Solvent rearrangements during the transition from hydrophilic to hydrophobic solvation

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We present an ab initio Born–Oppenheimer molecular dynamics study of the early time solvent dynamics after electron abstraction from aqueous iodide. An initial response occurs within ~75 fs, corresponding to a water molecule sharing almost one electron with the iodine. This is followed by the formation of a transient F−...OH2 complex within ~500 fs. Further insight into the driving forces for this complex are obtained using an energy decomposition analysis and frequency calculations of small clusters. It is shown that the anisotropic solvation shell structure of iodide before electron abstraction is likely to be an important factor in the formation of the complex.

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1. Introduction

Non-equilibrium processes play a crucial role in liquid phase reaction dynamics. Once the solute undergoes a perturbation, the possible outcomes are heavily determined by the structure and response of the solvent which surrounds it. As the vast majority of chemistry and biology occurs in solution, understanding these complex interactions is fundamental to many properties and processes.

Of particular importance are the processes involved in hydrophobic and hydrophilic solvation, which are considered the driving force for many biological processes [1,2]. The simplest example of this is the contrast between the solvation of halides with varying charge. Here significant differences between the solvation environments of the anions with respect to the cations are predicted. These can be traced to the different orientations of the water molecules in the primary solvation shell of the ions (H atoms pointing toward the anions and oxygen atoms toward the cations) [3–6]. Lynden-Bell, Rasaiah and co-workers [3,4] showed that the behaviour of solvated halogen atoms could be characterised as a function of charge with the entropy of solvation of the solute being minimal near zero charge because the water molecules are able to form a hydrogen bonded cavity around the halide (hydrophobic hydration). The solvation entropy gradually increases as a function of the solute charge, reflecting break-up of the cavity because the water molecules preferentially interact with the solute rather than themselves. Recently Wick et al. [7] used classical molecular dynamics (MD) with a polarisable force field to propose that for halides, the extinction of the hydrophobic cavity derives from a slight anisotropic solvation environment for which the polarisability is crucial. This was later confirmed by MD simulations in both a quantum mechanics/molecular mechanics (QM/MM) and a full density functional theory (DFT) framework [8].

The transition from hydrophobic to hydrophilic solvation could eventually best be visualised in time domain experiments, where it can be impulsively induced by a short laser pulse and then probed as a function of time. For this, X-ray absorption spectroscopy (XAS) is ideal as it offers a direct and element specific insight into the electronic structure of the absorbing atom and the solvent geometry around it [9]. To this end, Pham et al. [10] implemented static and time-resolved XAS, of photoexcited aqueous iodide, and extracted details of the solvation dynamics by exploiting the extended X-ray absorption fine structure (EXAFS) and X-ray absorption near edge structure (XANES) regions of the spectrum with pico- and femtosecond resolution [8,11]. They found significant photoinduced changes at the L1,3 edges 50 ps after excitation, which pointed to a reorganisation of the solvent shell around the solute after electron abstraction. The L1 edge sub-picosecond spectra [11], indicated the presence of a transient species that is not present at 50 ps. Quantum chemistry (QC) calculations and QM/MM MD simulations identified this transient species as an...
The simulations showed that upon electron abstraction most of the water molecules move away from iodine, while one comes closer to form the complex which survives for 3–4 ps. It was found that this time is governed by the reorganisation time of the solvation shell in particular the build up of a network of hydrogen bonds. Elles et al. [12] had previously carried out Monte Carlo simulations of the radial distribution functions (RDF) of Br− and Br2, and found that in the latter case, the RDF exhibits a small peak at short distances, which they attributed to formation of a three-electron (σ−σ+) bonded Br2...−OH2 complex.

There have been many investigations of photoexcited aqueous iodide using ultrafast optical spectroscopy, mostly aimed at characterising the formation of the aqueous electron via the charge transfer to solvent (CTTS) bands [13]. Neumark and co-workers [14] used photoelectron imaging on clusters of I (H2O)n=3–10 to measure the vertical detachment energies as a function of time after exciting the CTTS bands of the cluster, and found a drop of ~50 meV after a few tens of picoseconds, which they attribute to loss of the neutral iodine atom from the cluster. Interestingly this value is remarkably close to the binding energy of the I...−OH2 complex reported in Ref. [11]. In a similar study [15] the same authors investigated the relaxation dynamics of I (H2O)n=4–6 clusters. They reported that for n = 4, a simple population decay is observed, but in the cases of n = 5 and 6, a 500 fs decay in the average electron kinetic energy is observed, corresponding to an increase in stability. This was interpreted as the reorganisation of the water molecules in the larger clusters.

In an attempt to characterise the CTTS states Bradforth and Jungwirth [16] performed classical MD simulations. Using snapshots from these simulations they studied the ground state energies for both iodide and iodine and the triplet state energies of iodide. They reported that the excited state orbitals in these small clusters, avoid the solvent molecules and are highly delocalised. In contrast for the bulk, the CTTS are necessarily buried in the solvent and the vertical electron binding energy is almost an order of magnitude larger. In similar work, Kim and co-workers [17] characterised the structure of small iodide clusters and used ab initio molecular dynamics [18,19] to demonstrate that once excited into the CTTS states, the solvent undergoes a significant rearrangement to accommodate the photoelectron.

Here, we build on our previous work [8,10,11] and aim at describing the driving forces and the early time dynamics of the solvent rearrangement following photoabstraction of the electron from aqueous iodide. To this end, we perform ab initio MD simulations of both aqueous iodide and iodine, paying particular attention to the first 2 ps after electron abstraction. We show that in the first 75 fs, there is a significant response, characterised by the interaction between the iodine and one water molecule. Within 500 fs, a transient I...−OH2 complex is formed. The analysis of the MD simulations is supported by an energy decomposition analysis (EDA) and frequency calculations of optimised clusters. These indicate that the polarisation of the iodine originating from the anisotropic solvation shell structure of iodide before electron abstraction, is critical to the formation of the complex.

2. Theoretical approach and computational details

2.1. Ab initio molecular dynamics

The system consists of one iodide (or iodine) atom and 183 water molecules treated within periodic boundary conditions using a cubic simulation supercell of 18.15 Å sides. The initial configuration was obtained from a classical MD equilibration of 10 ns with a 1 fs time step using the Amber 7 package [20] and the nonpolarisable parm99 force field [21]. During this time the system was maintained at 300 K and 1 atm by the thermostat and barostat of Berendsen type, and the electrostatic interactions were treated using the particle mesh Ewald scheme [22].

The ab initio MD simulations were performed with the Born–Oppenheimer propagation scheme implemented in the CPMD package [23] using a time step of 15 a.u. The electronic part was described using DFT within the approximation of the BLYP xc potential [24,25]. The core electrons were treated using pseudopotentials of the Troullier–Martins type [26] and integration of the nonlocal parts of the pseudopotential were performed using the Kleinman–Bylander scheme [27]. The Kohn–Sham orbitals were expanded in plane-waves up to a kinetic energy cutoff of 100 Ry. Following this, a short preparation run of 2.0 ps was performed starting from the classically equilibrated geometry, this was followed by a production run of 3.0 ps that was used for the analysis of the iodide solvation geometries. Throughout the simulation a temperature of 300 K was maintained using the Nosé–Hoover thermostat [28,29] with a coupling constant of 2000 cm−1. An electron was then removed from the system and the calculation restarted from the last geometry of the iodide trajectory and the MD then run for a further 2.0 ps.

Given the computational expense of such calculations, only one simulation run is presented here. It is important to note that this does represent a limitation of the present work, for which ideally an ensemble of trajectories would be averaged to obtain statistical insight into the processes discussed. However, the results are in accordance with the QM/MM MD simulations presented in Ref. [11] and therefore we expect that a full statistical sampling would not significantly change the essence of the present analysis.

To analyse the electron density, the cell volume was partitioned into Voronoi polyhedra centred at each of the monomers and the corresponding electron density was monitored separately for each.

2.2. Quantum chemistry calculations

Geometry optimisations of the small clusters of the form I...−(H2)O=1, ...4 were performed at coupled cluster singles and doubles (CCSD) level [30] implemented within the Gaussian 09 quantum chemistry package [31]. Throughout the optimisation no symmetry constraints were imposed and for the case of the open shells a spin unrestricted coupled cluster singles and doubles (UCCSD) was used. A Dunning’s double zeta correlation consistent basis set augmented with diffuse functions was applied to the oxygen and the hydrogens while the iodine atom was described using a relativistic effective core potential, which retains the 5s and 5p electrons in the valence space [32]. In addition the optimised geometries of n = 1, 2 and 3 were used to calculate the normal mode frequencies in the standard approach implemented within the Gaussian 09 quantum chemistry package [31].

The energy decomposition analysis of the clusters were performed using the localised molecular orbitals energy decomposition analysis (LMOEDA) [33] implemented within the GAMESS quantum chemistry package [34]. The calculations were performed at MP2 level using the optimised geometries described above. The calculations were corrected for basis set superposition error using the Boys and Bernardi counterpoise method [35]. In the LMOEDA approach the total Hartree–Fock (HF) interaction energy is defined:

$$\Delta E^{HF} = \langle \phi_x | H_x | \phi_y \rangle - \sum_y \langle \phi_y | H_y | \phi_x \rangle$$

(1)

where x is the supermolecule consisting of y monomers. $\phi_x$ are the variational single determinant HF wavefunctions. The total HF interaction energy is decomposed into contributions from electrostatics
(\(E^e\)), exchange (\(E^x\)), repulsion (\(E^{rep}\)) and polarisation (\(E^{pol}\)) in the form:

\[
\Delta E^{tot} = \Delta E^e + \Delta E^x + \Delta E^{rep} + \Delta E^{pol}
\]

(2)

Dispersion is accounted for by the addition of dynamic correlation:

\[
\Delta E^{disp} = \Delta E^e + \Delta E^{disp}
\]

(3)

where \(\Delta E^{disp}\) represents the total interaction energy of the complex. This method has been applied to a wide variety of small supermolecules. These can be found along with a detailed derivation of the method in Ref. [33].

3. Results

3.1. Ab initio molecular dynamics

To describe the solvation dynamics of iodine in bulk water following removal of the electron and obtain information about the factors leading to the formation of the transient \(I^–\cdot\cdot\cdotOH_2\) complex previously reported in [11], we focus on the dynamics during the first 2 ps after the removal of the electron. As a result we do not show the equilibrium solvation shell structure of iodine which was presented in Ref. [11]. In addition we consider that the electron is ejected directly into the solvent without any dynamics via the CTTS states.

Fig. 1 shows the radial distribution function (RDF) for \(I^-\cdot\cdot\cdot\cdot O\) and \(I^-\cdot\cdot\cdot\cdot H\) integrated over the first 2 ps of the MD simulations. The time frame considered means that the RDF are not converged, however the important features show up. For iodide, the oxygens of the closest water molecules are at a distance \(\sim 3.5\) Å away, while the hydrogens are \(\sim 2.75\) Å away indicating, as previously reported [3], that the water molecules are oriented so that the hydrogens point towards iodide.

Following removal of the electron, the RDF broadens significantly reflecting the diffuse nature of the solvation shell. In addition this is accompanied by a rotation of the water molecules as the I–H distance increases by \(\sim 1.0\) Å. Most notably, the \(F^–\cdot\cdot\cdot O\) RDF (Fig. 1a) shows that while most of the water molecules move away, there is a small probability that one water molecule moves closer to the iodine. This corresponds to the transient \(F^–\cdot\cdot\cdotOH_2\) complex.

This is better seen in Fig. 2, which shows the I–O distance of all of the water molecules that come to within 3.5 Å of the iodine during the 2 ps MD trajectory. We consider that the water molecule is complexed to the iodine if the I–O distance is <3.0 Å, which is shown by the shaded green region. The criterion is based on the equilibrium distance of the \(F^–\cdot\cdot\cdotOH_2\) complex which is 3.1 Å [11,36]. From a starting configuration, taken from the iodide MD, initially the closest oxygens are \(\sim 4.0\) Å from the iodine. However, following removal of the electron, one water molecule (blue in Fig. 2) moves close to the iodine and reaches its minimum distance of 2.9 Å after 75 fs. This water does not form a complex and moves back to the bulk after a few tens of fs. Within 350 fs another water molecule (black in Fig. 2), moves close and remains complexed throughout the remaining 2 ps of the simulation. This time frame for the formation of the complexed water molecule is likely demonstrating that at early times the system is unable to form the complex because of the large rearrangements of the solvent structure, including reorientation of the water molecules and expansion of the primary solvent shell. From our previous QM/MM MD simulations [11] we estimated that these large rearrangements occur on a timescale of 300–400 fs, which is in agreement with Fig. 2 that shows that after \(\sim 300–400\) fs, the water molecule remains complexed for the 2 ps simulation with only a temporary exchange with another molecule at \(\sim 600\) fs.

To better understand the initial formation of the complex (\(\sim 75\) fs), we turn our attention to the initial electronic response, which acts as the driving force for the nuclear motion. In Fig. 3, we present a Voronoi analysis of the electronic density around iodine in the first 75 fs. At \(t = 0\), the solvent configuration is still that of iodide and the number of valence electrons attributed to the iodine is 6.8, reflecting its 5s25p5 configuration, with a small amount of electron density transferred to the hydrogen atoms on the closest water molecules as is the case for iodide. However, within 75 fs we observe a transfer of density corresponding to almost 1 full electron to the iodine. This electron is shared between the iodine
and the closest water molecule (blue in Fig. 2), forming the initial short lived complex. In the upper panel of Fig. 3 we plot the density at 0, 35 and 70 fs after removal of the electron. The water molecule (indicated with a red arrow) which forms the complex is just above and right of the iodine (green). Initially there is no interaction, however in the second frame one can observe a slight distortion of the density near the oxygen. After 70 fs there is a clear interaction with density being donated to the iodine from the water molecule.

This interaction has previously been described as a three electron bond [11], and has also been reported for Cl0 and Br0 [37,12]. Using a Mayer bond order analysis [38], we find for the initial I0–OH2 complex a bond order of 0.32, consistent with a three electron bond [39]. For such interactions, the bond order is lower than 0.5, typically found for one electron bonds, due to the destabilising effect of the electron repulsion. At later times along the trajectory the bond order varies between 0.22 and 0.37 indicating that the interaction is the same for the early and later time complexes.

3.2. Energy decomposition analysis of clusters

As demonstrated in the previous section, electronic distortions lead to the interaction between the closest water molecule and iodine. These act as the driving force for the formation of the complex. Here, to ascertain a more detailed understanding of the physical origin of this interaction we perform an energy decomposition analysis (EDA) on geometry optimised clusters, I–O distance for the analysis (EDA) on geometry optimised clusters, I0–(H2O)n clusters are shown in Tables S2, S3 and S4, respectively. For the monomeric species (n = 1) the largest difference between the neutral and anionic forms is, unsurprisingly, the electrostatic contribution, arising from the interaction between the iodide and the partial positive charges on the hydrogens. The interaction between the two monomers in the neutral complex derives mostly from exchange, shown by $E^{ex} = -11.81 \text{kcal/mol}$, showing that the hydrogen atoms point away from the iodine atom as expected.

The results of the EDA for the supermolecule are shown in Table 1, while the decomposition of the overall interaction energy into molecular pairs within the supermolecule (pairwise terms) for the I0–(H2O)2,3,4 clusters are shown in Tables S2, S3 and S4, respectively.

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![Fig. 3](image3.png) Upper panels: isosurfaces (isovalue = 0.025) of the electron density at 0 (a), 35 (b) and 70 fs (c) after abstraction of an electron. Bottom panel: the number of valence electrons attributed to iodine following a Voronoi analysis up to 75 fs following removal of the electron from iodide (lower panel).

![Fig. 4](image4.png) Optimised geometries of I0(H2O) (left) and I0(H2O) (right) for $n = 1$ (a), $n = 2$ (b), $n = 3$ (c) and $n = 4$ (d) obtained at CCSD level [11].
reflecting an increased orbital overlap between the two species, which is also responsible for an increase in $E^{\text{pol}}$. This leads to a larger distortion of the orbitals than in the anionic structure shown by the difference in $E^{\text{pol}}$, which is larger for the neutral case. In both cases $E^{\text{pol}}$ contributes to the stability of the structure, and it is well documented that, in the absence of a charged atom (i.e., iodide) for which the electrostatic interaction will dominate, dispersion forces play an important role in molecular properties [40–43]. In the present work, the ab initio molecular dynamics, using DFT (BLYP) are unable to describe dispersion. However, the complex still exists and yields a I–O distance comparable to the CCSD optimised geometries. Therefore, as shown in Table 1, although $E^{\text{pol}}$ contributes to the total interaction energy, it is $E^{\text{disp}}$ which is more important.

For the larger clusters, $E^r$ and $E^{\text{pol}}$ becomes increasingly attractive. This change is larger for the anionic clusters because for these structures the orbitals of the water molecules overlap both with the iodide and its nearest neighbours. Inspection of the pairwise terms (in the SI) shows that the strength of the OH$_2$–···I$^-$ interaction increases with the number of water molecules, while the I$^-$.OH$_2$ interaction decreases. This is due to finite size effects, reflecting the gradual convergence of the interactions towards bulk properties. Despite this the I$^-$.OH$_2$ interaction still dominates the supermolecule, a hallmark of hydrophilic solvation.

Importantly for the neutral clusters, changes in $E^r$ and $E^{\text{pol}}$ mainly derive from the OH$_2$–···OH$_2$ interaction, as additional water molecules do not have direct interactions with iodine, but rather form hydrogen bonds with each other. This would suggest, as expected, that the stability of the I$^0$–OH$_2$ complex shown in the neutral clusters is very dependent on the cluster size, because as the number of water molecules increases so will the hydrogen bond network, making it less energetically favourable for the complex to survive. In fact the stability of the complex (AE, see Tables S2, S3 and S4) is weaker than the hydrogen bond interactions. Therefore, as postulated in Ref. [11], it is likely that this complex will disappear when the more energetically favourable hydrogen bond network is formed. This is not the case for these small clusters.

$E^{\text{pol}}$ of the anionic clusters is a relatively small contribution in comparison to both $E^r$ and $E^{\text{pol}}$. Despite this, as previously reported [7,8] it plays an important role for the anisotropic solvation shell. For the neutral species the total $E^{\text{pol}}$ is larger for the $n = 1, 2$ and 3 clusters than in the anionic cluster. The pairwise terms show that the vast majority of this polarisation contribution energy derives from the I$^0$–OH$_2$ complex. In fact $E^{\text{pol}}$ is the largest stabilising contribution within the I$^0$–OH$_2$ complex and therefore critical to its formation. These observations add special importance to the anisotropy of the solvation shell of iodide reported in Refs. [7,8]. This anisotropy leads to a slight polarisation of the iodide, which upon removal of the electron will act as the initial driving force for the formation of this complex on short timescales in the absence of an extended hydrogen network, as shown by the complex at ~75 fs.

Finally, for the I$^0$–OH$_2$ complex, which has an open shell electronic structure, it is important to assess the effect of spin orbit coupling, which is large for iodine, $I^*$$(\Pi_{1,2})$–I$(\Pi_{1,2})$ = 0.94 eV [44]. For this, we have performed a geometry optimisation of the I$^0$–OH$_2$ complex, using the ADF quantum chemistry package [45] at DFT (BLYP) level of theory and a TZVP basis set. When no relativistic effects are included the optimisation yields an I–O distance of 2.98 Å and this slightly contracts (0.04 Å) upon inclusion of scalar relativistic (ZORA) effects. When adding the full relativistic treatment, including SOC effects, the bond length expands to 3.15 Å and this relatively small change in the interaction length is consistent with previous studies on the potential energy curves of iodine oxide [46] which reported only a small change to the I–O distance upon inclusion of SOC.

4. Discussion

The molecular dynamics simulations following electron abstraction from iodide in water show that a transient complex is formed within 75 fs, arising from an electron being shared between the iodine and the oxygen in the closest water molecule. This electronic interaction is understood using an EDA of the optimised clusters and shows that indeed only one water molecule interacts with the iodine because it is more energetically favourable for the remaining water molecules to form a hydrogen bonded network. In fact the I$^0$–OH$_2$ complex is only stabilised, in the absence of an extended hydrogen bond network, due to a significant contribution to the polarisation energy. This importance of the polarisation energy adds significance to the anisotropic solvation shell around the iodide [8] which will likely act as a driving force in forming the complex following abstraction of the electron.

Interestingly, the EDA suggests that for the small clusters, the hydrogen bond actually stabilises the I$^0$–OH$_2$ complex. This is demonstrated for the $n = 2$ and 3 clusters by the shortening of the I–O bond and an increase in the pair wise terms for the I$^0$–OH$_2$ complex (shown in Tables S2, S3 and S4). The origin of this increase is electrostatic and because the presence of one or two water molecules close to the complexed water molecule stabilises the charge transfer to the iodine. However for the $n = 4$ clusters the I$^0$–OH$_2$ complex is weakened, and this is likely demonstrating the effect of a H-bond network, which is first apparent for this cluster.

The initial complex formed in the MD simulations is unstable due to the large rearrangements of the solvent structure within the first 200 fs, as the binding energy of the complex (50 meV) is only two times larger than kT. This instability is shown by the exchanges of the water molecules which attempt to complex to the iodine. However there after a complex is formed beyond 350 fs and remains for the rest of the 2 ps simulation, though undergoing large amplitude oscillations during the first ps. In fact derived from the simulations of Ref. [11], its lifetime is expected to be around 3–4 ps. Interestingly the timescale for the formation of the complex has some agreement with the induction period (500 fs) of the vertical detachment energy reported by Neumark and co-workers [15] on the study of I$^+$ (H$_2$O)$_n$ clusters. They postulate that a change in the electron binding energy was due to reorganisation of the water molecules. This was observed for both the $n = 5$ and $n = 6$ clusters, but not for the $n = 4$ clusters, which they concluded could not rearrange efficiently to stabilise the excess electron transferred from iodide. In the present case the excess electron is neglected, however the agreement of these timescales does indicate that, despite the differences in the systems understudy, there are similarities in the ultrafast solvent response around iodine.

In a later study, Neumark and co-workers [14] reported a reduction in the vertical detachment energy of 50 meV, a few tens of picoseconds after photo excitation. They attribute this to the loss of the iodine atom from the cluster, and interestingly this energy is remarkably close to that of the I$^0$–OH$_2$ complex well depth [11,36]. In our case the separation of the water molecule from the complex it formed with the I$^0$ atom would be the analogue of the loss of the I$^0$. However, the processes are somewhat different. Indeed I$^0$ sits at the surface of the cluster [16] and a full solvation is probably never achieved (even with 10 molecules). Therefore, the dynamics for the clusters are likely determined by the initial conditions and the detachment of I$^0$ is then governed by thermal effects, which require long time scales (tens of picoseconds) to affect the cluster.

Finally, in Fig. 2, we see that the complex undergoes oscillations with periods of ~150–300 fs. The short time corresponds to a frequency of 200 cm$^{-1}$, which is close to the frequency of the in plane
bending mode of the \( \text{I}^0(\text{H}_2\text{O}) \) complex assigned by mass selective anion-ZEKE spectroscopy [47]. However here, these oscillations corresponds to the I–O stretching mode (shown by the I–O distance in Fig. 2), which has a reported frequency of 50 cm\(^{-1} \) [47]. Calculations of the frequencies of the geometry optimised clusters for \( \text{I}^0(\text{H}_2\text{O}) \), \( \text{I}^0(\text{H}_2\text{O})_2 \) and \( \text{I}^0(\text{H}_2\text{O})_3 \) indicates that the I–O stretching frequency of the iodine–water complex shifts from 86 cm\(^{-1} \) for \( \text{I}^0(\text{H}_2\text{O}) \) (in agreement with Ref. [36]) to 182 cm\(^{-1} \) in \( \text{I}^0(\text{H}_2\text{O})_2 \) which are close to the low and high frequency limit of the oscillations. This shift is derived from the presence of the additional water molecules, which appear to stabilise the complex for the \( n = 2 \) and 3 clusters, as previously discussed. The origin of the stabilisation is electrostatic. It is weakened for the \( n = 4 \) cluster, because this cluster shows the initial formation of a H-bond network. From this, one may conclude that the complexed water molecule undergoes oscillations on time scales that reflect an influence by the nearby molecules.

- Upon electron abstraction from iodide, an \( \text{I}^0 \cdots \text{OH}_2 \) complex forms in 75 fs, which is characterised by a transfer of electron density from the water molecule to the \( \text{I}^0 \) atom, reflecting the formation of a 3-electron bond, already discussed for \( \text{I}^0 \) [37] and \( \text{Br}^0 \) [12] complexed with water. The early formation of this complex is favoured by the anisotropy of the solvation shell that exists around \( \text{I}^0 \) prior to electron abstraction. This complex is short lived (<100 fs) due to the extensive solvent rearrangements still taking place.

- At later times (~400 fs) another \( \text{I}^0 \cdots \text{OH}_2 \) complex forms that undergoes large amplitude oscillation up to ~1.2 ps, then low amplitude ones around the equilibrium distance (~2.9 Å) of the isolated \( \text{I}^0 \cdots \text{OH}_2 \) complex [36,11]. The electronic structure of this complex (three electron bond) is the same as that of the short lived one, as supported by our sub-ps XAS measurements [11].

- Finally the large amplitude excursions the complexed water molecule undergoes makes below ~1.2 ps are characterised by time scales which reflect a changing stretch oscillation frequency due to the influence of the nearby water molecules.

The dynamics presented here do not involve the CTTS states, which are known to be highly complex. It has been reported for iodine, that the anisotropic solvation shell plays a significant role as, following excitation a contact pair of iodine and the electron has been following excitation a contact pair of iodine and the electron has been postulated as an intermediate, with the electron cloud filling the voids of the solvation shell in an anisotropic fashion [16]. Therefore further experimental and theoretical investigations are required to ascertain the role of this \( \text{I}^0 \cdots \text{OH}_2 \) complex to the dynamics of the CTTS states of aqueous iodide.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.chemphys.2012.10.008.

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