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Probing the Interaction of 1-octyl-3-methylimidazolium containing Ionic Liquids with Small Molecules

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Abstract

Ionic Liquids (ILs) have drawn a great deal of attention as carbon capture agents, and in order to understand them studies must be performed probing the CO₂–IL interaction. Many studies have focused upon measuring the solubility of CO₂ within ILs, with fewer studies directly probing the CO₂ adsorption environments within the IL. Understanding of the adsorption environments is of fundamental for the use of ILs industrially, if they are to be successfully applied within carbon capture and storage devices. Temperature programmed desorption (TPD) has been used to study the CO₂–IL interaction within two ionic liquids; 1-octyl-3-methylimidazolium tetrafluoroborate ([C₈C₁Im][BF₄]) and 1-octyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([C₈C₁Im][Tf₂N]). Experiments were performed utilising low temperature line of sight mass spectrometry (LTLOS MS), ensuring that only species desorbing from the surface are observed. Surfaces were formed through a coadsorption method, where IL was deposited by chemical vapour deposition at a rate of ≈ 1 layer per minute while CO₂ was simultaneously leaked into the chamber at pressures between 2×10^{-8} and 2×10^{-6} mbar. This study finds that CO₂ does not form a monolayer on a gold surface at ≈ 90 K, with no CO₂ TPD peak seen for those experiments, showing E_{des,CO_2} (the activation energy of desorption of CO₂) < 24.5 kJ mol⁻¹. When IL and CO₂ are coadsorbed the IL is seen to stabilise the CO₂, such that a TPD peak for CO₂ is seen, with the amount of stabilisation depending upon the IL used. Comparison of experimental TPD curves with calculated TPD profiles, using CO₂ states with a range of binding energies, shows that there are multiple CO₂ environments within the ILs. The use of TPD allowed the relative populations of these CO₂ adsorption environments to be measured, which is not possible using solubility measurements and Henry's constants, providing insights into the IL–CO₂ interaction. CO₂ was observed to desorb from sites within the bulk IL, which have activation energies of desorption in the range 24.5 to 43 kJ mol⁻¹. The CO₂ was seen to be stabilised most within the [C₈C₁Im][BF₄], giving a stabilisation in E_{des} of up to 18.5 kJ mol⁻¹. The [C₈C₁Im][Tf₂N] was typically seen to stabilise twice as much CO₂ as [C₈C₁Im][BF₄], which is consistent with the experimental Henry's constants.

Further to this a new experimental technique for determining surface structure, utilising high energy X-rays in the total reflection regime, to generate an X-ray standing wave (XSW) and detect the resulting photoelectrons from layered surfaces has been demonstrated. The variable period X-ray standing wave (VPXSW) technique relies on the fact that at low incident angles (typically $< 2^\circ$) total external reflection of X-rays is observed. The incident and reflected X-rays interact to generate an XSW along the surface normal, with nodes and antinodes at different heights, z , above a reflector for different angles of incidence. By scanning the incident angle of the X-ray from 0° upwards the periodicity of the XSW decreases, resulting in the nodes and antinodes sweeping towards the surface. As this sweeping occurs the nodes and antinodes pass through material adsorbed on the surface of the reflector, and the photoelectron signal fluctuates. Comparing the fluctuations in the measured photoelectron signal to a theoretical model allows surface layering to be detected at larger depths and with a higher information content than with other surface science techniques. This allows distance information, relative to the interfaces between different materials, to be obtained for different chemical species. Data is presented from a surface consisting of the ionic liquid $[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]$ on a Si(001) reflector, held at ≈ 90 K, with a thick IL layer adsorbed on the reflector and a CHCl_3 marker layer on top of the IL. Results from the frozen surface indicate a $12 \text{ \AA}$ layer of CHCl_3 and background water had been dosed on top of a $211 \text{ \AA}$ IL layer. These values agree well with what was expected for this model IL system with a thin marker layer, designed to test the technique. It is therefore shown that VPXSW with photoelectron emission can be used to successfully characterise thin films with thicknesses between $15 \text{ \AA}$ and $\approx 300 \text{ \AA}$ with chemical shift specificity, something not possible with current experimental techniques.

Declaration

This thesis is the result of my own investigations and is not being concurrently submitted in candidature for any degree.

Signed: _____ (Candidate)

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Abbreviations used within this work

A	Pre-exponential factor or amount
a	Area
AC	Alternating current
α	Incident angle of X-ray
α_c	Critical angle
α_m	Angle within layer m
amu	Atomic mass units
ARXPS	Angle resolved X-ray photoelectron spectroscopy
[B(CN) ₄]	Tetracyanoborate
BE	Binding energy
β	X-ray absorption index
[BETA]	Bis(pentafluoroethanesulfonyl)imide
[BF ₄]	Tetrafluoroborate
[C]	Concentration of CO ₂ per IL layer
[C ₂ C ₁ Im]	1-ethyl-3-methylimidazolium
[C ₄ C ₁ Im]	1-butyl-3-methylimidazolium
[C ₈ C ₁ Im]	1-octyl-3-methylimidazolium
CHA	Concentric hemispherical analyser
CHCl ₃	Trichloromethane (chloroform)
CO ₂	Carbon dioxide
$D(\alpha)$	Standing wave period
d	Layer thickness or diameter
d_{anal}	Analyser diameter
δ	Refractive index decrement
D_{hkl}	Layer spacing between (hkl) planes
EDC	Electron distribution curve
E_{des}	Activation energy of desorption
E_m	Electric field strength in layer m
E_m^R	Reflected electric field strength in layer m
[EtSO ₄]	Ethylsulfate
F^R	Fresnel reflection coefficient

F^T	Fresnel transmission coefficient
G	Gibbs free energy
H	Enthalpy
H_{gas}	Henrys constant of “gas”
h	Planck’s constant
h_{beam}	X-ray beam height
$h\nu$	Photon energy
I	Intensity
IL	Ionic liquid
IMFP	Inelastic mean free path
K_a	Langmuir isotherm constant and equilibrium constant
k	Proportionality constant, rate constant or wave vector
k_B	Boltzmann constant
KE	Kinetic energy
l	Length
λ	Attenuation length or wavelength
LOS	Line of sight
LTLOS	Low temperature line of sight
m	Mass of a molecule, mathematical label for an integer (XSW theory)
MEA	Monoethanolamine
MS	Mass spectrometry
m/z	Mass to charge ratio
n	Refractive index, order of diffraction, order of desorption, number of moles or number of molecules
N_A	Avogadro’s constant
[NFBS]	Nonafluorobutanesulfonate
NIXSW	Normal incidence X-ray standing wave
NOAA	National Oceanic and Atmospheric Administration
ν	Frequency
P	Pressure
p	Path length
Φ	Phase shift
ϕ	Work function

[PF ₆]	Hexafluorophosphate
<i>R</i>	Molar gas constant or reflectivity
<i>r</i>	Position or effective reflection coefficient
ρ	Density
<i>S</i>	Entropy or signal
σ	Peak width
σ_{abs}	Absorption cross section
SiO _x	Silicon oxide
SO ₂	Sulfur dioxide
<i>T</i>	Temperature
<i>t</i>	Time, thickness or effective transmission coefficient
τ	Residence time
<i>T_g</i>	Glass transition temperature
[Tf ₂ N]	Bis(trifluoromethylsulfonyl)imide
θ	Coverage (representing amount of material) or angle
TPD	Temperature programmed desorption
TSIL	Task specific ionic liquid
<i>U</i>	Internal energy
UHV	Ultra-high vacuum
<i>V</i>	Volume
<i>V_m</i>	Molar volume
VPXSW	Variable period X-ray standing wave
<i>x_{gas}</i>	Mole fraction of “gas”
XPS	X-ray photoelectron spectroscopy
XRR	X-ray reflectivity
XSW	X-ray standing wave
<i>z</i>	Position
<i>Z_{wall}</i>	Impingement rate

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Chapter 1

Introduction

1.1. An introduction to this thesis

This thesis looks at aspects within the broad topic of the surface structure of ionic liquids and their interaction with small molecules. Within this thesis there are two main branches of research. The first (chapter 4) is the development of a synchrotron based technique, variable period X-ray standing wave (VPXSW) analysis with photoelectron detection, which can be used to probe the surface structure and surface layering of thick layers (up to 100's Å). The second part (chapters 5 and 6) looks at the interaction between two imidazolium based ionic liquids (ILs) and the small molecule, carbon dioxide. These studies use temperature programmed desorption (TPD) with a newly developed low temperature line of sight mass spectrometry setup. This allows the study to focus on the strength of interaction rather than the solubility of CO₂ within the ionic liquids, which has already been well studied in the literature (see section 1.2.3).

1.1.1 Surface structure analysis

Any interaction between the two phases of a biphasic system occurs at an interface and in cases where one of these phases is vapour/vacuum the interface can be described as a surface (surface can also be used to describe the solid–liquid interface but not the liquid–liquid interface, although different people may have differing definitions). A large number of processes occur at surfaces varying from catalysis [1-5] and electrochemistry [2, 4] to gas capture [4, 6] and lubrication [7]. Surfaces are of particular interest due to the way that their properties vary from those of a bulk material, due to the fact that surface molecules are less coordinated than bulk molecules since the layer above them is different to every other layer of the material. This can lead to dangling bonds, and hence a greater reactivity, or can result in restructuring of the surface to minimise the energy penalty for the dangling bonds [2]. Functionalisation of porous surfaces with thin films has been observed to increase selectivity and yields in catalytic reactions [8], as well as keeping costs down for expensive

catalytic materials. The vast number of processes occurring at surfaces indicates the great importance of understanding the surface structure and having experimental techniques which have the ability to probe a range of different surfaces over length scales up to 100 nm.

It is the characterisation and determination of thin film composition that shall be focussed on within this study, an area for which many experimental techniques exist. Ellipsometry can be used to probe film thicknesses ranging from 0.1 to 100 nm [9] and can be used to give information on the dielectric constants of a thin layer. The technique utilises the change in the polarisation of a beam of optical light when it reflects from a surface, where the change in polarisation within the material on the surface is related to the optical constants of that material. These can then be used to determine the band gaps or the conductivities of the layers on the surface as well as the film thickness. The sensitivity of the technique is dependent upon the contrast between the optical constants of the substrate and the adsorbed layers [10]. Ellipsometry is analogous to specular X-ray reflectivity (XRR) in which an X-ray is reflected from a surface (for low incident angles, typically from 0° to 5°) and detected to probe the electron density perpendicular to the surface plane [11-13]. The X-rays are scattered by electrons, so in regions with higher electron density a greater degree of scatter occurs allowing the technique to determine layers of differing electron density. This means that there needs to be a large difference in the electron density of the substrate and the adsorbed layer for the best contrast and sensitivity in the results [10]. These techniques have the ability to probe thick surfaces in a non-destructive way due to the fact that the photons used are not attenuated significantly by the material they are travelling through, allowing them to be reflected from the substrate layer. These types of technique are suitable for looking at layering if prior information on the surface is available, but since they lack elemental analysis there is limited use for characterisation of thin films of unknown components and determining the structure of such surfaces.

X-ray photoelectron spectroscopy (XPS) [2, 14-16] uses an X-ray incident upon a surface at a large angle ($\approx 30^\circ$), such that it is transmitted into the surface and absorbed by the material within that surface. The absorption of the X-ray photons ionises the absorbers causing photoelectrons to be ejected

from the surface. In laboratory based sources the X-rays are typically generated from an aluminium anode, giving Al $K\alpha$ X-rays at an energy of 1486.6 eV [14]. The X-rays themselves are not highly attenuated by matter so penetrate the surface and are not surface sensitive, however the photoelectrons produced have attenuation lengths on the order of nanometres. This means that the photoelectrons can only escape from the top-most parts of the surface, before they are attenuated, allowing them to be used to probe films up to 10 nm thick. The surface sensitivity can be enhanced through the use of angle resolved X-ray photoelectron spectroscopy (ARXPS) [14, 15, 17, 18] in which the sample can be tilted, focussing on the top 1 to 3 nm of the surface. The background theory of XPS is discussed in more detail in section 2.2.

X-rays have also been used to characterise surfaces in X-ray standing wave (XSW) techniques of different forms [19]. The basic premise of all XSW techniques are similar; an incident X-ray and a reflected X-ray of the same wavelength and phase overlap in time and space, adding together to generate a standing wave which can be used to probe the layers adsorbed on a surface. One such set of XSW techniques rely on the satisfaction of the Bragg condition [4, 20],

$$n\lambda = 2D_{hkl}\sin(\theta)$$

by tuning either the X-ray photon energy (altering the wavelength, λ) or the angle relative to the diffracting plane (not the crystal surface), θ , to generate a reflected wave (n is the order of diffraction and D_{hkl} is the layer spacing between the planes with Miller indices (hkl)) [21-23]. The standing wave that is generated has a known standing wave period ($2D_{hkl}$ for first order diffraction) and behaves in a predictable fashion, with the phase of the X-ray standing wave shifting as the angle or photon energy is scanned through the Bragg condition. As an antinode passes through an adsorbed atom there is an observed increase in the detected signal (which can be photoelectrons, Auger electrons or X-ray fluorescence). By collecting XSW scans from a variety of different crystal planes the data sets can be used to triangulate the positions of the adsorbed atoms and identify the adsorption sites and orientation of the adsorbed molecules. For the traditional XSW technique the standing wave is set up from the crystal planes of the substrate, so for angles of incidence in the range 0° to 88° the crystal needs to be near perfect [21], which is not always the case, resulting in distortion of

the standing wave. Normal incidence X-ray standing wave (NIXSW) overcomes this issue by fixing the angle of incidence upon the diffracting plane to 90° (hence scanning of photon energy is required) which minimises the effect of the crystal imperfections and degree of collimation of the X-ray beam [22]. Since these XSW techniques rely upon diffraction from crystal planes the XSW wavelength is fixed, based upon the plane separation D_{hkl} , and is typically in the range 1 to 4 Å [24]. This provides the opportunity to probe a single atomic layer and bond lengths, however in the case of multi-layered adsorbates or large molecules there may be two or more antinodes within the adsorbed layer, producing multiple signals and making data very difficult to analyse. The XSW period can be increased by using artificially made layered substrates, such as the one described in ref. [24] where tungsten layers are separated by 25 Å using silicon as a spacer. This allows the XSW period to be increased allowing larger systems to be probed (such as the Langmuir–Blodgett films discussed in [24]), however the standing wave period is still fixed within a given experiment using a given substrate.

Another XSW technique that has been used to probe materials with larger layer thicknesses is variable period X-ray standing wave (VPXSW) analysis [25, 26], also referred to as total reflection XSW [27], grazing incidence XSW [28, 29] or glancing angle XSW [30, 31]. This relies upon the total external reflection of an X-ray from a flat surface, much in the same way as X-ray reflectivity, to produce the XSW. Since the reflection does not occur through diffraction of the X-rays from crystal planes by satisfying the Bragg condition the XSW wavelength is not fixed based upon the layer spacing D_{hkl} . Instead the standing wave period is related to the angle of incidence of the X-ray to the surface, where scanning the angle of incidence causes the XSW period to vary, for a fixed photon energy (hence the name of the technique is ‘variable period XSW’) [25, 32]. In much the same way as other XSW techniques the antinodes and nodes of the XSW can be used excite (or not, in the case of nodes) adsorbed layers of material on a surface. By scanning the incident angle of the X-ray the phase and the period of the XSW change which produce oscillating profiles as they pass through layers adsorbed on an X-ray reflector. This gives the VPXSW technique the ability to accurately probe adsorbed layers with thicknesses ranging from 10’s Å up to 1000 Å thick [25, 26, 32, 33]. Since the XSW is

produced from the reflection of X-rays, the standing wave only exists for low incident angles limiting the incident angle to a range of $\approx 0^\circ$ to 5° , although this is substrate and photon energy dependent. An evanescent wave is formed within the reflector surface, as a result of the total external reflection, and has a penetration depth which is dependent upon the intensity of the standing wave at the surface (which varies with incident angle). This evanescent wave has been used within total reflection XPS studies as the inelastically scattered background is low [14, 34]. The work discussed in ref. [34] could be considered to be a VPXSW study, although the author of the work made no comment on this in the paper.

All VPXSW experiments to date have utilised X-ray fluorescence as the detection method [25, 27, 29, 31, 33], in which the photons released from the decay of electrons into core holes emits photons [35]. The X-ray photon energies chosen to set up the standing waves in these studies have tended to be large (over 5 keV) to ensure the X-ray photons can ionise the core electrons in order to produce fluorescence, but also that the fluorescence photon produced has sufficiently large energy to be successfully transmitted through the adsorbed layer to the detector, rather than being absorbed by the overlayer [29]. The incident X-ray energy is tuned to optimise the signal from a given species, so in ref. [29] an X-ray energy of 15.2 keV was used to optimise detection of the Ge $K\alpha$ fluorescence peaks, whereas in ref. [32] an X-ray energy of 9.8 keV was chosen to optimally excite the Zn K fluorescence. This use of X-ray fluorescence does give elemental specificity, but requires some prior knowledge of the surface composition in order to optimise the X-ray energy, although this is true for most detection techniques. Use of X-ray fluorescence, however, limits the species that can be detected to ones with higher atomic weights as fluorescence yields are low for light atoms [24, 35, 36] such as carbon, nitrogen and oxygen. Although this allows good contrast in the fluorescence profiles to be obtained, as there is a heavy metal layer such as zinc [26, 32] or germanium [29] on top of hydrocarbon spacer molecules, it greatly limits the use of the technique in understanding many polymeric, organic and biological species, which are composed mainly from light elements such as carbon, nitrogen and oxygen. Utilising photoelectron detection can resolve these issues as photoelectrons have been used to characterise all species except hydrogen and helium. Not only do

photoelectrons allow elemental specificity, they can also be used to give information on the chemical environment of a particular photoelectron emitter. The fact that the produced photoelectrons are inherently surface sensitive, due to their attenuation lengths being on the 10's of Å scale [2, 14, 37], can also be used to provide extra information on the adsorbed layers at the surface. Through changing the photon energy used to generate the XSW the photoelectron kinetic energies and hence the attenuation lengths can be varied [2], allowing much thicker layers to be probed than with conventional XPS. The side effect of increasing the photon energy is a decrease in the photoionisation cross section [36], however experimental results described in this work show that reasonable absorption cross sections and attenuation lengths can be obtained for photon energies of 3 keV. It will be shown that VPXSW with photoelectron emission can be used to successfully characterise thin films with thicknesses between 15 Å and ≈ 300 Å with chemical shift specificity, something not possible with current experimental techniques.

1.1.2. Small molecule capture

The interaction of small molecules with ionic liquids is not only of importance from an academic perspective, as such studies will allow the suitability of ILs for new applications to be better understood. There is also a need for such applications with a global emergency arising from the emission of the small molecules generated upon burning fossil fuels such as coal, oil and natural gas. Worldwide energy consumption is increasing year on year, at an average rate of 1.9% for 2005 to 2015 [38], although it appears to be slowing with the 10 year average yearly consumption increase for 2007 to 2017 being 1.8% [39]. Over 80% of this energy is generated through the combustion of coal, oil and natural gas [39]. This is correlated to a statistically significant increase in the global temperature of over half a degree in the past century which, if left unchecked, could cause melting of the polar ice caps and increased sea levels [40]. Since it is understood by most scientists and political leaders that this rise in temperature is due to high emission of greenhouse gases, government bodies have agreed that action should be taken. This includes a legal obligation for countries to reduce greenhouse gas emissions by 40%, relative to the levels

measured in 1990, by the year 2030 [41] and to 80% of 1990 levels by 2050 [42].

Carbon dioxide (CO₂) has been identified as one of the major contributors to greenhouse gas levels (between 67% for the least developed countries and 81% for the most developed) [43]. The National Oceanic and Atmospheric Administration (NOAA) measure the concentration of CO₂ in dry air in Mauna Loa, Hawaii and have tracked the changes in the yearly average for global CO₂ levels. As of May 2017 the yearly average CO₂ level was 406.17 ppm [44] (which can be compared to the value of 280 ppm in 1800 [43]). Using this value as a mole fraction of CO₂ in the atmosphere (4.0617×10^{-4}) it can be seen that the partial pressure of CO₂ in the atmosphere is 0.412 mbar (given that atmospheric pressure is 1.01325 bar). The sharp increase in CO₂ levels has occurred mainly in the last 70 years (CO₂ level was 310 ppm in 1950), and is the reason many research projects and reviews have been and are being focussed on CO₂ capture and storage devices and strategies to prevent CO₂ generated from industrial processes escaping into the atmosphere [40, 45-48].

Present carbon dioxide capture technologies utilise amines of various forms to react chemically with the CO₂ molecules within flue gas from a power plant [46, 47, 49, 50]. This type of technology has been used since 1930 to separate CO₂ from natural gas and hydrogen with use of monoethanolamine (MEA) dissolved in water [49, 51]. Application of liquid MEA and other amines for removal of CO₂ from flue gas has been tested but some issues have arisen. These are largely to do with the financial implications of using the technology. During the CO₂ capture mechanism within amines a chemical reaction occurs and a carbamate ($R^1O_2CNR^2R^3$, with a chemical bond between the amine nitrogen and the CO₂ carbon) is formed. The regeneration of this carbamate is an energy intensive process, requiring temperatures of the order 130 °C for hours to get the CO₂ out of the carbamate using a “stripper” molecule [47, 50]. This regenerative process incurs the majority of the operational costs, responsible for 56% of the costs (the energy required for regeneration costs \$29 per ton of CO₂ captured whilst total costs are \$52 per ton of CO₂ captured) for use of amines (30% MEA solution) as carbon capture methods [49]. There are also issues arising from the reasonably high vapour pressures of the amines (MEA has a vapour pressure of $\approx$ 8.5 mbar at 293 K (capture temperature) and a vapour

pressure of ≈ 16 bar at 393 K (regeneration temperature)) and amine degradation processes, both leading to the cost of having to replace the amine as well as loss of the amine to the environment. Other issues include degradation of the amine species which can be induced thermally (generally above 200 °C, higher than the temperatures used during the general CO₂ capture process), through oxidative degradation by O₂, SO₂ and other oxides [49] or by carbamate polymerisation [47]. It has been found that using a wet amine can help regenerate some of the damaged species that form (urea groups) through thermal degradation [46]. As well as the cost of losing and replacing the amine it has also been found that the amines are very corrosive to the pipe networks used to transport them during the cycling from CO₂ capture to regeneration [47, 52]. This corrosion is found to vary with amine type, with high corrosion rates for the cheap and widely used MEA, occurring at an accelerated rate when the amine is loaded with CO₂ [52]. The use of ionic liquids within carbon capture and storage devices is seen by some as a viable alternative to amine technologies [47, 53].

1.2. Introduction to ionic liquids

Ionic liquids (ILs, also referred to as room temperature ionic liquids—RTILs) have been defined as liquids composed solely of ions, whilst having a melting temperature below 100 °C [54-56]. This is in contrast to an ionic solution, where ions are dissolved within another solvent, such as sodium chloride in water. It is noted by Seddon that the definition of 100 °C as the upper limit for melting temperature was a convenient, but arbitrary choice [56]. Interest in ILs has increased since 1998, when Freemantle noted the use of ILs as novel solvents for industrial processes [57] due to their low vapour pressures (hence preventing solvent evaporation contributions to air pollution), large liquid ranges and ability to dissolve “almost anything organic”. The wide variety of properties that an ionic liquid can have is made possible due to the highly tuneable nature of the ions from which the IL is composed. Ionic liquids have been synthesised with high liquid ranges and thermal stabilities [58], large electrochemical windows [59] and almost negligible vapour pressures [60, 61]. This has led to the development of many different uses for ILs such as solvents

for synthesis and catalysis of transition metal compounds [5, 62], lubricants in mechanical systems [7, 63], electrochemical solvents [64]—and therefore uses in chemical sensors [65] and in fuel cell devices [66]—but most relevant to this work is their application to the capture of small molecules [67-72]. It is very tempting to think that the term “ionic liquid” describes a molecular system in particular, when instead the term describes a broad range of species. It is important to understand that not all ILs have the same properties meaning that the suitability of an IL for a given application depends upon its chemical composition and the effects this has upon its physical properties.

As previously mentioned ionic liquids are made solely of ions, from their definition, which means they have strong coulombic interactions, just like in an ionic solid (such as sodium chloride). In an ionic solid these ionic interactions lead to very high melting temperatures (1074 K for NaCl [4]), however the difference in an ionic liquid is the type of ions that are used. Generally the cation is a bulky non-symmetric organic molecule, often with the charge localised on a nitrogen (such as in an imidazolium, ammonium, pyridinium or pyrrolidinium), with a large variety of anions which can vary from elemental ions (chloride) to inorganic (tetrachloroferrate(III)) and larger (tris(pentafluoroethyl)trifluorophosphate) anions. It is the use of the bulky and non-symmetric cations and anions which prevent effective packing leading to the liquid state of ILs, but also their strong cohesive forces and often very low vapour pressures at near ambient conditions [73-75] whilst the anions often give the chemical properties of the system [57]. The non-equilibrium vapour pressure of 1-ethyl-3-methylimidazolium ethylsulfate ($[\text{C}_2\text{C}_1\text{Im}][\text{EtSO}_4]$), being evaporated through a Bayard–Alpert pressure gauge, has been measured to be $\approx 5 \times 10^{-8}$ mbar at 500 K [76]. This value is much lower than the value obtained for the ionic liquid 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ($[\text{C}_4\text{C}_1\text{Im}][\text{Tf}_2\text{N}]$) measured using the Knudsen method, where the vapour pressure was seen to be 2.74×10^{-3} mbar at 507.54 K [77]. An empirical equation for the vapour pressure variation with temperature (as found using a Knudsen method) for $[\text{C}_4\text{C}_1\text{Im}][\text{Tf}_2\text{N}]$ is given in equation 2 of ref. [77], which when extrapolated to 298 K calculates the vapour pressure of $[\text{C}_4\text{C}_1\text{Im}][\text{Tf}_2\text{N}]$ to be $5 \times 10^{-12 \pm 2}$ mbar.

The fact that the ions in ILs are not necessarily monoatomic means that there is the possibility for many other interactions to occur between the ions and any other species. The formal charges on the ions means that interactions with other charged species or surfaces can be observed, which has been seen to result in effects such as ionic layering at a charged sapphire interface [78]. The charges on the ions could also interact with molecules which possess multipole moments (such as dipoles or quadrupoles). It has been discussed that the cations used in ILs are generally organic and bulky, with the bulky moiety usually being a hydrocarbon chain (also referred to as a hydrocarbon tail). As a result of the ions having hydrocarbon tails, which only have the ability to have dispersion interactions, phase segregation between the non-polar tails and the polar/ionic parts of the ions has been attributed as the driving force for layering at the liquid–gas interface [79, 80]. These topics (and more) are covered in a review on the structure of ILs, and the various interactions that have been observed within them, by Hayes, Warr and Atkin [81].

1.2.1. Ionic Liquids under ultra-high vacuum

It was discussed in section 1.2 that one of the reasons that ionic liquids are so popular is that they have the ability to be solvents which have very low vapour pressures [57]. For $[\text{C}_4\text{C}_1\text{Im}][\text{Tf}_2\text{N}]$ the vapour pressure was estimated to be $\approx 5 \times 10^{-12 \pm 2}$ mbar at 298 K, based upon the extrapolation of an empirical relationship between vapour pressure and temperature [77]. This vapour pressure is comparable to most laboratory based ultra-high vacuum (UHV) apparatus, which typically operate with base pressures below 10^{-9} mbar [2]. As a result ILs and their mixtures can be purified using UHV distillation techniques in order to produce spectroscopically pure materials and remove impurities that are not removed by low vacuum (or even high vacuum) drying techniques which affect the IL properties and hinder the ability of the IL to perform properly, such as affecting electrochemical onset potentials [82, 83]. Since some ILs have vapour pressures below that of the operating pressure for vacuum systems it is possible to study ILs using vacuum techniques in order to understand the IL structure further [84, 85]. Of particular interest is the surface structure of the ILs, as any molecule that attempts to interact with the IL from outside (i.e. not a

solute within the IL) will come into contact with the IL surface [17, 18]. Understanding how the IL surface is arranged for different cation–anion pairs will allow chemists to better design and modify ILs for the tasks that they are required to do [7, 86-88].

Surface science techniques such as XPS [61, 84, 89], XRR [78, 79, 90] and mass spectrometry based techniques [91], such as TPD [76, 92, 93], as well as vacuum scanning probe microscopy [94] have been performed on ILs. As XPS is sensitive to the top 5 to 10 nm of material in a layer it has been used to try and determine how the ionic composition affects surface layering within ILs. It has been observed using ARXPS that, as the cation chain length—on an imidazolium based cation or on the anion—is increased, the surface region becomes enriched with carbon suggesting that the IL arranges such that the alkyl chains are at the liquid–vacuum interface [18, 89]. An XRR study on an imidazolium IL with an 18-member carbon chain on the cation also showed that the carbon chain appears to protrude from the liquid surface into the vacuum, with ionic ordering occurring in the surface layers but decaying away with distance into the bulk liquid [79]. It was observed by ARXPS that the degree of surface enrichment, or layering, was dependent upon the relative sizes of the ions, with the surface structure being dominated by carbon for ILs in which cations had longer alkyl chains and smaller anions [17, 18]. This result however does not seem to be supported by all XRR studies of IL layering at the solid–liquid interface (solid was charged sapphire), where it was observed that $[\text{C}_4\text{C}_1\text{Im}][\text{PF}_6]$ (larger anion) shows a greater degree of layering than $[\text{C}_4\text{C}_1\text{Im}][\text{BF}_4]$ (smaller anion) [78]. Temperature programmed desorption studies have been used to probe IL surfaces to understand the kinetics of desorption [76, 95], composition in the vapour phase [88, 91] and interaction with small molecules.

Sticking probability and TPD experiments of water vapour interacting with the surface of $[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]$ and $[\text{C}_2\text{C}_1\text{Im}][\text{Tf}_2\text{N}]$ found that the water initially adsorbs to the IL surface before being absorbed into an ionic under layer [96]. The activation energies for desorption found from the TPD experiments could be used to elucidate the surface structure of the IL film, with the higher activation energy for absorption into the ionic under layer measured for the $[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]$ suggesting that the liquid–vapour interface is composed of

hydrophobic carbon tails. These findings are supported by XRR experiments in which an IL–water mixture was studied, showing that water could be observed to be adsorbed in the near surface region with the cations and the anions in the ionic under layer [90]. For ILs with long chains—in which the surface is composed of carbon tails—it would be expected that the solid IL glass, which is formed upon cooling to below the glass transition temperature of the IL, will be terminated by a carbonaceous layer. This was also suggested by TPD results in which the activation energies of desorption of water adsorbed on glassy layers of $[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]$ and $[\text{C}_2\text{C}_1\text{Im}][\text{Tf}_2\text{N}]$ were lower than the activation energy of desorption from water ice, suggesting that destabilisation of the water by the carbon chains has occurred [96].

Another TPD study looking at the interaction of $[\text{C}_2\text{C}_1\text{Im}][\text{Tf}_2\text{N}]$ with acetone exposed the frozen IL glass to acetone vapour at 100 K and observed that there was no stabilisation of the acetone by the IL, relative to acetone desorption from gold [88]. The IL was also dosed on top of a frozen acetone layer at 100 K (which is below the glass transition temperature for the IL) where it was observed that a “porous solid IL”, like an IL equivalent of snow, stabilised the acetone by up to 16 kJ mol^{-1} relative to desorption from the IL glass. This further suggests that the IL surface is composed from hydrophobic parts of the IL that cannot support interactions with ionic or polar regions. Furthermore this illustrates that the IL can have different morphologies in the solid phase depending upon the dosing method (dose then cool or dose onto a cooled surface). Understanding the surface structure of ILs in these different phases (IL glass or IL ‘snow’) will be useful in determining how incoming molecules interact with the IL surface and discovering whether they adsorb or reflect. Although ILs have attracted much attention for their surface properties and interaction with small gaseous molecules whilst under vacuum, the majority of work that has been performed to probe these interactions has been performed at ambient or elevated pressures with the IL in the liquid phase, as discussed in the following sections.

1.2.2. Ionic liquids as gas capture agents

As mentioned previously ionic liquids have been targeted as gas capture agents, specifically as replacements for amine technologies for CO₂ capture from the flue gas released at combustion power plants. There is a virtually limitless combination of ions that can be used to generate ILs [55], with modification of the ionic structure and composition affecting the physical properties of the IL. This has led to generation of task-specific ionic liquids (TSILs) [59, 60, 97] which have been specifically designed to perform a particular task. The first example of this included the addition of urea, thiourea and thioether groups onto imidazolium cations in order to capture mercury(II) and cadmium(II) metal ions from aqueous solutions [97]. This method utilised the phase separation behaviour between an aqueous layer and an IL layer and operated on the principle that the solvated metal ions would not enter the IL phase without an aqueous solvation shell unless the ion was complexed by the ligand groups attached to the IL. This allowed the metal ions to be removed from the aqueous solution by the IL and then the IL (containing the metal ions) to be separated from the aqueous phase.

In reality ILs are not composed solely of ions, often with impurities from synthesis or dissolved gases within the ILs. These impurities have been seen to affect many of the measureable properties of the ILs [82]. A study of such effects was performed by Seddon *et al.* showing that water impurities (due to absorption from atmospheric air) were seen to reduce the viscosity of imidazolium ILs whilst chloride impurities (from synthesis of the IL) were seen to increase the viscosity of the ILs [98]. For ILs used in gas capture it should be expected that the properties of the IL also vary upon absorption of the gases they capture. It has been observed that SO₂ (a component of flue gas from industrial processes) capture increases the viscosity of the ionic liquid 1,1,3,3-tetramethylguanidinium lactate, making transportation of the IL–gas mixture for separation more difficult. It was also observed that when there is SO₂ and water in the simulated flue gas the viscosity increase is not as large, with the added benefit being that there is no apparent effect on the SO₂ absorption capacity by the presence of the water [67]. The findings from these studies serves well as a reminder that it is not just the properties of the IL itself that need to be considered

when designing a new solvent or gas capture agent, but also the properties of the IL with the molecules of interest within it.

In the same way that there is a large variety of ions that can be used to compose ILs there is also a large range of different solute molecules that have been studied within ILs. Often when discussing the solubility of a molecule within an IL Henry's law is used to relate the mole fraction of the gas within the IL, x_{gas} , to the pressure of the gas above the IL, P_{gas} :

$$P_{\text{gas}} = H_{\text{gas}}x_{\text{gas}}$$

Using this convention the Henry's constant, H_{gas} , has units of pressure and is inversely proportional to the solubility, meaning that the lower the Henry's constant for a gas within a particular IL, the more soluble that gas is in the IL. Since Henry's law is only really applicable for low gas concentrations/mole fractions deviation from linearity is observed for high gas pressures [4]. Different gases have different sizes and polarities affecting their solubilities within different ILs, as observed in both experimental and theoretical studies [69, 99-102]. It is not surprising that there is not a single model for successfully describing the solubility of a gas within an IL given the huge quantity of variables involved, however it is acknowledged by many that the gas-anion [100, 101] and IL-IL interactions [103] are the most important factors [99]. A review by Hu *et al.* [99] looks into how the molecular characteristics of an IL influences the solubilities of different gases within ILs, concluding that the vibration and motion of the IL ions, to generate space in the IL network, is one of the most important factors in the physical absorption of gases (when chemical bonding is not considered).

Focusing on the characteristics of the IL which affect gas solubility, the interaction of the anion with the solute molecule is often seen to have a large influence on the solubility. This comes from experimental studies in which variation of the anion has a larger effect on the gas solubility than if the cation is changed, for a given gas [100, 104]. An infrared spectroscopy study has also been performed showing that the CO₂ associates with the anion in two imidazolium based ILs [105]. The findings in these experimental studies are reinforced by theoretical studies in which the contribution to the solute-IL interaction is found to be larger for the anion than for the cation [69, 106]. Many

of the commonly studied anions are heavily fluorinated (hexafluorophosphate $[\text{PF}_6]^-$, bis(trifluoromethylsulfonyl)imide $[\text{N}(\text{CF}_3\text{SO}_2)_2]^-$ (often written as $[\text{Tf}_2\text{N}]^-$) and tetrafluoroborate $[\text{BF}_4]^-$) meaning that the partial negative charges on the fluorine atoms can interact with any multipoles present on solute molecules and promote interaction through electrostatic forces [100, 101]. Theoretical calculations, however, have shown that the van der Waals interactions between both the anion and the cation, and the solute molecule are much larger than the coulombic contribution, irrespective of the solute molecule identity [69].

Aside from the anion–solute interaction it has been observed that there is an inverse relationship between the anion–cation interaction strength and the solubility of a solute within the IL [103, 106]. It is reasoned that a weaker anion–cation interaction will mean there is a smaller energy penalty when cavities are formed for the solute molecules to slot into, as well as the anion becoming more available for bonding with the solute [106]. The energetics relating to the formation of cavities, generating a large free volume for solutes to sit in, within the IL is regarded as one of the most important factors for gas capture [99, 102, 103, 106]. Such cavities can be formed through the motions of flexible side chains on the ions [99], with increases in solubility observed for imidazolium based ILs which have longer alkyl chains on the cations [45, 99, 100, 106]. There are however caveats to this trend of increasing solubility with increasing flexibility in the cation, which depend on the gas that is being studied (discussed later). Molecular dynamics simulations of the structures of a variety of imidazolium based ILs have shown that upon CO_2 adsorption there is not much variation in the radial distribution function of ions, suggesting the structure is not perturbed much by the CO_2 , supporting the idea that CO_2 (and other solutes) fill existing gaps within the IL network [104] rather than making new ones. The gaps in the IL network can be segregated into polar and non-polar domains [99, 107], depending on the environment of the IL surrounding the cavity, which in turn depends on the chemical structure of the ions (longer alkyl chains lead to a greater distribution of non-polar domains). The distribution of polar versus non-polar domains has been seen to affect the solubility of a given gases, with given characteristics, within ILs [69, 99, 102].

As well as looking at trends in solubility due to characteristics of the IL there are also a similar collection of observations on gas solubility based on the properties of the gas studied. It has already been discussed that solutes which interact strongly with the IL ions are more likely to be more soluble [69] (although this is not always the case—CO is an exception despite possessing a dipole moment and being reasonably polarisable, for a small molecule [100]). This means that often molecules which have large dipoles or quadrupoles, in relation to their size (such as CO₂, H₂S or N₂O), will interact strongly with ionic liquids and their charged regions or polar domains [69, 100]. This means that there is a trade-off between maximising cavity size (through large flexible ions) and ensuring that there are enough polar domains within the IL for the polar molecules to bind. The solubility of CO₂ within imidazolium ILs has been seen to be adversely affected by substitution of the C2 hydrogen (the one between the nitrogen atoms, fig. 3.5b) with a methyl group, resulting in an increase in the Henry's constant despite the greater free volume created for the gas to sit in, suggesting that CO₂ interacts with the imidazolium cation at this position [99, 104].

Higher solubilities are observed if gases can undergo specific interactions, such as hydrogen bonding or π - π stacking, with the ions within the IL [62, 100]. It is postulated that π - π stacking and other van der Waals forces could explain the high solubility of benzene observed within an imidazolium IL [100]. It has been observed through molecular dynamics simulations that water molecules interact strongly with the anion in 1-butyl-3-methylimidazolium tetrafluoroborate ([C₄C₁Im][BF₄]), at low water concentrations [108], despite many imidazolium ILs being observed to phase separate with water [75, 97]. For solute molecules which do not have any specific interaction or multipole moments, having a high polarisability, and hence the ability to interact through dispersion forces, appears to increase solubility [106]. This has been described in a review article which correlated solubility data for alkenes of different lengths within ILs. It was observed that as the length of the alkene increased the solubility of the alkene in all ILs studied also increased [5]. This idea is not supported by experiments which studied the solubilities of ethane and ethene, which have the same number of carbon atoms, within different ILs. Since the ethene has a double bond it has a higher quadrupole moment than ethane, and

was observed to have higher solubilities within three different imidazolium based ILs, despite ethane having a higher polarisability [100, 101]. The effect of gas polarisability is also cited for the higher solubility of SO₂ within ILs than CO₂ [106]. In scenarios where the gas molecules have weak interactions with the IL, such as homonuclear diatomics or monoatomics with low polarisabilities (H₂, Ar and N₂), the gas solubility is driven by the Gibbs free energy of forming cavities within the IL for the gas to fit into. As a result the higher gas solubilities are observed for ILs which have large flexible ions (such as cations with long tails which have a multiple degrees of freedom) [99]. The fact that a given IL (one designed to have a large volume of polar domains, for example) can solvate a particular type of gas (polar ones) readily and not others (hydrocarbons or N₂) makes them ideal candidates for gas separation, as the IL (in this case) becomes very selective towards certain gas molecules (the polar ones) [53, 99, 101, 102].

1.2.3. Ionic liquids for use in carbon dioxide capture

The general trends observed in experimental and theoretical studies for gas solubilities within ILs discussed so far can be applied to looking at IL–CO₂ systems specifically. There has been a large volume of work into this area [81] due to the fact that ILs have the ability to succeed in areas where amine technologies struggle (high thermal ranges, low volatilities and often utilising physical adsorption of CO₂ rather than chemical adsorption). Carbon dioxide does not have a dipole moment, due to its linear nature, but does have a reasonably large quadrupole moment [100, 109]. Owing to its small size CO₂ has a low polarisability in comparison to gases with a greater number of atoms (small hydrocarbons), but a larger polarisability than many of the small molecules (N₂, O₂) that may also be found in flue gas mixtures [100].

The characteristics of CO₂ have led many to conclude that CO₂ associates with the polar domains of an IL, which are mainly dictated by the anion in most ILs (where the cation doesn't have a functionalised hydrocarbon tail) [72, 100]. This has been observed in both theoretical calculations, with the CO₂ molecule sitting tangentially to the spherical [PF₆][−] and [BF₄][−] anions [104], and experimentally in infrared spectroscopy, where the CO₂ was observed to interact chemically with the [PF₆][−] and [BF₄][−] anions in a Lewis acid–base

type interaction, with the anions acting as Lewis bases [105, 106]. As a result it has been suggested that having a larger, more diffuse anion [102] with a greater degree of fluorination (such as the $[\text{Tf}_2\text{N}]^-$ anion) will lead to a greater CO_2 solubility within the IL [99]. This hypothesis was tested through measurement of the CO_2 solubility in $[\text{C}_2\text{C}_1\text{Im}]^+$ ILs with the anions $[\text{Tf}_2\text{N}]^-$, $[\text{BF}_4]^-$, bis(pentafluoroethanesulfonyl)imide ($[\text{BETA}]^-$) and nonafluorobutanesulfonate ($[\text{NFBS}]^-$) where the increased quantity of fluoroalkyl chains increase the degree of fluorination of the anion [110]. It was observed that the highest CO_2 solubility occurred in the $[\text{BETA}]^-$ containing IL, suggesting that degree of fluorination may be a factor in CO_2 solubility, however the $[\text{BETA}]^-$ anion was also the largest, so would have created the greatest free volume. It was also observed that the $[\text{NFBS}]^-$ anion had very similar CO_2 solubility properties to $[\text{Tf}_2\text{N}]^-$, despite a higher degree of fluorination in $[\text{NFBS}]^-$, but similar ion sizes (and hence free volumes). Further evidence for the fluorination of ions increasing the CO_2 solubility comes from studies in which the alkyl tails on cations have been substituted for fluorine containing tails, leading to reductions in the Henry's constants (CO_2 solubility increases) [72, 111]. One disadvantage of such systems was the increased viscosity of the heavily fluorinated IL relative to the non-fluorinated analogues, although it is discussed that this can be negated through tuning the ion design [111].

Studies, however, have also been published in which non-fluorous anions have had high CO_2 solubilities, such as the observation that ILs with the tetracyanoborate anion ($[\text{B}(\text{CN})_4]^-$) appear to be better at solvating CO_2 than the $[\text{Tf}_2\text{N}]^-$ containing analogues [68, 103]. It is suggested that this observation could be due to the weaker cation–anion interaction or the larger free volume and larger average pore size that occurs in $[\text{C}_2\text{C}_1\text{Im}][\text{B}(\text{CN})_4]$ (relative to the $[\text{Tf}_2\text{N}]^-$ analogue) [103]. The experimental study claims that the enthalpies of dissolution indicate the CO_2 – $[\text{Tf}_2\text{N}]^-$ interaction and the CO_2 – $[\text{B}(\text{CN})_4]^-$ interaction are similar in strength [68], whilst a computational paper says the CO_2 – $[\text{B}(\text{CN})_4]^-$ interaction is more attractive and is one of the reasons for the increased CO_2 solubility [103]. Addition of ether groups to the alkyl chains on the cation has been observed to increase the CO_2 solubility slightly (although ref. [53] claims there is little or no change in the CO_2 solubility in ether functionalised ILs). The solubility increase is thought to be caused both through

the increased free volume (due to extra flexibility in the chain given by the ether groups) [112] and the possibility the interaction of the CO₂ with the ether oxygen atoms, assuming analogies can be drawn from the interaction of CO₂ with dimethyl ether [112, 113]. Hopefully these discussions indicate that predicting the solubility of CO₂ within an IL is a complex issue with many factors affecting the outcome.

In addition to the aforementioned studies to try and understand what makes CO₂ bind to an IL, some research groups have simply utilised knowledge from current amine technologies, either by using ILs as a solvent for dissolving amines in [111] or by adding amine groups to the IL ions [114]. It was observed that there appears to be no significant increase in the solubility of CO₂ in [C₄C₁Im][Tf₂N] with addition of 2.7 weight % polyethyleneimine (Henry's constant in [C₄C₁Im][Tf₂N] was 37 ± 3 bar and 38 ± 3 bar with the addition of the amine) [111]. The use of ILs with amine groups within a polymer membrane has been shown to be a highly selective CO₂ transport mechanism across the membrane, although it was noted that water was required for the CO₂ capture by the amine groups on the IL [114], which will limit the use of this technology at higher temperatures (as the membrane will dry out).

Since there is no definitive adsorption model for CO₂ within ILs many different research groups have concluded that different characteristics are the most important factor for CO₂ adsorption within an IL. What is apparent from all of the literature is that there are multiple factors that need to be considered rather than just one most important characteristic of the IL for CO₂ capture. Further to this it is also important that the energetics of the CO₂–IL interaction are not neglected, since the majority of studies focus on the solubility (determined by the Henry's constants). The variation of Henry's constant with temperature gives an average enthalpy for adsorption of the CO₂ within the IL (strictly the average enthalpy is found from gradient of a graph of $\ln(H_{gas})$ vs. $1/T$, multiplied by the molar gas constant, R). As this only gives an average enthalpy value, it highlights the importance of experimental studies probing the variety of interaction energies and adsorption sites within an IL for CO₂ (and other solutes). The work in this thesis details a procedure by which to obtain the range of adsorption sites for CO₂ within two ILs, information which is of great

importance if ILs are to be utilised as substitutes for amine technologies, especially in studying the regeneration stage.

1.3. Introduction to synchrotron studies

A brief introduction to synchrotron radiation and synchrotron studies is given here, although the reader is directed to references [35], [115] and [116] for a more comprehensive review. A synchrotron is a roughly circular particle accelerator with circumferences ranging from ≈ 100 m to 2500 m (circumference of Diamond light source, UK, where the work in this study was undertaken is 562 m) [115] in which magnets are used to vary the trajectory of the electrons and maintain the correct path. To prevent the loss and scattering of electrons, resulting in reduction of the X-ray intensity too rapidly, the synchrotron storage ring is under UHV maintaining a pressure below 10^{-10} mbar, resulting in a lifetime for the electron beam of 10 to 20 hours [116]. The action of accelerating the electrons around a curved path by bending magnets produces low intensity (by synchrotron standards, but still much higher intensity than laboratory sources) bending magnet radiation which can be manipulated and used to probe surfaces. To generate much higher brilliance light (where brilliance encompasses photon flux and the area over which the light spreads out) devices are inserted into the path of the electrons. Devices such as undulators and wigglers force the electrons to undertake multiple oscillations along their path, generating X-rays which can be used [115]. The undulator radiation that is produced consists of a range of photon energies with different fluxes, so requires monochromating, focussing and shaping prior to use, with the desired parameters dependent upon the experiment to be performed.

Some of the surface science techniques discussed in this chapter require the use of synchrotron radiation sources due to the ability to provide an intense and well defined X-ray beam alongside the ability to tune the majority of the beam properties such as polarisation and beam energy [14, 35]. The X-ray standing wave techniques, discussed in section 1.1.1, make use of synchrotron sources to allow the photon energy ranges to be tuned during a scan (for XSW and NIXSW [21]) or to select the desired photon energy to optimise detection for a given element (VPXSW [29, 117]). The intense well defined X-ray beam

allows experiments to be performed for a fraction of the time of laboratory based X-ray sources whilst getting very high quality data with high resolution [14]. Furthermore it is often not possible to undertake such experiments with laboratory sources as the X-ray sources lack the sufficient brightness due to difficulties in focussing X-rays [116].

Synchrotron based VPXSW studies have been performed with X-ray fluorescence as the detection method to observe transitions in Langmuir–Blodgett films for a zinc arachidate bilayer adsorbed on top of a ω -tricosenoic acid bilayer on top of an octadecyl thiol coated gold reflector as a function of temperature [32]. It was observed that at low temperatures the Zn $K\alpha$ fluorescence signal contained clear oscillations that upon fitting implied a thin zinc layer was suspended 218 Å above the gold substrate. Ellipsometry gave the total film thickness to be 215 Å, however as the X-ray fluorescence was used to detect the signal it was not possible to determine the total film thickness in this study as it was not possible to measure the signal from the carbon species in the arachidate. It was calculated that the total film thickness as measured by VPXSW was 245 Å by making the assumption that the hydrocarbon chains are fully extended on top of the zinc layer. Under the assumption that the hydrocarbon chains were all fully extended and perpendicular to the mirror surface the total film thickness would have been expected to be 256 Å. This is 41 Å thicker than the ellipsometry measurement, representing a 16% error, suggesting that it may not have been valid to make this assumption. Upon heating of the sample to 105 °C the zinc layer was observed to change its position above a gold surface, yielding a VPXSW profile with fewer clear, well defined oscillations. It was noted by the author in ref. [32] that “The underlying structural change in the film that leads to this inward spread of the Zn layer cannot be completely determined from this result, since this measurement is only directly sensitive (via fluorescence) to the heavy-atom distributions in the film”. Further experimentation using simultaneous calorimetry and time resolved X-ray diffraction found that the temperature at which the VPXSW profile varied corresponded to the bulk melting temperature of the ω -tricosenoic acid [26]. It is possible that had photoelectron detection been utilised, within the studies discussed, the melting transition may have promoted changes in the relative intensities of chemically shifted carbon environments as the ω -tricosenoic acid

(which contains oxygen as carboxylic acid groups) collapse together. The same research group later showed that a system with 14 ω -tricosenoic acid bilayers between the gold sample and the zinc layer could also be analysed using the VPXSW technique with X-ray fluorescence [33]. This equated to successfully analysing a zinc layer 925 Å above the reflector surface showing that the VPXSW technique has the ability to be applied to a wide range of film thicknesses.

Later VPXSW studies at the DELTA synchrotron (Dortmund, DE) utilising fluorescence detection looked at the ability of the VPXSW profile to model thicker layers of a material [28, 29], rather than just thin layers of metals at elevated heights. Experiments consisted of studying germanium layers (thicknesses of 29, 76, 309 and 1010 nm, defined by the manufacturer but checked with XRR) adsorbed on silicon substrates. In order to get a fluorescence signal from the Ge a photon energy of greater than 11.1 keV (BE for Ge 1s level is 11.1 keV [36]) had to be used. The experimentally measured signals for the 29 and 76 nm samples showed some slight oscillations, due to nodes and antinodes passing into the thick layers, but these were less prominent than oscillations due to nodes and antinodes passing through the thin gold layer on top of polystyrene on silicon, also studied within their work. There were no clear oscillations observed for the VPXSW profiles of the 309 or 1010 nm Ge samples, with the experimental data looking like a smooth edged step which made fitting the VPXSW profiles difficult. The fitting for these layers gave layer thicknesses of 100 nm, suggesting that this may be an upper limit for the film thicknesses probed by this technique. It is discussed that this is due to the fact that there are multiple nodes and antinodes present within the thick layer of material producing an averaged fluorescence signal, which looks like a step [29]. This comes as a result of the fact that the photons produced by the fluorescence are not heavily attenuated by the material they travel through. With photoelectrons, which have attenuation lengths in the range 1 to 10 nm (energy dependent), the signal from an emitter decays exponentially with increasing distance of the emitter below the surface. In a VPXSW study of a thick layer this would result in slight oscillations when nodes or antinodes pass into the surface irrespective of thickness, as this is where the majority of photoelectrons are produced. Further to this the use of fluorescence as a detection method puts a

lower limit on the X-ray energy (11.1 keV in refs. [28, 29]), which has the effect of reducing the standing wave period relative to the energies that are typically used in photoelectron studies (1.5 to 3 keV) since the standing wave period decreases with X-ray energy [32]. This makes the issue of node and antinode averaging worse as having a shorter standing wave period means a greater number of nodes and antinodes enter the surface within a given angular range. This would require smaller angular steps to detect, however, in the absence of manipulators capable of making smaller angular steps, leads to an averaging of the signal. There will be a limit to the maximum thickness of the layer that can be probed by photoelectrons, as over 99% of the photoelectron signal comes from within the top 5λ of the surface (where λ is the photoelectron attenuation length). Eventually increasing the layer thickness will not affect the VPXSW profile as you will only be detecting the top x nm of a layer that is $x + y$ nm thick. Choosing an appropriate photon energy (which affects the kinetic energies of the photoelectrons) allows the attenuation lengths of the photoelectrons to be varied and a broad range of film thicknesses to be studied. The discussed studies which have used the VPXSW method with fluorescence reiterates the fact that photoelectron detection can provide information not currently available from existing VPXSW or surface science techniques.

1.4. References

- [1] Gasser, R.P.H., *An introduction to chemisorption and catalysis by metals*. Eds., Oxford University Press, New York, US, (1985)
- [2] Kolasinski, K.W., *Surface Science: Foundations of Catalysis and Nanoscience*. Eds., John Wiley & Sons, Chichester, UK, (2012)
- [3] Welton, T., Ionic liquids in catalysis. *Coord. Chem. Rev.*, **2004**, (248), pp. 2459-2477.
- [4] Atkins, P. and De Paula, J., *Atkins' Physical Chemistry 8th edition*. Crowe, J., Fiorillo, J. and Hughes, R., Eds., Oxford University Press, Oxford, (2006)
- [5] Haumann, M. and Riisager, A., Hydroformylation in room temperature ionic liquids (RTILs): Catalyst and process developments. *Chem. Rev.*, **2008**, (108), pp. 1474-1497.
- [6] Riisager, A., Fehrmann, R., Haumann, M. and Wasserscheid, P., Supported ionic liquids: versatile reaction and separation media. *Top. Catal.*, **2006**, (40), pp. 91-102.
- [7] Zhou, F., Liang, Y.M. and Liu, W.M., Ionic liquid lubricants: designed chemistry for engineering applications. *Chem. Soc. Rev.*, **2009**, (38), pp. 2590-2599.

- [8] Steinrück, H.P., Recent developments in the study of ionic liquid interfaces using X-ray photoelectron spectroscopy and potential future directions. *Phys. Chem. Chem. Phys.*, **2012**, (14), pp. 5010-5029.
- [9] Langereis, E., Heil, S.B.S., Knoops, H.C.M., Keuning, W., van de Sanden, M.C.M. and Kessels, W.M.M., In situ spectroscopic ellipsometry as a versatile tool for studying atomic layer deposition. *J. Phys. D Appl. Phys.*, **2009**, (42), pp. 073001.
- [10] Kohli, S., Rithner, C.D., Dorhout, P.K., Dummer, A.M. and Menoni, C.S., Comparison of nanometer-thick films by x-ray reflectivity and spectroscopic ellipsometry. *Rev. Sci. Instrum.*, **2005**, (76), pp. 023906.
- [11] Chason, E. and Mayer, T.M., Thin film and surface characterization by specular X-ray reflectivity. *Crit. Rev. Solid State*, **1997**, (22), pp. 1-67.
- [12] X-ray and neutron reflectivity: principles and applications 2nd edition. Dalliant, J. and Gibaud, A., Eds., Springer, Berlin, (2009)
- [13] Parratt, L.G., Surface Studies of Solids by Total Reflection of X-rays. *Phys. Rev.*, **1954**, (95), pp. 359-369.
- [14] Surface Analysis by Auger and X-ray Photoelectron Spectroscopy. Briggs, D. and Grant, J.T., Eds., IM Publications, Chichester, (2003)
- [15] Practical Surface Analysis Volume 1 - Auger and X-ray Photoelectron Spectroscopy. Briggs, D. and Seah, M.P., Eds., John Wiley & Sons, Chichester, (1990)
- [16] Steinhardt, R.G. and Serfass, E.J., X-ray Photoelectron Spectrometer for Chemical Analysis. *Anal. Chem.*, **1951**, (23), pp. 1585-1590.
- [17] Kolbeck, C., Cremer, T., Lovelock, K.R.J., Paape, N., Schulz, P.S., Wasserscheid, P., Maier, F. and Steinrueck, H.P., Influence of Different Anions on the Surface Composition of Ionic Liquids Studied Using ARXPS. *J. Phys. Chem. B*, **2009**, (113), pp. 8682-8688.
- [18] Lovelock, K.R.J., Kolbeck, C., Cremer, T., Paape, N., Schulz, P.S., Wasserscheid, P., Maier, F. and Steinrueck, H.P., Influence of Different Substituents on the Surface Composition of Ionic Liquids Studied Using ARXPS. *J. Phys. Chem. B*, **2009**, (113), pp. 2854-2864.
- [19] The X-Ray Standing Wave Technique: Principles and Applications. Zegenhagen, J. and Kazimirov, A., Eds., World Scientific, Singapore, (2013)
- [20] Bragg, W.L., The Diffraction of Short Electromagnetic Waves by a Crystal. *Proc. Camb. Philos. S.-M.*, **1913**, (17), pp. 43-57.
- [21] Jones, R.G., Shuttleworth, I., Fisher, C.J., Lee, J.J., Bastow, S.L., Ithnin, R., Ludecke, J., Skegg, M.P., Woodruff, D.P. and Cowie, B.C.C., Surface structure determination using X-ray standing waves. *Phys. Low-Dimens. Str.*, **2001**, (11-2), pp. 1-26.
- [22] Woodruff, D.P., Seymour, D.L., McConville, C.F., Riley, C.E., Crapper, M.D., Prince, N.P. and Jones, R.G., A Simple X-ray Standing Wave Technique for Surface Structure Determination - Theory and Application. *Surf. Sci.*, **1988**, (195), pp. 237-254.
- [23] Batterman, B.W., Effect of Dynamical Diffraction in X-ray Fluorescence Scattering. *Phys. Rev. A-Gen. Phys.*, **1964**, (133), pp. A759-A764.
- [24] Bedzyk, M.J., Bilderback, D.H., Bommarito, G.M., Caffrey, M. and Schildkraut, J.S., X-ray Standing Waves - A Molecular Yardstick for Biological Membranes. *Science*, **1988**, (241), pp. 1788-1791.

- [25] Zhang, R.T., Itri, R. and Caffrey, M., Membrane structure characterization using variable-period X-ray standing waves. *Biophys. J.*, **1998**, (74), pp. 1924-1936.
- [26] Wang, J., Caffrey, M., Bedzyk, M.J. and Penner, T.L., Structure Changes in Model Membranes Monitored by Variable Period X-ray Standing Waves - Effect of Langmuir-Blodgett Film Thickness on Thermal Behaviour. *J. Phys. Chem.*, **1994**, (98), pp. 10957-10968.
- [27] von Bohlen, A., Total reflection X-ray fluorescence and grazing incidence X-ray spectrometry - Tools for micro- and surface analysis. A review. *Spectrochim. Acta B*, **2009**, (64), pp. 821-832.
- [28] Kramer, M., von Bohlen, A., Sternemann, C., Paulus, M. and Hergenroder, R., X-ray standing waves: a method for thin layered systems. *J. Anal. Atom. Spectrom.*, **2006**, (21), pp. 1136-1142.
- [29] Kramer, M., von Bohlen, A., Sternemann, C., Paulus, M. and Hergenroder, R., Synchrotron radiation induced X-ray standing waves analysis of layered structures. *Appl. Surf. Sci.*, **2007**, (253), pp. 3533-3542.
- [30] Jach, T. and Bedzyk, M.J., Grazing Angle X-ray Standing Waves. *Phys. Rev. B*, **1990**, (42), pp. 5399-5402.
- [31] Jach, T. and Bedzyk, M.J., X-ray Standing Waves at Grazing Angles. *Acta Crystallogr. A*, **1993**, (49), pp. 346-350.
- [32] Bedzyk, M.J., Bommarito, G.M. and Schildkraut, J.S., X-ray Standing Waves at a Reflecting Mirror Surface. *Phys. Rev. Lett.*, **1989**, (62), pp. 1376-1379.
- [33] Wang, J., Bedzyk, M.J., Penner, T.L. and Caffrey, M., Structural Studies of Membranes and Surface Layers up to 1000 Å Thick using X-ray Standing Waves. *Nature*, **1991**, (354), pp. 377-380.
- [34] Henke, B.L., Ultrasoft X-ray Reflection, Refraction and Production of Photoelectrons (100-1000 eV Region). *Phys. Rev. A*, **1972**, (6), pp. 94-104.
- [35] *X-ray Science and Technology*. Michette, A.G. and Buckley, C.J., Eds., Institute of Physics Publishing, Bristol, (1993)
- [36] Thompson, A.C. and Vaughan, D., *X-ray Data Booklet*. Kirz, J., Eds., Lawrence Berkeley Laboratory, (2001)
- [37] Seah, M.P. and Dench, W.A., Quantitative electron spectroscopy of surfaces: A standard data base for electron inelastic mean free paths in solids. *Surf. Interface Anal.*, **1979**, (1), pp. 2-11.
- [38] BP Statistical Review of World Energy 2016, <http://www.bp.com/content/dam/bp/pdf/energy-economics/statistical-review-2016/bp-statistical-review-of-world-energy-2016-full-report.pdf> (accessed 31 May 2017)
- [39] BP Statistical Review of World Energy 2017, <http://www.bp.com/content/dam/bp/en/corporate/pdf/energy-economics/statistical-review-2017/bp-statistical-review-of-world-energy-2017-full-report.pdf> (accessed 31 May 2017)
- [40] Vandeginste, V. and Piessens, K., Pipeline design for a least-cost router application for CO₂ transport in the CO₂ sequestration cycle. *Int. J. Greenh. Gas Con.*, **2008**, (2), pp. 571-581.
- [41] European Commission 2030 Climate & Energy Framework, https://ec.europa.eu/clima/policies/strategies/2030_en#tab-0-0 (accessed 31 May 2017)

- [42] European Commission 2050 Low-Carbon Economy, https://ec.europa.eu/clima/policies/strategies/2050_en#tab-0-0 (accessed 31 May 2017)
- [43] Baumert, K.A., Herzog, T. and Pershing, J., *Navigating the Numbers: Greenhouse Gas Data and International Climate Policy*. Livernash, B., Eds., World Resources Institute, USA, (2005)
- [44] Dlugokencky, E. and Tans, P., NOAA/ESRL. www.esrl.noaa.gov/gmd/ccgg/trends/ (accessed May 31, 2017).
- [45] Chen, Y.H., Zhang, S.J., Yuan, X.L., Zhang, Y.Q., Zhang, X.P., Dai, W.B. and Mori, R., Solubility of CO₂ in imidazolium-based tetrafluoroborate ionic liquids. *Thermochim. Acta*, **2006**, (441), pp. 42-44.
- [46] Sayari, A. and Belmabkhout, Y., Stabilization of Amine-Containing CO₂ Adsorbents: Dramatic Effect of Water Vapor. *J. Am. Chem. Soc.*, **2010**, (132), pp. 6312-6314.
- [47] Yu, C.H., Huang, C.H. and Tan, C.S., A Review of CO₂ Capture by Absorption and Adsorption. *Aerosol Air Qual. Res.*, **2012**, (12), pp. 745-769.
- [48] Burghaus, U., Surface chemistry of CO₂ – Adsorption of carbon dioxide on clean surfaces at ultrahigh vacuum. *Prog. Surf. Sci.*, **2014**, (89), pp. 161-217.
- [49] Rochelle, G.T., Amine Scrubbing for CO₂ Capture. *Science*, **2009**, (325), pp. 1652-1654.
- [50] Haszeldine, R.S., Carbon Capture and Storage: How Green Can Black Be?, *Science*, **2009**, (325), pp. 1647-1652.
- [51] Bottoms, R.R. "Separating Acid Gases", U.S. Patent 1783901, (1930)
- [52] Veawab, A., Tontiwachwuthikul, P. and Chakma, A., Corrosion behavior of carbon steel in the CO₂ absorption process using aqueous amine solutions. *Ind. Eng. Chem. Res.*, **1999**, (38), pp. 3917-3924.
- [53] Bara, J.E., Carlisle, T.K., Gabriel, C.J., Camper, D., Finotello, A., Gin, D.L. and Noble, R.D., Guide to CO₂ Separations in Imidazolium-Based Room-Temperature Ionic Liquids. *Ind. Eng. Chem. Res.*, **2009**, (48), pp. 2739-2751.
- [54] Wilkes, J.S., A short history of ionic liquids - from molten salts to neoteric solvents. *Green Chem.*, **2002**, (4), pp. 73-80.
- [55] Rogers, R.D. and Seddon, K.R., Ionic liquids - Solvents of the future?, *Science*, **2003**, (302), pp. 792-793.
- [56] Seddon, K.R., Ionic liquids - A taste of the future. *Nat. Mater.*, **2003**, (2), pp. 363-365.
- [57] Freemantle, M., Designer solvents - Ionic liquids may boost clean technology development. *Chem. Eng. News*, **1998**, (76), pp. 32-37.
- [58] Heym, F., Etzold, B.J.M., Kern, C. and Jess, A., Analysis of evaporation and thermal decomposition of ionic liquids by thermogravimetric analysis at ambient pressure and high vacuum. *Green Chemistry*, **2011**, (13), pp. 1453-1466.
- [59] Armand, M., Endres, F., MacFarlane, D.R., Ohno, H. and Scrosati, B., Ionic-liquid materials for the electrochemical challenges of the future. *Nat. Mater.*, **2009**, (8), pp. 621-629.
- [60] *Ionic Liquids in Synthesis*. Wasserscheid, P. and Welton, T., Eds., Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, (2008)
- [61] Smith, E.F., Garcia, I.J., Briggs, D. and Licence, P., Ionic liquids in vacuo; solution-phase X-ray photoelectron spectroscopy. *Chem. Commun.*, **2005**, 5633-5635.

- [62] Crowhurst, L., Mawdsley, P.R., Perez-Arlandis, J.M., Salter, P.A. and Welton, T., Solvent-solute interactions in ionic liquids. *Phys. Chem. Chem. Phys.*, **2003**, (5), pp. 2790-2794.
- [63] Zhao, W.J., Zhu, M., Mo, Y.F. and Bai, M.W., Effect of anion on micro/nano-tribological properties of ultra-thin imidazolium ionic liquid films on silicon wafer. *Colloids and Surfaces A: Physicochem. Eng. Aspects*, **2009**, (332), pp. 78-83.
- [64] Xu, W. and Angell, C.A., Solvent-free electrolytes with aqueous solution - Like conductivities. *Science*, **2003**, (302), pp. 422-425.
- [65] Jin, X.X., Yu, L., Garcia, D., Ren, R.X. and Zeng, X.Q., Ionic liquid high-temperature gas sensor array. *Anal. Chem.*, **2006**, (78), pp. 6980-6989.
- [66] Lee, S.Y., Ogawa, A., Kanno, M., Nakamoto, H., Yasuda, T. and Watanabe, M., Nonhumidified Intermediate Temperature Fuel Cells Using Protic Ionic Liquids. *J. Am. Chem. Soc.*, **2010**, (132), pp. 9764-9773.
- [67] Ren, S., Hou, Y., Wu, W., Chen, X., Fan, J. and Zhang, J., Effect of H₂O on the Desulfurization of Simulated Flue Gas by an Ionic Liquid. *Ind. Eng. Chem. Res.*, **2009**, (48), pp. 4928-4932.
- [68] Makino, T., Kanakubo, M., Masuda, Y. and Mukaiyama, H., Physical and CO₂-Absorption Properties of Imidazolium Ionic Liquids with Tetracyanoborate and Bis(trifluoromethanesulfonyl)amide Anions. *J. Solution Chem.*, **2014**, (43), pp. 1601-1613.
- [69] Liu, H., Dai, S. and Jiang, D.-e., Solubility of Gases in a Common Ionic Liquid from Molecular Dynamics Based Free Energy Calculations. *J. Phys. Chem. B*, **2014**, (118), pp. 2719-2725.
- [70] Lee, B.-S. and Lin, S.-T., Screening of ionic liquids for CO₂ capture using the COSMO-SAC model. *Chem. Eng. Sci.*, **2015**, (121), pp. 157-168.
- [71] Kiefer, J., Molina, M.M. and Noack, K., The Peculiar Nature of Molecular Interactions between an Imidazolium Ionic Liquid and Acetone. *Chemphyschem*, **2012**, (13), pp. 1213-1220.
- [72] Hou, Y. and Baltus, R.E., Experimental measurement of the solubility and diffusivity of CO₂ in room-temperature ionic liquids using a transient thin-liquid-film method. *Ind. Eng. Chem. Res.*, **2007**, (46), pp. 8166-8175.
- [73] Easteal, A.J. and Angell, C.A., Phase Equilibria, Electrical Conductance and Density in Glass-Forming System Zinc Chloride and Pyridinium Chloride-A Detailed Low-Temperature Analog of Silicon dioxide and Sodium Oxide system. *J. Phys. Chem.*, **1970**, (74), pp. 3987-3999.
- [74] Vega, L.F., Vilaseca, O., Llovel, F. and Andreu, J.S., Modeling ionic liquids and the solubility of gases in them: Recent advances and perspectives. *Fluid Phase Equilibria*, **2010**, (294), pp. 15-30.
- [75] Wasserscheid, P., Chemistry - Volatile times for ionic liquids. *Nature*, **2006**, (439), pp. 797-797.
- [76] Armstrong, J.P., Hurst, C., Jones, R.G., Licence, P., Lovelock, K.R.J., Satterley, C.J. and Villar-Garcia, I.J., Vapourisation of ionic liquids. *Phys. Chem. Chem. Phys.*, **2007**, (9), pp. 982-990.
- [77] Paulechka, Y.U., Zaitsau, D.H., Kabo, G.J. and Strechan, A.A., Vapor pressure and thermal stability of ionic liquid 1-butyl-3-methylimidazolium Bis(trifluoromethylsulfonyl)amide. *Thermochim. Acta*, **2005**, (439), pp. 158-160.
- [78] Mezger, M., Schramm, S., Schroder, H., Reichert, H., Deutsch, M., De Souza, E.J., Okasinski, J.S., Ocko, B.M., Honkimaki, V. and Dosch, H.,

- Layering of BMIM⁺-based ionic liquids at a charged sapphire interface. *J. Chem. Phys.*, **2009**, (131), pp. 094701.
- [79] Mezger, M., Ocko, B.M., Reichert, H. and Deutsch, M., Surface layering and melting in an ionic liquid studied by resonant soft X-ray reflectivity. *Proc. Natl. Acad. Sci. U S A*, **2013**, (110), pp. 3733-3737.
- [80] Hammer, T., Reichelt, M. and Morgner, H., Influence of the aliphatic chain length of imidazolium based ionic liquids on the surface structure. *Phys. Chem. Chem. Phys.*, **2010**, (12), pp. 11070-11080.
- [81] Hayes, R., Warr, G.G. and Atkin, R., Structure and Nanostructure in Ionic Liquids. *Chemical Reviews*, **2015**, (115), pp. 6357-6426.
- [82] Taylor, A.W., Lovelock, K.R.J., Deyko, A., Licence, P. and Jones, R.G., High vacuum distillation of ionic liquids and separation of ionic liquid mixtures. *Phys. Chem. Chem. Phys.*, **2010**, (12), pp. 1772-1783.
- [83] Goodwin, S.E., Smith, D.E., Gibson, J.S., Jones, R.G. and Walsh, D.A., Electroanalysis of Neutral Precursors in Protic Ionic Liquids and Synthesis of High-Ionicity Ionic Liquids. *Langmuir*, **2017**, (33), pp. 8436-8446.
- [84] Smith, E.F., Rutten, F.J.M., Villar-Garcia, I.J., Briggs, D. and Licence, P., Ionic liquids in vacuo: Analysis of liquid surfaces using ultra-high-vacuum techniques. *Langmuir*, **2006**, (22), pp. 9386-9392.
- [85] Steinrück, H.P., Surface science goes liquid !, *Surf. Sci.*, **2010**, (604), pp. 481-484.
- [86] Rutten, F.J., Tadesse, H. and Licence, P., Rewritable imaging on the surface of frozen ionic liquids. *Angew. Chem. Int. Ed. Engl.*, **2007**, (46), pp. 4163-4165.
- [87] Villar-Garcia, I.J., Fearn, S., Ismail, N.L., McIntosh, A.J.S. and Lovelock, K.R.J., Fine tuning the ionic liquid-vacuum outer atomic surface using ion mixtures. *Chem Commun (Camb)*, **2015**, (51), pp. 5367-5370.
- [88] Hessey, S.G. and Jones, R.G., On the evaporation, bonding, and adsorbate capture of an ionic liquid on Au(111). *Chemical Science*, **2013**, (4), pp. 2519-2529.
- [89] Kolbeck, C., Killian, M., Maier, F., Paape, N., Wasserscheid, P. and Steinrueck, H.-P., Surface characterization of functionalized imidazolium-based ionic liquids. *Langmuir*, **2008**, (24), pp. 9500-9507.
- [90] Lauw, Y., Horne, M.D., Rodopoulos, T., Webster, N.A., Minofar, B. and Nelson, A., X-ray reflectometry studies on the effect of water on the surface structure of [C₄mpyr][NTf₂] ionic liquid. *Phys. Chem. Chem. Phys.*, **2009**, (11), pp. 11507-11514.
- [91] Deyko, A., Lovelock, K.R.J., Licence, P. and Jones, R.G., The vapour of imidazolium-based ionic liquids: a mass spectrometry study. *Phys. Chem. Chem. Phys.*, **2011**, (13), pp. 16841-16850.
- [92] Emel'yanenko, V.N., Verevkin, S.P., Heintz, A., Corfield, J.-A., Deyko, A., Lovelock, K.R.J., Licence, P. and Jones, R.G., Pyrrolidinium-based ionic liquids. 1-butyl-1-methyl pyrrolidinium dicyanoamide: Thermochemical measurement, mass spectrometry, and ab initio calculations. *J. Phys. Chem. B*, **2008**, (112), pp. 11734-11742.
- [93] Lovelock, K.R.J., Deyko, A., Corfield, J.A., Gooden, P.N., Licence, P. and Jones, R.G., Vaporisation of a dicationic ionic liquid. *Chemphyschem*, **2009**, (10), pp. 337-340.
- [94] Foulston, R., Gangopadhyay, S., Chiutu, C., Moriarty, P. and Jones, R.G., Mono- and multi-layer adsorption of an ionic liquid on Au(110). *Phys. Chem. Chem. Phys.*, **2012**, (14), pp. 6054-6066.

- [95] Deyko, A., *et al.*, Measuring and predicting Delta(vap)H298 values of ionic liquids. *Phys. Chem. Chem. Phys.*, **2009**, (11), pp. 8544-8555.
- [96] Deyko, A. and Jones, R.G., Adsorption, absorption and desorption of gases at liquid surfaces: water on C₈C₁Im BF₄ and C₂C₁Im Tf₂N. *Faraday Discuss.*, **2012**, (154), pp. 265-288.
- [97] Visser, A.E., Swatloski, R.P., Reichert, W.M., Mayton, R., Sheff, S., Wierzbicki, A., Davis, J.H. and Rogers, R.D., Task-specific ionic liquids for the extraction of metal ions from aqueous solutions. *Chem. Comm.*, **2001**, 135-136.
- [98] Seddon, K.R., Stark, A. and Torres, M.J., Influence of chloride, water, and organic solvents on the physical properties of ionic liquids. *Pure Appl. Chem.*, **2000**, (72), pp. 2275-2287.
- [99] Hu, Y.F., Liu, Z.C., Xu, C.M. and Zhang, X.M., The molecular characteristics dominating the solubility of gases in ionic liquids. *Chem. Soc. Rev.*, **2011**, (40), pp. 3802-3823.
- [100] Anthony, J.L., Anderson, J.L., Maginn, E.J. and Brennecke, J.F., Anion effects on gas solubility in ionic liquids. *J. Phys. Chem. B*, **2005**, (109), pp. 6366-6374.
- [101] Anderson, J.L., Dixon, J.K. and Brennecke, J.F., Solubility of CO₂, CH₄, C₂H₆, C₂H₄, O₂, and N₂ in 1-hexyl-3-methylpyridinium bis(trifluoromethylsulfonyl)imide: Comparison to other ionic liquids. *Acc. Chem. Res.*, **2007**, (40), pp. 1208-1216.
- [102] Shannon, M.S., Tedstone, J.M., Danielsen, S.P.O., Hindman, M.S., Irvin, A.C. and Bara, J.E., Free Volume as the Basis of Gas Solubility and Selectivity in Imidazolium-Based Ionic Liquids. *Ind. Eng. Chem. Res.*, **2012**, (51), pp. 5565-5576.
- [103] Liu, H., Dai, S. and Jiang, D.E., Molecular Dynamics Simulation of Anion Effect on Solubility, Diffusivity, and Permeability of Carbon Dioxide in Ionic Liquids. *Ind. Eng. Chem. Res.*, **2014**, (53), pp. 10485-10490.
- [104] Cadena, C., Anthony, J.L., Shah, J.K., Morrow, T.I., Brennecke, J.F. and Maginn, E.J., Why is CO₂ so soluble in imidazolium-based ionic liquids?, *J. Am. Chem. Soc.*, **2004**, (126), pp. 5300-5308.
- [105] Kazarian, S.G., Briscoe, B.J. and Welton, T., Combining ionic liquids and supercritical fluids: in situ ATR-IR study of CO₂ dissolved in two ionic liquids at high pressures. *Chem. Commun.*, **2000**, 2047-2048.
- [106] Damas, G.B., Dias, A.B.A. and Costa, L.T., A Quantum Chemistry Study for Ionic Liquids Applied to Gas Capture and Separation. *J. Phys. Chem. B*, **2014**, (118), pp. 9046-9064.
- [107] Zahn, S., MacFarlane, D.R. and Izgorodina, E.I., Assessment of Kohn-Sham density functional theory and Moller-Plesset perturbation theory for ionic liquids. *Phys. Chem. Chem. Phys.*, **2013**, (15), pp. 13664-13675.
- [108] Carrete, J., Mendez-Morales, T., Cabeza, O., Lynden-Bell, R.M., Gallego, L.J. and Varela, L.M., Investigation of the Local Structure of Mixtures of an Ionic Liquid with Polar Molecular Species through Molecular Dynamics: Cluster Formation and Angular Distributions. *J. Phys. Chem. B*, **2012**, (116), pp. 5941-5950.
- [109] Stogryn, D.E. and Stogryn, A.P., Molecular Multipole Moments. *Mol. Phys.*, **1966**, (11), pp. 371-393.
- [110] Watanabe, M., Kodama, D., Makino, T. and Kanakubo, M., CO₂ absorption properties of imidazolium based ionic liquids using a magnetic suspension balance. *Fluid Phase Equilibria*, **2016**, (420), pp. 44-49.

- [111] Baltus, R.E., Culbertson, B.H., Dai, S., Luo, H.M. and DePaoli, D.W., Low-pressure solubility of carbon dioxide in room-temperature ionic liquids measured with a quartz crystal microbalance. *J. Phys. Chem. B*, **2004**, (108), pp. 721-727.
- [112] Muldoon, M.J., Aki, S., Anderson, J.L., Dixon, J.K. and Brennecke, J.F., Improving carbon dioxide solubility in ionic liquids. *J. Phys. Chem. B*, **2007**, (111), pp. 9001-9009.
- [113] Van Ginderen, P., Herrebout, W.A. and van der Veken, B.J., van der Waals complex of dimethyl ether with carbon dioxide. *J. Phys. Chem. A*, **2003**, (107), pp. 5391-5396.
- [114] Hanioka, S., Maruyama, T., Sotani, T., Teramoto, M., Matsuyama, H., Nakashima, K., Hanaki, M., Kubota, F. and Goto, M., CO₂ separation facilitated by task-specific ionic liquids using a supported liquid membrane. *J. Membr. Sci.*, **2008**, (314), pp. 1-4.
- [115] Willmott, P., *An Introduction to Synchrotron Radiation: Techniques and Applications*. Eds., John Wiley and Sons, Chichester, (2011)
- [116] Margaritondo, G., *Elements of Synchrotron Light for Biological, Chemical and Medical Research*. Eds., Oxford University Press, New York, (2002)
- [117] Bedzyk, M.J., Bommarito, G.M., Caffrey, M. and Penner, T.L., Diffuse Double Layer at a Membrane-Aqueous Interface Measures with X-ray Standing Waves. *Science*, **1990**, (248), pp. 52-56.

Chapter 2

Background theory

2.1. Application of vacuum techniques

The experiments described within this thesis were all performed under ultra-high vacuum (UHV) conditions, with background pressures during measurements being below 1×10^{-9} mbar (not including surface preparation pressures which reached 2×10^{-6} mbar). Despite the fact that very few real world processes occur under UHV conditions (atmospheric pressure is ≈ 1000 mbar) application of UHV techniques is vital in gaining a fundamental understanding of everyday processes. The low pressures used in vacuum science result in longer mean free paths (average distance a species can travel before a collision occurs) for species within the vacuum chamber and hence fewer collisions of gaseous molecules with other species in the vacuum. The mean free paths for N_2 at 300 K and atmospheric pressure (1.01325 bar) can be calculated to be ≈ 68 nm, whereas under vacuum (1×10^{-7} mbar) and at 300 K the average distance travelled before a collision with another gas molecule is ≈ 680 m [1], which is larger than most vacuum chambers. As a result it is unlikely that species desorbing from a surface will be scattered prior to detection. Further to the increased mean free path of desorbing species using low pressures reduces the impingement rate (which is directly proportional to pressure) of molecules upon a surface such that at a pressure of 1×10^{-9} mbar a molecule hits a surface of area 1 cm^2 every 1000 seconds, on average [1]. The advantage of this is that a surface which has been prepared can be studied in the absence of collisions and interference from other contaminating species, allowing conclusions to be made on the interactions of the molecules that have been placed on the surface rather than having to consider the possible effect of the contaminant. Using UHV conditions reduces the number of variables within the experiment by simplifying the system somewhat.

Vacuum science also allows the use of experimental techniques which cannot be used under ambient conditions, often due to the short mean free paths of different species that can be studied. UHV conditions allow the detection of photoelectrons, which are readily absorbed or scattered by matter [1, 2], giving

elemental discrimination of species adsorbed upon a surface in techniques such as X-ray photoelectron spectroscopy (XPS). Near ambient pressure XPS techniques have been developed, in which the sample is held in a cell at higher pressure (over 1 mbar [3] and up to 250 mbar [4]) however the photoelectrons still pass into vacuum to be studied, as they have short mean free paths at elevated pressures. Apparatus such as mass spectrometers, providing identification of molecules based upon their mass to charge (m/z) ratios and fragmentation patterns, can be utilised to detect material desorbing from a surface in techniques such as temperature programmed desorption (TPD). Under ambient conditions this desorbing material would be scattered by background gases and there would be large signals being detected due to the background molecules making the species of interest harder to detect. To some extent this could be remedied by performing a subtraction of the background signals but there would still be a small signal to noise ratio.

Since vacuum chambers operate at low pressures the quantity of gas adsorbed to the walls of the vacuum chamber or the vacuum components becomes a factor which requires consideration. This is in contrast to ambient pressure studies within a chamber where the amount of gas adsorbed on the surface of the chamber is reasonably small in relation to the quantity of gas within the chamber. The result of having to consider species adsorbed onto the walls is that vacuum chambers will exhibit a memory effect, meaning that if a particular substance is released into the vacuum system it will adsorb to the walls and may slowly desorb from these surfaces over time, resulting in a persistent peak in whichever spectra are collected [1]. As with any desorption process application of heat can accelerate the desorption rate (a process referred to as baking), however this is not usually performed mid-experiment. As a result it may be necessary to consider 'wait' stages to allow desorption of species from the chamber walls, as performed within the CO₂ TPD studies discussed in this work, resulting in a lower background pressure and a better signal to noise ratio in collected data.

2.2 X-ray interaction with matter

Wilhelm Röntgen discovered X-rays on the 8th of November 1895 when observing that photosensitive films detected some form of radiation when covered by an optically opaque screen [5]. Röntgen immediately began utilising these X-rays for imaging materials and observed that materials consisting of light atoms (such as wood and flesh) were not as effective at attenuating the X-rays as materials made of heavy atoms (metal and bone) [6]. This was the first observation that X-rays were attenuated differently in different materials and gave birth to the use of X-rays in medical imaging, which was implemented just 3 months after the discovery of X-rays [5]. Further study of the interaction of X-rays with matter led to the discovery that X-rays were refracted from materials slightly differently to the way other light sources were refracted. It was observed, by Compton, that X-rays underwent total external reflection at grazing angles indicating that the refractive index of X-rays within matter is less than unity, with Compton measuring a value of 0.999995 from crown glass with an X-ray wavelength of 0.1279 nm (≈ 9700 eV) [5, 7]. Discussions relating to X-ray interactions in matter can be found in many textbooks, [5, 8-10], with a summary given in this work. The refractive index, n , of X-rays within any material can be written in the form

$$n = 1 - \delta - i\beta \quad \text{Equation 2.1}$$

where δ is the refractive index decrement, i represents the quantity $\sqrt{-1}$ and β is the X-ray absorption index [5, 10]. The values of δ and β depend on both the material to be studied and the X-ray energy or wavelength and have small values, with δ typically $\approx 10^{-4}$ and β typically $\approx 10^{-6}$, which can be estimated to a high degree of accuracy through predictive formulae [11].

$$n_1 \cos(\alpha_1) = n_2 \cos(\alpha_2) \quad \text{Equation 2.2}$$

Snell's law, eq 2.2, describes how the incident angle, α_1 , and the refracted angle, α_2 , are related for transmission of light across a boundary between two media of refractive indices n_1 and n_2 , as shown in fig. 2.1. Consider the case of an X-ray incident upon a surface under vacuum (so $n_1 = 1$ and α_1 shall be referred to as α) and n_2 is known to be less than 1 (eq 2.1). Mathematically the value of $\cos(\alpha_2)$ cannot be greater than 1, so there exists the case for small values of α (those below some critical angle, α_c) that Snell's law cannot be satisfied. It is in

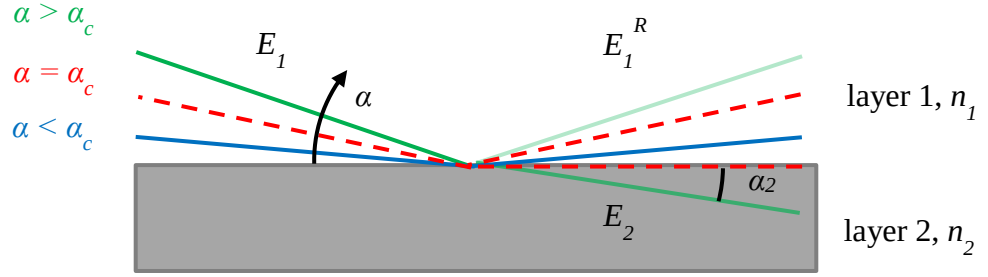


Figure 2.1: A diagrammatic representation of the way in which X-rays (with electric field strength E_1) at different incident angles, α , relative to the critical angle, α_c , reflect and refract (with transmitted angle α_2) from an interface between two layers. For incident angles below the α_c (blue lines) the X-ray is totally reflected, with the reflected angle the same as the incident angle, while an evanescent wave decaying into the reflector. For angles greater than α_c (green lines) a component of the incident X-ray is reflected (E_1^R) while the rest is transmitted (E_2). When the incident angle is equal to α_c (red dashed lines) then the transmitted component of the X-ray travels across the surface of the reflector.

this small angular regime that the incident X-ray beam is being totally reflected by the surface, blue line in fig. 2.1. The critical angle (in radians) can be estimated through evaluation of $\alpha_c \approx (\sqrt{2\delta})$ (derived in section 2.3.5) [10]. Total reflection of the incident X-ray continues as the angle of incidence is increased to the critical angle, $\alpha = \alpha_c$, at which point a travelling wave is also transmitted across the surface of the reflector, shown by the dashed red lines in fig. 2.1. Increasing the incident angle past the critical angle results in the reflected component of the X-ray decaying as the proportion of the X-ray transmitted into the surface increases, shown by the green line in fig. 2.1. It is this total reflection of the X-rays that is utilised to set up the standing wave in the variable period X-ray standing wave technique described in sections 1.1.1 and 1.3, and shall be discussed in more detail in section 2.3. In the case where multiple layers exist within a surface the presence of multiple interfaces results in multiple reflections and refractions (section 2.3).

For grazing angles of incidence the total external reflection is not truly ‘total’ as an evanescent wave penetrates the surface of the reflector, but its intensity decays rapidly with distance into the surface and the wave has a short, angle dependent, penetration depth into the surface [9, 10]. For angles of incidence greater than the critical angle X-rays penetrate the surface (being refracted slightly) and can interact with the material within the surface. X-rays interact with the electrons within a material and can either be scattered or absorbed, with the likelihood of interaction depending on the electron density

and the X-ray energy [10]. It is the scattering of X-rays by the electrons that leads to the reflection and refraction of X-rays, which has been discussed, with denser materials (such as gold) being better X-ray reflectors than materials such as silicon. This allows experimental techniques such as X-ray reflectivity to probe the electron density perpendicular to the surface plane to detect layering [8, 12]. In order to detect the elemental composition of a surface, absorption of the X-ray photons must be considered.

2.2.1. Absorption of X-rays by matter

X-rays, like all electromagnetic waves, can be considered as both particles and waves [13]. The macroscopic interaction of X-rays with matter, such as refraction and reflection, can be described by treating the X-ray as a wave which scatters from the electrons in the surface. In order to understand the absorption of X-rays by matter and the various processes which occur as a result of this absorption X-rays must be considered as particles, or photons. The photoelectric effect, characterised by the Einstein equation, eq 2.3, describes the properties of the photoelectron that is generated upon absorption of a photon and subsequent ionisation of the atom [13, 14].

$$KE = h\nu - \phi - BE \quad \text{Equation 2.3}$$

Equation 2.3 gives the relationship between the energy of the incident photon of energy, $h\nu$ (h is Planck's constant and ν is frequency in Hz), the effective binding energy of the electron, BE , the kinetic energy of the photoelectron, KE and the work function, ϕ . The work function accounts for the difference between the Fermi level (the energy halfway between the highest occupied energy level and the lowest unoccupied energy level at 0 K) and the vacuum level (energy at which the photoelectron is at rest 'just outside' the atom) and captures all of the uncertainties involved with surface contact potentials and the detector work function. The work function can be considered as a constant for a given experimental setup with a given surface but may vary if the surface is modified as the surface charging may vary, though is typically no larger than 5 eV [14]. It can be seen, from eq 2.3, that for a fixed photon energy and work function that the photoelectron kinetic energy is dependent upon the effective binding energy of the electron that has been ionised. It is these kinetic energies that are measured

in X-ray photoelectron spectroscopy (XPS) to characterise the material on the surface (section 2.2.2). A schematic of the processes occurring in photoemission is shown in fig. 2.2. In the example shown the incoming photon ($h\nu$) is absorbed by an electron, a core electron from the 1s orbital in fig. 2.2a (blue circle). Figure 2.2b shows the generation of a photoelectron with kinetic energy, KE (dictated by eq 2.3) and a core hole, $h^{\bullet+}$ (an electron deficiency).

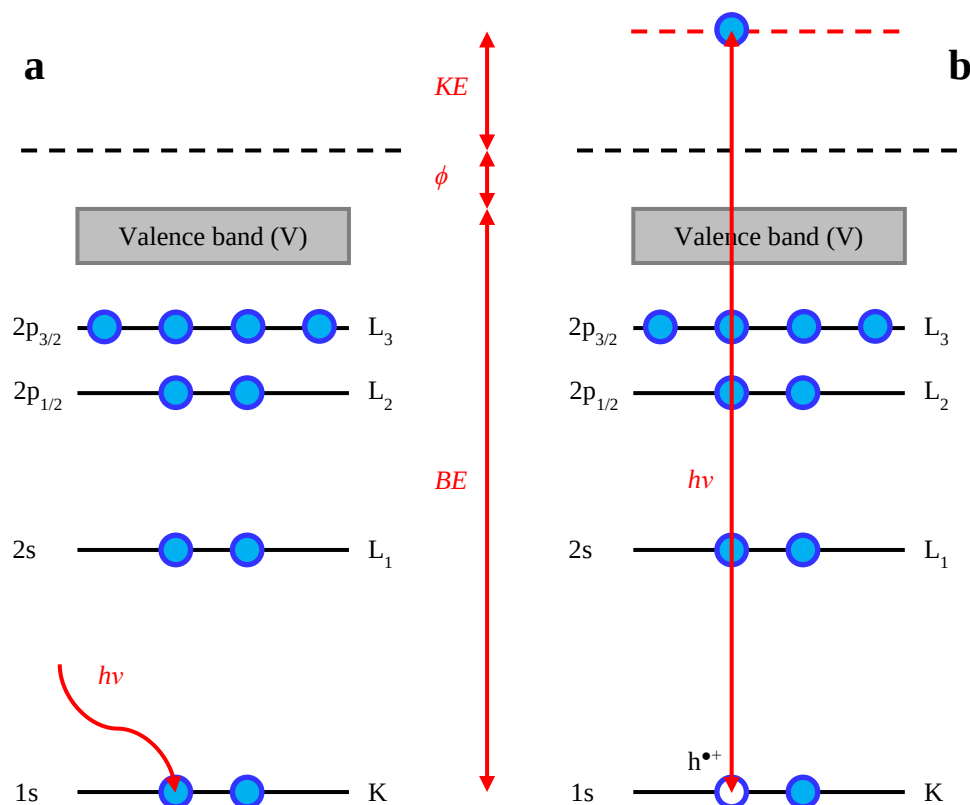


Figure 2.2: A diagram representing the photoemission process after (a) absorption of a photon with energy $h\nu$ by an electron (blue circle) in the 1s (K) level. (b) For sufficiently large photon energies ionisation leaves behind a core hole in the 1s level and generates a photoelectron with kinetic energy, KE , given by eq 2.3. The dashed black lines represent the vacuum level while the dashed red line represents the energy that is an energy $h\nu$ above the 1s level.

Often the binding energy of a photoelectron peak is quoted in XPS, rather than the kinetic energy. This is a result of the fact that the binding energies of the detected photoelectrons from a given core level (e.g. C 1s) do not vary with photon energy, whereas the kinetic energies do. Tables of electron binding energies exist allowing the peaks in the electron distribution curves (EDCs) to be identified and help elucidate the surface composition [14, 15]. The calculated binding energy can be used to identify not only the element that has emitted the photoelectron but also the chemical state that the atom is in, through analysis of initial state effects, also called chemical shifts [14, 16], assuming final state

effects (due to the core hole) are assumed to be constant. This is demonstrated within fig. 2.3 where two different carbon environments exist, one bound to another carbon atom (fig. 2.3a) and one where the carbon is bound to a nitrogen atom (fig. 2.3b). In the case where the carbon is bound to the nitrogen, the more electronegative nitrogen atom draws electron density away from the carbon, leaving the carbon in a slightly more electropositive environment. This means



Figure 2.3: An illustration of the initial state effects observed for two different carbon environments, in which the bonding environment of the photoelectron emitter affects the photoelectron kinetic energy, which in turn affects the apparent binding energies of the C 1s photoelectrons. The fact that the carbon in (b) is in an electropositive environment makes extraction of electrons more difficult, resulting in lower photoelectron kinetic energies than in neutral (a) or electronegative carbon environments.

that the carbon atom bound to the nitrogen will bind its core electrons more than the carbon atom which is bound to another carbon, resulting in a photoelectron with a lower kinetic energy and a higher binding energy. The observed effect in the photoelectron signal is a separation of the total signal into two states, which may be able to be fitted with two components, assuming the resolution is high enough and there are not too many other overlapping chemical states. For a C 1s electron in a simple hydrocarbon molecule the typical binding energy is 284.0 to 285.5 eV whilst carbon bound to nitrogen has a binding energy of 285.5 to 288.5 eV [14] depending on the system.

After generation of the photoelectron and core hole in the surface the excited atom will relax into its ground state, through an electron in a higher level decaying into the core hole level. The energy gained from this decay can either be used to generate an Auger electron or can generate an X-ray photon, as shown in fig. 2.4 [10, 14]. Figure 2.4a shows the processes that occur in Auger electron generation, where an electron in a higher level ($2p_{1/2}$ or L_2 level) relaxes into the core hole (1s or K level). This releases an energy equal to $BE(K) - BE(L_2)$ which can then be used to ionise an electron from the $2p_{3/2}$ (or L_3) level (purple arrow). The resulting Auger electron (referred to as a KL_2L_3 Auger electron due to the levels involved) will have kinetic energy approximately equal to

$$KE(KL_2L_3) = BE(K) - BE(L_2) - BE(L_3) - \phi \quad \text{Equation 2.4}$$

if interactions between the core holes and relaxations are neglected [10, 14]. It can be seen in eq 2.4 that the kinetic energy of an Auger electron does not depend on the X-ray photon energy as the X-ray only generates the core hole while the energy depends on the transitions between electron levels. Figure 2.4b shows the pathway for an atom with a core hole to relax, involving emission of a photon. As the transitions occur between bound electronic states they must obey

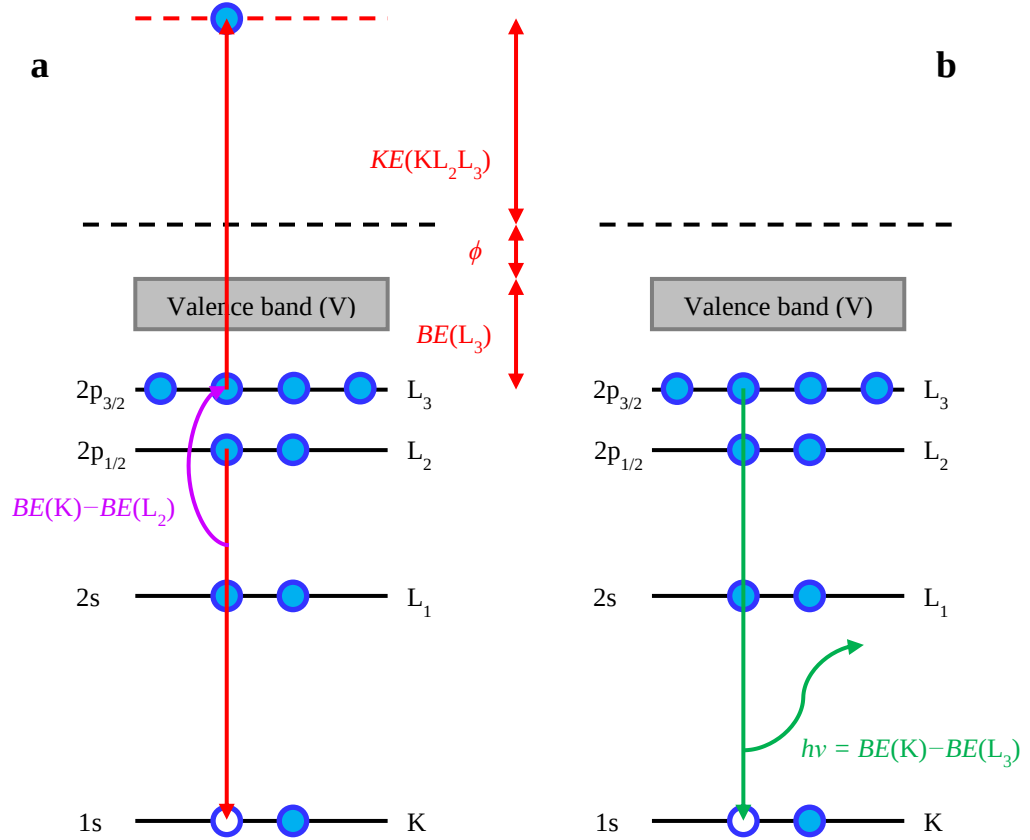


Figure 2.4: Energy level diagrams showing the two main competing methods for relaxation of an electron (filled blue circle) into a core hole (empty blue circle), either by (a) emission of an Auger electron or (b) emission of an X-ray photon. In the Auger emission the energy gained from an electron decaying into a core hole is transferred to another electron (purple line) to ionise that electron. In the X-ray fluorescence process the energy gained from an electron decaying into the core hole is released as an X-ray photon.

the selection rules $\Delta l = \pm 1$ (orbital angular momentum) and $\Delta s = 0$ (spin angular momentum) [10]. In fig. 2.4b an electron from the L₃ level decays into the K level emitting a $K\alpha_1$ photon (green arrow, in general any electron decaying from an L level to a K level is referred to as a $K\alpha$ photon with the subscripts used to denote spin orbit splitting). Auger electron emission and X-ray fluorescence are the main competing processes for relaxation of excited atoms [17] with Auger emission being the dominant decay process for lighter elements and

fluorescence being the more dominant process for heavier elements (cross over occurs at an atomic number ≈ 30 , zinc) [5, 10, 14]. As the emitter relaxes (usually over a time period of 100 fs [10, 14]) it is positively charged, doubly so if Auger emission has occurred, which can have an effect upon the outgoing photoelectron. Furthermore in cases where an electrical insulator is adsorbed upon a metallic conductor the motion of electrons from the metal to the adsorbed layer can also affect the photoelectron. These are referred to as final state effects (effects reliant upon the state of the photoelectron emitter after photoemission) and are usually neglected due to their small size in comparison to initial state effects (chemical shifts) [16].

2.2.2. Photoelectrons as a surface probe

It was discussed in section 2.2.1 that photoelectrons are generated as a consequence of the absorption of X-rays by matter. The photoelectrons that are generated have kinetic energies that can be measured by a concentric hemispherical analyser (CHA) to allow binding energies to be calculated using eq 2.3. The X-rays have attenuation lengths on the order of 1 μm in silicon for an X-ray at 1000 eV and 10 μm in silicon at 10000 eV [10], hence are not very surface sensitive. Photoelectrons are generated whenever X-rays interact with matter and are an effective tool to probe the surface structure of a material. This is a result of the short attenuation lengths, λ , of the photoelectrons with kinetic energies of ≈ 10 to 500 eV within matter giving $\lambda \approx 0.1$ to 3 nm [1, 2, 18]. The attenuation length encapsulates the scattering that occurs from both inelastic collisions (ones where energy is lost from the photoelectron, characterised by the inelastic mean free path, IMFP) and elastic collisions (where energy is conserved but the velocity of the electron has varied) of electrons with matter. The Beer–Lambert law, eq 2.5, can be used to give an expression for the intensity, I_d , of photoelectrons emitted from a thin layer of material a distance d below the surface, as shown in fig. 2.5.

$$I_d = I_0 \exp\left(\frac{-d}{\lambda \cos(\theta)}\right) \quad \text{Equation 2.5}$$

I_0 represents the photoelectron intensity measured from an uncovered layer of the material being probed (the blue species in fig. 2.5) and θ represents the angle between the surface normal and the detector vector. In many XPS setups the

value of θ is 0, meaning that $\cos(\theta) = 1$, however θ can be used to make the photoelectrons even more surface sensitive. By tilting the sample (increasing θ , fig. 2.5b) the photoelectrons from the blue layer of material travel through a greater quantity of green material, than when $\theta = 0^\circ$, leading to greater attenuation. This results in signal from the deepest layers being totally attenuated and hence increases the proportion of signal that is due to species closer to the surface. This is the principle behind angle-resolved XPS (ARXPS) which increases the surface sensitivity for a fixed photon energy, allowing enhancement of signal from the topmost layers of the surface.

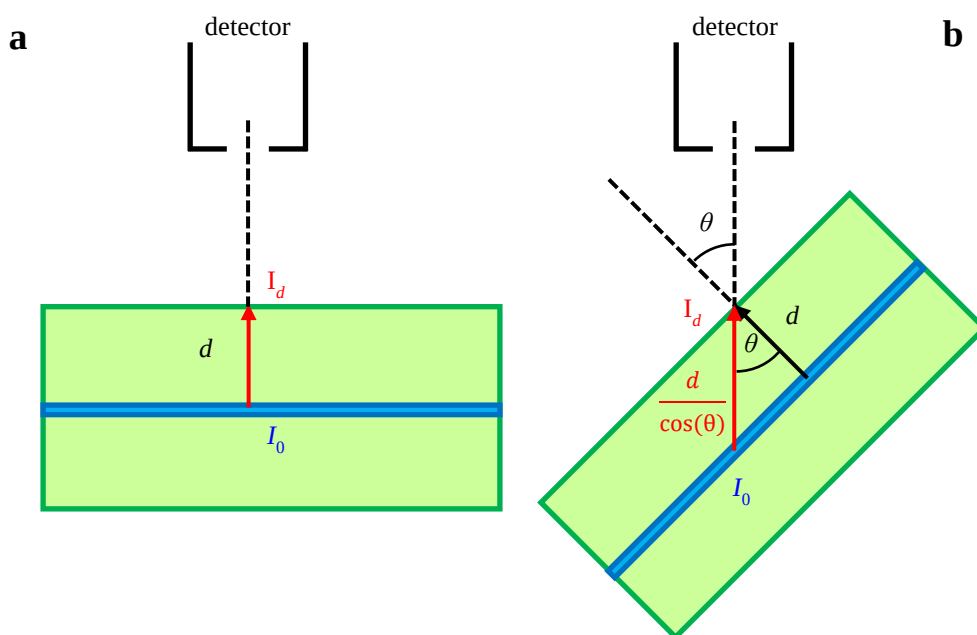


Figure 2.5: Diagrams illustrating the change in path length, and hence effect on photoelectron intensity through application of eq 2.5, for a sample in which the surface normal deviates from the detector vector by an angle θ . The diagram in (a) shows the setup when the surface normal points along the detector vector and a photoelectron emitter at a depth, d , with an emitted intensity I_0 , has a path length equal to d through the material. In (b) the angular deviation means that the photoelectron path length through the material is $d/\cos(\theta)$. Note that in (a) $\theta = 0$ so $\cos(\theta) = 1$, giving $d/\cos(\theta) = d$.

The surface sensitivity of photoelectrons can also be tuned through variation of the attenuation lengths, which depend upon the kinetic energies of the photoelectrons that have been produced from the surface. It can be observed from the universal electron curve for inelastic mean free paths [2] that as the electron energy is increased or decreased too much the IMFP increases, with a minimum in the IMFP of ≈ 1 nm occurring at ≈ 50 eV [1, 2, 18]. In order to probe thicker surface layers with photoelectrons the X-ray photon energy can be increased in order to generate photoelectrons with larger KE s, eq 2.3. The

disadvantage to this is that as the X-ray energy is increased the X-ray absorption cross section decreases [5, 10, 15]. The absorption cross section varies with $h\nu^{-3}$ but increases with atomic number as Z^4 [10]. For carbon (graphite) changing the photon energy from 1 keV to 10 keV results in a drop in the absorption coefficient by a factor of ≈ 100 , but the IMFP increases from ≈ 1.4 nm to ≈ 12 nm [18] allowing films 10 times thicker to be probed. Through use of synchrotron sources with high intensity X-ray beams the decrease in the absorption coefficient from increasing the photon energy can be somewhat negated, however X-ray induced effects such as surface charging and damage need to be considered [14, 19-21]. This X-ray damage can take many forms, such as bond breaking, cross linking, charge accumulation and stimulated desorption, as discussed in detail in chapter 9 of ref. [14]. These processes can occur either due to the irradiation by X-rays or by the generation of an intense photoelectron flux from a substrate by the X-ray photons. If damage is a significant issue it is advised that reduction of the X-ray flux will reduce the rate of damage of a surface, alternatively collection of spectra in a shorter time through reduction of the detector counting time (reducing the resolution) can help minimise sample damage [14]. It has also been observed that reducing the sample temperature can reduce the rate of damage to a surface, which is not solely explained by an Arrhenius factor, indicating that the effect is not simply due to reduced diffusion rates [22].

2.2.3. Calculating photoelectron attenuation lengths

The attenuation lengths for the photoelectrons studied within this work were estimated from the inelastic mean free paths (IMFP) using the relationship $\lambda = 0.8 \times \text{IMFP}$ [14]. The IMFPs can be estimated to a reasonable degree of accuracy (10% error compared to experimental measurements) using the TPP (Tanuma, Powell and Penn) method [18, 23, 24]. A program (NIST IMFP database) exists for calculating the IMFP for photoelectrons using this model for kinetic energies in the range 50 to 2000 eV based on the chemical formula, density, number of valence electrons and band gap [25], however this range does not cover all the photoelectron KEs that are used in this work. It was therefore necessary to estimate the IMFPs of photoelectrons through the different layers

based upon the calculation of IMFPs for high energy photoelectrons in ref. [18]. The two materials that the photoelectrons had to travel through in this work were a silicon oxide layer and a layer of frozen $[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]$, CHCl_3 and H_2O (organic material).

For the silicon oxide layer it was assumed that the attenuation properties would be similar to silica (SiO_2), which was a material for which values could be calculated in the computer database [25], meaning that the constants in the TPP equation had been optimised. The IMFP values for photoelectrons travelling at 1800 eV and 2000 eV through silica were calculated, using the program, to be 46.36 Å and 50.43 Å. A linear extrapolation was then performed to calculate the IMFP (Å) for the Si 2p and O 1s photoelectrons travelling through the silicon oxide layer with a given KE (eV) using the equation

$$IMFP_{\text{SiO}_2} = 50.43 + (KE - 2000) \times \frac{4.07}{200} \quad \text{Equation 2.6}$$

The values of 68.7 Å and 59.9 Å were calculated for photoelectrons with KE s of 2900 eV and 2467.7 eV (Si 2p and O 1s, respectively) and are shown in table 4.1. IMFPs for SiO_2 had not been calculated at high electron energies so comparison of the extrapolated IMFPs with literature values was not possible, however it was possible to compare the calculated IMFPs with those for silicon [18]. For a photoelectron with $KE \approx 1800$ eV through Si the IMFP was 39.2 Å, which is 7.16 Å less than what the database gave for SiO_2 (which was 46.36 Å). If the linear extrapolation is valid then similar differences should be observed for photoelectrons with other kinetic energies (assuming the rate of change in IMFP with energy is the same for Si and SiO_2). For photoelectrons with $KE \approx 2440$ eV (O 1s) the high energy calculation through Si gave an IMFP of 50.1 Å while the extrapolation for SiO_2 gave an IMFP of 59.4 Å, representing a difference of 9.3 Å. For the Si 2p photoelectron, the IMFP calculated for an electron with $KE \approx 2980$ eV through Si was 59.2 Å, while the extrapolated value for SiO_2 gave 70.4 Å, a difference of 11.2 Å. The differences observed for the extrapolation are of the correct order of magnitude (around 10 Å) but show that this extrapolation may not be the perfect method for obtaining the IMFPs, but does serve as a reasonable estimate.

For the layer composed of $[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]$, CHCl_3 and H_2O the photoelectron attenuation properties were assumed to be the same as glassy

carbon, for which IMFPs have been calculated for high electron KE s. This meant that an interpolative method could be used for finding the IMFPs within the organic layer. For photoelectron energies of 1998.2 eV and 2981.0 eV the IMFPs for the electrons transmitted through glassy carbon were calculated as 46.8 Å and 65.0 Å, respectively [18]. Assuming a linear interpolation this gave a gradient of $\Delta IMFP / \Delta KE = 18.2 / 982.8 \text{ Å eV}^{-1}$. Using this interpolation on data points within ref. [18] reproduced the IMFPs to 0.1 Å, suggesting that linear interpolation would be an appropriate method for calculating the IMFPs over this energy range. Since it is expected that there will be some difference between the glassy carbon and the organic layer that is being studied the IMFP for photoelectron attenuation within $[C_8C_1Im][BF_4]$ was calculated at 1998.2 eV, to allow a correction to be applied to convert from glassy carbon values to organic layer values. Using the TPP predictive formula in the NIST IMFP database [25] with a density of 1.115 g cm^{-3} [26], band gap of 8.2 eV [27], and 112 valence electrons an IMFP for an electron with $KE = 1998.2 \text{ eV}$ through $[C_8C_1Im][BF_4]$ was found to be 55.0 Å. It can be seen that this is 8.2 Å larger than for the glassy carbon so a correction of 8.2 Å must be added to the interpolated glassy carbon values to give IMFPs for photoelectrons through the organic layer (assumed to behave like the IL). The equation for calculating the IMFPs (Å) of a photoelectron with kinetic energy, KE (eV), transmitted through the organic layer used in this study is therefore

$$IMFP_{organic} = 46.8 + 8.2 + (KE - 1998.2) \times \frac{18.2}{982.8} \quad \text{Equation 2.7}$$

The “46.8” is the IMFP for a photoelectron with $KE = 1998.2 \text{ eV}$ travelling through glassy carbon and is the starting point for the interpolation while the “+8.2” is the required shift to correct the glassy carbon IMFP to the $[C_8C_1Im][BF_4]$ (which represents the organic layer) IMFP. This equation has been used to obtain the values of IMFP (and hence λ) used in this study, shown in table 4.2. These IMFPs (and hence attenuation lengths) are calculated assuming that the IL layer is in a form which has its normal liquid density, whereas the IL was deposited on a cooled surface producing what is assumed to be a less dense IL ‘snow’. The effects of the IL being in a snow-like morphology on the IMFP has not been accounted for, although it is believed that the IMFPs (and λ values) would increase in a less dense medium.

2.3. Variable period X-ray standing wave analysis

X-ray standing wave techniques were introduced in section 1.1.1 with a discussion of the different ways of generating X-ray standing waves. In the VPXSW technique the total reflection of X-rays from a surface is utilised to generate a reflected wave, of the same wavelength as the incident X-ray, allowing superposition of the incident and reflected waves to generate a standing wave above the reflector surface. This was mentioned in section 2.2 where it was discussed that for incident angles (α) below some critical angle (α_c , which is material dependent) the X-ray would be totally reflected, and for α larger than α_c the proportion of the X-ray that is reflected will decay as the X-ray is transmitted into the surface. The theory behind the reflection of X-rays from a polished surface using dynamic X-ray theory is based on work by Parratt in 1954 [12] with the topic being covered in many text books [8-10], whilst texts on the theory for VPXSW with X-ray fluorescence can be found in refs. [28-31]. The key procedures and results from these works are summarised in the following section.

2.3.1. Variable period standing wave intensity above a semi-infinite reflector

When looking at the reflection and refraction of X-rays by a surface the angles involved are very small (tens of milliradians) meaning that small angle approximations for expansions of (mainly trigonometric) functions are appropriate [9]. In a system with multiple layers the angle of refraction, in radians (all the angles considered will be in radians), within any given layer can be found using Snell's law (eq 2.2) and the expansion of cosine to a series with the small angle approximation [32]

$$\cos(x) = 1 - \frac{x^2}{2!} + \frac{x^4}{4!} - \dots \approx 1 - \frac{x^2}{2} \quad \text{Equation 2.8}$$

Considering a surface under vacuum ($\delta_1 = \beta_1 = 0$), and using the assumption that δ_m , β_m and α_m are suitably small such that combinations of these with power 3 or higher are neglected, and that δ_m and β_m are so small that any combination of these with power 2 or higher can be neglected then the angle of refraction of an

incident X-ray beam upon the m^{th} layer of a multilayer system with N layers will be [12, 29]

$$\alpha_m = (\alpha_1^2 - 2\delta_m - 2i\beta_m)^{1/2} \quad \text{Equation 2.9}$$

where α_1 is the incident angle (the same as α) in radians from within the $m = 1$ layer (vacuum). It can be seen that for a hypothetical interface between 2 layers of vacuum (where no refraction is expected) the refracted angle in the 2nd vacuum layer ($m = 2$), α_2 , would be equal to $(\alpha_1^2)^{1/2} = \alpha_1$ as δ_2 and β_2 would both equal zero for a vacuum layer. Considering now the interface between the first layer (vacuum) and a second layer consisting of a semi-infinite reflector (with non-zero values for δ_2 and β_2), as depicted in fig. 2.1, the X-ray incident upon the interface from the first layer ($m = 1$) has the form of a plane wave with an amplitude, E_1 , wave vector, $\mathbf{k}_1$, and propagates in the direction dictated by the vector, $\mathbf{r}$.

$$\psi_1 = E_1 \exp(i\mathbf{k}_1 \cdot \mathbf{r}) \quad \text{Equation 2.10}$$

The component of the wave which is reflected can be described by an amplitude, E_1^R , and a wave vector, $\mathbf{k}_1^R$, whilst the component of the wave transmitted into the second layer is described by the amplitude, E_2 , and the wave vector, $\mathbf{k}_2$, whilst the angle of refraction, α_2 , can be calculated using eq. 2.9. In order to calculate the proportion of the X-ray incident upon the interface between layers 1 and 2 that is reflected and transmitted the Fresnel reflection coefficient, $F_{1,2}^R$, and Fresnel transmission coefficient, $F_{1,2}^T$, are used [9, 12]. These represent the proportion of the X-ray amplitude (not the intensity, which is the absolute square of the amplitude) that is reflected or transmitted at an interface and are derived from consideration of Snell's law and the fact that at a phase boundary the wave and its derivative must be continuous [9]. For the 2 layer system discussed here the Fresnel coefficients can be calculated as [9, 12].

$$F_{1,2}^R = \frac{E_1^R}{E_1} \approx \frac{\alpha - \alpha_2}{\alpha + \alpha_2} \quad \text{Equation 2.11}$$

$$F_{1,2}^T = \frac{E_2}{E_1} \approx \frac{2\alpha}{\alpha + \alpha_2} \quad \text{Equation 2.12}$$

The reflectivity of the material at the layer 1–layer 2 interface at a given angle, $R(\alpha)$, is defined as the absolute square of the reflection coefficient, $|F_{1,2}^R|^2$. In order to calculate the intensity, $I(\alpha, z)$, of the standing wave some height, z ,

above the reflector for the incident angle, α , the absolute square of the sum of incident and the reflected X-rays needs to be calculated

$$I(\alpha, z) = |E_1 + E_1^R|^2 = (E_1 + E_1^R)(E_1^* + E_1^{R*}) \quad \text{Equation 2.13}$$

where the star (*) represents the complex conjugate. Expanding the brackets, substituting in for E_1^R and using the expression for the reflection coefficient, an expression can be obtained for the intensity which, after some factorising and substituting in for the reflectivity gives [29]:

$$I(\alpha, z) = |E_1|^2 \left[1 + R(\alpha) + 2\sqrt{R(\alpha)} \cos \left(\Phi(\alpha) - \frac{2\pi z}{D(\alpha)} \right) \right] \quad \text{Equation 2.14}$$

The term $|E_1|^2$ represents the intensity of the incident X-ray beam, $\Phi(\alpha)$ gives the phase shift between the incident and reflected X-rays and $D(\alpha)$ gives the period of the standing wave (spatial separation between two adjacent antinodes) above the reflector. The functions for the phase shift and the period are

$$\Phi(\alpha) = \tan^{-1} \left(\frac{\text{Im}(F_{1,2}^R)}{\text{Re}(F_{1,2}^R)} \right) \quad \text{Equation 2.15}$$

$$D(\alpha) = \frac{\lambda}{2 \sin(\alpha)} \quad \text{Equation 2.16}$$

respectively, where $\text{Im}(F_{1,2}^R)$ and $\text{Re}(F_{1,2}^R)$ represent the imaginary and real parts of the reflection coefficient (from eq 2.9 it can be seen that α_2 will be complex as $\beta_2 \neq 0$). These equations themselves are not of direct use in the VPXSW experiments that have been performed within this study as they are only applicable to a 2 layer model in which the first layer is vacuum and the second is a reflector. They do, however, demonstrate the procedures used in calculating the reflection and transmission coefficients and as a result the standing wave intensity. Use of the above standing wave intensity is limited to cases where a low concentration of molecules are adsorbed on a reflector surface, such that the adsorbed molecules do not cause total external reflection of the X-rays, and only interact with the standing wave field.

2.3.2. Variable period standing wave intensity in a multi-layered system

For systems with a greater number of layers than 2 (a 2 layer system only represents the vacuum and a semi-infinite reflector) additional factors need to be considered and the mathematics behind the science becomes more

complicated. Having a system composed of $N+1$ layers (where layer 1 is vacuum and layer N is adsorbed on a semi-infinite reflector) the interfaces between any two layers m and $m+1$ will reflect and transmit different components of the incident X-ray. In the general case the Fresnel reflection coefficient can be written as [9, 12, 29]

$$F_{m,m+1}^R = \frac{E_m^R}{E_m} \approx \frac{\alpha_m - \alpha_{m+1}}{\alpha_m + \alpha_{m+1}} \quad \text{Equation 2.17}$$

while the Fresnel transmission coefficient can be written as [9, 12, 29]

$$F_{m,m+1}^T = \frac{E_{m+1}}{E_m} \approx \frac{2\alpha_m}{\alpha_m + \alpha_{m+1}} \quad \text{Equation 2.18}$$

which can be seen to be the same as the reflection and transmission coefficients that were obtained for the case of the interface in the 2 layer model (between layers 1 and 2, $m = 1$). The α_m values in eqs 2.17 and 2.18 are calculated using eq 2.9 so the reflection and transmission coefficients are angle and material dependent. For a system with multiple layers, such as the one shown in fig. 2.6,

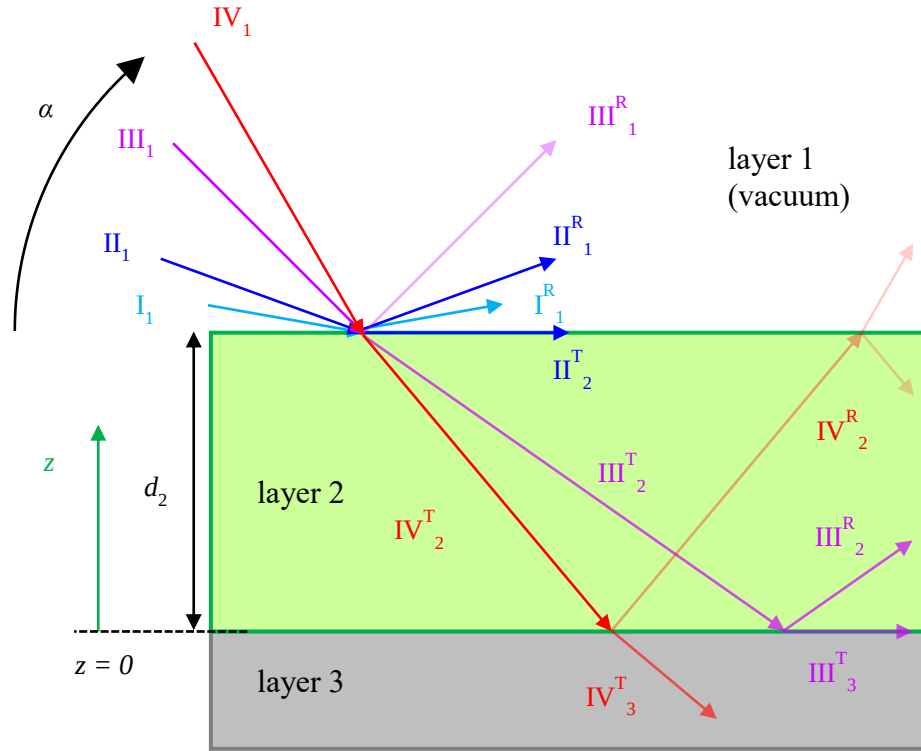


Figure 2.6: A ray diagram for a 3 layered system showing how X-rays incident at an angle of α reflect and refract from the different interfaces in the surface. The 4 rays shown (I, II, III, and IV) all have different values for α , which have been exaggerated for the purpose of this illustration. Ray I (light blue) has α less than $\alpha_{c,2}$, ray II (dark blue) has $\alpha = \alpha_{c,2}$, ray III (purple) has $\alpha = \alpha_{c,3}$ while ray IV (red) has α larger than $\alpha_{c,3}$ and shows multiple reflections within layer 2. Fading of lines shows that the amplitude is reduced as the X-ray has been partially reflected and partially transmitted from the interface.

it is possible to observe total reflection in the low angular regime ($\alpha < \alpha_c$, ray I, light blue). As the incident angle is increased it can match the critical angle of one of the layers, such as ray II (dark blue) which has $\alpha = \alpha_{c,2}$ or ray III (purple line) with $\alpha = \alpha_{c,3}$. This results in the refracted X-ray being a traveling X-ray propagating across the interface (rays II^T₂ and III^T₃). As critical angles are surpassed transmission through the layers occurs, and with each interface refracting and reflecting the X-ray multiple reflections become possible (as can be seen in ray IV, red line). The Fresnel reflection and transmission coefficients do not account for multiple reflections from the same interface. To account for multiple reflections Parratt's recursion formulation can be used, alongside the definition of an effective reflection coefficient at the interface of layers m and $m+1$,

$$r_{m,m+1} = \frac{E_m^R}{E_m} \quad \text{Equation 2.19}$$

to show that the effective reflection coefficient at the interface of layers $m-1$ and m is [9, 12, 29]

$$r_{m-1,m} = \frac{F_{m-1,m}^R + r_{m,m+1} \exp(-2ik_1 \alpha_m d_m)}{1 + F_{m-1,m}^R r_{m,m+1} \exp(-2ik_1 \alpha_m d_m)} \quad \text{Equation 2.20}$$

where d_m is the thickness of layer m measured in the z -direction (parallel to the surface normal, seen in fig. 2.6) and k_1 represents the magnitude of the wave vector for the incident X-ray

$$k_1 = |\mathbf{k}_1| = \frac{2\pi}{\lambda} \quad \text{Equation 2.21}$$

The exponential term represents the phase factor which comes as a result of the multiple reflections of the X-ray between the interfaces m and $m+1$. It can be noticed that in the case where a semi-infinite reflector is used as layer m , and $d_m = \infty$ (so there is then no interface between layers m and $m+1$ and so no multiple reflections) that the exponential term becomes zero ($e^{-\infty} = 0$) and the $r_{m-1,m}$ reduces to $F_{m-1,m}^R$. It can be seen that the recursion formula in eq 2.20 calculates the reflection coefficient for the $m-1, m$ interface considering factors from the $m-1, m$ and $m+1$ layers, so repeated use of this formula will eventually obtain the $r_{1,2}$ for the interface of the vacuum and the top layer of the surface ($m = 2$). Once obtained this effective reflection coefficient can then be used to find the reflectivity from the surface

$$R_{m,m+1} = |r_{m,m+1}|^2 \quad \text{Equation 2.22}$$

The reflectivity requires the recursion formula to be applied from the interface of the adsorbed layers and semi-infinite reflector (using $m = N+1$ in eq 2.20) and to be repeatedly applied for each layer in the surface [9, 12, 29]. An effective transmission coefficient, $t_{m-1, m}$ can be defined to account for the multiple reflections that occur in a multilayer system and are not accounted for in the Fresnel transmission coefficient.

$$t_{m-1, m} = \frac{E_m(d_m)}{E_{m-1}(d_{m-1})} \quad \text{Equation 2.23}$$

This gives the proportion of the X-ray amplitude that is transmitted at the $m-1, m$ interface into layer m , where $E_m(d_m)$ is the electric field amplitude within layer m a height d_m above the interface between layers m and $m+1$. As d_m is the thickness of the layer m , $E_m(d_m)$ is the electric field strength just below the $m-1, m$ interface (a height, z , of d_m above the $m, m+1$ interface). This electric field strength, $E_m(d_m)$, is calculated through consideration of all of the layers that the X-ray, incident upon the surface from the vacuum (with amplitude E_1), has passed through [29]

$$E_m(d_m) = E_1 \prod_{j=2}^m t_{j-1, j} \quad \text{Equation 2.24}$$

where this expression gives the X-ray electric field strength just below the interface of layer $m-1$ and layer m , where attenuation through layers 1 to m is accounted for by the β_m terms in the complex angles, α_m (eq. 2.9). The effective transmission coefficient can be calculated as [29]

$$t_{m-1, m} = \frac{(1 - F_{m-1, m}^R r_{m-1, m}) \exp(ik_1 \alpha_{m-1} d_{m-1})}{F_{m-1, m}^T} \quad \text{Equation 2.25}$$

The dependence of $t_{m-1, m}$ on $r_{m-1, m}$ (eq 2.20) is a result of the multiple reflections which result from a system with more than 2 layers.

Having defined all the necessary terms and expressions the intensity of the X-ray standing wave intensity at a height, z , above the $m, m+1$ interface within any layer, m , of a multilayer system can be calculated as a superposition of the incident and reflected X-rays above the $m, m+1$ interface [29]

$$I_m(\alpha, z) = |E_m(d_m)|^2 \exp(-2k_1 B_m d_m) \times [\exp(2k_1 B_m z) + R_{m, m+1} \exp(-2k_1 B_m z) + 2\sqrt{R_{m, m+1}} \cos(\Phi_m^R - 2k_1 A_m z)] \quad \text{Equation 2.26}$$

where the phase shift between the incident and the reflected X-rays, Φ_m^R , is defined in terms of the real and imaginary parts of the effective reflection coefficient

$$\Phi_m^R = \tan^{-1} \left(\frac{\text{Im}(r_{m,m+1})}{\text{Re}(r_{m,m+1})} \right) \quad \text{Equation 2.27}$$

and the functions A_m and B_m are defined as

$$A_m = \text{Re}(\alpha_m) \quad B_m = -\text{Im}(\alpha_m)$$

2.3.3. VPXSW with photoelectron detection in a 3 layer system

Having discussed the theory behind calculating the intensity of the VPXSW within any layer, m , for a system with any number, N , of layers, attention shall now be turned to 3 layer systems, like those studied within this work. In this work layer 1 is a vacuum layer and layer 3 is a silicon reflector, while the nature of layer 2 varies dependent upon the surface being studied (either SiO_x or $[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]$). The fact that a system with a known number of layers is being studied means that some of the expressions that have been discussed so far can be simplified. The standing wave intensity within layer 1 (the vacuum) need not be calculated as there is no species present to detect the XSW intensity, from the definition of a vacuum. The standing wave intensity within layer 2, $I_2(\alpha, z)$ can be calculated using eq 2.26 giving [29]

$$I_2(\alpha, z) = |E_2(d_2)|^2 \exp(-2k_1 B_2 d_2) \times [\exp(2k_1 B_2 z) + R_{2,3} \exp(-2k_1 B_2 z) + 2\sqrt{R_{2,3}} \cos(\Phi_2^R - 2k_1 A_2 z)] \quad \text{Equation 2.28}$$

where the expression for $E_2(d_2)$ can be shown to be $E_1 t_{1,2}$ using eq 2.24. The expression for $r_{2,3}$ (used in calculating $R_{2,3}$) simplifies to $F_{2,3}^R$ as the silicon reflector is assumed to be semi-infinite in size while the expression for $t_{1,2}$ becomes

$$t_{1,2} = \frac{1 - F_{1,2}^R r_{1,2}}{F_{1,2}^T} \quad \text{Equation 2.29}$$

as the exponential term becomes 1 due to the vacuum layer having an effective thickness of zero ($d_1 = 0$) as there is no matter capable of X-ray attenuation within it. All other expressions are defined as in sections 2.3.1 and 2.3.2. The XSW intensity within a 250 Å thick $[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]$ layer (layer 2) is shown as a 3D image in fig. 2.7, which shows how the XSW intensity varies with incident angle, α , and height above the reflector, z . The incident X-ray intensity has been

normalised to intensity of the incident X-ray ($E_1 = 1$), however, the XSW intensity is dependent upon the multiple reflections within the surface so is not simply 4 ($(E_1 + E_1^R)^2 = (1+1)^2$), as may be expected. The plot in fig. 2.7 shows that as the incident angle is swept from 0° upwards, oscillations in the XSW

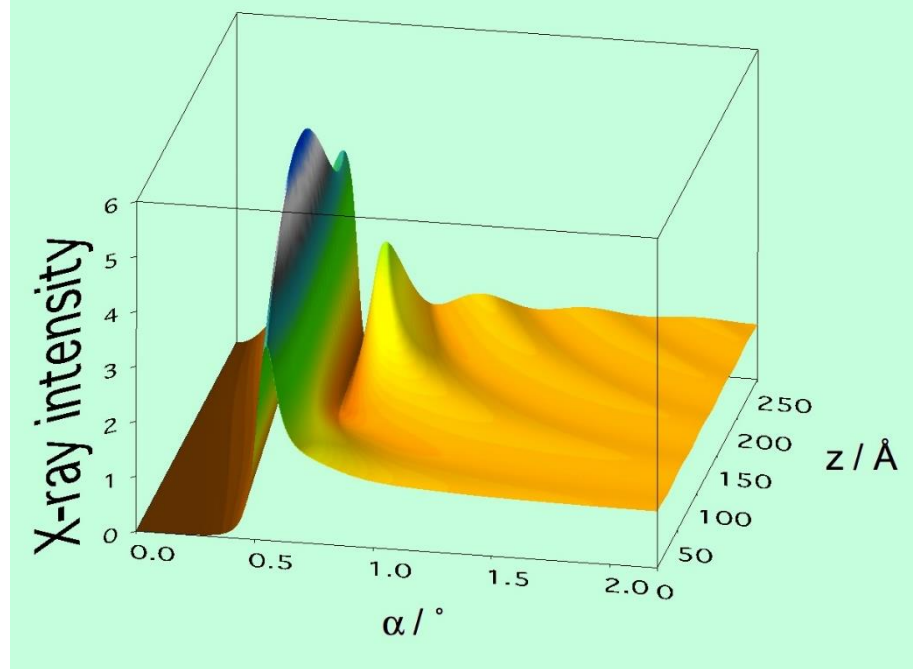


Figure 2.7: A 3D image of the X-ray standing wave intensity within a 250 Å $[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]$ layer on a silicon reflector. The X-ray intensity can be observed to be low below the critical angle of the IL ($\approx 0.43^\circ$) as only an evanescent wave probes the IL layer. For angles above the critical angle the X-ray intensity can be seen to oscillate, dependent upon the position of nodes and antinodes (which depend on z and α).

intensity occur at different heights above the reflector allowing layers at different heights to be distinguished. Looking at fig. 2.7 for a fixed value of angle shows how the XSW intensity varies above the reflector (i.e. at $\alpha = 1.5^\circ$ there are five antinodes within the surface).

In the studies performed within this thesis the XSW intensity was probed via photoemission. The photoelectron flux produced from within the material in layer 2 results from a combination of the X-ray intensity ($I_2(\alpha, z)$, which generates the photoelectrons), the number density of absorbing species within layer 2 ($\rho_2(z)$) and the attenuation of photoelectrons as they escape the surface. The generation of photoelectrons leaves behind core holes ($\text{h}^{\bullet+}$), which decay and produce X-ray fluorescence and Auger signals. The attenuation of photoelectrons is dependent upon the position of the electron emitter in relation to the vacuum layer (layer 1) and the material in layer 2, as described by eq 2.5 (it is assumed that $\theta = 0^\circ$). The 3 layer model is shown in fig. 2.8a, where $z = 0$

is defined as being at the surface of the reflector, shows that within layer 2 (total thickness of d_2) a layer located at position z is a distance $(d_2 - z)$ beneath the vacuum–layer 2 interface. The intensity of photoelectrons generated experimentally at the point z within a thin slice of the surface δz , $I_{e,0}(\alpha, z)$, is

$$I_{e,0}(\alpha, z) \propto \sigma_{abs} I_2(\alpha, z) \rho_2(z) \delta z \quad \text{Equation 2.29}$$

where σ_{abs} is the X-ray absorption cross section for the photoelectron being detected. In order to find the total photoelectron flux, $I_{e,tot}(\alpha)$, from a certain section of the IL layer, between z_1 and z_2 , the following integral must be performed

$$I_{e,tot}(\alpha) = \int_{z_1}^{z_2} I_{e,0}(\alpha, z) \exp\left(\frac{-(d_2 - z)}{\lambda_2}\right) dz \quad \text{Equation 2.30}$$

where λ_2 is the photoelectron attenuation length through layer 2. It is assumed that the angle of incidence is suitably small that the angular effect of tilting the sample by α does not affect the electron path length and hence the electron attenuation. The integral in eq 2.30 gives the photoelectron signal measured by an EDC at fixed incident angle, α , within an experiment. The experimental EDCs are then combined to form the experimental VPXSW profile—which is a function of angle.

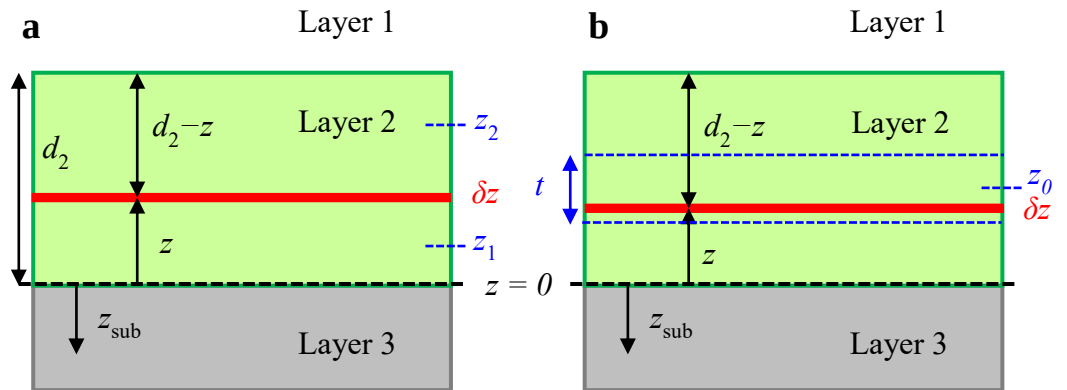


Figure 2.8: A diagram of a 3 layer model showing how the calculation for photoelectron signal from a surface is performed. The adsorbed layer (layer 2) has a thickness, d_2 , and $z = 0$ is defined as the reflector (layer 3) surface. The image in (a) shows how an integral could be performed over the range z_1 to z_2 , while (b) shows the calculation method used in analysis here, where a sum of the photoelectron signal over a layer of thickness t and centred at z_0 is performed. Note also how the surface of layer 3 is also defined as $z_{sub} = 0$, meaning that z_{sub} increases with distance below the vacuum layer (opposite direction to z).

In order to model the experimental VPXSW profiles the photoelectron signal had to be calculated. VPXSW profiles were normalised to a maximum value of 1, meaning that the differences in the absorption cross sections for different elements [15] could be ignored, as well as allowing comparison

between different datasets. The adsorbed material was also assumed to be uniform in density, so $\rho_2(z)$ is a constant, which will also be removed by the normalisation. The integral in eq 2.30 was not solved directly, to model the photoelectron VPXSW profile, due to the fact that the photoelectron intensity generated at position z depends upon $I_2(\alpha, z)$ making the mathematics behind the integration complicated. In order to calculate the total photoelectron flux from a segment of layer 2, within the analysis software used in this work [33], a section of layer 2 is defined with a thickness, t , centred at the position, z_0 , above the Si reflector (layer 3), as shown by the blue dashed lines in fig. 2.8b. The photoelectron signal from a slice of thickness $\delta z = 1 \text{ \AA}$ at a height z above the Si reflector (having to travel a distance $(d_2 - z)$ through layer 2) was then calculated using eq 2.5, assuming that the tilt of the surface did not affect the electron path length. The total photoelectron intensity for the model VPXSW profile in the layer specified, $I_{e, \text{mod}}(\alpha)$, is a sum of all of the $1 \text{ \AA}$ slices of layer 2 between $z_0 - t/2$ and $z_0 + t/2$ for a given α

$$I_{e, \text{mod}}(\alpha) = \sum_{z_0 - t/2}^{z_0 + t/2} I_{e,0}(\alpha, z) \exp\left(\frac{-(d_2 - z)}{\lambda_2}\right) \delta z \quad \text{Equation 2.31}$$

In order to calculate the total VPXSW profile the sum in eq 2.31 needs to be performed for all of the values of α within the experimental range. Like the experimentally measured signal, the VPXSW profile obtained from the model photoelectron signal is normalised to a maximum of 1, to remove any effects of the differences in absorption cross sections for different photoelectron peaks within layer 2 (after corrections have been applied, see section 2.3.4) and to allow different datasets to be compared. The calculations used within this study assume that the density of layer 2 is constant, for the surfaces in this work, however it is possible to use different density profiles within the software (such as a Gaussian for a thin layer which may diffuse from an original position). By tuning the values of z_0 and t the VPXSW profile for a thick slab (large t) or thin marker layer (small t) can be calculated.

As well as measuring the photoelectron signal and obtaining VPXSW profiles from the material within layer 2 it is also possible to measure the photoelectron signal from the silicon reflector (layer 3). As the reflector is modelled as semi-infinite the expression for the X-ray intensity in eq 2.26 is not suitable for modelling the X-ray intensity within the Si. The semi-infinite nature

of the reflector will mean that once an X-ray penetrates the Si layer it will not be reflected back, however there can still be multiple reflections within layer 2 which mean multiple rays enter the reflector. These multiple rays are accounted for in the expression for $E_m(d_m)$ (eq 2.24), as it depends upon the transmission coefficients (which itself accounts for the reflection coefficients) for the layers the X-ray has travelled through. In order to work out the amplitude of the X-ray that is transmitted into the Si reflector the Fresnel transmission coefficient at the layer 2–layer 3 interface, $F_{2,3}^T$ (eq 2.18), needs to be considered (as there are not multiple reflections from beneath layer 3) in the rearranged form

$$E_3 = E_2 \left(\frac{2\alpha_2}{\alpha_2 + \alpha_3} \right) \quad \text{Equation 2.32}$$

where E_2 and E_3 represent the electric field strength (amplitude) at the interface. As mentioned earlier eq 2.24 is not suitable for calculating E_3 as it assumes that the layer you are calculating the X-ray electric field strength (E_m) for is adsorbed on top of another layer. In order to calculate the X-ray amplitude E_2 just above the interface between layer 2 and the silicon reflector ($z = 0$) the electric field strength just below the layer 1–layer 2 interface, $E_2(d_2)$, can be used (from eq 2.24) and can be corrected to account for attenuation of the X-ray as it passes through layer 2 towards the reflector by using an exponential factor [9]

$$E_2 = E_2(d_2) \exp(k_1 \text{Im}(\alpha_2) d_2) \quad \text{Equation 2.33}$$

noting that although the exponential is a positive, that the imaginary part of α_2 is negative (eq 2.9). The X-ray amplitude just below the layer 2–layer 3 interface, E_3 , will be attenuated as it travels through the reflector layer meaning that the X-ray amplitude at a position z_{sub} below the reflector, $E_3(z_{\text{sub}})$ can be calculated by multiplication of an exponential factor

$$E_3(z_{\text{sub}}) = E_3 \exp(k_1 \text{Im}(\alpha_3) z_{\text{sub}}) \quad \text{Equation 2.34}$$

Despite the exponential power appearing to be positive the imaginary part of α_3 is negative resulting in the exponential decay that is expected for attenuation by the Beer–Lambert law, as was the case in eq. 2.33. To calculate the intensity of the X-ray at a position z_{sub} below the substrate surface for an incident angle, α , ($I_3(\alpha, z_{\text{sub}})$) the absolute square of $E_3(z_{\text{sub}})$ is required. Using equations 2.32 to 2.34 this can be shown to be equal to

$$I_3(a, z_{sub}) = |E_2(d_2)|^2 \exp(2k_1 \text{Im}(\alpha_2)d_2) \left| \left(\frac{2\alpha_2}{\alpha_2 + \alpha_3} \right) \right|^2 \exp(2k_1 \text{Im}(\alpha_3)z_{sub})$$

Equation 2.35

where eq 2.9 can be used to find the α_2 and α_3 values while eq 2.24 is used to calculate $E_2(d_2)$. It was not possible to simply use the intensity of the X-ray within layer 2 (eq 2.28) at $z = 0$ (just above the reflector surface) to find the intensity of the X-ray that would be transmitted through the layer 2–layer 3 interface. This is due to the fact that the X-ray intensity in layer 2 is composed from the X-rays that are incident upon interface 2, 3 and reflected from interface 2, 3, while the intensity within layer 3 is only concerned with the X-ray incident upon interface 2, 3.

Much like the case for the photoelectron signal in layer 2, the total photoelectron flux from the substrate (layer 3) will be dependent upon the density of photoelectron emitters, the absorption cross section and the X-ray intensity within the substrate. The number of photoelectrons produced within a thin layer δz_{sub} of the substrate $I_{e,sub,0}(\alpha, z_{sub})$ is

$$I_{e,sub,0}(\alpha, z_{sub}) \propto \sigma_{abs} I_3(\alpha, z_{sub}) \rho_3(z_{sub}) \delta z_{sub}$$

Equation 2.36

The photoelectrons then need to travel toward the detector which requires travelling through a thickness, z_{sub} , of silicon reflector and d_2 of the material in layer 2. Both of these layers will attenuate the photoelectrons, dependent upon the attenuation length, λ , of the photoelectron through the material. This gives the intensity of photoelectrons emitted from a thin slice of the substrate, δz_{sub} , positioned at z_{sub} and attenuated through the two layers (by repeated use of eq. 2.5 for each attenuating layer) reaching the detector to be

$$I_{e,sub}(\alpha, z_{sub}) = I_{e,sub,0}(\alpha, z_{sub}) \exp\left(\frac{-d_2}{\lambda_2}\right) \exp\left(\frac{-z_{sub}}{\lambda_3}\right)$$

Equation 2.37

where λ_2 and λ_3 are the photoelectron attenuation lengths through layer 2 and layer 3, respectively. The experimentally measured photoelectron signal, at a given angle α , is a sum across all of the thin slices of the semi-infinite substrate

$$I_{e,sub,mod}(\alpha) = \exp\left(\frac{-d_2}{\lambda_2}\right) \times \int_{z_{sub}=0}^{\infty} I_{e,sub,0}(\alpha, z_{sub}) \exp\left(\frac{-z_{sub}}{\lambda_3}\right) dz_{sub}$$

Equation 2.38

The photoelectron signals from each angle are then combined to generate a VPXSW profile which has its maximum intensity normalised to 1 to remove any effects resulting from differences in absorption cross section (the same as for the

VPXSW profiles from layer 2). It is also assumed that the small tilt of the sample (as α is varied) does not affect the photoelectron path length and that the density of the substrate is uniform.

For the analysis software used within this work [33] the experimentally measured photoelectron signal from the substrate was modelled by taking a sum of the photoelectron signal in 1 Å slices from $z_{\text{sub}} = 0$ Å to $z_{\text{sub}} = 1000$ Å for an uncovered substrate. Despite 1000 Å not being equal to infinity, given that the photoelectron attenuation lengths used in this work were all less than 100 Å, over 99.995% of the photoelectrons are emitted from top 1000 Å of the surface. This sum over the 1000 Å uncovered substrate was then attenuated by layer 2 (with thickness d_2) with one calculation. This gives the model photoelectron intensity, $I_{e,\text{sub},\text{mod}}(\alpha)$, to be

$$I_{e,\text{sub},\text{mod}}(\alpha) = \exp\left(\frac{-d_2}{\lambda_2}\right) \times \sum_{z_{\text{sub}}=0}^{1000} I_{e,\text{sub},0}(\alpha, z_{\text{sub}}) \exp\left(\frac{-z_{\text{sub}}}{\lambda_3}\right) \delta z_{\text{sub}}$$

Equation 2.39

The model photoelectron signal is calculated for each angle, α , then is assembled into a VPXSW profile prior to normalisation of the VPXSW profile to a maximum of 1, enabling it to be compared to the experimental VPXSW profiles, which are also normalised. The value used for λ_3 in the calculations in this work was 58 Å for Si 2p photoelectrons travelling through the silicon substrate. This value is larger than the expected attenuation length based upon high energy IMFP calculations (IMFP for Si 2p electrons through Si is 59.2 Å [18], see section 2.2.3). This inaccuracy, however, does not affect the photoelectron signal as the substrate layer used in the summation (eq 2.39) is thicker than the increased escape depth of the faster electron. The assumption of a 1000 Å thick reflector layer would not be sufficient for photoelectrons with attenuation lengths larger than 200 Å as then there would be a $\approx 1\%$ chance that a photoelectron from an emitter below 1000 Å is detected.

2.3.4. Corrections applied to calculated VPXSW profiles

The equations described in section 2.3.3 calculate the X-ray intensities and the photoelectron flux coming from the surface, for whichever photoelectron species is being studied. The detected signal, however, is different and in order to accurately model the detected photoelectron flux coming from the surface a

few corrections must be made. The first correction that is required is one relating to the path length for the X-rays through layers 2 and 3, as illustrated in fig. 2.9a. For a system in which layer 2 has thickness d_2 , the path length for the X-ray through layer 2, p_2 , (blue line) can be found from the definition of $\sin(x)$ to be

$$p_2 = \frac{d_2}{\sin(\alpha_2)} \quad \text{Equation 2.40}$$

This shows that for smaller angles there is an increased path length through layer 2, which results in a greater quantity of emitted species (photoelectrons, Auger electrons and X-ray fluorescence photons). This results in a larger experimental photoelectron signal for low angles than calculated by eq 2.31. To correct for the increased path length in the calculated photoelectron signal, division by $\sin(\alpha_2)$ is required. Under the assumption that the angles are small (so $\sin(x) \approx x$) and that $\alpha_2 \approx \alpha$ the calculated photoelectron signal can be divided by α to correct for the X-ray path length. A similar argument holds for the X-ray path through the reflector (layer 3), with the photoelectron signal also being corrected by division by α .

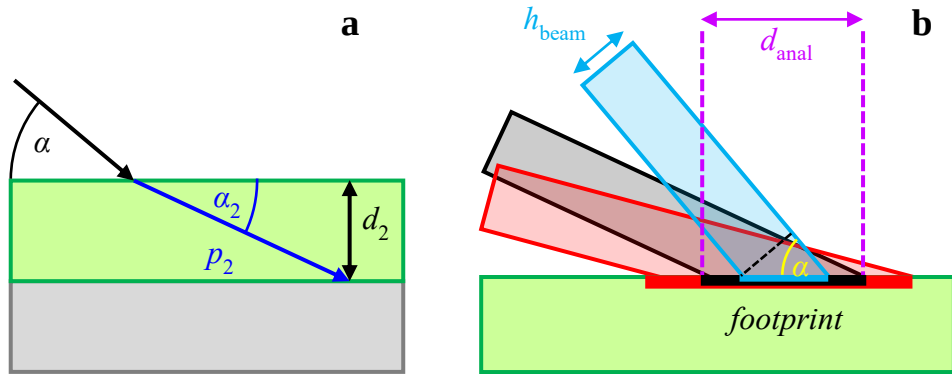


Figure 2.9: Diagrams depicting the two corrections made to the VPXSW signal within the analysis software in order to get a better match between the calculated and experimental profiles. The path length correction (a) accounts for the variation in path length through the adsorbed layer (layer 2) when the incident angle is changed. For smaller values of α the path length is longer, resulting in a higher photoelectron flux. The effect of α on the footprint is shown in (b), where smaller values of α result in larger footprints (h_{beam} is fixed). Since the analyser can only detect photoelectrons from an area characterised by the radius d_{anal} then for shallow angles ($\alpha < \alpha_{\text{foot}}$) a correction is required.

The second correction that is applied to the calculated photoelectron intensity is one which accounts for the changing X-ray footprint with angle. Figure 2.9b shows that the footprint of an X-ray with fixed beam height, h_{beam} , depends upon the angle of incidence, α , where smaller angles of incidence lead to larger X-ray footprints. This can be seen visually in fig. 2.9b as the largest footprint (thick red) is produced by the beam with the smallest angle of

incidence, while the largest angle of incidence (blue beam) generates the smallest footprint. Using the triangle shown within the blue beam of fig. 2.9b the footprint can be seen to be given by eq 2.41.

$$footprint = \frac{h_{beam}}{\sin(\alpha)} \quad \text{Equation 2.41}$$

The concentric hemispherical analyser has the ability to accept photoelectrons from an area on the sample characterised by a diameter, d_{anal} (purple dashed lines). For large incident angles (blue beam) the X-ray footprint is smaller than the analyser diameter and all of the photoelectrons that are produced can be detected (assuming emission along the surface normal). In this region no correction to the calculated photoelectron signal is required. For the case where the incident angle is suitably small, such that the X-ray footprint is larger than the analyser diameter (red beam), then not all of the produced photoelectrons are detected, but are included within the total calculated signal ($I_{e, mod}$). As a result the calculated photoelectron intensity will be too large for these smaller angles, so needs to be modified to match the experimentally measured signal ($I_{e, meas}$). The angles for which the correction needs to be applied are those below α_{foot} , the angle for which $footprint = d_{anal}$ (black beam). Using eq 2.41 it can be shown that

$$\sin(\alpha_{foot}) = \frac{h_{beam}}{d_{anal}} \quad \text{Equation 2.42}$$

It is assumed that the photoelectron flux (intensity per unit area) is constant, so for the low angle case where the footprint is larger than the analyser area, the photoelectron flux (PE flux) is given by

$$PE \text{ flux} = \frac{I_{e, meas}}{d_{anal}} \quad \text{Equation 2.43}$$

while for cases where the angle is sufficiently large and the footprint is smaller than the analyser area then

$$PE \text{ flux} = \frac{I_{e, mod}}{footprint} \quad \text{Equation 2.44}$$

Combining these equations into one, by setting the $PE \text{ flux}$ terms equal to each other, and rearranging gives

$$I_{e, meas} = I_{e, mod} \frac{d_{anal}}{footprint} \quad \text{Equation 2.45}$$

then substitution for $footprint$ using eq 2.41 gives

$$I_{e, meas} = I_{e, mod} \sin(\alpha) \frac{d_{anal}}{h_{beam}} \quad \text{Equation 2.46}$$

which can be rewritten, using eq 2.42, as

$$I_{e,meas} = I_{e,mod} \frac{\sin(\alpha)}{\sin(\alpha_{foot})} \quad \text{Equation 2.47}$$

This shows the required correction to the modelled photoelectron intensity ($I_{e, mod}$), such that it matches the experimentally measured intensity ($I_{e, meas}$). The value of $\sin(\alpha_{foot})$ used in this study was kept constant at 0.012 but was chosen to obtain the best fits to the data (h_{beam} was known to be 30 μm but d_{anal} was unknown). Using eq 2.42 to calculate the unknown value of d_{anal} using h_{beam} as 30 μm and $\sin(\alpha_{foot})$ as 0.012 gave a value of 2.5 mm for the analyser diameter on the surface, which seems to be a sensible value (i.e. not too far from the standard sample size of ≈ 1 cm). Variation of the ratio d_{anal}/h_{beam} can be observed to have a large effect upon the tail of the VPXSW signal (for angles greater than the one at which the peak maximum occurs) due to the effect of the footprint upon the intensity of the VPXSW peak maximum. As the peak maximum determines the normalisation factor for the VPXSW profile, if the VPXSW maximum changes so does the relative intensity of the signal at high angles (where the footprint correction is not applied). The switching over from the section of the VPXSW profile which has been corrected for the footprint (low angles) and the section which does not require correction (high angles) can be seen by a small kink in the VPXSW simulations, at around 0.7° . This correction is only an approximation as the X-ray intensity is not uniform across the whole footprint and also it is unlikely that the photoelectron capture efficiency is the same across the whole analyser diameter.

2.3.5. Calculated VPXSW profiles for different surface structures

Section 2.3.3 has discussed the mathematical form of the X-ray intensities and the photoelectron yield from within the adsorbed layer (layer 2) and the reflector (layer 3). The use of some example VPXSW profiles can aid in the visualisation of these mathematical functions, and in determining what effect changing the different parameters (such as layer thickness, layer position or attenuation length) within these functions has on the shapes of the model VPXSW profiles, after the corrections (section 2.3.4) have been applied. The critical angle, α_c , is important in determining the shape of the VPXSW profile and depends upon the material within the layer that the X-ray is incident upon

and the X-ray energy (as the δ and β values depend on the material and the X-ray energy). An approximation for the critical angle of a material (refractive index, n , given by eq 2.1) under vacuum ($n_1 = 1$) can be made through the application of Snell's law (eq 2.2) and knowing that at $\alpha_1 = \alpha_c$ then $\alpha_2 = 0$ radians, as a travelling wave is transmitted across the surface of the reflector.

$$\cos(\alpha_c) = (1 - \delta - i\beta) \quad \text{Equation 2.48}$$

Using the small angle approximation for $\cos(x)$ and the assumption that β is much smaller than δ (the ratio for β/δ is < 0.02 for $[\text{C}_8\text{C}_{10}\text{Im}][\text{BF}_4]$ with $h\nu = 3000$ eV [11]) the critical angle can be approximated to be

$$\alpha_c \approx \sqrt{2\delta} \quad \text{Equation 2.49}$$

As a result different materials and different X-ray energies will produce different VPXSW profiles. The examples that will be discussed within this section assume that the X-ray energy is 3000 eV and that the material within layer 2 is $[\text{C}_8\text{C}_{10}\text{Im}][\text{BF}_4]$ on top of a silicon reflector. For convenience the angles will be discussed in terms of degrees, rather than radians, despite the calculations all using the radian unit for angle. There are two main changes that are observed in the XSW as the incident angle is increased; as α is increased from 0° to α_c the phase shift between the incident and reflected rays changes from 180° (node at surface) to 0° (antinode at the surface, phase shift stays at 0° for $\alpha > \alpha_c$) [28, 34], and that the XSW period decreases as the incident angle increases, like a compressing bellows [28, 29]. These two effects will now be described in more detail with model VPXSW profiles to aid visualisation.

The XSW set up from a 3 layer surface, shown in fig. 2.7, for $\alpha = 0^\circ$ has a period of ∞ (so an antinode at ∞) and a node at the surface, so there is no X-ray interaction with matter. As the angle is increased, but is still below $\alpha_{c,2}$, the XSW period begins to decrease and the phase difference between the incident and reflected wave starts to change from 180° (out of phase) towards 0° (in phase, at $\alpha = \alpha_{c,2}$), such that there is a non-zero X-ray intensity at the surface [28, 34]. This results in an increase in the evanescent wave intensity at the surface and within the adsorbed layer, producing a photoelectron signal which rises with angle, giving a smooth leading edge in the data, however total external reflection means that only the top most layer is being probed (buried layers will not be producing photoelectrons if the top layer is sufficiently thick). As α

matches $\alpha_{c,2}$ a travelling wave propagates across the surface of the reflector (fig. 2.6, ray II, dark blue) [9] and produces a large photoelectron flux, and a peak in the VPXSW profile. As α is increased further the X-ray penetrates through layer 2 and sets up an X-ray standing wave from the surface of the reflector (or the next interface in a multi-layered surface). A smooth increase in the XSW intensity, resulting in photoelectron generation, from the substrate is observed as angle increases, in much the same way as it did for the second layer, initially with a node at the interface and the first antinode at ∞ (observed in fig. 2.7 for $z=0^\circ$, the reflector surface). As angle is increased further the XSW phase shifts and the XSW period decreases, with the evanescent wave caused by the phase shift producing photoelectrons from the reflector (which will be attenuated by the material in layer 2) and the XSW producing photoelectrons within layer 2. The XSW (within layer 2) has a period which decreases with angle, meaning that the antinodes start getting closer together as angle increases. As an XSW antinode impinges upon a thin layer within layer 2 photoelectrons are generated, while a node passing through a thin layer results in no photoelectron production. This means that the first antinode in the XSW will pass through layers which are at a greater height above the surface at a lower angle than the angle at which it will pass through layers which are deeper within the surface. Put simply—the smaller the angle for which a peak is observed in the signal, the closer to the vacuum that layer is. The effect of having nodes and antinodes passing through the surface results in the oscillatory VPXSW profiles, where the position of the oscillations (in angle) indicate the position of the layer in the surface (the layer height above the reflector).

The plot in fig. 2.10 shows the effect of changing the thickness, d_2 , of the layer being probed by the XSW on the VPXSW profile. The photoelectron attenuation length, λ_2 , being used in the calculations is 53 Å [18]. The leading edges (before the peak at $\alpha \approx \alpha_{c,2}$) are all very similar as the photoelectron intensity is affected only by the evanescent wave and the attenuation length. For the thinner layers (blue solid and blue dashed lines) the evanescent wave can probe the whole layer while for thicker layers the evanescent wave decays away before probing the entire layer, resulting in greater similarity in the leading edges for thicker layers (the leading edges of the red dashed and solid orange lines in fig. 2.10 are almost identical). All of the VPXSW profiles peak at an angle

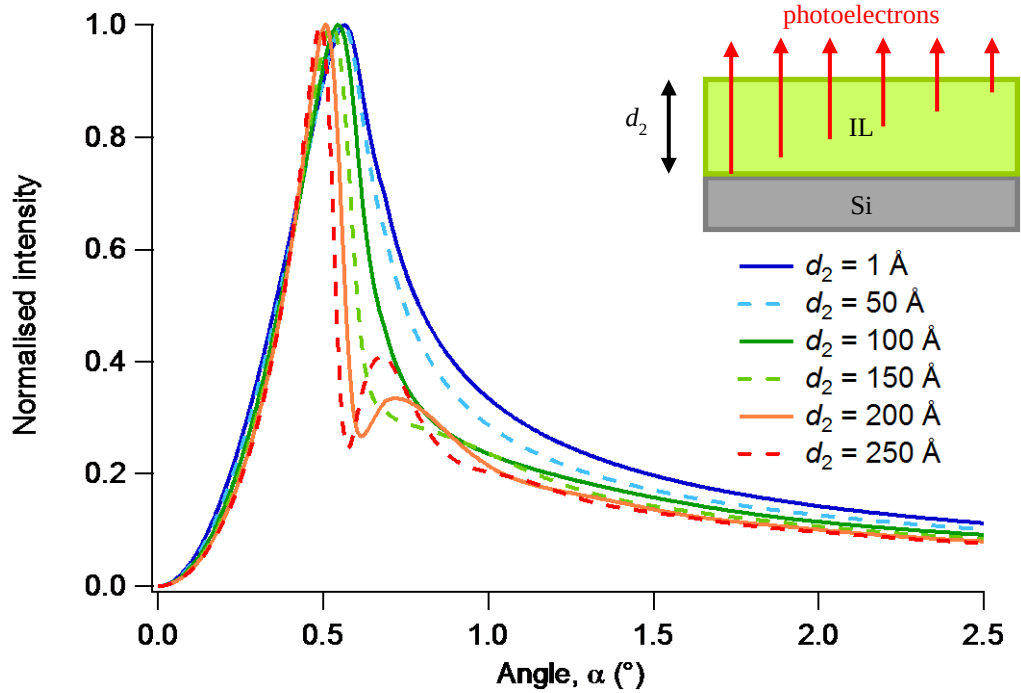


Figure 2.10: VPXSW profiles showing the calculated photoelectron signal (with corrections applied) for a silicon reflector with a $[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]$ layer adsorbed upon its surface. The different lines represent the profiles from IL layers with different thicknesses, d_2 . Thicker IL layers produce VPXSW profiles with a greater number of oscillations as more antinodes and nodes pass into the surface.

around the critical angle of $[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]$ ($\alpha_{c,2} = 0.4274^\circ$ [11]) as the travelling wave passes across the surface of the $[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]$. The X-ray then sets up a standing wave from the silicon reflector, where increasing the angle causes the antinodes and nodes to sweep towards the IL–Si interface. The thicker layers of IL meet the first incoming antinode at lower angles than the thinner layers, resulting in small peaks in the VPXSW signal (the peak in the red dashed line, $\alpha \approx 0.7^\circ$, occurs at a lower angle than the orange solid line, $\alpha \approx 0.8^\circ$). As the incident angle is increased further, and α surpasses $\alpha_{c,3}$, the XSW intensity and photoelectron signal begin to decay away as the reflected component of the X-ray decreases.

The silicon substrate photoelectron signal is observed in fig. 2.11 for surfaces with different IL layer thicknesses, where an attenuation length for the Si 2p photoelectrons through layer 2 of 58 Å was used [18]. The attenuation length for the Si 2p photoelectrons through the silicon used was also 58 Å despite 59.2 Å being more accurate [18]. This inaccuracy does not affect the final result as it only affects the number of photoelectrons reaching the silicon reflector surface, as the reflector is modelled as semi-infinite (see section 2.3.3). Since

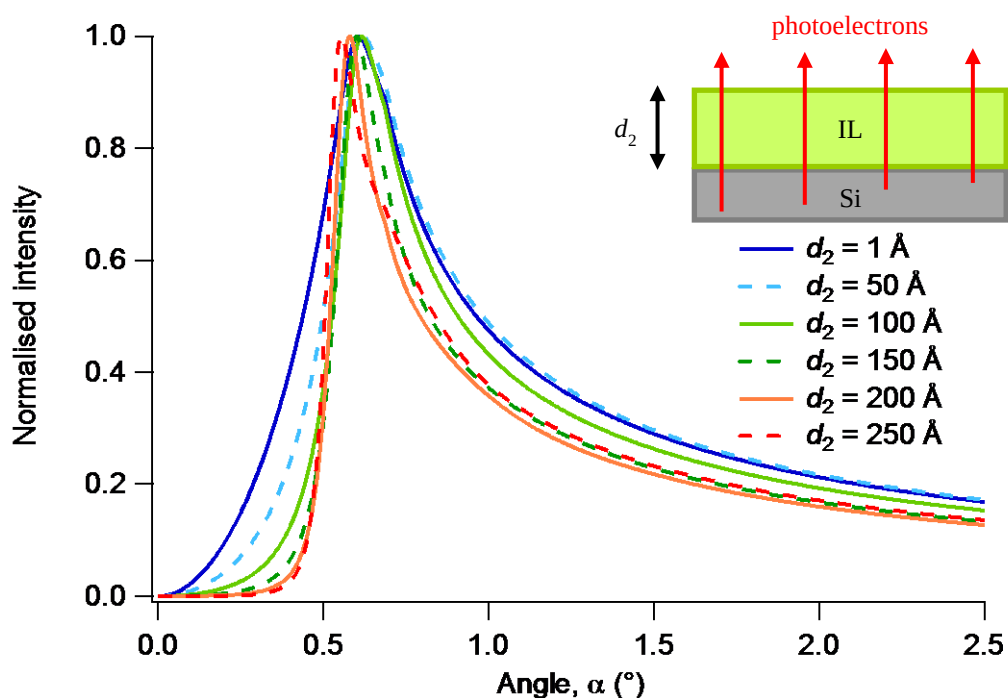


Figure 2.11: VPXSW profiles showing the calculated photoelectron signal (with corrections applied) from a silicon reflector beneath a $[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]$ layer of varying thickness. The different lines represent the profiles from beneath IL layers with thicknesses, d_2 , as given in the legend. Thicker IL layers produce substrate VPXSW profiles with a later leading edge onset as the depth that the evanescent wave probes increases with angle.

the VPXSW profile is normalised, the photoelectron intensity from the silicon prior to attenuation is not important, only the attenuation of the Si photoelectron signal through layer 2. The intensity of the evanescent wave increases with angle [9], allowing it to generate a significant signal from deeper within a layer. Surfaces in which d_2 is less than the depth for which the evanescent wave can probe produce a significant number of photoelectrons, at a given angle, resulting in a Si 2p photoelectron signal whilst the X-ray is being totally reflected at the layer 1–layer 2 interface. For the surfaces with thicker IL layers the evanescent wave doesn't reach the reflector, resulting in a flat section in the measured substrate VPXSW profiles. A trend of increased degree of flatness with layer 2 thickness can be seen in fig. 2.11 in the 0° to 0.5° angular range, with the thickest layer (red dashed line) having the lowest photoelectron signal for the largest angular range before a sharp rise in the photoelectron intensity as the X-ray penetrates through the IL layer and reaches the silicon substrate. The peak in the substrate VPXSW corresponds to the travelling wave across the IL–reflector interface at $\alpha = \alpha_{c,3} = 0.5971^\circ$ [11] before the signal decays away as the standing wave intensity decreases. The transmitted X-ray intensity through the substrate

continues to produce a non-zero photoelectron flux for all angles so the signal will not decay to zero.

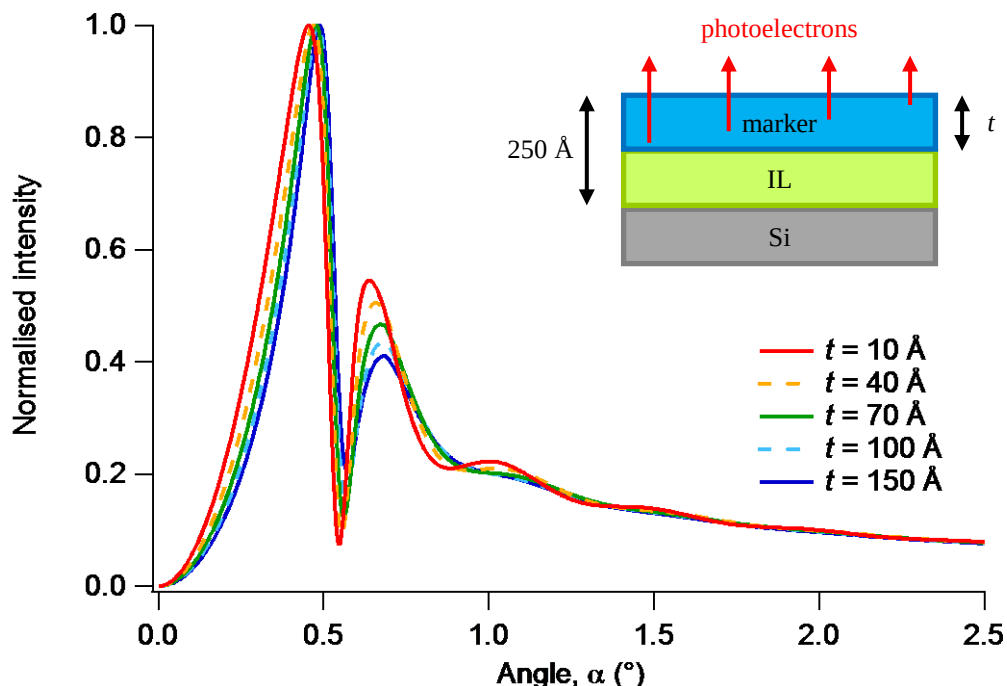


Figure 2.12: A comparison of calculated VPXSW profiles for photoelectrons produced by a marker layer of thickness t , which sits at the top of a 250 Å $[\text{C}_8\text{C}_{11}\text{Im}][\text{BF}_4]$ layer. As the thickness of the marker layer is increased the amplitude of the oscillations decreases (more prominent oscillations are observed for thinner layers) and the angular position of peaks increases slightly.

Having observed the variation in VPXSW profile with total layer thickness on the reflector in fig. 2.10, the signal from different segments of layer 2 can be calculated. This may be of use if layer 2 is assumed to be an “organic layer” which is composed of multiple organic species, with similar X-ray properties but differing photoelectron environments, adsorbed on the reflector. The differences in the photoelectron VPXSW profiles can be used to determine layering of organic species within the organic layer. Figure 2.12 shows the calculated VPXSW profiles for a layer with varying thickness, t , occupying the top t Å of layer 2, which had a total thickness, d_2 , of 250 Å and used $\lambda_2 = 53$ Å. It can be noticed that all of the VPXSW profiles in fig. 2.12 are very similar as they are all at the surface of the IL layer (which starts at $z = 250$ Å), meaning that they all experience the first antinode of the XSW at the same angle, producing a peak in the VPXSW profile. For the thinner marker layers (red line) the VPXSW profile oscillations are more distinct as the thin marker layer samples a narrower region of the XSW intensity, whereas for a thicker marker layer the photoelectron signal is an average of the entire XSW intensity within

the layer. This results in an averaging effect, within a layer which is thick enough (blue lines), resulting in a slight broadening of the oscillations observed above 0.5° and less clear modulations in the VPXSW profile.

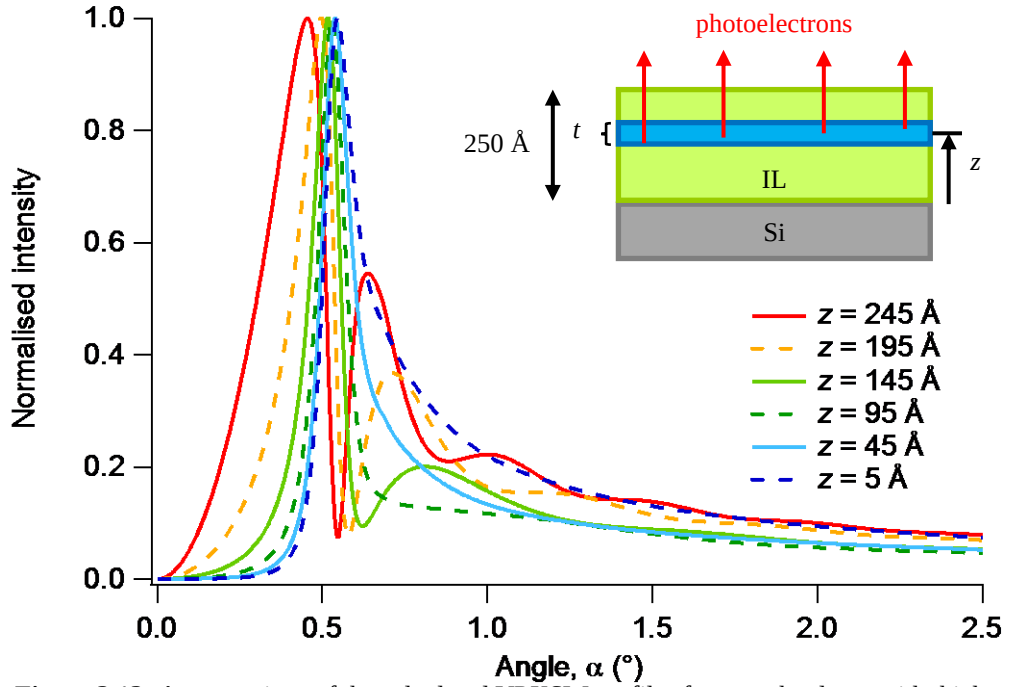


Figure 2.13: A comparison of the calculated VPXSW profiles for a marker layer with thickness, t , of 10 Å at different heights z above the silicon reflector surface. Layers closer to the surface have oscillations at lower angles as the nodes and antinodes of the XSW collapse from ∞ towards the reflector surface with increasing angle. Layers positioned closer to the reflector have later leading edges due to the fact that the evanescent wave produces more photoelectrons from deeper positions at increased angle.

It has been observed that thinner layers give VPXSW profiles with clearer oscillations, so by using a thin marker layer the effect of the layer position on the measured photoelectron flux can be observed. In order to probe the XSW intensity within layer 2 the VPXSW profiles for a thin layer ($t = 10$ Å) centred at different heights, z , above the reflector surface were calculated, fig. 2.13. The total thickness of layer 2, d_2 , was kept constant at 250 Å while the attenuation length, λ_2 , used was 53 Å [18]. Looking at the leading edge (below 0.5°) of the VPXSW profile a similar trend is observed to that in fig. 2.11 for the substrate signal, where an increased degree of flatness is observed for layers which are buried deeper within layer 2. It can also be seen that the angle at which the VPXSW profile peaks is dependent upon the relative position of the layer to the vacuum, with layers closer to the vacuum (red line) peaking at lower angles than marker layers at lower z values (solid blue line). For angles greater than 0.5° a large variation in the VPXSW shape can be observed, depending on the

marker layer position. This makes fitting thin marker layers easier and more accurate than fitting thick layers, as has been noted in VPXSW studies detecting the X-ray fluorescence [30, 34, 35]. It is observed that for marker layers at larger z positions (situated closer to the vacuum layer) a greater number of oscillations are observed and the oscillations occur at lower angles, as the antinodes move towards the reflector surface with increasing angle [28, 34].

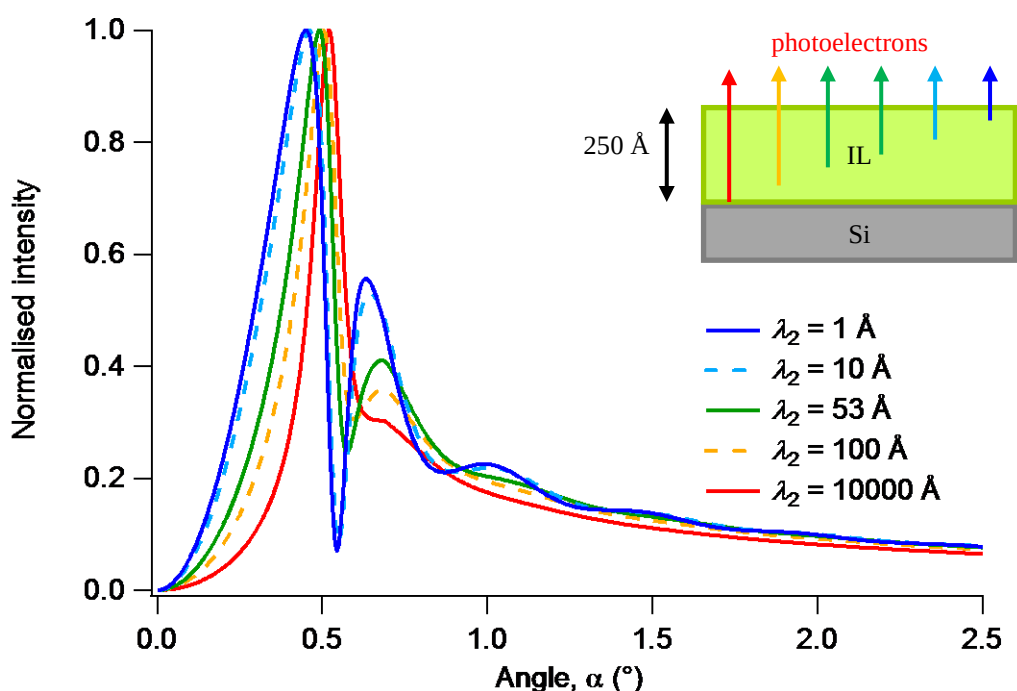


Figure 2.14: A comparison of the calculated VPXSW profiles from a 250 Å $[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]$ layer on top of a silicon reflector with different photoelectron attenuation lengths through the IL layer (λ_2). The $\lambda_2 = 53$ Å was the attenuation length used for the photoelectrons from the IL travelling through the IL within this work while $\lambda_2 = 10000$ Å is an approximate attenuation length for an X-ray fluorescence photon (so resembles the fluorescence VPXSW signal).

One of the advantages of using photoelectron detection in the VPXSW technique was the inherent surface sensitivity that comes as a result of the photoelectron attenuation length being on the order of 10 Å. The effect of the photoelectron attenuation length on the calculated VPXSW profile from a 250 Å IL layer is shown in fig. 2.14. Since 95% of the photoelectron signal comes from the top $3 \times \lambda_2$ [14], using a low attenuation length has the effect of probing a thin layer. This effect can be seen in the VPXSW using attenuation lengths of 1 Å (solid blue) and 10 Å (blue dashed) producing multiple, clear oscillations (similar to the marker layer VPXSW profiles in fig. 2.13). Larger attenuation lengths produce VPXSW profiles which are more featureless, with smaller oscillations (green and golden dashed lines only show one significant

oscillation). The red line in fig. 2.14 represents an attenuation length of $1\ \mu\text{m}$ ($= 10000\ \text{\AA}$) which is an estimate for the attenuation length of an X-ray photon, produced by X-ray fluorescence, with $h\nu \approx 3000\ \text{eV}$ [10]. The difference in the VPXSW profiles for $\lambda_2 = 53\ \text{\AA}$ and $\lambda_2 = 10000\ \text{\AA}$ demonstrates the advantage of using photoelectron detection over X-ray fluorescence as the VPXSW profile has a greater number of features, making it easier to model by the researcher. Photoelectron attenuation lengths also vary with the core level photoelectron peak that is being monitored (as they have different binding energies and hence different photoelectron kinetic energies) [14]. This allows more information to be extracted from the surface than with fluorescence detection where attenuation lengths will all be very similar. Aside from the leading edge and the first peak, the position of the oscillations within the VPXSW profile do not change much with attenuation length, with the main effect being upon the VPXSW intensity. Since it is the angular position of the oscillations that is used as the primary fitting criteria for the VPXSW profiles, rather than the intensity, any slight errors in the estimated attenuation lengths do not have a large effect on the fitting. This is a consequence of the XSW intensity being the dominant factor in the generated photoelectron signal, rather than the photoelectron attenuation. The main issue with photoelectron detection, however, is demonstrated by the similarity of the $1\ \text{\AA}$ (solid blue) and $10\ \text{\AA}$ (blue dashed) VPXSW profiles. As the attenuation length is not large enough to probe the full layer, only the top of layer 2 is probed resulting in two very similar VPXSW profiles. The only difference in the two VPXSW profiles is a slight change in the leading edge and position of the oscillation at $\approx 0.7^\circ$. This means that the true depth of the layer being probed cannot be determined and any buried layers would not be detected.

2.4. Temperature programmed desorption

Temperature programmed desorption (TPD) [1, 36, 37] is a destructive technique (the surface is destroyed during the experiment) which can be used to study the kinetics of desorption through the measurement of the activation energy of desorption (E_{des}). The activation energy of desorption can also give information on the binding environments within the surface. Low E_{des} values are indicative of physical adsorption (or physisorption) through van der Waals

interactions [38] whilst higher E_{des} values can indicate chemical adsorption (or chemisorption, typically $> 100 \text{ kJ mol}^{-1}$ [1]), in which electron transfer occurs and a chemical bond is formed between the adsorbed species and the surface. The premise of the TPD experiment is a simple one in which a surface is prepared and then heated, usually at a constant rate, whilst the desorbing species are monitored. The Polanyi–Wigner equation, eq 2.50[1], describes the decrease in surface coverage as the sample is heated for a simple system

$$-\frac{d\theta}{dT} \times \frac{dT}{dt} = \theta^n A_n(\theta) \exp\left(\frac{-E_{\text{des}}(\theta)}{RT}\right) \quad \text{Equation 2.50}$$

where θ is the relative coverage, t is time (s), n is the order of desorption, $A_n(\theta)$ is the pre-exponential factor (typically taken to be 10^{13} s^{-1} [37]), $E_{\text{des}}(\theta)$ is the activation energy for desorption (J mol^{-1}) and may be a function of coverage, R is the molar gas constant ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$) and T is the temperature of the surface (K). The relative coverage is defined in terms of layers, where $\theta = 1$ represents a monolayer of material. The change in the surface coverage can be related to the measured signal of the desorbing species $\left(-\frac{d\theta}{dt}\right)$ by noticing that the two terms on the left of eq 2.50 (the rate of coverage decrease with respect to temperature and the heating rate) can be combined into one term (the rate of coverage decrease with respect to time, which will be equal to the experimentally measured signal). For species in which the lateral interactions are suitably small the activation energy of desorption is not dependent on surface coverage, allowing it to be written simply as E_{des} , giving the Polanyi–Wigner equation in its more usual form:

$$-\frac{d\theta}{dt} = \theta^n A_n \exp\left(\frac{-E_{\text{des}}}{RT}\right) \quad \text{Equation 2.51}$$

In 1962 Redhead [37] demonstrated the linear sweep method of TPD (rather than flash desorption, in which the surface was rapidly heated) for some basic systems (argon on tungsten and hydrogen on tungsten) as a proof of concept. Up until this point flash desorption had been used to ensure that peaks in the pressure signal (the method of monitoring the desorption) were observed as vacuum systems were not able to pump gas away fast enough for slow heating rates to produce peaks (only a step up in the signal) [39]. Redhead found that the observed peak shape could be used to determine the order of desorption and

found ways of relating the activation energy of desorption to the temperature at which the peak maxima occurred [1].

As Redhead observed the order of desorption affects the peak shape observed in the TPD spectrum and can provide useful information on the desorption mechanism. Zero order desorption ($n = 0$) represents desorption from multilayers where there is no apparent variation in surface composition (as the molecule below the desorbing species is the same as the desorbing molecule, fig. 2.15a) [1]. First order desorption ($n = 1$) is observed for surfaces where the surface composition varies upon desorption as shown in fig. 2.15b, whilst other orders of desorption can indicate that a more complicated desorption mechanism occurs (e.g. combination of two species prior to desorption for a second order case) [1]. From eq 2.51 it can be seen that for $n = 0$ the desorption signal is independent of the surface coverage ($\theta^0 = 1$), so the experimental peak shape increases exponentially with temperature. Strictly zero order desorption doesn't provide a peak (just an exponential increase) but as the material on the surface

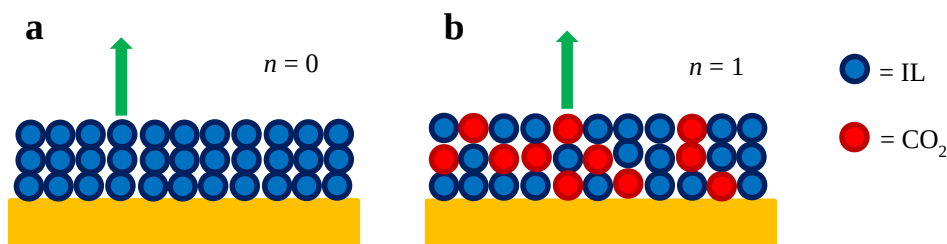


Figure 2.15: Diagram illustrating the difference between zero order desorption of IL (a) where the apparent surface composition is constant upon desorption and first order desorption of CO₂ (b) where there is an apparent change in surface composition (the number of CO₂ atoms which can be seen from above).

runs out the order of desorption ceases to be zero order, so the signal decreases sharply giving a peak in the data. As a result the maximum temperature for the desorption peak for a system observing zero order kinetics depends on the initial surface coverage, fig. 2.16a, where larger initial coverage result in higher temperatures for the peak maximum. The peak shape for first order desorption is different, having a maximum at a constant temperature, irrespective of initial coverage as shown in fig. 2.16b [1, 39]. This makes it possible to detect the point at which desorption changes from multilayer desorption (zero order) to monolayer desorption (first order), which is employed for finding the monolayer coverages for the ILs studied in this work (appendices 8.3 and 8.8). The areas

under the desorption curves, shown in fig. 2.16, are related to the initial surface coverages on the surface, so the integral of desorption rate can be used to find the initial coverage on the surface, which has been used in this work to determine the initial coverages of the IL layers studied.

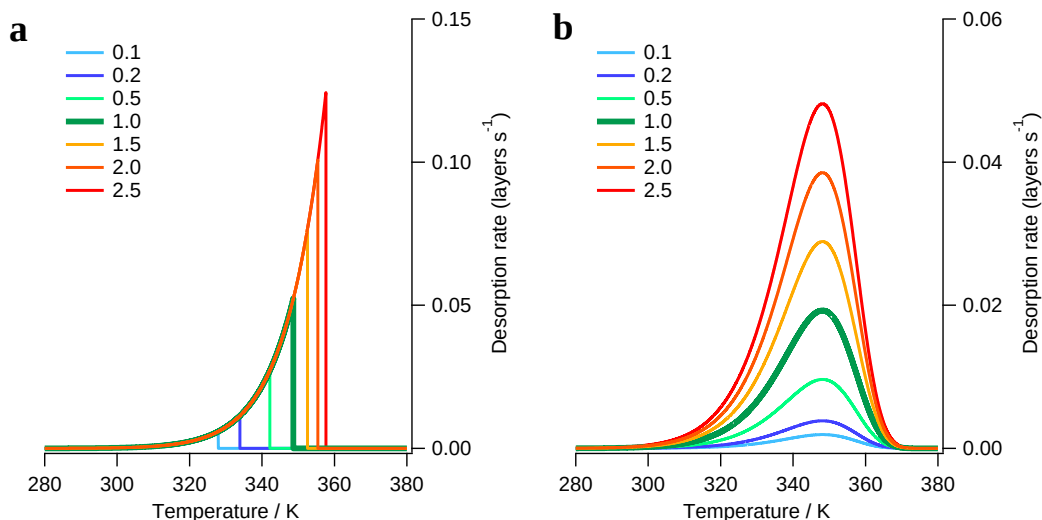


Figure 2.16: Temperature programmed desorption spectra calculated using eq 2.51 for varying initial coverages in the range 0.1 to 2.5 layers to observe the effect of order of desorption on the peak shape. The spectra in (a) observe zero order desorption, whilst the spectra in graph (b) obey first order desorption. The pre-exponential factor has been taken to be $A = 10^{13} \text{ s}^{-1}$ and the activation energy of desorption had a fixed value of 100 kJ mol^{-1} and a heating rate of 0.5 K s^{-1} .

As mentioned previously the Polanyi–Wigner equation can be used to find the activation energy of desorption for different species on a surface. In the case of zero order desorption ($n = 0$) eq 2.51 can be rearranged by taking natural logarithms of both sides to give:

$$\ln\left(-\frac{d\theta}{dt}\right) = \ln(A_n) - \frac{E_{des}}{R} \frac{1}{T} \quad \text{Equation 2.52}$$

Plotting a graph of $\ln\left(-\frac{d\theta}{dt}\right)$ versus $\frac{1}{T}$ will give a linear plot where the activation energy of desorption can be found from the gradient and the pre-exponential factor can be found from the y-axis intercept. Since the initial coverage affects the maximum temperature achieved for a zero order peak, and hence the temperature range over which desorption occurs, more accurate activation energies of desorption can be found for larger initial coverages, which have a greater number of data points. For cases where higher desorption orders are observed (such as $n = 1$) the parameters within the Polanyi–Wigner equation (θ , E_{des} and A_n) can be varied until a modelled TPD peak matches the experimentally observed TPD peak. Cases where experimental data cannot be adequately fitted

by a single peak modelled by the Polanyi–Wigner equation may indicate that multiple binding sites exist within the surface or a multi-step mechanism is involved. The total experimental desorption peak can then be modelled by a sum of desorption environments with varying E_{des} (and possibly A_n) values, as has been performed within this thesis.

2.5. Line of sight mass spectrometry

The use of line of sight (LOS) techniques, such as line of sight mass spectrometry (LOSMS) attempts to ensure that the experimental signal is only measured from a certain area within a sample, as defined by the line of sight area [40-43]. This greatly reduces the amount of molecules entering the detection region which reduces the background error that results from the detection of undesired species. The net result is an improved signal to noise ratio for the species of interest. There is also the benefit of knowing that the detected molecules originated from a specific part of the sample, as there is no way for species originating from other sources to enter the detector without reflecting from the sample. Such reflections from the sample often have a time delay, relative to the signal from the surface, so can be accounted for by subtractions which can be applied during data processing. The line of sight methods described in refs. [40-43] are set up with the use of a liquid nitrogen cooled shroud (boiling point of 77 K) made of copper, due to its high thermal conductivity, surrounding a detector. When gases collide with the wall of the LOS shroud the assumption is that the molecule is cryogenically frozen in place, or cryopumped. As a result any species desorbing or reflecting from the surface must pass thorough the line of sight tube without colliding with the LOS shroud. This results in a focal area existing on the surface—defined through the use of two apertures, assuming species travel only in straight lines (curved paths due to external fields are not considered)—as shown in fig. 2.17. The focal area consists of an umbra, of diameter d_U —from inside which a species adsorbed on the surface can see all of the detector—and a penumbra, of diameter d_P —from which an adsorbed species can only partially see the detector. The red dotted lines in fig. 2.17 show the boundaries for line of sight trajectories which result in detection for areas of the sample which are within the umbra, whilst black

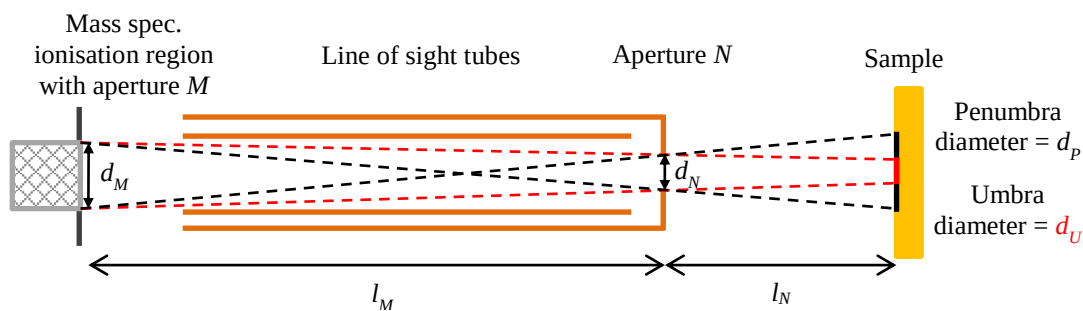


Figure 2.17: A diagram of a line of sight setup for a LOSMS experiment, showing the aperture diameters and distances required to calculate the umbra, d_U , and penumbra, d_P , diameters using eqs 2.53 and 2.54. It should be noted that there are two LOS tubes within the LTLOS setup, where the inner tube (≈ 45 K) is thermally shielded by the outer tube (≈ 80 K).

dashed lines show the allowed trajectories for species desorbing from the penumbra. As discussed the penumbra represents areas of the sample that can only partially see the detector, through line of sight, with areas of the sample at larger radii (from the centre of the LOS) seeing the least of the detector. The implication of this is that there is only a small fraction of the total signal that originates from the outer most parts of the penumbra, although the exact fraction does depend on the exact LOS geometry. This means that having a penumbra radius slightly larger than the area of the sample being studied is not too large an issue, although due to the quadratic nature of the area–radius relationship ($Area = \pi r^2$) large mismatches (10 to 20% difference) of the penumbra radius and the sample radius can lead to significant errors in the measured signal. The diameters of the umbra and penumbra defined by the apertures of radius d_M and d_N , a distance $l_M + l_N$ and l_N from the sample, respectively (as shown in fig. 2.17) can be calculated for a line of sight setup through consideration of basic trigonometry. Derivations for equations 2.53 and 2.54 can be found in appendix 8.1 and the supplementary information of reference [41].

$$d_U = d_N \left(1 - \frac{l_N}{l_M} \left(\frac{d_M}{d_N} - 1 \right) \right) \quad \text{Equation 2.53}$$

$$d_P = d_N \left(\frac{l_N}{l_M} \left(\frac{d_M}{d_N} + 1 \right) + 1 \right) \quad \text{Equation 2.54}$$

In reality not all molecules adsorb indefinitely to the liquid nitrogen cooled copper shroud, as the residence time of some species may be too low on the cooled copper tubes. The average residence time (the length of time a species will stick to a surface before it desorbs due to thermal energy), τ , can be calculated through use of the Frenkel equation (eq 2.55) [1]:

$$\tau = \tau_0 \exp\left(\frac{E_{des}}{RT}\right) \quad \text{Equation 2.55}$$

Here τ_0 is the time period between escape attempts (typically 10^{-13} s [38], the same as for a molecular vibration on a surface), E_{des} is the activation energy of desorption (J mol^{-1}), R is the molar gas constant ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$) and T is the kelvin temperature of the surface. Using a literature value for the activation energy of desorption of CO_2 on a $\text{Cu}(110)$ crystal of 21 kJ mol^{-1} [44], eq 2.55 for copper LOS tubes at 80 K gives a residence time of ≈ 5 s. This limits the effectiveness of the LOS technique on species with low E_{des} values such as N_2O , H_2S , CO_2 , N_2 , Ar and H_2 which are not effectively cryopumped with current experimental setups [40, 41]. This means that such species can be detected without travelling along the line of sight (they can bounce off of the LOS tubes) so studies of such species will not experience the benefits of the LOS system. In order to study CO_2 with line of sight techniques a new low temperature line of sight (LTLOS) apparatus has been developed in this work.

The operating principle is almost identical with the detector surrounded by a copper shroud, meaning that the only way to get a species in to the detector region is to travel along the line of sight. The cooling is provided by a helium refrigerator—which cools through the expansion of helium gas in a closed circuit—with two stage cooling allowing the use of two LOS tubes achieving ≈ 80 K and ≈ 45 K. The 80 K tube is placed outside the 45 K tube, as shown in fig. 2.17, to act as a thermal shield for the colder tube reducing the thermal load on the coldest part of the refrigerator. Despite the fact that the aperture is connected to the warmer outer tube, the cooler inner tube defines the line of sight. This is due to particles on non-LOS trajectories colliding with the inner tube, at which point it is assumed the particles adsorb to the cold inner tube indefinitely. The lower temperatures that can be achieved by the LTLOS apparatus allow a greater range of gases to be studied through line of sight methods. Looking again at the example of the CO_2 on the copper tubes ($E_{des} = 21 \text{ kJ mol}^{-1}$), the residence time for the CO_2 on the LTLOS tubes at 45 K is $\approx 2.4 \times 10^{11}$ s (≈ 7600 years). This demonstrates that once a CO_2 molecule collides with the LTLOS tubes, from a non-LOS trajectory, it will no longer interfere with the experiment. The detector region is also differentially pumped such that once molecules have made it through the line of sight they can be extracted after detection, which prevents a

build-up of species within the detection region. There are still limitations with the species which can be studied by the LTLOS setup as not all species will adsorb indefinitely on the copper tube. For a typical TPD experiment, which takes 2 hours to perform, in order for the LTLOS to be effective a minimum residence time of 2 hours is required to prevent species desorbing from the LOS tubes during the experiment. Using eq 2.55 with $\tau = 7200$ s and $\tau_0 = 10^{-13}$ s finds that the ratio E_{des}/T needs to be greater than $323 \text{ J K}^{-1} \text{ mol}^{-1}$ to ensure that the LOS setup will be suitable (the stay time will be over 2 hours) for a gas with a given E_{des} on the LOS tube. For the current LTLOS setup ($T = 45 \text{ K}$) species with an activation energy of desorption greater than 14.5 kJ mol^{-1} would be able to be studied but H_2 , Ar and N_2 are still not effectively cryopumped [41]. The experimental setup of the LTLOS apparatus used within this study (dimensions and distances) is described in section 3.2.2.

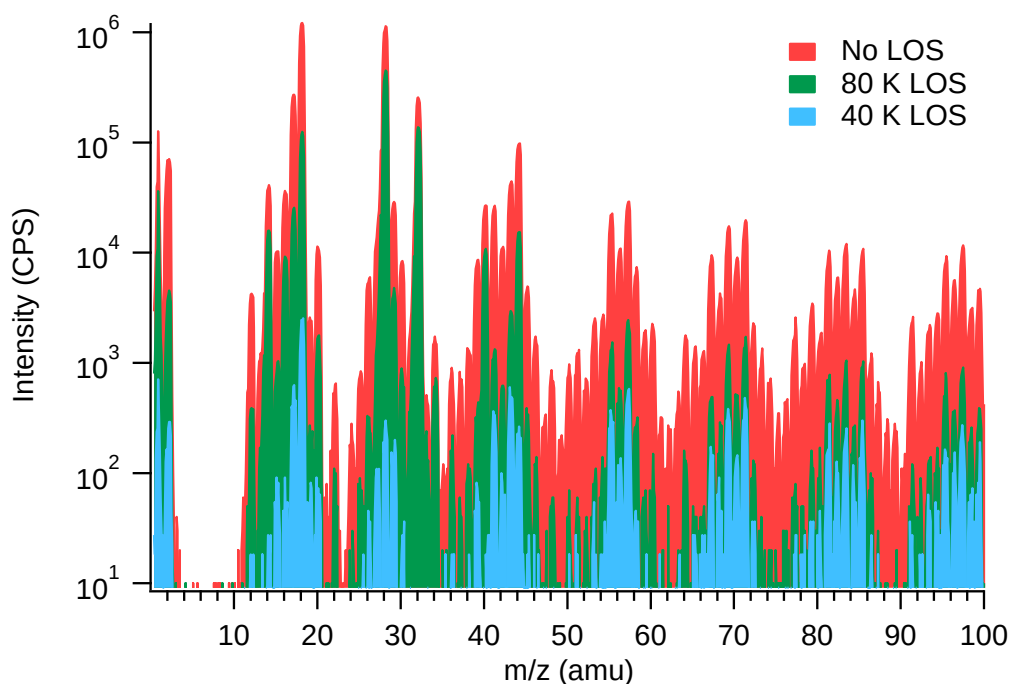


Figure 2.18: A graph showing the measured background mass spectrum for LOS tubes of different temperatures, with a logarithmic vertical scale. The sample was positioned into the LOS area, so material could be reflected into the mass spectrometer. The shown mass spectra are averages of 10 scans for line of sight tube temperatures of 298 K (room temperature, before the LOS was cooled), $\approx 80 \text{ K}$ (equivalent to liquid nitrogen cooled LOS) and $\approx 40 \text{ K}$ (LTLOS operating temperature).

The effect of using a LTLOS setup with a quadrupole mass spectrometer can be observed within fig. 2.18, which shows the background spectra (averaged over 10 cycles) for mass to charge ratios of 0 to 100 amu (emission current = $100 \mu\text{A}$, multiplier voltage = 2700 V) for different LOS tube temperatures, when

a room temperature gold sample is sitting in the LOS area. It can be seen that when the LTLOS is not operating and the tubes are at room temperature (red signal in fig. 2.18) the signals can be seen to be large ($\approx 10^6$ CPS for $m/z = 18$ and 28 amu). This is due to a combination of the matter entering the LOS aperture, which can be reflected from the tubes and detected, as well as material that is already adsorbed to the LOS tubes or within the mass spectrometer being able to desorb and be detected. Attempting to observe a small change in the signal of one of these peaks would be difficult, given the large background intensities. After cooling the LOS to approximately liquid nitrogen temperatures (as monitored by a thermocouple attached to the inner LOS tube) it can be seen that the intensities of all peaks have reduced, with many having a background level in the range 10^2 to 10^3 CPS (green data). Even at 80 K signals due to N_2 (28 amu), O_2 (32 amu) and CO_2 (44 amu) are still quite large with each of them being over 10^4 CPS. Once the LOS tubes reach ≈ 40 K it can be seen that the CO_2 background signal has dropped to $\approx 10^3$ CPS and most other mass fragments also have low signal intensities. With only H_2O ($m/z = 18$ amu) having an intensity over 10^3 CPS. This is a result of the sample reflecting background water along the line of sight into the mass spectrometer despite a background pressure below 1×10^{-8} mbar. A residual background signal will also exist for molecules which are within the region of the mass spectrometer (which itself is not cooled) as desorption from the surrounding chamber walls occurs. As well as reducing the detected signal from background species the restriction of the analysis area on the sample leads to a reduced signal intensity from the surface, relative to a system without line of sight, however the reduced background signal means a greater relative peak intensity is observed. For the LTLOS setup used within this work the desorbing signal from a surface is reduced by a factor of ≈ 12000 , relative to having the detector just above the surface [41]. This factor is affected by the geometry of the LOS setup, with systems in which the distance between the sample and detector is minimised and the LOS diameter is increased producing higher signals.

The TPD spectra in this study were detected using a quadrupole mass spectrometer rather than through variations in the measured pressure signal, which has been used for early studies [37, 39]. Quadrupole mass spectrometers [45, 46], like all mass spectrometers, allow separation of species with differing

mass to charge ratios (m/z). This allows a greater specificity to be achieved in molecular detection, however due to the fact that multiple species can have the same m/z ($\text{N}_2^{\bullet+}$, $\text{CO}^{\bullet+}$ and $\text{C}_2\text{H}_4^{\bullet+}$ all have $m/z = 28$ amu) dependence on a single m/z signal for a given species is not recommended. The quadrupole mass spectrometer utilises the fact that a charged particle will experience a force when exposed to electric fields. The electric fields are set up by four rods or poles (hence the name quadrupole), positioned every 90° on the circumference of a circle, running parallel to the direction of travel for a molecule travelling along the line of sight, fig. 2.19. The four poles are paired such that the potential on diametrically opposite rods are equivalent at any given time, resulting in a force exerted on the travelling ion which is perpendicular to its direction of travel. By

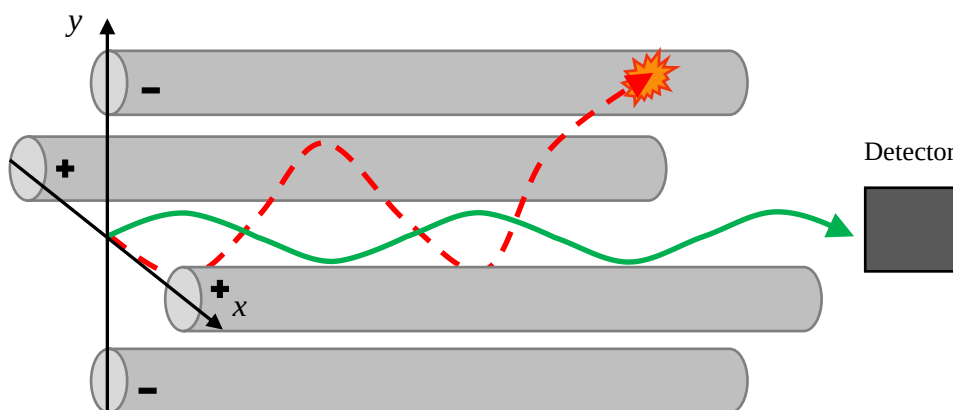


Figure 2.19: A schematic diagram showing the operating principles of the quadrupole mass spectrometer, in which four poles are used as a mass filter through periodic switching of the potentials applied to the poles. Only mass to charge ratios (m/z) which are stable for the voltages applied (green) at a given time are able to pass through to the poles to the detector, whilst other mass fragments collide with the poles and are eliminated.

oscillating the potentials applied to the rods an oscillating electric field will be set up causing the ion to oscillate as it travels along the mass spectrometer. The magnitude and stability of the oscillation of the ion will depend upon the frequency and magnitude of the oscillating potentials and the mass to charge ratio of the ion. The Mathieu equations [45, 47] equate the force experienced by the ion to the path of the ion through the oscillating field. Ions which have the correct m/z , for the given mass spectrometer settings, will experience a stable trajectory (green path in fig. 2.19), pass through the mass spectrometer and collide with the electron multiplier to generate a current which can be detected. Ions which do not experience a stable trajectory collide with one of the poles and are lost (red path in fig. 2.19). In practice, when selecting species with

different m/z to detect, the frequency of voltage oscillation is kept constant, as the voltages applied to the rods are the easiest parameters to vary electronically [46]. This allows rapid scanning and variation of the m/z that can be detected in the mass spectrometer meaning that the signals from certain mass fragments can be monitored with a temporal resolution of 100 ms, whilst still attaining a reasonable intensity. Quadrupole mass spectrometers have been shown to be suitable for use with TPD by previous studies [41, 42, 48, 49].

2.6. References

- [1] Kolasinski, K.W., *Surface Science: Foundations of Catalysis and Nanoscience*. Eds., John Wiley & Sons, Chichester, UK, (2012)
- [2] Seah, M.P. and Dench, W.A., Quantitative electron spectroscopy of surfaces: A standard data base for electron inelastic mean free paths in solids. *Surf. Interface Anal.*, **1979**, (1), pp. 2-11.
- [3] Salmeron, M. and Schlögl, R., Ambient pressure photoelectron spectroscopy: A new tool for surface science and nanotechnology. *Surf. Sci. Rep.*, **2008**, (63), pp. 169-199.
- [4] Ueda, K., Yoshida, M., Isegawa, K., Shirahata, N., Amemiya, K., Mase, K., Mun, B.S. and Kondoh, H., Operando Observation of NO Reduction by CO on Ir(111) Surface Using NAP-XPS and Mass Spectrometry: Dominant Reaction Pathway to N₂ Formation under Near Realistic Conditions. *J. Phys. Chem. C*, **2017**, (121), pp. 1763-1769.
- [5] *X-ray Science and Technology*. Michette, A.G. and Buckley, C.J., Eds., Institute of Physics Publishing, Bristol, (1993)
- [6] Röntgen, W.C., On a New Kind of Rays. *Nature*, **1895**, (53), pp. 274-277.
- [7] Compton, A.H., The total reflexion of X-rays. *Phil. Mag.*, **1923**, (45), pp. 1121-1131.
- [8] *X-ray and neutron reflectivity: principles and applications 2nd edition*. Dalliant, J. and Gibaud, A., Eds., Springer, Berlin, (2009)
- [9] Als-Nielsen, J. and McMorrow, D., *Elements of Modern X-ray Physics 2nd edition*. Eds., John Wiley & Sons, Chichester, (2011)
- [10] Willmott, P., *An Introduction to Synchrotron Radiation: Techniques and Applications*. Eds., John Wiley and Sons, Chichester, (2011)
- [11] Henke, B.L., Gullikson, E.M. and Davis, J.C., *X-ray interactions: photoabsorption, scattering, transmission, and reflection at E=50-30000 eV, Z=1-92*, Atomic Data and Nuclear Data Tables Vol. **54** (no. 2), 181-342 (July 1993). http://henke.lbl.gov/optical_constants/ (accessed July 2017).
- [12] Parratt, L.G., Surface Studies of Solids by Total Reflection of X-rays. *Phys. Rev.*, **1954**, (95), pp. 359-369.
- [13] Atkins, P. and De Paula, J., *Atkins' Physical Chemistry 8th edition*. Crowe, J., Fiorillo, J. and Hughes, R., Eds., Oxford University Press, Oxford, (2006)
- [14] *Surface Analysis by Auger and X-ray Photoelectron Spectroscopy*. Briggs, D. and Grant, J.T., Eds., IM Publications, Chichester, (2003)

- [15] Thompson, A.C. and Vaughan, D., *X-ray Data Booklet*. Kirz, J., Eds., Lawrence Berkeley Laboratory, (2001)
- [16] *Practical Surface Analysis Volume 1 - Auger and X-ray Photoelectron Spectroscopy*. Briggs, D. and Seah, M.P., Eds., John Wiley & Sons, Chichester, (1990)
- [17] Bambynek, W., Swift, C.D., Crasemann, B., Frend, H.U., Rao, P.V., Price, R.E., Mark, H. and Fink, R.W., X-ray Fluorescence Yields, Auger and Coster-Kronig Transition Probabilities. *Rev. Mod. Phys.*, **1972**, (44), pp. 716-813.
- [18] Tanuma, S., Powell, C.J. and Penn, D.R., Calculations of electron inelastic mean free paths. IX. Data for 41 elemental solids over the 50 eV to 30 keV range. *Surf. Interface Anal.*, **2011**, (43), pp. 689-713.
- [19] Lovelock, K.R.J., Smith, E.F., Deyko, A., Villar-Garcia, I.J., Licence, P. and Jones, R.G., Water adsorption on a liquid surface. *Chem. Commun.*, **2007**, 4866-4868.
- [20] Shkrob, I.A., Marin, T.W., Chemerisov, S.D., Hatcher, J.L. and Wishart, J.F., Radiation Induced Redox Reactions and Fragmentation of Constituent Ions in Ionic Liquids. 2. Imidazolium Cations. *J. Phys. Chem. B*, **2011**, (115), pp. 3889-3902.
- [21] Shkrob, I.A., Marin, T.W., Chemerisov, S.D. and Wishart, J.F., Radiation Induced Redox Reactions and Fragmentation of Constituent Ions in Ionic Liquids. 1. Anions. *J. Phys. Chem. B*, **2011**, (115), pp. 3872-3888.
- [22] Shaporenko, A., Zharnikov, M., Feulner, P. and Menzel, D., Quantitative analysis of temperature effects in radiation damage of thiolate-based self-assembled monolayers. *J. Phys.-Condens. Matt.*, **2006**, (18), pp. S1677-S1689.
- [23] Tanuma, S., Powell, C.J. and Penn, D.R., Proposed Formula for Electron Inelastic Mean Free Paths Based on Calculations for 31 Materials. *Surf. Sci.*, **1987**, (192), pp. L849-L857.
- [24] Tanuma, S., Powell, C.J. and Penn, D.R., Calculations of Electron Inelastic Mean Free Paths for 31 Materials. *Surf. Interface Anal.*, **1988**, (11), pp. 577-589.
- [25] Powell, C.J. and Jablonski, A., *NIST Electron Inelastic-Mean-Free-Path Database, version 1.2, SRD 71*. Eds., National Institute of Standards and Technology, Gaithersburg, MD, (2010)
- [26] Sanmamed, Y.A., Gonzalez-Salgado, D., Troncoso, J., Romani, L., Baylaucq, A. and Boned, C., Experimental methodology for precise determination of density of RTILs as a function of temperature and pressure using vibrating tube densimeters. *J. Chem. Thermody.*, **2010**, (42), pp. 553-563.
- [27] Nishi, T., Iwahashi, T., Yamane, H., Ouchi, Y., Kanai, K. and Seki, K., Electronic structures of ionic liquids $C_n\text{mim}^+ \text{BF}_4^-$ and $C_n\text{mim}^+ \text{PF}_6^-$ studied by ultraviolet photoemission, inverse photoemission, and near-edge X-ray absorption. ne structure spectroscopies. *Chem. Phys. Lett.*, **2008**, (455), pp. 213-217.
- [28] Bedzyk, M.J., Bommarito, G.M. and Schildkraut, J.S., X-ray Standing Waves at a Reflecting Mirror Surface. *Phys. Rev. Lett.*, **1989**, (62), pp. 1376-1379.
- [29] Zhang, R.T., Itri, R. and Caffrey, M., Membrane structure characterization using variable-period X-ray standing waves. *Biophys. J.*, **1998**, (74), pp. 1924-1936.
- [30] Kramer, M., von Bohlen, A., Sternemann, C., Paulus, M. and Hergenroder, R., Synchrotron radiation induced X-ray standing waves analysis of layered structures. *Appl. Surf. Sci.*, **2007**, (253), pp. 3533-3542.

- [31] Bedzyk, M.J., *X-Ray Standing Wave at the Total Reflection Condition*. In *X-Ray Standing Wave Technique: Principles and Applications*, Zegenhagen, J. and Kazimirov, A., Eds., World Scientific, Singapore, (2013), pp. 94-107.
- [32] Boas, M.L., *Mathematical Methods in the Physical Sciences, Second Edition*. Eds., John Wiley & Sons, New York, (1983)
- [33] VPXSW_3layer (written in Igor Pro 6.34), Contact: robert.g.jones@nottingham.ac.uk (accessed 2017)
- [34] Wang, J., Bedzyk, M.J., Penner, T.L. and Caffrey, M., Structural Studies of Membranes and Surface Layers up to 1000 Å Thick using X-ray Standing Waves. *Nature*, **1991**, (354), pp. 377-380.
- [35] Kramer, M., von Bohlen, A., Sternemann, C., Paulus, M. and Hergenroder, R., X-ray standing waves: a method for thin layered systems. *J. Anal. Atom. Spectrom.*, **2006**, (21), pp. 1136-1142.
- [36] King, D.A., Thermal Desorption from Metal Surfaces. *Surf. Sci.*, **1975**, (47), pp. 384-402.
- [37] Redhead, P.A., Thermal desorption of gases. *Vacuum*, **1962**, (12), pp. 203-211.
- [38] Deyko, A. and Jones, R.G., Adsorption, absorption and desorption of gases at liquid surfaces: water on C₈C₁Im BF₄ and C₂C₁Im Tf₂N. *Faraday Discuss.*, **2012**, (154), pp. 265-288.
- [39] Gasser, R.P.H., *An introduction to chemisorption and catalysis by metals*. Eds., Oxford University Press, New York, US, (1985)
- [40] Jones, R.G. and Fisher, C.J., Reaction and sticking probabilities using line of sight techniques: iodine on Al(111). *Surf. Sci.*, **1999**, (424), pp. 127-138.
- [41] Hessey, S.G. and Jones, R.G., Line-of-sight mass spectrometry: principles and practice. *Surf. Interface Anal.*, **2015**, (47), pp. 587-600.
- [42] Chan, A.S.Y., Skegg, M.P. and Jones, R.G., Line of sight techniques: Providing an inventory of all species arriving at and departing from a surface. *J. Vac. Sci. Technol. A*, **2001**, (19), pp. 2007-2012.
- [43] Jones, R.G., Turton, S. and Ithnin, R., Formation of translationally hot ethene by dissociative electron capture of adsorbed 1,2-dichloroethane. *Chem. Phys. Lett.*, **1996**, (261), pp. 539-544.
- [44] Ernst, K.H., Schlatterbeck, D. and Christmann, K., Adsorption of carbon dioxide on Cu(110) and on hydrogen and oxygen covered Cu(110) surfaces. *Phys. Chem. Chem. Phys.*, **1999**, (1), pp. 4105-4112.
- [45] Majer, J.R., *The Mass Spectrometer*. Mott, N. and Noakes, G.R., Eds., Wyekham Publications, London, (1977)
- [46] Herbert, C.G. and Johnstone, R.A.W., *Mass Spectrometry Basics*. Eds., CRC Press, Boca Raton, (2002)
- [47] Ruby, L., Applications of the Mathieu equation. *Am. J. Phys.*, **1996**, (64), pp. 39-44.
- [48] Lovelock, K.R.J., Deyko, A., Corfield, J.A., Gooden, P.N., Licence, P. and Jones, R.G., Vaporisation of a dicationic ionic liquid. *Chemphyschem*, **2009**, (10), pp. 337-340.
- [49] Emel'yanenko, V.N., Verevkin, S.P., Heintz, A., Corfield, J.-A., Deyko, A., Lovelock, K.R.J., Licence, P. and Jones, R.G., Pyrrolidinium-based ionic liquids. 1-butyl-1-methyl pyrrolidinium dicyanoamide: Thermochemical measurement, mass spectrometry, and ab initio calculations. *J. Phys. Chem. B*, **2008**, (112), pp. 11734-11742.

Chapter 3

Experimental section

The experiments discussed in this thesis were performed in two separate locations. The variable period X-ray standing wave analysis monitored through photoelectron detection experiments were performed at the Diamond Light Source, Oxfordshire, UK on the I09 beamline. The temperature programmed desorption experiments were performed within the School of Chemistry at the University of Nottingham, UK. All experiments were performed under ultra-high vacuum conditions, as detailed in the proceeding sections.

3.1. Diamond I09 beamline

The I09 beamline at the Diamond light source has a vacuum system which is composed of three chambers for sample introduction, sample preparation and sample analysis. The chambers are pumped with oil free pumps (turbomolecular pumps and ion pumps, backed by scroll pumps) to maintain a background chamber pressure of $\approx 1 \times 10^{-10}$ mbar in the analysis chamber. The experimental setup within the analysis chamber is depicted in fig. 3.1 with the sample placed on a manipulator which can translate in 3 dimensions and rotate

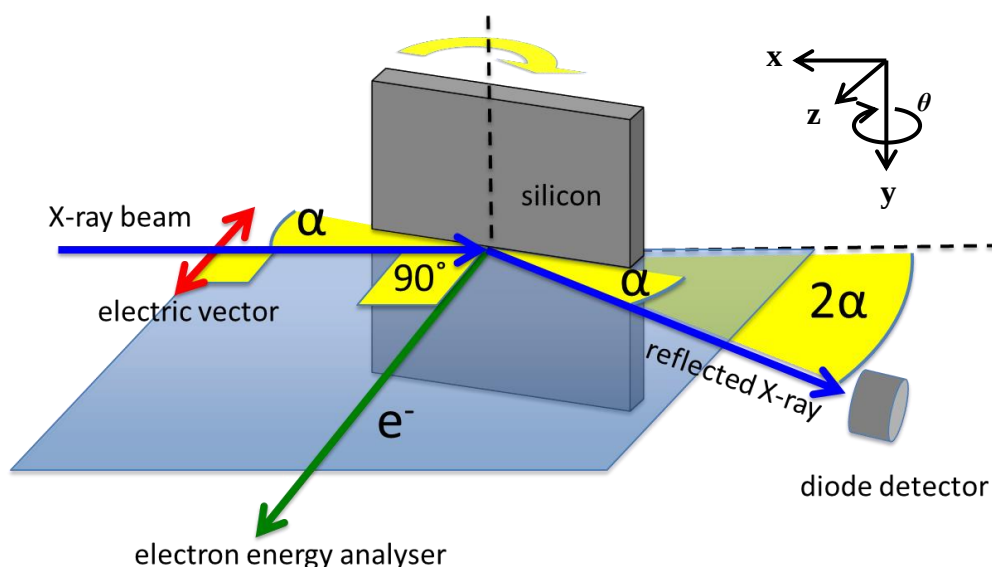


Figure 3.1: A schematic diagram of the experimental setup within the analysis chamber at the I09 beamline at the Diamond light source. The sample was mounted on a manipulator that could move in the x, y and z directions as well as rotate about the y-axis (and also the z-axis, though this was not used). The X-ray beam came in at 90° to the electron analyser and the diode detector was moved in order to collect the reflected beam.

about the y-axis, shown by the yellow arrow. A monochromatic X-ray beam is incident upon the sample at 90° to the concentric hemispherical analyser (CHA) and was polarised such that its electric field vector is parallel to the electron detector. Having the electric field polarised in this direction minimises the effect of non-dipole effects (which affect the angular distribution of photoelectrons that are emitted from the surface) [3, 4]. Variable period X-ray standing wave (VPXSW) profiles were obtained through the collection of electron distribution curves (EDCs) for different incident X-ray angles, α , at a fixed X-ray energy. Collection of a VPXSW profile for a given photoelectron peak (e.g. C 1s) was performed as follows. The value of α was scanned from 0° to 2.5° in 0.025° steps with a C 1s EDC collected at each step (101 scans in total), taking approximately 20 minutes per VPXSW profile. The VPXSW profile is then extracted from the variation of the fitted peak areas under the EDCs with angle using software written within the research group at Nottingham [6].

Despite the fact that the emission angle of the surface varies during the collection of the EDCs (which enhances the surface sensitivity and is the principle of operation in angle resolved X-ray photoelectron spectroscopy [7, 8]), no angular correction was made. This is due to the fact that the small angular range sampled here effects the escape depth by less than 0.1% (escape depth varies by a factor of $\cos(2.5^\circ)$, given in eq 2.5). EDCs of the photoelectrons leaving the surface were collected with a concentric hemispherical analyser (VG Scienta EW4000 10 keV, 200 mm radius hemisphere, lens acceptance angle $\pm 30^\circ$, resolution < 40 meV at 3000 eV) operating in snapshot mode, collecting signal from a range of kinetic energies at once (range dependent upon pass energy), with the total EDC being a sum of the snapshots over the energy range. A diode detector was used to align the sample through the use of two processes. The first involved using the diode detector to find 0° for the sample by initially moving the sample out of the way of the incident X-ray and letting the maximum X-ray intensity be measured by the diode detector. The sample (with $\alpha = 0^\circ$) was then moved along the positive z-direction until the measured X-ray intensity was half its maximum value (as the X-ray beam is cut by the edge of the sample surface). The second method used the diode detector positioned at 2° (relative to the incident X-ray) and scans α from 0° to 2° to find the angle at which the maximum reflectivity (which corresponds to $\alpha = 1^\circ$) occurs. If the reflectivity

maximum occurs at an angle which differs from $\alpha = 1^\circ$ (for the detector at 2°) then the angular range is shifted to ensure that maximum reflectivity occurs at $\alpha = 1^\circ$. The first and second alignment processes are repeated iteratively until the angular range does not require shifting, indicating the sample is correctly aligned. The diode detector also allowed simultaneous collection of the reflected X-ray (XRR) during experimental VPXSW scans. The sample preparation chamber was equipped with a quadrupole mass spectrometer (Hiden RC 511), allowing the purity of gaseous materials to be ascertained. The ionic liquid evaporator and its cooled collimator (taken from Nottingham, described in section 3.2.3) was attached the sample preparation chamber. The sample on the manipulator could be cooled to around 90 K and heated up to 650 K.

3.2. Temperature programmed desorption chamber

Temperature programmed desorption experiments were performed in a stainless steel vacuum chamber under UHV conditions—pumped by two oil diffusion pumps and a titanium sublimation pump—with the line of sight tubes acting as a cryopump. The chamber was baked at 150°C for 36 hours prior to

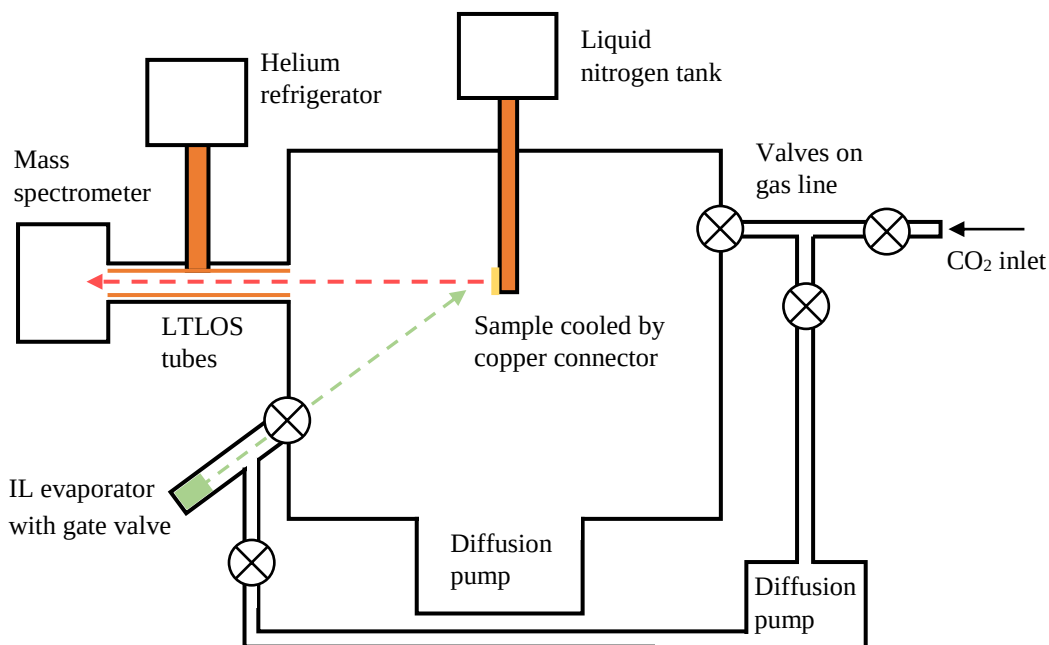


Figure 3.2: A schematic of the vacuum system used for the temperature programmed desorption studies described in this work. The gold sample is mounted on a manipulator which can translate in three dimensions and rotate about the z-axis (vertical axis), and is situated in the centre of the chamber such that all components point toward the sample. Circles with crosses in them represent valves whilst the dashed green line represents the IL beam trajectory upon evaporation and the dashed red line represents material desorbing along the line of sight into the mass spectrometer.

use (after being open to the air to attach new components) but not prior to each experimental run, achieving a base pressure of 5×10^{-10} mbar, as measured by a Bayard-Alpert type ionisation gauge (Vacuum Generators) calibrated for nitrogen gas. A schematic of the vacuum chamber is shown in fig. 3.2 with a photograph of the main analysis chamber shown in fig. 3.3. A disk shaped gold crystal (Au(111)) with a diameter 10 mm, was mounted on a manipulator capable of three dimensional translation as well as rotation about the z-axis, which could be cooled to a temperature of ≈ 88 K with liquid nitrogen. The surface was prepared for IL–CO₂ studies by annealing to 510 K to ensure that all physisorbed material had desorbed (leaving behind only material chemically bound to the surface, which would be unlikely to desorb during the experiment), as the interaction of the gold with the IL or CO₂ was not the focus of this study. The sample temperature was monitored through use of type K (chromel/alumel) thermocouples and was accurate to ± 2 K. Attached to the main analysis chamber via a gate valve was an IL evaporator (described in section 3.2.3), which could be independently pumped. There was also a gas line attached to the analysis chamber via a leak valve, which could be independently pumped, allowing gases to be dosed into the chamber.

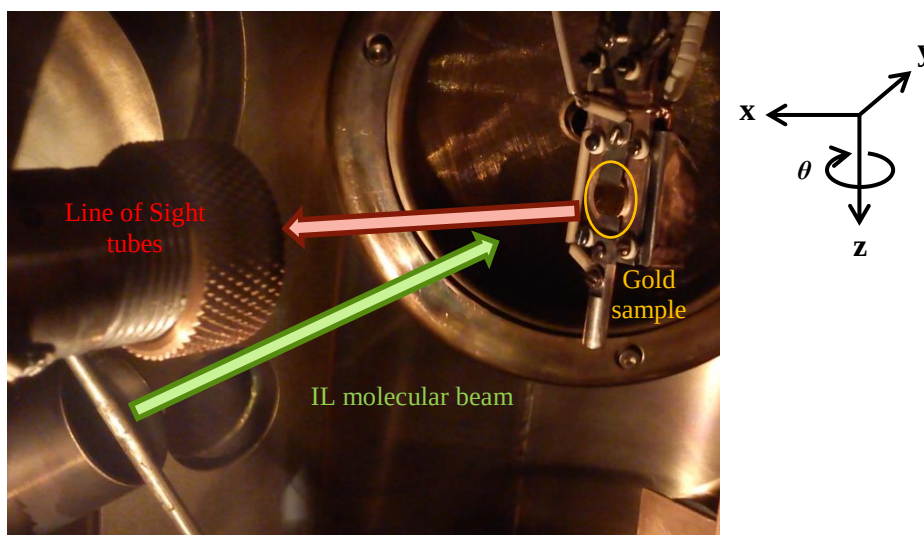


Figure 3.3: A photograph of the gold sample and manipulator used in this study, with a set of axis showing the translational and rotational capabilities of the sample manipulator. Ionic liquid is dosed by chemical vapour deposition in a molecular beam (green path). Only material desorbing and travelling along the line of sight (red path) are detected by the mass spectrometer.

3.2.1. Temperature programmed desorption setup

Temperature programmed desorption was performed by heating the sample with two tungsten filaments from the reverse side of the sample manipulator to which the gold crystal was affixed. Heating was performed in two regimes starting with a constant voltage (8.3 V AC), and therefore a constant power, heating regime from ≈ 88 K to ≈ 230 K before swapping to a constant heating rate (0.5 K s^{-1}) power supply (built in Nottingham) for ≈ 230 K to 510 K. During the CO_2 desorption the constant power heating regime was observed to produce a heating rate which was reasonably linear up to 200 K ($\approx 0.67 \text{ K s}^{-1}$) before a reduced heating rate was observed at higher temperatures. The heating regimes were swapped over after the CO_2 desorption had finished (generally by 180 K) but before the IL desorption had begun. The temperature at which the heating regimes were swapped was varied and was not seen to affect the measured TPD profiles of either the CO_2 or the IL. A constant heater power was required during the CO_2 desorption as the constant heating rate (0.5 K s^{-1}) supply used a feedback loop which turned the filaments on and off to control the temperature. The turning on and off of the filaments, for the lowest surface temperatures, caused non-linear heating rates and therefore spurious signals in the experimental data. TPD spectra were monitored through the use of low temperature line of sight mass spectrometry (section 2.5), where ion signals of interest were tracked by a Hiden RC 511 quadrupole mass spectrometer ($m/z = 1$ to 511 amu), using the MASSoft 7 software.

The general procedure for a temperature programmed desorption experiment is as follows. The surface of the gold crystal was heated to 510 K to clean the surface, before the surface was cooled to ≈ 90 K. Once the crystal had reached its minimum temperature the surface was formed (with various quantities of IL and/or CO_2). After the surface had been formed a 20 minute wait whilst keeping the surface at ≈ 90 K was performed. This wait allowed the background pressure to recover after dosing the CO_2 , giving a lower background in the mass spectrometer signal, as well as allowing any CO_2 which was only loosely bound on the surface to desorb (material which was not captured by the IL but had a stay time on the surface of a few minutes). After the 20 minute wait TPD was performed (first constant power heating then constant rate heating) up to 510 K, allowing the cycle to be performed again. The mass spectrometer was

used with a filament emission current of 1 mA, an electron energy of 70 eV and a multiplier voltage of 2700 V when tracking the mass fragments. The mass to charge ratios that were detected, for a counting time of 400 ms per point, during TPD for $m/z = 44$ ($\text{CO}_2^+\bullet$), 28 ($\text{CO}^+\bullet$, $\text{N}_2^+\bullet$), 20 ($\text{HF}^+\bullet$), 18 ($\text{H}_2\text{O}^+\bullet$) and 12 amu ($\text{C}^+\bullet$), as well as the fragments for the IL of interest; 195 ($[\text{C}_8\text{C}_1\text{Im}]^+$) and 96 amu ($[\text{C}_1\text{C}_1\text{Im}]^+$) for $[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]$ or 195 ($[\text{C}_8\text{C}_1\text{Im}]^+$) and 83 amu ($[\text{HC}_1\text{Im}]^+$) for $[\text{C}_8\text{C}_1\text{Im}][\text{Tf}_2\text{N}]$. Data was analysed using scripts and programs written within the research group using the Igor Pro 6.34A programming language.

3.2.2. Low temperature line of sight setup

The low temperature line of sight (LTLOS) apparatus has been developed to allow the study of the desorption of molecules which were not able to be studied by existing line of sight methods [9-11], for which only species that are successfully cryopumped at ≈ 77 K (with liquid nitrogen) could be successfully monitored. The theory behind the LTLOS setup is discussed in section 2.5, also showing a schematic diagram of the operating principle in fig. 2.17. The low temperature line of sight setup consists of two copper tubes of outer diameter 25 mm and 15 mm arranged concentrically (the smaller diameter tube will be referred to as the ‘inner’ tube and the larger diameter tube referred to as the ‘outer’ tube). The LOS tubes were attached to a Leybold Coolpak 4000 D helium refrigerator which maintained an inner tube temperature of ≈ 45 K and an outer tube temperature of ≈ 80 K, monitored by type K (chromel/alumel) thermocouples. The outer tube acts as a thermal shield from heat radiation and the majority of the chamber gas, reducing the thermal load on the inner tube. The LTLOS tubes were designed in such a way that it is not possible for a molecule to enter the mass spectrometer ionisation region from the sample chamber without passing through the line of sight tubes. For molecules that are cryopumped at 45 K, a detection in the mass spectrometer is only possible by desorption from or reflection from the sample and by travelling along the line of sight, as all other trajectories result in a collision with the inner tube and indefinite adsorption (an assumption of being cryogenically pumped). The outer tube had an aperture attached to it, of diameter 6 mm, positioned 10 cm from the sample to define a line of sight area on the sample. The mass

spectrometer ionisation region is also defined by an aperture of 6 mm, approximately 50 cm from the sample. Using this information the parameters $l_M = 400$ mm, $l_N = 100$ mm, $d_M = 6$ mm and $d_N = 6$ mm can be found and using eqs 2.53 and 2.54 a line of sight area with an umbra of diameter $d_U = 6$ mm and a penumbra of diameter $d_P = 9$ mm is defined on the sample surface. It is assumed that a molecule will only get a single pass through the mass spectrometer ionisation region to be detected before it is pumped away from the detector region. Using the known sample manipulator geometry and the dipstick attached to the bottom of the manipulator (which can be seen in fig. 3.3, below the gold sample) experiments, similar to those described in ref. [11] in which acetone vapour was reflected into the mass spectrometer by moving the dipstick across the LOS area, could be performed to detect the line of sight area from the increases in the detected signal. This ensured that the sample could be positioned such that the LOS area was focused solely upon the sample area during TPD experiments.

3.2.3. Ionic liquid evaporator

Ionic liquids were dosed onto the gold crystal through a chemical vapour deposition method, which has been used previously for IL systems [12-14] and has been seen to dose ILs intact (without thermal decomposition) [14]. An

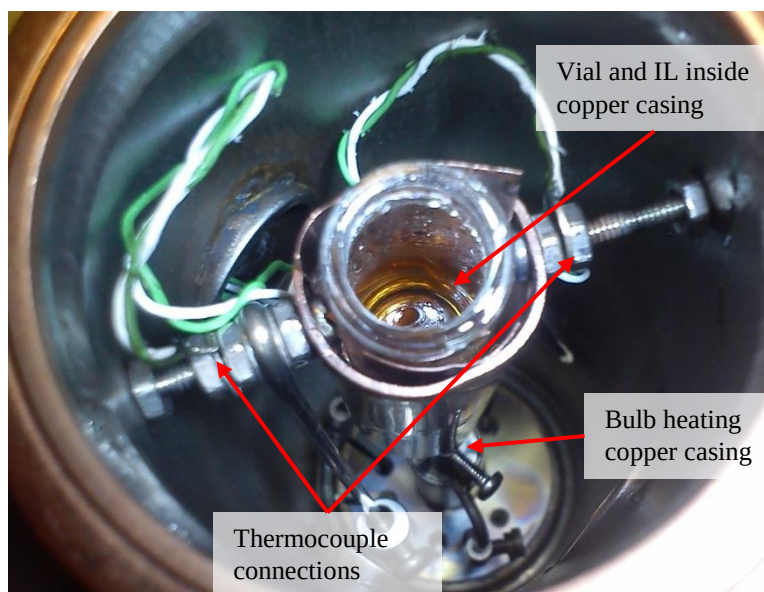


Figure 3.4: A photograph of the IL evaporator showing the setup with a vial containing IL in it. Beneath the copper tube a halogen bulb is situated which provides the heat to evaporate the IL. It can be seen that two bolts are used to keep the IL vial in the centre of the vacuum casing and also are where the thermocouples are connected to measure IL temperature.

evaporator was built in-house and consisted of a glass vial housed within a copper housing, which was heated by a halogen light bulb (20 W, 12 V), as shown in fig. 3.4. Note that due to the design of the copper housing for the glass vial (which contained the IL) there was not direct irradiation of the IL by light from the bulb, removing any possible effects of intense light (such as photodegradation) on the IL. The temperature of the IL was measured with the use of a type K (chromel/alumel) thermocouple in contact with the outside of the copper casing, so only gives the temperature of the IL accurate to ± 5 K. Since the evaporation rate is exponentially dependent upon the temperature (eq 2.51) a small change in temperature can result in a large change in desorption rate, however these variations in temperature and IL dose rate are accounted for by calibration of the IL coverage. The IL evaporator is mounted on the chamber at a 45° angle, as shown in the schematic diagram, fig. 3.2. Approximately 10 cm above the evaporator, along the IL evaporation path, a liquid nitrogen cooled collimator (8 mm diameter) was situated to capture any volatile gases released from the IL during evaporation. A gate valve was situated between the IL evaporator and the analysis chamber to allow the IL dose to be turned “on” or “off” by opening or closing the valve, once the IL had been heated to its evaporation temperature. The IL evaporator could be independently pumped by a diffusion pump which allows the IL to be degassed easily. The ILs were held at 373 K when not in use to prevent any gases being absorbed within the IL. The degassing process involved heating the IL to the temperature at which it begins to evaporate (IL dependent) ensuring that all volatile materials dissolved within the IL would be removed before introduction into the analysis chamber (see section 3.3). Potential impurities such as water or nitrogen were not observed in any of the mass spectra, so it is assumed they were removed by the degassing procedure. As a result water or other impurity content of the ILs was not checked before experimentation as this would not have been a reflection of the IL purity once under vacuum.

3.3. Materials used and beamline parameters

Two ionic liquids were studied in this work, 1-octyl-3-methylimidazolium tetrafluoroborate ($[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]$, ions **b** and **a** shown in fig.

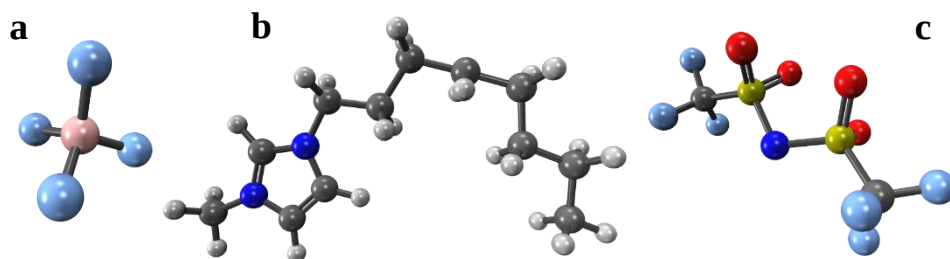


Figure 3.5: A diagram showing the ions used to compose the ionic liquids studied within this work where white atoms represent hydrogen, pink atoms represent boron, grey atoms represent carbon, dark blue atoms represent nitrogen, red atoms represent oxygen, light blue atoms represent fluorine and yellow atoms represent sulfur. The ion (**a**) is the tetrafluoroborate anion ($[\text{BF}_4]^-$), (**b**) is 1-octyl-3-methylimidazolium ($[\text{C}_8\text{C}_1\text{Im}]^+$) and (**c**) is the bis(trifluoromethylsulfonyl)imide ($[\text{Tf}_2\text{N}]^-$).

3.5) and 1-octyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ($[\text{C}_8\text{C}_1\text{Im}][\text{Tf}_2\text{N}]$, ions **b** and **c** in fig. 3.5). Both of the ILs were synthesised in Nottingham by members of the Licence group using procedures based upon those discussed in literature [15, 16] and were observed to be of high purity through the use of diagnostic spectrometry. ILs were introduced into the vacuum chamber with an initial slow degassing procedure to prevent violent release of volatile components and splatter of the IL. The slow degassing procedure consisted of iterative cycles of heating the IL ($\approx 373 \text{ K}$) isolated from vacuum conditions, followed by a slight reduction in pressure (to approximately half the original pressure), followed by heating and so on, over the period of 6 to 8 hours after which the IL was left exposed to UHV conditions. As mentioned previously the IL was left at 373 K under UHV conditions when not in use to aid in the removal of gaseous species. After the IL which had been introduced to the vacuum system had been degassed, prior to its first use for chemical vapour deposition the IL was prepared by heating it up to its evaporation temperature to ensure that all volatile species which may have been stable within the IL had been removed.

Surfaces within this study were exposed to the vapours CO_2 (99.8% British Oxygen Company, UK) and CHCl_3 (analytical standard, Sigma-Aldrich). Before use of the vapour from the liquid source (CHCl_3), the liquid was placed in a UHV compatible glass tube and attached to the vacuum chamber, frozen with liquid nitrogen and pumped on to remove any gaseous species that did not condense at liquid nitrogen temperatures. After allowing the liquids to thaw out aliquots of the gas were expanded into the gas line and their purity checked with residual gas analysers prior to dosing. For the CO_2 , only expansion

then pumping cycles were performed to remove any impurities in the gas line prior to use. All of the gases dosed onto the surfaces were seen to be pure with no major contaminants observed in the mass spectra during dosing.

The silicon crystal used in the VPXSW studies, described in chapter 4, was a polished Si(001) surface with dimensions 10×10×1 mm with a thin native oxide on its surface. Prior to introduction of the silicon crystal to the vacuum system it was rinsed in acetone. No attempt was made to remove the native oxide layer either by acid treatment or argon ion bombardment under vacuum. The X-ray beam used to study the silicon surface had its intensity reduced to prevent damage of materials that would be adsorbed onto its surface. The intensity was reduced by a factor of 200, where the beam was reduced by a factor of 20 by using slits in the beamline and was further reduced, by a factor of 10, by detuning the undulator gap. To further reduce the effects of beam damage each new VPXSW profile was collected on a fresh patch of the surface ensuring that the surface was as undamaged as possible when beginning the scan. Some X-ray damage of the surface was still observed as the sample had to be aligned at every position, meaning that prior to every VPXSW scan the surface had received between 30 and 60 seconds of X-ray irradiation. The X-ray beam itself had a height (perpendicular to surface plane) of 30 μm and a width (parallel to the surface plane) of 0.3mm. The photon energy was set to 3000 eV as this produced photoelectrons with reasonably large attenuation lengths ($\approx 50 \text{ \AA}$), allowing transmission of the photoelectrons through thicker layers than under traditional XPS (Al $K\alpha$ radiation has $h\nu = 1486.6 \text{ eV}$) with slower photoelectrons.

3.4. Surfaces studied

Each of the experiments performed within this study looked at slightly different surfaces, whether the IL was varied or the surface structure was varied. The synchrotron study looked at the ionic liquid $[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]$, with a thin layer on top of it. The temperature programmed desorption studies looked at the interaction of CO_2 with two different ILs but looked at the same surface structures, as described in the following sections.

3.4.1. VPXSW studies of silicon and its native oxide

Prior to the silicon surface having any $[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]$ deposited onto it VPXSW profiles of the silicon substrate with its native oxide layer were collected. These experiments were performed with a surface temperature of 293 K and photoelectrons were collected for the Si 2p ($KE \approx 2892$ to 2902 eV) and O 1s ($KE \approx 2457$ to 2473 eV) regions. The binding energies of the collected photoelectron peaks were calibrated such that the Si 2p_{3/2} signal from the silicon substrate was at the 99.42 eV literature value [17] to account for the work function of the spectrometer and any contact potentials that existed. This resulted in a correction of -1.46 eV being applied to the binding energies for the EDCs collected on this surface. A 3 layer model was used to calculate the theoretical VPXSW profiles of the surface in which the first layer was vacuum, the second layer was silicon oxide and the third layer was silicon substrate. The silicon oxide was assumed to be the same as SiO_2 (despite multiple oxide environments existing in reality [18, 19]) and had the X-ray parameters $\beta_2 = 4.1625 \times 10^{-6}$ and $\delta_2 = 5.1740 \times 10^{-5}$ giving a critical angle $\alpha_{c, 2} = 0.5828^\circ$ [2] (using the values for silica within the online database). Parameters for the silicon substrate were found to be $\beta_3 = 7.4998 \times 10^{-6}$ and $\delta_3 = 5.4303 \times 10^{-5}$ giving a critical angle $\alpha_{c, 3} = 0.5971^\circ$ [2] (using the values for Si within the ‘Index of Refraction’ online database [2]).

3.4.2. VPXSW studies of $[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]$ on silicon

After the silicon surface with its native oxide had been characterised the silicon was cooled to ≈ 90 K and a thick layer of $[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]$ was adsorbed onto the surface. The evaporator was set to 573 K and the surface was exposed to the IL for 30 minutes. It was not known what the IL layer thickness would be for such an IL dose as the IL evaporation had not been calibrated for the chamber at Diamond, but assuming the same deposition rate as in the chamber at Nottingham 30 minutes of IL would give a layer of IL approximately 30 layers (≈ 300 Å) thick. Since the sample temperature was 90 K, which was less than the glass transition temperature of $[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]$ ($T_g = 189.7$ K [20]), the IL is expected to have been deposited as a porous ‘snow’ (see section 3.4.3). After formation of the thick IL layer a thin CHCl_3 layer was deposited on the surface

(exposure of 5×10^{-6} mbar s). The sample was then left for ≈ 2 hours at 90 K, during which time background water adsorption occurred (which was not known to have occurred until data analysis had taken place), despite a background pressure of $\approx 1 \times 10^{-10}$ mbar, resulting in an exposure of 0.7×10^{-6} mbar s of water.

In order to obtain VPXSW profiles for the IL, CHCl_3 and substrate layers EDCs were collected for the Si 2p ($KE \approx 2893$ to 2903 eV), B 1s ($KE \approx 2794$ to 2810 eV), C 1s ($KE \approx 2701$ to 2717 eV), N 1s ($KE \approx 2585$ to 2602 eV), O 1s ($KE \approx 2455$ to 2470 eV), F 1s ($KE \approx 2301$ to 2316 eV) and Cl 1s ($KE \approx 158$ to 185 eV) photoelectrons. All of the collected EDCs were calibrated using the Si $2p_{3/2}$ substrate signal which could be seen through the organic (IL + CHCl_3) layer. A shift of -1.7 eV in binding energy was required to ensure that the BE of the detected Si $2p_{3/2}$ photoelectron peak matched the literature value of 99.42 eV [17], and was subsequently applied to the BE for each of the photoelectron spectra collected from this surface. The surface itself consisted of 6 layers (vacuum, H_2O , CHCl_3 , $[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]$, SiO_x , Si substrate) however a 3 layer model was used to calculate the X-ray standing wave intensities, in which the first layer was vacuum, the second layer was an organic layer and the third layer was a silicon substrate. This model assumes that the H_2O , CHCl_3 and $[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]$ can be modelled as a single organic layer, with the same X-ray parameters. Since the organic layer consisted mainly of the IL it was assumed that using the X-ray parameters of the IL would be best to define the organic layer. It can be seen from table 3.1 that the X-ray parameters and the critical

Table 3.1: The X-ray parameters obtained from the online database (reference [2]) for the components within the organic layer composed of H_2O , CHCl_3 and $[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]$. In the theoretical 3 layer model used for the analysis of the VPXSW profiles the organic layer used the IL X-ray parameters as the majority of the organic layer was IL. Given the similarity of the X-ray components for the constituent parts of the organic layer, the assumption made seems reasonable. Constants were calculated for a 3000 eV X-ray photon.

Component	H_2O	CHCl_3	$[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]$
Density (g cm^{-3})	1.00	1.4788 [1]	1.115 [5]
δ value	2.6161×10^{-5}	2.9278×10^{-5}	2.7828×10^{-5}
β value	6.4437×10^{-7}	6.4970×10^{-6}	5.1271×10^{-7}
α_c ($^\circ$)	0.3662	0.4384	0.4274

angles for the three components of the organic layer are similar, meaning that the use of the IL parameters should provide a reasonable approximation. As a result the X-ray parameters used for the second layer in the theoretical model

were $\beta_2 = 5.1271 \times 10^{-7}$ and $\delta_2 = 2.7828 \times 10^{-5}$ giving a critical angle $\alpha_{c,2} = 0.4274^\circ$ [2] (using a $[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]$ density of 1.115 g cm^{-3} at 283.15 K [5]). Using the 3 layer model also assumes that the silicon substrate and the silicon oxide layer can be modelled as a single layer. Previous XRR studies have modelled the silicon oxide and silicon as a single layer without any significant issues, due to their very similar X-ray constants [21]. Since the majority of the reflector is composed from silicon the X-ray parameters for silicon were used for layer 3 where $\beta_3 = 7.4998 \times 10^{-6}$ and $\delta_3 = 5.4303 \times 10^{-5}$ giving a critical angle $\alpha_{c,3} = 0.5971^\circ$ (using the values for Si within the ‘Index of Refraction’ online database [2]).

3.4.3. Surfaces studied whilst probing the IL–CO₂ interaction

As mentioned previously the interaction of CO₂ with the two ionic liquids $[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]$ and $[\text{C}_8\text{C}_1\text{Im}][\text{Tf}_2\text{N}]$, shown in fig. 3.5, was probed with TPD. Different surfaces were formed and studied on the gold crystal. After formation of the surface a 20 minute wait (arbitrarily chosen based on the rate of chamber pressure recovery) was employed before the TPD experiment was begun, in order to allow the chamber pressure to drop after exposure to CO₂ and allow any material which had a short stay time (due to a low activation energy of desorption) to desorb. This allowed for better quality data to be collected as the residual CO₂ in the chamber which remained from dosing (pressures used during dosing were up to $2 \times 10^{-6} \text{ mbar}$) had time to pump away so that it did not affect the observed CO₂ TPD signal. After the 20 minute wait TPD begun using initially a constant power heater before swapping to a constant rate heater after the CO₂ had desorbed (section 3.2.1).

Experiments to calibrate the IL coverage, through calculation of the monolayer coverage for each of the ILs (see appendices 8.3 and 8.8) were performed by measuring TPD spectra for the ILs for different initial coverages (dose lengths) of the IL, evaporated onto a room temperature gold surface. The mass fragments $m/z = 195$ and 96 amu were tracked during these experiments for $[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]$ and the fragments $m/z = 195$ and 83 amu were tracked for $[\text{C}_8\text{C}_1\text{Im}][\text{Tf}_2\text{N}]$ as they were found to be the most intense signals, which agrees with findings in the literature [22]. Similar TPD experiments were performed

for CO₂ by exposing the cleaned (by annealing only) gold surface, cooled to ≈ 90 K, to the CO₂ on its own to see if there was any adsorption (a TPD peak) in the absence of IL. No CO₂ TPD peak was observed during these experiments so instead the CO₂ signal was calibrated by looking at the mass spectrometer response to CO₂ being leaked into the chamber, as described in appendix 8.5.

Experiments in which each of the ILs and CO₂ were coadsorbed (the gold crystal was exposed to the IL molecular beam and the CO₂ simultaneously) at ≈ 90 K for timescales between 2 and 20 minutes were performed for the two ILs, with CO₂ pressures ranging from 2×10^{-8} to 2×10^{-6} mbar. IL molecular beams were formed as a result of the evaporator design (which has a liquid nitrogen cooled collimator) with the evaporator temperature set to 573 K for [C₈C₁Im][BF₄] and 519 K for [C₈C₁Im][Tf₂N]. Since the ILs were being deposited on a surface with a temperature ≈ 90 K, which is below their glass transition temperatures ($T_g = 189.7$ K for [C₈C₁Im][BF₄] [20] and $T_g = 189$ K for [C₈C₁Im][Tf₂N] [23, 24]), the ILs were not deposited as liquids. Instead they stuck where they landed in the conformations they arrived in, like an IL ‘snow’—which is a thicker, less dense layer than that of a liquid film containing the same quantity of IL. Deposition as an IL ‘snow’ has been observed with XPS and was observed to melt back into an IL film of the expected thickness upon heating [12]. Due to the fact that the IL condenses where it lands it is unlikely that the ion pairs will pack closely together, which results in pores for the CO₂ to adsorb within. These pores will be formed randomly and should represent the whole range of binding environments that are available for the CO₂ within the two ILs. This notion is supported by reference [25], which discusses the formation of thin metallic films being evaporated onto a surface and freezing into place, that it is “virtually impossible to produce vacuum deposits which are free from pinholes through which corrosive agents may penetrate”. Further observations of the growth of silver and platinum films observed that grainy surface growth occurred, rather than flat layers [26], which may be similar to the IL ‘snow’, which is expected to have some roughness to its surface. Such growth had also been observed for non-metallic species such as LiF where it was observed that layers up to 2 μm thick were porous and for thicker layers could develop inaccessible voids in its structure [27]. Diagrams representing the surfaces formed during experiments involving CO₂ and IL, demonstrating the

principle of dosing the IL at low temperatures to result in a porous ‘snow-like’ network, are shown in fig. 3.6. In each case the green layer represents the IL deposited on the surface, blue represents CO₂, yellow represents the gold crystal and white represents vacuum. The expected surface formed from a coadsorption experiment is shown in fig. 3.6a where the pores in the IL ‘snow’ structure are filled with CO₂ molecules.

In addition to the IL–CO₂ coadsorption experiments a variety of layered experiments were also performed, in an attempt to provide further insight into the IL–CO₂ interaction. Diagrammatic representations of these layered experiments are shown in figs. 3.6b–d, in which IL is evaporated onto the gold surface first and CO₂ is added to the surface afterwards, in some way. Figure 3.6b represents a surface in which 10 minutes of IL is deposited on a cold (≈ 90 K) gold surface, forming an IL ‘snow’, before being exposed to 10 minutes of CO₂ at a pressure of 5×10^{-7} mbar. It is expected that the IL ‘snow’ layer will be empty (the white spaces within the IL layer in the diagram), and once CO₂ is added one can probe whether the CO₂ diffuses into the pores in the IL snow. The

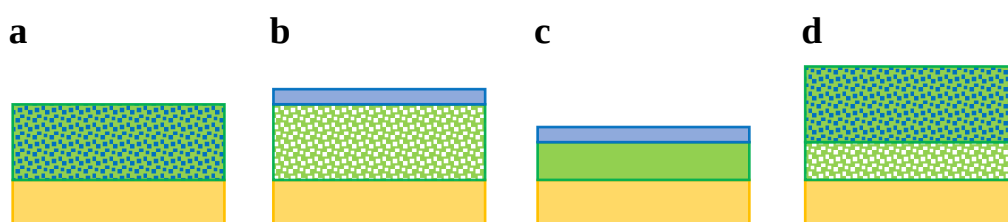


Figure 3.6: Diagrammatic representations of the different multicomponent surfaces (IL and CO₂) formed in this study. The gold rectangle represents the gold substrate, green sections represent the ionic liquid, blue sections represent the carbon dioxide and white represents spaces/pores. Image (a) shows the surface structure after a coadsorption (simultaneous adsorption) of IL and CO₂, with the CO₂ filling the pores in the IL ‘snow’, (b) shows a layer of IL ‘snow’ being exposed to a CO₂ dose, which may adsorb to the surface sites within the IL, (c) shows an IL glass layer (frozen from a liquid film so it’s non-porous) exposed to a CO₂ dose and (d) shows an IL–CO₂ coadsorption on top of an IL ‘snow’ layer.

quantities of IL and CO₂ used in this experiment were the same as for the 10 minute long IL–CO₂ coadsorption performed with a CO₂ pressure of 5×10^{-7} mbar, which will provide a direct comparison with the data from a coadsorbed system. Figure 3.6c represents a surface in which a 10 minute IL glass is formed prior to exposure to 10 minutes of CO₂ at a pressure of 5×10^{-7} mbar. The IL glass is formed by evaporating the IL onto the gold substrate at room temperature (it could be any temperature between the glass transition temperature and evaporation temperature) and then cooling the IL below its

glass transition temperature. The glass is not expected to be as porous as the IL 'snow' since it is expected that the IL glass will have the same structure as a liquid IL film, since the glass transition is one in which a viscous liquid solidifies as its temperature is reduced. The porosity of an IL film has been estimated by calculating the fractional free volume, which is 0.15 (15% free space) for [C₈C₁Im][BF₄] [28]. To reflect this the diagram of the glass layer is thinner but has no white spaces in it, demonstrating that for the same quantity of IL, but in a non-porous structure the layer would be expected to be thinner. Again the same quantity of IL and CO₂ are used as in the 10 minute, 5×10⁻⁷ mbar coadsorption and the CO₂-IL 'snow' layered surface allowing direct comparisons to be made. A third type of layered system was also studied in which a 10 minute IL-CO₂ coadsorption with a CO₂ pressure of 5×10⁻⁷ mbar was performed on top of 5 minutes dose of IL 'snow' (all on a 90 K surface). Figure 3.6d shows the structure of this surface in which the quantity of CO₂ deposited during the coadsorption is the same as in the other layered structures, with the total IL coverage being different due to the 5 minute IL snow beneath the coadsorption.

3.5. References

- [1] Lide, D.R., *CRC Handbook of Chemistry and Physics 8th Edition 2007-2008*. Eds., CRC Press, Taylor & Francis, Boca Raton, FL, (2007)
- [2] Henke, B.L., Gullikson, E.M. and Davis, J.C., *X-ray interactions: photoabsorption, scattering, transmission, and reflection at E=50-30000 eV, Z=1-92*, Atomic Data and Nuclear Data Tables Vol. **54** (no. 2), 181-342 (July 1993). http://henke.lbl.gov/optical_constants/ (accessed July 2017).
- [3] Fisher, C.J., Ithin, R., Jones, R.G., Jackson, G.J., Woodruff, D.P. and Cowie, B.C.C., Non-dipole photoemission effects in x-ray standing wavefield determination of surface structure. *J. Phys.-Condens. Mat.*, **1998**, (10), pp. L623-L629.
- [4] Lee, J.J., Fisher, C.J., Woodruff, D.P., Roper, M.G., Jones, R.G. and Cowie, B.C.C., Non-dipole effects in photoelectron-monitored X-ray standing wave experiments: characterisation and calibration. *Surf. Sci.*, **2001**, (494), pp. 166-182.
- [5] Sanmamed, Y.A., Gonzalez-Salgado, D., Troncoso, J., Romani, L., Baylaucq, A. and Boned, C., Experimental methodology for precise determination of density of RTILs as a function of temperature and pressure using vibrating tube densimeters. *J. Chem. Thermody.*, **2010**, (42), pp. 553-563.
- [6] EDCfitprog (written in Igor Pro 3.64), Contact: robert.g.jones@nottingham.ac.uk (accessed 2017)

- [7] *Practical Surface Analysis Volume 1 - Auger and X-ray Photoelectron Spectroscopy*. Briggs, D. and Seah, M.P., Eds., John Wiley & Sons, Chichester, (1990)
- [8] *Surface Analysis by Auger and X-ray Photoelectron Spectroscopy*. Briggs, D. and Grant, J.T., Eds., IM Publications, Chichester, (2003)
- [9] Jones, R.G. and Fisher, C.J., Reaction and sticking probabilities using line of sight techniques: iodine on Al(111). *Surf. Sci.*, **1999**, (424), pp. 127-138.
- [10] Chan, A.S.Y., Skegg, M.P. and Jones, R.G., Line of sight techniques: Providing an inventory of all species arriving at and departing from a surface. *J. Vac. Sci. Technol. A*, **2001**, (19), pp. 2007-2012.
- [11] Hessey, S.G. and Jones, R.G., Line-of-sight mass spectrometry: principles and practice. *Surf. Interface Anal.*, **2015**, (47), pp. 587-600.
- [12] Syres, K.L. and Jones, R.G., Adsorption, Desorption, and Reaction of 1-Octyl-3-methylimidazolium Tetrafluoroborate, [C₈C₁Im][BF₄], Ionic Liquid Multilayers on Cu(111). *Langmuir*, **2015**, (31), pp. 9799-9808.
- [13] Hessey, S.G. and Jones, R.G., On the evaporation, bonding, and adsorbate capture of an ionic liquid on Au(111). *Chemical Science*, **2013**, (4), pp. 2519-2529.
- [14] Foulston, R., Gangopadhyay, S., Chiu, C., Moriarty, P. and Jones, R.G., Mono- and multi-layer adsorption of an ionic liquid on Au(110). *Phys. Chem. Chem. Phys.*, **2012**, (14), pp. 6054-6066.
- [15] Bonhôte, P., Dias, A.P., Papageorgiou, N., Kalyanasundaram, K. and Grätzel, M., Hydrophobic, highly conductive ambient-temperature molten salts. *Inorg. Chem.*, **1996**, (35), pp. 1168-1178.
- [16] Fuller, J., Carlin, R.T. and Osteryoung, R.A., The room temperature ionic liquid 1-ethyl-3-methylimidazolium tetrafluoroborate: Electrochemical couples and physical properties. *J. Electrochem. Soc.*, **1997**, (144), pp. 3881-3886.
- [17] Thompson, A.C. and Vaughan, D., *X-ray Data Booklet*. Kirz, J., Eds., Lawrence Berkeley Laboratory, (2001)
- [18] Miyata, N., Shigeno, M., Arimoto, Y. and Ito, T., Thermal Decomposition of Native Oxide on Si(100). *J. Appl. Phys.*, **1993**, (74), pp. 5275-5276.
- [19] Kim, Y.B., Tuominen, M., Raaijmakers, I., de Blank, R., Wilhelm, R. and Haukka, S., Initial stage of the ultrathin oxide growth in water vapor on Si(100) surface. *Electrochem. Solid St.*, **2000**, (3), pp. 346-349.
- [20] Leys, J., Wubbenhorst, M., Menon, C.P., Rajesh, R., Thoen, J., Glorieux, C., Nockemann, P., Thijs, B., Binnemans, K. and Longuemart, S., Temperature dependence of the electrical conductivity of imidazolium ionic liquids. *J. Chem. Phys.*, **2008**, (128), pp. 064509.
- [21] Kohli, S., Rithner, C.D., Dorhout, P.K., Dummer, A.M. and Menoni, C.S., Comparison of nanometer-thick films by x-ray reflectivity and spectroscopic ellipsometry. *Rev. Sci. Instrum.*, **2005**, (76), pp. 023906.
- [22] Deyko, A., Lovelock, K.R.J., Licence, P. and Jones, R.G., The vapour of imidazolium-based ionic liquids: a mass spectrometry study. *Phys. Chem. Chem. Phys.*, **2011**, (13), pp. 16841-16850.
- [23] Zhang, S., Lu, X., Zhou, Q., Li, X., Zhang, X. and Li, S., *Ionic Liquids: Physicochemical Properties*. Eds., Elsevier, Amsterdam, (2009)
- [24] Gharagheizi, F., Keshavarz, M.H., Ilani-Kashkouli, P., Farahani, N. and Tumba, K., A group contribution method for estimation of glass-transition temperature of 1,3-dialkylimidazolium ionic liquids. *J. Therm. Anal. Calorim.*, **2013**, (114), pp. 1363-1382.

- [25] Holland, L., *Vacuum Deposition of Thin Films*. Eds., Chapman & Hall, London, (1956)
- [26] Andrade, E.N.D.C. and Martindale, J.G., The Structure and Physical Properties of Thin Films of Metal on Solid Surfaces. *Philos. T. R. Soc. A*, **1935**, (234), pp. 69-100.
- [27] Schulz, L.G., The Structure and Growth of Evaporation LiF and NaCl Films on Amorphous Substrates. *J. Chem. Phys.*, **1949**, (17), pp. 1153-1162.
- [28] Shannon, M.S., Tedstone, J.M., Danielsen, S.P.O., Hindman, M.S., Irvin, A.C. and Bara, J.E., Free Volume as the Basis of Gas Solubility and Selectivity in Imidazolium-Based Ionic Liquids. *Ind. Eng. Chem. Res.*, **2012**, (51), pp. 5565-5576.

Chapter 4

Development of the variable period X-ray standing wave technique with photoelectron detection

4.1. Introduction and background

Sections 1.1.1 and 1.3 discussed how X-rays have been used to characterise surfaces in previous studies for a variety of surface morphologies ranging from layers which are one molecular layer thick, using normal incidence X-ray standing waves [1-3], through ultra-thin films using X-ray photoelectron spectroscopy [4-7] to layers 100's Å thick using X-ray reflectivity [8-10]. It has been seen that for systems with thick adlayers variable period X-ray standing wave (VPXSW) analysis can be used through the detection of X-ray fluorescence [11-14], which has the advantage of giving elemental precision for very thick layers (up to 1000 Å), since X-ray photons are not highly attenuated by matter. Fluorescence yields, however, are low for lighter elements [16, 17] due to competition from Auger electron emission (the other method of relaxation for a core hole state). Consequently X-ray fluorescence studies are limited to use on surfaces which possess heavier atoms such as zinc [11] or germanium [12]. Using photoelectron emission as the detection method allows detection of all species except hydrogen and helium. This makes photoelectron techniques much more applicable to studies involving organic and biological molecules, which contain predominantly light elements (H, C, N and O), in an attempt to fully understand their nature. Photoelectrons also make it possible to gain not only elemental specificity but also discrimination between different chemical environments, through the chemical shift. The inherent surface sensitivity of photoelectrons, which are heavily attenuated by matter [7, 19, 20], can also provide extra information on the structure of adlayers on the substrate being studied. This comes as a result of the attenuation length for a photoelectron being related to the electron kinetic energy meaning different photoelectrons with different kinetic energies will have different escape depths from the surface.

4.2. Variable period X-ray standing wave analysis of the silicon substrate

The results discussed in the proceeding section were obtained from the experiments described in section 3.4.1. After introduction of the silicon substrate (Si(001)) into the vacuum chamber of beamline I09 at the Diamond light source, experimental data was collected for the surface prior to the surface being cooled ($T_{\text{surf}} = 293 \text{ K}$) or any material being deposited onto it. Since the substrate was only rinsed prior to use and not treated with acid or bombarded whilst under vacuum, the silicon substrate had a native oxide layer [5, 21], which is typically around $10 \text{ \AA}$ thick [22]. Electron distribution curves (EDCs) were collected for incident X-ray angles, α , in the range 0° to 2.5° for the silicon surface with an X-ray photon energy of $h\nu = 3000 \text{ eV}$. The EDCs were fitted and the VPXSW profiles were extracted using software developed and written within the research group [23] as was the software for comparing the experimental VPXSW profiles to theoretical ones [24].

4.2.1. Fitting the electron distribution curves for the silicon substrate

The EDCs collected at $\alpha = 2.5^\circ$ for the Si 2p and O 1s photoelectrons are shown in fig. 4.1a and fig. 4.1b, respectively. As discussed in section 3.4.1 the binding energies (BEs) of all peaks have been calibrated using the literature value of $\text{Si } 2p_{3/2 \text{ bulk}} = 99.42 \text{ eV}$ [25]. Figure 4.1a shows the spin-orbit split Si $2p_{1/2}$ ($BE \approx 100.0 \text{ eV}$) and $2p_{3/2}$ ($BE \approx 99.4 \text{ eV}$) photoelectron peaks due to silicon in the bulk silicon environment, whilst the spin-orbit pair at higher binding energies ($\approx 103 \text{ eV}$, shown in the inset) are due to silicon within the silicon oxide layer. The fits to the EDCs were obtained by modelling individual environments with Gaussian peak shapes of width σ , which were allowed to vary during fitting. The spin-orbit pairs had the area ratio of $2p_{3/2}:2p_{1/2}$ fixed to 2:1 [7] and the binding energy separation of the spin-orbit split peaks set to 0.6 eV , in accordance with the literature [21, 22, 25]. At $\alpha = 2.5^\circ$ the peaks for the Si_{bulk} environments had the width $\sigma = 0.3 \text{ eV}$, whilst the Si_{oxide} environments had larger widths of $\sigma = 0.7 \text{ eV}$ to accommodate the range of different oxide environments that exist within the oxide layer [21, 22]. The separation between

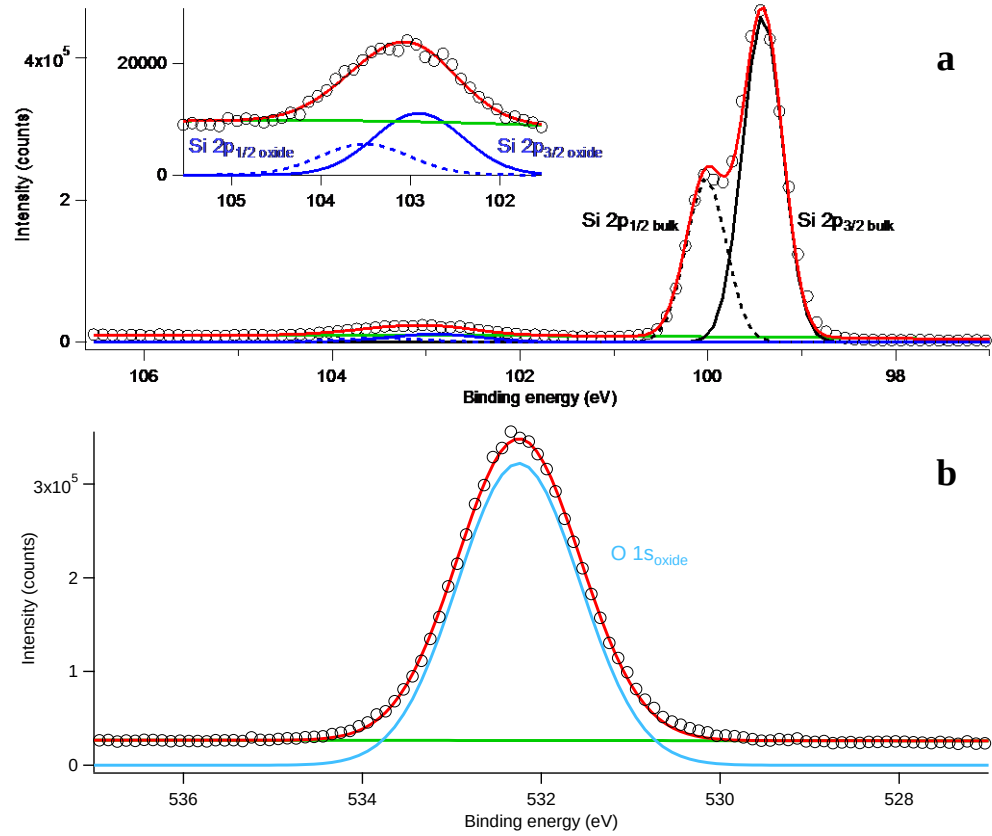


Figure 4.1: Electron distribution curves for the silicon substrate and its native oxide layer, showing both the Si 2p region (a) and the O 1s region (b). The black circles represent the experimental data whilst the red lines represent the fitted photoelectron signal, calculated from the sum of the background (green line) and the fitted components shown. The inset in (a) shows the shifted silicon environments in the native oxide.

the Si_{3/2} bulk and the Si_{3/2} oxide photoelectron peaks was found to be 3.5 eV, which is in agreement with literature values [21, 22]. Figure 4.1b shows the O 1s photoelectron peak with a single environment at a binding energy of ≈ 532 eV, corresponding to the silicon oxide. The fitting parameters for the EDCs at an

Table 4.1: Information extracted from the fitting of the electron distribution curves at $\alpha = 2.5^\circ$ for the silicon substrate with its native oxide layer. As mentioned the binding energies have been calibrated to the literature value for Si 2p_{3/2} bulk and a photon energy of 3 keV was used in the experiments. Inelastic mean free paths (IMFPs) have been calculated for electrons travelling through a silicon oxide layer where attenuation lengths (λ) derived from these ($\lambda = 0.8 \times \text{IMFP}$) [7] were used in the VPXSW fitting.

Photoelectron	Binding energy ± 0.1 (eV)	Kinetic energy ± 0.1 (eV)	IMFP ($\text{\AA}$), λ ($\text{\AA}$)	Gaussian width, σ , ± 0.1 (eV)
O 1s	532.3	2467.7	60, 48	1.0
Si 2p _{1/2} oxide	103.5	2896.5	69, 55	0.7
Si 2p _{3/2} oxide	102.9	2897.1		0.7
Si 2p _{1/2} bulk	100.0	2900.0		0.3
Si 2p _{3/2} bulk	99.4	2900.6		0.3

angle of 2.5° (the angle which gets closest to traditional XPS experiments, where α is typically $\approx 30^\circ$) are summarised in table 4.1.

4.2.2. Extraction and fitting of the substrate variable period X-ray standing wave profiles

The VPXSW profiles were obtained from the areas of the fitted Gaussian profiles to the experimental photoelectron peaks at the different incident angles, α . The VPXSW profiles for the silicon and oxygen environments are shown in fig. 4.2, where the maximum intensities have been normalised to one, to allow comparisons to be made with the theoretical model. It can be seen that the VPXSW profiles for the two bulk silicon environments (black circles, filled for Si $2p_{3/2}$ and empty for Si $2p_{1/2}$) are very similar, which is expected, but are different to the VPXSW profiles observed for the silicon oxide environments corresponding to the Si $2p_{3/2}$ oxide, Si $2p_{1/2}$ oxide and O $1s$ (filled blue squares, empty blue squares and blue triangles, respectively). This demonstrates that the VPXSW technique can identify species which are in different strata of a surface. The fact that the Si $2p_{\text{oxide}}$ and the O $1s$ VPXSW profiles match each other

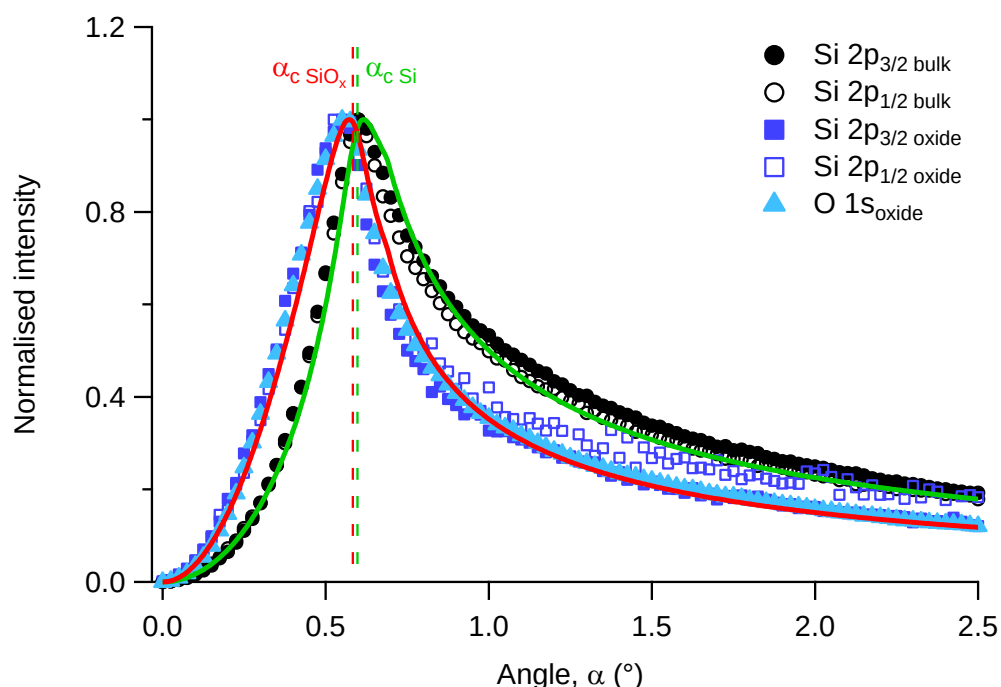


Figure 4.2: Variable period X-ray standing wave profiles for the photoelectrons detected for a silicon substrate with a silicon oxide layer. Markers represent experimental data points whilst the solid red line represents the VPXSW fit for a 15 Å thick SiO_x layer and the solid green line shows the VPXSW profile for the silicon substrate below. Dashed lines show the critical angles of the SiO_x and Si, which can be seen to match the peaks in the VPXSW profile reasonably well.

demonstrates that layers which overlap spatially can be monitored through different emitting species and give the same result for this technique, which is an essential trait for any experimental technique. The ability to detect the two different VPXSW profiles for the Si_{bulk} and the Si_{oxide} layers just from the Si 2p region is something which would not have been possible with the X-ray fluorescence technique and could save time (by only collecting the Si 2p EDCs) in the case of surfaces which evolve with time.

The experimental VPXSW profiles (markers in fig. 4.2) have been fitted with a calculated VPXSW profile (red line in fig. 4.2) which is based on a 3 layer model, in which the first layer is vacuum, the second layer is silicon oxide (SiO_x) and the third layer is silicon. The X-ray parameters for these layers are described in section 3.4.1, and give critical angles for the SiO_x and Si to be $\alpha_{c,2} = 0.5828^\circ$ and $\alpha_{c,3} = 0.5971^\circ$, respectively (with no critical angle for the vacuum layer as its refractive index is unity and it contains no matter to scatter the X-ray with). An X-ray incident on the surface will initially hit the SiO_x layer and for incident angles lower than $\alpha_{c,2}$ the X-ray is reflected, setting up a standing wave from the silicon oxide layer and an evanescent X-ray decaying into the SiO_x layer. This evanescent wave describes the observed photoelectron signal in the Si and SiO_x layers for angles below the critical angle, for which the X-ray is totally externally reflected. Since the intensity of the evanescent wave increases with the intensity of the X-ray standing wave at the surface, then as the incident angle increases towards the critical angle and the standing wave shifts its phase from having a node at the surface (at $\alpha = 0^\circ$) to having an antinode at the surface (at $\alpha = \alpha_{c,2}$), the VPXSW profile for SiO_x shows a steep increase with angle. The increase in the Si VPXSW profile is also due to the evanescent wave, and occurs since the SiO_x layer is only thin (a few Å), so some of the evanescent X-ray intensity is felt by the Si, explaining the shallower increase in the Si VPXSW profile than in the SiO_x profile. The photoelectron intensity for the SiO_x peaks near the critical angle, $\alpha_{c,2} = \alpha_{c, \text{SiO}_x}$, as a travelling X-ray propagates across the surface of the SiO_x layer for $\alpha = \alpha_{c,2}$, before an increase in the angle leads to a decay in the reflected component of the X-ray from the SiO_x layer (hence a decaying standing wave intensity from the SiO_x) and a travelling wave through the SiO_x surface towards the Si substrate below. The X-ray then reflects from the Si layer until the incident angle matches the critical angle of the Si layer (plus

the small angular deviation for refraction of the X-ray in the SiO_x layer) at which point a travelling wave propagates across the Si surface leading to a peak in the observed photoelectron intensity. For incident angles larger than the critical angle of silicon the component of the X-ray which is reflected decreases, leading to a decay in the intensity of the standing wave and hence an observed decay in the photoelectron intensity with increasing angle, α . The photoelectron intensity will continue to decay with angle until the point at which the intensity matches that of bulk XPS performed on the beamline (with a travelling X-ray through the surface). The fact that the X-ray standing wave only probed a thin film meant that the effects of having a variable period, where the period of the standing wave decreased as incident angle increased, were not observed (but would have been for thicker layers). In reality the observed VPXSW peak maxima differ to the critical angles due to surface roughness and undulations which make the apparent incident angle slightly different to the incident angle relative to the surface plane (see section 4.5).

The calculated VPXSW profile for the SiO_x layer, shown by the red line in fig. 4.2, corresponds to a 15 Å SiO_x layer on top of a silicon reflector. Attenuation lengths (λ) for photoelectrons were calculated to be 0.8×IMFP (inelastic mean free path) [7] for the different photoelectrons detected. The IMFPs of photoelectrons travelling through the native oxide layer were approximated by considering the native oxide to have the same electron scattering properties as SiO₂, and were calculated through use of the Tanuma, Powell and Penn method by extrapolation of values from a database [26], as described in section 2.2.3. IMFPs for photoelectrons of energy 2900.6 eV (for Si 2p photoelectrons) and 2467.7 eV (for O 1s photoelectrons) travelling through SiO₂ are shown in table 4.1, along with the attenuation lengths. For the calculated VPXSW profile shown in fig. 4.2 an attenuation length of 52 Å was used, which is an average of the attenuation lengths for the Si 2p and the O 1s photoelectrons. The photoelectron attenuation length only begins to have a significant effect on the VPXSW profile shape when the layer thickness is larger than the attenuation length, resulting in some of the photoelectron flux from deeper layers in the surface being significantly attenuated. The layer thickness was obtained through a method in which a variety of calculations with different SiO_x thicknesses were performed and compared to the experimental data, as

shown in fig. 4.3a. It can be seen that the 15 Å model is the best match to the experimental VPXSW profile, but due to either the noise in the data or some assumptions made in the theory (the layers can be approximated as cuboids) the true SiO_x thickness could be well modelled in some parts by the black 5 Å profile and in others by the green 25 Å profile, giving an error of ± 10 Å.

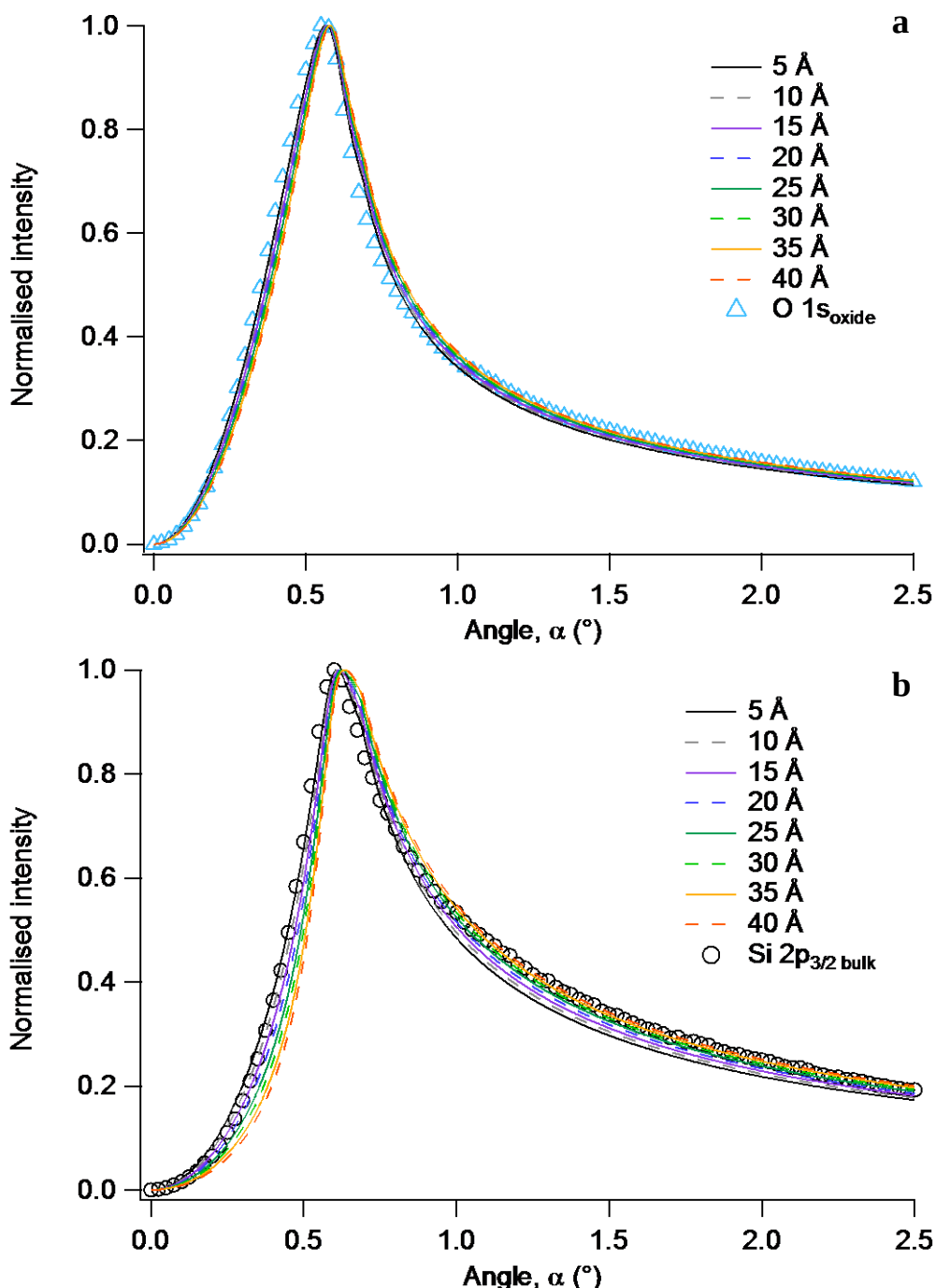


Figure 4.3: Variable period X-ray standing wave profiles for the photoelectrons detected from a silicon substrate with a silicon oxide layer. The markers represent experimental data for (a) the O 1s photoelectrons from the SiO_x layer and (b) the Si $2p_{3/2}$ photoelectron signal for the silicon substrate. Coloured lines represent theoretical models for different layer thicknesses to determine sensitivity of the VPXSW with respect to layer thickness, allowing errors to be determined.

The green line in fig. 4.2 shows the fit to the substrate VPXSW profile which results from a 15 Å layer of SiO_x being adsorbed on top of the silicon surface, agreeing with the results from the SiO_x layer. The substrate VPXSW profile can be seen to peak after the SiO_x VPXSW profile, which indicates that the SiO_x is closest to the vacuum layer. The green line is observed to be a good match to the experimental data for both the bulk Si 2p_{3/2} and Si 2p_{1/2} but would not be considered a good fit for the SiO_x layer. In a similar fashion to the SiO_x, the error for the Si substrate VPXSW profile was plotted alongside the VPXSW profiles that result from substrates with different SiO_x layer thicknesses on them, fig. 4.3b. The Si 2p_{3/2} VPXSW profile can be seen to match the low layer thicknesses very well for lower angles (below $\approx 1^\circ$), but then at higher angles is better matched by the thicker layers. Most of the experimental VPXSW profile is matched by layers in the thickness range 5 to 25 Å, giving an error of ± 10 Å for the SiO_x layer thickness determined by the substrate VPXSW profile. All of the VPXSW profiles have had the footprint and path length corrections, discussed in section 2.3.4, applied to them.

4.3. Variable period X-ray standing wave analysis of an ionic liquid slab with a chloroform marker layer

After the silicon substrate had been characterised, identifying the native oxide layer thickness, the substrate was cooled to 90 K prior to adsorption of the ionic liquid, [C₈C₁Im][BF₄]. A thick IL layer was evaporated onto the surface, as described in section 3.4.2, after which a thin chloroform (CHCl₃) layer was adsorbed on top. A thin layer of water was also adsorbed on the surface, adventitiously, from the background gases in the vacuum chamber. The B 1s, C 1s, N 1s and F 1s photoelectron peaks were detected to probe the IL layer, the Cl 1s for the CHCl₃ layer and the Si 2p and O 1s photoelectron peaks were detected to study the substrate, with the binding energies and kinetic energies for these photoelectrons shown in table 4.2. EDCs were collected for incident X-ray angles, α , of 0 to 2.5° in steps of 0.025° (101 in total) taking between 15 and 20 minutes per photoelectron peak studied. Each new set of EDCs, for each new element, was performed on a fresh part of the surface (by moving the sample vertically, perpendicular to the X-ray beam) in an attempt to reduce the

X-ray damage. Damage was observed in the setup scans of the surface and has also been observed in previous studies of $[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]$ systems after prolonged irradiation by X-rays [18].

Table 4.2: Information extracted from the fitting of the electron distribution curves at $\alpha = 2.5^\circ$ for photoelectrons detected from the silicon substrate beneath an organic layer ($[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]$ and CHCl_3). As mentioned the binding energies have been calibrated to the literature value for Si $2p_{3/2}$ bulk. Inelastic mean free paths (IMFPs) have been calculated for electrons travelling through an organic layer where attenuation lengths (λ) have been derived from these ($\lambda = 0.8 \times \text{IMFP}$) and were used in the VPXSW fitting.

Photoelectron	Binding energy ± 0.1 (eV)	Kinetic energy ± 0.1 (eV)	IMFP (Å), λ (Å)	Peak width, σ , ± 0.1 (eV)
Cl $1s_{\text{Cl}^\bullet}$	2825.6	174.4	11, 9	1.6
Cl $1s_{\text{CHCl}_3}$	2823.2	176.8		1.6
Cl $1s_{\text{Cl}^-}$	2821.0	179.0		1.3
F $1s_{\text{anion}}$	686.3	2313.7	61, 49	1.4
O $1s_{\text{water}}$	533.4	2466.6	64, 51	1.4
O $1s_{\text{small}}$	531.2	2468.8		1.0
N $1s_{\text{cation}}$	401.6	2598.4	66, 53	1.4
N $1s_{\text{damage}}$	399.6	2600.4		1.5
C $1s_{\text{hetero}}$	286.6	2713.4	68, 54	1.5
C $1s_{\text{alkyl}}$	284.9	2715.1		1.1
B $1s_{\text{anion}}$	194.2	2805.8	70, 56	1.1
Si $2p_{1/2}$ oxide	103.6	2896.4	72, 58	1.0
Si $2p_{3/2}$ oxide	103.0	2897.0		1.0
Si $2p_{1/2}$ bulk	100.0	2900.0		0.5
Si $2p_{3/2}$ bulk	99.4	2900.6		0.5

4.3.1. Fitting the electron distribution curves for the $[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]$ and the CHCl_3 layers

Figure 4.4a–d shows the EDCs collected at $\alpha = 2.5^\circ$ for the photoelectron peaks which correspond to the elements within the $[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]$, with figure 4.4e showing a colour coded structure representing the different chemical environments observed. All spectra show the experimental data (circular markers), the background (green line), the photoelectron components (coloured lines) and the sum of the fitted components (red line = background + components). As mentioned previously the photoelectron spectra have been calibrated, through matching the Si $2p_{3/2}$ bulk peak to the literature value of 99.42 eV [25], giving the required *BE* correction that has been applied to all

spectra (-1.7 eV, section 4.3.2). The doublet peak, which is not fitted but is observed at a $BE \approx 200$ eV, in fig. 4.4d corresponds to the Cl 2p emission from the chloroform layer, whilst the orange fit represents the peak due to the boron in the anion. The EDC in figure 4.4c shows the carbon environments observed within the IL cation, with the light grey peak corresponding to photoelectrons emitted from environments around the positively charged imidazolium ring, giving a higher BE than the photoelectrons emitted from the alkyl chain (black line). The relative peak positions of the C 1s_{hetero} and C 1s_{alkyl} photoelectron

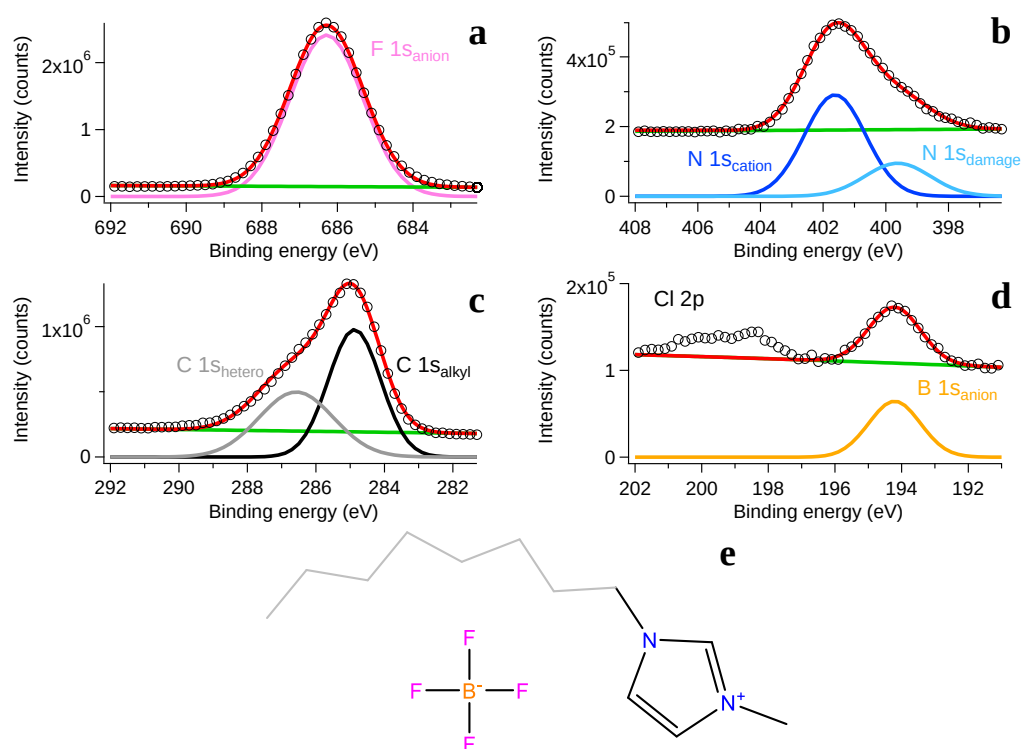


Figure 4.4: Electron distribution curves for the species within the $[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]$ overlayer for an incident angle, $\alpha = 2.5^\circ$, for the F 1s (a), N 1s (b), C 1s (c) and B 1s (d) regions. The colour coded diagram of the IL species (e) shows the origin of each photoelectron species based on the literature. All fits show the experimental data as black circles, background signals as green lines, photoelectron environments as coloured lines and total fits (background + components) as red lines.

peaks was fixed to 1.7 eV during the fitting procedure, which agrees with the literature value [15] but neither the widths nor intensities were constrained. Figure 4.4a shows the single fluorine environment due to the $[\text{BF}_4]^-$ anion where no constraints on peak position or width were used during fitting. The EDC for the N 1s region is given in fig. 4.4b where the peak widths (table 4.3) and peak separation (2.0 eV) were fixed to prevent peak ‘swelling’ (where one peak swells to take up more room to give a better fit mathematically, but does not make sense physically) which would affect the shape of the measured VPXSW

profiles. All of the fitted components of the EDCs for the IL have binding energies which match those observed in the literature for the pristine, undamaged IL [15], with the exception of the light blue nitrogen environment shown in fig. 4.4b. Table 4.3 shows a comparison of the binding energies observed in the fitting for the $[C_8C_1Im][BF_4]$ components in this study and the literature values for the same IL. Since the literature photoelectron spectra have been calibrated using the aliphatic carbon peak of the cation ($C\ 1s_{alkyl} = 285.0\text{ eV}$), in the same way that the spectra in this study have been calibrated to the $Si\ 2p_{3/2}$ peak, table 4.3 also shows the binding energy shifts relative to the $C\ 1s_{alkyl}$ peak. The difference in the ‘shift’ columns shows how well the experimental and literature photoelectron peak positions match, where it can be seen that the experimental shifts observed here agree with the literature shifts to 0.3 eV.

Table 4.3: Binding energies used within this study for the $[C_8C_1Im][BF_4]$ compared to literature values [15] for the binding energy for the same IL performed by XPS. Binding energy differences between the $C\ 1s_{alkyl}$ and the other photoelectron peaks are calculated (“shift” columns) to enable the two data sets to be compared due to the different calibrations used for the binding energy scales.

Photoelectron	Binding energy (eV)	Literature BE (eV) [15]	Shift relative to $C\ 1s_{alkyl}$ (eV)	Literature BE shift (eV)
F $1s_{anion}$	686.3	686.0	+401.4	+401.0
N $1s_{cation}$	401.6	402.0	+116.7	+117.0
N $1s_{damage}$	399.6	399.4 [18]	+114.7	+114.4
C $1s_{hetero}$	286.6	286.4	+1.7	+1.4
C $1s_{alkyl}$	284.9	285.0	0.0	0.0
B $1s_{anion}$	194.2	194.3	−90.7	−90.7

This new nitrogen environment at 399.6 eV is one which develops over the duration of the VPXSW experiment, as can be seen from fig. 4.5. The EDC shown in fig. 4.5a was collected for $\alpha = 0.025^\circ$, after approximately 30 seconds of X-ray irradiation, where it can be seen that only one nitrogen environment exists within the EDC at $\approx 402\text{ eV}$ in contrast to the two environments observed in fig. 4.4b. Figure 4.5b shows how the area of these two nitrogen environments vary as a function of angle, which is an indirect measure of exposure to X-rays and photoelectrons (the damage causing species). The plot shows that initially all of the nitrogen is in the cationic form (dark blue line) at the lowest angles, prior to the irradiation occurring, then as the angle and X-ray exposure increases

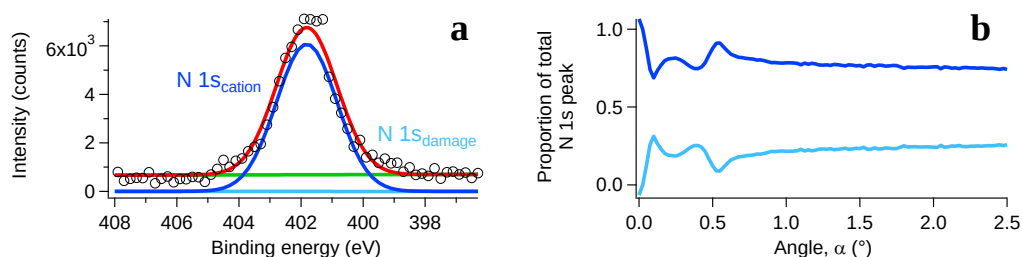


Figure 4.5: (a) An electron distribution curve for the N 1s region at an angle of $\alpha = 0.025^\circ$, prior to significant X-ray damage of the $[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]$ species. (b) The proportion of the total nitrogen photoelectron signal composed from each of the components as a function of angle (X-ray irradiation), with the dark blue line showing the cation and the light blue line shows the damage proportions.

an increase in the proportion of the total nitrogen peak composed of damaged species is observed. It would be expected that this increase in proportion of damaged species would be a smoother function than is shown by the light blue line in fig. 4.5b, especially in the angular range of 0.0° to 0.4° . The rate of damage is expected to increase with X-ray intensity, so the peak at around 0.4° ($\approx \alpha_c$ for the IL) could be due to the travelling wave across the IL surface. It is thought that charging of the frozen IL distorted the measured EDCs leading to peak ‘swelling’ (see section 4.4 for more details) making analysis of the data in fig. 4.5 very difficult.

Damage of the $[\text{C}_8\text{C}_1\text{Im}]^+$ cation has been observed previously within XPS studies, with the damage peak emerging at a $BE \approx 2.6$ eV lower than the N 1s_{cation} peak [18]. It can be seen that this shift is similar to the 2.0 eV shift in the damage peak observed in this study (table 4.3). The fact that the damage peak is observed at a lower binding energy than the cation peak suggests that the nitrogen in the damaged species is within a less positive environment, as the nitrogen had less of a hold on the emitted photoelectron, prior to emission. It has been suggested that the damaged nitrogen environment has a binding energy which corresponds to that of an uncharged nitrogen species [18]. It is expected that X-ray damage of all of the IL species should be observed due to the intense photon flux. Any damage in the imidazolium ring should also be observed in the C 1s EDCs, however it is believed that this carbon damage peak would reside beneath the cation envelope, making detection of this damage peak difficult. The lack of detection of damage peaks in the boron or fluorine EDCs could indicate that these species do not damage (which is unlikely), that the damage species

reside under existing photoelectron peaks or that the damaged species generated desorb into the vacuum after production (as discussed in section 4.3.4).

EDCs for the Cl 1s photoelectron peak, emitted from the CHCl_3 layer on top of the $[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]$ slab, are shown in figure 4.6 for incident angles of $\alpha = 0.025^\circ$ (4.6a) and $\alpha = 2.5^\circ$ (4.6b). It can be seen that the EDC for the fresh surface, prior to a large X-ray dose, is dominated by the pristine CHCl_3 chlorine environment (pink line fig. 4.6a), with only small contributions from the other chlorine environments. After exposure to X-rays for ≈ 20 minutes, the amount of time to collect 100 EDCs at different incident angles, it can be seen that new chlorine environments are observed to dominate the EDC collected for $\alpha = 2.5^\circ$ (fig. 4.6b). The environment, represented by light blue in fig. 4.6b, to the higher binding energy side of the pristine CHCl_3 peak must be in a more electropositive environment than the chlorine in CHCl_3 , which are themselves slightly electronegative. The chemical environment at lower BE, represented by the purple line in fig. 4.6b, must be in a more electronegative environment (making the photoelectron easier to eject). It is rationalised that, due to the BE shift of +2.4 eV for the light blue chemical environment and -2.6 eV for the purple environment, the low BE peak is due to chloride anions (Cl^-) and the high BE peak is due to a neutral chlorine environment ($\text{Cl}^\bullet$). The neutral chlorine cannot be in the form of Cl_2 as this has a vapour pressure of $\approx 10^{-4}$ mbar at 90 K [27],

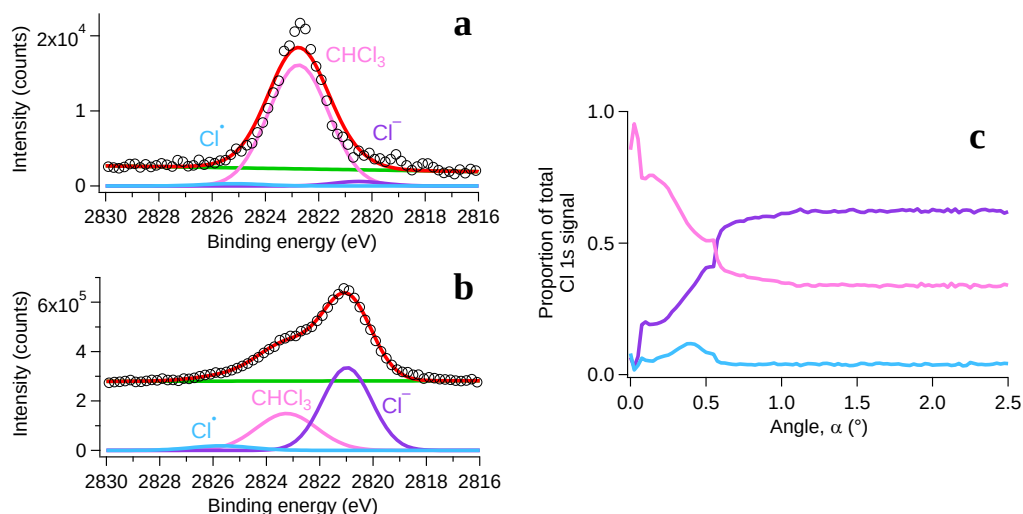
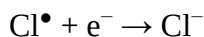


Figure 4.6: (a) An electron distribution curve for the Cl 1s region at an angle of $\alpha = 0.025^\circ$, prior to significant X-ray damage of the CHCl_3 species. (b) Shows an EDC collected at $\alpha = 2.5^\circ$ after X-ray damage has occurred. (c) The proportion of the total chlorine photoelectron signal composed from each of the components as a function of angle (X-ray irradiation), with the dark purple line showing the Cl^- species, the pink line showing the CHCl_3 species and the light blue line shows the $\text{Cl}^\bullet$ species.

so would be likely to desorb from the surface at the pressure experiments were carried out at ($\approx 10^{-10}$ mbar) even if it were stabilised by the ionic liquid. It is possible that formation of a chlorine radical has occurred which has adsorbed near the site of production, possibly near a $[\text{BF}_4]^-$ anion where the fluorine draws some of the electron density away from the $\text{Cl}^\bullet$. The contribution of the damage peaks to the overall chlorine signal is shown as a function of incident angle (which is an indirect measure of the total of X-ray exposure) in fig. 4.6c. It is observed that as the angle, and therefore X-ray dose, increases the proportion of the total Cl 1s photoelectron peak due to the CHCl_3 decreases rapidly. In response to this the proportion of the total chlorine peak due to the Cl^- environments increases, with the Cl^- environment being the dominant peak in the chlorine EDC for angles greater than $\approx 0.6^\circ$. The fact that the majority of the damage occurs for angles lower than 0.6° suggests that the X-ray is the primary source for damage. The XSW intensity is large within the organic layer for angles below the silicon critical angle, after which the X-ray is simply transmitted through all the layers (including the reflector) resulting in a larger photoelectron flux. The proportion of neutral chlorine environments stays approximately constant throughout the VPXSW scan. This result seems to suggest that the neutral chlorine environment does not result from a damaged species (as this would lead to a signal increase with angle), but also does not get damaged (as this would be shown by a signal decrease with angle). This could indicate some form of energy redistribution by chlorine atoms in these sites possibly suggesting that these chlorine species are at the CHCl_3 –IL interface. This could explain why the intensity of this peak is consistently low but constant, as the interfacial area will not vary with time, under the assumption that diffusion of the IL and CHCl_3 is not possible at 90 K. Being in an interfacial region with the IL would lead to either fluorine or the cations drawing electron density from the $\text{Cl}^\bullet$ making it appear to be in a more positive environment than in CHCl_3 . It is more likely that the $\text{Cl}^\bullet$ is a reaction intermediate for the damage reaction, initially increasing in concentration (formed from $\text{Cl}_{\text{CHCl}_3}$) before reaching a steady state concentration as it is converted to another damage product (Cl^-). This would suggest that the two processes





occur during X-ray irradiation of the CHCl_3 layer. Once again charging of the organic layer is believed to be the cause of the wiggles in the curves of fig. 4.6c for angles below 1° , as seen for the nitrogen damage species in fig. 4.5b.

4.3.2. Fitting the electron distribution curves for the substrate below the $[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]$ and CHCl_3 layers

As well as collecting EDCs for the adsorbed layers EDCs were also collected for the silicon substrate with its native oxide, shown in fig. 4.7. The EDC for the Si 2p region at $\alpha = 2.5^\circ$ (fig. 4.7a) shows the Si_{bulk} and Si_{oxide} chemical environments, however the spin-orbit split $\text{Si}_{3/2}$ and $\text{Si}_{1/2}$ peaks are no longer clearly resolved, as they were in fig. 4.1a. This can be seen quantitatively by comparing the peak widths (σ) of the substrate photoelectron signals in table 4.1 and 4.2, where it can be seen that the Si $2\text{p}_{3/2}$ bulk peaks before the organic layer was deposited were 0.3 eV, but 0.5 eV after deposition. This is due to use of different detector settings for the two sets of EDCs, as the detector was made more sensitive (at the cost of resolution) for observing the buried silicon layer. It is possible that the electric fields due to the adsorbed ion pairs within the IL may be interfering with the substrate photoelectrons, distorting the substrate peaks. Fitting has been performed including the spin-orbit split peaks, with the constraint that the Si $2\text{p}_{3/2}$ and Si $2\text{p}_{1/2}$ peaks are separated by 0.6 eV (based on literature values [25]) and had a 2:1 ratio of areas for Si $2\text{p}_{3/2}$:Si $2\text{p}_{1/2}$ [7]. Due to the lack of resolution between the spin-orbit pairs for the substrate peaks the widths had to be fixed to 0.5 eV for the bulk silicon environments and 1.0 eV for the silicon oxide environments. It can also be observed that the intensity of the Si $2\text{p}_{3/2}$ bulk peak is reduced when the organic layers are adsorbed on the surface relative to the clean substrate ($\Delta I \approx 450 \times 10^3$ and 250×10^3 counts respectively), due to the scattering of the photoelectrons by the IL and CHCl_3 layers. This reduction in the silicon peak intensity is not as large as would be expected for a thick film, due to the fact that the detector settings were not the same for these two sets of Si 2p EDCs in fig. 4.7a and fig. 4.1a. Calibration of the Si $2\text{p}_{3/2}$ bulk peak to the literature value of 99.4 eV [25] (corresponding to a BE shift of -1.7 eV) was performed and applied to all of the EDCs for the

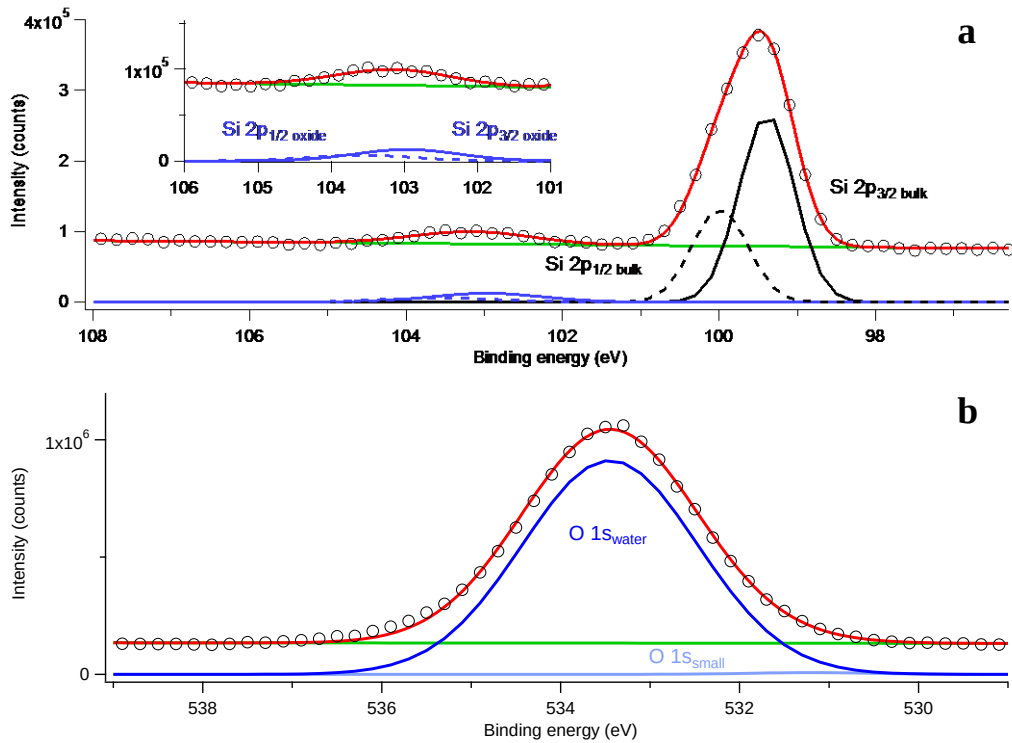


Figure 4.7: (a) An electron distribution curve for the Si 2p region at an angle of $\alpha = 2.5^\circ$, for a silicon substrate with its native oxide buried beneath a $[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]$ and CHCl_3 layer. (b) The EDC of the O 1s region in an attempt to see the native oxide from the substrate, instead showing the presence of water adsorbed from the background over a 2 hour period at $\approx 10^{-10}$ mbar. In both cases experimental data is shown by the black circles, background signal is shown by the green line, coloured lines show the different components of the fits and the red line shows the total fit (background + components).

Si/IL/ CHCl_3 surface to account for any contact potential and the work function of the spectrometer.

The fit to the O 1s photoelectron peak for $\alpha = 2.5^\circ$ is shown in fig. 4.7b where it can be seen that two environments have been fitted. The O 1s_{small} environment at $BE \approx 531$ eV has a high intensity for α in the range 0 to 0.75° , which is in the angular range that the travelling wave propagates along the surface, maybe suggesting this oxygen species corresponds to material at an interface. Initially it was expected that this O 1s EDC would show the photoelectrons emitted from the SiO_x layer, with a lower intensity due to attenuation of the photoelectrons by the overlayer. It is observed, however, that the peak intensity on fig. 4.7b ($\Delta I \approx 800 \times 10^3$ counts) is over twice as large as that for the uncovered SiO_x peak intensity in fig. 4.1b ($\Delta I \approx 300 \times 10^3$ counts, with the same detector sensitivity settings as the uncovered substrate). The VPXSW data (see section 4.3.5) conclusively proves that the oxygen species is positioned at a large height (≈ 200 Å) above the reflector surface, showing that the oxygen

environment is due to a species other than the SiO_x layer. There was a 2 hour time separation between surface preparation and the collection of EDCs and it is postulated that during this time background water adsorption occurred. Despite the background pressure being $\approx 10^{-10}$ mbar the 2 hour wait meant that the 90 K surface had been exposed to 7.2×10^{-7} mbar s of water (assuming all of the background pressure was due to water). Using the approximation that 1×10^{-6} mbar s is one langmuir (technically 1 L is 1×10^{-6} Torr s, so 1×10^{-6} mbar s can be considered a metric langmuir), which can be roughly approximated to one monolayer of material, then ≈ 0.7 layers of water could have adsorbed on the surface, giving a large oxygen photoelectron signal. The O 1s peak due to the SiO_x would be expected to be observed at $BE \approx 532$ eV, as it is in fig. 4.1b, but is masked by the peak due to the adsorbed water.

4.3.3. Extraction and fitting of the VPXSW profiles for the silicon substrate

After fitting of the substrate EDCs for all incident X-ray angles had been performed the VPXSW profiles could be extracted from the variation of area for the photoelectron environments at each angle. The VPXSW profiles extracted from the Si 2p EDCs for the Si_{bulk} environments are shown as black circles in fig. 4.8 and as blue squares for the Si_{oxide} environments. Due to the fitting constraints used for the substrate EDCs, described in section 4.3.2, the spin-orbit pairs ($2p_{3/2}$ and $2p_{1/2}$) have exactly the same VPXSW profiles, so only ‘bulk’ and ‘oxide’ profiles are shown. The ‘bulk’ VPXSW profile is a sum of the Si $2p_{3/2 \text{ bulk}}$ and Si $2p_{1/2 \text{ bulk}}$ components while the ‘oxide’ VPXSW profile is a sum of the Si $2p_{3/2 \text{ oxide}}$ and Si $2p_{1/2 \text{ oxide}}$ components (normalisation performed after the sum). The experimental data in fig. 4.8 can be seen to have a different shape to that observed in fig. 4.2, where initially the experimental VPXSW is seen to be flat until $\alpha \approx 0.3^\circ$, when the VPXSW intensity begins to rise sharply before peaking at $\alpha \approx 0.6^\circ$. This difference is due to the presence of an overlayer (the IL and CHCl_3) and the total reflection of the X-ray by this layer, which also has a thickness large enough to prevent the evanescent wave reaching the substrate below for low angles. The rise in VPXSW intensity is initially due to the evanescent wave decaying from the surface of the organic layer until the

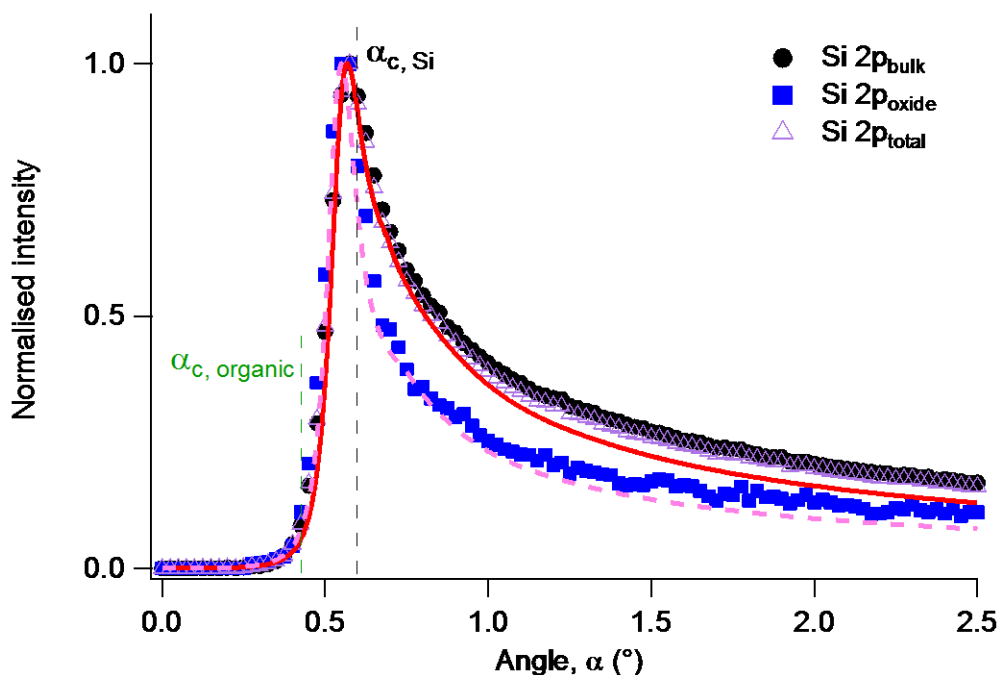


Figure 4.8: Extracted VPXSW profiles for the silicon substrate below the $[\text{C}_8\text{C}_{11}\text{Im}][\text{BF}_4]$ and CHCl_3 layers. Markers represent experimental data whilst the VPXSW profile for a theoretical model in which the silicon is buried beneath 223 Å of organic material is represented by a red line. The dashed pink line shows the model VPXSW profile for a 15 Å oxide layer buried beneath a 223 Å organic layer using $\lambda = 58$ Å (for Si through the IL). Since the EDC fitting used constraints on the peak areas and peak widths the VPXSW profiles for the $2p_{3/2}$ and $2p_{1/2}$ spin-orbit pairs are identical so there is not a VPXSW profile for each photoelectron peak. The Si $2p_{\text{total}}$ is a VPXSW profile for the total silicon substrate, where the individual VPXSW profiles were added together before normalisation.

incident angle surpasses that of the critical angle for the organic layer and the X-ray penetrates through to the silicon substrate. Once the X-ray illuminates the substrate a standing wave is set up which now probes the organic layer adsorbed on the silicon surface. As the incident angle is increased past the critical angle of the silicon reflector the intensity of the reflected X-ray decreases and the standing wave intensity decays, resulting in photoelectron signal from the X-ray penetrating into the silicon substrate.

The experimental surface is modelled by a 3 layer system in which the first layer is the vacuum above the surface, the second layer is organic material with a critical angle $\alpha_{c,2} = 0.4274^\circ$ and the third layer is the silicon reflector with a critical angle $\alpha_{c,3} = 0.5971^\circ$. The model assumes that the IL, CHCl_3 and H_2O can be modelled by the same X-ray parameters, which is a reasonable assumption given the similarity of their X-ray parameters (table 3.1). There is also the assumption that the SiO_x and Si layers can be modelled as a single substrate layer, which is reasonable given the similarity of their X-ray

parameters (so therefore their critical angles) and has been performed previously for silicon substrates [28]. The red line in fig. 4.8 shows the curve that is obtained if it is assumed that there is a 223 Å layer of organic material on top of the reflector and the attenuation length of the Si 2p photoelectrons through the organic layer is $\lambda = 58$ Å (table 4.2). The theoretical model matches the experimental data very well for low angular regimes (below 1°) but fails to reproduce the same signal intensity at higher angles. Increasing the layer thickness fits the VPXSW decay slightly better, but at the cost of a less good fit for low angles, however the exact decay could not be reproduced. The error in the layer thickness has been estimated as ± 15 Å by using the same method as described for the VPXSW profiles for the silicon without the organic layer dosed onto it (section 4.2.2). Essentially the experimental data is compared with a range of layer thicknesses to see which layer thicknesses could be deemed to fit the experimental data sufficiently well, with the plots for this process shown in appendix 8.2.

Both the Si 2p_{bulk} and Si 2p_{oxide} VPXSW are shown in fig. 4.8, where they can be seen to have good agreement for angles below the silicon critical angle, but differ at higher angles. This is due to the fact that in the calculation for the substrate VPXSW intensity the reflector is treated as very thick (1000 Å, section 2.3.3). By using a model to calculate the photoelectron signal from a 15 Å thick layer (representing the SiO_x) buried beneath a 223 Å organic layer (so total layer thickness was 238 Å), with $\lambda = 58$ Å, the pink dashed line in fig. 4.8 is obtained. This can be seen to model the Si 2p_{oxide} component reasonably well, with slight deviation at higher angles due to the noise which results from lower signal intensity for the oxide layer (see fig. 4.7). The substrate VPXSW profile for a 238 Å adsorbed layer is not significantly different to one with a 223 Å adsorbed layer, as shown in appendix 8.2. Since both the silicon and the native oxide were being modelled as a single layer a VPXSW profile was generated for the total silicon signal. This was done by adding the VPXSW profiles, before normalisation had been performed, for the Si 2p_{bulk} and Si 2p_{oxide} then normalising to generate the Si 2p_{total} profile (purple triangles) shown in fig. 4.8. The similarity of the Si 2p_{total} VPXSW profile to the Si 2p_{bulk} profile shows that the majority of the substrate signal comes from the bulk silicon layer. It is

possible that using a theoretical model with a greater number of layers (here it is a 3 layer system) may reproduce the Si 2p_{oxide} VPXSW more accurately.

4.3.4. Extraction and fitting of the VPXSW profiles for the [C₈C₁Im][BF₄] layer

The extracted VPXSW profiles for photoelectrons emitted from the [C₈C₁Im][BF₄] are shown in fig. 4.9 for the carbon (black triangles), boron (orange diamonds), fluorine (pink squares) and nitrogen (blue circles) species. The VPXSW profile shown for the carbon is a sum of the measured VPXSW profiles for the C 1s_{alkyl} and C 1s_{hetero} groups, where the intensities of the peaks were added prior to normalisation of the VPXSW profiles (different, incorrect, results are obtained if you normalise the individual VPXSW profiles then add them together as this has the effect of increasing the relative intensity of the least abundant species). The C 1s_{hetero} and C 1s_{alkyl} (and therefore C 1s_{total}) were observed to have very similar shapes indicating that both groups have the same distribution within the surface, which agrees with the fact that the environments are both present on the cation. The nitrogen VPXSW shown is also a sum of the

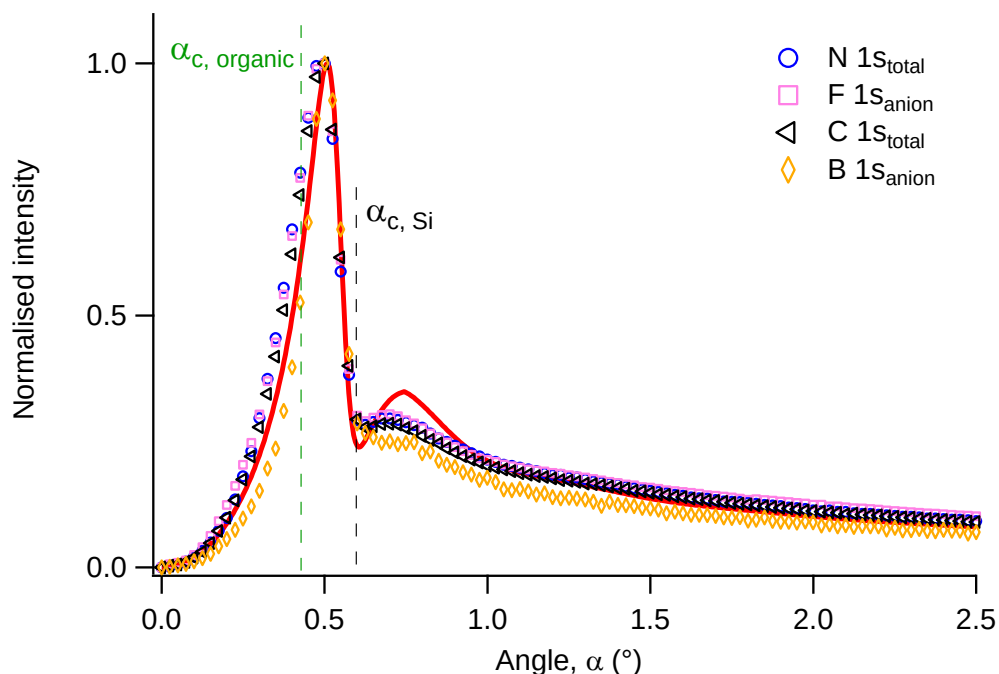


Figure 4.9: Extracted VPXSW profiles for the [C₈C₁Im][BF₄] layer adsorbed on a silicon substrate and beneath a CHCl₃ layer. Experimental data is shown as markers, where good agreement can be seen in the shapes of the VPXSW profiles for the nitrogen, carbon and fluorine with boron differing slightly. The red line shows the VPXSW profile for a model in which the bottom 211 Å of a 223 Å organic layer is emitting photoelectrons. Critical angles for the organic layer and the substrate are shown as dashed lines.

two observed nitrogen components, N 1s_{damage} and N 1s_{cation}, as seen in fig. 4.10. The two VPXSW profiles, prior to normalisation, for the N 1s_{cation} and the N 1s_{damage} (dashed lines within fig. 4.10) do not have the same shape, although they are similar. Since the damaged species is generated as the X-ray exposure (and therefore angle) increases the N 1s_{damage} has a higher relative intensity than the N 1s_{cation} at high angles, and continues to grow as angle increases. The peak in the damage species does appear to occur at a lower angle than N 1s_{cation} which may suggest that the damaged species has diffused to the surface (since layers closer to the surface experience peaks in their VPXSW profiles at lower angles). This is not likely as the surface is at 90 K with the IL frozen in place, making diffusion of species through it difficult. Presence of the damaged species at the surface could be a result of the X-ray traveling wave which propagates across the IL surface at the IL critical angle. It is also possible that the X-ray damage is highest at low angles (where the XSW exists in the organic layer) giving an early peak in the N 1s_{damage} VPXSW profile or is just an artefact of the fitting due to charging of the surface (see section 4.4). The VPXSW profiles of the N 1s_{cation} and the N 1s_{damage} were not able to be well modelled by any theoretical model independently due to the changing concentrations with time caused by the damage. It is rationalised that, due to the surface temperature being around 90 K, the damaged nitrogen species will remain in a similar position to the cation

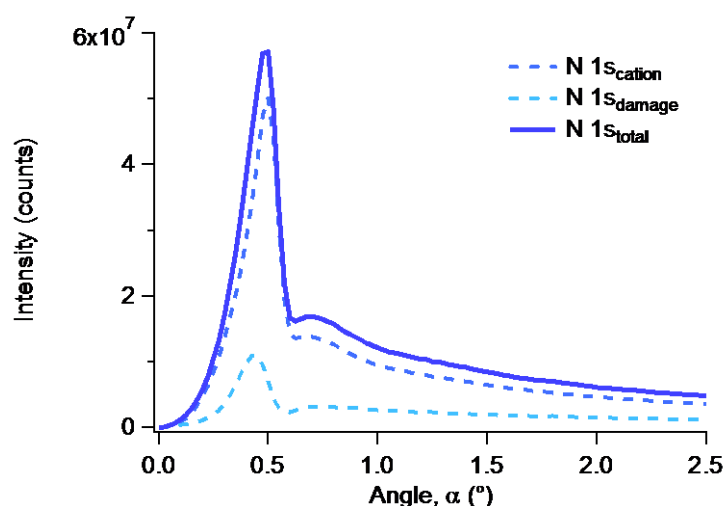


Figure 4.10: Extracted VPXSW profiles for the different nitrogen species within the [C₈C₁Im][BF₄] layer adsorbed on a silicon substrate and beneath a CHCl₃ layer. It can be seen that the shape of the VPXSW profiles for the damaged and cation species are different due to the fact that the amount of damaged species within the IL layer increases as a function of angle (X-ray irradiation). The total nitrogen photoelectron signal is found from adding the signals from the cation and damaged species.

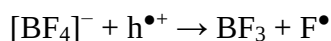
from which it was formed so the total nitrogen VPXSW profile ($N\ 1s_{\text{total}} = N\ 1s_{\text{damage}} + N\ 1s_{\text{cation}}$) should be suitable to probe the IL layer. It can be seen from fig. 4.9 that the $N\ 1s_{\text{total}}$ VPXSW profile is in good agreement with the profiles observed for fluorine and carbon signals from the IL.

The similarity of all of the VPXSW profiles for all individual $[C_8C_1Im][BF_4]$ components suggests that the IL is homogeneous due to randomly orientated ion pairs which have adsorbed where they land (since the surface temperature is lower than the IL glass transition temperature, $T_g = 189.7\text{ K}$ [29]) to form an IL ‘snow’. The IL VPXSW profiles can be fitted with a model (red line in fig. 4.9) which assumes that there is IL within the bottom 211 Å of a 223 Å organic layer adsorbed on the silicon reflector (in other words the top 12 Å of the organic layer doesn’t contain any IL, which agrees with the presence of a $CHCl_3$ layer on top of the IL). The error in the IL layer thickness was estimated as $\pm 10\text{ Å}$ through comparison of the experimental data for the IL species to theoretical models with IL layer thicknesses ranging from 196 Å to 221 Å , whilst keeping the organic layer thickness fixed to 223 Å (see appendix 8.2 for the plot). The attenuation length used for the VPXSW fit has been taken as an average of the attenuation lengths for the C $1s$, N $1s$, F $1s$ and B $1s$ photoelectrons travelling through the IL, table 4.2, giving $\lambda = 53\text{ Å}$. Description of how the attenuation lengths were calculated can be found in section 2.2.3.

Only the boron VPXSW profile, in fig. 4.9, differs significantly in its shape, having a delayed onset of the rise in the VPXSW profile and a less pronounced oscillation at $\alpha \approx 0.7^\circ$, relative to the C $1s_{\text{total}}$, N $1s_{\text{total}}$ and F $1s_{\text{anion}}$ VPXSW profiles which can be seen to match each other and the fit very well. In order to get a better fit for the boron VPXSW profile the IL layer needs to be 196 Å thick (appendix 8.2), suggesting that the boron is not present in the top 27 Å of the organic layer, or the top 15 Å of the IL layer. This boron deficiency could be related to self-assembly of the IL surface, which may have arranged in such a way as to ensure the surface structure consists solely of cations with the alkyl chains protruding from the surface, as has been observed in previous studies of IL systems [8, 30, 31]. This explanation, however, seems unlikely since the adsorption of the $[C_8C_1Im][BF_4]$ has occurred at approximately 90 K , so the IL is believed to have stuck where it lands in the conformation it arrived in as a ‘snow’ (not a liquid), making rearrangement of the ions unlikely (in the

absence of any surface heating by the X-ray beam). It is instead believed that the boron has undergone X-ray damage, despite not detecting a damaged boron species peak in the EDCs.

A study of radiation damage due to ionising radiation exposure (not necessarily X-rays) has been performed looking at the effects on the anions of ILs [32]. These studies were performed by freezing the ILs (a temperature of 50 K) to allow the study of the fragmentation pathways upon absorption of ionising radiation. It was observed that the ionising radiation produced electrons and “holes” ($h^{+\bullet}$, electron deficiencies on molecules), which could then go on to initiate reactions within surrounding molecular species. In the case of the $[\text{BF}_4]^-$ anion, interaction with a hole results in the following decomposition pathway (reaction (19) in ref. [32]):



It is rationalised that this pathway occurs through donation of the electron from the $[\text{BF}_4]^-$ to the hole and then fission of a B–F bond, rather than other decomposition methods such as the formation of F_2 and $^\bullet\text{BF}_2$ (observed for the $[\text{B}(\text{CN})_4]^-$ analogue) through energetics arguments (F_2 is not as stable as C_2N_2 so there is not enough energy gain to make it a thermodynamically viable option). The fluorine radical then goes on to react with nearby alkyl tails (C–H bonds) to generate HF (reaction (20) in ref. [32]). In the studies performed in this work the surface was held at 90 K, so assuming the same radiation induced decomposition reactions occur then formation of HF and BF_3 is expected. Using the Antoine equation [33] for calculating the vapour pressure

$$\log_{10}(P) = A - \frac{B}{(T+C)} \quad \text{Equation 4.1}$$

the vapour pressure, P (bar), for a species with known parameters A , B (K) and C (K) at a temperature, T (K) can be found. For HF the parameters for the temperature range 198.5 to 292.9 K are $A = 4.16129$, $B = 1142.985$ K and $C = -17.993$ K [34]. Extrapolating these values to 90 K gives a vapour pressure of $\approx 2 \times 10^{-12}$ bar ($\approx 2 \times 10^{-9}$ mbar) demonstrating that the HF would not desorb under the conditions of the study (pressure $\approx 10^{-10}$ mbar) if the HF is stabilised by the presence of the IL. For the BF_3 species the parameters are $A = 4.68215$, $B = 663.463$ K and $C = -30.795$ K for the temperature range of 118.5 K to 172.5 K [34]. Extrapolation of these values to 90 K gives the vapour pressure to be $\approx$

3×10^{-7} bar ($\approx 3 \times 10^{-4}$ mbar), meaning the BF_3 would be highly likely to desorb from the surface under the experimental conditions used in this study, even if it were stabilised due to dipole or van der Waals interactions with the surrounding IL molecules. As a result it would not be expected that photoelectron peaks due to the BF_3 would be observed, meaning only the $\text{B } 1s_{\text{anion}}$ should be observed, despite damage to the boron occurring. It is suspected that the fluorine photoelectron peak due to the presence of damaged HF is masked by the fluorine in the anion, whilst the inability for the HF to desorb may explain why the top 15 Å of the IL layer shows the presence of fluorinated species but no boron containing species.

4.3.5. Extraction and fitting of the VPXSW profiles for the CHCl_3 layer

It was observed in figure 4.6 that new chlorine environments (other than the pristine CHCl_3 environments) develop over the 20 minutes that the EDCs, from which the VPXSW profiles are generated, were collected. The VPXSW profiles, prior to normalisation, for these damaged species are shown as dashed lines in fig. 4.11 along with the total chlorine VPXSW profile (solid green line, total = $\text{CHCl}_3 + \text{Cl}^- + \text{Cl}^\bullet$). The shapes of the VPXSW profiles can be seen to reflect the fact that the CHCl_3 environment (dashed pink line) is decreasing over time and the damage species environments are growing in intensity with X-ray

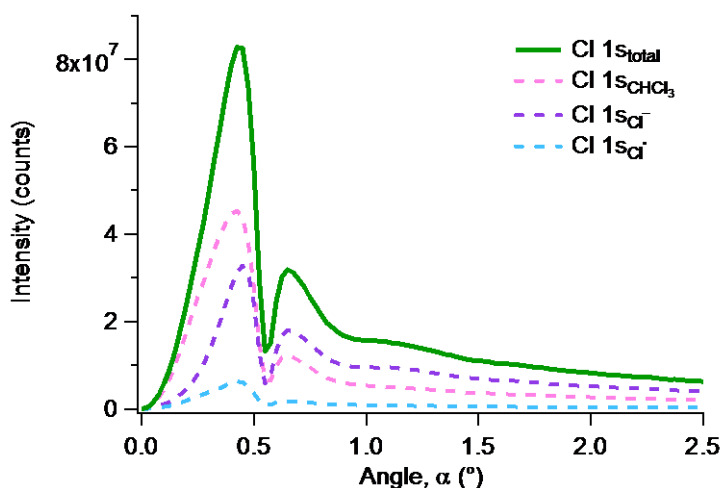


Figure 4.11: Extracted VPXSW profiles for the different chlorine species within the CHCl_3 layer adsorbed on a $[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]$ layer, on a silicon substrate. It can be seen that the shape of the VPXSW profiles for the damaged species is different to the CHCl_3 due to the fact that the amount of damaged species increases as a function of angle (X-ray irradiation). The total photoelectron signal is found from adding the signals from CHCl_3 and Cl^- and $\text{Cl}^\bullet$ species.

irradiation timescale. The hallmark of this is a higher relative intensity at higher angles for the damaged Cl^- environment (dashed purple line), since these represent longer X-ray doses as angle was scanned from 0° upwards. It was found in fig. 4.6c that the amount of the $\text{Cl}^\bullet$ environment doesn't appear to vary too much with angle, suggesting either that it is due to a species which does not damage with irradiation, possibly due to energy redistribution effects caused by being at the IL- CHCl_3 interface, or that it is a reaction intermediate. It is rationalised that as the surface is at 90 K the damaged species should not travel far from where they were generated, so fitting the $\text{Cl } 1s_{\text{total}}$ profile will be sufficient to model the CHCl_3 layer, despite the variation in the intensities of the chlorine environments with X-ray exposure and therefore angle.

The VPXSW profile for the $\text{Cl } 1s_{\text{total}}$ profile was modelled using the three layer model, described in section 4.3.3, in which the first layer is the vacuum, the second layer is an organic material (used to model the $[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]$, CHCl_3 and H_2O layers) with the third layer being the silicon substrate and its native oxide (treating them both as one layer). The $\text{Cl } 1s$ photoelectrons were calculated to have an attenuation length of $\lambda = 9 \text{ \AA}$ through the organic layer, which is much lower than the IL photoelectrons ($\lambda = 53 \text{ \AA}$) due to the low electron kinetic energy ($\approx 175 \text{ eV}$, table 4.2). The model for the normalised $\text{Cl } 1s_{\text{total}}$ VPXSW profile is shown in fig. 4.12 (red line) and used $\lambda = 9 \text{ \AA}$, whilst the experimental data shown as green squares. The fact that the CHCl_3 layer is only a thin overlayer results in a VPXSW profile with more pronounced oscillations than were observed in the IL VPXSW profiles. Oscillations come as a consequence of increasing the incident angle, α , which shortens the standing wave period so the antinodes and nodes of the standing wave pass through the CHCl_3 layer. At $\alpha \approx 0.55^\circ$ the signal nearly drops to zero as an XSW node passes through the CHCl_3 layer and at $\alpha \approx 0.7^\circ$ an antinode passes through the CHCl_3 layer generating a peak in the data. This is in contrast to the VPXSW profile observed for the $[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]$ profiles (fig. 4.9) where the IL was a thick layer so had less pronounced oscillations as the antinodes and nodes just pass into the surface rather than through the surface layer.

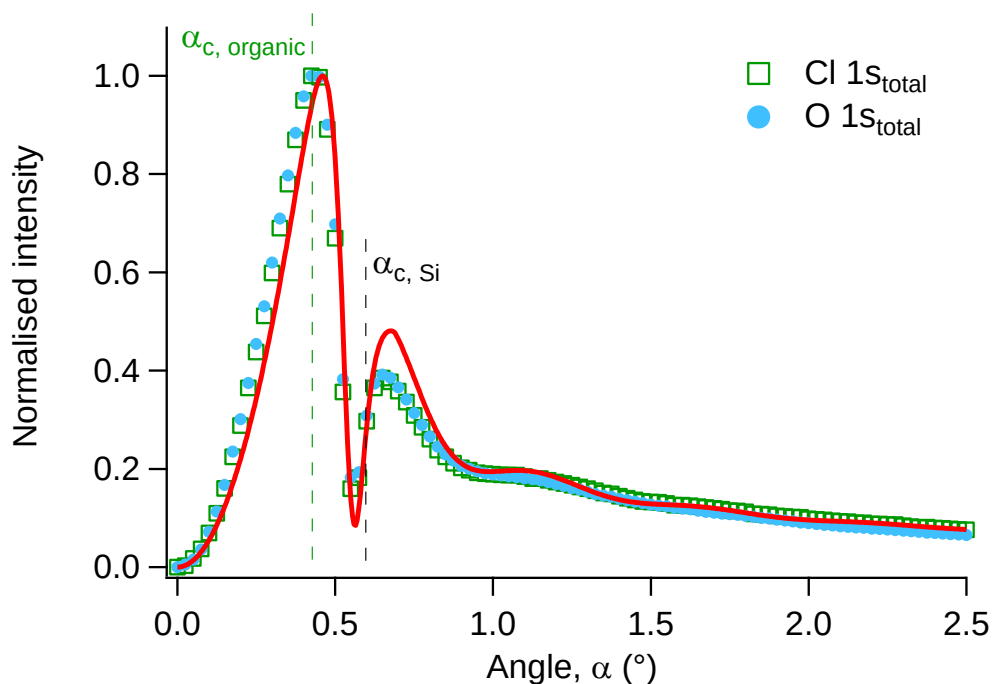


Figure 4.12: Extracted VPXSW profiles for the CHCl_3 and H_2O layers adsorbed on top of an $[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]$ layer, all of which is on a silicon substrate. Experimental data is shown as markers, and a good agreement can be seen in the shapes of the VPXSW profiles for the total chlorine and total oxygen profiles. The red line shows the VPXSW profile for a model in which the top 12 Å of a 223 Å organic layer is emitting photoelectrons. Critical angles for the organic layer and the substrate are shown as dashed lines.

Thinner layers at large distances (over 200 Å) above the surface plane will produce VPXSW profiles with more features in them, making them easier to model (peaks in the data are easier to model than monotonic decays). The theoretical VPXSW profile in fig. 4.12 assumes that the signal is coming from the top 12 Å of a 223 Å organic layer, which agrees with the VPXSW models from both the substrate VPXSW profiles and the IL VPXSW profiles. The error in the layer thickness is estimated to be ± 15 Å (see appendix 8.2 for plots and discussion). The VPXSW profile is not as sensitive to the variation in layer thickness as it is to the variation in layer position. Figure 4.13 shows the experimental data for the Cl $1s_{\text{total}}$ VPXSW profile alongside a range of theoretical VPXSW profiles for 12 Å thick CHCl_3 layers centred at different heights above a surface. It can be seen that as the layer position is increased the position of the local maxima at $\approx 0.7^\circ$ and $\approx 1.1^\circ$ decreases as the standing wave antinodes meet them at lower angles due to their higher position in the surface. From fig. 4.13 it can be seen that the blue line representing a 12 Å thick layer centred at 217 Å (which is the same model as one in which the top 12 Å of a 223 Å layer is composed of CHCl_3) is the best fit to the oscillation positions in

the experimental data. Consideration of the other models plotted in fig. 4.13 suggests that the positions of the experimental oscillations are within error of the 207 Å and 227 Å layers giving a ± 10 Å error in the position of the CHCl₃ layer. Fits to the individual chlorine environment VPXSW profiles shown in fig. 4.11 (CHCl₃, Cl⁻ and Cl[•]) were attempted, but suitable matches could not be found. This again confirms that the addition of all of the chlorine environments to make a Cl 1s_{total} VPXSW profile was suitable to model the CHCl₃ layer.

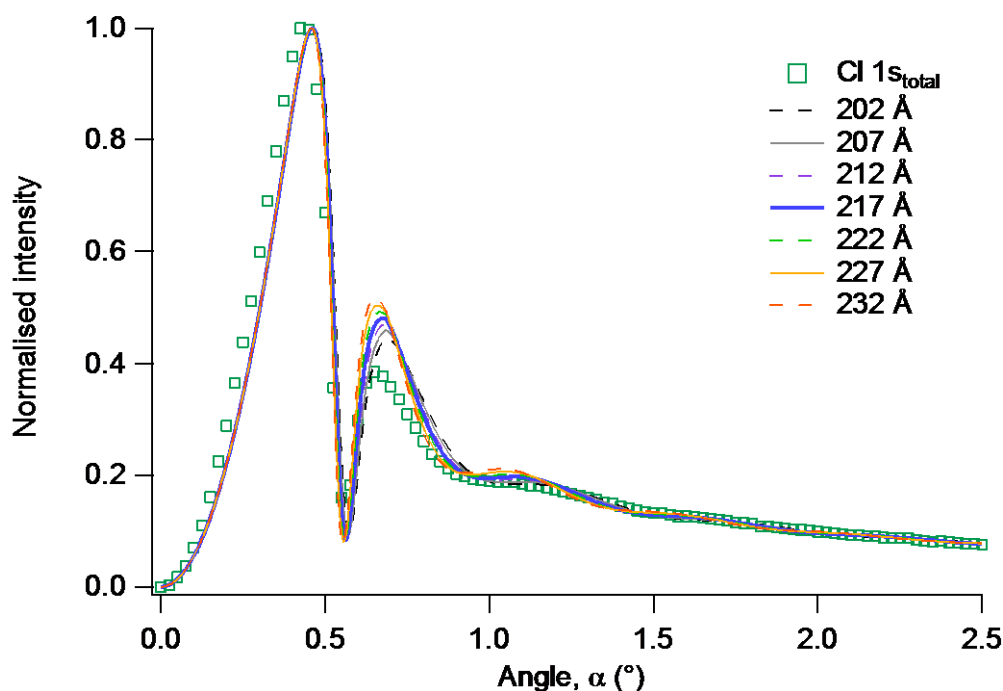


Figure 4.13: A comparison of the extracted VPXSW profiles for the total chlorine signal (green squares) to theoretical models with a thickness of 12 Å at a variety of heights above the surface in an attempt to estimate an error in the layer position. The legend indicates the position of the centre of the CHCl₃ layer at the top of the organic layer. An attenuation length of 9 Å was used in the theoretical models.

As well as showing the VPXSW profile for the sum of chlorine environments fig. 4.12 also shows the VPXSW profile for the O 1s signal (blue circles), which is thought to be due to background water adsorption as discussed in section 4.3.2. The fact that the O 1s VPXSW profile matches the chlorine VPXSW profile, and the VPXSW model for the top 12 Å of the 223 Å organic layer, so well is an indication that these layers are at very similar heights above the reflector surface. This supports the argument that the oxygen species is water which has adsorbed from the background over the period of 2 hours. The fact that the oxygen is not seen to be present throughout the whole organic layer is an indication that the background pressure (of water) was low enough to prevent

interference with the majority of the surface. The organic layer was deposited over a 30 minute period, meaning that there would have been 0.18 metric langmuirs of water spread over the 223 Å organic layer which was not concentrated enough to give a significant photoelectron signal. The exposure of the surface to the background water over a 2 hour period at 90 K gave a concentrated water layer, which was the crucial factor in the observation of the adventitiously adsorbed water.

4.4. Observation of photoelectron binding energy shifts with incident angle

Charging of the surface has already been mentioned in section 4.3.4 as the reason behind the growth of the N 1s_{damage} peak not being as smooth as one might expect (a peak might be expected at $\alpha = \alpha_{c, \text{organic}}$, where the travelling wave propagates across the surface of the organic layer promoting a greater quantity of damage). Aside from a few brief comments there has been no attempt to describe or discuss charging of the surface. X-ray charging [7, 15, 35-37] is observed on partially or non-conducting surfaces due to the release of photoelectrons, which are negatively charged, from the surface under X-ray irradiation. This leaves behind positively charged holes, or electron deficiencies, which has the effect of building up a positive charge on the surface. A conducting surface connected to the sample manipulator, which is grounded, simply draws electrons from the sample manipulator to balance out the lost photoelectrons. For a non-conducting surface this process cannot occur efficiently enough and the positive charge builds up on the surface shifting the photoelectron peaks to higher binding energies (the photoelectrons are retarded by the positive surface charge, hence giving a higher apparent binding energy) as well as distorting the shape of the photoelectron peaks (in the case of a non-uniform charge density where different parts of the surface have slightly different charges) [7, 35].

Charging was observed for all surfaces in this study although when no organic layer was present the charging of the surface was observed to be only by ≈ 0.6 eV in comparison to when the IL and CHCl₃ were adsorbed, where charging was observed to be on the order of 10 eV for the organic layer.

Charging of the substrate peaks below the organic layer is difficult to observe due to the fact that the X-ray is totally reflected from the organic layer, resulting in little or no X-ray intensity irradiating the silicon surface, in the angular range where charging is expected to be observed. The large difference in the amount of charging observed in the organic layer and in the substrate layer is due to the low surface temperature used in this study ($T_{\text{surf}} \approx 90$ K). When the IL is in the liquid state it is observed to be an electrical conductor, allowing it to be used as an electrochemical solvent [38-40], however at temperatures lower than its glass transition temperature ($T_g = 189.7$ K [29]) the IL will be a solid preventing the ions from migrating and neutralising the build-up of charge.

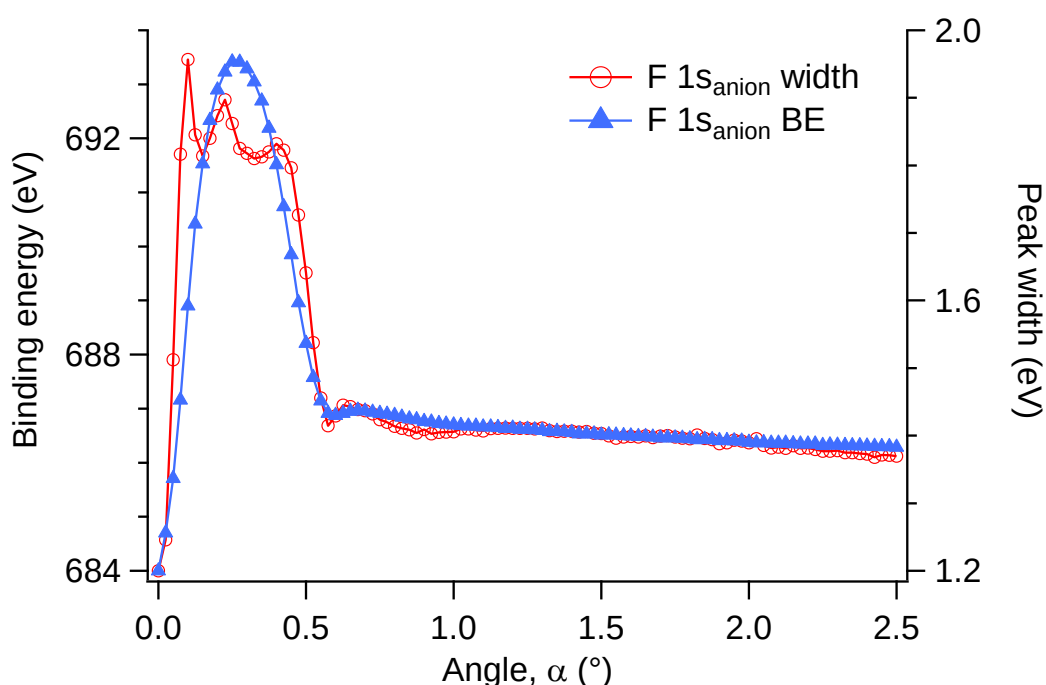


Figure 4.14: A comparison of the changes in the binding energy (blue triangles, left axis) and the width (red circles, right axis) of the Gaussian peak used to model the F 1s photoelectron intensity within the organic layer. The plots show that the angular range over which the binding energy shifts is the same as the angular range over which the width swells. Both of these effects have been related to surface charging in previous XPS studies and suggests that the surfaces studied here are also charging.

Figure 4.14 shows the effect of the observed charging on the binding energy and the peak width of the F 1s_{anion} component of the IL, which is representative of the charging observed in all of the IL photoelectron peaks. The X-ray charging has the effect of shifting the binding energy to more positive values, from ≈ 684 eV up to ≈ 693 eV, and broadening the peak from ≈ 1.2 to ≈ 2.0 eV, before both the *BE* and the width begin to decrease and reach stable values (approximately 686.3 eV and 1.4 eV, respectively). The angular range

over which the binding energy shifts and the peak width broadens is observed to be the same (0° to 0.55°) supporting the claim that these effects are due to charging of the surface. The fact that the surface appears to charge up by 10 V and then discharge is thought to be a result of the changing X-ray beam intensity at the surface, as well as the amount of the sample that is being irradiated by the X-ray (the X-ray footprint on the sample), as the incident angle is scanned. The charging observed in the IL is observed to be very similar to the charging in the CHCl_3 layer, as shown in fig. 4.15. Both photoelectron peaks are observed to shift in binding energy by ≈ 10 eV before the BE decreases and reaches a steady value.

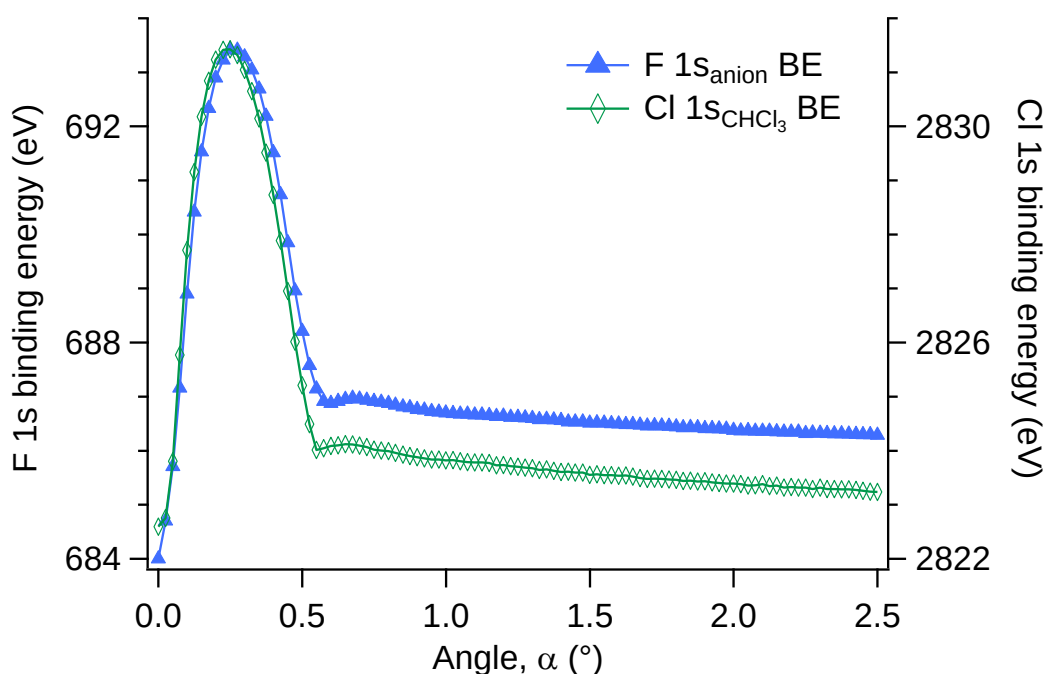


Figure 4.15: A comparison of the variation in binding energy for the IL species (represented by the $\text{F } 1s_{\text{anion}}$, blue triangles, on left axis) with the other component within the organic layer, the CHCl_3 (represented by the $\text{Cl } 1s_{\text{CHCl}_3}$, green diamonds, on right axis). The similarity in the binding energy shift for the two species indicates that the layers undergo similar charging processes.

Since it is thought that the X-ray intensity at the surface is related to the amount of surface charging observed, fig. 4.16 shows a comparison of the shift in the binding energy of the $\text{F } 1s_{\text{anion}}$ peak (blue triangles) with the $\text{F } 1s_{\text{anion}}$ VPXSW profile (pink squares). Here the VPXSW profile represents the X-ray intensity and the number of photoelectrons emitted from the IL layer, which should be related to the amount of charging within the IL layer. The peak in the VPXSW profile is observed to occur at $\approx 0.5^\circ$ (where a travelling wave

propagates across the organic layer surface) whereas the maximum *BE* shift is observed at $\approx 0.25^\circ$. These two angles are different as the number of photoelectrons released from the IL layer (monitored by tracking the F 1s electrons with a kinetic energy ≈ 2310 eV) is not necessarily representative of the total number of photoelectrons emitted from the surface. Had the drain current from the sample (the amount of current drawn by the sample from the sample manipulator) been measured it is expected that the drain current, which would have shown the amount of current drawn to compensate total photoelectron flux from the sample, would have mirrored the binding energy shift observed in the organic layer. Both the VPXSW profile and the *BE* shift drop to low levels at $\alpha = 0.55^\circ$, as the X-ray is transmitted through the organic layer and the X-ray standing wave is set up from the silicon reflector with a node within the IL layer. There is a slight increase in the binding energy shift of the F 1s_{anion} photoelectron peak at $\approx 0.7^\circ$, which is also the angle at which the small bump in the F 1s_{anion} VPXSW profile occurs. This is due to a standing wave antinode passing into the IL layer, supporting the claim that increased X-ray intensity (and hence photoelectron flux) is observed to increase the amount of charging and *BE* shift, which agrees with previous studies of X-ray charging [7].

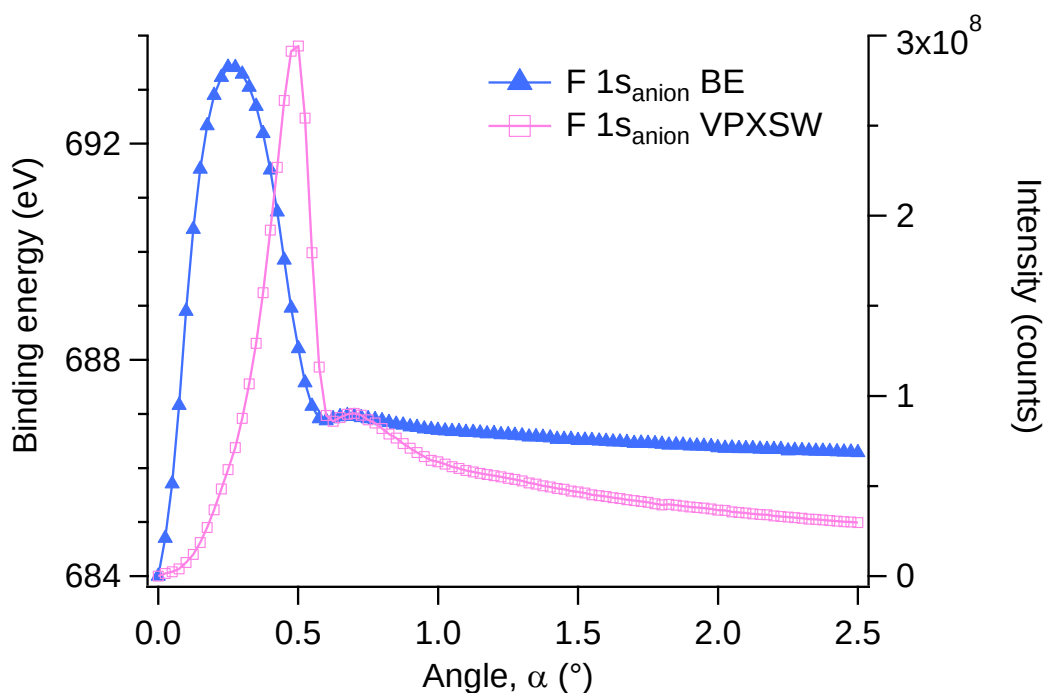


Figure 4.16: A plot comparing the binding energy of the Gaussian peak used to fit the F 1s_{anion} to the VPXSW profile extracted from the fits to the EDCs. It can be seen that the maximum binding energy (blue triangles, left axis), due to surface charging, and the maximum F 1s photoelectron flux (pink squares, left axis) do not occur at the same angle.

The amount of charging is thought to be related to the total photoelectron flux from the surface, which itself is determined by a combination of the X-ray intensity, X-ray path length through the surface and the X-ray footprint on the sample. This means that it is possible to produce a greater total photoelectron flux from the sample either by increasing the X-ray intensity or by increasing the area of the surface that is irradiated, through increasing the X-ray footprint on the sample. Since the X-ray intensity at the surface increases with incident angle, α , (section 2.3) but the X-ray path length and X-ray footprint decrease with incident angle then it seems sensible that a peak is observed in the plot of binding energy versus incident angle as these processes compete. By rearranging eq 2.41 (section 2.3.4) to make α the subject and using the *footprint = sample length* the angle at which the footprint becomes smaller than the sample, α_{foot} can be found.

$$\alpha_{foot} = \sin^{-1} \left(\frac{h_{beam}}{sample\ length} \right) \quad \text{Equation 4.2}$$

The experimental section (section 3.3) describes that the sample was 10 mm long and the X-ray beam height, h_{beam} , was 30 μm . Using these values finds the angle at which the footprint is the same length as the sample to be $\alpha_{foot} \approx 0.17^\circ$, which is reasonably close to the angle at which the maximum binding energy shift is observed. The difference in α_{foot} and the angle at which the binding energy is at a maximum could be a result of the X-ray not being in the centre of the sample, meaning that the apparent sample length (the length of the footprint at the point the footprint just crosses the edge of the sample) is smaller, leading to a larger α_{foot} value. This could be an indication that the maximum in surface charging occurs at the angle where the largest possible area of the sample is irradiated producing the largest photoelectron flux. Alternatively the effect of the X-ray path length could explain the slight variation of the maximum in the charging from α_{foot} , as the maximum path length through the material occurs for $\alpha > \alpha_c$ (when the X-ray starts to penetrate into the surface) causing the *BE* peak maximum to shift towards higher α values. Unfortunately the drain current was not measured during these experiments meaning that the relationship between the amount of surface charging and total photoelectron flux cannot be verified.

4.5. Overall surface structure determined by variable period X-ray standing wave analysis

This chapter has demonstrated the ability of the variable period X-ray standing wave technique to fit a large range of film thicknesses of different materials. The technique was able to detect the native oxide layer on a silicon wafer, despite the similarity of the optical properties of the two materials, with a native oxide thickness of $15 \pm 10 \text{ \AA}$ observed. A surface consisting of a thick layer of the ionic liquid $[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]$ with a thin layer of CHCl_3 on top was then prepared on the silicon surface. Using the VPXSW profile formed from the silicon substrate photoelectron peaks the thickness of the organic layer could be determined to be $223 \pm 15 \text{ \AA}$, although the substrate signal could not be used to work out how much of the organic layer was IL or CHCl_3 as the analysis software treated the whole organic layer as one species. The VPXSW profiles obtained from species within the IL (fluorine, nitrogen, carbon and boron) could be used to find the thickness of the IL layer, which was known to be deposited on the surface before the CHCl_3 . The VPXSW profiles could be successfully modelled by a theoretical curve which assumed that the photoelectron signal came from the bottom $211 \pm 10 \text{ \AA}$ of the organic layer. The CHCl_3 VPXSW profile was then compared to theoretical models to show that a good fit could be obtained if it was assumed that the photoelectron signal only came from the top $12 \pm 15 \text{ \AA}$ of the organic layer, but the position of this CHCl_3 layer was observed to be centred at $217 \pm 10 \text{ \AA}$, which agrees with the IL film thickness determined by VPXSW analysis. The errors discussed with this VPXSW technique are quite large however thicker layers will tend to have smaller errors in both position determination and thickness determination. Having a greater quantity of oscillations makes matching the phase of the experimental and theoretical oscillations easier, as varying the layer thickness slightly changes the phase of the oscillations in the VPXSW profile [11].

Combining all of the information gathered from the fitting of the different profiles the structure of the surface can be determined, with a pictorial representation shown in fig. 4.17. The VPXSW technique allowed the identity of an unknown oxygen containing species to be confirmed as an adsorbed water layer on the top of the organic layer. This discovery was somewhat serendipitous

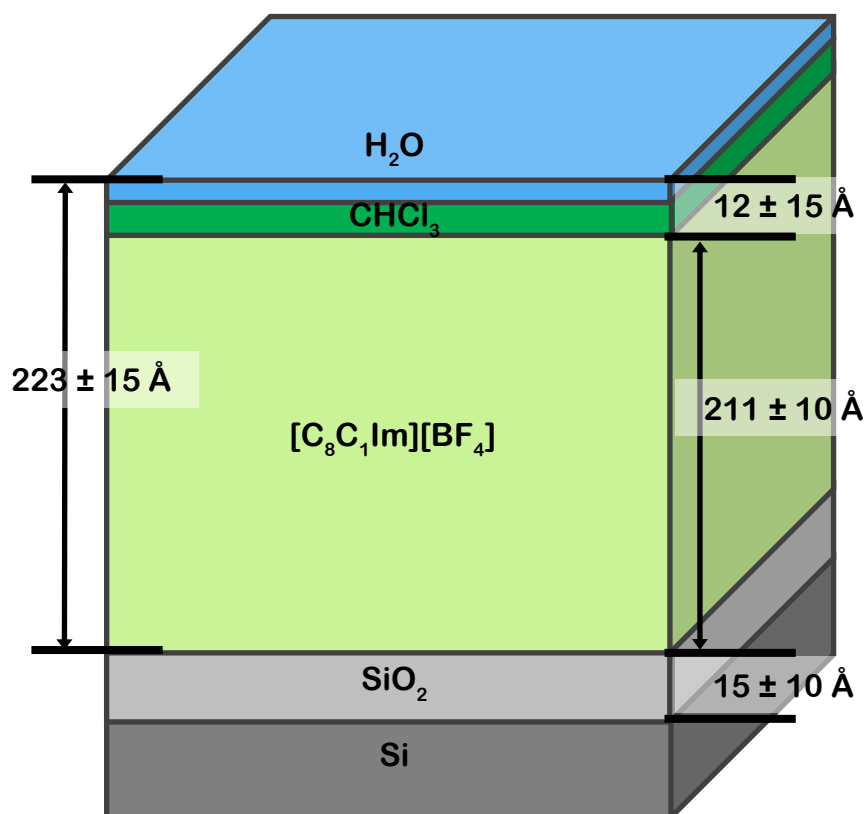


Figure 4.17: A diagrammatic representation of the surface formed and analysed within this study using the variable period X-ray standing wave technique with photoelectron emission. The layer thicknesses have been determined through matching the experimental VPXSW profiles to theoretical models, with all of the data agreeing with the surface structure shown. as the O 1s photoelectron peak was being studied to look at the native oxide, however a scan over the whole photoelectron kinetic energy range would identify species which were not known to be present on the surface. Without the VPXSW profile providing the information that the oxygen layer was on the surface (the VPXSW profile was the same as the CHCl₃ profile) it is unlikely that the identity of the oxygen species would have been found. This result shows that the VPXSW technique with photoelectron detection has great potential for determining surface layering. The fact that the work here only used a 3 layer model (vacuum, material in the layer, substrate) simplified the fitting and was fine for the native oxide layer on the silicon substrate. The model was also observed to be a sufficient approximation to a 6 layer system (vacuum, H₂O, CHCl₃, [C₈C₁Im][BF₄], SiO_x, Si), although it is not known whether using a 6 layer system would be of any benefit as this would introduce a greater number of variables which would take longer to optimise (the ‘fitting’ is presently performed by comparison of the experimental data and a model by a human). It

has however been observed that the buried Si 2p_{oxide} VPXSW profile did not match the buried Si 2p_{bulk} VPXSW, so it is possible that a 6 layer model could remedy this.

It has been observed that variable period X-ray standing wave analysis with photoelectron detection can be used to successfully determine the layering of a surface. There is still development of the technique required in order for it to become a tool that can be used on more complex systems as at present the fitting is not automated. Despite using an ionic liquid as a thick layer in this study, the fact that the surface temperature was around 90 K meant that the IL was not actually a liquid. This made finding a model for the surface much easier as it was known that the morphology of the surface would not vary in time (liquid surfaces can form droplets over time [41]). Another factor which made the fitting much easier was that the surface structure was known (with the exception of the water layer), in that it was known that the substrate would probably have a native oxide, onto which IL was dosed as a thick layer with a thin CHCl₃ on top. This meant that finding the correct model was easier than the case where there was no prior idea of where the different species might be, although after spending some time looking at the VPXSW profiles for different layers it becomes easier to deduce where different layers are based upon the profile shape (see section 2.3.5).

The shape of the leading edge, at the low angles, is a big factor in deducing the approximate position of a layer as species which are closest to the vacuum layer will have earlier rises in the leading edge, whilst buried interfaces will have a flat VPXSW profile before a sharp rise in the leading edge. Also the greater the number of oscillations or wiggles in the profile the closer that layer is to the vacuum layer, and the more pronounced the oscillation the thinner the layer (thick layers have ‘wiggles’, like the IL in this study). The chemicals used in this study were chosen as they had different elements within them which would make the photoelectron peak fitting easier. Using photoemission meant that different VPXSW profiles could be obtained from species with different chemical shifts however if the shift is not sufficiently large to be clearly resolved constraints must be used to prevent peak ‘swelling’ when fitting the EDCs. This issue is one which is commonplace in bulk XPS leading to databases of the chemical shifts of different compounds [7, 35].

All of the fits discussed in this work have assumed that the interfaces are perfectly flat and do not have any roughness. This is unlikely to be true in reality and may be the cause of the theoretical models not matching the experimental data perfectly in some of the cases described here. If the surface is too rough the X-rays will not be efficiently reflected and the standing wave will not be set up. This does not appear to have been the case here, but even small surface undulations affect the local angle of incidence of the X-ray, as shown in fig. 4.18, which will affect the measured VPXSW profile. Using angle θ as a measure for the local undulation, the fact that the angles in a triangle (composed of the blue line, black dashed line and green dashed line) must add up to 180° and that the angles along a line (the X-ray on the left) must also add up to 180° it can be found that an X-ray can be incident upon the surface at an angle of $\alpha + \theta$. If the angle $\alpha + \theta$ surpasses the critical angle, α_c , then the X-ray will not reflect from that local surface and will instead propagate into the material, emitting photoelectrons at angles below the critical angle. It is not known what the morphology of the IL ‘snow’ is, in terms of its surface roughness, however the ability to set up a standing wave from its surface must be an indication that it is reasonably flat.

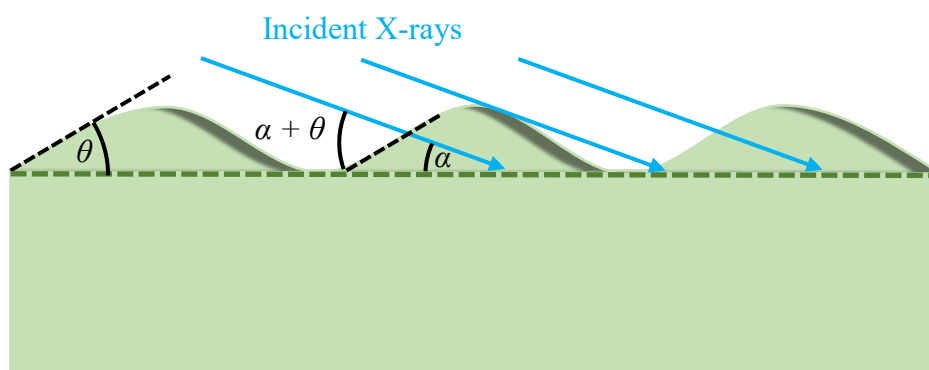


Figure 4.18: A diagrammatic representation of the effect of surface roughness on the VPXSW technique. X-rays are represented by the blue arrows incident upon the surface at an angle α relative to the surface plane (green dashed line). If the surface has a roughness, which can be characterised by an angle θ , then it can be seen that the X-ray may be incident upon a surface at an angle of anywhere between α (at the top of an undulation) and $\alpha + \theta$. Further to variation in the incident angle, surface undulations also cause shadows to be formed, where some areas are not irradiated by the X-rays.

X-ray induced effects such as surface charging and beam damage were observed within this study, complicating interpretation of some of the electron distribution curves. Use of photoelectron detection allowed damaging of the adsorbed species to be identified much more easily than if X-ray fluorescence

had been used due to the chemical shift specificity. The use of a low temperature sample ($T_{\text{surf}} \approx 90$ K) meant that some of the damaged species remained adsorbed to the sample (such as HF) allowing it to be detected, however more volatile suspected damage products (such as BF_3) were not observed. Damaging of the surface could be reduced through reduction in the X-ray beam intensity, as was employed within this study, however this also reduces the experimental signal. Surface charging was observed to affect the photoelectron binding energies and peak shapes, making extraction of VPXSW profiles from the EDCs difficult in some cases. This resulted in constraints being applied to the fits for the binding energies and peak widths of certain chemical components (especially ones where multiple environments were observed under one envelope such as CHCl_3 and N 1s_{damage}). It is not thought that the use of constraints affects the validity of the VPXSW profiles, but may explain why the binding energies of the IL components only matched the literature values to 0.3 eV.

4.6. References

- [1] Jones, R.G., Shuttleworth, I., Fisher, C.J., Lee, J.J., Bastow, S.L., Ithnin, R., Ludecke, J., Skegg, M.P., Woodruff, D.P. and Cowie, B.C.C., Surface structure determination using X-ray standing waves. *Phys. Low-Dimens. Str.*, **2001**, (11-2), pp. 1-26.
- [2] Woodruff, D.P., Seymour, D.L., McConville, C.F., Riley, C.E., Crapper, M.D., Prince, N.P. and Jones, R.G., A Simple X-ray Standing Wave Technique for Surface Structure Determination - Theory and Application. *Surf. Sci.*, **1988**, (195), pp. 237-254.
- [3] Roper, M.G., Skegg, M.P., Fisher, C.J., Lee, J.J., Dhanak, V.R., Woodruff, D.P. and Jones, R.G., Atop adsorption site of sulphur head groups in gold-thiolate self-assembled monolayers. *Chem. Phys. Lett.*, **2004**, (389), pp. 87-91.
- [4] Steinrück, H.P., Recent developments in the study of ionic liquid interfaces using X-ray photoelectron spectroscopy and potential future directions. *Phys. Chem. Chem. Phys.*, **2012**, (14), pp. 5010-5029.
- [5] Imamura, M., Matsubayashi, N., Fan, J., Kojima, I. and Sasaki, M., The determination of the thickness of the silicon oxide film by synchrotron radiation x-ray photoelectron spectroscopy (SR-XPS) analysis. *Meas. Sci. Technol.*, **2011**, (22), pp. 024007.
- [6] Brundle, C.R. and Roberts, M.W., Some observations on surface sensitivity of photoelectron spectroscopy. *P. R. Soc. A*, **1972**, (331), pp. 383-394.
- [7] Surface Analysis by Auger and X-ray Photoelectron Spectroscopy. Briggs, D. and Grant, J.T., Eds., IM Publications, Chichester, (2003)

- [8] Mezger, M., Ocko, B.M., Reichert, H. and Deutsch, M., Surface layering and melting in an ionic liquid studied by resonant soft X-ray reflectivity. *Proc. Natl. Acad. Sci. U S A*, **2013**, (110), pp. 3733-3737.
- [9] Lauw, Y., Horne, M.D., Rodopoulos, T., Webster, N.A., Minofar, B. and Nelson, A., X-ray reflectometry studies on the effect of water on the surface structure of [C₄mpyr][NTf₂] ionic liquid. *Phys. Chem. Chem. Phys.*, **2009**, (11), pp. 11507-11514.
- [10] Parratt, L.G., Surface Studies of Solids by Total Reflection of X-rays. *Phys. Rev.*, **1954**, (95), pp. 359-369.
- [11] Wang, J., Bedzyk, M.J., Penner, T.L. and Caffrey, M., Structural Studies of Membranes and Surface Layers up to 1000 Å Thick using X-ray Standing Waves. *Nature*, **1991**, (354), pp. 377-380.
- [12] Kramer, M., von Bohlen, A., Sternemann, C., Paulus, M. and Hergenroder, R., Synchrotron radiation induced X-ray standing waves analysis of layered structures. *Appl. Surf. Sci.*, **2007**, (253), pp. 3533-3542.
- [13] Bedzyk, M.J., Bommarito, G.M. and Schildkraut, J.S., X-ray Standing Waves at a Reflecting Mirror Surface. *Phys. Rev. Lett.*, **1989**, (62), pp. 1376-1379.
- [14] Zhang, R.T., Itri, R. and Caffrey, M., Membrane structure characterization using variable-period X-ray standing waves. *Biophys. J.*, **1998**, (74), pp. 1924-1936.
- [15] Villar-Garcia, I.J., Smith, E.F., Taylor, A.W., Qiu, F., Lovelock, K.R., Jones, R.G. and Licence, P., Charging of ionic liquid surfaces under X-ray irradiation: the measurement of absolute binding energies by XPS. *Phys. Chem. Chem. Phys.*, **2011**, (13), pp. 2797-2808.
- [16] *X-ray Science and Technology*. Michette, A.G. and Buckley, C.J., Eds., Institute of Physics Publishing, Bristol, (1993)
- [17] Bedzyk, M.J., Bilderback, D.H., Bommarito, G.M., Caffrey, M. and Schildkraut, J.S., X-ray Standing Waves - A Molecular Yardstick for Biological Membranes. *Science*, **1988**, (241), pp. 1788-1791.
- [18] Lovelock, K.R.J., Smith, E.F., Deyko, A., Villar-Garcia, I.J., Licence, P. and Jones, R.G., Water adsorption on a liquid surface. *Chem. Commun.*, **2007**, 4866-4868.
- [19] Kolasinski, K.W., *Surface Science: Foundations of Catalysis and Nanoscience*. Eds., John Wiley & Sons, Chichester, UK, (2012)
- [20] Seah, M.P. and Dench, W.A., Quantitative electron spectroscopy of surfaces: A standard data base for electron inelastic mean free paths in solids. *Surf. Interface Anal.*, **1979**, (1), pp. 2-11.
- [21] Kim, Y.B., Tuominen, M., Raaijmakers, I., de Blank, R., Wilhelm, R. and Haukka, S., Initial stage of the ultrathin oxide growth in water vapor on Si(100) surface. *Electrochem. Solid St.*, **2000**, (3), pp. 346-349.
- [22] Miyata, N., Shigeno, M., Arimoto, Y. and Ito, T., Thermal Decomposition of Native Oxide on Si(100). *J. Appl. Phys.*, **1993**, (74), pp. 5275-5276.
- [23] EDCfitprog (written in Igor Pro 3.64), Contact: robert.g.jones@nottingham.ac.uk (accessed 2017)
- [24] VPXSW_3layer (written in Igor Pro 6.34), Contact: robert.g.jones@nottingham.ac.uk (accessed 2017)
- [25] Thompson, A.C. and Vaughan, D., *X-ray Data Booklet*. Kirz, J., Eds., Lawrence Berkeley Laboratory, (2001)

- [26] Powell, C.J. and Jablonski, A., *NIST Electron Inelastic-Mean-Free-Path Database, version 1.2, SRD 71*. Eds., National Institute of Standards and Technology, Gaithersburg, MD, (2010)
- [27] Honig, R.E. and Hook, H.O., Vapor Pressure Data for some Common Gases. *Rca Review*, **1960**, (21), pp. 360-368.
- [28] Kohli, S., Rithner, C.D., Dorhout, P.K., Dummer, A.M. and Menoni, C.S., Comparison of nanometer-thick films by x-ray reflectivity and spectroscopic ellipsometry. *Rev. Sci. Instrum.*, **2005**, (76), pp. 023906.
- [29] Leys, J., Wubbenhorst, M., Menon, C.P., Rajesh, R., Thoen, J., Glorieux, C., Nockemann, P., Thijs, B., Binnemans, K. and Longuemart, S., Temperature dependence of the electrical conductivity of imidazolium ionic liquids. *J. Chem. Phys.*, **2008**, (128), pp. 064509.
- [30] Santos, C.S. and Baldelli, S., Gas-liquid interface of room-temperature ionic liquids. *Chem. Soc. Rev.*, **2010**, (39), pp. 2136-2145.
- [31] Hammer, T., Reichelt, M. and Morgner, H., Influence of the aliphatic chain length of imidazolium based ionic liquids on the surface structure. *Phys. Chem. Chem. Phys.*, **2010**, (12), pp. 11070-11080.
- [32] Shkrob, I.A., Marin, T.W., Chemerisov, S.D. and Wishart, J.F., Radiation Induced Redox Reactions and Fragmentation of Constituent Ions in Ionic Liquids. 1. Anions. *J. Phys. Chem. B*, **2011**, (115), pp. 3872-3888.
- [33] Antoine, C., Tensions des Vapeurs: Nouvelle Relation entre les Tension et les Temperatures. *C. R. Acad. Sci.*, **1888**, (107), pp. 681-684, 778-780, 836-837.
- [34] Stull, D.R., Vapor Pressure of Pure Substances - Organic and Inorganic Compounds. *Ind. Eng. Chem.*, **1947**, (39), pp. 517-550.
- [35] *Practical Surface Analysis Volume 1 - Auger and X-ray Photoelectron Spectroscopy*. Briggs, D. and Seah, M.P., Eds., John Wiley & Sons, Chichester, (1990)
- [36] Metson, J.B., Charge compensation and binding energy referencing in XPS analysis. *Surf. Interface Anal.*, **1999**, (27), pp. 1069-1072.
- [37] Cazaux, J., Mechanisms of charging in electron spectroscopy. *J. Electron Spectrosc. Relat. Phenom.*, **1999**, (105), pp. 155-185.
- [38] Taylor, A.W., Qiu, F., Villar-Garcia, I.J. and Licence, P., Spectroelectrochemistry at ultrahigh vacuum: in situ monitoring of electrochemically generated species by X-ray photoelectron spectroscopy. *Chem. Commun.*, **2009**, 5817-5819.
- [39] Xu, W. and Angell, C.A., Solvent-free electrolytes with aqueous solution - Like conductivities. *Science*, **2003**, (302), pp. 422-425.
- [40] Armand, M., Endres, F., MacFarlane, D.R., Ohno, H. and Scrosati, B., Ionic-liquid materials for the electrochemical challenges of the future. *Nat. Mater.*, **2009**, (8), pp. 621-629.
- [41] Syres, K.L. and Jones, R.G., Adsorption, Desorption, and Reaction of 1-Octyl-3-methylimidazolium Tetrafluoroborate, [C₈C₁Im][BF₄], Ionic Liquid Multilayers on Cu(111). *Langmuir*, **2015**, (31), pp. 9799-9808.

Chapter 5

Stabilisation of carbon dioxide within the ionic liquid 1-octyl-3-methylimidazolium tetrafluoroborate

5.1. Introduction

In section 1.2.3 the notion of utilising ionic liquids (ILs) to capture small molecules, including carbon dioxide (CO₂), was introduced. It was discussed that many factors contribute to the solubility of small molecules within ILs, including the nature of the small molecule itself, the way the small molecule interacts with the ions and the way that the cation and anion interact with each other. It was concluded by many studies that the free volume within an IL was one of the most important factors for gas solubility [1-4]. Systems which had a weaker interaction between the IL cation and anion, resulting in a greater space between the ions, had greater free volumes for gaseous species to fit into [3]. The nature of the gas should not be neglected in solubility considerations, with the solubility of the gas molecule within an IL often being related to its polarisability [4]. This relationship did not hold for all molecules and it was hypothesised that this was due to the presence of dipole moments, quadrupole moments and opportunities to hydrogen bond [5]. The effects of these different factors, across ILs in general, have been studied in order to maximise the solubility of gases within ILs, where gas solubility is discussed in terms of Henry's constants. The convention used in this text, when referring to Henry's constants is

$$P_{gas} = H_{gas}x_{gas}$$

where P_{gas} is the pressure of the gas above the IL, H_{gas} is the Henry's constant and x_{gas} is the mole fraction of the gas within the IL, such that the Henry's constant is inversely proportional to the solubility (a smaller Henry's constant means a higher gas solubility). In this convention H_{gas} has the same pressure units as P_{gas} .

In this study we chose to look at the IL 1-octyl-3-methylimidazolium tetrafluoroborate ([C₈C₁Im][BF₄]) largely due to the fact that it is an IL that has been well studied within the research group in Nottingham [6-9], so seemed to be a natural starting point. It has been shown, with the use of X-ray photoelectron

spectroscopy (XPS), that $[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]$ has been able to be deposited onto a surface using a chemical vapour deposition method without damaging or decomposing the IL. The photoelectron spectra of the $[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]$ which had been evaporated onto the surface were the same as the photoelectron spectra collected from a droplet of the bulk IL, introduced via a load lock [6]. This is a key result as the surfaces that have been studied here were prepared by chemical vapour deposition (see section 3.2.3).

In addition to being well studied within our research group $[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]$ has both a long alkyl chain, on the cation, and a fluorinated anion, both of which have been seen to increase CO_2 solubility [10]. It is commonly regarded, both experimentally and theoretically, that having an IL with a more fluorinated anion allows more favourable interactions between the partial negative charge on the fluorine atoms and the partial positive charges on the carbon of the CO_2 molecules' quadrupole moment [5, 11], however recent studies on $[\text{C}_2\text{C}_1\text{Im}]$ containing ILs show that there are exceptions to this rule [12]. This topic shall be discussed in more detail in chapter 6. The literature also suggests that there are interactions between the aromatic ring [13] and the hydrogen in the C2 position on the imidazolium ring of the cation (the carbon between the two nitrogen atoms) and the CO_2 molecules, due to the possibility of hydrogen bonding of this most acidic proton with solutes [14]. It was concluded that this CO_2 interaction was less significant than those with the anion, as substituting the proton attached to the 2-carbon with a methyl group did not have a drastic effect on the solubility of CO_2 within the ILs (A 10% change in the Henry's constant for $[\text{C}_4\text{C}_1\text{Im}][\text{BF}_4]$ at 25°C was observed upon substituting the $\text{C}_2\text{-H}$ for a $\text{C}_2\text{-CH}_3$, compared to a 50% change upon swapping the $[\text{BF}_4]$ for a $[\text{Tf}_2\text{N}]$ anion [11]). The effect of alkyl chain length, or more specifically the free volume of the pores that occur due to motions of the alkyl chain, has also been discussed as a factor which enhances the solubility of CO_2 within ILs [1, 4, 10]. It is argued that having a larger free volume means that there is more space for the CO_2 molecules to slot into without disturbing the IL from its bulk structure too much, hence reducing energy penalties to absorption.

Looking specifically at studies including $[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]$ and CO_2 , results show that Henry's constants increase with temperature [10], meaning that the solubility of CO_2 within the ILs decreases with temperature. This agrees with

the fact that CO₂ adsorption within ILs is an exothermic process (ΔS will be negative as the gas is confined to a smaller volume upon adsorption, so to ensure $\Delta G = \Delta H - T\Delta S < 0$ for a spontaneous process the reaction must be exothermic). This suggests that there are reasonably strong CO₂–[C₈C₁Im][BF₄] interactions formed upon adsorption. A large quantity of the previous work on [C₈C₁Im][BF₄]–CO₂ systems has focussed on measuring and calculating solubility of CO₂ and the effects of tuning the IL to increase the CO₂ solubility. Henry's constants for CO₂ within [C₈C₁Im][BF₄] at 300 K have been found to range from 15 to 55 bar [10, 15, 16] in a mixture of experimental and computational studies. It should be realised that solubility and stability are not necessarily the same thing, meaning that just because a lot of CO₂ can be dissolved within an IL does not mean the IL will be an effective carbon capture agent. It is important to factor in how tightly the IL holds onto the CO₂ molecule, as having a high CO₂ solubility would be futile if the IL does not bind the CO₂ reasonably well, requiring the CO₂ pressure to be far greater than 1 bar to capture it effectively. A similar argument can be made for the converse point, that use of an IL with too high a CO₂ binding energy means extraction of the CO₂ from the IL would require extreme conditions, as is required for amine technologies (see section 1.1.2). This point reiterates the importance of having measurements of the activation energy for desorption (to find the heat of adsorption) for CO₂ from ILs. Only a few studies have looked at the binding energies, or the heats of adsorption, of CO₂ molecules within [C₈C₁Im][BF₄]. These studies have included theoretical calculations [4, 16] with others obtaining thermodynamic values from solubility experiments [10, 15], which will represent average interaction enthalpies under high pressure conditions. As solubility measurements only give averaged CO₂ binding energies they do not give any idea of the range of binding sites that are available within the IL, or how these sites correlate to the molecular structure of the IL. This work aims to provide vital information on the types of adsorption sites present within imidazolium based ILs, to assist the design and implementation of future IL-based CO₂ capture devices [17].

5.2. Temperature programmed desorption of [C₈C₁Im][BF₄]

The theoretical description and experimental setup for temperature programmed desorption (TPD) can be found in earlier chapters, see sections 2.4 and 3.3. As mentioned previously, desorption of bulk [C₈C₁Im][BF₄] has been performed within the research group [7]. This was achieved by use of a silver dipstick sample, which could be immersed in a vial of IL to obtain a thick (enough to be visible with the naked eye) IL layer, and then by performing TPD. The enthalpy of vaporisation for the IL was calculated from the activation energy of desorption and an estimated change in heat capacity of $-94 \text{ JK}^{-1}\text{mol}^{-1}$, which was applied to all ILs despite it being estimated for [C₄C₁Im][Tf₂N] [18]. Differences for the change in heat capacity for [C₈C₁Im][BF₄] will have the effect of changing the enthalpy of vaporisation, but not the activation energy of desorption. As the TPD was performed using a thick [C₈C₁Im][BF₄] layer, comprising of millions of layers of ion pairs, the thermodynamic values obtained were accurate with reasonably small errors ($E_{\text{des}} = 137 \pm 3 \text{ kJ mol}^{-1}$, $\Delta_{\text{vap}}H_{298} = 162 \pm 3 \text{ kJ mol}^{-1}$) [7]. As a result these literature values can be used as a reference value for the parameters that are obtained from TPD within this study. The experiments discussed here probe ultra-thin IL films, no more than 30 ion pairs thick, which may have different desorption properties to the bulk films discussed previously so may yield different activation energies of desorption.

Prior to experiments being performed with CO₂ and [C₈C₁Im][BF₄] mixtures, calibrations were performed for the IL with the mass spectrometer. The number of counts that corresponded to a monolayer (a single IL layer) was determined for each of the mass channels used to detect the [C₈C₁Im][BF₄]. The mass channels detected for this IL were $m/z = 195$ and 96 amu, which are due to the ions [C₈C₁Im]⁺ (molecular cation) and [C₁C₁Im]⁺ (fragmentation loss of a seven membered alkyl chain, C₇H₁₇), respectively [19]. Monolayer calibration was achieved through collection of TPD spectra (m/z intensity vs. temperature) as the initial IL coverage on the gold sample was varied. The shape of the collected TPD spectrum could then be analysed, allowing the transition between first order peak shape and zero order peak shape to be the indication that multilayers had formed. The peak area of the monolayer could then be used to calibrate any experimental TPD peak of the [C₈C₁Im][BF₄], detected from the

$m/z = 195$ amu channel, to find the initial IL coverage of the sample. Discussion of this calibration, showing the variation in TPD peak shape, can be found in more detail in appendix 8.3. All experiments on $[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]$ were completed within 4 months of the IL monolayer calibration, meaning that aging of the electron multiplier within the mass spectrometer detector, among other factors affecting detection efficiency, can be assumed to be negligible.

As previously mentioned the IL films studied here were no thicker than 30 layers of the ion pair, so TPD spectra of just the IL film were collected to ensure that the behaviour of these thin films was comparable to that of bulk films

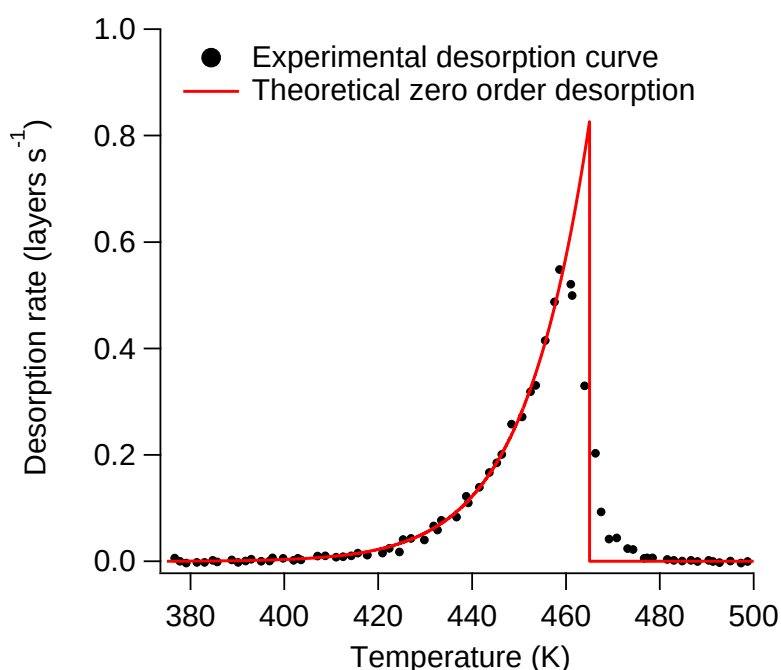


Figure 5.1: Experimental TPD data, detecting the cation parent ion ($m/z = 195$ amu), for a $[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]$ layer with an initial thickness of 21.6 ± 2.2 layers (black dots) with a zero order theoretical desorption peak for comparison (red line). The theoretical peak has been calculated using the parameters $E_{\text{des}} = 130 \text{ kJ mol}^{-1}$ and $A = 3.3 \times 10^{14} \text{ s}^{-1}$, found from leading edge analysis. Experimental data was collected with a heating rate of 0.5 K s^{-1} .

(such as those discussed in refs. [7, 20]), as well as ensuring that the IL itself did not produce TPD peaks which could be mistaken for CO_2 . Figure 5.1 shows the TPD spectrum for a surface consisting of 21.6 ± 2.2 layers. Leading edge analysis, described in section 2.4, can be used to determine the activation energy of desorption for an experimental data set, as shown in fig. 5.2. By comparison with eq 2.52, a plot of $\ln(\text{desorption rate})$ vs. reciprocal temperature was used to find the activation energy of desorption from the gradient of the line of best fit in fig. 5.2 and the pre-exponential factor from the y-axis intercept. For this 21.6 ± 2.2 layer $[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]$ surface E_{des} was found to be $130 \pm 2 \text{ kJ mol}^{-1}$, and A

was calculated to be $3 \times 10^{14 \pm 1} \text{ s}^{-1}$. The experimentally determined E_{des} is close to the literature value of $137 \pm 3 \text{ kJ mol}^{-1}$ [7], suggesting a thin IL layer behaves in a similar fashion to a bulk layer, which has been seen for other ILs [21]. The mismatch between the literature and experimental value for E_{des} is caused by having a much smaller dataset over which to perform leading edge analysis in this experiment, due to the much smaller quantity of IL on the surface.

The plot in fig. 5.1 also contains a theoretical zero order desorption profile, calculated using the Polanyi–Wigner equation [22] (eq 2.51, see section 2.4 for definition of terms). The parameters used in this theoretical curve are based on those determined from the fit in fig. 5.2, with $n = 0$, $E_{\text{des}} = 130 \text{ kJ mol}^{-1}$,

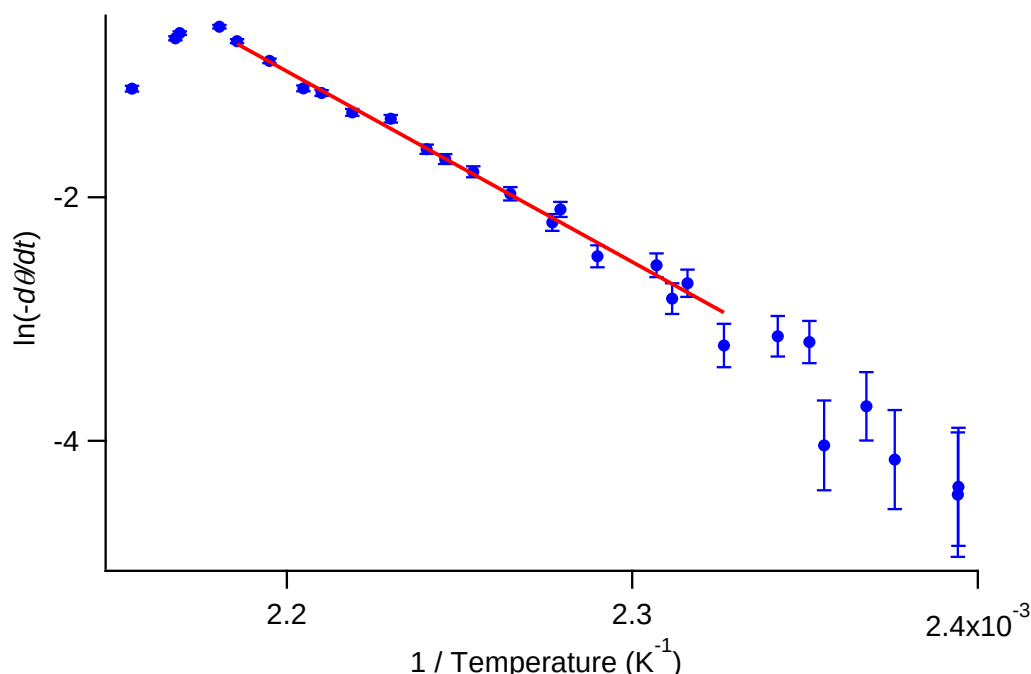


Figure 5.2: A plot showing the graph of $\ln(\text{desorption rate})$ vs. reciprocal temperature used in leading edge analysis for the 21.6 ± 2.2 layer $[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]$ sample. Blue markers represent experimental data with the red line showing a linear fit giving $E_{\text{des}} = 130 \pm 2 \text{ kJ mol}^{-1}$. The error bars come from the error in the experimental data points, which is a constant value, but due to the logarithmic scale the noise can be seen to have a smaller effect on the data points with a larger signal. Fitting was performed in the temperature range 430 to 458 K.

pre-exponential factor, $A = 3.3 \times 10^{14} \text{ s}^{-1}$ and heating rate of 0.5 K s^{-1} . The agreement between the theory and experiment is generally good, especially for lower temperatures before the IL layer depletes. Once the IL film gets to the final layer or two the experimental and theoretical curves begin to differ. This is due to factors such as possible surface patchiness [7] and interactions between the IL and the substrate stabilising the final layer of IL, with respect to the bulk, hence altering the desorption properties from zero order to first order.

Desorption of the IL was primarily monitored through analysis of the 195 amu mass fragment, as this is due to the molecular ion peak, with the 96 amu fragment being used to double-check that the IL was behaving as expected, since both fragments originate from the imidazolium cation.

The zero-order desorption of the IL was reproduced by the 96 amu fragment at the same temperature (≈ 450 K), as can be seen in appendix 8.4. An unexpected peak was also observed at lower temperatures (desorption occurs from 300 K), believed to be due to a decomposition product within the IL evaporator vial. Formation of contaminants has been observed previously through heating under vacuum, including HF, from hydrolysis of fluorinated anions by trace water [23], 1-alkyl-3-methylimidazolium-2-trifluoroborates, through reaction of the tetrafluoroborate anion with the C2 position on the imidazolium ring [24], and other unidentified products [25]. Presence of these is the reason for the use of a liquid nitrogen cooled collimator in the chamber setup (see section 3.2.3). Figure 5.3 shows the ratio of the contaminant peak area to the $[\text{C}_1\text{C}_1\text{Im}]^+$ peak area (ratio = peak area desorbing at 300 K $\div$ peak area desorbing at 450 K) as a function of IL evaporator uses. It can be seen that there are increases in the amount of contaminant present with number of uses (which has an approximate relation to time spent at an elevated temperature under vacuum). The increase in ratio is much steeper when the IL is running out, shown by the red line, with a clear decrease in ratio of contaminant to IL area when more IL was added to the vial (shown by the steep drop at index = 0). After replenishing the IL the ratio of contaminant to IL increases slowly with number of uses of the IL evaporator, which could be due to a larger reduction of IL with time than contaminant, resulting in a net contaminant concentration increase. Unfortunately the identity of the contaminant is unknown. The mass to charge ratio $m/z = 20$ amu (HF) was tracked during the experiment but no peak was seen, suggesting the contaminant had a different identity, possibly as that described in ref. [24] (1-octyl-3-methylimidazolium-2-trifluoroborate). It is not likely that the contaminant is 1-octyl-3-methylimidazolium-2-trifluoroborate, as this is seen to desorb at higher temperatures than the corresponding 1-alkyl-3-methylimidazolium tetrafluoroborate IL (otherwise distillation of the IL would not be possible), whereas here the contaminant is seen to desorb before the IL in the experimental TPD data. It would only be possible for the contaminant to be

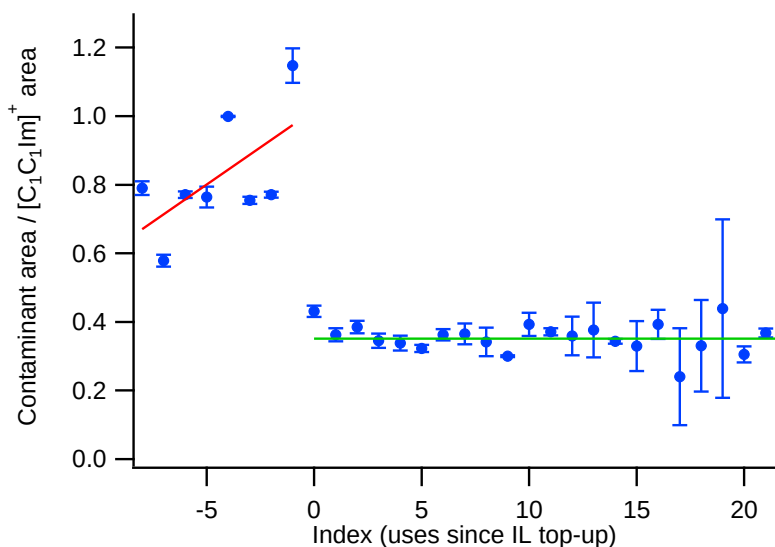


Figure 5.3: This plot shows how the ratio of the peak areas of the contaminant with $m/z = 96$ amu to the $[C_1C_1Im]^+$ cation (tracked by 96 amu) changes with number of uses of the IL evaporator (blue dots). The red and green lines are to guide the eye for the sections before and after the IL had been replenished in the evaporator respectively. Index = 0 represents the first experiment after topping up the IL vial.

1-octyl-3-methylimidazolium-2-trifluoroborate if it were heavily destabilised within the $[C_8C_1Im][BF_4]$, however this is thought to be unlikely due to the similarity of the molecules and the number of possible interactions. Experimental data used within this study correspond to indices 1–22, which have an approximately constant ratio of contaminant, so if CO_2 is stabilised by the contaminant we would expect it to stabilise the same proportion of CO_2 in each experiment, meaning any variations in CO_2 capture must be due to the IL. The presence of a contaminant is surprising given that XPS after chemical vapour deposition did not show any sign of a contaminant [6], though this could be due to the contaminant having a low surface concentration or having the same photoelectron binding energies as the IL. Furthermore there were no changes in the $m/z = 44$ amu TPD profile, which was to be used for monitoring CO_2 desorption, when a surface containing only IL was studied.

5.3. Temperature programmed desorption of CO_2 containing systems

As referred to in the experimental section (3.4.3) experiments were performed on a variety of CO_2 containing systems. The bulk of this work looked at IL and CO_2 coadsorption, that is exposing the gold substrate to the $[C_8C_1Im][BF_4]$ and the CO_2 simultaneously, but various layered systems were

also studied. The proceeding sections present and discuss at the results obtained from these various systems.

5.3.1. Desorption of CO₂ from a gold substrate

The gold substrate used in these studies was a Au(111) crystal, however neither the IL–Au(111) or CO₂–Au(111) interaction were the focus of these studies. Consequently the gold surface was not cleaned to regenerate the Au(111) crystal structure, through anneal and argon ion bombardment cycles. The gold–CO₂ and CO₂–CO₂ interaction (multilayer formation) have been discussed elsewhere, finding that physisorption of CO₂ on polycrystalline gold surfaces occurs at 77 K [26] with CO₂ multilayers also forming at 77 K [27]. In the work discussed here the gold surface was prepared only by annealing to 583 K, to ensure all the remnants of the previous surface had desorbed, a procedure similar to that discussed in ref. [26]. Figure 5.1 shows that 583 K is a suitable annealing temperature as the IL layer has finished desorbing by about 480 K, so any cracked or damaged fragments on the surface that are going to be able to desorb (i.e. are not chemisorbed to the surface) will have done so by 583 K.

The preliminary experiments included adsorption of solely CO₂ on the prepared gold crystal to see if there was a significant quantity of CO₂ physisorption on an 88 K surface, with results shown in fig. 5.4. The experimental data has had both a background subtraction and pressure subtraction applied to it, as discussed in detail within ref. [28], but summarised here. Figure 5.4a shows the data after background subtraction only, removing the base $m/z = 44$ amu signal, which originates from background gases in the vacuum system. The background is successfully modelled by a linear fit, however due to experimental noise the subtraction is responsible for making some of the data points negative. The pressure subtraction allows the removal of peaks from the TPD spectrum which are due to reflections of gas molecules from the analysis area into the detector. This subtraction is very important for the experimental setup discussed here since the sample manipulator has various components made from different materials, which all achieve different minimum temperatures (due to the manipulator design). The pressure

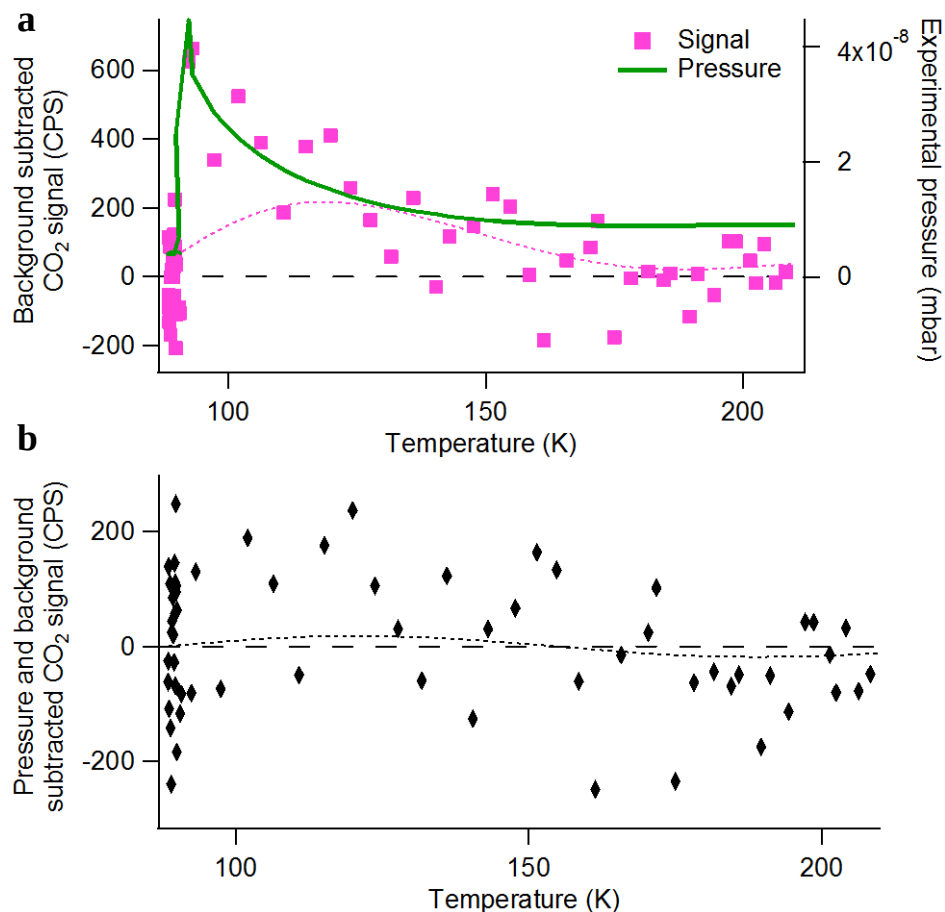


Figure 5.4: Experimental TPD data (heating rate of 0.67 K s^{-1}) for a surface prepared from a 10 minute dose of CO₂ at a pressure of $5 \times 10^{-7} \text{ mbar}$ on a gold surface at 88 K with (a) a background subtraction applied and (b) background and pressure subtractions applied. Markers show experimental data points, dashed lines show the 'zero line' and dotted lines are to smoothing splines to guide the eye. Peak area before pressure subtraction is 19000 ± 6000 counts and 2000 ± 4000 counts after pressure subtraction.

subtraction allows the removal of spurious signals which are due to CO₂ desorbing from those other areas (such as the liquid nitrogen reservoir or the filaments used to heat the sample), reflecting off the analysis region of the surface and contributing to the experimental signal. Practically this involves subtracting the pressure signal, multiplied by a constant (constant $\approx 2.0 \times 10^{10} \text{ CPS mbar}^{-1}$), from the experimental signal. The constant used varies slightly (by $\approx 0.2 \times 10^{10} \text{ CPS mbar}^{-1}$) between data sets as an $m/z = 44$ amu peak at higher temperatures, due to CO₂ desorbing off of colder parts of the manipulator, is used to find the constant. Figure 5.4b shows the effect of performing a pressure subtraction on the experimental data.

Looking at the experimental data itself the importance of applying a pressure subtraction can be seen in fig. 5.4a. After application of only a background subtraction the data gives a peak area for $m/z = 44$ amu of $19000 \pm$

6000 counts, suggesting that CO₂ is stabilised on the gold surface. This result was unexpected since the literature [26] shows adsorption of CO₂ at 77 K, which is a lower temperature than could be achieved with the experimental setup and CO₂ pressures discussed here. The experimental chamber pressure is shown as a solid green line in fig. 5.4a and behaves as expected for the initial stages of a TPD experiment. The pressure initially jumps from its base pressure as the TPD experiment begins and the filaments turn on, desorbing any material adsorbed on them (mainly CO₂ which was leaked into the chamber). Since the heater is operated in constant power mode the filaments remain on and the surrounding parts of the manipulator also heat up (gold sample included), promoting desorption of CO₂. As all the CO₂ desorbs from the surroundings and is pumped away the chamber pressure decays towards the base pressure. The chamber pressure is dominated by desorption of species which do not originate from the sample surface, so the approximation is made that the pressure subtraction does not remove signal which is due to species in the analysis region of the sample. Once the pressure subtraction has been performed, fig. 5.4b, the peak area for the $m/z = 44$ amu signal is given to be 2000 ± 4000 counts, indicating that no CO₂ is stabilised on the bare gold substrate, as originally expected. This demonstrates a standard method for removal of reflected signals from the TPD data, allowing detection of species that are adsorbed to the surface. These subtraction methods can be applied to the IL–CO₂ studies to ensure that only TPD peaks due to CO₂ interacting with the IL remain in the spectra.

The fact that CO₂ could not be stabilised on the gold substrate meant that a maximum activation energy of desorption could be estimated for the CO₂ on a gold substrate. As discussed in the experimental section (3.2.1) experiments incorporated a 20 minute wait between the end of surface preparation and the beginning of the TPD. During this time any CO₂ that may have been adsorbed must have desorbed from the surface, as no CO₂ TPD peak is observed, so the maximum residence time for the CO₂ on the gold is 1200 s. The lowest temperature, from all the CO₂ experiments, achieved by the gold sample was 88 K. Upon using the equation for surface residence time, eq 2.55 (see section 2.5 for definition of terms) with a typical value of $\tau_0 = 10^{-13}$ s, the maximum activation energy for desorption for CO₂ on gold can be found to be $\approx 27 \text{ kJ mol}^{-1}$. This value can be used as a reference for discussions involving the

$E_{\text{des, CO}_2}$ within ILs. Literature values for the enthalpy of sublimation for pure CO_2 at 100 K give the value for $\Delta_{\text{sub}}H_{100} = 26.8 \text{ kJ mol}^{-1}$ (this value is within error of both studies) [29, 30], which is comparable to the E_{des} found from the stay time calculation.

The inability to form a monolayer or multilayers of CO_2 on the gold substrate means that a monolayer calibration, like the one discussed for the IL in section 5.2, could not be performed. In order to perform a quantitative analysis of the CO_2 signal a calibration had to be completed. Since the experimental signal will vary depending on the experimental setup (emission current, multiplier voltage and chamber geometries) the calibration is only valid for the setup discussed here. The calibration involved monitoring the $m/z = 44$ amu signal as a function of CO_2 pressure, with details presented in appendix 8.5. The calibration allows the experimentally determined signal (in CPS) to be converted to a pressure of CO_2 . It is shown that for the experimental setup discussed here

$$P_{\text{CO}_2} = (3.45 \pm 0.04) \times 10^{-11} \times \Delta(S_{44}) \quad \text{Equation 5.1}$$

where, P_{CO_2} is the pressure of CO_2 (mbar), $\Delta(S_{44})$ is the change in mass spectrometer signal, from the baseline, for $m/z = 44.0$ amu channel (CPS) and the constant has units of mbar CPS^{-1} . This means that peak areas for desorption profiles, experimentally given in counts, can be converted to CO_2 coverages, expressed in mbar s . This will give a quantity of CO_2 which has been captured by the IL which is analogous to an exposure, but for the captured CO_2 .

5.3.2. Desorption of CO_2 from within $[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]$

Section 3.4.3 details the coadsorption experiments performed on the gold substrate, for which the cooled gold surface was exposed to CO_2 and $[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]$ simultaneously. Experimental data has been corrected to account for the flux of CO_2 reflected off of the sample into the mass spectrometer with pressure and background subtractions [28], as described in section 5.3.1. Figure 5.5 shows data for coadsorptions using a constant CO_2 pressure of 1×10^{-6} mbar but varying dose lengths, so therefore varying quantities of $[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]$. It can be observed that CO_2 desorption profiles, despite being reasonably noisy, are detected in the range 90 to 160 K. As fig. 5.4b shows that without the IL no CO_2 desorption peak is observed, the presence of the IL $[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]$ allows

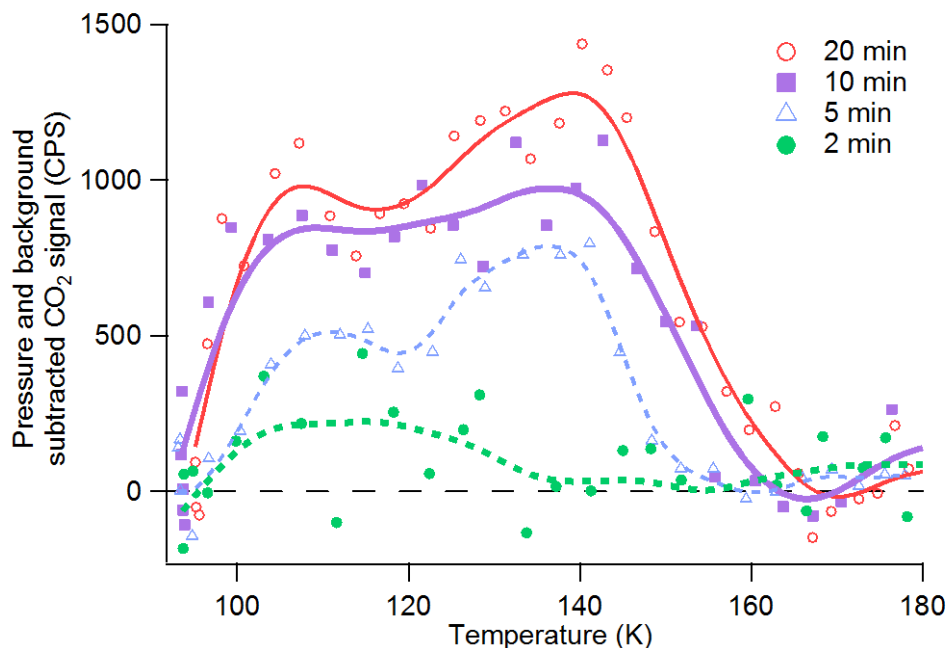


Figure 5.5: Experimental data for $[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]$ and CO_2 coadsorptions on gold at ≈ 90 K using a constant CO_2 pressure of 1×10^{-6} mbar. Open red circles represent the 20 minute coadsorption, purple squares the 10 minute coadsorption, open blue triangles the 5 minute coadsorption and green circles the 2 minute coadsorption. Coloured lines are smoothing splines through the experimental data to guide the eye through the shapes of the TPD profiles. The black dashed line shows the ‘zero line’ with points lying below it due to the background subtraction. The heating rate for TPD was approximately 0.67 K s^{-1} .

stabilisation of the carbon dioxide by 70 K. Furthermore it can be seen that the longer coadsorption times, meaning larger quantities of IL, have larger CO_2 desorption peaks. This suggests that the CO_2 is stabilised within the ‘bulk’ IL rather than only at the gold–IL or IL–vacuum interfaces, which would have resulted in the same quantity of CO_2 captured irrespective of dose length.

The peak areas for the experimental data shown in fig. 5.5 have been converted to CO_2 coverages, using eq 5.1 and are shown in table 5.1, along with the other CO_2 and $[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]$ coadsorption results. Data is expressed in ‘ $\times 10^{-6}$ mbar s’ or ‘metric langmuirs’ as an approximation to the langmuir unit, which is 1×10^{-6} Torr s, and is often taken to be roughly equal to a monolayer of material [22]. As mentioned previously all data has had pressure and background subtractions applied to them before integration of the TPD signal to obtain a result representing the quantity of CO_2 stabilised within the $[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]$, negating the effects of reflected CO_2 peaks. The relationship, observed in fig. 5.5, between the increased quantity of CO_2 stabilised for greater amounts of IL on the surface, for a given dose pressure of CO_2 , can be seen to hold for most of the experimental data in table 5.1. Exceptions occur for the shorter coadsorption

times due to smaller quantities of CO₂ being stabilised, making the results more susceptible to the effects of random fluctuations in the m/z = 44 amu baseline, detected by the mass spectrometer (which is the main contribution to the noise in the detected signal). Plots of the experimental data for the [C₈C₁Im][BF₄]-CO₂ coadsorptions at other pressures can be found in appendix 8.6.

The data within table 5.1 also shows that, when looking at fixed quantities of [C₈C₁Im][BF₄], e.g. the ‘20 minute’ column, the higher the pressure

Table 5.1: A table of all the collected experimental data for [C₈C₁Im][BF₄] coadsorptions, with errors. White rows show the IL coverage from time integrated TPD peaks divided by the IL monolayer coverage, light grey rows show experimentally measured CO₂ peak areas after pressure and background subtractions have been applied and dark grey rows show the peak areas converted to CO₂ coverages within the IL.

CO ₂ Dose Pressure	Coadsorption Dose Length	20 minutes	10 minutes	5 minutes	2 minutes
2×10 ⁻⁸ mbar	Initial IL coverage, θ_{IL}	—	10.8 ± 1.1	—	—
	CO ₂ peak area (counts)	—	7500 ± 2000	—	—
	CO ₂ coverage (10 ⁻⁶ mbar s)	—	0.26 ± 0.07	—	—
5×10 ⁻⁸ mbar	Initial IL coverage, θ_{IL}	22.2 ± 2.2	12.0 ± 1.2	4.7 ± 0.5	2.2 ± 0.2
	CO ₂ peak area (counts)	22000 ± 2500	20000 ± 5000	9100 ± 1500	6900 ± 1200
	CO ₂ coverage (10 ⁻⁶ mbar s)	0.76 ± 0.22	0.70 ± 0.17	0.31 ± 0.05	0.24 ± 0.04
1×10 ⁻⁷ mbar	Initial IL coverage, θ_{IL}	25.4 ± 2.5	12.8 ± 1.3	5.9 ± 0.6	3.0 ± 0.3
	CO ₂ peak area (counts)	28000 ± 2500	30000 ± 1000	12000 ± 2000	12000 ± 5000
	CO ₂ coverage (10 ⁻⁶ mbar s)	0.97 ± 0.25	1.05 ± 0.13	0.42 ± 0.07	0.42 ± 0.17
2×10 ⁻⁷ mbar	Initial IL coverage, θ_{IL}	27.4 ± 2.7	—	—	—
	CO ₂ peak area (counts)	42000 ± 3000	—	—	—
	CO ₂ coverage (10 ⁻⁶ mbar s)	1.46 ± 0.10	—	—	—
5×10 ⁻⁷ mbar	Initial IL coverage, θ_{IL}	19.5 ± 2.0	11.3 ± 1.1	5.0 ± 0.5	2.1 ± 0.2
	CO ₂ peak area (counts)	45000 ± 1500	31000 ± 2500	21000 ± 2500	10000 ± 2000
	CO ₂ coverage (10 ⁻⁶ mbar s)	1.57 ± 0.20	1.08 ± 0.11	0.73 ± 0.09	0.35 ± 0.07
1×10 ⁻⁶ mbar	Initial IL coverage, θ_{IL}	23.1 ± 2.3	11.7 ± 1.2	5.4 ± 0.5	2.1 ± 0.2
	CO ₂ peak area (counts)	72000 ± 1500	50000 ± 4000	25000 ± 1000	6400 ± 3000
	CO ₂ coverage (10 ⁻⁶ mbar s)	2.49 ± 0.23	1.71 ± 0.14	0.87 ± 0.03	0.22 ± 0.10
2×10 ⁻⁶ mbar	Initial IL coverage, θ_{IL}	21.7 ± 2.2	—	—	—
	CO ₂ peak area (counts)	86000 ± 2000	—	—	—
	CO ₂ coverage (10 ⁻⁶ mbar s)	2.97 ± 0.07	—	—	—

of CO₂ used during the coadsorption the greater the quantity of CO₂ captured. This is not an entirely surprising result as it is well known that the surface coverage of a gas on the surface is related to the pressure of the gas itself, as can be described by an adsorption isotherm. Increasing the surface coverage of CO₂ will increase the number of CO₂–IL interactions and would be expected to increase the amount of CO₂ stabilised within the IL. The experimental data is represented graphically for the variation in amount of CO₂ stabilised within a [C₈C₁Im][BF₄] layer, with applied CO₂ pressure, in appendix 8.6. Due to the use of vacuum apparatus in the discussed experimental setup there was an upper limit on the pressure of CO₂ that could be used during experiments. From section 1.1.2 the partial pressure of CO₂ in the atmosphere was approximated to be 0.4 mbar [31], which would have been too high a pressure to study within the setup used. Issues were present for the CO₂ pressure of 2×10^{-6} mbar, which caused a large quantity of background reflection from the sample, making analysis of that particular dataset difficult. Complications arose as the reflection peak, due to multilayers of CO₂ forming on colder parts of the sample manipulator and desorbing as it heated up, occurred at a temperature which overlapped with the TPD peak of CO₂ from the [C₈C₁Im][BF₄]. This made specifying a background region difficult and was the reason only one coadsorption experiment was performed using 2×10^{-6} mbar of CO₂.

It can be seen from table 5.1 that each surface studied had a slightly different IL coverage, θ_{IL} (units of IL layers), seen in the white rows of the table, even though the coadsorption times were the same. Since it has been seen that the quantity of IL affects the amount of CO₂, A_{CO_2} , captured by the surface (fig. 5.5), strictly the peak areas in table 5.1 cannot be compared directly to one another. To compensate for the effect of the variable IL coverage on the total quantity of CO₂ stabilised, the average amount of CO₂ stabilised per IL layer can be calculated. The data for the average CO₂ quantity per layer of [C₈C₁Im][BF₄] (10^{-6} mbar s layer⁻¹) is shown as a series of constant coverage curves in fig. 5.6, where the lines are solely to guide the eye and do not represent fits to an isotherm model. There are only 3 data points plotted for the 2 minute coadsorption data due to the erroneous 2 min., 1×10^{-6} mbar data point (obtained peak area for CO₂ captured was far too low), which has been discounted from

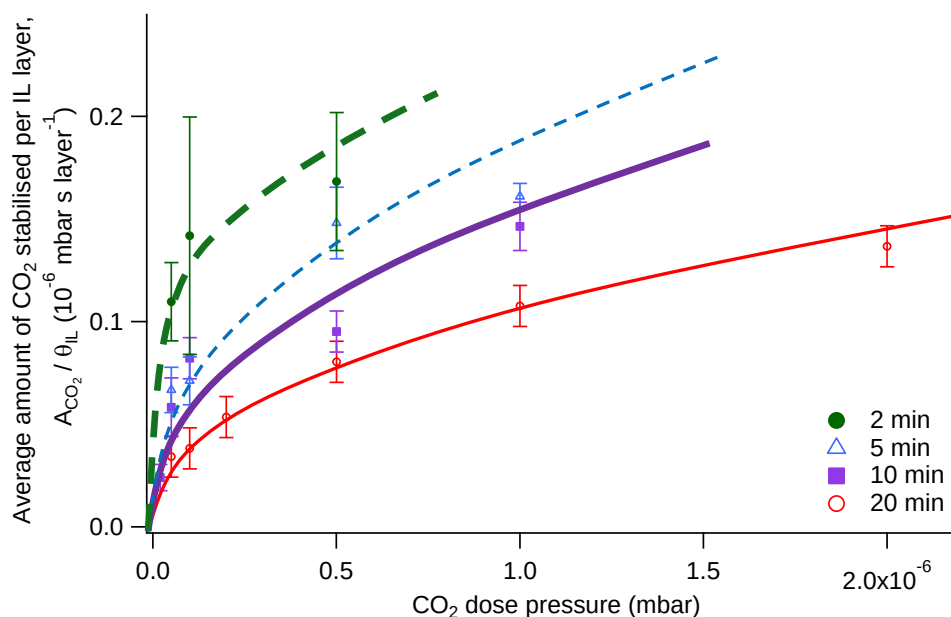


Figure 5.6: These constant coverage curves show the variation in the amount of CO₂ stabilised per layer of [C₈C₁Im][BF₄] as the dosing pressure of CO₂ is varied. It can be seen that the pressure of CO₂ used during dosing affects the quantity of CO₂ stabilised within the IL, with CO₂ capture more efficient for shorter coadsorption times. Lines are used solely to guide the eye for the 2 min (thick dashed), 5 min (thin dashed), 10 min (thick solid) and 20 min (thin solid) data sets.

the plot. Figure 5.6 shows that as the pressure of CO₂ used during coadsorption is increased, the quantity of CO₂ stabilised per IL layer also increases. It is already widely accepted that increasing the pressure of CO₂ above the IL will increase the concentration of CO₂ within the IL (so will increase the amount of CO₂ per IL layer), as this is simply Henry's law. The surprising result is that there is a variation in the average amount of CO₂ stabilised per IL layer for different coadsorption timescales. This suggests that the CO₂ capture efficiency is not constant throughout the experiment, moreover the results in fig. 5.6 show that CO₂ capture is most efficient for shorter coadsorption timescales. Since the CO₂ adsorption properties should not be time dependent, they must instead be dependent upon the thickness of the IL layer that is on the surface. The results indicate that there is a larger amount of CO₂ per layer of [C₈C₁Im][BF₄] for the thinner IL layers (shorter coadsorption times) than in the thicker layers. This is a result which is also observed in the [C₈C₁Im][Tf₂N]–CO₂ coadsorptions, and will be discussed in more detail in the next chapter, see section 6.3.2.

It can be seen that the quantity of CO₂ stabilised within the IL depends on both the quantity of IL dosed and the pressure of CO₂ used during dosing. Considering the results in table 5.1, a correction can be applied to allow

comparison of experimental datasets which have the same CO₂ exposure as each other during sample preparation (exposure = dose pressure × dose time). Since the actual IL and CO₂ coverages were roughly grouped corresponding to their coadsorption timescales, corrections have been applied to the data such that the 20 minute datasets have been corrected to 20 IL layers, 10 minute data has been corrected to 10 IL layers and so on (which assumes an IL deposition rate of 1 IL layer per minute). This correction is achieved through dividing the CO₂ peak area by the experimental IL coverage, to get the amount of CO₂ stabilised per IL layer, then multiplying this by the ‘desired IL coverage’ (a 20 minute coadsorption has a desired IL coverage of 20 layers). The corrected data are shown in table 5.2, which can now have coverages for equivalent CO₂ exposures compared directly. Comparison of CO₂ peak areas for the 5×10^{-7} mbar, 20 minute coadsorption data ($(1.61 \pm 0.20) \times 10^{-6}$ mbar s) and the 1×10^{-6} mbar, 10 minute coadsorption data ($(1.46 \pm 0.12) \times 10^{-6}$ mbar s) shows that there is a

Table 5.2: A table showing the amount of CO₂, A_{CO_2} , stabilised during [C₈C₁Im][BF₄] coadsorptions, with errors, after IL coverage correction has been applied (see text for details). Light grey rows show CO₂ peak areas in experimental units, after pressure and background subtractions have been applied and dark grey rows show the peak areas converted to CO₂ coverage within the IL. Since these data are corrected for IL coverage, experiments with the same exposures of CO₂ can be directly compared.

CO ₂ Dose Pressure	Coadsorption Dose Length	20 minutes	10 minutes	5 minutes	2 minutes
2×10^{-8} mbar	CO ₂ peak area (counts)	-	7000 ± 1900	-	-
	CO ₂ coverage (10^{-6} mbar s)	-	0.24 ± 0.06	-	-
5×10^{-8} mbar	CO ₂ peak area (counts)	19900 ± 2300	16900 ± 4200	9700 ± 1600	6400 ± 1100
	CO ₂ coverage (10^{-6} mbar s)	0.69 ± 0.20	0.58 ± 0.14	0.33 ± 0.05	0.22 ± 0.04
1×10^{-7} mbar	CO ₂ peak area (counts)	22200 ± 2000	23800 ± 800	10300 ± 1700	8200 ± 3400
	CO ₂ coverage (10^{-6} mbar s)	0.76 ± 0.20	0.82 ± 0.10	0.36 ± 0.06	0.28 ± 0.12
2×10^{-7} mbar	CO ₂ peak area (counts)	31000 ± 2200	-	-	-
	CO ₂ coverage (10^{-6} mbar s)	1.07 ± 0.20	-	-	-
5×10^{-7} mbar	CO ₂ peak area (counts)	46600 ± 1500	27600 ± 2200	21400 ± 2500	9800 ± 2000
	CO ₂ coverage (10^{-6} mbar s)	1.61 ± 0.20	0.95 ± 0.10	0.74 ± 0.09	0.34 ± 0.07
1×10^{-6} mbar	CO ₂ peak area (counts)	62400 ± 1300	42400 ± 3400	23300 ± 900	6200 ± 2900
	CO ₂ coverage (10^{-6} mbar s)	2.15 ± 0.20	1.46 ± 0.12	0.80 ± 0.03	0.21 ± 0.10
2×10^{-6} mbar	CO ₂ peak area (counts)	79200 ± 1800	-	-	-
	CO ₂ coverage (10^{-6} mbar s)	2.73 ± 0.20	-	-	-

greater amount of CO₂ stabilised within the 20 minute dose, despite the use of a lower dose pressure. This is reflected in the rest of the data in table 5.2, where the exposures are the same (5×10^{-8} mbar, 20 min. coad.; 5×10^{-7} mbar, 2 min. coad. and 5×10^{-8} mbar, 10 min. coad.; 1×10^{-7} mbar, 5 min. coad. to name a few). These comparisons for experiments with the same exposures are shown and discussed in appendix 8.10. Of the eight comparisons that can be made, where exposures are the same for the [C₈C₁Im][BF₄]-CO₂ system, in six of the cases the surface with more layers of IL has stabilised the greater quantity of CO₂. This indicates that not all CO₂ sites are equal, with some sites requiring larger dose pressures to access. One can speculate that these sites may involve small clusters of CO₂ near the IL molecule, although further experimentation and computational modelling may be able to clarify the situation further. This result also indicates that having a larger quantity of IL, and lower CO₂ pressure, will stabilise more CO₂ than having a higher pressure of CO₂, but smaller quantity of IL, which is consistent with the idea that an IL layer of given thickness will eventually saturate.

5.3.3. CO₂ adsorption within layered [C₈C₁Im][BF₄] systems

Since the experiments discussed have been performed under high vacuum conditions, a cooled (≈ 90 K) sample has had to be used in order to maximise the residence time of CO₂ on the sample surface, enhancing the probability of the CO₂ being captured by the IL. As the experiments performed were coadsorptions, where the [C₈C₁Im][BF₄] and CO₂ were dosed onto the substrate simultaneously, the IL was also dosed onto a cooled surface. Since the surface temperature was below the glass transition temperature for [C₈C₁Im][BF₄] ($T_g = 189.7$ K [32]), it was postulated that this would result in a porous IL network being formed. The conceptual analogy of water precipitation can be used for the ion pairs, which arrive individually and are expected to stick where they land, like snow, rather than forming a densely packed IL glass, like an ice sheet. Section 3.4.3 describes the layered systems studied here, providing more description of the solidified IL morphologies.

Experiments were performed in which layers of [C₈C₁Im][BF₄] were prepared as the IL ‘snow’ and IL glass, before being exposed to CO₂ at a pressure

of 5×10^{-7} mbar for 10 minutes. As discussed the IL ‘snow’ is formed by dosing the IL onto a surface with a temperature of ≈ 90 K (which is below that of the ILs glass transition temperature), whereas an IL glass is formed by dosing the IL onto a room temperature surface as a liquid (since $T_{\text{surf}} \geq T_{\text{g, IL}}$), then cooling the sample below $T_{\text{g, IL}}$ to ≈ 90 K. Such experiments allow the nature of the CO_2 –IL interaction to be probed further. The pressure and background subtracted results of these experiments are shown as the open green triangles (CO_2 on IL

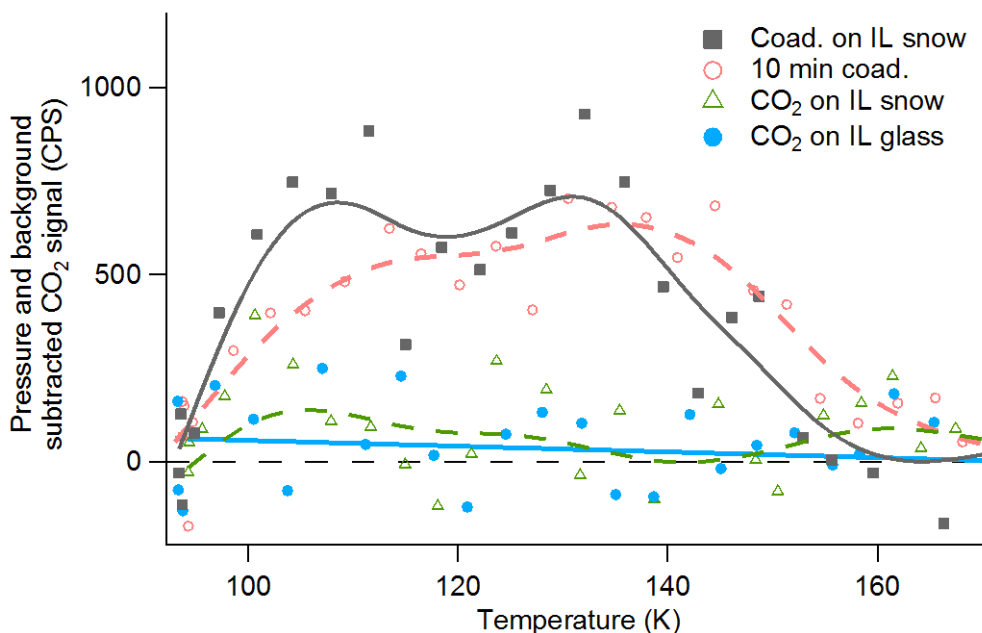


Figure 5.7: A comparison between layered and coadsorbed (coad.) $[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]$ – CO_2 surfaces after a pressure and background subtraction has been applied. In all cases CO_2 was dosed for 10 minutes at a pressure of 5×10^{-7} mbar, with data shown for CO_2 on 10 minutes of IL glass (filled blue circles), on 10 minutes of IL ‘snow’ (green triangles), coadsorbed (10 min.) on top of a 5 minute IL ‘snow’ (solid grey squares) and coadsorbed (10 min.) on gold (pink circles). Lines are smoothing splines used to guide the eye through the noise in the data. The dashed black line represents the ‘zero line’. The heating rate during TPD was 0.67 K s^{-1} .

‘snow’) and filled blue circles (CO_2 on IL glass) in figure 5.7. It can be seen that there does not appear to be any stabilisation of CO_2 on the IL glass, as the data is scattered about the ‘zero line’ which is also confirmed by the peak area (3000 ± 2000 counts). There does, however, appear to be a small quantity of CO_2 being stabilised in the ≈ 90 to 120 K temperature range for the CO_2 dosed onto the $[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]$ ‘snow’, although it is only just discernible (peak area of 7000 ± 3000 counts). The idea that CO_2 is stabilised within the IL ‘snow’ is supported by a comparison of the 10 minute coadsorption with $P_{\text{CO}_2} = 5 \times 10^{-7}$ mbar (pink open circles) and the 10 minute coadsorption ($P_{\text{CO}_2} = 5 \times 10^{-7}$ mbar) on top of 5 minutes of $[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]$ ‘snow’ (filled grey squares). It is not surprising that

these plots are similar as they both involve a 10 minute coadsorption with the same CO₂ pressure, however a difference is observed in the ≈ 90 to 120 K region. The data for the coadsorption on top of the IL ‘snow’ appears to show that more CO₂ is stabilised within the IL for the ≈ 90 to 120 K temperature range. It is possible that this discrepancy could be due to experimental errors, such as fluctuations in the 44 amu baseline, although this is the temperature region in which CO₂ was observed to be stabilised within the IL ‘snow’ layer. It is possible that some CO₂ is stabilised within the 5 minute (≈ 5 IL layers) IL ‘snow’ in addition to the CO₂ stabilised within the 10 minute coadsorption on top of this ‘snow’ layer, leading to an enhanced CO₂ signal observed in this temperature range, relative to the 10 minute coadsorption only data. This further supports the claim that the CO₂ peak seen for the desorption experiment from the IL ‘snow’ is real, despite the data being quite noisy.

This result suggests that the CO₂ can become stabilised through interactions which occur with the surface of the [C₈C₁Im][BF₄] ‘snow’, but is not stabilised by the surface of the IL glass. Since the IL ‘snow’ is believed to hit the cold surface and stick instantly where it lands, in the orientation it arrives in, it is expected that the surface of the [C₈C₁Im][BF₄] ‘snow’ will have regions which are non-polar (aliphatic chain of the cation) and some which are more ionic (imidazolium head group and anion). The surface structure for the [C₈C₁Im][BF₄] glass is expected to consist of aliphatic chains, as the structure of the surface should be the same as that of the IL liquid film before it was frozen [9]. (There is an ongoing debate in the literature, see review [33], over the exact surface structure of imidazolium based ILs, however current opinion favours the idea that the aliphatic chains protrude from the bulk film and into the vacuum [34]). TPD experiments have been performed at temperatures from 50 K showing that the activation energy for desorption of CO₂ on octadecanethiol self-assembled monolayers, which also have a surface layer of alkane chains, is $17.2 \pm 2 \text{ kJ mol}^{-1}$ [35]. This suggests that CO₂ would not stick to an aliphatic surface at the temperatures used in this study ($T_{\text{surf}} \approx 90 \text{ K}$, which gives $E_{\text{des}} \approx 27 \text{ kJ mol}^{-1}$), and supports the idea that the IL glass surface is made of aliphatic chains, whereas the surface of the [C₈C₁Im][BF₄] ‘snow’ is not made purely of aliphatic chains. For the data represented by green triangles in fig. 5.7 the CO₂ was dosed on top of an IL ‘snow’ layer, so the CO₂ molecules are only

interacting with the surface region of the IL ‘snow’. It is expected that the surface sites are less stable than bulk sites, due to the CO₂ being in a less coordinated site than it would be in the bulk. This is reflected in the experimental TPD peak in fig. 5.7 for the CO₂ dosed on [C₈C₁Im][BF₄] ‘snow’, with desorption occurring at lower temperatures (only ≈ 90 to 120 K, green triangles) rather than over the same temperature range as the TPD peak observed in the CO₂ and [C₈C₁Im][BF₄] coadsorption (≈ 90 to 160 K, grey squares).

5.3.4. Comparison of experimental CO₂ signal to the Polanyi–Wigner equation

Following the discussion about the existence of different types of binding site for CO₂ within the [C₈C₁Im][BF₄] ‘snow’ (section 5.3.3), it is clear that the TPD peaks observed in the coadsorption experiments are not due to a single CO₂ binding site. This means that CO₂ molecules exist in different environments within the IL, so the experimentally measured TPD peak is due to the sum of TPD peaks of CO₂ from the different binding sites. Each of these binding sites could have different activation energies of desorption, E_{des} , meaning that the experimental data in this study can be characterised by a range of $E_{\text{des, CO}_2}$ values. In order to evaluate this range of activation energies for CO₂ within the IL the experimental data must be fitted with theoretical peaks given by the Polanyi–Wigner equation [22] (eq 2.51, see section 2.4 for definition of terms), similar to the fitting that was performed with the [C₈C₁Im][BF₄] peak in section 5.2. Unlike the fitting of [C₈C₁Im][BF₄] there is not a known TPD peak area for 1 layer of CO₂ as there was with the IL coverage, due to the CO₂ not forming multilayers on the gold surface, making it impossible to determine the experimental signal for the desorption of a monolayer. The implication is that a desorption rate, in terms of layers per second, could not be determined meaning that finding the initial state population in layers of CO₂ was not possible. This meant that a relative scale has been used, where the most populated CO₂ state was assigned a relative population of one.

Theoretical TPD peaks for CO₂ desorption from within a [C₈C₁Im][BF₄] network were generated as a sum of TPD peaks from a series of theoretical CO₂ adsorption sites, weighted by their relative populations. All the theoretical CO₂

TPD peaks were assumed to be first order ($n = 1$), used a pre-exponential factor of $A = 10^{13} \text{ s}^{-1}$, which is typical for small molecules [21], and a heating rate similar to the one used during CO_2 desorption, which was $\approx 0.67 \text{ K s}^{-1}$. Theoretical CO_2 states were evenly spaced in activation energy of desorption from 26 kJ mol^{-1} upwards, in arbitrarily chosen steps of 1.5 kJ mol^{-1} . The fact that a monolayer coverage could not be calculated for CO_2 meant that the desorption rate could not be calibrated, so the assumption of $A = 10^{13} \text{ s}^{-1}$ had to be made. The pre-exponential factor, A , and the activation energy of desorption are not independent variables, with a change in A by an order of magnitude affecting E_{des} by 2 kJ mol^{-1} (had A been chosen as 10^{14} s^{-1} the lowest fitted $E_{\text{des, CO}_2}$ would have been 24 kJ mol^{-1}). Since the assumption made about A has an effect on the absolute values of E_{des} , conclusions can only really be drawn on the relative values of E_{des} , which is the same as the relative stabilisation of the CO_2 molecules.

The experimental data for the 10 minute $[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]$ and CO_2 coadsorption using a CO_2 pressure of $1 \times 10^{-6} \text{ mbar}$, pink line in fig. 5.8a expressed in terms of pressure, has been fitted by a sum of individual CO_2 states (blue lines) which have the relative populations shown in fig. 5.8b. The sum of theoretical states is shown as the black line in fig. 5.8a, and can be seen to match the shape of the experimental data reasonably well. It can be seen that an individual CO_2 state is much narrower than the experimentally observed desorption peak, meaning that it was not possible to fit the data with just a single CO_2 state. The CO_2 signal and relative populations have been expressed in terms of a pressure/exposure using eq 5.1 allowing a comparison to be made between the original dose ($600 \times 10^{-6} \text{ mbar s}$) and the stabilised quantity of CO_2 ($(1.71 \pm 0.14) \times 10^{-6} \text{ mbar s}$, table 5.1). About 0.3% of the CO_2 exposed to the 10 minute, $1 \times 10^{-6} \text{ mbar}$ coadsorption was captured, although the purpose of the experimental setup described here was not to capture CO_2 effectively, but probe the IL- CO_2 interaction. Capture efficiency may have been affected by the fact that experiments were performed at low temperature and low pressure meaning that the probability of a CO_2 molecule being in the correct place when an IL molecule is in the correct conformation is reduced relative to high temperature and pressure studies. This will be discussed further in chapter 6. As discussed previously correlating the experimental values to a desorption rate was not

possible, so the axes in fig. 5.8a have been scaled manually to obtain the best looking fit. This scaling does not affect the fit itself, or the values obtained from the fit provided, if the conversion between relative population and CO₂ state population is performed correctly. The simulated CO₂ state population (right hand axis on fig. 5.8b) was calculated by dividing the total quantity of CO₂ stabilised (in mbar s) by the sum of the relative populations, before multiplying by the individual relative populations to give the amount of mbar s stabilised within each state. It is important to stress that it can only be deduced that there is a distribution of CO₂ states within the IL, with an inability to elucidate the exact nature of the binding site from these experiments. It is not possible to infer the orientation of the CO₂ molecules, relative to the IL molecules, or the structure of the IL network, from the results collected here. Further experimentation would be required in conjunction with some form of computational modelling to calculate the interaction energy of CO₂ in different orientations around the [C₈C₁Im][BF₄] molecules.

Despite the simulated CO₂ adsorption sites not being directly related to any real conformations of CO₂ within the IL, information can still be extracted from the fitting. Studies found that CO₂ adsorbed on octadecanethiol self-assembled monolayers had an $E_{\text{des}} = 17.2 \pm 2 \text{ kJ mol}^{-1}$ [35], which has already been discussed as being lower than the minimum activation energy that can be

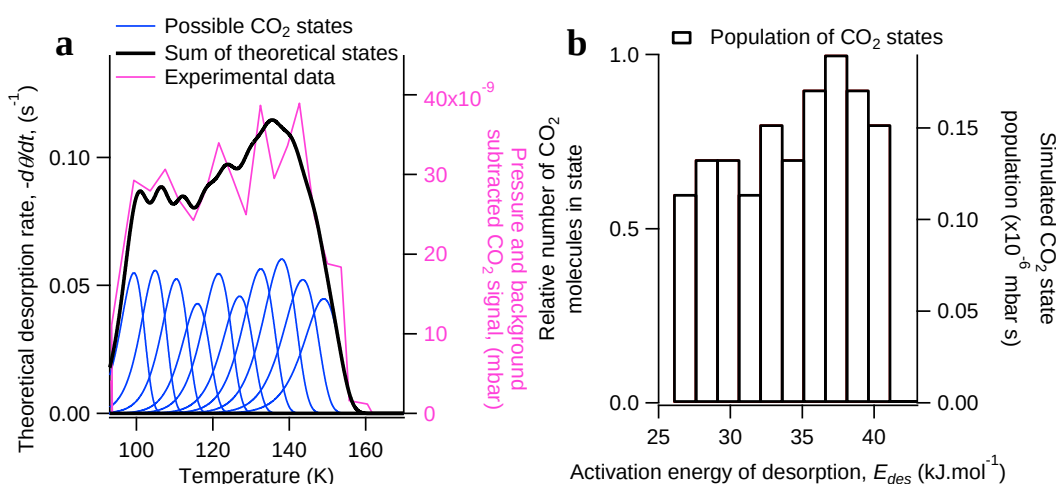


Figure 5.8: An example of the fitting performed to the TPD spectra, using the 10 minute coadsorption for which $P_{\text{CO}_2} = 1 \times 10^{-6}$ mbar, to find the distribution and population of theoretical CO₂ adsorption sites within the [C₈C₁Im][BF₄]. The plot in (a) shows the experimental data (heating rate = 0.67 K s⁻¹), converted to a pressure (pink line), after it has been fitted to a sum of theoretical states (black line). The individual CO₂ states used in the fitting are also shown (blue). The relative populations of the theoretical CO₂ states, found from the fitting are shown in (b), which has also been converted to a population using the CO₂ peak area.

probed in this study. For coadsorptions at low temperature the IL sticks where it lands on the surface, in the conformation it arrived in, meaning statistically there will be a wide variety of adsorption sites for CO₂. The CO₂ molecule itself has a quadrupole which would be able to interact strongly with other quadrupoles, dipoles or formal charges. It is postulated that sites where CO₂ has a large interaction with a non-polar domain, such as the aliphatic cation tail, will have lower activation energies of desorption, as there are only weak dispersion interactions available for bonding. It is thought that as the degree of ‘aliphatic nature’ of the pore decreases, the activation energy of desorption increases, due to the greater number of interactions with the ionic regions of the IL molecule. This argument suggests that the CO₂ is most tightly bound by the ionic regions of the IL, the imidazolium head group and the anion, as these are the sites which have the highest activation energies of desorption. This theory is in agreement with the literature which states that the nature of the anion is more important, when considering the interactions with CO₂, than the structure of the cation, for imidazolium based ILs [1, 5, 11].

Fitting of the experimental TPD profiles with the sum of theoretical states shows that the typical activation energy of desorption range for CO₂

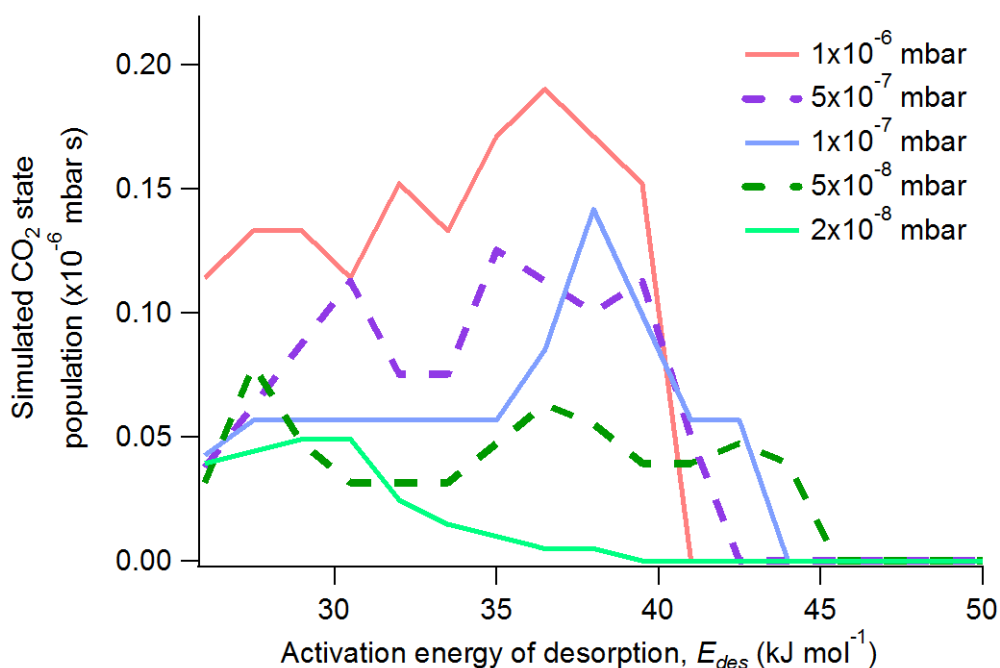


Figure 5.9: Plots showing how the population of CO₂ states with different E_{des} vary as the pressure of CO₂ used during coadsorption with [C₈C₁Im][BF₄] is varied. Data shown here is for coadsorptions with 10 minutes of IL, where state populations have been calculated from the relative populations found by fitting the TPD peak (heating rate = 0.67 K s⁻¹) with a sum of hypothetical CO₂ adsorption sites, as described in the text.

desorption from $[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]$ is $E_{\text{des}} = 26$ to 43 kJ mol^{-1} (table 5.3), representing a stabilisation of at least 17 kJ mol^{-1} (the term ‘at least’ is used in case the CO_2 binds to the surface at a temperature just below the minimum temperature obtained here, giving it an E_{des} just below 26 kJ mol^{-1}). It can be seen from fig. 5.8 that the population distribution of CO_2 within $[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]$ is not uniform, with a greater number of CO_2 molecules having $E_{\text{des}} = 32$ to 39.5 kJ mol^{-1} than have $E_{\text{des}} = 26$ to 32 kJ mol^{-1} . This is confirmed by the average activation energy of desorption, $E_{\text{des, ave}}$ for the 10 minute 1×10^{-6} mbar data being 33.3 kJ mol^{-1} (table 5.3 shows averages for all coadsorption data). The variation in CO_2 site populations for each experiment in the 10 minute $[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]$ – CO_2 coadsorptions can be compared, as shown in fig. 5.9. Looking at the 1×10^{-7} , 5×10^{-7} and 1×10^{-6} mbar population distributions, in fig. 5.9, higher CO_2 populations are observed for the more stable adsorption sites. A trend can also be seen that as the CO_2 pressure used during dosing is increased, a higher proportion of the CO_2 is stabilised within the sites with lower E_{des} , suggesting that some of these sites may require higher CO_2 pressures to access. The data for lower CO_2 dose pressures (2×10^{-8} and 5×10^{-8} mbar) does not seem to follow the trends discussed, with population distributions that are more uniform. This is also reflected in the low pressure data for different coadsorption timescales (see figures in appendix 8.7 for population distribution graphs for the 20 minute, 5 minute and 2 minute coadsorption data). It would be expected that the more stable CO_2 sites become populated first, at all pressures, as statistically these are the hardest to escape from once a CO_2 molecule has been captured (see residence time equation, eq 2.55). The fact that this trend is not always observed may suggest something about the capture process for the CO_2 molecules by the IL, which will be discussed further in chapter 6.

Table 5.3 shows the parameters obtained from fitting the experimental TPD peaks with a sum of hypothetical CO_2 adsorption sites. From this it can be confirmed that the typical range of activation energies of desorption for CO_2 from $[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]$ is $E_{\text{des}} = 26$ to 43 kJ mol^{-1} . The average activation energy of desorption, $E_{\text{des, ave}}$, is calculated by taking a weighted average of the data, that is

$$E_{\text{des, ave}} = \frac{\sum_i E_{\text{des}, i} \times \text{relative population}_i}{\text{total relative population}} \quad \text{Equation 5.2}$$

This results in a value which gives an idea of what the population distribution looks like, with larger values representing a higher population in the more stabilised states and a lower value representing a larger proportion of CO₂ molecules in the less stabilised adsorption sites. If the CO₂ population were uniformly distributed across all the adsorption sites over the range 26 to 42.5 kJ mol⁻¹ the calculation for $E_{\text{des, ave}}$ would yield 34.3 kJ mol⁻¹. It should be noted that the weighted average is sensitive to the E_{des} range, so care must be taken when drawing conclusions from data with different E_{des} ranges. The data in table 5.3 doesn't really show any clear trends in the $E_{\text{des, ave}}$ values, which could be a result of the experimental noise but may be an indication that there is no real trend in the data. This could be a result of the way in which the surface

Table 5.3: Table showing the parameters collected from performing fitting of the experimental TPD peaks with the hypothetical CO₂ adsorption sites within the [C₈C₁Im][BF₄]. The average activation energy of desorption has been calculated from a weighted sum, as described in the text. As the TPD fitting is judged by the human eye it is difficult to estimate errors for these values, however errors due to noise in the experimental data will be proportionally larger for the lower IL coverages and CO₂ pressures. Column headings give an approximate guide to the [C₈C₁Im][BF₄] layer thickness used in each case, but each surface has slight variation in IL coverage (as seen in table 5.1).

CO ₂ Dose Pressure	Coadsorption Dose Length	20 minutes (20 layers)	10 minutes (10 layers)	5 minutes (5 IL layers)	2 minutes (2 IL layers)
2×10 ⁻⁸ mbar	E_{des} range (kJ mol ⁻¹)	—	26.0 – 38.0	—	—
	Average E_{des} (kJ mol ⁻¹)	—	29.7	—	—
5×10 ⁻⁸ mbar	E_{des} range (kJ mol ⁻¹)	26.0 – 41.0	26.0 – 44.0	26.0 – 39.5	26.0 – 39.5
	Average E_{des} (kJ mol ⁻¹)	33.3	34.9	33.1	33.7
1×10 ⁻⁷ mbar	E_{des} range (kJ mol ⁻¹)	26.0 – 42.5	26.0 – 42.5	26.0 – 41.0	29.0 – 41.0
	Average E_{des} (kJ mol ⁻¹)	33.4	35.1	33.0	34.5
2×10 ⁻⁷ mbar	E_{des} range (kJ mol ⁻¹)	26.0 – 42.5	—	—	—
	Average E_{des} (kJ mol ⁻¹)	33.4	—	—	—
5×10 ⁻⁷ mbar	E_{des} range (kJ mol ⁻¹)	26.0 – 41.0	26.0 – 41.0	26.0 – 44.0	26.0 – 38.0
	Average E_{des} (kJ mol ⁻¹)	34.0	34.1	34.4	32.5
1×10 ⁻⁶ mbar	E_{des} range (kJ mol ⁻¹)	26.0 – 41.0	26.0 – 39.5	26.0 – 39.5	26.0 – 39.5
	Average E_{des} (kJ mol ⁻¹)	34.2	33.3	33.8	31.6
2×10 ⁻⁶ mbar	E_{des} range (kJ mol ⁻¹)	26.0 – 41.0	—	—	—
	Average E_{des} (kJ mol ⁻¹)	33.0	—	—	—

is prepared, where the lack of a trend may indicate that the CO₂ capture mechanism could be random (see section 6.3.2). Speculative conclusions could be drawn which suggest that the low pressure data has $E_{\text{des, ave}}$ values that are larger than 34.3 kJ mol⁻¹, suggesting that the CO₂ fills the high binding sites preferentially, as seen in fig. 5.9 (ignoring the 2×10^{-8} mbar data). For the higher pressures the $E_{\text{des, ave}}$ values tend to fall to approximately the value of 34.3 kJ mol⁻¹, which could suggest all the sites fill up more uniformly at higher pressures. Further conclusions cannot be drawn from comparisons of the $E_{\text{des, ave}}$ values due to the differences in E_{des} ranges for the adsorption sites in the experiments.

5.4. References

- [1] Hu, Y.F., Liu, Z.C., Xu, C.M. and Zhang, X.M., The molecular characteristics dominating the solubility of gases in ionic liquids. *Chem. Soc. Rev.*, **2011**, (40), pp. 3802-3823.
- [2] Shannon, M.S., Tedstone, J.M., Danielsen, S.P.O., Hindman, M.S., Irvin, A.C. and Bara, J.E., Free Volume as the Basis of Gas Solubility and Selectivity in Imidazolium-Based Ionic Liquids. *Ind. Eng. Chem. Res.*, **2012**, (51), pp. 5565-5576.
- [3] Liu, H., Dai, S. and Jiang, D.E., Molecular Dynamics Simulation of Anion Effect on Solubility, Diffusivity, and Permeability of Carbon Dioxide in Ionic Liquids. *Ind. Eng. Chem. Res.*, **2014**, (53), pp. 10485-10490.
- [4] Damas, G.B., Dias, A.B.A. and Costa, L.T., A Quantum Chemistry Study for Ionic Liquids Applied to Gas Capture and Separation. *J. Phys. Chem. B*, **2014**, (118), pp. 9046-9064.
- [5] Anthony, J.L., Anderson, J.L., Maginn, E.J. and Brennecke, J.F., Anion effects on gas solubility in ionic liquids. *J. Phys. Chem. B*, **2005**, (109), pp. 6366-6374.
- [6] Syres, K.L. and Jones, R.G., Adsorption, Desorption, and Reaction of 1-Octyl-3-methylimidazolium Tetrafluoroborate, [C₈C₁Im][BF₄], Ionic Liquid Multilayers on Cu(111). *Langmuir*, **2015**, (31), pp. 9799-9808.
- [7] Armstrong, J.P., Hurst, C., Jones, R.G., Licence, P., Lovelock, K.R.J., Satterley, C.J. and Villar-Garcia, I.J., Vapourisation of ionic liquids. *Phys. Chem. Chem. Phys.*, **2007**, (9), pp. 982-990.
- [8] Lovelock, K.R.J., Smith, E.F., Deyko, A., Villar-Garcia, I.J., Licence, P. and Jones, R.G., Water adsorption on a liquid surface. *Chem. Commun.*, **2007**, 4866-4868.
- [9] Deyko, A. and Jones, R.G., Adsorption, absorption and desorption of gases at liquid surfaces: water on C₈C₁Im BF₄ and C₂C₁Im Tf₂N. *Faraday Discuss.*, **2012**, (154), pp. 265-288.

- [10] Chen, Y.H., Zhang, S.J., Yuan, X.L., Zhang, Y.Q., Zhang, X.P., Dai, W.B. and Mori, R., Solubility of CO₂ in imidazolium-based tetrafluoroborate ionic liquids. *Thermochim. Acta*, **2006**, (441), pp. 42-44.
- [11] Cadena, C., Anthony, J.L., Shah, J.K., Morrow, T.I., Brennecke, J.F. and Maginn, E.J., Why is CO₂ so soluble in imidazolium-based ionic liquids?, *J. Am. Chem. Soc.*, **2004**, (126), pp. 5300-5308.
- [12] Watanabe, M., Kodama, D., Makino, T. and Kanakubo, M., CO₂ absorption properties of imidazolium based ionic liquids using a magnetic suspension balance. *Fluid Phase Equilibria*, **2016**, (420), pp. 44-49.
- [13] Holloczki, O., Kelemen, Z., Koenczoel, L., Szieberth, D., Nyulaszi, L., Stark, A. and Kirchner, B., Significant Cation Effects in Carbon Dioxide Ionic Liquid Systems. *Chemphyschem*, **2013**, (14), pp. 315-320.
- [14] Crowhurst, L., Mawdsley, P.R., Perez-Arlandis, J.M., Salter, P.A. and Welton, T., Solvent-solute interactions in ionic liquids. *Phys. Chem. Chem. Phys.*, **2003**, (5), pp. 2790-2794.
- [15] Zhang, J., Zhang, Q., Qiao, B. and Deng, Y., Solubilities of the gaseous and liquid solutes and their thermodynamics of solubilization in the novel room-temperature ionic liquids at infinite dilution by gas chromatography. *J. Chem. Eng. Data*, **2007**, (52), pp. 2277-2283.
- [16] Lee, B.-S. and Lin, S.-T., Screening of ionic liquids for CO₂ capture using the COSMO-SAC model. *Chem. Eng. Sci.*, **2015**, (121), pp. 157-168.
- [17] Yu, C.H., Huang, C.H. and Tan, C.S., A Review of CO₂ Capture by Absorption and Adsorption. *Aerosol Air Qual. Res.*, **2012**, (12), pp. 745-769.
- [18] Paulechka, Y.U., Zaitsau, D.H., Kabo, G.J. and Strechan, A.A., Vapor pressure and thermal stability of ionic liquid 1-butyl-3-methylimidazolium Bis(trifluoromethylsulfonyl)amide. *Thermochim. Acta*, **2005**, (439), pp. 158-160.
- [19] Deyko, A., Lovelock, K.R.J., Licence, P. and Jones, R.G., The vapour of imidazolium-based ionic liquids: a mass spectrometry study. *Phys. Chem. Chem. Phys.*, **2011**, (13), pp. 16841-16850.
- [20] Deyko, A., *et al.*, Measuring and predicting Delta(vap)H₂₉₈ values of ionic liquids. *Phys. Chem. Chem. Phys.*, **2009**, (11), pp. 8544-8555.
- [21] Hessey, S.G. and Jones, R.G., On the evaporation, bonding, and adsorbate capture of an ionic liquid on Au(111). *Chemical Science*, **2013**, (4), pp. 2519-2529.
- [22] Kolasinski, K.W., *Surface Science: Foundations of Catalysis and Nanoscience*. Eds., John Wiley & Sons, Chichester, UK, (2012)
- [23] Freire, M.G., Neves, C., Marrucho, I.M., Coutinho, J.A.P. and Fernandes, A.M., Hydrolysis of Tetrafluoroborate and Hexafluorophosphate Counter Ions in Imidazolium-Based Ionic Liquids. *J. Phys. Chem. A*, **2010**, (114), pp. 3744-3749.
- [24] Taylor, A.W., Lovelock, K.R.J., Jones, R.G. and Licence, P., Borane-substituted imidazol-2-ylidenes: syntheses in vacuo. *Dalton T.*, **2011**, (40), pp. 1463-1470.
- [25] Taylor, A.W., Lovelock, K.R.J., Deyko, A., Licence, P. and Jones, R.G., High vacuum distillation of ionic liquids and separation of ionic liquid mixtures. *Phys. Chem. Chem. Phys.*, **2010**, (12), pp. 1772-1783.
- [26] Brundle, C.R. and Roberts, M.W., Some observations on surface sensitivity of photoelectron spectroscopy. *P. R. Soc. A*, **1972**, (331), pp. 383-394.

- [27] Levenson, L.L., Condensation coefficients of argon, krypton, xenon and carbon dioxide measured with a quartz crystal microbalance. *J. Vac. Sci. Technol.*, **1971**, (8), pp. 629-635.
- [28] Hessey, S.G. and Jones, R.G., Line-of-sight mass spectrometry: principles and practice. *Surf. Interface Anal.*, **2015**, (47), pp. 587-600.
- [29] Bryson, C.E., Cazcarra, V. and Levenson, L.L., Sublimation Rates and Vapour Pressures of H₂O, CO₂ N₂O and Xe. *J. Chem. Eng. Data*, **1974**, (19), pp. 107-110.
- [30] Trusler, J.P.M., Equation of State for Solid Phase I of Carbon Dioxide Valid for Temperatures up to 800 K and Pressures up to 12 GPa. *J. Phys. Chem. Ref. Data*, **2011**, (40), pp. 043105.
- [31] Dlugokencky, E. and Tans, P., NOAA/ESRL. www.esrl.noaa.gov/gmd/ccgg/trends/ (accessed May 31, 2017).
- [32] Leys, J., Wubbenhorst, M., Menon, C.P., Rajesh, R., Thoen, J., Glorieux, C., Nockemann, P., Thijs, B., Binnemans, K. and Longuemart, S., Temperature dependence of the electrical conductivity of imidazolium ionic liquids. *J. Chem. Phys.*, **2008**, (128), pp. 064509.
- [33] Santos, C.S. and Baldelli, S., Gas-liquid interface of room-temperature ionic liquids. *Chem. Soc. Rev.*, **2010**, (39), pp. 2136-2145.
- [34] Mezger, M., Ocko, B.M., Reichert, H. and Deutsch, M., Surface layering and melting in an ionic liquid studied by resonant soft X-ray reflectivity. *Proc. Natl. Acad. Sci. U S A*, **2013**, (110), pp. 3733-3737.
- [35] Stein, O. and Asscher, M., Adsorption of H₂O, CO₂ and Xe on soft surfaces. *J. Phys. Chem. B*, **2008**, (112), pp. 3955-3962.

Chapter 6

Stabilisation of carbon dioxide within the ionic liquid 1-octyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide

6.1. Introduction

In chapter 5 it was seen that carbon dioxide could be captured within the ionic liquid 1-octyl-3-methylimidazolium tetrafluoroborate over an activation energy of desorption range of 26 to 43 kJ mol⁻¹. Since the CO₂ was not seen to form multilayers on the gold substrate, these results represented a stabilisation of the CO₂ within the [C₈C₁Im][BF₄] of up to 17 kJ mol⁻¹. The true stabilisation could be greater than this if it is found that the E_{des} for the CO₂ on the gold was actually a value smaller than 26 kJ mol⁻¹ (but isn't able to be measured by the setup here). As discussed the [C₈C₁Im][BF₄] had been well studied within the research group at Nottingham, largely contributing to the decision to study its interaction with CO₂. Within the field of ionic liquids, ILs containing the anion bis(trifluoromethylsulfonyl)imide ([Tf₂N]⁻) have been considered as some of the most hopeful options for carbon capture and storage devices, with large quantities of research into such ILs [1-6]. To allow comparisons to be drawn with this previous work and provide insights into future work it was decided that the interaction of carbon dioxide with the ionic liquid 1-octyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([C₈C₁Im][Tf₂N]) would be studied using temperature programmed desorption.

It is widely regarded that for ILs with a given cation the [Tf₂N]⁻ containing IL has a much higher CO₂ solubility than the [BF₄]⁻ containing analogue [2, 5, 7, 8]. This has been attributed to the increased degree of fluorination (quantity of fluorine atoms on anion) of the [Tf₂N]⁻ anion relative to the [BF₄]⁻ anion, rather than anion induced free volume differences. A molecular dynamics study looking at CO₂ solubility within [C₂C₁Im][Tf₂N] and [C₂C₁Im][BF₄] found that the cavity size distributions within these two ILs were very similar, indicating no major difference due to changing the anion [9]. Increased fluorination of the anion has been seen to increase the volume of polar domains within the IL which can interact with the quadrupole on the CO₂ molecule [10, 11]. Further experiments to investigate the effect of anion

fluorination on ILs used phosphate anions with varying length fluoroalkyl chains attached, which were seen to yield higher CO₂ solubilities than the [Tf₂N][−] containing ILs [8, 12]. It should be noted that, in the cases discussed, as the anion changes both the volume of the fluorinated domains and the free volume of the IL change. It is therefore possible that some of the solubility increase is due to the ability of CO₂ to slip into space generated due to the extra motion of the longer fluoroalkyl chains [12], observed as an increased free volume in the IL structure, rather than increase in volume of fluorinated domains. This increase in the number of degrees of freedom of alkyl tails, and hence free volume created within the IL structure, with chain length, is believed to be the cause of the slight CO₂ solubility variations that occur when the imidazolium cation is varied [7]. Studies also showed that, despite the anion often being the major contributing factor to CO₂ solubility [2, 3], fluorination of the alkyl chain on the imidazolium has been seen to increase CO₂ solubility significantly. The Henry's constants (which are inversely proportional to solubility) for [C₈C₁Im][Tf₂N] and its fluorinated cation analogue [C₈F₁₃C₁Im][Tf₂N] are 30 ± 1 bar and 4.5 ± 1 bar respectively [13]. The fluorinated cation makes the IL nearly seven times better at dissolving CO₂, however an undesirable increase in viscosity of the IL is observed when the cation is fluorinated, limiting the rate of CO₂ uptake and the ability to easily transport the IL, if used as an industrial processes. There are, however, studies where the degree of fluorination of the anion has been increased, but the CO₂ solubility has not [14]. This could have been due to the change in the anion structure from an imide to a sulfonate, suggesting there are multiple factors, not just the degree of fluorination, in determining CO₂ solubility within ILs.

The strength of the anion–cation interaction has also been cited as a factor in determining the ability of a given IL to dissolve CO₂, with the observed trend being that a weaker anion–cation interaction leads to a larger solubility of CO₂. This is related to the idea that for ions which are less attracted to each other the energy penalty for squeezing CO₂ between the ions, by increasing the ionic separation, is reduced [4, 9]. This would predict a larger solubility for CO₂ in [C₈C₁Im][Tf₂N] than in [C₈C₁Im][BF₄], if comparisons are drawn from the 1-ethyl-3-methylimidazolium analogues, where a stronger anion–cation interaction was calculated in [C₂C₁Im][Tf₂N] relative to [C₂C₁Im][BF₄] [9]. The

experimentally determined values of the Henry's constants of CO₂, at approximately 300 K, for the two [C₈C₁Im]⁺ containing ILs are 54 ± 3 bar for [C₈C₁Im][BF₄] [15] (an older reference has a value of 15 ± 0.1 bar for this IL [16], although they say that they see the correct trend in solubility but not the correct values) and 30 ± 1 bar for [C₈C₁Im][Tf₂N] [13]. For these Henry's constants (in units of pressure) the solubility of the gas is inversely proportional to the constant, which appears to support the inverse correlation of ion interaction and CO₂ solubility. Further to the effects of anion–cation interaction strength, calculations of the binding energy between the anions studied here ([Tf₂N][−] and [BF₄][−]) and the CO₂ molecule were performed in ref. [4]. These quantum calculations gave values of −15.79 kJ mol^{−1} for the interaction between CO₂ and [Tf₂N][−] and −21.55 kJ mol^{−1} for the CO₂–[BF₄][−] interaction (negative interactions are defined as attractive and stable). This, when compared to the Henry's constants from the literature, suggests that the solubility and stability of a gas within a given IL are not always related (results in refs. [2, 10] suggest that they are) despite the observation of increased solubility with interaction strength for some solute–IL combinations.

When considering the interaction between a CO₂ molecule and an IL molecule, chemical calculations from theoretical methods can be a vital tool in understanding the nature of the interaction. Care, however, should be taken when considering theoretical results as the experimental results obtained from bulk systems may not match up with single molecule calculations. One such example can be seen in ref. [4], where quantum calculations have predicted that the interaction between [C₂C₁Im][Tf₂N] ion pair and CO₂ occurs primarily through the carbon of CO₂ interacting with the oxygen on the anion, with the oxygen of the CO₂ also interacting with a hydrogen from the methyl group on the cation. Given the previous discussion, finding that the degree of fluorination is one of the key factors in determining the CO₂ solubility, it might be expected that the CO₂ interacts with the fluorine on the anion. Other calculations on the interaction between imidazolium cations and carbon dioxide also suggest that the most likely interaction between the CO₂ and the cation will involve the aromatic ring of the cation [17]. Molecular dynamics simulations using a model in which 90 ion pairs ([C₄C₁Im][PF₆]) and 10 CO₂ molecules have been performed [3]. The resulting radial distribution functions could be used to

conclude that the CO₂ aligned itself tangentially to the [PF₆][−] anion to maximise the favourable interactions with the fluorine atoms. Despite the anion in the quantum calculation from ref. [4] being different, it might still be expected that the CO₂ would become most stabilised by aligning itself near the fluorinated parts of the [Tf₂N][−]. Such an alignment would maximise the opportunity for Lewis acid–base interactions to occur between the CO₂ and the fluorine atoms [14], with the carbon on the CO₂ acting as the Lewis acid and the fluorine on the anion acting as the Lewis base (which is a different suggestion to ref. [14], which claims the Lewis acid–base interaction will be between the O in CO₂ and the F in the anion). It can be seen that the theoretical models agree that the CO₂ will interact most favourably with the anion, but exactly how is still not certain. It is likely that the observed differences in the quantum calculation and the molecular dynamics simulation are due to the presence of neighbouring molecules, which modify the potential felt by the CO₂ molecule such that the most stable binding site within a bulk IL domain is no longer the same as for the CO₂–ion pair interaction. To some extent this type of information could be gained from TPD studies by looking at the CO₂ interaction strength as a function of the IL layer thickness, as the IL layer goes from a ‘2D’ monolayer to a more bulk-like structure for increased thicknesses.

6.2. Temperature programmed desorption of [C₈C₁Im][Tf₂N]

The reader is referred to the previous chapters (sections 2.4, 2.5 and 3.2) for a detailed description of the theoretical principles of temperature programmed desorption (TPD) and the experimental conditions used in this study. Studies of the desorption of bulk [C₈C₁Im][Tf₂N] have been performed within the research group, in much the same way as described for [C₈C₁Im][BF₄] in chapter 5. To recap, the ILs were coated onto a silver dipstick by an immersion method, before withdrawing the dipstick from the IL to leave a bulk IL layer on the surface. The dipstick could then be heated in a linear fashion whilst the signals from the ion fragments of interest for the IL were monitored by line of sight mass spectrometry. From the desorption curve the activation energy of desorption, E_{des} , was obtained, which allowed further calculation of thermodynamic parameters. The values for the energies of desorption for bulk

[C₈C₁Im][Tf₂N] films were found to be $E_{\text{des}} = 131 \pm 2 \text{ kJ mol}^{-1}$ and $\Delta_{\text{vap}}H_{298} = 149 \pm 2 \text{ kJ mol}^{-1}$ [18]. The [C₈C₁Im][Tf₂N] films discussed in this work have thicknesses no larger than 20 layers of ion pairs, compared to the millions of layers of ion pairs in a bulk film (assuming a film has thickness 1 mm and an ion pair layer has thickness 10 Å the bulk layer is 10⁶ IL layers thick). As a result there may well be deviations for the experimentally measured activation energies of desorption here, from the literature values, as surface effects such as clustering and interactions with the gold substrate have a more significant effect on the desorption.

Studies of the desorption of [C₈C₁Im][Tf₂N] from the gold substrate alone were performed prior to the studies of IL coadsorption with CO₂, which allowed the quantity of [C₈C₁Im][Tf₂N] dosed to be converted from experimental counts to a surface coverage in terms of IL layers. The experimental signal for the [C₈C₁Im][Tf₂N] was recorded by monitoring the $m/z = 195$ and 83 amu mass fragments, which are due to the ions [C₈C₁Im]⁺ (molecular cation) and [HC₁Im]⁺ (fragmentation loss of the eight membered alkyl chain, C₈H₁₆), respectively [19]. By collecting TPD spectra for different initial coverages (controlled by varying the length of time that the gold sample was exposed to the IL vapour) the transition between first order desorption and zero order desorption could be determined, allowing a monolayer coverage to be obtained. The monolayer calibration for [C₈C₁Im][Tf₂N] is described in detail in appendix 8.8. These desorption studies of the IL on its own also allowed confirmation that the IL does not generate mass fragments that could be mistaken for CO₂ in later coadsorption experiments (meaning that the [C₈C₁Im][Tf₂N] does not generate an increase in the $m/z = 44$ amu fragment during desorption). Figure 6.1 shows an example of a [C₈C₁Im][Tf₂N] desorption profile for an initial IL coverage of 15.6 ± 1.6 layers, obtained from the experiments performed within this study. The experimental signal has been divided by the monolayer coverage to give a signal of desorption rate in layers s⁻¹, rather than in terms of mass spectrometer counts, which allows a direct comparison to be made with the theoretical desorption rate as predicted by the Polanyi–Wigner equation [20] (eq 2.51, see section 2.4). The theoretical model in fig. 6.1 has been fitted using the parameters found from the leading edge analysis, $\theta = 15.6$, $n = 0$, $E_{\text{des}} = 133 \text{ kJ mol}^{-1}$, pre-exponential factor, $A =$

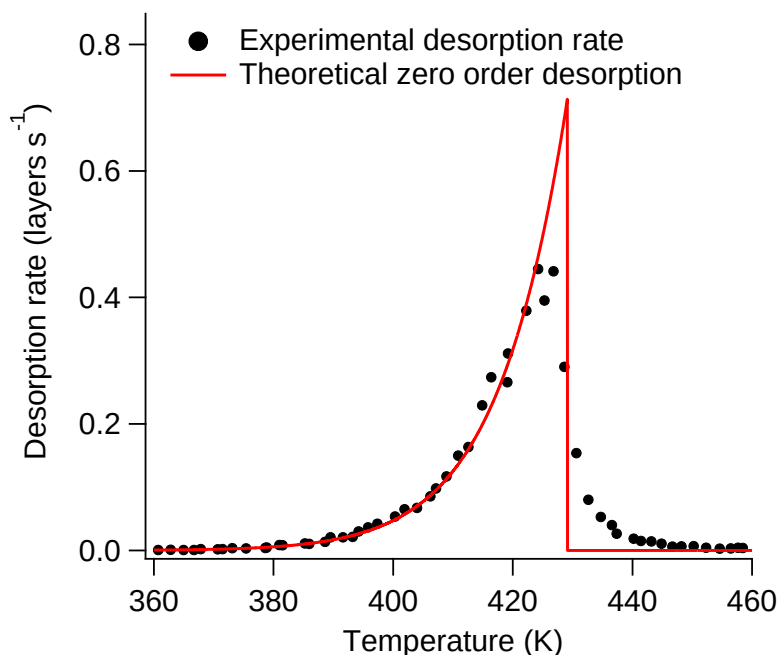


Figure 6.1: Experimental TPD spectrum (heating rate of 0.5 K s^{-1}) for a 15.6 ± 1.6 layer thick $[\text{C}_8\text{C}_1\text{Im}][\text{Tf}_2\text{N}]$ film, as detected by the $m/z = 195$ amu fragment (black dots), compared to a theoretical zero order desorption curve (red line) as modelled by the Polanyi–Wigner equation using the parameters $E_{\text{des}} = 133 \text{ kJ mol}^{-1}$ and $A = 1.1 \times 10^{16} \text{ s}^{-1}$, found from the leading edge analysis.

$1.1 \times 10^{16} \text{ s}^{-1}$ and heating rate of 0.5 K s^{-1} . The experimentally measured exponential leading edge can be seen to be well matched by the theoretical model, until around 420 K, at which point the theoretical model continues to increase exponentially, whilst the experimental signal starts to drop off gradually. The exact cause for the deviation of the experimental signal from the theoretical model is not known, as the deviation is influenced by a number of factors. These include possible surface patchiness [18] and substrate–IL interactions causing first order desorption for the final layer of IL, as described in chapter 5 for the case of $[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]$ desorption. The activation energy of desorption and pre-exponential factor for $[\text{C}_8\text{C}_1\text{Im}][\text{Tf}_2\text{N}]$ were found by performing leading edge analysis, utilising eq 2.52 (see section 2.4 for description). The plot of $\ln(\text{desorption rate})$ vs. reciprocal temperature is shown in fig. 6.2, giving a straight line with gradient $= -E_{\text{des}}/R$ and intercept $= \ln(A)$ for the desorption. The experimentally measured activation energy of desorption calculated from this leading edge analysis was found to be $133 \pm 3 \text{ kJ mol}^{-1}$ with a pre-exponential factor of $A = 1.1 \times 10^{16 \pm 1} \text{ s}^{-1}$. The activation energy of desorption is seen to be in good agreement with the literature value ($131 \pm 2 \text{ kJ mol}^{-1}$), despite the large difference in initial coverage [18].

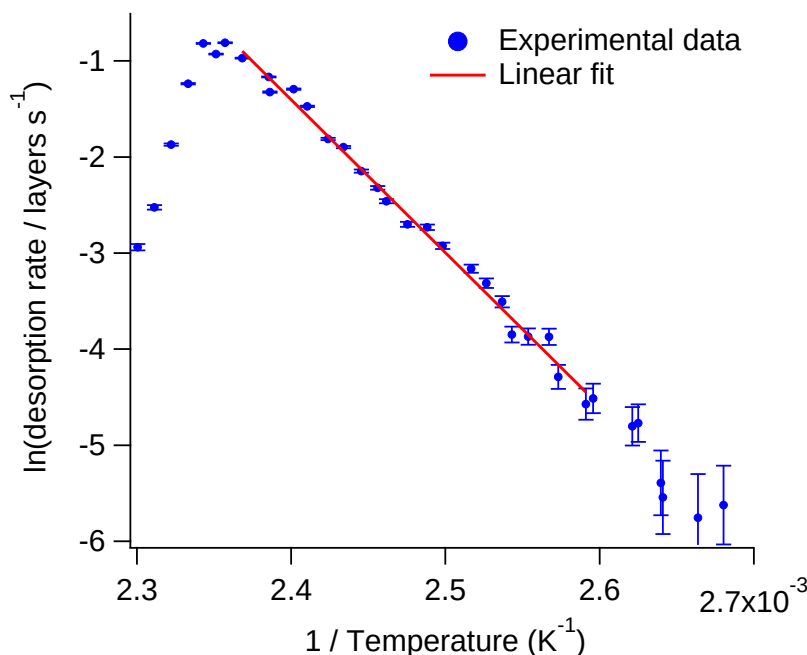


Figure 6.2: Leading edge analysis performed on the experimental data (blue dots) for desorption of $[\text{C}_8\text{C}_1\text{Im}][\text{Tf}_2\text{N}]$ from a film 15.6 ± 1.6 layers thick. Error bars represent the noise in the experimental signal, and are included to show how this is accentuated by taking the natural logarithm of the data. The linear fit has been applied over the temperature range 386 to 422 K. The values calculated from the gradient and intercept of the line of best fit are $E_{\text{des}} = 133 \pm 3 \text{ kJ mol}^{-1}$ and $A = 1.1 \times 10^{16 \pm 1} \text{ s}^{-1}$, respectively.

As mentioned previously the $[\text{C}_8\text{C}_1\text{Im}][\text{Tf}_2\text{N}]$ signal was monitored by following the intensity of the $m/z = 195$ and 83 amu fragments. The reason for tracking the 83 amu fragment rather than the 96 amu fragment (which was tracked in $[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]$) is a consequence of the signal intensity of the 83 amu peak being larger than the 96 amu peak. This result is also observed in the literature for the fragmentation of $[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]$ and $[\text{C}_8\text{C}_1\text{Im}][\text{Tf}_2\text{N}]$ ILs within a quadrupole mass spectrometer [19]. It should be noted that the smaller peak at lower temperature observed in the 96 amu signal for $[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]$ (discussed in fig. 5.3 and appendix 8.4) was not observed during desorption of $[\text{C}_8\text{C}_1\text{Im}][\text{Tf}_2\text{N}]$. This result suggests that the contaminant peak in $[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]$ is not induced by thermal decomposition of the cation, but instead is due to either a contaminant in the synthesised IL or a reaction induced by the presence of the $[\text{BF}_4]^-$ anion. The experimental TPD spectra do not show any desorption peaks for the contaminant HF ($m/z = 20$ amu), which has been seen to be produced in some fluorine containing ILs [21].

6.3. Temperature programmed desorption of CO₂ containing systems

Once the [C₈C₁Im][Tf₂N] had been observed to behave as expected, with respect to its evaporation and desorption, studies of [C₈C₁Im][Tf₂N]–CO₂ systems were performed. Section 5.3.1 has discussed the fact that when the CO₂ was dosed onto the cooled gold substrate (88 K) no CO₂ desorption peak was observed, after pressure and background subtractions had been applied [22]. This meant that the maximum activation energy for desorption that the CO₂ could have from the gold surface would be $\approx 27 \text{ kJ mol}^{-1}$, if the CO₂ had desorbed just below the minimum temperature that could be achieved experimentally by the gold substrate. The experimental details regarding surface formation can be found in section 3.4.3, with the discussion of the results obtained from these surfaces occurring in the proceeding sections.

6.3.1. Desorption of CO₂ from within [C₈C₁Im][Tf₂N]

The experimental procedure associated with these results has been discussed in section 3.2 and the presented experimental data has been corrected to compensate for signal due to CO₂ reflecting off of the sample into the mass spectrometer through application of pressure and background subtractions (discussed in section 5.3.1 and reference [22]). Experimental data for the surfaces formed from the coadsorption of [C₈C₁Im][Tf₂N] and CO₂, with a CO₂ pressure of 1×10^{-6} mbar, are shown in fig. 6.3. It can be seen that for all IL coverages shown (from 2 minutes, which is approximately 2 IL layers, up to 20 minutes, approximately 20 IL layers) that experimental CO₂ TPD peaks exist above the dashed zero line in fig. 6.3. This confirms that the CO₂ must be stabilised within the [C₈C₁Im][Tf₂N] under UHV conditions, as without the IL being present the CO₂ was not seen to be stabilised on the gold substrate (fig. 5.4). The data shows that as the quantity of IL is increased the CO₂ desorption peak area increases, suggesting that the CO₂ is being stabilised within the porous IL network, or ‘bulk’ IL, rather than just at the interfacial (IL–gold and IL–vacuum) regions. For CO₂ adsorbing into bulk IL sites, it is expected that having

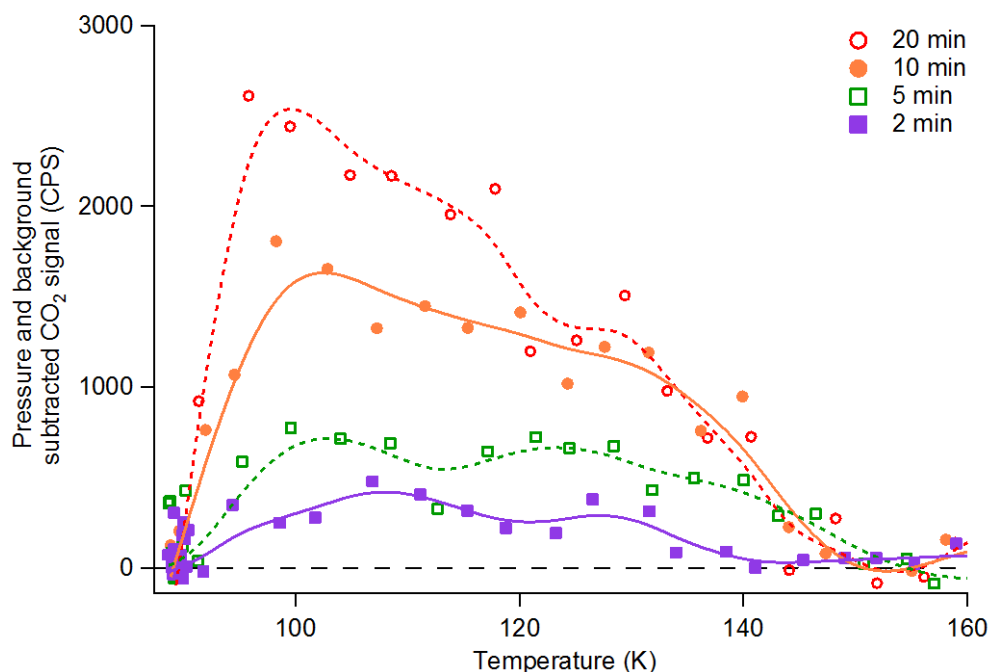


Figure 6.3: A comparison of the experimental data for the desorption of CO₂ from within the coadsorbed [C₈C₁Im][Tf₂N]–CO₂ network for a CO₂ dose pressure of 1×10^{-6} mbar with varying IL coverages. Experimental data points, after pressure and background subtractions have been applied, are shown by the markers whilst lines represent smoothing curves applied to the data to guide the eye. The dashed black line represents the ‘zero line’ for experimental signal. The heating rate during TPD was approximately 0.67 K s^{-1} .

larger quantities of IL will mean that more adsorption sites should exist, whereas there should be approximately the same quantity of interfacial adsorption sites for all layer thicknesses. (There will be a greater number of sites at the edges for a thicker layer, akin to a tower building having more windows than a house of the same floor area although this is negligible when the height is $\approx 200 \text{ \AA}$ but the floor area is $\approx 1 \text{ cm}^2$). This type of result was also observed for the experiments with [C₈C₁Im][BF₄] and CO₂ (section 5.3.2.). Similar trends in the peak areas are observed for other CO₂ dose pressures used during coadsorption, with a graphical representation of the data for these other pressures shown in appendix 8.9.

The experimental peak areas, representing the quantity of CO₂ stabilised within the [C₈C₁Im][Tf₂N] under different experimental conditions (initial IL coverages and CO₂ dose pressures) are shown in table 6.1. The peak areas are shown in both experimental counts (light grey rows) and in 10^{-6} mbar s (equivalent to a ‘metric langmuir’, where 1 true langmuir equates to 10^{-6} Torr s and is a rough approximation to a monolayer of material [20], dark grey rows). The conversion to mbar s was performed by application of eq 5.1 (see section

Chapter 6: Stabilisation of carbon dioxide within the ionic liquid 1-octyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide

Table 6.1: A table of all the collected experimental data for $[\text{C}_8\text{C}_1\text{Im}][\text{Tf}_2\text{N}]\text{-CO}_2$ coadsorptions, with errors. White rows show the IL coverage from time integrated TPD peaks divided by the IL monolayer coverage, light grey rows show experimentally measured CO_2 peak areas after pressure and background subtractions have been applied and dark grey rows show the peak areas converted to CO_2 coverages within the IL.

CO ₂ dose pressure	Coadsorption dose length	20 minutes	10 minutes	5 minutes	2 minutes
5×10^{-8} mbar	Initial IL coverage	17.6 ± 1.8	17.0 ± 1.7	4.3 ± 0.4	2.2 ± 0.2
	CO ₂ peak area (counts)	25000 ± 3000	35000 ± 9000	12000 ± 6000	11000 ± 3000
	CO ₂ coverage (10^{-6} mbar s)	0.85 ± 0.10	1.20 ± 0.31	0.42 ± 0.19	0.39 ± 0.10
1×10^{-7} mbar	Initial IL coverage	15.9 ± 1.6	12.0 ± 1.2	4.8 ± 0.5	2.1 ± 0.2
	CO ₂ peak area (counts)	34000 ± 4000	38000 ± 13000	4000 ± 3000	6000 ± 5000
	CO ₂ coverage (10^{-6} mbar s)	1.17 ± 0.15	1.32 ± 0.45	0.13 ± 0.10	0.20 ± 0.17
2×10^{-7} mbar	Initial IL coverage	19.1 ± 1.9	9.5 ± 1.0	4.1 ± 0.4	1.7 ± 0.2
	CO ₂ peak area (counts)	44000 ± 6000	22000 ± 7000	16000 ± 6000	6000 ± 4000
	CO ₂ coverage (10^{-6} mbar s)	1.52 ± 0.21	0.77 ± 0.22	0.56 ± 0.21	0.21 ± 0.15
5×10^{-7} mbar	Initial IL coverage	13.4 ± 1.3	11.0 ± 1.1	5.6 ± 0.6	1.8 ± 0.2
	CO ₂ peak area (counts)	49000 ± 2000	39000 ± 6000	20000 ± 4000	15000 ± 3000
	CO ₂ coverage (10^{-6} mbar s)	1.69 ± 0.07	1.34 ± 0.21	0.69 ± 0.15	0.53 ± 0.10
1×10^{-6} mbar	Initial IL coverage	16.7 ± 1.7	8.4 ± 0.8	5.0 ± 0.5	1.8 ± 0.2
	CO ₂ peak area (counts)	71000 ± 5000	60000 ± 10000	27000 ± 5000	12000 ± 3000
	CO ₂ coverage (10^{-6} mbar s)	2.46 ± 0.17	2.05 ± 0.36	0.92 ± 0.17	0.53 ± 0.10

5.3.1 for details) to the experimentally measured peak areas. Studying the data in table 6.1 it can be observed that increasing the quantity of IL or increasing the CO_2 dose pressure leads to a greater quantity of CO_2 being captured within the IL, and hence a larger desorption peak area. Exceptions to this trend can be seen and are generally accompanied by either large errors in the peak area, which is a consequence of only being able to use low dose pressures of CO_2 due to working under UHV (e.g. 10 minute, 1×10^{-7} mbar data), or experimental IL coverages which differed from those with the same coadsorption times (e.g. 10 minute, 5×10^{-8} mbar data). Random fluctuations in the mass spectrometer signal have a more significant effect on the data which has either a low initial IL coverage or a low CO_2 pressure, due to reduced signal intensities of these experiments leading to a lower signal to noise ratio. The ' 1×10^{-6} mbar' row in table 6.1 represents the experimental peak areas for the data shown in fig. 6.3, where it can be seen that the peak areas confirm quantitatively what is seen by

the trends in the graph qualitatively; that a larger initial IL coverage leads to a greater quantity of CO₂ captured, for a fixed CO₂ dose pressure.

The fact that the initial IL coverage varies, even for surfaces with the same coadsorption timescales, makes direct comparison of peak areas difficult, as fig. 6.3 shows that the CO₂ peak area is dependent upon initial IL coverage. This is a problem that can be solved by looking at either the average amount of CO₂ stabilised per IL layer or by correcting the CO₂ peak area to that of an ‘ideal IL coverage’ (i.e. 20 layers for a 20 minute coadsorption, 10 layers for a 10 minute coadsorption and so on). These two methods are essentially the same, as the experimental CO₂ peak area is divided by the IL coverage to give an average amount of CO₂ per IL layer, but the latter method multiplies the average amount of CO₂ stabilised per IL layer by the coadsorption time length. Figure 6.4 shows the experimental data for the amount of CO₂ stabilised per IL layer as a function of CO₂ pressure used during coadsorption, whilst table 6.2 shows the CO₂ peak areas after correction assuming a [C₈C₁Im][Tf₂N] dose rate of 1 IL layer min⁻¹ is observed. Figure 6.4 shows that thinner layers of IL appear to stabilise a

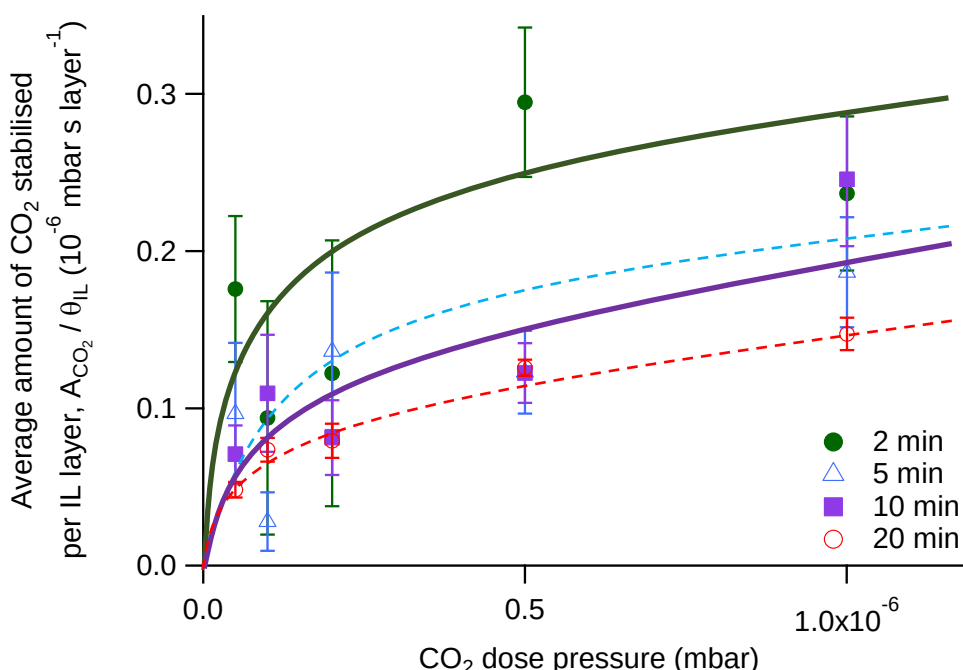


Figure 6.4: Experimental plots showing the variation in the average amount of CO₂ stabilised per layer within the porous [C₈C₁Im][Tf₂N] network as a function of the CO₂ dose pressure used during coadsorption. The markers show experimental data points, whilst the lines serve only to guide the eye through the experimental data and do not represent fits to an isotherm model. Line and marker colours have been matched up (red line for red markers) and solid lines have been used for filled markers whilst dashed lines have been used for hollow markers. The error in the data points has been calculated from the error in the integrated peak areas for the CO₂ desorption peaks.

greater quantity of CO₂ per layer, which would not be expected as all IL layers should be equal, and is discussed more in section 6.3.2.

Consideration of the corrected values in table 6.2 makes it clearer to see the trends in the experimental CO₂ peak areas than it was in table 6.1. The corrected data in table 6.2 confirms that the CO₂ peak area increases with IL coverage, for a given dose pressure, and also that the amount of CO₂ captured increases with CO₂ dose pressure, for a fixed initial IL coverage. Table 6.2 also allows experiments with the same CO₂ exposure (dose length × dose pressure)

Table 6.2: A table of all the experimental data for [C₈C₁Im][Tf₂N]–CO₂ coadsorptions, with errors, after IL coverage correction has been applied. Light grey rows show CO₂ peak areas in experimental units, after pressure and background subtractions have been applied and dark grey rows show the peak areas converted to CO₂ coverage within the IL. Since these data are corrected for IL coverage, experiments with the same exposures of CO₂ can be directly compared.

CO ₂ dose pressure	Coadsorption dose length	20 minutes	10 minutes	5 minutes	2 minutes
5×10 ⁻⁸ mbar	CO ₂ peak area (counts)	28000 ± 2800	21000 ± 5300	14000 ± 6500	10000 ± 2700
	CO ₂ coverage (10 ⁻⁶ mbar s)	0.96 ± 0.10	0.71 ± 0.18	0.48 ± 0.22	0.35 ± 0.09
1×10 ⁻⁷ mbar	CO ₂ peak area (counts)	43000 ± 4400	32000 ± 11000	4000 ± 2700	5400 ± 4300
	CO ₂ coverage (10 ⁻⁶ mbar s)	1.47 ± 0.15	1.09 ± 0.37	0.14 ± 0.09	0.19 ± 0.15
2×10 ⁻⁷ mbar	CO ₂ peak area (counts)	46000 ± 6300	24000 ± 6800	20000 ± 7300	7100 ± 4900
	CO ₂ coverage (10 ⁻⁶ mbar s)	1.59 ± 0.22	0.81 ± 0.23	0.68 ± 0.25	0.24 ± 0.17
5×10 ⁻⁷ mbar	CO ₂ peak area (counts)	73000 ± 3000	36000 ± 5500	18000 ± 3800	17000 ± 2800
	CO ₂ coverage (10 ⁻⁶ mbar s)	2.51 ± 0.10	1.23 ± 0.19	0.61 ± 0.13	0.59 ± 0.09
1×10 ⁻⁶ mbar	CO ₂ peak area (counts)	85000 ± 6000	71000 ± 12000	27000 ± 5100	14000 ± 2900
	CO ₂ coverage (10 ⁻⁶ mbar s)	2.95 ± 0.21	2.46 ± 0.43	0.93 ± 0.17	0.47 ± 0.10

to be compared, which can allow determination of whether a larger quantity of IL or a larger pressure of CO₂ is the more significant factor in CO₂ capture. An example of this is the comparison of the amount of CO₂ stabilised for the 1×10⁻⁷ mbar, 20 minute ((1.47 ± 0.15)×10⁻⁶ mbar s) and the 2×10⁻⁷ mbar, 10 minute ((0.81 ± 0.23)×10⁻⁶ mbar s) experiments. It can be seen that despite the exposure of the surface to the CO₂ being the same (1.2×10⁻⁴ mbar s), a greater quantity of CO₂ is captured in the case where the initial coverage of IL was larger. This comparison has been performed in detail in appendix 8.10, where it was found that of the twelve surfaces which had the same exposure to CO₂, eleven of them have a larger quantity of CO₂ stabilised when the initial [C₈C₁Im][Tf₂N]

coverage is larger. This is the same trend that was observed for the case of $[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]$ in section 5.3.2, which suggests that a greater quantity of carbon dioxide will be captured by these ILs if the IL is in large excess, rather than by increasing the CO_2 pressure.

The observation that quantity of IL is a more significant factor in CO_2 capture than CO_2 pressure is consistent with the idea that an IL layer of any given thickness will eventually saturate, as discussed previously 5.3.2. It is also possible that having too high a pressure will result in CO_2 reflection rather than CO_2 adsorption or capture as the surface coverage of CO_2 increases. A literature value for the enthalpy of sublimation for CO_2 in the temperature range 70 to 103 K is 27.2 kJ mol^{-1} [23]. This value is of the order of the maximum possible activation energy of desorption of CO_2 from gold hypothesised in section 5.3.1. Considering this result along with the idea that within solid CO_2 there are interactions from many neighbouring CO_2 molecules, meaning that the E_{des} for an isolated CO_2 molecule or pair will be lower, means CO_2 will not be likely to form clusters on the surfaces studied here. This lack of CO_2 cluster formation is supported by the experimental observation that CO_2 was not seen to be stabilised on the cooled gold crystal. Increasing the CO_2 pressure will mean that the CO_2 surface coverage increases, which means the probability of an incident CO_2 molecule hitting an adsorbed CO_2 increases. Since the temperature is too high for CO_2 – CO_2 interactions to be stable, such a collision results in reflection of the incident CO_2 , meaning it cannot be captured. By having a larger quantity of IL and a lower dose pressure the probability of an incident CO_2 hitting a pre-adsorbed CO_2 is lower, hence increasing the efficiency of CO_2 capture.

6.3.2. Comparison of the quantity of CO_2 captured within $[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]$ and $[\text{C}_8\text{C}_1\text{Im}][\text{Tf}_2\text{N}]$

It can be seen from fig. 6.4 that as the CO_2 dose pressure used during coadsorption is increased, then the amount of CO_2 captured is increased. This result matches Henry's law which states that the concentration of gas dissolved within a solution is proportional the partial pressure of the gas above the solution, where in the case here, 'solution' refers to the frozen IL network. It can be noticed, from the lines that guide the eye through the experimental data, that

there is not a linear relationship between the average amount of CO₂ stabilised per IL layer and the CO₂ dose pressure. Instead there appears to be a trend towards saturation at higher CO₂ pressures, where an increase in pressure will not generate an increase in amount of CO₂ stabilised, leading to a plateau in the data. This result is consistent with that of a Langmuir isotherm, where adsorption will occur up to a monolayer of material, at which point the surface coverage reaches saturation and adsorption ceases (multilayers are not allowed to form within the Langmuir adsorption model) [24, 25]. An interesting trend in fig. 6.4 can also be seen, with the average amount of CO₂ stabilised per IL layer being smaller for thicker IL films. This is a result that was also observed for the stabilisation of CO₂ within [C₈C₁Im][BF₄] (section 5.3.2, fig. 5.6). This suggests that not all IL layers are equal, since dosing a greater quantity of IL results in less CO₂ stabilised within each IL layer, on average. Considering the dosing mechanism used, where the IL is evaporated onto the cooled surface in a low pressure CO₂ atmosphere, there is no reason why the CO₂ atmosphere or IL vapour that is being dosed should change with time. What does change with time is the surface composition, as before dosing the surface does not have any IL on it, instead being a gold substrate, possibly with chemisorbed IL fragments on it. As dosing of the IL proceeds the gold surface becomes covered and the surface structure becomes that of the IL ‘snow’, which is assumed to be made of ion pairs in random orientations as they stick where they land in the conformations they arrive in. If it is assumed that these two types of surface, the gold with chemisorbed fragments and the IL ‘snow’, have different adsorption properties for the CO₂, then the following rationalisation for the observed results can be made. Assuming that for a CO₂ molecule on the gold with the carbonaceous cracked IL (containing charged or polar nitrogen groups) on its surface has a larger activation energy of desorption than for CO₂ on the IL ‘snow’, then CO₂ adsorbed on the gold surface would have a longer residence time and hence be more likely to be captured by the IL upon dosing. Once a few IL layers had been dosed then the gold surface would no longer be visible and CO₂ adsorption occurs on an IL ‘snow’ surface, which is composed of both charged ionic regions and alkyl tail regions. This would lead to an increased quantity of CO₂ captured within the first few layers of IL that were dosed, before a constant capture rate, characteristic of CO₂ on the IL ‘snow’, occurring for all subsequent IL layers. A

model of this form would explain the experimental observation in figs. 5.6 and 6.4, that the average amount of CO₂ captured per IL layer decreases as total IL coverage increases.

A model based on these assumptions can be proposed, where the concentration (in mbar s per IL layer) of CO₂ within the first two IL layers, $[C_1]$, is expected to be larger than the concentration (in mbar s per IL layer) of CO₂ within all subsequent IL layers, $[C_2]$, for a surface comprising of θ_{IL} layers of IL. This model is represented diagrammatically in fig. 6.5, showing the regions of the IL on the gold surface with different CO₂ concentrations, with the amount

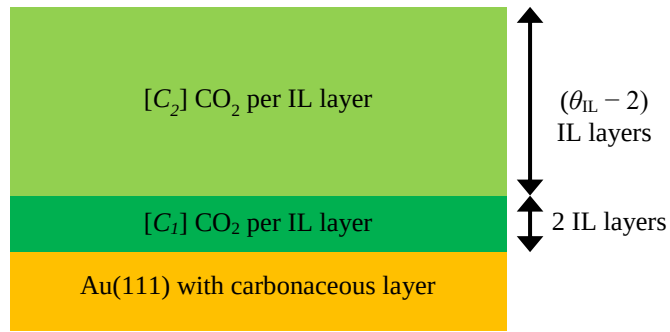


Figure 6.5: A diagrammatic representation of the proposed surface composition using the simple model proposed in the text. It is proposed that there are $[C_1]$ mbar s of CO₂ per IL layer stabilised within the first 2 IL layers and then $[C_2]$ mbar s of CO₂ per IL layer for subsequent IL layers. θ_{IL} is the total IL coverage (number of IL layers).

of CO₂ stabilised within a given region (in mbar s) being found from the multiple of the concentration and the layer thickness. By using fig. 6.5 the total amount of CO₂ stabilised within the θ_{IL} layers of IL, for a given dose pressure, can be found to be:

$$\text{Total CO}_2 \text{ stabilised (mbar s)} = 2[C_1] + (\theta_{IL} - 2)[C_2] \quad \text{Equation 6.1}$$

Assuming that $[C_2] = k[C_1]$, where k is a constant, then eq 6.1 becomes:

$$\text{Total CO}_2 \text{ stabilised (mbar s)} = [C_1](2 + k(\theta_{IL} - 2)) \quad \text{Equation 6.2}$$

For an equation describing the amount of CO₂ stabilised per IL layer, eq 6.2 can be divided by the IL coverage, θ_{IL} :

$$\text{CO}_2 \text{ stabilised per IL layer (mbar s)} = \frac{[C_1](2 + k(\theta_{IL} - 2))}{\theta_{IL}} \quad \text{Equation 6.3}$$

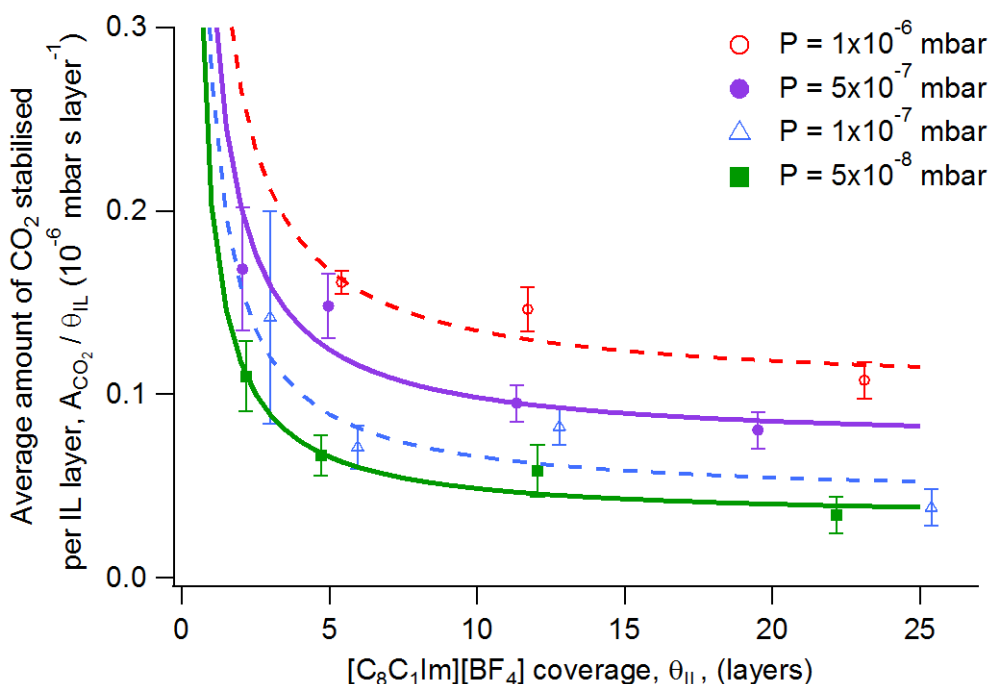


Figure 6.6: Experimental data for the average amount of CO₂ stabilised within a [C₈C₁Im][BF₄] layer (see section 5.3.2 for data) as a function of IL layer thickness, for the different pressures studied. Experimental data points (not the IL coverage corrected values) are shown as markers with lines representing fits of the form given in eq 6.3. The data clearly shows that increasing the pressure of CO₂ used during dosing increases the amount of CO₂ stabilised per IL layer.

The average amount of CO₂ stabilised per IL layer can be plotted as a function of the amount of IL dosed onto the surface, which will allow the experimental data to be fitted by the model in eq 6.3. This has been performed for the [C₈C₁Im][BF₄]-CO₂ coadsorption data (from table 5.1 in section 5.3.2) in fig. 6.6, where it can be seen from the least squares fits to the experimental data points that the average amount of CO₂ stabilised per IL layer decreases as the IL coverage increases. A clear trend can also be seen in the best fit lines,

Table 6.3: A table of all the fitting parameters, from eq 6.3 for the two IL-CO₂ systems studied here, as described in the main text. The fitting parameters correspond to the fits shown by the line in figs. 6.6 and 6.7. Errors in the [C₁] and *k* values come direct from the least squares fitting whilst errors in [C₂] have been calculated by multiplying the value of [C₁] by the error in *k*.

CO ₂ dose pressure (mbar)	[C ₈ C ₁ Im][BF ₄]			[C ₈ C ₁ Im][Tf ₂ N]		
	[C ₁] (10 ⁻⁶ mbar s per IL layer)	<i>k</i>	[C ₂] (= <i>k</i> × [C ₁]) (10 ⁻⁶ mbar s per IL layer)	[C ₁] (10 ⁻⁶ mbar s per IL layer)	<i>k</i>	[C ₂] (= <i>k</i> × [C ₁]) (10 ⁻⁶ mbar s per IL layer)
1×10 ⁻⁶	0.27 ± 0.03	0.38 ± 0.08	0.10 ± 0.02	0.24 ± 0.04	0.57 ± 0.13	0.14 ± 0.02
5×10 ⁻⁷	0.20 ± 0.03	0.36 ± 0.09	0.07 ± 0.02	0.26 ± 0.04	0.38 ± 0.10	0.10 ± 0.02
2×10 ⁻⁷	—	—	—	0.14 ± 0.06	0.53 ± 0.30	0.07 ± 0.03
1×10 ⁻⁷	0.16 ± 0.04	0.27 ± 0.14	0.04 ± 0.02	0.12 ± 0.08	0.60 ± 0.51	0.07 ± 0.06
5×10 ⁻⁸	0.12 ± 0.02	0.27 ± 0.11	0.03 ± 0.01	0.18 ± 0.07	0.20 ± 0.14	0.04 ± 0.01

showing that as the CO₂ dose pressure used during coadsorption is increased, the average amount of CO₂ stabilised per IL layer also increases, as is predicted by Henry's law. Similar fits, using the model in eq 6.3, have been applied to the experimental data points for [C₈C₁Im][Tf₂N] coadsorptions, shown in fig. 6.7. The fits to the experimental data for [C₈C₁Im][Tf₂N] do not form as nicely nested plots as is the case for [C₈C₁Im][BF₄], but when looking at the larger IL coverages the same trend with CO₂ pressure is observed, where having a higher pressure of CO₂ used during coadsorption leads to a greater quantity of CO₂ stabilised per IL layer. In both cases the fitting used the errors in the CO₂ peak areas in the weighting coefficients in the fits, meaning that points with larger errors are trusted less in the least squares fitting procedure. The fitting parameters for both IL–CO₂ systems are shown in table 6.3, where it can be seen that all of the k values are less than one. This confirms that the amount of CO₂ stabilised in the layers closest to the gold surface is greater than the amount of CO₂ captured by every other layer of IL.

Considering the '[C₈C₁Im][BF₄]' column in table 6.3 it can be seen that the fitting parameters [C_1] and [C_2] are larger for higher CO₂ dose pressures, as

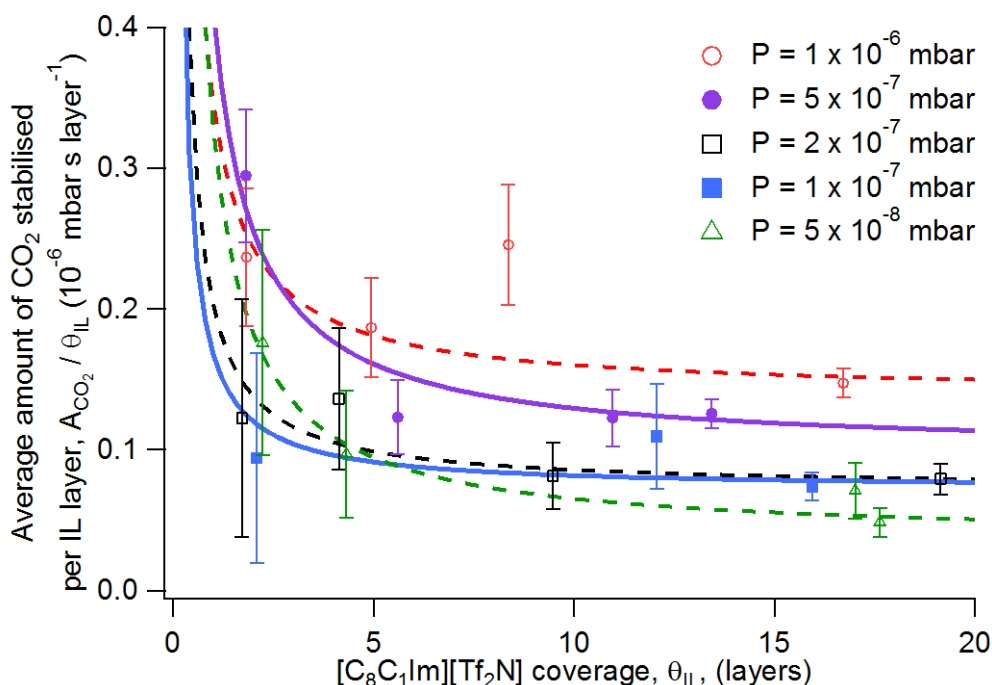


Figure 6.7: Experimental data for the average amount of CO₂ stabilised within a [C₈C₁Im][Tf₂N] layer as a function of IL layer thickness, for the different pressures studied. Experimental data points (not the IL coverage corrected values) are shown as markers with lines representing fits of the form given in eq 6.3. When looking at the fitted lines at higher IL coverages, it can be seen that increasing the pressure of CO₂ used during dosing increases the amount of CO₂ stabilised per IL layer.

expected from the trend observed in fig. 6.6 and Henry's law. Focussing on the values of k for $[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]$ it appears that there is no real trend in the values, with maybe a slight increase in k with increasing pressure. The value k is the fraction of CO_2 captured within the IL multilayers, relative to the first few IL layers, which appears to be constant and smaller than one, supporting the proposed model that CO_2 capture is more efficient in the first few layers than in subsequent IL layers. Thinking about the physical significance of k , one can rationalise that k represents the change in capture efficiency of CO_2 when the surface changes from 'gold with a carbonaceous layer' to that of an IL 'snow'. This constant may be related to factors such as the sticking probability of CO_2 on each of the two surfaces, but should not vary with CO_2 dose pressure as the pressure has no real influence on the gold or the frozen IL structure. It would be reasonable to assume that k will vary if either of the two surfaces (the 'gold with carbonaceous material' or the IL 'snow') were to change, as changing the surface will affect the CO_2 capture efficiency on that surface. It can be seen from table 6.3 that the value range of $0.30 \leq k \leq 0.38$ lies within the errors of all of the fitted k values for $[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]$.

The data for CO_2 captured within $[\text{C}_8\text{C}_1\text{Im}][\text{Tf}_2\text{N}]$ is also shown in table 6.3, where it can again be seen that there is a general increase in the fitted $[C_1]$ and $[C_2]$ parameters as the CO_2 pressure used during dosing is increased. The increase in $[C_2]$ is better behaved than the increase in $[C_1]$ with pressure, which is a consequence of the errors that occur in the experimental data, especially for the lower IL coverages. There is not a k range that is within the error bounds of all the fitted values for the case of $[\text{C}_8\text{C}_1\text{Im}][\text{Tf}_2\text{N}]$, as there was in the case of $[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]$. It is suspected that this is due to the fitting being affected by either or both of the 2 minute dose data points for the pressures 5×10^{-8} mbar and 1×10^{-6} mbar, which are at higher and lower y -positions than expected, respectively. Ignoring these two pressures it can be seen that the range $0.28 \leq k \leq 0.48$ lies within the errors of the other fitted k values for $[\text{C}_8\text{C}_1\text{Im}][\text{Tf}_2\text{N}]$, supporting that idea that k is a constant value and further supporting the proposed model.

Comparing the k ranges for the two IL- CO_2 systems we can see that the ranges are very similar, this is not surprising as the ILs are both very similar, so would be expected to have similar surface structures [26]. Taking the average of

the k ranges for the two ILs gives $k_{\text{ave}}([\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]) = 0.34$ and $k_{\text{ave}}([\text{C}_8\text{C}_1\text{Im}][\text{Tf}_2\text{N}]) = 0.38$. As discussed earlier the k value is expected to change as either the ‘before dosing’ or ‘after dosing’ surfaces are changed, and here the IL is different, affecting the ‘after dosing’ surface. This data appears to suggest that the CO_2 finds it easier to adsorb to the surface of $[\text{C}_8\text{C}_1\text{Im}][\text{Tf}_2\text{N}]$ (larger k_{ave} value) than to the surface of $[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]$. This can be interpreted as being due to either the increased stay time of a given CO_2 molecule on the $[\text{C}_8\text{C}_1\text{Im}][\text{Tf}_2\text{N}]$ surface or as a greater number of surface adsorption sites available in $[\text{C}_8\text{C}_1\text{Im}][\text{Tf}_2\text{N}]$, relative to the $[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]$. The latter argument would be consistent with the fact that larger Henry’s constants are observed for $[\text{C}_8\text{C}_1\text{Im}][\text{Tf}_2\text{N}]$ than $[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]$ [13, 15]. This conclusion is a speculative one, since the k ranges observed are very similar, and are only so if some of the experimental data is ignored (lower pressures for $[\text{C}_8\text{C}_1\text{Im}][\text{Tf}_2\text{N}]$). The fact, however, that the $[\text{C}_2]$ values, the amount of CO_2 stabilised per bulk IL layer, are seen to be larger for the $[\text{C}_8\text{C}_1\text{Im}][\text{Tf}_2\text{N}]$ data than for the $[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]$ data, at all pressures, is in agreement with the Henry’s constants from literature, and is a much more robust argument than the one regarding the k_{ave} values.

6.3.3. CO_2 adsorption within layered $[\text{C}_8\text{C}_1\text{Im}][\text{Tf}_2\text{N}]$ systems

So far CO_2 adsorption, or a lack of, has been studied on the bare gold surface and within the IL $[\text{C}_8\text{C}_1\text{Im}][\text{Tf}_2\text{N}]$ as part of a coadsorbed system, in which the IL and CO_2 are dosed onto the surface simultaneously. Experiments were also performed to see if CO_2 would adsorb onto, and be captured within, the $[\text{C}_8\text{C}_1\text{Im}][\text{Tf}_2\text{N}]$ network for a layered dosing mechanism, similar to the experiments discussed in section 5.3.3 for $[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]$. The minimum surface temperature achievable with the experimental setup discussed was ≈ 90 K, which is below the glass transition temperature for $[\text{C}_8\text{C}_1\text{Im}][\text{Tf}_2\text{N}]$ ($T_g = 189$ K [27, 28]). This enables IL surfaces to be formed as either an IL ‘snow’ (deposition of IL on a 90 K surface) or an IL glass (deposition of IL on a room temperature surface, then cooling to 90 K), with more detail on the different surfaces formed available in section 3.4.3. This allows CO_2 to be dosed onto the

different types of IL surface in an attempt to understand the CO₂ adsorption mechanism further.

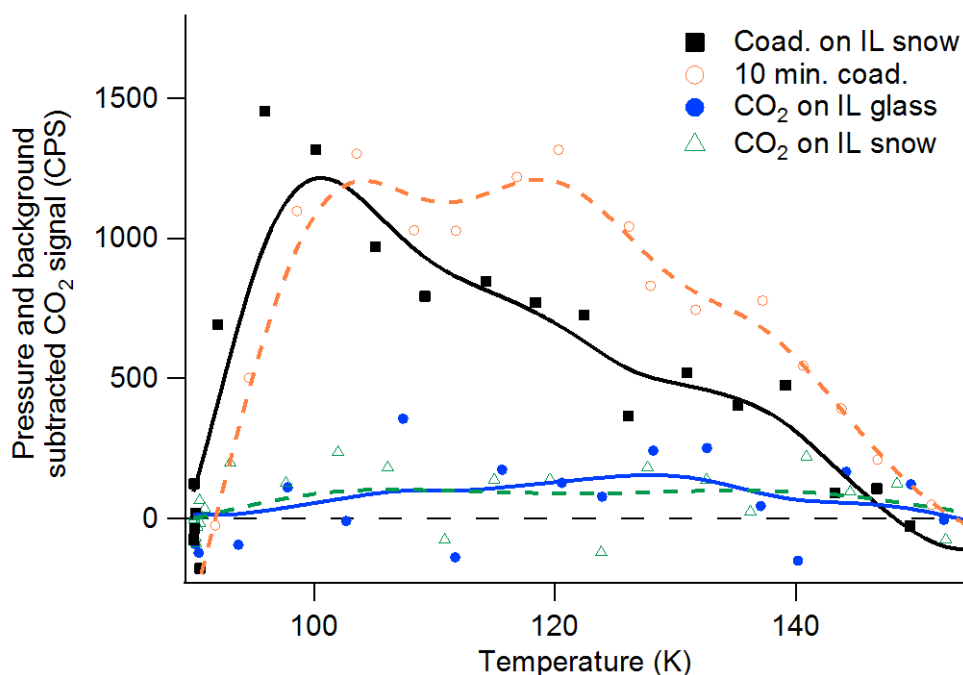


Figure 6.8: Experimental TPD curves, after application of pressure and background subtractions, for CO₂ desorption from different layered structures of CO₂ and [C₈C₁Im][Tf₂N]. Markers represent experimental data points while lines represent smoothing splines to guide the eye through the data. In all cases CO₂ was dosed for 10 minutes at a pressure of 5×10^{-7} mbar, with differences in the data occurring due to the nature of the IL dosing method, as described in the text. The dashed black line represents the zero level for the pressure and background subtracted TPD signal. The heating rate during desorption was approximately 0.67 K s^{-1} .

Separate experiments were performed where the IL was prepared as an IL glass layer and an IL ‘snow’ layer, both approximately ten IL layers thick, before being exposed to 10 minutes of CO₂ at a pressure of 5×10^{-7} mbar. The pressure and background subtracted TPD profiles for these experiments are shown in fig. 6.8, where the glass data shown as the blue filled circles with the blue line and the ‘snow’ data is shown as green open triangles with a dashed green line. There does not seem to be any significant difference between the CO₂ signal observed from the TPD experiments on the IL glass and IL ‘snow’, with both TPD peaks being only slightly above the black dashed zero line (peak areas of 4000 ± 3000 and 4000 ± 2000 counts, respectively). An experiment in which a 10 minute [C₈C₁Im][Tf₂N]–CO₂ coadsorption was performed on top of a five IL layer thick ‘snow’ layer (15 minutes of IL in total with no CO₂ in the bottom 5 layers). This was performed to investigate if doing coadsorption on top of an IL snow affected the quantity of CO₂ stabilised, relative to the 10 minute coadsorption experiment on gold. The data for these experiments are also shown

in fig. 6.8 as the filled black squares with solid black line and open orange circles with dashed orange line, respectively. The comparison of these two data sets shows that a greater quantity of CO₂ is captured if the adsorption is performed on the gold surface (39000 ± 6000 counts) rather than on the IL ‘snow’ surface (31000 ± 2000 counts). This could be due to a combination of factors such as the observation that the CO₂ prefers to adsorb to the gold than the IL ‘snow’ (section 6.3.2) however it is more likely to be a factor relating to the quantity of IL. Despite the fact that the coadsorption time scales are the same, there was a larger quantity of [C₈C₁Im][Tf₂N] deposited during the coadsorption on the gold surface than during the coadsorption on the IL ‘snow’. As a result only the shapes of the TPD profiles can really be compared, and in doing this it can be seen that there is a greater quantity of CO₂ desorbing at lower temperatures for the ‘coadsorption on snow’ data than for the ‘coadsorption on gold’ data. Although there is no significant low temperature TPD peak shown for the CO₂ on [C₈C₁Im][Tf₂N] ‘snow’ experiment (green triangles) it would be expected that any CO₂ stabilised in the surface region of the underlying 5 minute ‘snow’ layer would desorb at a lower temperature, to reflect the fact that the CO₂ is in a poorly coordinated surface state. This effect was seen in the case of CO₂ in layered [C₈C₁Im][BF₄] in section 5.3.3 (fig. 5.7), with the CO₂ on [C₈C₁Im][BF₄] ‘snow’ showing a TPD peak at low temperatures (≈ 90 to 120 K), so it would seem sensible for the same effect to be observed in [C₈C₁Im][Tf₂N]. The lack of any significant CO₂ desorption peak from the [C₈C₁Im][Tf₂N] ‘snow’ could, however, be an indication that the interaction strength between the [C₈C₁Im][BF₄] and the CO₂ is stronger than the interaction between the [C₈C₁Im][Tf₂N] and CO₂. The lack of any significant TPD peak for the CO₂ on the IL glass experiment is also in agreement with the discussion in section 5.3.3 in which it is argued that the IL glass surface is made up of alkyl chains for long chain imidazolium based ILs. Desorption of CO₂ from alkyl chains (octadecanethiol self-assembled monolayers) has been seen in the literature to occur with an activation energy of desorption equal to 17.2 ± 2 kJ mol⁻¹ [29], which is below the activation energy of desorption that can be probed with this experimental setup ($T_{\text{surf}} \approx 90$ K corresponds to $E_{\text{des}} \approx 27$ kJ mol⁻¹).

6.3.4. Comparison of experimental CO₂ signal to the Polanyi–Wigner equation

So far a lot has been discussed about the amount of CO₂ captured by the two ILs studied here, as can be seen in chapters 5 and 6. However, a relatively small amount has been discussed about the type of CO₂ environment that exists in [C₈C₁Im][Tf₂N]. It was seen in the previous chapter (section 5.3.3) that there was not just one single CO₂ binding site within [C₈C₁Im][BF₄] so it can be expected that a range of binding sites for CO₂ will also exist within [C₈C₁Im][Tf₂N]. In order to learn more about the nature of the CO₂–IL interaction the experimental data can be modelled by a sum of CO₂ TPD peaks, each of which is given by the Polanyi–Wigner equation (eq 2.51 [20]). Each of the hypothetical CO₂ environments is modelled by a first order desorption peak ($n = 1$), with the same parameters used as discussed in section 5.3.4 (pre-exponential factor of $A = 10^{13} \text{ s}^{-1}$, heating rate = 0.67 K s^{-1}). The hypothetical CO₂ states do not correspond to known adsorption sites or CO₂ geometries and the E_{des} values of the states have been chosen to vary from 26 kJ mol^{-1} by a multiple of 1.5 kJ mol^{-1} (the same scale as was used for [C₈C₁Im][BF₄] in section 5.3.4). Changes in the activation energy of desorption ranges, as the dosing pressure and IL quantity is varied, allows some suggestions to be made about the nature of the adsorption environments of the CO₂ within the ILs.

The pressure and background subtracted experimental data for the 10 minute, $1 \times 10^{-6} \text{ mbar}$ [C₈C₁Im][Tf₂N]–CO₂ coadsorption, converted to a pressure equivalent by use of eq 5.1, is shown as the pink line in fig. 6.9a. The blue lines represent the first order desorption curves from the equally spaced, hypothetical CO₂ adsorption sites within the IL with the thick black line representing the sum of the individual desorption curves. It can be seen that the width of an individual CO₂ desorption curve (blue) is much thinner than the total CO₂ TPD peak (pink), meaning that multiple CO₂ states are required to model the experimental data. The initial populations of each of the adsorption sites are varied manually until the black curve in fig. 6.9a matches the pink curve, with fig. 6.9b showing the initial populations corresponding to the fit. As discussed

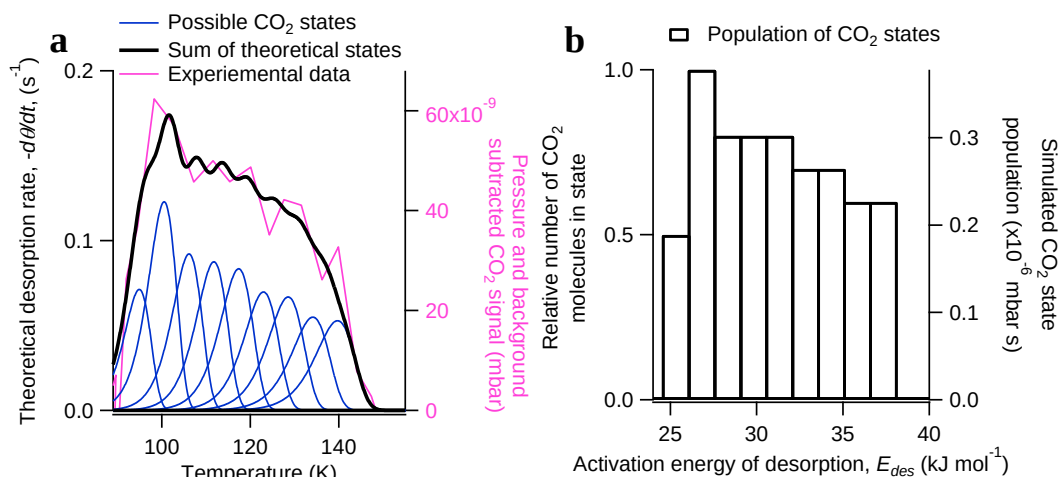


Figure 6.9: An example of the fitting performed to the data, using the 10 minute coadsorption for which $P_{CO_2} = 1 \times 10^{-6}$ mbar, to find the distribution and population of theoretical CO_2 adsorption sites within the $[C_8C_1Im][Tf_2N]$. The plot in (a) shows the experimental data, converted to a pressure (pink line), after it has been fitted to a sum of theoretical states (black line). The individual CO_2 states used in the fitting are also shown (blue). The relative populations of the theoretical CO_2 states, found from the fitting are shown in (b), which has also been converted to a population using the CO_2 peak area. The heating rate during TPD was $0.67\ K\ s^{-1}$.

in section 5.3.4, since the CO_2 coverage could not be calibrated (a monolayer would not form), the initial coverages could only be found using a relative scale (a maximum initial coverage for each site of one was defined for convenience). The relative coverage was then converted to a CO_2 state population, shown in fig. 6.9b, through use of the experimental peak area, the sum of the relative coverages and eq 5.1 (as described in section 5.3.4). The fit shown in fig. 6.9 can be seen to match the experimental data well and is representative of the majority of the fits performed, with fits becoming poorer at lower pressures and coadsorption time scales.

A comparison of the fitted 10 minute, 1×10^{-6} mbar data for a $[C_8C_1Im][Tf_2N]-CO_2$ system in fig. 6.9 and the corresponding data for the $[C_8C_1Im][BF_4]$ system, fig. 5.8, can be performed, provided that it is kept in mind that the IL coverages vary slightly (11.7 ± 1.2 layers for $[C_8C_1Im][BF_4]$ and 8.4 ± 0.8 layers for $[C_8C_1Im][Tf_2N]$). It can be seen that there is a greater experimental desorption signal and larger initial state population seen for CO_2 desorbing from $[C_8C_1Im][Tf_2N]$ than for CO_2 desorption from $[C_8C_1Im][BF_4]$, despite there being less IL on the $[C_8C_1Im][Tf_2N]$ surface. This agrees with the previous observations in this study and the literature values of the Henry's constant, that a greater quantity of CO_2 is captured by the $[C_8C_1Im][Tf_2N]$ than by $[C_8C_1Im][BF_4]$. The data shown in fig. 6.9 shows a greater proportion of CO_2

molecules in lower binding energy sites than were observed in the corresponding $[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]$ case. It can be seen that this appears to be characteristic of the CO_2 adsorption site distribution in $[\text{C}_8\text{C}_1\text{Im}][\text{Tf}_2\text{N}]$. The initial coverages for the hypothetical CO_2 adsorption sites, corresponding to the fits within a 20 minute $[\text{C}_8\text{C}_1\text{Im}][\text{Tf}_2\text{N}]$ layer are shown in fig. 6.10. These results differ to the distribution of adsorption sites within $[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]$, where it was observed that there was a greater quantity of CO_2 molecules captured within high binding energy sites than in low binding energy sites. As expected it can be observed

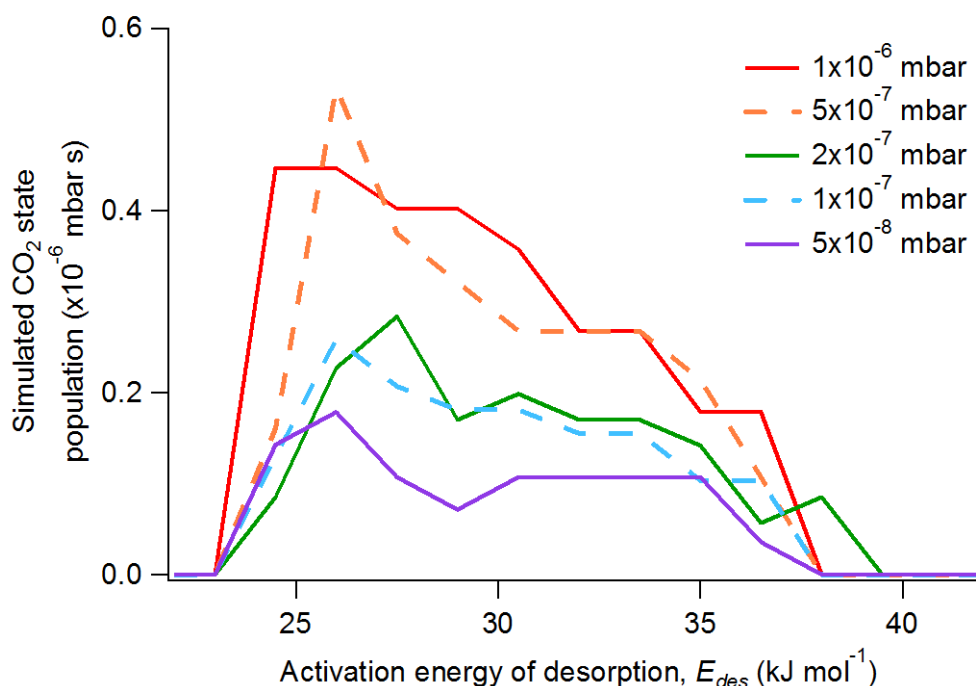


Figure 6.10: Plots showing how the population of CO_2 states with different E_{des} vary as the pressure of CO_2 used during coadsorption with $[\text{C}_8\text{C}_1\text{Im}][\text{Tf}_2\text{N}]$ is varied. Data shown here is for coadsorptions with 20 minutes of IL, where state populations have been calculated from the relative populations found by fitting the TPD peak with a sum of hypothetical CO_2 adsorption sites, as described in the text. The heating rate was assumed to be 0.67 K s^{-1} .

that initial populations of the adsorption sites increases as the CO_2 pressure used during coadsorption increases, with all sites increasing their population with pressure. Fits to the other experimental data have also been performed and the initial population distributions can be found in appendix 8.11. These initial populations also increase with the applied pressure during dosing, again by a similar proportion across the range of desorption sites. Another observation is that the E_{des} profiles for $[\text{C}_8\text{C}_1\text{Im}][\text{Tf}_2\text{N}]$ all appear to have a ‘top-hat’ like distribution, which is different to the ‘double peak’ distribution seen for the $[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]\text{--CO}_2$ coadsorptions.

The range of activation energies of desorption observed for each of the experiments performed have been obtained from the fitting procedure and are given in table 6.4. From table 6.4 it can be seen that the typical range of activation energy of desorption for CO₂ within [C₈C₁Im][Tf₂N] is $24.5 \leq E_{\text{des}} \leq 38.0$ kJ mol⁻¹. Since there was not the ability to form CO₂ multilayers it was not possible to observe a zero order desorption, which would have given a fixed value of the pre-exponential factor, A. Since the E_{des} can be affected by the value of A it is only possible to talk about relative E_{des} values, or stabilisation values,

Table 6.4: Table showing the parameters collected from performing fitting of the experimental TPD peaks with the hypothetical CO₂ adsorption sites within the [C₈C₁Im][Tf₂N]. The average activation energy of desorption has been calculated from a weighted sum, as described in the text. As the fitting of simulated profiles to experimental profiles is judged by the human eye it is difficult to estimate errors for these values, however errors due to noise in the experimental data will be proportionally larger for the lower IL coverages and CO₂ pressures.

CO ₂ dose pressure	Coadsorption dose length	20 minutes (20 layers)	10 minutes (10 layers)	5 minutes (5 IL layers)	2 minutes (2 IL layers)
5×10 ⁻⁸ mbar	E_{des} range (kJ mol ⁻¹)	24.5 – 36.5	24.5 – 38.0	24.5 – 38.0	26.0 – 41.0
	Average E_{des} (kJ mol ⁻¹)	29.6	30.7	30.5	34.3
1×10 ⁻⁷ mbar	E_{des} range (kJ mol ⁻¹)	24.5 – 36.5	24.5 – 41.0	24.5 – 36.5	26.0 – 36.5
	Average E_{des} (kJ mol ⁻¹)	29.8	31.7	29.3	32.2
2×10 ⁻⁷ mbar	E_{des} range (kJ mol ⁻¹)	24.5 – 38.0	24.5 – 38.0	24.5 – 36.5	24.5 – 35.0
	Average E_{des} (kJ mol ⁻¹)	30.3	30.1	30.8	29.0
5×10 ⁻⁷ mbar	E_{des} range (kJ mol ⁻¹)	24.5 – 36.5	26.0 – 38.0	24.5 – 35.0	24.5 – 38.0
	Average E_{des} (kJ mol ⁻¹)	29.6	31.0	30.0	31.5
1×10 ⁻⁶ mbar	E_{des} range (kJ mol ⁻¹)	24.5 – 36.5	24.5 – 36.5	24.5 – 36.5	24.5 – 35.0
	Average E_{des} (kJ mol ⁻¹)	29.3	30.2	31.0	29.7

as the assumptions made about A may be incorrect. The E_{des} range in [C₈C₁Im][Tf₂N] represents a stabilisation of at least 14.5 kJ mol⁻¹, which is less than in the case of [C₈C₁Im][BF₄], which had an upper limit of $E_{\text{des}} = 43$ kJ mol⁻¹ (minimum stabilisation of 18.5 kJ mol⁻¹). The obtained values from this study can be compared to E_{des} values determined experimentally for CO₂ on different surfaces, with typical values ranging from 21 kJ mol⁻¹ on clean Cu(110) [30] to 48.9 kJ mol⁻¹ on a MgO(100) surface [31]. It can be seen that CO₂ can be stabilised by [C₈C₁Im][BF₄] as effectively as on metals and their oxides (see in Table 5 of Ref. [31]), however the most stable site of CO₂ within the ILs is not

as stable as CO₂ within supported polyethylenimine (heat of sorption $\approx 66.1 \text{ kJ mol}^{-1}$) [32]. It is important to stress that nothing is known about the orientation of the CO₂ molecules within the IL, and that the values for the first order CO₂ states were chosen arbitrarily. The results can however be used to make suggestions on the nature of the CO₂–IL interaction.

The difference in the shape of the CO₂ desorption curves between the two ILs studied has been mentioned briefly, but this can be studied in greater detail by looking at the average activation energy of desorption, $E_{\text{des, ave}}$, in table 6.4. As discussed in section 5.3.4 $E_{\text{des, ave}}$ is calculated by taking an average of the E_{des} range, weighted by the initial populations of each state. As a reference, if the initial population were equally distributed across all the states across the typical range for [C₈C₁Im][Tf₂N] (24.5 to 38.0 kJ mol⁻¹) the $E_{\text{des, ave}}$ would be 31.3 kJ mol⁻¹. Values above this indicate that the distribution has a greater quantity of CO₂ stabilised within higher binding energy sites, whilst a lower value represents distributions where the CO₂ is stabilised primarily in low E_{des} sites. The weighted average is very sensitive to the E_{des} range over which the $E_{\text{des, ave}}$ is calculated, so strictly comparisons can only be made with other datasets with the same E_{des} range. Examining table 6.4 it can be seen that the majority of $E_{\text{des, ave}}$ values are equal to or below 31.3 kJ mol⁻¹, suggesting that the [C₈C₁Im][Tf₂N] stabilises the CO₂ in a larger quantity of weakly binding environments. This is in contrast to the binding in [C₈C₁Im][BF₄] where the shapes of the TPD peaks and the $E_{\text{des, ave}}$ values showed that a larger proportion of the CO₂ was stored in sites with higher binding energies. This result could come as a consequence of the difference in anion size between the two ILs. It has been discussed that the CO₂ is likely to bind to the more ionic regions of the IL, so with the larger [Tf₂N]⁻ anion, which will make up more of the IL surface area, there are likely to be a greater number of adsorption sites within the IL than with the smaller [BF₄]⁻ anion. To maximise the solubility of CO₂ within an IL, calculations suggest that the anion should be large and delocalised and the hydrocarbon bulk on the cation must be reduced [33] to promote more interactions of the CO₂ with the charged regions. Other groups, however, have suggested that the hydrocarbon bulk should be increased as this weakens the cation–anion interaction, which reduces the energy penalty for CO₂ squeezing into the structure [4]. Observations in this work suggest that the [BF₄]⁻ anion

has the ability to form stronger interactions with the CO₂ molecules, leading to larger E_{des} values, than the [Tf₂N][−] anion. This finding is supported by a computational study which calculated the [BF₄][−]–CO₂ binding energy to be −21.55 kJ mol^{−1} and the [Tf₂N][−]–CO₂ binding energy to be −15.79 kJ mol^{−1} [4].

The minimum temperature achieved during the [C₈C₁Im][Tf₂N] experiments was lower than during the [C₈C₁Im][BF₄] experiments, meaning that adsorption sites with lower E_{des} were able to be probed. This also means that the experimental peak areas, which have been compared and discussed qualitatively, are not truly comparable. This is due to the fact that there are some low E_{des} CO₂ sites available in the [C₈C₁Im][Tf₂N] studies that were not available for the [C₈C₁Im][BF₄] studies, but may have been able to be filled (which could have increased the amount of CO₂ stabilised). This can be compensated for by using the initial simulated coverages for the state with $E_{\text{des}} = 24.5$ kJ mol^{−1} and subtracting it from the total CO₂ coverage within the [C₈C₁Im][Tf₂N]. The CO₂ coverage of the 24.5 kJ mol^{−1} state is typically $\approx 0.1 \times 10^{-6}$ mbar s for low coadsorption timescales (2 and 5 minutes) or $\approx 0.2 \times 10^{-6}$ mbar s for longer coadsorption timescales (10 and 20 minutes), as can be seen from fig. 6.10 and appendix 8.11. Even if these approximate corrections were applied to the data in table 6.2 (the data shown in this table has not had the population of the lowest CO₂ state subtracted from it but has been corrected for differences in [C₈C₁Im][Tf₂N] coverage) the values would still be larger than the values in table 5.2 (IL coverage corrected values for [C₈C₁Im][BF₄]), in the general case. This indicates there is still a larger quantity of CO₂ stabilised within the [C₈C₁Im][Tf₂N] than the [C₈C₁Im][BF₄], despite the fact that [C₈C₁Im][BF₄] has a larger E_{des} range over which it can stabilise CO₂ (representing a larger possible range of binding environments). This result agrees qualitatively with the Henry's constants in literature, despite the experimental setup not being optimised for this type of measurement. The observations support the argument that solubility and strength of interaction are different quantities, and that just because there is a high solubility of CO₂ within a particular IL, it does not mean that CO₂ will bind to the IL effectively.

Up to this stage the energetics of the CO₂ binding has been discussed in terms of stabilities, relating to the difference in the activation energies of desorption that have been observed within this study, and the E_{des} that is just

below the detectable range for this experimental setup. Literature values for the enthalpy of sublimation for pure CO₂ at 100 K give the value for $\Delta_{\text{sub}}H_{100} = 26.8 \text{ kJ mol}^{-1}$ (this value is within error of both studies) [23, 34]. Using similar arguments to those made for calculating the enthalpy of vaporisation for ILs [18, 35] the enthalpy of sublimation for the CO₂ desorbing from the IL can be found for the data here. Since sublimation is occurring into a vacuum—so a negligible quantity of work is done upon expansion of the CO₂ into the gas phase—the activation energy of desorption, E_{des} , is equal to the change in internal energy for sublimation at the average temperature of desorption, $\Delta_{\text{sub}}U_{T_{\text{ave}}}$ (T_{ave} for CO₂ desorption from [C₈C₁Im][BF₄] was 130 K and 120 K for desorption from [C₈C₁Im][Tf₂N]). The enthalpy can be calculated from the internal energy using the expression $\Delta H = \Delta U + P\Delta V$, the ideal gas law, $P\Delta V = \Delta nRT$, and the knowledge that 1 mole of solid CO₂ will sublime to give 1 mole of CO₂ in the gas phase ($\Delta n = 1$). This gives the expression $\Delta_{\text{sub}}H_{T_{\text{ave}}} = \Delta_{\text{sub}}U_{T_{\text{ave}}} + RT_{\text{ave}}$ which for [C₈C₁Im][BF₄] with $T_{\text{ave}} = 130 \text{ K}$ gives $RT_{\text{ave}} = 1.1 \text{ kJ mol}^{-1}$ and for [C₈C₁Im][Tf₂N] with $T_{\text{ave}} = 120 \text{ K}$ gives $RT_{\text{ave}} = 1.0 \text{ kJ mol}^{-1}$. These values can be used to show that the maximum enthalpy of sublimation for the CO₂ from within [C₈C₁Im][BF₄] is $\Delta_{\text{sub}}H_{130} = 44.1 \text{ kJ mol}^{-1}$ and from within [C₈C₁Im][Tf₂N] is $\Delta_{\text{sub}}H_{120} = 39.0 \text{ kJ mol}^{-1}$. It can be seen that both of the enthalpy values for CO₂ desorption from within the IL are larger than the enthalpy of sublimation of pure CO₂ and represent stabilisation of the CO₂ by 17.3 and 12.2 kJ mol⁻¹ within [C₈C₁Im][BF₄] and [C₈C₁Im][Tf₂N], respectively. To the best of our knowledge there are no literature values for the enthalpies of sublimation of CO₂ from within different ILs (variations of Henry's constants with temperature can give enthalpies of solvation, which involves other processes such as mixing, meaning the results are not directly comparable). Comparisons can be made to a computational study which calculated the [BF₄]⁻–CO₂ binding energy to be $-21.55 \text{ kJ mol}^{-1}$ and the [Tf₂N]⁻–CO₂ binding energy to be $-15.79 \text{ kJ mol}^{-1}$ [4]. The calculation shows that the CO₂ is stabilised by 5.76 kJ mol^{-1} in the [BF₄]⁻ system relative to the [Tf₂N]⁻ system (under the assumption that the contributions to the CO₂ binding from the [C₈C₁Im]⁺ cation will be the same). This result is an agreement with the findings from this study

where it can be seen that the $[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]$ stabilises the CO_2 by 5.1 kJ mol^{-1} relative to $[\text{C}_8\text{C}_1\text{Im}][\text{Tf}_2\text{N}]$.

It was seen in section 5.3.4 that for the $600 \times 10^{-6} \text{ mbar s}$ CO_2 dose during coadsorption the $[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]$ had a capture efficiency of $\approx 0.29\%$, which is close to the capture efficiency observed for $[\text{C}_8\text{C}_1\text{Im}][\text{Tf}_2\text{N}]$ of $\approx 0.34\%$ (CO_2 coverage = $(2.05 \pm 0.36) \times 10^{-6} \text{ mbar s}$, table 6.1). It might have been expected that the capture efficiency of the two ILs would be significantly different to one another, to reflect the observation in the literature that the $[\text{C}_8\text{C}_1\text{Im}][\text{Tf}_2\text{N}]$ has a greater degree of fluorination and a smaller Henry's constant (larger CO_2 solubility). The difference in capture efficiency, and the capture efficiencies themselves, for the two ILs are small, which is probably a consequence of the way in which the surface is prepared. The surface preparation method used here means that the adsorbing CO_2 will probably be interacting with a solid phase IL, rather than a liquid phase IL which would have had the ability to rearrange and maximise favourable interactions with the CO_2 molecule.

6.4. Discussion of the CO_2 adsorption mechanism within imidazolium based ionic liquids

Throughout the CO_2 adsorption work in chapters 5 and 6 there have been some results and assumptions made which elucidate the nature of the CO_2 capture mechanism during coadsorption. It has been seen that the CO_2 does not form multilayers on the gold surface, and that the average amount of CO_2 captured per layer of IL increases with applied CO_2 pressure. This suggests that the surface coverage of the CO_2 could be modelled by a Langmuir isotherm [24, 25], in which the surface coverage increases with gas pressure but saturates at a monolayer. From the shapes of the experimentally observed TPD peaks for different CO_2 dosing pressures it has been seen that the expected behaviour, in which the more stable adsorption sites fill up first, does not occur. Upon adsorption it might be expected that, due to the low activation energy of desorption, the CO_2 would be allowed to diffuse around the surface until it finds a more stable site, from which the energy barrier to diffusion is sufficiently large to prevent further diffusion or the molecule desorbs. This would mean that at low pressures the more stabilised sites would fill up first, then as the applied

CO₂ pressure during dosing was increased the less stable sites would fill up once maximum occupancy of the most stable sites was achieved. The mechanism described (Langmuir–Hinshelwood) is observed in many adsorption studies and is the basis for most heterogeneous catalysis reactions [25, 36], but was not observed in these experiments (the shapes of the E_{des} profiles do not support this mechanism). Since the CO₂ has a sufficiently low activation energy of desorption on the gold or IL ‘snow’ surface it is argued that the amount of time that the CO₂ is adsorbed on the surface is so short that there is not much time for the CO₂ to diffuse around and find the most stable adsorption site. This suggests instead that the adsorption of CO₂ by the IL during coadsorption may be more similar to an Eley–Rideal mechanism [37, 38]. In the Eley–Rideal mechanism a reaction occurs when an incident molecule collides with an adsorbed species to form a new species. For the system discussed here the CO₂ is the species adsorbed on the surface at a particular instant, and the incoming ion pair collides with the adsorbed CO₂ to capture it. In this model the probability of the IL capturing a CO₂ molecule upon coadsorption is related to the surface coverage of CO₂, which can be described by the Langmuir isotherm model. With the assumption that the IL is dosed at a constant rate it can be shown (appendix 8.12) that for a system undergoing Eley–Rideal adsorption kinetics;

$$\frac{1}{\text{CO}_2 \text{ captured per IL layer}} = \frac{1}{k_2} + \frac{K_a}{k_2} \times \frac{1}{P_{\text{CO}_2}} \quad \text{Equation 6.4}$$

where P_{CO_2} is the pressure of CO₂ (mbar), K_a is the Langmuir adsorption isotherm constant (mbar) and k_2 is the rate constant for the adsorption of CO₂ (units of ‘per layer of IL’). The units of CO₂ captured ‘per IL layer’ can be converted to mbar s through the application of eq 5.1. Equation 6.4 can be used to determine the constants associated with Eley–Rideal kinetics, however treating the IL–CO₂ adsorption system with a Langmuir–Hinshelwood model also gives the same linear fit, but with a different interpretation of the constants (appendix 8.13). This means that the linear fit itself does not confirm Eley–Rideal kinetics, but can still be used to obtain useful information. In order to do this the experimental data for the ILs has been used to generate plots of 1/amount of CO₂ per IL layer vs. 1/pressure, with linear fits used to determine the parameters K_a and k_2 . Figure 6.11 shows the linear fits of the form shown in eq

6.4 to the $[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]$ coadsorption data, with the parameters obtained from the fitting shown in table 6.5.

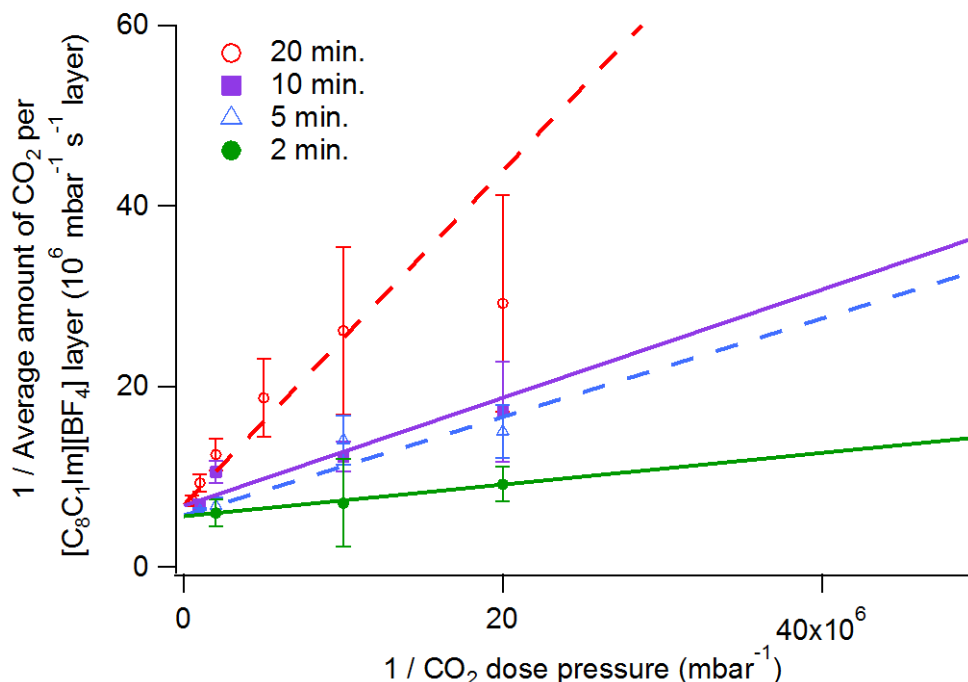


Figure 6.11: Experimental data for the $[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]$ – CO_2 coadsorptions plotted in such a way to determine the constants associated with Eley–Rideal kinetics, as described in the text. Data points are represented by individual markers with the corresponding linear fits represented by lines of the same colour as the markers. For added clarity the 5 minute and 20 minute markers are not filled and have dashed lines representing their fits. Data can generally be seen to be well modelled by linear fits.

Table 6.5: A table showing the fitting parameters corresponding to eq 6.4, for the $[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]$ – CO_2 coadsorptions to test whether Eley–Rideal kinetics are observed for CO_2 capture. The gradients and intercepts (measured directly from the graph) are shown as well as the parameters k_2 and K_a .

Coadsorption length	y-axis intercept ($10^6 \text{ mbar}^{-1} \text{ s}^{-1}$)	k_2 (10^{-6} mbar s)	Gradient (10^6 s^{-1})	K_a (mbar)
20 min.	6.8 ± 0.6	0.15 ± 0.01	$(18.5 \pm 4.4) \times 10^{-7}$	$(27.1 \pm 6.4) \times 10^{-8}$
10 min.	6.8 ± 0.6	0.15 ± 0.01	$(6.0 \pm 1.5) \times 10^{-7}$	$(8.9 \pm 2.2) \times 10^{-8}$
5 min.	5.7 ± 0.3	0.18 ± 0.01	$(5.5 \pm 1.4) \times 10^{-7}$	$(9.6 \pm 2.5) \times 10^{-8}$
2 min.	5.6 ± 1.7	0.18 ± 0.04	$(1.8 \pm 1.4) \times 10^{-7}$	$(3.2 \pm 2.4) \times 10^{-8}$

The $[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]$ coadsorption data appears to be well modelled by the linear fits, with the only major deviation occurring for the 20 minute point corresponding to the lowest pressure. This is a strong indication that Eley–Rideal kinetics are observed for this system, and maybe all CO_2 –IL coadsorptions performed with this method. Studying the values of the fit parameters in table 6.5 it can be seen that the values of k_2 , the rate constants for the capture of CO_2 , are all approximately the same value ($\approx 0.16 \times 10^{-6}$ per IL layer) which seems sensible as there should be no reason why the rate constant

for capturing CO₂ should vary with dose length. Data for the [C₈C₁Im][Tf₂N]–CO₂ coadsorptions has also been plotted in the form of eq 6.4, as shown in fig 6.12. It should be noted that the data points corresponding to the 5 minute, 1×10^{-7} mbar coadsorption (value of $(36 \pm 72) \times 10^6 \text{ mbar}^{-1} \text{ s}^{-1} \text{ layer}$) and 2 minute, 1×10^{-7} mbar coadsorption (value of $(10 \pm 40) \times 10^6 \text{ mbar}^{-1} \text{ s}^{-1} \text{ layer}$) have been removed from the plot as their errors were so large in comparison to all of the other values on the plot. Data points are shown as markers with the linear fits, based on eq 6.4, shown as lines. The fit parameters obtained from the linear fits to the [C₈C₁Im][Tf₂N]–CO₂ coadsorption data are shown in table 6.6. The values of k_2 for [C₈C₁Im][Tf₂N] appear to vary more than the ones for [C₈C₁Im][BF₄] do, and as discussed a variation in k_2 with IL layer thickness would not be expected. Since k_2 should be a constant the average value for [C₈C₁Im][Tf₂N] is $\approx 0.21 \times 10^{-6}$ per IL layer, which can be seen to be larger than the value for [C₈C₁Im][BF₄]. This suggests that the CO₂ is more effectively captured by the [Tf₂N][–] containing IL (a larger rate constant for CO₂ capture is observed), which is in agreement with the CO₂ solubilities and Henry's constants in the literature.

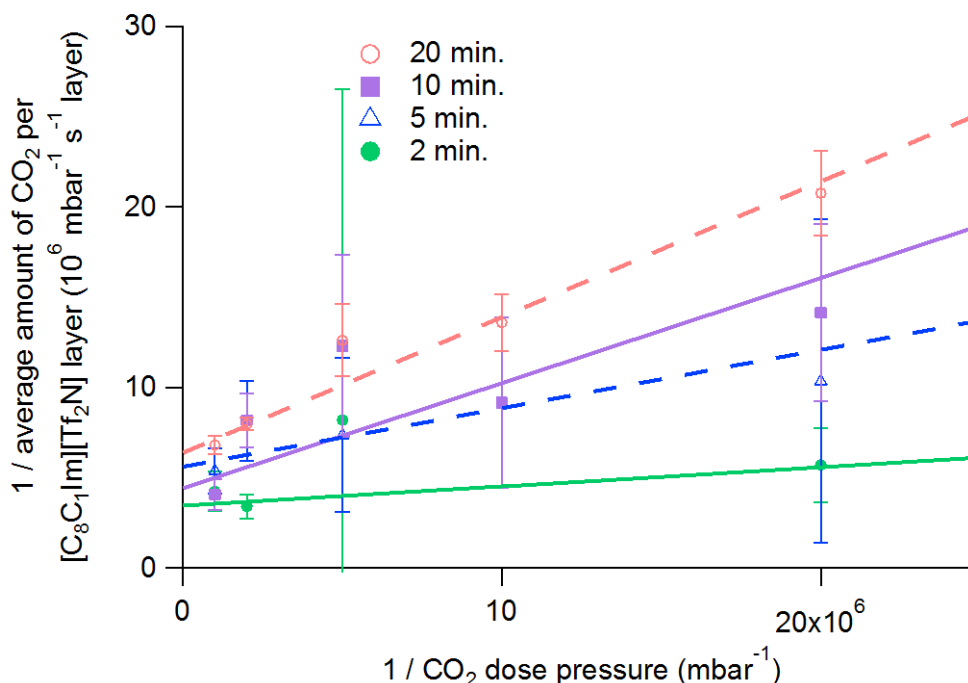
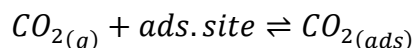


Figure 6.12: Experimental data for the [C₈C₁Im][Tf₂N]–CO₂ coadsorptions plotted in such a way to determine constants for CO₂ capture by the IL assuming Eley–Rideal kinetics, as described in the text. Data points are represented by individual markers with the corresponding linear fits represented by lines of the same colour as the markers. For added clarity the 5 minute and 20 minute markers are not filled and have dashed lines representing their fits. Data can generally be seen to be well modelled by linear fits.

Table 6.6: A table showing the fitting parameters corresponding to eq 6.4, for the $[\text{C}_8\text{C}_1\text{Im}][\text{Tf}_2\text{N}]\text{-CO}_2$ coadsorptions to test whether Eley–Rideal kinetics are observed for CO_2 capture. The gradients and intercepts (measured directly from the graph) are shown as well as the parameters k_2 and K_a .

Coadsorption length	y-axis intercept ($10^6 \text{ mbar}^{-1} \text{ s}^{-1}$)	k_2 (10^{-6} mbar s)	Gradient (10^6 s^{-1})	K_a (mbar)
20 min.	6.4 ± 0.4	0.157 ± 0.008	$(7.5 \pm 1.1) \times 10^{-7}$	$(11.8 \pm 1.7) \times 10^{-8}$
10 min.	4.4 ± 0.8	0.22 ± 0.04	$(5.8 \pm 2.4) \times 10^{-7}$	$(13.3 \pm 5.3) \times 10^{-8}$
5 min.	5.6 ± 1.3	0.18 ± 0.03	$(3.2 \pm 4.4) \times 10^{-7}$	$(5.8 \pm 7.9) \times 10^{-8}$
2 min.	3.4 ± 0.6	0.29 ± 0.05	$(1.1 \pm 1.1) \times 10^{-7}$	$(3.1 \pm 3.2) \times 10^{-8}$

Regarding the K_a values, the Langmuir adsorption isotherm constants, in tables 6.5 and 6.6 slight variations are seen as the amount of IL dosed during the coadsorption varies. The general trend shows that K_a increases as the coadsorption timescale increases. Thinking about the origin of the constant K_a , it can be seen that K_a represents the inverse of the equilibrium constant for the adsorption reaction [25];



so can be thought of as the equilibrium constant for the desorption reaction. It would make sense that the equilibrium constant for the desorption reaction would increase with IL coverage if the more favourable gold surface is being covered up and replaced with $[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]$ ‘snow’. Notice from the magnitude of the K_a values ($\approx 10^{-8}$) that the equilibrium lies a long way to the adsorbed CO_2 side (if K_a is the equilibrium constant for the forwards going desorption reaction). Comparing the K_a values for the two ILs studied here it can be seen that the values in $[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]$ appear to be slightly larger than those observed in $[\text{C}_8\text{C}_1\text{Im}][\text{Tf}_2\text{N}]$. This suggests that the CO_2 coverage on the $[\text{C}_8\text{C}_1\text{Im}][\text{Tf}_2\text{N}]$ surface will be higher than the CO_2 coverage on $[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]$ at any given CO_2 pressure, aiding in capturing a larger quantity of CO_2 .

An Eley–Rideal mechanism can aid in the explanation of why the CO_2 capture efficiencies in this study are so low (observed to be $\approx 0.3\%$). In order for the CO_2 to be captured the incoming ion pair must hit the adsorbed CO_2 in the correct orientation. Using the Langmuir adsorption isotherm (eq 8.6) with an approximate value for $K_a \approx 10 \times 10^{-8}$ it can be seen that the surface coverage of CO_2 at a pressure of $1 \times 10^{-6} \text{ mbar}$ on $[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]$ is about 0.91 and has a Gibbs free energy of desorption of $\approx 12 \text{ kJ mol}^{-1}$ (using $\Delta G = -RT \ln(K_a)$ at $T = 90 \text{ K}$, meaning the Gibbs free energy of adsorption is -12 kJ mol^{-1}). With such a large surface coverage of CO_2 it may be surprising that a greater quantity is

not captured by the incoming ion pair. It is thought that the efficiency of capture is highly dependent upon the orientation of the incoming ion pair as well as the temperature of the incoming IL molecule (which is ≈ 500 K from being evaporated). This means that the IL molecule comes in with $RT \approx 4.1$ kJ mol⁻¹, which may be enough to disperse weakly bound CO₂ from the surface, affecting the capture efficiency.

The IL orientation effect may explain why the [C₈C₁Im][Tf₂N] has a larger rate constant (k_2) for the capture of CO₂, as there is a larger ionic area due to the larger [Tf₂N]⁻ anion present than in [C₈C₁Im][BF₄]. This issue is unique to the experimental setup used here (cooled surface with frozen IL), as in liquid studies the IL can rearrange to accommodate the CO₂ molecule, whereas in this study the binding sites available are determined statistically. The benefit of this method is that the whole range of possible binding sites will be probed, which allows the nature of the IL–CO₂ binding to be better understood. The ionic area can be tuned through choice of ions so experiments with a [C₂C₁Im]⁺ cation may be expected to show slightly higher capture efficiencies due to the greater ionic area and therefore larger ‘reaction’ cross section for CO₂ capture.

6.5. Relating observed exposures (mbar s) to number of CO₂ layers

Over the previous two chapters the quantity of CO₂ stabilised has been discussed in terms of an exposure equivalent of ‘mbar s’, or ‘metric Langmuir’ which is 10⁻⁶ mbar s. As has been discussed in detail, this was due to the fact that CO₂ did not form multilayers on the gold surface studied here, so a monolayer calibration using TPD could not be performed. This meant that the experimental signal could not be related to an absolute number of CO₂ layers. The amount of ‘mbar s’ of CO₂ can be converted to a number of CO₂ layers if some approximations are made. It can be seen, from the kinetic theory of gases, that the rate of gas molecules colliding with a surface, Z_{wall} , can be given by [25]

$$Z_{\text{wall}} = \frac{P}{\sqrt{2\pi mk_B T}} \quad \text{Equation 6.5}$$

where P is the applied pressure of the gas (Pa), m is the mass of an individual gas molecule (kg), k_B is the Boltzmann constant (1.38×10^{-23} J K⁻¹) and T the gas temperature (K). Given that the area of the surfaces studied in this project were

$\approx 1 \text{ cm}^2 = 10^{-4} \text{ m}^2$ (see section 3.2) and the mass of a CO_2 molecule is $\approx 7.308 \times 10^{-26} \text{ kg}$ (molecular weight ($44.01 \times 10^{-3} \text{ kg}$) divided by Avogadro's constant) the number of CO_2 molecules that hit the surface due to 1 mbar s of exposure can be found. Noting that 1 mbar = 100 Pa and assuming the gas temperature is around room temperature ($\approx 300 \text{ K}$), the number of molecules (n_{area}) hitting a given area (a) in a given time (t) can be given by:

$$n_{\text{area}} = Z_{\text{wall}} a t \quad \text{Equation 6.6}$$

It can be seen that for a 1 mbar s exposure 2.294×10^{20} CO_2 molecules hit the 1 cm^2 surface, or are released from the surface, if looking at a 1 mbar s exposure equivalent during desorption. To convert the number of molecules into a number of layers the density of solid CO_2 is required (1663.0 kg m^{-3} at 90.15 K [39, 40]) then using the fact that the mass of 1 mole of CO_2 is $44.01 \times 10^{-3} \text{ kg}$ the molar volume of CO_2 can be found to be $V_m = 2.646 \times 10^{-5} \text{ m}^3$. The volume of 1 CO_2 molecule will be the molar volume divided by Avogadro's number giving a molecular volume of $4.395 \times 10^{-29} \text{ m}^3$. Under the assumption that the CO_2 molecule is a cube it can be rationalised that each CO_2 molecule will take up a surface area of $12.45 \times 10^{-20} \text{ m}^2$ (molecular volume cube rooted, then squared). As mentioned the gold surface had an area of $1 \times 10^{-4} \text{ m}^2$, so the number of CO_2 molecules that could fit on the gold surface (the surface area divided by the molecular area) is 8.03×10^{14} CO_2 molecules. This is an approximation of the number of CO_2 molecules within 1 layer on the surface.

Using this value and the number of molecules desorbing from the surface for 1 mbar s it is possible to find a conversion factor from mbar s to layers of CO_2 . Doing this gives the relationship $1 \text{ mbar s} = 2.857 \times 10^5$ molecular layers of CO_2 , or in terms of the 'metric Langmuir'; $1 \times 10^{-6} \text{ mbar s} = 0.2857$ layers of CO_2 . This conversion factor can be used to see that the 20 minute $[\text{C}_8\text{C}_1\text{Im}][\text{Tf}_2\text{N}]-\text{CO}_2$ coadsorption with a pressure of $1 \times 10^{-6} \text{ mbar}$ stabilised $(2.95 \pm 0.21) \times 10^{-6} \text{ mbar s}$ (table 6.2) or 0.84 ± 0.06 layers of CO_2 within 20 layers of IL. Using the same procedure as for the CO_2 calculation, assuming the ion pair can be approximated as cubic in shape, but using the molar volume of $[\text{C}_8\text{C}_1\text{Im}][\text{Tf}_2\text{N}] = 0.359 \times 10^{-3} \text{ m}^3 \text{ mol}^{-1}$ [18] it can be seen that one layer of IL is comprised of 1.412×10^{14} ion pairs. These numbers can then be used to find the average coordination number of the CO_2 by taking the ratio of the number of IL molecules in a layer to the number of CO_2 molecules in a layer. This means

that in the 20 minute, 1×10^{-6} mbar experiment each CO₂ is coordinated by 4.2 ± 0.3 [C₈C₁Im][Tf₂N] ion pairs, on average ((20 IL layers $\times$ 1.412×10^{14} molecules per IL layer) $\div$ (0.84 CO₂ layers $\times$ 8.03×10^{14} molecules per CO₂ layer)).

Studying instead at the 20 minute, 1×10^{-6} mbar CO₂ coadsorption for [C₈C₁Im][BF₄] it can be seen that 20 layers of IL stabilise $(2.15 \pm 0.20) \times 10^{-6}$ mbar s (table 5.2) or 0.61 ± 0.06 layers of CO₂. Using the molar volume of [C₈C₁Im][BF₄] = $0.255 \times 10^{-3} \text{ m}^3 \text{ mol}^{-1}$ [18] and assuming each ion pair can be modelled as cubic in shape it is found that there are 1.774×10^{14} ion pairs per layer. In a similar way to the case for [C₈C₁Im][Tf₂N] it can be seen that each CO₂ molecule is coordinated by 7.2 ± 0.6 [C₈C₁Im][BF₄] ion pairs, on

Table 6.7: A table of all the collected experimental data for both the [C₈C₁Im][BF₄]-CO₂ and [C₈C₁Im][Tf₂N]-CO₂ coadsorptions, showing the number of layers of CO₂ captured in each experiment and the average coordination number for each CO₂ molecule, with errors. White rows show the total amount of CO₂ captured by the ILs in units of layers of CO₂, using the calculations shown in the main text. Light grey rows show the average coordination number for a CO₂ molecule that is the average number of ion pairs per CO₂ molecule captured. Smaller average coordination numbers are an indication of more efficient CO₂ capture by the ionic liquid.

CO ₂ dose pressure	Coadsorption length	20 minutes	10 minutes	5 minutes	2 minutes
[C ₈ C ₁ Im][BF ₄]					
2×10^{-8} mbar	Layers of CO ₂	—	0.07 ± 0.02	—	—
	Coordination	—	32 ± 6	—	—
5×10^{-8} mbar	Layers of CO ₂	0.20 ± 0.06	0.17 ± 0.04	0.09 ± 0.01	0.06 ± 0.01
	Coordination	22 ± 5	13 ± 3	12 ± 2	7 ± 1
1×10^{-7} mbar	Layers of CO ₂	0.22 ± 0.06	0.23 ± 0.03	0.10 ± 0.02	0.08 ± 0.03
	Coordination	20 ± 4	9 ± 1	11 ± 2	6 ± 2
2×10^{-7} mbar	Layers of CO ₂	0.31 ± 0.06	—	—	—
	Coordination	14 ± 2	—	—	—
5×10^{-7} mbar	Layers of CO ₂	0.46 ± 0.06	0.27 ± 0.03	0.21 ± 0.03	0.10 ± 0.02
	Coordination	10 ± 1	8.1 ± 0.8	5.2 ± 0.6	4.5 ± 0.8
1×10^{-6} mbar	Layers of CO ₂	0.61 ± 0.06	0.42 ± 0.03	0.23 ± 0.01	0.06 ± 0.03
	Coordination	7.2 ± 0.6	5.3 ± 0.4	4.8 ± 0.2	7 ± 2
2×10^{-6} mbar	Layers of CO ₂	0.78 ± 0.06	—	—	—
	Coordination	5.7 ± 0.4	—	—	—
[C ₈ C ₁ Im][Tf ₂ N]					
5×10^{-8} mbar	Layers of CO ₂	0.28 ± 0.03	0.20 ± 0.05	0.14 ± 0.06	0.10 ± 0.03
	Coordination	13 ± 1	9 ± 2	6 ± 2	3.5 ± 0.7
1×10^{-7} mbar	Layers of CO ₂	0.42 ± 0.04	0.31 ± 0.11	0.04 ± 0.3	0.05 ± 0.04
	Coordination	8.4 ± 0.8	6 ± 1	22 ± 9	6 ± 3
2×10^{-7} mbar	Layers of CO ₂	0.45 ± 0.06	0.23 ± 0.07	0.19 ± 0.07	0.07 ± 0.05
	Coordination	7.7 ± 0.9	8 ± 2	5 ± 1	5 ± 2
5×10^{-7} mbar	Layers of CO ₂	0.72 ± 0.03	0.35 ± 0.05	0.17 ± 0.04	0.17 ± 0.03
	Coordination	4.9 ± 0.2	5.0 ± 0.7	5.0 ± 0.9	2.1 ± 0.3
1×10^{-6} mbar	Layers of CO ₂	0.84 ± 0.06	0.70 ± 0.12	0.27 ± 0.04	0.13 ± 0.03
	Coordination	4.2 ± 0.3	2.5 ± 0.4	3.3 ± 0.5	2.6 ± 0.5

average $((20 \text{ IL layers} \times 1.774 \times 10^{14} \text{ molecules per IL layer}) \div (0.614 \text{ CO}_2 \text{ layers} \times 8.03 \times 10^{14} \text{ molecules per CO}_2 \text{ layer}))$. Table 6.7 shows the total number of layers of CO₂ captured by each IL experiment and the average coordination numbers for CO₂ for each of the coadsorption experiments performed in this study for each of the ILs. It can be seen that the coordination number ranges from 2.5 to 20, depending on the experimental conditions used. Smaller coordination numbers accompany the higher pressure and shorter timescale coadsorptions, which is consistent with the other findings in this study. In all cases the CO₂ coordination numbers for the [C₈C₁Im][Tf₂N] experiments are smaller than the coordination numbers for the [C₈C₁Im][BF₄]. This result suggests that the [C₈C₁Im][Tf₂N] is able to interact with CO₂ molecules in a larger variety of ways, meaning that the orientation of the ion pair in relation to the CO₂ molecule is not as important as it is for [C₈C₁Im][BF₄]. The larger coordination number for the [C₈C₁Im][BF₄] indicates that only 1 in every 7.2 ion pairs arrives at an adsorbed CO₂ on the surface in a correct orientation to bind, whereas there is almost double the chance that a [C₈C₁Im][Tf₂N] ion pair will arrive in a correct orientation. This suggests a stronger, more directional interaction between the CO₂ and the [C₈C₁Im][BF₄], which would explain the observations in the E_{des} and $\Delta_{\text{sub}}H$ ranges, that the CO₂ is more stabilised within the [C₈C₁Im][BF₄] than in the [C₈C₁Im][Tf₂N].

The coordination number, defined as the number of IL molecules per CO₂ molecule can also be used to calculate the mole fraction of CO₂ within the IL, defined as the number of moles of CO₂ within one mole of the IL–CO₂ coadsorbed mixture. Working out the mole fraction, noticing that the Avogadro's constants cancel out, gives an expression in terms of the number of molecules of IL (*no. IL*) and CO₂ (*no. CO₂*), as:

$$x_{\text{CO}_2} = \frac{N_A \times \text{no. CO}_2}{N_A \times \text{no. CO}_2 + N_A \times \text{no. IL}} = \frac{\text{no. CO}_2}{\text{no. CO}_2 + \text{no. IL}} \quad \text{Equation 6.7}$$

From the definition of the coordination number then if *no. CO₂* is taken to be 1, then *no. IL* is equal to the coordination number, giving that the mole fraction can be worked out as:

$$x_{\text{CO}_2} = \frac{1}{1 + \text{coordination number}} \quad \text{Equation 6.8}$$

This then allows Henry's constants to be estimated for the CO₂ within the IL at 88 K (the temperature at which the CO₂ was captured), recalling that:

$$H_{CO_2} = \frac{P_{CO_2}}{x_{CO_2}} = P_{CO_2} \times (1 + \text{coordination number}) \quad \text{Equation 6.9}$$

It can be seen that, due to the low pressure values and low temperatures, the Henry's constants at 88 K are all of the order 10^{-6} mbar or 10^{-9} bar, indicating very high solubilities, relative to ≈ 300 K (where the Henry's constants are 54 ± 3 bar for $[C_8C_1Im][BF_4]$ [15] and 30 ± 1 bar for $[C_8C_1Im][Tf_2N]$ [13]). This is rationalised by the fact that the temperature is much lower for the Henry's constants from this work. It can be seen that the ratio of the Henry's constants at 300 K is 1.8:1 ($[C_8C_1Im][BF_4]:[C_8C_1Im][Tf_2N]$), and using the values of coordination number in table 6.7 the ratio of "coordination number + 1" values for the two ILs can be seen to agree with the 1.8:1 value. This suggests that the CO_2 is approximately twice as soluble in the $[C_8C_1Im][Tf_2N]$ as it is in the $[C_8C_1Im][BF_4]$ at 300 K and 88 K. Despite the fact that this experimental setup was not designed to be able to measure the Henry's constants of the CO_2 within the two ILs studied here, the fact that the experimentally observed ratio agrees with the ratio for literature values is a strong indication that the experiments undertaken in this study are consistent with the literature and can be trusted.

6.6. References

- [1] Muldoon, M.J., Aki, S., Anderson, J.L., Dixon, J.K. and Brennecke, J.F., Improving carbon dioxide solubility in ionic liquids. *J. Phys. Chem. B*, **2007**, (111), pp. 9001-9009.
- [2] Anthony, J.L., Anderson, J.L., Maginn, E.J. and Brennecke, J.F., Anion effects on gas solubility in ionic liquids. *J. Phys. Chem. B*, **2005**, (109), pp. 6366-6374.
- [3] Cadena, C., Anthony, J.L., Shah, J.K., Morrow, T.I., Brennecke, J.F. and Maginn, E.J., Why is CO_2 so soluble in imidazolium-based ionic liquids?, *J. Am. Chem. Soc.*, **2004**, (126), pp. 5300-5308.
- [4] Damas, G.B., Dias, A.B.A. and Costa, L.T., A Quantum Chemistry Study for Ionic Liquids Applied to Gas Capture and Separation. *J. Phys. Chem. B*, **2014**, (118), pp. 9046-9064.
- [5] Bara, J.E., Carlisle, T.K., Gabriel, C.J., Camper, D., Finotello, A., Gin, D.L. and Noble, R.D., Guide to CO_2 Separations in Imidazolium-Based Room-Temperature Ionic Liquids. *Ind. Eng. Chem. Res.*, **2009**, (48), pp. 2739-2751.
- [6] Makino, T., Kanakubo, M., Masuda, Y. and Mukaiyama, H., Physical and CO_2 -Absorption Properties of Imidazolium Ionic Liquids with Tetracyanoborate and Bis(trifluoromethanesulfonyl)amide Anions. *J. Solution Chem.*, **2014**, (43), pp. 1601-1613.

- [7] Hou, Y. and Baltus, R.E., Experimental measurement of the solubility and diffusivity of CO₂ in room-temperature ionic liquids using a transient thin-liquid-film method. *Ind. Eng. Chem. Res.*, **2007**, (46), pp. 8166-8175.
- [8] Anderson, J.L., Dixon, J.K. and Brennecke, J.F., Solubility of CO₂, CH₄, C₂H₆, C₂H₄, O₂, and N₂ in 1-hexyl-3-methylpyridinium bis(trifluoromethylsulfonyl)imide: Comparison to other ionic liquids. *Acc. Chem. Res.*, **2007**, (40), pp. 1208-1216.
- [9] Liu, H., Dai, S. and Jiang, D.E., Molecular Dynamics Simulation of Anion Effect on Solubility, Diffusivity, and Permeability of Carbon Dioxide in Ionic Liquids. *Ind. Eng. Chem. Res.*, **2014**, (53), pp. 10485-10490.
- [10] Liu, H., Dai, S. and Jiang, D.-e., Solubility of Gases in a Common Ionic Liquid from Molecular Dynamics Based Free Energy Calculations. *J. Phys. Chem. B*, **2014**, (118), pp. 2719-2725.
- [11] Zahn, S., *et al.*, Understanding ionic liquids from theoretical methods. *J. Mol. Liq.*, **2014**, (192), pp. 71-76.
- [12] Hu, Y.F., Liu, Z.C., Xu, C.M. and Zhang, X.M., The molecular characteristics dominating the solubility of gases in ionic liquids. *Chem. Soc. Rev.*, **2011**, (40), pp. 3802-3823.
- [13] Baltus, R.E., Culbertson, B.H., Dai, S., Luo, H.M. and DePaoli, D.W., Low-pressure solubility of carbon dioxide in room-temperature ionic liquids measured with a quartz crystal microbalance. *J. Phys. Chem. B*, **2004**, (108), pp. 721-727.
- [14] Watanabe, M., Kodama, D., Makino, T. and Kanakubo, M., CO₂ absorption properties of imidazolium based ionic liquids using a magnetic suspension balance. *Fluid Phase Equilibria*, **2016**, (420), pp. 44-49.
- [15] Zhang, J., Zhang, Q., Qiao, B. and Deng, Y., Solubilities of the gaseous and liquid solutes and their thermodynamics of solubilization in the novel room-temperature ionic liquids at infinite dilution by gas chromatography. *J. Chem. Eng. Data*, **2007**, (52), pp. 2277-2283.
- [16] Chen, Y.H., Zhang, S.J., Yuan, X.L., Zhang, Y.Q., Zhang, X.P., Dai, W.B. and Mori, R., Solubility of CO₂ in imidazolium-based tetrafluoroborate ionic liquids. *Thermochim. Acta*, **2006**, (441), pp. 42-44.
- [17] Holloczki, O., Kelemen, Z., Koenczoel, L., Szieberth, D., Nyulaszi, L., Stark, A. and Kirchner, B., Significant Cation Effects in Carbon Dioxide Ionic Liquid Systems. *Chemphyschem*, **2013**, (14), pp. 315-320.
- [18] Armstrong, J.P., Hurst, C., Jones, R.G., Licence, P., Lovelock, K.R.J., Satterley, C.J. and Villar-Garcia, I.J., Vapourisation of ionic liquids. *Phys. Chem. Chem. Phys.*, **2007**, (9), pp. 982-990.
- [19] Deyko, A., Lovelock, K.R.J., Licence, P. and Jones, R.G., The vapour of imidazolium-based ionic liquids: a mass spectrometry study. *Phys. Chem. Chem. Phys.*, **2011**, (13), pp. 16841-16850.
- [20] Kolasinski, K.W., *Surface Science: Foundations of Catalysis and Nanoscience*. Eds., John Wiley & Sons, Chichester, UK, (2012)
- [21] Freire, M.G., Neves, C., Marrucho, I.M., Coutinho, J.A.P. and Fernandes, A.M., Hydrolysis of Tetrafluoroborate and Hexafluorophosphate Counter Ions in Imidazolium-Based Ionic Liquids. *J. Phys. Chem. A*, **2010**, (114), pp. 3744-3749.
- [22] Hessey, S.G. and Jones, R.G., Line-of-sight mass spectrometry: principles and practice. *Surf. Interface Anal.*, **2015**, (47), pp. 587-600.

- [23] Bryson, C.E., Cazcarra, V. and Levenson, L.L., Sublimation Rates and Vapour Pressures of H₂O, CO₂, N₂O and Xe. *J. Chem. Eng. Data*, **1974**, (19), pp. 107-110.
- [24] Langmuir, I., The Adsorption of Gases on Plane Surfaces of Glass, Mica and Platinum. *J. Am. Chem. Soc.*, **1918**, (40), pp. 1361-1403.
- [25] Atkins, P. and De Paula, J., *Atkins' Physical Chemistry 8th edition*. Crowe, J., Fiorillo, J. and Hughes, R., Eds., Oxford University Press, Oxford, (2006)
- [26] Santos, C.S. and Baldelli, S., Gas-liquid interface of room-temperature ionic liquids. *Chem. Soc. Rev.*, **2010**, (39), pp. 2136-2145.
- [27] Gharagheizi, F., Keshavarz, M.H., Ilani-Kashkouli, P., Farahani, N. and Tumba, K., A group contribution method for estimation of glass-transition temperature of 1,3-dialkylimidazolium ionic liquids. *J. Therm. Anal. Calorim.*, **2013**, (114), pp. 1363-1382.
- [28] Zhang, S., Lu, X., Zhou, Q., Li, X., Zhang, X. and Li, S., *Ionic Liquids: Physicochemical Properties*. Eds., Elsevier, Amsterdam, (2009)
- [29] Stein, O. and Asscher, M., Adsorption of H₂O, CO₂ and Xe on soft surfaces. *J. Phys. Chem. B*, **2008**, (112), pp. 3955-3962.
- [30] Ernst, K.H., Schlatterbeck, D. and Christmann, K., Adsorption of carbon dioxide on Cu(110) and on hydrogen and oxygen covered Cu(110) surfaces. *Phys. Chem. Chem. Phys.*, **1999**, (1), pp. 4105-4112.
- [31] Burghaus, U., Surface chemistry of CO₂ – Adsorption of carbon dioxide on clean surfaces at ultrahigh vacuum. *Prog. Surf. Sci.*, **2014**, (89), pp. 161-217.
- [32] Wang, X. and Song, C., Temperature-programmed desorption of CO₂ from polyethylenimine-loaded SBA-15 as molecular basket sorbents. *Catal. Today*, **2012**, (194), pp. 44-52.
- [33] Shannon, M.S., Tedstone, J.M., Danielsen, S.P.O., Hindman, M.S., Irvin, A.C. and Bara, J.E., Free Volume as the Basis of Gas Solubility and Selectivity in Imidazolium-Based Ionic Liquids. *Ind. Eng. Chem. Res.*, **2012**, (51), pp. 5565-5576.
- [34] Trusler, J.P.M., Equation of State for Solid Phase I of Carbon Dioxide Valid for Temperatures up to 800 K and Pressures up to 12 GPa. *J. Phys. Chem. Ref. Data*, **2011**, (40), pp. 043105.
- [35] Deyko, A., *et al.*, Measuring and predicting Delta(vap)H₂₉₈ values of ionic liquids. *Phys. Chem. Chem. Phys.*, **2009**, (11), pp. 8544-8555.
- [36] Baxter, R.J. and Hu, P., Insight into why the Langmuir-Hinshelwood mechanism is generally preferred. *J. Chem. Phys.*, **2002**, (116), pp. 4379-4381.
- [37] Eley, D.D. and Rideal, E.K., The catalysis of the parahydrogen conversion by tungsten. *P. Roy. Soc. Lond. A Mat.*, **1941**, (178), pp. 0429-0451.
- [38] Eley, D.D. and Rideal, E.K., Parahydrogen conversion on tungsten. *Nature*, **1940**, (146), pp. 401-402.
- [39] Maass, O. and Barnes, W.H., Some thermal constants of solid and liquid carbon dioxide. *P. R. Soc. Lond. A-ContA*, **1926**, (111), pp. 224-244.
- [40] DETHERM database; We wish to acknowledge the use of the EPSRC funded National Chemical Database Service hosted by the Royal Society of Chemistry, (accessed May 2017)

Chapter 7

Conclusions

7.1 Variable period X-ray Standing wave

The first variable period X-ray standing wave experiments to be performed with photoelectron detection have been used to successfully determine the surface structure of a layered system. VPXSW relies on generation of an XSW that is set up from a reflector surface in the grazing angle regime ($\alpha \approx$ a few degrees), where total external reflection of X-rays occurs. The XSW period (separation between adjacent antinodes) varies as the incident angle is scanned, such that nodes and antinodes sweep through layers adsorbed on top of the reflector. This produces an oscillatory profile in the photoelectron signal, with the angular position and amplitude of the oscillations dependent upon the position and thickness of the adsorbed layer, which can then be compared to a calculated VPXSW profile from a model system. The VPXSW technique has been used previously with X-ray fluorescence detection [1, 2] however this limits the technique to studies in which thin layers of heavy elements (such as zinc [1] and germanium [3]) are present. Photoelectrons bring the advantage of chemical state specificity (using chemical shifts) and an inherent surface sensitivity (due to their short attenuation lengths) allowing a greater quantity of information to be gained from experiments, compared to X-ray fluorescence studies. The short attenuation lengths of photoelectrons does affect the maximum film thickness that can be probed. However photoelectron attenuation lengths can be increased by increasing the X-ray energy, to produce faster photoelectrons, at the cost of a reduction in the X-ray absorption cross section [4].

VPXSW with photoelectron detection was used to probe layered surfaces with thicknesses ranging from 15 Å up to around 230 Å with a resolution of ± 15 Å. VPXSW profiles of a Si(001) crystal with its native oxide layer could be measured by the Si 2p_{bulk}, Si 2p_{oxide} and the O 1s photoelectron peaks, where the substrate and oxide layer were observed to have clearly distinguishable experimental profiles. The calculation for the model VPXSW profiles assumed that the surface was composed of 3 layers (vacuum, SiO_x and Si) and could

successfully model the substrate and oxide layer when a $15 \pm 10 \text{ \AA}$ SiO_x layer on top of the Si reflector was used. The silicon and its native oxide then had a thick $[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]$ ‘snow’ layer adsorbed onto it, with a thin CHCl_3 layer adsorbed on top of the IL. There was also a thin layer of adventitiously adsorbed water from the background gases in the chamber on top of the CHCl_3 . This represented a 6 layer system (vacuum, H_2O , CHCl_3 , $[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]$, SiO_x , Si), with the XSW intensity modelled by calculations for a 3 layer system (vacuum, ‘organic’ layer, Si). The calculations for the photoelectron signal were not constrained to a 3 layer model with VPXSW profiles for the H_2O and CHCl_3 , $[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]$, SiO_x and Si reflector (5 layers including vacuum) all successfully modelled by the calculations using the XSW for a 3 layer system. The fitting gave a total organic layer thickness of $223 \text{ \AA}$, in which the $12 \text{ \AA}$ closest to the vacuum was composed of H_2O and CHCl_3 (so the $211 \text{ \AA}$ closest to the SiO_x/Si reflector was composed of IL). Although the SiO_x was treated as a reflector from the perspective of the XSW intensity calculations, treating the SiO_x as part of the reflector from the photoelectrons perspective did not provide a great fit to the Si $2p_{\text{oxide}}$ VPXSW profile. To model the Si $2p_{\text{oxide}}$ photoelectron signal, obtained from the SiO_x , the model required a $15 \text{ \AA}$ layer on top of the Si reflector to be buried beneath a $223 \text{ \AA}$ organic layer (total thickness of $238 \text{ \AA}$ on the Si reflector). This mismatch came as a result of the substrate VPXSW calculation assuming that the substrate layer is $1000 \text{ \AA}$ thick (semi-infinite substrate), which was not true for the SiO_x layer.

X-ray induced damage effects were detected within this study due to the ability of photoelectrons to differentiate between elements within different chemical environments (chemical shift specificity). Damage is expected to have occurred for all species within the ‘organic’ layer but was only directly observed for nitrogen and chlorine, although the top $15 \text{ \AA}$ of the IL layer was seen to be boron deficient. For low angles (which also represents low X-ray exposure) the majority of the nitrogen and chlorine photoelectron signals were from species with binding energies representative of the pristine, undamaged environments. However as the angle (and hence X-ray exposure) was increased the proportion of photoelectrons being emitted from damaged nitrogen and chlorine environments increased. Damage products have been postulated, with the damaged nitrogen species observed to have a binding energy characteristic of a

neutral nitrogen environment [5], while chlorine is seen to be converted into chloride ions from the CHCl_3 , possibly with a chlorine radical as an intermediate. The boron deficiency in the top 15 Å of the $[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]$ layer is thought to be due to X-ray induced decomposition of the $[\text{BF}_4]^-$ anion to BF_3 and HF. The BF_3 is thought to desorb, despite the surface temperature being around 90 K, but the HF is thought to remain as there is no observed fluorine deficiency in the VPXSW profile. Such information would not be available from an X-ray fluorescence study as the elements involved are light and the fluorescence does not provide chemical shift specificity.

As well as X-ray induced damage effects, surface charging was also observed to affect the surfaces studied. Charging is commonly observed in XPS studies for insulating samples [6]. However in standard XPS the angle of incidence is fixed and the X-ray intensity is constant. Within the VPXSW study the X-ray intensity varies with angle giving rise to a surface charging which is dependent upon angle. This results in a binding energy shift in the photoelectron peaks of up to 10 eV over the angular range of 0° to 0.5° ($\approx \alpha_c$), before dropping to a more constant value of around 3 eV, for higher incident angles. The charging mechanism is not completely understood but is thought to be due to the competition of the X-ray intensity within the organic layer (which increases with angle) and the X-ray path length within the organic layer and X-ray footprint (which decrease with incident angle).

Corrections to the modelled photoelectron signal had to be applied in order to match the experimental signal adequately. The first correction that was applied accounted for the change in the X-ray path length with incident angle, as X-rays transmitted into the adsorbed layer at shallower angles have longer path lengths. Longer path lengths allow a greater quantity of X-ray absorption and a greater photoelectron signal than is predicted from the theory, resulting in the model VPXSW having too low a photoelectron intensity at low angles (which overestimated the photoelectron intensity at high angles, due to normalisation of the VPXSW profiles). The second correction was to account for the X-ray footprint, which is larger for shallower angles of incidence. This correction was required as the CHA will only detect the photoelectrons emitted from within a given area of the sample, so for angles where the X-ray footprint was larger than the CHA detection area photoelectrons were being produced,

and included in the theoretical models, that were not detected. In the model VPXSW profile this gave a larger intensity than was observed in the experiments, hence a correction was applied for angles where the footprint was too large. Further improvements to the model VPXSW profiles could be observed if a greater number of layers were included in the XSW calculation as this would have allowed a better fit for the SiO_x layer beneath the organic material. Effects such as surface roughness (which affects the local angle of incidence) could be accounted for as the majority of real-world systems do not have well defined flat interfaces (an assumption of the theory used here). Overall, the ability of photoelectrons to easily detect all elements, except hydrogen and helium, and the success in modelling a simple layered system shows the possibility for VPXSW with photoelectron detection to study biological films and biomimetic systems, with thicknesses on the order of 250 Å, which are predominantly composed of light elements in differing chemical environments.

7.2 Temperature programmed desorption

It has been observed that ultra-thin layers (less than 30 IL layers thick) of $[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]$ and $[\text{C}_8\text{C}_1\text{Im}][\text{Tf}_2\text{N}]$ behave similarly to bulk layers (millions of IL layers thick), with respect to their desorption properties. This was measured through the activation energies of desorption, where for ultra-thin layers of $[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]$ E_{des} was measured to be $130 \pm 2 \text{ kJ mol}^{-1}$ (literature value for bulk film is $137 \pm 3 \text{ kJ mol}^{-1}$ [7]). In the case of $[\text{C}_8\text{C}_1\text{Im}][\text{Tf}_2\text{N}]$ leading edge analysis found that E_{des} was $133 \pm 3 \text{ kJ mol}^{-1}$ with the literature value for a bulk film being $131 \pm 2 \text{ kJ mol}^{-1}$ [7]. This confirmed that there was no decomposition of the ultra-thin IL films studied here upon adsorption onto the gold surface, giving confidence that studies with IL and CO_2 would be probing the IL- CO_2 interaction rather than the interaction of CO_2 with a decomposition product, or species which was not representative of the IL.

Low temperature line of sight mass spectrometry has been developed and successfully demonstrated to allow line of sight studies to be applied to experiments studying capture of CO_2 , which could not have been performed with existing line of sight setups. Null TPD experiments were performed in

which the gold surface, cooled to 88 K, was exposed to CO₂ at a pressure of 1×10^{-6} mbar in an attempt to form CO₂ multilayers. This would have allowed a reference value for the activation energy of desorption to be found for the CO₂ on the gold to allow comparisons to be made with the IL–CO₂ systems, as well as allowing the CO₂ coverage to be calibrated through the use of TPD. A CO₂ signal was not observed for these null experiments giving an estimation for the maximum possible E_{des} for CO₂ from the gold to be $\approx 27 \text{ kJ mol}^{-1}$, based upon a stay time of 1200 seconds at 88 K, although the true value could be lower than this. This value calculated from the stay time was seen to be similar to the enthalpy of sublimation of CO₂ at 100 K, $\Delta_{\text{sub}}H_{100} = 26.8 \text{ kJ mol}^{-1}$ [8, 9], indicating it was a suitable value to use for subsequent discussions of the stabilisation of CO₂ within the ILs.

Studies in which the CO₂ was coadsorbed with the ILs showed CO₂ TPD peaks, indicating that the CO₂ was successfully stabilised within the two ILs studied. It was seen that as the quantity of IL that was coadsorbed with the CO₂ was increased, the quantity of CO₂ captured increased. This unsurprising result confirmed that the CO₂ is captured within the bulk of the IL film, rather than just at the surface or interfacial layers (which would result in a fixed quantity of CO₂ being captured irrespective of amount of IL dosed). It was also seen that increasing the pressure of CO₂ whilst keeping the quantity of IL constant increased the amount of CO₂ captured, due to the increased CO₂ coverage that results from higher dose pressures. The CO₂ desorption curves could be compared to the Polanyi–Wigner equation to determine the range of activation energies of desorption for CO₂ within each of the ILs. It was not possible to model the experimental data with a single CO₂ adsorption site, indicating that multiple binding sites exist within the ILs. In the case of [C₈C₁Im][BF₄], the CO₂ was observed to exhibit E_{des} values up to 43 kJ mol^{-1} , which translates to a range for the enthalpy of sublimation of CO₂ from the [C₈C₁Im][BF₄] of 27.1 to 44.1 kJ mol^{-1} . Studies on the [C₈C₁Im][Tf₂N]–CO₂ coadsorption systems found that the experimental data could be modelled by a series of CO₂ desorption peaks with E_{des} in the range 24.5 to 38.0 kJ mol^{-1} , giving enthalpies of sublimation of 25.5 to 39.0 kJ mol^{-1} for CO₂ within [C₈C₁Im][Tf₂N]. None of the model CO₂ desorption peaks correspond to known adsorption geometries, as the E_{des} values used in the fitting were arbitrarily chosen. In order to gain further insights into

the arrangement of CO₂ around the IL ion pair or within the IL film quantum chemical calculations in for a wide variety of IL and CO₂ conformations would be required (current calculations have only looked at the most stable conformations).

The obtained values of enthalpy clearly show that the CO₂ is stabilised by up to 5.1 kJ mol⁻¹ more within the [C₈C₁Im][BF₄] than in the [C₈C₁Im][Tf₂N]. This experimentally observed stabilisation is close to the results of quantum calculations of different IL ion pairs and a CO₂ molecule, showing that the CO₂ is stabilised by 5.76 kJ mol⁻¹ more in a [BF₄]⁻ system relative to the [Tf₂N]⁻ system, based on the anion–CO₂ interaction [10]. This result may appear odd, at first, since it has been observed that CO₂ is more soluble in [C₈C₁Im][Tf₂N] than in [C₈C₁Im][BF₄] (Henry's constant for CO₂ in [C₈C₁Im][Tf₂N] is 30 ± 1 bar for [11] and in [C₈C₁Im][BF₄] is 54 ± 3 bar for [12], where a smaller Henry's constant denotes a larger solubility). This result demonstrates the fact that solubility (the amount of gas that can be held) and stability (how tightly that gas is held) are not necessarily related, highlighting the importance of studying not just the solubility of a gas within ILs, but also looking at the gas stability and trying to understand the bonding that occurs between the species.

As well as coadsorption studies between the CO₂ and the IL, experiments in which CO₂ was dosed onto IL glass layers and IL 'snow' layers were performed. In the case of [C₈C₁Im][Tf₂N] there was no significant CO₂ TPD peak on either the IL glass or IL 'snow', suggesting that CO₂ was not stabilised within the surface layers of the IL, at the IL–vacuum interface. For [C₈C₁Im][BF₄], CO₂ was not stabilised when exposing the IL glass, which is expected to have low porosity and a surface composed of aliphatic chains, to the gas. CO₂ was, however, captured by the surface of the [C₈C₁Im][BF₄] 'snow', which is expected to have both anions and cations exposed at the surface, in random orientations. The fact that the [C₈C₁Im][BF₄] 'snow' stabilises some CO₂, when the glass does not, suggests that the attractive interactions between the IL and the CO₂ occur between the ionic regions and the CO₂ molecule, and that the aliphatic chains do not interact strongly with the CO₂. The lack of any significant CO₂ stabilisation in the [C₈C₁Im][Tf₂N] 'snow', when CO₂ is seen to adsorb on [C₈C₁Im][BF₄] 'snow' could be explained in terms of interaction

strength between the IL and the CO₂. The weaker CO₂–[C₈C₁Im][Tf₂N] interaction strength means that in the less coordinated surface sites of the ‘snow’ surface the CO₂ cannot be captured effectively, however for the [C₈C₁Im][BF₄] the interaction with CO₂ is strong enough, even in the less coordinated sites, to capture the CO₂ resulting in a measured TPD peak. This argument with the interaction strengths agrees with the observation that the enthalpy range for CO₂ desorption from [C₈C₁Im][BF₄] is larger than the enthalpy range of desorption from [C₈C₁Im][Tf₂N]. The observation that the aliphatic chains prevent the CO₂ from being captured by the IL glass is concerning, if ILs are to be used in carbon capture, given that the surface structure of the IL (at the liquid vapour interface) is believed to be composed of aliphatic chains. This will result in an energy barrier to absorption of the CO₂ by the IL [13], limiting the effectiveness of certain methods of CO₂ extraction (e.g. just passing the gas over the IL surface may not capture CO₂ as effectively as bubbling the gas through the IL, which increases the IL surface area and hence the amount of CO₂ captured).

It was observed that the average quantity of CO₂ captured per IL layer decreased as the quantity of IL used in the coadsorption increased, for both liquids studied. This led to the conclusion that a greater quantity of CO₂ was captured in the first few IL layers than in the subsequent (bulk) layers. It was rationalised that since the IL layers themselves should be the same, irrespective of how much IL exists on the surface already, then the observed effect was a consequence of differences in the CO₂ coverage on the gold surface (which may have carbonaceous material and exposed charges chemisorbed to it) and the IL ‘snow’ surface. Comparisons of the amount of CO₂ captured per layer of ‘bulk’ IL showed that the CO₂ is more effectively captured by the [C₈C₁Im][Tf₂N] ((0.14 ± 0.02) × 10^{−6} mbar s of CO₂ captured per IL layer at 1 × 10^{−6} mbar) than by the [C₈C₁Im][BF₄] ((0.10 ± 0.02) × 10^{−6} mbar s of CO₂ captured per IL layer at 1 × 10^{−6} mbar). This observation agrees with the Henry’s constants from literature showing that CO₂ is more soluble in [C₈C₁Im][Tf₂N] than in [C₈C₁Im][BF₄]. This is believed to be due to the greater proportion of ionic regions in the [C₈C₁Im][Tf₂N] resulting from the larger, more diffuse anion.

The fact that surface coverage of CO₂ was such an important factor in determining the capture efficiency of the CO₂ gave an insight into the adsorption mechanism of CO₂ capture. A model in which the CO₂ is captured through an

Eley–Rideal type mechanism, where the incoming ion pair collides with an adsorbed CO₂ molecule to capture it, is proposed. It was observed that the experimental data could be adequately fitted by the equations derived from this proposed model. The Eley–Rideal mechanism could be confirmed, in future, with experiments in which the IL flux is varied (through use of different evaporator temperatures) to see if this affects the rate of CO₂ capture, with a higher IL flux leading to a higher rate of CO₂ capture if Eley–Rideal kinetics are observed (whereas the rate of CO₂ capture would be independent of the IL flux for a Langmuir-Hinshelwood type mechanism). It is shown, by the equilibrium constants for the desorption reaction obtained from the fits, that the equilibrium state is one in which CO₂ is mostly adsorbed, with a typical value for the equilibrium constant (10×10^{-8}) giving a CO₂ surface coverage on the IL at a pressure of 1×10^{-6} mbar of 0.91 (meaning the surface is 91% covered in CO₂), and a Gibbs free energy of adsorption in the IL ‘snow’ of ≈ -12 kJ mol⁻¹ at 90 K.

Using the kinetic theory of gases the number of CO₂ molecules captured by each of the ILs could be estimated, allowing the number of layers of CO₂ captured within the IL films to be calculated. It was observed that up to 0.05 ± 0.01 layers of CO₂ could be captured per layer of [C₈C₁Im][BF₄] and 0.09 ± 0.02 layers of CO₂ could be captured per layer of [C₈C₁Im][Tf₂N]. Using a simple model in which the IL and CO₂ molecules are modelled as cubes (so the area of an adsorbed molecule could be modelled as the cube root of the molar volumes, squared) CO₂ coordination numbers (the number of ion pairs per CO₂ molecule stabilised) could be calculated. It was shown that the coordination number of CO₂ in [C₈C₁Im][Tf₂N] was about half that of the CO₂ coordination in [C₈C₁Im][BF₄] (the average CO₂ molecule within [C₈C₁Im][BF₄] is surrounded by approximately twice as many IL molecules as a CO₂ molecule within [C₈C₁Im][Tf₂N]). Relating this coordination number to the mole fraction of CO₂ within the IL allows Henry’s constants, at ≈ 90 K, for CO₂ within each of the ILs to be estimated. The key result from this is that the Henry’s constant is proportional to the “CO₂ coordination + 1”, so it is seen that the ratio of Henry’s constants for [C₈C₁Im][BF₄]:[C₈C₁Im][Tf₂N] at ≈ 90 K is about 1.8:1, which is the same as the ratio of Henry’s constants for [C₈C₁Im][BF₄]:[C₈C₁Im][Tf₂N] at ≈ 300 K. This consistency of the ratio of Henry’s constants further validates the results collected and conclusions made within this study.

This study has focussed on vacuum studies of the IL–CO₂ interaction, resulting in systems that are not directly related to ambient conditions. Since the IL was dosed through evaporation onto a cold surface it adsorbed as an IL ‘snow’ rather than a liquid, which is not directly comparable to the IL morphology under ambient conditions. Studying the IL ‘snow’ allowed the entire range of possible CO₂ binding environments to be sampled, though studies in which the CO₂ adsorption environment within the liquid phase is probed should be performed. It is expected that this will result in a smaller variety of different binding environments, but with larger populations, as the IL will arrange in certain ways to accommodate the CO₂. Such studies would need to occur with higher temperatures, to ensure that the IL is in the liquid phase, and pressures, ensuring that the CO₂ coverage is sufficiently large to be captured by the IL. The IL itself could be dosed through a dipstick method (immersion followed by emersion), which could allow the IL to be saturated with CO₂ in a separate chamber then transferred to the analysis chamber to be coated onto the dipstick sample and studied. This could circumvent any issues from the inefficiency of CO₂ capture that would be a consequence of working at lower pressures due to the vacuum equipment in the analysis chamber.

7.3 **References**

- [1] Bedzyk, M.J., Bommarito, G.M. and Schildkraut, J.S., X-ray Standing Waves at a Reflecting Mirror Surface. *Phys. Rev. Lett.*, **1989**, (62), pp. 1376-1379.
- [2] Zhang, R.T., Itri, R. and Caffrey, M., Membrane structure characterization using variable-period X-ray standing waves. *Biophys. J.*, **1998**, (74), pp. 1924-1936.
- [3] Kramer, M., von Bohlen, A., Sternemann, C., Paulus, M. and Hergenroder, R., X-ray standing waves: a method for thin layered systems. *J. Anal. Atom. Spectrom.*, **2006**, (21), pp. 1136-1142.
- [4] Thompson, A.C. and Vaughan, D., *X-ray Data Booklet*. Kirz, J., Eds., Lawrence Berkeley Laboratory, (2001)
- [5] Villar-Garcia, I.J., Smith, E.F., Taylor, A.W., Qiu, F., Lovelock, K.R., Jones, R.G. and Licence, P., Charging of ionic liquid surfaces under X-ray irradiation: the measurement of absolute binding energies by XPS. *Phys. Chem. Chem. Phys.*, **2011**, (13), pp. 2797-2808.
- [6] *Surface Analysis by Auger and X-ray Photoelectron Spectroscopy*. Briggs, D. and Grant, J.T., Eds., IM Publications, Chichester, (2003)

- [7] Armstrong, J.P., Hurst, C., Jones, R.G., Licence, P., Lovelock, K.R.J., Satterley, C.J. and Villar-Garcia, I.J., Vapourisation of ionic liquids. *Phys. Chem. Chem. Phys.*, **2007**, (9), pp. 982-990.
- [8] Bryson, C.E., Cazarra, V. and Levenson, L.L., Sublimation Rates and Vapour Pressures of H₂O, CO₂, N₂O and Xe. *J. Chem. Eng. Data*, **1974**, (19), pp. 107-110.
- [9] Trusler, J.P.M., Equation of State for Solid Phase I of Carbon Dioxide Valid for Temperatures up to 800 K and Pressures up to 12 GPa. *J. Phys. Chem. Ref. Data*, **2011**, (40), pp. 043105.
- [10] Damas, G.B., Dias, A.B.A. and Costa, L.T., A Quantum Chemistry Study for Ionic Liquids Applied to Gas Capture and Separation. *J. Phys. Chem. B*, **2014**, (118), pp. 9046-9064.
- [11] Baltus, R.E., Culbertson, B.H., Dai, S., Luo, H.M. and DePaoli, D.W., Low-pressure solubility of carbon dioxide in room-temperature ionic liquids measured with a quartz crystal microbalance. *J. Phys. Chem. B*, **2004**, (108), pp. 721-727.
- [12] Zhang, J., Zhang, Q., Qiao, B. and Deng, Y., Solubilities of the gaseous and liquid solutes and their thermodynamics of solubilization in the novel room-temperature ionic liquids at infinite dilution by gas chromatography. *J. Chem. Eng. Data*, **2007**, (52), pp. 2277-2283.
- [13] Deyko, A. and Jones, R.G., Adsorption, absorption and desorption of gases at liquid surfaces: water on C₈C₁Im BF₄ and C₂C₁Im Tf₂N. *Faraday Discuss.*, **2012**, (154), pp. 265-288.

Appendices

8.1 Derivation of umbra and penumbra diameters for a line of sight setup

By using the schematic diagram of the setup of the LTLOS in fig. 2.17, expressions can be defined relating the diameter of the LOS umbra, d_U , and the diameter of the LOS penumbra, d_P , to the diameter of aperture N on the outer LTLOS tube closest to the sample, d_N , and the diameter of aperture M on the mass spectrometer, d_M . This can be done using trigonometry and noticing that within the geometry there are a collection of similar triangles (triangles with the same angles but different side lengths). A slightly less detailed version of this derivation can also be found in the supporting information of reference [1]. Figure 8.1 shows an accentuated version of the diagram in fig. 2.17, but now with the axis of symmetry along the centre shown as the dashed green line and the distances x and y defined. Considering the geometry of the umbra and the

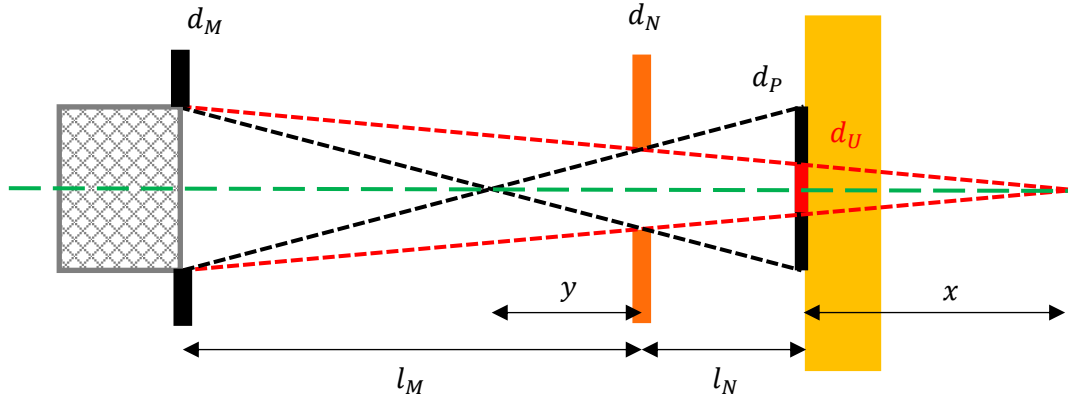


Figure 8.1: A diagram showing the setup for the LTLOS with the centre of symmetry (green dashed line) and the distances y (from aperture N to the point where the penumbra lines of sight cross) and x (from the sample surface to the point where the umbra lines of sight cross). These can be used to make triangles, allowing the equations for the umbra and penumbra diameters to be derived.

associated triangles that can be made, fig. 8.2, it can be seen that all of the triangles have the same angle, θ . Utilising this fact, the trigonometric ratio tangent and the information in fig. 8.2 the following simultaneous equations can be formed:

$$\frac{d_M}{2(l_M + l_N + x)} = \frac{d_N}{2(l_N + x)} \quad \text{rearranges to} \quad d_M l_N + d_M x = d_N l_M + d_N l_N + d_N x \quad 1)$$

$$\frac{d_M}{2(l_M + l_N + x)} = \frac{d_U}{2x} \quad \text{rearranges to} \quad d_M x = d_U l_M + d_U l_N + d_U x \quad 2)$$

$$\frac{d_N}{2(l_N + x)} = \frac{d_U}{2x} \quad \text{rearranges to} \quad d_N x = d_U l_N + d_U x \quad 3)$$

Where equation 1) is formed from considering triangles (a) and (b), equation 2) comes from triangles (a) and (c) and equation 3) comes from triangles (b) and (c). Substituting 2) and 3) into 1) (for the terms “ d_{MX} ” and “ d_{NX} ”, respectively)

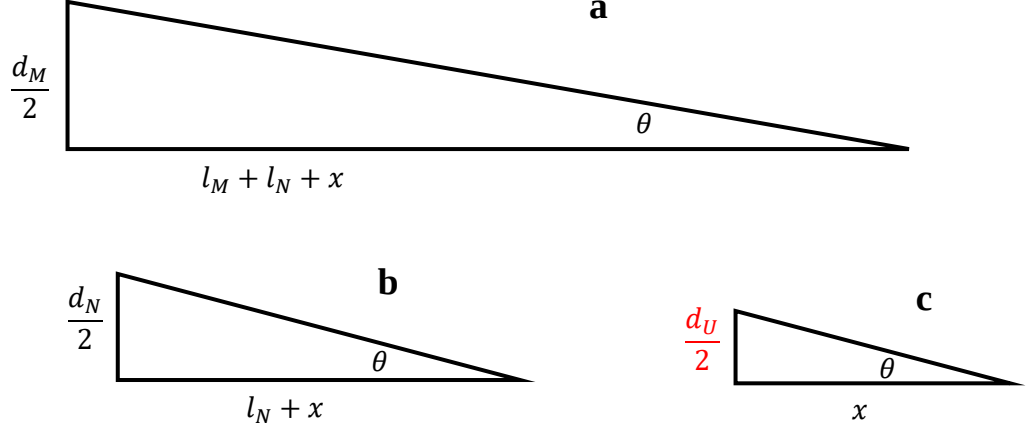


Figure 8.2: A diagram showing triangles, (a), (b) and (c) that can be formed when considering the umbra geometry from fig. 8.1. The geometry of the LOS setup means that all the triangles have the same angles, so the tangents can be equated allowing the value of d_U to be found.

gives the equation:

$$d_M l_N + (d_U l_M + d_U l_N + d_U x) = d_N l_M + d_N l_N + (d_U l_N + d_U x) \quad \text{Equation 8.1}$$

Noticing that the terms “ $d_U x$ ” and “ $d_U l_N$ ” are common to both the left and right sides of the equation, and that the diameter of the umbra, d_U , is the desired subject of the equation, then the above equation can be rearranged to:

$$d_U = \frac{d_N l_M + d_N l_N - d_M l_N}{l_M} = d_N + d_N \frac{l_N}{l_M} - d_M \frac{l_N}{l_M} \quad \text{Equation 8.2}$$

Through factorising the above equation the diameter of the umbra for a given LOS setup can be found to be given by eq 2.53:

$$d_U = d_N \left(1 + \frac{l_N}{l_M} \left(1 - \frac{d_M}{d_N} \right) \right) = d_N \left(1 - \frac{l_N}{l_M} \left(\frac{d_M}{d_N} - 1 \right) \right) \quad \text{Equation 2.53}$$

Considering now the penumbra, one can generate the similar triangles shown in figure 8.3. Since all these triangles are similar their tangents can be equated giving the three simultaneous equations

$$\begin{array}{lll} \frac{d_M}{2(l_M - y)} = \frac{d_N}{2y} & \text{rearranges to} & d_M y = d_N l_M - d_N y \quad \text{i)} \\ \frac{d_M}{2(l_M - y)} = \frac{d_P}{2(l_N + y)} & \text{rearranges to} & d_M l_N + d_M y = d_P l_M - d_P y \quad \text{ii)} \\ \frac{d_N}{2y} = \frac{d_P}{2(l_N + y)} & \text{rearranges to} & d_N l_N + d_N y = d_P y \quad \text{iii)} \end{array}$$

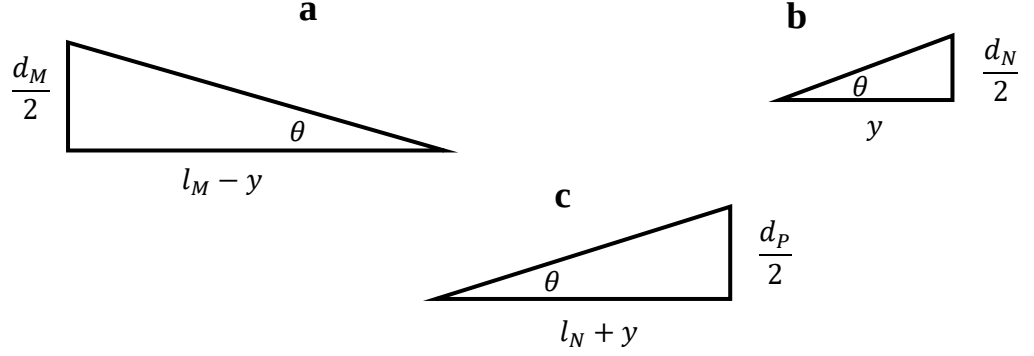


Figure 8.3: A diagram showing the three triangles, (a), (b) and (c) that can be formed when considering the penumbra geometry from fig. 8.1. From the geometry of the problem all the triangles have the same angles, which means that taking the tangent of all of the triangles gives fractions which can be compared and equated to solve for d_P .

Substituting equations i) and iii) into ii) (for the terms $d_M y$ and $d_P y$) gives the equation:

$$d_M l_N + (d_N l_M - d_N y) = d_P l_M - (d_N l_N + d_N y) \quad \text{Equation 8.3}$$

The “ $-d_N y$ ” terms cancel and since the diameter of the penumbra, d_P , is the desired subject of the equation rearrangement gives:

$$d_P = \frac{d_M l_N + d_N l_M - d_N l_N}{l_M} = d_M \frac{l_N}{l_M} + d_N - d_N \frac{l_N}{l_M} \quad \text{Equation 8.4}$$

By factorising the above equation the diameter of the penumbra can be found for a particular geometry of the LOS setup by using eq 2.54:

$$d_P = d_N \left(\frac{l_N}{l_M} \left(\frac{d_M}{d_N} + 1 \right) + 1 \right) \quad \text{Equation 2.54}$$

In all cases the units used for the diameters and lengths should be in the same, so if millimetres are used for the distances, the obtained diameters for the umbra and penumbra will also be in millimetres.

8.2 Determination of errors in layer thicknesses for VPXSW on Si

Determination of errors in the fitting of variable period X-ray standing wave (VPXSW) layer thicknesses is something which (at present) can only be performed by comparing the best model to the data with other subtly different models to the data (e.g. ones with different layer thicknesses) and seeing whether the new model could be considered to be within error of the experimental data. By performing this task iteratively the upper and lower bounds can be found for the layer thickness which successfully model the experimental data and hence errors can be found. This procedure is subject to the judgement of the Author

(or whomever is fitting the data) so may differ depending upon the user. This is the same procedure as the one described in section 4.2.2, in fig. 4.3, and shall be applied to the 3 layer model in which the silicon substrate is covered in an organic layer ($[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]$ and CHCl_3) beneath a vacuum layer.

By using the VPXSW profiles from the $\text{Si } 2p_{\text{bulk}}$, $\text{Si } 2p_{\text{oxide}}$ and $\text{Si } 2p_{\text{total}}$

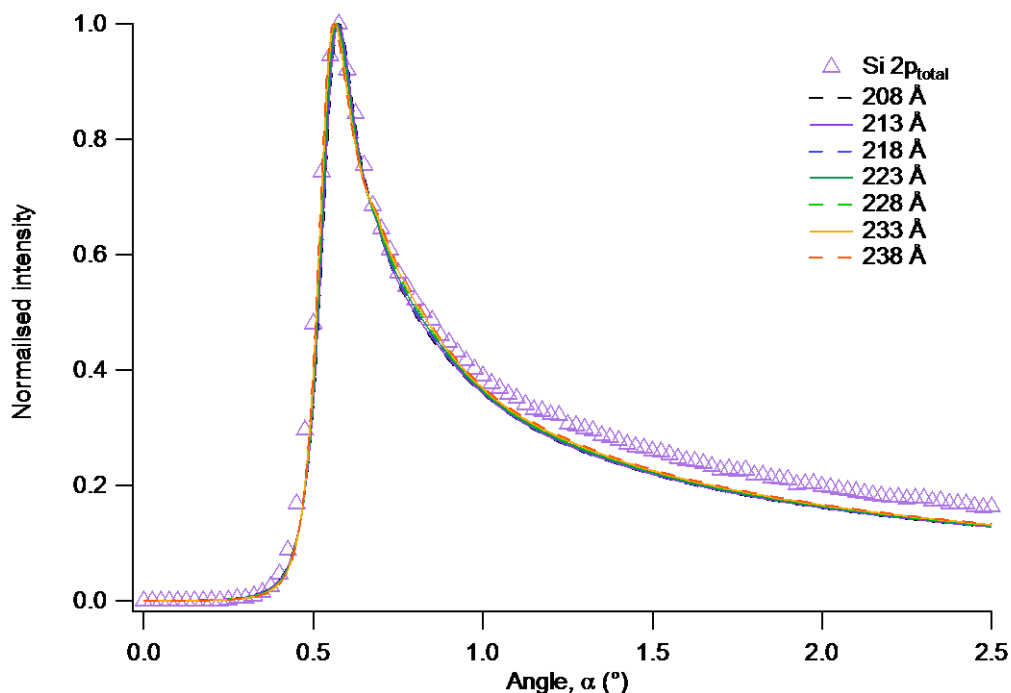


Figure 8.4: The total substrate signal ($\text{Si } 2p_{\text{total}}$, markers) has been compared to the theoretical models for a variety of organic layer thicknesses in an attempt to estimate the error in the organic layer thickness determined by VPXSW.

photoelectron peaks the organic layer was found to be 223 Å thick (section 4.3.3). Figure 8.4 shows the experimental data for the $\text{Si } 2p_{\text{total}}$ VPXSW profile compared with models in which the thicknesses range from 208 Å to 248 Å. The attenuation length used for the $\text{Si } 2p$ photoelectrons through the organic layer was 58 Å. It is observed that the VPXSW profiles for the substrate are all very similar, especially in the low angle (under 1°) regime, making it difficult to rely solely on the substrate VPXSW profile to determine film thickness. The decaying tail of the theoretical VPXSW profile can be seen to be a better match to the experimental data for thicker films, but as the film thickness increases the goodness of fit at low angles decreases. As a result the compromise of a film thickness of 223 Å (solid green line) is suggested for the best fit with an error of ± 15 Å.

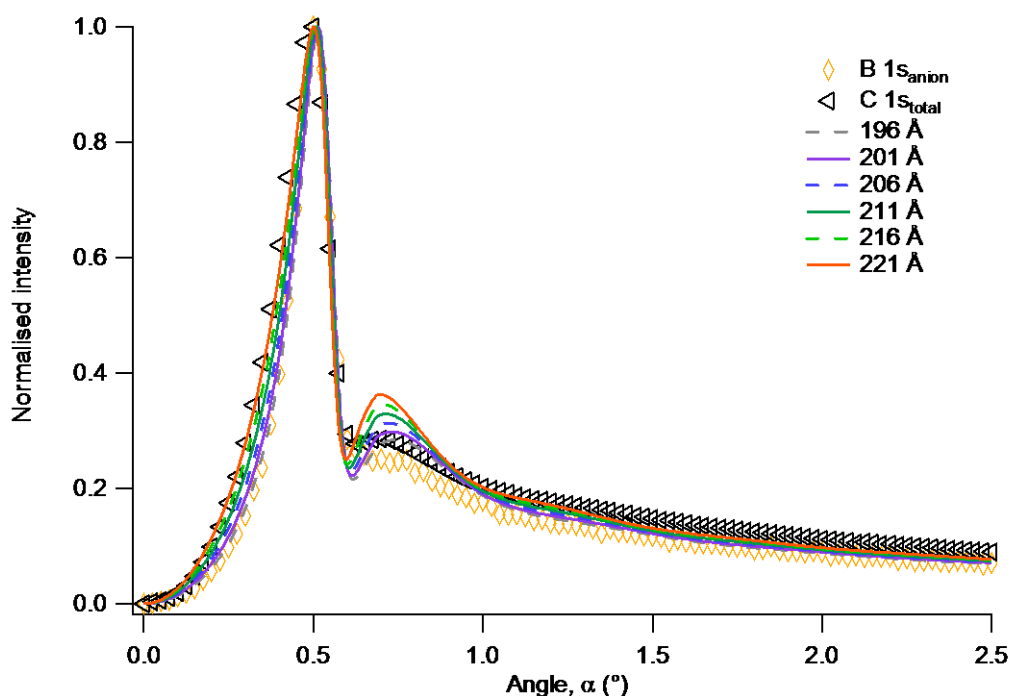


Figure 8.5: A comparison of the extracted VPXSW profiles for the IL components C 1s_{total} (black triangles) and B 1s_{anion} (orange diamonds) to theoretical models with varying layer thicknesses in an attempt to estimate an error in the layer thickness. It can be observed that the leading edge at low angles of the B 1s_{anion} VPXSW profile is fitted much better by a 196 Å layer than a 211 Å IL layer, which was observed to be the best fit of the other IL components. An attenuation length of 53 Å was used in the theoretical models.

To estimate the errors involved with the determination of the IL layer thickness a series of theoretical models were compared to the C 1s_{total} and B 1s_{anion} VPXSW profiles. The organic layer thickness was assumed to be 223 Å, as determined by the substrate VPXSW profile, and the attenuation length of the photoelectrons from the IL species within the organic layer was assumed to be 53 Å. The theoretical VPXSW profiles in fig. 8.5 show the effect of varying the thickness of the IL layer, whilst keeping the total organic layer thickness constant. It can be seen that in the lower angular regime (below 0.6°) the thicker IL layers are better models to the C 1s signal, but in the high angle regime (above 0.6°) the thinner IL layers are a better match to the C 1s VPXSW profile. It can be seen that the 211 Å layer is the best compromise, and hence is used as the best fit value. Since the majority of the data is successfully modelled by the thicknesses in the range 201 Å to 221 Å an error of ± 10 Å is estimated. It can be observed that the leading edge at low angles of the B 1s_{anion} VPXSW profile is fitted much better by a 196 Å layer than a 211 Å IL layer, which may

suggest that the boron species has been damaged at the surface and desorbed into the vacuum, as discussed in the main text (section 4.3.4).

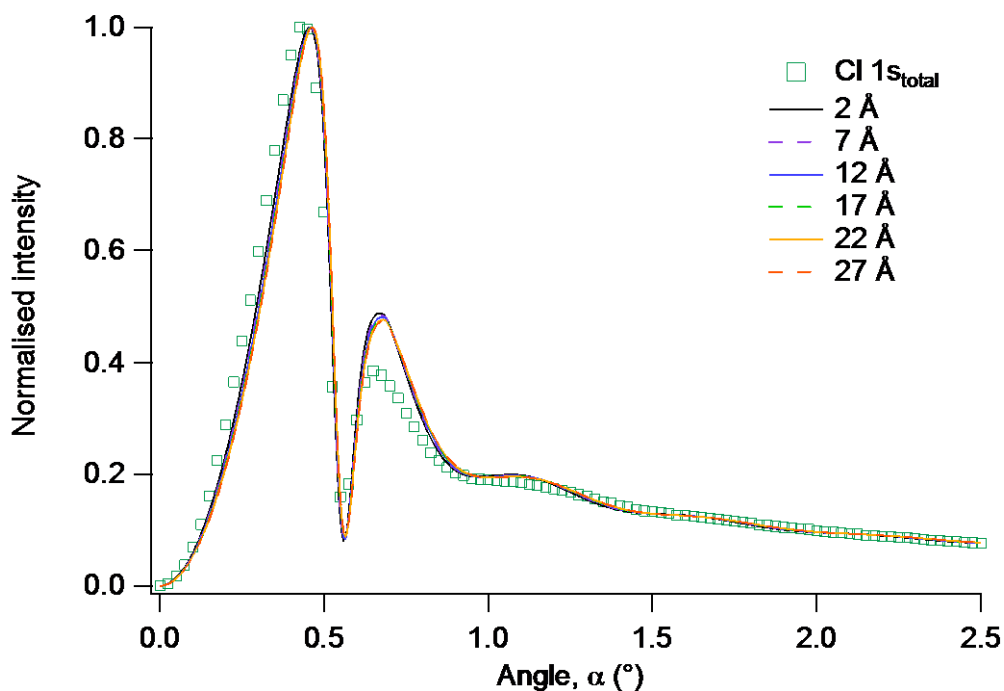


Figure 8.6: A comparison of the extracted VPXSW profiles for the total chlorine signal (green squares) to theoretical models with varying layer thicknesses in an attempt to estimate an error in the layer thickness. Only the thickness of the CHCl_3 layer is varied, not the thickness of the organic layer, with the legend indicating the thickness of the CHCl_3 layer at the top of the organic layer. An attenuation length of 9 Å was used in the theoretical models.

A plot to determine the error associated with the thickness of the CHCl_3 layer is shown in fig. 8.6, where the experimental data is shown as green squares and theoretical models for different layer thicknesses are shown as coloured lines. The total thickness of the organic layer was kept constant, so only the proportion of the organic layer composed of the CHCl_3 was varied (which varies the thickness of the IL layer to keep total organic layer thickness constant). The attenuation length used in calculations of the theoretical models for the Cl 1s photoelectrons through the organic layer was 9 Å. It can be seen that there is not too much variation in the theoretical VPXSW profiles as the layer thickness changes, due to the short attenuation length for the photoelectrons, with 87% of the photoelectron signal coming from the top 18 Å ($2 \times \lambda$) of the layer. The result of this is that increasing the layer thickness past this depth will not affect the VPXSW profile too much. This can be seen in fig. 8.6 as the 17 Å to 27 Å theoretical models are almost indistinguishable. This makes estimation of the error difficult as a layer 100 Å thick will give the same VPXSW profile as one that is 20 Å thick. Considering the theoretical model for the 2 Å layer (black

line) a slight shift in the position of the peak at $\approx 0.7^\circ$ is observed, but it is not a big enough shift to make it easily distinguishable from the 12 Å model (blue line). As a result of these considerations the error in the CHCl_3 layer is assumed to be the same as the error in the IL layer thickness as measured by the substrate signal, which is ± 15 Å.

In the case where the photoelectron attenuation length is sufficiently large the error will tend to decrease for thicker layers, in which a greater number of oscillations are present in the VPXSW profile, as errors are judged from the ability of the model to reproduce the experimentally observed oscillations. Having a greater quantity of oscillations makes matching the phase of the experimental and theoretical oscillations easier, as varying the layer thickness slightly changes the phase of the oscillations in the VPXSW profile [2]. The VPXSW profile is not as sensitive to layer thickness changes as it is to layer position changes (section 2.3.5 and 4.3.5).

8.3 Monolayer determination of $[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]$ using TPD

Determination of the monolayer coverage of $[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]$ was required to allow the IL coverage to be represented in terms of layers rather than the experimentally detected ‘counts’. The monolayer coverage was determined through a series of calibration experiments in which the detected mass spectrometer peak areas, from $[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]$ TPD peaks, were measured for a range of different initial quantities of IL on the gold surface. Experiments were performed on a room temperature sample, so the IL will have been deposited as a liquid, rather than an IL ‘snow’ which is observed when the IL is dosed onto a sample which is cold (≈ 88 K). The only expected difference between dosing at these temperatures, aside from the morphology of the IL, is the sticking probability of the IL on the surface, which will be closer to 1 for a cold surface than a room temperature one (at room temperature sticking probability is still expected to be close to 1 due to the low volatility of ILs). $[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]$ was dosed from an evaporator at 573 K, as discussed in section 3.4.3, with dose lengths varying between 0 and 600 seconds. The monolayer coverage was defined by the point at which the TPD peak shape went from first order (all peak maxima at the same temperature) to zero order (temperature of peak maximum

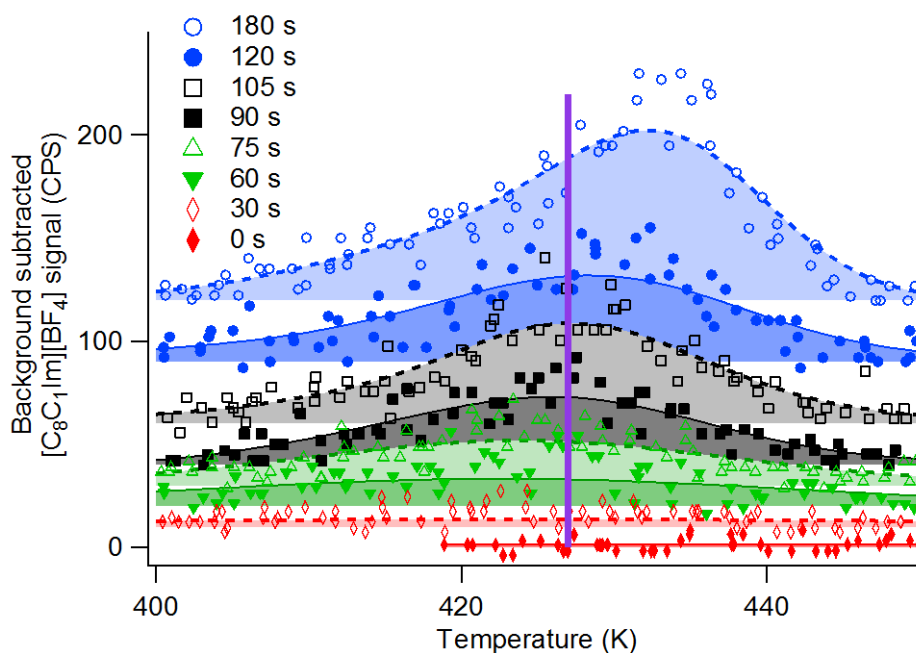


Figure 8.7: Experimental TPD data for $[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]$ desorption from a gold surface tracking the $m/z = 195$ amu mass channel (heating rate of 0.5 K s^{-1}). The gold surface was exposed to IL for timescales ranging from 0 to 180 seconds, with data shown as markers and smoothing splines have been added to guide the eye through the noise of the data. Solid lines and darker shading represent filled markers and dashed lines with lighter shading represent hollow markers with datasets offset for clarity. The purple line at $T = 427 \text{ K}$ represents the temperature at which the peak maxima sit for the first order TPD peaks.

increases with initial coverage), indicative of multilayer desorption. It is assumed the IL evaporation occurs at a constant rate, for a given evaporator temperature. This is because the evaporator has an excess of IL in it, so will observe zero order desorption kinetics, meaning that for a fixed temperature a constant desorption/evaporation rate occurs. Figure 8.7 shows $[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]$ TPD spectra, following the $m/z = 195$ amu fragment intensity, from a gold surface for initial dose lengths ranging from 0 to 180 seconds. The plots have been offset for clarity and smoothing splines have been used on the data to enable the temperature at which the intensity maximum occurs to be identified more easily. It is clear to see that for all $[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]$ dose lengths below 120 seconds the peak maxima (for the cases where a clear peak maximum can be seen) occur at $\approx 427 \text{ K}$ (purple line), with the peak for the 120 second IL dose (filled blue circles) being at 428 K . It is believed that the 120 second $[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]$ dose corresponds to the desorption of a monolayer from the gold surface. To find the number of counts (unit of experimentally measured peak areas) that correspond to this monolayer coverage a calibration curve of experimental peak area against dose length was generated, fig. 8.8, and modelled

by a straight line of the form $y = mx$. Fitting gave the gradient of the line to be 22.1 ± 0.3 counts per second of IL dosed. The equation of best fit was then used with the dose time of 120 seconds to obtain the monolayer coverage of 2650 ± 50 counts, which could be used to convert all of the $m/z = 195$ amu peak areas to IL coverages in layers. It can be seen that the error in the monolayer coverage itself, from the fit in fig. 8.8, is very small (less than 2% of the monolayer area). This error comes purely from the fitting and does not account for any error in the determination of the switching point from first order to zero order desorption. It can be seen, in fig. 8.7, that the 120 second TPD peak is first order in shape

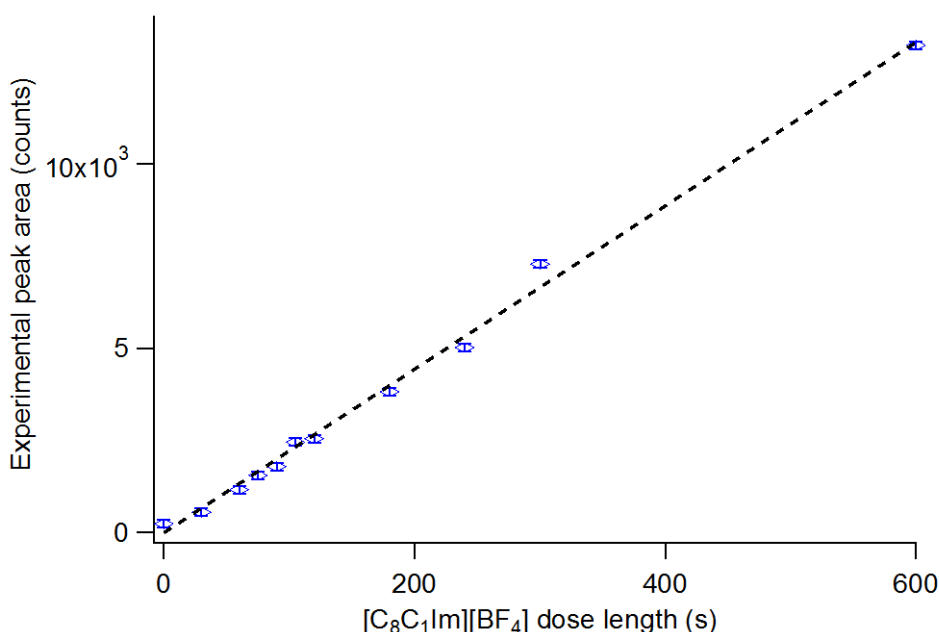


Figure 8.8: A calibration curve for the integrated peak area for the $m/z = 195$ amu TPD peak with dose length for $[C_8C_1Im][BF_4]$, where experimental data (blue markers) has been fitted by an equation of the form $y = mx$ (black dashed line). The gradient of the best fit equation was calculated to be 22.1 ± 0.3 counts per second of IL dosed.

and that the 180 second TPD peak is zero order, however it is possible that the switchover occurs for any dose length between 120 and 180 seconds. Using the fit from fig. 8.8 this would mean that the true monolayer coverage could lie anywhere between 2650 and 3980 counts, which represents a 50% error in the monolayer coverage (2650 ± 1330). Looking at how much the peak maximum for the 180 seconds dose has shifted from the purple line, it is apparent that the shift from first order to zero order shape occurred at a time closer to 120 seconds than 180 seconds. Hence an estimated error in the monolayer coverage of 10% (± 265 counts) has been assumed, in determining errors for $[C_8C_1Im][BF_4]$ layer thicknesses. As discussed in section 5.2 the IL was studied primarily through the

$m/z = 195$ amu peak, so a calibration was not performed on the $m/z = 96$ amu mass channel.

8.4 Temperature programmed desorption curve for $[C_1C_1Im]^+$

As mentioned in section 5.2 the desorption of $[C_8C_1Im][BF_4]$ was monitored through the $m/z = 195$ and 96 amu fragments corresponding to $[C_8C_1Im]^+$ and $[C_1C_1Im]^+$ respectively. The desorption profile for the $m/z = 195$ amu fragment is shown and discussed in section 5.2, with the corresponding desorption profile for the 96 amu fragment shown in fig. 8.9. It can be seen that there are two desorption peaks observed in the 96 amu trace, when only the one at ≈ 450 K, due to the $[C_1C_1Im]^+$, was expected, based on the 195 amu data. The possible origins of the unidentified peak at ≈ 300 K are discussed in the main text, although the exact identity of the contaminant is unknown. The experimental data shown in fig. 8.9 corresponds to the point with index -7 in fig. 5.3, which can be seen to have a higher concentration of the contaminant than during the CO_2 experiments, as the IL was running out. The 96 amu TPD

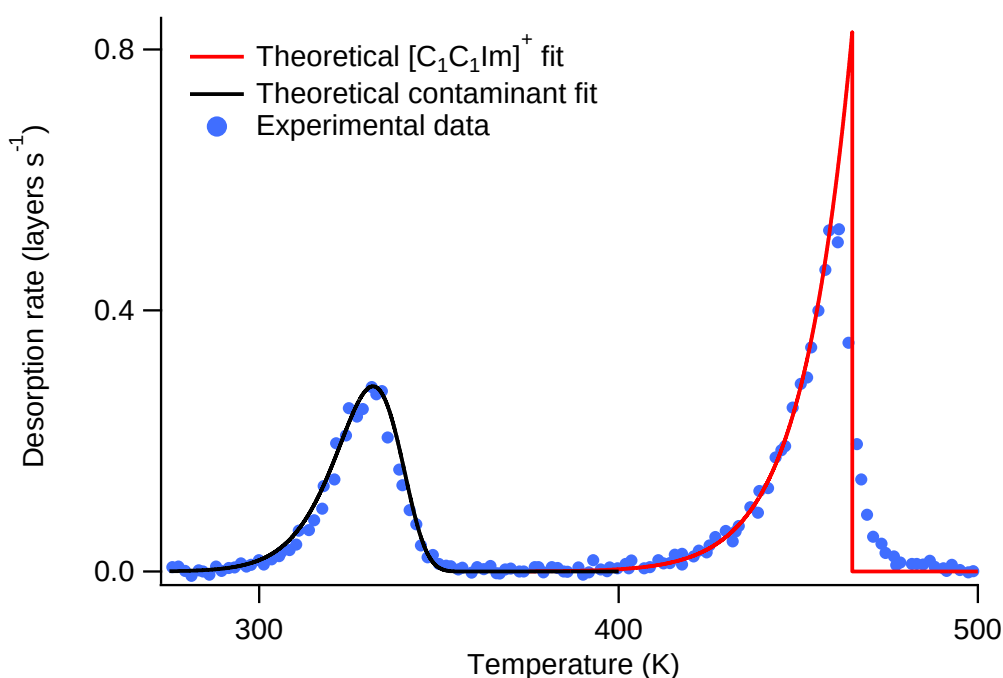


Figure 8.9: Experimental TPD data for the $m/z = 96$ amu mass fragment for a $[C_8C_1Im][BF_4]$ layer with an initial thickness of 21.6 ± 2.2 layers (blue dots) fitted with a zero order theoretical desorption peak for a fragment of the imidazolium cation ($[C_1C_1Im]^+$, red line) and a peak to describe a contaminant within the IL (black line). The heating rate was 0.5 K s^{-1} .

profile has been fitted with two theoretical peaks, shown as black and red lines in fig. 8.9, using the Polanyi–Wigner equation (eq 2.51). There is an added complication in the fitting of the $m/z = 96$ amu profile that a monolayer calibration was not performed for this ion fragment. As a result the desorption rate has been calculated by assuming that the peak on the right (due to $[C_1C_1Im]^+$) corresponds to 21.6 layers of IL, as found by the $m/z = 195$ amu plot. This number of IL layers was used to convert the zero order peak area for the 96 amu fragment (87760 counts) into a monolayer coverage equivalent of 4063 counts. This value was used to convert the 96 amu experimental data into a desorption rate, allowing it to be fitted with the theoretical peaks. The red line represents the desorption of the $[C_8C_1Im][BF_4]$ (21.6 ± 2.2 layers thick) and has parameters $n = 0$, $E_{des} = 130 \text{ kJ mol}^{-1}$, pre-exponential factor, $A = 3.3 \times 10^{14} \text{ s}^{-1}$ and heating rate of 0.5 K s^{-1} . The black line represents the theoretical fit to the contaminant peak with the parameters initial coverage = 13.8 layers, $n = 1$, $E_{des} = 97 \text{ kJ mol}^{-1}$, pre-exponential factor, $A = 1 \times 10^{14} \text{ s}^{-1}$ and heating rate of 0.5 K s^{-1} . The high temperature peak can be seen to be well modelled by the red line, which has the same fit parameters as for the $m/z = 195$ amu peak in fig. 5.1. The reasonably high E_{des} value for the contaminant within the IL suggests that some strong interactions are present, which could indicate some form of hydrogen bonding or dipolar interaction with the IL. This would explain why the degassing procedure to prepare the IL for use was unsuccessful in removing the contaminant, although does not give a definitive answer for the contaminant identity.

8.5 Calibration of experimental signal to a CO₂ pressure

Calibration of the CO₂ signal could not be performed by using the transition from first order TPD peak shapes to zero order TPD peak shapes for CO₂ adsorbed on the gold surface, like the $[C_8C_1Im][BF_4]$ was. This was due to the fact that the minimum sample temperature that could be reached in this study ($\approx 88 \text{ K}$) was not low enough to stabilise either monolayers or multilayers of CO₂ on the gold surface. Calibration of the experimental signal to a CO₂ pressure allows the results to be discussed in terms of quantities which are more relatable to both the amounts of CO₂ that the surface was initially exposed to and studies

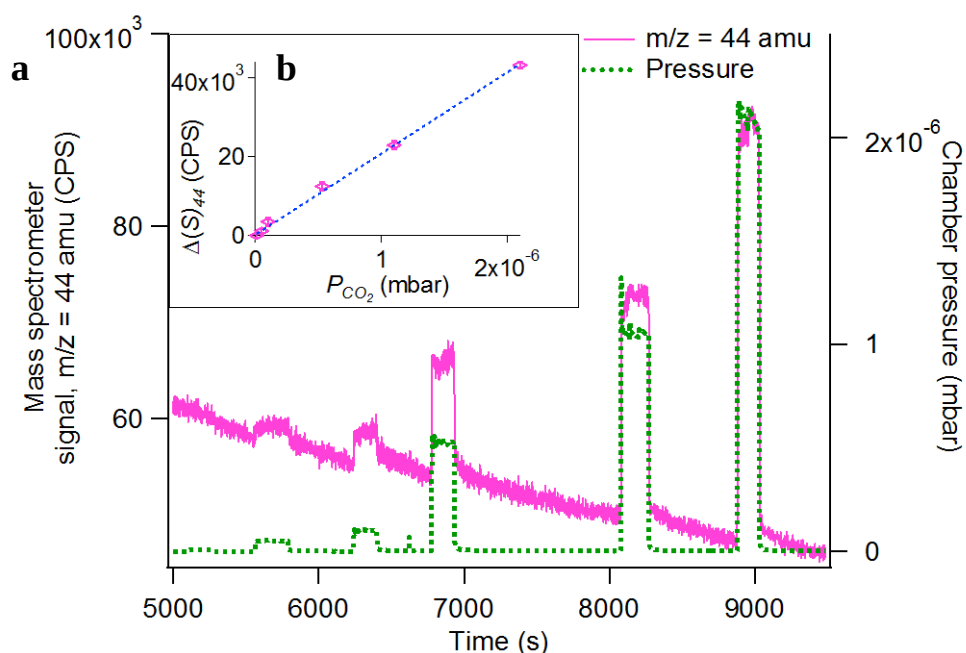


Figure 8.10: Results obtained from the calibration experiment to relate the CO_2 pressure to measured signal in the $m/z = 44$ amu fragment. The plot in (a) shows the measured quantities; pressure detected by the ion gauge (dashed green line) and the experimentally detected signal (pink line). Inset (b) shows the change in the 44 amu peak signal versus the pressure in the chamber due to CO_2 being leaked in, with the pink data points being obtained from (a). Data has been modelled with a fit of the form $y = mx$ (blue dashed line), where the gradient is $(2.07 \pm 0.04) \times 10^{10}$ CPS mbar $^{-1}$.

performed by other research groups. Calibration of the CO_2 signal, shown graphically in fig. 8.10, was performed by leaking CO_2 into the vacuum chamber at different pressures ranging from 1×10^{-8} mbar to 2×10^{-6} mbar, whilst collecting the $m/z = 44$ amu signal, with the same spectrometer settings that would be used for collection of experimental data. During calibration the gold substrate was at room temperature and was in the analysis position such that the CO_2 that would collide with the sample and would be reflected into the mass spectrometer. This meant that the chamber pressure and the CO_2 pressure local to the surface were the same, as the sticking probability of the CO_2 on the room temperature gold was assumed to be zero. As the LTLOS was in operation the pressure within the mass spectrometer is dictated by the local pressure above the gold surface. The change in $m/z = 44$ amu signal was plotted against the change in pressure, fig. 8.10b, to obtain a graph which could be fitted with the model $y = mx$. The gradient of the graph in fig. 8.10b is calculated to be $(2.07 \pm 0.04) \times 10^{10}$ CPS mbar $^{-1}$, so after correction for pressure gauge sensitivity from nitrogen to CO_2 (pressure gauge was calibrated for nitrogen) the equation of best fit for the calibration curve was found to be

$$\Delta(S_{44}) = (2.90 \pm 0.06) \times 10^{10} \times P_{CO_2} \quad \text{Equation 8.5}$$

where $\Delta(S_{44})$ is the change in the mass spectrometer signal for the $m/z = 44$ amu trace (CPS), and P_{CO_2} is the pressure of CO_2 in the chamber (which is the same as the local CO_2 pressure). This can be rearranged to give the expression for the pressure of CO_2 for an experimentally measured signal:

$$P_{CO_2} = (3.45 \pm 0.04) \times 10^{-11} \times \Delta(S_{44}) \quad \text{Equation 5.1}$$

Equation 5.1 can also be used to convert peak areas from the experimentally measured ‘counts’ to ‘mbar s’, as described in section 5.3.1. From the way in which the calibration was performed the CO_2 ‘pressure’ during a TPD experiment will be equivalent to the CO_2 pressure locally, above the gold surface. This differs from the chamber pressure as during an experiment the CO_2 desorbing from the gold expands into the vacuum, resulting in a chamber pressure which is lower than the local CO_2 pressure. The pressure seen by the mass spectrometer is also lower than the local CO_2 pressure, due to gas expansion into the LTLOS setup, which was differentially pumped. Since the LOS area is filled with the sample surface it is assumed that the pressure in the mass spectrometer is proportional to the pressure of CO_2 local to the surface, allowing the $m/z = 44$ amu signal to be related to a CO_2 pressure.

8.6 Graphical representations of experimental data for the variation in quantity of CO_2 stabilised within $[C_8C_1Im][BF_4]$ with varying IL coverage and CO_2 dose pressure

Further to the graph shown in fig. 5.5, in which the experimentally measured TPD peaks for CO_2 desorbing from $[C_8C_1Im][BF_4]$ for a variety of IL coverages and a fixed CO_2 dose pressure of 1×10^{-6} mbar are shown, this appendix includes plots of the experimental data for the other CO_2 pressures used where the IL coverage was varied. Although the peak areas and trends in this data can be determined from table 5.1, it can often be helpful to have a graphical representation of the data as well. All TPD spectra in this appendix were collected with a heating rate of 0.67 K s^{-1} . Looking at the data for the coadsorptions performed with a CO_2 pressure of 5×10^{-7} mbar, fig. 8.11, there

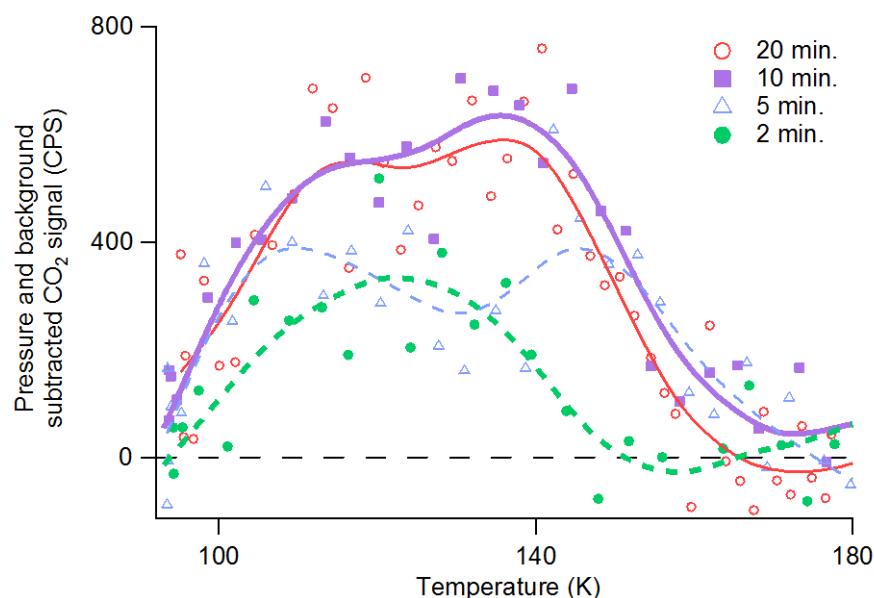


Figure 8.11: Experimental TPD curves, after application of pressure and background subtractions, for the $[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]\text{-CO}_2$ coadsorptions performed with a constant CO_2 pressure of 5×10^{-7} mbar. Markers represent true experimental data points, with the smoothing curves shown to guide the eye through the noise in the data. The colours of lines and markers correspond to each other, with the red line representing the smoothing curve for the red markers. The dashed black line represents the zero level in CO_2 signal.

isn't as clear a trend in the peaks as can be seen in fig. 5.5. What is also confusing is that the 10 minute peak appears to be larger than the 20 minute peak (from the smoothing curves) but gives a smaller peak area. This is the result of noise in a

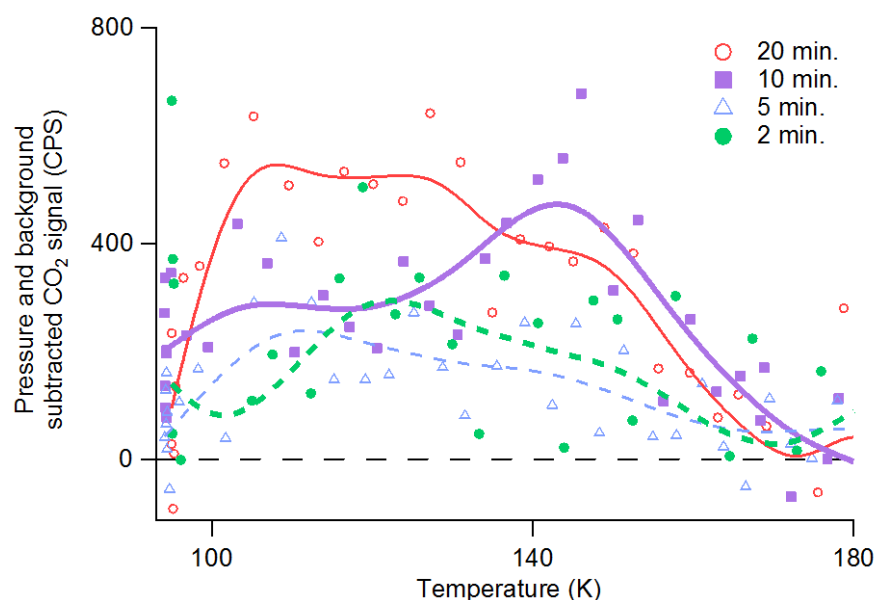


Figure 8.12: Experimental TPD curves, after application of pressure and background subtractions, for the $[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]\text{-CO}_2$ coadsorptions performed with a constant CO_2 pressure of 1×10^{-7} mbar. Experimental data is shown as coloured markers, with smoothing splines of the same colour used to guide the eye through the noise. The dashed black line represents the zero mark for the signal (signals below zero are possible due to the pressure and background subtractions).

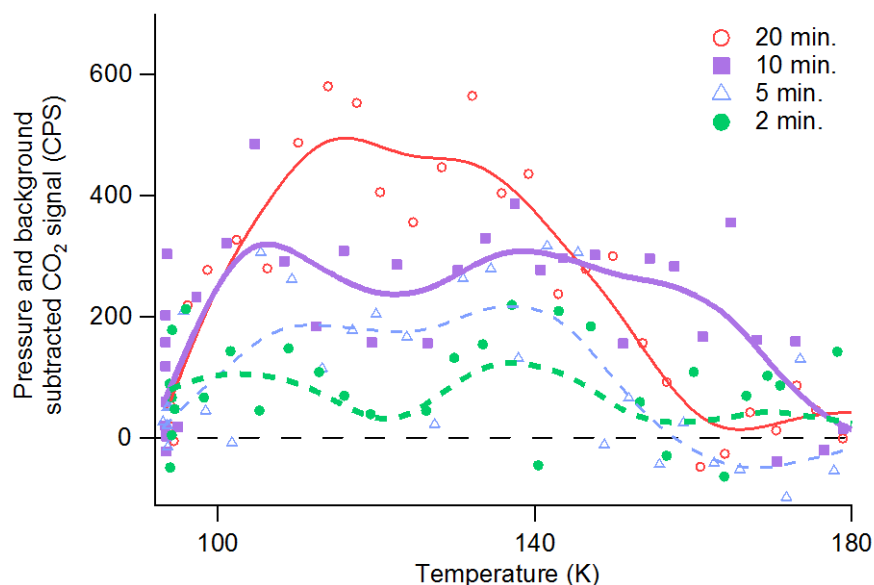


Figure 8.13: Experimental TPD curves, after application of pressure and background subtractions, for the $[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]\text{-CO}_2$ coadsorptions performed with a constant CO_2 pressure of 5×10^{-8} mbar. Markers represent data points for the different coadsorption timescales, with the lines representing smoothing splines through the data. Markers and lines of the same colour correspond to one another (i.e. purple markers and purple lines both correspond to 10 minute coadsorption). Black dashed line shows the zero position for the pressure and background subtracted signal.

few of the data points pulling the 20 minute smoothing spline to lower values, which is why the smoothing splines are used only as a rough visual guide. Figures 8.12 and 8.13 show the $[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]\text{-CO}_2$ coadsorption data for the 1×10^{-7} mbar and 5×10^{-8} mbar experiments, respectively. As was discussed in section 5.3.2, the effect of using lower pressures during coadsorption and hence stabilising smaller quantities of CO_2 means that the signal to noise ratio for these plots is lower. The general trend can still be seen in both graphs; that increasing the quantity of IL can be seen to stabilise a greater quantity of CO_2 , for a given pressure of CO_2 .

As well as looking at how the experimental data varies with changes in $[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]$ coverage for fixed CO_2 dose pressures, as shown in fig. 5.5 and the preceding section, the data can also be analysed by looking at how the peak shapes vary with CO_2 dose pressure for fixed initial $[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]$ coverages. The experimental data is largely the same as that shown in figs. 5.5 and 8.11 to 8.13, with a few extra datasets due to pressures that were only used once (e.g. 2×10^{-6} mbar in the 20 minute data), but are grouped by constant IL coverage (more accurately coadsorption timescale, since the IL dose rate is not always observed to be exactly 1 layer min^{-1}). The figures confirm what can be seen from

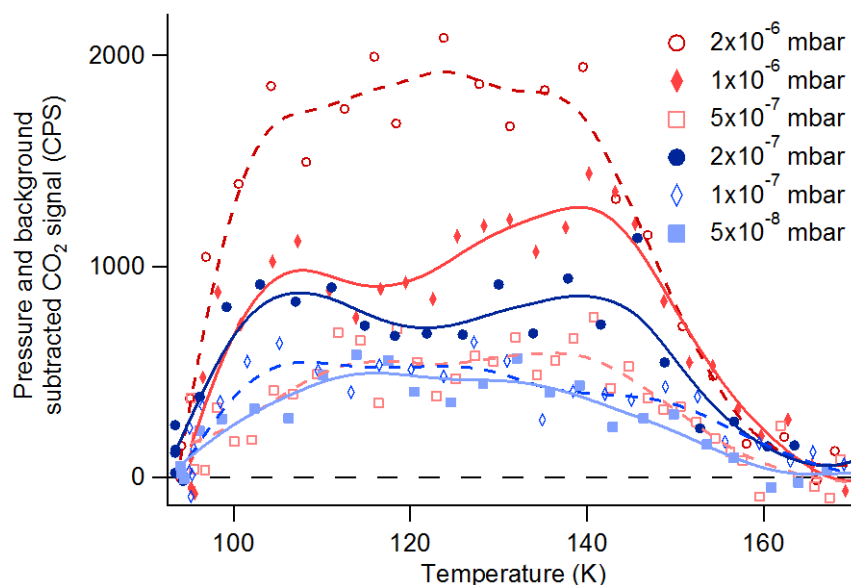


Figure 8.14: Experimental TPD curves, after application of pressure and background subtractions, for the 20 minute $[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]\text{-CO}_2$ coadsorptions, with varying CO_2 pressures. Markers represent true data points whilst lines with same colour as the markers represent smoothing splines for that data, to help guide the eye through the noise. Dashed lines correspond to open markers and solid lines to filled markers. The dashed black line represents the zero mark for the pressure and background subtraction axis.

the data in table 5.1; that increasing the dose pressure used during coadsorption increases the quantity of CO_2 captured by the IL. Figure 8.14 shows the data for the 20 minute coadsorptions, fig. 8.15 shows the data for the 10 minute

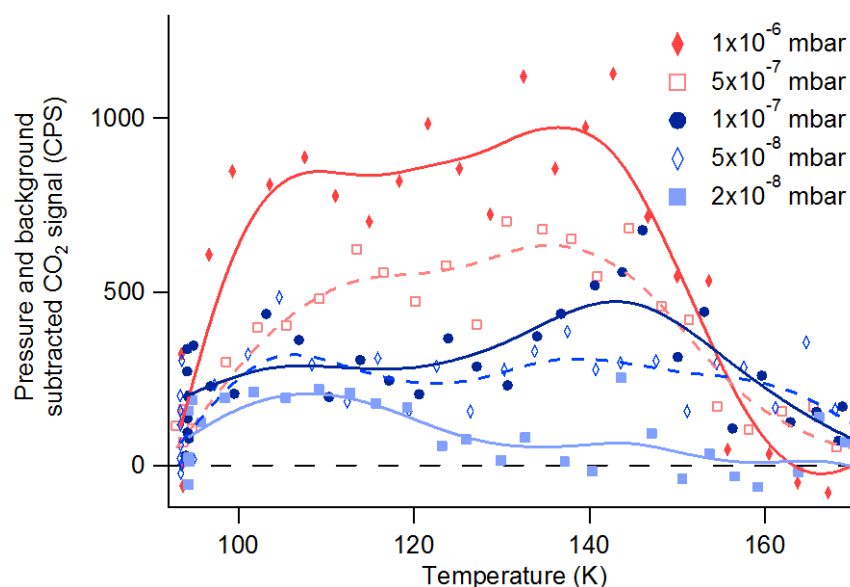


Figure 8.15: Experimental TPD curves, after application of pressure and background subtractions, for the 10 minute $[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]\text{-CO}_2$ coadsorptions, with varying CO_2 pressures. Markers represent true data points whilst lines with same colour as the markers represent smoothing splines for that data, to help guide the eye through the noise. Dashed lines correspond to open markers and solid lines to filled markers. The dashed black line represents the zero mark for the pressure and background subtraction axis.

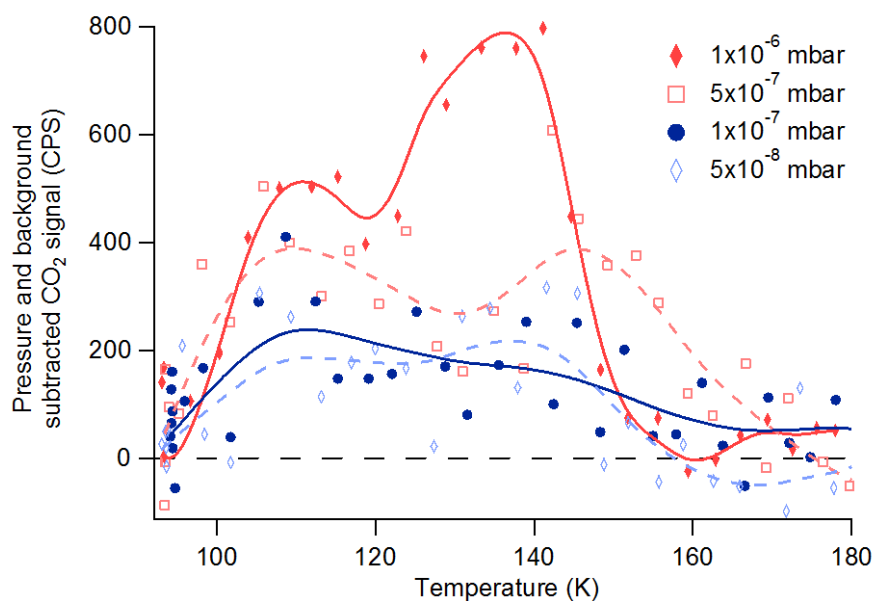


Figure 8.16: Experimental TPD curves, after application of pressure and background subtractions, for the 5 minute $[C_8C_1Im][BF_4]$ - CO_2 coadsorptions, with varying CO_2 pressures. Markers represent true data points whilst lines with same colour as the markers represent smoothing splines for that data, to help guide the eye through the noise. Dashed lines correspond to open markers and solid lines to filled markers. The dashed black line represents the zero mark for the pressure and background subtraction axis.

coadsorptions, fig. 8.16 shows the data for the 5 minute coadsorption data and fig. 8.17 shows the 2 minute coadsorption data. All graphs have smoothing splines to help guide the eye through the noise in the data, and a dashed black

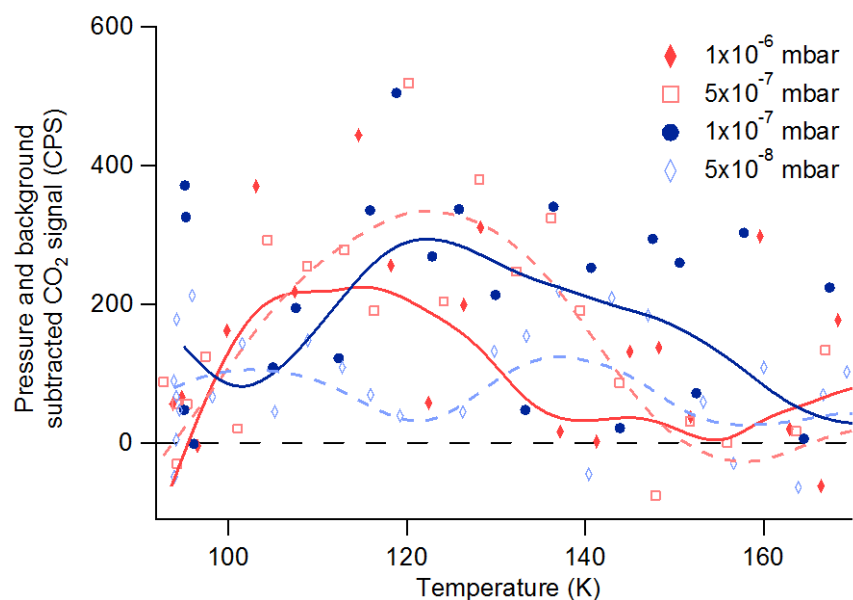


Figure 8.17: Experimental TPD curves, after application of pressure and background subtractions, for the 2 minute $[C_8C_1Im][BF_4]$ - CO_2 coadsorptions, with varying CO_2 pressures. Markers represent true data points whilst lines with same colour as the markers represent smoothing splines for that data, to help guide the eye through the noise. Dashed lines correspond to open markers and solid lines to filled markers. The dashed black line represents the zero mark for the pressure and background subtraction axis.

line to represent the zero level for the pressure and background subtracted data. The trend, increasing quantity of CO₂ captured with increase in pressure, is displayed most clearly in fig. 8.16, but can be seen in most of the plots. The 2 minute coadsorption data (fig. 8.17) visually do not seem to follow any trend as the smoothing splines are affected by the low signal to noise ratio. The CO₂ TPD profiles appear to have a ‘double peak’ appearance to them, which may be suggestive of two types of CO₂ binding environment within the [C₈C₁Im][BF₄] network, as discussed in section 5.3.4. Hopefully these plots have helped illustrate the trends observed in table 5.1, and have aided in understanding of the experimental data.

8.7 CO₂ population distributions for the [C₈C₁Im][BF₄]-CO₂ coadsorption data

Figure 5.9 shows the population distributions for the 10 minute [C₈C₁Im][BF₄]-CO₂ coadsorptions, which are obtained from fitting the experimental TPD spectra with a range of hypothetical CO₂ environments. These individual CO₂ environments have activation energies of desorption ranging from 26 kJ mol⁻¹ upwards (in steps of 1.5 kJ mol⁻¹), with the relative population of each state being varied to ensure that the sum of the hypothetical TPD profiles give the best fit to the experimental TPD profile. These fitted relative populations can be converted into a CO₂ coverage by using the relationship

$$\sum \text{Relative populations} = \text{Experimental Peak Area (mbar s)}$$

which means that the individual relative populations need to be multiplied by the experimental peak area divided by the total relative population. Figure 8.18 shows the fitted population profiles for the [C₈C₁Im][BF₄]-CO₂ coadsorption data for the 20 minute doses. As discussed in the main text there appears to be a greater proportion of the CO₂ stabilised in the 33 to 42 kJ mol⁻¹ range than there is in the 26 to 33 kJ mol⁻¹ range for the pressures of 5×10⁻⁷ mbar and 1×10⁻⁶ mbar. The highest pressure of 2×10⁻⁶ mbar appears to have a more even distribution of CO₂ environments, possibly indicating a requirement for a higher pressure to access certain environments. As was the case for the 10 minute coadsorption data, fig. 5.9, the lowest pressure results do not have the population

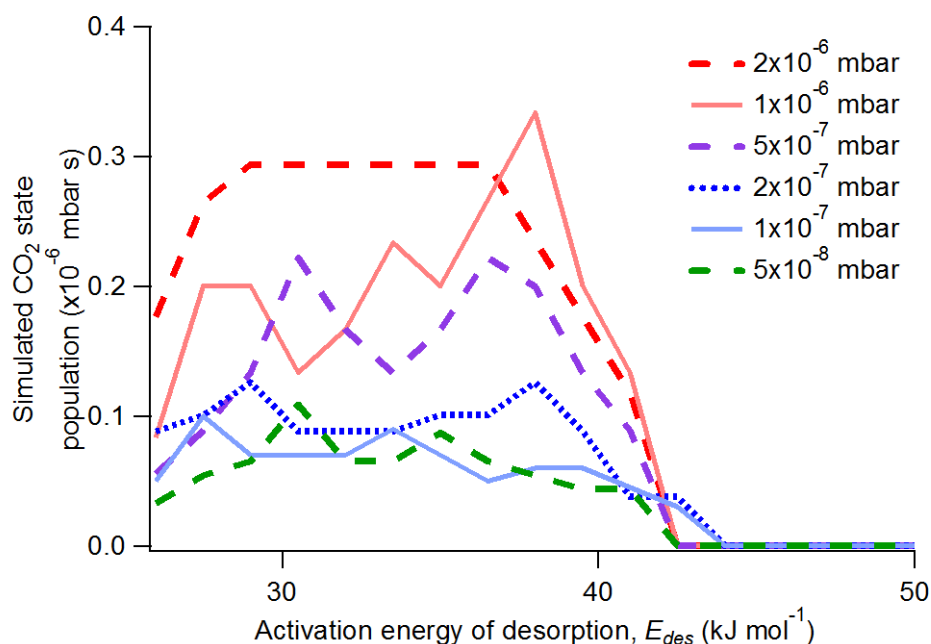


Figure 8.18: Fitted CO₂ TPD spectra for the 20 minute [C₈C₁Im][BF₄]-CO₂ coadsorption experiments. Pressures used are shown in the legend, with red colours used for the “10⁻⁶ mbar”, blues for “10⁻⁷ mbar” and greens for “10⁻⁸ mbar”. CO₂ states can be seen to have E_{des} values ranging from 26 to 43 kJ mol⁻¹.

distribution that would be expected (a higher quantity of CO₂ in more stabilised states), instead appearing to have a reasonably uniform distribution of states. Figures 8.19 and 8.20 show the population distributions from the 5 minute

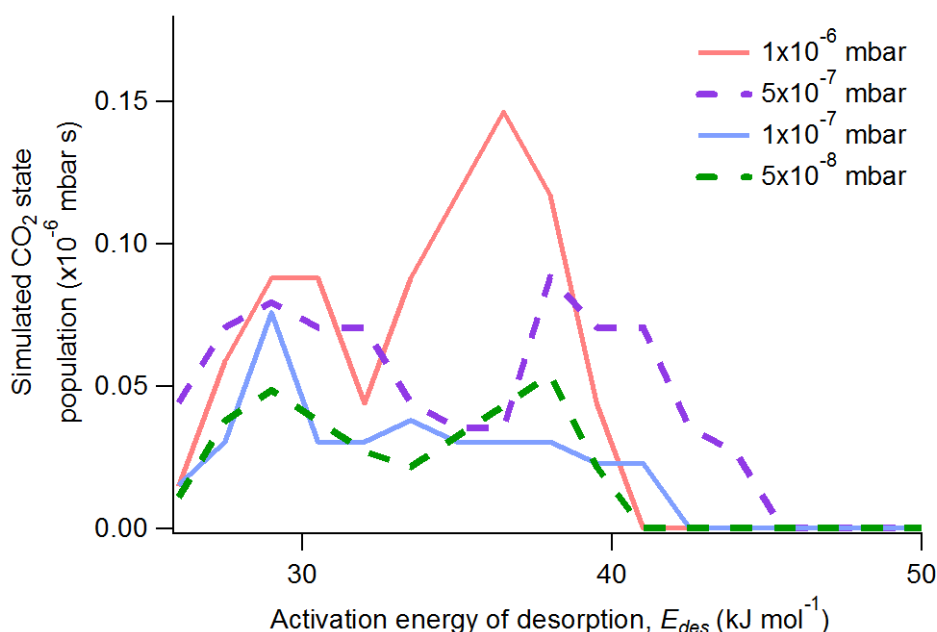


Figure 8.19: Fitted CO₂ TPD spectra for the 5 minute [C₈C₁Im][BF₄]-CO₂ coadsorption experiments. Pressures used are shown in the legend, with red colours used for the “10⁻⁶ mbar”, blues for “10⁻⁷ mbar” and greens for “10⁻⁸ mbar”. CO₂ states can be seen to have E_{des} values ranging from 26 to 44 kJ mol⁻¹. There appears to be a link between the dosing pressure and the CO₂ state population.

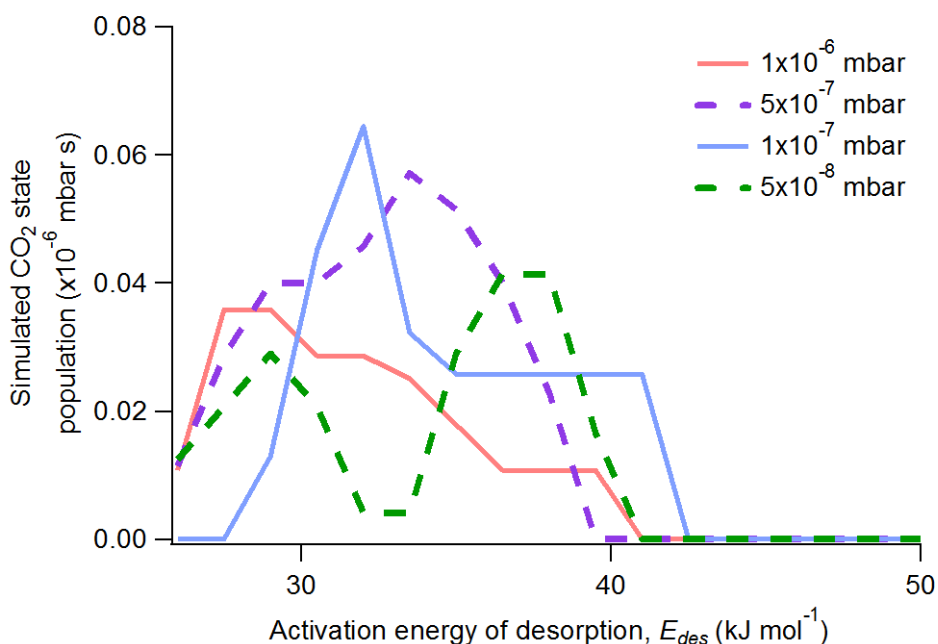


Figure 8.20: Fitted CO₂ TPD spectra for the 2 minute [C₈C₁Im][BF₄]-CO₂ coadsorption experiments. Pressures used are shown in the legend, with red colours used for the “10⁻⁶ mbar”, blues for “10⁻⁷ mbar” and greens for “10⁻⁸ mbar”. The data in this graph does not appear to exhibit any trends, since the experimental signal was of the same order as the background noise level, so is included only for completeness. There is no consistency in E_{des} range or population distribution shape for this data.

[C₈C₁Im][BF₄]-CO₂ and 2 minute [C₈C₁Im][BF₄]-CO₂ coadsorptions, respectively. These datasets are included for completeness as drawing any meaningful conclusions from them is difficult. The 5 minute data shows the trend that dosing with a higher CO₂ pressure stabilises more CO₂, with the CO₂ coverage for a given E_{des} value generally increasing with pressure. The population distributions appear to consist of two peaks, one at high E_{des} and one at low E_{des} , although this is possibly an artefact from the noise in the data and not an indication that the 5 minute IL dose has managed to order itself such that these two types of site exist. The 2 minute data in fig. 8.20 have not been discussed in the main text due to the fact that there is no trend seen in any of the data. The 1×10⁻⁶ mbar CO₂ dose (light red line), which is expected to have stabilised the most CO₂, can be seen to have some of the lowest CO₂ populations. This is a direct result of having small quantities of CO₂ desorbing from the surface, the intensities of which are comparable to the noise in the background $m/z = 44$ amu signal. It should be noted that, due to the high levels of noise associated with all of the CO₂ TPD spectra, the findings based on the shape of the population profiles are speculative, with further experimentation required to

confirm these results. The adsorption site distribution is assumed to be random, due to the nature of the IL dosing mechanism (IL molecule sticks where it lands in the conformation it arrived in), but there may be a statistical distribution of binding sites which could help explain the CO₂ population distributions seen here, and explain why the higher E_{des} sites are not the most occupied at low CO₂ dose pressures.

8.8 Monolayer determination for [C₈C₁Im][Tf₂N] using TPD

As described in appendix 8.3 the IL [C₈C₁Im][BF₄] was dosed onto the cooled gold substrate at a rate of approximately one layer of ion pairs per minute. This was a convenient dosing rate as it allowed quick judgements on the data to be made as the number of layers of IL was approximately the same as the length of the dose in minutes. The desorption temperature for [C₈C₁Im][BF₄] was inherited from previous studies on the IL within the group, however such studies of [C₈C₁Im][Tf₂N] had not been performed within the group previously. As a result it was decided that the temperature at which the IL [C₈C₁Im][Tf₂N] doses at a rate of one layer per minute, would be found. Experiments were performed in which the gold surface, at a temperature of 273 K, was exposed to 1 minute of [C₈C₁Im][Tf₂N] with the IL evaporator set to different temperatures (strictly the evaporator used a variable transformer, so a temperature could not be chosen, but would be attained through thermal equilibrium at a given voltage setting). The TPD spectra, following the $m/z = 195$ amu fragment, for the four temperatures studied are shown in fig. 8.21. From analysing the shapes of the desorption peaks the transition between first order TPD peak shape (characterised by peak maxima all being at the same temperature) and zero order TPD peak shape (characterised by the sharp drop off) can be seen to occur between the 519 K and 521 K spectra. The first order peak maxima occur at 381 K (purple dashed line), whereas the 521 K spectrum maximum occurs at a temperature of 383 K. Despite this being only a small difference, considering it alongside the fact that the 521 K data displays a pointier, more zero order shape than the 519 K data, means that it can be concluded that for the IL [C₈C₁Im][Tf₂N] a dose rate of a monolayer per minute is achieved with an evaporator with $T_{\text{evap}} \approx 519$ K.

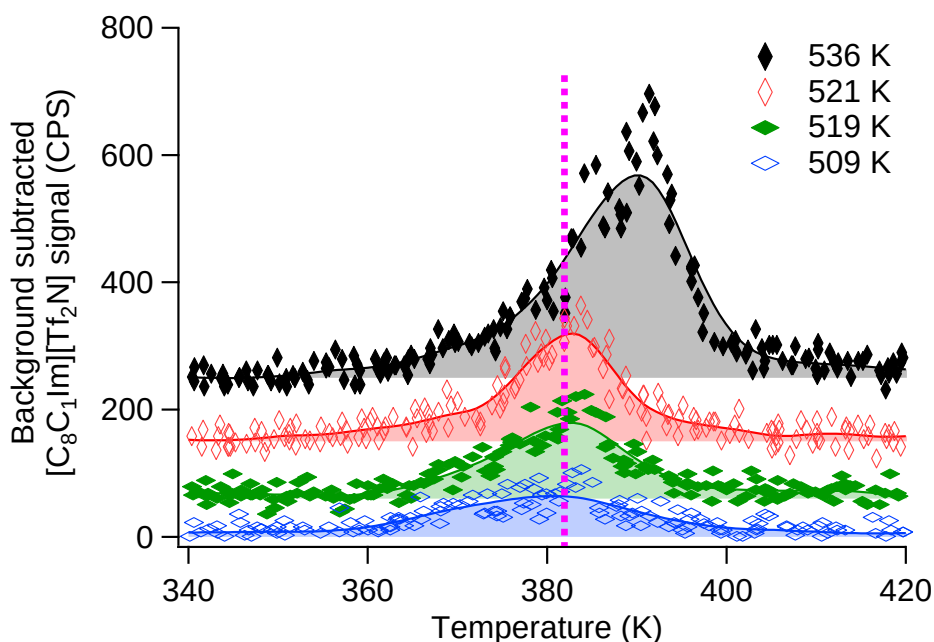


Figure 8.21: TPD spectra for the IL $[\text{C}_8\text{C}_1\text{Im}][\text{Tf}_2\text{N}]$, following the $m/z = 195$ amu fragment, for initial coverages corresponding to a 1 minute dose at the evaporator temperatures shown (509 to 536 K). Markers represent background subtracted experimental data and solid lines represent smoothing curves to guide the eye. The purple dotted line identifies $T = 381$ K, which can be seen to correspond to the maximum temperature for the first order TPD peaks (509 and 519 K). The heating rate during TPD was 0.5 K s^{-1} . Spectra have been offset for clarity.

Shortly after this calibration of the IL monolayer coverage had been performed, the mass spectrometer developed a fault and needed repairing. It was decided that another experiment to confirm the monolayer coverage should be performed, similar to the one described in appendix 8.3, in which the length of time the gold substrate was exposed to the IL for was varied. This would ensure that any errors induced by the fault in the mass spectrometer would be negated, as the monolayer coverage would be obtained with the repaired mass spectrometer. The room temperature gold surface was exposed to the IL $[\text{C}_8\text{C}_1\text{Im}][\text{Tf}_2\text{N}]$ for timescales between 60 and 240 seconds, using an IL evaporator temperature of 519 K. The resulting TPD spectra are shown in fig. 8.22 where it can be seen that the 60 second $[\text{C}_8\text{C}_1\text{Im}][\text{Tf}_2\text{N}]$ dose gives a first order peak shape, whilst larger doses (90 to 240 seconds) give more ‘triangular’ zero order peak shapes. The monolayer coverage, calculated from the integrated peak area underneath the 60 second background subtracted TPD spectrum (blue squares), was found to be 10960 ± 40 counts, with the small error resulting from the low background signal in the $m/z = 195$ amu. A larger source of error in the determination of the monolayer coverage is the determination of the exact dose

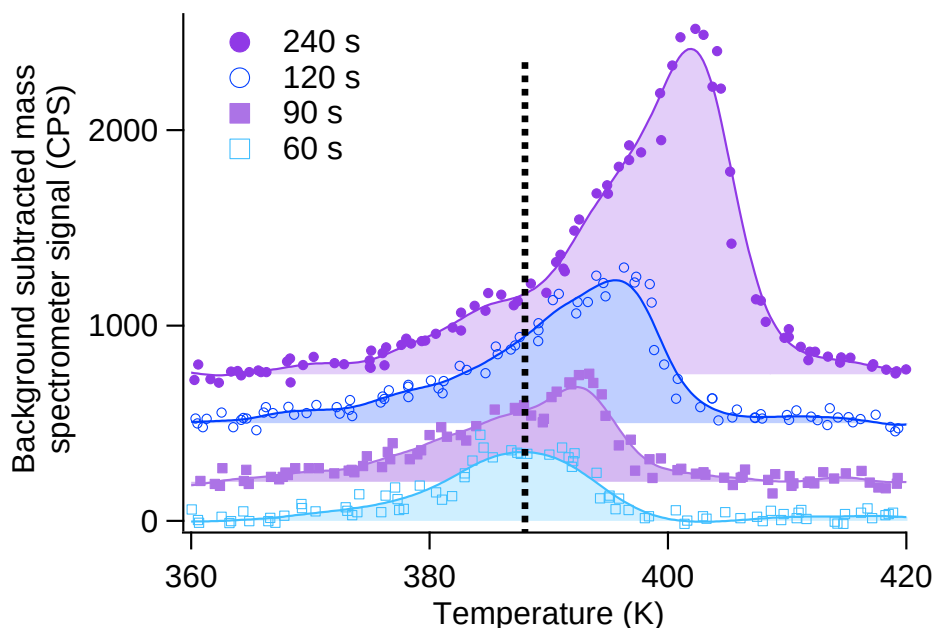


Figure 8.22: TPD spectra for the IL $[\text{C}_8\text{C}_1\text{Im}][\text{Tf}_2\text{N}]$, following the $m/z = 195$ amu fragment, for varying initial coverages between 60 and 240 seconds. Experimental data is shown as markers whilst solid lines represent smoothing curves to guide the eye through the shape of the data. The black dotted line can be seen to represent the position of the maximum of the first order TPD peak (387 K). Peak shapes for doses over 60 seconds exhibit zero order shapes. The heating rate during TPD was 0.5 K s^{-1} . Spectra have been offset for clarity.

length at which the transition from first order TPD peak to zero order peak occurs. The peak area corresponding to the 90 second dose length is $\approx 15050 \pm 60$ counts, and this can be seen to be a zero order TPD peak. As a result the transition between first and zero order (and hence the transition from monolayer to multilayer) in theory could have occurred anywhere between 60 seconds of dosing and 90 seconds of dosing. This would suggest an error in the monolayer coverage of 50%, however, from looking at how far the peak maximum has shifted in the 90 second dose spectrum relative to the 60 second dose, a more reasonable estimation of the error in the monolayer coverage is 10%. This 10% error in the monolayer coverage corresponds to a 10% error in the calculated $[\text{C}_8\text{C}_1\text{Im}][\text{Tf}_2\text{N}]$ coverage.

A comparison of the position of the first order TPD peak maxima in figs. 8.21 and 8.22 show that they are different ($T_{\text{max}} = 381 \text{ K}$ and 388 K , respectively). The physical interpretation of this shift in peak maximum is an increase in E_{des} for the IL, which may be due to the gold surface adjusting with subsequent desorption runs, as carbonaceous material chemisorbs to the surface during experimental runs.

8.9 Graphical representations of experimental data for the variation in quantity of CO₂ stabilised within [C₈C₁Im][Tf₂N] with varying IL coverage and CO₂ dose pressure

Figure 6.3 shows the experimentally measured TPD peaks for CO₂ from surfaces with varying initial [C₈C₁Im][Tf₂N] coverages but a fixed CO₂ dose pressure of 1×10^{-6} mbar used during coadsorption. The data representing the amount of CO₂ stabilised for all of the surfaces studied for this IL are shown in table 6.1, with graphical representations of these data shown in this appendix, for added clarity. Experimental data for the [C₈C₁Im][Tf₂N]–CO₂ coadsorptions for the 5×10^{-7} mbar studies are shown in fig. 8.23, where it can be seen that as the quantity of IL is increased, the CO₂ TPD peak increases, indicating a greater

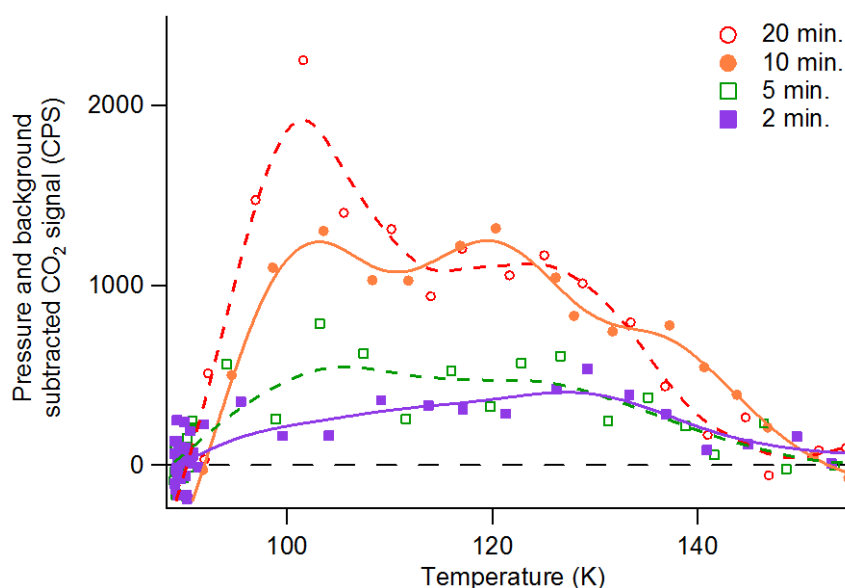


Figure 8.23: A comparison of the experimental data for the desorption of CO₂ from within the coadsorbed [C₈C₁Im][Tf₂N]–CO₂ network for a CO₂ dose pressure of 5×10^{-7} mbar with varying IL coverages (IL dose rate ≈ 1 layer per minute). Experimental data points, after pressure and background subtractions have been applied, are shown by the markers whilst lines represent smoothing curves applied to the data to guide the eye. Markers and lines which are the same colour correspond to each other. The dashed black line represents the ‘zero line’ for experimental signal. The heating rate during TPD was around 0.67 K s^{-1} .

quantity of CO₂ is stabilised. A similar trend can be seen in the plots for the coadsorption data for CO₂ pressures of 2×10^{-7} and 1×10^{-7} mbar, shown in figs. 8.24 and 8.25 respectively. Figure 8.26 shows the [C₈C₁Im][Tf₂N]–CO₂ coadsorption data for a CO₂ pressure of 5×10^{-8} mbar, however this data does not

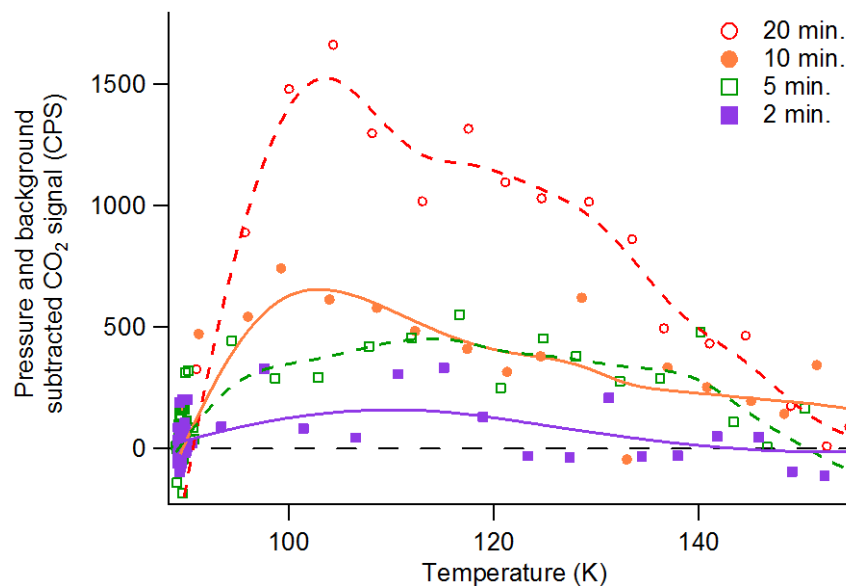


Figure 8.24: A comparison of the experimental data for the desorption of CO₂ from within the coadsorbed [C₈C₁Im][Tf₂N]–CO₂ network for a CO₂ dose pressure of 2×10^{-7} mbar with varying IL coverages. Experimental data points, after pressure and background subtractions have been applied, are shown by the markers whilst lines represent smoothing curves applied to the data to guide the eye. The times correspond to coadsorption timescales, where ≈ 1 layer of IL was deposited per minute. Markers and lines which are the same colour correspond to each other. The dashed black line represents the ‘zero line’ for experimental signal. The heating rate during TPD was around 0.67 K s^{-1} .

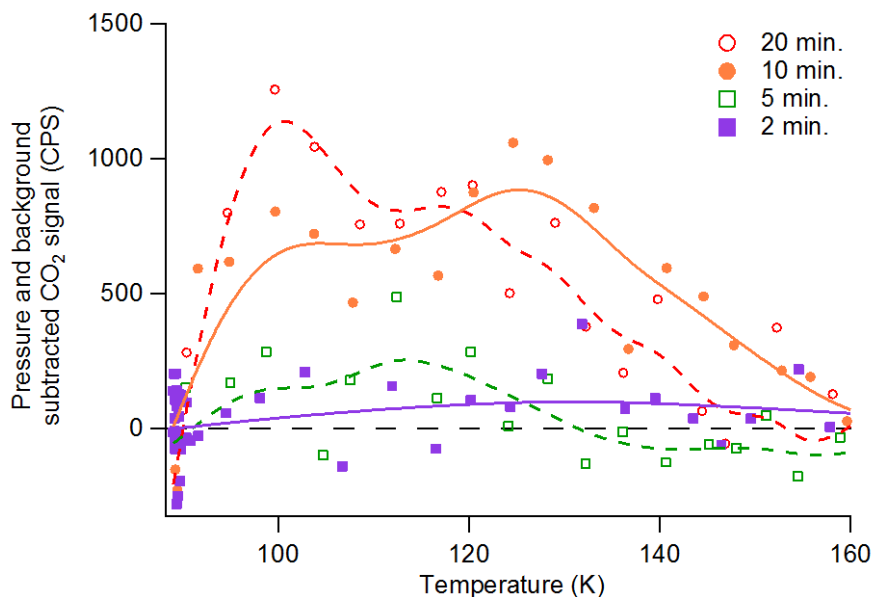


Figure 8.25: A comparison of the experimental data for the desorption of CO₂ from within the coadsorbed [C₈C₁Im][Tf₂N]–CO₂ network for a CO₂ dose pressure of 1×10^{-7} mbar with varying coadsorption timescales (≈ 1 IL layer per minute). Experimental data points, after pressure and background subtractions have been applied, are shown by the markers whilst lines represent smoothing curves applied to the data to guide the eye. Markers and lines which are the same colour correspond to each other. The dashed black line represents the ‘zero line’ for experimental signal. The heating rate during TPD was around 0.67 K s^{-1} .

appear to show the same trend as the other data sets, with the 10 minute (orange) data showing a larger peak area than the 20 minute (red) data (peak areas given in table 6.1). The reason for this discrepancy is unknown but is likely due to the

use of a low CO₂ pressure, resulting in a smaller quantity of CO₂ stabilised and

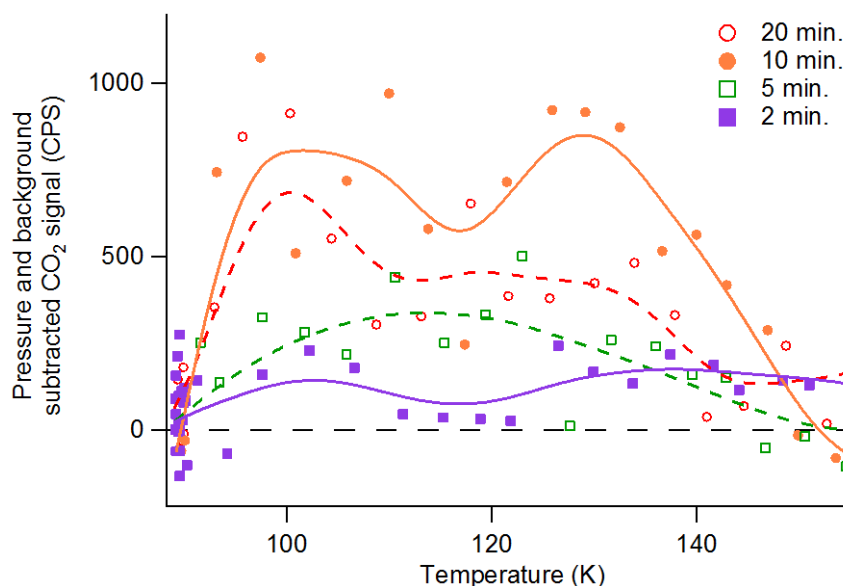


Figure 8.26: A comparison of the experimental data for the desorption of CO₂ from within the coadsorbed [C₈C₁Im][Tf₂N]–CO₂ network for a CO₂ dose pressure of 5×10^{-8} mbar with varying coadsorption timescales (≈ 1 IL layer per minute). Experimental data points, after pressure and background subtractions have been applied, are shown by the markers whilst lines represent smoothing curves applied to the data to guide the eye. Markers and lines which are the same colour correspond to each other. The dashed black line represents the ‘zero line’ for experimental signal. The heating rate during TPD was around 0.67 K s^{-1} .

a greater susceptibility to the effects of background noise.

Further to studying how the amount of CO₂ stabilised within the IL varies with a fixed CO₂ dose pressure and variation in initial IL coverage, it is also possible to look at the variation in CO₂ peak area as a function of dose pressure used for similar initial IL coverages (same coadsorption timescales). The data is exactly the same as that shown in figs. 6.3 and 8.23 to 8.26, but allows the trends with variation in pressure to be seen on the graphs, rather than the trends with IL quantity. Experimental data for the 20 minute coadsorptions can be seen in fig. 8.27, where a clear trend of increasing CO₂ peak area with increasing dose pressure can be seen. The experimental CO₂ TPD profiles all appear to be similar in shape, which could either be coincidental or an indication that there is a very even distribution of adsorption sites within the [C₈C₁Im][Tf₂N] network. Figure 8.28 shows the variation of the CO₂ TPD peak shapes as the CO₂ dose pressure was varied for the 10 minute coadsorption timescale (which results in an IL layer ≈ 10 ion pairs thick). Experimental data for the 5 minute and 2 minute coadsorption data sets are shown in figs. 8.29 and 8.30 respectively. The TPD profiles in figs. 8.28 to 8.30 show the general trend

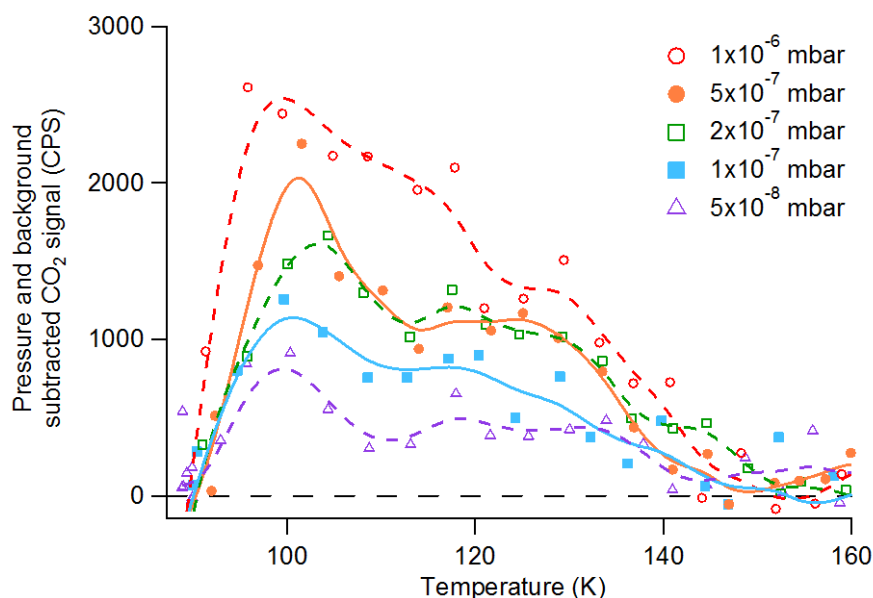


Figure 8.27: A comparison of the experimental data for the desorption of CO₂ from within the coadsorbed [C₈C₁Im][Tf₂N]–CO₂ network for varying CO₂ dose pressures, but a coadsorption timescale of 20 minutes (≈ 20 IL layers). Experimental data points, after pressure and background subtractions have been applied, are shown by the markers whilst lines represent smoothing curves applied to the data to guide the eye. Markers and lines which are the same colour correspond to each other. The dashed black line represents the ‘zero line’ for experimental signal. The heating rate during TPD was around 0.67 K s^{-1} .

of an increased CO₂ peak area results from a larger dose pressure used during coadsorption, but each figure has at least one exception where the data is not quite in the correct order. One of the causes for this is that although the

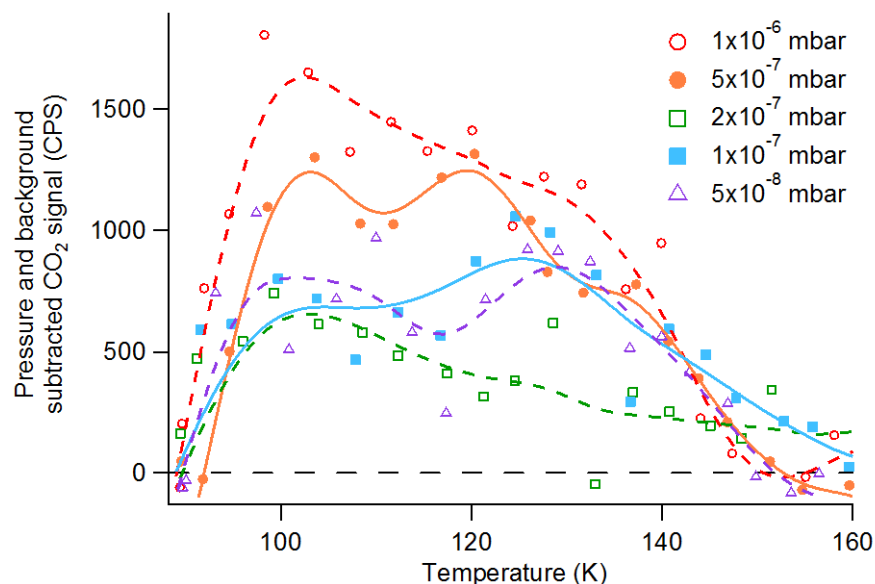


Figure 8.28: A comparison of the experimental data for the desorption of CO₂ from within the coadsorbed [C₈C₁Im][Tf₂N]–CO₂ network for varying CO₂ pressures, but a fixed coadsorption timescale of 10 minutes (≈ 10 IL layers). Experimental data points, after pressure and background subtractions have been applied, are shown by the markers whilst lines represent smoothing curves applied to the data to guide the eye. Markers and lines which are the same colour correspond to each other. The dashed black line represents the ‘zero line’ for experimental signal. The heating rate during TPD was around 0.67 K s^{-1} .

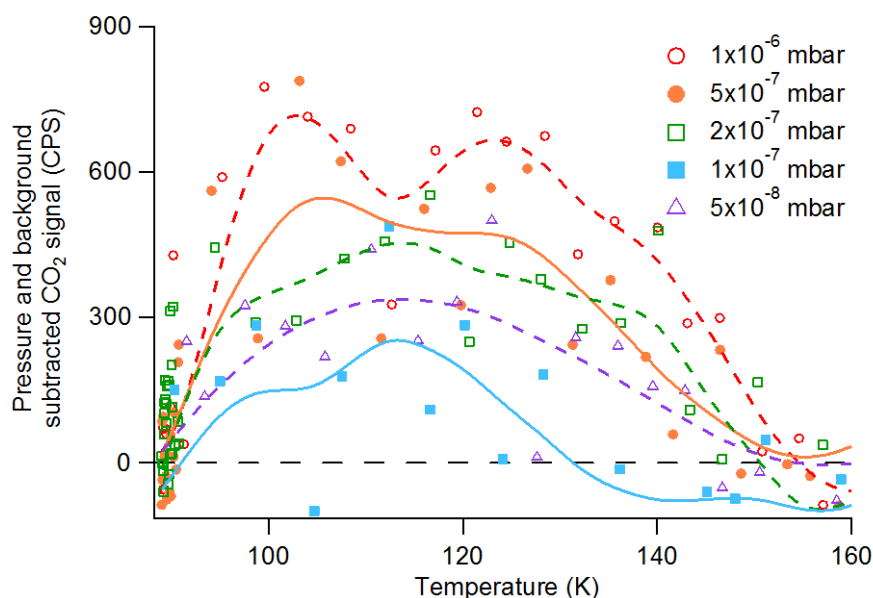


Figure 8.29: A comparison of the experimental data for the desorption of CO₂ from within the coadsorbed [C₈C₁Im][Tf₂N]–CO₂ network for varying CO₂ pressures, but a fixed coadsorption timescale of 5 minutes (≈ 5 IL layers). Experimental data points, after pressure and background subtractions have been applied, are shown by the markers whilst lines represent smoothing curves applied to the data to guide the eye. Markers and lines which are the same colour correspond to each other. The dashed black line represents the ‘zero line’ for experimental signal. The heating rate during TPD was around 0.67 K s^{-1} .

coadsorption timescales are the same the IL layers are not necessarily exactly the same thickness (layer thicknesses can vary by 25 to 50%). This is a result of

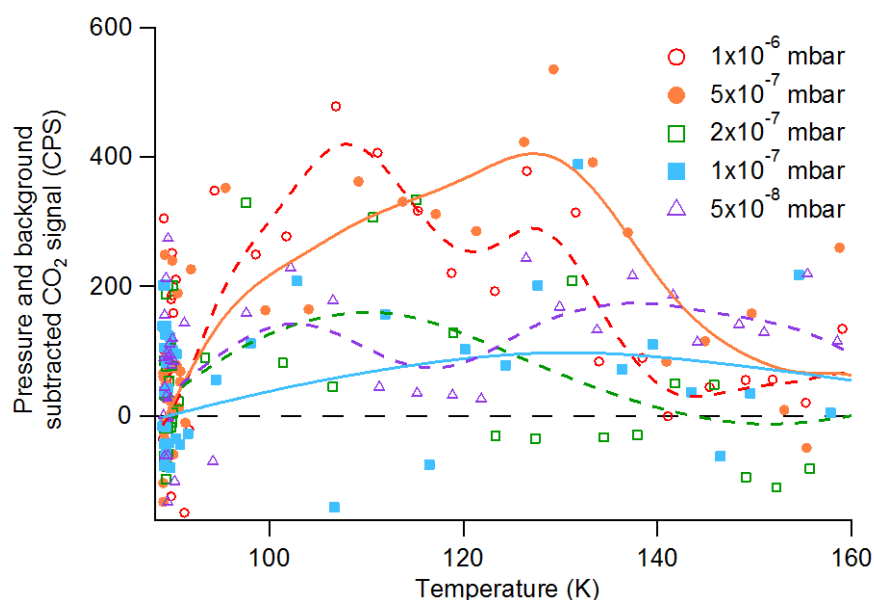


Figure 8.30: A comparison of the experimental data for the desorption of CO₂ from within the coadsorbed [C₈C₁Im][Tf₂N]–CO₂ network for varying CO₂ pressures, but a fixed coadsorption timescale of 2 minutes (≈ 2 IL layers). Experimental data points, after pressure and background subtractions have been applied, are shown by the markers whilst lines represent smoothing curves applied to the data to guide the eye. Markers and lines which are the same colour correspond to each other. The dashed black line represents the ‘zero line’ for experimental signal. The heating rate during TPD was around 0.67 K s^{-1} .

the evaporator temperature not being exactly the same, so the IL desorption rate is different, as discussed in the main text 3.2.3.

8.10 Comparison of corrected CO₂ desorption peak areas for experiments with the same CO₂ exposure

As discussed in section 5.3.2 a comparison of the corrected experimental peak areas—for the CO₂ desorption peak from the IL—from experiments where the same exposure (exposure = dose pressure × dose time) of CO₂ was performed. These comparisons can be used to help determine whether having a larger quantity of IL or having a larger dose pressure of CO₂ is the more significant factor in capturing a larger quantity of CO₂. In this appendix the comparisons are made for both of the ILs studied in this thesis.

For the studies of the [C₈C₁Im][BF₄]-CO₂ system the exposures of each of the experiments performed can be shown in table 8.1, where the exposures have been calculated in terms of ‘10⁻⁶ mbar minutes’, for ease of comparison. Cells in the table 8.1 which have the same exposure, and therefore the same

Table 8.1: The values in the table show experimental exposures, calculated in units of 10⁻⁶ mbar minutes from the equation exposure = dose pressure (in 10⁻⁶ mbar) × dose time (minutes), for the experiments with [C₈C₁Im][BF₄]-CO₂ coadsorptions. Cells with the same colour background represent experiments with the same exposure, and are compared in the main text.

CO ₂ Dose Pressure	Dose pressure in ‘10 ⁻⁶ mbar’	20 minutes	10 minutes	5 minutes	2 minutes
2×10 ⁻⁸ mbar	0.02	-	0.2	-	-
5×10 ⁻⁸ mbar	0.05	1	0.5	0.25	0.1
1×10 ⁻⁷ mbar	0.1	2	1	0.5	0.2
2×10 ⁻⁷ mbar	0.2	4	-	-	-
5×10 ⁻⁷ mbar	0.5	10	5	2.5	1
1×10 ⁻⁶ mbar	1	20	10	5	2
2×10 ⁻⁶ mbar	2	40	-	-	-

colour, are able to have their corrected peak areas (in counts from table 5.2) directly compared. These comparisons are listed below, with the smaller dose pressures and larger initial IL coverages on the left, for ease of comparison.

2×10 ⁻⁸ mbar, 10 minutes: 7000 ± 1900	and	1×10 ⁻⁷ mbar, 2 minutes: 8200 ± 3400
5×10 ⁻⁸ mbar, 20 minutes: 19900 ± 2300	and	1×10 ⁻⁷ mbar, 10 minutes: 23800 ± 800
5×10 ⁻⁸ mbar, 20 minutes: 19900 ± 2300	and	5×10 ⁻⁷ mbar, 2 minutes: 9800 ± 2000
1×10 ⁻⁷ mbar, 10 minutes: 23800 ± 800	and	5×10 ⁻⁷ mbar, 2 minutes: 9800 ± 2000
5×10 ⁻⁸ mbar, 10 minutes: 16900 ± 4200	and	1×10 ⁻⁷ mbar, 5 minutes: 10300 ± 1700
1×10 ⁻⁷ mbar, 20 minutes: 22200 ± 2000	and	1×10 ⁻⁶ mbar, 2 minutes: 6200 ± 2900
5×10 ⁻⁷ mbar, 20 minutes: 46600 ± 1500	and	1×10 ⁻⁶ mbar, 10 minutes: 42400 ± 3400

Appendices

5×10^{-7} mbar, 10 minutes: 27600 ± 2200 and 1×10^{-6} mbar, 5 minutes: 23300 ± 900

Of the eight direct comparisons for data with the same CO₂ exposure that can be made for the corrected peak areas for CO₂ desorption from [C₈C₁Im][BF₄], six of them (75%) exhibit a larger peak area for the case where a greater initial IL coverage is used.

A similar comparison can be performed for the corrected CO₂ peak areas for desorption from [C₈C₁Im][Tf₂N]. Table 8.2 shows the surface exposures to CO₂, in the convenient units of ‘ 10^{-6} mbar minutes’, where surfaces which had the same exposure are represented by cells with the same colour. The comparisons of peak areas (in counts, from table 6.2) are listed below, with smaller dose pressures and larger initial IL coverages on the left, for ease of comparison.

Table 8.2: The values in the table show experimental exposures, calculated in units of 10^{-6} mbar minutes from the equation exposure = dose pressure (in 10^{-6} mbar) $\times$ dose time (minutes), for the experiments with [C₈C₁Im][Tf₂N]–CO₂ coadsorptions. Cells with the same colour background represent experiments with the same exposure, and are compared in the main text.

CO ₂ Dose Pressure	Dose pressure in ‘ 10^{-6} mbar’	20 minutes	10 minutes	5 minutes	2 minutes
5×10^{-8} mbar	0.05	1	0.5	0.25	0.1
1×10^{-7} mbar	0.1	2	1	0.5	0.2
2×10^{-7} mbar	0.2	4	2	1	0.4
5×10^{-7} mbar	0.5	10	5	2.5	1
1×10^{-6} mbar	1	20	10	5	2

5×10^{-8} mbar, 20 minutes: 28000 ± 2800 and 1×10^{-7} mbar, 10 minutes: 32000 ± 11000

5×10^{-8} mbar, 20 minutes: 28000 ± 2800 and 2×10^{-7} mbar, 5 minutes: 20000 ± 7300

5×10^{-8} mbar, 20 minutes: 28000 ± 2800 and 5×10^{-7} mbar, 2 minutes: 17000 ± 2800

5×10^{-8} mbar, 10 minutes: 21000 ± 5300 and 1×10^{-7} mbar, 5 minutes: 4000 ± 2700

1×10^{-7} mbar, 20 minutes: 43000 ± 4400 and 2×10^{-7} mbar, 10 minutes: 24000 ± 6800

1×10^{-7} mbar, 20 minutes: 43000 ± 4400 and 1×10^{-6} mbar, 2 minutes: 14000 ± 2900

1×10^{-7} mbar, 10 minutes: 32000 ± 11000 and 2×10^{-7} mbar, 5 minutes: 20000 ± 7300

1×10^{-7} mbar, 10 minutes: 32000 ± 11000 and 5×10^{-7} mbar, 2 minutes: 17000 ± 2800

2×10^{-7} mbar, 10 minutes: 24000 ± 6800 and 1×10^{-6} mbar, 2 minutes: 14000 ± 2900

2×10^{-7} mbar, 5 minutes: 20000 ± 7300 and 5×10^{-7} mbar, 2 minutes: 17000 ± 2800

5×10^{-7} mbar, 20 minutes: 73000 ± 3000 and 1×10^{-6} mbar, 10 minutes: 71000 ± 12000

5×10^{-7} mbar, 10 minutes: 36000 ± 5500 and 1×10^{-6} mbar, 5 minutes: 27000 ± 5100

Of the twelve comparisons that can be made for surfaces which experience the same exposure to CO₂ eleven (92%) of them exhibit a larger peak area when a larger quantity of IL is used and a lower dose pressure, relative to using a smaller quantity of IL and a higher dose pressure. This is the same trend as was observed in the exposure comparisons for [C₈C₁Im][BF₄], and suggests that a greater

quantity of carbon dioxide will be captured if it is ensured that the quantity of IL is in an excess, rather than ensuring that the CO₂ pressure is high.

8.11 CO₂ population distributions for the [C₈C₁Im][Tf₂N]–CO₂ coadsorption data

Section 6.3.4 describes the fitting procedure that is performed to determine the activation energy of desorption range for the CO₂ captured within the IL [C₈C₁Im][Tf₂N] from the various coadsorption experiments. The pressure and background subtracted CO₂ TPD signal is compared to a sum of first order CO₂ TPD peaks, simulated from hypothetical adsorption environments with evenly spaced E_{des} values. The initial populations of each of the hypothetical CO₂ peaks are varied until the sum of CO₂ states matches the experimental signal. The distribution of these initial populations can be used to gain information on the CO₂–IL interaction. Here the hypothetical CO₂ states start with an $E_{\text{des}} = 24.5 \text{ kJ mol}^{-1}$, with the next CO₂ state having an E_{des} 1.5 kJ mol⁻¹ higher than the preceding one. A heating rate of 0.67 K s⁻¹ was used when simulating the TPD peaks. As discussed in section 6.3.4 and 5.3.4 a relative scale had to be used for the initial populations of the hypothetical CO₂ states. To

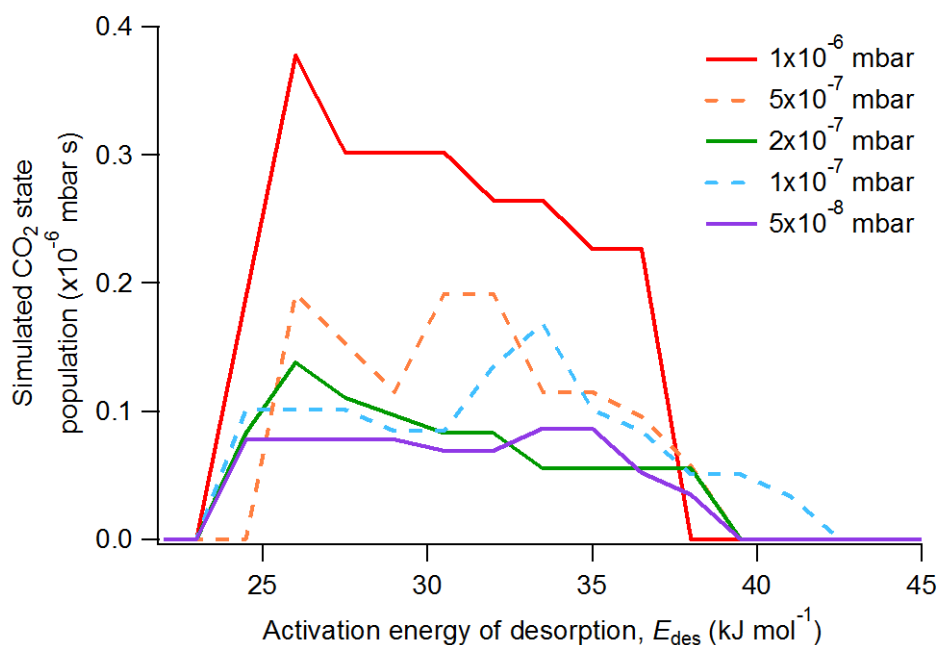


Figure 8.31: Plots showing how the population of CO₂ states with different E_{des} vary as the pressure of CO₂ used during coadsorption with [C₈C₁Im][Tf₂N] is varied. Data shown here is for coadsorptions with 10 minutes of IL, where state populations have been calculated from the relative populations found by fitting the TPD peak with a sum of hypothetical CO₂ adsorption sites, as described in the text.

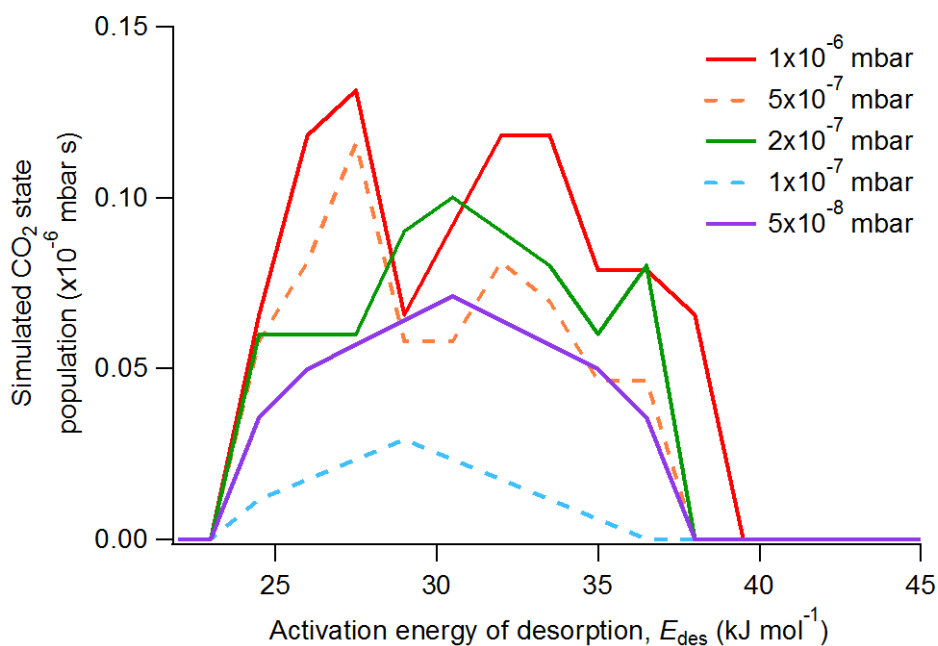


Figure 8.32: Plots showing how the population of CO₂ states with different E_{des} vary as the pressure of CO₂ used during coadsorption with [C₈C₁Im][Tf₂N] is varied. Data shown here is for coadsorptions with 5 minutes of IL, where state populations have been calculated from the relative populations found by fitting the experimental TPD peak with a sum of hypothetical CO₂ desorption peaks.

convert the populations from a relative scale to one which was comparable to the experimental data, the relative populations had to be multiplied by the

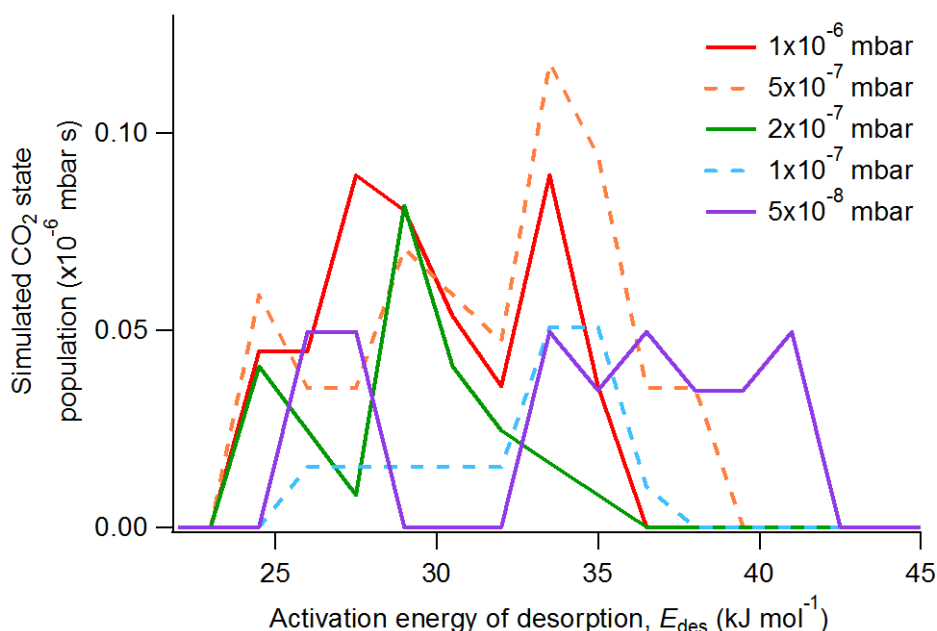
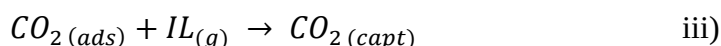


Figure 8.33: Plots showing how the population of CO₂ states with different E_{des} vary as the pressure of CO₂ used during coadsorption with [C₈C₁Im][Tf₂N] is varied. Data shown here is for coadsorptions with 2 minutes of IL, where state populations have been calculated from the relative populations found by fitting the experimental TPD peak with a sum of hypothetical CO₂ adsorption sites. As the 2 minute data gives the smallest CO₂ signal during TPD it is the most susceptible to experimental noise.

experimental TPD peak area $\div$ the sum of relative populations under the CO₂ peak. Figure 6.10 shows the initial population distributions for the 20 minute coadsorption data and whilst table 6.4 gives some data to help describe the distribution, graphs can also assist. Figure 8.31 shows the E_{des} distributions observed within the IL for the 10 minute coadsorption case where it can be seen that the typical range for the activation energy of desorption is $24.5 \leq E_{\text{des}} \leq 38.0 \text{ kJ mol}^{-1}$, as discussed in section 6.3.4. Population distributions for CO₂ within the 5 minute and 2 minute coadsorptions are shown in figs. 8.32 and 8.33 respectively, which also show similar E_{des} ranges. With the exception of the 2 minute data, which is the most susceptible to experimental noise due to the low signals, the E_{des} profiles all have a similar ‘top hat’ like distribution, where the population of all adsorption sites over the E_{des} range are approximately equal.

8.12 Probing Eley–Rideal reaction kinetics via graphical methods

It was discussed in section 6.4 that the capture of CO₂ by the ILs [C₈C₁Im][BF₄] and [C₈C₁Im][Tf₂N] during coadsorption might occur through an Eley–Rideal style mechanism. In order to test whether Eley–Rideal kinetics are observed the following processes occurring on the surface can be considered;



The coverage of CO₂ on the surface can be seen to depend on these three processes, however under the assumption that process iii) is slow (as the IL is dosed at a rate of approximately 1/60th of a monolayer per second, giving $\approx 1 \text{ layer min}^{-1}$) then the equilibrium coverage of CO₂(ads) on the surface is dictated solely by i) and ii), so can be described by an isotherm. The Langmuir adsorption isotherm, eq 8.6, seems a reasonable choice as the surface coverage saturates at 1 layer, which is in keeping with the fact that CO₂ multilayers are not observed on the gold surface.

$$P_{\text{CO}_2} = K_a \times \frac{\theta_{\text{CO}_2(ads)}}{(1 - \theta_{\text{CO}_2(ads)})} \quad \text{Equation 8.6}$$

where, P_{CO_2} is the pressure of CO_2 (mbar), K_a is the Langmuir adsorption isotherm constant (mbar) and $\theta_{CO_2(ads)}$ is the surface coverage of CO_2 in layers of CO_2 . The rate of formation of CO_2 (capt), v_r (layers of CO_2 per second), can be determined by considering the process in iii)

$$v_r = k_2 \times [CO_2(ads)] \times F \quad \text{Equation 8.7}$$

where, k_2 is the rate constant for the process (in ‘per layer of IL’), $[CO_2(ads)]$ is the surface concentration of CO_2 (layers of CO_2) and F is the flux of IL incident upon the surface per second (IL layers s^{-1}). If CO_2 is captured during a coadsorption experiment, by the IL landing on an adsorbed CO_2 molecule, over a time, t , then the total amount of CO_2 captured will be given by:

$$total\ CO_2\ captured = v_r \times t = k_2 \times [CO_2(ads)] \times F \times t \quad \text{Equation 8.8}$$

One can notice that $F \times t$ is the IL coverage (θ_{IL}), so it can be shown that the amount of CO_2 captured per IL layer can be given by:

$$CO_2\ captured\ per\ IL\ layer = \frac{v_r \times t}{F \times t} = k_2 \times [CO_2(ads)] \quad \text{Equation 8.9}$$

It can be seen that the amount of CO_2 stabilised per IL layer is dependent upon the surface concentration of CO_2 , so to effectively capture CO_2 there is a requirement for either a high CO_2 pressure or for the CO_2 to stick to the surface for a reasonable length of time. The Langmuir adsorption isotherm, eq 8.6, can be rearranged to make the surface coverage of CO_2 the subject;

$$\theta_{CO_2(ads)} = \frac{1}{\left(\frac{K_a}{P_{CO_2}} + 1\right)} \quad \text{Equation 8.10}$$

and then, using the knowledge that $[CO_2(ads)] = \theta_{CO_2(ads)}$, can be substituted into eq 8.9;

$$CO_2\ captured\ per\ IL\ layer = k_2 \times \frac{1}{\left(\frac{K_a}{P_{CO_2}} + 1\right)} \quad \text{Equation 8.11}$$

By taking the inverse of eq 8.11 the equation of a straight line can be obtained for a plot of 1/amount of CO_2 per IL layer vs. 1/pressure;

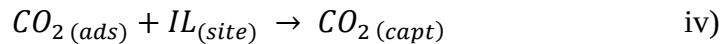
$$\frac{1}{CO_2\ captured\ per\ IL\ layer} = \frac{1}{k_2} + \frac{K_a}{k_2} \times \frac{1}{P_{CO_2}} \quad \text{Equation 6.4}$$

Any data which obeys this linear relationship will confirm that Eley–Rideal kinetics are observed in the adsorption system. If CO_2 capture occurred through a Langmuir–Hinshelwood type mechanism, where the CO_2 diffused into adsorption sites within the IL network, then due to the low IL dosing rate CO_2

saturation of the IL network would be expected. The gradients and y-axis intercepts of such a graph can be used to calculate the values of K_a and k_2 for the system.

8.13 Derivation of equations for a Langmuir–Hinshelwood mechanism of CO₂ capture by ILs

It has been discussed in section 6.4 and appendix 8.12 that the CO₂ capture by the ILs may occur through an Eley–Rideal type mechanism in which the CO₂ is adsorbed to the surface and then an incident IL molecule collides with the adsorbed CO₂ to capture it (provided the IL is in the correct orientation). The other commonly used model for surface reactions is the Langmuir–Hinshelwood mechanism in which the surface atoms are mobile and can diffuse into adsorption sites, if the stay time is long enough. Assuming a Langmuir–Hinshelwood kinetics system, in which the IL forms adsorption sites on the surface that the CO₂ can diffuse into in order to be captured, then the following processes are observed



Assuming that CO₂ adsorption (i) is a faster reaction than CO₂ capture (iii) and that the surface coverage of the CO₂ is such that it depends on the number of free sites (CO₂ will not adsorb on another CO₂ or a binding site within the IL—which would be an Eley–Rideal capture event—but can adsorb onto IL which is not in a CO₂ capture conformation (allowing adsorbed CO₂ to diffuse around on the surface). This means that coverage of the CO₂ can be found to be, as dictated by reactions i) and ii), a Langmuir isotherm for competitive adsorption of the form:

$$\theta_{CO_2(ads)} = \frac{1}{\left(\frac{K_a}{P_{CO_2}} + 1\right)} (1 - [IL_{(site)}]) \quad \text{Equation 8.12}$$

In this case $\theta_{CO_2(ads)}$ is the surface coverage of CO₂, K_a is the Langmuir isotherm constant in mbar (which is defined as the rate constant for the desorption reaction over the rate constant for the adsorption reaction), $[IL_{(site)}]$ is the surface

coverage of IL sites which can adsorb CO₂ and P_{CO_2} is the pressure of CO₂ (mbar). This isotherm can be derived from the consideration of the rates of adsorption and desorption. The rate of CO₂ adsorption is

$$Rate_{ads} = k_{ads}P_{CO_2}[free\ sites] \quad \text{Equation 8.13}$$

while the rate of CO₂ desorption is

$$Rate_{des} = k_{des}[CO_2(ads)] \quad \text{Equation 8.14}$$

where k_{ads} and k_{des} represent adsorption and desorption rate constants, respectively, $[free\ sites]$ represents the surface coverage of unoccupied states and $[CO_2(ads)]$ is the surface concentration of CO₂. Working in terms of the relative surface coverages (such the maximum surface coverage is 1) the following relationship can be found:

$$[free\ sites] = 1 - [CO_2(ads)] - [IL_{(site)}] \quad \text{Equation 8.15}$$

For a surface at equilibrium the rate of adsorption (eq 8.13) and desorption (eq 8.14) are equal, giving

$$k_{ads}P_{CO_2}[free\ sites] = k_{des}[CO_2(ads)] \quad \text{Equation 8.16}$$

By rearranging eq 8.16 and defining that the Langmuir Isotherm constant, K_a , as k_{des}/k_{ads} then

$$K_a = \frac{P_{CO_2}[free\ sites]}{[CO_2(ads)]} = \frac{P_{CO_2}(1 - [CO_2(ads)] - [IL_{(site)}])}{[CO_2(ads)]} \quad \text{Equation 8.17}$$

This can then be rearranged into the form shown previously (eq 8.12) by noting that $[CO_2(ads)] = \theta_{CO_2(ads)}$. Unlike in the Eley–Rideal case the capture of CO₂ does not occur through the IL landing on the adsorbed CO₂, instead the IL will stick to the surface (from evaporation) and may form an adsorption site. It is assumed that this adsorption site formation would be related to the orientation that the molecule lands in, so statistically it can be said that a proportion c_1 of the IL molecules stick to the surface in an orientation such that a CO₂ adsorption site is formed. The rate of surface site formation, $\nu_{r, site}$, will therefore be related to the flux of the incoming IL (F_{IL}) and the fraction of IL molecules that are in the correct orientation to form adsorption sites;

$$\nu_{r, site} = c_1 F_{IL} \quad \text{Equation 8.18}$$

This rate of adsorption site generation should not vary with IL dosing time or CO₂ pressure (it can be seen that this rate is independent of these two factors). This argument also implies that within 1 layer of IL then there will be c_1 layers

of IL binding sites formed (so c_1 IL binding sites per IL layer, giving a surface coverage of c_1). This means that the total number of IL binding sites within an IL layer of thickness θ_{IL} is

$$[IL_{(site)}]_{total} = \theta_{IL} \times c_1 \quad \text{Equation 8.19}$$

The total number of adsorption sites can also be obtained from multiplying the rate of formation by the time over which IL evaporation occurred (as flux is ‘per unit time’).

$$total\ number\ of\ IL\ sites = v_{r, site} \times t = c_1 F_{IL} t = c_1 \theta_{IL} \quad \text{Equation 8.20}$$

The result to take from this is that the surface coverage of the empty IL sites is constant (the unknown value c_1) when there is not any process reducing the coverage of the empty sites (no CO₂ adsorption). The rate of CO₂ capture, with a rate constant, k_3 , in equation iv) can be written as:

$$v_{r, capt} = k_3 \theta_{CO_2 (ads)} [IL_{(site)}] \quad \text{Equation 8.21}$$

In this Langmuir–Hinshelwood mechanism it is assumed that the IL is frozen in place and doesn’t diffuse around (unlike in most normal Langmuir–Hinshelwood mechanisms where both species are mobile). The CO₂ is able to diffuse around and find a stable site (if it reaches one within the stay time of a given CO₂ molecule). The CO₂ can be described by an isotherm as it is in equilibrium with the surface and gas phase, whereas the IL coverage cannot be described by an isotherm (unlike most other Langmuir–Hinshelwood mechanisms). Instead the fact that the IL has a fixed generation rate means that the surface concentration of IL sites will depend on the CO₂ pressure/coverage.

Assuming that the IL flux is very high in comparison to the rate of CO₂ capture within the IL ‘snow’ network (physically meaning that c_1 is small) the rate of change of IL sites is dictated only by the flux of incoming IL

$$\frac{d}{dt} [IL_{(site)}] = c_1 F_{IL} \quad \text{Equation 8.22}$$

Integration of eq 8.22 gives (assuming that at time = 0 there are no adsorption sites within the IL)

$$\int_0^{[IL_{(site)}]} d[IL_{(site)}] = \int_0^t c_1 F_{IL} dt \quad \text{Equation 8.23}$$

So the concentration of IL sites is

$$[IL_{(site)}] = c_1 F_{IL} t \quad \text{Equation 8.24}$$

Taking the expression for rate of CO₂ capture (eq 8.21) and substituting the expression for the CO₂ coverage gives

$$v_{r,capt} = k_3 \frac{1}{\left(\frac{K_a}{P_{CO_2}} + 1\right)} (1 - [IL_{(site)}])[IL_{(site)}] \quad \text{Equation 8.25}$$

Multiplying out the brackets on the right, and making the assumption that the surface concentration of IL sites is so small that higher powers (the squared term) can be ignored gives

$$v_{r,capt} = k_3 \frac{1}{\left(\frac{K_a}{P_{CO_2}} + 1\right)} [IL_{(site)}] \quad \text{Equation 8.26}$$

Substituting in for the concentration of IL sites we get

$$v_{r,capt} = k_3 \frac{1}{\left(\frac{K_a}{P_{CO_2}} + 1\right)} c_1 F_{IL} t \quad \text{Equation 8.27}$$

Where the flux of IL multiplied by the time is just the IL coverage, θ_{IL} . To look at the total CO₂ captured we need to multiply the rate by the time so

$$total\ CO_2\ captured = v_{r,capt} \times t = k_3 \frac{1}{\left(\frac{K_a}{P_{CO_2}} + 1\right)} c_1 \theta_{IL} \times t \quad \text{Equation 8.28}$$

The total amount of CO₂ captured per IL layer can then be found by dividing by the total IL coverage

$$total\ CO_2\ captured\ per\ IL\ layer = \frac{v_{r,capt} \times t}{\theta_{IL} \times t} = k_3 \frac{1}{\left(\frac{K_a}{P_{CO_2}} + 1\right)} c_1 \quad \text{Equation 8.29}$$

This is then virtually the same expression as was obtained for Eley–Rideal kinetics (eq 8.11) with the difference being that the rate constant (the rate of capture for Eley–Rideal, which was k_2) is now a combination of c_1 and k_3 (the proportion of IL that forms a CO₂ binding site and the rate constant for CO₂ capture). It makes sense that the equation is essentially the same as both of the processes are first order in kinetics (there is something immobile being hit by another species) with the assumed ‘immobile’ object being different in the two cases. This differs to most Langmuir–Hinshelwood kinetics seen in literature where there are two mobile species on the surface leading to second order kinetics for reaction. Note that in this derivation of Langmuir–Hinshelwood kinetics the assumption that IL flux is high was made, which is opposite to the assumption made in the Eley–Rideal derivation. If the IL flux is not assumed to be high then the CO₂ capture becomes controlled by the IL flux and saturation

of the IL would be expected to be seen (but isn't experimentally). The Eley-Rideal kinetics successfully describe why the most stable CO₂ adsorption sites within the IL are not observed to fill up first, whereas Langmuir-Hinshelwood kinetics assumes that the most stable sites will up first as the CO₂ will diffuse across the surface until it finds a stable site. To test whether Eley-Rideal or Langmuir-Hinshelwood kinetics are observed the IL flux would need to have been varied, as the rate of CO₂ capture is dependent upon the IL flux in the Eley-Rideal kinetics but is independent of the IL flux for Langmuir-Hinshelwood kinetics.

8.14 References

- [1] Hessey, S.G. and Jones, R.G., Line-of-sight mass spectrometry: principles and practice. *Surf. Interface Anal.*, **2015**, (47), pp. 587-600.
- [2] Wang, J., Bedzyk, M.J., Penner, T.L. and Caffrey, M., Structural Studies of Membranes and Surface Layers up to 1000 Å Thick using X-ray Standing Waves. *Nature*, **1991**, (354), pp. 377-380.