Supplementary Information

Probing the transition from hydrophilic to hydrophobic solvation with atomic scale resolution

Van-Thai Pham^{1}, Thomas J. Penfold^{1,2,3}, Renske M. van der Veen^{1,2†}, Frederico Lima¹, Amal El Nahhas¹, Steve Johnson², Paul Beaud², Rafael Abela², Christian Bressler^{1‡}, Ivano Tavernelli³, Chris J. Milne¹ and Majed Chergui¹*

¹ Ecole Polytechnique Fédérale de Lausanne, Laboratoire de spectroscopie ultrarapide, ISIC-FSB, Station 6, CH-1015 Lausanne, Switzerland

² Swiss Light Source, Paul-Scherrer-Institut, CH-5232 PSI-Villigen, Switzerland

³ Ecole Polytechnique Fédérale de Lausanne, Laboratoire de chimie et biochimie computationnelles, ISIC-FSB, CH-1015 Lausanne, Switzerland

Corresponding author : majed.chergui@epfl.ch

* Now at Pacific Northwest National Laboratory, 902 Battelle Blvd, Richland, WA 99352, USA

† Now at Physical Biology Center for Ultrafast Science & Technology, California Institute of Technology, Pasadena, CA 91125, USA

‡ Now at European XFEL, DESY, Notkestrasse 85, D-22607 Hamburg, Germany

SI. Experimental Methods

SI.1 Static X-ray absorption spectroscopy

Static L_1 and L_3 x-ray absorption of aqueous iodide were measured at the Micro-XAS beamline at the Swiss Light Source. The sample is circulated by a free-flowing jet of 200 μm thickness tilted at 45° . The ring current was 400 mA giving a flux at the sample position of $\sim 10^{12}$ photons/s at the L_1 and L_3 edges. The x-ray energy from the third harmonic of the U19 undulator can be tuned by a Si (111) double crystal monochromator, yielding an energy resolution of 0.8 eV at both edges. The beam is reshaped and attenuated with slits before passing through a pair of Kirkpatrick Baez (KB) mirrors which focuses it onto the sample. Two ion chambers (Oxford Danfysik, 30 cm length, bias 1.2 kV) filled with He measure the incoming and transmitted flux through the sample. The output current is amplified by a low noise current amplifier FEMTO DLPCA-200 with a typical gain of 10^6 to 10^9 V/A. The I_0 ion chamber absorbs only 0.19% of the incoming flux giving rise to 50 nA at 5 keV. The X-ray energy was calibrated with Ti and V foils, whose K edges were recorded and compared to the literature spectra. The absorption spectra were collected with an integration time of 10 s per data point giving a S/N (for the normalized spectra) of 400 and 1000 at an energy span of $8\text{\AA}^{-1}$ ($\Delta E=250$ eV) at L_1 and L_3 edges, respectively. The edge jumps of both L_1 and L_3 edges of iodine are in agreement with calculations using the known cross sections (via XOP, see ref. ¹). This edge height is later rescaled to estimate that of unpumped spectra to which the transient spectra were normalized (see below). Due to the rather small edge jump values of the unpumped spectra, this normalization procedure is only approximate.

SI.2 Picosecond X-ray absorption experiments:

The picosecond-resolved XAS measurements of aqueous iodide were carried out at the undulator beam line microXAS of the Swiss Light Source (SLS). The transient absorption of the L_1 and L_3 edges of iodine are measured using the 3rd harmonic of the radiator with an energy resolution of ~ 0.8 eV, provided by a Si (111) double crystal monochromator. The

monochromatic X-ray beam is focused onto the sample by Kirpatrick-Baez (KB) mirrors, which consist of two Rh-coated mirrors for horizontal and vertical focusing. The X-ray focus of $60 \times 120 \mu\text{m}^2$ (vertical x horizontal) at the sample position, ~ 50 cm after the KB mirrors, is determined by scanning a $50 \mu\text{m}$ pinhole. The samples and detectors are inside a chamber flushed with He gas in order to avoid attenuation of the X-ray flux by air. The ring is operated at 350 mA in the hybrid mode with a hybrid current of 2 mA at a repetition rate of 1.04 MHz and a pulse width of ~ 70 ps. The X-ray fluxes are ~ 1000 to 6000 photons/hybrid pulse at the sample position over the $L_{1,3}$ edges, respectively. The laser pump pulse at 400 nm is obtained by frequency doubling the 800 nm femtosecond laser (115 fs FWHM, 1 kHz). The laser spot size at the sample position is $180 \times 155 \mu\text{m}$ (vertical x horizontal), providing fluences up to $\sim 1.7 \text{ J/cm}^2$.

The samples consist of sodium iodide (NaI, 99.9% purity, Aldrich-Sigma) dissolved in deionized water at concentrations of 50 mM or 100 mM. The solution is a free flowing liquid jet that refreshes the sample after each laser/X-ray pulse pair. The $200 \mu\text{m}$ -thick liquid jet is rotated such that the flat jet surface is at 45° with the incident X-ray beam. The spatial overlap of the laser and X-ray beams is achieved by the $50 \mu\text{m}$ pinhole: the X-ray beam position on the sample is traced by the pinhole, which is at the same position as the sample. The laser beam is then centred to the pinhole to achieve the overlap.

The time delay between X-ray and laser is electronically controlled by a phase shift feedback loop. Briefly, the device controls the cavity length of the laser oscillator which is synchronized to the radio frequency (RF) master of the storage ring, the regenerative amplifier amplifies selective oscillator pulses while keeping its phase unchanged². The measurements were performed both in transmission and fluorescence modes. The X-ray signal is detected by a silicon avalanche photodiode (APD, C30703F, EG&G). Its output is electronically amplified by the FEMTO amplifier. The details of the data acquisition scheme are explained in ref. ³. Briefly, the hybrid pulse signal is integrated by electronic integrators with gate width of 20 ns. It is recorded at the laser excitation time and $500 \mu\text{s}$ later, where the sample is unexcited. To account for the background and long time drifts of the signal, ‘zero’ count rates are recorded at two positions between the hybrid and the multi bunch.

The transient absorption is given by $\Delta A = \ln(\frac{I_{\text{unpump}}}{I_{\text{pump}}})$, where I_{unpump} and I_{pump} are transmitted intensity of unpumped and pumped sample, respectively. Energy-resolved

measurements are carried out at different energy steps depending on the scanned energy ranges. ΔA is calculated using the weighed average of all I_{unpump} and I_{pump} data points at the respective energies.

SI.3 Femtosecond X-ray absorption experiments

The femtosecond hard X-ray pulses are generated using the slicing scheme.⁴ We use the same laser pump/X-ray probe technique as the one described above, except that the pump-probe synchronization is inherently established, since the time delay can just be controlled by moving a translation stage to change the optical path of the pump beam. The slicing scheme implies a significant loss of X-ray flux and the measurements become more tedious due to the longer data acquisition times. The fs X-ray polychromatic beam is monochromatized by a double crystal Ge (111) monochromator giving an energy resolution of ~ 2 eV at L_1 and L_3 edges of iodine. The beam is then focused at the sample position by KB mirrors, resulting in a spot size of $50 \times 100 \mu\text{m}$ (vertical $\times$ horizontal). The resulting X-ray flux at the sample position under 1 bar of He atmosphere is ~ 20 ph/pulse at the L_3 edge for the sliced beam and ~ 2 phs/pulse in the halo (i.e., the background arising from previous slicing events on the same hybrid pulse). At the L_1 edge, the flux is ~ 33 ph/pulse and ~ 1 ph/pulse for both beams, respectively. The X-ray beam probes the sample at 2 kHz only in transmission mode, since the fluorescence signal is too low to be detected. The sample is pumped by a fs laser at 400 nm, 1 kHz with a fluence of up to 1.2 J/cm^2 . The laser spot size is $\sim 200 \times 200 \mu\text{m}$ at the sample position. To compensate for the low signal-to-noise due to the weak X-ray flux, the sample concentration was high (0.43 M). Degraded samples were regularly replaced to ensure a negligible amount of I_2^- and I_3^- ($< 1.5 \text{ mM}$) that build up in the sample as a result of I^0 formation. All-optical pump/probe measurement shows that at this concentration, only a negligible amount of I_2 molecules is formed before 20 ps (see § S IV.1). The signal from the transmission APD feeds the two boxcars sequentially, one for the sliced beam and the other for the halo beam. The halo signal derived from the pulse just before the sliced one is electronically integrated by the boxcar. Its count rate is considered as a background of the transmitted slice signal. The data acquisition is done in the same way as in the picosecond XAS experiment. In addition, the electronic background drift is regularly measured by entirely blocking the X-rays. This was also done *in situ* by measuring the zero intensities, which should also correct for electronic background contributions. The time delay in the energy scans is calculated by compensating the change of X-ray path length

(due to the rotation of the monochromator crystal) with the delay line which controls the pump laser path length.

In this type of experiment, the spatial overlap is more difficult than in the picosecond experiment because the monochromatized probe beam is not visible by phosphorescence or burning paper. We therefore used a technique based on a knife-edge scan to initially mark the X-ray position. Two blades are mounted at right angle on a holder that is identical to the jet nozzle. The X-ray beam is scanned so that the center of the differentiated curve of the knife edge signal is located at the corner of the blades. This corner is marked by the attenuated pump laser before the blades are replaced by a 100 μm pinhole to precisely track the X-ray beam. The timing overlap is done using the more intense undispersed polychromatic beam with a fast photodiode. The time zero is then post corrected for the beam path length difference when the beam is dispersed by the monochromator. Once both overlaps are done, we start searching for a signal at a selected energy at which we previously found a large signal in the ps measurement. Since the probe flux is extremely low, a conventional time scan would take too long to find the signal and especially time zero. A more efficient way for finding time zero is the so-called binary search, where only signal at selective time points are measured. A range of time which potentially contains the time zero is divided into two regions. A difference in transient absorption of two ends of a region is measured. Temporal regions which show a zero signal indicate that both measured time points are at the same side of time zero, and should be excluded. The search continues in the other region and the process is repeated until the time zero uncertainty is about one ps.

During the actual data collection, the laser position on the sample is monitored online by a beamprofiler that collects the residual transmitted laser through the last mirror that directs the pump laser to the sample. We set the beamprofiler at the same distance to the mirror as the sample so that the beam on the beam profiler corresponds to a perfect conjugate image of the beam on the sample.

SI.4 Power dependence of the signal

Since the 400 nm beam is not absorbed by aqueous iodide, the excitation process is multi photon. Figure S1 shows the fluence dependence of the absorption by the solvated electron probed at 800 nm, 1 ps after excitation converted to the electron concentration via $c_{e^-} = \frac{\Delta OD}{\varepsilon \cdot l}$, where ΔOD , ε , l are, respectively, the transient absorption, the molar extinction of solvated

electron (16000 cm^{-1} , see ref. ⁵) and the sample thickness. The 400 nm pump excitation also generates electrons in pure water via multi photon absorption (Fig. S1). Therefore in Figure S1 the electron concentration is an upper limit of the concentration of iodine atoms, assuming each electron is generated from a photolysed iodide. Up to about 520 mJ/cm^2 , the power dependence is between quadratic and cubic, which implies electron ejection by 2 and/or 3 photon absorption events. However, given that the CTTS band reached by 2-photon excitation is strongly one-photon allowed, it is likely that the excitation process is dominated by 3-photon absorption. A maximum photolysis yield (ratio of product over reactant) of 3% ($1.5\text{ mM} / 50\text{ mM}$) is found at 860 mJ/cm^2 . The latter is still below the highest fluence used in our measurements but as seen later, the estimated yield is quite reasonable.

SII. Molecular dynamics simulations and quantum-chemical calculations

SII.1 Classical molecular dynamics

All of the classical molecular dynamics simulations were performed in a thermal isobaric ensemble (NPT) using the AMBER 10 package with the non-polarizable parm99 force field. The system was composed of either one Γ^- or I^0 solvated in 1192 TIP3P water molecules in a cubic box of $33.6\text{ \AA}$. The same force field parameters were used for both the iodide and the iodine. The structural properties were obtained from the last 5 ns of a 15 ns simulation maintained at 300 K and 1 atm by thermo- and barostats of the Berendsen type. All of the other parameters used in the simulations were the same as presented in ref. ⁶.

SII.2 QM/MM simulations

The QM/MM simulations were performed using the CPMD package⁷ and consisted of either a single Γ^-/I^0 atom or a single Γ^-/I^0 atom and 9 water molecules described at the DFT level of theory solvated in 1192 classical TIP3P water molecules in a box of $33.6\text{ \AA}$. The force field parameters used for the water molecules were the same as those employed in the classical MD simulations. The quantum part of the system was confined in a cubic box with $12\text{ \AA}$ ($20\text{ \AA}$ for the calculations with 9 quantum waters), but classical water molecules could enter the QM box. The core electrons for the anionic and neutral iodine were described using a Goedecker type pseudo potential which included dispersion-corrected atom-centred potentials (DCACPs) terms^{8,9}.

The radial distribution functions were computed from a single trajectory of 15 ps. This is significantly less than the classical simulations due to the computational expense involved. However, given the typical solvent reorganization times of water (1-2 ps¹⁰) they are largely sufficient to capture an equilibrated solvent shell. The RDF for the ensemble averaged calculations were obtained from an average over 10 different starting configurations at each time step.

SII.3. Quantum chemical calculations

Geometry optimisations of small clusters containing either anionic or neutral iodine and 1-4 water molecules were performed at CCSD level using the Molpro¹¹ and Gaussian09¹² quantum chemistry package. A Dunning's double zeta correlation consistent basis set (cc-PVDZ) was used to describe the oxygen, the hydrogens and the valence electrons for the iodine. The lowest 46 core electrons of the iodine were described using a Stuttgart/Cologne energy consistent pseudo potential generated by Dolg and co-workers¹³. Each optimization was performed at a range of starting geometries to ensure a minimum energy geometry. In the case of the iodine clusters this is significantly harder due to the very flat nature of the potential energy surface.

Figure S2 shows the I^0OH_2 potential along the I-O coordinate. It shows a shallow minimum of approx. 50 meV. Figure S3 shows the optimized geometries of the $\text{I}^-/\text{I}^0(\text{H}_2\text{O})_{n=1-4}$ clusters, whose structural parameters are listed in table S4.

SII.4. Core orbital shift calculations

The calculations of the orbital shifts for the diiodide and transient $\text{I}^0(\text{OH}_2)$ complex were performed at CCSD level of theory with a DGDZVP basis set. The relativistic effects were included through the relativistic scheme of eliminating small-component (RESC) of the four-component Dirac equation implemented within the Gaussian09 quantum chemistry package. The difference quoted is between the lone iodine and the optimised structures of diiodide and the transient $\text{I}(\text{OH}_2)$ complex.

SIII. Simulations of the transient EXAFS

The iodide L₃ edge absorption spectrum in energy space is reduced to EXAFS signal $\chi(k)$ using a standard data reduction procedure,¹⁴ where the energy is transformed to wave number k according to $k = \frac{\sqrt{2m_e(E - E_0)}}{\hbar}$ with m_e and E_0 being the electron mass and the ionization energy ($m_e = 9.1 \times 10^{-31}$ kg, $E_0 = 4559.4$ eV).

For the hydration shell of halogen anions, particularly those with large radii, the main contribution to the EXAFS signal is associated with the single scattering events that reflect a two-body interaction. Since we are dealing with disordered media, rather than using the usual discrete form of the EXAFS equation,¹⁵ the X-ray absorption fine structure for both Γ and Γ^0 is modeled as a function of the radial distribution function (RDF) $g(r)$ as¹⁶:

$$\begin{aligned} \chi(k) = & \int_0^\infty 4\pi\rho_O r^2 g_{I-O}(r) A_O(k, r) \sin(2kr + \phi_O(k, r)) dr \\ & + \int_0^\infty 4\pi\rho_H r^2 g_{I-H}(r) A_H(k, r) \sin(2kr + \phi_H(k, r)) dr \end{aligned} \quad (S1)$$

where r is the distance, ρ the density of atoms, $A(k, r)$ and $\phi(k, r)$ are the amplitude and phase functions. An average hydration shell structure, described by pair RDFs, can be extracted from the analysis of the EXAFS signal using Eq. S1. Theoretical EXAFS signal at the iodine L₃ edge associated with the oxygen and hydrogen atoms of the first shell water molecules, are calculated from Eq. S1 using the GNXAS program.^{16,17} The phase shifts $\phi(k, r)$ are calculated from a snapshot (the phase shifts were very similar for different snapshots of the same trajectory) of atomic coordination given by the MD simulations. A Hedin-Lundqvist (HL) plasmon-pole was used for the phase shift calculation with muffin-tin radii for iodide, oxygen and hydrogen of 2.28, 0.9, and 0.21 Å, respectively. Inelastic losses of the photoelectron are accounted for by complex potentials where the imaginary part includes the core-hole width of 3.08 eV for the 2p_{3/2} orbital.¹⁸ The $\chi(k)$ signal is mainly sensitive to a limited distance from the absorber due to the finite photoelectron mean-free path, this effect together with the spectral damping due to monochromator resolution are included in the scattering amplitude $A(k, r)$.

For the structural analysis, we simulate the Γ^0 EXAFS spectrum using the I-O $g(r)$'s from CMD and QMMM simulations using the same setting parameters (reduction amplitude S_0^2 , energy shift E_0 , $A(k, r)$ and $\phi(k, r)$) as for the EXAFS calculation of Γ , and we neglect the I-H $g(r)$'s. The transient EXAFS is then calculated as:

$$\Delta\chi(k) = \chi_{I^0}(k) - \chi_{I^-}(k) \quad (S2)$$

where $\chi_{I^-}(k)$ is the simulated spectrum of I^- . This spectrum is derived from the $g(r)$ obtained by QM/MM simulation, which gave the best agreement with the experimental spectrum¹⁴. The calculated $\Delta\chi(k)$ is then compared to the experimental transient with the only adjustable parameter being ΔE which is a chemical shift due to the change of the I oxidation state. The experimental transient EXAFS results from the edge-jump normalized transient absorption using equation (1) of the paper.

SIV. Extraction of the photolysis yield

Since obtaining the photolysis yield from independent laser-only measurements is not possible under the conditions of our laser pump/X-ray probe experiment (see below), we directly use our time resolved X-ray data to extract the photolysis yield. However we do make use of laser-only measurements to derive some parameters that are needed for fitting the X-ray data. The procedure that follows implies several steps, which we briefly outline before discussing each in detail:

1. We first demonstrate that for 50 mM and 100 mM samples the predominant photoproduct is I^0 at 50 ps time delay after excitation. This implies that we can express the transient absorption at 50 ps as:

$$\Delta A = c \cdot (\varepsilon_{I^0} - \varepsilon_{I^-}) \cdot d \quad (S3)$$

where c is concentration of photogenerated I^0 , ε_{I^0} , ε_{I^-} are the x-ray absorption coefficients of the only two species present in the sample. d is the sample thickness.

2. We fit the transient absorption of the L_1 edge at 50 ps time delay, to derive the concentration of generated I^0 species. This concentration is cross checked by a model-free method, which consists in reconstructing the I^0 spectrum for various concentrations and retaining those that deliver physically realistic spectra (the criterion for that is given below).

3. We apply the approach of point 2 to the L_3 edge for a 100 mM sample. To check the consistency of the extracted I^0 concentration, we fit the transient L_1 edge at 50 ps of this sample (identical pump condition) with Eq. S3 using the ε_{I^0} obtained in point 2. The I^0 concentration results identical for the transient fits at both edges.

The above steps have been carried out in the following way:

SIV.1 Photoproducts at 50 ps time delay:

Upon electron abstraction from iodide and formation of iodine atoms, several reactions take place, which are shown in the following scheme:

Scheme 1: Chemical reactions occurring upon photo excitation of aqueous iodide.

Reaction (S5) corresponds to the formation of the contact pair invoked in ref.¹⁹. Reaction S6 corresponds to the electron-neutral recombination, while reaction S7 to the formation of separated electron and iodine species. Therefore, rate constants k_p , k_n , k_d strongly influence the kinetics of photoproducts at early times. The rate equations for the species involved in reactions S4 to S7 are given by

$$\left\{ \begin{array}{l} \frac{d[I^-]}{dt} = -P(t) \cdot [I^-] + k_n \cdot [(I : e^-)] \\ \frac{d[I^{*-}]}{dt} = P(t) \cdot [I^-] - k_p \cdot [I^{*-}] \\ \frac{d[(I : e^-)]}{dt} = k_p \cdot [I^{*-}] - k_n \cdot [(I : e^-)] - k_d \cdot [(I : e^-)] \\ \frac{d[I]}{dt} = k_d \cdot [(I : e^-)] \\ \frac{d[e^-]}{dt} = k_d \cdot [(I : e^-)] \end{array} \right. \quad (S17)$$

In this set of equations the time convolution between pump and probe pulse is included as a Gaussian function $P(t)$ that models the pump laser:²⁰

$$P(t) = \frac{f \cdot \exp(-\frac{4t^2 \cdot \ln 2}{w^2})}{\sqrt{\frac{\pi w^2}{4 \ln 2}}} \quad (S18)$$

where f is excitation yield at time zero, w is the full width at half maximum of the cross correlation time, 200 fs .

The rate constant k_p (reaction S5) is assumed to be the same as under one-photon excitation,²¹ i.e. $(200 \text{ fs})^{-1}$. In order to derive the rate constants k_n and k_d , we need to record the population evolution of the iodide species. This can be done by probing the kinetics of the iodide bleach in the CTTS bands, under similar excitation conditions as in the X-ray experiment. However, this is not possible because: a) at the concentration of the X-ray experiment (100 mM), absorption of the CTTS bands is saturated; b) these bands undergo a red shift with temperature (Figure S5a).²² The intense laser excitation induces heating, which may therefore distort the measured kinetics of the bleach signal due to the shifting of the CTTS bands. Fortunately, the temperature dependence of the CTTS bands shows an isosbestic point at 211 nm. We therefore recorded the time evolution of the Γ bleach signal at this wavelength (Figure S5b) for a 20 mM sample (the reason for this concentration is to avoid saturation of absorption). The very early times are distorted by an experimental artefact and cannot be used. The trace is fitted to a numerical solution of the Γ population kinetics derived from the rate equations (Eq. S17).

The fitted parameters are k_d and k_n , the excitation yield f is fixed to the value estimated from the maximum bleach signal, which is $\sim 0.8\%$. The fit yields $k_d^{-1} = 59.4 \pm 6.7$ ps, $k_n^{-1} = 97.9 \pm 7.2$ ps. These values differ from those derived by Bradforth et al (70 ps and 33 ps, respectively)²¹ because they used one-photon excitation. We could also extract the rate constant k_4 (reaction S8 of the scheme) by recording the time trace at a probe wavelength of 419 nm where the signal (not shown here) is due to Γ_2 molecules and the solvated electron. The rate constants of reactions S9 to S16 are taken from the literature and are not really relevant here, as they only affect the population dynamics at the ns time scale. The entire set of rate constants is given in table S1.

Table S1: Rate constant values for the reactions S4-S16 in scheme 1.

Rate constant ($\text{M}^{-1}\text{s}^{-1}$)		Reference
k_p	5×10^{12}	²²
k_n	1.0×10^{10}	From fit
k_d	1.7×10^{10}	From fit
k_4	9.6×10^9	From fit
k_5	2.5×10^9	²³
k_6	1.5×10^{10}	^{23,24}
k_7	5×10^9	²⁴
k_8	7.2×10^2	²⁵
k_9	9.1×10^{10}	²⁶
k_{10}	6.4×10^9	²⁷
k_{11}	5×10^{10}	²⁸
k_{12}	3.5×10^{10}	²⁹

Figure S6 shows the temporal evolution of the photoproducts (scheme 1) for solutions of 50 and 100 mM concentrations, using the rate constants given in table S1. The reaction starts off with a photolysis yield of 15% at time zero. This value is purposely well over the estimated photolysis yield in § SI.4, but in spite of this, it can be seen that at 50 ps time

delay, the only photoproduct is I^0 to >98 % for a 50 mM sample and > 95% for a 100 mM solution. Nevertheless and to be on the safe side, we used a 50 mM concentration to extract the L_1 -edge line shape for deriving precisely the photolysis yield.

Table S2: Best fit parameters resulting from the fit of the Iodide L_1 transient to Eq. S3

<u>Parameter</u>	<u>Value</u>
Edge amplitude	1.01±0.04
MS amplitude	1.68±0.76
Atomic peak position	5184.97±0.08
Ionization potential	5193.31±0.28
MS position	5198.14±1.07
Atomic peak area	5.0±1.03
I^0 concentration	0.0024±0.0004
Edge width	0.844±0.442
MS width	6.370±2.932
Atomic peak width	3.082±0.304
Offset	0.00493±0.0140

The rising edge of ε_{I^0} is modelled by $A \cdot \arctg((E - E_{edge}) / w) / \pi + A / 2$ where A is edge amplitude, w is half width at half maximum (HWHM), E_{edge} is edge position. The MS feature is modelled by a Gaussian function $\frac{A \cdot \exp[-4 \cdot (E - E_0)^2 \cdot \ln 2 / w^2]}{\sqrt{(\pi \cdot w^2) / (4 \cdot \ln 2)}}$ where A is MS amplitude, E_0 is MS position, w is full width at half maximum (FWHM). The atomic transition is presented by a Lorentzian function $2 \cdot L \cdot w / [\pi \cdot (4 \cdot (E - E_0)^2 + w^2)]$ where L is atomic peak area, E_0 is peak position, w is the FWHM.

SIV.2. Fractional population of I^0 at 50 ps time delay:

We now use eq. S3 with $l=0.283$ mm to evaluate the effect of the possible $c_{I^0}(50ps)$ values for extracting the I^0 spectrum of a 50 mM solution at 50 ps time delay. Figure S7 shows the

concentration dependence of the I^0 absorption integrated between 5190.5 eV and 5191.6 eV, which is the minimum between the atomic $2s \rightarrow 5p$ resonance and the edge (Figure 1). Its lowest value can only be zero as negative values are unphysical. The lowest value of $c_{I^0}(50ps)$ that satisfies this condition is 1.85 mM (for a 50 mMol solution). The I^0 spectrum extracted for this value is shown in Figure S8. We model the extracted I^0 spectrum as a sum of: i) a Lorentzian for the $2s \rightarrow 5p$ transition; ii) an arctangent function for the edge jump; iii) a Gaussian function for the multiple scattering (MS) feature at ~ 5198 eV and use this modelled I^0 spectrum as $\varepsilon_{I^0}(E)$ in Eq. S3 to fit the transient absorption at the L_1 edge for a 50 mM sample. The resulting fit spectrum is shown in figure S9 and its parameters are listed in table S2. The best fit value $c_{I^0}(50ps) = 2.4 \pm 0.4$ mM is above the lower boundary of $c_{I^0}(50ps)$ (see Figure S7).

SIV.3 Fitting the I^0 absorption line shape at the L_3 edge

Using a similar approach for the $I^0 L_3$ edge, we model the XANES region with two Gaussian representing the two MS features at 4562 and 4572 eV, and one arctangent function for the edge step (Figure S10). The same fit is considered for the $I^0 L_3$ -edge spectrum but with a shift to higher energies. The reason for this is that the L_3 edge consists only of multiple and single scattering features (i.e., no bound-bound transitions like for the L_1 edge), with the edge shifted to higher energies due to the change of oxidation state. We then fit the transient L_3 edge for the 100 mM sample using Eq. S3 taking the width of the Gaussians, the edge energy and the concentration $c(50 ps)$ as adjustable parameters. The result is shown in Figure S11 and Table S3. An I^0 concentration of 3.2 ± 0.3 mM results from the fit. To check the consistency of this value, we fit a simulated L_1 transient spectrum measured for a 100 mM sample under the same conditions, with the $I^0 L_1$ spectrum derived in section SIV.2. The only adjustable parameter is the concentration of excited species and the results yields an I^0 concentration of 3.0 ± 0.5 mM (Figure S12). These two values are consistent. However the latter is more reliable because the $I^0 L_1$ spectrum is derived from a lower concentration which is less contaminated by subsequent products (Figure S6). Therefore the 3% photolysis yield at 100 mM concentration is used to reconstruct the $I^0 L_3$ edge (Figure 2).

Table S3: Best fit parameters resulted from the Iodide L₃ transient fit to Eq. S3

<u>Parameter</u>	<u>Value</u>
Edge amplitude	1.028±0.037
Edge position (eV)	4562.6±0.5
Edge width (eV)	0.77±0.22
Feature A amplitude *	1.34±0.23
Feature A position (eV)	4564.0±0.01
Feature A width (eV)	4.07±0.65
Feature B amplitude*	0.54±0.72
Feature B position (eV)	4577.3±3.0
Feature B width (eV)	6.9±7.3
I ⁰ concentration (M)	0.003217±0.00035
Offset	0.0539 ±0.0197

* Features A and B are shown in Figure S11

In summary, we have shown that at 50 ps time delay, the 50 and 100 mMol samples are negligibly contaminated by photoproducts other than I⁰. This allows us to fit the transient spectrum with a simple equation (Eq. S3) and extract the L₁ spectrum of I⁰. The iodide and iodine spectra are then used to optimally fit the transient and extract a reliable excitation yield. Employing this method for the transient L₃ edge, we get an excitation yield which is consistent with that derived from the L₁ transient. The extracted excitation yield is 3% for a 100 mM sample, and is used in the structural analysis of the transient.

Table S4: Detailed structural parameters for $\text{I}(\text{H}_2\text{O})_{n=1-4}$ (left) and $\text{I}^0(\text{H}_2\text{O})_{n=1-4}$ (right). These parameters correspond to the structures presented in figure 6. All distances are quotes in Å.

	$\text{I}-(\text{H}_2\text{O})$		$\text{I}^0-(\text{H}_2\text{O})$	
	I-O	I-H	I-O	I-H
N=1	3.63	2.69	3.13	3.72
		3.70		3.72
N=2	3.66	2.72	2.94	3.24
		3.75		3.39
		2.72	4.14	3.60
		3.75		4.59
N=3	3.80	2.95	2.81	3.17
		3.76		3.17
		2.95	4.06	3.51
		3.76		4.51
		2.95		3.51
		3.76		4.51
N=4	3.87	3.05	2.82	3.18
		3.84		3.18
		3.05	4.07	3.53
		3.84		4.29
		3.05	4.07	3.53
		3.84		4.29
		3.05	4.29	5.11
		3.84		5.11

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Figure S1: Pump fluence dependence of the solvated electron concentration at 1 ps time delay probed at 800 nm (black circles) for a 200 μm thick sample of 50 mM I^- in water pumped at 400 nm. The electron concentration dependence is fitted equally well with quadratic and cubic functions (green and red solid lines). The electron generated from pure water (blue circles) is best fitted with a cubic function (blue solid line).

Figure S2: Potential energy curve of $\text{I}^0(\text{OH}_2)$ as a function of the I-O distance. Obtained at CCSD level of theory using the same basis sets as the cluster calculations (see § S II.3).

Figure S3: Optimised geometries of $\text{I}(\text{H}_2\text{O})_{n-4}$ (left) and $\text{I}^0(\text{H}_2\text{O})_{n-4}$ (right) obtained at CCSD level of theory (see § S II.3). The I-H and I-O bond distances are given in table S4.

Figure S4: Probability as a function of time of a water molecule being at a distance between 0 and 3.2 Å from the iodine atom, obtained by integration of the I-O RDF in figure 5.

Figure S5: a) absorption of the CTTS bands of aqueous iodide in the temperature range 25-90 °C. The horizontal arrow indicates the direction of the CTTS band shift with temperature. The vertical arrow shows the position of the isosbestic point at 211 nm. b) I⁻ bleach signal probed at 211 nm upon 400 nm pump (open circles) and the fit (red trace) performed based on reaction S5-S8 and equation S18, with k_d and k_n being adjustable parameters.

Figure S6: Population kinetics of I^- (negative trace) I^0 (red positive trace) and I_2 (green positive trace) from [-100 to +200 ps] for the boundary values of the rate constants (table S1) for a 50 mM (dotted traces) and 100 mM (full traces) concentration samples. A photolysis yield of 15% at time zero for both samples was considered.

Figure S7: Averaged absorption between the 25ps peak and the edge step. The region of the weighted average is within the dashed vertical lines in Figure S8.

Figure S8: Normalized I^0 L_1 edge spectrum for $c_{I^0}(50 \text{ ps}) = 1.85 \text{ mM}$ (open circles) fitted by sum of a Lorentzian line shape for the atomic resonance line at 5185 eV, a step function for the edge and a Gaussian function for the multiple scattering feature at 5198 eV (fit parameters are given in table S2). The vertical lines denote the area that is averaged to derive the minimum I^0 concentration (see Figure S6).

Figure S9: Normalized transient L_1 edge spectrum at 50 ps of a 50 mM sample (circles with error bars) fitted with eq. S3 (blue trace). The absorption spectrum of I^0 product is assumed to be composed of one Lorentzian, one edge step and one Gaussian function (fit parameters are given in table S2).

Figure S10: Normalized iodide XANES L_3 edge fitted by Gaussian functions for the two MS features and one arctangent function for the edge step.

Figure S11: Normalized experimental transient L_3 edge spectrum of a 100 mM sample (circles with error bars) and its fit (blue trace) using eq. S3. The I^- and I^0 line shapes are modeled as explained in the text and the fit parameters are given in table S3.

Figure S12: Normalized L_1 edge transient spectrum of a 100 mM sample (circles with error bars) fitted by eq. S3 with the I^0 spectrum obtained in section IV. The best fit (blue trace) is obtained for a concentration of 3.0 ± 0.5 mM.