

Cross section for single and double ionization of carbon monoxide by electron impact from threshold up to 180 eV

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Electron impact ionization of carbon monoxide has been studied as a function of electron energy up to 180 eV with a double focusing mass spectrometer Varian MAT CH5. Absolute partial ionization cross section functions have been obtained for the processes $\text{CO} + e \rightarrow \text{CO}^+ + 2e$ and $\text{CO} + e \rightarrow \text{CO}^{2+} + 3e$ by normalization against the Ar^+ cross section with help of the method of molecular effusive flow. In the case of CO^{2+} the results suggest, in accordance with previous authors, that this ion exists in a metastable state with a mean half-life in the range of 6–15 μs . Using n th root extrapolation, the following minimum ionization potentials have been derived from the low energy cross section function: $\text{CO}^+(X^2\Sigma^+) = (14.07 \pm 0.05) \text{ eV}$ and $\text{CO}^{2+} = (41.8 \pm 0.5) \text{ eV}$. All experimental results presented are compared with previous determinations where available.

I. INTRODUCTION

The present paper is one in a series from this laboratory dealing with the upgrading of quantitative knowledge of electron impact ionization of free species.^{1–5} The present study is devoted to the parent molecule of carbon monoxide, with no attempt at the measurement of fragment ions. Very little work has been reported on the electron impact ionization of this diatomic heteronuclear system. Previous studies reporting partial cross section functions of the electron impact production of the various ions from CO include those of Vaughan⁶ and Defrance and Gomet.⁷ However, in both cases the cross section values $q(\text{CO}^+/\text{CO})$ ⁸ are much higher than estimated values of the upper limit to $q(\text{CO}^+/\text{CO})$ derived from the measurements of Rapp and Englander-Golden¹⁰ and Rapp *et al.*¹¹

Single ionization of CO near threshold yielding ionization and appearance potentials has been studied by numerous authors,¹² but only four previous electron impact mass spectrometer studies exist about the ionization potential of the doubly charged ion CO^{2+} .^{6,13–15} Otherwise important experimental information about the states of the doubly charged carbon monoxide comes from two mass spectrometric studies of metastable dissociation of CO^{2+} ,^{15,16} from the determination of the K–LL Auger electron spectra of CO^{2+} of Moddeman *et al.*,¹⁷ and from the investigation of ion pairs from fast decay processes (lifetimes $< 3 \mu\text{s}$) of CO^{2+} of Brehm and De Frenes.¹⁸

Newton and Sciamanna¹⁵ measured the appearance potential and the half-life of CO^{2+m} produced by electron impact on CO in a modified Dempster-type mass spectrometer and reported that unimolecular dissociation of CO^{2+m} occurs from a single metastable state with a half-lifetime of 20 (+ 10 or – 5) μs . Hirsch *et al.*¹⁶ employed a variable length, time-of-flight mass spectrometer to measure dissociative lifetimes of quasi-stable doubly charged molecular ions. They reported that electron impact results at 150 eV indicate a mean half-life of a metastable CO^{2+m} in the range of 9 μs with a 30% infinite lifetime component ($\tau > 10^{-4} \text{ s}$) to 16 μs with no infinite lifetime contribution, the latter in agreement with the results of Newton and Sciamanna.¹⁵

Brehm and De Frenes¹⁸ concluded from their experimental results that stable, metastable, and fast decaying CO^{2+} all have the same appearance potential within the error range, $\sim \pm 1.0 \text{ eV}$, of such measurements.

In an effort to obtain more quantitative information about the electron impact formation of the parent ion, ionization of CO has been studied as a function of electron energy E up to 180 eV. Results reported in the present study include absolute partial ionization cross section functions $q(E)$ for the processes $\text{CO} + e \rightarrow \text{CO}^+ + 2e$, and $\text{CO} + e \rightarrow \text{CO}^{2+} + 3e$. Values of the ionization potentials of the singly and doubly ionized parent molecule are presented.

II. APPARATUS AND TECHNIQUE

The experimental arrangement in the current study is identical with that previously described in detail.^{1,2} In short, it consists of a molecular type of electron impact source Varian MAT Intensitron M, a high resolution double focusing mass spectrometer, Varian MAT CH5, and a gas handling system. In the course of earlier work, the working conditions of the ion source have been improved,^{1,2,19} i.e.: The pusher electrode, which for measurement of mass spectra is sometimes operated positive with respect to the collision chamber, was put at the same potential as the collision chamber. The electron trap collector potential was raised to 24 V to ensure saturation of electron current at all electron energies. The range of the continuously selectable electron accelerating voltage was expanded up to 185 eV and the voltage of the electron focusing Wehnelt cylinder was maintained proportionally to the electron accelerating voltage in order to improve electron current collimation over the whole electron energy range. Thus stray electron currents could be reduced to $< 20\%$ of the electron current measured at the electron trap in the whole electron energy range.

Because of the difficulty in ascertaining the absolute collection efficiency of an ion source–mass spectrometer system, the primary value of mass spectrometric studies of ionization cross sections is in determining relative cross sections as a function of electron energy, i.e., $Cq(E)$, where it is hoped, and is according to

Kieffer and Dunn²⁰ usually assumed without being demonstrated, that C is constant. In order to demonstrate for the present system constant collection efficiency under certain operating conditions for each ionic species, a thorough study¹⁹ of the extraction characteristic for all rare gases has been made as a function of such experimental parameters as gas density in the collision chamber, gas temperature in the collision chamber, ion beam focusing conditions between ion source and mass spectrometer entrance, electron current, and electron energy. Detailed results have been reported in Ref. 19. With help of the information obtained from these studies it became possible to adjust the various ion source operating conditions in such a way that reproducible ($\pm 2\%$) and reliable ($\pm 5\%$) relative cross section functions could be measured with the present system.¹⁻⁵

Normalization of the currently measured relative cross section function $q(\text{CO}^+/\text{CO})$, to obtain absolute values, has been made by a method described previously,^{1,2} in which the relative cross section under study is compared at a particular electron energy with that of the measured value of $q(\text{Ar}^+/\text{Ar})$ for which absolute cross sections are taken from the literature. The comparison has been made at an electron energy of 136 eV, using the currently measured ratio $r = q(\text{Ar}^{2+}/\text{Ar})/q(\text{Ar}^+/\text{Ar}) = 0.084$ and the total ionization cross section $q(\text{Ar}) = 2.75 \times 10^{-16} \text{ cm}^2$ reported by Rapp *et al.*,¹² from which $q(\text{Ar}^+/\text{Ar}) = 2.29 \times 10^{-16} \text{ cm}^2$ is obtained. It should be mentioned, however, that in the literature values from 0.066 to 0.11 are reported for this ratio r at 150 eV.⁹ This uncertainty of the measured ratio would cause an error of up to $\pm 7\%$ in the value of $q(\text{Ar}^+/\text{Ar})$. In a similar way, the results of $q(\text{CO}^+/\text{CO})$ were used to normalize the relative cross section function $q(\text{CO}^{2+}/\text{CO})$ with the help of a measured cross section ratio of $q(\text{CO}^{2+}/\text{CO})/q(\text{CO}^+/\text{CO})$. As will be seen in the next paragraph, this ratio is strongly dependent on the value of the extraction potential applied (0–2 V) due to the metastable fraction of CO^{2+} ions.

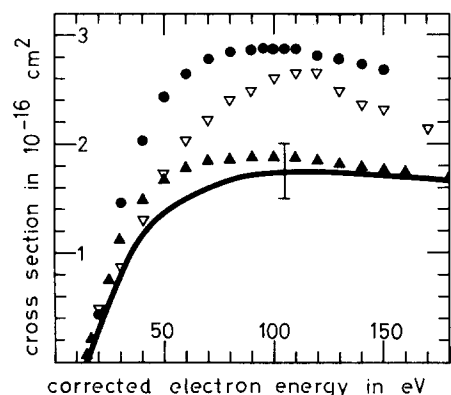


FIG. 1. Absolute partial ionization cross section function $q(\text{CO}^+/\text{CO})$ for the production of CO^+ via process $\text{CO} + e \rightarrow \text{CO}^+ + 2e$: full line, present data (error range shown $\pm 15\%$); Δ , data derived from results of Rapp *et al.*^{10,11}; ∇ , Defrance and Gomet⁷; \bullet , Vaughan.⁶ The energy scale of the present data was calibrated by means of the linear extrapolation method, taking the single ionization potential of Ar as 15.76 eV (spectroscopic value¹²).

In all normalization procedures the ion currents have been measured with a Faraday collector cup, and electron currents of 3–50 μA have been used. The gas temperature in the collision chamber was stabilized at 400 °K during measurements. The CO gas used was obtained from the Air Reduction Company, grade 3TM (Research). However, due to a small leak in the gas handling system, impurities (N_2 and O_2) were present. They have been analyzed mass spectrometrically and allowed for in the calibration procedures, e.g., signal $m/e = 14 \triangleq (\text{C}^{12}\text{O}^{16})^{2+}$ has been corrected for contributions of $^{14}\text{N}^+$ and $(^{14}\text{N}^{14}\text{N})^{2+}$ and signal $m/e = 28 \triangleq (\text{C}^{12}\text{O}^{16})^+$ for contributions of $(^{14}\text{N}^{14}\text{N})^+$. In addition, contributions of these impurity ions to the measured relative cross section curves have been subtracted accordingly. A correction has been made to all cross sections for the respective isotopic abundances.

The measurement of the ratio of the gas density of argon to the gas under study (CO) in the collision chamber necessary for the above absolute calibration has been made by means of the method of molecular effusive flow.^{1,2,10,21} The gas pressure in the gas reservoir has been measured with an absolute capacitance manometer. According to Rapp and Englander-Golden¹⁰ and Märk and Egger,² the results thus obtained are believed to be more accurate than those based on absolute McLeod-gauge measurements in each gas.

The reproducibility of the measured ion currents was in general better than $\pm 2\%$. However, for very low ion currents, e.g., as in the case of CO^{2+} , the statistical error could be as large as 5%–10%. The accuracy of the density ratio necessary for the absolute calibration of the cross section values depends on the accuracy of the measurement of the pressure (capacitance manometer Barocel $\pm 0.05\%$) and on the adequacy of the assumption of molecular flow. In accordance with Rapp and Englander-Golden¹⁰ and Märk *et al.*,^{2,19} the accuracy for repeated measurements at different molecular effusive flow conditions was found to be about $\pm 5\%$. The estimated maximum possible error, excluding that of the absolute value of $q(\text{Ar}^+/\text{Ar})$, is about 10%–20% for $q(\text{CO}^+/\text{CO})$ and about 20%–40% for $q(\text{CO}^{2+}/\text{CO})$.

III. RESULTS AND DISCUSSION

A. Single and double ionization cross section function

1. CO^+

The absolute cross section values obtained for the process $\text{CO} + e \rightarrow \text{CO}^+ + 2e$ are shown in Fig. 1 as a function of electron energy. A representative set of values of the cross sections measured in the present study is given in Table I.

Figure 1 also shows absolute ionization cross section data reported by previous authors. Points designated Δ in Fig. 1 represent an estimate of the upper limit to $q(\text{CO}^+/\text{CO})$ derived from measurements of Rapp and Englander-Golden¹⁰ and Rapp *et al.*¹¹ These authors made absolute measurements, using total ionization tubes, of the total ionization cross section function of CO and of the cross section function for the production

TABLE I. Absolute partial ionization cross sections $q(\text{CO}^+/\text{CO})$ and $q(\text{CO}^{2+}/\text{CO})$ for different corrected electron energies. Values of $q(\text{CO}^{2+}/\text{CO})$ are obtained under extraction and transmission conditions causing for CO^{2+} a transit residence time from time of formation to time of collection of $\sim 10 \mu\text{s}$.

E (eV)	$q(\text{CO}^+/\text{CO})$ (10^{-16} cm^2)	E (eV)	$q(\text{CO}^{2+}/\text{CO})$ (10^{-18} cm^2)
185	1.65	184	1.19
175	1.69	170	1.24
166	1.72	155	1.27
146	1.72	143	1.28
135	1.73	130	1.27
126	1.73	121	1.26
118	1.74	113	1.25
107	1.73	109	1.25
97	1.72	104	1.24
85	1.70	101	1.22
71.5	1.63	95	1.15
65	1.51	88	1.09
54	1.39	76	0.86
48	1.36	70	0.69
43	1.28	66	0.54
36.5	1.11	62	0.43
30	0.69	59	0.32
25.2	0.60	55	0.20
19.9	0.27	52	0.14
16.6	0.08	47	0.04

of ions in carbon monoxide with kinetic energies $> 0.25 \text{ eV}$. Hence, subtraction of the energetic ion curve (corrected by the present authors by 30% for dissociative ions with energies $< 0.25 \text{ eV}$) from the total ion curve should give an estimate of the cross section function for the production of $\text{CO}^+ + 2\text{CO}^{2+}$.²² It can be seen that the present cross section values are within the experimental error shown in Fig. 1, namely $\pm 15\%$, in agreement with the curve thus obtained from the data of Rapp *et al.*

It is interesting to compare this fact with a recent comparison of measured cross data of $q(\text{CO}_2^+/\text{CO}_2)$ ⁵ with the curve derived in a similar way as shown above from the data of Rapp *et al.*^{10,11} for carbon dioxide. The measured $q(\text{CO}_2^+/\text{CO}_2)$ curve differed from that obtained from the data of Rapp *et al.*, in magnitude, the measured curve being close to its maximum (100 eV) lower by about 21%. This difference in magnitude, besides being caused by the experimental error bars ($\pm 10\%$) and by a possible error in the value of $q(\text{Ar}^+/\text{Ar})$, used to normalize the measured $q(\text{CO}_2^+/\text{CO}_2)$ function, could be due to the uncertainty of the percentage of dissociative ions with energies $< 0.25 \text{ eV}$ used in the derivation of the Rapp *et al.* curve. As in both cases the same percentage of dissociative ions with energies $< 0.25 \text{ eV}$ (namely, 30%) has been used by the present authors to correct the energetic ion curve, it could be inferred from these results that CO_2 fragment ions have a larger fraction of ions with energies $< 0.25 \text{ eV}$ than CO fragment ions.

At this point of the discussion it is appropriate to mention that in the lower energy regime there seems to

be a systematic deviation between the currently determined $q(\text{CO}^+/\text{CO})$ and the curve obtained from the data of Rapp *et al.* This discrepancy could be explained, at least partly, by a fact recently reported by Köllmann.²³ For the investigation of dissociative ionization processes induced by electron impact, Köllmann has constructed an apparatus which allows one to measure the kinetic energy, angular distribution, and appearance potentials of produced fragment ions. He has found in the case of CO that, for instance, the fragment ion O^+ exhibits kinetic energy distributions which depend on the electron energy, i.e., with smaller electron energy a larger fraction of O^+ ions has kinetic energies near thermal. Thus the above mentioned derivation of cross section values $q(\text{CO}^+/\text{CO}) + 2q(\text{CO}^{2+}/\text{CO})$ from the data of Rapp *et al.* would yield values which are at low energy too high in relation to the values at higher energy. This fact could explain at least part of the difference in shape observed between the present results and the curve obtained from the data of Rapp *et al.*

Also shown in Fig. 1 is the CO^+ cross section curve reported by Defrance and Gomet⁷ and by Gomet.²⁴ According to the latter, CO cross sections reported in Ref. 7 are in units of 10^{-16} cm^2 and not in πa_0^2 . Defrance and Gomet⁷ have determined the partial ionization cross sections of CO by measuring the relative amounts of the produced ions (CO^+ , CO^{2+} , O^+ , and C^+) with a magnetic mass spectrometer CSF SM 100 and by normalizing their sum with the total CO ionization cross section. The latter has been measured by the same authors and has a maximum value of $2.74 \times 10^{-16} \text{ cm}^2$ ($E_e = 120 \text{ eV}$), which is close to that of Rapp and Englander-Golden¹⁰ of $2.64 \times 10^{-16} \text{ cm}^2$. It can be seen from Fig. 1 that the CO^+ curve obtained by Defrance and Gomet is some 50% higher at 110 eV than the present data. Their cross section curve also disagrees seriously in shape with the present results and with that obtained from the data of Rapp *et al.*^{10,11} In evaluating the accuracy of the magnitude of the CO^+ cross section values given by Defrance and Gomet,⁷ it is noteworthy that the sum of all cross section values of the CO fragment ions reported by these authors is much smaller than the cross section for the production of dissociative ions in CO with kinetic energies $> 0.25 \text{ eV}$ reported by Rapp *et al.*¹¹ It seems very likely that Defrance and Gomet⁷ were not able to measure with their mass spectrometer the correct fraction of fragment ions produced with excess kinetic energy. In the normalization procedure used by these authors this would lead to an overestimation of the parent cross section. Because of lack of experimental detail about the performance of their mass spectrometer (discrimination in the ion source, transmission, efficiency of ion collection) it is difficult to prove this point.

Figure 1 also shows $q(\text{CO}^+/\text{CO})$ values calculated from ionization efficiency measurements (number of ions formed per electron per cm path per mm pressure at 0°C) reported by Vaughan.⁶ Vaughan obtained the ionization efficiency curve of CO^+ by multiplying the total number of ions formed as given by Tate and Smith²⁵ by the percent of current carried by a particular ion (CO^+ , CO^{2+} , and C^+) and dividing by the charge on the

ion. The mass spectrometer apparatus employed by Vaughan⁶ in this experiment was the same as that used by Bleakney.²⁶ It can be seen from Fig. 1 that the CO^+ curve thus obtained by Vaughan⁶ is much higher than the present cross section function, some 65% at 110 eV. There are two reasons for this discrepancy. The total CO ionization cross section of Tate and Smith,²⁵ which Vaughan apparently used to calibrate the partial ion currents, has a maximum value some 16% higher than that of Rapp and Englander-Golden.¹⁰ The study of the latter authors seems at the moment the most reliable experimental determination of total cross sections and in the case of Ar and CO has been confirmed by Srinivasan and Rees.²⁷ Moreover, Vaughan has not included the fragment ion O^+ observed by Defrance and Gomet⁷ in their normalization. Vaughan reports "the O^+ ion, if formed, was entirely masked by the H_2O^+ (impurity) ion," a fact which is due to the small resolving power of the mass spectrometric apparatus²⁶ used. In addition, it must be noted that the cross section of the only fragment ion measured by Vaughan, C^+ , is much smaller than the cross section for the production of dissociative ions in CO with kinetic energies >0.25 eV reported by Rapp *et al.*¹¹ Thus, similar to the case discussed above, not all of the fragment ions produced in CO were detected with the apparatus used, owing to large discrimination effects for energetic dissociated ions. In the normalization procedure used by Vaughan, this fact, however, leads to an overestimation of the CO^+ cross section function.

2. CO^{2+}

Measured relative cross section values for the production of CO^{2+} have to be normalized with the help of a

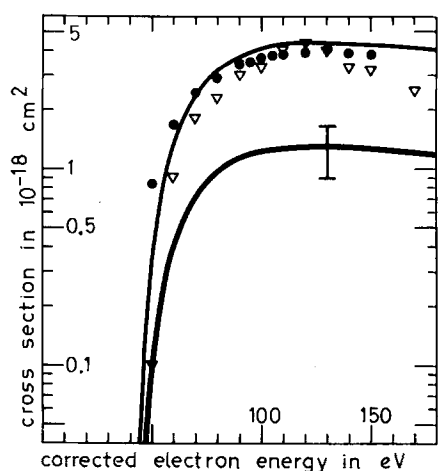


FIG. 2. Absolute partial ionization cross section function $q(\text{CO}^{2+}/\text{CO})$ for the production of CO^{2+} via process $\text{CO} + e \rightarrow \text{CO}^{2+} + 3e$: thick full line, present data for an ion transit residence time from time of formation to time of collection of $\sim 10 \mu\text{s}$ (error range shown $\pm 30\%$); upper thin full line, estimate of the upper limit of the production of metastable and stable CO^{2+} extrapolated to an ion residence time of $0 \mu\text{s}$; ∇ , Defrance and Gomet⁷; \bullet , Vaughan.⁶ The energy scale of the present data was calibrated by means of the square root extrapolation method, taking the double ionization potential of Ar as 43.39 eV (spectroscopic value¹²).

TABLE II. Partial ionization cross sections of the doubly ionized parent ion CO^{2+} divided by that of the singly ionized parent ion CO^+ in % at three different electron energies, as reported by Vaughan,⁶ Defrance and Gomet,⁷ in the present study¹ under extraction and transmission conditions causing a transit time from time of formation to time of collection of $\sim 10 \mu\text{s}$, and in the present study² an estimate of the upper limit of the production of the metastable molecular ion CO^{2+} extrapolated to an ion residence time of $0 \mu\text{s}$ (see also text).

Electron energy (eV)	50	100	150
Vaughan ⁶	0.35	1.27	1.42
Defrance and Gomet ⁷	0.06	1.25	1.36
Present study ¹	0.07	0.72	0.75
Present study ²	0.24	2.43	2.54

measured cross section ratio of $q(\text{CO}^{2+}/\text{CO})/q(\text{CO}^+/\text{CO})$ in order to obtain in the present study the absolute partial ionization cross section function $q(\text{CO}^{2+}/\text{CO})$. It was found, however, that this cross section ratio $q(\text{CO}^{2+}/\text{CO})/q(\text{CO}^+/\text{CO})$ is strongly dependent on the value of the extraction potential applied in the ion source, i. e., with higher extraction potential (corresponding to shorter transit times in the experimental apparatus from time of formation to time of collection) increasing cross section ratios $q(\text{CO}^{2+}/\text{CO})/q(\text{CO}^+/\text{CO})$ have been observed. This experimental behavior can be explained in accordance with previous studies with the metastability of the produced CO^{2+} . Previous authors have found that the doubly charged molecular ion CO^{2+} exists in quasistable electronic states which dissociate spontaneously by unimolecular decay with a mean half-life in the range of 5–30 μs .^{15,16}

The thick full line shown in Fig. 2, with an error range of $\pm 30\%$, represents cross section values $q(\text{CO}^{2+}/\text{CO})$ obtained in the present study under extraction and transmission conditions causing a transit time from time of formation to time of collection of CO^{2+} of $\sim 10 \mu\text{s}$. Measuring the rate of disappearance of CO^{2+} with transit time by determining the extraction voltage discrimination curve of the cross section ratio $q(\text{CO}^{2+}/\text{CO})/q(\text{CO}^+/\text{CO})$ and calibrating it against the stable system $q(\text{Ar}^{2+}/\text{Ar})/q(\text{Ar}^+/\text{Ar})$, it was possible to estimate an upper limit for the cross section of the production of the metastable molecular ion CO^{2+m} (upper thin full line in Fig. 2). The corresponding half-life is $\sim 6 \mu\text{s}$ with no significant infinite lifetime contribution. However, owing to the great uncertainty of the experimental data points it would also be possible to obtain a straight line semi-log plot of cross section ratio vs time leading to a half of $\sim 15 \mu\text{s}$. Both values lie within the range of half-lives reported by previous authors.^{15,16} The experimental points would also be compatible with the assumption that some of the CO^{2+} exists in stable or long-lived states.

Figure 2 also shows absolute ionization cross section

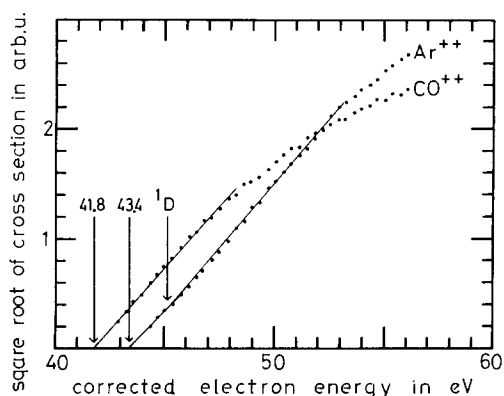


FIG. 3. Square root of the double ionization cross section function $q(\text{CO}^{2+}/\text{CO})$ and $q(\text{Ar}^{2+}/\text{Ar})$ near threshold. Energy scale calibration, see text.

data $q(\text{CO}^{2+}/\text{CO})$ reported by Vaughan⁶ and by Defrance and Gomet,⁷ whose experimental technique and calibration procedure has been described above. It can be seen from Fig. 2 that $q(\text{CO}^{2+}/\text{CO})$ measured by Defrance and Gomet⁷ exhibits a pronounced structure. Because of the lack of experimental detail given, it is difficult to discuss the origin of this structure, which seems to be a special feature of their work [see also $q(\text{CO}^+/\text{CO})$ in Fig. 1, where a similar structure has been reported by Defrance and Gomet].⁷ Because of the inconsistencies in absolute normalization (see the discussion of the CO^+ cross section function) it is not meaningful to compare the absolute values of $q(\text{CO}^{2+}/\text{CO})$ of Vaughan⁶ and

Defrance and Gomet⁷ with the present values, but rather the relative values, i.e., the ratio $q(\text{CO}^{2+}/\text{CO})/q(\text{CO}^+/\text{CO})$. Table II gives the ratio of the partial double and single ionization cross section of carbon monoxide at three different electron energies, 50, 100, and 150 eV. The agreement between the present results and those of the other authors is generally poor. Especially striking is the high ratio at 50 eV reported by Vaughan.⁶ This could be explained by impurity ions H_2O^+ masking the CO^{2+} signal at low electron energies due to the small resolving power of the mass spectrometric apparatus²⁶ used. As both authors^{6,7} were not aware of the quasi-bound nature of CO^{2+} and thus did not mention any residence time of their apparatus, it is difficult to make any further statements about their data.

It should be mentioned that there exists in addition a study of the transition probabilities of electron impact ionization of CO by Cuthbert *et al.*²⁸ From measured relative transition probabilities Cuthbert *et al.* calculated a value of $q(\text{CO}^{2+}/\text{CO}) = 0.001 \text{ \AA}^2$ for an electron energy 5 eV above threshold using the total cross section function of CO reported by Rapp and Englander-Golden.¹⁰ However, the residence time of CO^{2+} in their apparatus is not reported, thus preventing a comparison with other data.

B. Ionization potentials

From the behavior of the single ionization cross section function near threshold the ionization potential

TABLE III. Summary of previously reported appearance potentials of the doubly ionized parent molecule of carbon monoxide.

A. P. (eV)	Reference	Method	Remarks
43.0 ± 1.0	Vaughan (1931) ⁶	Linear extrapolation method	CO^{2+} signal near threshold falsified by impurity ions C^+ and H_2O^+ due to low mass resolution
42.0 ± 0.5	Hagstrum and Tate (1941) ¹³	Linear extrapolation method	...
41.8 ± 0.3 45.9	Dorman and Morrison (1961) ¹⁴	First differential plot	The higher value corresponds to a break in the excitation function of CO^{2+} observed by these authors
$41.17 - 42.8$	Hurley and Maslen (1961) ²⁹	Quantum mechanical virial theorem calculation	Because of lack of accurate knowledge of all the BN spectroscopic constants, particularly the dissociation energy, considerable uncertainty is associated with these values
41.5 ± 0.4	Newton and Sciamanna (1970) ¹⁵	n th Root extrapolation	In order to eliminate any interference from N^+ background in the measurement of A. P. (CO^{2+}) carbon monoxide enriched in ^{13}C was used
41.8 ± 0.5	Newton and Sciamanna (1970) ¹⁵	n th Root extrapolation	Measured A. P. of mass peaks centered about $m/e = 10.3$ and $m/e = 18.3$, respectively. These are the expected apparent mass values for the metastable dissociation of $\text{CO}^{2+} \rightarrow \text{C}^+ + \text{O}^+$
39.9 and 40.2	Moddemann <i>et al.</i> ¹⁷	K -LL Auger spectra	In molecules K -LL Auger data are available from more than one element. Reported minimum energy required for producing doubly charged CO corresponds to results obtained for C and O, respectively.
41.4 ± 1.0	Brehm and De Frenes ¹⁸	Coincidence time of flight	Their experimental apparatus discriminates strongly against CO^{2+} molecules with life times of more than $\sim 3 \mu\text{s}$
41.8 ± 0.5	Present study	n th Root extrapolation	

$\text{CO}^+(X^2\Sigma^+) = (14.07 \pm 0.05) \text{ eV}$ has been derived by means of the linear extrapolation method, using argon as reference gas and taking the single ionization potential of Ar as 15.76 eV (spectroscopic value).¹² No attempt has been made to improve the statistics so that breaks in the curve due to excited states of the ion could be identified.¹² The present value of the first ionization potential of CO is in excellent agreement with previous even more detailed measurements by various methods,¹² hence proving the correct calibration of the electron energy scale in the present study.

On the assumption that the n th power rule is correct, the minimum double ionization potential was taken in the present study as the point to which the square root of the extrapolated double ionization function met the energy axis, yielding A.P. (CO^{2+}) = $(41.8 \pm 0.5) \text{ eV}$, again using argon as reference gas with A.P. (Ar^{2+}) = 43.39 eV.¹² It should be noted that for the doubly ionized parent molecule of CO a square law dependence of the cross section has been found from threshold up to some 7 eV above onset (Fig. 3). In accordance with Newton and Sciamanna,¹⁵ the break in the ionization at 45.9 eV observed by Dorman and Morrison¹⁴ does not occur in the present results. On the other hand, a break in the ionization function Ar^{2+} was observed in agreement with Newton and Sciamanna¹⁵ and Morrison and Dorman,²⁹ corresponding to the metastable singlet state ¹D.

Several previous determinations of A.P. (CO^{2+}) are summarized in Table III. The present value agrees fairly well with that of previous experimental determinations and lies within the calculated range of values given by Hurley and Maslen.³⁰

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