

Solvent-dependent molecular structure of ionic species directly measured by ultrafast X-ray solution scattering

Ionic species plays an important role in many chemical and biological reactions. In particular, due to the charge present in ionic species, the solute-solvent interaction sensitively changes with the type of solvent, thus affecting the structure of the ions and the energy landscape of the reactions. The triiodide ion (I_3^-) in solution offers a good example. 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 photoexcited I_3^- ion, suggesting the existence of asymmetric (with unequal I-I bond lengths) and bent structure of the I_3^- ion, respectively. However, despite this evidence, the exact structure of the I_3^- ion has never been directly determined experimentally.

To determine the exact structure of the I_3^- ion, the researchers from a joint group of KAIST and KEK applied time-resolved X-ray solution scattering [1] to I_3^- ions in three different solvents: water, acetonitrile, and methanol [2]. The key ideas of the experiment and its data analysis are schematically summarized in Fig. 1. By taking the

difference between the scattering patterns measured before and 100 ps after the laser excitation, only the laser-induced changes of solution sample are extracted while all other background contributions are eliminated. To extract the structure of the I_3^- ion from the differences in the 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 the change in temperature. The theoretical scattering patterns were calculated by considering the solute contribution, the solvent hydrodynamics, and the contribution from the solute-solvent interaction. As a result, the lengths of the three bonds in the I_3^- ion were identified with sub-angstrom accuracy.

To reveal the symmetry breaking of the I_3^- ion induced by a hydrogen-bonding interaction with the solvent, the structure of the I_3^- ion was determined in three different solvents. The solvents of water, acetonitrile, and methanol have two, zero, and one functional groups available for hydrogen bonding, respectively. Figure 2 shows the experimental and theoretical differences scattering curves at 100 ps for the I_3^- ion in water and acetonitrile solutions. In water solution, the asymmetric and bent

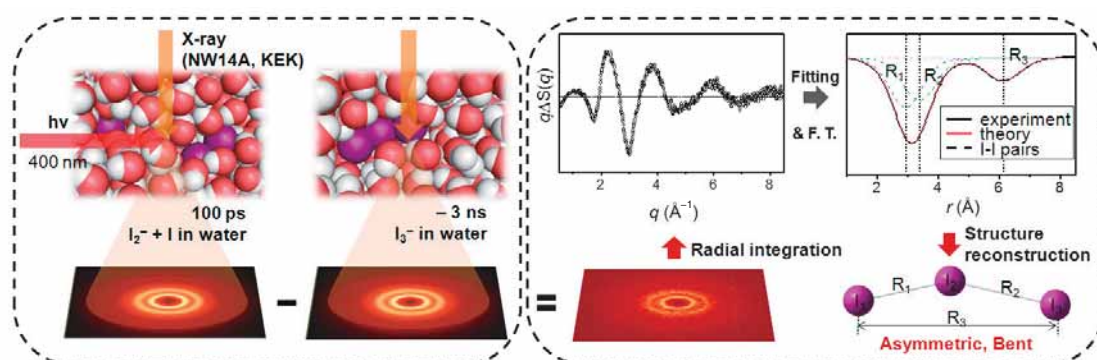


Fig. 1. Schematic of the experimental method (left) and the data analysis (right).

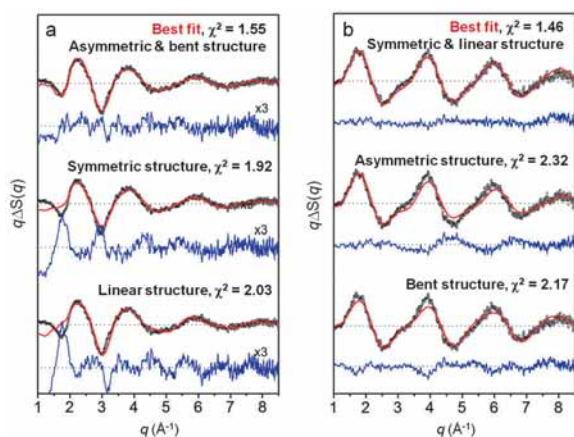


Fig. 2. Difference scattering curves from the I_3^- photolysis in water (left) and acetonitrile (right) solution. The experimental (black) and theoretical (red) curves using various candidate structures of the I_3^- ion are compared. The residuals (blue) obtained by subtracting the theoretical curve from the experimental one are displayed at the bottom.

structure of the I_3^- ion provided the best fit when every parameter was freely adjusted, while a fit with constraint to the linear structure deteriorated. In contrast, the same analysis indicates that the symmetric structure is favored in acetonitrile. The optimized structure in methanol lies in between the ones in water and acetonitrile solutions, as expected from the number of functional groups available for hydrogen bonding.

The distinction between the different structures of the I_3^- ion can be emphasized when the contribution of the I_3^- ion alone is extracted by subtracting the contributions of the I_2^- ion, the change in the temperature of the solvent, and the cage component. Figure 3 shows the extracted real-space features of only I_3^- ion in water and acetonitrile solutions. Each experimental curve (the black line) is formed by the sum of contributions from three I–I distances (the red line) optimized in the fitting analysis described in Fig. 2. Interestingly, as of the peak around 3 \AA , it is broader in water than in acetonitrile. This observation indicates that the I_3^- ion in water has two different I–I bond distances around 3 \AA suggesting an asymmetric structure. The asymmetric structure of the I_3^- ion in water is supported by the poor fit when using a symmetric structure. The peak centered at $\sim 6 \text{ \AA}$, which corresponds to the distance between the two end atoms, R_3 , can be used to determine whether the I_3^- ion has a linear or bent structure. In water, R_3 (6.13 \AA) is shorter than the sum of R_1 and R_2 (6.31 \AA), indicating the bent

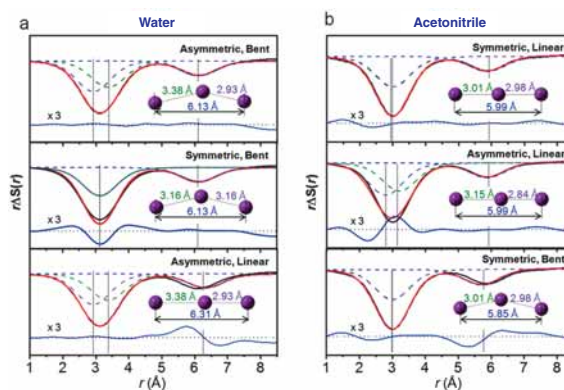


Fig. 3. Structure reconstruction of the I_3^- ion based on the extracted bond distances. The contribution of the I_3^- ion alone (the black solid line) was extracted. The theoretical curves (red) were generated by a sum of three I–I distances (the dashed lines). The residuals (the blue solid line) are displayed at the bottom.

structure of the I_3^- ion.

The results from the acetonitrile solution can be explained in the same manner. If an asymmetric structure of the I_3^- ion with two different bond lengths is used, the theoretical curve has a broader width than the experimental data. The distance between the end atoms (5.99 \AA) is the same as the sum of two other distances (5.99 \AA), indicating the linear structure of the I_3^- ion. In methanol, the structure of the I_3^- ion is asymmetric as indicated by a slightly broadened peak at $\sim 3 \text{ \AA}$, but to a lesser extent than in water. Based on this analysis, the symmetry breaking is clearly observed in water, weakly present in methanol, but does not exist in acetonitrile.

In summary, by applying time-resolved X-ray solution scattering, the researchers determined 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, they found that the I_3^- ion takes an asymmetric and bent structure, lowering the structural symmetry. This phenomenon is also weakly present in methanol but not in acetonitrile.

References

- [1] H. Ihee et al., *Science*, **309**, 1223 (2005).
- [2] K. H. Kim et al., *Phys. Rev. Lett.* **110**, 165505, (2013).