

Negative ion photoelectron spectroscopy of solvated electron cluster anions, $(\text{H}_2\text{O})_n^-$ and $(\text{NH}_3)_n^-$

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Abstract. The photodetachment spectra of $(\text{H}_2\text{O})_{n=2-69}^-$ and $(\text{NH}_3)_{n=41-1100}^-$ have been recorded, and vertical detachment energies (VDEs) were obtained from the spectra. For both systems, the cluster anion VDEs increase smoothly with increasing sizes and most species plot linearly with $n^{-1/3}$, extrapolating to a VDE ($n = \infty$) value which is very close to the photoelectric threshold energy for the corresponding condensed phase solvated electron system. The linear extrapolation of this data to the analogous condensed phase property suggests that these cluster anions are gas phase counterparts to solvated electrons, i.e. they are embryonic forms of hydrated and ammoniated electrons which mature with increasing cluster size toward condensed phase solvated electrons.

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1. Introduction

Although solvated electrons have been studied extensively in liquids and glasses, the microscopic nature of these species remains an intriguing topic [1–3]. In general, the individual molecules of solvated electron systems do not bind excess electrons. However, the corresponding condensed phase systems readily solvate them, implying that the association of electrons with these solvents is a multi-bodied interaction. In the past, this had sparked speculation that clusters of some size ought to bind excess electrons [4, 5], and several years ago, gas-phase water and ammonia cluster anions were observed in mass spectrometric studies [6–9]. Following this development, further experimental and theoretical interest arose in solvated electron cluster anions. Presently, an important question regarding these cluster anions concerns whether they are gas phase counterparts to condensed phase solvated electrons. Here, we discuss the results of our photoelectron (photodetachment) studies of water [10] and ammonia cluster anions [11], which reveal that ammonia

cluster anions ($n \geq 41$) and water cluster anions ($n \geq 11$) do indeed correlate to their bulk phase equivalents and exist as embryonic solvated electrons which mature with increasing cluster size.

2. Experimental

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 [12]. Briefly, negative ions are generated in a supersonic expansion cluster ion source, skimmed, and transported through a series of ion optical components into an $\mathbf{E} \times \mathbf{B}$ Wien velocity filter where they are mass selected. The mass selected ion beam is then crossed with the intracavity photon beam of an argon ion laser, and a small solid angle of the resulting photodetached electrons is accepted into a hemispherical electron energy analyzer, where the electrons are energy analyzed and counted. The supersonic expansion ion source used in these experiments has also been described previously [13]. In this source, ammonia or water vapor in the high pressure stagnation chamber is co-expanded with argon through a pinhole aperture into high vacuum, while a negatively biased hot filament injects relatively low energy electrons directly into the expanding jet, producing the cluster anions.

3. Results and interpretation

Water cluster anions, $(\text{H}_2\text{O})_{n=2-69}^-$

The water mass spectrum contains three regions whose intensity varies with source conditions. At very low concentrations of water, only the water dimer anion and its argon clusters are present, but as the water concentration is increased, the intensity of these clusters decreases, and new species such as $(\text{H}_2\text{O})_6^-$ and $(\text{H}_2\text{O})_7^-$ appear. At still

higher water concentrations the larger water cluster anions, $n \geq 11$, grow to dominate the mass spectrum, and the smaller cluster anions almost entirely disappear.

The photoelectron spectra of water cluster anions, $n = 2, 6, 7, 11-69$, are all presented in Fig. 1. The dimer anion's photoelectron spectrum exhibits one large peak with two less intense peaks toward higher binding energies. The main feature has a vertical detachment energy (VDE) of ~ 50 meV and is assigned as the origin-containing peak. The smaller peaks are vibrational features and are separated from the main peak by energies which correspond to those of water bending and stretching frequencies, respectively. The photoelectron spectra of the water hexamer and heptamer anions are similar to one another, and isotopic and source condition studies suggest that the two lowest electron binding energy (EBE) features in the spectra of $n = 6, 7$ may represent different isomers of each of these species. The highest EBE feature

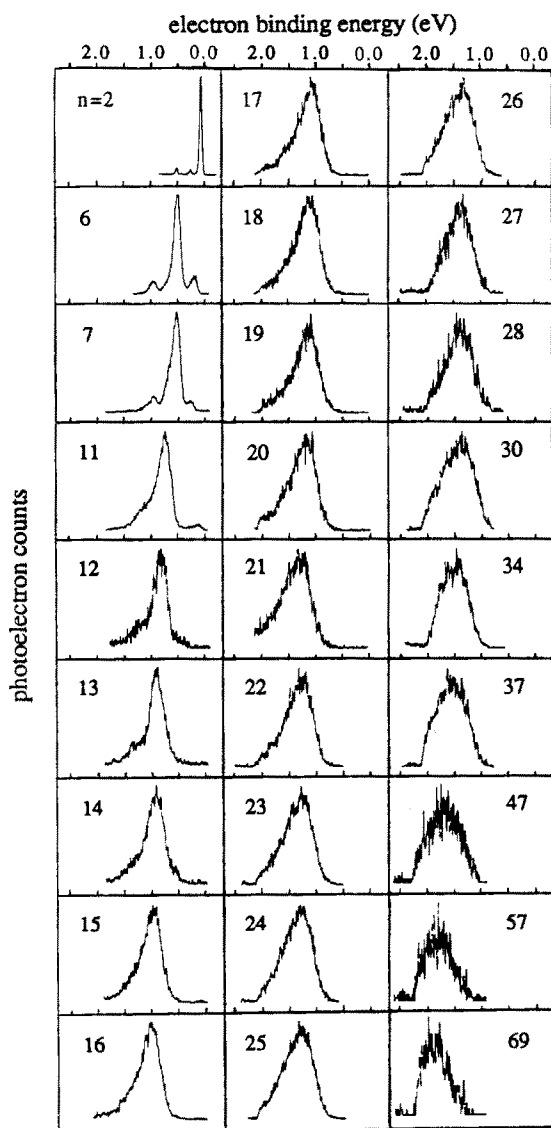


Fig. 1. The negative ion photoelectron (photodetachment) spectra of $(\text{H}_2\text{O})_n^-$, $n = 2, 6, 7, 11-69$, are presented above

is a vibrational feature and is separated from the main peak by an energy corresponding to a water stretching frequency. The spectra of the larger water cluster anions, $(\text{H}_2\text{O})_{n=11-69}^-$, are dominated by single broad asymmetric peaks. The EBEs of the peak maxima in these spectra are interpreted as the VDEs, and these shift to successively higher EBEs with increasing cluster size. For $n = 11-69$ the VDEs increase smoothly from 0.75 eV to 1.92 eV. Initially, the VDEs increase rapidly before showing asymptotic behavior at larger cluster sizes.

A particularly useful way to examine the asymptotic behavior of $\text{VDE}(n)$ is to plot the data vs $n^{-1/3}$. This is equivalent to plotting $\text{VDE}(n)$ vs R^{-1} , since the radius of a spherical cluster anion, R , can be related to n through $R = R_S n^{1/3}$, where R_S is the effective radius of a single solvent molecule. The intercept of such a plot represents the VDE at infinite cluster size, $\text{VDE}(\infty)$, which corresponds to the photoelectric threshold energy for the bulk solvated electron, i.e., the photon energy needed to initiate electron emission from a solvated electron solution at infinite dilution. Since the VDE and the photoelectric threshold both represent vertical ionization processes in the gas phase and the condensed phase, respectively, plotting VDE vs $n^{-1/3}$ provides an opportunity to compare these quantities.

For the lowest EBE isomers of $n = 6, 7$ and for $n \geq 11$, the VDEs plot linearly with $n^{-1/3}$ and extrapolate to an intercept of 3.3 eV, as demonstrated in Fig. 2. For the hydrated electron, the photoelectric threshold can be obtained indirectly from the sum of the photoconductivity threshold and V_0 , the width of the conduction band. For the hydrated electron in ice, the photoconductivity threshold is ~ 2.3 eV [14], while V_0 is ~ 0.9 eV [15, 16],

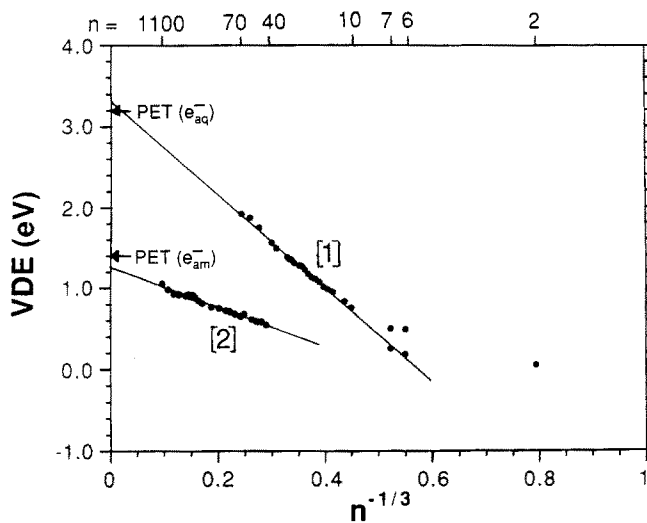


Fig. 2. The VDEs of $(\text{H}_2\text{O})_n^-$ [1] and $(\text{NH}_3)_n^-$ [2] are plotted vs $n^{-1/3}$. For water cluster anions, the VDEs for $n \geq 11$ (and for the lowest forms of $n = 6, 7$) show a linear dependence with $n^{-1/3}$ and extrapolate to an intercept [$\text{VDE}(\infty)$] of 3.3 eV. The photoelectric threshold for hydrated electrons [$\text{PET}(e_{aq}^-)$] is 3.2 eV. For ammonia cluster anions, the VDEs for $n = 41-1100$ are all linear with $n^{-1/3}$ and extrapolate to 1.25 eV. The PET for ammoniated electrons [$\text{PET}(e_{am}^-)$] is ≤ 1.4 eV

implying that the bulk photoelectric threshold is ~ 3.2 eV, in agreement with our extrapolated value. The linear extrapolation of the water cluster anion data to the analogous bulk property implies that water cluster anions of sizes $n \geq 11$ (and perhaps forms of $n = 6, 7$) are gas phase counterparts to bulk hydrated electrons, i.e., they are embryonic forms of solvated electrons which mature with increasing cluster size toward condensed phase hydrated electrons.

The VDE of water dimer anion and those of the higher binding energy forms of $n = 6, 7$ do not lie on the line described by the VDEs of $n \geq 11$, indicating they are different from the larger water clusters anions. The water dimer anion has been depicted by theoretical calculations as a dipole bound negative ion, in which the excess electron is weakly bound by the dipole field of a largely unperturbed neutral dimer. However, the photodetachment spectrum implies that water stretches and bends are excited during photodetachment and that at least one of the water subunits in the dimer anion is distorted relative to the neutral. The low intensity of the two smaller peaks suggests that the distortion is rather slight.

Ammonia cluster anions, $(\text{NH}_3)_{41-1100}^-$

The mass spectra of the ammonia cluster anions show distributions of cluster ions beginning at $(\text{NH}_3)_{35}^-$ and extending to larger sizes. At appropriate source conditions, the cluster distribution extends past $(\text{NH}_3)_{1350}^-$. The photoelectron spectra of ammonia clusters anions, $n = 41-1100$, each contain a single asymmetric peak, which tails toward high electron binding energy. Again, the EBEs of the peak maxima correspond to the VDEs, and these shift to successively higher EBEs with increasing cluster ion size. The VDEs for $(\text{NH}_3)_{n=41-1100}^-$ increase smoothly from 0.55 eV for $n = 41$ to 1.05 eV for $n = 1100$. Given the capabilities 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. Nevertheless, we were able to conduct reliable experiments under these conditions, primarily because the spectral shifts between the photoelectron spectra of adjacent-sized ammonia cluster anions are very small. Thus, even though the photoelectron spectrum of a given ammonia cluster anion may contain contributions from adjacent-sized cluster anions, it is not significantly altered. Indeed, the widths of the photoelectron peaks of very large ammonia cluster anions are not much greater than those of $n = 40-50$, where good mass selectivity was obtained.

As demonstrated previously, the data are most clearly presented as VDE vs $n^{-1/3}$. As shown in Fig. 2, the data plot linearly as VDE(n) vs $n^{-1/3}$ and extrapolate to an intercept of 1.25 eV. Several studies, all of which are in agreement, have examined the photoemission of electrons from ammoniated electron solutions [17–19]. Specifically, Häsing carried out examinations of the threshold region for the photoemission of electrons from metal-ammonia solutions and found the photoelectric threshold to range

from 1.42–1.45 eV for dilute solutions [17]. Given the usual uncertainties involved in threshold determinations, the presence of counter ions (alkali metal cations) in the metal-ammonia solutions, and the tendency for ammoniated electrons to spin-pair even at high dilution, our extrapolated value of VDE(∞) is in good agreement with this measurement and probably represents a lower limit for the photoelectric threshold. Thus, the linear extrapolation of the ammonia cluster anion data to the analogous condensed phase property strongly suggests that these cluster anions are gas phase counterparts to bulk solvated electrons.

4. Discussion

The linear relation observed between the electron binding energy and the inverse radius of the cluster is consistent with a classical electrostatic description of these systems. Over the years, dielectric sphere models have been developed describing such behavior. Specifically, the model developed by Jortner and more recently elaborated on by Jortner and Landman, describes the vertical detachment energy and the electron affinity of these clusters as a function of the inverse cluster radius (directly related to the number of solvent molecules in the cluster) [20]. The linear function for VDE vs $n^{-1/3}$ presented by Jortner and Landman is:

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

where VDE(∞) is the photoelectric threshold, R_s is the effective radius of a single solvent molecule ($R = R_s n^{1/3}$), D_s is the static dielectric constant of the medium, and D_{op} is the optical dielectric constant. This expression was developed for a spherically symmetric charge distribution in a homogeneous dielectric media, i.e., internal electron states which represent solvated electron-like environments.

For water cluster anions, the photodetachment data is consistent with this model because the VDEs for $n \geq 11$ are linear with $n^{-1/3}$; they extrapolate to the established photoelectric threshold, and the slope of the line best describing the experimental VDEs is nearly identical to the value predicted by the model. From the same model, Jortner and Landman also developed an analogous equation for describing the adiabatic electron affinity (EA_a) vs $n^{-1/3}$. Their model predicts that the EA_a s become positive at $n \sim 11$. Although we do not measure the EA_a in our experiment, this threshold corresponds to the observed onset for the continuous formation of water cluster anions and is in agreement with the implications of the experiments of Echt [21]. This supports the interpretation given above that water cluster anions of sizes $n \geq 11$ are developing forms of hydrated electrons.

Dielectric sphere models also provide an approximate description of ammonia cluster anions. Most significantly, the ammonia cluster anion VDEs are linear with $n^{-1/3}$ and extrapolate closely to the bulk photoelectric threshold. The specific form of Jortner and Landman's model

equation, however, does not describe the slope of the line fitting the experimental data as successfully. Perhaps the level of agreement is not as high for the ammonia cluster anions because bulk ammoniated electrons are thought to form large solvent cavities, and the model does not account for this additional complexity.

More rigorous theoretical treatments which explore the nature of the excess charge distribution in ammonia and water cluster anions include the quantum path integral and the molecular dynamic simulations by Landman and Jortner [20, 22–25] and by Klein [26]. These simulations attempt to describe the energetics and the excess electron localization modes in water and ammonia cluster anions over a range of sizes and temperatures.

For ammonia cluster anions, Klein found a marginally bound surface electron state to exist at $n = 16$; a stable surface state formed by $n = 36$, while both a stable surface state and a metastable internal state were found to exist at $n = 54$. Landman and Jortner concluded that the ammonia cluster anions, $n < 32$, exist only as weakly bound surface states, while $n > 32$ exist only as internal states. Both of these calculations are in qualitative agreement with our interpretation of the ammonia cluster anion data, for they predict that cluster anions $n > 40$ are internal states and, thus, counterparts to the bulk ammoniated electron. Quantitatively, however, the path integral results are not in accord with the experiment since they predict internal state VDEs which are larger than our measured values and which extrapolate to a photoelectric threshold that is substantially larger than the established value.

Landman and Jortner have also presented a quantum path integral description of water cluster anions, finding that cluster anions smaller than $(\text{H}_2\text{O})_{n=32}^-$ are surface states, while those larger than $(\text{H}_2\text{O})_{n=64}^-$ are internal states, with a surface-to-internal state transition occurring between $n = 32$ –64. Again, these calculations demonstrate substantial qualitative agreement with the experimental results, for both predict that small water cluster anions are surface states which give way at larger sizes to internal electron states. The experiment suggests the transition to internal states occurs by $n = 11$ (if not for isomers of $n = 6, 7$), while the path integral treatment locates the transition near $n = 32$ –64. However, as in the case of ammonia, there is quantitative disagreement concerning the magnitude of the water cluster anion VDEs. The calculated internal state VDEs for $n \geq 11$ are again larger than our measured values and extrapolate to a photoelectric threshold which is much larger than the likely value.

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References

- Hart, E.J., Anbar, M.: The hydrated electron. New York: Wiley-Interscience 1970
- Jolly, W.L.: Metal-ammonia solutions. Stroudsburg, Pennsylvania: Dowden, Hutchinson, and Ross 1972
- Dogonadze, R.R., Kalman, E., Kornyshev, A.A., Ulstrup, J.: The chemical physics of solvation, Part C: Solvation phenomena in specific physical, chemical, and biological systems. Amsterdam: Elsevier 1988
- Newton, M.: J. Phys. Chem. **79**, 2795 (1975)
- Chipman, D.M.: J. Phys. Chem. **83**, 1657 (1979)
- Armbruster, M., Haberland, H., Schindler, H.-G.: Phys. Rev. Lett. **47**, 323 (1981)
- Haberland, H., Schindler, H.-G., Worsnop, D.R.: Ber. Bunsenges. Phys. Chem. **88**, 270 (1984)
- Haberland, H., Langosch, H., Schindler, H.-G., Worsnop, D.R.: J. Phys. Chem. **88**, 3903 (1984)
- Haberland, H., Ludewigt, C., Schindler, H.-G., Worsnop, D.R.: J. Chem. Phys. **81**, 3742 (1984)
- Coe, J.V., Lee, G.H., Eaton, J.G., Arnold, S.T., Sarkas, H.W., Bowen, K.H., Ludewigt, C., Haberland, H., Worsnop, D.R.: J. Chem. Phys. **92**, 3980 (1990)
- Sarkas, H.W., Lee, G.H., Arnold, S.T., Eaton, J.G., Bowen, K.H. (to be published)
- Coe, J.V., Snodgrass, J.T., Freidhoff, C.B., McHugh, K.M., Bowen, K.H.: J. Chem. Phys. **84**, 618 (1986)
- Coe, J.V., Snodgrass, J.T., Friedhoff, C.B., McHugh, K.M., Bowen, K.H.: J. Chem. Phys. **87**, 4302 (1987)
- Kevan, L.: J. Phys. Chem. **76**, 3830 (1972)
- Baron, B., Hoover, D., Williams, F.: J. Chem. Phys. **68**, 1997 (1978)
- Onaka, R., Takahashi, T.: J. Phys. Soc. Jpn. **24**, 548 (1968)
- Häsing, J.: Ann. Phys. (Leipz.) **37**, 509 (1940)
- Aulich, H., Baron, B., Delahay, P., Lugo, R.: J. Chem. Phys. **58**, 4439 (1973)
- Teal, G.K.: Phys. Rev. **71**, 138 (1947)
- Barnett, R.N., Landman, U., Cleveland, C.L., Jortner, J.: J. Chem. Phys. **88**, 4429 (1988)
- Knapp, M., Echt, O., Kreisle, D., Recknagel, E.: J. Phys. Chem. **91**, 2601 (1987)
- Barnett, R.N., Landman, U., Cleveland, C.L., Jortner, J.: Phys. Rev. Lett. **59**, 811 (1987)
- Barnett, R.N., Landman, U., Cleveland, C.L., Jortner, J.: J. Chem. Phys. **88**, 4421 (1988)
- Barnett, R.N., Landman, U., Cleveland, C.L., Jortner, J.: Chem. Phys. Lett. **145**, 382 (1988)
- Barnett, R.N., Landman, U., Cleveland, C.L., Kestner, N.R., Jortner, J.: Chem. Phys. Lett. **148**, 249 (1988)
- Marchi, M., Sprik, M., Klein, M.L.: J. Chem. Phys. **89**, 4918 (1988)