

Formation of H_3O^+ by the soft X-ray ionization of ethanol clusters

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Abstract

Time-of-flight mass spectra have been measured for inner-shell ionization of ethanol molecules, its clusters, and methanol clusters at the oxygen K-edge regions. Only in the case of the ethanol clusters, a fairly intense signal corresponding to H_3O^+ has been observed. The measurements for ethanol- d_1 ($\text{C}_2\text{H}_5\text{OD}$) suggest that at least one H atom in the H_3O^+ ion originates from the C_2H_5 group of neighbouring ethanol. It is proposed that in addition to the O-H--OH type hydrogen bonding in the ethanol clusters, the H in the C_2H_5 group and OH interact with each other.

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1. Introduction

When a molecule is excited to highly excited states by soft X-ray photons, fragmentation follows in a few femtoseconds and intramolecular rearrangement reactions occur frequently [1-7]. In the rearrangement reactions, prior to fragmentation, one or more atoms 'migrate' in the molecule. In particular, the migration of H atom has been reported by several groups [1,3,5,6]. For example, CHF^+ was observed in the fragmentation products of the C 1s excited $\text{CF}_2=\text{CH}_2$ molecule [3]. In some cases, the products of the rearrangement reactions are only observed at a specific excitation energy, and site- and state-specific fragmentations are proposed for the migration of atoms [3,4]. It has also been reported that the ion yield does not depend significantly on the excitation energy [5,7]. Since the fragmentation processes are expected to proceed quite rapidly, the products of the rearrangement reactions usually provide useful information about the structure of the transition state of the unimolecular reactions.

In our previous paper, we reported the observation of an H_3O^+ rearrangement fragment by the oxygen K-edge excitation of ethanol clusters $[(\text{C}_2\text{H}_5\text{OH})_n]$ [8]. The observed formation of H_3O^+ in ethanol clusters was unexpected from a simple hydrogen-bonding interaction model for alcohol. In the simple hydrogen-bonding model [9,10], the O atom at the OH site of one molecule can interact and bind with the H atom at the OH site of another molecule: $-\text{O}-\text{H}\cdots\text{OH}$. Consequently, the simple fragmentation of alcohol clusters can produce only H_2O^+ and the participation of a third H atom is required to

form H_3O^+ . The ionic fragmentation of ethanol clusters has been investigated by electron impact [9] and VUV photoionization mass spectrometry [10,11]. Due to an intracuster ion-molecule reaction, which proceeds rapidly during cluster fragmentation, protonated clusters $[\text{H}(\text{C}_2\text{H}_5\text{OH})_n]^+$ become the dominant products for the hydrogen-bonding cluster [9-11]. However, the formation of H_3O^+ ions has not been reported in these studies. The objective of the present study is to verify whether the H_3O^+ ions originate from the ethanol clusters by the use of a time-of-flight (TOF) spectrometer with a higher resolving power to resolve the product ions more accurately. The measurement of ethanol was performed under effusive and supersonic beam conditions, and the obtained TOF mass spectra were compared. In addition, isotopically substituted samples were used and a comparison was made with the fragmentation process of methanol clusters.

2. Experimental

The experiments were conducted at the soft X-ray photochemistry beamline (BL27SU) in the SPring-8 facility [12,13]. The light source was the radiation from a ‘Figure-8’ undulator, which is capable of generating a linearly polarized photon beam [14,15]. The photon beam was dispersed using a soft X-ray monochromator with varied-line-spacing plane gratings and introduced into the ionization region of a coincidence measurement instrument. The experimental apparatus used in this study was described in detail in Ref. [8]. A TOF mass spectrometer was used instead of a double-field-type one to obtain a

higher resolution [16,17]. The ions and electrons resulting from the soft X-ray absorption were extracted toward opposite directions in the ionization region. In order to minimize mass discrimination effects, a high-intensity electrostatic field (1 kV/cm) was applied across the ionization region to collect the fragment ions; further, two lens systems were installed to focus the ions onto the detector. The electrons were detected by using a microsphere plate (MSP, EI-Mul) and the ions were detected using another MSP after the flight through the TOF tube. The electron signals were fed as start-pulse input to a multi-stop time-to-digital converter (FAST ComTec, 7886), and the ion signals were fed as stop-pulse input in order to obtain electron-ion coincidence (PEPICO) signals.

Methanol and ethanol clusters were produced by the seeded-beam method. A mixture of helium and room-temperature vapor of ethanol or methanol was expanded through a nozzle with a diameter of 30 μm . The supersonic beam was collimated using a skimmer (Beam Dynamics, diameter: 1.0 mm) and introduced into the main chamber. During the measurements, the pressures in the nozzle and in the main chamber were around 2×10^{-2} and 4×10^{-4} Pa, respectively.

In order to facilitate the comparison with the mass spectrum of the clusters, the spectra of the molecular ethanol were measured under an effusive beam condition. For this measurement, the pure sample vapor at room temperature was directly introduced into the ionization chamber through a 1/16-in. o.d. needle. During the effusive beam measurement, the pressure in the main chamber was 4×10^{-4} Pa. The methanol (purity: >99.9%), ethanol

(purity: >99.9%) and ethanol- d_1 (C_2H_5OD) [purity: D 99% (<5% D_2O)] were obtained from Wako Pure Chemical Industries, Ltd, and the He gas, with a stated purity of 99.99%, was purchased from Taiyo Toyo Sanso Co., Ltd.

3. Results and discussion

3.1. Observed mass spectra of fragment ions

Figure 1 shows the TOF mass spectra of the ethanol measured under the (a) seeded supersonic (He, 4 atm) and (b) effusive beam conditions. The spectra were acquired at a photon energy of 545.0 eV, which is higher than the O 1s ionization threshold of ethanol (538.6 eV) [18]. Under the effusive beam condition, only ions with an m/z smaller than 46 were observed; these ions were considered to originate from the ethanol molecule. Under the seeded supersonic beam condition, several ions with m/z greater than 46 were observed (Fig. 1a). The prominent peaks were assigned to protonated ethanol cluster ions, $H(C_2H_5OH)_n^+$ ($n = 1-6$). It is known that the protonated clusters, and not intact cluster ions, are the dominant products [9-11], and the results obtained in this study are consistent with those obtained from previous experiments of electron impact [9] and VUV photoionization [10,11] of ethanol clusters. In addition to the appearance of these cluster ions, certain differences were observed between the small-mass regions obtained in the measurements under the two beam conditions.

In order to observe these differences more clearly, the spectra of $m/z = 1-50$ are expanded; these are shown in Fig. 2. Significant differences can be observed at $m/z = 19$

and 45. At $m/z = 19$, a fairly intense peak was observed under the supersonic beam condition, whereas a very weak signal was observed under the effusive beam condition. At $m/z = 45$, a significant peak was observed only under the supersonic beam condition. The H_3O^+ and $\text{C}_2\text{H}_5\text{O}^+$ ions appear to characterize the supersonic beam condition. Since the difference in conditions between the supersonic and effusive beams is attributed to the presence of ethanol clusters, it can be inferred that these ions are formed due to the photoionization of the ethanol clusters.

3.2. Analysis of isotope effects

More detailed information regarding the H_3O^+ and $\text{C}_2\text{H}_5\text{O}^+$ ions was provided by the experiments on $\text{C}_2\text{H}_5\text{OD}$. Figure 3 shows the comparison of the TOF mass spectra of $\text{C}_2\text{H}_5\text{OD}$ and $\text{C}_2\text{H}_5\text{OH}$. In the TOF mass spectrum of $\text{C}_2\text{H}_5\text{OD}$, signals corresponding to D_2HO^+ ($m/z = 21$) were observed instead of those corresponding to H_3O^+ , and no signals corresponding to D_3O^+ ($m/z = 22$) were observed. This result indicates that at least one H atom in H_3O^+ observed in the $\text{C}_2\text{H}_5\text{OH}$ cluster experiment originates from a C_2H_5 group. In the $m/z = 45$ region, a peak at $m/z = 46$ that corresponds to $\text{C}_2\text{H}_4\text{OD}^+$ was observed; however, no peak at $m/z = 45$, for $\text{C}_2\text{H}_5\text{O}^+$, was observed in the $\text{C}_2\text{H}_5\text{OD}$ measurement. This suggests that in the $\text{C}_2\text{H}_5\text{OH}$ cluster experiment, wherein the H atom in the C_2H_5 group is eliminated, the ion at $m/z = 45$ is $\text{C}_2\text{H}_4\text{OH}^+$. As suggested in Introduction, the formation of H_3O^+ in ethanol clusters yields a crucial hint, because the formation of H_3O^+ is not expected from a

simple hydrogen-bonding interaction model for alcohol. The present isotope experiment thus suggests that the third H atom does not originate from the OH group of the third ethanol but from the C₂H₅ group as a result of the migration of an H atom. The significant formation of C₂H₄OH⁺, as confirmed by the isotope experiment, appears to be consistent with this mechanism. In this connection, preliminary photoelectron-photoion-photoion coincidence (PEPIPICO) spectra that we have observed recently show that one of the major products coincident with H₃O⁺ is C₂H₅O⁺.

3.3. Hydrogen atom migration

The migration of H atom has been observed in molecular ethanol. In the effusive beam measurement, significantly intense signals corresponding to H₂⁺, H₃⁺ and H₂O⁺ were observed, as shown in Fig. 2b. Hempelmann et al. reported similar rearrangement products for methanol and ascribed them to the high mobility of the H atoms [4]. Therefore, the formation of H₃O⁺ in ethanol clusters could be attributed to the concerted process of the abstraction of H in the O-H--OH type hydrogen bonding and the migration of the H atom from the C₂H₅ group. However, it was observed under the supersonic beam condition that the intensity of the signal corresponding to H₃O⁺ was considerably higher than that of the H₂O⁺ signal. Since the intensity of the signal corresponding to H₂O⁺ obtained under the effusive beam condition indicates the extent of the migration of H atom from the C₂H₅ group, the higher intensity of the H₃O⁺ signal suggests that more H atoms migrate from the C₂H₅

group. The TOF spectra of methanol measured under supersonic beam condition, i.e., the cluster-forming condition, are compared with those of the ethanol cluster in Fig. 4. In the case of methanol clusters (Fig. 4a) no signals corresponding to H_3O^+ were observed and only weak signals corresponding to H_2O^+ could be seen. This result suggests that the migration of H atom is ineffective in the methanol molecule or ethanol clusters. However, the H migration proceeds quite efficiently in the ethanol clusters as compared with that in methanol.

3.4. Internal rearrangement in ethanol clusters

The efficient rearrangement in the ethanol clusters can be ascribed to their structure. In a recent study, Dyczmons suggested the importance of the C-H--OH type hydrogen bonding as well as the O-H--HO type in ethanol dimers [19]. According to his theoretical study, relatively strong hydrogen bonding (O-H--OH) determines the distance between the molecules and the HO-H angle of the cluster, and one or two weak hydrogen bonds (C-H--OH) exist in the cluster. The conformational angles of the cluster was also determined; the distance between terminal CH_3 and O atom can be appreciably shortened as the alkyl chain - methyl to ethyl - length is increased.

It is observed in the present study that the clusters contain dimers and larger clusters, as shown in Fig. 1. Therefore, further explanation is required for larger clusters whose structures are yet unclear. Vibrational excitation may also be an important factor that needs

further consideration. The equilibrium geometries determined by a theoretical study can be distorted prior to the fragmentation, and this may enhance rearrangement reactions. Since the formation of H_3O^+ has not been observed in the outer-shell electron ionization, a multiple-charged intermediate resulting from the inner-shell electron excitation is expected to play an important role. One of the possible experimental approaches to study this phenomenon is the measurement of photoelectron-photoion-photoion coincidence spectra for ethanol clusters.

4. Summary

The H_3O^+ formation process has been studied for the soft X-ray photofragmentation of ethanol molecules and its clusters. The rearrangement reaction to form H_3O^+ has been observed only in ethanol clusters, in sharp contrast with methanol clusters. The study of $\text{C}_2\text{H}_5\text{OD}$ suggests the importance of not only the O-H--OH type hydrogen bond as well as the H migration from the C_2H_5 group in this reaction. The efficient H migration in ethanol clusters is consistent with the presence of C-H--OH type hydrogen bonding suggested in a theoretical study. The interaction of H in C_2H_5 with OH can be attributed to the longer alkyl chain in the cluster.

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Figure captions

- Fig. 1. TOF mass spectra of fragment ions obtained under the (a) seeded supersonic (He, 4 atm) and (b) effusive beam conditions. The excitation energy was 545.0 eV (higher than the ionization threshold). The spectra was obtained using the photoelectron-photoion coincidence method and converted to the TOF mass spectra.
- Fig. 2. Spectra similar to that shown in Fig. 1 with the spectral range of $m/z = 1-50$ expanded.
- Fig. 3. TOF mass spectra of fragment ions obtained under the supersonic beam condition (He, 4 atm): (a) C_2H_5OD and (b) C_2H_5OH .
- Fig. 4. Comparison between the TOF mass spectra of (a) methanol and (b) ethanol measured under the supersonic beam condition (He, 4 atm).

Figure 1

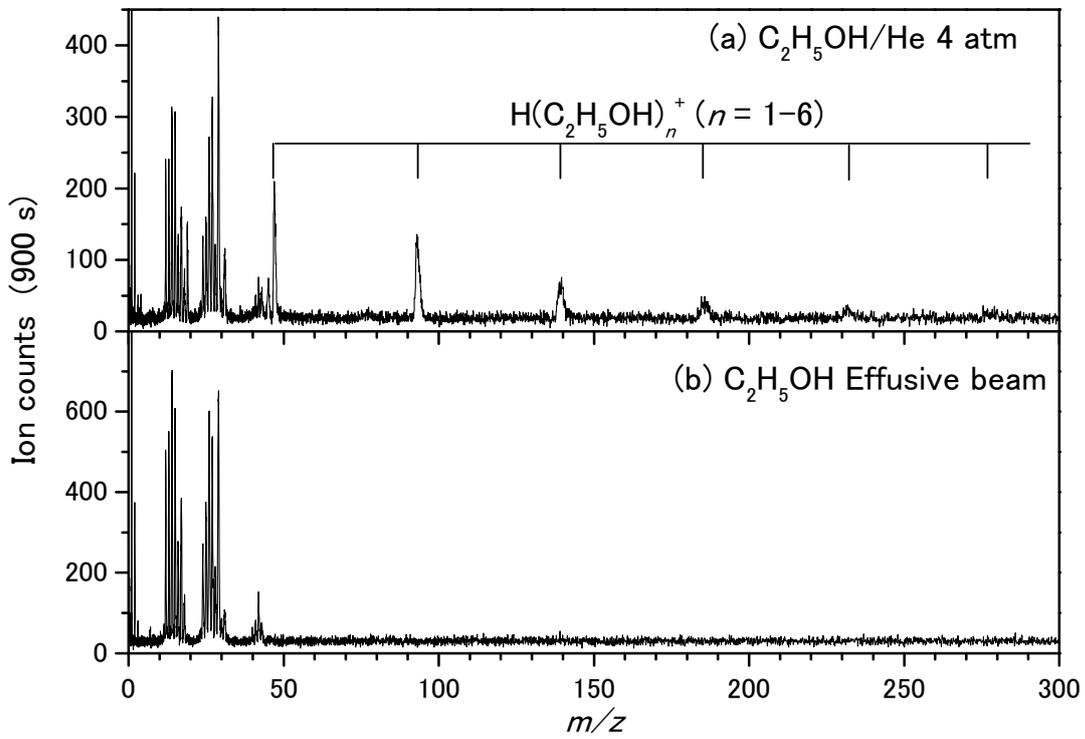


Figure 2

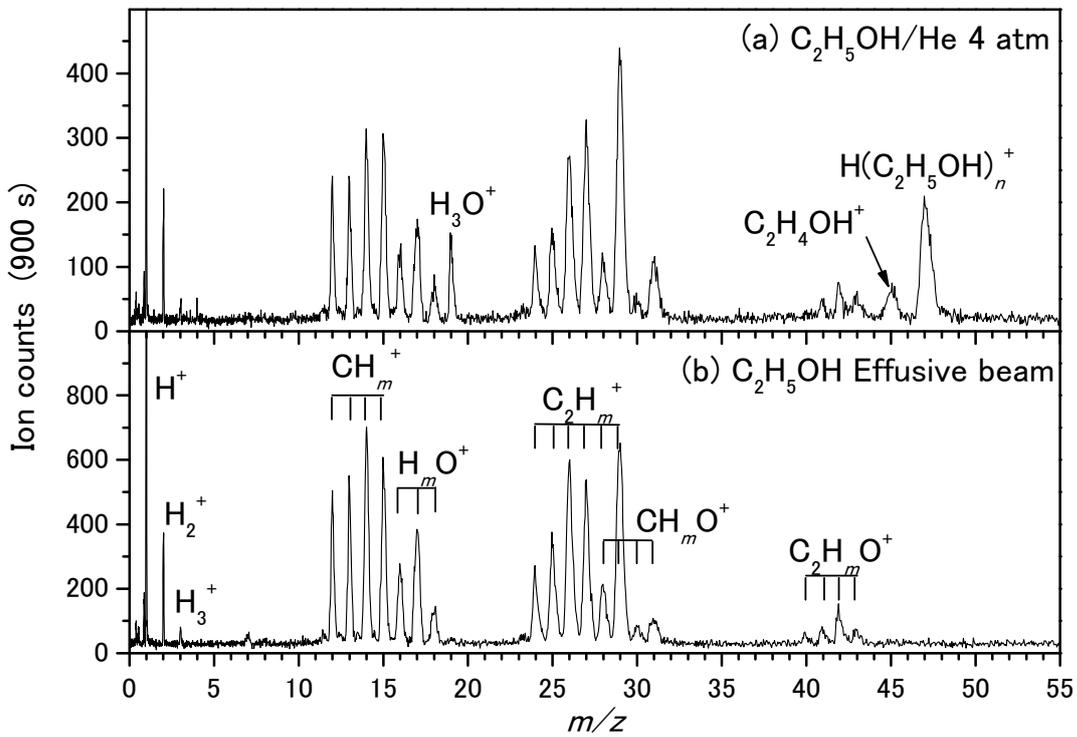


Figure 3

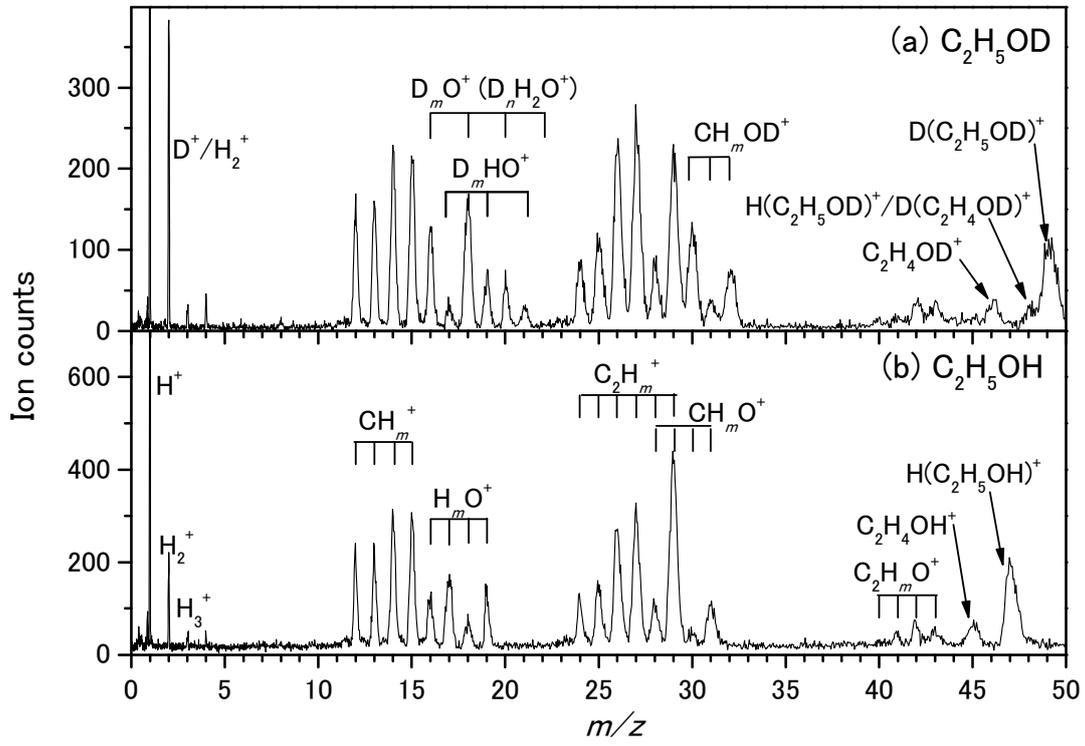
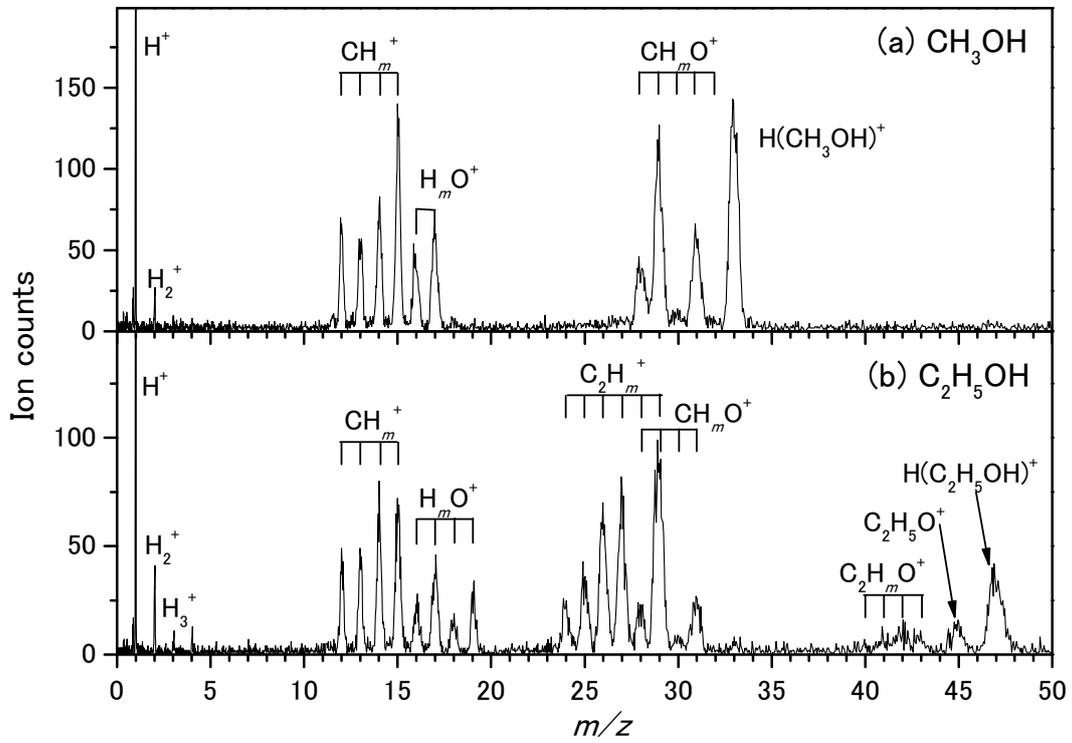


Figure 4



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