Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics. This journal is © the Owner Societies 2022

SUPPLEMENTARY INFORMATION: Probing the molecular structure of aqueous triiodide via X-ray photoelectron spectroscopy and correlated electron phenomena

Md Sabbir Ahsan^{1,3}, Vladislav Kochetov⁴, Dennis Hein^{2,5}, Sergey I. Bokarev⁴, and Iain Wilkinson^{1*}

¹Locally-Sensitive and Time-Resolved Spectroscopy, Helmholtz-Zentrum Berlin für Materialien und Energie, Hahn-Meitner-Platz 1, D-14109 Berlin, Germany

²Operando Interfacial Photochemistry, Helmholtz-Zentrum Berlin für Materialien und Energie, Hahn-Meitner-Platz 1, D-14109 Berlin, Germany

³Department of Physics, Freie Universität Berlin, Arnimallee 14, D-14195 Berlin, Germany

⁴Institut für Physik, Universität Rostock, Albert Einstein Str. 23-24, D-18059 Rostock, Germany

⁵Department of Physics, Humboldt-Universität zu Berlin, Newtonstrasse 15, D-12489 Berlin,

Germany

*Email: iain.wilkinson@helmholtz-berlin.de

A $I_{3(aq.)}^{-}$ sample preparation, UV-Vis absorption spectra, & characterisation of mixed $I_{3(aq.)}^{-}$ and $I_{(aq.)}^{-}$ solutions

Three different $I_{3(aq.)}^-$ solutions were implemented in the X-ray photoemission spectroscopy (XPS) experiments described in the main text. Specifically, 500 mM / 250 mM , 350 mM / 250 mM, and 420 mM / 210 mM NaI / I_2 mixtures were prepared in an aqueous solvent at room temperature. The former two mixtures were utilised in the BESSY II experiments, while the latter mixture was studied at PETRA III.

The solubility of iodine in an aqueous solvent is just 1.3 mM at $25^{\circ}C^{1}$. When I₂ is dissolved in water alone, I₂–H₂O charge-transfer complexes are known to be predominantly formed, with only a small fraction of the coordinated I₂ species oxidising water to form $I_{3(aq.)}^{-}^{2}$. Upon addition of excess iodide salts to such solutions, however, the water-coordinated I₂ molecules are consumed by the $I_{(aq.)}^{-}$ anions to form $I_{3(aq.)}^{-}$ and the effective solubility of I₂ increases significantly, see Reference 2 and Figure S1. Correspondingly, almost all of the solutions considered here were prepared by adding NaI to the aqueous solvent in excess quantities, with subsequent addition of I₂, followed by assisted dissolution and degassing in an ultrasonic bath. Adopting this approach, the triiodide anion is predominantly formed in aqueous solution by increasing the iodide and iodine reagent concentrations, driving the associated equilibrium towards the triatomic adduct, in accord with the following chemical equation³:

$$I_{2(aq.)} + I_{(aq.)}^{-} \rightleftharpoons I_{3(aq.)}^{-}$$
 (1)

The $I_{3(aq.)}^{-}$ sample and any residual $I_{2(aq.)}$ and $I_{(aq.)}^{-}$ solution concentrations produced via the aforementioned reagent mixing procedure were characterised over a wide range of concentrations using UV-Vis absorption spectroscopy measurements and the methodology described below. 10 μ m to 10 mm path length absorption

cells and a commercial UV-Vis spectrometer system (Shimadzu UV 2700i, with a useful operating range of 1.4-6.5 eV) were used to perform the associated measurements. Notably, these characterisation measurements were primarily sensitive to the bulk, *i.e.* average, solute concentrations within the prepared mixtures.

We begin by discussing potential XPS spectral contamination from residual I_{2(aq.)} molecules. Figure S1 shows UV-Vis absorption spectra of $I_{2(aq.)}$ (black curves) and $I_{2(aq.)}$ + NaI_(aq.) mixed (red, green, and blue curves) solutions with two different signal intensity scaling approaches. Both panels show 0.04 mM I_{2(aq.)} (black) and 0.15 mM $I_{2(aq.)}$ / 0.15 mM $NaI_{(aq.)}$ mixed (red) solution data, which were sequentially recorded using a 10 mm pathlength absorption cell. 5 mM $I_{2(aq.)}$ / 10 mM $NaI_{(aq.)}$ (green) and 210 mM $I_{2(aq.)}$ / 420 mM $NaI_{(aq.)}$ (blue) mixed solution data are also shown, as respectively recorded with 0.1 mm and 0.01 mm path length absorption cells. In Panel (a), the spectra are signal intensity normalised to the peak of the $I_{3(aq.)}^{-}$ C-band absorption, centred at \sim 3.5 eV^{4,5}, with the black I_{2(aq.)} curve intensity scaled by the same factor as implemented for the red 0.15 mM $I_{2(aq.)}$ / 0.15 mM NaI_(aq.) curve. The black curve and inset in Panel (a) highlights the visible absorption feature of the I_2 - H_2O charge-transfer complex, centred at ~ 2.7 eV. The corresponding red curve shows a vastly increased $I_{3(aa.)}^{-}$ absorbance at 3.5 eV, with just a moderate absorbance increase at \sim 2.7 eV when NaI is added to the solution to 0.15 mM concentration and the nominal $I_{2(aq.)}$ concentration is increased from 0.04 mM to 0.15 mM. The black and red curves correspondingly show how the I2 in the I2-H2O complex is consumed and converted to $I_{3(aq.)}^{-}$ as NaI is added to the $I_{2(aq.)}$ solution and the reagent concentrations are increased. Further increasing the nominal solute concentrations beyond the $I_{2(aq.)}$ -only solubility limit, by implementing a 2:1 excess of NaI to I₂, the \sim 2.7 eV band signal is found to further diminish with respect to the $I_{3(aq.)}^{-}$ \sim 3.5 eV band signal, as shown by the green and blue curves. Considering the full spectral range of Figure S1a, with increasing reagent concentrations, the green and blue curves highlight increasingly intense $I_{3(aq.)}^{-}$ absorption bands at ~2.8 eV, ~3.5 eV, and ~4.4 eV^{4,5}, as well as $I^-_{(aq.)}$ absorption bands at ~5.5 eV and ~6.5 eV^{6,7}, as further discussed below.



(a) Normalised UV-Vis spectra of $I^-_{2(aa.)}$, $Nal_{(aq.)}$ mixtures

(b) Path-length-scaled UV-Vis spectra of $I_{2(aq.)}^{-}$, NaI_(aq.) mixtures

Figure S1 $I_{2(aq.)}$ and concentration-dependent $I_{2(aq.)} + NaI_{(aq.)}$ mixed solution UV-Vis absorption spectra. Panel (a) shows the $\sim 3.5 \text{ eV} I_{3(aq.)}^-$ C-band peak normalised data. Panel (b) shows the same data without such normalisation but with intensity-scaling in accord with the absorption cell path lengths used to collect the data. See the main body of the text for details.

In Figure S1b, we present the data shown in Panel (a) with an alternative logarithmic intensity scaling. There, the as-recorded black and red curve absorption data are shown, with the as-measured green and blue mixed solution data intensity-scaled by factors of 100 and 1000, respectively. These high concentration data intensity scaling factors were set in accordance with the reduced relative absorption cell path lengths implemented in those measurements and the Beer-Lambert law, i.e. with the green and blue curve scaling factors respectively set as 10 mm/0.1 mm=100 and 10 mm/0.01 mm=1000. This facilitates a coarse comparison of the relative absorbance of the four different solutions, recorded with three different cell pathlengths. The scaled $I_{3(aq.)}^{-}$ C-band signals shown in Figure S1b correspondingly show that the $I_{3(aq.)}^{-}$ concentration increases by more than four orders of magnitude in going from a 0.15 mM/0.15 mM to a 210 mM/420 mM mixed $I_{2(aq.)}/NaI_{(aq.)}$ solution. In contrast, the overlapping $\sim 2.8 \text{ eV } I_{3(ac.)}^-$ and $\sim 2.7 \text{ eV } I_{2(aq.)}$ absorbance signals increase by around three orders of magnitude, which again indicates a consumption of $I_{2(aq.)}$ as $NaI_{(aq.)}$ is added in a 2:1 excess and the nominal solute concentrations are increased. Unfortunately, irrespective of the implemented data normalisation procedures, the near-complete spectral overlap of the $I_{2(aq.)}$ and $I^-_{3(aq.)}$ visible absorption features and generally-implemented high solute concentrations prevented us from using the data shown in Figure S1b alone to directly determine the $I_{3(aq.)}^{-}$ -to- $I_{2(aq.)}$ concentration ratio in the solutions used in the XPS experiments. We correspondingly rely on previously-reported thermodynamic data to extract this ratio and interpret the highconcentration UV-Vis spectra.

Considering Equation 1 and its associated equilibrium constant $(K=698\pm10)^3$, we can readily determine



Figure S2 UV-Vis absorption spectrum of a mixed 250 mM Nal and 125 mM I₂ aqueous solution (red curve). A cumulative Gaussian and exponentially modified Gaussian fit to the data is additionally shown (dashed-dotted black curve), including contributions from the B, C, D, and E electronically excited states of the $I_{3(aq.)}^{-}$ anion^{4,5} and the first ${}^{2}P_{\frac{3}{2}}$ and second ${}^{2}P_{\frac{1}{2}}$ charge-transfer-to-solvent (CTTS) states of the $I_{(aq.)}^{-}$ anion^{6,7} (coloured, dotted curves, labelled CTTS 1 and CTTS 2). The signatures of the $I_{3(aq.)}^{-}$ anion E state and lower $I_{(aq.)}^{-}$ anion CTTS state notably overlap (purple, dotted fit component) and cannot be distinguished from spectra recorded at fixed reagent concentrations.

the relative equilibrium concentrations of $I_{3(aq.)}^{-}$ with respect to $I_{2(aq.)}$ at fixed, known NaI_(aq.) concentrations. With 170–285 mM equilibrated NaI_(aq.) concentrations – which emerge in the solutions implemented in the XPS measurements, as determined in the forthcoming paragraphs of this section – a large $1.2 \cdot 1.8 \times 10^5 I_{3(aq.)}^{-}$ concentration-excess is expected. We further consider the relative peak molar extinction coefficients of the ~3.5 eV $I_{3(aq.)}^{-}$ C band (~16770 M⁻¹ cm⁻¹) and $I_{2(aq.)}$ ultraviolet charge-transfer band (~6.1 eV, ~9100 M⁻¹ cm⁻¹) reported in Reference 2, where the latter and cumulative Gaussian fits to the black curves in Figure S1b allow us to infer a related visible, 2.7-eV-band $I_{2(aq.)}$ peak extinction coefficient of ~290 M⁻¹ cm⁻¹. It can subsequently be estimated that the relative $I_{3(aq.)}^{-}$ contribution to the ~2.8 eV absorption feature in the blue mixed-solution spectra shown in Figure S1b is ~290 M⁻¹ cm⁻¹ / ~16770 M⁻¹ cm⁻¹ * ~1.5 × 10⁵ ≈ 2590 times higher than that of $I_{2(aq.)}$. That is, the $I_{2(aq.)}$ and high concentration conditions associated with the blue curves shown in Figure S1b and the UV-Vis data subsequently discussed in this Section. Furthermore, given the 1-2% signal-to-noise (S/N) ratio and up to few-percent relative signal area inaccuracies in all of the XPS data presented in the following Sections and main manuscript text, and reasonably assuming $I_{3(aq.)}^{-}$ and $I_{2(aq.)}$ contribution to the overall, concentrated-solution XPS signals also amounts to <0.1% and is correspondingly negligible.

In contrast to the $I_{2(aq.)}$ contributions to the sample solutions, the high-photon-energy regions of the green and blue curves shown in Panel (b) of Figure S1b indicate that residual $I^{-}_{(ac.)}$ content in the concentrated, mixed solutions may make significant contributions to the overall XPS signals. To define these contributions, additional UV-Vis absorption spectroscopy measurements were performed with minimum pathlength 10 μ m absorption cells over a broad solute concentration range. The primary associated aim was to accurately determine the degree of conversion of $I_{2(aq.)}$ to $I_{3(aq.)}^-$ and the concentration of residual $I_{(aq.)}^-$ as a function of the initial reagent concentrations. Corresponding $I_{3(aq.)}^{(aq.)}$ solutions were prepared with different I₂ concentrations spanning 25-250 mM and I₂-to-NaI concentration mixing ratios, defined as $[I_{(ac.)}^-]:[I_{2(aq.)}] = x:1$, where x = 1.4-10.0. An exemplary UV-Vis absorption spectrum recorded with an x value of 2.0 is shown in Figure S2, the data in which is notably free from absorption saturation effects. Four different peaks are directly visible in such UV-Vis spectra, denoted as C, D, E & CTTS 1, and CTTS 2 in Figure S2. A weaker additional peak, marked B (~2.75 eV, 451 nm), is also highlighted. This B state signal is thought to be associated with a low-energy singlet-to-triplet transition in $I_{3(aq.)}^{-4}$. The dominant, spin-orbit coupled C (~3.53 eV, ~351 nm) and D (~4.30 eV, ~288 nm) bands⁴ originate from the mixed singlet-singlet and singlet-triplet $n/\pi \rightarrow \sigma^*$ valence electronic transitions of $I_{3(aq.)}^{-}$, details of which are provided in the main text and Reference 5. Around 5.49 eV (226 nm, CTTS 1) and 6.44 eV (193 nm, CTTS 2), absorption peaks primarily and respectively associated with the lowest-energy $I_{(aq.)}^ {}^{2}P_{\frac{3}{2}}$ and $I_{(aq.)}^{-} {}^{2}P_{\frac{1}{2}}$ charge-transfer-to-solvent (CTTS) states are observed^{6,7}. Weaker contributions associated with the $I_{3(aq.)}^{-}$ anion also contribute to the former spectral region, as discussed below, with these signals being ascribed to a higher-energy triiodide excited state, labelled E. The $I_{3(aq.)}^-$ and $I_{(aq.)}^-$ spectral overlap at 5.5-6.0 eV excitation energies notably prevents a direct assessment of the residual $I_{(aq.)}^-$ content in the mixed solution based on the CTTS band intensities alone.

Considering the aforementioned UV-Vis spectral assignments^{4,5} and the general consistency of the UV-Vis spectra below 3.7 eV photon energies across the considered reagent concentration range ($[I_{2(aq.)}]_{nominal} \ge 25 \text{ mM}$, $[I_{(aq.)}]_{nominal} \ge 37.5 \text{ mM}$), the $I_{3(aq.)}^-$ signals in the vicinity of the $I_{3(aq.)}^-$ C-band were deemed to be spectrally isolated and unsaturated up to concentrations of $\le 200 \text{ mM}$. Notably, at the higher reagent concentrations investigated here, *e.g.* [I_2]_nominal >175 mM and [I^-]_nominal >350 mM, the D, CTTS 2 and potentially E and CTTS 1 band absorption signals were found to saturate with the 10 μ m, minimum path length absorption cell. Hence, the aforementioned spectrally isolated, and unsaturated, $I_{3(aq.)}^-$ C-band absorption signal area was selectively used to characterise the $I_{2(aq.)}$ -to- $I_{3(aq.)}^-$ conversion behaviour. The area of the C-band peak was correspondingly determined as a function of the nominal initial $I_{2(aq.)}$ concentration and $I_{(aq.)}^-$ -to- $I_{2(aq.)}$ mixing ratio to assess the $I_{3(aq.)}$ and, by extension, $I_{(aq.)}^-$ concentrations in the mixed XPS sample solutions. This was achieved by modelling



concentration, under excess of $I^-_{(aq)}$ conditions

Figure S3 (a) The relative $I_{3(aq.)}^{-}$ C-band absorption signals extracted from UV-Vis absorption spectra for nominal, initial I_2 concentrations of 50 mM (blue data), 100 mM (green data), and 200 mM (red data) as a function of the nominal, initial I^{-} -to- I_2 reagent mixing ratio. The C-band signal areas were normalised to the maximum signal values recorded for the 200 mM initial I_2 concentrations. (b) corresponding estimated conversion efficiencies of $I_{2(aq.)}$ to $I_{3(aq.)}^{-}$ as a function of reagent mixing ratio. (c) The average C absorption band area versus the nominal, initial iodine concentration at mixing ratios x > 4.0 and the associated results of a least-squares linear fit to the data. The error bars in the figure represent one standard deviation of the mean of the extracted peak areas or conversion efficiency at each mixing ratio. See the discussion in Section A for further details.

the recorded reagent-concentration-dependent UV-Vis spectra using a multi-peak fit routine and selectively extracting the contribution of the C-band component. This cumulative least-squares fit procedure modelled the B, D, E, CTTS 1, and CTTS 2 band features with Gaussian profiles, with the C-band feature being modelled with an exponentially modified Gaussian function. Exemplary UV-Vis absorption spectra fit results are shown as dashed and dot-dashed curves in Figure S2. More generally, Figure S3 summarises the C-band results of similar cumulative fits to UV-Vis spectra recorded from 22 different mixed solutions. There, Panel (a) shows the $I_{3(aq.)}^-$ C-band feature areas extracted for nominal, initial I₂ concentrations of 50 mM (blue data), 100 mM (green data), and 200 mM (blue data) as a function of $I_{(aq.)}^-$ -to- $I_{2(aq.)}$ mixing ratio. In all three initial I₂ concentration cases, the $I_{3(aq.)}^-$ signal generally rises with increased mixing ratio, before saturating at ratios of $x \ge 4$.

The most important results of the UV-Vis spectral analysis for the XPS measurements described in the main text are shown in Panels (b) and (c) of Figure S3. Assuming that the C-band signal saturation behaviour observed at mixing ratios of $x \ge 4$ in Panel (a) corresponds to a full (*i.e.* 100%) conversion of $I_{2(aq.)}$ to $I_{3(aq.)}^{-}$, the associated data is re-plotted in Panel (b) to show the $I_{2(aq.)}$ -to- $I_{3(aq.)}^{-}$ conversion efficiency as a function of the reagent mixing ratio. Up to the $x \sim 4$ mixing ratio, the degree of conversion from $I_{2(aq.)}$ and $I_{(aq.)}^-$ to $I_{3(aq.)}^-$ is correspondingly shown to depend both on the initial, nominal iodine concentration and iodide-to-iodine con-centration mixing ratio used to prepare the solutions. Beyond such mixing ratios, the C-band absorbance was found to be invariant, within the error bounds, up to $I_{2(aq.)}$ concentrations ≤ 210 mM, where the absorbance began to saturate. Correspondingly, the C-band areas at or above such mixing ratios, *i.e.* at x = 4 - 10, were averaged and have been plotted against the associated initial, nominal I2(aq.) concentrations over a 25-210 mM range in Panel (c) of Figure S3. To highlight the dependence of the $I_{3(ac)}^{-}$ concentration on the initial $I_{2(aq)}$ concentration under saturated conversion conditions, determine the average C-band area at >210 mM $I_{2(aq.)}$ concentrations by extrapolation, and quantify the $I_{2(aq.)}$ -to- $I_{3(aq.)}^{-}$ conversion efficiencies for the 250 mM / 350 mM, 210 mM / 420 mM, and 250 mM / 500 mM mixed $I_{2(aq.)}/I_{(aq.)}^-$ solutions used in the XPS experiments, a linear fit was applied to the data shown in Panel (c) of Figure S3. A near-linear dependence of the C-band signal, and seemingly the $I_{3(aq.)}^{-}$ concentration, on the $I_{2(aq.)}$ concentration is correspondingly confirmed. This suggests that $I_{3(aq.)}^{-}$ anions are predominantly formed under the conditions explored here and that any contributions of higher-order-polyiodide adducts, as potentially formed from multiple $I_{2(aq.)}$ moieties, are negligible⁸.

Panels (a), (b), and (c) of Figure S4 specifically show the UV-Vis spectra recorded of the three solutions implemented in the XPS experiments (light blue spectra). As mentioned above, with the available 10 μm minimum path length sample cells, it was not possible to record associated undistorted, *i.e.* unsaturated, UV-Vis spectra with such high iodine solute concentration mixtures. Consequently, half-concentration, mixed solution UV-Vis spectra analogues are additionally shown for each of the high concentration mixtures in Figure S4 to highlight the undistorted C, D, and E & CTTS band ratios associated with the $I_{3(aq.)}^-$ and $I_{(aq.)}^-$ solution components (orange spectra). Based on the confirmed (near-)linearity of the C-band signal and inferred $I_{3(aq.)}^{-}$ concentration dependence on the I_{2(aq.)} concentration, the signal ratios in the half-concentration spectra can be considered representative of the solutions used for the XPS measurements. For comparison, related UV-Vis spectra of NaI(aq.) solutions are additionally shown, with the NaI solute concentrations corresponding to the nominal, initial values implemented in the half-concentration, mixed solutions (green spectra). By applying the aforementioned cumulative least-squares peak fit to the half-concentration data and doubling the extracted C-band areas, the C-band signal area can be determined for the high initial, nominal $I_{2(aq.)}$ concentration solutions implemented in the XPS measurements. Furthermore, by dividing the resulting signal area by the signal area predicted by the extrapolated linear fit associated with Figure S3(c) - which is associated with fully converted conditions at either 210 mM or 250 mM $I_{2(aq.)}$ concentrations – the degree of $I_{2(aq.)}$ -to- $I_{3(aq.)}^{-}$ conversion in the solutions implemented in the XPS experiments can be established. Subsequently, the concentrations of the $I_{3(aq.)}^-$ and residual $I_{(aq.)}^-$ solutes are readily determined, assuming that equimolar $I_{2(aq.)}$ and $I_{(aq.)}^-$ contributions are needed to produce $I_{3(aq.)}^{-}$ anions. Adopting this procedure, the overall $I_{3(aq.)}^{-}$ concentrations of the solutions used in the XPS measurements are determined to be 228±4 mM, 177±8 mM, and 168±12 mM for the 250 mM / 500 mM, 210 mM / 420 mM, and 250 mM / 350 mM $I_{2(aq.)}$ / $I_{(aq.)}^-$ mixtures, respectively. This corresponds to respective 272 ± 4 mM, 243 ± 8 mM, and 182 ± 12 mM residual $I_{(aq.)}^{-}$ concentrations and respective $I_{2(aq.)}$ -to- $I_{3(aq.)}^{-}$ conversion efficiencies of 91 \pm 2%, 84 \pm 4%, and 67 \pm 4%.

As a final consideration of the UV-Vis absorption spectra of $I_{3(aq.)}^-$, Figure S4(d) shows the calculated UV-Vis spectra of the $I_{3(aq.)}^-$ anion at the **Lin** (dark blue curve) and **Bent** (red curve) geometries described in the main text. The two dominant, spin-orbit split C- and D-band peaks of the $I_{3(aq.)}^-$ anion are reproduced in the calculations, with an additional contribution being readily identified at around 5.5–6.0 eV, depending on the considered anion geometry, and marked as the E band. As mentioned above, this absorption feature overlaps with the intense CTTS bands associated with the residual $I_{(aq.)}^-$ anions in the experimental measurements. Still, in the experimental UV-Vis spectra recorded from the relatively low-mixing-ratio solutions – *i.e.* for the 500 mM



(a) 250/500 mM and 125/250 mM $\rm I_{2(aq.)}/NaI_{(aq.)}$ mixture, and 250 mM $\rm NaI_{(aq.)}$ solution spectra



(c) 250/350 mM and 125/175 mM $I_{2(aq.)}/NaI_{(aq.)}$ mixture, and 100 mM $NaI_{(aq.)}$ solution spectra



(b) 210/420 mM and 105/210 mM $I_{2(aq.)}/NaI_{(aq.)}$ mixture, and 210 mM $NaI_{(aq.)}$ solution spectra



(d) Background-subtracted experimental and Lin and Bent anion geometry calculated $I_{3(ac.)}^{-}$ UV-Vis absorption spectra

Figure S4 UV-Vis absorption spectra of $I_{(aq.)}^-$ and $I_{3(aq.)}^-$ mixed solutions. The D band signals are saturated in the UV-Vis absorption spectra for the 250 mM/500 mM, 210 mM/420 mM, and 250 mM/350 mM I_2 /Nal aqueous mixtures shown in Panels (a), (b), and (c), respectively. Hence, in each of the panels, unsaturated UV-Vis absorption spectra of 125 mM/250 mM, 105 mM/210 mM and 125 mM/175 mM I_2 /Nal mixtures are also respectively shown. UV-Vis absorption spectra of reference 250 mM, 210 mM and 100 mM Nal aqueous solutions are additionally shown Panels (a), (b), and (c), respectively. In Panel (d), the UV-Vis spectra calculated at the linear (Lin) and bent (Bent) nuclear structure geometries described in the main text are compared with the $I_{(aq.)}^-$ -background-signal-subtracted experimental UV-Vis spectrum, as extracted from a 250 M/125 mM Nal/I₂ mixed solution.

/ 250 mM, 420 mM / 210 mM, and 350 mM / 250 mM NaI / I₂ solutions implemented in the XPS measurements – the combined $I_{3(aq.)}^-$ E and $I_{(aq.)}^-$ CTTS 1 band feature is found to be blue shifted by approximately 40 meV with respect to the ${}^{2}P_{\frac{3}{2}}$ CTTS 1 band recorded from the pure $I_{(aq.)}^-$ solutions. Such an absorption feature shift supports the aforementioned existence of multiple, offset UV absorption bands in the mixed solutions at 5.5-6.0 eV. Correspondingly, we utilise our aforementioned experimental spectra analysis to determine that a residual $I_{(aq.)}^-$ concentration of 156±9 mM is present in a 250 mM / 125 mM NaI / I₂ aqueous mixture, the

UV-Vis absorption spectrum of which is notably unsaturated. Correspondingly intensity scaling a 125 mM $I_{(aq.)}^$ background absorption spectrum by a factor of 156 mM / 125 mM and subtracting the result from the mixed solution spectrum yields the isolated $I_{3(aq.)}^-$ experimental UV-Vis absorption spectrum (light blue curve), which is additionally shown in Figure S4d. The additional, relatively weak $I_{3(aq.)}^-$ UV absorption band feature, which we label E, is correspondingly confirmed with a peak centre at ~5.9 eV. Furthermore, comparing the calculated UV-Vis spectra to the $I_{3(aq.)}^-$ experimental results shown in Figure S4d, the calculated UV-Vis spectrum associated with the **Lin** geometry, particularly its C- and D-band intensity ratio, is found to be in much better agreement with the experimental spectra than the **Bent** geometry analogue. In this regard, the UV-Vis spectra results are fully consistent with the conclusions drawn from the XPS data, suggesting that the $I_{3(aq.)}^-$ anion predominantly takes on a near-linear, but bond-length asymmetric, geometry in the bulk of the aqueous solution.

To summarise this section, we estimated that any residual $I_{2(aq.)}$ in the concentrated mixed $I_{3(aq.)}^-$ and $I_{(aq.)}^-$ XPS sample solutions amounts to <0.1% of the $I_{3(aq.)}^{-}$ concentration. Such concentrations are expected to have a negligible influence on the XPS data. Further, mixed $I^-_{3(aq.)}/I^-_{(aq.)}$ solutions were prepared over a broad I^- and I_2 concentration range, associated UV-Vis absorption spectra were recorded, and the $I_{3(aq.)}^-$ C-band absorption signal areas were extracted from all of the spectra using a cumulative spectral fit routine. The high reagent mixing ratio aqueous solutions, with $I^-:I_2$ ratios of x > 4:1, were found to display signatures of full conversion from $I_{2(aq.)}$ to $I_{3(aq.)}^{-}$. The corresponding average C-band area was subsequently used to determine the conversion efficiency and solute concentrations of the equilibrated sample solutions at all considered mixing ratios, at least below the onset of UV-Vis absorption signal saturation. The UV-Vis C-absorption-band signals from $I_{3(aq.)}^{-}$ saturated with the available 10 μ m cells upon preparation from >200 mM nominal, initial I_{2(aq.)} concentrations. As a result, the lower reagent concentration data, a least-squares linear fit method, and an extrapolation approach were used to determine the average C-band signal area that corresponds to (near-)100% conversion at concentrations beyond the UV-Vis spectral saturation threshold. Subsequently, the $I_{2(aq.)}$ -to- $I_{3(aq.)}^{-}$ conversion efficiency and concentrations of $\rm I_{3(aq.)}^-$ in the 250 mM / 500 mM, 210 mM / 420 mM, and 250 mM / 350 mM $\rm I_{2(aq.)}$ / $I_{(aq.)}^-$ mixed solutions implemented in the XPS experiments were determined by taking ratios of measured and intensity-scaled C-band signal areas over the full conversion values calculated from the aforementioned fit and extrapolation. Moreover, experimental $I_{3(aq.)}^{-}$ UV-Vis absorption spectroscopy results were compared with associated spectral calculations. Spectral overlap of the $I_{3(aq.)}^-$ and $I_{(aq.)}^-$ anion absorption features was confirmed at photon energies of 5.0-6.0 eV, with the associated E-band $I_{3(aq.)}^-$ signal being isolated following $I_{(aq.)}^-$ background signal scaling and subtraction. The UV-Vis absorption calculations associated with the **Lin** geometric structure of $I_{3(aq.)}^-$, described in the main text, was importantly found to best reproduce the experimental spectra. Correspondingly, the UV-Vis absorption spectroscopy results and analysis are found to be in excellent agreement with the XPS spectral analysis.

B Experimental methods

To enable the XPS measurements, laminar jets of the aqueous solutions were introduced to the sample vacuum chambers by forcing the liquids through 30 μ m orifice diameter fused silica micro-capillaries using high-pressure liquid chromatography (HPLC) pumps⁹. The solution flow rate was set to 0.65-0.80 ml s⁻¹ and the jet temperature was stabilized to 5°C (SOL³PES instrument) or 10°C (EASI instrument) to minimize gas phase contributions to the measured XPS signals. The electrolyte solutions were electrically grounded to the XPS experimental setups ~30-50 cm prior to sample injection using a gold wire immersed in the flowing, electrically conductive solutions. The laminar regions of the liquid microjets were interrogated a few mm downstream from the fused silica nozzle and prior to subsequent collection and freezing at liquid nitrogen cold traps.

In the SOL³PES instrument¹⁰ experiments, a turbo pump (with $1740 \, l \, s^{-1}$ pumping speed for gaseous water) and two liquid nitrogen cold traps (2000 cm² total surface area, corresponding to a water-vapor-pumping speed of up to 30 000 l s⁻¹) were used to maintain a base pressure of 1×10^{-5} mbar in the sample chamber. The incoming soft X-ray beam was delivered orthogonally to the liquid microjet via a windowless, two-stage differential pumping assembly and was horizontally polarized, in the plane of the laboratory floor. The produced photo-

electrons (PEs) were detected using a differentially pumped hemispherical analyser system (Scienta Omicron HiPP-2), with its pre-lens axis aligned orthogonally to the light and liquid jet propagation axes, and correspondingly to the synchrotron polarization axis. This measurement configuration is referred to as the Perpendicular experimental geometry in the main text.

In the EASI instrument¹¹ experiments, a combination of turbo molecular pumping ($\sim 2700 \text{ l s}^{-1}$ pumping speed for water vapour) and three liquid nitrogen-filled cold traps (3000 cm² total surface area, up to a $\sim 45~000 \text{ l s}^{-1}$ pumping speed for water vapour) were used to maintain a pressure in the interaction chamber of $2-3 \times 10^{-5}$ mbar. The incoming soft X-ray beam was delivered orthogonally to the liquid microjet via another windowless, two-stage differential pumping assembly and was circularly polarized. The produced PEs were detected using a differentially pumped hemispherical analyser system (Scienta Omicron HiPP-3), with its pre-lens axis aligned at a 50° angle to the light propagation axis, close to the so called Magic Angle of 54.7°. This resulted in a near uniform detection efficiency of all PEs, irrespective of their angular emission distribution, with an expected angular signal variance amounting to less than 1%. We refer to this measurement configuration as the Magic Angle experimental geometry in the following and in the main text.

X-ray generated PEs were respectively produced ~500 μ m or ~800 μ m below the 500 μ m diameter SOL³PES or 800 μ m diameter EASI entrance apertures to the analyser pre-lens systems, which separated the first stages of the integrated differential pumping systems from the sample chambers. Consequently, the local pressures experienced by the emitted PEs were reduced by several orders of magnitude within 1 mm of their birth, minimizing the probability of inelastic electron scattering in the evaporating gas sheaths surrounding the liquid microjets. The ionising X-ray beam at beamline U49-2 PGM-1 had a focal spot size of 100 × 45 μ m² along the liquid-jet-propagation and orthogonal directions, respectively. A corresponding X-ray focus of 180 × 35 μ m² was achieved at beamline P04. These focal spot sizes resulted in relatively low gas-phase water and negligible I_{2(g)} contributions to the reported XPS spectra, in contrast to previous I_{3(aq.)} I 4d XPS spectra reports¹².

As mentioned in the main text, depending on the implemented photon energy and, hence, the KE of the directly produced PEs, the surface or bulk region of the liquid samples could be predominantly probed ¹³. It was previously theoretically illustrated ¹⁴ and experimentally supported ¹⁵ that NaI_(aq.) solution interfaces evolve to bulk conditions over a ~ 1 nm length scale. Assuming bulk conditions pertain over similar length scales in the mixed triiodide/iodide sample solutions, 150 eV or 200 eV photon energies were used to probe the aqueous-gas interface and record valence and I 4d⁻¹ core level spectra. Such photon energies resulted in PEs with KEs of 90–190 eV, engendering surface sensitive conditions, *i.e.* electron effective attenuation lengths (EALs) of ~ 1 nm¹³. In contrast, 600 eV photon energies resulted in KEs of 540–590 eV, allowing predominant investigation of the bulk region of the aqueous solution, via EALs of ~ 3 nm¹³. When probing the core I 3d⁻¹ levels, the photon energy was chosen to give a similar KE distribution as that recorded from the valence and I 4d⁻¹ core level spectra. 725 eV and 1175 eV photon energies were correspondingly and respectively implemented to yield surface- and bulk-sensitive EAL conditions for the aqueous triiodide I 3d⁻¹ core-level XPS spectra.

C Data Analysis Procedure

Figure S5 shows an as-measured, mixed $I_{3(aq.)}^-$ and $I_{(aq.)}^-$ XPS spectrum, including contributions from both liquidand gas-phase water, residual $I_{(aq.)}^-$ solute, $I_{3(aq.)}^-$ solute, $Na_{(aq.)}^+$ counter ions, and broad secondary and inelastically scattered electron background signals. All aqueous-solution XPS spectra recorded from liquid microjet sample sources exhibit such solvent, solute, and broad secondary electron and inelastically scattered background contributions, with the latter features being ubiquitous in condensed-phase XPS experiments¹⁶.

The sample solution associated with Figure S5 was produced by implementing nominal, initial 500 mM NaI and 250 mM I₂ aqueous solute concentrations. Based on the UV-Vis spectral analysis described in Section A, the XPS signals shown in Figure S5 were found to incorporate the total contributions from the evaporating gas and liquid phase water solvent, as well as 272 ± 4 mM $I_{(aq.)}^-$, 228 ± 4 mM $I_{3(aq.)}^-$, and 500 mM Na⁺ solute concentrations. To enable removal of the residual $I_{(aq.)}^-$ reagent, some of the Na⁺_(aq.) counterion, and the water solvent signal contributions from the mixed solution spectra, 250 mM NaI_(aq.) background photoelectron signal spectra were additionally recorded under the same experimental conditions as the mixed sample solution data (similar jet flow rate, jet temperatures, and resulting base pressure in the vacuum chambers).

Figure S6 highlights the analysis procedure used to produce the XPS figures shown in main text. Here, exemplary spectra associated with the sample solution (red curves), concentration-corrected background solution (black curves), and corresponding sample-background difference (green curves, produced via the to-bedescribed analysis procedure) are presented for a high photon energy data set. Therein, the valence and I 4d spectra are shown (Panels (a) and (b), respectively, as recorded at a 600 eV photon energy at PETRA III) along with corresponding solvent O 1s and solute I 3d spectra (Panels (c) and (d), respectively, recorded at a 1175 eV photon energy). A three-point rolling average smoothing algorithm was applied to the bulk-sensitive valence band data recorded at PETRA III to improve the signal-to-noise ratio, shown in Figure S6a (vertically offset, blue curve). The datasets recorded at BESSY II shown in the next sections were analyzed using a similar procedure, but were in this case smoothed using a 6-point rolling average method prior to fitting. To BE reference the valence and I 4d⁻¹ liquid-phase PE spectra in the presence of electrokinetic and ionization-induced sample charging^{9,17}, we used the commonly adopted liquid jet XPS procedures of pinning the lowest energy ionizing transition feature, $1b_{1(l)}^{-1}$, or core ionisation feature, $0 \ 1s^{-1}$, to predetermined (nearly-neat) liquid water reference BE values^{18,19}. In the latter case, O 1s spectra were separately recorded from the mixed triiodide/iodide and iodide reference solutions under the same conditions as the I $3d^{-1}$ spectra to engender the energy referenc-ing. Although we utilized this widely adopted referencing practice²⁰, we note its inadequacies in cases where an aqueous solute impacts the solvent BEs and ongoing efforts to improve on this approach^{19,21}. Notably, we expect these inadequacies to have a negligible effect on the relatively-low-solute-concentration results reported here, as evidenced by aqueous NaI spectra recorded at similar solute concentrations^{19,21}.

To implement the aforementioned, standard liquid jet XPS referencing procedure, the $I_{3(aq.)}^-$ sample and $I_{(aq.)}^-$ background valence and liquid water valence peaks of the mixed sample solutions and background reference spectra were cumulatively fit, as described in Section D. The spectra were subsequently BE shifted so that the solvent 1b₁ peak centres of the two solutions were set to a reference BE value of 11.33 \pm 0.03 eV with respect



Figure S5 As-measured valence and I 4d core-level XPS spectra recorded from a mixed 500 mM $Na^+_{(aq.)}$, ~272 mM $I^-_{(aq.)}$, and ~228 mM $I^-_{3(aq.)}$ solution at a photon energy of ~600 eV at BESSY II. The presented XPS spectrum contains a broad secondary electron background with an increasing spectral contribution from low to high BE¹⁶. The primary, direct photoelectron peaks of the solvent (liquid-phase, green labels, and gas-phase, light blue labels), $Na^+_{(aq.)}$ counter-ion (pink label), and $I^-_{3(aq.)}/I^-_{(aq.)}$ solute (dark blue) peaks are marked on the as-measured data. An additional artifact signal, associated with the residual second harmonic of the beamline and I 3d ionization is also highlighted by the 'I_{\$\substace\$} (SH)' label.



Figure S6 Panels (a), (b), and (d) respectively show bulk-sensitive valence, I 4d core, and I 3d core XPS spectra of the mixed $Na^+_{(aq.)}$, $I^-_{(aq.)}$, and $I^-_{3(aq.)}$ solutions (red curves), intensity-scaled Nal background solutions (black curves), and associated difference curves (green curves). The latter curves isolate the valence, I 4d, and I 3d contributions of the $I^-_{3(aq.)}$ solute. The difference curve associated with the valence band (blue curve) was additionally smoothed and vertically offset to better highlight its asymmetric structure. The Nal solution background/reference spectrum was obtained by intensity scaling an as-measured 210 mM Nal XPS spectrum to produce effective 243 mM solute peak heights, accounting for the residual $I^-_{(aq.)}$ contributions in the mixed solutions, as inferred from the UV-Vis spectral analysis. Exemplary 600 eV photon energy valence and I 4d⁻¹ XPS spectra are shown in figure Panels (a) and (b), respectively. Similar 1175 eV photon energy O 1s and I 3d⁻¹ spectra are respectively shown in Panels (c) and (d). The known (neat) liquid water 1b₁ peak BE was used to calibrate the BEs for the valence and I 4d measurements, whereas the known (neat) liquid water O 1s peak BE was used to calibrate the I 3d measurements. The spectra were recorded at PETRA III using a Magic Angle collection geometry, as further discussed in Section B and the main text.

to the local vacuum level^{18,19}, assuming that the (nearly-neat) liquid water 1b₁ BEs are unaffected by the solutes at the low implemented solute concentrations. The valence 1b₁ peak intensities for both the sample and reference solutions were then normalized to 1, accounting for any liquid jet spatial drifts or beamline flux variations between the mixed sample and background reference measurements. The signal intensity of the background NaI_(aq.) XPS spectra was then further scaled, according to the UV-Vis-spectroscopy-inferred residual $I_{(aq.)}^-$ concentration of the mixed solution, and then subtracted from the mixed solution spectrum. The resulting difference spectrum is shown in Figure S6a. In this example, the 210 mM reference NaI_(aq.) spectrum was recorded in close succession with the 210 mM/420 mM I₂ and I⁻ mixed solution spectrum and was intensity scaled by a factor $1.16\pm_{0.06}^{0.06}$ to account for the UV-Vis-analysis-determined 243±8 mM residual

 $I_{(aq.)}^-$ concentration. The I 4d core-level spectra were recorded under the same conditions as the valence XPS spectra. Correspondingly, the mixed solution $I_{3(aq.)}^-$ and background $NaI_{(aq.)}$ I 4d spectra were BE-shifted and intensity normalised using the values determined in the aforementioned valence spectra analysis. A subsequent $1.16\pm_{0.06}^{0.06}$ signal multiplication was applied to the background $NaI_{(aq.)}$ spectrum to correct the $I_{(aq.)}^-$ feature intensities according to the predetermined residual $I_{(aq.)}^-$ concentration in the mixed solutions. The normalised and scaled $NaI_{(aq.)}^-$ background spectrum was then subtracted from the mixed solution data to isolate the $I_{3(aq.)}^-$ anion I 4d signals and enable their associated analysis. The resulting spectra are shown in Figure S6b.

For the I 3d XPS analysis, the experimental-condition-dependent intensity signal scaling was initially performed using O 1s spectra associated with the solvent molecules in the sample and NaI_{aq}. background solutions, as shown in Figure S6c. Similar to the valence band data, the O 1s data was fit and shifted to reference BE values of 538.10 \pm 0.05 eV with respect to the local vacuum level^{19,22}, assuming that the liquid water O 1s/1a₁ BEs are unaffected by the solutes. In this case, Voigt profiles were used to fit the major liquid-phase and minor gas-phase features and a linear baseline correction was applied to the data. A I⁻_(aq.) concentration/signal-intensity correction was then applied to the shifted and normalised background NaI_(aq.) spectra – again in accord with the UV-Vis-spectroscopy-determined residual I⁻_(aq.) content in the solution – and the background spectra were finally subtracted from the corresponding mixed solution spectra to isolate the I⁻_{3(aq.)} I 3d peaks. The associated spectra are shown in Figure S6d.

D XPS Spectra Fitting Procedure

Figure S7, S8, and S9 show the background-subtracted experimental XPS spectra of aqueous triiodide solutions along with associated cumulative fits to the data. The spectra were recorded under a Perpendicular spectrometer collection axis alignment with respect to the incoming light polarisation at BESSY II. The XPS valence and corelevel spectra were BE-calibrated, the residual $I_{(aq.)}^-$ signal (and the related portion of the associated Na⁺_(aq.)) contributions were subtracted, as described in Section C. Prior to the data fitting, linear baseline corrections were also applied to the data, specifically over the 5-11 eV, 50-65 eV, and 618-636 eV and 632-645 eV BE ranges for the valence (Figure S7), I 4d (Figure S8), and I 3d $I_{3(aq.)}^{\bullet} \Omega = \frac{5}{2}$ and I 3d $I_{3(aq.)}^{\bullet} \Omega = \frac{3}{2}$ (Figure S9) ionisation spectra. The baseline corrections coarsley account for any secondary and scattered electron signals underlying the direct, primary PE peaks. The BESSY II $I_{3(aq.)}^-$ valence and core-level difference spectra were further smoothed using a 6-point moving average method prior to fitting.

The bulk-sensitive $I_{3(aq.)}^-$ valence PE spectra shown in Figure S7 were modelled using a pair of Gaussian peaks, allowing the individual spectral contributions and peak parameters to be extracted through fitting. The surface- and bulk-sensitive valence spectra were similarly modelled. The higher BE regions of the valence spectra are notably over-subtracted due to a reduced signal-to-background ratio in regions of spectral overlap with the intense liquid water valence feature and related errors in the background intensity scaling routine used to ensure subtraction of all $I_{(aq.)}^-$ signatures from the mixed solution spectra. Such over-subtraction leads to further uncertainties in the characterisation of the ~9.3 eV valence ionisation feature, denoted as Peak 2 in the main text and Table S1, particularly in the surface-sensitive data. Hence, the associated BE and FWHM values listed in Table S1 should be seen as lower limits.

The I 4d core level XPS spectra presented in Figure S8 can be expected to show more than five peak contributions originating from the ionic, terminal, and central atoms of $I_{3(aq.)}^-$ and its associated $I_{3(aq.)}^{\bullet}$ final-state spin-orbit splitting. However, due to the high density of accessible ionised states in the interrogated BE range, a number of the peaks overlap with each other. Figure S8 shows the surface-and bulk-sensitive, backgroundsubtracted and smoothed XPS I 4d⁻¹ core level spectra, where the two highest-BE peaks are due to multiactive-electronic ionization processes. In this case, the smoothed experimental spectra were modelled using cumulative, five-component Voigt-profile peak fits, which accounted for inhomogenous and any lifetime peak broadening effects.

The I 3d core-level, background-subtracted, and smoothed XPS spectra are shown in Figure S9. These spectra clearly display contributions from eight distinct peaks over the studied BE range. As a result, the



Figure S7 Background-subtracted and smoothed experimental data and fits to the valence band spectra of $I_{3(aq.)}^{-}$. Surface-sensitive (left) and bulk-sensitive (right) data sets are shown, as respectively produced using 200 eV and 600 eV photon energies at BESSY II.



Figure S8 Background-subtracted and smoothed experimental I 4d core-level XPS spectra of $I_{3(aq.)}^{-}$ and associated fivecomponent cumulative Voigt-profile fits. The surface (left) and bulk (right) regions of the aqueous solution were respectively and selectively probed using 200 eV and 600 eV photon energies at BESSY II.

I 3d core level spectra were modelled with cumulative eight-component Voigt-profile peak fits, which again accounted for inhomogenous and any lifetime peak broadening effects. The high resolution I 3d XPS spectra are additionally shown in Figure S10, as recorded at PETRA III under a Magic Angle geometry. This data set was analysed without spectral smoothing and was modelled and fit using the same routine as implemented with the BESSY II data.

We also compare our $I_{3(aq.)}^-$ I 4d and I 3d data to previously reported XPS spectra of I_3^- in ethanol solutions ^{12,23}. Figure S16 shows our cumulative Voigt-profile fits to the digitised ethanol solution I 4d (left) and I 3d (right) core-level spectra. The peak areas of the respective Voigt-profile fit components were used to determine the SU-to-main peak intensity ratio, as described in the main text and in Section F.

E I⁻ and I₂ mixing ratio dependence study in $I_{3(aq.)}^{-}$ preparation

Different concentrations of $I_{3(aq.)}^-$ were prepared by varying the mixing ratio between the NaI and I_2 solutes in aqueous solution, specifically 2:1 and 7:5 ratios. For example, ~228 mM or ~168 mM $I_{3(aq.)}^-$ solutions were prepared by mixing 500 mM NaI and 250 mM I_2 or 350 mM NaI and 250 mM I_2 in aqueous solution, respectively. Figures S11, S12, and S13 show a corresponding $I_{3(aq.)}^- / I_{(aq.)}^-$ concentration-dependent XPS study,



Figure S9 Background-subtracted and smoothed experimental, core-level I 3d XPS spectra of $I_{3(aq.)}^{-}$ and associated eightcomponent cumulative Voigt-profile fits. The surface-(left) and bulk-(right) sensitive data was respectively produced using 725 eV and 1175 eV photon energies at BESSY II.



Figure S10 Experimental core-level I 3d XPS spectra of $I_{3(aq.)}^{-}$ and associated Voigt-profile fits. The surface-(left) and bulk-(right) sensitive data were respectively produced using 725 eV and 1175 eV photon energies at PETRA III.



Figure S11 Valence surface-sensitive (left) and bulk-sensitive (right), smoothed XPS spectra of $I_{3(aq.)}^{-}$ recorded at BESSY II. ~228 mM and ~168 mM $I_{3(aq.)}^{-}$ solutions were prepared using NaI and I₂ solutes at different mixing ratios of x=2.0 and 1.4, respectively.

Table S1 Experimentally-determined, surface- and bulk-solution-sensitive aqueous triiodide valence (top section), core I 4d (middle section), and core I 3d (bottom section) electron BEs and peak FWHMs. The results associated with the surfacesensitive experiments are shown in the second and third columns of the table, with corresponding results associated with the bulk-sensitive experiments shown in the fourth and fifth columns. The BEs and widths of Peaks 1 and 2 were extracted from the cumulative Gaussian profile fits to the background subtracted XPS data, with the BEs representing final spin-orbit state averaged values denoted by a '*'. The spin-orbit-state resolved BEs and total FWHMs of the core-level features (Peaks 3-15) were determined via cumulative Voigt profile fits to the background subtracted data, which accounted for non-negligible lifetime broadening effects. The values reported here are the averages extracted from fits to all of the data shown in this document as well as additional spectra recorded at the P04 and U49-2 PGM-1 beamlines at PETRA III and BESSY II, respectively. As expected, the different experimental geometries adopted in the PETRA III and BESSY II experiments had no detectable effect on the determined BEs and peak FWHMs.

Peak	Surface Energetics		Bulk Energetics		
	BE (eV)	FWHM (eV)	BE (eV)	FWHM (eV)	
1	$7.88\pm0.05~^*$	1.34 ± 0.05	7.83 \pm 0.05 *	1.24 ± 0.04	
2	9.24 ± 0.04 *	0.83 ± 0.04	9.30 \pm 0.05 *	1.25 ± 0.11	
3	54.17 ± 0.04	0.84 ± 0.04	54.23 ± 0.05	0.97 ± 0.04	
4	55.52 ± 0.04	1.72 ± 0.09	55.62 ± 0.04	1.54 ± 0.04	
5	57.08 ± 0.05	0.75 ± 0.11	57.15 ± 0.04	0.87 ± 0.07	
6	58.96 ± 0.05	0.96 ± 0.16	59.05 ± 0.05	1.17 ± 0.06	
7	60.66 ± 0.12	1.33 ± 0.52	60.79 ± 0.06	1.14 ± 0.13	
8	624.20 ± 0.10	1.14 ± 0.02	624.12 ± 0.10	1.18 ± 0.07	
9	625.28 ± 0.10	1.27 ± 0.03	625.22 ± 0.10	1.31 ± 0.12	
10	627.27 ± 0.10	1.24 ± 0.06	627.32 ± 0.10	0.85 ± 0.07	
11	629.06 ± 0.10	1.31 ± 0.22	629.03 ± 0.10	1.59 ± 0.10	
12	635.66 ± 0.11	1.09 ± 0.01	635.64 ± 0.10	1.26 ± 0.09	
13	636.74 ± 0.10	1.27 ± 0.07	636.75 ± 0.10	1.31 ± 0.09	
14	638.69 ± 0.10	1.00 ± 0.17	638.78 ± 0.10	0.79 ± 0.05	
15	640.45 ± 0.11	1.66 ± 0.04	640.58 ± 0.11	1.84 ± 0.05	

as recorded at BESSY II under the same, Perpendicular electron collection geometry acquisition conditions. The spectra shown in S11, S12 and S13 were smoothed using a 6-point moving average routine. In our analysis, the reference NaI_(aq.) XPS spectra were scaled according to the residual $I_{(aq.)}^-$ concentrations that were determined through UV-Vis absorption spectroscopy (see Section A). As mentioned above, the scaling was performed in two steps, by normalising the liquid water 1b₁ signal level in the mixed and NaI reference solutions to 1 and then multiplying the background spectrum by a factor >1 to account for the higher $I_{(aq.)}^-$ concentration in the mixed solutions than the prepared reference/background solutions. As a result, both the 228 mM and 168 mM $I_{3(aq.)}$ valence spectra are over-subtracted above 9.5 eV. The over-subtraction is more prevalent in the surface-sensitive spectra due to the lower signal-to-background level in these experiments compared to the bulk-sensitive experiments.

Figure S11 shows the $I_{3(aq.)}^{-}$ valence XPS spectra recorded at two different concentrations, as prepared using mixing ratios of x=2.0 and 1.4. Figure S12 and S13 show the corresponding core-level PE spectra. The left panels of Figures S11, S12, and S13 show the surface-sensitive measurement results, while the right panels show the bulk-sensitive measurement results.

As discussed above, for a given amount of I_2 in aqueous solution, adding more I^- generally results in a higher (bulk) conversion of I_2 to I_3^- , at least until full conversion is achieved. Still, the SU-to-main peak intensity ratios shown in Table S2 are found to be unaffected by varying mixing ratio of I_2 and $I_{(aq.)}^-$ in preparing the $I_{3(aq.)}^-$ solutions, under the proviso the residual $I_{(aq.)}^-$ concentration in the mixed solutions is characterised and appropriately accounted for.



Figure S12 I 4d core-level surface-(left) and bulk-(right) sensitive smoothed XPS spectra of $I_{3(aq.)}^{-}$ recorded at BESSY II. 228 mM and 168 mM $I_{3(aq.)}^{-}$ concentrations were prepared using Nal and I₂ solutes at different mixing ratios of x=1.4 and 2.0, respectively.



Figure S13 | 3d core-level surface-(left) and bulk-(right) sensitive smoothed XPS spectra of $l_{3(aq.)}^{-}$ recorded at BESSY II. 228 mM and 168 mM $l_{3(aq.)}^{-}$ concentrations were prepared using Nal and l_2 solutes at different mixing ratios of x=1.4 and 2.0, respectively.

F Shake-up-to-main feature intensity ratio

The peak areas of all of the $I_{3(aq.)}^{-}$ XPS features were fit and tabulated, as described in Section D. To assess the molecular symmetry of the I_{3}^{-} anion in different solutions, the 2h1e SU features in a given core-level spectra have been added together to yield the total contribution of the SU processes. Similarly, the peak areas of the other, 1h peaks have been added together to produce the total contribution of the single-active-electron ionization processes. The ratio between these two spectral contributions has previously been noted to describe the degree of geometric structural asymmetry of $I_{3(aq.)}^{-}$ in different solvents²⁴.

Although the 500 mM NaI, 250 mM I₂ and 350 mM NaI, 250 mM I₂ aqueous solution mixtures results in different amounts of $I_{3(aq.)}^{-}$, the SU-to-main peak intensity ratios between the solutions are found to be equivalent within our uncertainty limits, as shown in Table S2. Thus, averaging the SU-to-main peak ratios extracted from the different solution concentration mixing ratios, surface- and bulk-sensitive values of 14.6±3.5% and 13.0±1.3% are respectively obtained for the I 4d core-levels in aqueous solution.

Similarly, for the I 3d data, the average SU-to-main peak intensity ratios are determined to be $18.1\pm2.1\%$ and $12.3\pm2.2\%$ for the aqueous surface- and bulk-sensitive experiments, respectively. Similar results are ob-

Table S2 Ratio between the 2h1e SU and 1h single-active-electron ionization contributions to the $l_{3(aq.)}^{-}$ core-level XPS spectra recorded under a Perpendicular electron collection geometry at BESSY II.

Experiment	Aqueous surface	Aqueous bulk	
I 4d core (250 mM/500 mM)	$15.1{\pm}2.0\%$	$12.2{\pm}1.2\%$	
I 4d core (250 mM/350 mM)	$14.2{\pm}4.5\%$	$14.7{\pm}1.5\%$	
I 3d core (250 mM/500 mM)	$16.2{\pm}1.8\%$	$12.3{\pm}2.5\%$	
I 3d core (250 mM/350 mM)	20.0±2.4%	12.3±1.9%	

tained for the 420 mM NaI, 210 mM I₂ data recorded under a Magic Angle collection geometry at PETRA III, 17.2 \pm 2.1% and 12.2 \pm 1.1%, respectively, as shown in Table S3. The results of similar SU-to-main peak intensity analyses of digitised, previously reported XPS spectra of I₃⁻ in ethanol^{12,23} are also reported in Table S3. Note that, unlike in the raw I_{3(aq.)} data reported here, the I₃⁻ in ethanol solution spectra reported in References 12,24 and 23 do not have any residual I⁻ contributions.

Table S3 Ratio between the cumulative 2h1e SU and 1h single-active-electron ionization signal contributions to the $l_{3(aq.)}^{-}$ core-level XPS spectra recorded under a Magic Angle collection geometry at PETRA III. SU-to-main peak intensity ratios of the $l_{3(aq.)}^{-}$ features in ethanol solutions are also reported, as obtained by digitising previously reported spectra^{12,23} and subsequently applying the same Voigt-profile fitting routine as implemented with the aqueous solution data.

Experiment	Aqueous surface	Aqueous bulk	Ethanol surface	Ethanol bulk
I 4d core (210 mM/420 mM)	-	8.6±1.4%	$5.3{\pm}0.8\%^{12}$	
I 3d core (210 mM/420 mM)	$17.2{\pm}1.3\%$	$12.2{\pm}1.1\%$		$8.9{\pm}0.6\%^{23}$

The SU-to-main peak intensity ratio errors shown in Table S2 and S3 were calculated by propagating the uncertainties in determining the I⁻ and I₃⁻ concentrations of the different solutions and the peak parameter uncertainties extracted from the fits to the data. In a first step, the SU-to-main peak intensity ratios were determined by considering the maximum or minimum limits of the solute concentration uncertainties determined using the UV-Vis measurements. Figure S14 shows the potential I₃⁻ signal intensity variations associated with the 420 mM NaI, 210 mM I₂ aqueous solution mixture and highlights the resulting maximum (Max. - 211 mM), mean (Mean - 188 mM), and minimum (Min. - 165 mM) I_{3(aq.)}⁻ concentrations for the bulk-sensitive core level I 4d (left panel) and I 3d (right panel) XPS spectra recorded at PETRA III. To establish the uncertainty ranges in the SU-to-main peak intensity ratio determinations, a similar fitting method as described in Section D was applied to the I_{3(aq.)}⁻ difference spectra data obtained by subtracting the I_(aq.)⁻ background spectra scaled to the maximum and minimum concentrations associated with uncertainty range of the I_{3(aq.)}⁻ concentration determined in the UV-Vis analysis. For example, the maximum (185 mM) and minimum (169 mM) potential I_{3(aq.)}⁻ concentrations determined for the I 4d data recorded at PETRA III, under bulk-sensitive conditions, and in the Magic Angle geometry result in I 4d SU-to-main peak intensity ratios of 9.2±1.4% and 8.3±1.3%, respectively. The same analysis was applied for the I 3d core level spectra to extract the maximum and minimum SU-to-main peak intensity ratio, again taking into account the maximum and minimum concentrations for I_(aq.)⁻ in the mixed sample solutions. The respectively determined ratios correspond to 12.1±0.7% and 12.7±1.5% .

G XPS spectra of I_3^- in ethanol and aqueous solutions

Here we compare our I_3^- aqueous solution XPS findings described in the main text to similar, previously reported results associated with I_3^- solutes in ethanol. As highlighted in Figure S15, which presents a comparison of our aqueous and previously published ethanol^{12,23} solution I_3^- XPS spectra, most of the single- and multi-active-electron ionization processes responsible for the different I 4d⁻¹ and I 3d⁻¹ peaks in the aqueous-phase data are also present in spectra recorded from solutions of I_3^- in ethanol. The left panel of Figure S15 compares our bulk-sensitive I 4d⁻¹, Magic Angle aqueous solution data to the digitised, ethanol solution data of Josefsson *et al.*¹², which was also recorded using a Magic Angle geometry but at a surface-sensitive photon energy of



(a) I⁻_{3(aq.)} I 4d Max., Mean, and Min. spectral contributions (b) I⁻_{3(aq.)} I 3d Max., Mean, and Min. spectral contributions

Figure S14 Minimum (Min.), mean, and maximum (Max.) signal intensities of the bulk-sensitive $I_{3(aq.)}^-$ core-level spectral features recorded at PETRA III, as determined by the $I_{(aq.)}^-$ concentration error bounds extracted from the UV-Vis spectroscopy measurements and analysis. The left and right panels show the I 4d and I 3d results, respectively. The intensity variations are due to the minimum and maximum $I_{(aq.)}^-$ concentrations potentially present in the solutions and the effects of the corresponding background signal subtraction. The effected regions of the resulting $I_{3(aq.)}^-$ spectra are highlighted by the red-shaded areas. These variations specifically occur in the spectral regions where $I_{(aq.)}^-$ and $I_{3(aq.)}^-$ contributions overlap. The results shown here are associated with samples prepared by mixing 210 mM of iodine with 420 mM of iodide.

100 eV. An overall ~-0.5 eV chemical shift is highlighted for the ethanol I $4d^{-1}$ spectra in comparison to the aqueous solution analogues, in agreement with the theory results of Josefsson *et al.*, reported in Reference 12. However, in contrast to that report, our alternative experimental background signal subtraction procedure – which was defined via experimentally-determined signal scaling parameters rather than expected I atom stoichiometries and assuming equivalent I_3^- and I^- ionisation cross-sections in the mixed solutions – reveals rather similar relative I $4d^{-1}$ XPS peak intensities for the two solutions. To better quantify the relative peak heights in the ethanol solution data, we applied our aqueous solution data fitting routines to the digitised ethanol data reported by Josefsson *et al.* (see the left panel of ESI Figure S12). We correspondingly determine an ethanol solution I $4d^{-1}$ SU-to-main peak intensity ratio of ~5.3±0.8%, which is significantly lower than the ratio extracted from the aqueous solution data shown in the left panel of Figure S15 (8.6±1.4%). We reiterate that even higher aqueous-phase XPS peak intensity ratios are extracted from our surface- (14.6±3.5%) and bulk- (13.0±1.3%) sensitive Perpendicular collection geometry data, indicating that the lower SU-to-main peak ratio observed from the ethanol solutions is not entirely associated with that data being recorded under surface-sensitive conditions. Correspondingly, using the methodology proposed by Norell *et al.*²⁴ and in full agreement with the predictions of Zhang and Lynden-Bell²⁵ and Jena *et al.*²⁶, the collective experimental I 4d⁻¹ XPS results and the SU-to-main XPS peak ratios indicate that the I_3^- anion has a reduced molecular symmetry in an aqueous solvent with respect to that in ethanol.

In the right panel of Figure S15 we compare our bulk-sensitive, Magic Angle aqueous solution I $3d^{-1}$ data to the analogous bulk-sensitive ethanol solution data reported by Arbman *et al.*²³; recorded using monochromatised Al K α radiation at ~1486 eV. In this case a ~-1.0 eV overall chemical shift is highlighted for the ethanol I $3d^{-1}$ spectra in comparison to the aqueous solution analogues. Similar main peak intensities are also highlighted in the I $3d^{-1}$ spectra recorded from the two solutions, with roughly 3:4 Peak 9-to-8 and Peak 13-to-12 intensity ratios determined in both cases. Notable spectroscopic differences are still apparent between the I_3^- I $3d^{-1}$ solute spectra from the two solutions, however. Particularly, Peaks 10 and 14 are present in the aqueous I_3^- solution data but are significantly suppressed, or perhaps even absent, in the ethanol solution spectra. This observation is another clear indication of a reduced molecular asymmetry of the aqueous solute in comparison to that in ethanol. To further explore this asymmetry, we quantified the relative peak intensities in the ethanol



Figure S15 Triiodide I 4d⁻¹ and I 3d⁻¹ core level X-ray PE spectra recorded from the aqueous bulk at the P04 beamline (blue, $'I_{3(aq.)}')$, and the bulk of an ethanol solution (reproduced from Reference 12 with permission from the PCCP Owner Societies and from Reference 23 with permission from Elsevier, orange curves, $'I_{3(EtOH)}')$. The ethanol I 4d⁻¹ core-level spectra show spectral shifts (Peak 3) and different peak ratios (peak 3 and 4) compared to the aqueous triiodide solutions. In the I 3d⁻¹ ionisation case, a spectral shift and an additional pair of peaks appear to be resolved in the aqueous solution data (Peaks 10 and 14) in comparison to the ethanol solution case.

solution data reported by Arbman *et al.* by applying the same fit routines implemented with our aqueous solution I $3d^{-1}$ XPS data (see the ethanol solution fit results shown in the right panel of ESI Figure S16). In this case we extract an ethanol solution SU-to-main peak intensity ratio of ~8.9±0.6%. Comparing the ethanol solution SU-to-main peak intensity ratio of ~8.9±0.6%. Comparing the ethanol solution SU-to-main peak intensity ratio of ~8.9±0.6%. Comparing the ethanol solution SU-to-main peak intensity ratio to that extracted from the aqueous solution spectrum shown in the right panel of Figure S10, the aqueous solution value is found to be significantly greater (12.2±1.1%). In agreement with the I $4d^{-1}$ XPS spectra results, the I $3d^{-1}$ data further indicates that the I₃⁻ anion adopts a more asymmetric molecular geometry, on average, in aqueous solutions with respect to ethanol solutions. This is once again in full agreement with the calculations of Jena *et al.*²⁶, which specifically suggest that this increased asymmetry corresponds to a greater disparity between the solute bond lengths, as opposed to a more bent solute geometry in aqueous solution.

As a further emphasis of this increased aqueous solute asymmetry, the more prominent aqueous-phase Peak 10 and 14 features in the I $3d^{-1}$ spectra suggest an increased probability of otherwise improbable or forbidden ionising transitions. Based on the simulated spectra reported here, these features can be tentatively attributed to ionisation of the *c* I-atoms of more asymmetric aqueous-phase solute molecules, the nuclear geometric bond-lenth and angular distributions of which have been calculated to be significantly broader than those in ethanol solutions²⁶. Alternatively, the increased Peak 10 and 14 feature intensities may be ascribed to a minor component of a bimodal geometric structural distributions. Proof of any of these explanations still requires more expansive and advanced molecular structure calculations and spectral simulations, however. In any regard, the differences between the aqueous-phase and ethanol XPS spectra further highlight the role of the solvent in modifying both the electronic and geometric structure of I_3^- , and particularly the lowering of its molecular symmetry.

In summary, similar I $4d^{-1}$ and I $3d^{-1}$ core-level XPS spectra are observed from aqueous and ethanol solutions. However, comparison of our aqueous solution SU-to-main XPS core-level peak ratios to those extracted from data recorded from ethanol solutions indicates a significant increase in the solute asymmetry in the former case. Furthermore, in comparison to I $3d^{-1}$ XPS spectra from ethanol solutions, more prominent or perhaps additional aqueous-phase-specific I $3d^{-1}$ XPS peaks are observed, which are tentatively attributed to more probable 2h1e SU ionisation of the *c* I atoms of asymmetric solute molecules in aqueous solution. Cumulatively, the comparison reported here supports the theory results of Jena *et al.*²⁶, which suggest narrower asymmetric bond length and bending potentials of the I_3^- anion in the ethanol solutions.



Figure S16 Digitised experimental core-level I 4d and I 3d XPS spectra of I_3^- in ethanol solution and associated cumulative Voigt-profile fits. The data were reproduced with permission from References 12 (I 4d⁻¹, left panel) and 23 (I 3d⁻¹, right panel).

Notes and references

- [1] H. Hartley and N. P. Campbell, Journal of the Chemical Society, Transactions, 1908, 93, 741–745.
- [2] B. K. Shrikanth, M. Hegde et al., Journal of Chemical Sciences, 2021, 133, 1–9.
- [3] D. Palmer, R. Ramette and R. Mesmer, Journal of Solution Chemistry, 1984, 13, 673–683.
- [4] W. Gabes and D. Stufkens, Spectrochimica Acta Part A: Molecular Spectroscopy, 1974, 30, 1835–1841.
- [5] A. S. P. Gomes, L. Visscher, H. Bolvin, T. Saue, S. Knecht, T. Fleig and E. Eliav, *The Journal of Chemical Physics*, 2010, 133, 064305.
- [6] M. J. Blandamer and M. F. Fox, Chemical Reviews, 1970, 70, 59–93.
- [7] S. E. Bradforth and P. Jungwirth, The Journal of Physical Chemistry A, 2002, 106, 1286–1298.
- [8] V. T. Calabrese and A. Khan, The Journal of Physical Chemistry A, 2000, 104, 1287–1292.
- [9] B. Winter and M. Faubel, *Chemical Reviews*, 2006, **106**, 1176–1211.
- [10] R. Seidel, M. N. Pohl, H. Ali, B. Winter and E. F. Aziz, *Review of Scientific Instruments*, 2017, 88, 073107.
- [11] S. Malerz, H. Haak, F. Trinter, A. B. Stephansen, C. Kolbeck, M. Pohl, U. Hergenhahn, G. Meijer and B. Winter, *Review of Scientific Instruments*, 2022, **93**, 015101.
- [12] I. Josefsson, S. K. Eriksson, N. Ottosson, G. Ohrwall, H. Siegbahn, A. Hagfeldt, H. Rensmo, O. Björneholm and M. Odelius, *Physical Chemistry Chemical Physics*, 2013, 15, 20189–20196.
- [13] S. Thürmer, R. Seidel, M. Faubel, W. Eberhardt, J. C. Hemminger, S. E. Bradforth and B. Winter, *Physical review letters*, 2013, **111**, 173005.
- [14] P. Jungwirth and D. J. Tobias, The Journal of Physical Chemistry B, 2002, 106, 6361–6373.
- [15] N. Ottosson, M. Faubel, S. E. Bradforth, P. Jungwirth and B. Winter, *Journal of Electron Spectroscopy and Related Phenomena*, 2010, **177**, 60–70.
- [16] S. Malerz, F. Trinter, U. Hergenhahn, A. Ghrist, H. Ali, C. Nicolas, C.-M. Saak, C. Richter, S. Hartweg, L. Nahon et al., Physical Chemistry Chemical Physics, 2021, 23, 8246–8260.
- [17] H. Siegbahn, The Journal of Physical Chemistry, 1985, 89, 897–909.

- [18] N. Kurahashi, S. Karashima, Y. Tang, T. Horio, B. Abulimiti, Y.-I. Suzuki, Y. Ogi, M. Oura and T. Suzuki, *The Journal of chemical physics*, 2014, **140**, 174506.
- [19] S. Thürmer, S. Malerz, F. Trinter, U. Hergenhahn, C. Lee, D. M. Neumark, G. Meijer, B. Winter and I. Wilkinson, *Chemical Science*, 2021, **12**, 10558–10582.
- [20] R. Seidel, S. Thürmer and B. Winter, The Journal of Physical Chemistry Letters, 2011, 2, 633–641.
- [21] M. N. Pohl, E. Muchová, R. Seidel, H. Ali, Š. Sršeň, I. Wilkinson, B. Winter and P. Slavíček, *Chemical science*, 2019, **10**, 848–865.
- [22] B. Winter, E. F. Aziz, U. Hergenhahn, M. Faubel and I. V. Hertel, *The Journal of chemical physics*, 2007, **126**, 124504.
- [23] M. Arbman, S. Holmberg, M. Lundholm, H. Siegbahn, O. Gropen and U. Wahlgren, *Chemical physics*, 1983, 81, 113–119.
- [24] J. Norell, G. Grell, O. Kühn, M. Odelius and S. I. Bokarev, *Physical Chemistry Chemical Physics*, 2018, **20**, 19916–19921.
- [25] F. Zhang and R. Lynden-Bell, Physical review letters, 2003, 90, 185505.
- [26] N. K. Jena, I. Josefsson, S. K. Eriksson, A. Hagfeldt, H. Siegbahn, O. Björneholm, H. Rensmo and M. Odelius, *Chemistry–A European Journal*, 2015, 21, 4049–4055.