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Study on Molecular Adsorption and Deliquescent Reaction Processes of Salt Nanocrystals

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Summary

Adsorption reaction of water on alkali halide nanocrystals gives a model of deliquescence of bulk salts. In this research, we investigate the adsorption reactions of water on sodium halide nanocrystal ions, for the purpose of unveiling the deliquescent processes of bulk crystals. The 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 and 23, which have rectangular block structures of (3×3×3) and (3×3×5), respectively.

In this report, before examining the reactions of nanocrystal ions with water, we have determined structures of the four sodium halide nanocrystal ion systems, $Na_nX_{n-1}^+$ and $Na_{n-1}X_n^-$ (X=F, I; n = 2~14) 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. Collision cross section of each ion is deduced from the observed arrival time which the injected ion spend in the cell. By comparing the experimental cross sections with those predicted theoretically, the geometrical structures of the nanocrystal ions were determined.

As an experimental result, we obtained a two-dimensional spectrum of nanocrystal size vs. arrival time (proportional to cross section). For all ion systems, the cross section increases with cluster size, n. By comparison of the cross sections obtained from the measurements with theoretical ones for n = 2~14, all of the ions were found to have most stable structures obtained in the calculation. In particular, those ions have rock-salt structures except for n = 7 and 10, which have specific compact structures in which one excess atom is encapsulated into the sodium halide cuboid lattice. However, the $Na_{n-1}I_n^-$ ions have distorted structures at n = 7 and 10, because of the large size of the excess I^- ion.