High-Resolution Electron Attachment to the Water Dimer Embedded in Helium Droplets: Direct Observation of the Electronic Conduction Band Formation

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ABSTRACT: For bulk liquid helium the bottom of the conduction band \( V_0 \) is above the vacuum level. In this case the surface of the liquid represents an electronic surface barrier for an electron to be injected into the liquid. Here we study the electronic conduction band for doped helium droplets of different sizes. Utilizing an electron monochromator, the onset of the \((\text{H}_2\text{O})_2^-\) ion yield corresponding to \( V_0 \) is determined for helium droplets doped with the water dimer. While for larger droplets the onset approaches the well-known bulk value of about 1 eV, the barrier does not continuously decrease with smaller droplet size. A minimum value of \( V_0 = 0.76 \pm 0.10 \) eV is observed, which corresponds to a droplet size of \( N_{\text{min}} = 1600 \pm 900 \). For droplet sizes below \( N_{\text{min}} \), a peak at \(-0.2 \) eV appears, which is well-known from neat H\(_2\)O clusters. Hence, we interpret \( N_{\text{min}} \) as the smallest droplet size in which the electronic band structure is formed in liquid helium droplets.

Clusters and droplets are known to be ideal systems for studying the transition between microscopic systems like single atoms or molecules and the macroscopic bulk matter. One fundamental property in this context is the electronic structure, which changes from the discrete levels of a single species to the electronic band structure of the bulk. In bulk liquid helium, the electron injection into the liquid is characterized by initial entry of the excess electron in the electronic conduction band with its minimum energy given by \( V_0 = 1.06 \) eV above the vacuum level,\(^{1,2}\) which reflects the subtle balance between long-range attractive polarization forces and short-range repulsive forces acting on the electron. The positive value of \( V_0 \) for helium indicates the dominant influence of repulsion (Pauli repulsion), i.e., the surface of the liquid represents an electronic barrier for an electron entering the liquid. We just note that bulk Ne shows the same property, while bulk media of the heavier rare gases Ar, Kr, and Xe possess a negative value of \( V_0 \), i.e., energy is released once the electron enters the medium.\(^{3}\) After thermalization of the electron in bulk liquid helium, within picoseconds,\(^{4}\) the excess electron is localized in an electron bubble with radius of about 17 Å.\(^{5}\)

In an earlier work by Martini et al., inelastic electron scattering from pure He droplets was studied.\(^{6}\) Droplets were formed by supersonic expansion of precooled helium through a nozzle. They observed an increase of the excitation threshold for the metastable 2s\(^3\)S level with decreased nozzle temperature, which corresponds to an increased average droplet size. This shift was attributed to the electronic surface barrier for electron injection into the liquid helium mentioned above. While at expansion temperatures of 10 and 11 K a barrier of 1.03 ± 0.20 eV was observed (in good agreement with the bulk value of \( V_0 \)), the barrier decreased to 0.78 ± 0.20 eV at 13.2 K and 0.68 ± 0.20 eV at 14.9 K. Values at other temperatures were not reported by Martini et al. The decrease of \( V_0 \) with increasing expansion temperature was ascribed to the droplet-size-dependent atomic density of the droplets, i.e., smaller droplets have a lower density, which leads to a decrease of \( V_0 \).

Interestingly, in previous photoionization studies of Kr- and Xe-doped He droplets using synchrotron radiation, a broad, unstructured peak was observed in the photoelectron spectra (in addition to a series of structured peaks).\(^{7}\) For large droplets with an average droplet size \( \langle N \rangle = 2.5 \times 10^3 \), this unstructured feature showed an onset close to 1 eV. Hence, this onset was attributed to the bulk band edge developed at this droplet size, which acts as an exit barrier for electrons leaving the droplet. It should be noted that the unstructured peak was observable only for droplets larger than \( \langle N \rangle \approx 1200 \). The authors of ref 8 pointed out two possibilities to explain this result: (i) at smaller droplet sizes the concept of a conduction band becomes invalid, or (ii) the attractive Coulomb potential between the photoelectron and the ion starts to alter the dynamics of the electron escaping the small droplet.

In the present study, we investigate the injection of a free electron into doped helium droplets, i.e., the reverse process of that studied in ref 8. As discussed in the following, we study...

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water dimers as dopants. Electron attachment to small water clusters shows particular features, which we exploit to determine the electronic surface barrier of helium droplets. By recording the dimer ion \((\text{H}_2\text{O})_2^-\) at different sizes of the helium droplet, we can extract unambiguous evidence on the development of the electronic conduction band in He droplets \((V_0)\) and estimate the minimum droplet size for which the electronic conduction band is developed.

Figure 1a presents the ion yield curve of the dimer recorded at the nozzle temperature of 9 K. The water pressure in the ion source chamber was \(0.4 \times 10^{-7}\) mbar for the measurement shown. The ion yield is characterized by one single resonance peaking close to 1.2 eV. As shown in the figure, the threshold energy of the measured peak is obtained by extrapolating the linear part of the low-energy side of the resonance to the noise level. By this method, we observe a threshold of \(0.96 \pm 0.05\) eV.

Before discussing this result in more detail, we shall briefly summarize the state of the art concerning electron attachment to (i) single water molecules in the gas phase, (ii) water clusters in the gas phase, and (iii) water clusters embedded in helium droplets. The free electron capture by isolated water molecules yields the fragment anions \(\text{O}^-\) and \(\text{H}^-\) via dissociative electron attachment. These channels are operative only within a series of three core-excited resonances in the energy range 6–15 eV, where two electrons occupy formerly unoccupied molecular orbitals.\(^{9,10}\) No isolated molecular anion of \(\text{H}_2\text{O}\) is observable on mass spectrometric time scales. Calculations showed that the binding energy of the electron to a single water molecule is exceedingly small and for equilibrium configuration of the nuclei undistinguishable from zero.\(^{11}\) However, in 1987 it was shown that electron attachment to water clusters (studied at the low electron energy resolution of about 1 eV) additionally leads to the nondissociated ionic complexes \((\text{H}_2\text{O})_n^-\) \((n \geq 11)\) which are formed within a resonance close to the threshold of \(\sim 0\) eV.\(^{12}\) Later, a study at ultrahigh-energy resolution (1 meV, restricted to the energy range below 80 meV) by means of a laser photoelectron attachment method\(^{13}\) yielded also smaller cluster ions \((\text{H}_2\text{O})_n^-\) \((n = 2, 6, 7, 11, 15)\) which are formed right at the threshold \((\sim 0\) eV) within a very narrow resonance (width < 20 meV). The observation of smaller water cluster anions was ascribed to a lower temperature of the clusters (hence depending on the experimental method used to produce the clusters). Helium droplets with a droplet temperature of \(\sim 0.4\) K provide an ideal heat bath to produce cold water clusters. Electron attachment to \((\text{D}_2\text{O})_n@\text{He}\) was studied in our laboratory\(^{14}\) with a low electron energy resolution of about 1 eV. The study revealed formation of \((\text{D}_2\text{O})_n^-\) \((n \geq 2)\) in a single resonance located at around 1.5 eV (the estimated accuracy of this value was a few tenths of an electronvolt). A precise determination of the peak onset was impossible because of the limited energy resolution of the electron beam. However, the ion yield for \((\text{D}_2\text{O})_2^-\) presented in ref 14 is at least in qualitative agreement with the present measurement.

The present ion yields for \((\text{H}_2\text{O})_2^-\) are measured at significantly improved electron energy resolution (100 meV) compared to the previous work. Hence, the onset of the resonance represents a measure of \(V_0\). The likely microscopic scenario for the electron attachment reaction under the conditions of Figure 1a is then as follows: An electron with an energy around 1 eV (in vacuum) impinges the target droplet containing water dimers. The electron is initially subjected to the short time electronic response (long-range attractive polarization interaction and short-range Pauli repulsion), thereby overcoming \(V_0\) and starting to propagate as a quasi free electron within the conduction band of the droplet.

Important to note in this scenario is the wavelength of the low-energy electron, which is in the order of the diameter of the He droplet. Hence, one can assume that electron attachment to the water dimer occurs prior to formation of the well-known excess electron bubble, the latter occurring on a comparatively longer time scale. In fact, the unexpected low electron mobility in bulk liquid He indicated excess electron localization;\(^{12,5,15}\) hence, the interior electron bubble state in bulk liquid He has been manifest for many years. The electron bubble state is energetically below that of the quasi free electron associated with \(V_0\). Excess electron bubbles also exist in He droplets, and the structure and energetics of them have been explored theoretically by Rosenblit and Jortner\(^{16}\) for droplet sizes ranging from \(N = 6.5 \times 10^3\) to \(N = 10^6\) He atoms. However, we can assume that for the present conditions, bubble formation can readily be excluded.

Accordingly, the formation of the dimer ion within the droplet can be viewed at threshold as direct electron attachment to the neutral dimer

\[
e^− + (\text{H}_2\text{O})_2 \rightarrow (\text{H}_2\text{O})_2^- \rightarrow (\text{H}_2\text{O})_2^- + \text{E}^* \tag{1}
\]

with \(\text{E}^*\) the electron affinity released to bind the extra electron to the dimer. This excess energy has to be dissipated within the droplet. This reaction is unlikely to be observed in the gas phase because of the restricted means to dissipate \(\text{E}^*\); hence, the formed water dimer anion is metastable. Desfrancois et al. reported a low (adiabatic) electron affinity of \(30 \pm 4\) meV for the water dimer.\(^{17}\) This value is much lower than the binding energy of the water dimer (155 meV\(^{17}\)). It is important to note
that for small water clusters, \( n < \sim 15 \), the electron affinity is smaller than the binding energy of a water molecule to the cluster.\(^3\) Dissipation of the excess energy by evaporation of single water molecules or fragmentation of the water cluster is not possible for those small sizes. Hence, the water dimer anion can be formed only by electron attachment to the neutral water dimer. However, the binding energy of He atoms in the droplet (0.62 meV bulk value, decreasing to 0.52 meV toward low droplet sizes\(^1\) is smaller than the electron affinity of the water dimer. Localization of the excess electron on the water dimer will lead to evaporation of only \( \sim 60 \) He atoms. Because bare water dimer anions are detected, these anions were expelled out of the helium droplets. One possible mechanism was reported earlier, in which a second electron is injected into the droplet.\(^1^9\) In this case Coulomb repulsion leads to bare dopant anions. Although the experiments are performed under single-collision conditions, it cannot be ruled out that such process happens. The single resonance observed near 1.2 eV indicates that reactions at the surface of the droplet can be excluded.

As noted by Martini et al., the value of \( V_0 \) depends on the helium droplet size. In order to relate the presently determined values of \( V_0 \) with the corresponding droplet sizes, the dependence of \( V_0 \) on the density of helium can be exploited. Taking the experimental barrier values determined as a function of the atomic density from ref\(^4\), we obtain an atomic density of \( 1.77 \pm 0.01 \times 10^{22} \text{ cm}^{-3} \) for \( V_0 = 0.96 \pm 0.05 \text{ eV} \). Effective densities of small helium droplets as a function of the droplet size were calculated by Harms et al.\(^2\) Using these density values we derive a droplet size of \( N = 11200 \pm 500 \) for the measured value of \( V_0 = 0.96 \pm 0.05 \text{ eV} \).

In subsequent measurements with the same droplet expansion conditions, we increased the water pressure in the pick-up cell. These measurements indicate that the peak threshold as well as peak maximum are strongly dependent on the water pressure. For example, Figure 1b shows the anion yield of the water dimer for three different pressures in the ion source chamber, \( 0.4 \times 10^{-7} \text{ mbar}, 1.0 \times 10^{-7} \text{ mbar}, \) and \( 1.7 \times 10^{-7} \text{ mbar} \). The data indicate that the peak maximum redshifts by more than 0.1 eV with increasing water pressure. The corresponding peak onsets are \( 0.96 \pm 0.05 \text{ eV}, 0.87 \pm 0.05 \text{ eV}, \) and \( 0.76 \pm 0.10 \text{ eV} \), respectively. Using the same procedure for the droplet size determination as described above, we obtain the droplet sizes \( N = 4500 \pm 500 \) for \( V_0 = 0.87 \pm 0.05 \text{ eV} \) and \( N = 1600 \pm 900 \) for \( V_0 = 0.76 \pm 0.10 \text{ eV} \), respectively. These results show that with increasing water pressure smaller droplets are doped with two water molecules, as expected. The present results can be compared with theoretical calculations on the droplet size dependency of \( V_0 \) by Rosenblit and Jortner.\(^5\) They predicted that \( V_0 \) increases from 0.95 eV at \( N = 6.5 \times 10^{3} \) to 1.02 eV at \( N = 1.9 \times 10^{3} \). These values are consistent with the present results and confirm the applicability of the presently used method to determine the helium droplet size for a given \( V_0 \).

Because the peak close to \( \sim 1.1 \text{ eV} \) is related to the presence of the electronic conduction band of the liquid helium droplet, we further investigated the evolution of the conduction band at even smaller droplet sizes. The latter were generated by further increasing the water pressure as well as increasing the temperature of the nozzle. Figure 2a shows the ion yields between \( \sim 0 \) and 2 eV recorded at the expansion temperature of 10.5 K (water pressure, \( 2.0 \times 10^{-7} \text{ mbar} \)) in comparison to the yield at 9 K (water pressure, \( 1.7 \times 10^{-7} \text{ mbar} \)). The resonance close to 1.1 eV is virtually identical at both temperatures.

![Figure 2](image)

**Figure 2.** Measured ion yields of the dimer anion \((\text{H}_2\text{O})_2^−\) resulting from electron attachment to helium droplets doped with water dimers. The electron energy range between \( \sim 0 \) and 2 eV is shown. (a) Data are shown for the water pressures \( p_{\text{H}_2\text{O}} = 1.7 \times 10^{-7} \text{ mbar} \) (nozzle temperature \( T = 9 \text{ K} \) ) (black line) and \( p_{\text{H}_2\text{O}} = 2.0 \times 10^{-7} \text{ mbar} \) (\( T = 10.5 \text{ K} \) ) (red line). While the peak close to 1 eV is virtually identical for both conditions, a peak close to 0 eV is present at higher pressure and temperature. The ion yield close to 0 eV indicates that in this case the water cluster captured an electron which did not enter the conduction band of the helium droplet. (b) The ion yield recorded at \( p_{\text{H}_2\text{O}} = 3.1 \times 10^{-7} \text{ mbar} \) (nozzle temperature \( T = 11 \text{ K} \) ). The disappearance of the resonance close to 1 eV indicates that no conduction band is present when the electron is captured by small doped droplets (see text).

However, in striking contrast, the ion yield at 10.5 K shows a pronounced peak at about 0 eV, i.e., at this electron energy the electron is attached to the water dimer without entering the conduction band. The observation of this 0 eV contribution can be explained in two ways: (i) the electron attaches to an almost bare water dimer or (ii) there exists a minimum size \( N_{\text{min}} \) for helium droplets, where the conduction band is present. The present experimental findings for the peak at about 1.1 eV strongly favor the latter explanation because the peak related to the conduction band obviously stops to shift to lower energies (see Figure 2a). The value \( V_0 = 0.76 \pm 0.10 \text{ eV} \) represents the lowest value, \( V_{\text{0,min}} \), obtained within the sensitivity of the present experiment. The existence of \( V_{\text{0,min}} \) is confirmed by the measurement at the expansion temperature of 11 K shown in Figure 2b (recorded at the water pressure of \( 3.1 \times 10^{-7} \text{ mbar} \)). In this case, the peak close to 1.1 eV completely vanished and only the 0 eV resonance is present. As mentioned above, for the presently obtained \( V_{\text{0,min}} \) a droplet size of \( N_{\text{min}} = 1600 \pm 900 \) is derived. This value is in good agreement with Wang et al.\(^5\) and confirms their previous assumption that the conduction band breaks down at a droplet size near \( 10^3 \) helium atoms.

In summary, the formation of water dimer anions emerging from electron attachment to \((\text{H}_2\text{O})_2\) doped He droplets is observed at an energy which is shifted by about 1.1 eV with respect to the corresponding reaction in the gas phase. The peak onset reflects the electronic surface barrier for the free electron to penetrate from vacuum into the He droplet, thus representing the bottom of the electronic conduction band in He droplets. We determined the threshold for different droplet sizes and derived the minimum droplet size, where the electronic band features of the liquid are developed. We note in this context that theory predicts for electron bubble...
formation in pure helium droplets a minimum droplet size of 4500 ± 700 (with the lower and upper limits representing the threshold of dynamic and energetic stabilities). Hence, excess electrons may remain delocalized in the conduction band of pure helium droplets in the size regime between about 1600 and 4500 and are highly mobile within such droplets before escaping into the vacuum.

**EXPERIMENTAL METHODS**

The present experiments are performed with a He droplet source combined with a pick-up cell containing H$_2$O vapor, an ion source, and a mass spectrometer system to analyze the resulting anions as previously described in detail. The helium droplet beam is formed by expansion of He through a nozzle of 5 μm diameter into vacuum at a temperature between 9 and 11 K and at a constant pressure of 20 bar. At a distance of 1 cm downstream, the He droplets pass a skimmer before they enter a differentially pumped chamber containing a pick-up cell, an ion source, and a mass analyzer. After passing the pick-up cell, the H$_2$O-doped helium droplets enter the collision region of the ion source, where free electron attachment to the doped droplets takes place. The electron beam is generated by a home-built hemispherical electron monochromator, which provides an electron beam with a full width at half-maximum of about 100 meV. The electron energy scale is calibrated by measuring the well-known resonance in SF$_6$ yielding SF$_{6-}$ close to threshold (~0 eV). Ion yields at negative electron energies are caused by the finite resolution of the electron beam. Anions formed are mass selected by a quadrupole mass filter and detected by a channel electron multiplier. In general, the number of pick-up events can be changed by adjusting the water pressure in the pick-up cell. All H$_2$O partial pressures mentioned were determined by an ion gauge mounted at the ion source chamber. Hence, the exact pressure in the pick-up cell is unknown; however, the chamber pressure can be considered a qualitative measure of the pressure in the pick-up cell.

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Notes

The authors declare no competing financial interest.

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