Infrared Photodissociation Spectra of Halomethane Halide Cluster Anions and Their Solvation Structures

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Solvation structures of $X^-(CH_3X)_n$ (X = Cl and Br) were studied by use of infrared photodissociation spectroscopy (925–1090 cm^{-1}) together with mass spectroscopy. The cluster anion, $X^-(CH_3X)_n$ ($n \geq 13$) was found to have an absorption peak at a vibrational wavenumber, which is comparable to that of the X–C–H bending mode of a free CH_3X molecule. On the other hand, $X^-(CH_3X)_{12}$ did not exhibit any detectable absorption at the wavenumbers studied. It was concluded that the first solvation shell of the cluster anion is completed at $n = 12$ (icosahedral structure), and that with a sub-shell is completed at $n = 18$ (capped icosahedral structure).

Solvation structures of cluster ions have been investigated extensively by using thermochemical, infrared photodissociation spectroscopic and photoelectron spectroscopic techniques. Kebarle,[1] Castleman[2] and Hiraoka[3] have measured the enthalpy of formation of cluster ions and determined the structures of the cluster ions in comparison with calculations. They have shown that an ion core is surrounded by its solvent molecules, which form a solvation shell; the cluster ion is stable when the solvation shell is closed. On the other hand, photodissociation spectroscopy and photoelectron spectroscopy have provided information on more detailed structures of the solvation shell such as inhomogeneous solvation. Lisy,[4] Okumura[5] and Johnson[6] have measured infrared photodissociation spectra of OH-containing cluster anions in the wavelength region where the OH stretching vibration can be observed, and revealed that the anion cores are located in the center (internal solvation) or on the surface (surface solvation) of the cluster anions. Neumark and his coworkers[7] have also shown details on the solvation structures of various cluster anions by using photoelectron spectroscopy.

We have so far investigated the solvation structures of larger cluster ions consisting of multi-solvation shells by using photodissociation spectroscopy in the 10-μm region.[8] We have demonstrated that the shell closure is manifested in a drastic wavenumber-shift of an absorption peak. In the present study, the infrared photodissociation spectra of $X^-(CH_3X)_n$ (X = Cl and Br) were measured in the wavenumber range of 925–1090 cm^{-1}.

The apparatus employed consists of a cluster ion source, two quadrupole mass filters and an octopole ion trap (OPIT, 50 cm in length) used for an optical absorption measurement.[9] A mixture of argon and sample gases was expanded through a 30-μm aperture into vacuum at the stagnation pressure of 4 atm. Clusters formed in the free jet expansion were ionized by electron impact (40 eV). Cluster anions thus produced were mass-analyzed in the first quadrupole mass filter (Extrel 162-8), and were introduced into OPIT by using a quadrupole deflector. The output of a continuous wave line-tunable (925–1090 cm^{-1}) CO_2 infrared laser (Edinburgh Instruments, PL5) was introduced coaxially through a Zn–Se window into OPIT and was allowed to pass through a Ge window outside the vacuum chamber. A power meter (Coherent, Field Master LM-100) was placed outside the exit Ge window to monitor the laser power (≈ 4 W). The diameter of the laser beam is larger than the effective diameter of the ion beam in the radial potential well of OPIT, so that all the ions in OPIT are irradiated fully by the laser beam. The complete overlap of the laser and the ion beams ensures the determination of the absolute photodissociation cross sections. Ions from the exit of OPIT were mass-analyzed by the second quadrupole mass filter after being bent by another quadrupole deflector, and were detected by a secondary electron multiplier (Murata, Ceratron EMS-1081B) with an ion conversion dynode (10-kV biased) in its front. The signal from the multiplier was processed by a microcomputer (NEC, PC-9801RA).

This photodissociation is considered to be a single-photon process, because the intensity of the product ion increases linearly with the laser power. Then, the photodissociation cross section, σ, is calculated as

$$\sigma = \frac{\pi r^2 h\nu}{Pt} \log \frac{I_0}{I}, \tag{1}$$

where I_0 and I represent the relative intensities of the parent cluster ions measured with the laser off and on, respectively, r, P and ν are the radius of the laser spot, the laser power and the frequency of the laser beam, respectively, t is the interaction time of the ion with the laser beam, and h is Planck's constant. A photodissociation spectrum is obtained by measuring I_0 and I with line-tuning the CO_2 laser through the region of interest. The statistical errors originating mainly from I_0 and I were estimated to be ± 40% (one standard deviation), while the systematic errors, which arise from a fluctuation of the laser power, a translational energy distribution and an ambiguity in determination of the radius of the interaction region, were estimated to be less than 10%. Therefore, the uncertainty in the absolute cross section turned out to be ≈ 50% (one standard deviation).

Figure 1 shows typical mass spectra of cluster anions, $X^-(CH_3X)_n$ (X = Cl and Br) produced by impact of 40-eV electrons on CH_3Br [panel (a)] and CH_3Cl [panel (b)]. These spectra exhibit abrupt intensity-changes at n =12 and 18 on otherwise smoothly distributed spectra. Figure 2 shows typical infrared-photodissociation spectra of $Br^-(CH_3Br)_n$ (n = 12, 13 and 18) [panels (a), (b) and (c)] and $Cl^-(CH_3Cl)_n$ (n = 12, 13 and 18) [panels (d), (e) and (f)]. In the spectra of $Br^-(CH_3Br)_n$ (n = 13 and 18), there is only peak at ≈ 960 cm^{-1} assignable to a

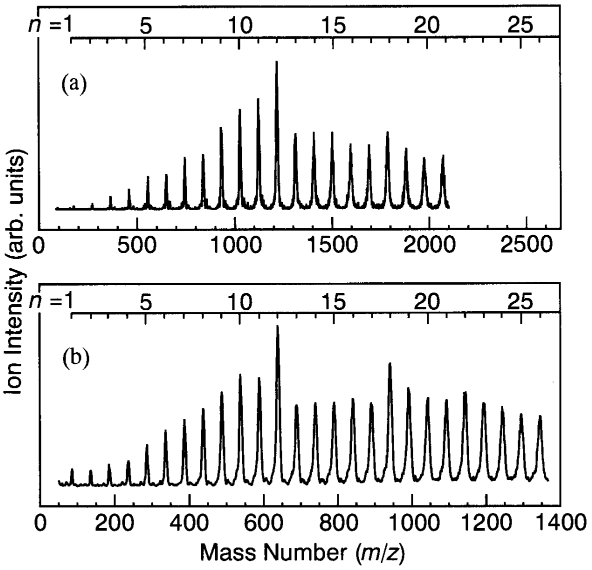

Figure 1. Mass spectra of $Br^-(CH_3Br)_n$ [panel (a)] and $Cl^-(CH_3Cl)_n$ [panel (b)].

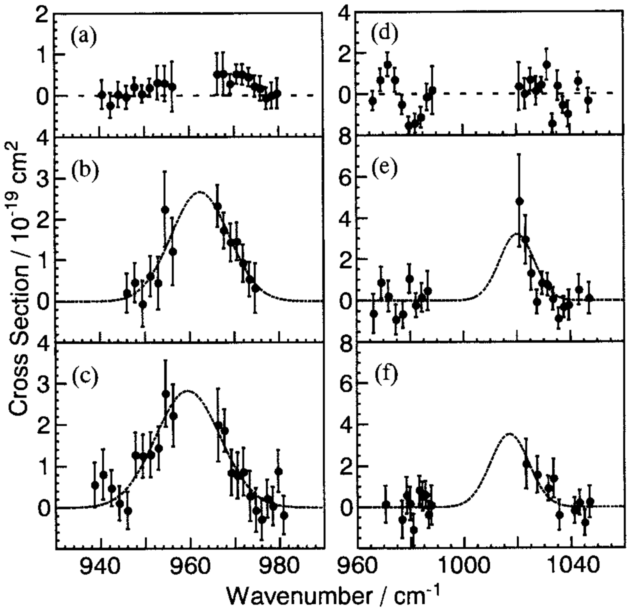

Figure 2. Infrared photodissociation spectra of $Br^-(CH_3Br)_n$ [(a) n =12, (b) n =13 and (c) n =18] and $Cl^-(CH_3Cl)_n$ [(d) n =12, (e) n =13 and (f) n =18]. The dashed lines show eye guides.

transition related to the Br–C–H bending mode (ν_5) of CH_3Br. This peak is present in the spectra of $Br^-(CH_3Br)_n$ ($13 \leq n$ 18), whereas is not in the spectrum of $Br^-(CH_3Br)_{12}$. The wavenumber of the peak (960 cm^{-1}) is comparable to that of the corresponding peak of a free CH_3Br molecule (955 cm^{-1}).[10] In the spectra of $Cl^-(CH_3Cl)_n$, one peak is present at ≈ 1020 cm^{-1}, which corresponds to the ν_5 mode of a free CH_3Cl molecule at 1017 cm^{-1}.[10] The spectrum of $Cl^-(CH_3Cl)_{12}$ exhibits no peak in the entire wavenumber range studied.

Although we have no definitive information on the structure of $X^-(CH_3X)_n$ (X=Cl and Br), we can reason on the structure from the known structure of $X^-(CH_3CN)_n$ and mass spectroscopic information obtained in the present experiment. Note that $X^-(CH_3CN)_n$ should resemble to $X^-(CH_3X)_n$ in geometric and electronic structures, because of similar chemical properties of CN to those of X. In comparison with the $X^-(CH_3CN)_n$ structure,[3] it is concluded that $X^-(CH_3X)_n$ is composed of an ion core, X^-, surrounded by CH_3X molecules with their X ends pointing outside. A stepwise change at n = 12 in the mass spectrum of $X^-(CH_3X)_n$ indicates that the first solvation shell is completed at n =12. Seemingly, $X^-(CH_3X)_{12}$ is an icosahedron with the X ends extruding outward. Another stepwise change at n =18 suggests that $X^-(CH_3X)_{18}$ is a capped icosahedron. This structure evolution resembles that of Xe_n^+; Xe_{13}^+ and Xe_{19}^+ are an icosahedron and a capped icosahedron, respectively.[11]

In the light of this structure model, one can explain the infrared photodissociation spectra of $X^-(CH_3X)_n$and its n-dependence. In $X^-(CH_3X)_n$ with $n \geq 13$, there are several CH_3X solvent molecules in the second solvation shell. Presumably, the wavenumbers of their ν_5 vibrations are comparable to that of a free CH_3X molecule because they are sufficiently apart from the ion core, X^-. Actually, the absorption peak in the spectra of $X^-(CH_3X)_n$ ($13 \leq n \leq 18$) is observed at almost the same wavenumber of the corresponding peak of a free CH_3X molecule, which is identified as the X–C–H bending mode (ν_5) as described previously. In $X^-(CH_3X)_{12}$, on the other hand, all the solvent CH_3X molecules are placed in the first solvation shell, and hence they are significantly influenced by the ion core, X^-. In fact, the peak observed in $X^-(CH_3X)_n$ with $13 \leq n \leq 18$ is not found in the spectra of $X^-(CH_3X)_{12}$ in the entire wavenumber range studied. It is inferred from a simple calculation on CH_3Cl and $Cl^-(CH_3Cl)$ that in $X^-(CH_3X)_n$with $n \leq 12$, several percents of the ion-core charge is donated to the solvent CH_3X molecules and each CH_3X molecule is polarized, so that electrons are intramolecularly transferred from C to X. Due to the slight charge transfer and the polarization, the peak corresponding to the ν_5 mode red-shifts; with increase in n, it blue-shifts and approach to the wavenumber of the ν_5 mode of a free CH_3X.

In this study, we elucidated the structural evolution of $X^-(CH_3X)_n$ with the cluster size, n, from the first solvation shell to that with a sub-shell; the completion of the solvation shell at n = 12 (icosahedral structure) and that with a sub-shell at n = 18 (capped icosahedral structure).

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References and Notes

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