

PROBING OF LOCAL ELECTRONIC STRUCTURE IN SMALL HYDROGEN BONDING CLUSTERS USING SOFT X-RAY PHOTOABSORPTION SPECTROSCOPY

Unlike valence orbitals, inner-shell orbitals are highly localized around an atom to which electrons originally belong. Inner-shell photoabsorption spectroscopy is therefore sensitive to the chemical environment of each atom and enables us to investigate the local geometric and electronic structures of matter [1]. This is applied not only to atoms and molecules in the gas phase but to those adsorbed on surfaces.

Inner-shell photoabsorption spectroscopy has also been applied to the analysis of gas phase clusters, which bridge a gap between an isolated molecule and a molecule in the condensed phase [2]. An inner-shell photoabsorption study of clusters is expected to become a useful probe for research on the local properties of electronic structures in small clusters, because higher unoccupied orbitals have further spatial extension and are strongly perturbed by surrounding molecules. From this viewpoint, inner-shell excitation spectra of small clusters have been extensively measured in recent years [2]. However, only few studies of the inner-shell excitation of hydrogen-bonding (HB) clusters have been reported. The purpose of our investigation is to elucidate the change in electronic structure by HB interaction at the cluster level [3].

Experiments were carried out at the soft X-ray photochemistry beamline **BL27SU**. The experimental setup is shown in **Fig. 1**. Ethanol clusters were produced by a seeded beam method. Helium at a pressure of 4 atm was bubbled through a sample reservoir containing room temperature ethanol, and the mixture was expanded through a nozzle of 30 μm diameter. A supersonic beam was collimated by a skimmer and led to the main chamber. In the main chamber, it was crossed with a soft X-ray beam in the ionization region of a double-field type time-of-flight (TOF) mass spectrometer. Ions and electrons formed by the soft X-ray absorption were extracted toward opposite directions in the ionization region. The electrons were detected by a micro-sphere-plate (MSP) and the ions were detected by another MSP after the flight through the TOF tube. Electron signals were fed into the start pulse input of a multi-stop time-to-digital converter and ion signals were fed into the stop pulse input to obtain electron-ion coincidence signals.

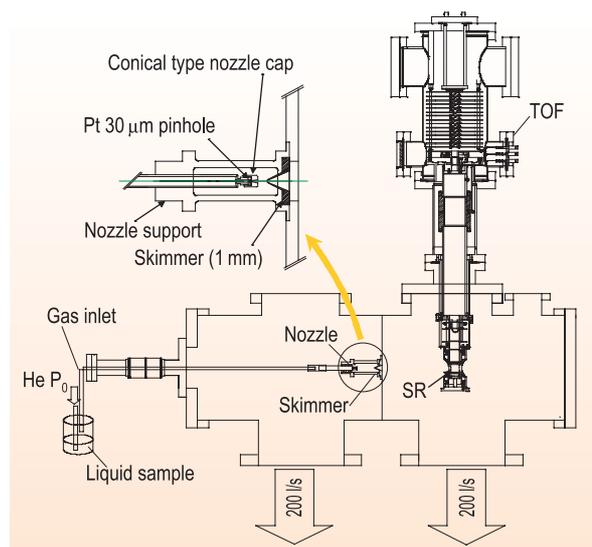


Fig. 1. Schematic layout of experimental chamber.

Figure 2 shows TOF mass spectra of ethanol measured under (a) seeded supersonic beam (He 4 atm) and (b) effusive beam conditions. Under the effusive beam condition, no ions larger than $m/z=45$ were found in the TOF mass spectrum. Because the effusive beam consists of only ethanol monomers, these ions are formed from the fragmentation of ethanol molecules. On the other hand, under the seeded supersonic beam condition, several ions larger than $m/z=45$ appear. Prominent peaks are assigned to protonated ethanol cluster ions, $\text{H}(\text{C}_2\text{H}_5\text{OH})_n^+$ ($n=1-6$). Owing to an intracluster ion-molecular reaction that proceeds rapidly during cluster fragmentation, the protonated cluster ions $\text{H}(\text{C}_2\text{H}_5\text{OH})_n^+$ become predominant products.

Inner-shell excitation spectra of ethanol clusters were obtained using the partial-ion-yield (PIY) method. The PIY spectra were obtained from the area of the peaks in the TOF spectra measured across the O K -edge. Soft X-ray photoabsorption spectra (XAS) of ethanol molecules and PIY spectra of $\text{H}(\text{C}_2\text{H}_5\text{OH})^+$ are shown in **Fig. 3**. A salient feature is that the PIY of $\text{H}(\text{C}_2\text{H}_5\text{OH})^+$ is very different from that of XAS of ethanol molecules. The PIY of $\text{H}(\text{C}_2\text{H}_5\text{OH})^+$ does not show any enhancement at 534.7 eV which is assigned to the transition

O(1s- $\sigma^*(\text{OH})$). A similar result, i.e., the loss of a pre-edge feature, has been observed by Nilsson *et al.* [4]. They observed that resonance pre-edge structures in the XAS of liquid water and ice are different from that of water molecules and ascribed this difference to the occurrence of the HB. They suggested that the OH group donating the hydrogen atom does not show the feature in the pre-edge region. The resonance pre-edge feature in the XAS comes from the free OH group that does not donate the hydrogen atom. Unoccupied molecular orbitals responsible for the resonance feature in the XAS of water molecules lose their p-character by participating HB. The present result suggests that a similar change in electronic structure occurs in ethanol clusters. In the case of ethanol clusters, the small clusters are expected to gather via the (H-O...H-O) network. Unlike water, ethanol molecule has only one OH; thus, no free OH remains in the HB clusters. This interaction leads to a drastic reduction in the intensity of $\sigma^*(\text{OH})$ excitation in PIY spectra.

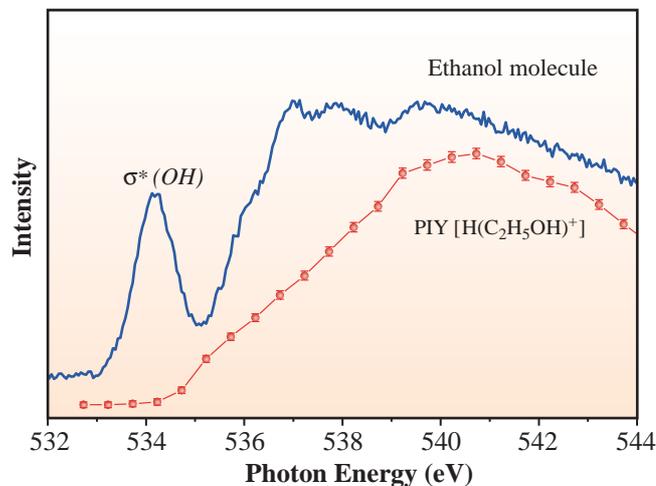


Fig. 3. Comparison of experimental soft X-ray absorption spectra of ethanol cluster (red) and molecule (blue).

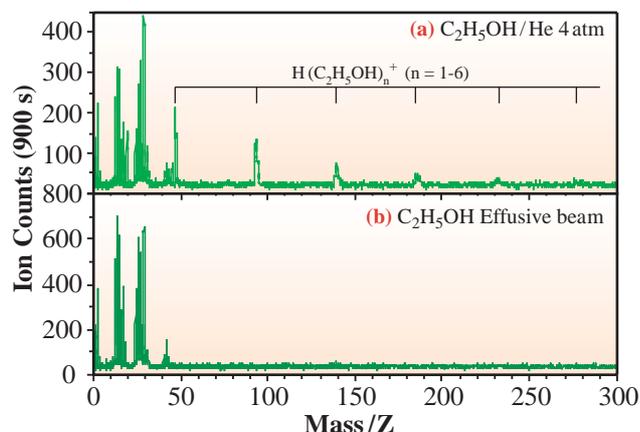


Fig. 2. Comparison of TOF mass spectra of ethanol measured under (a) seeded supersonic beam (He 4 atm) and (b) effusive beam conditions. The spectra were taken at a photon energy of 545.0 eV, which is higher than the O 1s ionization threshold of ethanol.

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References

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