Research Article

Formation of H₃O⁺ in the Ionization and Fragmentation of Ethanol Induced by Electron Beam Irradiation

Chao Ma, ¹ Jiaqi Zhou, ¹,2 Enliang Wang, ²,3 Tao Yang, ¹ Zhongfeng Xu, ¹ Shaokui Jia, ¹ Alexander Dorn, ² and Xueguang Ren ¹,2

¹MOE Key Laboratory for Nonequilibrium Synthesis and Modulation of Condensed Matter, School of Physics, Xi’an Jiaotong University, Xi’an 710049, China
²Max-Planck-Institut für Kernphysik, Saupfercheckweg 1, Heidelberg 69117, Germany
³J. R. Macdonald Laboratory, Department of Physics, Kansas State University, Manhattan, Kansas 66506, USA

Correspondence should be addressed to Zhongfeng Xu; zhfxu@mail.xjtu.edu.cn and Xueguang Ren; renxueguang@xjtu.edu.cn

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The single ionization and dissociation of ethanol molecules induced by low-energy electrons (E₀ = 90 eV) are investigated using multiparticle coincident momentum spectroscopy. By detecting two outgoing electrons (e₁ and e₂) and one fragment ion in coincidence, we obtain the energy deposition (E₀ − E₁ − E₂) during electron ionization of the molecule, i.e., the binding energy spectra, for production of the different ionic fragments C₂H₅OH⁺, C₂H₄OH⁺, COH⁺, and H₃O⁺. These data allow us to study the ionization channels for different ionic products. In particular, we focus on H₃O⁺ as a product of double hydrogen migration. It is found that this channel mainly originates from the ionization of outer-valance orbitals (3a″, 10a′, 2a″, 9a′, 8a′, 1a″, and 7a′). Additionally, there are minor contributions from the inner-valence orbitals such as 6a′, 5a′, and 4a′. Quantum chemistry calculations show two fragmentation pathways: concerted and sequential processes for formation of H₃O⁺.

1. Introduction

Particle beam and laser-induced ionization and fragmentation of molecules have attracted considerable interest for several decades [1–22]. Hydrogen or proton migration is a widely existing phenomenon during these processes, and it plays a vital role in various fields of physics, chemistry, and biology [1, 2, 7, 19, 20]. In particular, for small organic molecules [3–5] or molecular complexes [6–8], the isomerization process induced by intra- and intermolecular hydrogen transfer has been extensively studied due to its high relevance, e.g., in biological processes such as in DNA mutations [9, 10]. The ultrafast hydrogen migration can unlock new dissociation channels, such as hydrogen exchange [11], scrambling [12], and roaming [13, 14]. Recent studies showed that it can also stabilize the repulsive potential energy surface of dications before the direct Coulomb explosion occurs [15].

The ethanol molecule (C₆H₁₂O₆) contains both hydroxyl and methyl groups and is widely applied in the chemical industry as an important solvent. C₆H₁₂O₆ has attracted significant interest for studying hydrogen migration due to the relatively large number of hydrogen atoms bound to the various sites in the C-C-O skeleton. Here, of particular interest is the double hydrogen migration [23–26], forming a H₃O⁺ hydronium ion, which is central in acid-catalyzed reactions as the active protonating agent. Nevertheless, the understanding of the double H migration is incomplete since it is a rather complex process involving more than one C-H bond cleavage and at least two O-H bond formations.

H₃O⁺ formation has been studied by Raalte and Harrison in an electron impact ionization experiment with deuterated ethanol. Two reaction pathways were proposed, i.e., a concerted path and a sequential fragmentation path. For the concerted path, the two hydrogen migration directly follows single ionization of ethanol, while the sequential path
proceeds via the intermediate C₃H₄OH⁺ cation where initially hydrogen is abstracted and hydrogen migration occurs subsequently [23]. Later on, Niwa et al. performed an experiment on ethanol using the photodissociation technique (PEPICO) technique. By analyzing the breakdown diagrams and appearance energies (AE) for the different fragment ions, they concluded that H₂O⁺ was mainly formed by the sequential fragmentation [24]. Further studies using the time of flight (TOF) spectra and the quantum chemical calculations confirmed that the sequential process is the dominant pathway for the formation of H₂O⁺ in ethanol [25, 26].

In this work, we study the ionization and dissociation of ethanol irradiated by low-energy electrons using an (e, 2e + ion) method [27–30] in which all three final-state particles are detected in coincidence. We use the projectile energy of 90 eV, which is close to the mean energy of secondary electrons produced by high-energy primary radiation, such as X-rays, α-rays, γ-rays, fast electron, and ion beams [31]. Here, the momentum vectors and, consequently, kinetic energies of the outgoing electrons (scattered and ejected electrons) and fragment ions are determined. The contributions of different ionized orbitals for formations of C₂H₂OH⁺, C₂H₂OH⁺, COH⁺, and H₂O⁺ cations are obtained by measuring the energy deposition in the ionization process, i.e., the binding energy (BE) spectra. The BE is defined as the energy difference between the initial projectile electron energy E₀ and the energy sum of the scattered (Eₛ) and ejected (Eₑ) electrons: BE = E₀ − (Eₛ + Eₑ). The BE resolution of ∆E_{BE} = 3.7 eV, full width of half maximum (FWHM), has been achieved with a measurement on the ionization of helium. For ethanol, there are two conformers assigned as the trans and the gauche structures where the main difference is the dihedral angle between the hydroxyl and the carbon skeleton. Here, we consider the trans conformer with C₂ symmetry as the geometric structure of ethanol [32]. The ground-state electronic structure of the valence shell can be expressed as (4a¹⁻)² (5a¹⁻)² (5a¹⁻)² (6a¹⁻)² (7a¹⁻)² (1a³⁺)² (8a³⁺)² (8a³⁺)² (2a¹⁻)² (10a¹⁻)² (10a¹⁻)² (3a³⁻)².

2. Experiment

The experiment was performed using the multiparticle coincidence momentum spectrometer (reaction microscope) combined with a pulsed electron beam [33]. The details of the experimental setup can be found in the earlier work [27, 34]; thus, only a brief introduction is given here. A well-focused (about 1 mm in diameter) electron beam with an energy of 90 eV is crossed with an ethanol gas jet. The projectile electron beam is emitted from an electron gun in which a tantalum photocathode is irradiated by a pulsed ultraviolet laser beam. The wavelength, repetition rate, and pulse width of the laser beam are 266 nm, 40 kHz, and 0.5 ns, respectively. The energy per pulse of the laser is about 1 eV, and the flux of the projectile electron is about 5 nA/cm². The data accumulation time is about 100 hours for the present work. The gas jet is generated by the supersonic gas expansion of He (1 bar) with seeded ethanol vapor through a nozzle with a diameter of 30 μm and a two-stage differential pumping system. The ethanol gas was produced through the reservoir including the liquid ethanol at room temperature. The supersonic beam was collimated by two sequential skimmers (250 μm and 400 μm diameter, respectively) and transmitted into the reaction area of the main chamber. After traversing the jet, the nonscattered electron beam is guided into the central hole of the electron detector as a beam dump. The charged particles in the final state (two electrons and one ion) are extracted and guided by homogeneous electric and magnetic fields towards two-dimensional position- and time-sensitive microchannel plate detectors. Three-dimensional momentum vectors of the detected particles are determined from the time-of-flight and positions of the particles hitting the detectors. The ionization process can be expressed as follows:

\[
e^- + CH₃CH₂OH \rightarrow CH₃CH₂OH⁺ + 2e^- (1)
\]

3. Quantum Chemistry Calculations

The theoretical calculations are performed utilizing the Gaussian quantum chemistry package [35]. The ground-state equilibrium geometries of the singly charged ethanol molecule, the transition states (TSs), and intermediates (INTs) are optimized by the M06-2X method with the def2TZVP basis set. The zero-point energy (ZPE) correction is acquired by the M06-2X method with the def2TZVP basis set, and the electronic energy was calculated by employing the coupled-cluster single-double and perturbative triple (CCSD(T)) method with the aug-cc-pVQZ basis set. The validity of reaction pathways is confirmed by the NBO population and the intrinsic reaction coordinate (IRC) analysis which is carried out at the M06-2X/def2TZVP level.

4. Results and Discussion

The BE spectra for the formation of the C₂H₄OH⁺ parent ion and C₃H₄OH⁺ with H-loss are presented in Figure 1. The experimental data for C₂H₄OH⁺ correspond to a single peak located at about 10.8 eV, which is consistent with the ionization energy of the highest occupied molecular orbital (HOMO) of ethanol [32]. This result indicates that the C₂H₄OH⁺ parent ion is formed through the HOMO ionization, i.e., the 3a³⁻ orbital of the trans conformer [32]. For the H-loss channel, i.e., the C₂H₄OH⁺ cation, the measured BE spectrum shows a single peak located at about 12.6 eV which can be attributed to the ionization of the HOMO-1 (10a¹⁻) plus some amount of the internal energy (∼0.5 eV), leading to the subsequent H-loss.

Figure 2 presents the binding energy spectrum for the fragment ion with a mass-to-charge (m/z) ratio of 29 u. Due to the m/z degeneracy for COH⁺ and C₂H₃⁺, we are unable to distinguish them in our experiment. Hudson and McAdoo obtained the appearance energies (AE) of about 14.2 eV for COH⁺ and 12.7 eV for C₂H₃⁺ [24] by comparing the breakdown curves for C₂H₄OH⁺ and C₂D₄OD⁺. The present experimental data show a peak structure centered at about 15.3 eV and a shoulder structure at higher BE, and thus, we assigned the ionic product with 29 u to COH⁺ through the pathway of C-C bond breaking and two.
hydrogen loss from the C site [24]. The BE spectrum indicates that the ionization of several valence orbitals leads to the formation of COH +. The main peak located at 15.3 eV corresponds to ionization of 10a ′, 2a ″, 9a ′, 8a ′, 1a ″, and 7a ′ orbitals which cannot be resolved energetically. Additionally, ionization of inner-valence orbitals (6a ′, 5a ′, and 4a ′) can also contribute to the formation of COH +. We determine the branching ratios of about 55% and 45% for outer-valence and inner-valence ionization, respectively. It is also to be noted that the measured peaks at higher BE, e.g., 35.8 eV, may result also from the ionization plus excitation or from multiple scattering within ethanol clusters [36].

Concerning the production pathway of COH +, Hudson and McAdoo theoretically demonstrated a sequential process involving the H migration. First, a neutral H is ejected, and in the second step, the hydrogen transfers from hydroxyl to the methyl group, and then, the C α-C? bond breaks with the ejection of neutral methane [26]. The reaction process is expressed as follows:

\[
\text{CH}_3\text{CH}_2\text{OH}^+ \rightarrow \text{CH}_3\text{CHOH}^+ + \text{H}
\]

\[
\text{CH}_3\text{CHOH}^+ \rightarrow \text{CHO}^+ + \text{CH}_4
\]

It is considered that the CHO + production with H migration and the COH + formation without H migration are both involved in our experiment. The fragmentation channels induced by the ionization of inner-valence orbitals (6a ′, 5a ′, and 4a ′) may be concerned with the CHO + formation due to the higher deposited energy supporting for H migration. We notice that the formation of CHO + through hydrogen transfer from oxygen to carbon is different from the widely studied H migration process in ethanol where the migrated H is originated from carbon and moves to the oxygen side [15, 23–25].

The measured BE spectrum for the formation of H 3O + is presented in Figure 3, which exhibits a single-peak structure centered at about 15.1 eV and a tail structure at higher BE. The peak at BE ~15.1 eV can be attributed to the ionization of 10a ′, 2a ″, 9a ′, 8a ′, 1a ″, and 7a ′ orbitals which cannot be resolved energetically. Additionally, ionization of inner-valence orbitals (6a ′, 5a ′, and 4a ′) can also contribute to the formation of COH +. We determine the branching ratios of about 55% and 45% for outer-valence and inner-valence ionization, respectively. It is also to be noted that the measured peaks at higher BE, e.g., 35.8 eV, may result also from the ionization plus excitation or from multiple scattering within ethanol clusters [36].

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\]
the formation of $H_3O^+$ is dominated by the sequential process via the intermediate $CH_3CHOH^+$ cation. In the first step, one $C_\alpha$-H bond breaks and neutral hydrogen is ejected. After that, the fragmentation of $CH_3CHOH^+$ produces $H_3O^+$. The reaction process is expressed as follows:

$$CH_3CHOH^+ \rightarrow H_3O^+ + C_2H_2 \text{ (3) }$$

A theoretical work [26] demonstrated a reaction pathway where the two $H$ which migrate to form $H_2O^+$ originate from the methyl site and sequentially transfer to the hydroxyl site. On the other hand, recent experiments on deuterated ethanol showed a complete scrambling of the four hydrogens at the C-C site before migration to the hydroxyl site [25]. This is in agreement with an earlier study for deuterated $CH_3CD_2OH$ which mainly shows yields of $H_3O^+$ and $H_2DO^+$ in accordance with that expected for a $CH_3CDOH^+$ intermediate [23]. In addition, a small yield of $HD_2O^+$ shows that also the direct concerted fragmentation pathway contributes where both $H$ from the $C_\alpha$ site migrate:

$$CH_3CH_2OH^+ \rightarrow C_2H_3 + H_3O^+ \text{ (4) }$$

To trace the complete reaction pathways of double $H$ migration processes, we performed quantum chemical calculations for $H_3O^+$ formation in both concerted and sequential ways. The potential energy diagrams are shown in Figure 4 which exhibits the reaction pathways with transition states (TS1 and TS2) and intermediate states (INT1 and INT2). In Figure 4, the energy values are relative to the ionic ground state of $CH_3CH_2OH^+$, which is marked by 0.0 eV in Figure 4(a). The single point energy is calculated at the CCSD(T)/aug-cc-pVQZ level including the zero-point vibrational energy corrections. The reaction pathways are confirmed by the intrinsic reaction coordinate (IRC) calculation. The black, blue, and red balls represent carbon, hydrogen, and oxygen atoms, respectively.
process, higher internal energy is needed to overcome the potential barrier (TS1: 3.28 eV) in comparison with the concerted pathway (TS1: 1.05 eV). From this point of view, the concerted pathway is more accessible. However, fast H-loss channel is expected due to its lower energy barrier (0.40 eV). This can cause the observed dominance of the sequential process [23]. Nevertheless, future studies in both experiment and theory are required to unambiguously identify the concerted pathway.

5. Conclusions

We have presented results from the first (e, 2e + ion) study of the ionization-induced dissociation of ethanol induced by low-energy electron impact (90 eV). A multiparticle coincidence momentum spectrometer is used in which all three charged final-state particles, i.e., two outgoing electrons and one fragment ion, are detected in triple coincidence. The momenta and, consequently, the kinetic energies of all three final-state particles are obtained through the measurement of their TOFs and hit positions. We determine the binding energy (BE) spectra correlated with different ionic fragments, i.e., the parent ion C\textsubscript{2}H\textsubscript{5}OH\textsuperscript{+}, the H-loss channel C\textsubscript{2}H\textsubscript{4}OH\textsuperscript{+}, and the hydrogen migration channels of COH\textsuperscript{+} and H\textsubscript{2}O\textsuperscript{+} cations.

The present results confirm that the nondissociated C\textsubscript{2}H\textsubscript{5}OH\textsuperscript{+} ion product arises due to the HOMO (3a\textsuperscript{″}) orbital ionization, which is consistent with the results of previous appearance energy studies. The BE spectrum for the H-loss channel reveals a single-peak (12.6 eV) structure which can be assigned to the HOMO-1 (10a\textsuperscript{″}) orbital ionization. While for COH\textsuperscript{+} product, both the outer-valence (10a\textsuperscript{′}, 2a\textsuperscript{″}, 9a\textsuperscript{′}, 8a\textsuperscript{′}, 1a\textsuperscript{″}, and 7a\textsuperscript{″}) and inner-valence (6a\textsuperscript{′}, 5a\textsuperscript{′}, and 4a\textsuperscript{′}) orbital ionizations are observed from the measured BE spectrum. The BE spectrum for H\textsubscript{2}O\textsuperscript{+} product shows the similar feature in which the outer-valence (3a\textsuperscript{″}, 10a\textsuperscript{′}, 2a\textsuperscript{″}, 9a\textsuperscript{′}, 8a\textsuperscript{′}, 1a\textsuperscript{″}, and 7a\textsuperscript{″}) and inner-valence (6a\textsuperscript{′}, 5a\textsuperscript{′}, and 4a\textsuperscript{′}) orbital ionizations are involved. For the formation of H\textsubscript{2}O\textsuperscript{+} through double H migration, two fragmentation pathways (concerted and sequential processes) are identified using quantum chemistry calculations. The higher BE peaks can also result from the ionization plus excitation or from multiple scattering of the projectile in ethanol clusters. The present study can have implications for a better understanding of the ionization-induced isomerization mechanisms of molecules.

Data Availability

The experimental data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that there is no conflict of interest regarding the publication of this paper.

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