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# Desorption from Methanol and Ethanol Ices by High Energy Electrons: Relevance to Astrochemical Models

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ABSTRACT: Methanol and ethanol, precursors of prebiotic molecules, are found in interstellar and circumstellar environments. At low temperatures, electrons may interact with these frozen molecules on dust grain surfaces stimulating desorption of atomic and molecular ions and charged clusters. These heavy fragments released from the icy mantles could contribute to the abundance in the gas phase of organic molecules in such environments. In this work, we investigate the ionic fragments desorbed from methanol and ethanol pure ices due to high energy electron impact. Absolute desorption yields (ions/impact) for each fragment desorbed from the ice surface were determined. Several clusters and heavier molecular ions were observed at higher electron energies. Two mechanisms seem to be involved in the desorption process, namely, the Auger stimulated ion desorption and that of secondary electrons. These data may provide support to establish more accurate astrochemical models and contribute to explain the influence of solar wind on condensed alcohols.
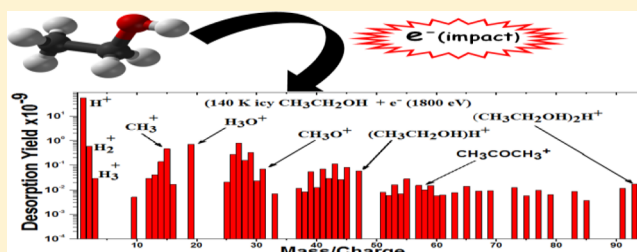
■ INTRODUCTION

Methanol (CH_3OH) and ethanol (CH_3CH_2OH) are important precursors of more complex prebiotic species. Both molecules were found in several astronomical environments, such as star formation regions, Sgr B2,[1] Orion KL,[2] W33A,[3] RAFGL 7009,[3] and in comets like Hale-Bopp.[4] In all these astronomical environments, due to low temperatures, molecules frozen on dust grain surfaces are subjected to several ionizing agents, like UV, X-ray photons, and charged particles such as protons and electrons, leading to the ionization, dissociation, and desorption processes. These fragments can lead to chemical reactions giving rise to new and more complex molecules. Some mechanisms were proposed for the formation of interstellar methanol and ethanol in the gas phase.[5] However, as pointed out by Millar and co-workers,[6] chemical reactions occurring in the gas phase are not enough to explain the relatively high abundances of these alcohols; therefore, reaction pathways on grains surfaces are required.

Andrade, Rocco, and Boechat-Roberty[7] investigated experimentally the contribution of positive and negative ion desorption from methanol ice stimulated by soft X-rays for producing chemically active ions in protoplanetary disks. The interaction of stellar radiation and charged particles with icy alcohols on grain surfaces produces neutral or ionic fragments such as H_2CO, CH_3O, HCO, CH_3, CO, and even H, C, and O free atoms. At surface temperatures around 50 K, these radicals can readily diffuse into the ice to form more complex molecules, like acetic acid (CH_3COOH), methyl formate ($HCOOCH_3$), and dimethyl ether (CH_3OCH_3).[7] Some series

of molecular clusters, like $(CH_3OH)_nH^+$ and $(CH_3OH)_nCH_3OH_2^+$, can also be produced.[8] Those chemical entities enrich the astrophysical ice composition and can sublimate from the ice surface by thermal or nonthermal desorption mechanisms. The nonthermal desorption mechanisms are those stimulated by the interaction with energetic photons, electrons, or ions. Such agents can promote different kinds of fragmentation pathways on the ice favoring, depending on the impact energy, the production of ionic species rather than neutral species. To understand the chemical evolution and to quantify the role of methanol, ethanol, and more complex organic molecules in the gas phase and in the icy mantles of interstellar grains, it is necessary to establish the main formation routes, which requires a detailed study of the ionization, dissociation, and desorption of these molecules caused by the interaction of already mentioned agents.

Hempelmann et al.[9] and Pilling et al.[10] studied the interaction of X-ray photons at energies around the C and O K-edges with gas phase methanol. They measured partial ion yields for the positive fragments using the photoelectron–photoion coincidence technique. Souza and co-workers[11] measured the mean kinetic energies, the relative abundances, and the dissociation pathways for the coincident fragments produced from the interaction of soft X-ray photons in the 100–310 eV energy range with gas phase methanol and
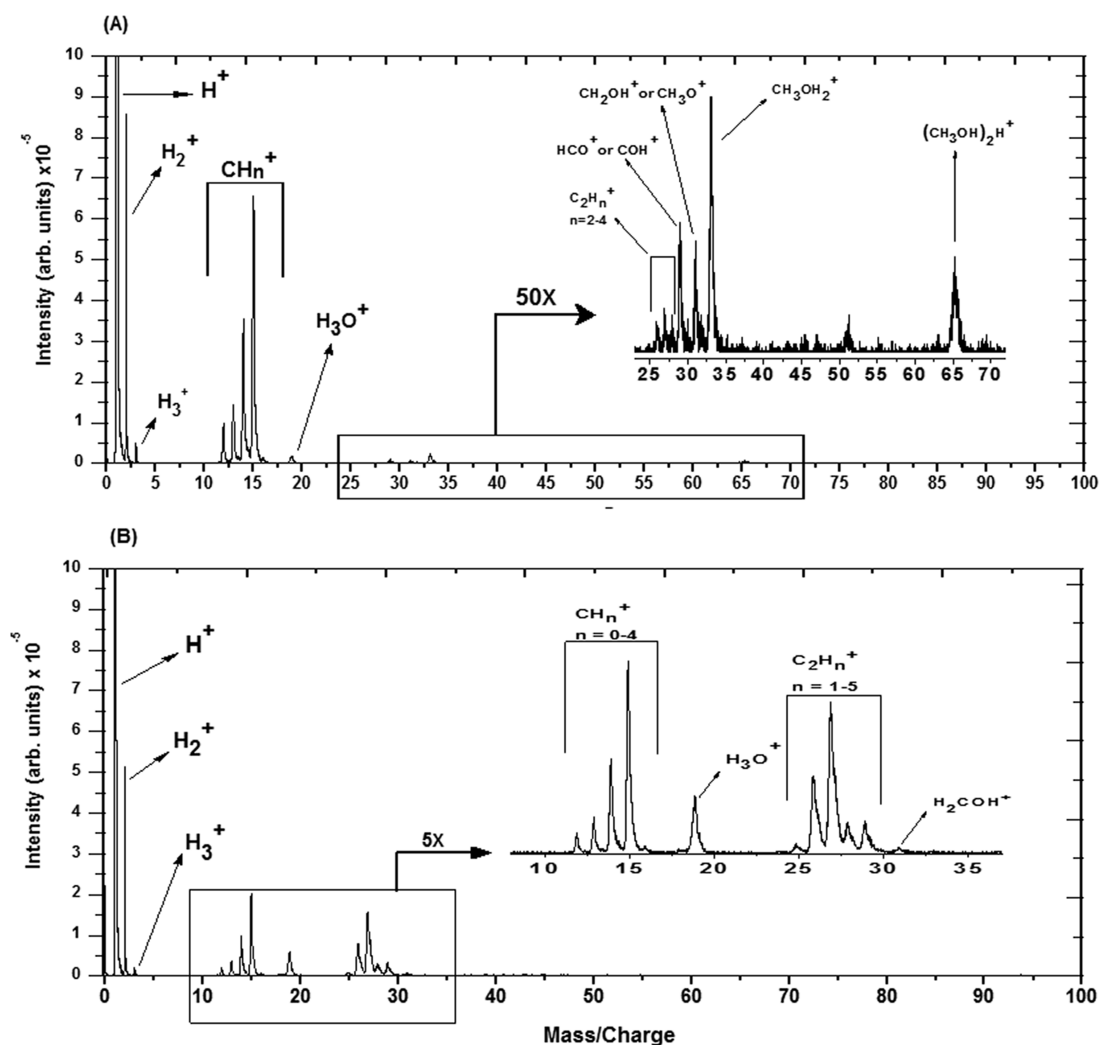
Figure 1. Mass spectra of ions desorbed from (A) methanol and (B) ethanol ices due to 900 eV electron impact.

ethanol. Sankar et al.[12] used the coincidence mapping technique to study the dissociation pathways of the ionic fragments produced by the impact of 1.2 MeV Ar^{8+} ions with methanol in the gas phase. In a recent work, D. Almeida et al.[13] studied the interaction of 1−4 keV H^-, O^-, and OH^- anion beams with water, nitromethane, methanol, and ethanol in the gas phase, using quadrupole mass spectrometry to identify the positive and negative fragments produced. Andrade and co-workers[8] studied the interaction of 65 MeV ions with methanol ice, measuring all positive fragments desorbed from the ice surface and identifying some clusters series, like CH_n^+, $C_2H_n^+$, and H_nCO^+. Palumbo and co-workers[14] studied through *in situ* infrared spectroscopy the interaction of 3−30 keV He^+ ions with methanol ices.

Dissociative electron attachment (DEA) of methanol, some deuterated methanols, and allylalcohol with analysis of the translational excess energy of the produced fragments was studied by Illenberger and co-workers.[15] The dissociative ionization cross sections of methanol, ethanol, and butanol were studied by electron impact in the energy range 5−60 eV, measuring C^+, O^+, H_3O^+, and CO^+ ions by Zavipoulo et al.[16] Partial ionization cross sections of the methanol molecule have also been studied by electron impact in the 20−500 eV energy range by Srivastava and co-workers[17] and using a time-of-flight mass spectrometer (TOF-MS) coupled with a two-dimensional

ion coincidence technique by Douglas and Price.[18] Rejoub et al.[19] measured absolute, partial, and total electron impact cross sections for methanol, ethanol, and 1-propanol in the energy range 13−1000 eV using a TOF-MS coupled with a position sensitive detector. All of these reported studies with energetic electrons were carried out in the gas phase.

In the ice phase, as far as we know, there are only a few studies. L. Sanche and co-workers[20] studied H^- desorption of condensed methanol films by low energy electron impact (0−20 eV). Kawanowa and co-workers[21] analyzed with TOF-MS fragments desorbed from 1.5 keV electron impact on methanol ices weakly physisorbed on a solid Ar substrate. Bennett et al.[22] analyzed quantitatively by Fourier transform infrared spectroscopy (FTIR) fragment ions produced by 5 keV electron impact on pure ices of amorphous methanol, identifying new species with the aid of high-level electronic structure calculations. Illenberger et al. studied negative ion desorption due to low energy electron impact (0−19 eV) from ethanol and trifluoroethanol condensed films.[23]

In the present work, we investigate ionic desorption from icy methanol and ethanol due to the impact of energetic electrons covering a broad energy range from 850 to 2200 eV. Absolute ion desorption yields per impact for all desorbed species were determined and the mechanisms involved discussed.

EXPERIMENTAL SETUP

Electron stimulated ion desorption (ESID) experiments on icy methanol and ethanol were performed using an experimental setup discussed in detail by Mendes et al.[24] Briefly, this setup consists of an *XYZ* sample manipulator, a commercial electron gun, and a homemade time-of-flight mass spectrometer (TOF-MS) housed in an ultrahigh vacuum (UHV) chamber with a base pressure of about 5×10^{-10} Torr. The TOF-MS has an electrostatic ion extraction system, a collimating electrostatic lens, a drift tube, and a pair of microchannel plate (MCP) detectors. After extraction, the positive ions travel through three metallic grids (each with a nominal transmission of ~90%) before reaching the MCP.

Methanol and ethanol were purchased commercially from Sigma-Aldrich with a purity greater than 99.8% and further degassed through several freeze–pump–thaw cycles before its vapor being admitted into the UHV chamber. The alcohol molecules were condensed in their pristine form on a stainless steel sample holder, which was connected to a commercially purchased gaseous nitrogen cooling system. The minimum temperature reached was about 140 K, which was sufficient to condense the icy films. A thermocouple was used to determine the temperature of the icy samples.

Icy methanol and ethanol were irradiated by a pulsed beam of monoenergetic electrons at various energies (150−1000 eV) using a commercial electron gun. The pulsed electron beam had a frequency of 80 kHz and a minimal pulse width of 20 ns. Constant positive potentials of +500 V and further +1200 V were applied to the sample. Incident electron currents of the order of nanoamperes were used throughout the measurements. The incident beam formed an angle of 60° with respect to the normal to the sample surface, situated about 10 mm away from the first grid of the TOF-MS. The start signal is provided by a pulse generator, which controls the electron gun. The stop signal corresponds to the detector output, processed using a standard system of counting pulses, consisting of a preamplifier and a discriminator. These signals are sent to a time-to-digital converter (TDC), with a time resolution of 1 ns per channel. Mass calibration was performed through computational simulations of the ion trajectories and flight times. The results were checked through the use of different extraction potentials applied to the sample and the standard equation of a linear TOF.

RESULTS AND DISCUSSION

ESID spectra for desorbed fragments from methanol and ethanol ices are shown in Figure 1. In both spectra, H^+ is the most intense peak followed by H_2^+, since they have low masses and high kinetic energies lowering the surface residence time and the probability of further reneutralization. H_3^+ formation is also presented in both spectra. This ion was also observed by Andrade and co-workers[8,25] on fragmentation studies of methanol and formic acid ices irradiated with 65 MeV ions. It is well-known[25−27] that H_3^+ could be produced via several collisions between H^+, H^0, H^-, H_2, and H_2^+ as a first stage of gas phase hydrogen clusterization. In addition, Pilling et al.[26] have shown that H_3^+ can also be produced via X-ray photodissociation of molecules containing the methyl group, like acetonitrile (CH_3CN), methylamine (CH_3NH_2), and methanol.

Like in some gas-phase studies[16,18,19] for the methanol molecule and in the recent study with anion collisions with the methanol and ethanol molecule,[13] the CH_n^+ series was also observed, although our results show that the CH_n^+ series is more intense for methanol than for ethanol. The $C_2H_n^+$ series is intense for ethanol and very weak for methanol. In fact, the $C_2H_n^+$ series is not observed in the fragmentation studies for methanol in the gas phase,[18,19] but this series was observed in the ice phase by interaction with 65 MeV ions.[8] To have a fragment of the type $C_2H_n^+$ for the methanol molecule, recombination between fragments must occur, which has low probability. For ethanol and alcohols with higher carbonic chains, the $C_2H_n^+$ series is clearly observed[13,16] and our measurements for ethanol are in good agreement with gas phase results. For ethanol, the enhanced intensity of the $C_2H_n^+$ series suggests a high efficiency in C−O bond breakage in the condensed phase. The absence of OH^+ in both spectra means that hydroxyl radical may be desorbing as a neutral or negative fragment. OH^+ was reported in the gas phase spectra of methanol measured at 200 eV electron impact by Douglas and Price,[18] but it was not observed by Rejoub et al.[19] at 100 eV electron impact. OH^- was reported in the gas phase in DEA studies with methanol and allylalcohol.[15] The recent gas phase study[13] with high energy anion impact reports the formation of both OH^+ and OH^- species. In the condensed phase, the OH^+ fragment was reported for the methanol molecule by high energy ion impact.[8] Low energy ESID studies for condensed ethanol and trifluoroethanol molecules showed no evidence for OH fragment formation.[23] Previous studies by Stockbauer et al.[28] pointed out the difficulty of O−H bond cleavage in the condensed phase due to hydrogen bonding. Therefore, the peak at $m/z = 29$, assigned as $C_2H_5^+$, may contain also a contribution of COH^+ and the peak at $m/z = 31$ is probably due to the CH_2OH^+ fragment, although this does not exclude the possibility of HCO^+ fragment formation for $m/z = 29$ and CH_3O^+ fragment formation for $m/z = 31$. Tables 1 and 2 present the suggested assignments for condensed methanol and ethanol, respectively.

In order to determine absolute desorption yield, Y, values presented in Tables 1 and 2, the following procedure was employed. First, the continuous electron current was measured for which a value of 6.8 μA was obtained at 900 eV electron impact. At pulsed conditions (80 kHz and 20 ns), a mean value

Table 1. Desorption Yield Y (Ions/Impact) of Ions from Icy Methanol at 140 K due to 900 eV Electron Impact

m/z	ions	$Y (\times 10^{-11})$ (ions/impact)	TOF (ns)	fwhm
1	H^+	2127.66	1172	17.5
2	H_2^+	18.30	1674	19.7
3	H_3^+	1.08	2059	20.5
12	C^+	2.11	4133	31.0
13	CH^+	3.04	4305	31.5
14	CH_2^+	7.60	4473	29.9
15	CH_3^+	13.92	4635	29.4
16	O^+ or CH_4^+	0.30	4782	25.7
19	H_3O^+	0.41	5204	44.4
26	$C_2H_2^+$	0.04	6105	46.9
27	$C_2H_3^+$	0.07	6217	37.4
28	CO^+ or $C_2H_4^+$	0.06	6344	30.3
29	HCO^+	0.21	6456	30.8
31	CH_2OH^+ or CH_3O^+	0.19	6676	33.8
33	$(CH_3OH)H^+$	0.48	6903	41.9
65	$(CH_3OH)_2H^+$	0.16	9701	61.8

Table 2. Desorption Yield Y (Ions/Impact) of Ions from Icy Ethanol at 140 K due to 1800 eV Electron Impact

m/z	ions	Y ($\times 10^{-11}$) (ions/impact)	TOF (ns)	fwhm
1	H^+	5411.70	747	15.2
2	H_2^+	58.46	1072	17.7
3	H_3^+	2.91	1325	22.1
9.5	H_3O^{2+}	0.50	2374	18.8
12	C^+	2.88	2672	19.0
13	CH^+	4.01	2784	18.6
14	CH_2^+	13.73	2892	18.4
15	CH_3^+	45.99	2997	17.1
16	O^+ or CH_4^+	1.64	3094	28.2
19	H_3O^+	70.56	3371	21.5
25	C_2H^+	2.05	3874	24.0
26	$C_2H_2^+$	26.71	3954	19.2
27	$C_2H_3^+$	78.12	4033	19.0
28	CO^+ or $C_2H_4^+$	15.56	4108	20.1
29	HCO^+ or $C_2H_5^+$	32.76	4181	19.3
30	$C_2H_6^+$ or $HCOH^+$	2.29	4249	33.8
31	CH_2OH^+ or CH_3O^+	6.93	4323	19.4
33	$(CH_3OH)H^+$	0.67	4464	19.6
37	$(H_2O)_2H^+$	1.15	4726	24.0
38	$(H_3O^+)_2$	0.81	4787	17.4
39	$C_2CH_3^+$	5.27	4854	20.8
40	C_2O^+	1.22	4916	35.4
41	C_2OH^+	6.87	4979	22.5
42	HC_2OH^+	2.86	5037	26.0
43	CH_2COH^+	11.15	5099	21.3
44	CH_3COH^+ or CO_2^+	2.58	5157	16.0
45	$CH_3CH_2O^+$	7.94	5217	21.0
47	$(CH_3CH_2OH)H^+$	5.81	5333	27.9
51	$(CH_3OH)H_3O^+$	0.79	5553	19.7
52	$(H_2O)_2O^+$	0.60	5611	24.8
53	$(H_2O)_2OH^+$	1.59	5663	21.2
54	$(H_2O)_2H_2O^+$	0.67	5718	11.0
55	$(H_2O)_2H_3O^+$	2.74	5773	21.7
57	$CH_3COCH_2^+$	1.52	5874	22.3
58	$CH_3COCH_3^+$	0.98	5924	24.5
60	CH_3COOH^+, $HOCH_2CHO^+$, $CH_3CH_2CH_2OH^+$, or $CH_3OCH_2CH_3^+$	0.57	6028	32.7
61	$(CH3COCH3)CH_3^+$ or $(CH_3OH)HCO^+$	0.62	6082	31.7
63	$(CH_3OH)CH_2OH^+$	0.76	6181	20.4
65	$(CH_3OH)_2H^+$	1.38	6277	26.5
67	$(CH_3OH)_2H_3^+$	0.88	6375	25.2
69	$C_4H_5O^+$	0.93	6470	23.2
73	$(H_2O)_3H_3O^+$	1.22	6654	32.9
75	$(CH_3CH_2OH)HCO^+$	0.57	6749	22.6
77	$(CH_3CH_2OH)CH_3O^+$	0.95	6837	27.6
79	$(CH_3CH_2OH)CH_3OH_2^+$	0.64	6926	26.1
83	$(CH_3OH)_2H_3O^+$	0.86	7094	26.4
85	$(CH_3CH_2OH)C_2C^+$	0.36	7182	13.7
91	$(CH_3CH_2OH)CH_3CH_2O^+$	1.15	7433	29.9
93	$(CH_3CH_2OH)_2H^+$	1.69	7513	41.1

of 8.5 nA was measured. This leads to a number of electrons per pulse equal to 6.6×10^5 which was used to normalize the data, given by

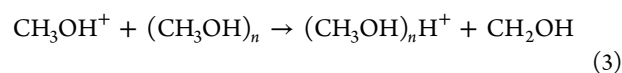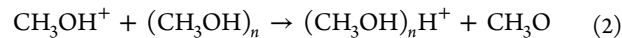$$Y_i = \frac{A_i}{N_{pulses} \cdot \frac{electrons}{pulse}} \qquad (1)$$

where Y_i is the number of ions desorbed per incident electron for each ion i and it was determined by dividing the peak area (A_i) by the number of pulses N_p and the number of electrons per pulse.

All fragments desorbed from icy methanol, and their absolute yields calculated by eq 1 are shown in Table 1. Figure 2 compares the absolute yields of each ion desorbed by 900 eV electron impact on methanol, emphasizing the strong contribution of hydrogen species and CH_n^+ ion yields.
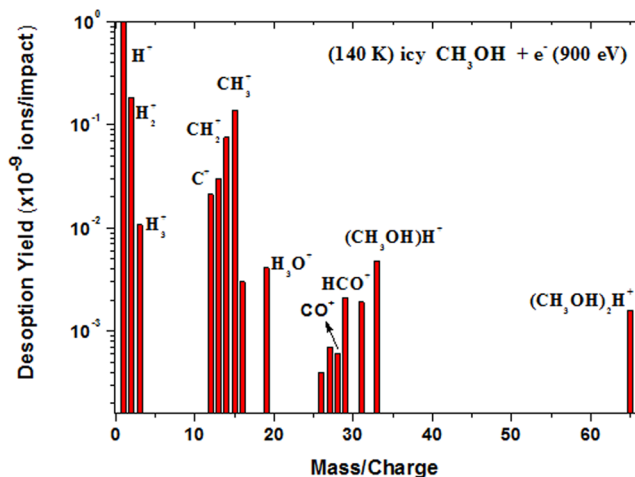
Figure 2. Absolute desorption yields of ions released from icy methanol due to 900 eV electron impact.

The H_3O^+ fragment is seen in both spectra of Figure 1. It is well-known[8,21] that water can be produced from alcohol dissociation on the ice phase. Some water cluster series like $(H_2O)_n(H_3O)^+$ were identified in the desorption spectrum of ethanol at energies higher than 1400 eV, as shown in Table 2. These clusters were also measured by Andrade et al.[8] on methanol ice desorption by interaction with californium fission fragments.

Only two clusters were observed in the methanol spectra. Kawanowa and co-workers[21] measured $(CH_3OH)_nH^+$ ($n = 1-4$) cluster series for icy methanol irradiated with 1.5 keV electrons. In this work, we could only observe the $n = 1$ and $n = 2$ members of this series, most probably because we have prepared very thick methanol films. Thick films, as mentioned by Kawanowa et al.,[21] can favor delocalization of valence holes in the molecule overlayer, due to hydrogen bonds. Such an effect reduces the Coulombic repulsion between the valence holes and lowers the probability of heavy fragments desorption. Kawanowa et al.[21] also mention that the proton transfer to the methanol molecule occurs during molecular collisions in the condensed phase. In fact, previous gas phase studies[16,18,19] showed no evidence of protonated molecular cluster formation. The formation of protonated cluster ions on the condensed phase is favored by hydrogen bonding, which becomes stronger with the ion–dipole interaction with H^+ ion. Protonated molecular clusters on the condensed phase are believed to be formed by the following pathways:[29]

$$CH_3OH^+ + (CH_3OH)_n \rightarrow (CH_3OH)_nH^+ + CH_3O \qquad (2)$$

$$CH_3OH^+ + (CH_3OH)_n \rightarrow (CH_3OH)_nH^+ + CH_2OH \qquad (3)$$
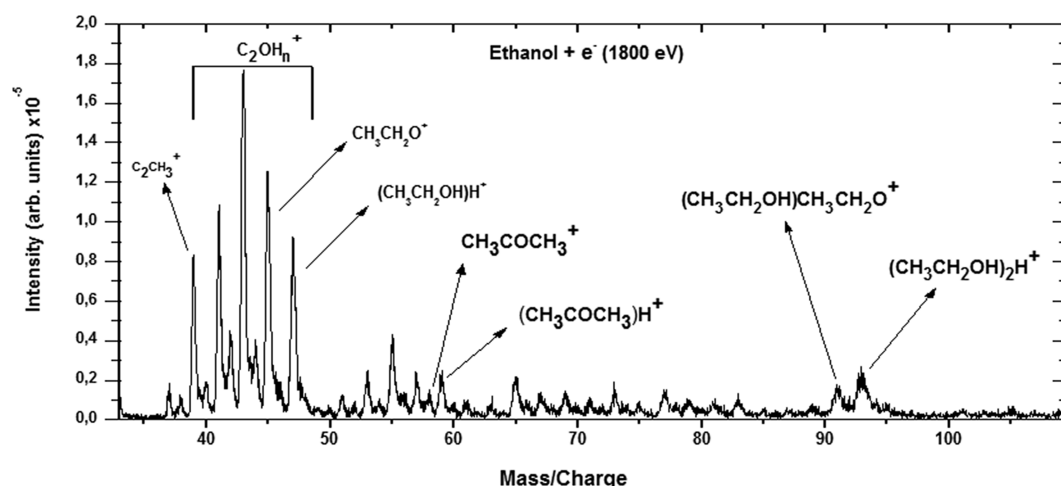
Figure 3. Mass spectrum of ions desorbed from ethanol ice due to 1800 eV electron impact.

Figure 3 shows the ethanol spectrum at 1800 eV electron impact for m/z greater than 35. Ethanol spectra at higher electron energies, around 1600−2200 eV, revealed a large number of heavier molecular fragments and molecular clusters, such as protonated ethanol $(CH_3CH_2OH)H^+$, $m/z = 47$, $[(CH_3CH_2OH)CH_3CH_2O^+]$, $m/z = 91$, and $[(CH_3CH_2OH)_2H^+]$, $m/z = 93$, related to the ethanol molecule while others like $[(CH_3OH)_2H^+]$, $m/z = 65$, $[(CH_3OH)_2OH^+]$, $m/z = 81$, and $[(CH_3OH)_2H_3O^+]$, $m/z = 83$, related to the methanol molecule, a clear evidence that methanol is formed on fragment desorption induced by electron impact in ethanol. Figure 4 compares the absolute
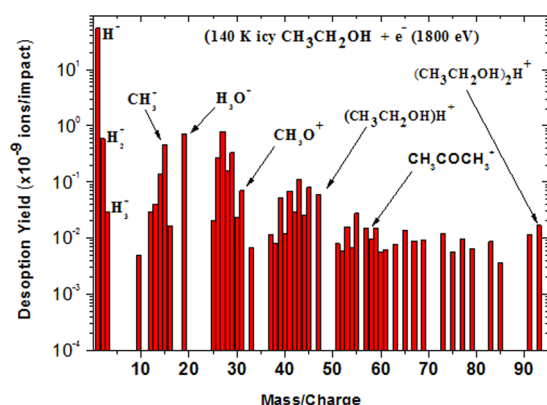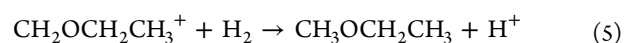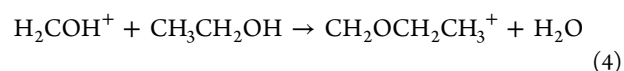

Figure 4. Absolute desorption yields of ions released by icy ethanol due to 1800 eV electron impact.

desorption yields of all fragments desorbed from ethanol by 1800 eV electron impact, showing the abundance of fragments resulting from the interaction of ethanol and the electron beam. Table 2 shows all fragments desorbed from the ethanol molecule by 1800 eV electron impact and their calculated absolute yields. This energy was chosen because it is representative of all ionic fragments measured for condensed ethanol.

Another molecule that is probably formed due to fragment recombination is acetone and protonated acetone identified by the peaks $m/z = 58$, $(CH_3COCH_3^+)$, and $m/z = 59$, $(CH_3COCH_3H^+)$, respectively. Acetone production was reported by Palumbo and co-workers[14] in the interaction of 3 keV He$^+$ ions with methanol ice. Bennett et al.[22] reported the

production of formaldehyde (CH_2O), methyl formate $(HCOOCH_3)$, $m/z = 60$, glycolaldehyde $(OHCH_2CHO)$, $m/z = 60$, and ethylene glycol $(HOCH_2CH_2OH)$, $m/z = 62$, from the interaction of 5 keV electrons with methanol ices. We could not identify peaks related to ethylene glycol in any of the impact energies employed here, but we could identify for energies higher than 1500 eV a peak at $m/z = 60$ that could be related to the production of methyl formate, glycoaldehyde, n-propyl alcohol $(CH_3CH_2CH_2OH)$, and methyl ethyl ether $(CH_3OCH_2CH_3)$. These observations are in agreement with the conclusion of Millar et al.[30] and Charnley et al.[31] that alcohols are a side product of grain surface chemistry on interstellar clouds and once released in the gas phase they can react with other fragments to form more complex molecules. One possible pathway for methyl ethyl ether production from ethanol could be explained by the ion−molecule interaction adapted from Millar et al.[6]

$$H_2COH^+ + CH_3CH_2OH \rightarrow CH_2OCH_2CH_3^+ + H_2O \tag{4}$$

$$CH_2OCH_2CH_3^+ + H_2 \rightarrow CH_3OCH_2CH_3 + H^+ \tag{5}$$

If an ethanol molecule is released into the gas phase by thermal desorption in a star-forming region or interacts with H_2COH^+ fragment and further with a H_2 molecule in the ice phase, methyl ethyl ether could be produced by the pathway given above. This is a reasonable pathway if we consider that H_2COH^+ fragment is produced by electron impact on condensed ethanol with an elevated yield per impact (Table 2), and hydrogen molecule is constantly produced by recombination between fragments produced during the impact.[32] The detection of methyl ethyl ether in the interstellar medium (ISM) remains doubtful. Fuchs et al.[33] mention that the confirmation of methyl ethyl ether in the interstellar medium would confirm the importance of ethanol in the grain mantle constitution. Theoretical calculations would be important to confirm the most favorable pathways for methyl ethyl ether production in the ISM.

Absolute ion yields in the energy range 850−1500 eV for the CH_n^+ and $C_2H_n^+$ series of fragments desorbed from ethanol ice are shown in Figure 5. All fragments desorbed at this energy range showed a similar behavior with curves presenting a broad maximum. The electron energies used here are high enough to induce both core and valence ionization processes. It is well-
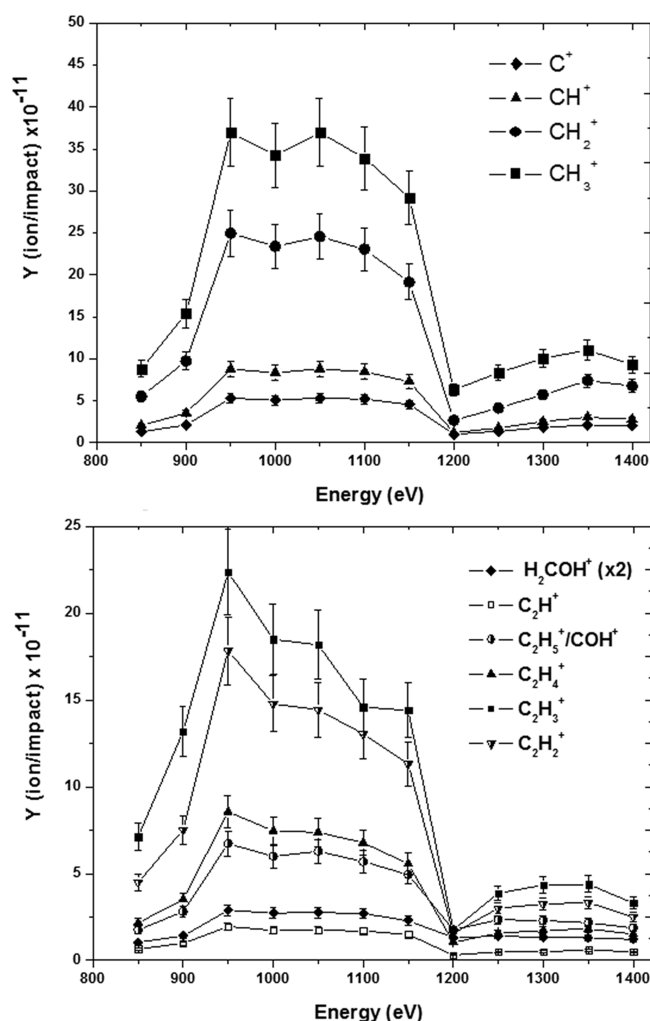
Figure 5. Absolute ion yield curves for the CH_n^+ and $C_2H_n^+$ series desorbed from ethanol ice in the energy range of 850–1400 eV electron impact.

Figure 6. Absolute ion yield curves for the CH_n^+ and $C_2OH_n^+$ series desorbed from ethanol ice in the energy range of 1350–2200 eV electron impact.

known that the Auger process is the dominant decay process for core ionization of light elements, such as carbon and oxygen.[34] The presence of localized valence holes may lead to fragmentation and desorption due to strong Coulombic repulsion. Generally, electron induced Auger cross sections have a maximum at energies corresponding to 2–3 or even 4 times the core ionization energy.[34,35] For alcohols, the C 1s and O 1s thresholds are about 292 and 539 eV, respectively.[9] The ethanol fragments present maximum desorption yields at an energy approximately 3.5 times higher than the carbon threshold, suggesting that the Auger mechanism may be the main process responsible for the desorption of these ionic species.[36] Fragments desorbed from icy methanol at this energy range showed the same behavior, and for this reason, the ionic yield curves are not presented here.

Figure 6 shows absolute yield curves for the CH_n^+ and $C_2OH_n^+$ series desorbed from the ethanol ice due to electrons at higher energies (1350–2200 eV). In this energy range, the ionic yields tend to increase with the increase of the electron energy. This behavior may characterize ionic desorption governed by secondary electrons. These low energy electrons inelastically scattered are mostly a result of outgoing energetic Auger electrons and photoelectrons, which induces valence excitations and ionizations on the ice surface, leading to bond
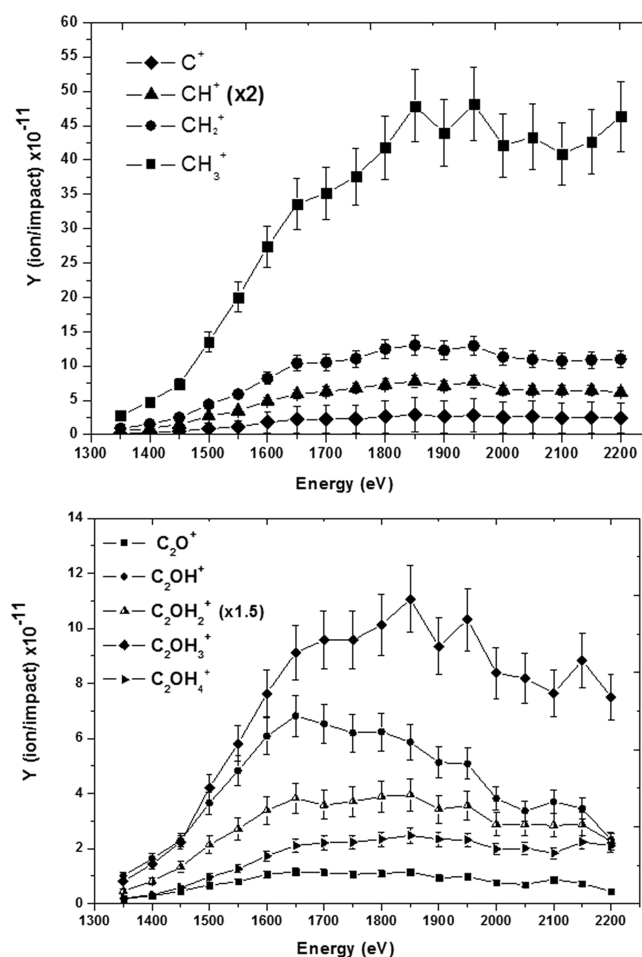
scissions and ionic fragmentation. This behavior is similar to the indirect X-ray induced electron stimulated desorption (XESD) mechanism[37,38] proposed for photon stimulated ion desorption (PSID).

Only at energies higher than 1600 eV, it was possible to observe significant ion yields for fragments like CH_3O^+, $CH_3CH_2O^+$, and $(CH_3CH_2OH)CH_3CH_2O^+$, which strongly suggests that electrons with energies higher than 1.6 keV (near the oxygen 1s threshold) can efficiently promote O–H bond breakage on alcohols.

■ CONCLUSIONS

As part of an experimental investigation on icy molecules of astrochemical interest, we have obtained absolute ion yields for all positive fragments desorbed from condensed methanol and ethanol stimulated by electron impact at energies ranging from 850 to 2200 eV. H_n^+ (n = 1−3) and CH_n^+ (n = 0−3) series for both methanol and ethanol and $C_2H_n^+$ (n = 1−5) and $C_2OH_n^+$ (n = 0−5) series for ethanol were clearly identified. Ionic yield curves for desorbed fragments show that ion desorption occurs mainly through the Auger mechanism in the energy range 850−1400 eV and by secondary electrons at higher impact energies.

$(CH_3OH)H^+$ and $(CH_3OH)_2H^+$ clusters were measured for methanol and several other clusters, and heavier molecular fragments were observed for ethanol at energies ranging from 1400 to 2200 eV. These molecular fragments point to the

production of more complex molecules, confirming previous observations[29−31] that when alcohol fragments desorb from grain mantles, passing to the gas phase, they can react with other fragments, leading to the formation of more complex organic molecules, such as ethers, esters, and aldehydes, observed in the hot cores of protostellar regions.

We believe that these data can be helpful for modeling astrochemical entities and explain the evolution of molecular complexity and abundance of astrophysical environments.

■ AUTHOR INFORMATION

Notes

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