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## COMMUNICATIONS

## Photoelectron spectroscopy of hydrated electron cluster anions, $(\text{H}_2\text{O})_{n=2-69}^-$

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Although the hydrated electron has been studied in condensed phases for about twenty-five years,<sup>1</sup> its microscopic nature continues to be an intriguing topic. Individual water molecules do not bind excess electrons,<sup>2</sup> yet bulk water readily solvates them, implying that the association of electrons with water is a multibodied interaction requiring a collection of molecules. This sparked speculation that water clusters of some size ought to bind excess electrons,<sup>3</sup> and several years ago, the long predicted, gas-phase water cluster anions,  $(\text{H}_2\text{O})_n^-$ , were observed mass spectrometrically by Haberland and co-workers.<sup>4</sup> Following this development, several experimental<sup>5-9</sup> and theoretical<sup>10-13</sup> studies on water cluster anions were undertaken, among them our work on the photodetachment of electrons from  $(\text{H}_2\text{O})_{n=2,6,7,10-69}^-$ ,  $(\text{D}_2\text{O})_{n=2,6,7,11-23}^-$ ,  $\text{Ar}_{m=1-3}(\text{H}_2\text{O})_2^-$ ,  $\text{Ar}_{m=1-3}(\text{D}_2\text{O})_2^-$ ,  $\text{Ar}(\text{H}_2\text{O})_{n=6,7}^-$ , and  $\text{Ar}(\text{D}_2\text{O})_{n=6,7}^-$ . Here, we present the photoelectron spectra of  $(\text{H}_2\text{O})_{n=2-69}^-$  as representative of these studies (see Fig. 1).

The spectra of  $(\text{H}_2\text{O})_{n=2,6,7}^-$  exhibit structure, with vibrational features observed on the high electron binding energy (EBE) side of the main peaks. Isotopic and source condition studies suggest that the two lowest EBE features in the spectra of  $n = 6$  and  $7$  may represent different isomers of each of these species. The spectra of  $(\text{H}_2\text{O})_{n>11}^-$  consist of single, broad, asymmetric peaks. The EBEs of the peak maxima in these spectra were interpreted as vertical detachment energies (VDEs), and these shift to successively higher EBEs with increasing  $n$ . In particular, for  $n = 11-69$  the VDEs increase smoothly from 0.75 eV to 1.92 eV with no abrupt changes.

An important question regarding water cluster anions concerns whether they are gas-phase counterparts to condensed-phase hydrated electrons. To address this issue, the

data is presented as VDE vs  $n^{-1/3}$  in Fig. 2. For  $n \geq 11$  and for the lowest EBE peaks of  $n = 6$  and  $7$ , the VDEs plot linearly with  $n^{-1/3}$  and extrapolate to an intercept of 3.3 eV. The intercept, VDE at  $n = \infty$ , should correspond to the photoelectric threshold for bulk hydrated electrons. This threshold can be determined indirectly from the sum of the photoconductivity threshold and  $V_0$ , the conduction band edge. For the hydrated electron in ice, the photoconductivity threshold is  $\sim 2.3$  eV,<sup>17</sup> while  $V_0$  is  $\sim 0.9$  eV,<sup>18</sup> implying that the bulk photoelectric threshold is  $\sim 3.2$  eV, in agreement with our extrapolated value. Several theoretical estimates of the photoelectric threshold range from 3–4 eV, further supporting the extrapolation to 3.3 eV.<sup>19</sup> (In addition, the same analysis of our data for  $(\text{NH}_3)_{n=41-1100}^-$  yields an intercept which is very close to the measured photoelectric threshold for bulk ammoniated electrons.<sup>20</sup>) The linear extrapolation of the water cluster anion data to the analogous bulk property implies that water cluster anions of sizes  $n \geq 11$  (and perhaps forms of  $n = 6, 7$ ) are counterparts to bulk hydrated electrons, i.e., they are embryonic forms of hydrated electrons which will mature with size toward condensed-phase hydrated electrons.

Landman and co-workers have developed a linear relation between VDE and  $n^{-1/3}$  which is based on a dielectric continuum model and which is valid for a spherical charge distribution in a uniform dielectric.<sup>11</sup> They expect this relationship to hold for water cluster anions having internal excess electron states, but not necessarily for those exhibiting surface electron states. Of the two, only cluster anions with internal states are consistent with solvated electron-like environments. In this VDE vs  $n^{-1/3}$  analysis, the intercept again corresponds to the bulk photoelectric threshold, while the slope is comprised of several factors, including  $R_s$ , the

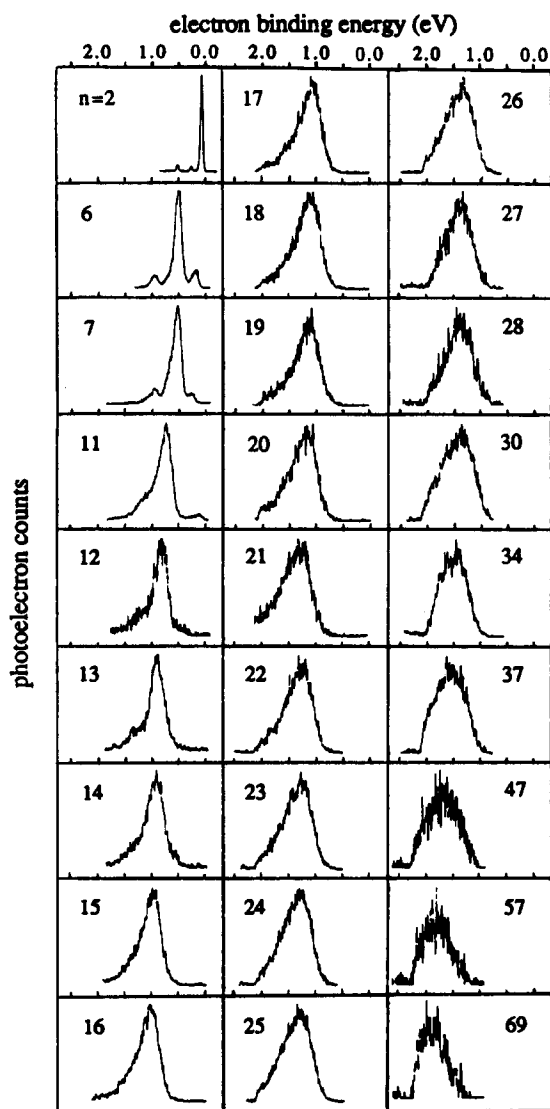


FIG. 1. The negative ion photoelectron (photodetachment) spectra of  $(\text{H}_2\text{O})_n^-$ ,  $n = 2, 6, 7, 11-28, 30, 34, 37, 47, 57, 69$  are presented above. These were recorded with visible photons and with an instrumental resolution of 30 meV. Our apparatus has been described previously.<sup>14</sup> Water cluster anions were generated in a supersonic expansion ion source, using Ar/ $\text{H}_2\text{O}$  mixtures.<sup>15</sup> Any  $\text{OH}^-(\text{H}_2\text{O})_n$  cluster anions which may have been present in small amounts could not have contributed to the spectra of  $(\text{H}_2\text{O})_n^-$  since  $\text{OH}^-(\text{H}_2\text{O})_n$ , and thus its larger analogs, do not photodetach at visible wavelengths.<sup>16</sup>

effective radius of a single solvent molecule. The data for  $n \geq 11$  and for the lowest EBE forms of  $n = 6, 7$  conform well to a straight line (see Fig. 2). The intercept agrees with theoretical and experimental estimates of the threshold, as demonstrated above, and the slope implies  $R_s = 1.95 \text{ \AA}$  which compares favorably with the bulk  $R_s$  value. This is consistent with water cluster anions  $n \geq 11$  (plus the lowest EBE forms of  $n = 6, 7$ ) existing as internal states, and thus, as embryonic hydrated electrons, supporting the interpretation given above. The dimer anion is, by definition, a surface state. Perhaps the higher EBE isomers of  $n = 6, 7$  are also surface states.

Quantum path integral MD simulations by Landman and co-workers find water cluster anions to be surface states

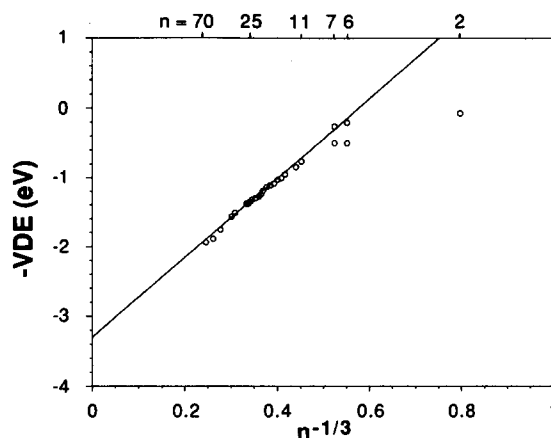


FIG. 2. The vertical detachment energies of  $(\text{H}_2\text{O})_n^-$ , including the two lowest EBE peaks of  $n = 6, 7$  which are believed to derive from different isomers, are plotted vs  $n^{-1/3}$ . The VDEs for  $n \geq 11$  (and for the lowest forms of  $n = 6, 7$ ) show a linear dependence vs  $n^{-1/3}$ . The linear least squares fit of the data corresponds to  $-VDE = -3.30 + 5.73n^{-1/3}$  (correlation coefficient of 0.998).

$n < 32$  and internal states for  $n \geq 64$ , with the transition occurring between  $n = 32-64$ .<sup>11</sup> Although their calculated surface state VDEs for  $n = 12, 18$ , and 32 are in accord with our measured VDEs, we observe no indication of a transition between  $n = 32-64$ , and the evidence presented above suggests the transition to internal states occurs by  $n = 11$ , if not by  $n = 6$ . These calculations are in qualitative agreement with our interpretation of the data, however, for they predict small water cluster anions to be surface states which evolve with size into internal electron states.

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## NOTES

The vibrational frequencies of  $\text{TiF}_n\text{Cl}_{4-n}$ ,  $n=0,4$ 

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In 1985 DeVore and Gallaher<sup>1</sup> measured the vibrational frequency of the product of a reaction of  $\text{TiCl}_4$  and  $\text{NaF}$  in quartz tube at 1000 K. Such a reaction may produce all products of the form  $\text{TiF}_n\text{Cl}_{4-n}$ , for  $n = 0,4$ , but based on available thermodynamic data DeVore and Gallaher concluded that the only product was  $\text{TiF}_4$ . They therefore assigned a band observed at  $772\text{ cm}^{-1}$  to the  $\nu_3$  (asymmetric stretching) mode of  $\text{TiF}_4$ . The observation of only one vibration in this region of the spectrum is consistent with an assignment to a molecule with  $T_d$  symmetry.

Very recently, however, Beattie and Jones have shown<sup>2</sup> that the  $\nu_3$  band of  $\text{TiF}_4$  lies at  $800\text{ cm}^{-1}$ . DeVore and Gallaher<sup>3</sup> agreed with this assignment, but questioned what species then gave rise to the  $772\text{ cm}^{-1}$  band they had previously observed.

In this work we report *ab initio* calculations for the vibrational frequencies of all of the possible  $\text{TiF}_n\text{Cl}_{4-n}$  products. Our calculations strongly suggest that the band at  $772\text{ cm}^{-1}$  is actually due to  $\text{TiFCl}_3$ .

The Ti basis set is derived from the (14s9p5d) primitive set of Wachters,<sup>4</sup> contracted to [8s4p3d] using his contraction 3. Two diffuse 2p functions ( $\alpha = 0.1523$  and 0.033) are added to describe the 4p orbital; the Hay<sup>5</sup> diffuse 3d function is also added. The F basis set is the Dunning<sup>6</sup> double-zeta contraction of the Huzinaga<sup>7</sup> primitive set. A diffuse p function ( $\alpha = 0.1$ ) is added to describe  $\text{F}^-$ . This yields an F basis of the form (9s6p)/[4s3p]. The Cl basis set is the (12s9p)/[6s5p]  $\text{Cl}^-$  basis set of McLean and Chandler.<sup>8</sup> The geometry is optimized at the SCF level and the frequencies and infrared intensities are computed using analytic derivative methods. We actually compute harmonic frequencies, but the difference between the harmonic values and fundamentals can be expected to be negligible for our present purpose: anharmonicities for transition metal diatomic fluorides are only a few  $\text{cm}^{-1}$ ,<sup>9</sup> and there should be no Fermi resonances that affect the fundamentals.

As we show below, the SCF results for  $\text{TiF}_4$  and  $\text{TiCl}_4$  in these small basis sets are in good agreement with experiment.