Absolute cross sections for electron-impact ionization of N_2O, H_2S, and CS_2 from threshold to 1000 eV

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Absolute partial and total cross sections for electron-impact ionization of N_2O, H_2S, and CS_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 N_2O^+, N_2^+, NO^+, N^+, and O^+ from N_2O; for production of $(H_2S^+ + HS^+ + S^+)$ and H^+ from H_2S; and for production of CS_2^+, S_2^+, CS^+, S^+, C^+, and CS_2^{2+} from CS_2. The total cross sections are obtained as the sum of these partial cross sections. The overall uncertainty in the absolute cross sections for most of the singly-charged ions is $\pm 6-8\%$. For all three targets the cross sections for production of lighter fragment ions are found to be greater than previously reported which is consistent with the presumption of incomplete collection of energetic ions in the earlier studies. Agreement with recent theoretical calculations is satisfactory for N_2O but not for H_2S or CS_2.
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I. INTRODUCTION

Ionization of molecules by electron-impact occurs in many natural and manmade plasmas and knowledge of the relevant electron-impact ionization cross sections is often essential for any meaningful physical understanding of the conditions in these environments. Accurate cross section data are also very important for the development of reliable quantitative theoretical descriptions of these fundamental processes. It has, however, been widely recognized that the reliability of much of the published research is questionable, particularly that conducted prior to the 1960s. This has prompted renewed activity in this area over the last decade with the result that a substantial body of modern data now exists. Notwithstanding these effort, there are still significant gaps in our knowledge of the cross sections for even some common triatomic molecules. In this paper, which is one in a series from this laboratory, cross sections for electron-impact ionization of N_2O, H_2S, and CS_2, all of which are of atmospheric interest, are reported. Of these targets, N_2O has received the most attention: the total N_2O cross section was measured by Rapp and Englander-Golden[1] and partial cross sections were measured by Adamczyk *et al.*,[2] Mark *et al.*,[3] and Iga *et al.*[4] For H_2S, total cross sections were measured by Belic *et al.*[5] and partial cross sections were measured by Rao and Srivastava.[6,7] The data for CS_2 are limited to partial cross section measurements by Freund *et al.*[8] and Rao and Srivastava.[9] Total cross sections for all three targets have been calculated by Kim *et al.*[10] and partial cross sections for H_2S have been calculated by Khare and Meath.[11]

Here we present absolute partial cross sections for production of N_2O^+, N_2^+, NO^+, N^+, and O^+ from N_2O; for production of $(H_2S^+ + HS^+ + S^+)$ and H^+ from H_2S; and for production of CS_2^+, S_2^+, CS^+, S^+, C^+, and CS_2^{2+} from CS_2 for electron energies from threshold to 1000 eV. Only the sum of the H_2S^+, HS^+, and S^+ cross sections is given since these ions could not be resolved by the mass spectrometer. The relatively large kinetic energies with which the N_2^+ and NO^+, and N^+ and O^+ ions are formed prevented the complete resolution of these ions in the time-of-flight spectra and a fitting procedure was therefore used to extract the individual cross sections.[12] 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.[13] Briefly, during a cross-section measurement the entire vacuum chamber is filled with the target gas at a pressure of approximately 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,[14] which records their arrival times and positions. The ion ar-

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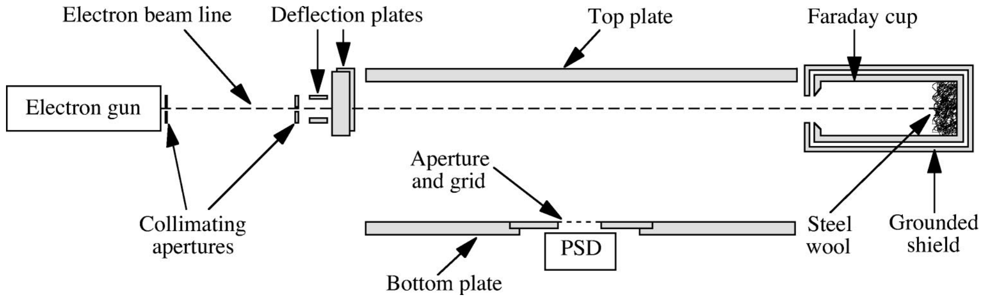

FIG. 1. Schematic diagram of the apparatus.

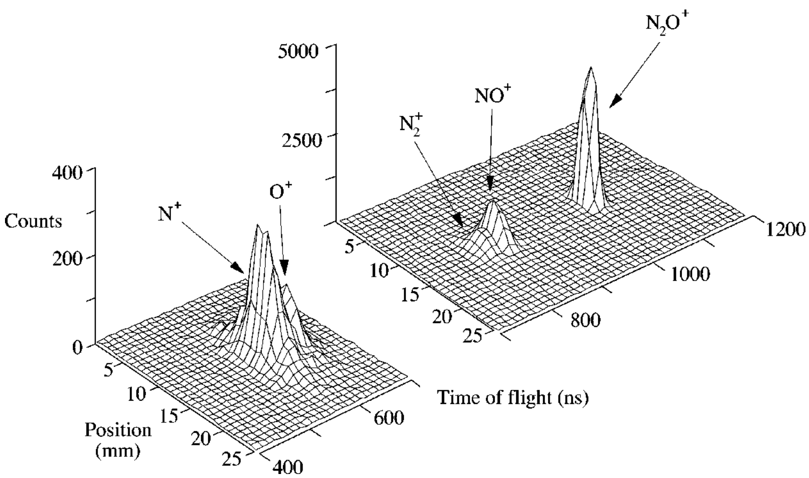

FIG. 2. Position and time-of-flight distribution of ions produced by 100 eV electron impact on N_2O. The position axis indicates the displacement of the ions perpendicular to the axis of the electron beam.

rival 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.[15] $\sigma(X)$ is then determined by measuring the four quantities on the right-hand side of Eq. (1).[13] Technical details concerning the PSD detection efficiency calibration and use of the capacitance diaphragm gauge may be found in Straub *et al.*[16] and Straub *et al.*,[17] respectively.

Complete collection of all product ions was confirmed by observing the arrival position distribution of the ions at the PSD. Figure 2 shows a plot in which the N_2O product ions' transverse arrival positions at the PSD (i.e., the displacement of ions perpendicular to the electron beam axis) have been combined with their flight times. The widths in both position and time of the singly-ionized parent molecule peak are due, primarily, to the transverse spatial extent of the electron beam while the widths for the fragment ion peaks are due to their initial velocities perpendicular to the electron beam in addition to the spatial extent of the electron beam. This figure thus gives some qualitative information about the relative energies of the various product ions.

The absolute uncertainties in the N_2O^+, $(H_2S^+ + HS^+ + S^+)$, H^+, CS_2^+, CS^+, S^+, and C^+ cross sections are ± 6–8%. The larger uncertainties in the individual N_2^+, NO^+, N^+, and O^+ cross sections, ± 10–15%, are due to the fitting procedure necessitated by the overlap of the N_2^+ and NO^+, and N^+ and O^+ peaks. The accuracies of the very small S_2^+ and CS_2^{2+} cross sections are limited primarily by the counting statistics to $\pm 30\%$ and $\pm 17\%$, respectively. 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. Note, however, that the N^+ and O^+ cross sections at low energies have been assigned smaller uncertainties because the time-of-flight peaks were well separated and fitting of the spectra was not necessary. The mean energy of the electron beam was established to within ± 0.5 eV.

III. RESULTS AND DISCUSSION: N_2O

The measured N_2O partial cross sections are listed in Table I and plotted in Fig. 3 together with the results of Märk *et al.*[3] and Iga *et al.*[4] whose associated uncertainties are given as, at least $\pm 10\%$ and $\pm 15\%$, respectively. The Adamczyk *et al.*[2] data are generally inconsistent with the other measurements and, moreover, have not been assigned an uncertainty and they are not shown on the graphs.

The N_2O^+ data of Märk *et al.*[3] [Fig. 3(a)] are in excellent agreement with the present work; and those of Iga *et al.*,[4] for the most part, also agree within the combined uncertainties. It should be noted that metastable N_2O^+ ions, fragmenting with a halflife of about 90 ns, have been observed by Newton and Sciammana[18] and that Mark *et al.*[3] reported evidence consistent with a significant N_2O^+ metastable population. In fact, Mark *et al.*[3] reported two N_2O^+ cross sections: one for the formation of stable N_2O^+ ions (shown in Fig. 3) and a much larger one which was thought to include an additional metastable component. No indication was found that metastable N_2O^+ ions were produced during the course of this investigation and it can now readily be shown, as a result of this study, that a key assumption which led Mark *et al.*[3] to deduce the presence of metastables is almost certainly incorrect. Mark *et al.*[3] inferred that metastable N_2O^+ ions were present in their experiment, and decomposing as they passed through the apparatus, by comparing two different normalization procedures which yielded very different results. In the first procedure, the results of which are plotted in Fig. 3, they correctly normalized their N_2O^+ data to the known Ar^+ cross section. In the second they normalized their N_2O^+ data to the cross section for production of low kinetic energy ions measured by Rapp *et al.*[19] which gave a much greater apparent N_2O^+ cross section. The tacit, assumption in the second normalization procedure is that the low energy product ions observed by Rapp and *et al.*[19] were all N_2O^+. However, as can be seen from Fig. 2, N_2^+ and NO^+ ions are also formed with relatively little kinetic energy and could therefore have contributed to the cross section reported by Rapp *et al.*[19] This contention is further supported by the fact that the sum of the present N_2^+ and NO^+ cross sections is consistent with the apparent metastable population seen by Mark *et al.*[3]

The N_2^+ and NO^+ cross sections of Iga *et al.*[4] shown in Fig. 3 generally agree with those measured here but their N^+ and O^+ cross sections are much smaller than observed in this investigation. As seen in Fig. 2, the N_2^+ and NO^+ ions are formed with little kinetic energy but the lighter N^+ and O^+ ions are much more energetic and therefore more easily escape detection. The differences between the present N^+ and O^+ cross sections and those of Iga *et al.*[4] are most probably due to incomplete collection of the lighter ions in that study. Such effects are not uncommon, e.g., Rejoub *et al.*[20]

TABLE I. Absolute partial cross sections for electron-impact ionization of N_2O. The uncertainties in the N_2O^+, N_2^+, NO^+, N^+, and O^+ cross sections are $\pm 6\%$, $\pm 15\%$, $\pm 10\%$, $\pm 10\%$, and $\pm 15\%$, respectively, unless otherwise indicated.

Energy (eV)	$\sigma(N_2O^+)$ (10^{-16} cm^2)	$\sigma(N_2^+)$ (10^{-17} cm^2)	$\sigma(NO^+)$ (10^{-17} cm^2)	$\sigma(N^+)$ (10^{-17} cm^2)	$\sigma(O^+)$ (10^{-17} cm^2)
14	0.067±0.008				
16	0.269±0.022				
18	0.411±0.029		0.131±0.026		
20	0.527	0.066±0.020	0.564		0.066±0.026
22.5	0.684	0.17±0.05	1.36	0.023±0.006	0.163±0.020
25	0.827	0.47±0.12	2.37	0.059±0.006	0.315±0.032
27.5	0.922	0.97±0.20	3.03	0.187±0.019	0.407±0.041
30	1.02	1.41	3.44	0.237±0.024	0.466±0.047
35	1.17	2.23	4.71	0.958	0.860
40	1.29	2.72	5.23	1.73	1.15
50	1.41	3.23	6.54	2.82	1.67
60	1.48	3.63	7.35	3.75	2.40
70	1.54	3.87	8.09	4.67	2.85
80	1.57	3.72	8.64	5.26	3.19
90	1.56	3.98	8.54	5.96	3.20
100	1.56	3.79	8.65	6.18	3.47
120	1.53	3.65	8.65	6.63	3.41
140	1.51	3.30	8.82	6.57	3.57
160	1.46	3.18	8.66	6.27	3.47
200	1.39	2.97	8.19	5.85	3.37
250	1.30	2.52	7.75	5.25	3.05
300	1.22	2.53	7.12	4.86	2.65
400	1.06	1.91	6.34	3.77	2.32
500	0.950	1.71	5.69	3.20	2.02
600	0.844	1.52	5.07	2.69	1.71
800	0.731	1.38	4.00	2.28	1.17
1000	0.666	1.17	3.53	2.03	0.807

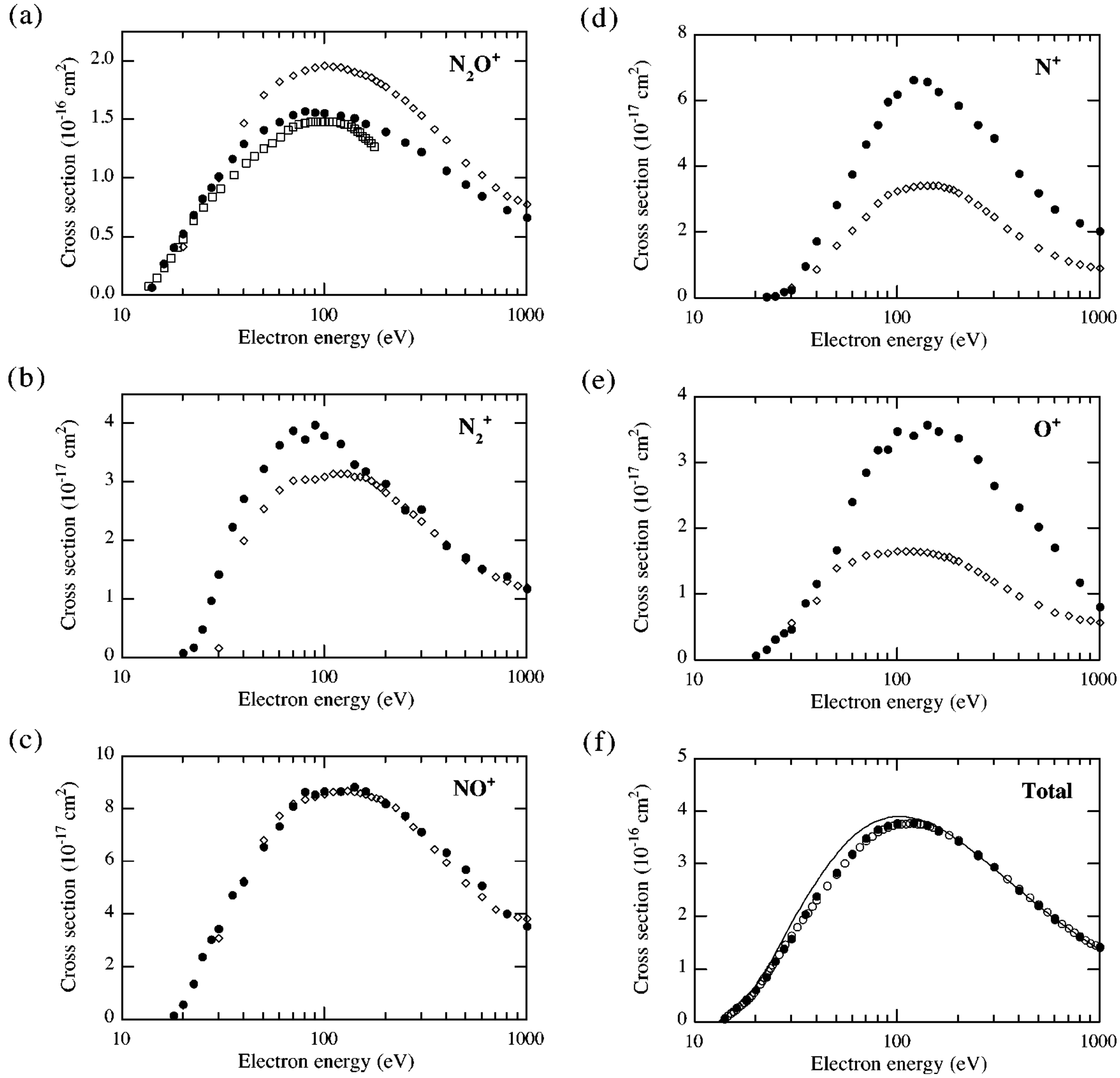

FIG. 3. Present N_2O cross sections (●) together with those of Rapp and Englander-Golden (Ref. 1) (○); Märk *et al.* (Ref. 3) (□); Iga *et al.* (Ref. 4) (◇); and the BEB calculations of Kim *et al.* (Ref. 10) (—). Note that the Märk *et al.* (Ref. 3) data are for production of stable N_2O^+ ions only.

The present N_2O total ionization cross section is shown in Fig. 3(f) together with that of Rapp and Englander-Golden[1] and the calculation of Kim *et al.*,[10] obtained using the binary-encounter-Bethe (BEB) method. Note that prior measurements from studies where incomplete ion collection seems probable are not shown in this plot and a similar approach is adopted for the H_2S and CS_2 targets discussed later. Clearly, the present cross section and that of Rapp and Englander-Golden,[1] whose uncertainty is $\pm 7\%$, are in excellent agreement. The calculated cross section of Kim *et al.*[10] also agrees extremely well with the experimental data, but it should be noted that, strictly speaking, this theoretical approach leads to an upper limit for the total ionization cross section and the agreement may therefore not be quite as good as it might appear.

IV. RESULTS AND DISCUSSION: H_2S

The present H_2S partial cross sections are listed in Table II and plotted in Figs. 4(a) and 4(b) together with the experimental results of Rao and Srivastava,[6] whose uncertainty is $\pm 13\%$, and the semiempirical calculations of

TABLE II. Absolute partial cross sections for electron-impact ionization of H_2S. The uncertainties in the H_nS^+ and H^+ cross sections are $\pm 6\%$ and $\pm 7\%$, respectively, unless otherwise indicated.

Energy (eV)	$\sigma(H_nS^+)$ (10^{-16} cm^2)	$\sigma(H^+)$ (10^{-17} cm^2)
16	2.11 ± 0.53	
18	2.92 ± 0.44	
20	3.87 ± 0.31	
25	4.51 ± 0.32	0.48 ± 0.12
30	4.88 ± 0.34	1.93
40	5.03	4.51
50	4.92	5.56
60	4.92	6.05
80	4.69	6.28
100	4.54	6.07
150	3.91	4.37
200	3.36	3.69
300	2.77	2.66
400	2.42	2.19
500	2.19	1.89
600	1.87 ± 0.17	1.44 ± 0.14
800	1.52 ± 0.18	1.36 ± 0.20
1000	1.29 ± 0.15	0.93 ± 0.23

Khare and Meath.[11] Although the magnitude of the H_nS^+ cross section reported by Rao and Srivastava[6] is not greatly dissimilar to the present cross section, the agreement is clearly very unsatisfactory. For the H^+ cross section the agreement is much worse than for the heavier product ions, the present data being about a factor of 5 greater than those of Rao and Srivastava,[6] a result consistent with incomplete collection of the lighter more energetic H^+ ions in the earlier study. The magnitude of the discrepancy seen here is larger than that observed for the N^+ and O^+ cross sections discussed above but similar to that reported for production of H^+ ions from NH_3.[20] The Khare and Meath[11] calculations considerably underestimate both the H_nS^+ and the H^+ cross sections which is not surprising given the extreme difficulty of calculating partial ionization cross sections for molecules.

Figure 4(c) shows the present H_2S total ionization cross section compared to the measurements of Belic and Kurepa[5] and the BEB calculations of Kim *et al.*[10] The Belic and Kurepa[5] measurement agrees quite well with the present data although the significance of this agreement is difficult to judge as no uncertainty was assigned to their cross section. Both BEB calculations considerably underestimate the measured cross section; the modified BEB (U/3) calculation being closest to the experimental data. The agreement is probably even less satisfactory than it might appear, however, as the BEB theory actually predicts an upper limit for the total cross section.

V. RESULTS AND DISCUSSION: CS_2

The present CS_2 partial cross sections are listed in Table III and are shown in Fig. 5 together with those of Freund *et al.*[8] and Rao and Srivastava,[9] whose relative uncertainties are $\pm 10\%$ and $\pm 15\%$, respectively. For CS_2^+ the agreement between the three measurements is good below 200 eV. Good agreement is also seen for the S_2^+ and CS^+ cross sections, with the exception of the region around 30 eV where Rao and Srivastava[9] observe uncharacteristically narrow peaks for which there is no clear evidence in the data presented here. There is, however, some slight suggestion of a peak in the present S_2^+ cross but it is impossible to be more definitive due to the scatter in the present data. Plainly there is no structure comparable to that seen by Rao and Srivastava[9] in the CS^+ cross section [Fig. 5(c)]. The present S^+ cross section and that of Rao and Srivastava[9] also disagree in that they peak at very different energies and have markedly different shapes. Furthermore, there are large discrepancies between the Rao and Srivastava[9] C^+ and CS_2^{2+} measurements and those presented here. No single explanation for all of these differences presents itself but it is noteworthy that the narrow structures seen by Rao and Srivastava[9] in the S_2^+, CS^+, and S^+ cross sections all appear at the same energy.

The present total cross section [Fig. 5(g)] is greater than the BEB calculation of Kim *et al.*[10] but the disagreement is considerably less than for H_2S. As for H_2S, the modified BEB (U/3) curve is an improvement on the simple BEB approach.

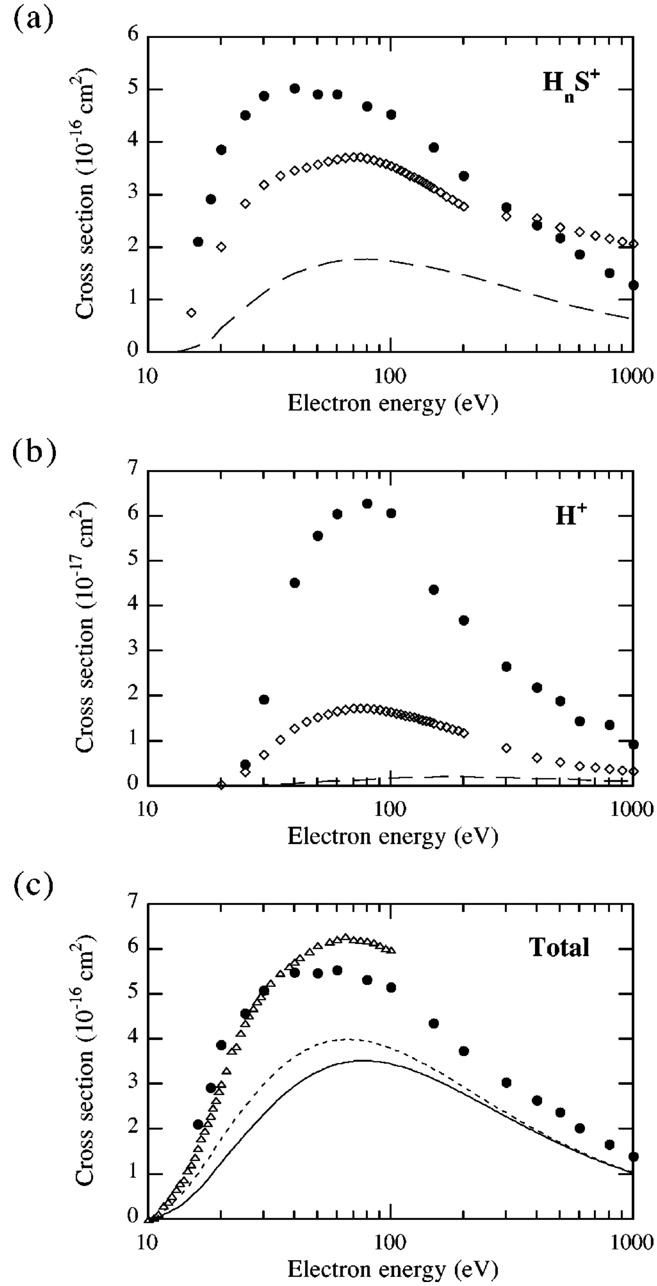

FIG. 4. Present H_2S cross sections (●) together with the those of Rao and Srivastava (Ref. 6) (◇); Belic and Kurepa (Ref. 5) (△); the semiempirical calculations of Khare and Meath (Ref. 11) (–––); the BEB calculations of Kim *et al.* (Ref. 10) (—); and the modified BEB (U/3) theory of Kim *et al.* (Ref. 10) (---).

VI. CONCLUSION

Absolute partial cross sections are reported for N_2O, H_2S, and CS_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. For all three targets the partial cross sections for production of lighter fragment ions are found to be considerably greater than previously reported which is consistent with incomplete collection of

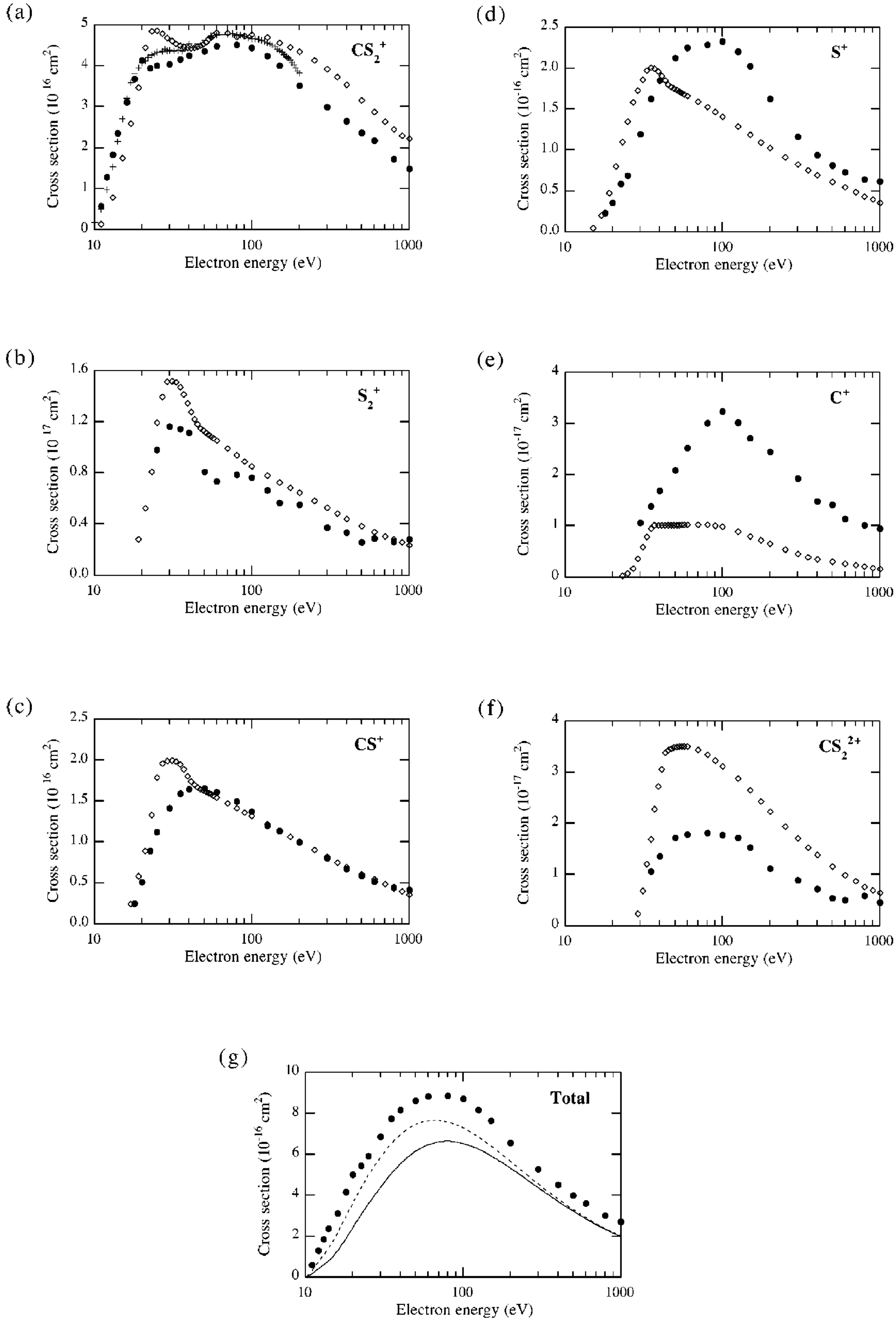

FIG. 5. Present CS_2 cross sections (●) together with those of Freund *et al.* (Ref. 8) (+); Rao and Srivastava (Ref. 9) (◇); the BEB calculations of Kim *et al.* (Ref. 10) (—); and the modified BEB (U/3) theory of Kim *et al.* (Ref. 10) (---).

TABLE III. Absolute partial cross sections for electron-impact ionization of CS_2. The uncertainties in the CS_2^+, S_2^+, CS^+, S^+, C^+, and CS_2^{2+} cross sections are ±6%, ±30%, ±6%, ±6%, ±8%, and ±17% respectively, unless otherwise indicated.

Energy (eV)	$\sigma(CS_2^+)$ (10^{-16} cm^2)	$\sigma(S_2^+)$ (10^{-17} cm^2)	$\sigma(CS^+)$ (10^{-16} cm^2)	$\sigma(S^+)$ (10^{-16} cm^2)	$\sigma(C^+)$ (10^{-17} cm^2)	$\sigma(CS_2^{2+})$ (10^{-17} cm^2)
11	0.58±0.09					
12	1.29±0.13					
13	1.84±0.18					
14	2.36±0.18					
16	3.11±0.24					
18	3.68±0.29		0.251±0.043	0.231±0.034		
20	4.14		0.507±0.086	0.354±0.060		
22.5	3.95		0.89±0.27	0.59±0.18		
25	4.00	1.0±0.6	1.12	0.684±0.068		
30	4.04	1.2±0.6	1.41	1.19	1.06±0.12	
35	4.16	1.1±0.6	1.59	1.63	1.39±0.14	1.06±0.53
40	4.25	1.1±0.5	1.64	1.85	1.68±0.17	1.36
50	4.36	0.81±0.40	1.66	2.12	2.09±0.21	1.72
60	4.47	0.73±0.36	1.61	2.25	2.52	1.78
80	4.51	0.79	1.49	2.29	3.01	1.81
100	4.44	0.76	1.37	2.32	3.24	1.77
125	4.23	0.66	1.20	2.20	3.02	1.71
150	4.00	0.56	1.13	2.02	2.71	1.53
200	3.51	0.55	0.999	1.63	2.45	1.12
300	2.99	0.37	0.800	1.16	1.93	0.888
400	2.65	0.33	0.670	0.937	1.48	0.722
500	2.37	0.26±0.18	0.584	0.813	1.42	0.535
600	2.18	0.29±0.20	0.513	0.726	1.13±0.11	0.502
800	1.73	0.26±0.18	0.445±0.036	0.641±0.064	1.02±0.15	0.581
1000	1.50	0.28±0.20	0.413±0.033	0.615±0.062	0.95±0.14	0.46±0.16

energetic ions in the earlier studies. The discrepancy observed for H_nS^+ suggests that another measurement of the H_2S^+, HS^+, and S^+ partial cross sections, which are not reported here, is very desirable. Agreement with recent theoretical calculations is satisfactory for N_2O but not for H_2S or CS_2.

ACKNOWLEDGMENT

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[1] D. Rapp and P. Englander-Golden, J. Chem. Phys. **43**, 1464 (1965).
[2] B. Adamczyk, K. Bederski, L. Wojcik, and T. Stanski, Folio Scientatis Scientiarum Lublinensis Mat.-Fiz.-Chem. **18**, 217 (1976).
[3] E. Märk, T. D. Märk, Y. B. Kim, and K. Stephan, J. Chem. Phys. **75**, 4446 (1981).
[4] I. Iga, M. V. V. S. Rao, and S. K. Srivastava, J. Geophys. Res. [Planets] **101**, 9261 (1996).
[5] D. S. Belic and M. V. Kurepa, Fizika (Zagreb) **17**, 117 (1985).
[6] M. V. V. S. Rao and S. K. Srivastava, J. Geophys. Res. [Planets] **98**, 13137 (1993).
[7] The early work of J. W. Otvos and D. P. Stevenson, J. Am. Chem. Soc. **78**, 546 (1956) and F. W. Lampe, J. L. Franklin, and F. H. Field, *ibid.* **79**, 6129 (1957) is not considered here.
[8] R. S. Freund, R. C. Wetzel, and R. J. Shul, Phys. Rev. A **41**, 5861 (1990).
[9] M. V. V. S. Rao and S. K. Srivastava, J. Geophys. Res. **96**, 17563 (1991).
[10] Y.-K. Kim, W. Huang, N. M. Weinberger, M. Ali, and M. E. Rudd, J. Chem. Phys. **106**, 1026 (1997).
[11] S. P. Khare and W. J. Meath, J. Phys. B **20**, 2101 (1987).
[12] B. G. Lindsay, M. A. Mangan, H. C. Straub, and R. F. Stebbings, J. Chem. Phys. **112**, 9404 (2000).
[13] H. C. Straub, P. Renault, B. G. Lindsay, K. A. Smith, and R. F. Stebbings, Phys. Rev. A **52**, 1115 (1995); **54**, 2146 (1996).
[14] R. S. Gao, P. S. Gibner, J. H. Newman, K. A. Smith, and R. F. Stebbings, Rev. Sci. Instrum. **55**, 1756 (1984).
[15] The N_2O used in this work was obtained from Matheson Gas Products, Inc. and has a specified purity of 99.99%. The H_2S and CS_2 were obtained from the Aldrich Chemical Company and have purities of 99.5% and 99.9%, respectively.
[16] H. C. Straub, M. A. Mangan, B. G. Lindsay, K. A. Smith, and R. F. Stebbings, Rev. Sci. Instrum. **70**, 4238 (1999).
[17] H. C. Straub, P. Renault, B. G. Lindsay, K. A. Smith, and R. F. Stebbings, Rev. Sci. Instrum. **65**, 3279 (1994).
[18] A. S. Newton and A. F. Sciamanna, J. Chem. Phys. **44**, 4327 (1966); **52**, 327 (1970).
[19] D. Rapp, P. Englander-Golden, and D. D. Briglia, J. Chem. Phys. **42**, 4081 (1965).
[20] R. Rejoub, B. G. Lindsay, and R. F. Stebbings, J. Chem. Phys. **115**, 5053 (2001).