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Study on Molecular Mechanisms in Dissolution and Deliquescence Processes of Salt Nanocrystals

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Summary

Adsorption reaction of water on alkali halide clusters gives a model of initial stage of dissolution or deliquescence of bulk salt crystals. We have examined adsorption reaction of polar molecules having hydroxyl group, ROH, on two sodium halide cluster ions, $Na_nF_{n-1}^+$ and $Na_nI_{n-1}^+$, by mass spectrometry coupled with a laser photodissociation technique in the ultraviolet region and also by theoretical calculations based on density functional theory.

The reactivity has a maximum at n = 13 for water (R=H), which suggests the role of some defect site, because the $Na_{13}X_{12}^+$ (X=F, I) ion has structures with one defect site from the stable cubic 3×3×3 structure of $Na_{14}X_{13}^+$. From the theoretical calculations, three possible isomeric structures were expected to coexist for $Na_{13}X_{12}^+$ in the beam; edge-defect, basket, and surface-defect structures. Among these isomers, the edge-defect structure is the most stable, although only the basket isomer was considered in the study of ammonia adsorption on $Na_nF_{n-1}^+$ nanocrystals by Whetten and his coworkers. In the present measurement, we have also found that the "magic" reactivity at n = 13 diminishes with increasing bulk size of adsorbates ROH from H_2O to CH_3OH, $(CH_3)_2CHOH$, and $(CH_3)_3COH$. This observation implies that the basket structure of $Na_{13}X_{12}^+$ has higher adsorption reactivity than others, in which the ROH molecules are adsorbed predominantly on the inside site. In other words, the adsorption reactivity is dominated by the steric hindrance in the adsorption at the inner defect site of the basket structure. This observation was also supported by DFT calculations, photofragment ion distribution from $Na_nI_{n-1}^+(CD_3OD)$ nanocrystal ions, and also by the simple estimation of inner space of the basket structure using atomic-ion radii for the alkali and halogen ions and van der Waals radii for adsorbates. Dependence of the reactivity on the basket size is also deduced from the experiment and theoretical calculations by comparing the results of $Na_nF_{n-1}^+$ and $Na_nI_{n-1}^+$.