

# Determination of active sites for H atom rearrangement in dissociative ionization of ethanol

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In an electron impact dissociative ionization experiment on  $C_2H_5OH$ , the formation of molecular ions requiring rearrangement of H atoms has been studied using a momentum spectrometer.  $H_3^+$ ,  $H_2^+$ ,  $HOH^+$ , and  $H_2OH^+$  observed in the experiment are molecular ions of this type. By comparing the mass spectrum of  $C_2H_5OH$  with that of its isotopomer  $C_2H_5OD$ , we determine the proportions of H-bond rearrangements involving carbon and oxygen sites. We find that the formation of  $H_3^+$  due to the breaking of the O-H bond and rearrangement of the H atoms on the  $CH_2$  site is about 2.5 times as likely as its formation involving atoms from the  $CH_3$  site alone. No such difference is seen in case of the  $H_2^+$  ion. The role of the O-H bond in formation of all observed ions has been assessed. Kinetic energy distributions of the molecular ions suggest that two or three electronically excited states contribute to their formation. © 2006 American Institute of Physics. [DOI: 10.1063/1.2234773]

## I. INTRODUCTION

Small molecules, such as alcohols, have often attracted attention of chemists and atomic physicists. Several spectroscopic and collisional studies, under a variety of excitation schemes, have been made. Partial cross sections for dissociative ionization of methanol and ethanol by electron impact have been measured by Duric *et al.*, Srivastava *et al.*, and Rejoub *et al.*<sup>1-3</sup> Beyond cross-section measurements are more interesting issues, such as the formation of molecular ions involving nonintuitive bond rearrangements.

The formation of  $H_2^+$  from  $CH_3OH$ ,  $C_2H_5OH$ , and  $C_3H_7OH$  by electron impact has been reported earlier by Rejoub *et al.*<sup>3</sup> Krishnamurthy *et al.* have reported and explained the formation of  $H_2^+$  ions in several alcohols by intense laser fields.<sup>4</sup> The observation of  $H_3^+$  from  $CH_3OH$  by photoabsorption has been reported by Ruhl *et al.*<sup>5</sup> The rates for rearrangement leading to  $H_3^+$  have been studied by Furukawa *et al.* in an experiment on  $CH_3OH$  in intense laser fields.<sup>6</sup> Another group of ions, viz.,  $HOH^+$  and  $H_2OH^+$ , from  $CH_3OH$ ,  $C_2H_5OH$ , and  $C_3H_7OH$  by electron impact have been observed by Rejoub *et al.*<sup>3</sup>

All ions mentioned here can only be formed by breaking of bonds between the H and skeletal C or O atoms followed by association of the H atoms or ions. Questions such as—are all bonds equally active in this rearrangement? which excited states are responsible for the observed fragment ions?—are pertinent to a better understanding of the formation of these unusual ions. We present here an attempt to answer these questions based on a combination of three techniques: ion momentum spectroscopy, ion-pair detection, and the use of isotopically altered, but electronically identical molecules. The process studied is dissociative ionization of  $C_2H_5OH$  upon 1300 eV electron impact. Four molecular

ions, namely,  $H_2^+$ ,  $H_3^+$ ,  $HOH^+$ , and  $H_2OH^+$ , have been studied. A comparative experiment was performed with  $C_2H_5OD$ .

## II. EXPERIMENTAL SETUP

The apparatus consists of a beam of target molecules crossed with an electron beam, and a momentum spectrometer, details of which can be found in Ref. 7. The beam of molecules was generated by effusion of alcohol vapor through a fine stainless steel capillary (0.15 mm inner diameter and 12 mm length). The alcohols were first purified by fractional distillation to remove traces of air and water contaminations in the target. The stagnation pressure behind the capillary was approximately 0.3 mbar, and the alcohol reservoir and delivery lines were maintained at room temperature. The mean free path of the molecules was about 2 mm, which is over ten times the capillary diameter. Under these circumstances clustering of molecules was unlikely. The target number density was  $10^{12} \text{ cm}^{-3}$ , with an interaction volume of  $2 \text{ mm}^3$ . The electron energy is kept fixed at 1300 eV. The momentum spectrometer is primarily a single field time-of-flight spectrometer with a large area multihit position-sensitive detector. Ions formed in the interaction region are extracted by a homogeneous electric field of magnitude 60 V/cm and subsequently detected by the position-sensitive detector. Electrons are extracted in the opposite direction and detected by a channel plate. Time of flight of ions is determined by an electron-ion coincidence and recorded by a multistop time-to-digital convertor. The timing and position data are written event-by-event into a list mode file. The flight time ( $t$ ) and the position ( $x, y$ ) of each ion in an event can be transformed into three momentum components ( $p_z, p_x, p_y$ ), respectively. The momentum, and hence the kinetic energy, distributions are obtained *post facto* from the event list.

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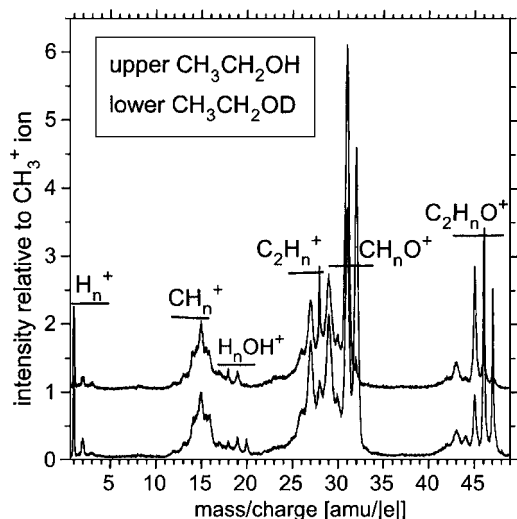


FIG. 1. Time-of-flight (TOF) spectrum of  $C_2H_5OH$  and  $C_2H_5OD$  under 1300 eV electron impact. The  $C_2H_5OH$  spectrum has been shifted by one unit along the intensity axis for clarity.

### III. CLASSIFICATION OF IONS IN THE MASS SPECTRUM

The time-of-flight spectra of ions from  $C_2H_5OH$  and  $C_2H_5OD$  were calibrated in terms of  $m/q$ , and are shown in Fig. 1. Twenty-two and 26 ions are seen in the two cases, respectively. The peaks at  $m/q=28, 32$  in the  $C_2H_5OH$  spectrum are due to air contamination, but these do not affect the analysis. The peak at  $m/q=47$  is the combined effect of natural fractions of isotopes of H, C, and O in  $C_2H_5OH$ . Corrections due to this have been taken into account in the analysis.

The spectra are normalized to the peak height of the methyl ion ( $CH_3^+$ ). The choice is based on the fact that this is an ion which can arise from a unique site, not involving the isotopically substituted bond. Thus, the intensity of all site-dependent fragments would be correctly represented with this normalization. We have verified that this normalization matches that with the total ion yield. It is obvious that differences in intensities of mass peaks point to reactions that involve the O–D bond.

The optimized structure of  $C_2H_5OH$  and  $C_2H_5OD$  is shown in Fig. 2. The structure suggests that there would be some fragments involving only the peripheral H atoms and some involving one or more of the skeletal C and O atoms. This, combined with the identification of the masses in the spectra, suggests that the whole spectrum can be logically

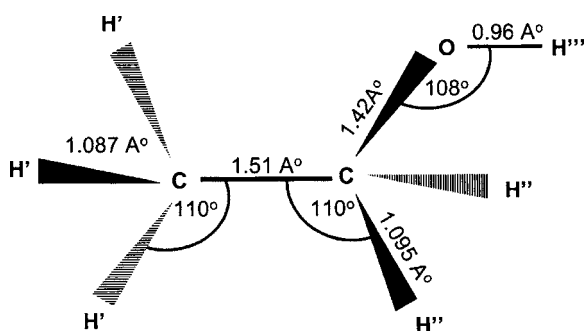


FIG. 2. Structure of  $C_2H_5OA$ ;  $A=H,D$ .

divided into six groups, namely, the  $H_n^+$ ,  $CH_n^+$ ,  $H_nOH^+$ ,  $C_2H_n^+$ ,  $COH_n^+$ , and  $C_2OH_n^+$  groups. This nomenclature is correct only in the case of  $C_2H_5OH$ . In the case of  $C_2H_5OD$ , there will be additional peaks, which are not reflected in this nomenclature. In both cases the peak at  $CH_2OA^+$ , where  $A$  is H or D, is the most intense.

Among the ion groups listed, the groups  $H_n^+$  and  $H_nOH^+$  involve rearrangements of H–bonds, while the others do not. We analyze the two categories separately.

#### A. Ions not requiring rearrangement of H–bonds

##### 1. The $CH_n^+$ group

The relative intensities of  $CH_n^+$  ion for a given  $n$  are equal for  $C_2H_5OH$  and  $C_2H_5OD$ . Thus the O–A bond is not relevant to the formation of ions in this group.

##### 2. $C_2H_n^+$ group

Peaks at mass 24, 25, 26, and 27 are assigned to the  $C_2^+$ ,  $C_2H^+$ ,  $C_2H_2^+$ , and  $C_2H_3^+$  ions, respectively. Mass 28 cannot be assigned to a single species, it could be either  $CO^+$  or  $C_2H_4^+$ . The peaks in this group are identical for the two molecules (barring contamination due to  $N_2^+$ ). Thus, formation of these ions does not require breaking of the O–A bond.

##### 3. $CH_nO^+$ group

This group ranges from mass 29 to 31 in case of  $C_2H_5OH$  and up to 32 in case of  $C_2H_5OD$ . Three ions, viz.,  $CH_3CH_2^+$ ,  $CH-O^+$ , and  $C-OH^+$  have mass 29. For the case of  $C_2H_5OD$ , the  $C-OD^+$  ion would appear at mass 30. This peak is seen in the spectrum, suggesting that  $C-OH^+$  is indeed formed from  $C_2H_5OH$ . However, it is not possible to rule out or confirm the formation of the two other ions. A scheme on the lines of that adopted for the  $H_n^+$  group may shed some light on this. For the scheme to succeed, it is necessary to determine the intensity of each peak accurately. However, broad mass peaks in this group preclude the possibility at the moment. The presence of the contaminant  $O_2^+$  peak would further hamper the attempt. Masses 31 and 32 are exclusively assigned to  $CH_2OA^+$ .

##### 4. The $C_2H_nO^+$ group

In case of  $C_2H_5OH$ , three structurally different ions, viz.,  $CH_3CH_2O^+$ ,  $CH_3CHOA^+$ , and  $CH_2CH_2OA^+$  appear at the same  $m/q$ , but in case of  $C_2H_5OD$ , the  $CH_3CHOA^+$  and  $CH_2CH_2OA^+$  ions would appear at  $m/q=46$ . The ratio of the intensity of the peak corresponding to loss of one H atom to the intensity of the parent ion is the same in both molecules. (This fact is not obvious from the peak heights in the mass spectrum, due to differing peak widths.) This indicates that only C–H bonds, and not the O–A bond, are broken in processes involving loss of a single H atom.

#### B. Ions requiring rearrangement of H–bonds

##### 1. The $H_n^+$ group

The  $C_2H_5OH$  spectrum has peaks at  $m/q=1,2,3$  corresponding to  $H^+$ ,  $H_2^+$ , and  $H_3^+$ , respectively. The  $C_2H_5OD$  spectrum, on the other hand, has peaks at  $m/q=1,2,3,4$

corresponding to  $H^+$ ,  $H_2^+$  or  $D^+$ ,  $H_3^+$  or  $HD^+$ , and  $H_2D^+$ , respectively. The comparison tells us that the formation of  $H_2^+$  or  $H_3^+$  from  $C_2H_5OH$  involves a rearrangement necessitating the breaking of the O–H bond.

To calculate the site-specific probability of formation of  $H_n^+$  ions, we proceed as follows. We assume that the sum of the normalized intensities of the peaks  $m/q=1, \dots, 3$  in case of  $C_2H_5OH$  equals the sum for  $m/q=1, \dots, 4$  in the case of  $C_2H_5OD$ . In other words, we assume that the sum of the cross sections for rearrangements involving the peripheral H (or D) bonds is the same for the two molecules. This is justified because the differences in vibrational energy levels between the two isotopomers are much smaller than the typical energy transfer during dissociative ionization at high impact energies. The sum of the intensities of all ions in this group is arbitrarily set to 1, and the intensity of each peak is renormalized to this sum.

We denote the contribution to the intensity of  $H_n^+$  due to rearrangement of the H–bonds on the  $CH_3$ ,  $CH_2$ , and OH sites by symbols with a prime, double prime, and triple prime, respectively. The symbol  $p$  is used for  $C_2H_5OH$  and  $P$  for  $C_2H_5OD$ , respectively. A rearrangement involving primed atoms alone is considered, as is one involving double and triple primed atoms together, but those involving primed and triple primed atoms or primed and double primed atoms are neglected. This scheme is justified on the grounds that the C–C bond is the longest and the  $H'$  atoms are far apart from the  $H''$  and  $H'''$  atoms. We get seven simultaneous equations which determine the site-specific probabilities for this group of ions. These are written below:

$$p_1 = 0.694 \pm 0.004 = 3p_{H'} + 2p_{H''} + p_{H'''}, \quad (1a)$$

$$p_2 = 0.189 \pm 0.001 = 3p_{H'H'} + p_{H''H''} + 2p_{H''H'''}, \quad (1b)$$

$$p_3 = 0.117 \pm 0.001 = p_{H'H'H'} + p_{H''H''H'''}, \quad (1c)$$

$$P_1 = 0.601 \pm 0.002 = 3P_{H'} + 2P_{H''}, \quad (2a)$$

$$P_2 = 0.216 \pm 0.001 = 3P_{H'H'} + P_{H''H''} + P_D, \quad (2b)$$

$$P_3 = 0.102 \pm 0.001 = P_{H'H'H'} + 2P_{H''D}, \quad (2c)$$

$$P_4 = 0.081 \pm 0.001 = P_{H''H''D}. \quad (2d)$$

We further assume that

$$p_{H'} = p_{H''} = P_{H'} = P_{H''}, \quad (3a)$$

$$p_{H'H'} = p_{H''H''} = P_{H'H'} = P_{H''H''}, \quad (3b)$$

$$p_{H'H'H'} = P_{H'H'H'}, \quad (3c)$$

$$p_{H''H''H'''} = P_{H''H''D}. \quad (3d)$$

The error in the probabilities is the net error due to statistical uncertainty and error in determining the base line of the mass peak. Solving these equations, we find that  $H^+$  formation has  $86 \pm 0.3\%$  contribution from the five C-sited bonds and  $14 \pm 0.3\%$  from the O-sited bond. The contribution to  $H_2^+$

from rearrangement of the bonds at the  $CH_3$  site is  $49 \pm 2\%$  and due to rearrangement of bonds at the  $CH_2$  and OH sites is  $51 \pm 2\%$ . Similarly,  $30 \pm 4\%$  of the  $H_3^+$  intensity is due to rearrangement of the bonds at the  $CH_3$  site, while  $70 \pm 4\%$  is due to the  $CH_2$  and OH sites together. The last result is surprising, because it implies a large probability of breaking of the strong O–H bond. This result may be compared with the formation of  $H_3^+$  by photoionization of  $CH_3OH$ , for which Ruhl *et al.* have reported rearrangement involving the O–H bond to be thrice as likely as the one not involving the O–H bond.<sup>5</sup>

## 2. The $H_nOH^+$ group

The peaks at masses 18 and 19 for the case of  $C_2H_5OH$  and the peaks at masses 19 and 20 for the case of  $C_2H_5OD$  confirm formation of  $HOA^+$  and  $H_2OA^+$  ions. As in case of the  $H_n^+$  group, the formation of these ions necessitate rearrangement of H–bond. The normalized intensity of  $HOH^+$  from  $C_2H_5OH$  equals that of  $HOD^+$  from  $C_2H_5OD$ . Similarly the intensities of  $H_2OH^+$  in  $C_2H_5OH$  and  $H_2OD^+$  in  $C_2H_5OD$  are equal within a percent. This implies that the O–A bond does not break in any of these rearrangements.

## C. Kinetic energy distributions for $H_n^+$ and $H_nOH^+$ groups

The molecular ions  $H^+$ ,  $H_2^+$ ,  $H_3^+$ ,  $HOH^+$ , and  $H_2OH^+$  may be formed from either singly or doubly charged  $C_2H_5OH$  ions as precursors. The probability of single ionization leading to dissociation is found to be five times that of double ionization leading to dissociation, based on a subsidiary observation of several ion pairs in this experiment. Since the formation of these ions requires bond rearrangement, there would be various vibrationally excited states involved in their formation. Furthermore, there may be more than one participating electronic state. The signatures of these excited states would be seen in the kinetic energy distributions (KEDs) of the fragment ions. In the present analysis no distinction is made between the precursor species while obtaining the KED.

The KED of  $H^+$ ,  $H_2^+$ , and  $H_3^+$  ions from  $C_2H_5OH$  is plotted in Fig. 3. The KED could not be determined unambiguously for  $HOH^+$  and  $H_2OH^+$  ions from  $C_2H_5OH$  as the mass peaks are not very well resolved. Instead, the KED of  $HOD^+$  and  $H_2OD^+$  ions arising from  $C_2H_5OD$  are plotted in Fig. 3 as these mass peaks are better resolved. We take the KED of  $HOD^+$  and  $H_2OD^+$  to be similar to those of  $HOH^+$  and  $H_2OH^+$ , respectively (barring a  $\sqrt{\mu}$  scaling due to differences in the reduced mass), because  $HOD^+$  and  $H_2OD^+$  ions arise from a similar rearrangement in  $C_2H_5OD$ . In interpreting the structures in the KED, it is necessary to have an idea of the instrumental spread of the kinetic energy. The KED of an undissociated molecular ion can be taken to be the instrumental width. While  $C_2H_5OH^+$  would be the obvious choice in this context, the presence of peaks at adjacent masses may lead to a false representation. We have instead shown the KED of  $CO_2^+$  ions arising from ionization of  $CO_2$  recorded

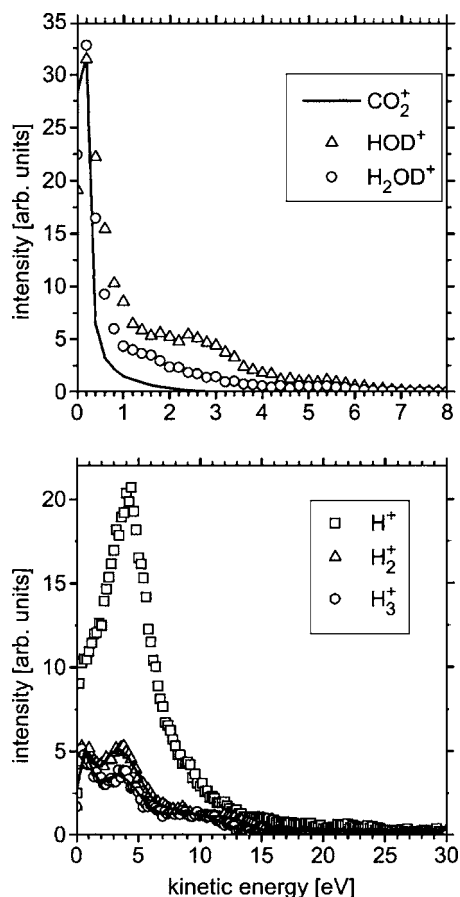


FIG. 3. (Upper) Distribution of kinetic energy of HOD<sup>+</sup> and H<sub>2</sub>OD<sup>+</sup> ions arising from C<sub>2</sub>H<sub>5</sub>OD. The continuous line is the KED of CO<sub>2</sub><sup>+</sup> ions from CO<sub>2</sub>, and may be taken to be the instrumental spread. This curve is arbitrarily normalized. (Lower) Distribution of kinetic energy of H<sup>+</sup>, H<sub>2</sub><sup>+</sup>, and H<sub>3</sub><sup>+</sup> ions from C<sub>2</sub>H<sub>5</sub>OH. For H<sub>2</sub><sup>+</sup> and H<sub>3</sub><sup>+</sup> distributions, the experimental data points are fitted to the sum of several Gaussian distributions, as indicated in the text.

under otherwise identical experimental conditions. The full width at half maximum (FWHM) of this distribution is  $\approx 160$  meV.

We attempted to fit the observed KEDs to sum of Gaussian distributions:

$$y = \sum_i \frac{a_i}{\sigma_i \sqrt{\pi/2}} \exp[-2[(x - \mu_i)/\sigma_i]^2].$$

This attempt succeeded partly for H<sub>2</sub><sup>+</sup> and H<sub>3</sub><sup>+</sup> ions, but not for the others, although the other ions also show a multiplex structure. For H<sub>2</sub><sup>+</sup> we obtain a fit of four Gaussian distributions ( $a_i, \mu_i, \sigma_i$ ): (480, 0.64, 1.1), (2249, 3.3, 3.5), (657, 8.0, 3.9), and (435, 12.4, 3.6), with  $\chi^2/\text{dof}=190$ . For H<sub>3</sub><sup>+</sup> the fit

consists of three Gaussian distributions ( $a_i, \mu_i, \sigma_i$ ): (533, 0.63, 1.2), (1588, 3.2, 3.6), and (836, 9.1, 5.1), with  $\chi^2/\text{dof}=237$ . We note that the first two Gaussian distributions are almost identical for these ions (barring the amplitude). This suggests that the two ions may arise from the same transition to the intermediate excited state. The presence of multiple peaks can be taken to be an indication of the participation of many electronically excited states. The vibrational structure of the electronic states also play a role. A proper interpretation of these peaks requires knowledge of the potential energy surfaces of the parent and intermediate species. If this information is available, then a procedure based on the reflection approximation, and a linear combination of excitation function from initial bound states to repulsive intermediate states can lead to an understanding of the dissociation dynamics. Such a scheme has been employed in recent times to the study of fragmentation of CO and H<sub>2</sub>O by ion impact.<sup>8,9</sup> A fuller understanding of our data requires the calculation of potential energy (PE) surfaces of ethanol.

#### IV. SUMMARY

Isotopic substitution of the H atom in the O–H bond of C<sub>2</sub>H<sub>5</sub>OH has been shown to be an extremely useful tool for determining the active sites in the formation of ions such as H<sub>2</sub><sup>+</sup> and H<sub>3</sub><sup>+</sup> by electron impact. Our analysis has shown that H<sub>3</sub><sup>+</sup> is far more likely to be formed by rearrangement of H atoms on the CH<sub>2</sub> and OH sites, rather than the CH<sub>3</sub> site. Kinetic energy analysis has shown that there are more than one electronically excited states of C<sub>2</sub>H<sub>5</sub>OH<sup>+</sup> or C<sub>2</sub>H<sub>5</sub>OH<sup>2+</sup> molecule which give rise to all four unusual ionic fragments, viz., H<sub>2</sub><sup>+</sup>, H<sub>3</sub><sup>+</sup>, HOH<sup>+</sup>, and H<sub>2</sub>OH<sup>+</sup>.

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