

Comment on “Characterization of Excess Electrons in Water-Cluster Anions by Quantum Simulations”

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The conclusion by Turi *et al.* (Reports, 5 August 2005, p. 914) that all experimental spectral and energetic data on water-cluster anions point toward surface-bound electrons is overstated. Comparison of experimental vertical detachment energies with their calculated values for $(\text{H}_2\text{O})_n^-$ clusters with surface-bound and internalized electrons supports previous arguments that both types of clusters exist.

Turi *et al.* (1) recently presented quantum simulations on water-cluster anions, $(\text{H}_2\text{O})_n^-$, with the specific goal of elucidating whether the excess electron in water clusters is bound to the surface of the cluster or is instead internalized within the cluster. According to the authors, the calculations “strongly support assignment of surface-bound electronic states to the water-cluster anions in published experimental studies thus far.” This interpretation differs from that drawn from recent photoelectron spectra reported by our group (2), where we found that we could make two classes of $(\text{H}_2\text{O})_n^-$ clusters (isomer I and isomer II) over a wide size range (up to $n = 200$), with isomer II clusters having considerably lower vertical detachment energies (VDEs) than isomer I clusters. On this basis, isomer II clusters were assigned to surface-bound states, whereas isomer I clusters, previously seen by Coe *et al.* (3), were assigned to internalized states, in agreement with their interpretation. Recent experimental results in our group (4) suggest a refinement in this assignment, with isomer I clusters between $n = 12$ and $n = 25$ representing a transitional regime between surface-bound and internalized states.

The Turi *et al.* study has made us think carefully about our interpretation of $(\text{H}_2\text{O})_n^-$ photoelectron spectra in terms of internally solvated versus surface-bound excess electrons. However, its unequivocal statements that “the available experimental energetic and spectral data are completely consistent with the

conclusion that the anionic water clusters observed to date bind the excess electron on the surface...”, and “the theory reproduces every observed energetic, spectral, and structural trend with cluster size” are problematic, particularly when one compares their calculated VDEs to the experimental VDEs for isomers I and II. In figure 3B in (1), the experimental VDEs for isomer I are shown to lie about halfway between the calculated VDEs for surface and interior states. The experimental VDEs for isomer II were not included in this plot. However, Fig. 1 below, adapted from (2), shows that there is extremely good agreement between isomer II VDEs and the calculated VDEs for the surface states, with four out of five calculated VDEs essentially matching the experimental values. This suggests that the calculated surface states correspond to our isomer II clusters, while the calculated VDEs for the internal states are fairly close to the isomer I VDEs (although agreement is not nearly as good). Hence, the calculated VDEs support rather than contradict our interpretation of the photoelectron spectra.

Furthermore, Turi *et al.* found another class of isomers with very low VDEs, formed in their simulations by attaching electrons to very cold clusters. Although no values are given, we speculate that this third set of clusters corresponds to the “isomer III” clusters shown in Fig. 1. If this correspondence were indeed to hold, then all three general types of clusters seen in the experiment appear in the simulations, further supporting our assignments.

Turi *et al.* find reasonable agreement between their calculated electronic spectra of $(\text{H}_2\text{O})_n^-$ with surface-bound electrons and the experimental spectra obtained by Ayotte and Johnson (5) on what we would now call isomer I clusters [figure 3A in (1)]. There are no experimental data on the electronic spectra of isomer II clusters, although we have some evidence that their electronic spectra are red-

shifted relative to isomer I clusters of the same size. Turi *et al.* also find in their simulations that surface states dominate at temperatures between 200 and 300 K for clusters with $n < 100$, while for $T = 100$ K, internal states dominate for $n \geq 66$. Hence, internal states are favored at low temperature in the calculations, whereas in our experiment, isomer II clusters were formed under conditions normally associated with generating colder clusters, namely higher stagnation pressure behind a pulsed molecular beam valve. These discrepancies may arise because isomer populations in both the experiment and the simulations reflect kinetic rather than thermodynamic effects.

Overall, we think that Turi *et al.* have overstated the case for interpreting all experimental observables on $(\text{H}_2\text{O})_n^-$ in terms of surface states. However, their study stimulates one to think about additional comparisons between experiment and theory to obtain further insight into the excess electron in $(\text{H}_2\text{O})_n^-$. For example, calculations on the excited-state dynamics of these clusters would provide an exceedingly useful point of comparison with experiment. We have measured the lifetimes of electronically excited states in isomer I and isomer II clusters (4, 6) and find significant differences in their values and size-dependent trends. On the experimental side, it is clearly of interest to generate very large $(\text{H}_2\text{O})_n^-$ clusters and measure their photoelectron spectra to search for additional isomers with higher VDEs than those found for the isomer I clusters. Finally, we point out that vibrationally resolved infrared spectra of $(\text{H}_2\text{O})_n^-$ are being measured over a wide size range by the

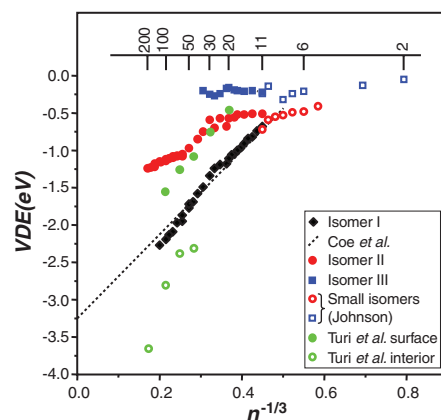


Fig. 1. Vertical detachment energies (VDEs) as a function of $1/n^{1/3}$ (where n is the cluster size) for various water-cluster anion isomers as measured by photoelectron spectroscopy. Symbols are assigned in the legend. Full green circles represent values calculated in (1) for surface-bound electrons, whereas open green circles represent values for internalized states of the electron at $T = 100$ K.

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Johnson group (7), providing a structural probe of the solvent network and the nature of its binding to the excess electron.

References and Notes

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