Ammonia cluster anions and their relationship to ammoniated (solvated) electrons: The photoelectron spectra of $(NH_3)^-_{n=41-1100}$

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We report the negative ion photoelectron spectra of $(NH_3)^-_{n=41-1100}$, recorded using 2.540 eV photons. The largest cluster anion in this series has a diameter of approximately 4.3 nm. The vertical detachment energies (VDEs) of these cluster anions increase smoothly from 0.55 eV for $n=41$ to 1.05 eV for $n=1100$. The VDEs throughout this size range are linear with $n^{-1/3}$ and extrapolate to a VDE ($n=\infty$) value, which is very close to the measured photoelectric threshold energy of condensed phase ammoniated electrons. The linear extrapolation of this data to an analogous condensed phase property implies that these cluster anions are gas-phase counterparts to ammoniated electrons, i.e., they are embryonic forms of ammoniated electrons which will mature with increasing cluster size to become condensed phase-solvated electrons. The VDE data further implies that these embryonic ammoniated electrons were generated in solid ammonia environments, consistent with the source conditions under which they were produced. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1451057]

I. INTRODUCTION

Almost two hundred years ago, Davy observed that sodium dissolved in liquid ammonia to produce a deep blue solution. Later, in 1864, Weyl described this phenomenon[1] in detail, and for many years, it was attributed to the formation of ordinary chemical complexes. Then, in 1908, after the properties of metal-ammonia solutions were studied more extensively, Kraus proposed that the blue color was due to solvated (ammoniated) electrons.[2] In modern times, solvated electrons have been found in a wide variety of other polar solvents, most notably in water, alcohols, amines, and ethers, and they are suspected of playing important roles in many chemical processes.[3–6] Despite the fact that solvated electrons have now been studied in condensed phases for several decades, however, the microscopic nature of these species remains an intriguing topic.

The individual molecules of solvated electron systems typically do not bind excess electrons, yet their bulk solvents readily solvate them, implying that the association of electrons with such solvents is a multi-bodied interaction requiring a collection of molecules. This inspired speculation over the years, by Newton,[7] by Herschbach, and by others, that clusters comprised of such solvent molecules also ought to bind electrons to form negative cluster ions, and that these might be gas-phase counterparts to condensed-phase solvated electron species. In the mid-1980s, these previously predicted species were finally observed by Haberland in ion production-mass spectrometric studies[8–11] of ammonia and water. Since then, interest in these cluster anions has grown, and the central issues concerning them have evolved from determining the minimum number of solvent molecules required to accommodate the excess electron to elucidating the relationship of these gas-phase entities to their corresponding condensed-phase solvated electrons.

Relative to water cluster anions, ammonia cluster anions have received less attention, despite the fact that our current understanding about the physical properties of solvated electrons has come largely from studies of ammoniated electrons. Nevertheless, there have been several important studies. In addition to the experimental work of Haberland,[8–11] Kondow[12,13] has formed ammonia cluster anions by attaching electrons to ammonia clusters via collisions with rare gas atoms in high Rydberg states. Both Haberland and Kondow found the minimum ammonia cluster anion size formed to be $n=35$ for $(NH_3)^-_n$ and $n=41$ for $(ND_3)^-_n$, with no evidence of smaller sizes. From theory, quantum path integral studies have been carried out by Klein and co-workers[14] and by Barnett and Landman[15,16] while dielectric screening models have been developed by Stampfli and Bennemann,[17] by Barnett and Landman,[15,16] by Makov and Nitzan,[18] and by Lakhno and colleagues.[19,20]

Here, we report photoelectron spectra for ammonia cluster anions in the size range $n=41-1100$, following up on our previous preliminary report.[21] Our work reveals that the ammonia cluster anions, like the negative cluster anions of water, are closely related to their corresponding solvated electrons in bulk, and that they exist as embryonic forms of solvated electrons, which mature with increasing cluster size. The photoelectron data further implies that the embryonic ammoniated electrons studied here exist in solid ammonia environments. Below, we present our results and discuss them in relation to theoretical treatments of ammonia cluster anions and to the results from related experiments on excess electron-containing clusters, including our own photoelectron studies of water cluster anions[21,22] and studies of metal atom-ammonia complexes by Hertel[23] and by Fuke.[24]

II. EXPERIMENT

Negative ion photoelectron spectroscopy is conducted by crossing a mass-selected beam of negative ions with a fixed-

frequency photon beam and energy analyzing the resultant photodetached electrons. Our negative ion photoelectron spectrometer has been described previously.[25] Anions generated in an ion source are accelerated, collimated, and transported via a series of ion optical components, before being mass-selected using an $E \times B$ Wein velocity filter. The mass-selected ion beam is then focused into a field-free, collision-free interaction region, where it is crossed with the intracavity photon beam of an argon ion laser operated at 488 nm (2.540 eV) and circulating powers of ~100 W. A small solid angle of the resulting photodetached electrons is accepted into the input optics of a magnetically shielded, hemispherical electron energy analyzer, where the electrons are energy analyzed and counted. The ammonia cluster anion photoelectron spectra presented here were all recorded at an instrumental resolution of 30 meV using a channel spacing of 8.5 meV.

Ammonia cluster anions were generated in a supersonic expansion cluster ion source similar in spirit to that employed by Haberland.[8–11] In this source, high pressure gas in the stagnation chamber is expanded through a pinhole aperture into high vacuum, while a negatively biased hot filament injects low-energy electrons directly into the condensation-prone environment of the expanding jet. In effect, the filament serves as a thermionic cathode, creating a quiescent plasma discharge, which is confined by a predominantly axial magnetic field to the region of the jet expansion. Similar plasma environments are known to possess high densities of very-low-energy electrons in addition to the primary electrons emitted directly from the cathode.[26,27] Probe measurements of electron energy distributions in plasmas have revealed that low-energy thermal electrons, with characteristic temperatures of only a few electron volts, are dominant in these environments, and exceed the number of primary electrons by factors often equaling several orders of magnitude.[27] It is therefore likely that primary electrons play only a minor role, if any, in the anion production process. Thus, generation of ammonia cluster anions in the present ion source is most likely to proceed via the attachment of low-energy thermal electrons to ammonia clusters during their formation and cooling in the supersonic expansion. To generate ammonia cluster anions in these experiments, the source was typically operated using emission currents of 2–8 mA and filament bias voltages of −25 V. Specific source conditions pertaining to this study included the use of a 25 μm sonic (pinhole aperture) nozzle and a stagnation chamber temperature of 0 °C. Typically, 4–7 atm of a 30% ammonia/argon mixture was expanded to produce the cluster anions, although production of the largest cluster ions required similar pressures of a 50% ammonia/argon mixture. Also, to produce the largest cluster anions, the source chamber pumping (VHS-10 diffusion pump at ~4000 l/s) was supplemented with a large surface area, dynamic, liquid nitrogen cryopump (~6000 l/s).

Under the source conditions given above, only cluster anions of the series $(NH_3)_n^-$ were generated. The production of these species began at size $n = 35$ and extended to rather large cluster anion sizes, i.e., $n > 1350$. Over the range of sizes where our mass spectra were resolved, their intensity profile closely resembled the higher resolution mass spectra of $(NH_3)_{n=35-100}^-$ obtained by Haberland[8–11] and by Kondow.[12,13] Given the limitations of our mass selector and the large cluster anion sizes involved in these experiments, it was not possible to obtain unit cluster anion mass selectivity over much of the ammonia cluster anion mass distribution. At the high mass range of the largest cluster anions studied here, the resolution of our mass selector was approximately 20. Accordingly, the photoelectron spectra of the largest ammonia cluster anions contain spectral contributions from approximately ±20 adjacent-sized cluster anions. Careful mass calibrations allowed cluster anion sizes to be accurately and reproducibly determined. Reliability was further enhanced by the fact that spectral shifts between the photoelectron spectra of adjacent-sized ammonia cluster anions were very small. Thus, even though the photoelectron spectrum of a given ammonia cluster anion may contain appreciable contributions from adjacent-sized cluster anions, this does not alter it significantly. Indeed, the widths of the photoelectron peaks of very large ammonia cluster anions are not much greater than those of $n = 40-50$, where the mass resolution was ~60 and good mass selectivity between adjacent size clusters was obtained. Finally, it should be noted that the mass intervals between the specific ammonia cluster anions examined in this study were carefully chosen to exceed the range over which spectral contributions from adjacent-sized cluster anions were expected.

III. RESULTS AND INTERPRETATION

The photoelectron spectra of ammonia cluster anions, $(NH_3)_{n=41-1100}^-$, are presented in Fig. 1. The photoelectron spectra for all sizes examined are qualitatively similar, each consisting of a single asymmetric peak which rises sharply and then tails toward high electron binding energy (EBE). The peak maximum in each spectrum corresponds to the vertical detachment energy (VDE), which corresponds to the energy of the most probable photodetachment transition. As compared to hydrated electron cluster anions[21,22] and color-center cluster anions of cesium iodide,[28] the widths of the photoelectron spectra of ammonia cluster anions are quite narrow. This might at first seem surprising, given the volume expansions that occur upon formation of bulk ammoniated electrons[29–31] and the expectation that large structural changes should translate into wide spectral widths. Ammonia/ammonia interactions, however, are quite weak; compare the ~0.26 eV interaction energy between a pair of nearest neighbor water molecules in the bulk with ~0.03 eV for the same quantity in ammonia.[32,33] Thus, because of weak intermolecular interactions in ammonia, even relatively large changes in solvent geometry result in only minor energetic changes and thus in narrow photoelectron spectral widths.

The VDE values for $(NH_3)_{n=41-1100}^-$, presented in Table I, increase smoothly from 0.55 eV for $n = 41$ to 1.05 eV for $n = 1100$, with no abrupt changes. The VDE values initially increase rapidly with increasing cluster anion size, and then appear to approach an asymptotic limit at larger cluster sizes. In order to correlate the electron binding in these ammonia
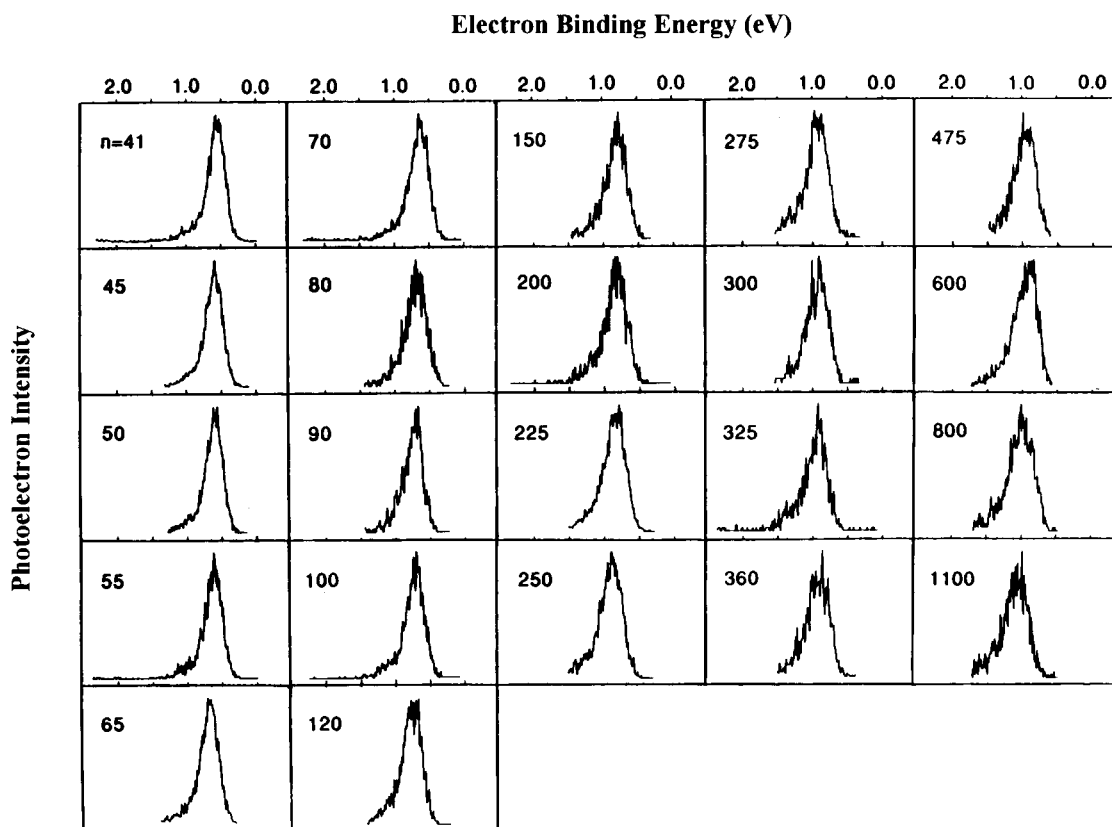
Electron Binding Energy (eV)

FIG. 1. The negative ion photoelectron spectra of $(NH_3)^-_{n=41-1100}$, recorded with 2.540 eV photons.

cluster anions with electron binding in bulk ammonia, one needs to know the asymptotic limit of the cluster anion VDEs.

The size-dependent evolution of electron binding energies for finite-sized metal and dielectric clusters has been described using classical electrostatic models.[34–37] The ob-

TABLE I. Vertical detachment energies (VDEs) of $(NH_3)^-_n$ cluster anions.

n	VDE (eV)
41	0.55 ± 0.1
45	0.59 ± 0.1
50	0.59 ± 0.1
55	0.61 ± 0.1
65	0.68 ± 0.1
70	0.65 ± 0.1
80	0.68 ± 0.1
90	0.71 ± 0.1
100	0.72 ± 0.1
120	0.75 ± 0.1
150	0.77 ± 0.1
200	0.81 ± 0.1
225	0.84 ± 0.1
250	0.88 ± 0.1
275	0.91 ± 0.1
300	0.90 ± 0.1
325	0.92 ± 0.1
360	0.90 ± 0.1
475	0.92 ± 0.1
600	0.93 ± 0.1
800	0.98 ± 0.1
1100	1.05 ± 0.1

served size dependencies of cluster electron binding energies are usually in good agreement (apart from small cluster sizes) with classical models, which predict that electron binding energies will increase linearly toward the corresponding bulk energy value as a function of R^{-1}, where R is the radius of the spherical cluster. Plotting the ammonia cluster anion VDEs as a function of R^{-1} is carried out by plotting VDE(n) versus $n^{-1/3}$ where n (the number of molecules in a given cluster anion) is related to the cluster radius by $R = r_s n^{1/3}$. In this expression, r_s is the effective radius of a single solvent molecule, which is usually derived from the density of the bulk solvent. The intercept of such a plot at $n^{-1/3} = 0$ provides the VDE at $n = \infty$. Thus, plotting the data in this manner elucidates the asymptotic behavior of VDE(n). A plot of the VDE(n) values for $(NH_3)^-_{n=41-1100}$ versus $n^{-1/3}$ is presented in Fig. 2. This plot gives a straight line, which extrapolates to a VDE(∞) value of 1.25 eV.

Let us now consider the physical significance of this VDE(∞) value in order to establish a link to the bulk. A framework for examining the energetics and photophysics of solvated electrons in both bulk and cluster anion systems has been put forth for the case of hydrated electrons by Coe and ourselves.[22,38] This same picture is applied here to ammonia cluster anions. The two energetic quantities most relevant to this discussion are the VDE(∞) and the bulk photoelectric threshold (PET). As stated, the VDE corresponds to the energy of the most probable photodetachment (photoemission) transition, while the PET corresponds to the minimum photon energy at which there is sufficient geometric overlap be-
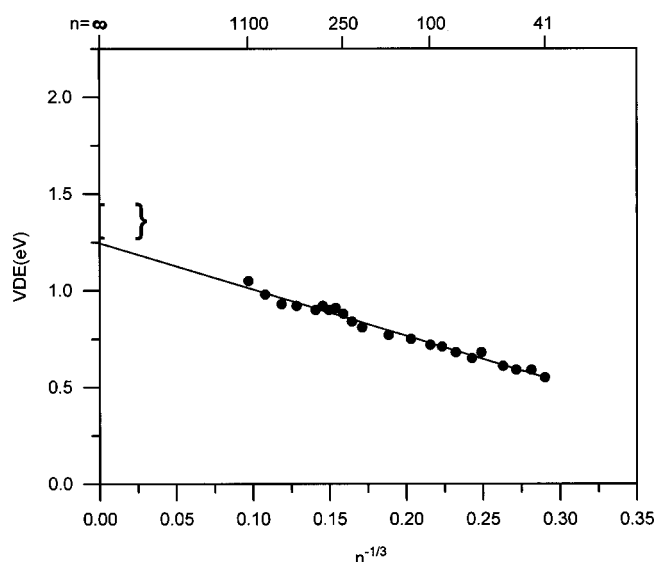
FIG. 2. Plot of VDE(n) vs $n^{-1/3}$ for $(NH_3)_{n=41-1100}^-$. The vertical detachment energies show a linear dependence with $n^{-1/3}$. The least squares fit of the data corresponds to VDE(n) = $1.25 - 2.41n^{-1/3}$ (correlation coefficient of 0.990). The range of variation among experimentally measured bulk PET values is bracketed along the ordinate.

tween the initial and final states to detect a photoelectron signal in the bulk. Studies on electron photoemission from bulk ammoniated electron solutions[39–43] have been concerned with determination of the PET value. They have not provided a value for the bulk VDE. In a strict sense, the bulk PET should be compared to the extrapolated value of the photoelectron spectral threshold at $n = \infty$, while the extrapolated value of the vertical detachment energy at $n = \infty$, VDE(∞), should be compared to the value of the bulk VDE. However, owing to the unavailability of the bulk VDE value, the inherent difficulties associated with determining thresholds accurately, and, most importantly, the observation that the energy differences between VDEs and threshold EBEs are relatively small in the photoelectron spectra of ammonia cluster anions, we will here compare the bulk PET with VDE(∞). The relatively narrow widths of ammonia cluster anion photoelectron spectra makes this a reasonable approximation.

Having established the close similarity between VDE and threshold values for this system, the extrapolated cluster anion VDE(∞) value and the bulk PET measurements can now be compared. The range of bulk PET values for ammoniated electrons in dilute solutions varies from 1.27 eV for the most dilute solutions studied to 1.45 eV for more concentrated solutions.[39,40] The measured bulk PET value decreases with concentration, and it is clear that its value at infinite dilution is the relevant quantity in the present study. Determining the bulk PET at the dilution limit was complicated by the fact that measurements were conducted at a temperature where the vapor pressure of ammonia was rather high (~45 Torr), making the detection of low-energy electrons difficult and increasing the apparent threshold energy. The presence of counterions in the bulk further increased the apparent threshold energy. Under these circumstances, our extrapolated VDE(∞) value of 1.25 eV, which itself must be

slightly higher than the photoelectron spectral threshold at $n = \infty$, is in reasonable agreement with the bulk PET value (1.27 eV) measured at the most dilute concentrations considered (see Fig. 2). Thus, the linear extrapolation of the ammonia cluster anion data to its analogous condensed phase property strongly suggests that all of these cluster anions are counterparts to bulk ammoniated electrons, i.e., they are embryonic forms of solvated electrons which mature with increasing cluster size to become condensed phase ammoniated electrons.

IV. DISCUSSION

Here, we discuss our results in relation to theoretical treatments of ammonia cluster anions and experimental results on related systems. Theoretical studies of ammonia cluster anions have been of two types. These are dielectric sphere models and quantum path integral calculations. We discuss the former first.

Dielectric continuum-based models have provided important frameworks for understanding solvation and ionization phenomena in condensed phases,[44–49] and microscopic adaptations of such models have made significant contributions to our understanding of discrete cluster systems. Using such a model, Stampfli and Bennemann[50] treated ammonia clusters as continuous dielectric spherical shells and found that by $n \cong 30$ the excess electron is bound inside the cluster by the electric field resulting from the polarization of the molecular dipole moments. This size threshold is in quite nice accord with mass spectral results. Their model also predicted the adiabatic electron affinities (EAs) for large ammonia clusters, demonstrating an asymptotic behavior toward EA(∞). However, their calculated values of EA(n) appear to be overestimations, given that they are larger than the corresponding experimental VDE(n) values, and that their EA(n) values appear to be on a course that would overestimate EA(∞), i.e., the literature value of ΔH_s for bulk ammoniated electrons.[51,52] In subsequent work, these authors explain that such overestimations are expected within this model, since it uses only a pair-potential approximation, neglecting induced polarization which would serve to decrease the effective polarization.[17]

Later, a refined dielectric sphere model was presented by Landman and co-workers,[15,16,53–55] and also by Stampfli and Bennemann themselves.[17] This model describes homogeneous dielectric clusters containing spherically symmetric charge distributions, and is thus appropriate for describing solvated electronlike environments. The expression describing the size dependence of the VDE within this model is

$$\text{VDE}(n) = \text{VDE}(\infty) - \frac{e^2}{2r_s}(1 + D_{op}^{-1} - 2D_s^{-1})n^{-1/3}, \quad (1)$$

where the intercept, VDE(∞), corresponds to the bulk vertical photodetachment energy, while the slope is comprised of several factors, including r_s, the effective radius of a single solvent molecule, D_{op}, the optical dielectric constant, and D_s, the static dielectric constant. In the case of ammoniated electron cluster anions, the PET for bulk ammoniated electrons is in reasonable accord with the intercept of the experi-

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mental VDE(n) versus $n^{-1/3}$ line, as was already discussed. However, in comparing the experimental slope with the dielectric sphere VDE(n) versus $n^{-1/3}$ line, care must be taken in selecting the proper parameters for bulk ammonia. Let us now focus on this slope.

As pointed out by Makov and Nitzan,[18] two rather different values for the slope of the dielectric sphere VDE(n) versus $n^{-1/3}$ line can be obtained, depending on whether parameters for solid or liquid ammonia are utilized. Only one is consistent with the experimental data. The reason for this difference stems primarily from the dissimilarity in the static dielectric constant values between ammonia in the liquid and solid phases, D_s, being $\sim$22 in the liquid phase,[56] but only $\sim$3.4 in the solid phase.[57] The reason for this difference has been attributed to lack of dipole rotation in the presence of an applied electric field for solid ammonia.[57] The disparity in D_s values is in sharp contrast to water, where D_s values are similar in both the solid and the liquid.[56] If the parameters for liquid ammonia are inserted into Eq. (1), the predicted dielectric sphere model VDE(n) versus $n^{-1/3}$ slope is 5.06 eV, over a factor of 2 larger than the experimentally determined slope of 2.41 eV. On the other hand, if the parameters for solid ammonia are inserted into the equation, a slope of 3.08 eV is obtained, and this value is much closer to the experimentally determined slope. Moreover, there are two effects that make it reasonable to expect the calculated value to be a little larger than the experimental value. Both effects derive from the fact that ammoniated electrons (and probably cluster anions in general) have a tendency to undergo volume expansions. For ammoniated electrons, this is the case even in the presence of counterions, and there are none present among gas-phase ammonia cluster anions, further increasing their tendency toward volume expansion. In any case, an increase in volume causes the *effective* radii (r_s) of ammonia molecules in each ammonia cluster anion to increase relative to those of free, ammonia molecules. In addition, the static dielectric constant, D_s, is density dependent, and it decreases as density decreases. Both effects reduce the calculated slope in the direction of the experimental slope. Thus, the agreement between the dielectric model slope, calculated with solid ammonia parameters, and the experimentally determined slope is relatively good, suggesting that the ammoniated electron cluster anions, $(NH_3)^-_{n=41-1100}$, studied here are in the solid phase.

Given this interpretation, it is interesting to consider whether the ammonia cluster anions produced in this study were likely to be in the solid or the liquid state based on the source conditions used to generate them. Electron diffraction studies on large clusters produced in supersonic flows reveal that solid clusters are produced in the cases of many simple polyatomic molecules (e.g., N_2, CO_2, CH_4).[58] Diffraction experiments by Bartell on large neutral ammonia clusters generated in neat supersonic expansions have shown that both solid and liquidlike species can be formed, with the production of liquid clusters occurring with the use of Laval nozzles, these being known to yield rather slow expansions.[59] The expansion conditions employed here differ significantly, however, in that pinhole aperture nozzles were used, and these characteristically result in rapid expansions.

In as much as jet expansions used to generate neutral clusters and those employed here can be compared, it is reasonable to expect that the use of a pinhole nozzle, coupled with high stagnation pressures, low stagnation temperatures, and argon carrier gas, resulted in the production of solid ammonia cluster anions, consistent with the interpretation presented above.

Before it was realized that the ammonia cluster anions in our study exist in the beam as solid entities, two analyses appeared in the literature.[17,55] In one of these,[17] its authors observed that only the experimental VDEs for $n>500$ seemed to lie on the dielectric sphere line for *liquid* ammonia, and they suggested that this might imply solvation structures different from the bulk for smaller species. In the other analysis,[55] it was argued that an $n^{-1/3}$ analysis should not apply to cluster anions smaller than $n \approx 150$, because the experimental VDEs did not appear to lie on the *liquid* ammonia-based dielectric sphere line. This analysis, however, also utilized a bulk PET value of 1.7 eV,[40] which was too large, as was later shown when the data (at that concentration) was reinterpreted to give a PET value of 1.45 eV.[60] The conclusions of these analyses were reached without considering the possibility that the clusters were in the solid phase, and, therefore, their validity is in question. Two years later, Makov and Nitzan[18] carried out a dielectric model analysis and concluded by stating, ''In particular it is suggested that the observed photodetachment energies from small $(NH_3)^-_n$ clusters are compatible with the dielectric predictions for electron solvation in solid ammonia.'' Thus, the observed slope, based on experimental VDEs, has physical significance across the entire size range ($n=41-1100$) investigated here. Specifically, the slope is consistent with a solid ammonia environment for these cluster anions.

Having discussed studies which utilized dielectric sphere models, we now comment on the pioneering quantum path integral treatments of ammonia cluster anions undertaken by Klein and co-workers[14] and by Landman, Barnett, and Jortner.[15,16] Both groups used quantum path integral simulations to explore, as functions of ammonia cluster size, the binding energy of the excess electron and the nature of the excess charge distribution. Klein's group performed quantum path integral Monte Carlo calculations and considered three cluster anion sizes, $(NH_3)^-_{n=16,36,54}$, between 100 and 200 K. They found stable cluster anions only at 100 K and concluded that stable ammonia cluster anions exist, at the smallest sizes, as surface electron states, which evolve with increasing cluster size toward internal, solvated electronlike excess electron states. The $n=16$ cluster anion was calculated by Klein *et al.* to be a marginally bound surface electron state, while a stable surface state (VDE of $\sim$0.2 eV) was predicted to exist for $n=36$. Both a stable surface state (VDE of $\sim$0.3 eV) and a metastable internal state (VDE of $\sim$1.2 eV) were predicted to exist at $n=54$. These calculations implied that rather large ammonia clusters, i.e., $n>200$, would be required to stabilize internal electron states. Our experiments, however, found no evidence for the coexistence of species exhibiting different electron binding behavior, in that all of the photoelectron spectra observed exhibited only single peaks.

Landman *et al.* performed quantum path integral molecular dynamic calculations, examining $(NH_3)^-_{n=16,24,32,64,128,256}$ at ~ 190 K. They concluded that ammonia cluster anions, $n < 32$, exist only as weakly bound surface states, while $n > 32$ exist only as internal excess electron states. Their calculated internal state VDEs ranged from 1.8 to 3.1 eV for $n = 32-256$. Qualitatively, the calculations of Landman *et al.* are in good agreement with our interpretation, since they predict that the cluster anions of ammonia ($n \geq 35$) should exist only as internally localized excess electron states, i.e., as solvated electronlike species. It should be noted, however, that for both quantum path integral studies, the calculated internal state VDEs are larger than the experimental values.

Finally, we discuss experimental results on metal atom–ammonia clusters, which are related to the ammoniated electron clusters studied here. Ionization potential (IP) measurements on neutral clusters composed of alkali metal atoms solvated by ammonia molecules (and by other polar molecules) were carried out by Hertel and co-workers[23] on $Na(NH_3)_{20 < n < 50}$, and by Fuke and co-workers[24] on $Cs(NH_3)_{n \leq 31}$. The results of both groups were presented in terms of $IP(n)$ versus $(n+1)^{-1/3}$ plots. In their analysis, "$n+1$" was used to account for the presence of the alkali atom. Hertel and co-workers report that their observations are consistent with a linear extrapolation of $IP(n)$ versus $(n+1)^{-1/3}$, giving a bulk value of 1.45 eV, while Fuke and co-workers observe a linear extrapolation of $IP(n)$ versus $(n+1)^{-1/3}$ to give a bulk value of 1.4 eV. The extrapolated $IP(\infty)$ values in these studies are consistent with the presence of an alkali counter-ion in the neutral species. Such cations, which were also present in the bulk ammoniated electron solution for which PET was measured, would be likely to enhance the electron binding abilities of the alkali metal atom-ammonia clusters.

V. CONCLUSION

We have presented the negative ion photoelectron spectra of $(NH_3)^-_{n=41-1100}$, from which vertical detachment energies (VDEs) have been obtained. The VDEs throughout this range are linear with $n^{-1/3}$ and extrapolate to a VDE(∞) value which is close to the photoelectric threshold energy for bulk ammoniated electrons. This suggests that these ammonia cluster anions exist as embryonic forms of bulk ammoniated electrons. The data further implies that these embryonic ammoniated electrons were generated in solid ammonia environments.

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