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Field detachment of  $(\text{H}_2\text{O})_2^-$  clustered with rare gases

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The electron affinity of  $(\text{H}_2\text{O})_2^-$  is estimated to be 17 meV, based on electric-field-detachment measurements. The shift of the electric field necessary for electron detachment from  $(\text{H}_2\text{O})_2^-$  clustered with Ar, Kr, and Xe is interpreted in terms of Fermi's theory of the pressure shift of Rydberg spectra, extended to a dipole-bound electron. The implications of these results for electron localization in gaseous and bulk water are briefly discussed.

Studies of electron localization in liquid and amorphous media have a history more than 100 years old.<sup>1-5</sup> In the last three decades electron localization in water has been a central point of these studies because of its extremely fast (less than 300 fs) relaxation and the biological and radiological implications.<sup>2-5</sup> Only recently has electron localization been studied in water clusters, both experimentally<sup>6-10</sup> and theoretically.<sup>11-16</sup> The motivation of the cluster work is manifold. First, there is an intrinsic interest in studying these systems because of their small finite size; second, new powerful theoretical methods make a computer simulation of the quantum path integral of the electron interacting with the cluster possible; third, the theoretical results can be better checked in a cluster than in the bulk; and fourth, there is hope that the cluster studies will shed new light on the bulk results. Data are presented here for the smallest electron-water system possible, one electron interacting with two water molecules to form  $(\text{H}_2\text{O})_2^-$ .

Closed-shell atoms and molecules do not in general have bound negative-ion states as monomers, if one excludes highly distorted nuclear configurations of the molecules. But 2 water molecules,<sup>7(b)</sup> 35 ammonia molecules,<sup>7</sup> and 3 mercury atoms<sup>17</sup> do have such states. These clusters at the threshold of stability can be expected to have a small electron affinity and consequently a diffuse electron orbital. A strong electric field can be used to detach the electron, a method which is used extensively for the detection of atoms in Rydberg states.<sup>18</sup> We have used this method to measure field detachment of  $(\text{H}_2\text{O})_2^-$  and  $(\text{H}_2\text{O})_2^-R_n$  ( $R = \text{Ar}$ ,  $n < 7$ ;  $R = \text{Kr}$ ,  $\text{Xe}$ ,  $n \leq 2$ ) and have extracted approximate electron affinities from these data. The results are compared to two recent calculations.<sup>14,16</sup>

The experiment is shown schematically in Fig. 1. Negative cluster ions are produced by injecting low-energy

electrons into a supersonic expansion.<sup>7,8</sup> Using a pure-water expansion, only  $(\text{H}_2\text{O})_n^-$  with  $n \geq 11$  are observed.<sup>6-9</sup> When the water vapor is seeded in a rare-gas expansion, which produces colder clusters, smaller  $(\text{H}_2\text{O})_n^-$  (with the exception of  $n = 1$  and  $n = 4$ ) are also observed, as well as  $(\text{H}_2\text{O})_n^-R_m$  where  $R = \text{Ar}$ ,  $\text{Kr}$ ,  $\text{Xe}$ .<sup>7</sup> The dimer anion is observed only in a strong expansion if the partial water pressure is below 2%.<sup>7(b)</sup> From a comparison with the experiment of Odutola and Dyke,<sup>19</sup> we expect a temperature lower than 20 K for  $(\text{H}_2\text{O})_2^-$ .

For field-detachment experiments, a high electric field is placed before the quadrupole mass spectrometer. No field detachment was ever observed for  $n > 2$ . All intensities were therefore normalized to that of  $(\text{H}_2\text{O})_6^-$ . Fig-

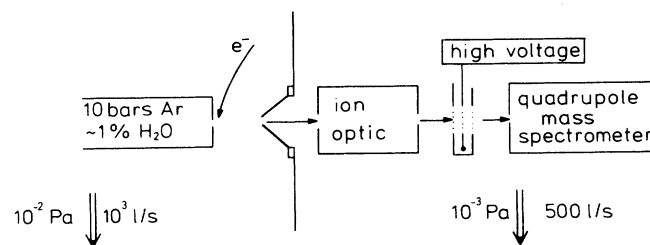


FIG. 1. Schematic of the experiment. A supersonic rare-gas expansion seeded with less than 1% of water is used to produce cold clusters. Slow electrons from a hot filament or a glow discharge are mixed into the expanding beam. Weakly bound and unstable cluster ions can be formed and are subsequently cooled by the expansion. The ions traverse a skimmer, are focused into a parallel beam, and traverse a high electric field produced by three planar grids. The field lines are parallel to the ion path. The ions are separated by a quadrupole mass spectrometer and detected by a channeltron.

ure 2 shows some data for Xe as carrier gas. We define, as the disappearance or detachment field, the point where the intensity has dropped to 1% of its zero-field value. Because of the steep slope of the intensity near this value, the detachment field depends only weakly on the setting of the ion optics. Above 3.1 MV/m  $(\text{H}_2\text{O})_2^-$  disappears. With the addition of one xenon atom this value shifts to 4.3 MV/m, while for  $(\text{H}_2\text{O})_2^- \text{Xe}_2$  this value is higher than 5.5 MV/m, the present limit of our apparatus. An isotope effect is observed; the value for  $(\text{D}_2\text{O})_2^-$  is 2.9 MV/m. All  $(\text{H}_2\text{O})_n^- R_m$  results are collected in Fig. 3. The experimental error on these numbers is  $\pm 0.1$  MV/m, except for Kr where it is  $\pm 0.2$  MV/m. Note that in the limit of arbitrarily many added rare-gas atoms this experiment corresponds to a matrix-isolation experiment on  $(\text{H}_2\text{O})_2^-$ .

No theory is known to us which can be used to obtain electron affinities from the data. A classical model, similar to that used for field detachment of Rydberg atoms, will be used to estimate binding energies.<sup>18</sup> The longest-range part of the electron-water dimer potential is the dipole-charge interaction.<sup>12</sup> We assume that the presence of the weakly bound electron does not change the dipole moment of the water dimer significantly. The long-range part of the potential including the electric field is then given by

$$V(\mathbf{r}) = -\frac{\boldsymbol{\mu} \cdot \mathbf{r}}{r^3} - Fz \quad (1)$$

Here  $\boldsymbol{\mu}$  is the dipole moment of the neutral water dimer<sup>19</sup> (1.02 a.u.), and  $\mathbf{r}$  is the electron coordinate. The dipole moment is large enough to support a bound electronic state if the rotational energy is low enough.<sup>12</sup> The electric field of strength  $F$  is applied in the  $z$  direction. The lowest rotational transitions of the neutral dimer<sup>19</sup> lie in the 6- to 200-GHz range. The dimer anion spends about 20 ns in

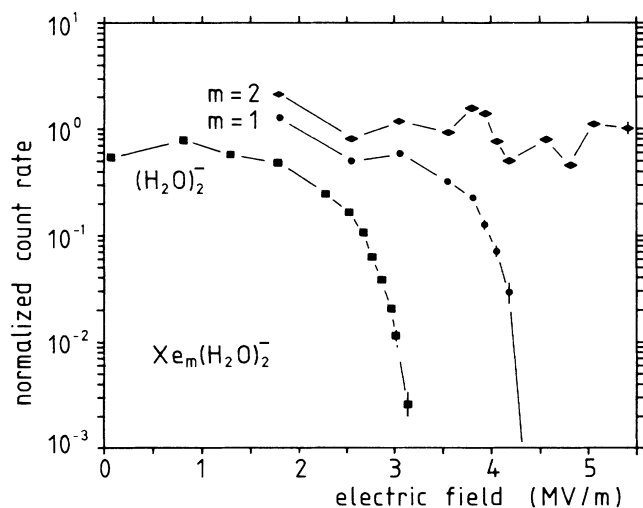


FIG. 2. Intensity of  $(\text{H}_2\text{O})_2^- \text{Xe}_m$ ,  $m=0,1,2$ , as a function of the electric field. Detachment of the weakly bound electron is observed for  $m=0$  and  $m=1$  at high enough fields, leading to the rapid decrease of signal intensity. The detachment field for  $m=2$  is above the present capability of the apparatus.

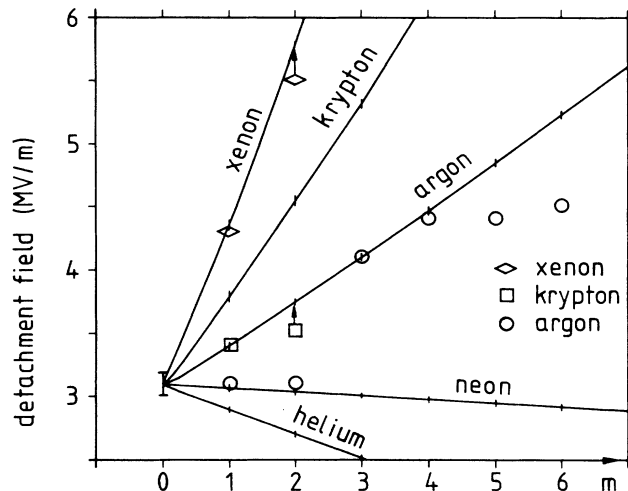


FIG. 3. Comparison of the experimental and calculated field detachment values. The agreement is surprisingly good, in spite of the simple model used. The solid lines give the calculated field detachment shifts as a function of the number of rare-gas atoms. The symbol ( $\dagger$ ) is used if only a lower bound could be obtained experimentally.

the high electric field. During this time there will be many occasions where the electric field is parallel to the rotating dipole moment. In this configuration the probability for detachment is highest. Field detachment is fast compared to rotation. From the analysis given below it follows that the electron is in a very diffuse state of about 40 a.u. diam. It takes less than 90 fs to accelerate it across this distance in an electric field of 3 MV/m. As this time is short compared to the time scale of relative motion of the molecules, the detachment threshold can be expected to measure the vertical and not the adiabatic electron affinity. Proceeding as in the case of Rydberg-atom field ionization, we look for the saddle point ( $z_s$ ) of Eq. (1) for a field of 3.1 MV/m, assuming that all vectors are parallel. This treatment neglects all Stark shifts, etc. For Rydberg atoms the value of  $-V(z_s)$  gives the correct electron affinity if the field strength rises slowly enough.<sup>18</sup> In this experiment the rate of field change is fast, at least  $10^{14}$  V/m.s. Atoms in Rydberg states show diabatic crossing of Stark levels at fast field changes, which leads to a lower field-detachment threshold. If and how this argument applies to a dipole-supported negative-ion state is unknown.

One obtains an electron affinity of 17 meV for  $(\text{H}_2\text{O})_2^-$  and 16 meV for  $(\text{D}_2\text{O})_2^-$ . Note that this is the first experimental estimate of this quantity.<sup>20</sup> Two quantum-path-integral calculations have very recently been performed for  $(\text{H}_2\text{O})_2^-$ . The electron affinity calculated by Wallqvist, Thirumalai, and Berne<sup>14</sup> is 3 to 6 meV, while Landman *et al.*<sup>16</sup> obtain 4 meV for the adiabatic and 15 meV for the vertical electron affinity. Field detachment from a dipole-supported state of an electronically excited organic molecule has been described by Lykke *et al.*<sup>21</sup> They find detachment for fields less than 70 V/cm at a binding energy of 0.6 meV. From Eq. (1) one would obtain a factor of about 20 less.

It would be extremely interesting to study if  $(\text{H}_2\text{O})_2^-$  is the weakly bound trap state which is thought to be the first step of electron localization in vaporous or liquid water.<sup>2-5</sup> Any (short-lived) neutral dimer could act as a shallow trap state for electrons. It has been debated in the literature if the transition from an initially delocalized electron in vaporous or liquid water to a localized state is mediated by a long-range dipolar interaction, or whether localization occurs on preexisting trapping sites.<sup>5</sup> It will require a major theoretical effort to see if the interaction of the  $(\text{H}_2\text{O})_2$ , suitably modified by its bulk environment, is strong enough for it to act as one of the trapping sites. As there are density fluctuations in the vapor or liquid corresponding to a dimer, the two possibilities do not contradict each other. There are dimers present, and they offer a long-range dipolar interaction.

Adding rare-gas atoms to  $(\text{H}_2\text{O})_2^-$  shifts the field-detachment values to higher fields for Ar, Kr, and Xe, except for  $(\text{H}_2\text{O})_2^- \text{Ar}$  and  $(\text{H}_2\text{O})_2^- \text{Ar}_2$  where no shift is observed. The red shift of optical transitions induced by rare-gas clustering has successfully been linked to the rare-gas polarizability.<sup>22</sup> We choose a different approach as (1) the correlation with polarizability is not good, and (2) the electron in  $(\text{H}_2\text{O})_2^-$  is very weakly bound and therefore in a very diffuse orbital. A mean diameter of 40 a.u. is calculated from Eq. (1) for an electron affinity of 17 meV. We adopt a theory originally developed by Fermi for the treatment of the pressure shift of Rydberg levels.<sup>23</sup> The theory has been extended and applied successfully in many cases.<sup>23,24</sup>

The outer electron is very weakly bound to the neutral water dimer. Consequently, the interaction of  $(\text{H}_2\text{O})_2^-$  with an atom  $A$  is dominated by the interaction of the electron with  $A$ , at least at large distances.<sup>16</sup> This gives the first term in Fermi's theory, the electron-rare-gas interaction  $\Delta E_1 = ah^2\rho/2\pi m$ , where  $a$  is the scattering length,  $m$  the electron mass, and  $\rho$  the density of the rare gas.<sup>23</sup> Fermi assumed that there are many atoms within the electron cloud, but the density should also be sufficiently small so that the electron interacts only with one atom at a time. The scattering length  $a$  is positive for

He and Ne and negative for Ar, Kr, and Xe. A negative value of  $a$  causes the Ramsauer-Townsend effect in low-energy electron scattering from rare gases and results from an attractive interaction, while a positive scattering length indicates a repulsive interaction.<sup>23</sup> The second term in the original Fermi theory is due to the positive-ion-rare-gas interaction.<sup>24</sup> We replace it by the water-dimer dipole  $\mu$  interacting with the rare-gas polarizability  $\alpha$ . Proceeding exactly as in Fermi's treatment, we obtain  $\Delta E_2 = -22\rho^2\mu^2\alpha$ .<sup>24,25</sup> This term is always negative, while the sign of the larger  $\Delta E_1$  depends on that of the scattering length. The number of atoms in a sphere of 40 a.u. radius was estimated from the bulk density of rare gases. Expressing the density  $\rho$  in  $\Delta E_1$  and  $\Delta E_2$  in terms of this value, the following changes of the electron affinity of  $(\text{H}_2\text{O})_2^-$  are calculated per atom inside the diffuse electron orbital:  $-0.74$  meV for He,  $-0.12$  (Ne),  $+1.18$  (Ar),  $+2.48$  (Kr), and  $+4.29$  (Xe). Using Eq. (1), these values can be converted to a field-detachment value.<sup>24,25</sup>

The results are given by the solid lines in Fig. 3. Despite the simple classical nature of the model, and the many approximations made, it predicts well the trend in detachment thresholds for Xe, Kr, and Ar. Note that no adjustable parameter is used. The discrepancy between model and experiment for  $(\text{H}_2\text{O})_2^- \text{Kr}$  and  $(\text{H}_2\text{O})_2^- \text{Ar}_n$  ( $n=1,2$  and  $5,6$ ) may reflect the simple procedure by which the density  $\rho$  in Fermi's theory is expressed by the number of attached rare-gas atoms. This ignores any geometrical effects coming from the orientation of the rare-gas atoms around the  $(\text{H}_2\text{O})_2$  dipole. A triangular structure for  $\text{Ar}(\text{H}_2\text{O})_2$  has recently been proposed<sup>26</sup> which is compatible with our experiment, as the overlap of the weakly bound electron with the Ar atom would be small. For He and Ne the electron affinity is lowered, due to the repulsive interaction of the electron with these atoms. If this is the reason for the nonobservation of He and Ne clustered to the dimer anion remains to be determined.

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