

# Solvent-dependent molecular structure of $I_3^-$ ion measured by ultrafast X-ray solution scattering

Kyung Hwan Kim,<sup>1,2</sup> Jae Hyuk Lee,<sup>1,2</sup> Hosung Ki,<sup>1,2</sup> Hyotcherl Ihee<sup>\*1,2</sup>

<sup>1</sup>Center for Nanomaterials and Chemical Reactions, Institute for Basic Science, Daejeon 305-701, Republic of Korea.

<sup>2</sup>Center for Time-Resolved Diffraction, Department of Chemistry, KAIST, Daejeon 305-701, Republic of Korea

## 1 Introduction

Ionic species play important roles 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 energy landscape of the reactions. Accordingly, aqueous solvation of ions has been a topic of intense studies. However, it is still challenging to describe the molecular-level change induced by solute-solvent interaction, for example, change in the structure of ionic species.

The triiodide ion ( $I_3^-$ ) in solution offers a good example that represents the role of solvent in determining the structure of ionic species. In the gas phase and aprotic solvents, the structure is linear and symmetric. In contrast, in protic solvents asymmetric and bent structures are possible. Here, by applying pump-probe X-ray solution scattering [1], we characterize the exact molecular structure of  $I_3^-$  ion in water, methanol, and acetonitrile.

## 2 Experiment

Time-resolved X-ray solution scattering data were acquired using the pump-probe method at the NW14A beamline at KEK. We applied time-resolved X-ray solution scattering (liquidography) to the  $I_3^-$  ion in three different solvents: water (H<sub>2</sub>O), acetonitrile (CH<sub>3</sub>CN), and methanol (CH<sub>3</sub>OH). Scattering data were collected for three time delays from 100 ps to 1 ns and, for each delay, the reference scattering curve was measured at -3 ns, which represents the unperturbed sample and is subtracted from the data measured at a positive time delay. By taking the difference between scattering patterns measured before and 100 ps after laser excitation, only the laser-induced changes of the solution sample are extracted with all other background contributions, mainly from unreacted solute molecules, being eliminated.

## 3 Results and Discussion

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. [2] In water solution, we 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. Our results provide direct evidence for broken symmetry of the triiodide ion in hydrogen-bonding solvents and clarify the subtle effect of solute-solvent interaction on the structure of ionic species.

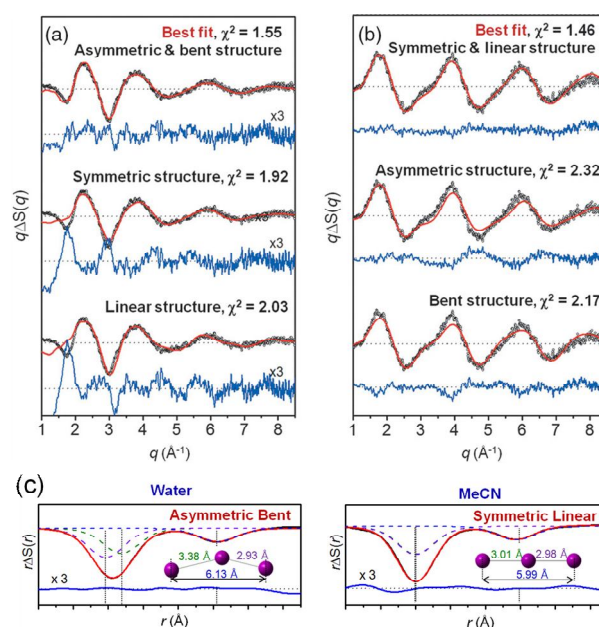


Fig. 1: Difference scattering curves from the  $I_3^-$  photolysis in water and acetonitrile solutions. Experimental (black) and theoretical (red) curves using various candidate structures of  $I_3^-$  ion are compared. Residuals (blue) obtained by subtracting the theoretical curve from the experimental one are displayed at the bottom. (a) In water,  $I_3^-$  ion was found to have an asymmetric and bent structure. (b) In acetonitrile,  $I_3^-$  ion was found to have a symmetric and linear structure. (c) Structure reconstruction of  $I_3^-$  ion based on the extracted bond distances. Theoretical curves (red) were generated by a sum of three I-I distances (dashed lines). The residuals (blue solid line) are displayed at the bottom.

## References

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

\* hyotcherl.ihee@kaist.ac.kr