Coordination structures of lithium-methylamine clusters from infrared spectroscopy and *ab initio* calculations

Tom E. Salter and Andrew M. Ellis^{a)}

Department of Chemistry, University of Leicester, University Road, Leicester LE1 7RH, United Kingdom

(Received 1 June 2007; accepted 3 August 2007; published online 12 October 2007)

Spectra of clusters formed between lithium atoms and methylamine molecules are reported for the first time. Mass-selective infrared spectra of $\text{Li}(\text{NH}_2\text{CH}_3)_n$ have been recorded in both the N–H and C–H stretching fundamental regions. The infrared spectra are broadly in agreement with *ab initio* predictions, showing redshifted N–H stretching bands relative to free methylamine and a strong enhancement of the N–H stretching fundamentals relative to the C–H stretching fundamentals. The *ab initio* calculations suggest that, for $n=3$, the methylamine molecules bunch together on one side of the lithium atom to minimize repulsive interactions with the unpaired electron density. The addition of a fourth methylamine molecule results in closure of the inner solvation shell and, thus, $\text{Li}(\text{NH}_2\text{CH}_3)_5$ is forced to adopt a two-shell coordination structure. This is consistent with neutron diffraction studies of concentrated lithium/methylamine solutions, which also suggest that the first solvation shell around the lithium atom can contain a maximum of four methylamine molecules.

© 2007 American Institute of Physics. [DOI: 10.1063/1.2776334]

I. INTRODUCTION

Clusters of alkali metal atoms with ammonia molecules have attracted considerable attention. These are intriguing species because of the ease with which alkali metals readily dissolve in bulk liquid ammonia.¹ Such solutions are colored and highly conducting on account of the formation of solvated electrons: these electrons derive from the outer valence electron originally on each alkali atom, which is lost to the solvent when the alkali dissolves. Small alkali-ammonia clusters may behave differently from the bulk solution and it is of interest to follow the transition towards bulklike behavior as the solvation number increases. Important questions include (i) how many solvent molecules are required for the alkali valence electron to fully transfer over to the solvent molecules, (ii) are distinct solvation shells formed and what are the structures of these solvation layers, and (iii) what is the unpaired electron distribution across the cluster?

Recently, we have performed the first mid-infrared spectroscopic study of $\text{Li}(\text{NH}_3)_n$ clusters.² Using a two-laser depletion technique that combines infrared (IR) excitation with photoionization, IR spectra of these clusters were recorded in the N–H stretching region as a function of solvation number n . The variation in band patterns for the $n=4-7$ clusters was interpreted in terms of a full first solvation shell at $n=4$, with subsequent NH_3 molecules entering a second, more remote, solvation shell. Additional support for this description of $\text{Li}(\text{NH}_3)_n$ clusters has come from a follow-up study of the photoionization threshold behavior.³

In addition to ammonia, the alkali metals are known to dissolve in ammonia derivatives, such as methylamine. The switch from ammonia to methylamine introduces some im-

portant changes to the solvent, including a change of dielectric constant and the introduction of a bulky methyl group onto the nitrogen atom. There have been a number of studies that have attempted to determine how the alkali cation and the solvated electron are affected by the switch from ammonia to methylamine. In the case of lithium/methylamine solutions, NMR,^{4,5} electron spin resonance,⁶ and optical spectroscopy⁷ have been employed to probe both the electronic and coordination structures. More recent studies using neutron diffraction have also been applied to lithium/methylamine solutions and indicate a solvation structure around the lithium ion consisting of approximately four methylamine molecules in the inner solvation shell.^{8,9}

As far as we are aware, spectroscopic studies of clusters of alkali atoms with ammonia derivatives have so far been restricted to a single report by Seegue *et al.*¹⁰ This investigation focused on the cationic clusters $\text{Cs}(\text{NH}_2\text{CH}_3)_n^+$, where $n=3-22$. Mass-selective photodissociation was achieved using IR absorption in the 1000–1100 cm^{-1} region (corresponding to excitation of the CN stretch) and, through a combination of the measured band shifts relative to free methylamine and Monte Carlo simulations, the tentative conclusion reached was that nine methylamine molecules are required to fill the first solvation shell. The only other reported spectroscopic study of metal-methylamine clusters was a zero electron kinetic energy study of CuNH_2CH_3 by Miyawaki *et al.*¹¹

In this paper, we describe the first spectroscopic investigation of lithium-methylamine clusters in the gas phase and, indeed, the first infrared spectroscopic study of methylamine clustered with any uncharged metal atom. Spectra are presented in both the N–H and C–H stretching regions for the $n=3-5$ clusters and a comparison is made with predictions from *ab initio* calculations also carried out as part of this work. The global potential energy minima adopted by these

^{a)} Author to whom correspondence should be addressed. Electronic mail: andrew.ellis@le.ac.uk Tel: +44(0)116 252 2138. Fax: +44 (0)116 252 3789.

clusters are based on reasonably strong Li–N bonds in the inner solvation shell, with the methyl groups pointing away from the lithium atom to minimize steric repulsion. The infrared spectra are consistent with this description, showing a strong redshift for the N–H stretching bands when compared to free methylamine and a dramatic reversal in the N–H/C–H stretching band intensity ratios. Both the calculations and the spectra are consistent with a full inner solvation shell at $n=4$, a conclusion that tallies with the neutron diffraction findings of bulk lithium-methylamine solutions.^{8,9}

II. EXPERIMENT

Full details of the experimental procedure have been provided elsewhere.² Briefly, the alkali-methylamine clusters are formed in a supersonic molecular beam by a standard laser ablation technique. This involves ablation of a lithium target using the second harmonic (532 nm) output of a small Nd:YAG laser (YAG denotes yttrium aluminum garnet). Clusters were formed by expanding methylamine gas (Aldrich, 98%) in argon (20:80 mixture) at a maximum pressure of 6 bars through a pulsed nozzle. The metal atoms produced by laser ablation were picked up by the methylamine/Ar gas flow and passed down a short clustering tube (~ 5 mm) to allow metal-solvent cluster formation prior to expansion. A skimmer was used to produce a molecular beam and at about 30 cm downstream of the nozzle the beam enters the source region of a linear time-of-flight mass spectrometer.

The molecular beam is intersected in this region by the UV output from a tunable pulsed dye laser to photoionize the clusters by single photon absorption. To record an infrared (IR) spectrum, the photoionization laser pulse is preceded by an IR radiation pulse generated through the combination of a tunable pulsed dye laser with a hydrogen-filled multipass Raman shifter cell. The IR pulse is timed to fire at ~ 50 ns prior to the photoionization laser and when resonant with a transition in a cluster, leads to signal depletion in the corresponding cationic signal after photoionization. Ions were detected using a time-of-flight mass spectrometer and subsequently recorded with a digital storage oscilloscope and computer.

III. COMPUTATIONAL DETAILS

To explore the geometric and electronic structures of lithium-methylamine clusters, as well as to aid in the assignment of the spectra, *ab initio* calculations were undertaken. Both density functional theory (DFT) (B3LYP) and MP2 methods were employed, and the highest quality calculations were performed using a 6-311++G(d,p) split-valence basis set. All calculations were carried out using GAUSSIAN 03 software.¹²

Since there have been no previous reports of *ab initio* calculations on $\text{Li}(\text{NH}_2\text{CH}_3)_n$ clusters, it was important to establish the structural landscape for each cluster size, and so, considerable effort was devoted to identifying as many isomers as possible. A trial-and-error procedure was initially employed to establish possible potential energy minima using a small basis set coupled with simple Hartree-Fock methodology. The geometry optimizations were carried out with-

out symmetry restrictions and many different starting structures were tried. Minima found from these low-level calculations were then refined with higher level calculations. This type of process will not find all possible isomers, especially higher energy isomers of the larger clusters. However, our primary concern is with low-lying isomers and stringent searches have been carried out to ensure that the global minimum and all significant low-lying isomers have been identified.

To ensure that true minima were located, all structures were checked using harmonic vibrational frequency calculations. The vibrational frequency calculations, along with calculated IR line strengths, were also used to predict the IR spectra of the clusters. In order to make a meaningful comparison with experiment, the calculated harmonic vibrational frequencies were scaled to reflect the tendency of such calculations to overestimate vibrational fundamentals. Scaling factors of 0.960 and 0.939 were applied to the DFT and MP2 predictions, respectively. These scaling factors were chosen to bring the calculated C–H and N–H stretching vibrations of free methylamine into best agreement with experiment^{12,13} and were then applied to the $\text{Li}(\text{NH}_2\text{CH}_3)_n$ clusters.

IV. RESULTS AND DISCUSSION

A. *Ab initio* calculations: Geometric and electronic structures

As will be seen later, the focus in the spectroscopic part of this study is on the $n=3, 4$, and 5 clusters. Consequently, the emphasis in the calculations presented here is on these larger clusters rather than the $n=1$ and 2 species. Nevertheless, calculations have been carried out on LiNH_2CH_3 and $\text{Li}(\text{NH}_2\text{CH}_3)_2$ and the findings for these smaller clusters are also briefly presented.

1. LiNH_2CH_3 and $\text{Li}(\text{NH}_2\text{CH}_3)_2$

Both DFT and MP2 calculations predict a single isomer for LiNH_2CH_3 with the lithium atom bonded directly to the nitrogen atom, as depicted in Fig. 1. $\text{Li}(\text{NH}_2\text{CH}_3)_2$ is more complex and three different isomers have been found; all three of which can be seen in Fig. 1. To distinguish between the isomers, we employ the notation $a+b$, where a is the number of methylamine molecules in the first solvation shell and b is the number in the second solvation shell. Distinguishing between solvent molecules in the first and second solvation shells is generally straightforward: those in the first solvation shell show a direct Li–N bond and, therefore, a short Li–N distance, whereas those solvent molecules in the second solvation shell are more distant from the lithium atom and are loosely attached to the cluster through hydrogen bonding with one or more of the inner shell solvent molecules.

The isomers found for $\text{Li}(\text{NH}_2\text{CH}_3)_2$ correspond to one 2+0 isomer and two different 1+1 structures. The lowest energy isomer is the 2+0 species, which adopts a strongly bent N–Li–N framework reminiscent of the bent global minimum structure found for the $\text{Li}(\text{NH}_3)_2$ cluster.¹⁵ Interestingly, the N–Li–N–C dihedral angle lies close to planarity in a configuration that brings the methyl groups into close prox-

FIG. 1. (Color online) Structures of the lowest energy isomers for the $n=1-3$ clusters of $\text{Li}(\text{NH}_2\text{CH}_3)_n$ derived from *ab initio* calculations. The relative energy (including zero point vibrational energy corrections) is shown for each isomer, the numbers with and without parentheses being the MP2 and DFT values, respectively. Missing MP2 or DFT energies imply that the particular calculation for this method did not converge.

imity. Calculations carried out for starting geometries with the methyl groups more remote from each other, in order to minimize steric repulsion, either did not converge or reverted back to the minimum energy isomer. The bent structure for $\text{Li}(\text{NH}_2\text{CH}_3)_2$ can be explained by considering the unpaired spin density distribution for the singularly occupied molecular orbital (SOMO), which is associated with the lithium atom and has a lobe pointing away from the methylamine molecules, as can be seen in Fig. 2. A bent structure is favored because it minimizes electrostatic repulsion between the SOMO and the methyl groups of the methylamine molecules.

2. $\text{Li}(\text{NH}_2\text{CH}_3)_3$

The number of potential energy minima was found to increase dramatically for $\text{Li}(\text{NH}_2\text{CH}_3)_3$. Twelve different isomers were located, with the three lowest energy isomers being shown in the bottom part of Fig. 1. As with $\text{Li}(\text{NH}_2\text{CH}_3)_2$, the lowest energy isomer of $\text{Li}(\text{NH}_2\text{CH}_3)_3$ contains all three ammonia molecules in a single solvation shell, yielding a 3+0 structure possessing approximate C_3 symmetry. Once again, there appears to be a sterically unfavorable bunching of the methyl groups on one side of the

FIG. 2. (Color) Calculated SOMO profile for the 2+0 isomer of $\text{Li}(\text{NH}_2\text{CH}_3)_2$ at the MP2 level of theory. The SOMO surface isovalue is 0.02 a.u.

lithium atom, which is driven by repulsion due to the concentrated lobe of SOMO density on the opposite side of the lithium atom.

The higher energy isomers take the form of a single 2+1 isomer, three 1+2 isomers, and eight 1+1+1 isomers. As all of the 1+1+1 and 1+2 isomers are >0.5 eV higher in energy than the 3+0 isomer, they are unlikely to be important in the spectroscopic work and are therefore discounted from further consideration. However, the 2+1 isomer is calculated to lie ~ 0.3 eV above the global minimum and cannot be so readily ignored, as discussed later.

3. $\text{Li}(\text{NH}_2\text{CH}_3)_4$

Fifteen isomers were found for $\text{Li}(\text{NH}_2\text{CH}_3)_4$, specifically one 4+0 isomer, one 3+1 isomer, four 2+2 isomers, six 1+2+1 isomers, one 1+3 isomer, and two 2+1+1 isomers. Many of these isomers are very similar in structure, subtly varying only by rotation of a single methylamine molecule, and, thus, the potential energy surface is expected to be relatively flat, particularly at higher energies. However, the global minimum was easy to establish and is found to be a 4+0 structure, as depicted in Fig. 3. Also shown in Fig. 3 are the two next lowest energy isomers, a 3+1 species and a 2+2 cluster, both of which lie at considerably higher energies than the 4+0 structure. The 4+0 cluster shows an approximately tetrahedral arrangement of the N atoms around the central lithium atom, with the methyl groups pointing away from the lithium atom to minimize steric repulsion. This arrangement of the nitrogen atoms is very similar to that found previously for $\text{Li}(\text{NH}_3)_4$.² The key structural parameters for $\text{Li}(\text{NH}_2\text{CH}_3)_4$ are summarized in Table I.

4. $\text{Li}(\text{NH}_2\text{CH}_3)_5$

Given the number of degrees of freedom, an attempt to search the structural landscape for $\text{Li}(\text{NH}_2\text{CH}_3)_5$ is a major challenge and was at the limit of our computational re-

FIG. 3. (Color online) Structures of the three lowest energy isomers for the $n=4$ clusters derived from *ab initio* calculations. The relative energy (including zero point vibrational energy corrections) is shown for each isomer, the numbers with and without parentheses being the MP2 and DFT values, respectively.

sources. A comprehensive search was not attempted, but a determined effort was made to establish all low-lying isomers likely to be of any importance in the spectroscopic work. These calculations revealed that the global potential energy minimum corresponds to a 4+1 isomer, i.e., four methylamine molecules in the inner solvation shell with an approximately tetrahedral coordination to the lithium atom, with a fifth solvent molecule entering a second solvation shell. The equilibrium structure of this isomer is illustrated in Fig. 4. The next lowest energy isomers were found to be a series of 3+2 species, all with substantially higher energies (>0.2 eV above the global minimum from MP2 calculations). Four distinct 3+2 isomers were found, but it is likely that with further computational effort other 3+2 isomers could have been located. However, it seems clear that all the 3+2 isomers will lie well above the global minimum and those 3+2 isomers that have been found can be regarded as representative of the “missing” 3+2 isomers, i.e., the latter are expected to show similar infrared spectra to the known 3+2 isomers.

FIG. 4. (Color online) Structure of $\text{Li}(\text{NH}_2\text{CH}_3)_5$ at its global potential energy minimum. MP2 and DFT calculations yielded essentially the same structures.

B. *Ab initio* calculations: Dissociation energies

The spectroscopic technique employed in the experimental part of this work is a depletion method which relies on the IR photon absorption inducing the loss of one or more solvent molecules. Unless the photon energy exceeds the binding energy of at least one methylamine molecule, the photo-depletion technique should fail. Consequently, in order to establish the feasibility and limitations of the photodepletion approach, it is useful to determine the dissociation energies of the clusters.

Table II lists the dissociation energies calculated for the lowest energy isomer of each cluster. These dissociation energies have been corrected to allow for the zero point vibrational energies of the cluster and its dissociation products and have also been subject to a counterpoise correction to minimize the basis set superposition error. Thus, we expect the values listed to be reasonably close to the true values, although the error margin may still amount to several hundred wave numbers. Further discussion of these dissociation energies will be met in later sections.

C. Infrared spectroscopy

Figure 5 shows a mass spectrum recorded in this work in the absence of the IR radiation. This photoionization mass spectrum displays a series of clusters containing both one and two lithium atoms with various numbers of methylamine molecules attached. Only the clusters containing a single lithium atom showed any dependence on the presence of IR radiation, so the $\text{Li}_2(\text{NH}_2\text{CH}_3)_n$ clusters will not be considered any further.

TABLE I. Key structural parameters calculated for the global minimum of $\text{Li}(\text{NH}_2\text{CH}_3)_4$.

		DFT	MP2
Bond length (Å)	LiN	2.112, 2.113, 2.114	2.088
	NC	1.481, 1.482, 1.482	1.480
	NH	1.022, 1.021	1.020
	CH	1.092, 1.096	1.092, 1.096
Bond angle (°)	LiNH	105.9, 106.0, 106.0, 105.7, 106.4, 106.1	109.2, 109.1
	LiNC	121.2, 121.1	116.6, 116.5
	HNH	104.6, 104.7	104.3
	HNC	109.0, 108.8, 108.9, 108.8	108.6, 108.4
	NCH	109.3, 113.3	113.3, 109.2
	HCH	108.4, 108.5, 107.8	108.5, 108.6, 108.0

Note that the structure predicted from DFT calculations possesses a lower symmetry than found for the MP2 calculations, hence the increased number of structural parameters for the former.

TABLE II. Calculated dissociation energies (D_0 in cm^{-1}) for $\text{Li}(\text{NH}_2\text{CH}_3)_n$.

n	DFT	MP2
1	4596	3990
2	3990	3623
3	4214	3527
4	2591	2206
5	1369	2449

When IR radiation was added, photodepletion was found to occur only for $n \geq 3$. The absence of depletion signals in the $n=1$ and 2 mass channels can be readily understood from the calculated dissociation energies shown in Table II, which lie above the single photon energies required to excite N–H stretching fundamentals, particularly for $n=1$. Consequently, on account of the absence of any IR-induced depletion spectra for LiNH_2CH_3 and $\text{Li}(\text{NH}_2\text{CH}_3)_2$, attention from here onwards will focus on the $n=3, 4$, and 5 clusters.

Notice also that the IR-induced depletion signals observed in the $n=3, 4$, and 5 mass channels are assumed to originate from IR absorption by the neutral clusters of the same size. In principle, subsequent IR absorption by one of the fragment clusters could lead to an ion “gain” signal in a lower mass channel. These positive-going signals can, in fact, be seen when the IR radiation is focused strongly onto the molecular beam. However, at the much lower IR intensities employed in the present work, there is no evidence of any distortion due to fragment IR absorption and, consequently, the depletion spectra observed in a particular mass channel are believed to reflect the IR absorption by the neutral cluster with the same molecular mass.

1. $\text{Li}(\text{NH}_2\text{CH}_3)_3$

The IR photodepletion spectrum of $\text{Li}(\text{NH}_2\text{CH}_3)_3$ is shown in Fig. 6. It consists of a single, weak band with a modest blue tail and a maximum at 3170 cm^{-1} . To interpret this spectrum, we first consider the IR spectrum of methylamine in the gas phase. The IR spectrum of methylamine at $>2800 \text{ cm}^{-1}$ is dominated by very strong C–H stretches at

2820 and 2961 cm^{-1} , along with another strong C–H stretching band at 2985 cm^{-1} .^{13,14} By comparison, the symmetric and antisymmetric N–H stretching bands at 3361 and 3427 cm^{-1} are more than an order of magnitude weaker.

We assign the band seen in Fig. 6 to excitation of one or more N–H stretching modes in $\text{Li}(\text{NH}_2\text{CH}_3)_3$. This assignment corresponds to a strong redshift in the frequency of the N–H stretching vibrations induced by the presence of a lithium atom. Equivalent behavior has been seen previously for $\text{Li}(\text{NH}_3)_n$ clusters and the redshift was attributed to the weakening of N–H bonds as a result of the formation of Li–N bonds.²

To further analyze the spectrum, we have carried out simulations of the IR spectrum based on *ab initio* calculations. Two simulations are shown beneath the experimental spectrum in Fig. 6, one derived from the 3+0 cluster and the other from the 2+1 cluster. DFT calculations have been used for these simulations, but the findings are very similar when MP2 calculations are employed. For ease of comparison with the experimental spectrum, each transition has been given a Gaussian profile with a full width at half maximum of 25 cm^{-1} .

Comparison of the simulated spectra with the experimental spectrum is encouraging. The scaling factor employed in the vibrational frequency calculations is an average derived from minimization of the root-mean-square difference between the theoretical and experimental C–H and N–H stretching IR band positions of gaseous methylamine, and so, exact agreement between the experimental and *ab initio* IR band positions is not expected. Nevertheless, the strong redshift of the N–H stretching bands is predicted by the calculations, and the wave number difference between the calculated and experimental peak maxima is relatively small, particularly for the simulation derived from the 3+0 cluster. Furthermore, the blue tail seen for the experimental spectrum is reproduced by the calculations.

Given the similarity between the predicted band profiles for the 3+0 and 2+1 clusters, it is not possible to ascertain definitively whether one or both isomers contributes to the experimental spectrum. Best agreement with experiment is

FIG. 5. (Color online) Photoionization mass spectrum showing a series of peaks due to $\text{Li}(\text{NH}_2\text{CH}_3)_n^+$ and a second series due to $\text{Li}_2(\text{NH}_2\text{CH}_3)_n^+$ cations. This particular spectrum was recorded using the 248 nm output from an excimer laser, but for IR spectroscopy longer photoionization wavelengths were employed to ensure minimal ion fragmentation.

FIG. 6. (Color online) IR photodepletion spectrum of $\text{Li}(\text{NH}_2\text{CH}_3)_3$ (upper trace) along with simulations derived from DFT calculations for the 3+0 and 2+1 isomers. In the experimental case, the red trace represents a single scan (30 laser shots per wavelength), while the black trace is an average of 13 separate scans.

obtained for the 3+0 isomer, both in terms of peak position and in terms of the width of the band profile. We do not know the temperature of the clusters in the molecular beam, but even if we assume relatively poor cooling and an internal temperature of 1000 K the 3+0 isomer is still expected to be present in much greater abundance in the molecular beam than the 2+1 isomer on the basis of the calculated energy difference between the two isomers. However, the calculated dissociation energy of the 3+0 isomer, presented in Table II, would suggest that this cluster should not undergo depletion when excited at $\sim 3200\text{ cm}^{-1}$. The DFT value shown in Table II is probably unreasonably high, and, thus, more weight is given here to the MP2 value, since MP2 calculations are known to yield more reliable estimates of alkali-solvent dissociation energies than DFT calculations.¹⁵ As mentioned earlier, a considerable error margin is expected for the dissociation energy given the level of approximations involved, and so, the 3+0 isomer cannot be ruled out on the basis of these dissociation energy calculations. Nevertheless, it is worth noting that the energy required to remove a methylamine molecule from the 2+1 cluster will be much lower than that of the 3+0 isomer on account of the weakly bound solvent molecule held in the outer shell for the former isomer. Consequently, the binding energy of the outer shell solvent molecule in the 2+1 cluster would be readily surpassed by absorption of an IR photon near 3000 cm^{-1} .

According to the *ab initio* calculations, the inclusion of methylamine molecules in a $\text{Li}(\text{NH}_2\text{CH}_3)_3$ cluster brings about a complete reversal of the intensity ratio of N–H/C–H stretching bands when compared with free methylamine. In principle, C–H stretching bands should be observable, but the signal-to-noise ratio in the experimental spectrum in Fig. 6 is relatively poor and would make their observation nigh on impossible. It is also worth noting that, if the 3+0 isomer is responsible for the experimental spectrum, C–H stretching excitation will almost certainly not deposit sufficient energy into the cluster to bring about solvent molecule ejection.

FIG. 7. (Color online) IR photodepletion spectrum of $\text{Li}(\text{NH}_2\text{CH}_3)_4$ (upper trace) along with simulations derived from DFT calculations for the 4+0, 3+1, and 2+2 isomers. In the experimental case, the red trace represents a single scan (30 laser shots per wavelength), while the black trace is an average of nine separate scans.

2. $\text{Li}(\text{NH}_2\text{CH}_3)_4$

Figure 7 shows the IR photodepletion spectrum of $\text{Li}(\text{NH}_2\text{CH}_3)_4$. The spectrum is dominated by a broad feature centered near 3190 cm^{-1} with a slightly asymmetric shape extending to the blue region. In addition, although not clear in Fig. 7, there is a convincing evidence from the recording of several spectra of weak but ill-defined C–H stretching features near 2900 cm^{-1} .

Simulations of the spectra from DFT calculations are included in Fig. 7 for the three lowest energy isomers. Comparison between theory and experiment clearly does not provide definitive identification of the isomer(s) responsible for the spectrum. Both the 4+0 and 3+1 simulations show some features in common with experiment, including a blue-degraded collection of N–H stretching bands located in approximately the correct position along with weak C–H stretching bands. Precise band intensities are not expected from the simulations, as demonstrated by MP2 calculations, which yield some common features in the N–H stretching region but with substantially different relative intensities when compared to the DFT predictions. Consequently, the best we can say for $\text{Li}(\text{NH}_2\text{CH}_3)_4$ is that both the 4+0 and 3+1 isomers could contribute to the spectrum.

3. $\text{Li}(\text{NH}_2\text{CH}_3)_5$

Figure 8 shows the experimental IR spectrum of $\text{Li}(\text{NH}_2\text{CH}_3)_5$ along with DFT simulations derived from the calculated lowest energy 4+1 isomer and the two lowest

FIG. 8. (Color online) IR photodepletion spectrum of $\text{Li}(\text{NH}_2\text{CH}_3)_5$ (upper trace) along with simulations derived from DFT calculations for the three lowest energy isomers. In the experimental case, the red trace represents a single scan (30 laser shots per wavelength) while the black trace is an average of 17 separate scans.

energy 3+2 isomers. There are two significant differences between the spectra of $\text{Li}(\text{NH}_2\text{CH}_3)_4$ and $\text{Li}(\text{NH}_2\text{CH}_3)_5$. First, the N–H stretching region is substantially broader for the latter, extending over nearly 300 cm^{-1} . Secondly, the $\text{Li}(\text{NH}_2\text{CH}_3)_5$ spectrum shows clear and relatively sharp C–H bands.

The signal-to-noise ratio for the $\text{Li}(\text{NH}_2\text{CH}_3)_5$ spectrum is considerably improved relative to $\text{Li}(\text{NH}_2\text{CH}_3)_4$, presumably because of the stronger ion signal in the $n=5$ mass channel (see Fig. 5). There is a clear evidence of structure within the broad N–H stretching feature, with at least two distinct maxima identifiable at 3206 and 3247 cm^{-1} . The much sharper C–H stretching bands are located at 2860 , 2900 , 2925 , and 2960 cm^{-1} . Given the signal-to-noise ratio achieved, the simulations for all three low energy isomers predict that C–H stretching bands should be observable. However, the calculations predict bunching of the main C–H transitions around 2880 cm^{-1} , with some very weak additional C–H stretching features around 2940 cm^{-1} . The presence of several distinct C–H stretching bands in the experimental spectrum could be taken to indicate a major discrepancy between theory and experiment. However, a more likely explanation is a breakdown of the harmonic oscillator approximation employed in the simulations. The simulations are unable to take into account combination and overtone bands, which may be important in both the C–H and N–H stretching regions. Indeed, we have previously suggested that discrepancies between the N–H stretching bands observed for $\text{Li}(\text{NH}_3)_4$ and simulations derived from *ab initio* harmonic oscillator calculations are likely to be the result

of the omission of an overtone band, which gains intensity through Fermi resonance with N–H stretching fundamentals.³ The inability of the simulations to predict the complexity in the C–H stretching region is therefore explicable by the inadequacy of the harmonic oscillator model through its neglect of overtone and combination contributions.

The increased span of the N–H stretching bands when compared to the $n=3$ and 4 clusters may be of some significance. Focusing solely on the simulated spectra of the lowest energy isomer for each cluster size, the N–H stretching region is predicted to be substantially broader for $\text{Li}(\text{NH}_2\text{CH}_3)_5$ than for $\text{Li}(\text{NH}_2\text{CH}_3)_3$ and $\text{Li}(\text{NH}_2\text{CH}_3)_4$. Indeed, the predicted span of the N–H stretching bands for the 4+1 isomer of $\text{Li}(\text{NH}_2\text{CH}_3)_5$ is remarkably close to the observed width, although the detailed intensity profiles for experiment and simulations do not match. The greater span of the N–H stretching region for $\text{Li}(\text{NH}_2\text{CH}_3)_5$ may indicate a switchover from a (dominant) single-shell solvation structure for $\text{Li}(\text{NH}_2\text{CH}_3)_4$ to a two-shell structure for $\text{Li}(\text{NH}_2\text{CH}_3)_5$, as predicted by the *ab initio* calculations. The broadening of the N–H stretching region for $\text{Li}(\text{NH}_2\text{CH}_3)_5$ can be attributed to the presence of methylamine molecules in two different solvation shells for $\text{Li}(\text{NH}_2\text{CH}_3)_5$, the contrasting environments producing a greater range of N–H stretching frequencies. A similar argument has been used previously to interpret the N–H stretching region of $\text{Li}(\text{NH}_3)_n$ clusters.² Thus, we tentatively propose that the width of the N–H stretching features observed in the IR spectra of $\text{Li}(\text{NH}_2\text{CH}_3)_n$ clusters provides support for the *ab initio* prediction that the inner solvation shell can contain a maximum of four methylamine molecules.

Finally, the marked contrast between the bandwidths in the C–H and N–H stretching regions merits comment. The source of the broadening in the N–H stretching region has not been established, but a significant factor may be lifetime broadening, i.e., the N–H stretching vibrations couple strongly to the dissociative continuum. On the other hand, the methyl group is effectively a spectator when it comes to the Li–N binding in the inner solvation shell or the hydrogen bonding between inner and outer shell solvent molecules. Consequently, the C–H stretching modes will couple more weakly to the dissociative continuum, yielding slower intramolecular vibrational redistribution and, thus, reducing the lifetime broadening when compared to the excited N–H stretching levels. This may account for the reduced widths of the C–H stretching bands when compared to the N–H stretching bands.

D. Comparison with neutron diffraction studies of lithium-methylamine solutions

Hayama *et al.* have applied neutron diffraction to concentrated lithium-methylamine solutions to explore the coordination structure around the alkali cation and the extent of electron delocalization.^{16,17} Their findings suggest a maximum of four methylamine molecules in the inner solvation shell, with an approximately tetrahedral coordination of the lithium atom by the nitrogen atoms in each methylamine

FIG. 9. (Color) Calculated SOMO profile for the lowest energy isomers of $\text{Li}(\text{NH}_2\text{CH}_3)_4$ and $\text{Li}(\text{NH}_2\text{CH}_3)_5$ at the MP2 level of theory. The SOMO surface isovalue in each case is 0.015 a.u.

molecule. This description fits nicely with the calculated global minimum energy structure for the $\text{Li}(\text{NH}_2\text{CH}_3)_4$ cluster calculated in the present work. The inner shell Li–N distance deduced by Hayama *et al.*, 2.1 Å, is in good agreement with the *ab initio* results shown in Table I. The neutron diffraction work has also been used to estimate the distance between the lithium atom and a second shell methylamine molecule. This quantity is quite strongly dependent on the concentration of the solution, but the Li–N separation was found to be in the region of 4.0 Å.¹⁷ The distance between the Li atom and the second shell N atom in the $\text{Li}(\text{NH}_2\text{CH}_3)_5$ cluster was calculated to be 4.14 Å using DFT and 3.93 Å with MP2, values which match the neutron diffraction estimate. Consequently, the calculations carried out on small clusters in the present work seem to provide a reasonable description of the coordination of lithium by methylamine in concentrated bulk solutions.

Finally, the unpaired electron density profiles for the lowest energy isomers of $\text{Li}(\text{NH}_2\text{CH}_3)_4$ and $\text{Li}(\text{NH}_2\text{CH}_3)_5$ are shown in Fig. 9. For the $n=4$ cluster, the electron density is tetrahedrally distributed around the Li atom, but the occupation of the second solvation shell in the $n=5$ cluster has a dramatic distorting effect on the SOMO density, concentrating it in the region near to the outer shell methylamine molecule and extending out well beyond the first solvation shell. This profile shows that the electron begins to fully detach from the lithium atom once the second solvation shell becomes occupied, although the localization of the unpaired electron density on one side of the cluster means that full solvated electron behavior is not achieved. An *ab initio* characterization of the transition to fully solvated electron behavior as the solvation number is increased beyond $n=5$ would be an interesting extension to this work.

V. CONCLUSIONS

The first infrared spectra of $\text{Li}(\text{NH}_2\text{CH}_3)_n$ ($n=3-5$) clusters have been recorded and compared with predictions

from *ab initio* calculations. The calculations indicate that the first solvation shell can accommodate up to four methylamine molecules in a tetrahedral coordination in which the Li atom binds to the N atom on each solvent molecule. To avoid steric repulsion, the bulky methyl groups point away from the Li atom. The infrared spectra seem to concur with this description, showing band profiles in the N–H stretching region suggestive of a two-shell solvent occupation for $\text{Li}(\text{NH}_2\text{CH}_3)_5$ but not for $\text{Li}(\text{NH}_2\text{CH}_3)_3$ or $\text{Li}(\text{NH}_2\text{CH}_3)_4$. Despite the additional bulk provided by the methyl group, $\text{Li}(\text{NH}_2\text{CH}_3)_n$ is able to accommodate the same number of solvent molecules in its inner solvation shell as $\text{Li}(\text{NH}_3)_n$ clusters. The findings of the present work agree rather well with the lithium coordination structure reported from neutron diffraction measurements on concentrated bulk lithium/methylamine solutions.

ACKNOWLEDGMENTS

The authors would like to thank the UK Engineering and Physical Sciences Research Council (EPSRC) and the Royal Society for grants in aid of this work. The EPSRC National Service for Computational Chemistry is also gratefully acknowledged for providing both software and hardware resources in support of this work.

- ¹ J. C. Thompson, *Electrons in Liquid Ammonia* (Oxford University Press, New York, 1976).
- ² T. E. Salter, V. A. Mikhailov, C. J. Evans, and A. M. Ellis, *J. Chem. Phys.* **125**, 034302 (2006).
- ³ T. E. Salter and A. M. Ellis, *J. Phys. Chem. A* **111**, 4922 (2007).
- ⁴ D. M. Holtom, P. P. Edwards, W. McFarlane, and B. Wood, *J. Am. Chem. Soc.* **105**, 2104 (1983).
- ⁵ P. P. Edwards, *J. Phys. Chem.* **88**, 3772 (1984).
- ⁶ H. Matsui, E. Yamada, S. Shimokawa, and Y. Nakamura, *J. Phys. Chem.* **97**, 4284 (1993).
- ⁷ C. M. Stupak, T. R. Tuttle, and S. Golden, *J. Phys. Chem.* **88**, 3804 (1984).
- ⁸ S. Hayama, J. C. Wasse, N. T. Skipper, and A. K. Soper, *Mol. Phys.* **99**, 779 (2001).
- ⁹ S. Hayama, J. C. Wasse, N. T. Skipper, and A. K. Soper, *J. Phys. Chem. B* **106**, 11 (2002).
- ¹⁰ T. J. Seegue, N. Moe, and J. M. Lisy, *Z. Phys. D: At., Mol. Clusters* **26**, 207 (1993).
- ¹¹ J. Miyawaki, K. Sugawara, S. Li, and D.-S. Yang, *J. Phys. Chem. A* **109**, 6697 (2005).
- ¹² M. J. Frisch, G. W. Trucks, H. B. Schlegel *et al.*, GAUSSIAN 03, Revision C.02, Gaussian, Inc., Wallingford, CT, 2004.
- ¹³ A. P. Gray and R. C. Lord, *J. Chem. Phys.* **26**, 690 (1957).
- ¹⁴ Y. Hamada, N. Tanaka, Y. Sugawara, A. Y. Hirakawa, M. Tsuboi, S. Kato, and K. Morokuma, *J. Mol. Spectrosc.* **96**, 313 (1982).
- ¹⁵ T. E. Salter and A. M. Ellis, *Chem. Phys.* **332**, 132 (2007).
- ¹⁶ S. Hayama, J. C. Wasse, N. T. Skipper, and J. K. Walters, *Mol. Phys.* **99**, 779 (2001).
- ¹⁷ S. Hayama, J. C. Wasse, N. T. Skipper, and A. K. Soper, *J. Phys. Chem. B* **106**, 11 (2002).