MATRIX-ISOLATION MAGNETO-OPTICAL SPECTROSCOPY OF DIATOMIC RADICAL MONOHYDRIDES

A thesis submitted in partial fulfilment of the requirements for the Degree of Doctor of Philosophy in Chemistry

in the University of Canterbury

by

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University of Canterbury

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Then the king's colour changed, and his thoughts alarmed him; his limbs gave way, and his knees knocked together. The king cried aloud to bring in the enchanters, the Chaldeans, and the astrologers. The king said to the wise men of Babylon, "Whoever reads this writing, and shows me its interpretation, shall be clothed with purple, and have a chain of gold around his neck, and shall be ruler in the third kingdom."

Daniel 5:6,7
Abstract

This PhD thesis presents the results of electronic magnetic-circular-dichroism (MCD) and absorption spectroscopy of CH, NH, OH, PH, and SH isolated in various noble-gas (argon, krypton, and xenon) matrices (XH/NG) at cryogenic temperatures, using a high-resolution simultaneous MCD and absorption spectrometer, MOD4. Experimental problems prevented the study of CH/Xe, NH/Xe, or OH/Xe matrices.

The results were interpreted in terms of a randomly oriented spin-orbit (SO) – crystal-field (CF) model previously developed by workers in this research group. SO and CF parameters were extracted by fitting the resulting data with parameterised equations derived from group-theoretical and quantum-mechanical considerations of the SO-CF model. In the cases of NH and PH, zero-field splitting (ZFS) parameters were also extracted. The SO-CF model worked well for CH, NH, and PH, but was found to fail for OH and SH.

Trends in the parameters of XH with varying noble-gas host were attributed to the external heavy-atom effect and/or motional effects within the matrix.

Preliminary attempts have been made to interpret spectral structure in terms of free or hindered rotation of the guest radicals within the host matrix. This has had a degree of success, especially for NH/Ar, however more theoretical work still needs to be done.
Acknowledgements

I thank my supervisor, Associate Professor Bryce Williamson, for his help and advice throughout the duration of my PhD. I have learnt a great deal because of his willingness to share his knowledge and expertise in the experimental and theoretical aspects of spectroscopy.

I also wish to thank Drs Robert Maclagan and Colin Freeman for valuable help.

I am grateful for the help I have received from the mechanical, electronics, and glassblowing workshops. I wish to thank (in no particular order) Steven Graham, Sandy Ferguson, Roger Merryweather, Russell Gillard, Danny Leonard, Geoff Speer, Nick Oliver, Wayne Mackay, Robert McGregor, and Dave MacDonald.

Financial support from the University of Canterbury, in the form of a Doctoral Scholarship, is appreciated.

Finally, I thank my family for all its support.
## Glossary of Acronyms and Terms

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<th>Acronym</th>
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<tr>
<td>A₀</td>
<td>zeroth absorption moment</td>
</tr>
<tr>
<td>@ term</td>
<td>a derivative-shaped MCD dispersion</td>
</tr>
<tr>
<td>AO</td>
<td>atomic orbital</td>
</tr>
<tr>
<td>@ term</td>
<td>a single-signed, temperature-independent MCD dispersion</td>
</tr>
<tr>
<td>B₀</td>
<td>@ term contribution to the zeroth MCD moment</td>
</tr>
<tr>
<td>C₀</td>
<td>@ term contribution to the zeroth MCD moment</td>
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<tr>
<td>c term</td>
<td>a single-signed, temperature-dependent MCD dispersion</td>
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<tr>
<td>CD</td>
<td>circular dichroism</td>
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<tr>
<td>CF</td>
<td>crystal field</td>
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<tr>
<td>CFP</td>
<td>coefficients of fractional parentage</td>
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<tr>
<td>CGC</td>
<td>Clebsch-Gordan coefficient</td>
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<tr>
<td>GOT</td>
<td>great orthogonality theorem</td>
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<tr>
<td>HSCC</td>
<td>high-symmetry coupling coefficient</td>
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<tr>
<td>IN</td>
<td>internuclear axis</td>
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<tr>
<td>irrep</td>
<td>irreducible representation</td>
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<tr>
<td>ISM</td>
<td>interstellar medium</td>
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<tr>
<td>LBW</td>
<td>leg before wicket</td>
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<tr>
<td>LCAO</td>
<td>linear combination of atomic orbitals</td>
</tr>
<tr>
<td>lcp</td>
<td>left circularly polarised</td>
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<tr>
<td>LIA</td>
<td>lock-in amplifier</td>
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<tr>
<td>LOT</td>
<td>little orthogonality theorem</td>
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<td>MCD</td>
<td>magnetic circular dichroism</td>
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<td>MI</td>
<td>matrix isolation</td>
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<tr>
<td>MO</td>
<td>molecular orbital</td>
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<tr>
<td>M₀</td>
<td>zeroth MCD moment</td>
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<tr>
<td>M₁</td>
<td>first MCD moment</td>
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<tr>
<td>MOD4</td>
<td>high-resolution simultaneous MCD/double-beam absorption spectrometer purpose built at the University of Canterbury</td>
</tr>
<tr>
<td>Nd(ODA)₃</td>
<td>Na₃[Nd(ODA)₃].2NaClO₄.6H₂O; a chiral crystal used as a CD calibrant</td>
</tr>
<tr>
<td>PEM</td>
<td>photoelastic modulator</td>
</tr>
<tr>
<td>PLL</td>
<td>phase-locked loop</td>
</tr>
<tr>
<td>PMT</td>
<td>photomultiplier tube</td>
</tr>
<tr>
<td>PSD</td>
<td>phase-sensitive detector</td>
</tr>
<tr>
<td>rcp</td>
<td>right circularly polarised</td>
</tr>
<tr>
<td>RS</td>
<td>rigid shift</td>
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<tr>
<td>RTC</td>
<td>rotation-translation coupling</td>
</tr>
<tr>
<td>SO</td>
<td>spin-orbit</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
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<td>--------------</td>
<td>------------------------------------------</td>
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<tr>
<td>SOC</td>
<td>spin-orbit coupling</td>
</tr>
<tr>
<td>SO-CF</td>
<td>spin-orbit + crystal-field</td>
</tr>
<tr>
<td>SS</td>
<td>spin-spin</td>
</tr>
<tr>
<td>S/N</td>
<td>signal-to-noise</td>
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<tr>
<td>UV</td>
<td>ultra-violet</td>
</tr>
<tr>
<td>VCC</td>
<td>vector coupling coefficient</td>
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<tr>
<td>WET</td>
<td>Wigner-Eckart theorem</td>
</tr>
<tr>
<td>ZFS</td>
<td>zero-field splitting</td>
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Appendix A: Matrix Elements of Angular Momentum Operators ................ A-1
1 Introduction

1.1 Outline

This research follows on from the work of Vaughan Langford,1-4 who measured the temperature and magnetic-field dependencies of the electronic magnetic-circular-dichroism (MCD) and absorption spectra of CH, NH, and OH isolated in argon matrices (XH/Ar). His results were interpreted in terms of a spin-orbit plus crystal-field (SO-CF) model, and provided insights into the extent of guest-host interactions in the matrix. However, he reached no definitive conclusions as to the mechanism by which host atoms perturb the electronic structure of the guest radical. A generalised description of Langford’s findings follows.

Table 1.1: Transitions for XH (X = C, N, O) with wavelengths for gas-phase transitions.

<table>
<thead>
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<th>XH</th>
<th>Transition</th>
<th>Wavelength</th>
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<tr>
<td>CH</td>
<td>A2Δ ← X2Π</td>
<td>430 nm</td>
</tr>
<tr>
<td></td>
<td>B2Σ− ← X2Π</td>
<td>389 nm</td>
</tr>
<tr>
<td>NH</td>
<td>A3Π ← X3Σ−</td>
<td>336 nm</td>
</tr>
<tr>
<td>OH</td>
<td>A2Σ+ ← X2Π</td>
<td>308 nm</td>
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</tbody>
</table>

The transitions investigated by Langford are listed in Table 1.1, along with the gas-phase wavenumbers of their origin bands. The main point of Langford’s SO-CF model is that spin and orbitally degenerate (Π, Δ, Φ...) states are simultaneously susceptible to SO coupling and CF effects in condensed phases. Since the corresponding operators do not commute, they have competing effects. To disentangle them, as many data as possible must be gathered. To this end, Langford simultaneously measured the MCD and double-beam absorption spectra over a range of temperatures and magnetic fields. He quantified the spectra using moment analysis (Section 4.2) with zeroth and first spectroscopic moments and then fitted the resulting data with parameterised equations derived from group-theoretical and quantum-mechanical considerations of the SO-CF model. In the case of A3Π ← X3Σ− for NH/Ar, where the orbital degeneracy is in the excited state, he resorted to more explicit methods of spectral simulation and comparison with experiment, finding that the only reasonable explanation was that NH undergoes essentially free rotation in its ground state, but not in its excited state.1-4 He also concluded that CH1-3 and OH1-2 in
Ar do not undergo rotation in any of their states. Langford’s conclusions were empirical and he did not attempt to explain any trends or the mechanisms by which they came about.

The original aim of this work was to augment the experimental results from Langford’s work with MCD and absorption data on CH, NH, and OH in krypton and xenon matrices, and the diatomic hydrides of the next row of the periodic table (SiH, PH, and SH) in all three matrix hosts (Ar, Kr, Xe). It was envisaged that a comprehensive model would be developed which would rationalise the differences between gas-phase and matrix, different isotopomers, different hosts, and different guests.

Preliminary experiments in this research were performed using the helium-refrigerator/electromagnet system (Section 6.2.1) in order to optimise matrix-deposition conditions, before higher-quality data were obtained using the matrix-injection system (Section 6.2.2), which requires copious quantities of liquid helium. The success of this approach assumes that optimum deposition conditions in the two systems are similar. Typically, this was not found to be the case. Some experiments that worked perfectly on the refrigerator/electromagnet setup (after much practice), were either of limited success or fail completely on the matrix-injection system. This was not helped by the fact that only five of these so-called “helium runs” could be carried out due to the cost of the cryogenic fluid. Langford\(^1\) also noticed these problems to a lesser extent during his investigations, particularly in the case of CH/Ar production where he observed OH impurities in the matrix on two separate experimental runs. He concluded that, “It seems apparent that water contamination is a major problem in the matrix injection system, probably due to condensation onto cool surfaces which are not readily outgassed before the sample is prepared.” Of the systems originally intended for research, only CH/Kr, NH/Kr, OH/Kr, PH/Ar, PH/Kr, PH/Xe, SH/Ar, SH/Kr, and SH/Xe could be analysed using the matrix-injection system.

The major drawbacks of this research project were the cost of liquid helium and the lack of resources. In New Zealand it costs about $50 to buy enough He gas to obtain one liquid litre. Typically a helium run costs about $1000, even when most of the helium is recovered. In USA, twenty times as many helium runs could easily have been carried out for a similar cost. Although New Zealand is not the ideal place to be doing this sort of research, lack of resources also plays a key role.
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Helium runs commenced in April 2001 after much preparatory work, however they were cut short that year because the helium budget had been ‘blown’, before resuming again in mid-2002. At this late stage in the candidate’s PhD it was not deemed appropriate to spend the additional time required to remedy the experimental problems, since they were unlikely to have been overcome without access to more liquid helium and a radical overhaul of the matrix-injection system.

It was also expected that Langford’s models would hold up to the new experiments undertaken as part of this research. This was largely the case for CH, NH, and PH, however significant problems started to appear when the SO-CF model gave unrealistic interpretations for data obtained on OH/Kr and SH/Ar. SH/Kr and SH/Xe had similar problems, and an experimental reinvestigation of OH/Ar produced different results from those obtained by Langford.\(^1\)\(^,\)\(^2\) For this reason, the candidate attempted to use a hindered-rotor model to explain the data. This had only limited success in the cases of OH and SH, however a purely rotational model had the greatest success for NH/Ar. These rotational simulations ignore centrifugal distortion, \(\Lambda\)-type doubling, spin uncoupling, and other higher-order effects\(^5\) because they can not be resolved in this work and are usually weak at the temperatures investigated.

1.2 Diatomic Radical Monohydrides

All six hydride radicals CH (methylidyne), NH (imidogen), OH (hydroxyl), SiH (silylidyne), PH (phosphinidene), and SH (mercapto) are well characterised in the gas phase,\(^5\) however their spectra in condensed phases are less well understood. In fact, matrix-isolated MCD spectra of SiH, PH, and SH have never been reported before, and reports of the matrix-isolated absorption spectra of SH\(^6\),\(^7\) and SiH\(^8\),\(^9\) are few.

These radicals are generally produced in high-energy processes such as electrical discharges or through vacuum-ultraviolet (VUV) photolysis. CH, NH and OH are the more common and important in terrestrial environments, being involved in a range of chemical reactions, e.g. the combustion of organic materials.\(^10\) On Earth, OH is the most important, being involved in many reactions in the atmosphere, even to sea level.\(^11\) It is the dominant oxidant in the troposphere, and is also responsible for 20% of the natural ozone loss.

All six monohydrides have been observed in extraterrestrial environments.
CH, NH, OH,\textsuperscript{12} and SH\textsuperscript{13} have all been detected in the interstellar medium, where their lifetimes are extended because of the very low particle concentrations. All have also been detected in the atmospheres of stars.\textsuperscript{13-21} Understanding the Zeeman effect of such diatomic molecules can help in the diagnosing of solar and stellar magnetic fields.\textsuperscript{22}

\section*{1.3 Literature Review}

The literature on CH, NH, and OH spectroscopy has been extensively reviewed by Langford\textsuperscript{1} and Rose,\textsuperscript{23} and so this chapter contains only cursory summaries for these cases. More detailed information is provided for SiH, PH, and SH.

\subsection*{1.3.1 Methylidyne (CH)}

Spectroscopic investigations of gas-phase CH are summarised by Herzberg and Huber.\textsuperscript{5} The most important work was carried out by Veseth \textit{et al.} in 1973.\textsuperscript{24} By re-analysing earlier experimental data, they were able to obtain molecular parameters and term values to a much greater precision than had been achieved previously.

Matrix-isolated CH and CD radicals, trapped in Kr, were first observed by Robinson and McCarty in 1960.\textsuperscript{25} CH/Ar was first investigated by Keyser,\textsuperscript{26} who assigned some of the structure in the \( B^{2}\Sigma^{-} \) and \( C^{2}\Sigma^{+} \leftarrow X^{2}\Pi \) bands to free rotation. Rose\textsuperscript{23} obtained the first MI-MCD data for CH/Ar and tried to interpret it using a rotational model.

Langford’s investigation of CH/Ar\textsuperscript{1,3} indicated that the CH guest molecules are randomly oriented and non-rotating. He found that there was a substantial quenching of the orbital angular momentum of the CH ground-state term, which was interpreted as resulting from a CF interaction with the surrounding Ar atoms. The fact that any MCD is observed at all is a direct consequence of the CF, which mixes the higher \( \Pi_{3/2} \) level into the lower, magnetically inactive \( \Pi_{1/2} \) level. Spectral structure was assigned to site and/or phonon effects.

\subsection*{1.3.2 Imidogen (NH)}

Eder first observed the \( A^{3}\Pi \leftarrow X^{3}\Sigma^{-} \) transition of NH in the late 19th
century. Subsequent studies by Funke, Dixon, and Veseth provided spectral assignments and various molecular parameters. Herzberg and Huber summarise many of the important studies of gas-phase NH.

McCarty and Robinson first trapped NH in an Ar matrix in 1958, and the following year published a comprehensive article on the electronic absorption spectra of NH and ND isolated in rare-gas matrices (Ar, Kr and Xe). They concluded that NH and ND undergo nearly free rotation in rare-gas lattices. By probing the vibrational relaxation of NH and ND in Ar and Kr matrices in 1975, Bondybey and Brus concluded that this near-free rotation only occurs in the $X^3\Sigma^-$ ground state, whilst in the $A^3\Pi$ state the guest undergoes libration. Lund et al. reported the first MI-MCD data for NH/Ar and NH/Xe. Rose later reinvestigated NH/NG and tried to interpret it using a rotational model.

Langford's investigation of NH/Ar indicated that the NH radicals undergo essentially free rotation in the ground state, with only the lowest rotational level being effectively populated at the temperatures investigated; but rotation is strongly hindered in the excited state. Spectral structure was attributed to excited state SO-CF splittings and couplings with librational modes and/or lattice phonons.

1.3.3 Hydroxyl (OH)

The UV emission spectrum due to the $2\Sigma^+ \rightarrow 2\Pi$ transition of OH had been observed for many years in electric discharges through water vapour or moist H₂ or O₂ before it was finally assigned by Watson in 1924 to OH. There has been a multitude of studies into gas-phase OH, the most important ones being summarised by Herzberg and Huber.

Robinson and McCarty made the first study of the $A^2\Sigma^+ \leftarrow X^2\Pi$ transition of OH trapped in an Ar matrix in 1958. Later studies of OH trapped in Kr and Xe showed similar fine structure, however this could not be assigned to guest rotation. The slight change in structure between OH and OD trapped in such matrices suggested that any such rotation would have to be strongly perturbed. Studies of OH/Ne and OD/Ne by Tinti and Brus and Bondybey showed appreciable isotopic variation, suggesting that the guest radicals undergo essentially free rotation. These observations were later explained using a model in which one Ar/Kr/Xe nearest neighbour forms a strongly bound linear complex with OH. There is minimal
interaction between Ne and OH. Rose\textsuperscript{23} obtained the first MI-MCD data and tried to interpret it using a rotational model.

Langford's investigation of OH/Ar\textsuperscript{1,2} indicated that the OH guest molecules are randomly oriented and non-rotating. He found that a reduction of the orbital angular momentum of the lowest electronic level of OH, which was interpreted as resulting from a CF interaction with the surrounding Ar atoms, was necessary to explain the data. Spectral structure was assigned to site effects.

1.3.4 Sillylidyne (SIH)

The spectrum of SiH was first observed in gas-phase emission, when a previously unrecorded band (410 – 420 nm) was observed by Professor A. Fowler on the photograph of a vacuum-arc spectrum of silicon in 1919 (cited in reference 44). He considered that it was probably due to SiH. In 1921, Prof. Wood (cited in reference 44), during his work on the hydrogen spectrum, observed a band of similar appearance and thought it was probably due to a compound of Si and H. The wavelengths of the main lines agreed well with Fowler’s, although the spectra obtained by the earlier worker contained more lines (due to SiN). The lines on Wood’s plate are now attributed solely to SiH with a strong head at 411.69 nm. Soon after, C. V. Jackson\textsuperscript{44} showed that Wood’s lines were due to a \( ^2\Delta - ^2\Pi \) transition. A. E. Douglas\textsuperscript{45} published a more thorough investigation of the emission spectrum of SiH in 1957.

In 1965, R. D. Verma\textsuperscript{46} published gas-phase absorption spectra for SiH (and SiD) prepared by flash photolysis in a tube of phenylsilane and hydrogen (\( \text{C}_6\text{D}_5\text{SiD}_3 \) and D\(_2\) for SiD) in a ratio of 1:50. Two new transitions were found. In addition to the previously known \( A \ ^2\Delta - X \ ^2\Pi \) transition, he found the \( B \ ^2\Sigma^+ - X \ ^2\Pi \) and the \( D \ ^2\Delta - X \ ^2\Pi \) transitions at 325 and 205 nm respectively. The \( B \) system is weak and the \( D \) system is diffuse due to strong predissociation, which is less pronounced for SiD.

In 1969, G. Herzberg \textit{et al.}\textsuperscript{47} found another transition near 190.7 nm in flash discharges through 1:50 mixtures of silane in hydrogen. This was assigned to the \( E \ ^2\Sigma^+ - X \ ^2\Pi \) transition.

In 1970 D. E. Milligan and M. E. Jacox\textsuperscript{8} trapped the products of the VUV photolysis of silane trapped in an argon matrix at 4 K and measured the IR and UV spectra. This study was more concerned with identifying the photolysis products (Si\(_2\),
SiH, SiH₂, and SiH₃) than with any rigorous spectroscopic analysis. An IR absorption pattern between 1950 and 2050 cm⁻¹ was attributed to SiH, but this was not conclusive. There was very little basis for assigning any UV absorption bands to SiH. However, they somehow concluded that the argon matrix leads to stabilisation of appreciable concentrations of Si₂, SiH₂, and SiH₃ and, almost certainly, of SiH.

In 1986, A. Lloret and L. Abouaf-Marguin⁹ published a paper in which products from a low-pressure silane plasma formed in a hot-cathode discharge were trapped in an argon matrix. (The study of plasma neutral fragments is of great importance to the growth and properties of thin films.) Once again SiH was trapped but spectroscopic methods (IR) were used only to identify its presence rather than to characterise its spectrum.

1.3.5 Phosphinidene (PH)

The gas-phase emission spectrum of PH at 340 nm was first reported by Geuter⁴⁸, ⁴⁹ in 1907 in an account of an investigation of spectra associated with phosphorus and obtained from a discharge tube containing phosphorus and hydrogen. The data were not good enough for detailed analysis of the fine structure of the band.

In 1930, R. W. B. Pearse⁴⁸ reinvestigated the 340-nm band using Geuter’s method of PH production, obtaining much better spectra by using a grating with higher dispersion. He was able to attribute the band to PH and assign it to a ³Π → ³Σ transition. In 1939, with M. Ishaque,⁵⁰ he made a study of the changes in the band structure when H was replaced by D, and found that the ³Σ-type ground state must be ³Σ⁻.

In 1968, A. E. Douglas and W. J. Balfour⁵¹ published a paper on the absorption spectrum of PH produced from a high-current pulsed discharge through a trace amount of phosphine in argon. They observed three new band systems – two from a previously unobserved a ¹Δ state, and a third attributed to B ³Π → X ³Σ⁻ at 143.5 nm (weak).

1.3.6 Mercapto (SH)

Until 1939, SH was the only hydride in the first two rows, with the exception of the noble-gas hydrides, whose spectrum had not been observed. M. N. Lewis and J. U. White⁵² reported the gas-phase absorption spectrum of SH in a pulsed radio-
frequency discharge through H₂S in 1939, after years of unsuccessful attempts by various investigators to observe the spectrum in emission. They observed one band, at 323.7 nm, which they assigned as $^2\Pi_{1} - ^2\Sigma$.

SH and SD were first studied by high resolution absorption spectroscopy in 1952 by D. A. Ramsay and co-workers. The radicals were produced by irradiation of H₂S or D₂S in a flash photolysis apparatus and the absorption spectrum recorded photographically. In addition to providing molecular parameters, it was discovered that the vibrationally excited states undergo rapid predissociation.

In 1966 B. A. Morrow reinvestigated the absorption spectra of SH and SD obtained by flash photolysis of H₂S/D₂S in the vacuum ultraviolet and found seven new electronic transitions between 123 and 200 nm. In addition to the $A^2\Sigma^+ - X^2\Pi$ (324 nm) transition, he observed transitions from the ground state to the following excited states: $B^2\Sigma, C^2\Delta, D^2\Delta, E^2\Sigma, F^2\Delta, G^2\Delta, H^2\Delta$. The $D, F, G,$ and $H$ states fit well into a Rydberg series, and were assigned to Rydberg states.

The first matrix-isolation (MI) absorption spectra of the SH and SD radicals were published in 1970 by N. Acquista and L. J. Schoen. They employed photolysis of H₂S or D₂S during deposition and trapped the radicals in argon matrices at 20.4 K. Further matrix work has since been conducted by L. Khriachtchev et al. in an investigation of the kinetics of the photolysis of H₂S in matrices of Ne, Ar, Kr and Xe. SH was observed using time-resolved luminescence methods and Fourier-transform IR spectroscopy, and it was found that their behaviour in these matrices resembled the tendencies for OH radicals.

1.4 Thesis Layout

Chapters 2 and 3 relate to the theoretical background required to understand the analysis of the data. Chapter 2 concerns the relationship between quantum mechanics, group theory, and angular momentum, while Chapter 3 delves into the construction of electronic and rotational wavefunctions for the diatomic radicals considered in this thesis.

Chapter 4 provides details on MCD and moment analysis, whereas Chapter 5 contains information on matrix isolation, including the external heavy-atom effect and the crystal-field hindered-rotor model for a diatomic molecule in a noble-gas matrix. Chapter 6 presents the experimental details for the MI-MCD conducted during this
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research, including a description of the spectrometer and the methods of sample preparation.

The main body of the thesis is encompassed by chapters 7, 8 and 9, where experimental data are presented, along with their analysis and interpretation, for the radicals within each periodic group; CH/(SiH), NH/PH and OH/SH, respectively. Each of these main chapters is intended to stand by itself to some degree so that future workers will not need to read the whole thesis in order to obtain the information they desire. This leads to a small amount of repetition for those reading the entire thesis.

The final chapter presents a synopsis of the conclusions from 7-9, presenting them in a coherent fashion and allowing the common trends to be identified and rationalised within the models that have been used. The potential of the hindered-rotor model is discussed and a summary for future work is presented. Also provided are details of how some of the practical problems encountered during this research might be overcome by future workers in the field.

1.5 References

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2 General Theory

This chapter contains a generalised overview of the theory necessary for the understanding of this thesis. Information largely comes from references 1-10, with additional references given where applicable. The theory is presented in a logical manner on the topics of quantum mechanics, group theory, angular momentum, vector-coupling coefficients, transformations under rotation, Wigner rotation matrices, rigid rotors, the Wigner-Eckart theorem, and the derivation of electronic matrix elements.

2.1 Quantum Mechanics

In classical mechanics, physical observables are represented by functions and parameters, but in quantum mechanics they are represented by quantum-mechanical operators, which act on wavefunctions. Generally, in quantum mechanics, one wishes to calculate integrals (sometimes called matrix elements) of the form

\[ I = \int \psi_i^* \Theta \psi_j \, d\tau = \langle \psi_i | \Theta | \psi_j \rangle \]  

(2.1)

where \( \psi_j \) is a wavefunction, \( \Theta \) is an operator, and \( \psi_i^* \) indicates the complex conjugate of \( \psi_i \). Eq. (2.1) represents the overlap integral of \( \psi_i \) with the outcome of \( \Theta \psi_j \), where \( d\tau \) is the volume element of the coordinates over which the integration is carried.

The expression on the right of Eq. (2.1) is written in the Dirac bra-ket notation. \( |\psi_j\rangle \) is a ket denoting the state with wavefunction \( \psi_j \), and \( \langle \psi_i | \) is a bra denoting the complex conjugate of \( \psi_i \). When connected by an operator, as in Eq. (2.1), integration is implied. Another way of thinking about this is that the bra and ket represent vectors in the Hilbert space that defines all possible states of a system. The ‘matrix element’ is then the scalar product of the vector representing \( \psi_i \) and that representing the action of \( \Theta \) on \( \psi_j \).

An experimental measurement yields an observable which is the eigenvalue of a corresponding eigenvalue equation.
The function \( \psi_i \) is said to be an eigenfunction, \( |\psi_i\rangle \) is an eigenvector, and \( \omega_i \) is its corresponding eigenvalue.

Each operator normally has many eigenvalues, which are usually chosen to be orthonormal. In the Hilbert-space model, this means that they are at 'right angles' to each other (orthogonal) and of unit length (normalised). Mathematically, this can be expressed as

\[
\int \psi_i^* \psi_j \, d\tau \equiv \langle \psi_i | \psi_j \rangle = \delta_{ij}
\]  

(2.3)

where \( \delta_{ij} = 1 \) when \( i = j \), and \( \delta_{ij} = 0 \) otherwise. The corresponding matrix elements reduce to

\[
\langle \psi_i | \mathcal{O} | \psi_j \rangle = \omega_i \delta_{ij}
\]  

(2.4)

In order for \( \omega_i \) to be real, \( \mathcal{O} \) must be linear and Hermitian. A linear operator has the properties

\[
\mathcal{O}(\psi_i + \psi_j) = \mathcal{O}\psi_i + \mathcal{O}\psi_j
\]  

(2.5)

\[
\mathcal{O}(c \psi_i) = c \mathcal{O}\psi_i
\]  

(2.6)

where \( c \) is a constant. Hermitian operators have the property

\[
\langle \psi_i | \mathcal{O} | \psi_j \rangle = \langle \psi_j | \mathcal{O} | \psi_i \rangle^*
\]  

(2.7)

The central quantum-mechanical problem in the study of molecules is finding the solution of the time-independent Schrödinger equation.

\[
\mathcal{H}\psi_n = E_n \psi_n
\]  

(2.8)
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Here $\mathcal{H}$ is the (Hermitian) Hamiltonian operator, $E_n$ is the energy (eigenvalue) of the $n$th state, and $\psi_n$ is the corresponding stationary state wavefunction (eigenfunction). The full set of such eigenfunctions is complete, meaning that any continuous function of the system with the same boundary conditions can be expanded as an infinite series in the $\psi_n$.

2.2 Commutators

Two operators are said to commute if the outcome of their successive operation on an arbitrary function $\phi$ is independent of the order in which they are applied; that is, for two operators $A$ and $B$

$$AB\phi = BA\phi \quad (2.9)$$

For this purpose we define the commutator

$$[A, B] = AB - BA \quad (2.10)$$

For observables $a$ and $b$ (respectively, eigenvalues of $A$ and $B$) to be simultaneously measurable, $A$ and $B$ must commute, that is, $[A, B] = 0$. In such a case it is possible to find a complete set of functions that are simultaneously eigenfunctions of both operators. If two functions belong to different eigenvalues of $A$

$$A\phi_i = a_i\phi_i \quad A\phi_j = a_j\phi_j \quad a_i \neq a_j$$

then

$$\langle \phi_i | B | \phi_j \rangle = 0 \quad (2.11)$$

where $B$ is any operator that commutes with $A$.

If an operator commutes with the Hamiltonian operator, $\mathcal{H}$, its eigenvalues are said to be good quantum numbers because all matrix elements of $\mathcal{H}$ connecting functions associated with different quantum numbers are necessarily zero. A couple of important operators that commute with $\mathcal{H}$ are $J^2 = \mathbf{J} \cdot \mathbf{J}$ (the square of the total
angular momentum) and $J_z$ (the projection of $J$ onto the laboratory $Z$-axis, defined by the direction of a magnetic or electric field).

The full set of *good* quantum numbers (corresponding to the largest set of mutually commuting operators) represents the maximum information that can be known about a quantum-mechanical system. Measuring another variable associated with an operator that does not commute will introduce uncertainty into at least one of the variables already measured.

### 2.3 Group Theory

For a molecule, $\mathcal{H}$ contains potential- and kinetic-energy operators to represent the interactions between, and the dynamics of, the electrons and nuclei. In nearly all cases it is impossible to solve the Schrödinger equation exactly, but group-theoretical techniques can provide means of vastly simplifying the task of obtaining a satisfactory approximation.

#### 2.3.1 Groups

A set $\mathcal{S}$ of operations or elements $a, b, c, \ldots$ forms a group if the following requirements are satisfied.

1. The *product* of any two elements also belongs to the set:
   
   If $a \in \mathcal{S}$ and $b \in \mathcal{S}$, then $ab \in \mathcal{S}$

2. The set contains an *identity* (unit) element, $E$, such that
   
   If $a \in \mathcal{S}$, then $EA = AE = a$

3. Each element, $a$, has an *inverse*, $a^{-1}$, which also belongs to $\mathcal{S}$:
   
   If $a \in \mathcal{S}$ then $a^{-1} \in \mathcal{S}$ such that $a^{-1}a = aa^{-1} = E$

4. The product of elements is *associative*
   
   If $a \in \mathcal{S}, b \in \mathcal{S}$, and $c \in \mathcal{S}$, then $a(bc) = (ab)c$

Groups having the additional property that all elements *commute* ($ab = ba$ for any $a$ and $b \in \mathcal{S}$) are called *Abelian groups*. A group $\mathcal{S}_1$ is a *subgroup* of $\mathcal{S}$ if all the symmetry elements of $\mathcal{S}_1$ also occur in $\mathcal{S}$. This is denoted $\mathcal{S} \supset \mathcal{S}_1$ or $\mathcal{S}_1 \subset \mathcal{S}$.
2.3.2 Point Groups

A *symmetry operation* of an object is an operation, such as a rotation or reflection, which leaves the object apparently unchanged. The full set of symmetry operations of a finite spatial object, for example a molecule, satisfies the requirements of a group when multiplication is taken to mean the successive application of symmetry operations. Since all of these symmetry operations necessarily intersect at a single point, such a group is called a *point group*. The number of operations in a point group is called the *group order* and is usually designated $h$. Point groups are classified in several ways:

- Groups having a finite number of elements are said to be finite groups. The point groups for all non-linear molecules are finite.
- Groups having an infinite number of elements are called infinite groups. These include point groups for linear molecules, $C_{nv}$ and $D_{nh}$, the spherical group, $O_3 = R_3$, and the group of all rotations, $SO_3$.
- A cyclic point group is one whose elements are obtained by raising one operation to various powers. Any cyclic group ($C_n$ or $S_n$) is also an Abelian group.

Important point groups which will be used in this thesis are:

- $O_3$ ($= R_3$), the infinite point group, which contains all the symmetry operations of a sphere (rotations and inversions); this is the point group of an atom.
- $SO_3$, the infinite point group of all rotations about all axes through a point; this is a subgroup of $O_3$ (with the centre of inversion removed) and does not represent the symmetry of any real atom or molecule.
- $D_{nh}$, the infinite point group which contains all the symmetry operations of a cylinder; this is the point group of homonuclear diatomic and polyatomic linear molecules.
- $C_{nv}$, the infinite point group which contains all the symmetry operations of a cone; this is the point group of heteronuclear diatomic molecules.
- $SO_2$ ($= C_{nv}$), the infinite point group of all rotations about a single axis ($C_{nv}$ without any mirror planes); as with $SO_3$, this does not represent the symmetry of any real molecule.
• $O_h$, the finite point group with octahedral symmetry.

The relevant group-subgroup chains are:

• $O_3 \supset SO_3 \supset SO_2$
• $O_3 \supset D_{oh} \supset C_{ov} \supset SO_2$
• $O_3 \supset O_h$

Note especially that $SO_2$ is Abelian, and that this fact, along with the subgroup relationships, will have a special importance later on.

### 2.3.3 Classes of a Group

Two elements $a$ and $b$ of the group $\mathcal{G}$ are conjugate to one another if they are related by a third symmetry operation $c$ according to a similarity transformation:

$$b = cac^{-1}$$

(2.12)

The entire group $\mathcal{G}$ can be subdivided into classes such that each class is a set of conjugates of a given element $a$ of the group $\mathcal{G}$. If a given element in $\mathcal{G}$ commutes with all the others, it necessarily forms a class by itself, e.g. the identity $E$.

### 2.3.4 Representatives and Representations

In order to explain the group theoretical concepts of representatives and representations, it is useful to imagine that the functions used to describe some aspect of the system correspond to vectors in a hyperspace, $L$. The number ($n$) of linearly independent (or orthogonal) vectors required to completely describe this space is called the dimension of $L$. In fact any set of $n$ linearly independent vectors will do this, and is said to form a complete basis for the space because any arbitrary vector in space $L$ can be written as a linear combination of the elements of the basis.

The effect of a point-group symmetry operation $R$ acting on the basis vectors of $L$ can be written as an $n$-dimensional square matrix, $D_L(R)$, which carries each vector of $L$ into a linear combination of other vectors of the same space. It turns out that the matrix-multiplication table of matrices $D_L(R)$ duplicates exactly (is
isomorphic with) the multiplication table of the operators $R$. The set of matrices $D_L(R)$ satisfies all the requirements of a group, and is known as a matrix group. Each $D_L(R)$ is a representative of the corresponding operator $R$ and the set of all representatives provides a representation, $\Gamma_l$, of the point group. A representation of a group $\mathcal{G}$ is thus a one-to-one mapping of the elements $R$ onto the operators $D_L(R)$ in the vector space $L$. The basis vectors (and also their corresponding functions) used to construct the representation are said to span or transform as the representation.

There are an infinite number of equivalent representations for a given point group. Furthermore, two sets of basis functions that describe entirely different aspects of the system can transform as the same representative, in which case they are said to have the same symmetry.

2.3.5 Character

All matrix representations that are related by unitary transformations are equivalent. This equivalence is characterised by specifying the traces (sum of the diagonal elements) of the matrices, which are invariant under all unitary transformations. In group theory, this trace is called the character of the representation and is denoted $\chi(R)$. It can be shown that the characters of a representative under operations belonging to the same class are equal and invariant to any similarity transformation of the basis of the representation.

2.3.6 Irreducible Representations

As the result of a suitable unitary transformation, it may happen that space $L$ divides into a number of subspaces, each of which is invariant with respect to all $D(R)$ associated with the point group $\mathcal{G}$. This essentially means that all the functions associated with each invariant subspace are transformed only into combinations of each other, and do not involve functions from other subspaces. In the language of matrices, an irreducible representation, or irrep for short, of a group is a representation for which there exists no unitary transformation (for all $R$) that will simultaneously transform all the matrix representatives into the same minimised (irreducible), block-diagonal form. In general, a reducible representation of dimension $n$ can be reduced into a number of irreps such that the sum of their dimensions is $n$. 
Orthogonality relationships exist between the components of the various irreps. For a group of order $h$ in which $d_l$ indicates the dimensionality of the $l$th irrep, and a representative $D^{(l)}(R)$, the great orthogonality theorem (GOT) can be stated mathematically as

$$\sum_R D^{(l)}_{jk}(R) * D^{(l)}_{mn}(R) = \frac{h}{d_l} \delta_{jl} \delta_{mn} \delta_{kn}$$  \hspace{1cm} (2.13)

A weaker form of this theorem is known as the little orthogonality theorem (LOT),

$$\sum_R \chi_l(R) * \chi_l(R) = h \delta_{ll}$$  \hspace{1cm} (2.14)

The LOT is essentially equivalent to saying that two vectors in the hyperspace are necessarily orthogonal unless they transform as the same irrep, whereas the GOT says, in addition, that two vectors are orthogonal unless they belong to the same row and column of that irrep. In the nomenclature that will be introduced later, they must transform as the same partner. The following properties of irreps can be derived from the two preceding orthogonality theorems.

1. The number of inequivalent irreps of a point group is equal to the number of classes of symmetry operations in the group.
2. The sum of the squares of the dimensions of the inequivalent irreps is equal to the order of the point group.
3. The sum of squared characters for each irrep is equal to the order of the group.
4. The characters of the matrices belonging to the same class are always the same for any representation (reducible or irreducible).
5. The number of times, $a_l$, that the $l$th irrep occurs in the reduced form of reducible representation $\Gamma$ is given (according to the LOT) by

$$a_l = \frac{1}{h} \sum_R \chi_l(R) * \chi(R)$$  \hspace{1cm} (2.15)
where $\chi(R)$ is the character of the irrep under symmetry operation $R$.

6. Every point group has a one-dimensional irrep, known as the totally symmetric irrep, whose basis remains unchanged under all symmetry operations of the group.

Rather than listing all of the representatives for all of the irreps of a point group, it is more convenient to designate them by labels. The basis functions of one-dimensional irreps are trivial and only a single label is required, although sometimes a second label is used to indicate the choice of the arbitrary phase factor. However we need additional labels to specify the basis functions of degenerate irreps – one for the irrep as a whole and one for each row (or column) within the representation. These additional specifiers are called partner labels. Generally, different choices of basis functions are indicated by different sets of partner labels, e.g. $x, y, z$, or $0, \pm 1$.

There are various systems for labelling irreps and their partners, such as the Mulliken\textsuperscript{2},\textsuperscript{11} or Butler systems.\textsuperscript{11} Generally, a function that transforms as the partner $\gamma$ of irrep $\Gamma$ is written in ket form as

$$|\Gamma \gamma\rangle$$

(2.16)

### 2.3.7 Double Groups

"Spin functions", corresponding to half-integral quantum numbers, can be accommodated within group theory by introducing a new operation, $Q$, to the point group, which corresponds to rotation about an axis through an angle $2\pi$. This operation commutes with all other point-group operators, $R$, but has the following peculiar properties:

$$Q \neq E$$

$$Q^2 = E$$

(2.17)

The group is now called a double group because for each $R$, there is another operation $RQ (= QR)$, the corresponding matrices of which have characters of opposite sign to those for $R$.

Double-group irreps come in two types: true (or single-valued) irreps, which correspond with the original point-group irreps, and spin (or double-valued) irreps,
which correspond to half-integral irreps and are represented in Mulliken notation by primes or half-integral subscripts and in Butler notation by half-integers.

2.3.8 Categories of Irreps

When using group theory to simplify quantum mechanical calculations it is useful to classify irreps into three categories according to their behaviour under complex conjugation.\textsuperscript{12}

1. Category-one irreps

Category-one irreps always have real characters and satisfy the relationship

\[ |\Gamma \gamma \rangle^* = |\Gamma \gamma^* \rangle \]  

(2.18)

The basis functions are boson-like (e.g. all orbital and even-spin irreps) and can always be written as a real basis, in which case \( \gamma = \gamma^* \). However, it is often very useful (for example when evaluating angular momenta) to transform to a complex basis for which \( \gamma \) and \( \gamma^* \) are not necessarily the same.

2. Category-two irreps

Category-two irreps also have real characters and satisfy Eq. (2.18). However the fermion-like basis functions (e.g. all odd-spin irreps) can never be rewritten in real form. Examples of these include degenerate spin functions such as \( |\frac{1}{2} \pm \frac{1}{2} \rangle \), which are referred to as Kramers doublets.

3. Category-three irreps

Category-three irreps satisfy the relationship

\[ |\Gamma \gamma \rangle^* = |\Gamma^* \gamma^* \rangle \]  

(2.19)

where \( \Gamma \neq \Gamma^* \) and \( \gamma \neq \gamma^* \). Like category-two irreps, the basis functions can never be rewritten in real form, but now some of the characters are complex. Category-three irreps are non-degenerate under spatial symmetry operations, but doubly-degenerate under time reversal. These degenerate pairs are known as Kramers pairs.
2.3.9 Ambivalent and Non-Ambivalent Groups

Ambivalent groups contain only category-one and -two irreps. Such groups include O_3 (the spherical group), SO_3 (the group of all rotations), C_{ov}, O_h, and D_4. Non-ambivalent groups – which contain category-three irreps and include C_5, T, S_6, and D_{5d} – will not be encountered in this research.

2.3.10 Chains of Groups

The transformation properties of the partners of a particular irrep are specified by designating a group-subgroup chain for the point group \( \mathcal{G} \) in question, \( \mathcal{G} \supset \mathcal{G}_a \supset \mathcal{G}_b \supset \ldots \supset \mathcal{C}_1 \), where \( \mathcal{G}_b \) is a subgroup of \( \mathcal{G}_a \), which is a subgroup of \( \mathcal{G} \), together with the character tables of each subgroup in the chain. The point group \( \mathcal{C}_1 \) contains only the identity operation (\( E \)) and is the point group with the lowest possible symmetry. In practice, the chain contains no new information, and may therefore be truncated at the first Abelian group \( S_n \) or \( C_n \) (including \( C_{ov} = SO_2 \)), since such groups are associated with only one-dimensional irreps. Chains terminating in \( C_2 \) are necessarily real, while those terminating in \( C_n \) (\( n > 2 \)) are said to be complex. This arises because the characters of all but the single-valued irreps of \( C_n \) are complex, while all those of \( C_2 \) are real. Often \( \mathcal{G} \) can be linked to a given Abelian subgroup via a number of different chains, each of which defines a different basis for \( \mathcal{G} \). The partner labels are determined by tracing the symmetry properties of the basis functions from \( \mathcal{G} \) to the Abelian subgroup. The corresponding functions can be written in ket form with the identifying irrep label first, followed sequentially by the irrep labels along the subgroup chain: thus for \( \mathcal{G} \supset \mathcal{G}_a \supset \ldots \supset \mathcal{G}_b \), the ket would be \( |\Gamma \Gamma_a \ldots \Gamma_b \rangle \). For practical purposes, however, the ket is normally written using the first and last labels \( |\Gamma \Gamma_b \rangle = |\Gamma \gamma \rangle \), where the second label (\( \Gamma_b \equiv \gamma \)) is taken to be the partner label.

2.3.11 Direct Products

The direct product (denoted by \( \otimes \)) of two representations of a group forms a new representation. In effect, the basis functions for the new representation comprise all possible products of the basis functions of the two original representations. If the two initial irreps are \( n \)- and \( m \)-dimensional, then the product representation is \( nm\)-
dimensional. Its characters are simply the products of the corresponding characters of
the initial irreps and it is generally reducible according to Eq. (2.15).

If both sets of basis functions span the same $n$-dimensional irrep, $\Gamma_a$, then
appropriately chosen linear combinations of the $n \times n$ product functions of $\Gamma_a \otimes \Gamma_a$
can be classified according to whether they are symmetric or anti-symmetric with
respect to the interchange of the two corresponding partner labels. Mathematically,

$$\Gamma_a \otimes \Gamma_a \equiv \Gamma_a^2 = [\Gamma_a^2] \oplus (\Gamma_a^2)$$  \hspace{1cm} (2.20)

where the square and round brackets indicate the symmetric and antisymmetric square,
respectively, each of which transforms as a different representation.

### 2.3.12 Application of Group Theory to Quantum Mechanics

The application of group theory to quantum mechanics relies on the fact that,
in the absence of external fields, the molecular Hamiltonian operator commutes with
the elements ($R$) of the point group of the molecule.

$$R \mathfrak{H} = \mathfrak{H} R$$ \hspace{1cm} (2.21)

Restated, this means that the Hamiltonian is invariant under the symmetry operations
of the “group of the Schrödinger equation,” i.e. $\mathfrak{H}$ is a scalar operator and transforms
as the totally symmetric irrep. This is intuitively obvious if one recognises that the
potential and kinetic energies of the electrons and nuclei are unchanged under a
rotation or reflection of the system.

The principal theorem relating group theory to quantum mechanics states that
the eigenfunctions of $\mathfrak{H}$ corresponding to a particular (degenerate) energy level form a
basis for an irrep of the molecular point group. This can be shown by applying the
operation $R$ to both sides of the Schrödinger equation, then invoking Eqs. (2.21) and
(2.8).

$$R \mathfrak{H} \psi_n = R E_n \psi_n$$

$$\mathfrak{H} R \psi_n = E_n R \psi_n$$  \hspace{1cm} (2.22)
Eq. (2.22) shows that if $\psi_n$ is an eigenfunction of $\mathcal{X}$, then $R\psi_n$ is also an eigenfunction with the same eigenvalue.

The most common quantum-mechanical operators are scalar, pseudo-scalar (a scalar which changes sign under inversion), vector, or pseudo-vector operators. These last two cases require special attention. Both have three components; however a true vector, such as position, linear momentum, or electric dipole moment, are antisymmetric (ungerade) with respect to inversion, whereas pseudo-vectors, including angular momenta and magnetic dipole moments, are symmetric (gerade) with respect to inversion. Pseudo-vectors actually transform as rotations about specified axes. The Cartesian components of vectors and pseudo-vectors are related to the complex spherical components by

$$V_{\pm l} = \frac{1}{\sqrt{2}}(V_x \pm i V_y) = \frac{1}{\sqrt{2}} V_\pm$$

$$V_0 = V_z$$

All quantum-mechanical operators have well-defined transformation properties in a given point group, further enhancing the usefulness of group theory to quantum mechanics. Of particular importance in the context of this thesis is the relationship between angular momenta and group theory.

### 2.4 Angular Momentum

According to classical mechanics, a particle of mass $m$ travelling with velocity $v$ has a linear momentum, $p$, given by

$$p = mv$$

and an angular momentum, $l$, about a given reference point of

$$l = r \times p$$

where $r$ is the position vector of the particle with respect to the reference point. The quantum-mechanical linear-momentum operator is
\[ p = -i\hbar \nabla \]  

(2.27)

where \( \nabla \) is the gradient operator

\[ \nabla = \frac{\partial}{\partial x} \hat{x} + \frac{\partial}{\partial y} \hat{y} + \frac{\partial}{\partial z} \hat{z} \]  

(2.28)

and \( \hat{x}, \hat{y}, \) and \( \hat{z} \) are the unit vectors in the \( x, y, \) and \( z \) directions respectively. Therefore the Cartesian components of \( I \) are

\[
\begin{align*}
I_x &= -i\hbar \left( y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right) \\
I_y &= -i\hbar \left( z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right) \\
I_z &= -i\hbar \left( x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right)
\end{align*}
\]  

(2.29)

The functional forms of Eq. (2.29) are appropriate for orbital angular momentum but not for quantum-mechanical spin, which has no functional form. In order to treat both types of angular momentum on an equal footing, it is convenient to define the corresponding pseudo-vector operator in terms of the commutation relations of their Cartesian components. For a generalised angular momentum operator \( J \)

\[ [J_i, J_j] = i\hbar \sum_k \varepsilon_{ijk} J_k \]  

(2.30)

where \( i, j, \) and \( k \) are some combination of \( x, y, \) and \( z. \) \( \varepsilon_{ijk} \) is known as the alternating tensor, the totally antisymmetric third-order tensor, or Levi-Civita density function. It is zero if any two coordinates are repeated, +1 if \( ijk \) is a cyclic permutation of \( xyz, \) or \(-1 \) for a non-cyclic permutation. The standard interpretation of these results is that no more than one component of the angular momentum can be measured simultaneously.

The square of the total angular momentum is
General Theory

\[ \mathbf{J}^2 = \mathbf{J}_x^2 + \mathbf{J}_y^2 + \mathbf{J}_z^2 \]  

(2.31)

It is straightforward to derive the following commutation relations\(^{13}\)

\[ [\mathbf{J}^2, \mathbf{J}_z] = [\mathbf{J}^2, \mathbf{J}_z] = [\mathbf{J}^2, \mathbf{J}_z] = 0 \]  

(2.32)

Hence \( \mathbf{J}^2 \) commutes with all components of \( \mathbf{J} \) and we can construct states \( |jm\rangle \) that are simultaneously eigenfunctions of \( \mathbf{J}^2 \) and one component of \( \mathbf{J} \), which is normally taken to be the \( z \) component. \( \mathbf{J}_x \) and \( \mathbf{J}_y \) can be combined to form the raising and lowering operators, which are given by

\[ \mathbf{J}_x = \mp \sqrt{2} \mathbf{J}_x = \mathbf{J}_x \pm i \mathbf{J}_y \]  

(2.33)

In the convention where angular momentum is measured in units of \( \hbar \), the following matrix elements can be obtained (see Appendix A)

\[ \langle j'm'| \mathbf{J}^2 | jm \rangle = j (j + 1) \delta_{jj'} \delta_{mm'} \]  

(2.34)

\[ \langle j'm'| \mathbf{J}_z | jm \rangle = m \delta_{jj'} \delta_{mm'} \]  

(2.35)

\[ \langle j'm'| \mathbf{J}_x | jm \rangle = [j (j + 1) - m (m \pm 1)]^{1/2} \delta_{jj'} \delta_{m, m' \pm 1} \]  

(2.36)

2.5 Coupling of Two Angular Momenta

Two angular momenta \((j_1, j_2)\) can be coupled to form a third \((J)\). If \(j_1\) and \(j_2\) refer to different physical systems (e.g. two different electrons or atoms) or independent parts of the same system (e.g. the orbital and spin angular momenta of a particle), then they will always commute, thus ensuring that \( \mathbf{J} \) obeys the relations of Eqs. (2.30) and (2.32).

There are two ways to describe such a compound system. In the uncoupled representation, the states \(|j_1m_1, j_2m_2\rangle = |j_1m_1\rangle |j_2m_2\rangle\) are eigenfunctions of the operators \(\mathbf{J}_1, \mathbf{J}_2, \mathbf{J}_{1z}, \) and \(\mathbf{J}_{2z}\). Therefore,

\[ j_1^2 |j_1m_1, j_2m_2\rangle = j_1 (j_1 + 1) |j_1m_1, j_2m_2\rangle \]
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\[ j_z^2 |j_1 m_1, j_2 m_2\rangle = j_2 (j_2 + 1) |j_1 m_1, j_2 m_2\rangle \]
\[ j_z |j_1 m_1, j_2 m_2\rangle = m_1 |j_1 m_1, j_2 m_2\rangle \]
\[ j_{zz} |j_1 m_1, j_2 m_2\rangle = m_2 |j_1 m_1, j_2 m_2\rangle \]  \hspace{1cm} (2.37)

In the coupled representation, the states \( |j_1 j_2 J M\rangle \) are eigenfunctions of \( j_1^2, j_2^2, J^2 \), and \( J_z \), where

\[ J^2 = (j_1 + j_2)^2 \]
\[ J_z = j_{1z} + j_{2z} \]  \hspace{1cm} (2.38)

Therefore the relations corresponding to Eq. (2.37) are

\[ j_1^2 |j_1 j_2 J M\rangle = j_1 (j_1 + 1) |j_1 j_2 J M\rangle \]
\[ j_2^2 |j_1 j_2 J M\rangle = j_2 (j_2 + 1) |j_1 j_2 J M\rangle \]
\[ J^2 |j_1 j_2 J M\rangle = J (J + 1) |j_1 j_2 J M\rangle \]
\[ J_z |j_1 j_2 J M\rangle = M |j_1 j_2 J M\rangle \]  \hspace{1cm} (2.39)

The unitary transformation connecting these representations is given by

\[ |j_1 j_2 J M\rangle = \sum_{m_1 m_2} \langle j_1 m_1, j_2 m_2 | J M \rangle |j_1 m_1, j_2 m_2\rangle \]  \hspace{1cm} (2.40)

The elements of the transformation \( \langle j_1 m_1, j_2 m_2 | J M \rangle \) are vector coupling coefficients (VCC), commonly called the Clebsch-Gordan coefficients (CGC) after the workers who first derived them. In this work (as is normally the case) the phases of these coefficients are chosen so that they are real, in which case the inverse relationship is

\[ |j_1 m_1, j_2 m_2\rangle = \sum_{J M} \langle j_1 m_1, j_2 m_2 | J M \rangle |j_1 j_2 J M\rangle \]  \hspace{1cm} (2.41)

For given \( j_1 \) and \( j_2, J \) must satisfy the triangle condition

\[ j_1 + j_2 \geq J \geq |j_1 - j_2| \]  \hspace{1cm} (2.42)
In classical terms, this can be regarded as the requirement that the three vectors form the sides of a triangle. It can also be understood group-theoretically because \( j_1 m_1 \) and \( j_2 m_2 \) transform as partners of irreps in the basis \( \text{SO}_3 \supset \text{SO}_2 \). When the direct product of the irreps labelled \( j_1 \) and \( j_2 \) is taken, the new representation can be reduced according to Eq. (2.42). From Eq. (2.38) it also follows that

\[
M = m_1 + m_2
\]  

(2.43)

Clebsch-Gordan coefficients can be tabulated for each point group.

An alternative way of documenting VCC is to use *high-symmetry coupling coefficients* (HSCC). These are related to CGC by

\[
\langle j_1 m_1, j_2 m_2 | J M \rangle = H(j_1 j_2 J) (2 J + 1)^{\frac{1}{2}} \begin{pmatrix} J \\ m_1 \end{pmatrix} \begin{pmatrix} j_1 \ j_2 \ J \\ m_1 \ m_2 \ -M \end{pmatrix}
\]  

(2.44)

\[
\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} = H(j_1 j_2 j_3) (2 j_3 + 1)^{\frac{1}{2}} \begin{pmatrix} j_3 \\ -m_3 \end{pmatrix} \langle j_1 m_1, j_2 m_2 | j_3 -m_3 \rangle
\]  

(2.45)

The six-element factors in brackets are called \( 3jm \) coefficients, while the \( 2jm \) phase is defined as

\[
\begin{pmatrix} j \\ m \end{pmatrix} = (-1)^{j-m}
\]  

(2.46)

An additional 'historical' phase factor, \( H(j_1 j_2 j_3) \), is used to make the \( 3jms \) compatible with the historical *Condon-Shortley phases*\(^2\) for VCC in the \( \text{SO}_3 \) point group.

\[
H(j_1 j_2 j_3) = (-1)^{-j_1 + j_2 - j_3} = (-1)^{j_1 - j_2 + j_3}
\]  

(2.47)

The advantage of using \( 3jms \) is that they are tabulated by Butler,\(^1\) and easily calculated using the computer program Racah.\(^1\)\(^4\) Also (and unlike CGC), they put the three angular momentum \( j \) quantum numbers on an equal footing, which permits
simple and symmetric relationships to be drawn between the 3jms that interrelate the same irreps; for example, 3jms are:

1) invariant in a cyclic permutation of the three columns;
2) multiplied by \((-1)^{J_1+J_2+J_3}\) in a permutation of two columns;
3) multiplied by \((-1)^{J_1+J_2+J_3}\) when the signs of \(m_1, m_2, \) and \(m_3\) are simultaneously changed.

For point groups other than \(S_03\), Eq. (2.44) is replaced by

\[
\langle \Gamma_A \gamma_A, \Gamma_B \gamma_B | \Gamma_C \gamma_C \rangle = |\Gamma_C|^{|\frac{1}{2}} \left( \begin{array}{c} \Gamma_C \Gamma_A \Gamma_B \Gamma_C^* \\ \gamma_C \gamma_A \gamma_B \gamma_C^* \end{array} \right)
\]

where \(|\Gamma_C|\) represents the degeneracy of the \(\Gamma_C\) irrep.

Clebsch-Gordan coefficients (and 3jms) can be expressed algebraically\(^1\) and the expressions for those coefficients (in \(S_03 \Rightarrow S_02\)) used in this thesis are contained in Table 2.1.

Table 2.1: Algebraic expressions for common Clebsch-Gordan coefficients in \(S_03 \Rightarrow S_02\).

| \(\langle j m-1,1 | j+1 m \rangle\) | \(\frac{(j + m)(j + m + 1)}{(2j + 1)(2j + 2)}\) |
| \(\langle j m-1,1 | j m \rangle\) | \(-\frac{(j + m)(j - m + 1)}{2j(j + 1)}\) |
| \(\langle j m-1,1 | j-1 m \rangle\) | \(\frac{(j - m)(j - m + 1)}{2j(2j + 1)}\) |
| \(\langle j m,0 | j+1 m \rangle\) | \(\frac{(j - m + 1)(j + m + 1)}{(2j + 1)(j + 1)}\) |
| \(\langle j m,0 | j m \rangle\) | \(\frac{m}{j(j + 1)^{\frac{1}{2}}}\) |
| \(\langle j m,0 | j-1 m \rangle\) | \(-\frac{(j - m)(j + m)}{j(2j + 1)}\) |
| \(\langle j m+1,1 | -j+1 m \rangle\) | \(\frac{(j - m)(j - m + 1)}{(2j + 1)(2j + 2)}\) |
| \(\langle j m+1,1 | j m \rangle\) | \(\frac{(j - m)(j + m + 1)}{2j(j + 1)}\) |
| \(\langle j m+1,1 | -j-1 m \rangle\) | \(\frac{(j + m + 1)(j + m)}{2j(2j + 1)}\) |
2.6 Transformations under Rotation

2.6.1 Unitary Transformations

If a linear transformation $U$ acts upon the function $|\psi_i\rangle$ of a system, it is (generally) changed into a new function $|\psi_f\rangle$

$$|\psi_f\rangle = U|\psi_i\rangle$$

(2.49)

It follows that

$$\langle \psi_i|\psi_f\rangle = \langle \psi_i|U^\dagger U|\psi_i\rangle$$

(2.50)

where $U^\dagger$ is the adjoint (transposed complex conjugate) of $U$. In order for the lengths of the vectors and the angles between any two of them to be the same in each vector space, we require that

$$U^\dagger = U^{-1}$$

(2.51)

since

$$U^{-1}U = I$$

(2.52)

where $I$ is the identity operator. Transformations that satisfy Eq. (2.51) are said to be unitary. It is important to know how operators change under unitary transformations. Let us define a matrix element, $Q_{ij}$

$$Q_{ij} = \langle \psi_i|Q|\psi_j\rangle$$

(2.53)

Using Eqs. (2.51) and (2.52), Eq. (2.53) can be rewritten as

$$Q_{ij} = \langle \psi_i|U^\dagger UQU^\dagger U|\psi_i\rangle = \langle \psi_i|QUQ^\dagger |\psi_i\rangle = Q'_{ij}$$

(2.54)

Therefore, a unitary transformation transforms an operator $Q$ into

$$Q' = QUQ^\dagger = UQU^{-1}$$

(2.55)
2.6.2 Rotations

A rotation is a unitary transformation that can be viewed in two ways. One can rotate the coordinate frame (passive rotation), keeping fixed each part of the physical system and its associated physical quantities, or one can rotate the physical system (active rotation), keeping the axes fixed. Whether we rotate the axes, or the physical system in the opposite direction, amounts to exactly the same thing. Thus, for a system of \( N \) particles, the wavefunction \( \psi(\mathbf{r}^{(1)}, \mathbf{r}^{(2)}, \ldots, \mathbf{r}^{(N)}) \) transforms under the rotation \( \mathcal{R} \) as

\[
\mathcal{R} \left[ \psi(\mathbf{r}^{(1)}, \ldots, \mathbf{r}^{(N)}) \right] = \psi(\mathbf{r}^{-1}^{(1)}, \ldots, \mathbf{r}^{-1}^{(N)}) = R \psi(\mathbf{r}^{(1)}, \ldots, \mathbf{r}^{(N)})
\]

(2.56)

where \( R \) is the unitary operator associated with \( \mathcal{R} \). This thesis uses a right-handed coordinate system. A positive rotation is defined so that it carries a right-handed screw in the positive direction (forward) along the axis of rotation.

2.6.3 Infinitesimal Rotations

Consider the positive rotation, \( \mathcal{R}_e(\alpha) \) by an angle \( \alpha \) about the \( z \)-axis, acting on the function \( \psi(x, y, z) \)

\[
\mathcal{R}_e(\alpha) \left[ \psi(x, y, z) \right] = \psi(x \cos \alpha + y \sin \alpha, -x \sin \alpha + y \cos \alpha, z)
\]

(2.57)

For an infinitesimal rotation \( (\alpha = \varepsilon) \),

\[
\mathcal{R}_e(\varepsilon) \left[ \psi(x, y, z) \right] = \psi(x + \varepsilon y, -x - \varepsilon y, z) + \varepsilon \left( \frac{\partial \psi}{\partial x} - x \frac{\partial \psi}{\partial y} \right)
\]

\[
= (1 - i \varepsilon \mathbf{J} \cdot \mathbf{L}) \psi(x, y, z)
\]

(2.58)

where a truncated Taylor's series expansion has been used in the second step, Eq. (2.29) (in units of \( \hbar \)) in the third, and \( \mathbf{J} \) is used to designate the rotational angular momentum of the system as a whole. Hence, the infinitesimal rotation operator has the form
or more generally,

$$R_n(\varepsilon) = 1 - i\varepsilon (J \cdot \hat{n})$$  \hspace{1cm} (2.60)$$

where \(\hat{n}\) is a unit vector along the axis of infinitesimal rotation. The operator \(J \cdot \hat{n}\) is therefore the generator of the infinitesimal rotation about \(\hat{n}\).

### 2.6.4 Finite Rotations

Any finite rotation can be regarded as a series of infinitesimal rotations. The corresponding operator is simply the product of these infinitesimal rotation operators.

$$R_n(\varphi + d\varphi) = R_n(d\varphi) R_n(\varphi) = \{1 - i(J \cdot \hat{n}) \, d\varphi\} R_n(\varphi)$$  \hspace{1cm} (2.61)$$

A Taylor's series expansion for \(R_n(\varphi + d\varphi)\) leads to the differential equation

$$\frac{d}{d\varphi} R_n(\varphi) = -i(J \cdot \hat{n}) R_n(\varphi)$$  \hspace{1cm} (2.62)$$

which integrates (using the condition \(R_n(0) = 1\)) to give

$$R_n(\varphi) = \exp\{ -i\varphi(J \cdot \hat{n}) \} = \sum_{n=0}^{\infty} \frac{( -i\varphi(J \cdot \hat{n}) )^n}{n!}$$  \hspace{1cm} (2.63)$$

Since \(R_n(\varphi)\) is unitary, \(J \cdot \hat{n}\) must be Hermitian; that is,

$$\{ -i\varphi(J \cdot \hat{n}) \}^\dagger = \{ i\varphi(J \cdot \hat{n}) \}$$  \hspace{1cm} (2.64)$$

This result shows the important connection in quantum mechanics between Hermitian operators for observables and unitary operators for transformations. \(R_n(\varphi)\) and \(J \cdot \hat{n}\)
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commute, and so the eigenvalues of $J \cdot \hat{n}$ remain unchanged under the transformation $R_n(\phi)$. If

$$(J \cdot \hat{n}) |\psi_\beta\rangle = \lambda |\psi_\beta\rangle$$

then from Eq. (2.63),

$$R_n(\phi) |\psi_\beta\rangle = \sum_{n=0} \frac{(-i\phi\lambda)^n}{n!} |\psi_\beta\rangle = \exp(-i\phi\lambda) |\psi_\beta\rangle$$  \hspace{1cm} (2.65)

$R_n(\phi)$ also commutes with $J^2$

$$[R_n(\phi), J^2] = \sum_{n=0} \frac{(-i\phi)^n}{n!} [(J \cdot \hat{n})^n, J^2] = 0$$ \hspace{1cm} (2.66)

2.6.5 Euler Angles

Using an active rotation of the physical system, the transformation from the $F = X, Y, Z$ (laboratory- or space-fixed) coordinate system to the $g = x, y, z$ (molecule-fixed) one is carried out by means of three successive positive, finite rotations through the Euler angles $\phi, \theta$ and $\chi$:

1. An anticlockwise rotation by $\phi$ about $Z (= z')$, which carries the $Y$ axis into the $y'$ axis.

$$\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = R_2(\phi) \begin{pmatrix} X \\ Y \\ Z \end{pmatrix}$$

where

$$R_2(\phi) = \exp(-i\phi J_2) = \begin{pmatrix} \cos\phi & \sin\phi & 0 \\ -\sin\phi & \cos\phi & 0 \\ 0 & 0 & 1 \end{pmatrix}$$  \hspace{1cm} (2.67)
2. An anticlockwise rotation by $\theta$ about $y'$, which carries the $Z$ axis into the $z\ (= z'')$ axis.

\[
\begin{pmatrix}
  x'' \\
  y'' \\
  z''
\end{pmatrix} = R_y(\theta) \begin{pmatrix}
  x' \\
  y' \\
  z'
\end{pmatrix}
\]

where

\[
R_y(\theta) = \exp(-i\theta J_y) = \begin{pmatrix}
  \cos\theta & 0 & -\sin\theta \\
  0 & 1 & 0 \\
  \sin\theta & 0 & \cos\theta
\end{pmatrix}
\] (2.68)

3. An anticlockwise rotation by $\chi$ about $z$, which carries $y'$ into the $y$ axis.

\[
\begin{pmatrix}
  x \\
  y \\
  z
\end{pmatrix} = R_z(\chi) \begin{pmatrix}
  x'' \\
  y'' \\
  z''
\end{pmatrix}
\]

where

\[
R_z(\chi) = \exp(-i\chi J_z) = \begin{pmatrix}
  \cos\chi & \sin\chi & 0 \\
  -\sin\chi & \cos\chi & 0 \\
  0 & 0 & 1
\end{pmatrix}
\] (2.69)

Figure 2.1: The Euler angles relating the space-fixed coordinate system to the molecule-fixed one. See text for more information.

The overall rotation can be expressed as
\[
\begin{pmatrix}
x \\
y \\
z
\end{pmatrix} = R(\phi, \theta, \chi)
\begin{pmatrix}
X \\
Y \\
Z
\end{pmatrix}
\]  

(2.70)

where

\[
R(\phi, \theta, \chi) = R_\chi(\chi) R_\gamma(\theta) R_\phi(\phi) = \exp(-i\chi J_z) \exp(-i\theta J_y) \exp(-i\phi J_z)
\]  

(2.71)

Eq. (2.71) involves angular momentum operators in two coordinate frames. It can be rewritten in one coordinate frame by making use of Eq. (2.55). \(\exp(-i\theta J_y)\) is the transform of \(\exp(-i\phi J_z)\) under \(\exp(-i\theta J_y)\); \(\exp(-i\chi J_z)\) is the transform of \(\exp(-i\chi J_z)\) under \(\exp(-i\theta J_y)\); and, since \(J_z\) commutes with itself, \(\exp(-i\chi J_z)\) is the transform of \(\exp(-i\chi J_z)\) under \(\exp(-i\phi J_z)\). These can be represented as

\[
\begin{align*}
\exp(-i\theta J_y) &= \exp(-i\phi J_z) \exp(-i\theta J_y) \exp(i\phi J_z) \\
\exp(-i\chi J_z) &= \exp(-i\phi J_z) \exp(-i\chi J_z) \exp(i\phi J_z) \\
\exp(-i\phi J_z) &= \exp(-i\theta J_y) \exp(-i\phi J_z) \exp(i\theta J_y)
\end{align*}
\]  

(2.72)

Inserting these into Eq. (2.71) gives

\[
R(\phi, \theta, \chi) = \exp(-i\phi J_z) \exp(-i\theta J_y) \exp(-i\chi J_z)
\]  

(2.73)

\(R(\phi, \theta, \chi)\) can also be expressed as a matrix.

\[
R(\phi, \theta, \chi) = \begin{pmatrix}
\cos\chi & \sin\chi & 0 \\
-sin\chi & \cos\chi & 0 \\
0 & 0 & 1
\end{pmatrix}
\begin{pmatrix}
\cos\theta & 0 & -\sin\theta \\
0 & 1 & 0 \\
\sin\theta & 0 & \cos\theta
\end{pmatrix}
\begin{pmatrix}
\cos\phi & \sin\phi & 0 \\
-sin\phi & \cos\phi & 0 \\
0 & 0 & 1
\end{pmatrix}
\]

(2.74)

Furthermore, for an arbitrary vector with Cartesian components \(r_F = (r_x, r_y, r_z)\) in the laboratory frame and \(r_g = (r_x, r_y, r_z)\) in the molecule-fixed frame,
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\[ r_F = \sum_g \Phi_{Fg}(\phi, \theta, \chi) r_g \]  \hspace{1cm} (2.75)

and

\[ r_g = \sum_{g'} \Phi_{g'F}(\phi, \theta, \chi) r_F \]  \hspace{1cm} (2.76)

where the \( \Phi_{Fg}(\phi, \theta, \chi) \) is the appropriate direction-cosine matrix elements of \( R(\phi, \theta, \chi) \) in Eq. (2.74) and the \( \Phi_{g'F}(\phi, \theta, \chi) \) are the direction cosine matrix elements of \( R^\dagger(\phi, \theta, \chi) \).

2.6.6 Anomalous Commutation Relations

The axis vectors associated with the three Euler angles can be expressed in terms of the Cartesian unit vectors in the space-fixed frame.

\[ \hat{n}_\phi = \hat{n}_Z \]
\[ \hat{n}_\theta = -\hat{n}_X \sin \phi + \hat{n}_Y \cos \phi \]
\[ \hat{n}_x = \hat{n}_X \sin \theta \cos \phi + \hat{n}_Y \sin \theta \sin \phi + \hat{n}_Z \cos \theta \]  \hspace{1cm} (2.77)

Since

\[ J \cdot \hat{n}_\alpha = -i \frac{\partial}{\partial \alpha} \]  \hspace{1cm} (2.78)

the above equations can be rewritten as

\[ -i \frac{\partial}{\partial \phi} = J_Z \]
\[ -i \frac{\partial}{\partial \theta} = -J_X \sin \phi + J_Y \cos \phi \]
\[ -i \frac{\partial}{\partial \chi} = J_X \sin \theta \cos \phi + J_Y \sin \theta \sin \phi + J_Z \cos \theta \]  \hspace{1cm} (2.79)

These can be solved to obtain
Commutation relations between these angular momentum operators can readily be verified.

\[
\begin{align*}
[J^2, J_x] &= [J^2, J_y] = [J^2, J_z] = [J^2, J_\pm] = 0 \\
[J_z, J_\pm] &= \pm J_\pm \\
[J_+, J_-] &= 2J_z \\
[J_x, J_y] &= iJ_z \\
[J_y, J_z] &= iJ_x \\
[J_z, J_x] &= iJ_y
\end{align*}
\] (2.81)

all of which conform to the conventional quantum-mechanical rules.

Expressions equivalent to Eqs. (2.77) – (2.81) can also be obtained in the molecule-fixed frame, but this time interesting and very important anomalous behaviour is revealed. Starting with the inverse transformation,

\[
\hat{n}_\phi = -\hat{n}_x \sin \theta \cos \chi + \hat{n}_y \sin \theta \sin \chi + \hat{n}_z \cos \theta \\
\hat{n}_\theta = \hat{n}_x \sin \chi + \hat{n}_y \cos \chi \\
\hat{n}_\chi = \hat{n}_z
\] (2.82)

we obtain
\[ \frac{-i \partial}{\partial \phi} = -J_z \sin \theta \cos \chi + J_y \sin \theta \sin \chi + J_z \cos \theta \]
\[ \frac{-i \partial}{\partial \theta} = J_x \sin \chi + J_y \cos \chi \]
\[ \frac{-i \partial}{\partial \chi} = J_z \]

(2.83)

These expressions can be solved to obtain

\[ J_x = -i \cos \chi \left( \cot \theta \frac{\partial}{\partial \chi} + \frac{1}{\sin \theta \partial \phi \partial \chi} \right) + i \sin \chi \frac{\partial}{\partial \theta} \]
\[ J_y = i \sin \chi \left( \cot \theta \frac{\partial}{\partial \chi} + \frac{1}{\sin \theta \partial \phi \partial \chi} \right) - i \cos \chi \frac{\partial}{\partial \theta} \]
\[ J_z = -i \frac{\partial}{\partial \chi} \]
\[ J_\pm = i \exp(\mp i \chi) \left( \left[ \left( \cot \theta \frac{\partial}{\partial \chi} + \frac{1}{\sin \theta \partial \phi \partial \chi} \right) \mp i \frac{\partial}{\partial \theta} \right] \right) \]

(2.84)

\[ J^2 = -\frac{\partial^2}{\partial \theta^2} - \cot \theta \frac{\partial}{\partial \theta} - \frac{1}{\sin^2 \theta} \left( \frac{\partial^2}{\partial \phi^2} + \frac{\partial^2}{\partial \chi^2} - 2 \cos \theta \frac{\partial^2}{\partial \phi \partial \chi} \right) \]

Commutation relations between these angular momentum operators can readily be determined.

\[ [\mathbf{J}^2, J_x] = [\mathbf{J}^2, J_y] = [\mathbf{J}^2, J_z] = [\mathbf{J}^2, J_\pm] = 0 \]
\[ [J_z, J_\pm] = \mp J_\pm \]
\[ [J_z, J_\mp] = -2 J_z \]
\[ [J_x, J_y] = -i J_z \]
\[ [J_y, J_z] = -i J_x \]
\[ [J_x, J_z] = -i J_y \]

(2.85)

The commutation relations of \( J_x, J_y, \) and \( J_z \) are therefore anomalous (compare Eq. (2.85) with (2.81)), differing from the normal commutation rules by a negative sign. All angular momenta describing rotations of the molecule-fixed frame relative to the laboratory frame obey these anomalous commutation relations. This result is
not simply an interesting piece of trivia, and if ignored it can lead to major phase
errors.

In order to apply angular-momentum techniques to molecular problems, the
corresponding operators must be defined with respect to a common centre, have the
same axes of quantisation, and obey the same commutation rules. A simple solution,
and the one adopted in this thesis, is to set the matrix elements of $J_x$ in the molecular
reference frame so that they behave as $J_\tau$ in the laboratory frame. If $\Omega$ is the
component of $J$ along the internuclear axis, then this means that, in the molecule-
fixed frame

$$
\langle J\Omega \mid J_x \mid J\Omega \rangle = [J(J + 1) - \Omega (\Omega \mp 1)]^{1/2} \delta_{J\tau} \delta_{\Omega \Omega \tau} \tag{2.86}
$$

instead of

$$
\langle J\Omega \mid J_x \mid J\Omega \rangle = [J(J + 1) - \Omega (\Omega \pm 1)]^{1/2} \delta_{J\tau} \delta_{\Omega \Omega \tau} \tag{2.86}
$$

The rationale can be seen if we envisage the two frames of reference that can
rotate about a common origin. An observer in one frame, rotating in one sense, will
see the other frame rotating in the opposite sense. This is analogous to reversal of the
time variable from $t$ to $-t$. The time-reversal operator $\Theta$ is antilinear and antiunitary.
An antilinear operator $\theta$ satisfies

$$
\theta(c_1 \psi_i + c_2 \psi_j) = c_1^* \theta \psi_i + c_2^* \theta \psi_j \tag{2.87}
$$

In addition to satisfying Eq. (2.87), an antiunitary operator $\theta$ satisfies

$$
\langle \theta \psi_i \mid \theta \psi_j \rangle = \langle \psi_i \mid \psi_j \rangle^* \tag{2.88}
$$

If $\Theta$ acts on a complex function it gives the complex conjugate of that function. For
angular momentum functions,

$$
\Theta J_\tau \Theta^{-1} = -J_\tau \tag{2.89}
$$

$$
\Theta J_x \Theta^{-1} = -J_x \tag{2.90}
$$
Therefore, all we have to do to relate $J$ in the space-fixed frame to the molecular-fixed one, is to apply time reversal to it, making $J_z$ behave as $J_z$.

### 2.6.7 Wigner Rotation Matrices

A rotation acting on the state $|JM\rangle$ cannot change the value of $J$ (Eq. (2.66)) but it can change $M$. Most generally

$$ R(\phi, \theta, \chi) |JM\rangle = \sum_M \mathcal{D}^J_{JM}(\phi, \theta, \chi) |JM'\rangle $$

(2.91)

The $\mathcal{D}^J_{JM}(\phi, \theta, \chi)$ are coefficients that depend on all of the quantum numbers and angles. Premultiplying Eq. (2.91) by $|JM'\rangle$, we obtain

$$ \mathcal{D}^J_{JM}(\phi, \theta, \chi) = |JM'\rangle R(\phi, \theta, \chi) |JM\rangle $$

(2.92)

$\mathcal{D}^J_{JM}(\phi, \theta, \chi)$ is unitary and referred to as a *Wigner rotation matrix*. An explicit expression for this rotation matrix will permit us to determine the transformations under rotation for any $|JM\rangle$. Using Eq. (2.73), Eq. (2.92) reduces to

$$ \mathcal{D}^J_{JM}(\phi, \theta, \chi) = |JM'\rangle \exp(-i\phi J_z) \exp(-i\theta J_y) \exp(-i\chi J_z) |JM\rangle $$

$$ = \exp(-i\phi M') \mathcal{d}^J_{JM}(\theta) \exp(-i\chi M) $$

(2.93)

where

$$ \mathcal{d}^J_{JM} = |JM\rangle \exp(-i\theta J_y) |JM\rangle $$

(2.94)

The evaluation of $\mathcal{d}^J_{JM}$ is reasonably difficult, but expressions do exist.\(^1\) The work presented in this thesis, however, does not require their explicit evaluation.

It is useful to know the behaviour of $\mathcal{D}^J_{JM}(\phi, \theta, \chi)$ under complex conjugation.

$$ \mathcal{D}^J_{JM}(\phi, \theta, \chi)^* = (-1)^{M'-M} \mathcal{D}^J_{J-M,M}(\phi, \theta, \chi) $$

(2.95)
For integral $J$, the rotation matrices are closely related to the spherical harmonics.

\[
\mathcal{D}^{L}_{M;0}(\phi, \theta, \chi) = \sqrt{\frac{4\pi}{2L + 1}} Y^{*}_{LM}(\theta, \phi) 
\]

(2.96)

\[
\mathcal{D}^{L}_{M;M}(\phi, \theta, \chi) = (-1)^{M} \sqrt{\frac{4\pi}{2L + 1}} Y^{*}_{LM}(\theta, \chi) 
\]

(2.97)

\[
\mathcal{D}^{L}_{0;0}(\phi, \theta, \chi) = P_{L}(\cos \theta)
\]

(2.98)

where $Y_{LM}(\theta, \phi)$ is a spherical harmonic,

\[
Y^{*}_{LM} = (-1)^{M} Y_{L,-M}
\]

(2.99)

and $P_{L}(x)$ is a Legendre polynomial.

### 2.6.8 Integrals over Products of Rotation Matrices

By applying a rotation to Eq. (2.41) and premultiplying by $\langle J_{1}M_{1} | J_{2}M_{2} \rangle$, we obtain

\[
\sum_{M_{1} \leq M_{2}} \mathcal{D}^{J}_{M_{1}M_{1}}(\omega) \mathcal{D}^{J}_{M_{2}M_{2}}(\omega) \langle J_{1}M_{1} | J_{2}M_{2} \rangle = \sum_{J_{1}} \sum_{M_{1}} \langle J_{1}M_{1} | J_{2}M_{2} \rangle \mathcal{D}^{J}_{M_{1}M_{1}}(\omega) \langle J_{1}M_{1} \rangle
\]

\[
\mathcal{D}^{J}_{M_{1}M_{1}}(\omega) \mathcal{D}^{J}_{M_{2}M_{2}}(\omega) = \sum_{J} \langle J_{1}M_{1} | J_{2}M_{2} \rangle \langle J_{1}M_{1} | J_{2}M_{2} \rangle \mathcal{D}^{J}_{M_{1}M_{1}}(\omega) \mathcal{D}^{J}_{M_{2}M_{2}}(\omega)
\]

(2.100)

where $\omega$ is introduced as a shorthand notation for $(\phi, \theta, \chi)$. Eq. (2.100) is known as the Clebsch-Gordan series. It proves to be useful in the evaluation of many important integrals over products of rotation matrices. Orthogonality relations for the $\mathcal{D}$ matrices can be evaluated and satisfy the equation

\[
\int d\Omega \mathcal{D}^{J}_{M_{1}M_{1}}(\omega) \mathcal{D}^{J}_{M_{2}M_{2}}(\omega) = \frac{8\pi^{2}}{2J_{1} + 1} \delta_{J_{1}J_{2}} \delta_{M_{1}M_{2}} \delta_{M_{1}M_{2}}
\]

(2.101)

The solid-angle element $d\Omega$ ensures that all relative orientations of the two reference frames are given equal weight as the angles run over their allotted ranges.
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\[ \int d\Omega = \int_0^\pi d\phi \int_0^\pi \sin \theta d\theta \int_0^{2\pi} d\chi \]  

(2.102)

If \( J_1 \) and \( J_2 \) are both integers or half-integers, then the orthogonality relation holds. However, if one is an integer and the other a half-integer, then the range of \( \phi \) integration must be doubled; that is, the value of the integral in Eq. (2.101) is multiplied by two. It is worthwhile noting that there is a close analogy between Eq. (2.101) and the GOT for finite groups (Eq. (2.13)).

The integral over a triple product of rotation matrices occurs in various applications, including the calculation of rotational line intensities and Zeeman matrix elements.

\[ \int d\Omega \mathcal{D}_{M'\ell}(\omega) \mathcal{D}_{m\ell}(\omega) \mathcal{D}_{M'\ell}(\omega) = \frac{8\pi^2}{2J_3 + 1} \langle J_1 M_1, J_2 M_2 | J_3 M_3 \rangle \langle J_1 M'_1, J_2 M'_2 | J_3 M'_3 \rangle \]

\[ = \frac{8\pi^2}{2J_3 + 1} \begin{pmatrix} J_3 \\ M_3 \end{pmatrix} \begin{pmatrix} J_1 & J_2 & J_3 \\ M_1 & M_2 & -M_3 \end{pmatrix} \begin{pmatrix} J_1 & J_2 & J_3 \\ M'_1 & M'_2 & -M'_3 \end{pmatrix} \]  

(2.103)

### 2.6.9 Rigid Rotors

The classical rotational kinetic energy, \( T \), for a rigid body with moment of inertia \( I_{ii} \) and angular momentum \( J_i \) about an axis \( i \) is given by

\[ T = \sum_i \frac{J_i^2}{2I_{ii}} \]  

(2.104)

The corresponding quantum-mechanical Hamiltonian operator is given by

\[ \mathcal{H}_{\text{rot}} = \frac{J_x^2}{2I_{xx}} + \frac{J_y^2}{2I_{yy}} + \frac{J_z^2}{2I_{zz}} \]  

(2.105)

where each \( J_i \) now represents a quantum-mechanical operator. In order to assign quantum numbers to the eigenfunctions of the Hamiltonian operator in Eq. (2.105), we need operators that commute with it. Since the operators \( J^2 \) and \( J_z \), with eigenvalues \( J(J + 1) \) and \( M \) respectively, commute with \( \mathcal{H}_{\text{rot}} \), their quantum numbers can be used to label the eigenfunctions. From Eq. (2.80), it is readily verified that
$\mathcal{D}_{MM}(\omega)^*$ is an eigenfunction of $J^2$ and $J_Z$.

$$J^2 \mathcal{D}_{MK}(\omega)^* = J(J+1) \mathcal{D}_{MK}(\omega)^*$$

$$J_Z \mathcal{D}_{MK}(\omega)^* = M \mathcal{D}_{MK}(\omega)^*$$  \hspace{1cm} (2.106)

Here $M$ is the component (in units of $\hbar$) of $J$ along the laboratory $Z$ axis, and $K$ is the component along the molecular $z$ axis. It is therefore apparent that the required eigenfunctions can depend only on the Euler angles $\omega$, so it is convenient to write them as a sum of $\mathcal{D}$ functions (which form a complete set). This gives

$$\psi(\omega) = \sum_K a_K \mathcal{D}_{MK}(\omega)^*$$  \hspace{1cm} (2.107)

for the rigid rotor. The coefficients $a_K$ depend on the moments of inertia, $I_{ii}$. If two of these moments are equal, then the rotor is a symmetric top and the Hamiltonian becomes

$$\mathcal{H}_{rot} = \frac{J_x^2 + J_y^2 + J_z^2}{2I_{zz}} = \frac{J_z^2}{2I_{zz}} + \left(\frac{1}{2I_{zz}} - \frac{1}{2I_{zz}}\right) J_z^2$$  \hspace{1cm} (2.108)

$\mathcal{D}_{MK}(\omega)^*$ is also an eigenfunction of $J_z$,

$$J_z \mathcal{D}_{MK}(\phi,\theta,\chi)^* = K \mathcal{D}_{MK}(\phi,\theta,\chi)^*$$  \hspace{1cm} (2.109)

Therefore each $\mathcal{D}$ function is an eigenfunction of a symmetric-top Hamiltonian, and the corresponding normalised wave function is given by

$$|JKM\rangle = \sqrt{\left(\frac{2J+1}{8\pi^2}\right)} \mathcal{D}_{MK}(\omega)^*$$  \hspace{1cm} (2.110)

---

* Technically $|JKM\rangle$ should be written as $\langle J\theta\phi |JKM\rangle$, because strictly speaking $|JKM\rangle$ is a vector, not a function of continuous variables. Throughout this thesis, the former will be employed purely as a simplified notation.
For a linear rotor with no electronic angular momentum, \( K = 0 \), meaning that \( J \) is necessarily perpendicular to the internuclear axis. In this case the symmetric-top wave function \( |J K M\rangle \) reduces to the spherical harmonic \( |J M\rangle \), where

\[
|J M\rangle = Y_{JM}(\theta, \phi)
\]  

(2.111)

The \( \mathcal{D} \) matrices are also eigenfunctions for a molecule where the component of the electronic angular momentum along the molecular symmetry (\( z \)) axis is non-zero (integral or half-integral). These kets are designated \( |J \Omega M\rangle \), where \( \Omega \) is the said component and replaces the previous \( K \) because of its different origins.

### 2.7 Scalars, Vectors, and Tensors

Physical quantities such as mass and energy, which have no directional properties and no dependence on the orientation of the coordinate system, are **scalars**. Quantities such as the position of a point in space or the velocity of a particle, which have a direction associated with them in addition to a magnitude, are called **vectors**. In the wider picture, scalars and vectors are examples of **tensors**.

An \( n \)th-rank **Cartesian tensor** in a three-dimensional Euclidean space has \( 3^n \) components.\(^\text{10}\) So a **zero-rank tensor** (a scalar) has only one component, can be described by a \( 1 \times 1 \) matrix, and is therefore invariant under rotation.

A vector, or **first-rank tensor**, has three components. If we specify vector \( A \) by its components \( (A_i) \) along three orthogonal axes, we find that rotating the system transforms \( A \) into \( A' \)

\[
A'_i = \sum_j a_{ij} A_j
\]

(2.112)

where the \( a_{ij} \) are the direction cosines for the rotation.

Now consider a second-rank Cartesian tensor \( T \), which transforms according to

\[
T'_{ij} = \sum_{kl} a_{ik} a_{jl} T_{kl}
\]

(2.113)

2-33
Since $T$ has nine components (of the kind $x^2$, $xy$, $yx$, $xz$, ...) the transformation coefficients form a $9 \times 9$ matrix (if the nine components are written as a column vector); that is they span a nine-dimensional representation in the group of all rotations (SO$_3$). However, $T$ is reducible into three irreps of dimension 1, 3, and 5 in the rotation group: a scalar, which corresponds to the trace of $T$

$$\sum_k T_{kk}$$

(2.114)

a rank-1 tensor (vector) which corresponds to the antisymmetric part of $T$

$$\tilde{T}_{ij} = \frac{1}{2} (T_{ij} - T_{ji})$$

(2.115)

and a rank-2 tensor, which corresponds to the traceless symmetric part of $T$

$$\overline{T}_{ij} = \frac{1}{2} (T_{ij} + T_{ji}) - \frac{1}{3} \delta_{ij} \sum_k T_{kk}$$

(2.116)

Under rotation, $\sum_k T_{kk}$ is invariant, while the components $\tilde{T}_{ij}$ transform amongst themselves, as do the $\overline{T}_{ij}$. These three tensors span the SO$_3$ representations $\mathbb{D}^0$, $\mathbb{D}^1$, and $\mathbb{D}^2$ respectively. Since the $\mathbb{D}^n$ are irreducible, the corresponding tensors are called spherical irreducible tensors.

Higher, rank-$n$ Cartesian tensors can be formed by taking the products of $(x, y, z)$ $n$ times. They can be reduced by determining the direct product of $\mathbb{D}^1$ with itself $n$ times, followed by taking appropriate linear combinations of the Cartesian basis functions to form functions which span the $\mathbb{D}^n$ in standard form.

### 2.7.1 Spherical Irreducible Tensors

Operators that transform under rotation in the same manner as the kets $|JM\rangle$ are of great importance. We can define a spherical irreducible tensor operator, $S^k$, with rank $k$ and $2k + 1$ components, such that
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\[ R(\omega) \mathbb{A}_{q}^{k} R^{-1}(\omega) = \sum_{q'} \mathbb{A}_{q}^{k}(\omega) \mathbb{A}_{q'}^{k} \]  \hspace{1cm} (2.117)

Since this is analogous to Eq. (2.91), the operators \( \mathbb{A}_{q}^{k} \) must behave like spherical-harmonic operators under rotation. (Spherical irreducible-tensor operators of half-integral rank, which interconvert boson and fermion angular-momentum states, are not considered in this work.) In fact, these operators satisfy the following commutation relations

\[ [J_{z}, \mathbb{A}_{q}^{k}] = q \mathbb{A}_{q}^{k} \]  \hspace{1cm} (2.118)
\[ [J_{\pm}, \mathbb{A}_{q}^{k}] = [k(k+1) - q(q \pm 1)]^{1/2} \mathbb{A}_{q \pm 1}^{k} \]  \hspace{1cm} (2.119)

It also proves useful to relate the components of spherical irreducible tensor operators in the molecule-fixed \((q)\) and space-fixed \((p)\) frames to each other. Slightly modifying Eq. (2.117), we obtain

\[ \mathbb{A}_{q}^{k} = \sum_{p} \mathbb{A}_{pq}^{k}(\omega) \mathbb{A}_{p}^{k} \]  \hspace{1cm} (2.120)

### 2.8 The Wigner-Eckart Theorem

The Wigner-Eckart theorem (WET) is one of the most remarkable group theoretical results in quantum mechanics and spectroscopy. For an operator in spherical irreducible tensorial form\(^*\) the Wigner-Eckart theorem allows the separation of matrix elements of an operator taken between angular-momentum eigenstates into two factors – a geometric part (coupling coefficient – see section 2.5) and a dynamical part (reduced matrix element). What follows is a simple proof (in \( \text{SO}_3 \supset \text{SO}_2 \)), which relies on the transformational properties of wave functions and operators.

If a rotation is applied to the product \( \mathbb{A}_{q}^{k} \left| \alpha JM \right> \) (where the symbol \( \alpha \) indicates any other quantum numbers needed to specify the state), we obtain, with the aid of Eqs. (2.91) and (2.117)

\(^*\) If the operators are in tesseral form, the WET can still be used. In such cases, all coupling coefficients in this real basis are calculated by taking appropriate combinations of those in the related complex basis.
General Theory

\[ R[\tilde{\mathcal{S}}^k_\alpha |\alpha J M] = R(\omega) \tilde{\mathcal{S}}^k_\alpha R^{-1}(\omega) R(\omega)|\alpha J M] \]

\[ = \sum_q \tilde{\mathcal{S}}^k_q(\omega) \tilde{\mathcal{S}}^k_q \sum_{M'} \mathcal{D}^{JM'}_M(\omega) |\alpha J M'] \]

\[ = \sum_{q, M'} \tilde{\mathcal{S}}^k_q(\omega) \mathcal{D}^{JM'}_M(\omega) [\tilde{\mathcal{S}}^k_q |\alpha J M'] \]  \hspace{1cm} (2.121)

This tells us that the products \( \tilde{\mathcal{S}}^k_\alpha |\alpha J M \) transform under rotation as the direct product representation \( \mathcal{D}^k \otimes \mathcal{D}^{J'} \) in \( S_0^3 \). In order to find the linear combination of these products that transform as the component \( |\beta K Q \rangle \) of the irreducible representation \( \mathcal{D}^K \), we use Eq. (2.40).

\[ |\beta K Q \rangle = \sum_{\tilde{\mathcal{S}}^k_\alpha} \langle kq, JM| KQ \rangle \tilde{\mathcal{S}}^k_\alpha |\alpha J M \rangle \]  \hspace{1cm} (2.122)

Using Eq. (2.41) this expression can be inverted, giving

\[ \tilde{\mathcal{S}}^k_\alpha |\alpha J M \rangle = \sum_{KQ} \langle kq, JM| KQ \rangle |\beta K Q \rangle \]  \hspace{1cm} (2.123)

Taking the matrix element with \( \langle \alpha' J'M'| \), we obtain

\[ \langle \alpha' J'M' | \tilde{\mathcal{S}}^k_\alpha |\alpha J M \rangle = \sum_{KQ} \langle kq, JM| KQ \rangle \langle \alpha' J'M'| \beta K Q \rangle \]  \hspace{1cm} (2.124)

A scalar product of the form \( \langle \alpha JM|\beta K Q \rangle \) can be rewritten as

\[ \langle \alpha JM|\beta K Q \rangle = \langle \alpha JM|R^{-1}(\omega) R(\omega)|\beta K Q \rangle = \sum_{M'Q} \mathcal{D}^{JM'}_M(\omega)^* \mathcal{D}^K_{MQ}(\omega) \langle \alpha JM'|\beta K Q \rangle \]  \hspace{1cm} (2.125)

Multiplying by \( d\Omega 8\pi^2 \) and integrating over the solid angle \( \Omega \) gives

\[ \langle \alpha JM|\beta K Q \rangle = \langle \alpha JM|\beta K Q \rangle = (2J + 1)^{-1} \delta_{\alpha\alpha} \delta_{K K} \delta_{MQ} \sum_{M'Q} \delta_{M'Q} \langle \alpha JM'|\beta K Q \rangle \]  \hspace{1cm} (2.126)
The scalar product \( \langle \alpha' \gamma' | \beta \gamma \rangle \) in Eq. (2.124) vanishes unless \( \alpha' = \beta, \gamma' = J, \) and \( M' = Q \). When this is satisfied, \( \langle \alpha' \gamma' | \beta \gamma \rangle \) is independent of \( M' \) and is usually written as

\[
\langle \alpha' \gamma' | \beta \gamma \rangle = (2J + 1)^{\frac{1}{2}} \langle \alpha \gamma | \sigma^k | \alpha \rangle \tag{2.127}
\]

which, when substituted into Eq. (2.124), gives

\[
\langle \alpha' \gamma' | \sigma^k | \alpha \gamma \rangle = (2J + 1)^{\frac{1}{2}} \langle \gamma' J \gamma | M \gamma J M' \gamma' | \gamma' \gamma \rangle \langle \alpha' \gamma | \sigma^k | \alpha \rangle \tag{2.128}
\]

\( \langle \alpha' \gamma | \sigma^k | \alpha \rangle \) is called the reduced matrix element and does not depend on the components of \( J \).

The Wigner-Eckart theorem can also be written in a form that incorporates \( 3jm \) coefficients. With the aid of Eq. (2.44), the theorem is

\[
\langle \alpha' \gamma' | \sigma^k | \alpha \gamma \rangle = \left( \begin{array}{c} J' \\ M' \end{array} \right) \left( \begin{array}{cc} J & k \\ -M' & q \end{array} \right) \langle \alpha' \gamma | \sigma^k | \alpha \rangle \tag{2.129}
\]

Although the Wigner-Eckart theorem is one of the most important quantum-mechanical applications of group theory and applies to any point group, group theory can not actually evaluate the reduced matrix elements.

For point groups other than \( SO_3 \), Eq. (2.129) is replaced by

\[
\langle \Gamma_A \gamma_A | \Gamma_O \gamma_O | \Gamma_B \gamma_B \rangle = \left( \begin{array}{ccc} \Gamma_A & \Gamma_A^* & \Gamma_B \\ \gamma_A & \gamma_A & \gamma_B \end{array} \right) \langle \Gamma_A \gamma_A | \Gamma_O \gamma_O | \Gamma_B \gamma_B \rangle \tag{2.130}
\]

The irrep and partner labels for the wavefunctions are easily determined, but we also need to know the transformation properties of the operators (Section 2.3.12). Table 2.2 gives the transformation properties of vectors and pseudo-vectors in the chains \( O_3 \supset SO_3 \supset SO_2 \) and \( O_3 \supset D_{coh} \supset C_{ov} \supset SO_2 \).
Table 2.2: Transformation properties of vectors (T) and pseudo-vectors (R) in terms of |j m|.

<table>
<thead>
<tr>
<th>(Pseudo-)vector component</th>
<th>O₃ ⊃ SO₃ ⊃ SO₂</th>
<th>O₃ ⊃ Dₐ₀h ⊃ Cᵥ ⊃ SO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tₓ</td>
<td>$\frac{i}{\sqrt{2}} { -1 } -</td>
<td>1 &gt; 1 } }$</td>
</tr>
<tr>
<td>Tᵧ</td>
<td>$\frac{i}{\sqrt{2}} { -1 } +</td>
<td>1 &gt; 1 } }$</td>
</tr>
<tr>
<td>Tₜ ≡ T₀</td>
<td></td>
<td>0 &gt; 0</td>
</tr>
<tr>
<td>T±₁</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rₓ</td>
<td>$\frac{i}{\sqrt{2}} { -1 } -</td>
<td>1 &gt; 1 } }$</td>
</tr>
<tr>
<td>Rᵧ</td>
<td>$\frac{i}{\sqrt{2}} { -1 } +</td>
<td>1 &gt; 1 } }$</td>
</tr>
<tr>
<td>Rₚ ≡ R₀</td>
<td></td>
<td>0 &gt; 0</td>
</tr>
<tr>
<td>R±₁</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

It is important to note that although the Wigner-Eckart theorem correctly predicts any vanishing matrix elements, some that are "apparently" non-zero may actually vanish because of other symmetry considerations. This includes some cases in which $A = B$ in Eq. (2.130), where the irrep category of the wavefunctions and whether the operator is real or complex must be taken into account (see Section 2.3.8). For real operators $\mathcal{R}_γ^R$, imaginary operators $\mathcal{J}_γ^I$, category-one irreps $Γ₁$, and category-two irreps $Γ₂$, we have

$$\langle Γ₁ γ_a | \mathcal{R}_γ^R | Γ₁ γ_b \rangle \neq 0, \text{ iff } Γ ∈ [Γ₂]² \quad (2.131)$$

$$\langle Γ₁ γ_a | \mathcal{J}_γ^I | Γ₁ γ_b \rangle = 0, \text{ iff } Γ ∈ (Γ_1^2) \quad (2.132)$$

$$\langle Γ₂ γ_a | \mathcal{R}_γ^R | Γ₂ γ_b \rangle \neq 0, \text{ iff } Γ ∈ (Γ_2^2) \quad (2.133)$$

$$\langle Γ₂ γ_a | \mathcal{J}_γ^I | Γ₂ γ_b \rangle \neq 0, \text{ iff } Γ ∈ [Γ₂^2] \quad (2.134)$$

### 2.9 Electronic Matrix Elements

Spin-orbit, crystal-field, Zeeman, and electric-dipole matrix elements are required in later chapters. This section explains the nature of the corresponding operators, and general procedures to derive the corresponding matrix elements.
2.9.1 Reduction to One-Electron Form

The process of deriving many-electron matrix elements is greatly simplified when the wavefunctions are in determinantal form and the operator \( F \) can be expressed as a sum of one-electron operators \( f(i) \).

\[
F = \sum_i f(i)
\]  

(2.135)

This process of simplification is achieved using the *Condon-Slater rules*.\(^\text{16}\) For a general matrix element \( \langle D_1 | F | D_2 \rangle \), the spin-orbitals in either \( D_1 \) or \( D_2 \) must be permuted so as to have as many as possible matching. The Condon-Slater rules are as follows:

1. If \( D_1 \) and \( D_2 \) are identical,

\[
\langle \phi_1 \phi_2 \phi_3 \ldots \phi_N | F | \phi_1 \phi_2 \phi_3 \ldots \phi_N \rangle = \sum_i \langle \phi_i | f(i) | \phi_i \rangle
\]

(2.136)

2. If \( D_1 \) and \( D_2 \) differ by only one spin-orbital \( (\phi_k \neq \phi_l) \),

\[
\langle \phi_1 \phi_2 \phi_3 \ldots \phi_l \ldots \phi_N | F | \phi_1 \phi_2 \phi_3 \ldots \phi_k \ldots \phi_N \rangle = \langle \phi_l | f(i) | \phi_k \rangle
\]

(2.137)

3. If \( D_1 \) and \( D_2 \) differ by two or more spin-orbitals, the matrix element is necessarily zero.

2.9.2 Spin-Orbit Coupling

Spin-orbit coupling is a relativistic phenomenon, arising from the interaction of an electron's relativistic electric dipole (classically, this is due to a Lorentz distortion of a spinning electron) and the internal electric fields of the molecule.\(^\text{17}\) Hence, only states with non-zero spin and orbital angular momentum will exhibit any SO splitting. Generally, SOC is treated as an effective interaction between the spin magnetic moment of an electron and a magnetic field generated by the component of that electron's orbital angular momentum about a nucleus.
For a hydrogen-like (one-electron) atom, the spin-orbit-coupling operator is given by

$$\mathcal{K}_{\text{SO}} = \xi(r) \mathbf{l} \cdot \mathbf{s}$$  \hspace{1cm} (2.138)

where $\mathbf{l}$ and $\mathbf{s}$ are the electronic orbital and spin-angular momentum of the electron respectively, and

$$\xi(r) = \frac{1}{2m_e^2c^2r} \frac{\partial U(r)}{\partial r}$$  \hspace{1cm} (2.139)

$U(r)$ is the central-field Coulomb potential energy, which for a given nucleus is determined only by the distance between the electron and nucleus ($r$).

$$U(r) = -\frac{Ze^2}{r}$$  \hspace{1cm} (2.140)

For a multi-electron molecule, the SO-coupling operator is written as a sum of one-electron operators:

$$\mathcal{K}_{\text{SO}} = \sum_{ik} \xi(r_{ik}) \mathbf{l}(i,k) \cdot \mathbf{s}(k)$$  \hspace{1cm} (2.141)

where the sum is over all $k$ electrons in open shells and all $i$ nuclei of the molecule. Strictly speaking this is not correct because it neglects spin-other-orbit interactions and the electrons no longer move in a central field. However, the radial integral over $\xi(r_{ik})$ is normally considered as an adjustable parameter called the spin-orbit coupling constant ($\zeta$), the value being determined from experiment.

### 2.9.3 Crystal Fields

In condensed phases (including noble-gas matrices), molecules will experience a “crystal field” (CF), which is essentially due to the electric fields of surrounding atoms. This can partially or entirely lower the orbital degeneracy, but does not directly affect the spin.
General Theory

A CF interaction between two orbitals \( h_1 \) and \( h_2 \), and their respective partners \( \theta_1 \) and \( \theta_2 \), requires that there are matrix elements of the form \( \langle h_1 \theta_1 | V_{\gamma}^I | h_2 \theta_2 \rangle \) which are non-zero. Here, \( V_{\gamma}^I \) is a real one-electron CF operator that transforms as partner \( \gamma \) of irrep \( I \) in the molecular point group. If \( h_1 \) and \( h_2 \) are the same (degenerate) orbital label \( (h) \), then the CF can lower the degeneracy, i.e. cause a splitting. In such a case it is required that \( \langle h \theta_1 | V_{\gamma}^I | h \theta_2 \rangle \) is non-zero, which partly depends on the nature of \( h \) (Sections 2.3.8 and 2.8). Since \( V_{\gamma}^I \) is a real operator and diagonalises the orbitals in a real basis, it is usually chosen so as to transform as a real combination of spherical harmonics, known as a tesseral harmonic. The WET is used to evaluate the matrix elements in terms of a parameter, denoted \( V \) in this work, which represents the magnitude of the splitting.

2.9.4 The Zeeman Effect

The electronic Zeeman Hamiltonian operator for a molecule in the presence of a magnetic field (in the direction of the laboratory Z axis) is given by

\[
\mathcal{K}_B = -\mu \cdot B = -\mu_B B = (L_Z + g_e S_Z) \mu_B B
\]

(2.142)

where \( \mu \) is the molecular electronic magnetic dipole moment associated with non-zero spin and orbital angular momenta. \( B \) is the magnetic flux density (which is also called the induction, but is commonly referred to as the magnetic 'field'), with magnitude \( B \) in tesla. \( \mu_B \) is the Bohr magneton (0.4869 cm\(^{-1}\) T\(^{-1}\)) and \( g_e \approx 2.0023 \) is the \( g \) value of an electron. The many-electron operators \( L_Z \) and \( S_Z \) are simple sums of the corresponding one-electron operators.

\[
L_Z = \sum_i l_z(i)
\]

\[
S_Z = \sum_i s_z(i)
\]

(2.143)

The Zeeman interaction between two states, \( |\alpha\rangle \) and \( |\kappa\rangle \), is given by the matrix element
When $|A\alpha\rangle$ and $|K\kappa\rangle$ are mutually degenerate (in the absence of the magnetic field), the matrix element is said to be first order; otherwise it is second or higher order. The Zeeman splitting between adjacent states from the same degenerate manifold is conventionally represented by $g\mu_B B$ where the $g$ value is a function of the molecular magnetic moment and its orientation in the field.

### 2.9.5 Transition Moments

All of the transitions considered in this thesis involve the interaction of the electric-field component of the electromagnetic radiation with the electric dipole moment of a diatomic molecule. For a transition from state $\psi_A$ to state $\psi_J$, the transition moment is given by

$$\mathcal{M}_{J \rightarrow A} = \int \psi_J^* m \psi_A \, d\tau = \langle \psi_J | m | \psi_A \rangle$$

(2.145)

where $m$ is the electric dipole moment operator. Essentially, the transition moment is a measure of the magnitude of the migration of charge accompanying the transition. The square of the transition moment is proportional to the intensity of the transition:

$$I_{J \rightarrow A} \propto |\langle \psi_J | m | \psi_A \rangle|^2$$

(2.146)

For $\psi_J \leftarrow \psi_A$ to be allowed, the orbital and electric-dipole-moment-operator irreps must fulfill the requirement

$$\Gamma_J \otimes \Gamma_m \otimes \Gamma_A \supset \Gamma^{(e)}$$

(2.147)

where $\Gamma^{(e)}$ is the totally symmetric irrep in the molecular point group. Since orbital irreps are category one, Eq. (2.147) can be rewritten

$$\Gamma_m \otimes \Gamma_A \supset \Gamma_J$$

(2.148)
The data analysis technique of taking ratios of spectroscopic moments (Section 4.2) means that only relative transition intensities need to be derived. Since \( m \) is a sum of one-electron operators, the many-electron transition moments of the type in Eq. (2.144) are converted to one electron form using the Condon-Slater rules (Section 2.9.1).

To improve the efficiency of this conversion process, the Wigner-Eckart theorem is employed and the results are expressions in terms of a reduced one-electron transition (excitation) moment, designated \( \mathcal{M} \). By these means it is possible to derive the relative intensities of the transitions between partner states of two different terms purely from symmetry considerations.

### 2.10 References


3 Heteronuclear Diatomic Molecules

3.1 Symmetry

A diatomic molecule consists of a pair of nuclei and a number of electrons, bound together by their mutual electrostatic interactions. Whereas the total electronic orbital angular momentum, \( L \), is a constant of the motion of the electrons in an atom, it is \( L_z \), the component of \( L \) along the internuclear (IN) axis, that is a constant of electronic motion in a diatomic molecule. This is essentially the same situation as an atom in a strong electric field where, in this case, the electric field is the two-centre field of the nuclei. \( L \) precesses about the IN axis with constant component \( M_L \) (in units of \( \hbar \)), which is given the symbol \( \Lambda \).

\[ \Lambda = M_L = L, L-1, L-2, L-3, \ldots, -L \]  

(3.1)

Reversing the direction of electron motion does not change the energy, but changes \( \Lambda \) into \(-\Lambda\). Therefore, electronic states of diatomic molecules are classified according to their value of \(|\Lambda|\). In molecular term symbols, states with \(|\Lambda| = 0, 1, 2, 3, \ldots \) are designated by the Greek letters \( \Sigma, \Pi, \Delta, \Phi, \ldots \) It is important to note that \( \Sigma \) terms are orbitally non-degenerate, whereas all the others are doubly degenerate.

The total spin angular momentum of the electrons, \( S \), in a diatomic molecule is not directly affected by the electric field of the nuclei. For \( \Sigma \) states, \( S \) is fixed in space as long as the molecule does not rotate and there is no external magnetic field. For other (\( \Lambda \neq 0 \)) states there is a net current of electrons around the IN axis, which produces a solenoidal magnetic field with strength proportional to \( \Lambda \). This magnetic field causes \( S \) to precess about the IN axis with constant component \( M_S \), which is given the symbol \( \Sigma \) (not to be confused with \( \Sigma \) states).

\[ \Sigma = M_S = S, S-1, S-2, \ldots, -S \]  

(3.2)

The component of total electronic angular momentum about the IN axis,

* Herzberg\(^1\) uses the convention \( \Lambda = |M_L|, \Sigma = M_S, \) and \( \Omega = |\Lambda + \Sigma| \), whereas this research uses the convention \( \Lambda = M_L, \Sigma = M_S, \) and \( \Omega = \Lambda + \Sigma \) employed by Zare,\(^2\) Judd,\(^3\) Hougen,\(^4\) and others. As well as being more logical, the latter system allows simpler notation of matrix elements and wavefunctions.
denoted \( \Omega \), is simply the algebraic sum of the components \( \Lambda \) and \( \Sigma \). The electronic states are classified according to their values of \( |\Omega| \) and components \( \pm |\Omega| \). (The use of \( |\Omega| \) is complicated when \( S > |\Lambda| > 0 \), however such cases do not arise in this research.)

The group theoretical irreps corresponding to \( |\Lambda| \) and \( |\Omega| \) for a heteronuclear diatomic molecule can be better understood by first considering those for the point group \( C_{\infty} \) (or \( SO_2 \)), which is the two-dimensional rotation group (the group of all rotations about a fixed axis). This is an Abelian group because all successive rotations about the axis commute. Furthermore, all irreps in this group are one-dimensional, and satisfy the relationship

\[
\Gamma(\phi_1) \Gamma(\phi_2) = \Gamma(\phi_1 + \phi_2)
\]  

(3.3)
as well as one of the cyclic boundary conditions

\[
\Gamma(0) = \Gamma(2\pi) \text{ for bosonic functions} \quad (3.4)
or
\[
\Gamma(0) = -\Gamma(2\pi) \text{ for fermionic functions} \quad (3.5)
\]

\( C_{\infty} \) is the point group for a particle moving around a circular ring, so it is to be expected that the exact eigenfunctions of the Schrödinger equation for this problem transform as irreps in \( C_{\infty} \). We can conclude that

\[
|m\rangle = \frac{1}{\sqrt{2\pi}} \exp(im\phi)
\]  

(3.6)
where

\[ m = 0, \pm 1, \pm 2 \ldots \text{ for bosonic irreps} \]

and

\[ m = \pm 1/2, \pm 3/2, \pm 5/2 \ldots \text{ for fermionic irreps}. \]

It can be shown\(^5\) that the \( z \) component of the angular momentum of state \( |m\rangle \) is determined only by the irrep.
\( J_z |m\rangle = m |m\rangle \)  
(3.7)

where (from Eq. (2.83) and changing \( \chi \) to \( \phi \))

\[ J_z = -i \frac{\partial}{\partial \phi} \]
(3.8)

\( C_{\infty v} \), the point group of a heteronuclear diatomic molecule, has all the symmetry elements of \( C_{\infty} \) as well as an infinite number of mirror planes, \( \sigma_v \), each of which includes the IN axis (conventionally called the \( z \) axis). Rotations about \( z \) by the same angle but in opposite directions, \( R_z(\phi) \) and \( R_z(-\phi) \), are related by a similarity transformation involving any \( \sigma_v \).

\[ R_z(\phi) = \sigma_v R_z(-\phi) \sigma_v \]  
(3.9)

As a result of this, basis functions that span \( |m\rangle \) and \( |-m\rangle \) in \( C_{\infty} \) transform as the partners of a common two-dimensional irrep in \( C_{\infty v} \). In more detail, the matrix representative for \( \sigma_v \) (at a particular angle) and \( R_z(\phi) \) acting on basis functions \( |m_i\rangle \) and \( |m_j\rangle \) that are interchanged by \( \sigma_v \) is given by

\[ D(\sigma_v) = \begin{pmatrix} 0 & a \\ b & 0 \end{pmatrix} \]  
(3.10)

where

\[ a \times b = 1 \]

Furthermore

\[ D(R_z(\phi)) = \begin{pmatrix} e^{im_1\phi} & 0 \\ 0 & e^{im_2\phi} \end{pmatrix} \]  
(3.11)

By substituting Eqs. (3.10) and (3.11) into Eq. (3.9), it can be verified that Eq. (3.9) is only satisfied if

\[ m_i = -m_j \]  
(3.12)
Therefore, as long as \( m \neq 0, |m\rangle \) and \(|-m\rangle\) span a two-dimensional irrep \( j = |m|\) with partners \( m = \pm j \). In the case where \( m = 0 \), \( D(\sigma_r) \) is diagonalisable and the representation is reducible to two one-dimensional irreps, labelled \( \Sigma^+ \) when \( \chi(\sigma_r) = 1 \) and \( \Sigma^- \) when \( \chi(\sigma_r) = -1 \). Table 3.1 gives the irrep labels and their partners in Mulliken and Butler notations\(^6,7\) for \( \text{C}_{\infty v} \). Table 3.2 gives the direct-product table for the irreps of \( \text{C}_{\infty v} \) (in Butler notation).

**Table 3.1:** The Mulliken and Butler irrep labels for \( \text{C}_{\infty v} \).

<table>
<thead>
<tr>
<th>Mulliken notation</th>
<th>Butler notation</th>
<th>Partners</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Sigma^+ )</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>( \Sigma^- )</td>
<td>( \tilde{0} )</td>
<td>0</td>
</tr>
<tr>
<td>( E_{1/2} )</td>
<td>( 1/2 )</td>
<td>( \pm 1/2 )</td>
</tr>
<tr>
<td>( \Pi )</td>
<td>1</td>
<td>( \pm 1 )</td>
</tr>
<tr>
<td>( E_{3/2} )</td>
<td>( 3/2 )</td>
<td>( \pm 3/2 )</td>
</tr>
<tr>
<td>( \Delta )</td>
<td>2</td>
<td>( \pm 2 )</td>
</tr>
<tr>
<td>( E_{5/2} )</td>
<td>( 5/2 )</td>
<td>( \pm 5/2 )</td>
</tr>
</tbody>
</table>

**Table 3.2:** Direct-product table for irreps of \( \text{C}_{\infty v} \), modified from reference 8. [ ] and ( ) represent symmetric and antisymmetric squares respectively.

<table>
<thead>
<tr>
<th>category</th>
<th>1</th>
<th>1</th>
<th>1</th>
<th>1</th>
<th>2</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>category</td>
<td>( \otimes )</td>
<td>0</td>
<td>( \tilde{0} )</td>
<td>( a ) (integer)</td>
<td>( b ) (integer)</td>
<td>( c ) (1/2-integer)</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>( \Box )</td>
<td>( a )</td>
<td>( b )</td>
<td>( c )</td>
<td>( d )</td>
</tr>
<tr>
<td>1</td>
<td>( \tilde{0} )</td>
<td>( \tilde{0} )</td>
<td>( a )</td>
<td>( b )</td>
<td>( c )</td>
<td>( d )</td>
</tr>
<tr>
<td>1</td>
<td>( a ) (integer)</td>
<td>( a )</td>
<td>( a ) ( \otimes ) ( \Gamma_{2b} ) ( \oplus ) ( \tilde{0} )</td>
<td>( \Gamma_{2b} ) ( \oplus ) (</td>
<td>a-b</td>
<td>)</td>
</tr>
<tr>
<td>1</td>
<td>( b ) (integer)</td>
<td>( b )</td>
<td>( b ) ( \Gamma_{2b} ) ( \oplus ) (</td>
<td>b-a</td>
<td>)</td>
<td>( \tilde{0} ) ( \otimes ) ( \Gamma_{2b} ) ( \oplus ) (</td>
</tr>
<tr>
<td>2</td>
<td>( c ) (1/2-integer)</td>
<td>( c )</td>
<td>( c )</td>
<td>( \Gamma_{2a} ) ( \oplus ) (</td>
<td>c-a</td>
<td>)</td>
</tr>
<tr>
<td>2</td>
<td>( d ) (1/2-integer)</td>
<td>( d )</td>
<td>( d )</td>
<td>( \Gamma_{2d} ) ( \oplus ) (</td>
<td>d-a</td>
<td>)</td>
</tr>
</tbody>
</table>

### 3.2 Hund's Cases

A free diatomic molecule has four general sources of angular momentum: electronic orbital angular momentum, 'spin' of the electrons and nuclei, and the rotational angular momenta of the nuclei as they 'orbit' the centre of mass. In this work, nuclear spin is disregarded.

The coupling between electronic and rotational motion is classified in terms of five limiting cases devised by Friedrich Hund.\(^1\) Only cases (a) and (b) need be
considered here because the radicals considered in this work fall between these limiting cases. Table 3.3 gives the angular momenta involved in Hund's coupling cases, along with the appropriate magnitude and (signed) internuclear-axis (IN-axis) projection quantum numbers.

<table>
<thead>
<tr>
<th>Type of angular momentum</th>
<th>Operator</th>
<th>Quantum numbers</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Total</td>
</tr>
<tr>
<td>Electronic orbital</td>
<td>( L )</td>
<td>( L )</td>
</tr>
<tr>
<td>Electronic spin</td>
<td>( S )</td>
<td>( S )</td>
</tr>
<tr>
<td>Rotational</td>
<td>( R )</td>
<td>( R )</td>
</tr>
<tr>
<td>Total</td>
<td>( J = R + L + S )</td>
<td>( J )</td>
</tr>
<tr>
<td>Total – Spin</td>
<td>( N = R + L )</td>
<td>( N )</td>
</tr>
</tbody>
</table>

*\( R \) is always perpendicular to the internuclear axis.

In both Hund’s cases, \( R \) is at right angles to the IN axis and \( L \) is strongly coupled (through its interaction with the electric fields of the nuclei) to the IN axis. In Hund’s case (a), \( S \) is also strongly coupled (through spin-orbit interactions) to the IN axis and the total angular momentum, \( J \), has projections \( M \) on the laboratory Z-axis and \( \Omega \) on the IN \( z \)-axis. In Hund’s case (b), \( S \) is only very weakly coupled to the IN axis. The result of this is that a non-zero \( \Lambda \) will couple with \( R \) to form resultant \( N \), which in turn couples with \( S \) to form the total angular momentum \( J \). It is worth noting that if \( \Lambda = 0 \) (i.e. \( \Sigma \) states), \( S \) is not coupled at all to the IN axis and \( \Omega \) is not defined. Most diatomic molecules actually lie between the limits of Hund’s cases (a) and (b). In such cases it is usually more convenient to use Hund’s case-(a) states as the basis from which to derive the more accurate wavefunctions.

The first step is to create purely electronic wavefunctions, excluding rotation. When spin-orbit coupling is not large, that is, when the energy levels fall into recognisable term multiplets, the electronic part of the wavefunction can be characterised by the ‘almost good’ quantum numbers \( \Lambda \), \( S \), and \( \Sigma \), and the truly good quantum number, \( \Omega \).

### 3.3 Construction of Electronic Wavefunctions

The process of constructing many-electron wavefunctions from a molecular-orbital (MO) configuration, ensuring that they span irreps of the point group of the electronic Hamiltonian (\( \mathcal{H}_e \)), will be outlined in this section. These electronic
wavefunctions are required to derive the SO-CF wavefunctions in subsequent chapters, and they also form the electronic part of the basis functions for the rotating-molecule Hund's case-(a) wavefunctions.

### 3.3.1 Molecular Orbitals

The first step is to determine the appropriate forms for the MOs. For small molecules, these are readily approximated by linear combinations of the parent atomic orbitals (LCAO). Determination of the combination coefficients, is not required for the purposes of this thesis. The only requirements are that the orbital symmetries and the ground- and excited-state electronic configurations be known. These can be determined from simple quantum-mechanical calculations.

The molecular orbitals transform as irreps of $C_{nv}$, and each is labelled according to its quantum number $\lambda$, which is determined by Eq. (3.1). (One-electron orbital labels are conventionally written in lower case.) The only one-electron molecular-orbital irreps required in this work are designated $\sigma^+$ and $\pi$. Since it is impossible for MOs to have $\sigma^-$ symmetry, $\sigma^+$ orbitals are often written as $\sigma$.

Generalised MO diagrams for XH are given in Figure 3.1. The present spectroscopic investigations of XH involve $\pi\leftrightarrow\sigma$ excitations where the $\pi$ orbitals are essentially non-bonding p orbitals of the non-hydrogen atom. These excitations are tabulated in Table 3.4.

![Figure 3.1: A generalised MO diagram for XH. When X = C, N or O, $n = 2$, whereas $n = 3$ for Si, P and S. The occupancy of the non-bonding $(n-1)\pi$ HOMO (open circles) increases from one (C and Si) to three (O and S) across each period. The spectroscopic transitions of concern in this thesis arise from the $(n-1)\pi \leftrightarrow (2n-1)\sigma$ excitation indicated by the arrow.](image-url)
3.3.2 Term Symbols

The next step is to derive molecular term symbols. Only electrons in partially filled orbitals contribute to the net angular momentum of the system, so only these need be considered in the construction of wavefunctions. The valence configurations applicable to this research are $\sigma_1$, $\pi_1$, $\sigma_2$, $\pi_2$, $\sigma_3$, and $\pi_3$.

Many-electron orbital irreps are determined by taking group-theoretical direct products of the appropriate single-electron orbital irreps in the appropriate point group. Because the spin is not directly coupled to the molecular axis, many-electron spin irreps are determined in the $SO_3$ point group by taking direct products of the single-electron spin irreps ($s = \frac{1}{2}$), which essentially comes down to application of the Clebsch-Gordan series.

The term symbol is conventionally written as $2S+1 \hbar$, where $\hbar$ is the many-electron orbital irrep label and $2S+1$ is the spin multiplicity. In deriving these term symbols it is of utmost importance to ensure that two or more electrons do not share all the same quantum numbers. This ensures that the resultant wavefunctions obey the Pauli exclusion principle; that is, they are antisymmetric with respect to the interchange of the coordinates of any two electrons.

3.3.3 SL Wavefunctions

In general, the operators $L^2$ and $L_z$ do not commute with $\mathcal{K}_\text{el}$, hence their corresponding quantum numbers are “poor” and do not provide a satisfactory basis by which to specify the electronic states. Instead, it is possible to classify the orbital functions by irreps ($h$) and their partners ($\theta$) in the molecular point group. On the other hand, before spin-orbit coupling has been included in the Hamiltonian, the operators $S^2$ and $S_z$ do still commute with $\mathcal{K}_\text{el}$ in SO$_3$. It is therefore appropriate to construct SL wavefunctions of the form $|S \ h \ M \ \theta\rangle$, where $S$ and $M$ denote quantum
numbers, which are effectively the spin irrep and partner labels in $SO_3$. Such functions always provide a suitable basis set because they form a complete set, and appropriate linear combinations of them are diagonal in $X_{SO}$. In this thesis, $|S h M \theta\rangle$ functions will often be written as $|a^n 2^{\nu+1} h M \theta\rangle$, where $a^n$ represents the electronic configuration.

### 3.3.3.1 One-electron SL wavefunctions

Simple one-electron SL wavefunctions can be derived by inspection. The following shorthand spin-orbital notation for an electron in the $\theta$ partner orbital will be used to simplify the expressions,

$$|\theta\rangle = |h \theta\rangle_{\frac{1}{2} \pm \frac{1}{2}}$$

where the first and second kets on the right represent the orbital and spin parts of the function, respectively.

#### $\sigma^1$

For a non-degenerate $\sigma (0)$ orbital, only two possible spin-orbital states exist:

$$|\sigma^1 \Sigma^+ 0 \pm \frac{1}{2} \rangle = |0^\pm\rangle$$

#### $\pi^1$

For a doubly degenerate $\pi (1)$ orbital (with partners $\pm 1$) there are four states,

$$|\pi^1 \Pi \pm 1 \pm \frac{1}{2}\rangle = |\pm 1^\pm\rangle$$

$$|\pi^1 \Pi \pm 1 \mp \frac{1}{2}\rangle = |\pm 1^\mp\rangle$$

### 3.3.3.2 Two-electron SL wavefunctions

Orbital and spin wavefunctions are derived separately, and then coupled together in such a way that the Pauli exclusion principle is satisfied.
The orbital irreps are given by

\[ \Lambda = 1 \otimes 1 = 0 \oplus 0 \oplus 2 = \Sigma^+ \oplus \Sigma^- \oplus \Delta \]  
(3.16)

The spin quantum numbers are obtained from the Clebsch-Gordan series:

\[ S = \frac{1}{2} \otimes \frac{1}{2} = |\frac{1}{2} + \frac{1}{2}| \ldots |\frac{1}{2} - \frac{1}{2}| = 0 \oplus 1 \]  
(3.17)

The orbital wavefunctions are generated according to

\[ |(h_1, h_2) \Theta \rangle = |\mathcal{A} | \frac{\mathcal{H}}{\Theta} \sum \left( \begin{array}{cc} h_1 & h_2 \{ \mathcal{H} \} \end{array} \right) |h_1 \Theta_1 \rangle |h_2 \Theta_2 \rangle \]  
(3.18)

where \( h \) and \( \Theta \) are the orbital irrep and partner for the many-electron wavefunction, \( h_1 \) and \( h_2 \) are the irreps of the orbital functions to be coupled, and the summation is made over all partners \( \Theta_1 \) and \( \Theta_2 \) for which the \( 3j \)s are non-zero.

The spin wavefunctions \( S_0 \) are generated according to

\[ |(s_1, s_2) S M \rangle = (-1)^{s_1 + s_2 + S} |S | \frac{1}{2} (-1)^{S-M} \sum \left( \begin{array}{ccc} s_1 & s_2 & S \end{array} \right) \sum \left( \begin{array}{ccc} M & m_1 & m_2 \end{array} \right) |s_1 m_1 \rangle |s_2 m_2 \rangle \]  
(3.19)

where \( S \) is the spin irrep of the many-electron spin function in \( S_0 \), and \( M \) is its partner. \( s_1 \) and \( s_2 \) are the irreps of the spin functions to be coupled, and the summation is made over all partners \( m_1 \) and \( m_2 \) for which the \( 3j \)s are non-zero.

Using Eqs. (3.18) and (3.19), the following orbital and spin wavefunctions are obtained for the \( \pi^2 \) configuration

\[ |(1 1) 0 0 \rangle = \frac{1}{\sqrt{2}} \{ |1 \ldots -1 | |1 \ldots 1 \rangle + |1 \ldots 1 \rangle |1 \ldots -1 \rangle \} \]

\[ |(1 1) \bar{0} 0 \rangle = \frac{1}{\sqrt{2}} \{ |1 \ldots -1 | |1 \ldots 1 \rangle - |1 \ldots 1 \rangle |1 \ldots -1 \rangle \} \]

\[ |(1 1) 2 \pm 2 \rangle = |1 \ldots 1 \rangle |1 \ldots \pm 1 \rangle \]  
(3.20)
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\[ |\begin{pmatrix} 1 \mathbf{1} \\ 0 \mathbf{0} \end{pmatrix} \mathbf{0} \mathbf{0} \rangle = \frac{1}{\sqrt{2}} \{ |\begin{pmatrix} 1 \mathbf{1} \\ 1 \mathbf{1} \end{pmatrix} \mathbf{1} \mathbf{1} - |\begin{pmatrix} 1 \mathbf{1} \\ 1 \mathbf{1} \end{pmatrix} \mathbf{1} \mathbf{1} \} \]

\[ |\begin{pmatrix} 1 \mathbf{1} \\ 1 \mathbf{0} \end{pmatrix} \mathbf{1} \mathbf{0} \rangle = \frac{1}{\sqrt{2}} \{ |\begin{pmatrix} 1 \mathbf{1} \\ 1 \mathbf{1} \end{pmatrix} \mathbf{1} \mathbf{1} + |\begin{pmatrix} 1 \mathbf{1} \\ 1 \mathbf{1} \end{pmatrix} \mathbf{1} \mathbf{1} \} \]

\[ |\begin{pmatrix} 1 \mathbf{1} \\ 1 \mathbf{1} \end{pmatrix} \mathbf{1} \mathbf{0} \rangle = \frac{1}{\sqrt{2}} \{ |\begin{pmatrix} 1 \mathbf{1} \\ 1 \mathbf{1} \end{pmatrix} \mathbf{1} \mathbf{1} - |\begin{pmatrix} 1 \mathbf{1} \\ 1 \mathbf{1} \end{pmatrix} \mathbf{1} \mathbf{1} \} \]

\[ |\begin{pmatrix} 1 \mathbf{1} \\ 1 \mathbf{1} \end{pmatrix} \mathbf{1} \mathbf{0} \rangle = \frac{1}{\sqrt{2}} \{ |\begin{pmatrix} 1 \mathbf{1} \\ 1 \mathbf{1} \end{pmatrix} \mathbf{1} \mathbf{1} + |\begin{pmatrix} 1 \mathbf{1} \\ 1 \mathbf{1} \end{pmatrix} \mathbf{1} \mathbf{1} \} \]  

(3.21)

The SL wavefunctions are the antisymmetric products of symmetric orbital functions with antisymmetric spin functions, and vice versa. The notation employed henceforth is normalised Slater determinantal form, which, for an N-electron system, is

\[ |\phi_1 \phi_2 \phi_3 \ldots \phi_N\rangle = \left(\frac{1}{\sqrt{N!}}\right)^{\frac{N-1}{2}} \sum_{\sigma_1} (-1)^\sigma |\phi_1\rangle |\phi_2\rangle |\phi_3\rangle \ldots |\phi_N\rangle \]

\[ = \left(\frac{1}{\sqrt{N!}}\right)^{\frac{N-1}{2}} \begin{vmatrix} |\phi_1\rangle & |\phi_2\rangle & |\phi_3\rangle \ldots & |\phi_N\rangle \\
|\phi_1\rangle & |\phi_2\rangle & |\phi_3\rangle \ldots & |\phi_N\rangle \\
\vdots & \vdots & \ddots & \vdots \\
|\phi_1\rangle & |\phi_2\rangle & |\phi_3\rangle \ldots & |\phi_N\rangle \\
\end{vmatrix} \]

(3.22)

where \(P_\sigma\) permutes the electrons. Thus,

\[ |\pi^2 \Sigma^- 0 \pm 1\rangle = |\pm 1 \pm 1\rangle \]

\[ |\pi^2 \Sigma^- 0 \pm 0\rangle = \frac{1}{\sqrt{2}} \{ |1^+ \pm 1\rangle + |1^- \pm 1\rangle \} \]

\[ |\pi^2 \Delta \pm 2 \pm 0\rangle = |\pm 1 \mp 1\rangle \]

\[ |\pi^2 \Sigma^+ 0 \pm 0\rangle = \frac{1}{\sqrt{2}} \{ |1^+ \pm 1\rangle - |1^- \pm 1\rangle \} \]

(3.23)

### 3.3.3.3 Three-electron SL wavefunctions

Wavefunctions for states with more than one open shell, \(a^m b^n\), are formed by sequentially coupling wavefunctions for each subconfiguration, using

\[ |(a^m(S_1 h_1), b^n(S_2 h_2)) S h M \theta\rangle = (-1)^{S-M} |\theta\rangle |S\rangle^{\frac{1}{2}} (-1)^{S-M} |h\rangle^{\frac{1}{2}} \]  

\[ \sum_{M_1, M_2} (S_1 S_2 S) \sum_{M_1 M_2} \left( \frac{h_1 h_2 h^*}{\theta_1 \theta_2 \theta} \right)^* \sum_{M_1 M_2} (S_1 S_2 S) \sum_{M_1 M_2} \left( \frac{h_1 h_2 h^*}{\theta_1 \theta_2 \theta} \right)^* |a^m S_1 h_1 M_1 \theta_1\rangle |b^n S_2 h_2 M_2 \theta_2\rangle \]

(3.24)
where \(|a^m \: S_1 \: h_1 \: M_1 \: \theta_1\rangle\) is the \(SL\) wavefunction corresponding to the \(a^m\) subconfiguration. The coupled wavefunction must be antisymmetrised to satisfy the Pauli exclusion principle, using

\[
|\mathcal{A}(a^m(S_1 \: h_1), b^n(S_2 \: h_2)) \: S \: h \: M \: \theta \rangle = \frac{[m! \: n! \: (m + n)!]^{-1/2}}{(m+n)!} \sum_v (-1)^v \: P_v |(a^m(S_1 \: h_1), b^n(S_2 \: h_2)) \: S \: h \: M \: \theta \rangle
\]  

(3.25)

where \(\mathcal{A}\) is the antisymmetrisation operator. The resulting \(SL\) wavefunction can now be expressed in Slater determinantal form, as follows.

\[\sigma^1 \pi^2\]

The states of the three-electron configuration \(\sigma^1 \pi^2\) are formed by coupling a \(\sigma\) electron to the states for the \(\pi^2\) configuration (derived above). The orbital irreps are given by

\[
\Lambda = 0 \otimes (0 \oplus \bar{0} \oplus 2) = 0 \oplus \bar{0} \oplus 2 = \Sigma^+ \oplus \Sigma^- \oplus \Delta
\]  

(3.26)

and the spin quantum numbers by

\[
S = \frac{1}{2} \otimes (0 \oplus 1) = \frac{1}{2} \oplus \frac{1}{2} \oplus \frac{1}{2}
\]  

(3.27)

Application of Eqs. (3.24) and (3.25) gives the following antisymmetrised \(SL\) wavefunctions.

\[
|\mathcal{A}(\sigma^1(\frac{1}{2} \: 0), \pi^2(0 \: 0)) \: \frac{1}{2} \: 0 \pm \frac{1}{2} \: 0\rangle = \frac{1}{\sqrt{2}} \{ |0^+ - 1^+ \: 1^-\rangle - |0^+ - 1^- \: 1^+\rangle\}
\]

\[
|\mathcal{A}(\sigma^1(\frac{1}{2} \: 0), \pi^2(1 \: \bar{0})) \: \frac{1}{2} \: \bar{0} \pm \frac{1}{2} \: 0\rangle = \frac{1}{\sqrt{2}} \{ |0^+ - 1^\pm \: 1^\mp\rangle - |0^\pm - 1^+ \: 1^-\rangle - |0^\pm - 1^- \: 1^+\rangle\}
\]

\[
|\mathcal{A}(\sigma^1(\frac{1}{2} \: 0), \pi^2(1 \: \bar{0})) \: \frac{1}{2} \: \bar{0} \pm \frac{1}{2} \: 0\rangle = |0^\pm - 1^\pm \: 1^\mp\rangle
\]

\[
|\mathcal{A}(\sigma^1(\frac{1}{2} \: 0), \pi^2(1 \: \bar{0})) \: \frac{1}{2} \: \bar{0} \pm \frac{1}{2} \: 0\rangle = \frac{1}{\sqrt{3}} \{ |0^+ - 1^\pm \: 1^\mp\rangle + |0^\pm - 1^+ \: 1^-\rangle + |0^\pm - 1^- \: 1^+\rangle\}
\]

\[
|\mathcal{A}(\sigma^1(\frac{1}{2} \: 0), \pi^2(0 \: 2)) \: \frac{1}{2} \: 2 \pm 2\rangle = -|0^+ \pm 1^- \pm 1^+\rangle
\]
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\[ |\Theta(\sigma^1(1^0 0), \pi^2(0 2))\rangle = -|0^- 1^- 1^+\rangle \]  

\(\pi^3\)

The states of three-electron configuration \(\pi^3\) are formed by coupling a single \(\pi\) electron to the states of the \(\pi^2\) configuration. Since a \(\pi^3\) configuration is the hole-particle equivalent of \(\pi^1\), the overall term is \(^2\Pi\) (refer to Eq. (3.15)). Of the 24 possible \(\pi^2-\pi\) functions, only 12 transform as \(^2\Pi\) and hence contribute to the correctly antisymmetrised final states. These 12 non-antisymmetrised wavefunctions are derived using Eq. (3.24).

\[ |(\pi^2(0 0), \pi^1(1 1))\rangle \pm 1 \pm 1\rangle = \frac{1}{\sqrt{2}} \{ |-1^+ 1^-\rangle |\pm 1^+\rangle - |-1^- 1^+\rangle |\pm 1^-\rangle \} \]

\[ |(\pi^2(0 0), \pi^1(1 1))\rangle \mp 1 \mp 1\rangle = \frac{1}{\sqrt{2}} \{ |-1^- 1^+\rangle |\pm 1^+\rangle - |-1^+ 1^-\rangle |\pm 1^-\rangle \} \]

\[ |(\pi^2(1 0), \pi^1(1 1))\rangle \pm 1 \pm 1\rangle = \frac{1}{\sqrt{6}} \{ |-1^+ 1^-\rangle |\pm 1^+\rangle + |-1^- 1^+\rangle |\pm 1^-\rangle - 2|-1^+ 1^-\rangle |\pm 1^-\rangle \} \]

\[ |(\pi^2(1 0), \pi^1(1 1))\rangle \mp 1 \mp 1\rangle = \frac{1}{\sqrt{6}} \{ |-1^- 1^+\rangle |\pm 1^+\rangle + |-1^+ 1^-\rangle |\pm 1^-\rangle - 2|-1^- 1^+\rangle |\pm 1^+\rangle \} \]

\[ |(\pi^2(0 2), \pi^1(1 1))\rangle \pm 1 \pm 1\rangle = -|\pm 1^- \pm 1^+\rangle |\mp 1^+\rangle \]

\[ |(\pi^2(0 2), \pi^1(1 1))\rangle \mp 1 \mp 1\rangle = -|\pm 1^+ \pm 1^-\rangle |\mp 1^-\rangle \]  

(3.29)

The four final antisymmetric \(^2\Pi\) states are formed by taking appropriate linear combinations of the 12 wavefunctions above, using “coefficients of fractional parentage” (CFP). This process is given by Eqs. (3.30) and (3.31).

\[ |a^n S_{1h_1} S_{2h_2} h M \Theta\rangle = \sum S_{1h_1} S_{2h_2} \langle a^n S_{1h_1} S_{2h_2} h | a^n S_{1h_1} S_{2h_2} h \rangle \times \]

\[ |(a^n S_{1h_1}, a^n S_{2h_2}) S_{1h_1} S_{2h_2} h M \Theta\rangle \]  

(3.30)

where the coefficients indicated by parentheses are the CFP. Thus,

\[ |\pi^3 \Pi M \Theta\rangle = (\pi^2 0 0, \pi^1 \pi^3 \Pi)(\pi^2 (0 0), \pi^1) \Pi M \Theta\rangle + \]

\[ (\pi^2 1 0, \pi^1 \pi^3 \Pi)(\pi^2 (1 0), \pi^1) \Pi M \Theta\rangle + \]

\[ (\pi^2 0 2, \pi^1 \pi^3 \Pi)(\pi^2 (0 2), \pi^1) \Pi M \Theta\rangle \]  

(3.31)
Although some CFP are tabulated, it is relatively straightforward to derive them from first principles. Essentially, they are chosen so that $|\pi^3 \Sigma M \Theta\rangle$ is antisymmetric and obeys the Pauli exclusion principle. Since, for example, the sum of all terms in $|1^+ 1^-\rangle|1^+\rangle$ in Eq. (3.31) must be zero, it is apparent that

\[
(p^2 0 0, \pi^1 |\pi^3 \Sigma\rangle) = -\frac{1}{\sqrt{3}}(p^2 1 0, \pi^1 |\pi^3 \Sigma\rangle)
\]

(3.32)

Once Eq. (3.32) has been inserted into Eq. (3.31), it is found that properly antisymmetric kets of the form in Eq. (3.22) will be obtained only if

\[
(p^2 0 2, \pi^1 |\pi^3 \Sigma\rangle) = \frac{\sqrt{2}}{\sqrt{3}}(p^2 1 0, \pi^1 |\pi^3 \Sigma\rangle)
\]

(3.33)

Eqs. (3.32) and (3.33) give the required CFP to within a phase factor. The phase is chosen so as to satisfy Eq. (3.34) when $n = 1$.

\[
|d^{2|\alpha|} 0 0 0 0\rangle = \sum_{\alpha_1 \alpha_2} |S|^{\alpha_1} |h_1|^{\alpha_2} \left[ \frac{(2|\alpha|)!}{n! (2|\alpha| - n)!} \right]^{\frac{1}{2}} |(a^n (S_1 h_1), d^{2|\alpha|-n} (S_2 h_2)) 0 0 0 0\rangle
\]

(3.34)

In this case, we want

\[
|\pi^4 0 0 0 0\rangle = |1^- 1^- 1^+ 1^-\rangle = |(\pi^1, \pi^3) 0 0 0 0\rangle
\]

(3.35)

Eq. (3.34) can only be satisfied if the CFP are

\[
(p^2 0 0, \pi^1 |\pi^3 \Sigma\rangle) = -\frac{1}{\sqrt{6}}
\]

\[
(p^2 1 0, \pi^1 |\pi^3 \Sigma\rangle) = \frac{1}{\sqrt{2}}
\]

\[
(p^2 0 2, \pi^1 |\pi^3 \Sigma\rangle) = \frac{1}{\sqrt{3}}
\]

(3.36)

The SL wavefunctions are therefore
3.3.3.4 Four-electron SL wavefunctions

\( \sigma^1 \pi^3 \)

The four-electron configuration \( \sigma^1 \pi^3 \) is formed by coupling a single \( \sigma \) electron to the states of the \( \pi^3 \) configuration.

\[
|\sigma^1(\frac{1}{2} 0), \pi^3(\frac{1}{2} 1) \, 0 \, 1 \, 0 \pm 1 \rangle = \frac{1}{\sqrt{2}} (|0^\pm - 1^- \pm 1^\mp 1^\pm \rangle - |0^- 1^+ \pm 1^\mp 1^\pm \rangle)
\]

\[
|\sigma^1(\frac{1}{2} 0), \pi^3(\frac{1}{2} 1) \, 1 \, 1 \, 0 \pm 1 \rangle = \frac{1}{\sqrt{2}} (|0^\pm - 1^- \pm 1^\mp 1^\pm \rangle + |0^- 1^+ \pm 1^\mp 1^\pm \rangle)
\]

\[
|\sigma^1(\frac{1}{2} 0), \pi^3(\frac{1}{2} 1) \, 1 \, 1 \, \mp \mp \pm \rangle = -|0^- - 1^\mp \mp 1^\pm \rangle
\]

\[
|\sigma^1(\frac{1}{2} 0), \pi^3(\frac{1}{2} 1) \, 1 \, \mp \mp \pm \pm \rangle = -|0^- - 1^\mp \mp 1^\pm \rangle
\]

3.3.4 Spin-Orbit Wavefunctions

When \( \mathcal{H}_{SO} \) is included in the Hamiltonian \( \mathcal{H} \), the operator \( S^2 \) no longer commutes with \( \mathcal{H} \); hence \( S \) is no longer a good quantum number. Furthermore, the orbital functions can no longer be classified by \( h \) and \( \theta \). It is the coupled double-group irreps, designated \( t \) with partners \( \tau \), which now span the eigenfunctions of \( \mathcal{H} \).

Before this coupling can be performed, however, the angular momentum \( (\text{SO}_3 \supset \text{SO}_2) \) spin basis \( |S \, M \rangle \) must be adapted to the molecular double group — \( C_{ov} \) in this case. The new spin functions are labelled as \( |S_i \, M_i \rangle \), where \( S_i \) and \( M_i \) are respectively the spin irrep and partner in the molecular double group. This adaptation is performed using Table 3.5.

Spin-orbit (SO) irreps are determined from the direct product of the spin and orbital irreps, both in the molecular point group:

\[
t = S_i \otimes h
\]
Table 3.5: Basis for $O_3 \supset D_{ab} \supset C_{nv} \supset C_\infty$ defined in terms of the $O_3 \supset SO_3 \supset SO_2$ ($\equiv C_\infty$) basis.

| $j$ | |$j^k(O_3) \ a^k(D_{ab}) a_1(C_{nv}) m(C_\infty)$| |$O_3 \supset SO_3 \supset SO_2$| |$|j^k m\rangle$| Equivalent |
|-----|-------------------------------------------------|------------------|------------------|------------------|
| 0   | $|0^+ 0^+ 0^+ 0^+\rangle$                         | $|0^+ 0^+\rangle$ |                  |                  |
| 1   | $|1^+ 0^+ 0^+ 0^+\rangle$                         | $|1^+ 0^+\rangle$ |                  |                  |
|     | $|1^+ 1^+ 1^+ \pm 1\rangle$                       | $|1^+ \pm 1\rangle$ |                  |                  |
|     | $|1^- 0^- 0^- 0^-\rangle$                         | $|1^- 0^-\rangle$ |                  |                  |
|     | $|1^- 1^- 1^- \pm 1\rangle$                       | $|1^- \pm 1\rangle$ |                  |                  |
| 2   | $|2^+ 0^+ 0^+ 0^+\rangle$                         | $|2^+ 0^+\rangle$ |                  |                  |
|     | $|2^+ 1^+ 1^+ \pm 1\rangle$                       | $\mp |2^+ \pm 1\rangle$ |                  |                  |
|     | $|2^+ 2^+ 2^+ \pm 2\rangle$                       | $|2^+ \pm 2\rangle$ |                  |                  |
|     | $|2^- 0^- 0^- 0^-\rangle$                         | $|2^- 0^-\rangle$ |                  |                  |
|     | $|2^- 1^- 1^- \pm 1\rangle$                       | $|2^- \pm 1\rangle$ |                  |                  |
|     | $|2^- 2^- 2^- \pm 2\rangle$                       | $|2^- \pm 2\rangle$ |                  |                  |

Normalised and orthogonal SO wavefunctions $|(S S_1, h) t \tau\rangle$ are derived using

$$
|(S S_1, h) t \tau\rangle = |t|^{1/2} \sum_{M_1 \theta} \left( \begin{array}{c} S_1 \ h \ t^* \\ M_1 \ \theta \end{array} \right)^* |S S_1 \ h \ M_1 \ \theta\rangle
$$

(3.40)

The $|(S S_1, h) t \tau\rangle$ functions are normally written as $|^{2S+1}h_i \ \tau\rangle$. Using Eq. (3.40), the following SO wavefunctions are derived.
3.3.4.1 One-electron SO wavefunctions

\begin{align*}
\sigma^1 \quad |^3\Sigma^+_1 \pm \frac{1}{2}\rangle &= |(\frac{1}{2}, 0) \frac{1}{2}, \pm \frac{1}{2}\rangle = -\frac{1}{2} |0 \pm \frac{1}{2}, 0\rangle = -|0^\pm\rangle \\
\pi^1 \quad |^3\Pi_{1/2} \pm \frac{1}{2}\rangle &= |(\frac{1}{2}, 1) \frac{1}{2}, \pm \frac{1}{2}\rangle = \mp \frac{1}{2} |1 \mp \frac{1}{2}, \pm 1\rangle = \mp |\pm 1^\mp\rangle \\
|\Sigma_{3/2} \pm \frac{1}{2}\rangle &= |(\frac{1}{2}, 0) \mp \frac{1}{2}, \pm \frac{1}{2}\rangle = \mp \frac{1}{2} |0 \pm \frac{1}{2}, \pm 1\rangle = \mp |\pm 1^\pm\rangle \\
|\Sigma_{1/2} \pm \frac{1}{2}\rangle &= |(\frac{1}{2}, 0) \pm \frac{1}{2}, \pm \frac{1}{2}\rangle = \pm \frac{1}{2} |0 \mp \frac{1}{2}, \pm 1\rangle = \pm |\pm 1^\pm\rangle \\
\end{align*}

3.3.4.2 Two-electron SO wavefunctions

\begin{align*}
\pi^2 \quad |\Sigma^+_0 0\rangle &= |(0, 0) 0, 0\rangle = |0 0 0 0\rangle = \frac{1}{\sqrt{2}}(-|0^+ 1^-\rangle - |0^- 1^+\rangle) \\
|\Sigma_0 0\rangle &= |(0, 0) 0, 0\rangle = -|1 0, 0 0\rangle = -\frac{1}{\sqrt{2}}(-|0^+ 1^-\rangle + |0^- 1^+\rangle) \\
|\Sigma^- 1\rangle &= |(1, 1) 1, 1\rangle = \mp |1 1 0 0\rangle = \mp |1^\pm 1^\mp\rangle \\
|\Delta_2 2\rangle &= |(0, 0) 2, 2\rangle = |0 0 2 2\rangle = -|0^\pm 0^\pm\rangle \\
\end{align*}

3.3.4.3 Three-electron SO wavefunctions

\begin{align*}
\sigma^1 \pi^2 \quad |^3\Sigma^+_1/2 \pm \frac{1}{2}\rangle &= |(\frac{1}{2}, 0) \frac{1}{2}, \pm \frac{1}{2}\rangle = -\frac{1}{\sqrt{2}} |0^+ - 1^-\rangle = -\frac{1}{\sqrt{2}} |0^- - 1^+\rangle \\
|\Sigma^+_1/2 \pm \frac{1}{2}\rangle &= |(\frac{1}{2}, 0) \pm \frac{1}{2}, \pm \frac{1}{2}\rangle = \pm \frac{1}{\sqrt{3}} |0^\pm 1^\mp\rangle \\
|\Sigma^- 1/2 \pm \frac{1}{2}\rangle &= |(\frac{1}{2}, 0) \mp \frac{1}{2}, \pm \frac{1}{2}\rangle = \mp \frac{1}{\sqrt{3}} |0^\mp 1^\pm\rangle \\
|\Delta_5 2\rangle &= |(0, 0) 2, 2\rangle = |0 0 2 2\rangle = |0^\pm 0^\pm\rangle \\
|\Delta_3 2\rangle &= |(0, 0) 2, 2\rangle = |0 0 2 2\rangle = |0^\pm 0^\pm\rangle \\
\end{align*}
\[ \pi^3 \]

\[ |^2\text{II}_1 \pm \rangle = |(\frac{1}{2}, 1, \frac{1}{2} \pm \rangle = \mp \frac{1}{\sqrt{2}} |1 \pm 1 \pm 1\rangle = \pm |-1^\pm 1^\pm 1^\pm \rangle \] (3.54)

\[ |^2\text{II}_2 \pm \rangle = |(\frac{1}{2}, 1, \frac{1}{2} \pm \rangle = -\frac{1}{\sqrt{2}} |1 \pm 1 \pm 1\rangle = |-1^\pm 1^\pm 1^\pm \rangle \] (3.55)

### 3.3.4.4 Four-electron SO wavefunctions

\[ \sigma^1 \pi^3 \]

\[ |^3\Pi_1 \pm \rangle = |(0, 0, 1, 1 \pm 1\rangle = |0 0 0 1 0 1 \rangle \]

\[ = \mp \frac{1}{\sqrt{2}} \{ |0^\pm 1^- 1^\pm 1^\pm \rangle - |0^\pm 1^\pm 1^\pm 1^\pm \rangle \} \] (3.56)

\[ |^3\Pi_0 \pm \rangle = |(1, 1, 1, 0 0 \rangle = \frac{1}{\sqrt{2}} |1 1 1 1 -1 \rangle + \frac{1}{\sqrt{2}} |1 1 1 -1 1 \rangle \]

\[ = \frac{1}{\sqrt{2}} \{ |0^+ 1^- 1^+ 1^- \rangle + |0^- 1^- 1^- 1^+ \rangle \} \] (3.57)

\[ |^3\Pi_0 \mp \rangle = |(1, 1, 1, 0 0 \rangle = \frac{1}{\sqrt{2}} |1 1 1 1 -1 \rangle - \frac{1}{\sqrt{2}} |1 1 1 -1 1 \rangle \]

\[ = -\frac{1}{\sqrt{2}} \{ |0^+ 1^- 1^- 1^+ \rangle - |0^- 1^- 1^- 1^+ \rangle \} \] (3.58)

\[ |^3\Pi_1 \pm \rangle = |(1, 0, 1, 1 \pm 1\rangle = \pm |1 0 1 0 \pm 1\rangle \]

\[ = \mp \frac{1}{\sqrt{2}} \{ |0^\pm 1^- 1^\pm 1^\pm \rangle + |0^\pm 1^\pm 1^\pm 1^\pm \rangle \} \] (3.59)

\[ |^3\Pi_2 \pm \rangle = |(1, 1, 2, 2 \pm \rangle = |1 1 1 1 \pm 1\rangle = - |0^\pm 1^- 1^\pm 1^\pm \rangle \] (3.60)

### 3.3.5 Matrix Elements

#### 3.3.5.1 SOC matrix elements

Details on spin-orbit coupling are given in Section 2.9.2. Matrix elements between SO wavefunctions are calculated using Eq. (2.141) and the Condon-Slater rules. These results are given in Chapters 7, 8, and 9 as required.

#### 3.3.5.2 CF matrix elements

Crystal fields were introduced in Section 2.9.3. A CF-induced splitting between a pair of degenerate \( \pi \) orbitals, requires that there are non-zero matrix elements of the type \( \langle 1 m_\pi V^\gamma \mid 1 m_\pi \rangle \), where \( V^\gamma \) is the component of CF that transforms
as partner $\gamma$ of irrep $\Gamma$ in the $C_{\text{ov}}$ point group. Since $V_{\gamma}$ is a real operator and $\pi$ is a category-one irrep (Section 2.8), these matrix elements will be non-zero only if

$$\Gamma \subset [\pi^2]$$  \hspace{2cm} (3.61)

Using Tables 3.2 and 3.1, the possible irreps of the potentially active components of the CF operator are therefore $\Sigma^+$ and $\Delta$. Since $\Sigma^+$ is the totally symmetric irrep of $C_{\text{ov}}$, the corresponding component of the CF shifts the energies of both orbitals in the same direction, having no effect on their degeneracy. In terms of the WET,

$$\langle 1 \pm 1| V^0_0|1 \pm 1 \rangle = \left( \begin{array}{cc} 1 & 1 \\ 1 & 0 \end{array} \right) \left( \begin{array}{cc} 1 & 0 \\ 0 & 1 \end{array} \right) C_{\text{ov}} \langle \pi||V^0||\pi \rangle = \frac{1}{\sqrt{2}} \langle \pi||V^0||\pi \rangle$$  \hspace{2cm} (3.62)

The CF operator of $\Delta$ symmetry ($\mathcal{K}_{\text{CF}}$) is chosen to transform as the tesseral harmonic $Z_{22}^C$ (which is essentially the functional form of the $d_{x^2-y^2}$ orbital).

$$Z_{22}^C = \frac{1}{\sqrt{2}} \{ |2 2 \rangle + |2 -2 \rangle \}$$

$$\mathcal{K}_{\text{CF}} = \frac{1}{\sqrt{2}} (V^2_2 + V_{-2}^2)$$  \hspace{2cm} (3.63)

The matrix elements of $V_{22}^2$ are evaluated using the Wigner-Eckart theorem

$$\langle 1 \pm 1| V_{22}^2|1 \mp 1 \rangle = \frac{1}{\sqrt{2}} \langle 1||V^2||1 \rangle = \frac{V}{\sqrt{2}}$$  \hspace{2cm} (3.64)

where $V$ is a parameter representing the magnitude of the splitting of the orbital components. Since these matrix elements are off-diagonal in the $|1 \pm 1\rangle$ basis, the CF will mix the states as well as lower their degeneracy.

**3.3.5.3 Zeeman matrix elements**

The Zeeman effect is briefly explained in Section 2.9.4. In the case of a non-rotating, randomly oriented diatomic molecule, the molecular $z$ axis may not
necessarily coincide with the laboratory Z axis. In such a case the Zeeman splitting depends on the projection of the magnetic field onto the IN axis. Therefore, the laboratory operator $\mu_Z$ must be related to the molecular operators $\mu_z$, $\mu_x$ and $\mu_y$, all of which have potentially non-zero matrix elements. In the case of diatomic molecules, it can be shown from Eq. (2.75) that

$$J_z = \sin \theta J_x + \cos \theta J_z$$

(3.65)

where $J$ is $L$ or $S$, and $\theta$ is the (Euler) angle between $z$ and $Z$.

The Zeeman effect for the state of a linear or axial molecule can be characterised by two principal $g$ values, which correspond to the cases with $B$ either parallel or perpendicular to the molecular $z$ axis; these values are designated $g_{\parallel} = g_z$ and $g_{\perp} = g_x = g_y$, respectively. The value of $g_{\parallel}$ is determined by the matrix elements of $\mu_z$, whereas that of $g_{\perp}$ is calculated from matrix elements of $\mu_x$ (or $\mu_y$).

### 3.3.5.4 Transition moments

Details on transition moments are given in Section 2.9.5. In this work, the spin selection rules ($\Delta S = \Delta M_S = 0$) are rigorously obeyed for transitions between basis states. The orbital selection rules are determined by the transformation properties of $m$. In $C_{\text{cov}}$, $m_0 = \Sigma^\dagger$, and $m_{\pm 1} = \Pi$. All excitations in this work are of the type $\pi \leftarrow \sigma$, hence the transitions are polarised perpendicular to the molecular $z$ axis. Transition moments between SO wavefunctions are calculated using the WET and the Condon-Slater rules.

### 3.4 Many-Electron Rotational Wavefunctions

#### 3.4.1 Hund’s Case-(a) Basis Set

When spin-orbit coupling is not large, $\Lambda$, $S$, and $\Sigma$ are almost good quantum numbers, the energy levels fall into recognisable term multiplets, and it is sufficient to characterise the electronic part (i.e. excluding rotation) of the wavefunction by $|\Lambda, S, \Sigma, h, \tau \rangle = |\Lambda, S, \Sigma, \Omega \rangle = |\Lambda, S, \Sigma \rangle$. In fact, $\Omega$ is the only truly good quantum number, but there is no need to specify it because of its simple relation to $\Lambda$ and $\Sigma$ (Table 3.3). This slight change in notation facilitates the representation of subsequent Hund’s
case-(a) basis functions and matrix elements.

The rotational part of the wavefunction is denoted by \( |J \Omega M \rangle \), where \( J \) is the total angular momentum (Table 3.3), and \( M = J, J - 1, \ldots, -J \) is the projection of \( J \) along the laboratory \( Z \) axis. Strictly speaking, \( \Omega \) is a quantum number only for the electronic part of the wavefunction (the eigenvalue of \( L_z + S_z \)), so it is included here simply as a parameter. Since it represents the projection of \( J \) along the internuclear axis, the rule \( J \geq |\Omega| \) applies. In terms of the \( D \) rotation matrices discussed in Section 2.6.7, the functional form of \( |J \Omega M \rangle \) is

\[
|J \Omega M \rangle = \sqrt{\frac{2J + 1}{4\pi}} D^J_M(\phi, \theta, 0)^* 
\]

(3.66)

This relationship is extremely important when it comes to determining some matrix elements, including transition moments and Zeeman matrix elements. Since a diatomic molecule only has two degrees of freedom, one of the Euler angles is redundant and \( \chi \) is chosen to be zero, which results in a change of normalisation factor (integration over \( \chi \) is no longer required). The integrals of Section 2.6.8 need to be altered to reflect this. The solid-angle element \( d\Omega \) is now given by

\[
\int d\Omega = \int d\phi \int_0^\pi \sin \theta d\theta
\]

(3.67)

and the integrals of Eqs. (2.101) and (2.103) become

\[
\int d\Omega \; D^J_{M_1 M}(\phi, \theta, 0)^* D^J_{M_2 M}(\phi, \theta, 0) = \frac{4\pi}{2J_1 + 1} \delta_{J_1 J_2} \delta_{M_1 M_2} \delta_{M_1 M}
\]

(3.68)

\[
\int d\Omega \; D^J_{M_1 M}(\phi, \theta, 0)^* D^J_{M_2 M}(\phi, \theta, 0) D^J_{M_3 M}(\phi, \theta, 0)
\]

\[
= \frac{4\pi}{2J_3 + 1} \langle J_1 M_1, J_2 M_2 | J_3 M_3 \rangle \left( \langle J_1 M_1' | J_2 M_2' \rangle | J_3 M_3' \rangle \right)
\]

(3.69)

The total case-(a) basis functions are simply products of the electronic \(|\Lambda S \Sigma \rangle\), vibrational \(|\nu \rangle\), and rotational \(|J \Omega M \rangle\) parts.

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where \( n \) represents any other information that is used to specify the electronic state of the system.

### 3.4.2 Hunds Case-(a) Basis-Set Matrix Elements

Important matrix elements in the Hunds case-(a) basis set are

\[
\begin{align*}
\langle J \Omega M | J^2 | J \Omega M \rangle &= J (J + 1) \\
\langle J \Omega M | J_z | J \Omega M \rangle &= \Omega \\
\langle J \Omega \mp 1 M | J_k | J \Omega M \rangle &= \left[ J (J + 1) - \Omega (\Omega \mp 1) \right]^{1/2} \\
\langle \Lambda \Sigma \Xi | L_\pm | \Lambda \Sigma \Xi \rangle &= \Lambda \\
\langle \Lambda \Sigma \Xi | S^2 | \Lambda \Sigma \Xi \rangle &= S (S + 1) \\
\langle \Lambda \Sigma \Xi | S_\pm | \Lambda \Sigma \Xi \rangle &= \Sigma \\
\langle \Lambda \Sigma \Xi \pm 1 | S_\pm | \Lambda \Sigma \Xi \rangle &= \left[ S (S + 1) - \Sigma (\Sigma \pm 1) \right]^{1/2}
\end{align*}
\]

Due to the anomalous commutation relations outlined in Section 2.6.6, Eq. (3.73) is based on Eq. (2.86). Matrix elements involving \( L_\pm \) are not listed because \( L \) is a poor quantum number.

### 3.4.3 Parity

The preceding Hund’s case-(a) basis functions (Eq. (3.70)) are not properly symmetrised because they are not eigenfunctions of the spatial inversion operator \( (i_{sp}) \), which replaces the laboratory-fixed Cartesian coordinates of all particles by their negatives. Ideally the molecular states should be classified as even (+) or odd (−) according to whether the corresponding wavefunction (apart from translation) remains the same or changes sign under this transformation. It can be shown\(^2, 9, 10\) that spatial inversion \( (i_{sp}) \) is equivalent to a rotation of the molecular frame by \( \pi \) about the \( x \) axis \( (C_2(x)) \) followed by a reflection of the molecule-fixed electronic coordinates in the \( yz \) plane \( (\sigma_v(yz)) \). Since the vibrational wavefunction \( |\nu\rangle \) depends only on the internuclear distance, it remains unchanged under spatial inversion. However the electronic and rotational parts are affected.
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\[ i_{sp} |n \Lambda S \Sigma; J \Omega M\rangle = \sigma_s(yz)C_2(x) |n \Lambda S \Sigma; J \Omega M\rangle = \sigma_s(yz) |n \Lambda S \Sigma\rangle C_2(x) |J \Omega M\rangle \]  
\[ \hspace{1cm} (3.78) \]

It can further be shown\(^2\),\(^9\),\(^10\) that

\[ \sigma_s(yz) |n \Lambda S \Sigma\rangle = (-1)^{S+w} |n -\Lambda S -\Sigma\rangle \]  
\[ \hspace{1cm} (3.79) \]

and

\[ C_2(x) |J \Omega M\rangle = (-1)^J |J -\Omega M\rangle \]  
\[ \hspace{1cm} (3.80) \]

where \( w \) is 1 for \( \Sigma^- \) states and zero otherwise. The overall parity relation can therefore be written as

\[ i_{sp} |n \Lambda S \Sigma; \nu; J \Omega M\rangle = (-1)^{J-S+w} |n -\Lambda S -\Sigma; \nu; J -\Omega M\rangle \]  
\[ \hspace{1cm} (3.81) \]

In order to form states of definite parity, the matrix for the \( i_{sp} \) operator must be diagonalised.

\[ \begin{bmatrix} 0 & (-1)^{J-S+w} \\ (-1)^{J-S+w} & 0 \end{bmatrix} \]  
\[ \hspace{1cm} (3.82) \]

The eigenfunctions of the matrix in Eq. (3.82) are the simple sum and difference linear combinations

\[ |n \Lambda S \Sigma; \nu; J \Omega M \rho^\pm \rangle = \frac{1}{\sqrt{2}} \{|n \Lambda S \Sigma; \nu; J \Omega M\rangle \pm |n -\Lambda S -\Sigma; \nu; J -\Omega M\rangle\} \]  
\[ \hspace{1cm} (3.83) \]

where \( \rho^\pm \) indicates the sign of the linear combination and corresponds to a parity of \( \pm (-1)^{J-S+w} \). As can be seen, each state is an admixture of basis functions with quantum numbers \( \pm \Omega \), but has a well-defined value of \( |\Omega| \). Furthermore, the only non-zero matrix elements of the molecular Hamiltonian operator are between states of the same parity, \( i.e. \) between states with the same eigenvalue of \( i_{sp} \).
3.4.4 Construction of Rotational Wavefunctions for States Intermediate Between Hund’s Cases (a) and (b)

With the aid of Table 3.3, the rotational Hamiltonian can be written as

\[ \mathcal{H}_{\text{rot}} = B_v \mathbf{R}^2 = B_v (J - L - S)^2 = B_v (J^2 + L^2 + S^2 - 2J \cdot S - 2J \cdot L + 2S \cdot L) \]  \hspace{1cm} (3.84)

\( B_v \) is the value of the rotational constant in the \( v \)th vibrational state

\[ B_v = \frac{1}{2I} = \frac{\langle \psi | 1/r^2 | \psi \rangle}{2\mu} \]  \hspace{1cm} (3.85)

where \( r \) is the bond length of the diatomic molecule and \( \mu \) is its reduced mass, a function of the masses of the two nuclei, \( m_A \) and \( m_B \).

\[ \mu = \frac{m_A m_B}{m_A + m_B} \]  \hspace{1cm} (3.86)

Since \( J_z = S_z + L_z \), the term \( B_v (J_z - S_z - L_z)^2 \) can be subtracted from Eq. (3.84) to give

\[ \mathcal{H}_{\text{rot}} = B_v (J^2 - J_x^2 - J_y^2 - J_z^2 - 2J \cdot S - 2J \cdot L + 2J \cdot S_x + 2J \cdot S_y + 2S \cdot L - 2S \cdot L_x) \]
\[ = B_v (J^2 - J_x^2 + L^2 - L_z^2 + S^2 - S_z^2 - 2J_s S_z - J_s L_z - J_s L - J_s L_x + S_s L_z + S_s L_x + S_s L_y) \]  \hspace{1cm} (3.87)

Matrix elements of \( L_x \) are necessarily zero, since, for a given \( |\Lambda| \), no orbital partners differ by \( \pm 1 \). Hence, the effective Hamiltonian becomes

\[ \mathcal{H}_{\text{rot}} = B_v (J^2 - J_x^2 + S^2 - S_z^2 + L_x^2 + L_y^2) - B_v (J_s S_z + J_s L_z) \]  \hspace{1cm} (3.88)

The first term of Eq. (3.88) is responsible for diagonal matrix elements

\[ \langle n \Lambda S \Sigma \psi; J \Omega M | \mathcal{H}_{\text{rot}} | n \Lambda S \Sigma \psi; J \Omega M \rangle = B_v \{J(J + 1) - \Omega^2 + S(S + 1) - \Sigma^2 + \langle L_x^2 + L_y^2 \rangle\} \]  \hspace{1cm} (3.89)
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whereas the second term contributes only to off-diagonal elements

\[
\langle n \Lambda S \Sigma \pm 1; v; J \Omega \pm 1 M | \mathcal{K}_{\text{rot}} | n \Lambda S \Sigma; v; J \Omega M \rangle = -B_v \{ S (S + 1) - \Sigma (\Sigma \pm 1) \}^{1/2} \{ J (J + 1) - \Omega (\Omega \pm 1) \}^{1/2}
\]  

(3.90)

The expectation value \( \langle L_x^2 + L_y^2 \rangle \) is problematic because \( L \) is not a good quantum number. However, since it is common to all of the diagonal matrix elements, it will only shift all rotational levels up or down in energy, so can be neglected when solving the secular determinant.

By calculating the appropriate matrix elements of \( \mathcal{K}_{\text{rot}} \) and \( \mathcal{K}_{\text{SO}} \) (Section 3.3.5.1), and solving the resulting secular determinant, one can obtain wavefunctions for any states intermediate between Hund’s cases (a) and (b), as follows. For convenience, the vibrational part of the wavefunction, plus the electronic \( n \), will now be dropped.

### 3.4.4.1 \( ^2 \Sigma^\pm_{1/2} \) states

The basis functions of definite parity are normalised linear combinations of the case-(a) wavefunctions

\[
| ^2 \Sigma^\pm_{1/2} J M p^- \rangle = \frac{1}{\sqrt{2}} \{ | 0 \frac{1}{2}; J \frac{1}{2} M \rangle - | 0 \frac{1}{2}; -J \frac{1}{2} M \rangle \}
\]

(3.91)

\[
| ^2 \Sigma^\pm_{1/2} J M p^+ \rangle = \frac{1}{\sqrt{2}} \{ | 0 \frac{1}{2}; J \frac{1}{2} M \rangle + | 0 \frac{1}{2}; -J \frac{1}{2} M \rangle \}
\]

(3.92)

There is no spin-orbit coupling within \( ^2 \Sigma^\pm \) states, and it turns out that these wavefunctions are already diagonal in \( \mathcal{K}_{\text{rot}} \), with the eigenvalues

\[
E( ^2 \Sigma^\pm; J p^-) = B_v [ J (J + 1) + \frac{1}{2} ] + B_v [ J (J + 1) + \frac{3}{2} ]^{1/2} = B_v (J + \frac{1}{2}) (J + \frac{3}{2})
\]

(3.93)

\[
E( ^2 \Sigma^\pm; J p^+) = B_v [ J (J + 1) + \frac{3}{2} ] - B_v [ J (J + 1) + \frac{1}{2} ]^{1/2} = B_v (J - \frac{1}{2}) (J + \frac{1}{2})
\]

(3.94)

### 3.4.4.2 \( ^2 \Pi \) states

The basis functions of definite parity are once again normalised linear
combinations of case-(a) wavefunctions

\[ |^2\Pi_{1/2} J M p^\pm \rangle = \frac{1}{\sqrt{2}} \{ |1 \frac{1}{2} - \frac{1}{2} J \frac{1}{2} M \rangle \pm | -1 \frac{1}{2} \frac{1}{2} J - \frac{1}{2} M \rangle \} \]  
(3.95)

\[ |^2\Pi_{3/2} J M p^\pm \rangle = \frac{1}{\sqrt{2}} \{ |1 \frac{1}{2} \frac{1}{2} J \frac{1}{2} M \rangle \pm | -1 \frac{1}{2} - \frac{1}{2} J - \frac{1}{2} M \rangle \} \]  
(3.96)

The matrix elements are the same for each parity block, which simplifies the problem. Each rotational level is therefore doubly degenerate. Remembering, from above, that \( J \geq |\Omega| \), the \( J = \frac{1}{2} \) level is associated exclusively with \(^2\Pi_{1/2}\)

\[ |^2\Pi_{1/2} \frac{1}{2} M p^\pm \rangle = \frac{1}{\sqrt{2}} \{ |1 \frac{1}{2} - \frac{1}{2} \frac{1}{2} M \rangle \pm | -1 \frac{1}{2} \frac{1}{2} M \rangle \} \]  
(3.97)

\[ E (^2\Pi; \frac{1}{2} p^\pm) = B_v - \frac{1}{2} A_v \]  
(3.98)

Here, \( A_v \) is the value of the SOC constant in the \( v \)th vibrational state. For \( J > \frac{1}{2} \) the secular determinant involves states with \( |\Omega| = \frac{1}{4} \) and \( \frac{3}{4} \), and has the form

\[ \begin{vmatrix} B_v [J (J+1) + \frac{1}{4}] - \frac{1}{2} A_v - E & -B_v [J (J+1) - \frac{1}{4}] \frac{1}{2} \\ -B_v [J (J+1) - \frac{3}{4}] \frac{1}{2} & B_v [J (J+1) - \frac{3}{4}] + \frac{1}{2} A_v - E \end{vmatrix} = 0 \]  
(3.99)

for which the eigenvalues are

\[ E (^2\Pi; J) = B_v [J (J+1) - \frac{3}{4} \pm \frac{1}{2} X] \]  
(3.100)

where

\[ X = [4J (J+1) + Y (Y - 4) + 1] \frac{1}{2} \]  
(3.101)

and

\[ Y = \frac{A_v}{B_v} \]  
(3.102)

The wavefunctions are denoted \( F_1 \) or \( F_2 \) depending on whether they correspond to the bottom or top line respectively of Eq. (3.100).

\[ |F_1 \rangle = \alpha J |^2\Pi_{1/2} J \rangle + \beta J |^2\Pi_{3/2} J \rangle \]
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\[
|F_2\rangle = -\beta_J |^3\Pi_{1/2} J\rangle + \alpha_J |^3\Pi_{3/2} J\rangle
\]  
(3.103)

where

\[
\alpha_J = \sqrt{\frac{X+ (Y-2)}{2X}}
\]

\[
\beta_J = \sqrt{\frac{X- (Y-2)}{2X}}
\]  
(3.104)

These wavefunctions can be used for both regular \( (A_v > 0) \) and inverted \( (A_v < 0) \) \(^3\Pi\) systems.

3.4.4.3 \(^3\Sigma^-\) states

The basis functions are

\[
|^{3}\Sigma_1^- J M M^p\rangle = \frac{1}{\sqrt{2}} (|0 1 1; J 1 M\rangle \pm |0 1 -1; J-1 M\rangle)
\]  
(3.105)

\[
|^{3}\Sigma_0^- J M\rangle = |0 1 0; J 0 M\rangle
\]  
(3.106)

Now, \( J = 0 \) is specifically associated with the \(^3\Sigma^-\) state, for which

\[
|^{3}\Sigma_0^- 0 0\rangle = |^{3}\Sigma_0^- 0 1 0; 0 0 0\rangle
\]  
(3.107)

\[
E(\ ^{3}\Sigma^-; 0) = 2B_v
\]  
(3.108)

For \( J > 0 \), there are still no spin-orbit coupling matrix elements, and, ignoring spin-spin splitting (Section 8.1.1.1.1), the secular determinant has the form

\[
\begin{vmatrix}
B_v J (J+1) - E & -2B_v [J (J+1)]^{1/2} & 0 \\
-2B_v [J (J+1)]^{1/2} & B_v [J (J+1) + 2] - E & 0 \\
0 & 0 & B_v J (J+1) - E
\end{vmatrix} = 0
\]  
(3.109)

In practice, rather than seeking analytical expressions for the eigenstates and eigenvalues, it is much easier to solve Eq. (3.109) numerically for a series of \( J \) values.
### 3.4.4.4 $^3\Pi$ states

The basis functions are

$$|^3\Pi_0 J M p^\pm\rangle = \frac{1}{\sqrt{2}} \{ [1 1 1; J 0 M] \pm [1 1 -1; J 0 M] \}$$  \hfill (3.110)$$

$$|^3\Pi_1 J M p^\pm\rangle = \frac{1}{\sqrt{2}} \{ [1 1 0; J 1 M] \pm [-1 1 0; J -1 M] \}$$  \hfill (3.111)$$

$$|^3\Pi_2 J M p^\pm\rangle = \frac{1}{\sqrt{2}} \{ [1 1 1; J 2 M] \pm [-1 1 -1; J -2 M] \}$$  \hfill (3.112)$$

The $J = 0$ level is exclusively associated with the $^3\Pi_0$ state.

$$|^3\Pi_0 0 0 p^\pm\rangle = \frac{1}{\sqrt{2}} \{ [1 1 1; 0 0 0] \pm [1 1 -1; 0 0 0] \}$$  \hfill (3.113)$$

$$E (^3\Pi_0; 0) = B_v + A_v$$  \hfill (3.114)$$

The $J = 1$ level is associated only with the $^3\Pi_0$ and $^3\Pi_1$ states. The eigenfunctions and eigenvalues are found by solving Eq. (3.115).

$$\begin{vmatrix} B_v [J (J + 1) +1] + A_v - E & \mp B_v [2J (J + 1)]^{1/2} \\ \mp B_v [2J (J + 1)]^{1/2} & B_v [J (J + 1) +1] - E \end{vmatrix} = 0$$  \hfill (3.115)$$

Although Eq. (3.115) can be solved analytically, there is little reason to do this given that the $J > 1$ levels (immediately below) have to be solved numerically anyway. For $J > 1$ the secular determinant is

$$\begin{vmatrix} B_v [J (J + 1) +1] + A_v - E & \mp B_v [2J (J + 1)]^{1/2} & 0 \\ \mp B_v [2J (J + 1)]^{1/2} & B_v [J (J + 1) +1] - E & -B_v [2J (J + 1) - 4]^{1/2} \\ 0 & -B_v [2J (J + 1) - 4]^{1/2} & B_v [J (J + 1) - 3] - A_v - E \end{vmatrix} = 0$$  \hfill (3.116)$$

which is best solved numerically.

### 3.4.4.5 $^2\Delta$ states

The basis functions are
Heteronuclear Diatomic Molecules

\[ H_{\text{2Δ3/2}} = \frac{1}{\sqrt{2}} \{ 2 \frac{1}{2} - \frac{1}{2}; J \frac{3}{2} M \} + \{ -2 \frac{1}{2} - \frac{1}{2}; J \frac{3}{2} M \} \]  \hspace{1cm} (3.117)

\[ H_{\text{2Δ4/2}} = \frac{1}{\sqrt{2}} \{ 2 \frac{1}{2} - \frac{3}{2}; J \frac{5}{2} M \} + \{ -2 \frac{1}{2} - \frac{3}{2}; J \frac{5}{2} M \} \]  \hspace{1cm} (3.118)

There is no first-order spin-orbit coupling because the contributions from the two HOMO π electrons, which occupy the same orbital with opposite spins, cancel (Section 7.1.1.2), so the secular determinant contains only matrix elements of \( \mathcal{H}_{\text{rot}} \).

The \( J = \frac{3}{2} \) level is exclusively associated with the \( ^2\Delta_{3/2} \) state.

\[ H_{\text{2Δ3/2}} = \frac{1}{\sqrt{2}} \{ 2 \frac{1}{2} - \frac{1}{2}; \frac{3}{2} \frac{3}{2} M \} + \{ -2 \frac{1}{2} - \frac{1}{2}; \frac{3}{2} \frac{3}{2} M \} \]  \hspace{1cm} (3.119)

\[ E ( ^2\Delta_{3/2}; \frac{3}{2} ) = 2B_v \]  \hspace{1cm} (3.120)

For \( J > \frac{3}{2} \) the secular determinant is

\[
\begin{vmatrix}
B_v [ J (J + 1) - \frac{3}{2} ] - E & -B_v [ J (J + 1) - \frac{15}{4} ]^{1/2} \\
-B_v [ J (J + 1) - \frac{15}{4} ]^{1/2} & B_v [ J (J + 1) - \frac{9}{4} ] - E
\end{vmatrix} = 0
\]  \hspace{1cm} (3.121)

which is best solved numerically.

### 3.4.5 Zeeman Matrix Elements

With the aid of Eq. (2.120), the Zeeman Hamiltonian can be written as

\[ \mathcal{H}_B = (L_z + g_e S_z) \mu_B B \]

\[ = \sum_q \left\{ \mathcal{D}^1_{pq}(\omega)^* L_q + g_e \mathcal{D}^1_{pq}(\omega)^* S_q \right\} \mu_B B \]  \hspace{1cm} (3.122)

where \( q \) labels spherical components in the molecular reference frame.

Matrix elements of \( \mathcal{H}_B \) are derived using Hund’s case-(a) basis functions. Details on how to derive electronic Zeeman matrix elements are given in Section 3.3.5.3. Matrix elements involving rotational bras, kets and \( \mathcal{D} \) matrices are related to the integral in Eq. (3.69) by
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\[ \langle J' \Omega' M' | \mathcal{D}_{pq}^{1}(\omega) | J \Omega M \rangle = \frac{2J + 1}{4\pi} \int d\Omega \mathcal{D}_{J \Omega M}^{*}(\phi, \theta, 0) \mathcal{D}_{pq}^{1}(\phi, \theta, 0) \mathcal{D}_{M \Omega}^{*}(\phi, \theta, 0) \]  
\[ (3.123) \]

The integral in Eq. (3.123) is solved by utilising Eq. (3.69). The CGC have been expressed algebraically (see Table 2.1) to give the following Zeeman matrix elements:

\[ \langle n \Lambda S \Sigma; J \Omega M | \mathbb{K}_{B} | n \Lambda S \Sigma; J \Omega M \rangle = (\Lambda + g_{e} \Sigma) \frac{\Omega M}{J(J + 1)} \mu_{B} \]  
\[ (3.124) \]

\[ \langle n \Lambda S \Sigma; J \Omega M | \mathbb{K}_{B} | n \Lambda S \Sigma; J \Omega M \rangle = \frac{g_{e} \mu_{B} B}{2J(J + 1)} \left( S(S + 1) - \Sigma(\Sigma + 1) \right)^{1/2} \left( J(J + 1) - \Omega(\Omega + 1) \right)^{1/2} \]  
\[ (3.125) \]

\[ \langle n \Lambda S \Sigma; J - 1 \Omega M | \mathbb{K}_{B} | n \Lambda S \Sigma; J \Omega M \rangle = \frac{(\Lambda + g_{e} \Sigma) \mu_{B} B}{J} \left( (J - M)(J + M) \right)^{1/2} \left( (J - \Omega)(J + \Omega) \right)^{1/2} \]  
\[ (3.126) \]

\[ \langle n \Lambda S \Sigma; J - 1 \Omega \pm 1 M | \mathbb{K}_{B} | n \Lambda S \Sigma; J \Omega M \rangle = \frac{g_{e} \mu_{B} B}{2J(J + 1)} \left( (J - M)(J + M)(J \mp \Omega)(J \mp \Omega - 1) \right)^{1/2} \left( S(S + 1) - \Sigma(\Sigma + 1) \right)^{1/2} \]  
\[ (3.127) \]

\[ \langle n \Lambda S \Sigma; J + 1 \Omega \pm 1 M | \mathbb{K}_{B} | n \Lambda S \Sigma; J \Omega M \rangle = \frac{g_{e} \mu_{B} B}{2J + 1} \left( (J - M + 1)(J + M + 1)(J \pm \Omega + 1)(J \pm \Omega + 2) \right)^{1/2} \left( S(S + 1) - \Sigma(\Sigma + 1) \right)^{1/2} \]  
\[ (3.128) \]

Determination of the complete eigenfunctions and eigenvalues is best achieved by creating matrices containing matrix elements for \( \mathcal{K}_{	ext{rot}} \), \( \mathcal{K}_{\text{SO}} \), and \( \mathbb{K}_{B} \) truncated at a suitably large value of \( J \). The Zeeman states are no longer diagonal in \( M \) and there is a small degree of mixing between different \( J \) levels, so the resulting secular equation must be solved numerically.

### 3.4.6 Transition Moments

The components of the electric dipole moment operator in the laboratory frame \((p)\) can be related to the components in the molecular frame \((q)\) by

\[ m_{p} = \sum_{q} \mathcal{D}_{pq}^{1}(\omega)^{*} m_{q}^{1} \]  
\[ (3.129) \]
The longitudinal Zeeman configuration of the experiments performed in this thesis permits $p$ to take only values of $\pm 1$, whereas, as outlined in Section 3.3.5.4, the electronic selection rules require that $q$ must also only take values of $\pm 1$ for the transitions investigated in this research. The transition dipole moment can be written as

$$
\langle n' \Lambda' S' \Sigma' ; J' \Omega' M' ; v' \mid m_p^1 | n \Lambda S \Sigma ; J \Omega M ; v \rangle
= \langle v'|v \rangle \sum_q \langle n' \Lambda' S' \Sigma' | m_q^1 | n \Lambda S \Sigma \rangle \langle J' \Omega' M' | D_{pq}^1(\omega) \mid J \Omega M \rangle
$$

(3.130)

<table>
<thead>
<tr>
<th>$\Delta J$</th>
<th>$\Delta \Omega$</th>
<th>$\Delta M$</th>
<th>$\langle J' \Omega' M' \mid D_{pq}^1(\omega) \mid J \Omega M \rangle$</th>
</tr>
</thead>
<tbody>
<tr>
<td>-1 -1 -1</td>
<td></td>
<td></td>
<td>$\frac{1}{2J} \frac{(J + M)(J + M - 1)(J + \Omega)(J + \Omega - 1)}{(2J - 1)(2J + 1)}$</td>
</tr>
<tr>
<td>-1 -1 1</td>
<td></td>
<td></td>
<td>$\frac{1}{2J} \frac{(J - M)(J - M - 1)(J + \Omega)(J + \Omega - 1)}{(2J - 1)(2J + 1)}$</td>
</tr>
<tr>
<td>-1 1 -1</td>
<td></td>
<td></td>
<td>$\frac{1}{2J} \frac{(J + M)(J + M - 1)(J - \Omega)(J - \Omega - 1)}{(2J - 1)(2J + 1)}$</td>
</tr>
<tr>
<td>-1 1 1</td>
<td></td>
<td></td>
<td>$\frac{1}{2J} \frac{(J - M)(J - M - 1)(J - \Omega)(J - \Omega - 1)}{(2J - 1)(2J + 1)}$</td>
</tr>
<tr>
<td>0 -1 -1</td>
<td></td>
<td></td>
<td>$\frac{1}{2J} \frac{(J + M)(J - M + 1)(J + \Omega)(J - \Omega + 1)}{2(J + 1)}$</td>
</tr>
<tr>
<td>0 -1 1</td>
<td></td>
<td></td>
<td>- $\frac{1}{2J} \frac{(J - M)(J + M + 1)(J + \Omega)(J - \Omega + 1)}{2(J + 1)}$</td>
</tr>
<tr>
<td>0 1 -1</td>
<td></td>
<td></td>
<td>- $\frac{1}{2J} \frac{(J + M)(J - M + 1)(J - \Omega)(J + \Omega + 1)}{2(J + 1)}$</td>
</tr>
<tr>
<td>0 1 1</td>
<td></td>
<td></td>
<td>$\frac{1}{2J} \frac{(J - M)(J + M + 1)(J - \Omega)(J + \Omega + 1)}{2(J + 1)}$</td>
</tr>
<tr>
<td>1 -1 -1</td>
<td></td>
<td></td>
<td>$\frac{1}{2J + 2} \frac{(J - M + 1)(J - M + 2)(J - \Omega + 1)(J - \Omega + 2)}{(2J + 1)(2J + 3)}$</td>
</tr>
<tr>
<td>1 -1 1</td>
<td></td>
<td></td>
<td>$\frac{1}{2J + 2} \frac{(J + M + 1)(J + M + 2)(J - \Omega + 1)(J - \Omega + 2)}{(2J + 1)(2J + 3)}$</td>
</tr>
<tr>
<td>1 1 -1</td>
<td></td>
<td></td>
<td>$\frac{1}{2J + 2} \frac{(J - M + 1)(J - M + 2)(J + \Omega + 1)(J + \Omega + 2)}{(2J + 1)(2J + 3)}$</td>
</tr>
<tr>
<td>1 1 1</td>
<td></td>
<td></td>
<td>$\frac{1}{2J + 2} \frac{(J + M + 1)(J + M + 2)(J + \Omega + 1)(J + \Omega + 2)}{(2J + 1)(2J + 3)}$</td>
</tr>
</tbody>
</table>

The first term on the right in Eq. (3.130) is a vibrational overlap factor. The second is the electronic transition dipole moment in the molecular reference frame,

3-30
which can be reduced to one-electron excitation form as outlined in Section 2.9.5. The third is an integral over rotation matrices, which are tabulated in Table 3.6 and were calculated using the methods employed in Section 3.4.5. It is worth noting that $p = \Delta M$, and $q = \Delta \Omega$.

### 3.5 References


4 Magneto-Optical Spectroscopy

4.1 Magnetic Circular Dichroism

Magnetic circular dichroism (MCD) is a form of magneto-optical spectroscopy which uses a longitudinal (axial) Zeeman configuration, meaning that the light is propagated parallel to the direction of the applied magnetic field (Figure 4.1).¹,²

![Diagram of longitudinal Zeeman spectroscopy](image)

Figure 4.1: In longitudinal Zeeman spectroscopy, the light is propagated parallel to the direction of the magnetic field.

It is defined as the difference between absorbance of left circularly polarised (lcp) and right circularly polarised (rcp) light of a sample in the presence of the field.

\[ \Delta A = A_{\text{lcp}} - A_{\text{rcp}} \]  

(4.1)

In similar terms, the conventional absorbance, \( A \), is defined as the average absorbance of lcp and rcp.

\[ A = \frac{A_{\text{lcp}} + A_{\text{rcp}}}{2} \]  

(4.2)

MCD is a useful technique for determining ground- and excited-state angular momenta in atoms and molecules, as well as for probing various environmental effects through their interactions with these angular momenta. To understand how these effects arise, it is necessary to consider the polarisation of radiation and the general nature of the Zeeman effect. Photons are bosons with angular momenta \( \sigma = 1 \) (in units of \( \hbar \)) and helicities \( m_\sigma = -1 \) and \( m_\sigma = +1 \), which correspond to lcp and rcp light respectively. (The absence of a state corresponding to \( m_\sigma = 0 \) is due to the fact that a photon doesn’t obey the usual angular momentum component rules because it is a massless particle travelling at the speed of light and therefore has no rest frame.)
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The electric ($F$) and magnetic ($B$) vectors associated with a photon trace out a helix along the axis of propagation such that the vector $F \times B$ always points along this axis.

The transitions in this research are all electric-dipole induced, and therefore involve the interaction of $F = (F_x, F_y, F_z)$ with the molecular electric dipole moment $m = (m_x, m_y, m_z)$. If the light is permitted to have any propagation direction with respect to the magnetic-field direction ($Z$ axis), this interaction is given by

$$-F \cdot m = -F_x m_x - F_y m_y - F_z m_z$$ (4.3)

which can be related to lcp ($F_{-1}$) and rcp ($F_{+1}$) components to give

$$-F \cdot m = -F_0 m_0 + F_{+1} m_{+1} + F_{-1} m_{-1}$$ (4.4)

From Eq. (4.4) it is seen that $m_{+1}$ interacts with $F_{-1}$ (lcp), and $m_{-1}$ interacts with $F_{+1}$ (rcp). This is consistent with the principle that angular momentum must be conserved; its loss or gain from the photon must be compensated by a gain or loss, respectively, by the molecule. Hence the operators $m_{+1}$ and $m_{-1}$ can be regarded as step-up ($\Delta M = +1$) and step-down ($\Delta M = -1$) operators for the angular momentum of the molecule, where $M$ is the component of the angular momentum along the magnetic field direction.

All molecules exhibit MCD to some extent. This phenomenon is best understood in terms of the Zeeman effect, in which the degeneracies of the angular momentum components of molecular states are lowered by the presence of a magnetic field. The field effectively defines an external (to the molecule) $Z$-axis, about which the angular momentum vectors precess so that that their projections onto this axis are quantised (spatial quantisation). Each of these angular-momentum states has a corresponding magnetic dipole moment, $\mu$, which depends on the charge of the dynamic particle, the total angular momentum $J$, and projection $M$, and is given by

$$\mu = \gamma (L + gS)$$ (4.5)

where $L$ is the orbital angular momentum of the particle; $S$ is its intrinsic internal angular momentum; $g$, known as the $g$ value, is a proportionality constant necessary
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to relate \( S \) to its associated magnetic moment; and \( \gamma = q/2m \) is the gyromagnetic ratio, where \( q \) is the charge and \( m \) the mass of the particle. (Classically, current loops create magnetic dipoles.) It is this dipole which interacts with the applied field and lifts the degeneracy. The quantum-mechanical Zeeman operator is given by

\[
\mathcal{H} = -\mu \cdot B
\]  

(4.6)

where \( \mu \) is the magnetic dipole operator and \( B \) is the magnetic flux density vector (also known as the magnetic inductance, but commonly referred to as the magnetic field strength).

Conventional Zeeman spectroscopy, which involves the measurement of band splittings and shifts as a function of magnetic-field strength is used for atoms and for some metal-ion complexes where the bandwidths are small compared with the Zeeman shifts. However, molecules generally have much larger bandwidths that obscure the small Zeeman splittings (typically of the order of 1 cm\(^{-1}\) or less) in a conventional Zeeman experiment. Because of the way it is detected (Section 6.3), MCD does not have this problem, making it an ideal method to probe the Zeeman states of molecules.

Natural circular dichroism (CD) is defined by Eq. (4.1) at zero magnetic field. Although it can be measured using the same apparatus as MCD, it has very different origins. Whereas MCD is exhibited by all molecules, CD is only exhibited by chiral molecules and depends on a quantity known as the rotational strength \( (\text{Rom}) \), the scalar product of the electric dipole and magnetic dipole transition moments. For a transition from \( \psi_o \) to \( \psi_m \),

\[
\text{Rom} = \langle \psi_m | \mu | \psi_o \rangle \cdot \langle \psi_o | m | \psi_m \rangle
\]  

(4.7)

For \( \text{Rom} \) to be non-zero, absorbing molecules must belong to point groups in which at least some components of the electric \( (m) \) and magnetic \( (\mu) \) dipole moment operators transform as the same irrep(s). This will only occur in point groups with no improper rotation axes, \textit{i.e.} chiral point groups. The distinction between natural CD and MCD can be understood by comparing the experimental results that would be obtained before and after the sample plus any applied field have been subjected to hypothetical
spatial inversion and time reversal transformations.\(^4\)

Spatial inversion of chiral molecules converts them to their enantiomers, thus the experimental observable in the case of CD will have equal but opposite values before and after this inversion, \(i.e. \Delta M\) is a pseudoscalar (a scalar which changes sign under inversion). Under time reversal, the chiral molecules are unchanged. We can therefore conclude that in the CD experiment, \(\Delta M\) is a time-even pseudoscalar.

Achiral molecules in an applied static magnetic field are unchanged by spatial inversion (a magnetic field is a pseudovector, \(i.e.\) a vector which remains unchanged under inversion). Since rotation of the sample and field about an axis perpendicular to the field changes the orientation relative to the light beam, which in turn changes the magnitude and sign of \(\Delta M\), we can conclude that \(\Delta M\) is a pseudovector. Under time reversal the molecules remain unchanged, but the magnetic field changes direction. We can therefore conclude that in the MCD experiment \(\Delta M\) is a time-odd pseudovector.

The observables are generated by operators of corresponding symmetries - CD by a time-even, odd-parity operator, and MCD by a time-odd, even-parity operator. The natures of the quantum states in each case are understandably very different. To undergo CD the initial and final states require mixed parity (associated with spatial dissymmetry of the molecule, \(i.e.\) "true" chirality), however to undergo MCD the states require mixed reversality (associated with dissymmetry due to the lack of time-reversal invariance, \(i.e.\) "false" chirality.)

The features observed in an MCD spectrum are often described as Faraday (\(\alpha, \beta, \text{and } \gamma\) terms.\(^2\) This terminology implies a number of simplifying assumptions, most of which are not applied in this thesis. However the \(\alpha, \beta, \text{and } \gamma\) nomenclature provides a useful shorthand notation for describing the features. Note that at zero field there is no MCD.

1. \(\alpha\) terms occur when either or both of the ground and excited states are degenerate (in the absence of the magnetic field), and their Zeeman splittings are different. Figure 4.2 gives the MCD for a general \(^1E \leftrightarrow ^1A\) transition. The excited \(^1E\) state, which is initially orbitally degenerate, splits in the magnetic field, causing the lcp and rcp transitions to occur at slightly different energies. The resultant \(\alpha\) term has a derivative shape, which can be
either positive (positive lobe at the higher energy) or negative (negative lobe at the higher energy), and is temperature independent.

Figure 4.2: A positive $\delta$ term resulting from a general $^1E \leftarrow ^1A$ transition. The resultant MCD is amplified by a factor of 100. (Adapted from reference 5.)

2. $\epsilon$ terms require a degenerate (in the absence of a magnetic field) ground-state manifold. Figure 4.3 gives the MCD spectrum for a general $^1A \leftarrow ^1E$ transition. The ground $^1E$ state splits in the magnetic field into two Zeeman states, the populations of which are given by the Boltzmann distribution and therefore depend on the temperature as well as the magnetic field strength. The intensities of lcp and rcp transitions are therefore temperature dependent, and the associated $\epsilon$ terms have an absorption-like dispersion, the sign of which depends on the polarisation of the transition from the lowest (and therefore most populated) Zeeman state. $\epsilon$ terms always coincide with $\delta$ terms, producing a lopsided derivative-shaped curve. However, the $\epsilon$ terms will normally dominate, especially at low temperatures, so that the effects of the $\delta$ terms are usually undiscernible.
3. Magnetic-field-induced mixing between electronic states of suitable symmetry (higher-order Zeeman interactions) gives rise to \( B \) terms. These are always present, but are generally weak (inversely proportional to the energy separation of the mixed states). They have an absorption-like dispersion of either sign and are temperature-independent. It is quite useful to think of \( B \) terms as corrections to the much larger \( \alpha \) and \( \epsilon \) terms (if these terms are present).

In the model for MCD due to Buckingham and Stephens,\(^1,2\) \( \alpha \), \( \beta \), and \( \epsilon \) terms are quantified by Faraday parameters \( \alpha_0 \), \( \beta_0 \), and \( \epsilon_0 \)^2. Conventionally MCD is treated in the "linear limit,"\(^2\) where the field is regarded as a weak perturbation, and it is assumed that the magnetic field Zeeman-shifts each individual Zeeman component contributing to the band, but does not change its shape. This is known as the rigid-shift (RS) approximation. More importantly, it is assumed that \( f(E) \) is field-independent. In these approximations

\[
\frac{\Delta A(E)}{E} = \gamma \mu_B B \{ \alpha_0 (-\partial f(E)/\partial E) + (\beta_0 + \epsilon_0 / kT) f(E) \} \tag{4.8}
\]

where \( \mu_B \) is the Bohr magneton, \( \gamma \) is a collection of physical constants including the concentration and pathlength of the sample, \( k \) is the Boltzmann constant (0.6954 cm\(^{-1}\) K\(^{-1}\)), \( f(E) \) is the normalised band-shape function (e.g. Gaussian or Lorentzian), and \( B \)
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is the magnetic field strength.

For a transition $J \leftarrow A$, the absorption is given by

$$
\frac{A(E)}{E} = \frac{\gamma}{2} \sum_{\alpha} P_{A\alpha} \left( |\langle J|\alpha|A\alpha\rangle|^2 + |\langle J|\bar{\alpha}|A\alpha\rangle|^2 \right) f(E)
$$

(4.9)

where $P_{A\alpha}^0$ is the zero-magnetic-field fractional population of the partner $\alpha$ within the $A$ manifold. Eq. (4.9) is applicable for molecules in isotropic point groups or for molecules that are oriented with their $z$ axes along the direction of the magnetic field.

$\Delta A(E)/E$ can be written in a similar manner

$$
\frac{\Delta A(E)}{E} = \gamma \sum_{\alpha} P_{A\alpha} \left( |\langle J|\alpha|A\alpha\rangle|^2 - |\langle J|\bar{\alpha}|A\alpha\rangle|^2 \right) f_{\alpha}(E)
$$

(4.10)

In this case, $P_{A\alpha}$ is the fractional population of the partner $\alpha$ within the $A$ manifold in the presence of a magnetic field.

$$
P_{A\alpha} = \frac{\exp(-E_{A\alpha}/kT)}{\sum_{\alpha} \exp(-E_{A\alpha}/kT)} = \frac{\exp(-E_{A\alpha}/kT)}{Q}
$$

(4.11)

where $Q$ is the partition function and $E_{A\alpha}$ is the Zeeman energy. The "linear limit" is so named because, for low magnetic fields and high temperatures (i.e. $g\mu_B B \ll 2kT$), $\Delta A$ effectively has a linear dependence on $B/T$. This can be shown by rearranging Eq. (4.11).

$$
P_{A\alpha} = \sum_{\alpha} \exp(-E_{A\alpha}/kT) \exp(-E_{A\alpha}/kT) \exp(\langle A\alpha|\mu_2|A\alpha\rangle B/kT)
$$

$$
= \exp(-E_{A\alpha}/kT) \exp(\langle A\alpha|\mu_2|A\alpha\rangle B/kT)
$$

$$
= \frac{1}{|A|} \left( 1 + \frac{\langle A\alpha|\mu_2|A\alpha\rangle B}{kT} \right)
$$

(4.12)
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where $E_{Aa}^0$ is the energy of the partner $\alpha$ within the $|A|$-fold $A$ manifold at zero magnetic field

$$E_{Aa} = E_{Aa}^0 - \langle A\alpha|\mu_z|A\alpha\rangle B$$  \hspace{1cm} (4.13)

and a truncated exponential series (which only holds if $\langle A\alpha|\mu_z|A\alpha\rangle/kT$ is small) has been used in the second step.

As the temperature decreases or the magnetic-field strength increases, the linear limit begins to fail because the population of the lowest ground-state Zeeman level becomes saturated. Using the general $^1A \leftarrow ^1E$ transition of Figure 4.3 as an example, the population difference between the lower and upper Zeeman levels of the ground state is given by

$$P_2 - P_1 = \frac{\exp(g\mu_B B/2kT) - \exp(-g\mu_B B/2kT)}{\exp(g\mu_B B/2kT) + \exp(-g\mu_B B/2kT)} = \tanh\left(\frac{g\mu_B B}{2kT}\right)$$ \hspace{1cm} (4.14)

where the Zeeman splitting is given by $g\mu_B B$. The hyperbolic tangent function of Eq. (4.14) is plotted in Figure 4.4.

![Figure 4.4: The population difference between the lower and upper Zeeman levels of the ground state of a general $^1A \leftarrow ^1E$ transition, plotted against $g\mu_B B/2kT$.](image)

For small values of $g\mu_B B/2kT$, $\tanh(g\mu_B B/2kT) \approx g\mu_B B/2kT$, and the linear limit is a good approximation. This region is shown in Figure 4.4 as the part of the curve that coincides with the dashed line. For sufficiently large values of $g\mu_B B/2kT$,
the population difference tends asymptotically to a constant value because essentially
the whole population shifts to the lower ground-state Zeeman level. The point where
the C-term contribution to $\Delta A$ has effectively reached a maximum value is a condition
that is known as saturation. Between these extremes is a region where $\Delta A$ has a non-linear dependence on $g\mu_B B/2kT$. In fact, this non-linear region provides the most
information, so in this work Eq. (4.8) is not utilised.

To treat randomly oriented non-rotating molecules, the absorption and MCD
equations (Eqs. (4.9) and (4.10)) need to be converted from the space-fixed ($X, Y, Z$)
to the molecule-fixed ($x, y, z$) frame of reference, using the Euler angles $\phi, \theta$ and $\chi$
defined in Section 2.6.5, and Eqs. (2.23) and (2.75). In this research, all transitions
are $x,y$-polarised (i.e. terms involving $\langle J\lambda|m_{\lambda}|A\alpha\rangle$ are zero), which greatly simplifies
the procedure. The results for molecules oriented at angle $\theta$ with respect to the
laboratory $Z$ axis are

$$
\frac{A(E, \theta)}{E} = \frac{\gamma(1 + \cos^2 \theta)}{4} \sum_{\alpha \lambda} P_{\alpha \lambda} \left( |\langle J\lambda|m_{+1}|A\alpha\rangle|^2 + |\langle J\lambda|m_{-1}|A\alpha\rangle|^2 \right) f_{\alpha \lambda}(E) \tag{4.15}
$$

$$
\frac{\Delta A(E, \theta)}{E} = \gamma \cos \theta \sum_{\alpha \lambda} P_{\alpha \lambda} \left( |\langle J\lambda|m_{+1}|A\alpha\rangle|^2 - |\langle J\lambda|m_{-1}|A\alpha\rangle|^2 \right) f_{\alpha \lambda}(E) \tag{4.16}
$$

For a randomly oriented ensemble, Eqs. (4.15) and (4.16) must be averaged
over $\theta$. A function $F(\theta)$ is averaged over $\theta$ to form $\bar{F}$ according to the relationship

$$
\bar{F} = \frac{1}{2} \int_{-1}^{1} F(\theta) \, d\cos \theta \tag{4.17}
$$

Upon application of Eq. (4.17), Eqs. (4.15) and (4.16) yield

$$
\frac{\bar{A}(E)}{E} = \frac{\gamma}{3} \sum_{\alpha \lambda} P_{\alpha \lambda} \left( |\langle J\lambda|m_{+1}|A\alpha\rangle|^2 + |\langle J\lambda|m_{-1}|A\alpha\rangle|^2 \right) f_{\alpha \lambda}(E) \tag{4.18}
$$

$$
\frac{\bar{\Delta A}(E)}{E} = \frac{\gamma}{2} \sum_{\alpha \lambda} \left( |\langle J\lambda|m_{+1}|A\alpha\rangle|^2 - |\langle J\lambda|m_{-1}|A\alpha\rangle|^2 \right) f_{\alpha \lambda}(E) \int_{-1}^{1} P_{\alpha \lambda} \cos \theta \, d\cos \theta \tag{4.19}
$$
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The integral in Eq. (4.19) must include $P_{\alpha\beta}$ because of its dependence on Zeeman energies, which themselves are orientation dependent.

### 4.2 Moment Analysis

Moment analysis is essentially the statistics of continuous distributions. The $n$th moment of a function $f(E)$ about reference point $E^0$ is defined as

$$
\langle f(E) \rangle_{n}^{E^0} = \int f(E) (E - E^0)^n \, dE
$$

(4.20)

where $f(E)$ must fall to zero at the integration limits.

When applied to MCD and absorption data, moment analysis makes possible the extraction of molecular parameters, although this can be difficult and the results are not always precise, for example, where there are strongly overlapping bands from different electronic transitions. For the purposes of experimental data, integration limits are taken between points where the band system “effectively” goes to zero. Hence it is important that all spectra are baselined correctly, otherwise errors will be introduced into the analysis.

The zeroth absorption ($A_0$) and MCD ($M_0$) moments are the areas under the respective bands.

$$
A_0 = \langle A(E)/E \rangle_0 = \int_{\text{band}} \frac{A(E)}{E} \, dE
$$

(4.21)

$$
M_0 = \langle \Delta A(E)/E \rangle_0 = \int_{\text{band}} \frac{\Delta A(E)}{E} \, dE = B_0 + C_0
$$

(4.22)

In Eq. (4.22), $M_0$ is the sum of the $B_0$ and $C_0$, the moments that correspond to $B$ and $C$ terms respectively, each of which is single-signed.

The first MCD moment about the band barycentre is given by

$$
M_1 = \langle \Delta A(E)/E \rangle_{1}^{E} = \int_{\text{band}} \frac{\Delta A(E)}{E} (E - E) \, dE
$$

(4.23)
The band barycentre, $\bar{E}$, is the average energy of the band, being defined according to the absorption so that

$$\bar{E} = \langle A(E)/E \rangle_0 / A_0$$  \hspace{1cm} (4.24)$$

which is equivalent to the requirement $\langle A(E)/E \rangle_1^\infty = 0$.

An unambiguous measure of bandwidth which can be applied to any absorption band is obtained from $2\sqrt{A_2/A_0}$, where

$$A_2 = \langle A(E)/E \rangle_2^\infty$$  \hspace{1cm} (4.25)$$

The spectra throughout this thesis consist of overlapping component bands and zeroth moments must therefore be taken over whole band systems, in which case

$$A_0 = \sum_i A_0(i)$$  \hspace{1cm} (4.26)$$

$$M_0 = \sum_i M_0(i)$$  \hspace{1cm} (4.27)$$

The $i$th component band, with zeroth moments $A_0(i)$ and $M_0(i)$, has a local barycentre $\bar{E}_i$, which is displaced from the overall barycentre by $\Delta_i$:

$$\bar{E} = \bar{E}_i - \Delta_i$$  \hspace{1cm} (4.28)$$

The expression for $M_1$ can now be expanded using Eqs. (4.27) and (4.28)

$$M_1 = \int \frac{\Delta A(E)}{E} (E - E) \, dE$$

$$= \sum_i \int \frac{\Delta A_i(E)}{E} (E - \bar{E}_i + \Delta_i) \, dE$$

$$= \sum_i \left\{ \Delta_i \int \frac{\Delta A_i(E)}{E} \, dE + \int \frac{\Delta A_i(E)}{E} (E - \bar{E}_i) \, dE \right\}$$
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\[ = \sum_i \{ \Delta_i \mathbf{M}_0(i) + \mathbf{M}_1(i) \} \quad (4.29) \]

For any single component transition between two discrete Zeeman states,

\[ \mathbf{M}_1(i) = 0 \quad (4.30) \]

and, with the help of Eq. (4.22), Eq. (4.29) can therefore be rewritten as

\[ \mathbf{M}_1 = \sum_i [\mathbf{B}_0(i) + \mathbf{C}_0(i)] \Delta_i \quad (4.31) \]

Hence \( \mathbf{B}_0 \) and \( \mathbf{C}_0 \), which can actually be separated on the basis of their field and temperature dependencies described earlier, can contribute to the first MCD moment.

Data analysis in this thesis involves the taking of ratios of \( \mathbf{M}_0/A_0 \) or \( \mathbf{M}_1/A_0 \). This has the advantage that the constant \( \gamma \) (Eqs. (4.9) and (4.10)) and the reduced one-electron transition moments (Sections 2.9.5 and 3.3.5.4), which occur in all these expressions, can be eliminated. The disadvantage is that we actually need an infinite number of moments to accurately reproduce a spectrum, so some information contained in the MCD spectra is inevitably lost.

An important aspect of moment analysis is that zeroth and first moments are invariant to unitary transformations of the excited-state basis. This has the advantage that simpler moment expressions can be obtained, but the disadvantage that little information about the excited-state crystal-field and spin-orbit effects can be ascertained. The invariance of zeroth moments is a consequence of the principle of spectroscopic stability. Consider the expression

\[ \sum_t \langle I | \mathbf{\Theta}_1 | t \rangle \langle t | \mathbf{\Theta}_2 | n \rangle \quad (4.32) \]

where \( | I \rangle \) and \( | n \rangle \) are arbitrary, and \( | t \rangle \) represents an orthonormal set of functions which can be related to another orthonormal set \( | \tau \rangle \) by a unitary transformation,

\[ | t \rangle = \sum_\tau | \tau \rangle \langle \tau | t \rangle \]
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\[
\langle t \rangle = \sum \langle t \mid \tau \rangle \langle \tau \mid t \rangle \tag{4.33}
\]

Using Eq. (4.33), Eq. (4.32) can be rewritten as

\[
\sum \langle I \mid \phi_1 \mid t \rangle \langle t \mid \phi_2 \mid n \rangle = \sum_{\tau \tau'} \langle I \mid \phi_1 \mid \tau \rangle \langle \tau \mid \phi_2 \mid n \rangle \langle \tau \mid t \rangle \langle t \mid \tau \rangle
\]

\[= \sum_{\tau} \langle I \mid \phi_1 \mid \tau \rangle \langle \tau \mid \phi_2 \mid n \rangle \delta_{\tau \tau'} = \sum_{\tau} \langle I \mid \phi_1 \mid \tau \rangle \langle \tau \mid \phi_2 \mid n \rangle \tag{4.34}\]

Eq. (4.34) is known as the principle of spectroscopic stability. To better understand how this result applies to MCD moments, expressions of the type \[\langle J\alpha | m_{z_1} | J\alpha \rangle \] (Eqs. (4.9) and (4.10)) must be rewritten in a form similar to Eq. (4.32).

\[
\langle J\alpha | m_{z_1} | J\alpha \rangle = -\langle A \alpha | m_{z_1} | J\alpha \rangle \langle J\alpha | m_{z_1} | A \alpha \rangle \tag{4.35}\]

Hence, from Eq. (4.34)

\[
\sum_{\lambda} \langle A \alpha | m_{z_1} | J\lambda \rangle \langle J\lambda | m_{z_1} | A \alpha \rangle = \sum_{\lambda} \langle A \alpha | m_{z_1} | J\lambda \rangle \langle J\lambda | m_{z_1} | A \alpha \rangle \tag{4.36}\]

Inspection of Eqs. (4.22) and (4.31) reveals that the moments \( M_0 \) and \( M_1 \) are therefore invariant to unitary transformations of the excited-state basis. Any excited-state basis (usually the one that leads to the simplest mathematical manipulations) can be used to derive these moment expressions as long as it is related to the "true" excited-state basis by a unitary transformation. In practice, the "true" nature of the excited state is inaccessible to the method of moments. It must be stressed here that moments are not invariant to unitary transformations of the ground-state basis because of population factors.

4.3 References


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5 Matrix Isolation

This chapter provides an overview of matrix isolation, followed by details on matrix shifts, the perturbation of rotational levels of diatomic molecules trapped in rare-gas matrices, and the external heavy-atom effect which causes variation in guest SOC constants.

5.1 An Overview of Matrix Isolation

This research utilises the matrix isolation (MI) technique, which was invented as a means of trapping reactive species, such as radicals, and studying them spectroscopically, but which now has a much wider range of applications. MI involves trapping the desired molecule in an inert host at cryogenic temperatures (≤15 K). The use of cryogenic temperatures is of direct benefit in MCD studies since it maximises the information content of the spectra (via the quantification of the temperature-dependent term contributions). However, MI also confers a number of other advantages:

- At sufficient dilution, MI results in isolation of guests from each other and hence removes the possibility of guest-guest interactions.
- Guest-host interactions can be minimised by using a noble gas (Ne, Ar, Kr, Xe) host. Since noble gases are relatively inert, they provide excellent long-lived (at low temperature) matrices for reactive radicals.
- The low temperatures required for MI have the advantage that "hot bands" are eliminated and only the lowest vibrational levels of an electronic-state manifold are significantly populated, resulting in simpler spectra.
- The bands obtained from the spectroscopy of MI species are usually relatively sharp compared with other condensed-phase methods.
- Noble-gas matrices have excellent optical properties. They are transparent from the far IR to the vacuum UV and optically isotropic, making them ideal for studies involving polarised light.

Although the guest-host interactions in noble-gas matrices are weaker than in solutions, they still occur. However, some of them can be of interest in themselves.
Matrix Isolation

They include:\(^1,^5\)

- Matrix shifts due to the ground and excited states of the guest interacting to different extents with the surrounding host.
- Orientational effects — generally non-rotating molecules are considered to be randomly oriented, although some orientation effects have been observed in the EPR spectra of molecules trapped in rare-gas matrices, such as VO/Ar.\(^6\)
- Crystal-field splittings of orbitally degenerate states.
- Vibronic effects resulting from coupling between the electronic states of the guest and the lattice phonons of the host.
- Spin-orbit coupling perturbations, resulting from the partial quenching of the electronic angular momenta of guests by interactions with the host.
- External heavy-atom effects which change the effective spin-orbit coupling parameters of the guest.

MI is not a perfect method for probing isolated molecules but it is simpler and cheaper than supersonic beam methods. Also, concentrations in supersonic beams are far too low to measure absorption or MCD under normal circumstances.

5.2 Matrix Shifts

As a rule, the energies of electronic and vibrational transitions of a guest trapped in a cryogenic matrix are observed to shift by less than 1% of the corresponding gas-phase energies.\(^1\) This gas phase-to-matrix shift arises because the ground and excited states of the guest interact with the host to different extents. The shift is a measure of the relative difference in interaction energy and does not give a measure of the absolute interaction energy of either state. Furthermore, such a shift can occur at lower or higher energy than the corresponding gas-phase transition.

Matrix shifts depend on the polarisability of the host.\(^1\) With very few exceptions, as this polarisability is increased, the observed spectrum shifts to longer wavelength. This red shift can be followed easily by considering a homologous series of solvents. In the case of the noble gases, the polarisability is correlated with atomic weight, so there is an increasing red shift in the energies of electronic and vibrational transitions of the guest as the host is varied from Ne to Xe. As will be demonstrated
in later chapters, this is consistent with the experimental observations in this thesis. Although complex quantum-mechanical calculations have been utilised to explain these matrix shifts, they are beyond the scope of this work.\(^5\)

### 5.3 External Heavy-Atom Effect

The effect on SOC in an atom or molecule due to nearby atoms of high atomic number, particularly when the neighbouring atoms are part of a solvent, is known as the external heavy-atom effect.\(^7\) It can arise from two types of interactions. The first, which can be termed 'mechanical' and is independent of mixing of the guest and host orbitals, arises from the fact that the orbital angular momentum of an electron confined to an orbital of a guest XH diatomic radical has components about nearby host nuclei, which are smaller than, and of the opposite sense to, that about the heavy (X) atom of the guest. The second is a consequence of components of the angular momentum about the heavy-atom nucleus that arise from 'covalent' mixing of the XH orbitals with host orbitals.

The contributions to SOC arising from these two effects will be proportional to the fourth power of the effective nuclear charge of the host atom and should therefore increase markedly as the host becomes heavier. But whereas the mechanical effect should always operate in the opposite sense to that of the free guest species, the covalent contribution can contribute in either direction, depending on the details of the mixing of guest and host states. Furthermore, for the latter, one would expect an inverse dependence on the cube of the principal quantum number of the outer orbitals of the guest atom.

The external heavy atom effect has been studied for alkali and noble metals trapped in noble-gas matrices by measuring the SOC constant of the excited \(2\text{P}\) states via MCD and conventional optical spectroscopy of the \(2\text{P} \leftarrow 2\text{S}\) transition.\(^7\) The one-electron SOC constants for the \(2\text{P}\) excited states of Li–Cs, Cu–Au are summarised in Table 5.1.

A uniform and important trend in the data presented in Table 5.1, is that the one-electron SOC constants of all of these systems are reduced (become more negative) as the size of the noble gas increases. Interestingly, these constants can be either greater or less than the corresponding gas-phase values. It would appear that the lighter atoms within each of the two series, have SOC constant that are reduced (in
comparison with the gas-phase value) by incorporation into an Ar matrix, whereas the heavier ones have SOC constants that are increased. In all cases there is a monotonic decrease as the atomic number of the matrix gas is increased.

Table 5.1: SOC constants (in cm\(^{-1}\)) for the \( ^2P \) excited states of Li,\(^8,9\) Na,\(^8\) K,\(^10\) Cs,\(^10\) Cu,\(^11\) Ag,\(^12\) Au,\(^12\) in noble-gas matrices and in the gas phase.

<table>
<thead>
<tr>
<th>Medium</th>
<th>Li</th>
<th>Na</th>
<th>K</th>
<th>Cs</th>
<th>Cu</th>
<th>Ag</th>
<th>Au</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas</td>
<td>0.23</td>
<td>11.5</td>
<td>38.5</td>
<td>369</td>
<td>166</td>
<td>614</td>
<td>2543</td>
</tr>
<tr>
<td>Ar</td>
<td>-16</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>124</td>
<td>783</td>
<td>3354</td>
</tr>
<tr>
<td>Kr</td>
<td>-70</td>
<td>*</td>
<td>-64</td>
<td>*</td>
<td>95</td>
<td>638</td>
<td>3110</td>
</tr>
<tr>
<td>Xe</td>
<td>-196</td>
<td>-213</td>
<td>-170</td>
<td>(\sim 100 - 150)</td>
<td>-23</td>
<td>583</td>
<td>2655</td>
</tr>
</tbody>
</table>

*No data available

A supermolecule approach\(^7\) has been used to calculate heavy-atom effects upon the SOC constant, or at least to try and predict whether they will increase or decrease relative to the gas phase. The supermolecule is taken to be MY\(_{12}\), where M is the metal located at a substitutional site in a face-centred cubic structure with 12 nearest neighbour noble-gas (Y) atoms. Essentially, it was found that the observed trends in SOC constants depend on the M-Y overlap integrals and mixing coefficients, as well as the ratio of the noble gas to metal SOC constants, with the latter being the major factor. For a particular metal, the size of its SOC constant primarily depends on the ratio of the noble-gas SOC constant to that of the metal in the gas phase.

5.4 Rotation in Matrices

There are two major models used by spectroscopists to calculate the perturbation of rotational levels of a diatomic molecule trapped in a rare-gas matrix. The first is a crystal-field model, developed by Devonshire\(^13\) and extended by Flygare.\(^14\) Generally this method is considered to be only marginally satisfactory for interpreting hindered rotational motion in matrices, however its similarities to the SO-CF non-rotating model make it a good starting point for investigation. The second is the rotation-translation coupling (RTC) model developed by Friedmann and Kimel.\(^15,16\) This is much more effective for interpreting the matrix spectra of small molecules, but the derivation of coupled states and their behaviour in the Zeeman effect is extremely complicated. Its application to the XH/NG spectra lies well beyond the
intended scope of this thesis and time constraints have prevented this from being investigated further.

5.4.1 Crystal-Field Hindered-Rotor Model

The following derivation of the interaction potential largely follows the approach taken by Flygare, but is extended to accommodate the case of open-shell electronic systems, which is relevant to radical molecules.

The crystal-field model assumes a rigid lattice with the perfect face-centred cubic structure of a rare-gas crystal. In such a structure, it is possible for a molecule to be located at an interstitial or substitutional site. Table 5.3 gives the types, symmetries, and nearest neighbour centre-to-centre distances of these sites.

<table>
<thead>
<tr>
<th>Type of site</th>
<th>Symmetry</th>
<th>Number of nearest neighbours</th>
<th>Nearest neighbour distances (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>substitutional</td>
<td>$O_h$</td>
<td>12</td>
<td>Ar</td>
</tr>
<tr>
<td>interstitial</td>
<td>$O_h$</td>
<td>6</td>
<td>3.75</td>
</tr>
<tr>
<td>interstitial</td>
<td>$T_d$</td>
<td>4</td>
<td>2.65</td>
</tr>
</tbody>
</table>

This model assumes that the substitutional $O_h$ site, which is surrounded by twelve equally spaced rare-gas atoms, is the preferred trapping site for small molecules because it is the largest (Table 5.3). Furthermore, it is assumed that the centre of mass of the molecule occupies the lattice point at all times. Removal of this last assumption allows the centre of mass to move around inside the cavity as the molecule rotates, which corresponds to the RTC model.

The dominant interactions between a trapped molecule and the surrounding rare-gas lattice are:

- attractive induced-multipole–induced-multipole forces
- attractive permanent-dipole–induced-dipole forces (if the trapped molecule has a permanent dipole moment)
- exchange forces (usually repulsive) caused by an overlap of the electronic distributions of the interacting systems
Matrix Isolation

The induction forces tend to increase the electron density at the outer part of the interacting systems, but decrease the density within the molecular bonds. This causes small increases in bond lengths and red shifts in the molecular vibrational frequencies relative to the gas phase, an effect which is greater with larger rare-gas atoms. A repulsive exchange interaction would have the opposite effect, causing an increase in vibrational frequency relative to the gas phase. Since red shifts of vibrational progressions are observed in this research, the following treatment assumes that the exchange interactions are negligible compared with the multipole interactions. If the trapped molecule has a smaller van der Waals radius than the substitutional lattice site, there will be negligible overlap of the two electronic charge distributions. This is more reasonable for diatomic monohydrides such as CH, NH, OH, but less so for SiH, PH, and SH.

Since the red shifts in the molecular vibrational frequencies are at most 1% of the gas-phase energies (Section 5.2), it is expected that the increase in bond lengths will only have a small effect on the rotational constants. Therefore, for the purposes of the following treatment, it is assumed that the molecular rotational constants ($B_v$) are the same in noble-gas matrices as they are in the gas phase.

The potential energy between the charges $e_i$ in a molecule and the charges $e_j$ (with separation distances $r_{ij}$) in a single atom whose position is fixed relative to the centre of mass ($a$) of the molecule is given by

$$V = \frac{1}{4\pi \varepsilon_0} \sum_{ij} \frac{e_i e_j}{r_{ij}}$$  \hspace{2cm} (5.1)

where $\varepsilon_0$ is the permittivity of free space. The factor $1/r_{ij}$ can be expressed in terms of distances relative to the molecular centre of mass by using a multipole expansion. Using electrostatic units, where $4\pi \varepsilon_0 = 1$, yields

$$V = \sum_{ij} e_i e_j \sum_{LM} \frac{4\pi}{2L + 1} Y_{LM}(\theta_{ai}, \phi_{ai}) Y_{LM}(\theta_{aj}, \phi_{aj})^* \frac{r_{ai}^L}{r_{aj}^{L+1}}$$  \hspace{2cm} (5.2)

where $r_{aj}$ is the distance between $a$ and the $j$th charge, and $(\theta_{ai}, \phi_{ai})$ represent the corresponding Euler angles. Eq. (5.2) implicitly requires that $r_{ai} > r_{aj}$, and can be
rearranged to give

\[ V = \sum_{ij} e_i e_j \sum_{LM} [T^L_M(i)_a][U^L_M(j)_a] \]

\[ = \sum_{ij} e_i e_j \sum_{LM} \left[ \bar{T}^L_K(i)_a \right][\mathcal{R}^L_M(\omega)^*][U^L_M(j)_a] \]  

(5.3)

where

\[ T^L_M(i)_a = \sqrt{\frac{4\pi}{2L+1}} r^{L}_{\text{aa}} Y^{LM}_{\theta_a \phi_a} \]

\[ U^L_M(j)_a = \sqrt{\frac{4\pi}{2L+1}} \frac{1}{r^{L+1}_{ij}} Y^{LM}_{\theta_j \phi_j}^* \]  

(5.4)

The \( T^L_M(i)_a \) act only on the molecular-charge distribution and represent the \( L \)th (single-charge) multipole moment about \( a \). The \( U^L_M(j)_a \) components act only on the atomic-surrounding charge distribution and represent the \( L \)th (single-charge) gradient of the \( j \)th electric potential at \( a \). In Eq. (5.3), the \( T^L_M(i)_a \) components referred to the laboratory reference frame have been converted into \( \bar{T}^L_K(i)_a \) in the molecular reference frame using Eq. (2.120).

Eq. (5.3) represents the multipole interaction between a rotating molecule and an atom fixed in space. When the molecule occupies a site in a rare-gas lattice, the rotational motion of the molecule will be much slower than the correlation time of the lattice electrons (Born-Oppenheimer approximation) and therefore \( \mathcal{R}^L_M(\omega)^* \) must be invariant under all symmetry operations of the point group of the site (in the space-fixed reference frame). From Table 5.3 it can be seen that the only non-zero components of \( \mathcal{R}^L_M(\omega)^* \) that transform as the totally-symmetric \((a_{1g})\) irrep under \( O_h \) symmetry have

\[ L = 0, 4, 6, 8, 9, 10, \ldots \]  

(5.5a)

and the potential can be expanded as

\[ V = V_0 + V_4 + V_6 + \ldots \]  

(5.5b)
Matrix Isolation

$V_0$ does not affect the relative rotational energies since it shifts all levels equally. $V_4$, the hexadecapole term, produces by far the largest perturbation on the rotational levels of a diatomic molecule, but in the remainder of this section, the model will be extended to include the 6th order term.

Table 5.3: Subduction from $SO_3$ to $O$.\textsuperscript{18} Note that inversion symmetry ($g$ or $u$) should be taken into account where applicable.

<table>
<thead>
<tr>
<th>$L$ ($SO_3$)</th>
<th>$O$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>$a_1$</td>
</tr>
<tr>
<td>1</td>
<td>$t_1$</td>
</tr>
<tr>
<td>2</td>
<td>$e + t_2$</td>
</tr>
<tr>
<td>3</td>
<td>$a_2 + t_1 + t_2$</td>
</tr>
<tr>
<td>4</td>
<td>$a_1 + e + t_1 + t_2$</td>
</tr>
<tr>
<td>5</td>
<td>$e + 2t_1 + t_2$</td>
</tr>
<tr>
<td>6</td>
<td>$a_1 + a_2 + e + t_1 + 2t_2$</td>
</tr>
<tr>
<td>7</td>
<td>$a_2 + e + 2t_1 + 2t_2$</td>
</tr>
<tr>
<td>8</td>
<td>$a_1 + 2e + 2t_1 + 2t_2$</td>
</tr>
<tr>
<td>9</td>
<td>$a_1 + a_2 + e + 3t_1 + 2t_2$</td>
</tr>
<tr>
<td>10</td>
<td>$a_1 + a_2 + 2e + 2t_1 + 3t_2$</td>
</tr>
<tr>
<td>...</td>
<td>...</td>
</tr>
</tbody>
</table>

The partners ($M$) for each $L$ that contributes to $a_{1g}$ in $O_h$, and the overall normalised form for $\sum_M D_{MK}^L(\omega)^*$ can be found in Butler\textsuperscript{19} for the chain $SO_3 \supset O \supset D_4 \supset C_4$. For $L = 4$ and 6,

$$\sum_M D_{MK}^4(\omega)^* = \sqrt{\frac{7}{12}} D_{0K}(\omega)^* + \sqrt{\frac{5}{24}} [D_{4K}(\omega)^* + D_{-4K}(\omega)^*]$$

$$\sum_M D_{MK}^6(\omega)^* = \sqrt{\frac{1}{8}} D_{0K}(\omega)^* - \sqrt{\frac{7}{16}} [D_{4K}(\omega)^* + D_{-4K}(\omega)^*]$$

(5.6)

The corresponding components of the potential can now be written as

$$V_4 = \sum_i \sum_K \left[ T_{K(i)}^4 \right] \left( \sqrt{\frac{7}{12}} D_{0K}(\omega)^* + \sqrt{\frac{5}{24}} [D_{4K}(\omega)^* + D_{-4K}(\omega)^*] \right)[3^4]$$

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\[ V_6 = \sum_i e_i \sum_K [\bar{T}_K(i)]_a \left( \sqrt{\frac{1}{8}} \mathcal{D}_{0K}(\omega)^* - \sqrt{\frac{7}{16}} \left[ \mathcal{D}_{4K}(\omega)^* + \mathcal{D}_{4K}^*(\omega)^* \right] \right) [\mathcal{K}] \] (5.7)

where the \( U^{J_0}_M(i)_a \) have been summed over the twelve nearest neighbours and the six next-nearest neighbours etc., to give

\[ \mathcal{K}_L = 12 \sum_j e_j \sum_M [U^{J_0}_M(i)_a] + 6 \sum_j e_j \sum_M [U^{J_0}_M(i)_a] + \ldots \] (5.8)

It is also required that the components of \( [\bar{T}_K(i)_a] \) and \( \mathcal{D}_{MK}(\omega)^* \) in the sums over \( K \) in Eq. (5.7) be invariant under all symmetry operations of the molecular point group (in the molecule-fixed reference frame). This is only satisfied when \( K = 0 \). Hence,

\[ V_4 = \sum_i e_i [\mathcal{F}_0(i)_a] \left( \sqrt{\frac{7}{12}} \mathcal{D}_{00}(\omega)^* + \sqrt{\frac{5}{24}} \left[ \mathcal{D}_{40}(\omega)^* + \mathcal{D}_{40}^*(\omega)^* \right] \right) [\mathcal{K}_4] \] \[ V_6 = \sum_i e_i [\mathcal{F}_0(i)_a] \left( \sqrt{\frac{1}{8}} \mathcal{D}_{00}(\omega)^* - \sqrt{\frac{7}{16}} \left[ \mathcal{D}_{40}(\omega)^* + \mathcal{D}_{40}^*(\omega)^* \right] \right) [\mathcal{K}_6] \] (5.9)

In a generalised basis designated \( |l; n \Lambda S \Sigma; J \Omega M \rangle \), where \( |l \rangle \) is the rare-gas atomic-electronic wavefunction, the perturbation matrix elements are given by

\[ \langle l; n \Lambda S \Sigma; J \Omega M | V | l; n \Lambda S \Sigma; J' \Omega M' \rangle = \] \[ \Gamma_0^4 \left( \sqrt{\frac{7}{12}} \langle J \Omega M | \mathcal{D}_{00}(\omega)^* | J' \Omega M' \rangle + \sqrt{\frac{5}{24}} \left[ \langle J \Omega M | \mathcal{D}_{40}(\omega)^* + \mathcal{D}_{40}^*(\omega)^* | J' \Omega M' \rangle \right] \right) \] \[ + \Gamma_0^6 \left( \sqrt{\frac{1}{8}} \langle J \Omega M | \mathcal{D}_{00}(\omega)^* | J' \Omega M' \rangle - \sqrt{\frac{7}{16}} \left[ \langle J \Omega M | \mathcal{D}_{40}(\omega)^* + \mathcal{D}_{40}^*(\omega)^* | J' \Omega M' \rangle \right] \right) + \ldots \] (5.10)

where \( \Gamma_0^L \) is a coupling constant, given by

\[ \Gamma_0^L = \langle l | \mathcal{K}_L | l \rangle \langle n \Lambda S \Sigma | \sum_i e_i [\mathcal{F}_0(i)_a] | n \Lambda S \Sigma \rangle \] (5.11)

The physical meaning of \( \Gamma_0^L \) is that it is the product of the \( 2^L \)-th-fold multipole
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moment of the molecule and the $L$th-order gradient of the electric potential at the molecular centre of mass (centre of the lattice site) due to all of the lattice charges.

The matrix elements in Eq. (5.10) are calculated by using the results given in Section 2.6.8:

$$
\langle J \Omega M | J' M' \rangle = (-1)^{2J-2L+M+\Omega} \sqrt{(2J+1)(2J'+1)} \times \left( \begin{array}{ccc}
J' & L & J' \\
M' & M & -M \\
\Omega & 0 & -\Omega
\end{array} \right)
$$

(5.12)

Using Eq. (5.12) in Eq. (5.10), and the fact that $L$ is necessarily an integer, gives

$$
\langle I; n \Lambda S \Sigma; J \Omega M | V | I; n \Lambda S \Sigma; J' \Omega M' \rangle = V_0 + \sqrt{(2J+1)(2J'+1)(-1)^{2J+M+\Omega}} \times
\left( \begin{array}{ccc}
J' & 4 & J \\
\Omega & 0 & -\Omega
\end{array} \right) \sqrt{\frac{7}{12} \left( M' 0 -M \right)} + \sqrt{\frac{5}{24} \left( M' 4 -M \right) + \left( M' -4 -M \right)}
+ \Gamma_0^6 \left( \begin{array}{ccc}
J' & 6 & J \\
\Omega & 0 & -\Omega
\end{array} \right) \sqrt{\frac{11}{18} \left( M' 0 -M \right)} - \sqrt{\frac{7}{16} \left( M' 4 -M \right) + \left( M' -4 -M \right)}
+ \ldots
$$

(5.13)

The effect of $V$ on the rotational Hund’s case-(a) energy levels can be calculated by incorporating Eq. (5.13) into a computer program to compute the Hamiltonian matrix and diagonalise it numerically. More details on this procedure will be given as required.

As a slight digression, it is useful to look at an alternative approach used by A. F. Devonshire in his classic 1935 paper “The Rotation of Molecules in Fields of Octahedral Symmetry.”13 Devonshire considered only $V_4$ and took a different approach than the one used here and by Flygare (who also considered only $V_4$). Using the identity

$$
D_{\Delta M}^L(\phi, \theta, \chi) = \sqrt{\frac{4\pi}{2L+1}} Y_{LM}(\theta, \phi)
$$

(5.14)

from Section 2.6.7, the potential can be written in terms of spherical harmonics. For $L = 4$ and 6,
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\[ V_4 = \sqrt{\frac{4\pi}{9}} \Gamma_0^4 \left( \sqrt{\frac{7}{12}} Y_{40}(\theta, \phi) + \sqrt{\frac{5}{24}} \left[ Y_{4d}(\theta, \phi) + Y_{-4d}(\theta, \phi) \right] \right) \]

\[ V_6 = \sqrt{\frac{4\pi}{13}} \Gamma_0^6 \left( \sqrt{\frac{1}{8}} Y_{60}(\theta, \phi) - \sqrt{\frac{7}{16}} \left[ Y_{6d}(\theta, \phi) + Y_{-6d}(\theta, \phi) \right] \right) \]  \hspace{1cm} (5.15)

The spherical harmonics can be expanded according to\(^{20}\)

\[ Y_{40}(\theta, \phi) = \frac{9}{16\sqrt{\pi}} \left( \frac{35}{3} \cos^4 \theta - 10 \cos^2 \theta + 1 \right) \]

\[ Y_{4d}(\theta, \phi) = \frac{3\sqrt{35}}{16\sqrt{2\pi}} \sin^4 \theta e^{\pm 4i\phi} \]  \hspace{1cm} (5.16)

\[ Y_{60}(\theta, \phi) = \frac{\sqrt{13}}{32\sqrt{\pi}} \left( 231 \cos^6 \theta - 315 \cos^4 \theta + 105 \cos^2 \theta - 5 \right) \]

\[ Y_{6d}(\theta, \phi) = \frac{3\sqrt{91}}{32\sqrt{2\pi}} (11 \cos^2 \theta - 1) \sin^4 \theta e^{\pm 4i\phi} \]  \hspace{1cm} (5.17)

Hence,

\[ V_4 = \Gamma_0^4 \frac{1}{8} \sqrt{\frac{7}{12}} \left( 35 \cos^4 \theta - 30 \cos^2 \theta + 3 + 5 \sin^4 \theta \cos 4\phi \right) \]  \hspace{1cm} (5.18)

\[ V_6 = \Gamma_0^6 \frac{1}{32\sqrt{2}} \times \]

\[ (231 \cos^6 \theta - 315 \cos^4 \theta + 105 \cos^2 \theta - 5 - 21(11 \cos^2 \theta - 1) \sin^4 \theta \cos 4\phi) \]  \hspace{1cm} (5.19)

The expression for \( V_4 \) in Eq. (5.18) has exactly the same form as Devonshire's potential:

\[ V_4 = -\frac{K}{8} \left( 35 \cos^4 \theta - 30 \cos^2 \theta + 3 + 5 \sin^4 \theta \cos 4\phi \right) \]  \hspace{1cm} (5.20)

where \( K \) is the barrier parameter. Hence, from Eqs. (5.18) and (5.20),

\[ K = -\sqrt{\frac{7}{12}} \Gamma_0^4 \]  \hspace{1cm} (5.21)
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The form of Eqs. (5.18), (5.19), and (5.20) is useful for determining minima and maxima in \( V \), and hence whether the potential is repulsive or attractive. For \( V_4 \) it turns out that when \( K \) is positive, \( V \) is repulsive (i.e. maxima occur when the diatomic molecules are aligned along the nearest-neighbour directions), and when \( K \) is negative, \( V \) is attractive (i.e. minima occur when the diatomic molecules are aligned along the nearest-neighbour directions).

At this point it also proves instructive (and also serves as a useful error check) to consider the case of a closed-shell electronic system and to see that the general result above converges to that obtained by earlier workers\textsuperscript{13, 14} when considering only \( V_4 \). In the closed-shell case, \( \Omega = 0 \), \( J' \) is an integer and Eq. (5.13) becomes

\[
\langle l; n 0 0 0; J 0 M | V_4 | l; n 0 0 0; J' 0 M' \rangle = -\sqrt{\frac{12(2J+1)(2J'+1)}{7}} (-1)^M K
\frac{\left( J' 4 J \right)}{\left( 0 0 0 \right)} \sqrt{\frac{7}{12}} \left( J' 4 J \right) + \sqrt{\frac{5}{24}} \left[ \left( J' 4 J \right) \left( J' 4 J \right) \right]
\]

The effect of \( V_4 \) on the rotational energy levels is calculated using a computer program Rotor, written by this author, which sets up a Hamiltonian matrix (to a sufficiently high value of \( J \)), containing the computed matrix elements of \( V_4 \) added to the diagonal elements for the unperturbed rotational energy \( B_v(J+1) \), then diagonalises it numerically. The results for a linear rotor \( (J=0, 1, 2, 3) \) are plotted in Figure 5.1. This replicates Figure 3 of Devonshire\textsuperscript{13} and Figure 1 of Flygare.\textsuperscript{14} Note that the results are plotted as \( E/B_v \) versus \( K/B_v \).

5.4.2 Rotation-Translation Coupling Model

Although the RTC model\textsuperscript{15-17} is not explicitly utilised in this research, it has proved very effective in the past for interpreting the matrix spectra of small molecules.

In addition to an electrostatic barrier to rotation (Section 5.4.1), the RTC model incorporates coupling between the rotational motion of the molecule and the oscillation of its centre of mass within the lattice site. A physical picture of this is that as the molecule rotates about its centre of mass, it undergoes a translation in order to bring the molecule to a position of lowest energy. Hence, for a symmetric molecule
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in which the centre of mass coincides with the centre of the lattice site, there is no RTC. The major features of this model are:

- Vibrational motion is decoupled from translation and rotation. Vibrational shifts can be calculated using Lennard-Jones potentials.
- The rotation-translation coupling arises from the torque acting on the molecule as a result of the non-coincidence of the centre of mass and the centre of the lattice site.
- The zero-order translational functions are harmonic-oscillator-type wavefunctions.

Figure 5.1: Rotational energy of a linear molecule (divided by the rotational constant $B_v$) as a function of the barrier parameter $K$, also divided by the rotational constant $B_v$. 

5-13
5.5 References


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6 Experimental Apparatus and Procedures

The experimental procedure involves the formation of matrices from mixtures of suitable precursor and noble gas (typically in a ratio of 1:100), undergoing a Tesla-coil discharge, deposited on a sapphire sample window held at a temperature below 20 K. Absorption and MCD spectra are measured simultaneously on a double-beam spectrometer known as MOD4.

This chapter gives details on how the matrices are formed and a description of the apparatus used to measure absorption and MCD spectra.

6.1 Matrix Formation

Mixtures of radical precursor and noble gas (~1:100) were made up to ~1 atmosphere, in Pyrex bulbs of 0.25 or 1 L capacity, using standard gas-line techniques. Due to the high cost of Kr and Xe, these gases were transferred between regions of the gas line by condensing them with liquid nitrogen, ensuring that none was wasted. The gases used in this project are given in Table 6.1, along with their sources and purities.

<table>
<thead>
<tr>
<th>Gas</th>
<th>Supplier</th>
<th>Purity</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄</td>
<td>Matheson</td>
<td>UHP 99.97%</td>
</tr>
<tr>
<td>NH₃</td>
<td>Matheson</td>
<td>anhydrous 99.99%</td>
</tr>
<tr>
<td>H₂O</td>
<td>University of Canterbury</td>
<td>milli-Q and freeze-pump-thaw purified</td>
</tr>
<tr>
<td>SiH₄</td>
<td>Matheson</td>
<td>semi-conductor 4N8 purity</td>
</tr>
<tr>
<td>PH₃</td>
<td>Matheson</td>
<td>ULSI 5N7 purity</td>
</tr>
<tr>
<td>H₂S</td>
<td>Aldrich</td>
<td>99.5%</td>
</tr>
<tr>
<td>Ar</td>
<td>Matheson</td>
<td>UHP 99.999%</td>
</tr>
<tr>
<td>Kr</td>
<td>Linde Minican</td>
<td>99.99 vol. %</td>
</tr>
<tr>
<td>Xe</td>
<td>Linde Minican</td>
<td>99.99 vol. %</td>
</tr>
<tr>
<td>N₂</td>
<td>BOC Gases</td>
<td>99.99%</td>
</tr>
</tbody>
</table>

The apparatus used to create the radicals and deliver the gas mixture to the deposition window is shown in Figure 6.1. The radicals were produced by subjecting the mixture, as it flows through a Pyrex or quartz tube, to a discharge induced by an
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Edwards High Vacuum Model TI Tesla coil. The discharge creates a weak noble-gas resonance-radiation field, which causes the formation of radicals, although the exact mechanism of this process is not well understood. A calibrated needle valve sets the flow rate to \(2 - 3 \text{ mmol hr}^{-1}\).

![Diagram of experimental apparatus](image)

**Figure 6.1:** The apparatus employed to produce radical species and deliver radical/matrix-gas mixture to the deposition window. The Al foil spreads out the Tesla-coil discharge, and the ridge prevents the tube being sucked into the vacuum.

**Table 6.2:** Gas mixtures used for preparation of matrices.

<table>
<thead>
<tr>
<th>Precursor ((XH_n))</th>
<th>Noble gas ((NG))</th>
<th>Ratio (XH_n:NG)</th>
<th>Bulb size (litres)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(CH_4)</td>
<td>Kr</td>
<td>1:100</td>
<td>1</td>
</tr>
<tr>
<td>(CH_4)</td>
<td>Xe</td>
<td>1:100</td>
<td>1</td>
</tr>
<tr>
<td>(NH_3)</td>
<td>Kr</td>
<td>1:100</td>
<td>0.25</td>
</tr>
<tr>
<td>(NH_3)</td>
<td>Xe</td>
<td>1:100</td>
<td>1</td>
</tr>
<tr>
<td>(H_2O)</td>
<td>Kr</td>
<td>1:100</td>
<td>0.25</td>
</tr>
<tr>
<td>(H_2O)</td>
<td>Xe</td>
<td>1:100</td>
<td>1</td>
</tr>
<tr>
<td>(SiH_4)</td>
<td>Ar</td>
<td>1:100</td>
<td>1</td>
</tr>
<tr>
<td>(SiH_4)</td>
<td>Kr</td>
<td>1:100</td>
<td>0.25</td>
</tr>
<tr>
<td>(SiH_4)</td>
<td>Ar</td>
<td>1:100</td>
<td>0.25</td>
</tr>
<tr>
<td>(PH_3)</td>
<td>Ar</td>
<td>1:100</td>
<td>1</td>
</tr>
<tr>
<td>(PH_3)</td>
<td>Kr</td>
<td>1:100</td>
<td>1</td>
</tr>
<tr>
<td>(PH_3)</td>
<td>Xe</td>
<td>1:100</td>
<td>0.25</td>
</tr>
<tr>
<td>(H_2S)</td>
<td>Ar</td>
<td>1:300</td>
<td>1</td>
</tr>
<tr>
<td>(H_2S)</td>
<td>Kr</td>
<td>1:100</td>
<td>0.25</td>
</tr>
<tr>
<td>(H_2S)</td>
<td>Xe</td>
<td>1:100</td>
<td>0.25</td>
</tr>
<tr>
<td>(NH_3)</td>
<td>(N_2)</td>
<td>1:100</td>
<td>0.25</td>
</tr>
</tbody>
</table>
6.2 Matrix-Isolation/Magnet Systems

Two matrix-isolation systems that have been used in this research – a helium refrigerator/electromagnet system and a matrix-injection system – are described in this section. Both systems are mounted on trolleys that can be wheeled in or out of the MOD4 spectrometer. More detailed descriptions are given by Langford.\textsuperscript{1, 2}

In each case, matrices are formed on c-cut sapphire windows. Sapphire is especially useful in these experiments because of its transparency, hardness and high thermal conductivity. The window is oriented so that the crystal c axis is parallel to the direction of propagation of light within the spectrometer. Sapphire is linearly birefringent if light does not propagate exactly along the c axis, so to minimise any effects of misalignment the matrix is deposited on the side closest to the light source. Even if some of the light does depolarise, this will occur after it has passed through the matrix and will have no effect on the signal detected by the photomultiplier tube (PMT).

6.2.1 Helium-Refrigerator/Electromagnet System

The main advantage of the helium-refrigerator/electromagnet system (Figure 6.2) is that it is very economical to run. Its major drawbacks are that it cannot be used to achieve high magnetic fields (> 0.7 T) or very low temperatures (< 12 K). Therefore its primary use is to optimise matrix-deposition conditions and to determine the energies (or wavelengths) and dispersion of the features of the spectra.

This set-up consists of an APD Cryogenics Inc. closed-cycle He refrigerator, comprising an HC-2D compressor and a Displex DE-202 expander, and an Alpha Magnetics Inc. 4800 U-frame electromagnet, powered by a Hewlett Packard 6269B 50-A, 40-V dc power supply. A current of 40 A gives a magnetic field of 0.64 T.

A Pfeiffer Balzers TSH172 170-L s\textsuperscript{-1} turbo-molecular pump is used to pump the system down to less than \textasciitilde 10\textsuperscript{-5} Torr. Once this is achieved, the refrigerator is turned on and cools to its base temperature of \textasciitilde 11 K in an hour. Matrices are formed on a c-cut sapphire sample window (\textasciitilde 9-mm diameter) mounted in a copper holder located at the tip of the second stage of the expander unit. The temperature of the sample can be estimated by measuring the resistance of a 100-\Omega Allen-Bradley carbon resistor, also located within this copper holder. Temperature gradients within the expander tip prevent accurate measurements of this sample temperature.
6.2.2 Matrix-Injection System

The MCD spectra of all the systems examined in this research project are temperature and magnetic-field dependent. The best quality data are obtained by using a large range of these parameters, extending to the lowest possible temperatures and magnetic fields up to about 5 T. The matrix-injection system can be used to achieve temperatures as low as \( \sim 1.4 \) K and magnetic fields as high as 6 T (although, such a high field scares the author's supervisor). In these respects it has major advantages over the refrigerator/electromagnet system. The one drawback is its
experimental cost, since it requires copious quantities of liquid helium, which costs about $50 per litre in New Zealand. A 60-L Dewar full permits about four days of operation. The helium gas is recycled to try to minimise the costs. Another drawback is that it is much more difficult to obtain good yields of radicals during matrix deposition using this system than with the refrigerator/electromagnet system. The reasons for this remain unclear.

The matrix-injection system (Figure 6.3) has been described in greater detail by Dunford.\textsuperscript{3, 4} It consists of an Oxford Instruments SpectroMag SM4 magneto-cryostat, a matrix-deposition chamber and a siphon rod, the tip of which contains a sapphire window. The sample is deposited, under vacuum (~10\textsuperscript{-5} Torr using a Pfeiffer Balzers TSH172 170 L s\textsuperscript{-1} turbo-molecular pump) in the deposition chamber, onto the window which is held at ~20 K via conduction from liquid helium (~2.5 L hr\textsuperscript{-1}) flowing through the sample rod. This liquid helium is drawn from a 60-L Dewar through a length of bellows by a Compton D/189 flow pump, with the flow controlled by an Oxford Instruments VC30 flow-control console.

Once deposition has been achieved, the gate valve is opened and the sample rod injected into the SM4 sample chamber, itself under vacuum using a Pfeiffer Balzers TPU170 170-L s\textsuperscript{-1} turbo-molecular pump. During this injection process, the space between the 'O'-ring sliding seals, situated above the deposition chamber, is pumped down to prevent any air entering the sample chamber. Once injected, the window is directly in the optical path of the MOD4 spectrometer and in the centre of the 6-T superconducting magnet, run by an Oxford Instruments PS75 magnet power supply and SG3 sweep generator.

Spectroscopic investigation can now begin. A needle valve is opened allowing cryogenic (liquid or cold gaseous) helium to flood into the sample chamber. Temperatures above the boiling point of He (~4.2 K) are monitored by a calibrated carbon resistor situated above the window in the sample rod. Temperature stability is maintained by using the set-point and error output signal from an Oxford instruments 3400 DC resistance meter to drive a mechanical valve that controls the flow rate of He gas exiting from the top of the sample chamber.\textsuperscript{5} Temperatures below ~ 4.2 K (down to ~ 1.4 K) are obtained by pumping the vapour above the liquid with a 450-L min\textsuperscript{-1} Welch 1397 rotary-vane pump and using an Oxford Instruments MNT manostat to maintain a steady helium vapour pressure (below 760 Torr) above the liquid He.
The vapour pressure is measured by a 1000-Torr MKS Baratron capacitance manometer (type 622A13TAE). The relationship between the vapour pressure and temperature is well established.\(^6\)

![Diagram of the matrix-injection system](image)

**Figure 6.3:** An overview of the matrix-injection system, consisting of an Oxford Instruments SpectroMag SM4 magneto-cryostat, a matrix-deposition chamber, and a siphon rod (adapted from reference 1).
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6.3 MOD4 Spectrometer

Double-beam absorption and MCD spectra are measured simultaneously on a spectrometer, known as MOD4, which was designed and built by Vaughan Langford, Bryce Williamson, and technical staff at the University of Canterbury. This section contains a brief overview of MOD4, followed by a look at some of the components necessary for the measurement of MCD. More detailed descriptions can be found in Langford’s PhD thesis,\(^1\) OH/Ar paper,\(^2\) and laboratory notes held in the University of Canterbury.

![Diagram of MOD4](Image)

Figure 6.4: A basic outline of MOD4.

Light from an ILC Technology LX300UV Xe-arc lamp is passed through a Jarrell Ash 78-463 Czerny-Turner scanning monochromator with a 1-m focal length and a 1180-groove/mm diffraction grating blazed at 300 nm. Optical filters are employed to remove stray light and higher orders of diffraction emerging from the entrance slit of the monochromator. A Corning 7-54 filter is used over the range 250 to 395 nm, and an Esco Products RG-395 filter from 395 to about 660 nm.

The light beam exiting the monochromator is collimated by a convex lens before passing through a Melles-Griot 15-mm Glan-Taylor polariser. The resulting
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Linearly polarised light passes to the photoelastic modulator (Hinds Instruments, Inc. PEM-80) which modulates the light between left and right circular polarisations at ~50 kHz.

In order to achieve double-beam measurement of absorption spectra, MOD4 uses a mechanical chopper (with a frequency of 11 Hz) which "chops" the light beam into a sample beam, which passes through the sample via an axial hole in the magnet, and a reference beam, in which the light beam hits the mirrored part of the chopper and is reflected around the reference path. Both beams are detected by a Hamamatsu R-376 photomultiplier tube (PMT), which has an approximate spectral range of 180 to 800 nm, and which is shielded from the magnetic field by a \( \mu \)-metal housing. A narrow, blackened metal strip on the chopper allows the measurement of the PMT's dark current (the signal measured when no light is incident on the detector), which is subtracted from the sample and reference signals. Electronic gating with the aid of a Schmidt trigger and optical-interrupter circuit ensures that the data collection occurs at the correct time during the chopper cycle.

The PMT output current is very small, typically 5 \( \mu \)A, and susceptible to interference. It is therefore preamplified at the earliest opportunity by a preamplifier with a current-to-voltage gain of \( \sim 5 \times 10^5 \) V/A. This preamplifier is mounted in the PMT housing to minimise the distance that the weak current signal has to travel. The preamplified signal then passes to the electronics and the Stanford Research Systems Model SR510 lock-in amplifier (LIA) which is referenced to the modulation frequency of the PEM and is used to extract the MCD data from a background of noise (Section 6.3.3.2). The LIA output then passes to an (inverting) integrating amplifier, which integrates the signal over the sample period to further improve the signal-to-noise (S/N) ratio.

All processing is done digitally by the 486SX CPU of an antiquated IBM-compatible PC. The interface card cannot deal with faster computers, but luckily no upgrade is necessary since this computer can easily cope with all that is required to run the spectrometer and collect the data. Wavelength scanning and data acquisition are controlled by an Advantech PCL-814B interface card. The monochromator has been modified by replacing the servomotor with a stepper, which allows computer control of the scan.
6.3.1 Glan-Taylor Polariser

A Glan-Taylor polariser takes advantage of double refraction, a phenomenon caused by birefringence. In uniaxial crystals such as calcite (CaCO₃) two refractive indices are observed – one denoted $n_e$ for light rays polarised parallel to the symmetry axis of the crystal (extraordinary rays), and the other denoted $n_o$ for rays polarised perpendicular to the symmetry axis (ordinary rays). A Glan-Taylor polariser, consisting of two calcite prisms separated by a small air gap (so small that beam displacement is negligible), creates a situation where, over a small range of angles, the ordinary ray undergoes total internal reflection at the prism/air interface before being absorbed by the prism housing, and the extraordinary ray is transmitted. (Since $n_o > n_e$ for calcite, the critical angle is lower for the ordinary ray.) The front and rear faces are normal to the optical axis of the spectrometer, and the inner faces are aligned parallel and lie close to Brewster's angle to minimise reflection loss of the extraordinary ray.

![Figure 6.5: A schematic diagram of a Glan-Taylor polariser.](image)

6.3.2 Photoelastic Modulator

The photoelastic modulator (Hinds Instruments, Inc. PEM-80) modulates light between left and right circular polarisations at ~50 kHz. Its operation utilises the phenomena of photoelasticity and piezoelectricity.

*Photoelasticity* is induced birefringence caused by the mechanical strain (compression or expansion) exerted on a transparent solid material; the effect is proportional to the resulting strain. Birefringence is a phenomenon in which different polarisations of light travel at different velocities through a medium. Although transparent solids are not necessarily naturally birefringent, they become so when placed under uniaxial mechanical strain. However, the induced birefringence does
not necessarily occur at the correct wavelengths or with a high enough magnitude for use in PEMs.

**Piezoelectricity** is the phenomenon where an applied current across a suitable material, such as quartz, induces a strain causes the material to change shape. If the current is an alternating one, the material can be set into vibration.

As Figure 6.6 shows, the PEM-80 consists of a rectangular quartz piezoelectric transducer attached to a rectangular, transparent and isotropic optical element made of fused silica. The two components are matched (by choice of length and knowledge of the speed of sound in the media) to the same longitudinal vibrational frequency of ~50 kHz. The transducer is driven by an alternating voltage with a frequency tuned to the PEM resonance and an amplitude that depends on the wavelength of the light.

![Diagram of PEM-80 photoelastic modulator](image)

**Figure 6.6**: A simple outline of the PEM-80 photoelastic modulator.

For the purposes of MCD, the long axis of the modulator is set at 45° to the plane of polarisation of an incoming linearly polarised light beam, which has just exited the Glan-Taylor polariser. When the long axis of the optical element is compressed, the polarisation component parallel to this axis travels slightly faster than the perpendicular component. The parallel component then leads the perpendicular one upon exiting the bar. Conversely, if the long axis is stretched, the parallel component lags behind the perpendicular one. This birefringence effect is at its maximum at the centre of the fused-silica bar. The phase difference between the components, which is a function of the instantaneous values of the refractive indices and the thickness of the optical element, is known as the retardation and has units of length.
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The voltage amplitude is set so that the maximum retardation, occurring when the bar is at its maximum displacement from equilibrium, is one quarter of the incident wavelength. This is called quarter-wave (or $\lambda/4$) retardation. Since one component either leads and lags the other, the net polarisation vector of the light emerging from the PEM traces out a spiral about the direction of propagation. Since the magnitude and sense of the retardation varies over a PEM cycle, the light oscillates between linear, elliptical, and circular polarisations. Left circularly polarised (lcp) and right circularly polarised (rcp) light, assigned according to the handedness of their helices, are produced at a frequency of $\sim 50$ kHz (Figure 6.7).

![Diagram of retardation over one PEM cycle](image)

**Figure 6.7:** The variation in retardation over one PEM cycle, and the corresponding polarisations. The light is elliptically polarised between the extrema and the points of inflection. In the PEM 80, the period of the cycle is $\sim 20$ μs, corresponding to a modulation frequency of $\sim 50$ kHz.

6.3.3 MCD Signal Extraction

6.3.3.1 Noise

Noise is an unwanted response by a detector (or other measuring device) and is always present in one form or another. When it obscures a desired signal, methods have to be employed to either reduce the noise or allow the signal to be selectively extracted from the detector response. Such processes are generically referred to as recovering or enhancing a signal, or improving the S/N ratio. Figure 6.8 shows typical power spectral densities (on a log-log scale) of common types of noise.

Deterministic noise ranges from discrete-frequency components, such as the power-line hum (at 50 Hz and its harmonics in New Zealand) from the mains supply, to wide-band (radio-frequency) interference caused by high-energy pulses, such as power-line switching spikes (e.g. flicking a switch on and off).
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![Diagram of power spectral densities of common types of noise](image)

**Figure 6.8:** The power spectral densities of common types of noise (adapted from reference 5).

Stochastic, or random, noise is found in all systems as white noise, which has a frequency-independent power density, and as flicker (or $1/f$) noise, where the power spectral density decreases with increasing frequency.

White, or fundamental, noise is found in two forms. Johnson (or thermal) noise is caused by the thermal motions of electrons in conductors, which generate a noise voltage even in the absence of a signal current. Shot noise, arising from the statistical nature of the flow of a signal current, is caused by the random arrival of electrons at the electrodes of various electronic components, and also the arrival of photons at the photocathode of a PMT.

Flicker, or excess, noise has many different origins. It can be caused by such things as the change in temperature throughout a year or a day, which can affect temperature sensitive electrical apparatus, or even opening and closing the door. Flicker noise still isn’t clearly understood, but it exhibits a $1/f^n$ power spectrum, where $n$ is normally in the range 0.9 to 1.35.

Noise arising from sources outside the experimental system is regarded as interference. The electrical mains supply is one such contributor, with interference frequencies at 50 Hz and harmonics thereof. Alternating magnetic fields caused by various electrical appliances around the lab, such as lights, heaters and other pieces of apparatus, can also cause interference. Pulse interference occurs when a large amount of power is dissipated suddenly by discharges in lasers, lamps and various other pieces of equipment. It has a large frequency spread and may be propagated directly as an electromagnetic wave or transmitted down the mains supply wiring. This is one of the major problems when the ILC Technology LX300UV Xe-arc lamp used in MOD4 is switched on.
Technically, a dc voltage is unvarying, so cannot carry information, but in practice, the term “dc signal” means a signal that includes zero frequency in its spectrum. Such signals are also called base-band signals, particularly when they are used to modulate a carrier frequency. The easiest way to improve the S/N ratio of dc signals is to use a low-pass filter to reduce the noise bandwidth.

For an ac signal, band-pass filtering is used. When the signal is particularly a weak one, a lock-in amplifier is employed.

### 6.3.3.2 Lock-in amplifier

A lock-in amplifier is a type of phase-sensitive detector used to extract an ac signal from a background of noise, which can often be many orders of magnitude more intense. Essentially it is a band-pass filter that achieves a much narrower bandwidth than conventional circuits by locking in to the frequency and phase of a reference signal, which can have a square or sinusoidal waveform. In addition to filtering, the LIA also provides gain, typically greater than $10^9$.

The Stanford Research Systems Model SR510 LIA employed in MOD4 amplifies the weak MCD signal which has a frequency of ~50 kHz corresponding to the modulation frequency of the PEM. This frequency is high enough to be well outside the regime of dominant flicker noise (Figure 6.8), and is far removed from the power-line and other common interferences. By detecting signals in only a narrow range of frequencies centred on the reference frequency, noise and interference at all other frequencies are rejected.

The SR510 LIA is programmable and connected to the computer via an RS-232 interface.

**The signal channel.** The preamplified signal from the PMT passes through two notch filters, which remove the line-frequency component and its first overtone. The signal then passes through an auto-tracking band-pass filter, which is set to within 1% of the reference frequency and removes most other unwanted signals. These three filters eliminate the majority of the noise before the signal is amplified and thus reduce the risk of overloading the amplifier input. Next the signal is amplified by a high-gain ac amplifier and passes to the linear phase-sensitive detector (PSD).

**The reference channel.** The reference sine wave with the same frequency as the modulation between lcp and rcp (~50 kHz) of the light, is produced by the PEM.
controller. This signal passes into the input discriminator of the LIA, where a reference sine wave is generated. The phase-locked loop (PLL) locks onto this sine wave and its output phase can be shifted relative to the input signal to maximise the output from the PSD. Before passing to the PSD, the signal goes through a precision sine converter to ensure the resulting sine wave is well formed.

The phase-sensitive detector (PSD). All LIAs use a PSD circuit, which consists of a mixer (linear multiplier) followed (in the case of the SR510) by two low-pass filters. The mixer combines the amplified and filtered signal with the reference sine wave. The output of the mixer contains a difference \((f_{\text{signal}} - f_{\text{reference}})\) frequency component near dc and a sum \((f_{\text{signal}} + f_{\text{reference}})\) frequency component near \(2f\). The difference is proportional to the amplitude of the signal. The two low-pass filters remove the \(2f\) frequency components and provide further noise reduction by narrowing the LIA’s detection bandwidth. The output of the filter stages is amplified by a dc amplifier to provide the LIA output.

6.3.4 Signal Processing

6.3.4.1 Absorption

According to the law of Beer and Lambert, the absorption \((A)\) at a particular wavelength is given by

\[
A = -\log_{10} \left( \frac{I}{I_0} \right)
\]  

(6.1)

where \(I_0\) is the intensity of the light incident on the sample, and \(I\) is the intensity transmitted by the sample. Since MOD4 measures intensities as voltages (output from the preamplifier), Eq. (6.1) is rewritten as

\[
A = -\log_{10} \left( \frac{V_{\text{sample}} - V_{\text{dark}}}{V_{\text{reference}} - V_{\text{dark}}} \right)
\]  

(6.2)

where \(V_{\text{sample}}\) and \(V_{\text{reference}}\) are, respectively, the average voltages for lcp and rcp passing through the sample and the reference beam (the reference intensities for lcp and rcp are equal), and \(V_{\text{dark}}\) is the dark voltage of the PMT.
6.3.4.2 Magnetic circular dichroism

From Section 4.1, the MCD is defined by

\[ \Delta A = A_{\text{lcp}} - A_{\text{rcp}} \]  

(6.3)

Since the incident intensities of lcp and rcp are both equal to \( I_0/2 \), we can rewrite Eq. (6.3), with the aid of Eq. (6.1), as

\[ \Delta A = - \log_{10} \left( \frac{2I_{\text{lcp}}}{I_0} \right) + \log_{10} \left( \frac{2I_{\text{rcp}}}{I_0} \right) = - \log_{10} \left( \frac{I_{\text{lcp}}}{I_{\text{rcp}}} \right) \]  

(6.4)

Using the expansion

\[ \log_{10} x = 2 \left( \frac{x - 1}{x + 1} + \frac{1}{3} \left( \frac{x - 1}{x + 1} \right)^3 + \frac{1}{5} \left( \frac{x - 1}{x + 1} \right)^5 + \ldots \right) \log_{10} e \]  

(6.5)

and the knowledge that \( \Delta A \) is generally much smaller than \( A \) (that is \( I_{\text{lcp}} - I_{\text{rcp}} \ll I_{\text{lcp}} + I_{\text{rcp}} \)), Eq. (6.4) can be rewritten as

\[ \Delta A = -2 \left( \frac{I_{\text{lcp}}}{I_{\text{rcp}}} \right) \log_{10} e \]  

(6.6)

This approximation is used by the MOD4 electronics in calculating the MCD. Since the light transmitted through the sample is elliptically polarised, the "experimental" MCD signal is usually expressed as an ellipticity, \( \theta \) (in millidegrees)

\[ \tan \theta = \frac{I_{\text{rcp}} - I_{\text{lcp}}}{I_{\text{rcp}} + I_{\text{lcp}}} = \frac{10^{-A_{\text{lcp}}} - 10^{-A_{\text{rcp}}}}{10^{-A_{\text{lcp}}} + 10^{-A_{\text{rcp}}}} \left( \frac{10^{(A_{\text{rcp}} - A_{\text{lcp}})/4}}{10^{(A_{\text{rcp}} + A_{\text{lcp}})/4}} \right) \]

\[ = \frac{10^{(A_{\text{rcp}} - A_{\text{lcp}})/4} - 10^{-4(A_{\text{rcp}} - A_{\text{lcp}})/4}}{10^{(A_{\text{rcp}} - A_{\text{lcp}})/4} + 10^{-4(A_{\text{rcp}} - A_{\text{lcp}})/4}} = \tanh \left( \frac{\Delta A \log_{10} e}{4} \right) \]  

(6.7)

Since \( \Delta A \) is generally small,
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\[ \theta = \frac{\Delta A \log_{10} e}{4} = \frac{\Delta A \log_{10} e}{8\pi} \times 3.6 \times 10^5 \text{ mdeg} = 32982 \Delta A \]  
(6.8)

The integrated MCD signal \( S_{MCD} \), which is proportional to the sample-beam intensity, is converted to \( \Delta A \) by

\[ \theta = \frac{S_{MCD} L f}{(10 \text{ mV})(32982 \text{ mdeg})(V_{\text{sample}} - V_{\text{dark}})} \]  
(6.9)

where \( f \) is an empirical calibration factor (obtained by using an optically pure solution of \( d-[\text{Co(en)}_3][\text{Cl}][\text{tartrate}]\cdot5\text{H}_2\text{O} \) with a known MCD) determined for a LIA sensitivity of 10 mV, and \( L \) (mV) is the LIA sensitivity.

As the MCD signal increases, the approximation in Eq. (6.6) breaks down and the corresponding error in the MOD4 output of \( \Delta A \) increases. With the aid of a rewritten Eq. (6.1)

\[ I = I_0 10^{-A} \]  
(6.10)

it is possible to rewrite Eq. (6.6) and relate the measured MCD to the true MCD.

\[ \Delta A_{\text{measured}} = -2 \log_{10} e \left( \frac{10^{-A_{\text{lcp}}} - 10^{-A_{\text{rcp}}}}{10^{-A_{\text{lcp}}} + 10^{-A_{\text{rcp}}}} \right) \]

\[ = -2 \log_{10} e \left( \exp \left[ -\ln(10) \left( \frac{A_{\text{lcp}} - A_{\text{rcp}}}{2} \right) \right] - \exp \left[ \ln(10) \left( \frac{A_{\text{lcp}} - A_{\text{rcp}}}{2} \right) \right] \right) \]

\[ = 2 \log_{10} e \tanh \left[ \ln(10) \left( \frac{A_{\text{lcp}} - A_{\text{rcp}}}{2} \right) \right] \]

\[ = \frac{2}{\ln(10)} \tanh \left[ \frac{\ln(10)}{2} \Delta A_{\text{true}} \right] \]  
(6.11)

It turns out that the approximation in Eq. (6.2), where \( V_{\text{sample}} \) is taken to be the average of the voltages for lcp and rcp, can also lead to problems if the MCD signal is strong. This can be shown in a similar manner to Eq. (6.11)
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\[ A_{\text{measured}} = -\log_{10}\left(\frac{I_{lcp} + I_{rcp}}{2I_0}\right) = -\log_{10}\left(\frac{10^{-A_{lcp}} + 10^{-A_{rcp}}}{2}\right) = -\log_{10}\left[\frac{1}{2}\left(10^{\frac{(A_{lcp} - A_{rcp})}{2}} + 10^{\frac{(A_{lcp} - A_{rcp})}{2}}\right) + 1\right] \]

\[ = \frac{A_{lcp} + A_{rcp}}{2} - \log_{10}\left[\frac{1}{2}\exp\left[-\ln(10)\left(\frac{A_{lcp} - A_{rcp}}{2}\right)\right] + 1\exp\left[\ln(10)\left(\frac{A_{lcp} - A_{rcp}}{2}\right)\right]\right] = A_{\text{true}} - \log_{10}\left[\cosh\left(\frac{A_{lcp} - A_{rcp}}{2}\ln(10)\right)\right] = A_{\text{true}} - \log_{10}\left[\cosh\left(\frac{\ln(10)}{2} \Delta A_{\text{true}}\right)\right] \tag{6.12} \]

In practice, all the MCD data collected in this research are sufficiently weak that the MOD4 electronics approximation holds to within a few percent.

6.4 References

7 Methylidyne (CH) and Silylidyne (SiH)

The spectroscopic investigations of methylidyne (CH) and silylidyne (SiH) in this thesis involve $\pi \leftrightarrow \sigma$ excitations (Table 3.4), where the $\pi$ orbitals are essentially non-bonding valence $p_{\perp}$ orbitals of the C/Si atom and the $\sigma$ orbitals are admixtures mainly of the valence $p_{\parallel}$ orbitals of the C/Si atom with the 1s orbital of the H atom (Figure 3.1). Since the two radicals are effectively isoelectronic, they can be treated together.

The states of the radicals are represented by SO wavefunctions, which were derived in Chapter 3 and are summarised in Table 7.1.

Table 7.1: SO wavefunctions for CH and SiH.

| $|^{2S+1}\Lambda|_{\Omega}$ | Normalised Slater determinants |
|--------------------------|--------------------------------|
| $|X^2\Pi_{1/2} \pm \frac{1}{2}\rangle$ | $\mp |0^+ 0^+ \pm 1^\pm\rangle$ |
| $|X^2\Pi_{3/2} \pm \frac{3}{2}\rangle$ | $- |0^- 0^+ \pm 1^\pm\rangle$ |
| $|a^4\Sigma^-_{1/2} \pm \frac{1}{2}\rangle$ | $- \frac{1}{\sqrt{3}} \left( |0^\pm -1^\pm 1^\pm\rangle + |0^\pm -1^+ 1^-\rangle + |0^\pm 1^- 1^+\rangle \right)$ |
| $|a^4\Sigma^-_{3/2} \pm \frac{3}{2}\rangle$ | $\pm |0^\pm -1^\pm 1^\pm\rangle$ |
| $|A^2\Delta_{3/2} \pm \frac{3}{2}\rangle$ | $\pm |0^\pm +1^- +1^\pm\rangle$ |
| $|A^2\Delta_{5/2} \pm \frac{5}{2}\rangle$ | $|0^\pm +1^- +1^\pm\rangle$ |
| $|B^2\Sigma^-_{1/2} \pm \frac{1}{2}\rangle$ | $- \frac{1}{\sqrt{6}} \left( 2 |0^\pm -1^\pm 1^\pm\rangle - |0^\pm -1^+ 1^-\rangle - |0^\pm 1^- 1^+\rangle \right)$ |
| $|C^2\Sigma^+_{1/2} \pm \frac{1}{2}\rangle$ | $- \frac{1}{\sqrt{2}} \left( |0^\pm -1^\pm 1^\pm\rangle - |0^\pm 1^- 1^+\rangle \right)$ |

The transitions $A^2\Delta \leftrightarrow X^2\Pi$, $B^2\Sigma^- \leftrightarrow X^2\Pi$ and $C^2\Sigma^+ \leftrightarrow X^2\Pi$ are allowed, whereas $a \leftrightarrow X$ is spin forbidden.

7.1 SO-CF Theory

7.1.1 SO-CF Wavefunctions

To construct the SO-CF wavefunctions for fixed CH/SiH molecules, SO and CF matrix elements must first be derived using the methods in Section 3.3.5.

7.1.1.1 $X^2\Pi$ state

Table 7.2 gives the SO and CF matrix elements for the $X^2\Pi$ state of CH/SiH in a noble-gas matrix. $A_\pi$ is the empirical SOC constant and $V_\pi$ is the one-electron reduced CF matrix element for a 1\pi electron in CH or a 2\pi electron in SiH.
Methylidyne (CH) and Silylidyne (SiH)

\[ A_{\pi} = \langle \pi | \xi(r) | \pi \rangle \]
\[ V_{\pi} = \langle \pi || V^2 || \pi \rangle \]  

(7.1)

Table 7.2: SO and CF matrix elements for the \( X^2 \Pi \) state of CH/NG and SiH/NG.

| \( \Sigma_{SO} + \Sigma_{CF} \) | \( |X^2 \Pi_{1/2} - \frac{1}{2}\rangle \) | \( |X^2 \Pi_{1/2} + \frac{1}{2}\rangle \) | \( |X^2 \Pi_{3/2} - \frac{1}{2}\rangle \) | \( |X^2 \Pi_{3/2} + \frac{1}{2}\rangle \) |
|------------------------|----------------|----------------|----------------|----------------|
| \( X^2 \Pi_{1/2} - \frac{1}{2} \) | \(-\frac{1}{2} A_{\pi} \) | 0 | 0 | \(-\frac{1}{2} V_{\pi} \) |
| \( X^2 \Pi_{1/2} + \frac{1}{2} \) | 0 | \(-\frac{1}{2} A_{\pi} \) | \frac{1}{2} V_{\pi} | 0 |
| \( X^2 \Pi_{3/2} - \frac{3}{2} \) | 0 | \frac{1}{2} V_{\pi} | \frac{1}{2} A_{\pi} | 0 |
| \( X^2 \Pi_{3/2} + \frac{3}{2} \) | \(-\frac{1}{2} V_{\pi} \) | 0 | 0 | \frac{1}{2} A_{\pi} |

The Hamiltonian matrix in Table 7.2 factors into two \( 2 \times 2 \) matrices, according to the value of \( \Sigma \). Diagonalisation of these matrices gives the SO-CF eigenfunctions for the \( X^2 \Pi \) term. The corresponding eigenvalues show that the \( X^2 \Pi \) term is split by a magnitude \( \Delta \), where

\[ \Delta = \sqrt{A_{\pi}^2 + V_{\pi}^2} \]  

(7.2)

The eigenfunctions are labelled \( ^2 \Pi_- \) and \( ^2 \Pi_+ \), which respectively designate the lower and upper SO-CF levels, and \( \pm \frac{1}{2} \) in the kets on the left-hand side denotes the value of \( \Sigma \).

\[ |^2 \Pi_{- \pm \frac{1}{2}} \rangle = \alpha |^2 \Pi_{1/2} - \frac{1}{2} \rangle \pm \beta |^2 \Pi_{3/2} \pm \frac{1}{2} \rangle \]
\[ |^2 \Pi_{+ \pm \frac{1}{2}} \rangle = \mp \beta |^2 \Pi_{1/2} - \frac{1}{2} \rangle + \alpha |^2 \Pi_{3/2} \pm \frac{1}{2} \rangle \]  

(7.3)

The mixing coefficients are given by

\[ \alpha = \sqrt{\frac{1 + \kappa}{2}} \]
\[ \beta = \sqrt{\frac{1 - \kappa}{2}} \]  

(7.4)

where \( \kappa \) is the orbital reduction factor, given by
Methylidyne (CH) and Silyldyne (SiH)

\[ \kappa = \frac{A}{\Delta} \quad (0 \leq \kappa \leq 1) \quad (7.5) \]

It is worthwhile here to introduce the crystal-field reduction factor, which is given by

\[ \eta = \sqrt{1 - \kappa^2} = \frac{V}{\Delta} \quad (0 \leq \eta \leq 1) \quad (7.6) \]

From Eq. (7.2) it can be seen that \( \kappa^2 + \eta^2 = 1 \). Furthermore, as \( V \) tends to zero (and \( \kappa \) tends to 1), the wavefunctions in Eq. (7.3) become the SO wavefunctions of Table 7.1.

![Energy-level diagram](energy-level-diagram.png)

**Figure 7.1:** Energy-level diagram, adapted from reference 1, showing the effects of SO, CF and Zeeman interactions on the \( X^2\Pi, A^2\Delta, B^2\Sigma^- \) and \( C^2\Sigma^+ \) states of CH/NG and SiH/NG.
7.1.1.2 \textit{A}^{2}\Delta \text{ state}

The \textit{A}^{2}\Delta \text{ term has no first-order SOC matrix elements because the contributions from the two }\pi\text{ electrons, which occupy the same orbital and have opposite spins, cancel. In addition, it has no first-order CF matrix elements – as outlined in Section 3.3.5.2, a first-order CF between a pair of degenerate }\pi\text{ orbitals requires a CF of }\Delta\text{ symmetry. Matrix elements of such an operator connecting states within a }^{2}\Delta\text{ term necessarily vanish due to the Condon-Slater rules and spin orthogonality.}

Langford and Williamson\textsuperscript{2} estimated the \textit{2}\Delta \text{ term of CH/Ar to have a weak splitting of }A_{\Delta} \lesssim 18 \text{ cm}^{-1}, \text{ which they attributed to higher-order SO effects (with }A_{\Delta} \approx 5 \text{ cm}^{-1})\text{ and a first-order CF of }\Gamma\text{ (4 in Butler notation) symmetry, with matrix elements}

\begin{align}
\langle \Delta_{3/2} \pm \frac{5}{2} | \mathcal{X}_{CF} | \Delta_{3/2} \mp \frac{3}{2} \rangle &= \pm \frac{1}{2} V_{\Delta} \\
\langle \Delta_{3/2} \pm \frac{3}{2} | \mathcal{X}_{CF} | \Delta_{1/2} \mp \frac{5}{2} \rangle &= \pm \frac{1}{2} V_{\Delta}
\end{align}

(7.7)

where \( V_{\Delta} \approx 15 \text{ cm}^{-1} \). However, since a one-electron operator of }\Gamma\text{ symmetry can not form non-zero matrix elements between }\sigma\text{ and }\pi\text{ orbitals, a non-vanishing }V_{\Delta}\text{ is only possible through higher-order inter-term CF interaction. In such a case }\mathcal{X}_{CF}\text{ in Eq. (7.7) should be regarded as an effective operator, and the effect will be weak on account of the energy differences between the different terms.}

7.1.1.3 \textit{B}^{2}\Sigma^{-} \text{ and }\textit{C}^{2}\Sigma^{+} \text{ states}

The \textit{B}^{2}\Sigma^{-} \text{ and }\textit{C}^{2}\Sigma^{+} \text{ states undergo no first-order spin-orbit or CF splitting due to their orbital non-degeneracy. However they are weakly mixed by higher-order SOC, and the }\textit{C}^{2}\Sigma^{+} \text{ state also weakly interacts with the }\textit{a}^{4}\Sigma^{-} \text{ state. The relevant matrix elements are}

\begin{align}
\langle \Sigma_{1/2}^{+} \pm \frac{1}{2} | \mathcal{X}_{SO} | \Sigma_{1/2}^{-} \pm \frac{1}{2} \rangle &= \frac{1}{\sqrt{3}} A_{x} \\
\langle \Sigma_{1/2}^{+} \pm \frac{1}{2} | \mathcal{X}_{SO} | \Sigma_{1/2}^{+} \pm \frac{1}{2} \rangle &= -\frac{2}{\sqrt{3}} A_{x}
\end{align}

(7.8), (7.9)
Methylidyne (CH) and Silylidyne (SiH)

but the energy differences between the terms are sufficiently large that the effects are not perceptible in this work.

7.1.2 Zeeman Matrix Elements

This section gives the angular momentum matrix elements for the various states. They are simply related to the Zeeman matrix elements as outlined in Section 2.9.4. For the purposes of a non-rotating diatomic molecule trapped in a matrix, \( g_x = g_y = g_\perp \).

7.1.2.1 \( X^2\Pi \) state

Table 7.3 gives the angular momentum matrix elements for the \( X^2\Pi \) SO-CF states of CH/NG and SiH/NG.

<table>
<thead>
<tr>
<th>( L_x + 2S_z )</th>
<th>( ^2\Pi L - \frac{1}{2} )</th>
<th>( ^2\Pi L + \frac{1}{2} )</th>
<th>( ^2\Pi \perp - \frac{1}{2} )</th>
<th>( ^2\Pi \perp + \frac{1}{2} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( ^2\Pi L - \frac{1}{2} )</td>
<td>(- (1 - \kappa))</td>
<td>0</td>
<td>( \eta )</td>
<td>0</td>
</tr>
<tr>
<td>( ^2\Pi L + \frac{1}{2} )</td>
<td>0</td>
<td>((1 - \kappa))</td>
<td>0</td>
<td>( \eta )</td>
</tr>
<tr>
<td>( ^2\Pi \perp - \frac{1}{2} )</td>
<td>( \eta )</td>
<td>0</td>
<td>(- (1 + \kappa))</td>
<td>0</td>
</tr>
<tr>
<td>( ^2\Pi \perp + \frac{1}{2} )</td>
<td>0</td>
<td>( \eta )</td>
<td>0</td>
<td>((1 + \kappa))</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>( L_x + 2S_x )</th>
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<th>( ^2\Pi \perp - \frac{1}{2} )</th>
<th>( ^2\Pi \perp + \frac{1}{2} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( ^2\Pi L - \frac{1}{2} )</td>
<td>0</td>
<td>( \eta )</td>
<td>0</td>
<td>( \kappa )</td>
</tr>
<tr>
<td>( ^2\Pi L + \frac{1}{2} )</td>
<td>( \eta )</td>
<td>0</td>
<td>(- \kappa )</td>
<td>0</td>
</tr>
<tr>
<td>( ^2\Pi \perp - \frac{1}{2} )</td>
<td>0</td>
<td>(- \kappa )</td>
<td>0</td>
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</tr>
<tr>
<td>( ^2\Pi \perp + \frac{1}{2} )</td>
<td>( \kappa )</td>
<td>0</td>
<td>( \eta )</td>
<td>0</td>
</tr>
</tbody>
</table>

From Section 2.9.4, the matrix elements in Table 7.3 are related to the principal \( g \) values according to the relationships

\[
\begin{align*}
g_\perp &= 2 \left( ^2\Pi \perp + \frac{1}{2}L_x + 2S_x^2(2^\perp \Pi L - \frac{1}{2}) \right) = 2\eta \\
g_\parallel^\pm &= 2 \left( ^2\Pi \perp + \frac{1}{2}L_z + 2S_x^2 ^2\Pi \perp + \frac{1}{2} \right) = 2(1 \pm \kappa)
\end{align*}
\]

\( g_\parallel^+ \) and \( g_\parallel^- \) are the \( g \) values for the upper and lower SO-CF levels, respectively, when the molecular \( z \) axis is aligned parallel to \( B \). \( g_\perp \) is the \( g \) value for both SO-CF levels.
when the molecular $z$ axis is aligned perpendicular to $B$.

### 7.1.2.2 $A^2\Delta$ state

The angular momentum matrix elements for the $A^2\Delta$ state of CH/NG and SiH/NG are given in Table 7.4.

| $L_z + 2S_z$ | $|^{1/2}\Delta_{3/2} - \frac{1}{2}\rangle$ | $|^{1/2}\Delta_{3/2} + \frac{1}{2}\rangle$ | $|^{1/2}\Delta_{5/2} - \frac{3}{2}\rangle$ | $|^{1/2}\Delta_{5/2} + \frac{3}{2}\rangle$ |
|-------------|-----------------|-----------------|-----------------|-----------------|
| $|^2\Delta_{3/2} - \frac{1}{2}\rangle$ | -1 | 0 | 0 | 0 |
| $|^2\Delta_{3/2} + \frac{1}{2}\rangle$ | 0 | 1 | 0 | 0 |
| $|^2\Delta_{5/2} - \frac{3}{2}\rangle$ | 0 | 0 | -3 | 0 |
| $|^2\Delta_{5/2} + \frac{3}{2}\rangle$ | 0 | 0 | 0 | 3 |

| $L_x + 2S_x$ | $|^{1/2}\Delta_{3/2} - \frac{1}{2}\rangle$ | $|^{1/2}\Delta_{3/2} + \frac{1}{2}\rangle$ | $|^{1/2}\Delta_{5/2} - \frac{3}{2}\rangle$ | $|^{1/2}\Delta_{5/2} + \frac{3}{2}\rangle$ |
|-------------|-----------------|-----------------|-----------------|-----------------|
| $|^2\Delta_{3/2} - \frac{1}{2}\rangle$ | 0 | 0 | 1 | 0 |
| $|^2\Delta_{3/2} + \frac{1}{2}\rangle$ | 0 | 0 | 0 | -1 |
| $|^2\Delta_{5/2} - \frac{3}{2}\rangle$ | 1 | 0 | 0 | 0 |
| $|^2\Delta_{5/2} + \frac{3}{2}\rangle$ | 0 | -1 | 0 | 0 |

### 7.1.2.3 $B^2\Sigma^-$ and $C^2\Sigma^+$ states

The $B^2\Sigma^-$ and $C^2\Sigma^+$ states have no orbital angular momentum, so the Zeeman splittings result purely from spin angular momentum. With $g_e \approx 2$,

\[ \langle \Sigma_{1/2} \pm \frac{1}{2} | L_z + 2S_z | \Sigma_{1/2} \pm \frac{1}{2} \rangle = \pm 1 \]  

\[ \langle \Sigma_{1/2} \pm \frac{1}{2} | L_z + 2S_z | \Sigma^*_{1/2} \pm \frac{1}{2} \rangle = \pm 1 \]

### 7.1.3 Oriented SO-CF Wavefunctions

The SO-CF model assumes that the CH/SiH molecules are not rotating in the matrix. Within this model it is therefore necessary to determine a set of wavefunctions and eigenvalues for a particular orientation of the XH internuclear axis ($z$) with respect to the direction of the magnetic field ($Z$). The result will then be extended to a randomly oriented ensemble by appropriate integration over the angle, $\theta$, between the magnetic field and the internuclear axis of the radical.
Laboratory-frame Zeeman matrix elements for the $X^2\Pi$ SO-CF states of OH/NG and SH/NG, calculated using Eq. (3.65) and Table 7.3, are given in Table 7.5. Note that $\sigma = \pm$ is a label representing the SO-CF levels of the $X^2\Pi$ state. Additional Zeeman matrix elements between the $^2\Pi_L$ and $^2\Pi_+$ levels are responsible for $\delta$ terms, which will be dealt with in Section 7.1.5.2.

Table 7.5: Zeeman matrix elements for the $X^2\Pi$ SO-CF states of CH/NG and SiH/NG.

| $\mu_B B(L_Z + 2S_z)$ | $|{}^2\Pi_\sigma - \frac{1}{2}\rangle$ | $|{}^2\Pi_\sigma + \frac{1}{2}\rangle$ |
|-----------------------|----------------------------------|----------------------------------|
| $\langle {}^2\Pi_\sigma - \frac{1}{2}\mid - \frac{1}{2}\cos\theta g_\parallel^\sigma \mu_B B$ | $\frac{1}{2}\sin\theta g_\parallel^\sigma \mu_B B$ |
| $\langle {}^2\Pi_\sigma + \frac{1}{2}\mid \frac{1}{2}\sin\theta g_\parallel^\sigma \mu_B B$ | $\frac{1}{2}\cos\theta g_\parallel^\sigma \mu_B B$ |

Diagonalisation of the matrix in Table 7.5 gives the energies of the raised and lowered magnetic-field-mixed SO-CF basis functions,

$$E_0(\pm) = \pm \frac{1}{2} g_\sigma^\sigma \mu_B B$$

(7.13)

where $g_\sigma^\sigma$ is given by

$$g_\sigma^\sigma = \sqrt{(g_\parallel^\sigma \cos\theta)^2 + (g_\perp^\sigma \sin\theta)^2}$$

(7.14)

The eigenfunctions in the Zeeman effect for the $^2\Pi_\sigma$ terms are given by

$$|{}^2\Pi_\sigma \pm\rangle = a_\sigma|{}^2\Pi_\sigma + \frac{1}{2}\rangle \pm b_\sigma|{}^2\Pi_\sigma - \frac{1}{2}\rangle$$

(7.15)

where the mixing coefficients $a_\sigma$ and $b_\sigma$ satisfy the relationships

$$|a_\sigma|^2 = \frac{(g_\parallel^\sigma \sin\theta)^2}{2g_\sigma^\sigma (g_\sigma^\sigma - g_\parallel^\sigma \cos\theta)}$$

$$|a_\sigma|^2 + |b_\sigma|^2 = 1$$

$$|a_\sigma|^2 - |b_\sigma|^2 = \frac{g_\parallel^\sigma \cos\theta}{g_\sigma^\sigma}$$

(7.16)
7.1.4 Transition Moments

Transition moments for $A^2\Delta \leftarrow X^2\Pi$, $B^2\Sigma^- \leftarrow X^2\Pi$ and $C^2\Sigma^+ \leftarrow X^2\Pi$ are evaluated using the Wigner-Eckart theorem (Section 2.8). The principle of spectroscopic stability has been used in choosing excited-state basis functions in the SO basis. $\mathcal{M}$ is the one-electron reduced transition moment for the orbital excitation $\pi \leftarrow \sigma$.

\[
\mathcal{M} = \langle \pi | m^1 | \sigma \rangle \quad (7.17)
\]

The applicable transition matrix elements are

\[
\langle 2\Sigma_{1/2}^+ | m_{z1}^1 | 2\Pi_{1/2} \pm \frac{1}{2} \rangle = \langle 2\Sigma_{1/2}^+ | m_{z1}^1 | 2\Pi_{3/2} \pm \frac{1}{2} \rangle = \frac{1}{\sqrt{3}} \mathcal{M} \quad (7.18)
\]

\[
\langle 2\Sigma_{1/2}^+ \pm \frac{1}{2} | m_{z1}^1 | 2\Pi_{1/2} \pm \frac{1}{2} \rangle = \pm \langle 2\Sigma_{1/2}^+ \pm \frac{1}{2} | m_{z1}^1 | 2\Pi_{3/2} \pm \frac{1}{2} \rangle = \frac{1}{\sqrt{3}} \mathcal{M} \quad (7.19)
\]

\[
\langle 2\Sigma_{1/2}^+ \pm \frac{1}{2} | m_{z1}^1 | 2\Pi_{1/2} \pm \frac{1}{2} \rangle = \pm \langle 2\Sigma_{1/2}^+ \pm \frac{1}{2} | m_{z1}^1 | 2\Pi_{3/2} \pm \frac{1}{2} \rangle = \frac{1}{3} \mathcal{M} \quad (7.20)
\]

Some of the matrix elements in Eqs. (7.18) to (7.20) differ from those obtained by Langford and Williamson\(^{1,2}\) due to minor phase discrepancies, which have no effect on the following analysis. Tables 7.6 to 7.9 give expressions for transition moments arising from the $X^2\Pi_\pm$ SO-CF states of CH/NG and SiH/NG.

**Table 7.6: Transition moments for the $A^2\Delta \leftarrow X^2\Pi_\pm$ SO-CF transitions of CH/NG and SiH/NG.**

| $m_{\pm 1}$ | $|^2\Pi_{- \frac{1}{2}}\rangle$ | $|^2\Pi_{+ \frac{1}{2}}\rangle$ | $|\Sigma_{\pm \frac{1}{2}} \rangle$ | $|\Pi_{\pm \frac{1}{2}}\rangle$ |
|-------------|-----------------|-----------------|-----------------|-----------------|
| $\langle 2\Delta_{3/2} - \frac{1}{2} \rangle$ | 0 | 0 | 0 | 0 |
| $\langle 2\Delta_{3/2} + \frac{1}{2} \rangle$ | $\frac{1}{\sqrt{2}} \alpha \mathcal{M}$ | 0 | $\frac{1}{\sqrt{2}} \beta \mathcal{M}$ | 0 |
| $\langle 2\Delta_{5/2} - \frac{1}{2} \rangle$ | 0 | 0 | 0 | 0 |
| $\langle 2\Delta_{5/2} + \frac{1}{2} \rangle$ | 0 | $\frac{1}{\sqrt{2}} \beta \mathcal{M}$ | 0 | $\frac{1}{\sqrt{2}} \alpha \mathcal{M}$ |
| $\langle 2\Sigma_{1/2}^+ \pm \frac{1}{2} \rangle$ | 0 | $\frac{1}{\sqrt{2}} \alpha \mathcal{M}$ | 0 | $-\frac{1}{\sqrt{2}} \beta \mathcal{M}$ |
| $\langle 2\Sigma_{1/2}^- \pm \frac{1}{2} \rangle$ | 0 | 0 | 0 | 0 |
| $\langle 2\Sigma_{1/2}^- \pm \frac{1}{2} \rangle$ | $-\frac{1}{\sqrt{2}} \beta \mathcal{M}$ | 0 | $\frac{1}{\sqrt{2}} \alpha \mathcal{M}$ | 0 |
| $\langle 2\Delta_{5/2} \pm \frac{1}{2} \rangle$ | 0 | 0 | 0 | 0 |
Table 7.7: Transition moments for the $B \Sigma^{-} \rightarrow X \Pi_{\lambda}$ SO-CF transitions of CH/NG and SiH/NG.

| $m_{+1}$ | $|^3\Pi_{-\frac{1}{2}}\rangle$ | $|^3\Pi_{+\frac{1}{2}}\rangle$ | $|^3\Pi_{+\frac{1}{2}}\rangle$ | $|^3\Pi_{+\frac{1}{2}}\rangle$ |
|----------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|
| $\langle \Sigma_{1/2}^{-} - \frac{1}{2} \rangle$ | $-\frac{3}{2} \beta M$ | 0 | $\frac{3}{2} \alpha M$ | 0 |
| $\langle \Sigma_{1/2} - \frac{1}{2} \rangle$ | 0 | $\frac{3}{2} \alpha M$ | 0 | $-\frac{3}{2} \beta M$ |

Table 7.8: Transition moments for the $A \Sigma^{+} \rightarrow X \pi_{\lambda}$ SO-CF transitions of CH/NG and SiH/NG.

| $m_{+1}$ | $|^3\Pi_{-\frac{1}{2}}\rangle$ | $|^3\Pi_{+\frac{1}{2}}\rangle$ | $|^3\Pi_{+\frac{1}{2}}\rangle$ | $|^3\Pi_{+\frac{1}{2}}\rangle$ |
|----------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|
| $\langle \Sigma_{1/2}^{+} - \frac{1}{2} \rangle$ | $-\frac{1}{2} \beta M$ | 0 | $\frac{1}{2} \alpha M$ | 0 |
| $\langle \Sigma_{1/2} + \frac{1}{2} \rangle$ | 0 | $-\frac{1}{2} \alpha M$ | 0 | $\frac{1}{2} \beta M$ |

Table 7.9: Transition moments for the $A \Delta_{A}, B \Sigma^{-}, C \Sigma^{+} \rightarrow X \Pi_{\lambda}$ transitions of CH/NG and SiH/NG.

| $m_{+1}$ | $|^3\Pi_{-}\rangle$ | $|^3\Pi_{+}\rangle$ | $|^3\Pi_{-}\rangle$ | $|^3\Pi_{+}\rangle$ |
|----------|-------------------|-------------------|-------------------|-------------------|
| $\langle \Delta_{3/2} - \frac{1}{2} \rangle$ | 0 | 0 | 0 | 0 |
| $\langle \Delta_{3/2} + \frac{1}{2} \rangle$ | $\frac{3}{2} a \alpha M$ | $\frac{3}{2} b \beta M$ | $\frac{3}{2} a \alpha M$ | $\frac{3}{2} b \beta M$ |
| $\langle \Delta_{5/2} - \frac{1}{2} \rangle$ | 0 | 0 | 0 | 0 |
| $\langle \Delta_{5/2} + \frac{1}{2} \rangle$ | $-\frac{3}{2} b \beta M$ | $\frac{3}{2} b \alpha M$ | $-\frac{3}{2} b \beta M$ | $\frac{3}{2} b \alpha M$ |
| $\langle \Sigma_{1/2} - \frac{1}{2} \rangle$ | $-\frac{3}{2} a \alpha M$ | $\frac{3}{2} b \alpha M$ | $-\frac{3}{2} a \alpha M$ | $\frac{3}{2} b \alpha M$ |
| $\langle \Sigma_{1/2} + \frac{1}{2} \rangle$ | $\frac{3}{2} b \alpha M$ | $-\frac{3}{2} a \alpha M$ | $\frac{3}{2} b \alpha M$ | $-\frac{3}{2} a \alpha M$ |

| $m_{-1}$ | $|^3\Pi_{-}\rangle$ | $|^3\Pi_{+}\rangle$ | $|^3\Pi_{-}\rangle$ | $|^3\Pi_{+}\rangle$ |
|----------|-------------------|-------------------|-------------------|-------------------|
| $\langle \Delta_{3/2} - \frac{1}{2} \rangle$ | $-\frac{3}{2} b \alpha M$ | $\frac{3}{2} a \alpha M$ | $\frac{3}{2} b \beta M$ | $-\frac{3}{2} a \beta M$ |
| $\langle \Delta_{3/2} + \frac{1}{2} \rangle$ | 0 | 0 | 0 | 0 |
| $\langle \Delta_{5/2} - \frac{1}{2} \rangle$ | $-\frac{3}{2} a \beta M$ | $\frac{3}{2} b \beta M$ | $\frac{3}{2} a \beta M$ | $\frac{3}{2} b \beta M$ |
| $\langle \Delta_{5/2} + \frac{1}{2} \rangle$ | 0 | 0 | 0 | 0 |
| $\langle \Sigma_{1/2} - \frac{1}{2} \rangle$ | $\frac{3}{2} a \alpha M$ | $-\frac{3}{2} b \alpha M$ | $\frac{3}{2} a \alpha M$ | $-\frac{3}{2} b \alpha M$ |
| $\langle \Sigma_{1/2} + \frac{1}{2} \rangle$ | $\frac{3}{2} b \alpha M$ | $-\frac{3}{2} a \alpha M$ | $\frac{3}{2} b \alpha M$ | $-\frac{3}{2} a \alpha M$ |
7.1.5 Moment Analysis

The analysis of experimental data involves the taking of ratios of the various MCD and absorption moments (Section 4.2). For this purpose, theoretical moment expressions need to be derived. Initially, this is restricted to the zeroth moments $A_0$ and $C_0$, where $C_0$ is the $C$-term contribution to the overall MCD zeroth moment. $B_0$, the $B$-term contribution, will be treated later by the application of non-degenerate perturbation theory.

7.1.5.1 $A_0$ and $C_0$

Start by considering a molecule oriented at angle $\theta$ with respect to the field. Using Eqs. (4.15) and (4.16), the expressions for $A_0^\theta$ and $C_0^\theta$ for transitions originating from the Zeeman eigenstates $(\pm)$ within each $^2\Pi_\sigma$ level, are given by

$$A_0^\theta(J\lambda \leftarrow ^2\Pi_\sigma \pm) = \frac{\gamma(1 + \cos^2 \theta)}{4} \sum_\lambda P_\sigma(\pm)(|\langle J\lambda|m_{\pm 1}|^2 \Pi_\sigma \pm|^2 + |\langle J\lambda|m_{-1}|^2 \Pi_\sigma \pm|^2) \quad (7.21)$$

$$C_0^\theta(J\lambda \leftarrow ^2\Pi_\sigma \pm) = \gamma \cos \theta \sum_\lambda P_\sigma(\pm)(|\langle J\lambda|m_{+1}|^2 \Pi_\sigma \pm|^2 - |\langle J\lambda|m_{-1}|^2 \Pi_\sigma \pm|^2) \quad (7.22)$$

As before, the superscripts $\theta$ indicate that the moment is specified for a particular orientation of the molecule with respect to the field axis (Z). $J$ and $\lambda$ are the irrep and partner labels appropriate to the excited state. The population factors $P_\sigma(\pm)$ depend on the relative populations of the $^2\Pi_\sigma$ levels; they vary with $g_\parallel^\sigma$ and $g_\perp$, as well as the magnetic field strength and temperature:

$$P_\sigma(\pm) = \frac{1}{Q} \exp \left( \mp \frac{g_\theta^\sigma \mu_\sigma B}{2kT} \right) \exp(\Delta/2kT)$$

$$P_\sigma(\pm) = \frac{1}{Q} \exp \left( \mp \frac{g_\theta^\sigma \mu_\sigma B}{2kT} \right) \exp(-\Delta/2kT) \quad (7.23)$$

$Q$ is the electronic partition function, given by
Methylidyne (CH) and Silylidyne (SiH)

\[ Q = \left[ \exp \left( -\frac{g_\theta \mu_B B}{2kT} \right) + \exp \left( -\frac{g_\theta^+ \mu_B B}{2kT} \right) \right] \exp(\Delta/2kT) + \]

\[ \left[ \exp \left( -\frac{g_\theta \mu_B B}{2kT} \right) + \exp \left( -\frac{g_\theta^+ \mu_B B}{2kT} \right) \right] \exp(-\Delta/2kT) \]

\[ = 2 \cosh \left( \frac{g_\theta \mu_B B}{2kT} \right) \exp(\Delta/2kT) + 2 \cosh \left( \frac{g_\theta^+ \mu_B B}{2kT} \right) \exp(-\Delta/2kT) \]  

(7.24)

The absorption and MCD zeroth moments for the three transitions are readily calculated using Eqs. (7.21) and (7.22), and Table 7.9. They are found to differ only by the factors \( \zeta_A(J) \) and \( \zeta_M(J) \), respectively, which are given in Table 7.10.

\[ A_\theta^0(J \leftarrow \Sigma^+) = \frac{\zeta_A(J)}{2} \gamma \left( 1 + \cos^2 \theta \right) \mathcal{M}^2 \]  

(7.25)

\[ C_\theta^0(J \leftarrow \Sigma^+) = \frac{\zeta_M(J)}{2} \gamma \left( 1 - \cos \theta \right) \mathcal{M}^2 \left[ \frac{g_\parallel^+}{g_\parallel^-} \sinh \left( \frac{g_\theta^+ \mu_B B}{2kT} \right) \exp(\Delta/2kT) - \right. \]

\[ \frac{g_\parallel^+}{g_\parallel^-} \sinh \left( \frac{g_\theta \mu_B B}{2kT} \right) \exp(-\Delta/2kT) \]  

(7.26)

Table 7.10: Absorption and MCD moment coefficients for the \( J \leftarrow \Sigma^+ \) transitions of CH/NG and SiH/NG.

<table>
<thead>
<tr>
<th>Excited term (J)</th>
<th>( \zeta_A(J) )</th>
<th>( \zeta_M(J) )</th>
<th>( \zeta(J) = \zeta_M(J)/\zeta_A(J) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A^2\Delta )</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>( B^2\Sigma^- )</td>
<td>( \frac{3}{2} )</td>
<td>( -\frac{3}{2} )</td>
<td>( -1 )</td>
</tr>
<tr>
<td>( C^2\Sigma^+ )</td>
<td>( \frac{1}{2} )</td>
<td>( -\frac{1}{2} )</td>
<td>( -1 )</td>
</tr>
</tbody>
</table>

The sign of the MCD zeroth moment is determined by the coefficient \( \zeta(J) \). Therefore, the transition \( A^2\Delta \leftarrow \Sigma^+ \) has positive MCD, and the other two transitions have negative MCD. This is the observed experimental result (see Section 7.3 below).

At low temperatures, the population of the upper SO-CF is small and effectively can be ignored. At weak fields, \( \sinh \left( \frac{g_\theta \mu_B B}{2kT} \right) \approx \left( \frac{g_\theta \mu_B B}{2kT} \right) \) and Eq. (7.26) becomes

7-11
According to Eq. (7.10), as \( \kappa \to 1 \) (i.e. as the magnitude of the CF decreases), \( g_{||}^{-} \) vanishes because the orbital and spin contributions to the magnetic moment cancel. So the fact that \( \mathcal{C} \) terms arise at all for CH/NG (and SiH/NG) matrices in the SO-CF model is a direct consequence of the CF which mixes \( ^{2}\Pi_{3/2} \) into the lower magnetically unsusceptible \( ^{2}\Pi_{1/2} \) level.

### 7.1.5.2 \( B_{\theta} \)

The \( \mathcal{B} \)-term contribution to \( M_{0} \) is considered by treating the magnetic-field-induced mixing of \( ^{2}\Pi_{L} \) and \( ^{2}\Pi_{+} \) by perturbation theory. This treatment assumes that the mixing of these levels is small compared to the first-order Zeeman effect, and that contributions from mixing with other terms are insignificant due to the large energy separations.

The field-induced perturbation modifies the Zeeman eigenfunctions \( ^{2}\Pi_{\sigma \pm} \) of Eq. (7.15), which become

\[
^{2}\Pi_{\sigma \pm} = ^{2}\Pi_{\sigma \pm}^{0} + ^{2}\Pi_{\sigma \pm}^{'}
\]

where the \( ^{0} \) and \( ^{'} \) respectively denote the states in the absence of the perturbation, and the correction for the perturbation. \( \mathcal{B} \) terms arise from the second term of Eq. (7.28), which can be expanded as

\[
^{2}\Pi_{L \pm}^{'} = -\frac{\mu_{B}B}{\Delta} \sum_{\nu=\pm} \left( ^{2}\Pi_{L \nu}^{0} \nu_{LZ} + 2S_{z}^{2}\Pi_{L \pm}^{0} \right)
\]

\[
^{2}\Pi_{+}^{'} = \frac{\mu_{B}B}{\Delta} \sum_{\nu=\pm} \left( ^{2}\Pi_{L \nu}^{0} \nu_{LZ} + 2S_{z}^{2}\Pi_{+}^{0} \right)
\]

where \( \nu \) labels the upper and lower Zeeman eigenfunctions of Eq. (7.15). These can be converted into \( \theta \)-dependent form using Eq. (3.65). The necessary Zeeman matrix elements are calculated using Table 7.3 and Eq. (7.15).
Methylidyne (CH) and Silylidyne (SiH)

\[ |^2 \Pi \pm \gamma' = -\frac{\mu_B B}{2\Delta} [(\cos \theta a_{g\pm} + 2 \sin \theta b_{\pm \kappa})|^2 \Pi + \frac{1}{2})^0 \pm (\cos \theta b_{g\pm} - 2 \sin \theta a_{\pm \kappa})|^2 \Pi + \frac{1}{2})^0 \pm (\cos \theta b_{g\pm} + 2 \sin \theta a_{\pm \kappa})|^2 \Pi + \frac{1}{2})^0 \pm (\cos \theta a_{g\pm} - 2 \sin \theta b_{\pm \kappa})|^2 \Pi + \frac{1}{2})^0 \pm \]

(7.30)

Transition moments from these corrected functions are derived in exactly the same manner as before (Section 7.1.4). The total transition moments are combined with the unperturbed ones according to Eq. (7.31).

\[ |\langle J | m_\pm | A \rangle |^2 = |\langle J | m_\pm | A \rangle |^2 + \langle \langle J | m_{\pm 1} | A \rangle \langle J | m_{\pm 1} | A \rangle^* \rangle + \langle \langle J | m_{\pm 1} | A \rangle^* \langle J | m_{\pm 1} | A \rangle \rangle \]

\[ = |\langle J | m_{\pm 1} | A \rangle |^2 + 2 \text{Re}(\langle J | m_{\pm 1} | A \rangle \langle J | m_{\pm 1} | A \rangle^* \rangle \]

\[ = |\langle J | m_{\pm 1} | A \rangle |^2 + [\langle J | m_{\pm 1} | A \rangle |^2 \]

(7.31)

\( A \) and \( J \) are the labels appropriate to the ground and excited states, respectively. The \( \Omega \)-term contribution (for an orientation \( \theta \)) to the zeroth MCD moment, \( B_0^\theta \), is formed by taking expressions of the form \( \cos \theta (|\langle J | m_{\pm 1} | A \rangle |^2 - |\langle J | m_{\pm 1} | A \rangle |^2) \), summing over all non-zero transitions weighted by their ground-state population factors, and multiplying by \( \gamma \). Thus, \( B_0^\theta \) is given by

\[ B_0^\theta(J \leftarrow ^2 \Pi) = -\sum_{M}(J) \gamma \langle g_{\pm \kappa} \cos \theta^2 \mu_B B | M_i^2 \left[ \cosh \left( \frac{g \mu_B B}{2kT} \right) \exp(\Delta/2kT) - \right. \]

\[ \left. \cosh \left( \frac{g \mu_B B}{2kT} \right) \exp(-\Delta/2kT) \right] \]

(7.32)

Note here that the \( \Omega \) terms are of opposite sign to the \( C \) terms for all transitions.

7.1.5.3 Moment ratios

In order to fit experimental data to the SO-CF theoretical model, \( B_0^\theta, C_0^\theta \), and \( A_0^\theta \) must be averaged over \( \theta \) as outlined in Section 4.2, before the appropriate ratios taken. The coefficients \( \gamma(J) = \sum_{M}(J)/\sum_{A}(J) \), which depend only on the symmetry of the excited state, are given in Table 7.10.
In Eqs. (7.33) and (7.34), the first and second terms in the square brackets respectively represents the contribution from the lower, $^2 \Pi_1$, and upper, $^2 \Pi_u$, levels.

### 7.2 Experimental

Preliminary matrix depositions were carried out using the He-refrigerator/electromagnet system, described in Section 6.2.1. Unfortunately, all attempts to make SiH/NG and CH/Xe, using the methods of Section 6.1, failed in these preliminary stages. The likely reason for the failure of SiH/NG is that the tesla-coil discharge of SiH/NG produces elemental Si and Si$_2$ etc.

The only CH or SiH matrix successfully investigated using the matrix-injection system (Section 6.2.2), was CH/Kr. The deposition time was 55 minutes, with the CH$_4$/Kr flow rate ~2-3 mmol hr$^{-1}$, and the window temperature ~20 K.

Spectral data were gathered using MOD4 (Section 6.3) in conjunction with a Xe-arc lamp, a 1180-groove/mm grating, and a Hamamatsu R-376 PMT. The monochromator slits were set to 200 µm (~0.16 nm resolution), and the chopper performed 30 cycles at each step of 0.05 nm over the main spectral features. An Esco Products GG-395 filter was used to eliminate second-order UV light for the $A^2 \Pi$ and $B^2 \Sigma^- \leftrightarrow X^2 \Pi$ transitions, while a Corning 7-54 filter was used to remove stray visible
light for the $C^2\Sigma^+ \leftarrow X^2\Pi$ transition.

### 7.3 Results

This section contains spectral data, obtained using the matrix-injection system, for the (0,0) bands of the three allowed transitions of CH/Kr ($A^2\Delta \leftarrow X^2\Pi$, $B^2\Sigma^- \leftarrow X^2\Pi$ and $C^2\Sigma^+ \leftarrow X^2\Pi$). The yield of CH/Kr was similar to that obtained using the refrigerator/electromagnet set-up. The spectra are similar to those of CH/Ar reported by Langford\textsuperscript{1, 2} and Rose,\textsuperscript{3} however the $\varepsilon$ terms are weaker and the $\varepsilon$ term associated with the $A^2\Delta \leftarrow X^2\Pi$ transition is more distinct. Table 7.11 gives the positions for the main absorption bands measured in this research, compared with those obtained by McCarty and Robinson\textsuperscript{4} and by Langford for CH/Ar.\textsuperscript{1, 2} The discrepancies in band positions between this work and McCarty and Robinson's are most likely due to minor calibration inconsistencies.

The transitions exhibit a consistent red shift from Ar to Kr, in accord with previous observations for molecules trapped in noble-gas matrices\textsuperscript{5} (Section 5.2). It is interesting to note that these shifts increase in going from the $A$ to $C$ transitions, indicating that the CH excited states interact with the host to different extents.

<table>
<thead>
<tr>
<th>Band</th>
<th>Band energy / cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Langford$^{1, 2}$ CH/Ar</td>
</tr>
<tr>
<td>$A^2\Delta \leftarrow X^2\Pi$</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>23234</td>
</tr>
<tr>
<td>2</td>
<td>23271</td>
</tr>
<tr>
<td>$B^2\Sigma^- \leftarrow X^2\Pi$</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>25507</td>
</tr>
<tr>
<td>2</td>
<td>25544</td>
</tr>
<tr>
<td>3</td>
<td>25587</td>
</tr>
<tr>
<td>4</td>
<td>25622</td>
</tr>
<tr>
<td>$C^2\Sigma^+ \leftarrow X^2\Pi$</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>31739</td>
</tr>
<tr>
<td>2</td>
<td>31780</td>
</tr>
</tbody>
</table>
7.3.1 \( \text{A}^2\Delta \leftarrow \text{X}^2\Pi \) (CH/Kr)

Figure 7.2 gives the temperature-dependent MCD (1.40 to 4.22 K at 1 T) and an averaged absorption spectrum for the \( \text{A}^2\Delta \leftarrow \text{X}^2\Pi \) transition of CH/Kr. There is noticeable temperature-dependence in the absorption spectrum, which becomes more intense at higher temperatures above \( \sim 4.2 \) K, possibly suggesting that CH is (partially) rotating. This is shown in Figure 7.3, which contains data for 10.5, 7.2, and 2.28 K at 5.01 T. Absorption data at 4.22 K were adversely affected by scattering due to bubbles of helium in the sample chamber and so are not included. The absorbance in Figure 7.2 was averaged over spectra below 4.22 K to obtain a better signal-to-noise ratio. There does appear to be small temperature and field dependencies below 4.22 K, but these are difficult to quantify due to the poor signal-to-noise ratio of the data and baselining problems caused by the scattering of light by the matrix itself.

Apart from the negative feature in the MCD near 23120 cm\(^{-1}\) (432.5 nm), which is due to a positive (temperature-independent) \( \sigma \) term, the MCD is largely single-signed and positive, showing the saturation behaviour indicative of \( \pi \) terms. This is illustrated for the MCD in Figure 7.2, and further in the field-dependence data at various temperatures between \( \sim 1.4 \) and 7.2 K in Figures 7.3 to 7.9.

Langford observed two maxima, at 23234 and 23271 cm\(^{-1}\), in the absorption spectrum of the \( \text{A}^2\Delta \leftarrow \text{X}^2\Pi \) transition of CH/Ar\(^{1,2}\) with a tailing-off to the blue. In the CH/Kr case the two bands have effectively merged into a single broad band centred at 23160 cm\(^{-1}\), and there is a similar tailing off to the blue. The MCD spectra are very similar to the CH/Ar case, with two main features being observed; a sharp \( \sigma \) term centred at \( \sim 23130 \) cm\(^{-1}\) and a broader \( \pi \) term to the blue with a maximum near 23200 cm\(^{-1}\). The \( \sigma \) term appears to be stronger than for CH/Ar, but this may be because the \( \pi \) terms are comparatively weaker or shifted further to the blue than with CH/Ar.
Figure 7.2: Absorption and temperature-dependent MCD (1 T) spectra of the $(0,0)$ band of the $A^2\Delta \leftarrow X^2\Pi$ transition of CH/Kr.

Figure 7.3: Absorption and temperature-dependent MCD (5 T) spectra of the $(0,0)$ band of the $A^2\Delta \leftarrow X^2\Pi$ transition of CH/Kr.
Methylidyne (CH) and Silylidyne (SiH)

Figure 7.4: Magnetic-field-dependent MCD (1.39 K) spectra of the (0,0) band of the $A^2\Delta \leftarrow X^2\Pi$ transition of CH/Kr.

Figure 7.5: Magnetic-field-dependent MCD (1.64 K) spectra of the (0,0) band of the $A^2\Delta \leftarrow X^2\Pi$ transition of CH/Kr.
Figure 7.6: Magnetic-field-dependent MCD (1.88 K) spectra of the (0,0) band of the $A^2\Delta \leftarrow X^2\Pi$ transition of CH/Kr.

Figure 7.7: Magnetic-field-dependent MCD (2.28 K) spectra of the (0,0) band of the $A^2\Delta \leftarrow X^2\Pi$ transition of CH/Kr.
**Figure 7.8:** Magnetic-field-dependent MCD (4.22 K) spectra of the (0,0) band of the $A^2\Delta \leftarrow X^2\Pi$ transition of CH/Kr.

**Figure 7.9:** Magnetic-field-dependent MCD (7.2 K) spectra of the (0,0) band of the $A^2\Delta \leftarrow X^2\Pi$ transition of CH/Kr.
7.3.2  $B^2\Sigma^+ \leftarrow X^2\Pi$ (CH/Kr)

Figure 7.10 gives an averaged (to obtain better signal to noise) absorption spectrum and temperature-dependent MCD spectra (1.39 to 3.11 K at 1 T) for the $B^2\Sigma^- \leftarrow X^2\Pi$ transition of CH/Kr. The response of the spectrometer decreases into the UV, hence the S/N of this transition is considerably poorer than that of $A^2\Delta \leftarrow X^2\Pi$, although the larger spacing between energy units in Figure 7.10 exaggerates this somewhat. The poor S/N made it difficult to confidently baseline the MCD data.

With the benefit of hindsight, it would have been wise to measure higher-temperature absorption spectra to see if there is any temperature dependence. The poor S/N of the absorption data actually obtained does not allow this to be tested. The MCD is single-signed and negative, showing the saturation behaviour indicative of $\epsilon$ terms. This is illustrated in the MCD of Figure 7.10, and further in the field-dependence data below 2.3 K in Figures 7.11 and 7.12.

Langford\(^1,2\) observed four maxima (at 25507, 25544, 25587 and 25622 cm\(^{-1}\)) in the absorption spectrum of the $B^2\Sigma^- \leftarrow X^2\Pi$ transition of CH/Ar. These were attributed to two “origins” separated by $\sim 80$ cm\(^{-1}\) with weaker bands $\sim 36$ cm\(^{-1}\) to the blue. In the CH/Kr case these have effectively merged into two broad bands centred at 25394 and 25464 cm\(^{-1}\). As seen in CH/Ar by Langford, there is also some evidence for broad shoulders located to the blue of the main bands.

The MCD spectra of CH/Kr are very similar to the CH/Ar case, with two main bands being observed, at $\sim 25380$ and $\sim 25480$ cm\(^{-1}\), both of which are negative and exhibit $\epsilon$-term behaviour.
Figure 7.10: Absorption and temperature-dependent MCD (1 T) spectra of the (0,0) band of the $B \Sigma^- \leftrightarrow X \Pi$ transition of CH/Kr.

Figure 7.11: Magnetic-field-dependent MCD (1.64 K) spectra of the (0,0) band of the $B \Sigma^- \leftrightarrow X \Pi$ transition of CH/Kr.
**Methylidyne (CH) and Silylidyne (SiH)**

\[ \lambda \text{ (nm)} \]

\[ \Delta A \]

\[ /10^3 \]

\[ E \text{ (cm}^{-1}\text{)} \]

**Figure 7.12**: Magnetic-field-dependent MCD (2.29 K) spectra of the (0,0) band of the \( B \, ^2\Sigma^- \leftrightarrow X \, ^2\Pi \) transition of CH/Kr.

### 7.3.3 \( C \, ^2\Sigma^+ \leftrightarrow X \, ^2\Pi \) (CH/Kr)

As for the \( B \, ^2\Sigma^- \leftrightarrow X \, ^2\Pi \) transition, the \( C \, ^2\Sigma^+ \leftrightarrow X \, ^2\Pi \) transition of CH/Kr has poor S/N. Figure 7.13 gives an averaged (to obtain better S/N) absorption spectrum and temperature-dependent MCD spectra (1.39 to 3.11 K at 1 T) for this transition. As found by Langford in his studies of CH/Ar, the matrix was also contaminated by OH, the \( A \, ^2\Sigma^+ \leftrightarrow X \, ^2\Pi \) transition of which partially overlaps the \( C \, ^2\Sigma^+ \leftrightarrow X \, ^2\Pi \) transition of CH/Kr. Subsequently, baselining of these MCD spectra was even more problematic than was the case for the \( A \) and \( B \) transitions.

The MCD is single-signed and negative, showing the saturation behaviour indicative of \( \Sigma \) terms. This is illustrated in the MCD of Figure 7.13, and further in the field-dependence data below 2.3 K in Figures 7.14 and 7.15. It would have been desirable to test for temperature dependence in the absorption spectra, especially at high-temperature. The poor S/N of the absorption data actually obtained does not allow this to be tested.
Two maxima (at 31739 and 31780 cm\(^{-1}\)) were observed by Langford in the absorption spectrum of the \(C^2\Sigma^+ \leftarrow X^2\Pi\) transition of CH/Ar. In the CH/Kr case these have merged into one broad band centred at 31542 cm\(^{-1}\). There is also a broad shoulder at \(~31700\) cm\(^{-1}\) and a weak shoulder located at \(~31510\) cm\(^{-1}\), just to the red of the main maximum. The MCD spectra are very similar to the CH/Ar case, with two main bands being observed, both of which are negative and show \(\epsilon\)-term behaviour.

![Spectra Diagram](image)

**Figure 7.13:** Absorption and temperature-dependent MCD (1 T) spectra of the \((0,0)\) band of the \(C^2\Sigma^+ \leftarrow X^2\Pi\) transition of CH/Kr.
Figure 7.14: Magnetic-field-dependent MCD (1.64 K) spectra of the (0,0) band of the \(^{3}\Sigma^{+} \leftarrow X^{2}\Pi\) transition of CH/Kr.

\[\text{CH/Kr: } C^{3}\Sigma^{+} \leftarrow X^{2}\Pi, \quad T = 1.64 \text{ K}\]

\[\Delta A \quad / 10^{-3}\]

\[E (\text{cm}^{-1})\]

Figure 7.15: Magnetic-field-dependent MCD (2.29 K) spectra of the (0,0) band of the \(^{3}\Sigma^{+} \leftarrow X^{2}\Pi\) transition of CH/Kr.

\[\text{CH/Kr: } C^{3}\Sigma^{+} \leftarrow X^{2}\Pi, \quad T = 2.29 \text{ K}\]
7.4 Moment Analysis

Zeroth MCD and absorption moments were obtained over the (0,0) band envelopes of each system by using the computer program MOMENT. Plots of the ratio \( \frac{M_0}{A_0} \) are given in Figures 7.16 – 7.22. (Note that Figures 7.16 and 7.17 are part of the same data set.) As reported in the previous section, the S/N ratio of the spectra is reasonably poor, especially for the \( B\, ^2\Sigma^- \leftarrow X^2\Pi \) and \( C\, ^2\Sigma^+ \leftarrow X^2\Pi \) transitions. This is reflected in relatively large errors in the moments.

The \( \frac{M_0}{A_0} \) plots show temperature dependence and non-linear magnetic-field dependence, both of which are indicative of significant \( \mathcal{C} \) terms. However, they also exhibit very unusual characteristics that provide evidence against dominant \( \mathcal{C} \) terms. These characteristics are most clearly evident for the \( A\, ^2\Delta \leftarrow X^2\Pi \) transition, which presents the best quality of data. Firstly, if \( \mathcal{C} \) terms were dominant, the moment ratios would trend to zero at infinite temperature \((1/kT = 0)\), whereas they appear to reach zero near \( \sim 6 \) K \((1/kT \approx 0.23 \text{ cm}^{-1}; \text{Figures 7.16 and 7.17})\). Secondly, \( \mathcal{C} \) terms exhibit magnetisation saturation, having a (quasi-) tanh dependence on the field strength and tending to a constant high field value. But at temperatures below \( \sim 2 \) K, the (absolute) magnitude of \( \frac{M_0}{A_0} \) is observed to reach a maximum at fields below \( 5 \) T \((\mu_B B \leq 2.3 \text{ cm}^{-1}; \text{Figure 7.18})\), with the field of the maximum decreasing with decreasing temperature. These observations point to the existence of strong \( \mathcal{B} \) terms of the opposite sign to the \( \mathcal{C} \) terms. The latter point is in accord with one of the predictions of the SO-CF model, as noted in Section 7.1.5.2.

![Figure 7.16](image-url)

Figure 7.16: Temperature-dependence of the moment ratio \( \frac{M_0}{A_0} \) as a function of \( 1/kT \) for CH/Kr \( A\, ^2\Delta \leftarrow X^2\Pi \). The curves are best fits to all the data using the randomly oriented SO-CF model, with \( A_\alpha = 10.9 \text{ cm}^{-1} \) and \( V_\alpha = 45 \text{ cm}^{-1} \).
Methylidyne (CH) and Silylidyne (SiH)

Figure 7.17: Temperature-dependence data for the moment ratio $M_0/A_0$ as a function of $1/kT$ for CH/Kr $A^2\Delta \leftarrow X^2\Pi$. The curves are best fits to all the data using the randomly oriented SO-CF model, with $A_n = 10.9 \text{ cm}^{-1}$ and $V_n = 45 \text{ cm}^{-1}$.

Figure 7.18: Magnetic-field-dependence data for the moment ratio $M_0/A_0$ as a function of $\mu_B B$ for CH/Kr $A^2\Delta \leftarrow X^2\Pi$. The curves are best fits to all the data using the randomly oriented SO-CF model, with $A_n = 10.9 \text{ cm}^{-1}$ and $V_n = 45 \text{ cm}^{-1}$.

Figure 7.19: Temperature-dependence data for the moment ratio $M_0/A_0$ as a function of $1/kT$ for CH/Kr $B^2\Sigma^- \leftarrow X^2\Pi$. The curve is a best fit to all the data using the randomly oriented SO-CF model, with $A_n = 14 \text{ cm}^{-1}$ and $V_n = 40 \text{ cm}^{-1}$.
Figure 7.20: Magnetic-field-dependence data for the moment ratio \( \frac{M_0}{A_0} \) as a function of \( \mu_0B \) for CH/Kr \( B^2\Sigma^- \leftrightarrow X^2\Pi \). The curves are best fits to all the data using the randomly oriented SO-CF model, with \( A_m = 14 \text{ cm}^{-1} \) and \( V_m = 40 \text{ cm}^{-1} \).

Figure 7.21: Temperature-dependence data for the moment ratio \( \frac{M_0}{A_0} \) as a function of \( \frac{1}{kT} \) for CH/Kr \( C^2\Sigma^+ \leftrightarrow X^2\Pi \). The curve is a best fit to all the data using the randomly oriented SO-CF model, with \( A_m = 11 \text{ cm}^{-1} \) and \( V_m = 30 \text{ cm}^{-1} \).

Figure 7.22: Magnetic-field-dependence data for the moment ratio \( \frac{M_0}{A_0} \) as a function of \( \mu_0B \) for CH/Kr \( C^2\Sigma^+ \leftrightarrow X^2\Pi \). The curves are best fits to all the data using the randomly oriented SO-CF model, with \( A_m = 11 \text{ cm}^{-1} \) and \( V_m = 30 \text{ cm}^{-1} \).
7.5 Discussion

7.5.1 SO-CF Model for CH

Fits to the experimental moment ratio data were achieved by employing the non-linear least-squares fitting program MAGPI, which uses the sum of Eqs. (7.33) and (7.34), with the integrals over \( \theta \) being evaluated numerically. The two (independent) fitting parameters are \( A_\pi \) and \( V_\pi \).

The best fits are shown as full curves superimposed on the experimental data in Figures 7.16 – 7.22. The results are very satisfactory for the \( A \leftarrow X \) transition, but somewhat less convincing for the \( B \leftarrow X \) and \( C \leftarrow X \) transitions, for which the experimental data are substantially less precise. It is encouraging to see that these fits reproduce the unusual zero-crossings in the temperature-dependence and the extrema in the field dependence, described in Section 7.4. The explanation is exactly as anticipated – relatively strong \( g \) terms of the opposite sign to the \( e \) terms.

An interesting point about the calculated curves is that after crossing zero in the plots against \( 1/kT \), they turn back to zero in the high-temperature \( (1/kT \rightarrow 0) \) limit. The reasons can be seen from inspection of Eqs. (7.33) and (7.34). As \( T \) increases, \( \sinh(g_\pi^2 \mu_B B/2kT) \) tends to zero, whereas \( \cosh(g_\pi^2 \mu_B B/2kT) \) and \( \exp(-A/2kT) \) tend to unity. Thus, the ratios \( C_0/A_0 \) and \( B_0/A_0 \) both tend to zero, but at different rates and for different reasons. In the case of the \( g \)-term contribution, both terms in the square brackets of Eq. (7.33) vanish as the populations between the two Zeeman levels within each SO-CF level are equalised. For the \( e \)-term contribution, neither of the terms vanishes; instead, they reach the same magnitude and, because they are of opposite sign, cancel at high temperatures. The magnitude of the \( g \)-term contribution changes throughout the range of temperatures investigated, whereas that for the (oppositely signed) \( g \) terms is essentially temperature independent in the regime where \( kT \ll A \). The zero-crossing corresponds to the temperature at which the \( g \)- and \( g \)-term magnitudes are equal. At higher temperatures (lower values of \( 1/kT \)), the \( g \)-terms are dominant, but then as they vanish, the value of \( M_0/A_0 \) turns back to zero. Unfortunately, data were not obtained at sufficiently high temperatures to properly test these theoretical predictions.

The best-fit parameters obtained for each of the \( A, B \) and \( C \) systems of \( CH/Kr \) are listed in Table 7.12, with two standard deviations uncertainty limits. One
would expect the parameters to be the same for each transition, as Langford found for CH/Ar.\textsuperscript{1,2} Although they do agree within the limits of uncertainty, this is mainly because the percentage errors for the parameters in the B and C transitions are very large due to the poor S/N ratios for the corresponding experimental data. In the following, the “best-fit” parameters for CH/Kr will be taken as those for $A^2\Delta \leftarrow X^2\Pi$. (This fit was performed without using data above 4.22 K, which has similar problems to the data in the $B$ and $C$ transitions.)

Table 7.12: Parameters for the $A^2\Delta$, $B^2\Sigma^-$ and $C^2\Sigma^+ \leftarrow X^2\Pi$ transitions of CH/Kr, obtained from a non-linear least-squares fit of the experimental data to the randomly-oriented SO-CF model. Quoted uncertainties are two standard deviations.

<table>
<thead>
<tr>
<th>Transition</th>
<th>$A_\pi$ (cm$^{-1}$)</th>
<th>$V_\pi$ (cm$^{-1}$)</th>
<th>$\Delta$ (cm$^{-1}$)</th>
<th>$\kappa$</th>
<th>$g_\parallel^-$</th>
<th>$g_\parallel^+$</th>
<th>$g_\perp$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A^2\Delta \leftarrow X^2\Pi$</td>
<td>10.9 ± 0.7</td>
<td>45 ± 6</td>
<td>46 ± 6</td>
<td>0.24 ± 0.05</td>
<td>1.53</td>
<td>2.47</td>
<td>1.95</td>
</tr>
<tr>
<td>$B^2\Sigma^- \leftarrow X^2\Pi$</td>
<td>14 ± 4</td>
<td>40 ± 20</td>
<td>40 ± 20</td>
<td>0.3 ± 0.3</td>
<td>1.37</td>
<td>2.63</td>
<td>1.90</td>
</tr>
<tr>
<td>$C^2\Sigma^+ \leftarrow X^2\Pi$</td>
<td>11 ± 2</td>
<td>30 ± 20</td>
<td>30 ± 20</td>
<td>0.3 ± 0.2</td>
<td>1.34</td>
<td>2.64</td>
<td>1.89</td>
</tr>
</tbody>
</table>

The parameters $A_\pi$ and $V_\pi$ for CH/Ar\textsuperscript{1,2} and CH/Kr are compared in Table 7.13.

The magnitude of $A_\pi$ in noble-gas matrices is reduced from the gas phase and further decreases as the size of the noble gas increases. This trend is a direct consequence of the external heavy-atom effect (see Section 5.3), in which the value of $A_\pi$ is perturbed by a nearby atom of high atomic number existing as part of the solvent shell. It seems likely that in this case the effect is largely mechanical in nature because of the small decrease of $A_\pi$ in going from the gas phase to krypton, however a small amount of mixing of the guest and host orbitals can not be ruled out.

Table 7.13: SOC coupling constants ($A_\pi$) for the $X^2\Pi$ state of CH in various media.

<table>
<thead>
<tr>
<th>Medium</th>
<th>Gas</th>
<th>Argon\textsuperscript{1,2}</th>
<th>Krypton</th>
<th>Xenon</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_\pi$ (cm$^{-1}$)</td>
<td>31.8$^6$</td>
<td>21 ±1</td>
<td>10.9 ± 0.7</td>
<td>*</td>
</tr>
<tr>
<td>$V_\pi$ (cm$^{-1}$)</td>
<td>–</td>
<td>78 ± 15</td>
<td>45 ± 6</td>
<td>*</td>
</tr>
</tbody>
</table>

*No data available.

Although no data could be collected on the CH/Xe system, the trend exhibited in Table 7.13 suggests that $A_\pi$ will be close to zero. In such a case, the contribution to $\mathbf{M}_0/A_0$ from $\mathcal{E}$ terms will be negligible and only $\mathcal{C}$ terms (which do not contribute to $\mathbf{M}_0$) and CF-induced $\mathcal{B}$ terms will be observed. The MCD will likely be even weaker than CH/Kr and it might be necessary to produce Xe matrices with much
higher optical density units of CH in absorption in order for good quality MCD spectra to be obtained.

SiH/NG matrices could be potentially very interesting to study, although it is possible that MCD might be too weak for the determination of $A_\pi$. Since the gas-phase value is 142.83 cm$^{-1}$, larger crystal fields than those encountered by CH will be required to mix enough of the upper $^2\Pi_{3/2}$ SO states into the lower Zeeman inactive $^2\Pi_{1/2}$ level to observe any $c$ terms. But it seems unlikely that these crystal fields could be considerably larger than those for CH/Ar and CH/Kr. Furthermore, if the external heavy-atom effect causes an increase in $A_\pi$ relative to the gas phase, as it does for PH (Chapter 8), the MCD will be even weaker; so the failure of SiH/NG experiments might not be such a disappointment after all.

### 7.5.2 Hindered-Rotor Model for CH

A number of previous workers, including Keyser, Rose, and Heaven, have assigned some structure, particularly in the $B^2\Sigma^- \leftarrow X^2\Pi$ and $C^2\Sigma^+ \leftarrow X^2\Pi$ transitions of CH/Ar and CH/Kr, to free rotation. Langford dismissed the possibility of rotation, but it is this author’s view that for a small diatomic radical the Hund’s case-(a) basis set should be able to explain the experimental data (because it is a complete set). The only obstacle to this is recognising the interactions between guest and host, and obtaining proper mathematical expressions for these.

Although the first-order Zeeman splitting of the lowest $J = \frac{1}{2}$ rotational levels of CH is zero, higher-order Zeeman interactions with other $J$ levels cause a small splitting. It is therefore possible to simulate a theoretical $M_0/A_0$ saturation curve for free-rotor CH.

As outlined in Section 3.4.4, the Hund’s case-(a) basis functions for the excited states of CH/SiH are

\begin{align*}
| ^2\Sigma_{1/2}^+ J M P^\pm \rangle &= \frac{1}{\sqrt{2}} \{ | 0 \frac{1}{2}, J \frac{1}{2} M \rangle \pm | 0 \frac{1}{2}, -\frac{1}{2}, J -\frac{1}{2} M \rangle \} \\
| ^2\Sigma_{1/2}^- J M P^\pm \rangle &= \frac{1}{\sqrt{2}} \{ | 0 \frac{1}{2}, J \frac{1}{2} M \rangle \pm | 0 \frac{1}{2}, -\frac{1}{2}, J -\frac{1}{2} M \rangle \} \\
| ^2\Delta_{3/2} J M P^\pm \rangle &= \frac{1}{\sqrt{2}} \{ | 2 \frac{1}{2}, -\frac{1}{2}, J \frac{1}{2} M \rangle \pm | 2 \frac{1}{2}, \frac{1}{2}, J -\frac{1}{2} M \rangle \}
\end{align*}

(7.35)  
(7.36)
Methylidyne (CH) and Silyldyne (SiH)

\[ |^2\Delta_{5/2} J M p^\pm \rangle = \frac{1}{\sqrt{2}} \{ | 2 \frac{1}{2} \frac{1}{2}, J \frac{3}{2} M \rangle \pm | -2 \frac{1}{2} -\frac{1}{2}, J -\frac{1}{2} M \rangle \} \tag{7.37} \]

while the basis functions for the \(^2\Pi\) ground state are

\[ |^2\Pi_{1/2} J M p^\pm \rangle = \frac{1}{\sqrt{2}} \{ | 1 \frac{1}{2} -\frac{1}{2}, J \frac{1}{2} M \rangle \pm | -1 \frac{1}{2} \frac{1}{2}, J -\frac{1}{2} M \rangle \} \]

\[ |^2\Pi_{3/2} J M p^\pm \rangle = \frac{1}{\sqrt{2}} \{ | 1 \frac{1}{2} \frac{1}{2}, J \frac{3}{2} M \rangle \pm | -1 \frac{1}{2} -\frac{1}{2}, J -\frac{3}{2} M \rangle \} \tag{7.38} \]

In order to simulate \(M_0/A_0\), only the matrix for the \(^2\Pi\) ground state, containing rotational (Section 3.4.4), Zeeman (Section 3.4.5) and, if required, crystal-field (Section 5.4.1) matrix elements, needs to be diagonalised. Due to the principle of spectroscopic stability (Section 4.2), the excited-state Hund’s case-(a) basis functions can be used to calculate transition moments. The necessary Zeeman matrix elements are given in Tables 7.14 and 7.15.

Table 7.14: J-diagonal Zeeman matrix elements for the \(^2\Pi\) ground state of CH/SiH.

| \(\mathcal{X}_B\) | \(|^2\Pi_{1/2} J M p^\pm \rangle\) | \(|^2\Pi_{3/2} J M p^\pm \rangle\) |
|----------------|-------------------------------|-------------------------------|
| \(\langle ^2\Pi_{1/2} J M p^\pm |\mathcal{X}_B|^2\Pi_{3/2} J+1 M p^\pm \rangle\) | 0 | \(\frac{\mu_B B M}{J (J+1)} \{ J (J+1) - \frac{3}{2} \}^{1/2}\) |
| \(\langle ^2\Pi_{3/2} J M p^\pm |\mathcal{X}_B|^2\Pi_{1/2} J+1 M p^\pm \rangle\) | \(\frac{\mu_B B M}{J (J+1)} \{ J (J+1) - \frac{3}{2} \}^{1/2}\) | \(\frac{3 \mu_B B M}{J (J+1)}\) |

Table 7.15: Non-J-diagonal Zeeman matrix elements for the \(^2\Pi\) ground state of CH/SiH.

| \(\langle ^2\Pi_{3/2} J M p^\pm |\mathcal{X}_B|^2\Pi_{3/2} J+1 M p^\pm \rangle\) | \(2 \frac{\mu_B B}{J+1} \frac{(J+\frac{3}{2}) (J+\frac{3}{2}) (J+1-M) (J+1+M)}{(2J+1) (2J+3)} \) |
| \(\langle ^2\Pi_{1/2} J M p^\pm |\mathcal{X}_B|^2\Pi_{3/2} J+1 M p^\pm \rangle\) | \(- \frac{\mu_B B}{J+1} \frac{(J+\frac{3}{2}) (J+\frac{3}{2}) (J+1-M) (J+1+M)}{(2J+1) (2J+3)} \) |
| \(\langle ^2\Pi_{3/2} J M p^\pm |\mathcal{X}_B|^2\Pi_{1/2} J+1 M p^\pm \rangle\) | \( \frac{\mu_B B}{J+1} \frac{(J+\frac{3}{2}) (J-\frac{3}{2}) (J+1-M) (J+1+M)}{(2J+1) (2J+3)} \) |

A Fortran computer program called CHDIAG.F was utilised to obtain the eigenfunctions and eigenvalues for CH using a sufficiently large basis set of Hund’s case-(a) functions. Gas-phase molecular parameters were used: \(A_\pi = 31.8 \text{ cm}^{-1}\) and \(B_{\nu_0}(X^2^\Pi) = 14.2082 \text{ cm}^{-1}\). The program calculates line strengths (Section 3.4.6) at any given temperature or magnetic-field strength, for left and right circularly
polarised radiation, between allowed rotational levels, weighted by the population factors of the ground levels. The average line strength gives $A_0$, whereas $M_0$ is the difference of lcp and rcp line strengths. A plot of $M_0/A_0$ against $1/kT$ for the $A^2\Delta \leftarrow X^2\Pi$ transition of free-rotor CH is given in Figure 7.23. The moment ratios for the $B^{2}\Sigma^{-} \leftarrow X^{2}\Pi$ and $C^{2}\Sigma^{+} \leftarrow X^{2}\Pi$ transitions are identical, and simply the negative of Figure 7.23. This program has not yet been extended to simulate absorption and MCD spectra, as has been done for NH in a later chapter (Chapter 8), due to time constraints.

![Figure 7.23](image)

**Figure 7.23:** Temperature-dependence simulations for the moment ratio $M_0/A_0$ as a function of $1/kT$ for the $A^2\Delta \leftarrow X^2\Pi$ transition of free-rotor CH. The moment ratios for the $B^{2}\Sigma^{-} \leftarrow X^{2}\Pi$ and $C^{2}\Sigma^{+} \leftarrow X^{2}\Pi$ transitions are the negative of those in the figure.

The program CHDIAG.F can not yet be used to accurately fit the hindered-rotor model to the experimental data, with the possibility of obtaining a different value for $A_{\pi}$ than the SO-CF model, until the non-linear least-squares fitting program associated with MAGPI has been converted from BASIC into Fortran. However, the program is capable of calculating $M_0/A_0$ ratios for a particular barrier parameter $K$, defined in Eqs. (5.20) and (5.21), using a fourth-order octahedral potential. To illustrate the promise of this model, it was found that by using the $A_{\pi}$ value obtained from the SO-CF model for CH/Kr and a value of $K = -267 \text{ cm}^{-1}$, plots of $M_0/A_0$ against $1/kT$ and $\mu_B B$ (Figures 1.24 and 1.25) exhibit similar trends to the CH/Kr plots in Figures 7.16 – 7.22. In particular, the simulated plots indicate that, at the lowest temperatures, the magnetic-field saturation of the positive $C$ terms is gradually overpowered by the negative $B$ terms whose magnitude increase with increasing field.
This situation is clearly observed in the experimental data of Figures 7.16 – 7.18. The major differences are that the strength of the $\beta$ terms compared to the $\epsilon$ terms is larger in the simulated moments than measured experimentally for CH/Kr, and that the field corresponding to the maximum $M_0/A_0$ increases with decreasing temperature whereas the experimental data show the opposite trend.

Setting aside this difference, the negative sign of $K$ indicates that the fourth-order octahedral potential is attractive and that the energy minimum occurs when CH is oriented along the direction of nearest noble-gas neighbours. Furthermore, when $K$ is positive or more strongly negative, the moment ratios become negative and the agreement with experiment is lost. It is important to note that the utilisation of the hindered-rotor model in this way assumes that the reduction in SOC constant is entirely mechanical in nature and that there is no overlap between noble-gas atomic and CH molecular orbitals. If there is appreciable overlap, it will be necessary to extend the hindered-rotor model by antisymmetrising the product of the noble-gas and molecular electronic wavefunctions.

It is essential that quantum-mechanical calculations be performed to investigate the CH-NG interaction in detail. Although the hindered-rotor model is promising, the extra information that would be provided by a quantum-mechanical calculation is essential, however it is beyond the scope of this investigation.

![Figure 7.24](image_url)

**Figure 7.24:** Magnetic-field-dependence simulations for the moment ratio $M_0/A_0$ as a function of $\mu_B B$ for the $A^2\Delta \leftarrow X^2\Pi$ transition of hindered-rotor CH with barrier parameter $K = -267$ cm$^{-1}$. 

7-34
Methylidyne ($CH$) and Silyldyne ($SiH$)

![Figure 7.25: Temperature-dependence simulations for the moment ratio $M_0/A_0$ as a function of $1/kT$ for the $A^2\Delta \leftarrow X^2\Pi$ transition of hindered-rotor CH with barrier parameter $K = -267 \text{ cm}^{-1}$.

7.6 Conclusions

Absorption and temperature- and magnetic-field-dependent MCD spectra have been obtained for the $A^2\Delta \leftarrow X^2\Pi$, $B^2\Sigma^- \leftarrow X^2\Pi$ and $C^2\Sigma^+ \leftarrow X^2\Pi$ transitions of CH/Kr. The MCD spectra are similar to those reported by Langford$^{1,2}$ for CH/Ar, however the $C$ terms are weaker and the $C$ term associated with the $A^2\Delta \leftarrow X^2\Pi$ transition is more distinct.

Although $M_0/A_0$ plots for CH/Kr clearly indicate the presence of significant $C$ terms, due to their characteristic temperature and magnetic-field dependence, they also show the existence of strong $B$ terms of the opposite sign to the $C$ terms, exactly as predicted from the SO-CF model.

Using a randomly oriented SO-CF model, the SOC constant ($A_\pi$) for the $X^2\Pi$ term of CH/Kr was found to be $10.9 \pm 0.7 \text{ cm}^{-1}$ and the crystal-field parameter ($V_\pi$) was found to be $45 \pm 6 \text{ cm}^{-1}$. The other two transitions have poor S/N in their MCD spectra, resulting in substantially poorer fits. The decrease in $A_\pi$ from the value of $21 \pm 1 \text{ cm}^{-1}$ for CH/Ar is attributed to the external heavy-atom effect.

A hindered-rotor model incorporating an attractive potential barrier to rotation provides a qualitative agreement with the experimental results for CH/Kr, however this model needs further refinement to give a completely accurate agreement within experimental error.
7.7 References

8 Imidogen \((\text{NH})\) and Phosphinidene \((\text{PH})\)

The spectroscopic investigations of imidogen \((\text{NH})\) and phosphinidene \((\text{PH})\) in this thesis involve the spectroscopically allowed transitions \(A^3\Pi \leftarrow X^3\Sigma^-\) arising from \(\pi \leftarrow \sigma\) excitations (Table 3.4), where the \(\pi\) orbitals are essentially non-bonding valence \(p_{\pm 1}\) orbitals of the \(N/P\) atom and the \(\sigma\) orbitals are admixtures mainly of the valence \(p_0\) orbitals of \(N/P\) with the \(1s\) orbital of the \(H\) atom (Figure 3.1). Since the two radicals are effectively isoelectronic, they can be treated together.

The states of the radicals are represented by SO wavefunctions, which were derived in Chapter 3 and are summarised in Table 8.1.

| \([2\Sigma^+]|A|\Sigma\Omega\) | Normalised Slater determinants |
|-------------------------------|--------------------------------|
| \(X^3\Sigma_0^- 0\)           | \(-\frac{1}{\sqrt{2}}\{0^+ 0^+ -1^+ 1^-\} + |0^- 0^+ -1^- 1^+\}\) |
| \(X^3\Sigma_1^- \pm 1\)       | \(\mp |0^- 0^+ -1^\pm 1^\pm\}\) |
| \(a^1\Delta_2 \pm 2\)         | \(- |0^- 0^+ \pm 1^- \pm 1^+\}\) |
| \(b^1\Sigma_0^- 0\)           | \(\frac{1}{\sqrt{2}}\{0^+ 0^+ -1^+ 1^-\} - |0^- 0^+ -1^- 1^+\}\) |
| \(A^3\Pi_0\pm 0\)             | \(-\frac{1}{\sqrt{2}}\{0^+ -1^- -1^+ 1^-\} \pm |0^- -1^- -1^- 1^+\}\) |
| \(A^3\Pi_1 \pm 1\)            | \(\mp \frac{1}{\sqrt{2}}\{0^\pm -1^\mp -1^\pm 1^\pm\} + |0^\pm -1^\mp \pm 1^\pm 1^\mp\}\) |
| \(A^3\Pi_2 \pm 2\)            | \(- |0^\pm -1^\mp \pm 1^\pm 1^\mp\}\) |
| \(c^1\Pi_1 \pm 1\)            | \(\mp \frac{1}{\sqrt{2}}\{0^\mp -1^\pm -1^\mp 1^\pm\} - |0^\mp -1^\pm \pm 1^\pm 1^\mp\}\) |

8.1 SO-CF Theory

8.1.1 SO-CF Wavefunctions

To construct the SO-CF wavefunctions, SO and CF matrix elements must first be derived using the methods in Section 3.3.5.

8.1.1.1 \(X^3\Sigma^-\) state

The \(X^3\Sigma^-\) state undergoes no first-order SO or CF splittings due to its orbital non-degeneracy, so this state is actually independent of the SO-CF model. However it does mix weakly with the nearby \(b^1\Sigma^+\) state due to higher order SOC. The relevant matrix element is
Imidogen (NH) and Phosphinidene (PH)

\[
\left\langle ^1\Sigma_0^+ \right| \mathcal{H}_{SO} \left| ^3\Sigma_0^- \right\rangle = 2A_\pi 
\]  
(8.1)

### 8.1.1.1 Spin-spin coupling

When a molecule contains two unpaired electrons with parallel spins \( S = 1 \), there is a zero-field splitting (ZFS) of the energy levels caused by spin-spin (SS) and higher-order spin-orbit coupling. This is particularly important in the \( X^3\Sigma^- \) state of NH and PH. The corresponding effective Hamiltonian is of the form

\[
\mathcal{H}_D = S \cdot D \cdot S
\]  
(8.2)

where \( D \) is the diagonalisable zero-field tensor comprising contributions \( D_{SO} \) and \( D_{SS} \). The former involves SO interactions with other electronic states whereas the later is due to intrastate interactions between the spin magnetic dipoles of the unpaired electrons.

The major non-zero contribution to the ZFS of \( X^3\Sigma^- \) from \( \mathcal{H}_{SO} \) results from mixing with the \( ^1\Sigma^+ \) state. From perturbation theory, and using Eq. (8.1)

\[
E_{SO} = \frac{\left\langle ^3\Sigma_0^- \right| \mathcal{H}_{SO} \left| ^1\Sigma_0^+ \right\rangle \left\langle ^1\Sigma_0^+ \right| \mathcal{H}_{SO} \left| ^3\Sigma_0^- \right\rangle}{E(3\Sigma_0^-) - E(1\Sigma_0^+)} = \frac{4A_\pi^2}{E(3\Sigma_0^-) - E(1\Sigma_0^+)}  
\]  
(8.3)

From the central expression of Eq. (8.3), one can see that this can be regarded as a diagonal interaction with an effective operator

\[
\frac{\left\langle ^3\Sigma_0^- \right| \mathcal{H}_{SO} \left| ^1\Sigma_0^+ \right\rangle \left\langle ^1\Sigma_0^+ \right| \mathcal{H}_{SO} \left| ^3\Sigma_0^- \right\rangle}{E(3\Sigma_0^-) - E(1\Sigma_0^+)}  
\]  
(8.4)

The contribution from \( \mathcal{H}_{SS} \) can be determined by firstly considering the classical Hamiltonian, \( \mathcal{H}_{\text{dip}} \), describing the interaction between two magnetic dipoles, which is given by

\[
\mathcal{H}_{\text{dip}} = \frac{\mu_1 \cdot \mu_2}{r^3} - \frac{3 (r \cdot \mu_1)(r \cdot \mu_2)}{r^5}  
\]  
(8.5)
where \( r \) is the distance between the dipoles. The quantum-mechanical operator is formed by the substitution \( \mu_i = g_e \mu_B s_i \), and rearranging to give

\[
\mathcal{K}_{SS} = \sum_p \sum_q D_{pq} S_p S_q = S \cdot D_{SS} \cdot S
\]  

(8.6)

where \( p, q = x, y, z \). The matrix elements in \( \mathcal{K}_{SS} \) are diagonal in the basis states of Table 8.1.

Since the SS and SO contributions associated with Eqs. (8.6) and (8.3) are both effectively diagonal, it is convenient to combine \( D_{SO} \) and \( D_{SS} \) into \( D \). The effective operator \( \mathcal{K}_D \) can then be rewritten as

\[
\mathcal{K}_D = D_{xx} S_x^2 + D_{yy} S_y^2 + D_{zz} S_z^2 = D \left( S_x^2 - \frac{1}{3} S^2 \right) + E \left( S_x^2 - S_y^2 \right)
\]  

(8.7)

where \( D = \frac{1}{2} D_{zz} \) and \( E = \frac{1}{2} (D_{xx} - D_{yy}) \). \( E \) is zero in the \( C_{ov} \) point group (because \( x \) and \( y \) are related by symmetry) and the effective spin-spin matrix elements for the \( X \ 3\Sigma^- \) state are those given in Table 8.2.

**Table 8.2: Spin-spin matrix elements for the \( X \ 3\Sigma^- \) state.**

| \( \mathcal{K}_{SS} \)        | \( |^3\Sigma_1^- \rangle - 1 \rangle \) | \( |^3\Sigma_0^- \rangle \) | \( |^3\Sigma_1^- \rangle + 1 \rangle \) |
|-------------------------------|----------------------------------------|-----------------------------|----------------------------------------|
| \( \langle ^3\Sigma_1^- - 1 \rangle \) | \( D/3 \)                               | 0                           | 0                                      |
| \( \langle ^3\Sigma_0^- \rangle \) | 0                                      | \( -2D/3 \)                 | 0                                      |
| \( \langle ^3\Sigma_1^- + 1 \rangle \) | 0                                      | 0                           | \( D/3 \)                              |

The major contribution to \( D \) for gas-phase NH arises from spin-spin coupling, which has been calculated, using \textit{ab initio} techniques\(^2\) to contribute 88% of the total ZFS (Table 8.3). This can be attributed largely to the spins being localised on the N atom, which increases the SS contribution, and the large energy difference (~21200 cm\(^{-1}\)) between the \( X \ 3\Sigma^- \) and \( b \ 1\Sigma^+ \) states which results in a small SO contribution. In the case of gas-phase PH, the major contribution arises from higher-order spin-orbit coupling effects, which have been calculated\(^2\) to contribute 91% of the total ZFS (Table 8.3). Here the spin is still largely localised on the large atom (P), however \( D_{SS} \) is reduced due to the expanded electron cloud, and \( D_{SO} \) is increased.
because the molecule is heavier.

Table 8.3: Calculated contributions to the ZFS of the \( X^{3\Sigma^-} \) states of gas-phase NH and PH.

<table>
<thead>
<tr>
<th>( X^{3\Sigma^-} )</th>
<th>( D_{\text{SS}} )</th>
<th>( D_{\text{SO}} )</th>
<th>( D_{\text{Calc}} )</th>
<th>( D_{\text{Exp}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH</td>
<td>1.624</td>
<td>0.224</td>
<td>1.848</td>
<td>1.67</td>
</tr>
<tr>
<td>PH</td>
<td>0.332</td>
<td>3.492</td>
<td>3.824</td>
<td>4.42</td>
</tr>
</tbody>
</table>

\( D_{\text{Calc}} = D_{\text{SS}} + D_{\text{SO}} \), all the tabulated values being taken from reference 2. Experimental values, \( D_{\text{Exp}} \), are taken from references 3 and 4 for NH and PH, respectively.

In the gas phase, the ZFSs of the various rotational levels are functions of \( D \) that also depend on the value of \( J \). As discussed in more detail in Section 8.5.1.1, these ZFSs can be substantially modified when the molecule is incorporated into a condensed phase. Of most concern in the discussion that follows is the ZFS of the lowest level of the \( X^{3\Sigma^-} \) term in a matrix. Following the notation employed by Weltner, the relevant splitting parameter is henceforth designated \( D' \).

8.1.1.2 A \( ^3\Pi \) state

Table 8.4 gives the SO and CF matrix elements for the \( A^{3\Pi} \) state of NH or PH in a noble-gas matrix. \( A_\pi \) is the empirical SO coupling constant and \( V_\pi \) is the one-electron reduced CF matrix element for a \( 1\pi \) electron in NH or a \( 2\pi \) electron in PH.

\[
A_\pi = \frac{1}{2} \langle \pi | \xi(r) | \pi \rangle \\
V_\pi = \langle \pi | V^2 | \pi \rangle
\] (8.8)

The treatment of the CF matrix elements is simplified if one uses a modified basis in which,

\[
| \frac{3}{2} \Pi_0 \mp 1 \pm 1 \rangle = \frac{1}{\sqrt{2}} \{ | \frac{3}{2} \Pi_0^+ 0 \rangle \pm | \frac{3}{2} \Pi_0^- 0 \rangle \} = -| 0^+ - 1^- \mp 1^+ \rangle
\] (8.9)

where the ket on the left-hand side now has the form \( | \frac{3}{2} \Pi_\Lambda \Lambda \rangle \). To remain consistent, all other basis kets will also be labelled using the same notation.
Table 8.4: SO and CF matrix elements for the $A^3\Pi$ state of NH/NG and PH/NG.

| $\mathcal{K}_{SO} + \mathcal{K}_{CF}$ | $|\hat{3}^3\Pi_0 +1 -1\rangle$ | $|\hat{3}^3\Pi_0 -1 +1\rangle$ | $|\hat{3}^3\Pi_1 -1 0\rangle$ | $|\hat{3}^3\Pi_1 +1 0\rangle$ | $|\hat{3}^3\Pi_2 -1 -1\rangle$ | $|\hat{3}^3\Pi_2 +1 +1\rangle$ |
|----------------------------------|----------------|----------------|----------------|----------------|----------------|----------------|
| $\langle \hat{3}^3\Pi_0 +1 -1|$ | $\alpha_{\pi}$ | 0 | 0 | 0 | 0 | $-\frac{1}{2} V_{\pi}$ |
| $\langle \hat{3}^3\Pi_0 -1 +1|$ | 0 | $\alpha_{\pi}$ | 0 | 0 | $-\frac{1}{2} V_{\pi}$ | 0 |
| $\langle \hat{3}^3\Pi_1 -1 0|$ | 0 | 0 | $\frac{1}{2} V_{\pi}$ | 0 | 0 | 0 |
| $\langle \hat{3}^3\Pi_1 +1 0|$ | 0 | 0 | $\frac{1}{2} V_{\pi}$ | 0 | 0 | 0 |
| $\langle \hat{3}^3\Pi_2 -1 -1|$ | 0 | $-\frac{1}{2} V_{\pi}$ | 0 | 0 | $-\alpha_{\pi}$ | 0 |
| $\langle \hat{3}^3\Pi_2 +1 +1|$ | $-\frac{1}{2} V_{\pi}$ | 0 | 0 | 0 | 0 | $-\alpha_{\pi}$ |

The $6 \times 6$ secular determinant formed from Table 8.4 can be factored into three $2 \times 2$ determinants. The kets $|\hat{3}^3\Pi_1 -1 0\rangle$ and $|\hat{3}^3\Pi_1 +1 0\rangle$ are mixed only by the CF, to give eigenstates separated by $V_{\pi};$

$$|\hat{3}^3\Pi_0 0\rangle = \frac{1}{\sqrt{2}} (|\hat{3}^3\Pi_1 1 0\rangle \pm |\hat{3}^3\Pi_1 -1 0\rangle)$$  \hspace{1cm} (8.10)

The SO-CF kets are labelled $^3\Pi_\pm$, which designate the lower and upper SO-CF levels, respectively; and 0 denotes the value of $\Sigma$. The remaining determinants give the SO-CF eigenfunctions and eigenvalues corresponding to the $\Sigma = \pm 1$ states of the $^3\Pi$ term;

$$|\hat{3}^3\Pi_\pm \pm 1\rangle = \alpha |\hat{3}^3\Pi_2 \pm 1 \pm 1\rangle + \beta |\hat{3}^3\Pi_0 \mp 1 \mp 1\rangle$$

$$|\hat{3}^3\Pi_\pm \mp 1\rangle = -\beta |\hat{3}^3\Pi_2 \pm 1 \pm 1\rangle + \alpha |\hat{3}^3\Pi_0 \mp 1 \mp 1\rangle$$  \hspace{1cm} (8.11)

The mixing coefficients are given by

$$\alpha = \sqrt{\frac{1 + \kappa}{2}}$$

$$\beta = \sqrt{\frac{1 - \kappa}{2}}$$  \hspace{1cm} (8.12)

where $\kappa$ is the orbital reduction factor;

$$\kappa = 2\alpha_{\pi} / \Delta \hspace{1cm} (0 \leq \kappa \leq 1)$$  \hspace{1cm} (8.13)
and $\Delta$ is the splitting between the $|^3\Pi_+\pm1\rangle$ and $|^3\Pi_-\pm1\rangle$ states;

$$\Delta = \sqrt{4A^2 + V^2} \quad (8.14)$$

It is worthwhile here to also introduce a crystal-field reduction factor, which is given by

$$\eta = \sqrt{1 - \kappa^2} = V/\Delta \quad (0 \leq \eta \leq 1) \quad (8.15)$$

Note that as $V$ tends to zero (and $\kappa$ tends to 1), the wavefunctions in Eq. (8.11) reduce to the SO wavefunctions in Table 8.1 and Eq. (8.9).

The incremental effects of the various effects on the state energies of the NH/NG and PH/NG systems are illustrated diagrammatically in Figure 8.1.

### 8.1.2 Zeeman Matrix Elements

This section gives the angular momentum matrix elements for the relevant states of NH and PH. These are simply related to the Zeeman matrix elements, as outlined in Section 2.9.4. For the purposes of a non-rotating diatomic molecule trapped in a matrix, $g_x = g_y = g_z$.

#### 8.1.2.1 $X^3\Sigma^-$ state

Although the $X^3\Sigma^-$ state has no orbital angular momentum, there is a non-zero spin magnetic dipole that can interact with a magnetic field to give a Zeeman splitting. Table 8.5 gives the relevant angular momentum matrix elements.

<table>
<thead>
<tr>
<th>$L_z + g_e S_z$</th>
<th>$^3\Sigma^-_{-1}$</th>
<th>$^3\Sigma^-_{0}$</th>
<th>$^3\Sigma^-_{+1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^3\Sigma^-_{-1}$</td>
<td>$-g_e$</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$^3\Sigma^-_{0}$</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$^3\Sigma^-_{+1}$</td>
<td>0</td>
<td>0</td>
<td>$g_e$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$L_x + g_e S_x$</th>
<th>$^3\Sigma^-_{-1}$</th>
<th>$^3\Sigma^-_{0}$</th>
<th>$^3\Sigma^-_{+1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^3\Sigma^-_{-1}$</td>
<td>0</td>
<td>$-g_e \sqrt{2}$</td>
<td>0</td>
</tr>
<tr>
<td>$^3\Sigma^-_{0}$</td>
<td>$-g_e \sqrt{2}$</td>
<td>0</td>
<td>$g_e \sqrt{2}$</td>
</tr>
<tr>
<td>$^3\Sigma^-_{+1}$</td>
<td>0</td>
<td>$g_e \sqrt{2}$</td>
<td>0</td>
</tr>
</tbody>
</table>
Imidogen (NH) and Phosphinidene (PH)

Figure 8.1: Energy-level diagram, adapted from reference 5, showing the effects of SO, SS, CF and Zeeman interactions on the states of NH/NG and PH/NG.

8.1.2.2 $A^3\Pi$ state

Table 8.6 gives the angular momentum matrix elements for the $A^3\Pi$ SO-CF states of NH/NG and PH/NG. From Section 2.9.4, the matrix elements in Table 8.6 are related to the principal $g$ values according to the relationship

$$g_{||}^+ = 2 \langle \Pi_+ | L_z + g_\sigma S_z | \Pi_+ +1 \rangle = 2(g_\sigma \mp \kappa)$$

(8.16)

$g_{||}^+$ and $g_{||}^-$ are the $g$ values for the upper and lower SO-CF levels, respectively, when the molecular $z$ axis is aligned parallel to $B$. 

8-7
Table 8.6: Angular momentum matrix elements for the $A^3\Pi$ SO-CF states of NH/NG and PH/NG.

| $J_z + 2S_z$ | $|^3\Sigma \text{I}_-|\text{I}$ | $|^3\Sigma \text{I}_+|\text{I}$ | $|^3\Sigma \text{I}_0\text{I}$ | $|^3\Pi \text{I}_0\text{I}$ | $|^3\Pi \text{I}_-1\text{I}$ | $|^3\Pi \text{I}_+1\text{I}$ |
|--------------|----------------|----------------|----------------|----------------|----------------|----------------|
| $^3\Sigma \text{I}_-1\text{I}$ | $-(g_e + \kappa)$ | 0 | 0 | 0 | $\eta$ | 0 |
| $^3\Sigma \text{I}_+1\text{I}$ | 0 | $(g_e + \kappa)$ | 0 | 0 | 0 | $-\eta$ |
| $^3\Sigma \text{I}_0\text{I}$ | 0 | 0 | 0 | 1 | 0 | 0 |
| $^3\Pi \text{I}_0\text{I}$ | 0 | 0 | 1 | 0 | 0 | 0 |
| $^3\Pi \text{I}_-1\text{I}$ | $\eta$ | 0 | 0 | 0 | $-(g_e - \kappa)$ | 0 |
| $^3\Pi \text{I}_+1\text{I}$ | 0 | $-\eta$ | 0 | 0 | 0 | $(g_e - \kappa)$ |

8.1.3 Oriented SO-CF Wavefunctions

The SO-CF model essentially assumes that the NH/PH molecules are not rotating in the matrix. Within this model it is therefore necessary to determine a set of wavefunctions and eigenvalues for a particular orientation of the NH/PH internuclear axis ($z$) with respect to the direction of the magnetic field ($Z$). The result will then be extended to a randomly oriented ensemble by appropriate integration over the angle, $\theta$, between the magnetic field and the internuclear axis of the radical.

Laboratory-frame Zeeman matrix elements for the $X^3\Sigma^-$ state of NH/NG and PH/NG are calculated using Eq. (3.65) and Table 8.5. Table 8.7 gives these elements, added to those arising from ZFS.

Table 8.7: ZFS and Zeeman Hamiltonian matrix elements for the $X^3\Sigma^-$ state of NH/NG and PH/NG.

| $\mathcal{K}_B + \mathcal{K}_D$ | $|^3\Sigma \text{I}_-1\text{I}$ | $|^3\Sigma \text{I}_0\text{I}$ | $|^3\Sigma \text{I}_+1\text{I}$ |
|----------------|----------------|----------------|----------------|
| $^3\Sigma \text{I}_-1\text{I}$ | $-g_e \cos \theta \mu_B B + D'/3$ | $-\sqrt{2}g_e \sin \theta \mu_B B$ | 0 |
| $^3\Sigma \text{I}_0\text{I}$ | $-\sqrt{2}g_e \sin \theta \mu_B B$ | $-2D'/3$ | $\sqrt{2}g_e \sin \theta \mu_B B$ |
| $^3\Sigma \text{I}_+1\text{I}$ | 0 | $\sqrt{2}g_e \sin \theta \mu_B B$ | $g_e \cos \theta \mu_B B + D'/3$ |
The resulting eigenfunctions have the general form

$$|^{3}\Sigma^{-} i\rangle = \sum_{j} C_{\Sigma,i} |^{3}\Sigma^{-} \Sigma\rangle$$  \hspace{1cm} (8.17)

where the mixing coefficients $C_{\Sigma,i}$ depend on $D', B$, and $\theta$. The indices $i = 1, 2, 3$ label the eigenfunctions in order of ascending energy, and each $|^{3}\Sigma^{-} i\rangle$ has energy $E_i$.

Laboratory-frame Zeeman matrix elements for the $A\ 3\Pi$ SO-CF states of NH/NG and PH/NG are calculated in a similar manner to those for the $X\ 3\Sigma^{-}$ state. Table 8.8 gives these elements. After adding the appropriate SO and CF contributions and diagonalising, final eigenstates and eigenvalues for the $3\Sigma$ term are obtained. The resulting energy levels are represented pictorially in Figure 8.1.

| $\Sigma_B$ | $|^{3}\Pi_{-1}\rangle$ | $|^{3}\Pi_{+1}\rangle$ | $|^{3}\Pi_{0}\rangle$ | $|^{3}\Pi_{0}\rangle$ | $|^{3}\Pi_{+1}\rangle$ | $|^{3}\Pi_{-1}\rangle$ | $|^{3}\Pi_{+1}\rangle$
<table>
<thead>
<tr>
<th></th>
<th></th>
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<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{3}\Pi_{-1}$</td>
<td>$-C_{g</td>
<td></td>
<td>}^{-}$</td>
<td>0</td>
<td>$S_{g\epsilon}(\alpha + \beta)$</td>
<td>$-S_{g\epsilon}(\alpha - \beta)$</td>
<td>$2C \eta$</td>
</tr>
<tr>
<td>$^{3}\Pi_{+1}$</td>
<td>0</td>
<td>$C_{g</td>
<td></td>
<td>}^{-}$</td>
<td>$S_{g\epsilon}(\alpha + \beta)$</td>
<td>$S_{g\epsilon}(\alpha - \beta)$</td>
<td>0</td>
</tr>
<tr>
<td>$^{3}\Pi_{0}$</td>
<td>$S_{g\epsilon}(\alpha + \beta)$</td>
<td>$S_{g\epsilon}(\alpha + \beta)$</td>
<td>0</td>
<td>$2C$</td>
<td>$S_{g\epsilon}(\alpha - \beta)$</td>
<td>$S_{g\epsilon}(\alpha - \beta)$</td>
<td></td>
</tr>
<tr>
<td>$^{3}\Pi_{+0}$</td>
<td>$-S_{g\epsilon}(\alpha - \beta)$</td>
<td>$S_{g\epsilon}(\alpha - \beta)$</td>
<td>0</td>
<td>$2C$</td>
<td>0</td>
<td>$S_{g\epsilon}(\alpha + \beta)$</td>
<td>$-S_{g\epsilon}(\alpha + \beta)$</td>
</tr>
<tr>
<td>$^{3}\Pi_{-1}$</td>
<td>$2C \eta$</td>
<td>0</td>
<td>$S_{g\epsilon}(\alpha - \beta)$</td>
<td>$S_{g\epsilon}(\alpha + \beta)$</td>
<td>$-C_{g</td>
<td></td>
<td>}^{+}$</td>
</tr>
<tr>
<td>$^{3}\Pi_{+1}$</td>
<td>0</td>
<td>$-2C \eta$</td>
<td>$S_{g\epsilon}(\alpha - \beta)$</td>
<td>$S_{g\epsilon}(\alpha + \beta)$</td>
<td>0</td>
<td>$C_{g</td>
<td></td>
</tr>
</tbody>
</table>

$C = \cos \theta \mu_0 B/2$; $S = \sin \theta \mu_0 B/2$.

### 8.1.4 Transition Moments

Transition moments for $A\ 3\Pi \leftarrow X\ 3\Sigma^{-}$ are evaluated using the Wigner-Eckart theorem (Section 2.8). The principle of spectroscopic stability is used in choosing excited-state basis functions in the SO basis (see next section). $\mathcal{M}$ is the one-electron reduced transition moment for the orbital excitation $\pi \leftarrow \sigma$,

$$\mathcal{M} = \langle \pi || m^{\dagger} || \sigma \rangle$$  \hspace{1cm} (8.18)

The applicable transition matrix elements are
Imidogen (NH) and Phosphinidene (PH)

\[
\langle \tilde{3} \Pi_1 \pm 1 \mid m_{\pm 1} \mid \tilde{3} \Sigma_0 \pm 1 \rangle = \langle \tilde{3} \Pi_2 \pm 1 \mid m_{\pm 1} \mid \tilde{3} \Sigma_1 \pm 1 \rangle = -\langle \tilde{3} \Pi_0 \mp 1 \mid m_{\pm 1} \mid \tilde{3} \Sigma_1 \pm 1 \rangle = \frac{\alpha \mathcal{M}}{\sqrt{2}}
\]  

Table 8.9: Transition moments for the \( \tilde{3} \Pi_1 \leftrightarrow \tilde{3} \Sigma \) transition of NH/NG and PH/NG.

<table>
<thead>
<tr>
<th>( m_{\pm 1} )</th>
<th>( \tilde{3} \Sigma_{1-1} )</th>
<th>( \tilde{3} \Sigma_{00} )</th>
<th>( \tilde{3} \Sigma_{11} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \langle \tilde{3} \Pi_1 \pm 1 \rangle )</td>
<td>(-\frac{\sqrt{2} \beta \mathcal{M}}{2})</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>( \langle \tilde{3} \Pi_1 \mp 1 \rangle )</td>
<td>0</td>
<td>0</td>
<td>( \frac{\mathcal{M}}{2} )</td>
</tr>
<tr>
<td>( \langle \tilde{3} \Pi_1 \pm 0 \rangle )</td>
<td>0</td>
<td>( \frac{\mathcal{M}}{2} )</td>
<td>0</td>
</tr>
<tr>
<td>( \langle \tilde{3} \Pi_1 \mp 0 \rangle )</td>
<td>( \pm \frac{\sqrt{2} \alpha \mathcal{M}}{2})</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>( \langle \tilde{3} \Pi_1 \pm 1 \rangle )</td>
<td>( \pm \frac{\sqrt{2} \beta \mathcal{M}}{2})</td>
<td>0</td>
<td>(-\frac{\sqrt{2} \beta \mathcal{M}}{2})</td>
</tr>
</tbody>
</table>

8.1.5 Moment Analysis

The analysis that follows involves the taking of ratios of various MCD and absorption moments (Section 4.2). For this purpose, theoretical moment expressions need to be derived. Since the MCD spectra of NH/NG and PH/NG consist of temperature-dependent pseudo-\( \mathcal{O} \) terms (essentially two oppositely signed \( \mathcal{C} \) terms which give the appearance of an \( \mathcal{O} \) term), the MCD data must be analysed using first moments \( M_1 \), which can be expressed as a sum of the zeroth moments \( B_0(i) \) and \( C_0(i) \) for each component transition, \( i \) (Eq. (4.31)). \( B_0 \) will be treated by the application of non-degenerate perturbation theory. The following analysis employs the ratio \( M_1/A_0 \).

Since zeroth and first moments obtained by integrating over an entire band system are invariant to unitary transformations of the excited-state basis (Section 4.2), they provide no information on the CF splitting of the \( A \tilde{3} \Pi \) term. Such information can only be determined from spectral simulations (if at all – see Section 8.5.2.1).

8.1.5.1 \( A_0 \) and \( C_0 \)

Using Eqs. (4.15) and (4.16), the expressions for \( A_0^\theta \) and \( C_0^\theta \) associated with transitions originating from the Zeeman eigenstates \( i \) within the \( \tilde{3} \Sigma^- \) manifold, are
given by

\[ A_{0}^{\theta}(3\Pi_{\pm} \Sigma \leftarrow 3\Sigma^{-} i) = \frac{\gamma(1 + \cos^{2}\theta)}{4} P_{i} |C_{\Sigma_{i}}|^{2} \left( |\langle 3\Pi_{\pm} \Sigma |m_{+1}|3\Sigma^{-} \Sigma \rangle|^{2} + |\langle 3\Pi_{\pm} \Sigma |m_{-1}|3\Sigma^{-} \Sigma \rangle|^{2} \right) \]  
(8.20)

\[ C_{0}^{\theta}(3\Pi_{\pm} \Sigma \leftarrow 3\Sigma^{-} i) = \gamma \cos \theta P_{i} |C_{\Sigma_{i}}|^{2} \left( |\langle 3\Pi_{\pm} \Sigma |m_{+1}|3\Sigma^{-} \Sigma \rangle|^{2} - |\langle 3\Pi_{\pm} \Sigma |m_{-1}|3\Sigma^{-} \Sigma \rangle|^{2} \right) \]  
(8.21)

The superscripts \( \theta \) indicate that the moments pertain to a particular orientation of the molecule with respect to the field axis (Z). The population factors \( P_{i} \) depend on the relative populations of the \( 3\Sigma^{-} \) levels.

\[ P_{i} = \frac{1}{Q} \exp(-E_{i}/kT) \]  
(8.22)

where \( Q \) is the electronic partition function

\[ Q = \sum_{i} \exp(-E_{i}/kT) \]  
(8.23)

The moment expressions \( A_{0}^{\theta} \) and \( C_{0}^{\theta} \) for individual transitions are given in Table 8.10. It is worth noting that the total absorption moment summed over all transitions, \( A_{0}^{\theta} \), is independent of temperature, magnetic-field strength, and ZFS, whereas the total \( C_{0}^{\theta} \) is zero.

### 8.1.5.2 B_{\theta}

The \( B \)-term contribution to \( M_{l} \) is determined by treating the magnetic-field-induced mixing of terms within the \( A^{3}\Pi \) manifold by perturbation theory. The assumption that these are the only important off-diagonal Zeeman interactions is reasonable because both the \( X^{3}\Sigma^{-} \) and \( A^{3}\Pi \) terms are well separated from other terms involving allowed transitions and the effects of any ground-state mixing are contained in the numerical diagonalisation process. \( B_{0}^{\theta} \) is given by
Imidogen (NH) and Phosphinidene (PH)

\[ B_0^\theta(3\Sigma \Sigma \leftarrow 3\Sigma^{-i}) = -2\gamma \cos \theta P_i \sum_{\sigma, \Sigma, \sigma, \Sigma} \left\langle \frac{3\Sigma_{\sigma} \Sigma | 3\Sigma^{-i} \rangle}{E(3\Sigma_{\sigma} \Sigma) - E(3\Sigma^{-i})} \sum_{m_{+1}} \left| \langle 3\Sigma_{\sigma} \Sigma | m_{+1} \rangle \left| 3\Sigma^{-i} \rangle \right|^2 \right. \]

\[ C_{\Sigma, i}^\theta \left( \left| \langle 3\Sigma_{\sigma} \Sigma | m_{+1} \rangle \left| 3\Sigma^{-i} \rangle \right|^2 \left( \langle 3\Pi_{\sigma} \Sigma | m_{+1} \rangle \left| 3\Sigma^{-i} \rangle \right|^2 \right)^* - \left( \langle 3\Pi_{\sigma} \Sigma | m_{-1} \rangle \left| 3\Sigma^{-i} \rangle \right|^2 \left( \langle 3\Pi_{\sigma} \Sigma | m_{-1} \rangle \left| 3\Sigma^{-i} \rangle \right|^2 \right)^* \right) \] (8.24)

\( \Re \) indicates the real part of everything to the right, and \( \sigma = \pm \) designates the upper and lower excited-state SO-CF levels. The moment expressions \( B_0^\theta \) for individual transitions are given in Table 8.10. It is worth noting that the total \( B_0^\theta \) is zero.

<table>
<thead>
<tr>
<th>Table 8.10: Moment expressions for individual (</th>
<th>3\Pi_{\sigma} \Sigma \rangle \leftarrow</th>
<th>3\Sigma^{-i} \rangle ) transitions of NH/NG and PH/NG.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Transition</td>
<td>( A_0^\theta )</td>
<td>( C_0^\theta )</td>
</tr>
<tr>
<td>(</td>
<td>3\Pi_+ \pm 1 \rangle \leftarrow</td>
<td>3\Sigma^{-i} \rangle )</td>
</tr>
<tr>
<td>(</td>
<td>3\Pi_0 \rangle \leftarrow</td>
<td>3\Sigma^{-i} \rangle )</td>
</tr>
<tr>
<td>(</td>
<td>3\Pi_0 \pm 1 \rangle \leftarrow</td>
<td>3\Sigma^{-i} \rangle )</td>
</tr>
<tr>
<td>( A \left</td>
<td>3\Pi \leftarrow</td>
<td>3\Sigma^{-} \right]\rangle )</td>
</tr>
</tbody>
</table>

\( K_A = \gamma \left| \mathcal{M} \right|^2 (1 + \cos^2 \theta)/8 \); \( K_M = \gamma \left| \mathcal{M} \right|^2 \cos \theta / 2. \)

8.1.5.3 Moment ratios

Using Eq. (4.31), an overall expression for \( M_1^\theta \) can be derived.

\[ M_1^\theta = \sum_{\sigma, \Sigma, i} \left( C_0^\theta \left| 3\Pi_{\sigma} \Sigma \leftarrow | 3\Sigma^{-i} \rangle \right| \Delta E_B \left| 3\Pi_{\sigma} \Sigma \leftarrow | 3\Sigma^{-i} \rangle \right| \right) \]

\[ + B_0^\theta \left| 3\Pi_{\sigma} \Sigma \leftarrow | 3\Sigma^{-i} \rangle \right| \Delta E_0 \left| 3\Pi_{\sigma} \Sigma \leftarrow | 3\Sigma^{-i} \rangle \right| \] (8.25)

where \( \Delta E_B \) and \( \Delta E_0 \) are, respectively, the transition energies in the presence and
Imidogen (NH) and Phosphinidene (PH)

absence of the magnetic field. After inserting the derived expressions from Table 8.10 into Eq. (8.25), one obtains

\[
\begin{align*}
M_i^0 \left( A^3 \Pi \leftarrow X^3 \Sigma \right) &= \gamma \cos \theta |\mathcal{M}|^2 \left[ \mu_0 B \cos \theta + 
\frac{1}{2} A_x \sum_i P_i \left( |C_{-1,i}|^2 - |C_{+1,i}|^2 \right) \right] 
\end{align*}
\]

(8.26)

In order to fit experimental data to the SO-CF theoretical model, \( M_i^0 \) and \( A_0^0 \) must be averaged over \( \theta \), as outlined in Section 4.2, before the ratio \( M_i/A_0 \) is taken.

\[
\begin{align*}
A_0 \left( A^3 \Pi \leftarrow X^3 \Sigma \right) &= \frac{1}{3} \gamma |\mathcal{M}|^2 \\
M_i \left( A^3 \Pi \leftarrow X^3 \Sigma \right) &= \gamma |\mathcal{M}|^2 \left[ \frac{1}{3} \mu_0 B + 
\frac{1}{2} A_x \int_{-1}^{1} \cos \theta \sum_i P_i \left( |C_{-1,i}|^2 - |C_{+1,i}|^2 \right) \cos \theta \right]
\end{align*}
\]

(8.27) (8.28)

The equation for the ratio \( M_i/A_0 \) is used to extract best-fit values for \( D' \) and \( A_x \) from the data.

\[
\begin{align*}
\frac{M_i \left( A^3 \Pi \leftarrow X^3 \Sigma \right)}{A_0 \left( A^3 \Pi \leftarrow X^3 \Sigma \right)} &= \mu_0 B + 
\frac{3}{2} A_x \int_{-1}^{1} \cos \theta \sum_i P_i \left( |C_{-1,i}|^2 - |C_{+1,i}|^2 \right) \cos \theta
\end{align*}
\]

(8.29)

Fits to the experimental saturation data (Section 8.4) are achieved using Eq. (8.29), where the integrals over \( \theta \) are evaluated numerically, and the parameters \( D' \) and \( A_x \) are varied by using a non-linear least-squares fitting program called ALLFIT.

8.2 Experimental

Preliminary matrix depositions were carried out using the He-refrigerator/electromagnet system described in Section 6.2.1. Matrices successfully investigated using the matrix-injection system are described in Table 8.11, along with
Imidogen (NH) and Phosphinidene (PH)

their deposition times. The matrix-injection system and the matrix-preparation
technique are described in Sections 6.2.2 and 6.1 respectively. Flow rates were ~2-3
mmol hr\(^{-1}\) and the sapphire window was held at ~20 K during deposition.

<table>
<thead>
<tr>
<th>Matrix</th>
<th>Deposition time (minutes)</th>
<th>Monochromator wavelength step (nm)</th>
<th>Number of chopper cycles</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH/Kr</td>
<td>60</td>
<td>0.05</td>
<td>40</td>
</tr>
<tr>
<td>NH/N(_2)</td>
<td>25</td>
<td>0.20</td>
<td>20</td>
</tr>
<tr>
<td>PH/Ar</td>
<td>41</td>
<td>0.10</td>
<td>20</td>
</tr>
<tr>
<td>PH/Kr</td>
<td>52</td>
<td>0.10</td>
<td>20</td>
</tr>
<tr>
<td>PH/Xe</td>
<td>60</td>
<td>0.10</td>
<td>20</td>
</tr>
</tbody>
</table>

All spectral data were gathered using the MOD4 spectrometer (Section 6.3)
in conjunction with a Xe-arc lamp, a 1180-groove/mm grating blazed at 500 nm, and
a Hamamatsu R-376 PMT. The monochromator slits were set to 300 \(\mu\)m (~0.24 nm
resolution), and a Corning 7-54 filter was used to remove stray visible light prior to
the sample. The number of chopper cycles per scan and wavelength step size are
given in Table 8.11.

8.3 Results

Spectral data for the \(A^3\Pi \leftrightarrow X^3\Sigma^-\) transitions of NH/Kr, NH/Xe, NH/N\(_2\),
PH/Ar, PH/Kr, and PH/Xe are presented in this section. The yields of PH/NG and
NH/N\(_2\) obtained by using the matrix-injection system were comparable to those
obtained using the refrigerator/electromagnet set-up. The quality of the spectra for
NH/Kr was severely worse than that obtained in trials, but was deemed good enough
for analysis. The yield of NH/Xe was the most adversely affected by the problems
with the matrix-injection system (Section 1.1), and no magnetic-field- and limited
temperature-dependent data could be obtained for this system.

The spectra that follow share a number of common features. The MCD
spectra have dispersion similar to that reported for NH/NG by Langford,\(^5,7\) Rose,\(^8\)
and Lund et al.\(^9\) Each comprises a pair of oppositely signed \(\varepsilon\) terms giving a (positive)
temperature-dependent pseudo-\(\varepsilon\) term, which exhibits saturation with respect to
(increasing) magnetic field and (decreasing) temperature.
Imidogen (NH) and Phosphinidene (PH)

As the atomic number of the noble-gas host atoms increases, there are two notable trends, which are quantified in the following section on moment analysis of the data. Firstly, the transitions exhibit red shifts, those for PH being larger than those for NH. These red shifts are in accord with previous observations for molecules trapped in noble-gas matrices\(^{10}\) (Section 5.2). Secondly, the bands become more diffuse and less structured, although, perhaps surprisingly, the overall bandwidth (as measured by the function \(2\sqrt{\Delta_2/\Delta_0}\) – see Section 4.2) does not change drastically. The bands for NH/N\(_2\) are at least three times broader than those for the NH/NG systems, suggesting the presence of much stronger guest-host interactions.

Note that \(E_0\) is the electronic energy of the lowest band feature, and is included to allow a more meaningful comparison with the transition wavenumbers in the gas-phase.

<table>
<thead>
<tr>
<th>Matrix</th>
<th>(E_0) / cm(^{-1})</th>
<th>(E) / cm(^{-1})</th>
<th>(2\sqrt{\Delta_2/\Delta_0}) / cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH/Ar</td>
<td>29620</td>
<td>29670</td>
<td>130</td>
</tr>
<tr>
<td>NH/Kr</td>
<td>29490</td>
<td>29550</td>
<td>130</td>
</tr>
<tr>
<td>NH/Xe</td>
<td>29420</td>
<td>29490</td>
<td>160</td>
</tr>
<tr>
<td>NH/N(_2)</td>
<td>29350</td>
<td>29710</td>
<td>500</td>
</tr>
<tr>
<td>PH/Ar</td>
<td>29000</td>
<td>29190</td>
<td>350</td>
</tr>
<tr>
<td>PH/Kr</td>
<td>28840</td>
<td>28980</td>
<td>360</td>
</tr>
<tr>
<td>PH/Xe</td>
<td>28500</td>
<td>28640</td>
<td>270</td>
</tr>
</tbody>
</table>

In most cases, weak temperature and magnetic-field dependence of the absorption spectra was observed, presumably due to thermal population of low-lying excited levels within the manifold of the ground electronic state. However, the relatively poor definition of structure within the band envelope, as well as limited temperature range at which investigations were possible (including the fact that bubbles in the liquid helium often precluded collection of useful data in the temperature range 4.2 – 2.2 K) prevented any definitive investigation of these phenomena.

### 8.3.1 Imidogen (NH)

Spectra were not measured for NH/Ar since data have been previously
Obtained for the system by Rose\textsuperscript{8} at the University of Virginia and (more comprehensively) by Langford in this laboratory.\textsuperscript{5,7} NH/N\textsubscript{2} was studied because of prior evidence\textsuperscript{11} that rotation of molecules usually does not occur in matrices, such as N\textsubscript{2}, with unsymmetrical trapping sites. It was hoped that this would provide insights into the purported free rotation of ground-state NH in rare-gas matrices.\textsuperscript{5,7,12,13}

\textbf{8.3.1.1 NH/Kr}

The quality of the NH/Kr matrices produced using the matrix-injection system (on two separate occasions) was very poor compared with the refrigerator/electromagnet set-up. The S/N is worse, and there is a steeply rising baseline due to the cloudiness of the matrix. Figure 8.2 gives a comparison of the absorption spectra for the $A^3\Pi \leftarrow X^3\Sigma^-$ transition in each case. A representative selection of magnetic-field- and temperature-dependent MCD spectra is shown in Figures 8.3 to 8.6.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure82.png}
\caption{Absorption spectra of the (0,0) band of the $A^3\Pi \leftarrow X^3\Sigma^-$ transition of NH/Kr using the matrix-injection system (top), and the refrigerator/electromagnet set-up (bottom). There is evidence of some temperature dependence at higher temperatures in the data obtained using the latter equipment.}
\end{figure}
Figure 8.3: Temperature-dependent MCD spectra (1 tesla) of the (0,0) band of the $^3\Pi \leftarrow X^3\Sigma^-$ transition of NH/Kr.

Figure 8.4: Magnetic-field-dependent MCD spectra (1.65 K) of the (0,0) band of the $^3\Pi \leftarrow X^3\Sigma^-$ transition of NH/Kr.
Imidogen (NH) and Phosphinidene (PH)

Figure 8.5: Magnetic-field-dependent MCD spectra (4.5 K) of the (0,0) band of the $A \ ^3\Pi \leftrightarrow \ X\ ^3\Sigma^-$ transition of NH/Kr.

Figure 8.6: Magnetic-field-dependent MCD spectra (10.5 K) of the (0,0) band of the $A \ ^3\Pi \leftrightarrow \ X\ ^3\Sigma^-$ transition of NH/Kr.
8.3.1.2 NH/Xe

NH/Xe was very easily prepared using the He-refrigerator/electromagnet system and has been successfully produced in reasonable yields by Rose at the University of Virginia using a matrix-injection system that is more primitive than the one in this laboratory. Frustratingly, however, a matrix failed to form on no fewer than ten attempts using the matrix-injection system. Therefore, this section contains only spectra obtained on the He-refrigerator/electromagnet system. The absorption and corresponding MCD of the (0,0) band of the $A^3\Pi \leftarrow X^3\Sigma^-$ transition of NH/Xe at 0.64 tesla and 11 K are given in Figure 8.7.

8.3.1.3 NH/N₂

The absorbance of the $A^3\Pi \leftarrow X^3\Sigma^-$ transition of NH/N₂ exhibited no temperature dependence and the spectra at all temperatures were therefore averaged to obtain better signal to noise. The result is shown in Figure 8.8 along with the temperature-dependent MCD (1.43 to 21.8 K at 1 T). As noted above, the spectra are much broader than the corresponding transitions in NH/NG. The temperature and magnetic-field dependencies of the MCD data are presented in Figures 8.8 to 8.11.
Imidogen (NH) and Phosphinidene (PH)

**Figure 8.8**: Absorption and temperature-dependent MCD spectra (1.00 T) of the (0,0) band of the $A^3\Pi \leftarrow X^3\Sigma^-$ transition of NH/N$_2$.

**Figure 8.9**: Magnetic-field-dependent MCD spectra (1.43 K) of the (0,0) band of the $A^3\Pi \leftarrow X^3\Sigma^-$ transition of NH/N$_2$. 

8-20
Figure 8.10: Magnetic-field-dependent MCD spectra (2.30 K) of the (0,0) band of the $A \ ^3\Pi \leftarrow X \ ^3\Sigma^-$ transition of NH/N₂.

Figure 8.11: Magnetic-field-dependent MCD spectra (10.2 K) of the (0,0) band of the $A \ ^3\Pi \leftarrow X \ ^3\Sigma^-$ transition of NH/N₂.
8.3.2 Phosphinidene (PH)

Minor temperature dependence was observed for the absorption spectra of PH/NG systems. But, as mentioned above, the details of this dependence were difficult to ascertain due to the absence of well-defined structure in the spectrum. This problem was exacerbated by a markedly sloped baseline, which was found to shift with changes of temperatures and magnetic field.

8.3.2.1 PH/Ar

The yield of PH/Ar produced on the matrix-injection system was much less than obtained using the refrigerator/electromagnet set-up. Figure 8.12 gives a comparison by way of the relative intensities in absorbance of the $A^3\Pi \leftarrow X^3\Sigma^-$ transition in both cases – note that the data for the matrix-injection system is amplified by a factor of four. The absorption spectrum has distinctive peaks at $\sim 29080$ and $29220$ cm$^{-1}$. A representative selection of magnetic-field- and temperature-dependent MCD spectra is given in Figures 8.13 to 8.19.

![Figure 8.12: Absorption spectra of the (0,0) band of the $A^3\Pi \leftarrow X^3\Sigma^-$ transition of PH/Ar using both the matrix-injection and refrigerator/electromagnet systems.](image-url)
Imidogen (NH) and Phosphinidene (PH)

Figure 8.13: Temperature-dependent MCD spectra (1.01 tesla) of the (0,0) band of the $A^3\Pi \leftrightarrow X^3\Sigma^-$ transition of PH/Ar.

Figure 8.14: Temperature-dependent MCD spectra (3.00 tesla) of the (0,0) band of the $A^3\Pi \leftrightarrow X^3\Sigma^-$ transition of PH/Ar.
Imidogen (NH) and Phosphinidene (PH)

Figure 8.15: Temperature-dependent MCD spectra (5.02 tesla) of the (0,0) band of the $A^3\Pi \leftrightarrow X^3\Sigma^-$ transition of PH/Ar.

Figure 8.16: Magnetic-field-dependent MCD spectra (1.7 K) of the (0,0) band of the $A^3\Pi \leftrightarrow X^3\Sigma^-$ transition of PH/Ar.
Imidogen (NH) and Phosphinidene (PH)

Figure 8.17: Magnetic-field-dependent MCD spectra (2.30 K) of the \((0,0)\) band of the \(A^3\Pi \leftarrow X^3\Sigma^-\) transition of PH/Ar.

![Magnetic-field-dependent MCD spectra](image1)

Figure 8.18: Magnetic-field-dependent MCD spectra (4.22 K) of the \((0,0)\) band of the \(A^3\Pi \leftarrow X^3\Sigma^-\) transition of PH/Ar.

![Magnetic-field-dependent MCD spectra](image2)
Imidogen (NH) and Phosphinidene (PH)

![Magnetic-field-dependent MCD spectra](image)

\[ \Delta A \]
\[ /10^{-3} \]
\[ \lambda \text{ (nm)} \]
\[ \Delta A \]
\[ /10^{-3} \]
\[ \lambda \text{ (nm)} \]
\[ \Delta A \]
\[ /10^{-3} \]
\[ \lambda \text{ (nm)} \]

**Figure 8.19:** Magnetic-field-dependent MCD spectra (9.9 K) of the (0,0) band of the \( A^3\Pi \leftarrow X^3\Sigma^- \) transition of PH/Ar.

### 8.3.2.2 PH/Kr

The yield of PH/Kr produced on the matrix-injection system was similar to that obtained using the refrigerator/electromagnet set-up. The \( A^3\Pi \leftarrow X^3\Sigma^- \) transition of PH/Kr is broader than, and shifted \( \sim 210 \text{ cm}^{-1} \) to the red of, the corresponding transition of PH/Ar. The absorption spectrum, which exhibits minor temperature and magnetic-field dependencies, is shown in Figure 8.20. A representative selection of magnetic-field- and temperature-dependent MCD spectra is given in Figures 8.21 to 8.27.
**Imidogen (NH) and Phosphinidene (PH)**

**Figure 8.20:** Absorption spectra of the (0,0) band of the \( A^3\Pi \leftarrow X^3\Sigma^- \) transition of PH/Kr using the matrix-injection system.

**Figure 8.21:** Temperature-dependent MCD spectra (1.00 tesla) of the (0,0) band of the \( A^3\Pi \leftarrow X^3\Sigma^- \) transition of PH/Kr.
Figure 8.22: Temperature-dependent MCD spectra (3.00 tesla) of the (0,0) band of the $A^3\Pi \leftarrow X^3\Sigma^-$ transition of PH/Kr.

Figure 8.23: Temperature-dependent MCD spectra (5.02 tesla) of the (0,0) band of the $A^3\Pi \leftarrow X^3\Sigma^-$ transition of PH/Kr.
Imidogen (NH) and Phosphinidene (PH)

**Figure 8.24:** Magnetic-field-dependent MCD spectra (1.71 K) of the (0,0) band of the $A^3\Pi \leftarrow X^3\Sigma^-$ transition of PH/Kr.

**Figure 8.25:** Magnetic-field-dependent MCD spectra (2.28 K) of the (0,0) band of the $A^3\Pi \leftarrow X^3\Sigma^-$ transition of PH/Kr.
Figure 8.26: Magnetic-field-dependent MCD spectra (4.22 K) of the (0,0) band of the $A^3\Pi \leftrightarrow X^3\Sigma^-$ transition of PH/Kr.

Figure 8.27: Magnetic-field-dependent MCD spectra (15.0 K) of the (0,0) band of the $A^3\Pi \leftrightarrow X^3\Sigma^-$ transition of PH/Kr.
8.3.2.3 PH/Xe

The yield of PH/Xe produced on the matrix-injection system was similar to that obtained using the refrigerator/electromagnet set-up. The $A \, ^3\Pi \leftarrow X \, ^3\Sigma^-$ transition of PH/Xe is broader than, and shifted $\sim 340$ cm$^{-1}$ to the red of, the corresponding transition of PH/Kr.

The absorption, which exhibits weak temperature and magnetic-field dependencies, is shown in Figure 8.28. A representative selection of MCD spectra is given in Figures 8.29 to 8.36.

![Figure 8.28: Absorption spectra of the (0,0) band of the $A \, ^3\Pi \leftarrow X \, ^3\Sigma^-$ transition of PH/Xe obtained using the matrix-injection system.](image-url)
Figure 8.29: Temperature-dependent MCD spectra (1.00 tesla) of the (0,0) band of the $^3\Pi \leftarrow X^3\Sigma^-$ transition of PH/Xe.

Figure 8.30: Temperature-dependent MCD spectra (3.00 tesla) of the (0,0) band of the $^3\Pi \leftarrow X^3\Sigma^-$ transition of PH/Xe.
Imidogen (NH) and Phosphinidene (PH)

Figure 8.31: Temperature-dependent MCD spectra (5.02 tesla) of the (0,0) band of the $A \ ^3\Pi \leftarrow X \ ^3\Sigma^-$ transition of PH/Xe.

Figure 8.32: Magnetic-field-dependent MCD spectra (1.43 K) of the (0,0) band of the $A \ ^3\Pi \leftarrow X \ ^3\Sigma^-$ transition of PH/Xe.
**Imidogen (NH) and Phosphinidene (PH)**

![Graph](image)

**Figure 8.33:** Magnetic-field-dependent MCD spectra (1.87 K) of the (0,0) band of the $A ^3\Pi \leftarrow X ^3\Sigma^-$ transition of PH/Xe.

![Graph](image)

**Figure 8.34:** Magnetic-field-dependent MCD spectra (2.97 K) of the (0,0) band of the $A ^3\Pi \leftarrow X ^3\Sigma^-$ transition of PH/Xe.
Figure 8.35: Magnetic-field-dependent MCD spectra (9.9 K) of the (0,0) band of the $A^3\Pi \leftarrow X^3\Sigma^-$ transition of PH/Xe.

Figure 8.36: Magnetic-field-dependent MCD spectra (27.8 K) of the (0,0) band of the $A^3\Pi \leftarrow X^3\Sigma^-$ transition of PH/Xe.
8.4 Moment Analysis

Band barycentres and bandwidths (Table 8.12) as well as zeroth absorption and first MCD (about the band barycentre) moments were obtained by numerical integration over the (0,0) band envelope of the $A^3\Pi \leftarrow X^3\Sigma^+$ transition of each system using the computer program MOMENT.

As alluded to in Section 8.3.1.1, the poor quality of the absorption data for NH/Kr obtained using the matrix-injection system made it difficult to obtain an accurate zeroth absorption moment and corresponding band barycentre. The barycentre used in moment analysis of the MCD was obtained from data collected on the He-refrigerator system.

Plots of the moment ratios $M_j/A_0$ against $1/kT$ and $\mu_0B$ are given below, as indexed by Table 8.13. These plots indicate strong saturation behaviour, especially with decreasing temperature but only slightly less marked with increasing magnetic field.

Table 8.13: Figure index for moment analysis plots.

<table>
<thead>
<tr>
<th>Dependence</th>
<th>NH/Kr</th>
<th>NH/Xe</th>
<th>NH/N₂</th>
<th>PH/Ar</th>
<th>PH/Kr</th>
<th>PH/Xe</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M_j/A_0$ vs $1/kT$</td>
<td>8.37</td>
<td>–</td>
<td>8.39</td>
<td>8.41</td>
<td>8.43</td>
<td>8.45</td>
</tr>
<tr>
<td>$M_j/A_0$ vs $\mu_0B$</td>
<td>8.38</td>
<td>–</td>
<td>8.40</td>
<td>8.42</td>
<td>8.44</td>
<td>8.46</td>
</tr>
</tbody>
</table>

8.4.1 NH/Kr

Figure 8.37: Temperature-dependence of the moment ratio $M_j/A_0$ as a function of $1/kT$ for NH/Kr $A^3\Pi \leftarrow X^3\Sigma^+$. The curves are best fits to all the data using the randomly oriented SO-CF model, with $A_\pi = 21 \text{ cm}^{-1}$ and $D' = 0 \text{ cm}^{-1}$.
8.4.2

**NH/N\(_2\)**

Figure 8.39: Temperature-dependence of the moment ratio \(\frac{M_1}{A_0}\) as a function of \(1/kT\) for NH/N\(_2\) \(A^3\Pi \leftarrow X^3\Sigma^-\). The curves are best fits to all the data using the randomly oriented SO-CF model, with \(A_s = 43.2\ \text{cm}^{-1}\) and \(D' = 0.61\ \text{cm}^{-1}\).
Imidogen (NH) and Phosphinidene (PH)

Figure 8.40: Magnetic-field-dependence data for the moment ratio \( M/I/A_0 \) as a function of \( \mu_B B \) for NH/N\(_2\) \( \Delta \Pi \leftarrow X \Sigma^+ \). The curves are best fits to all the data using the randomly oriented SO-CF model, with \( A_x = 43.2 \text{ cm}^{-1} \) and \( D' = 0.61 \text{ cm}^{-1} \).

8.4.3 PH/Ar

Figure 8.41: Temperature-dependence of the moment ratio \( M/I/A_0 \) as a function of \( 1/kT \) for PH/Ar \( \Delta \Pi \leftarrow X \Sigma^+ \). The curves are best fits to all the data using the randomly oriented SO-CF model, with \( A_x = 192 \text{ cm}^{-1} \) and \( D' = 1.62 \text{ cm}^{-1} \).
Imidogen (NH) and Phosphinidene (PH)

Figure 8.42: Magnetic-field-dependence data for the moment ratio $M_1/A_0$ as a function of $\mu_B B$ for PH/Ar $A^3\Pi \leftarrow X^3\Sigma^-$. The curves are best fits to all the data using the randomly oriented SO-CF model, with $\Delta_n = 192$ cm$^{-1}$ and $D' = 1.62$ cm$^{-1}$.

8.4.4 PH/Kr

Figure 8.43: Temperature-dependence of the moment ratio $M_1/A_0$ as a function of $1/kT$ for PH/Kr $A^3\Pi \leftarrow X^3\Sigma^-$. The curves are best fits to all the data using the randomly oriented SO-CF model, with $\Delta_n = 133$ cm$^{-1}$ and $D' = 1.4$ cm$^{-1}$.
**Imidogen (NH) and Phosphinidene (PH)**

Figure 8.44: Magnetic-field-dependence data for the moment ratio $M_1/A_0$ as a function of $\mu_B B$ for PH/Kr $A^3\Pi \leftarrow X^3\Sigma^-$. The curves are best fits to all the data using the randomly oriented SO-CF model, with $A_e = 133$ cm$^{-1}$ and $D' = 1.4$ cm$^{-1}$.

**8.4.5 PH/Xe**

Figure 8.45: Temperature-dependence of the moment ratio $M_1/A_0$ as a function of $1/kT$ for PH/Xe $A^3\Pi \leftarrow X^3\Sigma^-$. The curves are best fits to all the data using the randomly oriented SO-CF model, with $A_e = 107$ cm$^{-1}$ and $D' = 0.73$ cm$^{-1}$.
8.5 Discussion

8.5.1 The Randomly Oriented SO-CF Model

Non-linear least-squares fits of the $M_1/A_0$ data to the randomly oriented SO-CF model (Eq. (8.29)) were achieved using the program ALLFIT and the parameters listed in Table 8.14. The results, superimposed on the experimental data in Figures 8.37-8.46, reproduce the experimental data accurately and precisely over broad ranges of temperature and magnetic field for all of the systems investigated.

Table 8.14, which also contains the parameters for NH/Ar obtained by Langford\textsuperscript{5,7} provides quantitative evidence of the trends (described in Section 8.3) of the band wavenumbers and bandwidths with the host. Also very evident are significant and consistent trends in the values of the ground-state ZFS parameter, $D'$, and the excited state SOC coefficient, $A_x$. 

---

Figure 8.46: Magnetic-field-dependence data for the moment ratio $M_1/A_0$ as a function of $\mu_0B$ for PH/Xe $A^3\Pi \leftarrow X^3\Sigma^{-}$. The curves are best fits to all the data using the randomly oriented SO-CF model, with $A_x = 107$ cm$^{-1}$ and $D' = 0.73$ cm$^{-1}$. 

---

Imidogen (NH) and Phosphinidene (PH)
Table 8.14: Parameters for the $A^{3} \Pi \leftarrow X^{3} \Sigma^{-}$ transition of NH and PH in the gas phase and in inert-gas matrices, as obtained from moment analysis and non-linear least-squares fits of the experimental data to the randomly-oriented SO-CF model. Quoted uncertainties are two standard deviations.

<table>
<thead>
<tr>
<th>Matrix</th>
<th>$A_{\pi}$ / cm$^{-1}$</th>
<th>$D'$ / cm$^{-1}$</th>
<th>$\bar{E}$ / cm$^{-1}$</th>
<th>$E_{0}$ / cm$^{-1}$</th>
<th>$2\sqrt{A_{2}/A_{0}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH (gas)$^{6}$</td>
<td>34.79</td>
<td>1.67*</td>
<td>-</td>
<td>29807.4</td>
<td>-</td>
</tr>
<tr>
<td>NH/Ar</td>
<td>33.5 ± 0.3</td>
<td>-0.08 ± 0.03</td>
<td>29670</td>
<td>29620</td>
<td>130</td>
</tr>
<tr>
<td>NH/Kr</td>
<td>21 ± 2</td>
<td>0.01 ± 0.01</td>
<td>29550</td>
<td>29490</td>
<td>130</td>
</tr>
<tr>
<td>NH/Xe</td>
<td>-</td>
<td>-</td>
<td>29490</td>
<td>29420</td>
<td>160</td>
</tr>
<tr>
<td>NH/N$_{2}$</td>
<td>43.2 ± 0.3</td>
<td>0.61 ± 0.02</td>
<td>29710</td>
<td>29350</td>
<td>500</td>
</tr>
<tr>
<td>PH (gas)$^{6}$</td>
<td>115.71</td>
<td>4.42*</td>
<td>-</td>
<td>29498</td>
<td>-</td>
</tr>
<tr>
<td>PH/Ar</td>
<td>192 ± 3</td>
<td>1.62 ± 0.07</td>
<td>29190</td>
<td>29000</td>
<td>350</td>
</tr>
<tr>
<td>PH/Kr</td>
<td>133 ± 3</td>
<td>1.4 ± 0.1</td>
<td>28980</td>
<td>28840</td>
<td>360</td>
</tr>
<tr>
<td>PH/Xe</td>
<td>107 ± 1</td>
<td>0.73 ± 0.04</td>
<td>28640</td>
<td>28500</td>
<td>270</td>
</tr>
</tbody>
</table>

* Important note: In the gas phase, $D'$ is NOT manifest as a zero-field splitting of the lowest, $J = 1$, level of the $X^{3} \Sigma^{-}$ state – see text.

8.5.1.1 $X^{3} \Sigma$ zero-field splittings

An important point about the ZFS of a $^{3} \Sigma$ term is that it is not evident in the lowest ($J = 1$) rotational level of the freely rotating radical, which is necessarily triply degenerate in the absence of a magnetic field. (In essence, this is a reflection of the very weak coupling of $S$ to the internuclear axis – the Hund’s case-(b) behaviour expected for a $\Sigma$ state.) Instead, in the gas phase it is apparent as a splitting of higher rotational levels and its experimental value can only be calculated by analysis of transitions involving those levels. However, when the rotational motion of the molecule is constrained, the level with $J = 1$ parentage splits, according to Section 8.1.3, with a magnitude $D'$ (see Figure 8.1). The SO-CF model was developed under the assumption that the sample is an ensemble of randomly oriented trapped radicals, and that each guest radical has a fixed orientation on the timescale of the experiment. If the model were truly applicable, one would therefore expect, as a first approximation, that $D'$ would be independent of the host and determined by the guest species, with magnitudes close to the gas-phase values of $D_{NH} = 1.67$ cm$^{-1}$ and $D_{PH} = 4.42$ cm$^{-1}$.$^{3,4}$

Mechanisms have been described by which $D'$ can be modified on incorporation of the radical into condensed media. Two weak effects$^{1,14}$ that tend to increase $D'$ for trapped radicals are: exclusion forces, which push the unpaired electrons closer together, thereby increasing $D_{ss}$; and SO effects due to the molecular
Imidogen (NH) and Phosphinidene (PH)

electrons experiencing the electric fields due to electrons and nuclei of the surrounding matrix atoms.

Rotational effects\(^1\) cause a reduction of \(D'\), which can be rationalised in terms of motional averaging. This applies even for the librational zero-point motion of the radical within its matrix sites. Upon substitution of a heavier isotope within the molecule, a detectable increase in \(D'\) (effectively due to a reduction in the amplitude of motion) will confirm that such librational effects are appreciable. The other major effect that decreases \(D'\) arises from enhanced SO mixing of triplet and singlet molecular states, which should increase with the nuclear charge of the host.\(^1,14\)

For NH/NG and PH/NG, the ZFSs of the lowest level are severely quenched. In the extreme, for NH in Ar and Kr, \(D'\) is reduced effectively to zero. An explanation for this is that the system is acting essentially as a free rotor. This explanation, which was adopted by Langford,\(^5,7\) was also reached by McCarty and Robinson,\(^12\) based on the structure of the observed electronic absorption of NH/Ar, and by Bondebech and Brus,\(^13\) based on time- and wavelength-resolved laser-induced fluorescence experiments used to probe vibrational relaxation of NH in Ar and Kr matrices. This suggests that CF interactions of \(X^3\Sigma^-\) NH with Ar and Kr must be rather weak. In systems where the guest-host interactions are stronger, rotation will be more hindered, ultimately to the point where the molecule undergoes librational oscillations about one orientation. As the amplitude of the zero-point libration decreases, \(D'\) should increase to a maximum value, which, if the molecule were unperturbed by the host, would correspond to the gas-phase \(D\). \(N_2\) is known to form a strongly interacting matrix,\(^15\) and in the case of NH/\(N_2\) it is likely that the quenching of \(D'\) is caused by motional effects. (The small SO contribution to \(D_{\text{NH}}\) makes it unlikely that there are large matrix-induced SO effects.) A detectable increase in \(D'\) for the system ND/\(N_2\) would confirm that the librational effects are appreciable.

The maximum ZFS occurs for PH/Ar, with \(D'_{\text{PH}} = 1.6 \text{ cm}^{-1}\), 36% of the gas-phase value, then decreases to \(\sim 0.7 \text{ cm}^{-1}\) for PH/Xe. It would be tempting to assume that this indicates that PH is a less-hindered rotor when incorporated into matrices of heavier noble gases. However, PH differs from NH in that \(D_{\text{PH}}\) is mainly due to higher-order SOC, so there is a greater potential for quenching from SO effects. It is therefore impossible to say conclusively how the rotational motions are modified, but it is clear that PH is substantially more hindered than NH in all of the noble gases.
investigated.

### 8.5.1.2 Spin-orbit coupling

Any attempt to understand the trends in the SOC constants of NH and PH in rare-gas or nitrogen matrices requires consideration of the presence of the host atoms, in particular the external heavy-atom effect (see Section 5.3).

Table 5.1, containing one-electron SOC constants of the \(^2\)P excited states of Li–Cs and Cu–Au, is reproduced here in order to give a comparison with the two XH radicals that are the subject of attention in this chapter (Table 8.15).

<table>
<thead>
<tr>
<th>Medium</th>
<th>Li</th>
<th>Na</th>
<th>K</th>
<th>Cs</th>
<th>Cu</th>
<th>Ag</th>
<th>Au</th>
<th>NH</th>
<th>PH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas</td>
<td>0.23</td>
<td>11.5</td>
<td>38.5</td>
<td>369</td>
<td>166</td>
<td>614</td>
<td>2543</td>
<td>34.79</td>
<td>115.71</td>
</tr>
<tr>
<td>Ar</td>
<td>−16</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>124</td>
<td>783</td>
<td>3354</td>
<td>33.5</td>
<td>192</td>
</tr>
<tr>
<td>Kr</td>
<td>−70</td>
<td>*</td>
<td>−64</td>
<td>*</td>
<td>95</td>
<td>638</td>
<td>3110</td>
<td>21</td>
<td>133</td>
</tr>
<tr>
<td>Xe</td>
<td>−196</td>
<td>−213</td>
<td>−170</td>
<td>~100</td>
<td>−23</td>
<td>583</td>
<td>2655</td>
<td>*</td>
<td>107</td>
</tr>
</tbody>
</table>

The experimentally determined SOC constants for PH/NG, shown in the right-most columns of Table 8.15, follow the general trend of Ag. Namely a significant increase in \(A_n\) on incorporation into Ar, followed by a decrease with heavier host gas. In contrast, NH/NG is more like Cu/NG, exhibiting a slight decrease in Ar. On the basis of the data obtained in this work, one would expect \(A_n\) to be less than 21 cm\(^{-1}\) and greater than 0 cm\(^{-1}\) (if \(A_n\) was less than 0 cm\(^{-1}\), the MCD would appear as a negative pseudo-\(\alpha\) term). Since structure from the simulated MCD seems to correspond with that seen in the MCD spectra of NH/Ar, it is likely that there is minimal overlap between excited-state NH and nearby noble gas atoms. Hence, the observed trend in \(A_n\) is likely to be largely mechanical in nature.

Quantum-mechanical calculations must be performed to better understand the interactions between PH and matrix host, however at this stage it is reassuring to know that the experimental observations made in this work do have a precedent.

The increase in \(A_n\) to 43.2 cm\(^{-1}\) for NH/N\(_2\) relative to the gas phase of 35.79 cm\(^{-1}\) is most likely due to the overlap of excited-state NH with nearby N\(_2\) molecules. However because this matrix was a “one off,” intended to investigate the
Imidogen (NH) and Phosphinidene (PH)

rotational properties of the ground state, it is somewhat dangerous to speculate without performing quantum-mechanical calculations.

8.5.2 Free Rotor or Not? That is the Question.

8.5.2.1 SO-CF simulations

As described above, the SO-CF model gives an excellent fit to the moment-ratio data for NH/NG, NH/N₂, and PH/NG, and permits the trends of these data to be rationalised. However, it has serious weaknesses – it is based on an assumption that individual guest radicals have a fixed orientation on the timescale of the experiment, yet the reduced $D'$ values are interpreted to indicate that the radicals undergo (perhaps hindered) rotation in the ground state. Furthermore, it assumes that the only ground-state levels that carry significant populations at the experimental temperatures are those of $J = 1$ parentage. (For a $^3\Sigma^-$ term, the lowest rotational state has $J = 1$.) Thus, for the case of a hindered or free rotor, the model will fail to reproduce hot features that are observed as higher levels become populated, i.e. at higher temperatures and/or when the trapped molecules have small rotational constants. There is no scope within this model for any rotation in the excited state. A manifestation of these weaknesses is the fact, illustrated below, that spectral simulations for the $A^3\Pi \leftrightarrow X^3\Sigma^-$ transitions obtained using the SO-CF model are only partially successful.

Of all data that have been collected for these types of systems, those for NH/Ar provide the best test of any model because they exhibit the greatest detail of structure. Some of the spectroscopic data obtained by Langford on NH/Ar⁵,⁷ are reproduced in figures 8.47 and 8.48. These spectra exhibit several especially notable features that will be the subject of discussion later. Firstly, there are four relatively intense bands, labelled 1-4 in Figure 8.47. At high temperatures, the MCD of band 1 appears as a weak, positive @-term-like feature, but this transforms to a strong, negative @ term at lower temperatures. Band 2 is weak in absorption and is associated with a very weak, positive, temperature-dependent MCD feature. Bands 3 and 4 are broad and relate to positive C terms. In addition there are broad and weak features (bands 5 and 6) to the blue of the main band envelope, as well as a weak shoulder (band 7) to the red.

As well as the clearly evident temperature and magnetic-field dependencies exhibited by the MCD of NH/Ar, the absorption also shows significant temperature
Imidogen (NH) and Phosphinidene (PH)

dependence. The amplitudes of bands 1-4 decrease to various degrees as the temperature is increased. This phenomenon is stronger for the sharper bands (1 and 2) and is probably at least partly due to band broadening. The intensity of band 7 increases with temperature and is clearly associated with a hot transition arising from thermally excited levels within the manifold of the ground electronic state.

Langford’s SO-CF simulation for NH/Ar\textsuperscript{5, 7} concentrated on bands 1-4, which were assigned to transitions terminating in the $^3\Pi_1$, $^3\Pi_0$, $^3\Pi_0$, and $^3\Pi_1$ SO-CF states, respectively (Figure 8.1). According to this model, bands 1 and 2 are separated by $\delta = (A - V_n)/2$, which, with the aid of Eq. (8.14), provides an estimate of $V_n$ according to

$$V_n = \frac{A^2 - \delta^2}{\delta}$$  \hspace{1cm} (8.30)

Eq. (8.30) and Figure 8.47 give $\delta \sim 13 \text{ cm}^{-1}$ which (with $A_n = 33.5 \text{ cm}^{-1}$ from moment analysis) gives $V_n \approx 75 \text{ cm}^{-1}$.

![Figure 8.47: Absorption and temperature-dependent MCD spectra (0.50 T) of the (0,0) band of the $A^3\Pi \leftarrow X^3\Sigma^-$ transition of NH/Ar, as obtained by Langford.\textsuperscript{5, 7}](image)
Figure 8.48: Magnetic-field-dependent MCD spectra (1.58 K) of the (0,0) band of the $A^3\Pi \leftarrow X^3\Sigma^-$ transition of NH/A, as obtained by Langford.5,7

Figure 8.49: SO-CF-simulated absorption and temperature-dependent MCD spectra (1.00 K) of the (0,0) band of the $A^3\Pi \leftarrow X^3\Sigma^-$ transition of NH/A, with $A_e = 33.5$ cm$^{-1}$, $D' = 0$ cm$^{-1}$, and $V_e = 75$ cm$^{-1}$. The labels 1-4 indicate the four bands (HW1/eM of 5, 5, 30, and 30 cm$^{-1}$ respectively) generated in the simulation. Overlap between the broader bands 3 and 4 prevent them being resolved.
Imidogen (NH) and Phosphinidene (PH)

\[ \lambda \text{(nm)} \]

\[ 338 \quad 337 \quad 338 \quad 335 \quad 334 \]

\[ \Delta A \]

\[ 0.5 \text{T} \]

\[ 1.5 \text{T} \]

\[ 4.5 \text{T} \]

\[ \text{NH/Ar} \ A^3\Pi \leftarrow X^3\Sigma^- \]

\[ T = 1.58 \text{ K} \]

SO-CF simulation

Figure 8.50: SO-CF-simulated magnetic-field-dependent MCD spectra (1.58 K) of the (0,0) band of the \( A^3\Pi \leftarrow X^3\Sigma^- \) transition of NH/Ar, with \( A_\pi = 33.5 \text{ cm}^{-1}, D' = 0 \text{ cm}^{-1}, \) and \( V_\pi = 75 \text{ cm}^{-1}. \) The labels 1-4 indicate the four bands (HW/\( eM \) of 5, 5, 30, and 30 cm\(^{-1}\) respectively) generated in the simulation. Overlap between the broader bands 3 and 4 prevent them being resolved.

The simulated spectra obtained with \( D' = 0 \text{ cm}^{-1} \) (Figures 8.49 and 8.50) reveal reasonable agreement between theory and experiment, including roughly correct relative band intensities and MCD signs. Several problems still remain however. Although the simulation gives the right sort of dispersion, this is partly a result of an ad hoc choice of different widths for the various (Gaussian) bands (HW/\( eM \) of 5, 5, 30, and 30 cm\(^{-1}\) respectively). The simulation also does not explicitly account for bands 5-6 at the blue end of the spectrum, which were attributed by Langford to couplings with librational modes and/or lattice phonons. Finally, the limitations of the model do not allow for hot bands such as 7.

To see how the SO-CF model fares for related systems, simulations using Gaussian bands were also performed for NH/Kr and NH/N\(_2\), which have spectra that are broader and less structured than those for NH/Ar. Unlike the case of NH/Ar, estimates for \( V_\pi \) can not be determined directly by inspection of the spectra. The best simulations were determined visually while manually varying \( V_\pi \) and the bandwidths.

Figure 8.51 gives the simulation for NH/Kr, where \( V_\pi = 60 \text{ cm}^{-1} \) and the
Imidogen (NH) and Phosphinidene (PH)

Bandwidths are all 40 cm\(^{-1}\), whereas Figure 8.52 gives the simulation for NH/N\(_2\), where \(V_\pi = 200\) cm\(^{-1}\) and the bandwidths of bands 1-4 are 280, 280, 320, and 320 cm\(^{-1}\) respectively. These are to be compared with the experimental data in Figures 8.2 and 8.4 for the case of NH/Kr, and 8.8 and 8.9 for NH/N\(_2\). In both cases, the simulations give fairly good agreements with experiment. A feature of the experimental spectra, particularly for NH/Kr, is that the positive MCD structure lying to the blue is broader than the negative structure. The simulated MCD does not accurately reproduce this observation. The NH/Kr simulated absorption spectrum appears as two peaks of similar bandwidth and appearance, however the experimental absorption differs in that the lower-energy peak is narrower. No other bandwidth choices could simultaneously reproduce the experimental data. These discrepancies most likely arise from the fact that NH is rotating within the matrix.

SO-CF simulations were attempted for PH/NG, however no choices for \(V_\pi\) and the four bandwidths could simultaneously reproduce the MCD and absorption spectra at each temperature and magnetic field. This failure is possibly due to PH molecules occupying different sites, each site corresponding to a different value of \(V_\pi\).

![Graph showing absorption (bottom) and magnetic-field-dependent MCD (top) spectra for NH/Kr](image)

**Figure 8.51:** SO-CF-simulated absorption (bottom) and magnetic-field-dependent MCD (top) spectra (1.64 K) of the (0,0) band of the \(A^3\Pi \leftarrow \chi^3\Sigma^-\) transition of NH/Kr, with \(A_\pi = 21\) cm\(^{-1}\), \(D' = 0\) cm\(^{-1}\), and \(V_\pi = 60\) cm\(^{-1}\). The labels 1-4 indicate the four bands, with bandwidths of 40 cm\(^{-1}\) (HW1/eM). These simulations should be compared with the experimental data in Figures 8.2 and 8.4.
Imidogen (NH) and Phosphinidene (PH)

![Figure 8.52: SO-CF-simulated absorption (bottom) and magnetic-field-dependent MCD (top) spectra (1.43 K) of the (0,0) band of the \(A^3\Pi \leftrightarrow \chi^3\Sigma^-\) transition of NH/N\(_2\), with \(A_e = 43.2 \text{ cm}^{-1}\), \(D' = 0.61 \text{ cm}^{-1}\), and \(V_e = 200 \text{ cm}^{-1}\). Bandwidths are 280, 280, 320, and 320 cm\(^{-1}\) respectively (HW/eM). These simulations should be compared with the experimental data in Figures 8.8 and 8.9.]

8.5.2.2 Free-rotor simulations

In order to avoid the weaknesses of the SO-CF model, one needs to carry out simulations for the hindered-rotor case. However, the crystal-field potential for hindered rotation in an octahedral field (Section 5.4.1) corresponds to a unitary transformation and will have no effect on the overall \(M/A_0\) when it is applied to the excited state. In this case the best place to start is by performing simulations in which both the ground and excited states are free rotors.

As outlined in Section 3.4.4, the Hund’s case-(a) basis functions for the \(^3\Pi\) excited state of NH/PH are

\[
\begin{align*}
|^{3}\Pi_{0} J M \, p^{\pm}\rangle &= \frac{1}{\sqrt{2}}\{|-1 1 1; J 0 \, M\} \pm |1 1 -1; J 0 \, M\}
\end{align*}
\]

\[
\begin{align*}
|^{3}\Pi_{1} J M \, p^{\pm}\rangle &= \frac{1}{\sqrt{2}}\{|1 1 0; J 1 \, M\} \pm |-1 1 0; J -1 \, M\}
\end{align*}
\]
Imidogen (NH) and Phosphinidene (PH)

\[ |{^3\Pi_2 J M \pm^*}\rangle = \frac{1}{\sqrt{2}} \{|1 \, 1 \, 1; J \, 2 \, M\} \pm |1 \, 1 \, -1; J \, -2 \, M\}\]  \hspace{1cm} (8.31)

while the basis functions for the \(^3\Sigma^-\) ground state are

\[ |{^3\Sigma_1 J M \pm^*}\rangle = \frac{1}{\sqrt{2}} \{|0 \, 1 \, 1; J \, 1 \, M\} \pm |0 \, 1 \, -1; J \, -1 \, M\}\]  \hspace{1cm} (8.32)

\[ |{^3\Sigma_0 J M}\rangle = |0 \, 1 \, 0; J \, 0 \, M\rangle \]

Rotational energy levels are obtained by solving the appropriate equations in Section 3.4.4, with the inclusion of the appropriate Zeeman matrix elements (Section 3.4.5). The non-zero Zeeman matrix elements are given in Tables 8.16 to 8.19.

Table 8.16: J-diagonal Zeeman matrix elements for the \(^3\Sigma^-\) ground state of NH/PH.

<table>
<thead>
<tr>
<th>(\mathcal{K}_B)</th>
<th>(^3\Sigma_1 J M \pm^*)</th>
<th>(^3\Sigma_0 J M)</th>
<th>(^3\Sigma_1 J M \pm^*)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^3\Sigma_1 J M \pm^*)</td>
<td>(\frac{2 \mu_B M}{J (J + 1)})</td>
<td>(\mu_B M/J (J + 1))</td>
<td>0</td>
</tr>
<tr>
<td>(^3\Sigma_0 J M)</td>
<td>(\mu_B M/J (J + 1))</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>(^3\Sigma_1 J M \pm^*)</td>
<td>0</td>
<td>0</td>
<td>(\frac{2 \mu_B M}{J (J + 1)})</td>
</tr>
</tbody>
</table>

Table 8.17: Non-J-diagonal Zeeman matrix elements for the \(^3\Sigma^-\) ground state of NH/PH.

| \(\mathcal{K}_B\) | \(^3\Sigma_0 J M|\mathcal{K}_B|\Sigma_1 J \pm 1 \rangle\) | \(\frac{2 \mu_B B}{J + 1} \left[ J (J + 1) (J + 1 + M) (J + 1 + M) \right]^{1/2}\) |
|-----------------|----------------------------------|--------------------------------------------------|
| \(^3\Sigma_0 J M\) | \(\Sigma_1 J \pm 1 \rangle\) | \(\frac{2 \mu_B B}{J + 1} \left[ J (J + 1) (J + 1 + M) (J + 1 + M) \right]^{1/2}\) |
| \(^3\Sigma_1 J M \pm^*\) | \(\frac{2 \mu_B B}{J + 1} \left[ J (J + 1) (J + 1 + M) (J + 1 + M) \right]^{1/2}\) |
| \(^3\Sigma_1 J M \pm^*\) | \(\frac{2 \mu_B B}{J + 1} \left[ J (J + 1) (J + 1 + M) (J + 1 + M) \right]^{1/2}\) |

Table 8.18: J-diagonal Zeeman matrix elements for the \(^3\Pi\) excited state of NH/PH.

<table>
<thead>
<tr>
<th>(\mathcal{K}_B)</th>
<th>(^3\Pi_0 J M \pm^*)</th>
<th>(^3\Pi_1 J M \pm^*)</th>
<th>(^3\Pi_2 J M \pm^*)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^3\Pi_0 J M \pm^*)</td>
<td>0</td>
<td>(\pm \frac{g_s \mu_B B}{2 J (J + 1)})</td>
<td>0</td>
</tr>
<tr>
<td>(^3\Pi_1 J M \pm^*)</td>
<td>(\pm \frac{g_s \mu_B B}{2 J (J + 1)})</td>
<td>(\frac{\mu_B B}{2 J (J + 1)})</td>
<td>(\frac{2 J (J + 1) - 4}{J (J + 1)})</td>
</tr>
<tr>
<td>(^3\Pi_2 J M \pm^*)</td>
<td>0</td>
<td>(\frac{\mu_B B}{2 J (J + 1)})</td>
<td>(\frac{6 \mu_B B}{2 J (J + 1)})</td>
</tr>
</tbody>
</table>
Table 8.19: Non-J-diagonal Zeeman matrix elements for the $^3\Pi$ excited state of NH/PH.

<table>
<thead>
<tr>
<th>$^3\Pi_0$</th>
<th>$\mu_\mathrm{B} B \left( \frac{(J + 1 - M) (J + 1 + M)}{(2J + 1) (2J + 3)} \right)^{1/2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^3\Pi_1$</td>
<td>$\frac{\mu_\mathrm{B} B}{J + 1} \left( \frac{J (J + 2) (J + 1 - M) (J + 1 + M)}{(2J + 1) (2J + 3)} \right)^{1/2}$</td>
</tr>
<tr>
<td>$^3\Pi_2$</td>
<td>$\frac{3\mu_\mathrm{B} B}{J + 1} \left( \frac{(J - 1) (J + 3) (J + 1 - M) (J + 1 + M)}{(2J + 1) (2J + 3)} \right)^{1/2}$</td>
</tr>
<tr>
<td>$^3\Pi_0$</td>
<td>$\frac{\mu_\mathrm{B} B}{J + 1} \left( \frac{2 (J + 1) (J + 2) (J + 1 - M) (J + 1 + M)}{(2J + 1) (2J + 3)} \right)^{1/2}$</td>
</tr>
<tr>
<td>$^3\Pi_1$</td>
<td>$\frac{3\mu_\mathrm{B} B}{J + 1} \left( \frac{2 (J + 1) (J + 1 - M) (J + 1 + M)}{(2J + 1) (2J + 3)} \right)^{1/2}$</td>
</tr>
<tr>
<td>$^3\Pi_2$</td>
<td>$\frac{\mu_\mathrm{B} B}{J + 1} \left( \frac{2J (J - 1) (J + 1 - M) (J + 1 + M)}{(2J + 1) (2J + 3)} \right)^{1/2}$</td>
</tr>
</tbody>
</table>

8.5.2.2.1 NH

A Fortran computer program NHDIAG.F was utilised to calculate $\mathbf{M}_1/\mathbf{A}_0$ for the free-rotor at any given temperature or magnetic-field strength. The program first obtains the eigenfunctions and eigenvalues for NH by diagonalising a sufficiently large basis set of Hund’s case-(a) functions. The gas-phase molecular parameters were used: $A_\pi = 34.79$ cm$^{-1}$, $B_{\nu = 0}(X^3\Sigma^-) = 16.3748$ cm$^{-1}$, $B_{\nu = 0}(A^3\Pi) = 16.3018$ cm$^{-1}$, and $D = 1.67$ cm$^{-1}$. The program calculates line strengths (Section 3.4.6), for left and right circularly polarised radiation, between allowed rotational levels, weighted by the population factors of the ground levels. The average line strength gives $\mathbf{A}_0$, whereas $\mathbf{M}_1$ (about the band barycentre) is calculated from Eq. (4.31).

The results are depicted as dashed curves in Figures 8.53 and 8.54, which also provides a comparison with simulated moments (full curves) for NH/Ar using the SO-CF model and the parameters obtained by Langford. The latter essentially exactly reproduce the experimental behaviour. As these figures show, under any given conditions, $\mathbf{M}_1/\mathbf{A}_0$ for the free-rotor NH is larger and shows a lesser degree of saturation than the value determined by the SO-CF model.

The Zeeman splittings for the $^3\Sigma^-$ ground state SO-CF state ($D' = 0$) and the lowest rotational $J = 1$ level of NH are identical. It seems reasonable that the differences between the curves in Figures 8.53 and 8.54 arise purely from differences between the excited states, possibly due to differences in $\mathbf{B}$ terms. There is likely to be another
effect that has to be taken into account in order to reconcile these two models, such as RTC (Section 5.4.2).

**Figure 8.53:** Magnetic-field-dependence simulations for the moment ratio $M_1/A_0$ as a function of $\mu_B B$ for the $A \ ^3\Pi \to X \ ^3\Sigma^-$ transition of NH/Ar, using the SO-CF parameters obtained by Langford ($A_z = 33.5 \text{ cm}^{-1}, D' = 0 \text{ cm}^{-1}$; full line), and free NH (dashed line).

**Figure 8.54:** Temperature-dependence simulations for the moment ratio $M_1/A_0$ as a function of $1/kT$ for the $A \ ^3\Pi \to X \ ^3\Sigma^-$ transition of NH/Ar, using the SO-CF parameters obtained by Langford ($A_z = 33.5 \text{ cm}^{-1}, D' = 0 \text{ cm}^{-1}$; full line), and free NH (dashed line).
Once the energies of individual transitions and their moments have been calculated by NHDIAG.F, the spectra can be plotted using the BASIC program ROTPLOT, which assumes Gaussian bandshapes. The object of this was not to reproduce exactly the NH/Ar spectra, due to discrepancies between the two models, but to obtain a comparison. Hence bandwidths were arbitrarily chosen to be identical (5 cm⁻¹). The simulated spectra for freely rotating NH are given in Figures 8.56 to 8.58. Table 8.20 assigns transitions to the bands numbered 1-7, and Figure 8.55 gives the energy-level diagram for the appropriate rotational states.

The simulated absorption spectra in Figure 8.56 have a number of features in common with the NH/Ar experimental absorption spectra. Firstly, a direct correlation can be drawn with the observed bands. (Note that in the free-rotor NH model, bands 1 and 2 correspond to the same transition in absorption.) At low temperatures the series of bands, 1-6, drops off in intensity with increasing energy. In agreement with experiment, the amplitudes of these cold bands, particularly for the origin, are reduced as the temperature is increased. A weak, hot band observed to the red of the origin band can be correlated with band 7. It gains significant intensity only above ~10 K, which also accords well with the experimental observations.

The simulated magnetic-field-dependence of the MCD spectra of Figure 8.57 also has a number of features that are remarkably in common with experiment. There is a single, strong, negative band corresponding to the origin (band 1), and a number of weaker positive MCD bands (3, 4 and 6) which tail off to the blue. There is also a small positive MCD band, just to the blue of the origin, which is observed at high magnetic fields and correlates with band 2. Bands 1 and 2 correspond to the same transition in absorption, but in the presence of a magnetic field they are split into components corresponding to the Zeeman transitions \( \Delta M = -1 \) and 1 respectively. Encouragingly, the pattern of intensity for bands 3 and 4 is much more in accord with experiment than was the case for the SO-CF simulation (Figure 8.50).

The simulated temperature-dependence of Figure 8.58 also agrees generally with the experimental MCD spectra. More specifically band 1 reverts to positive \( \Delta \)-term-like at the higher temperatures. Bands 3 and 4 also gradually take on a two-signed character, resembling positive \( \Delta \) terms. The latter is not observed experimentally but could easily be obscured if these bandwidths are larger in the case of NH/Ar.
Incorporation of CF effects into the excited $A \ ^3\Pi$ state did not produce a closer agreement with experimental band energies and intensities. Consideration of RTC (Section 5.4.2) might be required to obtain this agreement.

Table 8.20: Band numbers in the simulated free-rotor transitions and their assignments, using notation from the gas-phase work of Dixon.\textsuperscript{21}

<table>
<thead>
<tr>
<th>Band number</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$R_1(1)$</td>
</tr>
<tr>
<td>2</td>
<td>$R_2(1)$</td>
</tr>
<tr>
<td>3</td>
<td>$^RQ_{21}(1)$</td>
</tr>
<tr>
<td>4</td>
<td>$^RQ_{31}(1)$</td>
</tr>
<tr>
<td>5</td>
<td>$^S!!!R_{21}(1)$</td>
</tr>
<tr>
<td>6</td>
<td>$^S!!!Q_{31}(1)$</td>
</tr>
<tr>
<td>7</td>
<td>$Q_1(2), \ ^Q!!!R_{12}(1)$</td>
</tr>
</tbody>
</table>

Figure 8.55: Energy-level diagram for some of the lines of the $^3\Pi \leftrightarrow \ ^3\Sigma^-$ transition of NH, reproduced from reference 5 with minor corrections. $J'$ and $N'$ are labels in the $^3\Pi$ term and $J''$ and $N''$ are labels in the $^3\Sigma^-$ term for Hund's cases (a) and (b), respectively. Note that splittings within the $N'' = 1$ levels of the $^3\Sigma^-$ term are too small to be shown in the scale of this diagram.
Imidogen (NH) and Phosphinidene (PH)

Figure 8.56: Simulated absorption spectra at 1.40, 10.0, and 17.0 K for the (0,0) band of the $A^3\Pi \leftrightarrow X^3\Sigma^-$ transition of free NH, using bandwidths of 5 cm$^{-1}$ (HW/εM).

Figure 8.57: Simulated magnetic-field-dependent MCD spectra (1.40 K) of the (0,0) band of the $A^3\Pi \leftrightarrow X^3\Sigma^-$ transition of NH, using bandwidths of 5 cm$^{-1}$ (HW/εM).
Figure 8.58: Simulated temperature-dependent MCD spectra (1.00 tesla) of the (0,0) band of the $A^3\Pi \leftrightarrow X^3\Sigma^-$ transition of NH, using bandwidths of 5 cm$^{-1}$ (HW/\delta M).

Although no experiments were performed on ND/NG in this work, Langford\textsuperscript{5,7} collected data on ND/Ar, obtaining the SO-CF parameters $A_\pi = 37.2$ cm$^{-1}$ and $D'=0$ cm$^{-1}$. Free-rotor simulations were also performed for ND, with gas-phase parameters $^3A_\pi = 34.58$ cm$^{-1}$, $B_{v=0}(X^3\Sigma^-) = 8.7913$ cm$^{-1}$, $B_{v=0}(A^3\Pi) = 8.7575$ cm$^{-1}$, and $D = 1.79$ cm$^{-1}$, and show very little deviation in the moment ratio $M_1/A_0$ from those of NH. The calculated moment ratios are slightly lower than the NH ones, reflecting the lower SOC and ground-state rotational constants. Higher ground-state rotational levels of ND become thermally populated at lower temperatures than NH, causing a small decrease in $A_0$. The reduced excited-state rotational constant also has negligible effect on $M_1/A_0$, although a simulated absorption spectrum would indicate more closely spaced bands than with NH. Such a simulation, however, has not been carried out due to time constraints. Langford’s data on ND/Ar indicated a small increase in $A_\pi$ relative to the gas phase, however the likelihood of NH contamination in the matrix, given the experimental problems already encountered in this work, make this hard to validate.
8.5.2.2.2 PH

A Fortran computer program called PHDIAG.F was utilised to perform calculations for free-rotor PH. This program is identical to NHDIAG.F except that gas-phase molecular parameters for PH are used:\textsuperscript{4, 6} $A_z = 115.71$ cm\textsuperscript{-1}, $B_{\nu=0}(X^3\Sigma^+) = 8.5371$ cm\textsuperscript{-1}, $B_{\nu=0}(A^3\Pi) = 8.0222$ cm\textsuperscript{-1}, and $D = 4.22$ cm\textsuperscript{-1}. Plots of the calculated values of $M_I/A_0$ against $1/kT$ and $\mu_B B$ are given in Figures 8.59 and 8.60. Figures 8.61 and 8.62 provide a comparison of the free-rotor moments with those obtained for PH/NG at 1.40 K and 5.00 T respectively. It is apparent that PH/NG deviates quite strongly from a free-rotor. This confirms the interpretation of the preceding SO-CF analysis.

A hindered-rotor simulation is unreasonable for PH/NG because the model explicitly assumes no overlap of PH with the noble-gas host. Such an overlap has already been established because of the large increase in $A_z$ due to the heavy-atom effect (Section 8.5.1.2).

![Figure 8.59: Magnetic-field-dependence simulations for the moment ratio $M_I/A_0$ as a function of $\mu_B B$ for the $A^3\Pi \leftrightarrow X^3\Sigma$ transition of free-rotor PH.](image)
Imidogen (NH) and Phosphindene (PH)

**Figure 8.60:** Temperature-dependence simulations for the moment ratio $M_l/A_0$ as a function of $1/kT$ for the $A^3\Pi \leftrightarrow X^3\Sigma^-$ transition of free-rotor PH.

**Figure 8.61:** Magnetic-field dependence (1.40 K) of the moment ratio $M_l/A_0$ as a function of $\mu_B B$ for the $A^3\Pi \leftrightarrow X^3\Sigma^-$ transition of free-rotor PH (dashed curve) and PH/NG (solid curves).
8.6 Conclusions

Absorption and temperature- and magnetic-field-dependent MCD spectra have been obtained for the \( A^3\Pi \leftarrow X^3\Sigma^- \) transitions of NH/Kr, NH/N\(_2\), PH/Ar, PH/Kr, and PH/Xe. The MCD spectra comprise pairs of oppositely signed \( \ell \) terms giving (positive) temperature-dependent pseudo-\( \ell \) terms, which exhibit saturation with respect to (increasing) magnetic field and (decreasing) temperature.

Using a randomly oriented SO-CF model, SOC constants \( (A_x) \) for the \( A^3\Pi \) terms and ZFSs \( (D') \) for the \( X^3\Sigma^- \) terms were extracted from the experimental data.

NH/NG exhibits a slight decrease in \( A_x \) on incorporation into Ar, followed by a decrease with heavier noble-gas host. However PH/NG exhibits a significant increase in \( A_x \) on incorporation into Ar, followed by a decrease with heavier host gas. These observations can be understood in terms of the external heavy-atom effect, in which the noble-gas host atoms perturb the guest radicals – the trend in PH results from strong guest-host orbital mixing; the trend in NH likely results from mainly mechanical effects.

For NH/NG and PH/NG, the ZFSs of the lowest levels are severely quenched. For NH in Ar and Kr, \( D' \) is reduced effectively to zero, consistent with the explanation that NH is a free rotor in its ground state. \( D' \) for NH/N\(_2\) is similarly...
Imidogen (NH) and Phosphinidene (PH) quenched by motional effects, although in this case NH is essentially librating. PH/NG exhibits a significant decrease in $D'$ on incorporation into Ar, followed by a further decrease with heavier host gas. Although it is clear that PH is substantially more hindered than NH in noble gases, the trend cannot be interpreted as PH becoming less hindered with heavier host gas because of the greater potential for $D'$ to be quenched by SO effects.

Absorption and MCD spectral simulations for free-rotor NH indicate a close agreement with the experimental results for NH/Ar, suggesting that the excited state is undergoing hindered rotation. The hindered-rotor model needs to be extended to include for the possibility of overlap between molecular guest and atomic host orbitals, as in the case of PH, and also needs to incorporate the rotation-translation-coupling model in which the molecule rotates about its centre of mass, which in turn is oscillating within the lattice site.

8.7 References


Imidogen (NH) and Phosphinidene (PH)


9 Hydroxyl (OH) and Mercapto (SH)

The spectroscopic investigations of hydroxyl (OH) and mercapto (SH) in this thesis involve the spectroscopically allowed transitions $A^2\Sigma^+ \leftarrow X^2\Pi$ arising from $\pi \leftarrow \sigma$ excitations (Table 3.4), where the $\pi$ orbitals are essentially non-bonding valence $p_{\pm 1}$ orbitals of the O/S atom and the $\sigma$ orbitals are admixtures of mainly the valence $p_0$ orbitals of the O/S atom with the 1s orbital of the H atom (Figure 3.1). Since the two radicals are effectively isoelectronic, they can be treated together.

The states of the radicals are represented by SO wavefunctions, which were derived in Chapter 3 and are summarised in Table 9.1.

| $|2\Sigma^+\rangle \langle \Lambda |_{\Omega} \Omega$ | Normalised Slater determinants |
|----------------|--------------------------------|
| $|X^2\Pi_{1/2} \pm \frac{1}{2}\rangle$ | $\pm |0^- 0^+ -1^- 1^+\rangle$ |
| $|X^2\Pi_{3/2} \pm \frac{3}{2}\rangle$ | $|0^- 0^+ -1^\mp 1^\pm\rangle$ |
| $|A^2\Sigma^+_{1/2} \pm \frac{1}{2}\rangle$ | $- |0^\pm -1^- 1^+ 1^+\rangle$ |

9.1 SO-CF Theory

9.1.1 SO-CF Wavefunctions

To construct the SO-CF wavefunctions for fixed OH/SH molecules, SO and CF matrix elements must first be derived using the methods in Section 3.3.5. The following derivation is similar to that of CH/SiH (Chapter 7), but is provided in full in order to make it easier to follow and to emphasise the differences between these systems.

9.1.1.1 $X^2\Pi$ state

Table 9.2 gives the SO and CF matrix elements for the $X^2\Pi$ state of OH/SH in a noble-gas matrix. $A_\pi$ is the empirical SO coupling constant and $V_\pi$ is the one-electron reduced CF matrix element for the valence $\pi$ electron in OH/SH.

$$A_\pi = \langle \pi | \xi (r) | \pi \rangle$$
$$V_\pi = \langle \pi | V^2 | \pi \rangle$$

(9.1)
Table 9.2: SO and CF matrix elements for the $X^2\Pi$ state of OH/NG and SH/NG.

| $\mathcal{X}_{SO} + \mathcal{X}_{CF}$ | $|X^2\Pi_{1/2} - \frac{1}{2}\rangle$ | $|X^2\Pi_{1/2} + \frac{1}{2}\rangle$ | $|X^2\Pi_{3/2} - \frac{1}{2}\rangle$ | $|X^2\Pi_{3/2} + \frac{1}{2}\rangle$ |
|-------------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|
| $(X^2\Pi_{1/2} - \frac{1}{2})$      | $\frac{1}{2}A_x$              | 0                               | 0                               | $-\frac{1}{2}V_\pi$            |
| $(X^2\Pi_{1/2} + \frac{1}{2})$      | 0                               | $\frac{1}{2}A_x$              | $\frac{1}{2}V_\pi$             | 0                               |
| $(X^2\Pi_{3/2} - \frac{1}{2})$      | 0                               | $\frac{1}{2}V_\pi$             | $-\frac{1}{2}A_x$              | 0                               |
| $(X^2\Pi_{3/2} + \frac{1}{2})$      | $-\frac{1}{2}V_\pi$             | 0                               | 0                               | $-\frac{1}{2}A_x$              |

The Hamiltonian matrix in Table 9.2 factors into two $2 \times 2$ matrices, according to the value of $\Sigma$. Diagonalisation of these matrices gives the SO-CF eigenfunctions for the $X^2\Pi$ term. The corresponding eigenvalues show that the $X^2\Pi$ term is split by a magnitude $\Delta$, where

$$\Delta = \sqrt{A_x^2 + V_\pi^2} \quad (9.2)$$

Figure 9.1: Energy-level diagram, reproduced from reference 1, showing the effects of SO, CF and Zeeman interactions on the $X^2\Pi$ and $A^2\Sigma^+$ states of OH/NG and SH/NG.
The eigenfunctions are labelled $^2\Pi_-$ and $^2\Pi_+$, which respectively designate the lower and upper SO-CF levels, and $\pm \frac{1}{2}$ in the kets on the left-hand side denotes the value of $\Sigma$. Note that these upper and lower SO-CF eigenfunctions are interchanged relative to Eq. (7.3).

$$
^2\Pi_+ \pm \frac{1}{2} = \alpha |^2\Pi_{1/2} \mp \frac{1}{2}\rangle \pm \beta |^2\Pi_{3/2} \pm \frac{1}{2}\rangle
$$

$$
|2\Pi_\pm \frac{1}{2}\rangle = \mp \beta |^2\Pi_{1/2} \pm \frac{1}{2}\rangle + \alpha |^2\Pi_{3/2} \pm \frac{1}{2}\rangle
$$

(9.3)

$\alpha$ and $\beta$ are mixing coefficients given by

$$
\alpha = \sqrt{\frac{1 + \kappa}{2}}
$$

$$
\beta = \sqrt{\frac{1 - \kappa}{2}}
$$

(9.4)

where $\kappa$ is the orbital reduction factor, given by

$$
\kappa = A_\pi / \Delta \quad (0 \leq \kappa \leq 1)
$$

(9.5)

It is worthwhile here to introduce the crystal-field reduction factor, which is given by

$$
\eta = V_\pi / \Delta \quad (0 \leq \eta \leq 1)
$$

(9.6)

From Eq. (9.2) it can be seen that $\kappa^2 + \eta^2 = 1$. Furthermore, as $V_\pi$ tends to zero (and $\kappa$ tends to 1), the wavefunctions in Eq. (9.3) become the SO wavefunctions of Table 9.1.

9.1.1.2 $^2\Sigma^+$ state

The $^2\Sigma^+$ state undergoes no first order spin-orbit coupling or CF splitting due to its orbital non-degeneracy.
9.1.2 Zeeman Matrix Elements

This section gives the angular momentum matrix elements for the various states. These are simply related to the Zeeman matrix elements, as outlined in Section 2.9.4. For the purposes of a non-rotating diatomic molecule trapped in a matrix, \( g_x = g_y = g_\perp \).

9.1.2.1 \( X^2\Pi \) state

Table 9.3 gives the angular momentum matrix elements for the \( X^2\Pi \) SO-CF states of OH/NG and SH/NG.

<table>
<thead>
<tr>
<th>( L_z + 2S_z )</th>
<th>( \langle \Pi^L - \frac{1}{2} \rangle )</th>
<th>( \langle \Pi^L + \frac{1}{2} \rangle )</th>
<th>( \langle \Pi^+ - \frac{1}{2} \rangle )</th>
<th>( \langle \Pi^+ + \frac{1}{2} \rangle )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \langle \Pi^L - \frac{1}{2} \rangle )</td>
<td>(- (1 + \kappa))</td>
<td>0</td>
<td>( \eta )</td>
<td>0</td>
</tr>
<tr>
<td>( \langle \Pi^L + \frac{1}{2} \rangle )</td>
<td>0</td>
<td>((1 + \kappa))</td>
<td>0</td>
<td>( \eta )</td>
</tr>
<tr>
<td>( \langle \Pi^+ - \frac{1}{2} \rangle )</td>
<td>( \eta )</td>
<td>0</td>
<td>(- (1 - \kappa))</td>
<td>0</td>
</tr>
<tr>
<td>( \langle \Pi^+ + \frac{1}{2} \rangle )</td>
<td>0</td>
<td>( \eta )</td>
<td>0</td>
<td>((1 - \kappa))</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>( L_x + 2S_x )</th>
<th>( \langle \Pi^L - \frac{1}{2} \rangle )</th>
<th>( \langle \Pi^L + \frac{1}{2} \rangle )</th>
<th>( \langle \Pi^+ - \frac{1}{2} \rangle )</th>
<th>( \langle \Pi^+ + \frac{1}{2} \rangle )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \langle \Pi^L - \frac{1}{2} \rangle )</td>
<td>0</td>
<td>( \eta )</td>
<td>0</td>
<td>(- \kappa )</td>
</tr>
<tr>
<td>( \langle \Pi^L + \frac{1}{2} \rangle )</td>
<td>( \eta )</td>
<td>0</td>
<td>( \kappa )</td>
<td>0</td>
</tr>
<tr>
<td>( \langle \Pi^+ - \frac{1}{2} \rangle )</td>
<td>0</td>
<td>( \kappa )</td>
<td>0</td>
<td>( \eta )</td>
</tr>
<tr>
<td>( \langle \Pi^+ + \frac{1}{2} \rangle )</td>
<td>(- \kappa )</td>
<td>0</td>
<td>( \eta )</td>
<td>0</td>
</tr>
</tbody>
</table>

From Section 2.9.4, the matrix elements in Table 9.3 are related to the principal \( g \) values according to the relationship

\[
g_\perp = 2 \langle \Pi^L + \frac{1}{2} | L_x + 2S_x | \Pi^L - \frac{1}{2} \rangle = 2\eta
\]
\[
g_\parallel = 2 \langle \Pi^L + \frac{1}{2} | L_x + 2S_x | \Pi^L + \frac{1}{2} \rangle = 2(1 + \kappa)
\]  

\( g_\parallel^+ \) and \( g_\parallel^- \) are the \( g \) values for the upper and lower SO-CF levels, respectively, when the molecular \( z \) axis is aligned parallel to \( B \). \( g_\perp \) is the \( g \) value for both SO-CF levels when the molecular \( z \) axis is aligned perpendicular to \( B \). The difference between Eq. (9.7) and Eq. (7.10) arises from the fact that the upper and lower SO-CF levels of Eq. (9.3) are interchanged relative to Eq. (7.3).
9.1.2.2 \( A^2\Sigma^+ \) state

The \( A^2\Sigma^+ \) state has no orbital angular momentum, so the Zeeman splitting results purely from spin angular momentum. With \( g_e \approx 2 \),

\[
\langle \Sigma^{1/2}_L \pm \frac{1}{2}|L_z + 2S_{iz}\Sigma^{1/2}_L \pm \frac{1}{2}\rangle = \pm 1
\]  

(9.8)

9.1.3 Oriented SO-CF Wavefunctions

The SO-CF model assumes that the OH/SH molecules are not rotating. Within this model it is therefore necessary to determine a set of wavefunctions and eigenvalues for a particular orientation of the OH/SH internuclear axis (\( z \)) with respect to the direction of the magnetic field (\( Z \)). The result will then be extended to a randomly oriented ensemble by appropriate integration over the angle, \( \theta \), between the magnetic field and the internuclear axis of the radical.

Laboratory-frame Zeeman matrix elements for the \( X^2\Pi \) SO-CF states of OH/NG and SH/NG, calculated using Eq. (3.65) and Table 9.3, are given in Table 9.4. Note that \( \sigma = \pm \) is a label representing the SO-CF levels of the \( X^2\Pi \) state. Additional Zeeman matrix elements between the \( 3\Pi_1 \) and \( 3\Pi_2 \) levels are responsible for \( \mathcal{B} \) terms, which will be dealt with in Section 9.1.5.2.

Table 9.4: Zeeman matrix elements for the \( X^2\Pi \) SO-CF states of OH/NG and SH/NG.

| \( \mu_B B(L_z + 2S_{iz}) \) | \( |^4\Sigma_{\sigma - \frac{1}{2}} \rangle \) | \( |^2\Pi_{\sigma + \frac{1}{2}} \rangle \) |
|-----------------------------|------------------------|------------------------|
| \( \langle 2\Pi_\sigma - \frac{1}{2} \pm 1 \rangle \) | \(-\frac{1}{2}\cos \theta g_{\|}\sigma\mu_B B\) | \(\frac{1}{2}\sin \theta g_{\perp}\mu_B B\) |
| \( \langle 2\Pi_\sigma + \frac{1}{2} \pm 1 \rangle \) | \(\frac{1}{2}\sin \theta g_{\perp}\mu_B B\) | \(\frac{1}{2}\cos \theta g_{\|}\sigma\mu_B B\) |

Diagonalisation of the matrix in Table 9.4 gives the energies of the raised and lowered magnetic-field-mixed SO-CF basis functions,

\[
E_\theta(\pm) = \pm\frac{1}{2}g_\theta^\sigma \mu_B B
\]  

(9.9)

where \( g_\theta^\sigma \) is given by

\[
g_\theta^\sigma = \sqrt{(g_{\|}\cos \theta)^2 + (g_{\perp}\sin \theta)^2}
\]  

(9.10)
The eigenfunctions in the Zeeman effect for the $^2\Pi_\sigma$ terms are given by

$$|^{2}\Pi_\sigma\pm\rangle = a_\sigma |^2\Pi_\sigma\pm\frac{\hbar}{2}\rangle \pm b_\sigma |^2\Pi_\sigma\mp\frac{\hbar}{2}\rangle$$

(9.11)

where the mixing coefficients $a_\sigma$ and $b_\sigma$ satisfy

$$|a_\sigma|^2 = \frac{(g_\perp \sin \theta)^2}{2g_\sigma(g_\sigma - g_\parallel \cos \theta)}$$

$$|a_\sigma|^2 + |b_\sigma|^2 = 1$$

$$|a_\sigma|^2 - |b_\sigma|^2 = \frac{g_\parallel \cos \theta}{g_\sigma}$$

(9.12)

### 9.1.4 Transition Moments

Transition moments for the $A^2\Sigma^+ \leftarrow X^2\Pi$ transition are evaluated using the Wigner-Eckart theorem (Section 2.8). The principle of spectroscopic stability has been used in choosing excited-state basis functions in the SO basis. $\mathcal{M}$ is the one-electron reduced transition moment for the orbital excitation $\pi \leftarrow \sigma$,

$$\mathcal{M} = \langle \pi||m^1||\sigma\rangle$$

(9.13)

The applicable transition moment matrix elements are

$$\langle ^2\Sigma^+_1/2 \pm \frac{1}{2}||m_{z1}||^2\Pi_{3/2} \mp \frac{1}{2}\rangle = \frac{1}{\sqrt{3}} \mathcal{M}$$

$$\langle ^2\Sigma^+_1/2 \pm \frac{1}{2}||m_{z1}||^2\Pi_{1/2} \mp \frac{1}{2}\rangle = \mp \frac{1}{\sqrt{3}} \mathcal{M}$$

(9.14)

### Table 9.5: Transition moments for the $A^2\Sigma^+ \leftarrow X^2\Pi_\sigma$ SO-CF transition of OH/NG and SH/NG.

| $m_{z1}$ | $|^2\Pi_{\frac{1}{2}} - \frac{1}{2}\rangle$ | $|^2\Pi_{\frac{1}{2}} + \frac{1}{2}\rangle$ | $|^2\Pi_{\frac{3}{2}} - \frac{1}{2}\rangle$ | $|^2\Pi_{\frac{3}{2}} + \frac{1}{2}\rangle$ |
|-----------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|
| $^2\Sigma^+_1/2 - \frac{1}{2}$ | $\frac{1}{\sqrt{3}} \alpha \mathcal{M}$ | 0 | $-\frac{1}{\sqrt{3}} \beta \mathcal{M}$ | 0 |
| $^2\Sigma^+_1/2 + \frac{1}{2}$ | 0 | $\frac{1}{\sqrt{3}} \beta \mathcal{M}$ | 0 | $-\frac{1}{\sqrt{3}} \alpha \mathcal{M}$ |
| $m_{-1}$ | $|^2\Pi_{\frac{1}{2}} - \frac{1}{2}\rangle$ | $|^2\Pi_{\frac{1}{2}} + \frac{1}{2}\rangle$ | $|^2\Pi_{\frac{3}{2}} - \frac{1}{2}\rangle$ | $|^2\Pi_{\frac{3}{2}} + \frac{1}{2}\rangle$ |
| $^2\Sigma^+_1/2 - \frac{1}{2}$ | $\frac{1}{\sqrt{3}} \beta \mathcal{M}$ | 0 | $\frac{1}{\sqrt{3}} \alpha \mathcal{M}$ | 0 |
| $^2\Sigma^+_1/2 + \frac{1}{2}$ | 0 | $\frac{1}{\sqrt{3}} \alpha \mathcal{M}$ | 0 | $\frac{1}{\sqrt{3}} \beta \mathcal{M}$ |
Table 9.6: Transition moments for the $A^2\Sigma^+ \leftrightarrow X^2\Pi_e$ transition of OH/NG and SH/NG.

| $m_{\pm 1}$ | $|^2\Pi_L ->\rangle$ | $|^2\Pi_L +\rangle$ | $|^2\Pi_e ->\rangle$ | $|^2\Pi_e +\rangle$ |
|-------------|------------------------|------------------------|------------------------|------------------------|
| $\langle \Sigma^+/2 - \frac{1}{2} \rangle$ | $\frac{1}{\sqrt{2}} a \cdot a \cdot M$ | $\frac{1}{\sqrt{2}} b \cdot a \cdot M$ | $-\frac{1}{\sqrt{2}} a \cdot b \cdot M$ | $-\frac{1}{\sqrt{2}} b \cdot b \cdot M$ |
| $\langle \Sigma^+/2 + \frac{1}{2} \rangle$ | $-\frac{1}{\sqrt{2}} b \cdot b \cdot M$ | $\frac{1}{\sqrt{2}} a \cdot \beta \cdot M$ | $\frac{1}{\sqrt{2}} b \cdot \alpha \cdot M$ | $\frac{1}{\sqrt{2}} a \cdot \alpha \cdot M$ |
| $\langle \Sigma^+/-2 \rangle$ | $\frac{1}{\sqrt{2}} a \cdot \beta \cdot M$ | $\frac{1}{\sqrt{2}} b \cdot \beta \cdot M$ | $\frac{1}{\sqrt{2}} a \cdot \alpha \cdot M$ | $\frac{1}{\sqrt{2}} b \cdot \alpha \cdot M$ |
| $\langle \Sigma^+/2 + \frac{1}{2} \rangle$ | $-\frac{1}{\sqrt{2}} b \cdot a \cdot M$ | $\frac{1}{\sqrt{2}} b \cdot \alpha \cdot M$ | $-\frac{1}{\sqrt{2}} b \cdot b \cdot M$ | $\frac{1}{\sqrt{2}} a \cdot \beta \cdot M$ |

Tables 9.5 and 9.6 give expressions for transition moments arising from the $X^2\Pi_e$ SO-CF states of OH/NG and SH/NG.

9.1.5 Moment Analysis

The analysis of any experimental data involves the taking of ratios of the various MCD and absorption moments (Section 4.2). For this purpose, theoretical moment expressions need to be derived. Initially this is restricted to the zeroth moments $A_0$ and $C_0$, where $C_0$ is the $c$-term contribution to the overall MCD zeroth moment. This overall MCD zeroth moment is the sum of $C_0$ and $B_0$, the $\beta$-term contribution, which will be treated later by the application of non-degenerate perturbation theory.

9.1.5.1 $A_0$ and $C_0$

Start by considering a molecule oriented at angle $\theta$ with respect to the field.

Using Eqs. (4.15) and (4.16), the expressions for $A_0^\theta$ and $C_0^\theta$ for the allowed transition from the Zeeman eigenstates ($\pm$) within each $^2\Pi_\sigma$ level to the $A^2\Sigma^+$ state, are given by

$$A_0^\theta(2\Sigma^+ \leftrightarrow 2\Pi_\sigma \pm) = \frac{\gamma(1 + \cos^2\theta)}{4} \sum_{\Omega} P_{\sigma}(\pm) |\langle 2\Sigma^+ \Omega | 2\Pi_{\sigma \pm} \rangle|^2$$

$$+ |\langle 2\Sigma^+ \Omega | 2\Pi_{\sigma \pm} \rangle|^2$$

(9.15)

$$C_0^\theta(2\Sigma^+ \leftrightarrow 2\Pi_\sigma \pm) = \gamma \cos \theta \sum_{\Omega} P_{\sigma}(\pm) (|\langle 2\Sigma^+ \Omega | 2\Pi_{\sigma \pm} \rangle|^2 - |\langle 2\Sigma^+ \Omega | 2\Pi_{\sigma \pm} \rangle|^2)$$

(9.16)

As before the superscripts $\theta$ indicate that the moment is specified for a particular orientation of the molecule with respect to the field axis (Z). The population factors
$P_{\sigma}(\pm)$ depend on the relative populations of the $^3\Pi_\sigma$ levels; they vary with $g_\parallel^0$ and $g_\perp$ as well as the magnetic field strength and temperature:

\[
P_{\sigma}(\pm) = \frac{1}{Q} \exp\left(\frac{g_\theta^+ \mu_B B}{2kT}\right) \exp(\Delta/2kT) \]
\[
P_{\pi}(\pm) = \frac{1}{Q} \exp\left(\frac{g_\theta^- \mu_B B}{2kT}\right) \exp(-\Delta/2kT) \quad (9.17)
\]

$Q$ is the electronic partition function, given by

\[
Q = \left[ \exp\left(-\frac{g_\theta^- \mu_B B}{2kT}\right) + \exp\left(\frac{g_\theta^+ \mu_B B}{2kT}\right) \right] \exp(\Delta/2kT) + \\
\left[ \exp\left(-\frac{g_\theta^+ \mu_B B}{2kT}\right) + \exp\left(\frac{g_\theta^- \mu_B B}{2kT}\right) \right] \exp(-\Delta/2kT) \\
= 2\cosh\left(\frac{g_\theta^\pm \mu_B B}{2kT}\right) \exp(\Delta/2kT) + 2\cosh\left(\frac{g_\theta^\mp \mu_B B}{2kT}\right) \exp(-\Delta/2kT) \quad (9.18)
\]

The absorption and MCD zeroth moments for the $A^2\Sigma^+ \leftarrow X^2\Pi_\perp$ transition are readily calculated using Eqs. (9.15) to (9.18).

\[
A_0^0(2\Sigma^+ \leftarrow 2\Pi) = \frac{\gamma}{8} \left(1 + \cos^2 \theta \right) \mathcal{M}^2 
\]
\[
C_0^0(2\Sigma^+ \leftarrow 2\Pi) = \frac{\gamma \kappa \cos^2 \theta \mathcal{M}^2}{Q} \left[ \frac{g_\theta^-}{g_\theta^+} \sinh\left(\frac{g_\theta^- \mu_B B}{2kT}\right) \exp(\Delta/2kT) - \\
\frac{g_\theta^+}{g_\theta^-} \sinh\left(\frac{g_\theta^+ \mu_B B}{2kT}\right) \exp(-\Delta/2kT) \right] 
\]

Therefore, the transition $A^2\Sigma^+ \leftarrow X^2\Pi$ has positive MCD, which is observed by experiment.

9.1.5.2 $B_0$

The $\beta$-term contribution to $M_0$ is considered by treating the magnetic-field-induced mixing of $^3\Pi_\perp$ and $^3\Pi_\perp$ by perturbation theory. This treatment assumes that the mixing of these levels is small compared to the first-order Zeeman effect, and that
Hydroxyl (OH) and Mercapto (SH)

contributions from mixing with other terms are insignificant due to the large energy separations.

The field-induced perturbation modifies the Zeeman eigenfunctions \( |^3 \Pi_\sigma \pm \rangle \) of Eq. (9.11) which become

\[
| ^3 \Pi_\sigma \pm \rangle = | ^3 \Pi_\sigma \pm \rangle^0 + | ^3 \Pi_\sigma \pm \rangle'
\]  

(9.21)

where the \( ^0 \) and \( ' \) respectively denote the states in the absence of the perturbation, and the correction for the perturbation. \( \beta \) terms arise from the second term of Eq. (9.21), which can be expanded as

\[
| ^3 \Pi_\pm \rangle' = -\frac{\mu_B}{A} \sum_{\nu=\pm} | ^3 \Pi_\nu \rangle_0 \langle ^3 \Pi_\nu | L_2 + 2S_2 | ^3 \Pi_\pm \rangle_0
\]

(9.22)

where \( \nu \) labels the upper and lower Zeeman eigenfunctions of Eq. (9.11). These can be converted into \( \theta \)-dependent form by using Eq. (3.65). The necessary Zeeman matrix elements are calculated using Table 9.3 and Eq. (9.11).

\[
| ^3 \Pi_\pm \rangle' = -\frac{\mu_B}{A} \left[ (\cos \theta a_{\pm} g_{\pm} + 2\sin \theta b_{\pm} \kappa) | ^3 \Pi_\pm \rangle_0 \pm (\cos \theta b_{\pm} g_{\pm} - 2\sin \theta a_{\pm} \kappa) | ^3 \Pi_\mp \rangle_0 \right]
\]

(9.23)

Transition moments from these corrected functions are derived in exactly the same manner as before. The total transition moments are combined with the unperturbed ones according to Eq. (9.24).

\[
\langle \langle \mathcal{J} m_{\pm \pm} | A \rangle^0 \vert A \rangle^0 \rangle^2 \approx \langle \langle \mathcal{J} m_{\pm \pm} | A \rangle^0 \vert \langle \langle \mathcal{J} m_{\pm \pm} | A \rangle^0 \rangle^* \rangle\]

\[
= \langle \langle \mathcal{J} m_{\pm \pm} | A \rangle^0 \vert \langle \langle \mathcal{J} m_{\pm \pm} | A \rangle^0 \rangle^* \rangle + \langle \langle \mathcal{J} m_{\pm \pm} | A \rangle^0 \vert \langle \langle \mathcal{J} m_{\pm \pm} | A \rangle^0 \rangle^* \rangle
\]

\[
= \langle \langle \mathcal{J} m_{\pm \pm} | A \rangle^0 \vert \langle \langle \mathcal{J} m_{\pm \pm} | A \rangle^0 \rangle^* \rangle + \langle \langle \mathcal{J} m_{\pm \pm} | A \rangle^0 \vert \langle \langle \mathcal{J} m_{\pm \pm} | A \rangle^0 \rangle^* \rangle
\]

(9.24)
$A$ and $J$ are the labels appropriate to the ground and excited states, respectively. The $\Theta$-term contribution (for an orientation $\theta$) to the zeroth MCD moment, $B_0^\Theta$, is formed by taking expressions of the form $\cos \theta \left( |m_{+1}|A^2 - |m_{-1}|A^2 \right)$, summing over all non-zero transitions weighted by their ground-state population factors, and multiplying by $\gamma$. Thus, $B_0^\Theta$ is given by

$$B_0^\Theta(2\Sigma^+ \leftarrow 2\Pi) = \frac{\lambda g_1 \cos \theta^2 \mu_B B}{2 \Omega A} \left[ \cosh \left( \frac{g_\theta^+ \mu_B B}{2kT} \right) \exp(\Delta/2kT) - \cosh \left( \frac{g_\theta^- \mu_B B}{2kT} \right) \exp(-\Delta/2kT) \right]$$

(9.25)

Note here that, in contrast to CH/NG, the $\Theta$ terms have the *same* sign as the $\Sigma$ terms. This difference is best seen by comparing this $2\Sigma^+ \leftarrow 2\Pi$ transition with the corresponding transition of CH. In both cases the $\Theta$ terms are positive. The difference arises from the sign of the $\Sigma$ terms, which depends on the polarisation of the transition from the lowest SO-CF level. Note that this all stems from the inverted nature of the SO-CF wavefunctions in Eq. (9.3) compared with Eq. (7.3).

### 9.1.5.3 Moment ratios

In order to fit experimental data to the SO-CF theoretical model, $B_0^\Theta$, $C_0^\Theta$ and $A_0^\Theta$ must be averaged over $\theta$ as outlined in Section 4.2, followed by the taking of appropriate ratios.

$$\frac{C_0(2\Sigma^+ \leftarrow 2\Pi)}{A_0(2\Sigma^+ \leftarrow 2\Pi)} = 3\kappa \left[ \exp(\Delta/2kT) \int_0^1 \frac{1}{Q} \frac{g_\pi^- \cos^2 \theta}{g_\pi^+} \sinh \left( \frac{g_\theta^+ \mu_B B}{2kT} \right) d\cos \theta - \exp(-\Delta/2kT) \int_0^1 \frac{1}{Q} \frac{g_\pi^+ \cos^2 \theta}{g_\pi^-} \sinh \left( \frac{g_\theta^- \mu_B B}{2kT} \right) d\cos \theta \right]$$

(9.26)
Hydroxyl (OH) and Mercapto (SH)

\[ \frac{B_0(2\Sigma^+ \leftarrow 2\Pi)}{A_0(2\Sigma^+ \leftarrow 2\Pi)} = \frac{3\mu_B B}{A} \exp(\Delta/2kT) \int_0^{\frac{\pi}{2}} \frac{1}{Q} (g_\perp \cos \theta)^2 \cosh \left( \frac{g_\perp \mu_B B}{2kT} \right) d\cos \theta - \exp(-\Delta/2kT) \int_0^{\frac{\pi}{2}} \frac{1}{Q} (g_\perp \cos \theta)^2 \cosh \left( \frac{g_\perp \mu_B B}{2kT} \right) d\cos \theta \]

(9.27)

These expressions can be simplified when only the \(^2\Pi_1\) level is significantly populated. In such a situation, \(P_\perp(\pm) = 0\), and \(Q\) (Eq. (9.18)) simplifies to

\[ Q = 2\cosh \left( \frac{g_\perp \mu_B B}{2kT} \right) \exp(\Delta/2kT) \]

(9.28)

Eqs. (9.20) and (9.25) can be rewritten to give

\[ C_0\left(\Sigma^+ \leftarrow \Pi\right) = \frac{\gamma \kappa g_\perp \cos^2 \theta |\mathcal{M}|^2}{2g_\perp \tanh \left( \frac{g_\perp \mu_B B}{2kT} \right)} \]

(9.29)

\[ B_0\left(\Sigma^+ \leftarrow \Pi\right) = \frac{\gamma |g_\perp \cos \theta|^2 \mu_B B |\mathcal{M}|^2}{4A} \]

(9.30)

Eqs. (9.26) and (9.27) now reduce to

\[ \frac{C_0(2\Sigma^+ \leftarrow 2\Pi)}{A_0(2\Sigma^+ \leftarrow 4\Pi)} = 3\kappa \int_0^{\frac{\pi}{2}} \frac{g_\perp \cos^2 \theta}{g_\perp \tanh \left( \frac{g_\perp \mu_B B}{2kT} \right)} d\cos \theta \]

(9.31)

\[ \frac{B_0(2\Sigma^+ \leftarrow 2\Pi)}{A_0(2\Sigma^+ \leftarrow 4\Pi)} = \frac{g_\perp^2 \mu_B B}{2A} \]

(9.32)

### 9.2 Experimental

Preliminary matrix depositions were carried out using the He-refrigerator/electromagnet system, described in Section 6.2.1. Matrices successfully investigated using the matrix-injection system are given in Table 9.7, along with their deposition times. The matrix-injection system is described in Section 6.2.2, and the matrix preparation technique is described in Section 6.1. Flow rates were \~2-3
mmol hr$^{-1}$ and the sapphire window held at $\sim$20 K.

Table 9.7: Deposition and spectroscopic scan conditions for successful OH/NG and SH/NG experiments using the matrix-injection system. See Chapter 6 for definitions of the terms.

<table>
<thead>
<tr>
<th>Matrix</th>
<th>Deposition time (minutes)</th>
<th>Monochromator wavelength step size (nm)</th>
<th>Monochromator slit width ($\mu$m)*</th>
<th>Number of chopper cycles</th>
</tr>
</thead>
<tbody>
<tr>
<td>OH/Ar</td>
<td>50</td>
<td>0.05</td>
<td>200</td>
<td>40</td>
</tr>
<tr>
<td>OH/Kr</td>
<td>43</td>
<td>0.04</td>
<td>150</td>
<td>10</td>
</tr>
<tr>
<td>SH/Ar</td>
<td>45</td>
<td>0.10</td>
<td>150</td>
<td>20</td>
</tr>
<tr>
<td>SH/Kr</td>
<td>40</td>
<td>0.10</td>
<td>300</td>
<td>20</td>
</tr>
<tr>
<td>SH/Xe</td>
<td>40</td>
<td>0.10</td>
<td>300</td>
<td>20</td>
</tr>
</tbody>
</table>

*100 $\mu$m corresponds to a resolution of $\sim$0.08 nm.

All spectral data were gathered using MOD4 (Section 6.3) in conjunction with a Xe-arc lamp, a 1180-groove/mm grating, and a Hamamatsu R-376 PMT. A Corning 7-54 filter was used to remove stray visible light. The monochromator slit widths, wavelength step size, and the number of chopper cycles per step are given in Table 9.7.

9.3 Results

Spectral data for the allowed $A \ ^3\Sigma^+ \rightarrow X \ ^3\Sigma^-$ transitions of OH/Ar, OH/Kr, OH/Xe, SH/Ar, SH/Kr, and SH/Xe are provided in this section. The yields obtained using the matrix-injection system were mostly lower than those obtained using the refrigerator/electromagnet set-up, but the data were still good enough to perform a full analysis. The yield of OH/Xe was most affected by the problems with the matrix-injection system (Section 1.1), and no field or temperature data could be obtained.

As the atomic number of the noble-gas host atoms increases, there are two notable trends in the absorption data. Firstly, the transitions exhibit red shifts, those for SH being larger than those for OH. These red shifts correspond with previous observations for molecules trapped in noble-gas matrices$^2$ (Section 5.2). Secondly, the overall bandwidths increase, as measured by the function $2\sqrt{A_2/A_0}$.

There is notable site structure in the absorption spectra of OH/Ar and OH/Kr. These sites are labelled 1-5 in the absorption spectra of Figures 9.2 and 9.9. Table 9.8
Hydroxyl (OH) and Mercapto (SH)

gives the positions of these site bands, compared with those measured by Langford for OH/Ar.$^{1,3}$

Table 9.8: Positions of band barycentres and bandwidths for the OH/SH matrices. The data for SH/NG is taken from absorption spectra measured using the helium-refrigerator/electromagnet setup.

<table>
<thead>
<tr>
<th>Matrix</th>
<th>$\bar{E}$ / cm$^{-1}$</th>
<th>$2\sqrt{A_2/A_0}$ / cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>OH/Ar</td>
<td>32170</td>
<td>130</td>
</tr>
<tr>
<td>OH/Kr</td>
<td>32070</td>
<td>210</td>
</tr>
<tr>
<td>OH/Xe</td>
<td>31850</td>
<td>350</td>
</tr>
<tr>
<td>SH/Ar</td>
<td>30400</td>
<td>240</td>
</tr>
<tr>
<td>SH/Kr</td>
<td>30110</td>
<td>300</td>
</tr>
<tr>
<td>SH/Xe</td>
<td>29660</td>
<td>360</td>
</tr>
</tbody>
</table>

Table 9.9: Band energies (in cm$^{-1}$) for the $A^2\Sigma^+ \leftrightarrow X^2\Sigma$ systems of OH/Ar and OH/Kr.

<table>
<thead>
<tr>
<th>Band number</th>
<th>OH/Ar</th>
<th>OH/Kr</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Langford$^{1,3}$</td>
<td>This work</td>
</tr>
<tr>
<td>1</td>
<td>32 025</td>
<td>32035</td>
</tr>
<tr>
<td>2</td>
<td>32 095</td>
<td>32115</td>
</tr>
<tr>
<td>3</td>
<td>32 165</td>
<td>32175</td>
</tr>
<tr>
<td>4</td>
<td>32 230</td>
<td>32230</td>
</tr>
<tr>
<td>5</td>
<td>32 285</td>
<td>32280</td>
</tr>
</tbody>
</table>

The MCD spectra that follow share a number of common features. They all have dispersion similar to that reported for OH/Ar by Langford,$^{1,3}$ and Rose.$^4$ Each comprises a positive $C_2$ term which exhibits saturation with respect to (increasing) magnetic field and (decreasing) temperature.

9.3.1 Hydroxyl (OH)

9.3.1.1 OH/Ar

Langford's original work included absorption and MCD data on OH/Ar.$^{1,3}$ However, data collected as part of the current research on a small amount of OH contamination in a SH/Ar matrix cast doubts on the earlier experimental results. It was therefore decided to investigate OH/Ar again, collecting more data than Langford obtained. A representative selection of magnetic-field- and temperature-dependent MCD spectra is shown in Figures 9.2 to 9.8. No significant temperature-dependence was observed in the absorption spectrum.
Figure 9.2: Absorption and temperature-dependent MCD (1 T) spectra of the (0,0) band of the \( \text{A} \ 2\Sigma^+ \leftarrow \chi \ 3\Pi \) transition of OH/Ar. The numbers 1-5 identify the five absorption bands attributed to different sites.

Figure 9.3: Temperature-dependent MCD (3 T) spectra of the (0,0) band of the \( \text{A} \ 2\Sigma^+ \leftarrow \chi \ 3\Pi \) transition of OH/Ar.
Figure 9.4: Temperature-dependent MCD (5 T) spectra of the (0,0) band of the $A^2\Sigma^+ \leftarrow X^2\Pi$ transition of OH/Ar.

Figure 9.5: Magnetic-field-dependent MCD (1.58 K) spectra of the (0,0) band of the $A^2\Sigma^+ \leftarrow X^2\Pi$ transition of OH/Ar.
Figure 9.6: Magnetic-field-dependent MCD (2.30 K) spectra of the (0,0) band of the $A^2\Sigma^+ \leftarrow X^2\Pi$ transition of OH/Ar.

Figure 9.7: Magnetic-field-dependent MCD (4.22 K) spectra of the (0,0) band of the $A^2\Sigma^+ \leftarrow X^2\Pi$ transition of OH/Ar.
Hydroxyl (OH) and Mercapto (SH)

Figure 9.8: Magnetic-field-dependent MCD (13.0 K) spectra of the (0,0) band of the $A \, ^2\Sigma^+ \leftarrow X \, ^2\Pi$ transition of OH/Ar.

9.3.1.2 OH/Kr

These data were collected near the conclusion of the first helium run, when the supply of liquid helium was nearing exhaustion. It was also thought that a similar number of spectra to those Langford recorded for OH/Ar would be enough for a complete analysis. About 15 spectra were measured for each of the (0,0) and (1,0) bands of the $A \, ^2\Sigma^+ \leftarrow X \, ^2\Pi$ transition of OH/Kr. With the benefit of hindsight, it would have been wiser to take more data concentrated solely on the (0,0) band.

A small leak, undetectable using standard ethanol leak-testing techniques, was later found in the needle valve by employing a helium leak detector. The sample used to prepare the matrix would therefore have been contaminated by a small amount of air. It is unknown whether this had any significant effect on the data collected.

The absorption data exhibited a small degree of magnetic-field and temperature dependence; however insufficient data were collected to perform a comprehensive study. Magnetic-field- and temperature-dependent MCD spectra are shown in Figures 9.9 to 9.12. The response of the spectrometer decreases into the UV, hence the S/N of the (1,0) band is considerably poorer than the (0,0) band.
Figure 9.9: Averaged absorption and temperature-dependent MCD (1 T) spectra of the (0,0) band of the $A^2\Sigma^+ \leftrightarrow X^2\Pi$ transition of OH/Kr. The numbers 1-5 identify the five absorption bands attributed to different sites.

Figure 9.10: Magnetic-field-dependent MCD (1.62-1.69 K) spectra of the (0,0) band of the $A^2\Sigma^+ \leftrightarrow X^2\Pi$ transition of OH/Kr.
Figure 9.11: Averaged absorption and temperature-dependent MCD (1 Tesla) spectra of the (1,0) band of the $A^2\Sigma^+ \leftarrow X^2\Pi$ transition of OH/Kr. The numbers 1-5 identify the five absorption bands attributed to different sites.

Figure 9.12: Magnetic-field-dependent MCD (1.63 K) spectra of the (1,0) band of the $A^2\Sigma^+ \leftarrow X^2\Pi$ transition of OH/Kr.
9.3.1.3 OH/Xe

OH/Xe could be formed using the He-refrigerator/electromagnet system, but the yield was somewhat small. Frustratingly, a matrix failed to form at least five times using the matrix-injection system. Therefore, this section contains only spectra obtained on the former system. The absorption and corresponding MCD spectrum of the (0,0) band of the $A^2\Sigma^+ \leftarrow X^2\Pi$ transition of OH/Xe at 0.64 tesla and 11 K are given in Figure 9.13.

![Absorption and MCD spectra](image)

Figure 9.13: Absorption and MCD spectra (0.64 tesla) of the (0,0) band of the $A^2\Sigma^+ \leftarrow X^2\Pi$ transition of OH/Xe using the refrigerator/electromagnet set-up.

9.3.2 Mercapto (SH)

9.3.2.1 SH/Ar

These data were collected during the first helium run, when it was thought that a similar number of spectra to those Langford recorded for OH/Ar would be enough for a complete analysis. Only 15 spectra at different fields and temperatures were measured for the (0,0) band of the $A^2\Sigma^+ \leftarrow X^2\Pi$ transition of SH/Ar. With the benefit of hindsight, it would have been wiser to take much more data.

The yield of SH/Ar obtained on the matrix-injection system was lower than
that obtained while using the refrigerator/electromagnet set-up, but adequate MCD data were still obtained. Figure 9.14 gives a comparison of the yields by way of the relative absorption intensities of the \( A^2\Sigma^+ \leftarrow X^2\Pi \) transition in both cases.

It was found that NH and OH were also obtained in the SH/Ar matrix, and that the (0,0) band of the OH \( A^2\Sigma^+ \leftarrow X^2\Pi \) transition obscured the (1,0) band of the SH \( A^2\Sigma^+ \leftarrow X^2\Pi \) transition. A small leak, undetectable using standard ethanol leak testing techniques, was later found in the needle valve by employing a helium leak detector. Air contamination of the sample is therefore the most likely reason for NH and OH being produced in the discharge process. Also, this is possibly the reason why the band barycentre has shifted ever so slightly to the red from its previous position measured using the refrigerator/electromagnet system (Figure 9.14). It is possible that the data collected may be adversely affected.

Magnetic-field- and temperature-dependent MCD spectra are shown in Figures 9.15 and 9.16.

---

**Figure 9.14:** Absorption spectra of the (0,0) band of the \( A^2\Sigma^+ \leftarrow X^2\Pi \) transition of SH/Ar using the matrix-injection system (bottom), and the refrigerator/electromagnet set-up (top).
Hydroxyl (OH) and Mercapto (SH)

**Figure 9.15:** Temperature-dependent MCD (1 T) spectra of the (0,0) band of the $A^2\Sigma^+ \leftarrow X^2\Pi$ transition of SH/Ar.

**Figure 9.16:** Magnetic-field-dependent MCD (1.69 K) spectra of the (0,0) band of the $A^2\Sigma^+ \leftarrow X^2\Pi$ transition of SH/Ar.
9.3.2.2 **SH/Kr**

A great deal more spectra on the (0,0) band of the $A^2\Sigma^+ \leftarrow X^2\Pi$ transition of SH/Kr were recorded than SH/Ar. The yield of SH/Kr obtained on the matrix-injection system was lower than that obtained while using the refrigerator/electromagnet set-up, but adequate MCD data were still obtained. Figure 9.17 gives a comparison of the yields by way of the relative absorption intensities of the $A^2\Sigma^+ \leftarrow X^2\Pi$ transition in both cases.

Some minor temperature and field dependence of the absorption was perceived, but the sloped baseline and poor signal to noise makes this hard to quantify. A representative selection of magnetic-field- and temperature-dependent MCD spectra is shown in Figures 9.18 to 9.25.

![Graph showing absorption spectra for SH/Kr comparison](image)

**Figure 9.17:** Absorption spectra of the (0,0) band of the $A^2\Sigma^+ \leftarrow X^2\Pi$ transition of SH/Kr using the matrix-injection system (bottom), and the refrigerator/electromagnet set-up (top).
Figure 9.18: Temperature-dependent MCD (1 T) spectra of the (0,0) band of the $A^2\Sigma^+ \leftarrow X^2\Pi$ transition of SH/Kr.

Figure 9.19: Temperature-dependent MCD (3 T) spectra of the (0,0) band of the $A^2\Sigma^+ \leftarrow X^2\Pi$ transition of SH/Kr.
Figure 9.20: Temperature-dependent MCD (5 T) spectra of the (0,0) band of the $A^2\Sigma^+ \leftarrow X^2\Pi$ transition of SH/Kr.

Figure 9.21: Magnetic-field-dependent MCD (1.37-1.38 K) spectra of the (0,0) band of the $A^2\Sigma^+ \leftarrow X^2\Pi$ transition of SH/Kr.
Hydroxyl (OH) and Mercapto (SH)

Figure 9.22: Magnetic-field-dependent MCD (1.89 K) spectra of the (0,0) band of the $A^2\Sigma^+ \leftarrow X^2\Pi$ transition of SH/Kr.

Figure 9.23: Magnetic-field-dependent MCD (3.00 K) spectra of the (0,0) band of the $A^2\Sigma^+ \leftarrow X^2\Pi$ transition of SH/Kr.
**Hydroxyl (OH) and Mercapto (SH)**

**Figure 9.24:** Magnetic-field-dependent MCD (4.22 K) spectra of the (0,0) band of the $A^2\Sigma^+ \leftarrow X^2\Pi$ transition of SH/Kr.

**Figure 9.25:** Magnetic-field-dependent MCD (21.2-22.0 K) spectra of the (0,0) band of the $A^2\Sigma^+ \leftarrow X^2\Pi$ transition of SH/Kr.
9.3.2.3 **SH/Xe**

A similar number of spectra for the (0,0) band of the $A^2\Sigma^+ \leftarrow X^2\Pi$ transition of SH/Xe were recorded as for SH/Kr. The yield of SH/Xe obtained on the matrix-injection system was lower than that obtained while using the refrigerator/electromagnet set-up, but adequate MCD data were still obtained. Figure 9.26 gives a comparison of the yields by way of the relative absorption intensities of the $A^2\Sigma^+ \leftarrow X^2\Pi$ transition. The quality of the matrix was the worst of all the SH/NG matrices, as indicated by the steep baseline which made base-lining the data all the more difficult. The S/N ratio of the MCD data is poor, meaning that $M_0$ is susceptible to more error.

From the data collected, it was impossible to verify any temperature or field dependence of the absorption. A representative selection of magnetic-field- and temperature-dependent MCD spectra is shown in Figures 9.27 to 9.33.

![Graph showing absorption spectra of SH/Xe](image)

Figure 9.26: Absorption spectra of the (0,0) band of the $A^2\Sigma^+ \leftarrow X^2\Pi$ transition of SH/Xe using the matrix-injection system (bottom), and the refrigerator/electromagnet set-up (top).
Figure 9.27: Temperature-dependent MCD (1 T) spectra of the (0,0) band of the $A^2\Sigma^+ \leftrightarrow X^2\Pi$ transition of SH/Xe.

Figure 9.28: Temperature-dependent MCD (3 T) spectra of the (0,0) band of the $A^2\Sigma^+ \leftrightarrow X^2\Pi$ transition of SH/Xe.
Figure 9.29: Temperature-dependent MCD (5 T) spectra of the (0,0) band of the \( A^2\Sigma^+ \leftarrow X^2\Pi \) transition of SH/Xe.

Figure 9.30: Magnetic-field-dependent MCD (1.39 K) spectra of the (0,0) band of the \( A^2\Sigma^+ \leftarrow X^2\Pi \) transition of SH/Xe.
Figure 9.31: Magnetic-field-dependent MCD (1.90 K) spectra of the (0,0) band of the $A^2\Sigma^+ \leftarrow X^2\Pi$ transition of SH/Xe.

Figure 9.32: Magnetic-field-dependent MCD (3.00 K) spectra of the (0,0) band of the $A^2\Sigma^+ \leftarrow X^2\Pi$ transition of SH/Xe.
9.4 Moment Analysis

Zeroth MCD and absorption moments were obtained over the (0,0) band envelopes of each system by using the computer program MOMENT. Plots of the ratio $M_0/A_0$ are given in Figures 9.34 – 9.44.

The $M_0/A_0$ plots show the temperature and magnetic-field dependence indicative of $C$ terms. In contrast to CH/Kr (Chapter 7), these $C$ terms dominate the $B$ terms more effectively because the lowest SO state for OH and SH is $^2\Pi_{3/2}$, which has a sizeable Zeeman splitting, whereas the lowest for CH is $^2\Pi_{1/2}$, which in the absence of a CF does not split in the presence of a magnetic field. The $M_0/A_0$ plots also show that the moment ratios decrease monotonically to zero at infinite temperature ($1/kT = 0$), due to the $B$ and $C$ terms having the same sign, in complete contrast to CH/Kr (Section 7.4).  

Langford plotted his data for OH/Ar using a ‘reduced’ abscissa of $\mu_B B/2kT$ and found that all of his data appeared to fall on the same curve, irrespective of the temperature or magnetic field strength. From Eqs. (9.31) and (9.32), it can be seen
that this type of behaviour would be expected if the MCD were very strongly dominated by $\mathcal{C}$ terms with negligible $\mathcal{B}$ terms. For the purposes of comparison, and to test this premise, all of the data for the OH/NG and SH/NG systems collected during the current research project are presented in similar plots.

In the cases of OH/Kr and SH/Ar, the data are limited and appear to conform to the same curve, independent of temperature and field; therefore only the plots against $\mu_B B/2kT$ are shown (Figures 9.37 and 9.38). But for SH/Kr and SH/Xe, more extensive data sets were obtained and all of the plots are given.

For all of the plots of $M_0/A_0$ against $\mu_B B/2kT$, the data fall on to 'isomagnetic' curves, which change from one field to another. The fact that the curves move to higher values with increasing field indicates the presence of positive $\mathcal{B}$ terms (of the same sign as the $\mathcal{C}$ terms), which, although weak, are far from negligible. In the case of OH/Ar in Figure 9.36, the data are compared directly with Langford's results, and significant discrepancies are found, both in terms of isomagnetic curves and the fact that all of Langford’s data fall substantially below those obtained in this work. The data obtained for OH contamination in the SH/Ar experiment indicates that this author’s results are reproducible. Possible reasons for the discrepancy with Langford’s will be discussed below.

### 9.4.1 OH/Ar

![Graph](image)

**Figure 9.34:** Temperature-dependence of the moment ratio $M_0/A_0$ as a function of $1/kT$ for the (0,0) band of OH/Ar $A^2\Sigma^+ \leftarrow X^2\Pi$. The curves are fits to all the data using the SO-CF model with unconstrained $\mathcal{X}$ – see Table 9.10.
Figure 9.35: Magnetic-field-dependence data for the moment ratio $M_0/A_0$ as a function of $\mu_B B$ for the (0,0) band of OH/Ar $A^2\Sigma^+ \leftarrow X^2\Pi$. The curves are fits to all the data using the SO-CF model with unconstrained $\kappa$ – see Table 9.10.

Figure 9.36: The moment ratio $M_0/A_0$ as a function of $\mu_B B/2kT$ for OH/Ar $A^2\Sigma^+ \leftarrow X^2\Pi$, with a comparison of data obtained by Langford. The curves are fits to all the data using the SO-CF model with unconstrained $\kappa$ – see Table 9.10. The differences between the isomagnetic curves are due to the presence of $\beta$ terms.

9.4.2 OH/Kr

Figure 9.37: The moment ratio $M_0/A_0$ as a function of $\mu_B B/kT$ for OH/Kr $A^2\Sigma^+ \leftarrow X^2\Pi$. Open circles represent data obtained by varying the temperature at a constant magnetic field of 1 T, while closed circles were obtained by changing the field at 1.64 K. The curve is a fit to all the data using the SO-CF model with unconstrained $\kappa$ – see Table 9.10.
9.4.3 SH/Ar

![Graph showing the moment ratio \( \frac{M_0}{A_0} \) as a function of \( \mu_B B / kT \) for SH/Ar. The graph shows data obtained by varying the temperature at a constant magnetic field of 1.01 T, with open circles representing this data. Closed circles were obtained by changing the field at 1.69 K. The curve is a fit to all the data using the SO-CF model with unconstrained \( \kappa \). See Table 9.10.](image)

**Figure 9.38:** The moment ratio \( \frac{M_0}{A_0} \) as a function of \( \mu_B B / kT \) for SH/Ar \( A^2\Sigma^+ \leftarrow X^2\Pi \). Open circles represent data obtained by varying the temperature at a constant magnetic field of 1.01 T, while closed circles were obtained by changing the field at 1.69 K. The curve is a fit to all the data using the SO-CF model with unconstrained \( \kappa \) — see Table 9.10.

9.4.4 SH/Kr

![Graph showing the moment ratio \( \frac{M_0}{A_0} \) as a function of \( \frac{1}{kT} \) for SH/Kr \( A^2\Sigma^+ \leftarrow X^2\Pi \).](image)

**Figure 9.39:** Temperature-dependence of the moment ratio \( \frac{M_0}{A_0} \) as a function of \( \frac{1}{kT} \) for SH/Kr \( A^2\Sigma^+ \leftarrow X^2\Pi \). The curves are fits to all the data using the SO-CF model with unconstrained \( \kappa \) — see Table 9.10.
Figure 9.40: Magnetic-field-dependence data for the moment ratio $M_0/A_0$ as a function of $\mu_B B$ for SH/Kr $A {^2}\Sigma^+ \leftrightarrow X {^2}\Pi$. The curves are fits to all the data using the SO-CF model with unconstrained $\beta$ – see Table 9.10.

Figure 9.41: The moment ratio $M_0/A_0$ as a function of $\mu_B B/2kT$ for SH/Kr $A {^2}\Sigma^+ \leftrightarrow X {^2}\Pi$. The curves are fits to all the data using the SO-CF model with unconstrained $\beta$ – see Table 9.10. The differences between the isomagnetic curves are due to the presence of $\beta$ terms.
9.4.5 SH/Xe

Figure 9.42: Temperature-dependence of the moment ratio \( \frac{M_0}{A_0} \) as a function of \( \frac{1}{kT} \) for SH/Xe \( A^2 \Sigma^+ \leftarrow X^2 \Pi \). The curves are fits to all the data using the SO-CF model with unconstrained \( \gamma \) – see Table 9.10.

Figure 9.43: Magnetic-field-dependence data for the moment ratio \( \frac{M_0}{A_0} \) as a function of \( \mu_0B \) for SH/Xe \( A^2 \Sigma^+ \leftarrow X^2 \Pi \). The curves are fits to all the data using the SO-CF model with unconstrained \( \gamma \) – see Table 9.10.
9.5 Discussion

9.5.1 SO-CF Model

Fits to the experimental moment ratio data were attempted by employing the non-linear least-squares fitting program MAGPI, which uses the sum of Eqs. (9.26) and (9.27), with the integrals over $\theta$ being evaluated numerically. Ideally, the fitting parameters should be limited to $A_x$ and $V_\pi$. However, when these were the only unconstrained parameters, the fits were found to be rather poor and to produce very low values of both parameters (Table 9.10). (Note that this is not an indication of an error in the program, which was checked very carefully.) The $C$-term contributions, which are responsible for the overall tanh-like (saturation) behaviour, can be readily modelled with sensible values of $A_x$ with $V_\pi$ set to zero. However it turns out that such a fit is highly insensitive to the value of $A_x$. Since the $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ levels remain unmixed in the absence of CF interactions, the effects of changing $A_x$ are seen only at temperatures sufficiently high that the upper $^2\Pi_{1/2}$ level starts to take on an appreciable population, that is for $A_x \lesssim 10 \text{ cm}^{-1}$ at the temperatures used in these experiments. The problem occurs when attempting to account for the $B$ term contributions, which cause the divergence of the isomagnetic curves seen in Figures 9.36, 9.41 and 9.44. In order to model the divergence, $V_\pi$ must be increased, but this
Hydroxyl (OH) and Mercapto (SH)

causes a reduction in $k$, which, in turn, reduces the magnitude of the $\Theta$-term contribution. Furthermore, since $\Delta$ increases with $V_\pi$, the $\Theta$ terms do not increase as rapidly as one might expect. The counter-intuitive consequence of these interactions is that both $A_\pi$ and $V_\pi$ take optimum values that are much lower than one might reasonably expect on the basis of the value of $A_\pi$ for the gas phase radical$^5$ (139.21 and 376.9 cm$^{-1}$ for OH and SH, respectively) and the CF parameters found for the $\Pi$ terms of CH and NH trapped in noble-gas matrices (typically $\sim$ 50 – 100 cm$^{-1}$).

In order to introduce an additional degree of freedom and to also allow for a possible error that could have contributed to the discrepancies between Langford’s data and those presented here for OH/Ar, an ad-hoc scaling parameter $\mathcal{K}$ was introduced to give

$$M_0/A_0 = \mathcal{K} (C_0 + B_0)/A_0$$

(9.33)

When $\mathcal{K}$ was unconstrained (along with $A_\pi$ with $V_\pi$) vastly better fits could be achieved with the fitting parameters listed on the right of Table 9.10. The corresponding calculated curves are the ones superimposed on the $M_0/A_0$ data in Figures 9.34 – 9.44. Once again $A_\pi$ with $V_\pi$ are still returned with remarkably small values. Interestingly, however, the parameters obtained by applying this modified model to Langford’s OH/Ar data and the experiments conducted as part of this research are now in close agreement except that the $\mathcal{K}$ values differ by a factor of $\sim$1.36.

<table>
<thead>
<tr>
<th>XH/NG</th>
<th>$\mathcal{K}$ constrained</th>
<th>$\mathcal{K}$ unconstrained</th>
</tr>
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<tr>
<td>OH/Ar$^1,3$ (Langford’s data)</td>
<td>$A_\pi$/cm$^{-1}$</td>
<td>$V_\pi$/cm$^{-1}$</td>
</tr>
<tr>
<td>OH/Ar</td>
<td>7.0±2.6</td>
<td>3.8±1.2</td>
</tr>
<tr>
<td>OH/Kr</td>
<td>3.4±0.6</td>
<td>4.1±0.3</td>
</tr>
<tr>
<td>SH/Ar</td>
<td>3.4±0.8</td>
<td>4.1±0.5</td>
</tr>
<tr>
<td>SH/Kr</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>SH/Xe</td>
<td>4.1±1.2</td>
<td>7.4±1.1</td>
</tr>
</tbody>
</table>

*No fit achievable
Putting aside, for the moment, concerns about the low values of $A_n$ and $V_n$, the differences between Langford's results and the ones found here will now be considered. Langford's approach was to assume, on the basis of the relatively large SOC constant for gas-phase OH (139.21 cm$^{-1}$), that the population of the upper SO-CF level of the $^2\Pi$ term was negligible due to the large energy difference, and he therefore utilised Eqs. (9.31) and (9.32). Also due to the large energy difference, he expected the $\beta$ terms to be small in comparison with the experimental uncertainty of the moment analysis. Although the latter assumption appears reasonable from an inspection of Langford's data, it is clear from the work in this thesis that insufficient data were collected to actually verify whether or not $\beta$ terms were significant. The results in this work indicate that, although small, they can not be ignored.

Using MAGPI, which explicitly considers both SO levels of the $^2\Pi$ term and includes all $\beta$ terms, fits to Langford's data produce the same low values for $A_n$ and $V_n$. The question then arises as to what has caused the differences between his data and the ones presented in this thesis. The current author has inspected Langford's results from raw data through all aspects of his analysis, and there appear to be no errors. One possibility is that there has been a change in the instrumental calibration, which would simply account for the factor of 1.36 difference between the best-fit $\chi$ values for OH/Ar in Table 9.10. However, tests performed at regular intervals over many years have shown the MOD4 calibration is very stable, so such an explanation is very unlikely. It therefore appears that the discrepancies reveal some fundamental difference between the samples.

It is possible that these differences arise from experimental technique. It has recently been shown$^6$ that a tesla-coil discharge of a 1:100 mixture of H$_2$O and Ar produces appreciable amounts of H$_2$O dimers and trimers, and H$_2$O$\cdot$HO, all held together by strong hydrogen bonds, as well as HO$_2$. It is possible that this author's H$_2$O/Ar mixture, the deposition conditions, and the technique were different from Langford's, resulting in the differing experimental results. One would expect that the species H$_2$O$\cdot$HO/Ar would absorb at a different wavelength than OH/Ar, but quantum-mechanical calculations need to be performed to verify this. This could possibly be the reason why there is such distinct site structure. Further structure could perhaps be due to (H$_2$O)$_2$$\cdot$HO, although there was no evidence for this in Langford's study.$^6$ In future, it might be wise to use lower H$_2$O:NG ratios to produce the matrices.
because the amount of $\text{H}_2\text{O}$$\cdot\text{OH}$ produced is lowered with decreasing $\text{H}_2\text{O}$ concentrations. Another possibility is that some of the OH radicals are preferentially oriented within the matrix (in the presence of the magnetic field). This would lead to an increase in $\text{M}_0/\text{A}_0$, but would be very difficult to verify experimentally.

Despite the very good fits that can be obtained for $A_x$ and $V_n$, these seem completely unreasonable in comparison with the results for the systems described in chapters 7 and 8. It can only be concluded that the SO-CF model is entirely inappropriate to the OH and SH samples obtained in this work. The reasons why are not known at present, but they might indicate very strong interactions of the guest species, perhaps involving preferential clustering with undissociated precursor molecules.

### 9.5.2 Hindered-Rotor Model

The failings of the SO-CF model suggest that that simulations performed for the hindered-rotor case might be more appropriate. Firstly, however, simulations will be performed assuming that the ground state is a free rotor.

As outlined in Section 3.4.4, the Hund’s case-(a) basis functions for the excited state of OH/SH are

$$\left| ^2\Sigma_{1/2}^+ J M p^\pm \right> = \frac{1}{\sqrt{2}} \left( |0 \frac{1}{2}, J \frac{1}{2} M \rangle \pm |0 \frac{1}{2}, J \frac{1}{2} M \rangle \right)$$

while the basis functions for the $^2\Pi$ ground-state term are

$$\left| ^2\Pi_{1/2} J M p^\pm \right> = \frac{1}{\sqrt{2}} \left( |1 \frac{1}{2}, J \frac{1}{2} M \rangle \pm |1 \frac{1}{2}, J -\frac{1}{2} M \rangle \right)$$

$$\left| ^2\Pi_{3/2} J M p^\pm \right> = \frac{1}{\sqrt{2}} \left( |1 \frac{3}{2}, J \frac{1}{2} M \rangle \pm |1 \frac{3}{2}, J -\frac{1}{2} M \rangle \right)$$

In order to simulate $\text{M}_0/\text{A}_0$, only the matrix for the $^2\Pi$ ground state, containing rotational (Section 3.4.4), Zeeman (Section 3.4.5) and, if required, crystal-field (Section 5.4.1) matrix elements, needs to be diagonalised. Due to the principle of spectroscopic stability (Section 4.2), the excited-state Hund’s case-(a) basis functions can be used to calculate transition moments. The necessary Zeeman matrix elements are given in Tables 9.11 and 9.12.
Hydroxyl (OH) and Mercapto (SH)

Table 9.11: J-diagonal Zeeman matrix elements for the $^2\Pi$ ground state of OH/SH.

<table>
<thead>
<tr>
<th>$\mathcal{K}_B$</th>
<th>$^2\Pi_{1/2} J M p^\pm$</th>
<th>$^2\Pi_{3/2} J M p^\pm$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\langle ^2\Pi_{1/2} J M p^\pm</td>
<td>\mathcal{K}_B</td>
<td>^2\Pi_{3/2} J M p^\pm \rangle$</td>
</tr>
</tbody>
</table>

Table 9.12: Non-J-diagonal Zeeman matrix elements for the $^2\Pi$ ground state of OH/SH.

| $\mathcal{K}_B | ^2\Pi_{3/2} J M p^\pm | ^2\Pi_{3/2} J M p^\pm \rangle$ | $\frac{2\mu_0 B}{J+1} \left\{ \frac{(J+\frac{3}{2}) (J-\frac{1}{2}) (J+1-M) (J+1+M)}{(2J+1)(2J+3)} \right\}^{1/2}$ |
|-----------------|----------------|----------------|
| $\langle ^2\Pi_{1/2} J M p^\pm | \mathcal{K}_B | ^2\Pi_{3/2} J M p^\pm \rangle$ | $-\frac{\mu_0 B}{J+1} \left\{ \frac{(J+\frac{3}{2}) (J-\frac{1}{2}) (J+1-M) (J+1+M)}{(2J+1)(2J+3)} \right\}^{1/2}$ |
| $\langle ^2\Pi_{3/2} J M p^\pm | \mathcal{K}_B | ^2\Pi_{1/2} J M p^\pm \rangle$ | $\frac{\mu_0 B}{J+1} \left\{ \frac{(J+\frac{3}{2}) (J-\frac{1}{2}) (J+1-M) (J+1+M)}{(2J+1)(2J+3)} \right\}^{1/2}$ |

A Fortran computer program called OHDIAG.F was utilised to obtain the eigenfunctions and eigenvalues for OH and SH using a sufficiently large basis set of Hund's case-(a) functions. Gas-phase molecular parameters were used:

$A_e = 139.21$ cm$^{-1}$ and $B_{e,0}(X^2\Pi) = 18.910$ cm$^{-1}$ for OH; and $A_e = 376.9$ cm$^{-1}$ and $B_{e,0}(X^2\Pi) = 9.461$ cm$^{-1}$ for SH. The program calculates line strengths (Section 3.4.6) at any given temperature or magnetic-field strength, for left and right circularly polarised radiation, between allowed rotational levels, weighted by the population factors of the ground levels. The average line strength gives $A_0$, whereas $M_0$ is the difference of lcp and rcp line strengths.

More so than the free-rotor simulations for CR, NH, and PH, the $A_0$ values for OH and SH exhibit noticeable increases in the presence of a magnetic field. For example at 1.4 K and 5.00 T, $A_0$ is increased by 8% relative to the value at zero field. This field dependence gradually reduces as the temperature is raised. Furthermore, there are essentially no $\delta$ terms, and plots of $M_0/A_0$ against $\mu_0 B/2kT$ for free-rotor OH and SH (Figure 9.45) indicate that if MCD experiments were performed on these, it would be nearly impossible to distinguish between them within experimental uncertainty. This essentially means that $M_0/A_0$ can provide no information on the magnitude of the SOC constant for these systems. Plots of $M_0/A_0$ against $1/kT$ and $\mu_0 B$ for free-rotor OH are given in Figures 9.46 and 9.47. The curves for SH are not shown, but are essentially identical to those for OH.
Figure 9.45: The simulated moment ratio $\frac{M_0}{A_0}$ as a function of $\frac{\mu_B B}{2kT}$ for the $A^2\Sigma^+ \leftarrow X^2\Pi$ transition of free-rotor OH and SH.

Figure 9.46: Simulated temperature-dependence of the moment ratio $\frac{M_0}{A_0}$ as a function of $1/kT$ for free-rotor OH $A^2\Sigma^+ \leftarrow X^2\Pi$. 

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Hydroxyl (OH) and Mercapto (SH)

The essential difference between the free-rotor simulations and the experimentally determined $M_0/A_0$ values is that the free-rotor curves do not saturate fast enough, although they give values of similar magnitude to the experimental ones. Figures 9.48 to 9.52 reproduce a number of experimental $M_0/A_0$ versus $\mu_B B/2kT$ plots from Section 9.4, showing comparisons with free-rotor simulations. The program OHDIAG.F has not yet been extended to simulate absorption and MCD spectra, as has been done for NH (Chapter 8), due to time constraints.

It now proves instructive to perform hindered-rotor simulations of $M_0/A_0$ plots. The program OHDIAG.F can not yet be used to accurately fit the hindered-rotor model to the experimental data until the non-linear least-squares fitting program associated with MAGPI has been converted from BASIC into Fortran. However, it is capable of calculating $M_0/A_0$ ratios for an arbitrary barrier parameter $K$, defined in Eqs. (5.20) and (5.21), using a fourth-order octahedral potential.

The hindered-rotor model lowers $M_0/A_0$ from the free-rotor values, regardless of the sign of the barrier parameter $K$. But as for the free-rotor case there are no significant $\Theta$ terms, due to the fact that all the isomagnetic curves are coincident in the $M_0/A_0$ versus $\mu_B B/2kT$. Also, the plots can provide no information on the magnitude of the SOC constant. Positive values of $K$ can be ruled out because
they cause an increase in the magnetic-field dependence of $A_0$ relative to the free-rotor case. Correspondingly, negative values of $K$ cause this field dependence to reduce. The fact that little or no field dependence is observed experimentally indicates that a negative value for $K$ is more plausible. A negative value for $K$ indicates that the potential is attractive and that the energy minimum occurs when OH or SH is oriented along the direction of nearest noble-gas neighbours.

Figures 9.48 to 9.52 reproduce a number of experimental $M_0/A_0$ versus $\mu_B^B/2kT$ plots from Section 9.4, showing comparisons with hindered-rotor simulations in which the barrier potential has been chosen so that the saturation behaviours can be easily compared. It is important to note that because of its lower ground-state rotational constant, SH is more sensitive to a rotational barrier than OH. The agreements between experiment and simulation are not fantastic, and often the simulation exhibits the wrong saturation behaviour. It is interesting to note that the agreement is better for OH/Kr and SH/Ar, the matrices that were contaminated by small quantities of air. OH/Ar and SH/Xe show the largest differences between calculation and experiment, and SH/Kr more closely agrees with the free-rotor case. In all cases, the rotational model fails to predict the existence of $\beta$ terms, which are clearly evident from the experimental data. Therefore, something is still missing from the hindered-rotor model, possibly involving rotation-translation coupling (Section 5.4.2). It must be emphasised here that for a small diatomic radical, the Hund’s case-(a) basis set should be able to explain the experimental data (because it is a complete set), however the obstacle to this is recognising the interactions between guest and host, and obtaining proper mathematical expressions for them.

**Figure 9.48:** The moment ratio $M_0/A_0$ as a function of $\mu_B^B/2kT$ for OH/Ar $A^2\Sigma^+ \leftarrow X^2\Pi$, compared with simulations for hindered-rotor OH, with barrier parameter $K = -382$ cm$^{-1}$, and free-rotor OH. The experimental data are described in Figure 9.36.
Figure 9.49: The moment ratio $M_0/A_0$ as a function of $\mu B/2kT$ for OH/Kr $A^2\Sigma^+ \leftarrow X^2\Pi$, compared with simulations for hindered-rotor OH, with barrier parameter $K = -382$ cm$^{-1}$, and free-rotor OH. The experimental data are described in Figure 9.37.

Figure 9.50: The moment ratio $M_0/A_0$ as a function of $\mu B/2kT$ for SH/Ar $A^2\Sigma^+ \leftarrow X^2\Pi$, compared with simulations for hindered-rotor SH, with barrier parameter $K = -200$ cm$^{-1}$, and free-rotor SH. The experimental data are described in Figure 9.38.

Figure 9.51: The moment ratio $M_0/A_0$ as a function of $\mu B/2kT$ for SH/Kr $A^2\Sigma^+ \leftarrow X^2\Pi$, compared with a simulation for free-rotor SH. The experimental data are described in Figure 9.41.
Hydroxyl (OH) and Mercapto (SH)

Figure 9.52: The moment ratio $M_0/A_0$ as a function of $\mu_B B/2kT$ for SH/Xe $A^2\Sigma^+ \leftrightarrow X^2\Pi$, compared with simulations for hindered-rotor SH, with barrier parameter $K = -550$ cm$^{-1}$, and free-rotor SH. The experimental data are described in Figure 9.44.

9.6 Conclusions

Absorption and temperature- and magnetic-field-dependent MCD spectra have been obtained for the $A^2\Sigma^+ \leftrightarrow X^2\Pi$ transitions of OH/Ar, OH/Kr, SH/Ar, SH/Kr, and SH/Xe. The MCD spectra are similar to those reported by Langford$^{1,3}$ for OH/Ar. Plots of $M_0/A_0$ clearly indicate the presence of significant $\mathcal{E}$ terms, due to their characteristic temperature and magnetic-field dependence, and also the existence of weak $\mathcal{B}$ terms of the same sign to the $\mathcal{E}$ terms.

Langford's OH/Ar study$^{1,3}$ was repeated and different results were obtained. The reasons for this are unknown but may arise from the formation of strongly hydrogen-bonded OH complexes such as H$_2$O•HO, or orientational effects. Fits to all the data using the MAGPI program yielded unrealistic parameters, suggesting a failure of the SO-CF model for these systems. This could be an indication of strong interactions between the target radicals and undissociated precursor molecules or other fragments of the tesla-coil discharge processes.

A hindered-rotor model incorporating an attractive potential barrier to rotation gives a similar magnitude to experimental plots of $M_0/A_0$, but often the wrong saturation behaviour. This model needs much refinement, possibly extending it to include rotation-translation coupling.
9.7 References


10 Conclusions

This PhD thesis has augmented the work of Dr. Vaughan Langford by presenting the electronic MCD and absorption spectra of CH, NH, OH, PH, and SH isolated in various noble-gas (argon, krypton, and xenon) matrices (XH/NG) at cryogenic temperatures. Attempts to form SiH/NG and CH/Xe matrices failed in preliminary stages, and NH/Xe and OH/Xe failed using the matrix-injection system, most likely due to water contamination.

Attempts were made to interpret the experimental results in terms of a randomly oriented SO-CF model in which orbital angular momentum is partially quenched by CF interactions with neighbouring noble-gas atoms in the matrix. The spectra were quantified using moment analysis with zeroth and first spectroscopic moments and then the resulting data were fitted with parameterised equations derived from group-theoretical and quantum-mechanical considerations of the SO-CF model.

All XHING transitions in this work exhibit red shifts with increasing noble-gas size. These red shifts are in accord with previous observations for molecules trapped in noble-gas matrices and are attributed to the polarisability of the host.5

The most successful aspect of this research comprised the study of the \( A^3\Pi \leftarrow X^3\Sigma^- \) transitions of NH/Kr, NH/N2, PH/Ar, PH/Kr, and PH/Xe. The MCD spectra each comprises a pair of oppositely signed \( \mathcal{E} \) terms giving a (positive) temperature-dependent pseudo-\( \mathcal{E} \) term which exhibits saturation with respect to (increasing) magnetic field and (decreasing) temperature. The data enabled the extraction of SOC constants \( (A_e) \) for the \( A^3\Pi \) terms and ZFS parameters \( (D') \) for the lowest level of the \( X^3\Sigma^- \) terms (see Tables 10.1 and 10.2). The trends in these parameters were explained in terms of motional and external heavy-atom effects. NH/NG exhibits a slight decrease in \( A_e \) on incorporation into Ar, followed by a decrease with heavier noble-gas host that can be attributed to largely mechanical effects. However for PH/NG, there is a significant increase in \( A_e \) on incorporation into Ar, followed by a decrease with heavier host gas, which can be understood in terms of strong overlap between the guest-host orbitals.

For NH/NG and PH/NG, the ZFSs of the lowest \( X^3\Sigma^- \) term are severely quenched. For NH in Ar and Kr, \( D' \) is reduced effectively to zero, consistent with the explanation that NH is a free rotor in its ground state. \( D' \) for NH/N2 is similarly

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quenched by motional effects, although in this case NH is essentially librating. PH/NG exhibits a significant decrease in $D'$ on incorporation into Ar, followed by a further decrease with heavier host gas. Although it is clear that PH is substantially more hindered than NH in noble gases, the trend cannot be interpreted as PH becoming less hindered with heavier host gas because of the greater potential for $D'$ to be quenched by SO effects.

Table 10.1: The trends in $A_\pi$ and $V_\pi$ for the $\Pi$ terms of NH, PH, and CH in the gas-phase and trapped in inert-gas matrices.

<table>
<thead>
<tr>
<th>Matrix</th>
<th>$A_\pi$ / cm$^{-1}$</th>
<th>$V_\pi$ / cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH (gas)$^5$</td>
<td>34.79</td>
<td>–</td>
</tr>
<tr>
<td>NH/Ar</td>
<td>33.5 ± 0.3</td>
<td>~ 75</td>
</tr>
<tr>
<td>NH/Kr</td>
<td>21 ± 2</td>
<td>~ 60</td>
</tr>
<tr>
<td>NH/Xe</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>NH/N$_2$</td>
<td>43.2 ± 0.3</td>
<td>~ 200</td>
</tr>
<tr>
<td>PH (gas)$^6$</td>
<td>115.71</td>
<td>–</td>
</tr>
<tr>
<td>PH/Ar</td>
<td>192 ± 3</td>
<td>undetermined</td>
</tr>
<tr>
<td>PH/Kr</td>
<td>133 ± 3</td>
<td>undetermined</td>
</tr>
<tr>
<td>PH/Xe</td>
<td>107 ± 1</td>
<td>undetermined</td>
</tr>
<tr>
<td>CH (gas)$^7$</td>
<td>31.8</td>
<td>–</td>
</tr>
<tr>
<td>CH/Ar</td>
<td>21 ±1</td>
<td>78 ± 15</td>
</tr>
<tr>
<td>CH/Kr</td>
<td>10.9 ± 0.7</td>
<td>45 ± 6</td>
</tr>
<tr>
<td>CH/Xe</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

All attempts to produce CH/Xe and SiH/NG matrices failed, however data were obtained for the $A^2\Delta \leftarrow X^2\Pi, B^2\Sigma^- \leftarrow X^2\Pi$ and $C^2\Sigma^+ \leftarrow X^2\Pi$ transitions of CH/Kr, although the S/N ratios of the last two were reasonably poor. The MCD spectra are similar to those for CH/Ar,$^1,3$ however in this case the $\epsilon$ terms are weaker and the $\zeta$ term associated with the $A^2\Delta \leftarrow X^2\Pi$ transition is more distinct. Unusually, the $\epsilon$ terms are not dominant and there is clear evidence for the existence of strong $\zeta$ terms of the opposite sign to the $\epsilon$ terms, exactly as predicted from the SO-CF model. $A_\pi$ for the $X^2\Pi$ term of CH/Kr was found to be 10.9 ± 0.7 cm$^{-1}$, the decrease from the value of 21 ±1 cm$^{-1}$ for CH/Ar being attributed to the external heavy-atom effect.
Table 10.2: The trends in $D'$ for the $X^2\Sigma^-$ ground-state terms NH and PH in the gas-phase and trapped in inert-gas matrices. Values for the gas phase are $D$, which is not manifest in the lowest ($J = 1$) rotational level of the term.

<table>
<thead>
<tr>
<th>Matrix</th>
<th>$D'/\text{cm}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH (gas)$^6$</td>
<td>1.67</td>
</tr>
<tr>
<td>NH/Ar</td>
<td>$-0.08 \pm 0.03$</td>
</tr>
<tr>
<td>NH/Kr</td>
<td>$0.01 \pm 0.01$</td>
</tr>
<tr>
<td>NH/Xe</td>
<td>$-0.01 \pm 0.01$</td>
</tr>
<tr>
<td>NH/N$_2$</td>
<td>$0.61 \pm 0.02$</td>
</tr>
<tr>
<td>PH (gas)$^6$</td>
<td>4.42</td>
</tr>
<tr>
<td>PH/Ar</td>
<td>$1.62 \pm 0.07$</td>
</tr>
<tr>
<td>PH/Kr</td>
<td>$1.4 \pm 0.1$</td>
</tr>
<tr>
<td>PH/Xe</td>
<td>$0.73 \pm 0.04$</td>
</tr>
</tbody>
</table>

Data were also collected for the OH/NG and SH/NG systems, each consisting of strong positive $\cdots$ terms in the MCD. Langford's OH/Ar study was repeated and different results were obtained. The reasons for this are unknown but may arise from the formation of strongly hydrogen-bonded OH complexes such as H$_2$O•HO, or orientational effects. Fits using the MAGPI program yielded parameters that can not be regarded as physically reasonable for a truly 'isolated' guest radical, which suggests that the SO-CF model is inappropriate for these systems, perhaps as a consequence of strong interactions between the target guest species and other contaminants including, perhaps, undissociated precursor molecules and other fragments of the discharge processes used to create the radicals.

Preliminary absorption and MCD spectral simulations for free-rotor NH indicate promising agreement with the experimental results for NH/Ar, suggesting that the excited state is undergoing some sort of hindered rotation. This bodes well for the further development of the crystal-field hindered-rotor model, in which the diatomic molecule is assumed to occupy a substitutional site within the perfect face-centred cubic structure of a rare-gas crystal. The barrier parameter, $K$, is a measure of the magnitude of the octahedral CF field. For the $X^2\Pi$ states of CH, OH, and SH, the most reasonable values for $K$ are all negative, indicating that the potential is attractive and that the energy minimum occurs when the radical is oriented along the direction of nearest noble-gas neighbours.

Considerable further development of the hindered-rotor model is required to extend it to include the possibility of overlap between molecular guest and atomic
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A more comprehensive model should also incorporate the rotation-translation-coupling, where the molecule rotates about its centre of mass, which in turn oscillates within the lattice site.

The original aim of obtaining a comprehensive model that would rationalise the differences between gas-phase and matrix, different isotopomers, different hosts, and different guests has only been partially achieved, and there remains much work necessary for the completion of this. An important part of this work should involve quantum-mechanical calculations of XH-NG complexes, with particular attention being paid to how the SOC constants are perturbed by surrounding heavy atoms.

Future work must include finding new and novel ways to obtain funding for liquid helium, such as sausage sizzles, and performing an overhaul of the matrix-injection system. A possible remedy for the problem of adsorbed water is to build a liquid nitrogen 'jacket' around the sample chamber so that any water adsorbed on the metal surfaces inside, while under vacuum, will stick to the inside of the jacket, which has a larger surface area. The design of this jacket will require a great deal of expertise and planning.

Problems with forming CH/Xe and SiH/NG matrices could be overcome by employing different methods of radical production. A possible replacement method involves the pyrolysis of suitable precursor molecules using a nozzle similar in design to that developed by Peter Chen. This was briefly investigated at the start of this author's PhD project, however was deemed too expensive and time-consuming given the amount of work that could be successfully completed with the procedures that were then readily available in the laboratory. This method might also enable higher yields of radicals to be produced than with the tesla-coil method, and could (hopefully) be fine-tuned to minimise the amounts of, or eradicate completely, undesirable side-products.

Even though alternative methods for radical formation might improve the yields, there is still the problem of the sloping baselines which present a major problem with small absorbances. This might be overcome by utilising phase-sensitive detection of the absorption, in a manner similar to measuring MCD spectra.

An original aim of this work was to investigate the matrix-isolated deuterated analogues of CH, NH, OH, SiH, PH, and SH. This could not be done, partly due to a lack of financial resources to purchase the gases, but mostly because of the problems with the experimental apparatus, the uncertainty that the radicals produced in the
Conclusions

matrix would not be partially protonated and the fact that the experiments and analysis that were conducted consumed more time than had initially (and over-optimistically) been anticipated. These experiments should still be performed, especially in the cases of ND/N\textsubscript{2} and PD/NG, in which the ground \( ^3\Sigma^- \) state exhibits a ZFS. In the case of hindered rotation or libration, the experimentally determined ZFS parameters should vary substantially from the non-deuterated cases, and a measure of the corresponding "static" ZFS can be obtained. In fact, it would be interesting to measure the ZFS for various \( A^3\Pi \leftarrow X^3\Sigma^- \) systems such as SO, AsH, SbH, BiH, NF, PF, NCl, and PCl, and examine their trends with noble-gas host.

It was also originally planned to measure ESR spectra on the matrix-isolated radicals studied in this thesis, but this could not be done because of time restrictions. This would have given much more precise information on the electronic ground state, since conventional ESR involves transitions between the Zeeman levels of that state.

By trapping NH or PH in mixed matrices of equal amounts of Ar, Kr, and Xe it might be possible to eliminate rotation by disrupting the lattice to such a degree that all the trapping sites are unsymmetrical. PH/N\textsubscript{2} would be interesting to study, but the tesla-coil method would lead to the formation of small amounts of NH/N\textsubscript{2}, the \( A^3\Pi \leftarrow X^3\Sigma^- \) transition of which overlaps slightly with that of NH, especially considering the very broad bands observed for NH/N\textsubscript{2}.

The MCD Group has, at other times, utilised selective line-narrowing spectroscopic techniques to obtain better resolution over normal MCD and absorption experiments in which, under ideal circumstances, Zeeman shifts can be measured directly.

Hole-burning spectroscopy\textsuperscript{9} can overcome the problem of inhomogeneous broadening of bands (due to molecules experiencing slightly different environments) by using a laser beam of narrow spectral linewidth to selectively excite a narrow band of molecules. These molecules then (hopefully) either decay to a new ground state with a different transition energy, or undergo a photochemical change. Regardless of which of these mechanisms occur, a sharp dip or "hole" is observed in the absorption spectrum at the energy corresponding to the energy of the laser, as well as at the energies corresponding to vibrational and rotational sidebands. This method could give important rotational information for the XH radicals in their ground electronic
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states. Utilising this method will require access to a tunable ultraviolet laser, which would necessitate further sausage sizzles.

Fluorescence line-narrowing (FLN) and selective excitation spectroscopies have also been utilised within the MCD Group. In FLN, a laser beam of narrow linewidth and fixed energy excites a narrow band of molecules. The frequency of the observed luminescence is scanned by a monochromator, and the resulting spectrum gives a measure of the ground-state rotational and vibrational frequencies. In selective excitation, the laser wavelength is scanned across a series of absorption bands as the emission is recorded at a fixed wavelength. The resulting spectrum gives a measure of the excited-state rotational and vibrational frequencies. However this technique still requires a tunable UV laser.

Other ideas for future work could include modifying the matrix-injection system so that XH/Ne matrices can be studied (which would require a much colder deposition window), performing molecular-beam spectroscopic studies of XH-NG complexes, or obtaining further MCD saturation data for OH/Ar as the ratio of the initial H2O:Ar precursor mixtures are varied.

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Appendix A

Matrix Elements of Angular Momentum Operators

Since $J^2$ commutes with all components of $J$, it is possible to construct states, designated $|jm\rangle$, that are simultaneously eigenfunctions of $J^2$ and one component of $J$, which is normally taken to be the $z$ component

$$J^2 |jm\rangle = \lambda_j |jm\rangle$$
$$J_z |jm\rangle = m |jm\rangle$$

(A.1)

From the definition of $J^2$ in Eq. (2.31), Eq. (A.1) can be rewritten as

$$(J^2 - J_z^2) |jm\rangle = (J_x^2 + J_y^2) |jm\rangle = (\lambda_j - m^2) |jm\rangle$$

(A.2)

Since $J$ is a Hermitian operator (and therefore has real eigenvalues) $J^2, J_x^2, J_y^2$ and $J_z^2$ must all have positive eigenvalues. Therefore,

$$\lambda_j - m^2 \geq 0$$
$$|m| \leq \lambda_j$$

(A.3)

This implies that there are minimum and maximum values of $m$ ($m_{\text{min}}$ and $m_{\text{max}}$) for a given $j$. Using the raising and lowering operators (Eq. (2.33)), the following commutation relations may be derived

$$[J^2, J_z] = 0$$
$$[J_z, J_x] = \pm J_x$$
$$[J_x, J_z] = 2 J_z$$

(A.4)

These relations can be used to show that $J_z |jm\rangle$ is an eigenfunction of both $J^2$ and $J_z$.

$$J^2 J_z |jm\rangle = J_z J^2 |jm\rangle = \lambda_j J_z |jm\rangle$$
Appendix A

\[ J_± J_± |j m\rangle = (J_x J_± ± J_± J_x) |j m\rangle = (m ± 1) J_± |j m\rangle \]  

(A.5)

From these relationships it can be seen that \( J_\pm \) leaves the eigenvalue of \( J^2 \) unaltered, but changes \( m \) by \( ± 1 \). It follows that

\[ J_± |j m\rangle = C_± |j (m ± 1)\rangle \]  

(A.6)

where \( C_± \) is a constant. Since \( m \) must lie between \( m_{\text{min}} \) and \( m_{\text{max}} \) (inclusive),

\[ J_+ |j m_{\text{max}}\rangle = 0 \]  

(A.7)

\[ J_- |j m_{\text{min}}\rangle = 0 \]  

(A.8)

If we apply \( J_- \) to Eq. (A.7), we obtain

\[ J_- J_+ |j m_{\text{max}}\rangle = (J_x - iJ_y) (J_x + iJ_y) |j m_{\text{max}}\rangle \]
\[ = (J_x^2 + J_y^2 + i [J_x, J_y]) |j m_{\text{max}}\rangle \]
\[ = (J^2 - J_z^2 - J_z) |j m_{\text{max}}\rangle \]
\[ = \lambda_j - m_{\text{max}} (m_{\text{max}} + 1) \]
\[ = 0 \]  

(A.9)

Similarly if we apply \( J_+ \) to Eq. (A.8), we obtain

\[ J_+ J_- |j m_{\text{min}}\rangle = (J_x + iJ_y) (J_x - iJ_y) |j m_{\text{min}}\rangle \]
\[ = (J_x^2 + J_y^2 - i [J_x, J_y]) |j m_{\text{min}}\rangle \]
\[ = (J^2 - J_z^2 + J_z) |j m_{\text{min}}\rangle \]
\[ = \lambda_j - m_{\text{min}} (m_{\text{min}} - 1) \]
\[ = 0 \]  

(A.10)

From these equations we obtain

\[ m_{\text{max}} (m_{\text{max}} + 1) = m_{\text{min}} (m_{\text{min}} - 1) \]

or
Appendix A

\[(m_{\text{max}} + m_{\text{min}}) (m_{\text{max}} - m_{\text{min}} + 1) = 0\]  \hfill (A.11)

Since \(m_{\text{max}} \geq m_{\text{min}}\), the only solution to this equation is

\[m_{\text{max}} = -m_{\text{min}}\]  \hfill (A.12)

As already established, successive \(m\) values differ by 1. Hence, \(m_{\text{max}} - m_{\text{min}}\) must be a non-negative integer. If we denote this non-negative integer by \(2j\) (where \(j\) is an integer or half-integer), it becomes apparent that

\[m_{\text{max}} = j\]
\[m_{\text{min}} = -j\]  \hfill (A.13)

Substituting Eq. (A.13) into Eqs. (A.9) or (A.10) gives

\[\lambda_j = j (j + 1)\]  \hfill (A.14)

We can now evaluate \(C_{\pm}\) from Eq. (A.6) by using the identity

\[J_x J_x = J^2 - J_z (J_z + 1)\]  \hfill (A.15)

Note that the phase is chosen to make \(C_{\pm}\) real.

\[
|C_{\pm}|^2 = j (j + 1) - m (m \pm 1)  \hfill (A.16) \\
C_{\pm} = [j (j + 1) - m (m \pm 1)]^{1/2}  \hfill (A.17)
\]

In the convention where angular momentum is measured in units of \(\hbar\), the following matrix elements can be obtained

\[\langle j' m' | J^2 | j m \rangle = j (j + 1) \delta_{jj'} \delta_{mm'}\]  \hfill (A.18)
\[\langle j' m' | J_z | j m \rangle = m \delta_{jj'} \delta_{mm'}\]  \hfill (A.19)
\[\langle j' m' | J_\pm | j m \rangle = [j (j + 1) - m (m \pm 1)]^{1/2} \delta_{jj'} \delta_{mm' \pm 1}\]  \hfill (A.20)