

Observation of the Solvent Shell Reorganization around Photoexcited Atomic Solutes by Picosecond X-ray Absorption Spectroscopy

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Solvation dynamics, the process of solvent shell reorganization upon electronic structure changes in a solute, is one of the most studied processes in chemical dynamics. This is based on its importance in liquid phase chemistry and in biology, where the solvent shell has an active role in assisting, hindering, or triggering chemical reactions. Solvation dynamics has been much studied using different ultrafast optical UV–vis and IR laser techniques since the 1980s,^{1–3} as well as by theoretical models and simulations.^{4–6} In the experimental studies, a short laser pulse excites a dye molecule in a solvent, inducing a sudden dipole moment change, to which the solvent molecules react by minimizing the free energy. This rearrangement is probed by recording, on the femtosecond time scale, the fluorescence, the excited-state absorption, or the stimulated emission of the dye molecule.

Optical methods have, however, their limitations; namely, the solvent shell structure in the ground state is solute-dependent, such that the solvent rearrangement in the excited state reflects a departure from a specific initial structure. Optical methods cannot deliver the *structure* of the solvent shell before, during, and after solvent rearrangement. In a previous publication,⁷ we proposed an approach based on solvated atomic ions, whose electronic structure is modified by a short laser pulse, while probing is done by picosecond X-ray pulses from a synchrotron storage ring. The detection is based on X-ray absorption spectroscopy (XAS). XAS is a well-established method that delivers precise information both about the electronic structure (via X-ray absorption near edge structure or XANES) and about the occupancy of valence orbitals, which are those that take part in chemical processes. It also probes the short-range geometric structure (via extended X-ray absorption fine structure or EXAFS) around the atom of interest.⁸ Furthermore, it is able to detect optically silent species, such as neutral atoms in liquids. Here, we report the first implementation of this method to detect the changes in the solvation shell in the case of photoexcited aqueous iodide (I^-).

The optical absorption spectrum of I^- in water is characterized by two broad bands (the so-called charge transfer-to-solvent or CTTS bands) with maxima at 225 and 200 nm. Excitation of these bands leads to abstraction of the electron from the negatively charged atom. The solvated electron is easily detected by its strong and broad near-IR (centered at 780 nm) absorption. The kinetics of the latter is characterized by a multiexponential decay over femtoseconds to nanoseconds, which has been well characterized in previous studies.^{9–12} Important here is that the electron population corresponds to the number of photolyzed I^- atoms. In particular, after the initial fast processes of electron-atom recombination, nearly 20% of the initial population of photolyzed species remains in the

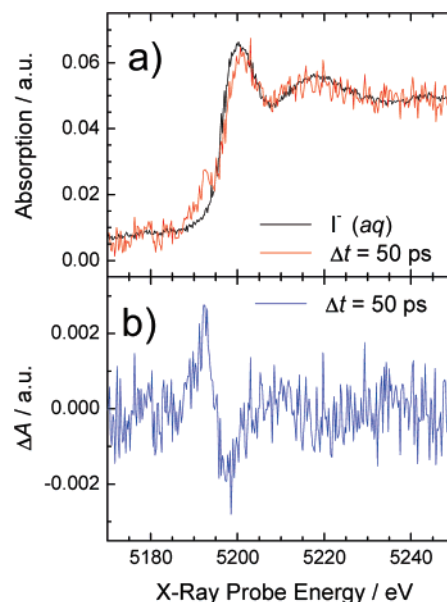


Figure 1. (a) L_1 -edge absorption spectra of aqueous I^- ($I^-(aq)$); (b) difference absorption spectrum (ΔA) 50 ps after laser excitation. In (a), the red trace is the reconstructed L_1 -edge absorption spectrum of photogenerated aqueous I^0 atoms (at $\Delta t = 50$ ps) using the spectra of the reactant (a, black trace) and the transient spectra (b), and taking a 20% fractional population of I^0 species (see text for details).

sample for hundreds of picoseconds. On the basis of these findings, we have probed the population of I^0 species, by X-ray absorption spectroscopy at the L_1 and L_3 edges, 50 ps after electron abstraction by the pump laser.

The details of the optical pump/X-ray probe experiment have already been described.^{13,14} Here we just mention that the sample is a recirculating liquid jet of 500 mM of NaI dissolved in water that is renewed after each laser pulse. Two-photon excitation at 400 nm into the CTTS bands was carried out using 150 fs pulses (energy/pulse 350 μ J, repetition rate 1 kHz). The laser beam was focused onto the sample in a 200 μ m diameter spot congruently with the X-ray probe beam having a diameter of 100 μ m. X-ray pulses from the Swiss Light Source storage ring (Villigen), with a pulse width of 70 ps, were used. We record the transient difference X-ray absorption (difference absorption spectra between the unpumped and the pumped sample) as a function of time delay between the laser pump and the X-ray probe pulse.

Figure 1 shows the L_1 (initial core orbital: 2s) absorption before laser excitation, the transient difference XAS spectrum 50 ps after excitation, and the reconstructed absorption spectrum (as explained in ref 8) of the I^0 species, based on a fractional population of the photodetached iodide of 20%, which we determined from separate

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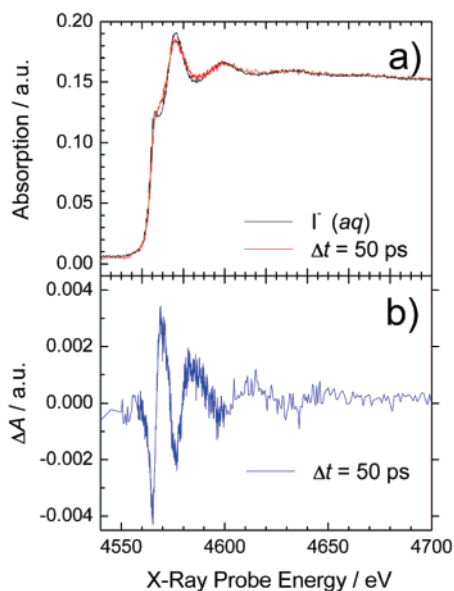


Figure 2. (a) L_3 -edge absorption spectra of aqueous I^- ; (b) difference absorption spectrum (ΔA) 50 ps after laser excitation. In (a), the red trace is the reconstructed L_3 -edge absorption spectra of photogenerated aqueous I^0 atoms (at $\Delta t = 50$ ps) using the spectra of the reactant (a, black trace) and the transient (b) spectra, and taking a 10% fractional population of I^0 species (see text for details).

laser-only pump–probe experiments under similar conditions. The I^- XAS is characterized by an edge around 5.2 keV, followed by marked modulations at higher energies. Being isoelectronic with Xe, I^- does not show bound–bound core transitions at the L_1 edge, and the modulations in the XANES region are all due to above-ionization threshold multiple scattering of the photoelectron on the solvent species.¹⁵ Removal of the electron from I^- should lead to formation of I^0 with a hole in the 5p shell that can then be accessed by excitation of the 2s core orbital.⁷ Therefore, appearance of the $2s \rightarrow 5p$ resonance is a fingerprint of I^0 formation. Figure 1b shows the transient difference absorption spectrum recorded 50 ps after laser excitation. Interestingly, it shows an increase of absorption in the pre-edge region at ~ 5.19 keV. In addition, there is evidence of significant changes above the edge, which point to a solvent reorganization around the solute. This can be better seen by recording the transient absorption at the L_3 edge (due to transitions originating from the $2p_{3/2}$ core orbital), for which the signal is more intense and entirely due to multiple scattering, since no atomic resonance line is expected (the $2p \rightarrow 5p$ transition is forbidden). Figure 2 shows the static (a) and the transient difference (b) L_3 -edge absorption spectra. Figure 2a shows the reconstructed L_3 -edge absorption spectra. Figure 2a shows the reconstructed L_3 -edge absorption spectrum of the I^0 species. The changes in the above-edge region clearly confirm that significant structural reorganization has occurred.

In the case of the L_1 spectrum of the I_2 molecule, the $2s \rightarrow 5p$ pre-edge resonance is slightly higher than the edge jump itself,⁷ whereas in Figure 1a, we find it to be 1/3 of the edge height. Since XANES probes the occupancy of valence orbitals, this suggests a partial refilling of the 5p orbital with back electron transfer from the solvent molecules, maybe concomitant with the solvent reorganization we observe in the above-edge regions. The latter could correspond to a tumbling over of the water molecules, with their oxygen side pointing toward the solute. DFT calculations are underway to determine the exact structure of the water shell around I^0 , and preliminary results point to the above scenario.

The above results represent the first example of the observation of the changes in the solvent shell structure after light-induced electronic structure changes in an atomic solute. They could not have been retrieved by optical techniques. Although they do not probe the actual solvation process, due to time resolution, they demonstrate the power of time-resolved X-ray absorption spectroscopy as an ideal tool for the study of solvation dynamics. With the extraction of ultrashort X-ray pulses from synchrotrons, based on the slicing scheme, it will soon be possible to follow the process of shell rearrangement in real-time on the femtosecond time scale.

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