IR Photodissociation Spectroscopy of Ion-Molecule Complexes as Chemical Intermediates

(Hiroshima Univ.) Yoshiya INOKUCHI

[Introduction]

Ion-molecule complexes play significant roles as chemical intermediates in a number of chemical reactions. For example, the formation of the chemical bond between unsaturated groups such as C=C and C=O and ions is thought to be primary processes in nucleophilic additional reactions catalyzed by acid and base. In this study, we apply IR photodissociation (IRPD) spectroscopy in the 1000–2300 cm⁻¹ region to the (CO₂)₂⁺, (OCS)₂⁺, and (CS₂)₂⁺ ions. The IRPD spectra are measured as action spectra of the Ar loss through the IR irradiation of the (CO₂)₂⁺Ar, (OCS)₂⁺Ar, and (CS₂)₂⁺Ar ions. In these dimer ions, an intermolecular covalent bond will be formed between a molecular radical cation (M⁺) and a neutral molecule (M) via the interference between the singly occupied molecular orbital (SOMO) of M⁺ and the highest occupied MO (HOMO) of M. We discuss the characteristics of the structure and the intermolecular bond formed in the dimer ions on the basis of the IRPD results with the aid of quantum chemical calculations.

[Experimental]

Figure 1 shows a schematic drawing of the IRPD spectrometer used in this study.¹ ² A mixture of the sample gas (CO₂, OCS, or CS₂, ~1%) and Ar is injected into a source chamber through a pulsed nozzle with a stagnation pressure of 0.8 MPa and ionized with an electron impact ion source. The cluster ions produced are accelerated into a flight tube, and only target parent ions are mass-selected by a mass gate. Parent ions are irradiated by an output of a pulsed IR laser. Resultant fragment ions are mass-analyzed by a reflector and detected by a multichannel plate. IRPD spectra of parent ions are obtained by plotting normalized yields of fragment ions against wavenumber of the IR laser. We also carry out the geometry optimization and the vibrational analysis of the (CO₂)₂⁺, (OCS)₂⁺, and (CS₂)₂⁺ ions with GAUSSIAN03 program package at the B3LYP/6-311+G* level of theory.

[Results and discussion]

The (CO₂)₂⁺, (OCS)₂⁺, and (CS₂)₂⁺ ions are expected to have in-phase and out-of-phase combination modes of the ν₁ and ν₃ stretching vibrations of the two components. Figure 2 displays the in-phase (a) and out-of-phase combination modes of the ν₃ vibrations for the (CO₂)₂⁺ ion. If the (CO₂)₂⁺ ion has a planar C₂ᵥ structure, the in-phase combination of ν₃ is IR forbidden, though the ν₃ vibration of CO₂ is strongly IR active. Therefore, the number of the IR bands of the dimer ions suggests the structural planarity. Figures 3(a), 3(c), and 3(e) show the IR spectra of the dimer ions in the ν₂ region. In the case of (CO₂)₂⁺ and (CS₂)₂⁺ ions, only one band appears in the spectra, suggesting...
that these dimer ions have a planar C$_{2h}$ structure. In contrast, the (OCS)$_2^+$ ion has two IR bands, which implies a C$_2$ structure for (OCS)$_2^+$. The IRPD results of (CO$_2$)$_2^+$ and (OCS)$_2^+$ are consistent with the results of the geometry optimization shown in Fig. 3; these dimer ions have a C$_{2h}$ and a C$_2$ structure, respectively. However, the density functional theory (DFT) calculation provides a C$_2$ structure for the (CS$_2$)$_2^+$ ion, which does not agree with the IRPD result in Fig. 3(e). The disagreement in the (CS$_2$)$_2^+$ case demonstrates incomplete representation of the intermolecular interaction by the DFT calculations. In order to examine the stability of the planar form of the dimer ions, we calculate the potential energy surface (PES) of the dimer ions along the intermolecular out-of-plane bending mode (Fig. 4). The steepness of the PES is substantially lower for the (CS$_2$)$_2^+$ ion than for the (CO$_2$)$_2^+$ and (OCS)$_2^+$ ions, suggesting that the (CS$_2$)$_2^+$ ion has a floppier structure than that of (CO$_2$)$_2^+$ and (OCS)$_2^+$. The (OCS)$_2^+$ and the (CS$_2$)$_2^+$ ions have a double-minimum potential, and the potential barrier between the minima is substantially higher for the (OCS)$_2^+$ ion (391 cm$^{-1}$) than for the (CS$_2$)$_2^+$ ion (92 cm$^{-1}$). The DFT calculation predicts that the zero-vibrational level along the dihedral angle is located lower than the potential barrier even in the case of the (CS$_2$)$_2^+$ ion. It is probable that the DFT calculations cannot reproduce the intermolecular PES properly for the (CS$_2$)$_2^+$ ion because of a much weaker intermolecular interaction in (CS$_2$)$_2^+$. In Figs. 3(b), 3(d), and 3(f), the IRPD spectra of the trimer ions are shown for comparison. As seen in Fig. 3(b), the (CO$_2$)$_3^+$ ion core in the (CO$_2$)$_3^+$ trimer ion has a C$_2$ structure; the solvation of one CO$_2$ molecule to the (CO$_2$)$_2^+$ ion core easily distorts the planar structure of the dimer ion, even though the (CO$_2$)$_2^+$ ion has the highest tension of the planar form among the dimer ions of CO$_2$, OCS, and CS$_2$.

**References**
