

Probing solvation at a molecular scale using Infra-red depletion spectroscopy

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Nitika Bhalla – Probing solvation at a molecular scale using infrared depletion spectroscopy

Infrared spectroscopy, coupled with mass spectrometry has been used to investigate a specific sized gas phase clusters. In particular, alkali metals i.e. lithium or lanthanides such as ytterbium in the presence of ammonia derivative solvents, has been explored observing both the electronic and vibrational spectral characteristics. *Ab initio* work has been carried out in support of experimental work which has given some vital clues to help assign some spectra.

Firstly, the first electronic spectrum of $\text{Li}(\text{NH}_3)_4$ has been observed. Strong absorption is observed in the near-infrared and the band system is assigned to the $\tilde{A}^2T_2 - \tilde{X}^2A_1$ transition in the tetrahedral complex. The vibrational structure is indicative of a substantial Jahn-Teller effect in the excited electronic state. Following this, LiNH_3 was the next complex to be investigated, the spectra is consistent with two electronic transitions in close proximity, the $\tilde{A}^2E - \tilde{X}^2A_1$ and $\tilde{B}^2A_1 - \tilde{X}^2A_1$ systems. Vibrational structure is seen in both systems and the prominence of a particular band is attributed to a Herzberg-Teller coupling.

The electronic spectrum of the Li-methylamine cluster was attempted, this spectrum occurs in the near-infrared and shows provisional bands assigned to the $\tilde{A}^2A - \tilde{X}^2A_0^0$, $\tilde{B}^2A - \tilde{X}^2A_0^0$ and possibly the $\tilde{C}^2A - \tilde{X}^2A_0^0$ electronic transitions.

An effort was made to try and record the IR depletion spectrum of a mixed cluster, such as $\text{Li}(\text{NH}_3)_n(\text{Ma})_m$, despite the additional bulk of the methylamine group, up to four solvent molecules were able to reside within the first solvation shell.

Finally, the electronic spectrum of the rare earth complex, YbNH_3 has been recorded using two colour resonance-enhanced multiphoton ionisation spectroscopy (REMPI). The spectrum arises from a spin-forbidden transition between the 1A_1 ground electronic state and a 3E excited electronic state. Some vibrational structure is also observed in the REMPI spectrum which has been assigned.

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Chapter 1 – Introduction

1.1 Introduction

Solvation is a fundamental concept in chemistry and the investigation of solute-solvent interactions is, naturally enough, usually carried out in the liquid phase. Information can be extracted from bulk liquid solutions to give an insight into the dissolution process between a solute and a solvent. One interesting area of solvation chemistry is the formation of solvated electrons, which is essentially when an electron originally on an atom or molecule is detached by some means and becomes embedded in the solvent medium. Solvated electrons can be formed in a number of ways, most commonly for example by dissolving alkali-metals in liquid ammonia.¹

In a classic experiment first performed by Sir Humphrey Davy in 1808,² the colour of an alkali metal-ammonia solution was found to depend on the alkali/ammonia ratio. A distinct deep blue colour was observed for a dilute solution but this changed to a bronze colour at high concentration (near saturation). Accompanying this colour change was an increase in solution conductivity and approximately 200 years later, these changes in colour were attributed to the formation of solvated electrons.^{3,4}

However, a full understanding of the dissolution process and indeed the solvated electron is still lacking. This is a rather difficult thing to tackle in the condensed phase, because of the intrinsic complexity. To try and simplify matters, it has therefore become popular in recent years to explore the structural and dynamical issues of solvation through studies of molecular clusters in the gas phase, where the cluster contains both the solute and the solvent. Such systems are clearly highly simplified but the hope is that they can act as a model system that can reveal some of the underlying features of the more complex, real, solutions.

As a result, one of the major growth areas in gas phase spectroscopy is the study of solute-solvent clusters (in this thesis we are specifically concerned with metal-solvent

clusters). Essentially, by varying the size of the cluster, spectroscopic information relevant to solvation behaviour in bulk solutions can potentially be extracted, if clusters of sufficient size are considered. Clusters of alkali metal atoms with ammonia molecules are among those that have attracted considerable attention because of the formation of solvated electrons in these solutions, as mentioned above.

The study of uncharged metal-ammonia and related clusters were studied in the gas phase and the work is reported in this thesis. These clusters were subjected to a series of investigations using infrared spectroscopy and one of the key aims of this type of work is to try and ascertain how many solvent molecules are required around the central metal atom for the cluster to start to resemble bulk-like solution properties. At a more detailed level we could also ask; (i) how many solvent molecules are required for the valence electron to completely detach itself and become embedded into the solvent medium? (ii) what are the reaction mechanisms for forming solvent shells? and (iii) what is the unpaired electron distribution across the cluster and how does it vary with the number of solvent molecules?

These are some of the most important issues that will need to be resolved. Prior to describing this work in later chapters, some background information is given here on previous relevant studies.

1.2 Previous work on metal-solvent clusters

In recent years there has been a dramatic increase in the number of studies of metal-containing clusters using spectroscopic analysis.^{5,6} Several research groups have made important contributions in this research field. The spectroscopic study of charged metal-solvent clusters is generally favoured, since a charge makes mass-selective spectroscopy convenient. When mass selection is carried out before spectroscopic excitation, the exact identity of the cluster species can be established.

Most of the work on metal ion-solvent species has focused on singly charged metal-solvent cations. For example, Duncan and co-workers used infrared (IR) photodissociation spectroscopy to explore complexes of singly charged transition metals cations, such as vanadium, iron, nickel and aluminium.⁷ A variety of solvent molecules have been investigated, including ethene, ammonia and carbon dioxide.⁷ Both single photon absorption and IR multiphoton absorption have been used to record vibrational photodissociation spectra as a function of solvent number for these types of complexes.

Stace and co-workers⁸ have tried to bridge the gap between isolated gas phase species and the condensed phase by exploring metal-solvent ions where the metal has a chemically realistic charge state. In particular, the Stace group have developed the means to produce clusters of multiple charged metal ions in the gas phase. Using this so-called ‘pick-up’ method, spectra of clusters such as $[\text{Cu}(\text{H}_2\text{O})_n]^{2+}$ have been prepared⁸ and electronic photodissociation spectra of transition metal complexes, such as $[\text{Ag}(\text{pyridine})_4]^{2+}$ and $[\text{Cu}(\text{pyridine})_4]^{2+}$, have been recorded.⁹

The above studies are only a brief selection from a substantial portfolio of research on metal-solvent clusters. Another group that has carried out significant work in this area is the Lisy group, who use photodissociation spectroscopy to obtain the IR spectra of alkali-metal cations solvated with a range of solvents.¹⁰

1.3 Alkali-metal solvent clusters

Spectroscopic studies of alkali-solvent clusters in the gas phase were first performed by Hertel *et al.*¹¹ In particular they explored the photoionisation thresholds of $\text{Na}(\text{NH}_3)_n$ clusters as a function of n . A reduction in the ionisation energies of the clusters was observed as the number of solvent molecules increased from $n = 0$ to 4. This was followed by a slower

decline in the ionisation energy for clusters from $n = 5$ to 10. For clusters $n = 11$ to 16 the ionisation energies seem to plateau and then decline again from $n = 16$ to $n = 20$.¹² By construction of a model potential, the photoionisation energies provided circumstantial evidence for the completion of the first solvation shell at $n = 4$ and an increased tendency for the unpaired electron on the alkali metal to transfer into the solvent medium as n increases. Moreover, the calculations showed that, for complexes with $n > 4$, the formation of a solvated electron developed and started to penetrate around the solvent network.¹¹ For larger clusters there was an indication that the cluster formed a two-centre species for complexes $n = 11$ to 16, where the electron from the singly occupied molecular orbital (SOMO) was completely detached from the metal into the solvated medium. Essentially, an ion pair was formed between the metal cation and the electron. Furthermore, at cluster sizes $n > 16$, the progressive addition of ammonia molecules resulted in the electron now being completely solvated in the solvent medium and the complex strongly resembled a bulk solution in this respect.¹¹

However, extracting information on the solvation properties of alkali-solvent clusters on the basis of photoionisation measurements alone is somewhat limited and unreliable. Photoionisation studies provide little or no information on the structures of these clusters, which is important information for elucidating the role of the solvent molecules. In these circumstances, optical spectroscopy has much to offer, since structural information is part of the information content of many spectroscopic techniques.

The simplest alkali-ammonia complex is LiNH_3 , since it contains the lightest alkali metal atom and only a single NH_3 molecule. However, the only previous spectroscopic studies of LiNH_3 have been carried out in solid argon matrices. In these studies matrix infrared spectroscopy was carried out, the fundamental frequencies of several vibrational modes of LiNH_3 and its deuterated analogues were determined.^{12,13}

The next heaviest alkali metal is sodium (Na) and the vibrationally-resolved resonance-enhanced multiphoton ionization (REMPI) spectrum of NaNH_3 has been recorded.^{14,15} Unfortunately, this technique will not extend to larger $\text{Na}(\text{NH}_3)_n$ clusters, since the low-lying excited electronic states of the larger clusters undergo non-radiative decay that is too rapid for successful REMPI measurements.¹⁶

A set of experiments carried out by Schulz and co-workers¹⁶ provided a means of recording spectra of neutral molecules and clusters with some degree of mass selectivity. Their studies utilised the method of photodepletion spectroscopy, a technique that underlies the basis of several experiments reported in this thesis. In particular the photodepletion spectroscopy of $\text{Na}(\text{NH}_3)_n$ clusters, including their deuterated isotopes, was investigated. The depletion experiment results in the dissociation of the $\text{Na}(\text{NH}_3)_n$ complexes following photoexcitation leading to the formation of smaller clusters, which are subsequently ionised. The depletion spectra of $\text{Na}(\text{NH}_3)_2$ and $\text{Na}(\text{ND}_3)_2$ were recorded in this initial study.¹⁶ In addition to this investigation, the first electronically excited state of $\text{Na}(\text{NH}_3)_n$ clusters by means of depletion spectroscopy were identified by Schulz and co-workers.¹⁶ A UV laser was used for photoionisation and a second tuneable OPO laser was used prior to photoionisation in order to allow photodissociation to occur. The electronic spectra were broad and did not contain any sharp lines associated with a specific vibrational progression. Furthermore, $\text{Na}(\text{NH}_3)_n$ clusters up to $n = 22$ were investigated and the conclusion from the study was that the first solvation shell was complete at $n = 4$. A decrease of the excitation energy from the $3p \leftarrow 3s$ transition of the Na atom $\sim 16,950 \text{ cm}^{-1}$ down to 6000 cm^{-1} for the $\text{Na}(\text{NH}_3)_4$ cluster was observed. For larger clusters the excitation energy increases only slightly toward the bulk value $\sim 6300 \text{ cm}^{-1}$, which represents the absorption of the solvated electron in liquid ammonia.¹⁶

Recently, infrared spectra of neutral solute-solvent complexes have been recorded by the Leicester group, where the primary focus has been on alkali-ammonia and ammonia derivatives. The mid-IR (pure vibrational) spectra of $\text{Li}(\text{NH}_3)_n$ clusters for $n = 4$ to 7 in the N-H stretching region were determined. The mid-IR spectra and associated *ab initio* calculations provided the first information which could be linked *directly* to the structures of $\text{Li}(\text{NH}_3)_n$. In particular, strong evidence was provided that the completion of the first solvation shell occurred at $n = 4$.¹⁷ In addition, the favoured geometry of the $\text{Li}(\text{NH}_3)_4$ cluster was found to be tetrahedral, i.e. corresponding to a 4+0 complex (the 4+0 terminology refers to the number of solvent molecules present in the first and second solvation shells, respectively).

Several *ab initio* studies of alkali-ammonia complexes have been reported and vibrational frequencies have also been calculated using the coupled electron pair approximation (which incorporates electron correlation) was used to predict the anharmonic vibrational frequencies for the LiNH_3 complex.^{18,19} Interestingly this study demonstrated how complexation to a metal can impact the IR absorption intensities of the ammonia molecule, causing a significant increase in magnitude (by more than two orders of magnitude) of the N-H stretching line strength compared to the free ammonia molecule.

Furthermore, Mierzwicki and Latajka²⁰ carried out MP2 and DFT calculations using a 6-311+G(d,p) basis set on $\text{Li}(\text{NH}_3)_n$ and $\text{Li}(\text{NH}_3)_n^+$ for $n = 1-4$ in an attempt to explore the many-body interactions in clusters composed of more than one solvent molecule. As part of their work, Mierzwicki and Latajka determined both equilibrium structures and total interaction energies.²⁰ Hashimoto and co-workers, employing Hartree-Fock and single-point MP2 calculations with double zeta + polarization quality basis sets, predicted the equilibrium structures and binding energies for $\text{Na}(\text{NH}_3)_n$ and $\text{Na}(\text{NH}_3)_n^+$, where $n = 1-6$.^{21,22}

Moreover the complexes LiNH_3 and $\text{Li}(\text{NH}_3)_2$ and their cationic equivalents have been studied using computational chemistry.²³ These high quality calculations, using the dunning basis set aug-cc-pVQZ, revealed accurate Li-N bond dissociation energies, as well as equilibrium structures of each complex and their harmonic vibrational frequencies. These calculations on the simplest of lithium and ammonia complexes provided a benchmark to which calculations on other large $\text{Li}(\text{NH}_3)_n$ complexes can be compared to.

1.4 Photodepletion spectroscopy of solute-solvent complexes: the mechanism

The incentive to study neutral metal-solvent clusters is derived from the fact that the metal solute will adopt the charge state dictated by the solvent, which in the limit of a large number of solvent molecules should tally with the charge state in the bulk solution. In particular, uncharged clusters allow the potential to explore charge separation as a function of solvent number, i.e. the formation of both cations and anions *within the same cluster*. The study of neutral clusters also has the advantage of actually being a good model for highly concentrated bulk solutions. Thus, spectroscopic study of neutral metal-solvent clusters offers information complementary to that of charged solute-solvent clusters containing a single cation or anion.

The disadvantage the absence of charge imposes is that mass-selection of clusters becomes difficult.¹⁷ It is not possible to select a specific cluster prior to spectroscopic excitation. For this reason, the spectroscopic study of neutral solute-solvent clusters has been rather limited.

The investigations described above have provided a foundation to which we are able to apply the concept of IR photodepletion spectroscopy (see Figure 1.1) to study neutral metal-solvent gas phase clusters. Within the Leicester spectroscopy group investigations have concentrated on recording the mid-infrared spectra (vibrational photodepletion spectroscopy) of alkali-ammonia clusters for $n > 1$ via IR photodepletion spectroscopy.

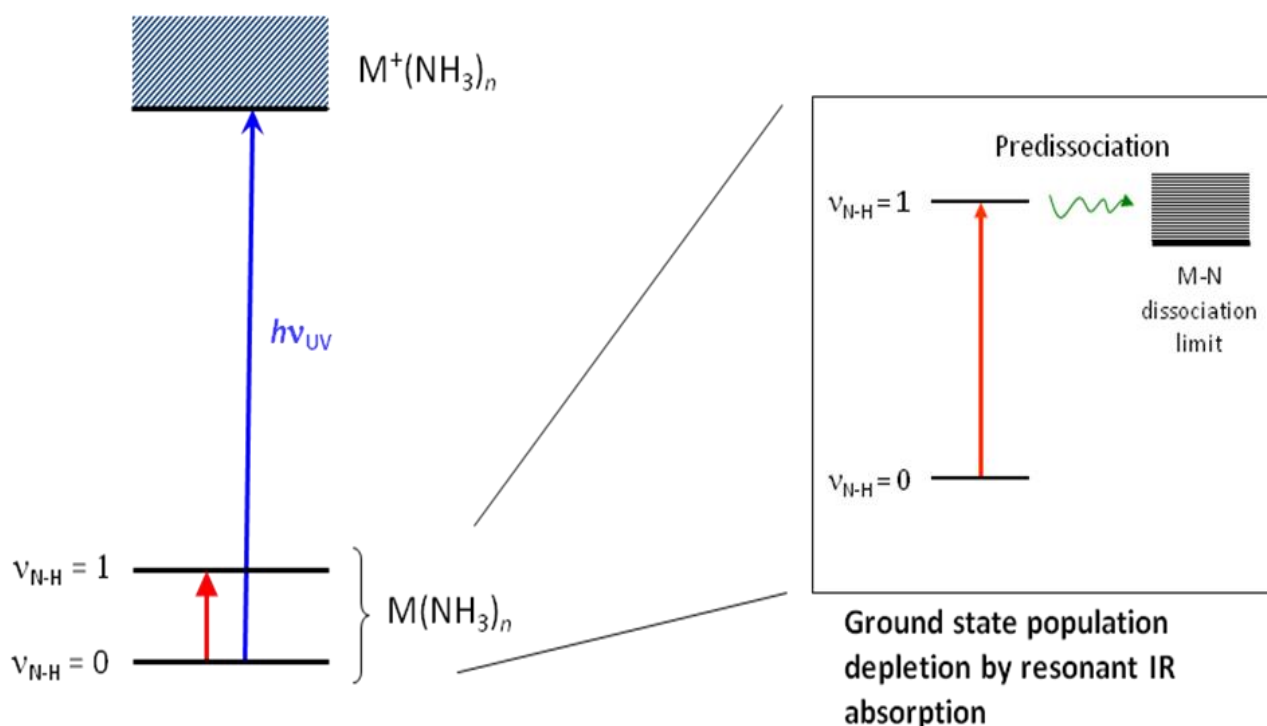


Figure 1.1: Mechanism for IR depletion spectroscopy.

According to the scheme given in Figure 1.1, the alkali-solvent clusters can be spectroscopically probed and detected by a two-laser experiment. Firstly, once the clusters have been formed, an IR beam of a particular wavelength (corresponding to the N-H stretching region, for example) is directed towards the neutral clusters. If the IR beam is resonant with a specific vibrational transition then it can be absorbed. If the energy is then redistributed within the complex then cluster fragmentation can result, providing the energy injected is sufficient to exceed the M-N binding energy. Next, a UV laser is used to photoionise the fragmented cluster. Thus it becomes possible to record a mass selective IR spectrum of $M(NH_3)_n$ through IR-induced depletion of the $M^+(NH_3)_n$ signal.

1.5 Aims and thesis content

The primary aim of this work was to extract and produce new spectroscopic information on metal-solvent clusters using optical spectroscopy. The emphasis was mainly on lithium-containing species and employed near and MID-IR spectroscopy, to investigate several new species.

Chapters 2 and 3 give details on the experimental setup employed and the methodology of the supporting *ab initio* calculations. The first piece of spectroscopic work reported in this thesis deals with the complex $\text{Li}(\text{NH}_3)_4$. The aim of this experiment was to try and record the first electronic spectrum of this particular complex and is described in Chapter 4. As will be discussed later, the electronic spectrum was found to show some remarkable similarities to that of an electron in liquid ammonia.

In addition, the electronic spectrum of the simplest alkali-ammonia complex, i.e. LiNH_3 , has also been recorded for the first time (details reported in Chapter 5). Within this spectrum, vibrational structure was observed and assigned with the aid of isotope substitution studies, along with a series of supporting *ab initio* calculations. Building on this work, the first spectra of LiNH_2CH_3 have also been recorded and this study is disseminated in Chapter 6.

In Chapter 7 the effect of a mixed solvent system in the form of $\text{Li}(\text{Ma})_m(\text{NH}_3)_n$ is explored, where $\text{Ma} = \text{NH}_2\text{CH}_3$. The aim here was to record vibrational spectra in the N-H stretching region which could be compared with previously recorded spectra of $\text{Li}(\text{NH}_3)_n$ and $\text{Li}(\text{Ma})_n$ to investigate the effect of a mixture of solvent molecules on cluster structure.

The first spectroscopic study of a lanthanide-ammonia complex, YbNH_3 , is reported in Chapter 8. One of the significant features of Yb is that, similar to the alkali and some alkaline earth metals, it dissolves readily in liquid ammonia. Thus the interest in seeing if any

evidence for solvated electrons in $\text{Yb}(\text{NH}_3)_n$ clusters can be found. The investigation of YbNH_3 was carried out, via its electronic spectrum.

Finally, some general conclusions drawn from all the work reported in the preceding chapters will be summarised in Chapter 9, including some discussion of possibilities for future work.

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Chapter 2 - Experimental Methods

This chapter describes the experimental apparatus employed in the thesis work. It begins with an experimental overview of the apparatus and then the particular items of equipment used are described in more detail.

2.1 Overview

At the heart of the experimental setup are two vacuum chambers; a primary chamber, which is where the desired cluster production and cooling takes place, and a secondary chamber where spectroscopic and mass spectrometric measurements are made. The molecules and clusters of interest are produced in a pulsed supersonic expansion. Metal-containing species are formed upstream, by a laser ablation process, which generates metal atoms that can then combine with molecular species seeded into the stagnation gas. The supersonic expansion then cools the molecules/clusters and the expanding mixture is skimmed to form a collimated molecular beam, whereupon it enters the second vacuum chamber.

The molecular beam enters the ion source region of a time-of-flight mass spectrometer in the second chamber, where ions are produced by UV laser photoionisation. For spectroscopic measurements, a second laser beam, from an optical parametric oscillator/amplifier (OPO/OPA) is used, counterpropagating the UV laser beam. Both laser beams are guided in a direction perpendicular to the direction of travel of the molecular beam, as represented in Figure 2.1.

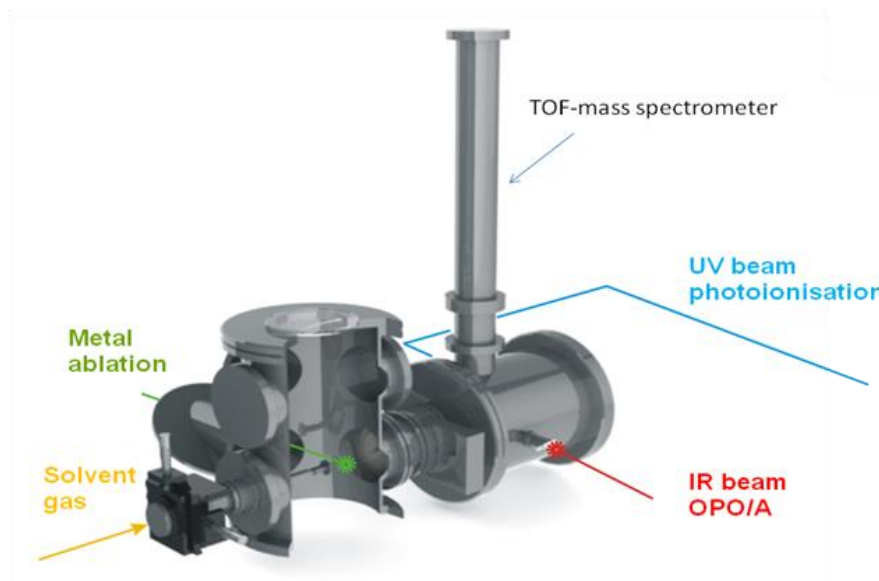


Figure 2.1: Schematic layout of the experimental setup.

2.2 Vacuum system

The vacuum chambers were custom built within the departmental mechanical workshop, the primary chamber is where the metal ablation takes place and the actual spectroscopy of the complex occurs at the secondary chamber. The experimental chambers were constructed from stainless steel and are described fully elsewhere.¹ Consequently only a brief overview is given here.

The primary (source) chamber features nine access ports to which a variety of steel flanges or windows can be attached to provide flexibility to the system. The chamber is pumped by a 3000 l s^{-1} diffusion pump (Leybold DIP 3000 S) fitted with a water-cooled baffle to prevent backstreaming of oil, which can contaminate the vacuum system. The diffusion pump is in turn backed by a $40 \text{ m}^3 \text{ hour}^{-1}$ mechanical two-stage rotary pump (Leybold Trivac D 40 B) fitted with $505 \text{ m}^3 \text{ hour}^{-1}$ roots booster (Leybold Ruvac WA 501) for dealing with high gas loads. The maintenance of a low base pressure ($<10^{-5} \text{ mbar}$) is desired because, as the base pressure increases, this will

somewhat disturb the supersonic expansion process. The chamber base pressure is typically 7×10^{-6} mbar, which is increased to an average pressure of about $\sim 8 \times 10^{-5}$ mbar when the pulsed nozzle is fired.

The pulsed nozzle is mounted on an XYZ translation stage (MiniAx, VG Scienta) to assist in the alignment of the nozzle with respect to the skimmer. This gives independent movement of 20 mm in each of the x , y and z directions, where z is parallel to the axis along which the molecular beam travels. Electrical input to the pulsed nozzle is delivered via a high vacuum compatible electrical feedthrough, which is attached to the front flange.

The gas mixture enters the pulsed valve via PTFE tubing, usually from a gas cylinder. Through the use of a regulator, the gas pressure can be varied from 0-8 bar. The translation of the pulsed nozzle can be achieved whilst under vacuum, thereby allowing the optimum position of the nozzle with respect to the skimmer. This can be determined by making positional adjustments while observing mass spectrometric signals on an oscilloscope (see later section). A skimmer (Beam Dynamics, Inc.) with an aperture of 1.0 mm diameter is mounted on the far side of the primary chamber, just before a gate valve. The purpose of the gate valve is to allow isolation of either vacuum chamber, if required.

The secondary chamber contains a custom-built time-of-flight mass spectrometer (TOF-MS), which is mounted vertically on the top of the chamber. On both sides are two CaF_2 coated windows, mounted at Brewster's angle, which are attached to short arms. The purpose of these windows is to allow the laser beams (in particular the UV and IR beams) to perpendicularly intersect the molecular beam. Furthermore, there is a window at the end of the chamber, whose main purpose is to allow the alignment of the

nozzle and the skimmer to be visibly optimised. The secondary chamber is pumped by an 800 l s^{-1} turbomolecular pump (Leybold Turbovac 1000), backed with a $25 \text{ m}^3 \text{ h}^{-1}$ two stage rotary vane pump (Leybold Trivac D 25 B). This pumping system achieves a chamber base pressure in the region of 9×10^{-7} mbar, rising to $\sim 1 \times 10^{-6}$ mbar when the nozzle is operating under standard gas stagnation conditions.

2.3 Supersonic expansion

The cooling of molecules and molecular clusters is an important aspect of the experiment. In particular, the reduction of temperature can result in a much simpler and/or sharper spectrum that will assist the assignment process. At relatively high temperatures, vibrational and rotationally excited states are likely to be occupied, such that the molecules can undergo numerous transitions out of these states. Furthermore, the increased thermal content can sometimes cause the rapid fragmentation of transient species such as ions, free radical and van der Waals clusters. Consequently, to prolong the lifetime of the relevant species, decreasing the internal temperature of the molecules/clusters is often vital.

A supersonic jet is produced when a sample of gas is expanded from a relatively high pressure region into a vacuum through a small orifice. The aim is to cool the molecules in the gas without leading to excessive condensation. Ordinarily the molecules of interest are diluted in an inert carrier gas to minimise condensation. Figure 2.2 illustrates the process of molecular cooling in supersonic jets: this diagram shows the velocity distribution of atoms/molecules before and after the expansion process. The numerous collisions that take place in the orifice region result in the conversion of random thermal motion of the gas molecules into a directed flow after the nozzle. This delivers a narrow distribution of particle velocities, which is characteristic of a low

translational temperature. By this means it is possible to achieve translational temperatures as low as 1 K.²

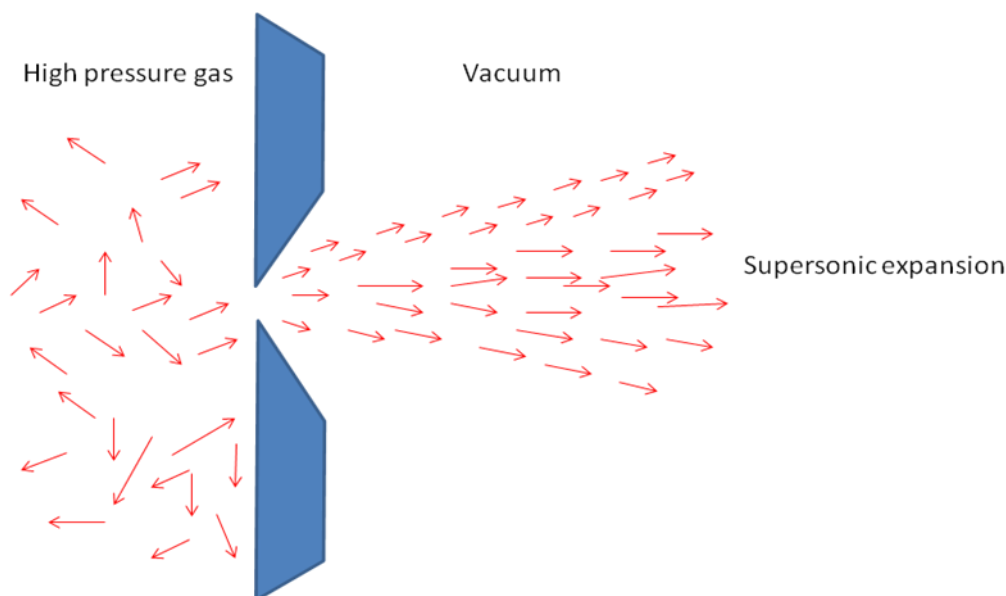


Figure 2.2: Representation of cooling in a supersonic jet.

In the early stages of the expansion there are collisions that lead to an exchange of energy between the vibrational and rotational degrees of freedom and the translational motion. Since argon (a monatomic gas and typical carrier gas) is often the carrier gas used, it does not possess any vibrational or rotational degrees of freedom. Consequently, when the argon atoms collide with any molecules in the nozzle region, internal energy within the molecules can be converted to translational energy of the argon atoms. Equilibration between translational and rotational degrees of freedom tends to be very fast and it is possible to cool the molecular rotational motion to a very low temperature, sometimes to <10 K.³ The vibrational $\rightarrow$ translational relaxation is much slower, and the final vibrational temperature in the supersonic jet is usually considerably higher than the final translational temperature; typical values are in the range 100–300 K.³

2.4 Laser systems

Lasers were used throughout the experimental work for both photoionisation and spectroscopic excitation. Key properties of lasers include a high light intensity, high monochromaticity and a collimated beam profile.⁴ Various types of lasers have been used in this work, as described below. Due to the pulsed nature of the experiment, all of the lasers employed are pulsed and operate at a repetition rate of 10 Hz.

2.4.1 Laser ablation source (*Minilite*)

The species of interest in the present work are derived from the reactions of metal atoms. Consequently, some means of producing metal atoms in the gas phase is required. In this work, laser ablation has been employed to generate gaseous atoms. This is a standard technique for generating metal atoms in combination with supersonic gas expansion.

Laser ablation of the solid metal target was carried out using the second harmonic (532 nm) output of a small Nd:YAG laser (Continuum Minilite). This laser typically delivers 20-25 mJ pulse⁻¹. The radiation from this laser is focused onto the surface of the metal using a lens with a focal length 25 cm. The firing of this laser is timed to coincide with the arrival of a gas pulse from the pulsed nozzle (see later), in order to allow formation of metal-solvent clusters.

Ordinarily, the metal target employed was static throughout the experiment. One problem with this is that during the ablation process if a hole in the metal is formed relatively quickly, then the signal can rapidly decay to an unacceptable level. This was not found to be a serious problem with lithium, the main metal employed in this work. However, laser ablation experiments on ytterbium proved to be more problematic, and thus signal intensities varied significantly across long spectral scans. To prevent this

problem, a rotating/translating rod system can be used. This works by rotating the metal sample so that a fresh surface area is exposed to the high intensity laser beam at each laser shot. The aim of this system is to improve the stability of the sample over long periods. The device is designed so that a metal ablating rod can be placed in its holder and with the control of an electrical motor, the metal rod can rotate and translate at different speeds, hence exposing different areas of the metal sample to the ablation laser. In actual fact, for the experiments reported herein the rotating/translating rod was not used due to an electrical problem with the motor.

2.4.2 Dye laser

A dye laser allows access to wavelength-tuneable laser light over the entire range of the visible spectrum and into the near-ultraviolet (UV). The active lasing medium within the dye laser is a conjugated aromatic organic dye molecule dissolved in a suitable solvent, usually methanol. This produces broadband emission when optically pumped, but dye lasers also contain a diffraction grating within the laser cavity to yield a monochromatic output and tunability.

The dye laser employed for the work describe in this thesis was a Sirah Cobra-Stretch system. This was pumped by a Continuum Surelite Nd:YAG laser operating at either 532 or 355 nm, depending on the desired output wavelength from the dye laser. The Cobra-Stretch laser was fitted with a frequency doubling unit to allow operation in the near-UV.

2.4.3 Optical parametric oscillator/amplifier (OPO/A)

Vibrational and electronic transitions of the molecules and clusters studied in this work have been excited by tuneable IR output from an optical parametric oscillator/amplifier (OPO/A) system (LaserVision). This tuneable light source essentially converts an input laser wavelength into two output waves of lower frequency (ω_s and ω_i) by means of a non-linear optical effect. From the conservation of energy the sum of the output wave frequencies must be equal to the input wave frequency: $\omega_s + \omega_i = \omega_p$. The two output waves are called the *signal* (ω_s), consisting of a higher photon energy (shorter wavelength), and the *idler* (ω_i), which is of lower energy (longer wavelength).

The initial pump beam is the 1064 nm output from a Nd:YAG laser (Continuum Surelite II-10). This laser beam, which has a typical input pulse energy of 585 mJ, is introduced into the OPO/A unit and is split into two pathways, as illustrated in Figure 2.3. The first part enters a frequency doubling crystal (KTP crystal (C1) potassium titanyl phosphate) to produce a 532 nm beam. Following this conversion, the residual 1064 nm pump beam is dumped at D1. The 532 nm beam is steered into the oscillator cavity, which contains a second KTP crystal (C2), and is where optical parametric oscillation occurs. The signal wave is horizontally polarised while the idler is vertically polarised (as is the 532 nm pump beam). The polarity of the two beams can be exchanged (using a custom half-wave plate, WP1) before entering the OPA stage of the laser and the signal portion is dumped (at the half-wave plate).

It is at the OPA stage, the amplifier stage, where the generation of tuneable mid-infrared radiation is achieved. Initially, the 1064 nm pump beam is combined with the idler output from the OPO stage in crystals C3-6. Two further signal and idler waves are generated in a difference frequency mixing process within the KTA (potassium titanyl arsenate) crystals. These beams pass from the crystals with the 1064 nm beam

into a dichroic mirror (Dc2). The residual 1064 nm beam is reflected and dumped at D2, and the remaining signal and idler beams then pass into the polarised filter (polariser). The orientation of the polariser is crucial in determining which wavelength of light is allowed to pass. For example, if the polariser is placed in the ‘U’ position then this permits the signal wave (higher energy) to pass through the laser aperture. On the contrary, if the polariser is placed in the ‘C’ position, this will allow the idler wave (lower energy) to pass through the aperture.

In a particular experiment, it is desirable for the OPO/A to function with the idler wavelength, since this works in the range of 2.1-5.0 μm in the mid-IR and (710-880 nm) in the near IR.

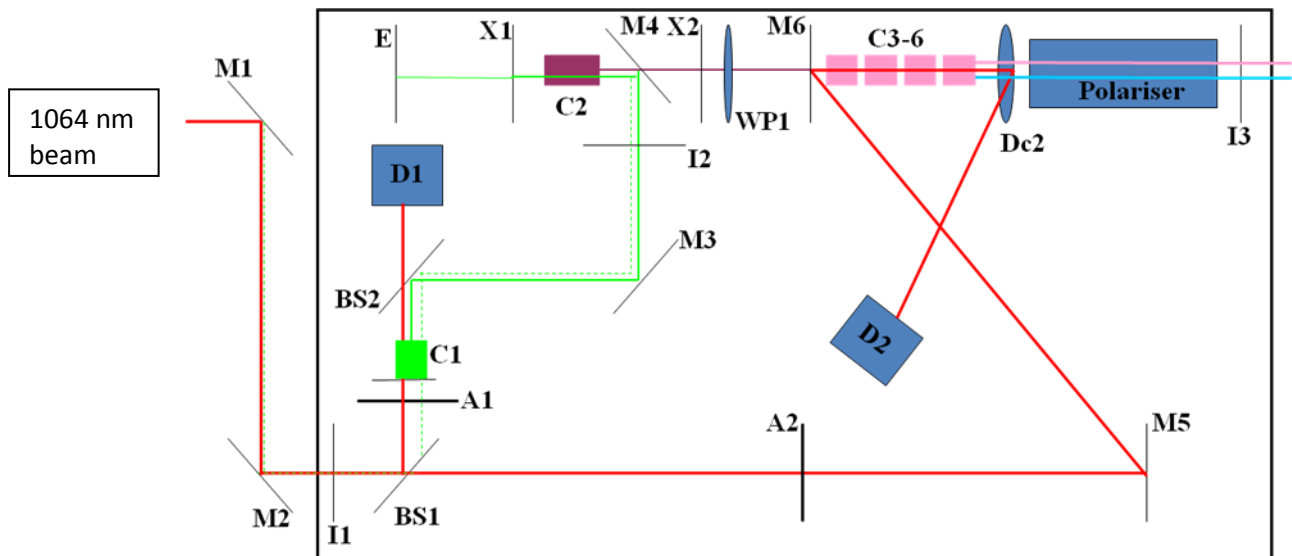


Figure 2.3: Schematic diagram of the OPO/A system.

During the alignment procedure it is at times necessary to take regular burn patterns to ensure good optical alignment. This is essential to achieve the maximum

output of IR energy. Figure 2.4(a) shows the burn patterns of the incoming beams after the KTA crystals in the case where there is good beam alignment: here the smooth oval shape of the beam profile gives a good indication that the beam is not being ‘clipped’ by any of the four KTA crystals. On the other hand, Figure 2.4(b) shows an example where the alignment is poor. The beam profile in this case is no longer symmetrical and the presence of additional features at the top of the main beam profile suggests that there is a divergence of the output beam, which is likely to be due to major ‘clipping’ of the laser beam with the KTA crystals, i.e. the beam is not centred correctly through all four crystals.

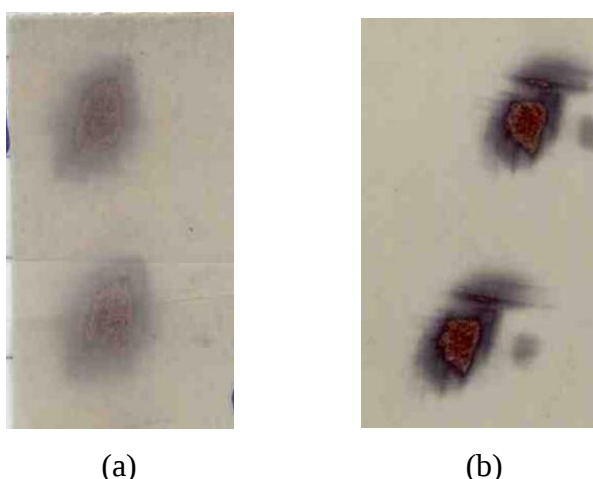


Figure 2.4: Burn patterns of beams after the OPA stage.

Where (a) represents the beam with no clipping and (b) illustrates where the laser beam is being clipped by the non linear crystals.

In general, once correctly aligned, the OPO/A laser is capable of producing tunable infra-red radiation. The oscillator acting alone is capable of generating approximately 3 mJ of energy at 771-815nm. For electronic spectroscopy experiments only the OPO crystal was used and the amplifier stage was bypassed by the use of carefully positioned mirrors and lens to enhance the focusing of the IR beam. When the OPA was used IR

output with pulse energies of 10-15 mJ were achieved at wavelengths 2900-3300 nm. Outside of these wavelengths pulse energies continuously fall away and the pulse energy will start to drop significantly, down to 5-6 mJ.

In addition to the KTP and the KTA crystals, there is also an additional crystal, an AgGaSe₂ crystal. The AgGaSe₂ crystal is for *external* difference-frequency mixing of the signal and idler waves from the OPA stage to generate light that is tunable from 5 to 18 microns (2000-555 cm⁻¹). Relatively low frequency vibrations can therefore be excited with the use of this external crystal. The AgGaSe₂ crystal was not used in any of the experiments described in this thesis, due to time constraints. The operating wavelength of the OPO/A system was under computer control. Changes in wavelength were provided by adjusting the positions of the crystals in the OPO and OPA states using computer-controlled motors. Furthermore, there are important equations unique to the OPO systems which deserve a mention. For example, a concept important to OPO/A's is that of energy conservation and phase matching. These two requirements can be summarised below.

Energy conservation is given by equation [2.1]

$$E_{\text{pump}} = E_{\text{signal}} + E_{\text{idler}} \rightarrow 1/\lambda_{(p)} = 1/\lambda_{(s)} + 1/\lambda_{(i)} \quad [2.1]$$

Where E_{pump} is the energy of the 1064 nm pump laser beam and the E_{signal} and E_{idler} are the energies two types of frequency wavelengths produced. In the current system there are two stages of this process are summarised and which is known as the frequency conversion equation. For example,

OPO process: $E_{532} (= 2.E_{1064}) = E_{\text{signal}} + E_{\text{intermediateIR}}$

OPA process: $E_{1064} = E_{\text{intermediateIR}} + E_{\text{midIR}}$

(Subtracting) $E_{1064} = E_{\text{signal}} - E_{\text{midIR}}$

OR, $E_{\text{signal}} = E_{\text{midIR}} + E_{1064}$

= $1/\lambda_{(\text{signal})} = 1/\lambda_{(\text{mid-IR})} + 1/\lambda_{(1064)}$

Hence $\lambda_{\text{signal}} = [1/\lambda_{(\text{mid-IR})} + 1/\lambda_{(1064)}]^{-1}$ **[2.2]**

To convert between the near IR and mid IR, the expression in equation [2.2] is used. Finally, the need to indicate how a wavelength scan is performed is worth mentioning, using the in-house LabView software programme the wavelength is set to scan continuously from an initial to final wavelength (nm) at a chosen speed rate. Full details of this procedure can be found in the data acquisition section.

2.4.4 Laser calibration

Laser wavelength calibration is an essential part of the experimental procedure. Our approach to wavelength calibration was to exploit photoacoustic spectroscopy. The setup used has been described in detail previously,¹ so only a brief account is given here. The photoacoustic cell is a closed system containing an acoustic microphone. IR radiation from the OPO/A enters the cell through a glass window and illuminates the cell contents, which is a gas or vapour. If absorption takes place, the temperature of the sample momentarily increases and then the gas sample expands, generating a pressure (acoustic) wave. This acoustic wave is detected by the microphone, producing an electrical signal that can be captured by the oscilloscope.

The current photoacoustic cell is made of glass with two Young's taps. Figure 2.5 shows the photoacoustic spectrum of water vapour alongside a simulated spectrum of water taken from the HITRAN database.⁸ The spectrum represented in figure 2.5 illustrates the fundamental O-H stretching region of water vapour. From initial observations the experimental and simulation spectra look almost identical, the experimental spectrum (via a photoacoustic cell) has been recorded by measuring the water vapour content in air by creating a partial vacuum within the cell. Hence, the presence of other IR absorbing trace gases species may possibly be contributing to the overall IR spectrum. The experimental spectrum has not been shifted with respect to the simulated spectrum: the two spectra were already in good agreement with one another, which indicates that the OPO/A laser is fairly well calibrated.

Generally, after laser calibration the calibration can be sustained for a particular set of experiments recorded on the same day, and sometimes over several days. However, it is good practise when starting a new experiment to check the laser calibration, just to make sure no wavelength shift has occurred.

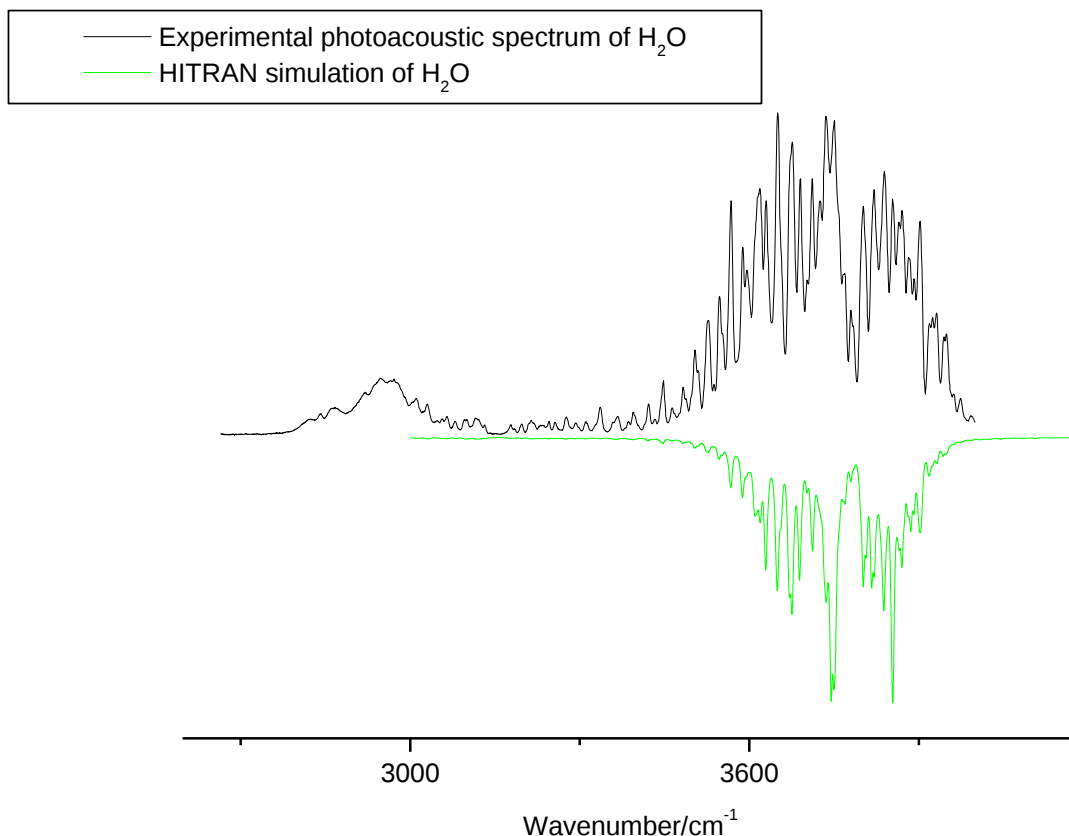


Figure 2.5: HITRAN simulation and experimental photoacoustic spectrum of H₂O.

2.5 Time-of-flight mass spectrometer

To detect molecular ions, a time-of-flight mass spectrometer (TOF-MS) was used. TOF mass spectrometers are based on the principle that ions of different mass/charge (m/z) ratios can be separated and their mass spectra recorded due to different arrival times at an ion detector. An electric field (E) is used to inject ions into a field-free drift region, i.e. the flight tube. If the ions travel a fixed distance (l) to the detector, then the ‘time-of-flight’ is given by the equation [2.3].

$$t = l \sqrt{m/2zeV} \quad [2.3]$$

Here z is the ion charge, e is the fundamental electronic charge, V is the accelerating voltage, and m is the mass of the ion. Essentially, lighter ions will reach the detector before the heavier ions, and therefore by measuring the flight time (t) of ions from the ion source to the detector, the ion mass can be determined.

The first practical TOF-MS instrument was designed by Wiley-McLaren in 1955.⁹ They devised a time-lag focusing scheme that improved mass resolution by simultaneously correcting for the initial spatial and kinetic energy distributions of the ions.

Our current mass spectrometer is based on the Wiley-McLaren design. The analyte gas enters the ionisation region between the ‘repeller’ and ‘grid’ electrodes (see Figure 2.6). Ions are produced by laser photoionisation, which essentially starts the ‘clock’ for ion time-of-flight measurements. In theory, ions should be accelerated from the same space/location between the two plates, so should have the same kinetic energy travelling to the detector, located at the end of the drift region. However, due to the possibility of a divergent molecular beam this assumption is flawed. Instead, ions of the same m/z ratio can potentially have different drift velocities and thereby arrive at the detector at different times. This is because identical ions may not be located at the same spatial position, and thus those ions located near the upper electrode will have a shorter distance to travel as opposed to the identical ion located nearer to the lower electrode. The effect of this can lead to very poor mass resolution, making the instrument virtually useless.

Wiley and McClaren solved this problem by introducing a draw-out grid electrode. The draw-out grid is a second wire mesh electrode with a potential set slightly less than that of the repeller. The potential difference between the accelerator

and grid provides the main acceleration, which is the same for all ions. However, the first stage of the acceleration process depends on the spatial position of the ions such that those ions further away from the grid will receive additional kinetic energy, but consequently have further to travel to reach the detector when compared to those ions located in close proximity to the grid.

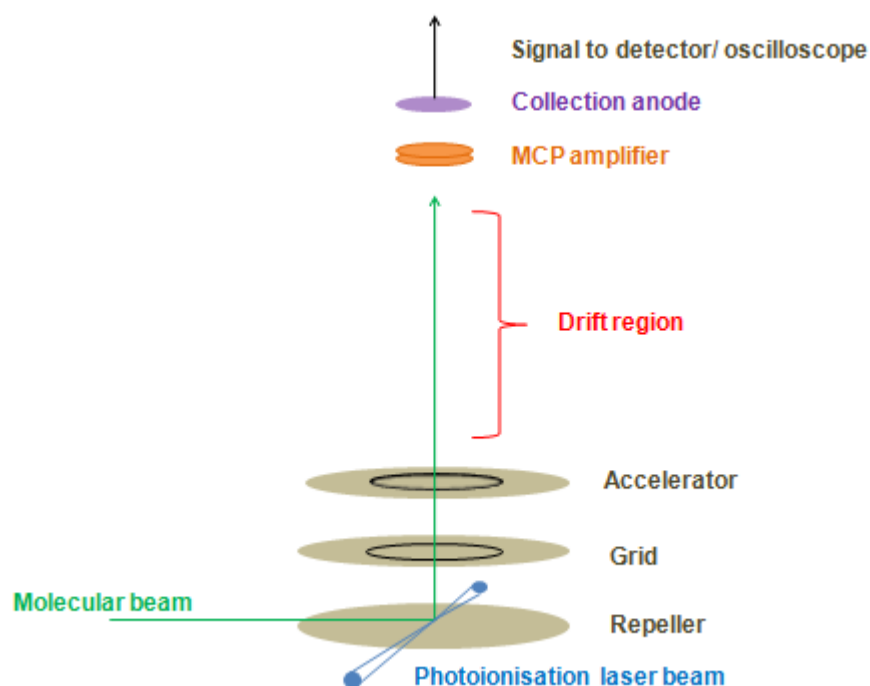


Figure 2.6: Schematic representation of a TOF-MS.

Essentially, the voltages of the grid and repeller can be carefully tuned so that the overall mass resolution of peaks can be improved. This method of reducing the time spread and the initial energy distribution of ions is known as first order spatial focusing.⁹

For simplicity, the time of flight (t_1) and the mass of a known ion (m_1) are often used to calculate the corresponding mass of an unknown ion (m_2) using its measured time of flight (t_2), i.e. using equation [2.4]:

$$t_1/t_2 = \sqrt{m_1}/\sqrt{m_2} \quad [2.4]$$

This approximation works best when there are two ions of similar masses, when this formula is used for ions of different masses the approximation becomes less accurate.

A microchannel plate (MCP) detector assembly was used for ion/electron detection. An MCP is essentially an amplifier for charged particle signals. The output was further amplified using a preamplifier unit and then sent to a digital oscilloscope (see next section).

2.6 Data acquisition and processing

Data capture and storage is achieved using a combination of a digital oscilloscope (DSO) (LeCroy Waverunner LT332) and a personal computer. Firstly, the output from the MCP on each laser shot is sent to the DSO. The collected signal images are continuously averaged over multiple shots, to reduce any signal ‘spikes’, and are then transferred to the PC.

Data collection, instrument control, and data processing is provided by an in-house written script using National Instruments LabView (version 6.0.2) software. The main function of this software is to scan the OPO laser over a desired wavelength range and at a particular scan rate. In addition to this, the software collects the mass spectral data from the DSO and processes the data to produce a spectrum. The LabView software allows several (up to seven) specific mass channels to be ‘gated’ and analysed individually. This means that spectra can be recorded in up to seven different mass channels, and therefore potentially for seven different species. A spectrum is recorded by scanning the OPO wavelength while integrating the signal within a specific ion gate.

2.7 Pulse synchronisation

The lasers and the gas valve used in these experiments are pulsed. Consequently, it is essential that they are appropriately synchronised. In order to achieve this, electronic delay generators were employed. The start of this synchronisation process comes from the driver unit for the pulsed valve (IOTA ONE). This unit is set to fire the valve at a 10 Hz repetition rate and effectively acts as the master clock, providing the starting pulse against which all other pulses are delayed. When it fires, the IOTA ONE generates a reference TTL pulse, which will be referred to as the T_0 pulse, from which the rest of the experiment is triggered. This is fed into a Stanford Research Systems DG535 delay generator consisting of four output channels, A, B, C and D. These are used to externally trigger the flashlamps and Q-switches of the two Nd:YAG pump lasers (pumping the dye laser and the OPO/A). The laser timing events are labelled as follows:

T_0 = Start pulse

$$A = T_0 + T_{UV \text{ Flashlamp}}$$

$$B = A + T_{UV \text{ Q-switch}}$$

$$C = A - T_{IR \text{ Flashlamp}}$$

$$D = C + T_{IR \text{ Q-switch}}$$

The firing times of the flashlamp and Q-switch on each Nd:YAG laser are set by optimising the mass spectral signal on an oscilloscope. A second delay generator (EG&G Princeton Applied Research 9650A) is also triggered from the initial timing pulse, T_0 . This delay generator is used to trigger the flashlamp on the small Nd:YAG laser (Continuum Minilite), which is used for laser ablation. Again, the optimum timing for the firing of this laser is determined by monitoring the ion signal on an

oscilloscope. The typical values for the timings of the lasers are given in figure 2.7, although these timings are subject to modest changes from one experiment to another.

The delay settings will necessarily determine the portion of the pulsed molecular beam that is probed by the lasers. Previous experiments have found that the most efficient cooling occurs for the gas molecules close to the front of the gas pulse.¹ However, the largest signal is usually found further upstream in the gas pulse, which can be accessed by delaying the probe lasers such that the central part of the gas pulse is probed.¹ The experimental timing is illustrated in figure 2.7:

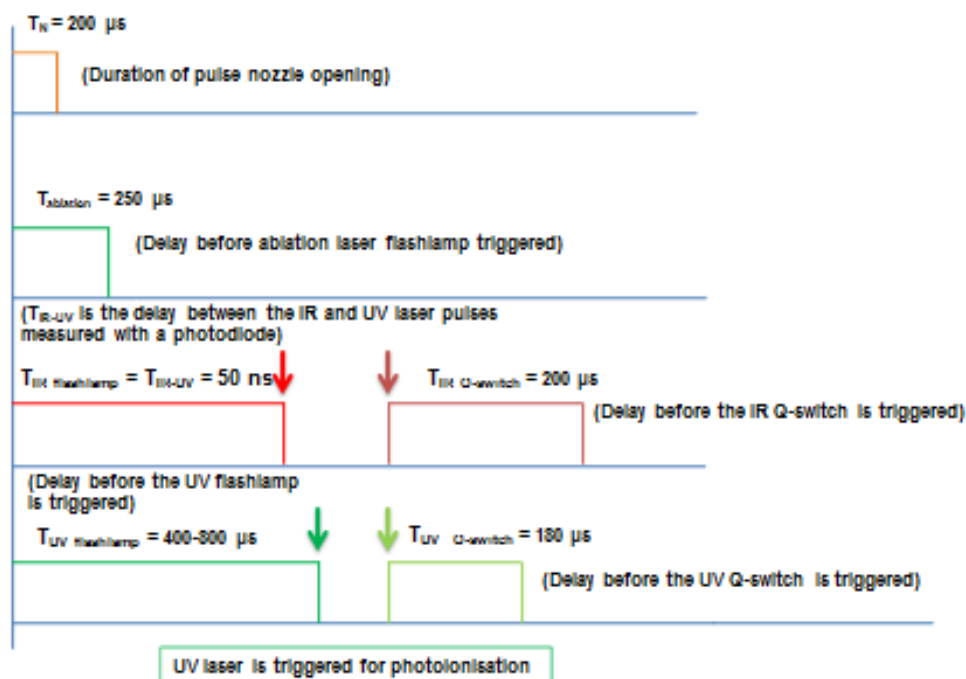


Figure 2.7: Pulse timing diagram.

(The typical valve opening time is around $200 \mu s$ and all other timings will be relative to this).

2.8 Electronic spectroscopy

The role of electronic spectroscopy will be an important part of our experiments since many of the complexes will be probed in the near IR. Essentially electronic spectroscopy is concerned with the transition of an electron from a lower energy state to an excited one, of a molecule. For a good approximation, the electrons in a molecule can be considered to be in molecular orbitals (MO). Electronic spectroscopy is able to provide detailed information on the electronic structure of molecules. It can also provide information on molecular vibrations and rotations since vibrational and rotational structure can often be resolved, especially for small molecules in the gas phase.

In addition, vibrational transitions can also accompany electronic transitions to produce a vibronic spectrum. The set of bands associated with this spectrum is known as an electronic band system. However, transitions between vibrational levels in different electronic states must satisfy the Franck-Condon principle.⁴ This states that the most probable transition is a vertical transition involving no change in equilibrium nuclear positions. There will be little evidence of vibrational structure if the upper and lower electronic states have very similar equilibrium structures. However, a long vibrational progression is expected if there is a marked change in equilibrium structure between the two electronic states.⁴

2.8.1 Selection rules and symmetry

It is important to note that in order for a transition to actually occur a set of formal constraints must be satisfied. Electronic transitions must satisfy the spin selection rule, which states that the total electronic spin of a molecule must be unchanged ($\Delta S = 0$) on absorption or emission of a photon.⁴ For example, The emission processes where photons are emitted from excited electronic states in transitions back down to lower

electronic states, include fluorescence: $\Delta S = 0$ is fast because this process is spin-allowed. Whereas phosphorescence (due to inter-system crossing): $\Delta S \neq 0$ therefore is a slow process because it is spin-forbidden.

The transition probability, $|R^{nm}|^2$, equation [2.5], is also related selection rules where the transition probability is zero for a forbidden transition and non-zero for an allowed transition.⁴

$$R^{nm} = \int \psi_n^* \mu \psi_m d\tau \quad [2.5]$$

Where R^{nm} is the transition moment, ψ is the wavefunction of the upper and lower states and μ is the electric dipole moment operator.

Since vibrational spectroscopy will be a central focus of the experiments, in a fundamental vibration, the molecule is excited from its ground state ($v = 0$) to the first excited state ($v = 1$). The symmetry of the ground-state wave function is the same as that of the molecule. It is, therefore, a basis for the totally symmetric representation in the point group of the molecule. It follows that, for a vibrational transition to be allowed, the symmetry of the excited state wave function must be the same as the symmetry of the transition moment operator. With the use of character tables, the point group of a metal-solvent complex can be used to deduce whether a particular transition will be allowed or not.

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Chapter 3 - *Ab initio* methods

3.1 Introduction

Ab initio calculations have played an important role in describing the behaviour of molecules and clusters investigated in this thesis. These calculations complement experimental studies by aiding spectroscopic assignment and also by providing information on the targeted species that are inaccessible from the experiments. The calculations are a valuable tool, as they can firmly establish important parameters such as equilibrium geometries, bond dissociation energies and vibrational frequencies.

This particular chapter outlines key concepts of *ab initio* theory, including the hardware and software used in the present study. A detailed discussion of the underlying theoretical principles will not be provided; more detailed information on quantum mechanical theory can be found elsewhere.¹

3.2 Fundamentals of *ab initio* calculations

Standard *ab initio* methods aim to approximate the many-electron time-independent Schrödinger wave equation:

$$H\psi = E\psi \quad [3.1]$$

The Schrödinger equation is very simply expressed as equation [3.1], where H represents the Hamiltonian operator and ψ is the wavefunction of the system of interest.

Equation [3.2] illustrates how the Hamiltonian can be constructed. The first part of the equation essentially indicates the kinetic energy (T) operators for the electrons and nuclei present in the system. The second set of terms are the potential energy (V) operators corresponding to electron-electron and nuclear-nuclear repulsions, as well as the electron-nuclear attractive forces.

$$H = T_n + T_e + V_{en} + V_{ee} + V_{nn} \quad [3.2]$$

A more detailed and complete Hamiltonian for an N -electron system consisting of P distinct nuclei and N electrons can be written as:

$$H = -\frac{\hbar^2}{2} \sum_{A=1}^P \frac{1}{M_A} \nabla_A^2 - \frac{\hbar^2}{2m_e} \sum_{i=1}^N \nabla_i^2 - \sum_{i=1}^N \sum_{A=1}^P \frac{Z_A e^2}{4\pi\epsilon_0 r_{iA}} + \sum_{i=1}^N \sum_{j>i}^N \frac{e^2}{4\pi\epsilon_0 r_{ij}} + \sum_{A=1}^P \sum_{B>A}^P \frac{Z_A Z_B e^2}{4\pi\epsilon_0 R_{AB}} \quad [3.3]$$

where Z_A is the charge and M_A is the mass of nucleus A , m_e is the mass of the electron, R_{AB} is the distance between the nuclei A and B , r_{ij} is the distance between electrons i and j , r_{iA} is the distance between the electron i and nucleus A and ϵ_0 is the permittivity of free space.

Solving the Schrödinger equation using this Hamiltonian can, in principle, yield the full set of wavefunctions and the corresponding energies for the system under investigation. However, the resulting Schrödinger equation is far too complex for an exact solution when more than one electron is present in the molecule.² Consequently, approximations are needed to solve the Hamiltonian for a multi-electron system. One such approximation is the assumption that nuclear motion is much slower than electron motion, essentially because nuclei are much heavier than electrons.³ This is the underlying basis of the Born-Oppenheimer approximation, which allows the nuclear kinetic energy part of equation [3.2] to be removed, and the resulting simplified electronic Schrödinger equation can then be more readily solved. The Born-Oppenheimer approximation implies that the electrons respond instantaneously to changes in nuclear coordinates, such that the energy of the electrons becomes part of the potential field in which the nuclei move. Thus we can

focus on a more restricted Hamiltonian, shown in equation [3.4], which applies for a fixed nuclear position.

$$H_e = T_e + V_{ee} + V_{en} \quad [3.4]$$

Even with the Born-Oppenheimer approximation, the Schrödinger equation still cannot be solved exactly for a multi-electron system. In particular, further approximations are required to simplify the problem of electron-electron interactions. The Hartree-Fock method is the most basic method for doing this.² Essentially, the individual electrons are assumed to reside in *orbitals*, denoted as ψ . By confining each electron to a specific wavefunction, ψ , each of these individual electrons will move and experience the average repulsive field generated by the other electrons, as well as the attractive force of the nucleus. This is sometimes called the *mean field approximation*, because it simplifies the way in which electron-electron repulsion is treated.

In addition to electron-electron repulsion, the electrons need to be described in terms of their spin. This is achieved using spin orbitals, χ , which are products of the one-electron orbital wavefunction and the spin function, given by:

$$\chi = \begin{matrix} \psi(r)\alpha \\ \text{or} \\ \psi(r)\beta \end{matrix} \quad [3.5]$$

where α and β are spin wavefunctions and r describes the spatial coordinates of an electron. In the HF method, the wavefunction for a closed-shell molecule is formed

from a single Slater determinant. A Slater determinant ensures the antisymmetry of the electronic wave function (from the Pauli Principle) and takes the general form

$$\psi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(\mathbf{x}_1) & \chi_2(\mathbf{x}_1) & \cdots & \chi_n(\mathbf{x}_1) \\ \chi_1(\mathbf{x}_2) & \chi_2(\mathbf{x}_2) & \cdots & \chi_n(\mathbf{x}_2) \\ \vdots & \vdots & & \vdots \\ \chi_1(\mathbf{x}_n) & \chi_2(\mathbf{x}_n) & \cdots & \chi_n(\mathbf{x}_n) \end{vmatrix} \quad [3.6]$$

where x_i collectively describes both the spatial and spin coordinates of the electron. The individual electrons are represented by different rows in the determinant, which means that interchanging the coordinates of two electrons is equivalent to interchanging two rows in the determinant.² Essentially, the Slater determinant can be used to describe the ground state wavefunction of an atom or molecule. Substitution of the Slater determinant into the electronic Schrödinger equation and subsequent application of the variation principle leads to the Hartree-Fock (HF) equations. There is essentially one HF equation for each electron but the operators appearing in the HF equations are functions of the orbitals that we wish to generate. Consequently, it is necessary to solve these equations by an iterative procedure, which is called the self-consistent field (SCF) procedure.

As implied above, the HF method does not fully account for electron-electron interactions. Each electron is assumed to interact with the averaged charge cloud formed by the sum of all other electrons distributed within fixed molecular orbitals.⁴ This loss of flexibility causes the electrons to actually come closer to each other than would otherwise be possible, resulting in extra repulsion energy and thus the overall energy of

the system is increased. The difference in energy omitted by the inaccurate treatment of electron-electron interaction is termed the correlation energy. Although small in absolute terms, it can be extremely important in the description of some molecular properties, e.g. the determination of bond dissociation energies. Consequently, to improve the accuracy of an electronic structure calculation some method of accounting for this electron correlation must be included beyond a simple Hartree-Fock calculation. This will be discussed in a later section.

3.3 Basis sets

Molecular orbitals are usually expressed in terms of a linear combination atomic orbitals (LCAO). This collection of ‘atomic orbitals’ is known as a basis set. A basis set provides a collection of functions, usually centred on each atom present in the molecule, which can be used to expand the molecular orbitals. The basis functions will ideally possess some of the expected properties of real atomic orbitals. The LCAO expansion takes the form shown below:

$$\psi_i = \sum_i c_i \phi_i(r) \quad [3.7]$$

where ψ_i is the molecular orbital, i , c_i is the expansion coefficient and ϕ_i is the spatial basis function. For a perfect description of molecular orbitals the basis set would require an infinite number of terms in the expansion. However, in computational chemistry a compromise must obviously be reached between the accuracy of the calculation and the computational cost.

Early *ab initio* calculations employed basis sets constructed from Slater-type orbitals. These particular basis functions were initially chosen since they closely

resemble the exact solutions of the Schrödinger equation for the hydrogen atom.² However these basis functions were later largely abandoned because they led to integrals appearing in the calculations that were time consuming to calculate. In their place primitive Gaussian functions are now almost always used instead and have shown to be more cost effective. An expanded Gaussian function takes the form of equation [3.8]

$$g_{ijk}(r) = Nx^i y^j z^k e^{-\alpha r^2} \quad [3.8]$$

where, x , y and z represent spatial coordinates with respect to the nucleus of the appropriate atom, i , j , and k are non-negative integers, α is an orbital exponent and N is a normalisation constant. Generally, the number of Gaussian-type orbitals required to reproduce a result found using Slater type orbitals will be significantly larger. Despite these limitations, Gaussian type orbitals are generally chosen to build a basis set due to the relative ease in evaluating their two-electron integrals.²

There are many examples of standard basis sets, which are now available in basis set ‘libraries’. One of them is the so-called minimal basis set, which uses the smallest number of functions possible to represent all the electrons present in the molecule. The most common example of this minimal basis set is the STO-3G basis set. Here each atomic orbital has been expanded into three Gaussian functions, where the values of the Gaussian exponents and the expansion coefficients have been determined by least squares fits to Slater-type functions. This basis set is not sufficient to accurately describe the chemistry of a molecular system. Consequently, the use of additional functions is required that can provide a better description of the electron distribution.

Examples of basis sets which incorporate a higher level of flexibility are the split valence basis sets.^{2,5} These offer more functions than the minimal basis set: core atomic orbitals are represented by one set of functions while the valence orbitals have additional functions. The Pople basis sets, 3-21G and 6-31G, are prime examples of split valence basis sets.² For instance, the 3-21G basis set implies a contraction of three primitive Gaussian functions to represent the core atomic orbitals and two different contractions are used to represent the valence electrons. More explicitly, one of the two valence contractions contains two primitive Gaussian functions and the second contains just one. Larger basis sets, may be produced using three or four additional Gaussian functions to offer a more accurate description of the valence electron distribution. The split valence basis sets are preferred over the minimal basis sets since they better describe the spatial distribution of electrons when they form chemical bonds.

To supplement the basis set, diffuse functions can also be added. These functions can correct for the poor behaviour of the wavefunction at large distances from the nucleus. A prime example would be in excited electronic state calculations for a molecule, where the promoted electron may be only loosely associated with the specific atoms. The inclusion of diffuse functions is often denoted by a + sign added to the basis set label, e.g. 6-31+G. Diffuse functions are particularly important in describing weakly interacting species, such as van der Waals complexes, because of their large internuclear separation.

Another widely used group of basis sets are the Dunning correlation-consistent basis sets.⁶ These add functions to a core set of atomic Hartree-Fock functions that are consistent with the effects of electron correlation. An example of these are the (aug)-cc-p(C)VXZ basis set. Here the “aug” refers to the addition of diffuse functions and the “C” means core and is used to include electron correlation functions. In addition to this,

X represents the number of contracted basis functions used to represent the valence orbitals. If $X = 2$ we have a so-called double zeta basis set, $X = 3$ is a triple zeta basis set, and so on. Although the expansion of the electron distribution becomes more accurate as more basis functions are added, the computational expense can rise exceptionally quickly. It is therefore normally good practice to start a trial calculation using either a minimal or a small split valence basis set before computationally more expensive basis sets are employed.

3.4 Møller-Plesset perturbation theory

Møller-Plesset perturbation theory (MPPT) is a post-HF method which incorporates some of the effects of electron correlation.⁷ MPPT assume that the difference between the two Hamiltonians, i.e. the complete H and the approximate (from HF) $H^{(0)}$, is small. This difference between the two is referred to as the perturbation to the system. Thus, the incorporation of a small perturbation to the HF Hamiltonian in the form of a Taylor expansion series is added to the unperturbed Hamiltonian in which λ is an expansion parameter, as given below.

$$\hat{H} = \hat{H}^{(0)} + \lambda \hat{H}^{(1)} + \lambda^2 \hat{H}^{(2)} + \lambda^3 \hat{H}^{(3)} \dots \quad [3.9]$$

If enough terms are included in this expansion series the result will eventually yield the actual Hamiltonian. Expanding the exact wavefunction and energy yields

$$E = E^{(0)} + \lambda E^{(1)} + \lambda^2 E^{(2)} + \lambda^3 E^{(3)} \dots \quad [3.10]$$

$$\psi = \psi^{(0)} + \lambda \psi^{(1)} + \lambda^2 \psi^{(2)} + \lambda^3 \psi^{(3)} \dots \quad [3.11]$$

In equation [3.10] the zero order energy term $E^{(0)}$ provides the energy of the spin orbitals and the first order term $E^{(1)}$ adds a correction such that the sum of the two gives the HF energy. The subsequent higher order corrections are required to include electron correlation effects. However, the addition of many perturbation terms within a calculation is computationally very expensive, and therefore the second order perturbation theory, i.e. MP2, is often the only one used. Importantly, this usually recovers the majority of the dynamic correlation energy.

3.5 Other electron correlation methods

An alternative to the Møller-Plesset method for incorporating electron correlation energy is the Configuration Interaction (CI) method. This method is based on the use of an overall electronic wavefunction resulting from a linear combination of the ground state electronic wavefunction (obtained from the HF theory) and all the possible excited electronic states formed via the excitation of electrons from occupied to unoccupied molecular orbitals. This is actually referred to as full configuration interaction, and since the numbers of electronically excited states is potentially infinite, this would give the exact solution to the Schrödinger equation if it could be achieved.

However, in practice a finite expansion must be employed. Consequently, the final energy will not be the same as would result from solution of the full Schrödinger equation, and therefore CI calculations are only approximations. The crudest approximation makes use of only single-electron promotion, i.e. only Slater determinants corresponding to single electron promotions are included in the CI expansion. This CI-Singles (CIS) method leads to no improvement of the HF energy or wavefunction, but it does allow very crude estimates of electronic excitation energies.

A simple procedure that actually does lead to a slight improvement over the HF method is called the CISD method, where both single and two (double) electron excitations are included.² One important problem with CI methods is their size-inconsistency, which means the energy of two infinitely separated particles is not double the energy of the single particle.

Coupled (CC) cluster theory⁸ is another technique that can be used to take into account the effects of electron correlation. Instantaneous Coulomb repulsion between two interacting electrons can be disrupted to such an extent that this can cause the excitation of an electron from an occupied spin orbital to a virtual orbital with a specific probability, and this disturbance from an orbital into a virtual orbital is known as a pair cluster. The effect of this on the wavefunction can be expressed as

$$\psi = e^{\hat{T}} \psi_0 \quad [3.12]$$

Here $\hat{T}$ is the excitation operator acting on the ψ_0 (which is a Slater determinant constructed from the HF molecular orbitals) to produce a linear combination of excited Slater determinants, as illustrated in equation [3.6]. The effect of this is to produce a new wavefunction that will include the excitations of occupied spin orbitals into virtual spin orbitals. The global cluster excitation operator is given by equation [3.13]:

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3 \dots \quad [3.13]$$

where the truncation of the excitation operator will define the method used. For example, $\hat{T}_3$ will suggest that three occupied spin orbitals are being replaced by virtual spin orbitals, i.e. a triple excitation. The CC method is primarily limited to single and

double excitations (these excitations are used to calculate the energy of a given state), since anything beyond that will require a hugely increased amount of computational time. The most common method used is CCSD(T), where the single (S) and double (D) excitations are calculated via this method and triple (T) excitations are determined at a much lower cost via perturbation theory.

In general, as the level of excitation increases so does the cost of computational time, to achieve a sufficient accuracy the Coupled cluster method (with a suitable basis set) is generally more accurate than the MP2 and CIS methods. Furthermore, CCSD(T) is regarded as the ‘gold standard’ in terms of *ab initio* calculations for the compromise between accuracy and cost. However, for large molecular systems CCSD(T) calculations are considered unfavourable due to time and cost issues. In Full-CI all possible occupation schemes are allowed hence, you will have single, double, triple, quadruple etc... excitations occurring, however full-CI is not practical except for very small systems. The main aim of methods such as CCSD and/or MP2 is to get close to the full-CI energy; hence, why the inclusion of triple excitations gives you more accurate energies than if you only include single and double excitations.

3.6 Basis Set Superposition Error

The calculation of bond dissociation energies can be deduced by the supermolecule approach

$$\text{Binding (bond)energy} = (E)_{\text{cluster}} - \Sigma(E)_{\text{fragments}} \quad [3.14]$$

Although intuitive, an interaction energy calculated in this way is likely to be artificially high. This effect is a result of basis set truncation and is termed the basis set superposition error (BSSE). This arises when two fragments that make up the molecule approach one another and in a sense, they begin to share their basis functions. Effectively this causes an increase in the overall basis set resulting in a lowering of the calculated energy. However, when the fragments of the overall molecule are treated separately their individual energies are relatively high since they can no longer share additional basis functions from the other fragment.

To overcome this deficiency the counterpoise correction method was introduced by Boys and Bernardi.⁹ Essentially, this correction requires an additional calculation where the fragment in question contains its electrons and nucleus, but the basis functions from the second fragment, the so called ‘ghost species’ are added, and vice-versa. The corrected interaction energy, $E_{CC}[AB]$ of dimer AB can then be calculated using a modified supermolecule approach i.e.

$$E_{CC}[AB] = E_{AB}[A] + E_{AB}[B] - E_{AB}[AB] - E_A[A] - E_B[B] \quad [3.15]$$

where $E_{AB}[A]$ is the energy of the fragment A using the basis functions from the dimer AB, $E_{AB}[B]$ is the energy of fragment B using the basis functions from the dimer AB and $E_{AB}[AB]$ is the energy of the entire molecule,

3.7 Geometry optimisation

A key quantity often required from *ab initio* calculations is the equilibrium structure(s) of a molecule. These correspond to minima on the potential energy surface and

therefore can be calculated by finding the minimum energy. This process is known as geometry optimisation.

To ensure that a particular optimised geometry is positioned at a stationary point, harmonic frequencies must be calculated (see next section). A true minimum will yield a complete set of real (positive) vibrational frequencies. On the other hand, one or more imaginary (negative) frequencies will occur if the structure is not at a real minimum.

Geometry optimisation calculations increase in cost very rapidly as the size of the molecule increases, because the energy optimisation has to be done in $3N-6$ dimensional space, where N is the number of atoms. Furthermore, larger structures are likely to consist of several isomers. This can be troublesome as the geometry optimisations would ideally be carried out on all individual isomers, ensuring that the global minimum and local minima are identified. This is a challenging requirement and is not always viable.

3.8 Harmonic vibrational frequency calculations

Once a stationary point has been found, it is then important to carry out a vibrational frequency analysis to determine if the molecule is at a true potential energy minimum. In addition, for many applications reported in this thesis the vibrational frequencies were of value in interpreting the spectra. The vibrational frequencies calculated in this work use the simple harmonic oscillator approach.

For a non-linear polyatomic molecule, there will be $3N-6$ degrees of vibrational freedom, where N is equal to the number of atoms present in the molecule. The partial derivatives of the energy with respect to each of the $3N-6$ independent geometrical coordinates (R_i) are zero at a potential energy minimum i.e.

$$\frac{\partial V}{\partial R_i} = 0 \quad i = 1, 2, \dots, 3N - 6 \quad [3.16]$$

Therefore in the many dimensional case, each coordinate, R_i results in $3N-6$ second derivatives²

$$\frac{\partial^2 V}{\partial R_i \partial R_1}, \frac{\partial^2 V}{\partial R_i \partial R_2}, \frac{\partial^2 V}{\partial R_i \partial R_3}, \dots, \frac{\partial^2 V}{\partial R_i \partial R_{3N-6}} \quad [3.17]$$

This leads to a matrix of second derivatives, i.e. the so called Hessian matrix,² which can be used to calculate the harmonic vibrational frequencies of a molecule. When comparing the calculated vibrational frequencies with fundamental frequencies, the calculated results will normally overestimate the vibrational frequencies because the former are harmonic frequencies, and so do not account for anharmonicity. One solution to this is to introduce some scaling,¹⁰ where the computed harmonic frequency is brought closer to the ‘true’ fundamental frequency through some rational scaling factor.¹¹ The scaling factor is a theoretical construction that can be derived via a ‘trial and error method,’ e.g. by investigating a series of molecules and then applying a scaling factor that brings theory and experiment into best agreement. It should be understood that the scaling parameter is both method and basis set dependent. It is, of course, also approximate.

3.9 Computational hardware and set up

All calculations were performed using Gaussian 03¹² and all input scripts were edited in GaussView 03.¹³ Several different computer hardware systems were used. Each is a cluster running under a Linux-based operating system and had the following specifications.

Marvin has two AMD Opteron 244 64-bit processors in one node, with 6 GB of RAM per node and 140 GB scratch disk per node. This particular cluster is a custom-built system, exclusively for the spectroscopy group at the University of Leicester.

The majority of calculations were run on two other systems: *Magellan*, which is run by the National Service for Computational Chemistry Software, and the *Newton* cluster, which is a part of the University of Leicester's Mathematical Modelling centre.

Finally the *Alice* cluster is a recent high performance computing cluster installed at the University of Leicester and has been used for the remainder of the calculations. The system is composed of 256 computer nodes, two login nodes, two management nodes and a high performance parallel file system of 100 TB capacity. Each computer node has a pair of quad-core 2.67 GHz Intel Xeon X5550 CPUs and 12 GB of RAM. In total, there are 2048 CPU cores available for running jobs.

All geometry optimisations were run with Cartesian co-ordinates with no symmetry constraints to permit a full variation of all degrees of freedom. After this, vibrational frequency analysis was used to ensure that a true potential energy minimum was achieved by checking for imaginary values. The highest level of theory used in the present calculations was second order Møller-Plesset perturbation (MP2 theory). In addition to this, for visualisation of output files, Chemcraft¹⁴ was utilised. This is a graphical program for displaying the findings of quantum chemistry calculations. Chemcraft is mainly developed as a graphical user interface for Gaussian program packages.

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Chapter 4 - The Electronic Spectrum of $\text{Li}(\text{NH}_3)_4$

4.1 Introduction

This following chapter has been adapted from the published paper by the Ellis group.¹ $\text{Li}(\text{NH}_3)_4$ has been proposed as a key entity in lithium-ammonia solutions, but its spectral signature has so far proved impossible to distinguish from other species in these solutions. In this chapter, the first electronic spectrum of $\text{Li}(\text{NH}_3)_4$ in the gas phase will be investigated, which was recorded using mass-selective depletion spectroscopy. Strong absorption is observed in the near-infrared and the band system is assigned to the $\tilde{A}^2T_2$ - $\tilde{X}^2A_1$ transition in a nominally tetrahedral complex. However, the vibrational structure is indicative of a substantial Jahn-Teller effect in the excited electronic state. The broad and structured spectrum confirms a recent theoretical prediction that the electronic spectrum of $\text{Li}(\text{NH}_3)_4$ will strongly overlap with the spectrum of the solvated electron in lithium-ammonia solutions.²

4.2 Previous studies on Lithium-ammonia molecules

Solutions of lithium in liquid ammonia have attracted attention because of their intriguing and unusual properties. These properties include the solution colour and the electrical conductivity, both of which can change dramatically over a relatively modest concentration range. Despite being studied for many decades, the contents of a typical lithium/ammonia solution at the molecular scale are still poorly understood to this day. The complexity of these solutions has been illustrated in a recent comprehensive study by Zurek *et al.*,² who applied molecular orbital calculations, in the form of density functional theory, to an array of neutral molecules, anions and cations that might be plausible constituents of a lithium/ammonia solution under a variety of concentration regimes. Potential species

identified included $\text{Li}(\text{NH}_3)_4$ and $\text{Li}(\text{NH}_3)_4^+$, the solvated electron (denoted as $e^-@(\text{NH}_3)_n$), and clusters formed from combinations of these species, see figure 4.1.

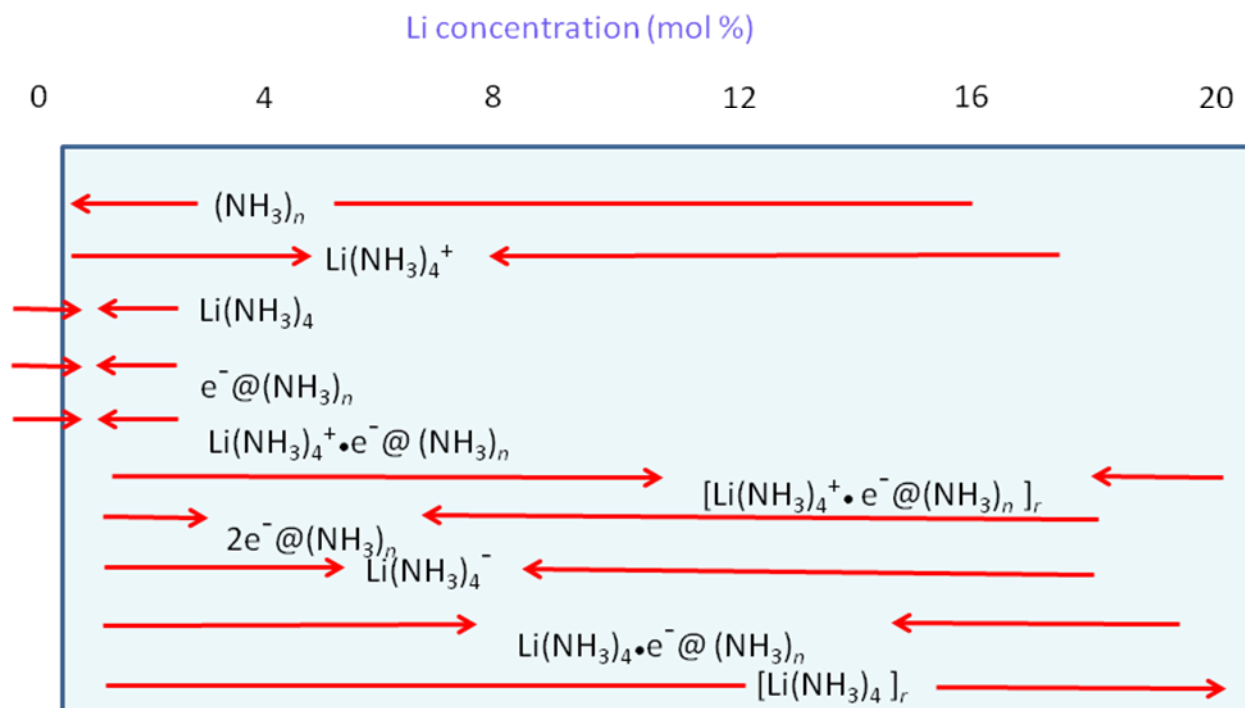


Figure 4.1: Likely substituent's of Li/ NH_3 solution as predicted by DFT calculations.²

In an attempt to understand the characteristic optical spectra of lithium/ammonia solutions, which show a peak absorption in the near-infrared, time-dependent density functional theory (TD-DFT) was also applied to calculate the electronic transitions for various ion pairs, as well as for neutral $\text{Li}(\text{NH}_3)_4$.² Remarkably, both solvated electrons and $\text{Li}(\text{NH}_3)_4$ are predicted to have similar vertical transition energies, which suggests that optical spectroscopy may be inadequate for identifying the optically active species in a solution of specific concentration.²

In order to explore this further, it would be valuable to know the electronic spectrum of $\text{Li}(\text{NH}_3)_4$. The band maximum of this molecule in the gas phase was predicted to be close to 6900 cm^{-1} (1450 nm) by the TD-DFT calculations of Zurek and co-workers,² but there were no experimental data against which this could be compared. Here we provide this information and, as will be shown below, the TD-DFT calculations do well in predicting the absorption maximum but by their very nature are unable to reveal the richness of the actual spectrum, which shows resolvable vibrational structure and a clear absorption onset. Evidence for a large Jahn-Teller effect in the excited electronic state is also found, which further complicates the spectral appearance and the assignment. The Jahn-Teller effect will be explained in more detail in this chapter, however in brief, this effect arises when a molecule is in an orbitally degenerate state. Therefore the Jahn-Teller effect will involve a distortion of the molecule in order to remove this degeneracy and improve the stability of the molecule overall.

4.3 Current experimental studies on $\text{Li}(\text{NH}_3)_4$ cluster

The spectrum of $\text{Li}(\text{NH}_3)_4$ has been recorded using a depletion technique which has been applied previously in our group to record the mid-infrared (pure vibrational) spectrum of this and other $\text{Li}(\text{NH}_3)_n$ clusters, Figure 4.2 and 4.3 represent the mass spectrum and the IR depletion spectrum of lithium-ammonia clusters, including $\text{Li}(\text{NH}_3)_4$.³

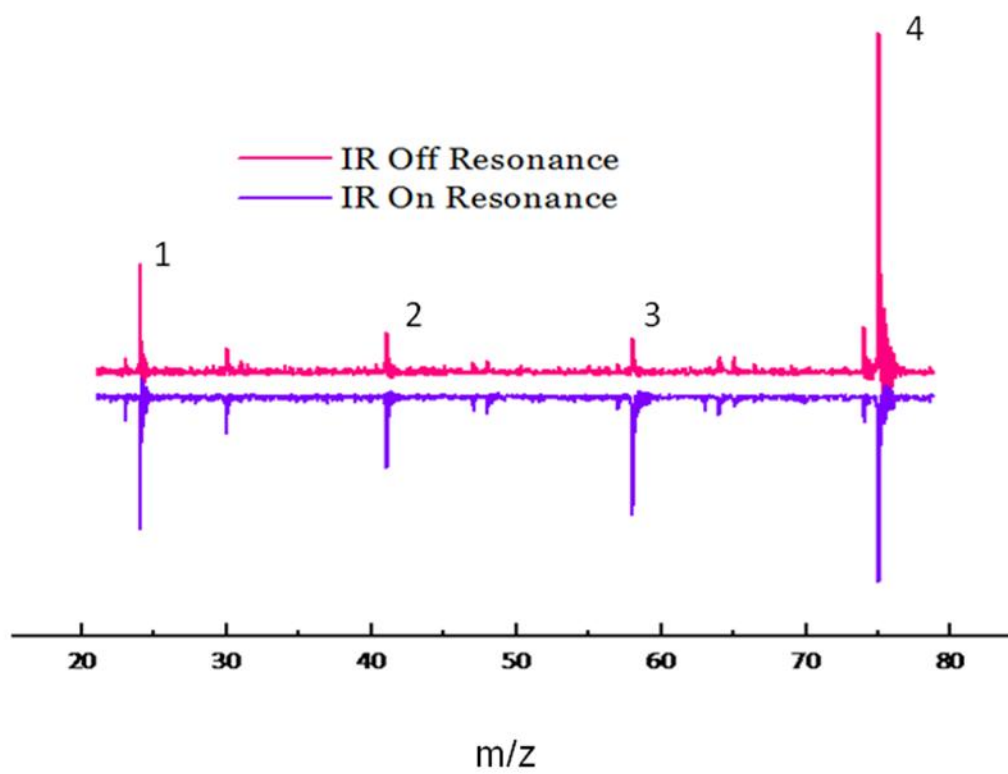


Figure 4.2: Mass spectrum of $\text{Li}(\text{NH}_3)_n$ clusters, where $n = 1$ to 4.

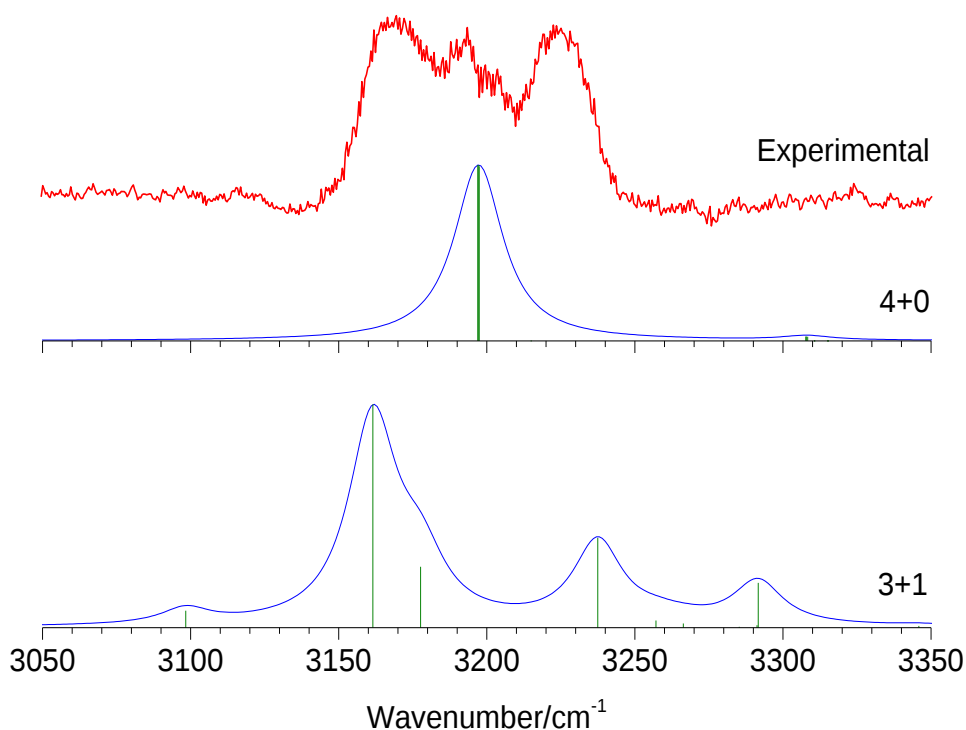


Figure 4.3: An enlarged view of the IR spectrum of $\text{Li}(\text{NH}_3)_4$ in the N-H stretching region is shown in the upper panel. Below the experimental spectrum are the DFT simulations for the 3+1 and 4+0 conformers.³

The experimental procedure is an adaption of earlier work on $\text{Na}(\text{NH}_3)_n$ clusters by Brockhaus and co-workers,⁴ who recorded near-infrared spectra that showed no assignable structure (except for $n = 1$). Briefly, the $\text{Li}(\text{NH}_3)_4$ clusters were formed in the gas phase by laser ablation of a lithium target in the presence of gaseous ammonia (NH_3 anhydrous 99% Aldrich) or (ND_3 99 atom % (Aldrich)). The resulting mixture was expanded into a vacuum to form a supersonic expansion and then passed into a second vacuum chamber for laser interrogation. A pulsed laser operating in the near-ultraviolet was used to ionize $\text{Li}(\text{NH}_3)_n$ clusters and the various ions present were registered by a time-of-flight mass spectrometer. Ablation and expansion conditions were chosen such that $\text{Li}(\text{NH}_3)_4^+$ ion was

the largest signal, although other cluster ions were also observed. Note that dissociative photoionization of larger neutral clusters makes a negligible contribution to the $\text{Li}(\text{NH}_3)_4^+$ signal, as shown by operation at wavelengths just above the $\text{Li}(\text{NH}_3)_4$ ionization threshold.⁵ Infrared spectra were recorded by crossing the molecular beam with the output from a pulsed tuneable optical parametric oscillator prior to the ultraviolet laser pulse. The spectrum is registered by a decrease in the $\text{Li}(\text{NH}_3)_4^+$ signal on resonant absorption, which is induced by predissociation following injection of the photon energy into the neutral cluster. This mass-selective technique allows the optical absorption to be assigned to a cluster of a specific size. Further details of the experimental setup and the equipment employed can be found in chapter two of this thesis.

4.4 Results and discussion

Figure 4.4 compares the near-infrared spectra of $\text{Li}(\text{NH}_3)_4$ and $\text{Li}(\text{ND}_3)_4$. The deuterated and non-deuterated spectra are similar but the former is shifted to lower energy. At higher frequencies there is almost continuous absorption punctuated by some evidence of band structure. Unfortunately, the region above 7400 cm^{-1} is not accessible with our current laser system.

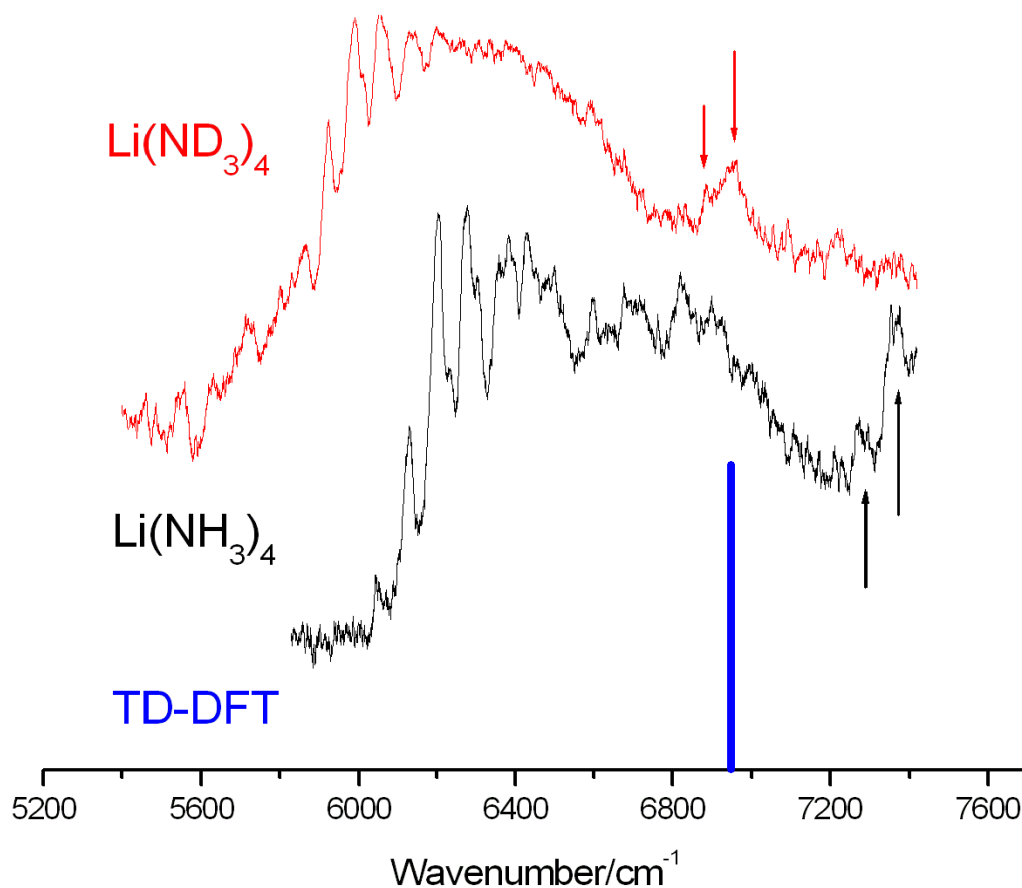


Figure 4.4: Near-infrared spectra of $\text{Li}(\text{NH}_3)_4$ and $\text{Li}(\text{ND}_3)_4$.

For ease of comparison the spectrum of $\text{Li}(\text{ND}_3)_4$ has been vertically displaced relative to that of $\text{Li}(\text{NH}_3)_4$. Bands marked with arrows are attributed to excitation of the totally symmetric NH_3 umbrella vibration (ν_{11}) (with or without combination with ν_3). For other band assignments see Table 4.1 and text. Beneath the two spectra is the vertical transition energy predicted from time-dependent density functional theory (TD-DFT).²

An expanded view of the low frequency region of the $\text{Li}(\text{NH}_3)_4$ spectrum is provided in Figure 4.5. The first band appears at 6060 cm^{-1} , which is tentatively assigned to the electronic origin transition (0_0^0), since careful searches to lower energy have revealed no additional bands. Virtually all of the peaks, which arise from vibrational structure, can be assigned on the basis of two active vibrational modes, one with a wavenumber of $\sim 74\text{ cm}^{-1}$ and the other at $\sim 186\text{ cm}^{-1}$. Deuteration shifts these vibrational intervals to 65 and 149

cm^{-1} , which shows that the modes responsible are dominated by motion of the LiN_4 framework (see below for further justification). The contribution to the spectrum from ‘hot’ and sequence transitions is thought to be negligible since the main spectral features were found to be invariant to changes in supersonic expansion conditions.

4.5 *Ab initio* calculations on $\text{Li}(\text{NH}_3)_4$ cluster

Ab initio calculations of the harmonic vibrational frequencies of $\text{Li}(\text{NH}_3)_4$ in its ground electronic state have been carried out, while Burns *et al.* and Pinsook *et al.* have performed similar calculations on $\text{Li}(\text{NH}_3)_4^+$.^{6,7} This data is gathered together in Table 4.1. In all three cases a tetrahedral (T_d) equilibrium structure is calculated and the vibrational frequencies are similar for both the neutral cluster and the cation. Vibrational frequency calculations for the excited electronic state would particularly assist the vibrational assignment in the current study but repeated attempts to converge CASSCF calculations proved unsuccessful. Consequently, we use the combined information from the *ab initio* calculations on the ground state neutral and cationic clusters as a guide to the most likely excited electronic state vibrational assignment. The 186 cm^{-1} interval is readily assigned to the totally symmetric (a_1) Li-N stretch, since all other vibrational modes have significantly higher or lower frequencies. (Note: no anharmonic frequency calculations were carried out due to the significant computational time this would have taken up). This assignment is consistent with the small shift on deuteration predicted for this mode, as summarized in Table 4.1.

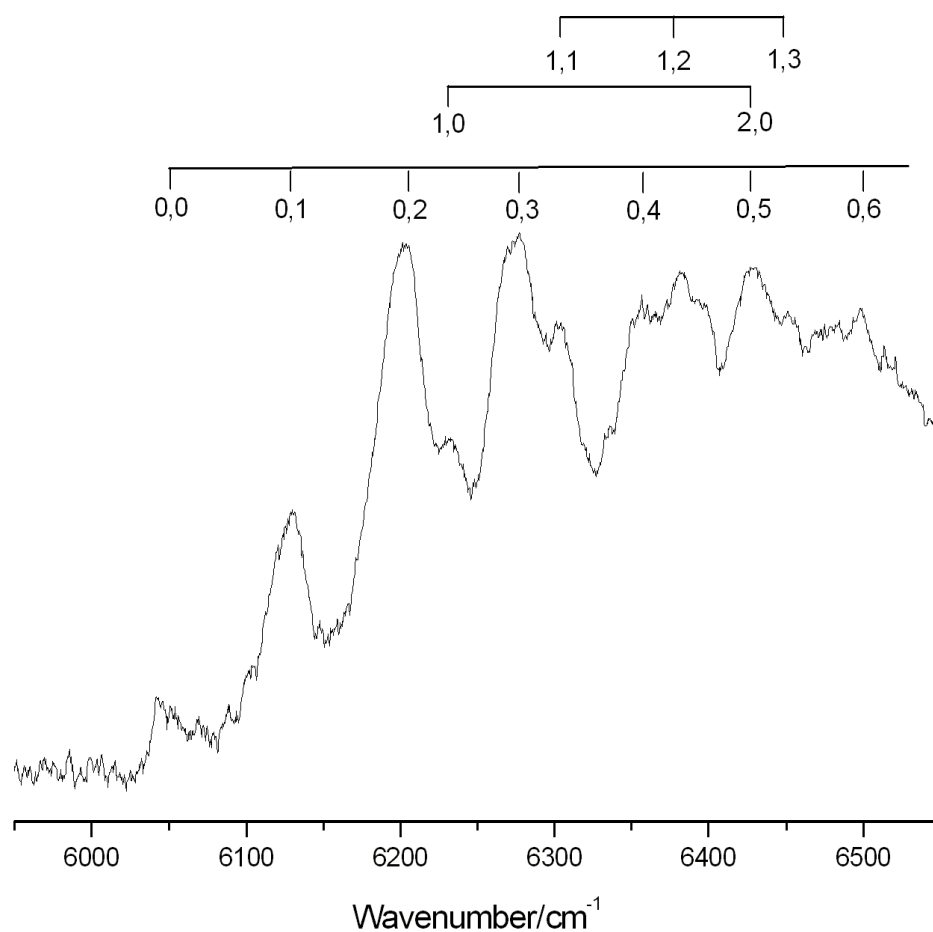


Figure 4.5: Expanded view of the low frequency structure in the near-infrared spectrum of $\text{Li}(\text{NH}_3)_4$.

All transitions are assumed to originate from the zero point vibrational level in the ground electronic state. The labels used to assign the vibrational structure in the figure denote the vibrational quantum number for two modes, ν_3 and ν_5 , in the *upper* electronic state (see text for definitions of these modes).

Table 4.1: Predicted and measured vibrational wavenumbers of $\text{Li}(\text{NH}_3)_4$, $\text{Li}(\text{ND}_3)_4$ and $\text{Li}(\text{NH}_3)_4^+$.

		$\text{Li}(\text{NH}_3)_4$		$\text{Li}(\text{ND}_3)_4$		$\text{Li}(\text{NH}_3)_4^+$	
Mode	Symmetry	Theory ^{a)}	Expt ^{b)}	Theory ^{a)}	Expt ^{b)}	Ref. 5 ^{d)}	Ref. 6 ^{d)}
ν_1	a_2	51		35		31	
ν_2	t_1	66		47		56	
ν_3	e	68	74	59	65	68	73
ν_4	t_2	76		65		106	113
ν_5	a_1	231	186	212	(149) ^{c)}	217	218
ν_6	t_1	311		231		327	
ν_7	t_2	322		260		343	347
ν_8	e	402		304		419	
ν_9	t_2	494		472		550	
ν_{10}	t_2	1165		886		1186	
ν_{11}	a_1	1172	1242	890	1026 ^{c)}	1202	

a) are the unscaled harmonic vibrational wavenumbers calculated for the 2A_1 electronic *ground* state using MP2/aug-cc-pVTZ calculations. Only those vibrations with frequencies $< 1500 \text{ cm}^{-1}$ are included here. b) represent the measured vibrational wavenumbers for the 2T_2 *excited* electronic state and c) are derived from tentative band assignments owing to uncertainty in the position of the origin transition of $\text{Li}(\text{ND}_3)_4$. Finally, d) values come from the MP2 calculations.

For the lower frequency (74 cm^{-1}) active vibration we can say with certainty that it must derive from a non-totally symmetric vibration in T_d symmetry, since the symmetric Li-N stretch is by far the lowest frequency totally symmetric mode predicted in all of the *ab initio* calculations on $\text{Li}(\text{NH}_3)_4$ and $\text{Li}(\text{NH}_3)_4^+$. The most likely assignment is to a doubly degenerate (e) vibration, whose frequency is predicted to be close to 70 cm^{-1} in the calculations on both $\text{Li}(\text{NH}_3)_4$ and $\text{Li}(\text{NH}_3)_4^+$. This vibration involves a non-totally

symmetric distortion of the LiN_4 framework by twisting of one N-Li-N plane relative to the other.

Crucially, this low frequency mode cannot be Franck-Condon active by virtue of its symmetry if $\text{Li}(\text{NH}_3)_4$ is perfectly tetrahedral in both ground and excited electronic states. Since there is considerable evidence to suggest that $\text{Li}(\text{NH}_3)_4$ is tetrahedral in the ground electronic state, we focus here on the excited state.

4.6 Elucidation of vibronic spectra using spectroscopy theory

To picture the basic electronic symmetry, as a first (and crude) approximation the lowest allowed electronic transition can be thought of as a $2p \leftarrow 2s$ transition on the Li atom. In a tetrahedral environment this would make the lowest allowed transition a ${}^2T_2 \leftarrow {}^2A_1$ transition. However, the triple degeneracy in the excited electronic state makes it susceptible to Jahn-Teller distortion, which can be induced by vibrations of e or t_2 symmetry.^{8,9} Both our own calculations of the LUMO characteristics and the TD-DFT calculations of Zurek *et al.*² indicate that the unpaired electron in the excited state is not localized on the Li atom, but instead enters an orbital where the bulk of the electron density is in lobes that protrude well beyond the LiN_4 framework as illustrated in figure 4.6.

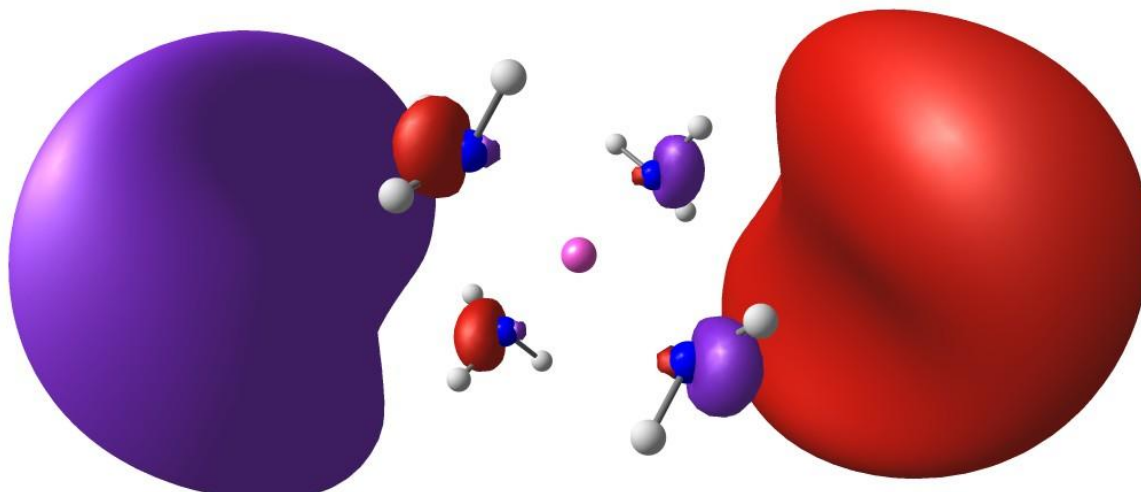


Figure 4.6: Shape of the t_2 LUMO derived from an MP2/aug-cc-pVTZ calculation. The red and purple colors indicate opposite phases of the orbital.

Consequently, significant coupling between the orbital angular momentum in the 2T_2 electronic state and the vibrational angular momentum of the lowest frequency framework (e) vibration is plausible. The extensive vibrational progression in the Jahn-Teller active mode (ν_3) is consistent with a substantial *static* Jahn-Teller distortion. This effect arises if the ground state or lowest energy level of a molecule is degenerate and so the system will distort spontaneously so as to remove the degeneracy. The result of this distortion is to lower the overall energy of the system by either elongation or compression of the Li-N bond length, hence lowering the symmetry of the complex. The Li complex itself is degenerate thereby upon electronic excitation the $2P_{xy}$ orbital will split into a derived E state and the $2P_z$ will split into a 2A_1 state. The proof of this theorem is based on perturbation theory,¹⁰ in which the influence on nuclear displacements as a result of vibronic interactions is considered as a perturbation to the degenerate states. The main

effect of electronic degeneracy is that it produces a *special coupling between the electronic and nuclear motion* that results in a series of observable effects, which are jointly called the Jahn-Teller vibronic coupling effects.¹¹ The presence of this effect in the electronically degenerate states of molecules will result in the lowering of the potential energy for the configurations in which the arrangement of the nuclei has a reduced symmetry.

In effect, the molecular symmetry is lowered from T_d to D_{2h} by the Jahn-Teller distortion such that the Jahn-Teller active vibration becomes totally symmetric in this lower symmetry environment and is subject to a normal Franck-Condon progression. The direction of the ν_3 mode stretch is illustrated in Figure 4.7.

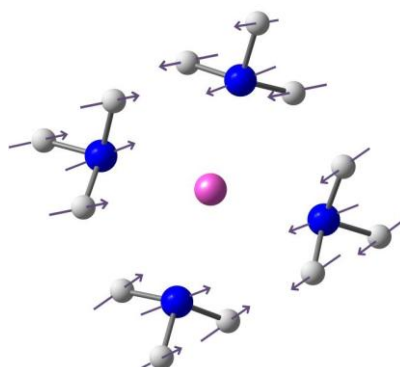


Figure 4.7: Jahn-Teller active mode (ν_3), LiN_4 deformation (e) in $\text{Li}(\text{NH}_3)_4$.

Essentially the change in the point group is important in determining whether this particular electronic transition is allowed or forbidden. It is the transition moment equation which is used to determine this, see Chapter 2, section 2.8.1. In addition group theory can be used to prove this concept, for example the character tables of the point groups T_d and D_{2h} as shown in Figure 4.8 and 4.9 respectively.

Table 4.2: Character table for a Td point group.

	E	8C ₃	3C ₂	6S ₄	6σ _d	linear, rotations	quadratic
A ₁	1	1	1	1	1		x ² +y ² +z ²
A ₂	1	1	1	-1	-1		
E	2	-1	2	0	0		(2z ² -x ² -y ² , x ² -y ²)
T ₁	3	0	-1	1	-1	(R _x , R _y , R _z)	
T ₂	3	0	-1	-1	1	(x, y, z)	(xy, xz, yz)

Table 4.3: character table for a D_{2h} point group

	E	C ₂ (z)	C ₂ (y)	C ₂ (x)	i	σ (xy)	σ (xz)	σ (yz)	linear, rotations	quadratic
A _g	1	1	1	1	1	1	1	1		x ² , y ² , z ²
B _{1g}	1	1	-1	-1	1	1	-1	-1	R _z	xy
B _{2g}	1	-1	1	-1	1	-1	1	-1	R _y	xz
B _{3g}	1	-1	-1	1	1	-1	-1	1	R _x	yz
A _u	1	1	1	1	-1	-1	-1	-1		
B _{1u}	1	1	-1	-1	-1	-1	1	1	z	
B _{2u}	1	-1	1	-1	-1	1	-1	1	y	
B _{3u}	1	-1	-1	1	-1	1	1	-1	x	

From Table 4.2, calculating the probability of a transition is as followed; the excited state has been assigned as the T₂ band, therefore using the number of irreducible representations, $(3 \times 1) + (0 \times 8) + (-1 \times 3) + (-1 \times 6) + (1 \times 6) = 0$ since this is zero it is therefore a forbidden transition when in this particular point group. However upon the Jahn-teller distortion, the complex will change to a lower symmetry point group such as D_{2h} and hence resulting an transition moment of non-zero and producing an allowed transition.

$\text{Li}(\text{NH}_3)_4$ and $\text{Li}(\text{ND}_3)_4$ both show evidence of a third active vibration in their spectra, which is consistent with excitation of the symmetric umbrella mode of the ammonia ligands. In the $\text{Li}(\text{NH}_3)_4$ spectrum the two bands near to the high wavenumber limit are attributed to this mode in combination with the low frequency deformation. The likely vibrational frequency is listed in Table 4.1 for both isotopomers and the large shift on deuteration is consistent with the vibrational assignment.

The spectrum of $\text{Li}(\text{NH}_3)_4$ in liquid ammonia is likely to differ from the gas phase spectrum of $\text{Li}(\text{NH}_3)_4$ because of the impact of the surrounding solvent. One anticipated effect of the solvent will be a broadening of absorption features, leading to loss of vibrational structure and thus a quasi-continuous absorption envelope. The work described here provides a basis for defining the shape of this absorption profile and we expect that the solution phase spectrum will show an oscillatory profile over a wide wavelength range owing to extensive vibrational excitation in the excited state along with contributions from the two other electronic states correlating with the tetrahedral 2T_2 limit. Using a standard dielectric continuum model, the TD-DFT calculations of Zurek *et al.* predict a solvent shift of -0.11 eV for the absorption maximum when $\text{Li}(\text{NH}_3)_4$ is transposed into a liquid ammonia solution.² Application of this shift to the gas phase spectrum gives an absorption onset of 0.64 eV (5160 cm^{-1}) in the solution phase, which can be compared with the experimentally observed absorption onset of ~ 0.5 eV for the solvated electron in dilute solutions of lithium in ammonia.¹² Consequently, the electronic spectra of the solvated electron and $\text{Li}(\text{NH}_3)_4$ will strongly overlap throughout the near infrared, except perhaps near the absorption onset for the solvated electron.

4.7 Conclusions

The first electronic spectrum of $\text{Li}(\text{NH}_3)_4$ in the gas phase has been recorded using mass-selective depletion spectroscopy. Strong absorption is observed in the near-infrared and the band system is assigned to the $\tilde{A}^2T_2 - \tilde{X}^2A_1$ transition. However, the vibrational structure is indicative of a substantial Jahn-Teller effect in the excited electronic state. The broad and structured spectrum confirms a recent theoretical prediction that the electronic spectrum of $\text{Li}(\text{NH}_3)_4$ will strongly overlap with the spectrum of the solvated electron in lithium-ammonia solutions.

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Chapter 5 - Observation of the Electronic Spectrum of LiNH_3

5.1 Introduction

The following chapter has been adapted from a published paper by the Ellis group.¹

The study of clusters of alkali metal atoms with ammonia molecules in the gas phase (as opposed to the liquid phase)² provides a means of probing the impact of the solute/solvent ratio on the electronic properties in a system of finite size. The latter is particularly valuable because small complexes are, in principle, amenable to high quality *ab initio* calculations, which can then be compared directly with experimental findings.³ The smallest, the simplest, alkali-ammonia cluster is LiNH_3 . Any attempt to understand small alkali-ammonia clusters, and to extrapolate their properties as a function of cluster size, should include this most fundamental complex. However, the only previous experimental studies of LiNH_3 have been carried out in solid argon matrices.^{4,5} In these matrix studies infrared spectroscopy was used to identify several fundamental vibrational modes of LiNH_3 and its deuterated analogues.

Here we report the first observation of the electronic spectrum of LiNH_3 . This is part of a series of investigations of alkali/ammonia clusters and complements our earlier spectroscopic work on the ground electronic states of these complexes.^{6,7} The only previous study of the electronic spectroscopy of $\text{Li}(\text{NH}_3)_n$ clusters was a recent investigation of $\text{Li}(\text{NH}_3)_4$ originating from our laboratory, which employed photodissociation spectroscopy.⁸ Very recently, this work has been complemented by a velocity map imaging study to explore the photodissociation dynamics in the first excited electronic state of $\text{Li}(\text{NH}_3)_4$.⁹ More extensive spectroscopic work has been carried out on small $\text{Na}(\text{NH}_3)_n$ clusters and the first such study was reported by Schulz and co-workers,¹⁰ who successfully obtained spectra for clusters with $n = 1-6$ and showed that the lowest-lying electronic

transitions all occur in the near-infrared. These transitions correlate asymptotically with the $3p \leftarrow 3s$ transition of atomic sodium. The spectra obtained were broad and unresolved, with the exception of the NaNH_3 complex. Subsequent work by Schulz and co-workers,^{11,12} and also by Rodham and Blake,¹³ on both NaNH_3 and NaNd_3 , has yielded resolved vibrational structure. One of the defining features of the NaNH_3 electronic spectrum is strong vibronic coupling, as evinced by intense bands originating from excitation of a low frequency degenerate bending vibration, whose observation should be symmetry forbidden in the Franck-Condon limit for a molecule of C_{3v} symmetry. The origin of this vibronic coupling, whether a Jahn-Teller effect or Herzberg-Teller coupling, or indeed a combination of the two, has not been determined. Predictions of the vertical transition energies to low-lying excited electronic states of both LiNH_3 and NaNH_3 have recently been published,^{14,15} but neither geometries nor vibrational frequencies were reported for these complexes in their excited electronic states.

Electronic spectra of both LiNH_3 and its partially- and fully-deuterated analogues are presented in the current study. These spectra were successfully obtained using both two-colour resonance-enhanced multiphoton ionization (REMPI) and a photodepletion technique. The spectra show a number of features, which appear to be vibrational or vibronic in origin, and their assignment is discussed in the light of results obtained for partially- and fully-deuterated molecules.

5.2 Experimental

The experimental procedure and apparatus employed were similar to that described in previous studies⁶⁻⁸ and thoroughly Chapter 2 of this thesis. Briefly, LiNH_3 complexes were produced by laser ablation of a solid lithium target in the presence of gaseous NH_3 and the resulting mixture was expanded into vacuum to form a supersonic jet. The central portion of the jet was extracted by a skimmer and the resulting molecular beam passed into the source region of a time-of-flight mass spectrometer. To gain some information on the species formed during the expansion, single-photon ionization in the near-UV was employed using the output from a pulsed dye laser. The dominant ions present were LiNH_3^+ and $\text{Li}(\text{NH}_3)_4^+$, although significant quantities of other $\text{Li}(\text{NH}_3)_n^+$ ions were also observed.

To record optical spectra, the output from a LaserVision optical parametric oscillator/amplifier (OPO/A) was employed. This system was pumped by the output from an injection-seeded Nd:YAG laser (Surelite II-10), although the injection seeder was not essential for the experiments described here, since it did not affect the observable resolution. Since all of the spectra were recorded in the near-infrared, only the OPO part of the OPO/A system was used. This gave a wavelength-tuneable output capable of pulse energies of up to 15 mJ, although the pulse energy incident on the molecular beam was typically measured at 0.5 mJ. The beam from the OPO was gently focused into the source region of the mass spectrometer and aligned such that it spatially overlapped the UV laser beam. The delay between the firing of the two laser pulses was controlled using a delay generator.

Ammonia was sourced from a standard liquid ammonia cylinder (BOC Gases, 99% purity) and was used without purification. To assist with spectral assignments some experiments were also carried out using ND₃ (Sigma Aldrich, 99% D). The backing pressure used throughout the experiments was approximately 0.5 bar.

5.3 Computational details

Ab initio calculations on LiNH₃ have been carried out in support of the experimental work. We have previously reported *ab initio* calculations on the ground electronic state of LiNH₃ at levels up to and including UCCSD(T) with an aug-cc-pVQZ basis set.¹⁶ These high level calculations were used to predict both the vibrational frequencies and the Li-N bond dissociation energy. The aims of the new calculations were twofold: (1) to predict vibrational isotopic shifts for the ground state and (2) to explore the low-lying excited electronic states. For the ground state calculations, UMP2/6-311++G** calculations were initially performed, using the GAUSSIAN 03 program, revision E.01.¹⁷ Spin contamination was found to be negligible, as shown by the calculated value of $\langle S^2 \rangle = 0.7501$. The geometry was optimized and harmonic vibrational frequencies calculated at the potential energy minimum. In addition, RCCSD(T) calculations were also performed by Tim Wright, University of Nottingham, with again both geometry optimization and harmonic frequency calculations being undertaken: these calculations employed MOLPRO 2008.¹⁸ For N and H, standard Dunning aug-cc-pVTZ basis sets were employed. For Li, the cc-pVTZ basis set was extended by adding a single set of diffuse *s*, *p* and *d* basis functions, extrapolated in an even-tempered fashion from the existing basis functions with the smallest exponents.

Hashimoto and Daigoku have recently computed the vertical transition energies to low-lying electronic states of LiNH_3 using multireference calculations (MRCI-SD).¹⁵ In the current study, we undertook a series of CASSCF and CASSCF+MRCI calculations (Tim Wright, University of Nottingham). For the CASSCF calculations, the basis set was as described above for the RCCSD(T) calculations, while for the CASSCF+MRCI calculations, we employed aug-cc-pVDZ basis sets for N and H and the cc-pVDZ basis set for Li. MOLPRO 2008¹⁸ was used for all of the CASSCF and CASSCF + MRCI calculations. The aim was to obtain excitation energies, as well as geometries and vibrational frequencies for the ground and excited states. These calculations proved to be far from straightforward, especially with regard to calculation of the vibrational frequencies.

Initially, the strategy adopted was to use state-averaged CASSCF, with the triple- ζ basis set mentioned above. The four lowest energy roots arising from the interaction of Li with NH_3 were considered, where Li had the unpaired electron in either the 2s or 2p orbitals. As will be discussed in more detail later, these four roots correspond to the $\tilde{X}^2A_1$, $\tilde{A}^2E$ and $\tilde{B}^2A_1$ states, where C_{3v} symmetry is assumed in these labels. Both the Li and N 1s orbitals were kept doubly occupied during this procedure, although their coefficients were allowed to vary. Analytic gradients were employed for optimizing the geometry, by using the RS2 procedure within MOLPRO,¹⁸ but not allowing any excitations; however, the second derivatives were calculated numerically and this required convergence at all displaced geometries. Unfortunately, even with small step sizes in the numerical gradient calculation, the vibrational frequencies for the 2E state came out with imaginary frequencies and severe non-degeneracy of the vibrational modes with nominal e symmetry (although

the geometries and the energies of the two components of this state were essentially identical). Indeed, the two components of the 2E state, calculated separately, did not give vibrational frequencies in even approximate agreement with each other. Even for the non-degenerate $\tilde{X}$ and $\tilde{B}$ states, non-degeneracy in the e vibrations was observed, even when C_{3v} symmetry was imposed. Similar results were obtained when each root was considered separately in single-reference CISD calculations.

Further calculations were then undertaken where multireference CI was performed on the CASSCF wavefunctions obtained with the double- ζ basis set. It was found that the values obtained for the $\tilde{X}$ state were now in good agreement with those from the RCCSD(T)/aug-cc-pVTZ calculations. There were, however, still non-degenerate and imaginary vibrational frequencies for the $\tilde{A}{}^2E$ state. As a consequence, we have been unable to obtain vibrational frequencies for the 2E state. The same set of calculations did, however, yield a full set of real vibrational frequencies for the $\tilde{X}{}^2A_1$ state and the $\tilde{B}{}^2A_1$ states, and which also showed the expected degeneracies, and the results of this latter set of calculations are discussed below.

5.4 Results and discussion

5.4.1 *Ab initio* calculations

We begin with a discussion of the results from the *ab initio* calculations, since these provide information that has proved important in achieving a spectral assignment. The minimum energy structures in all three electronic states of LiNH_3 , derived from CASSCF + MRCI calculations, are summarized in Table 5.1.

Table 5.1: Calculated equilibrium parameters for LiNH_3 and LiNH_3^+ .

	LiNH_3				LiNH_3^+
	RCCSD(T)	CASSCF + MRCI			(R)CCSD(T)
Parameter	$\tilde{X}^2A_1$	$\tilde{X}^2A_1$	$\tilde{A}^2E$	$\tilde{B}^2A_1$	$\tilde{X}^1A_1$ ^{a)}
$R_{\text{LiN}} / \text{\AA}$	2.022	2.042	2.043	1.966	1.985
$R_{\text{NH}} / \text{\AA}$	1.018	1.021	1.018	1.031	1.019
$\theta_{\text{LiNH}} / ^\circ$	112.4	112.1	112.2	114.4	113.9
T_e / cm^{-1}	0	0	11463	11806	34535

a) Note that these parameters for the cation agree closely with those described in ref. 16, which were also calculated using UCCSD(T) methodology.

For comparison purposes, we also include structures for the ground states of both LiNH_3 and LiNH_3^+ obtained from CCSD(T) calculations. Caution is needed in interpreting the theoretical findings for the $\tilde{A}^2E$ state since, as mentioned earlier, some imaginary vibrational frequencies were calculated for the two components of this state. Nevertheless, in all of the neutral and ionic states the minimum energy structure was found to correspond to C_{3v} symmetry. According to the calculations the minima of the $\tilde{A}^2E$ and $\tilde{B}^2A_1$ states are separated by $<350 \text{ cm}^{-1}$, a point of significance which will be encountered again later. It should also be noted that the calculated adiabatic ionization energy obtained from these calculations, 4.32 eV (inclusive of zero-point vibrational energy), is in excellent agreement with the experimentally determined value of $4.339 \pm 0.003 \text{ eV}$.¹⁹ An important take-home message from these calculations is that the change in structure in moving from the $\tilde{X}^2A_1$ state to the $\tilde{A}^2E$ state is small, whereas excitation to the $\tilde{B}^2A_1$ state leads to a much more significant change in structure, specifically in the Li-N bond length. Indeed the Li-N bond is found to be even shorter in the $\tilde{B}^2A_1$ state than in the cation, which would not be

expected if the unpaired electron was simply a non-bonding electron. In fact in the limit of a non-bonding electron the $\tilde{A}^2E$ state should possess the shortest bond, since the orientation of the unpaired electron, which would now lie in orbitals that correlate with the $2p_{x,y}$ orbital pair on the Li atom, would expose the N atom to an increase in effective positive charge on the Li atom. By way of contrast, in the $\tilde{B}^2A_1$ state the Li-N bond length would be expected to be longer than that in the $\tilde{X}^2A_1$ state, since increased electron-electron repulsion would arise from the unpaired electron residing in what is approximately a $2p_z$ orbital pointing directly at the N atom. This simple electrostatic picture is clearly deficient for LiNH_3 and suggests that the unpaired electron has a significant *covalent* bonding role, particularly in the $\tilde{B}^2A_1$ state.

Under C_{3v} symmetry LiNH_3 will have six distinct vibrational frequencies and Table 5.2 shows the *ab initio* predictions alongside experimental values for the ground electronic state of LiNH_3 derived from IR matrix isolation spectroscopy.^{4,5}

Table 5.2: Vibrational frequencies) (in cm^{-1}) of the $\tilde{X}^2A_1$ states of LiNH_3 and LiND_3 .

Vibration a)	Description b)	LiNH_3 RCCSD(T)/ aug-cc-pVTZ	LiNH_3 Matrix IR c)	LiND_3 RCCSD(T)/ aug-cc-pVTZ	LiND_3 Matrix IR c)
$\nu_1 (a_1)$	Symm N-H stretch	3408	3278	2438	2372
$\nu_2 (a_1)$	Umbrella	1194	1135	910	882
$\nu_3 (a_1)$	Li-N stretch	439	320	429	(311)
$\nu_4 (e)$	Antisymm N-H stretch	3540	3380	2603	2516
$\nu_5 (e)$	NH ₂ scissor	1657	1606	1201	1175
$\nu_6 (e)$	Li-N-H bend	371	381	283	(293)

a) The experimental data are vibrational fundamental frequencies while the calculated values are unscaled harmonic vibrational frequencies.

b) These descriptions describe the *approximate* character of the vibrational modes.

c) From infrared spectra of LiNH_3 and LiND_3 isolated in an argon matrix (refs 4 and 5). The values for LiND_3 in parentheses were estimated from a force field analysis (ref. 5).

Although the argon matrix will perturb the vibrations, the effect on the vibrational frequencies is normally small and the shifts relative to the gas phase tend to be a few cm^{-1} at most. Confirmation that the matrix IR assignments are reasonable is provided by the relatively good agreement with our *ab initio* vibrational frequencies. The only exception to this statement is for mode ν_3 , the Li-N stretch, where a significant discrepancy between theory and experiment is seen. The same conclusion has been reached in a recent DFT study of MNH_3 complexes,²⁰ where $\text{M} = \text{Li-Fr}$, and therefore the matrix assignment of the Li-N stretching frequency in LiNH_3 looks to be erroneous. Also shown in Table 5.4 are corresponding data for LiND_3 . The effect of deuteration in the matrix experiments is

faithfully reproduced by the calculated vibrational frequencies, a fact that will become important later in the spectral assignment process.

Table 5.3: Compares the vibrational frequencies calculated for the $\tilde{X}^2A_1$ state with those obtained for the $\tilde{B}^2A_1$ state of LiNH_3 and the $\tilde{X}^1A_1$ state of LiNH_3^+ .

Vibration	LiNH ₃			LiNH ₃ ⁺
	$\tilde{X}^2A_1$ RCCSD(T)	$\tilde{X}^2A_1$ CASSCF + MRCI	$\tilde{B}^2A_1$ CASSCF+ MRCI	$\tilde{X}^1A_1$ RCCSD(T)
$\nu_1 (a_1)$	3408	3446	3297	3447
$\nu_2 (a_1)$	1194	1218	1294	1315
$\nu_3 (a_1)$	439	434	560	554
$\nu_4 (e)$	3540	3572	3410	3541
$\nu_5 (e)$	1657	1683	1644	1677
$\nu_6 (e)$	371	384	688	521

There is good agreement between the CASSCF/MRCI and RCCSD(T) vibrational frequencies for the $\tilde{X}^2A_1$ state of LiNH_3 . The CASSCF/MRCI calculations also yielded vibrational frequencies for the $\tilde{B}^2A_1$ state. Of note, is the very large increase in the frequency of the Li-N stretching vibration, ν_3 , on excitation from the $\tilde{X}^2A_1$ state of LiNH_3 to the $\tilde{B}^2A_1$ state. Indeed the calculated frequency for ν_3 in the $\tilde{B}^2A_1$ state substantially exceeds that in the ground state of the cation, a finding that fits with the shorter Li-N bond for the former species discussed earlier.

5.4.2 Survey scan for LiNH_3

Initial attempts to observe the near-infrared electronic spectrum of LiNH_3 were made using photodepletion spectroscopy, as used for other $\text{Li}(\text{NH}_3)_n$ complexes in our laboratory.^{6,8} In the case of LiNH_3 this technique involves monitoring the LiNH_3^+ ion signal, produced by laser photoionisation at a wavelength of 283 nm, while scanning the wavelength of the OPO. In order to register IR absorption, this process must induce fragmentation of the neutral, which then leads to a reduction in the monitored LiNH_3^+ signal; consequently, IR absorption is registered by dips in this ion signal. UCCSD(T) calculations of the Li-N bond dissociation energy of LiNH_3 (4430 cm^{-1})¹⁶ suggest that this energy is easily exceeded by the photon energies used in the present work. Successful observation of a depletion spectrum is also determined by intramolecular decay dynamics, since some of the energy from the initial IR absorption must move into the Li-N stretching vibration, such that Li-N fragmentation can occur on the timescale of the experiment. Since we have electronic excitation of LiNH_3 , and the dissociation process must take place on the ground state potential energy surface, the rate of internal conversion is critical.

The spectrum in Figure 5.1 is a survey scan of LiNH_3 obtained in photodepletion mode. This spectrum covers the region from $11300\text{--}13600 \text{ cm}^{-1}$ and consists of several well-resolved bands accompanied by a number of weaker and more congested features on the high frequency side of the spectrum. All of the bands are relatively broad, with full widths at half maximum of approximately 40 cm^{-1} . The linewidth of the OPO is approximately 3 cm^{-1} , so the widths of these bands must be dominated by other factors. We can rule out power broadening, since experiments using reduced OPO pulse energies showed no significant decrease in observed band widths. Consequently, the most likely

source is lifetime broadening, most probably caused by rapid internal conversion following laser excitation. As a result, no rotational information is obtained from the current work.

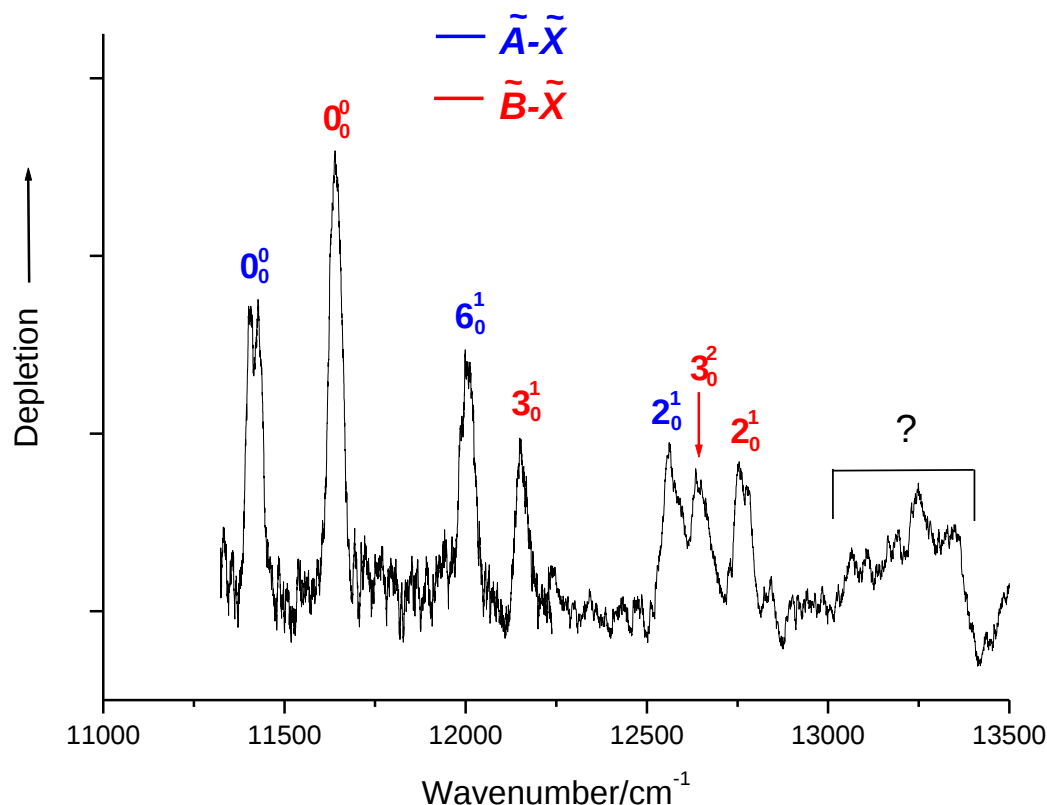


Figure 5.1: Electronic spectrum of LiNH_3 in the near-infrared obtained using photodepletion spectroscopy (signal averaging 1:63).

This spectrum was constructed from two separate scans which are joined at 12250 cm^{-1} . See text for details of the assignment.

One problem with depletion spectroscopy is that laser-induced dissociation of higher mass complexes can sometimes lead to contributions to the ion signal in a particular lower mass channel. For example, depletion of $\text{Li}(\text{NH}_3)_2$ to produce LiNH_3 will ultimately lead to an increase in LiNH_3^+ signal on photoionisation. This leads to ion signal enhancements which can be seen as structure in the spectrum pointing in the opposite direction to those bands seen in Figure 5.1. From the low signal levels of the corresponding

cations in the mass spectrum, we conclude that $\text{Li}(\text{NH}_3)_2$ and $\text{Li}(\text{NH}_3)_3$ are more than an order of magnitude less abundant than LiNH_3 in the gas mixture. Furthermore, the fact that no positive-going signals are seen in Figure 5.1 is further indication that larger complexes are not involved. Nevertheless, these observations do not definitively rule out contributions from one or more larger complexes, since there is some possibility, albeit small, of coincident positive- and negative-going signals cancelling each other out.

Firm proof that the spectrum arises only from LiNH_3 was obtained by recording the two-colour REMPI spectrum in the LiNH_3^+ mass channel. The wavelength of the frequency doubled dye laser was set at 288 nm, introducing a photon with an energy just below the ionization threshold of LiNH_3 .¹⁹ When the IR output was added and the wavelength scanned, a REMPI spectrum was observed in which all of the main bands seen for LiNH_3 in the photodepletion mode were also obtained in the REMPI spectrum. However, the signal/noise ratio for this spectrum (not shown here) was not as good as that recorded by photodepletion, presumably because the decay of the excited electronic state of LiNH_3 is so rapid, which is also consistent with the broad but relatively intense photodepletion bands.

5.4.3 Spectral assignments

The positions of the bands observed in the electronic spectra of LiNH_3 and LiND_3 are summarized in Table 5.4. To assist with the assignment, we can gain useful clues from previous work, including matrix isolation IR studies of LiNH_3 , previous work on the electronic spectroscopy of NaNH_3 , and *ab initio* calculations, including our own.

Table 5.4: Band positions ^{a)} and assignments for LiNH₃.

LiNH ₃ band position/cm-1 b)	LiND ₃ band position/cm-1 b)	Assignment
11423 (0)	11459 (0)	$\tilde{A} - \tilde{X} \ 0_0^0$
11656 (0)	11612 (0)	$\tilde{B} - \tilde{X} \ 0_0^0$
12035 (612)	11940 (481)	$\tilde{A} - \tilde{X} \ 6_0^1$
12162 (506)	12108 (496)	$\tilde{B} - \tilde{X} \ 3_0^1$
12596 (1173)	12342 (883)	$\tilde{A} - \tilde{X} \ 2_0^1$
12676 1020)		$\tilde{B} - \tilde{X} \ 3_0^2$
12808 (1152)	12551 (939)	$\tilde{B} - \tilde{X} \ 2_0^1$

a) Only bands that have significant signal/noise ratios and are clearly resolved are listed in this table. b) The numbers in parentheses show the positions of the bands relative to the respective assigned electronic origin transition.

We will begin by discussing the low frequency part of the spectrum in Figure 5.1. We will start with LiNH₃ and will then subsequently draw on a comparison with its partially- and fully-deuterated analogues to check the consistency of the assignments made. The band observed at the lowest wavenumber in the spectrum of LiNH₃ is at 11423 cm⁻¹. Scans further to the red, extending down to 10500 cm⁻¹, found no other identifiable bands,

suggesting that this band is likely to be an electronic origin (0_0^0) transition. The $\tilde{A}^2E$ - $\tilde{X}^2A_1$ transition is expected to correlate with the strongly allowed $2p \leftarrow 2s$ transition of atomic lithium.⁸ In the free Li atom this transition takes place at 14903 cm^{-1} and so in LiNH_3 it is shifted substantially to the red by the presence of the NH_3 group. This parallels the behavior seen previously for NaNH_3 .¹⁰⁻¹³ Assuming C_{3v} point group symmetry for LiNH_3 , the $\tilde{A}^2E$ state will correlate with the $2p_{x,y}$ orbitals and the $\tilde{B}^2A_1$ state has the Li $2p_z$ orbital as its principal contributor. It is plausible that transitions to both excited electronic states could be observed in our spectra if the states are close enough in energy.

The two lowest frequency vibrations of LiNH_3 are, by a large margin, the Li-N stretch (ν_3) and the Li-N-H bend (ν_6). If we assume that the lowest frequency band, at 11423 cm^{-1} , originates from the $\tilde{A}^2E$ - $\tilde{X}^2A_1$ 0_0^0 transition, then we cannot achieve a sensible band assignment for the three bands immediately above this nominal origin band based on a single electronic transition, even invoking the non-totally symmetric (e symmetry) ν_6 bending mode (also known as the rocking mode). This suggests a contribution from two distinct electronic transitions, the $\tilde{A}^2E$ - $\tilde{X}^2A_1$ and $\tilde{B}^2A_1$ - $\tilde{X}^2A_1$ transitions. To gain further information, we also recorded spectra for LiNH_2D , LiNHD_2 and LiND_3 . Figure 5.2 shows a comparison of the spectra of these isotopologues with that of LiNH_3 .

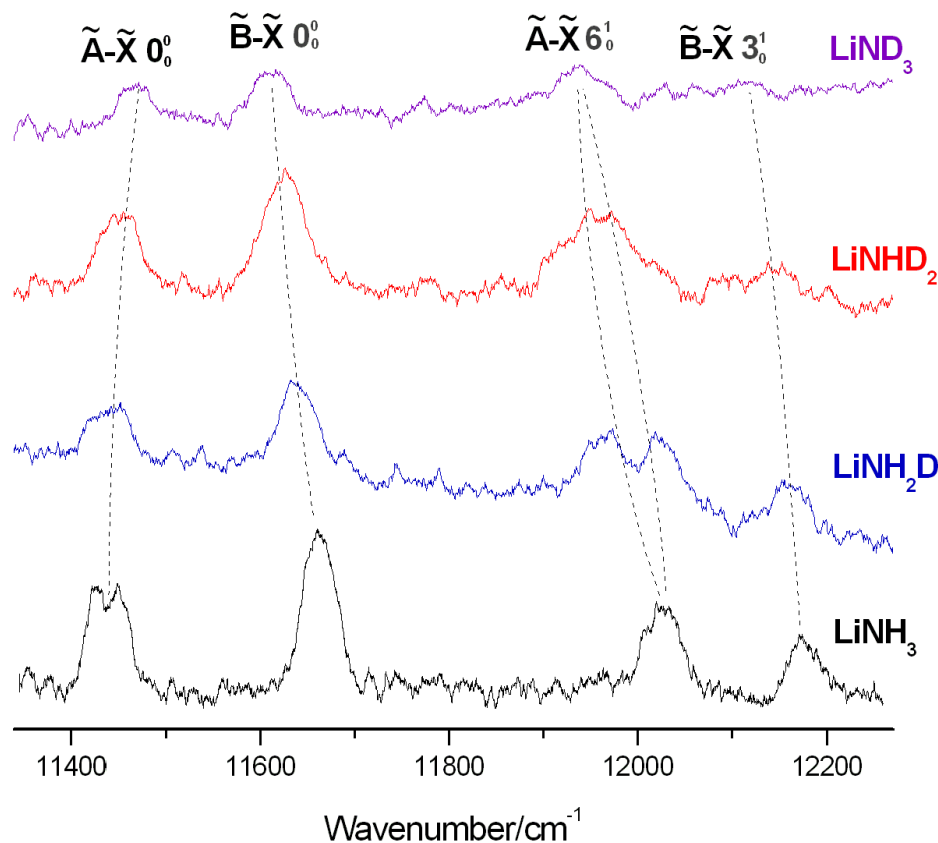


Figure 5.2: Comparison of the low frequency regions in the spectra of LiNH_3 , LiNH_2D , LiNHD_2 and LiND_3 .

The spectra for the partly and fully deuterated isotopologues were recorded simultaneously by gating the signals for the respective cations in the mass spectrum. A small quantity of ND_3 was injected into the NH_3 flow, allowing the H and D atoms to exchange. This results in continuously changing isotopologue ratios as the spectral scan progresses and so these spectra are intended only to show correlations in band positions on isotope substitution: the intensity ratios will not be reliable. For each spectra a signal averaging 1:63 was used.

We begin our assignment with the aforementioned assumption that the lowest frequency band, at 11423 cm^{-1} , corresponds to the $\tilde{A}^2E - \tilde{X}^2A_1\ 0_0^0$ transition. We can then use the isotopic shifts, along with other information, to assign vibrational features in the spectrum. The ratio of frequencies in a given vibrational mode for the non-deuterated

versus fully deuterated molecule should be approximately retained from one electronic state to another. Our calculations for the $\tilde{X}^2A_1$ and $\tilde{B}^2A_1$ states confirm this, with the vibrational frequency ratios for the two states agreeing to within 1% for all of the vibrational modes. Consequently, we expect to be able to predict a reliable estimate of this ratio in the $\tilde{A}$ state, even though *ab initio* vibrational frequency calculations on the $\tilde{A}$ state were unsuccessful, by making use of the *ab initio* data for the $\tilde{X}$ state, which has a very similar equilibrium geometry, as noted above. The assignment of the third lowest energy band of LiNH_3 , at 12035 cm^{-1} , to the 6_0^1 transition, leads to a response to deuteration in line with expectations (experimental ν_6 D/H ratio is 0.79 versus 0.76 from theory). Furthermore, we have carried out additional *ab initio* calculations on the various isotopologues of LiNH_3 in its $\tilde{X}$ state, which support this assignment. As can be seen from Table 5.5, the calculations show that the degenerate 6_0^1 band should split into two distinct bands in LiNH_2D (an Li–N–H bend and an Li–N–D bend). Accordingly, we see in the spectra a clear splitting of the tentatively assigned 6_0^1 feature into two bands, with an approximate separation of 60 cm^{-1} , in going from LiNH_3 to LiNH_2D (see Figure 5.2). The *ab initio* calculations predict a smaller splitting for LiNHD_2 and a significant shift to the red for the two resulting features. In agreement with this prediction we see a clearly broadened, but unresolved, band in Figure 5.2 which shows a notable red-shift relative to the 6_0^1 band of LiNH_3 . The bending mode assignment is further confirmed by the additional red shift seen on full deuteration to give LiND_3 .

Table 5.5: Comparison of the calculated vibrational frequencies of the $\tilde{X}^2A_1$ state of LiNH_3 with its partially and fully deuterated analogues. ^{a)}

Description ^{b)}	LiNH_3	LiNH_2D	LiNHD_2	LiND_3
Li-N-H bend	400 (371)	384 (363)	341 (326)	
Li-N-D bend		320 (306)	297 (283)	295 (283)
Li-N stretch	450 (439)	435 (438)	432 (435)	424 (429)
Umbrella	1223 (1194)	1126 (1103)	1015 (994)	930 (910)
H-N-H bend	1658 (1657)	1616 (1624)		
H-N-D bend		1408 (1417)	1471 (1272)	
D-N-D bend				1274 (1201)

^{a)} The values not in parentheses are from MP2/6-311++G** calculations, while those in parentheses are from RCCSD(T) calculations using a triple- ζ basis set (see text for details). The harmonic frequencies shown are unscaled. Only those vibrations with frequencies below 2000 cm^{-1} , the region of interest in the current work, are listed here.

^{b)} These descriptions give the *approximate* character of the vibrational modes.

Immediately beyond the 6_0^1 band is a second band which is also red-shifted on deuteration. The only other low frequency vibration which could possibly be responsible for this band is the ν_3 vibration, where ν_3 is the Li-N stretch. Unlike the 6_0^1 transition, which is nominally forbidden on the basis of simple symmetry arguments, the 3_0^1 transition is symmetry allowed in the Franck-Condon limit. The absence of any splitting of this band on deuteration is consistent with this vibrational assignment. This band could be assigned to the 3_0^1 transition in the $\tilde{A}^2E - \tilde{X}^2A_1$ system, but this would require a huge increase in the frequency of ν_3 , from roughly 440 to 739 cm^{-1} . Not only do the molecular structure changes

predicted for the $\tilde{A}^2E - \tilde{X}^2A_1$ transition (see Table 5.1) not support this large change in ν_3 , but also a comparison with the corresponding band in LiND₃ gives a drastically different ratio of vibrational frequencies (0.87) when compared with the *ab initio* prediction (0.98).

To achieve a sensible assignment, we attribute the bands at 11565 and 12068 cm⁻¹ to the $\tilde{B}^2A_1 - \tilde{X}^2A_1$ 0_0^0 and 3_0^1 transitions, respectively. Comparison with the corresponding transitions seen for LiND₃ now gives a fully deuterated/non-deuterated ν_3 frequency ratio of 0.98, in perfect agreement with the value predicted from *ab initio* calculations. In addition, the frequency extracted for ν_3 in the $\tilde{B}^2A_1$ state, 506 cm⁻¹, is close to the MRCI harmonic estimate of 560 cm⁻¹ (see Table 5.2).

The conclusions drawn so far, based on the first four bands in the LiNH₃ spectrum, are that there are two electronic transitions, the $\tilde{A}^2E - \tilde{X}^2A_1$ and $\tilde{B}^2A_1 - \tilde{X}^2A_1$ transitions, in close proximity. Specifically, we obtain a separation of only 233 cm⁻¹ between the two electronic origins. Our CASSCF/MRCI calculations predict a T_e separation of 343 cm⁻¹, which is certainly consistent with the experimental separation given the margins of error that are typical for such excited state transition energy calculations. Previous calculations by Hashimoto and Daigoku using MRCI methodology predicted a separation of *vertical* transitions of around 1200 cm⁻¹,¹⁵ which again is reasonably close to the observed separation in view of the likely margin of error in those calculations. Furthermore, Hashimoto and Daigoku predicted almost identical oscillator strengths for the two electronic transitions, which is in accord with the similar band intensities seen in the spectrum in Figure 5.1. It is also interesting to note the effect of deuteration on the electronic origin transition energies. For a transition where the binding is stronger in the excited electronic state, deuteration would normally shift the origin transition to the red.

This is indeed the case for the $\tilde{B} - \tilde{X}$ system, where both the ν_3 vibrational assignment and the *ab initio* predictions point to a marked strengthening of the Li-N bond on electronic excitation. Interestingly, the $\tilde{A} - \tilde{X} \ 0_0^0$ transition shows a modest blue-shift on deuteration. A small blue-shift has also been reported previously for the $\tilde{A}^2E - \tilde{X}^2A_1 \ 0_0^0$ transition of NaNH_3 and this was tentatively explained by the suggestion that the binding in the NH_3 entity was weakened by electronic excitation.¹¹ The *ab initio* calculations carried out in the present work do not provide any specific support for this suggestion in the case of LiNH_3 , but these calculations were hampered by an inability to calculate vibrational frequencies for the $\tilde{A}^2E$ state.

Having found ν_6 structure in the $\tilde{A}^2E - \tilde{X}^2A_1$ system, we might reasonably look for evidence of excitation of the other low frequency vibration, ν_3 . However, we see no additional low frequency features which would allow such an assignment. The conclusion we draw is that either the ν_3 structure is hidden beneath existing bands, e.g. the 3_0^1 and 6_0^1 bands coincide, or the 3_0^1 band is simply very weak and is therefore not observed. The latter suggestion is plausible given the negligible change in the Li-N bond length predicted by the *ab initio* calculations (see Table 5.1), which would confer a small Franck-Condon factor to the 3_0^1 transition.

Likewise, in the $\tilde{B}^2A_1 - \tilde{X}^2A_1$ manifold we have successfully identified structure due to ν_3 but not to ν_6 . However, single quantum excitation of ν_6 is forbidden in the absence of vibronic coupling (see next section) and we would not expect any first-order vibronic coupling in the $\tilde{B}^2A_1$ state.

To close this section on band assignments, we turn to the collection of weaker bands in the higher frequency section of the spectra. There is a trio of bands lying between 12500 and 13000 cm^{-1} in Figure 5.1. An unambiguous assignment for these bands is not possible because more than one plausible transition can contribute. Furthermore, the data from partly and fully deuterated molecules are less definitive for these and higher bands because of their low intensities and the increased congestion. Nevertheless, we have viable suggested assignments which are summarized in Table 5.4. A totally symmetric vibration that could be active in this region is the NH_3 umbrella mode, ν_2 . Bands have been assigned to 2_0^1 in both the $\tilde{A}-\tilde{X}$ and $\tilde{B}-\tilde{X}$ systems for both LiNH_3 and LiND_3 . On the basis of the $\tilde{A}-\tilde{X} 2_0^1$ assignment, the frequency of ν_2 in the $\tilde{A}$ state is 1173 cm^{-1} , which is close to the calculated ground state value of 1194 cm^{-1} (Table 5.2; RCCSD(T) value). The D/H ratio of vibrational frequencies is 0.75, which is very similar to that expected for the electronic ground state (0.76) based on *ab initio* calculation, lending further credence to this assignment. The corresponding ν_2 frequency in the $\tilde{B}$ state is 1152 cm^{-1} , which is significantly below the 1294 cm^{-1} prediction from the CASSCF/MRCI calculations (Table 5.3. Furthermore, the experimental D/H ratio is 0.83, suggesting that $\tilde{B}-\tilde{X} 2_0^1$ assignment in LiNH_3 or LiND_3 , or perhaps both, may not be sound.

There are additional, weak, bands above 13000 cm^{-1} , but there is major congestion in this region and therefore specific assignments would be highly speculative. However, we note that several transitions could plausibly lie within this region, including the $\tilde{B}-\tilde{X} 3_0^3$ band and combination bands such as the $\tilde{A}-\tilde{X} 2_0^1 6_0^1$ band.

5.3.3 Pgopher simulations on band contours

The full range IR photodepletion spectra are a set of useful results that can be used to determine peak assignments for the vibronic spectrum of LiNH₃. However, in addition to this individual peak scans have been carried out to try and gain specific information on band contours. For the purpose of the experimental the peaks which will be analysed are the $\tilde{A}-\tilde{X} 0_0^0$ and the $\tilde{B}-\tilde{X} 0_0^0$ peaks which seem to show individual structure, as illustrated in Figure 5.3.

A program called Pgopher has been used to analyse the individual peaks; this program is used for simulating and fitting rotational, vibrational and electronic spectra aswell as fitting can be to line positions, intensities or band contours.²¹ Full rotational resolution is not possible in our current experiments because of the relatively large linewidth of the OPO (3 cm⁻¹). Nevertheless, the rotational contours of specific bands may provide some useful information.

Figure 5.3 show the contours of the $\tilde{A}-\tilde{X} 0_0^0$ and $\tilde{B}-\tilde{X} 0_0^0$ bands of LiNH₃. In interpreting the rotational contours, the LiNH₃ is a prolate symmetric top and the *ab initio* calculations give estimated rotational constants of $A = 6.321 \text{ cm}^{-1}$ and $B = 0.723 \text{ cm}^{-1}$ in the ground electronic state.

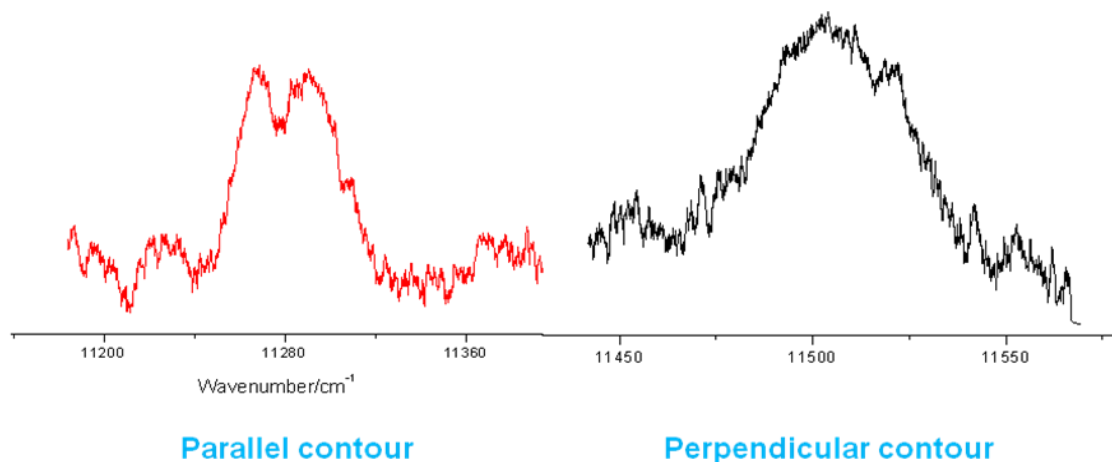


Figure 5.3: Rotational contours of the $\tilde{A}-\tilde{X} 0_0^0$ (left) and $\tilde{B}-\tilde{X} 0_0^0$ (right) bands of LiNH_3 .

The contours of the two bands are very different. The $\tilde{A}-\tilde{X} 0_0^0$ band appears to show P and R branch structure typical of a parallel transition. On the other hand, the $\tilde{B}-\tilde{X} 0_0^0$ band shows structure that is more characteristic of a perpendicular band, where coarse structure due to changes in the K rotational quantum number dominate.

At first sight these structural features are surprising, since the $\tilde{A}^2E-\tilde{X}^2A_1 0_0^0$ band should show the classic perpendicular structure. This could be taken to indicate the transition we are observing is to the 2A_1 state instead. However, there is an alternative explanation which would be consistent with the $\tilde{A}^2E-\tilde{X}^2A_1$ transition. The effective rotational constant for coarse rotational structure arising from the $\Delta K = \pm 1$ selection rule is given by $A(1-\zeta)-B$, where A and B are the usual prolate rotor rotational constants and ζ is the effective vibronic angular momentum. For the zero point level of the $\tilde{A}^2E$ state, there is only an electronic contribution, ζ_e , to ζ . Consequently, as pointed out by Herzberg,²¹ it is

possible for the $\tilde{A}^2E - \tilde{X}^2A_1 0_0^0$ band to show parallel-like structure if $\zeta_e \approx 1$. On the other hand, in the $\tilde{B} - \tilde{X} 0_0^0 = 1$ level of the $\tilde{A}^2E$ state the additional contribution to ζ from the vibrational angular momentum can now bring about a transition that shows perpendicular structure. The Pgopher simulations have been carried out for each transition using a variety of parameters, which have been determined from experiment/*ab initio* calculations such as origin peak and rotational constants, including variable parameters for example temperature effect, to try and closely correlate with the experimental spectra produced. The two Pgopher simulated plots for the $\tilde{A} - \tilde{X} 0_0^0$ and $\tilde{B} - \tilde{X} 0_0^0$ origin transitions can be viewed in Figure 5.3.

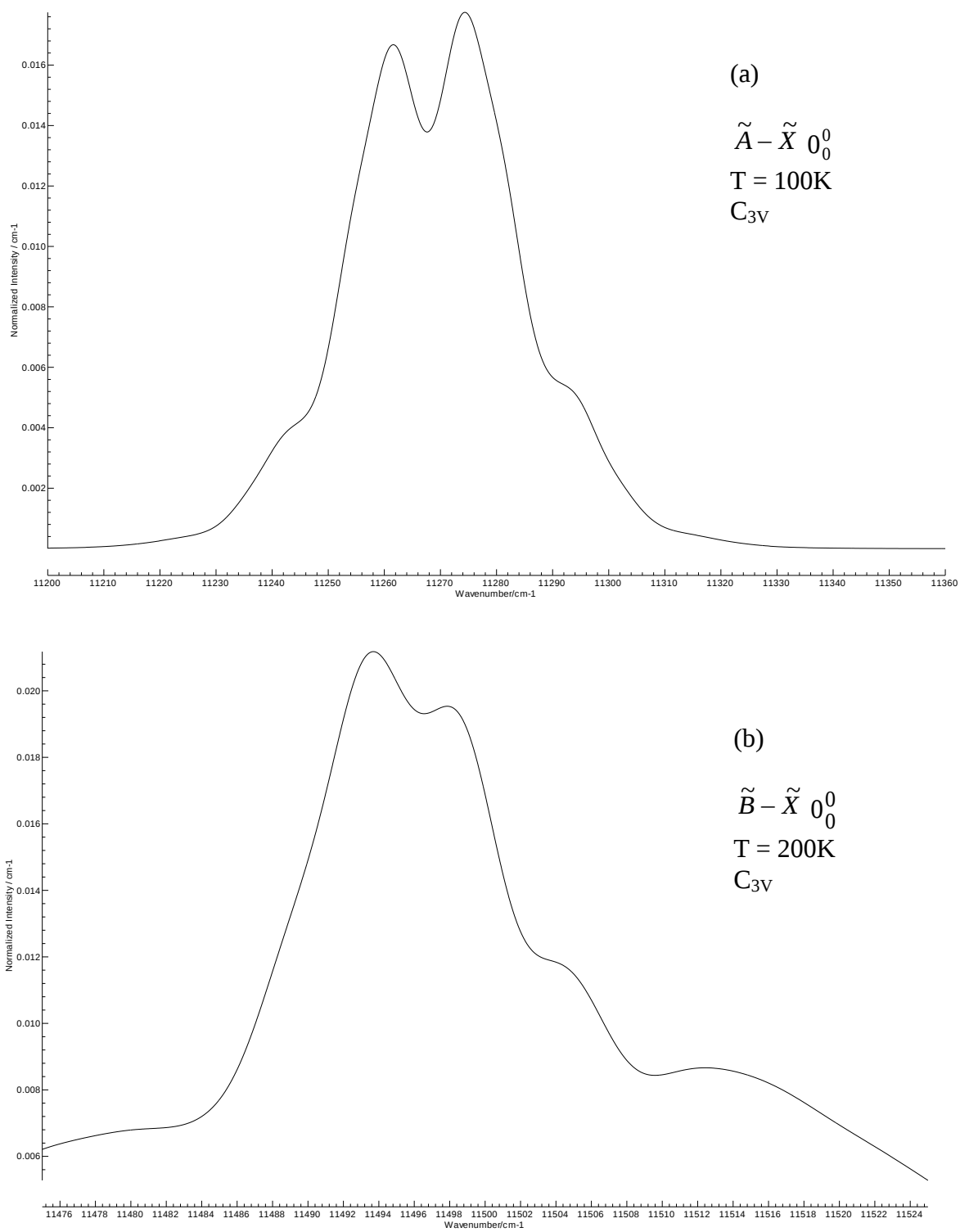


Figure 5.4: Pgopher simulated plots for (a) $\tilde{A} - \tilde{X} \ 0_0^0$ and (b) $\tilde{B} - \tilde{X} \ 0_0^0$ transitions.

5.3.4 Vibronic coupling

The observation of activity in ν_2 and ν_3 in the spectrum of LiNH_3 is not unexpected, since these vibrations are totally symmetric. More surprising is the prominence of the 6_0^1 band in the $\tilde{A}^2E - \tilde{X}^2A_1$ system, since mode ν_6 is non-totally symmetric in the C_{3v} point group and its excitation is therefore symmetry-forbidden at the single quantum level ($\Delta v = \pm 1$) in the Franck-Condon limit, if this point group symmetry is maintained in both electronic states. We note that a prominent 6_0^1 band has also been reported in the corresponding spectrum of NaNH_3 and there has been some (unresolved) debate about whether this arises from a Jahn-Teller effect or Herzberg-Teller coupling.¹³ Evidence is presented here that shows that Herzberg-Teller coupling dominates in LiNH_3 .

The Jahn-Teller effect arises from the coupling of vibrational angular momentum with electronic orbital angular momentum within a degenerate electronic state of a non-linear molecule. When this coupling is significant, the vibrational quantum numbers for Jahn-Teller active vibrations are no longer good quantum numbers, but they can still be used in an approximate sense as a guide to the expected vibrational behavior. In particular, if Jahn-Teller coupling is prominent, we would expect vibrational selection rules for the active vibration(s) of $\Delta v = \pm 0, \pm 1, \pm 2$, etc.²³ In effect, Jahn-Teller distortion converts a nominally non-totally symmetric vibration into a totally symmetric one, in the point group of the distorted structure, subject to the normal Franck-Condon selection rules, and thus a progression in this mode is possible. On the other hand, in Herzberg-Teller coupling, the corresponding vibrational selection rule for the active non-totally symmetric vibration is $\Delta v = \pm 1, \pm 3$, etc.²⁴ We cannot use these selection rules to distinguish between Herzberg-Teller

and Jahn-Teller coupling in LiNH_3 since the 6_0^2 and 6_0^3 bands would lie in congested regions of the spectrum where other bands are also clearly present.

However, we have other evidence from the present work which points to a dominant role for Herzberg-Teller coupling. In particular, Herzberg-Teller coupling can persist as the vibrational symmetry is lowered, whereas Jahn-Teller coupling cannot, since all vibrational angular momentum is quenched for LiNH_2D and LiND_2H . Consequently, no significant ν_6 structure would be expected for LiNH_2D and LiND_2H if Jahn-Teller coupling was responsible for the 6_0^1 bands seen in the spectra of LiNH_3 and LiND_3 . Furthermore, although the vibrational symmetry is lowered for LiNH_2D and LiND_2H , making all vibrational transitions fully allowed in the Franck-Condon limit even without Jahn-Teller or Herzberg-Teller coupling, observable progressions in what were previously non-totally symmetric vibrations would not be expected because there is no change in the equilibrium structure of the molecule on isotopic substitution. Since we observe the 6_0^1 band just as readily for LiNH_2D and LiND_2H as we do for LiNH_3 and LiND_3 , we therefore conclude that Herzberg-Teller coupling is responsible for the appearance of the nominally forbidden 6_0^1 band.

The prominence of this band must derive from substantial intensity ‘stealing’ from one or more electronically allowed transitions. The vibrational wavefunction for the $\nu_6 = 1$ level in LiNH_3 has e symmetry and can potentially mix with the wavefunction of the $\tilde{A}^2E$ state to give *vibronic* states with A_1 and E symmetries. An A_1 vibronic state would now have the correct symmetry to interact with other electronic states of A_1 symmetry, and in particular the nearby $\tilde{B}^2A_1$ state. According to the *ab initio* predictions by Hashimoto and

Daigoku the $\tilde{B}^2A_1 - \tilde{X}^2A_1$ electronic transition has virtually the same oscillator strength as the $\tilde{A}^2E - \tilde{X}^2A_1$ transition.¹⁵ Consequently, the ‘stealing’ of substantial intensity from the $\tilde{B}^2A_1 - \tilde{X}^2A_1$ transition is a plausible source of the strong vibronically-allowed 6_0^1 band seen in the $\tilde{A}^2E - \tilde{X}^2A_1$ system of LiNH₃.

5.4 Conclusions

The electronic spectrum of the prototypical alkali-ammonia cluster, LiNH₃, has been recorded for the first time. This spectrum, occurring in the near-infrared, shows bands assigned to both the $\tilde{A}^2E - \tilde{X}^2A_1$ and $\tilde{B}^2A_1 - \tilde{X}^2A_1$ electronic transitions. In particular the origin bands for these two transitions are found to be in very close proximity ($\sim 200 \text{ cm}^{-1}$). Vibrational structure in these two band systems has been identified and assigned with the aid of isotope substitution studies and a series of supporting *ab initio* calculations.

The $\tilde{A}^2E - \tilde{X}^2A_1$ system is characterized by prominent activity of the Li-N-H bending vibration (ν_6), implying strong vibronic coupling in the excited electronic state. Jahn-Teller activity is possible in the $\tilde{A}^2E$ state, which could give rise to observation of Franck-Condon-forbidden features, such as the intense 6_0^1 band. However, evidence from isotope substitution experiments suggests that the vibronic activity is a consequence of Herzberg-Teller coupling. In particular, the proximity of the $\tilde{B}^2A_1$ state to the $\tilde{A}^2E$ state provides the opportunity for strong vibronic coupling.

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Chapter 6 – Near Infrared Spectroscopy of Lithium

Methylamine Complex

6.1 Introduction

Ammonia is not the only solvent to show solvated electron behaviour when alkali metals are dissolved within it. Other solvents such as water, ammonia and ammonia derivatives i.e. methylamine (Ma), water have also been shown to exhibit solvated electron behaviour but there are some subtle differences, including different solution electrical conductivities for a given solute/solvent ratio when compared to ammonia.¹ The introduction of an ammonia derivative (by the substitution of a methyl group for a hydrogen atom) is likely to result in some changes to the solvent structure around the metal atom.² In particular steric hindrance in the form of the bulky methyl substituent on the nitrogen atom may have a significant impact on the ability to pack solvent molecules around the metal atom. Furthermore, subtle differences in properties of the metal-solvent complexes in the gas phase might be expected, such as ionisation energies.

Recent neutron diffraction studies on lithium-methylamine solutions suggest that approximately four solvent molecules can reside in the inner solvation shell.³ This was also evident in gas phase experimental studies carried out previously in our laboratory, where IR spectroscopic data on $\text{Li}(\text{Ma})_n$ complexes indicated that four methylamine molecules were required to fill the first solvation sphere.²

The study of clusters of alkali metal atoms with ammonia molecules in the gas phase provides a means of probing the impact of the solute/solvent ratio on the electronic properties in a system of finite size. In particular smaller clusters, such as LiNH_3 or LiMa are amenable to high quality *ab initio* calculations, which can then be compared directly with experimental findings.⁴ The smallest, and simplest, alkali-Ma complex is LiMa , where just one solvent molecule is attached to the Li atom. This

isolated complex has not been subject to any previous studies, experimental or theoretical.⁴ Any attempt to understand the fundamental properties of small alkali-Ma clusters as a function of cluster size should include this basic complex.

One example of metal-Ma complexes studied in the gas phase is spectroscopic work carried out on $\text{Al}(\text{NH}_2\text{CH}_3)$, $\text{Al}(\text{NH}(\text{CH}_3)_2)$ and $\text{Al}(\text{N}(\text{CH}_3)_3)$.⁵ Spectra of these complexes were obtained using threshold photoionisation and zero-electron-kinetic-energy photoelectron spectroscopies and interpreted using density functional and *ab initio* calculations.⁵ The AlMa data revealed the formation of low-lying electronic states of several charged Al-containing complexes, including AlMa, $\text{Al}(\text{Ma})_2$ and $\text{Al}(\text{Ma})_3$. The partial substitution of a methyl group in place of a hydrogen atom leads to a lower molecular symmetry (C_s) and more complex spectra consisting of metal–ligand stretching and bending progressions. In addition, the spectroscopic measurements and theoretical calculations showed that methyl substitution for the AlNH_3 complex has a significant impact on the ionisation energies and metal–ligand binding.⁵ The electronic spectra of $\text{Al}(\text{Ma})_n$ become increasingly more complicated with successive Ma substitutions: the Al–NH_3 spectrum is dominated by a single vibrational progression of the cationic structure, whereas AlMa showed three vibrational progressions and $\text{Al}(\text{Ma})_2$ and $\text{Al}(\text{Ma})_3$ displayed four and six modes, respectively.

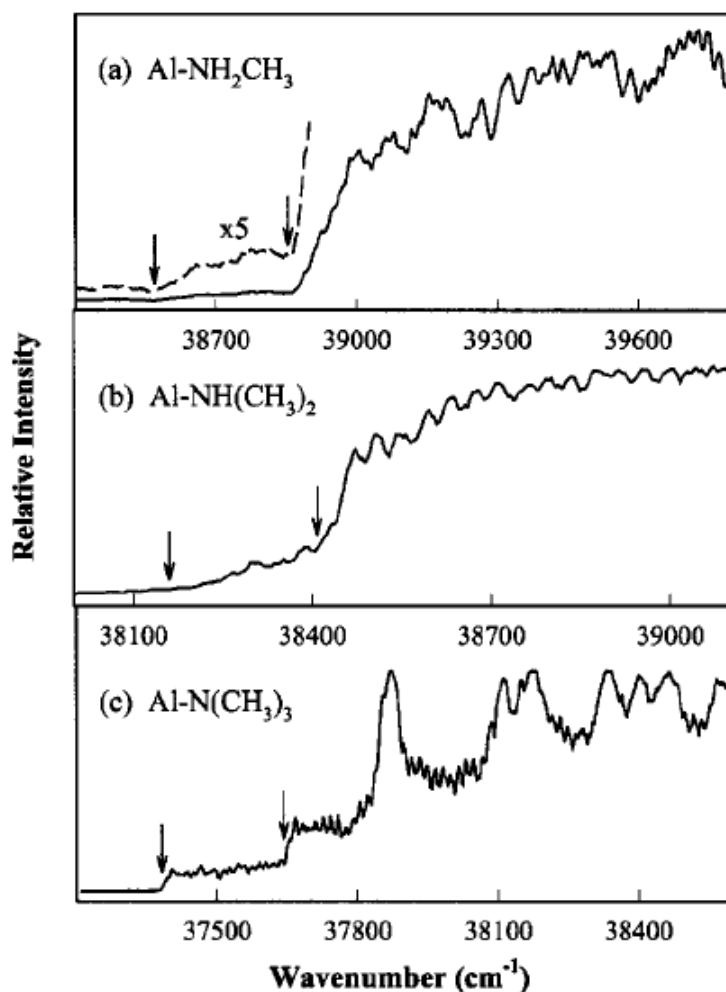


Figure 6.1: Photoionisation efficiency spectra of Al-NH₂CH₃ (a) and Al-NH(CH₃)₂ (b) in helium and Al-N(CH₃)₃ (c) in argon. Taken from reference 5.

Following on from the first study of the electronic spectrum of LiNH₃ in the gas phase,⁶ which was reported in Chapter 5, the first study of LiMa is described in the present chapter. As for LiNH₃, the spectrum recorded for LiMa was an electronic spectrum. Electronic spectra of both LiMa and its partially- and fully-deuterated analogues are presented in the current chapter. These spectra were successfully obtained using a photodepletion technique. The spectra show a number of features, which appear to be vibronic in origin, and their preliminary assignment is discussed in the light of

results obtained for partially deuterated methylamine, as well as through a comparison with LiNH_3 .

6.2 Experimental

The experimental procedure and apparatus employed has been described extensively in Chapter 2 of this thesis. Briefly, LiMa complexes were produced by laser ablation of a solid lithium metal target in the presence of gaseous methylamine and the resulting mixture was expanded into vacuum to form a supersonic jet. The central portion of the jet was extracted by a skimmer (2 mm aperture diameter) and the resulting molecular beam was then passed into a second vacuum chamber for cluster detection via time-of-flight mass spectrometry. Single-photon ionisation was employed to create cluster cations using the output from a pulsed dye laser. The dominant ions present were LiMa^+ , although significant quantities of larger cluster ions, $\text{Li}(\text{Ma})_n^+$, up to $n = 14$ were also observed. The proportion of larger clusters could be altered by varying the experimental conditions, such as backing pressure and laser pulse timings.

To record photodepletion spectra, the output from a LaserVision optical parametric oscillator/amplifier (OPO/A) was employed. This system was pumped by the output from a Nd:YAG laser (Surelite II-10). Since all of the spectra were recorded in the near-infrared region, only the OPO part of the OPO/A system was used. The beam from the OPO was gently focused into the source region of the mass spectrometer, since a more diffuse beam allowed a greater chance of overlap with the UV laser beam (greater details of the OPO operation including wavelength and intensity is describes in Chapter 2 of this thesis). Furthermore, a strongly focused beam into the chamber results in saturation of the signal and hence produces less well resolved spectra. The delay between the firing of the two laser pulses was controlled using a delay generator. The

accuracy of the two laser timings was initially set by the use of a photodiode and then the incoming IR beam timing was adjusted by monitoring the signal on an oscilloscope and optimising for the best possible signal depletion.

Methylamine was sourced from a standard anhydrous methylamine cylinder (Sigma Aldrich, 98%) and was used without further purification. To assist with spectral assignments some experiments were also carried out using ND₃ (Sigma Aldrich, 99% D). The production of the other isotopic species was achieved by allowing methylamine and deuterated ammonia gases to exchange in the gas line; the equilibration was fast and this resulted in the formation of partially deuterated methylamine being produced. It is important to note that ‘fast’ exchange only occurred for the amino groups, i.e. the exchange process for the methyl group is too ‘slow’ on the timescale of our experiment.

6.3 Computational details

To aid in the assignment of the spectroscopic data, *ab initio* calculations were undertaken on LiMa and its deuterated analogues using GAUSSIAN 03, Revision E.01.⁷ Geometry optimisation and vibrational frequency calculations were performed using a 6-311++G** split valence basis set in combination with MP2 methodology, using a tight convergence. To ensure that a true potential energy minimum was obtained, all calculations were run without specifying any symmetry constraints to allow variations in all degrees of freedom. In addition to this, all optimised clusters were checked using the vibrational frequencies such that there were no imaginary frequencies found. Furthermore, the harmonic vibrational frequencies obtained from the calculations have been scaled by a factor of 0.9375 for comparison with experiment. This scaling factor was chosen to bring the calculated N-H frequencies of the free

methylamine molecule into best agreement with the experimental fundamental vibrational frequencies. The restriction to N-H stretching frequencies was dictated by the experiment, since the spectra shown in this chapter focus on the N-H stretching region.

Configuration-interaction singles (CIS) calculations were also carried out to explore the possible excited electronic states being accessed in the experimental work. CIS is, however, a very crude method for calculating electronic excited states, so this needs to be taken into account when interpreting the spectra.

6.4 Results and Discussion

The most prominent signal in the mass spectrum corresponds to LiMa^+ (and its partially deuterated analogues when ND_3 was added). Although other species were seen in the mass spectra, the focus here is on LiMa and its partially deuterated analogues.

Photodepletion spectra were obtained for LiNH_2CH_3 (LiMa), LiNHDCH_3 and LiND_2CH_3 , by gating the corresponding cation signals in the mass spectrum and scanning the OPO output wavelength over the range $10600\text{--}13000\text{ cm}^{-1}$. Scans immediately above and below this range were not possible with the current OPO system. The IR photodepletion spectrum gives three prominent depletion peaks for LiMa and approximately four/five peaks for LiNHDCH_3 and LiND_2CH_3 , as illustrated in Figure 6.2. All depletion peaks produced were reproducible with a reasonable signal-to-noise ratio.

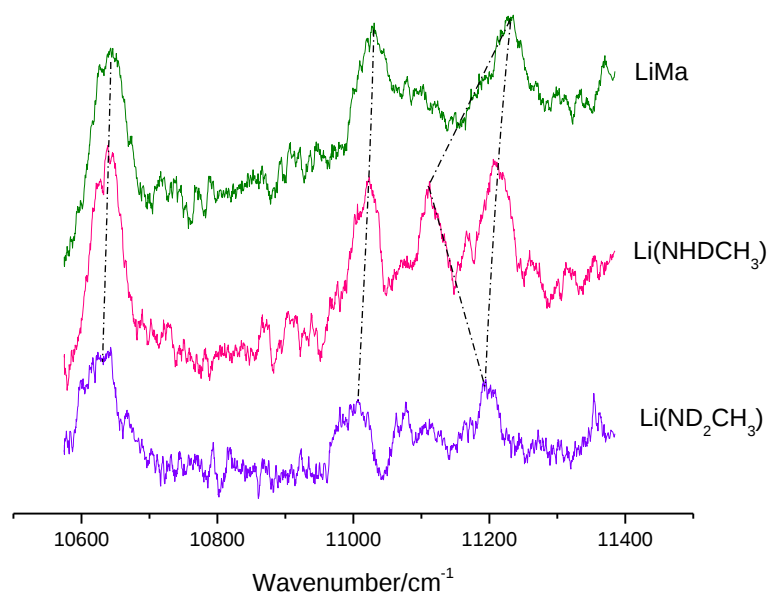


Figure 6.2: IR photodepletion spectra of LiMa (green), Li(NHDCH₃) (pink) and Li(ND₂CH₃) (purple). Spectra were recorded with a signal averaging of 1:63.

LiNH₃ has C_{3v} point group symmetry. As reported in Chapter 5, the electronic spectrum of LiNH₃ was interpreted in terms of two closely lying excited electronic states that derive from the degenerate Li $2p_{x,y}$ orbitals ($\tilde{A}^2E$ state) and the Li $2p_z$ orbital ($\tilde{B}^2A_1$ state). However, LiMa must possess a lower symmetry than LiNH₃ due to the presence of the methyl group, which has replaced one of the hydrogen atoms. Thus for LiMa we might expect to see the effect of the lower symmetry through loss of any excited state degeneracy seen in LiNH₃, i.e. through observation of three closely lying electronic states corresponding to the three distinct Li $2p$ orbitals, rather than the two seen for LiNH₃. This assumes that the loss of electronic state degeneracy is resolvable in the current experiments.

The three spectra in Figure 6.2 all show an intense peak near 10640 cm^{-1} . For LiMa this is centred at 10642 cm^{-1} and becomes slightly red-shifted on deuteration, i.e. occurs at 10639 cm^{-1} and 10632 cm^{-1} for Li(NHDCH₃) and Li(ND₂CH₃), respectively. The positions of the bands in the spectra are summarised in Table 6.1. Given the restrictions on the OPO scan range, scans further to the red were impossible to obtain. Thus, while assigning the lowest wavenumber peak, which is also the most intense spectral signal, to the $\tilde{A}-\tilde{X}\ 0_0^0$ transition, we do so tentatively because it is unclear what might lie further to the red.

For LiNH₃ the $\tilde{A}-\tilde{X}\ 0_0^0$ band was located at 11423 cm^{-1} , and scans further to the red, extending down to 10500 cm^{-1} , revealed no other identifiable bands. Consequently, the LiMa origin band is already shifted substantially to the red when compared to LiNH₃. When considering the vibrational frequency calculations, the isotope shift is very small for this band that there is no conceivable assignment to anything other than the origin transition. Hence, we take this as circumstantial evidence that we have found the $\tilde{A}-\tilde{X}\ 0_0^0$ transition of LiMa.

Table 6.1: Calculated MP2 vibrational frequencies for the ground electronic states of LiNH_2CH_3 , LiNHDCH_3 and LiND_2CH_3 .^{a)}

Description ^{b)}	LiNH_2CH_3 (cm^{-1})	Description ^{b)}	LiND_2CH_3 (cm^{-1})	Description ^{b)}	LiNHDCH_3 (cm^{-1})
Antisymm N-H stretch	3357	Antisymm N-D stretch	2472	N-H stretch	3319
Symm N-H stretch	3278	Symm N-D stretch	2373	N-D stretch	2420
C-H symmetric stretch	2889	C-H stretch	2994	C-H stretch	2971
C-H antisymmetric stretch	2994	C-H asymmetric stretch	2971	C-H asymmetric stretch	2994
N-H bending	1541	C-H twisting/bend	1441	NHDCH ₃ twisting	1443
C-H rocking	1443	C-H bend	1388	C-H scissoring	1430
C-H bend	1429	ND ₂ CH ₃ rocking	1159	NHDCH ₃ scissoring	1394
C-H wagging	1386	ND ₂ CH ₃ bend	1106	NHDCH ₃ twisting	1193
NH ₂ -CH ₃ twist	1157	ND ₂ -CH ₃ stretch + N-D bend	955	NHDCH ₃ twist	1130
NH ₂ -CH ₃ stretch	990	ND ₂ -CH ₃ twist	755	NHDCH ₃ stretch	981
Ma bending	930	ND ₂ CH ₃ bend	739	NHDCH ₃ twist	760
Li-N-H bend	416	Li-N-D bend	324	Li-NHDCH ₃ stretch+twist	390
Li-N stretch	389	Li-N stretch	380	Li-NHDCH ₃ bending	355
whole molecule rocking	169	Li-ND ₂ CH ₃ rocking	158	Li-NHDCH ₃ rocking	159

a) The calculated vibrational frequencies are scaled harmonic values.

b) An approximate description only.

The second peak in the spectrum of LiMa, at 11028 cm^{-1} , is shifted approximately 386 cm^{-1} to the blue of the first peak. Upon deuteration this peak is again shifted to the red. In particular, for LiND_2CH_3 the band is shifted 13 cm^{-1} relative to LiMa. From initial observations, this second peak could have arisen from a vibrational feature, so *ab initio* calculations were used to help with possible vibrational assignments. The calculations focus only on the ground electronic state whereas the vibrational spacings in the experimental spectrum will correspond to vibrational frequencies for the electronic excited state(s). However, by analogy with LiNH_3 we do not expect any large changes in vibrational frequency on electronic excitation and in any case the ground state values will provide valuable information on the *percentage* shift in vibrational frequency on deuteration, which is almost independent of the electronic state. When comparing the photodepletion spectra of LiNH_3 (Figure 5.1 and Figure 6.2, the prominent Li-N-H non-totally symmetric (*e* symmetry) ν_6 bending mode (also known as the rocking mode) present in LiNH_3 may also be active in LiMa. In LiNH_3 this vibration was non-totally symmetric and therefore gained intensity through vibronic coupling. However, in LiMa it is now a totally symmetric vibration and could appear in a Franck-Condon sense very easily.

The calculations may provide some clarity here, since they predict a vibrational frequency at 389 cm^{-1} compared to the measured value of 386 cm^{-1} . Furthermore for complexes LiNHDCH_3 and LiND_2CH_3 the relative shifts to their origin bands is 384 and 383 cm^{-1} respectively. These are actually in reasonable agreement with the *ab initio* calculations since the predicted vibrational frequencies closest to these values are 380 and 355 cm^{-1} respectively. This could give a clue to the possible assignment of this band, but it is also important to include the results obtained from the theoretical

calculations of the LiNH_3 ,⁷ where a band at 371 cm^{-1} was assigned at the non totally symmetric ν_6 mode. However, interestingly this second band for the LiNHDCH_3 complex in Figure 6.2 is not split into two. In addition to this, if this band was a bending vibration then it would be expected that the Li-N-H bend to stay in roughly the same place as for LiNH_2CH_3 but the Li-N-D bend would shift to a lower frequency, which does not fit with the current spectrum. Therefore, it is likely that this band is probably the Li-N stretch (this can be assigned as ν_3 just to compare with the LiNH_3 complex). Perhaps to justify this assignment further it would be useful if the 3_0^2 band could be observed, this particular band is estimated to be around 11412 cm^{-1} . However, this does not seem evident in the experimental spectrum or perhaps it is too weak to be observed amongst the noise.

The third band at around 11200 cm^{-1} for LiMa , LiNHDCH_3 and LiND_2CH_3 is shifted approximately $+590$, $+575$, $+560\text{ cm}^{-1}$ from the origin transitions respectively. The *ab initio* calculations do not show a vibrational mode with a frequency that could sensibly be assigned to this particular peak. The total shift upon deuteration is 30 cm^{-1} , which is lower than for any of the lowest frequency vibrations (for example the rocking or symmetric stretching modes), so this can be ruled out. It therefore seems more likely that the transition corresponding to 11200 cm^{-1} is the $\tilde{B} - \tilde{X}\ 0_0^0$ transition. It is important to take note of the double split band, in which the split band is difficult to assign at the moment, since it is not clear to which mode this may belong to. This could be as a result of a shift in frequency therefore further work will be required in order to fully deduce this tentative assignment.

Figure 6.3 shows scans from 11250 - 13250 cm^{-1} , which go beyond the bands shown in Figure 6.2. There does not seem to be any evidence of significant additional

peaks until roughly 12850 cm^{-1} , although the signal/noise (S/N) level is rather poor and this may mask other bands. The 12850 cm^{-1} band is present only for $\text{Li}(\text{NH}_2\text{CH}_3)$ and $\text{Li}(\text{NHDCH}_3)$ but this maybe, once again, just be a consequence of the poor (S/N) ratio. The band is red-shifted by 24 cm^{-1} on partial deuteration. This is a small isotope shift and again there does not seem to be a calculated vibrational frequency showing such a small isotope shift. A possible explanation is that this particular band could be a new electronic origin i.e. the $\tilde{C} - \tilde{X} 0_0^0$ transition.

The S/N ratio is an important factor in trying to assign the spectrum, therefore future attempts will have to be made in order to try to improve this. For example, focusing the lasers inside the chambers may help in this to ensure the desired complexes are formed. A change in the composition of solvent gas and argon can also be tested to see if this improves the S/N ratio.

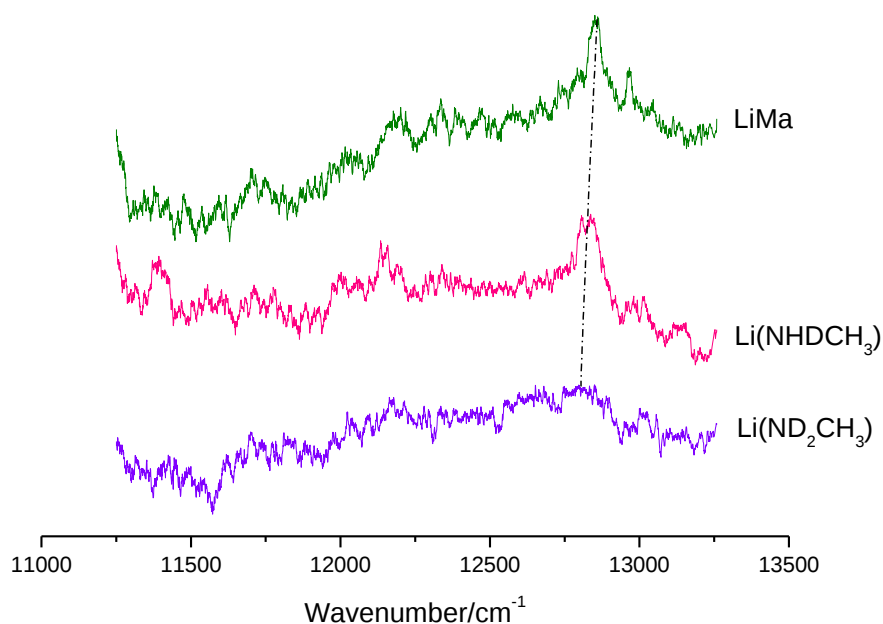


Figure 6.3 : IR photodepletion of LiMa (green), Li(NHDCH₃) (pink) and Li(ND₂CH₃) (purple). All spectra were recorded with a signal averaging of 1:63.

As the transitions involved in this particular cluster will involve the formation of electronically excited states, some *ab initio* calculations have been attempted which address these excited states. The method used was configuration-interaction singles (CIS method). It is important to recognise that the CIS method is not suitable for an accurate determination of electronic excited states, but may still be able to provide some useful information. According to the CIS calculations, the origin bands present in LiMa have the following transition energies: 11000, 11086 and 15159 cm⁻¹, which represent transitions to the first, second and third electronically excited states, respectively. The CIS prediction for the $\tilde{A}-\tilde{X}$ origin transition is fairly close to the experimentally measured origin band at 10642 cm⁻¹, given the expected limitations of the CIS method. Furthermore, theory and experiment seem to be in agreement for the $\tilde{B}-\tilde{X}$ origin

transition, i.e. 11086 cm^{-1} (CIS) and 11028 cm^{-1} (experiment). On the other hand, the CIS method predicts a transition energy to the third excited electronic state at 15159 cm^{-1} , which is far above any of bands seen in the present work. Even though the CIS predictions are unreliable, it would be constructive to repeat the investigation both experimentally and theoretically. For example, repeating the experiment may give better S/N ratio which could help to generate better defined spectral features. It would be particularly beneficial to see calculations on LiMa excited electronic states using a more robust and reliable treatment of excited electronic states, e.g. MRCI calculations.

Table 6.2: Electronic transition energies of LiMa from CIS calculations.

Excited electronic state	Predicted transition frequency (cm^{-1})
$\tilde{A}^2A - \tilde{X}^2A$	11000
$\tilde{B}^2A - \tilde{X}^2A$	11086
$\tilde{C}^2A - \tilde{X}^2A$	15159

Table 6.3: Band positions and potential assignments for LiMa. The numbers in parentheses show the positions of the bands relative to the respective assigned electronic origin transition.

Li-NH ₂ CH ₃ band position/cm ⁻¹	Li-NHDCH ₃ band position/cm ⁻¹	Li-ND ₂ CH ₃ band position/cm ⁻¹	Assignment
10642 (0)	10639 (0)	10632 (0)	$\tilde{A} - \tilde{X} \ 0_0^0$
11028 (386)	11025 and 11110	11005 (373)	$\tilde{A} - \tilde{X} \ 6_0^1$
11231 (589)	11210 (571)	11200 (568)	$\tilde{B} - \tilde{X} \ 0_0^0$
12854 (0)	12831(0)	12801(0)	$\tilde{C} - \tilde{X} \ 0_0^0$

6.5 Conclusions

The electronic spectrum of the Li-methylamine cluster has been recorded for the first time. This spectrum, occurring in the near-infrared, shows bands assigned to the $\tilde{A}^2A - \tilde{X}^2A \ 0_0^0$, $\tilde{A} - \tilde{X} \ 3_0^1$ (using the same notation as LiNH₃), $\tilde{B}^2A - \tilde{X}^2A \ 0_0^0$, and possibly the $\tilde{C}^2A - \tilde{X}^2A \ 0_0^0$ electronic transitions. However, it is important to state that at this stage the assignments are tentative and that further work will need to be carried out to firmly assign the spectrum of the LiMa complex.

Supporting *ab initio* calculations provide some support for the electronic state assignments, particularly for the $\tilde{A} - \tilde{X}$ and $\tilde{B} - \tilde{X}$ assignments. However, the CIS method is a very crude approximation and it would be an improvement to consider alternative methods for calculating excited electronic states. One possibility would be

time-dependent DFT calculations, which are available in standard software packages such as Gaussian 03, Revision E.01 and which are readily affordable.

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Chapter 7 – Spectroscopic Analysis of the $\text{Li}(\text{NH}_3)_n(\text{Ma})_m$ Mixed Clusters

7.1 Introduction

The microscopic solvation of a lithium atom in water-ammonia mixed clusters has recently been investigated using *ab initio* calculations.¹ In particular the low energy structures of $\text{Li}(\text{H}_2\text{O})_n(\text{NH}_3)$ for $n = 1-5$ complexes were considered and one of the primary objectives of this study was to see how electron solvation is affected by the combination of two different solvents. Additionally, the relative stability of these mixed solvent clusters was calculated and it was found that there is an effective repulsive interaction among the solvent molecules in the first solvation shell due to steric effects, which leads to an increase in the Li–O distance in the first solvation shell.

However according to vertical ionisation energy data, it was observed that a near spontaneous ionisation of the Li atom occurs when it is associated with four water and/or ammonia solvent molecules in the first solvation sphere, despite the steric hindrance effect.¹ For small clusters, the singly occupied molecular orbital (SOMO) electron density is found to be distributed mainly in the vicinity of the Li atom. On the other hand, for the larger clusters i.e. clusters bound to greater than four solvent molecules, the SOMO extends out between water and ammonia molecules, rather than being mainly in the vicinity of the Li atom.¹

There have been no previous experimental studies of alkali-solvent clusters with more than one type of solvent. Rather than investigate mixed water/ammonia systems, which would be a major leap from other work reported in this thesis, the work described in this chapter focuses on lithium with both methylamine and ammonia attached. In any mixed cluster experiment, the different sizes of the solvent molecules may have an impact on the solvent shell structure. Also, the different electronic properties of the two solvents may be significant, and in particular may affect solvated electron behaviour. In

the case of ammonia and methylamine, we would expect such electronic impacts to be minimal but structural effects may be more significant. In the experiments reported herein $\text{Li}(\text{NH}_3)_n(\text{Ma})_m$ clusters (Ma = methylamine) were studied via IR depletion spectroscopy in the N-H stretching region. These two solvents were chosen because extensive studies have previously been carried out in the Ellis group on the mid-IR spectroscopy of lithium- and sodium-containing complexes with ammonia or methylamine complexes.^{5,9} This will be the first example of an uncharged *mixed* ligand alkali-containing cluster studied in the gas phase using IR depletion spectroscopy.

7.2 Experimental

The experimental procedure and apparatus employed has been described in detail in Chapter 2 of this thesis. Briefly, $\text{Li}(\text{NH}_3)_n(\text{Ma})_m$ mixed complexes were produced by laser ablation of a solid lithium metal target in the presence of gaseous methylamine (Sigma Aldrich, 98%) and ammonia (Sigma Aldrich, anhydrous, > 99.99% purity). Both gases were used without further purification. The gases were allowed to mix within the gas line prior to arrival at the pulsed valve at a backing pressure of approximately 0.5-1 bar and the resulting mixture was then expanded into vacuum to form a supersonic jet. The central portion of the jet was extracted by a skimmer (2 mm aperture diameter) and the resulting molecular beam was then passed into the secondary chamber so that detection via the time-of-flight mass spectrometer is possible. Photoionisation of the clusters was achieved using the output from a pulsed dye laser. A variety of mixed solvent complexes were observed such as $\text{Li}(\text{NH}_3)_n(\text{Ma})$ and $\text{Li}(\text{NH}_3)(\text{Ma})_n$, where $n = 1 \rightarrow 3$. Furthermore, other neat complexes such as $\text{Li}(\text{Ma})_n$ and $\text{Li}(\text{NH}_3)_n$ were also detected in the mass spectrum (see Figure 7.1).

To record photodepletion spectra, the output from a LaserVision optical parametric oscillator/amplifier (OPO/A) was employed. This gave tuneable mid-IR output with pulse energies of up to 15 mJ, although only approximately 0.5 mJ of this energy was able to reach the molecular beam, owing to energy losses at various optical components. The IR beam was only gently focused into the source region of the mass spectrometer, since a more diffuse beam would allow greater chance of overlap with the UV laser beam. The delay between the firing of the two laser pulses was controlled using a delay generator.

7.3 Computational details

To aid the spectroscopic assignment *ab initio* calculations were carried out in order to predict the optimised geometries of relevant complexes, as well as their vibrational frequencies. In addition to this, bond dissociation energies have been calculated to deduce which solvent molecule (ammonia or methylamine) is more strongly bound to the lithium atom. The calculations were carried out using Møller-Plesset perturbation theory to second order (MP2), as implemented in GAUSSIAN 03, Revision E.01.¹¹ For all MP2 calculations the basis set chosen was 6 311++G (*d*, *p*), with tight convergence (SCF = tight). Bond angles and bond lengths were generated from the GAUSSIAN output via the Chemcraft software.¹⁰

All calculations were run without specifying any symmetry constraints to allow all variations in degrees of freedom. In addition to this, a check for a true potential energy minimum was made by calculating the vibrational frequencies to check for imaginary frequencies. Finally, the vibrational frequencies obtained from the output calculations of the clusters have been scaled by a factor of 0.9375 derived in house to

bring the calculated N-H stretches of a free ammonia molecule into best agreement with experiment.

7.4 Results and discussion

The mass spectrum in Figure 7.1 illustrates the variety of complexes that were produced in the experiments, i.e. $\text{Li}(\text{NH}_3)_n(\text{Ma})_m$ complexes as well as neat clusters containing only ammonia or methylamine solvent molecules in combination with lithium. For the purpose of this chapter, the focus will be on $\text{Li}(\text{NH}_3)_3(\text{Ma})$, $\text{Li}(\text{NH}_3)(\text{Ma})_3$ and $\text{Li}(\text{NH}_3)_2(\text{Ma})_2$.

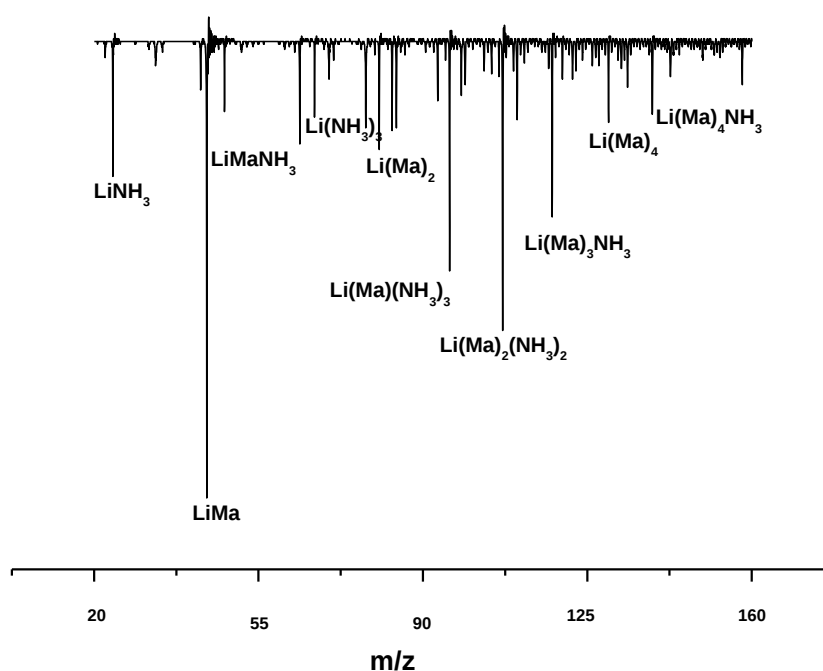


Figure 7.1: A mass spectrum of the $\text{Li}(\text{NH}_3)_n(\text{Ma})_m$ mixed cluster system.
(Signal averaging – 1000 shots)

7.4.1 $\text{Li}(\text{NH}_3)_3(\text{Ma})$

An IR spectrum of the $\text{Li}(\text{NH}_3)_3\text{Ma}$ complex is shown in the upper trace of Figure 7.2.

This scans the region where N-H stretching fundamentals are expected to be seen.

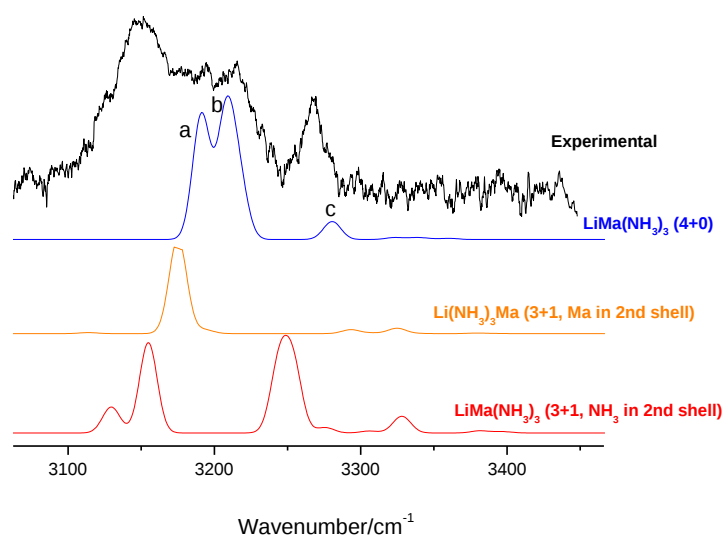


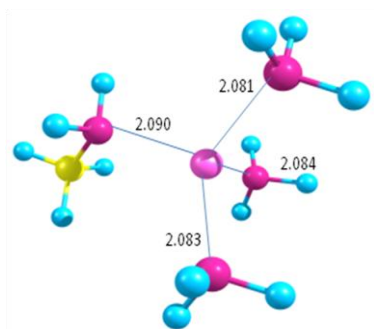
Figure 7.2: IR spectrum of $\text{Li}(\text{NH}_3)_3(\text{Ma})$ in the N-H stretching region (black).

(Below the experimental spectrum are MP2 simulations for the 4+0 and the two 3+1 conformers. The calculated harmonic vibrational frequencies have been scaled by a scaling factor of 0.9375. The individual transitions have been convoluted with Gaussian profiles (full width at half maximum = 15 cm^{-1}) to generate the simulated spectra. The spectrum was recorded with a 1:63 average).

The $\text{Li}(\text{NH}_3)_3\text{Ma}$ spectrum consists of four partially resolved bands spanning the region of approximately $3100\text{--}3300\text{ cm}^{-1}$, although there could be more bands hidden within the broad band profiles. Several scans were extended to lower wavenumbers, down as far as 2600 cm^{-1} , to see if any C-H stretching peaks could be seen. However, no other features were observed, this particular stretch is weak and therefore cannot be observed over the S/N ratio.

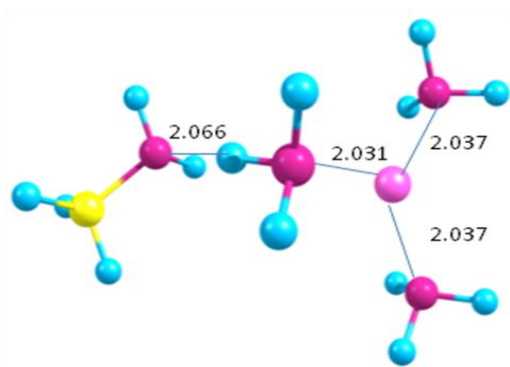
For comparison purposes, it should be noted that the isolated ammonia molecule has an IR spectrum showing two N-H fundamental stretches, the symmetric and asymmetric stretches at 3337 and 3444 cm^{-1} , respectively. The N-H stretching bands of methylamine, as observed in argon matrix studies, also show two bands, these lying at 3361 and 3427 cm^{-1} and with essentially the same assignment as in ammonia. Thus it is clear that the N-H stretching bands seen for $\text{Li}(\text{NH}_3)_3\text{Ma}$ in Figure 7.2 show a comparatively marked red-shift relative to the corresponding bands of the free solvent molecules.

There have been no previous studies of lithium-ammonia/methylamine mixed complexes, and consequently, *ab initio* calculations were carried out on these species in order to assist with the spectroscopic assignment. In the case of $\text{Li}(\text{NH}_3)_3(\text{Ma})$ the first step was to identify the possible isomers that might contribute to the experimental spectrum. Four plausible equilibrium structures of $\text{Li}(\text{NH}_3)_3(\text{Ma})$ isomers were identified and these are illustrated in Figure 7.3 along with their calculated relative total energies. All molecular structures were produced via a graphical program designed for quantum chemistry calculations.⁹

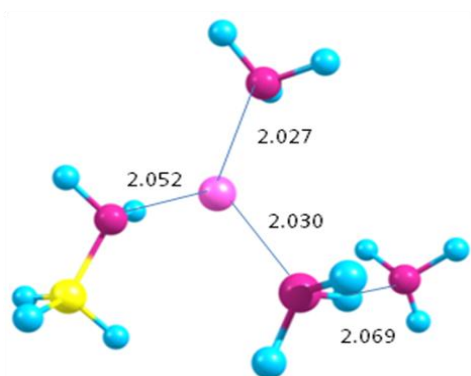
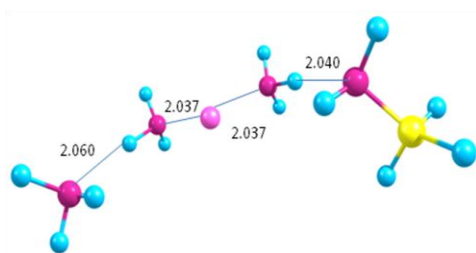


0 eV

4+0

0.30 eV
shell)

3+1 (Ma in 2nd

0.33 eV
shell)3+1 (NH₃ in 2nd

0.70 eV

2+2

Figure 7.3: Calculated isomers of $\text{Li}(\text{NH}_3)_3(\text{Ma})$.

(The relative energies of the isomers are shown and were obtained from MP2 calculations. All Li-N are in angstroms

(Å). (Please note: Blue – Hydrogen, Pink – Nitrogen, Light pink – Lithium and Yellow – Carbon)).

The lowest energy isomer was found to be the 4+0 isomer, i.e. where all four of the solvent molecules reside in the primary solvation shell and there are no molecules in the second shell. In this case, each of the nitrogen-containing substituents is coordinated to the Li metal centre via the nitrogen lone pair. Thus, despite the additional bulk of the methyl group (which incidentally point away from the Li metal centre to minimise steric repulsion), the $\text{Li}(\text{NH}_3)_3(\text{Ma})$ cluster is capable of containing up to four solvent molecules in the primary shell according to the *ab initio* calculations, i.e. the same as $\text{Li}(\text{NH}_3)_4$. Previous studies from the Leicester spectroscopy group have found the same structure for $\text{Li}(\text{Ma})_4$,⁹ so this finding is not surprising.

The second lowest energy isomer is a 3+1 isomer, (0.3 eV) where all three ammonia molecules are situated in the first solvation shell and the methylamine molecule resides in the second shell. In this case the methylamine molecule is coordinated to the complex through a hydrogen bonding interaction with one of the NH_3 molecules, rather than being ‘shared’ between two or more NH_3 molecules. The next lowest energy isomer is another 3+1 cluster, (0.33 eV) but in this case the methylamine group is now in the inner shell and thus an ammonia molecule is situated in the outer shell. The two 3+1 isomers have very similar total energies, and so if these energies alone dictate the abundances then they should be present in similar quantities in the gas phase. One other isomer that has been identified is a 2 + 2 isomer, but this corresponds to a substantially higher total energy and is unlikely to contribute to the experimental spectrum. This isomer will therefore not be discussed further.

Figure 7.2 shows simulated spectra from the three lowest energy isomers, derived from MP2 calculations. The simulation for the 4+0 isomer shows several features in common with the experimental spectrum, and in particular predicts the observed red-shifts relative to spectra of NH_3 and CH_3NH_2 , but the breadth of structure

seen in the experimental spectrum is not reproduced. Thus it seems likely that more than one type of isomer contributes to the overall experimental spectrum. The possibility of combination or overtones bands may exist and contribute to the overall spectrum; therefore, it is necessary to repeat these experiments to confirm this.

The two most intense peaks in the 4+0 simulation, labelled *a* and *b*, correspond to N-H symmetric stretching vibrations in the NH₃ molecules. The positions and the comparable intensities of these bands match the middle two bands in the experimental spectrum rather well. The simulation also shows a third peak, labelled *c*, which arises from the N-H symmetric stretch of the methylamine group. This weaker peak could plausibly give rise to the highest energy peak in the experimental spectrum. Although the intensity of this peak in the simulation is much less than that in the experimental spectrum, previous studies suggest that relative intensities are not always reliable from MP2 calculations.⁵

However, the 4+0 simulation does not account for the most intense band in the experimental spectrum. The 3 + 1 isomer, where the methylamine group is in the second solvent shell, produces a different simulation with only one strong band. This is a promising candidate for the most intense feature in the experimental spectrum because this band is predicted to lie to the red of those from the 4+0 isomer. The calculations show that this 3+1 band arises from N-H stretches in the NH₃ molecules and the fact that these are not resolved suggests a ‘quasi’ *C*_{3v} symmetry. Furthermore, the discussion of the relative abundances of the isomers does deserve a mention and could possibly help in determining the relative contributions of the 4+0 and 3+1 isomers. Assuming a temperature of 298 K (since the temperature of the system is not known), then the abundances of the two 3+1 clusters relative to the 4+0 cluster are 8.49×10^{-6} (when

ammonia is in the primary shell, 3+1 (a)) and 2.64×10^{-6} (as methylamine occupying the primary solvation shell, 3+1 (b)), assuming a Boltzmann distribution. This clearly predicts a very small contribution from a 3+1 isomer. Even if the temperature is assumed to be much higher, 1000 K, the abundance of the 3+1 isomers is still fifty times less than the 4+0 species due to its low concentration. . However, from analysing the dissociation energy data (discussed later in this section) it is reasonable to suggest that the 4+0 isomer should not dissociate at all, unless very ‘hot’. On the other hand, the 3+1 isomers are capable of dissociating on the N-H stretch excitation despite their low relative abundance.

The observation here is that the main band in the 3+1 (NH₃ in primary shell) spectrum has a line strength that is more than 1.5 times greater than that of any band in the 4+0 spectrum. However the factor of 1.5 is highly insignificant since there would need to be at least a factor of 50 to match the 4+0 signal, given the low abundance of the 3+1 isomers. For the other 3+1(b) isomer, there is an NH₃ in the second solvent shell and a methylamine molecule in the first solvent shell. The bands in the simulation (figure 7.2) for this isomer are spread over a slightly larger range than those in the experimental spectrum. There are approximately four bands predicted which does not seem to account to any possible experimental structure. Furthermore, the bands themselves do not easily correlate to any specific bands seen in the experimental spectrum. For this reason it is proposed that this particular 3+1 isomer does not contribute to the experimental spectrum, despite having almost the same predicted total energy as the other 3+1 isomer. A contribution from the calculated 2 + 2 structure is also dismissed, both because it has a substantially higher energy and the fact that the predicted vibrational spectrum (not shown here) is very different from the experimentally observed spectrum.

Table 7.1: Calculated IR vibrational frequencies and line intensities $\text{Li}(\text{NH}_3)_n(\text{Ma})_m$ for the 4+0 and 3+1 isomers (a) and (b).

	Vibration	Frequency (cm^{-1})	Line intensity (cm^{-1})
4+0 isomer	Free N-H stretch	3191	4848
	Free N-H stretch	3208	4783
	N-H stretch (Ma)	3217	2014
3+1 isomer (3+1 (a))	Free N-H stretch	3175	7406
	N-H stretch (NH_3 involved in H-bonding)	3325	414
3+1 isomer (3+1(b))	N-H symmetric stretch (All NH_3 's)	3130	505
	NH_3 symmetric stretch	3154	1760
	N-H stretch (Ma)	3244	1334
	N-H stretch (NH_3 in second shell)	3254	1279

It is necessary to try to account for the apparent selective formation of the 3+1 isomer with methylamine in the second solvent shell, despite its low concentration. Therefore, dissociation energies will be calculated to explore any energetic possibilities. It would be useful to explore this issue in more detail, e.g., through a study using *ab initio* molecular dynamics, but currently this information is unavailable.

From interpretation of the infrared spectra, it is apparent that single photon IR absorption is responsible for depletion of the mass signal in a given mass channel. For this particular mechanism to occur the photon energy must exceed the binding energy of at least one solvent molecule. However, in the case of the 3+1 complex it does not necessarily have to be the Li-N binding energy, since in this case the 2nd shell solvent molecule will be the one that is most easily lost on energetic grounds. To see this, *ab initio* calculations of the binding energies were carried out using the supermolecule approach, i.e.

$$D_0[\text{Li}(\text{NH}_3)_n(\text{Ma})_m] = E[\text{NH}_3] + E[\text{Li}(\text{NH}_3)_{n-1}(\text{Ma})_m] - E[\text{Li}(\text{NH}_3)_n(\text{Ma})_m] \quad [7.1]$$

where E represents the total energy of the complex or fragment at equilibrium, including the zero point vibrational energy, and D_0 is the dissociation energy. By using equation [7.1] the energy required to remove an NH_3 or Ma molecule from a $\text{Li}(\text{NH}_3)_n(\text{Ma})_m$ complex can be calculated. MP2 calculations have again been employed and the counterpoise correction was utilised to remove the basis set superposition error.

The binding energy for the removal of methylamine from the 4+0 complex is 3839 cm^{-1} while removal of NH_3 requires 4060 cm^{-1} . This difference in dissociation energy clearly indicates that the removal of a methylamine molecule is favoured as it occurs at a lower energy. However, and more importantly, it is evident that the dissociation energies for removal of either methylamine or ammonia are far greater than the energies injected by the IR absorption, assuming single photon absorption dominates. To explain the contribution of the 4+0 isomer to the photodepletion spectrum, we suggest that there is a subset of clusters that are hot, and thus dissociation

is assisted by this additional internal energy. Given the violence of the laser ablation process and the subsequent gas phase chemistry prior to supersonic expansion, this is a viable possibility. One attempt to try and prove this could be to measure the temperature inside the chamber.

By comparison, the binding energies for the outer solvent molecule in the 3+1 isomers are much lower than in the 4+0 isomers. This binding energy is calculated to be 1338 cm^{-1} when NH_3 is in the second solvent shell and 1428 cm^{-1} when methylamine is in the second solvent shell. Thus all of the 3+1 clusters will receive sufficient energy to dissociate when N-H stretch excitation takes place, whereas only a very small subset of hot 4+0 clusters can do so. Hence through this scenario we can explain the disproportionately high contribution of the 3+1 isomer to the photodepletion spectrum of $\text{Li}(\text{NH}_3)_3\text{Ma}$ spectrum.

For now any assignment made to the spectrum is tentative and despite the low concentration of the 3+1 (a) isomer (where all three ammonia's reside in the primary shell). The low dissociation energy could account for the reason why this particular isomer makes a reasonable contribution to the overall photodepletion spectrum; hence, energetic factors will play a vital role in explaining this assignment further.

7.4.2 $\text{Li}(\text{Ma})_3(\text{NH}_3)$

With three molecules of methylamine, $\text{Li}(\text{Ma})_3\text{NH}_3$ is a bulkier cluster than $\text{Li}(\text{NH}_3)_3\text{Ma}$. Mass selective infrared depletion spectra of $\text{Li}(\text{Ma})_3\text{NH}_3$ have been recorded in both the N-H and C-H stretching regions. No evidence of any C-H stretching peaks have been found, but spectra have been successfully recorded in the N-H stretching region. An illustrative spectrum is shown in Figure 7.4. Only two bands are clearly observed in the experimental spectrum: one at 3095 cm^{-1} and the other, stronger,

band centred at 3228 cm^{-1} . The S/N ratio in the experimental spectrum is relatively poor and does not allow the clear observation of any other features.

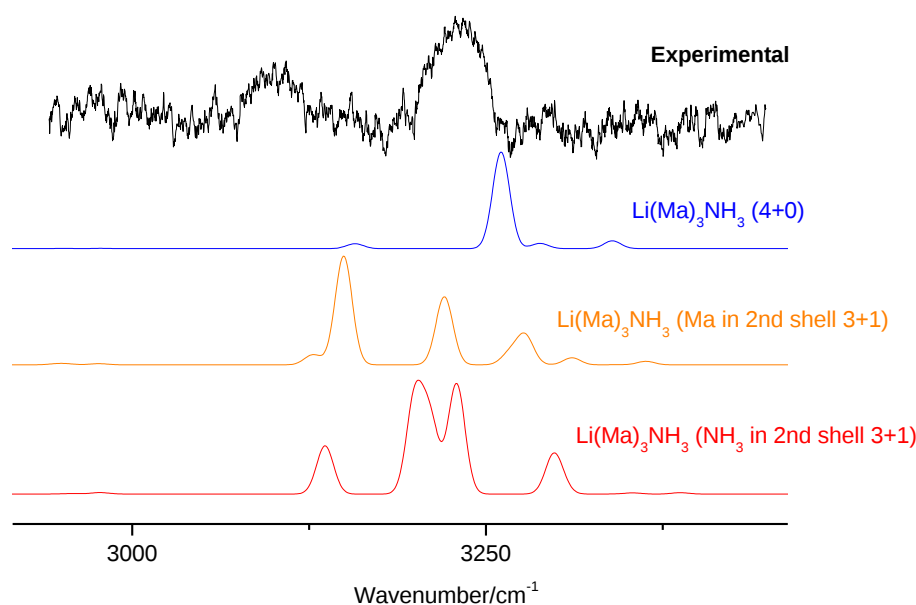


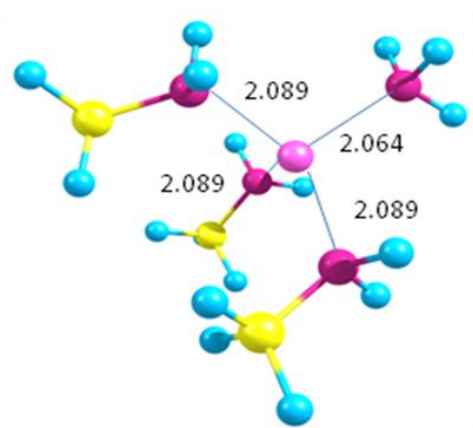
Figure 7.4: IR spectrum of $\text{Li}(\text{Ma})_3\text{NH}_3$ in the N-H stretching region (Black).

(Beneath the experimental spectrum are MP2 simulations for the 4 + 0 and two 3 + 1 conformers. The calculated harmonic vibrational frequencies were scaled by a factor of 0.9375. The individual transitions have been convoluted with Gaussian profiles (full width at half maximum = 15 cm^{-1}). The spectrum was recorded with a signal average of 1:63).

In an attempt to interpret the spectrum, a series of *ab initio* calculations have been performed. The global potential energy minimum corresponds to the 4+0 isomer. The 4+0 cluster shows an approximate tetrahedral arrangement of the N atoms around the central lithium atom, with the methyl groups pointing away from the lithium atom to minimise steric repulsion. 3+1 isomers were also found in which NH_3 was in the first or second solvent shell. The structures and relative energies of these isomers are

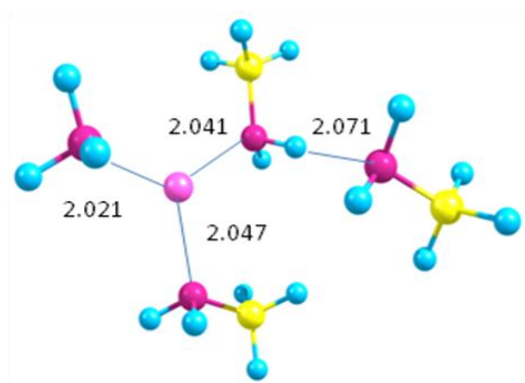
summarised in Figure 7.5. Furthermore, the calculated bond dissociation energies have also been calculated and show some interesting results. Firstly, for the 4+0 isomer, the energy needed to remove NH_3 and methylamine groups are 4754 and 4497 cm^{-1} , respectively. The high dissociation energy of the bulky methylamine group maybe due to the steric hindrance is likely to play a key factor such that removing this molecule will probably require less energy than the smaller NH_3 group. However, the most significant point here is that the dissociation energies are very high, hence this is likely to make depletion highly unlikely and may explain the weak signal seen in the experiment. There are two 3+1 isomers, the first of which contains the methylamine group in the second shell (3+1 (a)) and the second isomer (3+1 (b)) has NH_3 in the second shell. Both of these isomers have similar dissociation energies, at 2363 and 2401 cm^{-1} . The total energies of the 3+1 isomers of $\text{Li}(\text{Ma})_3\text{NH}_3$ relative to the 4+0 isomer are roughly the same as for the $\text{Li}(\text{NH}_3)_3\text{Ma}$, however the dissociation energies are very different, which again may account for the poor signal to ratio seen in the experimental spectrum. So by analogy it is plausible that one or both of the 3+1 isomers could contribute to the spectrum of $\text{Li}(\text{Ma})_3\text{NH}_3$.

The simulated spectrum for the 4+0 isomer is dominated by a single peak at 3294 cm^{-1} , which corresponds to the N-H symmetric stretch of two of the methylamine molecules. This predicted peak is reasonably close to the strongest experimental peak,



0 eV

4+0

0.32 eV
shell)

3+1c (Ma in 2nd

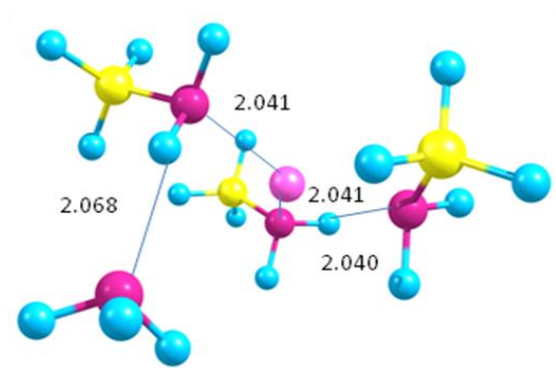
0.36 eV
in 2nd shell)3+1d (NH₃

Figure 7.5: Calculated isomers of $\text{Li}(\text{Ma})_3\text{NH}_3$.

(The relative energies of the isomers are shown and were obtained from MP2 calculations).

The next lowest energy isomer is the 3+1(c) (the 3+1 isomer of $\text{Li}(\text{Ma})_3\text{NH}_3$ where Ma is in the second shell). Three bands with substantial intensities are apparent in the simulated spectrum. The strongest of those bands in the simulation is at 3149 cm^{-1} and could potentially account for the lowest energy band in the experimental spectrum. Although the peak in the simulation is blue-shifted from the experimental peak, the same is also true for the strong band in the 4+0 simulation. However, the absence of any trace of the other predicted bands makes this assignment hard to justify. It could however be very possible that in this case the MP2 band intensities are actually quite poor representations of the true band intensities.

Any contribution from 3+1(d) isomer (3+1 complex of $\text{Li}(\text{Ma})_3\text{NH}_3$ where NH_3 is in the second shell) certainly seems implausible. The bands seen in the simulation do not match those seen in the experimental spectrum, and in this case even if the relative intensities are unreliable it is hard to see how the experimental spectra can be interpreted using the simulated spectrum. Similarly for the $\text{Li}(\text{NH}_3)_3(\text{Ma})$ complex the 3+1(b) isomer did not make a significant contribution to the depletion spectrum due to kinetic factors which could disfavour the formation of this particular cluster. Therefore, it seems likely that the same reasoning can be applied to the 3+1(d), explaining why this cluster does not contribute to the experimental spectrum.

7.4.3 $\text{Li}(\text{NH}_3)_2(\text{Ma})_2$

The last of the complexes considered in this chapter is $\text{Li}(\text{NH}_3)_2(\text{Ma})_2$. The photodepletion spectrum for this complex is shown in Figure 7.6, along with simulations for several possible isomers.

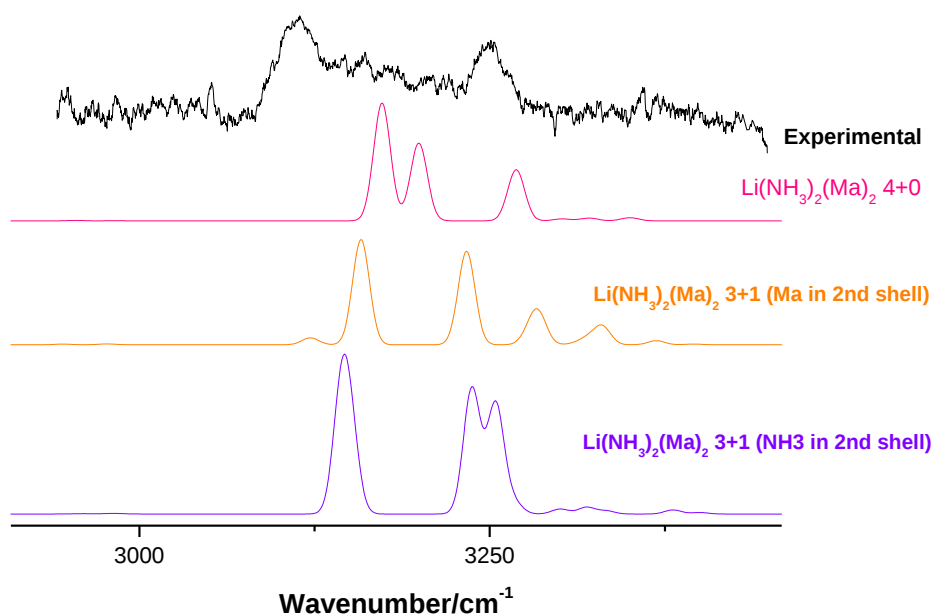


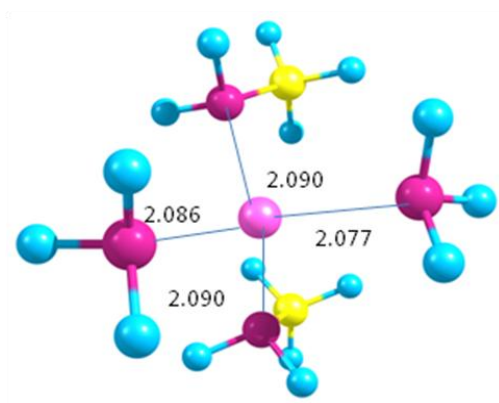
Figure 7.6: IR spectrum of $\text{Li}(\text{NH}_3)_2(\text{Ma})_2$ in the N-H stretching region (Black).

(Beneath the experimental spectrum are MP2 simulations for the 4 + 0 and two 3 + 1 conformers. The harmonic vibrational frequencies have been scaled by a scaling factor of 0.9375. The individual transitions have been convoluted with Gaussian profiles ($\text{FWHM} = 15 \text{ cm}^{-1}$). The spectrum was recorded with a signal average of 1:63)).

There are two obvious peaks in the IR photodepletion spectrum of the $\text{Li}(\text{NH}_3)_2(\text{Ma})_2$ complex, with a broad but ill-defined absorption clearly taking place between those two peaks. The first of the two peaks is centred at 3109 cm^{-1} and the second is at 3245 cm^{-1} . Simulations from MP2 calculations are also included in Figure 7.6 for the three lowest isomers, and the structures of these isomers are shown in Figure 7.7. None of the simulated spectra provide a definitive identification of any single isomer responsible for the experimental spectrum. However, both the 4+0 and 3+1 isomers (where the ammonia is in the second shell) show some features in common with the experimental spectrum. For example, the 4+0 isomer has three peaks spanning

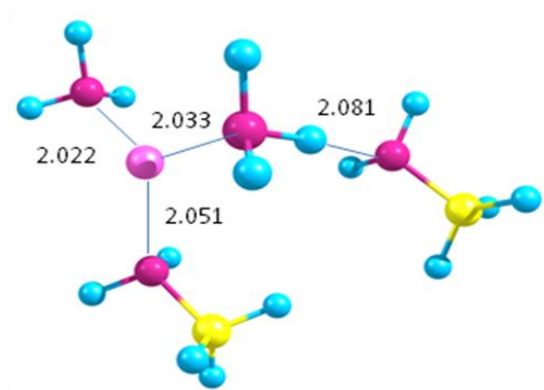
from 3173 to 3266 cm^{-1} , with some additional, very weak, peaks towards the blue end of the spectrum. The first of the two peaks is centred on 3173 cm^{-1} and corresponds to the N-H antisymmetric stretch of the two NH_3 molecules. If this is responsible for the lowest frequency peak in the experimental spectrum then the calculated frequency is substantially blue shifted. The second of three peaks is located at 3199 cm^{-1} and also derives from N-H antisymmetric stretching motion of the NH_3 units. This peak does not fit any identifiable feature in the experimental spectrum, although it could contribute to the broad absorption profile between the two main peaks. Finally, the third peak in the 4+0 isomer simulation is centred at 3266 cm^{-1} and could plausibly be attributed to the highest energy peak in the experimental spectrum. According to the simulation this peak arises from the symmetric N-H stretch in both methylamine molecules.

Of the two 3+1 isomers, some contribution from the isomer where methylamine is in the second shell seems most likely (3+1(e) where the Ma is in the second shell of the $\text{Li}(\text{NH}_3)_2(\text{Ma})_2$ complex). With a red-shift of the simulated spectrum, we can account for the experimental spectrum to a considerable degree. Although this combination does not fully account for the seemingly broad absorption between the two main peaks in the experimental spectrum, the inclusion of a contribution from this particular 3+1 isomer does at least introduce some intensity between the two main peaks. By contrast, the other 3+1(f) (where the NH_3 is in the second shell of the $\text{Li}(\text{NH}_3)_2(\text{Ma})_2$ complex) (NH_3 in second shell) isomer does not assist the assignment of the spectrum in any way.



0 eV

4+0



0.32 eV 3+1e (Ma in 2nd shell)

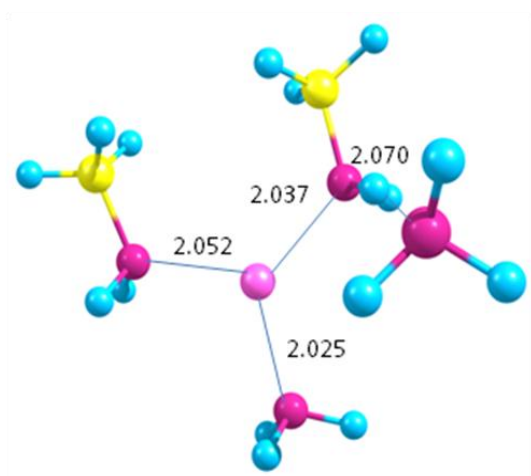
0.30 eV 3+1d (NH₃ in 2nd shell)

Figure 7.7: Calculated isomers of $\text{Li}(\text{NH}_3)_2(\text{Ma})_2$.

(The relative energies of the isomers are shown and were obtained from the MP2 calculations).

The calculations suggest that the removal of an ammonia fragment requires slightly greater energy (4139 cm^{-1}) than removing the bulkier methylamine molecule (3963 cm^{-1}). In addition to this, 3+1 isomers show another interesting behaviour where the removal of ammonia or methylamine in the outer shell is 1581 cm^{-1} and 1534 cm^{-1} respectively.

7.5 Conclusions

The mixed solvent complexes $\text{Li}(\text{NH}_3)_3(\text{Ma})$, $\text{Li}(\text{NH}_3)(\text{Ma})_3$ and $\text{Li}(\text{NH}_3)_2(\text{Ma})_2$ have been investigated by means of photodepletion spectroscopy and *ab initio* calculations. For $\text{Li}(\text{NH}_3)_3(\text{Ma})$ the calculations indicate that both the 4+0 and 3+1 (a) isomer contribute to the overall experimental spectrum. This is due to the uncertainty in temperature of the experimental chamber, thus the high temperatures present could potentially give enough energy to a sub-set of the 4+0 isomers to actually help them to dissociate given that the calculated bond dissociation energies of the 4+0 isomer are high.

The results obtained from the $\text{Li}(\text{NH}_3)(\text{Ma})_3$ were generally similar to the $\text{Li}(\text{NH}_3)_3(\text{Ma})$ cluster. For example, both complexes showed a contribution from the two 4+0 (from each complex), 3+1(a) ($\text{Li}(\text{NH}_3)_3(\text{Ma})$ where Ma is in the second shell) and 3+1(c) isomers ($\text{Li}(\text{Ma})_3(\text{NH}_3)$ with Ma again in the second solvation shell). However the 3+1(b) and 3+1(d) (where ammonia is in the second shell for complexes $\text{Li}(\text{NH}_3)_3(\text{Ma})$ and $\text{Li}(\text{Ma})_3\text{NH}_3$ respectively), isomers did not contribute significantly, if at all, to the overall experimental spectrum.

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Chapter 8 - Electronic Spectroscopy of Jet-Cooled YbNH₃

8.1 Introduction

The rare earth element ytterbium (Yb) shows many parallels with alkaline earth elements.¹ This derives from the filled and compact $4f$ sub-shell of Yb, which leaves it with an active valence configuration of $6s^2$. One way in which the similarity between the alkaline earths and Yb manifests itself is through their ability to dissolve in liquid ammonia. The resulting solutions possess properties that strongly depend on the metal concentration,^{1,2} a property also shared by the alkali metals.² At high concentrations the solutions have a metallic sheen and a high electrical conductivity. On the other hand, at low metal concentrations the conductivity is many orders of magnitude smaller and the blue colour of the solutions is characteristic of the formation of a solvated electron.³ Consequently, as the metal/ammonia ratio is decreased, the ability of the metal to fully release one of its valence electrons increases, leading (at some sufficient dilution level) to an electron that escapes the confining potential of the metal cation.

In several laboratories, including our own, spectroscopic work on $M(\text{NH}_3)_n$ clusters in the gas phase, where M is an alkali metal, has been employed to try to gain some insight into the behaviour of these metallic elements when dissolved in liquid ammonia.⁴⁻¹⁰ This spectroscopic work can provide information on properties such as solvent shell formation and on the ability of the metal to release an electron into the solvent medium as the solvent number (n) increases.

Here we present the findings from our first attempt to record gas phase spectra of an ytterbium-ammonia cluster, focusing on the simplest species, YbNH_3 and its deuterated analogue, YbND_3 . While there have been many spectroscopic studies of Yb-containing diatomics, most notably YbF and YbO ,^{11,12} there has only been one previous study of a polyatomic Yb-containing molecule, YbOH .¹³ In the current work we have successfully recorded the electronic spectrum of YbNH_3 using two-colour two-photon

resonance-enhanced multiphoton ionization (REMPI) spectroscopy. The spectrum obtained is assigned to a spin-forbidden transition in which the transiting electron is retained largely in the vicinity of the Yb atom, i.e. is a metal-centred transition.

8.2 Experimental

The experimental procedure and apparatus employed was similar to that described in previous studies ⁴⁻⁶ and in Chapter two of this thesis. Briefly, YbNH₃ clusters were produced by laser ablation of a solid ytterbium (99.9% purity, Sigma Aldrich) target in the presence of gaseous NH₃ and the resulting mixture was expanded into vacuum to form a supersonic jet. The central portion of the jet was extracted by a skimmer (with an aperture of 2 mm diameter) and the resulting molecular beam passed into the source region of a time-of-flight mass spectrometer, where it was photoionised by the output from a pulsed dye laser (pumped by a Nd:YAG laser).

To record optical spectra, the output from a LaserVision optical parametric oscillator/amplifier (OPO/A) was employed. This system was pumped by the output from an injection-seeded Nd:YAG laser (Surelite II-10), although the injection seeder was not essential for the experiments described here since it did not affect the observable resolution. Since all of the spectra were recorded in the near-infrared, only the OPO part of the OPO/A system was used. This gave a wavelength tuneable output with a pulse energy of up to 15 mJ. However, only a small fraction of this energy was used in the current study, due to the energy losses as the IR beam path was directed through a variety of optics and lens. The beam from the OPO was gently focused into the source region of the mass spectrometer such that it overlapped strongly with the UV laser beam. The delay between the firing of the two laser pulses was controlled using a delay generator and was determined via a photodiode.

Ammonia was sourced from standard liquid ammonia cylinder and was used with no further purification. To assist with spectra assignments some experiments were also carried out using ND₃, both gases were from sigma Aldrich in the anhydrous form at > 99.9% atom purity. During each experiment the valve of the ammonia gas was opened for a limited duration at a backing pressure of approximately 0.5 bar, which meant that a small quantity of ammonia could enter the chamber to form metal-solvent clusters whilst the large quantity of gas can be preserved in the cylinder for future experiments. In turn the deuterated solvent ND₃ was then introduced into the chamber. To record a pure LiND₃ spectrum, it was important that most of the ammonia gas was purged out of the system. This is because the addition of all partially and fully deuterated analogues can sometimes over-complicate the spectrum especially if definite mass peaks or time-of-flights have not been deduced.

8.3 Computational details

Ab initio calculations on YbNH₃ have been carried out in support of the experimental work. The aims of the new calculations were twofold: (1) to predict vibrational frequencies for the ground state and (2) to explore the low-lying excited electronic states. For the ground state calculations, UMP2/6-311++G** basis set was used, in combination with the basis set exchange to deduce the basis set for using Yb. Calculations were initially performed using the GAUSSIAN 03 program, Revision E.01.¹⁴ Spin contamination was found to be present, as shown by the calculated value of $\langle S^2 \rangle = 2.001$. The geometry was optimized and harmonic vibrational frequencies calculated at the potential energy minimum in all cases. The aim was to obtain excitation energies, as well as geometries and vibrational frequencies for the ground and excited states.

Essentially calculations were carried out the MP2 level and the energies were compared in both the singlet and triplet ground states. The relative difference of these energies were then used to establish a theoretical transition energy, for the YbNH_3 complex, which was found to be at 12945.20 cm^{-1} and the experimental origin band was observed at just over 1000 cm^{-1} at 14008 cm^{-1} . Although these are just crude estimations these provide some support to the experimentally observed bands and thus more highly sophisticated *ab initio* calculations will be required to deduce accurate transition energies.

8.4 Results and discussion

8.4.1 Mass spectrometry

Figure 8.1 shows the photoionisation mass spectrum of the Yb/NH_3 system.

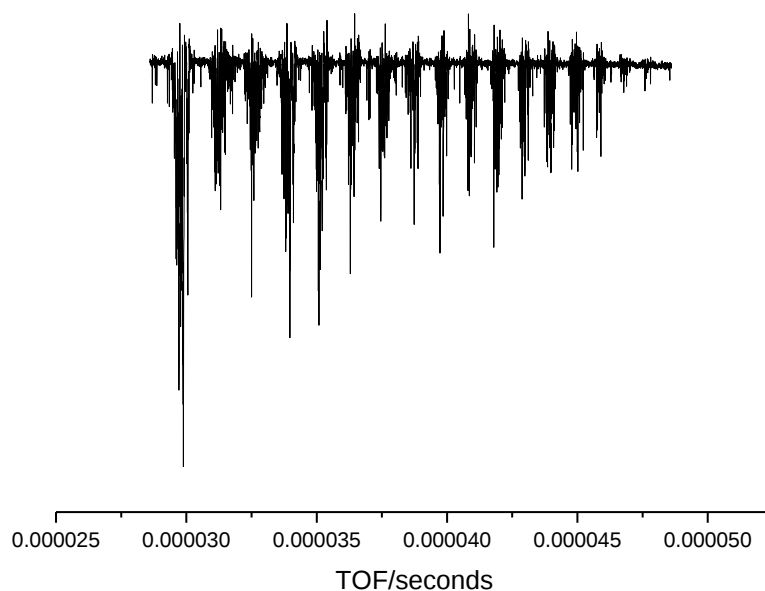


Figure 8.1: The photoionisation mass spectrum of $\text{Yb}(\text{NH}_3)_n$ complexes.

(The first mass peak represents the Yb metal and the rest of the mass peaks are $\text{Yb}(\text{NH}_3)_n$ complexes with n progressively increasing one ammonia molecule).

Many peaks can be seen, all of which can be assigned to Yb^+ and various $[\text{Yb}(\text{NH}_3)_n]^+$ clusters, where we have seen n extending out to values as high as 16. At the photoionisation wavelength used in the present work (250 nm) the ion signal shows a decline in intensity from $n = 0$ -2, and then an increase at $n = 3$ before declining again across the cluster series. We attribute the maximum at $n = 3$ to a change from two-photon non-resonant ionization to single photon ionization, i.e. the first ionization energy of the $\text{Yb}(\text{NH}_3)_n$ clusters declines with n and single photon ionization becomes possible for $n \geq 3$, with a concomitant increase in ionization cross section. For each Yb atom there are six abundant isotopes present when observing the mass spectrum and all isotopes will need to be considered, for example as illustrated in Figure 8.2 for the $\text{Yb}(\text{NH}_3)_2$ complex. We are planning to explore this threshold photoionisation behaviour in detail and will report on this elsewhere.

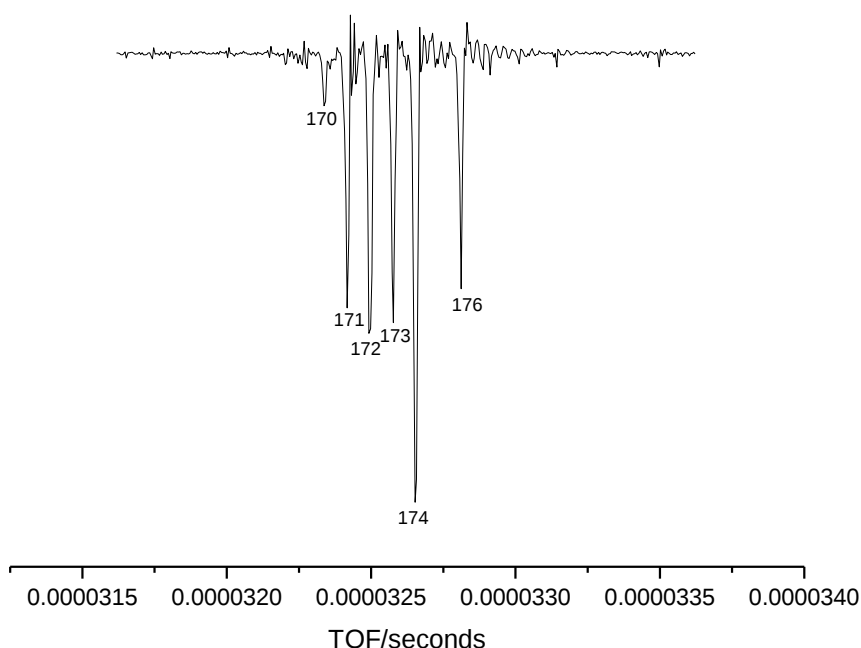


Figure 8.2: The photoionisation spectrum of $\text{Yb}(\text{NH}_3)_2$, including all isotopomers of ytterbium present.

The focus here is on YbNH_3^+ , and in particular the dramatic enhancement in the signal when the OPO output is added and tuned to an appropriate wavelength. This shows a huge increase in the YbNH_3^+ signal and is the result of REMPI excitation of YbNH_3 . By scanning the OPO wavelength and monitoring the YbNH_3^+ signal, a REMPI spectrum of YbNH_3 could be obtained. Yb has several isotopes of comparable abundance, as can be seen from the fine structure in each $[\text{Yb}(\text{NH}_3)_n]^+$ peak, Figure 8.3. In recording electronic spectra we have set the data collection gate to include all isotopomers, i.e. no distinction between different isotopes of Yb has been made.

8.4.2 Electronic spectra: electronic structure

Figure 8.3 (a) compares the REMPI spectra of YbNH_3 and YbND_3 . The electronic spectrum of YbNH_3 is remarkably simple and is dominated by three strong peaks with similar relative intensities. The first-second and second-third peak separations are 232 and 249 cm^{-1} respectively, with the first peak being located at 14008 cm^{-1} . On initial inspection the peak separation would seem suitable for a vibrational interval, but the abrupt end of the progression at the third member, together with a small but negative anharmonicity, would suggest otherwise.

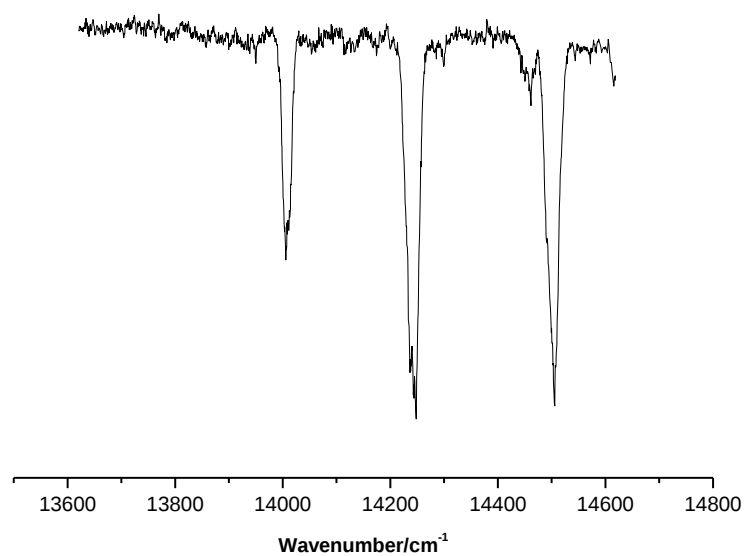


Figure 8.3 (a): Vibronic spectrum of YbNH₃, showing a triplet structure.

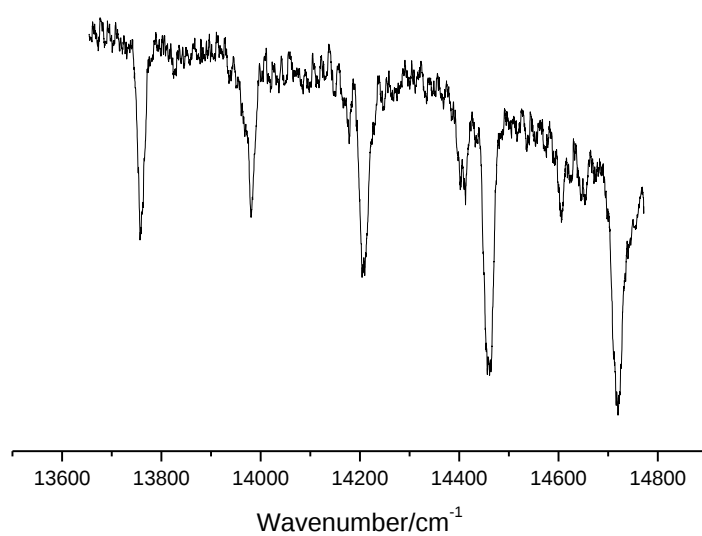


Figure 8.3 (b): YbND₃ also shows this triplet structure.

(With smaller intervals of 221 and 226 cm⁻¹. Furthermore, there are additional peaks in the YbND₃ spectrum that are not seen for YbNH₃).

To assign these spectra, we draw analogies with other $M(\text{NH}_3)_n$ clusters, and in particular M = alkali species such as LiNH_3 and NaNH_3 .^{7-10,17} For these clusters the low energy electronic spectroscopy is dominated by metal-centred transitions, albeit substantially perturbed by the presence of the NH_3 group. If we assume that YbNH_3 behaves similarly, then we can draw upon the electronic energy levels of Yb to construct an electronic structure model for YbNH_3 . In particular, the lowest energy electronic transition in atomic Yb involves excitation of one of the 6s electrons to a 6p orbital, as shown in Figure 8.4. There are both singlet-singlet and singlet-triplet versions of this transition, but the latter occurs at much lower energy and is the one that is related to the YbNH_3 transitions seen in Figure 8.3(a). If YbNH_3 has C_{3v} point group symmetry, then the ^3P excited state of atomic Yb will correlate with two possible excited states of YbNH_3 , a 3E state and a 3A_1 state. These two states arise from the different orientations of the 6p orbital when placed in a C_{3v} environment: the electron can be excited to either the degenerate pair of $6p_{x,y}$ orbitals, which have e symmetry, or to an a_1 orbital that correlates with the Yb $6p_z$ orbital. The 3E excited state is expected to have the lower energy because of the reduced electron density along on the Yb-N axis, which allows the N atom to be exposed to a high partial positive charge on the Yb atom.

We assign the triplet structure in the YbNH_3 and YbND_3 spectra to spin-orbit splitting in the excited electronic state. Consequently, the assignment is to a $^3E^{-1}A_1$ transition, with access to all three spin-orbit sub-states, $^3E_{(0)}$, $^3E_{(1)}$ and $^3E_{(2)}$ from the ground electronic state, Figure 8.4 represents the atomic energy levels of atomic ytterbium and then the energy levels when the ytterbium is complexed to an ammonia molecule. The observation of spin-orbit splitting is clear confirmation that YbNH_3 has C_{3v} symmetry. This also agrees with our *ab initio* calculations, which finds C_{3v} symmetry for both the lowest singlet and triplet electronic states. Furthermore, because

the two states that we observe are the lowest states of their respective multiplicity, we can obtain reasonable description of these states without recourse to multi-reference wavefunctions. We obtain a value of 12940 cm^{-1} for the separation between the $\tilde{X}^1A_1$ and $\tilde{a}^3E$ states, which is reasonably close to the true value given the approximations involved.

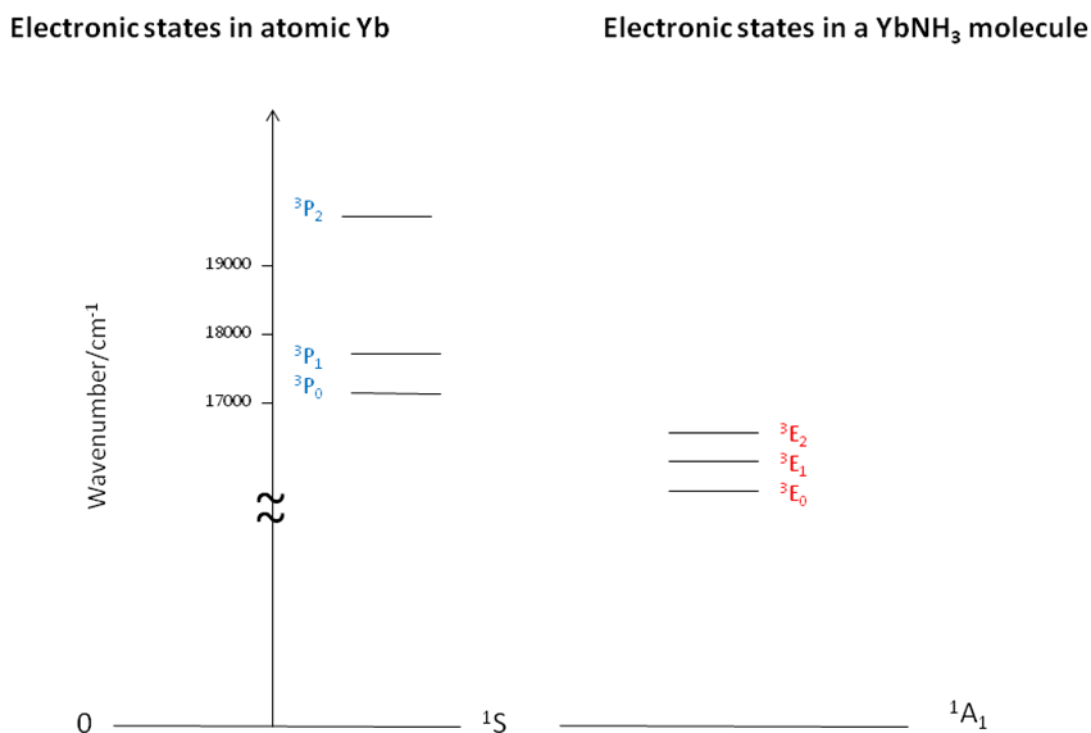


Figure 8.4: A diagram showing how the low-lying electronic states of YbNH₃ correlate with those of atomic Yb.

For a linear molecule in the Russell-Saunders limit, the spin-orbit components should be located at position $T_0 + A\Lambda\Sigma$, where T_0 represents the unperturbed transition frequency (i.e. in the absence of spin-orbit coupling), Λ is the orbital projection of the electronic orbital angular momentum on the C_3 axis and Σ is the corresponding value for the spin angular momentum. Russell-Saunders coupling will only approximately apply to YbNH₃ because of the heavy Yb atom, and of course it is a non-linear molecule and

so Λ in particular is no longer a good quantum number. Nevertheless, if the molecule retains C_{3v} symmetry then it will possess orbital angular momentum in its 3E excited state and therefore spin-orbit components of the 3E excited state should occur at $T_0 - A$, T_0 , and $T_0 + A$. This is illustrated in Figure 8.4. The prediction of an equally spaced spin-orbit triplet matches the observed spectrum very closely. The spin-orbit coupling constants obtained, $A_{YbNH_3} \approx 243$ and $A_{YbND_3} \approx 221 \text{ cm}^{-1}$, are much smaller than the spin-orbit coupling of the corresponding state of atomic Yb, i.e. $A({}^3P) = 708 \text{ cm}^{-1}$.¹⁸ The explanation may lie in the off-axis H/D atoms, which can partially quench the electronic orbital angular momentum, and thus reduce the effective spin-orbit coupling.

It is also noteworthy that $A_{YbNH_3} \neq A_{YbND_3}$. The difference is not huge, but it is significant given that the spin-orbit coupling would normally be expected to be isotope invariant. The fact that they are not may suggest substantial perturbations are in action, as noted recently for the $\tilde{A}^2\Pi$ states of BaOH and BaOD.¹⁹

Another profound effect which can arise from heavy metals, resulting in spin orbital coupling is relativistic effects. The study of complexes of heavy elements by *ab initio* quantum chemical methods requires the incorporation of relativistic effects.^{20,21} Essentially, the presence of relativistic effects has the ability to cause dramatic changes to chemical properties, such as ionisation potentials, orbital energies and atomic radii.²¹ These changes become more apparent as the system increases in the number of electrons, i.e. for heavy metal atoms, a prime example can be that of the lanthanides. One such example, is the so called lanthanide contraction²⁰ this effect is predominately caused by the incomplete shielding of the nucleus by the $4f^{14}$ electrons, therefore this results in the large effective core charge which contracts the 5p, 5d, 6s orbitals.

A full exact relativistic treatment of electronic motion in a molecule is very difficult, but approximate calculations of useful accuracy can be made. For example, the

calculations assume that the core electrons remain unchanged in molecule formation and replace their detailed influence on valence electrons by relativistic effective core potentials (RECP).²¹

The design of RECPs is a compromise between two requirements: first they have to imitate the interactions of core electrons of a many electron atom with the valence electrons. Second, this imitation of core electrons has to be limited only to the valence region. Hence, these calculations will ensure a ‘valence only’ basis set is used for the atom in question (details of quantum theory and *ab initio* calculations can be found in Chapter 3 of this thesis).

8.4.3 Electronic spectra: vibrational structure

We now turn to additional features in the spectra, which are particularly evident in the case of YbND₃. The appearance of a second prominent triplet, starting at 701 cm⁻¹ above the first triplet, is indicative of vibrational excitation in the *a*³*E* excited electronic state. Assuming *C*_{3v} symmetry, YbNH₃ will have six distinct vibrational modes, with approximate descriptions and symmetries as follows: the Yb-N stretch (*a*₁), the Yb-N-H bend (*e*), the NH₃ umbrella vibration (*a*₁), a degenerate H-N-H bending mode (*e*), a symmetric N-H stretch (*a*₁) and an antisymmetric N-H stretch (*e*).

To gain some idea of the frequencies of these vibrations, we refer to *ab initio* predictions on YbNH₃ and YbND₃ in their lowest singlet and triplet electronic states. Table 8.1 shows the predicted vibrational frequencies for the lowest triplet state. Only totally symmetric vibrations are expected to be active in the Franck-Condon limit. The only plausible candidate for the 701 cm⁻¹ interval in the YbND₃ spectrum is the ND₃ umbrella mode, which is predicted to occur at 898 cm⁻¹. This is substantially lower than

the predicted frequency for this mode, suggesting that the calculations do not accurately describe the vibrational behaviour of YbNH₃ and YbND₃.

Table 8.1: *Ab initio* vibrational frequencies of YbNH₃ and Yb ND₃ (in cm⁻¹).

Vibratio n	Description ^{b)}	YbNH ₃ $\tilde{X}^1A_1$	YbND ₃ $\tilde{X}^1A_1$	YbNH ₃ $\tilde{A}^3E$	YbND ₃ $\tilde{A}^3E$
$\nu_1 (a_1)$	Symm. N-H stretch	3223	2304	3039	2125
$\nu_2 (a_1)$	Umbrella	1133	864	1155	898
$\nu_3 (a_1)$	Yb-N stretch	177	164	298	291
$\nu_4 (e)$	Antisymm N-H stretch	3365	2476	3108	2213
$\nu_5 (e)$	N-H scissor	1524	1103	1453	1025
$\nu_6 (e)$	Yb-N-H bend	285	211	313	281

^{a)} See Computational Details section for more information on the procedure used. The vibrational frequencies shown above have been obtained by multiplying the calculated harmonic vibrational frequencies by a scaling factor

(0.9375)

^{b)} These descriptions describe the *approximate* character of the vibrational modes.

8.5 Conclusions

The electronic spectra of YbNH₃ and YbND₃ have been recorded for the first time. This is also the first spectroscopic study of a complex consisting of a rare earth atom in combination with ammonia. Using two colour resonance-enhanced multiphoton ionisation spectroscopy, the lowest energy electronic transition of YbNH₃ has been found in the near-infrared. The spectrum arises from a spin-forbidden transition between the 1A_1 ground electronic state and a 3E excited electronic state. The transition is metal-centered and can be approximately described as an Yb 6*p* ← 6*s* transition. The observation of clear spin-orbit structure in the spectrum confirms the C_{3v} symmetry of

YbNH₃. Some vibrational structure is also observed in the REMPI spectrum which has been successfully assigned.

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Chapter 9 – Summary and overall conclusions

9.1 Summary of findings

The objective of the work described in this thesis was to explore new metal-ammonia and related complexes using size-selective spectroscopy. The focus was on the alkali metals and in effect the onset of solvation by ammonia and its derivatives was studied at the molecular scale.

One of the highlights of this work was the recording of the first electronic spectrum of $\text{Li}(\text{NH}_3)_4$, which was achieved using mass-selective depletion spectroscopy. Strong absorption was observed in the near-infrared and the band system assigned to this particular complex was the $\tilde{A}^2T_2 - \tilde{X}^2A_1$ electronic transition. The vibrational structure in the spectrum suggests a tetrahedral complex, but one with a substantial Jahn-Teller effect in the excited electronic state. The location of the spectrum confirmed a recent theoretical prediction¹ that the electronic spectrum of $\text{Li}(\text{NH}_3)_4$ will strongly overlap with the spectrum of the solvated electron in lithium-ammonia solutions.

To gain further understanding of the lithium-ammonia cluster complexes, it was decided to investigate the simplest lithium-ammonia complex, LiNH_3 . Unlike $\text{Li}(\text{NH}_3)_4$, spectra for LiNH_3 could be recorded by REMPI spectroscopy. Electronic spectra of LiNH_3 and its partially and fully deuterated analogues were recorded in the near-infrared. The two electronic transitions observed are in close proximity and were assigned as the $\tilde{A}^2E - \tilde{X}^2A_1$ and $\tilde{B}^2A_1 - \tilde{X}^2A_1$ systems. Although vibrational structure was seen in both systems, the Li-N-H bending vibration (ν_6) was dominant in the $\tilde{A}^2E - \tilde{X}^2A_1$ system and the Li-N stretch (ν_3) in the $\tilde{B}^2A_1 - \tilde{X}^2A_1$ system. The prominence of the 6_0^1 band in the $\tilde{A}^2E - \tilde{X}^2A_1$ spectrum was attributed to Herzberg-Teller coupling, which is essentially caused by ‘intensity stealing’ from higher lying electronically excited states. The proximity of the

$\tilde{B}^2A_1$ state, which lies little more than 200 cm^{-1} above the $\tilde{A}^2E$ state, is likely to be the primary contributor to this strong vibronic coupling.

To further investigate the vibronic nature of simple Li-solvent systems, the spectroscopy of the lithium-methylamine (LiMa) complex was explored. This represents a change in the solvent molecule, but is the closest relative to NH_3 . Thus it was expected to yield spectra in roughly the same region as LiNH_3 . So far only preliminary spectra have been recorded, with room for improvement in the signal/noise ratio. This spectrum, occurring in the near-infrared, showed bands assigned to the $\tilde{A}-\tilde{X}$, $\tilde{B}-\tilde{X}$ and possibly the $\tilde{C}-\tilde{X}$ electronic transitions. In particular the origin bands for the first two transitions are found to be in very close proximity ($\sim 386\text{ cm}^{-1}$), but the symmetries of the excited states are not clear. Further experiments and *ab initio* calculations will need to be carried out in order to firmly assign the spectrum of LiMa and its deuterated analogues.

Due to the success of mid-IR experiments previously undertaken, IR depletion spectroscopy was investigated of lithium complexes with mixed solvents. The complexes considered were $\text{Li}(\text{NH}_3)_3\text{Ma}$, $\text{Li}(\text{Ma})_3\text{NH}_3$ and $\text{Li}(\text{NH}_3)_2(\text{Ma})_2$ and successful attempts were made to record vibrational spectra in the N-H stretching region. The assignment of the spectral bands in the $\text{Li}(\text{NH}_3)_3\text{Ma}$ spectrum is only tentative. However isomers, namely those of the $3 + 1$ type, seem to make a significant contribution to the overall spectrum. The exceedingly high dissociation energies for $4+0$ are highly suggestive of the presence of ‘hot’ molecules within the system, such that without this subset of molecules, the dissociation of the complex will probably not occur. Therefore energetic factors will have a contributing factor since the bond dissociation energies if the $3+1$ isomers are lower, Hence observing a significant contribution from the $3+1$ complex.

For the $\text{Li}(\text{Ma})_3\text{NH}_3$ complex, again the spectral assignment is only tentative. The bands seen in the *ab initio* simulation do not exactly match those seen in the experimental spectrum. All assignments made in Chapter 7 are tentative and further work will need to be carried out in order to fully assign the spectrum of these mixed complexes.

The final metal-solvent system explored contained the metal ytterbium in combination with ammonia. The electronic spectrum of YbNH_3 was recorded for the first time. The two-colour REMPI spectrum was observed in the near-infrared and was attributed to a spin-forbidden transition between the 1A_1 ground electronic state and a 3E excited electronic state. The transition is metal-centred and can be approximately described as an $\text{Yb } 2p \leftarrow 2s$ transition. The observation of clear spin-orbit structure in the spectrum confirms the C_{3v} symmetry of YbNH_3 .

9.2 Suggestions for future work

There is potential for improving on the experiments and calculations carried out in this thesis work. For example, for the $\text{Li}(\text{NH}_3)_4$ complex we could record spectra of higher energy electronic transitions using a dye laser. In addition, supporting high quality *ab initio* calculations on the excited electronic states will be very useful. It would also be interesting to explore the spectra of larger $\text{Li}(\text{NH}_3)_n$ complexes, where the solvated electron behaviour should become even more obvious as the second solvation shell becomes populated.

In terms of improving the LiMa investigation, the experimental spectra will no doubt need to be improved to gain a better signal to noise ratio. Furthermore, in order to accurately assign the spectra, high quality excited state *ab initio* calculations will be

required to allow the symmetries of the excited states to be determined and to predict the electronic state separations.

In terms of exploring the lanthanide metals, larger $\text{Yb}(\text{NH}_3)_n$ clusters should also be investigated through photodepletion experiments. In addition photoionisation threshold experiments of the $\text{Yb}(\text{NH}_3)_n$ experiment may provide some useful information, such as indirect information on solvent shell closings. This is work that has not been attempted before and should be relatively straightforward to do.

Finally, a simple variation to these experiments would be to use nitrogen-containing solvents other than ammonia, for example, dimethylamine, ethylamine or even trimethylamine.

The prospects of taking this research further provide numerous opportunities to explore different metal-solvent systems, such as the coinage metals, i.e. copper, silver and gold. The interesting aspect of investigating these metals is that, firstly, they all have a single electron in their outer shell, which bears a superficial resemblance to the alkali metals. However since these particular metals are less electropositive than the alkali metals, the coinage metals are likely to show greater reluctance to release the 'solvated electron' into the solvent medium. The observation of complexes of the coinage metals with ammonia and other solvents would make it possible to see how the solvation process changes with these less electropositive metals. Furthermore exploration of common solvents, such as water, would provide an important direction for this work.

References

1. E. Zurek, P.P Edwards and R. Hoffmann, *Ang. Chem. Int. Ed.* **48**, 8198 (2009)

Record of achievement

Publications

- The electronic spectrum of $\text{Li}(\text{NH}_3)_4$, L. Varriale, N. M. Tonge, N. Bhalla, and A. M. Ellis, *J. Chem. Phys.* **132**, 161101 (2010)
- Near-infrared spectroscopy of LiNH_3 : first observation of the electronic spectrum, L. Varriale, N. Bhalla, N. M Tonge and A.M. Ellis, in *J. Chem. Phys*, **134**, 124304 (2011)
- Electronic spectroscopy of jet-cooled YbNH_3 , *J. Chem. Phys*, **136**, 064305 (2012)

Conferences and presentations attended

During the course of my PhD I have attended numerous conferences and seminars. These have included; the spectroscopy and Dynamics Group (SDG) meeting, Midlands Universities group (MUGS) meeting and the 65th International Symposium on Molecular Spectroscopy at Ohio State University, Columbus, Ohio, USA. During these meetings I have had the opportunity to present my work through oral and poster presentations.