Electron-impact ionization of the methyl halides

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(Received 31 May 2002; accepted 19 July 2002)

Absolute partial and total cross sections for electron-impact ionization of CH_3F, CH_3Cl, CH_3Br, and CH_3I 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. Data are presented for the production of CH_nF^+, CH_nCl^+, CH_nBr^+, CH_nI^+, $CH_n{}^+$, F^+, Cl^+, Br^+, I^+, and H^+, where $n=0-3$. Data are also reported for production of $H_2{}^+$, $H_3{}^+$, and doubly charged species at 100 eV. The total cross section for each target is obtained as the sum of the partial cross sections. The overall uncertainty in the absolute cross sections for most of the singly charged ions is $\pm 6\%$. It is observed that, although the Deutsch–Märk and the binary-encounter-Bethe theoretical formalisms are able to predict some features of the measured total cross sections, neither is consistently accurate. The simple *ab initio* method of Vallance *et al.* can apparently predict the value of the cross section maxima as well as the other more sophisticated approaches.
[DOI: 10.1063/1.1506152]

I. INTRODUCTION

The importance of electron-impact ionization in areas of science and technology as diverse as plasma processing and astrophysics has long been recognized. In recent years considerable efforts have been made to accurately determine the cross sections for ionization of molecules. The resultant data are often of significant practical value and are critical for the development of reliable quantitative theoretical models of these fundamental processes. Consequently there have been numerous comparisons of theory and experiment presented in the literature.[1] While it is very useful to compare experimental and theoretical cross sections for a specific molecular target, it is potentially even more informative to carry out such a comparison for a group of related molecules. Recently Vallance *et al.*[2] adopted this approach in their study of the CH_3X series, where $X=$H, F, Cl, Br, or I. The apparatus used for their study was, however, only capable of determining the total electron-impact ionization cross sections. We have already reported both partial and total cross sections for CH_4 (Ref. 3) and here we present new data for CH_3F, CH_3Cl, CH_3Br, and CH_3I.

Absolute cross sections are reported for production of CH_nF^+, CH_nCl^+, CH_nBr^+, CH_nI^+, $CH_n{}^+$, F^+, Cl^+, Br^+, I^+, and H^+, where $n=0-3$, for energies from threshold to 1000 eV. Data are also reported for production of $H_2{}^+$, $H_3{}^+$, and doubly charged species at 100 eV. Only the sums of the cross sections for $CH_3{}^+$, $CH_2{}^+$, CH^+, and C^+ and for CH_3X^+, CH_2X^+, CHX^+, and CX^+ ($X=$F, Cl, Br, or I) are given since the ionic species within each group could not be fully resolved by the mass spectrometer. The total ionization cross sections are obtained as the sum of the measured partial cross sections.

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.[4] Briefly, during a cross section measurement the entire vacuum chamber is filled with the appropriate methyl halide at a pressure of 2×10^{-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,[5] 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.[6] $\sigma(X)$ is then determined

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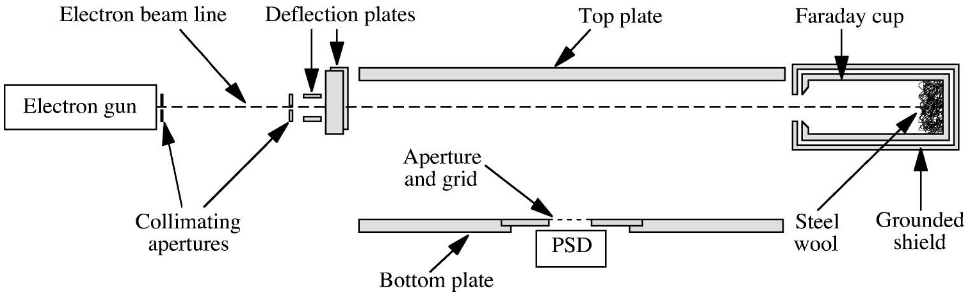

FIG. 1. Schematic diagram of the apparatus.

by measuring the four quantities on the right-hand side of Eq. (1).[4] Technical details concerning the PSD detection efficiency calibration and use of the capacitance diaphragm gauge may be found in Refs. 7 and 8, respectively.

The absolute uncertainties in the CH_nF^+, CH_nCl^+, CH_nBr^+, CH_nI^+, $CH_n{}^+$, and H^+ (where $n=0-3$) partial cross sections are $\pm6\%$. Those for F^+, Cl^+, Br^+, and I^+ are $\pm20\%$, $\pm7\%$, $\pm6\%$, and $\pm6\%$, respectively. Most of these uncertainties are slightly greater than those for our other recent measurements[9] because the methyl halides adversely affected the performance of the electron gun. The relatively large F^+ uncertainty is due to the proximity of this peak to the much larger $CH_n{}^+$ peak. Near the threshold for formation of each species the uncertainties in the cross sections are generally greater than those quoted above and are given in the tables. The mean energy of the electron beam was established to within ±0.5 eV.

III. RESULTS AND DISCUSSION

The measured partial cross sections for CH_3F, CH_3Cl, CH_3Br, and CH_3I are listed in Tables I–IV. No other measurements or calculations are currently available with which they may be compared.

Total cross sections obtained as the sum of these partial cross sections are shown in Fig. 2 together with previously published data.[2,10,11] Vallance *et al.*[2] reported CH_4 measurements in addition to the methyl halide measurements and our earlier data for CH_4 are therefore reproduced here.[3,12] It should be noted that the measurements of Vallance *et al.*,[2] Torres *et al.*,[10] and Rapp and Englander-Golden[11] are for total charge production while the present data represent total ion production. Very few multiply charged ions are produced, however, and the two cross sections are thus essentially identical (see below). Vallance *et al.*[2] estimated a maximum experimental uncertainty of 4% for their data, but they

TABLE I. Absolute partial cross sections for electron-impact ionization of CH_3F. The uncertainties in the CH_nF^+, $CH_n{}^+$, F^+, and H^+ cross sections are $\pm6\%$, $\pm6\%$, $\pm20\%$, and $\pm6\%$, respectively, unless otherwise indicated.

Energy (eV)	$\sigma(CH_nF^+)$ (10^{-16} cm^2)	$\sigma(CH_n{}^+)$ (10^{-16} cm^2)	$\sigma(F^+)$ (10^{-18} cm^2)	$\sigma(H^+)$ (10^{-17} cm^2)
14	0.070 ± 0.011			
16	0.300 ± 0.030			
18	0.513 ± 0.041			
20	0.651	0.160 ± 0.016		
22.5	0.852	0.314		
25	1.03	0.488		
30	1.23	0.776		0.123 ± 0.012
35	1.38	1.01		0.497 ± 0.050
40	1.51	1.21		0.989 ± 0.099
50	1.59	1.46	2.99 ± 0.90	2.05
60	1.64	1.57	3.75	2.80
80	1.68	1.64	5.34	3.79
100	1.67	1.66	5.77	4.20
125	1.61	1.60	6.08	4.43
150	1.56	1.57	5.99	4.17
200	1.40	1.39	5.24	3.80
300	1.19	1.21	4.30	2.95
400	1.06	1.05	3.73	2.39
500	0.911	0.897	3.07	1.97
600	0.798	0.780	2.34	1.53
800	0.645	0.638	1.90	1.25
1000	0.546	0.558	1.70	1.02

TABLE II. Absolute partial cross sections for electron-impact ionization of CH_3Cl. The uncertainties in the CH_nCl^+, $CH_n{}^+$, Cl^+, and H^+ cross sections are ±6%, ±6%, ±7%, and ±6%, respectively, unless otherwise indicated.

Energy (eV)	$\sigma(CH_nCl^+)$ (10^{-16} cm^2)	$\sigma(CH_n{}^+)$ (10^{-16} cm^2)	$\sigma(Cl^+)$ (10^{-17} cm^2)	$\sigma(H^+)$ (10^{-17} cm^2)
14	0.385 ± 0.042			
16	1.03 ± 0.07			
18	1.45 ± 0.10	0.344 ± 0.034		
20	1.81	0.698 ± 0.056		
22.5	2.24	1.12 ± 0.08		
25	2.51	1.58 ± 0.11		0.092 ± 0.023
30	2.71	2.20	0.575	0.502 ± 0.035
35	2.90	2.49	1.87	0.732
40	2.99	2.67	3.25	1.45
50	3.06	2.83	4.57	2.97
60	3.14	2.85	6.38	4.37
80	3.15	2.92	6.57	5.70
100	3.12	2.87	5.97	5.76
125	3.01	2.75	5.55	5.51
150	2.85	2.62	5.19	4.83
200	2.61	2.28	4.33	4.18
300	2.15	1.89	3.14	3.00
400	1.81	1.63	2.39	2.25
500	1.56	1.37	1.87	1.93
600	1.39	1.21	1.55	1.59
800	1.15	0.986	1.22	1.20
1000	0.983	0.844	0.959	0.997

also state that this figure does not necessarily reflect their absolute accuracy. The uncertainty in the CH_3F data of Torres *et al.*[10] is ±10% while that for the CH_4 data of Rapp and Englander-Golden[11] is ±7%. Of the prior work only that of Vallance *et al.*[2] encompasses all five targets and it is seen that, while there is superficial agreement between their data and the new results presented here, there are serious discrepancies in the near threshold regime and also to a lesser extent at the higher energies. The threshold behavior of the present cross sections is clearly consistent with the known ionization potentials for these species [9.5–12.6 eV (Ref. 13)] while it is difficult to reconcile the low-energy measurements of Vallance *et al.*[2] with such small ionization potentials. The measurements of Rapp and Englander-Golden[11] for CH_4 are seen

TABLE III. Absolute partial cross sections for electron-impact ionization of CH_3Br. The uncertainties in the CH_nBr^+, $CH_n{}^+$, Br^+, and H^+ cross sections are ±6% unless otherwise indicated.

Energy (eV)	$\sigma(CH_nBr^+)$ (10^{-16} cm^2)	$\sigma(CH_n{}^+)$ (10^{-16} cm^2)	$\sigma(Br^+)$ (10^{-16} cm^2)	$\sigma(H^+)$ (10^{-17} cm^2)
13	0.382 ± 0.042			
14	0.729 ± 0.066			
16	1.35 ± 0.12	0.158 ± 0.024		
18	1.82 ± 0.13	0.415 ± 0.037		
20	2.16	0.684 ± 0.048		
22.5	2.57	0.958 ± 0.067	0.080 ± 0.032	
25	3.01	1.25	0.167 ± 0.033	
30	3.24	1.66	0.334 ± 0.037	0.154
35	3.43	2.02	0.497	0.603
40	3.53	2.29	0.657	1.04
50	3.59	2.49	0.824	1.87
60	3.58	2.60	0.961	2.70
80	3.57	2.69	1.04	3.79
100	3.52	2.62	1.02	4.11
125	3.27	2.54	0.932	4.03
150	3.10	2.38	0.852	3.67
200	2.82	2.07	0.657	3.03
300	2.36	1.72	0.489	2.28
400	2.02	1.51	0.366	1.89
500	1.77	1.29	0.302	1.69
600	1.58	1.14	0.248	1.49
800	1.22	0.876	0.186	1.25
1000	1.09	0.799	0.154	1.06

TABLE IV. Absolute partial cross sections for electron-impact ionization of CH_3I. The uncertainties in the CH_nI^+, $CH_n{}^+$, I^+, and H^+ cross sections are $\pm 6\%$ unless otherwise indicated.

Energy (eV)	$\sigma(CH_nI^+)$ (10^{-16} cm^2)	$\sigma(CH_n{}^+)$ (10^{-16} cm^2)	$\sigma(I^+)$ (10^{-16} cm^2)	$\sigma(H^+)$ (10^{-17} cm^2)
13	0.77 ± 0.15			
14	1.29 ± 0.26			
16	2.10 ± 0.21			
18	2.77 ± 0.28			
20	3.43 ± 0.27	0.080 ± 0.016	0.061 ± 0.012	
22.5	3.95	0.107 ± 0.011	0.529 ± 0.079	
25	4.14	0.277 ± 0.028	0.951 ± 0.095	
30	4.36	0.740 ± 0.059	1.54 ± 0.15	
35	4.56	1.39	1.89 ± 0.19	0.376 ± 0.038
40	4.66	1.72	2.03	0.811 ± 0.081
50	4.70	1.98	2.23	1.61 ± 0.16
60	4.67	2.17	2.29	2.25
80	4.66	2.30	2.33	3.53
100	4.58	2.25	2.28	4.56
125	4.31	2.15	2.17	5.31
150	4.02	2.02	2.02	5.26
200	3.63	1.84	1.75	4.87
300	3.03	1.51	1.36	3.95
400	2.55	1.28	1.15	3.52
500	2.18	1.08	0.942	3.03
600	1.92	0.970	0.819	2.69
800	1.58	0.803	0.689	2.32
1000	1.41	0.707	0.601	2.11

to be in complete agreement with the present data over the entire energy range. It is noteworthy that very good agreement between the work of this laboratory and that of Rapp and Englander-Golden[11] is observed for all thirteen atoms and molecules jointly studied by the two laboratories.[9,14] The congruence of the results of these two independent laboratories is viewed as compelling evidence for the correctness of their collective data. The only other pertinent experimental data for the methyl halides are those of Torres *et al.*[10] for CH_3F, which are seen to be in good accord with the present measurements.

Calculations by Vallance *et al.*[2] using the semiclassical Deutsch–Märk formalism (DM), the binary-encounter-Bethe model (BEB), and a simple *ab initio* approach based on an electrostatic model are shown for comparison in Fig. 2. The analogous DM calculation for CH_4 performed by Deutsch *et al.*,[15] which differs somewhat from the Vallance *et al.*[2] DM calculation, is also shown. Evidently, although all three theories are able to reproduce some features of the measured cross sections, none are able to acomplish this with consistent accuracy. The DM theory agrees with the data when the heavier halogen atoms are involved and the BEB theory agrees better with molecules containing lighter halogens. The BEB approach consistently predicts the energy at which the cross sections peak more accurately than the DM theory which predicts lower maxima than are observed. The *ab initio* method of Vallance *et al.*[2] is only able to predict the value of the cross section maximum; however, it seems able to accomplish this as well as the two more sophisticated theories.

Table V gives cross sections for production of minor ionic products measured at an electron energy of 100 eV. For all targets small numbers of $H_2{}^+$ ions were observed, but only in two cases were $H_3{}^+$ ions observed. It is not known why production of $H_3{}^+$ should be much more likely for CH_3Cl and CH_3Br than for the other methyl halides. It was initially thought that perhaps the physical shape of the molecule or its dipole moment might play a role. However, there is little variation in the bond angles or the dipole moments for this molecular series and no obvious trend explains our finding that $H_3{}^+$ is only produced for two of the four targets. Only very small numbers of doubly charged ions were observed, much less than 1% of the total cross section, and therefore the total charge production cross section and the total cross section are essentially identical.

IV. CONCLUSION

Absolute partial and total cross sections are reported for electron-impact ionization of CH_3F, CH_3Cl, CH_3Br, and CH_3I for electron energies from threshold to 1000 eV. The apparatus geometry is of simple design embodying a short-

TABLE V. Absolute cross sections for production of $H_2{}^+$, $H_3{}^+$, and CH_nX^{2+} by 100 eV electron impact on the methyl halides. No measurable $H_3{}^+$ peak was observed in the CH_3F or CH_3I spectra. It was also not possible to determine a value for $\sigma(CH_3F^{2+})$ because of the overlapping OH^+ background peak.

Target	$\sigma(H_2{}^+)$ (10^{-18} cm^2)	$\sigma(H_3{}^+)$ (10^{-18} cm^2)	$\sigma(CH_nX^{2+})$ (10^{-19} cm^2)
CH_3F	2.40 ± 0.24	—	—
CH_3Cl	2.23 ± 0.22	2.46 ± 0.25	1.9 ± 0.5
CH_3Br	2.17 ± 0.22	1.40 ± 0.21	3.0 ± 0.9
CH_3I	1.56 ± 0.16	—	4.3 ± 1.3

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. The peak total cross sections reported by prior investigators agree fairly well with the present measurements. It is observed that, although the DM and the BEB theoretical formalisms are able to predict some features of the measured total cross sections, neither is consistently accurate. The simple *ab initio* method of Vallance *et al.*[2] can apparently predict the value of the cross section maxima as well as the other more sophisticated approaches.

It is hoped that the body of experimental data now available for the methyl halides will stimulate further theoretical investigations of this series of similar, and relatively simple, molecular targets.

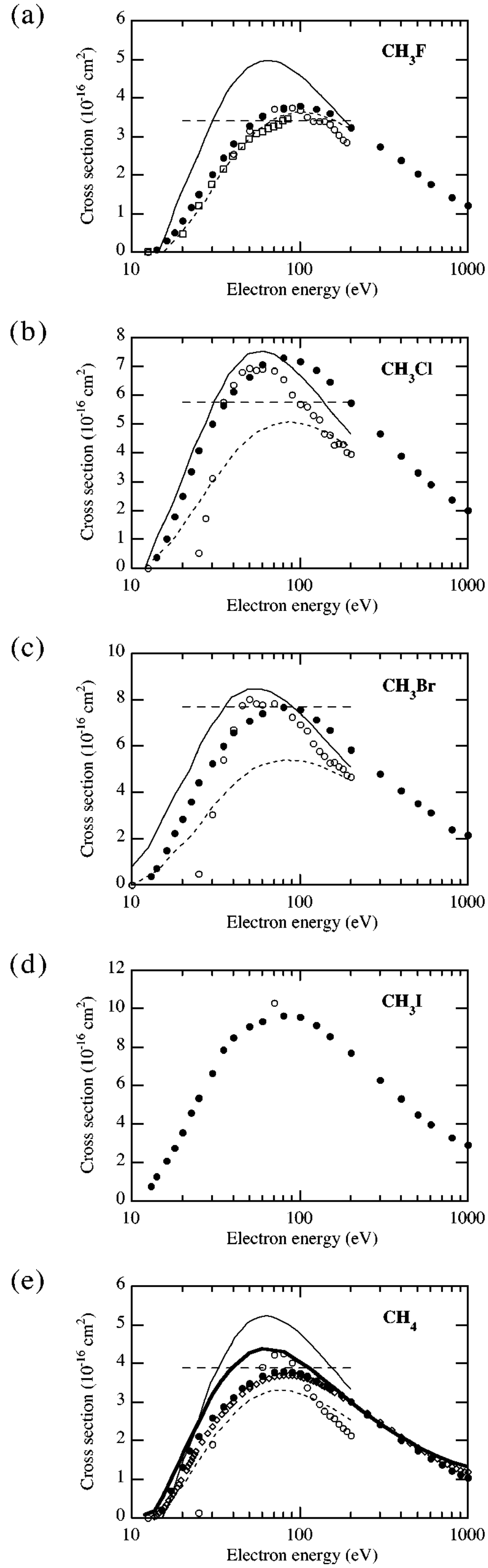

FIG. 2. Total cross sections: present results (●); Vallance *et al.* (Ref. 2) (○); Torres *et al.* (Ref. 10) (□); Rapp and Englander-Golden (Ref. 11) (◇); DM calculation of Vallance *et al.* (Ref. 2) (—); DM calculation of Deutsch *et al.* (Ref. 15) (—); BEB calculation of Vallance *et al.* (Ref. 2) (– – –); *ab initio* calculation of Vallance *et al.* (Ref. 2) (– – –).

ACKNOWLEDGMENTS

The authors gratefully acknowledge support by the Robert A. Welch Foundation and useful conversations with Dr. P. R. Brooks and Dr. P. W. Harland.

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