

# LETTERS TO THE EDITOR

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## COMMUNICATIONS

### Electron transfer collisions between small water clusters and laser-excited Rydberg atoms

C. Desfrancois, N. Khelifa, A. Lisfi, and J. P. Schermann  
*Laboratoire de Physique des Lasers, Université Paris-Nord, 93430 Villetaneuse France*

J. G. Eaton and K. H. Bowen  
*Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland 21218*

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#### I. INTRODUCTION

The interaction of an electron with an assembly of water molecules has been the subject of several experimental<sup>1-7</sup> and theoretical<sup>8-10</sup> studies. While individual water molecules do not attach electrons to form stable water anions,<sup>11</sup> excess electrons injected into bulk water thermalize and lead to the formation of hydrated electrons.<sup>12</sup> In between these two extreme situations, negatively charged water clusters offer an opportunity for studying the association of excess electrons with water.

Water cluster anions have been prepared by mixing electrons with neutral clusters in an adiabatic expansion<sup>2,4</sup> and by low energy ( $< 1$  eV) electron attachment to pre-existing cold water clusters.<sup>3,5</sup> Depending on source conditions and electron energy distributions, their mass spectra were observed to vary considerably. Especially interesting is the electron energy range near  $kT$  which is encountered in the solvated electron formation process in bulk water. In this thermal energy range, however, free electron sources are very difficult to achieve experimentally. As an alternative, Kondow and co-workers<sup>5</sup> introduced a method of cluster anion formation in which collisions with free electrons were replaced by collisions with electrons weakly bound in Rydberg atoms. Only water cluster anions  $(\text{H}_2\text{O})_N^-$  with  $N$  equal to or larger than 11 were observed with Rydberg electrons in Kondow's experiment. Haberland, on the other hand, had detected all water cluster anions, except for the tetramer (and of course, the monomer) with  $N = 2, 6,$  and  $7$  being the predominantly observed species below  $N = 11$ . In order to investigate the origin of the differences between these experimental observations and in particular between free electron and Rydberg electron results, we present here the results of our study of the Rydberg electron energy ( $\epsilon$ ) dependence for the formation of small water cluster anions. Our use of laser excited Rydberg atoms allows us to span the electron energy range between  $\epsilon = 9$  and  $168$  meV (corresponding to principal quantum number  $n = 40-9$ ), as compared to the essentially fixed Rydberg electron energy range of  $\epsilon = 10-20$  meV in the Kondow experiment.<sup>5</sup>

#### II. EXPERIMENT

Our experimental setup is similar to that already described.<sup>13</sup> A pulsed beam of metastable xenon atoms is created by electron bombardment and further excited towards  $n$  Rydberg states by means of a pulsed tunable dye laser pumped by an amplified YAG laser. The Rydberg atoms cross a skimmed pulsed supersonic beam of water clusters obtained by expanding room temperature water vapor (20 Torr) with 4 bar helium. The collision region, situated at 10 cm from the room temperature nozzle, is the ion extraction zone of a conventional 2 m long Wiley-McLaren time-of-flight mass spectrometer.

Because of the presence of a Rydberg ionic core, Rydberg electron sources can lead to the formation of Coulombic complexes with cluster anions.<sup>14</sup> This effect, which is predominant for low  $n$  values (large Rydberg electron energies), is here avoided by using helium as seeding gas. As has been previously shown,<sup>15</sup> the high relative collision energy prevents complex formation for  $n \geq 8$  and, thus, all created water anions are observable when helium is used as the seed gas. Any observed cluster anions must be stable or possess autodetachment lifetimes longer than their time of flight ( $\geq 25$   $\mu\text{s}$ ).

A calibration is performed by adding a very small amount of  $\text{SF}_6$  to the expansion mixture and directly measuring the ratios between the  $\text{SF}_6^-$  and  $(\text{H}_2\text{O})_N^-$  signals. The Rydberg electron energy dependence for the formation of  $\text{SF}_6^-$  ions from  $\text{SF}_6$  seeded in helium has been previously measured<sup>15</sup> and is used as a relative calibration reference.

#### III. RESULTS

Figure 1 shows mass-spectra obtained for different values of the Rydberg electron energy  $\epsilon$  (principal quantum number  $n$ ). The main observed features are the following: at large Rydberg electron energy values, a strong signal corresponding to the  $(\text{H}_2\text{O})_2^-$  dimer is present, together with weaker  $(\text{H}_2\text{O})_{6,7}^-$  signals. These diminish rapidly in intensity with decreasing Rydberg electron energy. Figure 2 displays the Rydberg electron energy dependence for the

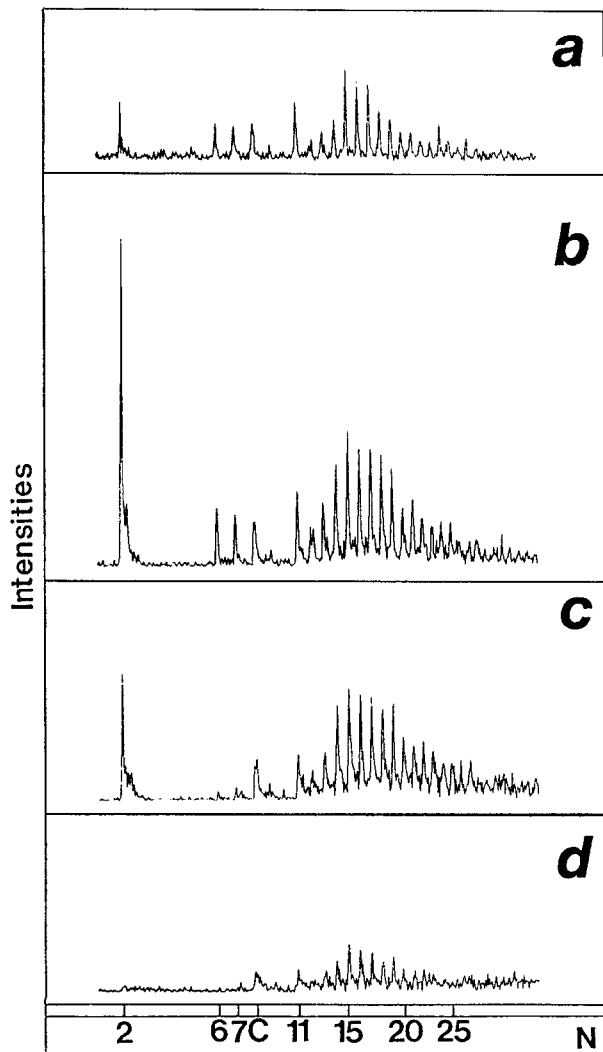


FIG. 1. Negative  $(\text{H}_2\text{O})_N^-$  cluster ion mass spectra for different Rydberg mean electron energies: (a) 168 meV ( $n=9$ ), (b) 95 meV ( $n=12$ ), (c) 60 meV ( $n=15$ ), (d) 22 meV ( $n=25$ ). Ion signal labeled C corresponds to the calibration  $\text{SF}_6^-$  signal. The tunable laser (Coumarine 480) power is not constant over the Rydberg excitation spectral range and is responsible for the variations of the observed signal to noise ratio.

formation of the negative water dimer, hexamer, and heptamer when helium is used as the seed gas. All of these small cluster ions nearly completely disappear for electron energies smaller than 50 meV. It is thus not surprising that they were not observed in the experiments of Kondow and co-workers. Another contributing reason may be that Kondow used a neat hot water vapor expansion while in the results presented here, we used less than 1% concentration of water in inert seed gas.

In order to test the influence of the relative collision energy, different carrier gases have been used. Using helium as the seeded gas, the calculated relative collision energy for dimers is 360 meV with a width of 100 meV (FWHM). By using neon and argon as seeded gases, the relative collision energies drop down to  $90 \pm 40$  meV (FWHM) in neon and  $60 \pm 30$  meV (FWHM) in argon (for dimers). As the Rydberg electron energy is decreased,

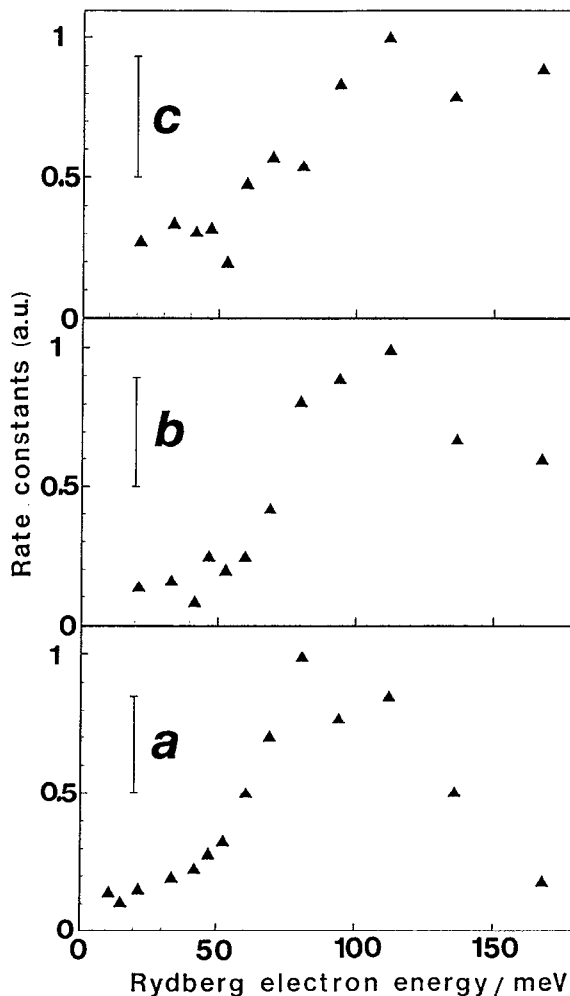


FIG. 2. Rydberg mean electron energy dependence of the  $(\text{H}_2\text{O})_N^-$ ,  $N=2$  (a), 6 (b), and 7 (c) ion cluster formation rate constants.

clear onsets for the formation of water dimer anions appear at respective values of  $\epsilon = 120 \pm 30$  meV in neon and  $\epsilon = 90 \pm 30$  meV in argon. For the hexamer and heptamer water anions, the maxima of the creation rates are shifted towards larger values of Rydberg electron energies and we do not observe any energy onset in helium. In neon and argon, the weakness of the ion signals precludes a quantitative determination of the energy onsets.

The cluster distribution in the  $11 \leq N \leq 50$  range depends upon source conditions and Rydberg electron energies but always presents a sharp onset for  $N=11$  (with the exception that a very weak signal for  $N=10$  was observed for  $\epsilon \approx 120$  meV ( $n=10$  and 11)). This sharp onset is followed by weaker signals for  $n=12, 13$ , and 14 and again strong signals for  $N=15$  and above. This behavior for these water clusters is somewhat typical, i.e., smooth anion distributions for  $N \geq 15$  and rather different distributions from one experiment to another for  $11 \leq N \leq 15$ .

For large Rydberg electron energies ( $\epsilon \approx 120$  meV),  $(\text{H}_2\text{O})_2^- \text{He}_{1,2}$  were observed in this work. Haberland and co-workers<sup>2</sup> have measured field detachment thresholds of

inhomogeneous for  $(\text{H}_2\text{O})_2^- \text{R}_N$  ( $\text{R} = \text{Xe}, \text{Kr}, \text{Ar}$ ) clusters, but did not observe any anions when  $\text{R}$  was helium or neon. Also, Bowen and co-workers<sup>4</sup> have measured photoelectron (photodetachment) spectra for  $(\text{H}_2\text{O})_2^- \text{Ar}_{1-3}$ .

#### IV. DISCUSSION

The formation of cluster anions in charge transfer collisions between neutral clusters and Rydberg atoms can be thought of as a two-step process:<sup>14</sup> first, at some rather large internuclear distance comparable to the Rydberg atom radius, a sudden attachment of the quasifree Rydberg electron takes place leading to the formation of a Coulombic positive ionic core-cluster anion complex. In a second step, the Coulombic complex dissociates if its kinetic energy  $E_k$  exceeds the electrostatic attraction interaction. In fact, the condition for dissociation of the Coulombic complex is  $\epsilon \leq E_k + EA$ , or at threshold,  $\epsilon = E_k + EA$ , where  $EA$  is the cluster electron affinity. The Rydberg energy  $\epsilon$  is actually a mean value averaged over the electron energy distribution in state  $nl$ , equal to the ionization potential  $IP(nl)$  of the Rydberg atom in state  $nl$ .

Near threshold for Coulombic complex dissociation, there is a strong interaction between the positive ionic core and the cluster anion due to the short closest approach distances involved.<sup>15</sup> This leads to energy conversion between vibrational and translational degrees of freedom.<sup>14</sup> The nascent cluster anions can then be internally relaxed, and the observed electron affinity,  $EA$ , tends towards the adiabatic electron affinity  $EA_{ad}$ . These relaxation effects may be important in the water dimer anion due to the diffuse nature of its electronic cloud.<sup>2</sup>

On the other hand, far from threshold (towards small values of  $\epsilon$  or large values of  $E_k$ ), the cluster anion trajectories always remain far from the positive ionic core corresponding to a quasifree electron attachment. The electron affinity in question then tends towards the vertical electron affinity,  $EA_v$ .

From the calculated values of the relative collision energies and the observed thresholds for water dimer anion formation in argon and neon, we deduce an estimate of the adiabatic electron affinity equal to  $0 \pm 40$  meV for water dimer. With this value, the threshold for helium would be equal to  $\epsilon = 360$  meV, well beyond our maximum attainable  $\epsilon$  value of 168 meV. For helium, the results tend towards the quasifree electron behavior limit. There, one can expect a resonant shape of the Rydberg electron energy dependence when the attached electron energy  $\epsilon$  is close to the vertical electron affinity. This suggests a value of  $EA_v$  equal to  $-90 \pm 50$  meV for water dimer. In the past, Bowen and co-workers<sup>4</sup> have measured the vertical detachment energy (VDE) of water dimer anion to be  $0.048 \pm 0.006$  eV. Taken together, these three results (VDE,  $EA_{ad}$ ,  $EA_v$ ) can lead to a clearer picture of the relationship between the potential surfaces of water dimer and its anion.

The variety of water anion mass spectra which have been obtained by different groups can be largely explained, at least for the small clusters ( $N \leq 11$ ), by the here observed

influence of the excess electron energy upon the anion formation. For larger water clusters, source conditions as well as electron energy distributions must be considered and are the object of further investigations.

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