Structures of Small Li$(NH_3)_n$ and Li$(NH_3)_n^+$ Clusters ($n = 1-5$): Evidence from Combined Photoionization Efficiency Measurements and ab Initio Calculations

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Photoionization threshold measurements have been carried out for small Li$(NH_3)_n$ clusters ($n = 1-5$) and have been combined with ab initio calculations to determine structural information. The calculated adiabatic ionization energy for the lowest-energy isomer of each cluster is found to be in excellent agreement with the corresponding experimental photoionization threshold, providing evidence that the calculated structures are correct. The combination of the photoionization efficiency curve and the calculated adiabatic ionization energies also confirms the tentative assignment of the infrared spectrum of Li$(NH_3)_4$ reported by Salter and co-workers (*J. Chem. Phys.* **2006**, *125*, 34302); i.e., the 3 + 1 isomer does not contribute and the spectrum is due solely to the 4 + 0 isomer. The findings are consistent with an inner solvation shell that can hold a maximum of four ammonia molecules around the central lithium atom.

1. Introduction

The solvation of alkali metals in liquid ammonia is an interesting phenomenon, not least because these solutions exhibit a strong color due to the formation of solvated electrons.[1] To gain insight into the microscopic behavior of such solutions, alkali−ammonia clusters, M$(NH_3)_n$, can be used as solvation models. These clusters provide a finite system to which spectroscopic and ab initio computational techniques can be applied and from which it is possible to learn about the factors affecting the detachment of the electron from the alkali metal and its location within the solvent environment. A prerequisite for the successful adoption of this strategy is to determine the structural arrangement of the solvent molecules around the metal atoms.

This paper deals with the structures of small neutral and cationic lithium-ammonia clusters, up to and including $n = 5$. Previous experimental studies of small Li$(NH_3)_n$ clusters are sparse. Photoionization thresholds have been measured for these clusters from $n = 1$ up to 28 and have been used to deduce some structural information.[2] However, more explicit and direct structural information could be extracted from spectroscopic studies. $LiNH_3$ has been successfully studied by matrix isolation infrared spectroscopy,[3,4] but larger clusters have not succumbed to this technique. However, in a recent investigation we were able to obtain mass-selective infrared spectra of larger lithium−ammonia clusters.[5] This work provided the first infrared spectra for the $n = 4-7$ clusters, focusing on the N−H stretching region. A notable finding was a marked change in spectral features when n was increased from 4 to 5, which was attributed to the filling of the first solvation shell at $n = 4$ and the presence of the fifth ammonia molecule in Li$(NH_3)_5$ in a second solvation shell. Although this switchover from a single solvation shell structure for $n = 4$ to a two-shell structure for $n = 5$ was supported by ab initio calculations, the same calculations were not able to fully reproduce the vibrational features observed in the IR spectra of these clusters. Consequently, there is still some uncertainty about the structures of the $n = 4$ and 5 clusters.

Several theoretical studies of lithium−ammonia clusters have been reported. The earliest calculations employing a level of theory incorporating electron correlation were performed by Flügge et al.[6,7] This group used the coupled electron pair approximation (CEPA-1) to assess the role of electron correlation on the binding and spectroscopic properties of $LiNH_3$ and $LiNH_3^+$. More recently, Wu et al. have employed MP2 methodology to interpret mass spectrometric data and have predicted the structures and Li−N bond dissociation energies of $LiNH_3$ and $LiNH_3^+$ [22].[8] In another study, Mierzwicki and Latajka carried out MP2 and DFT calculations using a 6-311+G-(d, p) basis set on Li$(NH_3)_n$ and Li$(NH_3)_n^+$ for $n = 1-4$ in an attempt to explore many-body interactions in clusters composed of multiple solvent molecules.[9] Very recently, we have reported a detailed ab initio study of $LiNH_3$ and Li$(NH_3)_2$ and their monopositive cations using a variety of levels of theory, up to and including CCSD(T) with an aug-cc-pVQZ basis set.[10]

In this paper we draw upon data from several sources to obtain definitive structural information for Li$(NH_3)_n$ and Li$(NH_3)_n^+$ clusters with $n = 1-5$. As part of this work, we have recorded the photoionization efficiency (PIE) curves in the threshold region for each neutral cluster in order to obtain more precise adiabatic ionization energies than previously reported.[2] This information is combined with high-level ab initio calculations on the neutral and cationic clusters, and also the findings of our recent infrared spectroscopic study of Li$(NH_3)_4$ and Li$(NH_3)_5$, to confirm the structural changes taking place on ionization. In particular, we show that the data are entirely consistent with a single-shell tetrahedral arrangement of ammonia molecules around the Li atom in Li$(NH_3)_4$, whereas Li$(NH_3)_5$ adopts a two-shell structure because the inner solvation shell is full at $n = 4$.

2. Experimental

Our experimental apparatus and procedure is essentially the same as that described elsewhere.[5] Briefly, Li$(NH_3)_n$ clusters

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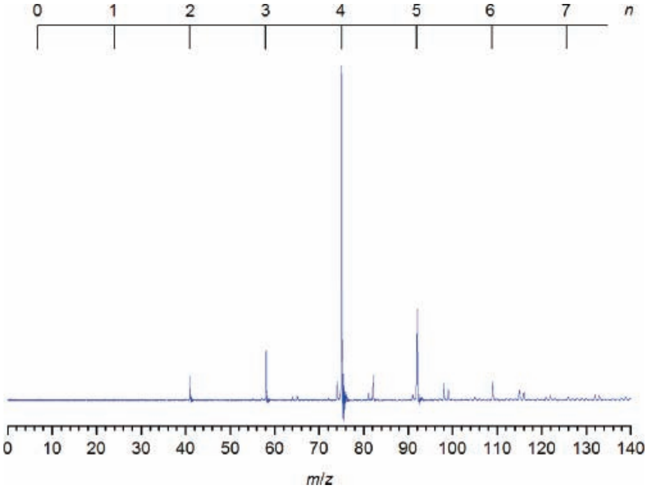

Figure 1. Photoionization mass spectrum obtained at a wavelength of 340 nm, which is just above the threshold for single photon ionization of $Li(NH_3)_2$.

are formed in a supersonic expansion by laser ablation of a solid lithium target in the presence of gaseous ammonia. The expansion is skimmed to form a molecular beam, which then enters the source region of a time-of-flight mass spectrometer. For the particular experiments carried out here, the mixture of clusters is interrogated in this region by the output from a single pulsed tunable dye laser, which is used to photoionize the clusters. A photoionization efficiency curve for each cluster is then obtained by recording the ion current in a given mass channel as a function of the laser wavelength. Care has been taken to ensure that we operate at sufficiently low laser intensities to allow only single-photon ionization of the clusters.

3. Computational Procedure

In support of the experimental work, ab initio calculations were carried out on both $Li(NH_3)_n$ and $Li(NH_3)_n^+$ clusters for $n = 1-5$. Both DFT and MP2 methods were used along with the standard 6-311++G(d, p) basis set. The aim was to calculate the equilibrium structures and total energies of each cluster to predict the adiabatic ionization energies. Various isomers were considered to ensure that the global potential energy minimum was found for each cluster size. Calculations were carried out using Gaussian 03[11] on the Columbus computer cluster maintained by the UK National Service for Computational Chemistry and the Newton supercomputer at the University of Leicester Mathematical Modeling Centre.

4. Results and Discussion

4.1. Photoionization Efficiency Curves and Ionization Energies. Figure 1 shows a typical mass spectrum and Figure 2 shows the threshold regions of the photoionization efficiency (PIE) curves determined for $n = 1-5$. There are some marked differences between the clusters. The $n = 1$ cluster shows a very steep rise in its PIE curve in the threshold region, as does the $n = 4$ cluster. The adiabatic ionization energies (AIEs) can easily be determined from these profiles by a linear extrapolation of the steepest part of the profile back to the baseline signal level. The values obtained are 4.339 ± 0.003 eV ($n = 1$) and 3.025 ± 0.001 eV ($n = 4$), which are similar to those reported previously by Fuke and co-workers,[2] although the current values have a higher precision.

The $n = 2$, 3, and 5 clusters show a slower rise in their PIE curves in the threshold region, and this is particularly marked for the $n = 2$ cluster. This makes it more difficult to establish the precise ionization onset. A simple extrapolation by eye to the baseline should provide a satisfactory estimate of the AIE for $Li(NH_3)_3$ and $Li(NH_3)_5$ and gives $3.195^{+0.001}_{-0.004}$ and $2.866^{+0.002}_{-0.003}$ eV, respectively, where the error margins reflect our estimated uncertainty in the extrapolation process. Once again, these ionization energies are in good agreement with those reported previously.[2] For $Li(NH_3)_2$ an extrapolation to the baseline yields an ionization energy of 3.560 eV. Given the slow rise of the PIE for this particular cluster, it is impossible to extract meaningful margins of error on this value, but it is likely that this is an overestimate of the true AIE. In support of this statement, we note that the high quality ab initio calculations on $LiNH_3$ and $Li(NH_3)_2$ in ref 10 yield an AIE for $LiNH_3$ that is an excellent agreement with the experimental value derived here, the difference being 0.01 eV, whereas the AIE for $Li(NH_3)_2$ determined from the present work is 0.17 eV higher than the calculated value.

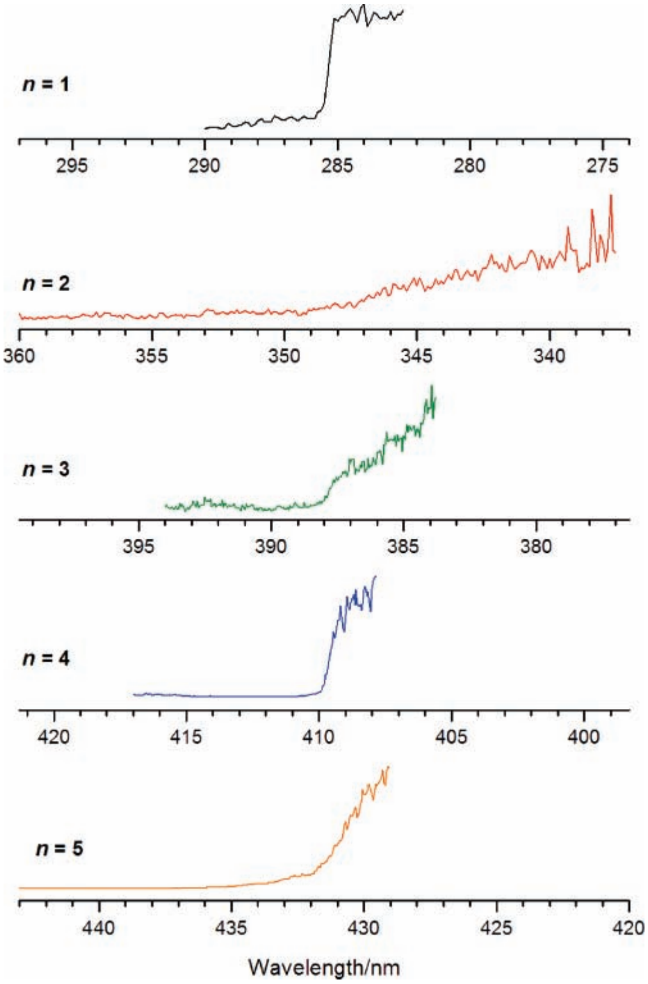

Figure 2. Photoionization efficiency (PIE) curves for $Li(NH_3)_n$, where $n = 1-5$. The PIE curve for $n = 5$ was recorded on a different day from those of the $n = 1-4$ clusters and shows a low-energy tail which is most likely due to the presence of a small proportion of vibrationally hot clusters. This weak tail has been ignored in the determination of the adiabatic ionization energy (see text). All curves have been normalized to the laser intensity and their maximum amplitudes have been adjusted so that they are roughly the same in the figure for each cluster size.

The sharp rise in the PIE curves for $LiNH_3$ and $Li(NH_3)_4$ is indicative of small structural changes on ionization for these two clusters. In contrast, the slow rise in the PIE curve for $Li(NH_3)_2$ suggests a substantial change in equilibrium structure

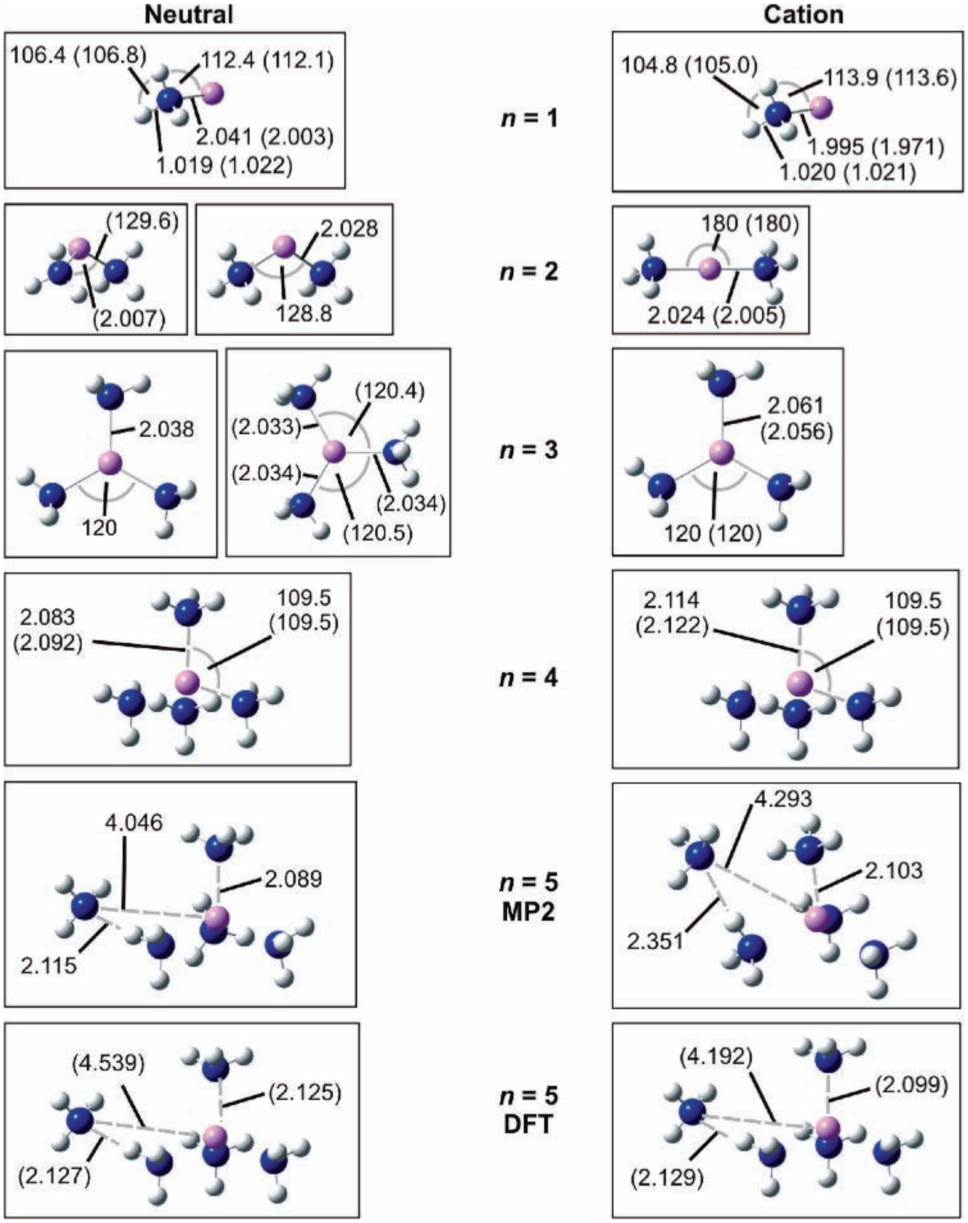

Figure 3. Calculated structures of the lowest energy isomers of the neutral and cationic clusters for $n = 1-5$. Numerical values of key structural parameters are highlighted and are derived from MP2 and DFT calculations (DFT results are in parentheses, unless otherwise specified).

on ionization. The $n = 3$ and $n = 5$ clusters represent an intermediate case, showing neither the sharp rises of the $n = 1$ and $n = 4$ clusters nor the slow rise of the $n = 2$ cluster.

4.2. Ab Initio Calculations. The primary aim of this work is to show that the PIE curves are consistent with ab initio calculations, a combination that should pin down the structures of both the neutral and ionic clusters. The calculations carried out in the present work were at the DFT and MP2 levels using a 6-311++G(d, p) basis set. We have previously ‘calibrated’ this level of theory using higher quality calculations on $LiNH_3$ and $Li(NH_3)_2$ clusters and their cations.[10] Specifically, those earlier calculations were carried out using the CCSD(T) method and an aug-cc-pVQZ basis set. It was found that lower level calculations of the type employed in the present work provided very similar structures and similar energetics (dissociation and ionization energies) to those deduced from the higher level calculations. We therefore deem the present set of calculations as acceptable for describing the main structural features of $Li(NH_3)_n$ and $Li(NH_3)_n^+$ clusters and for estimating ionization energies.

Attempts were made to identify as many structural isomers as possible in order to ascertain the global potential energy minimum for each cluster. For $n = 1-4$ we find that structures with the ammonia molecules in a single solvation shell give by far the lowest energy, i.e., each ammonia molecule is attached to the Li atom through a Li−N bond. However, in $Li(NH_3)_5$ there are four ammonia molecules bound directly to the Li atom and the fifth ammonia molecule is more loosely attached through hydrogen bonding to one of the inner shell solvent molecules. We designate this two-shell structure as the 4 + 1 isomer, signifying that there are four ammonia molecules in the inner solvation shell and one in a second (outer) solvation shell. The structures calculated for the lowest energy isomers of each cluster are summarized in Figure 3. Figure 4 shows a comparison of the calculated adiabatic ionization energies versus the measured values (from this work) and Table 1 summarizes the numerical values. The trend in ionization energies is reproduced by both the DFT and MP2 calculations, with the former consistently overestimating the experimental ionization energy by a modest margin, while the latter provides underestimates.

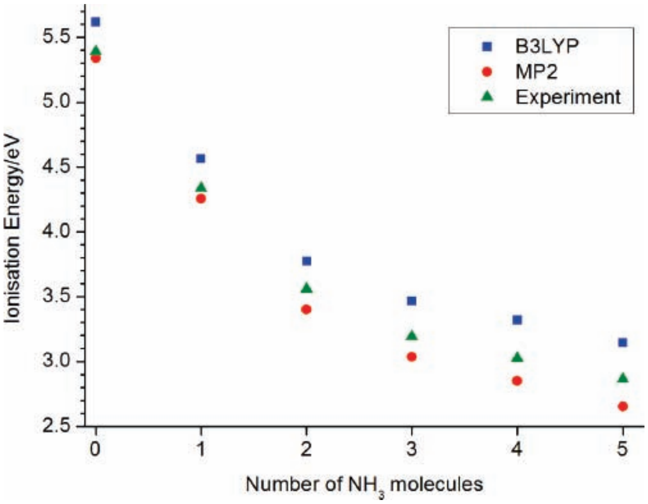

Figure 4. Comparison of the calculated adiabatic ionization energies of $Li(NH_3)_n$ and the measured values (from this work). All calculated values are for the lowest energy isomer for each value of *n*.

TABLE 1: Experimental and Calculated First Ionization Energies of $Li(NH_3)_n$ Clusters (Lowest-Energy Isomer Only)

cluster	AIE (expt) (eV)	AIE (MP2) (eV)	AIE (DFT) (eV)
$LiNH_3$	4.339 ± 0.003	4.257	4.565
$Li(NH_3)_2$	3.560[a]	3.400	3.775
$Li(NH_3)_3$	$3.195^{+0.001}_{-0.004}$	3.035	3.466
$Li(NH_3)_4$	3.025 ± 0.001	2.850	3.318
$Li(NH_3)_5$	$2.866^{+0.002}_{-0.003}$	2.654	3.144

[a] No error margin is quoted for this AIE because of uncertainties in the extrapolation process. As described in more detail in the text, this AIE is likely to be an upper limit.

The good agreement between the calculated and experimental ionization energies provides strong indication that the present set of calculations yields a satisfactory description of the structures and energetics of the $Li(NH_3)_n$ and $Li(NH_3)_n^+$ clusters.

In previous work using high-quality calculations, we have shown that the small change in equilibrium structure between $LiNH_3$ and $LiNH_3^+$ leads to co-incident adiabatic and vertical ionization energies for $LiNH_3$.[10] On the other hand, the same type of calculations show a major structural change for $Li(NH_3)_2$ on ionization. $Li(NH_3)_2^+$ is found to be a linear molecule whereas $Li(NH_3)_2$ is bent with a N−Li−N angle of 140°. Similar findings are obtained from the somewhat lower level calculations employed in the present work, although the change in the N−Li−N angle on ionization is found to be even larger (50°). This major structural change is entirely consistent with the slowly rising PIE curve for $Li(NH_3)_2$ shown in Figure 2. In addition, the N−Li−N bending vibration is a low-frequency mode (harmonic frequency ~70 cm^{-1}) and thus transitions from vibrationally excited states in the neutral cluster may also contribute to the long low-energy tail in the $Li(NH_3)_2$ PIE curve.

The calculations show a change in structure on ionization of $Li(NH_3)_3$, but a more modest change than that seen for $Li(NH_3)_2$. Both the neutral and cation possess C_{3h} symmetry at the MP2 level, with a slight elongation of the Li−N bond in the cation. At the DFT level, the cation has essentially the same geometry as the MP2 findings, but the structure of the neutral cluster differs between the two types of calculation. The neutral DFT structure possesses C_s symmetry, with two of the ammonia molecules occupying equivalent environments. The change in structure on ionization at the DFT level is more significant, with the rotation of one ammonia group by 27°. In view of the PIE curve for the $n = 3$ cluster, which indicates a significant degree of structural change on ionization, it would seem that the DFT calculations provide the best description of the structural change.

The calculations for $Li(NH_3)_4$ and $Li(NH_3)_4^+$ reveal similar structures for the 4 + 0 isomers at both the DFT and MP2 levels. However, for the higher-energy 3 + 1 isomer, which contains one ammonia molecule in a second solvation shell, there are significant differences in structure between the neutral cluster and the cation. The most pronounced structural change on ionization is for the N1−N2−Li bond angle, where N2 is in the outer shell ammonia molecule and N1 is in the inner shell ammonia molecule that is hydrogen-bonded directly to the outer shell molecule. This bond angle changes from 94° to 115° at the MP2 level and 95° to 114° at the DFT level. This is a sizable change in bond angle which would lead to substantial off-diagonal Franck−Condon factors for this ionization process, and therefore a slow rise in the PIE curve in the threshold region. Other structural changes are also found and the implications of these findings will be considered in the next section.

For the lowest-energy $n = 5$ isomer, the 4 + 1 species, ionization changes the N1−N2-Li bond angle from 105° to 119° according to the DFT calculations. At the MP2 level the neutral cluster has almost the same structure as in the DFT case. However, the cation now shows two inner shell ammonia molecules bonded to the outer shell ammonia. Although this does not require a major change in the N1−N2−Li bond angle, the second inner shell ammonia must tilt toward the outer shell ammonia in order to participate in the hydrogen bonding on ionization. We cannot establish whether the DFT or MP2 structure provides the best description of the structure of $Li(NH_3)_5$ on the basis of the present data. However, in both cases the modest but significant structural changes predicted for the $n = 5$ cluster are consistent with the observed photoionization threshold, which is not as sharp as for $n = 1$ or $n = 4$.

4.3. 4 + 0 versus 3 + 1 Isomers for $Li(NH_3)_4$: Comparison with the Infrared Spectrum.

In a previous infrared study of $Li(NH_3)_4$ clusters, supporting ab initio calculations were unable to reproduce the observed vibrational structure in the N−H stretching region of the spectrum.[5] Although the red shift of the N−H stretching bands relative to those of free ammonia was predicted quite accurately, only a single strong band was expected for tetrahedral (4 + 0) $Li(NH_3)_4$ in harmonic oscillator calculations whereas three closely spaced bands were observed in practice. As a result, the spectral assignment to the 4 + 0 isomer was not definitive and a contribution from the 3 + 1 isomer could not be ruled out. Our calculations predict that the 3 + 1 isomer has an energy ~0.3 eV above that of the 4 + 0 isomer, which is a substantial difference. However, the laser ablation source used to produce the $Li(NH_3)_n$ clusters is highly energetic and it is possible that higher energy isomers could be formed and some might survive the subsequent supersonic expansion.

To assess the likelihood that the 3 + 1 isomer contributes to the infrared spectrum, we have calculated its adiabatic ionization energy. The values obtained are 3.260 and 2.834 eV at the DFT and MP2 levels, respectively. The absolute values of the calculated ionization energies for the 4 + 0 and 3 + 1 clusters are not sufficiently different by themselves to allow us to distinguish between the two isomers. However, both DFT and MP2 calculations predict a clear lowering of the ionization energy in moving from the 4 + 0 to the 3 + 1 cluster, the difference being 0.058 eV for DFT and 0.016 eV for MP2. Although small in absolute terms, these correspond to red shifts of approximately 8 and 2 nm, respectively, with respect to the

4 + 0 ionization onset, which should easily be observable on the scale shown in Figure 2. Furthermore, as discussed in the previous section, we expect a relatively sharp ionization threshold for the 4 + 0 cluster, whereas that of the 3 + 1 cluster should be much more gradual because of substantial structural changes on cluster ionization.

The calculations show that if the 3 + 1 cluster was present in a significant amount in the experiment, then the first ionization threshold should correspond to this isomer and there would be a slow rise in the ionization cross section as the laser wavelength is decreased. This would be punctuated at higher energy by a sharp step in the ion current on passing the ionization threshold of the 4 + 0 cluster. Since we observe the latter, but no trace of the former, we conclude that the 4 + 0 isomer is the sole contributor to the PIE curve. Consequently, under our experimental conditions, the proportion of $Li(NH_3)_4$ existing as the 3 + 1 isomer must be negligibly small. This is entirely consistent with the assignment of the infrared spectrum of $Li(NH_3)_4$ reported by Salter et al.,[5] which was tentatively attributed to the 4 + 0 isomer.

5. Conclusions

Photoionization threshold measurements have been combined with ab initio calculations to confirm structural information for small $Li(NH_3)_n$ clusters with $n = 1-5$. The calculated adiabatic ionization energy for the lowest energy isomer of each cluster is found to be in good agreement with the corresponding experimental photoionization threshold. The data are consistent with an inner solvation shell that can hold a maximum of four ammonia molecules.

The marked difference in Franck−Condon behavior expected for the 4 + 0 and 3 + 1 isomers of $Li(NH_3)_4$ has been used to show that the infrared spectrum reported previously for this cluster is due only to the 4 + 0 species.[5] The increased complexity of the N−H stretching region when compared to that predicted from harmonic oscillator calculations must therefore have an alternative origin. One possibility is that Fermi resonance is responsible. Fermi resonance between the $2\nu_4$ overtone and the N−H stretching fundamentals in NH_3 is well-known and gives rise to additional band structure in the N−H stretching region. This process may also be in operation in the case of $Li(NH_3)_n$ clusters and could account for the unexpected complexity in the $Li(NH_3)_4$ spectrum.

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