

Comment on ‘Iodine effect on the relaxation pathway of photoexcited $I^-(H_2O)_n$ clusters’ [Chem. Phys. Lett. 335 (2001) 475]

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In the Letter ‘Iodine effect on the relaxation pathway of photoexcited $I^-(H_2O)_n$ clusters’, Chen and Sheu [1] propose a new interpretation based on ab initio calculations for the time-dependent dynamics we observed by femtosecond photoelectron spectroscopy (FPES) of $I^-(H_2O)_n$ and $I^-(D_2O)_n$ ($n = 4–6$) clusters [2]. In our experiments on these and related clusters [3–5], the cluster analog of the charge-transfer-to-solvent (CTTS) band [6] was excited with a femtosecond pump pulse that transfers an electron from the I^- anion to the network of solvent molecules in the cluster. The resulting dynamics were monitored by photodetachment with a femtosecond probe pulse and measurement of the photoelectron spectrum. While we attributed the temporal evolution of the FPE spectra of $I^-(H_2O)_n$ clusters primarily to electron solvation dynamics induced by rearrangement of the water molecules,

Chen and Sheu interpret our results in terms of I atom dissociation dynamics from the excited cluster. In this comment, we address their interpretation of our experiment and present a more recent piece of data to clarify the issue.

Fig. 1a,b show the FPE spectra previously reported for $I^-(D_2O)_4$ and $I^-(H_2O)_5$ taken at pump and probe photon energies of 4.71 and 1.57 eV. Fig. 1c shows a new FPE spectrum of $I^-(H_2O)_4$ at slightly lower pump and probe energies of 4.52 and 1.51 eV. These spectra illustrate how the vertical detachment energy (VDE) of the excess electron varies with time. In the $n = 5$ spectrum, the VDE undergoes an abrupt increase of ~ 0.25 eV within 500 fs of the excitation pulse. Similar shifts are seen for larger clusters. We attributed this shift to electron solvation dynamics that occur following excitation of the CTTS band. Specifically, excitation of the CTTS band promotes the excess electron into a diffuse and weakly bound electronic state, and the water molecules subsequently rearrange to stabilize the excess electron, resulting in a larger VDE. This abrupt shift in VDE is absent in the FPE spectrum

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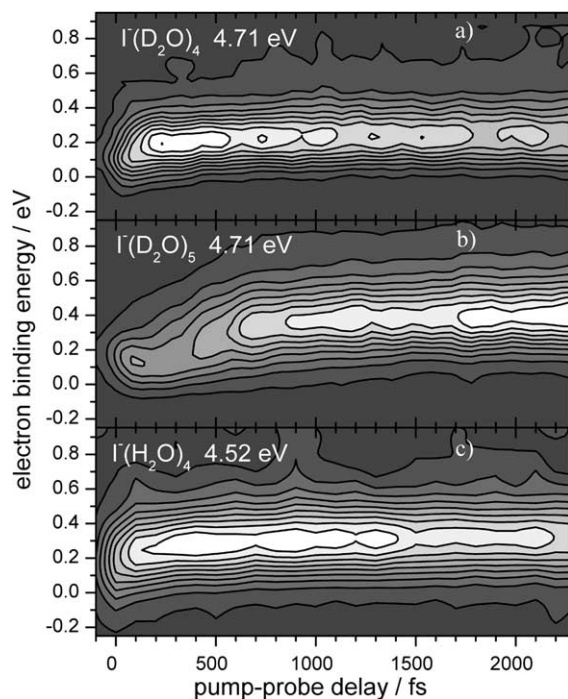


Fig. 1. Femtosecond photoelectron spectra showing electron binding energy vs. time for (a) $\text{I}^-(\text{D}_2\text{O})_4$ at a pump energy of 4.71 eV, (b) $\text{I}^-(\text{D}_2\text{O})_5$ at 4.71 eV, and (c) $\text{I}^-(\text{H}_2\text{O})_4$ at 4.52 eV. The probe photon energy is 1/3 the pump energy in all three spectra.

of $\text{I}^-(\text{D}_2\text{O})_4$ and $\text{I}^-(\text{H}_2\text{O})_4$ at the same pump/probe energies (Fig. 1a). Thus it appears that a minimum of five waters is needed for these solvation dynamics to occur prior to the excess electron leaving the cluster. The overall signal decays at considerably longer times, an effect attributed to thermionic emission from vibrationally excited $\text{I} \cdot (\text{H}_2\text{O})_n^-$ species. The interaction of the neutral I atom with the excited electron and with the water molecules was neglected in our interpretation of the results.

Chen and Sheu (CS) offer a radically different interpretation, based on electronic structure calculations [7] on electronically excited $\text{I}^-(\text{water})_n$ clusters with $n = 4, 5, 6$. They calculated the VDE for increasingly larger water I distances, with the geometry of the water molecules frozen at the geometry of the ground state $\text{I}^-(\text{H}_2\text{O})_n$ cluster. The calculations indicate that just after excitation the electronic wavefunction is diffuse as we assumed, but that there is a repulsive interaction between the I atom and excited diffuse electron. CS claim that

this repulsion causes rapid dissociation to $\text{I} + (\text{H}_2\text{O})_n$, accompanied by an increase in the VDE because the repulsive interaction decreases as the fragments separate (Fig. 1 in CS). The spectra at long times (after 2–3 ps) are then attributed to bare $(\text{H}_2\text{O})_n^-$ anions rather than to the $\text{I} \cdot (\text{H}_2\text{O})_n^-$ species. In essence, CS propose that dissociation to $\text{I} + (\text{H}_2\text{O})_n^-$ happens before solvent rearrangement, whereas we assumed that electron/solvent dynamics occurs well before the I atom leaves the cluster, if it ever does.

The electronic structure calculations have addressed an important point, namely the role of the I atom in the excited state cluster dynamics. In our interpretation of the FPE spectra, we assumed that in the excited diffuse state the I atom was an inert spectator, playing no role in the subsequent dynamics. Chen and Sheu's results indicate that due to orbital repulsion, the I atom reduces the electron binding energy and changes the electronic wave function. We agree that our original assumptions regarding the I atom may have been an oversimplification. However, we disagree with the conclusion by CS that the short-time dynamics revealed by the FPE spectra are exclusively due to dissociation of the cluster to $\text{I} + (\text{H}_2\text{O})_n^-$ rather than solvent interaction with the excess electron. Specifically, we take issue with two aspects of their interpretation. First, their interpretation of our results for $\text{I}^-(\text{H}_2\text{O})_4$ is not supported by previous and more recent experimental results. Second, the experimentally observed isotopic dependence of the dynamics for the $n = 5$ and 6 clusters argues in favor of assigning the VDE shifts to vibrational/libration motion of the solvent molecules rather than dissociation.

We first consider the proposed dissociation of the $n = 4$ cluster. CS claim that the VDE shift in our experiments is from I atom dissociation, not electron solvation dynamics, and should be present for all three cluster sizes. Their calculated shifts are in reasonable agreement with experiment for the $n = 5$ and 6 clusters, but not for the $n = 4$ clusters where the experiments do not exhibit an abrupt VDE shift. To account for this discrepancy, CS assert that the excited state dissociation for $n = 4$ occurs within the first 100–200 fs and that we miss most of the shift in the VDE due to our time res-

olution of about 100 fs. They reason that I atom dissociation occurs more rapidly for the $n = 4$ cluster than for $n = 5$ and 6, because our pump pulse deposits a large amount of excess energy in the CTTS state for $n = 4$, but not as much for $n = 5$ or 6. In our original experiment, the pump photon energy was 0.31 eV above the $n = 4$ CTTS state, and 0.17 and 0.10 eV above the CTTS state for the $n = 5$ and 6 clusters (these values are based on their calculated CTTS excitation energies). CS postulate that the larger the excess energy, the faster the I atom leaves the cluster, and that our time-resolution is not capable of monitoring the dissociation dynamics of the fastest cluster $n = 4$.

There are two problems with this argument. First, our time resolution is sufficient to monitor dynamics on a sub-100 fs time scale. In experiments on I_2^- , we had no trouble resolving the time-dependence of direct dissociation of I_2^- on a repulsive excited state with our FPES instrument [8]. For this diatomic, we deposited 0.57 eV of energy above the dissociation limit on the excited state surface, and dissociation was complete on a time-scale of about 250 fs. It is unlikely that dissociation of excited $I^-(H_2O)_4$ would be significantly faster than this.

More importantly, CS state that if ‘a lower excitation energy is used in the experiment, a dynamics similar to the $n = 5$ and 6 [clusters] is expected for $n = 4$ ’. In fact, this is not the case. Although we did not report this data at the time, Fig. 1c of this paper shows that FPE spectra of $I^-(H_2O)_4$ at a pump energy of 4.52 eV (an excess energy of 0.1 eV) are very similar to those recorded previously at the higher pump energy of 4.71 eV, and are still quite different from the $I^-(H_2O)_5$ FPE spectra. The main difference between the old and the new $n = 4$ FPE spectra is a slightly longer excited state lifetime in the new spectrum, as expected for a process such as thermionic emission that depends on excess energy. Hence, the dynamics of $I^-(H_2O)_4$ subsequent to the CTTS excitation are fundamentally different from those of the larger clusters regardless of the excess energy. This is in clear contradiction to the claim of CS.

We next consider the origin of the abrupt VDE shift in clusters with $n \geq 5$, which CS attribute to dissociation to $I + (H_2O)_n^-$. However, as discussed in our original paper [2], the FPE spectra exhibit a

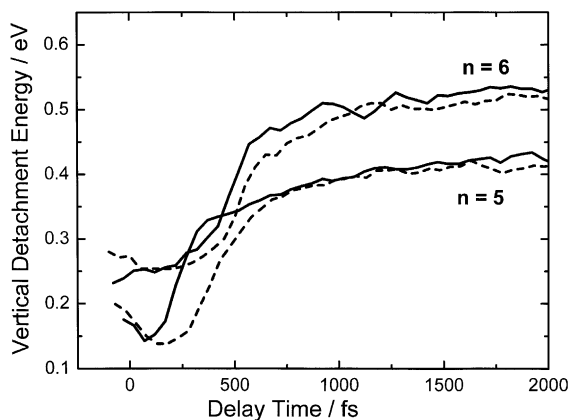


Fig. 2. Time dependence of vertical detachment energy (VDE) for $I^-(H_2O)_{5,6}$ (solid lines) and $I^-(D_2O)_{5,6}$ (dashed lines). VDEs for the $I^-(D_2O)_n$ clusters have been shifted upward by 0.02 eV to line up with the $I^-(H_2O)_n$ clusters at long times.

clear isotope effect. This can be seen in Fig. 2, which displays a plot of VDE vs. time for the $I^-(D_2O)_n$ and $I^-(H_2O)_n$ ($n = 5, 6$) clusters and shows that the shift in VDE occurs more rapidly for the H_2O than the D_2O clusters. It therefore appears more reasonable to attribute the VDE shifts to librational and rotational motion of the water molecules, motions in which the hydrogen atoms are directly involved, than to dissociation to $I + (H_2O)_n^-$, for which isotope effects, primarily due to different reduced masses of the recoiling fragments, will be very small. Note that no $(H_2O)_n^-$ fragments from the pump laser alone were observed in our reflectron mass analyzer, but their absence is not definitive since these species might be formed with sufficient vibrational excitation to decay by thermionic emission during their transit time through the reflectron (several μs) before they can be detected.

Assuming that the main result from Chen and Sheu’s electronic structure calculation is correct, namely that there is a repulsive interaction between the I atom and excited electron in the CTTS state of the cluster, then what is the origin of the apparent discrepancies between their interpretation of the excited state dynamics and the experimental results? In all of Chen and Sheu’s calculations, the orientations of the water molecules are fixed at the ground state geometry of $I^-(H_2O)_n$, and only relative translation between the I atom and the frozen

water cluster is considered. However, the repulsive interaction in the excited state can be reduced not only by displacing the I atom, but also through water librations and rotations. Any such motions will involve light atoms (H or D) and are therefore likely to be rapid compared to the relative translational motion of the much heavier I atom and water cluster. This point is supported by a recent theoretical study by Vila and Jordan [9] on $I^-(H_2O)_4$.

While we prefer not to speculate on the detailed excited state dynamics, one possible 'final' (i.e. 2–3 ps) structure may simply be a geometry in which all the water molecules have changed their orientation so that the H atoms not involved in inter-water hydrogen bonding, point away from the I atom instead of toward it as they do in the anion ground state. The excess electron then would then reside on the other side of the cluster, far from the I atom and bound only by its interaction with the water molecules. Hence this state could be described as $I \cdot (H_2O)_n(e^-)$, with the solvent network interposed between the I atom and excess electron. In this scenario, the I atom would be bound to the cluster via its van der Waals attraction to the water molecules, or could leave the system without substantially altering the VDE since its electrostatic interaction with the excess electron would be small.

Further insight into the interpretation of the FPE spectra could be gained from excited state molecular dynamics simulation. Such calculations might well show that the excited state dynamics reflect repulsion between the I atom and excess electron as well as stabilization of the excess electron through solvent reorganization, in analogy to the CTTS dynamics in aqueous solution [10]. Calculations on the time-dependent photodetachment cross section from the excited state would also be of

considerable interest. Our results showed a rather surprising transient increase in the photodetachment cross-section for the $n \geq 5$ clusters 1–2 ps after the excitation pulse, and this was tentatively attributed to localization of the excess electron due to solvent reorganization. On the experimental side, it would be desirable to analyze in more detail the neutral and ionic products at long times after the excitation pulse in order to clarify further the final products of the dynamics. Such experiments are being planned in our laboratories.

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References

- [1] H.Y. Chen, W.S. Sheu, *Chem. Phys. Lett.* 335 (2001) 475.
- [2] L. Lehr, M.T. Zanni, C. Frischkorn, R. Weinkauff, D.M. Neumark, *Science* 284 (1999) 635.
- [3] A.V. Davis, M.T. Zanni, C. Frischkorn, D.M. Neumark, *J. Electron Spectrosc. Relat. Phenom.* 108 (2000) 203.
- [4] C. Frischkorn, M.T. Zanni, A.V. Davis, D.M. Neumark, *Faraday Discuss.* (2000) 49.
- [5] M.T. Zanni, C. Frischkorn, A.V. Davis, D.M. Neumark, *J. Phys. Chem. A* 104 (2000) 2527.
- [6] D. Serxner, C.E.H. Dessent, M.A. Johnson, *J. Chem. Phys.* 105 (1996) 7231.
- [7] H.Y. Chen, W.S. Sheu, *J. Am. Chem. Soc.* 122 (2000) 7534.
- [8] M.T. Zanni, V.S. Batista, B.J. Greenblatt, W.H. Miller, D.M. Neumark, *J. Chem. Phys.* 110 (1999) 3748.
- [9] F.D. Vila, K.D. Jordan, *J. Phys. Chem. A*, in press.
- [10] J.A. Kloepfer, V.H. Vilchiz, V.A. Lenchenkov, A.C. Germaine, S.E. Bradforth, *J. Chem. Phys.* 113 (2000) 6288.