

Practical Approaches to Simulating X-ray Spectroscopy with Quantum Chemistry

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Dedication

To Jane and Emad, wouldn't have done it without your love and support.

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Abstract

Developments on simulating X-ray spectroscopy using quantum chemistry are presented. Topics are introduced in Chapter 1 via two separate reviews on X-ray spectroscopy and quantum chemistry. The introduction is followed by four independent investigations across four chapters, aimed at developing robust and accurate simulations to support new experimental findings in X-ray spectroscopy.

In Chapter 2, the performance of gaussian basis sets for density functional theory based calculations of core electron spectroscopies is assessed. The convergence of core-electron binding energies and core-excitation energies using a range of basis sets, including split-valence, correlation consistent, polarisation consistent and individual gauge for localized orbitals basis sets is studied. For Δ self-consistent field calculations of core-electron binding energies and core-excitation energies of first row elements, relatively small basis sets can accurately reproduce the values of much larger basis sets but second row element calculations are more challenging. Time-dependent density functional theory based calculations of core-excitation energies show less sensitivity to the basis set, in contrast, X-ray emission energies are highly dependent on the basis set. The results are applied to understanding the charge distribution associated with individual components in functionalised ionic liquids being tuned by careful manipulation of the substituent groups. Δ self-consistent field calculations of core-electron binding energies calculated using the pcSseg-2 basis set support X-ray photoelectron spectroscopy experimental findings. The experimental measurements and supporting calculations revealed an unexpected variation in the charge density distribution within the ionic liquid cation when the oxygen atom in a poly-ether containing side chain is moved by just one atomic position.

In Chapter 3, the simulation of X-ray emission spectra of organic molecules using time-dependent density functional theory (TDDFT) is explored. TDDFT calculations using standard hybrid exchange-correlation functionals in conjunction with large basis sets can predict accurate X-ray emission spectra provided an energy shift is applied to align the spectra with experiment. The relaxation of the orbitals in the intermediate state is an important factor, and neglect of this relaxation leads to considerably poorer predicted spectra. A short-range corrected functional is found to give emission energies that required a relatively small energy shift to align with

experiment. However, increasing the amount of Hartree-Fock exchange in this functional to remove the need for any energy shift led to a deterioration in the quality of the calculated spectral profile. To predict accurate spectra without reference to experimental measurements, we use the CAM-B3LYP functional with the energy scale determined with reference to a Δ self-consistent field calculation for the highest energy emission transition.

Chapter 4 sees the resonant inelastic soft X-ray scattering maps for the water molecule simulated by combining quantum chemical calculations of X-ray spectroscopy with *ab initio* molecular dynamics. The resonant inelastic scattering intensity is computed using the Kramers-Heisenberg formalism which accounts for channel interference and polarisation anisotropy. Algebraic diagrammatic construction and density functional theory based approaches for the calculation of the x-ray transition energies and transition dipole moments of the absorption and emission processes are explored. Conformational sampling of both ground and core-excited intermediate states allows the effects of ultra-fast dynamics on the computed maps to be studied. Overall, it is shown how resonant inelastic scattering maps can be simulated with a computationally efficient protocol that can be extended to investigate larger systems.

In Chapter 5, a highly accurate resonant inelastic soft X-ray scattering simulation is performed on the open-shell nitric oxide molecule. The inelastic scattering contains detailed insights into the complex nature of the Rydberg and valence excited states. The high level multi-reference, restricted active space self consistent field and restrictive active space second order perturbation theory methods are employed, performing a comprehensive analysis of the resonant inelastic x-ray scattering map. Furthermore, insights from the simulations are given to the striking vertical broadening feature in the experimental map. The calculations show that excitation and emission energies in this region correspond to π^* emission from doubly excited core excited states, where a π electron as well as the nitrogen $1s$ electron have gone into the antibonding π^* shell. The occurrence of these states is dependant on the nature of the absorption measurement in the RIXS. Potential energy curves between the core excited Rydberg $3s\sigma$ and first doubly excited state D_1 show an adiabatic state crossing directly in the Franck-Condon region of the ground state. If the RIXS absorption is measured by fluorescence, this indicates the possibility of ultrafast two-electron-one-photon processes happening on the timescale of the absorption process.

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Motivation

The aims of the research are to develop and provide methods to accurately and efficiently simulate X-ray spectroscopy using quantum chemistry which are able to replicate experimental observables and provide insights into the underlying chemical and physical processes behind them. The capability to accurately simulate X-ray spectroscopy will aid the interpretation and understanding gained from X-ray spectroscopy and widen its applicability with chemistry. A wide range of quantum chemical techniques across available modern software packages will be considered and applied within the limits of typically accessible computational resources. The fundamental physics of X-ray spectroscopy is discussed in order to provide a platform to develop robust simulations. Careful consideration of the experimental environment will be required to put the quantum chemical calculations into the correct context. New plotting methods are developed to facilitate the interpretation and increase the information gained from X-ray spectroscopy simulations. It is hoped that the outcomes of this work will make reliable simulations of X-ray spectroscopy more accessible to researchers who are not specialists at quantum chemical simulation; driving the widespread development of X-ray spectroscopy as a fundamental analytical tool across chemistry.

Author Publication List

Contributing to this work:

1. “Assessment of basis sets for density functional theory-based calculations of core-electron spectroscopies” Fouda, A. E. A.; Besley, N. A. *Theor. Chem. Acc.* **2017**, *137*, 6. (**Chapter 1**)
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3. “Probing the electronic structure of ether functionalised ionic liquids using X-ray photoelectron spectroscopy” Dick, E.; Fouda, A. E. A.; Besley, N. A.; Licence, P. *Phys. Chem. Chem. Phys.* **2020**, *22*, 1624–1631. (**Chapter 1**)
4. “Improving the predictive quality of time-dependent density functional theory calculations of the X-ray emission spectroscopy of organic molecules” Fouda, A. A. E.; Besley, N. A. *J. Comput. Chem.* **2020**, 1–10. (**Chapter 3**)
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Further Publications:

6. “Does the DFT Self-Interaction Error Affect Energies Calculated in Proteins with LargeQM Systems?” Fouda, A.; Ryde, U. *J. Chem. Theory Comput.* **2016**, *12*, 5667–5679.
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Glossary

XAS: X-ray absorption spectroscopy

XANES: X-ray absorption near edge structure

EXAFS: Extended X-ray absorption fine structure

XPS: X-ray photoelectron spectroscopy

XES: X-ray emission spectroscopy

RXES: Resonant X-ray emission spectroscopy

RIXS: Resonant inelastic X-ray scattering

TRXAS: Time resolved X-ray absorption spectroscopy

SXRS: Stimulated X-ray raman scattering

ATAS: Attosecond transient absorption spectroscopy

Chapter 1

Introduction

1.1 X-Ray Spectroscopy Overview

An understanding of the evolution of the electronic structure of molecular systems on an ultrafast time scale underpins many modern technological developments. At the forefront of driving our understanding in electronic structure and its response to polyatomic nuclear dynamics, is the cooperation between cutting edge X-ray spectroscopy experiments and their simulation. Spectroscopy with high energy X-rays is atom specific and sensitive to both intermolecular and intramolecular environments, and single photon X-ray techniques (top row Figure 1.1) are emerging as one of the most powerful analytical tools for the study of the geometric and electronic structure. They can elucidate types of chemical bonding and probe the properties of materials. One attraction of these techniques is that they provide an element specific, local probe of geometric and electronic structure, and have been applied to study systems within a wide variety of applications, ranging from materials to biological systems.^{1,2} Furthermore, the development of X-ray free-electron lasers (XFELs) that can deliver short femtosecond pulses of X-rays has opened up the possibility of resolving ultrafast chemical processes at an atomic level.³ Recent examples of experimental work include studies on liquid water,^{4,5} the composition of an active site in a metalloprotein,⁶ the nature of bonding in metal containing complexes⁷ and the real-time monitoring of bond breaking of carbon monoxide adsorbed on a metal surface,⁸ illustrating the breadth of system that can be studied using single photon X-ray spectroscopic techniques. Single photon X-ray experiments are well established and the techniques shown in the top row of Figure 1.1 will be discussed in detail in the following subsections.

Studies investigating photoinduced phenomena on ultrafast time scales are now possible due to the development of ultrafast multiphoton light sources allowing the

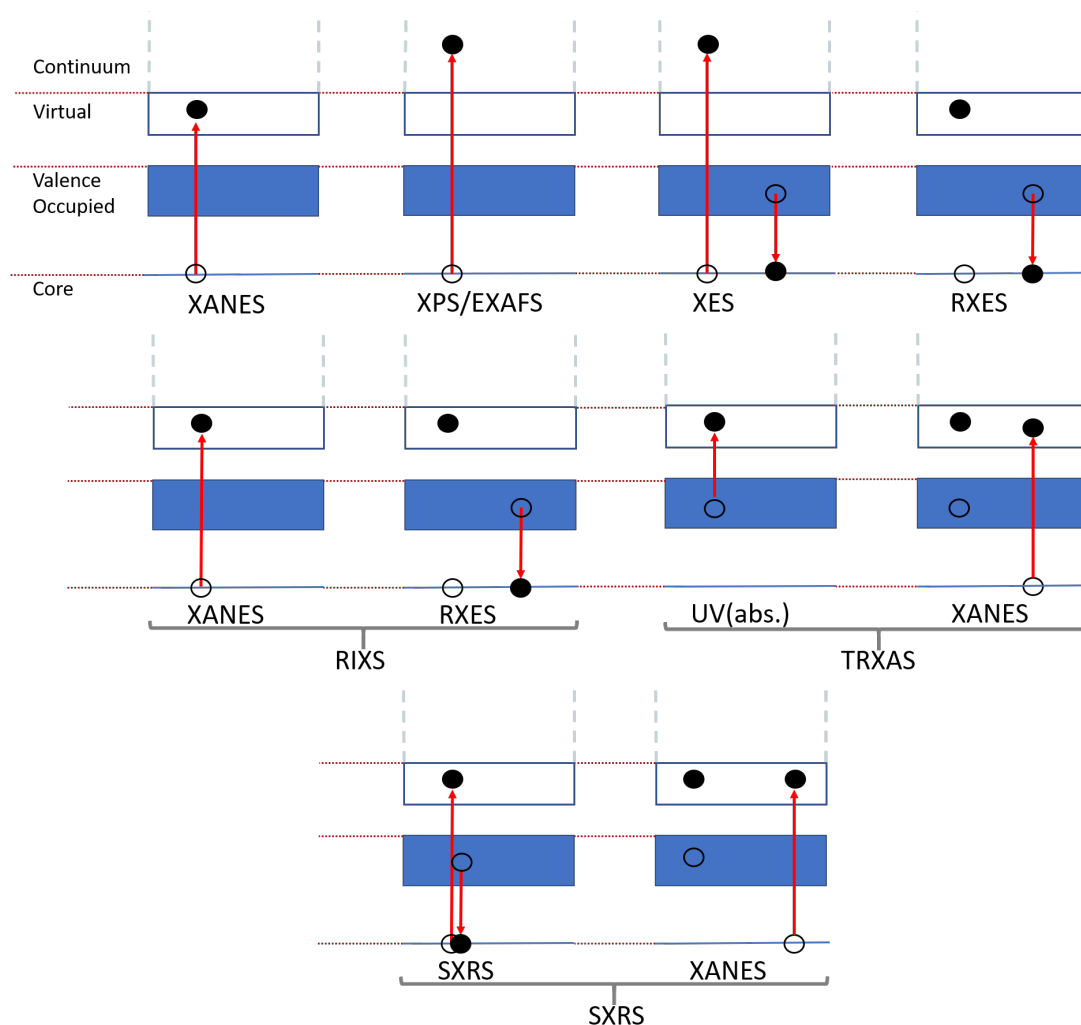


Figure 1.1: Schematic diagrams of the electron transitions involved in contemporary X-ray spectroscopy, abbreviations are given in the text. Core, valence and virtual refers to types of orbital, continuum refers to non-bound electronic states.

nature of excited states and non-adiabatic dynamics to be probed using two-photon experiments involving X-rays (middle row Figure 1.1).^{9–11} Information on fluorescent and non-fluorescent transitions are gained by the photochemical tracking of relaxation pathways following electronic excitation. The development of ultrafast multiphoton experiments is vital for understanding energy transfer dynamics in complex photochemical processes such as vision and photosynthesis.¹² Transient X-ray absorption spectroscopy (TRXAS), also referred to as time resolved X-ray absorption spectroscopy, is able to directly probe the non-adiabatic dynamics occurring in valence excited states.^{13–15} Optically bright valence excited states are generated by femtosecond UV pump pulses, the dynamics of these states can be monitored at femtosecond time intervals by femtosecond pulsed X-ray probes. The X-ray pulse provides a localised probe on the excited state dynamics via X-ray absorption near

edge structure (XANES) (see subsection 1.1.2), the diagram in Figure 1.1 shows the XANES core to pre-edge virtual orbital transition, but a more direct indication of dark relaxation processes will be the core to lowest energy singly occupied molecular orbital (SOMO) transition, which is available in TRXAS experiments. The femtosecond resolution of this experiment allows the excited state nuclear motion to be studied, whilst the recent development of attosecond transient absorption spectroscopy (ATAS) at XFEL facilities now enables electron dynamics to be probed.¹⁶ Resonant inelastic X-ray scattering (RIXS), is a two photon X-ray spectroscopy technique, discussed in depth in subsection 1.1.4. In contrast to TRXAS, RIXS involves incident X-rays, generating core-excited states, which then undergo spontaneous emission processes. There are many spontaneous processes that can occur in the transient core excited state, including Auger decay. However in RIXS, X-ray photons are detected when inelastic scattering occurs from electrons in occupied ground state orbitals collapsing to the core hole. RIXS has become a popular technique in solid state materials¹⁷ and solutions¹⁸ due to its ability to probe both the unoccupied and occupied orbitals of the system. Subsection 1.1.4 will give a review on the various phenomena present in the gas phase dynamics of RIXS, which is the focus of chapters 4 and 5. The final states in RIXS are valence excited states and they can be inaccessible states in UV absorption as a result of being dipole forbidden, however they can be accessed via the core hole intermediate state in RIXS. A new X-ray spectroscopy technique, known as stimulated X-ray Raman scattering (SXRS)^{19–21} (bottom row Figure 1.1), is still in the early stages of development, and probes the excited state dynamics of valence excited states generated via a core hole. The spontaneous emission in RIXS allows significant time (< 10 fs) for core excited state dynamics to impact the nature of the final valence excited states. Stimulated X-ray Raman emission can prevent this by stimulating attosecond time scale emission once the core excited state is generated. Then the valence excited final state dynamics, considered to be “unperturbed” by core hole dynamics relative to RIXS final states, can thus be monitored by femtosecond time-delayed X-ray pulses, similar to TRXAS. TRXAS and SXRS are beyond the scope of this work, but simulating the photon processes involved in XPS, XANES, XES and RIXS will provide the building blocks towards accurate TRXAS and SXRS simulation, whilst interpreting the core hole dynamics effects in RIXS spectra is vital for analysis of spectra across multiphoton X-ray spectroscopy.

This work will show how state of the art theory and computation can support experimental measurements, providing key insights into the underlying electronic structure and dynamics. Chapter 2 will present benchmarks of the optimal basis sets required to study core hole states for XPS, XANES and XES²² and the

results will be applied to the interpretation of experimental X-ray photoelectron spectroscopy (XPS) in ether-functionalised ionic liquids.²³ Chapter 3 will then investigate the role of the exchange-correlation functional in time-dependent density functional theory (TDDFT) on its accuracy for the calculation of XES in organic molecules.²⁴ Chapter 4 will investigate practical simulation methods describing the effects of ultra-fast dissociation in the gas phase RIXS of water.²⁵ Chapter 5 will apply advanced theoretical methods to analyse the experimental RIXS map of nitric oxide and the effect of the core excited nuclear dynamics.

1.1.1 X-Ray Photoelectron Spectroscopy

The XPS process is shown in Figure 1.1, it is similar to the EXAFS technique discussed in the following subsection. Both techniques involve the photoionisation of core electrons into the continuum. The difference is in the detection, EXAFS detects the absorption of X-ray radiation whereas XPS measures the kinetic energy of the ionised electrons via the photoelectric effect. For solid and liquid samples, where XPS is routinely applied, this process requires sufficient incident energy for the core ionised electron to leave the bulk sample and reach the vacuum. Therefore the kinetic energy of the photoelectron E_K , is determined by the following energy conservation rules,

$$h\nu = E_B + E_K \quad (1.1)$$

where $h\nu$ is the photon energy and E_B the binding energy, relative to the vacuum of the core electron prior to ionisation. In bulk conditions however, the binding energy will be relative to the Fermi level. In this case E_B is replaced by the binding energy relative to the Fermi level, $\tilde{E}_B$, plus the work function Θ for leaving the bulk sample giving,

$$h\nu = \tilde{E}_B + \Theta + E_K. \quad (1.2)$$

Due to the bulk conditions, energy loss features may occur from inelastic scattering. This effects the photoemission processes as the core ionised electron may impact surrounding molecules or atoms, ionising outer shell electrons as a result. Despite this, XPS has high chemical sensitivity in relation to bonding and oxidation states and is a well established and commonly applied surface analysis technique.^{26,27} XPS can provide detailed information about the electronic environment and charge distribution associated with individual components at, or near to, the surface of a material. High-level atomistic data can be used to inform the design of more efficient processes, by delivering insight into local surface composition and orientation²⁸⁻³⁰ and complex interactions that can exist between charge carriers and solutes alike.

1.1.2 X-Ray Absorption Spectroscopy

XAS refers to techniques involving incident X-rays, typically from synchrotron light sources, exciting core level electrons to unoccupied bound states near the ionisation threshold in XANES, or to ionise core electrons to the continuum in EXAFS. The combination of XANES and EXAFS is a powerful and widely applied technique, allowing the formal oxidation state and coordination environment of the absorbing atom be to probed by XANES and the bond distances, coordination number and species of atoms surrounding the absorbing atom to be determined by EXAFS. The combination of the two techniques is known as X-ray absorption fine structure (XAFS). Unlike XPS, XAFS is not surface sensitive as the incident X-rays penetrate deeply in matter, but XAFS techniques have the same atom selectivity as XPS. XAFS is particularly sensitive to the formal oxidation states of the core excited atom and local geometric coordination structure, therefore it is a valuable tool in metal complex coordination chemistry.^{31–33} Synonymous with all wavelengths of absorption spectroscopy, the probability that a core electron will absorb an incident X-ray via the photoelectron effect is governed by Beer's Law,

$$I = I_0 e^{-\mu t}, \quad (1.3)$$

the absorption coefficient μ gives the probability that X-rays will be absorbed, I_0 is the intensity of the incident X-ray, t is the thickness of the sample and I the intensity transmitted through the sample. The intensity is proportional to the number of photons. The absorption coefficient can be estimated by,

$$\mu \approx \frac{\rho Z^4}{AE^3}, \quad (1.4)$$

where ρ is the sample density, Z is the atomic number, A the atomic mass, and E the X-ray energy. The Z^4 dependence on μ is the reason why X-ray spectroscopy is highly atom selective. The size of the absorbing nucleus will effect the energy of the incident X-ray by several orders of magnitude. The incident X-ray energy range is from approximately 200 eV to 500 keV, enabling the study of elements across the periodic table. When the energy of the incident X-ray is equal to the core electron binding energy (CEBE), there will be a spike in the absorption which defines the absorption edge. XANES and EXAFS look at the energy dependence on μ just before and just after the absorption edge respectively. Absorption edges can be labelled with respect to the angular momentum of the absorbing core orbital. The K-edge corresponds to absorption from the s-shell, L-edge the p-shell and the M-edge the d-shell. This work only considers small organic molecules and all core-hole spectroscopy will be considered at the K-edge. Once the core electron has been excited to the edge, the core excited state lifetime is only a few femtoseconds before

core hole decay processes commence. There are two main mechanisms by which this can occur: X-ray fluorescence and Auger decay. In X-ray fluorescence, electrons in orbitals higher than in energy to the core hole collapse to the core hole, emitting X-rays of well defined energy. In the Auger decay de-excitation process, an electron from a higher orbital fills the core hole and second electron is ejected in the process. The absorption coefficient can either be measured by transmission, Equation 1.5, or by de-excitation (Auger and fluorescence), Equation 1.6,

$$\mu(E) = \log \left(\frac{I_0}{I} \right) \quad (1.5)$$

$$\mu(E) \propto I_f/I_0 \quad (1.6)$$

where I_f is the detected fluorescence or electron emission intensity associated with the X-ray absorption process.

1.1.3 X-Ray Emission Spectroscopy

X-ray emission spectroscopy (XES) ionizes a core electron, similar to XPS and EXAFS, but measures the X-ray emission following the collapse of electrons in occupied orbitals to the core hole. When the core electron is ionised, it can be considered as emission performed under non-resonant conditions and classed as non-resonant XES (NRXES). However, if the core electron is excited to a bound or near ionisation threshold state via XANES, then the emission would be in resonant conditions, this is classed as resonant XES (RXES), the photon-in photon-out process in this case is known as RIXS and will be discussed in-depth in the following section. XES probes the occupied molecular orbitals and is complementary to X-ray absorption spectroscopy (XAS) which is sensitive to the unoccupied orbitals, and the combination of the two can provide an extensive description of the electronic structure of the system.³⁴ XES is a widely used technique that has been used to probe the structure of liquids⁵ and the adsorption of molecules on surfaces.^{1,35} Furthermore, it can be applied to transition metal complexes and identify the nature of surrounding ligands, via metal center core-ionisation and emission via the collapse of electrons from ligand sites.³⁶⁻³⁸ Chapter 3 provides a computationally cheap and accurate protocol to simulate XES on small organic molecules .

1.1.4 Resonant Inelastic X-Ray Scattering

RIXS is part of the latest advancements in high energy photon sources at synchrotron facilities and is a fast developing technique.³⁹ It combines the element specific nature of X-ray spectroscopic techniques with the flexibility to probe different intermediate states, and is not limited by optical selection rules. RIXS has become a ubiquitously

powerful tool for understanding the electronic structure of molecular systems and materials. It involves a two step procedure where the ground state of the system is excited to an intermediate core-excited state and a spontaneous emission from this state leads to valence excited final states. For direct scattering, RIXS can be viewed as synonymous with resonant X-ray emission (RXES).

RIXS probes the response of the electronic structure to ultrafast nuclear dynamics. The screening effect,⁴⁰ of excited electrons on the ground state occupied orbitals can be observed via the inelastic scattering of X-ray photons as electrons in occupied orbitals collapse to the core hole during spontaneous emission processes. This provides an extensively detailed technique in which both the occupied and unoccupied states of the system are simultaneously mapped. The femtosecond core excited nuclear dynamics have a direct impact on the spectral outcomes which is naturally calibrated within the core hole lifetime. This technique has wide implications for areas in fundamental molecular physics to materials science and biology.^{41–47}

RIXS studies have been reported for a range of molecules.^{42–49} Small gas phase molecules, are of high importance both technologically and environmentally. They provide a platform for RIXS studies to obtain new structural insights not possible in larger systems. Water has been studied in great detail, namely for the presence of core excited ultrafast dissociation^{25,43,50} and the ability to selectively gate ground state vibrational modes.⁵¹ Furthermore, combined experimental and theoretical studies in resonant X-ray scattering have attained a rich source of physical spectroscopic knowledge of linear molecules in the gas phase. Glans et al. demonstrated the presence of the parity selection rule for homonuclear diatomic systems via the RXES of di-nitrogen.⁵² Rubensson and co-workers explored the near ionisation threshold states of nitrogen and found that the core excited electron acts as a pure spectator in the resonant emission process.⁵³ Another homo-nuclear diatomic system studied with RIXS was oxygen, Pietzsch et al. demonstrated how the vibrational progression in dissociative core excited states differing by their spin produced spatial quantum beats in the X-ray scattering.⁵⁴ Heteronuclear diatomic molecules are also of spectroscopic interest. Couto et al.’s work on X-ray Raman scattering of carbon monoxide alluded to the presence of dark two-electron-one-photon (TEOP) final states attained via non-adiabatic dynamics in the final states driven by Coulomb coupling.⁵⁵

The RIXS intensity is a function of both the excitation and emission processes. The theory of two-photon cross-section scattering was originally set out by Kramer and Heisenberg,⁵⁶ and later developed by Gel’mukhanov and co-workers to account

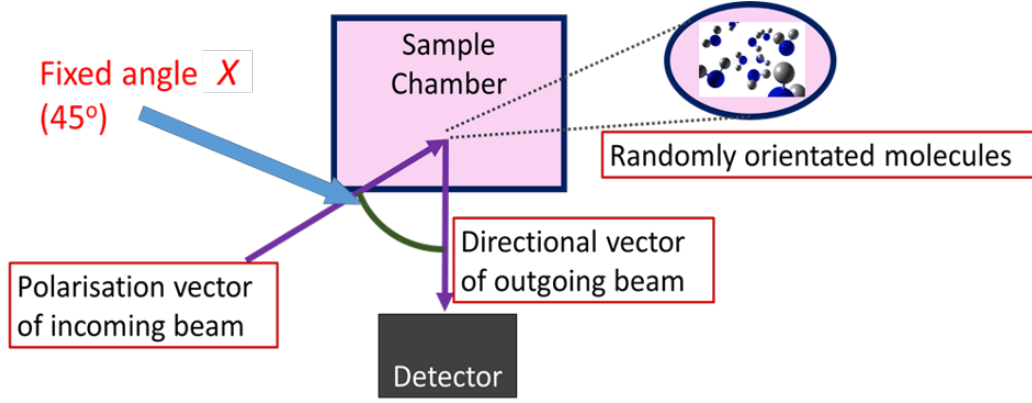


Figure 1.2: Diagram of the gas phase experimental RIXS setup.

for channel interference and polarisation anisotropy effects.^{57–60} The two dimensional RIXS maps displayed in this work are calculated using expressions from two-photon scattering theory and are readily applicable to small molecules involving one core orbital resonantly excited by an incident photon. The formula for calculating the two photon RIXS spectra is derived from the Kramer-Heisenberg (KH) equation,

$$\sigma(\omega, \omega') \propto \sum_N \sum_{F_N} \left| \frac{\langle \psi_N | D | \psi_I \rangle \langle \psi_{F_N} | D | \psi_N \rangle}{\omega - \omega_{I,N} + i\Gamma_N} \right|^2. \quad (1.7)$$

The equation accounts for the two photon RIXS intensity $\sigma(\omega, \omega')$, summing over the core excited intermediates ψ_N and each of the corresponding valence excited final states ψ_{F_N} and ψ_I is the initial ground state. ω and ω' are the incoming and outgoing photon frequencies, whilst D is the dipole operator, for operators see Section 1.2.1. $\omega_{I,N}$ is the excitation frequency between the ground and core excited intermediate. Γ_N is the lifetime broadening term of the core excited state⁶¹ and prevents the equation from going to infinity in the case of resonance ($\omega = \omega_{I,N}$).

In order to use quantum chemical calculations to calculate gas phase RIXS spectra, an unpolarised (in all directions) RIXS intensity I_0 is expressed by a scattering channel interference term⁵⁷ $\zeta_{F_N}^I$, which is presented in the resonance condition to give,

$$\zeta_{F_N}^I = \frac{\alpha \omega_{I,N} \omega_{N,F_N}}{i\Gamma_N} d_{I,N} d_{N,F_N}, \quad (1.8)$$

where

$$I_0 \propto \zeta_{F_N}^I {}^* \zeta_{F_N}^I. \quad (1.9)$$

Equations 1.8 and 1.9 enable RIXS intensities to be calculated from excitation and emission energies to give $\omega_{I,N}$ and ω_{N,F_N} and dipole moments for $d_{I,N}$ and d_{N,F_N} . These quantities can be generated by the quantum chemical methods discussed in Sections 1.2.2-6. α is the fine structure constant equal to 137^{-1} and can be omitted

from the calculation due to the proportionality relation between the intensity and interference in Equation 1.8.

Due to the polarisation anisotropy dependence of RIXS on randomly orientated molecules in the gas phase, it is appropriate to represent the RIXS intensity as a function of not only the excitation and emission processes but also the angle between the vector of the linearly polarised incident X-ray and the directional vector of the outgoing scattered X-rays, shown in Figure 1.2. The polarised angular dependent intensity $I(\theta)$, where $\theta = 45^\circ$, can be derived from the following equations as detailed in previous studies,^{25,57,62} where

$$I(\theta) = I_{\perp}(\theta) + I_{\parallel}(\theta), \quad (1.10)$$

$$I_{\perp}(\theta) = \frac{1}{2}I_0[1 - R], \quad (1.11)$$

$$I_{\parallel}(\theta) = \frac{1}{2}I_0[1 + R(3\sin^2\theta - 1)]. \quad (1.12)$$

The perpendicular and parallel components of the polarised intensity, $I_{\perp}(\theta)$ and $I_{\parallel}(\theta)$, are dependent on the polarisation anisotropy parameter R , which is in turn dependent on ϕ ; the angle between the dipole moment vectors of the excitation and emission processes,

$$R = \frac{1}{5}(3\cos^2\phi - 1). \quad (1.13)$$

To produce the simulated RIXS maps, the peaks are generated by 2-dimensional Gaussian functions with $I(\theta)$ as the height of the peak and ω and ω' expressed on the x and y coordinates respectively,

$$\Phi\{(\omega - \omega_1)(\omega' - \omega'_1)\} = I(\theta)e^{-\left\{\frac{(\omega - \omega_1)^2}{2\sigma_{\omega}^2} + \frac{(\omega' - \omega'_1)^2}{2\sigma_{\omega'}^2}\right\}}. \quad (1.14)$$

1.2 Calculating X-Ray Spectroscopy

Computational simulations of X-ray spectroscopy often play an important role in the interpretation of experimental data. As X-ray spectroscopy directly probes the core and bonding orbitals of molecular systems and materials, they must be treated quantum mechanically rather than classically, in simulations. This section will give an overview on how X-ray spectroscopy can be simulated using quantum chemistry. It will begin by introducing the core principles of quantum mechanics and how it is applied to chemistry, followed by a theoretical review of the quantum chemical techniques used in this work. A number of contemporary methods in quantum

chemistry are used in this project and examples from the literature will be provided. These are not the only methods used to compute X-ray spectroscopy; XAS can be computed using the transition potential method⁶³ and the Bethe-Salpeter equation.⁶⁴ CEBEs for XPS have been calculated through an unrestricted generalised transition state method,^{65,66} however these methods are beyond the scope of this work.

1.2.1 Background in Quantum Mechanics for Chemistry

Wave-Nature of Matter

Due to the small size of electrons, atoms and molecules, they cannot be adequately described by Newtonian mechanics but are instead treated quantum mechanically. In general, molecules and atoms exist with discrete energy values known as quantum states. An exception, would be an electron ionized from a molecule and the ion-electron system having continuous spread in kinetic energy.

Light can be described as photons; particles of energy $E = h\nu$, where ν is the frequency of the photon and h is the Planck's constant, by which the energy of the photon is discretized. Considered alongside the quantization of molecular energy levels, this forms the basis of the spectroscopic techniques discussed in the previous sections. In-fact, electrons themselves have wave like nature. This appears in molecules via the superposition of atomic orbitals to give molecular orbitals, where bonding orbitals are given by in-phase combinations of atomic orbitals and anti-bonding orbitals from out-of-phase combinations.

Both light and matter behave as both particles and waves, this is known as “wave-particle duality”, originally expressed by de Broglie⁶⁷ in the following relationship,

$$\lambda = \frac{h}{p}, \quad (1.15)$$

λ is the wavelength and p the momentum; h is Planck's constant $h = 6.626 \times 10^{-34} \text{ Js}$ and sets the length/velocity/time scales that wave-particle duality becomes significant in.

The Wavefunction

The wave nature of matter is quantitatively expressed via a wavefunction, ψ . The wavefunction is a quantity defined at all points in space (3N dimensions, N being the number of particles in the system), which varies in time and all physical properties

of the system are determined by. The wavefunction is single valued, finite everywhere and normalised (probability of being located in its given space equal to 1).

$$\int \psi^* \psi d\tau = 1. \quad (1.16)$$

The Born interpretation⁶⁸ tells us that the square-norm of a wavefunction, $|\psi|^2$, is equal to its probability density and that $\psi^2(x)dx$ is the probability of finding the quantum object between x and $x + dx$.

The Schrödinger Equation

How do we determine the wavefunction and calculate its properties? An equation is needed that considers the nature of the matter (mass, charge etc.), boundary conditions (description of the edges of the space occupied) and its starting position at a given time. This is all provided for by the Schrödinger equation,⁶⁹ describing the evolution of the wavefunction in time, also known as the time-dependent Schrödinger equation,

$$\hat{H}\psi = i\hbar \frac{\partial \psi}{\partial t}. \quad (1.17)$$

which can also be considered when the system is in a “stationary state” (invariant with respect to time), in what is known as the time-independent Schrödinger equation for a wavefunction,

$$\hat{H}\psi = E\psi. \quad (1.18)$$

In the time-independent equation, E is a constant ($\hbar = \frac{h}{2\pi}$) and therefore $\hat{H}$ must also have dimension of energy. $\hat{H}$ is the Hamiltonian operator. Operators act on and transform the mathematical function to their right and $\hat{H}$ is the operator associated with the energy observable.

Quantum Mechanical Operators

All observable quantities of a quantum system will have a corresponding quantum-mechanical operator. For example, the linear momentum operator, $\hat{p}_x$, applied to a wavefunction will behave like the Hamiltonian operator in Equation 1.18 and return a constant times the original wavefunction.

$$\psi_k = \exp(ikx) \quad (1.19)$$

$$\hat{p}_x \psi_k = -i\hbar \frac{\partial}{\partial x} \exp(ikx) = \hbar k \psi_k \quad (1.20)$$

$\hat{p}_k$ has eigenfunction ψ_k and eigenvalue $\hbar k$ which is the linear momentum in the x coordinate. ψ_k is an eigenfunction of both the the energy and momentum operators,

the consequence is that the order in which the operators are applied does not matter and the commutator, $[\hat{H}, \hat{p}_x]$, between the two operators is zero,

$$[\hat{H}, \hat{p}_x] = \hat{H}\hat{p}_x - \hat{p}_x\hat{H} = 0, \quad (1.21)$$

which means they commute. Operators that commute with the Hamiltonian, will have a common set of eigenfunctions and therefore quantum states with a definite value corresponding to the physical property of the operator.

If two operators that do not commute, they will not have simultaneous eigenvectors and eigenvalues, thus the order in which they are applied to an eigenvector will effect the result (and the commutator will not equal zero). For two non-commuting quantum mechanical operators, there is no simultaneous wavefunction between the operators. Measuring both physical properties simultaneously in an experiment will have its precision limited by the Heisenberg Uncertainty principle.⁷⁰ The value of a property P belonging to operator $\hat{P}$, is defined as an expectation value between the wavefunction and operator in the case where a normalised wavefunction is not necessarily an eigenfunction.

$$\langle P \rangle = \langle \psi | \hat{P} | \psi \rangle \quad (1.22)$$

Dirac Bra-Ket Notation

Equation 1.22 introduces the Dirac bra-ket notation which allows wavefunctions to be described as vectors in infinite multidimensional space (Hilbert space). The “ket”, $|\psi\rangle$, defines the vector and the “bra”, $\langle\psi|$ its complex conjugate, which results in the bra-ket notation denoting an inner product in Hilbert space when the bra-ket is closed. So for any normalised wavefunction,

$$\langle\psi|\psi\rangle = 1, \quad (1.23)$$

which is equivalent to Equation 1.16.

The Born-Oppenheimer Approximation and the Potential Energy Surface

The theory of quantum mechanics presents equations to determine all desired properties of chemical systems. The problem is finding solutions to practical examples becomes overly complex and the scale of the calculations goes beyond reasonable computing time and resources. The following sections will detail several techniques used to approximately solve the Schrödinger equation in molecular systems in the context of X-ray spectroscopy, but first will detail a widely applied approximation applied to all of the methods discussed. The Born Oppenheimer (BO) approximation⁷¹ arises from the relatively large separation in speeds between the fast moving

electrons and slow moving nuclei. This allows the generation of a simplified Hamiltonian which represents the nuclei as fixed and the electrons moving in the electrostatic potential generated by nuclei at these coordinates. To begin with, the full Hamiltonian, explicitly containing both electron and nuclear degrees of freedom is generated from the classical energy expression in terms of the coordinates and momenta, where the momenta p_x , is replaced by $\frac{d}{dx}$ and expressed in atomic units (a.u) to give,

$$\hat{H} = - \sum_{i=1}^N \frac{1}{2} \nabla_i^2 - \sum_{A=1}^M \frac{1}{2M_A} \nabla_A^2 - \sum_{i=1}^N \sum_{A=1}^M \frac{Z_A}{r_{iA}} + \sum_{i=1}^N \sum_{j>i}^N \frac{1}{r_{ij}} + \sum_{A=1}^M \sum_{B>A}^M \frac{Z_A Z_B}{R_{AB}}, \quad (1.24)$$

$$\nabla = \left(\frac{\delta}{\delta x}, \frac{\delta}{\delta y}, \frac{\delta}{\delta z} \right). \quad (1.25)$$

In Equation 1.24 M_A is the mass and Z_A the atomic number of nucleus A. r_{iA} , r_{ij} and R_{AB} are the electron-nuclear, electron-electron and nuclear-nuclear distances respectively. Therefore, the first and second terms in Equation 1.24 are the kinetic energy operators of the electrons and nuclei respectively; the third term is the Coulomb attraction between the electrons and nuclei and the fourth and fifth terms are the repulsion of the electrons and nuclei. In the BO approximation, terms corresponding to the kinetic energy and repulsion of the nuclei can be neglected because any constant added to an operator only adds to the operator eigenvalues and has no effect on the eigenfunctions. This leads to the electronic Hamiltonian describing the motion of N electrons in the field of M nuclear point charges.

$$\hat{H}_{\text{elec}} = - \sum_{i=1}^N \frac{1}{2} \nabla_i^2 - \sum_{i=1}^N \sum_{A=1}^M \frac{Z_A}{r_{iA}} + \sum_{i=1}^N \sum_{j>i}^N \frac{1}{r_{ij}}, \quad (1.26)$$

This allows the time-independent electronic Schrödinger equation for fixed nuclear geometry $\{R_A\}$ to be written as,

$$\hat{H}_{\text{elec}} \psi_{\text{elec}} = E_{\text{elec}} \psi_{\text{elec}} \quad (1.27)$$

where the eigenfunction is the electronic wavefunction and eigenvalue the electronic energy at $\{R_A\}$,

$$E_{\text{elec}} = E_{\text{elec}}(\{R_A\}) \quad (1.28)$$

and the total energy for a fixed nuclear coordinate can be generated by adding in the nuclear repulsion term.

$$E_{\text{total}} = E_{\text{elec}}(\{R_A\}) + \sum_{A=1}^M \sum_{B>A}^M \frac{Z_A Z_B}{R_{AB}}. \quad (1.29)$$

Now the electron coordinates depend parametrically on the nuclei and varying R_A will give the total energy as a function of the nuclear coordinates, constituting

what is known as a potential energy surface (PES). The concept of the PES is fundamental to solving problems in many areas of chemistry.

The next challenge is the solution of the time-independent electronic Schrödinger equation in Equation 1.18 which involves more approximations to be discussed in the following subsection (1.2.2) on the Hartree-Fock theory, including the application to excited state wavefunctions. However Hartree-Fock theory is not widely applied to X-ray spectroscopy due to its omission of electron correlation treatment in the electron interaction term $1/r_{ij}$ in Equation 1.26. However, Hartree-Fock theory lays the foundation of the rest of the theories discussed, in particular the widely implemented Kohn-Sham Density functional Theory (KSDF) and time-dependent DFT (TDDFT) discussed in subsection 1.2.3. Subsections 1.2.4-7 will look at various wavefunction methods also based on the Hartree-Fock model and capable of accurate X-ray spectroscopy simulations, using propagator functions, equations of motion (EOM) and multi-determinantal wavefunctions.

1.2.2 Hartree-Fock Theory and the Self Consistent Field Procedure

The Hartree Product

Hartree-Fock theory is the foundation of the vast majority of modern quantum chemical methods. It is the implementation of molecular orbital theory, involving the approximation of molecular orbitals by a linear combination of atomic orbitals (LCAO). It solves the time-independent electronic Schrödinger using mean field theory, each electron moves in a mean field potential of the surrounding electrons.

We begin by expressing the fermionic nature of electrons as single particle wavefunctions known as spin orbitals $\chi(\mathbf{x})$, where $\mathbf{x}$ has both a spatial $\psi(\mathbf{r})$ and spin coordinate, $s(\omega)$ of either $\omega = \alpha$ or β ($+\frac{1}{2}$ or $-\frac{1}{2}$),

$$\chi(\mathbf{x}) = \psi(\mathbf{r})s(\omega). \quad (1.30)$$

Most systems of interest will have more than one electron, which will require the consideration of many one electron spin orbitals. If electrons in the system are not interacting with each other then the Hamiltonian of an N electron system could be expressed as,

$$\hat{H} = \sum_{i=1}^N h(i) \quad (1.31)$$

where $h(i)$ is the operator for the kinetic and potential energy of attraction to nuclei of electron i . The eigenfunctions of $\hat{H}$ can be found by describing the N

electron wavefunction as a product of spin orbitals as $\hat{H}$ is a sum of one electron Hamiltonians ($h(i)$),

$$\Psi^{HP}(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) = \chi_i(\mathbf{x}_1)\chi_j(\mathbf{x}_2)\dots\chi_k(\mathbf{x}_N), \quad (1.32)$$

$$\hat{H}\Psi^{HP} = E\Psi^{HP}, \quad (1.33)$$

which gives eigenvalue E. This many electron wavefunction is known as the Hartree-Product and is an uncorrelated many electron wavefunction; i.e the position of electron $\mathbf{x}_i$ is only effected by an averaged mean field representation of its repulsion interaction with other N-1 electrons in the system. The development of correlated electron-electron repulsion methods is a key focus point of modern quantum chemistry development.

Slater Determinants

Another deficiency of the Hartree-Product is that it does not account for the Pauli anti-symmetry principle, where the interchange of the space and spin of coordinates of two electrons changes the sign of the wavefunction. Representing the N electron wavefunction as a Slater determinant does however satisfy the antisymmetry principle.

$$|\Psi\rangle = \Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) = (N!)^{-1/2} \begin{vmatrix} \chi_i(\mathbf{x}_1) & \chi_j(\mathbf{x}_1) & \cdots & \chi_k(\mathbf{x}_1) \\ \chi_i(\mathbf{x}_2) & \chi_j(\mathbf{x}_2) & \cdots & \chi_k(\mathbf{x}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_i(\mathbf{x}_N) & \chi_j(\mathbf{x}_N) & \cdots & \chi_k(\mathbf{x}_N) \end{vmatrix} \quad (1.34)$$

The determinant is normalised by the factor $(N!)^{-1/2}$. The wavefunction now obeys the Pauli-exclusion principle and all the electrons are indistinguishable from one another. The ket notation in Equation 1.33 will be used to describe Slater determinants herein, since they are used throughout Hartree-Fock theory and in post Hartree-fock theories.

The Linear Variation Principle and Basis Sets

The variation principle states that the expectation value of the energy of the Hartree-Fock wavefunction, or in fact any approximate wavefunction, will be higher in energy than the value of the exact ground state energy.

$$\langle \Psi^{HF} | \hat{H} | \Psi^{HF} \rangle \geq E_{\text{exact}} \quad (1.35)$$

It would be too complex to optimise all the parameters of the HF wavefunction to minimise the expectation value in line with the variational principle. Therefore, it is

more convenient to expand the orbitals in the wavefunction as a linear combination of fixed parameter atom centred basis functions $|\Phi\rangle$ and optimise the corresponding expansion coefficients c_i , shown in Equation 1.36, with respect to minimising the energy. The basis functions form a basis set that will describe the radial behaviour of the orbitals and can be chosen for optimal efficiency and accuracy depending on the system under investigation. The optimal basis set design for various X-ray spectroscopy techniques is discussed and applied to XPS of ionic liquids in Chapter 2.

$$|\Psi^{HF}\rangle = \sum_{i=1}^N c_i |\Phi\rangle \quad (1.36)$$

The Roothan-Hall Hartree Fock Equations

The normalisation constraint of the wavefunction, $\langle\Psi|\Psi\rangle = 1$ allows the Lagrangian method of undetermined multipliers to perform constrained minimisation to minimise the energy and the linear expansion of the wavefunction in a basis set allows operators and wavefunctions to be represented in a matrix form to generate,

$$\mathbf{FC} = \mathbf{SC}\epsilon. \quad (1.37)$$

This is known as the Roothan-Hall Hartree Fock equations in the non-orthogonal atomic orbital basis, $\mathbf{F}$ represents the Hamiltonian and is the Fock operator in its matrix representation. The interested reader is referred to Szabo and Ostlund's thorough discussion on the Hartree-Fock method.⁷² The coefficients in Equation 1.36 form the coefficient matrix in the atomic orbital basis and are variationally optimised to generate the minimum total energy. ϵ represents a diagonal matrix of the orbital energies. The fixed basis functions used are normalised but not orthogonal. $\mathbf{S}$ is the overlap matrix compensating for this and used to construct an orthogonalisation transformation matrix. To solve the Hartree-Fock equations, the Fock operator is diagonalised in the orthogonal molecular orbital basis then transformed back into the AO basis to calculate the energy. Several techniques are available to orthogonalise the orbitals into the MO basis, such as symmetric and canonical orthogonalization. The Fock matrix can be split into one and two electron parts,

$$\mathbf{F} = \mathbf{h} + \mathbf{G}. \quad (1.38)$$

The one electron matrix $\mathbf{h}$, represents the operators in the non-interacting Hamiltonian in Equation 1.31. The two electron matrix can be further split into the Coulomb, $\mathbf{J}$, (electrostatic) and exchange, $\mathbf{K}$, (anti-symmetrised) electron-electron interaction matrices,

$$\mathbf{G} = \mathbf{D}[2\mathbf{J} - \mathbf{K}] \quad (1.39)$$

therefore,

$$\mathbf{F} = \mathbf{h} + \mathbf{D}[2\mathbf{J} - \mathbf{K}]. \quad (1.40)$$

There is another term in the equation of the Fock matrix, $\mathbf{D}$ which is the density matrix. In a similar fashion to the square-norm of wavefunction $|\psi|^2$ being equal to its probability density, the density matrix is calculated in a set of known AO basis functions Φ_μ , in an N-electron closed shell system by

$$D_{\mu\nu} = 2 \sum_i^{N/2} C_{\mu i} C_{\nu i}^*. \quad (1.41)$$

The Self Consistent Field Procedure

Now we can observe one of the most important aspects to practically solving problems in quantum chemistry, the Fock matrix is diagonalised to give the coefficient matrix $\mathbf{C}$, but also requires $\mathbf{C}$. The Fock matrix is a function of the density (Equations 1.40 and 1.41). This allows for a guess density to initiate an iterative self consistent field (SCF) process to find the optimal $\mathbf{C}$ and hence optimal density, to then calculate the Hartree-Fock electronic energy via,

$$E_{\text{elec}} = \mathbf{D}(\mathbf{h} + \mathbf{F}). \quad (1.42)$$

The steps in the SCF procedure, used across modern quantum chemistry packages, are:

1. Specify the molecular system and choose a suitable basis set.
2. Calculate the integrals for the one electron $\mathbf{h}$ and two electron $\mathbf{G}$ matrices.
3. Use $\mathbf{S}$ to generate a transformation matrix, $\mathbf{X}$, to orthogonalise the non-orthogonal AO orbitals.
4. Obtain guess $\mathbf{D}$ (common to diagonalise $\mathbf{h}$ and construct $\mathbf{D}$ from the resulting eigenvectors).
5. Calculate $\mathbf{G}$ using $\mathbf{D}$, add $\mathbf{h}$ to make Fock matrix $\mathbf{F}$ (the effective Hamiltonian).
6. Use $\mathbf{X}$ to transform $\mathbf{F}$ into the orthogonal MO basis $\mathbf{F}'$.
7. Diagonalise $\mathbf{F}'$ to $\mathbf{C}'$ and ϵ .
8. Back transform $\mathbf{C}'$ into the non-orthogonal AO basis $\mathbf{C}$ using $\mathbf{X}$.
9. Form new $\mathbf{D}$ from the new $\mathbf{C}$.
10. Check for convergence between the new $\mathbf{D}$ and old $\mathbf{D}$, if not converged go back to step 5.

Unrestricted Hartree-Fock

The above notation applies to closed shell ground state systems where the α and β electrons can be treated on an equal footing and by a single Slater determinant,

known as restricted Hartree-Fock. The present work, primarily concerns itself with excited states and in Chapter 5, open shell systems, where the electrons cannot be treated on the same footing with regards to their spin. In such cases the previous notation cannot be used. To perform calculations on these systems one begins with the unrestricted Hartree-Fock equations, where there are separate matrices for the α and β electrons,

$$\mathbf{F}_\alpha = \mathbf{h} + \mathbf{D}_\alpha \mathbf{J} + \mathbf{D}_\beta \mathbf{J} - \mathbf{D}_\alpha \mathbf{K} \quad (1.43)$$

$$\mathbf{F}_\beta = \mathbf{h} + \mathbf{D}_\beta \mathbf{J} + \mathbf{D}_\alpha \mathbf{J} - \mathbf{D}_\beta \mathbf{K} \quad (1.44)$$

$$E_{\text{elec}} = \frac{1}{2} \mathbf{D}_\alpha (\mathbf{h} + \mathbf{F}_\alpha) + \frac{1}{2} \mathbf{D}_\beta (\mathbf{h} + \mathbf{F}_\beta) \quad (1.45)$$

The density matrix for each spin, $\mathbf{D}_\alpha$ and $\mathbf{D}_\beta$, will come from coefficient matrices of corresponding spin $\mathbf{C}_\alpha$ and $\mathbf{C}_\beta$ in a similar fashion to Equation 1.41 but summing over N in each spin rather than the total number of electron over two (number of occupied orbitals for a closed shell system).

Excited State Wavefunctions and the Maximum Overlap Method

The unrestricted Hartree-Fock equations can be applied to any open shell or excited state system where the α and β electrons need to be treated on a separate footing. How can one then optimise the coefficients of an excited state wavefunction in the framework of energy minimisation in the variation principle? One widely used method that allows for non-aufbau configurations of the system to be attained, excited state wavefunctions to be calculated and applicable to any variational quantum chemical technique is the maximum overlap method (MOM).⁷³ Rather than the orbitals being solely constrained to be an orthonormal set during the energy minimisation, they can also be chosen to maximise the overlap with the orbitals of the previous cycle. By adding this extra constraint in the SCF procedure, MOM can maintain electronic configurations higher in energy than the ground state. By using the optimised ground state as the initial guess for the excited state calculation, an electron can then be promoted to an unoccupied orbital at the start of the SCF cycle, then MOM will prevent variational collapse during the SCF procedure.

To perform MOM, initially an orbital overlap matrix between the molecular orbitals of the current cycle, $\mathbf{C}^n$, and previous cycle, $\mathbf{C}^{n-1}$, is generated.

$$\mathbf{O} = (\mathbf{C}^{n-1})^\dagger \mathbf{S} \mathbf{C}^n \quad (1.46)$$

The matrix element O_{ij} represents the overlap between the i^{th} previous cycle orbital and the j^{th} current cycle orbital. Summing over the rows of the overlap

matrix will generate a vector of projections, $\mathbf{P}_j$ for the new orbital space, orbitals with the largest $\mathbf{P}_j$ s will become the new occupied orbitals.

$$\mathbf{P}_j = \sum_i^{occ} \mathbf{O}_{ij} = \sum_l^{occ} \left[\sum_k^{occ} \left(\sum_i^{occ} C_{ik}^{n-1} \right) S_{kl} \right] C_{lj}^n \quad (1.47)$$

Due to the underlying energy minimisation, the MOM method still has the potential to collapse to the ground state or any lower energy state in the same symmetry group. It should be used with caution and variational collapse becomes more likely with promotion to higher energy orbitals and larger sized systems, there have been several recent attempts to develop new theories for converging excited state wavefunctions,^{74–76} but these are not yet as practical and cannot be applied as a “black-box” method in the same way that MOM can. MOM will be used throughout this work to generate core excited and core ionised reference states with single determinant quantum chemical methods.

The Δ SCF Method

In recent years, very few spectroscopic and in-particular X-ray spectroscopic publications, have used results from Hartree-Fock calculations. Hartree-Fock theory lays the foundations of the majority of quantum chemical methods but it misses the energetically crucial component of the electron correlation energy. The correlation energy describes the difference between the Hartree-Fock and the exact energy of the system. It originates from the correlated motion of electrons (dynamic correlation) and the interaction between near degenerate electron configurations (static correlation). The subsequent sections of this chapter discuss methods that explicitly include the electron correlation into the solution of the Schrödinger equation. MOM can be applied to any of these methods and generate core-ionised and core-excited wavefunctions which can be used to calculate spectra by the energy difference between the ground and excited (or ionised) state. The following equations are used for the transition energy and oscillator strengths between initial and final states respectively,

$$\Delta E = E_F - E_I \quad (1.48)$$

$$f \propto |\langle \phi_I | \hat{\mu} | \phi_F \rangle|^2 \quad (1.49)$$

the indexes I and F represent initial and final states and $\hat{\mu}$ is the dipole operator. E represents the energies of the states and ϕ the orbitals involved in the electronic transitions. This is a commonly used approach known as Δ -self-consistent field (Δ SCF) and has routinely been used to compute CEBEs.^{77–80}

1.2.3 Density Functional Theory

The Hohenberg-Kohn Theorems

Until now the chemical system has been described by a wavefunction. In the many electron wavefunction each electron and nucleus is described by a three dimensional coordinate space resulting in a $3N$ dimensional system. A much simpler description of the chemical system can be given by its density, $\rho(\mathbf{r})$. We saw in the previous section that the square norm of a wavefunction is equal to its probability density, meaning the electron density is an extractable observable from the wavefunction. Integrating over the density of system will give the number of electrons, N .

$$\int d\mathbf{r} \rho(\mathbf{r}) = N \quad (1.50)$$

The electron density of a molecule will have peaks at the nuclei and the slope of the density around the nuclei will correspond to the nuclear charge. This means that the number of electrons, the position and the charge of the nuclei are provided by the ground state density, which therefore contains all the information needed about the system. The density can generate a Hamiltonian to solve the Schrödinger equation and provide a wavefunction for the ground state system. Hohenberg and Kohn presented two theorems in relation to this;⁸¹

1. The density specifies the Hamiltonian, hence a ground-state energy functional exists: $E[\rho]$
2. The energy functional in Theorem 1. is variational: $E[\rho'] \geq E_{\text{exact}}$.

The energy density functional put forward in the theorems can be split into two parts,

$$E[\rho] = E_{\text{HK}}[\rho] + \int d\mathbf{r} \rho(\mathbf{r}) \nu_{\text{nuc}}(\mathbf{r}) \quad (1.51)$$

the first term is the unknown, but universal, density functional. The second is known and specifies the nature of the system. Solving the universal functional has proven to be extremely challenging. The universal functional is of the form,

$$E_{\text{HK}}[\rho] = T[\rho] + J[\rho] + E_{\text{xc}}[\rho] \quad (1.52)$$

the Coulomb energy functional, $J[\rho]$, is a large proportion of the total energy functional and is known. The relatively small contribution from the exchange and correlation functional $E_{\text{xc}}[\rho]$, is unknown. $T[\rho]$ is the kinetic energy functional and presents the largest unknown contribution HK-DFT energy.

Kohn Sham Density Functional Theory

Kohn-Sham DFT (KS-DFT) provides the means for practical solutions to DFT by re-introducing the Slater determinant,⁸² this overcame two of the primary limita-

tions to the application of HK-DFT. Theorem 2 of HK-DFT states that the density functional is variational. This requires minimisation to occur over densities corresponding to an antisymmetric wavefunction, provided by the Slater determinant representation of a wavefunction. In HK-DFT, the functional for the kinetic energy provided the largest unknown. In KS-DFT the kinetic energy functional is split into non-interacting $T_s[\rho]$ and correlated $T_c[\rho]$ contributions by introducing one-electron atomic orbitals expressed via a Slater determinant. $T_s[\rho]$ is analogous to the one electron kinetic energy of the Hartree-Fock Hamiltonian and is exactly solvable and $T_c[\rho]$ is now included in $E_{xc}[\rho]$. The new formula for the energy density functional is,

$$E[\rho] = T_s[\rho] + J[\rho] + E_{xc}[\rho] + \int d\mathbf{r} \rho(\mathbf{r}) \nu_{\text{nuc}}(\mathbf{r}) \quad (1.53)$$

The KS-DFT energy can be found by minimizing the energy with respect to orbitals that form a Slater determinant, i.e. minimising the orbital coefficients corresponding to a linear combination of known basis functions. This means that the same algorithms solving Hartree-Fock can be applied to KS-DFT via analogous Kohn-Sham equations,

$$\hat{f}_{\text{KS}}\psi_i = \epsilon_i\psi_i \quad (1.54)$$

where $\hat{f}_{\text{KS}}$ is derived from the functional derivative of $E[\rho]$,

$$\hat{f}_{\text{KS}} = -\frac{1}{2}\nabla^2 + \nu_J + \nu_{\text{xc}} + \nu_{\text{nuc}}. \quad (1.55)$$

The only unknown term in KS-DFT is the exchange-correlation potential, ν_{xc} . In the adiabatic approximation, the exchange-correlation potential reacts instantly and without memory to any perturbation to the density, allowing the potential to be expressed as,

$$\nu_{\text{xc}}(\mathbf{r}) = \frac{\partial E_{\text{xc}}[\rho]}{\partial \rho(\mathbf{r})}. \quad (1.56)$$

The expression of E_{xc} has been the main focus of KS-DFT development in recent years and there are a vast number of functionals which are used across multiple applications. The first models were based on the description of a uniform electron gas. This model, called the local density approximation (LDA)⁸³ provides a good description of the exchange-correlation where a uniform density is a good approximation, such as in metallic solids. Unfortunately in molecular systems, the density is far from uniform. Modifying the LDA approximation to take into account in the gradient of the density, in the generalised gradient approximation (GGA), provides a better description of molecular systems. The accuracy of the GGA model can be further improved by the meta-GGA approximation, where the second derivative of the density or kinetic energy density is included. This hierarchy of exchange correlation functionals is known as Jacobs ladder.

Hybrid Kohn-Sham Density Functional Theory

The exchange-correlation functionals discussed in the previous section are considered as pure DFT. The inaccuracy associated to these functionals can be partly attributed to the correlated part of the kinetic energy is not adequately described within the exchange-correlation functional.

$$E_{xc}[\rho] = \{V_{ee}[\rho] - J[\rho]\} + \{T[\rho] - T_s[\rho]\} = \{V_{ee}[\rho] - J[\rho]\} + T_c[\rho] \quad (1.57)$$

Becke found that including some Hartree-Fock exchange into the BLYP functional to form a hybrid functional, B3LYP, partially corrected this.⁸⁴

$$E_{xc}^{B3LYP}[\rho] = (1 - a)E_x^S[\rho] + aE_x^{HF} + bE_x^{B88}[\rho] + cE_c^{LYP}[\rho] + (1 - c)E_c^{VWN}[\rho] \quad (1.58)$$

$$a = 0.20 \quad b = 0.72 \quad c = 0.81 \quad (1.59)$$

B3LYP in KSDFT is one of the most widely used methods in quantum chemistry and has supported chemical research across a multitude of disciplines as a good all-rounder for the description of the exchange-correlation. KS-DFT has provided an accurate correlated method of the same computational scaling as Hartree-Fock; which has driven its evolution into a widely used black box method. One deficiency, partially alleviated by inclusion of Hartree-Fock exchange, is the self-interaction error (SIE). This results from the DFT approximate exchange not cancelling the self interaction included in the DFT Coulomb energy, allowing the electrons to experience “their own potential”. As a consequence the electron density in charge transfer systems is poorly described. The SIE becomes worse at larger electron-electron interaction distances, which is a consequence of the exchange potential behaving as $-0.2r^{-1}$, instead of $-r^{-1}$. The development of the long range corrected analogue of B3LYP, Coulomb-attenuating method B3LYP (CAM-B3LYP),⁸⁵ corrects this by separating the electron-electron ($1/r_{12}$) interaction into long and short range parts and applying more Hartree-Fock exchange (exact exchange) into the long range interaction.

$$\frac{1}{r_{12}} = \frac{1 - [\alpha + \beta \cdot \text{erf}(\mu r_{12})]}{r_{12}} + \frac{\alpha + \beta \cdot \text{erf}(\mu r_{12})}{r_{12}} \quad (1.60)$$

The first term accounts for the short range and the second the long range. The α controls the amount of Hartree-Fock exchange and the β controls the DFT exchange included. This exchange-correlation functional is popular in time-dependent DFT described in the next section, as this method is used for excited states which involve the transfer of electron density. In X-ray spectroscopy, short range electron-electron interactions are important as an accurate description of the core hole is required. The short-range corrected analogues of CAM-B3LYP, the SRC functionals, have proven to give accurate core excitation energies in TDDFT^{86,87} and are given by the

following partition scheme,

$$\begin{aligned} \frac{1}{r_{12}} = & C_{\text{SHF}} \frac{1 - \text{erf}(\mu_{\text{SR}} r_{12})}{r_{12}} + C_{\text{LHF}} \frac{1 - \text{erf}(\mu_{\text{LR}} r_{12})}{r_{12}} \\ & - C_{\text{SHF}} \frac{1 - \text{erf}(\mu_{\text{SR}} r_{12})}{r_{12}} + C_{\text{LHF}} \frac{1 - \text{erf}(\mu_{\text{LR}} r_{12})}{r_{12}} + \frac{1}{r_{12}}, \end{aligned} \quad (1.61)$$

C_{SHF} and C_{LHF} are parameters that control the portion Hartree-Fock exchange in the long and short range interactions. μ_{SR} and μ_{LR} are the long and short range attenuation parameters that allow more control over the range separation. The SRC-R functionals have been designed for XAS calculations, Chapter three explores their application to XES TDDFT calculations and to what degree they can be modified to generate more accurate results.

Linear Response Time Density Functional Theory

Time-dependent DFT (TDDFT) was first presented by Runge and Gross,⁸⁸ who introduced an external electric field potential, into solving the time-dependent Schrödinger equation via a functional of the density. This led to the development of the time dependent Kohn-Sham equations,

$$\hat{f}_{\text{KS}}(\mathbf{r}, t) \psi(\mathbf{r}, t) = i\hbar \frac{\partial \psi(\mathbf{r}, t)}{\partial t}, \quad (1.62)$$

$$\hat{f}_{\text{KS}}(\mathbf{r}, t) = -\frac{1}{2} \nabla^2 + \nu_{\text{ext}}(\mathbf{r}, t) + \int \frac{\rho(\mathbf{r}', t)}{r_{12}} + \frac{E_{\text{xc}}[\rho_t(\mathbf{r})]}{\rho(\mathbf{r})}. \quad (1.63)$$

The exchange-correlation energy term is a functional of $\rho_t(\mathbf{r})$, the $\rho(\mathbf{r}, t)$ at evaluated at fixed time t , owing to the adiabatic approximation being local in time. The widely implemented formalism of TDDFT uses the linear response (LR) of the dynamic polarizability ($\alpha(\omega)$). Where a time dependent perturbation in the dynamic polarizability $\alpha(\omega)$ is applied to an unperturbed molecule for which the ground state equations have been solved for. The response of the unperturbed system to an applied electric field will generate an absorption spectrum by the following equations,

$$\alpha(\omega) = \sum_I \frac{f_I}{\omega_I^2 - \omega^2}, \quad (1.64)$$

$$f_I = \frac{2}{3} (|\langle \Psi_0 | \hat{x} | \Psi_I \rangle|^2 + |\langle \Psi_0 | \hat{y} | \Psi_I \rangle|^2 + |\langle \Psi_0 | \hat{z} | \Psi_I \rangle|^2), \quad (1.65)$$

$$\omega_I = E_I - E_0. \quad (1.66)$$

The poles of the dynamic polarizability determine the excitation energies, ω_I and the residues, f_I , determine the corresponding oscillator strengths of the spectrum.

Implementation of LR-TDDFT usually adopts the formalism of Casida.⁸⁹ In the frequency domain, the response of the Kohn-Sham density matrix, $\delta\mathbf{P}(\omega)$ in the applied electric field $b(\omega)$ is given by,

$$\left\{ \omega \begin{bmatrix} -1 & 0 \\ 0 & -1 \end{bmatrix} - \begin{bmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B} & \mathbf{A} \end{bmatrix} \right\} \begin{pmatrix} \delta\mathbf{P}(\omega) \\ \delta\mathbf{P}^*(\omega) \end{pmatrix} = \begin{pmatrix} b(\omega) \\ b^*(\omega) \end{pmatrix} \quad (1.67)$$

where,

$$A_{ia\sigma,jb\tau} = \delta_{ij}\delta_{ab}\delta_{\sigma\tau}(\epsilon_{a\sigma} - \epsilon_{i\tau}) + (ia\sigma|jb\tau) + (ia\sigma|f_{xc}|jb\tau) \quad (1.68)$$

$$B_{ia\sigma,jb\tau} = (ia\sigma|jb\tau) + (ia\sigma|f_{xc}|jb\tau) \quad (1.69)$$

which are defined by,

$$(ia\sigma|jb\tau) = \int \int \psi_{i\sigma}^*(\mathbf{r}_1)\psi_{a\sigma}^*(\mathbf{r}_1)\frac{1}{r_{12}}\psi_{j\tau}(\mathbf{r}_2)\psi_{b\tau}(\mathbf{r}_2)d\mathbf{r}_1d\mathbf{r}_2 \quad (1.70)$$

and

$$(ia\sigma|f_{xc}|jb\tau) = \int \psi_{i\sigma}^*(\mathbf{r}_1)\psi_{a\sigma}^*(\mathbf{r}_1)\frac{d^2E_{xc}}{d\rho_{\sigma}(\mathbf{r}_1)d\rho_{\tau}(\mathbf{r}_2)}\psi_{j\tau}(\mathbf{r}_2)\psi_{b\tau}(\mathbf{r}_2)d\mathbf{r}_1d\mathbf{r}_2. \quad (1.71)$$

Equation 1.64, suggests that a frequency corresponding to an excitation energy will generate a finite perturbation but the response in the density matrix will be infinite. Meaning that Equation 1.67 in the case of an excitation frequency is re-written as,

$$\omega_I = \begin{bmatrix} -1 & 0 \\ 0 & +1 \end{bmatrix} - \begin{bmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B} & \mathbf{A} \end{bmatrix} = 0 \quad (1.72)$$

which allows for the excitation energies to be solved as a pseudo-eigenvalue problem.

$$\begin{bmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B} & \mathbf{A} \end{bmatrix} \begin{pmatrix} \mathbf{X}_I \\ \mathbf{Y}_I \end{pmatrix} = \omega_I \begin{bmatrix} +1 & 0 \\ 0 & -1 \end{bmatrix} \begin{pmatrix} \mathbf{X}_I \\ \mathbf{Y}_I \end{pmatrix} \quad (1.73)$$

A widely used approximation applied to LR-TDDFT is the Tamm-Dancoff approximation (TDA).⁹⁰ LR-TDDFT-TDA is computationally cheaper than full LR-TDDFT, without much loss in accuracy of the excitation energies, by setting $\mathbf{B} = 0$ in the Casida equations to give,

$$\mathbf{A}\mathbf{X}_I = \omega_I\mathbf{X}_I. \quad (1.74)$$

All TDDFT calculations in this work have been performed as LR-TDDFT-TDA. Another computational application involves reducing the single excitation space of the TDDFT calculation. Calculating all possible excitations of the system is often not computationally practical. This is addressed by the Davidson procedure, leading to the development of Krylov subspace methods, which solve for the lowest eigenvalues first.⁹¹ This poses as a problem for calculating XAS with TDDFT, many excited

state roots would be calculated before core excitations are reached, making calculations prohibitively expensive. Many computational chemistry software packages give the option to reduce the excitation window, which allows the user to specify a specific orbital in which to excite from. The capability to choose specific core orbitals makes TDDFT a practical tool for simulating X-ray spectroscopy. TDDFT has been used to simulate XAS^{87,92} and also XES.^{37,93,94} XES is simulated through the use of a reference determinant with a core-hole. TDDFT can be readily combined with the MOM procedure to create an unperturbed reference system which is in-fact an excited or ionised state. Enabling TDDFT to simulate two-photon spectroscopy techniques such as RIXS^{25,95} which is implemented in Chapter 4.

Ab-initio Molecular Dynamics

This review of quantum mechanical methods primarily concerns itself with the solving the electronic Schrödinger equation within the BO approximation. The effect of nuclear motion is not explicitly accounted for and only incorporated by manually altering the geometry and re-optimising the electronic structure. Whilst accurate description of the electronic structure is vital for spectroscopic calculations, experiments probe the response of the electrons under in the presence of an external field with respect to the motion of the nuclei. One key focus of spectroscopy, in particular X-ray spectroscopy, is to probe non-adiabatic dynamics involving nuclear motion on multiple potential energy surfaces mediated by conical intersections. “Dark” relaxation processes are fundamental to understanding photochemical applications such as photosynthesis and vision. It is therefore just as important to consider the nuclear dynamics as well as the electronic structure and understand how they effect each other in-order to accurately simulate advanced spectroscopic techniques. Explicitly implementing quantum dynamics is not in the scope of this work. However, the study in Chapter 5 shows evidence for ultrafast state-crossing in core excited nitric oxide and highlights the requirement for the development of theoretical methods to accurately calculate non-adiabatic core-excited state dynamics.

Nuclear dynamics simulations play an important role in simulating the effects of ultra-fast dissociation in the RIXS of water in Chapter 4. It has been previously shown that conformer sampling can give significant improvements to simulated XES spectra.⁹⁶ The nuclear dynamics method used stays within the Born-Oppenheimer approximation and is referred to as *ab initio* molecular dynamics (AIMD).⁹⁷ AIMD is based on the classical trajectories widely implemented in force-field dynamics, but rather than using a pre-parametrised molecular mechanics (MM) force field, AIMD generates the interatomic forces F_I from *ab initio* electronic structure calculations.

There are two main approaches to AIMD simulations, the Car-Parrinello method propagates the wavefunction parameters as classical degrees freedom and the Born Oppenheimer approach recomputes the electronic structure at each time step.⁹⁸ The Car-Parrinello technique only requires a single *ab initio* calculation and is hence computationally less intensive and applicable to large systems such as liquids. This work primarily deals with small systems in the gas phase and hence employs the Born Oppenheimer AIMD,

$$F_I = -\nabla_R \Phi(\mathbf{R}) \quad (1.75)$$

where $\Phi(\mathbf{R})$ is the potential energy function and is calculated by,

$$\Phi(\mathbf{R}) = E[\{\psi_i\}; \mathbf{R}] = E^{KS}[\{\psi_i[\rho(\mathbf{r})]\}; \mathbf{R}] + E_{II}(\mathbf{R}) \quad (1.76)$$

AIMD is a semi-classical method, the electrons are described quantum mechanically and the nuclei classically, this reduces its relative cost greatly and large scale AIMD simulations are widely implemented.^{99,100} This work uses KS-DFT-B3LYP driven dynamics, to improve spectra simulated by TDDFT in Chapters 3 and 4 and EOM-CSSD in Chapter 5.

1.2.4 Intermediate State Representation of the Algebraic Diagrammatic Construction Method

A similar approach to calculating X-ray spectroscopy using linear response functions is to use a polarisation propagator function,

$$\Pi_{pq,rs}(\omega) = \sum_n \frac{\langle \Psi_0 | c_q^\dagger c_p | \Psi_n \rangle \langle \Psi_0 | c_r^\dagger c_s | \Psi_n \rangle}{\omega + E_0 - E_n} + \sum_n \frac{\langle \Psi_0 | c_r^\dagger c_s | \Psi_n \rangle \langle \Psi_0 | c_q^\dagger c_p | \Psi_n \rangle}{\omega + E_0 - E_n} \quad (1.77)$$

$$= \Pi_{pq,rs}^+(\omega) + \Pi_{pq,rs}^-(\omega), \quad (1.78)$$

This formalism uses the notation of the creation and annihilation operators, $c_q^\dagger$ and c_q ($c_q^\dagger$ acts on a wavefunction to create an electron in orbital q and c_q acts on a wavefunction to create a hole in orbital q), which is a useful form of notation for quantum chemical methods concerning spectroscopy and correlation. The summation goes over all electronically excited states $|\Psi_n\rangle$ with energies E_n . Much like a response function, the polarisation propagator, $\Pi(\omega)$ has poles at the vertical excitation energies and the residues are related to the oscillator strength. When solving $\Pi(\omega)$, $\Pi_{pq,rs}^+(\omega)$ and $\Pi_{pq,rs}^-(\omega)$ contain the same information so only one needs to be considered. $\Pi(\omega)$ can be written in a compact diagonal representation,

$$\Pi(\omega) = \mathbf{x}^\dagger (\omega \mathbf{1} - \mathbf{\Omega})^{-1} \mathbf{x}, \quad (1.79)$$

where,

$$\Omega_n = E_n - E_0, \quad (1.80)$$

and

$$x_{rs}^n = \langle \Psi_n | c_r^\dagger c_s | \Psi_0 \rangle. \quad (1.81)$$

A diagonal matrix of vertical excitations energies is yielded by Ω and x is the matrix of oscillator frequencies. One polarization propagator approach which has recently become a popular choice for two-photon spectroscopy simulations, is known as the algebraic-diagrammatic construction (ADC). ADC was originally confined to ground-to-excited state transitions but the development of the intermediate state representation (ISR) allowed the ADC formalism to explicitly represent excited wavefunctions, enabling two-photon spectroscopy applications. The ADC method presents a “non-diagonal” representation of $\Pi(\omega)$ in the compact matrix form shown below,

$$\Pi(\omega) = \mathbf{f}^\dagger (\omega \mathbf{1} - \mathbf{M})^{-1} \mathbf{f}, \quad (1.82)$$

where,

$$M_{IJ} = \langle \Psi_I | \hat{H} - E_0 | \Psi_J \rangle \quad (1.83)$$

and

$$f_{J,rs} = \langle \Psi_J | c_r^\dagger c_s | \Psi_0 \rangle \quad (1.84)$$

The ADC secular matrix $\mathbf{M}$, is constructed as the shifted Hamiltonian with respect to the intermediate states $|\Psi_I\rangle$ and $\mathbf{f}$ is the matrix of effective transition amplitudes. The eigenvalues of $\mathbf{M}$ are the excitations energies and can be solved in the following eigenvalue problem,

$$\mathbf{M}\mathbf{X} = \mathbf{X}\mathbf{Q} \quad (1.85)$$

where

$$\mathbf{X}^\dagger \mathbf{X} = \mathbf{1}. \quad (1.86)$$

The form of the diagonal eigenvalue matrix $\mathbf{Q}$ is expressed in Equation 1.80 the eigenvectors $\mathbf{X}$ can construct the excited states, $|\Psi_n\rangle$ in the basis of the intermediate states.

$$|\Psi_n\rangle = \sum_J X_{Jn} |\Psi_J\rangle \quad (1.87)$$

The intermediate states themselves can be explicitly constructed from an initial state, via a set of so-called correlated excited states,

$$|\Psi_J^0\rangle = \hat{C}_J |\Psi_0\rangle \quad (1.88)$$

where $\hat{C}_J$ is constructed using a successive Gram-Schmidt orthonormalisation of excitation classes represented by the creation and annihilation operators shown below,

$$\{\hat{C}_J\} \equiv \{c_a^\dagger c_k; c_a^\dagger c_b^\dagger c_k c_l, a < b, k < l; \dots\}. \quad (1.89)$$

This explicit construction of excited state wavefunctions allows for the ISR/ADC method to generate excited state to excited state properties and be directly applied to multiphoton spectroscopy. The excitation classes correspond to 1-particle-1-hole ($c_a^\dagger c_k$), 2-particle-2-hole ($c_a^\dagger c_b^\dagger c_k c_l$) and so forth. The degree to the size of the particle-hole classes is dependent on the order of perturbation employed. In the ADC method, the $\mathbf{F}$ and $\mathbf{M}$ matrices are perturbatively expanded,

$$\mathbf{M} = \mathbf{M}^{(0)} + \mathbf{M}^{(1)} + \dots \quad (1.90)$$

$$\mathbf{f} = \mathbf{f}^{(0)} + \mathbf{f}^{(1)} + \dots \quad (1.91)$$

Second order ADC, noted as ADC(2) will be truncated at the 2-particle-2-hole excited state class type. Furthermore, the ground state wavefunction $|\Psi_0\rangle$ and energy $|E_{(0)}\rangle$ are parametrised for use in the equations in $\mathbf{M}$ and $\mathbf{F}$ via the Møller-Plesset perturbation scheme (detailed in subsection 1.2.6). Hence, the ground state wavefunction in ADC(2) is the described by the Møller-Plesset second order perturbation theory (MP2) method. An extension to the ADC(2) method is ADC(2)-x, which gives a better description of doubly excited states by a implementing a first order expansion in the 2-particle-2-hole block, $M_{22}^0 + M_{22}^0$. Furthermore core excited states can be generated by ADC methods by applying core-valence separation approximation (CVS) which zeros all integrals between the core and valence orbitals, exploiting the highly local and non-interacting nature of core orbitals with respect to the valence orbitals. A CVS-ADC scheme has been developed to simulate RIXS¹⁰¹ and Chapter 4 employs the CVS-ADC(2)-x method coupled with AIMD and MOM to produce accurate RIXS spectra.

1.2.5 Equations of Motion Coupled Cluster Theory

Coupled cluster methods are among the group of wavefunction methods that improve on the Hartree-Fock solution to the electronic Schrödinger equation by explicitly including electron correlation via excited state configurations. The coupled cluster wavefunction $|\Psi_{CC}\rangle$ is of the form,

$$|\Psi_{CC}\rangle = \prod_{\mu} (1 + t_{\mu} \hat{\tau}_{\mu}) |0\rangle = \prod_{\mu} \exp(t_{\mu} \hat{\tau}_{\mu}) |0\rangle = \exp \left(\sum_{\mu} t_{\mu} \hat{\tau}_{\mu} \right) |0\rangle \quad (1.92)$$

where $|0\rangle$ is the Hartree-Fock wavefunction and $\hat{\tau}_{\mu}$ is the excitation operator (annihilation followed by creation) of the order μ , corresponding to single, double etc. excitations. The coupled cluster operator $\hat{T}$, allows the representation as,

$$|\Psi_{CC}\rangle = e^{\hat{T}} |0\rangle \quad (1.93)$$

where,

$$\hat{T} = \sum_{\mu} t_{\mu} \hat{\tau}_{\mu} \quad (1.94)$$

For coupled cluster singles doubles, CCSD, the exponential nature allows for higher order terms than double excitations to be included into the wavefunction which makes CCSD a widely used high accuracy quantum chemical technique for inclusion of the electron correlation energy.

$$|\Psi_{CCSD}\rangle = e^{(\hat{T}_1 + \hat{T}_2)} |0\rangle \quad (1.95)$$

$$|\Psi_{CCSD}\rangle = \left[1 + \hat{T}_1 + \left(\hat{T}_2 + \frac{1}{2} \hat{T}_1^2 \right) + \left(\hat{T}_1 \hat{T}_2 + \frac{1}{6} \hat{T}_1^3 \right) + \dots \right] |0\rangle \quad (1.96)$$

The ground state energy is found by diagonalising the similarity transformed Hamiltonian in the basis of the reference (Hartree-Fock),

$$e^{-\hat{T}} \hat{H} e^{\hat{T}} |0\rangle = E |0\rangle. \quad (1.97)$$

In equations of motions (EOM) CCSD equations for excited state calculations, the similarity transformed Hamiltonian will be expressed as $\bar{H} = e^{-\hat{T}} \hat{H} e^{\hat{T}}$, and is diagonalised in an eigenvalue problem where the eigenfunctions are described by applying general excitation operators to the reference $|0\rangle$,

$$\bar{H} \hat{R} = E \hat{R}, \quad (1.98)$$

$$\hat{L} \bar{H} = E \hat{L}, \quad (1.99)$$

$$\hat{L}_I \hat{R}_J = \delta_{IJ}, \quad (1.100)$$

where $\hat{R}$ and $\hat{L}$ are excitation and de-excitation operators usually truncated to the same order as $\hat{T}$ and excitation energies between states $|0\rangle$ and $|f\rangle$ are generated with respect to a reference state $|\tilde{0}\rangle$,

$$\omega_{0f} = \frac{\langle \tilde{0} | L(f) [\bar{H}, R(f)] | \tilde{0} \rangle}{\langle \tilde{0} | L(f) R(f) | \tilde{0} \rangle} \quad (1.101)$$

The interested reader is referred to the review on EOM-CCSD by Krylov;¹⁰² EOM-CCSD methods have been used to simulate XAS,^{103,104} XES¹⁰⁵ and RIXS.¹⁰⁶ In the present study it is combined with core-ionised nuclear dynamics via MOM-AIMD to compute XES spectra of nitric oxide in Chapter 5.

1.2.6 Multi-Configurational Self Consistent Field Methods

So far, all discussed methods have involved variationally optimising a single Slater determinant wavefunction $|\Psi\rangle$ or reference wavefunction. In CCSD, we saw the use of excited state configurations generated from $|0\rangle$ by excitation operators $\hat{\tau}_{\mu}$.

Expressing the wavefunction as a linear combination of all possible excited state determinants will give an exact solution (in the limit of the basis set) in the full configuration interaction (FCI).

$$|\Psi_{CI}\rangle = |0\rangle + \sum_{ia} c_a^i \hat{\tau}_i^a |0\rangle + \frac{1}{4} \sum_{ij,ab} c_{ab}^{ij} \hat{\tau}_{ij}^{ab} |0\rangle + \dots \quad (1.102)$$

It is clear that in an FCI calculation, the number of determinants will increase rapidly with respect to the number of electrons and orbitals in the system. Hence FCI calculations are only applied to small systems and small basis sets; being used as a accurate benchmark for quantum chemical method development and multireference CI methods have been used to accurately compute XAS and XES.¹⁰⁷ Active space methods however, provide accurate, computationally applicable approach that performs an FCI calculation within a subset of orbitals, known as an active space. The rest of the occupied and virtual orbitals in the system are either, inactive (the stay doubly occupied, Hartee-Fock space) or frozen (do not take part in the SCF optimisation cycles). This is known as the complete active space self consistent field (CASSCF) method. Active space methods are not considered “black-box” (unlike the other methods used in this work), due to the careful selection of the active space that is required. There is no formula for determining the active space and it will be a different consideration for each application. However, once the active space is chosen correctly, the accuracy can be unrivalled. Active space methods are regularly performed in conjunction with experimental studies to provide the highest level of accuracy possible. They can be applied to a range of complex systems, such as open-shell species and excited states. One extension to CASSCF, which is able to increase the active space at reduced cost and more importantly, generate core-hole states, is the restricted active space (RAS) method. RAS methods are discussed and used to study nitric oxide RIXS in Chapter 5 and reviewed in the following subsections.

The Restricted Active Space Self Consistent Field Method

The restricted active space self consistent field method is discussed in detail within the context of X-ray spectroscopy in Chapter 5, but the RAS concept is summarised here. The active space is split into three subspaces RAS1, RAS2 and RAS3. For the orbitals in the RAS1 space, the number of holes is restricted to one, RAS2 orbitals contain arbitrary occupations, resembling the active space in a CASSCF calculation (FCI space) and the orbitals in the RAS3 space have the number of electrons restricted to one. Besides providing the capacity to describe core-hole states, this method enables the overall active space to be increased without adding to

much cost to the calculation and can be applied to larger systems than in CASSCF, with more orbitals of interest.

The Restricted Active Space Second Order Perturbation Theory

Though active space methods explicitly take into account static correlation, involving the interaction between near degenerate electronic configurations, the truncation of the active space can result in a significant loss of dynamic correlation (correlated motion of electrons). There are many double excitations neglected from the inactive orbitals into the active space and into the virtual orbitals. This can be partly recovered by second order perturbation theory, which improves the energy of the RASSCF (and CASSCF) wavefunction. Perturbation theory is a technique applied throughout physics, and widely applied in single determinant quantum chemistry as second order Møller-Plesset perturbation theory (MP2), which uses the Hartree-Fock determinant as a reference. We will summarise perturbation theory in the context of MP2, then discuss its application to CASSCF for CASPT2, showing how a similar approach is adopted for RASPT2.

In MP2 we start by partitioning the Hamiltonian of the time-independent electronic Schrödinger in Equation 1.18 $\hat{H}$, into an exactly solvable part, $\hat{H}_0$ and a perturbation, $\lambda\hat{H}_1$, expandable in a Taylor series and obeying the condition that $\langle\hat{H}_1\rangle$ is relatively small compared to $\langle\hat{H}\rangle$.

$$\hat{H}(\lambda) = \hat{H}_0 + \lambda\hat{H}_1 \quad (1.103)$$

which is substituted into the Schrödinger equation to give,

$$(\hat{H}_0 + \lambda\hat{H}_1)|\Psi(\lambda)\rangle = \hat{E}(\lambda)|\Psi(\lambda)\rangle \quad (1.104)$$

expressed in a Taylor expansion,

$$(\hat{H}_0 + \lambda\hat{H}_1)(|0\rangle + \lambda|1\rangle + \lambda^2|2\rangle + \dots) = (E_0 + \lambda E_1 + \lambda^2 E_2 + \dots)(|0\rangle + \lambda|1\rangle + \lambda^2|2\rangle + \dots) \quad (1.105)$$

By separating the terms in the Taylor expansion by order in λ and rearranging the equation to equal zero, shows that all λ coefficients must equal zero separately and gives the following equations,

$$\hat{H}_0|0\rangle = E_0|0\rangle \quad (1.106)$$

$$\hat{H}_0|1\rangle + \hat{H}_1|0\rangle = E_0|1\rangle + E_1|0\rangle \quad (1.107)$$

$$\hat{H}_2|1\rangle + \hat{H}_1|1\rangle = E_0|2\rangle + E_1|1\rangle + E_2|0\rangle. \quad (1.108)$$

The zeroth order equation is already solved, the energies and eigenfunctions of the higher order terms can be solved by rearranging and expressing them as a function of

the lower order terms. For example Equation 1.107 can be rearranged to express the first order energy correction in terms of the zeroth order wavefunctions.

$$E_1 = \langle 0 | \hat{H}_1 | 0 \rangle \quad (1.109)$$

Representing the first order wavefunction $|1\rangle$, as a linear combination of the zeroth order wavefunction,

$$|1\rangle = \sum_n c_n |0_n\rangle = \sum_n c_n |n\rangle \quad (1.110)$$

will allow the first order wavefunction to be solved, which in turn can generate a second order energy correction by rearranging Equation 1.108 and expressing in terms of the first order perturbation.

$$E_2 = \langle 0 | \hat{H}_1 - E_1 | 1 \rangle \quad (1.111)$$

This can be applied to Hartree-Fock by calling the Hartree-Fock Hamiltonian the reference $\hat{H}_0$, and the zeroth order energy as the sum of the Hartree-Fock eigenvalues,

$$\hat{H}_0 |0\rangle = E_0 |0\rangle \quad (1.112)$$

and

$$E_0 = \langle 0 | \hat{H}_0 | 0 \rangle = \sum_{i=1}^n \epsilon_i. \quad (1.113)$$

This is not the Hartree-Fock energy however, summing the orbital energies double counts the electron-electron interaction as each orbital energy from Hartree-Fock includes the interaction from the other electrons (mean field approximation). By expressing the perturbing Hamiltonian as the difference between the exact Hamiltonian and the Hartree-Fock Hamiltonian,

$$\hat{H}_1 = \hat{H} - \hat{H}_0 \quad (1.114)$$

$$\hat{H}_1 = \sum_{i < j}^{N-1} \frac{1}{r_{ij}} - \sum_i \hat{J}_i - \hat{K}_i \quad (1.115)$$

the interelectronic energy, $E_1 = \langle 0 | \hat{H}_1 | 0 \rangle$ can be generated by the following,

$$\langle 0 | \hat{H}_1 | 0 \rangle = \langle 0 | \hat{H} | 0 \rangle - \langle 0 | \hat{H}_0 | 0 \rangle \quad (1.116)$$

which is the Hartree-Fock energy minus the sum of the orbital energies. The second order energy can then be found by the expression,

$$E_2 = \langle 0 | \hat{H}_1 - E_1 | 1 \rangle \quad (1.117)$$

which requires an expression for the first order wavefunction which can be derived from the first order equation (Equation 1.107) and by expanding $|0\rangle$ in FCI space

using excitation operators.

Unfortunately this is not directly applicable to CASSCF as there is no similar single determinant reference to use. However a reference can be chosen to be relatively simple and contain single and double excitations, of the form,

$$\hat{H}_0 = \hat{P}_0 \hat{F} \hat{P}_0 + \hat{P}_{SD} \hat{F} \hat{P}_{SD} \quad (1.118)$$

where, $\hat{P}_0$ is the projector into the CAS space, $\hat{P}_{SD}$ is the projector to single and double excitation space, the interacting configurations space and $\hat{F}$ is the generalised Fock operator, involving excitation operators acting on the Fock matrix, which can occur from outside the active space,

$$\hat{F} = \sum_{p,q} F_{pq} \hat{E}_{pq}, \quad (1.119)$$

and the CASPT2 equation can be represented in matrix form as,

$$(\mathbf{F} - \mathbf{E}_0 \mathbf{S})\mathbf{c} = -\mathbf{R}. \quad (1.120)$$

Applying this to RASSCF becomes conceptually more challenging, due to the restrictions of the RAS1 and RAS3 spaces, however the same form of $\hat{H}_0$ can be used but more subspaces incorporated.

The Restricted Active Space State Interaction Method

In order to calculate the dipole moments between states calculated in the RASPT2 calculations, the restricted active space interaction method is applied. This method computes matrix elements over a basis of wavefunctions (such as those computed in a state averaged RASSCF calculation), each with its own set of optimised orbitals. This is done by expanding the set of Slater determinants to a set of biorthonormal orbitals, enabling the computation of one or two body operators, such as dipole operators, $\hat{\mu}$ between wavefunctions. This group of RAS methods have been used extensively in X-ray spectroscopy, simulating XAS,¹⁰⁸ TRXAS¹⁵ and RIXS.^{46,55}

Chapter 2

Core Electron Spectroscopy Basis Sets Assessment and Application to X-ray Photoelectron Spectroscopy Calculations of Ether Functionalised Ionic Liquids

2.1 Assesement of Basis Sets for Density Functional Theory Based Calculations of Core Electron Spectroscopy

2.1.1 Introduction

The first section of this chapter is an extract from ref. 22 The results from this study were used in a collaboration with experiment to study the XPS of ionic liquids²³ which is described in the second half of the chapter.

A common feature to all approaches for simulating core electron spectroscopies is the choice of basis set used in the calculation. In many applications, the simulation of core electron spectroscopy can be computationally demanding. For example, in the study of large systems such as metalloprotein active sites or the study of liquids where is necessary to incorporate averaging over conformations. Consequently, it is important to understand which are the most efficient basis sets for these calculations, i.e. which basis sets provide a good approximation to the complete basis set limit with fewest basis functions. In this work we focus on the Gaussian basis sets

and there are a number of well established families of Gaussian basis sets, including the split-valence basis sets of Pople^{109–115} and the correlation-consistent basis sets of Dunning.^{116–121} More recently, Jensen has introduced the polarisation consistent basis sets.^{122–124} A common feature of all of these basis sets is that they are designed for the calculation of properties that primarily depend on the nature of the valence electrons. Consequently, their performance for the calculation of properties that depend on the core electrons is less well understood. In order to describe core orbitals accurately it is often necessary to add additional tight basis functions and correlation-consistent basis sets are available with functions that describe core electron correlation (cc-pCVXZ). The calculation of nuclear magnetic (NMR) shielding constants represents an example of a molecular property that requires a good representation of the orbitals near the nuclei, and basis sets have been designed for the calculation of NMR properties. For example, the individual gauge for localized orbitals (IGLO) basis sets^{125,126} are often used for the calculation of magnetic properties, however, they have only been defined for hydrogen and the first- and second-row p-block elements. A family of segmented contracted basis sets, denoted pcSseg-n, optimized for the calculation of nuclear magnetic shielding constants has also been reported.¹²⁷

Similar to calculations of NMR spectroscopy, accurate calculations of spectroscopy in the X-ray region also rely on a correct description of the core orbitals. Several studies have considered the basis set dependence of CEBEs calculations using a Δ SCF approach in conjunction with DFT or Møller-Plesset perturbation theory.^{80,128–133} It has been reported that the core-valence correlated triple-zeta basis set (cc-pCVTZ) to be accurate and efficient compared with the cc-pV5Z basis set. It was also found that exponent scaled basis sets did not perform well.¹²⁸ In another study using a Δ SCF approach it was found that by optimising the exponents and contraction coefficients of relatively small basis sets for the core-hole state allowed CEBEs calculated with much larger basis sets to be reproduced to within 0.2 eV.¹³⁰ The use of Slater-type basis functions has also been explored for the calculation of CEBEs and the results indicate that polarized triple-zeta basis set of Slater-type orbitals would be adequate.¹³¹ In more recent work, the performance of a range of basis sets and exchange-correlation functionals was investigated for the calculation of CEBEs of first row hydrides and glycine.¹³³ The inclusion of polarisation and diffuse functions on the heavy atoms was found to have a significant effect for medium sized basis sets, such as 6-311G. Several density functionals were found to perform well with large basis sets that have considerable flexibility in the core region. For example, the B3LYP5 and TPSSh functionals had a mean unsigned error of less than 0.2 eV with a fully uncontracted triple zeta quality basis set augmented with diffuse

and polarization functions. The majority of studies of CEBEs have only considered excitations from the 1s orbitals of first row elements. Segala and Chong assessed DFT based calculations of CEBEs for a set of 40 sulfur and phosphorous containing molecules.¹³⁴ An additional complication for second row elements is that relativistic effects become significant and an empirical correction to account for these effects was used. A wide variety of exchange-correlation functionals were considered, and the most accurate functional was found to be VS8,¹³⁵ with an average unsigned error of 0.43 eV. A few studies have considered core-excitation energies in addition to CEBEs. In calculations on the formaldehyde molecule it was concluded that diffuse basis functions were important for simulating X-ray absorption spectra but less important for CEBEs and X-ray emission spectra.¹³² In a study of core excitation energies and CEBEs, it was found that using the 6-311G** basis set with uncontracted basis functions gave results that were comparable with the much larger cc-pCVQZ basis set.⁸⁰ There has been much less attention to the basis set dependence of X-ray emission energies, although one study has found that X-ray emission energies of transition metal complexes computed using TDDFT were highly dependent on the basis set used.⁹⁴

In this chapter we explore the basis set dependence of DFT based calculations of a range of core electron spectroscopies, including CEBEs computed using a Δ SCF approach, core-excitation energies computed using Δ SCF and TDDFT, and X-ray emission energies computed using TDDFT. We consider a set of 34 molecules that includes excitations from first and second row s- and p-block elements and wide range of basis sets with the goal of identifying the most efficient and reliable basis sets for calculations of core-electron spectroscopies.

2.1.2 Computational Details

CEBEs were computed using a Δ SCF approach in conjunction with DFT using the B97-1 exchange-correlation functional.¹³⁶ The focus of this study is the variation of the computed core-electron properties with basis set, and the B97-1 functional is assumed to be representative of DFT exchange-correlation functionals. This is explored further in this work where the basis set dependence of difference exchange-correlation functionals is compared. The core-ionised states were optimised using an overlap criterion⁷³ to maintain the core-hole during the SCF process. In a similar manner, Δ SCF core-excitation energies were computed for the lowest excitation energy arising from an excitation from the relevant core orbital to the lowest unoccupied molecular orbital (LUMO). Core excitation energies were also computed for the core to LUMO transitions with TDDFT. TDDFT can be applied to compute

Table 2.1: Molecules used in this study. Bold font indicates element with the core-hole.

s-block	LiH	LiF	LiCl	LiCH₃
	BeF₂	BeCl₂	Be₂H₄	NaH
	NaF	NaCH₃	MgF₂	MgCl₂
	Mg₂H₄			
p-block	BH₃	CH₄	CO	CO₂
	CH₃OH	N₂	NH₃	HCN
	CH₃CN	N₂H₂	H₂O	BF₃
	F₂	AlH₃	Si₂H₂	SiH₄
	PH₃	PF₃	H₂S	H₂CS
	HCl			

core-excitation energies through limiting the single excitation subspace to include only excitations from the relevant core orbital(s).⁹² It is well known that standard exchange-correlation functionals underestimate core excitation energies when computed using TDDFT, and several groups have developed functionals specifically designed for core excitation energies.^{86,137–139} However, in this study we use the B97-1 functional throughout since we are not primarily concerned with a direct comparison with experiment. X-ray emission energies were computed for the highest occupied molecular orbital (HOMO)→core transition by applying TDDFT to a Kohn-Sham determinant with a core hole in a procedure described in more detail elsewhere.⁹³ All calculations use an unrestricted Kohn-Sham formalism except the TDDFT calculations of core excitation energies. A range of molecules (shown in Table 2.1) including first and second row s- and p-block elements was considered, with the structure of the molecules optimised at the B97-1/6-311G(d,p) level of theory. This set of molecules was chosen to include the core excitations from the range of elements in the first and second rows of the periodic table.

The basis sets considered in this study are shown in Table 2.2 and include small, medium and large basis sets from three widely used families of basis sets including split-valence, correlation-consistent and polarisation consistent basis sets. Correlation-consistent basis sets with additional core-valence correlation functions are also considered. For these basis sets, the standard regular correlation-consistent basis set is used for hydrogen. In addition, the IGLO-II and IGLO-III basis sets are included since these have been optimised for the calculation of NMR and have

Table 2.2: Basis sets used in this study.

Split-Valence	Ahlrichs	IGLO	ANO (ROOS)	Correlation Consistent	Polarisation Consistent
STO-3G	VDZ	IGLO-II	aug-VTZ	cc-pVDZ	pcS-0
6-31G(d,p)	VTZ	IGLO-III		cc-pCVDZ	pcSseg-0
6-311G(2df,2pd)				cc-pVTZ	pcS-1
u6-31G(d,p)				cc-pCVTZ	pcSseg-1
				cc-pVQZ	pcSseg1
				cc-pV5Z	pcS-2
					pcSseg-2
					aug-pcSseg-2
					pcS-3
					pcSseg-3
					pcS-4
					pcSseg-4

been observed to previously to perform well for the calculation of core-electron excitations^{140,141} as well as the basis sets of Ahlrichs¹⁴² and a triple zeta quality atomic natural orbital (ANO) basis set.^{143,144} Here we only include widely used basis sets that are available for the majority of elements and we do not consider specially designed or modified basis sets, with the exception that the 6-31G(d,p) with uncontracted core basis functions (denoted u6-31G(d,p)) is included. The errors in the computed energies are assessed relative to the largest segmented polarisation consistent (pcSseg-4) basis set. This is a very large basis set and is considered to give a good approximation to the complete basis set limit. Although the error relative to the largest correlation-consistent basis set (cc-pV5Z) is also considered. In order to compare the performance of the different basis sets with respect to their size, N , where N is the number of contracted basis functions for a first and second row p-block atom is introduced as a measure of the size of the basis set. In determining N a pure representation of the d and higher angular momentum basis functions is assumed. All calculations were performed with the Q-Chem software package.¹⁴⁵

2.1.3 Results and Discussion

Δ SCF Core-Electron Binding Energies and Core Excitation Energies

Table 2.3 gives the mean absolute deviations (MADs) with the associated standard deviation and maximum absolute errors between the computed CEBEs and

Table 2.3: Error in calculated core electron binding energies (in eV) relative to pcSseg-4. MAE: Maximum absolute error, standard deviation given in parenthesis.

Basis set	s-block Δ^{MAD}	p-block Δ^{MAD}	total Δ^{MAD}	MAE	N
STO-3G	3.00 (4.83)	5.69 (6.68)	4.69	29.68 (PF ₃)	14
pcS-0	6.86 (6.24)	5.13 (3.89)	5.77	14.40 (MgCl ₂)	22
pcSseg-0	9.09 (8.54)	4.64 (4.19)	6.29	18.80 (NaH)	22
Ahlrichs VDZ	13.16 (8.42)	6.03 (5.21)	8.68	23.78 (MgCl ₂)	22
6-31G(d,p)	9.09 (8.47)	5.93 (5.50)	7.10	20.35 (NaH)	32
cc-pVDZ	10.14 (8.53)	6.51 (5.77)	7.10	20.60 (NaH)	32
Ahlrichs VTZ	3.92 (2.65)	2.43 (4.37)	2.98	18.10 (PF ₃)	37
pcS-1	1.30 (0.40)	2.86 (3.25)	2.28	11.94 (PF ₃)	38
pcSseg-1	1.98 (0.56)	2.23 (2.53)	2.14	12.38 (PF ₃)	38
u6-31G(d,p)	7.50 (7.78)	5.99 (6.73)	6.55	24.48 (H ₂ CS)	42
cc-pCVDZ	2.24 (1.62)	2.25 (3.91)	2.25	18.04 (PF ₃)	45
IGLO-II	-	0.89 (1.85)	-	8.47 (H ₂ CS)	57
cc-pVTZ	6.42 (6.88)	2.99 (3.62)	4.20	15.30 (NaF)	64
6-311G(2df,2pd)	0.58 (1.00)	1.42 (2.43)	1.11	9.02 (H ₂ CS)	68
pcS-2	0.86 (0.92)	1.09 (2.23)	1.00	2.23 (H ₂ CS)	68
pcSseg-2	0.89 (0.76)	1.05 (0.82)	0.99	4.34 (H ₂ CS)	68
IGLO-III	-	0.89 (1.80)	-	8.15 (H ₂ CS)	79
ROOS aug-VTZ	5.49 (6.23)	3.16 (3.80)	4.03	14.05 (NaH)	96
cc-pCVTZ	0.69 (1.00)	0.88 (1.78)	0.81	8.05 (H ₂ CS)	102
aug-pcSseg-2	0.59 (0.98)	1.32 (2.48)	1.05	10.56 (H ₂ CS)	105
cc-pVQZ	5.72 (6.66)	3.13 (3.88)	4.09	14.97 (NaF)	114
pcS-3	0.66 (1.17)	0.79 (1.79)	0.74	8.26 (H ₂ CS)	150
pcSseg-3	0.68 (1.17)	0.15 (0.12)	0.35	4.32 (MgCl ₂)	150
cc-pV5Z	1.11 (1.47)	0.30 (1.12)	0.60	5.20 (H ₂ CS)	186
pcS-4	0.93 (1.38)	0.93 (1.74)	0.93	7.78 (H ₂ CS)	244

the values computed with the pcSseg-4 basis set. These MAD values are denoted $\Delta^{\text{MAD}}(\text{pcSseg-4})$. Values are given for s-block and p-block elements, as well as a combined value. This is necessary since the IGLO-II and IGLO-III basis sets are only available for the p-block elements. The small basis sets of double zeta and lower quality show a large deviation from the large basis set for both s- and p-block elements, and a typical error of 4.5 to over 8 eV is found. For the large majority

of molecules the smaller basis set give a CEBE that is too large. This is a result of the smaller basis set providing a relatively poor description of the core-ionised state. The average change in energy between the pcSseg-4 and 6-31G(d,p) basis sets is 1.8 eV and 8.9 eV for the ground state and core-excited state, respectively. For the heavier nuclei this effect can be significant, for example for H₂S the ground state energy is lowered by 1.3 eV with the larger basis set while for the core-ionised state the energy is lowered by 15.9 eV. If CEBEs were computed for the 1s electrons of heavier nuclei, such as transition metal elements, the size of this disparity would increase further. One explanation for this is that the smaller basis sets, such as 6-31G(d,p), do not have the flexibility to describe the core-ionised state which has a different effective nuclear charge. Adding core correlation functions to cc-pVDZ with the cc-pCVDZ basis set leads to a large improvement in the calculated CEBEs. The error with respect to the large basis set is reduced by over 4 eV. The overall error of cc-pCVDZ is 2.25 eV which is a little larger than for the pcSseg-1 basis set. It is surprising that the 6-31G(d,p) basis set with uncontracted core basis functions does not lead to a large improvement in performance, since this is contrary to the findings of earlier work.⁸⁰ As will be discussed in more detail later, this error is associated to CEBEs of the row two nuclei and these systems were not included in previous studies. Overall none of these small basis sets provides an adequate description of the complete set of molecules, with some large maximum errors observed.

The larger basis sets Ahlrichs VTZ, pcS-1 and pcSseg-1 lead to a significant reduction in the error associated with the basis set. Both pcS-1 and pcSseg-1 perform well with $\Delta^{\text{MAD}}(\text{pcSseg-4})$ of 2.28 eV and 2.14 eV, respectively. Although, these two basis sets perform particularly well for the s-block elements while for the p-block elements the error remains over 2 eV. For the p-block elements, the IGLO-II basis set has a much lower error (<0.9 eV) than basis sets of comparable size. It is difficult to understand in detail the reason for the excellent performance of the IGLO-II basis set since it may be a consequence of a balance between several different factors. One notable difference between the IGLO-II basis set and 6-31G(d,p) is the exponents of the gaussian functions of the inner 1s orbital are larger in IGLO-II. If H₂S is taken as an example, the CEBE is computed to be 2485.0 eV with 6-31G(d,p) and 2468.9 eV with IGLO-II compared with a value of 2470.3 eV for pcSseg-4, consistent with the better performance of IGLO-II. However, if the exponents of the gaussian functions of the core basis function of 6-31G(d,p) are scaled by 1.1 for sulfur the CEBE becomes 2473.4 eV. This demonstrates that relatively modest changes to the basis function of the core orbital can have a large effect on the computed CEBE. The large split-valence basis set is also relatively accurate with an overall error of 1.42 eV, with good performance for both s- and p-block elements.

Table 2.4: Error in core electron binding energies for row 1 and row 2 nuclei (in eV).

Basis set	Row 1	Row 2
	$\Delta^{\text{MAD}}(\text{pcSseg-4})$	$\Delta^{\text{MAD}}(\text{pcSseg-4})$
6-31G(d,p)	1.98	13.53
cc-pVDZ	2.72	14.52
Ahlrichs VTZ	2.31	4.22
pcSseg-1	1.64	2.81
u6-31G(d,p)	1.28	13.23
cc-pCVDZ	1.54	3.19
IGLO-III	0.06	2.23
cc-pVTZ	0.58	7.26
6-311G(2df,2pd)	0.59	1.75
pcS-2	0.61	1.53
pcSseg-2	0.99	1.02
IGLO-III	0.04	2.29
cc-pCVTZ	0.09	1.74
cc-pVQZ	0.34	8.89
pcSseg-3	0.06	0.72

The large basis sets pcS-2, pcSseg-2, pcS-3 and pcSseg-3 all have overall MADs of 1 eV or less with a well balanced performance between s- and p-block elements. For the pcSseg-2 basis set, the errors for the large majority of the molecules lie in the range of 0 to 1.5 eV with a few molecules showing significantly larger errors with a largest error of 4.3 eV for H_2CS . The inclusion of diffuse basis functions in aug-pcSseg-2 leads to a decrease in the accuracy of the calculated CEBEs compared with pcSseg-4. However, assessment of this basis set relative to a very large basis set that includes diffuse functions might be more appropriate. The pcSseg-3 basis set has an overall error of 0.35 eV with an error of 0.15 eV for the p-block elements which represents a very good level of accuracy. The IGLO-III basis set also performs well, but it is surprising that IGLO-III shows no improvement over IGLO-II. The results also show that the basis set errors for the pcSseg-n basis sets are smaller than for their counterpart pcS-n basis sets, with the exception of pcS-0 and pcSseg-0. This, and the good performance of the IGLO basis sets demonstrates that basis sets designed for the prediction of NMR also perform well in the calculation of CEBEs. One feature of the data is the poor performance of the standard correlation-consistent basis sets. Similar behaviour is observed for the ANO basis

Table 2.5: Variation in basis set error for different exchange-correlation functionals (in eV). Experimental data from references^{131,146,147}

Molecule	Experiment	Method	pcSseg-4	pcSseg-3	cc-pCVTZ	IGLO-III	pcSseg-2	pcSseg-1
CH ₄	290.91	B97-1	291.13	+0.08	+0.03	-0.02	+1.04	+1.28
		PBE0	290.31	+0.08	+0.03	-0.02	+1.01	+1.23
		M06	290.30	+0.00	-0.09	-0.07	+0.94	+1.17
		HF	290.71	+0.09	+0.01	-0.04	+0.99	+1.21
NH ₃	405.56	B97-1	406.87	-0.06	-0.04	-0.02	+1.09	+1.20
		PBE0	406.01	-0.05	-0.04	-0.02	+1.06	+1.16
		M06	404.90	-0.10	-0.04	-0.07	+1.05	+1.33
		HF	405.30	-0.02	-0.05	-0.04	+1.06	+1.21
H ₂ O	539.90	B97-1	539.96	+0.09	-0.09	-0.06	+1.13	+1.19
		PBE0	538.79	+0.09	-0.07	-0.06	+1.12	+1.15
		M06	539.15	+0.04	-0.14	-0.09	+1.10	+1.40
		HF	539.28	+0.11	-0.03	-0.03	+1.11	+1.24
PH ₃	2150.69	B97-1	2151.40	+0.33	-0.04	-1.44	+0.76	+2.06
		PBE0	2150.52	+0.24	-0.04	-1.55	+0.66	+1.89
		M06	2152.46	+0.20	-0.04	-1.60	+0.66	+1.80
		HF	2154.04	+0.22	-0.05	-1.50	+0.68	+2.13
H ₂ S	2478.58	B97-1	2478.60	+0.37	-1.50	-1.54	+0.89	+1.98
		PBE0	2477.73	+0.37	-1.51	-1.55	+0.89	+1.95
		M06	2479.67	+0.35	-1.68	-1.55	+0.88	+1.98
		HF	2481.56	+0.35	-1.48	-1.52	+0.93	+2.19

set. In general, the correlation-consistent basis sets perform poorly, particularly for the s-block elements. For these basis sets, large errors remain for the cc-pVTZ and cc-pVQZ basis sets and this is significantly reduced for the cc-pV5Z basis set. This trend is also observed in the MADs are evaluated relative to the cc-pV5Z values, with an error of over 4 eV for the cc-pVQZ basis set relative to the cc-pV5Z basis set. In comparison, the pcSseg-2 and pcSseg-3 basis sets have overall Δ^{MAD} of 1.19 eV and 0.61 eV relative to the cc-pV5Z basis set. There is a substantial improvement in performance of the correlation-consistent basis sets with core-valence correlation functions. The cc-pCVTZ basis set has an error of <1 eV for s- and p-block elements. This basis set has been observed to be accurate in previous studies.¹²⁸

Table 2.3 shows that the maximum error observed generally occurs for a CEBE for a second row nucleus. To explore this further, Table 2.4 shows the errors in the

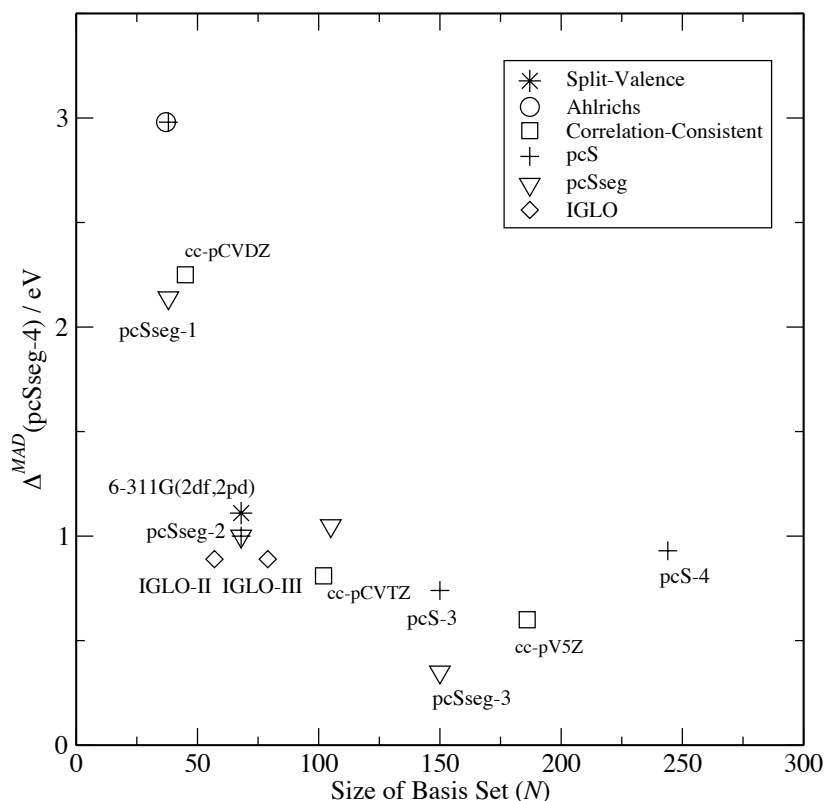


Figure 2.1: Variation in the basis set error for core-electron binding energies with the size of the basis set.

CEBEs for a selection of the basis sets studied partitioned into nuclei from the first and second rows of the periodic table. For the first row nuclei several basis sets have $\Delta^{\text{MAD}}(\text{pcSseg-4})$ of less than 1 eV. In particular, IGLO-II, IGLO-III, cc-pCVTZ and pcSseg-3 are very accurate with errors of less than 0.1 eV. For these elements the standard correlation consistent basis sets cc-pVTZ and cc-pVQZ also perform well and uncontracting the core basis function in 6-31G(d,p) also leads to a significant improvement. Much larger errors are observed for CEBEs for the second row nuclei. For these systems the standard correlation consistent basis sets perform poorly and there is a large improvement with the inclusion of core correlation basis functions. The polarisation consistent basis sets show the best performance for these elements, and pcSseg-2 is noteworthy in that it has a similar error for first and second row nuclei.

All of the results presented are for the B97-1 exchange-correlation functional and it is of interest whether the behaviour observed for B97-1 is representative of other functionals. Table 2.5 shows that variation in the computed CEBE for B97-1 and two other functionals, PBE0¹⁴⁸ and M06,¹⁴⁹ in addition to Hartree-Fock (HF) theory. The computed CEBE for the pcSseg-4 basis set has been corrected for rel-

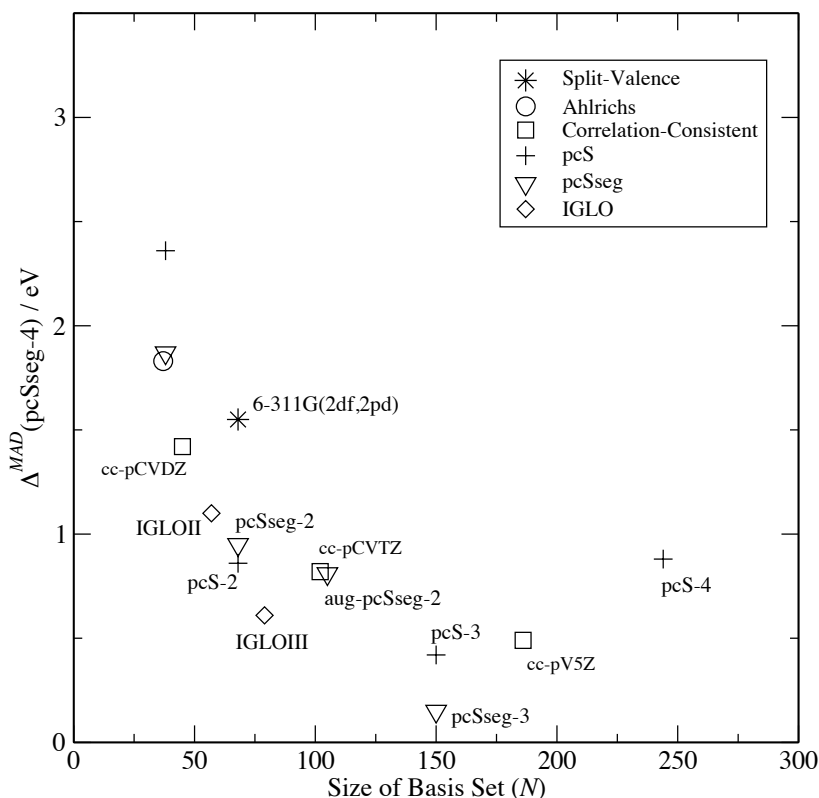


Figure 2.2: Variation in the basis set error for core→LUMO excitation energies with the size of the basis set.

ativistic effects. Here, we have applied corrections of +0.08, +0.17, +0.31, +6.50 and +8.28 eV for carbon, nitrogen, oxygen, phosphorous and sulfur, respectively, consistent with previous studies.¹⁵⁰ For all five of the molecules, the experimental value lies within the range of values predicted by the different methods with the pcSseg-4 basis set demonstrating that the large basis set leads to values consistent with experiment. The variation in the computed CEBEs for the different basis sets is remarkably similar for the different methods. This indicates that the general observations for the B97-1 functional can be interpreted more broadly to other functionals.

In order to identify efficient basis sets that give a good approximation to the complete basis set limit with the fewest basis functions, $\Delta^{\text{MAD}}(\text{pcSseg-4})$ is plotted against a measure of the size of the basis set (N) for the basis sets with $\Delta^{\text{MAD}}(\text{pcSseg-4}) < 3$ eV. N is the number of contracted basis functions for a first and second row p-block atom and provides a rough measure of the size of the basis sets. The graph shows that, in general, the error arising from the basis set decreases as the size of the basis increases. However, it does highlight basis sets that show good or poor performance in relation to their size. For the correlation-consistent basis sets without core-valence correlation functions, the large cc-pV5Z basis set is required

Table 2.6: Error in calculated Δ SCF core $\rightarrow$ LUMO excitation energies (in eV) relative to pcSseg-4. MAE: Maximum absolute error, standard deviation given in parenthesis.

Basis set	s-block Δ^{MAD}	p-block Δ^{MAD}	total Δ^{MAD}	MAE
STO-3G	2.18 (2.54)	4.48 (3.38)	3.69	11.51 (HCl)
pcS-0	7.00 (5.74)	5.42 (4.29)	6.01	14.09 (MgF ₂)
pcSseg-0	9.15 (8.83)	4.96 (4.54)	6.52	19.47 (Mg ₂ H ₄)
Ahlrichs VDZ	13.08 (7.81)	6.68 (5.75)	9.06	22.20 (MgCl ₂)
6-31G(d,p)	8.79 (8.55)	6.88 (5.93)	7.59	20.14 (NaH)
cc-pVDZ	10.15 (8.74)	7.46 (6.35)	8.46	20.39 (NaH)
Ahlrichs VTZ	3.83 (2.63)	0.65 (1.53)	1.83	10.67 (Be ₂ H ₄)
pcS-1	1.29 (0.56)	2.99 (2.69)	2.36	6.95 (F ₂)
pcSseg-1	2.05 (0.64)	1.77 (1.13)	1.87	6.27 (F ₂)
u6-31G(d,p)	7.57 (7.95)	5.41 (6.39)	6.21	17.10 (NaH)
cc-pCVDZ	1.95 (1.67)	1.11 (0.64)	1.42	5.37 (MgF ₂)
IGLO-II	-	1.10 (1.51)	-	6.87 (F ₂)
cc-pVTZ	6.46 (7.04)	3.27 (3.52)	4.45	15.01 (NaF)
6-311G(2df,2pd)	0.73 (1.54)	2.04 (4.03)	1.55	17.49 (Si ₂ H ₂)
pcS-2	0.62 (0.27)	1.00 (1.47)	0.86	6.87 (F ₂)
pcSseg-2	0.65 (0.47)	1.12 (1.22)	0.95	6.20 (F ₂)
IGLO-III	-	0.61 (0.62)	-	1.57 (AlH ₃)
ROOS aug-VTZ	5.40 (6.04)	2.97 (3.68)	3.87	13.94 (NaH)
cc-pCVTZ	0.88 (1.49)	0.78 (0.83)	0.82	5.47 (Mg ₂ H ₄)
aug-pcSseg-2	0.73 (1.52)	0.85 (1.43)	0.81	6.86 (F ₂)
cc-pVQZ	5.54 (6.64)	3.56 (4.11)	4.30	14.67 (NaF)
pcS-3	0.36 (0.42)	0.45 (0.55)	0.42	1.25 (HCl)
pcSseg-3	0.11 (0.17)	0.18 (0.12)	0.15	0.65 (Mg ₂ H ₄)
cc-pV5Z	1.16 (1.43)	0.10 (0.11)	0.49	3.99 (MgF ₂)
pcS-4	1.06 (1.87)	0.77 (0.78)	0.88	6.67 (Mg ₂ H ₄)

to achieve a reasonable level of accuracy with respect to the basis set limit. However, the use of such a large basis set is not practical for the majority of calculations.

The IGLO basis sets show the best performance of the smaller basis sets, and IGLO-II is a particularly cost effective basis set. Unfortunately, these basis sets

Table 2.7: Error in core→LUMO excitation energies for row 1 and row 2 nuclei (in eV), relative to pcSseg-4.

Basis set	Row 1 Δ^{MAD}	Row 2 Δ^{MAD}
6-31G(d,p)	2.21	15.06
cc-pVDZ	2.69	16.45
Ahlrichs VTZ	2.27	1.64
pcSseg-1	1.70	2.08
cc-pCVDZ	1.37	1.33
IGLO-II	0.94	1.35
cc-pVTZ	0.77	9.28
6-311G(2df,2pd)	0.78	2.82
pcS-2	0.98	0.71
pcSseg-2	1.21	0.58
IGLO-III	0.10	0.87
cc-pCVTZ	0.30	1.55
cc-pVQZ	0.45	9.54
pcSseg-3	0.11	0.23

are not available for the s-block elements. The pcS-2 and pcSseg-2 are the smallest basis sets that perform well for both s- and p-block elements (an error of about 1 eV or less), and the large split-valence basis set also does quite well in this regard. To achieve higher levels of accuracy it is necessary to use the cc-pCVTZ or pcSseg-3 basis sets, with an overall error of less than 0.5 eV for the pcSseg-3 basis set. To put this in context in terms of the computational cost, a single point energy calculation for PF_3 with the pcSseg-2 and pcSseg-3 basis sets take about 1% and 6% of the time for the pcSseg-4 basis set when run on a single processor.

Extending the analysis to consider core-excitation energies Tables 5.1 and 2.7 along with Figure 2.2 show the corresponding analysis for the ΔSCF calculated core→LUMO excitation energies. The trends evident for the calculated CEBEs are largely observed for these excitation energies and there is a strong correlation with the performance of the basis sets for CEBEs. Basis sets of double zeta or lower quality have large average errors of over 4 eV. The series of polarisation consistent basis sets (pcS-n and pcSseg-n) perform well. There is a reduction in the size of the errors as n increases. The pcSseg-1 basis set has a low overall error of 1.87 eV, and cc-pCVTZ is the smallest basis set to achieve an error of less than 1 eV for

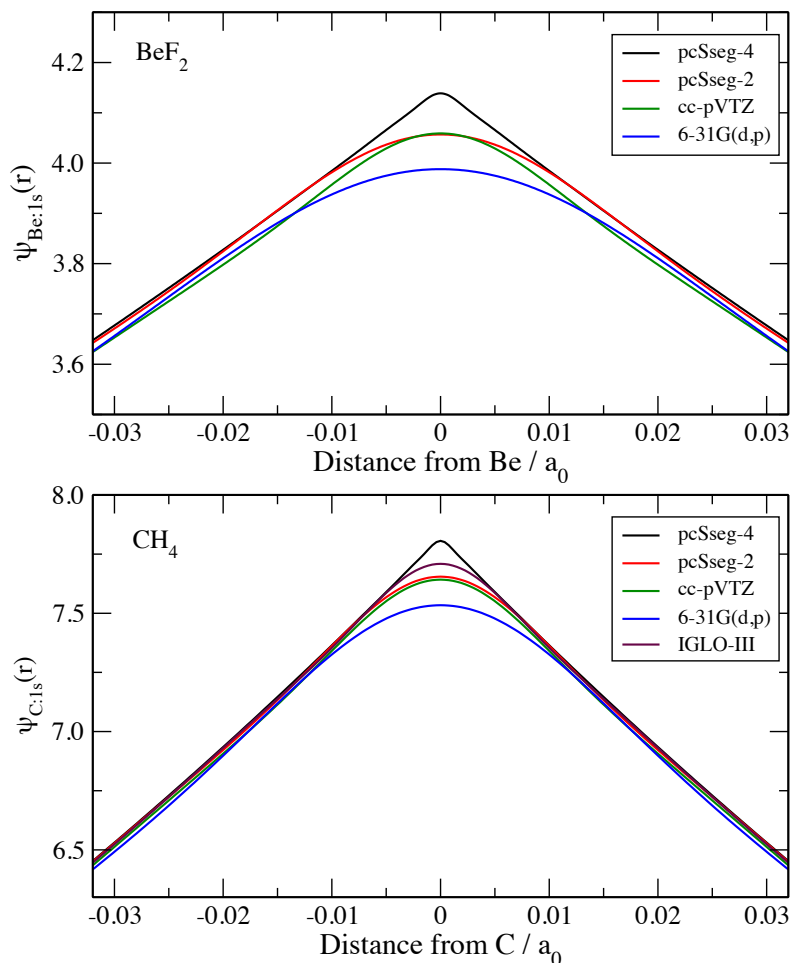


Figure 2.3: Radial behaviour of the core 1s orbitals for **BeF₂** and **CH₄** with different basis sets.

both s- and p-block elements. There is a very small error for the pcSseg-3 basis set. Focusing on the p-block elements, the IGLO basis sets perform well and there is a large reduction in the error for the IGLO-III basis set compared with IGLO-II. The large split-valence basis set performs less well compared with the CEBEs calculations. Again for these core→LUMO excitation energies there is a large error for the correlation consistent basis sets with core-correlation basis functions and it is necessary to use the very large cc-pV5Z basis set to reduce the error to a reasonable level. Similar to the CEBEs, the correlation-consistent basis sets with core-valence correlation functions lead to a significantly improved performance and the cc-pCVDZ and cc-pCVTZ basis sets have overall errors of 1.42 eV and 0.82 eV, respectively. For the small molecules considered here the LUMO will comprise both valence and Rydberg orbitals. For states of Rydberg character it is likely to be necessary to include diffuse basis functions in order to achieve a good agreement with experiment. Augmented polarisation consistent basis sets are available and diffuse basis functions are also available for the IGLO basis sets.¹⁵¹

Table 2.8: Error in calculated TDDFT core excitation energies (in eV).

Basis set	s-block	p-block	total
	$\Delta^{\text{MAD}}(\text{pcSseg-4})$	$\Delta^{\text{MAD}}(\text{pcSseg-4})$	$\Delta^{\text{MAD}}(\text{pcSseg-4})$
6-31G(d,p)	0.50 (0.27)	1.01 (0.66)	0.82
cc-pVDZ	0.47 (0.33)	0.87 (0.47)	0.72
Ahlrichs VTZ	2.47 (2.35)	0.50 (0.31)	1.23
pcSseg-1	0.39 (0.35)	0.32 (0.32)	0.34
cc-pCVDZ	0.26 (0.27)	0.49 (0.50)	0.41
IGLO-II	-	0.28 (0.32)	-
cc-pVTZ	0.48 (0.48)	0.50 (0.40)	0.50
pcSseg-2	0.09 (0.06)	0.10 (0.12)	0.10
IGLO-III	-	0.14 (0.16)	-

Figure 2.3 shows the radial behaviour of the 1s orbital at the beryllium and carbon nuclei in BeF_2 and CH_4 , respectively. For both orbitals, the large pcSseg-4 basis set results in a core orbital that has a greater value and is more steeply peaked at the nuclei compared with the relatively low quality 6-31G(d,p) basis set. This can be largely attributed to the much larger value of the highest exponent basis functions present in the larger basis set. For BeF_2 the orbital for the pcSseg-2 basis set closely follows that of the pcSseg-4 basis set apart from in the region very close to the nucleus where it has a lower value. The 1s orbital for the cc-pVTZ basis set is close to the pcSseg-2 basis set at the nucleus but is close to the 6-31G(d,p) basis set further from the nucleus. This is indicative of the poor performance of the correlation-consistent basis sets for the s-block elements. For CH_4 the orbitals arising from the pcSseg-2 and cc-pVTZ basis sets show a similar behaviour. However, for this molecule the orbital for the IGLO-III basis set is significantly closer to the large basis set and may underlie the strong performance of this basis set for the p-block elements.

TDDFT Core Excitation and Emission Energies

Table 2.8 shows $\Delta^{\text{MAD}}(\text{pcSseg-4})$ for the core $\rightarrow$ LUMO transition energies computed using TDDFT. These calculations are performed for a subset of the basis sets. The variation in the computed excitation energies between the different basis sets is considerably smaller for the TDDFT calculations compared to the ΔSCF calculations. As a consequence very large basis sets are not necessary for TDDFT calculations of

Table 2.9: Error in calculated TDDFT emission energies (in eV), relative to pcSseg-4.

Basis set	s-block Δ^{MAD}	p-block Δ^{MAD}	total Δ^{MAD}
6-31G(d,p)	18.38 (17.28)	14.09 (12.81)	15.69
cc-pVDZ	18.79 (17.54)	13.79 (12.03)	15.64
Ahlrichs VTZ	5.21 (3.46)	1.61 (1.98)	2.94
pcSseg-1	3.75 (1.123)	3.52 (1.43)	3.60
cc-pCVDZ	4.37 (3.60)	2.45 (1.74)	3.16
IGLO-II	-	1.67 (1.92)	-
cc-pVTZ	11.89 (12.84)	4.72 (7.11)	7.38
pcSseg-2	1.21 (0.65)	2.05 (1.33)	1.74
IGLO-III	-	1.27 (1.41)	-
pcSseg-3	0.36 (0.38)	0.58 (0.72)	0.50

core excitations. With the exception of the Ahlrichs VTZ basis set, all of the basis sets shown have an overall error of less than 1 eV, and this includes the 6-31G(d,p) and correlation consistent basis sets. The pcSseg-1 and pcSseg-2 basis sets reproduce the values for the larger basis set very well, and for the p-block elements the IGLO basis sets also perform well. As discussed earlier, the large error associated with the basis set in ΔSCF calculations arises predominantly from the calculation of the core-ionised or core-excited state. The TDDFT calculations are based upon the ground state molecular orbitals which are described relatively well by the small basis sets with the result that the basis set is a less crucial factor.

In contrast to TDDFT calculations of core excitation energies, the TDDFT calculations of the X-ray emission energies do show a large dependence on the basis set particular for the second row elements. This sensitivity to the basis set has been noted in previous work.⁹⁴ The approach to simulating the emission energies uses the core-ionised Kohn-Sham determinant in the TDDFT calculation. Consequently, by extension of the arguments made above, a large dependence on the basis set is to be expected since the smaller basis sets do not describe the core-ionised state well. The size of the basis set error for the smaller 6-31G(d,p) and cc-pVDZ basis sets is over 15 eV which is considerably larger than for the ΔSCF calculations of CEBEs and core-excitation energies. Another factor that appears to be significant is in TDDFT calculations of X-ray emission energies the transition is to an unoccupied

Table 2.10: Basis set dependence of the computed oscillator strengths for core→LUMO transitions.

Molecule	Method	pcSseg-4	pcSseg-3	cc-pCVTZ	IGLO-III	pcSseg-2	pcSseg-1	cc-pVDZ
CO	TDDFT	0.031	0.031	0.034	0.032	0.032	0.033	0.033
	Δ SCF	0.018	0.018	0.018	0.018	0.018	0.018	0.017
HCN	TDDFT	0.037	0.038	0.047	0.041	0.042	0.045	0.049
	Δ SCF	0.025	0.025	0.026	0.025	0.026	0.026	0.024
H ₂ O	TDDFT	0.006	0.006	0.013	0.009	0.008	0.010	0.013
	Δ SCF	0.006	0.006	0.007	0.006	0.006	0.006	0.007
AlH ₃	TDDFT	0.004	0.004	0.004	0.005	0.004	0.004	0.004
	Δ SCF	0.004	0.004	0.004	0.004	0.004	0.005	0.003
H ₂ S	TDDFT	0.002	0.003	0.004	0.004	0.003	0.004	0.005
	Δ SCF	0.003	0.003	0.003	0.003	0.003	0.003	0.002

core orbital, which also seems to lead to greater sensitivity to the basis set. For the emission energies the pcSseg-2 basis set has an error of 1.74 eV compared with 0.10 eV for the core excitation energies. The pcSseg-3 basis set has an error of 0.50 eV and shows that large basis sets are required to eliminate error associated with the basis set in these calculations.

For simulations of X-ray absorption spectra it is also important to accurately determine the intensities of the transitions. Table 2.10 shows the computed oscillator strengths for the core→LUMO transitions of a selection of molecules for a range of basis sets. The oscillator strengths have been computed within the Δ SCF and TDDFT approaches. The oscillator strengths computed from the Δ SCF calculations show little variation between the different basis sets, and even the cc-pVDZ basis set gives oscillator strengths in close agreement with the much larger basis sets. For the TDDFT calculations some variation in the computed oscillator strengths is observed. For HCN, which has the most intense transition, the smaller basis sets and cc-pCVTZ predict intensities that are a little larger than pcSseg-4.

2.1.4 Conclusions

The basis set dependence of DFT based calculations of spectroscopy in the X-ray region has been assessed. Δ SCF calculations of CEBEs and core→LUMO excitation energies, and TDDFT calculations of core-excitation and emission energies

have been studied for a range of molecules including excitations from the core orbitals of elements from the first and second rows of the periodic table. A range of widely used basis sets have been used with the aim of identifying relatively small basis sets that perform well for these calculations. For Δ SCF calculations at the K-edge of first row elements, relatively small basis sets can accurately reproduce core-electron binding energies and core-excitation energies of much larger basis sets. The IGLO-II, IGLO-III and cc-pCVTZ basis sets perform well, with IGLO-II being a particularly cost effective basis set. However, application of the IGLO basis sets is limited to p-block elements and for s-block elements the cc-pCVTZ or large split-valence (at least 6-311G(d,p) quality) is recommended. Calculations for second row elements are more challenging and the pcSseg-2 basis set has the best performance of the smaller basis sets, with pcSseg-3 required for a greater level of accuracy significantly better than 1 eV. The standard correlation-consistent basis sets have large errors. However, the core-valence correlation versions of the basis sets (cc-pCVXZ) are much more accurate but less accurate than pcSseg-n basis sets of comparable size. For these calculations, the basis set error is predominantly associated with the calculation of the core-excited or core-ionised state. This suggests that many of the smaller basis sets lack the flexibility to adjust for the change in effective nuclear charge associated with removing a core electron. Furthermore smaller basis sets provide a poor description of the radial behaviour of the 1s orbital and some correlation between the quality of the description of the core orbital and size of the basis set error. The TDDFT calculations of the core-excitation energies show less sensitivity to the basis set used and relatively small basis sets reproduce the excitation energies of the larger basis sets well. For these calculations the pcSseg-1 and pcSseg-2 perform well, although the versions augmented with diffuse basis functions may be more appropriate for some applications. In contrast, TDDFT calculations of X-ray emission energies show a high dependence on the basis set used. This can be rationalised by the fact that TDDFT calculations of excitation energies are based upon the ground state Kohn-Sham determinant, while TDDFT calculations of emission energies used the core-ionised determinant. For these calculations the IGLO-II, IGLO-III and pcSseg-2 basis sets provide a good level of accuracy for the K-edge of both row 1 and row 2 elements. The results from this study led to the development of the (Z+1) group of basis sets within the research group,¹⁵² which are based of Pople Gaussian basis sets and the core orbitals are described by the element 1 atomic number higher, to give a higher degree of flexibility to the core and provide a low cost and accurate description of the wavefunction for core-hole spectroscopy. The (Z+1) basis sets are used in Chapter 3 for the TDDFT simulation of XES.

2.2 Probing the Electronic Structure of Ether Functionalised Ionic Liquids with X-ray Photoelectron Spectroscopy

2.2.1 Introduction

The outcomes of this benchmarking study were applied to an experimental collaboration on probing the electronic structure of ether functionalised ionic liquids (ILs) using X-ray photoelectron spectroscopy (XPS).²³ The XPS technique provides detailed information about the electronic environment and charge distribution associated with individual components at, or near to, the surface of a material. High-level atomistic data can be used to inform the design of more efficient processes by guiding the structural modification of ionic liquids and that enable hydrogen bonding or anion recognition to generate highly functionalised performance molecules or so-called “designer solvents”.^{153–155}

Ether-functionalised ILs demonstrate great potential for sustainable chemical applications.¹⁵⁶ The polyethene (PEG) moiety can be naturally derived from biorefinery and plant waste via solvolysis of soft wood biomass,¹⁵⁶ or the catalytic conversion of cellulose into ethylene glycol and ethylene glycol monoethers.¹⁵⁷ Ether and PEG substituted systems show improved catalytic performance and reduced viscosities, when compared to alkyl substituted analogues^{153,158–160} and find application as alternative solvents or performance molecules across multiple aspects of science, technology and engineering.^{161–165}

A recent XPS study on surface enrichment in equimolar mixtures of nonfunctionalised and ether-functionalised imidazolium-based ILs, by Heller et al.,¹⁶⁶ showed that the electronic structure of the aromatic region of the imidazolium cation is shifted to significantly higher CEBEs when compared to $[C_8C_1Im]^+$, when the ether oxygen is directly bound to the imidazolium charge carrier. This study combines a higher resolution, monochromated, X-ray source and carefully designed DFT based CEBE calculations, employing new insights gained from the basis set benchmarking discussed in the earlier sections to evaluate intra-molecular interaction between the polyether oxygen and the imidazolium charge carrier group. It is shown that manipulation of the position of the oxygen atom, nearest to the cationic charge carrier, can delicately tune the electronic properties of the resulting ionic liquid. There is a distinct overall change in the profile of the C1s photoemission envelope, showing the relative position of the oxygen atom has a marked impact upon on the immediate side chain chemistry of the IL, while exhibiting minimal impact on the imidazolium ring itself. The DFT calculations, using basis sets identified to be accurate and

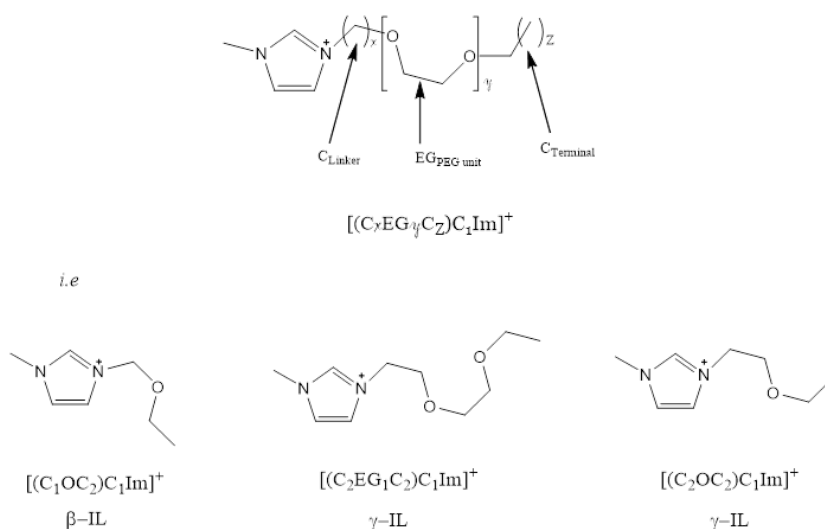


Figure 2.4: Nomenclature system adopted for functionalised ionic liquids studied in this work.

computationally efficient in the previous section and provide a detailed model for deconstructing which specific atomic sites alter the spectral profile with respect to the imidazolium substituent functionalisation. Figure 2.4 depicts a relatively simple nomenclature system designed to minimize ambiguities of visualising the structures. The system is defined by short hand notations ascribed to each N-based substituent in turn. Structures studied herein include functionalised substituents, so the descriptor for the complex substituent must reflect this. The DFT modelling shows strong agreement to experimental findings allowing a modified deconstruction model for ether containing systems to be proposed.

2.2.2 Computational Details

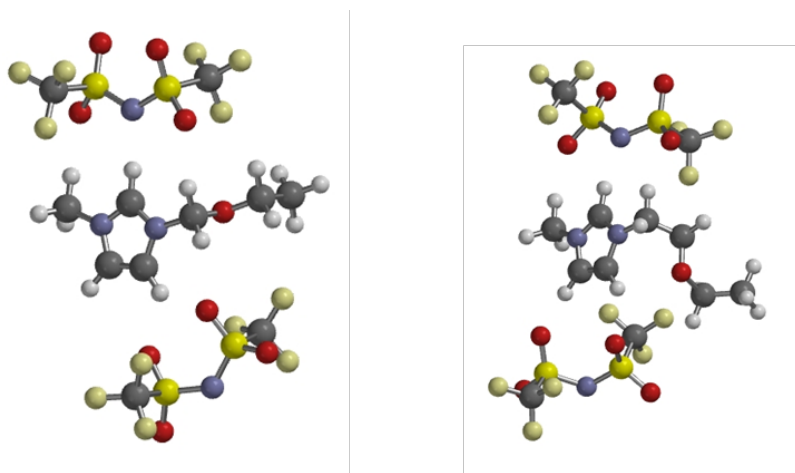


Figure 2.5: Optimized DFT structure for non-methylated β (left) and γ (right) ILs.

The experimental procedure of this work is detailed in ref.²³ Here we describe the computational model supporting the experiment based on DFT. The structure was optimized with the B97-1 exchange-correlation functional,¹³⁶ and the pcSseg-1 basis set.¹²⁷ The structural model utilized for the calculations consist of the cation with two counterions placed near the imidazole ring, structures for the $[(C_2EG_1C_2)C_1Im][Tf_2N]$ and $[(C_2EG_2C_2)C_1Im][Tf_2N]$ IL calculations are shown in Figure 2.4. The electron BEs were computed using a Δ self-consistent field (Δ SCF) approach,⁸⁰ with the PBE functional,¹⁶⁷ and larger pcSseg2 basis set. These basis sets have been shown to be accurate for the calculation of core ionisation energies earlier in this chapter. These calculations used the optimised trimer structure in conjunction with the polarised continuum model (PCM),^{168–170} with a dielectric constant of 15.0 to capture long range electrostatic effects.

2.2.3 Results and Discussion

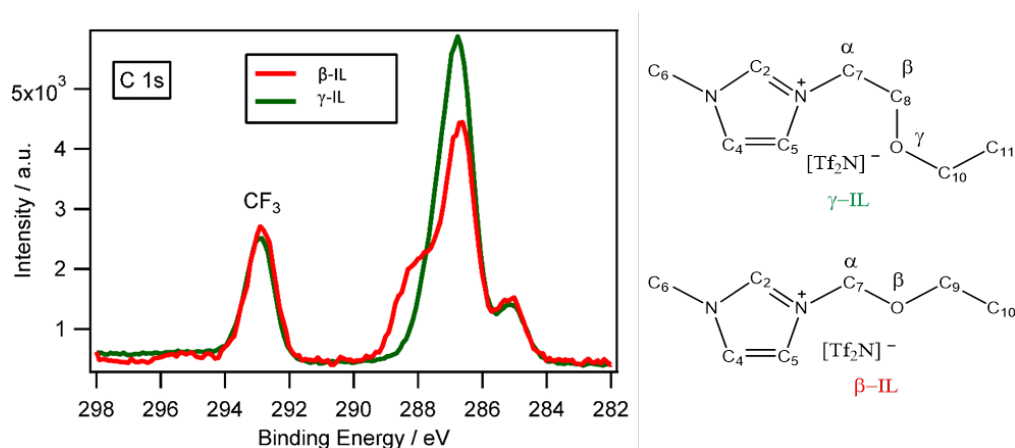


Figure 2.6: Overlaid C 1s high resolution spectra (taken from ref²³) for γ -IL, $[(C_2OC_2)C_1Im][Tf_2N]$ (green) and β -IL, $[(C_1OC_2)C_1Im][Tf_2N]$ (red), highlighting significant higher binding energy shift and difference in photoemission intensity. The number of carbon atoms in γ -IL is one greater than that of β -IL and the intensity normalized to the area of the CF_3 1s for γ -IL. Charge correction for both ILs was achieved indirectly by setting the value of the F 1s photoemission equal to that observed in a standard reference material, (F = 688.8 eV).¹⁷¹

It is clear, simply by inspection, that the photoemission line shapes for the ILs are different, whereby β -IL has a clear shoulder at approximately 288 eV. On a structural level, moving the O, by just a single atom position closer to the imidazolium charge carrier in the substituent chain could have a notable impact in the electronic structure, and hence potential for hydrogen bonding both inter-molecularly and indeed intra-molecularly. This striking change in electronic structure is so pronounced

that it motivated the need for further interrogation. In order to establish which carbon atoms in the structure are impacted to the greatest extent, and to consider if this observation could be used in the design and engineering of solvents on the molecular level further analysis is required to firmly establish which individual carbon components were being influenced most directly by the change in proximity of the oxygen atom. Overlaying the XP high resolution photoemission spectra of β -IL and γ -IL in Figure 2.6 shows that the region with the highest photoemission intensity for β -IL, is considerably lower than you would expect for the IL, suggesting that there is a shift of at least one of the C 1s photoemission components to higher BE.

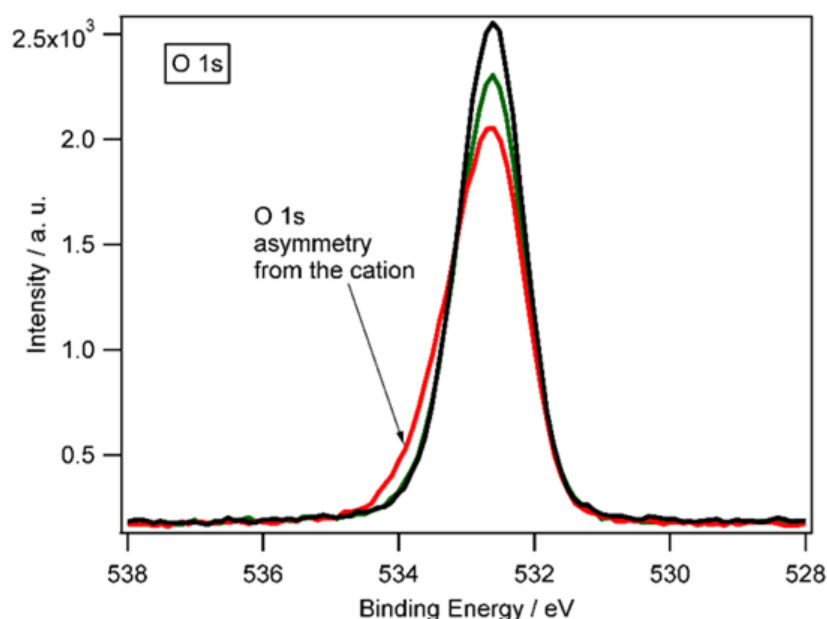


Figure 2.7: O 1s high resolution spectra (taken from ref²³) for β -ILs, red, γ -IL, green, and $[C_4C_1Im][Tf_2N]$, blue, showing asymmetry in the photoemission spectra for β -IL. Intensity normalized to the area of the N_{cation} 1s for γ -IL.

A review of the O 1s region is given in Figure 2.7, ref²³ shows the N 1s XPS data for the three ILs investigated exhibited a similar binding energy, suggesting that the electronic structure of the N 1s component for β -ILs is not perturbed relative to γ -IL and $[C_4C_1Im][Tf_2N]$. This data also strongly suggests minimal impact on the electronic structure of the cationic component C2 1s, C4,5 1s for β -ILs, when the polyether oxygen at β position. In contrast the O 1s region in Figure 2.7 for β -IL revealed an asymmetry at 533.5 eV. This binding energy is much higher than those observed for the γ -IL and alkyl substituted ILs, i.e 532.6 eV for both ILs, with a binding energy difference, (ΔBE) equal to 0.9 eV. This is significantly higher than the experimental error and similar to those observed in a range of polymers.¹⁷² Therefore, the higher BE shift was attributed to the electron withdrawal by the C7

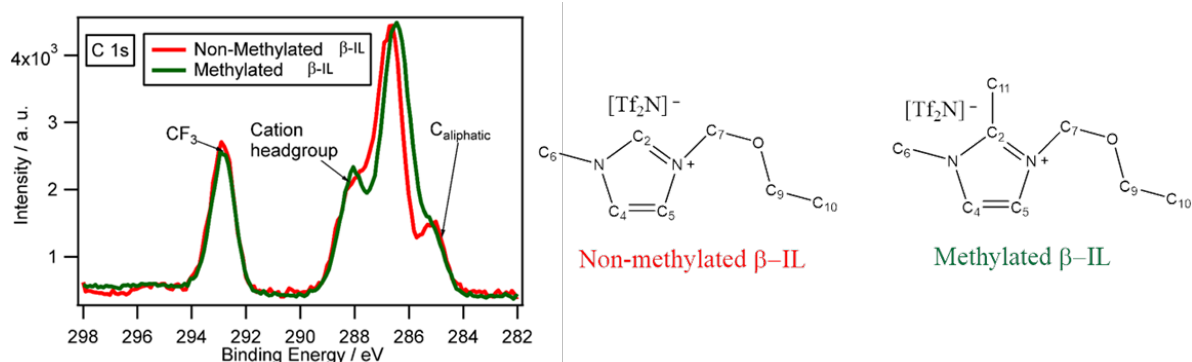


Figure 2.8: Overlaid C 1s high resolution XP spectra for non-methylated (red) and methylated (green) β -IL, $[(C_1OC_2)C_1\text{Im}][\text{Tf}_2\text{N}]$ and $[(C_1OC_2)C_1C_1\text{Im}][\text{Tf}_2\text{N}]$ respectively. Intensity normalized to the area of the CF_3 1s for non-methylated β -IL, $[(C_1OC_2)C_1\text{Im}][\text{Tf}_2\text{N}]$. Charge correction is achieved indirectly by setting the value of the F 1s photoemission equal to that observed in a standard reference material $[\text{C}_8\text{C}_1\text{Im}][\text{Tf}_2\text{N}]$, (F = 688.8 eV).¹⁷¹

Table 2.11: Comparison of XPS measurements and DFT core binding energy calculations for β -IL and γ -IL.

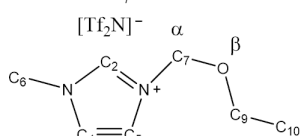
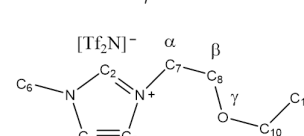
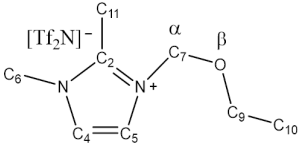
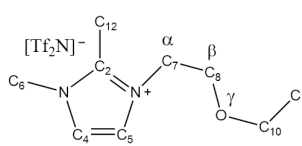
β -IL 			γ -IL 		
XPS Bulk /eV	Cationic component	DFT /eV	XPS Bulk /eV	Cationic component	DFT /eV
287.7	C_2	290.7	287.7	C_2	290.7
287.0	$C_4(C_{4,5})$	289.8	287.1	$C_4(C_{4,5})$	289.6
287.0	$C_4(C_{4,5})$	289.5	287.1	$C_5(C_{4,5})$	289.5
286.5	$C_6(C_{\text{hetero}})$	290.0	286.5	$C_6(C_{\text{hetero}})$	289.9
288.3	C_7	291.4	286.5	$C_7(C_{\text{hetero}})$	290.1
-	C_8	-	286.5	$C_8(C_{\text{hetero}})$	290.1
286.5	$C_9(C_{\text{hetero}})$	289.9	-	C_9	-
285.1	$C_{10}(C_{\text{aliphatic}})$	288.3	286.5	$C_{10}(C_{\text{hetero}})$	289.8
-	C_{11}	-	285.1	$C_{11}(C_{\text{aliphatic}})$	288.2
533.5	O_{cation}	536.3	532.7	O_{cation}	536.0
402.0	$N_{\text{cation}}(+)$	405.4	402.0	$N_{\text{cation}}(+)$	405.3
402.0	N_{cation}	405.6	402.0	N_{cation}	405.4

Table 2.12: Comparison of XPS measurements and DFT core binding energy calculations for methyl- β -IL and methyl- γ -IL.

methyl- β -IL			methyl- γ -IL		
					
XPS Bulk /eV	Cationic component	DFT /eV	XPS Bulk /eV	Cationic component	DFT /eV
287.9	C ₂	291.1	287.7	C ₂	291.1
286.9	C ₄ (C _{4,5})	289.7	287.0	C ₄ (C _{4,5})	289.5
286.9	C ₄ (C _{4,5})	289.7	287.0	C ₅ (C _{4,5})	289.5
286.5	C ₆ (C _{hetero})	289.9	286.5	C ₆ (C _{hetero})	289.9
288.3	C ₇	291.5	286.5	C ₇ (C _{hetero})	290.1
-	C ₈	-	286.5	C ₈ (C _{hetero})	290.0
286.5	C ₉ (C _{hetero})	290.0	-	C ₉	-
285.2	C ₁₀ (C _{aliphatic})	288.2	286.5	C ₁₀ (C _{hetero})	289.8
-	C ₁₁	289.1	285.0	C ₁₁ (C _{aliphatic})	288.2
-	C ₁₂	-	286.0	C ₁₂	289.2
533.4	O _{cation}	536.3	532.6	O _{cation}	536.0
401.9	N _{cation} (+)	405.3	401.9	N _{cation} (+)	405.3
401.9	N _{cation}	405.4	401.9	N _{cation}	405.3

carbon directly bonded it. This data indicates that the C7 1s component for β -IL is significantly electron deficient and pulls electron density away from the highly electronegative O atom directly bound to it. Therefore, the observed higher binding shift for β -IL was attributed to the C7 1s component. This interesting observation could be rationalized as a consequence of inductive electron withdrawal effect, initiated by the electron deficient imidazolium cationic charge carrier, which pulls electron density away from the C7 carbon, thus making it highly electron deficient. This observation was interrogated further by methylating the C2 position of the β -IL, which has the effect of turning off hydrogen bonding interaction within the site, and distorting charge transfer between the C2 and other potential interaction sites.^{173–175} This allowed for direct comparison of electronic interaction between the methylated and non-methylated β -ILs. From the overlaid spectra for both ILs, (Figure 2.7), there is broadening of the region with the highest intensity for the methylated β -IL (green colour) at 86.0 eV. This is indicative of the presence of the methyl group directly bonded to the C2 carbon. While the region with the highest

binding energy (288.5 eV) exhibited good alignment between the two XP spectra. This suggests that the C2 1s component in both ILs are in the same electronic environment, and independent of the methylation at the C2 position. This data has therefore established the fact that the electronic structure of the C2 1s component is not impacted by substituting polyether oxygen at β position to the imidazolium ring.

In order to firmly establish the carbon atom that is mostly impacted in the β -IL, data from XPS experiment was investigated further by evaluating core binding energy calculation using DFT calculations. The BEs from the DFT calculations in Tables 2.11 and 2.12 are higher than the experimental values. This difference can be attributed to the exchange-correlation functional and basis set used. Furthermore, the finite structural model used is likely to underestimate the long-range electrostatic interactions. However, these effects will be constant for the different systems, and crucially the trends in the computed BEs are in good agreement with the experimental data. In particular, the calculations confirm that the C7 1s component for the non-methylated and methylated β and γ -ILs exhibits higher BEs in comparison to the C2 1s. The calculations also confirm that the electronic structure of the N_{cation} 1s for β -IL is relatively unperturbed, when compared to a notable impact upon the BE of the O_{cation} 1s component in the β -IL.

2.2.4 Conclusions

The designer aspect of ionic liquids was exploited to graft polyether groups into IL structural framework, thus creating an opportunity to investigate fundamental interactions within the IL, using XPS. Although XPS studies of ether-functionalised systems have been previously undertaken, the effect of structural changes to IL ether substituent on fundamental intramolecular interaction within the system, has not been analysed in great depth. This work addresses this knowledge gap, in which the use of monochromated XPS provided the opportunity to further probe subtle intramolecular interaction and electron density distribution within ether-functionalised systems. A systematic investigation of two distinct ether functionalised systems suggests that the electronic structure of the imidazolium cation can be significantly perturbed by tuning the position of the polyether oxygen in the ether substituent. This can have profound impact on ionic liquid interaction with solvents and solute, for example, IL-catalyst interaction and dissolution of solutes. From our data, it was apparent that tuning the position of the polyether oxygen from γ to β position, results in highly electropositive substituent groups (C7 1s and O_{cations} 1s) for β -IL, in comparison to that observed for γ -IL. Interestingly, the electronic structure of the components within the aromatic region of the imidazolium cation headgroup

(C2 1s, C4,5 1s and N_{cation} 1s) for the β -IL were not perturbed as they recorded binding energy values similar to their γ -ILs counterparts. The above XPS data was supported by DFT core-electron binding energy calculations which showed excellent agreement with the experimental observations. The C 1s environment for β -IL was consequently fitted based upon the data obtained from both XPS experiment and DFT calculation. This data has provided critical insight that can aid the design of new materials with specific properties that can potentially impact hydrogen bonding, both intermolecularly and intramolecularly. This study has added to the depth of information already established for ether-functionalised systems that are useful in underpinning the development of new materials for specific chemical applications, including catalysis, dissolution and metal extraction.

Chapter 3

Improving the Predictive Quality of Time-Dependent Density Functional Theory Calculations of the X-ray Emission Spectroscopy of Organic Molecules

3.1 Introduction

In this chapter, TDDFT calculations of XES are discussed and the work has been published in reference 24. Accurate simulation of X-ray emission spectra can play a vital role in the assignment of the spectral bands and enable the full interpretation of the experimental data. A number of different theoretical approaches have been developed and applied to the study of XES. The most formally straightforward approach to determine the energy and associated oscillator strengths for the various valence to core transitions required to simulate an X-ray emission spectrum is to approximate the transitions energies using the energy difference between the orbital energies

$$\Delta E = \epsilon_v - \epsilon_c \quad (3.1)$$

and estimate the oscillator strengths from

$$f \propto |\langle \phi_c | \hat{\mu} | \phi_v \rangle|^2 \quad (3.2)$$

where ϕ_c is a core orbital and ϕ_v is a valence orbital. This approach has been used successfully in many studies, for example the study of valence-to-core XES of transition metal complexes.^{96,176} One of the important advantages of this approach is

that it allows the spectra to be determined directly from the wavefunction^{177–180} or KSDFT¹⁷⁶ calculations.

Following ionization of a core electron, the effective nuclear charge of the relevant nuclei increases by one, and as a consequence the molecular orbitals will adapt to the new environment. This relaxation of the electronic structure in the presence of the core-hole was applied in the previous chapter in the Δ (SCF) approach. This approach has been shown to provide accurate core-ionization energies,^{80,181–184} however it is difficult to apply to large systems owing to the number of individual SCF calculations required, and the challenge of performing SCF calculations for arbitrary electronic states. This has led to the development of methods that incorporate the electronic relaxation while avoiding the practical limitations of Δ SCF. For example, in the $Z+1$ approximation an increased nuclear charge is used for the absorbing atom³⁶ or the transition potential approach where a half filled core orbital is used providing a balance between final and initial states.³⁵

More recently an alternative approach to computing X-ray emission spectra using conventional response theory methods, such as TDDFT, was introduced. In this scheme, the determinant for the state with a core-hole is used as a reference and the transitions of interest are found as those with negative eigenvalues.⁸⁷ In this approach the relaxation of the orbitals in the presence of the core-hole is captured by the core-ionized reference determinant. This has been applied within the context of EOM-CCSD,¹⁰⁵ TDDFT⁹³ and ADC methods.¹⁸⁵ An advantage of this approach compared with Δ SCF is that the complete spectrum can be determined in a single calculation. The XES of transition metal systems have been studied using TDDFT,^{37,94,186} and it has been shown that the experimental spectra are reproduced well although an energy shift needs to be applied to the calculated spectra to align with experiment. This compromises the predictive power of TDDFT and is a consequence of deficiencies in the exchange-correlation functional associated with the electron self-interaction error.⁹³ There has been less focus on the calculation of the XES of organic molecules, although studies of water³⁴ and a small selection of organic molecules⁹³ have been reported. In the latter study, an attempt was made to parameterise a hybrid exchange-correlation functional to describe the X-ray emission energies more accurately. However, although the systematic overestimation of the excitation energies was reduced by increasing the fraction of Hartree-Fock exchange in the functional, the calculated spectral profiles were adversely affected.

In Chapter 2 we saw that a choice of Gaussian basis set has emerged as another important factor in the accuracy of these calculations.²² The higher effective nuclear

charge results in a contraction of the electron density in the core-ionized state. Small or moderately sized basis sets can provide a poor description of the core-ionized state since they do not have the flexibility to describe the more compact electron density. This is particularly a problem for the study of XES at the K -edge of heavier nuclei. One solution is to simply use very large basis sets such as large Dunning basis sets with core-correlation functions, such as cc-pCVTZ and cc-pCVQZ, which have been shown to be effective.⁹⁴ However, this can severely restrict the size of system that can be studied. Alternative basis sets that achieve a balanced description of the ground and core-ionized states have been proposed including using exponents for the basis functions midway between the element and the element with a nuclear charge of one higher¹⁸⁷ and explicitly including basis functions for the $Z+1$ element in the basis set.¹⁵²

In this chapter we investigate the accuracy of TDDFT calculations for a range of organic molecules, and explore the dependence of the computed spectra on factors such as basis set, exchange-correlation functional and the relaxation of the intermediate state. It is shown that accurate spectra can be computed from first principles following the application of an energy shift derived from DFT calculations for the highest energy transition and that the CAM-B3LYP functional provides a reliable description of the spectra band profile, providing a new protocol for reliably predicting XES spectra.

3.2 Methodology

X-ray emission spectra were computed with TDDFT within the Tamm-Dancoff approximation⁹⁰ using a protocol described previously.⁹³ Following a Kohn-Sham DFT calculation for the ground state, a further DFT calculation is performed for the core-ionized state with the maximum overlap method⁷³ used to maintain the core-hole during the SCF procedure and in a subsequent TDDFT calculation using the core-ionized state as a reference the emission energies appear as negative eigenvalues. Calculations were performed for the following molecules: methanol (carbon K -edge), ammonia (nitrogen K -edge), acetone and dimethyl sulfoxide (DMSO) (oxygen K -edge), fluorobenzene (fluorine K -edge), H_2S (sulphur K -edge), CH_3Cl and CF_3Cl (chlorine K -edge) and compared with experimental data adapted from references 188–193. The structures of the molecules were optimized at the B3LYP/6-311G** level of theory. Relativistic effects can also be significant and these effects are accounted for by applying an energy shift to the computed transition energies which is estimated from the difference in the 1s orbital energy between relativistic and non-

relativistic HF/cc-pCVQZ-DK¹⁹⁴ with the relativistic effects modelled using the Douglas-Kroll-Hess Hamiltonian. This gives values of +0.13, +0.25, +0.44, +0.47, +0.74, +10.01, +13.08 and +13.08 eV for methanol, ammonia, acetone, DMSO, fluorobenzene, H₂S, CH₃Cl and CF₃Cl, respectively. All calculations were performed with the Q-CHEM software package.¹⁴⁵ Computational spectra were generated by convoluting the computed energies and oscillator strengths with gaussian functions with full-width at half maximum of 0.25 eV.

3.3 Results and Discussion

We begin our analysis by demonstrating the accuracy that can be achieved using TDDFT with a standard hybrid functional to simulate X-ray emission spectra before proceeding to explore how various approximations affect the quality of the computed spectra and the dependence on the exchange-correlation functional. The accuracy that can be obtained from TDDFT calculations of XES is represented in Figure 3.1 which shows a comparison between the computed and experimental spectra for a range of molecules at the *K*-edge involving a variety of nuclei. The spectra are computed with the cc-pCVQZ basis set and the B3LYP exchange-correlation functional, and an energy shift has been applied to each spectra so that the most intense peak aligns with the experimental data. The cc-pCVQZ basis set is large and has been shown to give emission energies that are converged with respect to the basis set.²² The computed spectra reproduce the experimental spectra remarkably well. For all of the molecules, the computed spectra predict the peak heights and their relative energy spacing with a high degree of accuracy. In some spectra, most notably ammonia and H₂S, the experiment has bands at higher emission energy which can be associated with elastic scattering and multi-electron transitions.^{190,191} Multi-electron transitions of this type will not be described by the TDDFT methodology used here. In some cases the relative intensities of the bands are not predicted in line with experiment, for example for ammonia and acetone. However, a uniform broadening has been applied and a single structure considered, and so the effects of nuclear dynamics are not accounted for. Consideration of nuclear dynamics can affect the relative intensities of the bands, as demonstrated in the following chapter.

As noted above and in the figure caption, an energy shift is required to align the computed spectra with experiment. The calculations systematically overestimate the emission energies. This is in contrast to TDDFT calculations of X-ray absorption spectra where the transition energies are underestimated. However, both of these errors are a manifestation of the self-interaction error. In the context of X-ray

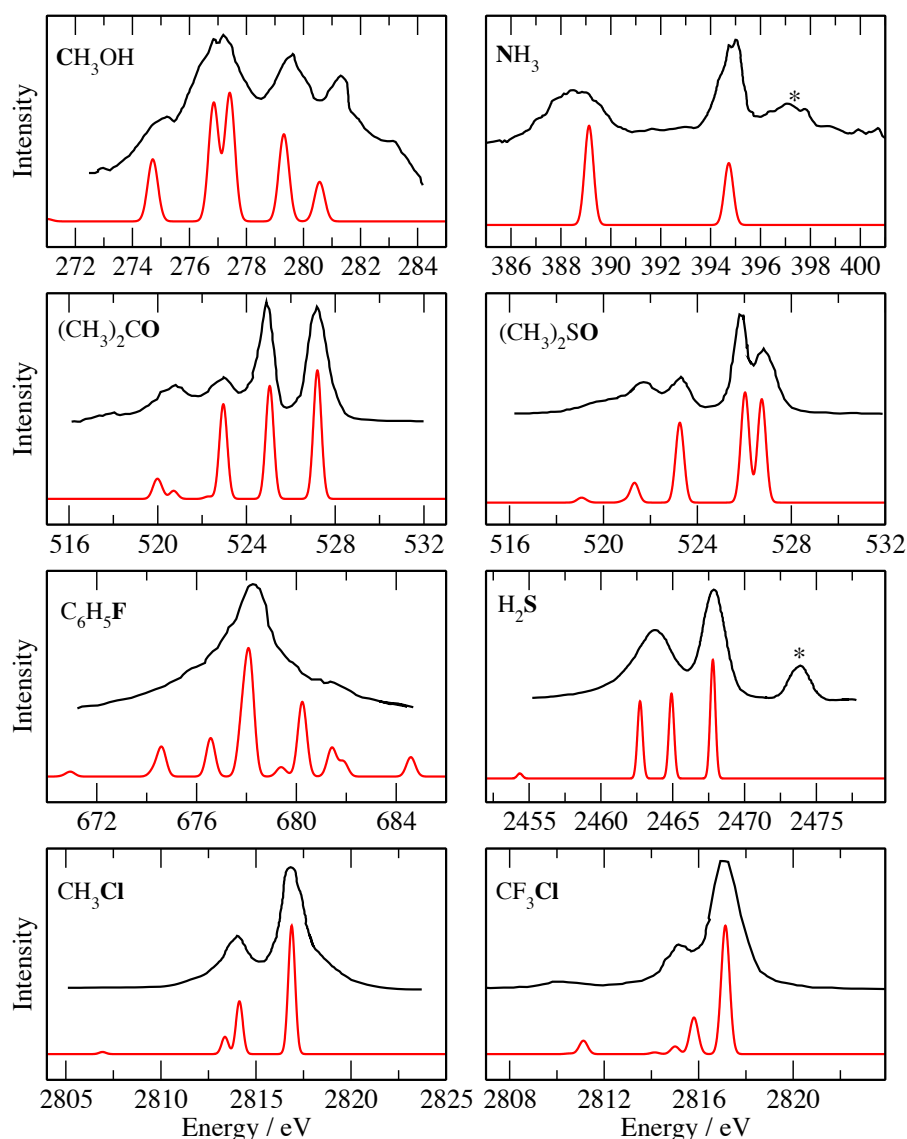


Figure 3.1: Calculated B3LYP/cc-pCVQZ and experimental X-ray emission spectra for CH_3OH , NH_3 , $(\text{CH}_3)_2\text{CO}$, $(\text{CH}_3)_2\text{SO}$, $\text{C}_6\text{H}_5\text{F}$, H_2S , CH_3Cl and CF_3Cl , with bold font denoting the atom that has been core-ionised. Black line: experiment and red line: calculation. * indicates a multi-electron feature. The following energy shifts have been applied to the calculated spectra to align them with experiment CH_3OH : -6.3 eV, NH_3 : -6.9 eV, $(\text{CH}_3)_2\text{CO}$: -8.8 eV, $(\text{CH}_3)_2\text{SO}$: -8.6 eV, $\text{C}_6\text{H}_5\text{F}$: -7.9 eV, H_2S : -33.7 eV, CH_3Cl : -32.9 eV and CF_3Cl : -32.9 eV

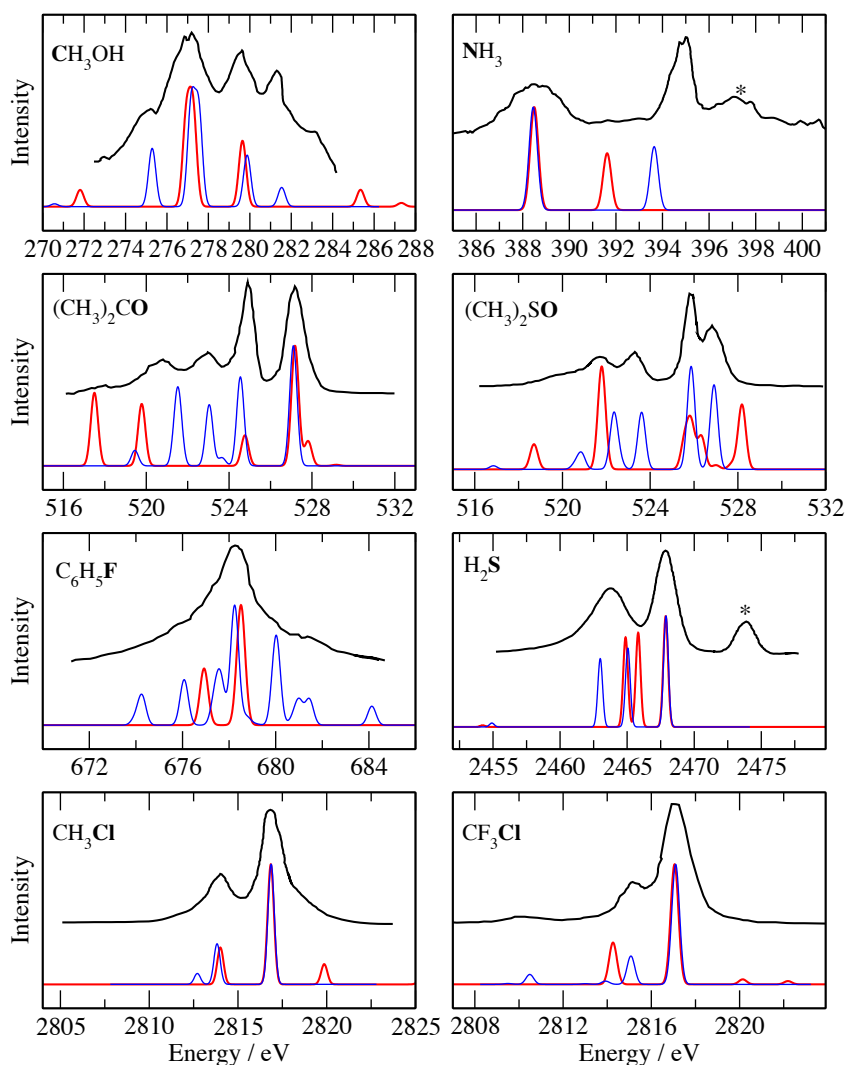


Figure 3.2: Calculated TDDFT B3LYP/cc-pCVQZ (red line), Kohn-Sham DFT B3LYP/cc-pCVQZ (blue line) and experimental X-ray emission spectra (black line) for **CH**₃OH, **NH**₃, (**CH**₃)₂CO, (**CH**₃)₂SO, **C**₆H₅F, **H**₂S, **CH**₃Cl and **CF**₃Cl, with bold font denoting the atom that has been core-ionised. * indicates a multi-electron feature. The following energy shifts have been applied to the calculated spectra to align them with experiment **CH**₃OH: -25.2 eV, **NH**₃: -30.9 eV, (**CH**₃)₂CO: -46.0 eV, (**CH**₃)₂SO: -46.6 eV, **C**₆H₅F: -34.4 eV, **H**₂S: -86.7 eV, **CH**₃Cl: -91.1 eV and **CF**₃Cl: -91.6 eV for TDDFT and **CH**₃OH: +11.1 eV, **NH**₃: +11.9 eV, (**CH**₃)₂CO: +13.5 eV, (**CH**₃)₂SO: +13.6 eV, **C**₆H₅F: +18.5 eV, **H**₂S: +47.1 eV, **CH**₃Cl: +49.7 eV and **CF**₃Cl: +50.2 eV for Kohn-Sham DFT.

absorption calculations the self-interaction error leads to the energy of the occupied core orbitals being too high resulting in an under-estimation of the core→virtual orbital energy differences. For X-ray emission calculations it leads to the energy of the unoccupied core orbital in the reference core-ionized state being too low leading to an overestimation of the valence→ virtual-core orbital energy differences. This artefact is less prevalent in Δ SCF calculations where the orbitals are optimized for each state and the virtual orbitals do not play a direct role. The magnitude of the shift applied increases as the nuclear charge of the ionized nuclei increases. For the examples shown here, the size of the shift applied varies from -6.3 eV for the methanol carbon and -32.9 eV for the chlorine in CF_3Cl .

Analogous spectra computed with TDDFT where there is no electronic relaxation in the intermediate state are shown in Figure 3.2. These spectra are computed using the same approach except the reference determinant is comprised of the orbitals for the neutral ground state with a vacancy introduced to the appropriate core orbital. The neglect of relaxation leads to a large change in the calculated spectra and the resulting spectra show a considerably worse agreement with experiment, and for some of the molecules the calculated spectra show little resemblance to experiment. Also shown in Figure 3.2 are spectra computed based upon the Kohn-Sham ground state orbitals using equations 3.1 and 3.2. This approach to computing the spectra also does not incorporate any orbital relaxation in the core-ionized state but in contrast to the TDDFT calculations provides an accurate representation of the experimental spectra. This suggests that there is some cancellation of errors between approximating the transition as the orbital energy difference and the relaxation in the intermediate state. The two conditions studied here, namely full and no relaxation, represent the two extreme situations. Depending on the relative timescales of the electronic relaxation and the core-hole lifetime, it is possible to conceive of situations where only partial relaxation may occur.

We investigate next the role of the basis set on the calculated spectra. Figure 3.3 shows the calculated spectra for a range of basis sets of varying quality for DMSO and CF_3Cl . For these spectra no energy shift has been applied. The results show that varying the quality of the basis set has a relatively small effect on the spectral profile but does have a significant effect on the calculated emission energies, particularly at the Cl K -edge. This is consistent with the findings of previous studies.²² It is of interest to have small basis sets that are able to replicate the results of the much larger basis sets at a vastly reduced computational cost. In this regard the IGLO-II basis set performs well, and this has been recognized previously in the literature.^{195,196} The (Z+1)6-31G* basis set also performs well. This is a non-standard

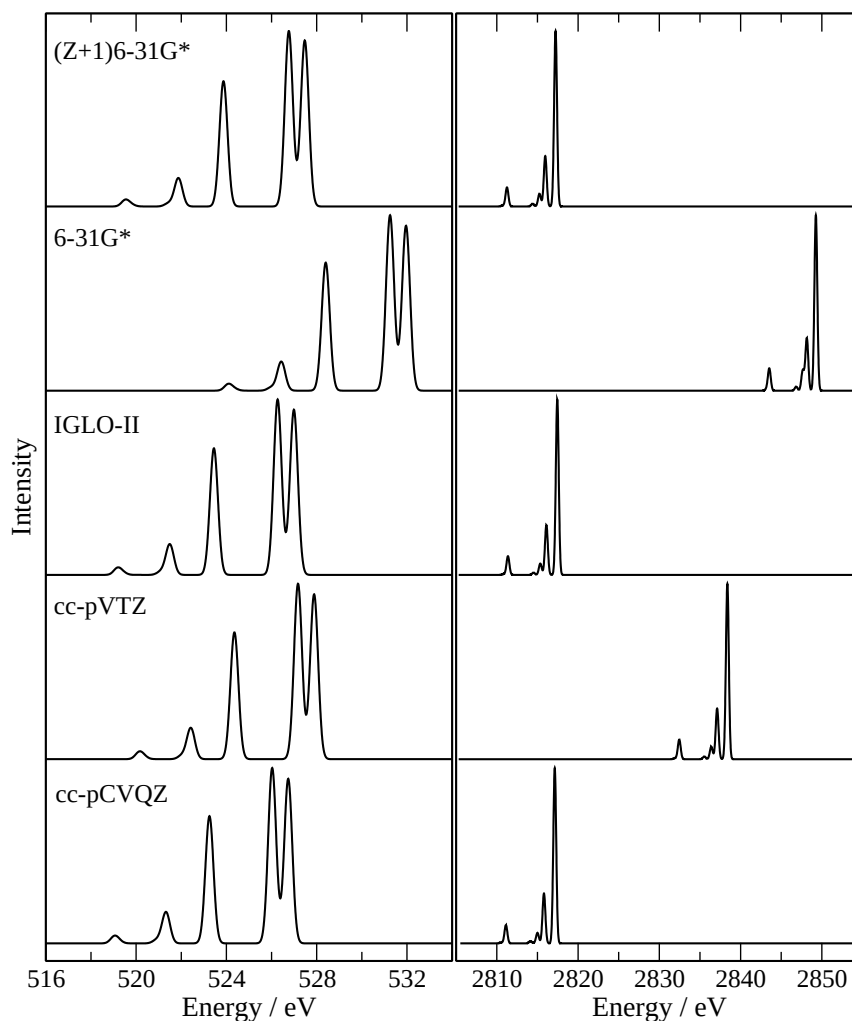


Figure 3.3: Variation of the calculated spectra with basis set for DMSO (left) and CF_3Cl (right). Spectra computed with the B3LYP exchange-correlation functional.

approach that was introduced recently,¹⁵² and involves supplementing the 6-31G* basis set with basis functions for the element with nuclear charge one greater for the element being ionized. While the IGLO basis sets are only available for a subset of the elements, this (Z+1) protocol can be applied to generate basis sets for all elements.

Figures 3.4 and 3.5 show computed spectra for fluorobenzene, H_2S , CH_3Cl and CF_3Cl with the exchange-correlation functionals: B3LYP, PBE,¹⁶⁷ CAM-B3LYP,¹⁹⁷ CAM-QTP(01)¹⁹⁸ and SRC1-R2⁸⁶ evaluated using the cc-pCVQZ basis set. In these figures, the spectra are plotted relative to the energy of the highest energy band to allow an easier comparison of the spectral profiles. The functionals were chosen from

a survey of a wide range of functionals as providing X-ray emission energies close to the experimental values. SRC1-R2 is a short-range corrected functional that was parameterized for X-ray absorption spectroscopy, while CAM-B3LYP and CAM-QTP(01) are range-separated functional with 100% HF exchange in the long range. The CAM-QTP(01) functional is parameterized so that the Kohn-Sham eigenvalues are approximately equal to the vertical ionization energies.

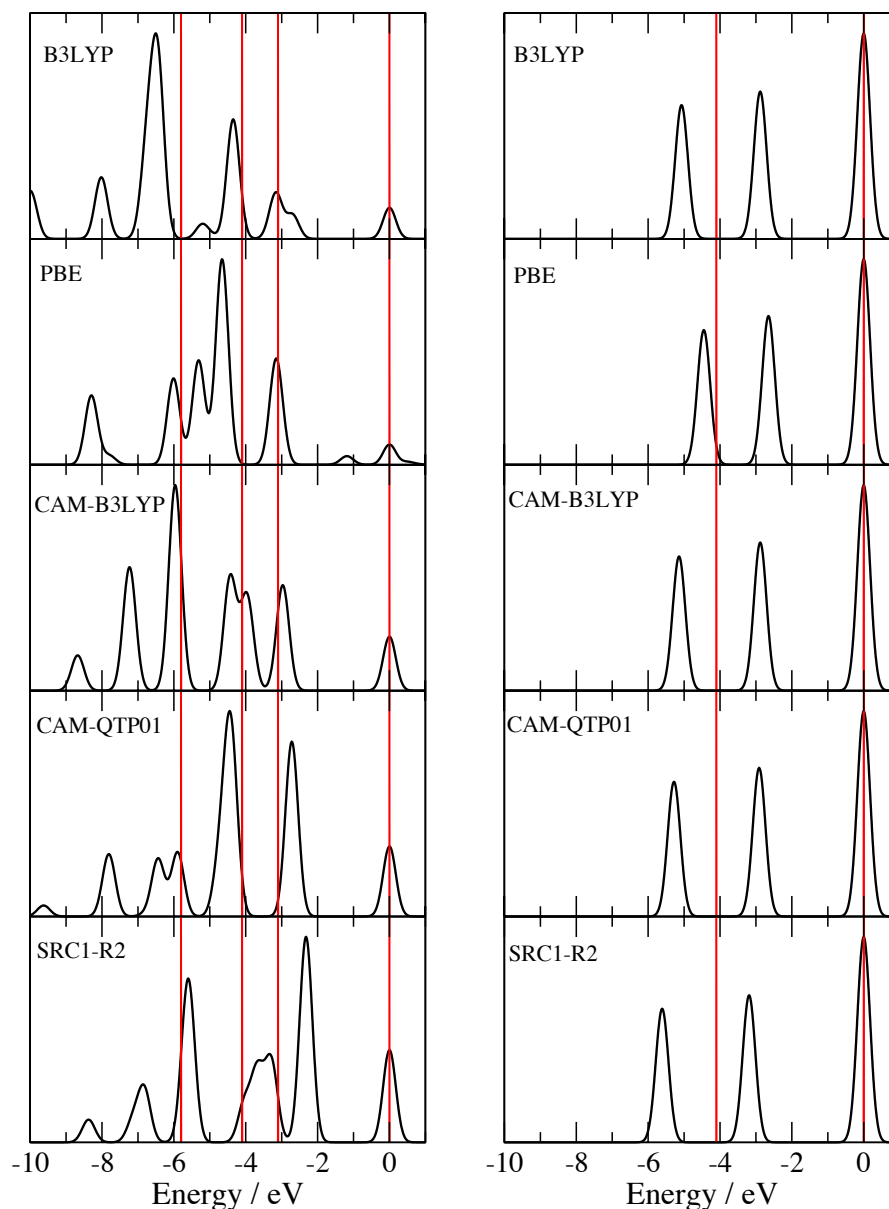


Figure 3.4: Variation of computed X-ray emission spectra with exchange-correlation functional for $\text{C}_6\text{H}_5\text{F}$ (left) and H_2S (right). The spectra are plotted relative to the energy of the highest energy band which is set to zero, and the vertical red lines indicate the position of the bands in the experimental spectra.

The spectral profiles predicted by the different functionals are qualitatively sim-

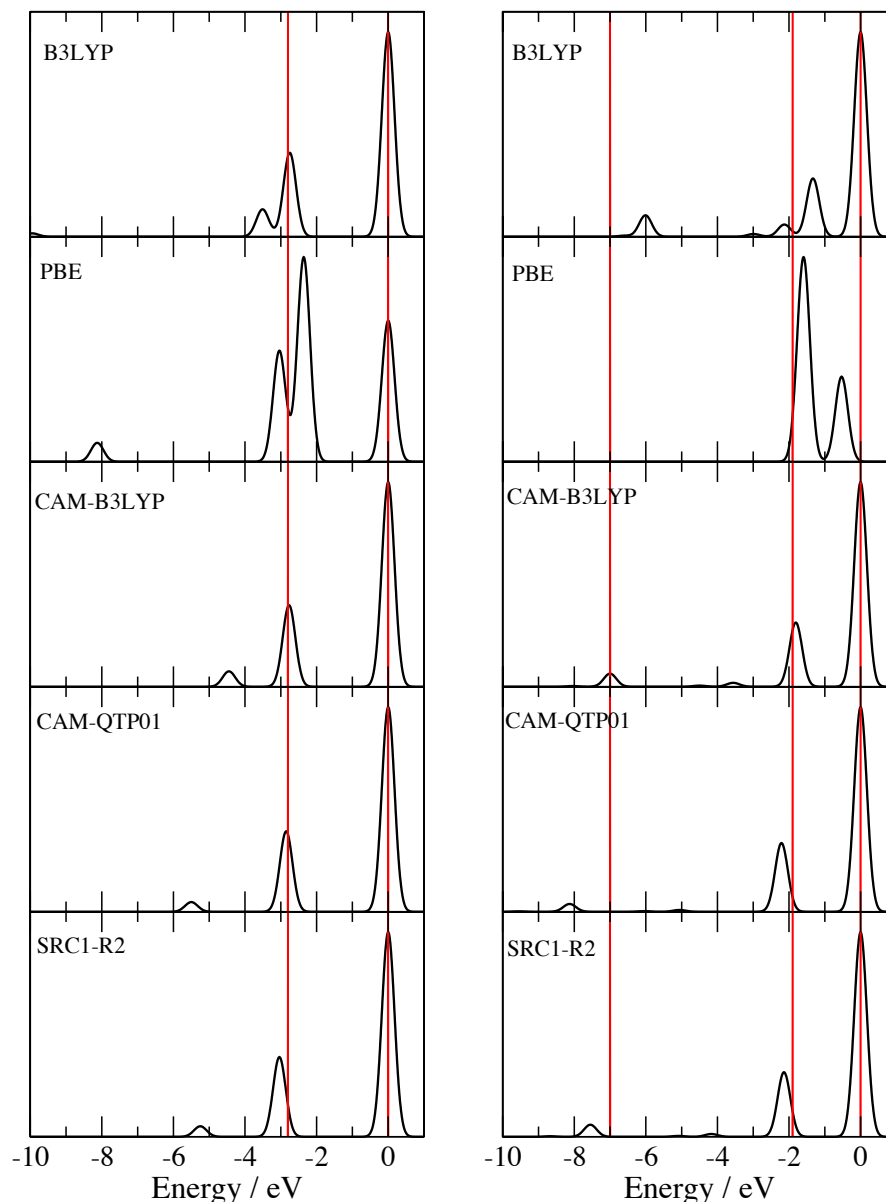


Figure 3.5: Variation of computed X-ray emission spectra with exchange-correlation functional for CH_3Cl (left) and CF_3Cl (right). The spectra are plotted relative to the energy of the highest energy band which is set to zero, and the vertical red lines indicate the position of the bands in the experimental spectra.

ilar. The exception to this is PBE which gives distinctly poorer spectra for acetone, DMSO and CF_3Cl . On balance, the CAM-B3LYP functional gives a good description of the relative energies of the bands observed in experiment, showing some improvement over B3LYP. We now focus on which functional gives predicted excitation energies that are in agreement with experiment so that no energy shift is required to align the calculated spectra with experiment. Table 3.1 shows the energy difference between the calculated spectra and experiment for the most intense band. All of the functionals considered overestimate the transition energies but a

Table 3.1: Variation of the computed energy of the most intense band relative to experiment with exchange-correlation functional evaluated using the cc-pCVQZ basis set.

Molecule	B3LYP	PBE	CAM-B3LYP	CAM-QTP(01)	SRC1-R2
CH₃OH	+6.4	+7.3	+6.0	+4.7	+4.7
NH₃	+6.8	+7.9	+6.8	+5.7	+4.2
(CH₃)₂CO	+8.6	+10.6	+8.6	+7.4	+4.7
(CH₃)₂SO	+8.7	+10.9	+8.7	+7.5	+6.2
C₆H₅F	+7.9	+14.0	+7.8	+5.0	+1.3
H₂S	+33.7	+44.4	+34.7	+31.9	+7.6
CH₃Cl	+38.2	+50.8	+39.2	+36.3	+8.0
CF₃Cl	+37.6	+50.9	+38.7	+35.8	+7.5

common pattern emerges across the molecules. The GGA functional PBE shows the greatest overestimation, while the values for B3LYP and CAM-B3LYP are quite similar. The CAM-QTP(01) is parameterized such that the Kohn-Sham eigenvalues are equal to the vertical ionization energies. While this leads to an improvement relative to B3LYP, the transition energies remain too high. SRC2-R2 is the functional that gives transition energies closest to experiment, and this is the only functional for which there is not a large increase for the *K*-edge of the heavier nuclei. This functional was designed for X-ray absorption spectroscopy and has a high proportion of HF exchange (91%) in the short-range, and this leads to a large change in the core-orbital energies. The R2 parameterization was for elements Na $\rightarrow$ Ar, but we use these parameters for all elements here.

It would be desirable to have a functional that provides emission spectra that do not require an energy shift to align with experiment. Previous work has found that a high fraction (66%) of HF exchange is required in a standard hybrid functional to provide emission energies close to experimental values.⁹³ A consequence of this modification of the functional is that the properties of the valence orbitals are adversely affected and the quality of the computed spectra deteriorates. The SRC2-R2 functional used here has 91% HF exchange in the short-range. Increasing the percentage of HF to 100% leads to only a small shift to lower emission energies. To reduce the emission energies further requires modification of the short-range attenuation parameter. This leads to a similar problem to the hybrid functionals, i.e. the quality of the computed spectra becomes poor. The fundamental difference between

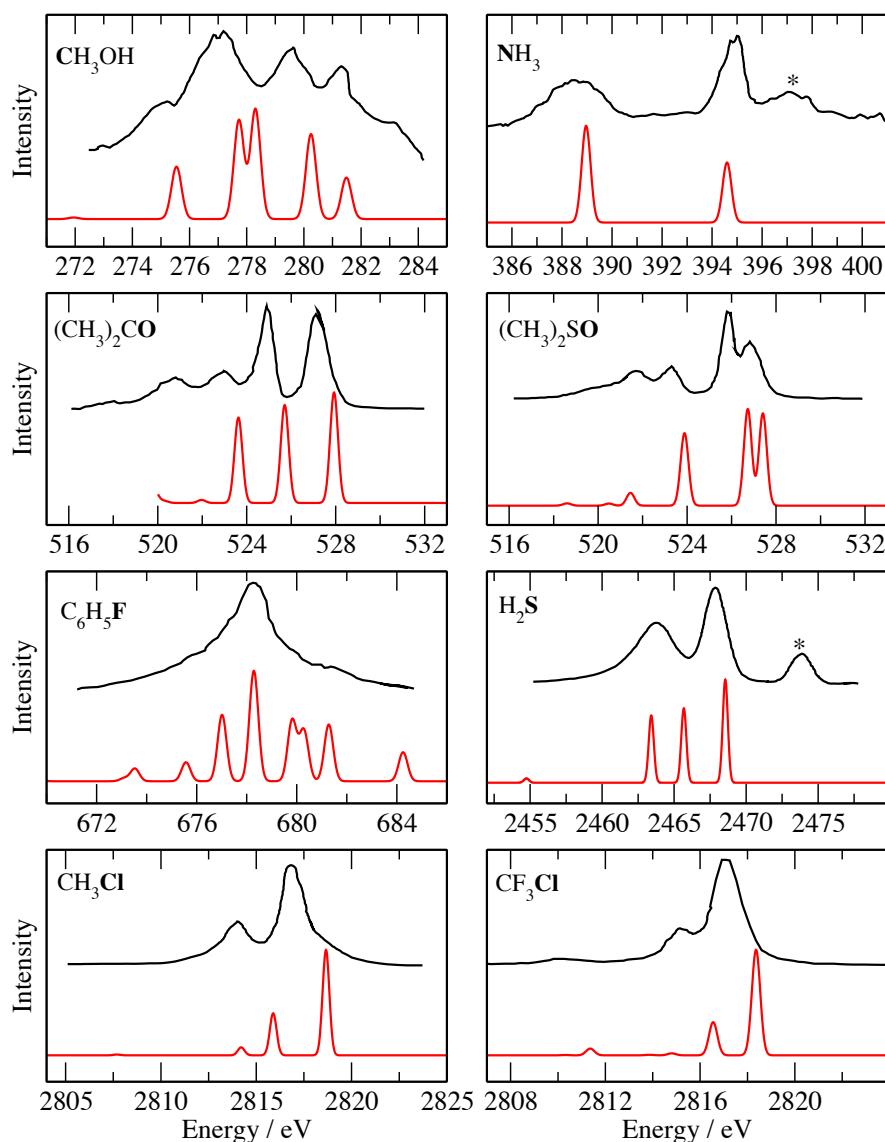


Figure 3.6: Calculated CAM-B3LYP/cc-pCVQZ with energy shift based upon Δ SCF calculation and experimental X-ray emission spectra. Black line: experiment and red line: calculation. * indicates a multi-electron feature.

the design of functionals for XAS and XES is that for X-ray emission the relevant core orbital is unoccupied. This means that the properties of this orbital are being influenced indirectly through orthogonalisation with respect to the occupied orbital space rather than directly for occupied core orbitals, which is the case for X-ray absorption. This could underlie the need for functional parameters that lead to a poor description of the occupied orbitals.

To generate spectra that require no information from experiment we adopt a strategy that is often used in the calculation of X-ray absorption spectra, where an energy shift that is applied to the TDDFT computed spectra.^{199,200} This shift

is determined from a Δ SCF calculation, more specifically, here an extra calculation to determine the ground state energy of the cation is performed. The energy shift is then determined from the difference between the energy of the highest energy transition in the TDDFT calculation and the corresponding transition energy from a Δ SCF ($E_{\text{core-ionized}} - E_{\text{cation}}$) calculation. The resulting spectra for the CAM-B3LYP/cc-pCVQZ calculations are shown in Figure 3.6. The position of the spectral bands agrees well with experiment. There remains an overestimation of the transition energies of about 2 eV for the two chlorine containing molecules. This error may in part be associated with estimation of the relativistic correction which becomes increasingly significant for the chlorine *K*-edge. However, the calculations do show that TDDFT approach does provide a relatively computationally inexpensive method that can be readily applied to give X-ray emission spectra that form a reliable basis to interpret and assign experimental spectra.

3.4 Conclusions

TDDFT provides an efficient approach for the calculation of X-ray emission spectroscopy. In this work the different factors that affect the accuracy of these calculations are explored. Computed spectra evaluated with a large basis set and shifted in energy to align with experiment are in excellent agreement with experiment for the *K*-edge of a range of nuclei. The electronic relaxation of the core orbitals in the intermediate state is an important effect and the neglect of this relaxation leads to spectra that are significantly different from experiment. The calculation of spectra that do not require an additional energy shift to align with experiment is challenging. Investigation of a wide range of available exchange-correlation functionals found the functional predicting emission energies closest to experiment was a short-range corrected functional. However, the calculated emission energies were still systematically too high. Modification of this functional led to a deterioration in the relative energies of the emission bands and worse spectra. Spectra can be calculated by using a Δ SCF calculation of the highest energy transition as a basis to determine the energy shift that needs to be applied. This leads to calculated spectra that provide a reliable description of experiment.

Chapter 4

Simulation of Ultra-Fast Dynamics Effects in Resonant Inelastic X-Ray Scattering of Gas Phase Water

4.1 Introduction

The focus of this chapter is the water molecule and this work has been published in reference 25. X-ray absorption and X-ray emission studies have played a central role in an on-going debate regarding the structure of liquid water,^{4,5,201} which has led to the concept of high density and low density water structures.^{202–204} The first non-resonant XES study of gas phase water was reported by Guo *et al.*²⁰⁵ More recently, gas phase RIXS spectra of H₂O and D₂O were measured with a higher signal to noise ratio and covering a range of intermediate states. Shifts in energy, variation in the relative intensities of the emission lines for different intermediate states and new features associated with dissociated H₂O were observed.⁴³ RIXS studies have also shown that control and selection of vibrational excitation can be achieved by selectively tuning core-excited molecular bands.^{51,206} Gas-phase water often serves as a precursor to examining liquid water and a number of studies have investigated the RIXS of liquid water.^{205,207–211}

Computational simulations can play an important role in understanding and interpreting RIXS spectra measured in experiment. In comparison to calculations of X-ray absorption and emission spectra, the application of quantum chemical based methods to simulate RIXS is considerably less well developed. The previous chapter discussed the method of simulating X-ray emission spectra directly from a Kohn-

Sham DFT calculation. This approach was extended to simulate RXES in a two-step procedure where a reference determinant describing the intermediate core-excited state is used in the Kohn-Sham DFT calculation.^{96,212} It was necessary to average over a number of structures from a molecular dynamics simulation in the core-excited state to achieve agreement with experiment.

RIXS can be simulated based upon the formalism of Kramers and Heisenberg who introduced electronic coherence effects between two photon transitions in atomic systems.⁵⁶ Their formalism was later developed by Gel'mukhanov and co-workers,^{57,59,60} who incorporated consideration of the polarisation anisotropy and channel interference between the excitation and resonant emission processes as discussed in Chapter 1. The interaction between the linearly polarised incident photon, the orientation of the molecule and the transition dipole moments between the core electron excitation and the subsequent collapse of the valence electrons to the core all result in an angular dependence of the intensity of resonant emission and the overall RIXS cross-section. An overview of this approach is available elsewhere.⁵⁸

Calculations of the RXES of liquid water have been reported.^{62,209} These studies use small water clusters to represent different hydrogen bonding environments present in liquid water. The intensities of the bands in the emission spectra were determined using a group theory formalism⁶² and from the p orbital population of the excited atom.²⁰⁹ It has been established that vibrational interference effects can play an important role in X-ray emission spectroscopy,^{213,214} The Kramers-Heisenberg formalism has been used to describe vibrational interference effects in the X-ray emission spectrum of the water dimer, and this work is summarised in the review by Nilsson *et al.*²¹⁵ The intermediate state representation (ISR) within ADC²¹⁶ provides a framework for describing excited states and determining excited state properties.²¹⁷ Very recently, Rehn *et al.*²¹⁸ developed a ADC/ISR scheme to provide a first principles description of inelastic scattering through the integration of complex polarisation propagator theory into the Kramers-Heisenberg (KH) equation. Determining RIXS 'maps' reported in experimental studies⁴³ presents several challenges to quantum chemical based calculations. It is necessary to have a reliable description of the both the excitation and emission processes, the resulting RIXS cross-sections need to be determined via (for example) the KH equation and these intensities need to be combined to give a resulting map. A further complicating factor is that consideration of nuclear dynamics can be important, and the dynamics of the core-excited intermediate state may differ significantly from the ground state. Ideally this should be achieved using approaches that can be applied to relatively large systems. A semiclassical approximation to the KH equation has been

introduced for the modelling of core-hole induced dynamics.²¹⁹ In this approach the initial conditions are sampled from the quantum zero-point position and momentum distributions of the OH vibration and it has been applied to study liquid methanol and ethanol,^{220,221} in addition to water.²¹⁹ Recently, this approach has been extended to consider resonant X-ray emission.²²²

In this study, we simulate the RIXS spectrum of a water molecule using an approach that explicitly considers the intermediate state. The vibrational degrees of freedom are sampled by averaging over structures derived from *ab initio* molecular dynamics (AIMD) simulations²²³ for both the ground and intermediate states and the use of both wavefunction and DFT based methods to describe the absorption and emission processes is explored.

4.2 Method and Computational Details

An overview of the different steps in determining the RIXS maps are as follows, with further details of the calculations described subsequently

1. AIMD simulations are performed for the ground and core-excited states and the structures sampled from each simulation.
2. The absorption and emission energies and associated transition dipole moments are determined using electronic structure calculations.
3. The RIXS intensities for the different absorption and emission energies are determined from the KH equation.
4. Normalised spectra for each structure are fitted to independent 2-dimensional Gaussian functions and summed and renormalised to produce a RIXS map.

Ab Initio Molecular Dynamics Simulations

AIMD calculations were performed using DFT with the B3LYP exchange-correlation functional and aug-cc-pCVTZ basis set. The inclusion of core-valence correlation functions in the basis set has been shown to be important for describing core-excited states.²² The purpose of these simulations is to provide representative structures for the ground and core-excited states. Simulations were performed for the ground state and 4a₁ and 2b₂ core-excited states. It is known that the 4a₁ undergoes ultra-fast dissociation, as a consequence of this and the lifetime of the core-excited state being approximately 3.6 fs, a short simulation time of 3.8 fs is used for 4a₁ and 2b₂ core-excited state simulations. In practice, the life-time of the intermediate state is not fixed and is represented by an exponential decay. Consequently, it is possible for the

intermediate state to have a longer lifetime than the typical 3.6 fs. Furthermore, it is also possible for the water molecule to dissociate on a faster time scale depending on the initial conditions. When comparing the computed spectra with experiment (see later) we also consider the presence of fully dissociated $\text{H}^+ - \text{OH}^-$. The water molecule represents an example of where the nuclear dynamics of the intermediate state are very different from the ground state, making explicit consideration of the molecular dynamics of the core-excited intermediate state necessary. The core-excited state simulations were run using the maximum overlap method (MOM)⁸⁰ to prevent variational collapse. MOM calculations start with an initial guess formed by removing one selected core orbital from the spin-beta space of the converged neutral orbitals and prevents the excited state from collapsing by maintaining maximum overlap of orbitals between successive iterations of the self-consistent field (SCF) procedure. In the application of MOM to study core-excited states it can be useful to consider the overlap with the initial guess, rather than the previous iteration of the SCF calculation.²²⁴ Ground state dynamics were run for a longer simulation period of 13.2 fs, capturing the full extent of the ground state conformations. All simulations were initiated with thermally derived velocities using a temperature of 383 K, consistent with the experimental conditions.⁴³ It has been shown that for dissociative states large zero-point energy in the OH stretch can have a significant influence on the resulting dynamics.²¹⁹ However, in this study we do not explicitly consider sampling of the initial conditions from the quantum distributions. For the DFT calculations, 40 structures were sampled at equally spaced time intervals from each simulation. The different simulation times for the core-excited and ground state dynamics results in time-steps of 0.096 fs and 0.24 fs, for the core-excited and ground state simulations, respectively. For the ADC calculations, only 10 structures were sampled for each simulation owing to the comparatively high cost of ADC calculations. To maximise the extent of conformational sampling and the channel interference between initial and final states, each individual ground state structure was linked to each core excited state structure through the KH equation for both core-excited states. This results in 3200 spectra of unique coordinate combinations for the DFT calculations.

Electronic Structure Calculations

Electronic structure calculations were performed based upon the ADC and DFT methods using the aug-cc-pCVTZ basis set. Within the framework of the ADC method, core-excited states can be determined using the core-valence separation (CVS) approach where the coupling between the valence and core is assumed to be zero. Further details of this method have been reported.^{225,226} Core-excited

states were determined for the ground state structures using the extended second order CVS-ADC (CVS-ADC(2)-x) method as recommended by Neville *et al.*²²⁷ The ground state wavefunction of ADC(2) is calculated by second order Møller-Plesset perturbation theory (MP2). In the approach used here, the resonant emission energies and their associated transition dipole moments were calculated by performing ADC(2)-x on a core excited wavefunction generated by using MOM and MP2. The CVS approximation is not required because the relevant transition energies are negative.

For the DFT calculations, X-ray absorption energies and transition dipole moments were determined for the ground state structures using TDDFT within the Tamm-Dancoff approximation (TDA).⁹⁰ The SRC1-R1 exchange-correlation functional⁸⁶ was used, this functional has been shown to be accurate for core-excited states for a range of systems.²²⁸⁻²³¹ Two different approaches were investigated for the calculation of the emission spectra for the different intermediate states. In the first approach, the emission energies and transition dipole moments are determined directly from the Kohn-Sham DFT calculation using Equations 1.47 and 1.48. It has also been shown that this method gives good agreement with experiment for RIXS spectra when used in conjunction with the B3LYP functional.⁹⁶ In addition, the emission spectra were determined using TDDFT with the TDA and B3LYP functional. In these calculations the relevant core-excited determinant is used as the reference for the TDDFT calculation. All electronic structure calculations were performed using the QCHEM software package.¹⁴⁵ The calculations do not include relativistic effects. For the oxygen K-edge it is common to include a correction of +0.3 eV to account for relativistic effects.²³² This correction has been included in the calculated energies and the one dimensional spectra compared with experiment.

Map Generation

RIXS maps are formed by fitting 2D gaussian functions to the individual peaks of a normalised spectrum. 1600 RIXS maps containing both $4a_1$ and $2b_2$ core-excited intermediate states are generated from the structures sampled from the AIMD simulations. The Gaussian functions are summed on a grid and then the final grid is renormalised. Gaussian broadening of 0.25 eV and 0.30 eV was applied to the excitation and emission energy coordinates respectively in the maps. All 1D spectra presented in this study were broadened by 0.20 eV.

4.3 Results and Discussion

The structural changes that occur during the AIMD simulations have a critical role in the appearance of the simulated RIXS spectra. The lifetime of the core-excited states is of the order of femtoseconds enabling the ultra-fast dissociation phenomena often attributed to core-excited states to be probed. The dissociation of the water molecule in the $4a_1$ core-excited state has been observed in X-ray fragment diffraction and Auger spectroscopy studies.^{233,234} The length of the AIMD simulations for the core-excited states is 3.8 fs which reflects the lifetime of this state, and Table 4.1 summarises the changes in the O-H bond lengths that occur during the AIMD simulations for the $4a_1$ and $2b_2$ core-excited states. For both core-excited states the O-H bond lengths increase during the simulations. In the $4a_1$ intermediate state the lengthening of the bonds is asymmetric with one bond stretching more. This represents the early stages of dissociation and for longer simulations dissociation is observed. We note that the AIMD simulations performed will not account for non-adiabatic effects and hence an accurate estimation of the core-lifetime is not to be expected. In contrast to for $4a_1$, the $2b_2$ state has a more symmetric extension of the bonds. The RIXS spectra that result from sampling the structures from these dynamics simulations will reflect the changing symmetry of the water molecule that occurs during the relaxation in the intermediate state.

Table 4.1: Maximum bond lengths for the $4a_1$ and $2b_2$ core-excited states during a 3.8 fs B3LYP/aug-cc-pCVTZ AIMD simulation and their deviation from the initial equilibrium ground state structure ($r_{OH}=0.962$ Å).

State	Bond	r_{max} / Å	Δr / Å
$4a_1$	r_{OH1}	1.055	0.094
	r_{OH2}	1.170	0.208
$2b_2$	r_{OH1}	1.159	0.194
	r_{OH2}	1.158	0.196

Detailed analysis of the X-ray absorption and X-ray emission spectra of water are reported elsewhere.^{62,209} In the water molecule, the three highest occupied valence orbitals are the $1b_2$, $3a_1$ and $1b_1$ orbitals, while the two lowest unoccupied orbitals are the $4a_1$ and $2b_2$ orbitals. The RIXS spectrum measured in experiment⁴³ considers the two higher energy $2b_1$ and $5a_1$ in addition to the $4a_1$ and $2b_2$ states. In our calculations, the MOM procedure is unable to describe the $5a_1$ state, and in this study we focus on the lower energy $4a_1$ and $2b_2$ intermediate states. The calculation of higher lying states is problematic for this approach, however, progress

in overcoming these limitations is being made.⁷⁴ Table 4.2 shows the core-excitation energies calculated at the equilibrium ground state structure for CVS-ADC(2)-x and TDDFT methods. The CVS-ADC(2)-x values underestimate the experimental values by 1.0 eV however, this underestimation is consistent for the two states. Consequently, the energy difference between the two states is predicted correctly. An advantage of DFT based calculations is that they can be more readily applied to study larger systems, owing to their lower computational cost. TDDFT excitation energies have been computed with the SRC1-R1 exchange-correlation functional.⁸⁶ This functional is designed for the calculation of core-excitation energies and the calculated excitation energies are closer to experiment. Although, the separation between the two states is predicted less accurately.

Table 4.2: Calculated and experimental XAS transition energies (in eV) with the errors with respect to experiment²³⁵ given in parentheses, including a correction of +0.3 eV for relativistic effects.²³²

State	Exp.	CVS-ADC(2)-x	TDDFT: SRC1-R1
4a ₁ (1s→4a ₁)	534.0	533.0 (-1.0)	534.8 (+0.8)
2b ₂ (1s→2b ₂)	535.9	534.9 (-1.0)	536.1 (+0.2)

Table 4.3: Calculated and experimental RXES transition energies (in eV), including a correction of +0.3 eV for relativistic effects.,²³² with the errors with respect to experiment⁴³ given in parentheses. TDDFT emission energies have been shifted by -9 eV.

Intermediate State	Emission Line	Exp.	ADC(2)-x	KS-DFT	TDDFT
4a ₁	1b ₁	526.6	526.2 (-0.4)	526.4 (-0.2)	526.2 (-0.4)
	3a ₁	524.2	523.9 (-0.3)	524.6 (+0.4)	524.0 (-0.2)
	1b ₂	522.1	520.1 (-2.0)	521.6 (-0.5)	522.3 (+0.2)
2b ₂	1b ₁	526.8	526.2 (-0.6)	526.5 (-0.3)	526.4 (-0.4)
	3a ₁	524.6	523.9 (-0.7)	524.9 (+0.3)	524.5 (-0.1)
	1b ₂	520.8	520.2 (-0.6)	521.4 (+0.6)	522.1 (+1.3)

The resonant X-ray emission energies for the two intermediate states are shown in Table 4.3. The ADC(2)-x method tends to underestimate the size of the transition energies. The separation between the different transitions is predicted accurately

with the exception of the $1b_2$ emission line for the $4a_1$ intermediate state. However, as shown later, this state is significantly affected when the dynamics of the intermediate state are taken into account. The KS-DFT values calculated with the B3LYP exchange-correlation functional are in good agreement with the experimental values. This is the computationally least expensive of the three methods and has the potential to be applied to study much larger systems. The transition energies computed with TDDFT are too high owing to self interaction error in DFT,^{93,236} and a shift of -9 eV has been applied to the transition energies shown. Once this shift is applied, the TDDFT calculations provide a good description of the emission energies.

The structures extracted from the AIMD simulations have C_s symmetry, and the orbitals of a_1 and b_1 symmetry will have a' symmetry and b_2 orbitals will be a'' . However, in the calculated RIXS maps we retain the C_{2v} point group labels. The evolving nature of the molecular orbitals and associated transition dipole moments during the molecular dynamics simulations will be reflected in the channel interference and the polarisation anisotropy effects of resonant emission. These effects are important for an accurate description of the RIXS intensity and are described by the KH equation. In a RIXS experiment of a gas-phase sample, the molecules will have random orientation and the incident X-ray beam is linearly polarised by the undulator source with the detector positioned at a fixed angle from the polarisation vector (45 degrees in this case⁴³). The probability of excitation will depend on the relationship between the polarisation vector and the transition dipole moment between the core and unoccupied valence excited state. Furthermore, the intensity of the emission will be dependant on the symmetry of the intermediate state.

The simulated RIXS spectral maps based upon ADC, DFT and TDDFT methods are shown in Figures 4.1-4.3. For each method, maps are presented based upon the single equilibrium structure also when averaging over conformation is included. This allows the effect of nuclear dynamics and the different computational methodologies to be assessed. In the computed RIXS maps, the intensity is color-coded as a function of absorption and emission intensities and can be compared directly with the experimental data reported previously.⁴³ There are a number of features observed in experiment that can be used to assess the accuracy of the computational simulations. For the $3a_1^{-1}$ and $1b_1^{-1}$ states there is a shift to higher energy with increasing excitation energy, while the $1b_2^{-1}$ emission band only has a small shift. This is referred to as the spectator shift and arises from screening effects and from the angular isotropy of the emission process.⁴⁰ The most intense peak in the map is the $1b_1^{-1}$ band for the $2b_2$ intermediate state. A further feature of the maps is the evidence of nuclear dynamics, with additional features visible for the $4a_1$ state.

These features were associated with OH fragments formed following dissociation in the intermediate state.

The ADC RIXS map for a single conformer shows peaks at approximately the correct energies, although the absorption energies are underestimated a little, and correctly predicts the $1b_1^{-1}$ peak for the $2b_2$ intermediate state to be the most intense. However, there is little evidence of spectator shifts. The elastic scattering peaks (participant electron emission) are also described well in terms of their energies and relative intensities. On the inclusion of molecular dynamics some noticeable changes become evident. These are most significant for the $1b_2^{-1}$ emission, where there is a loss of intensity for the $2b_2$ intermediate state and a large degree of broadening of the emission energy for the $4a_1$ intermediate state. Similar broadening is also observed for the elastic scattering lines. There is a small spectator shift in the energy of the $3a_1$ emission band but not for the $1b_1^{-1}$ band.

For the ADC simulations the RIXS maps only a limited amount of conformational averaging was performed. For the computationally less demanding DFT methods, more extensive sampling can be used more readily. Consequently, it is informative to establish how these methods perform for the simulation of RIXS maps. Figure 4.2 shows the RIXS map generated using TDDFT to describe the absorption process and the properties of the emission determined directly from the Kohn-Sham DFT calculation. The map for a single conformation shows that this approach provides a qualitatively correct description. The absorption and emission energies for the spectral bands are consistent with experiment, and the correct peak is identified as the most intense. The largest discrepancy for this method is the energies of the elastic peaks, which are too high. On the inclusion of conformational sampling the peaks are broadened significantly, particularly in the $4a_1$ emission line, and spectator shifts are observed for the $3a_1^{-1}$ and $1b_1^{-1}$ bands. A key observation is that the effects of ultra-fast dissociation are evident in the simulations for the $4a_1$ intermediate state. In the AIMD simulation for the $4a_1$ intermediate state the water molecule is not fully dissociated. The experimental spectrum shows distinct features associated with OH^- arising from a fully dissociated water molecule. We will return to discuss these features later. One potential improvement in the simulation protocol would involve multiple AIMD simulations for the core-excited states, each started at different ground state conformations. Such an approach has been used in AIMD investigations combined with Auger spectroscopy,²³⁷ but would result in a significant increase in computational cost. A more complete sampling of initial conditions has also been given in other studies.²¹⁹ Other avenues for improvements would be the use of high level quantum nuclear dynamical methods such as the variational multi-

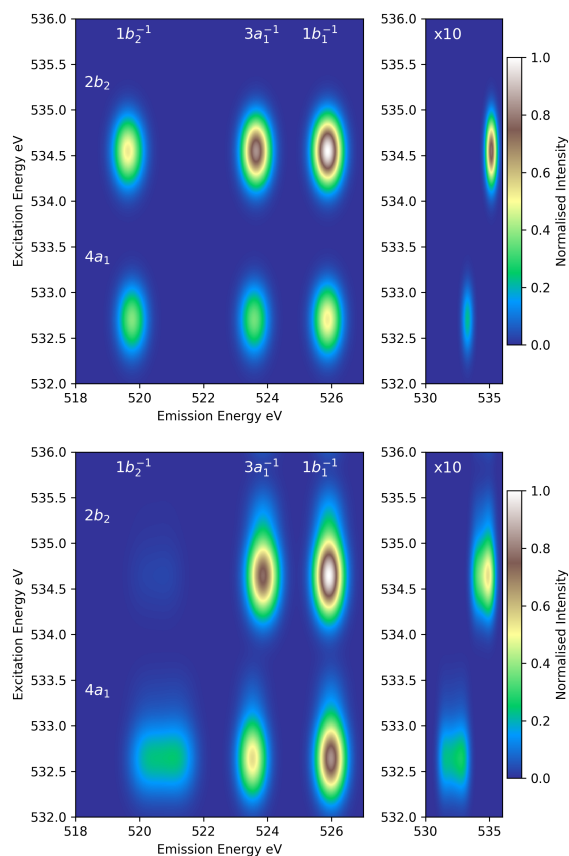


Figure 4.1: Simulated RIXS maps of gas phase water calculated with ADC methods for the equilibrium water structure (top) and sampling structures attained from AIMD simulations (bottom). Left panels shows the inelastic region (spectator emission) and the right panel shows the elastic scattering peaks (participant emission).

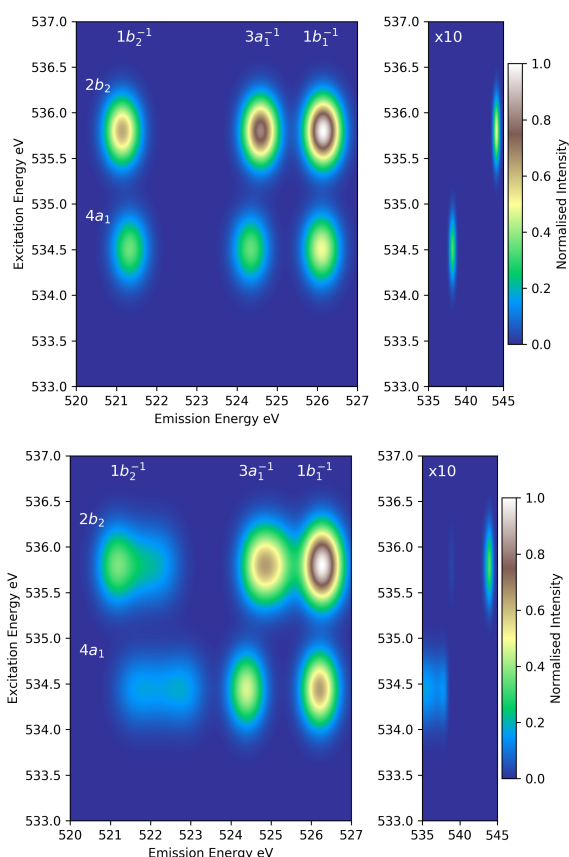


Figure 4.2: Simulated RIXS maps of gas phase water calculated with TDDFT for the absorption and Kohn-Sham DFT for the emission for the equilibrium water structure (top) and sampling structures attained from AIMD simulations (bottom). Left panels shows the inelastic region (spectator emission) and the right panel shows the elastic scattering peaks (participant emission)

configurational Gaussian (vMCG) method.²³⁸

Using TDDFT to describe the emission process also provides a good description of the RIXS maps, with the relative energies and intensities of the peaks predicted accurately (see Figure 4.3). However, the computed energies are systematically too high, which is associated with the self-interaction error present with the B3LYP exchange-correlation functional.⁹³ However, this error is systematic and applying a constant shift to the emission energies of about -9 eV brings the map into alignment with the experiment. An advantage of the TDDFT approach is that the relative energies of the elastic scattering peaks relative to the spectator peaks is predicted correctly.

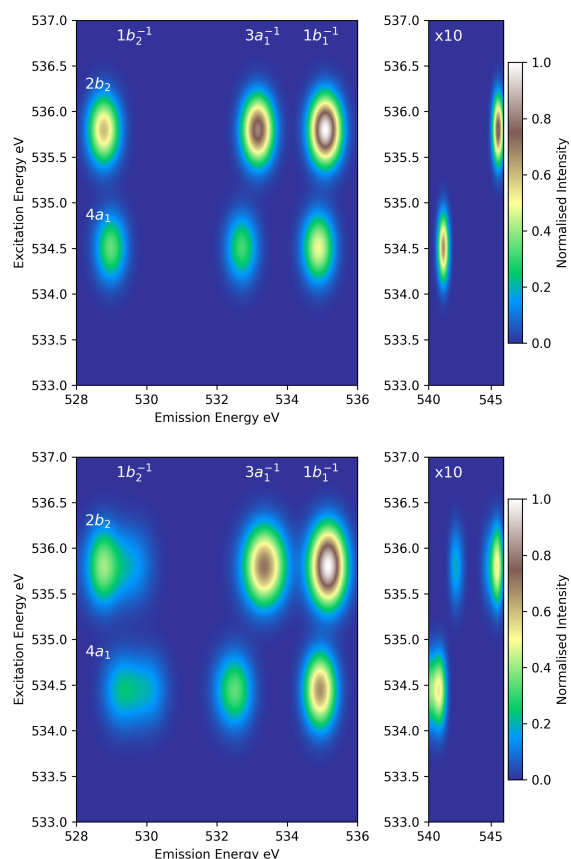


Figure 4.3: Simulated RIXS maps of gas phase water calculated with TDDFT methods for the equilibrium water structure (top) and sampling structures attained from AIMD simulations (bottom). Left panels shows the inelastic region (spectator emission) and the right panel shows the elastic scattering peaks (participant emission)

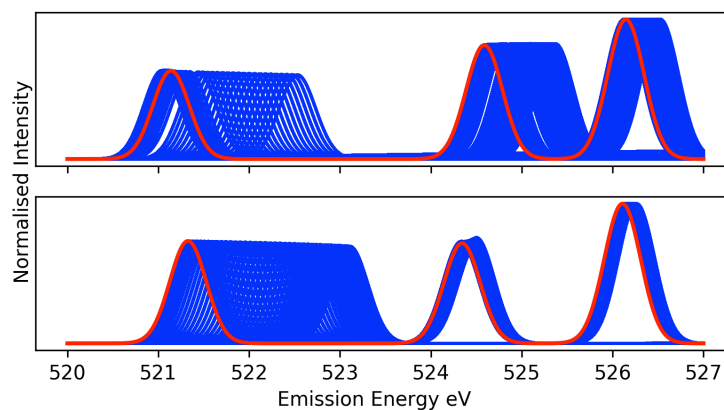


Figure 4.4: Resonant emission spectra for gas phase water computed using Kohn-Sham DFT (B3LYP), comparing single equilibrium conformer (red) against multiple spectra obtained from AIMD simulations (blue). Top: $2b_2$ intermediate state, Bottom: $4a_1$ intermediate state.

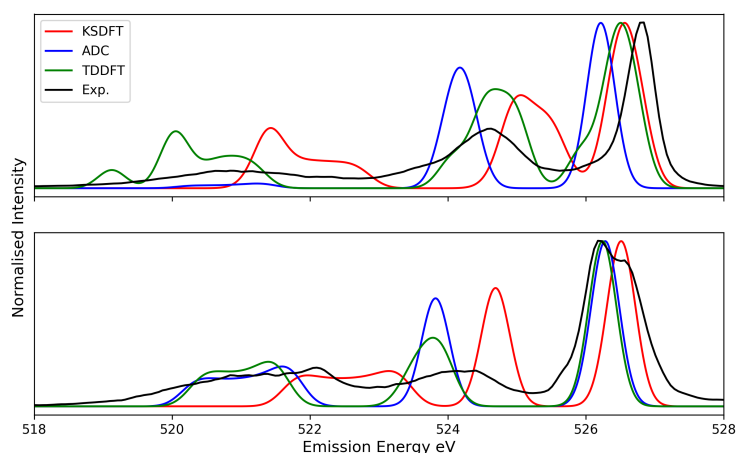


Figure 4.5: 1-dimensional RIXS spectra for ADC, Kohn-Sham DFT and TDDFT methods incorporating conformational sampling. Experimental data from reference 8. Top: $2b_2$ intermediate state, Bottom: $4a_1$ intermediate state.

Figure 4.4 illustrates the variation of the resonant X-ray emission spectra along core-excited trajectories for the $4a_1$ and $2b_2$ core-excited states. The spectra for the dynamics (blue curves) along with the spectra for the ground state equilibrium starting structure (red curve). This shows how the spectra evolve as the structure of the water molecule changes. Data is shown for the Kohn-Sham DFT calculations of the emission, but this is representative of the ADC and TDDFT calculations. A number of observations can be made. Firstly, for all states the emission energies increase as the structure changes in the core-excited state, and this effect is largest for the $1b_2^{-1}$ state. As discussed previously, there is a important difference between the structures in the intermediate $4a_1$ and $2b_2$ states, where in the $4a_1$ state one O-H bond is lengthens significantly and dissociates. The $1b_1^{-1}$ and $3a_1^{-1}$ emission peaks are broadened more in the $2b_2$ state resulting in a greater spectral shift, while the $1b_2^{-1}$ emission peak is more affected for the $4a_1$ state.

Figure 4.5 shows the 1-dimensional RIXS spectra for the two intermediate states along with the experimental data.⁴³ This allows a more direct comparison between the different electronic structure methods used to describe the emission. The TDDFT spectrum has been shifted by -9 eV so that it can be compared with the other methods. Initially we will discuss the $2b_2$ state. Both Kohn-Sham DFT and TDDFT predict the energy of $1b_1^{-1}$ line to be closer to the experimental value than ADC. However, Kohn-Sham DFT underestimates the energy separation between $1b_1^{-1}$ and the lower energy bands, while TDDFT predicts the energy of these bands accurately. All three methods show significant broadening of the $1b_2^{-1}$ band. For the $4a_1$ state, experiment shows two bands for the $1b_1^{-1}$ line. The higher energy of these corresponds to $1b_1^{-1}$ while the lower energy component was proposed to arise from

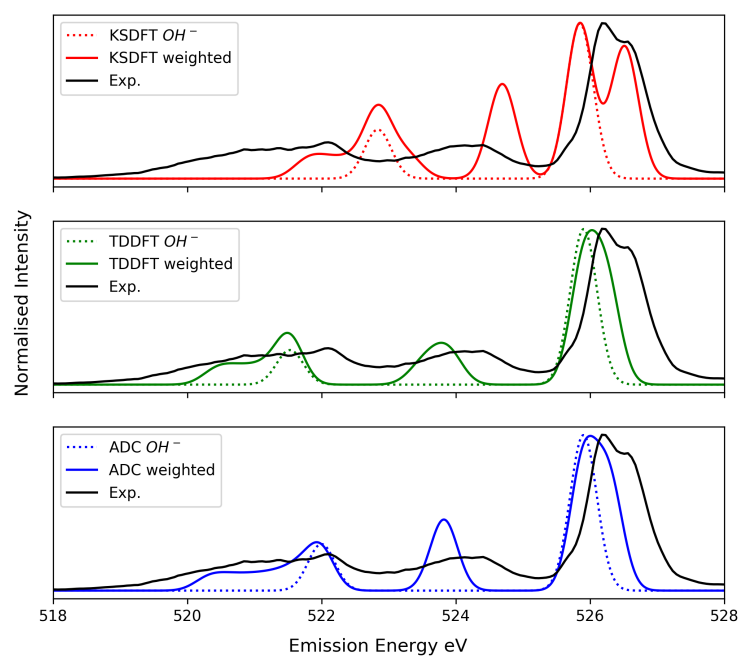


Figure 4.6: 1-dimensional RIXS spectra for the $4a_1$ intermediate state computed with Kohn-Sham DFT (upper panel), TDDFT (middle panel) and ADC (lower panel) methods. Broken lines show the spectra for OH^- and the solid lines the weighted spectra for 25% of the H_2O being dissociated. Experimental data from reference 8.

the $1e^{-1}$ emission of OH^- following dissociation. The Kohn-Sham DFT $1b_1^{-1}$ band agrees well with experiment, but similar to the $2b_2$ state the separation with the lower energy bands is underestimated. Both ADC and TDDFT predict the energy of the bands in quite good agreement with experiment, with the main discrepancy being the energy for $1b_1^{-1}$ is too low. The experimental data suggests that to achieve a complete description of the $4a_1$ state requires consideration of OH^- . Figure 4.6 shows the spectra for the three methods that include 25% of OH^- . This proportion of OH^- was chosen to achieve the correct relative heights of the two components of the $1b_1^{-1}$ band. OH^- gives bands at about 526 eV ($1e^{-1}$) and 522 eV ($3a_1^{-1}$). A further consequence of introducing OH^- is that the relative intensity of the $3a_1^{-1}$ band is reduced since OH^- does contribute at this energy, and this has the effect of improving the computed spectra. Overall, once a constant energy shift is applied to the emission energies, TDDFT provides an accurate description in comparison with experiment and ADC. The magnitude of this shift can be determined from comparison with ΔSCF calculations, which means that TDDFT provides a potentially accurate approach that can be applied to study larger systems.

4.4 Conclusions

This study has shown how soft inelastic scattering maps can be simulated through a combination of electronic structure X-ray spectroscopy calculations and AIMD, with the RIXS intensities evaluated using the Kramers-Heisenberg formalism. Incorporating averaging over conformation, explicitly considering the core-excited intermediate state, is necessary to achieve an accurate representation of experimental data. For the water molecule, spectator shifts in the emission bands are observed and evidence of ultra-fast dynamics, particularly for the dissociative $4a_1$ state are observed. The three approaches used to describe the emission process, namely ADC(2)-x, Kohn-Sham DFT and TDDFT with the B3LYP exchange-correlation functional all provide a similar response to the nuclear dynamics. The DFT methods are computationally less expensive and can be more readily applied to study large systems and to incorporate extensive conformational sampling. Once a constant shift is applied to the emission energy scale, TDDFT is able to describe both inelastic and elastic scattering, while for Kohn-Sham DFT no energy shift is required but the energy of the elastic scattering bands are not predicted accurately. Furthermore, Kohn-Sham DFT tends to underestimate the energy separation between the $1b_1^{-1}$ band and the lower energy bands. For the $4a_1$ state good agreement with experiment can be achieved if a proportion of dissociated water molecules (OH^-) is included. Consequently, TDDFT provides a potentially accurate approach that can be applied

to study larger systems. The challenge for the methodology is the MOM procedure can fail to prevent variational collapse for high lying core-excited states and progress in this aspect is required to improve the robustness of the approach.

Chapter 5

Observations of Double Excitations in the Resonant Inelastic X-ray Scattering of Nitric Oxide

5.1 Introduction

One heteronuclear diatomic molecule yet to be studied by RIXS, is nitric oxide (NO). NO is a stable open-shell molecule with a $X^2\Pi$ ground state and is important in many chemical and biological processes including the formation of smog and acid rain, the depletion of ozone in the atmosphere, and it has a role in the control of blood circulation, nerve transmission and the function of the immune system.²³⁹ Furthermore, the selective catalysis of nitric oxide to oxygen and nitrogen is an active area of research as no by-products are produced.²⁴⁰ The complex electronic structure of nitric oxide is less well understood than other diatomic species due to its ground state radical nature. The electronic spectrum of NO in the UV region has been studied in detail.^{241–243} The $\pi \rightarrow \pi^*$ transition leads to set of valence excited states including $B^2\Pi$, $L'\Psi$ and $L^2\Pi$, while excitation to the $3s$ and $3p$ Rydberg orbitals gives $A^2\Sigma^+$, C^2 and $D^2\Sigma^+$ states.

There have been fewer studies focused on the core-excited states of NO. The X-ray absorption spectrum of NO at the nitrogen K-edge has been measured using electron energy-loss spectroscopy^{244,245} and also in a high resolution photoionization study.²⁴⁶ The spectrum is dominated by an intense band at approximately 400 eV arising from the $1s \rightarrow \pi^*$ transitions with weaker bands at higher energies arising from transitions to Rydberg states. The $1s^{-1}\pi^{*2}$ electron configuration gives rise

to four electronic states, namely $4\Sigma^-$, $2\Sigma^-$, 2Δ and $2\Sigma^+$, shown in Figure 5.1, and transitions to the doublet states contribute to the intense band. There has been some debate regarding the energy ordering of these three doublet states, but high level calculations suggest the order is, from low to high energy, 2Δ , $2\Sigma^-$, $2\Sigma^+$.²⁴⁷ There is a significant lengthening of the bond in these core-excited states relative to the ground state, and vibrational structure is observed. Vibrationally resolved X-ray absorption spectra for NO at the oxygen K-edge have also been reported.²⁴⁸ Theoretical simulations of the absorption and de-excitation spectra associated with the $1s \rightarrow \pi^*$ transitions have been reported²⁴⁷ using potential energy surfaces determined from the multiconfiguration reference coupled electron pair approximation. The calculations gave good agreement with the experimental core-excitation energies. Other studies have measured the angular distribution of the nitrogen K-edge photoelectron ionization and Auger decay of NO.^{249,250} An early study identified a broad dissociative region around 404 eV as associated with the $2p\sigma^*$ state.²⁵¹ However, a recent theoretical study using the non-orthogonal configuration method proposed that this feature belongs to a doubly excited state.²⁵²

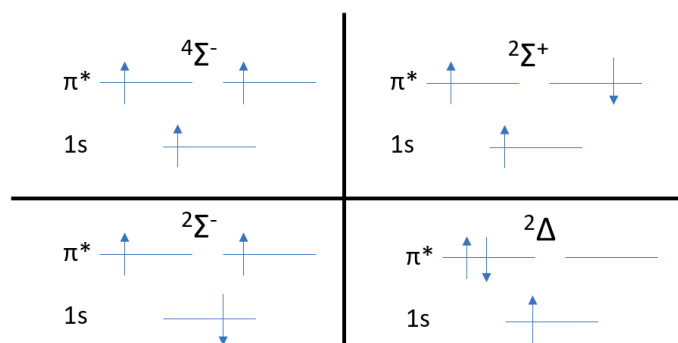


Figure 5.1: Four states of the $N1s^{-1}\pi^{*2}$ orbital configuration.

This combined experimental and theoretical study applies RIXS to a heteronuclear diatomic open shell species for the first time. A detailed picture of the core-excited electronic structure of NO and insight into the processes that occur on the lifetime of the core-excited states is provided. The measured RIXS map is interpreted using simulated maps based upon multiconfigurational perturbation theory calculations allowing the observed features to be assigned to electronic states. The results reveal the presence of doubly excited states and evidence in the form of simulated RIXS maps and potential energy curves suggest that these could arise from non-adiabatic dynamics occurring in the core-excited intermediate state.

The numerous near degeneracies between the excited states of NO present a

complicated picture of the RIXS and further insights are gained. Herein, we present an extensive review on the excited states of NO and provide RIXS maps, potential energy curves and XAS, XES and RXES spectra.

5.2 Computational and Theoretical Details

5.2.1 RIXS Electronic Structure Calculations

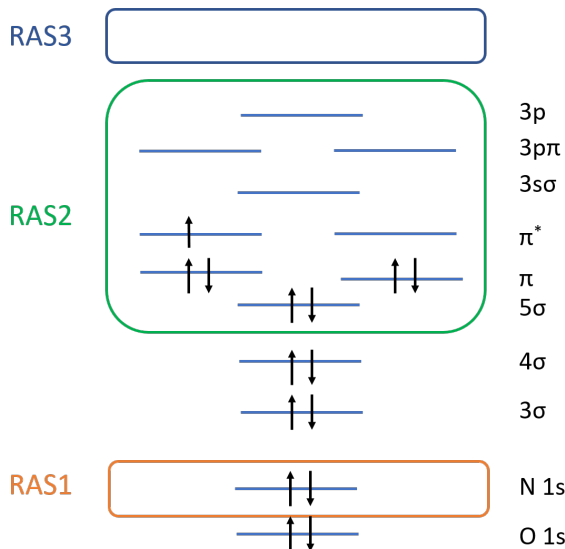


Figure 5.2: MO diagram depicting the wave-function used in the RASSCF calculations.

There have been a number of single determinant methods for simulating RIXS in the literature, including EOM-CCSD¹⁰⁶ ISR/ADC²¹⁸ and TDDFT.⁹⁵ However for diatomic molecules the electronic state is characterized by the projection of the total orbital angular momentum onto the molecular z-axis and has reflection symmetry in the plane containing the internuclear axis, therefore single-determinant approaches will not provide an accurate description of the RIXS. NO further requires a multi-reference treatment as a result of the open shell nature and near degenerate spin configurations. All states involved in the RIXS calculations have been calculated by the restricted active space self consistent field (RASSCF)²⁵³ method and the state energies improved via addition of dynamical correlation using restricted active space second order perturbation theory (RASPT2).^{253,254} Transition dipole moments between states were computed using the restricted active space state interaction method (RASSI).^{255,256} All restricted active space methods have been performed using the Molcas 8.2^{257,258} software package. The calculation details follow a similar protocol to previous RIXS studies.^{46,50,51,55,206} The RASSCF wavefunction is shown

in Figure 5.2. The active space of the wave-function was built by placing the nitrogen 1s orbital into RAS1 and restricting the maximum number of electron holes to one. The oxygen 1s orbital was frozen and to further reduce computational cost and simplify analysis of the final states, the 3σ and 4σ orbitals were frozen at the Hartree-Fock level. The remaining doubly occupied 5σ , π and π orbitals and the singly occupied, π^* anti-bonding orbital were placed in RAS2 (full configuration interaction active space). In addition, the unoccupied π^* anti-bonding and Rydberg $3s$, doubly degenerate $3p_\pi$ and $3p_\sigma$ orbitals were included in the active space. and the overall level of theory for computing the RIXS states can be represented as RASPT2(9,1,0;1,9,0). This uses the RAS($n,l,m;i,j,k$) representation¹⁰⁸ where, n , l and m refer to total number of active electrons, the maximum number of holes allowed in RAS1 and the maximum number of electrons in RAS3 respectively, and i , j and k refer to the number of MOs in RAS1, RAS2 and RAS3. No symmetry was used, however the N 1s orbital was locked into an individual sub-symmetry group to prevent orbital rotation and the highly-excited-state scheme (HEXS)¹⁰⁸ was applied to eliminate doubly occupied N 1s states and force the generation of core hole states when required. Scalar relativistic effects are included via the combination of the second order Douglas-Kroll-Hess (DKH) Hamiltonian^{259,260} and the atomic mean field (AMFI) approximation.²⁵⁶ The relativistic ANO-RCC-VTZP basis set²⁶¹ was used and to describe Rydberg orbitals, an additional ANO-RCC-VDZP (8s8p8d) diffuse basis fixed at the NO cation centre of charge function was augmented to the basis set.

In order to capture the necessary states, two state averaged calculations containing 30 core-excited intermediate and 30 valance excited final states were computed in the RASPT2 and RASSI methods. Due to the bi radical nature of nitric oxide’s excited states, resulting in multiconfigurational spin states, and the diffuse nature of Rydberg orbitals; state classification of this system is non trivial. A combination of orbital, orbital occupation number, angular momentum analysis and KH intensities were used to correctly couple intermediates states to their corresponding final states.

5.2.2 Calculating the XES spectra with EOM-CCSD and AIMD

Here we detail rational to the methodology behind the non-resonant emission spectra shown in Figure 5.4 c). The electronic structure of states involved in the non-resonant XES spectra of NO are less complex than the RIXS and single determinant EOM-CCSD methods sampled over core-ionised nuclear dynamics have been used with a core-hole reference state generated by MOM.

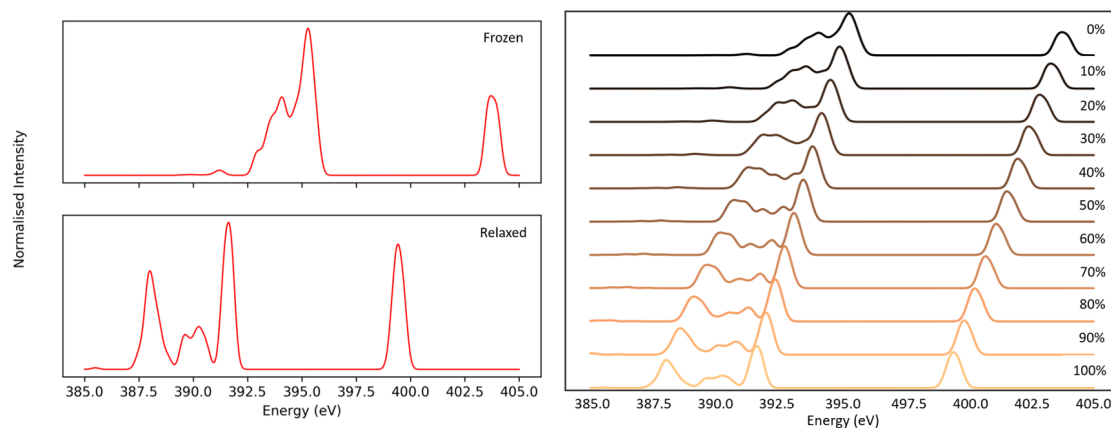


Figure 5.3: EOM-CCSD calculated X-ray emission spectroscopy calculations as a percentage of core hole relaxation. Calculated by sampling over conformers of core ionised AIMD dynamics. Spectra are broadened by 0.25 eV.

Both α and β spin core ionisation need to be considered as the two spectra differ depending on the spin of the unpaired π^* electron, fixed to α spin. There Core ionised AIMD simulations were ran separately for the α and β ionised cases using MOM to generate the core-hole and DFT-B3LYP with the aug-cc-pCVTZ basis set employed to generate the trajectory forces. The dynamics were ran over 250 timesteps with a timestep of 1.92 fs. 22 structures were sampled for both runs and a bond displacement of 0.082 Å was sampled for the alpha core ionised state and displacement of 0.080 Å sampled for the beta core ionised state. EOM-CCSD calculations were performed with a reference core-ionised state generate by MOM. In chapter 3, core-hole relaxation via MOM improved the simulated spectra for all molecules involved in the study. This is not the case however for NO. In Figure 5.3, the left two panels shows the spectra calculated when the core hole was not relaxed via MOM (frozen). The bottom panel shows the spectra calculated when the core ionised state was fully relaxed via MOM. The frozen spectra resembles the experimental spectrum more than the relaxed spectra. Though neither produce an accurate result, the frozen calculation overestimates the π emission (highest energy emission peak) whilst the relaxed spectra underestimates. To understand how much core relaxation is required to accurately simulate the non-resonant XES spectra for NO, the right side of Figure 5.3 explores what percentage of core hole relaxation is required to reproduce the experimental spectra. It is shown that going above 50% core relaxation distorts the spectra and separates the energies of the 5σ and π emission lines, whilst 20% core hole relaxation accurately describes the effect of core-hole relaxation in the experiment; this value was used in the non-resonant XES spectra in Figure 5.4 c).

5.3 Results and Discussion

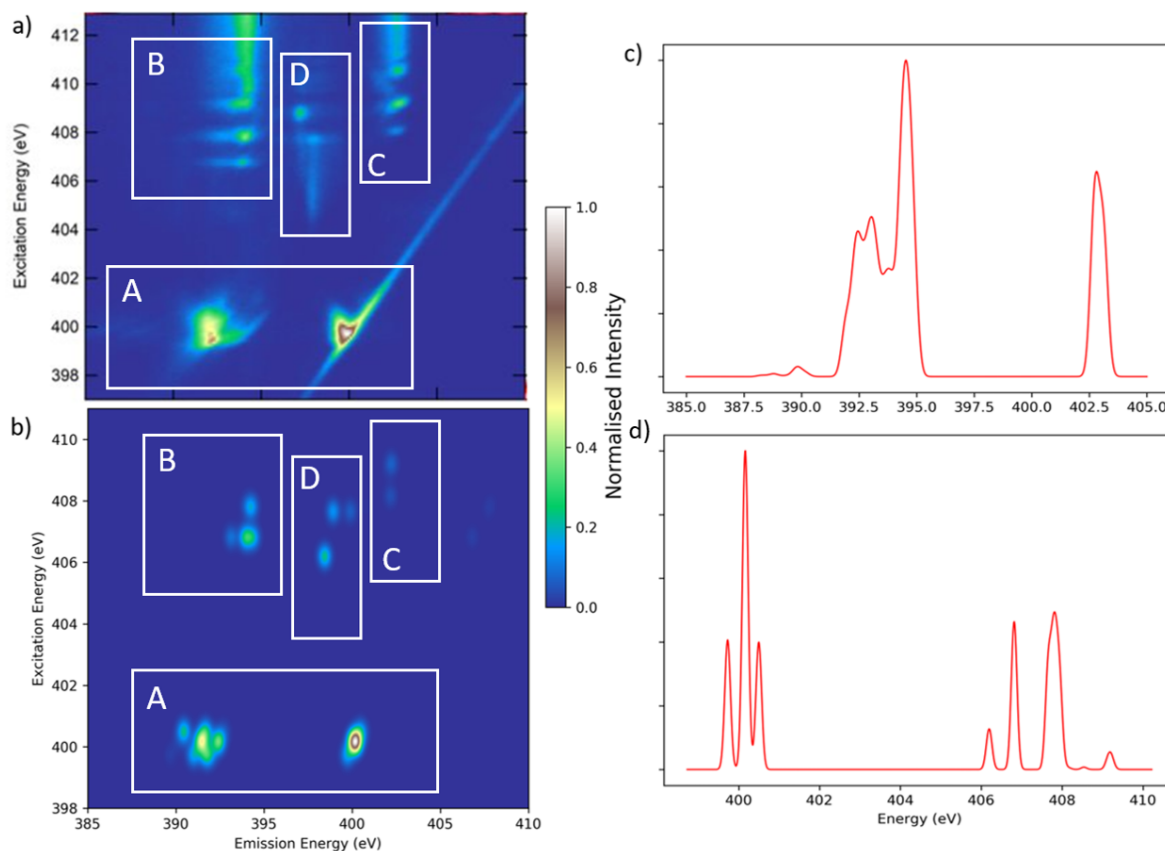


Figure 5.4: a) Experimental nitric oxide RIXS map b) Map simulated by RASPT2 at the ground state equilibrium bond length. The intensities in the region above 404 eV excitation energy have been amplified by a factor of 10. c) XES spectra calculated by MOM-AIMD-EOM-CCSD, gaussian broadening of 0.25 eV and 20% core hole relaxation used. d) XAS spectra calculated by RASPT2 and used in the generation of RIXS map, presented with gaussian broadening of 0.1 eV.

Figure 1 shows the measured RIXS map for gas-phase NO (a). This map was measured by Lothar Wheindhart, Linsey Sietz and Clemens Heske and provided to our group for assistance in the analysis of complex spectral features; which forms the topic of discussion in this chapter. Below in (b) is the simulated map based upon ab initio calculations (b). A number of distinct features are evident in the map, and the different regions of the map have been labelled A-D. To achieve an accurate description of the ground, excited and core-excited states the RASSCF method had been used, with the state energies improved via addition of dynamical correlation using RASPT2 and the RIXS intensity evaluated using the Kramers-Heisenberg formalism. The simulated spectrum is in good agreement with experiment and provides a good foundation for a detailed analysis of the observed peaks.

Region A is dominated by two intense and broad bands at an adsorption energy of about 400 eV and with emission energies of about 400 eV and 392 eV. This is the region of the spectrum that has been most well characterized. The peak at 392 eV corresponds to inelastic scattering and arises from the $1s \rightarrow \pi^*$ excitation which gives the $N1s\pi^{*2}$ electron configuration leading to $^2\Delta$, $^2\Sigma^-$, $^2\Sigma^+$ states, we note that we do not consider $^4\Sigma^-$ state since this does not have significant intensity. The calculated excitation energies and XAS spectrum for these states are given in Table 5.1 and Figure 5.4 respectively and agree well with the experimental spectrum and predict an energy ordering of the states consistent with previous multiconfiguration reference coupled electron pair approximation calculations.²⁴⁷ The broad and non-symmetric nature of the observed experimental band is also reflected in the simulated spectrum. This can be largely attributed to the energy separation of these states which is calculated to be 0.8 eV, with further broadening arising from nuclear dynamics. The peak comprises six contributions arising from emission from π and 5σ orbitals for the three $N1s\pi^{*2}$ states. These emission energies are also given in Table 5.1 and show the emission energy for the π orbital to be greater than for the 5σ orbital for all three of the states. The multiple contributions to this feature are consistent with the non-symmetric feature observed in experiment. In the simulated spectrum distinct contributions to this band are evident, however, some additional broadening may arise from nuclear dynamics which are not accounted for in the simulation. These states also demonstrate the need for a multiconfigurational description of the electronic structure since single determinant-based methods do not adequately describe the energy separation between these states.²⁵²

Region B of the experimental map contains a broad band that lies at an emission energy of about 394 eV. Distinct bands are observed between excitation energies of 407 eV and 408 eV, then a continuous band is present above 409 eV. Region C is similar but occurs at an emission energy of 402 eV with the first band observed at an excitation energy of 408 eV. The simulated spectrum also predicts peaks in these regions which correspond to intermediate states arising from $1s \rightarrow$ Rydberg excitations. In the simulated spectrum only excitation to the $3s$, $3p_\pi$ (Rydberg p orbitals perpendicular to internuclear axis) and $3p_\sigma$ (Rydberg p orbital parallel to internuclear axis) are included and consequently will only capture the lower excitation energy parts of the experimental features. Excitation to these Rydberg orbitals generates a large number of potential intermediate states. Excitation to the $3s$ and $3p_\sigma$ orbitals will lead to three $^2\Pi$ states and one $^4\Pi$ state each. Whereas excitation to the $3p_\pi$ orbital will give six doublet states (three $^2\Delta$, two $^2\Sigma^+$ and $^2\Sigma^-$), in addition to two further quartet states. This results in a total of twelve doublet intermediate

Table 5.1: Calculated absorption and emission energies (in eV) by RASPT2.

State	Absorption	π^*	π	5σ
$^2\Delta$	399.7	399.7	391.7	391.0
$^2\Sigma^-$	400.2	400.2	392.4	391.4
$^2\Sigma^+$	400.5	400.5	391.7	390.5
D_1	406.2	397.4-398.4		
$R_1(3s)$	406.8	400.8	394.4	394.0
D_2	407.7	398.8-399.9		
D_3	407.7	398.8-399.9		
$R_2(3p_\pi)$	407.8	400.8	394.3	394.0
$R_3(3p_\sigma)$	407.8	400.8	394.2	394.2
$R_4(3p_\pi)$	407.9	400.9	394.3	394.0
$R_5(3p_\pi)$	408.0	401.0	394.4	394.0
D_4	408.0	399.1-400.2		
$R_6(3s)$	408.0	402.0	394.3	395.1
$R_7(3s)$	408.2	402.2	394.5	395.3
$R_8(3p_\pi)$	409.2	401.2	395.6	394.4
$R_9(3p_\pi)$	409.5	401.6	395.0	394.6
$R_{10}(3p_\pi)$	409.5	401.6	395.0	394.6
$R_{11}(3p_\pi)$	409.1	402.1	395.5	395.3
$R_{12}(3p_\sigma)$	409.1	402.1	395.5	395.5
$R_{13}(3p_\sigma)$	409.1	402.1	395.5	395.5
$R_{14}(3p_\pi)$	409.2	402.2	395.7	395.4

states included in the simulations. Here we denote the Rydberg states which arises from the $1s \rightarrow \theta$ transition as $R_i(\theta)$, where θ is a Rydberg orbital, and the calculated absorption and emission energies for these states are summarized in Table 5.1.

The simulated map predicts bands arising from the Rydberg intermediate states consistent with features observed in experiment. In particular, the lowest energy feature in Region B is associated with emission from the 5σ and π orbitals for the intermediate state arising from the $1s \rightarrow 3s$ transition, while the feature at higher energy is predominantly associated with the Rydberg $3p_\pi$ and Rydberg $3p_\sigma$ intermediate states. Higher excitations energies will lead to higher energy Rydberg states, however, these are not included in the calculations. The lowest energy band in Region C lies at an excitation energy of about 408 eV, this is associated with π^* emission for

the Rydberg $3p_\pi$ and Rydberg 3σ intermediate states, and both in experiment and the simulation the emission from this orbital for the lowest energy Rydberg $3s$ intermediate state is not evident. Other features are also reproduced by the calculations, notably the emission energies for the Rydberg states are approximately 2 eV higher than for the valence states in region A, this is a consequence of screening effects. In addition, the spectator effect of the Rydberg electron to the occupied ground state is present as there is little overall red shift in the emission energies for the Rydberg states. As the core excitation to Rydberg states increases they converge towards the XES spectra. The screening effect by the core-excited electron to the ground state occupied orbitals is reduced and the core-excited electron acts as a spectator in the emission process,⁵³ as the excitation energy approaches the ionisation threshold.

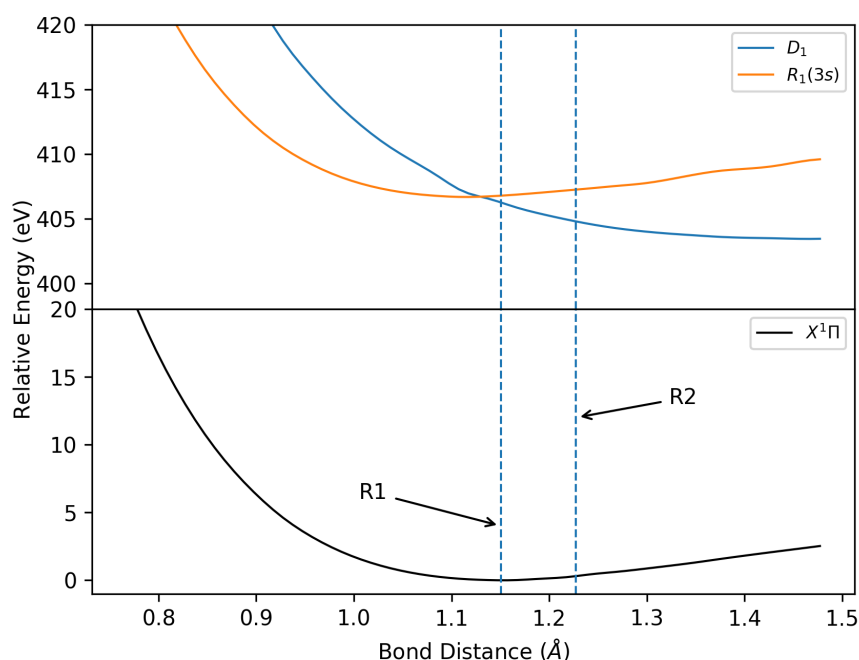


Figure 5.5: Calculated RASPT2 ground and core-excited potential energy curves, R1 is the ground state equilibrium bond length (1.151 Å) and R2 (2:1.228 Å) is an extended bond length.

Region D lies at emission energies of about 397 eV where the experimental map shows a striking vertically broadened feature at this energy. Within a single electron excitation and emission framework there are no transitions that are predicted to lie this region indicating a more complex explanation for the origin of these features. The simulated map does show peaks with significant intensity in this region which arise from doubly excited states, which correspond to $1s \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ excitations. The large number of possible doubly excited states makes a comprehensive account of all these states beyond our calculations and Table 5.1 shows four relevant doubly

excited states included in the simulation (denoted D_i). In the context of NEX-AFS spectroscopy there has been some discussion of the nature of the states in this energy region and earlier work has assigned them to a dissociative $1s \rightarrow 2\sigma^*$ transition.²⁵¹ However, our calculations are consistent with a recent theoretical study²⁵² in their assignment to doubly excited states. These two-electron one-photon states are not optically bright in the single excitation picture and in order to investigate on how these states are generated we consider potential energy curves for the low-lying core-excited states, which are shown in Figure 5.2. The key feature of these curves is a crossing between the $R_1(3s)$ and D_1 , states directly in the vertical excitation region. This suggest that the D_1 state could be readily formed from excitation to $R_1(3s)$, followed by crossing to the D_1 state via a conical intersection. Furthermore, the potential energy curves show the D_1 state to be dissociative, which is possibly a consequence of there being three electrons in the π^* anti-bonding orbitals. This suggests that this doubly excited state is present in the RIXS map as consequence of an ultra-fast non-adiabatic process.

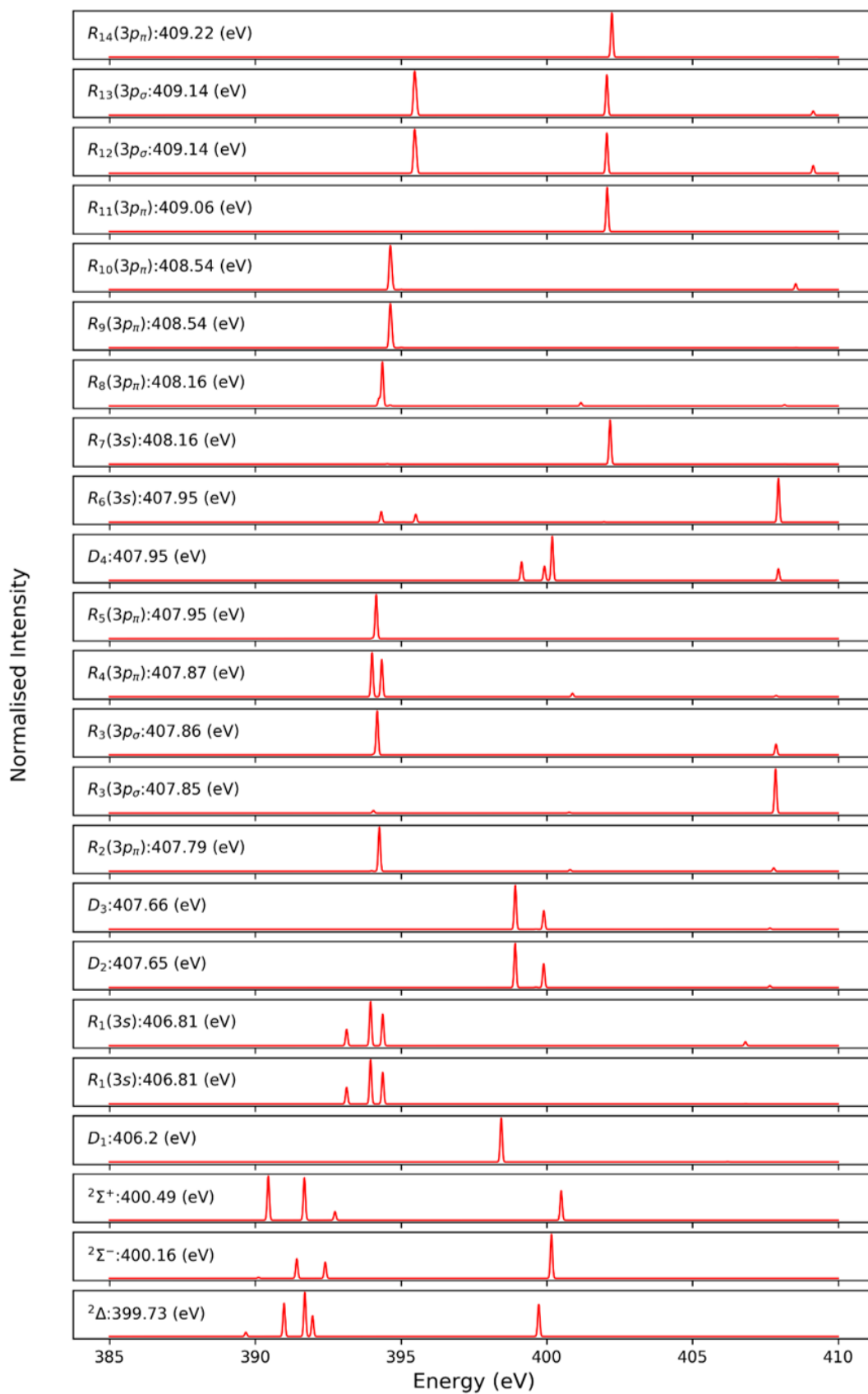


Figure 5.6: RASPT2 RXES spectra for intermediate states contributing to the simulated RIXS map in Figure 5.4.

The transition dipole moments calculated between Rydberg and doubly excited states are relatively low compared to transition dipole moments associated to the $1s \rightarrow \pi^*$ excitation, as a result many of the calculated peaks do not appear in the map, despite all the peaks above 404 eV being amplified by a factor of 10. In order to generate a spectral overview of all possible intermediates in the RIXS, including peaks not appearing in the simulated map, but potentially contributing to experimental features, RXES spectra for each intermediate calculated are presented in Figure 5.6. This presents a 1-dimensional picture of the regions highlighted in the maps, as the spectra are ordered from lowest (bottom) to highest (top) excitation energy. It can be observed that the $R_1(3s)$ intermediate has three peaks as there are two peaks for the π emission. The peak of highest intensity was included in Table 5.1 and this highlights the complexities associated with open-shell linear molecules in RIXS studies. One reason for this energy split, may stem from whether the emitting π orbital is perpendicular or parallel to the singly occupied π^* orbital.

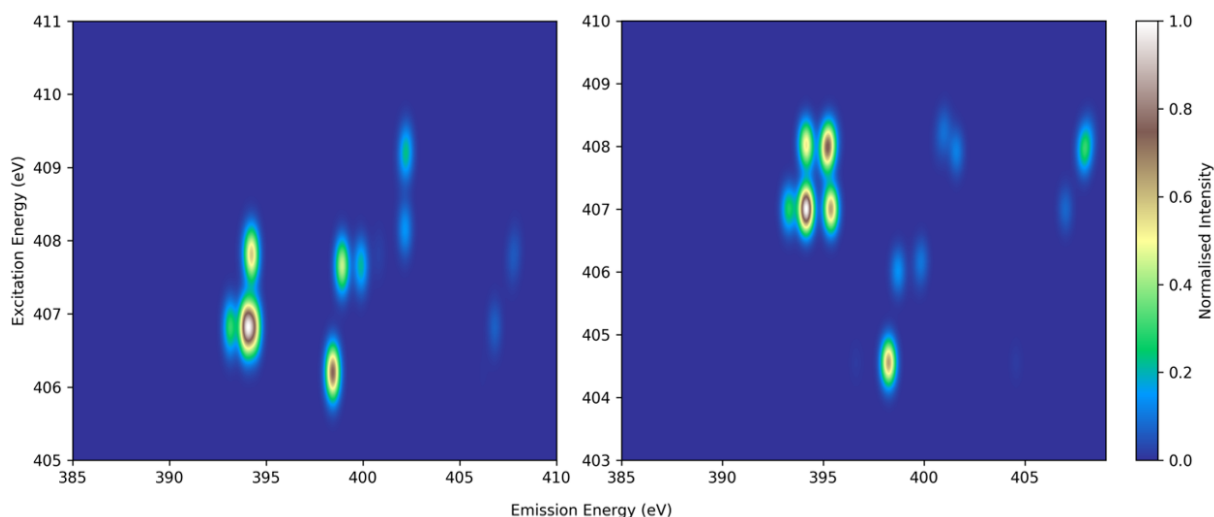


Figure 5.7: Simulated RIXS maps for the Rydberg and double excitations at the ground state (left) and extended bond lengths (right).

We now explore the dissociative nature of the D_1 state in more detail. In the experimental map the feature arising from the double excitations shows a significant vertical broadening. Figure 5.7 shows simulated RIXS map for this region based upon the ground state bond length R_1 and also an extended bond length R_2 . The maps show that the excitation energies of the Rydberg states are not greatly affected by the increase in the bond length, however, the energy of the D_1 state is lowered significantly which correlates with the vertical broadening of this feature. The inelastic region of the valence region of the maps show a distinct blue shift of the π emission in the $^2\Sigma^-$ intermediate between present in both R_1 and R_2 and is enhanced by an increase in bond length. This behaviour can be correlated to a

similar feature in the experimental map. The rationalisation of this, provided by the calculations, is shown in the energy level diagram in Figure 5.8. The ordering of the states with respect to the orbital angular momentum quantum numbers differs between the intermediate and final states. The consequence is that the $^2\Pi$ state corresponding to a π emission in the $^2\Sigma^-$ intermediate is at a lower energy than the $^2\Phi$ final state corresponding to π in the $^2\Delta$ intermediate. The broadening in the experimental map in this region indicates that it is clear that the bond length has an effect on the energy separation with respect to the interplay of spin and angular momentum in the electron correlation of excited states in open shell linear molecules.

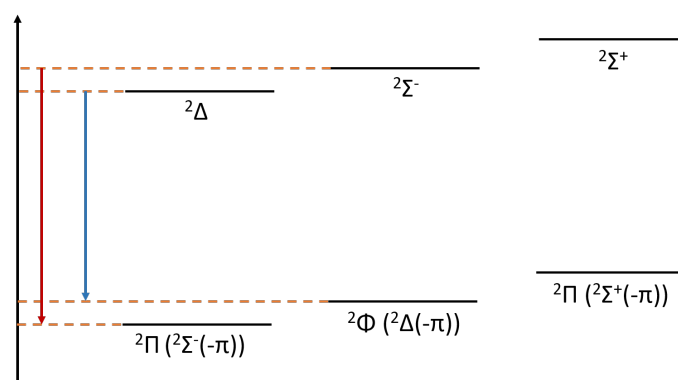


Figure 5.8: Energy level diagram (not to scale) of the core excited valance intermediate states and corresponding final states when an electron from a π orbital collapses to the ground state.

5.4 Conclusions

This study has combined both experiment and theory to extensively map the core and valence excited states of Nitric Oxide concerning both the valence and Rydberg orbitals of the system. It is the first RIXS study on an open shell linear molecule and has provided many new insights into the electronic structure and nuclear dynamics of NO. The presence of doubly excited core excited states in the experimental map was identified by the calculations. Evidence has been provided by RASPT2 calculated potential energy curves and by simulating the map at an extended nuclear geometry, for the contribution of these doubly excited states to the striking vertical broadening feature in the map. The mechanism for this features appearance in the absorption measurement has not yet been fully identified. This study has proposed evidence of ultra-fast non-adiabatic state crossing followed by dissociative nuclear dynamics. There is an ongoing investigation into this spectral phenomena that will involve non-adiabatic nuclear dynamics simulations.

Chapter 6

Conclusions

This research has shown that a variety of X-spectroscopy methods can be accurately and efficiently simulated using of quantum chemical techniques. Particularly when careful considerations are made.

In particular “black-box” single determinant quantum chemical methods, both wavefunction and density functional based, can be readily implemented tools to produce accurate X-ray spectra. It is important however to use a basis set that sufficiently describes the core hole for Δ -SCF calculations of CEBEs and for TDDFT calculations of XES using a core-ionised reference (via MOM). For CEBE calculations, useful for interpreting XPS experiments, relatively small basis sets can be used, provided the core orbitals are well described, this allows large systems such as ionic liquids to be accurately and efficiently simulated.

TDDFT can accurately simulate XES spectra of organic molecules, using a relaxed core-hole reference, in terms of relative energy spacing and peak heights. However the energies are required to be aligned to experiment. It was found that this is amendable by a secondary Δ -SCF calculation that can calculate the shift based of the HOMO to core-hole energy. This increases the predictive power of TDDFT to compute XES.

KS-DFT, TDDFT and ADC methods can produce accurate energies for the peaks associated to the RIXS of gas phase water. However the intensity distribution will not be accurately represent unless conformer sampling using AIMD is applied. Sampling a single trajectory can vastly improve the simulated spectra making this a relatively straightforward method to produce accurate RIXS simulations.

Open-shell linear molecules remain a challenge for single determinant quantum chemistry, however multi-reference methods like RAS based methods are available in open source quantum chemistry packages. There is a rich source of literature available to guide effective simulations. The results of these calculations produce highly accurate results and provide an important utility for simulating X-ray spectroscopy

experiments on complex multiconfigurational systems.

Looking forward, the X-ray spectroscopy methods simulated and methods used are already widely implemented across diverse applications. The next generation of X-ray spectroscopy experiments such as TRXAS and SXRS will provide new simulation challenges and the interpretations of the experiments will become more complex. The findings in this work provide a platform for the next stages of method development. However new simulation techniques will require the explicit incorporation of non-adiabatic dynamics simulation in-order to exploit the exploration of dynamics across multiple potential energy surfaces promised by the next generation of X-ray spectroscopy.

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