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Prediction and Observation of a New, Ground State, Dipole-Bound Dimer Anion: The Mixed Water/Ammonia System

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The first study of very low energy electron attachment to mixed water-ammonia clusters is reported here. A "magic" cluster anion distribution with strong similarities to that of pure water cluster anions is observed. The mixed $(H_2O\ldots NH_3)^-$ dimer is created under very specific experimental conditions and its existence is a test of the theory of electron binding by a dipole. This fragile species has a very small electron binding energy as inferred from field detachment experiments.

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The interaction of an electron with homogeneous assemblies of both water and ammonia molecules has generated considerable interest [1]. While individual molecules of neither water nor ammonia can bind excess electrons to form stable molecular anions, in the condensed phase both water and ammonia readily solvate them. This implies that the association of electrons with these solvents is a collective interaction requiring an assemblage of solvent molecules. These observations formed the basis of speculation some years ago that both water and ammonia clusters at some size(s) ought to be able to bind excess electrons, the existence of the resultant cluster anions depending on a delicate interplay between electron-molecule, molecule-molecule, and electron-multimolecule interactions. Following a period of searching by several investigators, both water and ammonia cluster anions, $(H_2O)_N{}^-$ and $(NH_3)_N{}^-$, were observed by Haberland *et al.* [2], and thereafter experiments on them were conducted in several laboratories [3–7]. Ammonia forms no cluster anions until size $N=34$, beyond which all cluster anion sizes are observed. Water, on the other hand, forms all cluster anion sizes (except $N=4$), but with $N=2$, 6, and 7 being overwhelmingly the most abundant species observed below $N=11$, the practical onset for the continuing formation of water cluster anions. The experimental observation of small water anions requires specific conditions, i.e., cold neutral parents and very low energy (in the meV range) attached electrons [2,5,7].

Clearly, these two polar systems experience drastically different interactions with electrons. Because of the vast differences in behavior between ammonia and water cluster anions at small sizes, the very existence of small, mixed water/ammonia cluster anions was, until now, an open question. It was not clear how similar or dissimilar small cluster anions, made up of a mixture of rather different solvents, would be to their homogeneous counterparts.

While relatively little information exists about the nature of water hexamer and heptamer anions, much more is known about the water dimer anion. Theoretical calculations [8–11] and experimental observations [2,5,7] have characterized the water dimer anion as a ground state, dipole-bound anion with a very diffuse excess electron charge distribution; i.e., the excess electron is bound by the long-range, dipole field of the neutral water dimer. There is a substantial body of theoretical work concerning the binding of electrons by dipole fields [12–14]. This is supported by high resolution spectroscopy on excited state, dipole-bound anions [15]. For finite, rotating dipoles the critical dipole moment for electron binding is thought to be $\approx 2D$, the exact value depending on the dipole length, the rotational constants of the system, and its rotational state. The dipole moment of the water dimer neutral is known from molecular beam electric resonance (MBER) studies to be $\approx 2.6D$ [16], and it binds an electron to give the water dimer anion. The dipole moment of ammonia dimer neutral is known, also from MBER, to be $\approx 0.7D$ [17], and, as already mentioned, there is no evidence for the existence of the ammonia dimer anion. The mixed water/ammonia dimer neutral has also been studied via MBER, and its dipole moment is $\approx 2.9D$ [18]. Thus, based on these considerations, there was substantial reason for us to suspect *a priori* that the water/ammonia dimer anion might exist as a dipole-bound anion.

Here, we present the results of our study of small water-ammonia cluster anions. These species were formed via electron transfer collisions between small cold water/ammonia clusters and laser-excited Rydberg atoms. This method [6,7,19] provides not only very low energy electrons, but also unusually fine control of their energies, both important assets in the formation of fragile anionic species. The presence of the Rydberg ionic core interaction with the nascent cluster anion during the collision also appears to be an efficient means of stabilizing anions against autodetachment [7].

The experimental apparatus has been described previously [20]. In brief, a pulsed beam of metastable xenon atoms created by electron bombardment is further excit-

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ed downstream by means of a pulsed, tunable dye laser towards *nf* Rydberg states. The Rydberg atomic beam intersects a pulsed cluster beam obtained by flowing 3 bars of helium over an ammonia and water liquid mixture (vapor pressure ~100 Torr) and expanding this gas mixture through a 0.15 mm room temperature nozzle. The cluster beam is first skimmed before penetrating into the collision region which is the extraction zone of a conventional Wiley McLaren time-of-flight (TOF) mass spectrometer. The Rydberg *n* dependences of the rate constants for cluster anion production are obtained by comparison with signals of SF_6^- production in collisions with a thermal beam of SF_6. The high relative collision energies obtained with helium as the carrier gas (from 0.5 eV for dimers up to 2 eV for the largest observed clusters) guarantee that no Coulombic pairs between the Xe^+ core and the anions will be formed [7]. Electric field detachment of electrons can provide estimates of excess electron binding energies. This is performed for dimer anions by means of three planar grids perpendicular to the ion path. The two external grids are grounded while the internal one is set to a positive high voltage. In order to ensure a sufficient field homogeneity, the grids are equally spaced by 2.25 mm which is 4 times the mesh. A fourth grid placed just before the microchannel plate detector can be either grounded to detect both ions and neutrals or biased at -2.5 kV in order to repel anions, since their energy is 1.65 keV. We measured the ratio of the number of detected neutrals over the total number of anions plus neutrals as a function of the electric field inside the three-grid region. The TOF tube being coaxial with the cluster beam, even at zero field, 30% to 40% of the detected particles are already neutrals produced by dissociating and detaching collisions with the background helium gas. Dimer anions spend more than 10 ns between the grids which is much longer than their rotational period so that field detachment can occur in the most favorable relative orientation between their dipole moments and the electric field.

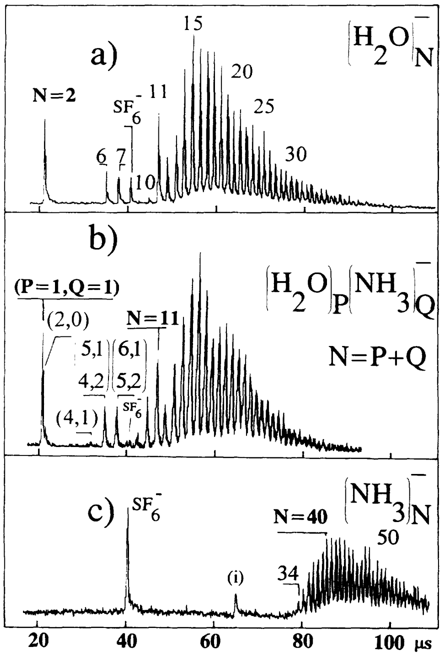

FIG. 1. Mass spectra of (a) $(H_2O)_N^-$, (b) mixed $[(H_2O)_P(NH_3)_Q]^-$, and (c) $(NH_3)_N^-$ cluster anions, resulting from collisions of laser-excited $Xe^{**}(13f)$ atoms with water, mixed water/ammonia, and ammonia neutral clusters, respectively [in (c), (i) is an impurity emitted by the electron gun].

Figure 1 shows for comparison the mass spectra of $(H_2O)_N^-$, $(NH_3)_N^-$, and $[(H_2O)_P(NH_3)_Q]^-$, the latter obtained via a water-ammonia mixture with helium as the carrier gas. This constitutes the first observation of mixed ammonia-water cluster anions. The mass identification is more than adequate to ensure that the $[(H_2O)_P(NH_3)_Q]^-$ mass spectrum is not just $(H_2O)_N^-$. A striking magic number pattern of mixed $[(H_2O)_P(NH_3)_Q]^-$ anions appears with magic numbers $N=P+Q=2$, 5, 6, 7, 9, and above. Ammonia seems to substitute easily for the role of water, at least for one or two monomer units.

Figure 2 displays the *n* dependences of relative rate constants for the production of $(H_2O)_2^-$, $(H_2O\ldots NH_3)^-$, and $(D_2O\ldots ND_3)^-$ dimer anions via electron transfer during collisions of $Xe^{**}(nf)$ Rydberg atoms and neutral clusters with helium carrier gas. While the water dimer anion is observed over a rather wide range of Rydberg quantum numbers ($10 \leq n \leq 20$), sizable signals corresponding to the mixed $(H_2O\ldots NH_3)^-$ or $(D_2O\ldots ND_3)^-$ anions appear only over a somewhat narrower range ($n=12$ to 16) without any isotopic effect. This suggests that mixed dimer anion formation conditions may be rather specific. The maximum value is obtained for all these dimer anions at nearly the

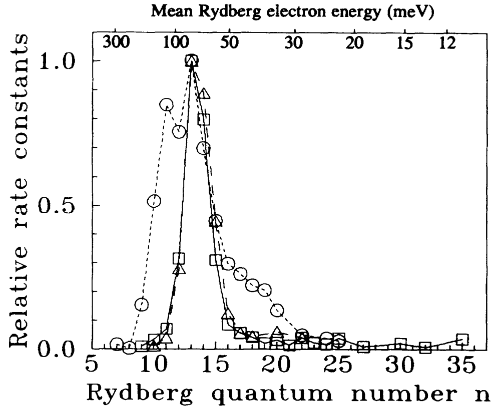

FIG. 2. The *n* dependences of relative rate constants for the formation of the $(H_2O)_2^-$ (circles), $(H_2O\ldots NH_3)^-$ (squares), and $(D_2O\ldots ND_3)^-$ (triangles) dimer anions in collisions of $Xe^{**}(nf)$ atoms with, respectively, water, mixed water/ammonia, and deuterated water/ammonia neutral clusters in He carrier gas.

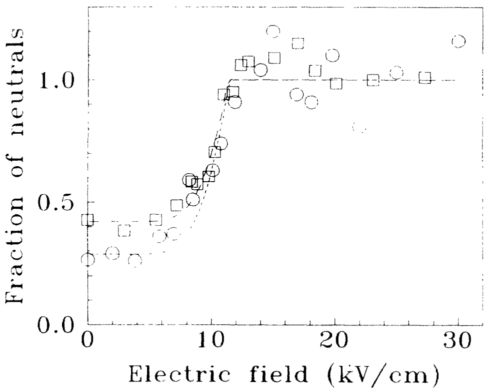

FIG. 3. Fraction of $(H_2O)_2$ (circles) and $(H_2O...NH_3)$ (squares) neutral dimers detected after field detachment of the corresponding anions, as a function of the applied electric field. The dotted lines correspond to the respective fits (see text).

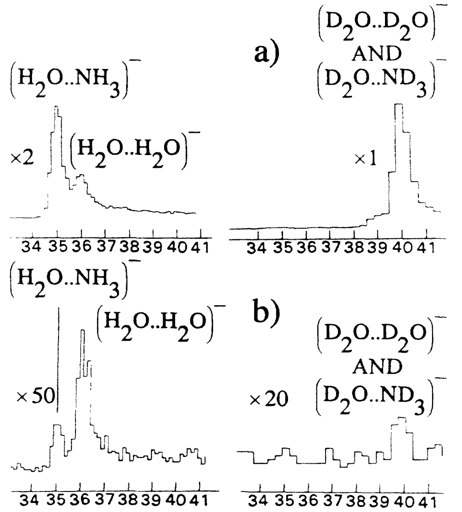

FIG. 4. Isotopic dependence of the mass spectra of water and mixed water/ammonia dimer anions due to collisions of (a) Xe**(13f) and (b) Xe**(18f) Rydberg atoms with the corresponding neutral parents. The mean Rydberg electron energies are 80 and 42 meV, respectively.

same n value, around $n=13$ [7].

The results of field detachment experiments are displayed in Fig. 3, where the fraction of arriving neutrals is plotted as a function of electric field, for both $(H_2O)_2^-$ and $(H_2O...NH_3)^-$ ions. An electric field of 12 kV/cm is, in both cases, enough to detach all the remaining anions, while a previous experiment [21] found this threshold to be 31 kV/cm for $(H_2O)_2^-$. This discrepancy can be attributed to the internal energies of the anions which are created under very different conditions as well as to the different time dependences of the effective electric fields experienced by the anions. To model our results, we assumed that the excess electron is bound by a pure dipole field, and we used known dipole moment values for parent neutral dimers [16,18]. The calculation of the tunneling probability through the potential barrier, when the electric field and the dipole moment are parallel, provided us with best fits for electron binding energies close to 9 meV in both cases.

The high energy tails of free electron sources [2-5] can lead to dissociative attachment. The well controlled energy distributions of Rydberg electron sources, on the other hand, are likely to preclude dissociative attachment. This is confirmed by the isotopic study displayed in Fig. 4 which establishes that the peak at mass 35 can be unambiguously identified as $(H_2O...NH_3)^-$ [and not as $(H_2O)OH^-$]. With deuterated water and ammonia, the single peak at mass 40 corresponds to both $(D_2O...ND_3)^-$ and $(D_2O...D_2O)^-$ species while no ion at mass 38, corresponding to $(D_2O)OD^-$, is detected. From MBER studies [18], the neutral mixed dimer structure is known, and there is no evidence for charge transfer in the gas phase. The anion we form thus does not originate from electron attachment to preexisting neutral $(NH_4{}^+OH^-)$ ammonium hydroxide. Furthermore, a large barrier for an intra-anion proton transfer can be estimated from available energetic data, and we can thus assert that the mixed water-ammonia anion corresponds to attachment of a low energy electron to a weakly bound neutral $(H_2O...NH_3)$ dimer.

The results presented above show that small, mixed water/ammonia cluster anions behave, in most ways, rather similarly to small water cluster anions. The evidence is of three types: magic numbers, Rydberg electron energy dependences for anion formation, and field detachment thresholds. Mass spectra of water/ammonia cluster anions show most of the same magic numbers as do mass spectra of water cluster anions, i.e., $n=2$, 6, 7, and from 11 on up (see Fig. 1). Some differences are observed in the water/ammonia case via the appearance of relatively intense mass peaks at $n=5$, 9, and 10. The Rydberg electron energy dependences of water dimer anions and of water/ammonia dimer anions show maxima at the same mean Rydberg electron energy (see Fig. 2). Differences appear in regard to the widths of their electron energy dependences. Field detachment studies show that both water dimer anions and water/ammonia dimer anions field detach at the same electric field (see Fig. 3).

Four different theoretical calculations [8-11] have characterized the water dimer anion as a ground state, dipole-bound anion. Three of the calculations found the electron binding energy to be very small (<6 meV) and the most stable structure of the dimer anion to be the same as that of the neutral dimer. A more recent calculation [11] found a somewhat higher dipole moment structure with a correspondingly higher electron binding energy. Three experiments have probed the water dimer anion. Field detachment experiments [21] found it to have a low electron binding energy, consistent with its characterization as a dipole-bound anion. From experiments employing collisions between neutral water clusters and laser-excited Rydberg atoms [7], the adiabatic electron affinity of the water dimer was estimated to be rather small. Photoelectron experiments [5] measured the vertical detachment energy of the water dimer anion to be 42 meV and found vibrational features in its spectrum, indicating that the structure of the dimer anion is at least slightly different from that of the neutral water dimer.

Based on the similarities between its behavior and that of the water dimer anion, the water/ammonia dimer anion is probably a largely dipole-bound species. In fact, there may be a whole class of ground state, dipole-bound anions which are formed by the interaction of electrons with appropriate weakly bound neutral dimers (and perhaps some trimers) and which can provide a new set of experimental reference points for the testing and further development of dipole-bound electron theory. The weakly bound neutral dimers in this test class must meet two requirements: (1) They must be composed of molecules which, on their own, cannot bind electrons, and (2) the dipole moments of these dimers must have been measured. Having met these specifications, the existence or nonexistence of specific dimer anions in this class would provide a basis for comparison with the predictions of dipole-bound electron theory. Since, for practical purposes, existence is being equated here with observation, it is important, at least initially, to attempt the formation of such fragile species with the most gentle experimental techniques available, and we have done so. Up to now, the water dimer anion has been the only precedent for the existence of such a system, and the ammonia dimer anion has served as an example of a negative existence result. The observation and characterization of the water/ammonia dimer anion reported here has been the first deliberate step in the exploration of this class of species. In the future, for those dimer and trimer anions found to exist, accurate measurements of their electron binding energies will also be valuable tools for advancing the theory.

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