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Study on Deliquescent Reaction Processes of Salt Nanocrystals

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Summary

Adsorption reaction of water on alkali halide nanocrystals gives a model of initial stage of dissolution or deliquescence of bulk salt crystals. In this research project, we investigate the adsorption reactions on sodium halide nanocrystal ions, for the purpose of unveiling the deliquescent reaction processes of bulk crystals. The alkali halide nanocrystals, which are composed of alkali cations and halogen anions, are known to have stable substructures of bulk rock-salt crystals. For example, the $Na_nF_{n-1}^+$ ions are stable at the sizes of n = 14, 23, and 38, which have rectangular block structures of (3×3×3), (3×3×5), and (3×5×5), respectively.

In this report, before examining the reactions of nanocrystal ions with water, we have determined structures of small sodium halide nanocrystal ions, $Na_nX_{n-1}^+$, (X=F, I) by ion mobility mass spectrometry coupled with theoretical calculations. In the ion mobility spectrometry, pulsed ions are injected into a drift cell, in which He buffer gas is introduced and an electrostatic field is applied. Then collision cross section of each ion is deduced from the observed arrival time, which the ion spend in the cell. By comparing the experimental cross sections with those determined theoretically, we can determine the geometrical structures of the nanocrystal ions.

As an experimental result, we obtained a two-dimensional spectrum of nanocrystal size vs. arrival time (proportional to cross section). We also obtained mass spectrum from the two-dimensional spectrum. In the mass spectrum of $Na_nF_{n-1}^+$ ions, cuboid ions with near regular hexahedron were predominantly observed as magic numbers. This size distribution was obtained as a result of collision induced dissociation of nanocrystal ions just after injection into the drift cell, producing stable ions with relatively high dissociation energies. By comparison of the collision cross sections obtained from the ion mobility measurements with theoretical ones for n = 5-14, we have experimentally shown that all of the ions except for n = 7 and 10 have stable rock-salt structures. By contrast, the ion structures of n = 7 and 10 are found to be specific compact ones in which one sodium atom is encapsulated into the sodium fluoride cuboid lattice.