

# Structures of $[(\text{N}_2\text{O})_n\text{H}_2\text{O}]^+$ ( $n = 2-7$ ) Cluster Ions Studied by Photodissociation Spectroscopy

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**[Introduction]** One of the basic subjects of molecular cluster ions to be revealed is the charge distribution in clusters. To answer this question, we have been studying the structures and charge distribution of various kinds of molecular cluster ions by IR photodissociation (IRPD) spectroscopy. In the present study, we present study of  $[(\text{N}_2\text{O})_n\text{H}_2\text{O}]^+$  cluster ions. We already showed that in  $(\text{N}_2\text{O})_n^+$  cluster ions the positive charge is localized in the  $\text{N}_4\text{O}_2^+$  dimer ion core. We examined how an additional  $\text{H}_2\text{O}$  molecule changes the structure of  $(\text{N}_2\text{O})_n^+$  clusters.

**[Experimental]** A gas mixture of water vapor and  $\text{N}_2\text{O}$  is injected into a vacuum chamber through a pulsed nozzle and ionized by an electron-impact. Then the created cations are accelerated into a time-of-flight mass spectrometer and only a target ion is selected by a mass gate. Ions are then irradiated by an IR laser in the  $1100-3800\text{ cm}^{-1}$  region. IRPD spectra are obtained by plotting yields of fragment ions against wavenumber of the IR laser. In addition, quantum chemical calculations are performed at the B3LYP/6-311++G(d,p) level of theory.

**[Results and Discussions]** Figure 1 shows the IRPD spectra of the  $[(\text{N}_2\text{O})_n\text{H}_2\text{O}]^+$  ( $n = 2-7$ ) ions in the  $1100-3800\text{ cm}^{-1}$  region. The IRPD spectra show  $\nu_1$  and  $\nu_3$  vibrations of  $\text{N}_2\text{O}$  components at around  $1250$  and  $2200\text{ cm}^{-1}$  and the OH stretching vibrations of the  $\text{H}_2\text{O}$  part in the  $2400-3800\text{ cm}^{-1}$  region. In the  $n = 2$  spectrum, a sharp band is observed at  $3452\text{ cm}^{-1}$ , which is ascribed to the free OH stretching vibration. Since the frequency of this band is intermediate between the vibrations of  $\text{H}_2\text{O}$  and  $\text{H}_2\text{O}^+$ , a part of the positive charge is thought to be shared by the  $\text{H}_2\text{O}$  component. In the  $2000-2300\text{ cm}^{-1}$  region, there are two bands, which are ascribable to solvent  $\text{N}_2\text{O}$  molecules and an ion core, indicating that one  $\text{N}_2\text{O}$  molecule also has some amount of the positive charge. These results suggest that the  $(\text{N}_2\text{O}\cdot\text{H}_2\text{O})^+$  ion core exists in the clusters. In order to determine the structure of the  $(\text{N}_2\text{O}\cdot\text{H}_2\text{O})^+$  ion core and its solvation features, we carried out the geometry optimization and the vibrational analysis at the B3LYP/6-311++G(d,p) level of theory. Figure 2 shows the optimized structure of  $(\text{N}_2\text{O}\cdot\text{H}_2\text{O})^+$  and an intermolecular bonding MO. In the  $(\text{N}_2\text{O}\cdot\text{H}_2\text{O})^+$  ion core, the oxygen atoms of  $\text{H}_2\text{O}$  and  $\text{N}_2\text{O}$  are directly bonded to each other. In larger clusters, solvent  $\text{N}_2\text{O}$  molecules form hydrogen-bonds to the OH groups of the  $(\text{N}_2\text{O}\cdot\text{H}_2\text{O})^+$  ion core.

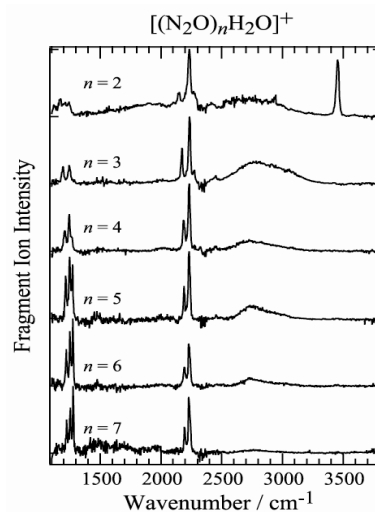


Fig.1 IRPD spectra of  $[(\text{N}_2\text{O})_n\text{H}_2\text{O}]^+$  ( $n = 2-7$ )

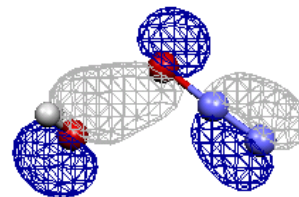


Fig.2 Ion core structure of  $[(\text{N}_2\text{O})_n\text{H}_2\text{O}]^+$