

## Photodetachment Spectroscopy of Cluster Anions

Photoelectron Spectroscopy of  $\text{H}^-(\text{NH}_3)_1$ ,  $\text{H}^-(\text{NH}_3)_2$  and the Tetrahedral Isomer of  $\text{NH}_4^-$

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The dominant peaks in the photoelectron spectra of the gas-phase, negative cluster ions  $\text{H}^-(\text{NH}_3)_1$  and  $\text{H}^-(\text{NH}_3)_2$  provide evidence for describing them as ion-molecule complexes comprised of intact hydride ions which are solvated by ammonia. Vertical detachment energies and approximate ion-single-solvent dissociation energies are obtained. Other spectral features reveal the complexation-induced distortion of the ammonia solvent(s) by their hydride sub-ions. In the photoelectron spectra of  $\text{H}^-(\text{NH}_3)_1$  an additional peak appears which is small and unusually narrow and which does not shift upon deuteration. Evidence is presented for interpreting this peak as arising due to the photodetachment of a tetrahedral isomer of  $\text{NH}_4^-$ . This previously unknown ammonium anion is not a cluster species, and it is described as a  $\text{NH}_4^+$  ion core with two Rydberg-like electrons.

The study of gas-phase cluster anions provides an avenue for addressing open questions in topics as diverse as ion solvation, excess electrons in fluids, ion-molecule reactions, ion-induced nucleation and electronic band structure in solids. In the past, experimental investigations of negative cluster ions have included thermochemical,<sup>1-3</sup> kinetic,<sup>4</sup> electron-attachment<sup>5,6</sup> and spectroscopic studies, with the latter exploring total photodestruction,<sup>7,8</sup> photodissociation<sup>9,10</sup> and photodetachment<sup>11</sup> processes. At the same time, theoretical studies have dealt with the related topics of negative-ion solvation,<sup>12-14</sup> trapped and solvated electron states<sup>15,16</sup> and the variation of metal-cluster electron affinities with cluster size.<sup>17-19</sup>

The photodetachment of electrons from mass-selected cluster anions yields incisive information not only about individual sizes of cluster anions but also about their corresponding neutral clusters. When conducted as a function of cluster size, photodetachment experiments can contribute to our understanding of interatomic and intermolecular phenomena in the size regime between single atomic or molecular species and the condensed phase. In recent years, dramatic progress in the photodetachment of negative cluster ions and related anionic species has been occurring in several laboratories. Using pulsed negative ion photoelectron spectroscopy, Smalley and his colleagues<sup>20-27</sup> have recorded the spectra of  $\text{C}_{n=2-30,48-84}^-$ ,  $\text{Cu}_{n=6-41}^-$ ,  $\text{Ag}_{n=3-21}^-$ ,  $\text{Au}_{n=2-21}^-$ ,  $\text{Nb}_{n=4-12}^-$ ,  $\text{Pb}_{n=2-12}^-$ ,  $\text{Si}_{n=3-20}^-$ ,  $\text{Ge}_{n=3-15}^-$ ,  $\text{Sn}_{n=2-12}^-$  and  $\text{Al}_{n=3-32}^-$ ; Johnson's group<sup>28-31</sup> has measured the spectra of  $(\text{O}_2)_{n=2-6}^-$ ,  $\text{O}_2^-(\text{N}_2)_1$ ,  $\text{NO}^-(\text{NO})_1$ ,  $(\text{CO}_2)_{n=2-13}^-$ ,  $\text{O}_2^-(\text{H}_2\text{O})_1$  and  $\text{NO}_2^-(\text{N}_2\text{O})_1$ ; Neumark *et al.*<sup>32-34</sup> have recorded the spectra of  $(\text{ClHCl})^-$ ,  $(\text{IHl})^-$ ,  $(\text{BrHBr})^-$ ,  $(\text{FHCl})^-$ , and  $(\text{BrHCl})^-$ ; and Meiwes-Broer and co-workers<sup>35,36</sup> have taken the spectra of  $\text{Al}_{n=3-14}^-$ ,  $\text{Ag}_{n=3-22}^-$  and  $\text{Ni}_{n=2-18}^-$ . Using ion-cyclotron resonance photodetachment spectroscopy, Brauman *et al.*<sup>37-39</sup> have investigated a variety of solvated anions of the form  $(\text{ROHF})^-$ . Using continuous-beam, negative-ion photoelectron spectroscopy, Lineberger's group<sup>40-48</sup> has measured the spectra of  $\text{Cu}_{n=2-10}^-$ ,  $\text{Fe}_2^-$ ,  $\text{Co}_2^-$ ,

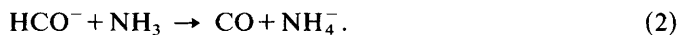
$\text{Ag}_{n=2-6}^-$ ,  $\text{Re}_2^-$ ,  $\text{Ni}_{n=2-8}^-$ ,  $\text{Pd}_3^-$ ,  $\text{Pt}_{n=2,3}^-$ ,  $(\text{Na}_m\text{F}_n)^-$ ,  $\text{Fe}(\text{CO})_{n=1-4}^-$ ,  $\text{Ni}(\text{CO})_{n=1-3}^-$ ,  $\text{H}^-(\text{H}_2\text{O})_1$  and  $\text{D}^-(\text{D}_2\text{O})_1$ ; Ellison *et al.*<sup>49</sup> have taken the spectrum of  $\text{Si}_2^-$ ; and in our laboratory<sup>50-54</sup> we have recorded the photoelectron spectra of  $\text{NO}^-(\text{N}_2\text{O})_{n=1-5}$ ,  $\text{H}^-(\text{NH}_3)_{n=1,2}$ ,  $\text{D}^-(\text{ND}_3)_1$ ,  $\text{NH}_2^-(\text{NH}_3)_{n=1,2}$ ,  $\text{ND}_2^-(\text{ND}_3)_{n=1,2}$ ,  $\text{NO}^-(\text{Ar})_1$ ,  $\text{NO}^-(\text{Kr})_1$ ,  $\text{NO}^-(\text{Xe})_1$ ,  $\text{O}_2^-(\text{Ar})_1$ ,  $\text{NO}^-(\text{H}_2\text{O})_{n=1,2}$ ,  $\text{NO}^-(\text{D}_2\text{O})_{n=1,2}$ ,  $(\text{CO}_2)_2^-$ ,  $(\text{N}_2\text{O})_2^-$ ,  $(\text{CS}_2)_2^-$ ,  $(\text{SO}_2)_2^-$ ,  $(\text{H}_2\text{O})_{n=2,6,7,10-25,30,34,37,40}^-$ ,  $(\text{D}_2\text{O})_{n=2,6,7,11-23}^-$ ,  $\text{Ar}(\text{H}_2\text{O})_{n=2,6,7}^-$ ,  $\text{Ar}(\text{D}_2\text{O})_{n=2,6,7}^-$ ,  $\text{Ar}_2(\text{D}_2\text{O})_6^-$ ,  $\text{Na}_{n=2-5,7}^-$ ,  $\text{K}_{n=2-7}^-$ ,  $\text{Rb}_{n=2,3}^-$ ,  $\text{Cs}_{n=2,3}^-$ ,  $(\text{NaK})^-$ ,  $(\text{Na}_2\text{K})^-$ ,  $(\text{KRb})^-$ ,  $(\text{KCs})^-$ ,  $(\text{K}_2\text{Cs})^-$  and  $(\text{RbCs})^-$ . Clearly, progress in cluster-anion photodetachment spectroscopy has been rapid, and the field is beginning to flourish across a chemically diverse range of systems.

Here we illustrate our work in negative-cluster ion photoelectron (photodetachment) spectroscopy with a specific study, that of  $\text{H}^-(\text{NH}_3)_n$ . Previously, we reported<sup>50</sup> the negative-ion photoelectron spectra of  $\text{H}^-(\text{NH}_3)_1$  and  $\text{D}^-(\text{ND}_3)_1$ . In this paper we elaborate on these earlier results; we report the photoelectron spectrum of  $\text{H}^-(\text{NH}_3)_2$ ; and we present evidence for a tetrahedral isomer of  $\text{NH}_4^-$ .

The hydride ion-ammonia complex has long been implicated in liquid-ammonia solutions<sup>55-58</sup> as an intermediate in the proton-transfer reaction



The first observation of  $\text{NH}_4^-$  in the gas phase, however, did not occur until 1982, when Nibbering and co-workers<sup>59</sup> generated it in a Fourier-transform ion-cyclotron spectrometer *via* the reaction



Deuterium labelling experiments demonstrated that all of the hydrogen atoms in  $\text{NH}_4^-$  were not equivalent, and these investigators concluded that  $\text{NH}_4^-$  is comprised of a hydride ion solvated by an ammonia molecule, *i.e.*  $\text{H}^-(\text{NH}_3)_1$ .

Of the cluster anions studied thus far by negative-ion photoelectron spectroscopy,  $\text{H}^-(\text{NH}_3)_1$  is currently the most thoroughly investigated by theoretical methods. The first calculations on  $\text{H}^-(\text{NH}_3)_1$  were performed twenty years ago by Ritchie and King.<sup>60</sup> More recently, *ab initio* computations on  $\text{NH}_4^-$  have also been carried out by Rosmus *et al.*,<sup>61</sup> by Squires,<sup>62</sup> by Schleyer and co-workers,<sup>63</sup> by Cremer and Kraka,<sup>64</sup> by Cardy *et al.*,<sup>65</sup> by Hirao and Kawai,<sup>66</sup> and by Ortiz<sup>67</sup> all of whom agree that the most stable configuration of  $\text{NH}_4^-$  is an  $\text{H}^-(\text{NH}_3)_1$  ion-dipole complex in which the hydride ion is bound at a relatively long distance to only one of the ammonia hydrogens almost collinearly with a N—H bond of ammonia. Also, of the five studies that have considered the issue, all found  $\text{H}^-(\text{NH}_3)_1$  to be more stable than the alternative ion-molecule complex,  $\text{NH}_2^-(\text{H}_2)_1$ . Furthermore, most of these computations also found values for the dissociation energy of  $\text{H}^-(\text{NH}_3)_1$  breaking into  $\text{H}^-$  and  $\text{NH}_3$  that were in good agreement with the value determined in our photoelectron study<sup>50</sup> of  $\text{H}^-(\text{NH}_3)_1$ . In addition to a hydrogen-bonded  $\text{NH}_4^-$  ion-molecule complex, calculations by Schleyer *et al.*,<sup>63</sup> by Cremer and Kraka,<sup>64</sup> by Cardy and colleagues<sup>65</sup> and by Ortiz<sup>67</sup> also found a bound, higher energy, nitrogen-bonded  $\text{NH}_4^-$  isomer of tetrahedral symmetry. Recent *ab initio* calculations on double Rydberg molecular anions by Simons and co-workers<sup>68</sup> also found a tetrahedral  $\text{NH}_4^-$ . In addition, semi-empirical calculations by Glidewell<sup>69</sup> have predicted the tetrahedral configuration to be the most stable form of  $\text{NH}_4^-$ .

## Experimental

In continuous-beam, negative-ion photoelectron spectroscopy, a steadily operating, mass-selected beam of negative ions is crossed with a fixed-frequency, c.w. photon beam, and the resultant photodetached electrons are energy-analysed. Subtraction of the centre-of-mass electron kinetic energy of an observed spectral feature from the photon

energy gives the transition energy (the electron binding energy) from an occupied level in the negative ion to an energetically accessible level in the corresponding neutral. Our apparatus, which has been described previously,<sup>70</sup> employs a Wien velocity filter for mass selection, an argon-ion laser operated intracavity in the ion-photon interaction region, and a magnetically shielded, hemispherical electron-energy analyser. Mass selection is a particularly important attribute of this technique because it allows us to 'purify' our starting sample of negative ions before photodetachment and thus to obtain interference-free photoelectron spectra of specific negative cluster ions.

We did not utilize the Nibbering formation mechanism in preparing our ion sample. Negative cluster ions of  $\text{H}^-(\text{NH}_3)_{n=1-4}$  were generated in this work, with a supersonic expansion-ion source similar in spirit to that developed by Haberland *et al.*<sup>71</sup> The operation of this source involves the injection of electrons from a biased hot filament into an expanding supersonic jet in the presence of magnetic fields, and our version of it has been described previously.<sup>52</sup> Typical source operation conditions were as follows: a nozzle diameter of 18  $\mu\text{m}$ , a stagnation pressure of *ca.*  $3 \times 10^5$  Pa of ammonia, a beam voltage of  $-500$  V, a filament bias of  $-70$  V relative to the nozzle, a filament emission of *ca.* 15 mA, an extraction voltage of *ca.* 1300 V and a nozzle temperature of *ca.* 0 °C. Currents measured at the Faraday cup beyond the ion-photon interaction region were usually *ca.*  $6 \times 10^{-10}$  A of  $\text{H}^-(\text{NH}_3)_1$  and *ca.*  $1 \times 10^{-10}$  A of  $\text{H}^-(\text{NH}_3)_2$ . Typical mass spectra obtained by using neat  $\text{NH}_3$  and  $\text{ND}_3$  in the nozzle-ion source are presented in fig. 1 on aligned mass scales. Mass assignments were confirmed by photodetaching ions with well known photoelectron spectra such as  $\text{NH}_2^-$  and  $\text{OH}^-$ . While cluster-anion series of the form  $\text{H}^-(\text{NH}_3)_n$  and  $\text{NH}_2^-(\text{NH}_3)_n$  were observed in these mass spectra, no homologous series of the form  $\text{NH}_2^-(\text{H}_2)_n$  was seen.

## Results and Interpretation of Spectra

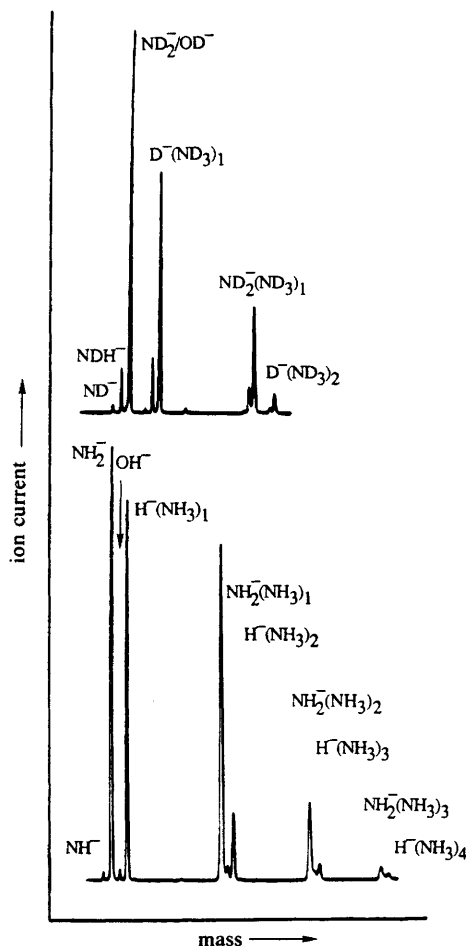
### Data

The photoelectron spectrum of  $\text{H}^-(\text{NH}_3)_1$  is presented in fig. 2, along with the photoelectron spectrum of  $\text{H}^-(\text{NH}_3)_2$  and a sketch of the spectrum of  $\text{H}^-$  (a single peak), all on aligned centre-of-mass electron kinetic-energy scales. Magnified versions of the photoelectron spectra of  $\text{H}^-(\text{NH}_3)_1$  at mass 18 and of  $\text{D}^-(\text{ND}_3)_1$  at mass 22 are presented in fig. 3. The similarity of these spectra confirms that mass 22 is the deuterated version of mass 18, and together with mass-spectral data, this strongly suggests that both ions are comprised of four hydrogens and one nitrogen, *i.e.*  $\text{NH}_4^-$  and  $\text{ND}_4^-$ . In all of the spectra shown here the photon energy was 2.540 eV† (4880 Å), the electron energy channel spacing was 8.5 meV, and the analyser's instrumental resolution was 30 meV. Also, the mass resolution typically used during these experiments was that shown in fig. 1. The photoelectron spectrum of  $\text{OH}^-$  (or of  $\text{ND}_2^-/\text{OD}^-$  in deuterated cases) was recorded before and after each cluster-ion spectrum for calibration purposes. Peaks were fitted to the functional form of asymmetric Gaussians. Peak positions, intensities and widths are presented in table 1, and the day-to-day variation in  $\text{H}^-(\text{NH}_3)_1$  peak intensity ratios is shown in table 2. The photoelectron spectrum of  $\text{H}^-(\text{NH}_3)_1$  was recorded at photon energies of 2.409, 2.497, 2.540 and 2.707 eV.‡ The electron binding energies of all features in the spectrum remained unchanged at each of these four photon energies.

The photoelectron spectra of  $\text{H}^-(\text{NH}_3)_1$  and  $\text{H}^-(\text{NH}_3)_2$  are both dominated by large peaks which we have designated as peaks A and A', respectively, in fig. 2. The  $\text{H}^-(\text{NH}_3)_1$  spectrum also exhibits a smaller peak on the low electron kinetic-energy side (the high electron binding-energy side) of peak A, which we have labelled as peak B. The shoulder

†1 eV  $\approx 1.60218 \times 10^{-19}$  J.

‡The C/A peak intensity ratio increased steadily with decreasing photon energies.

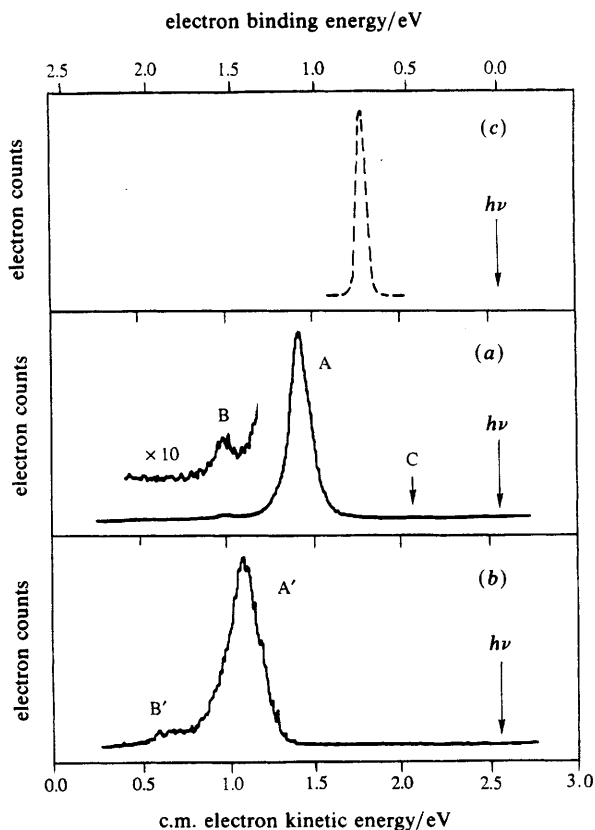


**Fig. 1.** Negative-ion mass spectra showing the cluster anions generated when  $\text{NH}_3$  and  $\text{ND}_3$  were used in our supersonic expansion ion source. These ion currents were measured at a Faraday cup beyond the ion-photon interaction region. Although not shown here, large currents of  $\text{H}^-$  were also detected.

on the low electron kinetic-energy side of peak A' in the  $\text{H}^-(\text{NH}_3)_2$  spectrum is marked in fig. 2 as feature B'. A much smaller third peak also exists in the  $\text{H}^-(\text{NH}_3)_1$  spectrum, and this is designated as peak C. We find no evidence for a counterpart to peak C in the  $\text{H}^-(\text{NH}_3)_2$  spectrum. In the sections that follow, we interpret these spectra by discussing in turn peaks A and A', then peaks B and B', and lastly peak C.

### Peaks A and A'

Peaks A and A' arise due to the photodetachment of electrons from the solvated hydride ion 'chromophores' within  $\text{H}^-(\text{NH}_3)_1$  and  $\text{H}^-(\text{NH}_3)_2$ , respectively. For this reason, both peaks resemble the photoelectron spectrum of free  $\text{H}^-$  except for being broadened and shifted to progressively lower electron kinetic energies owing to the stabilizing effect of solvation. The  $\text{H}^-(\text{NH}_3)_{n=1,2}$  ions are examples of cluster anions in which the system's



**Fig. 2.** The photoelectron spectra of (a)  $\text{H}^-(\text{NH}_3)_1$  and (b)  $\text{H}^-(\text{NH}_3)_2$ , both recorded with 2.540 eV photons. The spectrum of  $\text{H}^-$  has been sketched in for comparison (c).

excess negative charge is largely localized on a specific component of the cluster ion to form a sub-ion which interacts with the remaining components. When this occurs, the photoelectron spectra of the resulting ion-molecule complexes may be viewed as the spectra of their perturbed sub-ions, some additional examples being  $\text{NO}^-(\text{N}_2\text{O})_{n=1-5}$ ,  $\text{H}^-(\text{H}_2\text{O})_1$ ,<sup>42</sup>  $\text{NH}_2^-(\text{NH}_3)_{n=1,2}$ ,  $\text{O}_2^-(\text{N}_2)_1$ <sup>29</sup> and  $\text{NO}^-(\text{Ar})_1$ .

Before discussing the energetic implications of peaks A and A', let us first consider the energetic relationships between the generic negative cluster ions,  $\text{X}^-(\text{Y})_n$ , and their corresponding neutral clusters,  $\text{X}(\text{Y})_n$ . These are expressed through the identities

$$E_A[\text{X}(\text{Y})_n] = E_A[\text{X}] + \sum_{m=0}^{n-1} D[\text{X}^-(\text{Y})_m \cdots \text{Y}] - \sum_{m=0}^{n-1} D_{\text{WB}}[\text{X}(\text{Y})_m \cdots \text{Y}] \quad (3)$$

and

$$E_A[\text{X}(\text{Y})_n] = E_A[\text{X}(\text{Y})_{n-1}] + D[\text{X}^-(\text{Y})_{n-1} \cdots \text{Y}] - D_{\text{WB}}[\text{X}(\text{Y})_{n-1} \cdots \text{Y}] \quad (4)$$

where  $E_A[\text{X}(\text{Y})_n]$  denotes the adiabatic electron affinity of the  $\text{X}(\text{Y})_n$  cluster,  $D[\text{X}^-(\text{Y})_m \cdots \text{Y}]$  is the ion-neutral dissociation energy (the absolute value of the solvation energy) for the loss of a single neutral solvent Y from a given negative cluster ion, and  $D_{\text{WB}}[\text{X}(\text{Y})_m \cdots \text{Y}]$  is the weak-bond dissociation energy for the loss of a single solvent Y from a given neutral cluster. Since ion-solvent interaction energies generally

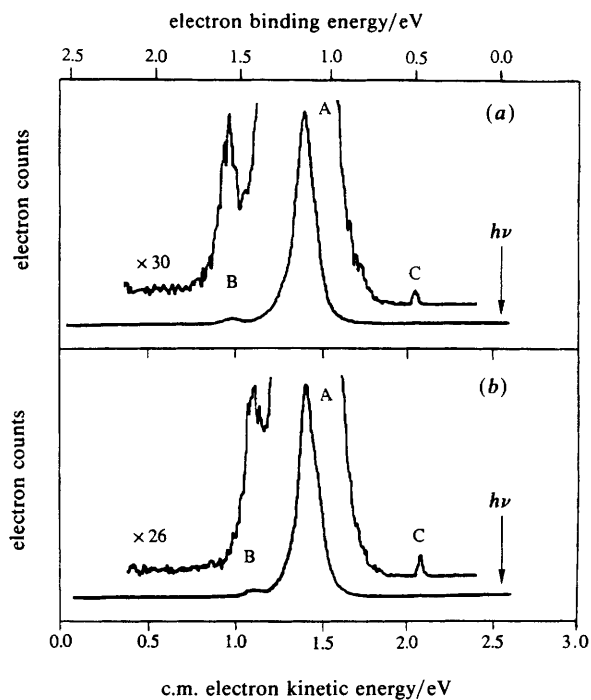


Fig. 3. The photoelectron spectra of (a)  $\text{H}^-(\text{NH}_3)_1$  and (b)  $\text{D}^-(\text{ND}_3)_1$  along with magnified versions of each. Both spectra were recorded with 2.540 eV photons.

Table 1. Peak positions, widths and intensities for the photoelectron spectra of  $\text{H}^-(\text{NH}_3)_1$ ,  $\text{D}^-(\text{ND}_3)_1$  and  $\text{H}^-(\text{NH}_3)_2^a$

peak labels	peak centre positions			
	c.m. electron kinetic energy/eV	electron binding energy/eV	peak widths, f.w.h.m./eV	relative intensities
		$\text{H}^-(\text{NH}_3)_1$		
C	2.068	0.472	0.032	14
A	1.431	1.109	0.144	5978
B	0.999	1.541	0.140	176
		$\text{D}^-(\text{ND}_3)_1$		
C	2.066	0.474	0.027	33
A	1.419	1.121	0.146	7467
B	1.113	1.427	0.188	271
		$\text{H}^-(\text{NH}_3)_2$		
A'	1.085	1.455	0.223	440

<sup>a</sup> Photon energy = 2.540 eV.

**Table 2.** Day-to-day variation in  $\text{H}^-(\text{NH}_3)_1$  peak intensity ratios

A/B	A/C
38	164
36	312
37	60
38	227
34	417
36	167

exceed van der Waals bond strengths, it is evident from these relations that the electron affinities of clusters should increase with cluster size, and that clustering can be expected to stabilize the excess electronic charges on negative ions.

Physically, the electron binding energies of peaks A and A' correspond to the energies needed to detach excess electrons from the stabilized  $\text{H}^-$  sub-ions within  $\text{H}^-(\text{NH}_3)_1$  and  $\text{H}^-(\text{NH}_3)_2$ . The electron binding energies of the centres of peaks A and A' are 1.109 and 1.455 eV, respectively. Formally, these numbers are vertical detachment energies, measures of the energy difference between the occupied states of an anion and the portion of its neutral's potential surface which corresponds to the instantaneous configuration of the anion during photodetachment. While little is known about the topology of this region of the neutral  $\text{NH}_4$  potential surface, it seems likely that the photodetachment of  $\text{H}^-(\text{NH}_3)_1$  is accessing a portion of it not far in energy above the  $\text{H} + \text{NH}_3 + e^-$  dissociation asymptote, and that a conceptually analogous situation is occurring in the case of  $\text{H}^-(\text{NH}_3)_2$ . The van der Waals interaction between a neutral hydrogen atom and an ammonia molecule probably results in a shallow, broad well only slightly lower in energy than its dissociation asymptote, and again we suspect that an analogous situation holds for the doubly solvated complex. For these reasons, these vertical detachment energies are not only upper limits to the dissociative detachment energies of  $\text{H}^-(\text{NH}_3)_1$  and  $\text{H}^-(\text{NH}_3)_2$  and to the adiabatic electron affinities of their corresponding neutral complexes, they are also approximations to them. We should also mention that the vertical detachment energy of  $\text{D}^-(\text{ND}_3)_1$  is 1.121 eV, slightly different from that of  $\text{H}^-(\text{NH}_3)_1$ . This difference is interpreted as being due to net differences in zero-point energies.

The calculations by Ortiz<sup>67</sup> provide some quantitative perspective to these qualitative expectations. In a particularly extensive study, Ortiz calculated the vertical detachment energy of  $\text{H}^-(\text{NH}_3)_1$  to be 1.205 eV, the van der Waals well depth of the  $\text{H}(\text{NH}_3)_1$  neutral complex (in  $C_s$  symmetry) to be only *ca.* 0.001 eV, and the adiabatic electron affinity of the complex to be 1.127 eV (zero-point energies not having been included). Since the difference between his vertical detachment energy and his adiabatic electron affinity values should be relatively insensitive to zero-point energy effects along the neutral surface, this implies that the photodetachment of  $\text{H}^-(\text{NH}_3)_1$  is accessing a point on the potential surface of its corresponding neutral which is only 0.077 eV above the  $\text{H} + \text{NH}_3$  dissociation asymptote. While his calculation does not claim this degree of accuracy, it does provide a sense of the magnitudes involved, and it leads us to suggest that the dissociative detachment energy of  $\text{H}^-(\text{NH}_3)_1$  and the adiabatic electron affinity of its corresponding neutral are both probably smaller than the measured vertical detachment energy by only *ca.* 0.1 eV or less. While the situation for  $\text{H}^-(\text{NH}_3)_2$  is less clear, one can imagine (1) that the  $\text{H}(\text{NH}_3) + \text{NH}_3$  dissociation asymptote of its neutral's surface is only slightly lower in energy than the  $\text{H} + \text{NH}_3$  dissociation asymptote, and (2) that, in the case where the hydride ion in  $\text{H}^-(\text{NH}_3)_2$  were hydrogen-bonded equally to both

ammonia molecules, the photodetachment of  $\text{H}^-(\text{NH}_3)_2$  would be accessing a point on the potential surface of its corresponding neutral which is roughly 0.15 eV (*i.e.*  $2 \times 0.077$  eV) in energy above its dissociation asymptote.

An upper limit to the ion-solvent dissociation energy for  $\text{H}^-(\text{NH}_3)_1$  breaking into  $\text{H}^-$  and  $\text{NH}_3$  is given by the difference between the vertical detachment energy of  $\text{H}^-(\text{NH}_3)_1$  and the electron affinity of the hydrogen atom (0.754 eV). This value is 0.36 eV. Likewise, an upper limit to the ion-single-solvent dissociation energy for  $\text{H}^-(\text{NH}_3)_2$  breaking into  $\text{H}^-(\text{NH}_3)_1$  and  $\text{NH}_3$  is given by the difference between the vertical detachment energies of  $\text{H}^-(\text{NH}_3)_2$  and  $\text{H}^-(\text{NH}_3)_1$ , and this value is 0.35 eV. Alternatively, these same estimates can be taken from eqn (4) if cluster electron affinities are approximated by vertical detachment energies and if van der Waals dissociation energies are assumed to be negligible compared to ion-neutral dissociation energies. Either approach, of course, is equivalent to saying that the spectral shifts between the centres of the origin peaks of adjacent-sized ions and cluster ions are approximately equal to the ion-solvent dissociation energies for the larger of the cluster ions losing single solvent molecules. If the Ortiz difference corrections are applied to these upper limit values in order better to estimate the actual ion-single solvent dissociation energies, one obtains *ca.* 0.28 and *ca.* 0.27 eV for  $\text{H}^-(\text{NH}_3)_1$  and  $\text{H}^-(\text{NH}_3)_2$ , respectively.

The ion-solvent dissociation energy for  $\text{H}^-(\text{NH}_3)_1$  breaking into  $\text{H}^-$  and  $\text{NH}_3$  has been calculated during the course of several theoretical studies. The calculations of Ritchie and King<sup>60</sup> found a value for  $D_e$  of 0.27 eV. Kalcher *et al.*<sup>61</sup> calculated that  $D_e = 0.36$  eV and that  $D_0 \geq 0.24$  eV. Squires<sup>62</sup> determined  $D_0$  to be 0.23 eV. Kos *et al.*<sup>63</sup> found that  $D_e = 0.46$  eV and that  $D_0 = 0.35$  eV. Cremer and Kraka<sup>64</sup> calculated that  $D_e = 0.65$  eV. Cardy *et al.*<sup>65</sup> found  $D_e$  to be 0.27 eV. [Cardy *et al.* also calculated the lower limit to the ionization potential of  $\text{H}^-(\text{NH}_3)_1$  to be 0.93 eV.] Hirao and Kawai<sup>66</sup> determined  $D_0$  to be 0.33 eV, and Ortiz<sup>67</sup> found that  $D_e = 0.38$  eV. In addition to these calculations, Leopold and Lineberger<sup>72,73</sup> have measured the electron affinity of  $\text{HCO}$  and have utilized it in a thermochemical cycle [involving eqn (2)] to estimate a lower limit of  $0.32 \pm 0.09$  eV for the ion-solvent dissociation energy of  $\text{H}^-(\text{NH}_3)_1$ . Thus the preponderance of information available from other studies is in reasonably good agreement with our value for the dissociation energy of  $\text{H}^-(\text{NH}_3)_1$ , and is supportive of our interpretation.

The ion-single-solvent dissociation energies determined in our work are also sequential gas-phase solvation energies. In the cases of  $\text{H}^-(\text{NH}_3)_1$  and  $\text{H}^-(\text{NH}_3)_2$ , these values are comparable (whether one chooses to consider their upper limits of 0.36 and 0.35 eV or their corrected estimates of 0.28 and 0.27 eV, respectively). Guidance in appreciating the similarity of these values is provided by thermochemical studies of gas-phase ion-clustering processes by Kebarle and by Castleman.<sup>1,74</sup> Stepwise enthalpy changes have been measured for the addition of solvent molecules onto a variety of negative ions in which the ions' corresponding neutrals are usually species with relatively high electron affinities. Often in negative cluster ions with large (*ca.* 1 eV) first solvation energies, the second solvation energy is much smaller (often *ca.* 50% of the first), while in cluster ions with first solvation energies of *ca.* 0.5 eV, for example, the second solvation energy is only slightly smaller (often by only *ca.* 10% of the first). In light of these trends it is not surprising that in the case of  $\text{H}^-(\text{NH}_3)_{n=1,2}$ , where the first solvation energy is *ca.* 0.28 eV (or the upper limit of 0.36 eV), the second solvation energy is only slightly smaller. These effects can probably be understood, at least in part, in terms of partial charge transfer between the anion and its solvent(s).<sup>74</sup> While the first and second ion-single-solvent dissociation energies calculated by Hirao and Kawai<sup>66</sup> are not as close to each other as are ours, they are nevertheless in reasonable accord with the expected trends. For  $\text{H}^-(\text{NH}_3)_1$  they calculate that  $D_0$  is 0.33 eV, while for  $\text{H}^-(\text{NH}_3)_2$  they find two geometries, both with  $D_0$  values of *ca.* 0.27 eV.



The full widths at half maximum of peaks A and A' are 0.144 and 0.223 eV, respectively, considerably broader than the 0.030 eV instrumental resolution. In the case of  $D^-(ND_3)_1$ , the full widths at half maximum of its peak A is 0.146 eV, not significantly different from that of peak A in the spectrum of  $H^-(NH_3)_1$ . The broadening of these peaks is probably due to contributions from several sources including (a) excited weak-bond vibrations in the cluster ion, (b) vibrational excitations in the resulting neutral and (c) access to a repulsive portion of the neutral's potential surface. (a) If the internal temperature of the cluster ions is not rather cold, then weak-bond hot bands could contribute to the broadening, especially on the high electron kinetic-energy sides of peaks A and A'. Even though our cluster ions were generated in a supersonic expansion ion source where strong collisional cooling conditions exist, we do not presently possess a reliable means of determining their temperature. In fact, it seems likely that while the cluster ions generated in this fashion are relatively cool by the standards usually applied to ions, they are also considerably warmer than neutral clusters generated in a comparable expansion. Thus, a contribution to the broadening due to weak-bond hot bands may well be present to some extent. (b) Vibrational excitations in the resulting neutral would contribute to broadening on the low electron kinetic-energy sides of peaks A and A'. As will be discussed in the next section, peaks B and B' arise owing to the excitation of stretching modes in the ammonia solvent(s) during photodetachment. If bending modes were also excited, they could easily lie unresolved under the low electron kinetic-energy sides of peaks A and A', thereby contributing to the broadening. The observation of a slight asymmetry in peak A, with tailing to its low electron kinetic-energy side, suggests that this is indeed occurring. On the other hand, the similarity in the peak A full widths at half maximum in the spectra of  $H^-(NH_3)_1$  and  $D^-(ND_3)_1$ , along with the low intensity of peak B (in both), imply that this source of broadening is relatively minor. In the case of peak A' in the  $H^-(NH_3)_2$  spectrum, where there are two ammonia molecules to excite, this type of broadening may make a greater contribution. (c) Broadening could also arise owing to the projection of the cluster anion's wavefunction onto the repulsive portion of the resulting neutral's potential surface. Recall that the calculations by Ortiz<sup>67</sup> found the photodetachment of  $H^-(NH_3)_1$  to be sampling a point on its neutral potential surface *ca.* 0.077 eV above the  $H + NH_3 + e^-$  dissociation asymptote. If the anion's reflected wavefunction were wide enough to encompass the dissociation asymptotic region of the neutral's potential surface, and if the repulsive part of the potential were of relatively constant slope over the portion being accessed, then the broadening due to this mechanism would be *ca.* 0.150 eV. This is close to the observed full widths at half maximum of peak A, and it suggests that this broadening mechanism may be an important one in this system. If this is the case, then additional implications are that the repulsive portion of the potential is fairly gently sloping in the region where it is accessed, and that the van der Waals well regime of the neutral's potential is being accessed during photodetachment, *i.e.* the origin transition is represented under the high electron kinetic energy side of peak A. The greater its photodetachment accessing a point on its corresponding neutral's surface that is higher in energy and therefore more steeply sloping than in the case of  $H^-(NH_3)_1$ .

### Peaks B and B'

Peak B in the photoelectron spectrum of  $H^-(NH_3)_1$  is primarily due to the excitation of a stretching mode in the ammonia solvent during photodetachment, and the same interpretation holds for peak B in the spectrum of  $D^-(ND_3)_1$ . Physically this comes about in the following way. Within the  $H^-(NH_3)_1$  ion-molecule complex, the hydride ion interacts with its ammonia solvent and distorts it from its equilibrium geometry. At

the moment of photodetachment, the ammonia portion of the resulting neutral possesses the same structure exhibited by ammonia in the ion-molecule complex an instant earlier. Thus, some of the ammonia molecules within their resultant neutrals are prepared in a vibrationally excited state. Alternatively stated, there is Franck-Condon overlap between the distorted ammonia in the ion-molecule complex and the vibrationally excited modes of ammonia in the resultant neutral. Of course, most of the overlap occurs with the ground vibrational state of ammonia in the resulting neutral.

Vibrational excitation in the resultant neutral manifests itself in the photoelectron spectrum as a spectral feature (peak B) with an electron binding energy which is higher than that of the origin-containing peak (peak A) by an energy equal to the vibrational excitation. Fig. 3 presents the photoelectron spectra of  $\text{H}^-(\text{NH}_3)_1$  and  $\text{D}^-(\text{ND}_3)_1$  along with magnified versions of each. In the  $\text{H}^-(\text{NH}_3)_1$  spectrum the centre of peak A is separated from the centre of peak B by  $3480 \pm 40 \text{ cm}^{-1}$ , where the cited uncertainty is a conservative estimate of the statistical errors involved in locating the peak centres. In  $\text{NH}_3$  the band centre for the asymmetric stretch occurs at  $3443 \text{ cm}^{-1}$ , while that for the symmetric stretch occurs at  $3336 \text{ cm}^{-1}$ . The A-B peak spacing observed in the  $\text{H}^-(\text{NH}_3)_1$  spectrum not only supports our interpretation of peak B as arising from the excitation of an ammonia stretching mode; it also implies that the dominant mode of excitation is the asymmetric stretch.<sup>†</sup> Of course, there may also be a contribution to peak B from the symmetric stretch. If this is the case, however, it appears to be less intense than the asymmetric stretch and to serve primarily to broaden peak B.

In the  $\text{D}^-(\text{ND}_3)_1$  spectrum, peak B undergoes an isotope shift which moves it closer to peak A. There, the separation between the centres of peak A and peak B is  $2470 \pm 40 \text{ cm}^{-1}$ , where again the uncertainty is a conservative estimate of the statistical errors involved in locating peak centres. In  $\text{ND}_3$  the band centre for the asymmetric stretch occurs at  $2564 \text{ cm}^{-1}$ , while that for the symmetric stretch occurs at  $2420 \text{ cm}^{-1}$ . The observed A-B spacing in  $\text{D}^-(\text{ND}_3)_1$  is not only indicative of a deuterated ammonia stretch; its isotope shift also provides confirmation that the A-B spacing in the  $\text{H}^-(\text{NH}_3)_1$  spectrum is indeed due to an ammonia stretch. With regard to symmetric *vs.* asymmetric stretches, the observed A-B spacing in the deuterated spectrum lies between the symmetric and the asymmetric stretches of  $\text{ND}_3$ , and this observation alone is indeterminate. Note, however, that peak B in the  $\text{D}^-(\text{ND}_3)_1$  spectrum suffers from substantially greater peak-pulling effects (due to peak A) than does peak B in the  $\text{H}^-(\text{NH}_3)_1$  spectrum. This makes the A-B spacing in the deuterated spectrum appear to be smaller than it actually is. For this reason, the A-B spacing observed in the deuterated spectrum is consistent with our interpretation of peak B in the undeuterated spectrum, *i.e.* peak B arises primarily from the excitation of an asymmetric stretch in the ammonia solvent.

The A-B spacings in these spectra also provide further support for characterizing the species we have photodetached as  $\text{H}^-(\text{NH}_3)_1$  and  $\text{D}^-(\text{ND}_3)_1$  rather than as  $\text{NH}_2^-(\text{H}_2)_1$  and  $\text{ND}_2^-(\text{D}_2)_1$ . If peak A were the origin-containing peak for the photodetachment of an amide-ion-hydrogen-molecule complex, and if peak B were due to the excitation of a hydrogen stretch, then the A-B spacings in such spectra would be equal to the stretching frequencies of hydrogen and deuterium, which are 0.546 and 0.386 eV, respectively. The observed A-B spacings in the undeuterated and the deuterated spectra are 0.432 and 0.306 eV, respectively. In the same units, the asymmetric and symmetric stretching frequencies of  $\text{NH}_3$  are 0.427 and 0.414 eV, while the asymmetric and symmetric stretching frequencies of  $\text{ND}_3$  are 0.318 and 0.300 eV, respectively.<sup>75-79</sup> These data strongly suggest that the solvent in these ion-solvent complexes is ammonia and not hydrogen.

As mentioned earlier, theoretical calculations find a lowest-energy configuration of  $\text{H}^-(\text{NH}_3)_1$  in which the hydride ion is bound to only one of the ammonia molecule's

<sup>†</sup>Earlier we reported the A-B spacing as indicative of a symmetric stretch in ammonia. This interpretation was incorrect. Upon further analysis of these bands, it is evident that the A-B spacing in the spectrum of  $\text{H}^-(\text{NH}_3)_1$  is closer to the frequency of an asymmetric stretch.

hydrogens and not to all three. This should induce an asymmetric structural distortion of the ammonia solvent, as opposed to the symmetric distortion that would be expected if the hydride ion were to interact along the  $C_{3v}$  axis equally with all three hydrogens. Thus, if the theoretically predicted structure of this complex is correct, there should be a tendency to excite the asymmetric stretching mode of the ammonia solvent at the moment of photodetachment. Our data indicating that peak B arises primarily from the excitation of an asymmetric stretch in the ammonia solvent is supportive of the predicted structure. While the earlier work of Nibbering and co-workers<sup>59</sup> concluded that  $\text{NH}_4^-$  is comprised of a hydride ion and an ammonia solvent, it did not specify the structural relationship of these two components. The present work goes a step further and provides the first experimental evidence in support of an asymmetrical hydrogen-bonded complex.

Peak B is a direct manifestation of the complexation-induced distortion of the solvent by its anion in  $\text{H}^-(\text{NH}_3)_1$ . Presumably, the intensity of peak B is a measure of the extent to which the solvent is distorted. The small Franck-Condon factor observed for peak B therefore suggests only a slight distortion, and this is in agreement with the results of several calculations. We have observed analogous distortion-induced spectral peaks in the photoelectron spectra of  $\text{NH}_2^-(\text{NH}_3)_1$ ,  $(\text{H}_2\text{O})_2^-$ ,  $(\text{H}_2\text{O})_6^-$  and  $(\text{H}_2\text{O})_7^-$ , and Lineberger and coworkers<sup>42</sup> have seen such a feature in the photoelectron spectrum of  $\text{H}^-(\text{H}_2\text{O})_1$ . In the case of  $\text{NH}_2^-(\text{NH}_3)_1$ , where we found the ion-solvent interaction energy to be greater than in  $\text{H}^-(\text{NH}_3)_1$ , the spectral feature analogous to peak B was substantially more intense. These findings are consistent with calculations by Squires<sup>62</sup> which predict a negligible solvent distortion in  $\text{H}^-(\text{NH}_3)_1$ , yet a significant elongation of an ammonia N-H bond in  $\text{NH}_2^-(\text{NH}_3)_1$ .

Feature B' is an unresolved shoulder on the side of peak A' in the photoelectron spectrum of  $\text{H}^-(\text{NH}_3)_2$ . While its intensity is greater than that of peak B, its extent to the low electron kinetic energy side of peak A' is essentially the same as the A-B energy spacing in the spectrum of  $\text{H}^-(\text{NH}_3)_1$ . We interpret feature B' as arising from a complexation-induced solvent distortion mechanism analogous to that which gave us peak B. The lack of structure in feature B', along with its higher intensity, are probably related to the excitation of two sets of ammonia modes.

### Peak C

Peak C occurs only in the photoelectron spectra of  $\text{NH}_4^-$  and  $\text{ND}_4^-$ . We find no evidence for an analogous feature in the  $\text{H}^-(\text{NH}_3)_2$  spectrum. In the  $\text{H}^-(\text{NH}_3)_1$  spectrum peak C is centered at a c.m. electron kinetic energy of 2.068 eV with a f.w.h.m. of 32 meV, while in the  $\text{D}^-(\text{ND}_3)_1$  spectrum it is located at a c.m. electron kinetic energy of 2.066 eV with a f.w.h.m. of 27 meV (see fig. 3 and table 1). The locations of these peak centres are essentially unshifted upon isotopic substitution, and their peak widths are comparably narrow. As will be discussed below, our interpretation of peak C is that it arises due to the photodetachment of a tetrahedral isomer of  $\text{NH}_4^-$ .

Before presenting the evidence in support of our interpretation, we first discuss several other possible explanations of peak C which can be eliminated from further consideration. First, since the negative ions in this experiment are mass-selected before photodetachment, the presence of peak C in the photoelectron spectra of both  $\text{H}^-(\text{NH}_3)_1$  and  $\text{D}^-(\text{ND}_3)_1$  is good evidence that it does not arise due to the photodetachment of an impurity ion. Mass leakage due to  $\text{OH}^-$ ,  $\text{NH}_2^-$  or  $\text{NH}^-$  can be eliminated as the source of peak C because, with 2.540 eV photons, none of these ions produces photoelectrons at the laboratory electron kinetic energy at which peak C occurs. Also, peak C is not due to the possible presence of small amounts of  $\text{NH}_2^-(\text{H}_2)_1$ . Peak C occurs at too high an electron kinetic energy (and is too narrow) to be  $\text{NH}_2^-$ , and the solvation of  $\text{NH}_2^-$  by  $\text{H}_2$  to form  $\text{NH}_2^-(\text{H}_2)_1$  would be expected to shift the amide sub-ion's peak

toward even lower electron kinetic energies and to broaden it even more. Furthermore, the prospect can also be eliminated that peak C is due to the photodetachment of some hypothetical isomer of the hydride-ion-ammonia complex having a very low ion-solvent dissociation energy. Even if the ion-solvent stabilization energy of such a species were negligibly small, its major peak (analogous to peak A) would still be located at a considerably lower electron kinetic energy than that of peak C.

Narrow peaks that do not show isotope shifts are usually indicative of photodetachment either from atomic negative ions or from internally cool molecular anions whose corresponding neutrals have nearly identical equilibrium structures. While we will argue in the coming paragraphs that peak C is due to the latter, we should nevertheless consider the possibility that peak C might somehow be due to the former. The photodissociation of  $\text{H}^-(\text{NH}_3)_1$  into  $\text{H}^-$  and  $\text{NH}_3$  followed by the photodetachment of electrons from the nascent  $\text{H}^-$  is a two-step process which is energetically accessible with visible photons. It is clear, however, that this is not the source of peak C. A hydride ion formed from the photodissociation of  $\text{H}^-(\text{NH}_3)_1$  would have the vertical detachment energy of  $\text{H}^-$  (the electron affinity of the hydrogen atom) and the kinematic correction of  $\text{H}^-(\text{NH}_3)_1$ , since it would have essentially the same velocity. Its peak would occur in the photoelectron spectrum at a (laboratory or c.m.) electron kinetic energy that is 0.282 eV lower than the (laboratory or c.m.) electron kinetic energy of peak C. The fact that  $\text{H}^-$  and  $\text{D}^-$  would have rather different kinematic corrections and the observation that peak C does not undergo an isotope shift together provide further insurance against this scenario. In addition, we find that the intensity of peak C varies linearly with laser power, and while not proof in itself, this is consistent with a single-photon process.

Having reviewed possible explanations for peak C that can be discarded, we turn now to the evidence for our interpretation of peak C. The ion-formation environment of an ion source varies from day to day due to slight variations in source conditions. Table 2 shows examples of the day to day variation in the  $\text{H}^-(\text{NH}_3)_1$  peak intensity ratios, A/B and A/C. While the relative intensities of peaks A and B are essentially constant from day to day, the relative intensity of peak C changes substantially. Such variation in the relative intensity of a spectral feature is usually indicative of a photodetachment transition which originates from a higher-energy form of the anion, and this is often seen for vibrationally excited states of negative ions. Hot-band peaks, however, tend to be members of a progression of such peaks, and peak C stands alone. More importantly, hot-band peaks would shift upon deuteration, and peak C does not. Thus peak C appears to be due to a photodetachment transition which originates from a higher-energy form of the anion, but not a vibrationally excited form. Peak C behaves as if it arises from an electronically higher-energy form of  $\text{NH}_4^-$ . Since a low-lying, electronically excited state of  $\text{H}^-(\text{NH}_3)_1$  seems unlikely, the evidence leads us to the conclusion that peak C is due to the photodetachment of a higher-energy isomer of  $\text{NH}_4^-$ . Peak C is remarkably narrow, even though the cluster-anion peaks, A and B, in the same spectrum are considerably broader than typical peaks in unclustered molecular-anion photodetachment spectra. In fact, the width of peak C is probably limited by the resolution of the electron energy analyser. Such a narrow width implies that the structure of the anion and the equilibrium structure of its corresponding neutral are very similar. Thus the structure of the  $\text{NH}_4^-$  isomer in question and the equilibrium structure of  $\text{NH}_4$  neutral are inferred to be very similar. The ground electronic state of  $\text{NH}_4$  is a Rydberg radical of tetrahedral configuration which is thought to possess a barrier to dissociation.<sup>80-87</sup> Thus, we are led by this trail of evidence to conclude that peak C arises owing to the photodetachment of a previously unknown tetrahedral isomer of  $\text{NH}_4^-$ . We find the vertical detachment energy of  $\text{NH}_4^-(T_d)$  to be 0.472 eV. Because of the high degree of structural similarity between this anion and its corresponding neutral, the adiabatic electron affinity of  $\text{NH}_4(T_d)$  has the same value, *i.e.* 0.472 eV.

Certainly,  $\text{NH}_4^-(T_d)$  should not be envisaged as a hydride ion trying to interact with the lone-pair electrons of ammonia. Our picture of  $\text{NH}_4^-(T_d)$  is that it is best described as a  $\text{NH}_4^+$  cation core surrounded by two diffuse, Rydberg-like electrons. It is the tetrahedral structure of the ammonium cation that gives  $\text{NH}_4^-(T_d)$  its tetrahedral geometry. Thus there exist tetrahedral ammonium cations, tetrahedral ammonium neutrals and tetrahedral ammonium anions, and essentially these are each ammonium cations with 0, 1 and 2 associated Rydberg-like electrons, respectively. The tetrahedral ammonium anion is probably formed in the nozzle-ion source by electron attachment to  $\text{NH}_4$  neutral, which was presumably formed by electron neutralization of  $\text{NH}_4^+$ , a particularly abundant ion in ammonia plasmas.

The existence of  $\text{NH}_4^-(T_d)$  is supported by theoretical calculations, by analogy with the ammonium radical's unified atom, and by related observations in electron transmission spectroscopy. Although unusual, double Rydberg anions are not without precedent. Electron transmission spectroscopy has characterized a variety of temporary negative-ion states as consisting of two Rydberg electrons loosely attached to a positive-ion core.<sup>88</sup> Compound anion states of this kind have also been observed in ammonia.<sup>89</sup> Unlike these temporary negative ions, however, the tetrahedral ammonium anion appears to be relatively stable with respect to autodetachment. The unified atom for the ammonium radical is sodium. The ionization potential of the sodium atom is 5.139 eV, while for the ammonium radical it is comparable at 4.73 eV. The electron affinity of the sodium atom is 0.548 eV. The electron affinity of the species responsible for peak C is 0.472 eV. Just as  $\text{Na}^-$  possesses an  $s^2$  electron configuration,  $\text{NH}_4^-(T_d)$  should have the totally symmetric molecular equivalent.

*Ab initio* calculations by Schleyer *et al.*,<sup>63</sup> by Cremer and Kraka,<sup>64</sup> by Cardy *et al.*,<sup>65</sup> by Ortiz<sup>65</sup> and by Simons and co-workers<sup>68</sup> all find bound tetrahedral configurations of  $\text{NH}_4^-$ . Schleyer *et al.* were the first to find a tetrahedral structure for  $\text{NH}_4^-$ . They predicted tetrahedral  $\text{NH}_4^-$  to be less stable than the  $\text{H}^-(\text{NH}_3)_1$  ion-molecule complex by 0.47 eV. Cremer and Kraka predicted tetrahedral  $\text{NH}_4^-$  to be less stable than the  $\text{H}^- + \text{NH}_3$  asymptote by 0.056 eV. Together with their value for the ion-molecule dissociation energy of  $\text{H}^-(\text{NH}_3)_1$ , this implies that tetrahedral  $\text{NH}_4^-$  lies 0.71 eV in energy above the  $\text{H}^-(\text{NH}_3)_1$  ion-molecule complex. Cardy *et al.* find the energy of tetrahedral  $\text{NH}_4^-$  above the  $\text{H}^- + \text{NH}_3$  asymptote to be 0.26 eV; and when this number is added to their value for the ion-molecule dissociation energy of  $\text{H}^-(\text{NH}_3)_1$ , it implies that tetrahedral  $\text{NH}_4^-$  lies 0.53 eV above the ion-molecule complex. Cardy also calculates the electron affinity of  $\text{NH}_4^-(T_d)$  to be 0.31 eV and the barrier for the dissociation of  $\text{NH}_4^-(T_d)$  into  $\text{H}^- + \text{NH}_3$  to be 0.81 eV. This barrier height is higher than that predicted for neutral  $\text{NH}_4$ , and Cardy speculates that tetrahedral  $\text{NH}_4^-$  may have a sufficiently long lifetime to be observed experimentally. Ortiz emphasizes the Rydberg-like character of the two electrons surrounding the  $\text{NH}_4^+$  core in tetrahedral  $\text{NH}_4^-$ . He calculates that tetrahedral  $\text{NH}_4^-$  lies 0.42 eV above the  $\text{H}^-(\text{NH}_3)_1$  ion-molecule complex, and that the vertical detachment energy of tetrahedral  $\text{NH}_4^-$  is also 0.42 eV. Simons and co-workers have recently performed extensive calculations on 'double-Rydberg' molecular anions, *i.e.* anionic systems comprised of a closed-shell cation with two Rydberg-like outer electrons. Their results imply a vertical detachment energy for tetrahedral  $\text{NH}_4^-$  of 0.45 eV. Several of these studies also find or imply that the vibrational frequencies of the tetrahedral ammonium anion are similar to those of the ammonium cation. Clearly there is a substantial body of theoretical support for the existence of tetrahedral  $\text{NH}_4^-$ .

Before concluding, let us consider some of the energetic implications of our work. Determining the relative energies of tetrahedral  $\text{NH}_4^-$  and the  $\text{H}^-(\text{NH}_3)_1$  ion-molecule complex is hindered by the uncertainty in the relative energies of the neutral  $\text{NH}_4$  ground state and the  $\text{H} + \text{NH}_3$  dissociation asymptote. The relative energies of the tetrahedral  $\text{NH}_4^-$  ground state,  $E(\text{NH}_4^-, T_d)$ , and the  $\text{H}^- + \text{NH}_3$  dissociation asymptote,

$E(\text{H}^- + \text{NH}_3)$ , is given by

$$E(\text{NH}_4^-, T_d) - E(\text{H}^- + \text{NH}_3) = E_A(\text{H}) - E_A(\text{NH}_4, T_d) + \Delta E \quad (5)$$

where  $E_A(\text{H})$  and  $E_A(\text{NH}_4, T_d)$  denote the electron affinities of H and tetrahedral  $\text{NH}_4$ , respectively, and  $\Delta E$  is the energy difference between the neutral  $\text{NH}_4$  ground state and the  $\text{H} + \text{NH}_3$  dissociation limit:

$$\Delta E = E(\text{NH}_4, T_d) - E(\text{H} + \text{NH}_3). \quad (6)$$

Using the literature value for  $E_A(\text{H})$  and our value for  $E_A(\text{NH}_4, T_d)$ , we obtain the relationship

$$E(\text{NH}_4^-, T_d) - E(\text{H}^- + \text{NH}_3) = 0.28 + \Delta E. \quad (7)$$

Thus if  $\Delta E > -0.28$  eV, then the ground state of tetrahedral  $\text{NH}_4^-$  lies above the  $\text{H}^- + \text{NH}_3$  dissociation asymptote. The transit time from the ion source to the ion-photon interaction for  $\text{NH}_4^-$  in our spectrometer is *ca.* 27  $\mu\text{s}$ . If tetrahedral  $\text{NH}_4^-$  does lie above the dissociation asymptote, it must have a barrier to dissociation as calculated by Cardy *et al.* If this is the case, then part of the reason for the narrowness of peak C could be explained in terms of a self-refrigerating effect, *i.e.* rotationally and vibrationally excited  $\text{NH}_4^-(T_d)$  ions would tend to tunnel towards dissociation more rapidly than cooler ground-state ions. Using our value of *ca.* 0.36 eV for the ion-molecule dissociation energy of  $\text{H}^-(\text{NH}_3)_1$ , one can see that the energy difference between tetrahedral  $\text{NH}_4^-$  and the  $\text{H}^-(\text{NH}_3)_1$  ion-molecule complex is equal to 0.64 eV +  $\Delta E$ . The theoretical calculations mentioned above are reasonably consistent with this energetic relationship.

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