

## Study on Molecular Adsorption and Deliquescent Reaction Processes of Salt Nanocrystals

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### Summary

Adsorption reactions of water on alkali halide nanocrystals gives a model of deliquescence of bulk salts. In this research, we investigate the adsorption 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, have stable substructures of bulk rock-salt crystals. For example, the  $\text{Na}_n\text{F}_{n-1}^+$  ions are stable at  $n = 14$  and  $23$ , which have rectangular block structures of  $(3 \times 3 \times 3)$  and  $(3 \times 3 \times 5)$ , respectively.

In the past two years, structures of  $\text{Na}_n\text{X}_{n-1}^+$  and  $\text{Na}_{n-1}\text{X}_n^-$  ( $\text{X}=\text{F}, \text{I}; n = 2-14$ ) were assigned by ion mobility mass spectrometry. In this method, a collision cross section of an ion is determined from an ion velocity in an ion drift cell, in which He buffer gas was introduced and an electrostatic field was applied. As a result, we found that most of the nanocrystal ions have rock-salt structures.

This year, adsorption reactions of water or methanol on the  $\text{Na}_n\text{F}_{n-1}^+$  ions were observed, by mixing small amount of the reactant gas with He buffer gas in the ion drift cell. We detected molecular-adsorbed nanocrystal ions for some cluster size. In particular, the molecular-adsorbed ions were observed for the cluster ions with  $n = 1$  to  $3$  sizes smaller than  $n = 14$  and  $23$  having rectangular block structures. Also the cross section of  $\text{Na}_{13}\text{F}_{12}^+(\text{CH}_3\text{OH})$  was larger than that of the bare  $\text{Na}_{14}\text{F}_{13}^+$  ion, whereas the cross section of water-adsorbed  $\text{Na}_{13}\text{F}_{12}^+(\text{H}_2\text{O})$  was comparable with that of  $\text{Na}_{14}\text{F}_{13}^+$ .

We have also developed a new apparatus for electrospray ionization-ion mobility mass spectrometry for hydrated nanocrystal ions. In a measurement of positive and negative ion mass spectra, we detected a doubly-charged  $\text{Na}_n\text{F}_{n-2}^{2+}$  ion series in addition to  $\text{Na}_n\text{F}_{n-1}^+$  and  $\text{Na}_{n-1}\text{F}_n^-$  monocations.