Electron-impact ionization of the simple alcohols

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Absolute partial and total cross sections for electron-impact ionization of methanol, ethanol, and 1-propanol are reported for electron energies from threshold to 1000 eV. The product ions are mass analyzed using a time-of-flight mass spectrometer and detected with a position-sensitive detector whose output demonstrates that all product ion species are collected with equal efficiency irrespective of their initial kinetic energies. The total cross section for each target is obtained as the sum of the partial cross sections. The overall uncertainty in most of the absolute cross sections is $\pm 6\% - 8\%$. Significant discrepancies are seen between the only prior methanol partial cross section determination and this study but the majority of published total cross section measurements and calculations are in good agreement with this work. © *2003 American Institute of Physics.*
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I. INTRODUCTION

The discovery of simple alcohols in interstellar space and in the atmospheres of planets in our own solar system has prompted recent laboratory work on the electron-impact ionization of these molecules. Prior to the studies of Duric *et al.*[1] and Srivastava *et al.*[2] there had apparently been no quantitative determination of the ionization cross sections for these species. Despite these two investigations the information available on the alcohols has remained quite limited as Srivastava *et al.*[2] only studied methanol and the work of Duric *et al.*[1] was confined to determination of the total cross sections for the three simplest alcohols. Here we provide a further determination of these cross sections and extend the earlier work to include total and partial cross sections for all three simple alcohols: methanol, ethanol, and 1-propanol. Additionally, the methanol data are compared to those for CD_3OD.

The development of sound electron-impact ionization theories requires that reliable quantitative data be available for comparison and, as noted in our recent paper on the methyl halides,[3] comparison of measurements and calculations for a group of similar molecules has the potential to be advantageous in this regard.[4] It is hoped, therefore, that the availability of cross sections for this series of related molecules will also encourage further theoretical investigation of these systems.

II. APPARATUS AND EXPERIMENTAL METHOD

The apparatus, which is shown in Fig. 1, consists of an electron gun, a time-of-flight mass spectrometer with a position-sensitive detector (PSD), and an absolute capacitance diaphragm pressure gauge (not shown). It has been described in detail previously.[5] Briefly, during a cross-section measurement the entire vacuum chamber is filled with the appropriate methyl halide at a pressure of about 3×10^{-6} Torr. The electron gun produces 20 ns long pulses at a repetition rate of 10 kHz. These pulses are directed through an interaction region, located between two plates maintained at ground potential, and are collected in a Faraday cup. Approximately 250 ns after each electron pulse, a 3 kV pulse is applied to the top plate to drive any positive ions formed by electron impact toward the bottom plate. Some ions pass through a grid-covered aperture in the bottom plate, are then accelerated and subsequently impact a PSD,[6] which records their arrival times and positions. The ion arrival times are used to identify their mass-to-charge ratios and the ion arrival positions are used to determine the effectiveness of product ion collection. Under conditions in which very few of the incident electrons produce an ion, the partial cross section $\sigma(X)$ for production of ion species X is given by

$$\sigma(X) = \frac{N_i(X)}{N_e n l}, \tag{1}$$

where $N_i(X)$ is the number of X ions produced by a number N_e of electrons passing a distance l through a uniform gas target of number density n.[7] $\sigma(X)$ is then determined by measuring the four quantities on the right-hand side of Eq. (1).[5] Technical details concerning the PSD detection efficiency calibration and use of the capacitance diaphragm gauge may be found in Straub *et al.*[8] and Straub *et al.*,[9] respectively.

The particular strength of this experimental arrangement is the ability to ensure that all fragment ions are collected irrespective of their kinetic energies. This is achieved, however, at the expense of high mass resolution and for these targets it was not possible to separate all of the individual ionic species, whose masses often only differed from one another by one atomic mass unit. Hence, most of the reported partial cross sections pertain to groups of ions with

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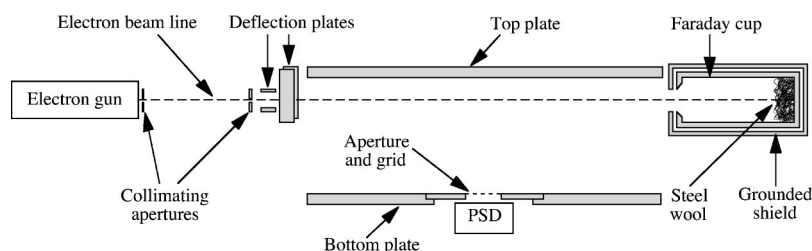[c]Electronic mail: lindsay@rice.edu

FIG. 1. Schematic diagram of the apparatus.

similar masses. For instance, the sum of the cross sections for production of CH_3O^+, CH_2O^+, CHO^+, and CO^+ ions is presented as $\sigma(CH_nO^+)$, where $n=0-4$. The total ionization cross sections are obtained as the sum of the measured partial cross sections.

III. RESULTS AND DISCUSSION

The mass spectra of methanol, ethanol, and 1-propanol are compared in Fig. 2. The limitations of the apparatus in the study of these molecules is apparent, in that, in many instances individual mass peaks are not fully resolved. The situation is further complicated by the fact that some fragment ions, such as CO^+ and $C_2H_4^+$, have identical masses. Several qualitative observations may, however, be made. The peak at around 120 ns which is visible in all of the spectra clearly shows that all of the alcohols produce substantial numbers of protons. By contrast, the relative abundance of the heavier mass peaks changes conspicuously from one target to the next. In methanol, for example, there is a significant CH_3OH^+ peak which is notably absent in the other alcohol spectra, and both ethanol and 1-propanol have prominent $C_2H_n^+$ peaks which are, of course absent from the methanol spectrum. It is also worth noting that, while a small number of H_2O^+ ions are observed for all three targets, and a comparable number of H_3O^+ ions are observed for ethanol and 1-propanol, no H_3O^+ ions are produced by methanol.

The measured partial cross sections for methanol, ethanol, and 1-propanol are listed in Tables I–III. The absolute

uncertainties are typically $\pm 6\% - 8\%$. The uncertainties for the ethanol and 1-propanol cross sections, particularly those for $\sigma(CH_n^+ + H_nO^+)$, are somewhat greater than for methanol because the more complex alcohols adversely affected the performance of the electron gun. Near the threshold for formation of each species the uncertainties are generally greater and are given in the tables. The mean energy of the electron beam was established to within ± 0.5 eV. As indicated above because of the limited resolution of the mass spectrometer employed most of these partial cross sections are for the production of groups of ions with closely similar mass-to-charge ratios rather than single ionic species. In previous studies involving H_2O and NH_3 this limitation was overcome by simply using the deuterated form of the compound.[10,11] However, that strategy was not effective here because of the heavier molecular masses of the alcohols and because kinetic energy partitioning between the alcohol fragments, which can be of comparable mass, broadens the time-of-flight peaks much more than for H_2O and NH_3 where one fragment is always much more massive than the other. Initial investigations with CD_3OD did, nonetheless, provide one in-

TABLE I. Absolute partial ionization cross sections for electron-impact ionization of methanol. The uncertainties in the CH_nO^+, $(CH_n^+ + H_nO^+)$, H^+, and H_2^+ cross sections are $\pm 6\%$, $\pm 6\%$, $\pm 6\%$, and $\pm 8\%$, respectively, unless otherwise indicated.

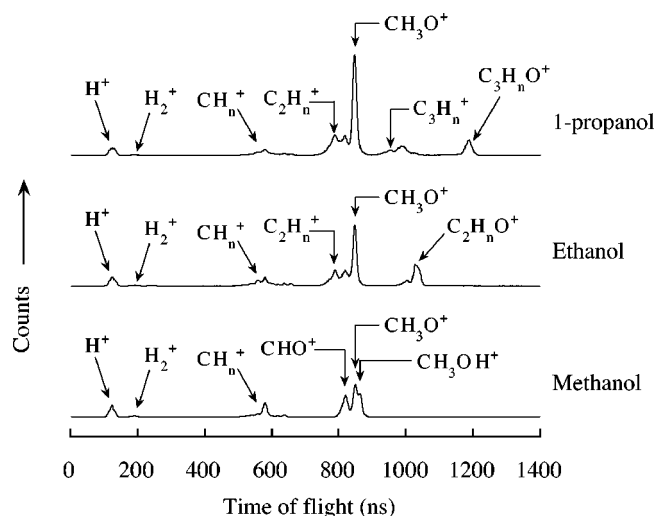| Energy (eV)	$\sigma(CH_nO^+)$ (10^{-16} cm^2)	$\sigma(CH_n^+ + H_nO^+)$ (10^{-16} cm^2)	$\sigma(H^+)$ (10^{-17} cm^2)	$\sigma(H_2^+)$ (10^{-18} cm^2)
13	0.151±0.012			
14	0.335±0.027			
16	0.609±0.043	0.015±0.003		
18	0.913	0.063±0.006		
20	1.22	0.115±0.009		
22.5	1.60	0.214±0.017		
25	1.95	0.298		
30	2.39	0.428	0.379±0.030	0.32±0.08
35	2.74	0.563	0.892	0.93±0.09
40	2.98	0.673	1.52	1.59±0.13
50	3.28	0.821	2.62	3.28±0.26
60	3.39	0.901	3.55	4.72
80	3.48	0.998	4.88	6.04
100	3.37	1.01	5.30	6.45
125	3.30	0.980	5.53	6.02
150	3.18	0.930	5.40	5.66
200	2.86	0.847	4.68	4.88
300	2.41	0.686	3.54	3.55
400	2.05	0.571	2.70	2.77
500	1.79	0.488	2.23	2.16
600	1.62	0.435	1.86	1.89
800	1.33	0.352	1.42	1.40
1000	1.14	0.295	1.17	1.13

FIG. 2. Time-of-flight spectra for ions produced by 100 eV electron-impact on methanol, ethanol, and 1-propanol. The magnitudes of the spectra are proportional to the measured cross sections.

TABLE II. Absolute partial ionization cross sections for electron-impact ionization of ethanol. The uncertainties in the $C_2H_nO^+$, $(CH_nO^+ + C_2H_n^+)$ $(CH_nO^+ + C_2H_n^+)$, $(CH_n^+ + H_nO^+)$, H^+, and H_2^+ cross sections are $\pm 6\%$, $\pm 6\%$, $\pm 7\%$, $\pm 6\%$, and $\pm 12\%$ respectively, unless otherwise indicated.

Energy (eV)	$\sigma(C_2H_nO^+)$ (10^{-16} cm²)	$\sigma(CH_nO^+ + C_2H_n^+)$ (10^{-16} cm²)	$\sigma(CH_n^+ + H_nO^+)$ (10^{-16} cm²)	$\sigma(H^+)$ (10^{-17} cm²)	$\sigma(H_2^+)$ (10^{-18} cm²)
16	0.86±0.16	0.82±0.22			
18	0.94±0.11	1.42±0.28			
20	1.07±0.09	1.74±0.17			
22.5	1.19±0.10	2.09±0.21			
25	1.32±0.11	2.43±0.24			
30	1.43	3.03	0.24±0.05		
35	1.49	3.49	0.42±0.09	0.048±0.011	
40	1.59	3.85	0.58±0.10	0.70±0.06	
50	1.68	4.27	0.83±0.10	1.82±0.15	2.00
60	1.74	4.52	0.97	2.82	3.30
80	1.73	4.69	1.12	4.15	4.45
100	1.70	4.54	1.14	4.82	4.84
125	1.63	4.32	1.09	4.55	4.77
150	1.56	3.98	0.965	4.00	4.11
200	1.40	3.64	0.817	3.04	3.85
300	1.24	3.19	0.618	2.33	3.16
400	1.09	2.72	0.512	1.92	2.88
500	0.977	2.42	0.457	1.58	2.26
600	0.888	2.21	0.419	1.41	1.91
800	0.743	1.91	0.353	1.07	1.83
1000	0.635	1.72	0.316	0.948	1.58

teresting observation. As expected, the partial cross sections for CH_nO^+, H^+, and H_2^+ were found to be identical, to within $\pm 2\%$, with those for CD_nO^+, D^+, and D_2^+; but the $(CH_n^+ + H_nO^+)$ cross section was found to be approximately 15% smaller than that for $(CD_n^+ + D_nO^+)$. This unexpected result was confirmed with different batches of methanol and deuterated methanol and contamination of the CD_3OD by H_2O was also eliminated as a possible cause. In the absence of any other viable explanation it would appear that this isotope effect is genuine and as such it warrants further investigation using a higher resolution instrument than that presently available.

The only partial cross sections with which the present data may be compared are those of Srivastava *et al.*[2] who measured the individual partial cross sections for methanol to within a quoted uncertainty of $\pm 15\%$. Figure 3 shows that, while there is good agreement as to the CH_nO^+ cross section, there is considerable disagreement as to the $(CH_n^+$

TABLE III. Absolute partial ionization cross sections for electron-impact ionization of 1-propanol. The uncertainties in the $C_3H_nO^+$, $(C_2H_nO^+ + C_3H_n^+)$, $(CH_nO^+ + C_2H_n^+)$, $(CH_n^+ + H_nO^+)$, H^+, and H_2^+ cross sections are $\pm 8\%$, $\pm 8\%$, $\pm 7\%$, $\pm 20\%$, $\pm 8\%$, and $\pm 20\%$ respectively, unless otherwise indicated.

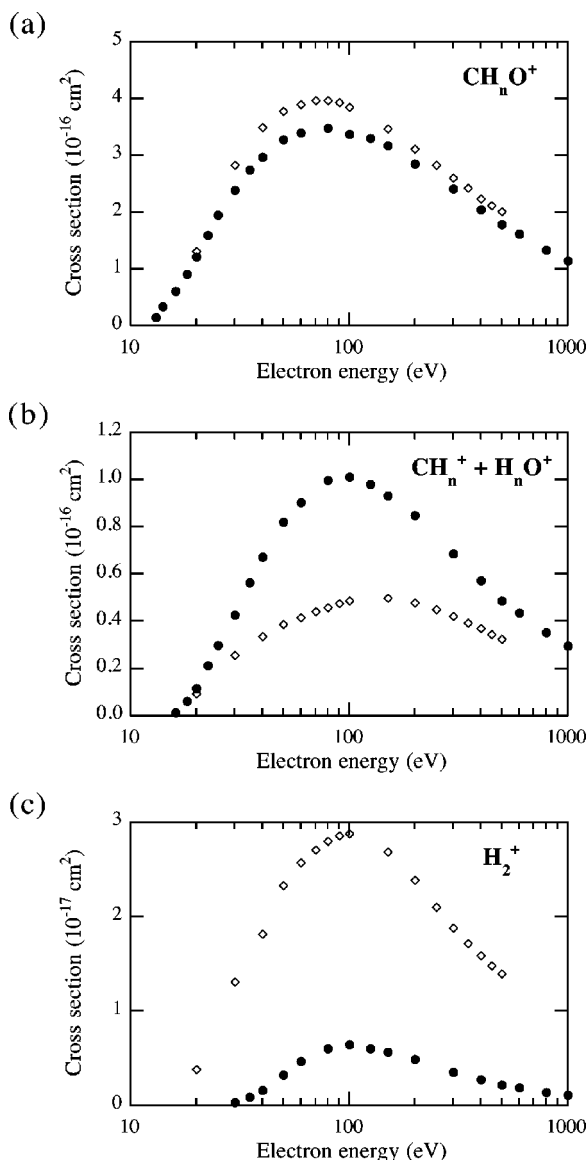| Energy (eV)	$\sigma(C_3H_nO^+)$ (10^{-16} cm²)	$\sigma(C_2H_nO^+ + C_3H_n^+)$ (10^{-16} cm²)	$\sigma(CH_nO^+ + C_2H_n^+)$ (10^{-16} cm²)	$\sigma(CH_n^+ + H_nO^+)$ (10^{-17} cm²)	$\sigma(H^+)$ (10^{-17} cm²)	$\sigma(H_2^+)$ (10^{-18} cm²)
16	0.53±0.18		1.30±0.35			
18	0.49±0.12	0.22±0.22	1.71±0.38			
20	0.73±0.18	0.41±0.20	2.53±0.56			
22.5	0.64±0.11	0.51±0.11	2.91±0.35			
25	0.89±0.11	0.69±0.12	3.87±0.43			
30	0.92±0.11	1.17±0.20	5.36±0.48			
35	1.03±0.12	1.30±0.16	6.37±0.51			
40	1.12±0.13	1.36±0.16	6.83		1.0±0.5	
50	1.18±0.14	1.42±0.17	7.11	4.6±1.4	1.71±0.27	0.9±0.5
60	1.19	1.48±0.15	7.18	6.3±1.9	2.49±0.30	5.0±1.5
80	1.17	1.44±0.14	7.28	7.4	3.34	4.2
100	1.08	1.46	6.95	7.6	4.11	4.7
125	1.01	1.43	6.76	7.2	3.95	4.2
150	0.941	1.33	6.54	6.9	3.74	3.7
200	0.879	1.22	5.97	6.3	3.44	3.5
300	0.728	0.999	5.03	5.1	2.72	3.1
400	0.645	0.798	4.21	3.7	2.31	2.4
500	0.561	0.726	3.70	3.1	1.82	1.6±0.8
600	0.521	0.697	3.37	2.6±0.8	1.63	
800	0.463	0.636	3.01	3.4±2.2	1.26	
1000	0.402	0.582	2.83	3.0±1.5	1.03±0.12	

(a)

(a)

(b)

(b)

(c)

(c)

FIG. 3. Methanol partial cross sections: present results ($\bullet$); Srivastava et al. (Ref. 2) ($\diamond$).

FIG. 4. Total alcohol cross sections: present results ($\bullet$); Duric et al. (Ref. 1) ($\circ$); Srivastava et al. (Ref. 2) ($\diamond$); DM calculation of Deutsch et al. (Ref. 12) (—).

$+H_nO^+$) and H_2^+ cross sections. A possible explanation for the ($CH_n^+ + H_nO^+$) discrepancy is that all of the fragment ions were not collected in the earlier study, which is consistent with our previous observations, e.g., Rejoub et al.[11] The H_2^+ discrepancy on the other hand cannot be explained so easily. The fact that a significant H^+ cross section is seen here, much greater than that for H_2^+, while Srivastava et al.[2] report only an H_2^+ cross section and do not indicate that any H^+ ions were observed at all, does, however, suggest that the low mass peak observed in their study was misidentified as H_2^+.

It seems apparent that the measurements of Srivastava et al.[2] and those reported here are somewhat complementary. The higher resolution afforded by their mass spectrometer results in better separation between the closely spaced peaks, whereas the apparatus utilized here provides more reliable ion collection and thus better absolute cross sections. The most accurate partial cross sections for the heaviest mass ions may be derived therefore by combining the present
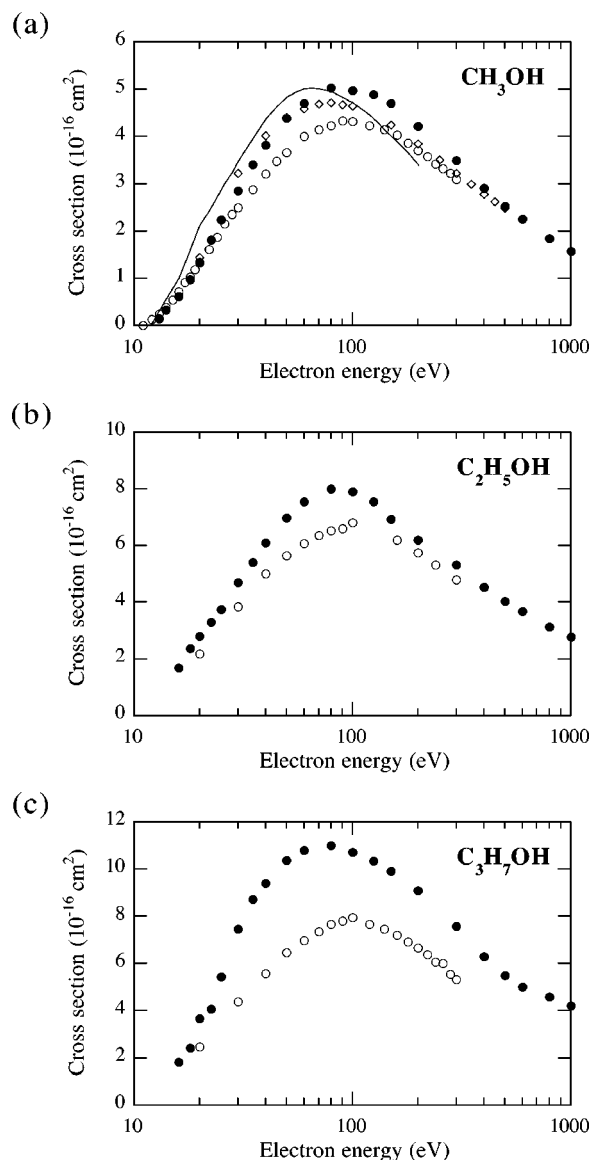
CH_nO^+ composite cross sections with the relative abundances reported by Srivastava et al.[2]

Total cross sections obtained as the sum of these partial cross sections are shown in Fig. 4 together with the measurements of Srivastava et al.,[2] those of Duric et al.,[1] and the calculations of Deutsch et al.[12] The data of Duric et al.,[1] whose uncertainty is $\pm 10\%$, are for total charge production but, as no multiply-charged ions were observed, the charge production cross sections should be equivalent to the total ion production cross sections.[13] For methanol and ethanol the agreement between different investigations is good. The semiclassical Deutsch–Märk (DM) calculation of Deutsch et al.[12] also reproduces the measured methanol cross section quite well. Why the 1-propanol data do not exhibit similarly good agreement is puzzling.

Besides the species listed in the tables very small numbers of H_3^+ ions were also observed. The measured cross sections for production of H_3^+ ions by 100 eV electron im-

pact on methanol, ethanol, and 1-propanol are 1.16 ± 0.15 $\times10^{-18}$ cm^2, $1.35\pm0.34\times10^{-18}$ cm^2, and 1.1 ± 0.6 $\times10^{-18}$ cm^2, respectively.

IV. CONCLUSION

Absolute partial and total cross sections are reported for electron-impact ionization of methanol, ethanol, and 1-propanol for electron energies from threshold to 1000 eV. The apparatus geometry is of simple design embodying a short-path-length time-of-flight mass spectrometer and position-sensitive detection of the product ions, which unequivocally demonstrates that all fragment ion species are collected with equal efficiency irrespective of their initial kinetic energy. Significant discrepancies are seen between the only prior methanol partial cross section determination and this study but the majority of the previous total cross section measurements and calculations are in good agreement with the present work. Comparison of the present CH$_3$OH measurements with those for CD$_3$OD indicates that, contrary to our observations for other simple molecules, the isotopic composition of the methanol target is important.

ACKNOWLEDGMENTS

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[13] Duric *et al.* (Ref. 1) provide their ethanol and 1-propanol data in the form of ratios relative to their methanol cross section. The absolute ethanol and 1-propanol data shown in Fig. 3 were therefore obtained by multiplying these ratios by their absolute methanol cross section.