

SPECTROSCOPY OF SUBSTITUTED BENZENE MOLECULES

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Abstract

Consistent assignment of vibrational motions across substituted benzene derivatives is a long-standing desire amongst spectroscopists. In this thesis, the S_1 electronic states of monohalosubstituted benzene molecules and their deuterated isotopologues are investigated, using resonance enhanced multiphoton ionisation spectroscopy. The observed vibrational bands are assigned using the M_i nomenclature proposed by Gardner and Wright where ring-localised vibrations having the same atomic motion are given the same label, allowing straightforward comparisons of vibrational motions across monosubstituted benzene molecules to be achieved.

Detailed investigation showed that it would not be possible to apply the same M_i nomenclature labels to the *para*-disubstituted benzene derivatives owing to the different vibrational motions of mono- and disubstituted benzene molecules. As a consequence a new nomenclature, D_i , for labelling the vibrational motions of *para*-disubstituted benzene molecules is proposed in this work. The D_i labelling scheme is based on the vibrations of the *para*-difluorobenzene molecule. S_0 state vibrations of symmetric and asymmetric *para*-dihalobenzene species, *para*-fluorotoluene and *para*-xylene are studied in detail, showing that the ring-localised vibrational motions of *para*-disubstituted benzene species are being described by the same label.

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1. Introduction

Electronically excited molecules are important intermediates to chemical reactions and an improved understanding of chemical reaction mechanisms is an ultimate goal for the physical chemistry community. Vibrational activity observed during a transition between electronic states or upon ionisation needs to be well understood, as it indicates the geometry changes, which in turn can be used to deduce changes that have occurred in the electronic structure of the molecule during the process. Additionally, vibrational activity is also often used to gain understanding of other photophysical processes that are happening, such as photodissociation, internal conversion (IC), intersystem crossing (ISC), and intramolecular vibrational energy redistribution (IVR).

Substituted benzene molecules are of great interest spectroscopically. They can be the simplest deviation from the parent benzene molecule with an atomic substitution, or can have a lengthy organic side chain, as do a large number of substituted benzene species. These prototypical aromatic molecules provide links to the building blocks of biological molecules and are used widely in the pharmaceutical industry.^{1,2,3}

Improving our understanding of these simpler molecules is therefore of significant importance, and as mentioned above, the vibrational activity of a species during a transition conveys much more information about its geometry and electronic structure. Despite this, the vibrational

assignments of substituted benzene species are often inconsistent and not complete. The work in this thesis tackles the confusion arising when different vibrational labelling schemes are used, and in Chapter 3 the M_i nomenclature proposed by Gardner and Wright in 2011⁴ for monosubstituted benzene species is employed in the study of the S_1 state of the monohalosubstituted benzene molecules and their deuterated analogues. As is presented in Chapter 3, the M_i nomenclature allows one to label the same vibrational motion with the same label for a wide range of monosubstituted benzene molecules, enabling much easier and more consistent comparison across species. Chapter 4 addresses symmetric and asymmetric *para*-disubstituted benzene molecules in their S_0 states and the consistency in their vibrational assignments with a new labelling scheme, D_i , proposed in this thesis. The D_i nomenclature applies to a wide range of *para*-disubstituted benzene species and gives the same label to the ring-localised vibrations across different benzene molecules when motions are the same.

1.1 Vibrational motion

In order to represent the vibrational motion of a molecule, the Born-Oppenheimer approximation needs to be applied. The approximation is based on the great difference between the masses of the nuclei and electrons and enables one to treat the motions of the nuclei and electrons separately, with the result being that the electrons are able to respond almost immediately when the nuclei change their position.

Taking this approximation into account, the total wavefunction, Ψ_{tot} , can be factorised into electronic (Ψ_e) and nuclear parts (Ψ_n):

$$\Psi_{\text{tot}} = \Psi_e(r, R) \Psi_n(R) \quad \text{Equation 1}$$

where r denotes electronic coordinates, and R , the nuclear coordinates respectively. Here the electronic wavefunction still contains the nuclear coordinates but only as fixed parameters. The nuclear part of the wavefunction can be further factorised into vibrational, rotational and nuclear spin contributions yielding a total wavefunction product:

$$\Psi_{\text{tot}} = \Psi_e \Psi_{\text{vib}} \Psi_{\text{rot}} \Psi_{\text{spin}} \quad \text{Equation 2}$$

The Hamiltonian operator ($\hat{H}$) of the molecule can be separated into a sum of electronic and nuclear parts:

$$\hat{H} = \hat{H}_e + \hat{H}_{\text{nuc}} \quad \text{Equation 3}$$

where the time-independent Schrödinger equation is:

$$\hat{H}\psi = E\psi \quad \text{Equation 4}$$

This enables the total energy (E_{tot}) to be represented as:

$$E_{\text{tot}} = E_e + E_{\text{vib}} + E_{\text{rot}} + E_{\text{spin}} \quad \text{Equation 5}$$

resulting in vibrations being treated separately from other contributions to the total energy.

For a non-linear molecule with N atoms, there are $(3N-6)$ vibrational normal modes, where every individual mode can be thought of as a single harmonic oscillator associated with its own frequency. For a diatomic molecule harmonic oscillator is a simple model used to illustrate vibrational motion, where equally spaced energy levels in the well go up infinitely. The harmonic oscillator model provides a great advantage as one can depict individual bonds vibrating independently. However it is a poor representation because real molecules will dissociate at higher energy and if deviation of the potential energy from a quadratic dependence occurs, dissociation can occur even at lower energy. The deviation from harmonic behaviour will increase with increasing energy. This results in asymmetry in the potential about the equilibrium position, and is known as anharmonicity. The Morse potential, however, depicts a more realistic representation where energy levels get closer together until they almost converge at the dissociation limit, see Figure 1.1 below.

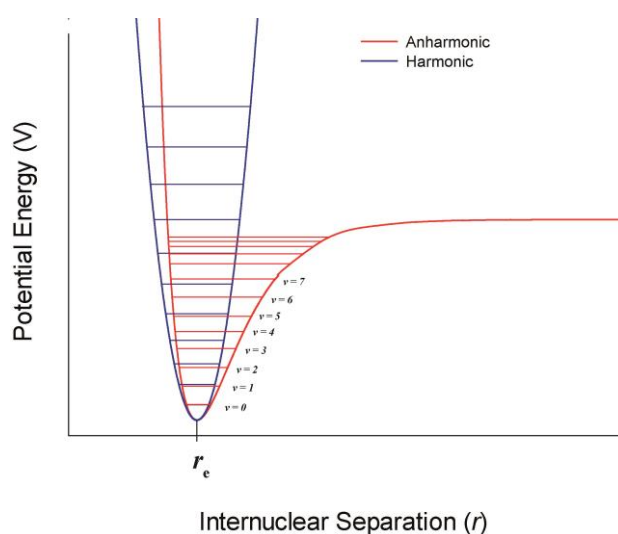


Figure 1.1. The parabolic potential (pink line) of a harmonic oscillator is compared to the Morse potential (blue line) which is a more realistic representation of the vibrational levels in a molecule.

The potential energy (V) of a diatomic molecule in a harmonic oscillator depends on the displacement x and obeys Hooke's law:

$$\frac{dV}{dx} = kx \quad \text{Equation 5}$$

where k is a force constant. Integrating equation 6 leads to:

$$V = \frac{1}{2} kx^2 \quad \text{Equation 7}$$

The Morse potential energy can be expressed as:

$$V = D_e \left(1 - e^{-a(r-r_e)}\right)^2 \quad \text{Equation 8}$$

where r is the distance between atoms, r_e is an equilibrium bond distance, D_e is the well depth and a is related to the width of the potential well.

Although it is convenient to refer to the vibration of an individual bond in isolation, in reality in polyatomic molecules there are many such bonds and the vibration of one bond will have an effect on the others. The potential energy expression then becomes more complex:

$$V = \frac{1}{2} \sum_{ij} k_{ij} x_i x_j \quad \text{Equation 9}$$

where x_i and x_j represent the Cartesian displacement of each atom in the molecule and the k_{ij} are generalised force constants. As Cartesian displacement of one atom affects the Cartesian displacement of other atoms, the normal coordinates are chosen to eliminate those 'cross terms'

by finding the linear combination, q_i , of the above two atom displacements, $x_i x_j$. The potential energy expression in terms of normal modes of a molecule becomes:

$$V = \frac{1}{2} \sum_i k_i q_i^2 \quad \text{Equation 10}$$

The Hamiltonian for a single quantum mechanical harmonic oscillator then is:

$$\hat{H} = \frac{-\hbar^2}{2\mu} \frac{d^2}{dx^2} + \frac{1}{2} k x^2 \quad \text{Equation 11}$$

where μ denotes a reduced mass, and vibrational energies are given by:

$$E_{\text{vib}} = \left(v + \frac{1}{2} \right) h\nu \quad \text{Equation 12}$$

where $\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$ is fundamental frequency of the oscillator and v is defined here as the vibrational quantum number.

1.2 Vibrational level coupling

In the harmonic approximation the vibrational modes are not coupled to one another, meaning the representation of the Hamiltonian is diagonal, with no off-diagonal elements being present. Normal vibrational modes in the harmonic approximation are referred to as zero-order states (ZOSs). An eigenstate can be expressed as a superposition of normal

vibrational modes. The linear superposition of normal modes can be expressed with the following equation:

$$|n\rangle \approx \sum_i a_i \phi_i \quad \text{Equation 13}$$

where a_i is a coefficient (the contribution from each zero-order state) and ϕ_i is a zero-order state. Two zero-order states are said to be mixed with each other if they both make a contribution to the same eigenstate. The extent of the mixing depends on the strength of the coupling and the energy separation of the normal modes of vibration. If a two energy level system is taken, then the real eigenfunctions can be written in terms of the ZOSs:

$$|n\rangle = a_1 \phi_1 + a_2 \phi_2 \quad \text{Equation 6}$$

This coupling of normal modes causes off-diagonal terms to appear in the Hamiltonian, compromising the independence of the normal modes, and leading to the coupling of the vibrational motions. This causes the upper energy level to go up in energy and the lower energy level to go down. Anharmonic coupling is only permitted between levels that have the same symmetry and are close in wavenumber. Fermi resonance (FR) is the simplest example of such coupling, see Figure 1.2 on the next page.

In practice it is vibrational eigenstates that are probed experimentally, and if the two ZOSs couple to form two vibrational eigenstates then, for example, a zero-electron kinetic energy spectrum (ZEKE) recorded via each vibrational eigenstate will consist of two bands, corresponding to

the two ZOSs. Relative intensities of those bands will reflect the amount of each ZOS that is present in each vibrational eigenstate as well as any photoionisation cross-sections.

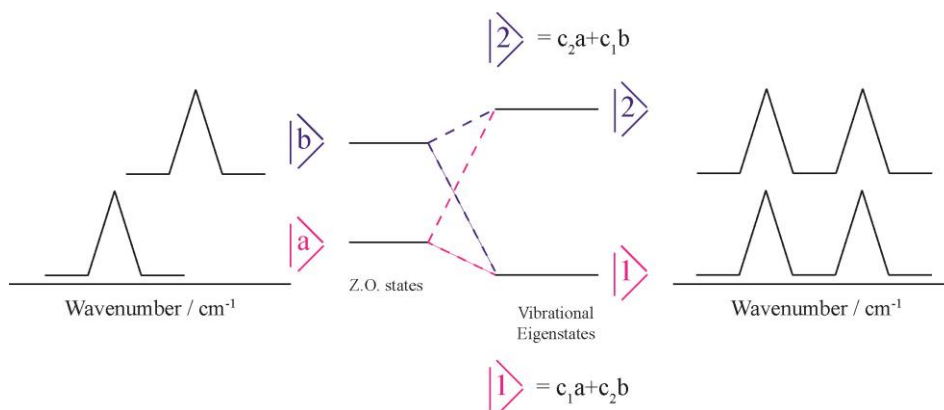


Figure 1.2. Schematic diagram of the coupling observed between two ZOSs where c_1 and c_2 are coefficients of contributions of states a and b.

For the two level system, the energy of the resulting eigenstates can be calculated:

$$E^{+/-} = \frac{1}{2}(E_0 + E_1) + / - \sqrt{(E_0 - E_1)^2 + 4H_{12}H_{21}} \quad \text{Equation 7}$$

where H_{12} and H_{21} are coupling matrix elements.

Such vibrational state couplings can be resolved via frequency-resolved experiments or time-resolved experiments. In frequency-resolved experiments, lasers with sufficiently narrow bandwidths are used to probe a single eigenstate, where intensity of a transition and energy difference of the molecular eigenstate are measured. In time-resolved experiments, short laser pulses (usually in the order of femtosecond) excite a number of molecular eigenstates coherently, forming a

vibrational wavepacket. The evolution of these eigenstates over a period of time is studied, gaining insight into the IVR behaviour as a function of time delay. The time evolution occurs because constructive and destructive interference happens as excited vibrational eigenstates vibrate in and out of phase, often referred to as the energy flow between 'bright' (Franck-Condon active) and 'dark' (optically inactive) states. IVR lifetimes and sometimes the assignments of the dark and doorway states can be identified (A doorway state provides a route through which the bright state is coupled to numerous other states). However the IVR lifetime must be higher than the laser pulse duration. Time-dependence is not observed if only one eigenstate is excited. Felker and Zewail⁵ have pioneered time-resolved experimental techniques and understanding of the IVR processes.

1.3 Vibrational motion nomenclatures

The vibrational state of the molecule is specified by the label of a particular vibrational mode. In previous work on substituted benzene species, the majority of the assignments of the vibrational bands have been in terms of Wilson,⁶ Varsányi⁷ or Mulliken⁸ notations. When those studies are considered, an enormous task arises in muddling through various vibrational motion labelling schemes and the inconsistencies that appear in the vibrational labels used across them. The confusion perhaps dates back to much earlier papers, with authors utilising these three well known different labelling schemes because of the advantages and disadvantages they carry.

The Wilson nomenclature,⁶ perhaps the best known one, gives a vibrational normal mode a unique label notifying which atoms are moving during a vibration and what motion they are undergoing. Wilson labels are based on the vibrations of the benzene molecule itself. However the form of those vibrations changes considerably even with the simplest of substitutions. This arises because upon substitution the overall symmetry of the molecule is lowered (for example, from D_{6h} to C_{2v} in the case of monohalobenzene species) and the form of the vibrational motions changes significantly. Also, with a substituted atom, changes in the bonding lead to a different force constant being present which is expected to have an effect on the fundamental frequencies. As a result, although a lot of papers on substituted benzene species refer to the Wilson vibrational motion label, many of the vibrational motions of the substituted molecule do not correspond to the vibrational motion of benzene. This issue has been previously highlighted for the fluorobenzene (FBz) molecule by Butler et al.,⁹ Pugliesi et al.¹⁰ and previous papers by the Wright group, ref. 4 and 11, where it has been shown that the Wilson labels are inappropriate for describing the phenyl ring-localized vibrations in substituted benzene molecules.

Varsányi in his nomenclature⁷ attempted to account for the inconsistencies seen with the Wilson scheme. Using knowledge and understanding from the analysis of many infrared (IR) and Raman spectra, he proposed likely wavenumber ranges for various categories of substituted benzene species. He suggested labels based on Wilson-type labels for a very large number of substituted benzene molecules and their

vibrations. However, his scheme also has limitations in its use because of its arbitrary division of the substituents into heavy or light groups, leading to the same vibrational mode being represented by different labels in even quite similar molecules, or a different vibration being described by the same Wilson label. This aspect is of great importance in this chapter, as fluorine is considered a -light- substituent whereas chlorine and bromine are considered a -heavy- substituents by Varsányi in his book⁷ giving a number of vibrations different labels in FBz, chlorobenzene (ClBz) and bromobenzene (BrBz) molecules, despite the fact that, as was shown briefly in ref 4, the atomic motions of the vibrations in these molecules are very similar. In addition such complications make the wide use of the Varsányi scheme with the same symbols as Wilson labels somewhat misleading when describing vibrational motion of substituted benzene species.

The third, Mulliken notation⁸ (sometimes referred to as Herzberg notation¹²), lists the vibrations in order of decreasing wavenumber in symmetry blocks. These are specific to each molecular point group and are in a predetermined order so that in the case of a C_{2v} molecule, they would always be listed in the order a_1 , a_2 , b_1 , and b_2 symmetry blocks. Vibrations then are assigned a number, starting at 1 for the highest wavenumber a_1 mode, through to 30 (in the case of the monosubstituted halobenzene species), for the lowest wavenumber b_2 mode. This is seemingly a very straightforward alternative to the Wilson scheme, however, there are drawbacks too.

The Mulliken scheme⁸ does not provide direct information on what atomic motion occurs during a vibration, with energetic ordering leading to similar motions being renumbered if the symmetry of a molecule changes, or if the substituent is a polyatomic then its internal vibrations will contribute to the numbering list, altering the numbering once again, leading to the same complication as described above in the Wilson scheme, where the same vibrational motion will have a different label in a different molecule. All of the inconsistencies mentioned above contribute to the complexity when one wishes to compare and correlate vibrational behaviour across different substituted benzene species. In Figure 1.3 on the next page part of the ClBz- h_5 (1+1) REMPI spectrum is presented that was recorded in this project using the experimental techniques and apparatus outlined in Chapter 2.

The origins of each spectrum have been shifted to zero for straightforward comparison and assigned vibrational bands have been labelled using the schemes outlined above. What is clear to see is how vibrational bands in the same spectrum of the same molecule have been assigned to different vibrational labels and how many inconsistencies occur, making it extremely tricky to compare previous work of the same molecule by different experimental groups, and making it even harder to keep track of similar vibrations across different closely-related molecules. Where some inconsistencies could be attributed to the different spectral assignments rather than inconsistent application of the different nomenclatures however for majority inconsistent vibrational band assignments seen in Figure 1.3 this would be highly unlikely

because different labels describing such bands have large energy differences between them and even different symmetries. For example the most intense vibrational band above the origin has been assigned as mode ‘12’ or as mode ‘1’ by some, both of such modes are of same symmetry and very close in wavenumber so simple band missassignment can be attributed. However vibrational band that has been assigned as mode ‘15’ or ‘18b’ in the spectra below is most probably attributed to the complexity in the vibrational nomenclatures as energetic difference between such modes is around 700 cm^{-1} .⁷

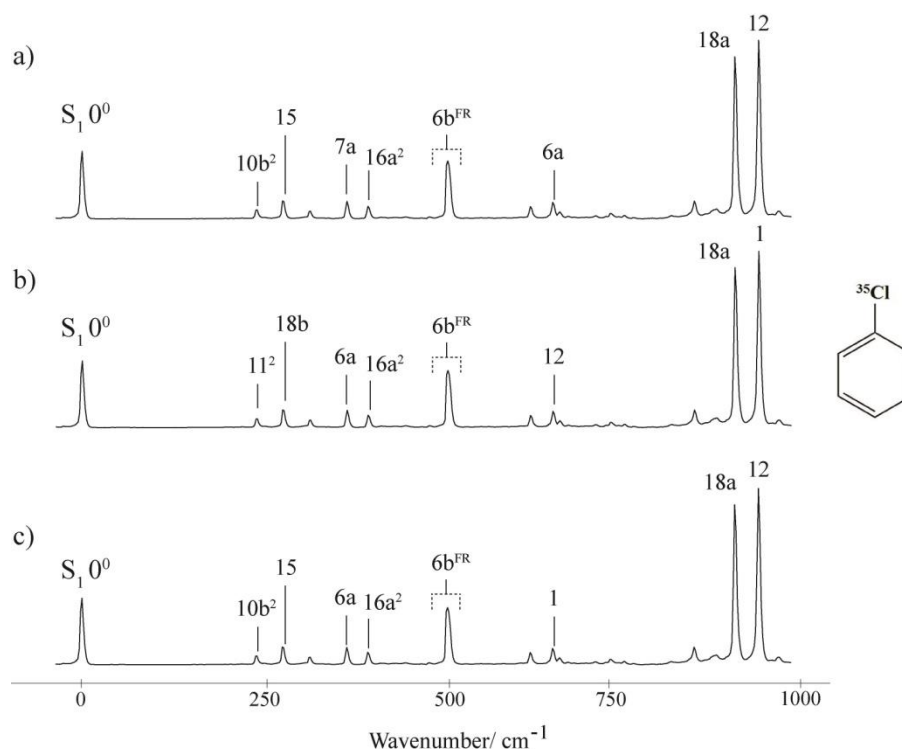


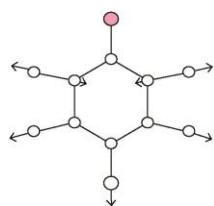
Figure 1.3. (1+1) REMPI spectrum of the $^{35}\text{ClBz-}h_5$ molecule in the $0\text{--}1000\text{ cm}^{-1}$ range of the $S_1 \leftarrow S_0$ transition above the S_1 origin. The recorded spectrum in this work has been reproduced 3 times and vibrational assignments were labelled using different schemes outlined above: a) Varsányi labels are utilised from ref. 7 b) Wilson nomenclature used by Wright et al. in ref. 13 and c) Varsányi labels used by Imhof and Kleinermanns work from ref.14.

1.4 M_i nomenclature

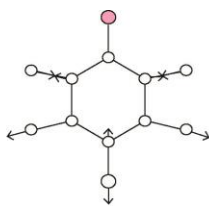
In order to get around the different issues highlighted within the nomenclatures outlined above, Gardner and Wright in 2011¹⁴ put forward a new consistent assignment method for labelling the ring-localized vibrational modes of monosubstituted benzene molecules. The same vibrational modes have the same unique label, M_i , irrespective of which substituent is present in the molecule, as can be seen in ref 4, 15 and 16. In the Gardner-Wright scheme, FBz is used as a prototypical system, whose ring-localised vibrational modes in the S_0 state serve as a model upon which benzene derivative vibrations are labelled, as seen in Figure 1.4 here. Each normal mode corresponding to a vibration is given the symbol M_i , where i denotes the number of the vibration. M_i labels for the vibrations of the S_0 state of FBz- h_5 are formulated the same way as in the Mulliken (Herzberg) notation, but the vibrations in the deuterated isotopologue, FBz- d_5 , and other halobenzene molecules are based on the ring-localised vibrations of the FBz- h_5 molecule and so are assigned by direct comparison of the atomic motions, or by looking at the generalized Duschinsky matrix, see Figure 3.2 of Chapter 3, section 3.4.1.

In a case where the substituent on the phenyl ring is not an atom, it is treated as a point mass, so that the benzene derivative species are always of C_{2v} symmetry, preventing changes in the point group symmetry. Vibrations that have the same atomic motion are given the same label regardless of the energy ordering, allowing straightforward comparison between monosubstituted benzene molecules. For the

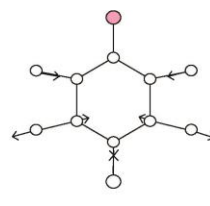
substituent-localised modes, a different nomenclature would need to be employed.



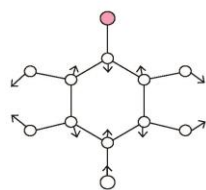
$M_1(a_1)$



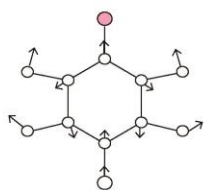
$M_2(a_1)$



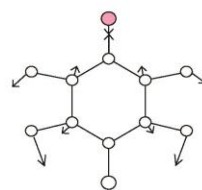
$M_3(a_1)$



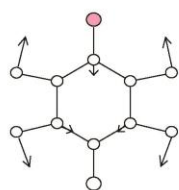
$M_4(a_1)$



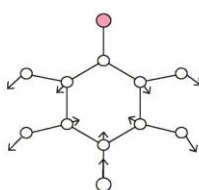
$M_5(a_1)$



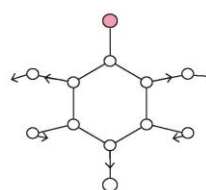
$M_6(a_1)$



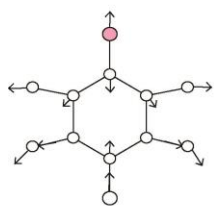
$M_7(a_1)$



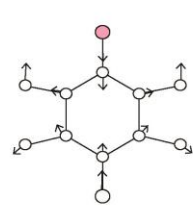
$M_8(a_1)$



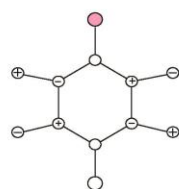
$M_9(a_1)$



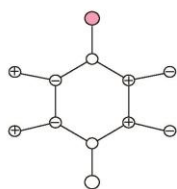
$M_{10}(a_1)$



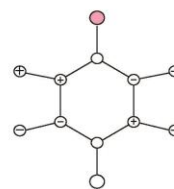
$M_{11}(a_1)$



$M_{12}(a_2)$



$M_{13}(a_2)$



$M_{14}(a_2)$

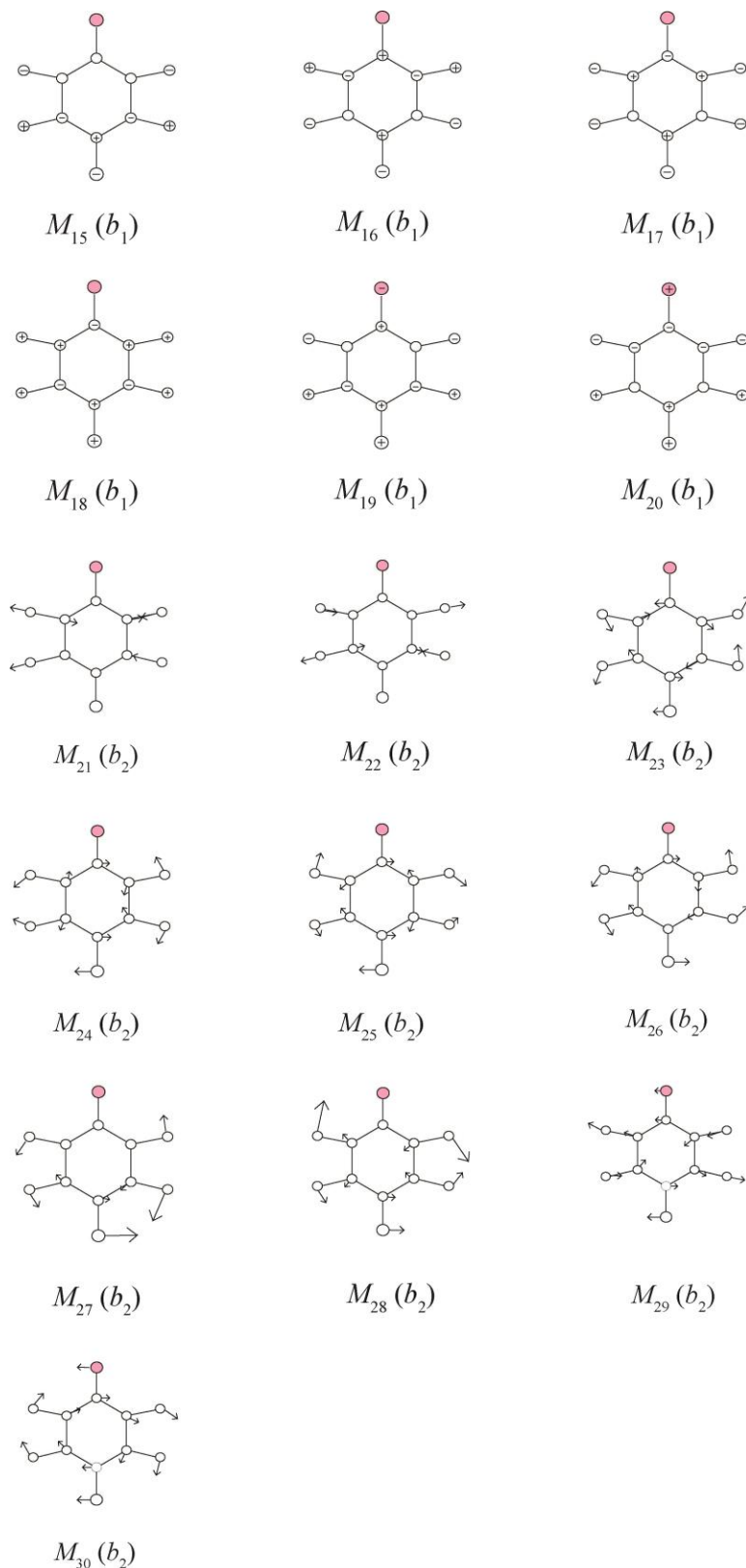


Figure 1.4. Calculated vibrational modes for FBz (B3LYP/aug-cc-pVTZ), labelled using the Gardner-Wright scheme. The vibrations here match extremely well the ones in Figure 5 in ref. 4 that were calculated with the B3LYP/aug-cc-pVDZ level of theory.

1.5 References

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2. Experimental Methodology

In the present thesis, resonance-enhanced multiphoton ionisation (REMPI) spectroscopy was used to probe the first electronically excited states of monohalosubstituted benzene molecules and their perdeuterated isotopologues. In the following is a brief description of the experimental apparatus used and of the REMPI technique employed to probe the excited states of interest.

2.1 Resonance-enhanced multiphoton ionisation

REMPI spectroscopy is a widely used technique that is employed to probe the (ro)vibrational levels of an electronically excited state of a neutral molecule. In non-resonant multiphoton ionisation, the desired molecule is irradiated with photons and if the energy is sufficient the ionisation will occur, Figure 2.1a. REMPI achieves this ionisation via a two-step process. In the first step a neutral molecule is promoted to an excited vibronic state following the absorption of one or more photon(s); this step is known as the ‘pump’ step. In the second step absorption of one or more photons of sufficiently high energy ionises the molecule, known as the ‘probe’ step. In the pump step the total photon energy must be resonant with a transition energy band gap for a transition to occur and selection rules must be satisfied. By proceeding via an intermediate state not all of the photons need to be absorbed simultaneously resulting in a significant increase in ion yield with a resonant scheme. As the number

of photons needed for the absorption step increases, the probability of the absorption happening decreases accordingly.¹ The REMPI technique can be one-colour, where a single laser wavelength is used for both steps, or two-colour, where two different laser wavelengths are used in the two-colour REMPI scheme. $(n+m)$ is the notation for one-colour REMPI, where n and m are the number of photons of the same wavelength that are used for each step. $(n+m')$ indicates a two-colour process where photons of different wavelengths are used for each step. Schematic representations of $(1+2)$ REMPI and $(1+1')$ REMPI are shown in Figure 2.1 below.

In a one-colour scheme excess energy in the ionisation step can lead to the fragmentation of a sample which can contribute to structure in the spectrum.

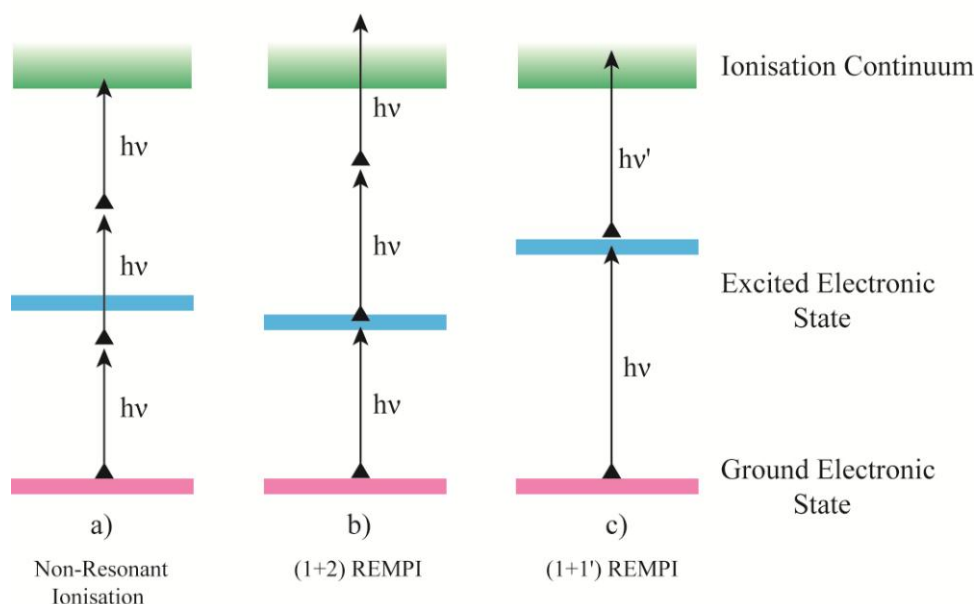


Figure 2.1. Schematic representation of a) non-resonant multiphoton ionisation, b) $(1+2)$ REMPI and c) $(1+1')$ REMPI.

The structure seen in the REMPI spectrum is associated with the intermediate state in the molecule of interest, where each band corresponds to a transition to a (ro)vibrational level in the excited electronic state.

2.2 Apparatus

A schematic of the experimental apparatus employed to record (1+1) REMPI spectra of monosubstituted benzene molecules and their deuterated isotopologues is shown in Figure 2.2, with a photograph in Figure 2.3.

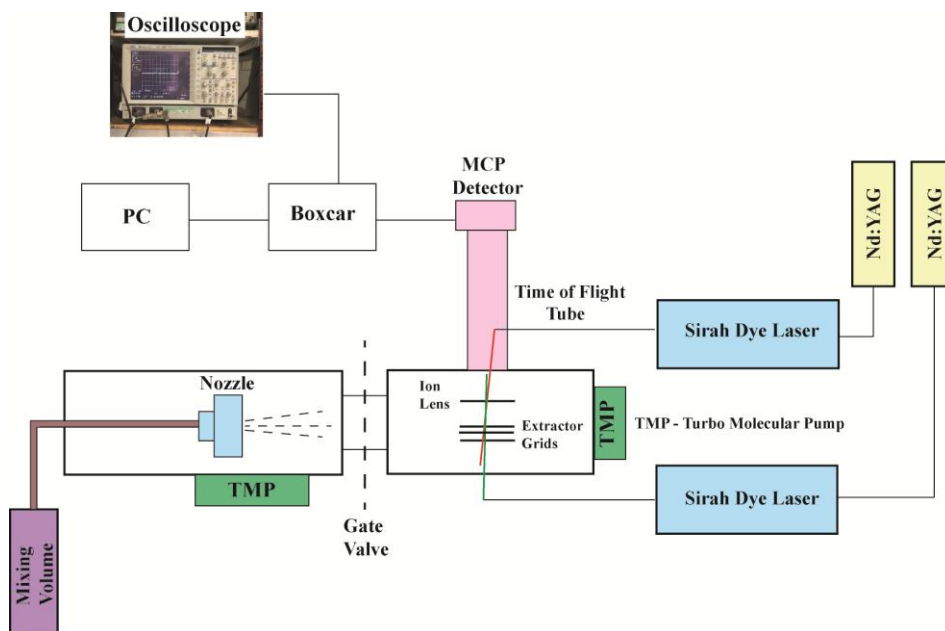


Figure 2.2. Schematic diagram for the (1+1) and (1+1') REMPI experiments. Adapted from ref. 2.

The third harmonic (355 nm) of a neodymium-doped yttrium aluminium garnet laser (Nd:YAG, Surelite III, 10 Hz) was used to pump a tunable dye laser (Sirah Cobra Stretch). For monosubstituted benzene molecules and their deuterated isotopologues, the pump and probe steps were both achieved with a dye laser operating on Coumarin 503. The fundamental in the visible region produced by the dye laser was frequency-doubled using a beta-barium borate (BBO) crystal to allow tunable UV radiation to be obtained across the energetic regions of interest. The bandwidth of these lasers (0.2 cm^{-1} ; 0.1 cm^{-1} in the dye laser fundamental) is able to resolve numerous vibrational bands of the samples, sometimes identifying partially-resolved rotational branches of the associated rotational envelopes.

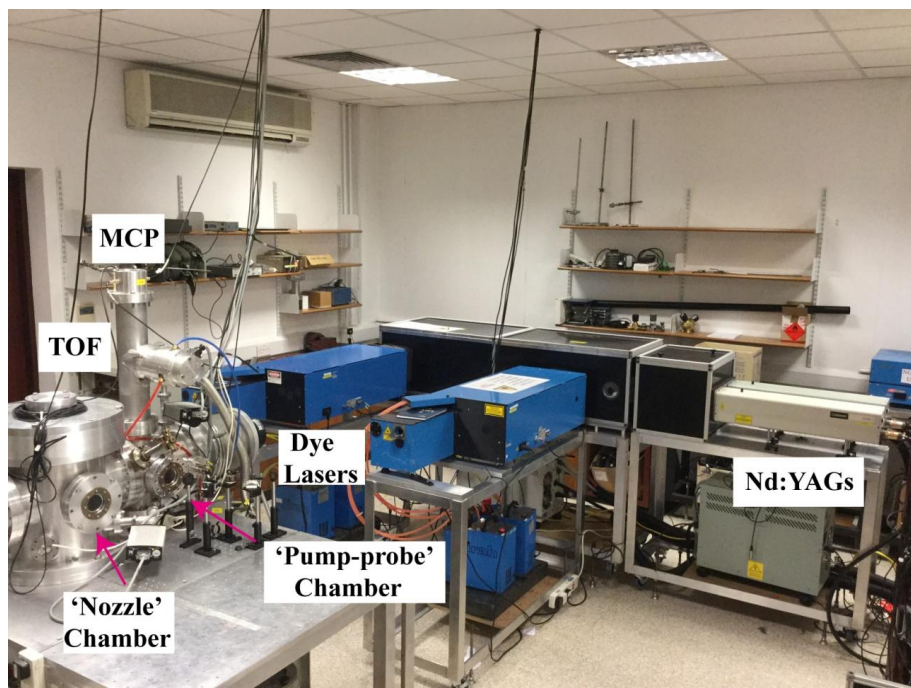


Figure 2.3. Picture of the SOCAR group experimental apparatus.

A small amount of gaseous sample is seeded in backing gas (typically held at ~ 2 -5 bar, argon or helium) and the mixture is passed into the nozzle chamber through a general pulsed valve (750 μm orifice, opening time ~ 150 -200 μs) creating a supersonic jet expansion (please see Section 2.3 for explanation). This expansion proceeds from the 'nozzle chamber' into the 'pump-probe' chamber where it intersects perpendicularly with focused UV light from a dye laser, and ionisation subsequently occurs. The extraction region is formed by two grids, which have different positive charges applied, creating an electric field between them. The resulting ions are extracted and accelerated down the 1 m Wiley-McLaren time-of-flight (TOF) mass spectrometer. A microchannel plate (MCP) detector (consisting of two MCPs in a chevron arrangement) is located at the end of the TOF tube, whose responsibility it is to convert charged particle collisions (ion count) into a voltage signal. The signal is then passed onto an oscilloscope (LeCroy LT342 Waverunner) for monitoring, and a boxcar (SRS SR250) for integrating and averaging; this signal is then relayed to a computer for storage and analysis.

The supersonic jet expansion, direction of propagation of the dye lasers and TOF tube are arranged so as to be mutually perpendicular. The timing of the production of laser pulses relative to the opening and closing of the pulsed nozzle is achieved using a digital delay generator (SRS DG535). The delays are varied to achieve optimum conditions for the sample of interest to produce well-resolved REMPI spectra, where the coldest molecules will be at the front of the expansion.

The spectral calibration for substituted benzene molecules was achieved by comparing the position of the S_1 origin bands to previous spectra.³ For some spectra more sophisticated non-linear calibration techniques were employed using a mathematical function, but results from these were found to be of the same quality as the above method for the first $\sim 1500\text{ cm}^{-1}$ with small discrepancies seen above that. Estimated overall uncertainty in the band positions in this work is $\pm 0.2\text{ cm}^{-1}$ up to 1500 cm^{-1} above the S_1 origin and $\pm 1\text{ cm}^{-1}$ for higher energy bands.

2.3 Supersonic jet expansion

It is desirable to cool the molecular gas sample, as at room temperature a large number of rotational and vibrational levels are populated, leading to congested spectra. The spectra of molecules at room temperature will consist of transitions out of many different energy levels, resulting in broad bands consisting of unresolved vibrational and rotational structure. If the resolution is enough then a large number of transitions will give rise to an extremely high density of (ro)vibronic lines making assignment of those an impossible task.

A supersonic jet expansion overcomes many of the difficulties outlined above as it results in successful cooling of translational, rotational and vibrational internal degrees of freedom. A molecular gas sample is seeded in a carrier gas (typically an atomic gas such as argon or helium) and held in a container at a pressure of several atmospheres, usually. When this mix is passed through an orifice with a diameter considerably higher than the mean free path of the sample into a vacuum, a supersonic

jet expansion is formed. The term 'supersonic expansion' is derived from the fact that the molecules in the free jet expansion have a velocity much higher than the local speed of sound. The speed of the sample is expressed in terms of a Mach number, M , and when the number is >1 the expansion is supersonic.¹ As the sample passes through the orifice many collisions between departing sample molecules and the carrier gas molecules occur resulting in rotational and vibrational energy of the sample being converted into translational energy in the atomic carrier gas. The relative translational temperature of the sample will be also dramatically reduced as the distribution of speeds is reduced significantly with the large number of collisions averaging the translational energy across gas particles, Figure 2.4.

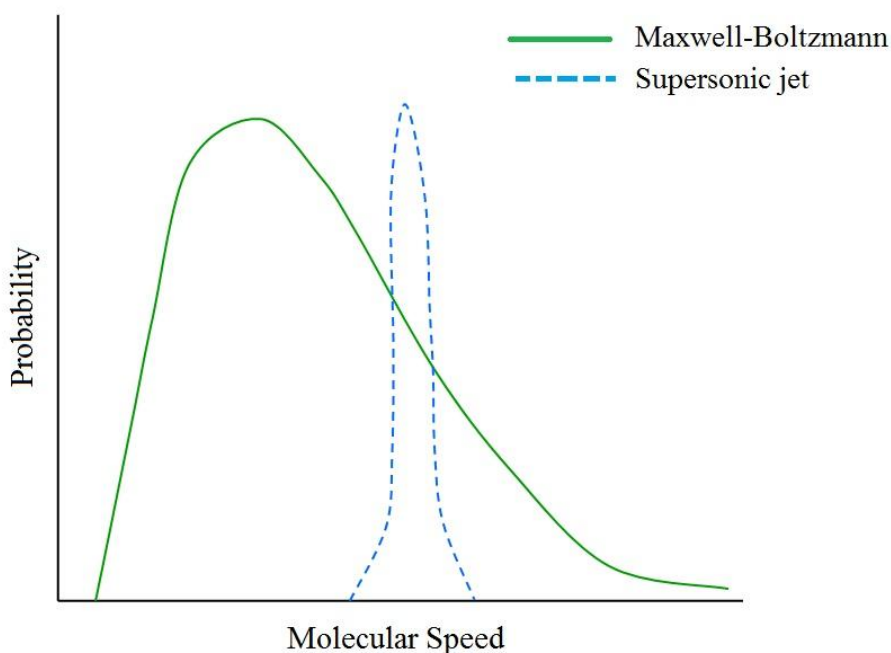


Figure 2.4. Comparison of the speed distributions in the gas reservoir (Maxwell-Boltzmann distribution) and in the supersonic jet downstream of the orifice. Two plots are not to scale and the areas under both curves are roughly the same.

2.4 References

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² R. J. Plowright, PhD Thesis, *Spectroscopy and Interaction of Metal and Metal Cation Complexes*, University of Nottingham, 2010.

³ Please see Chapter 3, sections 3.4.1, 3.4.2 and 3.4.3, for detailed calibration information on fluorobenzene, chlorobenzene and bromobenzene molecules and their deuterated isotopologues respectively.

3. Electronic spectroscopy of monohalobenzene molecules and their perdeuterated isotopologues.

In this chapter vibrationally-resolved spectra of the $S_1 \leftarrow S_0$ transition of monohalobenzene molecules recorded using resonance-enhanced multiphoton ionisation (REMPI) spectroscopy are presented. Under study are halobenzene- h_5 species (halo = fluoro, chloro and bromo) as well as their perdeuterated isotopologues, halobenzene- d_5 molecules. Changes in the form of the vibrational modes between the isotopologues and also between the S_0 and S_1 electronic states are discussed for each species. Vibrational bands are assigned utilising quantum chemical calculations, previous experimental results and isotopic shifts. The use of Wilson or Varsanyi labels describing the vibrational normal modes of substituted benzene species has often been inappropriate, therefore the M_i vibrational labelling scheme¹ is applied to all of the halobenzene molecules in this project. Previous work and assignments of the S_1 spectra are discussed. Additionally, the vibrations in the ground state cation, D_0^+ , are considered, since these have also been used by some previous workers in assigning the neutral excited state spectra. The results included here are based on recently published work, found in refs. 2, 3 and 4, where the REMPI spectra of the S_1 states of the halobenzene- d_5 molecules were presented for the first time with comprehensive vibrational band assignments.

3.1 Introduction

The simplest types of monosubstituted benzene species are the monohalobenzenes. Halobenzene molecules are widely used as intermediates in the synthesis of other benzene containing organic compounds, as well as being used as solvents. Chlorobenzene in particular remains to be the most widely used halobenzene species on an industrial scale. Its uses range from production of perfume, the pesticide DDT and others, to being a solvent in the production of various plastics and coatings, as well as being used in dyes.^{5,6,7}

In the following chapter, abbreviations to the titular molecules will be applied, for example chlorobenzene will be referred to as ClBz. The isotopologues will be noted with a presuperscript, 35 or 37, and/or a suffix $-h_5$ or $-d_5$ as appropriate, so that $^{37}\text{ClBz-}d_5$ represents the ^{37}Cl isotopologue of the perdeuterated chlorobenzene molecule.

With the $3N-6$ possible vibrational modes, there are a total of 30 different normal modes for monohalobenzene species. Of course not all of these will be present in the spectrum when an electronic state is being probed spectroscopically. For the vibronic transitions to happen Franck-Condon factors⁸ must be favourable as the intensity of an allowed transition is dependent upon them, and symmetry selection rules must be followed too. In this project, for substituted benzene species only totally-symmetric vibrations should be observed according to the symmetry selection rules. However intense, non-totally-symmetric fundamentals are also seen in electronic spectra of the $S_1 \leftarrow S_0$ transition

for substituted benzenes. These modes are specifically of b_2 symmetry for monosubstituted benzenes, where the molecular plane is located in the yz plane. The appearance of these bands arises from Herzberg-Teller vibronic coupling between the S_1 ($\tilde{A}^1B_2$) state and a higher-energy $^1A_1$ state;⁹ the coupling occurs via various b_2 vibrations, and so these appear in the recorded spectrum.

3.2 Computational Details

The experimental set-up and the technique for obtaining experimental results was described in detail in Chapter 2. As an aid to the assignment of the spectra recorded in this work, the normal mode frequencies for each monohalobenzene molecule and its deuterated isotopologue were calculated using the GAUSSIAN 09 software package.¹⁰ For the S_0 ($\tilde{X}^1A_1$) electronic state and the ground cation D_0^+ ($\tilde{X}^2B_1$) electronic state, (U)B3LYP/aug-cc-pVTZ calculations were used, whereas for the S_1 ($\tilde{A}^1B_2$) state TD-B3LYP/aug-cc-pVTZ calculations were employed. For the Br atom, the fully relativistic effective core potential, ECP10MDF, was used alongside corresponding aug-cc-pVTZ-PP valence basis sets. All of the calculated wavenumbers were harmonic and the usual factor of 0.97 was used to scale vibrational frequencies. For the unrestricted calculations $\langle S^2 \rangle$ values were all ~ 0.76 showing that spin contamination was minimal.

For the S_1 states of both the BrBz- h_5 and BrBz- d_5 molecules, the M_{14} fundamental frequency returned imaginary values, something that was also obtained by the authors of ref. 11 employing TDDFT with triple zeta

basis sets equivalent to those used here, in the GAUSSIAN 09 software package. There, imaginary frequencies were obtained for both the M_{14} and M_{20} fundamental modes, with some others being very low in value. These abnormalities were explained as an artefact of the computational procedure, since allowing the geometry to optimise away from the real C_{2v} symmetry to a structure of C_s leads to acceptable frequencies, implying that the geometry optimisation algorithms find the minimum energy structure with some atoms unphysically out of the plane of the benzene ring. Harmonic frequency calculations for the S_0 and D_0^+ states were unaffected by the issue.

The vibrational modes of the $XBz-h_5$ ($X = Cl$ and Br) S_0 states were labelled by comparing the molecular vibrational displacements with those of $FBz-h_5$ via a generalised Duschinsky matrix approach¹² and by visualisation of the actual vibrational motion, both employing the FC-LabII program.¹³ A Duschinsky matrix allows the molecular vibrations of an excited state to be expressed as a linear combination of vibrations in the ground state (a classic Duschinsky matrix), or it can be used to express the molecular vibrations of one molecule in terms of molecular vibrations of another molecule. Where normal modes become mixed between electronic states or molecules, this is known as Duschinsky mixing. Here, Duschinsky mixing allows examination of how well the normal modes of heavier monohalobenzene molecules correspond to those of FBz , providing a clear assignment of the phenyl ring-localized vibrations. For $FBz-d_5$, $ClBz-d_5$ and $BrBz-d_5$, the molecular vibrational motions were compared to those of $FBz-h_5$,

ClBz- h_5 and BrBz- h_5 respectively in their S_0 states via a generalized Duschinsky approach using FC-LabII. Similarly, vibrations in the S_1 and D_0^+ states were compared to those of the respective S_0 state, and those of each molecule's S_1 and D_0^+ states to each other. The first example of a Duschinsky matrix employed in this project is seen in Figure 3.2. The mixing information is displayed as a matrix, where diagonal elements close to 1 (black square = 1.00) indicate the vibrational modes in two states have very similar vibrational motion. White squares indicate elements with a contribution of zero, and where mixing of the vibrational motions is present across two states, the element is coloured grey. In this work, mixing criteria were taken as follows: coefficient values > 0.2 are termed major contributions, with dominant contributions having mixing coefficients > 0.5 . Minor contributions have values between 0.05 and 0.2. If there is more than one contribution of each type, these are presented in order of decreasing magnitude. Vibrations with a mixing coefficient < 0.05 are ignored.

All transitions here are denoted by the upper vibrational level, since all transitions, unless noted, are from the $v=0$ vibrational level in the ground electronic state.

3.3 Previous work

3.3.1 Fluorobenzene- h_5 and Fluorobenzene- d_5

It is not surprising that there has been a significant number of studies with detailed spectroscopic analysis performed on the FBz- h_5 molecule as it is one of the simplest substituted benzene species. It is often thought

of as a prototypical substituted benzene, as it is the lightest molecule with a single atomic substitution, excluding deuterium.

Whiffen's study¹⁴ along with Lipp and Seliskar's study,¹⁵ from 1956 and 1978 respectively, are some of the earliest assignments of the fundamental vibrational modes in the S_0 state of FBz- h_5 , where the symmetry was deduced from rotational profiles of the bands. Varsányi¹⁶ has suggested assignments for 29 out of 30 fundamental vibrational modes in his book, and more recently in 2007 Butler et al.¹⁷ confirmed previous vibrational assignments of the ground electronic state by employing dispersed fluorescence (DF). IR spectra of the region of some of the CH stretches have been recorded recently by Scotoni et al.¹⁸ which allowed investigation of interactions between these vibrational modes. The above findings have been summarised before by Gardner and Wright in ref.1.

The S_1 state of FBz- h_5 has been probed by Vasudev and Brand¹⁹ in 1979 with a two-photon spectrum reported where different activity was observed compared to a one-photon spectrum from the same study. As with the ground state, Lipp and Seliskar²⁰ published one of the first detailed studies on the S_1 state of FBz- h_5 in the 1981 using UV absorption spectroscopy, where bands were identified by expected wavenumber and rotational contours. A sister paper to that study was published in the same year and issue, focussing on hot bands featured in the spectrum.²¹ More recently, Butler et al.¹⁷ have carried out thorough laser induced fluorescence (LIF) experiments, with activities in the DF spectra being used to confirm S_1 band assignments. Pugliesi et al.²² in

2008 produced a very comprehensive study on the $S_1 \leftarrow S_0$ transition of FBz- h_5 employing REMPI spectroscopy, zero-electron-kinetic-energy (ZEKE) spectroscopy, Franck-Condon (FC) simulations and quantum chemical calculations; the latter were used to gain insight into the S_0 , S_1 and D_0^+ electronic states and mode mixing therein. FC simulations and quantum chemical calculations were also employed in recent years by He et al.²³ to gain deeper understanding into the fluorescence from the S_1 state. The Lawrance group²⁴ in 2011 employed two-dimensional laser-induced fluorescence (2D-LIF) spectroscopy in order to attempt to unravel overlapping structures and vibrational couplings seen in the spectra recorded by this technique.

Vibrations of the FBz- h_5 cation were examined using ZEKE spectroscopy by Pugliesi et al.,²² one-photon excitation mass-analyzed threshold ionisation (MATI) spectroscopy by Kwon et al.,²⁵ as well as two-colour (1+1') MATI work by Lembach and Brutschy²⁶ and REMPI-PES experiments by the Boesl group.²⁷ Experimental results by Kwon et al. are in excellent agreement with the two-photon MATI results of Lembach and Brutschy; all studies will be discussed in more detail in section 3.4.1.

Compared to its perhydrogenated isotopologue, FBz- d_5 has been studied much less. The first study was by Steele and co-workers,²⁸ employing IR and Raman spectroscopies in 1960 to obtain vibrational band assignments of the S_0 state of FBz- d_5 . They reported 24 out of 30 fundamental vibrations with approximate atomic motion descriptions. A study by Lipp and Seliskar²⁹ in 1978 confirmed Steele's assignments with

their higher resolution study. However, Wilson mode labels in that study differed from those of the Varsányi¹⁶ study from 1974 and this will be discussed further in the section 3.4.1.

In the S_1 state, only half of the fundamental vibrations of FBz- d_5 have been reported by Lipp and Seliskar.²⁹ No other work on the S_1 state of FBz- d_5 has been published.

In contrast to its non-deuterated isotopologue, for the FBz- d_5 cation no experimental studies in the literature were available.

In the results section 3.4.1 vibrational assignments of the FlBz- h_5 and FBz- d_5 REMPI spectra are discussed in the 0-1800 cm^{-1} range above the origin employing M_i nomenclature, and assignments reported in the references mentioned above are also confirmed.

3.3.2 Chlorobenzene- h_5 and Chlorobenzene- d_5

The ClBz- h_5 molecule has been studied even more abundantly than FBz- h_5 , making it one of the most- studied monosubstituted benzene species. IR and Raman studies up to 1956 were summarized by Whiffen,¹⁴ and early studies of the $S_1 \leftarrow S_0$ transition were reported by Purvis,³⁰ with Sponer and Wollman³¹ obtaining the first vibrationally-resolved UV absorption spectra of ClBz- h_5 at different temperatures in 1941. Cvitaš and Hollas³² in 1970 reported a measured S_1 origin position at $37048.2 \pm 0.2 \text{ cm}^{-1}$ from a high-resolution study, where the spectra were partially rotationally-resolved. One of the most comprehensive studies on ClBz- h_5 was undertaken by Jain, Bist and

coworkers,^{33,34,35} who assigned the majority of the normal modes in the ground and first electronically-excited states, reporting them in a series of publications divided into: planar vibrations of the S_1 state;³³ planar vibrations of the S_0 state;³⁴ and out-of-plane vibrations of the ground and excited states.³⁵ In a paper by this group,¹ Gardner and Wright have discussed previous assignments of the works mentioned above on the S_0 state vibrations of ClBz- h_5 .

The REMPI technique has been implemented by a large number of groups for studying the ClBz- h_5 molecule, providing assignments for the vibrational modes in the S_1 state.^{36,37,38} Murakami et al. used two-photon excitation, followed by ionisation,³⁶ whereas the experiments by Anderson et al.³⁷ and Walter et al.³⁸ were one-photon excitation followed by a further subsequent one-photon ionisation. The Ortiz group³⁹ have employed high-resolution, one-photon excitation REMPI spectroscopy with a supersonic molecular beam to obtain photoionisation spectra of the origin band of the S_1 state. The first study where the authors considered the two naturally occurring isotopes of chlorine in the $^{35}\text{ClBz-}h_5$ and $^{37}\text{ClBz-}h_5$ molecules was a high-resolution, one-photon excitation REMPI spectroscopy with a supersonic molecular beam experiment by the Ortiz group³⁹ where photoionisation spectra of the origin band of the S_1 state were obtained at a rotational temperature of 1 K; this allowed them to determine the shift of the origin band between the $^{35/37}\text{Cl}$ isotopologues. They report a shift of $0.14 \pm 0.02 \text{ cm}^{-1}$, which is within the resolution of the present work, therefore the origin band shift is not detected in this work. However, shifts of vibrational bands can be

larger, and such shifts are observable here and will be commented on later in section 3.4.2. Imhof and Kleinermanns⁴⁰ are the only authors to date who have recorded a laser-induced fluorescence spectrum of ClBz-*h*₅, also dispersing the fluorescence from several S₁ vibrational states. Other workers have reported a lack of success in obtaining fluorescence spectra for the ClBz-*h*₅ molecule using a discharge lamp⁴¹ or electron impact^{42,43,44} for excitation.

There are quite a large number of photoelectron studies on the vibrations in the ClBz-*h*₅⁺ cation, covering conventional HeI PES,⁴⁵ REMPI-PES,^{37,38,46} ZEKE spectroscopy,⁴⁷ and also one-photon⁴⁸ and two-photon, two-colour MATI spectroscopy.⁴⁹ Such studies are of great relevance to the assignments of the S₁ vibrations, since in the two-colour experiments, the assignment of the cation vibrations have often been used to aid the assignments of the intermediate vibrational level. The assignments in the papers mentioned will be compared to the quantum chemical calculations obtained in this project, as well as provide insight into the vibrational assignments of the S₁ state of the ClBz-*h*₅ and ClBz-*d*₅ molecules.

ClBz-*d*₅ is much less studied compared to its non-deuterated isotopologue. Nanney et al.⁵⁰ have reported vibrational assignments using IR and Raman spectroscopies. Those assignments were made in terms of symmetry and an approximate description of the atomic motions as well as comparing wavenumbers of the corresponding vibrations in the ClBz-*h*₅ and FBz-*h*₅ molecules. Varsányi¹⁶ has featured Nanney's vibrational assignments in his book. The recording of the S₁ ← S₀

REMPI spectrum is implied in a paper by Asselin et al.;⁴⁶ however, no spectra are included, as the emphasis was on REMPI-PES spectra.

3.3.3 Bromobenzene- h_5 and bromobenzene- d_5

Far less prior work is available on BrBz- h_5 compared to the ClBz- h_5 and FBz- h_5 molecules. The IR and Raman spectra of BrBz- h_5 have been detailed by a number of groups^{14,16,51,52,53} with the first spectra being reported over 75 years ago in 1941, and with the study by Whiffen¹⁴ being the most comprehensive to date. The assignments of the S_0 spectra have been achieved in terms of symmetry, the band-type (rotational contours), and also taking into account expected positions of vibrations based upon various mass-scaling rules. Wilson-type⁵⁴ labels for the vibrations have been employed by Varsányi¹⁶ and by Walter et al.²⁷ albeit with some (unexplained) switches in the latter work. As noted and discussed in section 1.3, the Varsányi labels are used inconsistently across the monohalobenzene species, making it problematic to compare vibrational activity across different monosubstituted benzene species, or even between different studies done on the same molecule.

Walerstein⁵⁵ and Sreeramamurty⁵⁶ produced brief reports of the UV absorption spectrum of BrBz- h_5 vapour, and a study by Prakash and Singh⁵⁷ has reported a reasonably detailed UV absorption spectrum of BrBz- h_5 vapour, predominantly at 0 °C. Klimusheva et al.⁵⁸ have reported absorption spectra of BrBz- h_5 in both vapour (20 K) and crystals (4 K), but experimental spectra are absent from that paper and very little experimental detail is given. Those studies are commented on in more detail in section 3.4.3.

Jet-cooled studies of the BrBz- h_5 $S_1 \leftarrow S_0$ transition have been reported by Dietz et al.⁵⁹ and Boesl et al.^{27,60} where Wilson⁵⁴ and Varsányi¹⁶ labelling nomenclatures were employed respectively. The Wilson and Varsányi vibrational assignments between the two main studies^{27,59} were not particularly consistent which can be attributed to the fact that vibrational labels across these two nomenclatures do not always uniquely correspond to the same vibrational motion as discussed in section 1.3. Just as was done for the S_0 state vibrations, the above authors have taken into account assignments of similar molecules as well as predicted mass and electronic shifts that arise with the BrBz- h_5 molecule to aid in their assignments.

To probe the vibrations of the cation, conventional PES^{45,61} REMPI-PES²⁷ and one-photon MATI studies⁴⁸ have been employed by various groups. In 2015 Powis and Holland et al.⁶² published photoelectron spectra of various BrBz- h_5 states including that of the $\tilde{X}^2B_1$ state using linearly polarized synchrotron radiation. The vibrational structure associated with these photoelectron bands has also been simulated with the calculated FC factors connecting the neutral ground and ionic states aiding the vibrational progression assignments. In the case of the REMPI-PES experiments, the assignment of the photoelectron spectrum and the resonant S_1 level are linked, and so will be discussed in the BrBz results section 3.4.3 below. A number of computational studies have also been performed on the BrBz- h_5 molecule in order to assist with the interpretation of the photoelectron, ultraviolet (UV) and vacuum ultraviolet (VUV) spectra.^{11,63}

As was seen for the FBz- d_5 and ClBz- d_5 species, BrBz- d_5 is also a much less studied molecule compared to its non-deuterated isotopologue, with only a few studies delivering information on the vibrations in the S_0 electronic state. Vibrationally-resolved IR and Raman spectra of the S_0 state have been reported by Nanney et al.,⁶⁴ where assignments were given in Mulliken notation and cautiously describing atomic motions, and comparison was also made to the wavenumbers of the corresponding vibrations in ClBz- d_5 and FBz- d_5 . In the literature there have been no previous reports of the $S_1 \leftarrow S_0$ BrBz- d_5 transition or any photoelectron spectra for this isotopologue.

3.3.4 Iodobenzene- h_5 and Iodobenzene- d_5

IBz- h_5 and IBz- d_5 are the least studied of the monosubstituted benzene species, with little previous work available on these isotopologues. S_0 state vibrational wavenumbers have been reported by a Whiffen¹⁴ study (with the same study including information on the FBz- h_5 , ClBz- h_5 and BrBz- h_5 molecules), and the work of Griffiths and Thompson.⁵³

No REMPI spectra for the $S_1 \leftarrow S_0$ transition of IBz- h_5 nor IBz- d_5 have been recorded in this project as the excited state is known to be extremely short lived. For monohalobenzene molecules, the S_1 state is a bound delocalised $\pi\pi^*$ state of predominantly singlet character, which interacts with a repulsive $n\sigma^*$ state of mainly triplet character via spin-orbit coupling. The dissociation rate of the $\pi\pi^*$ state increases with increasing mass of the halogen atom in the substituted benzene molecule since the spin-orbit coupling is strongly enhanced by the presence of a heavy substituent. These were the findings when the dissociation dynamics of

IBz, BrBz and ClBz were studied upon excitation at 266nm by femtosecond pump probe spectroscopy by M. Kadi et al.⁶⁵ Upon excitation of BrBz for example, the molecule was promoted to its first excited singlet state ($\pi\pi^*$). This state is predissociative due to the coupling with the repulsive triplet state ($n\sigma^*$).⁶⁶ However, this coupling is expected to be weaker here than for the IBz molecule since the Br atom is lighter than I. Accordingly, the dissociation rate of excited BrBz was found to be much slower compared to that of IBz. Two fast dissociation channels of ~ 350 and ~ 700 fs were observed in the IBz molecule, where the faster of the two dissociation rates is due to direct dissociation of the antibonding $n\sigma^*$ state.⁶⁷ In the BrBz molecule, the dissociation rate was 28 ps, and in ClBz the excited state lifetime was no longer than 1 ns. No fluorescence or REMPI spectra have been previously reported for IBz which is attributed to this short lifetime. However, it was possible for Kwon et al.²⁵ to record a one-colour MATI spectrum of IBz, since the predissociating S_1 state is bypassed. The PES studies of Holland et al.⁶⁸ and Potts et al.⁴⁵ each measured only two vibrational separations.

Moving onto the vibrations for S_0 IBz- d_5 , again one can see that there is very little work available, but experimental values and assignments are presented in a paper by Nanney et al.,⁶⁴ which were given Wilson-like⁵⁴ labels by Varsányi.¹⁶ There seems to be no experimental data or previous calculations available for the IBz- d_5 cation or indeed the S_1 state.

Quantum chemical calculations and vibrational assignments of the S_0 and D_0^+ states of IBz- h_5 and IBz- d_5 molecules were obtained in this project

for completeness and are presented in ref. 4 for the first time; however, with no accompanying REMPI spectrum for either of the two isotopologues, those results are not discussed in detail here.

3.4 Results

3.4.1 Fluorobenzene- h_5 and Fluorobenzene- d_5

The FBz- h_5 and FBz- d_5 (1+1) REMPI spectra recorded in this project are shown in Figure 3.1 where the main progressions of vibrational bands have been marked. Both of the spectra have been shifted to zero for straightforward comparison and the origin bands of the FBz- h_5 and FBz- d_5 molecules are at $37816.2 \pm 1 \text{ cm}^{-1}$ and at $37989.8 \pm 1 \text{ cm}^{-1}$ respectively, calibrated to the Lipp and Seliskar²⁰ spectra (itself calibrated using iron/neon hollow cathode lines). This FBz- h_5 origin value is also in good agreement with the band position given by Pugliesi et al.²² and Butler et al.¹⁷ The observed vibrational bands are not fully rotationally resolved; the position of an observed dip in the band profile of the coldest spectra was taken to be indicative of the rotationless transition in each vibrational feature. Rotational temperature was not explicitly measured in this case but the observation of the “rotationless dip” in all of the monohalobenzene spectra recorded here indicates a value of around 5 K; this is supported by previous work on toluene⁷⁶ in which the rotational temperature was explicitly estimated by simulations, and similar dips in spectral structure were taken as indicative of such temperature.

The FBz- h_5 REMPI spectrum is in very good agreement with previously published work,^{17,22} whereas there is no REMPI or LIF spectra available for comparison for the FBz- d_5 molecule. The FBz- d_5 isotopologue was studied in absorption by Lipp and Seliskar²⁰ therefore vibrational band positions from the spectra recorded here are further compared with theirs in this section. A good agreement exists between the FBz- h_5 and FBz- d_5 spectra, where a few bands undergo isotopic shifts, which is not at all surprising as participation of the hydrogen atoms is mode specific and the degree of their participation in the vibrational modes varies. Before analysis of the REMPI spectra for both isotopologues can be undertaken in detail, the origin of the M_i vibrational labels for the S_1 states need to be explored.

Table 3.1 below includes the calculated vibrational wavenumbers for the FBz- h_5 and FBz- d_5 molecules in the S_0 state, as well as previous experimental assignments. (See Table 1 of ref. 2 for the M_i labels in terms of Wilson labels).

The calculated B3LYP/aug-cc-pVTZ S_0 vibrational frequencies (harmonic values scaled by 0.97) for FBz- h_5 are in very good agreement with the B3LYP and RICC2 values reported by Pugliesi et al.²² employing a def2-TZVPP basis sets.

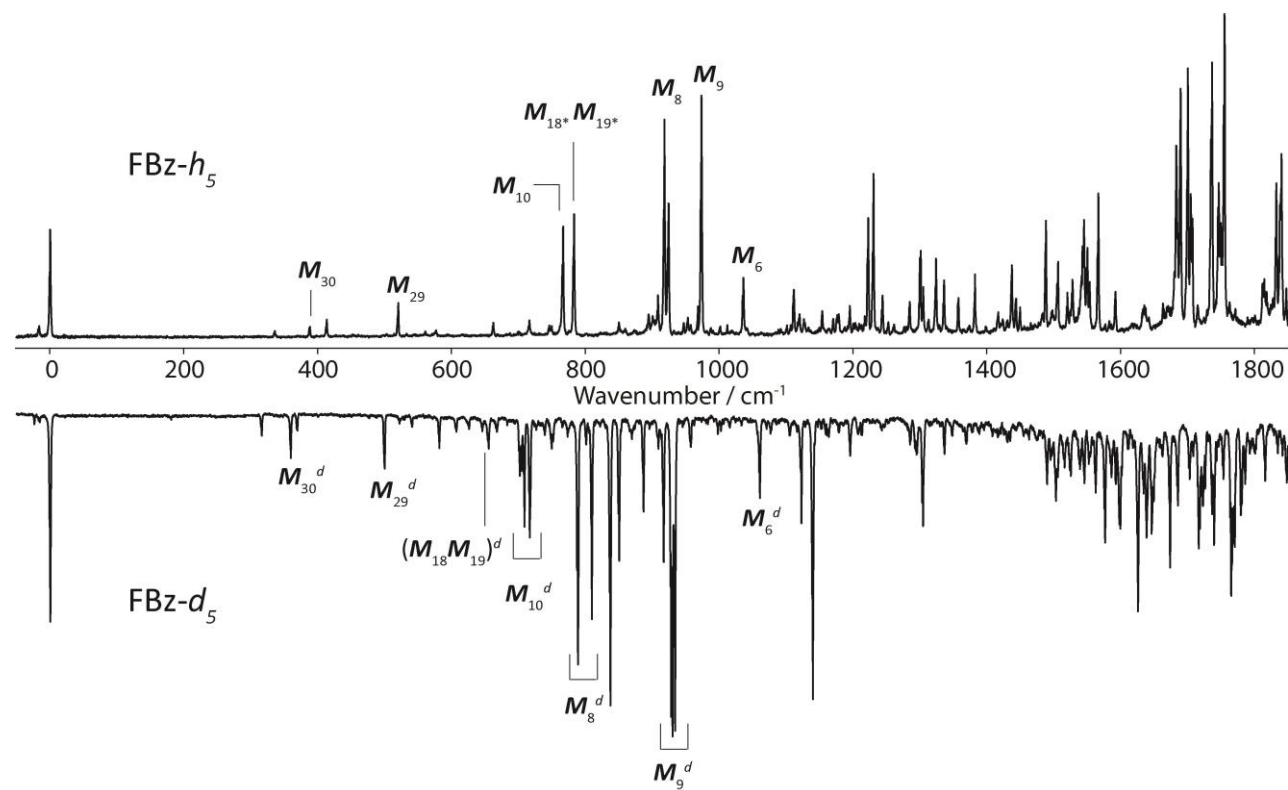


Figure 3.1. Complete spectral range scans of the $S_1 \leftarrow S_0$ (1+1) REMPI spectrum of $\text{FBz-}h_5$ (top trace, upright) and $\text{FBz-}d_5$ (bottom trace, inverted) where the main vibrational features up to 1150 cm^{-1} have been marked.

Table 3.1. Calculated and experimental vibrational wavenumbers (cm^{-1}) for the S_0 states of the FBz- h_5 and FBz- d_5 molecules.

Mode Label	FBz- h_5					Mode Label	FBz- d_5		
	Calculated			Experiment			Calc.	Experiment	
	This work ^a	Ref. b	Ref. c	Ref. d	Ref. e		This work ^a	Ref. d	Ref. e
a_1									
M_1	3108	3205.7	3241.7	3100	3094.4	M_1^d	2303	2320	-
M_2	3097	3194.9	3231.6	3087	3080.2	M_2^d	2291	-	2291.4
M_3	3077	3174.1	3209.6	3067	3061.0	M_3^d	2269	2295	-
M_4	1584	1640.1	1631.8	1603	1604.8	M_4^d	1551	1578	1579.2
M_5	1481	1529.7	1520.2	1499	1500.3	M_5^d	1371	1389	1395.9
M_6	1206	1248.0	1252.2	1220	1232.4	M_6^d	1148	1163	1172.4
M_7	1141	1179.1	1176.6	1156	1156.3	M_7^d	859	880	877.2
M_8	1010	1042.6	1036.3	1020	1022.7	M_8^d	808	817	819.8
M_9	993	1023.4	1014.3	1009	1008.6	M_9^d	951	959	963.9
M_{10}	799	825.1	818.2	806	808.7	M_{10}^d	741	753	752.5
M_{11}	509	526.7	516.5	520	517.1	M_{11}^d	496	505	502.8
a_2									
M_{12}	955	1003.2	962.9	955	957.4	M_{12}^d	776	(789)	776.2
M_{13}	812	874.7	839.1	818	817.6	M_{13}^d	632	682	636.1
M_{14}	413	456.7	426.2	[400] ^f	413.9	M_{14}^d	359	350	362.6
b_1									
M_{15}	977	1014.9	955.1	980	977.8	M_{15}^d	815	(825)	-
M_{16}	893	944.9	901.9	896	894.8	M_{16}^d	756	717	759.0
M_{17}	752	812.5	770.4	752	754.1	M_{17}^d	619	627	624.7
M_{18}	678	723.6	665.7	685	686.7	M_{18}^d	545	563	552.9
M_{19}	495	546.8	512.1	501	497.7	M_{19}^d	424	438	426.6
M_{20}	230	265.9	238.2	242	248.6	M_{20}^d	217	229	233.7
b_2									
M_{21}	3106	3203.1	3239.4	3053	-	M_{21}^d	2299	-	-
M_{22}	3085	3183.1	3218.3	3040	3069.5	M_{22}^d	2279	-	2280.8
M_{23}	1593	1645.8	1638.8	1597	-	M_{23}^d	1561	1564	-
M_{24}	1445	1494.4	1479.5	1460	1460.5	M_{24}^d	1325	1311	1311.7
M_{25}	1305	1355.7	1429.6	1290	1300.7	M_{25}^d	1021	1035	1035
M_{26}	1286	1331.8	1321.6	1326	-	M_{26}^d	1286	1281	-
M_{27}	1144	1186.6	1177.9	-	1127.7	M_{27}^d	831	843	843.2
M_{28}	1058	1093.3	1087.6	1066	1066.1	M_{28}^d	796	806	806.7
M_{29}	609	630.9	613.7	615	614.1	M_{29}^d	584	590	591.5
M_{30}	394	412.5	401.9	405	400.4	M_{30}^d	376	388	384.9

^a. B3LYP/aug-cc-pVTZ values scaled by 0.97

^b. B3LYP/def2-TZVPP from ref.22, unscaled

^c. RICC2/def2-TZVPP from ref.22, unscaled

^d. From ref. 16

^e. From ref. 15 and 20

^f. Estimated value.

Table 3.1 also includes previous experimental assignments for the FBz- h_5 fundamental vibrations. Yet again, good agreement is present between harmonic calculated values in this work and IR/Raman results obtained by Varsányi¹⁶ and Lipp and Seliskar.²⁰ It is worth pointing out that although each M_i label is assigned to a Wilson⁵⁴ or a Wilson-type Varsányi label, in reality, Wilson labels are not always an accurate representation of the atomic vibrational motion that occurs in substituted benzene species, something that was already brought to light by the work of Pugliesi et al.,²² Butler et al.¹⁷ and previous paper from this group.¹

To see how the FBz- d_5 vibrational modes correlate with the FBz- h_5 ones in the S_0 state, the Duschinsky matrix in Figure 3.2 below should be referred to.

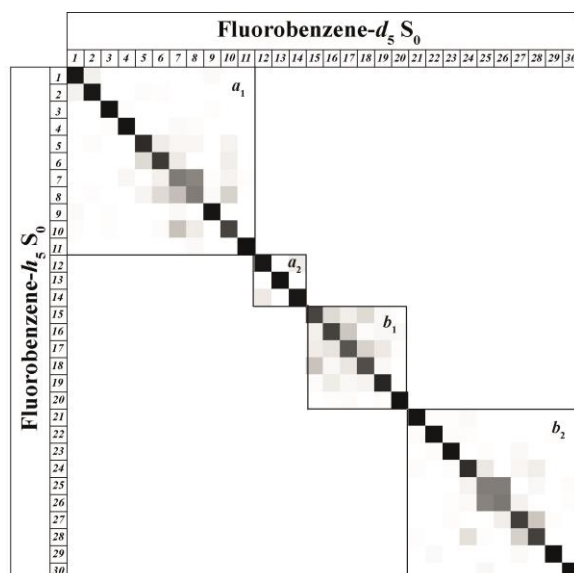


Figure 3.2. Generalized Duschinsky matrix showing how the S_0 state FBz- d_5 vibrational modes can be expressed in terms of the FBz- h_5 ones. Black shading indicates a normalized coefficient value of 1.00, while white indicates a value of 0.00, with the level of the grey shading indicating intermediate values. See section 3.2.

Overall diagonalisation is seen in Figure 3.2 where a single dominant contribution to the FBz- d_5 vibrational modes from those of FBz- h_5 can be identified with relative ease, informing one that the vibrational motion seen in the FBz- d_5 modes is very similar to the motion seen in the FBz- h_5 molecule. The only significant mixing is present for the M_7 and M_8 , and the M_{25} and M_{26} modes.

The vibrational modes of FBz- d_5 , or indeed any monohalosubstituted perdeuterated benzene molecule, are referred to as M_i^d modes, with the post-superscript d indicating the reference to the pentadeuterated molecule. Where overtones and combination bands are concerned the superscript d is added outside of parentheses; the lack of such a superscript indicates the reference to the non-deuterated isotopologue.

There are no other computational studies in the literature so there is no opportunity to compare the FBz- d_5 harmonic wavenumbers calculated in this project to others, however, the agreement between previous experimental values and those calculated here for the S_0 state of FBz- d_5 is generally good. (see Table 3.1) Compared to the Varsányi¹⁶ values, Lipp and Seliskar²⁰ have obtained slightly more precise values, both from vibrational spectroscopy, but also from observed hot bands in the electronic transition in the case of a_1 and b_2 symmetry modes.²¹ Across the set of experimental values in Table 3.1, good agreement is present. However, some values for vibrational modes by Steele et al.²⁸ did not match well with those from Varsányi nor Lipp and Seliskar and so those fundamentals were not included in the table (they are however available in ref. 28).

For the FBz- h_5 and FBz- d_5 molecules, each S_1 vibrational mode can be expressed in terms of S_0 modes. The mixing that occurs in the Duschinsky matrix, Figure 3.3 below, is the usual vibrational mixing one can anticipate upon electronic excitation due to changes in the electronic structure. Overall diagonalisation is present and vibrational motion in the S_1 state can be assigned to the corresponding S_0 vibration with confidence for both of the FBz isotopologues.

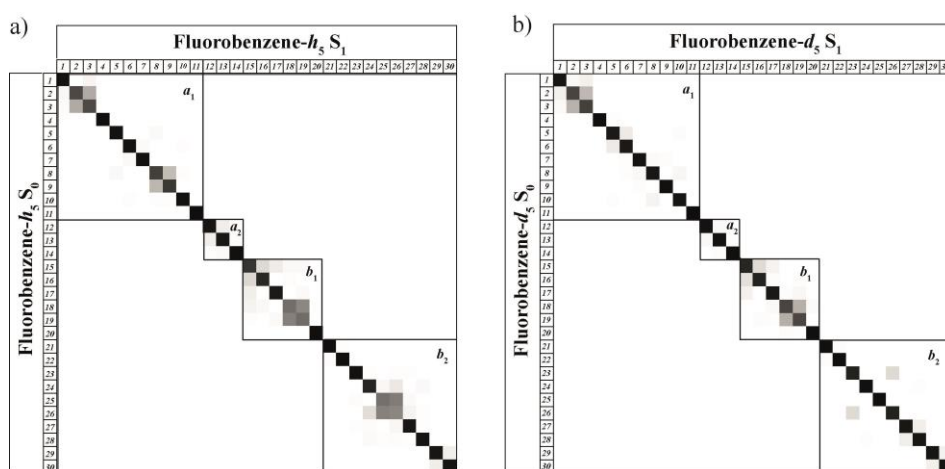


Figure 3.3. Duschinsky matrices showing how the S_1 vibrational modes are related to the S_0 ones for FBz- h_5 (a) and FBz- d_5 (b). Black shading indicates a normalized coefficient value of 1.00, while white indicates a value of 0.00, with the level of the grey shading indicating the intermediate values. Mode numbers along axes refer to M_i labels in the corresponding state.

Although Figure 3.3 provides a powerful tool of pictorially representing vibrational mixings, in Tables 3.2 and 3.3 one can find expressed the S_0 modes that make up the S_1 state vibrations for each isotopologue respectively. It was found that the FBz- h_5 S_1 M_{15} and M_{16} modes, although mixed, can be expressed in terms of the S_0 vibrations, with a dominant contribution in each case, and so these are labelled in the S_1 state with the same M_i label as in the ground state. The M_8 and M_9 modes

in FBz- h_5 molecule yet again look much more mixed compared to the FBz- d_5 case; however, they too have corresponding dominant contributions. In contrast, the M_{18} and M_{19} modes are each significant mixtures of the corresponding S_0 modes.

To highlight this, these modes are labelled in the S_1 state as M_{18}^* and M_{19}^* in the case of FBz- h_5 , with the M_{19}^* having the lower wavenumber. The M_{26} mode does not have a dominant contribution, but is highly mixed with the M_{25} mode in S_1 , even though the M_{25} mode does have a dominant contribution; as above this is highlighted by representing the M_{25} and M_{26} modes as M_{25}^* and M_{26}^* , with the M_{26}^* having the lower wavenumber. It is worth mentioning here that in the paper on FBz isotopologues (ref. 2) a different notation was applied to the mixed transitions in the S_1 state for the FBz- h_5 molecule. M_{18} and M_{19} transitions were labelled as $M_{[18/19]a}$ and $M_{[18/19]b}$ respectively and M_{25} and M_{26} were labelled as $M_{[25/26]a}$ and $M_{[25/26]b}$. However in the ClBz study (ref. 3) vibrations in the S_1 state that had a significant contribution from multiple S_0 modes were labelled with a * symbol for clarity; here, the same was employed for FBz for clarity and to be consistent across monosubstituted species.

There is also mode mixing for the FBz- d_5 molecule but there is always a dominant contribution leading to a unique M_i^d label being assigned to all 30 vibrational modes, but noting that some of the S_1 modes will be significantly mixed forms of the S_0 ones.

Tables 3.2 and 3.3 also include TD-DFT B3LYP/aug-cc-pVTZ vibrational wavenumbers for the S_1 states of FBz- h_5 and FBz- d_5 molecules respectively, calculated during this project. For the FBz- h_5 isotopologue, RICC2/def2-TZVPP calculated values for the S_1 state from ref. 22 are also included in Table 3.2. No such calculations are available in ref. 22 for FBz- d_5 , so “isotopically-scaled” versions of these are included where the isotopic shift between FBz isotopologues as calculated at the TD-DFT B3LYP/aug-cc-pVTZ level of theory was applied to the FBz- h_5 S_1 RICC2/def2-TZVPP values. For the FBz- h_5 molecule most of the TD-DFT B3LYP/aug-cc-pVTZ and RICC2/def2-TZVPP vibrational wavenumbers are in good agreement with each other. A number of scaled harmonic values calculated in this project are in better agreement with experimental results than are the RICC2 values. Butler et al.¹⁷ and Pugliesi et al.²² with the help of LIF and REMPI experiments respectively, have assigned the majority of the S_1 vibrational structure, and where available those assignments have been confirmed by DF and ZEKE. With the work of Pugliesi et al.²² coming a number of years after Butler et al.¹⁷ they have added refinements to the Butler et al. assignments, particularly emphasising how some modes in the S_1 state are mixtures of the S_0 vibrational modes, where some mixtures are of complex character. In this work there is essentially full agreement with the previous assignments of Butler et al. and Pugliesi et al., where only minor modifications are employed. Previous vibrational assignments give a great advantage in labelling the vibrational features seen in the S_1 (1+1) REMPI spectrum of the FBz- d_5 molecule.

In the cases where the FBz- h_5 S_1 vibrational wavenumber has been experimentally determined, the ratio between the TD-B3LYP value and the experimental one is utilised as a scaling factor to give new “experimental scaled” values for FBz- d_5 from its TD-B3LYP values. In the process of spectral assignments, all of the different calculated values were considered, but more weight was given to the “experimental scaled” values.

The next section will tackle a detailed vibrational band assignment of the (1+1) REMPI recorded spectra for the FBz- h_5 and FBz- d_5 molecules.

Table 3.2. Calculated and experimental vibrational wavenumbers (cm^{-1}) for the S_1 state of FBz- h_5 .

Mode Label	Mixing ^a	FBz- h_5					
		Calculated	Experimental				
		This Work ^b	Ref. c	Ref. d	Ref. e	Ref. f	This work ^g
a_1							
M_1	M_1	3134.3	3262.4	-	-	-	-
M_2	M_2, M_3	3118.9	3246.3	-	-	-	-
M_3	M_3, M_2	3091.9	3220.6	-	-	-	-
M_4	M_4	1513.4	1546.7	-	-	-	-
M_5	M_5	1408.9	1431.3	-	-	-	-
M_6	M_6	1210.7	1244.0	1220	1230	1220.4	1230.0
M_7	M_7	1115.7	1143.5	922	-	-	-
M_8	M_8, M_9	932.2	936.1	916	917	911.0	917.8
M_9	M_9, M_8	963.2	978.3	968	969	963.0	970.0
M_{10}	M_{10}	774.4	780.1	765	765	761.1	766.2
M_{11}	M_{11}	459.8	459.4	460	460	457.6	[456.0]
a_2							
M_{12}	$M_{12}(M_{13})$	622.3	597.1	-	643	-	[643.8]
M_{13}	$M_{13}(M_{12})$	482.5	486.9	-	509	-	[509.2]
M_{14}	M_{14}	152.2	208.7	206	206	204.9	[206.6]
b_1							
M_{15}	$M_{15}(M_{16}, M_{17})$	799.5	738.1	-	755	-	[756.0]
M_{16}	$M_{16}(M_{15})$	681.8	610.9	-	661	-	[661.8]
M_{17}	$M_{17}(M_{15})$	588.7	570.9	555	555	-	[555.3]
M_{18}^*	M_{18}, M_{19}	472.4	458.4	-	451	-	[451.7]
M_{19}^*	M_{19}, M_{18}	301.6	333.5	-	331	328.4	[331.1]
M_{20}	M_{20}	173.0	174.2	168	168	166.4	[167.8]
b_2							
M_{21}	M_{21}	3130.1	3258.6	-	-	-	-
M_{22}	M_{22}	3112.5	3240.0	-	-	-	-
M_{23}	M_{23}	1470.5	1691.4	-	-	-	-
M_{24}	$M_{24}(M_{26})$	1382.7	1398.9	-	-	-	-
M_{25}^*	$M_{25}, M_{26}(M_{24})$	1411.2	1530.9	1589	1589	-	-
M_{26}^*	M_{25}, M_{26}	1265.3	1284.0	-	-	-	-
M_{27}	M_{27}	1134.1	1161.7	-	-	-	-
M_{28}	M_{28}	982.1	986.9	976	955	-	952.6
M_{29}	$M_{29}(M_{30})$	508.9	514.4	519	518	515.7	520.0
M_{30}	M_{30}	381.6	383.7	387	388	385.0	388.0

^a. Duschinsky mixing of the S_0 state vibrations to form the S_1 state ones.

^b. Present work. TD-B3LYP/aug-cc-pVTZ scaled by 0.97.

^c. RICC2/def2-TZVPP values from ref. 22

^d. Absorption spectroscopy from ref. 20

^e. LIF spectroscopy from ref. 17

^f. REMPI spectroscopy from ref. 22

^g. Values in square brackets are derived from overtones or combination bands, other values are from fundamentals. Values in parentheses indicate that the spectral feature is part of a FR and so the actual position of the fundamental is not definitive.

Table 3.3. Calculated and experimental vibrational wavenumbers (cm^{-1}) for the S_1 state of FBz- d_5 .

Mode Label	Mixing ^a	This Work ^b	FBz- d_5		Ref. e	This work- Experiment ^f
			RICC2 scale of this work ^c	Exp. scaling of this work ^d		
$\mathbf{a_1}$						
M_1^d	M_1^d	2320.5	2415.4	-	-	-
M_2^d	M_2^d, M_3^d	2301.8	2395.8	-	-	-
M_3^d	M_3^d, M_2^d	2279.8	2374.7	-	-	-
M_4^d	M_4^d	1475.6	1508.1	-	-	-
M_5^d	$M_5^d(M_6^d)$	1291.6	1312.2	-	-	-
M_6^d	$M_6^d(M_5^d)$	1134.3	1165.5	1153.6	1137	1139.6
M_7^d	M_7^d	832.4	853.1	-	836	-
M_8^d	M_8^d	788.8	792.1	774.4	786	788.6
M_9^d	M_9^d	919.6	934.0	926.4	932	(931.0)
M_{10}^d	M_{10}^d	710.2	715.4	702.0	747	(709.4)
M_{11}^d	M_{11}^d	447.9	447.5	444.1	-	-
$\mathbf{a_2}$						
M_{12}^d	M_{12}^d	512.3	491.5	533.8	-	[530.2]
M_{13}^d	M_{13}^d	379.7	383.2	406.4	-	[401.6]
M_{14}^d	M_{14}^d	129.3	177.3	183.7	179	[179.8]
$\mathbf{b_1}$						
M_{15}^d	$M_{15}^d(M_{16}^d)$	688.9	636.0	645.4	-	[651.3]
M_{16}^d	$M_{16}^d(M_{15}^d)$	599.1	536.8	579.1	-	-
M_{17}^d	M_{17}^d	466.5	452.4	433.1	-	[443.2]
M_{18}^d	M_{18}^d, M_{19}^d	255.3	247.7	234.6	-	[234.2]
M_{19}^d	M_{19}^d, M_{18}^d	374.5	414.1	404.0	-	[411.4]
M_{20}^d	M_{20}^d	162.3	163.4	157.1	158	[158.1]
$\mathbf{b_2}$						
M_{21}^d	M_{21}^d	2311.5	2406.4	-	-	-
M_{22}^d	M_{22}^d	2291.2	2385.0	-	-	-
M_{23}^d	$M_{23}^d(M_{26}^d)$	1436.8	1652.6	-	-	-
M_{24}^d	M_{24}^d	1222.1	1236.4	-	-	-
M_{25}^d	M_{25}^d	1004.1	1018.9	-	-	-
M_{26}^d	$M_{26}^d(M_{23}^d)$	1404.4	1523.6	-	-	-
M_{27}^d	$M_{27}^d(M_{28}^d)$	818.0	837.9	-	-	-
M_{28}^d	$M_{28}^d(M_{27}^d)$	768.5	772.2	739.0	-	739.0
M_{29}^d	M_{29}^d	490.7	496.0	501.8	498	499.0
M_{30}^d	M_{30}^d	363.7	365.7	370.1	368	369.4

^a. Duschinsky mixing of the S_0 state vibrations to form the S_1 state ones. S_1 state vibrational motion is matched to the S_0 one. More detailed discussion on how scheme is constructed can be found in Section 3.2.

^b. Present work. TD-B3LYP/aug-cc-pVTZ values scaled by 0.97

^c. Used the RICC2-B3LYP ratio in FBz- h_5 to scale the FBz- d_5 B3LYP values.

^d. Used the experimental-TD-B3LYP ratio in FBz- h_5 to scale the FBz- d_5 TD-B3LYP values

^e. From ref. 20 and 21

^f. Values in square brackets are derived from overtones or combinations bands, other values are from fundamentals. Values in parentheses indicate that the fundamental is part of a Fermi resonance and so the actual position of the fundamental is not definitive.

1. Low wavenumber range (0 - 550 cm⁻¹)

Figure 3.4 below is the expanded view of the low-wavenumber range of the FBz-*h*₅ and FBz-*d*₅ REMPI spectra.

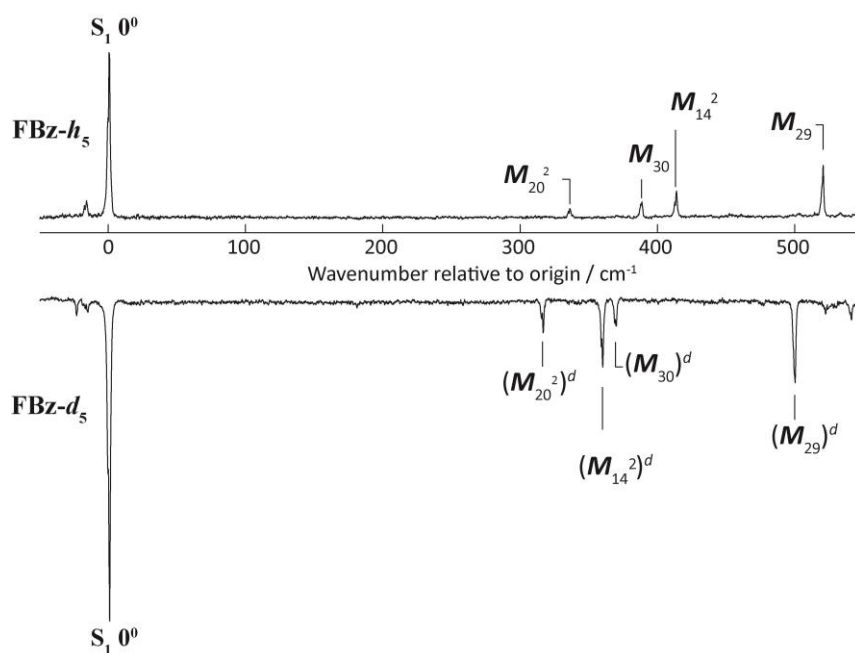


Figure 3.4. Expanded views of the low wavenumber regions (0–550 cm⁻¹) of the S₁ ← S₀ (1+1) REMPI spectra of FBz-*h*₅ (top trace, upright) and FBz-*d*₅ (bottom trace, inverted).

In both of the spectra presented in Figure 3.4 a strong origin band is observed with much weaker features appearing to higher wavenumber. Generally, experimental vibrational wavenumbers obtained in this project agree almost exactly with the values of Lipp and Seliskar²⁰ and Butler et al.,¹⁷ whereas Pugliesi et al.²² values tend to be 3 to 5 cm⁻¹ lower than the ones obtained here; such discrepancies are unable to be accounted for. Below 450 cm⁻¹, three main bands are observed for the FBz-*h*₅ molecule,

in agreement with Butler et al.¹⁷ and Pugliesi et al.²² The vibrations are assigned as the M_{20}^2 , M_{30} and M_{14}^2 modes. All three of the experimental values for these modes are in good agreement with the RICC2 calculated vibrational wavenumbers by Pugliesi et al.²² B3LYP values calculated in this work for the M_{20} and M_{30} fundamental modes are also in good agreement with experimental positions; however, the M_{14} mode is in poor agreement with the RICC2 result (and with experiment) but as was explained in section 3.2 the B3LYP method is unable to describe this motion well, something experienced by other groups too.¹¹

In the FBz- d_5 spectrum, there are also three main bands that appear below 450 cm^{-1} and these again were also observed by Lipp and Seliskar²⁰ although the lowest wavenumber feature, here $(M_{20}^2)^d$, was unassigned by them. The assignments here for the other two vibrational bands match the assignments given by Lipp and Seliskar, although they used Wilson notation. Owing to isotopic shifts, the $(M_{14}^2)^d$ vibration now appears in between the $(M_{20}^2)^d$ and M_{30}^d bands, see Figure 3.4.

In the FBz- h_5 spectrum, Pugliesi et al.²² identified a very weak band at 457.6 cm^{-1} assigned to M_{11} , confirming it with ZEKE spectroscopy and quantum chemical calculations, where the weak intensity is attributed to the small geometric change experienced along this coordinate during the $S_1 \leftarrow S_0$ transition. No such feature was observed here or by Butler et al.¹⁷ or by Lipp and Seliskar²⁰ work. There was also no equivalent vibrational band seen in the FBz- d_5 spectrum.

The next observed vibrational band is intense for both of the isotopologues, located at 520.0 cm⁻¹ in FBz-*h*₅ and 499.0 cm⁻¹ in FBz-*d*₅, attributed to the *M*₂₉ and *M*₂₉^{*d*} fundamentals respectively. The *M*₂₉ vibration in both isotopologues corresponds to the classic “*ν*_{6b}” mode of benzene, which appears in the S₁ ← S₀ spectrum of benzene as a result of vibronic coupling with the second electronically-excited state; leading to intensity borrowing.

2. Medium wavenumber range (550 - 1000 cm⁻¹)

From 550 cm⁻¹ onwards the spectra for both FBz-*h*₅ and FBz-*d*₅ molecules become much busier with vibrational features. As with the low wavenumber section, assignments for the FBz-*h*₅ vibrations reported previously by Lipp and Seliskar,²⁰ Butler et al.¹⁷ and Pugliesi et al.²² over this wavenumber range are very comprehensive so in this project the perhydrogenated isotopologue is straightforwardly assigned based on those, with only the most intense features being mentioned here as seen in Figure 3.5 where expanded views are presented.

A band at 662.2 cm⁻¹ in the FBz-*h*₅ spectrum (top spectrum, Figure 3.5) is assigned to the *M*₁₉*² mode which was also assigned as such by Butler et al.,¹⁷ but as was noticed by Pugliesi et al.²² fundamental *M*₁₉* vibration is better described in the S₁ state as the mixture of the *M*₁₈ and *M*₁₉ modes, where mixing was visible in the Duschinsky matrix presented in Figure 3.2a. The weak band at 715.8 cm⁻¹ was assigned as *M*₁₃*M*₁₄ by Butler et al. which was confirmed by dispersed fluorescence; this is also confirmed by the RICC2 calculated wavenumbers. The two very strong lines at

766.2 and 782.8 cm^{-1} are a Fermi resonance between the M_{10} and the combination $M_{18}^*M_{19}^*$, confirmed by the similar structure observed when dispersing the fluorescence from each feature.¹⁷

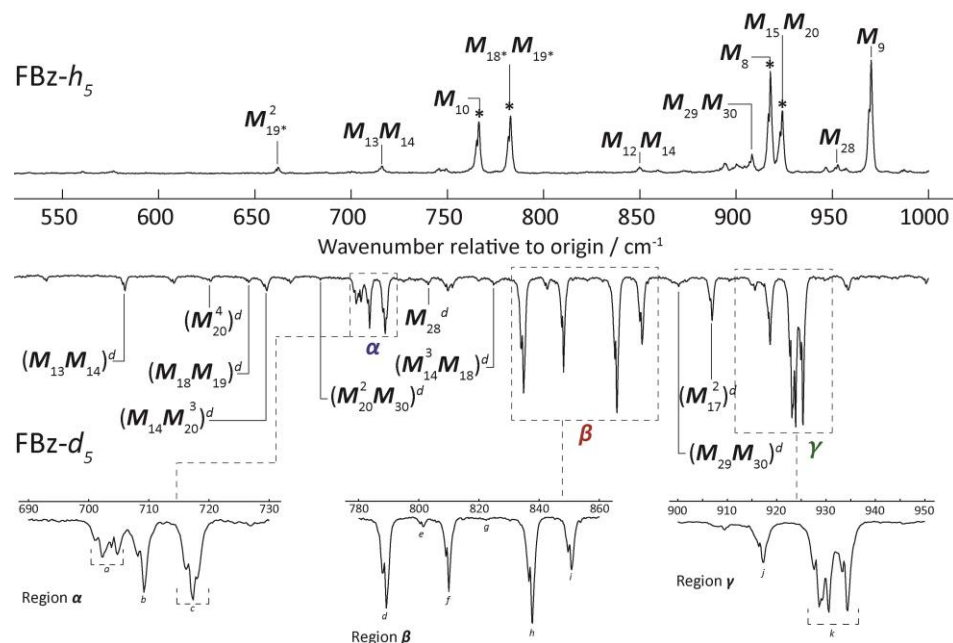


Figure 3.5. Expanded views of the medium wavenumber regions (550–1000 cm^{-1}) of the $S_1 \leftarrow S_0$ (1+1) REMPI spectra of FBz- h_5 (top trace, upright) and FBz- d_5 (bottom trace, inverted). The zoomed-in sections at the bottom are those for Regions α , β and γ of FBz- d_5 , which are indicated by dashed boxes in the main spectrum, a detailed assignments of these are discussed in section 3.4.1.

Straight away from Figure 3.5 one can spot how much more congested the FBz- d_5 spectrum is compared to its perhydrogenated isotopologue. Lipp and Seliskar²⁰ paper reported no features in the region of 500–736 cm^{-1} and only a few vibrational bands were noted in the 770 - 850 cm^{-1} range, whilst in the recorded spectrum here many features are present, including some of high intensity.

Knowing the FBz- h_5 vibrational activity is a great advantage as similar vibrational activity is expected in the FBz- d_5 molecule since the changes in the equilibrium geometry are the same for the two isotopologues. Of course there will also be difference; as isotopic shifts occur, vibrations will move in and out of Fermi Resonance (FR) with each other. As mentioned before not only the calculated TD-DFT/B3LYP scaled frequencies will be relied upon in assignments, but the scaled 'RICC2' frequencies will also be considered, where FBz- d_5 TD-DFT/B3LYP values were scaled by the same factor as the ratio of the TD-DFT/B3LYP and RICC2 values for FBz- h_5 . Table 3.4 summarises assigned vibrational features present in the FBz- d_5 spectrum that are of reasonable intensity, whereas Table 3.5 includes possible assignments for the α , β and γ regions, enlarged sections of low intensity regions seen in Figure 3.5.

One of the first features to consider is the $M_{10}/M_{18}M_{19}^*$ FR seen in the FBz- h_5 spectrum, here however that FR is not observed because due to the isotopic shift the vibrations have moved apart significantly, with the $(M_{18}M_{19})^d$ combination band and the M_{10}^d vibration expected to appear close to 640 cm^{-1} and 705 cm^{-1} respectively. A weak feature at 645.6 cm^{-1} has been assigned to $(M_{18}M_{19})^d$ and the weakness of this feature (Figure 3.5, bottom trace) is in line with the corresponding vibration being optically dark in the FBz- h_5 molecule and having gained intensity from M_{10} through FR, as suggested by Butler et al. in ref.17. The calculated position of the M_{10}^d vibration in the FBz- d_5 spectrum seems to provide intensity for the many features seen in Region α of Figure 3.5, where such features are absent in the FBz- h_5 spectrum. Table 3.5 lists the

vibrations that are likely to be contributing to this feature, however as these vibrations are likely to be mixed in a “complex FR”, Table 3.5 simply lists probable contributors. If one wished to disentangle this further, DF or ZEKE spectroscopy could be employed; or, given the energetic proximity of these features, a time-resolved study could be attempted with a picosecond pulse producing a wavepacket consisting of all vibrational eigenstate contributions.^{47,69,70}

Region β in the wavenumber range 780–860 cm^{-1} contains four intense bands, *d*, *f*, *h* and *i* as designated in Figure 3.5 and Table 3.4, with two additional, much weaker associated features. Table 3.5 lists possible contenders for these bands and as these are quite intense it is expected that equivalent bands would have been seen in the FBz-*h*₅ spectrum but there are no obvious candidates close in wavenumber. Proposed vibrational band assignments in Table 3.5 are done to the best of ones ability based on this work, due to the convoluted nature of the region further techniques would have to be employed in order to confirm the assignments with certainty. Some strong features in the FBz-*h*₅ spectrum that could isotopically-shift into this range were the next favourable contenders and the M_8^d vibration is expected to lie in the 775 - 790 cm^{-1} range from the calculated values. That fits the position of band *d* very well, and even though there are other possibilities for this feature, there is no other strong feature that would fit the M_8^d vibration so well. The $(M_{15}M_{20})^d$ vibration is expected in this wavenumber region as it was quite intense in the FBz-*h*₅ spectrum, and so it seems likely that one of the bands *e* or *f* is due to this combination. Lipp and Seliskar²⁰ have observed

two vibrational bands in this range, although it is difficult to assign with certainty which exact two bands they have observed.

A band at 886.4 cm^{-1} is assigned to the $(M_{17}^2)^d$ vibration as it is expected to appear at $865\text{--}900\text{ cm}^{-1}$. The $(M_{13}^2)^d$ vibration is expected to be positioned in the $765\text{--}815\text{ cm}^{-1}$ range and, although the agreement is not as close as desired, the only reasonable choice is to assign this as band *h* with the discrepancy attributable to deficiencies in the calculated scaled values, and perhaps also shifts due to FR. *f* and *i*, the two less intense bands may then be assigned as vibrations that gain intensity from FR with the M_8^d and $(M_{13}^2)^d$ states being the optically allowed ones, with no definitive assignments known; Table 3.5 lists the most plausible candidates. For example, if one takes the assignment of band *h* as $(M_{13}^2)^d$ and assumes that band *i* arises from FR, then assignments to M_7^d or $(M_{17}M_{19})^d$ are possible (as they have the same symmetry), with a gain in intensity from the FR in FBz-*d*₅ perhaps being the explanation for their non-observance in the FBz-*h*₅ spectrum.

The next region, γ , is the most complex of the three regions as it contains a number of overlapping features, with the main one being labelled as *k*. A weaker feature at 916.6 cm^{-1} , labelled *j*, has its likely contributions listed in Table 3.5. Feature *k* corresponds well to the expected position of the M_9^d vibration, which is intense in the case of FBz-*h*₅, see Figure 3.5, with no other obvious intense band being expected in this region. It is concluded that there are several bands that make up a complex FR in the $927\text{--}935\text{ cm}^{-1}$ range, with all candidates being included in Table 3.5.

With M_9^d being the main intensity carrier, only candidates of overall a_1 symmetry are able to gain intensity from the M_9^d . Although plausible candidates are proposed, again further evidence from ZEKE, DF or time-resolved studies will be required to unravel the complicated interactions and confirm assignments.

Table 3.4. A summary of the assigned vibrational features from the present work for the $S_1 \leftarrow S_0$ transition of FBz- d_5 .

Experimental Band (cm ⁻¹) ^a	Assignment ^b	This work B3LYP ^c	From experimental fundamental ^d	Overall symmetry
316.2	(M_{20}^2) ^d	324.6	316.2 ^e	a_1
359.6	(M_{14}^2) ^d	258.6	359.6 ^e	a_1
369.4	M_{30}^d	363.7	369.4 ^e	b_2
499.0	M_{29}^d	490.7	499.0 ^e	b_2
581.4	($M_{13}M_{14}$) ^d	509.0	581.4 ^e	b_2
626.0	(M_{20}^4) ^d	649.2	632.4	a_1
645.6	($M_{18}M_{19}$) ^d	629.8	645.6 ^e	a_1
654.6	($M_{14}M_{20}^3$) ^d	616.2	654.1	a_1
667.4			-	
683.6	($M_{20}^2M_{30}$) ^d	688.3	685.6	b_2
701.0 <i>a</i>	[($M_{14}^3M_{20}$) ^d]	550.2	697.5	a_1
702.2 <i>a</i>	[M_{10}^d]	710.2	709.4 ^{e,f}	a_1
703.8 <i>a</i>	[($M_{14}M_{20}M_{30}$) ^d]	655.3	707.3	a_1
704.8 <i>a</i>	[($M_{18}M_{20}^3$) ^d]	742.2	708.5	a_1
708.4 <i>b</i>	[($M_{12}M_{14}$) ^d]	641.6	710.0 ^e	a_1
716.6 <i>c</i>	[(M_{14}^4) ^d]	517.2	719.2	a_1
717.8 <i>c</i>			-	
726.8	($M_{14}^2M_{30}$) ^d	622.3	729.0	b_2
739.0	M_{28}^d	768.5	739.0 ^e	b_2
749.8			-	
773.6	($M_{14}^3M_{18}$) ^d	643.2	773.6	b_2
788.6 <i>d</i>	[M_8^d]	788.8	788.6 ^e	a_1
800.8 <i>e</i>			*	
809.4 <i>f</i>	[($M_{15}M_{20}$) ^d]	851.2	809.4 ^e	b_2
822.2 <i>g</i>	[M_{27}^d]	818.0	822.2 ^e	b_2
837.0 <i>h</i>	[(M_{13}^2) ^d]	759.4	803.2	a_1
850.0 <i>i</i>	[M_7^d]	832.4	850.0 ^e	a_1
866.4	-			
869.6	($M_{29}M_{30}$) ^d	854.4	868.4	a_1
886.4	(M_{17}^2) ^d	933.0	886.4	a_1
916.6 <i>j</i>	($M_{17}M_{20}^3$) ^d	953.4	917.5	a_1
927.6 <i>k</i>			*	
928.6 <i>k</i>			*	
929.2 <i>k</i>			*	
930.6 <i>k</i>	[M_9^d]	919.6	931.0 ^{e,f}	a_1
933.2 <i>k</i>			*	
934.4 <i>k</i>			*	
957.0	[($M_{18}M_{19}M_{20}^2$) ^d]	954.4	961.8	a_1
1006.4	[($M_{18}M_{19}M_{14}^2$) ^d]	888.4	1005.2	a_1
1015.6	[($M_{18}M_{19}M_{30}$) ^d]	993.5	1015.0	b_2
1060.4	(M_{12}^2) ^d	1024.6	1060.4 ^e	a_1

1122.2	$(M_{15}M_{20})^3$ ^d	1175.8	1125.6	a_1
1139.6	M_6 ^d	1134.3	1139.6 ^e	a_1

^{a.}The letters correspond to the peaks identified in Figure 3.5 and in Table 3.5, and which are discussed in the text.

^{b.} Assignments in square brackets are those which are less certain, due to a number of possibilities for the feature, but which are thought to be the most sensible of the selection available. Asterisks indicate bands where there are many possible assignments. These are given for certain features in region γ , and the possible assignments for these features are given in Table 5.

^{c.} S_1 state vibrations have been calculated employing TDDFT/B3LYP level of theory.

^{d.}All values come from experimental fundamentals.

^{e.} An experimental fundamental is taken from this feature.

^{f.} This fundamental is part of a FR and so the actual position of the fundamental is not definitive.

Table 3.5. Possible assignments for the features in Regions α , β and γ - as marked in Figure 3.5.

FBz-d_5							
Region	Feature	Exp. band cm^{-1} _a	Calculated band position (cm^{-1})			Exp. _e	Possible Contributions _f
			This work _b	RICC2- scaled _c	Exp. scaled _d		
α	a	701.0	550.2	695.3	708.2	697.5	$(M_{14}^3 M_{20})^d (b_2)$
	b	702.2	710.2	715.4	702.0	-	$M_{10}^d (a_1)$
		703.8	655.3	706.4	710.9	707.3	$(M_{14} M_{20} M_{30})^d (a_1)$
		704.8	742.2	737.9	705.9	708.5	$(M_{18} M_{20}^3)^d (a_1)$
		708.4	641.6	668.8	717.5	710.0	$(M_{12} M_{14})^d (a_1)$
	c	716.6	517.2	709.2	734.8	719.2	$(M_{14}^4)^d$
		717.8					
	d e f	788.6 800.8 809.4	788.8	792.1	774.4	-	M_8^d
			739.5	788.2	784.9	782.0	$(M_{11} M_{14} M_{20})^d$
			748.3	790.7	788.4	783.4	$(M_{14} M_{18} M_{30})^d$
			835.2	822.2	783.4	784.6	$(M_{18}^2 M_{20}^2)^d$
			851.2	799.4	802.5	-	$(M_{15} M_{20})^d$
			759.4	766.4	812.8	803.2	$(M_{13}^2)^d$
			706.5	802.1	811.5	803.7	$(M_{11} M_{14}^2)^d$
			802.2	836.1	810.0	806.3	$(M_{14} M_{18}^2 M_{20})^d$
			754.2	797.3	810.4	813.0	$(M_{13} M_{19})^d$
			854.4	784.5	813.7	813.3	$(M_{16} M_{18})^d$
			811.6	813.2	814.2	813.5	$(M_{11} M_{30})^d$
			815.3	822.8	816.0	815.2	$(M_{20}^2 M_{29})^d$
β	g h i	822.2 837.0 850.0	749.0	828.2	808.0	822.8	$(M_{19}^2)^d$
			769.2	850.0	836.6	828.0	$(M_{14}^2 M_{18}^2)^d$
			818.2	813.3	829.1	831.1	$(M_{14} M_{15})^d$
			818.0	837.9	-	-	M_{27}^d
			832.4	853.1	-	-	M_7^d
			865.5	858.6	835.8	836.4	$(M_{11} M_{28} M_{20})^d$
			782.3	836.7	842.6	836.9	$(M_{14} M_{20} M_{29})^d$
			874.3	861.1	839.3	837.8	$(M_{18}^2 M_{30})^d$
			846.2	835.6	839.5	844.8	$(M_{13} M_{17})^d$
			841.0	866.5	837.1	854.6	$(M_{17} M_{19})^d$
			749.3	850.6	869.2	858.6	$(M_{14}^2 M_{29})^d$
	j	916.6	828.4	918.2	901.9	907.4	$(M_{14} M_{19} M_{20}^2)^d$
			958.5	942.9	913.3	912.5	$(M_{11} M_{18}^2)^d$
			875.3	921.0	920.1	913.0	$(M_{14} M_{18} M_{29})^d$
			953.4	942.6	904.4	917.5	$(M_{17} M_{20}^3)^d$
			800.6	901.2	930.9	919.3	$(M_{13} M_{14}^2 M_{20})^d$
γ	k	927.6 928.6 929.2 930.6 933.2 934.4	919.6	934.0	926.4	-	$M_9^d (a_1)$
			795.4	932.1	928.5	929.1	$(M_{14}^2 M_{19} M_{20})^d (a_1)$
			905.7	912.3	933.6	929.1	$(M_{13} M_{20} M_{30})^d (a_1)$
			892.0	874.7	940.2	931.8	$(M_{12} M_{13})^d (a_1)$
			1021.2	990.8	938.4	936.8	$(M_{18}^4)^d (a_1)$
			900.5	943.2	931.2	938.9	$(M_{19} M_{20} M_{30})^d (b_2)$
			920.4	956.5	931.0	939.2	$(M_{14} M_{17} M_{20}^2)^d (b_2)$
			886.8	905.6	937.8	941.6	$(M_{12} M_{19})^d (b_2)$
	l	940.0 941.0	940.0	941.0	940.0	941.0	$(M_{14} M_{18} M_{20})^d$
			941.0	942.0	941.0	942.0	$(M_{14} M_{18} M_{20})^d$

^a Observed peak positions are given although these will slightly different to the band origin positions.

^b TD-B3LYP values scaled by 0.97.

^c Used the RICC2-B3LYP ratio in FBz- h_5 to scale the FBz- d_5 B3LYP values.

^d Used the experimental-B3LYP ratio in FBz- h_5 to scale the FBz- d_5 B3LYP values.

^e These values are based solely on the experimental values where available; otherwise they are a combination of available experimental values and Exp.-scaled values for vibrations that were not observed. The possible assignments are ordered by this column.

^f Overall symmetries are given for the possible contributions to the more-complicated features.

3. High energy region (1000 - 1800 cm⁻¹)

It was easy to spot from Figure 3.1 the many features arising past the medium wavenumber range, with the 1500–1800 cm⁻¹ region being particularly dense with vibrational bands for the FBz-*d*₅ molecule.

Butler et al.¹⁷ have assigned a number of vibrational bands in this range for the FBz-*h*₅ molecule, with lower wavenumber assignments being extrapolated to the higher wavenumber region with overtones and combination bands coming into play, which is at all not surprising as the spectrum does become more complex and awash with such features including FRs. The same region in the FBz-*d*₅ molecule is even more complex compared to its perhydrogenated isotopologue, making deducing vibrational band assignments a more hands-on task. Starting with the band at 1060.4 cm⁻¹, this has been assigned to $(M_{12}^2)^d$. The $(M_{10}M_{11})^d$ combination band was first considered as an assignment for the feature appearing at 1122.2 cm⁻¹ because it interacts with the *M*₆ mode in FBz-*h*₅ and is expected to shift but such an assignment is unlikely since the derived value for *M*₁₁ would then be too far from the calculated value. $(M_{15}M_{20}^3)^d$ is a better candidate for the 1122.2 cm⁻¹ feature because the expected wavenumber is very close to the observed one, and if this assignment is correct, then it leads to the understanding that the $(M_{10}M_{11})^d$ vibration has now moved too far away from *M*₆^{*d*} to interact with it, and so now is very weak. The $M_{15}M_{20}^3$ combination band does not appear in the FBz-*h*₅ spectrum, and so its appearance in FBz-*d*₅

suggests that it is in Fermi resonance with M_6 and therefore gaining its intensity from it.

Lipp and Seliskar²⁰ appointed a value for the M_6^d (designated ν_{7a} in their work) at 1137.3 cm^{-1} , which is in very good agreement with the value of 1139.6 cm^{-1} from the present work; however, it is noted that the intensity of this band relative to the origin in Lipp and Seliskar work is reported as being rather low, while in the present work the M_6^d feature is somewhat more intense than the origin, and this can only partially be attributed to variations in laser intensity due to the dye. Again, a feature seen here at 1122.2 cm^{-1} is not reported by them. As with the other features missing from Lipp and Seliskar's paper,²⁰ there is no explanation for the differences regarding these two spectral features.

4. Cation

In ref. 2 the ground cationic state of FBz- h_5 and FBz- d_5 was not studied but in ref. 3 and 4 for ClBz and BrBz molecules respectively, the D_0^+ state was looked at, as its assignments can relate to the vibrational mode assignments in the S_1 state. Here the D_0^+ states of both of the FBz isotopologues are also looked at to be consistent with other monohalobenzene molecules. In the results section above, it was shown how the M_i nomenclature can be applicable to the S_0 and S_1 states and it also works just as well for the D_0^+ state. For clarity in the discussion, a post-superscript + is added to each label as it helps to identify that a cationic vibration is being referred to.

Below in Figure 3.6 are the ionisation Duschinsky matrices for the FBz- h_5 and FBz- d_5 species.

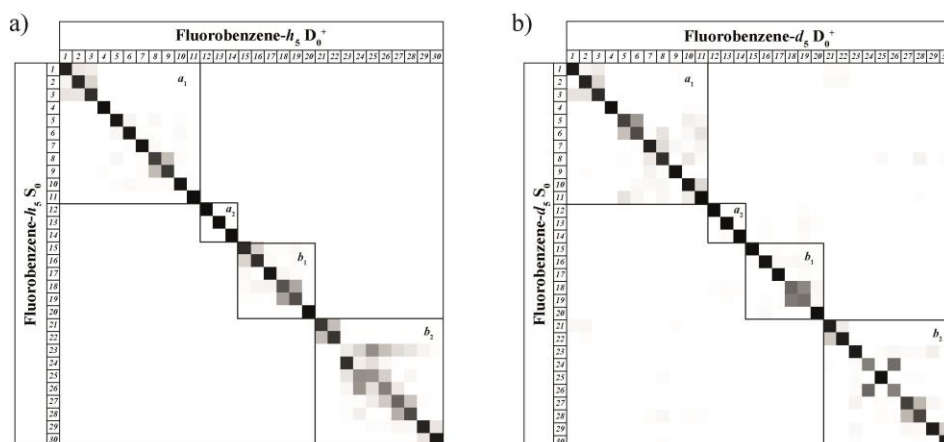


Figure 3.6. Generalized Duschinsky matrices between the vibrational modes of S_0 and D_0^+ states for the a) FBz- h_5 and b) FBz- d_5 molecules. Shadings indicate the normalized coefficient values where the numbers are the i values for each M_i/M_1^+ mode.

For both of the species, the matrices are fairly diagonal, illustrating that the vibrational motion in the cationic state is largely the same as in the neutral states, despite some mixing being present, predominantly in the b_2 modes. The relationship between the S_1 and D_0^+ states of both isotopologues was also checked with the aid of Duschinsky matrices, where a similar scenario emerged and vibrational motion in the ground cationic state was correlated to the first electronically excited state albeit with some mixed character.

The aim of this project was to meticulously assign S_1 vibrational spectra of deuterated halobenzene molecules with the new nomenclature and to compare vibrational behaviour across different monohalobenzene species, and although the D_0^+ state vibrational assignments provide insight into the S_1 state vibrations, only REMPI was implemented here.

However, a few other groups did utilise ZEKE,²² MATI²⁶ and REMPI-PES²⁷ methods to yield a few vibrational band assignments.

Values from the scaled harmonic frequencies calculated here are compared to some of these studies in Table 3.6 for FBz-*h*₅. As there are no previous results on the FBz-*d*₅ molecule, calculated vibrational frequencies are included in Table 3.6 for this isotopologue for consistency only.

Table 3.6 shows that calculated fundamentals in this work match well with the few experimental values provided by Walter et al.²⁷ and Lembach and Brutschy.²⁶

Table 3.6. Assignments, calculated and experimental vibrational wavenumbers (cm^{-1}) for the ground state cation, D_0^+ , of $\text{FBz-}h_5$ and $\text{FBz-}d_5$.

FBz-h_5					FBz-d_5	
Mode Label	Calculated	Experimental			Mode Label	Calculated
	This work ^a	Ref. b	Ref. c	Ref. d		This work ^a
a_1						
M_1^+	3120.3				M_1^{d+}	2316.7
M_2^+	3109.8				M_2^{d+}	2297.8
M_3^+	3098.9				M_3^{d+}	2289.9
M_4^+	1616.6	1610		1620	M_4^{d+}	1578.7
M_5^+	1438.3	1502			M_5^{d+}	1367.0
M_6^+	1313.1	1274			M_6^{d+}	1181.4
M_7^+	1156.7	1168	1164	1170	M_7^{d+}	841.8
M_8^+	943.4			980	M_8^{d+}	815.2
M_9^+	973.6		959	970	M_9^{d+}	932.8
M_{10}^+	786.4	804	791 ^e	810	M_{10}^{d+}	719.7
M_{11}^+	499.3	500	500	500	M_{11}^{d+}	486.0
a_2						
M_{12}^+	984.4				M_{12}^{d+}	795.8
M_{13}^+	766.1				M_{13}^{d+}	594.2
M_{14}^+	345.6				M_{14}^{d+}	302.4
b_1						
M_{15}^+	992.8				M_{15}^{d+}	834.7
M_{16}^+	932.8				M_{16}^{d+}	780.2
M_{17}^+	788.6	763			M_{17}^{d+}	674.1
M_{18}^+	585.6				M_{18}^{d+}	307.6
M_{19}^+	359.5	479			M_{19}^{d+}	462.4
M_{20}^+	178.2	182	181		M_{20}^{d+}	165.8
b_2						
M_{21}^+	3117.9				M_{21}^{d+}	2313.1
M_{22}^+	3108.4				M_{22}^{d+}	2295.3
M_{23}^+	1490.3	1574			M_{23}^{d+}	1244.8
M_{24}^+	1354.0	1464			M_{24}^{d+}	1291.3
M_{25}^+	1361.6	1299			M_{25}^{d+}	1026.5
M_{26}^+	1262.1	1339			M_{26}^{d+}	1412.0
M_{27}^+	1121.3	1106			M_{27}^{d+}	820.4
M_{28}^+	1049.3	1071			M_{28}^{d+}	808.4
M_{29}^+	506.5	606	505	510	M_{29}^{d+}	492.3
M_{30}^+	395.0	402	400	410	M_{30}^{d+}	377.2

^a. UB3LYP/aug-cc-pVTZ, scaled by 0.97

^b. MATI via one-photon VUV absorption from ref. 25

^c. (1+1') MATI from Ref. 26

^d. MPI-PES from Ref. 27

^e. Taken from a combination band from ref. 26

Exciting via an M_8 transition, Walter et al.²⁷ obtained a spectrum where a frequency was determined to be $\sim 980 \text{ cm}^{-1}$ (122 meV) with another band being positioned above the M_8^+ transition at $\sim 1620 \text{ cm}^{-1}$ (201 meV). The $\sim 1620 \text{ cm}^{-1}$ spacing was assigned to the totally symmetric mode ν_{8a} by the authors (M_4^+ here) and this spacing is a characteristic feature of nearly all PE spectra of FBz in that work. Both of these values match well with the calculated frequencies here but both of those transitions were not observed by Lembach and Brutschy²⁶ who employed MATI spectroscopy to investigate the dissociation process of a FBz-Ar complex. Both of the groups however obtained a value for the M_9^+ transition (18a in their work) with Lembach and Brutschy exciting via the S_1 origin and Walter et al. via the 18a itself. Both of the values are in good agreement across those two works and with the one calculated here. The study by Kwon et al.²⁵ summarizes previously published results. However they did not include M_8^+ and M_9^+ values (but included other fundamentals) of Walter et al.²⁷ or the M_9^+ experimental value from Lembach and Bruschy in their table, perhaps because Kwon et al. themselves did not observe M_8^+ or M_9^+ vibrations experimentally.

Kwon et al. measured many more vibrational frequencies compared to the two other studies; however, as seen in Table 3.6, although some of their values coincide well with other studies and the calculated values, M_{11}^+ , M_{20}^+ , M_{29}^+ and M_{30}^+ for example, some others do not.

5 Summary

Here were presented the $S_1 \leftarrow S_0$ electronic spectra of both FBz- h_5 and FBz- d_5 up to 1800 cm^{-1} . The FBz- d_5 spectral assignments were quite straightforward since largely the same vibrational activity was expected to be present as in the FBz- h_5 spectrum. However, fundamentals as well as overtones and combination bands did move in and out of resonance compared across the two isotopologues as a result of isotopic shifts, leading to new FRs being formed and different bands being seen. This in itself is a very interesting aspect of the spectra as it shows that even only a simple mass change can have a large impact on the observed spectral structure.

3.4.2 Chlorobenzene- h_5 and Chlorobenzene- d_5

The next part of this work applies the nomenclature introduced by Gardner and Wright by showing its application not just for the prototypical FBz molecule but other monohalosubstituted benzene species too. ClBz- h_5 and its perdeuterated isotopologue, ClBz- d_5 , are discussed in detail here.

The spectral assignments for the ClBz- h_5 and ClBz- d_5 molecules are based upon calculated vibrational frequencies, experimental values for the lower wavenumber fundamentals, and in the case of ClBz- h_5 , previous experimental results also aided the assignments. To confirm the assignments, shifts upon deuteration were examined. As the chlorine atom has two naturally abundant isotopes, ^{35}Cl and ^{37}Cl , both of these isotopologues were recorded for the fully hydrogenated and fully

deuterated chlorobenzene species, resulting in 4 different isotopic spectra being produced for this section. Spectra of $^{37}\text{ClBz}$ are very similar to those of $^{35}\text{ClBz}$ due to only small isotopic shifts occurring, for instance the M_{20}^2 and M_{14}^2 bands shift by only 0.4 and 0.2 cm^{-1} respectively. The M_{11} vibration, according to calculated vibrational wavenumbers undergoes the biggest isotopic shift of $\sim 5\text{cm}^{-1}$ (for both $\text{ClBz-}h_5$ and $\text{ClBz-}d_5$ isotopologues) which is clearly visible once the $^{35/37}\text{ClBz-}h_5$ spectra are overlayed, allowing one to narrow down possible vibrational assignments when multiple candidates are present.

Here only the ^{35}Cl spectra and data are presented, where information on the $^{37}\text{ClBz-}h_5$ and $^{37}\text{ClBz-}d_5$ isotopologues can be found in Supplementary Material of ref. 3, although $^{37}\text{ClBz}$ isotopologues will be mentioned here when the need arises.

The (1+1) REMPI spectra recorded of $\text{ClBz-}h_5$ (upright, top trace) and $\text{ClBz-}d_5$ (inverted, bottom trace) from 0 – 3000 cm^{-1} are shown in Figure 3.7. As with FBz both of the spectra presented in Figure 3.7 had their origin bands shifted to zero and have been plotted on a relative scale for straightforward comparison between different isotopologues.

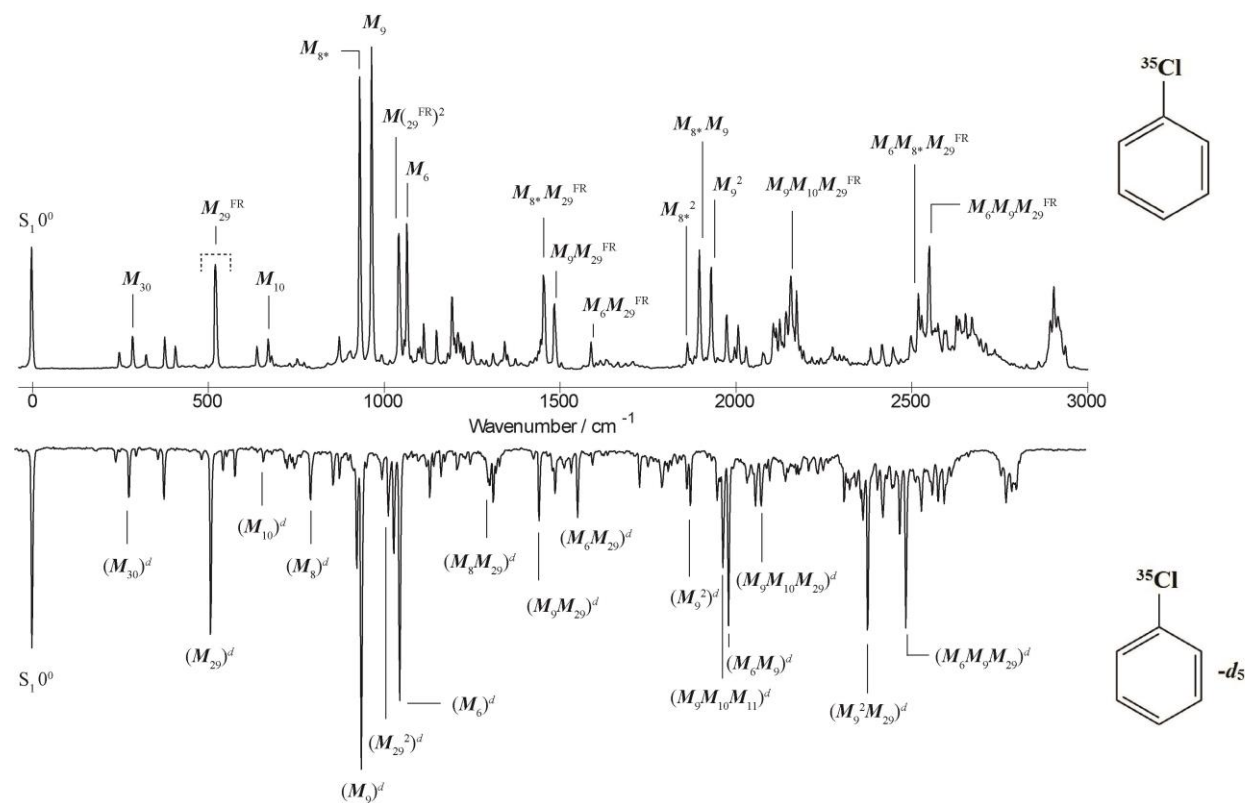


Figure 3.7. Complete 0–3000 cm⁻¹ spectral range scan of the S₁ ← S₀ (1+1) REMPI spectra of ClBz-h₅ (top trace, upright) and ClBz-d₅ (bottom trace, inverted) showing selected assignments – see text in this section for further discussion.

By analogy with the FBz (1+1) REMPI spectra, the rotational temperature here is estimated to be $\sim 5\text{K}$ again, as the appearance of the spectra for both of the ClBz isotopologues matches those of FBz spectra. The wavenumber of the most intense part of each vibrational band was taken, since the vibrational bands are not fully rotationally resolved in either the ClBz- h_5 or ClBz- d_5 spectra. Relative band positions are estimated to be precise to $\pm 0.5\text{ cm}^{-1}$. Just as was done for the FBz- d_5 isotopologue, M_i^d labels are employed to designate the vibrational modes of a deuterated species, with the post-superscript (d) indicating that reference is to a vibration of the perdeuterated molecule.

By simulating the S_1 band origin using PGOPHER⁷⁴ and using the rotational constants reported in ref. 32 it was possible to compare the experimental (1+1) REMPI origin to the band profile given in the latter work, and so calibrate the $^{35}\text{ClBz-}h_5$ spectrum to the ref. 32 band origin of $37048.2 \pm 0.2\text{ cm}^{-1}$. It was then found that the position of the $^{37}\text{ClBz-}h_5$ origin band was in the same position, within experimental uncertainty here, showing that the S_1 origin bands of the ^{35}Cl and the ^{37}Cl isotopologues are within 0.2 cm^{-1} of each other, in agreement with the work of de la Cruz et al.³⁹ The ClBz- d_5 origin transition occurs at $37215.6 \pm 0.5\text{ cm}^{-1}$ with an isotopic blue shift of 167.4 cm^{-1} compared to the ClBz- h_5 origin transition, giving it a favourable agreement with the Dimicoli group's⁴⁶ origin band position of 37218.1 cm^{-1} (itself calibrated using time- of- flight (TOF) -energy calibration curve).

The ClBz- h_5 spectrum presented here is in excellent agreement with previously published work, but there are no previous vibrationally

resolved spectra of ClBz- d_5 . When one accounts for the mode specific participation of H atoms leading to different magnitudes of H/D isotopic shifts, the ClBz- h_5 and ClBz- d_5 spectra are in reasonably good agreement (see Figure 3.7), noting that the observed vibrational bands in the ClBz- d_5 spectrum are generally red shifted from their ClBz- h_5 positions. This is discussed and shown in more detail later on, but before that can be done, the vibrational labels using the new nomenclature need to be established.

Figure 3.8a expresses ClBz- h_5 S_0 state vibrations in terms of those of FBz- h_5 S_0 . Although the Wilson modes of benzene (Bz) do not always clearly correspond to a single calculated vibrational mode of a monosubstituted benzene molecule unambiguously, those of FBz- h_5 do. The diagonalization seen indicates that the normal modes of ClBz all have a dominant contribution from one FBz mode. Figure 3.8b displays the ClBz- d_5 S_0 vibrational motions expressed in terms of those of ClBz- h_5 S_0 , via a generalized Duschinsky matrix. Again the overall diagonalization observed here suggests that the majority of the vibrations in the ClBz- d_5 species are very similar to the vibrational motion seen in the S_0 state for ClBz- h_5 . M_6/M_8 , M_{17}/M_{18} , M_{25}/M_{26} and M_{27}/M_{28} are four pairs of significantly mixed vibrations, but despite this, all thirty vibrational modes of ClBz- d_5 show a dominant contribution from a ClBz- h_5 vibration allowing all ClBz- d_5 vibrational modes to be numbered with the ClBz- h_5 labels, but bearing in mind that some of these vibrations are of significantly mixed form.

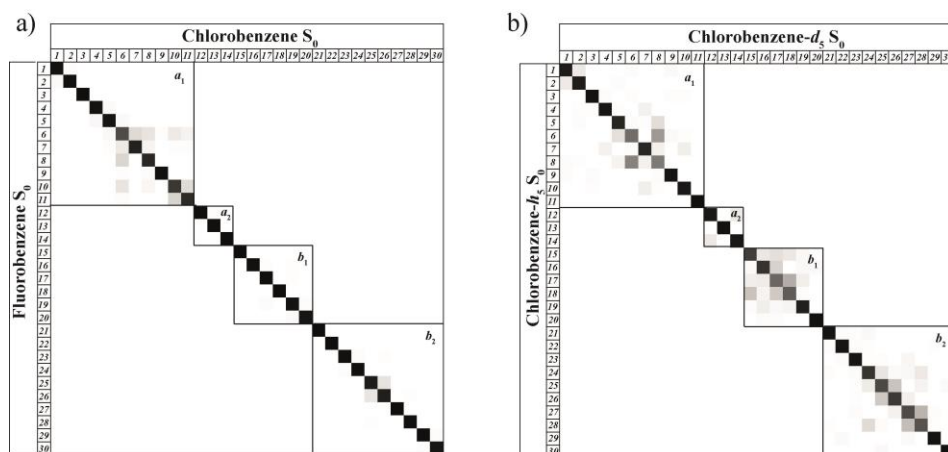


Figure 3.8. Generalized Duschinsky matrix between vibrational modes of the S_0 states of a) FBz- h_5 and ClBz- h_5 and b) ClBz- h_5 and ClBz- d_5 . Shadings indicate the mixing coefficient values, with black = 1.00 while white = 0.00, with the level of the grey shading indicating intermediate values. The numbers are the i values for each M_i mode where vibrational mode frequencies were obtained using DFT/UB3LYP level of theory.

S_0 state

Calculated vibrational wavenumbers for the S_0 states of the ClBz- h_5 and ClBz- d_5 molecules are presented in Table 3.7 on next page along with previous experimental results. Very good agreement exists between previous experimental results and the values calculated here, with an average deviation of $\sim 1\%$ from experimental results observed. Imhof and Kleinermanns's study⁴⁰ includes calculated frequencies where a number of different levels of theory have been used. The B3LYP/6-311G(d,p) results are in reasonable agreement with the values presented here; the MP2/6-311G(d,p) values are in better agreement for some modes but are in much poorer agreement for a few vibrations with both the wavenumbers calculated here and also for the experimental results presented in Imhof and Kleinermanns's study. Quite poor agreement is seen for the CAS(8,7) frequencies with those calculated here and the experimental values, as shown in Table 3.7 below.

Table 3.7. Assignments, calculated and experimental vibrational wavenumbers (cm^{-1}) for the S_0 state of $^{35}\text{ClBz-}h_5$ and $^{35}\text{ClBz-}d_5$.

Mode Label	ClBz- h_5						Mode Label	ClBz- d_5	
	Calculated			Experiment				Calc.	Exp.
	This Work ^a	Ref. b	Ref. c	Ref. d	Ref. e	Ref. f		This Work a	Ref. g
a_1									
M_1	3109	3204	3240	3383	3082		M_1^d	2303	2295
M_2	3097	3191	3230	3368	3054		M_2^d	2291	2288
M_3	3076	3169	3209	3344	3031		M_3^d	2268	-
M_4	1571	1628	1632	1725	1586		M_4^d	1535	1563
M_5	1466	1509	1508	1622	1483		M_5^d	1333	1346
M_6	1065	1098	1129	1177	1092	1097	M_6^d	1015	1038
M_7	1161	1197	1199	1271	1153		M_7^d	852	865
M_8	1013	1098	1044	1149	1025		M_8^d	814	816
M_9	990	1016	1004	1064	1003	1006	M_9^d	949	959
M_{10}	687	754	718	767	706	710	M_{10}^d	656	667
M_{11}	401	417	422	443	417	417	M_{11}^d	394	412
a_2									
M_{12}	962	978	904	997	961		M_{12}^d	783	760
M_{13}	825	841	816	856	832		M_{13}^d	642	680
M_{14}	404	414	394	433	403	404.5 ^h	M_{14}^d	351	367
b_1									
M_{15}	983	1003	897	1028	981		M_{15}^d	820	-
M_{16}	903	917	855	933	902		M_{16}^d	747	747
M_{17}	739	708	718	753	741		M_{17}^d	612	618
M_{18}	681	703	365	726	685		M_{18}^d	541	542
M_{19}	467	480	441	513	467		M_{19}^d	408	420
M_{20}	183	187	183	204	198 ⁱ	185.5 ^h	M_{20}^d	172	182
b_2									
M_{21}	3107	3202	3237	3380	3096		M_{21}^d	2299	-
M_{22}	3084	3178	3218	3355	3067		M_{22}^d	2278	-
M_{23}	1576	1624	1631	1718	1598		M_{23}^d	1541	1543
M_{24}	1435	1478	1445	1577	1448		M_{24}^d	1309	1260
M_{25}	1306	1343	1474	1443	1326		M_{25}^d	1018	1022
M_{26}	1277	1183	1181	1191	1271		M_{26}^d	1274	1322
M_{27}	1146	1318	1326	1311	-		M_{27}^d	831	842
M_{28}	1064	1043	1098	1101	1068	1063	M_{28}^d	807	800
M_{29}	609	628	617	661	615	616	M_{29}^d	584	591
M_{30}	286	298	296	317	295	294	M_{30}^d	271	282

^a. B3LYP/aug-cc-pVTZ values, scaled by 0.97.

^b. B3LYP/6-311G(d,p), unscaled, ref.40.

^c. MP2/6-311G(d,p), unscaled, ref.40.

^d. CAS(8,7)/6-31++G(d,p), unscaled, ref.40.

^e. As summarized in ref.47, taken from ref. 35 and 34.

^f. Dispersed fluorescence results from ref.40.

^g. Ref.50

^h. M_{14} and M_{20} fundamentals have been obtained from overtones reported in ref.40.

ⁱ. Denotes a Raman value in liquid sample from ref.34.

For the ClBz- d_5 isotopologue, the only previous results that are available are from Nanney et al.⁵⁰ and there is a good agreement between those IR/Raman values and the calculated frequencies, seen in Table 3.7.

No previous S_0 results are available for the $^{37}\text{ClBz-}h_5$ or $^{37}\text{ClBz-}d_5$ isotopologues making it impossible to compare those experimentally or theoretically; however, as the isotopic wavenumber shift is generally small and the calculated values in this work for $^{35}\text{ClBz-}h_5$ and $^{35}\text{ClBz-}d_5$ proved to be in very good agreement with the experimental IR and Raman values, confidence is placed in their reliability and they are included in the Supplementary Material in ref. 3.

S_1 state

The S_1 state vibrations in terms of the S_0 vibrations for both ClBz isotopologues are expressed via a generalised Duschinsky matrix approach in Figures 3.9a and 3.9b.

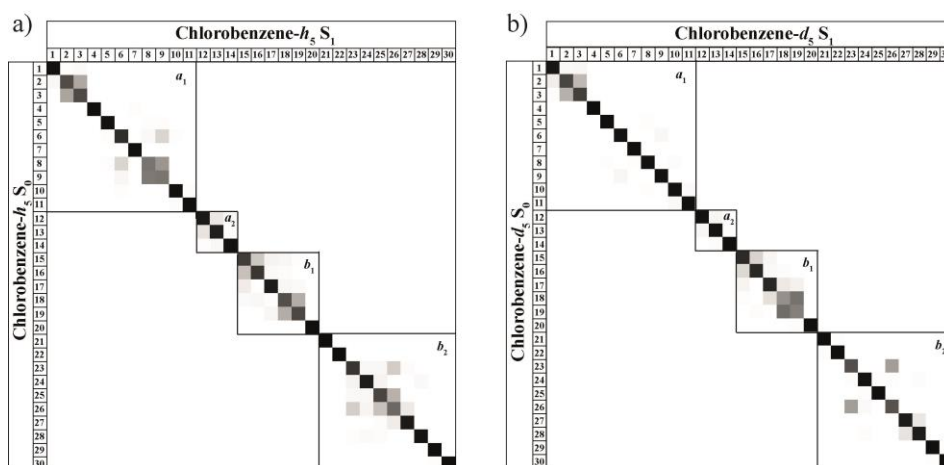


Figure 3.9. Generalized Duschinsky matrices between the vibrational modes of the S_1 and S_0 states for: (a) ClBz- h_5 and (b) ClBz- d_5 . Shadings indicate the mixing coefficient values, with black = 1.00 while white = 0.00, with the level of the grey shading indicating intermediate values. The numbers are the i values for each M_i or M_i^d mode. Vibrational frequencies were calculated using TDDFT/B3LYP level of theory.

It can be seen that for both ClBz- h_5 and ClBz- d_5 , dominant contributions are present for each vibration despite the changes that occur in the electronic structure and geometry upon excitation. The S_1 vibrations are labelled with the same M_i (or M_i^d) label as in the ground state. The M_8 vibration in ClBz- h_5 is an exception; it shows the most mixed character (having a dominant contribution of only 0.52) and so is a significant mixture with the corresponding S_0 M_9 mode; to reflect this, this mode is given the label M_{8*} . The M_{18}^d and M_{19}^d modes show significant mixtures of the corresponding S_0 modes (largest coefficients of 0.51 and 0.54, respectively) in the ClBz- d_5 molecule and therefore these mixed modes in the S_1 state will be denoted M_{18*}^d and M_{19*}^d , with M_{18*}^d being of higher energy. In reality all vibrations have small mixtures of other vibrations of the same symmetry in them, but each vibrational motion largely resembles the motion of the dominant M_i mode (please refer to Figure 1.4 for vibrational motions).

Calculated B3LYP/aug-cc-pVTZ vibrational wavenumbers for the S_1 states of $^{35}\text{ClBz-}h_5$ and $^{35}\text{ClBz-}d_5$ are included in Table 3.8. Overall a good agreement is present between the $^{35}\text{ClBz-}h_5$ B3LYP values and previous experimental values by Jain and Bist,^{34,35} Wright et al.⁴⁷ and Imhof and Kleinermanns.⁴⁰ Much poorer agreement is seen between the CAS(8,7) values from ref. 40 and those calculated here, as was seen for the S_0 state.

Table 3.8. Assignments, calculated and experimental vibrational wavenumbers (cm^{-1}) for the S_1 state of $^{35}\text{ClBz-}h_5$ and $^{35}\text{ClBz-}d_5$.

Mode Label	ClBz- h_5						Mode Label	ClBz- d_5	
	Calculated		Experiment					Calc.	Exp.
	This Work ^a	Ref. b	This Work	Ref. c	Ref. d	Ref. e		This Work ^a	This Work
a_1									
M_1	3135	3404		-	3158.2		M_1^d	2320	
M_2	3116	3386		-	3118.7		M_2^d	2301	
M_3	3087	3365		-	3083.4		M_3^d	2276	
M_4	1478	1659		-	1564.3		M_4^d	1434	
M_5	1402	1540		-	1489.0		M_5^d	1238	
M_6	1034	1131	1066.0 ^h	1066	1065.1	1064.2	M_6^d	1003	1032.4
M_7	1129	1241		-	980.6		M_7^d	833	
M_{8^*}	946	1028	932.2	932	965.7	929.2	M_8^d	785	783.2
M_9	969	970	964.8	965	931.3	964.2	M_9^d	918	926.2
M_{10}	673	709	671.6	-	671.3		M_{10}^d	641	650.4
M_{11}	374	412	377.4	-	378.2	378.2	M_{11}^d	367	371.2
a_2									
M_{12}	642	659	649.3 ^g	-			M_{12}^d	532	540.7 ^g
M_{13}	523	574	522.1 ^g	-			M_{13}^d	412	407.0 ^g
M_{14}	119	284	203.8 ^g	-	203.07 ^f		M_{14}^d	100	177.1 ^g
b_1									
M_{15}	825	719		-			M_{15}^d	704	
M_{16}	694	640	694.4 ^g	-			M_{16}^d	594	594.1 ^g
M_{17}	580	551	557.3 ^g	-			M_{17}^d	455	456.7 ^g
M_{18}	474	474	471.1 ^g	-			$M_{18^*}^d$	383	382.6 ^g
M_{19}	340	272	319.7 ^g	-	320.49 ^f		$M_{19^*}^d$	291	268.2 ^g
M_{20}	136	118	123.9 ^g	-			M_{20}^d	129	117.5 ^g
b_2									
M_{21}	3129.9	3399		-	3076.0		M_{21}^d	2310	
M_{22}	3108.8	3376		-	3056.0		M_{22}^d	2287	
M_{23}	1446.0	1848		- ^h	1584.4		M_{23}^d	1376	
M_{24}	1375.5	1503		- ^h	1483.2		M_{24}^d	1205	
M_{25}	1263.9	1401		1564 ⁱ	1210.1		M_{25}^d	999	
M_{26}	1393.4	1649		-	1194.3		M_{26}^d	1413	
M_{27}	1133.2	1253		-	1149.4		M_{27}^d	819	
M_{28}	977.6	1015		-	1089.7		M_{28}^d	775	
M_{29}	512.1	587	520.6 ^j	521.3	521.0	521.8	M_{29}^d	493	501.8
M_{30}	286.0	307	286.0	287.8	287.3	288.2	M_{30}^d	271	272.2

^a. TD-DFT, B3LYP/aug-cc-pVTZ, scaled by 0.97.

^b. CAS(8,7)/ 6-31++G(d,p), ref.40.

^c. Ref.47.

^d. Ref. 33 and 35.

^e. Ref.46.

^f. Derived from an overtone band from ref.35.

^g. Derived from a combination band or overtone. Italicized values are less certain.

^h. Values are given in ref. 47 for these vibrations, but these have been reassigned here to combination bands.

ⁱ. Seen in two-photon REMPI experiments, ref.36.

^j. Fermi resonance component – see text.

Again the M_{14} fundamental mode has a much lower calculated value here compared to previous results, something that was also the case for the FBz molecule, hence the experimental assignment of this vibration was based on previous experimental work, previous calculated values using other methods for the FBz molecule and the fact that there were no other possible assignment for the M_{14}^2 band in the spectra, as will be seen later.

There do not seem to be any previous values for the S_1 state vibrations of the ClBz- d_5 molecule, nor are there any values to compare to for the ^{37}Cl isotopologue calculations.

Now detailed vibrational assignments of the spectra seen in Figure 3.7 above can be presented. To break down the discussion into more manageable chunks and to make it more approachable, three wavenumber range regions are considered separately.

1. Low wavenumber range (0 - 530 cm^{-1})

ClBz- h_5

Figure 3.10 illustrates the expanded low energy regions of the ClBz- h_5 (top, upright trace) and ClBz- d_5 (bottom, inverted trace) spectra recorded in this project. The low wavenumber region was straightforward to assign with the use of calculated vibrational wavenumbers and by comparison to previous ClBz work and spectra of other monosubstituted benzenes. Assignments of the $^{35}\text{ClBz-}h_5$ spectra are presented in Table 3.9 and Table 3.10 includes $^{35}\text{ClBz-}d_5$ assignments.

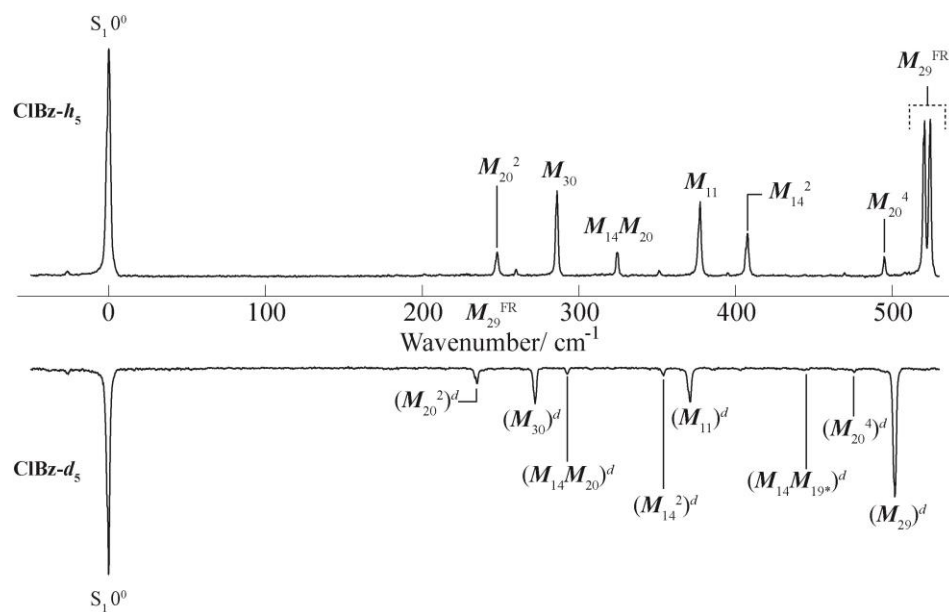


Figure 3.10. Expanded views of the low wavenumber regions (0-530 cm^{-1}) of the $S_1 \leftarrow S_0$ (1+1) REMPI spectra of ClBz- h_5 (top trace, upright) and ClBz- d_5 (bottom trace, inverted).

Bar the origin transition, the most intense transition in the ClBz- h_5 spectrum in this region is the M_{29} fundamental appearing just above 500 cm^{-1} , which is in FR with a band assigned to the $M_{14}M_{19}$ combination (both of b_2 symmetry). This feature is labelled as M_{29}^{FR} in Figure 3.10 for conciseness. Cvitaš and Hollas³² were the first to assign this FR, partnering the M_{29} fundamental with the $M_{14}M_{20}$ combination. Jain and Bist³⁵ confirm their assignment but reassigned the interacting combination to $M_{14}M_{19}$, which is concurred with here. The FR assignments since then have been confirmed via REMPI-PES,⁴⁶ ZEKE⁴⁷ and MATI⁴⁹ studies, with spectra suggesting that the lower wavenumber component at 520.6 cm^{-1} has a majority contribution from the M_{29} zero order state (ZOS) and the component at 524.2 cm^{-1} having a majority contribution from the $M_{14}M_{19}$ ZOS. For example, ZEKE spectra recorded

by Wright et al.⁴⁷ via each eigenstate exhibited two peaks, with the relative intensity of each being representative of the amount of each ZOS present in each vibrational eigenstate. In the ³⁷ClBz-*h*₅ spectrum recorded here (not shown) the FR feature appears essentially as an identical doublet, which is in line with the calculated vibrational wavenumbers suggesting each feature has an isotopic shift of only $\sim 0.1\text{ cm}^{-1}$, making the changes in the FR coupling small enough as not to be discernible at the resolution of this experiment.

Vibrational bands appearing at 286.0 cm^{-1} and 377.4 cm^{-1} are attributed to the *b*₂ symmetry mode, *M*₃₀, and the *a*₁ mode, *M*₁₁, respectively. There is excellent agreement between these experimental fundamentals and the calculated B3LYP values in this work, as can be noted in Table 3.8 along with other vibrational band assignments for the ClBz-*h*₅ and ClBz-*d*₅ molecules. The two weaker intensity overtone bands *M*₂₀² and *M*₁₄² are seen at 247.8 cm^{-1} and 407.6 cm^{-1} respectively. A combination band of overall *b*₂ symmetry, *M*₁₄*M*₂₀, is present here at 324.4 cm^{-1} but no observation of such a band was present in the FBz-*h*₅ spectrum, described in section 3.4.1 and in a recent publication.²

The ClBz-*h*₅ spectrum recorded during this project is an improvement over those previously available. Bist and coworkers^{33,35} observed the *M*₃₀, *M*₁₁, *M*₂₀² and *M*₁₄² vibrations in their absorption spectra but not the *M*₁₄*M*₂₀ combination. The REMPI study by Anderson et al.³⁷ does not show the spectrum below $\sim 500\text{ cm}^{-1}$, and the work of Murakami et al.³⁶ had a break in the spectrum in this wavenumber region, and hence none of the aforementioned four features were presented. The REMPI

spectrum from Walter et al.³⁸ does show all four of these features, but these are not discussed nor assigned, which is similar to the Wright et al.⁴⁷ REMPI spectrum where only the M_{30} and M_{11} features were assigned in this region and the cold spectrum reported in that work does actually show all of the cold features assigned here.

ClBz- d_5

The M_{29}^{FR} in the ClBz- h_5 spectrum described above is not observed in the ClBz- d_5 spectrum; perhaps unsurprising, since the contributing ZOSs have shifted in wavenumber; the M_{29}^d band now appears at 501.8 cm^{-1} whilst the $(M_{14}M_{19*})^d$ band can be identified from the calculated vibrational wavenumbers as a feature of very weak intensity at 446.6 cm^{-1} . This weakness in the ClBz- d_5 spectrum is consistent with the $M_{14}M_{19}$ vibration in ClBz- h_5 “borrowing” intensity from the M_{29} vibration due to close energetic proximity. Upon deuteration this no longer occurs, and the intensities now are representative of the Franck-Condon factors (FCFs) for the largely uncoupled M_{29}^d and $(M_{14}M_{19*})^d$ vibrations.

As was also seen with the M_{29}^{FR} in ClBz- h_5 , a weak feature to slightly lower wavenumber of the M_{29}^d in Figure 3.10 is the third overtone of the M_{20} vibration, $(M_{20}^4)^d$.

The ClBz- d_5 spectrum below 450 cm^{-1} presents the same vibrational structure as ClBz- h_5 , but with significant shifts which are attributed to the deuteration of the molecule. Most notably the $(M_{14}^2)^d$ vibrational band shifts by $\sim 54 \text{ cm}^{-1}$ due to its vibrational motion being concentrated on the

D atoms. As a consequence it appears to lower wavenumber than the M_{11}^d band with other vibrations shifting by smaller amounts. Such observations are consistent with the corresponding spectra of FBz- h_5 and FBz- d_5 described in Section 3.4.1 previously.

Table 3.9. A summary of the assigned vibrational features from the present work for the $S_1 \leftarrow S_0$ transition of the $^{35}\text{ClBz-}h_5$.

$^{35}\text{ClBz-}h_5$				
Experimental band (cm^{-1}) ^a	Assignment ^b	This work B3LYP ^c	From experimental fundamentals ^d	Overall symmetry
-26.6	$[0^0 + \text{Ar}]$	-	-	-
0.0	0^0	-	-	-
247.8	M_{20}^2	272.7	247.8 ^e	a_1
286.0	M_{30}	285.9	286.0 ^e	b_2
324.4	$M_{14}M_{20}$	255.5	327.7	b_2
377.4	M_{11}	374.5	377.4 ^e	a_1
407.6	M_{14}^2	238.4	407.6 ^e	a_1
494.8	M_{20}^4	545.3	495.6	a_1
520.6	M_{29}	512.1	520.6 ^e	b_2
524.2	$M_{14}M_{19}$	459.4	523.5	b_2
538.0 [†]	$M_{20}^2M_{30}$	558.7	533.8	b_2
621.0	$M_{14}M_{20}M_{30}$	541.5	613.7	a_1
	$M_{11}M_{20}^2$	647.1	625.2	a_1
639.4	M_{19}^2	680.5	639.4 ^e	a_1
646.0 [†]	$M_{13}M_{20}$	659.5	646.0 ^e	b_2
665.6	$M_{11}M_{30}$	660.4	663.4	b_2
671.6	M_{10}	672.5	671.6 ^e	a_1
681.2	$M_{17}M_{20}$	716.4	681.2 ^e	a_1
693.4	$M_{14}^2M_{30}$	524.4	693.6	b_2
753.8	M_{11}^2	748.9	754.8	a_1
759.0	$M_{14}M_{17}$	699.2	761.1	b_2
773.2 [†]	$M_{20}^2M_{29}$	784.8	768.4	b_2
	$M_{14}M_{19}M_{20}^2$	732.1	771.3	b_2
	$M_{12}M_{20}$	778.3	773.2 ^e	b_2
874.0	$M_{17}M_{19}$	920.3	877.0	a_1
898.2 [†]	$M_{14}M_{16}$	813.2	898.2 ^e	b_2
902.8	-			
905.6	$[M_{8^*} + \text{Ar}]$		-26.6 from M_{8^*}	
927.2	$M_{14}^2M_{29}$	750.5	928.2	b_2
	$M_{14}^3M_{19}$	697.8	931.1	b_2
	$M_{19}^2M_{30}$	966.4	925.4	b_2
	$M_{13}M_{20}M_{30}$	945.5	932.0	a_1
932.2	M_{8^*}	945.8	932.2 ^e	a_1
938.8	$[M_9 + \text{Ar}]$		- 26.5 from M_9	
957.2	$M_{10}M_{30}$	958.5	957.6	b_2
	$M_{14}M_{18}M_{30}$	879.7	961.0	a_1
964.8	M_9	968.7	964.8 ^e	a_1
973.0	M_{28}	977.6	973.0 ^e	b_2
	$M_{17}M_{20}M_{30}$	1002.4	967.2	b_2
	$M_{12}M_{19}$	982.2	969.0	b_2
993.2 [†]	$M_{13}M_{18}$	997.7	993.2 ^e	b_2
1017.0	$M_{11}M_{19}^2$	1054.9	1016.8	a_1
	$M_{11}M_{13}M_{20}$	1034.0	1023.4	b_2
1043.0	$M_{17}M_{18}$	1054.5	1028.4	a_1
	$M_{18}M_{19}M_{20}^2$	1087.4	1038.6	a_1
	$M_{11}^2M_{30}$	1034.9	1040.8	b_2
	M_{29}^2	1024.2	1041.2	a_1
	M_{13}^2	1046.4	1044.2	a_1
	$M_{14}M_{19}M_{29}$	971.5	1044.1	a_1
	$M_{10}M_{11}$	1047.0	1049.0	a_1
1047.4	$M_{14}^2M_{19}^2$	918.8	1047.0	a_1
	$M_{14}M_{17}M_{30}$	985.2	1047.1	a_1

1057.8	$M_{11}M_{14}M_{18}$	968.1	1052.3	b_2
	$M_{13}M_{14}^2M_{20}$	897.9	1053.6	b_2
	$M_{20}^2M_{29}M_{30}$	1070.8	1054.4	a_1
	$M_{11}M_{17}M_{20}$	1090.8	1058.6	a_1
	$M_{12}M_{20}M_{30}$	1064.3	1059.2	a_1
1066.0	M_6	1034.3	1066.0 ^e	a_1
1078.2	$M_{13}M_{17}$	1103.2	1079.4	b_2
	$M_{10}M_{14}^2$	910.9	1079.2	a_1
1113.8	M_{17}^2	1160.1	1114.6 ^e	a_1
1191.8	$M_{10}M_{29}$	1184.6	1192.2	b_2
1194.8	$M_{10}M_{14}M_{19}$	1131.9	1195.1	b_2
1220.0	$M_8^*M_{30}$	1231.8	1218.2	b_2
1252.4	M_9M_{30}	1254.7	1250.8	b_2
1453.4	$M_8^*M_{29}$	1457.9	1452.8	b_2
1457.2	$M_8^*M_{14}M_{19}$	1405.2	1455.7	b_2
1485.0	M_9M_{29}	1480.8	1485.4	b_2
1488.2	$M_9M_{14}M_{19}$	1428.2	1488.3	b_2
1587	M_6M_{29}	1546.4	1586.6	b_2
1591	$M_6M_{14}M_{19}$	1493.8	1589.5	b_2
1865	M_8^2	1891.6	1864.4	a_1
1898	$M_8^*M_9$	1914.5	1897.0	a_1
1931	M_9^2	1937.5	1929.6	a_1
1976	$M_8^*M_{10}M_{11}$	1992.8	1981.2	a_1
1999	$M_6M_8^*$	1980.1	1998.2	a_1
2009	$M_9M_{10}M_{11}$	2015.7	2013.8	a_1
2031	M_6M_9	2003.1	2030.8	a_1
2128	$M_8^*M_{10}M_{29}$	2130.4	2124.4	b_2
	$M_8^*M_{10}M_{14}M_{19}$	2077.7	2127.3	b_2
2159	$M_9M_{10}M_{29}$	2153.4	2157.0	b_2
	$M_9M_{10}M_{14}M_{19}$	2100.7	2159.9	b_2
2386	$M_8^2M_{29}$	2403.7	2385.0	b_2
2390	$M_8^2M_{14}M_{19}$	2351.0	2387.9	b_2
2418	$M_8^*M_9M_{29}$	2426.6	2417.6	b_2
	$M_8^*M_9M_{14}M_{19}$	2373.9	2420.5	b_2
2449	$M_9^2M_{29}$	2449.6	2450.2	b_2
2455	$M_9^2M_{14}M_{19}$	2396.9	2453.1	b_2
2522	$M_6M_8^*M_{29}$	2492.2	2518.8	b_2
	$M_6M_8^*M_{14}M_{19}$	2439.5	2521.7	b_2
2551	$M_6M_9M_{29}$	2515.2	2551.4	b_2
	$M_6M_9M_{14}M_{19}$	2462.5	2554.3	b_2

^a. Features above 1500 cm⁻¹ are quoted to 1 cm⁻¹ only as no 0.2 cm⁻¹ stepsize scans were taken of the high wavenumber region for this isotopologue.

^b. A bold assignment indicates a favoured choice where multiple options are possible; if multiple options are given but none is bolded, the assignment is not known definitively. A † next to an assignment indicates a tentative assignment, but where there appears to be little else to choose from or it is the best from the options available. An * indicates a mixed vibration; see text for details.

^c. TD-DFT/B3LYP level of theory was employed. Please see Section 3.2 for more details.

^d. All values are computed entirely from experimental fundamentals.

^e. An experimental fundamental is taken from this feature.

Table 3.10. A summary of the assigned vibrational features from the present work for the $S_1 \leftarrow S_0$ transition of the $^{35}\text{ClBz-d}_5$.

$^{35}\text{ClBz-d}_5$				
Experimental band (cm^{-1})	Assignment ^a	This work B3LYP	From experimental fundamentals seen ^b	Overall symmetry
-26.2	$[0^0 + \text{Ar}]$	-	-	-
0	0^0	-	-	-
235.0	$(M_{20}^2)^d$	257.1	235.0 ^c	a_1
272.2	$(M_{30})^d$	271.3	272.2 ^c	b_2
292.8	$(M_{14}M_{20})^d$	228.8	294.6 ^c	b_2
354.2	$(M_{14}^2)^d$	200.5	354.2 ^c	a_1
371.2	M_{11}^d	366.7	371.2 ^c	a_1
446.6	$(M_{14}M_{19}^*)^d$	391.3	445.3	b_2
475.8	$(M_{20}^4)^d$	514.2	470.0	a_1
501.8	M_{29}^d	492.6	501.8 ^c	b_2
536.4	$(M_{19}^*)^d$	582.0	536.4 ^c	a_1
570.6	$(M_{17}M_{20})^d$	583.6	574.2	a_1
625.6	$(M_{14}^2M_{30})^d$	471.7	626.4	b_2
633.6	$(M_{14}M_{17})^d$	555.2	633.8	b_2
650.4	M_{10}^d	640.6	650.4	a_1
675.2 [†]	$(M_{13}M_{19}^*)^d$	703.2	675.2 ^c	b_2
693.4	-			
711.6 [†]	$(M_{16}M_{20})^d$	722.9	711.6 ^c	a_1
	$(M_{14}^4)^d$	400.9	708.4	a_1
717.8 [†]	$(M_{12}M_{14})^d$	632.0	717.8 ^c	a_1
	$(M_{17}M_{19}^*)^d$	746.0	724.9	a_1
729.4	$(M_{17}M_{19}^*)^d$	746.0	724.9	a_1
	$(M_{18}^*M_{20}^3)^d$	768.9	735.1	a_1
737.0	$(M_{20}^2M_{29})^d$	749.7	736.8	b_2
742.8	$(M_{11}^2)^d$	733.5	742.4	a_1
	$(M_{14}^2M_{19}^*M_{20})^d$	620.0	739.9	a_1
			- 26.6 from	
756.6	$[M_8^d + \text{Ar}]$		M_8^d	
	$(M_{11}M_{19}^*M_{20})^d$	786.3	756.9	a_1
779.6	M_{28}^d	775.3	-	b_2
783.2	M_8^d	785.3	783.2 ^c	a_1
789.6 [†]	$(M_{13}M_{18}^*)^d$	795.4	789.6 ^c	b_2
846.0	$(M_{17}M_{20}M_{30})^d$	854.9	846.4	b_2
	$(M_{14}M_{20}M_{30}^2)^d$	771.4	839.0	b_2
	$(M_{14}^2M_{18}^*M_{20})^d$	712.2	854.3	a_1
849.8	$(M_{14}^2M_{29})^d$	693.0	856.0	b_2
	$(M_{14}^2M_{18}^*M_{20})^d$	712.2	854.3	a_1
864.4 [†]	$(M_{13}M_{17})^d$	867.2	863.7	b_2
	$(M_{16}M_{19}^*)^d$	885.3	862.3	a_1
	$(M_{14}M_{17}M_{20}^2)^d$	812.4	868.8	b_2
889.6	$(M_{14}^2M_{19}^*)^d$	782.5	890.6	a_1
	$(M_{19}^*M_{20}M_{29})^d$	912.2	887.5	b_2
	$(M_{14}^2M_{30}^2)^d$	743.0	898.6	a_1
			- 26.2 from	
900.0	$[M_9^d + \text{Ar}]$		M_9^d	
904.4	$(M_{14}M_{17}M_{30})^d$	826.5	906.0	a_1
	$(M_{11}M_{19}^*)^d$	948.5	907.6	a_1
913.4	$(M_{17}^2)^d$	910.0	913.4 ^c	a_1
920.2	$(M_{10}M_{30})^d$	911.9	922.6	b_2
	$(M_{12}M_{18}^*)^d$	915.0	923.3	b_2
926.2	M_9^d	917.6	926.2 ^c	a_1

939.4	$(M_{13}M_{14})^3{}^d$	712.8	938.3	a_1
	$(M_{16}M_{20})^3{}^d$	979.9	946.6	a_1
983.4	$(M_{16}M_{20}M_{30})^d$	994.1	983.8	b_2
	$(M_{14}M_{19})^3{}^d$	973.3	981.7	b_2
	$(M_{14})^3M_{17})^d$	755.7	988.0	b_2
993.2	$(M_{14}M_{19}M_{30})^2{}^d$	933.8	989.7	b_2
	$(M_{18}M_{20})^2{}^d$	1023.6	1000.2	a_1
	$(M_{12}M_{17})^d$	986.8	997.4	b_2
	$(M_{17}M_{19}M_{30})^d$	1017.3	997.1	b_2
	$(M_{11}M_{14})^2M_{30})^d$	838.5	997.6	b_2
	M_{25}^d	999.3	-	b_2
1001.4	$(M_{11}M_{14}M_{17})^d$	922.0	1005.0	b_2
	$(M_{13}M_{16})^d$	1006.4	1001.1	b_2
	$(M_{18}M_{20}M_{29})^d$	1004.4	1001.9	b_2
	$(M_{29})^2{}^d$	985.2	1003.6	a_1
	$(M_{10}M_{14})^2{}^d$	841.0	1004.6	a_1
	$(M_{14}M_{16}M_{20})^2{}^d$	951.6	1006.2	b_2
1017.0	$(M_{10}M_{11})^d$	1007.3	1021.6	a_1
	$(M_8M_{20})^2{}^d$	1042.5	1018.2	a_1
	$(M_{12}M_{14})^2M_{20})^d$	860.8	1012.4	b_2
	$(M_{11}M_{18}M_{19})^d$	1041.0	1022.0	a_1
1032.6	M_6^d	1002.6	1032.4 ^c	a_1
1149.0	$(M_{10}M_{29})^d$	1133.2	1152.2	b_2
1281.4	$(M_8M_{29})^d$	1277.9	1285.0	b_2
1425.4	$(M_9M_{29})^d$	1410.1	1428.0	b_2
1533.6	$(M_6M_{29})^d$	1495.2	1534.2	b_2
1850.6	$(M_9)^2{}^d$	1835.1	1852.4	a_1
1941.2	$(M_9M_{10}M_{11})^d$	1924.9	1947.8	a_1
1956.4	$(M_6M_9)^d$	1920.1	1958.6	a_1
2047.8	$(M_6M_{10}M_{11})^d$	2009.9	2054.0	a_1
2072.4	$(M_9M_{10}M_{29})^d$	2050.7	2078.4	b_2
2348.4	$(M_9)^2M_{29})^d$	2327.7	2354.2	b_2
2455.0	$(M_6M_9M_{29})^d$	2412.7	2460.4	b_2

^a A bold assignment indicates a favoured choice where multiple options are possible; if multiple options are given but none is bolded, the assignment is not known definitively. An $\dagger$ next to an assignment indicates a tentative assignment, but where there appears to be little else to choose from or it is the best from the options available.

^b All values computed entirely from experimental fundamentals.

^c An experimental fundamental is taken from this feature.

2. Medium wavenumber range (530 - 1120 cm^{-1})

The expanded spectra over this region for ClBz- h_5 and ClBz- d_5 can be seen in Figure 3.11 below. This spectral range is dominated by new fundamental bands which give rise to overtones and combination bands with the vibrations that have been assigned below 530 cm^{-1} .

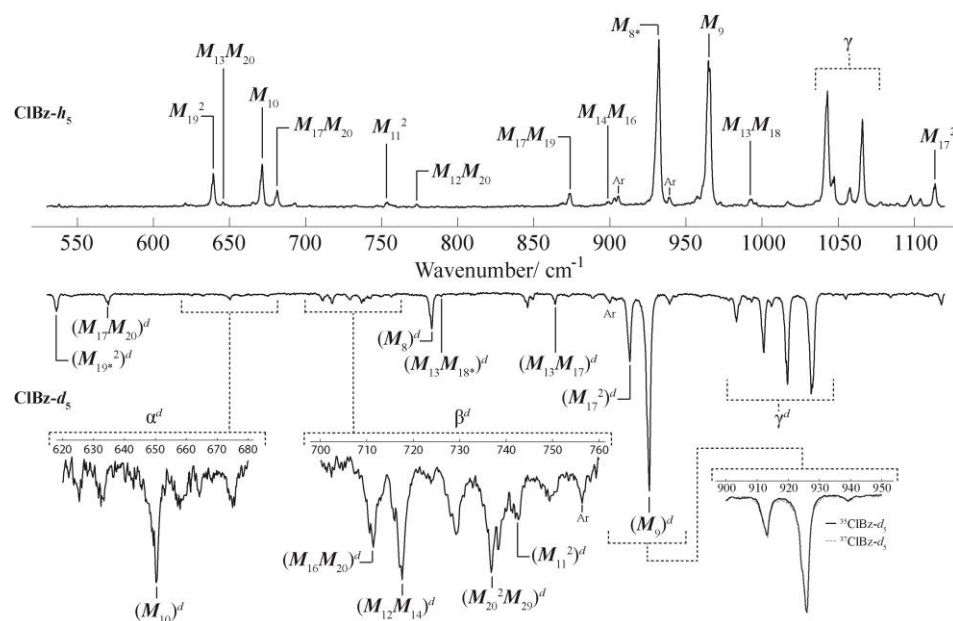


Figure 3.11. Expanded views of the medium wavenumber regions (530–1120 cm^{-1}) of the $S_1 \leftarrow S_0$ (1+1) REMPI spectra of ClBz- h_5 (top trace, upright) and ClBz- d_5 (bottom trace, inverted). As indicated, expanded views are shown of three sections of the ClBz- d_5 spectrum. Assignments are discussed in the text and summarized in Tables 3.9 and 3.10; suggested assignments for some of the weaker features are also given in these tables. Some weak bands, marked with “Ar” are attributed to the ClBz-Ar complex.

ClBz- h_5

In the 600 – 700 cm^{-1} range there are three main features at 639.4, 671.6 and 681.2 cm^{-1} as well as a number of weaker features. One of the more intense features at 671.6 cm^{-1} is attributable to the M_{10} vibration. One

may have thought that the $M_{18}M_{19}$ combination band which is seen in FR with the M_{10} vibration in FBz and toluene would also be nearby; however, the M_{10} vibration is more sensitive to the change in the mass of the substituent than the M_{18} and M_{19} vibrations, consequently moving much lower in wavenumber in ClBz than the $M_{18}M_{19}$ combination, resulting in no such FR being present in ClBz- h_5 . A good approximation to the experimental value of M_{19} can be deduced from the average wavenumber of M_{29}^{FR} , one ZOS of which is $M_{14}M_{19}$. The mean value of the two FR components is 522.4 cm^{-1} and the M_{14}^2 wavenumber is known as it was seen in the low wavenumber range, indicating that the M_{19} vibrational wavenumber is $\sim 320 \text{ cm}^{-1}$. That suggests the M_{19}^2 vibration is responsible for the band at 639.4 cm^{-1} . The third feature at 681.2 cm^{-1} is preliminarily assigned to the $M_{14}M_{18}$ and $M_{17}M_{20}$ combination bands based on the vibrational wavenumbers for this isotopologue, however, with no ZEKE or DF spectra recorded via this band it is difficult to say which one of the two combinations is responsible for this feature. $^{35/37}\text{Cl}$ shifts are expected to be small in both cases and the shifts upon deuteration are extremely similar so they are of no help either. The $M_{17}M_{20}$ combination band seems to be the more plausible assignment because M_{17}^2 is seen in the FBz spectrum and here a feature at 1113.8 cm^{-1} matches the expected position for the M_{17}^2 overtone in the ClBz- h_5 spectrum. This then gives very good agreement with the 570.6 cm^{-1} feature being $M_{17}M_{20}$. If this assignment is correct then it may be that this vibration is in FR with the M_{10} vibration and so evidence for this would be seen in the vibrational activity in ZEKE or DF spectra. (In contrast, if

the $M_{14}M_{18}$ vibration were the correct assignment, no such interaction would occur, owing to the different symmetries.)

Two dominant features in this wavenumber range at 932.2 and 964.8 cm^{-1} were easy to assign to the M_{8*} and M_9 vibrations respectively. Those vibrational levels have been used as intermediate states in REMPI-PES experiments,⁴⁶ ZEKE experiments⁴⁷ and DF work,⁴⁰ concluding the assignment of these more concretely. The wavenumber ordering of these vibrations in the S_1 state is reversed from the order in the S_0 state, something that also happens in FBz and toluene. The $^{35}\text{Cl}/^{37}\text{Cl}$ shift for the M_{8*} and M_9 vibrations is calculated to be within our experimental precision, in line with the observations in the spectra.

ClBz- d_5

The ClBz- d_5 spectrum also contains three features between 530–660 cm^{-1} , with the third being part of the region labelled α^d , see the expanded view of Figure 3.11. Here the M_{10}^d vibration is assigned to a vibrational band at 650.4 cm^{-1} and the $(M_{19*})^d$ overtone is assigned to a band at 536.4 cm^{-1} . These assignments fit the calculated shifts upon deuteration, as well as the $^{35}\text{Cl}/^{37}\text{Cl}$ shifts, where in the latter case the M_{19*}^2 vibration essentially does not shift upon Cl-isotope change, while the M_{10} vibration undergoes a 1–2 cm^{-1} red shift. A third feature at 570.6 cm^{-1} corresponds to the $(M_{17}M_{20})^d$ combination based on the ClBz- h_5 spectrum, calculated shift upon deuteration, and also on the identification of the $(M_{17}^2)^d$ band.

A weak set of features between 700–750 cm^{-1} , marked β^d in Figure 3.11, have no corresponding set of features in ClBz- h_5 and have almost

identical appearance and wavenumber values between the $^{35}\text{ClBz-d}_5$ and $^{37}\text{ClBz-d}_5$ spectra, ruling out combinations involving the M_{11}^d vibration for the main features. Suggested assignments to these are included in Table 3.10. Such small differences in weak features between the ClBz-h_5 and ClBz-d_5 spectra are likely attributable to small changes in vibrational wavenumbers and transition strengths and hence slightly different Franck-Condon factors (FCFs).

The M_{8^*} and M_9 vibrational bands are next to each other and very dominant in the ClBz-h_5 spectrum (Figure 3.11) but in the ClBz-d_5 sample the M_8^d vibration is calculated to have a red shift of 149 cm^{-1} upon deuteration. Taking the calculated shift into account and the behaviour of the FBz isotopologues for comparison, the M_8^d vibration is assigned to the band at 783.2 cm^{-1} . The M_9^d vibration is assigned to the feature at 926.2 cm^{-1} with a much smaller isotopic shift, 39 cm^{-1} . The M_9^d vibration in ClBz-d_5 is almost the same intensity as it is for the ClBz-h_5 isotopologue but the M_8^d band is much weaker than the M_{8^*} . The difference in intensity is not explained by FR as those two bands are not in FR with one another in ClBz-h_5 .⁴⁷ The difference in intensity however can be explained through the Duschinsky mixing approach. In ClBz-h_5 the M_{8^*} and M_9 vibrations are heavily mixed in the S_1 state as already mentioned previously but in the ClBz-d_5 sample such mixing is much less. It is postulated then that the motion along the M_9 coordinate is what gives the main contribution to the intensity for these vibrations, and the mixed nature of the M_{8^*} and M_9 modes in ClBz-h_5 leads to both being

intense, while in ClBz- d_5 the significantly weaker mixing means the M_9^d band is far more intense than the M_8^d one.

It was difficult to assign the feature at 913.4 cm^{-1} at first because on the basis of expected wavenumbers the suitable candidates were the $(M_{11}M_{19*}^2)^d$ and $(M_{11}M_{30}^2)^d$ combinations. However, the band in the spectrum is essentially insensitive to the $^{35}\text{Cl}/^{37}\text{Cl}$ isotopic change (please see the expanded view on the bottom right of Figure 3.11) so they can not be the correct assignments due to the M_{11} band having an isotopic shift of $\sim 5\text{ cm}^{-1}$. In fact, this feature was assigned to the $(M_{17}^2)^d$ overtone because this vibration is not expected to shift appreciably upon $^{35/37}\text{Cl}$ substitution; an analogous overtone is seen in the FBz spectrum. This then leads to the M_{17}^d fundamental being at 456.7 cm^{-1} , which compares very favourably with the calculated value of 455.0 cm^{-1} . As the $(M_{17}^2)^d$ is extremely close to the M_9^d vibration at 926.2 cm^{-1} they could be in FR with one another but ZEKE or DF spectra would have to be recorded in order to confirm this. With the $(M_{17}^2)^d$ assignment confirmed here it was possible to find a band that was assignable to the corresponding M_{17}^2 vibration in the ClBz- h_5 spectrum at 1113.8 cm^{-1} .

Regions γ and γ^d

Both the ClBz- h_5 and ClBz- d_5 spectra show regions of complexity around 1000 cm^{-1} labelled as γ in Figure 3.11 for ClBz- h_5 , and the analogous region in ClBz- d_5 , labelled γ^d . An enlargement of this region is shown in Figure 3.12, where both the corresponding ^{35}Cl and ^{37}Cl traces are included in each case as the comparison between four isotopologues

was of great help when trying to understand this spectral region. The detailed discussion of the assignments follows after Figure 3.12, with Tables 3.9 and 3.10 having full vibrational assignments.

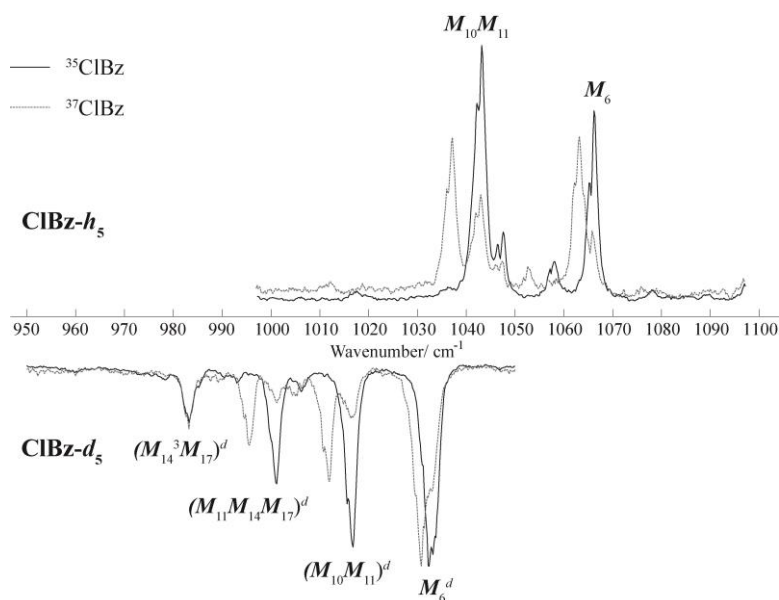


Figure 3.12. Expanded views of regions γ and γ^d of the spectra in Figure 3.11 for ClBz- h_5 (upright, upper trace) and ClBz- d_5 (inverted, lower trace). The solid lines are the traces for the ^{35}Cl isotopologues, while the dashed lines are those for the ^{37}Cl isotopologues. (It is noted that it was not possible to exclude completely the $^{35}\text{ClBz}$ isotopologue mass signal from the $^{37}\text{ClBz}$ mass gate, and so some contributions of the former may be contributing to the spectrum of the latter in the “unshifted” positions.)

ClBz- h_5

For the ClBz- h_5 sample, two intense features are noticed straight away amongst weaker contributions. The $M_{10}M_{11}$ combination band and the M_6 vibration are expected to be present in this region of the spectrum according to calculated wavenumbers and previous work on ClBz as well as the FBz and toluene molecules. They are not expected to be of low intensity here because in toluene, employing time-resolved spectroscopy

and ZEKE, two such vibrations have been found to be 'bright' vibrations, and they were both also seen in FBz. As M_{10} and M_{11} experimental values have already been established from the low wavenumber region of the spectrum, the expected position of the $M_{10}M_{11}$ combination is at $\sim 1049 \text{ cm}^{-1}$ and taking into account anharmonicity, a band at 1043 cm^{-1} is assigned to the $M_{10}M_{11}$. Additionally, upon $^{35/37}\text{Cl}$ substitution, a shift of $\sim 6 \text{ cm}^{-1}$ occurs, consistent with the involvement of the M_{11} vibration as seen in Figure 3.12. Again based on the calculated wavenumber (the M_6 vibration was calculated to be a few tens of cm^{-1} lower than was experimentally observed for FBz, and it is reasonable to expect it to be so here too) and a slight shift to the red upon $^{35/37}\text{Cl}$ substitution due to the vibrational motion including halogen atom stretching motion (just as was for the M_{11} mode), the band at 1066 cm^{-1} is assigned to the M_6 vibration.

Other weaker contributions to this region at ~ 1041 , 1044 and 1047 cm^{-1} have been attributed to M_{29}^2 , $M_{14}M_{19}M_{29}$ and $M_{14}^2M_{19}^2$ respectively. The M_{29}^2 and $M_{14}M_{19}M_{29}$ components are the closest in wavenumber to the $M_{10}M_{11}$ combination and so can interact and contribute to the 1043.0 cm^{-1} feature.

The bands at 1017.0 cm^{-1} and at 1057.8 cm^{-1} undergo a shift upon $^{35/37}\text{Cl}$ substitution in line with contributions from M_{11} vibration being present, therefore the feature at 1017.0 cm^{-1} is assigned to the $M_{11}M_{19}^2$ combination and 1057.8 cm^{-1} is attributed to the $M_{11}M_{17}M_{20}$ combination, i.e. M_{11} plus the $M_{17}M_{20}$ combination discussed earlier.

ClBz- d_5

Having assigned the ClBz- h_5 spectrum in Figure 3.12, it is expected that the ClBz- d_5 sample will also have the $(M_{10}M_{11})^d$ and M_6^d vibrations as bright ZOSs. Based on the experimental values for M_{10}^d and M_{11}^d , the band at 1017.0 cm^{-1} in the $^{35}\text{ClBz-}d_5$ spectrum is assigned to the $(M_{10}M_{11})^d$ combination band, with a feature in the $^{37}\text{ClBz-}d_5$ spectrum undergoing roughly the correct red shift for such an assignment to hold true. The band at 1032.6 cm^{-1} likely arises mainly from the M_6^d ; again, it shows a small red shift in line with expectations.

The feature at 1001.4 cm^{-1} is consistent with the expected position for the $(M_{29}^2)^d$ overtone, but it is noted that more than one contribution is associated with this feature. From Figure 3.12 it is seen that a significant shift occurs between the $^{35/37}\text{Cl}$ isotopologues, and with the M_{11}^d being present, the $(M_{11}M_{14}M_{17})^d$ vibration is another possible assignment for the feature that is overlapped with the $(M_{29}^2)^d$, please see Table 3.10.

3. High wavenumber range ($1120 - 3000\text{ cm}^{-1}$)

ClBz- h_5

Above 1100 cm^{-1} , the spectra of both ClBz- h_5 and ClBz- d_5 become much richer in structure. In the ClBz- h_5 spectrum, it is possible to identify pairs of bands that arise from combinations involving M_6 , M_8 and M_9 vibrations as well as the M_{29}^{FR} feature, and a number of these are labelled in Figure 3.7, as well as being included in Table 3.9. It is then seen that the same combinations are seen in ClBz- d_5 although here only those involving the M_9^d and M_{29}^d vibrations are immediately obvious, as these

are much more intense than those involving M_6^d and M_8^d , in line with the observed intensities for the fundamentals.

This spectral region is not only occupied by intense bands, as a number of very weak features are present in the ClBz- h_5 spectrum from $\sim 1120 - 1400 \text{ cm}^{-1}$ which are not straightforward to assign. For the more intense features, located between $1200-1260 \text{ cm}^{-1}$, it is possible to come up with likely assignments based on expected wavenumber and isotopic shifts. For many other weaker contributions in this region a comprehensive assignment of these is largely a fruitless task. The more intense pairs of features are expected to include contributions from M_8M_{30} and M_9M_{30} , and the $^{35/37}\text{Cl}$ shifts of $\sim 2 \text{ cm}^{-1}$ are consistent with these assignments.

Straight after this low intensity region, a pair of features between $1450-1500 \text{ cm}^{-1}$ are almost certainly the M_{29}^{FR} components in combination with the M_8 and M_9 bands, since each feature is split (consistent with containing contributions from M_{29}^{FR}) and shows almost no $^{35/37}\text{Cl}$ shift. Between $\sim 1700-2000 \text{ cm}^{-1}$, a set of bands are present at 1865 cm^{-1} , 1898 cm^{-1} and 1931 cm^{-1} that match well the expected positions of the M_8^2 , M_8M_9 and M_9^2 vibrations, to which these are assigned, respectively. After these bands in the range $1970-2015 \text{ cm}^{-1}$ the vibrational structure can be attributed to the combination bands, $M_8M_{10}M_{11}$, $M_9M_{10}M_{11}$, M_6M_8 and M_6M_9 . These main features do not demonstrate a significant $^{35/37}\text{Cl}$ shift (as expected for the suggested assignments), but there are other bands here that do, and so clearly there are more contributions here than those highlighted. To higher

wavenumber much more congestion appears in the vibrational structure with the prominent bands becoming surrounded by weaker ones, the assignments of which are unclear.

ClBz- d_5

The ClBz- d_5 spectrum compared to that of ClBz- h_5 in this higher wavenumber region contains less intense features and it is even less straightforward to assign individual features since the clear pairing of features seen for the M_8 and M_9 combination bands in ClBz- h_5 is not present for M_8^d and M_9^d in ClBz- d_5 . Utilising the ClBz- h_5 assignments as a guide and the wavenumber values obtained from the lower region of the spectrum, key features incorporating the M_6^d , M_9^d and M_{29}^d fundamentals were identified, indicated in Figure 3.7 and Table 3.10. Towards 3000 cm^{-1} much more congestion is seen where distinguishing between individual contributions is something that cannot be achieved.

4. Cation

Figure 3.13a shows the Duschinsky matrix for ClBz- h_5^+ between the vibrational modes of the S_0 state and the D_0^+ state in the cation ($\tilde{X}^2B_1$ state). Each vibrational mode in the ground cationic state has a dominant contribution from the neutral ground state pictorially represented by the resulting diagonal nature of the matrix although small contributions from other modes are present. As a consequence, M_i labels are used, but it is noted that the cation's vibrational motions will not be identical to those of the neutral ground state. For clarity in the discussion, a post-superscript +

to each label is added as it helps to identify that a cationic vibration is being referred to.

Figure 3.13b portrays a generalised Duschinsky matrix for the S_1 and D_0^+ states of the ClBz- h_5 molecule. The diagonalisation that is observed indicates that the D_0^+ vibrational modes can be assigned with confidence to the corresponding S_1 state modes based on their motion and wavenumber.

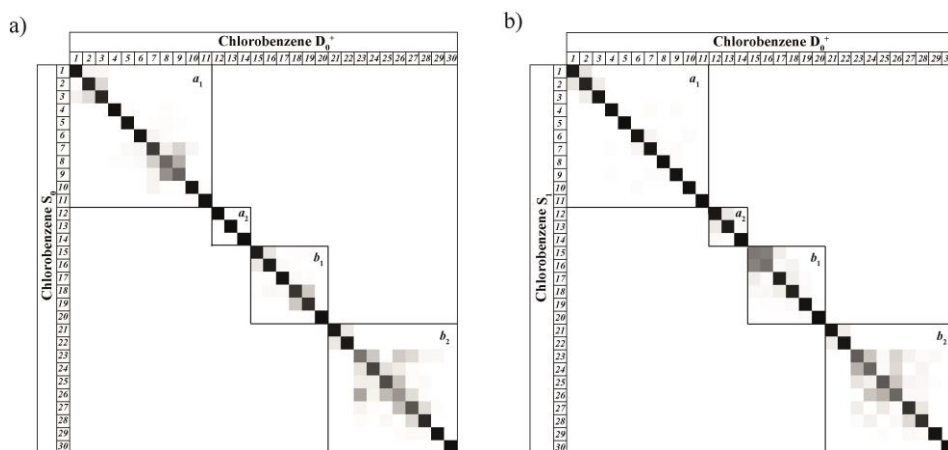


Figure 3.13. Generalized Duschinsky matrices between the vibrational modes of: (a) the S_0 and D_0^+ states for ClBz- h_5 and (b) the S_1 and the D_0^+ states for ClBz- h_5 . Shadings indicate the normalised coefficient values, with black = 1.00 while white = 0.00, with the level of the grey shading indicating intermediate values. The numbers are the i values for each M_i/M_i^+ mode.

ClBz- d_5 Duschinsky matrices comparing D_0^+ vibrational modes in terms of the S_0 and S_1 state modes have yielded very similar results to those presented in Figure 3.13a and b and therefore are not included here. M_i^{d+} labels are used, with the motions in the D_0^+ state being very similar to the motion seen in the S_0 state but not being identical.

Table 3.12 gives the calculated vibrational wavenumbers for the ground state $^{35}\text{ClBz-}h_5^+$ and $^{35}\text{ClBz-}d_5^+$ isotopologues and includes both experimental and theoretical values from previous works. Fairly good agreement exists between calculated values in this work using the B3LYP/aug-cc-pVTZ level of theory and RHF/6-31G* calculated values from ref. 47; however, the frequencies here are more in line with the experimental values when compared across different studies.

In previous studies, Wilson nomenclature was employed by most workers, but the inconsistent application of these labels makes it difficult to discuss the observed activity, in particular since the assignment of the cation's vibrations in resonant experiments is often dependent on the identified vibrational level in the intermediate state (or vice versa). In light of this, in this discussion the M_i^+ modes referred to in previous work are assigned from the wavenumber values given in the respective studies.

One-photon MATI spectra of ClBz- h_5 , for both ^{35}Cl and ^{37}Cl isotopologues, were recorded by Kwon et al.⁴⁸ in 2002. Table 3.11 includes their wavenumber assignments and those are in good agreement with previous work and calculated vibrational frequencies in this work. The M_5^+ vibration at 1411 cm^{-1} was omitted however as it does not agree well with either the ZEKE value, nor the calculated value here. Kwon et al.'s other suggestion for this band, which seems to correspond to $(M_9M_{11})^+$, seems to fit the calculated and previous experimental values better. Potts et al.⁴⁵ have recorded conventional HeI PES spectra and the overall appearance looks similar to the MATI spectra. Analysis of the vibrational structure in the first photoelectron band, yielded vibrational

wavenumbers of 417, 1112 and 1460 cm^{-1} , which are assigned to M_{11}^+ , $(M_{10}M_{11})^+$ and, plausibly, the M_5^+ or $M_8M_{29}^{\text{FR}}$ vibrations. The 1460 cm^{-1} band might also be assignable to $(M_9M_{11})^+$, similar to the Kwon et al.⁴⁸ 1411 cm^{-1} band, given the likely error in the HeI PES vibrational spacings.

REMPI-PES spectra were recorded via the S_1 origin, M_{30} , M_{11} and M_{29} levels by Anderson et al.³⁷ with no vibrational structure seen via the origin. Spacings of 270, 450 and 730 cm^{-1} were observed via the M_{30} level which were assigned to M_{30}^+ , M_{29}^+ and the combination vibration, $(M_{29}M_{30})^+$ but those are only approximate values as the spacings were measured to the nearest meV and the bands were broad. The ZEKE study of Wright et al.⁴⁷ agreed with the M_{30}^+ assignment but thought that the 730 cm^{-1} feature is actually due to the $(M_{11}M_{29})^+$ combination. Additionally, the 450 cm^{-1} spacing between features corresponds to M_{11}^+ . Asselin et al.⁴⁶ saw the M_{30}^+ fundamental to be the most intense feature when exciting via the M_{30} intermediate level, followed by combinations with M_{11}^+ , whereas excitation via M_{11} produced a progression in M_{11}^+ as well as a feature due to M_{10}^+ at $\sim 730 \text{ cm}^{-1}$.

Table 3.11. Assignments, calculated and experimental vibrational wavenumbers (cm^{-1}) for the ground state cation, D_0^+ , of $^{35}\text{ClBz-}h_5$ and $^{35}\text{ClBz-}d_5$.

Mode Label	ClBz- h_5^+						Mode Label	ClBz- d_5^+	
	Calc.		Experimental					Calc.	Exp.
	This Work ^a	Ref. b	Ref. c	Ref. d	Ref. e	Ref. f		This Work a	Ref. c
a_1									
M_1^+	3122	3052					M_1^{d+}	2317	
M_2^+	3111	3043					M_2^{d+}	2299	
M_3^+	3099	3030					M_3^{d+}	2289	
M_4^+	1589	1619				1554	M_4^{d+}	1548	
M_5^+	1422	1393		1429			M_5^{d+}	1250	
M_6^+	1084	1072	1106	1116	1115	1118	M_6^{d+}	1059	
M_7^+	1181	1174	1182	1200	1194	1193	M_7^{d+}	851	
M_8^+	960	885	981	975	971	974	M_8^{d+}	801	760
M_9^+	977	961	1016	995	992	991	M_9^{d+}	932	
M_{10}^+	700	673	728	716	714	713	M_{10}^{d+}	665	
M_{11}^+	414	401	421	422	420	419	M_{11}^{d+}	405	413
a_2									
M_{12}^+	989	1010					M_{12}^{d+}	802	
M_{13}^+	786	808					M_{13}^{d+}	611	
M_{14}^+	344	347	342	348	343		M_{14}^{d+}	300	
b_1									
M_{15}^+	1000	1015	909				M_{15}^{d+}	843	
M_{16}^+	944	960	812				M_{16}^{d+}	771	
M_{17}^+	769	771	603			771	M_{17}^{d+}	652	
M_{18}^+	589	586	558			600? ^g	M_{18}^{d+}	470	
M_{19}^+	376	396	388	394	393	[482] ^g	M_{19}^{d+}	324	
M_{20}^+	144	144	165			141	M_{20}^{d+}	134	
b_2									
M_{21}^+	3120	3050					M_{21}^{d+}	2313	
M_{22}^+	3109	3038					M_{22}^{d+}	2295	
M_{23}^+	1373	1365				1593	M_{23}^{d+}	1237	
M_{24}^+	1483	1485					M_{24}^{d+}	1394	
M_{25}^+	1249	1317					M_{25}^{d+}	1021	
M_{26}^+	1345	1113					M_{26}^{d+}	1299	
M_{27}^+	1122	1035					M_{27}^{d+}	825	
M_{28}^+	1070	1220					M_{28}^{d+}	821	
M_{29}^+	523	496	526	531	526	527	M_{29}^{d+}	507	
M_{30}^+	293	294	322	311		[286] ^g	M_{30}^{d+}	278	

^a. UB3LYP/aug-cc-pVTZ, scaled by 0.97.

^b. RHF/6-31G*, scaled by 0.89, ref.47

^c. Two-colour REMPI-PES, ref. 46 The assignment of M_8^{d+} is suggested in the present work, please see text.

^d. Two-colour ZEKE spectroscopy, ref.47. The assignment of the 1116 cm^{-1} feature was ambiguous as a band at 1147 cm^{-1} was also mentioned in the text of that work, please see discussion in this section.

^e. Two-colour MATI spectroscopy, ref. 49

^f. One-colour MATI spectroscopy, ref. 48

^g. value marked with a “?” was uncertain in ref.48, values in square brackets are deemed unreliable by ourselves by comparison with previous work – see text.

Excitation via one of the M_{29}^{FR} components (it was not clear which one exactly) by the Anderson et al.³⁷ group produces progressions with spacings of 450, 660 and 1150 cm^{-1} . The first of these is likely to be a M_{11}^+ progression in combination with M_{29}^+ , although the initial spacing would be expected to be different from the others, or perhaps there was an error in identifying the zero on the energy scale. The 660 cm^{-1} progression was assigned to M_{10}^+ , but would be expected to be in combination with an allowed b_2 vibration – perhaps $(M_{14}M_{19})^+$; the 1150 cm^{-1} spacing was likely assigned to the $(M_{11}M_{29})^+$ combination, which was also observed in the corresponding ZEKE,⁴⁷ MATI⁴⁹ and REMPI-PES⁴⁶ spectra. It should also be noted that both the M_{29}^{FR} components at $\sim 520 \text{ cm}^{-1}$ were excited by Asselin et al.⁴⁶ who were able to see that the spectra were progressions of M_{11}^+ but with one quantum of M_{29}^+ when exciting via the lower wavenumber component, and one quantum of $(M_{14}M_{19})^+$ when exciting via the upper one, with these results being in agreement with the ZEKE⁴⁷ and MATI⁴⁹ work.

The only group to record REMPI-PES spectra of the ClBz- d_5 molecule was the work by Asselin et al.⁴⁶ Excitations through the S_1 origin and M_{11}^d levels were undertaken, leading to the observation of progressions of 413 cm^{-1} , assigned to M_{11}^{d+} , which is in good agreement with the calculated value obtained here (please see Table 3.11). Also, a combination band at 1171 cm^{-1} was tentatively assigned as involving the M_{11}^{d+} vibration, which would allow another a_1 fundamental vibration of $\sim 760 \text{ cm}^{-1}$ to be derived, the best suggestion for this vibration being the M_8^{d+} (Table 3.11).

In the ClBz- h_5 REMPI spectrum the two features at 932.2 and 964.8 cm^{-1} must be assigned with caution. When expressed in terms of the S_0 vibrations, the Duschinsky matrix indicates that the lower wavenumber vibration (denoted M_{8^*} here) in the S_1 state has a majority contribution from M_8 , but that there is a significant contribution from M_9 , while the upper wavenumber vibration (denoted M_9 here) is predominantly M_9 motion, with some M_8 . These vibrations can be viewed as having switched order from the S_0 state – a phenomenon also seen for FBz, as discussed above and in ref.2. In the Wright et al.⁴⁷ ZEKE study, a feature at $\sim 965 \text{ cm}^{-1}$ was assigned as M_9 as exciting via this level yielded a very strong $\Delta v = 0$ band, corresponding to M_9^+ , together with the M_{11}^+ fundamental and the $(M_9M_{11})^+$ combination band (the latter was part of a doublet, with the partner being assigned as M_5^+). Excitation via the M_{8^*} level at $\sim 932 \text{ cm}^{-1}$ produced two ZEKE bands of very similar intensities, assigned as M_8^+ and M_9^+ . The observation of two strong components was taken as implying that this level had mixed character in the S_1 state. It is noted that the observation of two strong components does not fit in with the appearance of the Duschinsky matrix for the S_1 and D_0^+ vibrations (Figure 3.13b), which suggests that these vibrations are of very similar forms in the S_1 and D_0^+ states; whereas based on the ZEKE intensities, the M_9^+ is expected to have a motion very similar to that of M_9 in the S_1 state, and M_8^+ to be a mix of the S_1 M_{8^*} and M_9 motions (i.e. a similar situation as that between the S_0 and S_1 states). This could mean that the calculations here are misleading or that these states do mix to some extent during the $D_0^+ \leftarrow S_1$ ionisation and if the M_9 vibration has a

significantly higher photoionisation cross section than the M_{8*} vibration, this could explain to some degree the appearance of the ZEKE spectra.

One-colour MATI spectra have been compared to the older conventional HeI PES spectra of Potts et al.⁴⁵ The appearance of the early part of the HeI spectrum (see Figure 1(b) of ref. 45) is similar to that of the MATI spectrum (see Figure 2(a) of ref. 48). Potts et al. analysed vibrational structure in the first photoelectron band, yielding vibrational wavenumbers of 417, 1112 and 1460 cm^{-1} . They have been assigned to the M_{11}^+ , $(M_{10}M_{11})^+$ and, plausibly, the M_5^+ or $M_8M_{29}^{\text{FR}}$ vibrations. The band at 1460 cm^{-1} could also be assigned to $(M_9M_{11})^+$, similar to the Kwon et al. 1411 cm^{-1} band, given the likely error in the HeI PES vibrational spacings.

DF spectra of the ClBz- h_5 molecule were recorded by Imhof and Kleinermanns⁴⁰ via various S_1 vibrational levels from which ZEKE spectra have also been recorded by Wright et al.⁴⁷ The assignment of the S_1 vibrational level should be evident from the vibrational structure seen for the S_0 state from DF spectroscopy. However, although the DF spectra recorded from low wavenumber bands in the S_1 state of ClBz- h_5 are largely consistent with the assignments from the photoionisation studies discussed above, those from higher wavenumber features are not.

The DF spectra recorded via the origin mostly showed in S_0 activity from a_1 vibrations, with the most intense band arising from the M_9 vibration, but the b_2 mode, M_{29} , was also observed, although much more weakly than in the DF spectra of FBz. The M_{30} band assignment was confirmed

when fluorescence was dispersed from that band, the $\Delta v = 0$ propensity rule was obeyed since an intense band corresponding to the ClBz ground state M_{30} vibration was seen. This result is in agreement with the ZEKE spectrum.⁴⁷ DF spectra were also recorded via two bands at 384 and 380 cm^{-1} , which were extremely similar, and assignments were made to the $^{35}\text{ClBz-}h_5$ and $^{37}\text{ClBz-}h_5$ S_1 M_{11} modes.

The M_{29}^{FR} was also looked at, where DF spectrum via each component was reported by Imhof and Kleinermauns.⁴⁰ It was confirmed that the lower component arose from the eigenstate with more M_{29} character, while the upper one had more of the $M_{14}M_{19}$ combination band character, a finding that is in agreement with previous ZEKE spectra,⁴⁷ MATI spectra⁴⁸ and REMPI-PES work.⁴⁶

When DF spectra from the two levels at 932.2 and 964.8 cm^{-1} (cited at 934 and 966 cm^{-1} in ref. 40) were produced, they were of a complicated nature and some assignments by the authors were puzzling. In order to account for the observations, significant mixing between the vibrations was suggested as an explanation. Some of the suggested mixings however, such as between M_9 and M_{28} , cannot occur since these are of different symmetry. The overall conclusion was that the lower wavenumber band was assignable to M_9 , but only on the basis that this was the assignment put forward in the ZEKE paper by Wright et al.⁴⁷ In reality, the M_9 fundamental was not seen in the DF spectrum, although a feature assigned as the $M_{12}M_{28}$ vibration (b_2 symmetry) was observed.

The 964 cm^{-1} band was assigned in ref. 40 to the b_2 symmetry band, M_{28} , although previous studies had established this band to be at 1068 cm^{-1} .

To gain more insight into the DF spectra recorded via the 934 and 966 cm^{-1} bands, the DF spectra of FBz by Butler et al. were examined, who also dispersed the fluorescence from equivalent levels. Looking at the DF spectrum for FBz when exciting M_9 , strong bands corresponding to M_9 , M_9^2 and M_9M_{10} , M_{10} fundamental and many other higher wavenumber features are observed. To be consistent with the assignment of the 966 cm^{-1} band to M_9 , the DF spectrum for ClBz- h_5 should show bands at 1006 and 2012 cm^{-1} , which are not seen. At first it was thought that there had been a misassignment of the ClBz DF spectrum in ref. 40 but the wavenumbers of the observed features do appear to be consistent with the assignments offered.

A possible explanation for this confusion may lie in the fact that the S_1 states of the halobenzenes undergo rapid predissociation via intersystem crossing to a repulsive region of a triplet $n\sigma^*$ state and this becomes more marked as the atomic number of the halogen atom increases, owing to the crossing point becoming increasingly closer to the minimum along the carbon-halogen bond (the reason why no IBz REMPI work was undertaken here or has been recorded before). It is noted that Deguchi et al.⁷¹ have measured the lifetime of the origin of the S_1 state using a picosecond laser as 520 ps ; and that Liu et al.⁷² have undertaken an ultrafast dynamics study of ClBz, exciting to the S_1 state at a wavenumber of $\sim 37495\text{ cm}^{-1}$ using a femtosecond laser which was

centred roughly on M_{29} , but with a width of $\sim 550 \text{ cm}^{-1}$. The lifetime of these levels was measured as having two components of $152 \pm 3 \text{ fs}$ and $749 \pm 21 \text{ ps}$. The population of the S_1 state was monitored via photoionisation in the latter two experiments.

Lifetimes shorten with increasing mass of the halogen because of intersystem crossing (ISC) and predissociation, full explanation in section 3.3.4. And as it is expected for the lifetimes to shorten at higher wavenumbers, making it difficult to obtain a reliable DF spectrum as population is being rapidly lost and/or transferred to different levels.

In the DF spectra of Imhof and Kleinermanns,⁴⁰ the intensity of the M_{8*} and M_9 transitions and higher-wavenumber bands are much weaker than they are in the present REMPI spectrum, suggesting the short lifetime of the state is a reasonable explanation for the complicated spectral observations. The reason this lifetime effect is not evident in the REMPI spectra here is because REMPI spectroscopy relies on ionisation, which is extremely rapid and hence is far less susceptible to effects seen in fluorescence spectroscopies which require the excited state to exist long enough to emit a photon. With that being a main requirement it follows then, that the emission observed from halobenzene energy levels is likely to be not purely due to the initial excited vibrational level in the S_1 state, but rather to what remains of this, plus any emitting levels to which the population has transferred. Bass and Sponer⁷³ commented that they did not detect any phosphorescence in their experiments, consistent with ISC resulting in predissociation being the likely mechanism for the loss of signal.

A similar explanation applies to the band at 932.2 cm^{-1} , which is assigned as M_{8*} in the present work, and is observed in the previous REMPI-PES and ZEKE studies. It is less straightforward to compare the DF spectrum from this band with that of FBz, as it has been shown that in FBz the M_8 mode is in Fermi resonance with the $M_{15}M_{20}$ combination band.

Discussion of the previous work in this section has demonstrated the application of the M_i nomenclature to the ground cationic state of the ClBz- h_5 molecule and its perdeuterated isotopologue, even though the vibrational mode motions deviates from the modes of the S_0 state. Vibrational assignments taken from a number of different studies are referred to with the same label for the same vibration (based on wavenumber) making it much more convenient to compare across a breadth of work.

5. Summary

Electronic spectra of the $S_1 \leftarrow S_0$ transition of ClBz- h_5 and ClBz- d_5 up to 3000 cm^{-1} were presented here with detailed assignments of the first 1100 cm^{-1} and fairly comprehensive assignments up to 2500 cm^{-1} . For ClBz- h_5 previous studies have been of great aid including those using DF, REMPI-PES, ZEKE and MATI. However, some reassignments have been made and discrepancies between those studies accounted for.

The shifts in the calculated vibrational wavenumber upon deuteration have allowed the assignments of the vibrations in the $^{35}\text{ClBz-}d_5$ isotopologue to be established. $^{35/37}\text{Cl}$ isotopic shifts have proven useful in deciding between possible assignments for many features.

It is clear from the above discussed assignments that a number of possible FRs exist in these isotopologues, in addition to a well known one at 520 cm^{-1} in the ClBz- h_5 sample. As a result it would be of benefit in the future to explore those features with DF, ZEKE, MATI and REMPI-PES studies as was done for a number of bands already.

In the next section, vibrational assignments of BrBz- h_5 and its perdeuterated isotopologue will be discussed with (1+1) REMPI spectra presented, examining in detail the trends in the vibrational structure that occur across monohalobenzene species.

3.4.3 Bromobenzene- h_5 and Bromobenzene- d_5

The (1+1) REMPI spectra of BrBz- h_5 (upright, top trace) and BrBz- d_5 (inverted, bottom trace) from $0\text{--}3050\text{ cm}^{-1}$ are shown in Figure 3.14 with the main vibrational band assignments marked. As was true for the chlorine atom, bromine has two naturally abundant isotopes, and although $^{35}\text{Cl}/^{37}\text{Cl}$ isotopic shifts were of great use in establishing the vibrational assignment when there was more than one possibility available, as the isotopic shift of Cl is significant enough to differentiate between modes, little use was made of the $^{79}\text{Br}/^{81}\text{Br}$ isotopic shifts as these are extremely small, $< 1\text{ cm}^{-1}$ for 29 out of the 30 vibrational modes. The M_{11} mode has an isotopic shift of 1.6 cm^{-1} between BrBz- h_5 and BrBz- d_5 isotopologues. Only the spectra for the ^{79}Br isotopologues are included in Figure 3.14 and other spectra presented here. BrBz- h_5 and BrBz- d_5 refer to the ^{79}Br isotopologue, with ^{81}Br only being mentioned in

passing on two occasions. Calculated vibrational wavenumbers of the S_0 , S_1 and D_0^+ states of $^{81}\text{BrBz-}h_5$ and $^{81}\text{BrBz-}d_5$ are given in Supplementary Material of ref. 4.

The $\text{BrBz-}h_5$ and $\text{BrBz-}d_5$ isotopic shifts are of a much larger magnitude and are mode specific as participation of the hydrogen atoms is different for each vibration. As with the FBz and ClBz isotopologues, these shifts are easily spotted in the comparison of the spectra, seen in Figure 3.14 and thereafter.

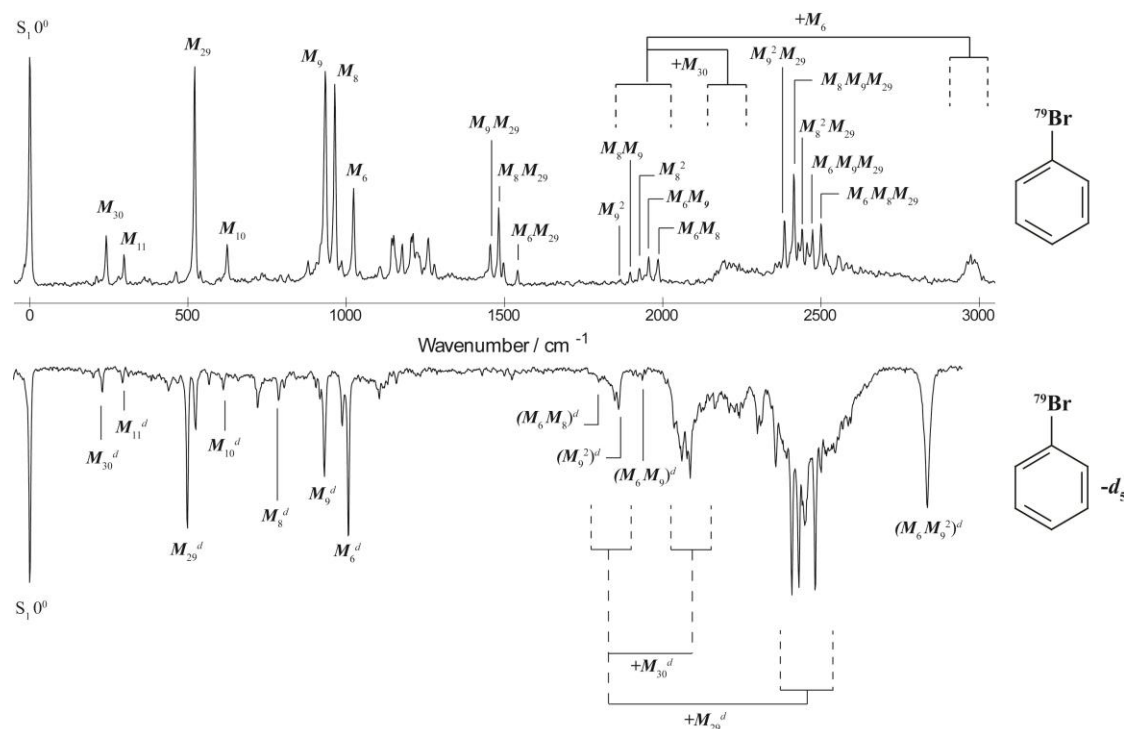


Figure 3.14. 0–3050 cm^{-1} spectral range scan of the $S_1 \leftarrow S_0$ (1+1) REMPI spectra of $\text{BrBz-}h_5$ (top trace, upright) and $\text{BrBz-}d_5$ (bottom trace, inverted). The assignments are discussed in detail in the text below. The “combs” indicate regions of the spectrum whose contributors also appear to higher wavenumber in combination with another vibration, although the precise assignment of the individual features is not necessarily clear.

The $^{79}\text{BrBz-}h_5$ spectrum was calibrated to the band origin of $36991.5 \pm 0.2 \text{ cm}^{-1}$ by comparing with a simulation of the origin band using PGOPHER⁷⁴ and the rotational constants taken from the work of Cvitas;⁷⁵ this also allowed a rotational temperature of 20–30 K to be established. It was found that the BrBz spectra were warmer than the FBz and ClBz spectra; however, there were difficulties with vibrationally and rotationally cooling the BrBz samples. At first, Ar was utilised as the carrier gas, but broad features were always present, attributable to dimers and trimers etc. where dissociation of these formed warm monomers; only with the use of He as a carrier gas were the spectra cooled successfully. With a PGOPHER simulation it was found that the $^{81}\text{BrBz-}h_5$ origin band was at the same position, within the bandwidth of the laser employed, showing that the S_1 origin bands of the ^{79}Br and the ^{81}Br isotopologues are within 0.5 cm^{-1} of each other, consistent with the result found by the work of the de la Cruz group,³⁹ with the difference equal to $< 0.02 \text{ cm}^{-1}$. (PGOPHER aides with the calibration process as by simulating the origin band from rotational constant one is able to compare recorded band profile in this work against that as band origin values reported by other groups give band centre, however it is unclear where band centre is within the precision of quoted value.)

For the BrBz- d_5 transition origin, an isotopic blue shift from the BrBz- h_5 origin of 171.4 cm^{-1} is determined from the recorded spectrum, locating the origin at $37162.9 \pm 0.5 \text{ cm}^{-1}$. The origins of the recorded spectra were shifted to zero just as for the FBz and ClBz molecules to make the

comparisons of the vibrations observed more straightforward and easier on the eye.

Before the vibrational assignments in Figure 3.14 of the BrBz- h_5 and BrBz- d_5 molecules can be discussed and compared in more detail, vibrations for the S_0 state should be touched upon first. BrBz- h_5 S_0 state vibrations were briefly mentioned previously in terms of the M_i vibrations in the publication by Gardner and Wright¹ so it is sufficient to only mention here that the motions are very different to those of the Bz molecule itself, and so Wilson modes are inappropriate. The corresponding motions between FBz- h_5 and BrBz- h_5 correlate well to one another as seen in Figure 3.15a. Figure 3.15b presents a Duschinsky matrix of BrBz- d_5 ground state vibrations against those of the BrBz- h_5 ground state. The matrix in Figure 3.15b shows that the vibrational motions of the BrBz- d_5 molecule (M_i^d vibrations) are very similar to those of BrBz- h_5 (M_i modes) in most cases; however, the wavenumber ordering of the vibrations changes, as it did for the FBz and ClBz molecules seen previously.

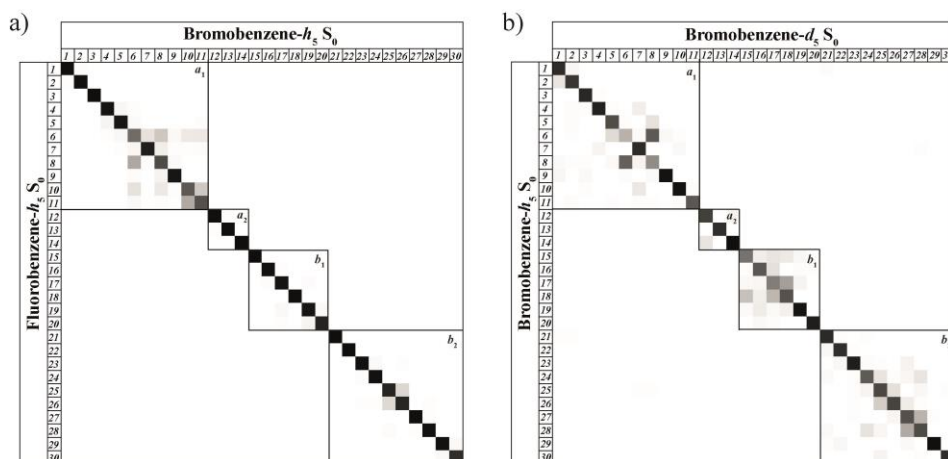


Figure 3.15. Generalized Duschinsky matrix between vibrational modes of the S_0 states of a) FBz- h_5 and BrBz- h_5 and b) BrBz- h_5 and BrBz- d_5 . Shadings indicate the mixing coefficient values, with black = 1.00 while white = 0.00, with the level of the grey shading indicating intermediate values. The numbers are the i values for each M_i mode.

For FBz- h_5 , the energetic ordering of the vibrational modes is $M_9 < M_8 < M_7 < M_6$ (by construction), while for FBz- d_5 the ordering is $M_8^d < M_7^d < M_9^d < M_6^d$; for ClBz- h_5 the vibrational ordering is $M_9 < M_8 < M_6 < M_7$, while for ClBz- d_5 the ordering is again $M_8^d < M_7^d < M_9^d < M_6^d$ as it was for FBz- d_5 . For BrBz, the same orderings were found in the S_0 states as for the respective ClBz isotopologues. The M_6^d and M_8^d modes are quite heavily mixed in the S_0 state of BrBz- d_5 (compared to BrBz- h_5 , see Figure 3.15b), with the off-diagonal coefficients suggesting their order should be changed; however, it is clear from the spectra here and our previous assignments of these modes for FBz and ClBz samples, that it is in fact the M_8^d vibration that has lower wavenumber. Also, the vibrational motion itself was followed and matched across modes from the BrBz- h_5 molecule. The M_6 and M_8 modes are extremely similar in their vibrational motions as may be seen in Figure 1.4 in Chapter 1, with the major difference being the stretching of the carbon–substituent bond.

As the substituent gets heavier, this motion becomes smaller, and determining the difference between these two modes in the Duschinsky procedure becomes less clear, although these can be identified by looking at the actual motion of the calculated atomic displacements in the FC-LabII program.¹³ The comparison of the BrBz- h_5 and - d_5 spectra with the corresponding spectra of FBz and ClBz does, however, make the assignment of these modes more clear.

Table 3.12 summarises calculated vibrational frequencies for the BrBz- h_5 and BrBz- d_5 molecules in the S_0 state with previous experimental results. Excellent agreement is shown between experimental IR/Raman results by Whiffen¹⁴ and Nanney et al.⁶⁴ (for BrBz- h_5 and BrBz- d_5 molecules respectively) and calculated vibrational frequencies in this project (employing B3LYP/aug-cc-pVTZ theory). It is worth mentioning that the estimated M_2^d mode value of 2275 cm^{-1} from the Nanney et al. paper is consistent with the calculated value of 2269 cm^{-1} for M_3^d . The wavenumber of M_8^d is uncertain in ref. 64, as a band at 817 cm^{-1} was observed in the IR spectrum but in the Raman spectrum a band was located at 826 cm^{-1} and both of these are close to the calculated value of 815 cm^{-1} and so it is not possible to decide between the two definitively. Apart from the work by previous members of this group (ref.1), there are no other calculated frequencies to compare to for either isotopologue of BrBz in the S_0 state.

Figure 3.16 shows the Duschinsky matrices for the S_1 vibrations in terms of the S_0 vibrations for each of the BrBz isotopologues. As was the case for the FBz and ClBz molecules, a little bit more mixing is present in

BrBz- h_5 than BrBz- d_5 , indicating there is more rotation of the vibrational coordinates present in the perhydrogenated isotopologue signifying that some of the vibrations in the S_1 state will be somewhat different to those in the S_0 state, which is not surprising in itself as upon excitation change in electronic structure and geometry occur. In particular, it was found that the M_8 and M_9 modes are significantly mixed (as was the case for ClBz), and those are individually labelled here to be consistent with previous work.

The calculated vibrational wavenumbers for the S_1 states of the $^{79}\text{BrBz-}h_5$ and $^{79}\text{BrBz-}d_5$ molecules have been used to aid the assignment of the recorded spectra and are presented in Table 3.13 on the next page, together with previously reported experimental assignments for the $^{79}\text{BrBz-}h_5$ molecule and experimental fundamentals deduced from the recorded spectra in this project.

Table 3.12. Assignments, calculated and experimental vibrational wavenumbers (cm^{-1}) for the S_0 state of $^{79}\text{BrBz-}h_5$ and $^{79}\text{BrBz-}d_5$.

⁷⁹ BrBz- <i>h</i> ₅				⁷⁹ BrBz- <i>d</i> ₅		
Mode Label	Calculated		Experimental	Mode Label	Calculated	Experimental
	This work ^a	Ref. 1 ^b	IR/Raman ^c		This work ^a	IR/Raman ^d
<i>a</i> ₁						
<i>M</i> ₁	3109	3212	3069	<i>M</i> ₁ ^{<i>d</i>}	2304	2296
<i>M</i> ₂	3097	3200	3050	<i>M</i> ₂ ^{<i>d</i>}	2291	2275 ^e
<i>M</i> ₃	3077	3178	3029	<i>M</i> ₃ ^{<i>d</i>}	2269	2270
<i>M</i> ₄	1567	1616	1580	<i>M</i> ₄ ^{<i>d</i>}	1530	1551
<i>M</i> ₅	1463	1489	1473	<i>M</i> ₅ ^{<i>d</i>}	1328	1346
<i>M</i> ₆	1052	1080	1070	<i>M</i> ₆ ^{<i>d</i>}	995	1020
<i>M</i> ₇	1164	1191	1176	<i>M</i> ₇ ^{<i>d</i>}	853	865
<i>M</i> ₈	1009	1036	1020	<i>M</i> ₈ ^{<i>d</i>}	815	817 or 826 ^f
<i>M</i> ₉	988	1003	1001	<i>M</i> ₉ ^{<i>d</i>}	948	958
<i>M</i> ₁₀	662	676	669	<i>M</i> ₁₀ ^{<i>d</i>}	633	644
<i>M</i> ₁₁	305	312	315	<i>M</i> ₁₁ ^{<i>d</i>}	298	305
<i>a</i> ₂						
<i>M</i> ₁₂	961	977	963	<i>M</i> ₁₂ ^{<i>d</i>}	783	760
<i>M</i> ₁₃	825	836	832	<i>M</i> ₁₃ ^{<i>d</i>}	642	680
<i>M</i> ₁₄	401	415	409	<i>M</i> ₁₄ ^{<i>d</i>}	348	350
<i>b</i> ₁						
<i>M</i> ₁₅	980	1000	988	<i>M</i> ₁₅ ^{<i>d</i>}	816	817
<i>M</i> ₁₆	902	914	903	<i>M</i> ₁₆ ^{<i>d</i>}	742	743
<i>M</i> ₁₇	732	746	735	<i>M</i> ₁₇ ^{<i>d</i>}	607	614
<i>M</i> ₁₈	677	701	681	<i>M</i> ₁₈ ^{<i>d</i>}	538	543
<i>M</i> ₁₉	456	472	458	<i>M</i> ₁₉ ^{<i>d</i>}	401	403
<i>M</i> ₂₀	162	168	181	<i>M</i> ₂₀ ^{<i>d</i>}	152	172
<i>b</i> ₂						
<i>M</i> ₂₁	3106	3210	3069	<i>M</i> ₂₁ ^{<i>d</i>}	2299	2280
<i>M</i> ₂₂	3085	3186	3056	<i>M</i> ₂₂ ^{<i>d</i>}	2278	2270
<i>M</i> ₂₃	1573	1623	1577	<i>M</i> ₂₃ ^{<i>d</i>}	1538	1541
<i>M</i> ₂₄	1432	1458	1445	<i>M</i> ₂₄ ^{<i>d</i>}	1304	1316
<i>M</i> ₂₅	1306	1341	1323	<i>M</i> ₂₅ ^{<i>d</i>}	1017	1012
<i>M</i> ₂₆	1275	1316	1264	<i>M</i> ₂₆ ^{<i>d</i>}	1271	1278
<i>M</i> ₂₇	1146	1172	1159	<i>M</i> ₂₇ ^{<i>d</i>}	831	841
<i>M</i> ₂₈	1064	1092	1068	<i>M</i> ₂₈ ^{<i>d</i>}	809	800 ^e
<i>M</i> ₂₉	608	621	615	<i>M</i> ₂₉ ^{<i>d</i>}	583	586
<i>M</i> ₃₀	240	249	254	<i>M</i> ₃₀ ^{<i>d</i>}	226	238

^a. B3LYP/aug-cc-pVTZ values, scaled by 0.97

^b. B3LYP/aug-cc-pVDZ values, unscaled.

^c. Ref. 14

^d. Ref. 64

^e. Estimated value from ref. 64

^f. In ref.64, a band at 817 cm^{-1} was observed in the IR spectrum, but moved to 826 cm^{-1} in the Raman spectrum.

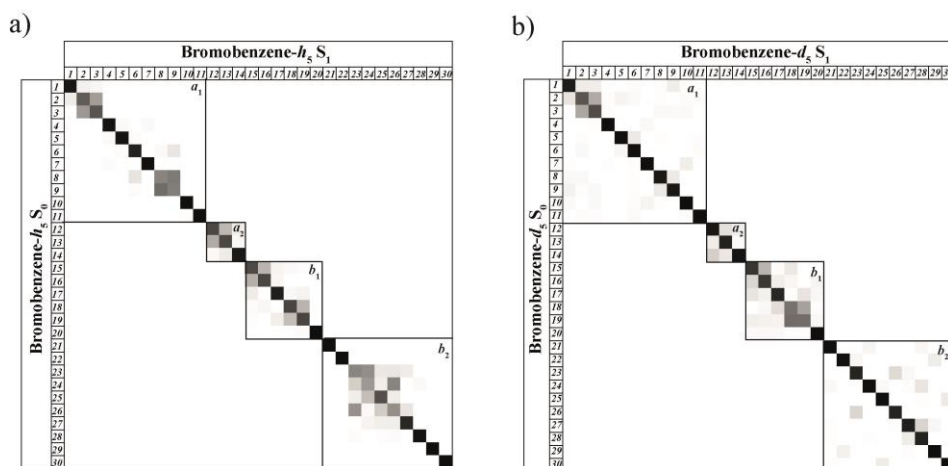


Figure 3.16. Generalized Duschinsky matrices between the vibrational modes of the S_0 and S_1 states for: (a) BrBz- h_5 and (b) BrBz- d_5 . Shadings indicate the mixing coefficient values, with black = 1.00 while white = 0.00, with the level of the grey shading indicating intermediate values. The numbers are the i values for each M_i or M_i^d mode.

With the calculated S_1 frequencies in place for both isotopologues a detailed assignment of the spectra presented in Figure 3.14 can be undertaken. As with the FBz and ClBz molecules, the discussion is split into three main wavenumber regions: low wavenumber range (0-750 cm^{-1}), medium wavenumber range (750-1050 cm^{-1}) and high wavenumber range (1050-3050 cm^{-1}) for the $^{79}\text{BrBz-}h_5$ and $^{79}\text{BrBz-}d_5$ molecules, with the assignments for the ^{81}Br isotopologues being the same. To assign the spectra, previous BrBz assignments were used as a guide, where the main reliance lay on the calculated wavenumbers and previous assignments of the FBz and ClBz spectra for both $-h_5$ and $-d_5$ variants.

Table 3.13. Assignments, calculated and experimental vibrational wavenumbers (cm^{-1}) for the S_1 states of $^{79}\text{BrBz-}h_5$ and $^{79}\text{BrBz-}d_5$.

⁷⁹ BrBz- <i>h</i> ₅						⁷⁹ BrBz- <i>d</i> ₅		
Mode Label	Calc.	Exp.				Mode Label	Calc.	Exp.
	This work ^a	This work	Ref. 59 ^b	Ref. 58 ^c	Ref. 57		This work ^a	This work
<i>a</i> ₁								
<i>M</i> ₁	3135					<i>M</i> ₁ ^{<i>d</i>}	2320	
<i>M</i> ₂	3115					<i>M</i> ₂ ^{<i>d</i>}	2301	
<i>M</i> ₃	3079					<i>M</i> ₃ ^{<i>d</i>}	2271	
<i>M</i> ₄	1445			1447		<i>M</i> ₄ ^{<i>d</i>}	1394	
<i>M</i> ₅	1401					<i>M</i> ₅ ^{<i>d</i>}	1239	
<i>M</i> ₆	993	1022.5	1019.1	1017	1019	<i>M</i> ₆ ^{<i>d</i>}	965	996.6
<i>M</i> ₇	1125			1141		<i>M</i> ₇ ^{<i>d</i>}	833	
<i>M</i> ₈	949	934.5	931.4	929	931	<i>M</i> ₈ ^{<i>d</i>}	787	779.1
<i>M</i> ₉	974	963.0	960.3	959	961	<i>M</i> ₉ ^{<i>d</i>}	917	921.1
<i>M</i> ₁₀	641	623.0	620.8	650	620	<i>M</i> ₁₀ ^{<i>d</i>}	614	604.1
<i>M</i> ₁₁	295	297.0	294.1	(333)		<i>M</i> ₁₁ ^{<i>d</i>}	289	290.6
<i>a</i> ₂								
<i>M</i> ₁₂	612			709		<i>M</i> ₁₂ ^{<i>d</i>}	511	
<i>M</i> ₁₃	511	560 ^d				<i>M</i> ₁₃ ^{<i>d</i>}	412	405.5 ^d
<i>M</i> ₁₄	-- ^e	181.0 ^f		231	296	<i>M</i> ₁₄ ^{<i>d</i>}	-- ^e	154.6 ^f
<i>b</i> ₁								
<i>M</i> ₁₅	843	825.4 ^d		871		<i>M</i> ₁₅ ^{<i>d</i>}	711	
<i>M</i> ₁₆	680				678 ^g	<i>M</i> ₁₆ ^{<i>d</i>}	581	
<i>M</i> ₁₇	575	579 ^f				<i>M</i> ₁₇ ^{<i>d</i>}	449	
<i>M</i> ₁₈	486	486.8 ^d				<i>M</i> ₁₈ ^{<i>d</i>}	393	
<i>M</i> ₁₉	344	311 ^h				<i>M</i> ₁₉ ^{<i>d</i>}	297	264.1 ^f
<i>M</i> ₂₀	119	105.6 ^f			120	<i>M</i> ₂₀ ^{<i>d</i>}	112	99.1 ^f
<i>b</i> ₂								
<i>M</i> ₂₁	3130					<i>M</i> ₂₁ ^{<i>d</i>}	2310	
<i>M</i> ₂₂	3106				3082 ⁱ	<i>M</i> ₂₂ ^{<i>d</i>}	2285	
<i>M</i> ₂₃	1426			1476		<i>M</i> ₂₃ ^{<i>d</i>}	1316	
<i>M</i> ₂₄	1360			1328		<i>M</i> ₂₄ ^{<i>d</i>}	1199	
<i>M</i> ₂₅	1253			1257		<i>M</i> ₂₅ ^{<i>d</i>}	996	
<i>M</i> ₂₆	1372					<i>M</i> ₂₆ ^{<i>d</i>}	1401	
<i>M</i> ₂₇	1121			1199		<i>M</i> ₂₇ ^{<i>d</i>}	816	
<i>M</i> ₂₈	973					<i>M</i> ₂₈ ^{<i>d</i>}	775	
<i>M</i> ₂₉	511	521.5	518.9	519	518	<i>M</i> ₂₉ ^{<i>d</i>}	491	493.6
<i>M</i> ₃₀	242	242.0		282	234	<i>M</i> ₃₀ ^{<i>d</i>}	228	227.1

^a. TDDFT, B3LYP/aug-cc-pVTZ, scaled by 0.97 ^b. Dietz et al. REMPI study

^c. All values in the vapour phase at 20 K, except for the parenthesised value which was from a 4 K crystalline sample.

^d. Derived from a combination band and so there may be an anharmonic shift.

^e. The M_{14} mode calculations in the S_1 state give unrealistic values, as for the lighter monohalobenzenes, and so is not reported here – see text.

^f. Derived from an overtone band and so there may be an anharmonic shift.

^g. Assigned in the present work from hot bands in refs. 56 and 57.

^h. Tentatively assigned from assuming the overtone is contributing to the feature at 623 cm^{-1} .

ⁱ. Reassigned (tentatively) in the present work – please see discussion.

1. Low wavenumber range (0 - 750 cm⁻¹)

BrBz-*h*₅

In the low-wavenumber region below 300 cm⁻¹, a similar pattern of features is seen as was previously observed for the FBz and ClBz molecules, therefore these were assigned straightforwardly as shown in Figure 3.17 and Table 3.14. Figure 3.17 shows the low energy region being dominated by the origin transition and the M_{29} level for both isotopologues. A first assignment of the M_{14}^2 transition was considered for the feature at 462 cm⁻¹, however, this assignment was rejected since it goes against the trend of falling wavenumber for the M_{14} vibration with increasing substituent mass. Instead, the M_{14}^2 was assigned to the weak feature at 362 cm⁻¹, which then allowed the identification of the band at 278.5 cm⁻¹ as the $M_{14}M_{20}$ combination transition- a corresponding band was seen in the ClBz-*h*₅ spectrum.

The band at 462 cm⁻¹ still required an assignment and the guidance for that was taken from the ClBz spectrum. In ClBz-*h*₅, the M_{29} vibration is in FR with the $M_{14}M_{19}$ combination, where the two bands are almost isoenergetic at 529 cm⁻¹, and of almost the same intensity. Here, the $M_{14}M_{19}$ combination, occurs at 462 cm⁻¹ which is shifted in ClBz-*h*₅ from its non-perturbed value by the FR. This combination band assignment leads to the M_{19} fundamental value. Taking into the account calculated frequency and comparison of the calculated and experimental values in ClBz-*h*₅, it is expected that the M_{19} vibration will be at ~ 310 cm⁻¹, and hence the $M_{14}M_{19}$ vibration should appear at ~491 cm⁻¹. Considering anharmonicity, FR and uncertainty in the values, the assignment of the

462 cm^{-1} band becomes reasonable, but further evidence from dispersed fluorescence or ZEKE spectroscopy is needed to confirm this assignment.

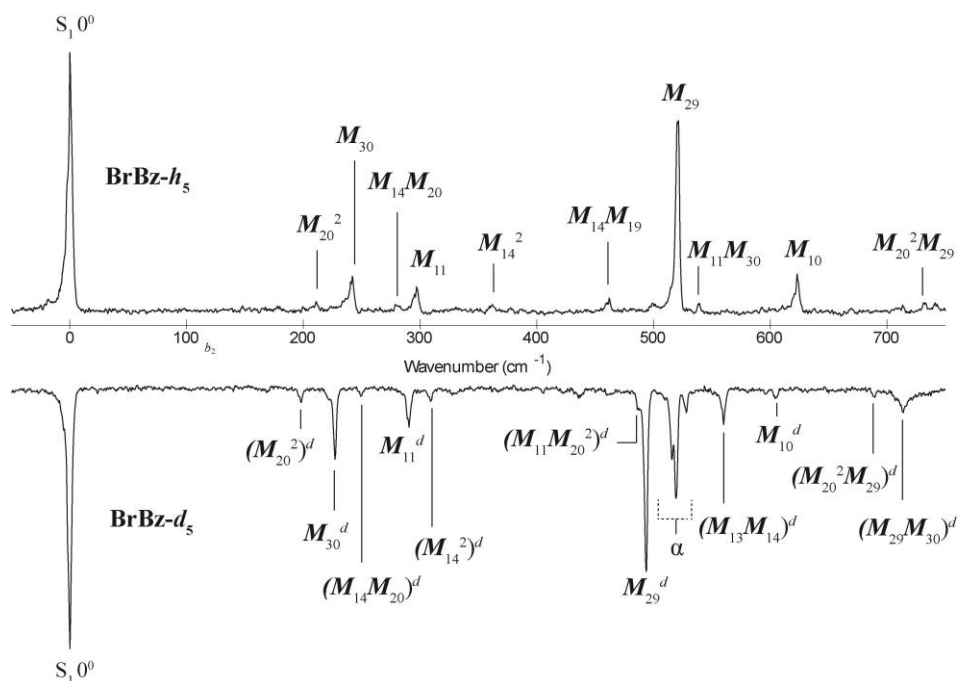


Figure 3.17. Expanded views of the low wavenumber regions (0–750 cm^{-1}) of the $S_1 \leftarrow S_0$ (1+1) REMPI spectra of BrBz- h_5 (top trace, upright) and BrBz- d_5 (bottom trace, inverted). Assignments are discussed in the text and summarized in Tables 3.14 and 3.15; suggested assignments for some of the weaker features and the region marked α are also given in these tables.

At 521.5 cm^{-1} , the intense, vibronically-allowed M_{29} transition appears. Unlike in the ClBz- h_5 spectrum where this transition is in FR with the $M_{14}M_{19}$ combination band, here it stands alone. The assignment of the M_{29} band at $\sim 520 \text{ cm}^{-1}$ is consistent with the assignment made by Dietz et al.⁵⁹ to the close-to-pure ν_{6b} Wilson mode, and to a non-totally-symmetric vibration by Walerstein.⁵⁵ The assignment of M_{29} has also been confirmed in the REMPI-PES study of Walter et al.,³⁸ which shall

be commented on further below, and in the absorption study of Prakash and Singh.⁵⁷

The M_{29} transition is followed by a weak feature at 539.0 cm^{-1} that can be assigned to $M_{11}M_{30}$, and then by the M_{10} band at 623.0 cm^{-1} . The weak feature at 733.0 cm^{-1} is in the correct position to be the $M_{20}^2M_{29}$ transition, while the 741.0 cm^{-1} band is tentatively assigned to the $M_{13}M_{14}$ combination.

Dietz et al.⁵⁹ and Prakash and Singh⁵⁷ also saw the M_{11} feature and assigned it to the ν_{6a} Wilson mode; however, as mentioned before the M_{11} mode is of very mixed Wilson-mode character and in fact the M_{10} mode corresponds more strongly to the Wilson ν_{6a} mode. The M_{10} mode itself corresponds to what was reported in ref. 59 as Wilson mode 1 at 620.8 cm^{-1} , which is in agreement with the spectrum here, and such a feature was also seen in ref. 57. Transition assignments in this low wavenumber range are in good agreement with the results of Klimusheva et al.⁵⁸ for the vibrational wavenumbers from their absorption spectrum, but their values for M_{11} , M_{14} and M_{30} are somewhat higher than other reported values and those obtained here (please refer to Table 3.13).

BrBz- d_5

The assignments of the BrBz- d_5 spectrum rely on the calculated vibrational wavenumbers/isotopic shifts and previous assignments of the two lighter deuterated monohalobenzene molecules discussed in previous sections because no previous studies were found on this isotopologue. In the low wavenumber region, the three vibrations observed in the BrBz- h_5

spectrum below 300 cm^{-1} are seen here with relatively similar positions in figure 3.17, consistent with the small calculated isotopic shifts for these, seen in Table 3.13.

Based on the expected large H/D isotopic shift and consistent with the FBz and ClBz samples, a band at 309.1 cm^{-1} is assigned as the $(M_{14}^2)^d$ transition. This gives a predicted position for the $(M_{14}M_{20})^d$ combination at $\sim 254\text{ cm}^{-1}$, so the weak band at 249.1 cm^{-1} can be cautiously assigned to this vibration, with the small difference attributable to anharmonicity.

The M_{29}^d band at 493.6 cm^{-1} , as was true for BrBz- h_5 , is the most intense transition here bar the origin band. There appears to be no obvious band that can be assigned to $(M_{14}M_{19})^d$ which is attributed to its being too separated in wavenumber from the M_{29}^d and thus unable to gain intensity from it via FR, with the combination band expected to be $\sim 419\text{ cm}^{-1}$ based on fundamentals assigned below and knowledge from the ClBz spectra.

To slightly higher wavenumber from the M_{29}^d band there is a small group of features, marked α . From the calculated wavenumbers, and the spectrum of BrBz- h_5 , the $(M_{11}M_{30})^d$ transition is expected to appear here at $\sim 518\text{ cm}^{-1}$. In the perhydrogenated sample the $(M_{11}M_{30})^d$ transition is weak and for this combination to be seen more intensely in the BrBz- d_5 sample, it must be in FR with the nearby feature, M_{29}^d .

A feature at 560.1 cm^{-1} is tentatively assigned to the $(M_{13}M_{14})^d$ combination band due to the fact it matches a corresponding band in BrBz- h_5 and the calculated shifts upon deuteration. From this a fundamental value for M_{13}^d can be established to be around $\sim 406\text{ cm}^{-1}$;

resulting in $(M_{13}M_{20})^d$ being a possible contributor to feature α . This combination band of b_2 symmetry could be in Fermi resonance with the M_{29}^d and/or $(M_{11}M_{30})^d$ bands, which could explain why it is seen in the spectrum of BrBz- d_5 but not in that of BrBz- h_5 .

The M_{10}^d transition is assigned in the BrBz- d_5 spectrum to the weak band seen at 604.1 cm^{-1} . In the FBz- d_5 and ClBz- d_5 spectra, the same transition was also weak and this was attributed to its being involved in complex Fermi resonances, but this seems not to be the case here. A band at 714.0 cm^{-1} in this region is the last one that is high enough in intensity to be noticed and it is assigned to the $(M_{29}M_{30})^d$ combination band as the most plausible assignment. Very similar vibrational transitions occur in both BrBz- h_5 and BrBz- d_5 isotopologues in the low wavenumber region, as was the case for FBz and ClBz molecules.

Table 3.14. A summary of the assigned vibrational features from the present work for the $S_1 \leftarrow S_0$ transition of $^{79}\text{BrBz-}h_5$.

	Experimental band (cm^{-1}) ^a	Assignment ^b	This work B3LYP	From experimental fundamental ^c	Overall Symmetry
	0.0	0^0	-	-	a_1
	211.5	M_{20}^2	239	211.5 ^d	a_1
	242.0	M_{30}	242	242.0 ^d	b_2
	278.5	$M_{14}M_{20}$	- ^e	286.6	b_2
	297.0	M_{11}	295	297.0 ^d	a_1
	362.0	M_{14}^2	- ^e	362.0 ^d	a_1
	462.0	$M_{14}M_{19}$	- ^e	492.0	b_2
	501.5	$M_{11}M_{20}^2$	533	508.4	a_1
	521.5	M_{29}	511	521.5 ^d	b_2
	539.0	$M_{11}M_{30}$	537	539.0	b_2
	592.5	$M_{18}M_{20}$	606	592.5 ^d	a_1
	623.0	M_{10}	641	623.0 ^d	a_1
	669.5	$M_{14}M_{18}$	- ^e	667.0	b_2
	733.0	$M_{20}^2M_{29}$	750	732.7	b_2
	741.0	$M_{13}M_{14}$	691	741.0	a_1
	880.0	$M_{14}^2M_{29}$	- ^e	883.5	b_2
	905.5	$M_{14}M_{18}M_{30}$	- ^e	909.0	a_1
		$M_{10}M_{14}M_{20}$	- ^e	909.6	b_2
Region β	918.0	$M_{10}M_{11}$	936	920.0	a_1
	931 ^f	$M_{15}M_{20}$	963	931.0 ^d	a_1
	934 ^f	M_8	949	934.0 ^d	a_1
	963.0	M_9	974	963.0 ^d	a_1
	985.0	$M_{10}M_{14}^2$	- ^e	985.0	a_1
	1022.5	M_6	994	1022.5 ^d	a_1
	1107.5	$M_{10}M_{30}^2$	1126	1107.0	a_1
	1143.5	$M_{10}M_{29}$	1153	1144.5	b_2
	1150.0	$M_8M_{20}^2$	1187	1146.0	a_1
	1157.5	M_{17}^2	1150	1157.5	a_1
	1174.5	$M_9M_{20}^2$	1212	1174.5	a_1
	1176.5	M_8M_{30}	1191	1176.6	b_2
	1203.5	M_9M_{30}	1216	1205.0	b_2
	1211.0	$M_{18}^2M_{30}$	1198	1214.0	b_2
	1231.5	M_8M_{11}	1243	1231.6	a_1
	1258.5	M_9M_{11}	1268	1260.0	a_1
	1455.0	M_8M_{29}	1460	1456.1	b_2
	1474	$M_8M_{11}M_{30}$	1486	1473.6	b_2
	1482	M_9M_{29}	1485	1484.5	b_2
	1498	$M_9M_{11}M_{30}$	1510	1502.0	b_2
	1542	M_6M_{29}	1505	1544.0	b_2
	1868	M_8^2	1897	1869.2	a_1
	1898	M_8M_9	1922	1897.6	a_1
	1926	M_9^2	1947	1926.0	a_1
	1956	M_6M_8	1942	1957.1	a_1
	1986	M_6M_9	1967	1985.5	a_1
	2386	$M_8^2M_{29}$	2409	2390.7	b_2
	2414	$M_8M_9M_{29}$	2434	2419.1	b_2
	2440	$M_9^2M_{29}$	2459	2447.5	b_2

2474	$M_6M_8M_{29}$	2454	2478.6	b_2
2500	$M_6M_9M_{29}$	2478	2507.0	b_2
2892	$M_6M_8^2$	2891	2891.7	a_1
2948	$M_6M_9^2$	2941	2948.5	a_1
2974	$M_6^2M_8$	2936	2979.6	a_1

^a Features above 1460 cm⁻¹ are quoted to the nearest 1 cm⁻¹ only since only scans with 2 cm⁻¹ resolution were undertaken for this isotopologue.

^b Selected assignments given for the region > 1000 cm⁻¹. If more than one option is given, the assignment is not known definitively.

^c All values have been computed from experimental fundamentals.

^d An experimental fundamental is taken from this feature.

^e M_{14} calculated B3LYP frequency was unrealistic; see text for details.

^f Overlapping bands, and so the position is an estimate.

Table 3.15. A summary of the assigned vibrational features from the present work for the $S_1 \leftarrow S_0$ transition of $^{79}\text{BrBz-d}_5$.

	Experimental band (cm^{-1}) ^a	Assignment ^b	This work B3LYP	From experimental fundamentals ^c	Overall symmetry
	0.0	0^0	-	-	-
	198.1	$(M_{20}^2)^d$	224	198.1 ^d	a_1
	227.1	M_{30}^d	228	227.1 ^d	b_2
	249.1	$(M_{14}M_{20})^d$	- ^e	253.7	b_2
	290.6	M_{11}^d	289	290.6 ^d	a_1
	309.1	$(M_{14}^2)^d$	- ^e	309.2 ^d	a_1
	487.6	$(M_{11}M_{20}^2)^d$	513	488.7	a_1
	493.6	M_{29}^d	491	493.6 ^d	b_2
α	515.6	$(M_{13}M_{20})^d$	524	504.6	b_2
	518.1	$(M_{11}M_{30})^d$	517	517.7	b_2
	528.1	$(M_{19}^2)^d$	- ^e	528.1 ^d	a_1
	560.1	$(M_{13}M_{14})^d$	- ^e	560.1 ^d	a_1
	604.1	M_{10}^d	615	604.1 ^d	a_1
	714.1	$(M_{29}M_{30})^d$	719	720.7	a_1
	779.1	M_8^d	787	779.1 ^d	a_1
	796.1	$(M_{14}^2M_{29})^d$	- ^e	802.8	b_2
	895.1	$(M_{10}M_{11})^d$	898	894.7	a_1
	906.6	$(M_{10}M_{14}^2)^d$	- ^d	915.7	a_1
	921.1	M_9^d	917	921.1 ^d	a_1
	977.1	$(M_8M_{20}^2)$	1011	977.3	a_1
	996.6	M_6^d	965	996.6 ^d	a_1
	1086.6	$(M_8M_{14}^2)^d$	- ^e	1088.3	a_1
	1093.6	$(M_{10}M_{29})^d$	1106	1097.7	b_2
	1117.1	$(M_9M_{20}^2)^d$	1141	1119.3	a_1
	1147.6	$(M_9M_{30})^d$	1145	1148.2	b_2
	1209.1	$(M_9M_{11})^d$	1206	1211.7	a_1
	1222.6	$(M_6M_{30})^d$	1193	1223.7	b_2
	1225.1	$(M_9M_{14}^2)^d$	- ^e	1230.1	a_1
	1286.1	$(M_6M_{11})^d$	1253	1287.2	a_1
	1415.1	$(M_9M_{29})^d$	1408	1414.7	a_2
	1439.6	$(M_9M_{11}M_{30})^d$	1434	1438.8	b_2
	1464.6	$(M_8M_{18}M_{19})^d$	- ^e	1468.1	b_2
	1484.6	$(M_6M_{29})^d$	1456	1490.2	b_2
	1843	$(M_9^2)^d$	1834	1842.2	a_1
	2057	$(M_8^2M_{29})^d$	2065	2051.8	b_2
	2067	$(M_6M_8M_{11})^d$	2041	2066.3	a_1
	2277	$(M_6M_8M_{29})^d$	2243	2269.2	b_2
	2335	$(M_9^2M_{29})^d$	2326	2335.8	b_2
	2385	$(M_6M_8M_{10})^d$	2366	2379.8	a_1
	2457	$(M_9^2M_{10})^d$	2449	2446.3	a_1

^a Features above 1500 cm^{-1} are quoted to the nearest cm^{-1} as only 2 cm^{-1} resolution scans were taken of the high wavenumber region for this isotopologue.

^b Selected assignments given for the region $> 1000\text{ cm}^{-1}$.

^c All values come from experimental fundamentals.

^d An experimental fundamental is taken from this feature.

^e M_{14}^d calculated B3LYP frequency is imaginary.

2. Medium wavenumber range (750 - 1050 cm^{-1})

Figure 3.18 below presents (1+1) REMPI spectra in the medium wavenumber range of BrBz- h_5 (top, upright) and BrBz- d_5 (bottom, inverted). Between 750-1050 cm^{-1} many more transitions occur in the BrBz- d_5 sample, whereas the BrBz- h_5 spectrum is dominated by three main features at $\sim 934 \text{ cm}^{-1}$, $\sim 963 \text{ cm}^{-1}$ and $\sim 1023 \text{ cm}^{-1}$ with very little other structure present in this range.

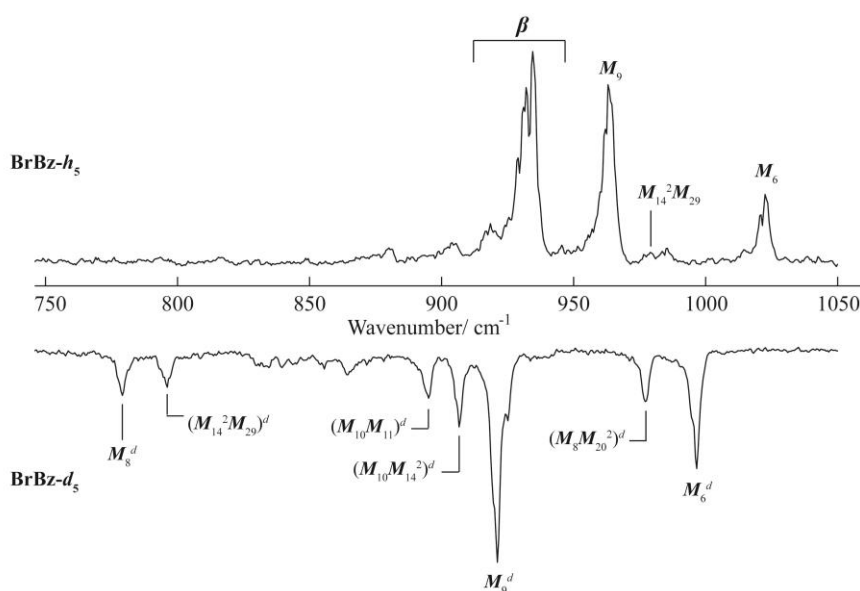


Figure 3.18. Expanded views of the medium wavenumber regions (750–1050 cm^{-1}) of the $S_1 \leftarrow S_0$ (1+1) REMPI spectra of BrBz- h_5 (top trace, upright) and BrBz- d_5 (bottom trace, inverted). Assignments are discussed in the text and summarized in Tables 3.14 and 3.15.

BrBz- h_5

The main contributors to the three dominating features in this range are the M_8 , M_9 and M_6 fundamentals, respectively. The agreement between the calculated wavenumbers for the M_8 and M_9 vibrations and the observed positions is good, whilst the value for the M_6 is calculated to be

$\sim 30 \text{ cm}^{-1}$ too low compared to its position; the same pattern was seen previously for the two lighter monosubstituted benzenes.

The two higher-wavenumber features, M_9 and M_6 , have a vibrational band width consistent with a single contribution, and so these are labelled in Figure 3.18. M_8 , the lowest wavenumber feature, has a width suggestive of further contributors than M_8 ; it is marked as the β region in Figure 3.18, where Table 3.14 features other possible contributions to the band. The $M_{10}M_{11}$ combination band is a possible contributor to the β region, as it has a_1 symmetry and therefore could be in FR with the M_8 vibration. $M_{10}M_{11}$ is expected at $\sim 920 \text{ cm}^{-1}$, calculated from the sum of the wavenumbers of the two contributors; when both anharmonicity and FR are taken into account, it is expected of the band to shift to lower wavenumber. It is therefore extremely plausible that this transition is associated with a weak feature on the low wavenumber ($\sim 918 \text{ cm}^{-1}$) side of region β , which is also consistent with a small red shift seen for this feature in the $^{81}\text{BrBz-}h_5$ spectrum arising from the M_{11} component (not shown). No other obvious fundamentals exist of a_1 or b_2 symmetry that could contribute to the region β , nor is there an overtone, but looking to the FBz spectrum again, the $M_{15}M_{20}$ combination band was seen in FR with the M_8 band, and so it could be a contributing band to the central region at $\sim 931 \text{ cm}^{-1}$ of the BrBz- h_5 spectrum, and be in FR here too with the M_8 vibration. This then would give the M_{15} fundamental a value of $\sim 825 \text{ cm}^{-1}$, which is in reasonable agreement with the calculated value of 843 cm^{-1} . It is worth noting that the $M_{15}M_{20}$ combination band is not seen to be in FR with the M_8 in the ClBz and toluene.

The Dietz et al. study⁵⁹ saw the three main bands that make up this wavenumber range, however, the complexity of the structure in the feature at $\sim 934\text{ cm}^{-1}$, assigned as the M_8 here, was not noted in the above work. Three vibrational bands at $\sim 934\text{ cm}^{-1}$, $\sim 963\text{ cm}^{-1}$ and $\sim 1023\text{ cm}^{-1}$ were employed as intermediate levels to record REMPI-PES spectra by Walter et al.,²⁷ although their stated wavenumber for the M_8 feature seems to be incorrect. The obtained spectrum does suggest that this was indeed the intermediate state employed (see later discussion of the photoelectron spectra).

Vibrations with wavenumbers of 933, 963 and 1020 cm^{-1} which correspond to M_8 , M_9 and M_6 , respectively, were noted by both Walerstein⁵⁵ and Sreeramamurty.⁵⁶ Klimusheva et al.⁵⁸ have reported very similar values. Their study also reports a value for M_{12} , but this is in very poor agreement with the calculated value in this work and no contribution from this vibrations was seen experimentally in the current work nor any other previous studies on BrBz- h_5 .

BrBz- d_5

Previous discussions above for FBz and ClBz molecules have demonstrated that there is a significant red shift for the M_8 vibration upon deuteration, with smaller red shifts for the M_9 and M_6 vibrations. M_9 and M_6 modes therefore were assigned with relative ease to the bands seen at 921.1 cm^{-1} (M_9^d) and at 996.6 cm^{-1} (M_6^d). As explained previously, the identification of the M_6^d and M_8^d vibrations from the calculations here is not as straightforward as one would have liked for the BrBz- d_5 molecule, but luckily their wavenumbers and isotopic shifts are different enough for

the assignment to be achieved successfully; as mentioned before, the M_6 and M_8 motions are very similar, with the main difference being the greater motion of the substituent in the M_6 vibration. The calculated wavenumbers and comparison with the FBz and ClBz spectra allowed the bands at 779.1 cm^{-1} to be assigned to the M_8^d transition.

A feature at 796.1 cm^{-1} can be assigned to the $(M_{14}^2M_{29})^d$, consistent with the appearance of such a band in the BrBz- h_5 spectrum. There are then two features to the red of the M_9^d band at 895.1 cm^{-1} and 906.6 cm^{-1} , the first is an excellent match for the expected position of the $(M_{10}M_{11})^d$ transition, and this feature red shifts by $\sim 1.5\text{ cm}^{-1}$ for $^{81}\text{BrBz-}d_5$ (the same isotopic shift was seen for the BrBz- h_5 samples). The second band is then $(M_{10}M_{14}^2)^d$ and the corresponding vibration may be in FR with M_9^d . The band to the red of M_6^d at 977.1 cm^{-1} is in the correct position to be $(M_8M_{20}^2)^d$ and the two vibrations could also form a FR but further work, such as use of the ZEKE technique, would have to be performed in order for this observation to be confirmed.

3. High wavenumber range ($1050 - 3050\text{ cm}^{-1}$)

Higher in wavenumber, more and more features arise and the number of potential candidates for such features also increases. There is the possibility too of complications arising from anharmonic shifts and FRs; for these reasons a detailed discussion of the individual band assignments of this higher region is not presented here, but certain points are brought to attention. The most intense progressions of vibrational bands seen below 1500 cm^{-1} will be present in this wavenumber range but now

involving overtones and combinations with each other, particularly for example with the M_8 and M_9 pair of features in the BrBz- h_5 molecule. Once these were identified, much of the main structure of the high-wavenumber regions was assigned. Selected assignments of intense features in this region are labelled in the full range REMPI spectrum in Figure 3.14, and are summarized in Tables 3.14 and 3.15. Dietz et al.⁵⁹ have identified some high-wavenumber ($< 1580 \text{ cm}^{-1}$) features in their work and their assignments largely (but not completely) match those here, when the nomenclature change is accounted for (their work used Wilson labels). The M_8^2 , M_8M_9 and M_9^2 features occur close together which is not surprising as the fundamental bands were in close proximity to one another in the BrBz- h_5 spectrum, such features were also present in the FBz and ClBz spectra at high wavenumber. The M_6M_8 and M_6M_9 combination bands are another set of features present to higher wavenumber therefore combination bands of these transitions with other vibrations will also appear close together, and such features are indicated in Figure 3.14. With regard to previous work, it is noted that Prakash and Singh⁵⁷ assigned a good number of the bands up to 4382 cm^{-1} and, although there are shifts of a few cm^{-1} from the present values, many assignments are consistent with those here. It is worth pointing out that the feature at 3082 cm^{-1} is assigned to a b_2 mode here, M_{22} , whereas at first it was hypothesised by Prakash and Singh that this could be due to a totally-symmetric fundamental vibration of 2564 cm^{-1} that was in combination with M_{29} ; such spacing was also identified by Walterstein,⁵⁵

however, no obvious match for that is found from calculations in this work.

Klimusheva et al.⁵⁸ reported values for M_7 , M_{23} , M_{24} , M_{25} and M_{27} that are in moderately good agreement with calculated values here, but contributions from these vibrations were not seen in the present work, nor have they been reported by others, see Table 3.13.

The M_8^d fundamental vibration shifts in the BrBz- d_5 spectrum by a large amount and appears with much less intensity, therefore not many combinations with this fundamental are easily identifiable to higher wavenumber. The M_9^d mode, however, is of similar intensity in the BrBz- d_5 spectrum as it was for BrBz- h_5 , with very little shifting occurring, making it much easier to pick out the corresponding combinations involving M_9^d , and these are labelled in the inverted bottom trace of Figure 3.14.

4. Cation

Just as with FBz and ClBz, the BrBz cation has not been studied experimentally here but there are a number of groups who did carry out such studies and their work is considered here as sometimes the vibrations in the ground state cation, D_0^+ , have been used in assigning the excited neutral state spectra. The Duschinsky matrix for the BrBz- h_5 isotopologue showing the relationship between the S_0 and D_0^+ state vibrations is presented in Figure 3.19a. The largely diagonal matrix depicts the vibrational motion in the cation ground state being largely the same as in the neutral ground state, although some vibrations will deviate slightly in motion. However, a vibration in the cation can be correlated

with one in the neutral ground state with confidence. Figure 3.19b below shows a generalized Duschinsky matrix between the vibrational modes of the S_1 and the D_0^+ states for BrBz- h_5 where a strong diagonal nature is present once again, correlating vibrational motion in the cation to that of the S_1 state. Generalized Duschinsky matrices for the BrBz- d_5 sample (not shown here) present a similar relationship as for the BrBz- h_5 molecule between S_0 and D_0^+ state vibrations and for the S_1 and D_0^+ states. Based on this and previous work on FBz and ClBz species, it is expected that for most cases the $\Delta v = 0$ propensity rule works well for the $D_0^+ \leftarrow S_1$ ionisation, and so the selected intermediate vibrational level, for example in a REMPI-PES experiment, does correspond to that of the most intense cation band, allowing such experiments to gain more insight into the S_1 state vibrational band assignments.

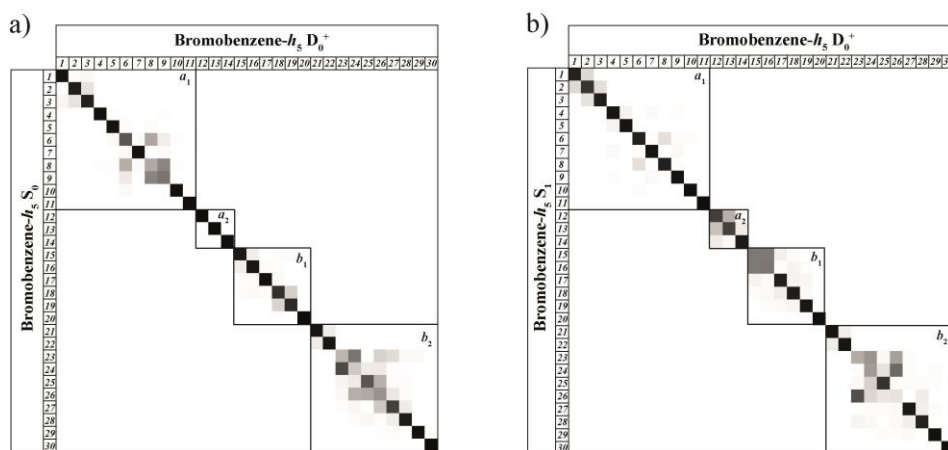


Figure 3.19. Generalized Duschinsky matrices between the vibrational modes of: (a) the S_0 and D_0^+ states for BrBz- h_5 and (b) the S_1 and the D_0^+ states for BrBz- h_5 . Shadings indicate the normalized coefficient values, with black = 1.00 while white = 0.00, with the level of the grey shading indicating intermediate values.

The vibrational wavenumbers of $\text{BrBz-}h_5^+$ and $\text{BrBz-}d_5^+$ were calculated in this project and are presented in Table 3.16 along with available experimental results. As mentioned in the introduction there are no previous experimental results on the $\text{BrBz-}d_5^+$ sample and so the calculated wavenumber frequencies presented in Table 3.16 are for completeness.

Assignments given in the work of Walter et al.³⁸ are not consistent with the ones in the Dietz et al.⁵⁹ study, nor do they match most of the assignments given to the vibrational bands in this chapter. However, the observed structure in their REMPI-PES spectra makes assignments more clear. Firstly it was noted that exciting via the origin Walter et al. observed a progression of bands with spacings of 320 cm^{-1} , which matched the calculated value of 323 cm^{-1} from this work, assigned to M_{11}^+ , extremely well. Walter et al. assigned this as Wilson mode ν_{6a} ; but M_{11} is quite mixed in the monosubstituted benzenes, and ν_{6a} is essentially M_{10} for the heavier species. When excitation was performed via the M_{29} level, a series of bands with spacings of 540 cm^{-1} were observed which matched extremely well the calculated value of 534 cm^{-1} for M_{29}^+ in this work. Walter et al.³⁸ have also observed a spacing of 950 cm^{-1} , which is in best agreement with the value for M_8^+ in the present work. When excitation was done via the M_8 intermediate level, progressions of 950 cm^{-1} and 320 cm^{-1} were seen which match the spacings mentioned above. Another observed spacing of 1530 cm^{-1} best matches here the calculated M_4^+ value. Excitation via the M_9 mode (erroneously given as an overtone in Table 1 of ref. 38 but as a fundamental, ν_{18a} , in their text) gives

progressions involving spacings of 320 and 980 cm^{-1} , where the M_9^+ is assigned to the latter value from calculated values seen in Table 3.16 on next page.

As one now considers the region towards higher energy, there does seem to be some confusion in the experimental assignments when excitation occurs via intermediate levels in that energy range. Walter et al.³⁸ cite an intermediate level of $\sim 1080 \text{ cm}^{-1}$ above the S_1 origin, where Dietz et al.⁵⁹ locate the same level at 1019 cm^{-1} . Owing to the lack of structure in the $\Delta v = 0$ region in their REMPI-PES spectrum, Walter et al. assigns this level as Wilson mode ν_{9b} (but to add to confusion they maintain a ν_{9a} label in other places in the paper). The spacings seen by them (134 meV) of 1080 cm^{-1} (but mistyped as 1180 cm^{-1} therein) are in best agreement with those for the M_6^+ vibration and therefore confirm an assignment of the intermediate level to M_6 , and not to a b_2 symmetry vibration.

Kwon et al.,⁴⁸ in the same study that included FBz and ClBz species, have also recorded one-photon, mass-analyzed threshold ionisation (MATI) spectra of the $^{79/81}\text{BrBz-}h_5$ molecules, noting that the largest shifts between the ^{79}Br and ^{81}Br isotopologues are equal to only a few cm^{-1} , with their assignments being included in Table 3.16 on next page.

Table 3.16. Assignments, calculated and experimental vibrational wavenumbers (cm^{-1}) for the ground state cation, D_0^+ , of $^{79}\text{BrBz-}h_5$ and $^{79}\text{BrBz-}d_5$.

⁷⁹ BrBz- <i>h</i> ₅ ⁺					⁷⁹ BrBz- <i>d</i> ₅ ⁺	
Mode Label	Calculated	Experimental			Mode Label	Calculated
	This work ^a	Walter et al. ^b	Kwon et al. ^c	PES ^d		This work ^a
<i>a</i> ₁						
<i>M</i> ₁ ⁺	3121				<i>M</i> ₁ ^{<i>d</i>+}	2316
<i>M</i> ₂ ⁺	3111				<i>M</i> ₂ ^{<i>d</i>+}	2299
<i>M</i> ₃ ⁺	3098		3083 ^e		<i>M</i> ₃ ^{<i>d</i>+}	2289
<i>M</i> ₄ ⁺	1573	1530	1577		<i>M</i> ₄ ^{<i>d</i>+}	1532
<i>M</i> ₅ ⁺	1425				<i>M</i> ₅ ^{<i>d</i>+}	1251
<i>M</i> ₆ ⁺	1040	1080 ^f	1073		<i>M</i> ₆ ^{<i>d</i>+}	1016
<i>M</i> ₇ ⁺	1181		1193		<i>M</i> ₇ ^{<i>d</i>+}	854
<i>M</i> ₈ ⁺	966	950			<i>M</i> ₈ ^{<i>d</i>+}	801
<i>M</i> ₉ ⁺	981	980	1008	1020 (1016)	<i>M</i> ₉ ^{<i>d</i>+}	933
<i>M</i> ₁₀ ⁺	669		678		<i>M</i> ₁₀ ^{<i>d</i>+}	639
<i>M</i> ₁₁ ⁺	323	320	331	330 (330)	<i>M</i> ₁₁ ^{<i>d</i>+}	315
<i>a</i> ₂						
<i>M</i> ₁₂ ⁺	988				<i>M</i> ₁₂ ^{<i>d</i>+}	802
<i>M</i> ₁₃ ⁺	792				<i>M</i> ₁₃ ^{<i>d</i>+}	616
<i>M</i> ₁₄ ⁺	346		396		<i>M</i> ₁₄ ^{<i>d</i>+}	301
<i>b</i> ₁						
<i>M</i> ₁₅ ⁺	998				<i>M</i> ₁₅ ^{<i>d</i>+}	840
<i>M</i> ₁₆ ⁺	944				<i>M</i> ₁₆ ^{<i>d</i>+}	765
<i>M</i> ₁₇ ⁺	758		791		<i>M</i> ₁₇ ^{<i>d</i>+}	637
<i>M</i> ₁₈ ⁺	587				<i>M</i> ₁₈ ^{<i>d</i>+}	328
<i>M</i> ₁₉ ⁺	378				<i>M</i> ₁₉ ^{<i>d</i>+}	472
<i>M</i> ₂₀ ⁺	131		126		<i>M</i> ₂₀ ^{<i>d</i>+}	122
<i>b</i> ₂						
<i>M</i> ₂₁ ⁺	3119				<i>M</i> ₂₁ ^{<i>d</i>+}	2312
<i>M</i> ₂₂ ⁺	3108				<i>M</i> ₂₂ ^{<i>d</i>+}	2294
<i>M</i> ₂₃ ⁺	1479		1523 ^g		<i>M</i> ₂₃ ^{<i>d</i>+}	1244
<i>M</i> ₂₄ ⁺	1341				<i>M</i> ₂₄ ^{<i>d</i>+}	1381
<i>M</i> ₂₅ ⁺	1254				<i>M</i> ₂₅ ^{<i>d</i>+}	1019
<i>M</i> ₂₆ ⁺	1380		1307		<i>M</i> ₂₆ ^{<i>d</i>+}	1313
<i>M</i> ₂₇ ⁺	1129				<i>M</i> ₂₇ ^{<i>d</i>+}	827
<i>M</i> ₂₈ ⁺	1074				<i>M</i> ₂₈ ^{<i>d</i>+}	823
<i>M</i> ₂₉ ⁺	534	540	593		<i>M</i> ₂₉ ^{<i>d</i>+}	517
<i>M</i> ₃₀ ⁺	246		257		<i>M</i> ₃₀ ^{<i>d</i>+}	232

a. UB3LYP/aug-cc-pVTZ, scaled by 0.97

b. Ref. 38

c. Ref. 48

d. Ref. 61 and, in parenthesis, ref. 45

e. Reassigned in the present work.

f. Reassigned vibrational band.

g. Assigned to a fundamental in ref.48, but value is far from any calculated b_2 symmetry vibration here.

As seen in Table 3.16, good agreement exists between many of Kwon et al.'s⁴⁸ experimentally determined vibrational energies and calculated values in this work, but a few anomalies do exist. The M_{29}^{+} mode value of 593 cm^{-1} seems far from the REMPI-PES value and the value calculated here, with the M_{23}^{+} value of 1523 cm^{-1} also being far from the calculated value in this work. The band at 3083 cm^{-1} agrees best with the M_3^{+} calculated value and therefore has been reassigned here and in ref. 4. The M_9^{+} mode being assigned to the band at 1008 cm^{-1} is questionable because it does not match the REMPI-PES value well, and has a larger discrepancy with the calculated value here compared to other vibrations. However the resolution in the MATI study is much better, and the M_9^{+} energy from Kwon et al.⁴⁸ is also closer to the value from the conventional PES studies by Potts et al.⁶¹ and Holland et al.⁴⁵ and with that in mind it is taken to be more reliable than Walter et al.'s³⁸ value. Both of the conventional PES studies mentioned above give values for M_{11}^{+} that match well with other experimental and the present calculated values.

5. Summary

The (1+1) REMPI spectra of the BrBz- h_5 and BrBz- d_5 molecules presented here have been assigned successfully in detail up to 1050 cm^{-1} , along with the major features thereafter. The assignments for BrBz- d_5 are presented here for the first time.

3.5 Concluding remarks and future work

In this chapter, the $S_1 \leftarrow S_0$ electronic spectra are reported of both halobenzene- h_5 and halobenzene- d_5 isotopologues (halo = F, Cl and Br). These are assigned in detail up until $\sim 1500\text{ cm}^{-1}$, along with the major features thereafter. Assigning the halobenzene- d_5 spectra was relatively straightforward since they were expected to have largely the same vibrational activity as was observed in the corresponding halobenzene- h_5 spectrum since they have the same electronic structure and geometry changes upon excitation, but with some vibrations coming in and out of resonance as a result of the isotopic shifts. This led to the differences between the two spectra which are sometimes significant, for example the M_8 vibration. Considering the fact that there is only a simple mass change between the two isotopologues, some very interesting aspects of the spectra were uncovered and discussed throughout this chapter. This led to different FR being seen, although only some of those noted in the perhydrogenated isotopologue persist in the perdeuterated species or vice versa.

It was more challenging to obtain a good-quality REMPI spectrum of BrBz than ClBz and FBz given the short lifetime that precludes the possibility of obtaining an LIF spectrum. However, obtaining such a spectrum of IBz appears not to be possible as discussed in Section 3.3.4, owing to rapid internal conversion leading to predissociation.

The M_i nomenclature was introduced in 2011 by Gardner and Wright¹ to alleviate a large number of discrepancies that arise from the use of Wilson, Varsanyi and Mulliken numbering in describing vibrational motions. Since the $\pi^* \leftarrow \pi$ transition is localized on the phenyl ring, the vibrational activity should be similar in all monosubstituted benzene molecules; in order to be able to discern this, similar vibrational modes should be given the same label, something that the M_i nomenclature does successfully. Here, application of the M_i nomenclature was implemented in the assignment of the FBz, ClBz and BrBz (1+1) REMPI spectra as well as the spectra of their fully deuterated isotopologues, with the aim to investigate further if indeed one can have a very consistent vibrational band assignment across different monosubstituted benzene species. Figure 3.20 on next page shows that the assignments given using the M_i nomenclature in fact do give the same label when the same vibrational motion is being described.

Figure 3.20 combines spectra recorded in this project and the work on the toluene molecule by previous members of the group,⁷⁶ with the first 700 cm^{-1} being assigned and compared. The same vibrational motions have the same M_i label for the monosubstituted benzene molecules regardless of the energetic ordering of vibrations or changes in molecular symmetry, allowing straightforward comparison between species.

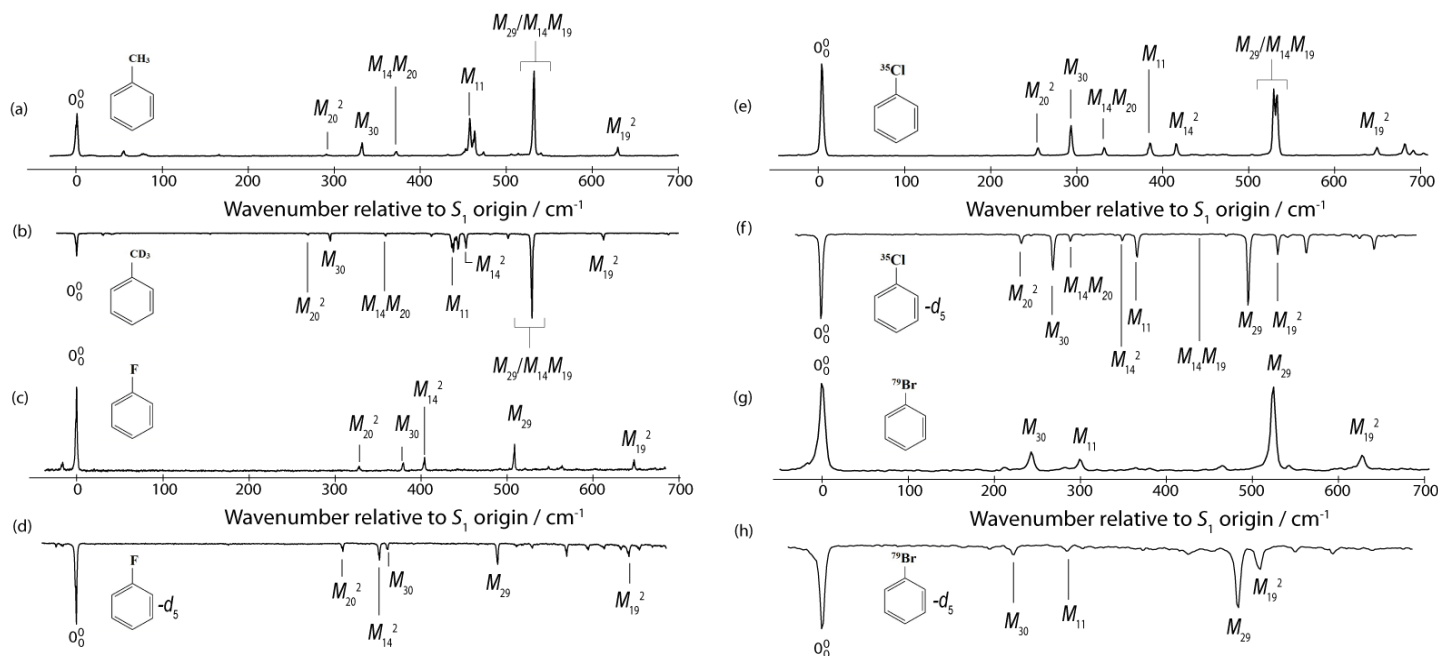


Figure 3.20. Expanded views of the low wavenumber regions (0–700 cm^{-1}) of the $S_1 \leftarrow S_0$ (1+1) REMPI spectra of a and b) Toluene (top trace, upright) and toluene- d_3 (bottom trace, inverted), spectra taken from ref.76. c and d) FBz- h_5 (top trace, upright) and FBz- d_5 (bottom trace, inverted). e and f) ClBz- h_5 (top trace, upright) and ClBz- d_5 (bottom trace, inverted). g and f) BrBz- h_5 (top trace, upright) and BrBz- d_5 (bottom trace, inverted). Assignments a and b are taken from ref. 76, assignments of others are discussed in the text and summarized in Tables 3.4, 3.9, 3.10, 3.14 and 3.15.

There are several cases where it is difficult to be unambiguous in the assignments of the recorded spectra, especially in the higher wavenumber range owing to the rapid build-up of the number of overtone and combination bands. This study also suggests a number of future possible areas of interest to unpick various FRs. In these cases, firmer assignments will have to await ZEKE or time-resolved studies for confirmation as was previously already undertaken by this group for the *para*-fluorotoluene⁷⁷ and toluene molecules.⁷⁶ It is also intended to perform standard and two-dimensional dispersed fluorescence experiments on some of the species studied in this project and the results of these will be complementary to the ZEKE studies.

In this chapter it was demonstrated how the M_i nomenclature proposed by Gardner and Wright¹ is applicable to the study of the vibrations of monosubstituted benzene species. What happens when disubstituted species are concerned? Can one use the three traditional and well-known nomenclatures in describing the vibrational motions, and compare with ease across different molecules? If not, could the M_i nomenclature then be applied or would there be a need for a new scheme in describing the vibrations of *para*-disubstituted benzene species? These are the questions that will be answered in the next chapter.

3.6 References

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4. Consistent assignment of the vibrations of symmetric and asymmetric *para*-disubstituted benzene molecules.

In this chapter, the consistent assignment nomenclature, D_i , for the vibrations of *para*-disubstituted benzene derivatives is presented for the first time. The nomenclature is based on the vibrational modes of the *para*-difluorobenzene (*p*DFB) molecule which are labelled employing Mulliken labelling under C_{2v} point group symmetry making the D_i nomenclature applicable to both symmetrically- and asymmetrically-substituted benzene species. The description of the phenyl-ring-localised vibrational modes of the ground states of the *para*-disubstituted benzene molecules is provided. In this work symmetric and asymmetric *para*-dihalobenzene molecules are considered as well as *para*-xylene (*p*-xylene) and *para*-fluorotoluene (*p*FT). A more general form of the presented work can be found in ref. 1, which also includes additional *para*-disubstituted benzene molecules but these are not included here since work on those molecules was carried out by different members of the group.

4.1 Introduction

The importance of having a consistent vibrational labelling scheme for substituted benzene molecules was demonstrated in Chapter 3 where it was shown how a vibrational motion in one molecule and its labelling

needs to be similar in a different molecule if one wishes to compare across different benzene derivatives.

In the same chapter it was demonstrated how extant work on substituted benzene species employs one of three well-known vibrational nomenclatures: Wilson,² Varsányi³ or Mulliken,⁴ and how numerous inconsistencies occur when one of these labelling schemes is used as each scheme has flaws associated with it. As a consequence, the same vibrational motion in different molecules is being described by different labels, or even a different label is applied to the same vibrational motion in the same molecule by different groups, see Sections 1.3 and 3.4 of Chapters 1 and 3 respectively. These aspects have made it very time consuming and difficult to compare vibrational activity across different substituted benzene derivatives but such challenges were largely overcome with the introduction of the M_i nomenclature for monosubstituted benzene molecules by Gardner and Wright.⁵ In the Gardner and Wright scheme fluorobenzene (FBz) is a prototypical molecule, whose vibrational motions serve as a model upon which the M_i nomenclature is based. FBz normal modes impose Mulliken ordering on all of the monosubstituted benzene species, so the M_i modes are ordered in symmetry blocks and decreasing wavenumber value. For any substituent that has more than one atom and therefore whose vibrations would contribute to the ordered list of vibrations, for example the CH₃ group in the toluene molecule, the substituent-localised vibrations are separated from the list, ensuring that only the thirty phenyl-ring-localised normal contribute to the M_i vibrations. The application of the M_i

nomenclature to monohalobenzene species and their deuterated isotopologues was studied in refs. 6, 7 and 8 as well as being presented in detail in Chapter 3. It was shown in the aforementioned works that the same vibrational motions in the monosubstituted benzene molecules are given the same label, making it much more straightforward to compare across different monosubstituted benzene species, easing the task of studying for example intramolecular vibrational energy redistribution (IVR) rates across different monosubstituted benzene molecules.

Firstly it was investigated here if Wilson benzene modes² can successfully describe vibrational motion in *para*-disubstituted benzene derivatives. By comparing the vibrational modes of benzene to those of *para*-difluorobenzene (*p*DfB) via mass trends and the Duschinsky matrix approach one is able to see how mixed the vibrations of *p*DfB are in terms of those of benzene. In addition, comparing how the FBz vibrational modes evolve into those of *p*DfB demonstrates here too that M_i nomenclature for monosubstituted benzene molecules is not unambiguously applicable to other substituted benzene molecules, for example *para*-disubstituted species. This leads to the new D_i nomenclature being presented here and ref. 1 for the first time. *p*DfB ground state (S_0) vibrational modes are described and the new nomenclature is built upon them. S_0 vibrational normal modes for a range of *para*-disubstituted benzenes are then studied, for both symmetric ($p\text{-C}_6\text{H}_4\text{X}_2$) and asymmetric ($p\text{-C}_6\text{H}_4\text{XY}$) molecules, where X and Y are halogen groups or a CH_3 group. In Section 4.4 of the Results previous

experimental S_0 state assignments are discussed in detail and compared to the calculated harmonic frequencies obtained here.

4.2 Motivation and previous work

When disubstituted benzene species are considered, two substituents can be arranged relative to one another in three positions on the benzene ring: *para*, *ortho* and *meta*. In this chapter only *para*-disubstituted benzene molecules are investigated. Mono- and di- substituted derivatives of benzene molecules have gained a lot of attention as each system has one or more excited electronic states that are suitably low-lying in energy to make them accessible with UV laser sources. The commercial and scientific importance of monosubstituted benzene molecules, especially monohalosubstituted benzenes, was addressed in Chapter 3 and *para*-disubstituted benzenes are no different.

Para-disubstituted benzene molecules play an important role in biological systems, for example tyrosine being an essential components for the production of several important neurotransmitters.^{9,10} A benzene ring with two substituents also play a vital role in pharmaceutical medicinal synthesis, for example chloramphenicol antibiotic.¹¹ More specifically *para*-dihalobenzenes are widely implemented in the pesticide, disinfectant and deodorant industries.^{12,13} Spectroscopically, the *p*DFB and *p*FT molecules remain among the most studied substituted benzene derivatives to date. The *p*-xylene molecule, although much less studied spectroscopically compared to *p*DFB and *p*FT has an arguably

wider application on the industrial scale with its use being implemented in fibre production, specifically polyester manufacturing.¹⁴

Even though benzene derivative molecules have been studied extensively for the past three decades, they remain of great interest because a lot more is yet to be understood and explained about such systems. In recent years, the *p*FT and *p*DFB molecules have been the subjects mainly of IVR studies, where for *p*FT the focus has been primarily concentrated on the methyl group. The internal rotation of the methyl group is hypothesised to be responsible for an increase in IVR rate in *p*FT compared to *p*DFB. The measured rate constants of the IVR for those two molecules differ by approximately two orders of magnitude for comparable vibrational levels.¹⁵ The increased rate of IVR is potentially rationalised by a large number of additional states that are able to couple in *p*FT through the exchange of energy between the ring vibration and methyl group torsion.¹⁶ The two molecules have similar ring structures, and so if internal rotation in *p*FT was ignored then one would expect similar IVR dynamics in the two species. Any differences can be attributed to the methyl group in *p*FT, bringing in extra degrees of freedom. What is interesting though is that moving the methyl group from the *para* to the *meta* position on the benzene ring will further accelerate the rate of IVR.¹⁷ Such results are surprising as *p*FT and *meta*-fluorotoluene (*m*FT) have comparable density of states. The increase in IVR rate can be rationalised here by the lower symmetry in *m*FT (C_s point group) compared to *p*FT symmetry (C_{2v} point group) where *m*FT has a change in the shape and height of the barrier to internal

rotation along with displacement of the axis of internal rotations relative to the molecular axis of highest symmetry. This clearly shows that substitutions of functional groups in *para*-disubstituted benzene molecules is a powerful tool in studying IVR differences and dynamics across a range of benzene derivatives and at the heart of understanding such processes is the knowledge of the ring-localised vibrations and their coupling to different levels. The need for a consistent vibrational nomenclature across different *para*-disubstituted benzene species for ring-localised vibrations is essential as when one vibrational level is labelled, in order to avoid confusion or comparison with the wrong level altogether, the same label has to correspond to the same vibrational motion in other *para*-disubstituted benzene species. The newly proposed D_i nomenclature resolves a large number of labelling inconsistencies seen with the Wilson,² Varsányi³ and Mulliken⁴ schemes.

4.3 Computational Details

For each *para*-disubstituted benzene molecule harmonic vibrational frequencies were obtained for the S_0 ($\tilde{X}^1A_1$) electronic state using B3LYP/aug-cc-pVTZ calculations. For bromine and iodine, the fully relativistic effective core potentials, ECP10MDF and ECP28MDF respectively, were used with corresponding aug-cc-pVTZ-PP valence basis sets. All of the calculated harmonic vibrational wavenumbers were scaled by the usual factor of 0.97 as an approximate method of obtaining anharmonic wavenumber values. All of the calculations were performed via the GAUSSIAN 09 software package.¹⁸

All of the calculated frequencies were harmonic but as was shown in Chapter 3 for the monohalobenzene species and in ref. 6, 7, and 8, calculated scaled harmonic frequencies, except for the M_{14} and M_{20} low wavenumber vibrations, match very well with previous experimental results and with the experimental results obtained via (1+1) REMPI spectra recorded in that work. Also, in the work on toluene by previous members of the Wright group,^{19,20} it was found that scaled harmonic values were at least as reliable as the explicitly calculated anharmonic values, with scaled harmonic wavenumbers having an additional advantage of being much less computationally expensive to calculate.

As in the previous chapter, the Duschinsky matrix approach²¹ is used here too in order to correlate S_0 vibrational modes of symmetric and asymmetric *para*-disubstituted halobenzene (halo = F, Cl, Br and I), *p*FT and *p*-xylene molecules with the S_0 vibrational modes of the *p*DFB molecule. A detailed description of the Duschinsky procedure is given in Section 3.2 of Chapter 3, and here an analogous method was applied in the FC-LabII program.²² The information on mixing of vibrational levels obtained from a matrix is interpreted as before in Chapter 3, where diagonal elements close to 1 (black square = 1.00) indicate that the vibrational modes in two states have very similar vibrational motions. White squares indicate a contribution of zero from one vibrational mode to another. The element is coloured grey when mixing of vibrational motions is present across two states, and in this work the depth of shading relates to the degree of mixing. In this work mixing criteria were taken as follows: coefficient values > 0.2 are termed major contributions,

with dominant contributions having mixing coefficients > 0.5 . Minor contributions have values between 0.05 and 0.2. If there is more than one contribution of each type, these are presented in order of magnitude. Vibrations with a mixing coefficient < 0.05 were ignored.

In this work vibrational wavenumbers calculated for the actual molecule are referred to as “explicit” and are used throughout unless stated otherwise. However vibrations have also been calculated in this project that used one molecule’s force field, where the mass of one or two atoms has been artificially changed to match those of substituents (atomic or otherwise), those are referred to as “iso” here and in ref. 1.

4.4 Normal vibrational mode mass trends from benzene to *p*DFB

Vibrational modes of benzene molecule were found not to have a one to one correspondence to the FBz vibrational modes, as demonstrated in Figure 4 of ref. 23 and Figure 4a of ref. 5. Based on that one would not expect the normal modes of benzene to have the same vibrational motion as those of *para*-disubstituted benzene molecules, for example in *p*DFB, as upon adding substitutions to the benzene molecule the point group symmetry is lowered and the need arises to compensate for the motion of two fluorine atoms instead of hydrogen. Figure 4.1 on the next page shows how the benzene Wilson normal modes are related to those of *p*DFB. In the Duschinsky matrix presented, which concerns itself with ground state of each molecule, only five of those modes have a 1 : 1 correspondence, meaning that only those particular motions have stayed the same across the two molecules and all of the remaining vibrational

modes have significant mixing. The majority of the *p*DFB vibrational modes cannot be uniquely described by a benzene Wilson mode. From Figure 4.1 it is concluded that Wilson labels are not appropriate in describing vibrational motions of *para*-disubstituted benzene species, except for the a_2 symmetry vibrational modes.

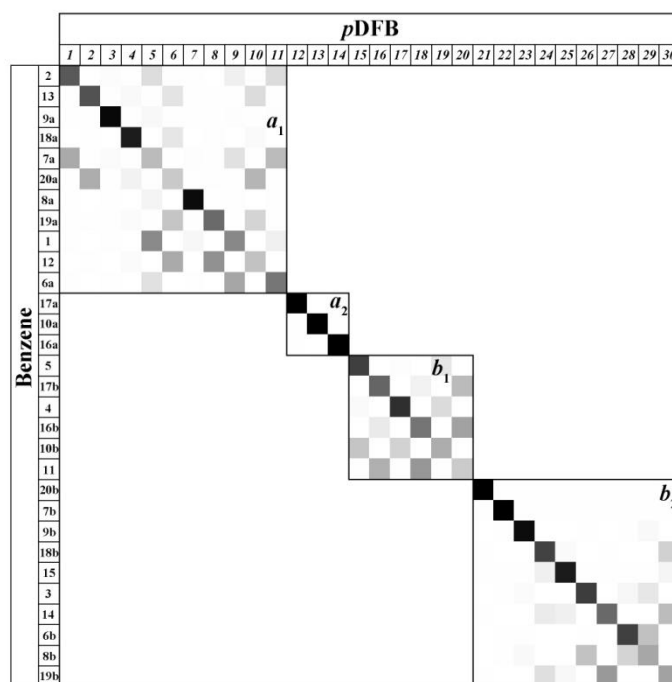


Figure 4.1. Generalized Duschinsky matrix showing vibrational modes of *p*DFB being expressed in terms of the benzene modes for the ground state of each molecule. Significant mixing of the benzene vibrational modes occurs. Black shading indicates a normalized coefficient value of 1.00, while white indicates a value of 0.00, with grey shading indicating intermediate values, see section 4.2 for further explanation.

In order to understand the mixings observed in greater detail, changes to the vibrational wavenumbers in the normal modes of benzene were explored as the masses of *ipso*- and *para*-positioned hydrogen atoms were varied from 1 to 19 amu simultaneously whilst the force field stayed the same, see Figure 4.2. In the figure the vibrations have been

separated into C_{2v} symmetry blocks where the same symbols are used to connect similar vibrational modes between benzene and *p*DFB. On the left-hand side of the diagram the vibrational modes are those of the benzene molecule where each mode is labelled with the appropriate Wilson label, and on the right-hand side of the diagram are the vibrational modes of the *p*DFB molecule which have been labelled with a D_i label, with the D representing “disubstituted” and i being determined by the Mulliken ordering of the vibrations of *p*DFB in the C_{2v} point group.

Straight away one can spot how some modes almost remain unchanged as the mass is increased for the two *para*-positioned hydrogen atoms, for example vibrations of a_2 symmetry, whereas other vibrations are very much mass dependent. Some curves in the a_1 , b_1 and b_2 symmetry blocks look like they undergo “avoided crossings”. In this context the explanation for an “avoided crossing” is that the vibrations that change form when going from benzene to *p*DFB become close to one another with their motions becoming mixed, and at the region of a crossing the normal modes look like superpositions of the motions of the two separated vibrations. After the avoided crossing the vibrations gradually exchange forms, yielding two vibrations of the original atomic motions but now switched in energy. This is analogous to the behaviour of avoided crossings for potential energy curves of diatomic molecules. This behaviour of the vibrational modes was first noted and described in ref. 5 for the M_i nomenclature.

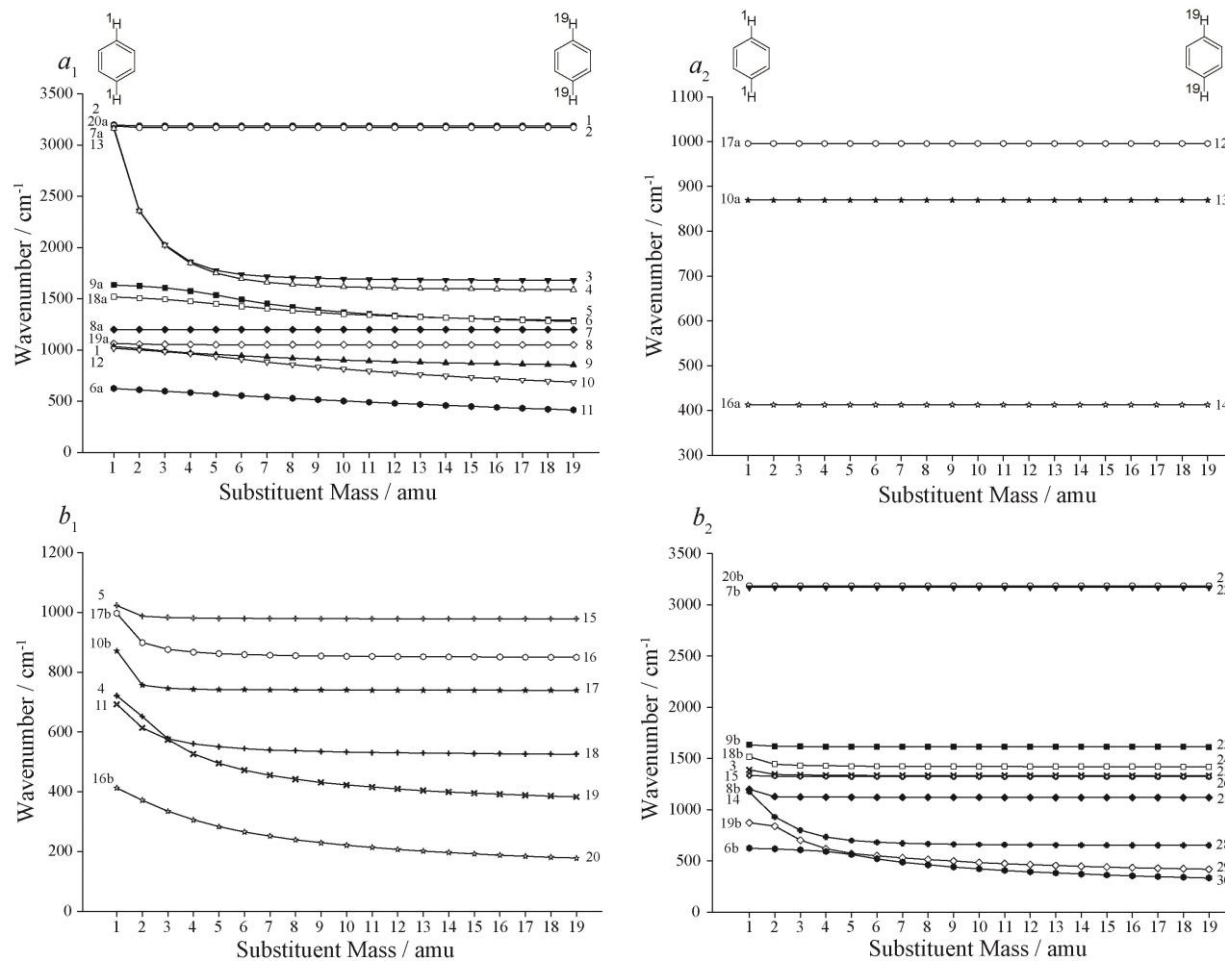


Figure 4.2. Mass-correlated vibrational wavenumbers showing how the vibrations of benzene molecule evolve into those of *p*DFB molecule. The force field of benzene is employed and the masses of the *ipso* and *para* hydrogen atoms are artificially varied from 1 to 19 amu. The vibrations have been grouped into their C_{2v} symmetry groups: a_1 , a_2 , b_1 and b_2 . The Wilson labels have been included on the left, while on the right hand side the numbers refer to the D_i modes.

Below is a more detailed description of how the *p*DFB D_i vibrational modes compare to the benzene Wilson vibrational modes as illustrated in Figure 4.2.

a_1 vibrations

From Figure 4.2 it can be seen that some a_1 vibrations change in wavenumber quite dramatically as the mass of the *ipso* and *para* substituents is increased whereas some other vibrational modes remain almost unchanged. The first two vibrational modes in the a_1 symmetry block, D_1 and D_2 , are the highest-wavenumber vibrational modes in the *p*DFB molecule. These two modes in *p*DFB have dominant contributions from Wilson modes ν_2 and ν_{13} , and major contributions from ν_{7a} and ν_{20a} modes. In the benzene molecule there are four high-wavenumber vibrations but as the mass of the *ipso*- and *para*-positioned hydrogen atoms is increased a sharp fall in wavenumber is observed from benzene to *p*DFB for the D_3 and D_4 modes. D_3 and D_4 come from ν_{7a} and ν_{13} Wilson modes, with Wilson modes ν_{9a} and ν_{18a} also presenting dominant contributions due to mixing. The ν_{7a} and ν_{20a} modes appear again as non-dominant and minor contributions to other *p*DFB a_1 symmetry vibrations.

When one looks at the actual vibrational motion of the ν_2 , ν_{7a} , ν_{13} and ν_{20a} modes, all of these modes have H motion at the *ipso*- and *para*-positions and so one would expect that all four modes would fall in wavenumber as the mass of the *ipso*- and *para*-positioned hydrogen atoms is increased. However as seen in Figure 4.2 that is not the case as

only modes D_3 and D_4 fall in wavenumber. One of the possible explanations is that motions mix quite significantly when D_i modes are formed which results in the D_1 and D_2 modes having very little motion of the *para*-positioned hydrogen atoms. D_1 is made up from ν_2 and ν_{7a} Wilson modes which are in- and out-of-phase motions of the *para*-hydrogens and these vibrational motions cancel in forming D_1 , while the enhanced *ipso* and *para* motion of the other vibrations formed upon substitution causes a decrease in wavenumber, seen in modes D_3 and D_4 , which is due to the ν_{7a} mode mixing with other a_1 vibrations, all the way down to D_{11} . A similar explanation holds for the formation of the D_2 vibrational mode from ν_{13} and ν_{20a} . Contributions of Wilson mode ν_{20a} to the vibrations of *p*D₂FB includes modes as low in energy as D_{10} .

Modes D_5 and D_6 become quite mixed from benzene to *p*D₂FB in terms of Wilson modes, and cannot be labelled with a single Wilson label. The next two modes, D_7 and D_8 , are easily assignable as they do not mix and have essentially the same motions as the Wilson modes ν_{8a} and ν_{19a} in the benzene molecule respectively. However the same cannot be said about modes D_9 and D_{10} as these are heavily mixed in terms of Wilson modes and so can only be unambiguously identified with their D_i label. The last mode of a_1 symmetry is the D_{11} mode which has a dominant contribution from Wilson mode ν_{6a} .

a_2 vibrations

The three vibrational modes of a_2 symmetry, D_{12} , D_{13} and D_{14} in Figure 4.2 do not involve the movement of the substituted *para*-positioned

atoms which explains the small change occurring in their vibrational wavenumber from 1 to 19 amu. These three modes have very similar atomic motion to the corresponding Wilson modes in benzene (ν_{17a} , ν_{10a} and ν_{16a}). This small change in wavenumber from benzene to *p*DFB is also reflected in the Duschinsky matrix (Figure 4.1) where no mixing is present for these modes. These three modes can be accurately described with any of the three vibrational nomenclature schemes that were discussed in Chapter 3 and mentioned in the introduction here.

b_1 vibrations

b_1 vibrations in Figure 4.2 are quite straightforward to track from D_i modes back to benzene. The first two modes, D_{15} and D_{16} , in the *p*DFB molecule have dominant contributions from Wilson modes ν_5 and ν_{17b} respectively. These are in- and out-of-phase, out-of-plane motions of the *ipso* and *para* hydrogens. Also, the motion of mode ν_{10b} , which has a similar out-of-plane C-H motion as ν_5 , also contributes to these vibrations through mixing. The low-wavenumber ν_{11} vibration contributes to the D_{15} and D_{16} modes too, therefore making these two D_i modes different in motion from the original Wilson modes. The next mode D_{17} is still straightforward to track even though it becomes a mixed version of Wilson mode ν_{10b} . The next two vibrations, D_{18} and D_{19} , undergo an avoided crossing which results in wavenumber re-ordering, and the modes themselves are mixed versions of Wilson modes ν_4 and ν_{11} respectively. The last and lowest wavenumber mode of b_1 symmetry is D_{20} which has its major contribution from ν_{16b} . However Wilson mode

ν_{16b} is also a dominant contributor to D_{18} causing vibrations in the b_1 block to be highly mixed and making Wilson labels inappropriate when used to describe vibrations of the *p*DFB molecule.

b_2 vibrations

The first four vibrations of b_2 symmetry, D_{21} to D_{24} , have motions that are very close to the corresponding benzene vibrations ν_{20b} , ν_{7b} , ν_{9b} and ν_{18b} respectively, which explains why very little wavenumber deviation is observed in Figure 4.2 for most of the symmetry block. For the next two modes, D_{25} and D_{26} , the wavenumber ordering swaps but the vibrational motion of the modes can still be well described by Wilson modes ν_{15} and ν_3 . Modes D_{27} and D_{28} have dominant contributions from Wilson modes ν_{14} and ν_{6b} respectively but these are not in the same wavenumber order as in the benzene molecule. The two lowest wavenumber modes D_{29} and D_{30} are mixed in terms of Wilson modes. The D_{29} vibration mainly consists of the ν_{8b} Wilson mode, although this Wilson mode also contributes to other b_2 vibrations. The D_{30} mode largely arises from a dominant contribution from ν_{19b} .

Although wavenumber ordering changes in a number of the D_i vibrations they can still be connected to the Wilson modes, but vibrational motions will be highly mixed therefore the same Wilson label used to describe a vibrational motion in the benzene molecule cannot be applied to the *p*DFB, and therefore other *para*-disubstituted derivatives, unambiguously. However, how would the M_i nomenclature labels by Gardner and Wright⁵ for monosubstituted benzene species relate to the

D_i vibrational modes of p DFB? It is not unreasonable to suspect that vibrational motions of p DFB will differ from those of the FBz molecule because of the change in the motion that was observed when one goes from benzene to FBz5 and benzene to p DFB. If so, application of the M_i nomenclature to *para*-disubstituted benzene molecules will not be favourable or appropriate. The next section explores how vibrational M_i modes of the FBz molecule evolve into D_i modes, and to what extent mixing occurs.

4.5 Normal vibrational mode mass trends from FBz to p DFB

Figure 4.3 shows a Duschinsky matrix where p DFB ground state vibrations have been expressed in terms of those of FBz.

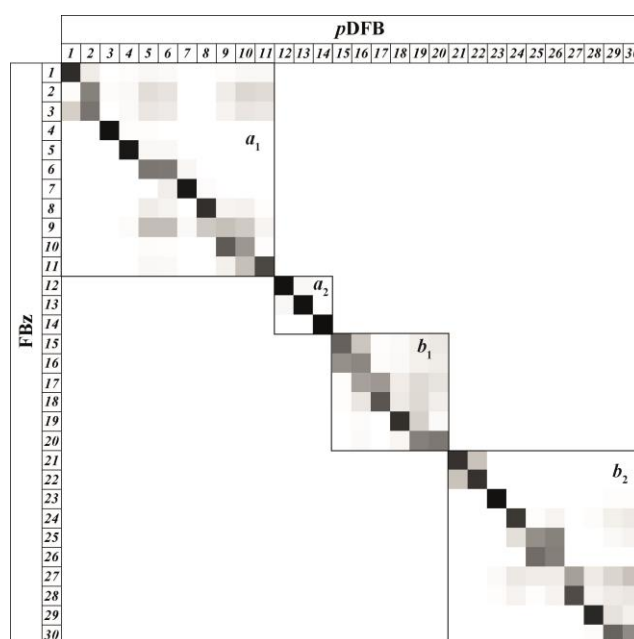


Figure 4.3. Generalized Duschinsky matrix showing how the vibrational modes of p DFB can be expressed in terms of those of FBz for the ground state. Although overall diagonalisation is observed, a lot of mixing is still present.

The matrix shows how M_i vibrational modes map onto the one of the simplest *para*-disubstituted benzene species, and although diagonalisation is present to a large degree, significant mixing between vibrational modes is evident too. Taking into account the mixings seen here it becomes questionable whether the M_i nomenclature can be applicable to species other than monosubstituted benzene derivatives.

In order to explore mixings between FBz and *p*DFB vibrational modes, the evolution of the FBz M_i modes into *p*DFB D_i modes was followed as the mass of the hydrogen in the *para* position in the FBz molecule was increased from 1 to 19 amu whilst the force field of FBz was kept constant, see Figure 4.4. In the figure the vibrations have been separated into C_{2v} symmetry groups, just as in Figure 4.2, where same symbol lines are used to connect modes in the *p*DFB molecule to the most comparable FBz vibrational mode. In Figure 4.4 on the left-hand side of the diagram vibrational modes of the benzene molecule are presented where each mode is labelled using Wilson nomenclature. These modes are then followed through to the FBz molecule where the fundamentals are here labelled with the M_i scheme. A version of this part of the figure, comparing the Wilson modes of benzene to those of FBz can be seen in Fig. 2 of ref. 5. The same behaviour and trends are observed here compared to the original figure, but larger basis set was implemented in the calculations for this project. The vibrational modes of FBz are in the middle of Figure 4.4 where their evolution into *p*DFB modes is examined. This illustrates how, despite some notable successes, the

*p*DFB D_i modes cannot be described with the M_i labels unambiguously for all of the 30 ring-localised vibrations.

a_1 vibrations

The two highest wavenumber modes for the *p*DFB molecule, D_1 and D_2 , have dominant contributions from the M_1 and M_3 vibrational modes of the FBz molecule respectively. FBz mode M_2 falls in wavenumber leading to it contributing to a number of D_i modes all the way down to D_{11} . Modes D_3 and D_4 in *p*DFB have their dominant contributions from the M_4 and M_5 vibrational modes of FBz. The next two D_i modes, D_5 and D_6 are extremely mixed in terms M_i modes; both have dominant contributions from M_6 and so these vibrations can only unambiguously be identified with their D_i labels. The D_7 mode has essentially the same vibrational motion as the M_7 mode of FBz, and likewise the D_8 mode is strongly associated with the M_8 mode. Modes D_9 and D_{10} are once again heavily mixed, just as D_5 and D_6 were. D_9 and D_{10} both have dominant contributions from the M_{10} FBz mode and so they too can only be identified accurately by their D_i label. D_{11} has a dominant contribution from the FBz M_{11} mode.

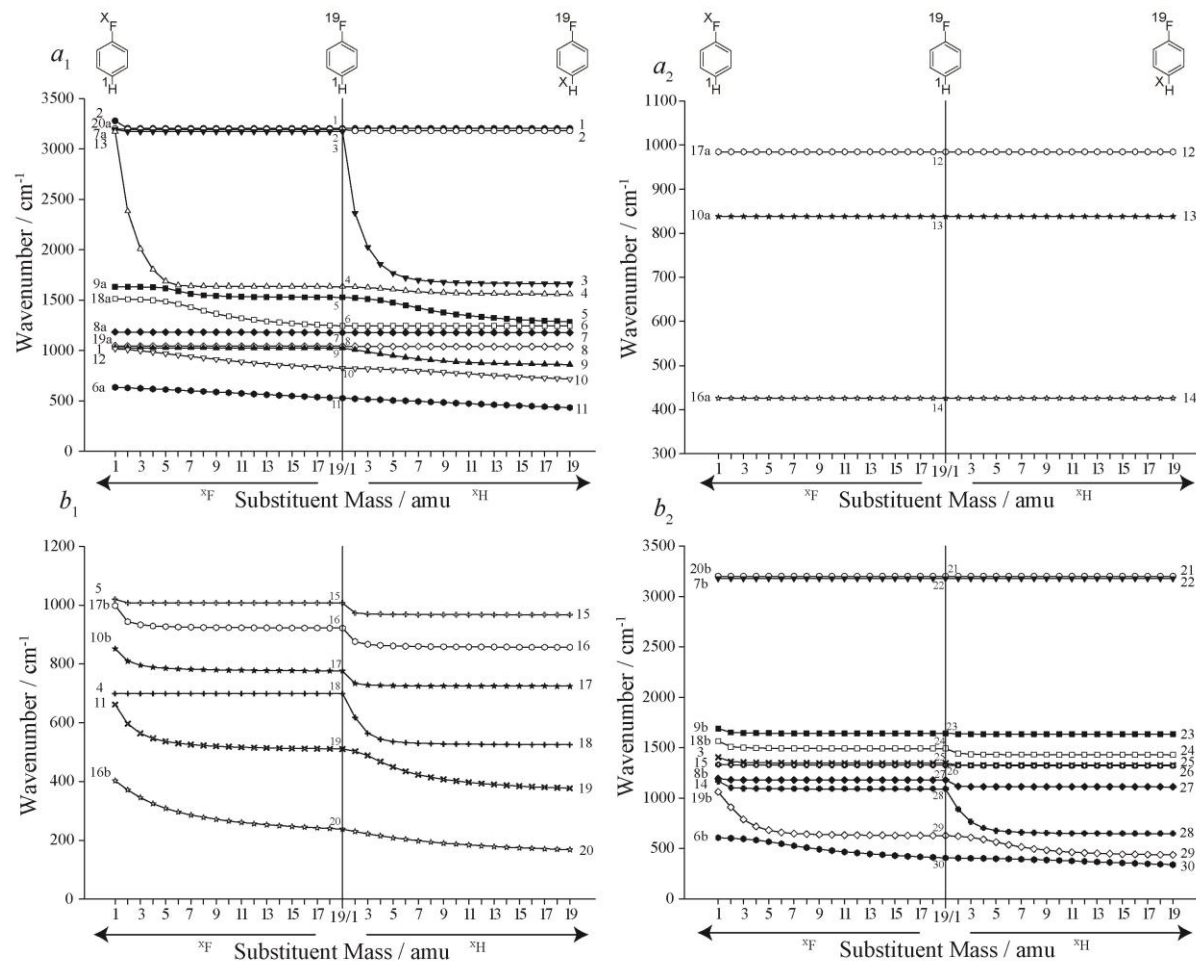


Figure 4.4. Mass-correlated vibrational wavenumbers showing how the vibrations of FBz molecule (centre) evolve into those of benzene (left) and to those of *p*DFB (right). Lines and symbols refer to “iso” calculations where the force field of FBz is employed and the mass of the fluorine atom is artificially varied from 19 to 1 amu when moving to the left (representing the benzene molecule), and then that of the *para* hydrogen is varied from 1 to 19 amu when moving to the right (representing the *p*DFB molecule). The vibrations have been grouped into their C_{2v} symmetry groups: a₁, a₂, b₁ and b₂. The Wilson labels have been included on the left; in the centre the numbers refer to the M_i modes, while on the right hand side, the numbers refer to the D_i modes.

a_2 vibrations

When one tracks vibrational modes of a_2 symmetry from FBz to p DFB, they are seen to stay constant as the mass is increased from 1 to 19 amu, something that was also observed going from the benzene molecule to p DFB in the same symmetry block, Figure 4.2. Here too these three vibrational modes can be described well with either Wilson, Varsányi or Mulliken schemes, as well as with the M_i nomenclature.

b_1 vibrations

When b_1 symmetry vibrations in Figure 4.4 are examined in detail from FBz to p DFB they are mainly straightforward to assign. Modes D_{15} and D_{16} are mainly made up of M_i modes M_{15} and M_{16} respectively, whereas modes D_{17} to D_{20} are mixed versions of the corresponding M_i vibrations and therefore cannot be described by a single M_i vibrational motion contribution unambiguously.

b_2 vibrations

Vibrational modes D_{21} to D_{24} of b_2 symmetry, Figure 4.4, stay almost constant in their wavenumber from FBz to p DFB and are likely to correspond well in motion to their respective M_i modes. Here p DFB modes D_{25} and D_{26} are a mixture of the M_{25} and M_{26} vibrations with the M_{26} mode being the dominant contribution to the D_{25} mode and a major contribution to D_{26} mode. The D_{27} vibration is a mixture of the M_{27} and M_{28} vibrational modes of the FBz molecule, whereas D_{28} is largely made up from the M_{29} FBz mode. The two lowest modes D_{29} and D_{30} are mixed

in terms of their M_i vibrations with the M_{30} being the dominant contribution to both of these D_i modes alongside a minor contribution coming from the M_{27} mode but there is no dominant contributions from the FBz M_{27} mode to any D_i mode.

The previous two sections presented how Wilson2 or M_i modes⁵ show that neither provide a good description when vibrations of *para*-disubstituted benzene molecules are being considered. Collectively those two schemes show a significant amount of mixing when *p*DFB vibrational modes are compared to modes of benzene or FBz. The M_i nomenclature has worked exceptionally well for monosubstituted benzene molecules where other schemes showed inconsistencies when comparing vibrational behaviour across such species (Chapter 3), so next will be shown how the *p*DFB molecule and its ring localised D_i vibrational modes form a basis for a new scheme, whose application can be extended to a large variety of *para*-disubstituted benzene species.

4.6 D_i nomenclature

FBz is a prototypical molecule upon whose vibrations the M_i nomenclature is built. In the case of *para*-disubstituted benzene species, the vibrational modes of *p*DFB serve as a model for the D_i nomenclature, where i denotes the number of the vibration and D notifies one that it is applied to a *para*-disubstituted benzene derivative. Ring-localised vibrational modes are ordered in C_{2v} symmetry group blocks and then by decreasing wavenumber. For the *p*DFB molecule the mode numbering is essentially in Mulliken ordering but for other *para*-disubstituted benzene

species the actual vibrational motions would have to be compared to the *p*D_{2h} modes in order to identify which vibration it is so the numbering for other *para*-disubstituted benzene species will not necessarily be in Mulliken order especially if the substituent is a functional group rather than an atom.

Figure 4.5 presents the vibrational mode diagrams of the D_i modes for the *p*D_{2h} molecule. *p*D_{2h} and other symmetric *para*-disubstituted benzene species that have both substituents as atoms, have D_{2h} point group symmetry, but in order for the D_i nomenclature to be applicable to a wider range of *para*-disubstituted benzene species, including asymmetrically-substituted derivatives, C_{2v} symmetry is employed in the D_i scheme. Vibrational motions presented in Figure 4.5 for the 30 ring-localised D_i modes have been seen to remain the same overall across the different *para*-disubstituted benzene derivatives studied here, although localised deviations do occur when heavier mass substituents are considered, and symmetric versus asymmetric molecules are compared.

Now that the D_i nomenclature construction is established, it will next be seen if one can use the vibrational mode labels of the *p*D_{2h} molecule for other symmetric and asymmetric *para*-disubstituted halobenzene species as well as the *p*FT and *p*-xylene molecules. In the following, the experimental and “explicit” calculated values are included in the tables for all of the benzene derivatives studied.

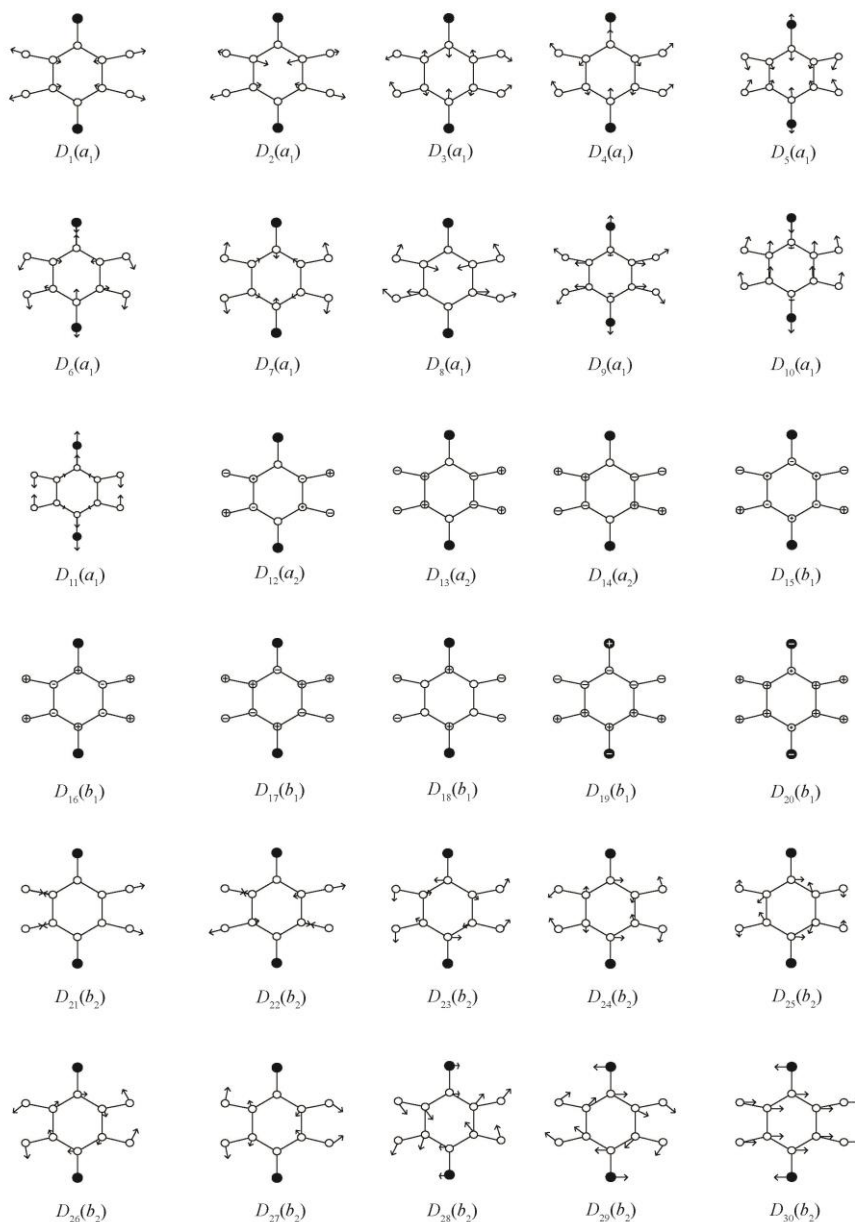


Figure 4.5. Calculated vibrational modes for *p*DFB (B3LYP/aug-cc-pVTZ), labelled using the D_i notation in the present work.

The *p*FT and *p*-xylene molecules have a non-atomic CH_3 group substituent and the vibrational modes that are substituent-localized are produced in the calculations and observed experimentally but these do not form part of the labelled ring-localised vibrations and are treated

separately. Such modes are straightforwardly identified from their calculated vibrational motion when visualised in the FC-Lab II program. When Duschinsky matrix comparisons are made involving *p*FT and *para*-xylene molecules then the “artificial isotope” (“iso”) calculated frequencies are employed.

4.7 Symmetric $p\text{C}_6\text{H}_4\text{X}_2$ benzene derivatives (X = halogen, CH₃)

In this part of the results, the ring-localised vibrational modes of the symmetric *para*-dihalobenzene and *p*-xylene molecules are the focus of attention.

Figure 4.6 compares the calculated artificial isotopic (“iso”) frequency values (shown on the plots as the lines) with previous experimental results (shown as the symbols) for the *para*-dihalosubstituted benzene and *p*-xylene molecules in their ground state. Artificial isotopic frequencies were achieved by taking the force field of the *p*DFB molecule in the calculations and artificially changing the mass of the two F atoms from 15 amu through to 127, with the lightest mass representing a CH₃ group and the heaviest one representing an iodine atom.

When one first considers the mass trends from *p*-xylene molecule to *para*-diiodobenzene (*p*DIB) using only the calculated frequencies, at first it can be seen that some variations in wavenumber exist as the mass is increased but no vibrational mode decreases in wavenumber as much as was experienced in Figure 4.2 going from benzene to *p*DFB (the same also applies to the Figure 4.4). Avoided crossings or evidence of significant vibrational mode mixings are also not present here.

Regarding the comparison between the “iso” values and the previous experimental results, for the S_0 state it may be seen from the figure that the agreement is very good for most of the D_i vibrations. The vibrational modes with poorer agreement between the iso values and experimental ones are the modes where the dominant motion is of the C-X bond, or where multiple D_i modes share a common dominant M_i contribution from the FBz modes. For example, M_{10} for D_9 and D_{10} , M_{20} for D_{19} and D_{20} , and M_{30} for D_{29} and D_{30} . This poorer agreement may indicate that these motions are sensitive to any electronic structure changes induced by the substituent, and that the changes in the force field from that of the *p*DFB molecule contribute to the differences between experimental and iso values. Such iso calculations can be utilised as a tool to study and map out any changes in the vibrational wavenumbers that occur only from the mass effect.

In Figure 4.7 Duschinsky matrices for the ground state vibrations of *p*-xylene, *para*-dichlorobenzene (*p*DCIB), *para*-dibromobenzene (*p*DBrB) and *para*-diiodobenzene (*p*DIB) are presented where the comparison is being made with the *p*DFB ground state vibrations in all cases. Strong diagonalisation is seen for all of the four molecules compared where only very slight mixing is present in the vibrational modes of a_1 symmetry. This signifies that the *p*DFB vibrational motion is close to those of the respective molecules, and the vibrations can be given the same D_i label across different symmetric *para*-disubstituted benzene species.

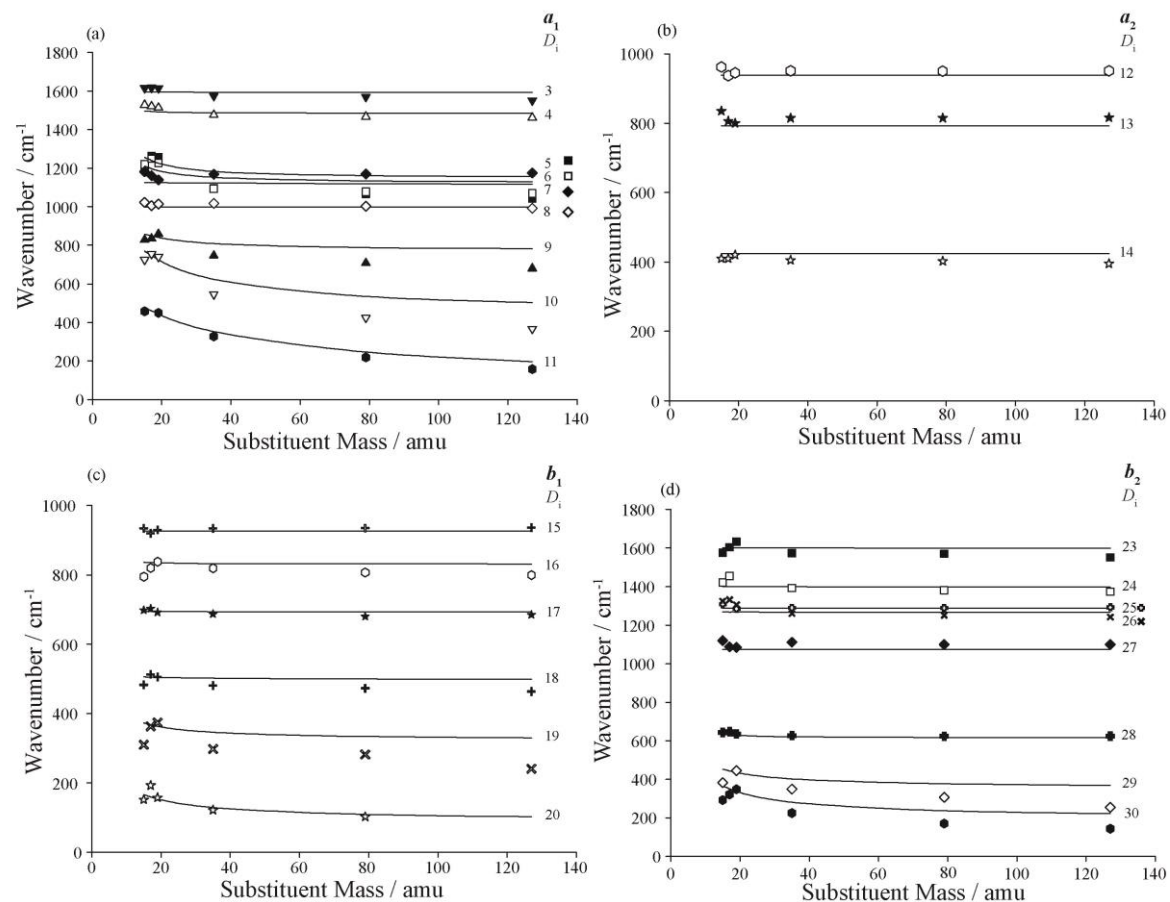


Figure 4.6. Variation in vibrational wavenumbers for symmetric *para*-disubstituted benzenes. The vibrations have been grouped into their C_{2v} symmetry groups: a_1 , a_2 , b_1 and b_2 . The lines are plotted from “iso” calculations taking the force field for *p*DFB and artificially varying the masses of the two fluorine atoms simultaneously from 15 to 127 amu. The symbols are the experimental values discussed in the text and given in Table 1. The significantly higher wavenumber C–H stretches, D_1 and D_2 (a_1 symmetry) and D_{21} and D_{22} (b_2 symmetry) are omitted for clarity.

In Figure 4.6 comparison was made between the iso frequencies and previous experimental results. Table 4.1 summarises explicitly calculated wavenumbers and previous experimental results for the symmetric molecules under study here, as well as assigning the vibrational wavenumbers to the D_i modes. Table 4.1 also includes the D_{2h} Mulliken symmetry labels for each of the D_i vibrations as previous assignments of symmetric *para*-disubstituted halobenzene derivatives were mainly done under such symmetry, employing Mulliken nomenclature.

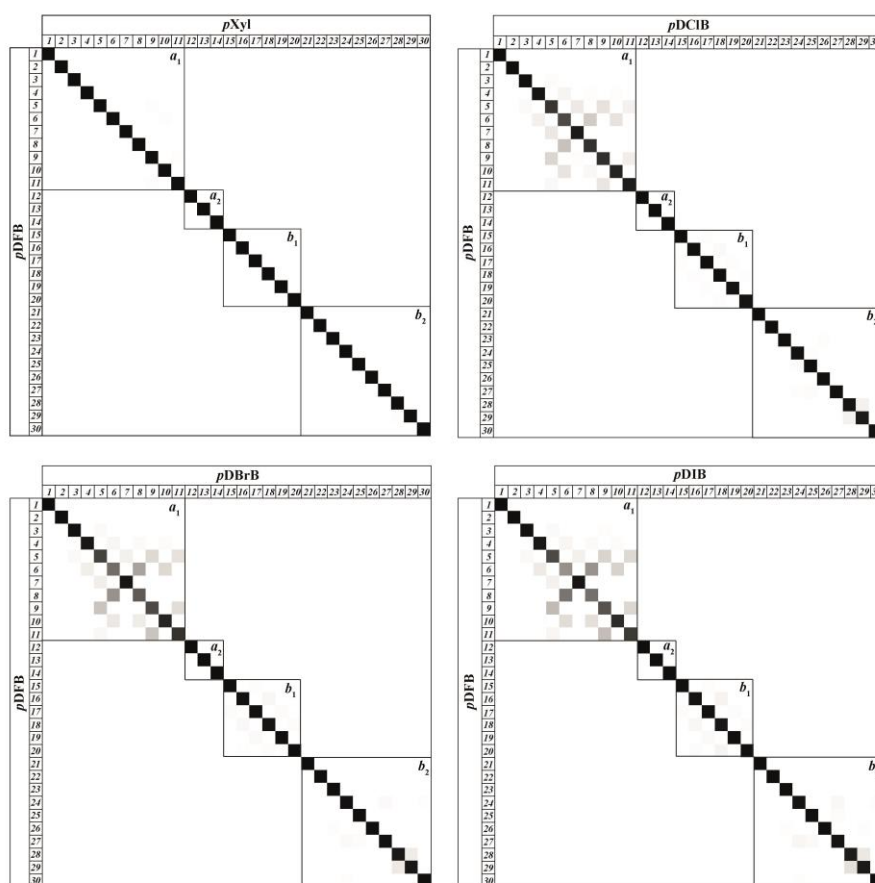


Figure 4.7. Generalised Duschinsky matrix showing how the vibrational modes of *p*-xylene, using the *p*DFF force field and changing the mass of both fluorine atoms to 15 amu, and explicitly calculated symmetric *para*-dihalobenzenes can be expressed in terms of those of *p*DFF. Black shading indicates a normalized coefficient value of 1.00, while white indicates a value of 0.00, with grey shading indicating intermediate values.

Varsányi's³ book includes very comprehensive assignments for over 700 substituted benzene derivatives using Wilson-like labels for the vibrational assignments, including *para*-disubstituted benzene species. However Varsányi has divided *para*-disubstituted benzene species into “heavy” and “light” molecules (as was mentioned in Chapter 3 for monosubstituted benzene molecules), resulting in the *p*DFB vibrations being included in the “light” category and other dihalobenzene molecules being part of the “heavy” category. This leads to numerous discrepancies in assignments and comparisons between different molecules because even though *para*-disubstituted benzene derivatives have the same or very similar ring-localised vibrations they are being described by different labels. As a result, Varsányi's experimental assignments for *para*-disubstituted benzene species are not among the ones that were chosen in this project for comparisons.

As the foundations of the D_i nomenclature have been outlined here, each benzene derivative under investigation will be discussed individually in detail in the next section in terms of its vibrational modes and by reference to previous experimental work in the ground state. Calculated scaled harmonic frequencies throughout the following results sections are labelled utilising new D_i labels for both symmetric and asymmetric *para*-disubstituted benzene derivatives. Previous experimental assignments used Wilson or Wilson-type labels. However here results from previous works have also been assigned in terms of the D_i labels.

*p*DFB molecule

For the *p*DFB molecule most of the experimental fundamental vibrational wavenumbers in Table 4.1 came from vapour-phase IR/Raman study by Zimmerman and Dunn.²⁴ Their work on the ground state of *p*DFB has been used as the key reference for vibrational wavenumbers in all of the later studies. There is very good agreement between the B3LYP/aVTZ harmonically scaled frequencies calculated in this project and previous experimental wavenumbers, especially for the a_2 and b_1 symmetry vibrations, Table 4.1. However, as was investigated here there are some vibrations that do not have unambiguous assignments, or that have been assigned incorrectly in ref. 24.

The wavenumber for the D_{12} vibration (a_u symmetry in the D_{2h} point group, expected to be both IR and Raman inactive) is taken from ref. 24, but originally comes from a hot band in the two-photon electronic spectrum of Robey and Schlag.²⁵ This vibration was later confirmed by the combined laser induced fluorescence and dispersed fluorescence study of Knight and Kable.²⁶

Vibrational mode D_{21} is assigned to a feature at 3073 cm^{-1} in the table in ref. 24 but was referred to as a feature at 3091 cm^{-1} in the text of the same work. The value of 3091 cm^{-1} for this vibration matches well with the corresponding value for *p*DCIB molecule from the same work but the value of 3073 cm^{-1} agrees more with the corresponding value for *p*DBrB one, Table 4.1. The calculated values in this work are not able to differentiate between these two vibrations.

Zimmermann and Dunn²⁴ have reassigned the D_{25} vibrational mode from a feature observed at 1286 cm^{-1} by earlier works to a band at 1306 cm^{-1} on the basis of their IR measurements, as according to them it was too low. The newer assignment is consistent with the calculated wavenumber value from this work and lies well with the trend that can be observed across the symmetric dihalobenzene derivative series.

*p*DCIB molecule

The experimental vibrational wavenumbers in Table 4.1 for *p*DCIB come from two sources, a gas phase IR work by Saëki²⁷ and an IR/Raman study by Scherer and Evans²⁸ from 1962 and 1963 respectively. A study by Green²⁹ from 1970 on the ground state vibrations of *p*DCIB molecule tends to be the study which later works refer to, but Green also includes values from these two earlier studies, while mainly confirming the assignments made by Stojiljković and Whiffen.³⁰

The D_{25} vibration in the *p*DCIB molecule was originally assigned to a band seen at 1260 cm^{-1} in the IR spectrum by Stojiljković and Whiffen.³⁰ Scherer and Evans²⁸ have reassigned this feature to a combination band and have assigned the D_{25} fundamental to a band observed at 1221 cm^{-1} . The calculated vibrational wavenumber in this project for the D_{25} vibration was found to be 1264 cm^{-1} which matches the value from Stojiljković and Whiffen of 1260 cm^{-1} much better, and 1260 cm^{-1} value also matches well the trend in wavenumbers that is seen across the symmetric *para*-disubstituted halobenzene species for the D_{25} vibration.

Table 4.1. Vibrational wavenumbers for *para*-C₆H₄X₂ (X = F, Cl, Br, I and CH₃)^a

Mode			<i>p</i> Xyl		<i>p</i> DFB		<i>p</i> DCIB		<i>p</i> DBrB		<i>p</i> DIB	
<i>D_i</i>	<i>D</i> _{2h} ^b	<i>C</i> _{2h} ^c	Exper.	Calc. ^d	Exper.	Calc. ^d	Exper.	Calc. ^d	Exper.	Calc. ^d	Exper.	Calc. ^d
<i>a</i> ₁												
<i>D</i> ₁	1(<i>a_g</i>)	1(<i>a_g</i>)	3059 ^e	3073	3088 ^f	3114	3070 ^h	3114	3068 ⁱ	3113	3056 ⁱ	3109
<i>D</i> ₂	10(<i>b</i> _{1<i>u</i>})	21(<i>b_u</i>)	3045 ^e	3054	3073 ^f	3100	3098 ⁱ	3100	3068 ^k	3098	3055 ⁱ	3094
<i>D</i> ₃	2(<i>a_g</i>)	2(<i>a_g</i>)	1616 ^e	1606	1615 ^f	1595	1574 ^h	1563	1570 ⁱ	1551	1552 ⁱ	1540
<i>D</i> ₄	11(<i>b</i> _{1<i>u</i>})	22(<i>b_u</i>)	1520 ^e	1505	1514 ^f	1492	1478 ⁱ	1463	1468 ^k	1458	1463 ⁱ	1455
<i>D</i> ₅	3(<i>a_g</i>)	3(<i>a_g</i>)	1203 ^e	1186	1257 ^f	1226	1096 ^h	1067	1067 ⁱ	1045	1044 ⁱ	1031
<i>D</i> ₆	12(<i>b</i> _{1<i>u</i>})	23(<i>b_u</i>)	1225 ^e	1203	1228 ^f	1187	1094 ⁱ	1067	1078 ^k	1056	1069 ⁱ	1055
<i>D</i> ₇	4(<i>a_g</i>)	4(<i>a_g</i>)	1183 ^e	1173	1140 ^f	1126	1169 ^h	1160	1170 ⁱ	1166	1175 ⁱ	1173
<i>D</i> ₈	13(<i>b</i> _{1<i>u</i>})	24(<i>b_u</i>)	1026 ^e	1011	1014 ^f	999	1017 ⁱ	1000	1003 ^k	991	993 ⁱ	982
<i>D</i> ₉	5(<i>a_g</i>)	5(<i>a_g</i>)	830 ^e	813	859 ^f	841	747 ^h	730	708 ⁱ	699	680 ⁱ	680
<i>D</i> ₁₀	14(<i>b</i> _{1<i>u</i>})	25(<i>b_u</i>)	694 ^e	712	740 ^f	724	545 ⁱ	523	424 ^k	410	361 ⁱ	356

D_{11}	$6(a_g)$	$6(a_g)$	454^e	449	450^f	443	328^h	318	218^i	205	157^i	153
a_2												
D_{12}	$7(a_u)$	$12(a_u)$	972^e	961	945^f	939	951^h	954	950^k	956	951^i	959
D_{13}	$9(b_{1g})$	$17(b_g)$	832^e	830	800^f	792	815^h	809	815^k	810	816^i	814
D_{14}	$8(a_u)$	$13(a_u)$	410^e	408	422^g	424	410^h	406	402^k	402	$(400)^i$	397
b_1												
D_{15}	$15(b_{2g})$	$18(b_g)$	930^e	935	928^f	927	934^h	941	935^k	940	936^i	942
D_{16}	$28(b_{3u})$	$14(a_u)$	795^e	792	838^f	835	819^i	821	807^k	812	799^i	803
D_{17}	$16(b_{2g})$	$19(b_g)$	700^e	701	692^f	694	687^h	692	$(680)^k$	685	$(685)^i$	676
D_{18}	$29(b_{3u})$	$15(a_u)$	481^e	484	505^f	505	480^i	483	473^k	473	464^i	465
D_{19}	$17(b_{2g})$	$20(b_g)$	312^e	300	374^f	363	298^h	288	282^k	258	241^i	233
D_{20}	$30(b_{3u})$	$16(a_u)$	132^e	132	158^f	154	125^h	99	103^k	74		59
b_2												
D_{21}	$18(b_{2u})$	$26(b_u)$	3056^e	3070	3091^f	3113	3098^i	3113	3078^k	3111	$(3050)^i$	3107
D_{22}	$23(b_{3g})$	$7(a_g)$	3042^e	3054	3085^f	3102	3065^h	3102	3068^i	3099	3056^i	3095

D_{23}	24(b_{3g})	8(a_g)	1578 ^e	1564	1617 ^f	1601	1574 ^h	1563	1565 ^k	1557	1552 ⁱ	1545
D_{24}	19(b_{2u})	27(b_u)	1400 ^e	1395	1437 ^f	1400	1393 ⁱ	1378	1381 ^k	1370	1374 ⁱ	1363
D_{25}	20(b_{2u})	28(b_u)	1320 ^e	1281	1306 ^f	1287	1260 ^j	1264	1251 ⁱ	1260	1242 ⁱ	1252
D_{26}	25(b_{3g})	9(a_g)	1313 ^e	1306	1285 ^f	1268	1290 ^h	1282	1290 ^k	1285	1292 ⁱ	1289
D_{27}	21(b_{2u})	29(b_u)	1099 ^e	1107	1085 ^f	1074	1112 ⁱ	1090	1100 ^k	1091	1100 ⁱ	1092
D_{28}	26(b_{3g})	10(a_g)	643 ^e	640	635 ^f	628	626 ^h	621	623 ⁱ	618	624 ⁱ	617
D_{29}	27(b_{3g})	11(a_g)	389 ^e	374	446 ^g	435	350 ^h	343	307 ^k	301	(255) ⁱ	271
D_{30}	22(b_{2u})	30(b_u)	285 ^e	277	348 ^f	337	225 ⁱ	213	171 ^k	158	140 ^l	126

^a. Values in parentheses have been estimated in the cited work. ^b. Numbered according to the Mulliken convention in the D_{2h} point group with the symmetry given in parentheses. For D_{2h} the order of the symmetry groups used in assigning the numbering comes from Table 14 in Herzberg II³¹ and has the order A_g , A_u , B_{1g} , B_{1u} , B_{2g} , B_{2u} , B_{3g} , B_{3u} ; the symmetry breakdown of the thirty vibration is $6A_g+2A_u+1B_{1g}+5B_{1u}+3B_{2g}+5B_{2u}+5B_{3g}+3B_{3u}$. ^c. Labelled according to the Mulliken convention in the C_{2h} point group with the symmetry given in parentheses, where the order of the symmetry groups used in assigning the numbering comes from Table 13 in Herzberg II³¹ and is A_g , A_u , B_g , B_u ; the symmetry breakdown of the thirty vibration is $11A_g+5A_u+4B_g+10B_u$. ^d. This work. B3LYP/aVTZ scaled by 0.97. ^e. Vapour phase IR and Raman from Ref. 34. ^f. Vapour phase IR from Ref.24. ^g. Dispersed fluorescence from Ref.26. ^h. From Ref.28. ⁱ. Vapour Phase IR from Ref. 27. ^j. From Ref. 30. ^k. From Ref.29. ^l. From Ref.33

*p*DBrB molecule

In Table 4.1, the experimental wavenumbers for the *p*DBrB molecule come from the same two sources as the *p*DClB assignments: Green's study²⁹ and the work of Stojiljković and Whiffen work.³⁰ Mode D_{26} at 1290 cm^{-1} is the only exception as its assignment comes from the work of Herz et al.³² The experimental wavenumbers are in good agreement with the calculated harmonic frequencies obtained in this work, something that was already seen for the *p*DFB and *p*DClB molecules. Fair agreement also exists between the assignments of Green²⁹ and Stojiljković and Whiffen,³⁰ apart from for the D_{25} vibration. Green assigns the D_{25} fundamental to the feature at 1212 cm^{-1} but Stojiljković and Whiffen assign this fundamental to the band at 1251 cm^{-1} . The calculated wavenumber obtained in this work for D_{25} is 1260 cm^{-1} which is closer to the Stojiljković and Whiffen assignment; therefore, that is the one which is included in Table 4.1. Although Green has only estimated a value for the D_{17} fundamental in his work, it is a perfect match with the one calculated here.

*p*DIB molecule

Previous assignments for *p*DIB are taken from the work of Stojiljković and Whiffen³⁰ except for the D_{30} fundamental, the value for which is obtained from the solution phase IR spectrum of Griffiths and Thompson.³³ As was seen for other *para*-dihalobenzene derivatives, previous experimental assignments match the calculated wavenumbers from this work really well. The D_{14} , D_{17} and D_{29} values in Table 4.1

taken from ref. 30 are only estimates by the authors but they are in very good agreement with the calculated values from this work.

The wavenumber of the D_{25} fundamental is also being queried here as it was for *p*DBrB. Green²⁹ assigns the D_{25} vibration to the 1212 cm^{-1} band, whereas Stojiljković and Whiffen³⁰ place this mode at 1242 cm^{-1} . Again, here the Stojiljković and Whiffen assignment is favoured over that of Green as it matches better the calculated result and the trend in wavenumber as one moves from *p*DFB to the *p*DIB molecule. Inconsistencies also arise with the D_{20} vibration. Griffiths and Thompson³³ assign it to the 105 cm^{-1} feature but the calculated value is lower than the observed one by 60 cm^{-1} . Both *p*DCIB and *p*DBrB had experimental frequencies higher than the calculated values for the D_{20} fundamental but not by a such large amount, which leads to the conclusion that the D_{20} experimental assignment is incorrect as one would expect it to lie lower than 105 cm^{-1} based on the decreasing trend in wavenumber seen for this vibration from *p*DFB to *p*DCIB and *p*DBrB. It has been left blank in Table 4.1. (A possible assignment for the 105 cm^{-1} feature being the D_{29} - D_{30} ($255 - 144 = 111$) cm^{-1} difference band.)

p-xylene molecule

The last molecule left to discuss from Table 4.1 and for this section is *p*-xylene . The vibrational wavenumbers in Table 4.1 are summarised from the IR/Raman study of Draeger³⁴ which match well the calculated values. However, the calculated values suggest that D_{25} has a lower vibrational wavenumber than the D_{26} fundamental, but experimentally

derived wavenumbers assigned to these vibrations do not reproduce this. Selco and Carrick³⁵ have recorded emission spectra of *p*-xylene and reported six vibrational wavenumbers. Comparing those to the Draeger³⁴ and Green²⁹ studies and then to the calculated wavenumbers in this work, a good agreement was observed overall but there were some exceptions. The D_3 vibration is assigned to the 1656.7 cm^{-1} band by Selco and Carrick,³⁵ but the calculated value for this fundamental is much lower than that and agrees more closely with the value from Draeger³⁴ and Green²⁹ of 1616 cm^{-1} . Selco and Carrick assign the D_9 mode to 842.3 cm^{-1} , but Draeger assigns this vibration to a band at 830 cm^{-1} . The calculated wavenumbers cannot unambiguously assign this vibration, but the higher wavenumber value matches closely with the $D_{11}D_{29}$ combination band wavenumber which is expected to be present based on previous experimental results.

4.8 Asymmetric *para*-C₆H₄XY benzene derivatives (X and Y = halogen and CH₃)

In this results section the application of the D_i nomenclature to *para*-asymmetrically disubstituted benzene derivatives is explored in more detail, specifically, the asymmetric dihalobenzene and *p*FT molecules. The simplest cases of asymmetric molecules to consider are species where one of the substituents is the fluorine atom and the second substituent in the *para*-position is a different halogen. The easiest way to present mass trends for such species is to map out the trends observed between previous experimental results and the “iso” wavenumbers obtained. “Iso” wavenumbers here refer to calculations where the *p*DFB

force field was used but where the mass of one fluorine atom was artificially changed in mass from 19 to 35, 79 and 127 to emulate halogen atoms, and mass 15 to represent a methyl group, similar to the procedure for producing the mass trends for symmetric benzene cases, as was seen in Figure 4.6.

From Figure 4.8 it is evident that the mass trends obtained from the “iso” wavenumbers (indicted by lines) are overall in very good agreement with previous experimental results (indicated by symbols). The agreement seems to be slightly better here compared to the symmetrically-substituted benzene mass plots in Figure 4.6, but the vibrational modes that do show a larger deviation from experimental results have changes in their force field which is an indication that electronic effects may need to be considered for such vibrations. In the D_9/D_{10} and D_{29}/D_{30} vibrations, the lower wavenumber mode deviates further from the “iso” line with increasing mass than the higher wavenumber mode. The higher wavenumber vibration is localized to the C–F bond and follows the “iso” line more closely suggesting that the local mode nature of these vibrations is largely a result of the differences between the halogens, for example evolving electronic effects arising from the size and electronegativity of the halogen atoms.

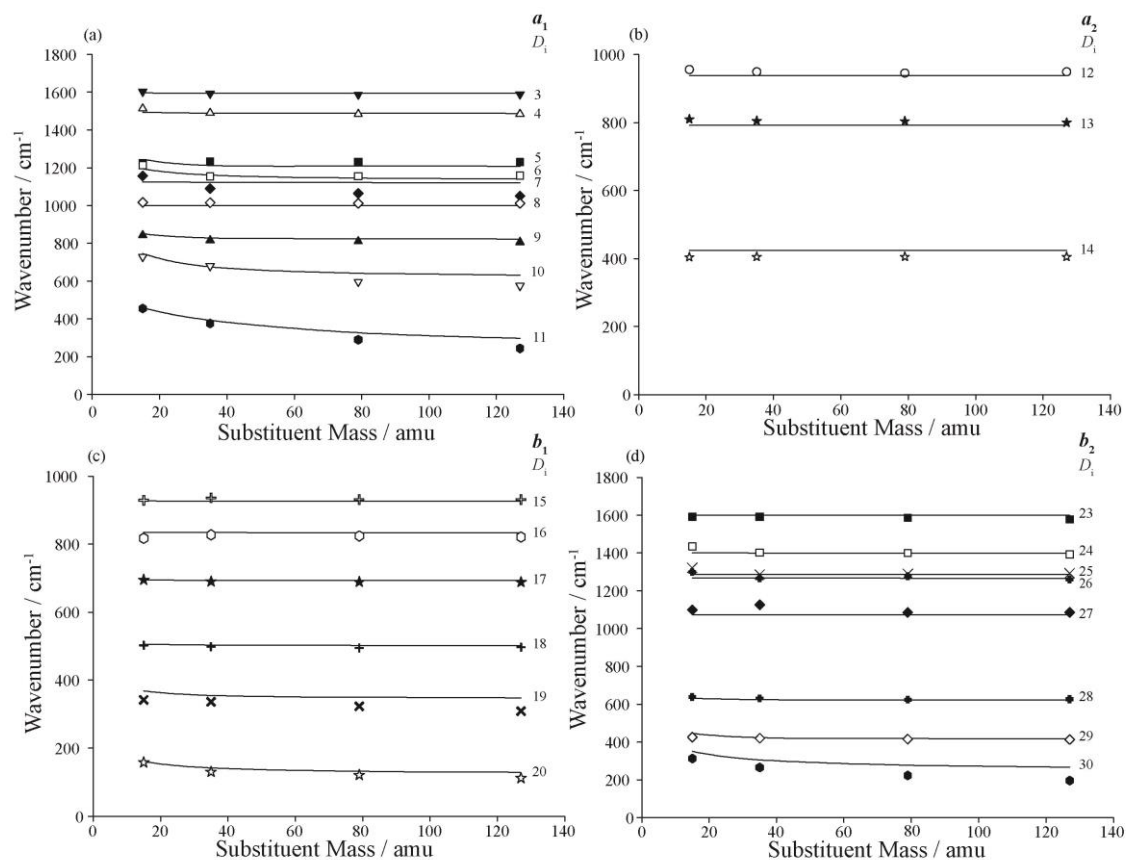


Figure 4.8. Variation in vibrational wavenumbers for asymmetric *para*-disubstituted benzene derivatives. The vibrations have been grouped into their C_{2v} symmetry groups: a_1 , a_2 , b_1 and b_2 . The lines arise from “iso” calculations taking the force field for *p*DfB and artificially varying the mass of the *para* fluorine atom from 15 to 127 amu. The symbols are the experimental values discussed in the text and given in Table 1. The high wavenumber C–H stretches, D_1 and D_2 (a_1 symmetry) and D_{21} and D_{22} (b_2 symmetry) are omitted for clarity.

Duschinsky matrices for the asymmetric *para*-disubstituted *p*FT, *para*-chlorofluorobenzene (*p*ClFB), *para*-bromofluorobenzene (*p*BrFB) and *para*-iodofluorobenzene (*p*IFB) molecules are shown in Figure 4.9.

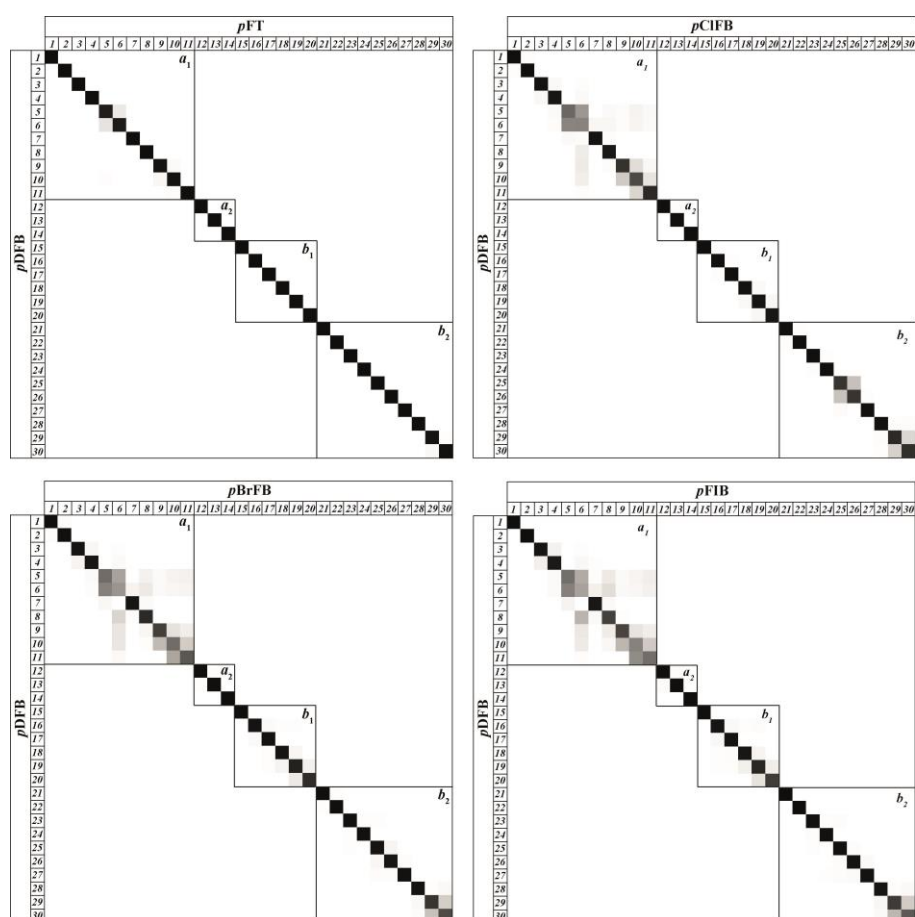


Figure 4.9. Generalised Duschinsky matrices showing how the vibrational modes of *p*FT and asymmetric *para*-dihalobenzene derivatives can be expressed in terms of the *p*DFB ones. For the *p*FT molecule the *p*DFB force field was used and the mass of one fluorine atom was changed to 15 amu whereas the asymmetric *para*-dihalobenzenes used explicitly calculated wavefunctions. Black shading indicates a normalized coefficient value of 1.00, while white indicates a value of 0.00, with grey shading indicating intermediate values.

In agreement with the observations that were seen for the symmetric *para*-disubstituted benzenes, the matrices here also show diagonalisation. Such diagonal behaviour indicates that the vibrational motion of asymmetric *para*-disubstituted benzene species can be described in terms of the vibrations of *p*DFB with confidence as although some mixed character is present, on the whole the ring-localised motions are conserved.

Such diagonalisation was also observed for a large number of different species, for example other *para*-dihalotoluenes and *para*-dihalophenols.¹ Those findings along with the mass trends, all lead to the conclusions that the D_i labels can be used for asymmetric derivatives as well as the symmetric cases. In order to solidify the fundamentals of the D_i nomenclature the ground state assignments for a number of asymmetrically *para*-disubstituted benzene molecules are presented in Table 4.2 and discussed in detail further on.

Table 4.2. Vibrational wavenumbers for *para*-C₆H₄XY: asymmetric *para*-dihalobenzenes^a

<i>D_i</i> Mode	<i>p</i> ClFB		<i>p</i> BrFB		<i>p</i> FIB		<i>p</i> BrClB		<i>p</i> ClIB		<i>p</i> BrIB		<i>p</i> FT	
	Exper.	Calc. ^b	Exper.	Calc. ^b	Exper.	Calc. ^b	Exper.	Calc. ^b	Exper.	Calc. ^b	Exper.	Calc. ^b	Exper.	Calc. ^b
<i>a</i>₁														
<i>D</i> ₁	3076 ^c	3114	3076 ^c	3113	3072 ^c	3111	3070 ^c	3113	3067 ^c	3111	3069 ^c	3111	3068 ^c	3103
<i>D</i> ₂	3076 ^c	3099	3076 ^c	3099	3072 ^c	3097	3070 ^c	3099	3052 ^d	3097	3069 ^c	3096	3068 ^c	3071
<i>D</i> ₃	1592 ^c	1581	1587 ^c	1576	1589 ^c	1572	1570 ^c	1557	1567 ^c	1552	1553 ^c	1546	1603 ^c	1598
<i>D</i> ₄	1490 ^c	1477	1485 ^c	1474	1484 ^c	1471	1471 ^c	1461	1470 ^c	1459	1467 ^c	1457	1513 ^c	1499
<i>D</i> ₅	1233 ^c (C-F)	1211 (C-F)	1236 ^d (C-F)	1211 (C-F)	1230 ^c (C-F)	1211 (C-F)	1087 ^c (C-Cl)	1067 (C-Cl)	1090 ^c (C-Cl)	1068 (C-Cl)	1069 ^c (C-Br)	1057 (C-Br)	1241 ⁱ (C-F)	1209 ^(C-F)
<i>D</i> ₆	1096 ^d (C-Cl)	1064 (C-Cl)	1069 ^d (C-Br)	1046 (C-Br)	1050 ^c (C-Cl)	1037 (C-Cl)	1068 ^c (C-Br)	1051 (C-Br)	1054 ^c (C-Br)	1042 (C-Br)	1052 ^c (C-Cl)	1038 (C-Cl)	1215 ⁱ (C-Me)	1192 ^(C-Me)
<i>D</i> ₇	1153 ^d	1141	1157 ^d	1144	1158 ^c	1147	1166 ^c	1163	1172 ^c	1167	1171 ^c	1170	1157 ^c	1145
<i>D</i> ₈	1017 ^d	1002	1015 ^d	1000	1011 ^c	998	1009 ^c	996	1005 ^c	992	1000 ^c	987	1001 ^j	1005
<i>D</i> ₉	815 ^e	809	812 ^e	805	806 ^d	802	730 ^c	716	722 ^c	709	697 ^c	690	843 ⁱ	827
<i>D</i> ₁₀	639 ^d	616	600 ^d	580	575 ^c	565	496 ^c	477	476 ^c	460	397 ^c	386	730 ^k	715

D_{11}	375 ^c	364	282 ^c	278	244 ^c	236	258 ^c	251	220 ^c	214	180 ^c	177	453 ⁱ	446
a_2														
D_{12}	949 ^c	948	945 ^c	949	949 ^c	951	951 ^c	955	951 ^c	957	954 ^c	957	956 ^c	953
D_{13}	805 ^c	800	804 ^c	800	800 ^c	801	812 ^c	809	(815) ^c	811	(813) ^c	812	810 ^c	808
D_{14}	(405) ^c	416	(405) ^c	414	(405) ^c	411	405 ^c	404	400 ^c	402	(400) ^c	400	404 ^c	418
b_1														
D_{15}	936 ^c	935	931 ^c	934	931 ^c	935	935 ^c	941	936 ^c	942	936 ^c	941	929 ^c	931
D_{16}	830 ^d	829	827 ^d	826	821 ^c	823	812 ^c	817	809 ^c	813	803 ^c	808	819 ^l	817
D_{17}	690 ^c	693	689 ^c	690	688 ^c	685	686 ^c	689	686 ^c	685	(685) ^c	681	695 ^c	698
D_{18}	498 ^d	497	496 ^d	495	497 ^c	493	480 ^c	479	476 ^c	475	470 ^c	469	502 ^c	500
D_{19}	337 ^d	326	322 ^d	312	309 ^c	300	291 ^c	273	275 ^c	261	261 ^c	246	321 ⁱ	330
D_{20}	130 ^c	123	127 ^h	108	112 ^c	98	112 ^c	86	103 ^c	78	97 ^c	66	158 ^c	141
b_2														
D_{21}	3076 ^c	3112	3076 ^c	3112	3072 ^c	3110	3082 ^c	3112	3073 ^c	3110	3089 ^c	3109	3040 ^c	3102
D_{22}	3076 ^c	3101	3046 ^c	3101	3072 ^c	3099	3082 ^c	3100	3073 ^c	3098	3089 ^c	3097	3040 ^c	3071

D_{23}	1592 ^c	1583	1587 ^c	1581	1579 ^c	1577	1557 ^g	1559	1560 ^h	1554	1553 ^c	1551	1592 ^c	1586
D_{24}	1402 ^c	1389	1400 ^c	1384	1393 ^c	1380	1390 ^c	1374	1387 ^c	1370	1374 ^c	1366	1435 ^c	1395
D_{25}	1266 ^c	1278	1277 ^c	1279	1260 ^c	1282	1216 ^c	1283	1215 ^c	1286	1213 ^c	1287	1300 ^c	1283
D_{26}	1287 ^c	1274	1290 ^c	1273	1293 ^c	1268	1290 ^c	1262	1289 ^c	1257	1296 ^c	1256	1321 ^c	1292
D_{27}	(1086) ^f	1082	1086 ^c	1082	1086 ^c	1082	1100 ^c	1091	1100 ^c	1092	1100 ^c	1092	1099 ^c	1090
D_{28}	630 ^c	624	624 ^c	622	626 ^c	620	624 ^g	619	624 ^h	618	623 ^h	617	640 ⁱ	633
D_{29}	419 ^c	412	416 ^d	407	413 ^c	405	333 ^g	326	324 ^d	317	294 ^c	288	426 ⁱ	414
D_{30}	265 ^c	254	218 ^d	212	196 ^c	185	194 ^c	182	173 ^c	161	155 ^c	141	313 ^c	298

^a. Values in parentheses have been estimated in the cited work. Where the same wavenumber value is given for two vibrations of the same symmetry group, the assignment is assumed to be uncertain. The pairs of modes, D_5/D_6 and D_{29}/D_{30} become more localized modes here, while they were in- and out-of-phase combinations for the symmetric cases. The higher value corresponds to a C–X stretch involving the lighter atom, while the lower value corresponds to the corresponding mode involving the heavier atom.^b. This work: B3LYP/aVTZ scaled by 0.97. ^c IR values from Ref. 29. ^dVapour phase IR from Ref.36.^e From Ref. 37. ^f. Estimate, this work. ^g Liquid phase Raman values from Refs.38 and 39. ^h Solution phase Raman from Ref.45. ⁱ Electronic emission spectrum from Ref. 44. ^j Dispersed fluorescence spectra from Ref. 43. ^k Rotationally resolved gas phase IR from Ref. 42. ^l Rotationally resolved gas phase IR from Ref. 41.

Table 4.2 presents “explicit” calculated harmonic frequencies from this work and previous experimental vibrational wavenumbers and assignments for the asymmetric *para*-substituted dihalobenzenes as well as the *p*FT molecule. It was fairly straightforward to assign vibrational modes and as was seen for the symmetric substituted cases in Table 4.1, here too the calculated frequencies matched well with the previous experimental results.

*p*ClFB, *p*BrFB and *p*FIB molecules

Most of the experimental values for the *p*ClFB and *p*BrFB molecules are taken from a liquid phase IR study by Green²⁹ and a vapour phase IR study by Narasimham et al.³⁶ For both of the molecules, the D_9 fundamental value is taken from the liquid phase Raman spectrum by Patel et al.³⁷ All three studies have excellent overall agreement with each other for each respective molecule. The values for the *p*FIB molecule in Table 4.2 are taken from liquid phase IR and Raman studies by Green²⁹ and Narasimham et al.³⁶ respectively as there are no gas phase results available.

*p*BrClB, *p*ClIB and *p*BrIB molecules

For these three molecules there are no available gas phase results. The *p*BrClB values are taken from a paper by Green²⁹ with the exception of the D_{23} , D_{28} and D_{29} fundamentals the values for which come from works by Paulsen³⁸ and Herz et al.³⁹

Experimental results for *p*ClIB and *p*BrIB are taken from both Green²⁹ and Stojiljković and Whiffen.⁴⁰

pFT molecule

The calculated scaled harmonic frequencies obtained here match well with previous experimental results which were taken from the following works: the D_{10} and D_{16} pFT fundamental values in Table 4.2 come from Ghosh^{41,42} and the D_8 value is taken from Okuyama et al.⁴³ Other previous experimental fundamental frequencies are from Green²⁹ and Ha et al.⁴⁴

For the D_{20} mode the experimental value of 180 cm^{-1} given by Okuyama et al.⁴³ seems a little high, but from currently unpublished work by the Wright group this band is believed likely to arise from a torsion-vibration level. In light of this Green's²⁹ value of 158 cm^{-1} is included in Table 4.2 for this vibration, which is more in line with the trend for this mode,¹ and with the calculated value.

Also in Table 4.2, the D_{30} fundamental has been assigned the value of 313 cm^{-1} from Green study²⁹ to be in line with other values for halotoluenes¹ as the frequencies of 288 and 287 cm^{-1} from Ha et al.⁴⁴ and Okuyama et al.⁴³ respectively for this fundamental seem to be $10\text{-}15\text{ cm}^{-1}$ too low compared to other halotoluenes (as was also the case with the D_{20} mode).

4.9 Summary and Future Work

Following on from Chapter 3, Chapter 4 has explored vibrational motions of substituted benzene derivatives even further, concentrating on the *para*-disubstituted benzene molecules, where both symmetric and asymmetric derivatives were studied.

Firstly, the vibrational modes of benzene (Wilson modes) were mapped out onto those of *p*DfB. For most of the ring-localised vibrations, the *p*DfB vibrational modes had more than one contribution from the benzene modes, resulting in a high degree of mixing and indicating that although some of the vibrations can be described by Wilson-type labels, the majority cannot. Following from that, the application of the M_i nomenclature for *para*-disubstituted benzene species was explored with the *p*DfB molecule. Essentially mapping out the evolution of the FBz vibrational modes onto *p*DfB. Here too, although some vibrations underwent only small changes, or larger changes associated with “avoided crossings”, many of the vibrational modes became mixed going from FBz to *p*DfB, indicating that the vibrational motions of *para*-disubstituted benzene derivatives cannot be described with the M_i nomenclature unambiguously.

Following that, a new nomenclature for *para*-disubstituted benzene species, D_i , is proposed in this chapter. D_i labels are based on the vibrations of the *p*DfB molecule, ordered by decreasing wavenumber in symmetry blocks under C_{2v} point group symmetry so that the scheme is applicable to both symmetrically and asymmetrically *para*-disubstituted benzene molecules. The same D_i label is given to the same vibrational motion in different *para*-disubstituted benzene species making comparisons across different derivatives much more straightforward aiding the study of IVR and other photophysical processes.

In this chapter, only assignments for the S_0 state were explored for symmetrically and asymmetrically-disubstituted *para*-dihalobenzene, *p*-xylene and *p*FT molecules.

Although the D_i scheme is presented here in a comprehensive manner, due to time constraints not all aspects of it were studied as wished during the duration of this PhD. In future work fully deuterated symmetric and asymmetric *para*-disubstituted species could be considered in order for a similar analysis to be done as was undertaken in Chapter 3 on monosubstituted benzene molecules.

Application of the D_i nomenclature to the first electronically excited states (S_1) of *para*-disubstituted benzene molecules is the most desired next step, as upon excitation changes in electronic structure necessarily occur and it will be interesting to see what consequences this will have on vibrational motion. The computational aspect of the project pertaining to the S_1 state was already performed during this PhD for a number of molecules, but those preliminary results are not included here since they are out of the scope of this thesis. Duschinsky matrices for symmetric *para*-dihalobenzenes, *p*FT and *p*-xylene molecules have showed almost complete diagonalisation indicating that even upon excitation with some modes having deviations in vibrational motion, the majority of the vibrations hold on to their motion and can be described by the same D_i label. It would be of great benefit if computational results obtained for the S_1 state could be compared to experimentally recorded REMPI and ZEKE spectra which are currently being recorded for the *p*DFB, *p*FT and *p*-xylene molecules at the time of writing.

As mentioned in the introduction there are three arrangements in which two substituents can be arranged on the benzene ring: *ortho*, *meta* and *para* where it is the latter that has been investigated here. Study of the *ortho*- and *meta*-disubstituted benzene molecules is the next step for future work. Wilson modes have been found again to be inappropriate in describing vibrational motions of *ortho*- and *meta*-disubstituted benzene species, and the D_i nomenclature has also been found incompatible. Therefore, separate vibrational nomenclatures are required for the *ortho*- and *meta*-disubstituted benzene derivatives based on the *ortho*-difluorobenzene and *meta*-difluorobenzene modes respectively. Following methodologies similar to those outlined in this chapter, preliminary results have been obtained for the ground state vibrations of symmetric and asymmetric *ortho*- and *meta*-disubstituted benzene molecules. Those results can be found in the master's dissertation of Jonathan Wakefield,⁴⁶ an MChem student who jointly worked on this project.

4.10 References

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