

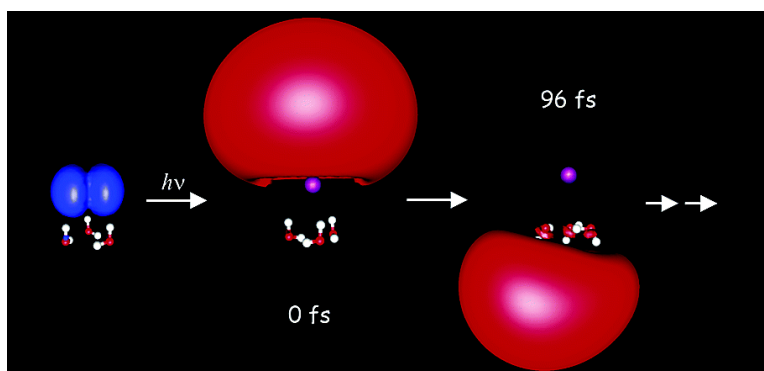
Communication

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Further Insight into the Relaxation Dynamics of Photoexcited $\text{I}^-(\text{H}_2\text{O})_n$ Clusters

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One of the fascinating features of anions dissolved in water, especially halides, is the possibility of photochemical transfer of an electron from the ion to the bulk solvent. The electron will be stabilized by the field of polar solvent molecules, giving rise to so-called charge-transfer-to-solvent (CTTS) excited states, which eventually lead to the solvated electron. In 1996, Johnson and co-workers were able to experimentally observe cluster analogues of the bulk CTTS states in clusters of iodide with one to four water molecules.¹ It was found that subsequent relaxation of the excited cluster may lead to the ejection of the neutral iodine atom and formation of a dipole-bound water cluster anion $(\text{H}_2\text{O})_n^-$.

It is now well established that small to medium sized iodide–water clusters tend to have surface structures, where the iodide ion tends to sit at the surface of the hydrogen-bonded water network.^{7,8} The cluster structures are governed by a combination of the interaction of the negatively charged I^- with the dipole moment of the entire water network, and the hydrogen-bonding interactions of the “dangling” hydrogen atoms with the iodide ion.⁷ Upon photoexcitation, it was shown unambiguously that an electron from a I^- valence p orbital is transferred to a very diffuse solvent molecular orbital, where it is supported by the stabilizing interaction with the dipole moment of the solvent network, reflecting actual charge transfer to solvent.^{9,10} As a matter of fact, the excited electron distribution in the excited state of iodide–solvent clusters in the Franck–Condon region has been found to be very similar to the electronic structure of the corresponding dipole-bound solvent cluster anions. The only significant difference between excited $[\text{I}^-(\text{H}_2\text{O})_n]^*$ and $(\text{H}_2\text{O})_n^-$ is the presence of the neutral iodine atom which destabilizes the excited electron. Moreover, the ion–dipole interactions, which kept the ion and solvent molecules together in the ground state, no longer exist in the excited state. Thus, profound structural changes are expected as the system relaxes after photoexcitation.

Neumark and co-workers applied femtosecond photoelectron spectroscopy techniques to study the relaxation dynamics of photoexcited $\text{I}^-(\text{H}_2\text{O})_n$ clusters ($n = 4–6$), unveiling interesting dynamical characteristics of the excited electron in clusters of different sizes.² For the smallest cluster investigated, $\text{I}^-(\text{H}_2\text{O})_4$, the electron binding energy was found to remain constant throughout the measurement time window (2 ps), and the population of photoexcited clusters decayed exponentially because of the spontaneous ejection of the dipole-bound electron from the vibrationally excited water cluster. On the other hand, for $\text{I}^-(\text{H}_2\text{O})_5$ and $\text{I}^-(\text{H}_2\text{O})_6$, an induction period of ca. 500 fs was observed, during which the electron binding energy is constant, before it increases by ~ 0.3 eV, and the population of excited clusters starts decaying until the end of the observation time (2 ps). To rationalize their observations, Neumark and co-workers put forward the hypothesis that the rise in electron binding energy after the first 500 fs is due to reorganization of the water molecules in $\text{I}^-(\text{H}_2\text{O})_5$ and $\text{I}^-(\text{H}_2\text{O})_6$

clusters.^{2,3} While the four water molecules in $\text{I}^-(\text{H}_2\text{O})_4$ may not be able to rearrange and efficiently stabilize the excess electron transferred from iodide, five and six water molecules are known to bind an excess electron in a number of cluster configurations. Therefore, in the 500 fs following photoexcitation, the water molecules in $\text{I}^-(\text{H}_2\text{O})_5$ and $\text{I}^-(\text{H}_2\text{O})_6$ clusters are assumed to gain configurations which can support the excess electron much more efficiently than in the initial cluster configuration. This model is based solely on the consideration of solvent dynamics, neglecting the possible role of the neutral iodine atom formed by photoexcitation, and is hereafter referred to as the “solvent-driven” relaxation dynamics model. This model also accounts for the pronounced isotope effects observed, that is, a longer induction period for $\text{I}^-(\text{D}_2\text{O})_n$ than for $\text{I}^-(\text{H}_2\text{O})_n$.^{2,3}

Recently, Chen and Sheu proposed an alternative interpretation for the femtosecond experiments, based on quantum-chemical calculations, in which the stabilization of the excited electron is rationalized by the ejection of the neutral iodine atom from the water cluster.^{4,5} Quantum-chemical calculations show that the presence of the neutral iodine atom can considerably destabilize the excited electron in excited $\text{I}^-(\text{H}_2\text{O})_n$ clusters, and thus, as the iodine atom leaves the water cluster, the electron binding energy must increase significantly. According to this “iodine-driven” model of relaxation dynamics, a $\text{I}^-(\text{H}_2\text{O})_4$ cluster would undergo iodine atom ejection on a very fast time scale, that is, less than 100 fs, and only the dynamics of the $(\text{H}_2\text{O})_4^-$ cluster product could be monitored. On the other hand, iodine would leave photoexcited $\text{I}^-(\text{H}_2\text{O})_5$ and $\text{I}^-(\text{H}_2\text{O})_6$ clusters more slowly, giving rise to the experimentally observed induction period. The main problem with the latter model is that it is based on static quantum-chemical calculations, which have the water cluster moiety frozen in the geometry of the cluster before photoexcitation. Excited-state quantum-chemical calculations of $\text{I}^-(\text{H}_2\text{O})_4$ clusters by Vila and Jordan indeed showed that the excited-state potential energy surface is repulsive along the hydrogen atom “flip” coordinate, which further supports the importance of solvent motion.⁶

None of the models proposed so far to interpret femtosecond experiments treats the relaxation of iodide–water clusters as a whole, neglecting either the role of the iodine atom or that of solvent reorganization. In the present Communication, we report preliminary results from ab initio molecular dynamics simulations of $\text{I}^-(\text{H}_2\text{O})_3$ relaxation. The electronic structure calculations were performed with the CASSCF technique,¹¹ as implemented in the MOLPRO program.¹⁶ Computational details, including the active space and basis sets used,^{6,12–15} as well as the molecular dynamics simulation procedure¹⁷ are given in the Supporting Information. Despite its small size, $\text{I}^-(\text{H}_2\text{O})_3$ possesses the crownlike structure characteristic of $\text{I}^-(\text{H}_2\text{O})_n$ clusters with $n \leq 6$, and, even though there are no explicit experimental data on the relaxation dynamics for this cluster size, it can serve as a good model to gain some insight into the

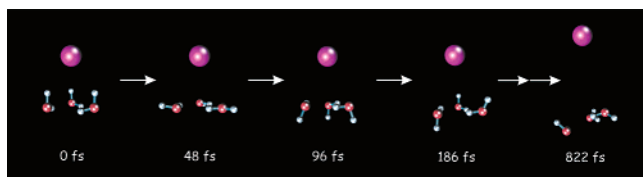


Figure 1. Snapshots of selected configurations along the trajectory of photoexcited $\text{I}^-(\text{H}_2\text{O})_3$ relaxation.

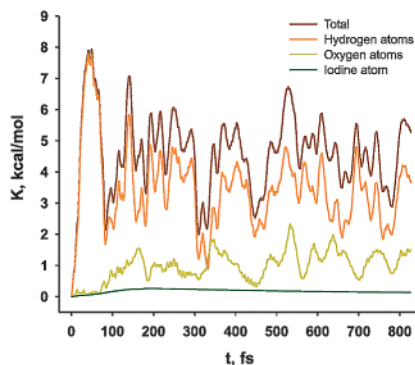


Figure 2. Time-evolution of the kinetic energy for the photoexcited $\text{I}^-(\text{H}_2\text{O})_3$ cluster: total kinetic energy, kinetic energy of the iodine atom, and kinetic energy of all oxygen and all hydrogen atoms.

general features of the excited-state time-evolution of larger $\text{I}^-(\text{H}_2\text{O})_n$ species.

According to our simulations, the “dangling” hydrogen atoms which formed hydrogen bonds with iodide in the ground state start moving away from the iodine atom, and in less than 50 fs the structure of the water cluster becomes almost flat (Figure 1, 48 fs), which is accompanied by a drop in the system potential energy. Yet because of the kinetic energy acquired, hydrogen atoms keep moving, until the water cluster moiety reaches an “inverted crown” structure (Figure 1, 96 fs). The latter structure is higher in energy than the “flat” structure, and the hydrogen atoms thus continue their oscillatory motion. In general, the relaxation process involves rapid oscillatory motion of the water molecules which results in abrupt oscillations in the system potential and kinetic energies (cf. Figure 2). After the first oscillation, the synchronicity of the water motion appears to be disrupted (Figure 1, 186 fs), as energy is transferred to other cluster vibrational modes, and the oxygen atoms and the hydrogen atoms which are involved in the water–water hydrogen bonding start gaining additional kinetic energy (cf. Figure 2). The water network undergoes deformations during the trajectory, and water–water hydrogen bonds break and form back and forth a few times. Meanwhile, the heavy iodine atom is slowly departing from the water cluster: the distance between iodine and the center of mass of the $(\text{H}_2\text{O})_3$ moiety reaches 6.3 Å in less than 900 fs (Figure 1, 822 fs), while it is only 3.44 Å in the initial Franck–Condon geometry. As is evident from Figure 2, the kinetic energy gained following photoexcitation appears mainly partitioned into the rotational and vibrational modes of water molecules.

The main features of the relaxation of photoexcited iodide–water clusters that emerge from this preliminary study are the oscillatory motion of water molecules and the slow recoil motion of the neutral iodine atom. Rapid changes in the relative orientation of the water molecules that result from the interconversion of “crown” and “inverted crown” structures cause rapid changes in the total dipole moment of the $(\text{H}_2\text{O})_n$ moiety, and in the excited electron distribution that follows the aggregate dipole. Thus, the binding energy of the excited electron must also undergo oscillatory changes

along a given trajectory. However, in the femtosecond experiments of Neumark and co-workers, the measured electron binding energy is changing quite smoothly.² This may be explained by the fact that, at finite experimental temperatures, ground-state $\text{I}^-(\text{H}_2\text{O})_n$ clusters exist in various configurations and isomers. The observed experimental signal is an average over the whole ensemble of possible initial cluster structures, which may lead to observed smooth changes in ensemble-averaged electron binding energies. A large number of trajectories, starting with many different initial cluster configurations, will thus be needed to make a thorough connection with experiment for larger clusters. However, the present simulations already suggest that the relaxation of photoexcited $\text{I}^-(\text{H}_2\text{O})_n$ clusters is a complex process, where both the role of iodine and solvent motion must be included to fully rationalize experimental observations.² While the rapid motion of water molecules observed in our simulations clearly supports the “solvent-driven” model of relaxation dynamics, the role of iodine motion may also be critical in determining the time-evolution of the electron binding energy following photoexcitation, which is consistent with the “iodine-driven” model of cluster relaxation dynamics.

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Supporting Information Available: Computational details (PDF), atomic coordinates along the trajectory (XYZ), and trajectory animation (MPEG). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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