

# Double Rydberg anions: Photoelectron spectroscopy of $\text{NH}_4^-$ , $\text{N}_2\text{H}_7^-$ , $\text{N}_3\text{H}_{10}^-$ , $\text{N}_4\text{H}_{13}^-$ , and $\text{N}_5\text{H}_{16}^-$

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We report the discovery and photoelectron spectroscopic study of the four double Rydberg anions:  $\text{N}_2\text{H}_7^-$ ,  $\text{N}_3\text{H}_{10}^-$ ,  $\text{N}_4\text{H}_{13}^-$ , and  $\text{N}_5\text{H}_{16}^-$ ; of three solvated double Rydberg anions; and of a previously unseen feature in the spectrum of the double Rydberg anion,  $\text{NH}_4^-$ . In each case, vertical detachment energies were measured and vibrational features tentatively assigned. In the case of solvated double Rydberg anions, anion–neutral interaction energies were also determined. © 2002 American Institute of Physics. [DOI: 10.1063/1.1499491]

## I. INTRODUCTION

The term “double Rydberg anion” refers to a negative ion which is composed of a closed-shell cation and two Rydberg-type outer electrons. The first double Rydberg molecular anion to be discovered was  $\text{NH}_4^-$ . We observed it during photoelectron studies of the anion–molecule complex,  $\text{H}^-(\text{NH}_3)_1$ , a system in which the hydride anion is solvent stabilized by an ammonia molecule.<sup>1</sup> Because  $\text{H}^-(\text{NH}_3)_1$  and  $\text{NH}_4^-$  have identical masses, the photoelectron spectra of both appeared in the same spectrum, and fortuitously, the features of the  $\text{H}^-(\text{NH}_3)_1$  spectrum were well separated from the spectrum of  $\text{NH}_4^-$ .

As originally recorded, the spectrum of  $\text{NH}_4^-$  consisted of a single, weak intensity peak. The experimental evidence for it being a double Rydberg anion was based on the following observations. The intensity of this peak fluctuated from day to day relative to the intensities of the  $\text{H}^-(\text{NH}_3)_1$  portion of the spectrum, indicating that it was not part of the  $\text{H}^-(\text{NH}_3)_1$  spectrum. It showed no significant deuterium isotope shift, implying that it was not a vibrational excitation. The lone peak was extraordinarily narrow with a nearly instrumentally limited width, implying a high degree of Franck–Condon overlap with its corresponding neutral. From these observations, we inferred that  $\text{NH}_4^-$  is a separate electronic entity with a structure which must be very similar to that of  $\text{NH}_4$ . The neutral  $\text{NH}_4$  molecule, however, was already known from the work of Herzberg and others<sup>2–5</sup> to be the molecular Rydberg radical,  $(\text{NH}_4^+)^-$ . Moreover, because its core was the tetrahedral  $\text{NH}_4^+$  cation, the geometry of  $\text{NH}_4$  was also tetrahedral. From this reasoning came our conclusion that the  $\text{NH}_4^-$  species we were observing must be the anion of the  $\text{NH}_4$  Rydberg molecule, thus the term, double Rydberg anion. This implied the appropriate representation of  $\text{NH}_4^-$  to be  $(\text{NH}_4^+)^-$ , i.e., a cationic core of  $\text{NH}_4^+$  with two electrons occupying diffuse Rydberg-type orbitals.

Since the  $\text{NH}_4^-$  double Rydberg anion was also built on a tetrahedral cation, its structure was presumed to be essentially tetrahedral as well. The vertical detachment energy (VDE) of  $\text{NH}_4^-$  that we measured was 0.472 eV. Given the close similarity between the structures of this ion and its corresponding neutral, this is also its adiabatic electron affinity (E.A.<sub>a</sub>). Herzberg had earlier noted that the united atom of  $\text{NH}_4$  is sodium, and that the ionization potentials of Na and  $\text{NH}_4$  are quite similar at 5.139 and 4.73 eV, respectively. Interestingly, the electron affinities of Na and  $\text{NH}_4$  are also quite similar at 0.548 and 0.472 eV, respectively.

Theory has provided strong support for the existence of  $\text{NH}_4^-$  as a double Rydberg anion. Prior to our experimental work, Cremer and Kraka<sup>6</sup> as well as Cardy and co-workers<sup>7</sup> both found tetrahedral configurations of  $\text{NH}_4^-$ . Immediately after our initial experiments on  $\text{NH}_4^-$ , Ortiz<sup>8,9</sup> confirmed it to be a viable double Rydberg anion, characterizing the Rydberg-type nature of the two diffuse electrons around its  $\text{NH}_4^+$  core and predicting its VDE to be 0.42 eV. Gutowski and Simons<sup>10–12</sup> next performed calculations on the  $\text{NH}_4^-$  double Rydberg anion, predicting its VDE to be 0.45 eV. In addition, theoretical studies on  $\text{NH}_4^-$  were also conducted by Boyd<sup>13</sup> and by Gordon *et al.*<sup>14</sup>

Here, we report the photoelectron spectroscopic study of the four new double Rydberg anions:  $\text{N}_2\text{H}_7^-$ ,  $\text{N}_3\text{H}_{10}^-$ ,  $\text{N}_4\text{H}_{13}^-$ , and  $\text{N}_5\text{H}_{16}^-$ ; of at least three solvated double Rydberg anions; and of a previously unseen feature in the spectrum of  $\text{NH}_4^-$ . In each case, vertical detachment energies were measured and vibrational features tentatively assigned. In the case of solvated double Rydberg anions, anion–neutral interaction energies were also determined.

## II. EXPERIMENT

Negative ion photoelectron spectroscopy is conducted by crossing a mass-selected anion beam with a fixed frequency photon beam and energy analyzing the resultant photodetached electrons. This is a direct approach to determining electron binding energies (EBE), and it is governed by the energy-conserving relationship

$$h\nu = \text{EKE} + \text{EBE}, \quad (1)$$

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where  $h\nu$  is the photon energy, and EKE is the measured electron kinetic energy. Our apparatus has been described previously.<sup>15</sup> The species studied in these experiments were generated in a nozzle-ion source in which 1–2 atm. of cool, neat ammonia was expanded through a 20  $\mu\text{m}$  diameter nozzle, with a biased thoriated iridium filament used as the electron source. Most probably, the microplasma outside the nozzle consisted of  $\text{NH}_4^+$  ( $\text{NH}_3$ )<sub>*n*</sub> cations,  $\text{NH}_4(\text{NH}_3)_n$  neutral Rydberg radicals, low-energy electrons, and anions. This soup was the incubator for forming double Rydberg anions, probably by electron attachment to neutral Rydberg radicals. These were then extracted into the spectrometer along with other anions. These negative ions were then mass selected by a magnetic sector with a mass resolution of  $\sim 500$  and photodetached with  $\sim 100$  circulating watts of 488 nm (2.540 eV) photons, one anion composition at a time. Finally, the resultant photoelectrons were energy analyzed by a hemispherical electron energy analyzer with a resolution of  $\sim 25$ – $30$  meV.

### III. RESULTS

The photoelectron spectra of the species studied here are presented in Fig. 1. Each spectrum contains contributions both from an anion–molecule complex,  $\text{H}^-(\text{NH}_3)_n$ , and from a double Rydberg anion system,  $(\text{N}_n\text{H}_{3n+1})^-$  of the same composition. In each case, the spectral contributions from the hydride–ammonia complex species are more intense, broader, and occur at higher electron binding energies than those from their double Rydberg anion counterparts. To distinguish the spectral contributions of these two types of species in Fig. 1, we have magnified the intensity of the double Rydberg anions and plotted them as solid, dark insets, while the spectra of the anion–molecule complexes have been presented as dotted, subdued traces. For both the anion–molecule complexes and double Rydberg anions, the electron binding energies (EBE) of each discernible spectral feature in Fig. 1, along with their assignments, spacings, and solvation shifts, are listed in Table I.

### IV. DISCUSSION

#### A. Hydride–ammonia complexes

While hydride anion–ammonia complexes are not the focus of this work, they nevertheless provide useful information on anion solvation. In the past, we studied<sup>1</sup> the species,  $\text{H}^-(\text{NH}_3)_1$  and  $\text{H}^-(\text{NH}_3)_2$ . Here, as a by-product of our search for new double Rydberg anions, we have recorded these again as well as the spectra of  $\text{H}^-(\text{NH}_3)_{n=3-5}$ . In all of these  $\text{H}^-(\text{NH}_3)_n$  systems, however, the story is qualitatively similar. Their spectra resemble the photoelectron spectrum of the hydride anion except for being broadened and shifted to progressively higher electron binding energies, owing to the stabilizing effect of solvation by ammonia molecules. This results in the broad peaks (FWHM = 130–240 meV) which dominate these spectra. The EBEs of the main peaks maxima are interpreted as their VDEs in each case. These are listed in Table I. From these,

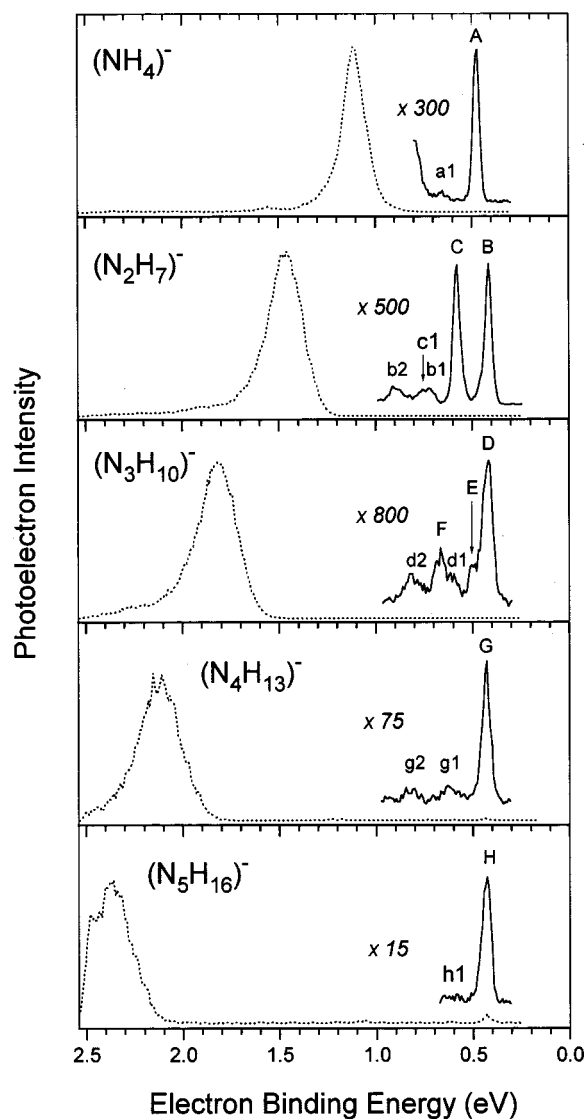


FIG. 1. The photoelectron spectra of  $(\text{N}_n\text{H}_{3n+1})^-$ ,  $n=1-5$  measured with 2.540 eV photons.

estimates of sequential solvation energies can be extracted via standard energetic cycles,<sup>15</sup> and these are also tabulated there.

In the cases of the first three complexes ( $n=1-3$ ), a second, much weaker intensity feature can also be seen to the high EBE sides of their main peaks. This feature is due to the excitation of an ammonia stretching motion during photodetachment. The energy spacings between the maxima of the main peak (their VDEs) and the maxima of these weaker peaks are essentially the same in each case, at 0.436 eV or 3514  $\text{cm}^{-1}$ . Ammonia's symmetric and asymmetric stretching frequencies are 3336 and 3444  $\text{cm}^{-1}$ , respectively.<sup>16</sup>

#### B. Double Rydberg anion systems

##### 1. $\text{NH}_4^-$

When we first recorded the photoelectron spectrum of the  $\text{NH}_4^-$  double Rydberg anion some years ago, it was extremely weak in intensity compared to the main peak in  $\text{H}^-(\text{NH}_3)_1$ . Since then, our skill with the source has im-

TABLE I. Electron binding energies (EBE) of peak positions, assignments, spacings, and solvation shifts. Energies are in eV (VDE=vertical detachment energy).

Anion composition	Solvated hydride anions				Double Rydberg anions			
	EBE <sup>a</sup>	Assignment	Spacing	Shift	EBE <sup>b</sup>	Assignment <sup>c</sup>	Spacing	Shift
NH <sub>4</sub> <sup>-</sup>	1.110	VDE of H <sup>-</sup> (NH <sub>3</sub> )	...	...	0.472 ( <b>A</b> )	VDE of (NH <sub>4</sub> <sup>+</sup> ) <sup>=</sup>	...	...
	1.546	NH <sub>3</sub> stretch	0.436		0.651 ( <b>a1</b> )	$\nu_4$ of NH <sub>4</sub>	0.179 ( <b>a1-A</b> )	
N <sub>2</sub> H <sub>7</sub> <sup>-</sup>	1.460	VDE of H <sup>-</sup> (NH <sub>3</sub> ) <sub>2</sub>	...	0.350	0.415 ( <b>B</b> )	VDE of (N <sub>2</sub> H <sub>7</sub> <sup>+</sup> ) <sup>=</sup>	...	...
	1.896	NH <sub>3</sub> stretch	0.436		0.578 ( <b>C</b> )	VDE of (NH <sub>4</sub> <sup>+</sup> ) <sup>=</sup> (NH <sub>3</sub> )	...	0.106 ( <b>C-A</b> )
					0.723 ( <b>b1</b> )	Proton motion	0.308 ( <b>b1-B</b> )	
					0.757 ( <b>c1</b> )	$\nu_4$ of NH <sub>4</sub>	0.179 ( <b>c1-C</b> )	
N <sub>3</sub> H <sub>10</sub> <sup>-</sup>					0.894 ( <b>b2</b> )	N <sub>2</sub> H <sub>7</sub> stretch	0.479 ( <b>b2-B</b> )	
	1.820	VDE of H <sup>-</sup> (NH <sub>3</sub> ) <sub>3</sub>	...	0.360	0.424 ( <b>D</b> )	VDE of (N <sub>3</sub> H <sub>10</sub> <sup>+</sup> ) <sup>=</sup>	...	...
	2.256	NH <sub>3</sub> stretch	0.436		0.495 ( <b>E</b> )	VDE of (N <sub>2</sub> H <sub>7</sub> <sup>+</sup> ) <sup>=</sup> (NH <sub>3</sub> )	...	0.080 ( <b>E-B</b> )
					0.660 ( <b>F</b> )	VDE of (NH <sub>4</sub> <sup>+</sup> ) <sup>=</sup> (NH <sub>3</sub> ) <sub>2</sub>	...	0.082 ( <b>F-C</b> )
					0.605 ( <b>d1</b> )	N <sub>3</sub> H <sub>10</sub> umbrella	0.181 ( <b>d1-D</b> )	
N <sub>4</sub> H <sub>13</sub> <sup>-</sup>					0.824 ( <b>d2</b> )	N <sub>3</sub> H <sub>10</sub> stretch	0.400 ( <b>d2-D</b> )	
	2.111	VDE of H <sup>-</sup> (NH <sub>3</sub> ) <sub>4</sub>	...	0.289	0.427 ( <b>G</b> )	VDE of (N <sub>4</sub> H <sub>13</sub> <sup>+</sup> ) <sup>=</sup>	...	...
					0.632 ( <b>g1</b> )	N <sub>4</sub> H <sub>13</sub> umbrella	0.205 ( <b>g1-G</b> )	
N <sub>5</sub> H <sub>16</sub> <sup>-</sup>					0.803 ( <b>g2</b> )	N <sub>4</sub> H <sub>13</sub> stretch	0.376 ( <b>g2-G</b> )	
	2.360	VDE of H <sup>-</sup> (NH <sub>3</sub> ) <sub>5</sub>	...	0.249	0.434 ( <b>H</b> )	VDE of (N <sub>5</sub> H <sub>16</sub> <sup>+</sup> ) <sup>=</sup>	...	...
					0.610 ( <b>h1</b> )	N <sub>5</sub> H <sub>16</sub> umbrella	0.176 ( <b>h1-H</b> )	

<sup>a</sup>Errors for the main peaks in the solvated hydride anion spectra are  $\pm 0.010$  eV, while those for the NH<sub>3</sub> stretch peaks are  $\pm 0.060$  eV.

<sup>b</sup>Errors for peaks labeled with capital letters are  $\pm 0.005$  eV (except for peak *E* which is 0.015 eV), while those for vibrations labeled with lower case letters are  $\pm 0.060$  eV.

<sup>c</sup>VDEs listed here for double Rydberg anions are also equivalent to adiabatic electron affinities, EA<sub>a</sub>.

proved, and we have learned how to make higher intensities. As a result, the new spectrum of NH<sub>4</sub><sup>-</sup> shown in the top panel of Fig. 1 is substantially more intense than earlier spectra. In terms of peak location and peak width, the main peak (**A**) in this new spectrum of NH<sub>4</sub><sup>-</sup> is essentially unchanged from that previously reported,<sup>1</sup> i.e., VDE=0.472 and  $\sim 40$  meV, respectively. The enhancement in intensity provided benefits which were more than cosmetic, however, because it allowed us to observe a previously unseen, weak feature in the spectrum of NH<sub>4</sub><sup>-</sup>. This is peak **a1**, seen in the top panel of Fig. 1. The center of peak **a1** is spaced 0.179 eV ( $1442\text{ cm}^{-1}$ ) to the high EBE side of the center of peak **A**, and we assign it as being due to a vibrational excitation in NH<sub>4</sub><sup>-</sup>'s corresponding neutral, i.e., NH<sub>4</sub>. Recent calculations by Ortiz<sup>17</sup> found  $\nu_4$ , the triply degenerate umbrella mode in neutral NH<sub>4</sub>, to be  $1355\text{ cm}^{-1}$ . This is likely to be the vibration we have observed, given the uncertainty in precisely locating the center of such a weak, broad peak and the fact that peak **a1** is subject to strong, peak-pulling effects from the fast-rising intensity tail of the H<sup>-</sup>(NH<sub>3</sub>)<sub>1</sub> spectrum immediately to its high EBE side. Still higher frequency NH<sub>4</sub> vibrational transitions may also be buried under the tail of the H<sup>-</sup>(NH<sub>3</sub>)<sub>1</sub> spectrum.

Recall that NH<sub>4</sub><sup>+</sup>, NH<sub>4</sub>, and NH<sub>4</sub><sup>-</sup> all have tetrahedral symmetries, because they are all built on NH<sub>4</sub><sup>+</sup> cation templates. However, since each of these is made up of an NH<sub>4</sub><sup>+</sup> core with 0, 1, or 2 excess electrons, respectively, their N-H bonds should not be expected to be exactly the same. Indeed, the observation of a  $\nu_4$ (NH<sub>4</sub>) vibrational excitation in the photoelectron spectrum of NH<sub>4</sub><sup>-</sup> reflects the fact that the equilibrium structures of NH<sub>4</sub><sup>-</sup> and NH<sub>4</sub> are not precisely the same. In perspective, however, these results are also consistent with their structures being very similar, albeit slightly

different, further supporting the characterization of NH<sub>4</sub><sup>-</sup> as a double Rydberg anion.

## 2. N<sub>2</sub>H<sub>7</sub><sup>-</sup>

The double Rydberg anion portion of the N<sub>2</sub>H<sub>7</sub><sup>-</sup> spectrum (low EBE, dark spectral traces in the second panel of Fig. 1) exhibits two strong, narrow peaks (**B** and **C**) and several weaker features (**b1**, **c1**, and **b2**) to their high EBE sides. The ratio of the intensities of peaks **B** and **C** varied from day to day, implying that they arose from separate entities. We interpret peak **B** to be a new double Rydberg anion, i.e. (N<sub>2</sub>H<sub>7</sub><sup>+</sup>)<sup>=</sup>, and peak **C** to be the NH<sub>4</sub><sup>-</sup> double Rydberg anion solvated by an ammonia molecule, i.e., NH<sub>4</sub><sup>-</sup>(NH<sub>3</sub>)<sub>1</sub>.

Peak **B** in this spectrum occurs at EBE=0.415 eV (its VDE). This is 0.057 eV lower in energy than the position of peak **A** in the spectrum of NH<sub>4</sub><sup>-</sup>. We attribute this downshift in EBE to a decreased positive charge density on N<sub>2</sub>H<sub>7</sub><sup>+</sup> as compared to that on NH<sub>4</sub><sup>+</sup>. The Rydberg-type electrons do not interact as strongly with the more dispersed positive charge on N<sub>2</sub>H<sub>7</sub><sup>+</sup>, and thus they detach at a slightly lower EBE. In recent work, Ortiz<sup>17</sup> calculated the VDE of this new double Rydberg anion to be 0.41 eV, in excellent agreement with our result. He also computed the structures of both this anion and its corresponding neutral, finding significant differences in the proton to nitrogen bond lengths in these hydrogen-bridged structures. This structural difference could easily translate into a vibrational excitation during photodetachment, and Ortiz<sup>17</sup> predicted this motion to have a frequency of  $2938\text{ cm}^{-1}$ . We observe the **b1-B** peak spacing in the spectrum to be 0.308 eV ( $2482\text{ cm}^{-1}$ ). Given that  $2938\text{ cm}^{-1}$  was calculated under the harmonic approximation, and the fact that peak **c1** may partially obscure its location, peak **b1** may well arise largely from this motion.

Peak **b2** is located at  $\text{EBE}=0.894$  eV, and we are also inclined to assign it as a vibration associated with peak **B** (the new double Rydberg anion based on the  $\text{N}_2\text{H}_7^+$  cation) rather than with peak **C** (the solvated double Rydberg anion). The **b2**–**B** peak spacing is  $0.479$  eV ( $3861$   $\text{cm}^{-1}$ ). Our interpretation is based on two observations. (1) It is difficult to see how peak **b2** could arise from the solvated complex,  $\text{NH}_4^-(\text{NH}_3)_1$ . Neither neutral  $\text{NH}_4$  nor  $\text{NH}_3$  provide vibrations consistent with the observed **b2**–**C** peak separation. (2) Similarly spaced high EBE vibrational features appear in the double Rydberg anion spectra of  $\text{N}_3\text{H}_{10}^-$  and  $\text{N}_4\text{H}_{13}^-$ . In both of these, their highest EBE vibrational features are very likely associated with their peak **B** analogs, i.e., peak **D** in the spectrum of  $\text{N}_3\text{H}_{10}^-$  and peak **G** in the spectrum of  $\text{N}_4\text{H}_{13}^-$ . Thus, peak **b2** is probably due to the photodetachment-induced excitation of a stretching motion in the neutral Rydberg molecule,  $\text{N}_2\text{H}_7$ . This is roughly consistent with the frequencies found for  $\text{N}_2\text{H}_7^+$  by Lee and co-workers.<sup>18</sup> These are relevant since the vibrational frequencies of a given neutral Rydberg species can be expected to be similar to those of its corresponding cation.

We interpret peak **C**, located at  $\text{EBE}=0.578$  eV (its VDE), as being due to a  $\text{NH}_4^-$  double Rydberg anion solvated by an ammonia molecule, i.e.,  $\text{NH}_4^-(\text{NH}_3)_1$ . This is the first cluster containing a double Rydberg anion to be seen. Ortiz's calculations<sup>17</sup> found a potential minimum corresponding to an ion–molecule complex composed of tetrahedral  $\text{NH}_4^-$  with  $\text{NH}_3$ . His calculated VDE for this complex was  $0.60$  eV, in quite good agreement with the VDE which we observed. The spectral shift between peak **A** in the spectrum of  $\text{NH}_4^-$  and peak **C** in the present spectrum is  $0.106$  eV. This is a good estimate of the interaction energy between  $\text{NH}_4^-$  and  $\text{NH}_3$  in the  $\text{NH}_4^-(\text{NH}_3)_1$  complex, i.e., the dissociation energy of  $\text{NH}_4^-(\text{NH}_3)_1$  separating into  $\text{NH}_4^-$  and  $\text{NH}_3$ . This, however, is a small interaction energy compared to most anion/ammonia interaction energies. Consider, for example, the  $0.35$  eV shift between the spectra of  $\text{H}^-$  and  $\text{H}^-(\text{NH}_3)$ .<sup>1</sup> This is the interaction energy between  $\text{H}^-$  and  $\text{NH}_3$ . We attribute the comparatively small interaction energy between  $\text{NH}_4^-$  and  $\text{NH}_3$  to the highly diffuse nature of the Rydberg-type electrons on  $\text{NH}_4^-$  with which the ammonia solvent molecule interacts, i.e., the charge density of the excess electronic charge on the double Rydberg  $\text{NH}_4^-$  anion is significantly lower than that found around most normal anions. The sharp spectral features seen in the spectra of all double Rydberg anions are, in fact, also characteristic of other highly diffuse excess electron systems, such as dipole-bound anions.<sup>19</sup>

Last, we turn to the interpretation of peak **c1**. Its assignment as a vibrational excitation associated with peak **C** is straightforward. The spectrum of  $\text{NH}_4^-(\text{NH}_3)_1$  can be thought of as a perturbed  $\text{NH}_4^-$  spectrum with the  $\text{NH}_4^-$  moiety acting as the chromophore for photodetachment. As such, it should exhibit the same spectral features as those seen in the spectrum of bare  $\text{NH}_4^-$ , just shifted to new positions by the stabilizing effects of ammonia solvation. In the spectrum of bare  $\text{NH}_4^-$ , peak **a1** appears  $0.179$  eV ( $1442$   $\text{cm}^{-1}$ ) to the high EBE side of the origin-containing main peak (**A**). That same vibration is discernible in the spectrum of  $\text{NH}_4^-(\text{NH}_3)_1$

as peak **c1**. It is located  $\sim 0.18$  eV to the high EBE side of peak **C**, just where it should be.

### 3. $\text{N}_3\text{H}_{10}^-$

The three peaks, labeled **D**, **E**, and **F**, in the double Rydberg anion portion of the  $\text{N}_3\text{H}_{10}^-$  spectrum are interpreted as arising from three different double Rydberg anion species. They are located at  $0.424$ ,  $0.495$ , and  $0.660$  eV, respectively. These values also correspond to their respective VDEs. Peak **F** is due to  $\text{NH}_4^-$  being solvated by two ammonia molecules, i.e.,  $\text{NH}_4^-(\text{NH}_3)_2$ . Peak **E** is due to the double Rydberg anion,  $(\text{N}_2\text{H}_7)^-$ , being solvated by one ammonia molecule, i.e.,  $\text{N}_2\text{H}_7^-(\text{NH}_3)$ . Peak **D**, the highest intensity feature, is due to a double Rydberg anion which can be characterized as  $(\text{N}_3\text{H}_{10})^=$ . Thus, both peaks **E** and **F** are due to Rydberg anion–neutral complexes, while peak **D** is due to a new double Rydberg anion. The low intensities of peaks **E** and **F** are probably due to the multiple collisions necessary to form anion–neutral complexes compared to the more direct mechanism involved in forming unclustered double Rydberg anions.

The spectral shift between  $\text{NH}_4^-(\text{NH}_3)_1$  and  $\text{NH}_4^-(\text{NH}_3)_2$ , i.e., the spacing between peak **C** in the  $(\text{N}_2\text{H}_7)^-$  spectrum and peak **F** in the  $(\text{N}_3\text{H}_{10})^-$  spectrum, is a good estimate of the sequential solvation energy experienced when an additional ammonia molecule is added to  $\text{NH}_4^-(\text{NH}_3)_1$ . Its value is  $0.082$  eV, slightly less than, but comparable to, the  $0.106$  shift between  $\text{NH}_4^-$  and  $\text{NH}_4^-(\text{NH}_3)_1$ . This is reasonable, since second solvation energies are usually slightly less than first solvation energies. The spectral shift from the new double Rydberg anion,  $(\text{N}_2\text{H}_7)^-$  (peak **B** in the  $\text{N}_2\text{H}_7^-$  spectrum) to  $\text{N}_2\text{H}_7^-(\text{NH}_3)$  (peak **E** in the  $\text{N}_3\text{H}_{10}^-$  spectrum) is  $0.080$  eV. It is reasonable that the interaction energy between the  $\text{N}_2\text{H}_7^-$  double Rydberg anion and  $\text{NH}_3$  should be a little less than that between the  $\text{NH}_4^-$  double Rydberg anion and  $\text{NH}_3$ , given that the negative charge density on  $\text{N}_2\text{H}_7^-$  is probably less than that on  $\text{NH}_4^-$ . Thus, the solvation energies of  $\text{NH}_4^-(\text{NH}_3)_1$ ,  $\text{NH}_4^-(\text{NH}_3)_2$ , and  $\text{N}_2\text{H}_7^-(\text{NH}_3)$  are all consistent and mutually supportive of our interpretation of them as ion–molecule complexes.

As already mentioned, we interpret peak **D** as being due to a new double Rydberg anion which can be characterized as  $(\text{N}_3\text{H}_{10})^=$ . While the cation,  $\text{N}_3\text{H}_{10}^+$ , is no doubt closely related to  $\text{N}_2\text{H}_7^+$ , it is also a closed-shell cation in its own right. An interesting observation about peak **D** is that its VDE is slightly higher than that of peak **B** in the spectrum of  $\text{N}_2\text{H}_7^-$  (see Table I). Indeed, the VDE of peak **G** in the spectra of  $\text{N}_4\text{H}_{13}^-$  as well as that of peak **H** in the spectrum of  $\text{N}_5\text{H}_{16}^-$  also continue to increase slightly compared to the position of peak **B**. Remembering that peak **B** in the spectrum of  $\text{N}_2\text{H}_7^-$  had shifted in the opposite direction relative to peak **A** in the spectrum of  $\text{NH}_4^-$ , this is a curious trend. It looks as if the delocalization of positive charge on  $\text{N}_2\text{H}_7^+$  is partially reversed in  $\text{N}_3\text{H}_{10}^+$ , and that this trend continues, albeit gradually, for  $\text{N}_4\text{H}_{13}^+$  and  $\text{N}_5\text{H}_{16}^+$  despite the increasing physical size of these cations.

There are two more discernible peaks in the  $\text{N}_3\text{H}_{10}^-$



double Rydberg anion spectrum, peaks **d1** and **d2**. These are, in all likelihood, vibrational features, and since neither peak **E** nor peak **F** is intense enough to exhibit observable vibrational intensities of their own, we attribute both peaks **d1** and **d2** to peak **D**. Peak **d1** is separated from peak **D** by 0.181 eV ( $1458\text{ cm}^{-1}$ ). This is very close to the frequency of the  $\nu_4$  umbrella motion in both  $\text{NH}_4^-$  ( $1355\text{ cm}^{-1}$ )<sup>17</sup> and  $\text{NH}_4^+$  ( $1447\text{ cm}^{-1}$ ).<sup>20</sup> A similar motion is probably embedded in the available vibrations of neutral  $\text{N}_3\text{H}_{10}$ , i.e., in  $(\text{N}_3\text{H}_{10}^+)^-$ , and it is apparently excited during photodetachment. Peak **d2** is separated from peak **D** by 0.400 eV ( $3224\text{ cm}^{-1}$ ), and in analogy to peak **b2** in the spectrum of  $(\text{N}_2\text{H}_7)^-$ , it is probably due to the excitation of a stretching motion in the neutral Rydberg molecule,  $\text{N}_3\text{H}_{10}$ . As already mentioned, since the vibrational frequencies of a given neutral Rydberg species and its corresponding cation can be expected to be similar, the vibrations of ammoniated ammonium cations can be helpful in rationalizing the observed vibrational features found in our spectra. In general accord with our assignment of **d2**, Schwarz<sup>21</sup> found stretching modes in  $\text{NH}_4^+(\text{NH}_3)_2$  at  $\sim 3300\text{ cm}^{-1}$ , and Lee<sup>18</sup> found stretching frequencies in this ion around  $\sim 3400\text{ cm}^{-1}$ .

#### 4. $\text{N}_4\text{H}_{13}^-$

In this spectrum, there are only three discernible features, peak **G**, peak **g1**, and peak **g2**. Gone are the spectral features due to Rydberg anion–molecule complexes that enriched the spectra of  $\text{N}_2\text{H}_7^-$  and  $\text{N}_3\text{H}_{10}^-$ . In the spectrum of  $\text{N}_4\text{H}_{13}^-$ , peak **G** is due to the new double Rydberg anion,  $(\text{N}_4\text{H}_{13}^+)^-$ , and its VDE is 0.427 eV. The peaks **g1** and **g2** are due to vibrations associated with it. Peak **g1** is separated from peak **G** by 0.205 eV ( $1652\text{ cm}^{-1}$ ). Given the uncertainty in locating the center of this relatively weak peak, this vibration is probably of the same type as **d1**, described immediately above. Likewise, peak **g2** is separated from peak **G** by 0.376 eV ( $3030\text{ cm}^{-1}$ ), and it is likely due to the excitation of a stretching motion in the neutral Rydberg molecule,  $\text{N}_4\text{H}_{13}$ . There is a good correspondence, in fact, between this frequency and the range of frequencies seen by Lee and co-workers<sup>18</sup> in the infrared spectrum of  $\text{NH}_4^+(\text{NH}_3)_3$ .

#### 5. $\text{N}_5\text{H}_{16}^-$

The spectrum of this anion consists of a strong peak, labeled as **H**, and a weak peak, labeled as **h1**. This spectrum is as simple as that of  $\text{NH}_4^-$ . We interpret peak **H** as being due to the photodetachment of the new double Rydberg anion,  $(\text{N}_5\text{H}_{16}^+)^-$ . Its VDE is 0.434 eV. No clustered double Rydberg anions are seen with this composition. Peak **h1** is separated from peak **H** by 0.176 eV ( $1418\text{ cm}^{-1}$ ). A vibrational feature with a similar separation is common to every one of the five spectral panels in Fig. 1. In the spectra of  $\text{NH}_4^-$ ,  $\text{N}_3\text{H}_{10}^-$ ,  $\text{N}_4\text{H}_{13}^-$ , and  $\text{N}_5\text{H}_{16}^-$ , they are associated with the new, unclustered double Rydberg anionic species. In  $\text{N}_2\text{H}_7^-$ , however, this feature is observed in association with  $\text{NH}_4^+(\text{NH}_3)_1$ . [It may also be present and associated with the unclustered double Rydberg anion,  $\text{N}_2\text{H}_7^-$  (peak **B**), but if so, it is obscured by peak **C**.] As mentioned above, the vibration

responsible for this feature is probably a simple motion which is available to all of the double Rydberg anions studied here.

The scale magnification factors shown on each of the double Rydberg anion spectra are especially interesting. For comparison, we have plotted the strongest peak in each double Rydberg anion spectrum to be essentially the same height as the main peak in its corresponding anion–molecule complex spectrum. This allows one to easily judge the fraction of photodetachment signal (as measured by peak heights) coming from the strongest double Rydberg anion peak versus that coming from the anion–molecule complex's main peak. Since the vast majority of the photodetachment signal in any given  $(\text{N}_n\text{H}_{3n+1})^-$  composition comes from the latter, this approximates the fraction of total photodetachment signal coming from a given double Rydberg anion. For example, the photodetachment signal from peak **A** ( $\text{NH}_4^-$ ) is 1/300 that from the main peak in the  $\text{H}^-(\text{NH}_3)_1$  spectrum. Likewise, peak **B**'s photodetachment signal is 1/500 of the main peak in the  $\text{H}^-(\text{NH}_3)_2$  spectrum (peak **C** is of the same fraction), and peak **D** is 1/800 that from the main peak in the  $\text{H}^-(\text{NH}_3)_3$  spectrum. At the  $\text{N}_4\text{H}_{13}^-$  composition, however, something unexpected happens. The fraction of photodetachment signal from peak **G** has become 1/75 of the main anion–molecule peak in the  $\text{H}^-(\text{NH}_3)_4$  spectrum, and at the composition of  $\text{N}_5\text{H}_{16}^-$ , the double Rydberg anion at peak **H** accounts for 1/15 of the photodetachment signal! (One can see these effects in the unmagnified baseline.) Because the total ion currents (those of the hydride–ammonia complexes plus their corresponding double Rydberg anion species at the same mass) for each composition differ substantially (decreasing with  $n$ ), an absolute comparison between double Rydberg anion species is not feasible here. Nevertheless, one can still see that the fraction of double Rydberg anion content is low at  $\text{NH}_4^-$ , decreases for the next two compositions, and then reverses itself starting at the composition of  $\text{N}_4\text{H}_{13}^-$ , becoming a significant fraction of the photodetachment signal by  $\text{N}_5\text{H}_{16}^-$ .

In the case of the  $\text{N}_5\text{H}_{16}^-$  composition, a likely explanation presents itself for the enhanced fraction of double Rydberg anion signal. Studies by Castleman,<sup>22</sup> by Nishi,<sup>23</sup> and by Fuke<sup>24</sup> all found the  $\text{NH}_4^+(\text{NH}_3)_4$  cation to be a magic number in their mass spectral distributions of  $\text{NH}_4^+(\text{NH}_3)_n$  cluster ions. Thus, the observed fractional enhancement of  $\text{N}_5\text{H}_{16}^-$  double Rydberg anion photodetachment signal may simply be due to an enhanced abundance of the  $\text{N}_5\text{H}_{16}^+$  cation in our nozzle expansion plasma (rather than to a high photodetachment cross section). In turn, the abundance of the  $\text{N}_5\text{H}_{16}^+$  cation may well be due to its particular stability. The  $\text{NH}_4^+(\text{NH}_3)_4$  cation has four ammonia molecules tetrahedrally coordinated to  $\text{NH}_4^+$ , suggesting an opportunity for enhanced stability. An abundance of  $\text{N}_5\text{H}_{16}^+$  may then lead to a relative abundance of neutral  $\text{N}_5\text{H}_{16}$ , from which  $\text{N}_5\text{H}_{16}^-$  is formed. Last, while it is definitely not as stable as  $\text{NH}_4^+(\text{NH}_3)_4$ , the  $\text{NH}_4^+(\text{NH}_3)_{16}$  cation,<sup>25</sup> with 12 ammonia molecules in its second shell, is the next highly symmetric  $\text{NH}_4^+(\text{NH}_3)_n$  cation which may be capable of forming an enhanced fraction of its double Rydberg anion, i.e.,  $(\text{N}_{17}\text{H}_{52})^=$ . It would be interesting to look for it.

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