



Editor's choice

Infrared spectroscopy of $\text{Ca}(\text{NH}_3)_n$ complexes

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ABSTRACT

Infrared spectra of $\text{Ca}(\text{NH}_3)_n$ complexes in the gas phase have been recorded for the first time. The spectra are consistent with structures where the Ca atom resides inside one or more solvation shells of NH_3 molecules. IR spectra were recorded using a photodissociation technique. A comparison of the spectra with those predicted from *ab initio* calculations suggests that $\text{Ca}(\text{NH}_3)_8$ has all NH_3 molecules in a single solvent shell around the Ca atom, whereas the spectra of $\text{Ca}(\text{NH}_3)_9$ and $\text{Ca}(\text{NH}_3)_{10}$ are consistent with two-shell structures.

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1. Introduction

The study of metals dissolved in liquid ammonia has a history stretching back to original work by Humphry Davy in the early 19th century [1]. Davy was the first to see the remarkable colours of alkali/ammonia solutions, which range from metallic bronze at high metal concentrations to deep blue at low concentrations. It is now known that the blue colour results from the formation of solvated electrons, whereas the highly reflective bronze sheen derives from metallic-like solutions with large electrical conductivities. There have been various attempts over many decades to learn more about these solutions. However, as described in a relatively recent review article [2], these are complex solute/solvent systems and the full range of species active in these solutions is poorly understood.

Detailed information about solute-solvent interactions is difficult to extract from a multi-component bulk solution. An alternative way of learning something about the underlying interactions between metal atoms and ammonia molecules is through the study of small metal-ammonia complexes in the gas phase. Spectroscopic techniques, such as mass-selective laser spectroscopy, can be used to determine the structures adopted by such complexes. Furthermore, quantum chemical calculations on relatively small complexes are viable and their combination with spectroscopic measurements is a particularly powerful way of exploring solute-solvent interactions.

In the case of alkali metals, the earliest experimental studies of $\text{M}(\text{NH}_3)_n$ complexes employed photoionization mass spectrometry, and in particular the measurement of ionization energies as a function of n [3–7]. Unfortunately mass spectrometry provides limited

structural information and so more recent work has exploited optical spectroscopy, including resonance-enhanced multiphoton ionization spectroscopy and photodepletion spectroscopy [8–14]. Other experimental techniques, such as photoelectron spectroscopy [15] and electric deflection measurements [16], alongside various theoretical studies [17–21], have provided a considerably detailed picture of the solvation of alkali atoms by ammonia molecules.

By comparison with the alkali metals, complexes between alkaline earth metals and ammonia have received scant attention. In fact until very recently the only study was restricted to $\text{Mg}(\text{NH}_3)_n$, and in particular photoionization measurements and associated *ab initio* calculations [22]. In marked contrast to alkali-ammonia complexes, where the alkali metal is surrounded by ammonia molecules (which we will call an interior complex) in the lowest energy structure, $\text{Mg}(\text{NH}_3)_n$ complexes adopt a surface structure in which the Mg atom sits on the surface of an $(\text{NH}_3)_n$ cluster. A surface location is favoured energetically because the closed shell ground state of the Mg atom interacts rather weakly with individual NH_3 molecules, and so there is no energetic gain in disrupting the hydrogen bonding in the ammonia network. This observation most probably explains the very low solubility of magnesium in liquid ammonia [23].

By way of contrast Ca, Sr and Ba all readily dissolve in liquid ammonia and generate solvated electrons in sufficiently dilute solutions [24]. This suggests that these heavier alkaline earth metals have a stronger interaction with ammonia molecules. To probe this interaction, we report here the first infrared (IR) spectra of alkaline earth-ammonia complexes, focusing on $\text{Ca}(\text{NH}_3)_n$. The IR spectra were recorded in the NH stretching region using a photodepletion technique. As will be described, only complexes with sufficiently low ammonia binding energies, which correspond to relatively large complexes, yield IR depletion spectra. We are able

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to show that these spectra are consistent with interior structures where the Ca atom is surrounded by ammonia molecules.

2. Experimental

The apparatus employed has been described in detail previously [11]. Briefly, $\text{Ca}(\text{NH}_3)_n$ complexes were made by laser ablation of the solid alkaline earth metal in an atmosphere of pure ammonia. The ammonia was delivered by a pulsed valve and flowed over the surface of the metal target at a typical pressure of 2 bars before expanding into vacuum to generate a supersonic jet. The laser pulse was provided by a Nd:YAG laser operating at 346 nm and was synchronized to arrive at the metal target at the same time as the pulse of ammonia gas. We used 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.

The jet was then skimmed to form a molecular beam and entered the source region of a Wiley-McLaren time-of-flight mass spectrometer, where it was crossed by two pulsed laser beams. One laser, operating in the ultraviolet, was used for photoionization of the complexes. The other laser pulse, timed to arrive just before the ultraviolet pulse, was used to excite spectroscopic transitions in the infrared (from a LaserVision optical parametric oscillator/amplifier). IR absorption was achieved by a form of action spectroscopy involving the dissociation of $\text{Ca}(\text{NH}_3)_n$ following photon absorption, usually by loss of a single NH_3 molecule. The dissociation event can be registered through a fall in the $\text{Ca}(\text{NH}_3)_n^+$ signal measured via the mass spectrometer. In this sense the spectroscopy is mass selective.

However, there are two potential complications to note. First, if the IR photon energy is below the dissociation energy of the complex, and/or the dissociation process is very slow, then photodepletion spectroscopy is not viable. Second, any loss in $\text{Ca}(\text{NH}_3)_n^+$ signal caused by photodissociation of $\text{Ca}(\text{NH}_3)_n$ can be countered by new signal for $\text{Ca}(\text{NH}_3)_n^+$ created from photodissociation of $\text{Ca}(\text{NH}_3)_{n+1}$, assuming both neutral complexes absorb at the same IR wavelength. To try and minimise the effects of this potential clash of opposing signals, we have deliberately adjusted the expansion conditions in the current series of experiments such that the $\text{Ca}(\text{NH}_3)_n^+$ ion signal is significantly larger than the $\text{Ca}(\text{NH}_3)_{n+1}^+$ signal prior to any addition of IR radiation. Under these conditions any signal enhancement from dissociation of $\text{Ca}(\text{NH}_3)_{n+1}$ registered in the $\text{Ca}(\text{NH}_3)_n^+$ mass channel should be smaller than the depletion in the same mass channel derived from absorption by $\text{Ca}(\text{NH}_3)_n$.

3. Computational details

To support the experimental work, *ab initio* calculations were performed on a series of $\text{Ca}(\text{NH}_3)_n$ complexes. These calculations employed second-order Møller-Plesset perturbation theory (MP2) in conjunction with 6-311++G(d,p) basis sets on the atoms. This basis set was selected because it is reasonably large and flexible without being too computationally demanding for the relatively large complexes considered in this work. The calculations used GAUSSIAN 03 software [25].

In addition to predicting equilibrium geometries, IR spectra were also calculated for each complex considered. The theoretical spectra were based on the harmonic approximation but employed a scaling factor to partly account for anharmonic effects on the band positions. This was obtained from a comparable calculation on a single NH_3 molecule and choosing a scaling factor (0.936)

which brought theory and experiment into best agreement. This scaling factor was then applied to $\text{Ca}(\text{NH}_3)_n$ vibrational predictions.

4. Results and discussion

Fig. 1(a) shows a photoionization mass spectrum recorded for $\text{Ca}(\text{NH}_3)_n$ in the absence of the IR laser beam. Under the conditions used the highest intensity occurs for $\text{Ca}(\text{NH}_3)_8^+$ and then declines for higher mass species. In fact the $\text{Ca}(\text{NH}_3)_8^+$ ion shows a relatively high abundance under a wide variety of experimental conditions (different NH_3 stagnation pressures, valve opening-ablation laser delays, and UV wavelengths), suggesting that this ion is particularly stable (a magic number ion).

Fig. 1(b) shows a mass spectrum recorded under the same conditions but now with the IR radiation added. The IR output was fixed at 3153 cm^{-1} for this measurement, a position which overlaps with one of the broad absorption bands seen for several complexes (see later). A pronounced change in the mass spectrum occurs, with clear evidence of neutral $\text{Ca}(\text{NH}_3)_n$ photodissociation leading to signal enhancement in lower mass channels at the expense of signal in higher mass channels. We can therefore use this signal depletion to record IR spectra of neutral clusters and Fig. 2 shows some examples. For simplicity we will refer to the spectrum collected by detecting $\text{Ca}(\text{NH}_3)_n^+$ as being from the neutral $\text{Ca}(\text{NH}_3)_n$ species. In fact we expect this neutral complex to be the dominant contributor but we cannot rule out some contribution from larger species, not least because photoionization may lead to the loss of one or more NH_3 molecules.

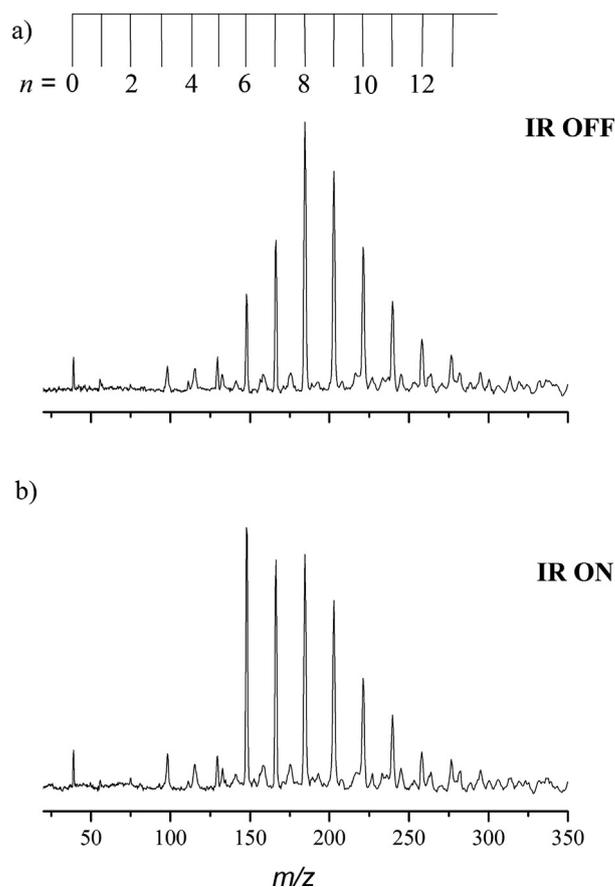


Fig. 1. Photoionization mass spectra obtained for $\text{Ca}(\text{NH}_3)_n$ at a laser wavelength of 346 nm. Spectrum (a) was obtained in the absence of the IR laser whereas spectrum (b) was recorded in the presence of the IR laser operating at 3153 cm^{-1} .

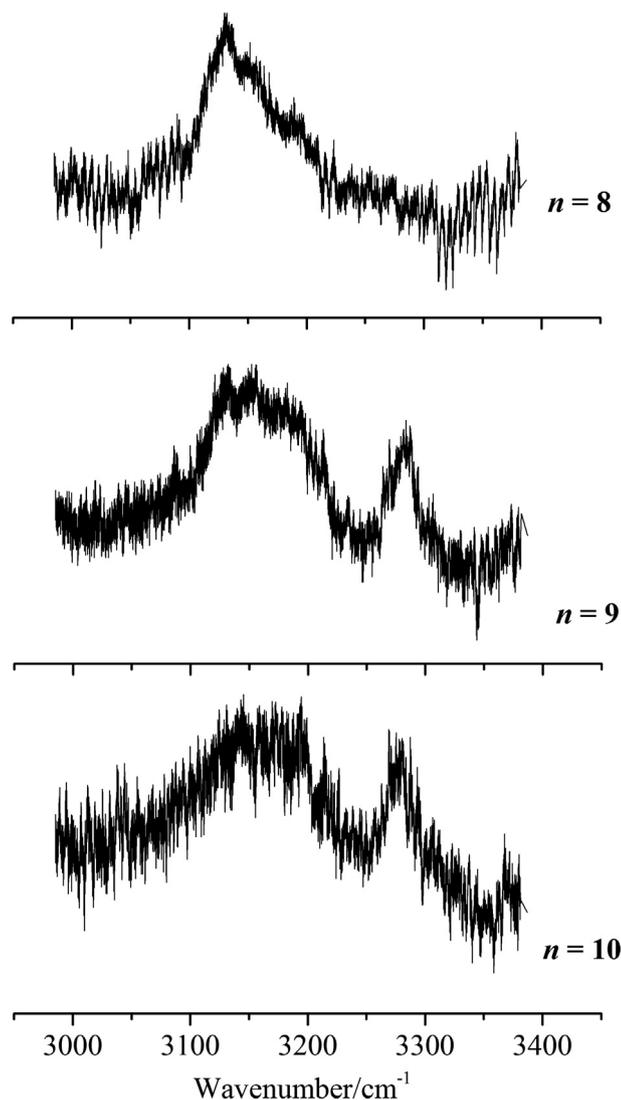


Fig. 2. IR spectra attributed to $\text{Ca}(\text{NH}_3)_8$, $\text{Ca}(\text{NH}_3)_9$ and $\text{Ca}(\text{NH}_3)_{10}$. These were obtained by measuring IR-induced signal depletion for the $\text{Ca}(\text{NH}_3)_8^+$, $\text{Ca}(\text{NH}_3)_9^+$ and $\text{Ca}(\text{NH}_3)_{10}^+$ ions, respectively.

For $n = 6$ and 7 we see only resonant ion enhancement, suggesting that the IR wavelength-dependent signal changes in the $\text{Ca}(\text{NH}_3)_6^+$ and $\text{Ca}(\text{NH}_3)_7^+$ mass channels derive from the depletion of larger neutral clusters. Signal depletion is only seen for $\text{Ca}(\text{NH}_3)_n$ complexes with $n \geq 8$ and the significance of this threshold will be discussed later.

The IR spectrum of $\text{Ca}(\text{NH}_3)_8$ consists of a single broad absorption peaking at *ca.* 3130 cm^{-1} . This band extends asymmetrically to the blue, suggesting that more than one transition underlies this feature. Similar but somewhat more symmetrical bands are seen at the same position in the spectra recorded for $\text{Ca}(\text{NH}_3)_9$ and $\text{Ca}(\text{NH}_3)_{10}$. However, the spectra of these larger complexes also show a second band peaking near 3280 cm^{-1} , a feature which is absent from the $\text{Ca}(\text{NH}_3)_8$ spectrum.

To try and understand these observations we have performed *ab initio* calculations on $\text{Ca}(\text{NH}_3)_n$ complexes. To be of any assistance the calculations must address relatively large complexes in this work and so some compromises must be made to make the calculations feasible and affordable. The compromise we have adopted avoids trying to calculate all conceivable minima on the potential energy surface of each complex. Instead, we have focused on low energy minima based around a central location for the Ca

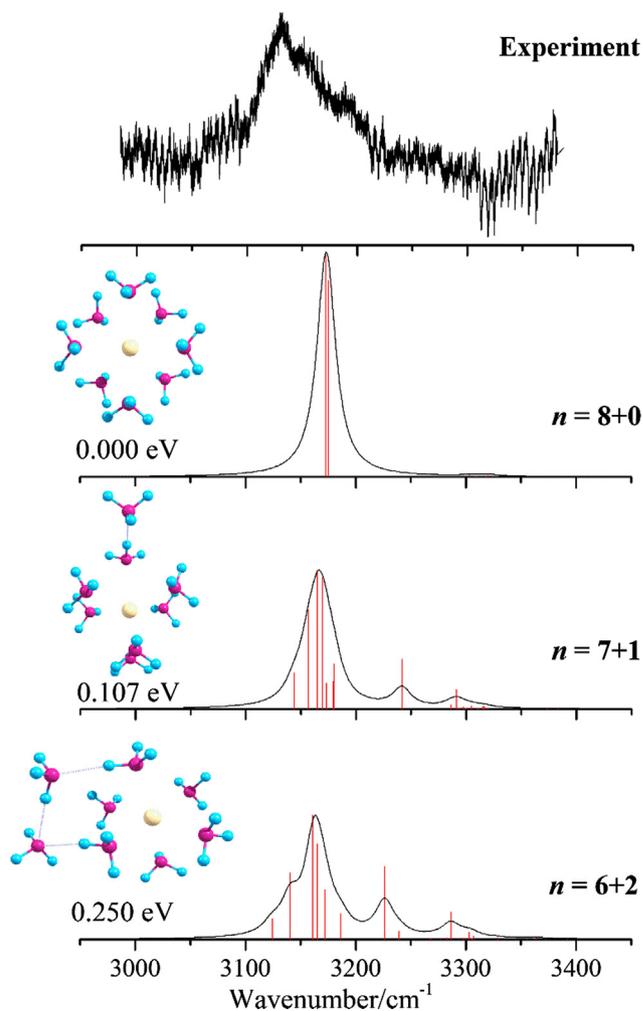


Fig. 3. Comparison of the experimental spectrum for $\text{Ca}(\text{NH}_3)_8$ with predictions from *ab initio* calculations for three possible equilibrium structures. Next to images of the structures are the relative energies of the complexes.

atom, which is the most likely location given that metallic calcium will dissolve in liquid ammonia [24]. For $\text{Ca}(\text{NH}_3)_8$, the lowest energy isomer found has the NH_3 molecules symmetrically distributed around a central Ca atom. Since all eight NH_3 molecules reside in a single solvation shell, we refer to this as the $8+0$ isomer, *i.e.* 8 solvent molecules in the inner shell and none in the second. Other isomers have been found with one or more NH_3 molecules in a second solvation shell and we show the predicted effect on the IR spectra in simulations shown in Fig. 3. The additional isomers, the $7+1$ and $6+2$ isomers, have energies significantly above that of the $8+0$ isomer. Under cold conditions the $8+0$ isomer would dominate but the large amount of energy injected into the system by laser ablation means we must also consider the possibility that higher energy isomers could be produced.

According to the *ab initio* calculations, the symmetrical arrangement of solvent molecules in the $8+0$ complex should result in a single intense band at around 3175 cm^{-1} . This is somewhat higher than the strongest band seen in the experimental spectrum (3130 cm^{-1}), but still reasonably close. The $7+1$ and $6+2$ isomers are also predicted to have a similar dominant band but here additional, weaker, bands are expected at higher frequency. Put simply, the higher frequency bands signify occupancy of the second solvation shell. The experimental spectrum for $\text{Ca}(\text{NH}_3)_8$ is in reasonable agreement with the predicted spectrum for the $8+0$ isomer, although we cannot rule out the possibility that other isomers

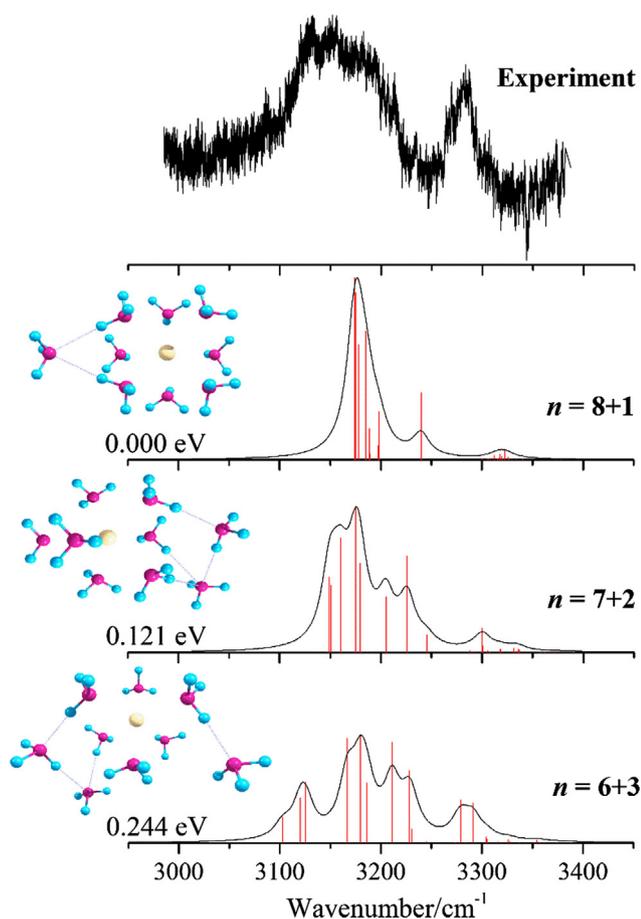


Fig. 4. Comparison of the experimental spectrum for $\text{Ca}(\text{NH}_3)_9$ with predictions from *ab initio* calculations for three possible equilibrium structures. Next to images of the structures are the relative energies of the complexes.

contribute to this spectrum given the observed asymmetric broadening of the absorption band.

For $\text{Ca}(\text{NH}_3)_9$ and $\text{Ca}(\text{NH}_3)_{10}$, the calculations find that it is no longer possible to squeeze all of the solvent molecules in a single shell around the Ca atom. Now the second shell must be occupied and the lowest energy isomer for $\text{Ca}(\text{NH}_3)_9$ is the 8 + 1 isomer. Fig. 4 shows a comparison of the experimental spectrum for $\text{Ca}(\text{NH}_3)_9$ with the calculated spectra for several isomers, including the 8 + 1 isomer. The experimental spectrum is now characterised by two distinct bands and although the relative intensities do not agree, the separation of the highest frequency band from the stronger lowest frequency band in the calculated spectrum of the 8 + 1 isomer (143 cm^{-1}) is similar to that seen in the experimental spectrum (*ca.* 150 cm^{-1}). This is consistent with the claim made earlier that the higher frequency peak is representative of occupation of a second solvation shell around the Ca atom. We interpret the higher frequency peak in the spectrum of $\text{Ca}(\text{NH}_3)_{10}$ in the same way, although the lowest energy isomer for this complex is an 8 + 2 species. The poor agreement between theory and experiment when it comes to the relative intensities of the two bands might be a reflection of the limited quality of the *ab initio* calculations. However, it should also be borne in mind that the photodepletion signal is a convolution of the IR absorption probability and the subsequent dissociation probability for the neutral complex. The latter is likely to be strongly energy dependent and the higher than expected intensity of the higher energy absorption band may simply reflect an increased rate of unimolecular dissociation when more energy is pumped into the complex.

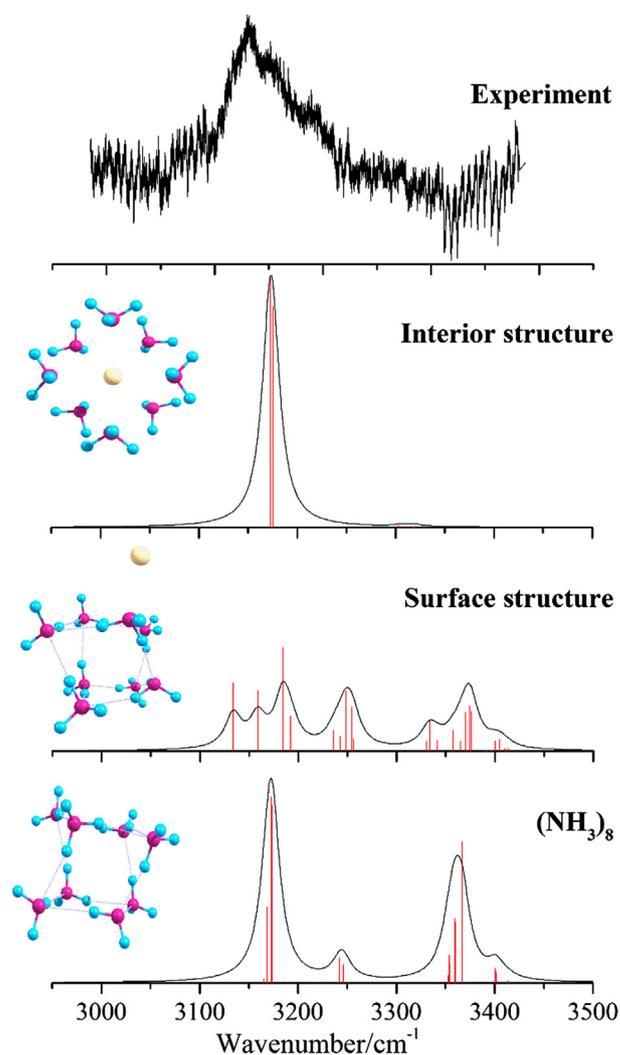


Fig. 5. Comparison of the experimental spectrum for $\text{Ca}(\text{NH}_3)_8$ with predictions from *ab initio* calculations for the lowest energy (8 + 0) structure and a surface structure (a Ca atom sat on the outside of an $(\text{NH}_3)_8$ cluster). Also shown for comparison is the predicted spectrum for a bare $(\text{NH}_3)_8$ cluster.

Note that we have considered the alternative possibility that the Ca atom resides on the outside of a $(\text{NH}_3)_n$ cluster, *i.e.* forms a surface-bound complex. Fig. 5 shows the predicted structure and IR spectrum (NH stretching region only) for a surface-bound $\text{Ca}(\text{NH}_3)_8$ complex. This isomer is calculated to be 1.74 eV above the energy of the global minimum of $\text{Ca}(\text{NH}_3)_8$, the 8 + 0 interior isomer. This is a large energy difference and it therefore seems unlikely that the surface structure would contribute to the experimental spectrum, but it needs to be eliminated. For comparison, Fig. 5 also shows calculated spectra for the 8 + 0 interior complex and for a pure $(\text{NH}_3)_8$ cluster. The spectrum of a surface-bound $\text{Ca}(\text{NH}_3)_8$ complex might be expected to be similar to that of a pure $(\text{NH}_3)_8$ cluster, since the former is essentially an $(\text{NH}_3)_8$ cluster perturbed by a Ca atom attached to the exterior. In practice the calculated spectra are quite different in their details but similar in the sense that absorption is spread over a much wider range than seen in the experimental spectrum. This confirms that there is no contribution from a surface structure.

Having established that the IR spectra arise from structures in which NH_3 molecules solvate around the Ca atom, an obvious question is why do we see depletion only for $n \geq 8$? To try and answer this question, we have calculated dissociation energies

Table 1

Calculated dissociation energies (D_e) for removing a single NH_3 molecule from $\text{Ca}(\text{NH}_3)_n$.

n	D_e/cm^{-1}
1	3347
2	3366
3	4371
4	4841
5	5349
6	6129
7	3581
8	3195
9	2391 ^a
10	2437 ^a

^a Calculated for the 8 + 1 and 8 + 2 isomers of $n = 9$ and 10, respectively.

for the complexes and these are shown in Table 1. The dissociation energies correspond to the loss of a single NH_3 molecule from the lowest energy isomer. The values obtained do not take into account the basis set superposition error (BSSE) and so are likely to be overestimates of the true dissociation energy. Note also that there will inevitably be some residual internal energy from the laser ablation process even after supersonic cooling, and we do not know how much each complex possesses. Nevertheless, the findings provide an explanation for the absence of depletion signal for $n \leq 7$. The dissociation energies for $n = 9$ and 10 are relatively small (a consequence of the presence of a more weakly bound NH_3 molecule in the second solvent shell) and lie well below the energy deposited into the complex by absorption of an IR photon near to 3100 cm^{-1} . The calculated dissociation energy for the 8 + 0 structure of $\text{Ca}(\text{NH}_3)_8$ is very close to this photon energy and, given that BSSE is not taken into account, the true value is likely to fall below this threshold. By way of contrast, the dissociation energy for $n = 6$ is way above the energy of such an IR photon, so this complex would not undergo IR-induced photodissociation. The $n = 7$ complex is clearly an intermediate case but, even allowing for some overestimation from BSSE, it is expected to have a dissociation energy significantly above 3100 cm^{-1} . The calculations are therefore consistent with depletion being accessible only for complexes with $n \geq 8$.

Finally, we comment on the bonding in $\text{Ca}(\text{NH}_3)_n$ complexes. In contrast to the alkali case, where the outer valence electron on the alkali metal atom readily transfers into the surrounding solvent sphere, the Ca atom in $\text{Ca}(\text{NH}_3)_n$ retains much of its electron density for complexes of the sizes we have considered. One measure of this is the calculated Mulliken charge on the Ca atom, which hovers close to zero for all of the complexes, sometimes being slightly positive and sometimes negative, with no significant pattern as a function of n . As would be expected, the N atoms show negative charges (averaging close to $-0.5e$) on account of the polar N–H bonds. These findings suggest that the principal binding interaction between the Ca and N is covalent in character. Furthermore, there is no tendency towards solvated electron formation in small $\text{Ca}(\text{NH}_3)_n$ complexes. We attribute the drop in dissociation energy in going from $n = 6$ to $n = 7$ to the increased importance of repulsive interactions between the negatively charged N atoms as steric crowding escalates. Beyond $n = 8$ that crowding is too severe and any further added NH_3 molecules go into a second solvation shell and are held in place solely by inter-shell hydrogen bonding.

5. Conclusions

The first spectra of $\text{Ca}(\text{NH}_3)_n$ complexes in the gas phase have been recorded. These complexes were formed by laser ablation in the presence of ammonia gas and entrained within a molecular beam. IR spectra in the NH stretching region were obtained by a photodepletion technique for $n \geq 8$. The absence of depletion spectra for smaller complexes is attributed to high binding energies of the NH_3 molecules to the complex, which exceed the energy injected by a photon in the NH stretching region. Only for larger complexes, and particularly those where the second solvation shell becomes occupied, does depletion spectroscopy become possible.

The IR spectra are consistent with a structure of $\text{Ca}(\text{NH}_3)_n$ in which the NH_3 molecules surround a central Ca atom. Furthermore, the spectra establish that the first solvation shell is full once eight NH_3 molecules surround the Ca atom. Any subsequently added NH_3 molecules enter the second solvation shell in the lowest energy structures.

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