Absolute partial cross sections for electron-impact ionization of CO from threshold to 1000 eV

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Abstract. Absolute partial cross sections for electron-impact ionization of CO are reported for electron energies from threshold to 1000 eV. The product ions are mass analysed using a time-of-flight mass spectrometer and detected with a position-sensitive detector whose output unequivocally demonstrates that the various product ions are collected with equal efficiency irrespective of their initial kinetic energies. Data are presented for the production of CO^+, C^+, O^+ and CO^{2+}, and for the total cross section which is obtained as the sum of these partial cross sections. The overall uncertainty in the absolute cross section values is $\pm 5\%$ for singly charged parent ions and $\pm 6\%$ for fragment ions. Comparison is made with prior experiments and calculations.

1. Introduction

Ionization of atoms and molecules by electron impact is of fundamental importance in atmospheric science, plasma processing and mass spectrometry. Historically, the accurate determination of absolute partial electron-impact ionization cross sections for molecular targets has proven particularly challenging, largely due to the difficulty of completely collecting energetic fragment ions. The present paper is devoted to the study of carbon monoxide which is a common pollutant in the terrestrial atmosphere. Furthermore, collisions of electrons with CO provide an important energy loss mechanism for energetic electrons in many astrophysical environments and in planetary atmospheres (Liu and Victor 1994).

A number of previous experimental studies of electron-impact ionization of carbon monoxide have been reported. Total cross sections were measured by Tate and Smith (1932), Schulz (1962), Asundi *et al* (1963), Rapp and Englander-Golden (1965) and Srinivasan and Rees (1967). Partial cross sections were measured by Vaughan (1931), Defrance and Gomet (1966), Adamczyk *et al* (1976), Hille and Märk (1978) and Freund *et al* (1990), while partial and total cross sections have been reported by Orient and Srivastava (1987) and Tian and Vidal (1998). Theoretical investigation includes a classical calculation by Bauer and Bartky (1965), a partial cross section calculation by Pal *et al* (1997), and two total ionization cross section calculations performed by Jain and Khare (1976) and Hwang *et al* (1996).

In light of all the previous studies the justification for further work on CO is not immediately apparent. On closer inspection, however, it becomes clear that the final word on these cross sections has not yet been written. The earliest studies, such as that of Tate and Smith (1932), are generally not very reliable because those investigators did not have instrumentation to accurately determine their target gas pressure. In the 1960s Rapp and Englander-Golden

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(1965) effectively used a similar approach in the study of numerous atoms and molecules; and their work has been widely accepted as the *de facto* standard for quite some time. These early studies generally only provided cross sections for total charge production. However, for all targets other than atomic hydrogen, more than one ionic species may result and primary interest centres on the partial cross sections for these different ions. The determination of the individual cross sections requires a mass spectrometer. Numerous studies have demonstrated that it is extraordinarily difficult to ensure that all product ions originating from a well characterized region are detected, particularly when mass spectrometers with a long path length or narrow apertures are used. This problem is exacerbated in studies involving molecules where fragment ions may be created with considerable kinetic energy. This often leads to underestimation of the fragment ion cross sections and, consequently, when normalization is achieved by comparing the sum of the partial cross section to the known total cross section, to a corresponding overestimation of the parent ion cross section.

Ideally, partial cross sections should be obtained without recourse to normalization. For CO, however, with the exception of the work of Freund *et al* (1990) all previously reported measurements of partial cross sections have been normalized to the absolute measurements of others. The experimental technique employed here embodies the simplicity of the parallel-plate arrangement, utilized by Rapp and Englander-Golden (1965), coupled with an extremely short path length mass spectrometer together with a position-sensitive detector. All quantities needed for the determination of the partial cross sections are directly measured and absolute partial cross sections for the production of CO^+, C^+, O^+ and CO^{2+} by electron-impact ionization of carbon monoxide are reported for electron energies from threshold to 1000 eV. The total ionization cross section is then obtained as the sum of the measured partial cross sections.

2. Apparatus and experimental method

The apparatus shown in figure 1 consists of an electron gun, a time-of-flight mass spectrometer with a position-sensitive detector (PSD), and an absolute pressure gauge (not shown). It has been described in detail previously (Straub *et al* 1995, 1996). Briefly, during a cross section measurement the entire vacuum chamber is filled with carbon monoxide at a pressure of approximately 5×10^{-6} Torr. The electron gun produces 20 ns long pulses, each containing approximately 2500 electrons, at a repetition rate of the order of 2.5 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 200 ns after each electron pulse, a 480 V cm^{-1} electric field is applied across the interaction region to drive any positive ions
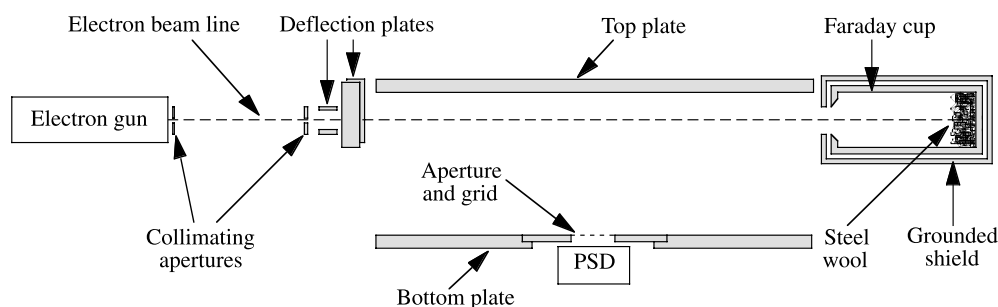

Figure 1. Schematic diagram of the apparatus.

formed by electron impact toward the bottom plate. This electric field is generated by applying a 3 kV pulse with a 55 ns rise time to the top plate. Some ions pass through a grid-covered aperture, of length 1.91 cm in the direction parallel to the electron beam, in the bottom plate. These ions are then accelerated to an energy of 5.4 keV and subsequently impact a PSD, comprising a pair of 25 mm diameter microchannel plates and a resistive-encoded anode (Gao *et al* 1984), 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

$$\sigma(X) = \frac{N_i(X)}{N_e nl} \tag{1}$$

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 carbon monoxide target of number density n. Determination of an absolute cross section requires measurement of all four quantities on the right-hand side of equation (1) and has been described previously in detail (Straub *et al* 1995, 1996). Briefly, the number of electrons N_e is determined by collecting the electron beam in a Faraday cup and measuring the current with an electrometer operating in the charge collection mode. Measurement of $N_i(X)$ is accomplished by recording the time-of-flight spectrum, counting the number ions in an appropriate portion of the spectrum, and accounting for the detection efficiency of the PSD and the transparency of the grid. The overall detection efficiency was determined to be $(37.2 \pm 0.6)\%$ and to be independent of ion species by repetitively directing an ion beam of appropriate species and energy alternately onto the PSD and into a second Faraday cup (not shown in figure 1) (Straub *et al* 1999). The effective path length l from which detected ions originate is determined by the aperture directly in front of the PSD, although, due to slight non-uniformities in the pulsed electric field, l is 2% smaller than the actual length of this aperture. In the present measurements, a few of the energetic fragment ions that are created in the region directly above the aperture with velocities parallel to the electron-beam axis will escape detection. However, the translational symmetry of the apparatus along the electron-beam axis ensures that for every ion produced in the region directly above the PSD that escapes detection, one from outside this region will be detected. The target number density n is obtained from measurements of the gas pressure using a capacitance diaphragm gauge (Straub *et al* 1994).

The CO used in this work was obtained from Matheson Gas Products and has a minimum specified purity of 99.9%. It is transported from the gas cylinder through stainless-steel tubing and introduced to the vacuum chamber through a leak valve. The effectiveness of these procedures in preventing contamination can be seen from the absence of spurious peaks in the time-of-flight spectrum shown in figure 2. The CO^+ peak is completely resolved but the resolution of the apparatus is insufficient to allow the CO^{2+} peak to be resolved independently of the C^+ and O^+ peaks. This very slight overlap causes an additional uncertainty in the measured C^+ and O^+ partial cross sections of less than 1%.

Complete collection of all product ions from the path length l was confirmed by observing the arrival position distribution of the ions at the PSD. Figure 3 shows a plot in which the transverse arrival positions of the product ions at the PSD (i.e. the displacement of the 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 of the fragment ion peaks are due to their initial velocities perpendicular to the electron beam in addition to the
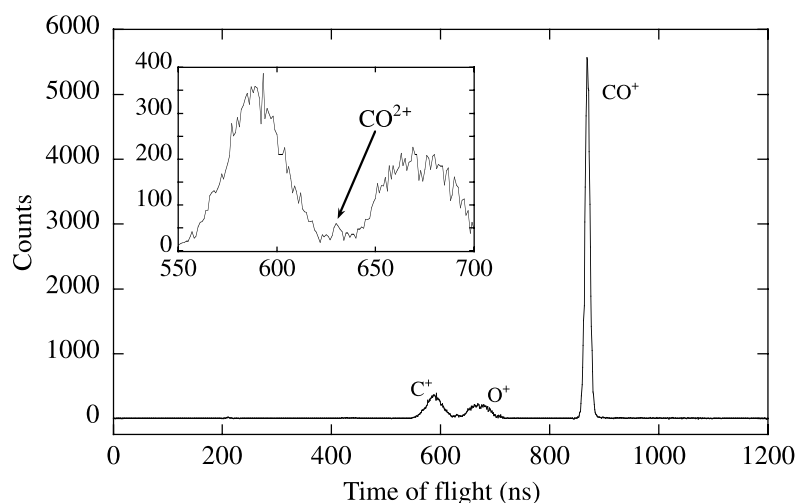
Figure 2. Time-of-flight spectrum for ions produced by 100 eV electron impact on CO.
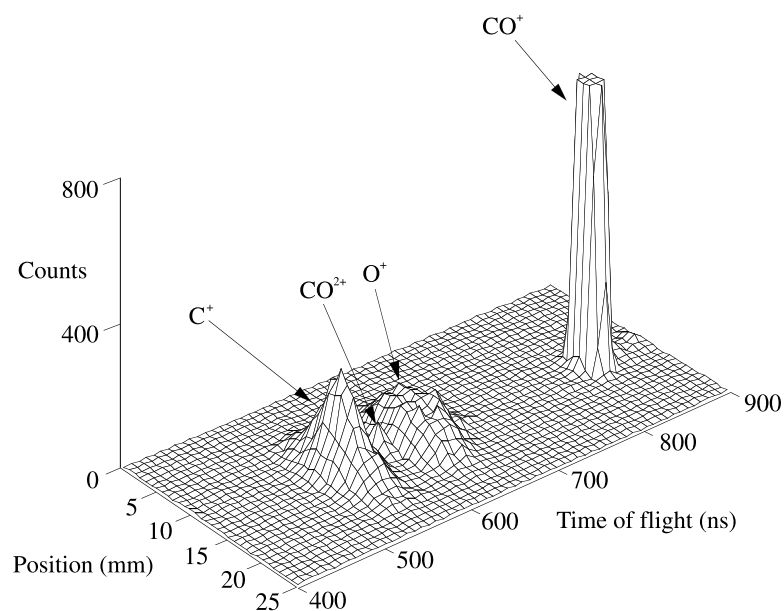

Figure 3. Position and time-of-flight distribution produced by 100 eV electron impact on CO. The position axis indicates the displacement of the ions perpendicular to the axis of the electron beam.

spatial extent of the electron beam. The figure thus gives some qualitative information about the relative energies of the various product ions.

Measurement of all the quantities on the right-hand side of equation (1) allows a direct determination of the absolute partial cross sections. Pressure measurements using the capacitance diaphragm gauge, that are needed for determination of the number density n, are, however, very time consuming. Absolute measurement of the cross sections was therefore

made at an electron energy of 100 eV, and the cross sections at other energies were determined relative to the cross section at 100 eV.

3. Results and discussion

A detailed analysis of the experimental uncertainties has been given previously (Straub *et al* 1995, 1996). However, in the light of experience gained with this apparatus over a number of years the uncertainty in the absolute cross section for parent ions, such as CO^+ (where the counting statistics are $\pm 1\%$ or better), is now considered to be closer to $\pm 5\%$ rather than the $\pm 3.5\%$ figure which was typically quoted in earlier publications. This $\pm 5\%$ uncertainty should also be applied to the earlier data. The uncertainties in the C^+ and O^+ cross sections, which may be as large as $\pm 6\%$, are slightly greater than that for the CO^+ parent ion because of the small overlap between these peaks and the CO^{2+} peak. It was not possible to determine the CO^{2+} cross section from the time-of-flight spectra alone with any degree of accuracy. However, by utilizing the additional information provided by the position data (figure 3) it was possible to estimate this cross section. Because of the poor statistics and the background presented by the neighbouring C^+ and O^+ peaks, the uncertainty in the present CO^{2+} cross section is ± 30–40%. The energy of the electron beam was established to better than ± 1 eV by observing the threshold for He^+ formation.
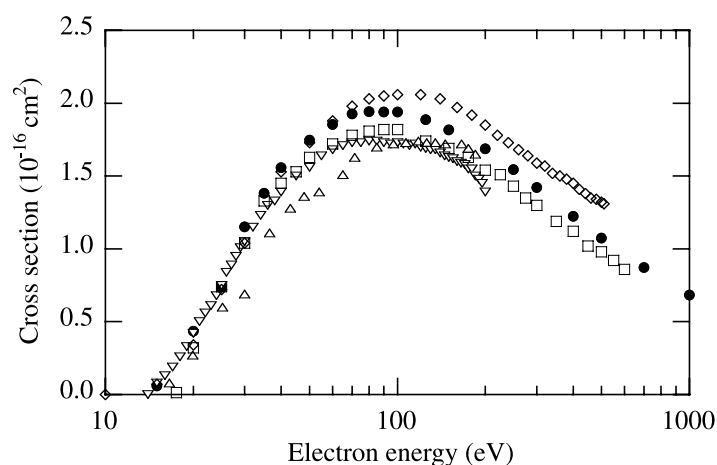
In presenting data for processes that have been studied extensively in the past, it is often difficult to know precisely which of the earlier data should be included and which should be omitted. It seems reasonable to take the position that, as a field matures and new techniques and procedures are brought to bear, inclusion of all data obtained by earlier methods is no longer appropriate. For CO some of the earlier data are, in fact, clearly incorrect and are omitted here because their inclusion serves only to obscure the real picture. Total cross section data, which were normalized using the data of others, sometimes by circuitous routes, are also not included because the normalization process itself typically forces agreement between different data sets, often without adding anything new. The recent partial cross section calculations of Pal *et al* (1997) are inconsistent with the experimental data and are not included in the following figures. Although the magnitudes of their parent ion cross sections are in fair agreement with the current work, their C^+ and O^+ cross sections are a factor of two smaller than those reported here and peak at energies approximately 100 eV higher than the present experimental data. This lack of agreement is not unanticipated since even the calculation of total cross sections remains difficult (Deutsch *et al* 2000). Nevertheless, it serves to illustrate the very real need for better theoretical approaches to this type of problem.

The present CO^+ cross section is given in table 1 and shown in figure 4 together with the other measurements. Besides the present data only the work of Freund *et al* (1990) is absolute in its own right, albeit obtained by a technique which, when viewed against that employed here, is extremely complex. Their measurements, which have an uncertainty of $\pm 10\%$, are in reasonable agreement with those presented here, although the sharp decrease in the cross section observed by them beyond 180 eV is not in accord with the data presented here.

The data of Hille and Märk (1978), Orient and Srivastava (1987) and Tian and Vidal (1998), for which the respective experimental uncertainties are $\pm 15\%$, $\pm 15\%$ and $\pm 10\%$, are relative and have all been normalized using the absolute measurements of others. The results of Tian and Vidal (1998) are in good agreement with the present measurements above 25 eV, but their cross section appears anomalously small near threshold. The results of Orient and Srivastava (1987) are in accord with the present measurements within the combined uncertainties. The magnitude of the cross section reported by Hille and Märk (1978) is also in agreement with

Table 1. Present absolute partial cross sections for CO. The uncertainties in the CO^+, C^+, O^+ and CO^{2+} cross sections are $\pm5\%$, $\pm6\%$, $\pm6\%$ and $\pm30\%$, respectively, unless otherwise indicated.

Energy (eV)	$\sigma(CO^+)$ (10^{-16} cm²)	$\sigma(C^+)$ (10^{-17} cm²)	$\sigma(O^+)$ (10^{-17} cm²)	$\sigma(CO^{2+})$ (10^{-18} cm²)
15	0.060			
20	0.435			
25	0.741	0.150		
30	1.15	0.532	0.090	
35	1.38	1.18	0.380	
40	1.56	1.71	0.618	
50	1.75	2.50	1.32	0.14 ± 0.06
60	1.85	2.88	1.99	0.55 ± 0.22
70	1.93	3.33	2.50	0.75
80	1.94	3.51	2.78	0.97
90	1.94	3.74	2.98	1.30
100	1.94	3.76	3.09	1.12
125	1.89	3.80	3.16	1.11
150	1.82	3.58	3.13	1.32
200	1.69	3.17	2.74	1.04
250	1.54	2.84	2.45	0.95
300	1.42	2.44	2.16	0.89
400	1.22	1.98	1.75	0.82
500	1.07	1.67	1.43	0.49 ± 0.20
700	0.871	1.25	1.15	0.34 ± 0.14
1000	0.683	0.952	0.816	0.29 ± 0.12

Figure 4. CO^+ cross section: ●, present results; □, Tian and Vidal (1998); ▽, Freund *et al* (1990); ◇, Orient and Srivastava (1987); and △, Hille and Märk (1978).

that presented here, but the energy dependence of their cross section differs significantly from that of all other investigators.

For C^+ and O^+, only the present measurements are independently absolute and are shown in figures 5 and 6 together with the data of Orient and Srivastava (1987) and Tian and Vidal (1998). For both ions, there is agreement, within the combined uncertainties, between the present measurements and those of Tian and Vidal (1998). The results of Orient and Srivastava
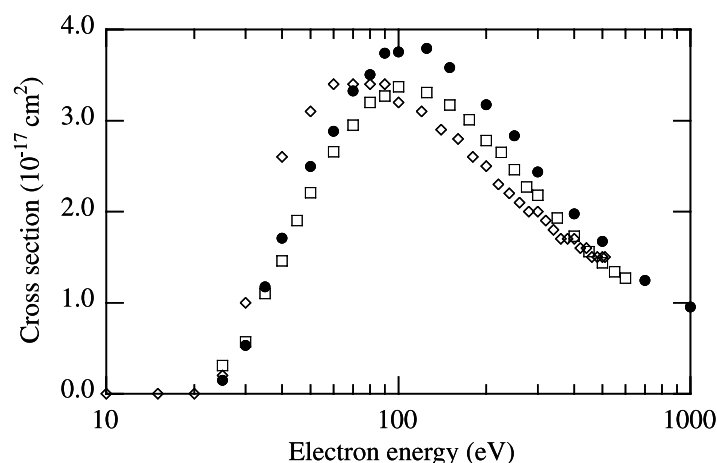
Figure 5. C^+ cross section: ●, present results; □, Tian and Vidal (1998); and ◇, Orient and Srivastava (1987).
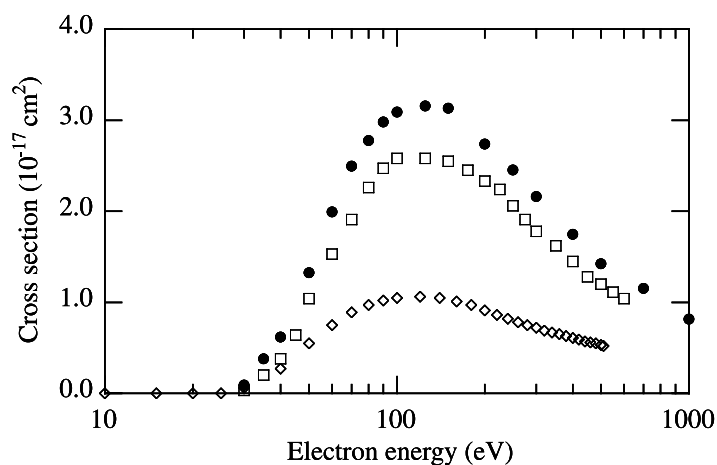

Figure 6. O^+ cross section: ●, present results; □, Tian and Vidal (1998); and ◇, Orient and Srivastava (1987).

(1987) for C^+, however, have a markedly different energy dependence, while for O^+ their data are significantly lower than both the present measurements and those of Tian and Vidal (1998). This probably indicates the loss of energetic O^+ fragments by these workers.

The present absolute CO^{2+} cross section is shown in figure 7 together with the normalized data of Hille and Märk (1978) and Tian and Vidal (1998). The uncertainty in the present data is approximately ±30% at the peak of the cross section. Hille and Märk (1978) state that the maximum uncertainty in their data is ±20–40%, while Tian and Vidal (1998) give an uncertainty on the order of ±15%. The present data agree with the results of Hille and Märk (1978) and of Tian and Vidal (1998) to within the combined uncertainties. It has been found previously that CO^{2+} is quasi-stable and may spontaneously dissociate via unimolecular decay. Newton and Sciammana (1970) determined that the half-life for CO^{2+} ions produced by electron-impact ionization was in the region of 15–30 μs. Hille and Märk (1978) give a value
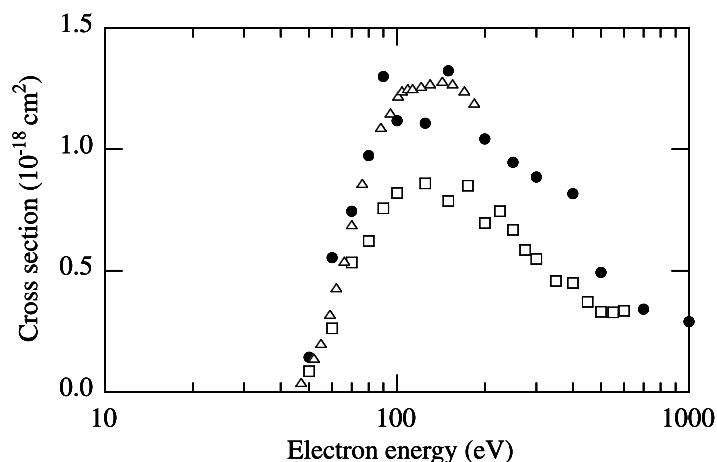
Figure 7. CO^{2+} cross section: ●, present results; □, Tian and Vidal (1998); and △, Hille and Märk (1978). Note that any apparent structure in the present cross section is almost certainly a consequence of the ± 30–40% uncertainty in these data.
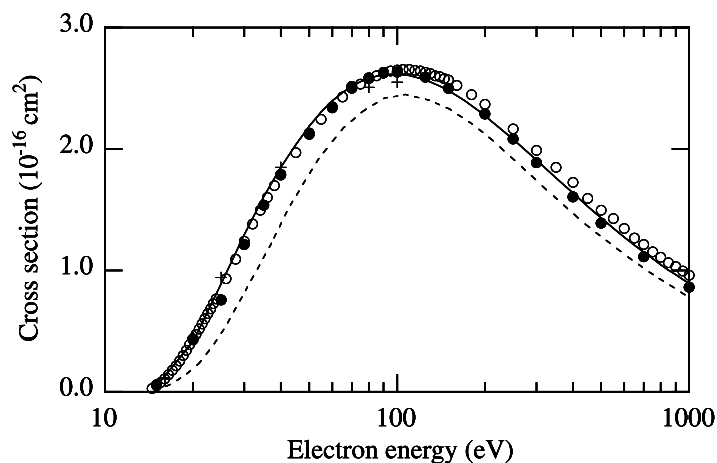

Figure 8. Total cross section: ●, present results; +, Srinivasan and Rees (1967); ○, Rapp and Englander-Golden (1965); ——, Hwang *et al* (1996); and – – –, Jain and Khare (1976).

of 6–15 μs, and Hirsch *et al* (1975) give a value in the 9–16 μs range. However, in a relatively recent study, Safvan and Mathur (1993) found a mean lifetime of only 1 ± 0.25 μs which is comparable to that for CO^{2+} ions produced by photoionization (Field and Eland 1993). In the present study the time from formation to detection of the CO^{2+} ions is less than 1 μs, in that of Hille and Märk (1978) it was ~ 10 μs, and in the Tian and Vidal (1998) study it was ~ 2 μs. The present measured CO^{2+} production cross section should therefore be the largest, followed by that of Tian and Vidal (1998), and the Hille and Märk (1978) cross section should be the smallest. Although the uncertainties involved are relatively large, this does not appear to be the case, and therefore, based on the data in figure 7 alone, it is not possible to make a definitive statement about the half-life of the CO^{2+} ion.

The present CO total electron-impact ionization cross section is shown in figure 8 together with the absolute data of Rapp and Englander-Golden (1965) and those of Srinivasan and Rees

(1967). Both of the early measurements are for total charge production, whereas the present data were obtained by summing the partial cross sections. These data are directly comparable because of the very small number of multiply charged ions observed for CO. The present total cross section is in excellent agreement with the measurements of Rapp and Englander-Golden (1965), and those of Srinivasan and Rees (1967). Also shown in figure 8 are the theoretical calculations of Jain and Khare (1976) and Hwang *et al* (1996). The total electron-impact ionization cross section of Hwang *et al* (1996), obtained by use of the binary-encounter-Bethe model (BEB), is in excellent agreement with the present measurements. Previous calculations for CH_4, SO_2, NO and NO_2 using the BEB method have also been in good agreement with the experimental work performed in this laboratory (Kim *et al* 1997, Lindsay *et al* 2000). The BEB cross section is clearly in much better agreement with the experimental data than the early semi-empirical calculations of Jain and Khare (1976).

4. Conclusion

Absolute partial cross sections for the production of CO^+, C^+, O^+ and CO^{2+} from electron-impact ionization of CO are reported for 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. Additionally, determination of the ions' detection efficiency and direct measurement of the gas pressure using a capacitance diaphragm gauge allows the cross sections to be measured absolutely. The previously published partial cross section data are generally in reasonable agreement with the present measurements. It should be noted that the partial cross sections presented here are the only truly absolute measurements available in the sense that they do not rely on normalization to the absolute data of other investigators. The present total cross section is in excellent agreement with the only other reliable independent measurements of the total ionization cross section, both from the 1960s. Agreement with the most recent theoretical calculations is also excellent.

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