A study of microscopic solvent effect in S_N2 reaction : $I^-(CH_3I)(H_2O)_n$ (n = 1-7)

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[Introduction]

There have been many experimental and theoretical researches in reactions of methyl halides with halide anions ($X^- + CH_3Y \rightarrow XCH_3 + Y^-$) in condensed phase. It is well known that protic solvents highly inhibit these reactions. However, concrete features of the solvation effect are not well understood at the microscopic level. In this work, we discuss the structure of complexes of the S_N2 reactants with protic solvent molecules in molecular level by using cluster ion complexes.

[Experimental]

A gas mixture of H_2O / CH_3I / Ar is injected into a vacuum chamber and ionized by electron-impact. Cluster ions produced are accelerated into a time-of-flight mass spectrometer. Target cluster ions are selected by a mass gate and irradiated with an IR laser in the 2800-3800 cm^{-1} region. IR photodissociation (IRPD) spectra are obtained by plotting yields of fragment ions as a function of the IR laser frequency.

[Results and Discussion]

Fig. 1 shows the IRPD spectra of $I^-(CH_3I)(H_2O)_n$ (n = 1-7) cluster ions in the 2800-3800 cm^{-1} region. In the CH stretching region (2800-3200 cm^{-1}), only the n = 2 ion exhibits two strong bands at 2940 and 3030 cm^{-1}, while the larger cluster ions than n = 2 ion don't exhibit any bands. In the OH stretching region (3200-3800 cm^{-1}), we found that the spectra are similar to those of $I^-(H_2O)_n$[1,2]. Therefore, the hydration structure of I^- ion seems to be hardly affected by the introduction of one CH_3I molecule. We performed geometry optimization and vibrational analysis for the n = 1-4 ions at MP2/ECP/aug-cc-pVDZ +diff level[3]. Fig. 2 shows stable structures of n = 1-4 ions. It is found that n = 1 and 2 complex ions have the structure in which I^- and CH_3I have a direct contact. On the other hand, the n = 3 and 4 ions take structures in which the CH_3I molecule is attached outside the hydrated shell formed around the I^- ion. The calculated IR spectrum of these structures reproduce the IRPD spectra well. We concluded that the I^- + CH_3I S_N2 reaction is effectively inhibited by the presence of only several H_2O molecules.

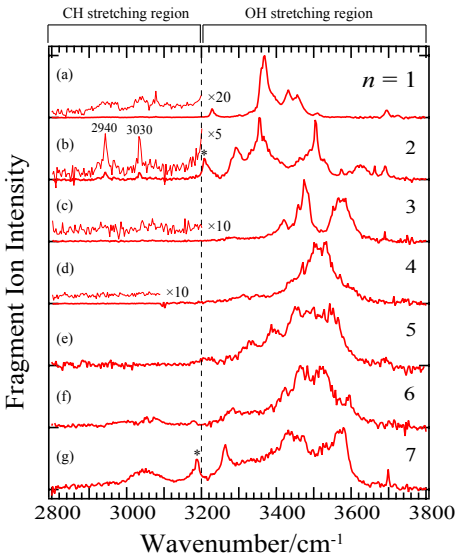

Fig. 1 IRPD spectra of $I^-(CH_3I)(H_2O)_n$

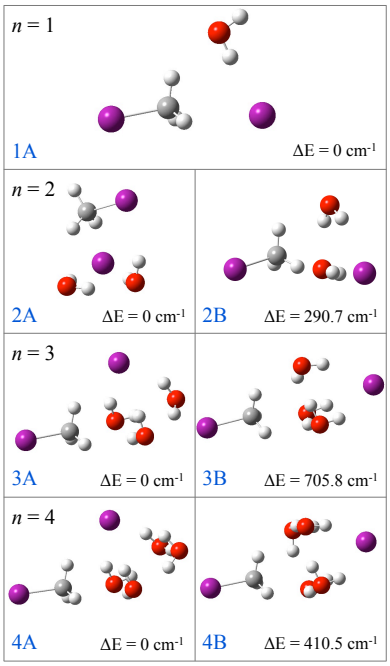

Fig. 2 The optimized structures of n = 1-4 cluster ions at MP2/ECP/ aug-cc-pVDZ+diff level.

[Reference]

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[3] H. M. Lee, K. S. Kim, *J. Chem. Phys.* ,**114**, 446 (2001)