

Observation of Large Water-Cluster Anions with Surface-Bound Excess Electrons

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Anionic water clusters have long been studied to infer properties of the bulk hydrated electron. We used photoelectron imaging to characterize a class of $(\text{H}_2\text{O})_n^-$ and $(\text{D}_2\text{O})_n^-$ cluster anions ($n \leq 200$ molecules) with vertical binding energies that are significantly lower than those previously recorded. The data are consistent with a structure in which the excess electron is bound to the surface of the cluster. This result implies that the excess electron in previously observed water-cluster anions, with higher vertical binding energies, was internally solvated. Thus, the properties of those clusters could be extrapolated to those of the bulk hydrated electron.

The hydrated electron (I), which is localized and supported within a cavity formed by surrounding water molecules, plays a prominent role in many areas of condensed-phase science such as radiation physics, biological activity, electron transfer, and charge-induced reactivity. Gas-phase clusters of solvent molecules have also been observed to carry an extra charge (2), and they represent microscopic analogs to their bulk counterparts, assuming that sufficient solvent molecules are present. For water clusters, however, the critical size beyond which the cluster anion resembles the bulk hydrated electron has remained a contro-

versial issue. Specifically, there are believed to be two localization modes for an excess electron in a water cluster: an internally solvated electron, akin to the bulk; and an electron localized on the surface of the cluster (3).

Significant theoretical effort has been devoted to understanding the nature of the excess electron in water clusters, $(\text{H}_2\text{O})_n^-$. Path-integral molecular dynamics simulations found that surface states are more stable at sizes up to $n = 32$ molecules, whereas the internal electron is more stable for $n \geq 64$ (3). Electron vertical binding energies (VBEs), which correspond to the minimum amount of energy required to remove the electron from the cluster anion with no molecular rearrangement, were predicted to be considerably lower for the surface states than for the internal states. Thus, photoelectron (PE) spectroscopy of $(\text{H}_2\text{O})_n^-$ clusters should yield the size at which the surface-to-internal structural transformation occurs.

However, PE spectra measured by Coe *et al.* (4) showed no evidence for a surface-to-internal transition in the predicted size range. Instead, the measured VBEs from $(\text{H}_2\text{O})_{11}^-$ up to $(\text{H}_2\text{O})_{69}^-$ scaled linearly with the inverse of the cluster radius or, equivalently, as $n^{-1/3}$. Such a correlation is expected for an internally solvated electron within a simple dielectric model (5), which recovers the observed gradient using the known dielectric constants of bulk water (4, 6). Furthermore, extrapolation of the VBE to infinite size (the bulk) yielded a value of 3.3 eV, which is close to the photoelectric threshold of water, 3.2 eV, estimated by Coe *et al.* (4). This result supports the idea that there is an internally solvated electron in these clusters. However, the measured VBEs are in good agreement with VBEs calculated for surface states (3), providing the alternative interpretation that surface states were observed in the experiments. There is a similar inconsistency in the electronic absorption spectra of $(\text{H}_2\text{O})_n^-$ ($15 \leq n \leq 50$) (7), in which the maxima also scale linearly with $n^{-1/3}$ and extrapolate to the observable bulk value (I). But, those spectra were also found to be in agreement with the calculated values for surface rather than internal states (8). Finally, even though PE spectra of $\Gamma(\text{H}_2\text{O})_n^-$ clusters showed a VBE-versus- $n^{-1/3}$ correlation with the same gradient as $(\text{H}_2\text{O})_n^-$ clusters (9), there is consensus that the iodide resides on the surface of small- to medium-sized clusters (10, 11).

The issue of internal versus surface structures has reemerged in the context of two recent time-resolved PE spectroscopy studies focusing on the dynamics of $(\text{H}_2\text{O})_n^-$ clusters after electronic excitation (12, 13). Measurement of the internal conversion lifetime of $(\text{H}_2\text{O})_n^-$ as a function of size ($n = 25$ to 50) extrapolated to a bulk value of 50 fs, supporting a nonadiabatic

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