

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

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(Received 1 February 1978)

Electron impact ionization of carbon dioxide has been studied as a function of electron energy up to 180 eV with a double focussing mass spectrometer. Absolute partial ionization cross section functions have been measured for the processes $\text{CO}_2 + e \rightarrow \text{CO}_2^+ + 2e$ and $\text{CO}_2 + e \rightarrow \text{CO}_2^{++} + 3e$ by normalization against the Ar^+ ionization cross section. Using n th root extrapolation, the following minimum ionization potentials have been derived from the low energy cross section function: $\text{CO}_2^+(X^2\Pi_g) = 13.79 \pm 0.05$ eV and $\text{I.P.}(\text{CO}_2^{++}) = 37.2 \pm 0.5$ eV. For the doubly ionized parent molecule, a square law dependence of the cross section has been found from threshold up to some 10 eV above onset. All results obtained 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 gas species.¹⁻⁴ The current study is devoted to carbon dioxide, which is the dominant constituent of the atmospheres of Mars and Venus, and is also being used in a high-power laser.⁵

Previous studies reporting partial cross section functions for the production of various ions from CO_2 include those of Peresse and Tuffin,⁶ Adamczyk *et al.*,⁷ Crowe *et al.*,⁸ and Gomet.⁹ However, only two^{6,9} of these include results concerning the doubly ionized molecule CO_2^{++} . Two of the studies^{6,7} have used normalization procedures later questioned by Crowe *et al.*,⁸ whereas the CO_2^+ ionization curves of Peresse *et al.*⁶ and Gomet⁹ are quite different from measurements by other authors.^{7,8,10} Furthermore, the present authors are aware of one study of the temperature dependence of the electron impact ionization of CO_2 up to 1500 K, yielding the result that in this temperature range the relative cross section for forming the primary ion CO_2^+ is temperature independent.¹³ Ionization of CO_2 near threshold yielding ionization and appearance potentials has been studied by several authors¹⁴; however, only two previous electron impact studies exist of the ionization potential of the doubly charged ion CO_2^{++} .^{15,16}

In an effort to obtain more quantitative information about the electron impact formation of the parent ion, ionization of CO_2 has been studied as a function of electron energy E up to 180 eV. Results reported in the current study include absolute partial ionization cross section functions $q(E)$ ¹⁷ for the processes $\text{CO}_2 + e \rightarrow \text{CO}_2^+ + 2e$ and $\text{CO}_2 + e \rightarrow \text{CO}_2^{++} + 3e$. 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, and a high resolution double focussing mass spectrometer (Varian

MAT CH5) with a total dynamic range of 1×10^8 . 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 high electric field at the collector surface also prevented secondary electrons from entering the collision region. The range of the continuously selectable electron accelerating voltage was expanded up to 185 eV and the voltage of the electron focussing Wehnelt cylinder was maintained proportionally to the electron accelerating voltage in order to improve electron current collimation over 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., $C \cdot q(E)$, where it is hoped and is, according to Kieffer and Dunn,²⁰ 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 focussing 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 and reliable relative ($\pm 5\%$) cross section functions can be measured with the present system.¹⁻⁴

Because of the contact potential difference between the electrode in the electron gun and the collision region in the ion source, the energy scale needs to be calibrated. This was done by measuring the cross section curve of

the simultaneously admitted calibrating gas Ar, where the ionization potential is known spectroscopically, and treating these data with the linear extrapolation method. The difference between the observed ionization potential and the spectroscopic ionization potential for Ar was then added to the energy scale (see Fig. 1).

Normalization of the measured relative cross section function $q(\text{CO}_2^+/\text{CO}_2)$, 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 known from the literature. The comparison has been made at an electron energy of 105 eV, using the presently measured ratio $q(\text{Ar}^{2+}/\text{Ar})/q(\text{Ar}^+/\text{Ar}) = 0.082$ and the total ionization cross section $q(\text{Ar}) = 2.84 \times 10^{-16} \text{ cm}^2$ reported by Rapp *et al.*,¹² from which $q(\text{Ar}^+/\text{Ar}) = 2.43 \times 10^{-16} \text{ cm}^2$ is obtained. In a similar way, the results of $q(\text{CO}_2^+/\text{CO}_2)$ were used to normalize the relative cross section function $q(\text{CO}_2^{2+}/\text{CO}_2)$ with the help of a measured cross section ratio of $q(\text{CO}_2^{2+}/\text{CO}_2)/q(\text{CO}_2^+/\text{CO}_2) = 0.011$ at $E = 105 \text{ eV}$. This ratio is the mean value of repeated measurements under various extraction conditions (1 to 10 V extraction potential). In all normalization procedures, the ion currents have been measured with a Faraday collector cup.

The measurement of the ratio of the gas density of argon to the gas under study (CO_2) in the collision chamber necessary for the above absolute calibration has been made by means of the method of molecular effusive flow.^{1,2,12,21} The gas pressure in the gas reservoir is measured with an absolute capacitance manometer. According to Rapp and Englander-Golden¹² and Märk and Egger,² the results thus obtained are believed to be more accurate

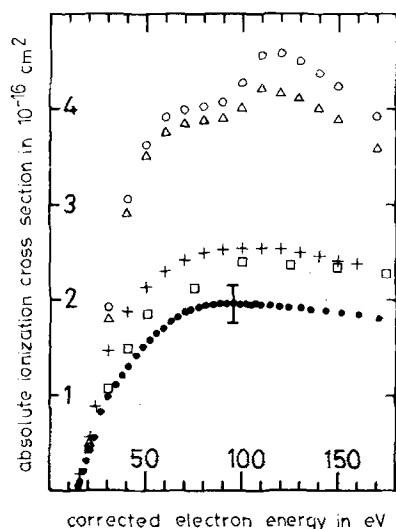


FIG. 1. Absolute partial ionization cross section for the production of CO_2^+ as a function of corrected electron energy: •, present data; +, curve derived from measurements of Rapp *et al.*^{11,12} for $q(\text{CO}_2^+ + 2\text{CO}_2^{2+}/\text{CO}_2)$; Δ , Peresse and Tuffin⁶; \square , Adamczyk *et al.*⁷; and \circ Gomet⁹. The energy scale of the present data has been calibrated with argon by means of the linear extrapolation method, taking the ionization potential of Ar at 15.76 eV (spectroscopic value).

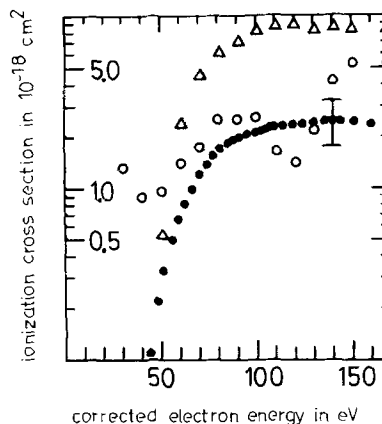


FIG. 2. Absolute partial ionization cross section for the production of CO_2^+ as a function of corrected electron energy: • present data; Δ , Peresse and Tuffin⁶; and \circ , Gomet⁹.

than those based on absolute McLeod gage measurements in each gas.

The accuracy 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^{2+} , the statistical error could be as large as 5% to 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-Golden¹² and Märk *et al.*,^{2,19} the accuracy for repeated measurements at different molecular effusive flow conditions was found to be about $\pm 4\%$. Thus, the estimated maximum possible error, excluding that of the absolute value of $q(\text{Ar}^+/\text{Ar})$, is about 10% for $q(\text{CO}_2^+/\text{CO}_2)$ and about 20% to 30% for $q(\text{CO}_2^{2+}/\text{CO}_2)$.

The CO_2 gas used was purified by distillation *in vacuo* with -10 , -80 , and -180°C cold traps. Impurities still present have been determined mass spectrometrically (H_2O , N_2 , and $\text{O}_2 < 0.5\%$). Electron currents of 10 to 50 μA have been used; however, for most of the calibration work, an electron current of 50 μA has been used. The gas temperature in the collision chamber has been stabilized at 400 K during measurements.

III. RESULTS AND DISCUSSION

A. Single and double ionization cross section function

1. CO_2^+

The absolute cross sections obtained for the processes $\text{CO}_2 + e \rightarrow \text{CO}_2^+ + 2e$ and $\text{CO}_2 + e \rightarrow \text{CO}_2^{2+} + 3e$ are shown as a function of electron energy in Figs. 1 and 2, respectively. It can be seen that the CO_2^+ curve has its peak near 95 eV, while the CO_2^{2+} curve peaks around 145 eV. A representative set of values of the cross sections measured in the present study is given in Table I. Figures 1 and 2 also show absolute ionization cross section curves of CO_2^+ and CO_2^{2+} reported by previous authors.

Points designated + in Fig. 1 represent a rough esti-

TABLE I. Absolute partial ionization cross sections $q(\text{CO}_2^+/\text{CO}_2)$ and $q(\text{CO}_2^{++}/\text{CO}_2)$ for different corrected electron energies.

E (eV)	$q(\text{CO}_2^+/\text{CO}_2)$ (10^{-16} cm^2)	$q(\text{CO}_2^{++}/\text{CO}_2)$ (10^{-18} cm^2)
171.1	1.81	2.20
160.3	1.84	2.36
151.2	1.86	2.47
143.4	1.88	2.47
130.0	1.92	2.42
119.0	1.92	2.36
109.1	1.95	2.31
102.1	1.95	2.14
91.5	1.96	1.98
84.4	1.95	1.81
77.1	1.92	1.54
70.0	1.87	1.21
62.8	1.77	0.82
55.6	1.65	0.49
52.0	1.58	0.33
48.4	1.51	0.22
44.8	1.42	0.11
40.8	1.31	0.05
37.6	1.21	...
34.0	1.12	...
30.4	0.98	...
26.8	0.82	...
23.1	0.55	...
21.4	0.43	...
17.7	0.20	...
15.9	0.083	...
15.2	0.042	...
14.1	0.021	...

mate of the upper limit to $q(\text{CO}_2^+/\text{CO}_2)$ derived from measurements of Rapp and Englander-Golden¹² and Rapp *et al.*¹¹ These authors made absolute measurements, using total ionization tubes, of the total ionization cross section of CO_2 and of the cross section for the production of ions in CO_2 with kinetic energies > 0.25 eV. Hence, subtraction of the energetic ion curve, corrected by 30% for dissociative ions with energies < 0.25 eV, from the total ion curve, should give an estimate for the cross section function for the production of $\text{CO}_2^+ + 2\text{CO}_2^{++}$. The cross section values of Rapp *et al.*¹¹ for ions with energies > 0.25 eV have been reduced before this subtraction by 6%, so that these values are consistent with the total cross section values of Rapp and Englander-Golden.¹² This reduction is necessary because of corrections introduced in the latter work to correct for errors of the McLeod pressure measurement. The curve thus obtained from the data of Rapp *et al.* is in good agreement with the shape of the relative cross section function $q(\text{CO}_2^+/\text{CO}_2)$ reported by Crowe *et al.*⁸ The curve of Crowe *et al.*,⁸ which is not shown in Fig. 1 for the sake of preserving clarity, peaks in the 85–90 eV region, whereas the curve derived from the data of Rapp *et al.* has a broad maximum in the 90–110 eV region. Both curves also agree well in shape with the present curve, which has its peak around 95 eV. However, the present curve differs from that obtained from the data of Rapp *et al.*, in magnitude, the present

curve being lower by about 21% at 100 eV. This difference in magnitude, besides being due to the experimental error bars, and due to the uncertainty of the percentage of dissociative ions with energies < 0.25 eV used for the above derivation, could be caused by an error in the value of $q(\text{Ar}^+/\text{Ar})$ used to normalize the present $q(\text{CO}_2^+/\text{CO}_2)$ function. $q(\text{Ar}^+/\text{Ar})$ has been obtained, using the presently measured ratio $r = q(\text{Ar}^{++}/\text{Ar})/q(\text{Ar}^+/\text{Ar}) = 0.082$ at 105 eV and the total ionization cross section of argon reported by Rapp and Englander-Golden.¹² In the literature, however, values from 0.05 to 0.10 are reported for this ratio r at 100 eV.¹⁸ This uncertainty of the measured ratio would cause an error of up to $\pm 7\%$ in the value of $q(\text{Ar}^+/\text{Ar})$.

Also shown in Fig. 1 are the absolute $q(\text{CO}_2^+/\text{CO}_2)$ values reported by Adamczyk *et al.*⁷ These authors have obtained absolute cross section values by normalizing the sum of the CO_2^+ , CO^+ , O^+ , C^+ , and O_2^+ ionization efficiency curves, measured by them with a cycloidal mass spectrometer,²² to the absolute total ionization cross section of CO_2 reported by Rapp and Englander-Golden.¹² The present curve agrees very closely in shape and within the experimental error, in magnitude, with that obtained by Adamczyk *et al.*⁷ It should be noted, however, that according to Crowe and McConkey,⁸ the O_2^+ signal observed by Adamczyk *et al.*⁷ could only be produced in a secondary process as a result of the pressure in their system being too high. Moreover, the CO^+ signal is at an electron energy of 100 eV, by far the dominant dissociative ion in the study of Adamczyk *et al.*,⁷ whereas from the data of Crowe *et al.*,⁸ it follows that O^+ is the dominant fragment ion of CO_2 . The findings of Crowe *et al.* have been confirmed by a recent work of Jackson, Brackmann, and Fite.¹³

Figure 1 also shows $q(\text{CO}_2^+/\text{CO}_2)$ values reported by Peresse and Tuffin.⁶ These cross section values were obtained by normalizing the sum of the CO_2^+ , O^+ , CO^+ , and CO_2^{++} ionization efficiency curves measured by them mass spectrometrically to an absolute total ionization cross section of CO_2 also measured by them. Their cross section curve disagrees seriously in both magnitude and shape (pronounced structure in the region of the peak of the curve) with the present work, the results of Adamczyk *et al.*,⁷ of Crowe and McConkey,⁸ and with that obtained from the data of Rapp *et al.*^{11,12} The peak cross section $q(\text{CO}_2^+/\text{CO}_2) = 4.2 \times 10^{-16} \text{ cm}^2$ at an electron energy of 110 eV reported by these authors is more than a factor of 2 higher than the present value at this energy. Lack of experimental detail in the work of Peresse and Tuffin⁶ makes it difficult to evaluate their work. It is interesting to note, however, that the total CO_2 ionization cross section of Peresse and Tuffin, which they used to calibrate their partial cross section curves, has a maximum value which is some 30% higher than that of Rapp and Englander-Golden,¹² the latter being in good agreement with the semiempirical calculation of Jain and Khare.²³ Similar discrepancies have been noted by Crowe and McConkey²⁴ between the absolute total cross section of N_2 reported by Peresse and Tuffin⁶ and those of Rapp and Englander-Golden¹² and Tate and Smith.²⁵

Moreover, Peresse and Tuffin have not included the

fragment ion C^+ in their normalization, even though the magnitude of its cross section is, according to Adamczyk *et al.*⁷ and Crowe and McConkey,⁸ comparable to those of the other CO_2 fragment ions O^+ and CO^+ . In addition, it should be noted that both the O^+ cross section and the CO^+ cross section values of Peresse and Tuffin are appreciably lower than those of Adamczyk *et al.*⁷ and Crowe and McConkey.⁸ The omission of C^+ and the small relative intensities of CO^+ and O^+ , however, can only account for part of the observed discrepancy.

Also shown in Fig. 1 is the CO_2^+ cross section reported very recently by Gomet.⁹ Gomet has determined the partial ionization cross sections of CO_2 by measuring the relative amounts of the produced ions with a linear rf mass spectrometer²⁶ and by normalizing their sum with the total CO_2 ionization cross section. The latter has been measured by the same author and has a maximum value which is some 30% higher than that of Rapp and Englander-Golden.¹² It is interesting that some of the total ionization cross sections measured by Gomet show similar discrepancies in magnitude when compared with established data, e.g., the values of the absolute total cross section of H_2O reported by Gomet are a factor of about 2 higher than the values reported by Schutten *et al.*,²⁷ and the values of the absolute total cross section of NH_3 reported by Gomet are also a factor of about 2 higher than the experimental values reported by Märk *et al.*⁴ It can be seen from Fig. 1 that the CO_2^+ curve thus obtained by Gomet lies higher than the present data and that of Adamczyk *et al.*⁷ by a factor of 2.3 at 120 eV. In addition, the pronounced structure in the region around 80 eV of Gomet's curve is not evident in the curve of Adamczyk *et al.*,⁷ of Rapp *et al.*,^{11,12} of Crowe and McConkey,⁸ or of the present work. In evaluating the accuracy of the magnitude of the CO_2^+ cross section reported by Gomet, it is noteworthy that all cross sections of the CO_2 fragment ions measured by Gomet are considerably lower than those of Adamczyk *et al.*⁷ and Crowe and McConkey,⁸ although the cross sections of the CO_2 fragment ions reported by the latter have not been corrected for dissociatively produced ions with energies < 0.25 eV. Again, the small relative intensities of the CO_2 fragment ions measured by Gomet and used for the calibration can only account for part of the observed discrepancy.

2. CO_2^{++}

Figure 2 shows, beside the present data, ionization cross section curves of CO_2^{++} reported by Peresse and Tuffin⁶ and by Gomet.⁹ Their cross section curves disagree seriously in both shape and magnitude with the present work. In both previous studies, the partial ionization cross section functions have been determined by measuring the relative amounts of the produced ions of CO_2 mass spectrometrically and by normalizing their sum on the total CO_2 ionization cross section. The latter has been measured by the same authors and, as already discussed above, has a maximum value which is some 30% higher than that of other results.^{12,28} Because of the difference in absolute normalization (see also discussion of the CO_2^+ cross section function), it is not

meaningful to compare the absolute values of the CO_2^{++} cross section curves, but rather the shape or the relative values, i.e., the ratio $q(CO_2^{++}/CO_2)/q(CO_2^+/CO_2)$. It can be seen from Fig. 2 that the $q(CO_2^{++}/CO_2)$ curve of Peresse and Tuffin⁶ and even more the curve of Gomet⁹ exhibit pronounced structures. Because of the lack of experimental detail given, it is difficult to discuss the origin of these structures, which seem to be a special instrumental feature of their work (see also the $q(CO_2^+/CO_2)$ cross section function, where similar structures have been reported by Peresse and Tuffin and by Gomet). In addition to the pronounced structure, their cross section curve peaks around 110 to 120 eV⁶ and around 200 eV,⁹ while the present curve peaks in the 135–150 eV region. Especially striking is the cross section value reported by Gomet at an electron energy of 30 eV, which is well below the established appearance potential of CO_2^{++} (see below).

At that point of the discussion it is appropriate to report that Newton and Sciamanna¹⁶ have observed that part of the CO_2^{++} ions (about 30%) that they produced by electron impact at an electron energy of 80 eV appeared to be in a metastable state dissociating into $CO^+ + O^+$ with a half-life of $2.3 \pm 0.2 \mu s$. Whereas ion residence times of $\geq 10 \mu s$ in the present study do not allow us to monitor an appreciable amount of this metastable state at m/e of CO_2^{++} , the high ratio of $q(CO_2^{++}/CO_2)/q(CO_2^+/CO_2)$ measured by Peresse and Tuffin⁶ could be partly due to the measurement of this metastable state in their instrument. However, because of the lack of experimental detail given by these authors, it is not possible to prove this point.

B. Ionization potentials

From the behavior of the single ionization cross section function near threshold, the ionization potential $CO_2^+(X^2\Pi_g) = (13.79 \pm 0.05)$ eV has been derived by means of the linear extrapolation method. 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.¹⁴ The present value of the first ionization potential of CO_2 is in excellent agreement with previous, even more detailed measurements by various methods.¹⁴

On the assumption that the n th power rule is correct,

TABLE II. Summary of previously reported ionization potentials of the doubly ionized parent molecule of carbon dioxide.

I. P. (eV)	Reference	Method
36.4 ± 0.3	Dorman and Morrison (1961) ¹⁵	First differential plot
38.0 ± 0.2	Newton and Sciamanna (1964) ¹⁶	n th root extrapolation
38.13	Newton and Sciamanna (1964) ¹⁶	Energy balance estimate
36.2 ± 0.4	Samson <i>et al.</i> (1977) ²⁸	Photoionization
37.2 ± 0.5	Present study	n th root extrapolation

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 $I. P. (CO_2^{2+}) = (37.2 \pm 0.5) \text{ eV}$. Several previous determinations are summarized in Table II. Dorman and Morrison¹⁵ reported from measurements of the first derivative of the ionization efficiency curve of CO_2^{2+} that a square law is followed some 5 eV above onset. The curve then changes abruptly to a slower rate of increase. In the present study, a square threshold law is followed for some 10 eV above onset, in good agreement with the threshold behavior observed by Newton and Sciamanna¹⁶ in their study of the ionization efficiency curve of CO_2^{2+} close to threshold.

ACKNOWLEDGMENTS

The authors are grateful to the Österreichischer Fonds zur Förderung der wissenschaftlichen Forschung for financial assistance under Project Nos. 1490, 1727, and 2781. The authors wish to thank Professor M. Pahl, head of the department, for the opportunity to use the mass spectrometric system Varian MAT CH5. We are grateful for a critical reading of the manuscript by guest professor R. N. Varney.

¹T. D. Märk, *J. Chem. Phys.* **63**, 3731 (1975).

²T. D. Märk and F. Egger, *Int. J. Mass Spectrom. Ion Phys.* **20**, 89 (1976).

³T. D. Märk and F. Egger, *J. Chem. Phys.* **67**, 2629 (1977).

⁴T. D. Märk, F. Egger, and M. Cheret, *J. Chem. Phys.* **67**, 3795 (1977).

⁵N. N. Sobolev and V. V. Sobovikov, *Vth ICPEAC*, Leningrad, edited by L. Branscomb, p. 49.

⁶J. Peresse and F. Tuffin, *Meth. Phys. D'Anal. (GAMS)* **3** (1967).

⁷B. Adamczyk, A. J. H. Boerboom, and M. Lukasiewicz, *Int. J. Mass Spectrom. Ion Phys.* **9**, 407 (1972).

⁸A. Crowe and J. W. McConkey, *J. Phys. B* **7**, 349 (1974).

⁹J. Gomet, Thèse, l'Université de Rennes, 1977.

¹⁰Compare also with the ionization cross section values de-

rived when the absolute cross section for production of ions from CO_2 with energies $> 0.25 \text{ eV}$, as measured by Rapp *et al.*,¹¹ is subtracted from the absolute total ionization cross section for CO_2 , as measured by Rapp and Englander-Golden¹². For more detail see Ref. 8.

¹¹D. Rapp, P. Englander-Golden, and D. D. Briglia, *J. Chem. Phys.* **42**, 4081 (1965).

¹²D. Rapp and P. Englander-Golden, *J. Chem. Phys.* **43**, 1464 (1965).

¹³W. M. Jackson, R. T. Brackmann, and W. L. Fite, *Int. J. Mass Spectrom. Ion Phys.* **13**, 237 (1974).

¹⁴J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Draxl, and F. H. Field, *Natl. Stand. Ref. Data Ser. Natl. Bur. Stand.* **26**, (1969).

¹⁵F. H. Dorman and J. D. Morrison, *J. Chem. Phys.* **35**, 575 (1961).

¹⁶A. S. Newton and A. F. Sciamanna, *J. Chem. Phys.* **40**, 718 (1964).

¹⁷Following Kieffer,¹⁸ a nomenclature is used in the present paper, whereby $q(X^+/X)$ designates the cross section for the production of X^+ from X via the process $X + e \rightarrow X^+ + 2e$.

¹⁸L. J. Kieffer, Joint International Laboratory on Astrophysics Report, No. 6, Boulder, CO, 1968.

¹⁹T. D. Märk, F. Egger, E. Hille, M. Cheret, H. Störi, and K. Stephan, *Proceedings of Xth International Conference on the Physics of Electronic and Atomic Collisions*, Paris, 1977, p. 1070; E. Hille, T. D. Märk, and H. Störi, *Proceedings of the 1st Symposium on Atomic and Surface Physics*, Tirol, 1978, p. 59; and K. Stephan, T. D. Märk, and H. Helm, *Proceedings of the 1st Symposium on Atomic and Surface Physics*, Tirol, 1978, p. 77.

²⁰L. J. Kieffer and G. H. Dunn, *Rev. Mod. Phys.* **38**, 1 (1966).

²¹C. Brunnee and H. Voshage, *Massenspektrometrie* (Thiemig, München, 1964), pp. 97-100.

²²B. Adamczyk, *Ann. Univ. Mariae Curie-Skłodowska Sect. AA* **20**, 141 (1969).

²³D. K. Jain and S. P. Khare, *J. Phys. B* **8**, 1429 (1976).

²⁴A. Crowe and J. W. McConkey, *J. Phys. B* **6**, 2108 (1973).

²⁵J. T. Tate and P. T. Smith, *Phys. Rev.* **39**, 270 (1932).

²⁶J. C. Gomet and J. J. Le Jeune, *C. R. Acad. Sci. Ser. B* **273**, 612 (1971).

²⁷J. Schutten, F. J. de Heer, H. R. Moustafa, A. J. H. Boerboom, and J. Kistemaker, *J. Chem. Phys.* **44**, 3924 (1966).

²⁸A. R. Samson, P. C. Kemeny and G. N. Haddad, *Chem. Phys. Lett.* **51**, 75 (1977).