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Measurements of electron-impact-ionization cross sections of N_2, CO, CO_2, CS, S_2, CS_2, and metastable N_2

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Electron-impact-ionization cross sections to form the parent ions of N_2, CO, CO_2, CS, S_2, and CS_2 have been measured with the same apparatus used recently to measure ionization cross sections of 27 atoms with an absolute accuracy of ±10%. The ionization cross sections for CS, S_2, and CS_2 are measured here for the first time to our knowledge. The results for N_2, CO, and CO_2 generally agree with previous measurements. A remeasurement of the ionization cross sections of metastable N_2 improves upon our previous measurement.

I. INTRODUCTION

Despite the many years that electron-impact ionization cross sections have been measured,[1,2] few species have been studied by more than one or two different laboratories. Without independent measurements it is difficult to assess the accuracy of the measurements which are available. Another approach to assess measurement accuracy is to examine the results from a single laboratory for a number of species with known cross sections, and use systematic deviations of the results to indicate systematic measurement errors with that apparatus. This approach also has been of limited applicability since few laboratories have reported ionization cross sections for more than five different species.

Recently, we reported measurements of ionization cross sections for 27 atoms.[3] In the present work, the same apparatus is used to measure cross sections for ionization of three molecules whose cross sections have been measured more than four times before (N_2, CO, and CO_2), and three other molecules whose cross sections have never been measured to our knowledge (CS, S_2, CS_2). In addition, we improve upon our previous measurement of the ionization cross section of metastable N_2.[4]

II. EXPERIMENT

The apparatus is described in detail in previous papers.[3,5,6] Briefly, a beam of molecules is prepared by charge-transfer neutralization of a mass separated ion beam and is then ionized by a well-characterized electron beam. The product ions are focused at the entrance of a hemispherical energy analyzer, which separates parent ions from fragment ions. Absolute measurements are made by measuring the neutral beam flux with a pryoelectric detector, calibrated with respect to the well-known ionization cross sections of Ar and Kr. Based on the discussion in Ref. 3, we estimate these cross sections to be accurate to ±10% (1σ).

Beams of neutral molecules were prepared from the source and charge-transfer gases listed in Table I. Figure 1 shows as an example the mass spectrum of ions formed from a CS_2 discharge and the neutral molecules formed by symmetric charge transfer with CS_2. The three major neutral molecules which form are studied in this work; the S atom was studied previously.[3] The ion at mass 38 is probably $CS_2{}^{2+}$ and the one at mass 28 is probably $N_2{}^+$ from outgassing or from a small leak in the source; neither is neutralized significantly. Formation of electronically and vibrationally excited states by charge transfer is discussed below. The intensity of signal from Rydberg states, formed by charge transfer, is below the level of detection, so no correction for them is necessary.

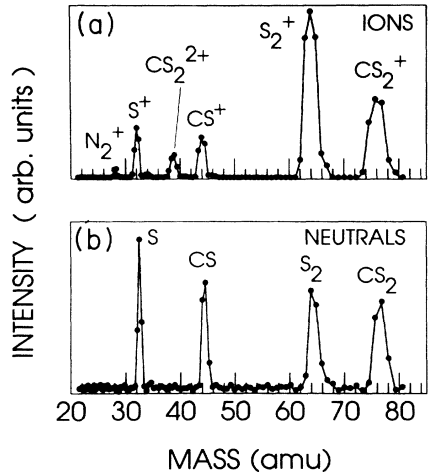

FIG. 1. Mass spectra of CS_2. (a) Mass spectrum of ion beam. (b) Mass spectrum of neutral beam formed by charge-transfer neutralization with CS_2.

TABLE I. Source and charge-transfer gases.

Molecule studied	Source gas	Charge-transfer gas
N_2	N_2	N_2, triethylamine
CO	CO	CO_2, CO, triethylamine
CS	CS_2	cyclopropane, ethane
S_2	CS_2	cyclopropane, ethane, butadiene
CO_2	CO_2	CO_2
CS_2	CS_2	CS_2, cyclopropane

III. RESULTS AND DISCUSSION

A. Thresholds

The ionization thresholds (Fig. 2) give information on whether or not the molecules are in their ground states. CO_2 and CS_2 must be in their ground electronic states, since their lowest-lying excited electronic states are many eV above the ground states,[7] and the measured cross sections would show easily detected signals below the ground-state thresholds if excited electronic states were present. The thresholds for both of these molecules show only a small amount of curvature, consistent with the electron energy spread, so there is little or no vibrational excitation. Since these molecules are formed by symmetric charge transfer with only $v=0$ significantly populated in the room-temperature gas, $v=0$ is expected to form preferentially.

The S_2 threshold shows slightly more curvature. Its first excited electronic state is at only 0.6 eV,[8] and so might be populated. Alternatively, there could be approximately 0.3 eV of vibrational energy corresponding to up to $v=3$ (the vibrational quantum of S_2 is 0.09 eV).[7]

For N_2, CO, and CS, the major thresholds correlate well with the ground-state ionization potentials.[9] However, there are significant signals extending several eV below the ground-state threshold. These result from the presence of metastable excited states, the lowest of which lies at 6 eV in CO, in 6.5 eV in N_2, and at 3.4 eV in CS.[7] Of course, excited vibrational levels of the ground state could also be populated, although for CO and N_2, for which symmetric charge transfer is used, neutralization to $v=0$ should be favored.

Further information on the contribution of metastable states of N_2 and CO is given by the thresholds shown in Fig. 3. Use of triethylamine (TEA) as a nonsymmetric charge-transfer gas greatly increases the intensity of the signal arising from metastable neutrals. This is apparently because a metastable electronic state is present in the ion beam and is neutralized to a metastable state of the neutral molecule, a process which is nearly resonant with TEA [with an ionization potential (IP) of 8.1 eV (Refs. 10 and 11)] but not with a N_2 or CO charge-transfer gas. The appropriate energy levels of N_2 are illustrated in Fig. 8 of Ref. 4. Similarly, for CO, the energy difference between $CO^+(A\ ^2\Pi)$ and the lowest vibrational level of $CO(a'\ ^3\Sigma)$ is 9.66 eV, close to the IP of TEA [neutralization directly to $CO(a\ ^3\Pi)$ requires a 2-electron transition and so should be unimportant].

The effect of the radiative lifetime of a metastable CO ion is shown in Fig. 4. The radiative lifetime of CO^+ $A\ ^2\Pi$ is known to vary from 3.5 to 2.4 μs for $v=1$ to 8.[7] This lifetime is close to the time of flight (TOF) for CO^+ to travel 40.6 cm from the ion source to the charge-transfer cell, calculated to be 4.8 μs for a 1-keV beam, 3.4 μs for a 2-keV beam, and 2.8 μs for a 3-keV beam (the actual TOF is somewhat longer since the beam energy is lower in the einzel lens and during initial acceleration from the ion source). The relatively low intensity (Fig. 4) of signal below the ground-state threshold for the 1-keV beam is consistent with its longer TOF allowing more of the metastable ions to radiate to their ground state before they reach the charge-transfer cell. The variation with beam energy should be smaller in N_2 because the radiative lifetime of $N_2^+(A\ ^2\Pi)$ is longer than the TOF, vary-

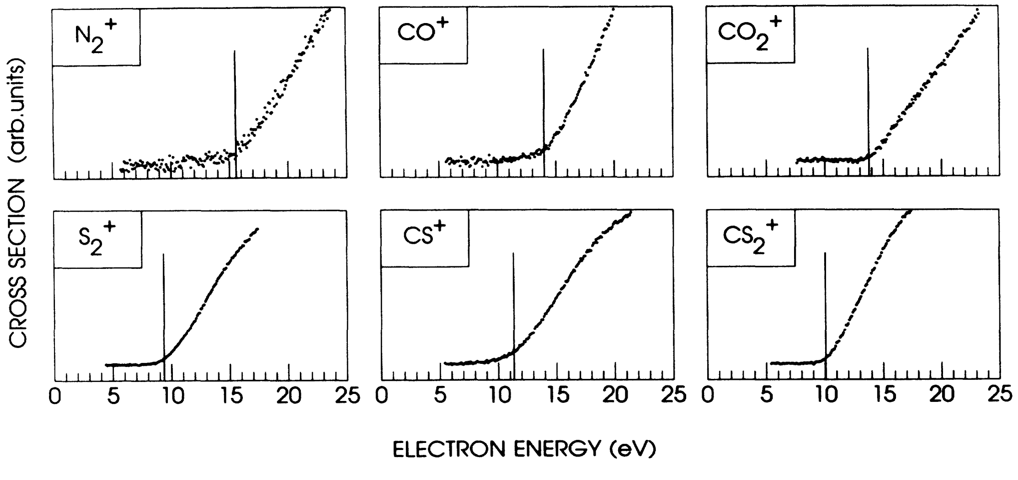

FIG. 2. Ionization thresholds measured with the first charge-transfer gas listed in Table I. Vertical lines indicate the ground-state ionization potentials.

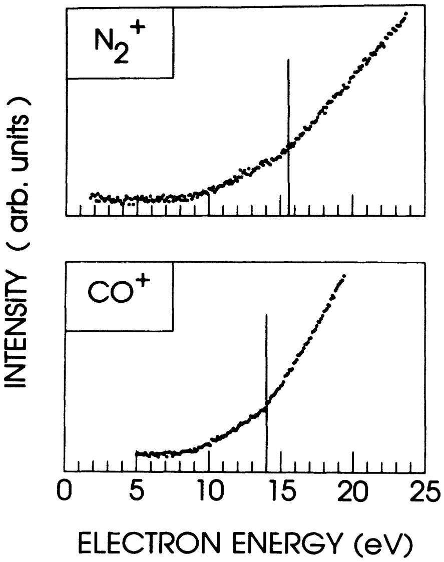

FIG. 3. Thresholds for N_2 and CO formed by charge transfer with triethylamine, showing the presence of metasable states in the neutral beams.

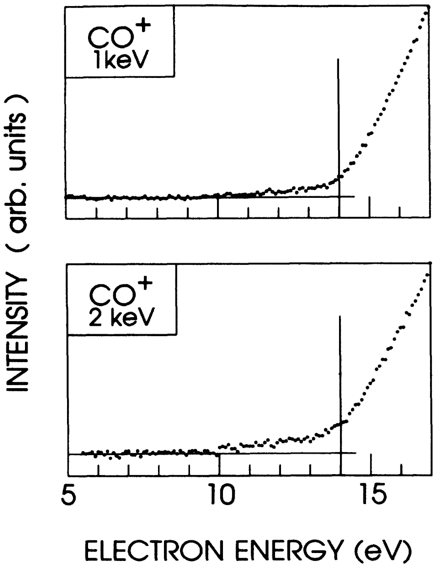

FIG. 4. Thresholds for CO formed by charge transfer with CO_2, showing that there is more metastable state present in the 2-keV beam.

ing from 13.9 to 7.3 μs for vibrational levels from $v=1$ to 8, the levels likely to be populated in the ion beam.

B. Measured cross sections

Measured ionization cross sections for formation of parent ions of 70-eV electron impact are given in Table II. The standard deviations for 4 to 6 measurements are all smaller than ±5%. These 70-eV values are used to normalize the relative cross sections measured from threshold to 200 eV. The results are given in Fig. 5 and Table III. Shape corrections, less than 5%, were made below 50 eV and above 150 eV according to Eq. (15) in Ref. 5.

Separate ionization cross sections for the ground state σ_G and for the metastable state σ_M of N_2 have been derived from the cross sections measured with N_2 and TEA charge-transfer gases, denoted as σ_N and σ_T, respectively. (The subscripts G and M are used to refer to ground and metastable states, respectively, and the subscripts N

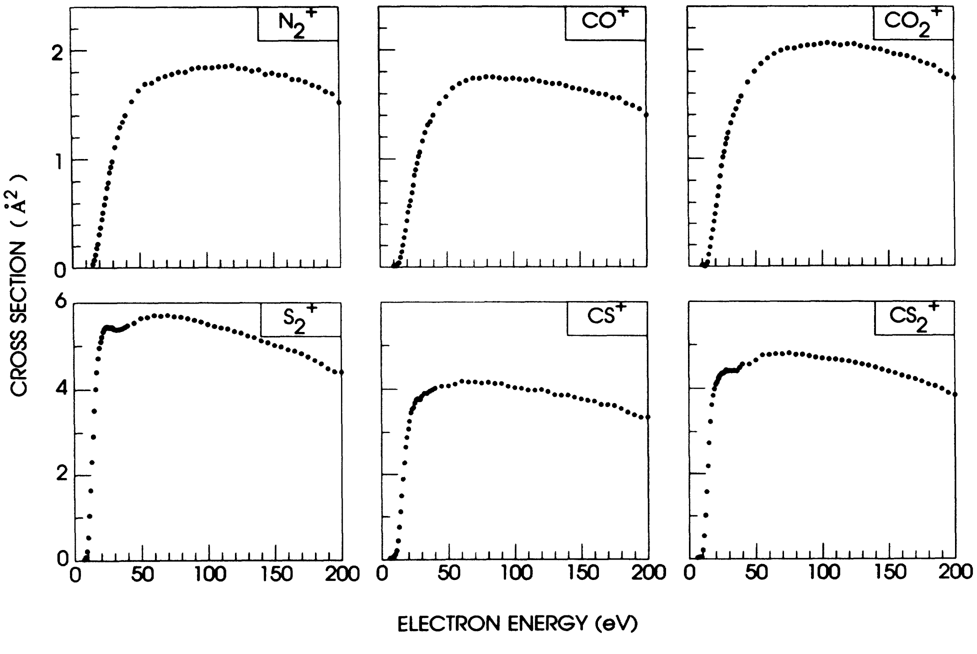

FIG. 5. Single ionization cross sections from 0 to 200 eV.

TABLE II. Measurements of absolute cross sections at 70 eV.

Run No.	N_2[a]	N_2[b]	CO	CO_2	CS	S_2	CS_2
1	1.76	1.85	1.88	2.03	3.98	5.45	4.93
2	1.72	1.94	1.71	1.98	3.97	5.58	4.72
3	1.78	1.87	1.69	1.90	3.98	5.86	4.78
4	1.85	1.80	1.64	2.01	3.92	6.02	4.65
5			1.74			5.56	
6						5.49	
Average	1.78	1.87	1.73	1.98	3.96	5.66	4.76
St. dev.	0.05	0.06	0.08	0.05	0.03	0.21	0.12
St. dev.%	2.6	3.2	4.7	2.5	0.7	3.7	2.6

[a] With N_2 charge-transfer gas.
[b] With TEA charge-transfer gas.

TABLE III. Cross sections (Å^2) for electron-impact single ionization to the parent ion.

Electron energy (ev)	N_2[a]	N_2[b]	N_2[c]	N_2[d]	CO	CS	S_2	CO_2	CS_2
6						0.00			0.00
7						0.01	0.00		0.01
8						0.02	0.04		0.02
9			0.00	0.00		0.05	0.17		0.02
10			0.01	0.03		0.09	0.46		0.18
11		0.00	0.02	0.06		0.18	0.91		0.51
12		0.03	0.07	0.15		0.39	1.53		0.98
13		0.04	0.10	0.21		0.70	2.23	0.00	1.54
14		0.03	0.13	0.32	0.00	1.05	2.84	0.03	2.15
15		0.03	0.16	0.42	0.08	1.40	3.44	0.10	2.71
16	0.00	0.06	0.23	0.58	0.13	1.78	3.95	0.17	3.21
17	0.03	0.11	0.30	0.69	0.19	2.15	4.32	0.25	3.59
18	0.09	0.17	0.35	0.72	0.26	2.51	4.67	0.33	3.81
19	0.12	0.22	0.42	0.82	0.33	2.73	4.93	0.41	3.96
20	0.21	0.30	0.51	0.91	0.42	2.91	5.04	0.48	4.07
21	0.27	0.36	0.56	0.97	0.50	3.09	5.16	0.56	4.12
22	0.35	0.45	0.65	1.08	0.56	3.27	5.28	0.65	4.20
23	0.41	0.51	0.71	1.14	0.61	3.36	5.36	0.73	4.26
24	0.48	0.59	0.80	1.24	0.68	3.39	5.43	0.83	4.30
25	0.54	0.66	0.87	1.36	0.75	3.49	5.45	0.92	4.33
26	0.64	0.74	0.93	1.34	0.84	3.57	5.39	1.00	4.33
27	0.69	0.80	0.98	1.42	0.89	3.58	5.37	1.05	4.36
28	0.79	0.88	1.04	1.42	0.95	3.56	5.37	1.12	4.40
29	0.84	0.93	1.10	1.50	1.01	3.57	5.38	1.17	4.37
30	0.89	0.99	1.16	1.55	1.05	3.64	5.37	1.22	4.38
32	1.03	1.12	1.26	1.59	1.15	3.71	5.33	1.31	4.37
34	1.13	1.21	1.32	1.62	1.23	3.71	5.32	1.38	4.38
36	1.22	1.30	1.41	1.71	1.30	3.76	5.34	1.44	4.37
38	1.25	1.35	1.50	1.88	1.33	3.79	5.41	1.51	4.45
40	1.31	1.42	1.54	1.91	1.39	3.83	5.42	1.56	4.53
45	1.46	1.54	1.65	1.95	1.50	3.87	5.48	1.69	4.53
50	1.57	1.65	1.73	2.00	1.56	3.87	5.59	1.79	4.62
55	1.63	1.71	1.79	2.06	1.64	3.91	5.63	1.86	4.74
60	1.63	1.72	1.81	2.12	1.68	3.98	5.67	1.91	4.75
65	1.67	1.76	1.85	2.16	1.71	3.96	5.64	1.95	4.76
70	1.69	1.78	1.87	2.18	1.73	3.96	5.68	1.98	4.76
75	1.71	1.80	1.88	2.17	1.73	3.94	5.65	2.00	4.78
80	1.74	1.82	1.87	2.14	1.74	3.95	5.64	2.00	4.75

TABLE III. (*Continued*).

Electron energy (ev)	N_2[a]	N_2[b]	N_2[c]	N_2[d]	CO	CS	S_2	CO_2	CS_2
85	1.75	1.82	1.88	2.12	1.74	3.92	5.63	2.02	4.75
90	1.78	1.85	1.88	2.08	1.73	3.92	5.59	2.03	4.72
95	1.80	1.86	1.88	2.06	1.72	3.86	5.55	2.03	4.68
100	1.79	1.86	1.89	2.09	1.73	3.84	5.51	2.04	4.66
105	1.79	1.86	1.90	2.09	1.72	3.82	5.48	2.05	4.65
110	1.81	1.87	1.89	2.04	1.71	3.77	5.43	2.04	4.64
115	1.81	1.87	1.90	2.04	1.72	3.78	5.42	2.03	4.62
120	1.82	1.88	1.88	2.02	1.70	3.79	5.36	2.04	4.60
125	1.79	1.85	1.85	1.99	1.69	3.75	5.32	2.04	4.56
130	1.80	1.85	1.83	1.94	1.68	3.68	5.22	2.02	4.53
135	1.78	1.83	1.83	1.94	1.68	3.66	5.21	2.01	4.50
140	1.76	1.84	1.83	1.99	1.66	3.66	5.14	2.00	4.46
145	1.75	1.80	1.82	1.95	1.64	3.62	5.11	1.99	4.41
150	1.74	1.81	1.81	1.94	1.63	3.57	5.04	1.97	4.37
155	1.73	1.79	1.80	1.93	1.62	3.55	5.01	1.95	4.33
160	1.73	1.79	1.78	1.89	1.60	3.53	4.95	1.94	4.27
165	1.70	1.75	1.77	1.90	1.59	3.45	4.89	1.93	4.23
170	1.69	1.75	1.76	1.89	1.58	3.44	4.83	1.91	4.19
175	1.67	1.73	1.73	1.87	1.55	3.42	4.77	1.88	4.14
180	1.64	1.70	1.71	1.84	1.55	3.37	4.69	1.86	4.07
185	1.63	1.68	1.68	1.79	1.50	3.28	4.59	1.84	4.03
190	1.58	1.63	1.65	1.78	1.48	3.22	4.47	1.79	3.96
195	1.56	1.61	1.63	1.76	1.45	3.17	4.44	1.76	3.87
200	1.52	1.54	1.60	1.75	1.39	3.18	4.41	1.73	3.82

[a] Derived for the ground state.

[b] Measured with N_2 charge-transfer gas.

[c] Measured with triethylamine (TEA) charge-transfer gas.

[d] Derived for the metastable state.

and T refer to beams formed by charge transfer with N_2 and TEA, respectively.) Two assumptions are necessary: (1) both the ground-state and the metastable-state ionization cross sections are linear for the first 10–15 eV above threshold, and (2) the slopes near threshold are proportional to the peak cross sections. These assumptions are only approximately true, so we do not expect the derived cross sections to be highly accurate. If we denote the threshold slopes of the ground and metastable states by s_G and s_M, respectively, and their peak cross sections by σ_{pG} and σ_{pM}, then the fractions of the beam in the metastable and the ground state are given by

$$F_M = S_M \sigma_{pG} / (S_G \sigma_{pM} + S_M \sigma_{pG}) \tag{1}$$

and

$$F_G = 1 - F_M \ . \tag{2}$$

The measured cross sections can be expressed as

$$\sigma_N = F_{GN} \sigma_G + F_{MN} \sigma_M \tag{3}$$

and

$$\sigma_T = F_{GT} \sigma_G + F_{MT} \sigma_M \ . \tag{4}$$

For σ_T (Fig. 3), the slope of the foot in arbitrary units (from 10 to 15 eV) due to the metastable state is 0.75. The slope of the contribution from the ground state in the same units (from 15 to 25 eV), after subtracting the contribution of the metastable state, is 1.00. For σ_N (Fig. 2), the slope of the metastable foot is 0.22 and the slope of the ground state is 1.67. We solve Eqs. (1)–(4) with three iterations, starting with $\sigma_{pM} = \sigma_{pG}$ and find that $F_{GN} = 0.89$, $F_{MN} = 0.11$, $F_{GT} = 0.62$, and $F_{MT} = 0.38$. The resulting cross sections for ground and metastable nitrogen are given in Fig. 6 and Table III. The noise on the cross section for metastable N_2 is large, because the separation process amplifies the measurement noise.

The presence of metastable molecules in the CO and CS beams suggests that their ground-state cross sections are also slightly smaller than the measured cross section, perhaps, as for N_2, by about 2%. No correction has been applied to the CO and CS data reported here, however, since the correction is so small and uncertain. The measurements necessary to derive separate ground and metastable cross sections were not made.

C. Comparisons to previous measurements

The present results for formation of the parent ions of N_2, CO, and CO_2 are compared to previous measurements in Figs. 7–9.

The total ionization cross section of N_2 is, to a good approximation, equal to $\sigma(N_2{}^+) + \sigma(N^+) + 2\sigma(N_2{}^{2+}) + 2\sigma(N^{2+})$. The measurement of Rapp and Englander-

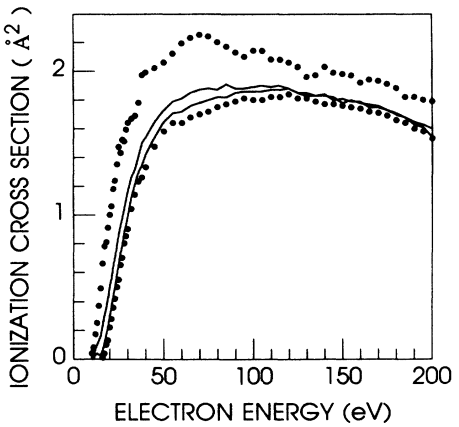

FIG. 6. Single ionization cross sections from 0 to 200 eV for the mixed ground and metastable states of N_2 formed by charge transfer with N_2 (lower solid line) and TEA (upper solid line), and the derived cross sections for the ground (lower dots) and metastable (upper dots) states.

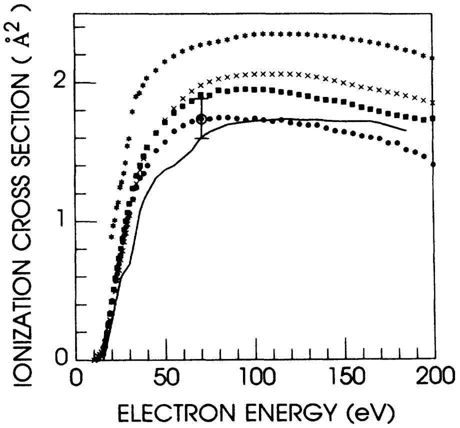

FIG. 8. Comparisons of the present measurements of σ ($CO \rightarrow CO^+$) (●●●●) to previous measurements of Rapp and Englander-Golden (Ref. 12) (■■■■); Hille and Märk (Ref. 20) (——); Adamczyk *et al.* (Ref. 23) (******); and Orient and Srivastava (Ref. 27) (××××××).

Golden[12] (REG) is probably the most accurate available, with an estimated uncertainty of ±7%. For comparison to the present measurement a value of $\sigma(N_2{}^+)$ can be derived from their measured total ionization cross section. For the dissociative ionization cross section $\sigma(N^+)+2\sigma(N^{2+})$ we use the data of Rapp, Englander-Golden, and Briglia[13] (REGB) who measured the cross sections for all ions with kinetic energies >0.25 eV. Two corrections to their data are made: One, as pointed out by Crowe and McConkey,[14] is to lower the REGB value by 7.1%, to correct for McLeod gauge errors. The other is to add to $\sigma(N^+)$ a contribution for ions with energies less than 0.25 eV, which were not detected by REGB. The magnitude of this correction has in the past been estimated to be 0% (Ref. 14) or 5%.[15] Here, we have measured the area under the kinetic-energy distribution of N^+ reported by Locht[16] and found that approximately 9% of the ions have less than 0.25 eV of kinetic energy. For the value of $\sigma(N_2{}^{2+})$, there are three published measurements[15,17,18] in good agreement with each other. The result (Fig. 7) for $\sigma(N_2{}^+)$ is about 5–10 % larger than the present data, well within the combined uncertainties.

An analogous treatment of the REG data for CO gives the result in Fig. 8. Measurements by Locht[19] of C^+ and O^+ fragment ions show that a higher percentage of the fragment ions, about 25%, has kinetic energy below 0.25 eV. The measured value of $\sigma(CO^{2+})$ comes from Hille and Märk[20] (about 0.012 Å^2 at the peak). The agreement between the present measurement and the value for $\sigma(CO^+)$ derived from REG is fairly good, the difference being about 12%.

For CO_2, we could not find published data on the kinetic energy distributions, so a correction for fragment ions with kinetic energy less than 0.25 eV is more difficult

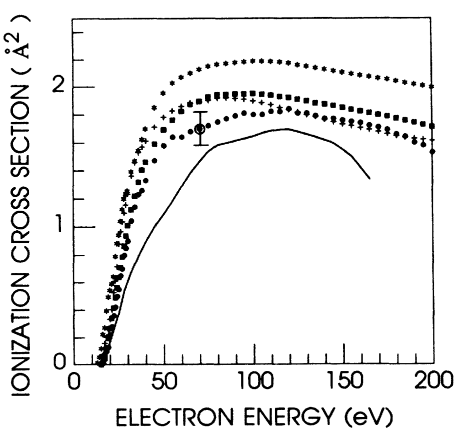

FIG. 7. Comparisons of the present measurements of the cross section for $N_2 \rightarrow N_2{}^+$ (●●●●) to previous measurements of Rapp and Englander-Golden (Ref. 12) (■■■■); Märk (Ref. 15) (——); Crowe and McConkey (Ref. 14) (++++++); and Halas and Adamczyk (Ref. 18) (******).

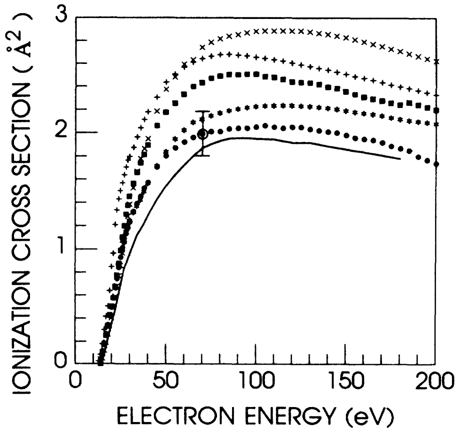

FIG. 9. Comparisons of the present measurements of σ ($CO_2 \rightarrow CO_2{}^+$) (●●●●) to previous measurements of Rapp and Englander-Golden (Ref. 12) (■■■■); Märk and Hille (Ref. 21) (——); Crowe and McConkey (Ref. 28) (++++++); Adamczyk *et al.* (Ref. 24) (******); and Orient and Srivastava (Ref. 27) (××××××).

to make. The principal fragment ion is CO^+, and since its mass is greater than that of O, its dissociation partner, it carries less kinetic energy. In analogy to CO, significant fractions of the C^+ and O^+ fragments also probably have low kinetic energy. Thus we estimate that 50% of the fragments have less than 0.25-eV kinetic energy (Märk and Hille[21] estimated 30%), and correct the dissociative ionization data of REGB accordingly. $\sigma(CO_2{}^{2+})$ is about 0.012 Å^2 at 70 eV.[21] The value of $\sigma(CO_2{}^+)$ derived from these values and REG's data (Fig. 9) is larger than the present measurement by about 20%, possibly due to the large uncertainty in the cross section for dissociative ionization.

All three of these molecules were also studied by Märk and Hille.[15,20,21] They measured their cross sections directly in a mass spectrometer, using $\sigma(Ar^+)$ to calibrate the apparatus. Their resulting values are slightly smaller than or about the same as the present measurements, within the combined uncertainties. Actually their values should be increased slightly, since they used $\sigma(Ar^+)=2.29$ Å^2 at 70 eV, derived from REG's total ionization cross section for Ar and measurements of the ratio $\sigma(Ar^{2+})/\sigma(Ar^+)$ which were then available. More recent values[5,22] of the ratio would raise the calculated $\sigma(Ar^+)$ to 2.40 or 2.42 Å^2. Our directly measured $\sigma(Ar^+)$ (Ref. 5) is slightly larger still, 2.57 Å^2. Use of one of these values for $\sigma(Ar^+)$ would increase their cross section by 5–12%, leading to slightly better overall agreement with the present measurements.

Adamczyk *et al.*[18,23,24] measured relative cross sections for formation of parent and fragment ions and normalized the charge-weighted sum to the total ionization cross sections of REG. This method does not rely on the data of REGB, but it is very sensitive to any error in their measured ratio of fragment to parent ions. Their resulting value for $\sigma(N_2{}^+)$ (Ref. 18) is about 15% larger than the present measurement. The discrepancy may result from their value of $\sigma(N^+)$ being too small; it is less than half as large as the other previous measurements.[17,14] If their $\sigma(N^+)$ value had been as large as these previous values, their normalized value of $\sigma(N_2{}^+)$ would have agreed well with the present measurements. Their result for $\sigma(CO^+)$ (Ref. 23) is also larger than all of the other measurements. It is difficult to assess whether or not the ratio of fragment to parent ions is too small, since there is much disagreement among the other available measurements of the fragment cross sections.[23,25–27] Their result for $\sigma(CO_2{}^+)$ (Ref. 24) agrees quite well with the present measurement. Questions have been raised,[28] however, about the conditions of their experiments, which might alter the ratios of the fragment ions and therefore affect the normalization to REG. Thus, the agreement between the data of Adamczyk *et al.* and the present data may not be significant.

Crowe and McConkey[14,28] measured the relative cross sections for formation of $N_2{}^+$ and $CO_2{}^+$ and normalized them to the values of $\sigma(N_2{}^+)$ or $\sigma(CO_2{}^+)$ they derived by combining the total ionization cross section of REG, dissociative ionization from REGB, and double ionization. They included a 7.1% McLeod gauge correction in the dissociative ionization cross section, but did not correct for ions with less than 0.25-eV kinetic energy. Their result for $N_2{}^+$ (Ref. 14) agrees with the present measurement. Inclusion of a 9% increase to the data of REGB to account for low-kinetic-energy ions would lower their value by only 1%. Their result for $CO_2{}^+$ (Ref. 28) is significantly higher than the present measurement. It is larger than the data labeled REG in Fig. 9 because we show their data as they normalized them to REG, whereas the data marked REG in Fig. 9 include a correction to account for the existence of low-kinetic-energy fragment ions.

Orient and Srivastava[27] measured $\sigma(CO^+)$ and $(CO_2{}^+)$ directly, using the relative flow technique to normalize their measured data to cross sections for the rare gases. Their results are larger than most of the other measurements.

Measurements by Vaughan[25] and by Defrance and Gomet[26] disagree with the other measurements discussed here. Hille and Märk[20] have addressed this disagreement, so we do not repeat the discussion here.

The present value for the ionization cross section of metastable N_2 is about twice our earlier value.[4] We have more confidence in the present measurement, which was made with signal levels so much larger than before that data could be obtained in 1 h rather than 30 h. It is certain from the present data that the metastable N_2 cross section is larger than that of the ground state, since the cross section of the beam with a larger fraction of metastable has a larger cross section. In the earlier work,[4] the cross section for the mixed ground and metastable states [denoted $\sigma(NO)$ in that work to represent nitrogen ions formed by charge transfer with NO] was about 20% smaller than the pure ground-state cross section. To be consistent with the present results, $\sigma(NO)$ would have had to be about 5% larger than the ground-state cross section, a 25% difference, which is at the quoted error limit in the earlier work. Separation of the ground and metastable state contributions then amplified this error.

There are no previous measurements of the cross sections for CS, S_2, and CS_2. The cross sections of these sulfur-containing molecules are about 2 to 3 times larger than those of N_2, CO, and CO_2, although this comparison is not entirely meaningful, since we should really compare total ionization, not just the parent ionization cross sections. The other noticeable difference is that the cross sections for all three sulfur-containing molecules (Fig. 5 and Table III) show peaks between 25 and 30 eV which are absent for the lighter molecules. These features appear to be related to sulfur, but do not show up in ionization of the sulfur atom.[3] They may reflect autoionization resulting from excitation from $2p$ molecular orbitals.

IV. CONCLUSIONS

Measurements have been presented of the single ionization cross sections to the parent ions of N_2, CO, CO_2, CS, S_2, and CS_2. Approximate agreement of the present N_2, CO, and CO_2 cross sections with several previous measurements serves to confirm the accuracy of the apparatus and the measurement procedures.

Overall, the measurements from each laboratory tend to group together as smaller or larger than the measurements from other laboratories. The measurements of Märk and Hille are the smallest. The present measurements are next, then the parent ionization cross sections derived from measurements of REG, then those of Adamczyk *et al.* The measurements of Orient and Srivastava tend to be the largest. The differences among the cross sections from different laboratories are not large, ranging from somewhat less than to somewhat more than the combined stated uncertainties.

The present measurements for N_2, CO, and CO_2 agree best with those of Märk *et al.*, lying within the combined uncertainties. They also agree with cross sections for the parent ion derived from the total ionization cross sections of Rapp and Englander-Golden, but the present values are lower by 5–20 %. This comparison is complicated by the scarcity of accurate data for the ionization cross sections to form fragment ions with less than 0.25-eV kinetic energy.

The cross section for ionization of metastable N_2 was remeasured with the benefit of a greatly improved apparatus and found to be about twice the value previously reported.

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