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

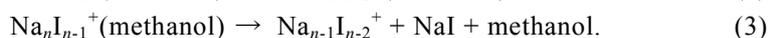
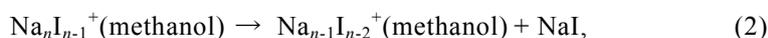
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### Summary

Adsorption reaction of water or methanol on alkali halide (AH) clusters gives a model of initial stage of dissolution or deliquescence of bulk AH solid. We have examined structures and stability of AH clusters adsorbed with methanol by a photodissociation technique of mass-selected cluster ions and by theoretical calculations based on density functional theory. In a mass spectrum of  $\text{Na}_n\text{I}_{n-1}^+$  with methanol, the cluster ions  $\text{Na}_n\text{I}_{n-1}^+(\text{CH}_3\text{OH})_m$  with  $n = 6, 13, 15, 19$  were more efficiently observed than other  $n$ . In the photodissociation measurements, we first examined the photolysis of bare  $\text{Na}_n\text{I}_{n-1}^+$  in the excitation energy of 4.8-6.0 eV. A neutral NaI molecule is found to be dissociated from the  $\text{Na}_n\text{I}_{n-1}^+$  ions for  $n=3-8$ ;



From the theoretical calculation, we found excited states predominantly due to the electron excitation of  $\text{I } 5p \rightarrow \text{Na } 3s$ . This electron transfer weakens the interatomic Coulomb attraction, and thus the neutralized NaI is ejected from the cluster ions. In the photodissociation of  $\text{Na}_n\text{I}_{n-1}^+(\text{methanol})$ , following two reactions were mainly observed;



However, elimination of only methanol was scarcely observed in this experiment. Therefore we concluded that NaI is firstly ejected from the cluster ions via the excited states as in  $\text{Na}_n\text{I}_{n-1}^+$ , and the methanol molecule is subsequently dissociated by consuming the residual excess energy.

From the size dependence of the obtained photofragment ion intensities, we found that the methanol loss (3) is more efficient from  $n=5$  cluster ion than from neighboring sizes. These results imply that the adsorption reactivity is higher for  $n=4$  and 6 than for  $n=5$ . This observation can be qualitatively explained by the calculated stable structures of  $\text{Na}_n\text{I}_{n-1}^+(\text{CH}_3\text{OH})$  for  $n=4-6$ ; the bare  $n=5$  ion has a compact crystal structure ( $3 \times 3 \times 1$  sheet), and thus  $\text{CH}_3\text{OH}$  may ligate to the ion weakly. By contrast, the methanol adsorbed on the  $n=4$  and 6 probably have higher binding energies, in which the O atoms of the molecule are located at defect sites of the AH cluster ions.