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[Introduction]

The reaction ($\text{X}^- + \text{CH}_3\text{Y} \rightarrow \text{XCH}_3 + \text{Y}$) is a typical example of $\text{S}_{\text{N}}2$ reactions, which are inhibited highly by protic solvents. We have investigated the structure of $\text{I}^-(\text{CH}_3\text{I})(\text{H}_2\text{O})_n$ ($n = 0-4$) cluster ions as a microsolvation system of the ($\text{I}^- + \text{CH}_3\text{I}$) reaction.[1] In this study, we extend the study to the structure of $\text{Br}^-(\text{CH}_3\text{Br})(\text{H}_2\text{O})_m$ ($m = 0-2$) cluster ions to investigate halogen-atom-dependence on the ($\text{X}^- + \text{CH}_3\text{X}$) reaction in the water. We determine the cluster structure by measuring IR photodissociation (IRPD) spectra and by calculating the structure at the MP2/aug-cc-pVDZ + diffuse level.

[Experimental]

A gas mixture of CH_3Br (0.1-0.5%) / H_2O (0.1-0.6%) / 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 mass spectrometer, and target ions $\text{Br}^-(\text{CH}_3\text{Br})(\text{H}_2\text{O})_m$ ($m = 0-3$) were isolated by a mass gate. These target ions were irradiated by an IR laser in the $2800 - 3800\text{cm}^{-1}$ region, producing some fragment ions. The fragment ions were mass-analyzed by a reflectron and were detected by an MCP. 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 1(b) show the IRPD spectra of $\text{I}^-(\text{CH}_3\text{I})(\text{H}_2\text{O})_1$ and $\text{Br}^-(\text{CH}_3\text{Br})(\text{H}_2\text{O})_1$ complexes, respectively. In spectra (a) and (b), the bands in the $3270 - 3500\text{cm}^{-1}$ region are hydrogen bonded OH-stretching bands of H_2O , and the bands at 3690cm^{-1} are free OH-stretching bands. Then, the band at 3230cm^{-1} is the overtone OH-bending band appeared by Fermi resonance the H-bonded ν_{OH} . Spectral features of the IR spectra can be assigned to the two isomers 1A and 1B shown in Fig.2. On the basis of the relative intensity, 1B is thought to exist more than 1A in $\text{I}^-(\text{CH}_3\text{I})(\text{H}_2\text{O})_1$, while in $\text{Br}^-(\text{CH}_3\text{Br})(\text{H}_2\text{O})_1$, 1A and 1B exist almost equally. This isomer abundance ratio is thought to be controlled by the difference in charge density between CH_3I and CH_3Br . Natural Bond Orbital (NBO) calculations (table1) show that Br in CH_3Br is more negative (-0.09) than I in CH_3I (-0.01). As a result, Br in CH_3Br core accepts the proton of H_2O stronger than I in CH_3I . This gives higher abundance of 1A for the $\text{Br}^-(\text{CH}_3\text{Br})$ system.

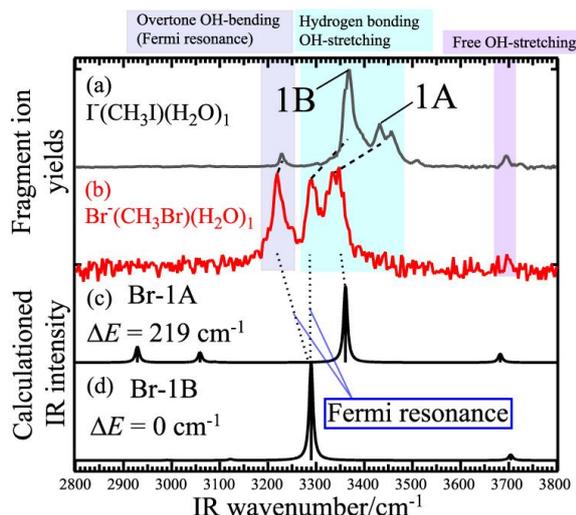


Fig.1 The IRPD spectra of (a) $\text{I}^-(\text{CH}_3\text{I})(\text{H}_2\text{O})_1$ and (b) $\text{Br}^-(\text{CH}_3\text{Br})(\text{H}_2\text{O})_1$. (c, d)The calculated IR spectra of $\text{Br}^-(\text{CH}_3\text{Br})(\text{H}_2\text{O})_1$ isomers for Br-1A and Br-1B.

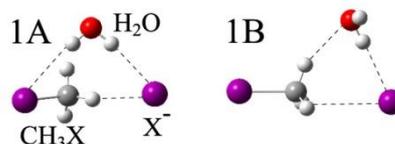


Fig.2 The stable structures of $\text{X}^-(\text{CH}_3\text{X})(\text{H}_2\text{O})_1$.

Table.1 The calculated NBO of 1A at the MP2/aug-cc-pVDZ_pp + diffuse level.

	X ⁻	C	X
I	-0.87	-0.54	-0.01
Br	-0.87	-0.45	-0.09

[1] Doi et al., submitted to J. Am. Chem. Soc.