

# XAFS Analysis of Triiodide Ion in Solutions

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## Abstract

Iodine K-edge XAFS of triiodide ions in various solvents were measured at SPring-8 BL01B1 and analyzed. Though the anion takes a linear and symmetric form, the second peak expected from enhanced multiple scatterings can be hardly observed because of its large vibrations. The bond distances and the Debye-Waller factors for the I-I couple vary when protic solvents were used and they were similar when aprotic solvents were used. It was indicated that the larger the Mayers' acceptor number  $A_N$  of the solvent, the larger the Debye-Waller factor. Also found was that among the aprotic solvents, the larger the Gutmann's donor number  $D_N$ , the smaller the Debye-Waller factor.

## Experimental

### Samples

Solute: NaI and I<sub>2</sub> (NaI<sub>3</sub> solution), \*tetra-*n*-propylammonium triiodide (TPAI<sub>3</sub> solution)

Solvent: acetone (AC)\*, *N,N*-dimethylacetamide (DMA)\*, nitromethane (NM), *N,N*-dimethylformamide (DMF), tetrahydrothiophen-1, 1-dioxide (TMS), methanol (MeOH)\*, acetonitrile (AN)\*, dimethylsulfoxide (DMSO)\*, ethanol (EtOH), water (aq)

Concentration: 0.01 mol/L I<sub>3</sub><sup>-</sup>  
(aqueous solution: 0.04 mol/L NaI and 0.01 mol/L I<sub>2</sub>)

### XAS measurements

Conditions: transmission mode at room temperature  
Monochromator: silicon double crystal monochromator in Si(311) diffraction mode. Rh-coted quartz mirror  
Path length: 5 – 20 cm

### Analysis

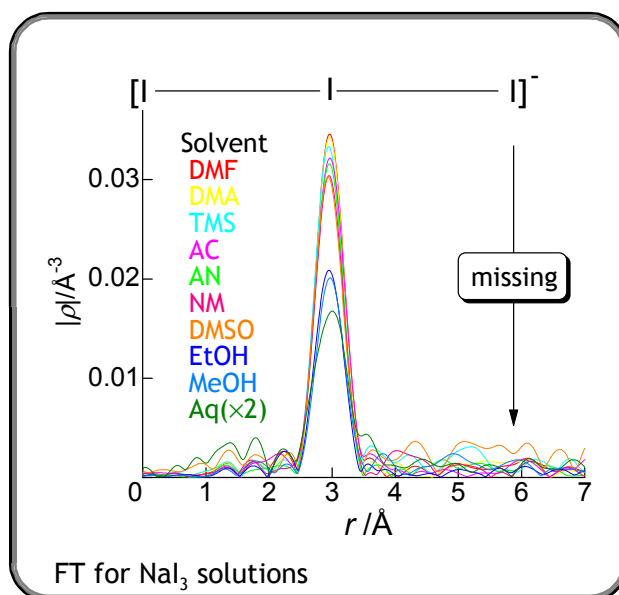
Software: Xanadu (Sakane *et al.*, 1993)

Parameters: Calculated with FEFF 6.01a for TPAI<sub>3</sub> crystal structure model.

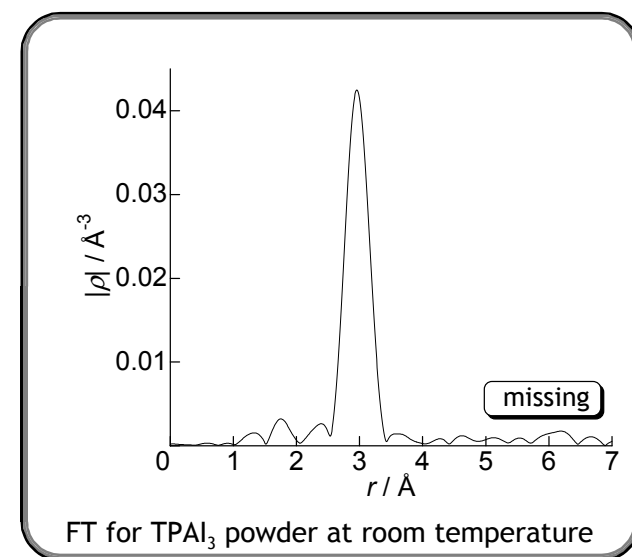
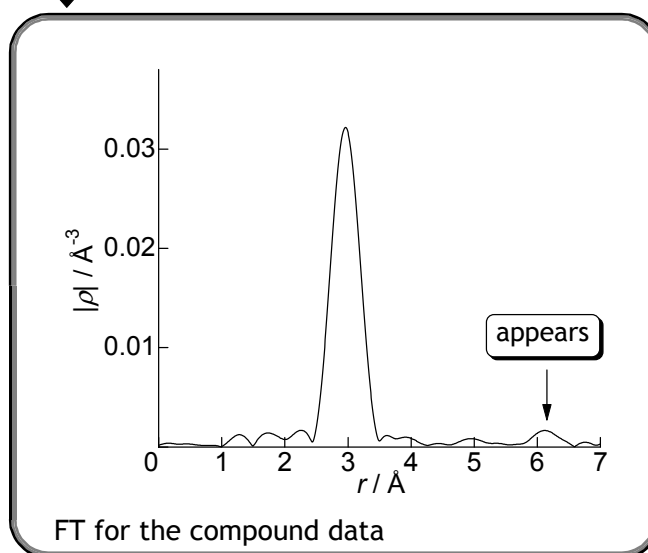
Fourier transforms:  $k$ -range of 3.6 – 15.4 Å<sup>-1</sup>. Hamming window function. Phase shifts and backscattering amplitude were corrected.

Curve fitting:  $k$ -range of 3.75 – 13.95 Å<sup>-1</sup>

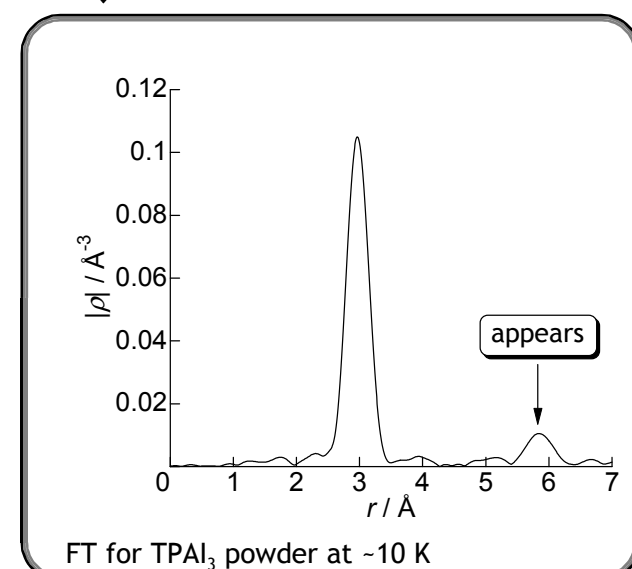
## Search for the second peak



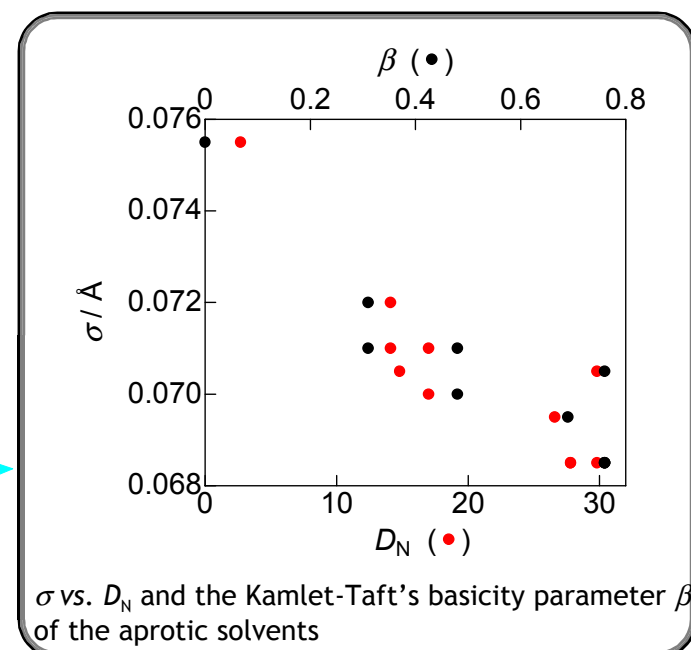
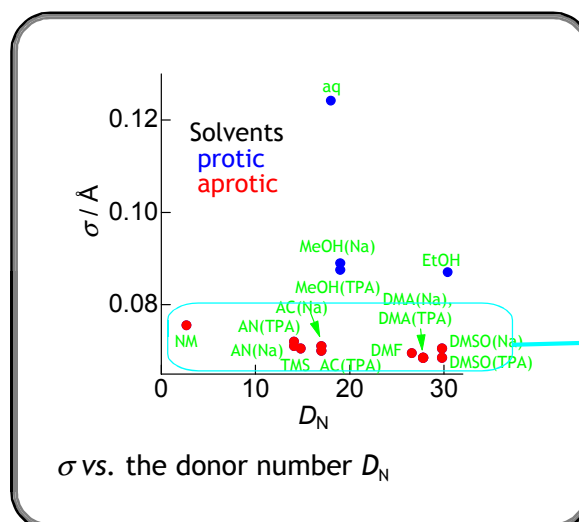
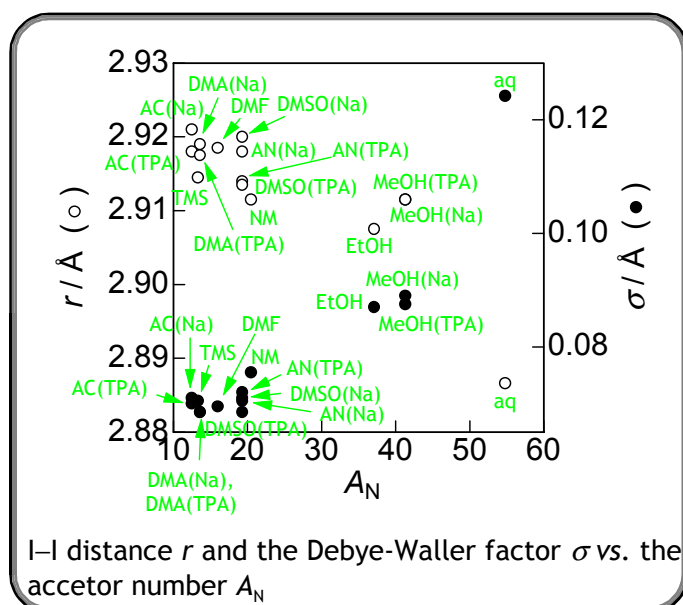
summation of 12 independent spectra



cool until -10 K



## Relations to solvent parameters



## Conclusion

The second peak, including enhanced multiple scatterings, of polyiodine species is found for the first time. It results from the highest quality of the spectra obtained from SPring-8 BL01B1 and the proper analysis treatments.

Protic solvent, water and alcohols, solutions behave correlation of decrease of the I-I distance  $r$  and increase of the Debye-Waller factor  $\sigma$  with increasing the acceptor number  $A_N$ . The group of the aprotic solvents also lies on the correlation.  $\sigma$  for the aprotic solvent solutions is declining lines with the

donor number  $D_N$  and the Kamlet-Taft basicity parameter  $\beta$ . These relations can be unified as the more the electron of I<sub>3</sub><sup>-</sup> is withdrawn by solvent molecules and the lower the electron density on the anion, the larger its  $\sigma$  becomes and then the weaker the bond in the anion is. According to simple molecular orbital interpretations, HOMO of I<sub>3</sub><sup>-</sup> has antibonding character. But, from this study HOMO should be bonding. A problem of this unified interpretation is the limited application scope of the each solvent parameters. The classification that a

solvent is either protic or aprotic has been found for Br<sup>-</sup> and I<sup>-</sup> solvation studies by XAFS and may reflect a feature of anion-solvent interactions.  $r$  becomes smaller when its  $\sigma$  becomes larger. This phenomenon cannot be understood by common knowledge. For the aqueous solution,  $\sigma$  is so large that the thermal vibration of I<sub>3</sub><sup>-</sup> would not be approximated with the Debye-Waller factor alone. Higher order cumulants should be considered in the aqueous solution. Other solutions conclude that the solvent effects affect the I-I bond strength in I<sub>3</sub><sup>-</sup> in a complex manner.