

1B3b The structure of micro-solvated clusters in S_N2 reaction systems: $\Gamma(\text{CH}_3\text{I})(\text{H}_2\text{O})_n$ and $\Gamma(\text{CH}_3\text{I})(\text{MeOH})_m$

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[Introduction]

The reaction ($\text{X}^- + \text{CH}_3\text{Y} \rightarrow \text{XCH}_3 + \text{Y}^-$) is a typical S_N2 reaction. It is known that protic solvents highly inhibit this reaction. However, a detail of this effect is not well understood at the microscopic level. So we have investigated the structure of $\Gamma(\text{CH}_3\text{I})(\text{H}_2\text{O})_n$ ($n = 0-4$) cluster ions and $\Gamma(\text{CH}_3\text{I})(\text{MeOH})_m$ ($m = 1-2$) as a microscopic system of the ($\Gamma + \text{CH}_3\text{I}$) reaction in protic solvent.

[Experimental]

We determine the cluster structure by measuring the IR photodissociation (IRPD) spectra and by *ab initio* calculation at the MP2/aug-cc-pVDZ + diffuse level.

A gas mixture of CH₃I/ H₂O or MeOH/ Ar was expanded into a vacuum chamber through a pulse nozzle and ionized by an electron gun. The generated molecular cluster ions were mass-selected by a time-of-flight (TOF) mass spectrometer, and target ions $\Gamma(\text{CH}_3\text{I})(\text{H}_2\text{O})_n$ ($n = 0-4$) and $\Gamma(\text{CH}_3\text{I})(\text{MeOH})_m$ ($m = 1-2$) were isolated by a mass gate. These ions were irradiated by an IR laser in the 3000 – 3800 cm⁻¹ region, producing fragment ions. The fragment ions were mass-analyzed by a reflectron TOF tube and were detected by an MCP detector. The IRPD spectra were obtained by plotting yields of the fragment ions as a function of the IR laser frequency.

[Results and Discussion]

Figs.1(a) and (c) show the IRPD spectra of $\Gamma(\text{CH}_3\text{I})(\text{MeOH})_1$ and $\Gamma(\text{CH}_3\text{I})(\text{MeOH})_2$, respectively, in the OH-stretching bands region. The bands at 3160 – 3410 cm⁻¹ are the H-bonded OH-stretching bands. Fig.1 also shows the *ab initio* calculated structures for $\Gamma(\text{CH}_3\text{I})(\text{MeOH})_1$ and $\Gamma(\text{CH}_3\text{I})(\text{MeOH})_2$. In $\Gamma(\text{CH}_3\text{I})(\text{MeOH})_1$, only one isomer is obtained and in $\Gamma(\text{CH}_3\text{I})(\text{MeOH})_2$, two isomers with similar stabilization energies are obtained. In $\Gamma(\text{CH}_3\text{I})(\text{MeOH})_2$, two MeOH molecules are H-bonding to Γ so that they interfere Γ to approach to CH₃ site of CH₃I, which will inhibit the S_N2 reaction. Figs.1(b), (d), and (e) show the calculated vibrational spectra for the stable structures of $\Gamma(\text{CH}_3\text{I})(\text{MeOH})_1$ and $\Gamma(\text{CH}_3\text{I})(\text{MeOH})_2$. The assignment of the bands is illustrated in Fig.1. As to the unassigned bands, the band at 3370 in Fig.1(a) is either the band due to other isomer or the combination band of 3305 cm⁻¹. Similarly, the band at ~3160 cm⁻¹ in Fig.1(c) may be due to other isomer.

In the future, we will extend study to $m = 3$ and 4, which will be compared with those of $\Gamma(\text{CH}_3\text{I})(\text{H}_2\text{O})_n$.

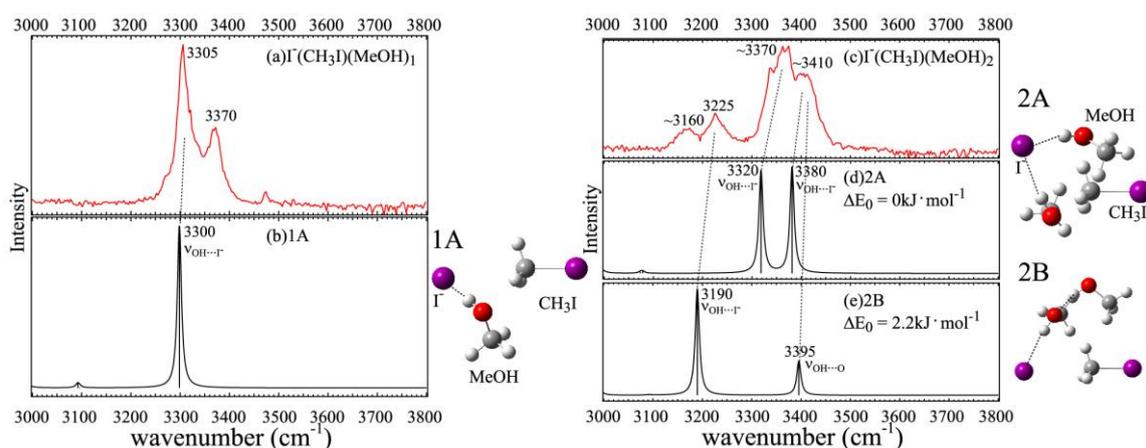


Fig.1 (a), (c): The IRPD spectra of $\Gamma(\text{CH}_3\text{I})(\text{MeOH})_1$ and $\Gamma(\text{CH}_3\text{I})(\text{MeOH})_2$ respectively.
(b), (d), (e): The calculated vibrational spectra in the stable structure of $\Gamma(\text{CH}_3\text{I})(\text{MeOH})_1$ and $\Gamma(\text{CH}_3\text{I})(\text{MeOH})_2$.
 ΔE_0 : The gap of stabilization energy corrected zero point energy between the 2A and the 2B. The 2A is the most stable isomers obtained by calculation.