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 of the solvent, the larger the Debye-Waller factor. Also found was that among the aprotic solvents, the larger the Gutmann’s donor number \( D_\text{g} \), the smaller the Debye-Waller factor.

Experimental

Samples

Solute: NaI and I\(_3\) (NaI solution), “tetra-n-propylammonium triiodide (TPA)”, solution

Solvent: acetone (AC), nitromethane (NM), N, N-dimethylacetamide (DMA), tetrahydrofuran (THF), methanol (MeOH), acetonitrile (AN), dimethylsulfoxide (DMSO), ethanol (EoH), water (aq)

Concentration: 0.01 mol/L I\(_3\) (aq)

Solute: NaI and I\(_2\) (NaI\(_3\) solution), tetra-n-propylammonium triiodide (TPA) solution

XAS measurements

Conditions: transmission mode at room temperature

Monochromator: silicon double crystal monochromator in Si(311) diffraction mode. Rh-coated quartz mirror

Path length: 5 – 20 cm

Analysis

Software: Xanadu (Sakane et al., 1993)

Parameters: Calculated with FEFF 6.01a for TPAI\(_3\) crystal structure model.

Fourier transforms: \( k \)-range of 3.6 – 15.4 Å\(^{-1}\), Hamming window function. Phase shifts and backscattering amplitude were corrected.

Curve fitting: \( k \)-range of 3.75 – 13.95 Å\(^{-1}\)

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 solvents, 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 \( A_\text{g} \). The group of the aprotic solvents also lies on the correlation. \( \sigma \) of the aprotic solutions is declining lines with the donor number \( D_\text{g} \) and the Kamlet-Taft’s basicity parameter \( \beta \). This phenomenon cannot be understood by common knowledge. For the aqueous solution, \( \sigma \) is so large that the thermal vibration of I\(_3\) 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\(_3\) in a complex manner.