Negatively Charged Water Clusters, or the First Observation of Free Hydrated Electrons

Martin Armbruster, Hellmut Haberland, and Hans-Georg Schindler
Fakultät für Physik, Universität Freiburg, D-7800 Freiburg, Germany

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We report the experimental observation of free negatively charged water clusters, i.e., $(H_2O)_n^-$ with $n \geqslant 8$. These species have been postulated to occur in irradiated liquids or high-density vapors—the so-called hydrated electrons—but have never been observed so far in the gas phase.

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We report in this Letter the first observation of free, negatively charged water clusters, $(H_2O)_n^-$ with $n \geqslant 8$. These fragile and elusive species have been postulated to exist in solids and liquids, the so-called "solvated" or "hydrated" electrons,[1] but have never been observed so far[2-4] in the gas phase. Their bulk properties, which resemble in many respects those of the F centers in alkali-halide crystals, are well studied.[1] Even commercial applications are known.[1c]

The H_2O molecule itself does not have a stable negative ion state. Electron scattering experiments indicate a strong electron dipole interaction,[5] and the existence of a resonant or virtual state of near zero energy. But the water dipole moment of $0.73ea_0$ ($=1.85$ D) is not strong enough to support a bound state. A point dipole can bind an electron[6] if its dipole moment is larger than $0.639ea_0$. Garrett[7] has shown that the influence of the finite size of a real molecule pushes this value to roughly ea_0. Although many molecules are known which have larger dipole moments,[2,7-10] no such dipole bound states have been observed so far unambiguously.[2,8]

Stillinger and David[11] calculated a dipole moment of $1.82ea_0$ for a cold, neutral water cluster $(H_2O)_n$ with $n = 8$, so that one can expect that a large water cluster is able to bind an electron. The existence of electrons bound to clusters of dipolar molecules has been proposed[12] to account for many properties of excess electrons in polar fluids and vapors.[1]

Many attempts have been made to produce free, negatively charged water clusters in the gas phase in order to check these ideas. Electron attachment,[2] or charge transfer by alkali beams[3] to water clusters, or high-pressure mass spectrometry[4] were not successful.

Our apparatus is shown schematically in Fig. 1. Water vapor of 100 to 1000 Torr and roughly 400 K is irradiated with electrons from a β^--radioactive ^{63}Ni foil. The electrons ($E_{max} = 66$ keV) are quickly thermalized, and from all prior experience[1,12] one knows that some solvated electrons are formed. The water vapor is expanded through a 60 μm hole into a vacuum. Within several microseconds the transition from a high density to free molecular flow is completed. Some of the charged clusters either survive this rapid expansion or, more likely, are formed during it. Because of the large pressure ratio of 10^6 to 10^7 no Mach disk[13] develops, which could destroy any fragile species. Even without charged particles, clustering of the water beam can be expected.[13] As the dipole moment of a cluster will depend on its temperature, a low cluster temperature can be expected if the electron is really dipole bound in $(H_2O)_n^-$.

Charged particles are accelerated by an electronic field between nozzle and skimmer, focused by an ion optical system, and mass analyzed by a time-of-flight (TOF) mass spectrometer (home built), or a quadrupole mass spectrometer (Balzers QMG511). Neutral particles in the beam can be monitored by electron impact ionization. The total mass flux through the nozzle is roughly

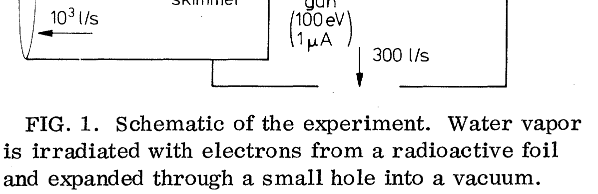

FIG. 1. Schematic of the experiment. Water vapor is irradiated with electrons from a radioactive foil and expanded through a small hole into a vacuum. Charged particles are accelerated by the electrically isolated skimmer, focused by the ion optics, and mass dispersed by two different methods.

10^{18} water molecules/sec, while only a total ion current of 10^4 to 10^5 ions/sec is observed. Because of this extremely small charge fraction, the free expansion is practically undisturbed. A radioactive source, or corona discharge in a high-pressure nozzle source, has been used previously to softly ionize large organic molecules with extreme sensitivity.[14]

Figure 2 shows TOF spectra of negatively charged ions for different electric fields between source and skimmer. One sees a regular procession of peaks, separated by 18 atomic mass units (u), the molecular weight of the water molecule. The resolution is not sufficient enough to resolve single masses, as the usual tricks[15] to increase the velocity resolution of a TOF spectrometer were not applicable, as a result of the field between nozzle and skimmer. There is some mass discrimination at higher masses.[16] The average cluster size is very much larger than that expected for neutral clusters.[13] It is well known, that clustering about ions is much more efficient than about neutrals.[17] Figure 2 shows a strong decrease of the average cluster size for increasing electric field. This field accelerates the ions, where the pressure is still quite high. They spend less time in the expansion zone, where the clusters are growing, and in addition the clusters are fragmented because of the many collisions they experience with particles from the neutral beam.[14c] Surprisingly these two processes yield mainly masses near multiples of mass 18. For pure water expansions we never observed negative ions smaller than roughly 72 u, corresponding to masses near $(H_2O)_4^-$, while for CO_2[2,16] or mixed CO_2-H_2O[16,18] expansions many smaller clusters are observable. Also the mass spectra of positively charged water clusters show many masses below 72 u.

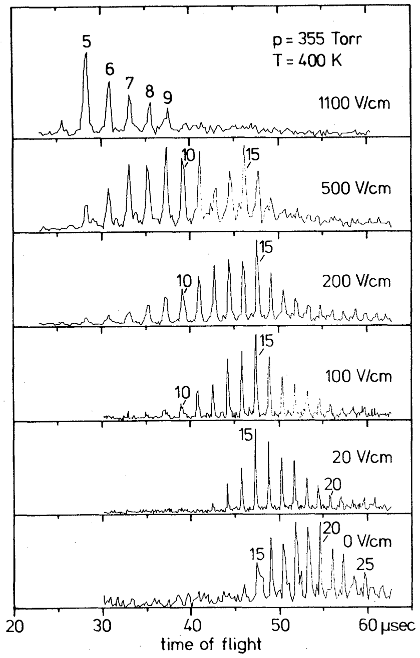

FIG. 2. Time-of-flight spectra of negatively charged clusters from a pure water expansion for different electric fields between the nozzle and the skimmer. The numbers on the peaks give the nominal number of water molecules in a cluster. The strong fragmentation is discussed in the text.

Figure 3 shows two scans with the quadrupole mass sepctrometer. In Fig. 3(a) the peak corresponding to eleven water molecules plus one electron has the highest intensity. We interpret this peak at mass 198 as the first observation of free hydrated electrons. The mass scale of the quadrupole was carefully calibrated before this run and checked for zero drift afterwards. Figure 3(b) shows a mass spectrum around 90 u, or roughly five water molecules per cluster. Within statistical error no $(H_2O)_5^-$ is observed in this spectrum. Under different experimental conditions a very small peak was sometimes observed at mass 90, so that we cannot place a lower limit on the number of water molecules sufficient to bind an electron. But eight H_2O molecules will definitively be sufficient. A lower limit of six water molecules has been calculated previously.[12a] We purposely do not give an intensity distribution of the negative water clusters, as this depended sensitively on many source parameters.[16] The scan of Fig. 3(b) was taken with somewhat better resolution than that of Fig. 3(a).

The O^- and OH^- ions are stable, and clusters of the form $(H_2O)_nX^-$, $X = O$, OH are well known.[2] The peaks at 91 or 199 u can be interpreted as $(H_2O)_nH^-$, $n = 5$ or 11. This ion has never been observed in the gas or liquid phase, but H^- has been postulated to occur in irradiated solids.[19] Peaks similar to that at M-3 (mass 87) in Fig. 3(b) were observed also for some heavier clusters. The only possible interpretation seems to be a structure of the type $[(H_2O)_3O(OH)]^-$. Also the other peaks, which are labeled by their mass only, have not been observed so far.

It would be very interesting to perform photodetachment experiments with a mass-selected water cluster beam. We conjecture that the unstructured optical absorption continuum[1] observed in the liquid and solid phase will show

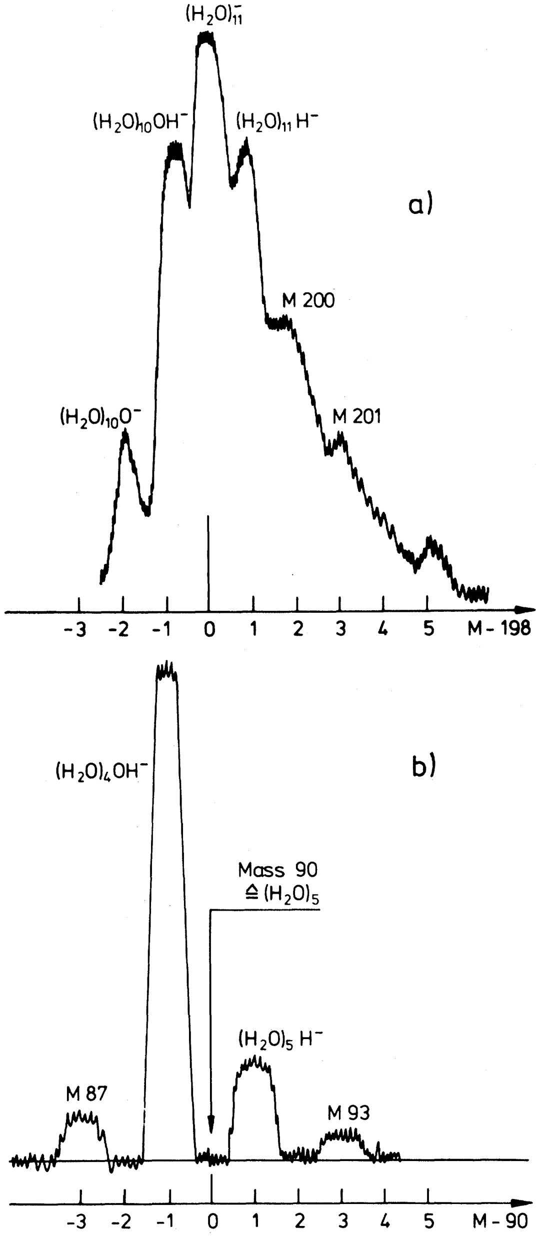

FIG. 3. (a) Negative-ion mass spectrum with use of the quadrupole mass spectrometer. We interpret the peak at mass 198 as a negatively charged cluster of eleven water molecules. This is the first observation of a free hydrated electron, which has so far only been postulated to exist in liquids or high-density vapors. The electron might be dipole bound only. The field between nozzle and skimmer was $E_{ns} = 100$ V/cm. (b) Mass spectrum for $E_{ns} = 500$ V/cm. No intensity is observed for mass 90 corresponding to five water molecules per cluster.

some structure. If the electron in $(H_2O)_n^-$ is dipole bound, it will be in an extremely diffuse orbital.[10b] Its charge density close to the water molecules would then be nearly negligible, so that the internuclear force field should not change too much, if the electron is removed. Photodetachment from a cold, mass-selected, negative cluster beam can therefore be expected to give no fragmentation of the clusters. As far as we know, no other method has so far been proposed which would give a mass-selected neutral cluster beam. Unfortunately, the intensities are presently many orders of magnitude too low for these kinds of experiments. We recorded only 80 counts/sec for the $(H_2O)_{11}^-$ peak in Fig. 3(a).

Localized electrons in liquid helium are well studied,[1,20] and large He clusters (n up to 10^8) have been produced.[21] With use of our method one could look for some He^- cluster ions, with the electron in a bubble state.[1,20]

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Influence of Singlet-Triplet Mixing on the Hyperfine Structure of 5*snd* Rydberg States in ^{87}Sr

R. Beigang, E. Matthias, and A. Timmermann
Institut für Atom- und Festkörperphysik, Freie Universität Berlin, D-1000 Berlin 33, West Germany

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A systematic study of the hyperfine structure of 5*snd* $^1D_2$ and $^3D_2$ states of ^{87}Sr was carried out by Doppler-free two-photon excitation. In the region of strong singlet-triplet mixing around $n = 16$, the hyperfine structure exhibits a marked n dependence which is related to the amount of singlet-triplet mixing.

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For excited states of two-electron systems the hyperfine structure (hfs) provides a sensitive probe both for the type of coupling and for possible admixtures of other states. A typical example is the hyperfine structure of 1*snd* ^1D levels in ^{3}He which has been shown to arise from admixture of ^3D states.[1] In their recent study of the hfs of various levels of ^{3}He, Liao *et al.*[2] emphasized the crucial role of the Fermi contact interaction of the inner s electron to the electronic structure of high-n Rydberg states. The singlet-triplet mixing effects observed in ^{3}He are expected to also occur in other two-electron systems. It is therefore of interest to investigate the hfs of Rydberg states of alkaline-earth atoms, particularly in regions of the principal quantum number n where mixing of states is indicated by other experiments. The first results on a few levels in Ba point indeed towards strong perturbations of the levels investigated.[3] A more favorable case is Sr, for which Esherick[4] has shown that strong singlet-triplet mixing occurs in 5*snd* states around $n = 16$, while for $n \leq 10$ and $n \geq 30$ the ^1D and ^3D can be regarded as being "pure" states. Wynne, Armstrong, and Esherick[5] verified that the g factors of 5*snd* $J = 2$ states accurately reflect the change of admixture. For the same reason we expect the hfs of ^{87}Sr to vary with the principal quantum number between $n = 10$ and 30. It is the purpose of this Letter to present a first systematic study of the hfs of 5*snd* Rydberg states of ^{87}Sr for a wide range of n and to demonstrate the drastic influence of singlet-triplet mixing on the hfs. We expect that this will be of importance also for other two-electron systems.

The energy difference between the ground state and the 5*snd* states[6] in strontium can be bridged by two-photon excitation. In our experimental