

Solvent-Dependent Molecular Structure of Ionic Species Directly Measured by Ultrafast X-Ray Solution Scattering

Triiodide ion has a molecular structure that sensitively changes depending on the type of solvent and its symmetry can be broken by strong solute-solvent interaction. Here, by applying pump-probe X-ray solution scattering, we characterize the exact molecular structure of the I_3^- ion in water, methanol and acetonitrile with sub-angstrom accuracy. The data reveal that the I_3^- ion has an asymmetric and bent structure in water. In contrast, the ion keeps its symmetry in acetonitrile, while the symmetry breaking occurs to a lesser extent in methanol than in water.

The triiodide ion (I_3^-) in solution offers a good example of the role played by solvent in determining the structure of ionic species. In the gas phase and aprotic solvents, the structure is linear and symmetric with equal I-I bond lengths. In contrast, in protic solvents such as water and methanol, an antisymmetric stretching mode was observed in the resonance Raman spectrum and a rotationally excited I_2^- fragment was detected in the transient anisotropy measurement of the photoexcited I_3^- ion, suggesting the existence of an asymmetric and bent structure of the I_3^- ion, respectively. However, despite these evidences, the exact structure of the I_3^- ion has never been directly characterized experimentally.

To characterize the exact structure of the I_3^- ion, we applied time-resolved X-ray solution scattering [1] to the I_3^- ion in three different solvents: water, acetonitrile, and methanol [2]. The key ideas of the experiment and data

analysis are schematically summarized in Fig. 1. By taking the difference between scattering patterns measured before and 100 ps after laser excitation, only the laser-induced changes of solution sample are extracted with all other background contributions being eliminated. To extract the structure of the I_3^- ion from the difference in scattering intensity, the maximum likelihood estimation with chi-square estimator was employed with five variable parameters. The parameters are three bond distances for the I_3^- ion, the bond distance for the I_2^- fragment, and temperature change. The theoretical scattering patterns were calculated by considering solute contribution, solvent hydrodynamics, and the contribution from solute-solvent interaction (cage). As a result, the lengths of the three bonds in the I_3^- ion are identified with sub-angstrom accuracy.

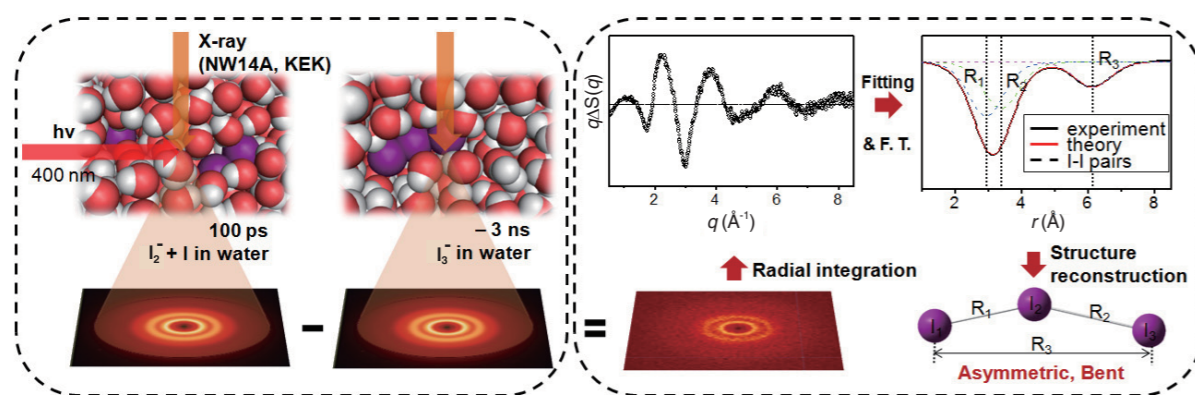


Figure 1: Schematic of our experimental method (left) and the data analysis (right).

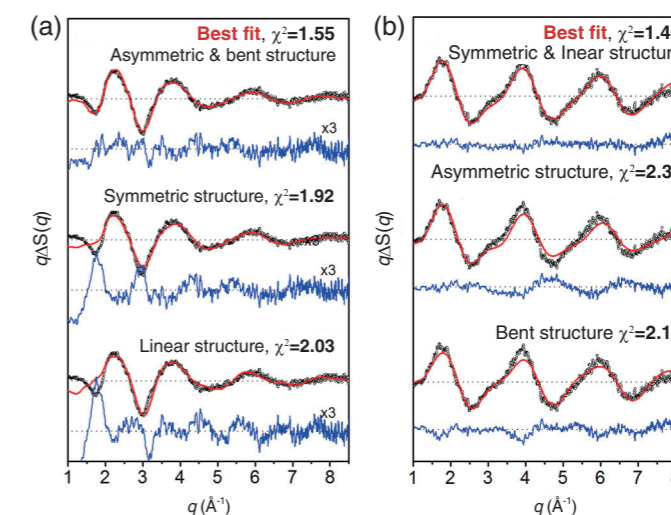


Figure 2: Difference scattering curves from the I_3^- photolysis in water (a) and acetonitrile (b) solution. Experimental (black) and theoretical (red) curves using various candidate structures of I_3^- ion are compared. Residuals (blue) obtained by subtracting the theoretical curve from the experimental one are displayed at the bottom.

To reveal the symmetry breaking of the I_3^- ion induced by hydrogen-bonding interaction with the solvent, the structure of the I_3^- ion was characterized in the three different solvents. The solvents of water, acetonitrile, and methanol have two, zero, and one functional group available for hydrogen bonding, respectively. Figure 2 shows experimental and theoretical difference scattering curves at 100 ps for the I_3^- ion in water and acetonitrile solutions. In water solution, the asymmetric and bent structure of the I_3^- ion gave the best fit when every parameter was adjusted freely. If a symmetric structure or a linear structure is assumed as a constraint, the fit between theory and experiment deteriorates. In contrast, in acetonitrile, the symmetric and linear structure gave the best fit within the error range when every parameter was adjusted freely. If an asymmetric structure or a bent structure is assumed as a constraint, the agreement deteriorates. The optimized structure in methanol lies between those in water and acetonitrile solutions, as expected from the number of functional groups available for hydrogen bonding.

Our experimental results well account for the results of previous experimental and theoretical studies [3, 4]. For example, the I-I-I angle of the bent I_3^- ion in water was estimated to be 153° from transient anisotropy measurement. This estimated value closely matches the value extracted from our data. Also, a theoretical study using MD simulation suggested an asymmetric structure of I_3^- in water with one bond longer by 0.49 \AA than the

other. This prediction is very similar to the result of our measurement (0.45 \AA).

In summary, by applying time-resolved X-ray solution scattering, we characterized the structure of the I_3^- ion in three different solvents, elucidating subtle structural changes of the ion depending on the hydrogen-bonding ability of the solvent. In water solution, the I_3^- ion was found to take an asymmetric and bent structure, lowering the structural symmetry. This phenomenon is also weakly present in methanol but not in acetonitrile.

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