Electron-impact ionization of CCl_4 and CCl_2F_2

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Absolute partial and total cross sections for electron-impact ionization of CCl_4 and CCl_2F_2 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 production of CCl_3^+, CCl_2^+, CCl^+, C^+, Cl_2^+, and CCl_3^{2+} from CCl_4; and for production of CCl_2F^+, $CClF_2^+$, $CClF^+$, $(CCl^+ + CF_2^+)$, Cl^+, CF^+, F^+, and C^+ from CCl_2F_2. Data are also reported for formation of (CCl_2^+, Cl^+) and (CCl^+, Cl^+) ion pairs from CCl_4. 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 $\pm 5-7\%$. The present partial cross sections for lighter fragment ions are found to be considerably greater than had been previously reported but the most recent total cross section measurements agree well with those reported here. Neither the binary-encounter-Bethe theory nor the Deutsch–Märk theory reproduces the experimental cross sections correctly for both targets. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1761055]

I. INTRODUCTION

Electron-impact ionization of molecules is one of the most ubiquitous collision processes. Accurate electron-impact ionization data for molecular targets are necessary for understanding the physics of a wide range of environments, and for the development of quantitative theoretical descriptions of this fundamental process. Consequently, it has received much attention over the years from both experimenters and theorists and a definitive body of quantitative data has now been accumulated for the most commonplace molecules. However, for less frequently encountered molecules, there are still generally few or no reliable data to be found in the literature. Here we present partial and total cross sections for CCl_4 and CCl_2F_2. Both of these gases are atmospheric pollutants that contribute to the greenhouse effect and to ozone depletion. Hence, one object of this paper is to provide reliable partial cross section data to those concerned with understanding the effects of these gases on our atmosphere.

Partial cross sections for both CCl_4 and CCl_2F_2 have been reported by Leiter *et al.*[1,2] Total cross sections have been reported by Hudson *et al.*[3] for CCl_4, and by Pejcev *et al.*[4] and Bart *et al.*[5] for CCl_2F_2. A number of older studies[6–8] and one recent relative study[9] have also been published. The CCl_2F_2 work performed prior to 1997 has been reviewed by Christophorou *et al.*[10]

Here, absolute cross sections are reported for production of CCl_3^+, CCl_2^+, CCl^+, C^+, Cl_2^+, and CCl_3^{2+} from CCl_4; and for production of CCl_2F^+, $CClF_2^+$, $CClF^+$, $(CCl^+ + CF_2^+)$, Cl^+, CF^+, F^+, and C^+ from CCl_2F_2. Data are also reported for formation of (CCl_2^+, Cl^+) and (CCl^+, Cl^+) ion pairs from CCl_4. A few of the product ion mass peaks are not fully resolved because of their close proximity to the neighboring peaks in the time-of-flight spectra and because of the kinetic energies with which the ions are formed. In consequence, a fitting procedure is used to extract the partial cross sections for production of Cl^+ and CF^+ from CCl_2F_2, and only the aggregate $(CCl^+ + CF_2^+)$ cross section is reported. 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.[11] Briefly, during a cross-section measurement the entire vacuum chamber is filled with either CCl_4 or CCl_2F_2 at a pressure of approximately 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

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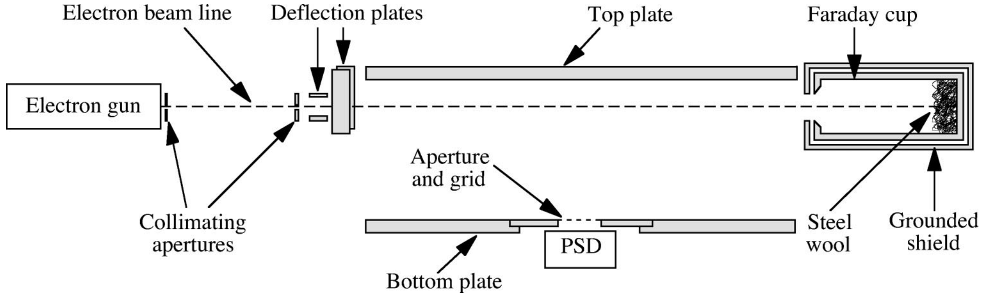

FIG. 1. Schematic diagram of the apparatus.

plate, are then accelerated and subsequently impact a PSD,[12] 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.[13] $\sigma(X)$ is then determined by measuring the four quantities on the right-hand side of Eq. (1).[11] Technical details concerning the PSD detection efficiency calibration and use of the capacitance diaphragm gauge may be found in Straub *et al.*[14] and Straub *et al.*,[15] respectively.

III. RESULTS AND DISCUSSION

For CCl_4 the ion peaks are all well resolved by the mass spectrometer. However, for CCl_2F_2, some of the product ions are formed with very nearly the same mass-to-charge ratios and cannot be separated by the time-of-flight apparatus. Fortunately, when multiply charged species, with very small cross sections, are formed in the vicinity of a much larger singly charged ion peak their presence may be neglected without compromising the quoted uncertainties. The tiny cross sections for production of doubly charged species reported by Leiter *et al.*[2] provide quantitative support for this approach. In one instance, two singly charged ions, $CClF_2^+$ and CCl_2^+, are formed in very close proximity to each other, but because the CCl_2^+ cross section has been found to be more than two orders of magnitude smaller than that for $CClF_2^+$ (Ref. 2) this peak is attributed to the dominant $CClF_2^+$ ion only. Furthermore, the Cl^+ and CF^+ time-of-flight peaks overlap and the two cross sections are comparable. In this case, there is sufficient separation between the two peaks to allow the individual cross sections to be determined by fitting the sum of two modified Gaussian distributions to the spectra.[16] For CCl^+ and CF_2^+, none of these approaches is applicable and the aggregate cross section is reported.

During the course of this work it was found that pairs of positive ions may result from electron impact of CCl_4 via

$$e+CCl_4 \rightarrow CCl_2^+ + Cl^+ + \cdots, \tag{2}$$

TABLE I. Absolute partial ionization cross sections for electron-impact ionization of CCl_4. The uncertainties in the CCl_3^+, CCl_2^+, CCl^+, Cl^+, C^+, Cl_2^+, and CCl_3^{2+} cross sections are ±5%, ±6%, ±6%, ±5%, ±7%, ±22%, and ±25%, respectively, unless otherwise indicated.

Energy (eV)	$\sigma(CCl_3^+)$ (10^{-16} cm^2)	$\sigma(CCl_2^+)$ (10^{-16} cm^2)	$\sigma(CCl^+)$ (10^{-16} cm^2)	$\sigma(Cl^+)$ (10^{-16} cm^2)	$\sigma(C^+)$ (10^{-17} cm^2)	$\sigma(Cl_2^+)$ (10^{-18} cm^2)	$\sigma(CCl_3^{2+})$ (10^{-18} cm^2)
15	1.5±0.5						
20	4.03±0.61	0.35±0.11					
25	5.38	1.19±0.10	0.62±0.11	0.085±0.030			
30	6.14	1.77±0.14	1.72±0.14	0.415±0.031	0.38±0.10	2.9	
35	6.59	1.70	2.15	0.979	1.50	5.9	1.9±0.6
40	6.36	1.64	2.23	1.66	2.11	9.1	3.5
50	6.19	1.62	2.18	2.76	2.61	9.1	5.7
60	6.53	1.69	2.20	3.43	3.12	8.8	6.1
80	6.66	1.64	2.17	3.74	3.52	8.8	7.6±3.0
100	6.85	1.70	2.01	3.97	3.78	8.5	7.6
125	6.85	1.69	1.89	3.75	3.73	8.2	6.1
150	6.63	1.62	1.76	3.57	3.49	7.7	6.0
200	6.12	1.46	1.47	2.88	2.78	5.9	6.0
300	5.47	1.31	1.17	2.15	2.07	4.9±2.3	4.4±2.3
400	4.75	1.11	0.954	1.77	1.65	4.0±1.8	3.6±1.6
500	4.25	0.998	0.867	1.53	1.46	2.8±1.1	4.2
600	3.89	0.880	0.715	1.18	1.24	2.6±1.2	3.3±1.4
800	3.18±0.19	0.724±0.110	0.574±0.086	1.04	1.03±0.27	3.1±2.2	2.4±1.8
1000	2.72±0.19	0.622±0.099	0.520±0.083	0.888	0.76±0.29	2.4±1.9	1.4±1.2

TABLE II. Absolute cross sections for production of (CCl_2^+,Cl^+) and (CCl^+,Cl^+) ion pairs by electron-impact ionization of CCl_4. The uncertainties in $\sigma(CCl_2^+,Cl^+)$ and $\sigma(CCl_2^+,Cl^+)$ are ±25%, unless otherwise indicated.

Energy (eV)	$\sigma(CCl_2^+,Cl^+)$ (10^{-17} cm^2)	$\sigma(CCl^+,Cl^+)$ (10^{-17} cm^2)
50	2.6	3.7
60	3.1	4.7
80	3.0	5.3
100	2.8	5.5
125	2.9	5.9
150	2.5	5.3
200	1.9	4.0±1.2
300	1.5±0.8	2.8
400	1.4±0.5	2.6±1.1
500	1.0±0.6	2.2
600	0.79±0.64	2.3
800		1.0±0.5
1000		1.4±1.0

$$e + CCl_4 \rightarrow CCl^+ + Cl^+ + \cdots \tag{3}$$

Cross sections for production of (CCl_2^+,Cl^+) and (CCl^+,Cl^+) ion pairs were obtained by utilizing an electronic gating technique which has been described previously.[17] Observations of ion pair production from CCl_2F_2 are discussed below.

For CCl_4, the absolute uncertainties in the CCl_3^+, CCl_2^+, CCl^+, Cl^+, C^+ cross sections are ±5%, ±6%, ±6%, ±5%, and ±7%, respectively (Table I). The uncertainties in the Cl_2^+ and CCl_3^{2+} cross sections are ±22% and ±25%; and those in the (CCl_2^+,Cl^+) and (CCl^+,Cl^+) pair production cross sections are also ±25%. For CCl_2F_2, the uncertainties in the $CClF_2^+$, $CClF^+$, and ($CCl^+ + CF_2^+$) cross sections are ±5%; those in the CCl_2F^+, Cl^+, CF^+, F^+, and C^+ cross sections are ±6%, ±12%, ±15%, ±12%, and ±6%, respectively. The relatively large uncertainties in $\sigma(Cl^+)$ and $\sigma(CF^+)$ result from the fitting procedure necessitated by the overlap of these two peaks in the mass spectra. The large F^+ uncertainty is a consequence of the underlying water vapor background. The uncertainty in the total cross sections is ±5%. Near the threshold for formation of each species the uncertainties in the cross sections are typically 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.

The measured partial cross sections are listed in Tables I–III and plotted in Figs. 2 and 3. As noted by Leiter *et al.*,[1] no stable CCl_4^+ parent ions are observed. The $CCl_2F_2^+$ parent ion peak is identifiable in the present time-of-flight spectra but the cross section is difficult to determine with any degree of accuracy. It is estimated as $1.5\pm0.6\times10^{-18}$ cm^2 at 100 eV, which is consistent with the value of $1.1\pm0.1 \times10^{-18}$ cm^2 reported by Leiter *et al.*[2]

From Fig. 2(a), it can be seen that the present CCl_3^+ cross section and that of Leiter *et al.*,[1] whose absolute uncertainty is ±20%, agree fairly well in magnitude and also seem to exhibit similar structure near 35 eV. When all of the partial cross section plots are viewed, the most obvious trend observed is that the Leiter *et al.*[1] cross sections become progressively smaller relative to the present measurements as the mass of the fragment ion decreases. This is consistent with incomplete collection of the lighter more energetic fragment ions in the earlier study. Such effects are extremely common[18] and are almost invariably present when secondary ions are analyzed with mass spectrometers embodying long path lengths. Even the large discrepancies for Cl^+ and C^+ [Figs. 2(d) and 2(e)] are not surprising when it is remembered that these are the lightest and most energetic ions formed. Recently, Karwasz *et al.*[19] noted that the CCl_4 data of Leiter *et al.*[1] are too low because of incomplete ion col-

TABLE III. Absolute partial ionization cross sections for electron-impact ionization of CCl_2F_2. The uncertainties in the $CClF_2^+$, $CClF^+$, and ($CCl^+ + CF_2^+$) cross sections are ±5%; those in the CCl_2F^+, Cl^+, CF^+, F^+, and C^+ cross sections are ±6%, ±12%, ±15%, ±12%, and ±6%, respectively, unless otherwise indicated.

Energy (eV)	$\sigma(CCl_2F^+)$ (10^{-17} cm^2)	$\sigma(CClF_2^+)$ (10^{-16} cm^2)	$\sigma(CClF^+)$ (10^{-17} cm^2)	$\sigma(CCl^+ + CF_2^+)$ (10^{-16} cm^2)	$\sigma(Cl^+)$ (10^{-16} cm^2)	$\sigma(CF^+)$ (10^{-17} cm^2)	$\sigma(F^+)$ (10^{-17} cm^2)	$\sigma(C^+)$ (10^{-17} cm^2)
15		0.72±0.12						
20	1.53±0.19	2.43±0.19		0.049±0.009				
25	3.00±0.27	3.50±0.25	0.74±0.08	0.263±0.021	0.046±0.007	0.90±0.16		
30	3.99	3.82±0.23	1.59±0.11	0.538±0.038	0.190±0.027	3.44±0.55		
35	4.31	3.88	1.92±0.12	0.742	0.443	5.28		0.238±0.024
40	4.61	3.85	2.20±0.13	0.858	0.731	5.92	0.26±0.13	0.712±0.071
50	5.22	3.98	2.52	1.02	1.19	5.68	0.57±0.10	1.29
60	5.64	4.18	2.90	1.10	1.48	5.85	0.866	1.69
80	5.87	4.21	3.18	1.15	1.75	6.35	1.60	2.25
100	6.14	4.19	3.26	1.17	1.83	6.14	2.19	2.57
125	6.09	4.09	3.12	1.11	1.76	6.18	2.52	2.66
150	5.99	3.91	3.03	1.06	1.72	5.94	2.51	2.64
200	6.02	3.78	2.96	1.01	1.59	5.07	2.54	2.37
300	5.28	3.16	2.50	0.826	1.18	4.21	1.95	1.86
400	4.67	2.76	2.26	0.706	0.968	3.40	1.65	1.51
500	4.11	2.44	1.92	0.591	0.793	2.98	1.31	1.23
600	3.91	2.23	1.66	0.542	0.709	2.67	1.20	1.06
800	3.42	1.88	1.41±0.11	0.453	0.568	2.17	0.891	0.86
1000	3.03	1.62	1.23±0.11	0.377±0.030	0.442	1.82	0.765	0.723

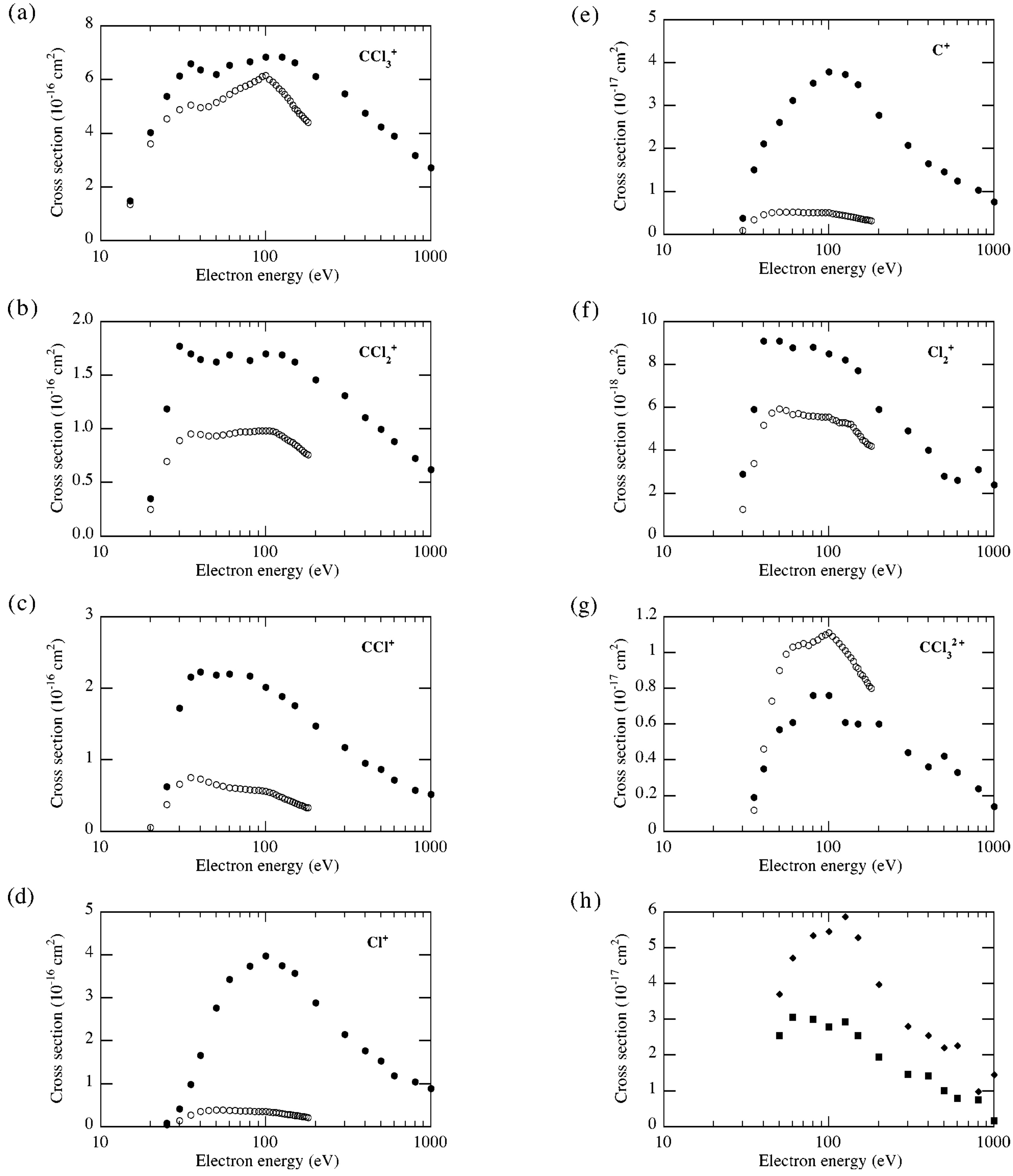

FIG. 2. Present CCl_4 partial cross sections (●) together with the data of Leiter *et al.* (Ref. 1) (○). The cross sections for production of (CCl_2^+, Cl^+) ion pairs (■); and (CCl^+,Cl^+) ion pairs (◆) are shown in (h).

lection and they attempted to correct the data to account for this.

For CCl_2F_2 (Fig. 3), the agreement between the present data and those of Leiter *et al.*,[2] whose uncertainty is $\pm 10\%$ for singly charged ions, is much better overall than for CCl_4. This is apparently a consequence of improvements to the experimental technique adopted by Leiter *et al.*[1,2] after the CCl_4 study was published, and to the fact that there are more slow heavy ions formed in the CCl_2F_2 case, and complete ion collection is therefore less problematic. It is however clear from the figure that even in the later Leiter *et al.*[2] study complete collection of the lightest ions is still not achieved.

Comparison of the Cl^+ and CF^+ cross sections [Figs. 3(e) and 3(f)] provides an interesting example of the influence of the molecular fragmentation dynamics on the laboratory observations. The Cl^+ and CF^+ fragment ions have similar masses, CF^+ is in fact slightly lighter, and one would expect, based on the above collection efficiency argument,

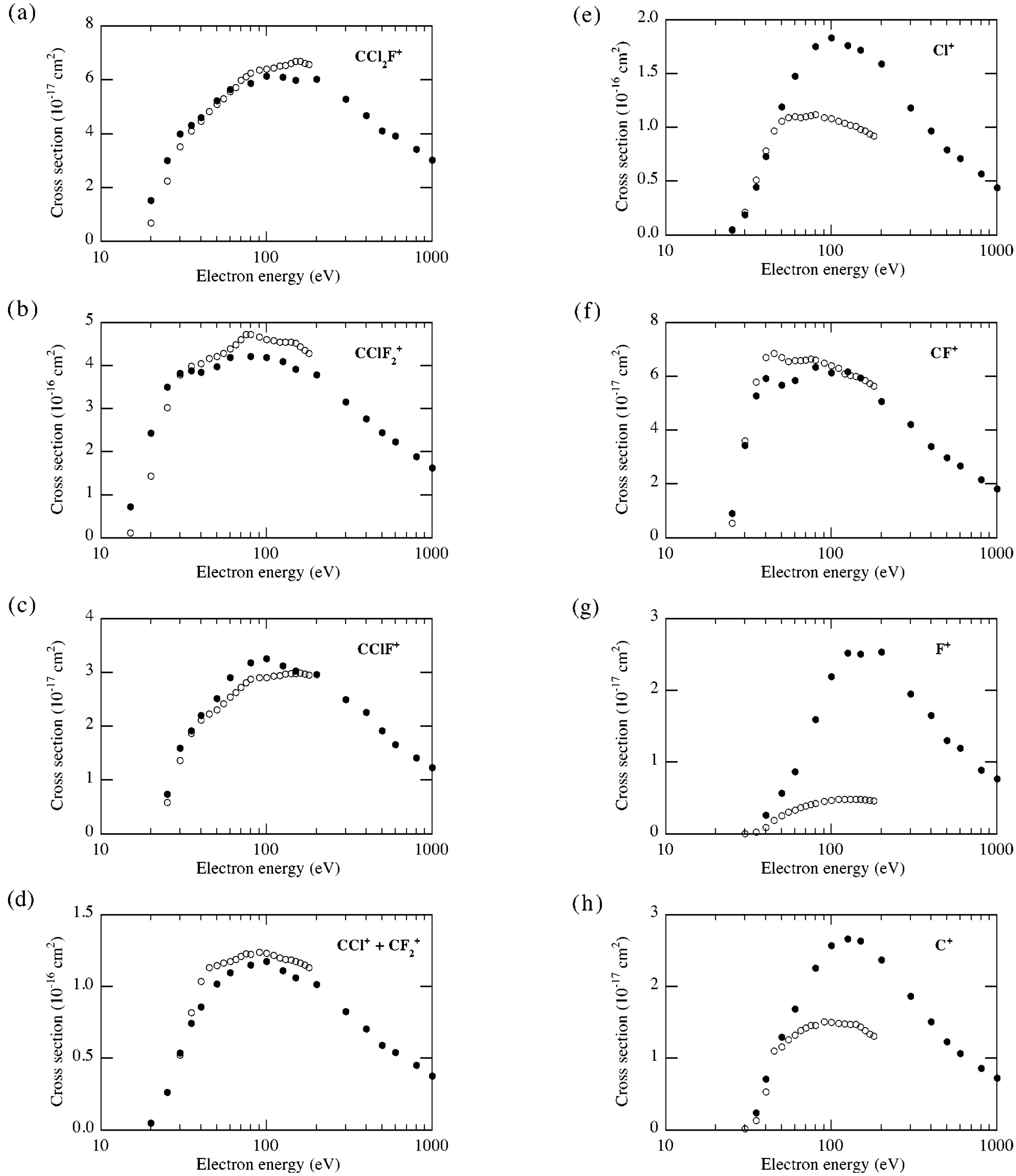

FIG. 3. Present CCl_2F_2 partial cross sections (●) together with the data of Leiter *et al.* (Ref. 2) (○).

that the disagreement between the present data and those of Leiter *et al.*[2] might be greater for CF^+ than for Cl^+. This is clearly not the case. This circumstance may, however, be explained by considering the relative kinetic energies of the two fragments which is obtainable from their arrival distributions on the PSD. At 100 eV, the full width at half maximum of the Cl^+ distribution, in the direction perpendicular to the electron beam, is 5.2 mm but for the CF^+ fragment the corresponding figure is only 3.9 mm. The fact that the CF^+ ions have considerably less kinetic energy, a consequence of the fragmentation dynamics of the molecule, explains why these ions are more easily collected and why the agreement for CF^+ is actually better than for Cl^+.

The cross sections for formation of (CCl_2^+, Cl^+) and (CCl^+, Cl^+) ion pairs from CCl_4 are shown in Fig. 2(f) and tabulated in Table II. In the case of CCl_2F_2, production of (CF_2^+, Cl^+) ion pairs was observed but due to the complex nature of the mass spectra it was not possible to determine

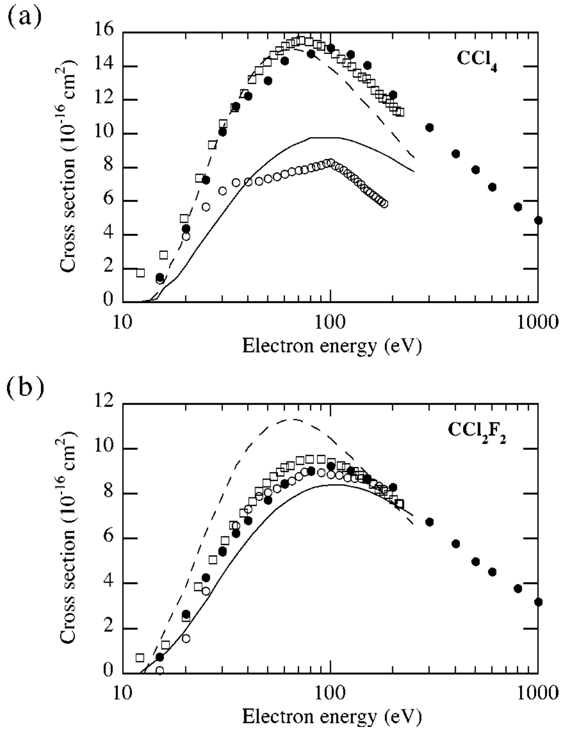

FIG. 4. (a) CCl_4 total cross section: present results (●); Leiter *et al.* (Ref. 1) (○); Hudson *et al.* (Ref. 3) experiment (□); Hudson *et al.* (Ref. 3) BEB (——); Hudson *et al.* (Ref. 3) DM (— — —). (b) CCl_2F_2 total cross section: present results (●); Leiter *et al.* (Ref. 2) (○); Bart *et al.* (Ref. 5) experiment (□); Bart *et al.* (Ref. 5) BEB (——); Bart *et al.* (Ref. 5) DM (— — —).

this cross section accurately. At 100 eV, $\sigma(CF_2^+, Cl^+)$ is estimated as $2.9\pm1.2\times10^{-17}\,cm^2$. Presently no other experimental or theoretical data exist with which to compare any of these cross sections, however, similar processes have been observed in CF_4,[17] SF_6,[20] NH_3,[18] and CH_4.[21]

Total cross sections obtained as the sum of these partial cross sections are shown in Fig. 4 together with previously published data. It should be noted that the measurements of Hudson *et al.*[3] and Bart *et al.*,[5] which are from the same laboratory, 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. Hudson *et al.*[3] and Bart *et al.*[5] estimated maximum experimental uncertainties of 4% for their data, but, as indicated by Vallance *et al.*[22] this figure does not necessarily reflect their absolute accuracy. For CCl_4, the data of Hudson *et al.*[3] agree well with the present measurements; the cross section of Leiter *et al.*[2] is considerably smaller than the other measurements as expected given their collection efficiency problems. For CCl_2F_2, it is gratifying to see that very good agreement exists between all three experiments. Calculations by Hudson *et al.*[3] and Bart *et al.*[5] obtained using the semiclassical Deutsch–Märk formalism (DM) (Ref. 23) and the binary-encounter-Bethe model (BEB) (Refs. 24 and 25) are also shown for comparison in Fig. 4. Evidently, neither theory is consistently able to reproduce the experimental cross section. The BEB approach predicts the energy at which the cross sections peak more accurately than the DM theory which predicts lower maxima than are observed. However, an improved version of the DM theory,[26] which has been applied to atomic targets, predicts slightly higher energy maxima than the version used for the calculations shown in Fig. 4.

IV. CONCLUSION

Absolute partial and total cross sections are reported for electron-impact ionization of CCl_4 and CCl_2F_2 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. The present partial cross sections for lighter fragment ions are found to be considerably greater than had been previously reported which is attributed to incomplete ion collection in the earlier studies. The most recent total cross section measurements agree well with those reported here but neither the BEB theory nor the DM theory was able to reproduce the experimental cross sections for both targets.

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[1] K. Leiter, K. Stephan, E. Märk, and T. D. Märk, Plasma Chem. Plasma Process. **4**, 235 (1984).
[2] K. Leiter, P. Scheier, G. Walder, and T. D. Märk, Int. J. Mass Spectrom. Ion Processes **87**, 209 (1989).
[3] J. E. Hudson, C. Vallance, M. Bart, and P. W. Harland, J. Phys. B **34**, 3025 (2001).
[4] V. M. Pejcev, M. V. Kurepa, and I. M. Cadez, Chem. Phys. Lett. **63**, 301 (1979).
[5] M. Bart, P. W. Harland, J. E. Hudson, and C. Vallance, Phys. Chem. Chem. Phys. **3**, 800 (2001).
[6] J. D. Craggs, C. A. McDowell, and J. W. Warren, Trans. Faraday Soc. **48**, 1093 (1952).
[7] R. E. Fox and R. K. Curran, J. Chem. Phys. **34**, 1595 (1961).
[8] J. A. Beran and L. Kevan, J. Chem. Phys. **73**, 3866 (1969).
[9] P. Limão Vieira and R. F. M. Lobo, Vacuum **52**, 19 (1999).
[10] L. G. Christophorou, J. K. Olthoff, and Y. Wang, J. Phys. Chem. Ref. Data **26**, 1205 (1997).
[11] H. C. Straub, P. Renault, B. G. Lindsay, K. A. Smith, and R. F. Stebbings, Phys. Rev. A **52**, 1115 (1995); **54**, 2146 (1996).
[12] R. S. Gao, P. S. Gibner, J. H. Newman, K. A. Smith, and R. F. Stebbings, Rev. Sci. Instrum. **55**, 1756 (1984).
[13] The CCl_4 used in this work was obtained from Sigma-Aldrich Inc. and had a specified purity of 99.9%. The CCl_2F_2 sample was originally obtained from Matheson Gas Products Inc.
[14] H. C. Straub, M. A. Mangan, B. G. Lindsay, K. A. Smith, and R. F. Stebbings, Rev. Sci. Instrum. **70**, 4238 (1999).
[15] H. C. Straub, P. Renault, B. G. Lindsay, K. A. Smith, and R. F. Stebbings, Rev. Sci. Instrum. **65**, 3279 (1994).
[16] B. G. Lindsay, M. A. Mangan, H. C. Straub, and R. F. Stebbings, J. Chem. Phys. **112**, 9404 (2000).
[17] M. R. Bruce, C. Ma, and R. A. Bonham, Chem. Phys. Lett. **190**, 285 (1992); M. R. Bruce, L. Mi, C. R. Sporleder, and R. A. Bonham, J. Phys. B **27**, 5773 (1994); D. R. Sieglaff, R. Rejoub, B. G. Lindsay, and R. F. Stebbings, *ibid.* **34**, 799 (2001).
[18] R. Rejoub, B. G. Lindsay, and R. F. Stebbings, J. Chem. Phys. **115**, 5053 (2001).

[19] G. P. Karwasz, R. S. Brusa, and A. Zecca, Riv. Nuovo Cimento **24**(4), 1 (2001).
[20] R. Rejoub, D. R. Sieglaff, B. G. Lindsay, and R. F. Stebbings, J. Phys. B **34**, 1289 (2001).
[21] B. G. Lindsay, R. Rejoub, and R. F. Stebbings, J. Chem. Phys. **114**, 10225 (2001).
[22] C. Vallance, S. A. Harris, J. E. Hudson, and P. W. Harland, J. Phys. B **30**, 2465 (1997).
[23] H. Deutsch, K. Becker, S. Matt, and T. D. Märk, Int. J. Mass. Spectrom. **197**, 37 (2000).
[24] Y.-K. Kim, W. Hwang, N. M. Weinberger, M. A. Ali, and M. E. Rudd, J. Chem. Phys. **106**, 1026 (1997).
[25] It should be noted that because the BEB approach assumes the target molecule will ionize when energetically possible the calculated cross section is, strictly speaking, an upper limit to the total ionization cross section [H. Nishimura, W. M. Huo, M. A. Ali, and Y.-K. Kim, J. Chem. Phys. **110**, 3811 (1999)].
[26] H. Deutsch, P. Scheier, K. Becker, and T. D. Märk, Chem. Phys. Lett. **382**, 26 (2003); Int. J. Mass. Spectrom. **233**, 13 (2004).