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

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**Abstract:** In response to the Comment by Neumark and co-workers, we reiterate that the conclusions of the title Report are based on identifiable characteristic trends in several observables with cluster size. The numerical comparison between simulated and experimental vertical detachment energies emphasized in the Comment reflect quantitative limitations of our atomistic model, but, in our opinion, do not undermine these conclusions.

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The comment by Neumark and co-workers (1) challenges the strength of our simulation-based conclusion (2) that all experimental spectral and energetic data on water cluster anions to date is attributable to surface-bound electronic states. However, our comparison of the calculated trends in properties to the data of Ayotte et al (3), and to Coe et al (4), is consistent in all respects with surface states, and the measured data is not overall consistent with the characteristics calculated for interior states. This is evident for the vertical detachment energies included in Fig. 1 of the Comment, manifesting linear variation for surface, but not interior, states, but it is more dramatic for the spectral moments (reflected in the radii and kinetic energies, Fig. 4 of (2)). The conclusion that we draw is that the states denoted as Isomer I by Neumark and co-workers (5), and equivalent to those measured by these other authors (3,4), are also surface states. The additional inference we make is that if Isomer I is a surface state, so are the other isomers (II, III) identified in (5), which bind the electron considerably more weakly. This logic is explicit in the Report (2) and the numerical issues made in the Comment are acknowledged: *“There are quantitative shortcomings in the calculated values compared with experimental reports. The calculated VDE values are closer to those only recently measured by Neumark for the identified surface states (denoted there as Isomer II) than to the Coe data considered here. However, the surface and interior electron binding morphologies lead to distinctly different trends in measured physical properties: vertical detachment energy, optical absorption spectra, kinetic energy, and electronic radius. The comparison of the trends to the corresponding published experimental data strongly*

*supports the conclusion that the available experiments reporting these results reflect only clusters characterized by electronic surface states.”*

We agree with the discussion of temperature effects on morphology in the Comment. It is reasonable that the coldest clusters manifest non-equilibrium factors, for both the experiment and simulation, as we suggested was possible in our Report (2). In the simulation, we start the electron internally, and in the experiment it is attached to a pre-formed water cluster, i.e., initially externally, so non-equilibrium can lead to differences. Johnson and co-workers (6) have provided a rationale for the difference between Isomer I and the more weakly binding isomer II that is consistent with our conclusions. Based on detailed spectral analysis of relatively small clusters, they attribute the difference to the presence (isomer I) or absence (isomer II) of proximal water molecules with both molecular hydrogen atoms oriented toward, and penetrating into, the electronic distribution. Whether this conjecture is manifest in simulations of larger anionic clusters is being investigated.

We agree with the Comment that there is an important place for new experiments and for further calculations to fill in the picture robustly. It would certainly be of interest to extend the PES measurements into the range predicted for the stable interior states of larger clusters. As shown in Fig. 1 of the Comment (1), these are predicted to lie at deeper energies than the bulk hydrated electron. At the same time, the beautifully executed excited state dynamics experiments reported by Neumark and co-workers (5) provide a rich set of data which strongly motivates theoretical study of dynamics. These

excited state dynamics studies are more challenging for the theoretical community, paralleling the challenges now overcome by the experimental community. These challenges form the next hurdle for simulation.

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