Photoionization and infrared laser spectroscopy of molecular complexes: the transition from the molecular to the nanoscale

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by

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Abstract

The microscopic nature of neutral alkaline earth metal-ammonia complexes, namely $Ca(NH_3)_n$, $Sr(NH_3)_n$, and $Ba(NH_3)_n$ have been investigated in a molecular beam. *Ab initio* calculations undertaken in support of the experimental results provided valuable insight into the structures of these complexes. In addition, calculations have also been carried out on other complexes, namely, $Mg(NH_3)_n^+$ and $Eu(NH_3)_n$.

Ionization energies have been determined by photoionization for $Ca(NH_3)_n$, and $Sr(NH_3)_n$ complexes and combined with *ab initio* calculations to assist the interpretation of the photoionization data. Good agreement between the experimental photoionization threshold and theoretical ionization energies based on the lowest energy structures of the complexes is found, indicating that predicted lowest energies structures dominate in the molecular beam.

Infrared spectra in the N-H stretching region have been recorded for the $Ca(NH_3)_n$, $Sr(NH_3)_n$ and $Ba(NH_3)_n$ complexes for the first time using mass-selective photodissociation spectroscopy. The IR spectra of all of these complexes are red-shifted from those of the free ammonia molecule, suggesting that the M-N interaction weakens the N-H bond. The IR spectra and *ab initio* calculations confirm that the interior structure, in which a metal is surrounding by a number of ammonia molecules is favoured over a structure in which the metal atom sits upon a cluster of ammonia molecules (a 'surface' structure).

Ab initio calculations predict that the first solvation shell of the $Mg(NH_3)_n^+$ complexes can hold up to six NH₃ molecules. In the case of the Eu(NH₃)_n complexes, the theoretical calculations predict that the interior structure is energetically favoured, similar to the neutral alkaline earth metals. Calculations show that the first solvation shell is found to close with eight ammonia molecules around the central europium atom.

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Chapter 1

Introduction

1.1 On the nature and signatures of electron solvation in ammonia

The nature of the solvated electron in liquid ammonia has inspired numerous experimental and computational investigations since the first discovery by Humphry Davy in the early 19th century.¹ Wilhelm Wely² described this phenomenon in detail, and subsequently, the first theoretical calculations reported by Ogg³ supported the experimental insights on the solvated electron. In addition, the term "solvated electron" for excess electron states in liquid ammonia was first introduced by Gibson and Argo.⁴ A large number of studies have since focused on the absorption spectra, magnetic behaviour, conductivities, electrical properties and the nature of the cavity structure, and solvation dynamics.⁵⁻¹⁰ However, the microscopic nature of the solvated electron in ammonia is still not completely understood with respect to the individual properties. The strong interest in this fascinating system comes from a rich variety of different phases from a phase separation and metal insulator transitions (electrolytic conductors) to metallic properties (metallic state) and liquid-liquid phase equilibria with a single-phase region in these solutions. The intriguing and unusual properties of electron solvation therefore, remains of sustained interest.¹¹⁻²³

Alkali, alkaline and some rare earth metals dissolve freely in pure, anhydrous liquid ammonia without chemical reaction²⁴, resulting in a free electron and a positively charged metal ion. This dissolution of metal in ammonia produces an intense blue colour for dilute solutions and a bronze/gold colour for concentrated solutions, as shown in Figures 1.1(a) and 1.1(b), respectively. When the solution is dilute, the valence electrons are not attached to the metal ion but are contained within a cavity of liquid ammonia by the electrostatic energy of the oriented ammonia molecules surrounding the cavity.²⁵ These excess electrons can be

considered as a negative charge in the cavity surrounded by ammonia molecules, as suggested by Kraus in 1908.²⁶ He noted that "*The negative ion constitutes a new species of anion. It consists of a negative charge, an electron, surrounded by an envelope of solvent molecules.*" This solution behaves like an ideal electrolytic where the solvated electron is localized in a cavity in the liquid ammonia^{27,28}, and are displayed in Figure 1.1(a). When the concentration of the metal is between approximately 10^{-3} - 10^{-2} MPM (mole percent metal)²⁹, the equivalent conductance decreases, with the onset of ion-pair association (M⁺, e⁻) in this solution. This solution remains electrolytic in nature at these low concentrations and has an intense blue colour. Extensive studies have provided insights into the evolution of the nature of the microscopic structure of electron solvation, giving evidence for ion pair in a cavity.^{6,30-33}

For metal concentrations exceeding 1 MPM, magnetic measurement of metal-ammonia solutions provide evidence that electron spin-pairing occurs - (e⁻ M⁺ e⁻) or (e⁻ M⁺ e⁻ M⁺), the latter being referred to as bipolarons.^{34,35} Hoffmann *et al.*²⁷ reported the various microscopic entities and magnetic properties which can co-exist in the paramagnetic to diamagnetic transition region. At intermediate metal concentrations between 1 and 10 MPM, the transition to a total metallic state (TMS) takes place, where the electrical conductivity increases as the concentration of metal is increased. At these concentrations, conversion from a localized state of the electron to a delocalized one occurs, and a remarkable change in the solution's colour from deep blue to bronze results, as shown in Figure 1.2. Numerous studies give evidence for a non-metallic solution transition into a metallic state in this concentration range.^{21,36-38} One of the first studies to show the direct determination of a composition induced non-metallic to metallic transition was recorded by Cady in 1897.³⁹ He had observed that in the case of a sodium-ammonia solution "…*it will be noticed that the molecular conductivity rises with concentration, contrary to that of electrolytes ….the solution then seems to conduct like a metal <i>not as an electrolyte.*" Moreover, he also reported an absence of polarization effects in this

solution, suggesting that this solution may conduct in a metallic fashion. Cooling at an intermediate concentration of about 4 MPM leads to physical separation of this solution into two distinct liquid layers; a dark blue non-metallic phase and bright bronze/gold phase which floats above the dilute electrolyte phase with a remarkable low density, where the reducing electrons are clearly delocalized.^{5,36,40,41} Liquid-liquid phase separation is easily observed due to the metallic bronze colour and the deep blue colour of the separated components.

Near to saturation at approximately 20-21 MPM (see bottom right hand side of Figure 1.2), the appearance of solutions become metallic due to an order of magnitude increase in the electrical conductivity. The solution now behaves as a liquid metal and has a bronze/gold colour.²⁷ Moreover, at this concentration, the density of the metal/ammonia solution is considerably lower than that of either of its components.⁴²⁻⁴⁴ In particular, the electrical conductivity of lithium-ammonia solutions (where the ratio Li: NH₃ is 1:4) has an electrical conductivity about three times that of sodium-ammonia. Furthermore, the conductivity of lithium-ammonia solutions exceeds the value of liquid mercury.⁴⁵ Note that the electrical conductance of mercury is of the order of $10^4 \Omega^{-1} \text{ cm}^{-1}$. In addition, mercury is an example of a superconductor which shows nearly ideal superconducting behaviour.^{46,47}

In a saturated metal/ammonia solution, the metal atom is surrounded by a sufficiently high number of ammonia molecules. For instance, lithium-ammonia complexes were found to be approximately tetrahedrally solvated by four ammonia molecules in the first solvation shell, which has also been thus found to be the case in the gas phase⁴⁸⁻⁵⁰, with the nearest neighbour Li-N distance occurring at around 2Å. Much interest has focused on the microscopic structure of these solutions, particularly the nature of saturated liquid lithium-ammonia, giving insights into the transition to a metallic state and show that the solvated lithium ions in ammonia display a tetrahedron T_d symmetry and the electrons are apparently fully delocalized in these solutions.⁵¹⁻⁵³



Figure 1.1 Schematic representation of the metal-ammonia solutions at (a) at a dilute metal concentration and (b) at high concentration.



Figure 1.2 Schematic representation of the colour change of lithium-ammonia solutions with concentration. This image was taken from ref.²⁷

The solvated electron in ammonia has distinct spectroscopic properties and can be detected through its intense optical absorption in a highly dilute solution. The absorption spectrum of this electron is located in the near infrared (NIR) region.

The optical absorption spectrum of the solvated electron in such dilute solution shows a single absorption band with a maximum ranging from 0.8-0.88 eV. This band is a very intense, broad and asymmetric absorption line, which peaks in intensity at around 0.85 eV, as shown in Figure 1.3. It can be seen in this figure that the optical absorption band has a tail extending into the near infrared or visible ranges. The shape and location of the electronic transition for alkali, alkaline earth, and rare earth metals such as europium and ytterbium in ammonia solutions, have been found to have similar absorption spectra as the concentration is increased.⁵ A number of theoretical methods have been used to characterize the transition of the solvated electron in ammonia and its absorption spectrum.⁵⁴⁻⁵⁶ However, the description of the solvated electron in a cavity and the behaviour of solvated electrons in the liquid ammonia environment is far from complete. The first and most basic model which describes the solvated electron within a liquid ammonia cavity was reported by Ogg.^{57,58} He proposed "…..two electrons trapped in the same cavity are appreciably stable with respect to either two electrons trapped in separate cavities or one trapped and one conducting electron." He assumed the electron is surrounded by a spherical cavity of radius *R* and this electron may be found in its cavity either alone or paired. The ammonia molecules generate an effective potential well with an infinitely high repulsive barrier to the electron. However, Ogg's model does not represent the relatively weakly bound states of the solvated electron.

The improved cavity model which has given a reasonable explanation of the electronic transition of the electron solvation in metal-ammonia solution was provided by Jortner.^{25,55} He has explained the optical absorption spectrum as being the result of the 1s-2p transition state of the solvated electron in a cavity of radius 3-3.2 Å. This theoretical prediction showed an excellent agreement with experiment data.⁵⁹ Therefore, the 1s-2p transition is assumed to be responsible for the intense blue colour characteristic of the dilute metal-ammonia solutions. Consequently, the intense blue colour solution is attributed to a broad single optical absorption band in the near IR spectrum. Note that the potential well formed by the interaction of the electron with the medium was taken as a constant potential within it and a varying potential outside the cavity (see Figure 1.4). However, Jortner's model does not accurately describe the

long tail of the absorption band, which may arise from transitions to higher electronic states. Attempts to improve this model have been given by Catterall and Mott.⁶⁰ They proposed that the solvated electron resides in a natural hole in the liquid ammonia formed by molecular dipoles made up of a few ammonia molecules from the surrounding solvation shell.⁶¹ In other words, Catterall and Moot suggested that the large volume of the cavity is formed by a 'loosening' of the ammonia structure around a natural hole in liquid ammonia.

Hoffmann *et al.*²⁷ have recently studied the structures and charge distributions of a number of species which might be present in a Li/ammonia solution. This theoretical study focused on a detailed microscopic model of the interactions between species in these solutions and their electronic excitation. DFT and TD-DFT have been performed with a variety of high quality basis sets. Their calculations on models of electron solvation clusters comprised of a number of negatively charge ammonia molecules, illustrate an electron trapped in a cavity of the solvent. The unpaired electron is found to be located near to the cavity surface and not in the centre of the cavity, hence weakening hydrogen bonding. These results have been confirmed by Chandra and Marx⁶² and Jortner's model.²⁵



Figure 1.3 Optical absorption spectrum due to the solvated electron in a lithium-ammonia solution. Image reproduced from ref.²⁷



Figure 1.4 Wavefunctions and energy levels for electron solvation. The trapping potential is V(r). This image is taken from ref.²⁷

1.2 Spectroscopic properties of the complex as a function of size

Complexes, consisting of weakly bound of atoms or molecules bound by non-covalent interactions, constitute a bridge from the gas phase to the condensed phase.⁶³⁻⁶⁸ For example, Farrar and co-workers⁶⁹⁻⁷¹ have studied $M(Sol)_n^+$ complexes, where M is an alkaline earth metal atom and Sol is a solvent such as ammonia, water or methanol. Electronic photodissociation spectroscopy has been applied as a function of complex size. Large red shifts of the excitation frequency were shown as the first solvation shell filled, corresponding to a considerable change in electronic structure. Results from *ab initio* calculations have been found to be in agreement with the experimental findings. The valance electron on the metal ion experiences characteristic changes in size and shape as the number of solvent molecules are added, and when sufficiently large can reside in the solvent shell.

Studies on size-selected complexes provide insight into the origin of solvation effects. Therefore, size effects of complexes have been of considerable interest in a number of research groups.⁷²⁻⁷⁷ There are basically two distinct domains of size-dependent effect:⁷² the first type is specific size effects which are related to the magic numbers (referring to the observation of anomalously intense peaks) corresponding to shell closure effects for small complexes and irregularities in size dependencies. The second type of size effect are smooth complex size effects which take place for large complexes and can be extrapolated to the bulk values. In this size domain, Jortner introduced a model to explain the quantitative description for the "transition" of a property in region of the smooth various with complex size. An example is the ionization energy of a complex, such as an alkali metal-ammonia complex, which for a complex of radius R_c is given by

$$I(R_c) = I(\infty) + C(R_c) \tag{1.1}$$

Here $I(R_c)$ is the ionization energy of the specific complex and $I(\infty)$ is the ionization energy of the bulk. An underlying assumption here is that complexes are spherical. The correction term, $C(R_c)$ consists of the contribution from the electrostatic interaction of the charge with the excluded region in the range from R_c to(∞). Equation (1.1) is applicable when continuum dielectric theory is applied, and the conductivity of the solvent stays constant. In this case the ionization energy of weakly bound complexes, $C(R_c)$ is given by;

$$C(R_c) = \frac{e^2}{2R_c} \left(1 - \frac{1}{\epsilon}\right) \tag{1.2}$$

Here ϵ is the dielectric constant of the bulk. The value of ϵ has been calculated by Makov and Nitzan for both interior and surface of a spherical complex and compared with the known dielectric constant of liquid or solid ammonia.⁷⁸ As a consequence, plotting the ionization energy from the measured complex sizes as a function of R_c^{-1} generates a linear relationship with the slope $C(R_c)$ and an intercept, $I(\infty)$.

Jortner's model has been applied to the ionization potentials (IPs) of Na(NH₃)_n complexes by Steinbach and Buck.⁶⁸ Instead of plotting the IP against the complex radius, it was instead plotted as a function of $(n+1)^{-1/3}$. The rationale here is that, for spherical clusters, $(n+1)^{-1/3}$ is effectively the inverse of the complex radius. Data were reported spanning the size range from n = 10 to n = 1500 in order to predict the behaviour for large n. A linear trend in IPs for $n \ge 18$, and further steps at n = 24, 35 and 59 were observed. The steps in this linear region were concluded as strong evidence for a substructure of the ammonia molecules around electron solvation or metal ion. A further insight into the stepwise behaviour at n = 24, 35 and 59 was explained by the partial closed-shell with ammonia molecules. The localization of the solvated metal valence electron in ammonia molecules was determined. For $1 \le n \le 9$, where the IPs decrease linearly, they assumed a one-centre model with the valence electron trapped around the sodium which is surrounded by a shell of solvating NH₃ molecules. A two centre model with the sodium ion and a separated electron by the solvating NH₃ molecules and localization of the electron placed at the surface of the complex for $10 \le n \le 17$. For larger complexes in which $n \ge 18$, a two-centre interior model assumed with complete solvation of the electron by the NH₃ molecules inside the complex in a cavity structure. They concluded that the electronic structure of the Na(NH₃)_n complexes does not change significantly at $n \ge 18$.

1.3 Previous studies of alkali metal-ammonia complexes

Much of the gas-phase exploration of alkali metal-ammonia complexes, $M(NH_3)_n$, has been through photoionization investigations. Early studies were reported by Hertel and coworkers.^{79,80} In the case of ammonia molecules, they explored the photoionization threshold of Na(NH₃)_n with increasing complex size. The observed ionization threshold energies decrease rapidly as the number of ammonia molecules increases from n = 0 to n = 4. However, for $n \ge 5$, it becomes constant and the ionization energy (IE) value is nearly equal to the IE of bulk ammonia. A similar trend has been observed in photoionization thresholds of Li(NH₃)_n complexes, which were measured for $n \le 28$ by Takasu *et al.*^{81,82} Moreover, the same behaviour was also observed when Li and Na were replaced by Cs.⁸³

Salter and Ellis⁴⁹ used photoionization mass spectrometry to record the photoionization efficiency (PIE) curves for small Li(NH₃)_n complexes (n = 1-5). Alongside this *ab initio*

calculations were carried out on both the neutral and cationic complexes to determine geometrical structural information, and thus to interpret any structural changes occurring on ionization. LiNH₃ and Li(NH₃)₄ displayed a sharp rise in the photoionization efficiency curve in the threshold region, indicating that the neutral and cation complexes possess similar structures. Li(NH₃)₂ was very different and showed a more slowly rising trend in its PIE, suggesting large differences in the equilibrium structures between the neutral and cationic complexes. A gradual decrease in the photoionization efficiency profiles was shown for n = 3 and 5, suggesting small structural change on ionization for the neutral and cationic geometries. Similar work has been described by Nitsch and co-workes⁸⁴ and Hashimoto and Morokuma^{85,86} for Na(NH₃)_n complexes.

Optical spectroscopy has also been applied to alkali-ammonia complexes. The first electronically excited state of Na(NH₃)_n complexes for $n \le 22$ was investigated by Schulz and co-workers using photodepletion spectroscopy.⁸⁷ A change in the excitation energy was observed as a function of complex size. A sharp decrease of the excitation energy from 16950 cm⁻¹ for atomic Na down to 6000 cm⁻¹ for the Na(NH₃)₄ complex was seen. For $n \ge 5$, the absorption energy showed a slight increase towards the bulk value at 6300 cm⁻¹, which corresponds to the absorption band of the solvated electron in liquid ammonia. It was suggested that there is a change in the electronic structure of the complex at n = 4, i.e. the electron becomes partly solvated for $n \ge 5$. This indicates a strong non-covalent interactions, since the nitrogen atom attached to sodium metal undergoes significant structural rearrangement on excitation. Moreover, a similar spectroscopic study was also employed for Na(NH₃)_n by Hertel and co-workers.⁷⁹

The first vibrational spectra for Na(NH₃)_n complexes was obtained by Ellis and coworkers.⁸⁸ Spectra were recorded in the N-H stretching region for n = 3-8 and *ab initio* calculations were also carried out to support the spectroscopic work. The IR photodepletion spectra for n = 3-6 were found to be similar and showed two distinct bands. The similarity between these spectra suggested the ammonia molecules are in similar environments, which was presented as evidence of a single solvation shell with six ammonia molecules. For larger complexes where n = 7 and 8, much broader bands were reported however. The appearance of higher vibrational frequency N-H stretching bands for n = 7 and 8 was concluded to be the result of closure of the first solvation shell with six ammonia molecules. The IR spectra are in accord with the theoretical calculations. The theoretical calculations predicted that the lowest energy structure possesses all six ammonia molecules in a single solvation shell. However, for the n = 7 and 8 complexes, two solvation shell have been shown, i.e. these clusters consist of six ammonia molecules in the first solvation shell and additional ammonia molecules in the second shell.

Similar photodepletion measurements and theoretical calculations were also performed for Li(NH₃)_n complexes by Ellis and co-workers.⁴⁸ The IR photodepletion spectra concur with theoretical calculations and provided strong evidence that completion of the first solvation shell occurs at n = 4. This is in agreement with previous studies by Mierzwicki and Lataja.^{27,89,90}

1.4 Previous studies of alkaline earth metal-solvent complexes

The few spectroscopic studies of alkaline earth metal-solvent complexes have focused almost entirely on singly charged alkaline earth cations. Such ions are isoelectronic with the neutral alkali atoms. Moreover, working with charged complexes makes spectroscopy easier through the use of mass selection prior to spectroscopic excitation.

Most of the work on these complexes have employed electronic photodissociation spectroscopy because the valence electron on the metal gives rise to strongly allowed electronic transitions in the visible and ultraviolet regions. For example, Fuke and co-workers⁹¹⁻⁹⁴, Duncan and co-workers⁹⁵⁻⁹⁷ and Farrar and co-workers⁹⁸⁻¹⁰² have applied mass-selected photodissociation spectroscopy of singly charged alkaline earth metal cations complexed with a variety of solvents including water, methanol and ammonia. Single photon and multiphoton absorption have been performed to record spectra as a function of the number of solvent molecules for these types of clusters. The change of the electronic states with increasing number of solvent molecules has been determined. In the case of ammonia, the electronic spectra of $M(NH_3)_n^+$ complexes showed a large red shift of the excitation frequency with increasing complex size. The red shift was explained as being due to the considerable change in the electronic structure. The magnitude of excitation frequency shift caused by the strength of the non-covalent interactions that present in complexes. In other words, the large red shift reflects a non-covalent contribution to the M⁺ – N binding, accompanying with weakening of the N-H bonds.

In addition to spectroscopic studies, *ab initio* calculations on these complexes have been performed to help with the interpretation of the experimental results.¹⁰³⁻¹⁰⁸ For example, Bauschlicher and co-workers¹⁰⁹⁻¹¹² reported extensive theoretical calculations on singly charged alkaline earth metal-solvent systems with small numbers of solvent molecules. These studies showed the spectroscopic properties predicted are in an excellent agreement with those measured.

A limited number of studies on the neutral alkaline earth metal-solvent complexes have been reported. The ionization energies (IEs) of Mg(H₂O)_n, $(n \ge 9)$ and Ca(H₂O)_n $(n \ge 8)$ were measured by Fuke and co-workers using photoionization threshold measurements.¹¹³ The IEs were found to decrease with increasing complex size. This study showed that the formation of a structure where the Mg atom sits on the surface of a water cluster is a marked preference for Mg(H₂O)_n complexes, while interior structure (Ca surrounded by water molecules) is preferred for Ca(H₂O)_n complexes. Cabanillas-Vidosa *et al.* have reported an experimental and theoretical study of the photoionization of Ba(H₂O)_n complexes (n = 1-4).¹¹⁴ This study showed good agreement between the experimental results and theoretical calculations. Similar to the Ca(H₂O)_n complexes, the preferential structure of Ba(H₂O)_n complexes is an interior structure, where the Ba metal is embedded within a shell of H₂O molecules, rather than sitting on the surface of (H₂O)_n clusters.

1.5 Motivation and overview of thesis

Besides those mentioned above, ammonia clusters containing neutral alkali atoms or singly charged alkaline earth metal ions have been studied in the gas phase. In these complexes, the valence electron of the metal is expected to be transferred to the solvent in the limit of large *n*. In neutral alkaline earth metal-ammonia complexes in the gas phase, the photoionization mass spectroscopy and infrared spectroscopy are currently only poorly understood.

The main aim of the work presented in this thesis was to study uncharged alkaline earth metal-ammonia complexes in the gas phase. In contrast to analogous clusters containing alkali metals and positively charged alkaline earth metal, the neutral complexes have received little research attention. Here the first infrared spectra of these complexes are reported. To do this, mass-selective IR photodepletion spectroscopy has been applied.

The structure of this thesis is organized as follows. After a description of the experimental set up in Chapter 2, Chapter 3 describes a theoretical study of the neutral alkaline earth metal-ammonia complexes to investigate their lowest energy structures, and to build a theoretical picture to help understand the spectroscopic signatures of the complexes. The core tools and concepts of theoretical work are introduced in this chapter. Photoionization mass spectra of $Ca(NH_3)_n$ and $Sr(NH_3)_n$ complexes are reported in Chapter 4, allowing their first

ionization energies to be determined. In Chapter 5, the first mass-selected infrared photodepletion spectra of $Sr(NH_3)_n$ complexes are presented for n = 6-14. IR spectra of neutral $Ba(NH_3)_n$ complexes are reported in Chapter 6 while IR spectra of $Ca(NH_3)_n$ are presented in Chapter 7. In Chapter 8, the first *ab initio* calculations of a lanthanide-ammonia system, $Eu(NH_3)_n$, are reported. In the same chapter high-level calculations are described on $Mg(NH_3)_n^+$ complexes. Finally, this thesis is concluded with a summary of the key experimental and theoretical results and some recommendations for future scientific work.

References

- (1) Thomas, S. J. M.; Edwards, P. P.; Kuznetsov, V. L. *Chemphyschem* **2008**, *9*, 59.
- (2) Weyl, W. Ann. Phys. 1864, 199, 350.
- (3) Ogg Jr, R. A. *Phys. Rev.* **1946**, *69*, 668.
- (4) Gibson, G.; Argo, W. J. Am. Chem. Soc. 1918, 40, 1327.
- (5) Thompson, J. C. *Electrons in liquid ammonia*; Oxford University Press, 1976.
- (6) Edwards, P. P. Adv. Inorg. Chem. **1982**, 25, 135.
- (7) Golden, S.; Tuttle, T. R. J. Chem. Soc., Faraday Trans. 2 1982, 78, 1581.
- (8) Edwards, P. P. Phys. Chem. Liquidsl 1981, 10, 189.
- (9) Suezer, S.; Andrews, L. J. Am. Chem. Soc. 1987, 109, 300.
- (10) Maeda, K.; Lodge, M. T.; Harmer, J.; Freed, J. H.; Edwards, P. P. J. Am. Chem. Soc. **2012**, *134*, 9209.
- (11) Lagowski, J. Synth. React. Inorg., Metal-Org. Nano-Metal Chem. 2007, 37, 115.
- (12) Edwards, P. P.; Rao, C.; Kumar, N.; Alexandrov, A. S. *ChemPhysChem* 2006, 7, 2015.
- (13) Lindner, J.; Unterreiner, A. N.; Vöhringer, P. ChemPhysChem 2006, 7, 363.
- (14) Edwards, P. P. *Nature* **1988**, *331*, 564.

- (15) Tuttle Jr, T. R.; Golden, S. J. Phys. Chem. 1991, 95, 5725.
- (16) Becker, E.; Lindquist, R.; Alder, B. J. Chem. Phys. 1956, 25, 971.
- (17) Chuev, G. N.; Quémerais, P. J. Chem. Phys. 2008, 128, 144503.
- (18) Orabi, E. A.; Lamoureux, G. J. Chem. Theory Comput. 2013, 9, 2324.
- (19) Lee, I. R.; Lee, W.; Zewail, A. H. ChemPhysChem 2008, 9, 83.
- (20) Edwards, P. P. Journal of superconductivity 2000, 13, 933.
- (21) Edwards, P. P.; Sienko, M. Acc. Chem. Res. 1982, 15, 87.
- (22) Seel, A. G.; Swan, H.; Bowron, D. T.; Wasse, J. C.; Weller, T.; Edwards, P. P.; Howard, C. A.; Skipper, N. T. *Angew. Chem.* 2017.
- He, L.-L.; Zhang, S.-Y.; Sun, T.-T.; Zhao, C.-L.; Zhang, C.; Yang, Z.-Z.; Zhao, D.-X.
 Molecular Simulation 2017, 1.
- (24) Cottrell, F. J. Phys. Chem. 1914, 18, 85.
- (25) Jortner, J. J. Chem. Phys. 1959, 30, 839.
- (26) Kraus, C. A. J. Am. Chem. Soc. 1908, 30, 1323.
- (27) Zurek, E.; Edwards, P. P.; Hoffmann, R. Angew. Chem. Int. Ed. 2009, 48, 8198.
- (28) Vöhringer, P. Annual review of physical chemistry **2015**, 66, 97.
- (29) MPM= [moles of metal/(moles of metal+moles of solvent)]×100. For calibration purposes: 1 MPM ~ 2 x 10²⁰ electron cm⁻³.
- (30) Deng, Z.; Martyna, G. J.; Klein, M. L. Phys. Rev. Lett. 1993, 71, 267.
- (31) Deng, Z.; Martyna, G. J.; Klein, M. L. J. Chem. Phys. 1994, 100, 7590.
- (32) Deng, Z.; Klein, M. L.; Martyna, G. J. J. Chem. Soc., Faraday Trans. 1994, 90, 2009.
- (33) Carrera, A. l.; Marceca, E. J. Phys. Chem. A 2015, 119, 4207.
- (34) Lelieur, J.; Damay, P.; Lepoutre, G. J. Phys. Chem. 1975, 79, 2879.
- (35) Mott, N. J. Phys. Chem. 1975, 79, 2915.
- (36) Kraus, C. A. J. Am. Chem. Soc. 1907, 29, 1557.

- (37) Chieux, P.; Sienko, M. J. Chem. Phys. 1970, 53, 566.
- (38) Hartweg, S.; West, A. H.; Yoder, B. L.; Signorell, R. Angew. Chem. Int. Ed. 2016, 55, 12347.
- (39) Cady, H. P. J. Phys. Chem. 1897, 1, 707.
- (40) Pitzer, K. S. J. Am. Chem. Soc. 1958, 80, 5046.
- (41) Edwards, P. P.; Sienko, M. J. Am. Chem. Soc. 1981, 103, 2967.
- (42) Kraus, C. A.; Lucasse, W. W. J. Am. Chem. Soc. 1921, 43, 2529.
- (43) Kraus, C. A.; Carney, E. S.; Johnson, W. C. J. Am. Chem. Soc. 1927, 49, 2206.
- (44) Johnson, W. C.; Meyer, A. W. J. Am. Chem. Soc. 1932, 54, 3621.
- (45) Morgan, J.; Schroeder, R.; Thompson, J. J. Chem. Phys. 1965, 43, 4494.
- (46) Schirber, J.; Swenson, C. Phys. Rev. 1961, 123, 1115.
- (47) Finnemore, D.; Mapother, D.; Shaw, R. Phys. Rev. 1960, 118, 127.
- (48) Salter, T. E.; Mikhailov, V. A.; Evans, C. J.; Ellis, A. M. J. Chem. Phys. 2006, 125, 034302.
- (49) Salter, T. E.; Ellis, A. M. J. Phys. Chem. A 2007, 111, 4922.
- (50) Sommerfeld, T.; Dreux, K. M. J. Chem. Phys. 2012, 137, 244302.
- (51) Thompson, H.; Wasse, J. C.; Skipper, N. T.; Hayama, S.; Bowron, D. T.; Soper, A. K.
 J. Am. Chem. Soc. 2003, *125*, 2572.
- (52) Thompson, H.; Wasse, J. C.; Skipper, N. T.; Howard, C. A.; Bowron, D. T.; Soper, A. K. *J. Phys.: Condens. Matter* 2004, *16*, 5639.
- (53) Garroway, A.; Cotts, R. *Physical Review A* **1973**, *7*, 635.
- (54) Blandamer, M. J.; Fox, M. F. Chem. Rev. 1970, 70, 59.
- (55) Jortner, J. J. Chem. Phys. 1957, 27, 823.
- (56) Douthit, R. C.; Dye, J. L. J. Am. Chem. Soc. 1960, 82, 4472.
- (57) Ogg Jr, R. A. J. Chem. Phys. **1945**, 13, 533.

- (58) Ogg Jr, R. A. J. Chem. Phys. 1946, 14, 114.
- (59) Lepoutre, G.; Sienko, M. J. Mémoires et travaux. Université catholique. Lille 1964.
- (60) Catterall, R.; Mott, N. Adv. Phys. **1969**, 18, 665.
- (61) Bjerrum, N. Science **1952**, 115, 385.
- (62) Chandra, A.; Marx, D. Angew. Chem. Int. Ed. 2007, 46, 3676.
- (63) Duncan, M. A. Int. J. Mass spectrom. 2000, 200, 545.
- (64) Duncan, M. A. Int. Rev. Phys. Chem. 2003, 22, 407.
- (65) Walker, N. R.; Walters, R. S.; Duncan, M. A. New J. Chem. 2005, 29, 1495.
- (66) Buck, U.; Steinbach, C. J. Phys. Chem. A 1998, 102, 7333.
- (67) Steinbach, C.; Buck, U. *PCCP* **2005**, *7*, 986.
- (68) Steinbach, C.; Buck, U. J. Chem. Phys. 2005, 122, 134301.
- (69) Farrar, J. M. Int. Rev. Phys. Chem. 2003, 22, 593.
- (70) Lee, J. I.; Qian, J.; Sperry, D. C.; Midey, A. J.; Donnelly, S. G.; Farrar, J. M. J. Phys. Chem. A 2002, 106, 9993.
- (71) Lee, J. I.; Sperry, D. C.; Farrar, J. M. J. Chem. Phys. 2004, 121, 8375.
- (72) Jortner, J. Z. Phys. D At., Mol. Clusters 1992, 24, 247.
- (73) Jortner, J. Z. Phys. Chem. 1994, 184, 283.
- (74) Jortner, J. J. Chim. Phys. Phys. Chim. Biol. 1995, 92, 205.
- (75) Alivisatos, A. P. *Science* **1996**, *271*, 933.
- (76) Rips, I.; Jortner, J. J. Chem. Phys. 1992, 97, 536.
- (77) Roduner, E. *Nanoscopic materials: size-dependent phenomena*; Royal Society of Chemistry, 2006.
- (78) Makov, G.; Nitzan, A. J. Phys. Chem. 1994, 98, 3459.
- (79) Hertel, I.; Hüglin, C.; Nitsch, C.; Schulz, C. Phys. Rev. Lett. 1991, 67, 1767.
- (80) Schulz, C.; Gerber, A.; Nitsch, C.; Hertel, I. Z. Phys. D At., Mol. Clusters 1991, 20, 65.

- (81) Takasu, R.; Misaizu, F.; Hashimoto, K.; Fuke, K. J. Phys. Chem. A 1997, 101, 3078.
- (82) Takasu, R.; Hashimoto, K.; Fuke, K. Chem. Phys. Lett. 1996, 258, 94.
- (83) Misaizu, F.; Tsukamoto, K.; Sanekata, M.; Fuke, K. Chem. Phys. Lett. 1992, 188, 241.
- (84) Nitsch, C.; Schulz, C.; Gerber, A.; Zimmermann-Edling, W.; Hertel, I. Z. Phys. D At., Mol. Clusters 1992, 22, 651.
- (85) Hashimoto, K.; He, S.; Morokuma, K. Chem. Phys. Lett. 1993, 206, 297.
- (86) Hashimoto, K.; Morokuma, K. J. Am. Chem. Soc. 1995, 117, 4151.
- (87) Brockhaus, P.; Hertel, I. V.; Schulz, C. P. J. Chem. Phys. 1999, 110, 393.
- (88) Salter, T. E.; Mikhailov, V.; Ellis, A. M. J. Phys. Chem. A 2007, 111, 8344.
- (89) Mierzwicki, K.; Latajka, Z. Chem. Phys. Lett. 2000, 325, 465.
- (90) Mierzwicki, K.; Latajka, Z. Chem. Phys. 2001, 265, 301.
- (91) Sanekata, M.; Misaizu, F.; Fuke, K. J. Chem. Phys. 1996, 104, 9768.
- (92) Misaizu, F.; Sanekata, M.; Fuke, K.; Iwata, S. J. Chem. Phys. 1994, 100, 1161.
- (93) Yoshida, S.; Daigoku, K.; Okai, N.; Takahata, A.; Sabu, A.; Hashimoto, K.; Fuke, K.
 J. Chem. Phys. 2002, *117*, 8657.
- (94) Yoshida, S.; Okai, N.; Fuke, K. Chem. Phys. Lett. 2001, 347, 93.
- (95) Yeh, C.; Pilgrim, J.; Willey, K.; Robbins, D.; Duncan, M. Int. Rev. Phys. Chem. 1994, 13, 231.
- (96) France, M.; Pullins, S.; Duncan, M. Chem. Phys. 1998, 239, 447.
- (97) Walker, N.; Walters, R.; Tsai, M.-K.; Jordan, K. D.; Duncan, M. J. Phys. Chem. A 2005, 109, 7057.
- (98) Shen, M.; Farrar, J. J. Phys. Chem. 1989, 93, 4389.
- (99) Shen, M.; Farrar, J. J. Chem. Phys. 1991, 94, 3322.
- (100) Donnelly, S.; Farrar, J. J. Chem. Phys. 1993, 98, 5450.

- (101) Sperry, D. C.; Midey, A. J.; Lee, J. I.; Qian, J.; Farrar, J. M. J. Chem. Phys. 1999, 111, 8469.
- (102) Qian, J.; Midey, A.; Donnelly, S.; Lee, J.; Farrar, J. Chem. Phys. Lett. 1995, 244, 414.
- (103) Watanabe, H.; Iwata, S. J. Phys. Chem. A 1997, 101, 487.
- (104) Watanabe, H.; Iwata, S.; Hashimoto, K.; Misaizu, F.; Fuke, K. J. Am. Chem. Soc. 1995, 117, 755.
- (105) Martyna, G. J.; Klein, M. L. J. Phys. Chem. 1991, 95, 515.
- (106) Lu, W.; Yang, S. J. Phys. Chem. A 1998, 102, 825.
- (107) Reinhard, B. M.; Niedner-Schatteburg, G. J. Chem. Phys. 2003, 118, 3571.
- (108) Rodgers, M.; Armentrout, P. Chem. Rev. 2016, 116, 5642.
- (109) Sodupe, M.; Bauschlicher, C. W. Chem. Phys. Lett. 1992, 195, 494.
- (110) Bauschlicher Jr, C. W.; Sodupe, M.; Partridge, H. J. Chem. Phys. 1992, 96, 4453.
- (111) Sodupe, M.; Bauschlicher Jr, C. W.; Partridge, H. J. Chem. Phys. 1991, 95, 9422.
- (112) Sodupe, M.; Bauschlicher, C. W. Chem. Phys. Lett. 1993, 212, 624.
- (113) Okai, N.; Ishikawa, H.; Fuke, K. Chem. Phys. Lett. 2005, 415, 155.
- (114) Cabanillas-Vidosa, I.; Rossa, M.; Pino, G. A.; Ferrero, J. C.; Cobos, C. J. PCCP 2012, 14, 4276.
Chapter 2

Experimental methods

This chapter, which describes the experimental procedure and equipment used in this thesis, is divided into sections covering the following topics: a description of the overall apparatus and an outline of the operating procedure, followed by specifics on the vacuum systems, supersonic expansion, the laser systems, and the time-of-flight (TOF) mass spectrometer.

2.1 General Description of the experimental set up

Figure 2.1 presents a simplified view of the experimental layout. The apparatus features two vacuum chambers: a primary chamber used for complex production and supersonic jet expansion, and a secondary chamber used for optical excitation and mass spectrometric measurement.

The metal-solvent complexes of interest are produced by the collision of gas (solvent) molecules with metal atoms formed by pulsed laser ablation by a Nd:YAG laser. The mixture is then expanded into vacuum to form a supersonic jet, where the metal-solvent complexes are cooled. The expansion is then skimmed to form a collimated molecular beam that enters the second vacuum chamber.

The molecular beam enters the ionization source area of a TOF mass spectrometer, where complexes are ionized by a pulsed dye laser operating in the ultraviolet (UV). A second laser beam from an optical parametric oscillator/amplifier (OPO/OPA) is available for carrying out infrared (IR) spectroscopy experiments. The beams from the two lasers pass into the second vacuum chamber from opposite directions and perpendicular to the molecular beam.

The ions generated are then accelerated into the TOF mass spectrometer and are

detected by a micro-channel plate detector system. The delay between the pulsed gas valve and the firing of the pulsed lasers is synchronized using digital delay generators to optimize the observed ion signals. The TOF MS signal is fed into a digital storage oscilloscope and transferred to a personal computer through an IEEE-488.2 interface.



Figure 2.1 Schematic diagram of the experimental setup.

2.2 Vacuum Systems

Two vacuum chambers comprise the heart of the experimental apparatus. Both chambers were constructed from stainless steel and were custom-built in the departmental mechanical workshop. Since full details of both vacuum chamber systems are provided elsewhere¹, only a brief account is given here.

The first vacuum chamber has nine access ports in a variety of sizes (seven ports on the side and one each at the top), which provide flexibility to the system. The chamber is pumped by a 3,000 l/s diffusion pump (Leybold DIP 3000 S). A gate valve, located between the chamber and the diffusion pump, isolates the pump so it can remain on when the vacuum chamber is vented to atmospheric pressure. To minimize oil vapour from reaching the chamber, a water-cooled baffle is provided above the diffusion pump. The diffusion pump is backed by a mechanical pump comprised of a 505 m³/hour roots blower (Leybold Ruvac WA 501) and a two-stage rotary pump operating at 40 m³/hour (Leybold Trivac D 40 B). Maintaining a pressure below 10^{-4} mbar is desirable in the first vacuum chamber. The base pressure of the chamber is about 5×10^{-5} mbar when the gas valve is off and about 7×10^{-5} mbar under pulsed gas load.

The pulsed valve is coupled to a three-dimensional translation stage (Miniax, VG Scienta) that can be adjusted from outside the first vacuum chamber. This is necessary to accurately align the nozzle with respect to the fixed skimmer. This system has been designed to provide independent movement in the plane perpendicular in each (x, y, and z) direction.

The gas used in the experiment enters the first vacuum chamber via PTFE tubing, generally from a gas cylinder. The pressure of gas can be varied between 0 and 8 bar. A skimmer (Beam Dynamics, Inc.), which is used to collimate the molecular beam, has an aperture diameter of 1 mm and is located between the first and second vacuum chambers.

The second vacuum chamber comprises a custom-made, vertically mounted TOF mass spectrometer. Two CaF_2 windows, allow the IR and UV beams to cross the molecular beam in the ionization region of the TOF-MS. The windows are mounted at Brewster's angle to minimize laser beam scattering. A third window, located at the end of the chamber, allows alignment of the nozzle and the skimmer to be visibly optimized. The top of the second chamber is connected to the Wiley-McLaren TOF-MS (see section 2.5).

An 800 l/s turbomolecular pump (Leybold Trivac 1000), assisted by a 25 m³/h twostage rotary vane pump (Leybold Trivac D 25 B), is used to pump the second vacuum chamber. The base pressure in the second chamber is typically in the range of 1×10^{-8} mbar, rising to about 4×10^{-8} mbar with the pulsed gas load from the first chamber entering.

A gate valve is situated between the first and second vacuum chambers. The gate valve isolates the two chambers from each other, allowing the nozzle to be accessed for maintenance without breaking the high vacuum in the second chamber.

2.3 Supersonic Expansion

The generation of cold molecules and molecular complexes by supersonic gas expansion was an important aspect of the experiments performed in this work.^{2,3} The population of rotational and vibrational states in a molecular gas at room temperature is exacerbated when the temperature is significantly raised. Under these circumstances, multiple vibrational and rotational excited states are likely to be occupied and therefore the molecules will undergo transitions out of many different energy levels. This results in spectral congestion and broadened bands consisting of unresolved rotational and vibrational structure, thus making it difficult, if not impossible, to assign the spectra and extract useful information. By cooling the molecules in a supersonic expansion, spectra congestion can be reduced. Additionally, in the case of highly reactive molecules and complexes, the supersonic cooling may also have the effect of increasing their lifetimes.

The concept of the supersonic jet is based on the cooling of translational degrees of freedom by passing a gas sample from a relatively high-pressure region to a low-pressure region through a small nozzle orifice.⁴ Figures 2.2 illustrates how the gas molecules/atoms have different distributions of velocities. The supersonic expansion narrows the velocity distribution by transforming the random velocities in a normal Maxwell-Boltzmann distribution into directed flow. This narrowing only occurs if the nozzle orifice diameter is much larger than the mean free path of the gas. When this occurs many collisions in the nozzle region will occur in the high-density region near the nozzle. These collisions accelerate the gas and increase the directed flow through the aperture, generating a dense jet with a relatively narrow velocity distribution that is kinetically "cold".^{5,6} This narrow distribution is consistent with a low translational temperature and values below 1 K are possible.⁶

At the beginning of expansion, the jostling between gas atoms and molecules results in an exchange between the rotational and vibrational degrees of freedom and translation, leading to the cooling of rotational and vibrational degree of freedom. This happens through two-body collisions relatively early on in the expansion. Through this process, the cooling process is transferred to the internal degrees of freedom of the molecules via energy exchange with the translational degrees of freedom. The exchange of energy between the rotational and translational degrees of freedom is more efficient than the vibrational degrees of freedom because the energy gaps between vibrational levels are usually much larger than that between rotational levels. Thus it is often possible to cool the molecular rotational motion to approximately 10 K, and sometimes even lower, while the translational temperature may be in the range of approximately 1 K.⁷ The result is that the recorded spectra are simplified and peaks observed are then sharper.



Figure 2.2 Process for cooling molecules in a supersonic jet.

2.4 Laser Systems

The characteristic properties of lasers include highly monochromatic output, very high light intensities and a collimated beam profile that is ideal for spectroscopic investigation.⁸ These properties of lasers can be used to acquire new information about molecular structure. Various types of lasers were used in the experiments reported in this thesis. A common feature of them all is pulsed operation, generally at a 10 Hz repetition rate.

2.4.1 Pulsed laser ablation source

In this work laser ablation has been employed as a means of generating metal atoms in the gas phase. Figure 2.3 shows a schematic of the laser ablation assembly. Laser ablation of a solid metal target was performed by applying the second harmonic output (532 nm) of a small Nd:YAG laser (Continuum Minilite II): this laser can deliver up to 26 mJ/pulse. A lens with a focal length of 25 cm was used to focus the laser beam onto the surface of the metal target within the first vacuum chamber. When the focused laser beam strikes the solid metal target, which is placed inside a cylindrical aluminium holder, ablation occurs. The firing of the ablation laser pulse and the arrival of the pulse of gas from the pulsed nozzle (typical opening time 200 µs) were synchronized to generate supersonically-cooled solute-solvent complexes. The resulting mixture is then carried along a small channel and expanded into source reign.

The main drawback with the laser ablation technique is the formation of a hole in the metal target, which grows in depth over time because the target is stationary. As a result, the spectroscopic signals can rapidly decrease and can also become unstable. A solution is to use a rotating and translating metal target but this has not been used in the work reported in this thesis.



Figure 2.3 Schematic drawing of laser ablation apparatus for production of metalcontaining complexes and complexes.

2.4.2 Dye laser

A key property of the dye laser is its wavelength tuneability, which is based on dyes as the gain medium. The active media within the dye laser are aromatic organic molecules dissolved in a solvent and which show strong, broad transitions of their conjugated π electrons. By selection of the appropriate dye and solvent, access to tuneable wavelength light over the near-UV to the near-infrared (NIR) is possible.

The dye laser used was a Sirah Cobra-Stretch system pumped by a Nd:YAG laser (Continuum Surelite) running at either 335 or 532 nm, according to the desired output wavelength of the dye laser. The Cobra-Stretch laser was supplied with a frequency doubling unit to provide operation in the near-UV.

2.4.3 Optical parametric oscillator/ amplifier (OPO/A) theory and background

A combined optical parametric oscillator (OPO) and optical parametric amplifier (OPA) system has been used for generating tunable infrared (IR) radiation. A simple illustration of the OPO/A is shown in Figure 2.4. An OPO comprises a non-linear crystal located within an optical resonator. When a sufficiently powerful pump beam is input to the system, the pump wave of frequency ω_p (the input) can be converted into two waves of lower frequencies (the output), represented by the signal and idler waves with frequencies ω_s and ω_i , respectively, with $\omega_s \ge \omega_i$ by definition. In this parametric process, the sum of the output wave frequencies must equal the input wave frequency in order to conserve energy, i.e. $\omega_p = \omega_s + \omega_i$.

The pump laser is a Nd-YAG laser (Continum Surelite II-10), producing roughly 600 mJ per pulse at 1064 nm. A beam splitter (BS) separates the horizontally polarized incoming pump at 1064 nm into two pathways, as illustrated in Figure 2.4. The first beam is frequency doubled in a KTP (KTiOPO4) (C1) crystal to produce the green (532 nm) beam for the OPO, while the other pump beam (1064 nm) passes through a delay line. The 532 nm beam is passed into the OPO resonator which consists of a second KTP crystal (C1), and where optical parametric oscillation take place. In other words, in the OPO stage, tunable signal (higher energy) and idler (lower energy) beams are generated. The residual beam at 1064 nm then combines with the lower frequency (idler) output of the OPO in the amplifier (A) stage. By combining the idler wavelength from the OPO stage with the 1064 nm pump beam in the OPA stage, further waves are created by difference frequency mixing. For both the OPO and OPA, each of the crystals used is equal in length and counter-rotated to compensate for beam displacement. At the OPO stage, one KTP crystal is used. This stage divides the 532 nm beam into a visible signal beam (710–770 nm) and near-IR idler beam (2.1–1.35 μ m), while the OPA stage uses four KTA (KTiOAsO4) crystals to generate the tunable mid-IR radiation.

An orientation of the polarizer, which is placed behind the dichroic mirror (Dc2), is used to isolate either vertically polarized idler ('C' position, 2.1-5 μ m) or the horizontally polarized signal wave ('U' position, 1.3-2.1 μ m) from the OPA output. Because all of the spectra are recorded in the mid-infrared region in this thesis work, the polarizer is placed in the 'C' position to allow the idler wave to pass through the aperture.

In addition to the KTP and KTA crystals, which are used internally within both the OPO and OPA stages, an AgGaSe₂ crystal is available for external difference frequency combining of the signal and idler output from the OPA stage to produce tunable radiation in the range 2000–555 cm⁻¹. However, in this research the AgGaSe2 crystal was not used. To adjust the position of the crystals in both the OPO and OPA, all OPO and OPA crystals are manipulated by computer-controlled motors. Because the optimization of crystal angle depends strongly on the wavelength, the wavelength is controlled by these motors and these are in turn controlled by some proprietary software.





(C1–2: KTP crystals; BS1–2: beam splitters; M4–6: mirrors; I1–3: irises; WP1: wave plate; C3–6: KTA crystals; Dc1–2: dichroic mirrors; H: horizontal sign; V: vertical sign).

2.5 Time-of-Flight Mass Spectrometer

To analyse the composition of a molecular beam as a function of mass, a Time-of-Flight mass spectrometer (TOF-MS) was used. TOF-MS is based on the principle that ions of different masses (mass-to-charge ratio) with the same kinetic energy will travel with different velocities, thereby allowing them to separate according to the time of ion flight, which differs according to the mass-to-charge ratio of the ion. When the ions travel through a fixed length of a fieldfree drift tube (*D*) and kinetic energy (*E*) is used to insert ions into the drift region, the mass of ion (*m*) signal can be estimated using its time of flight(t_f) as follows:

$$t_f = D_{\sqrt{m/2E}} \tag{2.1}$$

A schematic view of the TOF mass spectrometer is presented in Figure 2.5 and a photograph of the electrode assembly is shown in Figure 2.6. The molecular beam enters the second (ionization) chamber region between two acceleration plates. Ions are produced by photoionization and are then accelerated towards the field-free tube region, known as the flight tube, by the difference between the potential applied at the repeller and upper electrode. Because all ions should acquire the same kinetic energy, ions with lighter mass should arrive at the detector faster than heavier ones. This ideal situation occurs only if it is assumed that all ions of the same mass-to-charge value are accelerated from the same position within the acceleration region. In practice this assumption does not hold because the ions nearest to the upper electrode will have a shorter journey and will be exposed to a smaller potential difference than those starting near the repeller. If not corrected this leads to poor mass resolution.

To solve this problem, Wiley and McLaren⁹ added a two-stage acceleration zone in place of a single acceleration region, where the acceleration zone is divided into two regions of different electric field strength. This two-stage acceleration is directed perpendicular to the direction of travel of the molecular beam. The first region is determined by voltages applied to the repeller and grid and the second acceleration region is applied by a potential which is set to a voltage slightly less than that of the repeller. The potential difference between the grid and accelerator electrodes provides the main acceleration, which is the same for all ions. Assuming the complex ions beam pass the first electric region centrally between the repeller and grid, then the ions acquire the same kinetic energy. These ions are then accelerated towards the fieldfree region by a difference of potential applied between the accelerator and grid, thereby arriving at the detector at virtually the same moment in time if the conditions are correctly chosen. By suitable choice of the voltages applied to the repeller and grid, the mass resolution of peaks can be improved by reducing kinetic energy contributions and the time spread of ions.

Ordinarily, the time of flight (t_1) and mass of a known ion (m_1) are used to determine the corresponding mass of an unknown ion (m_2) using its time of flight (t_2) , as shown in equation 2.2 (which follows from equation 2.1).

$$t_1/t_2 = \sqrt{m_1}/\sqrt{m_2}$$
 (2.2)

This equation is more accurate when there are two ions of similar mass and becomes less accurate for ions of very different masses.

At the end of the flight tube, a microchannel plate (MCP) detector is used to detect and amplify the ion signal. The MCP output is then sent to a digital storage oscilloscope (DOS) (see the next section).



Figure 2.5 Schematic drawing of the TOF mass spectrometer.



Figure 2.6 Photograph of the accelerating electrode assembly in the TOF mass spectrometer.

2.6 Experimental Control

The opening of the nozzle and the firing of the lasers must be synchronized for a successful experiment. The timing of these events is controlled by two delay generators (Stanford Research Systems DG535 and BNC 555). The data acquisition system consists of a digital oscilloscope (DSO) (LeCroy Waverunner LT332) which captures ion signals and these are then transmitted via a general-purpose interface GPIB to a personal computer (PC) for storage and manipulation. These data are controlled by a script written in-house using the National

Instruments LabView (version 13.0) software package. This software also communicates with the OPO/A and sets the start wavelength and the rate at which the wavelength is scanned.

2.6.1 Synchronization process and timing

Figure 2.7 illustrates the timing and synchronisation of our system. The driver unit for the pulsed valve (IOTA ONE) serves as the 10 Hz master clock. This is achieved via a reference TTL pulse (T₀) from which the whole experiment is triggered. This TTL pulse is sent to the first delay generator (BNC 555), which has four channels labelled A, B, C, and D. These channels are used to externally trigger the firing of the flashlamps and their respective Q-switches for the first two Nd-YAG lasers. Channels A and B of the first delay generator are used for pumping the small Nd-YAG laser (Continuum Minilite), which is used for ablation. Channel C is used to trigger the flash lamp of the UV laser, which is used the UV dye laser for photoionization, while channel D triggers the Q-switch roughly 180 μ s later. The second digital delay generator (Stanford Research Systems DG535, SRS DG535) is configured to trigger the YAG laser that pumps the OPO/A, with a shared T₀ pulse synchronising the two delay generators. The UV laser is typically fired 50 ns after the IR laser. The laser timing events are represented in Table 2.1.



Figure 2.7 Pulsed timing illustration.

Table 2.1Timing and Setting of delay generator.

Delay generator	Channel	Timing control	
SRS DG535	T _N	200 μs 250 μs	Pulsed nozzle opening duration (all other timing in this research is relative to this valve) Delay before ablation laser flashlamp triggered
	В	400 μs	Internally trigged
	С	400-800 μs	Delay before UV flashlamp triggered
	D	180 µs	Delay before UV Q-switch triggered
BNC 555	T_N	200 µs	Pulsed nozzle opening duration
	A	50 µs	Delay between the IR and UV laser pulses measured with a photodiode
	В	200 µs	Delay before IR Q-switch triggered

2.7 Infrared photodepletion spectrum of Li(NH₃)₄

Before recording new IR spectra in this study, a test experimental was performed in using Li(NH₃)₄. The IR photodepletion spectrum of this complex was previously recorded by Salter *et al.* in our laboratory¹, using a combination of a dye laser unit with Raman shifting to generate the IR radiation. Consequently, this affords an opportunity to test the OPO/A and make sure that the wavelength scanning works correctly for this study.

2.7.1 Experimental set up

Details of the experimental set up for the Li(NH₃)₄ complex has already been described in the thesis of Salter.¹ Briefly, the Li(NH₃)₄ complexes were formed in the gas phase by laser ablation of a lithium target in the presence of gaseous ammonia (BOC,> 99.93%). The resulting mixture was expanded into a vacuum chamber to form a supersonic expansion and then passed into a second vacuum chamber via a skimmer for laser interrogation. It noteworthy that we use pure ammonia rather than ammonia seeded into an inert carrier gas as the former gives much stronger spectroscopic signals. However, this improved signal comes at the expense of poorer cooling in the supersonic expansion, although we have no means of directly measuring the temperature of the gas.

2.7.2 Results

Figures 1(a) and 1(b) represent the IR depletion spectrum of $Li(NH_3)_4$ complex in the present work and in the previously studied¹, respectively. As can be seen in the figure 1(a), three partly resolved IR bands of $Li(NH_3)_4$ are seen and all three bands can be attributed to N-H stretching vibrations. The two spectra are very similar, although the S/N ratio is better in the experiment by Salter *et al*, which indicates that the satisfactory performance of the OPO/A laser in generating mid-IR radiation. It should be noted that the wavelength of the OPO/A laser was not precalibrated in this work using photoacoustic spectroscopy.



Figure 2.8 Photodepletion spectra of $Li(NH_3)_4$ in the N-H stretching region. a) recorded in this work and b) taken from ref.¹

References

- (1) Salter, T. E. University of Leicester 2007.
- (2) Krems, R.; Friedrich, B.; Stwalley, W. C. *Cold molecules: theory, experiment, applications*; CRC press, 2009.
- (3) Levy, D. H. Annual Review of Physical Chemistry 1980, 31, 197
- (4) Campargue, R. J. Chem. Phys. 1970, 52, 1795.
- (5) Miller, T. A. *Science* **1984**, *223*, 545

- (6) Hyes, J. M. Chsm. Rev. 1987, 87, 745.
- (7) Levy, D. H. Science **1981**, 214, 263.
- (8) Hollas, J. M. *Wiley* **2007**.
- (9) Wiley, W.; McLaren, I. H. Rev. Sci. Instrum. 1955, 26, 1150.

Chapter 3

Ab initio calculations

3.1 Introduction

Ab initio calculations are essential for studying the behaviour of the molecules and complexes investigated in this thesis. These calculations are used to complement the experimental studies by obtaining a more complete picture of the spectroscopic assignments and in providing information on selected species that are inaccessible from experiments. *Ab initio* calculations therefore play an important role in identifying and understanding key parameters such as equilibrium geometries, vibrational frequencies, ionization potentials, and bond dissociation energies. This chapter describes only the most common *ab initio* methods used: more detailed information on *ab initio* calculations can be found elsewhere.¹

3.2 Fundamentals of *ab initio* calculations

The main concept behind the theoretical prediction of molecular structure and other properties is to find an approximate solution to the time-independent Schrödinger wave equation

$$H\Psi = E\Psi \tag{3.1}$$

for an *N* electron system. Ψ is the electronic wavefunction and *E* is the energy of a specific state. The Hamiltonian can be written as the sum of kinetic and potential energy terms and is given as:

$$H = T_n + T_e + V_{ee} + V_{en} + V_{nn}$$
(3.2)

The first two terms (T_n and T_e) of (3.2) represent the kinetic energy operators for the nuclei and the electrons in the system. The final three terms are potential energy operators, where V_{en} represents the electron-nuclei attractive forces and V_{ee} and V_{nn} represent electron-electron and nuclear-nuclear repulsions, respectively. In general, the Hamiltonian for a molecular system comprising *N* nuclei and *n* electrons can be written as:

$$H = -\frac{\hbar}{2} \sum_{A=1}^{N} \frac{1}{M_A} \nabla^2 - \frac{\hbar^2}{2m_e} \sum_{i=1}^{n} \nabla^2 - \sum_{i=1}^{n} \sum_{A=1}^{N} \frac{Z_A e^2}{4\pi \mathcal{E}_o r_{iA}} + \sum_{i=1}^{n} \sum_{j>1}^{n} \frac{e^2}{4\pi \mathcal{E}_o r_{iA}} + \sum_{A=1}^{N} \sum_{B>A}^{N} \frac{Z_A Z_B e^2}{4\pi \mathcal{E}_o R_{AB}}$$
(3.3)

where M_A is the mass of nucleus A, \hbar is Plank's constant divided by 2π , m_e is the mass of the electron, ∇^2 is the Laplacian operator, Z_A and Z_B are the charges on nuclei A and B, e is the charge on the electron, r_{iA} is the distance between electron i and nucleus A, r_{ij} is the distance between electron i and nucleus A, r_{ij} is the distance between electron i and j, ε_0 is the permittivity of free space, and R_{AB} is the distance between nuclei A and B.

The time-independent Schrödinger equation derived from this Hamiltonian in (3.3) is too complex to solve exactly for systems with more than one electron.^{2,3} Consequently, approximations are necessary. One such approximation is the Born-Oppenheimer approximation, which assumes that nuclei move far slower than electrons because of the large mass difference. In the Born-Oppenheimer approximation, the Schrödinger equation is solved for a system with fixed nuclear coordinates. In other words, the nuclear kinetic energy term of equation (3.3) can be ignored when solving for the electronic wavefunctions and energies.⁴

Although the Born-Oppenheimer approximation provides a degree of simplification, challenges remain. In particular we have the complication of electron-electron repulsion. The most fundamental solution to the e-e problem is to employ the Hartree-Fock (HF) approximation. The essence of the HF approximation is to assume that the electrons can be assigned to molecular orbitals and the total electronic wavefunction can then be expressed as a product of those molecular orbitals. However, a simple product is insufficient because the wavefunction must also satisfy the Pauli Exclusion Principle, which requires that the overall

wavefunction is antisymmetric to exchange of any two electrons. To achieve this requirement the wavefunction is formed from a Slater determinant of *N* spin orbitals given by:

$$\psi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1^{(X_1)} & \chi_2^{(X_1)} \cdots \cdots \chi_n^{(X_1)} \\ \chi_1^{(X_2)} & \chi_2^{(X_2)} \cdots \cdots \chi_n^{(X_2)} \\ \vdots & \vdots & \vdots \\ \chi_1^{(X_n)} & \chi_2^{(X_n)} \cdots \cdots \chi_n^{(X_n)} \end{vmatrix}$$
(3.4)

where χ_i is used to indicate both the spatial and spin coordinates of the electron labelled (x*i*). Interchanging any two rows of a Slater determinant, which corresponds to interchange of two electrons, changes the sign of the determinant. Because the HF approximation employs a single determinant for the wavefunction (for a closed-shell system), it does not accurately account for the correlated motion of electrons. The neglected correlation between electrons is a major weakness of the HF method.

3.3 Density functional theory

An alternative to HF calculations for solving the Schrödinger equation is to apply density functional theory (DFT). This method is based on electron density, whereas the HF method focuses on a wavefunction approach. An important advantage of DFT is that it does provide some of the missing electron correlation inherent in the HF method. DFT yields, in principle, a good description of the interacting system of electrons through its first-order ground state density (i.e., not via its many-body wavefunction)^{5,6}, as follows:

$$\rho(\vec{r}) = N \int \cdots \cdots \int \left| \Psi\left(\vec{x}_{1}, \vec{x}_{2} \cdots \cdots \vec{\chi}_{N}\right) \right|^{2} d\vec{\chi}_{1} d\vec{\chi}_{2} \cdots \cdots d\vec{\chi}_{N}$$
(3.5)

where $\rho^{(\vec{r})}$ is the probability of finding any of the *N* electrons at position $d\vec{\chi}_N$, resulting in the calculation complexity being reduced to three coordinates rather than 3N interacting electrons.

In describing the foundation of the DFT method, Hohenberg and Kohn state that the many-electron ground state is a unique functional of $\rho^{(\vec{r})}$ because the fixed potential of the nuclei is a unique functional of $\rho^{(\vec{r})}$. If sufficient electron density in three-dimensional space is used in constructing the full electronic Hamiltonian, the result leads to a possible solution to the Schrödinger equation and therefore, any ground state property for a particular set of nuclear coordinates.⁷

Kohn and Sham⁸ introduced a practical solution to Hohenberg and Kohn theory. The key to Kohn-Sham density functional theory is describing the behaviour of the ground state electron density and electronic energy functions of the many-electron system. In practice, the sizes and shapes of molecules can be estimated. Kohn and Sham's DFT solution demonstrates that the ground state spin densities and energy E can be solved iteratively as a set of one-electron Schrödinger equations. However, the most crucial problem of Kohn and Sham's DFT is the unknown term for exchange-correlation energy. Consequently, this term must be approximated. The main types of approximations that may be used are local density approximations (LDA), the generalized gradient approximation (GGA), and hybrid functional approximations.

Although DFT is versatile and computationally efficient, the accuracy of results is affected by the choice of the exchange-correlation functional.

3.4 Møller–Plesset perturbation theory

Møller–Plesset (MP) perturbation theory⁹ is a simple post-HF method that incorporates the effects of electron correlation. The MP perturbation theory assumes that the Hamiltonian operator used in the calculations can be split into two parts: a perturbation \hat{H}' and an unperturbed Hamiltonian $H^{(0)}$,

$$\widehat{H} = H^{(0)} + \widehat{H}' \tag{3.6}$$

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Here $H^{(0)}$ is taken as the HF Hamiltonian. The difference between these two Hamiltonians is assumed to be small in order that the perturbation expansion converges and may be expanded in a Taylor series in the order parameter λ :

$$\widehat{H} = \widehat{H}^{(0)} + \lambda \widehat{H}^{(1)} + \lambda^2 \widehat{H}^{(2)} + \lambda^3 \widehat{H}^{(3)} + \lambda^4 \widehat{H}^{(4)} \dots \dots$$
(3.7)

Here $H^{(1)}$, $H^{(2)}$, etc. are the first, second and higher order corrections to the Hamiltonian. The energy and wavefunction of the correlated system can be written as

$$E_n = E_n^{(0)} + \Delta E_n \tag{3.8}$$

As clearly seen, these expressions for E depend on the expansion parameter. If enough terms are included in the expansion series, the outcome of any calculation will approach the solution for the actual Hamiltonian. The expansion of the actual wavefunction and energy can be described, as follows:

In equation (3.8), $E^{(0)}$ is the HF one-electron energy, which is the solution to Schrodinger equation $\hat{H}^{(0)}\Psi^{(0)} = E^{(0)}\Psi^{(0)}$. The second-order term and higher order corrections are needed to include electron correlation effects. Although the addition of several perturbation terms yields more accurate predictions and may be used to determine a near exact energy, such calculations are computationally very expensive. Consequently, truncation to second-order is normally used giving rise to MP2 perturbation theory. Despite the truncation this level of theory usually recovers the majority of the dynamic correlation energy in a molecule.

3.5 Basis sets

The molecular orbitals in the HF and DFT methods are normally expanded as linear combinations of atom-centred basis functions, as shown below:

$$\psi(r) = \sum_{i} c_{i} \varphi_{i}(r) \tag{3.10}$$

Here $\psi(r)$ is a molecular orbital for electron *i*, $\varphi(r)$ is atomic orbital-type functions and c_i is the expansion coefficient. An optimal description of the molecular orbitals would be achieved by an infinitely large basis set, but of course this is impractical. Therefore, in computational chemistry compromise must be reached between the accuracy of the calculation and the computational time needed.

Early *ab initio* calculations employed Slater Type Orbitals (STOs)^{10,11} in their basis sets, which are described by quantum numbers (*n*, *m* and *l*), an exponent ζ to describe the spatial extent of the orbital, and a spherical harmonic, $Y_{l,m}$, to describe the angular distribution. An STO has the form

$$\chi_{\zeta,n,l,m}(r,\theta,\varphi) = NY_{l,m}(\theta,\varphi)r^{n-1}e^{-\zeta r}$$
(3.11)

Here *r* is the distance from the nucleus and *N* is a normalization constant. Although these basis functions have a form similar to the exact solutions of the Schrödinger equation for the hydrogenic atom,¹² such functions are not favourable for calculating the many multicentre twoelectron integrals encountered for molecules because of the excessive computer time. This predicament can be overcome by replacing STOs by Gaussian Type Orbitals (GTOs),¹³ where the exponential term, $\exp(-\zeta r)$, in an STO is replaced by $\exp(-\alpha r^2)$ in a GTO,¹⁴ Integrals involving GTOs are faster to calculate than those involving STOs because the product of two Gaussian functions is a single Gaussian situated between the different nuclei centres.¹⁵

GTOs have the form

$$g_{ijk}(r) = Nx^i y^j z^k e^{-\alpha r^2}$$
(3.12)

Here *i*, *j* and *k* are non-negative integers, *N* is a normalization constant, *x*, *y*, and *z* are spatial coordinates measured from the nucleus of an atom and α is the orbital exponent, which determines the size or the diffuseness of the basis function. A large exponent represents a small

and dense function (a tight Gaussian), while a small exponent indicates a large and diffuse function.

The computation of integrals involving GTOs is much faster than for STOs but unfortunately GTOs provide a less effective description of the shape of an atomic orbital. One possible way to achieve an acceptable level of accuracy with the least amount of computational effort is to use a linear combination of several GTOs to mimic the behaviour of STOs.

There are several types of standard basis sets, which are now available in basis set libraries. One of them is known as a minimal basis set and uses the smallest possible number of functions to represent all types of occupied atomic orbitals in the separated atoms within a molecule. These basis sets are not capable of giving highly accurate results and do not provide reliable physical properties of molecules. The most common minimal basis set is STO-*n*G, where *n* is the number of primitive GTOs are used to approximate STO, where n = 2, 3, or 6. These basis sets typically give significantly less accuracy in providing reliable physical properties of molecules. As a consequence, to provide a better description of the electron distribution, the use of additional functions is required.

Examples of basis sets that combine high levels of flexibility are split valence basis sets, such as the Pople basis sets.¹⁶ These basis sets employ more functions than the minimal basis set by adding extra functions to describe the spatial distribution of the valence electrons. Prime examples of split valence basis sets are 3-21G and 6-31G, where the first digit represents the number of Gaussian primitives that are used to construct the core atomic orbitals and the second and third digits indicate the number of primitives used to describe the valence orbitals: this kind of basis set is named a double zeta basis set because there are two groups of GTOs used to describe the valence orbitals. For more improvement, a triple-zeta (TZ) or even larger basis sets can be chosen to provide a more accurate description of the valence electron distribution.

To further improve the basis set, diffuse functions can be included to describe the behaviour of electrons when they are far from the nucleus. These basis sets are often denoted by the notation + (to the heavy atom) or ++ (to hydrogen atoms). Diffuse functions are typically important in describing the electron density in anions or intermolecular species, such as van der Waals complexes.

An important addition to a basis set is the inclusion of one or more polarisation functions. One of the key gains offered by polarization functions is that they allow valence orbitals to change shapes from those adopted in atoms. These functions significantly improve the description of molecular geometries (bond lengths and angles) and relative energies. For example, the first polarization function that would be added to a hydrogen atom would be a ptype function.

3.6 Relativistic effective core potential

Heavy atoms like Sr, Ba and Eu, all of which are encountered elsewhere in this thesis, have a large number of core electrons which are generally not significantly affected by changes in chemical properties. However, the effect of these electrons cannot be completely ignored. Not only do they make a large contribution to the total energy of a molecule, they also show significant relativistic effects because the core electrons are close to the highly charged nucleus and therefore reach high velocities. A simple and satisfactory way to account for the core electrons is to employ an effective core potential (ECP) (often also called the pseudopotential basis set or relativistic effective core potentials, RECP). This approach works because the effective core potential (ECP) accounts for the effect of core electrons in a cost-effective way.

The most recently developed effective core potential (ECP) families are available in the EMSL basis set exchange library¹⁷ for a range of elements. Commonly used ones are the Los Alamos National Laboratory (LANL) families of Hay and Wadt^{18,19,20}, the Consistent Effective Potential (CEP) of Stevens *et al.*²¹ and the Stuttgart 1997 ECP.^{22,23,24} One type of ECP has been

employed in this thesis: the Stuttgart 1997 ECP, which is popular for heavy atoms. The Stuttgart 1997 ECP is available with both small cores (Stuttgart RSC 1997 ECP) and large cores (Stuttgart RLC 1997 ECP). MWB*n*ECP and MDH*n*ECP are used to specify the Stuttgart 1997 ECP, where *n* is the number of core electrons which are replaced by effective core potential, and M indicates that the potential is developed for a neutral atom. The other two terms specify the theoretical level of the potential: WB stands for Wood-Boring quasi-relativistic and DF is for Dirac-Fock relativistic.

3.7 Computational details

All calculations were carried out using Gaussian 03.²⁵ The majority of calculations were run on ALICE, a recent high performance computing (HPC) cluster installed at Leicester University. In this system there are 208 computer nodes, two login nodes and two management nodes. A high performance Panasa system provides 550 TB of storage for user data. Each computer node has a pair of eight core 2.6 GHz Intel Xeon Iny Bridge CPUs and 64 GB of RAM.

All geometry optimizations in this work were run with Z-matrix coordinates without symmetry to permit full variation of all degrees of freedom. Such calculations were always followed by a vibrational frequency analysis (see next section 3.8) to ensure that a true potential energy minimum was found by checking for imaginary frequencies. The highest level of theory used in the calculation was second-order Møller–Plesset perturbation theory (MP2). Chemcraft was used for visualisation of output files.²⁶

3.8 Harmonic vibrational frequency calculations

To identify equilibrium geometries and to obtain IR spectra and zero point energies, it is necessary to determine vibrational frequencies. Because the number of vibrational normal modes varies with the number of atoms, N, in molecules (3N-6 for non-linear molecules and

3*N*-5 for linear molecules), each normal mode has a characteristic resonance frequency which is usually determined experimentally and/or theoretically. For the potential energy surface (PES) to have a minimum, the vibrational frequencies must be real, i.e., no imaginary frequencies.

The stationary points with respect to each of the 3N-6 independent geometrical coordinates (R_i) have first derivatives of energy equal to zero at a minimum, i.e.

$$\frac{\partial V}{\partial R_i} = 0 \qquad i = 1, 2, 3, \dots \dots \dots 3N - 6 \tag{3.13}$$

The second derivatives form the so-called Hessian matrix whose components are given by:

$$\frac{\partial^2 V}{\partial R_i R_1}, \frac{\partial^2 V}{\partial R_i R_2}, \frac{\partial^2 V}{\partial R_i R_3}, \dots, \frac{\partial^2 V}{\partial R_i R_{3N-6}}$$
(3.14)

The Hessian can be used to calculate the harmonic vibrational frequencies of a molecule.

With methods such as HF and MP2 the calculated harmonic frequencies are larger than the experimentally observed vibrational frequencies. This overestimation can vary from one method to another by up to 10%. The main reason for this disagreement is neglecting the effect of vibrational anharmonicity. Anharmonic effects are seldom calculated because of their high computational cost. The simplest and most common alternative is to introducing a scaling factor (specific to each method/basis set combination) to bring theory into closer agreement with experimentally observed frequencies.

References

- Atkins, P. W.; Friedman, R. S. *Molecular quantum mechanics*; Oxford university press, 2011.
- Green, N. J. B. *Quantum mechanics 1: foundations*; Oxford University Press: Oxford, 1997.
- Green, N. J. B. *Quantum mechanics 2: the toolkit*; Oxford University Press: New York, 1998.

- (4) Born, M.; Oppenheimer, R. Ann. Phys. **1927**, 389, 457.
- (5) Kohn, W.; Becke, A. D.; Parr, R. G. J. Phys. Chem. 1996, 100, 12974.
- (6) Springborg, M. Density-functional methods in chemistry and materials science; Wiley Chichester, 1997.
- Rode, B. M.; Hofer, T. S.; Kugler, M. D. *The basics of theoretical and computational chemistry*; Wiley-VCH, 2007.
- (8) Kohn, W.; Sham, L. J. *Phys. Rev.* **1965**, *140*, A1133.
- (9) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618.
- (10) Slater, J. C. Phys. Rev. **1930**, *36*, 57.
- (11) Slater, J. Phys. Rev. 1932, 42, 33.
- (12) Harris, F. E. Int. J. Quantum Chem. 2002, 88, 701.
- (13) Leach, A. R. *Molecular modelling: principles and applications*; Prentice Hall: New York;Harlow, England;, 2001.
- (14) Boys, S. F. Proce. R. Soc. **1950**, 200, 542.
- (15) Jensen, F. Introduction to computational chemistry; John Wiley & Sons: Hoboken,
 NJ;Chichester, England;, 2007.
- (16) Pople, J. A. Rev. Mod. Phys. 1999, 71, 1267.
- (17) <u>https://bse.pnl.gov/bse/portal</u>.
- (18) Hay, P. J.; Wadt, W. R. J. Chem. Phys. 1985, 82, 299.
- (19) Hay, P. J.; Wadt, W. R. J. Chem. Phys. 1985, 82, 270.
- (20) Wadt, W. R.; Hay, P. J. J. Chem. Phys. 1985, 82, 284.
- (21) Stevens, W. J.; Krauss, M.; Basch, H.; Jasien, P. G. Can. J. Chem. 1992, 70, 612.
- (22) Bergner, A.; Dolg, M.; Küchle, W.; Stoll, H.; Preuß, H. Mol. Phys. 1993, 80, 1431.
- (23) Kaupp, M.; Schleyer, P. v. R.; Stoll, H.; Preuss, H. J. Chem. Phys. 1991, 94, 1360.
- (24) Dolg, M.; Stoll, H.; Preuss, H.; Pitzer, R. M. J. Phys. Chem. 1993, 97, 5852.

- (25) Frisch, M. J. T., G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb,; M. A.; Cheeseman, J. R. M., J. A., Jr.; Vreven, T.; Kudin, K.; N.; Burant, J. C. M., J. M.; Iyengar, S. S.; Tomasi, K.; Barone, V.;; Mennucci, B. C., M.; Scalmani, G.; Rega, N.; Petersson, G. A.;; Nakatsuji, H. H., M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.;; Ishida, M. N., T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li,; X.; Knox, J. E. H., H. P.; Cross, J. B.; Bakken, V.; Adamo, C.;; Jaramillo, J. G., R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.;; Cammi, R. P., C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.;; Voth, G. A. S., P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich,; S.; Daniels, A. D. S., M. C.; Farkas, O.; Malick, D. K.; Rabuck, A.; D.; Raghavachari, K. F., J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A.; G.; Clifford, S. C., J.; Stefanov, B. B.; Liu, G.; Liashenko, A.;; Piskorz, P. K., I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham,; M. A.; Peng, C. Y. N., A.; Challacombe, M.; Gill, P. M. W.;; Johnson, B. C., W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian Inc., Wallingford, CT* **2004**, *26*.
- (26) <u>http://www.chemcraftprog.com</u>.

Chapter 4

Photoionization of Ca(NH₃)_n and Sr(NH₃)_n complexes

4.1 Introduction

The study of solvent-solute complexes have received significant theoretical and experimental attention in recent years because of their intriguing and unusual properties.^{1,2} Although bulk solutions have been extensively studied, there are aspects of solvent-solute complex behaviour that are still not fully understood. In the case of alkali/ammonia solutions, even the main entities present at the molecular scale have not been established, and extracting such information from bulk solutions through techniques such as spectroscopy, where broad spectral absorptions may overlap, has proven to be a major challenge.

An alternative tactic for extracting information on the types of species that might be present in an alkali/ammonia solution is to study alkali-ammonia complexes of the type $M(NH_3)_n$ in the gas phase. The benefit of working in this environment is that fundamental information about the interactions between a single metal atom and a limited number of surrounding ammonia molecules can be established through systematic size-selective studies of these complexes. Furthermore, such systems are amenable to *ab initio* quantum chemical calculations, which helps maximise the information gained from the accompanying experimental work.

Like alkali metals, solvated electrons are produced when certain alkaline earth and several rare earth metals are dissolved in liquid ammonia.^{3,4} However, these solutions have not been as extensively studied as alkali-ammonia solutions. Likewise, the corresponding isolated $M(NH_3)_n$ complexes in the gas phase, where M is an alkaline earth metal, have also received little attention to date. For the alkaline earth metals, the only $M(NH_3)_n$ complexes that have

been studied previously have been $Mg(NH_3)_n$, (n = 1-37) where photoionization mass spectrometry was employed.⁵ This work revealed that the Mg atom is preferentially bound to the surface of an $(NH_3)_n$ cluster, in marked contrast to the alkali metal atoms, where an interior location for the metal atom is preferred. A surface location is favoured because the interaction between Mg and the N atoms of the NH₃ molecules is much weaker than for the alkalis.

This chapter reports the first experimental study of $Ca(NH_3)_n$ and $Sr(NH_3)_n$ complexes. Photoionization mass spectrometry was used to measure the first ionization energies for n = 2-6. Help in interpreting the experimental measurements was provided by *ab initio* calculations on both the neutral complexes and their cations.

4.2 Photoionization efficiency curves

Photoionization was used to obtain the ion yield as a function of photon energy (wavelength): such data are known as photoionization efficiency (PIE) curves. In principle, the ionization energy of a specific complex can be determined from its PIE.

Different approaches have been developed to extract the adiabatic ionization energy (AIE) from a PIE. An early method was described by Watanabe *et al.*⁶ and further developed with respect to AIE determination for a number of molecules, including NO, CS_2 , C_6H_6 , and CH_3I .^{7,8} In this method, a distinct point in the PIE curve for a molecule was identified where a linear region at longer wavelengths abruptly changed to a plateau at shorter wavelengths, as seen in Figure 4.1. This transition point (called a curved transition point energy) was assigned to be equivalent to the AIE for the species of concern because values determined in this way for a number of small diatomic and triatomic molecules were found to be in close agreement with those reported from earlier spectroscopic studies. The level of agreement found by this

approach led to it being adopted by a number of other workers and extended in subsequent studies to larger molecules containing more atoms.⁹



Figure 4.1 PIE curves for CS_2 and CH_3l indicating the points corresponding to the respective molecular AIE values (marked as IP = ionization potential). This figure is reproduced from ref.⁷

Guyon and Berkowitz¹⁰ reinterpreted the PIE curves of the larger polyatomic molecules reported by Watanabe and co-workers such as CS_2 , C_6H_6 , and CH_3I and questioned the validity/accuracy of the earlier work. Rather than taking the curved transition point energy as the AIE, Guyon and Berkowitz suggested that a simple extrapolation of the data in the linear region of the PIE curve to the abscissa (ion yield = 0) would give a more accurate value for the AIE, as seen in Figure 4.2.

AIEs for the molecules considered by Guyon and Berkowitz were found to be significantly lower than those determined by Watanabe. This is because the Watanabe approach
overestimates the AIEs for larger molecules by inherently including an additional contribution equivalent to the average vibrational energy of the species. For large molecules with low frequency vibrations, better estimates of the AIEs are obtained by extrapolation of the PIE to the point of zero ionization intensity. Berkowitz and co-workers extended this approach in a number of subsequent studies involving other species, including SiH_n $(n = 1-4)^{11}$ and C_{60.}¹²



Figure 4.2 PIE curve for S_6 showing the linear extrapolation approach for evaluating AIE. Image reproduced from ref.¹⁰

Wucher *et al.* reported PIE data for a series of indium clusters, $In_n (2 \le n \le 35)$, formed by laser sputtering of a solid indium target and detection of cluster products using a laser ionization time-of-flight mass spectrometer (TOF-MS).¹³ To analyse the PIE curves produced for these clusters, the variation in threshold behaviour was considered as a series of step functions shifted by a factor equivalent to the average vibrational energy, as described by Guyon and Berkowitz. This led to the following linear parameterisation expression:

$$PIE^{\circ}(E) = \begin{cases} (E) = \{a(E - E_1), & \text{for } E \ge E_1 \\ 0, & \text{for } E < E_1 \end{cases}$$
(4.1)

where E_1 is the adiabatic ionization energy, and *a* is the slope of the linear region.

For the smallest cluster, In_2 , which approaches the dimensions of smaller diatomic molecular species, it was found that the same AIE (5.5 eV) was determined using both the Watanabe and linear extrapolation methods because of the large internal excitation of the sputtered In_2 cluster. However, for larger clusters, the AIE values obtained from the two methods diverged, with the Watanabe approach consistently overestimating values.

Knickelbein *et al.*, reported on nickel clusters, Ni_n, with $3 \le n \le 90$.¹⁴ As with previous studies,¹³ laser photoionization (TOF-MS) was employed to generate PIE curves for the different clusters and to determine respective AIE values using both the Watanabe approach and the linear extrapolation method of Guyon and Berkowitz. It was found that for the smaller clusters in the series, AIEs from the two methods were generally in good agreement, whilst values for larger clusters diverged, consistent with the reasons given previously.

Yang and Knickelbein subsequently used the same methods to deduce the AIEs for Fe and Co clusters and for Sc_nO clusters.^{15,16} They noted a correlation between the shape of the PIE curve and cluster size, with the applicability of the Watanabe method decreasing with increasing cluster size in favour of increased accuracy using the linear extrapolation method.

Kooser *et al.*¹⁷ reported the cluster size dependent AIEs for the Se_n clusters (n = 2-8) based on linear extrapolation of experimentally derived partial ion yields from vacuum evaporation of a Se source using the photoelectron-photoion coincidence technique. Figure 4.3 shows the PIE data for all eight clusters, as indicated in each panel. Kooser *et al.* noted some

differences in their estimated AIE values compared with previously reported and theoretically predicted values. Most likely, these differences are a result of the inherent assumptions made in using the linear extrapolation approach.



Figure 4.3 Photoion yield data for Se_n microclusters (n = 2-8) with cluster AIE values determined by linear extrapolation. Image was taken from ref.¹⁷

To summarise for this section, the two primary methods for evaluating molecular and cluster AIEs from PIE curves have been outlined. The original Watanabe approach identifies the AIE as a transition point in the PIE curve where an abrupt change delineates linear and plateau regions. For small gas-phase cluster species, subsequent studies have shown this approach to be valid. However, for larger molecules and clusters, this approach overestimates AIE values because it does not account for the average vibrational energy, and the linear extrapolation method introduced by Guyon and Berkowitz has been shown to be more accurate. Given that relatively large complexes are encountered in this chapter, the linear extrapolation method has been employed for determining ionization energies.

4.3 Experimental section

The experimental apparatus and procedures have been described in detail in Chapter 2 of this thesis, and therefore only a brief account is given here. $M(NH_3)_n$ complexes, where M = Ca or Sr, were generated by pulsed laser ablation (using the second harmonic output of a Nd:YAG laser, at 532 nm) of the solid alkaline earth metal in the presence of gaseous ammonia (BOC > 99.93%). This was conducted at a maximum pressure of 2 bar using a pulsed nozzle with an opening duration of 200 µs, and the resulting gas mixture was then expanded into a vacuum to produce a supersonic jet. The mixture was collimated with a skimmer to form a molecular beam and passed into an orthogonal acceleration TOF-MS. The UV output from a pulsed tunable dye laser with frequency-doubling capability was used to ionize the complexes in the source region of the TOF-MS. To focus the UV laser into the ionization region of the TOF-MS, a lens of focal length 250 mm was used. Photoionization efficiency curves for each complex were generated by recording the ion signal in a given mass channel as a function of the output wavelength from the dye laser. Ion signals were accumulated in a digital storage oscilloscope and were typically averaged over 1000 laser shots before the wavelength was changed.

4.4 Computational Details

Ab initio calculations were carried out to assist in the interpretation of the photoionization data and to predict specific structures of the $M(NH_3)_n$ (M = Ca and Sr) complexes and their corresponding cations for n = 1-10. For each complex, several possible starting structures were considered, and geometry optimization was then used to find potential energy minima. There is no guarantee that such a crude approach will identify all possible isomers, but we suspect that all low energy isomers for all of the complexes explored in this research have been identified. To ensure that geometry optimization yielded true minima on the potential energy surface, harmonic vibrational frequencies were calculated for each isomer found. In the following calculations, the total energies of neutral complexes and ions have been corrected for zero-point vibrational energies. All calculations were performed using the GAUSSIAN 03 suite of programs¹⁸, as described in Chapter 3.

4.4.1. $Ca(NH_3)_n$ complexes

The calculations on $Ca(NH_3)_n$ (n = 1-10) used both density functional theory DFT(B3LYP) and second-order Møller-Plesset perturbation theory (MP2). In both cases, the Pople 6-311++G(d,p) basis set was employed for all atoms. This basis set was chosen because it is reasonably large and flexible but still viable for use on relatively large complexes.

4.4.2. $Sr(NH_3)_n$ complexes

Owing to the large number of core electrons, the standard 6-311++G basis set is not available for the strontium atom. In this case, a different basis set was sought. For Sr, a double-zeta basis set with a relativistic effective core potential (ECP28MWB), known as the Stuttgart RSC 1997 ECP, was chosen¹⁹, which includes d-type polarization functions.²⁰ To keep a balanced overall basis set, the standard Pople double zeta 6-31+G(d,p) basis sets were used for the N and H atoms.

4.5 Results and discussion

4.5.1. Mass spectrometry and ionization energy measurements

Typical photoionization mass spectra of Ca(NH₃)_n and Sr(NH₃)_n complexes are depicted in Figures 4.4 and 4.5, respectively. These mass spectra were recorded at the relatively short wavelength of 346 nm to illustrate the full range of complexes formed in the molecular beam. It is expected, from a comparison with the behaviour of alkali-ammonia complexes, that the first ionization energy of the complexes will decrease as each ammonia molecule is added. The photon energy at 346 nm (3.58 eV) is just below the threshold for producing M(NH₃)_n⁺ (M = Ca or Sr) for n = 1-3 (see later discussion). However, complexes with $n \ge 3$ can be ionized by a single photon at this wavelength. The significant abundance of M⁺ relative to MNH₃⁺ presumably reflects the much higher abundance of free metal atoms in the molecular beam, which can be ionized by two-photon non-resonant absorption. In addition to ions of the type M(NH₃)_n⁺, weak peaks are seen which can be assigned to Ca₂(NH₃)_n⁺ (n = 3-7). Ca₂⁺ is not observed in the mass spectrum but Ca₂(NH₃)_n⁺ complexes are, presumably because the ionization energy of Ca₂ is above the UV photon energy. As expected, NH₃⁺ is not observed in the mass spectrum because of its high ionization energy (10.07 eV).²¹



Figure 4.4 Photoionization mass spectrum from $Ca(NH_3)_n$ complexes. The laser wavelength used was 346 nm. The main series of peaks originate from $Ca(NH_3)_n^+$ ions. In addition the peaks marked by an asterisk (*) are from $Ca_2(NH_3)_n^+$ for $n^*=3-7$.



Figure 4.5 Photoionization mass spectrum from $Sr(NH_3)_n$ complexes. The laser wavelength used was 346 nm.

4.5.2. Photoionization efficiency curves

In this thesis, linear extrapolation at the steepest part of the PIE curves has been used to estimate the AIE for each complex (see section 4.2 for more details.)

Besides the ionization energy, the shape of the PIE curve is also of interest. A steep rise in the slope of the PIE curve indicates that there is no major change in equilibrium structure between the neutral complex and the corresponding cation, in which case the adiabatic and vertical ionization energies are almost identical. A gentle rise in the slope of the PIE curve indicates that the equilibrium structures of the neutral complex and its cationic analogue differ significantly, which gives rise to a large disparity in the vertical and adiabatic ionization energies. The shapes of the PIE curves are dictated by the Franck-Condon principle.

In this thesis, the experimental photoionization efficiency curves of $Ca(NH_3)_n$ and $Sr(NH_3)_n$ have been determined for the first time. To aid the interpretation of the PIE spectra, *ab initio* calculations were undertaken on both the neutral and cationic structures (see section 4.4) to assign the structures of the complexes of interest.

Figures. 4.6 and 4.7 show PIE curves measured as a function of the photon energy of the ionizing laser. It is important to note that the intensity of the laser was kept sufficiently low to eliminate multiphoton absorption processes, and therefore these results represent the photon energy dependence of the cross sections for single-photon ionization of each complex at a particular laser wavelength.

Generally, to derive reasonable experimental adiabatic ionization energy values, it is necessary to make a least squares fit (linear regression) to the experimental data in the threshold region. The margin of error for the AIE from the fit is no more than ± 0.02 eV in each case, which is mainly due to the uncertainly of the first linear increase of the PIE curves.



Figure 4.6 Photoionization efficiency curves for $Ca(NH_3)_n$ (n = 2-6). Also shown on these plots are the linear regression, whose extrapolation to the baseline was used to predict the adiabatic ionization energy for the neutral complex.



Figure 4.7 Photoionization efficiency curves for $Sr(NH_3)_n$ (n = 2 - 6). Also shown on these plots are the linear regression, whose extrapolation to the baseline was used to predict the adiabatic ionization energy for the neutral complex.

The photoionization efficiency rises steeply with photon energy in the threshold region for n = 2 for the Ca(NH₃)_n complexes and for n = 2 and 6 for the Sr(NH₃)_n complexes. This suggests that the neutral complexes and their corresponding cations have similar equilibrium structures. For n = 3 - 6 of Ca(NH₃)_n and n = 3 - 5 of Sr(NH₃)_n the PIEs show a slower rise, implying that there is a more significant change in the equilibrium structure between the neutral and the cation upon ionization when compared to n = 2. Note that the AIEs for the n = 1complexes have not been determined in this thesis might be due to these adiabatic ionization energies (see Tables 4.1 and 4.2) may require a multi-photon UV experiment, which was provided by the output of a pulsed tunable dye laser has insufficient energy to facilitate ionization. The AIE values determined for Ca(NH₃)_n and Sr(NH₃)_n are summarised in Tables 4.1 and 4.2. Also shown in Tables 4.1 and 4.2 are calculated AIEs and VIEs for the complexes. As can be seen, the calculated values are in good agreement with the experimental findings in the case of AIEs, as also illustrated in Figures 4.8 and 4.9. The AIEs gradually decrease with an increasing number of ammonia molecules, until they begin to plateau. This behaviour is interpreted in terms of the appreciable lowering of ionization energy, which essentially results from the formation of a solvated electron. For small complexes, an increasing number of ammonia molecules surround the Ca and Sr atoms allows the valence electrons on the metal atom to become more delocalized but not detached. The ionization energies decrease continuously until marking the closing of the first solvation shell, which will be discussed in more detail in the next section. Eventually an electron separates from the Ca and Sr cations and is shielded dielectrically by the solvated molecules. For large complexes, a more delocalized electron is produced, and the ionization energies remain nearly constant. In other words, the shape of the PIEs can be explained by increased screening of the valence electrons on the alkaline earth metal from the positive charge as ammonia molecules are added.

	MP2/eV		DFT/eV		EXP./eV
n	AIE	VIE	AIE	VIE	
0	6.154	-	6.150	-	6.113 ^(a)
1	4.872	4.881	5.206	5.206	-
2	4.185	4.243	4.361	4.522	4.111 ± 0.15
3	3.759	3.800	4.075	4.115	3.997 ± 0.08
4	3.511	3.542	3.756	3.829	3.719 ± 0.03
5	3.424	3.474	3.677	3.730	3.549 ± 0.06
6	3.267	3.267	3.561	3.592	3.224 ± 0.06
7	3.143	3.195	3.494	3.494	-
8	3.078	3.078	3.343 ^(c)	3.343	-
9	2.930 ^(b)	2.930	3.196 ^(c)	3.196	-
10	2.823 ^(b)	2.823	3.131 ^(c)	3.131	-

Table 4.1First ionization energies of $Ca(NH_3)_n$ complexes. The MP2 and DFT results are
corrected for zero point vibrational energies in the neutral and ion complexes.

(a) Experimental 1^{st} ionization energy of atomic Ca taken from ref.²²

- (b) Calculated for the 8+1 and 8+2 isomers of n = 9 and 10, respectively, at the MP2 level.
- (c) Calculated for the 7+1, 7+2 and 7+3 isomers for n = 8, 9 and 10, respectively. As detailed in the text, these were the lowest energy structures for Ca(NH₃)_n for n = 8-10 at the DFT level.

Table 4.2	First ionization energies of Sr(NH ₃) _n complexes. The MP2 and DFT results are
	corrected for zero point vibrational energies in the neutral and ion complexes.

	MP2/eV		DFT/eV		EXP./eV
n	AIE	VIE	AIE	VIE	
0	5.467	-	5.758	-	5.695 ^(a)
1	4.702	4.702	4.970	4.970	-
2	4.122	4.122	4.398	4.398	4.342 ± 0.05
3	3.682	3.738	3.952	4.018	3.932 ± 0.02
4	3.349	3.401	3.650	3.708	3.619 ± 0.04
5	3.329	3.247	3.536	3.611	3.494 ± 0.05
6	3.143	3.076	3.453	3.487	3.317 ± 0.28
7	3.074	3.004	3.376	3.376	-
8	3.039	2.966	3.298	3.334	-
9	2.791 ^(b)	2.791	3.197 ^(b)	3.197	-
10	2.689 ^(b)	-	3.006 ^(b)	3.008	-

(a) Experimental 1st ionization energy of atomic Sr taken from ref.²³

(b) Calculated for 8+1 and 8+2 isomers of n = 9 and 10, respectively.



Figure 4.8 Plot of the calculated and experimental adiabatic ionization energy versus n for Ca(NH₃)_n.



Figure 4.9 Plot of the calculated and experimental adiabatic ionization energy versus n for Sr(NH₃)_n.

According to a quantitative classical interpretation, the ionization energy IE, which is the energy required to remove an electron from an infinitesimal distance δ to infinity, is given by

$$IE = \lim_{\delta \to 0} e^2 \left[\frac{1}{4\delta} + \frac{3}{8R} + \frac{Z}{R} \right]$$
(4.2)

in the limit as $\delta \to 0$, where δ is the distance from the small very particle surface to infinity,^{24,25} *R* is the complex radius consisting of *m* particles. In the limit as $R \to \infty$, i.e. the surface of the sphere become more like a flat surface, $IE = e^2/4\delta$. Thus the *IE* becomes equivalent to the surface work function (*WF*) and the IE to remove an electron from the bulk solid is

$$IE = WF + 3e^2/8R (4.3)$$

Here *r* is written using the number density of electrons ρ as

$$r(m) = [(3m/4\pi\rho)]^{-1/3}$$
(4.4)

The ionization energy is proportional to $m^{-1/3}$ for a complex of *m* particles, which can be approximated by a sphere. If we apply this approximate description to an ML_n complex of the type met in this chapter, then the IEs can be expected to be (one metal atom plus *n* solvent molecules) proportional to $(n + 1)^{-1/3}$. The observed size dependent evolution of ionization energies for complexes are usually in good agreement with classical models,^{26,27,28} which predict that the ionization energy will decrease linearly towards the corresponding bulk energy value as a function of $(n + 1)^{-1/3}$.

To explore the relationship between the IE and $(n + 1)^{-1/3}$ for the complexes studied in this chapter, the experimental ionization energies (AIEs) are plotted in Figures 4.10 and 4.11 as a function of $(n + 1)^{-1/3}$ for the Ca(NH₃)_n and Sr(NH₃)_n complexes, respectively. As can be seen in these figures, the experimental results decrease almost linearly with increasing $(n + 1)^{-1/3}$, suggesting that the classical model does reasonably well in predicting how the IE changes with the number of NH₃ molecules. The AIEs can also be extrapolated to an infinite complex size $(n \rightarrow \infty)$, giving a limiting value of 0.382 eV for the Ca(NH₃)_n. This experimental value is much lower than the vertical detachment energy (VDE) of the ammoniated electron in the bulk (1.25 eV).²⁹ The extrapolation for Sr(NH₃)_n in the limit of $n \rightarrow \infty$ gives the even more bizarre value of -0.086 eV. Part of the problem may be that we are extrapolating from to infinity form the AIEs from complexes with relatively small values of n. Small complexes deviate from classical behaviour, presumably because they cannot be adequately described by near spherical structures. The non-delocalization of the valence electrons from the metal may also play a role here.



Figure 4.10 Plot of the experimental adiabatic ionization energy versus $(n+1)^{-1/3}$ for Ca(NH₃)_n.



Figure 4.11 Plot of the experimental adiabatic ionization energy versus $(n+1)^{-1/3}$ for Sr(NH₃)_n.

4.5.3. Calculated equilibrium structures

In order to assist in the interpretation of the experimental results, a series of *ab initio* calculations have been carried out on $Ca(NH_3)_n$ and $Sr(NH_3)_n$ complexes and their corresponding cations without symmetry constraints. Because there have been no prior published theoretical studies of these complexes, it was important to establish the structural landscape for the complexes in order to determine possible minima for each complex size. Attempts were made to find as many low-lying structural isomers as possible to assess whether a single isomer, the global potential energy minimum, dominates for each complex, or whether it is necessary to consider contributions to the PIE curves from several different isomers.

Ionization energies were then calculated for each complex and compared with the experimental values, as mentioned above.

To establish possible potential energy minima, initial search calculations were performed using a small basis set and a simple level of theory, the Hartree Fock method. This enabled trial calculations at many different starting geometries for each complex due to the low computational cost in searching the potential energy landscape. When minima were found, the resulting structures were then re-investigated with a higher level theory and a larger basis set.

The notation p + q is used to help distinguish between isomers, where p is the number of ammonia molecules in the first (inner) solvation shell and q is the number in the second (outer) shell around the central metal atom. The ammonia molecules in the second shell are expected to be attached to the first shell ammonia molecules by hydrogen bonds. The structural parameters for low-lying geometry structures found for both the neutral and cationic complexes are given in Tables 4.3 and 4.4, respectively, and graphical depictions of the calculated global potential energy minima for Ca(NH₃)_n and Sr(NH₃)_n complexes and their cations are shown in Figures 4.12 and 4.13, respectively.

For the simple binary complex, MNH_3 (M = Ca or Sr), only one isomer was found, and this consisted of a direct bond between the M and N atoms, predicting a structure with C_{3v} point group symmetry. Comparing the calculated equilibrium structures between the neutral complex and the corresponding cation, no significant changes in geometry occur upon ionization, which means that the adiabatic and vertical ionizations will be almost identical. In fact, this coincidence between the adiabatic and vertical ionization energies applies for the larger complexes too.

	Parameter(a)	MP2		B3LYB	
n		Neutral	Cation	Neutral	Cation
	Ca-N1	2.574	2.510	2.682	2.587
1	N- H	1.020	1.021	1.023	1.023
	Ca-N1-H3	112.5	114.0	112.1	113.5
	H-N-H	106.3	104.6	106.8	105.1
	Ca-N-H	112.5	114.0	112.1	113.5
	Ca-N	2.567, 2.567	2.542,2.542	2.530,2.530	2.495,2.495
	N1-Ca-N2	80.4	96.9	84.9	179.9
2	N-N	3.313	3.803	3.413	4.910
	H6-N2-H4	105.8	104.6	106.5	105.6
	H4-N2-Ca	108.9	110.7	109.4	113.1
	Ca-N	2.546,2.511,2.511	2.574,2.533,2.533	2.538,2.495,2.495	2.542,2.508,2.508
	N1-Ca-N2	86.7	88.8	93.5	101.9
3	N-H	1.020		1.025	1.022
	H1-N1-H3	106.2	104.9	106.7	105.7
	N2-Ca-N3	177.5		177.9	156.1
	Ca-N	2.510,2.530,2.530	2.548,2.578,2.548	2.497,2.519,2.522	2.536,2.538,2.540
4		2.510	2.548	2.498	2.538
4	N-Ca-N	91.3	88.7	94.3	90.8
	N-H	1.025	1.019	1.026	1.022
	Ca-N	2.518,2.517,2.522	2.557,2.557,2.586	2.522,2.522,2.529	2.542,2.541,2.566
		2.556,2.558	2.556,2.558	2.517,2.518	2.535,2.536
5	N3-Ca-N4	178.6	177.6	174.6	173.9
5	N-H	1.024	1.019	1.026	1.022
	N3-Ca-N5	90.7	89.5	90.2	89.9
	N1-Ca-N3	89.7	88.5	91.9	91.8
	Ca-N	2.531,2.531,2.531	2.547,2.547,2.547	2.547,2.547,2.548	2.562,2.562,2.563
	N3-Ca-N4	2.531,2.531,2.531	2.547,2.547,2.547	2.548,2.548,2.548	2.561,2.562,2.561
	N-H	175.2	175.8	179.9	175.8
6	H1-N1-H18	1.024	1.023	1.025	1.024
	N3-Ca-N5	105.5		105.9	105.4
	N1-Ca-N3	87.7	104.8	88.4	91.6
	N6-Ca-N4	89.1	89.4	91.6	88.5
	Ca-N	2.588,2.568,2.590	2.604,2.584,2.608	2.607,2.593,2.614	2.623,2.609,2.627
		2.570,2.569,2.569	2.587,2.584,2.587	2.594,2.592,2.594	2.609,2.609,2.609
	N3-Ca-N4	2.588	2.608	2.616	2.634
7	N-H	78.6	79.0	82.4	82.6
	H1-N1-H2	1.024	1.022	1.025	1.023
	N3-Ca-N5	105.4	104.9	105.8	105.4
	N1-Ca-N3	78.6	79.0	82.8	82.7
	N6-Ca-N4	140.2	141.8	149.1	150.5
	Ca-N	2.626,2.626,2.6256	2.642,2.642,2.642	2.657,2.661,2.659	2.673,2.677,2.675
8		2.626,2.626,2.626	2.642,2.642,2.642	2.659,2.659,2.661	2.677,2.675,2.678
	N3-Ca-N4	2.626,2.626	2.642,2.642	2.661,2.660	2.677,2.676
	N-H	72.3	72.3	79.9	79.9
	H1-N1-H2	1.024	1.022	1.024	1.022
	N3-Ca-N5	105.2	104.7	105.8	105.4
	N1-Ca-N3	80.9	80.6	72.2	72.2
	N6-Ca-N4	72.3	72.3	72.3	72.3
	N8-Ca-N2	145.5	145.1	112.4	112.4
		77.5	77.7	112.7	112.7

Table 4.3Key calculated structural parameters for the lowest energy isomers of $Ca(NH_3)_n$ complexes and their cations. Distances are in Å and angles in degrees.

	Ca-N	2.574,2.566,2.574	2.588,2.582,2.579	2.603,2.620,2.609	2.612,2.607,2.604
		2.587,2.566,2.594	2.596,2.584,2.602	2.603,2.510,2.603	2.603,2.616,2.632
		2.571	2.510	2.575	2.608
	Ca-N2	4.576	4.877	4.714	4.927
ø	N3-Ca-N4	80.9	79.7	74.4	77.1
0 (7+1)	N-H	1.024	1.022	1.024	1.023
(1+1)	H1-N1-H2	105.4	104.8	105.8	105.4
	N3-Ca-N5	121.4	123.6	113.7	109.2
	N1-Ca-N3	96.5	103.3	78.3	78.4
	N6-Ca-N4	94.2	90.5	128.6	152.7
	N1-Ca-N6	80.9	79.9	83.9	78.7
	Ca-N	2.626,2.628,2.621	2.638,2.648,2.6322.	2.663,2.667,2.661	2.675,2.688,2.673
		2.621,2.623,2.623	632,2.634,2.6362.6	2.661,2.653,2.654	2.673,2.669,2.669
		2.654,2.627	40,2.642	2.663,2.658	2.675,2.666
	Ca-N2	4.778	4.866	4.887	4.984
	N3-Ca-N4	72.1	71.8	71.7	71.4
9	N-H	1.019	1.018	1.011	1.018
(8+1)	H1-N1-H2	105.9	105.2	106.6	105.9
	N3-Ca-N5	79.1	78.8	79.4	79.3
	N1-Ca-N3	99.3	102.1	101.1	103.8
	N6-Ca-N4	143.5	142.7	143.7	143.7
	N8-Ca-N2	79.6	80.2	79.4	79.2
	N9-Ca-N1	48.6	50.6	52.9	57.4
	Ca-N	2.612,2.627,2.63	2.614,2.6456,2.646	2.656,2.654,2.671	2.663,2.669,2.686
		2.633,2.625,2.618	2.646,2.639,2.634	2.670,2.664,2.655	2.671,2.669,2.679
		2.626, 2.622	2.646, 2.628	2.648, 2.662	2.671, 2.664
	Ca-N1	5.047	5.081	5.749	6.832
	Ca-N9	4.683	4.687	4.778	4.785
	Ca-N10	73.3	73.7	73.7	73.0
10	N3-Ca-N4	1.011	1.019	1.019	1.017
(8+2)	N-H	105.4	104.8	106.7	106.3
	H1-N1-H2	81.6	81.9	81.2	80.8
	N3-Ca-N5	80.4	81.2	75.3	68.1
	N1-Ca-N3	144.1	76.8	143.7	142.4
	N6-Ca-N4	140.7	140.1	142.4	143.5
	N8-Ca-N2	45.7	46.2	50.3	43.0
	N9-Ca-N7	80.3	80.5	79.6	79.6

Table 4.3(Continued)

a) A single N-H distance has been given since all calculated N-H distances were found to be the same to within \pm 0.001 Å.

Parameter		Ν	IP2	B3LYP		
п	(a)	Neutral	Cation	Neutral	Cation	
	Sr-N1	2.743	2.685	2.686	2.637	
	N- H	1.019	1.011	1.023	1.023	
1	Sr -N1-H3	112.3	113.9	112.1	113.6	
	H2-N1-H3	106.5	104.8	106.8	105.	
	Sr -N1-H2	112.3	113.8	111.9	113.5	
	Sr -N2	2.699,2.699	2.697,2.697	2.678,2.678	2.681,2.681	
	H-N	1.019	1.011	1.019	1.022	
2	H2-N2-H1	106.8	105.1	107.1	105.4	
	N1- Sr -N2	179.9	179.9	179.1	178.4	
	H4-N1- Sr	112.0	113.6	112.2	113.5	
	Sr -N	2.718,2.717,2.674	2.724,2.723,2.688	2.691,2.691,2.661	2.694,2.694,2.676	
	N1- Sr -N2	74.6	80.2	78.5	91.5	
3	N2-H3	1.021	1.019	1.025	1.023	
5	H6-N1-N4	106.3	104.9	106.6	105.	
	N1-Sr-N3	143.7	140.1	140.6	134.3	
	N3-Sr-N2	141.7	139.8	140.6	134.3	
	Sr -N	2.689,2.689,2.688	2.724,2.724,2.724	2.698,2.692,2.692	2.723,2.723,2.723	
		2.688	2.712	2.698	2.723	
	N3- Sr -N1	88.2	89.7	85.4	90.1	
4	N1-Sr-N2	91.8	90.3	101.6	90.1	
_	N2-Sr-N4	88.2	89.7	85.4	90.1	
	N4-Sr-N3	91.8	90.3	88.7	90.1	
	N-H	1.025	1.024	1.019	1.022	
	H6-N1-H4	106.3	105.0	106.5	1.019	
	Sr -N	2.699,2.702,2.699	2.686,2.721,2.721	2.681,2.691,2.690	2.699,2.724,2.727	
		2.699,2.689	2./11,2./11	2.701,2.699	2.725,2.724	
	$N_{5} - Sr - N_{2}$	88.5	89.0 80.1	90.0	89.0 01.6	
5	NJ-SI-INI N H	00.4	09.1 1.025	92.0	91.0	
5		1.022	1.025	1.020	1.024	
	$\frac{14-111-110}{N3}$	100.2	105.5	100.4	105.0	
	N_{1-} Sr $-N_{1-}$	8/ 8	81.5	87.6	87.1	
	N4-Sr-N2	84.8	89.0	92.4	93.6	
	Sr -N	2 703 2 703 2 703	2 725 2 725 2 725	2 717 2 716 2 717	2 737 2 736 2 736	
	DI IV	2,703,2,703,2,703	2.725 2.725 2.725	2,717,2,718,2,716	2,737,2,738,2,736	
	N3- Sr -N4	89.6	89.5	89.8	89.8	
	N-H	1.023	1.021	1.026	1.024	
6	H4-N1-H6	106.1	105.3	106.3	105.5	
	N3- Sr -N5	87.2	87.8	87.3	87.2	
	N1- Sr -N3	89.6	89.4	89.1	89.3	
	N6- Sr -N4	175.4	175.9	174.3	174.7	
7	Sr-N	2.722,2.722,2.728	2.745,2.745,2.754	2.741,2.748,2.752	2.764,2.771,2.774	
		2.724,2.724,2.729	2.749,2.749,2.757	2.749,2.755,2.746	2.771,2.778,2.769	
	N3- Sr -N4	2.734	2.755	2.753	2.777	
	N-H	95.8	92.1	110.8	110.8	
	H4-N1-H5	1.023	1.021	1.026	1.024	
	N3- Sr -N5	106.3	105.5	106.4	105.6	
	N1- Sr -N3	80.9	80.9	79.7	79.8	
	N6- Sr -N4	75.9	76.5	75.5	75.7	
	N7- Sr –N6	122.1	124.0	119.2	119.8	
		144.6	141.5	154.9	154.3	

Table 4.4Key calculated structural parameters for the lowest energy isomers of $Sr(NH_3)_n$
complexes and their cations. Distances are in Å and angles in degrees.

	Sr -N	2.757,2.757,2.757	2.782,2.781,2.781	2.793,2.793,2.793	2.815,2.815,2.815
		2.757,2.757,2.757	2.781,2.782,2.782	2.793,2.793,2.793	2.815,2.815,2.815
		2.757,2.757	2.782,2.781	2.793,2.793	2.815,2.815
	N3- Sr –N2	80.0	79.1	81.2	81.0
	N-H	1.021	1.011	1.024	1.023
	H5-N1-H6	105.9	105.3	106.2	105.6
8	N3- Sr –N7	78.9	79.0	78.8	78.3
	N1- Sr –N8	80.0	79.1	78.8	78.3
	N6- Sr -N4	80.1	79.1	81.2	81.0
	N7- Sr –N1	80.1	79.1	81.2	81.0
	N8- Sr –N5	80.1	79.2	81.2	81.0
	N6-Sr-N2	79.	79.0	78.8	78.3
	N4-Sr-N5	80.0	79.0	78.8	78.3
	Sr -N	2.757,2.761,2.762	2.776,2.785,2.791	2.790,2.795,2.799	2.816,2.818,2.821
		2.756,2.754,2.764	2.776,2.774,2.785	2.792,2.799,2.805	2.801,2.816,2.809
		2.755,2.752	2.776,2.778	2.774,2.792	2.806,2.816
	Sr-N5	4.685	5.035	4.855	5.044
	N3- Sr -N4	139.0	142.2	143.6	144.2
9	N-H	1.021	1.020	1.024	1.023
(8+1)	H6-N1-H4	105.8	105.4	106.1	105.7
	N3- Sr -N5	73.2	83.1	59.63	79.0
	N1- Sr -N3	145.3	142.4	141.6	141.5
	N6- Sr -N4	72.2	71.6	71.9	71.9
	N7- Sr –N6	72.4	71.5	71.6	71.8
	N9- Sr –N6	142.7	144.8	142.7	141.1
	Sr -N	2.741,2.746,2.745	2.751,2.757,2.756	2.780,2.805,2.798	2.806,2.812,2.811
		2.739,2.744,2.743	2.750,2.751,2.751	2.805,2.779,2.799	2.812,2.806,2.811
		2.733,2.738	2.742,2.749	2.783,2.785	2.797,2.797
	Sr-N3	5.005	5.056	5.088	5.113
	Sr-N2	4.826	4.832	5.083	5.115
10	N3- Sr -N4	37.9	37.9	50.3	38.0
(8+2)	N-H	1.028	1.024	1.025	1.024
(012)	H6-N1-H4	105.8	105.9	106.3	105.6
	N3- Sr –	38.4	38.2	34.3	38.0
	N10	81.5	81.2	78.0	78.8
	N1- Sr –N9	81.5	82.5	80.7	79.8
	N6- Sr –N8	81.5	79.8	80.4	79.2
	N8- Sr –N5	41.8		34.3	38.1

Table 4.4(Continued)

a) A single N-H distance has been given since all calculated N-H distances were found to be the same to with ± 0.001 Å.



Figure 4.12 Calculated structures of neutral $Ca(NH_3)_n$ and it cationic counterparts from calculations at the MP2 level.



Figure 4.12 (Continued)



Figure 4.13 Calculated structures of neutral $Sr(NH_3)_n$ and it cationic counterparts from calculations at the MP2 level.



Figure 4.13 (Continued)

For complexes with up two ammonia molecules, more than one isomer can be identified, and attempts were made to find these isomers and establish which has the lowest energy. For $M(NH_3)_2$ (M = Ca or Sr), two possible ammonia molecule arrangements were found, giving rise to the 2+0 and 1+1 isomers. The 2+0 isomer is significantly lower in energy than the 1+1 isomer, the difference being 0.093 eV for MP2 and 0.150 eV for DFT-B3LYP

calculations. For Sr(NH₃)₂ the corresponding energy differences are 0.305 eV for MP2 and 0.261 eV for DFT-B3LYP. These large differences for the lowest-lying isomers mean that the most stable isomer is the 2+0 isomer in these complexes, and the M-N bonding is stronger than the hydrogen bonding between inner and outer shell ammonia molecules. It therefore seems likely that the 2+0 isomer will be more abundant than the 1+1 complex in the molecular beam. In fact, we find that the same general principle applies to larger complexes, i.e. the structure that maximises occupancy of the inner solvation shell is found to be the global potential energy minimum.

The above considerations hold true for $M(NH_3)_n$ for n = 3 - 7 (M = Ca or Sr) on the basis of comparing the energy differences between their isomers [(n + 0, (n - 1) + 1 and (n - 2) + 2)]. As a result, in what follows the emphasis will be on the n + 0 complexes on the assumption that this will be the principal contributor to the photoionization data.

According to the DFT-B3LYP calculations there is a significant change in equilibrium structure for Ca(NH₃)₂ on ionization. DFT-B3LYP finds that Ca(NH₃)₂ is bent, with a N-Ca-N angle of 85° , while Ca(NH₃)₂⁺ is found to be a linear, with a N-Ca-N angle of 179.9° . The MP2 calculations find that both the neutral and the cation are bent with N-Ca-N angles of 80° (neutral) and 97° (cation). To establish the correct equilibrium structure for Ca(NH₃)₂⁺, a higher level of theory is needed. Therefore, MP3 calculation carried out with the same basis set used here to perform a geometry optimization for Ca(NH₃)₂⁺. Clearly, the MP3 level of theory displays the same equilibrium structure for Ca(NH₃)₂⁺ as the MP2 method and the minimum structure is still bent, with a N-Ca-N angle of 96.1° .

Ca(NH₃)₈ is something of a transition point in terms of structures. For the MP2 calculations, the 7+1 structure is higher in energy than the 8+0 isomer by 0.11 eV, whereas the DFT-B3LYP calculations predict that the 8+0 isomer is higher in energy than the 7+1 structure by 0.035 eV. For n = 9, both the MP2 and DFT-B3LYP calculations show that no stable 9+0

structure can be found, and the lowest-lying energy isomer is the 8+1 isomer. For n = 10, the MP2 level of theory predicts that the 8+2 is lower than that of the 7+3 isomer by 0.117 eV, while the DFT-B3LYP calculations predict that the 7+3 isomer is lower in energy than the 8+2 structure by 0.038 eV. Therefore, these calculations suggest that the first solvation shell of Ca(NH₃)_n is full once eight ammonia molecules are present.

The findings from the calculations for $Sr(NH_3)_n$ complexes and their cations are broadly similar to those for $Ca(NH_3)_n$ and $Ca(NH_3)_n^+$. However, one difference between the $Ca(NH_3)_8$ and $Sr(NH_3)_8$ complexes is that for $Sr(NH_3)_8$ complexes the MP2 and DFT-B3LYP calculations agree that the global minimum for n = 8 is the 8+0 isomer. In contrast to the calculations for $Ca(NH_3)_9$, the MP2 and DFT-B3LYP calculations for $Sr(NH_3)_9$ complexes have established that nine ammonia molecules can be accommodated in a single shell around a central strontium atom. However, the calculations predict that the total energy of the 8+1 isomer is lower than that of the 9+0 isomer by 0.021 eV and 0.133 eV at the MP2 and DFT-B3LYP levels, respectively. Together, these results provide important insights regarding the first solvation shell, which is excessively crowded for n = 9, and the release of this "strain" energy by switching to an 8+1 arrangement is beneficial energetically. For n = 10 the 8+2 structure clearly has the lowest energy. Thus, the calculations suggest that only 8 ammonia molecules can comfortably fit into the first solvation around Sr.

In principle, there are two broad types of structures possible between a metal atom and ammonia molecules. One option is 'interior solvation, where the metal atom is surrounded by ammonia molecules: this is the type of structure already considered above, However, it is also important to consider the possibility of a 'surface' structure, where the metal atoms reside on the surface of an ammonia cluster. Consequently, the possibility that $Ca(NH_3)_n$ and $Sr(NH_3)_n$ might adopt "surface" structures must also be considered. A prior published study has noted that the Mg atom is preferentially bound to the surface of an $(NH_3)_n$ cluster rather than adopting

an interior structure.⁵ Calculations were therefore carried out on two representative complexes, Ca(NH₃)₅ and Sr(NH₃)₅, to see if these might also adopt surface structures. These calculations predict that the surface and interior structures behave significantly differently. In particular, the surface structure shows a longer M-N distance and a much higher energy than the interior structure. For Ca(NH₃)₅, the total energies for the optimised surface structure are higher than the global minimum interior structure by 1.1 eV and 1.3 eV at the MP2 and DFT-B3LYP levels, respectively. For Sr(NH₃)₅, the corresponding energy differences are 1.0 eV and 0.98 eV. These are large energy differences and so it seems very unlikely that the surface structures would form in the experiments employed here.

We can confirm that surface structures are not made in the experiments by calculating the AIEs. The AIEs for the surface structures were found to be 4.392 eV and 3.903 eV for the surface structures of Sr(NH₃)₅ at the MP2 and DFT-B3LYP levels and 4.112 eV and 4.427 eV for the surface structure of Ca(NH₃)₅, respectively. These values are considerably higher than the experimental values of 3.549 and 3.490 eV for Ca(NH₃)₅ and Sr(NH₃)₅, respectively (see Tables 4.1 and 4.2). By comparison, the calculated AIEs of the interior structures for these complexes are in far better agreement with experiment and this shows that only the interior structures are formed in the molecular beam experiments reported here.

4.6 Conclusions

The experimental ionization efficiency curves of alkaline earth metal-ammonia complexes have been recorded for the first time and compared with the results of *ab initio* calculations. There is good agreement between the experimental AIEs and theoretical ionization energies based on the lowest energy structures of the complexes, suggesting that the calculated lowest energy isomers dominate in the molecular beam. The *ab initio* calculations predict that the neutral $Ca(NH_3)_n$ complexes can accommodate up to eight ammonia molecules in the first solvation shell, although these calculations have not established whether the 8+0 structure is more stable than the 7+1 isomer. For neutral $Sr(NH_3)_n$, the calculations clearly predict that the first solvation shell can accommodate up to eight ammonia molecules, and any additional ammonia molecules then enter a second shell.

The work in this chapter sets the scene for the experiments reported in Chapters 5 and 7, which describe the first IR spectra of $Sr(NH_3)_n$ and $Ca(NH_3)_n$, respectively.

References

- (1) Thompson, J. C. *Electrons in liquid ammonia*; Oxford University Press, 1976.
- (2) Lagowski, J. Synth. React. Inorg., Met.-Org. Nano-Metal Chem. 2007, 37, 115.
- (3) Cottrell, F. J. Phys. Chem. 1914, 18, 85.
- (4) Thompson, J. C. Oxford University Press: Oxford, **1967**.
- (5) Elhanine, M.; Dukan, L.; Maître, P.; Breckenridge, W.; Massick, S.; Soep, B. J.
 Chem. Phys. 2000, *112*, 10912.
- (6) Watanabe, K.; Marmo, F.; Inn, E. C. *Phys. Rev.* **1953**, *91*, 1155.
- (7) Watanabe, K. J. Chem. Phys. 1954, 22, 1564.
- (8) Watanabe, K.; Nakayama, T.; Mottl, J. J. Quant. Spectrosc. Radiat. Transf. 1962, 2, 369.
- (9) Rayane, D.; Melinon, P.; Cabaud, B.; Hoareau, A.; Tribollet, B.; Broyer, M. J. Chem.
 Phys. **1989**, *90*, 3295.
- (10) Guyon, P. M.; Berkowitz, J. J. Chem. Phys. 1971, 54, 1814.
- (11) Berkowitz, J.; Greene, J.; Cho, H.; Ruščić, B. J. Chem. Phys. 1987, 86, 1235.

- (12) Yoo, R.; Ruscic, B.; Berkowitz, J. J. Chem. Phys. 1992, 96, 911.
- Wucher, A.; Staudt, C.; Neukermans, S.; Janssens, E.; Vanhoutte, F.; Vandeweert, E.;
 Silverans, R.; Lievens, P. *New J. Phys.* 2008, *10*, 103007.
- (14) Knickelbein, M. B.; Yang, S.; Riley, S. J. J. Chem. Phys. 1990, 93, 94.
- (15) Yang, S.; Knickelbein, M. B. J. Chem. Phys. 1990, 93, 1533.
- (16) Yang, S.; Knickelbein, M. B. Z. Phys. D At., Mol. Clusters 1994, 31, 199.
- (17) Kooser, K.; Ha, D.; Itälä, E.; Laksman, J.; Urpelainen, S.; Kukk, E. J. Chem. Phys.
 2012, 137, 044304.
- (18) Frisch, M. J. T., G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb,; M. A.; Cheeseman, J. R. M., J. A., Jr.; Vreven, T.; Kudin, K.; N.; Burant, J. C. M., J. M.; Iyengar, S. S.; Tomasi, K.; Barone, V.;; Mennucci, B. C., M.; Scalmani, G.; Rega, N.; Petersson, G. A.;; Nakatsuji, H. H., M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.;; Ishida, M. N., T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li,; X.; Knox, J. E. H., H. P.; Cross, J. B.; Bakken, V.; Adamo, C.;; Jaramillo, J. G., R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.;; Cammi, R. P., C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.;; Voth, G. A. S., P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, et al. *Gaussian Inc., Wallingford, CT* 2004, *26*.
- (19) <u>https://bse.pnl.gov/bse/portal</u>.
- (20) Hay, P. J.; Wadt, W. R. J.Chem. Phys. 1985, 82, 299.
- (21) Lias, S.; NIST, Gaithersburg MD, 1998.
- (22) <u>http://physics.nist.gov/PhysRefData/Handbook/Tables/calciumtable1.htm</u>.
- (23) http://physics.nist.gov/PhysRefData/Handbook/Tables/strontiumtable1.htm.
- (24) Wood, D. M. Phys. Rev. Lett. 1981, 46, 749.
- (25) Smith, J. M. AIAA Journal 1965, 3, 648.
- (26) Takasu, R.; Hashimoto, K.; Fuke, K. Chem. Phys. Lett. 1996, 258, 94.

- (27) Hertel, I.; Hüglin, C.; Nitsch, C.; Schulz, C. Phys. Rev. Lett. 1991, 67, 1767.
- (28) Misaizu, F.; Tsukamoto, K.; Sanekata, M.; Fuke, K. *Chem. Phys. Lett.* 1992, 188, 241.
- (29) Lee, G.; Arnold, S.; Eaton, J.; Sarkas, H.; Bowen, K.; Ludewigt, C.; Haberland, H. Z Phys. D At., Mol. Clusters 1991, 20, 9.

Chapter 5

IR spectroscopy of Sr(NH₃)_n complexes

5.1 Introduction

Alkali metals provide a good example for studying electron solvation. These metals readily dissolve in ammonia, where the electrons originate from the outer valence electrons on the metal atom and are lost to the solvent.^{1,2,3} Equally important, alkaline earth metals are also known to dissolve in liquid ammonia ⁴ and can be considered as molecular models for the metal-ammonia complex, presenting microscopic details about the solvated electrons.⁵ However, by contrast with the alkali metals, complexes of alkaline earth metals with ammonia in the gas phase have received scant attention. For heavier alkaline earth metals there have been no studies of their complexes with ammonia molecules prior to the work reported in Chapter 4 of this thesis. In Chapter 4 a photoionization investigation of the Ca(NH₃)_n and Sr(NH₃)_n complexes was reported along with *ab initio* calculations. The calculations suggest that the formation of interior structures, that is, an alkaline earth atom surrounded by one or more shells of ammonia molecules, is favoured over surface structures. However, the structures deduced from the calculations could not be confirmed using mass spectrometry. To attempt to confirm the preference for interior structures, infrared spectra of the heavier alkaline earth-ammonia complexes in the gas phase are reported in this chapter using a photodepletion technique.

There has been only one prior study of the infrared spectroscopy of alkaline earthammonia complexes, which focused on cationic $Mg^+(NH_3)_n$ complexes.⁶ Infrared spectroscopy in the N-H stretching region was applied to these complexes using mass selective photodissociation. Supporting theoretical calculations predicted that a single hydrogen bond between ammonia molecules would be observed in a band significantly red-shifted from free ammonia molecules relative to the N-H stretching frequency of the gas phase ammonia molecule. The infrared photodissociation experiments found IR absorption bands only from 3000 to 3500 cm⁻¹. These infrared photodissociation results show no clear evidence of large frequency reduction were observed for the N-H stretches of ammonia, suggesting that either all of the ammonia molecules were directly interacting with the Mg⁺ ion or an additional ammonia molecules in the second solvent shell were weakly interacting with two ammonia molecules in the inner solvation shell via hydrogen bonds.

The aim of the current chapter is to explore the microscopic nature of solvation by using IR photodepletion spectra in the N-H stretching region for $Sr(NH_3)_n$ complexes. As will be seen, this only works for relatively large complexes because of their low metal-ammonia binding energies.

5.2 IR photodepletion spectroscopy mechanism

Infrared spectroscopy on complexes has been possible for many years using conventional absorption spectroscopy. However, this technique is not an option for molecules in molecular beams because of the low density of molecules. Consequently other, more sensitive, techniques are needed.

Infrared photodissociation spectroscopy has proven to be a powerful tool for investigating the structural properties of metal-solvent complexes in the gas phase, especially if accompanied by sophisticated quantum mechanical calculations to aid the interpretation of the vibrational spectra obtained. The infrared photodissociation spectroscopy of complexes relies on the rapid distribution of the absorbed photon energy. The deposited energy is transferred internally from the initially excited vibrational mode to other vibrational modes (i.e., nearly isoenergetic states), a process known as intramolecular vibrational energy redistribution (IVR). Eventually, this process can lead to dissociation of part of the complex. In the spectroscopic work reported here the energy redistribution is assumed to be sufficiently fast to overcome the binding energy of the M-N bond, yielding a photofragment that has at least one less NH₃ molecule than the original absorbing complex.

The mechanism of IR photodepletion spectroscopy can be grasped from Figure 5.1. A pulsed UV laser is used to ionize $M(NH_3)_n$ complexes in the gas phase, and the intensity of the ion signal is observed by a mass spectrometer. The IR laser pulse, which is introduced just prior to the UV laser pulse, can induce photodissociation of the complex via excitation of the fundamental N-H stretching modes in ammonia molecules. Excitation of these vibrations, which usually fall within the 3000 to 3500 cm⁻¹ region, can lead to dissociation of the M-N bond via IVR. As a consequence, by scanning the IR laser frequency, IR spectra of mass-selected complexes can be observed as the decreasing intensity of the ion signal for the ionized parent complex with the wavenumber of the IR laser. With this mechanism, a mass selective IR spectrum of $M(NH_3)_n$ can be recorded via IR-induced depletion of the $M(NH_3)_n^+$ ion signal.



Figure 5.1 Mechanism for IR photodissociation spectroscopy.

There are two possible complications with the IR photodissociation spectroscopy technique. One important challenge arises when the photon energy is too small to cause any dissociation of the complex, and therefore the IR photodissociation technique will not register any absorption. Another experimental challenge comes from the dissociation of the $M(NH_3)_n$ complexes after photodepletion. This may lead to the formation of smaller complexes, which can be ionized by the UV laser, leading to an increase in the new ion signal for $M(NH_3)_{n-1}^+$ created from depletion of $M(NH_3)_n$. Consequently, any attempt to record the depletion spectrum by following the $M(NH_3)_{n-1}^+$ signal is complicated by the possibility of contributions from both depletion and production.

There are steps that can be taken to minimise this competition between signal production and signal depletion. In particular, if we alter the expansion conditions such that the $M(NH_3)_{n}^+$ ion signal is significantly larger than the $M(NH_3)_{n+1}^+$ signal, then any depletion of the latter will make only a small 'production' contribution to the former. Wherever possible we have tried to operate under such conditions, as will be seen later.

5.3 Experimental section

Full details of the experimental setup and apparatus are provided in Chapter 2 of this thesis, and so only a summary is presented here. $Sr(NH_3)_n$ complexes were formed by laser-ablating a solid strontium target with the second harmonic (532 nm) of a small Nd:YAG laser in an atmosphere of pure ammonia. Neat ammonia at a typical pressure of 2 bar was delivered from a pulsed valve and passed over the surface of the metal target before expanding into the source chamber to form a supersonic jet, thereby cooling translational and rotational degrees of freedom. The jet-cooled expansion was introduced into an ionization chamber of a Wiley-McLaren time-of-flight mass spectrometer via a skimmer to form a molecular beam. In this ionization region, the molecular beam is intersected by two pulsed laser beams. The first beam operated in the ultraviolet (UV) and was provided by the output of a pulsed tunable dye laser with frequency doubling. This pulsed laser beam is used to ionize the complexes by single photon ionization. The pulses in the second (IR) beam, firing at ~ 50 ns prior to the UV laser pulse, excite spectroscopic transitions. Note that the time delay between the IR and UV lasers could be varied from ~ 0 ns to several hundred nanoseconds with little impact on the infrared spectra. For the work reported in this chapter the delay was kept close to 50 ns. Because all of the spectra were recorded in the mid-infrared region in this thesis, the output from a LaserVision tunable OPO/A was employed. When the IR beam is resonant within a stretching vibrational transition of a specific Sr(NH₃)_n complex, the absorption process can then be detected if the energy absorption leads to removal of at least one ammonia molecule. This photoabsorption is evident by the decrease in the Sr(NH₃)_n⁺ signal detected by the mass spectrometer.

5.4 Computational Details

The *ab initio* calculations using the GAUSSIAN 03 program package⁷ were carried out on the $Sr(NH_3)_n$ (n = 1-10) complexes using both second-order Møller-Plesset perturbation theory (MP2) and density functional theory (DFT with the B3LYP functional) to aid in interpreting the experimental results.

The basis sets used in this thesis were carefully selected. For the strontium atom, a double-zeta basis set with a relativistic effective core potential (ECP28MWB), known as the Stuttgart RSC 1997 ECP, proved to be the best choice⁸ due to the large number of core electrons in the strontium atom (see complete details in Chapter 3 in the thesis). It includes d-type
polarization functions.⁹ When exploring a range of complexes with up to ten ammonia molecules, a trade-off must be made between calculation accuracy and computational cost. Therefore, larger basis sets have not been used here and to maintain a balanced overall basis set the standard Pople double zeta 6-31+G(d,p) basis sets were used for hydrogen and nitrogen atoms.

Calculations were carried out for both the neutral and cationic complexes. The optimized structures for each of the neutral and cation $Sr(NH_3)_n$ complexes were checked to ensure that they were true minima by making sure that there were no imaginary vibrational frequencies. All theoretical calculations were run without symmetry constraints to allow variation in all degrees of freedom.

To compare the theoretical calculations with the experimental IR spectra, the calculated harmonic vibrational frequencies were scaled by multiplying factors of 0.932 and 0.949 using the MP2 and DFT-B3LYP methods, respectively, with the same basis sets employed here. These scaling factors were chosen to bring the calculated N-H stretching vibrational frequencies of the isolated ammonia molecule into best agreement with the experimental values.

It is to be noted that the equilibrium structures predicted by MP2 and DFT-B3LYP methods show slight differences in the orientation of the ammonia molecules. However, the prediction of the equilibrium geometries is largely the same in both the cases. Also all theoretical calculations predicted by both the MP2 and DFT-B3LYP methods have similar harmonic vibrational frequencies with different scaling factors. Therefore, the results from DFT-B3LYP calculations are not shown in this chapter, unless otherwise stated.

5.5 Results and Discussion

5.5.1 Mass spectrometry

Both Figures 5.2(a) and 5.2(b) show typical mass spectra derived from the $Sr(NH_3)_n$ complexes (n = 1-14) as a function of the mass-to-charge ratio (m/z), which were recorded under the same expansion conditions at the relatively short UV laser wavelength of 346 nm (3.584 eV). A wavelength of 346 nm was selected to show the range of complexes formed in the molecular beam.

Figure 5.2(a) shows a typical photoionization mass spectrum in the absence of the IR laser pulse. The most intense peak in this particular mass spectrum corresponds to $Sr(NH_3)_8^+$, indicating that this complex is formed preferentially and likely has some enhanced stability relative to the neighbouring complex ions. The mass spectrum shows a steady decrease in ion signal with *n* for *n* > 8, an observation that is also due to the closing of the first solvation shell around the strontium atom, as discussed in more detail in Chapter 4. As expected at a wavelength of 346 nm, only complexes with $n \ge 3$ are ionized by a single photon. The substantial Sr⁺ signal is presumed to result from two-photon ionization.

In Figure 5.2(b), a mass spectrum of $Sr(NH_3)_n$ is shown with the IR laser frequency fixed at 3153 cm⁻¹ and timed to fire 50 ns prior to the ionizing laser pulse. The IR beam was mildly focused into the ionization chamber and possessed a typical pulse energy of at most 2.5 mJ per pulse at a repetition rate of 10 Hz. When the IR laser pulse is in resonance with an N-H stretching transition of one or more of the complexes, photofragmentation involving the loss of one or more NH₃ molecules can be observed. The mass spectrum shows a signal reduction of ~ 75% in the $n \ge 8$ channels, which is a relatively large effect. This behaviour may be attributed to photodepletion of corresponding neutral complexes, indicating that the binding energies for $n \ge 8$ are smaller than the energy of the IR photon. Moreover, in this figure, the IR spectrum shows ion production for n = 6 and 7. All of these IR depletion and production ion signals are discussed in more detail later.



Figure 5.2 Mass spectra recorded for $Sr(NH_3)_n$ complexes, where (a) IR laser was blocked and (b) IR laser is on resonance. The UV laser wavelength used was 346 nm and IR laser was set at 3153 cm⁻¹. The two spectra are the result of 1000 consecutive laser shots and recorded on exactly the same vertical scale.

5.5.2 Infrared photodissociation spectroscopy

The infrared photodepletion spectra of the isolated $Sr(NH_3)_n$ complexes for n = 8-10 have been recorded in the N-H stretching region for the first time in this thesis, as shown in Figure 5.3. Moreover, we have successfully recorded IR photodepletion spectra for $Sr(NH_3)_n$ complexes up to n = 14 under different experimental conditions, which will be explained in more detail in section 5.5.3. For cluster sizes $n \ge 15$ it was not possible to record spectra because of the low signal-to-noise ratio.

As previously mentioned, there are possible challenges with the IR photodissociation technique used here (See Section 5.2 for more details). These challenges may arise when there is resonance with a vibrational mode of the $Sr(NH_3)_n$ complex which induces dissociation into $Sr(NH_3)_{n-1}$ and NH_3 . In this case the $Sr(NH_3)_n^+$ signal will be depleted by the IR absorption. However, the resulting $Sr(NH_3)_{n-1}$ can be ionized by the UV laser pulse, which leads to an increase in the amount of $Sr(NH_3)_{n-1}^+$. Thus ion production may lead to decreased ion signal when we try to look for the photodissociation spectrum of $Sr(NH_3)_{n-1}$ by depletion. Competition between photoproduction and IR photodepletion could distort the IR spectrum and lead to misleading conclusions about contributions from heavier complexes, unless this cascade effect is very small. Furthermore, the mass spectra displayed in Figure 5.2 show a monotonic decrease in complex ion intensity with increasing complex size for $n \ge 8$, indicating that the change in ion signal in a particular mass channel for $n \ge 8$ should be dominated by contributions from depletion of the neutral complexes.

The IR photodissociation spectra for n = 8-10, shown in Figure 5.3, exhibit two strong IR depletion bands between 3100 and 3250 cm⁻¹. These bands have similar relative intensities and almost identical positions for the three different sized complexes. However, an additional band is seen for Sr(NH₃)₁₀ shifted to higher vibrational frequencies compared to the other two IR absorption bands. For comparison, the IR spectrum of the isolated ammonia molecule shows two N-H stretching bands: the N-H symmetric stretch (v_1) at 3334 cm⁻¹ and the N-H antisymmetric stretch (v_3) at 3444 cm⁻¹.¹⁰ Therefore, the bands of Sr(NH₃)_n are considerably red-shifted from those of free ammonia. These observations will be discussed in more detail in the following sections along with the theoretical calculation spectra for each structure, taking each complex in turn.



Figure 5.3 Experimental IR photodepletion spectra of $Sr(NH_3)_n$ for n = 8-10 in the N-H stretching region.

5.5.2.1 <u>Sr(NH₃)</u>8

In Figure 5.4 the IR photodepletion experimental spectrum for the N-H stretching region (top panel) by monitoring the $Sr(NH_3)_8^+$ ion depletion. The IR spectrum was measured by considering the loss of the channel ammonia molecule. Two distinct IR depletion bands were observed within the frequency range of 3100 -3200 cm⁻¹ for $Sr(NH_3)_8^+$ spectrum. The first of the two strong bands peaks at ~ 3145 cm⁻¹, and the second band is centred at ~ 3191 cm⁻¹, evidently representing a marked redshift from that of the N-H stretching bands of gaseous ammonia as mention earlier due to the coordination between the Sr metal and the ammonia

molecules via the Sr-N bond. This large red shift upon coordination indicates the strong Sr-NH₃ interaction, which will discuss in more detail farther in this chapter.

To investigate and provide details about the geometric structure and relative energies of the complex, the experimental IR photodissociation spectrum is compared with the predictions from theoretical calculations in Figure 5.4. The notation p + q is used to distinguish between possible isomers, where p is the number of ammonia molecules nominally within the first solvation shell and q is the number of ammonia molecules in the second shell around the central Sr atom. The predicted IR spectra of the corresponding four isomers, 8+0, 7+1, 6+2, and 5+3 were carried out with MP2 and DFT-B3LYP methodologies level of theories. The first three lowest energies structures with relative energies and their IR spectra are shown in Figure 5.4.

The calculations find that the n = 8+0 structure has the lowest optimized energy, corresponding to a geometry with eight ammonia molecules in a single shell around the central strontium atom. Each ammonia molecule attaches to the Sr atom via a bond with the N atom. This result was already presented in Chapter 4. The 7+1 structure is higher in energy than the 8+0 isomer by 0.263 eV at the MP2 level and 0.520 eV at the DFT-B3LYP level. All the inner seven ammonia molecules are directly bonded to the metal atom, forming the first solvation shell. The eighth ammonia molecule is in a second shell and is bonded to two ammonia molecules in the first solvation shell via distorted hydrogen bonds according to the MP2 calculations. However, the DFT-B3LYP calculations predicted a single hydrogen bond between the NH₃ molecule found in the second solvation shell and one ammonia molecule in the inner solvation shell. As shown in the lowest panel of Figure 5.4, the 6+2 structure is 0.545 eV and 0.312 eV above the global minimum at MP2 and DFT-B3LYP levels, respectively. The 5+3 isomer structure has such a high energy that it is likely to make a negligible contribution

to the experimental spectra. Accordingly, this structure will not be considered as a part of discussion.

The results obtained from the predicted IR spectra of all the above mentioned three isomers by MP2 calculations are compared with the experimental IR spectrum in an attempt to identify the possible geometric structures that may contribute to the experimental IR spectrum. The theoretical IR absorption spectrum for the 8+0 structure predicts two peaks at low resolution, which are demonstrated as a single strong IR absorption band. As shown in the second top panel of Figure 5.4, the 8+0 spectrum exhibits an intense peak at ~ 3183 cm⁻¹ and a medium intensity peak at ~ 3186 cm⁻¹. Each of these peaks is composed of very closely spaced two different N-H peaks. The predicted peak predicted at ~ 3183 cm⁻¹ is composed of two strong peaks having similar wavenumber and intensity. These two peaks possess similar mode of the vibrational frequency and corresponds to the vibrations of the ammonia molecules moving in-plane and out-of-plane towards each other. The peak of medium intensity at ~ 3186 cm⁻¹ arises due to the asymmetric N-H stretching vibration of the eight ammonia molecules around the central strontium atom. The symmetric stretching frequency of the NH₃ molecules is substantially weaker, thus it can hardly be identified in the experimental IR spectrum.

The calculations show that the less symmetric 7+1 spectrum has more N-H stretching bands, as seen in Figure 5.4. Moreover, the ammonia molecule in the second solvation shell is redshifted to a lesser extent than those in the first solvation shell. Hence, this mode is actually attributable to the asymmetric N-H stretching of NH₃ in the first solvation shell. The calculated IR bands are spread over a slightly larger range 3100–3300 cm⁻¹, indicating that the n = 7+1structure does not relate to any possible experimental structure. Moreover, in order to estimate could possibly determine the relative contribution of the 8+0 and 7+1 complexes, assuming a Boltzmann distribution. The energy difference between 8+0 and 7+1 complexes is 0.263 eV, then the abundance of the 7+1 complex relative to the 8+0 complex is 3.58×10^{-5} . This gives rise to the abundance of the 7+1 complex with respect to 8+0 of less than 0.008% at a temperature of 298 K (since the temperature of the gas is not known as mention in chapter 2 of this thesis). Even if the temperature is assumed to be much higher (say 1000 K) the abundance of the 7+1 complex is still less than the 8+0 due to its low concentration. Therefore, the 7+1 complex is considered an unlikely to dominate the molecular beam.

In the 6+2 structure the predicted IR bands are also found to spread over a considerably wider spectral range ($3100-3350 \text{ cm}^{-1}$) than those observed in the experimental IR spectrum ($3100-3200 \text{ cm}^{-1}$). Consequently, this does not contribute to the experimental IR photodepletion spectrum.



Figure 5.4 IR photodepletion spectra of Sr(NH₃)₈ in the N-H stretching region (top spectrum). Calculated MP2 spectra for different isomers are shown in the lower panels.

It is worthwhile comparing the experimental IR photodepletion spectrum for $Sr(NH_3)_8$ with those of $Mg(NH_3)_n^+$ complexes reported by Ohashi *et al.*⁶ The findings of Ohashi *et al.* are shown in Figure 5.5 for n = 3-6. The IR spectra for $Mg(NH_3)_n^+$ show two partly resolved bands for n = 5 and 6, one peaking at 3095 cm⁻¹ and the second band at 3135 cm⁻¹.

The experimental IR spectrum of $Sr(NH_3)_8$ is similar to these spectra of $Mg(NH_3)_5^+$ and $Mg(NH_3)_6^+$ reported by Ohashi *et al.* are seen in Figure 5.5. Both are dominated by two distinct IR bands and these bands that are red-shifted with respect to these in free NH₃. Moreover, the interesting aspect of these spectra is the spacing between these two absorption IR bands for all of complexes. The spacing between two bands for Sr(NH₃)₈ is found to be nearly the same as for $Mg(NH_3)_n^+$ complexes, signifying the ammonia molecules in each complexes exist in similar environments. The similarity of these spectra implies that all of these complexes have all ammonia molecules bound directly to the metal center, and there are not ammonia molecules in bridging sites in the second solvation. However, while Ohashi et al. have seen two partly resolved bands in each spectra, they provided no explanation, why there might be two bands when theory predicts only one. In order to enable a full interpretation of these vibrational spectra, it is expected that anharmonic coupling including overtone and combination modes is required to accurately predict the vibrational spectrum of $Sr(NH_3)_n$ complexes. It is therefore possible that the splitting is caused by an anharmonic effect. Another possible explanation is that more than one low lying potential energy minimum energy structure may be found in the molecular beam, all based on a single solvation shell with eight ammonia molecules around the central Sr metal, and thus the observed spectrum may comprise of contributions from these isomers.

In the calculated IR spectrum, the substantial redshift bands with respect to free ammonia is predicted in agreement with the experimental IR photodepletion bands. Thus, this suggests that the vibrations of the eight ammonia molecules within the $Sr(NH_3)_n$ complex are perturbed by interactions with the strontium metal.



Figure 5.5 IR photodepletion spectra of isolated $Mg(NH_3)_n^+$ complexes in the N-H stretching region. This figure is reproduced from ref.⁶

5.5.2.2 <u>Sr(NH₃)</u>9

The experimental IR photodepletion spectrum of the $Sr(NH_3)_9$ complex is shown in the upper panel of Figure 5.6 with corresponding calculated IR spectra in the three panels below. In the IR photodepletion spectrum two strong IR depletion bands are present at ~ 3146 and ~ 3196 cm⁻¹, which is very similar to the $Sr(NH_3)_8$ case.

Three typical structures of the $Sr(NH_3)_9$ complex, namely the 9+0, 8+1 and 7+2 structures, with relative calculated energies and their IR spectra are summarized in Figure 5.6. The lowest energy structure of the n = 8+1 is found to have two solvation shell structures. The structure of n = 9+0, in which all the ammonia molecules are directly bonded to the Sr atom has a slightly geometric distortion in order to minimize the steric interactions. The bond distance of Sr-N bond where the bond is formed between the strontium atom and nitrogen of the three ammonia molecules is predicted to be 2.859 Å. The bond distance of these three ammonia molecules is notably longer than the bond distance of the other six ammonia molecules bound with the Sr atom, which predicted as 2.785 Å. As has already been mentioned in Chapter 4 of this thesis, the theoretical calculations predict that this structure is higher in energy than the 8+1 structure by an amount of 0.021 eV. It could be observed that there is a similarity in the predicted energy between the n = 9+0 and 8+1 isomers, which has become an area of particular interest in this study. The next lowest energy isomer of the 7+2 structure is predicted to be higher in energy than the 8+1 structure by 0.231 eV and 0.138 eV by the MP2 methods and by at the DFT-B3LYP calculations, respectively.

The 8+1 spectrum shows intense band centered at ~ 3180 cm^{-1} with a weak band extending to the higher frequency of the N-H stretching region, indicating that the presence of a ninth ammonia in the outer solvation shell, which is hydrogen bonded and shared between two inner solvation shell ammonia molecules. The spectrum for 9+0 structure is predicted to be considerably more intense band which appear at ~ 3190 cm^{-1} . The calculated IR spectrum for the 7+2 structure is predicted to produce more peaks with lower intensity for the N-H stretch, spreading over the large region between 3100 and 3300 cm⁻¹. This is attributed to the fact that the presence of the ammonia molecules in the outer solvation shell, which is more unlikely observed in the experimental IR spectrum.

The small difference between the energy of 9+0 and 8+1 structures may mean that both isomers would form in the molecular beam and contribute to the experimental IR spectrum. In other words, the experimental spectrum of $Sr(NH_3)_9$ with well-resolved absorption bands could plausibly be attributed to one or both structures.



Figure 5.6 IR photodepletion spectra of isolated Sr(NH₃)₉ in the N-H stretching region (top spectrum). Calculated MP2 spectra for different isomers are shown in the lower panels.

5.5.2.3 Sr(NH₃)10

Figure 5.7 shows the experimental IR photodepletion in the upper panel and the predicted IR spectra in the lower four panels of the isolated $Sr(NH_3)_{10}$ complex for the N-H stretching region, which is determined as the depletion of the ion signal caused by the vibrational frequency. There are two prominent IR absorption bands centred at ~ 3146 and ~ 3199 cm⁻¹ with an additional band at around 3271 cm⁻¹ as observed from the IR experimental spectrum as depicted in the figure. The absorption intensity of these two bands are found to be lesser than that of the experimental IR depletion bands for the *n* = 9 and 8.

The calculations predict the complex $Sr(NH_3)_{10}$ to have four isomer structures, namely 10+0, 9+1, 8+2, and 7+3 structures and are summarized in Figure 5.7 with relative calculated energies and their IR spectra. The theoretical calculations predict that the lowest energy structure, adopting a 8+2 with the two outer-shell ammonia molecules are attached to three inner-shell ammonia molecules by forming two hydrogens bonds. The second lowest energy isomer, n = 9+1, has a small difference in the predicted energy from 8+2 isomer by 0.021 eV. The next lowest energy isomer for the n = 10+0 which has a slightly geometric distortion, with ten ammonia molecules bonded directly to the strontium atom like that of the n = 9+0 structure. The proximity of the two ammonia molecules leads to weak bonding with the strontium atom. It is reasonable to expect the presence of two NH₃ molecules in the first solvation shell. This structure is predicted to be higher in energy than the 8+2 structure by 0.119 eV. The third lowest energy structure, the 7+3 isomers, is found to be higher in energy than the 8+2 structure by 0.185 eV. Therefore, this isomer is considered an unlikely candidate for the molecular beam and should not contribute to the experimental IR spectrum.

As a consequence, a comparison of the theoretical spectrum with that of the experimental IR depletion spectrum in terms of energy and the position bands for the 8+2 and 9+1 structures is highly consistent with the experimental IR spectrum. Thus, this structure has the maximum probability to be formed in the molecular beam. Moreover, assuming the Boltzmann distribution and taking into account the possibility of the relative contribution of the 8+2, 9+1 and 10+0 isomers in the molecular beam, then the abundance of the 9+1 and 10+0 isomers relative to the 8+2 are 0.442 and 9.73×10^{-3} , respectively, at a temperature of 298 K (since the temperature of the system is not known). These results clearly predict a very a small contribution from a 10+0 isomer and much higher abundance of 9+1 isomer to the experimental IR spectrum. Therefore, 8+2 and 9+1 isomers would form in the molecular beam.



Figure 5.7 IR photodepletion spectra of Sr(NH₃)₁₀ in the N-H stretching region (top spectrum). Calculated MP2 spectra for different isomers are shown in the lower panels.

5.5.3 Larger $Sr(NH_3)_n$ complexes (n = 11-19)

5.5.3.1 Mass spectrometry

In Figures 5.8(a) and 5.8(b), typical photoionization mass spectra of the larger sized $Sr(NH_3)_n$ complexes recorded under different experimental conditions are shown. Worth noting is that the short wavelength of the ionization laser is maintained at 346 nm (3.584 eV). Pure ammonia gas at ~ 2 bar was employed with the same background pressure used in Figures 5.2a and 5.2(b) (see section 5.5.1 in this chapter).



Figure 5.8 Mass spectra recorded for $Sr(NH_3)_n$ complexes, where (a) the IR laser off resonance and (b) IR laser on resonance. The UV laser wavelength used was 346 nm and the IR laser was set at 3153 cm⁻¹. The two spectra are the result of 1000 consecutive laser shots and recorded on exactly the same vertical scale.

Relative to the mass spectra recorded for $Sr(NH_3)_n$ complexes where $n \le 10$, the differences between the spectra for these larger complexes are obtained by adjusting the delay between the ionization laser firing and the cooling gas pulsed valve opening. The delay time for the Nd:YAG ablation laser with respect to the pulsed nozzle opening was set in such a manner that maximum, and hence the size distribution of complexes. The rest of the settings for the experiments remain similar as has been recorded mass spectra for $n \le 10$.

It is useful to compare these results to those obtained in section 5.5.1 for complexes produced under different experimental conditions. The Figure 5.8(a) shows a typical

photoionization mass spectrum of the isolated $Sr(NH_3)_n$ complexes up to n = 19 which were made in the absence of the IR laser pulse.

Figure 5.8(b) shows a mass spectrum of the $Sr(NH_3)_n$ complexes with the IR laser frequency fixed at 3153 cm⁻¹ and timed to fire ~ 50 ns prior to the ionizing laser pulse for inducing a resonant photodepletion of the complex via vibrational excitation. There is similarity of the spectra of Figures 5.8(b) and 5.2(b), although there are moderate differences in their respective band intensities. It is therefore evident that the majority of depletion takes place for $n \ge 8$, as was expected. A comparison between the two IR depletion mass spectra, Figure 5.2(b) and 5.8(b), showed that the ion signal of the IR spectrum in Figure 5.8(b) reached a value of 40%.

5.5.3.2 Infrared photodissociation spectroscopy

The experimental vibrational predissociation spectra of the $Sr(NH_3)_n$ complexes for the n = 11-14 are shown in Figure 5.9. These spectra simply have a broad IR absorption bands ranging from 3100 to 3400 cm⁻¹, unlike that of the IR depletion spectra found for the n = 8-10 (see section 5.5.2). It should be mentioned that the theoretical calculations of the larger sized $Sr(NH_3)_n$, where $n \ge 11$ complexes, have not yet done in this thesis because of the high computational cost in searching the potential energy surface than for $n \le 10$. An attempt to analyse these spectra has made by analogy with $Sr(NH_3)_{10}$. The broader IR absorption bands can be attributed to the presence of ammonia molecules in two different solvation shells for these complexes. As seen in this figure strong IR bands are observed in the 3150-3250 cm⁻¹ region corresponding to absorption the first shell ammonia molecules whereas these bands blue-shifted band is probably due to the excitation of other ammonia molecules which are not attached to the central strontium metal, which have vibrational structure near the frequency of the free ammonia frequency.



Figure 5.9 Experimental IR photodepletion spectra of $Sr(NH_3)_n$ for n = 11-14 in the N-H stretching region.

5.5.4 Infrared photoproduction spectroscopy

The IR spectra of the Sr(NH₃)_n complexes for n = 6 and 7 have two distinct bands as seen in the lower panel of Figures 5.10(b) and 5.11(b), respectively. A strong intense band peaked at ~ 3148 cm⁻¹ and less intense band centred at ~ 3194 cm⁻¹ are shown in the n = 6 complex. The spectrum of the n = 7 complex has a strong intense band at ~ 3146 cm⁻¹ and a slightly less intense band at ~ 3197 cm⁻¹. It should be noted that these observed IR photoproduction spectra were recorded under the same expansion conditions as the IR photodepletion spectra reported for $n \le 10$ as mentioned earlier in this chapter. In comparison of the IR photoproduction spectra for n = 6 and 7(lower panel, Figures 5.10 and 5.11, respectively) with absorption IR photodepletion spectra for n = 8 and 9 (upper panel, Figures 5.10 and 5.11, respectively), finds that the IR photoproduction spectra are in good agreement with the photodepletion spectra. The IR depletion observed in the n = 8 channel approximately mirrors production in n = 6. The IR photoproduction for n = 7 and absorption IR photodepletion spectrum for n = 9 are also found to be approximately mirror images of each other. This results provide strong evidence that the ion production in the n = 6 and 7 channels arise from photodepletion in n = 8 and 9 through loss of more than one NH₃ molecule after absorption of the IR photon.



Figure 5.10 Experimental IR photoproduction (a) of $Sr(NH_3)_8$ and photoproduction (b) of $Sr(NH_3)_6$.



Figure 5.11 Experimental IR photoproduction (a) of $Sr(NH_3)_9$ and photoproduction (b) of $Sr(NH_3)_7$.

5.5.5 Dissociation energies

As already observed in the interpretation of the IR depletion spectra, the efficiency of single photon IR absorption is strongly enhanced in a given mass channel. This makes resonance on a vibrational fundamental possible, which means that the intramolecular vibrational energy redistribution (IVR) transfers energy throughout the complexes and the Sr-N binding energy is weakest, so that the Sr-N bond is easier to break. A complete understanding of the infrared photodepletion spectra of the Sr(NH₃)_n complexes therefore requires exploration of the Sr-N bond dissociation energy (D_0). The energy required to remove at least one ammonia molecule from the complexes for the range n = 1-10 has been investigated at both the MP2 and the DFT-B3LYP level of theories.

To calculate the dissociation energies of complexes, only the lowest-energy structure have been taken into account in each case. The theoretical calculations use the supermolecule approach, i.e.

$$D_0[Sr(NH_3)_n] = E[NH_3] + E[Sr(NH_3)_{n-1}] - E[Sr(NH_3)_n]$$
(5.1)

Here, D_0 represents the dissociation energy for the removal of at least one ammonia molecule from a given complex, and *E* amounts to the total energy of the isolated complex or fragment at equilibrium structure, including the zero point vibrational energy. The IR-induced photodepletion of Sr(NH₃)_n complexes has been found to take place between n = 8 and 14. The results are shown in Table 5.1 and depicted in Figure 5.12 as a function of increasing number of ammonia molecules.

It can be clearly seen in Table 5.1 that the dissociation energies for MP2 and DFT-B3LYP are not in perfect agreement, although the results show similar trends. The dissociation energy shows a gradual increase up to n = 6, with the exception of n = 2, which displays a rapid increase. Then a rapid decrease is evident for n = 7-10, although the additional ammonia molecules are entering the same solvation shell probably because of the steric strain between ammonia molecules as they pack the first solvation shell. The increase in bond dissociation energy for n = 2 is presumably due to compensation by the energy that is necessary to form Sr(NH₃)₂ from its bent structure to the linear equilibrium geometry, as shown in Figure 4.9 in Chapter 4. This linear equilibrium structure seen of the strontium complex is preferred when the ammonia molecules spread out around the strontium metal.

What it is clear from Table 5.1 and shown in Figure 5.12 is that excitation of N-H stretching in small complexes where n = 1, 3, and 4 are predicted to receive sufficient energy to remove NH₃ molecules. This is inconsistent with experiment, since no photodissociation was seen for those small complexes. This could result from the calculations employed here not

being sufficient by accurate to predict the dissociation energies for these small complexes. Therefore, high quality calculations will be required to make accurate predictions in these complexes. The CCSD(T) method provide to be the most accurate method for predicting dissociation energies. Due to the associated computational expense, this method was not undertaken for these complexes.

As seen from Figure 5.12 that the two different computational methods, MP2 and DFT-B3LYP are not in agreement with the n = 8 complex. The DFT-B3LYP methods predict that the dissociation energy for n = 8 to be low enough that a one photon IR absorption at 3153 cm⁻¹ which can dissociate the complex, while the MP2 calculations predict the dissociation energy to be higher. Take into account the approximate nature of the calculations and the possibility of thermally excited complexes, it is likely that there is sufficient energy under the present experimental conditions to permit photodepletion of $Sr(NH_3)_8$ and this would fit with the experimental observation. In the case of the large complexes for $n \ge 9$, the dissociation energies have been predicated to be lower which meant that absorption of a photon in the N-H stretching region was enough to dissociate ammonia molecules that are not directly bonded to strontium atom.

n	MP2/ cm ⁻¹	DFT/ cm ⁻¹	
1	2393	2859	
2	3351	3595	
3	2245	2430	
4	3082	2993	
5	3782	3598	
6	4588	4393	
7	3435	2388	
8	3225	2010	
9	947 ^(a)	904 ^(a)	
10	854 ^(a)	463 ^(a)	

Table 5.1Calculated dissociation energies for isolated Sr(NH₃)_n complexes.

(a) Calculated for 8+1 and 8+2 isomers of n = 9 and 10, respectively.



Figure 5.12 Dissociation energy for loss of one ammonia molecule from isolated $Sr(NH_3)_n$ complexes. Dashed horizontal line indicates experimental vibrational excitation energy.

5.5.6 Possible surface structure

The metal atom could be solvated within a shell of ammonia molecules in the interior structure or sitting on the exterior of a hydrogen-bonded complexes in a surface structure. To further surface versus interior solvation, the N-H stretching bands for the surface structure of large $Sr(NH_3)_n$ complexes were predicted using the MP2 and the DFT-B3LYP level of computations.

The vibrational frequencies predicted for interior, surface structures of $Sr(NH_3)_8$ and free (NH₃)₈ spectra are presented in Figure 5.13 along with experimental IR spectrum. The calculated IR spectrum for the surface structure indicates a series of high intensity peaks spanning the range 3100-3500 cm⁻¹. Some of these bands are substantially blue shifted when compared with those calculated for the interior structure. To obtain a clearer picture of the solvation structure, the free (NH₃)₈ cluster has been predicted. It can be observed from the bottom panel of Figure 5.13 that the predicted IR spectrum of the free (NH₃)₈ cluster shows many intense peaks in the higher frequency region within the range of 3100 to 3500 cm⁻¹. The surface structure of Sr(NH₃)₈ complex and the free (NH₃)₈ cluster demonstrate a very rich vibrational structure. In addition, the theoretical calculations predict that the total energy for surface structure is a much higher in energy than the interior structure by 1.566 eV. Therefore, the surface structure is unlikely formed in the molecular beam.



Figure 5.13 Comparison between two types of the structures (interior and surface) for the $Sr(NH_3)_8$ spectra and the free $(NH_3)_8$ spectrum with the experimental IR depletion spectrum in the N-H stretching region.

As a consequence, the experimental IR depletion of the Sr(NH₃)₈ spectrum, as shown in the upper panel of Figure 5.13, found no evidence for vibrational frequencies corresponding to the surface structure. Thus it can be explained in terms of the interior structure dominating the experimental IR photodepletion spectra reported in this chapter.

5.6 Conclusions

In this chapter the IR photodepletion spectra of $Sr(NH_3)_n$ complexes were reported for n = 6–14 for the first time. The complexes studied showed a substantial red shift of the N-H stretching vibrations, as anticipated resulting from the strong interaction between the strontium atom and ammonia molecules.

The theoretical considerations undertaken in support of the experimental IR spectroscopy provided valuable insight into the structure of gas-phase complexes. It has been shown that the lowest energy isomer for n = 1-8 contains ammonia molecules in a single solvation shell, whereas the isomers n = 9 and 10 contain two shells

With the increase in the size of complexes which is achieved by photodepletion of IR spectra from $n \ge 11$, strong resonances are shown to the blue shift for the N-H stretches. Broad IR depletion spectra were displayed which is closer to the stretching region of the free ammonia molecules. An additional blue-shift evolves over a broader wavelength range in the hydrogenbonding region which confirms the fact that when a sufficient number of ammonia molecules are filled the first solvation shell, the IR predissociation can take place by removal of ammonia molecules from the second solvation shell.

Therefore, this Chapter is a stepping stone to a more detailed exploration of the structure of heavier alkaline earth metal-ammonia complexes, which will be extended to barium metal with ammonia complexes in Chapter 6.

References

- (1) Hart, E. J. Solvated electron; ACS Publications, 1965.
- (2) Golden, S.; Tuttle, T. R. J. Chem. Soc., Faraday Trans. 2 1982, 78, 1581.
- (3) Deng, Z.; Martyna, G. J.; Klein, M. L. J. Chem. Phys. 1994, 100, 7590.
- (4) Cottrell, F. J. Phys. Chem. **1914**, 18, 85.
- (5) Glaunsinger, W.; Von Dreele, R.; Marzke, R. F.; Hanson, R.; Chieux, P.; Damay, P.;Catterall, R. J. Phys. Chem. 1984, 88, 3860.
- (6) Ohashi, K.; Terabaru, K.; Inokuchi, Y.; Mune, Y.; Machinaga, H.; Nishi, N.; Sekiya,
 H. *Chem. Phys. Lett.* 2004, *393*, 264.
- (7) Frisch, M. J. T., G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb,; M. A.; Cheeseman, J. R. M., J. A., Jr.; Vreven, T.; Kudin, K.; N.; Burant, J. C. M., J. M.; Iyengar, S. S.; Tomasi, K.; Barone, V.;; Mennucci, B. C., M.; Scalmani, G.; Rega, N.; Petersson, G. A.;; Nakatsuji, H. H., M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.;; Ishida, M. N., T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li,; X.; Knox, J. E. H., H. P.; Cross, J. B.; Bakken, V.; Adamo, C.;; Jaramillo, J. G., R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.;; Cammi, R. P., C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.;; Voth, G. A. S., P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, et al. *Gaussian Inc., Wallingford, CT* 2004, *26*.
- (8) <u>https://bse.pnl.gov/bse/portal</u>.
- (9) Hay, P. J.; Wadt, W. R. J. Chem. Phys. 1985, 82, 299.
- (10) Beu, T. A.; Buck, U. J. Chem. Phys. 2001, 114, 7853.

Chapter 6

IR spectroscopy of Ba(NH₃)_n complexes

6.1 Introduction

The heavier alkaline earth metals, namely Ca, Sr, and Ba, all readily dissolve in liquid ammonia and produce solvated electrons in sufficiently dilute solutions.¹ Observations involving these heavier alkaline earth metals suggest a stronger interaction with ammonia molecules than for Mg, which probably explains the very low solubility of magnesium in liquid ammonia.² In Chapter 4 of this thesis, a study of the dissolution of calcium and strontium with ammonia molecules in the gas phase was presented and demonstrated. Thus, gas phase studies of these solvated complexes may provide a tool for understanding fundamental solvation processes. To assist in the extraction of this information, electronic structure calculations have been employed to support the experimental findings.

To extract more information on the microscopic structure of these types of complexes, Chapter 5 showed infrared photodepletion spectra of $Sr(NH_3)_n$ complexes in the N-H stretching region. The assignment of the IR spectra was achieved through comparison with theoretical calculations. It was been shown that the $Sr(NH_3)_n$ complexes possess a single solvation shell for $n \le 8$, while larger complexes contain two solvation shell. The IR photodepletion spectra and theoretical calculations confirm that the interior structures are favoured over surface structures for the $Sr(NH_3)_n$ complexes. Therefore, building upon these results for $Sr(NH_3)_n$ complexes, a logical extension of this work is to expand the study to heavier alkaline earth metals.

In this chapter IR spectra of $Ba(NH_3)_n$ complexes are reported. In addition, theoretical investigations of the ionization and dissociation energies of the $Ba(NH_3)_n$ complexes are presented.

6.2 Experimental section

The apparatus employed has been described in detail in Chapters 2 and 5 of this thesis. Therefore, only a summary description of the basic setup is given here. The $Ba(NH_3)_n$ complexes were produced by laser ablation of a barium target in the presence of gaseous ammonia (NH₃ anhydrous 99% Aldrich) at a maximum pressure of 2 bar through a pulsed nozzle. The pulsed nozzle was operated at 10 Hz, with an opening duration of 250 µs. The resulting mixture was expanded into a vacuum to form a supersonic jet.

The expansion jet was skimmed to form a molecular beam, and then the resulting molecular beam was passed into the ionization region. In the ionization vacuum chamber, the molecular beam was crossed by two pulsed laser beams: a frequency-doubled UV laser beam was used for ionizing complexes, and an IR laser beam was used for vibrational excitation. The UV and IR lasers were directed into the ion source region from opposite directions. Care was taken to ensure that both laser beams spatially overlapped between the repeller and the central grid plate in the mass spectrometer ionization source region with the molecular beam. A single photon ionization of the UV beam was employed. The IR laser pulse fired at ~ 50 ns prior to the UV laser pulse. As mentioned in Chapter 5, all of the spectra have been recorded in the mid-infrared region in this thesis. The IR pulse laser is generated from a LaserVision optical parametric oscillator/amplifier (OPO/A) that was pumped by the output from a Nd:YAG laser (Surelite II-10). More details regarding the OPO/A system, including wavelength and intensity, are presented in Chapter 2 of this thesis.

6.3 Computational Details

In support of the experimental findings, *ab initio* calculations were performed on the neutral and cationic states of Ba(NH₃)_n complexes for n = 1-10 using the GAUSSIAN 03

computational package.³ All theoretical calculations have been carried out using both MP2 and DFT-B3LYP level of computations.

Because the barium atom is a heavy atom having a large number of core electrons, a double-zeta basis set with a relativistic effective core potential (ECP46MWB), known as the Stuttgart RSC 1997 ECP ⁴, was used. This basis set included d-type polarization functions.⁵ To maintain a balanced overall basis set for hydrogen and nitrogen atoms, the standard Pople double zeta 6-31+G(d,p) basis sets were used.

Vibrational frequency analysis was carried out for each optimized structure of the neutral and cation $Ba(NH_3)_n$ complexes. All calculations were run without symmetry constraints to permit a full variation of all degrees of freedom. Note that the geometric optimizations calculated using both MP2 methods and the DFT-B3LYP level of theories show slight differences in the orientation of the ammonia molecules but were otherwise very similar. The same was also true for the predictions of vibrational spectra and so we show mainly the results of MP2 calculations in this chapter, unless otherwise stated.

For comparison with experimental results of the IR depletion spectra, all computed vibrational frequencies were scaled using the MP2 and the DFT-B3LYP levels of theory with the same basis set employed here. A scaling factor of 0.932 was used for the harmonic MP2 method, and a value of 0.949 was used for the harmonic DFT-B3LYP calculations for a full range of vibrations studied here. It should be pointed out that the zero point vibrational energies (ZPVE) also have been scaled with these results and used to correct all the total energies.

6.4 Results and Discussion

6.4.1. Mass spectrometry

A typical photoionization mass spectrum from the Ba(NH₃)_n complexes (n = 1-16) is shown in Figure 6.1. This mass spectrum was recorded at a UV laser wavelength of 346 nm (3.584 eV).

As can be seen in this figure, the mass spectrum displays an increased peak intensity (magic number) for the n = 9 complex. Therefore, for complexes larger than Ba(NH₃)₉, the intensity of the complexes decreased rapidly with increasing complex size.



Figure 6.1 Photoionization mass spectrum from $Ba(NH_3)_n$ complexes. The laser wavelength used was 346 nm.

6.4.2. Photoionization energy predictions

To achieve a deeper understanding of the microscopic solvation process of the $Ba(NH_3)_n$ complexes in the gas phase, the adiabatic ionization energy (AIE) and vertical ionization energies (VIE) have been investigated. Experimental ionization energies for $Ba(NH_3)_n$ complexes were not determined due to time constraints. However, the calculated adiabatic and vertical ionization results determined are summarized in Table 6.1. The comparison of (AIEs) determined with the MP2 and DFT-B3LYP calculations in Figure 6.2 demonstrate that the evolution of the ionization energies decrease monotonically with an increasing size of the complexes, until they begin to plateau. This behaviour is interpreted in terms of the appreciable lowering of ionization energy trend for $Ba(NH_3)_n$ complexes is similar to that shown for the Ca(NH₃)_n and Sr(NH₃)_n complexes (see Chapter 4).

Table 6.1First ionization energies of the isolated $Ba(NH_3)_n$ complexes. The MP2 and
DFT results are corrected for zero point vibrational energies in the neutral and
cation complexes.

n	MP2/eV		DFT/eV		EXP./eV
	AIE	VIE	AIE	VIE	
0	4.918	-	5.233	-	5.212 ^(a)
1	4.323	4.324	4.606	4.609	-
2	3.899	4.047	4.185	4.209	-
3	3.548	3.796	3.806	4.035	-
4	3.246	3.667	3.569	3.629	-
5	3.112	3.411	3.457	3.517	-
6	3.043	3.268	3.389	3.448	-
7	2.954	3.249	3.324	3.391	-
8	2.908	3.685	3.290	3.358	-
9	2.852	3.433	3.234	3.319	-
10	2.689 ^(b)	3.321	3.086 ^(b)	-	-

(a) Experimental 1st ionization energy of atomic Ba taken from ref.⁶

(b) Calculated for 9+1 isomer of n = 10.



Figure 6.2 Plot of the calculated adiabatic ionization energy versus n for the isolated Ba(NH₃)_n.

When dealing with small complexes, the valence electrons on the barium atom become more delocalized but not detached as an increasing number of ammonia molecules surround the Ba atom. A continuous decrease in the ionization energies is observed until the first solvation shell is closed, as discussed in more detail in the next section. Eventually, the Ba cation releases an electron, which is shielded dielectrically by the solvated molecules. In contrast, a more delocalized electron is produced for large complexes while nearly constant ionization energies remain.

6.4.3. Calculated equilibrium structures.

Ab initio calculations have been carried out in support of the experimental work. Because there have been no previous theoretical studies of $Ba(NH_3)_n$ complexes, establishing the structural landscape for the complexes was important to determine possible minima for each complex size. To assess for a single isomer whether the global potential energy minimum dominates for each complex, attempts were made to identify as many low-lying structural isomers as possible.

Initial searches for minima were performed using a small basis set and a simple level of theory, the Hartree Fock method. This approach permitted trial calculations at many different starting geometries for each complex in a cost-effective manner. The resulting structures were then reinvestigated with a higher level theory and a larger basis set.

As mentioned previously in Chapters 4 and 5, the notation p + q is used to distinguish between isomers. The values of p and q represent the number of ammonia molecules in the first and the second solvation shell, respectively. The ammonia molecules in the second solvation shell are expected to be bonded to the first shell ammonia molecules by hydrogen bonds, whereas those ammonia molecules in the first solvation shell show a direct Ba-N bond.

Full descriptions of the key geometric parameters for the low-lying energy isomers of the neutral complexes and their corresponding cations are shown in Table 6.2 and the optimized structures of the global potential energy minima are illustrated in Figure 6.3. As expected, BaNH₃, is found to have only one isomer, where the ammonia molecule is directly bonded to the Ba atom via the N atom. This outcome predicts a structure with C_{3v} point group symmetry. There is little change in the equilibrium structures between the neutral complex and the corresponding cation occur upon ionization.

Table 6.2Key calculated structural parameters for the lowest energy isomers of the
isolated Ba(NH₃)_n complexes (n = 1-10) and their cations. Distances are in Å
and angles in degrees.

	Parameter	MP2		B3LYB	
n	(a)	Neutral	Cation	Neutral	Cation
	Ba-N	2.848	2.830	2.811	2.798
1	N1- H3	1.020	1.020	1.024	1.023
	Ba -N1-H3	112.4	113.8	111. 9	113.5
	H2-N1-H3	106.4	104.8	106.9	105.2
	Ba -N1-H2	112.4	113.9	111.9	113.4
	Ba -N	2.875,2.875	2.889,2.889	2.859,2.859	2.861,2.861
	N1- Ba -N2	179.8	179.9	169.2	156.6
2	N-H	1.019	1.020		
	H1-N1-H3	106.6	105.0	106.9	105.3
	H1-N1- Ba	112.3	113.6	111.2	112.9
	Ba -N	2.890,2.863,2.889	2.904,2.886,2.904	2.869,2.861,2.869	2.868,2.869,2.868
	N1- Ba -N2	143.9	140.9	141.5	120.8
3	N2-H9	1.019	1.019	1.023	1.022
_	H6-N3-N4	106.2	105.1	106.6	105.4
	NI-Ba-N3	/1.9	78.2	76.5	118.6
	N3-Ba-N2	144.0	140.9	141.5	120.6
	Ba -N	2.908,2.891,2.889	2.932,2.932,2.932	2.889,2.895,2.896	2.926,2.929,2.930
	N2 Do N1	2.903	2.932	2.889	2.920
	$N_{1} D_{2} D_{3} - N_{1}$	121.0	1/9.9	85.2	89.3 84.7
4	N1 - Da - N2 N2 $P_0 N4$	121.9	69.0 170.0	86.0	04.7
	N_2 -Da- N_4 N_4 R_0 N_3	75.5	80.6	00.2 103.0	90.2
	N4-Da-N3 N1 U1	1 020	1 018	1 024	1.021
	H2 N1 H1	1.020	105.1	1.024	1.021
	Ba N	2 007 2 001 2 007	2 942 2 944 2 944	2 900 2 902 2 900	2 030 2 044 2 030
	Da -IN	2.907,2.901,2.907	2.942,2.944,2.944	2.900,2.902,2.900	2.939,2.944,2.939
	N3- Ba –N2	132.1	137.6	128 5	130.3
	N5-Ba-N1	76.9	146.9	81.7	79.3
5	N1-H1	1.02021	1.019	1.025	1.022
	H1-N1-H2	106.090	105.2	106.6	105.7
	N3- Ba -N5	150.126	74.7	151.8	150.9
	N1- Ba–N4	145.349	75.4	152.2	151.1
	Ba -N	2.904,2.904,2.904	2.933,2.933,2.933	2.919,2.917,2.919	2.944,2.940,2.942
		2.904,2.904,2.904	2.933,2.933,2.933	2.916,2.916,2.918	2.939,2.940,2.942
	N3- Ba -N4	139.3	85.5	166.9	167.8
(N1-H1	1.021	1.020	1.026	1.024
0	H1-N1-H2	106.0	105.2	106.3	105.5
	N3- Ba -N5	84.6	79.0	82.6	84.4
	N1- Ba-N3	133.8	79.0	86.6	86.6
	N6- Ba -N4	133.9	79.1	103.6	103.4
	Ba -N	2.924,2.924,2.923	2.948,2.952,2.953	2.953,2.951,2.940	2.976,2.973,2.964
7		2.922,2.926,2.926	2.948,2.950,2.950	2.933,2.936,2.939	2.959,2.961,2.963
	N3- Ba-N4	2.932	2.952	2.948	2.971
	N1-H3	92.3	125.3	82.6	82.7
	N3- Ba -N5	1.021	1.020	1.025	1.023
	N1-Ba -N3	82.3	82.3	78.2	78.3
	N6- Ba -N4	76.4	76.5	77.5	77.6
	N7- Ba –N6	82.3	76.2	77.6	77.7

8	Ba -N	2.947,2.947,2.947	2.974,2.974,2.974	2.980,2.979.2.980	3.004,3.003,3.004
		2.947,2.947,2.947	2.974,2.974,2.974	2.979,2.980,2.980	3.003,3.004,3.004
		2.947,2.947	2.974,2.974	2.979,2.979	3.003,3.003
	N3- Ba –N2	140.7	114.3	139.6	140.1
	N1-H5	1.022	1.020	1.025	1.023
	H3-N1-H2	106.0	105.4	106.3	105.7
	N3- Ba –N7	77.6	72.9	77.7	77.7
	N1- Ba –N8	80.0	114.3	81.9	81.1
	N6- Ba -N4	144.6	76.5	146.4	145.6
	N7- Ba –N1	140.7	139.7	139.5	140.1
	N8- Ba –N5	77.6	72.9	77.5	77.7
	N6-Ba-N2	77.6	72.9	77.8	77.7
	Ba -N	2.973,2.973,3.005	2.998,2.998,3.028	3.017,3.018,3.036	3.039,3.051,3.042
		3.005,2.973,2.973	3.028,2.998,2.998	3.035,3.021,3.018	3.066,3.048,3.051
		2.973,3.005,2.973	2.998,3.028,2.998	3.017,3.034,3.021	3.039,3.047,3.048
	N3- Ba -N4	138.6	138.8	138.4	139.
	N1-H1	1.021	1.020	1.024	1.022
9	H1-N1-H2	105.9	105.4	106.3	105.8
	N3- Ba -N5	75.5	75.2	76.0	76.2
	N1- Ba-N3	134.9	134.8	135.3	134.1
	N6- Ba -N4	90. 1	90.5	89.3	92.2
	N7- Ba –N6	138.6	138.8	138.4	139.4
	N9-Ba –N6	138.6	138.8	138.3	138.3
	Ba -N	2.970,2.970,3.000	2.996,2.994,3.020	3.025,3.015,3.030	3.045,3.037,3.047
		2.965,2.967,3.001	2.989,2.994,3.018	3.015,3.019,3.025	3.039,3.044,3.049
	D 1440	2.969,2.963,3.004	2.991,2.985,3.027	3.026,3.005,3.037	3.049,3.024,3.046
	Ba-N10	5.096	5.123	5.183	5.206
	N3- Ba -N4	75.0	/4.0	72.5	72.3
10	N6-H9	1.020	1.020	1.023	1.022
(9+1)	H9-N6-H8	106.4	105.9	106.9	106.5
	N3- Ba -N5	76.9	76.1	80.5	79.6
	NI-Ba-N3	136.2	135.3	135.8	136.1
	N6-Ba -N4	69.4	69.6	70.5	70.7
	N/-Ba-N6	133.9	/0./	135.9	134.9
	N9- Ba –N3	68.3	68.2 26.2	67.3	67.5
	N10-Ba –N8	40.4	39.9	40.3	40.1

Table 6.2(Continued)

a) A single N-H distance has been given since all calculated N-H distances were found to be the same to within ± 0.001 Å.



Figure 6.3 Calculated structures of neutral $Ba(NH_3)_n$ and cationic counterparts from calculations at the MP2 level.



Figure 6.3 (Continued)

For Ba(NH₃)₂, 2+0 and 1+1 structures have been identified. The 2+0 structure has a considerably lower energy than the 1+1 isomer, the difference being 0.342 eV for the MP2 calculation and 0.325 eV for DFT-B3LYP. These large differences clearly indicate that the most stable isomer for Ba(NH₃)₂ complex is that the 2+0 isomer, which is presumably a consequence of the Ba-N bonding being stronger than the hydrogen bonding between the first
and the second solvation shell ammonia molecules. Therefore, it seems likely that the 2+0 isomer will be more abundant than the 1+1 complex in the molecular beam.

Similar results are obtained in the case of $Ba(NH_3)_n$ for n = 3-8, based on a comparison of energies between their isomers [(n + 0, (n - 1) + 1 and (n - 2) + 2)]. As a result, an emphasis was placed on the n + 0 complexes, assuming that this would be the principal contributor to the experimental data. This progression in geometric structures is similar to the case of the Ca(NH_3)_n and Sr(NH_3)_n complexes (see Chapter 4).

A comparison between experiment and *ab initio* calculations for larger complexes is more challenging because of the increasing number of isomers and increased computational difficulty. For the Ba(NH₃)₉ complex, the lowest energy isomers have been theoretically identified, giving rise to the 9+0 and 8+1 isomers. The total energy of the 8+1 isomer is higher than that of the 9+0 isomer by 0.134 eV at the MP2 level of theory. For complexes of up ten ammonia molecules, although many different starting structures have been tried, no structure was found in which all of the ten ammonia molecules fill a single solvation shell. On the basis of these results, the theoretical investigations suggest that the first solvation shell of the Ba(NH₃)_n complex is filled when nine ammonia molecules are present.

To gain further insight, calculations have been performed for "surface" structures, as also encountered in earlier chapters. For interior solvation, the metal atom is embedded inside the complex and surrounded by ammonia molecules, as per the examples above. However, in a surface structure the metal atom is situated on an ammonia cluster. As a consequence, it is important to consider the possibility that Ba(NH₃)₉ complexes might adopt "surface" structures. For the optimised surface structure, the total energies are higher than for the global minimum interior structure by 1.04 eV and 1.03 eV at the MP2 and DFT-B3LYP level of computations, respectively. It is evident from these calculations that the surface structures seem very unlikely to be favourably arranged for this type of structure.

6.4.4 Mass spectrometry

Figures 6.4(a) and 6.4(b) show a comparison of the typical mass spectra by monitoring the $Ba(NH_3)_n^+$ complexes with a function of the mass-to-charge ratio (*m/z*). The data in both figures have been recorded under the same expansion conditions at UV laser wavelength of 346 nm (3.584 eV) as mentioned earlier but they differ in that in (a) there is no IR laser pulse whereas this is present for (b).

In the photoionization mass spectrum recorded in the absence of the IR laser pulse $Ba(NH_3)_n^+$ ions containing up to 14 or more ammonia molecules are seen. This figure shows that the most intense peak in this particular mass spectrum corresponds to $Ba(NH_3)_9^+$, suggesting that this ion has some enhanced stability relative to the neighbouring complex ions. This mass spectrum shows a gradual decrease in the ion signal with *n* for *n* > 9, suggesting a closing of the first solvation shell around the central barium atom at *n* = 9 in the cation.

Figure 6.4(b) shows a mass spectrum of Ba(NH₃)_n complexes with the IR laser frequency fixed at 3150 cm⁻¹ and timed to fire at ~ 50 ns prior to the ionizing laser pulse. It is worth emphasizing that this mass spectrum was obtained with an IR laser beam mildly focused into the ionization chamber. In this figure, the IR mass spectrum shows ion signal of the Ba(NH₃)_n complexes depletions > 75 % for some ions. This behaviour can be explained by the photodepletion of corresponding neutral complexes, thus indicating that the binding energies of the $n \ge 9$ neutral complexes are less than the IR photon energy. Moreover, as shown in Figure 6.4(b), net ion production occurs from n = 4 to n = 7. A more detailed discussed about these IR photodepletion and production ion signals is presented later.



Figure 6.4 Mass spectra recorded for isolated $Ba(NH_3)_n$ complexes, where (a) the IR laser is off and (b) the IR laser is on. The UV laser wavelength used was 346 nm and the IR laser was set at 3150 cm⁻¹ (with pulse energy fixed at 2.5 mJ in this case). The two spectra are the result of 1000 consecutive laser shots and are recorded on exactly the same vertical scale.

6.4.5 Infrared photodissociation spectroscopy

Figure 6.5 shows IR photodepletion spectra of $Ba(NH_3)_n$ complexes for n = 8-10 in the N-H stretches region between 3000 and 3400 cm⁻¹. Attempts have been made to change the experimental conditions to increase the abundance of larger complexes, such as the timing

between the ionization laser pulse and the pulsed valve opening. However, the resulting signals were too weak to extract IR photodepletion spectra.

Here, it is worth briefly commenting on the possible challenges with the IR photodissociation experiments used (for more details see section 5.2 in Chapter 5). A major challenge in the IR photodissociation experiments is that the photodepletion in one mass channel leads to ion photoproduction in another. In particular, this is a concern for the ion signal for Ba(NH₃)_n⁺ lost from depletion of the Ba(NH₃)_n followed by photoionization of the resulting Ba(NH₃)_{n-1}, which leads to an increase in the Ba(NH₃)_{n-1}⁺ signal on photoproduction and IR photodepletion in ion signals may compete, thus distorting the IR spectrum and leading to misleading conclusions about contributions from heavier complexes. However, we expect that because the ion intensity decreases with increasing complex size for $n \ge 9$, the change in ion signal in a particular mass channel for $n \ge 9$ should be dominated by contributions from depletion of the neutral complexes.

As shown in Figure 6.5, the IR depletion spectra for each of the complexes for n = 8 - 10 have two strong IR depletion bands between 3100 and 3240 cm⁻¹. These observed absorption bands have similar relative intensities and almost identical positions for the three different sized complexes. However, in the IR spectrum of Ba(NH₃)₁₀, there is an additional and weaker band at around 3288 cm⁻¹. For comparison , note that gaseous ammonia has an IR spectrum showing two peaks in the N-H stretching region, the symmetric stretch (v_1) at 3334 cm⁻¹ and the N-H antisymmetric stretch (v_3) at 3444 cm⁻¹.⁷ Therefore, in the experimental IR photodepletion bands, all of the N-H stretches are shifted significantly to lower frequencies from the position of the free ammonia molecules. These red-shifts derive from weakening of the N-H bonds by the formation of Ba-N bonds. We now consider each of the complexes in more detail.



Figure 6.5 Experimental IR photodepletion spectra of $Ba(NH_3)_n$ (n = 8-10) in the N-H stretching region.

6.4.5.1 Ba(NH₃)8

The vibrational spectrum measured by monitoring $Ba(NH_3)_8^+$ is shown in the upper panel of Figure 6.6, along with the theoretical spectra of the isolated complex in the lower three panels in the region of the N-H stretching. Two strong IR depletion bands are observed with significant intensity; the first band peaking at ~ 3143 cm⁻¹ and the second at ~3193 cm⁻¹.

To interpret this IR spectrum, four low-lying structures, namely 8+0, 7+1, 6+2 and 5+3 were considered. The first three structures are presented in Figure 6.6, along with their predicted relative total energies and their IR spectra. The lowest energy structure is the 8+0 structure, i.e. where all eight ammonia molecules occupy the first solvation shell. The 7+1 structure is predicted to be more than 0.321 and 0.181 eV higher in energy than the 8+0 structure at the MP2 and DFT-B3LYP levels, respectively. The 6+2 structure is much higher in energy relative to the 8+0 isomer, by 0.613 eV at the MP2 level and by 0.440 eV at the DFT-B3LYP level. A fourth isomer, a 5+3 structure, was found to even higher in energy and consequently, is most unlikely to contribute to the experimental IR spectrum. Accordingly, this structure will not be discussed further in this chapter.

The predicted spectrum for the 8+0 isomer shows remarkable similar in predicted band shape to the predicted spectrum for n = 8+0 of Sr(NH₃)₈ (see Chapter 5). Although two peaks are predicted for the 8+0 isomer, at low resolution they merge into a single peak. Two peaks seen here likely arises from similar modes in/out of phase with each other. The third peak with a medium intensity appearing at a higher wavenumber arise from the N-H asymmetric stretching modes of all ammonia molecules in the first solvation. For the 7+1 structure, the predicted IR spectrum show more vibrational structure in the N-H stretching region. Moreover, these peaks are spread over a wider range than for the 8+0 structure because of excitations of the N-H symmetric stretching vibrations of the ammonia molecule in the second solvation shell. Although the spectrum in the n = 6+2, as shown in the lowest panel of Figure 6.6, has two separately resolved bands similar to the experimental IR bands, the third band on the higher frequency side of 2^{nd} band, which is a signature of the occupation of the second solvation shell is not consistent with experiment. Any contribution from the 6+2 structure is therefore negligible in the molecular beam.



Figure 6.6 The upper panel shows the experimental IR photodepletion spectrum of $Ba(NH_3)_8$. The spectra below are MP2 predictions for three different isomers (see text for more details).

In comparing the theoretical predictions for the 8+0 and 7+1 structures with the experimental IR spectrum, the 7+1 structure is predicted to have a relatively broad spectrum and therefore fits the experimental IR spectrum less well due to the additional feature on the higher side of the main band which is not observed in the experimental IR spectrum. In the case of the 8+0 structure, this structure is predicted to have only one strong band. A similar features was found in the predict spectrum of the Sr(NH₃)₈ (see Chapter 5 of this thesis), where the predicted spectrum was dominated by one band and did not match the observed spectrum

that showed two strong bands. As suggested in Chapter 5, the explanation for such splitting is an anharmonic effect (e.g. a combination band) or to more than one low lying isomer being present in the molecular beam and contributing to the spectrum.

The experimental IR photodepletion spectra of $Ba(NH_3)_8$ and $Sr(NH_3)_8$ are quite similar, suggesting similar structures for the complexes. This indicates that there is significant perturbation in this structure by the central barium metal. Consequently, the agreement between these observed spectra of both complexes can be explained in terms of the *n* =8 structure dominating the experimental IR photodepletion spectrum.

6.4.5.2 Ba(NH3)9

Both the experimental (top panel) and the predicted IR depletion spectra (the bottom three panels) for Ba(NH₃)₉ are presented in Figure 6.7. The Ba(NH₃)₉ spectrum has two distinct IR absorption bands: the first band occurs at 3198 cm⁻¹ and the second is centred at ~3150 cm⁻¹. Moreover, the appearance of the experimental IR spectrum is very similar to that observed for n = 8, indicating that the ammonia molecules are in similar environments in both complexes.

Three plausible equilibrium structures, namely 9+0, 8+1 and 7+3, have been identified and are presented in Figure 6.7, along with their predicted relative total energy. The global potential energy minimum is calculated to be the 9+0 structure. The second lowest energy structure, an 8+1 structure, is predicted to be 0.134 eV above the 9+0 isomer at the MP2 level, while the 7+2 is 0.385 eV above the global minimum.

The predicted IR spectrum from the lowest energy 9+0 isomer shows a single band with greatest intensity near to 3204 cm⁻¹. The predicted IR spectrum of the 9+0 isomer is very similar to the corresponding 8+0 spectrum but with a slightly smaller red shift, suggesting that the solvation of these two structures by ammonia molecules is very similar. The N-H stretch region

of the 8+1 structure is similar to that of the 9+0 isomer but the strongest band is asymmetric, with a tail on the blue side which derives from an ammonia molecule in the second solvation shell. This asymmetric band does not provide a particularly good match to the experimental IR spectrum. Therefore, the experiments strongly suggest that the 9+0 structure is formed in molecular beam. However, as the strongest band in the 8+1 spectrum falls within the range of the two bands seen in the experimental spectrum, it is possible that the experimental spectrum contains contributions from both the 9+0 and 8+1 isomers.



Figure 6.7 IR photodepletion spectra of Ba(NH₃)₉ in the N-H stretching region (upper panel). Also shown are the predicted MP2 spectra for three different structures.

6.4.5.3 <u>Ba(NH₃)10</u>

The IR photodepletion spectrum measured by monitoring $Ba(NH_3)_{10}^+$ is shown in the top panel of Figure 6.8 and is compared to predicted IR spectra in the bottom four panels. The experimental spectrum shows at least three distinct bands. The two strongest bands are at ~ 3200 and ~ 3149 cm⁻¹, and a weaker band is seen at ~ 3288 cm⁻¹.

Four typical structures of the Ba(NH₃)₁₀ have been determined and are shown in Figure 6.8. As previously mentioned, no minimum energy structure could be found for the n = 10+0 complex, and thus the lowest energy structure is the 9+1 structure. In fact two distinct 9+1structures have been predicted. In the first structure, three hydrogen bonds are shared between the ammonia molecule in the outer solvation shell and three ammonia molecules in an inner solvation shell, and this is referred to as 9+1(3HBs). The next lowest energy structure is another 9+1 structure but in this structure, the ammonia molecule in the second solvation shell has hydrogen bonds with only two of the ammonia molecules in the first solvation shell: this structure is referred to as 9+1(2HBs). The energy difference between these two structures is predicted to be 0.016 eV, so is very small. The next lowest energy structure, the 8+2 isomer, is predicted to lie 0.119 eV above the 9+1 structure at the MP2 level of calculation. The less symmetric 7+3 structure is calculated to be 0.412 eV higher in energy than the 9+1 structure, again at the MP2 level.

As observed in Figure 6.8, both the 9+1 (3HBs) and the 9+1 (2HBs) structures are dominated by a single band, with several additional peaks shift to the blue derived from the presence of tenth ammonia molecules in the second solvation. The n = 8+2 spectrum shows more vibrational structure, with weak bands shifted towards high frequency. It is clear from the lowest panel of Figure 6.8 that the 7+3 structure gives rise to two bands that have roughly the appropriate separation; however, the intensities of the two IR bands do not correspond well to the IR photodepletion experimental spectrum. Therefore, this structure is most unlikely to contribute to the IR photodepletion experimental spectrum.

The theoretical calculations predict no minimum energy structure for the n = 10+0 isomer. Consequently, comparison between the experimental and theoretical calculations results is made in Figure 6.8, assuming that the preference for the Ba(NH₃)₁₀ complex is one or both of the 9+1 structures, although we cannot completely rule out the possibility of an 8+2 structure contribution. It is therefore clear that the lowest energy structure for this complex contains two solvation shells.



Figure 6.8 IR photodepletion spectrum of Ba(NH₃)₁₀ (upper panel). The lower panels show IR spectra from MP2 calculations for three different structures.

6.4.6. Infrared photoproduction spectroscopy

Figure 6.9 shows the experimental IR photoproduction spectra in the upper four panels and IR photodepletion spectra in the lower three panels of the isolated $Ba(NH_3)_n$ complexes. The position of these bands in the depletion and production spectra are similar, spanning the frequency range from 3100 to 3250 cm⁻¹. These IR N-H stretch bands are again red-shifted from that of free ammonia.

As observed in Figure 6.9 (a-d), the IR photoproduction spectra of four complexes, which show two strong and moderate intensity IR bands, are present at ~ 3143 and 3189 cm⁻¹ for n = 4, and around 3146 and 3193 cm⁻¹ for n = 5. For n = 6, approximately 3150 and 3197 cm⁻¹ are exhibited. Two intense bands were appeared at ~3157 and ~ 3201 cm⁻¹ for n = 7. It can be seen from the lower three panels of Figure 6.9(e-g), IR photodepletion spectra for the larger complexes, namely larger complexes where n = 8-10 is accompanied by ion production in smaller spectra where n = 4-7. Therefore, it is expected that the majority of depletion from the larger complexes (n = 8-10) result in ion production in the small complexes where n = 4-7 (through loss of one or more NH₃ molecules after absorption of the IR photon).



Figure 6.9 Experimental IR photoproduction spectra of $Ba(NH_3)_n$ for n = 4 - 7 (a-d) and IR photodepletion for n = 8 - 10 (e-g).

6.4.7. Dissociation energies

The IR-induced photodepletion of $Ba(NH_3)_n$ complexes has been found to take place between n = 8 and 10. The energy required to remove at least one ammonia molecule from the complexes for the range n = 1-10 has been determined by both MP2 and DFT-B3LYP calculations.

To obtain the dissociation energies (D_0) , only the lowest energy isomer structures for each complex have been taken into account. The calculations used the supermolecule approach:

$$D_0[Ba(NH_3)_n] = E[NH_3] + E[Ba(NH_3)_{n-1}] - E[Ba(NH_3)_n]$$
(6.1)

Here, D_0 represents the dissociation energy for the removal of one ammonia molecule from a given complex, and *E* is the total energy of the isolated complex or fragment at equilibrium structure, including the zero point vibrational energy (ZPVE). Dissociation energy calculations were predicted without basis set superposition error (BSSE). The predicted D_0 values are presented in Table 6.3 and depicted in Figure 6.10 as a function of increasing number of ammonia molecules.

Analysis of dissociation energies predicted from the MP2 and the DFT-B3LYP methods do not show perfect agreement, as seen in Table 6.3, but they do show a generally similar trend. The Ba-N bond dissociation energies displayed in Figure 6.10 show a similar trend to the Sr(NH₃)_n complexes (see section 5.5.3 in Chapter 5); that is, the most dramatic decrease takes place up to $n \ge 8$ at the DFT-B3LYP methods and $n \ge 9$ at the MP2 calculations.

Excitation in the N-H stretching region of the ammonia molecule occurs at around 3150 cm⁻¹, which is indicated in Figure 6.10 with a horizontal dashed line. The dissociation energy of n = 8 predicted using DFT-B3LYP is low enough that a one photon IR absorption at 3150 cm⁻¹ can dissociate the complex. In the case of the MP2 calculations, the dissociation energy of n = 8 is far more than the energy of a photon required to excite the N-H stretches. Taking into account the approximate nature of the calculations and the possibility of thermally excited complexes formed in the experiment, it is likely that there is sufficient energy under the present experimental conditions to permit photodepletion of Ba(NH₃)₈ and this would fit with the experimental observation. For large complexes for the $n \ge 9$, there is a significant shift towards lower dissociation energy suggesting that the dissociation energy of NH₃ molecules that are not directly bound to the central barium metal is less than for those that are bound. In other words, large complexes will receive sufficient energy to dissociate when the N-H stretching excitation occurs.

п	MP2/ cm ⁻¹	DFT/ cm ⁻¹
1	3388	3684
2	4304	4117
3	2898	2932
4	3140	3074
5	3289	2991
6	3732	3622
7	3770	3009
8	3580	2531
9	1053	972
10	1009 ^(a)	722 ^(a)

Table 6.3Calculated dissociation energies for the isolated Ba(NH₃)_n complexes.

(a) Calculated for 9+1 isomers of n = 10.



Figure 6.10 The dissociation energy for loss of one ammonia molecule from $Ba(NH_3)_n$ (n = 1-10). The dashed horizontal line indicates the experimental vibrational excitation energy (3150 cm⁻¹) for the lower frequency band.

As previously mentioned in section 6.4.3, both surface and interior structures are possible for $Ba(NH_3)_n$. The theoretical investigations confirm that the interior structures discussed in the earlier parts of this chapter are energetically favoured. To explore this further, and in particular to see what the IR spectrum would look like if we had a surface structure, the IR spectrum of the surface structure of $Ba(NH_3)_5$ complex have been investigated by both MP2 and DFT-B3LYP calculations. As seen in the middle and lower panels of Figure 6.11, the calculated IR spectrum of the surface structure of $Ba(NH_3)_5$ and the free $(NH_3)_5$ cluster are similar; that is, they show more peaks with several high intensities in the N-H stretching region, spread over a large region between 3100 and 3500 cm⁻¹. Moreover, these peaks are much closer to the positions of the bands of free ammonia molecules than seen in the IR spectra reported in this chapter. This can be understood based on the fact that the ammonia molecules are arranged in hydrogen bonding networks in the free ammonia clusters and the surface structure. The situation is completely different in the interior structure.



Figure 6.11 Comparison between the predicted IR spectra for two types of the structures (interior and surface) for Ba(NH₃)₅ and the free (NH₃)₅ spectrum.

The extent to which the surface and interior structural differences in the N-H stretching region of $Ba(NH_3)_n$ complexes continue at larger complex sizes, calculations have been carried out on two surface structures (identified as structure 1 and structure 2) of $Ba(NH_3)_9$. As shown in Figure 6.12, in both surface structures, the N-H stretching region is substantially broader, extending over nearly 700 cm⁻¹, which reflects the larger hydrogen-bond network in both surface structures of the $Ba(NH_3)_9$ complex. As a consequence, both surface spectra do not fit with the experiment spectrum. Moreover, the *ab initio* calculations of surface structure 1 and structure 2 are predicted to be considerably higher in total energy than the interior structures by 2.021 and 2.081 eV, respectively.



Figure 6.12 Comparison between two types of the structures for the Ba(NH₃)₉ spectra and the free (NH₃)₉ spectrum with the experimental IR depletion spectrum in the N-H stretching region.

Clearly, there is no spectral evidence for the surface structure of the complexes in the observed IR absorption spectra. Therefore, interior structures are confirmed as the source of the experimental IR spectra reported in this chapter. This is also consistent with the observed IR spectra for $Ca(NH_3)_n$ and $Sr(NH_3)_n$.

6.5 Conclusions

IR spectroscopy has been applied to neutral $Ba(NH_3)_n$ complexes for the first time. The IR spectra for n = 8-10 each show two distinct bands with considerable red-shifting of the N-H stretching bands from that of gaseous ammonia. The IR photodepletion spectra are very similar in appearance for n = 8 and 9, suggesting that these complexes are dominated by isomers where all ammonia molecules are bound directly to the barium metal centre.

Ab initio calculations and the IR vibrational spectroscopy confirm that the first solvation shell of neutral Ba(NH₃)_n complexes can contain up to nine ammonia molecules, suggesting that the Ba(NH₃)_n complexes possess structures in which the barium metal is situated in the interior of the complex, whereas the second solvation shell is occupied for n = 10.

The Ba-N bond dissociation energies of the $Ba(NH_3)_n$ complexes for n = 1-10 have been calculated for the first time. The calculations predict that a sharp decrease in dissociation energy occurs when the first solvation shell is filled, which makes it possible to record the IR spectra in a photodepletion mode.

References

- (1) Jolly, W. L. Progress in Inorganic Chemistry 1959, 1, 235.
- (2) Loomis, A. G. J. Am. Chem. Soc. 1922, 44, 8.

- (3) Frisch, M. J. T., G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb,; M. A.; Cheeseman, J. R. M., J. A., Jr.; Vreven, T.; Kudin, K.; N.; Burant, J. C. M., J. M.; Iyengar, S. S.; Tomasi, K.; Barone, V.;; Mennucci, B. C., M.; Scalmani, G.; Rega, N.; Petersson, G. A.;; Nakatsuji, H. H., M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.;; Ishida, M. N., T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li,; X.; Knox, J. E. H., H. P.; Cross, J. B.; Bakken, V.; Adamo, C.;; Jaramillo, J. G., R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.;; Cammi, R. P., C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.;; Voth, G. A. S., P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, et al. *Gaussian Inc., Wallingford, CT* 2004, 26.
- (4) <u>https://bse.pnl.gov/bse/portal</u>.
- (5) Hay, P. J.; Wadt, W. R. J. Chem. Phys. 1985, 82, 299.
- (6) <u>http://physics.nist.gov/PhysRefData/Handbook/Tables/bariumtable1.htm</u>.
- (7) Beu, T. A.; Buck, U. J. Chem. Phys. 2001, 114, 7853.

Chapter 7

IR spectroscopy of Ca(NH₃)_n complexes

7.1 Introduction

The spectroscopy of metal-solvent complexes in the gas phase as a function of the number of added solvent molecules is often viewed as a bridge between the gas phase and bulk solutions. Complexes containing highly electropositive metal atoms and ammonia molecules provide information on the microscopic nature of solvation upon the dissolution of metal atoms and the formation of solvated electrons^{1,2} via extrapolation of the well-defined structural and energy properties in the gas phase to the bulk limit at a molecular level.^{3,4} In particular, alkali-ammonia complexes has been investigated by various spectroscopic techniques and theoretical calculations as the alkali/ammonia system is perhaps the classic solvated electron system. ⁵⁻¹⁰

The alkaline earth metals are also known to dissolve in liquid ammonia.^{11,12} However, spectroscopic studies of complexes of alkaline earth metal atoms with ammonia molecules are far fewer than those involving alkali metals. In Chapter 4 of this thesis, the ionization energies of $Ca(NH_3)_n$ and $Sr(NH_3)_n$ complexes were presented and then interpreted using theoretical investigations. The predictions from *ab initio* calculations are in good agreement with the experimental findings.

To provide more direct structural information on the properties of alkaline earth/ammonia complexes, IR photodepletion spectra of the neutral complexes have also been recorded. In Chapters 5 and 6 of this thesis, the gas-phase complexes of heavier alkaline earth metals, namely $Sr(NH_3)_n$ and $Ba(NH_3)_n$, were studied. There we reported the first IR photodepletion spectra of these complexes and focused on the N-H stretching region. The spectra were found to be consistent with interior structures of the complexes, *i.e.* the metal atom is surrounded by ammonia molecules rather than residing on the surface of an ammonia cluster.

Motivated by the above, the current chapter describes the first spectroscopic study of $Ca(NH_3)_n$ complexes. As in the previous chapters, this experimental study will be supported by *ab initio* calculations in an attempt to understand the resulting IR spectra.

7.2 Experimental section

The experimental apparatus has been described in detail in Chapter 2 of this thesis, and so only a brief account is given here. Neutral $Ca(NH_3)_n$ complexes were generated by laser ablation of a solid calcium target with the second harmonic (532 nm) of a Nd:YAG laser in the presence of gaseous ammonia. Calcium-ammonia complexes were formed by expanding ammonia gas at a maximum pressure of 2 bar via a pulsed nozzle into a vacuum. The pulsed valve operated at a repetition rate of 10 Hz and with a nominal opening time of 250 µs.

The jet-cooled expansion was skimmed to form a molecular beam which then entered the ionization region of a Wiley-McLaren time-of-flight mass spectrometer. In this region the molecular beam was intersected by two pulsed laser beams. The first laser beam was from a UV laser, which was provided by the output from a tunable dye laser equipped with frequency doubling capability. This laser is used to photoionize the complexes by single photon ionization close to the ionization threshold (in order to try and avoid ion fragmentation). The second laser was a tunable mid-infrared laser (LaserVision OPO/A), which was used to excite vibrational transitions. Both UV and IR laser beams were directed into the ion source region from opposite directions and overlap with the molecular beam takes place between the repeller and the central grid electrodes in the mass spectrometer ionization source region. The IR pulse was fired 50 ns prior to the UV laser pulse. The intention of the IR laser is to cause resonant photodepletion of one or more $Ca(NH_3)_n$ complexes via vibrational excitations. This photodepletion can be registered from a decrease in the corresponding $Ca(NH_3)_n^+$ signal in the mass spectrometer.

7.3 Computational Details

In order to aid the interpretation of the experimental IR depletion spectra and to determine the possible molecular structures, *ab initio* calculations were performed. These calculations were carried out using the GAUSSIAN 03 suite of programs.¹³ The background to these calculations was provided in Chapter 3. Calculations were performed using MP2 and DFT-B3LYP methodologies and the Pople 6-311++G(d,p) basis set was used for all atoms. This basis set was selected because it is reasonably large and flexible while not being too computationally demanding to tackle relatively large complexes.

In order to ensure that the geometry optimization found true minima on the potential energy surface, harmonic vibrational frequencies were calculated to make sure no imaginary frequencies were found. Such calculations were also used to predict the IR spectra. The energies of neutral and ionic complexes were corrected for zero-point vibrational energies. No symmetry constraint was employed during the geometry optimizations to allow variations in all of the degrees of freedom available for the complexes studied.

To facilitate comparison between the experimental IR depletion and theoretically calculated spectra, the predicted N-H vibrational stretch frequencies were scaled by a factor of 0.936 for the MP2 calculations and 0.955 for the DFT-B3LYP calculations. These scaling factors were those required to bring the calculated harmonic frequencies of the N-H stretching modes of the free ammonia molecule into close agreement with experimental fundamental frequencies for the same modes.

7.4 Results and Discussion

7.4.1. Mass spectrometry

Typical mass spectra of Ca(NH₃)_n (n = 1-13) complexes are presented in Figures 7.1(a) and 7.1(b). Both spectra were recorded under the same expansion conditions at a UV wavelength of 346 nm (3.584 eV). However, the difference between the two spectra is that the spectrum in Figure 7.1(b) was obtained with the addition of the OPO/A laser, whereas that in 7.1(a) is for UV photoionization only.

The mass spectrum of Ca(NH₃)_n complexes recorded with the IR laser frequency fixed at 3153 cm⁻¹ is given in Figure 7.1(b). The firing of the IR laser was optimized to give the maximum depletion signal and this was found to occur when the IR laser fired ~ 50 ns prior to the ionizing laser pulse. Note that the IR photodepletion pulse energy is kept at a constant value of 2.5 mJ and mildly focused into the ionization chamber. Clearly the mass spectrum with the IR laser switched on has a different intensity distribution from that with the IR laser switched off, showing that photodepletion has occurred in the former case. A comparison between the two mass spectra shows that the ion signals from ionization of Ca(NH₃)_n complexes for $n \ge 8$ is depleted by up to 40 %, which is a relatively large effect. Again, this is consistent with the behaviour found previously for the Sr(NH₃)_n and Ba(NH₃)_n complexes in Chapters 5 and 6 of this thesis, respectively. Moreover, as shown in Figure 7.1(b), the IR mass spectrum shows ion production for n = 6 and 7. This indicates that Ca(NH₃)_n for $n \ge 8$ have a binding energy that is sufficiently below the energy of the IR photon to allow photodepletion, whereas this might not be the case for smaller complexes. More discussion of these IR depletion and production ion signals will be provided later.



Figure 7.1 Mass spectra recorded for isolated $Ca(NH_3)_n$ complexes (n = 1-13), where (a) the IR laser is off and (b) the IR laser is on. The UV laser wavelength used was 346 nm and IR laser was set at 3153 cm⁻¹ (with pulse energy fixed at 2.5 mJ in this case) The two spectra are the result of 1000 consecutive laser shots and are recorded on exactly the same vertical scale.

7.4.2. Infrared photodissociation spectroscopy

The IR depletion spectra recorded in different mass channels are shown in Figure 7.2. These spectra were obtained by detecting $Ca(NH_3)_n^+$ ions for n = 8-10. Attempts to obtain spectra of satisfactory quality for larger complexes were made, e.g. by varying the experimental conditions, but the ion signal intensities for these complexes were too weak and so gave poor quality spectra.

Photodepletion is clearly seen in the mass channels for $n \ge 8$. The IR depletion spectrum for n = 8 consists of a single vibrational band at around 3150 cm⁻¹ shown in the upper panel of Figure 7.2. In the observed IR spectra for n = 9 and 10, two IR absorption bands are found in the region of 3100-3300 cm⁻¹ (middle and the bottom panels of Figure 7.2, respectively). For the purpose of comparison, it is worth noting that gaseous ammonia has an IR spectrum showing two peaks in the N-H stretching region, the symmetric stretch at 3334 cm⁻¹ and the N-H antisymmetric stretch at 3444 cm⁻¹.¹⁴ Formation of Ca-N bonds is expected to weaken the N-H bonds and therefore the shift to lower frequencies for Ca(NH₃)_n is reasonable.^{15,16}



Figure 7.2 Experimental IR photodepletion spectra of $Ca(NH_3)_n$ (n = 8-10) in the N-H stretching region.

7.4.2.1 Ca(NH₃)₈

The experimental IR spectrum of this complex, which is assumed to derive from photodepletion of $Ca(NH_3)_8$ and was obtained by monitoring $Ca(NH_3)_8^+$, consists of a single unresolved but asymmetric band. It shows a peak maximum at ~ 3143 cm⁻¹ and a shoulder on the higher frequency side of this band, with the latter indicating that there may be one or more additional unresolved bands.

To aid in the interpretation of the experimental IR photodepletion spectrum, calculations were performed to gain some geometrical information on the Ca(NH₃)₈ complex. Four plausible lowest energy structures were identified, namely the 8+0, 7+1, 6+2 and 5+3 isomers. The first three have the lowest energies and are shown in Figure 7.3 along with their calculated relative total energies. This figure shows the results from MP2 calculations but the DFT predictions are similar (and are therefore not shown, unless otherwise stated). In order to explore which structures might contribute to the experimental IR spectrum, the calculated IR spectra are shown in Figure 7.3.

The lowest energy structure was found to be the 8+0 isomer, *i.e.* where all eight ammonia molecules form a single shell. The NH₃ molecules are bonded to the Ca atom via their nitrogen atoms. The second lowest energy structure is the 7+1 isomer, in which seven ammonia molecules are found in the first solvation shell and an eighth is in the second shell. According to MP2 calculations, this structure is 0.107 eV above the global minimum. The 6+2 structure is 0.250 eV above the global minimum, an energy which makes it most unlikely to contribute to the observed IR spectrum. Consequently, the 6+2 structure, and the even higher energy 5+3 structure, will not be discussed further.

It is worth noting a significant change between the MP2 and DFT calculations. In the latter, the 8+0 structure is predicted to be higher in energy than the 7+1 structure by 0.035 eV.

Clearly, on the basis of both MP2 and DFT calculations, we cannot be certain whether it is the 8+0 or 7+1 structure that is the global minimum energy structure.



Figure 7.3 The upper panel shows the IR photodepletion spectrum of Ca(NH₃)₈ complex in the N-H stretching region. The spectra below show MP2 predictions for three different isomers (see text for more details).

A comparison of the experimental IR spectrum with the theoretical predictions for the 8+0 and 7+1 structures is not definitive. Both are dominated by a single intense IR absorption and the predicted positions are quite close to the peak maximum in the experimental spectrum. Of course the 8+0 spectrum should consist of a single absorption band if the predicted high

symmetry is maintained. However, the experimental spectrum is clearly more complex, with evident asymmetry on the higher frequency side of the peak maximum. This could certainly be consistent with a contribution from the 7+1 isomer, since this is predicted to have weak absorption features at energies above the peak maximum. Of course other effects, such as anharmonic coupling, can introduce extra vibrational structure. Nevertheless, the possibility exists that the observed absorption feature arises from contributions from both 8+0 and 7+1 isomers.

It is worth noting that the predicted IR spectra presented in Figure 7.3 are similar in appearance to those of the predicted IR spectra presented in Figures 5.4 and 6.6 in Chapters 5 and 6 of this thesis, respectively, for Sr(NH₃)₈ and Ba(NH₃)₈. This suggests that the ammonia molecules are similarly perturbed by the central calcium metal and adopt the same basic geometric structure.

7.4.2.2 Ca(NH₃)9

Figures 7.4 and 7.5 compare the experimental IR depletion spectrum of $Ca(NH_3)_9$ with spectra obtained from MP2 and DFT calculations, respectively. The experimental spectrum is very different from that of $Ca(NH_3)_8$. There is an intense and very broad band with a mid-point at roughly 3160 cm⁻¹, which is similar to the strong band seen for $Ca(NH_3)_8$. However, there is also a second fully resolved band at ~ 3280 cm⁻¹ which has significant intensity.

The results of the *ab initio* calculations on Ca(NH₃)₉ are summarized in Figure 7.4. The MP2 calculations predict that the lowest energy structure is 8+1: no equilibrium structure could be found for a 9+0 structure, and therefore the lowest-lying energy structure is concluded to be the 8+1 structure. The next lowest structure is the 7+2 isomer, which is predicted to be higher in energy than the 8+1 structure by 0.121 eV at the MP2 level. The 6+3 structure is of very high energy and will not be discussed further. As for Ca(NH₃)₈, the energy ordering for the

calculated structures in MP2 and DFT calculations are not in agreement. Thus the DFT 7+2 isomer is lower in energy than that of the 8+1 isomer by 0.031 eV.



Figure 7.4 IR photodepletion spectra of Ca(NH₃)₉ complex in the N-H stretching region (upper panel). Also shown are calculated MP2 IR spectra for three different structures.



Figure 7.5 IR photodepletion spectra of Ca(NH₃)₉ in the N-H stretching region (upper panel). Also shown are the predicted DFT spectra for three different structures.

None of the calculated spectra show close agreement with experiment. However, it seems likely that the prominent band at 3280 cm⁻¹ is a signature of the occupation of the second solvation shell. This agrees well with theoretical calculations, which found that no minimum energy structure for n = 9+0 was found in the first solvation shell for calcium-ammonia complexes; that is, the lowest energy isomer for this complex contains two occupied solvation shells.

All of the calculated spectra from both MP2 and DFT predict such a feature, although the relative intensities vary considerably. The spectrum that produces the best agreement with experiment is probably the 7+2 DFT spectrum. However, given the width of the lower frequency absorption, which is the dominant band in the experimental spectrum, there is probably a contribution from more than one isomer to this feature. We certainly can't rule out some contribution from the 8+1 isomer but the 6+3 isomer does not seem to fit the experimental observations.

7.4.2.3 Ca(NH₃)10

The experimental and predicted IR absorption spectra for $Ca(NH_3)_{10}$ are shown in Figures 7.6 and 7.7. The experimental spectrum is similar to that from $Ca(NH_3)_9$, although the S/N ratio is less favourable. Nevertheless, we can interpret this spectrum in much the same way as for $Ca(NH_3)_9$. Thus the ammonia molecules must be in comparable environments and a two-shell structure is assumed.

In MP2 calculations the lowest energy structure has been identified as the 8+2 structure (see Figure 7.6). According to the MP2 calculations the 7+3 structure is the next lowest in energy, lying about 0.117 eV above the 8+2 structure. However, the energy ordering is reversed in the DFT calculations, with the 7+3 isomer lying lower in energy than the 8+2 structure by 0.038 eV. In the DFT calculations the 6+4 structure is only marginally (0.015 eV) above the 8+2 structure whereas in the MP2 calculations it is substantially higher in energy. Once again the calculated spectra do not seem to yield perfect agreement with the experimental IR spectrum. It seems unlikely that a single isomer could account for the entire spectrum but a mixed contribution from the 8+2 and 7+3 isomers would account for the main features.



Figure 7.6 IR photodepletion spectrum of Ca(NH₃)₁₀ (upper panel). The lower panels show IR spectra from MP2 calculations for three different structures.



Figure 7.7 IR photodepletion spectrum of Ca(NH₃)₁₀ (upper panel). The lower panels show IR spectra from DFT calculations for three different structures.

7.4.3 Infrared photoproduction spectroscopy

There is no evidence for depletion features in the IR spectra recorded by detecting Ca(NH₃)_n⁺ ions with n < 8. However, photoproduction IR spectra were acquired by monitoring the Ca(NH₃)_n⁺ ion channels for n = 6 and 7, as presented in Figure 7.8. As seen in the upper panel of this figure, for n = 6, there is one intense band centred at ~ 3163 cm⁻¹, with shoulders on both sides. In the case of n = 7, two large IR production bands were observed at ~ 3177 and ~ 3282 cm⁻¹, as seen in the bottom panel of this Figure. The first of these bands is quite broad with the shoulder on the higher frequency side of the broad band, peaking at ~ 3217 cm⁻¹. It

should be noted that these IR photoproduction spectra were recorded under the same expansion conditions as the IR photodepletion spectra reported earlier in this chapter.

A comparison of the photoproduction spectrum for n = 7 (see the lower panel of Figure 7.8) with the photodepletion spectrum for n = 8 (see the top panel of Figure 7.3) shows that these spectra are not in perfect agreement; that is, they are not mirror images of each other. Nevertheless, the peak near 3280 cm⁻¹ in the n = 7 is very similar to that in the depletion spectrum for n = 8. Where the spectra differ is in the lower energy band, which actually peaks at a higher frequency for n = 7 than for n = 8. It is noteworthy that there is some evidence of depletion between 3100 and 3150 cm⁻¹, and so possible competition between ion depletion and ion production might create a distorted peak. This would explain the lack of a mirror image between the n = 7 photoproduction and n = 8 photodepletion channels. The n = 6 photoproduction spectrum shows less evidence of distortion and is closer to (but not identical with) a mirror image of the n = 8 spectrum. It might be that the n = 6 spectrum also has photoproduction contributions from IR absorption and subsequent photodepletion of Ca(NH₃)₇ and Ca(NH₃)₈ (through loss of two NH₃ molecules after absorption of the IR photon).



Figure 7.8 Experimental IR photoproduction of $Ca(NH_3)_n$ for n = 6 and 7 in the N-H stretching region.

7.4.4 Dissociation energies

To establish the feasibility and limitations of the IR photodepletion technique for $Ca(NH_3)_n$ complexes, the Ca-N bond dissociation energy (D_0) has been explored. These bond dissociation energies have not been previously determined and therefore estimates of the energy required to remove at least one ammonia molecule have been investigated by both MP2 and DFT-B3LYP calculations.

As has already discussed in Chapters 5 and 6 of this thesis, the dissociation energies were calculated from the expression:

$$D_0[Ca(NH_3)_n] = E[NH_3] + E[Ca(NH_3)_{n-1}] - E[Ca(NH_3)_n]$$
(6.1)

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Here D_0 corresponds to the dissociation energy for the removal of one ammonia molecule from a given complex and *E* is the total energy of the isolated complex or fragment at its equilibrium structure. No allowance has been made for the basis set superposition error, which makes it likely that the calculated dissociation energies will overestimate the true dissociation energies.

The results are presented in Table 7.1 and depicted in Figure 7.9. Agreement between MP2 and DFT is not perfect but a clear trend of decreasing dissociation energies with increasing complex size can be identified in both cases. This behaviour is similar to that seen for $Sr(NH_3)_n$ and $Ba(NH_3)_n$. According to the MP2 calculations, only the n = 9 and 10 complexes of Ca(NH₃)_n have dissociation energies low enough to undergo NH₃ loss after absorption of a photon in the low frequency part of the N-H stretching region (as shown by the dashed line in Figure 7.9). However, Ca(NH₃)₈ is very close to this threshold and so, allowing for a margin of error, could also be subject to IR photodissociation. In fact, this fits very nicely with experiment since the smallest complex for which photodissociation is very clearly seen is Ca(NH₃)₈. The situation changes for DFT because the lowest energy complex for Ca(NH₃)₈ is the 7+1 complex, which has a weakly bound NH₃ molecule in the second solvation shell. Both MP2 and DFT calculations agree that there should be no photodepletion for n = 1-6 complexes and this is entirely consistent with experiment. i.e. for n = 1-6, the dissociation energy is clearly in excess of the single photon energy required to excite N-H stretching vibrations. Therefore, this is likely to make net ion photoproduction for n = 6 and 7 highly likely, as shown in section 7.3.3. However, note that the even for $Ca(NH_3)_7$ the MP2 dissociation energy is not too far above that of the energy needed to excite N-H stretching vibrations. This might account, and especially for a 'hot' molecule, for the evidence for some depletion signal when recording in the $Ca(NH_3)_7^+$ channel, as mentioned earlier.
n	MP2/ cm ⁻¹	DFT/ cm ⁻¹
1	3347	3249
2	3366	4202
3	4371	4274
4	4841	4079
5	5349	4926
6	6129	4621
7	3581	1548
8	3195	1287 ^(b)
9	2391 ^(a)	1034 ^(b)
10	2437 ^(a)	1217 ^(b)

Table 7.1Calculated dissociation energies for isolated Ca(NH₃)_n complexes.

- (d) Calculated for the 8+1 and 8+2 isomers of n = 9 and 10, respectively, at the MP2 level.
- (e) Calculated for the 7+1, 7+2 and 7+3 isomers for n = 8, 9 and 10, respectively. As detailed in the text, these were the lowest energy structures for Ca(NH₃)_n for n = 8-10 at the DFT level.



Figure 7.9 Dissociation energy for loss of one ammonia molecule from isolated Ca(NH₃)_n complexes. The dashed horizontal line show the photon energy corresponding to the strongest peak seen in the experimental spectra of Ca(NH₃)_{7,8,9}.

7.4.5 Possible surface structure

It is important to be able to eliminate possible contributions to the IR spectra from complexes where the metal atoms sits upon the surface of an $(NH_3)_n$ cluster, rather than being embedded within it. The frequency shift relative to free ammonia varies with the strength of the metalammonia interaction. To explore this, the N-H stretching bands for the surface structure of some selected Ca(NH₃)_n complexes have been predicted by both MP2 and the DFT-B3LYP calculations. Note that the predicted IR spectra for the MP2 calculations are very similar to those from DFT-B3LYP calculations and therefore only the former are shown.

The Ca(NH₃)₈ complex has been chosen to illustrate the findings. As well as calculations on the surface structure of Ca(NH₃)₈, Figure 7.10 shows the predicted IR spectra for the interior structure of Ca(NH₃)₈ (the 8+0 complex) and the pure (NH₃)₈ cluster in the absence of calcium. There is some resemblance between the calculated spectra for the surface structure of Ca(NH₃)₈ and the pure (NH₃)₈ cluster, in the sense that bands are spread over a relatively wide frequency range. However, this is very different from the experimental spectrum, which is in much better agreement with the 8+0 prediction. Moreover, the calculations predict that the total energy for the optimised surface structure is far higher than the global minimum interior structure, by 1.741 eV at the MP2 theory. It is therefore possible to rule out the surface structure of Ca(NH₃)₈ as a contributor to the experimental IR spectrum. This is also consistent with the findings for the Sr(NH₃)_n and Ba(NH₃)_n complexes described in the previous two chapters. Moreover, in the surface structure, the distance between nitrogen and the central calcium metal exceeded those in the interior structure.



Figure 7.10 Comparison between the two possible types of structures for the $Ca(NH_3)_8$ spectra and the free $(NH_3)_8$ spectrum with the experimental IR depletion spectrum in the N-H stretching region.

7.5 Conclusions

The gas phase vibrational spectroscopy of $Ca(NH_3)_n$ complexes has been investigated via infrared photodissociation spectroscopy in the N-H stretching region for the first time. As shown with the aid of *ab initio* calculations, the IR spectra are not consistent with a surface bound structure, in which a Ca atom essentially sits astride an ammonia cluster. Instead, the ammonia molecules cluster around a central metal atom, giving a so-called interior structure. The experimental IR photodepletion spectra show one broad band for n = 8 and one broad and one sharper, and somewhat weaker, IR band for the n = 9 and 10 complexes. The bands for the latter cases signify clear occupation of the second solvation shell around a central Ca atom. For complexes smaller than Ca(NH₃)₈ the dissociation energies are unfavourable for photodepletion experiments.

References

- (1) Thomas, S. J. M.; Edwards, P. P.; Kuznetsov, V. L. *Chemphyschem* **2008**, *9*, 59.
- (2) Lagowski, J. Synth. React. Inorg., Met.-Org. Nano-Metal Chem. 2007, 37, 115.
- (3) Thompson, J. C. *Electrons in liquid ammonia*; Oxford University Press, 1976.
- (4) Edelmann, F.; Abel, E.; Stone, F.; Wilkinson, G. by EWAbel, FGA Stone, G. Wilkinson, and MF Lappert, Pergamon, Oxford **1995**, 4, 11.
- (5) Salter, T. E.; Ellis, A. M. J. Phys. Chem. A 2007, 111, 4922.
- (6) Hertel, I.; Hüglin, C.; Nitsch, C.; Schulz, C. Phys. Rev. Lett. **1991**, 67, 1767.
- Nitsch, C.; Schulz, C.; Gerber, A.; Zimmermann-Edling, W.; Hertel, I. Z. Phys. D At.,
 Mol. Clusters 1992, 22, 651.
- (8) Takasu, R.; Hashimoto, K.; Fuke, K. Chem. Phys. Lett. 1996, 258, 94.
- (9) Castleman, A. W., Jr. J. Phys. Chem. 1996, 100, 12911.
- (10) Steinbach, C.; Buck, U. J. Chem. Phys. 2005, 122, 134301.
- (11) Cottrell, F. J. Phys. Chem. 1914, 18, 85.
- (12) Glaunsinger, W.; Von Dreele, R.; Marzke, R. F.; Hanson, R.; Chieux, P.; Damay, P.;Catterall, R. J. Phys. Chem. 1984, 88, 3860.
- (13) Frisch, M. J. T., G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb,; M. A.; Cheeseman, J. R. M., J. A., Jr.; Vreven, T.; Kudin, K.; N.; Burant, J. C. M., J. M.; Iyengar, S. S.; Tomasi, K.; Barone, V.;; Mennucci, B. C., M.; Scalmani, G.; Rega, N.; Petersson, G. A.;; Nakatsuji, H. H., M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.;; Ishida, M.

N., T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li,; X.; Knox, J. E. H., H. P.; Cross,
J. B.; Bakken, V.; Adamo, C.;; Jaramillo, J. G., R.; Stratmann, R. E.; Yazyev, O.;
Austin, A. J.;; Cammi, R. P., C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.;; Voth,
G. A. S., P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, et al. *Gaussian Inc., Wallingford, CT* 2004, 26.

- (14) Beu, T. A.; Buck, U. J. Chem. Phys. 2001, 114, 7853.
- (15) Suezer, S.; Andrews, L. J. Am. Chem. Soc. 1987, 109, 300.
- (16) Joseph, J.; Jemmis, E. D. J. Am. Chem. Soc. 2007, 129, 4620.

Chapter 8

Theoretical calculations of other metal-ammonia complexes

Section (A): Mg(NH₃)_{*n*}⁺ complexes

8A.1 Introduction

Spectroscopic studies on $Mg(NH_3)_n^+$ complexes have employed mass-selected photodissociation for electronic spectroscopy to examine the change of the electronic states with increasing number of ammonia molecules. A large red shift of the excitation frequency with increasing complex size were observed. The red shift has been explained as a result of the considerable change in the electronic structure as the first solvation shell fills.¹⁻⁴ Vibrational absorption spectroscopy has also been performed on $Mg(NH_3)_n^+$ complexes (for n = 3-6) in the N-H stretching region to obtain further insight into the vibrational frequencies and geometric structures.⁵ Although, this study finds that the Mg^+ -N binding causes the N-H stretches of ammonia to be red shifted from the frequencies of the free ammonia molecule, no evidence has been shown that either all of the ammonia molecules are bound directly to the metal cation.

To date theoretical calculations reported for Mg^+ with various small solvent molecules have been carried out to elucidate their structures and reactions.⁶⁻¹⁰ In the case of $Mg(NH_3)_n^+$ complexes, density functional theory with B3LYP functional and a 6-31G(d) basis set was used by Hokinson and co-workers in an attempt to determine the optimized structures for *n* up to 6.⁶ Although, the structural information was obtained the calculations were not definitive in establishing the size of the inner solvation shell.

Despite many published experimental and theoretical studies for Mg^+ with ammonia molecules, the size of the first solvation shell in $Mg(NH_3)_n^+$ complexes is still a matter of debate. To gain a more complete picture of the solvation structure at the molecular level for

the $Mg(NH_3)_n^+$ complexes, a comprehensive set of *ab initio* calculations are performed, in particular MP2 and DFT-B3LYP calculations with larger basis sets. Therefore, the aim of this section is to explore the microscopic structure in an attempt to obtain a better of the nature of the metal cation solvation process.

8A.2 Computational Details

In order to clarify the lowest energy structures and relative energies of $Mg(NH_3)_n^+$ complexes, *ab initio* calculations were employed. Calculations were carried out by using the GAUSSIAN 03 suite of programs.¹¹ Theoretical calculations were employed both MP2 calculations and DFT methods with the B3LYP functional. The calculations focused on $Mg(NH_3)_n^+$ complexes for n = 1-7. It should be noted that no MP2 calculations were undertaken for n = 7 because of the associated computational expense. Theoretical calculations used a reasonably large basis set, 6-311++G(d,p). The reliability of this basis set can be seen in the earlier studies on calcium-ammonia complexes, as shown in Chapter 4 and Chapter 7 of this thesis. Moreover, this basis set was identified as a good compromise between cost and accuracy.

All geometry optimizations have been confirmed to be real minima by checking for imaginary vibrational frequencies. No symmetry constraints were imposed during calculations to permit the variation of all degrees of freedom.

The predicted vibrational frequencies were scaled by a factor of 0.936 and 0.955 at the MP2 and the DFT-B3LYP calculations, respectively to bring experimental and calculated N-H stretching frequencies of gaseous ammonia into agreement. Note that both methods predicted similar vibrational frequencies and therefore only the results from the DFT-B3LYP calculations are presented in this chapter, unless otherwise stated.

8A.3 Results and Discussion

8A.3.1. Calculated equilibrium structures

As already been mentioned in previous chapters in this thesis, the notation (p + q) is used distinguish isomers, where the values of p is the number of ammonia molecules bound directly to the metal while q is the number of ammonia molecules in the second solvation shell bound to the first shell via hydrogen-bonding.

The key calculated structural parameters for the lowest energy structures of magnesium cation-ammonia complexes are presented in Table 8A.1. The structures of $Mg(NH_3)_n^+$ complexes are shown in Figures 8A.1, together with their relative energies. As shown in this figure, the calculations show that the n + 0 isomer is significantly lower in energy than the (n - 1) + 1 isomer for n = 1-6. An attempt to optimize structures with seven ammonia molecules directly bound to magnesium cation was made but no structure was found where seven ammonia molecules fill a single solvation shell. The lowest-lying energy isomer is found to be the 6+1 isomer, where the seventh NH₃ molecule resides in the second solvation shell and is hydrogen bonded to two of the inner ammonia molecules.

Table 8A.1 Key calculated structural parameters for the lowest energy isomers of $Mg(NH_3)_n^+$ complexes (n = 1-7) and their cations. Distances are in Å and angles in degrees.

п	Parameter (a)	MP2	DFT
	Mg-N1	2.200	2.196
	N1- H3	1.022	1.023
1	Mg -N1-H3	113.5	113.1
	H2-N1-H3	105.2	105.6
	Mg -N1-H2	113.5	113.1
	Mg -N	2.207,2.207	2.228,2.227
	N1- Mg -N2	100.5	102.6
2	N1-H4	1.019	1.022
	H6-N1-H4	105.3	105.5
	H1-N2- Mg	109.1	109.1

Table 8A.1	(Continued)
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	Ma N	2 242 2 242 2 242	2 220 2 240 2 240
	NIG -IN	2.242,2.242,2.242	2.239,2.240,2.240
	NI-Mg-N2	98.30	100.5
	N1-H4	1.020	1.021
- 3	H4-N1-H6	104.5	106.0
	N2- Mg -N3	98.30	100.3
	N3- Mg -N1	98.30	100.5
	Mg N	2 161 2 161 2 161	2 163 2 164 2 164
	Nig -IN	2.101,2.101,2.101	2.105,2.104,2.104
		2.101	2.104
	NI- Mg -N2	109.5	109.7
1	NI-H4	1.026	1.027
-	H4-N1-H6	105.6	105.8
	N2- Mg -N3	109.4	109.3
	N3- Mg -N4	109.5	109.5
	N4- Mg -N1	109.5	109.6
	N1- Mg -N3	109.5	109.4
	Mg -N1	2.197,2.231,2.197	2.205,2.241
	-	2.197,2.231	2.203,2.201
	N1- Mg -N2	89.28	2.238
	N1-H4	1.026	88.46
5	H4-N1-H6	105.3	1.024
5	N2- Mg -N3	89.36	105 5
	N3- Mg -N4	119.9	89.42
	N/- Mg -N1	120.03	119.2
	$M_{1} = M_{2} = M_{1}$	110.0	119.2
	INT-Mg-INS	2 252 2 252 2 252	2266226722266
	Mg -N I	2.252,2.252,2.252	2.200,2.207,2.200
	NI M. NO	2.232,2.232,2.232	2.207,2.203,2.200
	NI-Mg-N2	89.88	90.08
	N1-H3	1.023	1.024
	HI-NI-H3	104.8	105.3
6	N2- Mg -N3	89.83	89.69
	N3- Mg -N4	176.2	176.6
	N4- Mg -N1	87.49	87.32
	N1-Mg -N3	89.84	90.01
	N5- Mg -N3	92.94	92.81
	N6- Mg -N4	3.182	90.2
	Mg -N1		2.261,2.259,2.254
			2.270,2.264,2.270
	Mg -N7		4.553
	N1- Mg -N2		92.65
	N1-H4		1.025
_	H4-N1-H6		105.4
7	N2- Mg -N3	-	88.39
(6+1)	N3- Mg -N4		90.84
	N4- Mg -N1		88.62
	N1-Mg-N3		178.8
	N5_ Mg_N3		88 51
	$N6 M \sim N4$		177.2
	$\frac{100-101g}{Ma} - \frac{104}{Ma}$		
	IN / - IVIS -INO		92.20

a) A single N-H distance has been given since all calculated N-H distances were found to be the same to within ± 0.001 Å.



Figure 8A.1 Calculated structures of $Mg(NH_3)_n^+$ from DFT-B3LYP calculations.



Figure 8A.1 (Continued)

8A.3.2 Predicted infrared spectra

The predicted IR spectra in the N-H stretching region of $Mg(NH_3)_n^+$ for n = 5-7 have been chosen here to probe a specific sized gas phase complexes, and are shown in Figures 8A.2-8A.4, along with several low-lying isomer spectra. It can be seen from these figures that these spectra show large red shifts from the corresponding stretches of the free ammonia molecule. These shifts confirm the coordination of ammonia molecules to the central magnesium cation, similar to that seen previously for the neutral heavier alkaline earth metal-ammonia complexes (see Chapters 5-7 of this thesis).

The predicted vibrational spectrum for the 5+0 structure has an intense band at ~ 3168 cm⁻¹ and several weaker bands in the range 3166-3206 cm⁻¹, which will combine to make a single band at low resolution (see the upper panel of Figure 8A.2). The calculated spectra of structures 4+1(isomer 1) and 4+1(isomer 2) show more vibrational structure, with several high intensity bands spread over a wide spectral range of 2850-3400 cm⁻¹. Each spectrum for these structures displays an intense band below 3000 cm⁻¹ which arises because of the inter-shell hydrogen bonding.

The predicted vibrational spectrum from the 6+0 isomer of $Mg(NH_3)_6^+$ is dominated by an intense band at ~ 3190 cm⁻¹, as shown in the top panel of Figure 8A.3. Both 5+1 and 4+2 structures show one intense band and several less intense bands on top of a broad resonance ranging from 2980 to 3400 cm⁻¹. Again, any intense transitions below 3000 cm⁻¹ are a result of the hydrogen bonding.

The 6+1 structure spectrum in the upper panel of Figure 8A.4, which appears as multiple peaks structure, shows one intense band at ~ 3180 cm⁻¹ and a weak intensity band on the higher frequency side of the N-H stretching region. Predicted harmonic spectra of 5+2(Isomer 1) and 5+2(Isomer 2) structures are similar to each other. A broad spectral absorption range from ~ 2940 cm⁻¹ to ~ 3400 cm⁻¹ is predicted for the 4+3 structure.



Figure 8A.2 Predicted IR spectra of $Mg(NH_3)_5^+$ in the N-H stretching region.



Figure 8A.3 Predicted IR spectra of $Mg(NH_3)_6^+$ in the N-H stretching region.



Figure 8A.4 Predicted IR spectra of $Mg(NH_3)_7^+$ in the N-H stretching region.

Only one experimental study of the IR spectroscopy of $Mg(NH_3)_n^+$, by Ohashi *et al.*, has been reported.⁵ This study observed two distinct IR absorption bands for the spectrum of $Mg(NH_3)_5^+$, at 3095 and 3135 cm⁻¹ (see Figure 8A.5(c)). A similar spectrum is obtained for $Mg(NH_3)_6^+$, albeit slightly blue shifted (see Figure 8A.5 (d)).

A comparison of the predicted spectra of n = 5+0 and 6+0 structures (see the top panel of Figure 8A.2 and 8A.3, respectively) with these experimental IR spectra seen by Ohashi *et al.* show that the width and relative intensities are quite close. 4+1(Isomer 1) and 4+1(Isomer 2) structure spectra (see the middle and lower panel of Figure 8A.2, respectively) did not match either the spacing or relative intensities of the experimental IR bands of n = 5, and are in poor agreement with the experimental spectrum. Moreover, the predicted spectra of 5+1 and 4+2structures (see the middle and lower panel of Figure 8A.3, respectively) have a wider range of spectral bands than that observed in the experimental IR spectrum, and so do not provide a particularly good match to the experimental IR spectrum of the n = 6 structure. Consequently, it is very unlikely that the predicted spectra of 4+1(Isomer 1), 4+1(Isomer 2), 5+1 and 4+2 structures contribute significantly to the experimental spectrum.

Given the similarities between the experimental and theoretical spectra for the n = 5+0and 6+0 structures, the IR spectra support the notion that all of the ammonia molecules occupy the first solvation shell and thus the first shell can hold at least six ammonia molecules. For the largest complex investigated (n = 7), the existence of two solvation shells was found, probably in a 6+1 configuration. Therefore, it is concluded that the first solvation shell can accommodate up to six ammonia molecules. Note that no experimental IR spectrum of the n = 7 complex is currently available for comparison with the theoretical results.

The experimental and theoretical IR spectra of $Mg(NH_3)_n^+$ complexes provide a useful comparison to that of the heavier alkaline earth metal-ammonia complexes (see previous chapters of this thesis). The spectra of $Mg(NH_3)_n^+$ for n = 5 and 6 are found to be similar in appearance to the general shape of the IR spectra for $Sr(NH_3)_8$ and $Ba(NH_3)_9$ complexes. The experimental IR spectra for these complexes show two strong and closely spaced bands. The similarity of these spectra of $Mg(NH_3)_5^+$ and $Mg(NH_3)_6^+$ indicates that the ammonia molecules are in similar environments in these two complexes. However, Ohashi *et al.* provided no explanation as to why these are two bands in each spectra when only one is expected from theory. This is a similar problem to what we see in the IR spectra of $Sr(NH_3)_8$ and $Ba(NH_3)_9$. One point that cannot be left out is that these metals perturb the vibrational frequencies of the N-H ammonia and result in a red shift of the N-H stretching frequencies associated with the metal bound NH₃.



Figure 8A.5 IR photodissociation spectra of $Mg(NH_3)_n^+$ complexes in the N-H stretching region. This figure is reproduced from ref.⁵

8A.4 Conclusions

Ab initio calculations for $Mg(NH_3)_n^+$ for n = 1-7 have been performed. Geometry optimizations and vibrational frequency analysis are employed. The geometric structures of the n = 1-6complexes reveal a single solvation shell. For n = 7 the addition of the seventh ammonia molecule leads to a structure where an ammonia molecules resides in the second solvation shell.

Calculations predict that the widths and intensities of IR bands from the n = 5 and 6 spectra are close to that of those of the experimental IR photodissociation spectra, suggesting that the ammonia molecules are arranged in a single shell structure for these complexes.

Section (B): Eu(NH₃)_n complexes

8B.1 Introduction

In addition to alkali and alkaline earth metals, rare earth metals, such as europium and ytterbium, are also known to dissolve in liquid ammonia.^{12,13} Until now the equilibrium geometries and energies of rare earth- ammonia complexes in the gas phase have received scant attention. Europium (Eu) and Ytterbium (Yb) are considered to be lanthanide analogues for alkaline earth metals.^{14,15}

The only experimental study of a rare earth metal- ammonia complex in the gas phase applied photoionization mass spectrometry and associated *ab initio* calculations to Yb(NH₃)_n complexes, where n = 1 - 10.¹⁶ The combined findings from experimental photoionization results and theoretical data are consistent with the formation of an "interior" structure where the ytterbium atom is solvated within a shell of ammonia molecules, rather than sitting on the exterior of hydrogen-bonded (NH₃)_n clusters, as also found for the alkaline earth metals with ammonia in this thesis. The *ab initio* predictions suggest that the first solvation shell of the Yb atom can accommodate up to eight ammonia molecules before steric repulsion makes occupancy of the second solvation shell more energetically favourable.

Here we extend this theoretical work to $Eu(NH_3)_n$ complexes.

8B.2 Computational Details

Equilibrium geometries of neutral and cationic $Eu(NH_3)_n$ complexes (where n = 1-10) have been calculated using the MP2 calculations and DFT methods with the B3LYP and the PBE1 functions to identify the optimized structures, ionization energies, vibrational frequencies and Eu-N bond dissociation energy. Due to the associated computational expense, the MP2 calculations were not undertaken for n > 8. All calculations were performed using the GAUSSIAN 03 program package.¹¹ All optimized geometries were determined without any symmetry constraint.

A test of the quality of the calculations was to calculate the ionization energy of the Eu atom. In doing so, the ground state spin, S=7/2, has been assumed. The predicted first ionization energy of Eu using the chosen theory can then be compared directly with the experimental value of 5.670 eV.¹⁷ The MP2, DFT-B3LYP and DFT-PBE1 values calculated here are 5.529 eV, 5.370 eV and 5.531 eV, respectively. These values are in good agreement with experiment.

The Eu atom has 63 electrons and clearly including all these electrons in a calculation would greatly increase the computational cost. To reduce the cost a relativistic effective core potential (ECP28MWB), known as the Stuttgart RSC 1997 ECP, was used to simulate the effects of the core electrons.¹⁸ The valance space was represented by a double-zeta basis set that includes d-type polarization functions.¹⁹ Further details are provided in Chapter 3 of this thesis. It was found that the ECP of the Eu atom is the best available in the literature and shows excellent agreement with experimental findings.²⁰⁻²² The use of the standard Pople double-zeta 6-31+G(d,p) basis sets was applied for nitrogen and hydrogen atoms in order to keep a balanced overall basis set for the complexes.

A vibrational frequency calculation was carried out at each optimized structure to confirm that a true potential energy minimum was obtained. Again, the predicted vibrational frequencies from all methods are very similar, therefore throughout this chapter we will refer to the predictions of vibrational frequencies obtained from DFT-PBE1 methods, unless otherwise stated. Vibrational frequencies were scaled by 0.932, 0.935 and 0.949 for the MP2, DFT-PBE1 and DFT-B3LYP calculations, respectively.

8B.3 Results and Discussion

8B.3.1 Photoionization energy predictions.

In order to obtain insights into the behaviour of $Eu(NH_3)_n$ complexes (n = 1-10) and the ability of Eu metal to release an electron into ammonia as the number of NH₃ molecules increases, the adiabatic ionization energies have been investigated. The calculated adiabatic ionization energies for the global minima of the Eu(NH₃)_n complexes are provided in Table 8B.1. A graphical summary of the predicted ionization energies is shown in Figure 8B.1.

What is clear from the table and figure is that the adiabatic ionization energies decrease smoothly as the number of ammonia molecules increases, until they begin to plateau. This is similar to the corresponding alkaline earth metal complexes. This decrease in the adiabatic ionization energy is mainly due to the formation of a solvated electron, as interpreted in the previous chapters. Note, no experimental results are available for the ionization energies of the Eu(NH₃)_n (n = 1-10) complexes.

To show how the presence of the metal affects the bonding with ammonia molecules, both surface and interior structures have been considered. Evidence for both internal and external solvation structures have been investigated in the previous chapters of this thesis. As clearly shown in these chapters, the neutral alkaline earth metal-ammonia complexes show a marked preference for an interior structure. Calculations were therefore performed on Eu(NH₃)₅ to see if this might adopt surface structures. These calculations predict that the total energy for the surface structure is found to be higher than the lowest energy interior structure by 0.979 eV, 0.989 eV and 1.317 eV at the DFT-PBE1, MP2 and DFT-B3LYP methods respectively. In terms of bond distance, the surface structure shows a longer Eu-N distance than interior structure. Therefore, an interior structure for Eu(NH₃)_n complexes is assumed to be preferred.

Table 8B.1First ionization energies of $Eu(NH_3)_n$ complexes (n = 1-10). The DFT-PBE1,
MP2 and DFT-B3LYP results are corrected for zero point vibrational energies
in the neutral and ion complexes.

n	DFT-PBE1 /eV	MP2/eV	DFT-B3LYP /eV	EXP./eV
0	5.531	5.529	5.730	5.670 ^(a)
1	4.718	4.656	4.902	-
2	4.187	4.036	4.349	-
3	3.732	3.540	3.899	-
4	3.454	3.157	3.615	-
5	3.357	3.053	3.520	-
6	3.308	3.039	3.462	-
7	3.228	2.958	3.390	-
8	3.174	2.862	3.346	-
9	3.005	-	3.183	-
10	2.836	-	3.056	-

(a) Experimental 1st ionization energy of atomic Eu taken from ref.¹⁷



Figure 8B.1 Plot of the calculated and experimental adiabatic ionization energy versus n for Eu(NH₃)_n (n =1-10).

8B.3.2. Calculated equilibrium structures

In order to obtain more information on the microscopic nature of solvation, various possible structural isomers have been investigated. The structural landscape for the complexes have been established in the same way as the work for the alkaline earth metal-ammonia complexes, by determining possible potential energy minima for each complex size to establish the structural landscape using a small basis set and a simple level of computation. Once minima were found, the resulting structures were recalculated using a higher level of computation in combination with the larger basis set. The key structural parameters from the MP2 and DFT calculations for both neutral and cationic complexes are listed in Table 8B.2. The geometric structures of the predicted global potential energy minima for the complexes studied are illustrated in Figure 8B.2.

The lowest energy structure found for EuNH₃ has C_{3v} symmetry. For complexes with two or more ammonia molecules, more than one isomer has been found. Once the first NH₃ molecule is bound to the Eu atom, the second ammonia molecule has two different ways it can bind: one is to directly bind to the Eu metal, giving rise to the 2+0 structure. The second way is through hydrogen bonding to the existing NH₃ molecule, giving the 1+1. The calculations predict that the 2+0 structure is significantly lower in energy than the 1+1 isomer, the difference being 0.302, 0.312 and 0.281 eV for the DFT-PBE1, MP2 and DFT-B3LYP calculations, respectively. We conclude that the Eu-N bonding is stronger than the hydrogen bonding between the first and the second solvation shell ammonia molecules, making the 2+0 structure the global energy minimum.

Similar to the alkaline earth metal-ammonia complexes, the lowest energy structures of the n = 3-7 complexes were found to be n + 0 isomers.

	Parameter	MP2		DFT-PBE1		DFT-B3LYB	
п	(a)	Neutral	Cation	Neutral	Cation	Neutral	Cation
	Eu-N1	2.635	2.576	2.654	2.599	2.683	2.625
	N1-H3	1.020	1.021	1.021	1.021	1.024	1.024
1	Eu-NI-H3	111.9	113.5	111.8	113.4	112.6	113.84
	H2-N1-H3	106.9	105.2	106.9	105.3	106.9	105.3
	$Eu-INI-\Pi Z$	2 626 2 626	115.5	111.0	115.4	110.9	112.7
	Eu-IN N1-Eu-N2	2.020,2.020	2.032,2.032	2.000,2.000	2.030,2.033	2.084,2.084	2.088,2.088
2	H6-N2-H4	1/9.9	105.3	107.2	105 4	107.2	105 /
4	H4-N2-Eu	1117	113.4	111.5	113.2	1117	113.3
-	Eu-N	2.644.2.596	2.646.2.625	2.674.2.636	2.658.2.658	2.698.2.6584	2.693.2.678
	241	2.643	2.646	2.671	2.658	2.698	2.693
	N1-Eu-N2	143.0	138.9	141.9	119.9	140.8	130.7
3	N1-H3	1.022	1.020	1.022	1.021	1.025	1.023
	H2-N1-H3	107.6	105.2	106.6	105.9	106.6	106.1
	N2-Eu-N3	142.9	138.9	140. 7	120.4	140.9	131.3
	N3-Eu-N1	73.9	82.0	77.3	119.7	78.2	97.9
	Eu-N	2.625,2.646	2.674,2.674	2.685,2.670	2.712,2.711	2.700,2.701	2.735,2.735
		2.646,2.625	2.674,2.674	2.669,2.683	2.711,2.711	2.702,2.701	2.736,2.735
	N1-Eu-N2	78.2	89.9	83.8	89.8	88.3	90.4
	N1-H3	1.022	1.019	1.021	1.019	1.026	1.023
4	H1-N1-H3	107.8	105.5	107.1	105.9	107.2	105.9
	N2-Eu-N3	85.4	90.0	109.9	91.9	93.2	90.4
	N3-Eu-N4	78.2	89.9	83.7	91.0	87.8	90.1
	N4-Eu-N1	121.4	90.0	86.3	89.1	94.1	90.4
	En N	137.3	1/0.0	100.9	109.8	2 710 2 670	2 7501 2 729
	Eu-IN	2.039,2.032	2.087,2.087	2.088,2.087	2.720,2.720	2.710,2.070	2.7501,2.758
		2.038,2.041	2.087,2.087	2.070,2.077	2.719,2.719	2.709,2.092	2.751,2.745
	N1-Eu-N2	128.4	134 1	107.4	1167	85 3	80.6
	N1-H3	1.021	1.021	1.022	1.021	1.025	1.024
5	H1-N1-H3	106.9	105.9	106.7	105.8	106.8	106.0
_	N2-Eu-N3	130.7	135.7	150.1	150.3	150.4	153.1
	N4-Eu-N1	79.1	149.6	151.1	151.0	84.4	79.6
	N5-Eu-N3	149.5	148.2	128.1	131.1	85.0	80.5
	Eu-N	2.648,2.648	2.667,2.667	2.692,2.2	2.713,2.713	2.723,2.723	2.745,2.745
		2.648,2.648	2.667,2.667	2.692,2.692	2.713,2.713	2.723,2.723	2.745,2.745
		2.648,2.648	2.667,2.667	2.692,2.692	2.713,2.713	2.723,2.723	2.745,2.745
	N1-Eu-N2	84.6	81.2	84.8	82.9	88.9	89.0
	NI-H3	1.023	1.022	1.024	1.021	1.027	1.024
6	HI-NI-H3	106.1	105.2	106.2	105.4	106.2	105.5
0	N3-EU-N4	84.5	81.8	84.7	83.1	89.1	89.0
	N1-EU-INS N6 Eu N4	80.5 104.5	82.0 120.0	80.4 84.8	82.0	80.2	80.0
	Fu-N	2 661 2 666	2 686 2 689	2 721 2 716	02.9	09.2	07.2
	Lu-IN	2.001,2.000	2.080,2.089	2.721,2.710	2.743,2.737	2.747,2.740	2.772,2.709
		2.669.2.672	2.696 2.69	2.734,2.720	2.734,2.745	2.735,2.740	2.701,2.771
		2.682	2.709	2.735	2.755	2.760	2.782
	N1-Eu-N2	74.32	74.6	74.9	75.2	74.7	74.9
	N1-H3	1.024	1.021	1.022	1.022	1.026	1.023
	H1-N1-H3	105.9	105.3	106.1	105.4	106.2	105.5
7	N4-Eu-N1	119.7	122.5	114.0	114.2	113.5	113.8
	N1-Eu-N3	76.7	76.5	77.7	77.8	77.9	77.9
	N5-Eu-N3	157.81	157.1	156.2	155.7	156.4	155.9
	N6-Eu-N4	157.8	157.1	155.9	155.5	156.3	155.8

Table 8B.2Key calculated structural parameters for the lowest energy isomers of $Eu(NH_3)_n$ complexes and their cations (n = 1-10). Distances are in Å and angles in degrees.

	Eu-N	2,704,2,704	2.728.2.728	2.766.2.766	2,786,2,786	2.796.2.796	2.818.2.819
	2011	2.704.2.704	2.728.2.728	2.766.2.766	2.786.2.786	2.796.2.796	2.819.2.819
		2.704.2.704	2.728.2.728	2.766.2.766	2.787.2.787	2.796.2.796	2.819.2.819
		2.704.2.704	2.728.2.728	2.766.2.766	2.786.2.786	2.796.2.796	2.819.2.818
	N1-Eu-N2	145.8	145.7	79.6	79.2	79.7	79.3
	N1-H3	1.022	1.021	1.023	1.020	1.025	1.023
	H1-N1-H3	105.8	105.2	106.1	105.4	106.2	105.5
	N2-Eu-N3	80.9	80.6	79.6	79.3	79.7	79.4
8	N3-Eu-N4	145.8	145.7	79.5	79.2	79.7	79.4
	N4-Eu-N1	139.7	139.6	142.8	142.7	142.9	142.8
	N1-Eu-N3	72.4	72.6	72.0	72.2	71.9	72.2
	N5-Eu-N3	113.2	113.7	112.5	112.9	112.3	112.7
	N6-Eu-N4	80.9	80.6	112.7	113.1	112.5	112.9
	N7-Eu-N6	139.7	139.6	142.8	142.8	142.9	142.8
	N8-Eu-N6	145.8	145.7	72.1	72.3		
	Eu-N			2.762,2.769	2.779,2.777	2.793,2.799	2.812,2.809
				2.753,2.764	2.778,2.783	2.786,2.794	2.808,2.817
				2.762,2.762	2.782,2.781	2.793,2.792	2.815,2.814
				2.761,2.771	2.782,2.791	2.791,2.801	2.816,2.821
	Eu-N5			5.037	4.884	5.119	4.969
	N1-Eu-N2			72.3	73.0	72.19	72.92
9	N1-H3			1.023	1.021	1.026	1.023
(8+1)	H1-N1-H3			106.3	105.6	106.4	105.6
	N2-Eu-N3	-	-	116.8	112.9	116.1	112.8
	N3-Eu-N4			73.9	69.9	73.7	70.0
	N4-Eu-N1			109.5	113.7	109.8	113.6
	N1-Eu-N3			72.4	73.2	72.2	73.0
	N5-Eu-N3			38.4	43.3	37.6	42.5
	N6-Eu-N4			76.7	74.0	77.2	73.9
	N8-Eu-N6			73.8	75.1	73.8	74.8
	N9-Eu-N6			117.9	118.8	117.5	117.8
	Eu-N			2.757,2.755	2.774,2.772	2.796,2.776	2.806,2.806
				2.765,2.768	2.783,2.783	2.793,2.813	2.814,2.817
				2.765,2.768	2.780,2.787	2.801,2.807	2.812,2.819
	-			2.760,2.756	2.776,2.774	2.791,2.784	2.807,2.809
	Eu-N9			4.833	4.979	4.836	5.085
	Eu-N10			5.033	5.038	5.103	5.128
10	NI-Eu-N2			83.8	80.5	113.6	81.1
10	NI-H3			1.021	1.019	1.026	1.022
(8+2)	HI-NI-H3	-	-	106.4	105.7	106.1	105.7
	N2-Eu-N3			79.2	/6./	/3.5	//.8
	N3-Eu-N4			80.2	80.4	/9.3	80.1
	N4-EU-N1			143.6	143.6	143.5	143.4
	N1-EU-N3 N5 E., N2			08.4	09.2	12.4	09.5 72 5
	NG E. NA			71.2	/ 3.0	70.5	73.5
	NO-EU-IN4			11.2	/1.5	70.7	/1.2 76.2
	IN / -EU - INO N2 Ev N10			/0. /	13.4	12.5	10.5
	NJ En NO			140.1	143.9	141.8 75.2	141./
	INI-EU-IN9			41.3	30.3	13.5	57.9

a) A single N-H distance has been given since all calculated N-H distances were found to be the same to within ± 0.001 Å.



Figure 8B.2Calculated structures of neutral $Eu(NH_3)_n$ and it cationic counterparts
from DFT-PBE1 calculations.



For Eu(NH₃)₈ the DFT-PBE1 and DFT-B3LYP methods predict that the 8+0 structure is lower in energy than the 7+1 structure by 0.155 eV and 0.122 eV, respectively. The optimized geometry of this structure is quite similar to the Ca(NH₃)₈, Sr(NH₃)₈ and Ba(NH₃)₈ complexes (see earlier chapters in this thesis) and to Yb(NH₃)₈.¹⁶

For Eu(NH₃)₉ complex, the 8+1 structure is predicted to be the lowest energy structure, the difference being 0.078 eV and 0.095 eV at the DFT-PBE1 and DFT-B3LYP methods respectively. The 8+2 structure is found to be lower in energy than the 9+1 structure, the corresponding energy difference being 0.050 eV for DFT-PBE1 calculations and 0.119 eV for DFT-B3LYP calculations. Note, no minimum could be found for a 10+0 structure.

8B.3.3 Predicted infrared spectra

Harmonic vibrational frequency analysis and the lowest energy structures, along with their predicted relative total energies are shown in Figures 8B.3 – 8B.5, together with different low lying isomer spectra for n = 8-10. The predicted vibrational frequencies of Eu(NH₃)_n complexes shift to lower frequencies compared to those same vibrations in the free ammonia molecule, upon bonding with the europium atom.

The 8+0 isomer spectrum is dominated by the one band in the top panel of Figure 8B.3. This band is composed of two strong peaks of similar wavenumber and intensity, and one peak with a medium intensity. The two strong peaks are shown at ~ 3172 cm⁻¹, while the medium intensity peak at ~ 3175 cm⁻¹. This result is similar to the predicted IR spectrum for the 8+0 structure of $M(NH_3)_n$ complexes, where M = Ca, Sr and Ba (for further details see the previous chapters) which adopt structures in which all NH₃ molecules coordinate directly with the metal. The predicted IR spectra shown in the middle and lower panel of Figure 8B.3 correspond to the 7+1 and 6+2 isomer structures, respectively and show more bands with several at high intensity between 3100 and 3350 cm⁻¹. Moreover, extremely weak bands which are shown at higher frequency in these spectra are due to the asymmetric N-H structure) or two (for 6+2 structure) ammonia molecules in the second solvation shell via hydrogen bonding.

The 8+1 spectrum consists of a main (higher intensity) band and a much weaker intensity band. The n = 9+0 complex shows has an intense feature at 3178 cm⁻¹ and several weak peaks which combine to make a single band at low resolution. The 7+2 and 6+3 isomer spectra show additional weaker bands in the presence of the loosely held ammonia molecules in the outer solvation shell.





Predicted IR spectra of Eu(NH₃)₈ in the N-H stretching region









Predicted IR spectra of $Eu(NH_3)_{10}$ in the N-H stretching region.

8B.3.4. Dissociation energies

The energy required to remove at least one ammonia molecule for n = 1-10 has been investigated by both the DFT-PBE, MP2 and the DFT-B3LYP level of theories for the first time in this chapter. The Eu-N bond dissociation energies were calculated using the standard supermolecule expression:

$$D_0[Eu(NH_3)_n] = E[NH_3] + E[Eu(NH_3)_{n-1}] - E[Eu(NH_3)_n]$$
(8.1)

Here, D_0 corresponds to the dissociation energy for the removal of at least one ammonia molecule from a given complex, and *E* is the total energy of the isolated complex or fragment at equilibrium structure. Note that the total energy includes the zero point vibrational energy (ZPVE). Dissociation energy calculations were performed without compensation for the basis set superposition error.

n	DFT-PBE1/ cm ⁻¹	MP2/ cm ⁻¹	DFT-B3LYP/ cm ⁻¹
1	3637	2819	2819
2	4387	3958	3631
3	3112	2528	2423
4	3381	2915	2895
5	3601	3405	2980
6	4053	4493	3928
7	3416	3861	2561
8	2624	2991	2000
9	1101 ^(a)	-	663 ^(a)
10	1215 ^(a)	-	843 ^(a)

Table 8B.3Calculated dissociation energies for Eu(NH₃)_n complexes.

(a) Calculated for 8+1 and 8+2 isomers of n = 9 and 10, respectively.



Figure 8B.6Dissociation energies for loss of one ammonia molecule from isolated
 $Eu(NH_3)_n$ complexes.

The predicted Eu-N bond dissociation energies, given in Table 8B.3 and Figure 8B.6 show a similar trend to the $Sr(NH_3)_n$ and $Ba(NH_3)_n$ complexes (for further details see previous chapters of this thesis); that is, the most dramatic decrease takes place up to $n \ge 8$, suggesting again that the dissociation energy of NH₃ molecules that are not directly bound to the central europium atom is less than for those that are bound. Therefore, it is most likely that the mass-selected infrared photodepletion spectra of Eu(NH₃)_n complexes would successfully record in the N-H stretching region.

8B.4 Conclusions

Ab initio calculations for the neutral and their cationic equivalents $Eu(NH_3)_n$ complexes for n = 1-10 have been reported for the first time. A smooth decrease in predicted ionization energy

as a function of complex size is shown at all theory levels of computations. These ionization energies show a similar trend for alkaline earth metal complexes with ammonia, suggesting that the valence electron of Eu atom is transferred to ammonia at sufficiently large n. The theoretical calculations predict that the neutral Eu(NH₃)_n complexes can accept up to eight ammonia molecules in the first solvation shell.

The IR spectra of $Eu(NH_3)_n$ complexes have been predicted. The Eu-N bond dissociation energies calculated per ammonia molecule added show a monotonically decreasing trend as a function of complex size and it looks highly likely that photodepletion spectroscopy of $Eu(NH_3)_n$ complexes would succeed.

References

- (1) Lee, J. I.; Sperry, D. C.; Farrar, J. M. J. Chem. Phys. 2004, 121, 8375.
- (2) Liu, H.; Guo, W.; Yang, S. J. Chem. Phys. 2001, 115, 4612.
- (3) Yoshida, S.; Okai, N.; Fuke, K. Chem. Phys. Lett. 2001, 347, 93.
- (4) Yoshida, S.; Daigoku, K.; Okai, N.; Takahata, A.; Sabu, A.; Hashimoto, K.; Fuke, K.
 J. Chem. Phys. 2002, *117*, 8657.
- (5) Ohashi, K.; Terabaru, K.; Inokuchi, Y.; Mune, Y.; Machinaga, H.; Nishi, N.; Sekiya,
 H. *Chem. Phys. Lett.* 2004, *393*, 264.
- (6) Shoeib, T.; Milburn, R. K.; Koyanagi, G. K.; Lavrov, V. V.; Bohme, D. K.; Siu, K. M.;
 Hopkinson, A. C. *Int. J. Mass spectrom.* 2000, 201, 87.
- (7) Daigoku, K.; Hashimoto, K. J. Chem. Phys. 2004, 121, 3569.
- (8) Bauschlicher, C. W.; Partridge, H. Chem. Phys. Lett. 1991, 181, 129.
- (9) Andersen, A.; Muntean, F.; Walter, D.; Rue, C.; Armentrout, P. B. J. Phys. Chem. A 2000, 104, 692.

- (10) Chan, K. W.; Wu, Y.; Liu, Z.-F. J. Phys. Chem. A 2008, 112, 8534.
- (11) Frisch, M. J. T., G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb,; M. A.; Cheeseman, J. R. M., J. A., Jr.; Vreven, T.; Kudin, K.; N.; Burant, J. C. M., J. M.; Iyengar, S. S.; Tomasi, K.; Barone, V.;; Mennucci, B. C., M.; Scalmani, G.; Rega, N.; Petersson, G. A.;; Nakatsuji, H. H., M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.;; Ishida, M. N., T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li,; X.; Knox, J. E. H., H. P.; Cross, J. B.; Bakken, V.; Adamo, C.;; Jaramillo, J. G., R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.;; Cammi, R. P., C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.;; Voth, G. A. S., P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, et al. *Gaussian Inc., Wallingford, CT* 2004, 26.
- (12) Warf, J. C.; Korst, W. L. J. Phys. Chem. 1956, 60, 1590.
- (13) Catterall, R.; Symons, M. Journal of the Chemical Society (Resumed) 1965, 3763.
- (14) Hitzbleck, J.; O'Brien, A. Y.; Deacon, G. B.; Ruhlandt-Senge, K. *Inorg. Chem.* 2006, 45, 10329.
- (15) Müller, W. *Physics Letters* **1965**, *17*, 82.
- (16) Guttridge, M. J.; Don, S. H.; Ellis, A. M. ChemPhysChem 2013, 14, 723.
- (17) <u>http://physics.nist.gov/PhysRefData/Handbook/Tables/europiumtable1.htm.</u>
- (18) https://bse.pnl.gov/bse/portal.
- (19) Hay, P. J.; Wadt, W. R. J. Chem. Phys. 1985, 82, 299.
- (20) Cao, X.; Dolg, M. Theor. Chem. Acc. 2002, 108, 143.
- (21) Cao, X.; Dolg, M. J. Chem. Phys. 2001, 115, 7348.
- (22) Xiaoyan, C.; Wenjian, L.; Dolg, M. Sci. China Ser. B: Chem. 2002, 45, 91.

Chapter 9

Conclusions

9.1 Thesis summary

The motivation behind the present work was the desire to explore new metal-ammonia complexes using molecular beam techniques. This work focused on the neutral alkaline earth metals and affect the onset of solvation by ammonia to analysis solvation on the molecular scale.

The photoionization efficiency (PIE) curves for the Ca(NH₃)_n and Sr(NH₃)_n complexes were measured for the first time. The measured adiabatic ionization energies (AIE) for each complex were compared to theoretical predictions. Good agreement was found between experiment and theory when the latter assumed the lowest energy structures. Consequently, it is concluded that the lowest energy structures dominate in the molecular beam. In contrast to the case of Mg(NH₃)_n⁺, which has been studied previously¹ and where the metal atom prefers to sit on the surface of an (NH₃)_n cluster, interior structures are formed in Ca(NH₃)_n and Sr(NH₃)_n, in which the Ca and Sr atoms reside within one or more shells of ammonia molecules. Moreover, this piece of work suggests that the first solvation shell around calcium and strontium atoms can take a maximum of eight and nine ammonia molecules, respectively.

To gain further understanding of the neutral alkaline earth metal-ammonia complexes, mass selected infrared photodepletion spectroscopy was applied to these complexes for the first time. The experimental IR spectra were compared with the results of *ab initio* calculations. A substantial red shift of the N-H stretching vibrations was found when compared with the free ammonia molecule. This red shift reflects a weakening of the N-H bonds by the strong interaction between the metal atom and ammonia molecules in the first solvation shell. IR spectra were recorded for $Sr(NH_3)_n$ complexes for n = 6-14. Two strong IR absorption bands between 3100 and 3250 cm⁻¹ were observed for n = 8 and 9. For $Sr(NH_3)_{10}$ a similar pair of bands is accompanied by a weaker band at higher frequency. The additional band is taken as an indicator of closure of the first solvation shell, which implies that the first shell can accommodate a maximum of nine NH₃ molecules. Over the size range from n = 11 to n = 14 much broader IR absorption bands are seen with additional peaks at higher frequency. Specific assignments of these bands have not been made but these spectra must arise from complexes with ammonia molecules in two different shells.

Infrared spectra of $Ba(NH_3)_n$ complexes in the N-H stretching region have been obtained for n = 4-10. Two distinct IR absorption bands were seen for both $Ba(NH_3)_8$ and $Ba(NH_3)_9$ complexes. The similarity between these spectra indicate that the ammonia molecules in each complex must exist in similar environments. In the case of $Ba(NH_3)_{10}$, two strong bands and a much weaker absorption band at around 3280 cm⁻¹ are seen. This weak band were assigned to the presence of the tenth ammonia molecule located in the second shell, leading to the conclusion that the first solvation fills with nine ammonia molecules. These conclusions fit nicely with the predictions from a supporting theoretical study.

In contrast to the experimental IR photodepletion spectra for $Sr(NH_3)_n$ and $Ba(NH_3)_n$ complexes, the IR spectra of $Ca(NH_3)_n$ complexes showed a single broad IR band for n = 8. For n = 9 and 10, much broader IR absorption bands were observed with a second, fully resolved band, located towards the higher frequency part of the spectrum. This suggests that the first solation shell of $Ca(NH_3)_n$ can contain a maximum of eight NH₃ molecules.

The observation of IR depletion spectra relies upon sufficiently rapid dissociation of the $M(NH_3)_n$ once vibrationally excited. To gain more information about the viability of this process, it is necessary to know the M-N dissociation energies. The M-N bond dissociation

energies were therefore calculated for n = 1-10. A gradual decrease in dissociation energy is seen as the first solvation shell fills and a large decrease occurs for any NH₃ molecules that occupy the second shell.

The predicted IR spectra of $Mg(NH_3)_n^+$ complexes were investigated and compared with IR photodissociation spectra reported in the literature.² The close agreement between the theoretical and experimental spectra was found. Possible geometries, ionization energies and harmonic vibrational frequencies were predicted. These results suggested that the lowest energy structure for *n* =1-6 to contain a single solvation shell, whereas *n* =7 contain two shells.

The microsolvation geometric structures and ionization energies of $Eu(NH_3)_n$ complexes where n = 1-10 were also investigated by means of *ab initio* calculations. The calculations show that the n = 10 complex consists of ten ammonia molecules arranged around a central europium metal atom; eight ammonia molecules are bound directly to Eu atom, while two ammonia molecules adopt a looser arrangement. However, the lowest energy structure for n = 10 is found to be the 8+2 structure.

9.2 Recommendations for future work

It would be interesting to see the work described in this thesis extended to include other metals, most notably certain lanthanide metals that are known to dissolve in liquid ammonia. A good example is europium, hence the theoretical study reported above. The calculations, and in particular the dissociation energies, indicate that photodepletion spectroscopy on $Eu(NH_3)_n$ complexes is viable.

It would also be interesting to extend the experimental and theoretical work to mixed solvent system to explore the effect of a mixture of solvent systems. Some work has already bene attempted on this in the case of alkali metals, most notably for $Li(NH_3)_n(CH_3NH_2)_m$

mixed³ and Li(H₂O)_{*n*}(NH₃) complexes.⁴ A second interesting area of research would be to investigate the neutral alkaline earth metals in other solvents than ammonia in order to show how the presence of the metal affects the solvated electron and complex geometry. Methylamine has bene chosen previously for this type of work and resulted in IR spectra of Li(NH₂CH₃)_{*n*} complexes.⁵

Interest in the prospect of neutral alkaline earth metals-ammonia complexes could be extended to record size-selective electronic spectra to show an absorption feature that may be attributable to the solvated electron. This study has been employed previously to investigate Li(NH₃)₄ and LiNH₃.^{6,7} It would also be expected that new experimental techniques with higher resolution and sensitivity will emerge in the future to identify the elucidation of details of the contribution of different isomers in the molecular beam through the technique of spectral hole-burning.⁸

References

- Elhanine, M.; Dukan, L.; Maître, P.; Breckenridge, W.; Massick, S.; Soep, B. J. Chem.
 Phys. 2000, 112, 10912.
- (2) Ohashi, K.; Terabaru, K.; Inokuchi, Y.; Mune, Y.; Machinaga, H.; Nishi, N.; Sekiya, H. *Chem. Phys. Lett.* 2004, *393*, 264.
- (3) Bhalla, N., *PhD Thesis*, University of Leicester, 2012.
- (4) Pratihar, S.; Chandra, A. J. Chem. Phys. 2008, 129, 024511.
- (5) Salter, T. E.; Ellis, A. M. J. Chem. Phys. 2007, 127, 144314.
- (6) Varriale, L.; Tonge, N. M.; Bhalla, N.; Ellis, A. M. J. Chem. Phys. 2010, 132, 161101.
- (7) Varriale, L.; Bhalla, N.; Tonge, N. M.; Ellis, A. M.; Wright, T. G. J. Chem. Phys. 2011, 134, 124304.
- (8) Zwier, T. S. Nat. Chem. 2009, 1, 687.
