Cross Sections for Electron Collisions With Carbon Dioxide

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Cross section data have been compiled for electron collisions with carbon dioxide (CO_2) molecules, based on 75 references. Collision processes considered are: total scattering, elastic scattering, momentum transfer, excitations of vibrational and electronic states, ionization, electron attachment, and emission of radiation. Molecular properties of CO_2 are summarized as far as they are helpful in understanding those collisional processes. With an evaluation of the compiled data, recommended values of the cross section are presented in a tabular form. The literature was surveyed through early 2001, but more recent data available to the author are also considered. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1481879]

Key words: attachment, carbon dioxide, CO_2, cross section, dissociation, elastic scattering, electron collision, emission, excitation, ionization, momentum transfer, recommended data, total scattering

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1. Introduction

Carbon dioxide (CO_2) is one of the fundamental constituents of the planetary atmosphere. In particular, it is the most abundant molecule in the atmospheres of Venus and Mars. On Earth, its behavior is carefully scrutinized with respect to the global warming process. In a laboratory, CO_2 is widely used in gaseous discharges or low-temperature plasma devices. Since CO_2 is one of the simplest polyatomic molecules, its study is also of interest from the viewpoints of atomic and molecular physics.

An electron collision with CO_2 is one of the basic processes involving the molecule. Since the 1920s, the process has been studied both theoretically and experimentally by many authors. A large number of papers have been published to report cross section data for the process. In view of the wide interest of CO_2 as described above, it is desirable to compile those cross sections and present them in tabular or graphical form. In 1971, recognizing its importance in the upper atmosphere of Mars, Itikawa and Shimizu[1] reviewed the process of electron collision with CO_2 and compiled the relevant cross section data as far as available at that time. Tawara[2] noticed the role of the process in nuclear fusion devices and published a review of the data on the electron-impact cross section of CO_2. Recently Shirai *et al.*[3] revised the work. Karwasz *et al.*[4] published a review article on the electron-impact cross section of a number of polyatomic molecules, including CO_2.

Very recently an extensive collection and evaluation of cross section data has been carried out for electron collisions with molecules.[5] This work has provided a comprehensive set of cross sections recommended for a number of specific processes (i.e., total scattering, elastic scattering, momentum transfer, excitations of vibrational and electronic states, ionization, and electron attachment) for more than 70 molecular species. In the present paper, a complete data set is assembled for electron collision with CO_2, mainly based on the result of that data compilation,[5] but with some significant additional information (e.g., emission cross sections, more recent data on vibrational excitation, etc.) which are either outside the scope of the compilation or reported after the completion of the compilation.

The literature has been surveyed through early 2001, except for a few papers published since then.

2. Properties of CO_2

The carbon dioxide molecule in its electronically ground state is linear. Electronically excited states are discussed in Sec. 6. The equilibrium C–O distance is

$$r_{CO} = 0.11600\ \text{nm}.$$

This was obtained from an analysis of infrared (IR) spectra[6] and confirmed by the electron-diffraction experiment.[7]

The ionization energy of CO_2 recommended by Lias[8] is

$$E_i = 13.777\ (\pm 0.001)\ \text{eV}.$$

The energy to dissociate CO_2 into O–CO was recommended by Darwent[9] to be

$$D = 5.451\ (\pm 0.004)\ \text{eV}.$$

The ground state CO_2 has D_∞ symmetry and no permanent electric dipole. It has an electric quadrupole, whose moment is

$$\Theta = -3.239\ \text{a.u.} = -4.357 \times 10^{-26}\ \text{esu cm}^2.$$

This is a result of very elaborate calculation[10] (i.e., taking a proper account of electronic correlation). There are several measurements of Θ (see Maroulis and Thakkar[10]), but, considering their uncertainties, it is better to adopt the most accurate theoretical value above.

The electrostatic dipole polarizability of CO_2 is a tensor, only two components of which are independent. The isotropic and the anisotropic components are defined, respectively, by

$$\bar{\alpha} = \alpha_0 = \tfrac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}), \tag{1}$$

$$\Delta\alpha = \tfrac{3}{2}\alpha_2 = \alpha_{zz} - \alpha_{xx}, \tag{2}$$

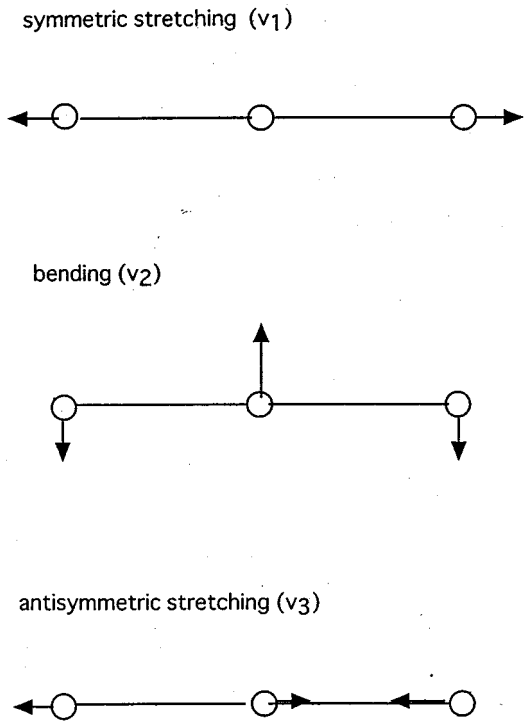

FIG. 1. Normal vibrational modes of CO_2 in its ground electronic state.

where the z axis is taken along the molecular axis. Similarly to the case of the quadrupole moment described above, the isotropic component $\bar{\alpha}$ has been determined by an elaborate theory to be[10]

$$\bar{\alpha}=17.63\ \text{a.u.}=2.613\ \text{Å}^3.$$

Since there is a difference between two large quantities, the anisotropic component $\Delta\alpha$ is amenable to a cancellation error and difficult to obtain theoretically. Instead the value directly determined from a measurement of the Kerr effect[11] is adopted here:

$$\Delta\alpha=13.2\ \text{a.u.}=1.96\ \text{Å}^3.$$

The vibrational (and rotational) spectra of CO_2, mostly in the IR region, have been studied extensively. The spectra and the molecular constants derived from them are collected in a volume of the Landolt–Börnstein series.[12] It contains many works, among which the most comprehensive determination of the energy levels and the line intensities is the one reported by Rothman *et al.*[13] Their result is incorporated into the database HITRAN. According to their analysis, the vibrational and rotational energy levels of CO_2 can be expressed as

$$E(v,J)=G_v+B_vJ(J+1)-D_v[J(J+1)]^2. \qquad (3)$$

CO_2 has three normal modes of vibration as shown in Fig. 1.

TABLE 1. Spectroscopic constants in Eq. (3)[a]

v[b]	G_v (cm^{-1})	B_v (cm^{-1})	D_v (10^{-7} cm^{-1})
000	0	0.3902	1.333
010 ($l_2=1$)	667.4	0.3906	1.353
020[c] ($l_2=0$)	1285	0.3905	1.571
100[c]	1388	0.3902	1.149
001	2349	0.3871	1.330

[a]Determined by Rothman *et al.*[13]
[b]Vibrational states are denoted by $v=(v_1,v_2,v_3)$, where v_1,v_2,v_3 represent the symmetric-stretching, bending, and antisymmetric stretching states, respectively. The quantum number l_2 denotes angular momentum associated with bending vibration.
[c]Due to the Fermi resonance, these two states have a mixed character of (020) and (100).

In Eq. (3), v denotes collectively the vibrational states, i.e., $v=(v_1,v_2,v_3)$, where v_1,v_2, and v_3 represent the vibrational quantum numbers of the symmetric-stretching, bending, and antisymmetric stretching modes, respectively. The rotational quantum number is denoted by J. The spectroscopic constants appearing in Eq. (3) are given in Table 1 for the ground and the lowest excited states.[13]

The following two special features of the CO_2 spectra should be noted:

(1) *Fermi resonance.* In CO_2, the energy levels of (100) and (020) are very close. This accidental degeneracy of the levels is called the Fermi resonance. Due to this resonance, the two levels perturb each other. Table 1 shows the resultant two levels (often called a Fermi dyad), which have both the characters of (100) and (020) (i.e., mixture of the two).

(2) *Vibrational angular momentum quantum number.* The bending mode of a linear molecule is doubly degenerate. This degeneracy causes an angular momentum around the molecular axis. Here we introduce the quantum number l_2 associated with the resulting angular momentum. It takes the value

$$l_2=v_2,v_2-2,\ldots,1 \ \text{or}\ 0. \qquad (4)$$

Thus, in Eq. (3), v_2 should be replaced with a set of quantum numbers (v_2,l_2) to designate the bending mode. Each level (v_2,l_2) with $l_2\neq 0$ is doubly degenerate.

From the rotational–vibrational spectra observed, the molecular constants (i.e., harmonic frequency, anharmonicity constant, etc.) can be determined. Those molecular constants are also tabulated in the Landolt–Börnstein volume.[12] A more recent attempt of the determination is reported by Tashkun *et al.*,[14] who derived the constants from the experimental spectra reported by Rothman *et al.*[13]

Two of the fundamental bands of CO_2 are IR active. They are associated with the bending (v_2) and the antisymmetric stretching (v_3) vibrations. The corresponding IR absorption intensities are[13]

$$S=83065\times10^{-22}\ \text{cm molecule}^{-1} \quad \text{for}\ (000)\rightarrow(010),$$

$$S=916076\times10^{-22}\ \text{cm molecule}^{-1} \quad \text{for}\ (000)\rightarrow(001).$$

TABLE 2. Measurements of total scattering cross section for CO_2

Author	Energy range (eV)
Ferch *et al.*[16]	0.07–4.5
Buckman *et al.*[17]	0.1–5
Szmytkowski *et al.*[18]	0.5–3000
Kimura *et al.*[19]	0.8–500
Sueoka and Mori[20a]	1–400
Kwan *et al.*[21]	1–500
Hoffman *et al.*[22b]	2–50
Garcia and Manero[23]	400–5000

[a]Superseded by Kimura *et al.*[19]
[b]Superseded by Kwan *et al.*[21]

3. Total Scattering Cross Section

The total scattering cross section Q_T for electron collisions with CO_2 was measured by a number of authors. Table 2 lists those measurements published since 1980. Zecca *et al.*[15] recently determined the best value of Q_T. In the lowest energy range (<1 eV) they adopted the experimental data obtained by Ferch *et al.*[16] and Buckman *et al.*,[17] which are in good agreement with each other. In the energy range 1–1000 eV, the three sets of cross sections, obtained by Szmytkowski *et al.*,[18] Kimura *et al.*,[19] and Kwan *et al.*,[21] have an energy dependence consistent with each other. Since there is no special reason to reject any one of them, Zecca *et al.*[15] averaged the three sets of cross sections with equal weight to obtain the recommended values. The resulting cross sections are consistent with the measurement by Garcia and Manero[23] in the higher energy range (>400 eV). Figure 2 and Table 3 show the values of Q_T recommended by Zecca *et al.*[15]

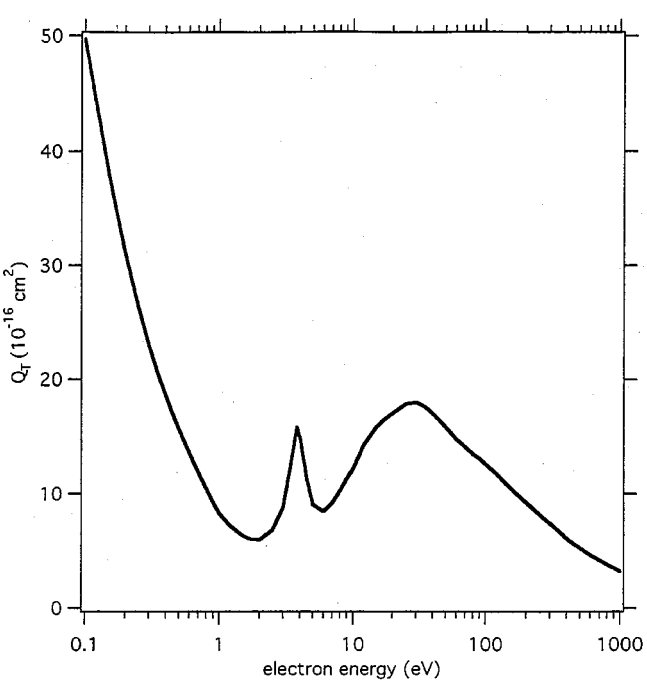

FIG. 2. Recommended values of total electron scattering cross section Q_T of CO_2.

Below 1 eV, Q_T rises with decreasing energy. Recently this was confirmed by Field *et al.*,[24] who used a very low energy electron beam generated by a photoionization of the Ar atom. From an analysis of their cross section data, they ascribed this rapid rise to the effect of a virtual state of the electron in the field of CO_2.

4. Elastic-scattering and Momentum-transfer Cross Sections

Recently Buckman *et al.*[25] determined the best values of the elastic cross section Q_{elas} in the energy range 1–100 eV. Those are based on the elastic differential cross section (DCS) measured by Register *et al.*,[26] Tanaka *et al.*,[27] and Gibson *et al.*[28] Shirai *et al.*[3] report similar recommended data on Q_{elas}. Their result almost agrees with the values recommended by Buckman *et al.*[25] Shirai *et al.*[3] extended the energy range to 1000 eV, taking into account a recent beam measurement by Iga *et al.*[29] in the higher energy region (100–400 eV). In the present paper, the result of Buckman *et al.*[25] in the range 1–60 eV is combined with the values of Shirai *et al.*[3] at 100–1000 eV. The two sets of data can be smoothly connected. The resulting cross sections are shown in Fig. 3 and Table 4. Buckman *et al.*[25] estimated an uncertainty of the data to be ±30%. In the higher energy region (>100 eV), the 18% uncertainty of the original data of Iga *et al.*[29] can be adopted.

Broadly speaking, there are two experimental ways of obtaining the momentum-transfer cross section Q_m. The first one is a beam-type measurement. Once the elastic differential cross section q_{elas} is derived from a beam measurement, the Q_m can be calculated as

$$Q_m = 2\pi \int_0^{\pi} (1-\cos\theta) q_{elas}(\theta) \sin\theta \, d\theta. \tag{5}$$

Another method is a swarm-type experiment. In the experiment, a set of cross sections is determined so as to reproduce the measured values of the transport properties of electrons in a gas. This method is practically suitable to give Q_m at a very low energy of electrons (say, <1 eV), where the data on Q_m have a prime importance. As the collision energy increases, it becomes harder to derive the cross section set without any ambiguity, because a number of different collision processes should be taken into account simultaneously. Elford *et al.*[30] determined their recommended value of Q_m from a recent swarm measurement of Nakamura,[31] corrected with the beam data at higher energies. In the procedure, they took into account the same beam experiments as considered in the case of Q_{elas} above. Their results of Q_m are shown in

TABLE 3. Total scattering cross section

Energy (eV)	Cross section (10^{-16} cm^2)
0.1	49.7
0.12	44.3
0.15	38.1
0.17	34.9
0.2	31.1
0.25	26.4
0.3	23.0
0.35	20.5
0.4	18.6
0.45	17.0
0.5	15.7
0.6	13.6
0.7	11.9
0.8	10.5
0.9	9.25
1	8.29
1.2	7.22
1.5	6.32
1.7	6.02
2	5.94
2.5	6.81
3	8.77
3.5	13.3
3.8	15.8
4	14.9
4.5	11.3
5	9.06
6	8.44
7	9.21
8	10.3
9	11.3
10	12.2
12	14.2
15	15.8
17	16.4
20	17.0
25	17.8
30	18.0
35	17.6
40	17.0
45	16.4
50	15.8
60	14.8
70	13.5
80	13.5
90	13.1
100	12.6
120	11.8
150	10.6
170	10.0
200	9.24
250	8.20
300	7.39
250	6.73
300	7.39
350	6.73
400	6.08
450	5.62
500	5.23
600	4.63
700	4.16
800	3.78
900	3.47
1000	3.20

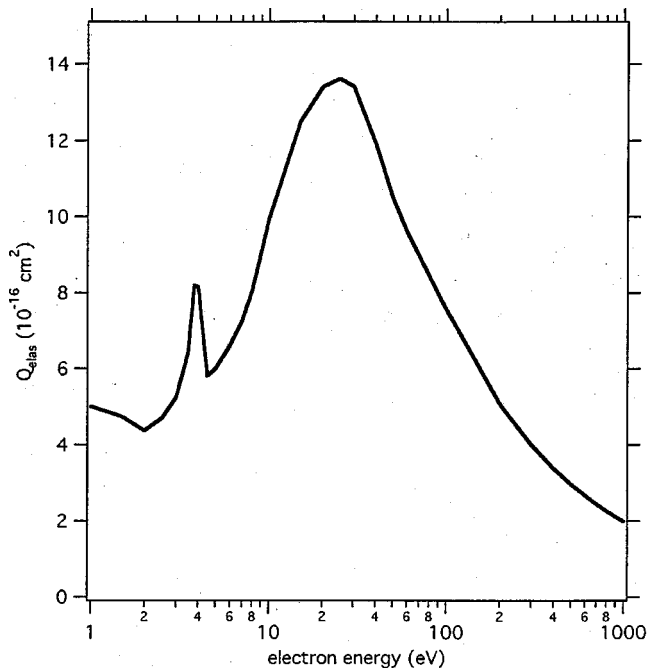

FIG. 3. Recommended values of elastic electron scattering cross section Q_{elas} of CO_2.

TABLE 4. Elastic scattering cross section

Energy (eV)	Cross section (10^{-16} cm^2)
1.0	5.00
1.5	4.73
2.0	4.37
2.5	4.70
3.0	5.25
3.5	6.40
3.8	8.20
4.0	8.15
4.5	5.80
5.0	6.00
6.0	6.60
7.0	7.25
8.0	8.06
10.0	9.95
15	12.5
20	13.4
25	13.6
30	13.4
40	11.9
50	10.5
60	9.6
100	7.55
200	5.07
300	4.01
400	3.39
500	2.98
600	2.68
700	2.45
800	2.26
900	2.11
1000	1.99

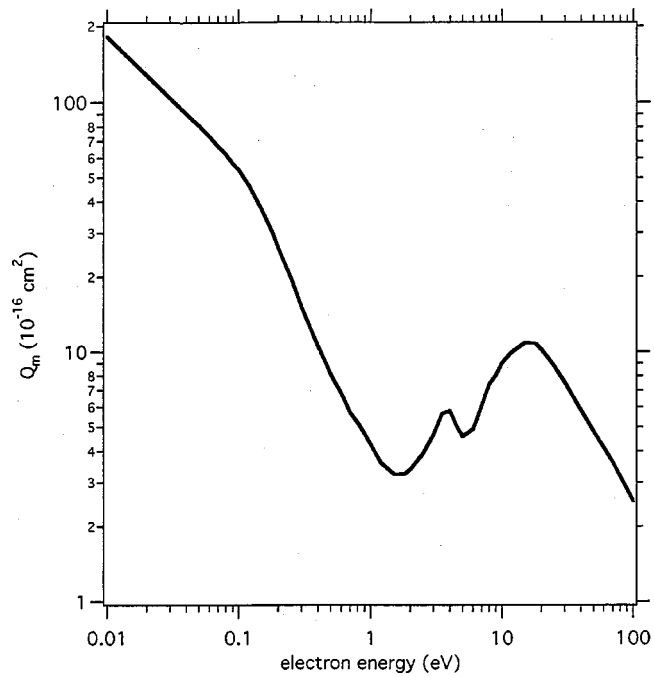

FIG. 4. Recommended values of momentum transfer cross section Q_m for the electron scattering from CO_2.

Fig. 4 and Table 5. Elford *et al.*[30] estimated an uncertainty of the Q_m to be $<5\%$ for 0.01–0.5 eV, $<10\%$ for 0.5–20 eV and $<20\%$ for 20–100 eV.

5. Vibrational Excitation

Kitajima *et al.*[32] made a very comprehensive measurement of the DCS for the vibrational excitation of CO_2. Their DCS is consistent with the results of previous beam-type experiments,[26,33] although the latter measurements were done at only a few points of collision energy. Kitajima *et al.*[32] reported their DCS over the scattering angles of 20°–130°, except at 4 eV, where the smallest angle was extended to 10°. In his master's thesis, Watanabe[34] attempted to extrapolate the DCS in both the forward and the backward directions to obtain integral cross sections (ICSs). As a guideline for the extrapolation, he referred to the calculation by Takekawa and Itikawa.[35,36] It is well known that for a dipole-allowed transition, the Born approximation can give a fairly accurate DCS at the small scattering angles, if properly taking into account the electron interaction with the molecular dipole.[37] CO_2 has no permanent dipole moment. But, once the nuclear coordinates deviate from their equilibrium positions, CO_2 may have a dipole moment. The nuclear-coordinate dependence of the dipole moment induces the absorption/emission of infrared radiation. Similarly the nuclear-coordinate dependence of the electron–dipole interaction is the dominant origin of the excitation of an IR-active vibration, particularly at the small scattering angles. Since the electron–dipole interaction has a long range, its contribution can be well evaluated with the Born approximation.

TABLE 5. Momentum transfer cross section

Energy (eV)	Cross section (10^{-16} cm^2)
0.01	182
0.015	148
0.02	128
0.03	104
0.04	90.0
0.05	80.6
0.06	73.2
0.07	66.8
0.08	61.9
0.09	56.8
0.1	53.6
0.12	46.4
0.15	37.2
0.18	30.1
0.2	26.2
0.25	19.8
0.3	15.05
0.4	10.48
0.5	8.09
0.6	6.77
0.7	5.69
0.8	5.18
0.9	4.69
1	4.25
1.2	3.59
1.5	3.24
1.8	3.24
2	3.39
2.5	3.91
3	4.67
3.5	5.64
4	5.79
4.5	5.02
5	4.58
6	4.91
7	6.08
8	7.40
9	8.09
10	9.02
12	10.00
15	10.86
18	10.76
20	10.17
25	8.74
30	7.51
40	5.84
50	4.79
60	4.15
70	3.61
80	3.19
90	2.83
100	2.53

In the present paper, the experimental DCS of Kitajima *et al.*[32] is extrapolated to obtain ICS in the following manner. In the forward direction (i.e., $<20°$) for the dipole-allowed transitions, (000)→(010), (001), the Born-dipole result is used and otherwise the result of Watanabe's extrapolation is

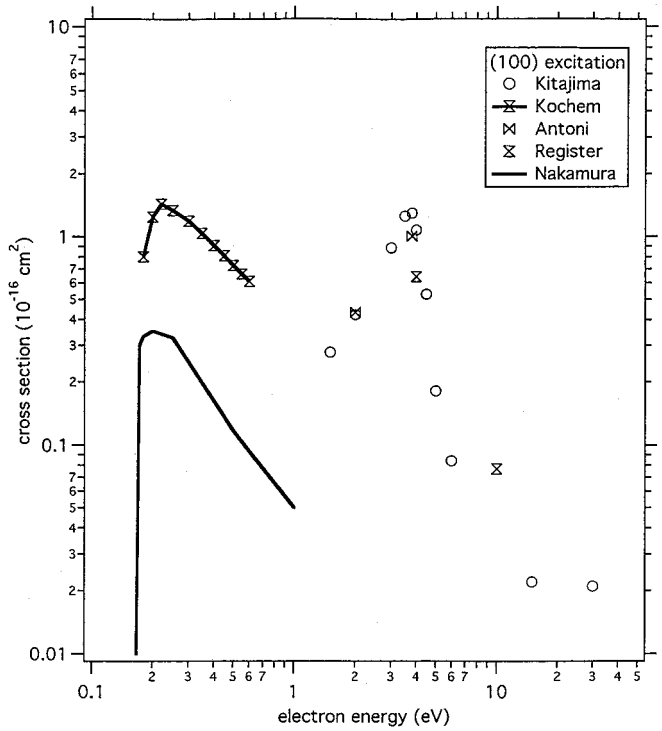

FIG. 5. Cross sections for the electron-impact excitation of the vibrational state (100) of CO_2. Comparison of the beam experiments by Kitajima *et al.*,[32] Antoni *et al.*,[33] Register *et al.*,[26] and Kochem *et al.*,[38] and the swarm result of Nakamura[31] is shown.

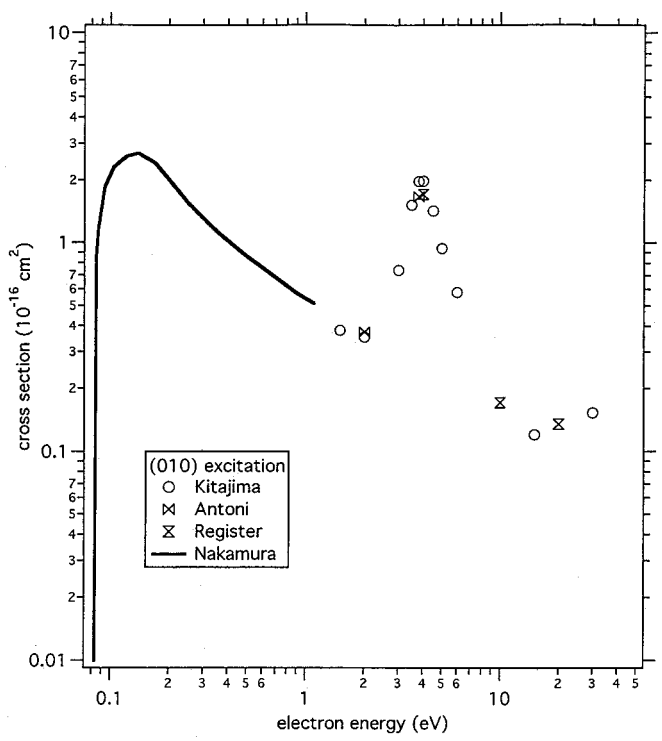

FIG. 6. Cross sections for the electron-impact excitation of the vibrational state (010) of CO_2. Comparison of the beam experiments by Kitajima *et al.*,[32] Antoni *et al.*,[33] and Register *et al.*,[26] and the swarm result of Nakamura[31] is shown.

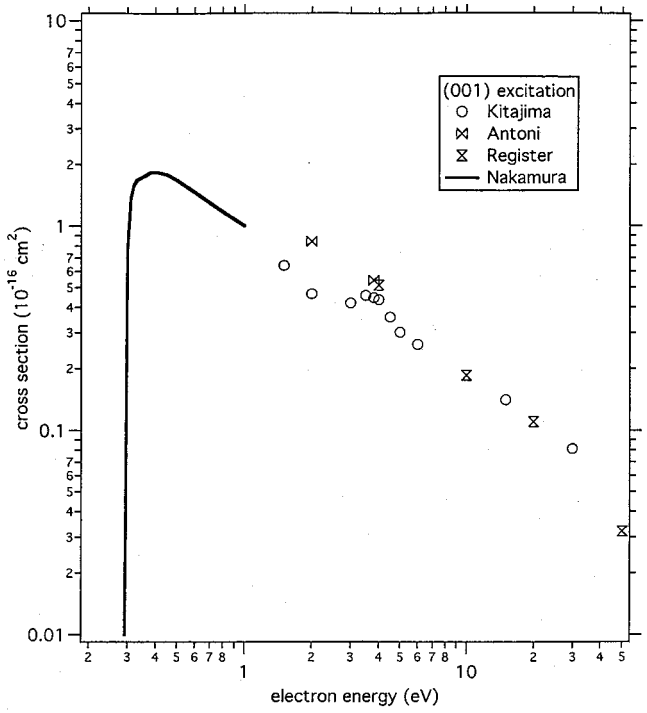

FIG. 7. Cross sections for the electron-impact excitation of the vibrational state (001) of CO_2. Comparison of the beam experiments by Kitajima *et al.*,[32] Antoni *et al.*,[33] and Register *et al.*,[26] and the swarm result of Nakamura[31] is shown.

adopted as it is. The resulting ICSs are compared with the previous data of Register *et al.*[26] and Antoni *et al.*[33] in Figs. 5–7. The present and the previous data are overlapped almost consistently. It should be noted that Kitajima *et al.*[32] assigned an uncertainty of 30% to their measured DCS. As is stated in Sec. 2, there is a Fermi resonance between the (100) and (020) modes of vibration. According to the conventional notation, the higher of the Fermi dyad (with $\Delta E = 0.172$ eV) is called (100) and the lower ($\Delta E = 0.159$ eV) is called (020) here. Kitajima *et al.*[32] obtained the DCS separately for the two states. More discussion about this is given at the end of this section

The vibrational cross section (ICS) can also be derived from a swarm experiment, as in the case of momentum-transfer cross section (see Sec. 4). In such a manner, Nakamura[31] determined the vibrational cross sections for CO_2. As is discussed for Q_m, the swarm result should be most reliable in the low energy region. The values of Nakamura[31] at the energies below 1 eV are plotted in Figs. 5–7. For the excitation of (010) and (001) modes, the present values of ICS are consistent with the swarm data. For the (100) mode, however, a large inconsistency seems to appear between the swarm and the beam results. In the energy range below 1 eV, the cross section for (100) excitation is much smaller than those for the other two modes. From the principle of swarm analysis, smaller cross sections have larger uncertainties. In 1985, Kochem *et al.*[38] made a beam experiment at the energies below 1 eV. For the (100) mode, they

TABLE 6. Vibrational excitation cross sections

Energy (eV)	Cross section (10^{-16} cm^2)		
	(100)[a]	(010)[a]	(001)[a]
1.5	0.277	0.378	0.639
2	0.420	0.350	0.464
3	0.878	0.734	0.417
3.5	1.25	1.51	0.456
3.8	1.29	1.96	0.443
4	1.07	1.97	0.433
4.5	0.526	1.42	0.356
5	0.181	0.938	0.300
6	0.0840	0.576	0.262
15	0.0221	0.120	0.141
30	0.0210	0.153	0.0815

[a]Vibrational states are denoted by $v=(v_1,v_2,v_3)$, where v_1,v_2,v_3 represent the symmetric-stretching, bending, and antisymmetric stretching states, respectively.

TABLE 7. Excited electronic states of CO_2

State[a]	Excitation energy (eV) from the ground state			
	Nakatsuji[44b]	Rabalais *et al.*[42c]	Chan *et al.*[43d]	Lee *et al.*[52e]
$^1\Pi_u$	11.39		11.28	
$^3\Pi_u$	11.31			
$^1\Sigma_u^+$	11.00	11.08	10.3	
$^1\Delta_u$	9.32	8.41	8.38	9.95
$^1\Sigma_u^-$	9.27	6.53		9.73
$^3\Sigma_u^-$	9.19			9.73
$^1\Pi_g$	8.93	9.31	9.30	
$^3\Delta_u$	8.80			9.13
$^3\Pi_g$	8.73			
$^3\Sigma_u^+$	8.15	4.89		8.53

[a]Assignment following Nakatsuji.[44]
[b]Vertical excitation energy calculated by Nakatsuji.[44]
[c]Photoabsorption study by Rabalais *et al.*[42]
[d]Photoabsorption study by Chan *et al.*[43]
[e]Excitation energy employed in the cross section calculation by Lee *et al.*[52]

succeeded in deriving ICS in the energy range below 0.6 eV. The cross sections of Kochem *et al.*[38] are also shown in Fig. 5. The present values are more consistent with Kochem *et al.*[38] than with Nakamura[31] for the (100) excitation.

Here we recommend the vibrational cross sections derived from the beam experiment by Kitajima *et al.*[32] Table 6 presents the ICS derived from their DCS. If one needs the cross section for the energies below 1 eV, the swarm data obtained by Nakamura[31] can be used for the excitations of (010) and (001) modes. For the (100) excitation, the beam data of Kochem *et al.*[38] are preferred to the swarm data of Nakamura,[31] but should be used with caution.

The experiment of Kitajima *et al.*[32] shows that the (020) mode is excited significantly in the region around the 3.8 eV resonance. Particularly in the energy range of 4–6 eV, the cross section for the (020) excitation has a magnitude comparable to that for (100). Below and above the region, the (020) excitation has a DCS more than 1 order of magnitude less than the corresponding value of (100). The swarm analysis of Nakamura[31] does not distinguish the Fermi dyad. Below 1 eV, however, the (020) excitation is assumed to have no contribution compared with that of the excitation (100). The energy dependence of the cross sections (DCS) of the Fermi dyad has been studied in more detail by Allan.[39] In the resonance region, other overtone bands of the vibrational modes are known to be excited (see, for example, Allan[40]), but no quantitatively reliable data are available for the cross section.

6. Excitation of Electronic States

Although the electronic ground state of CO_2 has a linear equilibrium geometry, many of the excited states are supposed to have a bent structure. It is difficult to determine spectroscopically the structure of the bent state, because they show only weak feature in the absorption spectra. Except for the Rydberg states (which are known to be linear), for instance, Herzberg lists four excited states in his book,[41] but gives no details about them. There is still no definite consensus about the assignment of the excited electronic-states of CO_2. Table 7 shows the present situation.

In 1971, Rabalais *et al.*[42] reviewed electronic spectroscopy of linear triatomic molecules. They extensively surveyed the experimental and theoretical results available by then and also reported their own measurement of absorption spectra. Their study was concentrated on the excited states below about 11 eV. For CO_2, they confirmed five excited states in the energy region. Those are listed in Table 7. Note that the lowest state they found ($^3\Sigma_u^+$) was identified only from emission spectra so that it has a bent geometry.

The most recent photoabsorption study of CO_2 was done by Chan *et al.*[43] They employed the electron-impact (e,e) spectroscopy. Below the ionization threshold, they confirmed four distinct states. Those are also listed in Table 7.

There are many theoretical calculations of the electronic structure of CO_2. One of the elaborate calculations is the symmetry-adapted cluster method with CI (SAC-CI) study by Nakatsuji.[44] In his calculation he assumed a linear geometry. From the characteristics of the molecular orbitals, however, he indicated the possibility of bent geometry of some excited states he obtained. On the other hand, Spielfiedel *et al.*[45,46] investigated the bent structure of the excited states. They found that the electronic energy depends critically on the details of the nuclear configuration (i.e., the two C–O distances and the O–C–O angle). It needs very elaborate treatment of electron correlation to obtain reliable values of the electronic energy of CO_2. Recently Buenker *et al.*[47] attempted theoretically to reveal the bent structure of the excited states. Their results are not necessarily in agreement with those of Spielfiedel *et al.*[45,46]

Although electron energy loss spectroscopy has been applied rather extensively in the study of electronic structure of CO_2 (see Green *et al.*[48] and the references therein), very few experimental results have been reported for the excitation cross section. Klump and Lassettre[49] measured DCS for two

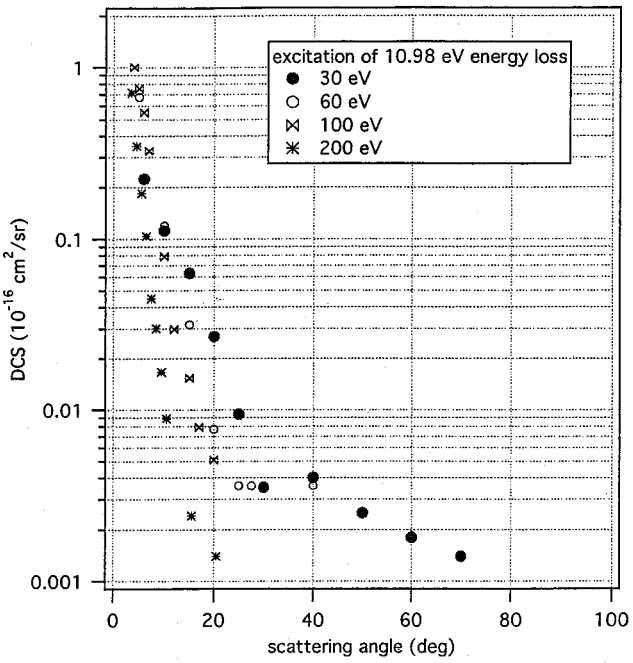

FIG. 8. DCSs for the electron-impact excitation of the excited electronic state with the energy loss of 10.98 eV of CO_2, measured by Green *et al.*[48] The data obtained at the incident electron energies of 30, 60, 100, and 200 eV are shown.

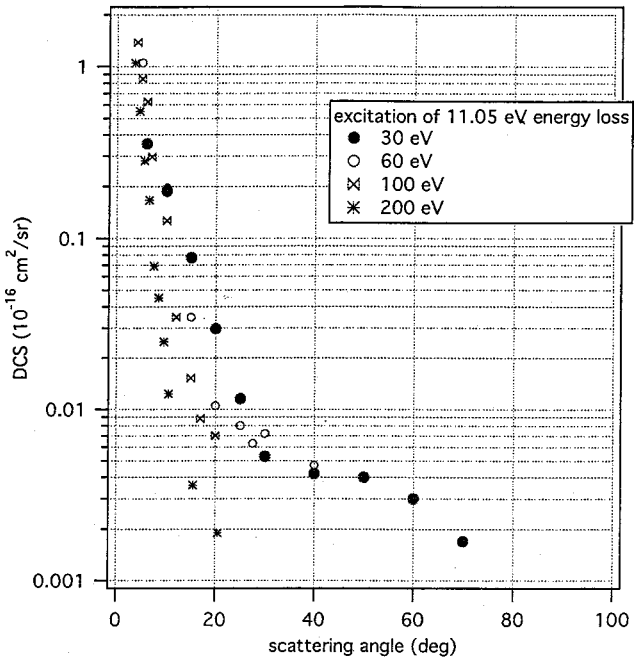

FIG. 9. DCSs for the electron-impact excitation of the excited electronic state with the energy loss of 11.05 eV of CO_2, measured by Green *et al.*[48] The data obtained at the incident electron energies of 30, 60, 100, and 200 eV are shown.

prominent transitions (at 11.05 and 11.40 eV). Their primary aim was to obtain a generalized oscillator strength (GOS), from which they extract the corresponding optical oscillator strength. For this reason, their measurement was limited to very high energies of electrons and at very small scattering angles. Recently Green *et al.*[48] made a more extensive measurement of the cross section for the excitation of the 10.8–11.5 eV energy-loss states. In their energy-loss spectra, they found four clearly distinct peaks at about 10.98, 11.05, 11.16, and 11.40 eV. As is stated above, an identification of the excited electronic states of CO_2 is still controversial. Green *et al.*[48] tentatively assigned those peaks as

$$^1\Sigma_u^{+\prime} \text{ or } ^1\Sigma_u^+ \quad \text{for } 10.98 \text{ eV},$$

$$^1\Sigma_u^+ \text{ or } ^1\Delta_u \quad \text{for } 11.05\,\text{eV},$$

$$C' \quad \text{for } 11.16 \text{ eV},$$

$$^1\Pi_u \quad \text{for } 11.40 \text{ eV}.$$

They measured DCS for the transitions to those states at the collision energy of 20–200 eV. The actual measurement was done independently at two places: Flinders University in Adelaide and Sophia University in Tokyo. A good agreement is found between the two sets of measurements when they are overlapped. Here those measured at the Sophia University[48] are plotted in Figs. 8–11. Green *et al.*[48] claimed an uncertainty of 30% for the result. Since the experimental DCS is available only for a very limited range of scattering angle, it is impossible to derive an integral cross section from them.

There are several attempts to calculate electronic excitation cross sections of CO_2. McCurdy and McKoy[50] applied the Born approximation to the calculation of GOSs for a number of optically allowed excitations. The GOS for the excitation of the $^1\Pi_u$ state is in relatively good agreement with the measurement of the 11.40 eV transition of Klump and Lassettre,[49] but the GOS for $^1\Sigma_u^+$ is much smaller than the corresponding experimental data (i.e., 11.05 eV transition). The same conclusion is drawn from a comparison of the theoretical GOS and the recent experimental data of Green *et al.*[48]

Using a distorted-wave method, Lee and McKoy[51] calculated the cross section for the excitation of eight low-lying states ($^3\Sigma_u^+$, $^3\Pi_g$, $^3\Delta_u$, $^1\Pi_g$, $^1\Delta_u$, $^1\Sigma_u^+$, $^3\Pi_u$, and $^1\Pi_u$) at the collision energies of 25–60 eV. It should be noted that Lee and McKoy[51] show no transition energies for those states. Recently Lee *et al.*[52] employed a close-coupling method to calculate similar cross sections for five excited states (see Table 7). The agreement of the two sets of calculations is not necessarily good. Furthermore Lee *et al.*[52] compared their calculations with three and nine channels coupled to find a rather sensitive effect of the strong coupling among the excited states. Finally, for the excitations of $^1\Sigma_u^+$ and $^1\Pi_u$ states, the theoretical DCS can be compared with the experimental one of Green *et al.*[48] The agreement is very poor, although there is some ambiguity in the assignment of the states. In conclusion a much more elaborate calculation is

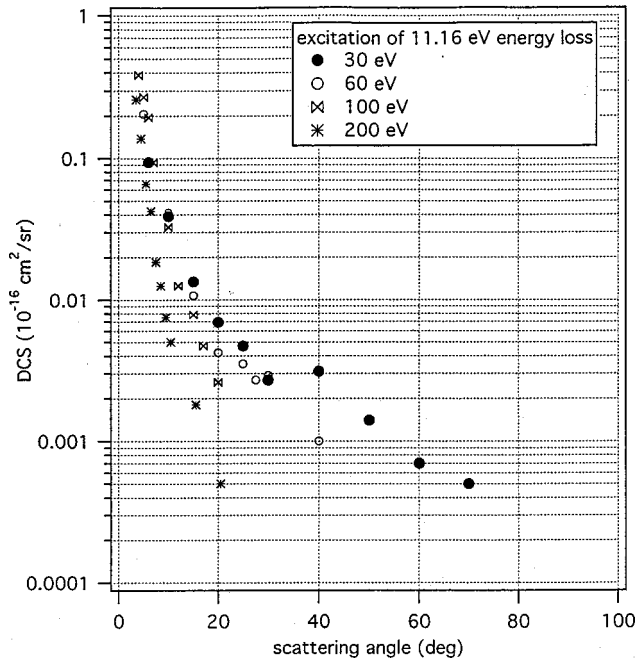

FIG. 10. DCSs for the electron-impact excitation of the excited electronic state with the energy loss of 11.16 eV of CO_2, measured by Green *et al.*[48] The data obtained at the incident electron energies of 30, 60, 100, and 200 eV are shown.

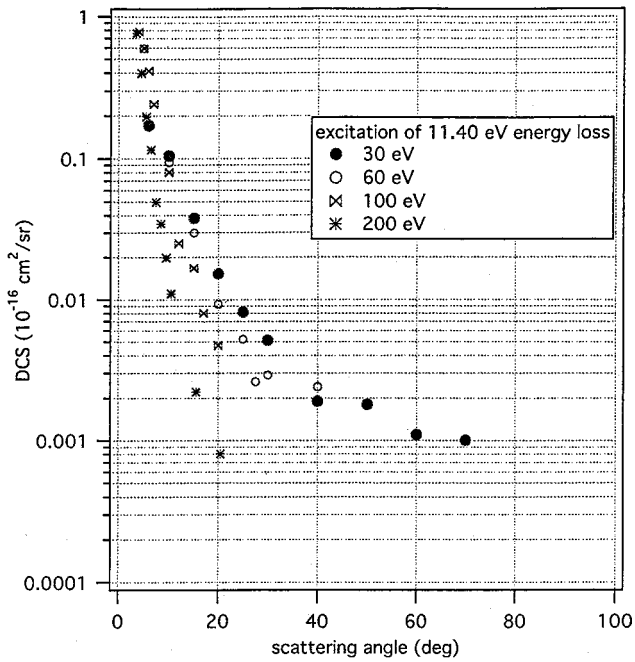

FIG. 11. DCSs for the electron-impact excitation of the excited electronic state with the energy loss of 11.40 eV of CO_2, measured by Green *et al.*[48] The data obtained at the incident electron energies of 30, 60, 100, and 200 eV are shown.

needed to produce reliable cross sections for the electronic excitation of CO_2.

7. Ionization

When an electron collides with a CO_2 molecule, many different kinds of positive ions are produced:

$$
\begin{aligned}
e+CO_2\rightarrow \quad & CO_2^+ && 13.8\ \text{eV},\\
& CO^+ && 19.5\ \text{eV},\\
& O^+ && 19.1\ \text{eV},\\
& C^+ && 27.8\ \text{eV},\\
& CO_2^{++} && 37.4\ \text{eV},\\
& C^{++} && 51.2\ \text{eV},\\
& O^{++} && 54.2\ \text{eV}.
\end{aligned}
$$

The energy given at the right side of each channel shows the appearance energy of the respective ion (see, for example, Tian and Vidal[53]). There are two types of measurements of the ionization cross section. The first one is the measurement of the total ion current, from which the total ionization cross section Q_{ion}(tot) is derived. (Actually the ion-current measurement gives a gross ionization cross section but, as is shown below, the production of multiply charged ions is much less frequent. Hence the gross ionization cross section is practically the same as the total ionization cross section.) This type of experiment is relatively easy to perform so that reliable data can be produced, particularly for their absolute values. In fact, the rather old data of Rapp and Englander-Golden[54] are still taken as a standard of the total ionization cross section for CO_2.

The second kind of ionization experiment is the separate measurement of each product ion with the use of some kind of mass spectrometer. When a dissociative ionization occurs, the fragment ion may have a significant amount of kinetic energy. It is not easy to completely collect the fragment ions, particularly fast ones. Therefore special care should be taken in evaluating experimental data available on the partial (dissociative) ionization cross section.

Recently, after a critical survey of available experimental data, Lindsay and Mangan[55] have determined their recommended values of ionization cross sections. Their result is given in Tables 8–10 and Figs. 12 and 13. Their partial cross sections are based on a very elaborate measurement of the product ions with a time-of-flight (TOF) mass spectrometer by Straub *et al.*[56] It should be noted that Straub *et al.*[56] made their cross sections absolute without resorting to any other data for normalization. For the total cross section below 25 eV, Lindsay and Mangan[55] adopted the values of Rapp and Englander-Golden,[54] instead of Straub *et al.*,[56] because the latter obtained cross sections only at a few energy points. According to Lindsay and Mangan,[55] the uncertainties for the partial cross sections for the productions of CO_2^+, CO^+, C^+, O^+, and the total ionization cross section are 5% for the energies above 25 eV. The cross sections for the energies

TABLE 8. Ionization cross section: total and CO_2^+ production

Energy (eV)	CO_2^+ (10^{-16} cm^2)	Total (10^{-16} cm^2)
14.5	0.055	0.055
15	0.097	0.097
15.5	0.135	0.135
16	0.174	0.174
16.5	0.215	0.215
17	0.255	0.255
17.5	0.293	0.293
18	0.333	0.333
18.5	0.373	0.373
19	0.428	0.428
19.5	0.452	0.452
21	0.577	0.577
21.5	0.623	0.623
22	0.676	0.676
22.5	0.727	0.727
23	0.777	0.777
23.5	0.828	0.828
24	0.880	0.880
25	0.969	1.04
30	1.34	1.58
35	1.53	1.95
40	1.70	2.25
45	1.84	2.50
50	1.94	2.71
55	2.00	2.88
60	2.06	3.06
65	2.10	3.18
70	2.13	3.27
75	2.15	3.36
80	2.19	3.45
85	2.20	3.51
90	2.22	3.56
95	2.23	3.60
100	2.25	3.64
110	2.23	3.66
120	2.23	3.66
140	2.19	3.63
160	2.12	3.52
180	2.08	3.43
200	2.01	3.32
225	1.95	3.21
250	1.87	3.05
275	1.83	2.97
300	1.75	2.82
350	1.62	2.58
400	1.54	2.43
450	1.43	2.23
500	1.35	2.09
550	1.27	1.96
600	1.21	1.85
650	1.16	1.76
700	1.10	1.68
750	1.06	1.61
800	1.01	1.53
850	0.964	1.45
900	0.941	1.41
950	0.909	1.36
1000	0.876	1.30

under 25 eV have uncertainties of 7%. The uncertainties for the productions of CO_2^{++}, C^{++}, and O^{++} are 6%, 11% and 11%, respectively.

The energy distribution of the ejected (secondary) electrons produced by the electron-impact ionization is of practical importance. For instance, to determine how much energy the incident electron loses upon the ionizing collision, we need the energy distribution of the electrons after the collision. The electron energy distribution, often called the single differential cross section (SDCS) of ionization, was measured for CO_2 by Opal *et al.*[57,58] at the impact of 500 eV electron. Later Shyn and Sharp[59] extended the measurement to the lower energies, 50, 100, 200 and 400 eV. The values of SDCS obtained by Shyn and Sharp[59] are given in Table 11. Both groups derived their SDCS from the measurement of the angular distribution of the secondary electrons.

8. Emission Cross Section

Upon an electron collision with a molecule, radiations of various wavelengths are emitted. The detection of those emissions is a diagnostics tool of the molecular gas or plasma. In the case of CO_2, for instance, the electron-impact emission plays an important role in the study of the upper atmospheres of Mars and Venus (see, for example, the review articles by Fox[60] and Fox and Bougher[61]).

(1) *Emission from* CO_2^+. Emissions corresponding to the following transitions are detected:

$$A\,^2\Pi_u \rightarrow X\,^2\Pi_g \quad \text{at} \quad 293.3-438.4 \ \text{nm}$$

$$B\,^2\Sigma_u^+ \rightarrow X\,^2\Pi_g \quad \text{at} \quad 218.9-226.8 \ \text{nm}.$$

It should be noted that both the ground and excited states of CO_2^+ are known to be linear.[41] There are three papers reporting emission cross sections for them.[62–64] The peak values of the cross sections measured by the three groups for the above emissions are almost in agreement with each other. (Note that the cross sections reported by McConkey *et al.*[62] should be corrected as noted in Mentall *et al.*[65]). The cross section of Ajello[63] has too steep an energy dependence near threshold, compared with the other two sets of data.[62,64] Here the cross sections obtained by Tsurubuchi and Iwai,[64] which are newer than the data of McConkey *et al.*,[62] are adopted as the recommended data. They are shown in Fig. 14 and Table 12. Tsurubuchi and Iwai[64] assigned an uncertainty of 25% to their data.

(2) *Emission from* CO^+. Only Ajello[63] measured the cross section for the emission of CO^+

$$B\,^2\Sigma^+ \rightarrow X\,^2\Sigma^+ \quad (\text{first negative system}).$$

The values of Ajello[63] are shown in Fig. 15 and Table 13.

(3) *Emission from CO*. The following band emissions from CO are reported:

TABLE 9. Dissociative ionization cross sections

Energy (eV)	CO^+ (10^{-16} cm^2)	C^+ (10^{-16} cm^2)	O^+ (10^{-16} cm^2)	C^{++} (10^{-18} cm^2)	O^{++} (10^{-18} cm^2)
25	0.0279		0.0419		
30	0.139	0.0024	0.0986		
35	0.247	0.0280	0.150		
40	0.281	0.0782	0.195		
45	0.299	0.121	0.245		
50	0.319	0.149	0.299		
55	0.339	0.178	0.352		
60	0.362	0.208	0.407		
65	0.369	0.229	0.452		
70	0.379	0.246	0.485		
75	0.380	0.261	0.526		
80	0.386	0.278	0.556	0.0179	
85	0.389	0.285	0.584	0.0215	
90	0.390	0.296	0.606	0.0311	
95	0.390	0.306	0.622	0.0506	0.0169
100	0.389	0.310	0.640	0.0520	0.0197
110	0.386	0.322	0.663	0.0751	0.0324
120	0.378	0.323	0.671	0.108	0.0721
140	0.365	0.331	0.680	0.157	0.133
160	0.340	0.321	0.670	0.186	0.159
180	0.333	0.309	0.647	0.249	0.217
200	0.314	0.301	0.631	0.279	0.233
225	0.300	0.288	0.606	0.256	0.271
250	0.278	0.273	0.572	0.291	0.286
275	0.269	0.260	0.553	0.247	0.304
300	0.250	0.245	0.524	0.252	0.276
350	0.226	0.215	0.470	0.216	0.249
400	0.211	0.202	0.433	0.224	0.215
450	0.193	0.183	0.388	0.198	0.193
500	0.178	0.169	0.361	0.177	0.192
550	0.165	0.154	0.339	0.184	0.168
600	0.154	0.145	0.311	0.145	0.156
650	0.145	0.136	0.299	0.169	0.142
700	0.139	0.127	0.283	0.147	0.176
750	0.132	0.123	0.268	0.157	0.147
800	0.124	0.116	0.252	0.139	0.127
850	0.119	0.108	0.238	0.129	0.127
900	0.113	0.105	0.229	0.0965	0.100
950	0.110	0.101	0.222	0.0897	0.116
1000	0.103	0.0964	0.209	0.0984	0.103

$$A\,^1\Pi \rightarrow X\,^1\Sigma^+ \quad \text{(fourth positive system)},$$

$$a\,^3\Pi \rightarrow X\,^1\Sigma^+ \quad \text{(Cameron system)}.$$

Ajello[63] measured both of them. The emission cross section for the fourth positive system is shown in Fig. 16. The emission is very weak and Ajello[63] could not measure the cross section near threshold (13.48 eV). For the Cameron system, Ajello[63] reported only the relative magnitudes of the cross section for the emission of the (0, 1) band at 215.8 nm. The upper state ($a\,^3\Pi$) of this emission is metastable and has a long radiative lifetime. Furthermore, being a dissociative fragment, CO ($a\,^3\Pi$) is known to have kinetic energy. Accordingly the emission of the Cameron system is very weak and easily blended with other emissions, unless the excitation energy is small. Erdman and Zipf[66] tried to remeasure the emission cross section of the Cameron system. They gave an absolute magnitude of the total Cameron system emission cross section of 2.4×10^{-16} cm^2 at 80 eV. Because of the difficulty of the measurement, however, the value is likely to have a large uncertainty by as much as a factor of 2. No recommended cross sections, therefore, are presented here for the Cameron system of emission.

(4) *Emission from O at 130.4 nm.* The two sets of cross sections measured for this emission[63,67] are in a large disagreement with each other (see Fig. 17). Mumma *et al.*[67] obtained their cross section with the normalization to the Lyman α emission at the electron collision with H_2.[68] Their

TABLE 10. Ionization cross section for the production of CO_2^{++}

Energy (eV)	CO_2^{++} (10^{-18} cm^2)
45	0.166
50	0.393
55	0.686
60	1.06
65	1.26
70	1.59
75	1.72
80	2.06
85	2.19
90	2.27
95	2.46
100	2.65
110	2.85
120	2.90
140	2.94
160	2.90
180	2.85
200	2.72
225	2.57
250	2.32
275	2.31
300	2.03
350	1.83
400	1.75
450	1.65
500	1.41
550	1.28
600	1.25
650	1.13
700	1.06
750	0.986
800	0.961
850	0.883
900	0.823
950	0.741
1000	0.723

cross section for the latter process is rather old. If the most recent cross section is employed for the normalization (see van der Burgt *et al.*[69]), the values of Mumma *et al.*[67] should be multiplied by 0.61. Then the two sets of cross sections come closer. However, a difference of a factor of 3 remains near threshold. At present it is difficult to decide which data would be better.

There are many other emissions than those presented above, but they have much smaller cross sections. For instance, Kanik *et al.*[70] reported cross sections for the emissions of wavelengths 40–125 nm, measured at the collision energy of 200 eV. Those are the emissions from O, O^+, C, C^+, CO, and CO^+. All the cross sections reported by Kanik *et al.*,[70] however, are less than 10^{-18} cm^2 (see also a review by van der Burgt *et al.*[69]).

9. Dissociative Attachment

Recently Itikawa[71] reviewed the cross section data for electron attachment to molecules. Here his conclusion for

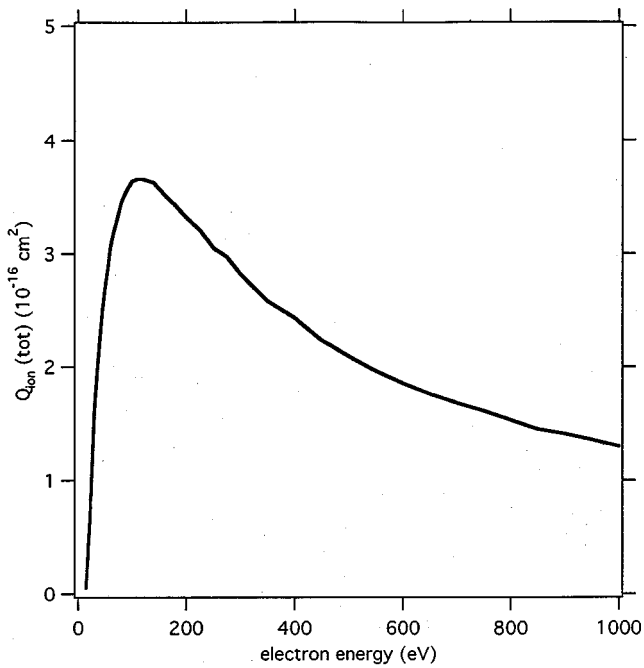

FIG. 12. Recommended values of total ionization cross section Q_{ion}(tot) for the electron collision with CO_2.

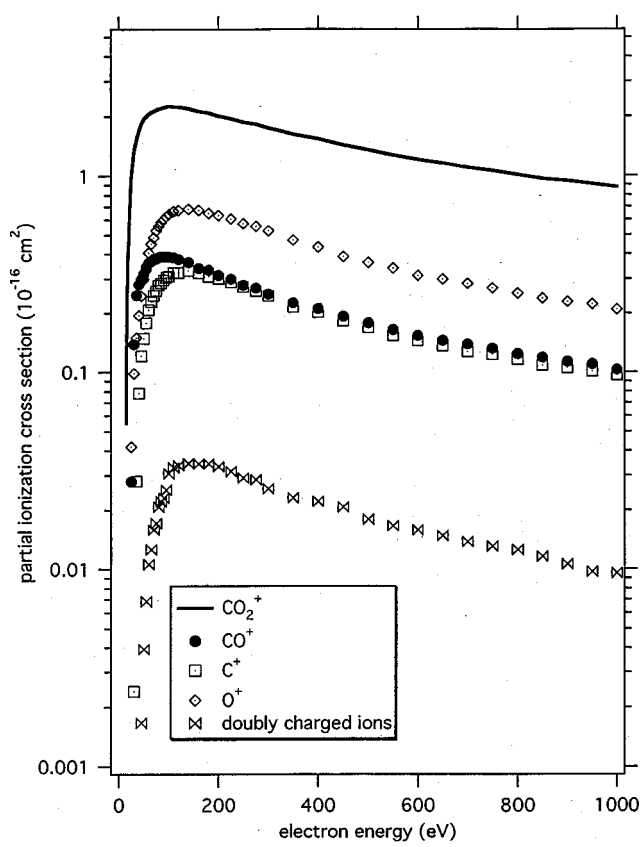

FIG. 13. Recommended values of the partial ionization cross sections for the production of CO_2^+, CO^+, C^+, O^+, and the sum of doubly charged ions (i.e., CO_2^{++}, C^{++}, and O^{++}) upon electron collision with CO_2.

TABLE 11. Single differential cross sections (10^{-18} cm^2 eV^{-1}) for ionization

E_s[a] (eV)	Incident electron energy (eV)			
	50	100	200	400
1	16.08	22.38	15.66	12.66
2	25.47	27.62	19.29	12.50
3	23.37	26.62	20.12	14.44
4	16.57	19.94	17.52	11.43
5	14.60	17.53	14.44	10.51
6	13.51	19.40	12.90	9.32
8	12.79	12.85	10.64	7.70
10	12.50	10.12	8.76	6.30
12	11.26	8.55	7.39	5.47
15	9.61	8.18	5.77	4.52
20		6.18	4.46	3.26
25		4.18	3.22	2.38
30		3.14	2.52	1.76
35		2.87	1.77	1.32
40		2.65	1.32	1.04
50			0.81	0.687
65			0.56	0.401
80			0.49	0.277
100				0.188
120				0.137
140				0.131
160				0.129
180				0.123

[a]Energy of secondary electron.

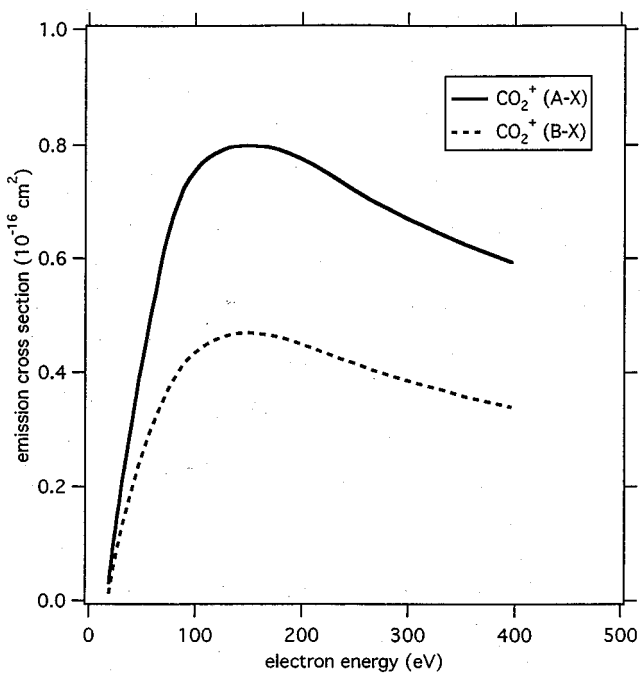

FIG. 14. Recommended values of the cross sections for the emissions $A\,^2\Pi_u \rightarrow X\,^2\Pi_g$ and $B\,^2\Sigma_u^+ \rightarrow X\,^2\Pi_g$ from CO_2^+ upon electron collision with CO_2.

TABLE 12. Cross sections for the emissions from CO_2^+

Energy (eV)	Cross sections (10^{-16} cm^2)	
	$A \rightarrow X$	$B \rightarrow X$
18.8	0.0314	0.0121
19.9	0.0494	0.0247
21.1	0.0682	0.0384
22.4	0.0873	0.0517
23.7	0.107	0.0653
25.1	0.128	0.0797
26.6	0.150	0.0932
28.2	0.168	0.106
29.8	0.191	0.120
31.6	0.214	0.134
33.5	0.233	0.147
35.4	0.256	0.162
37.5	0.280	0.176
39.8	0.304	0.191
42.1	0.331	0.207
44.6	0.356	0.222
47.2	0.388	0.239
50.0	0.416	0.256
53.0	0.445	0.272
56.1	0.476	0.288
59.5	0.508	0.304
63.0	0.541	0.321
66.7	0.579	0.337
70.7	0.615	0.353
74.8	0.646	0.371
79.3	0.675	0.386
88.9	0.723	0.415
94.2	0.740	0.425
99.8	0.754	0.434
106	0.767	0.443
112	0.776	0.451
119	0.784	0.457
126	0.790	0.462
133	0.796	0.466
141	0.796	0.468
149	0.798	0.469
158	0.796	0.467
167	0.796	0.466
177	0.791	0.462
188	0.784	0.457
199	0.775	0.449
211	0.763	0.441
223	0.750	0.432
236	0.734	0.423
250	0.718	0.414
265	0.702	0.404
281	0.687	0.395
298	0.671	0.386
315	0.656	0.377
334	0.640	0.368
354	0.624	0.357
375	0.609	0.348
397	0.593	0.339

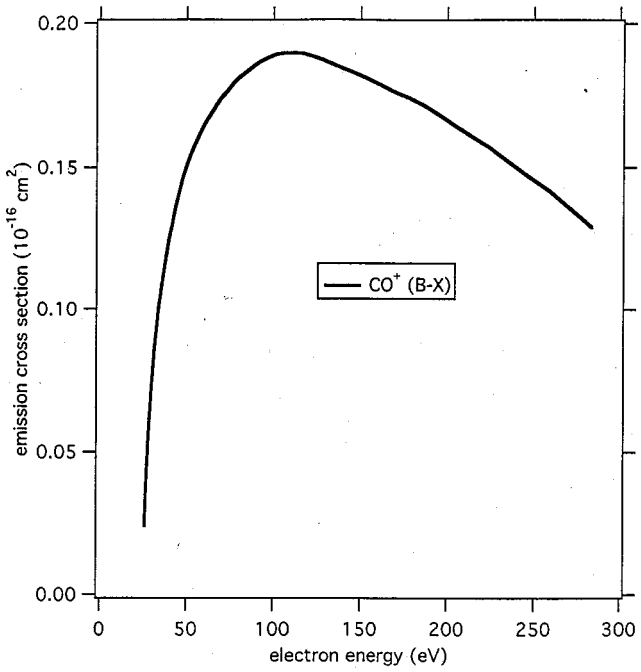

FIG. 15. Recommended values of the cross section for the emission $B\,^2\Sigma^+ \rightarrow X\,^2\Sigma^+$ from CO^+ upon electron collision with CO_2.

CO_2 is adopted. Rapp and Briglia[72] measured absolute values of the cross section for the production of negative ions from CO_2. They used the total ionization method, i.e., the measurement of the total current of negative ions. Using a mass spectrometric method, Orient and Srivastava[73] obtained the cross section for the O^- production. Their values are in agreement with those of Rapp and Briglia[72] within the uncertainty of the cross section ($\pm 20\%$) and the energy scale (± 0.1 eV). Here the cross section measured by Rapp and Briglia[72] is recommended as the cross section for the production of O^- from CO_2. They are shown in Fig. 18 and Table 14.

Spence and Schulz[74] measured cross sections for the production of C^- ions. The cross section has a value in the energy range 14–21 eV with its maximum of about 2×10^{-21} cm^2.

10. Dissociation to Produce Neutral Fragments

Electron collisions with CO_2 produce neutral fragments, CO, C, and O. When those fragments emit radiation, they can be detected easily. The corresponding emission cross sections are compiled in Sec. 8.

Although a few qualitative studies have been reported on the detection of metastable fragments, a direct, quantitative detection of neutral fragments has been made only for O (^1S). With the use of a solid Xe detector, LeClair and McConkey[75] succeeded in measuring the cross section for the production of O (^1S). Their result is shown in Fig. 19 and Table 15. They claimed an uncertainty of 12% for their

TABLE 13. Cross section for the emission from CO^+ (B)

Energy (eV)	Cross section (10^{-16} cm^2)
26.0	0.0240
26.7	0.0346
27.2	0.0440
27.3	0.0521
28.6	0.0594
29.3	0.0663
30.0	0.0729
30.7	0.0791
31.4	0.0845
32.1	0.0897
32.9	0.0942
33.7	0.0984
34.5	0.102
35.3	0.106
37.0	0.114
39.6	0.124
41.6	0.130
43.6	0.136
45.7	0.141
47.9	0.146
50.2	0.151
52.6	0.155
55.1	0.159
57.8	0.162
60.5	0.165
63.4	0.168
66.5	0.171
69.7	0.174
73.0	0.176
76.5	0.179
80.2	0.181
84.0	0.183
88.0	0.185
92.3	0.187
96.7	0.188
101	0.189
106	0.190
111	0.190
117	0.190
122	0.189
128	0.187
134	0.186
141	0.184
147	0.182
154	0.181
162	0.178
170	0.176
178	0.174
186	0.172
195	0.168
204	0.164
214	0.161
224	0.157
235	0.152
247	0.147
258	0.142
271	0.136
284	0.129

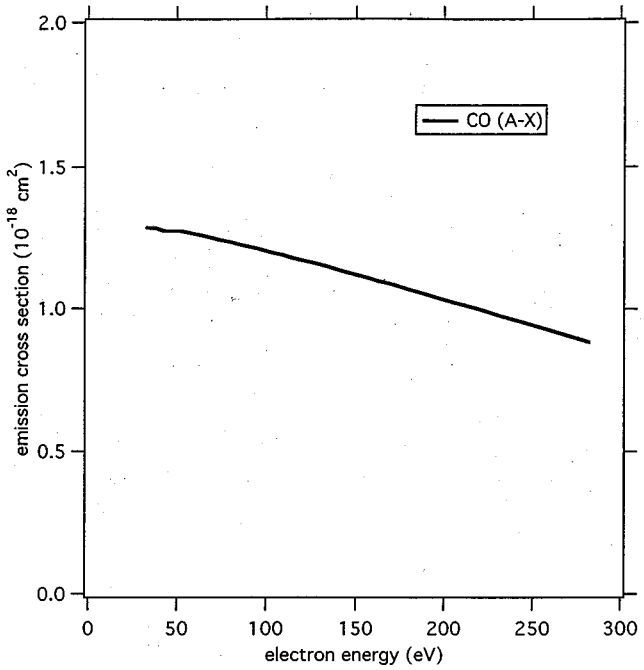

FIG. 16. Cross section for the emission $A\ ^1\Pi \rightarrow X\ ^1\Sigma^+$ from CO measured by Ajello.[63]

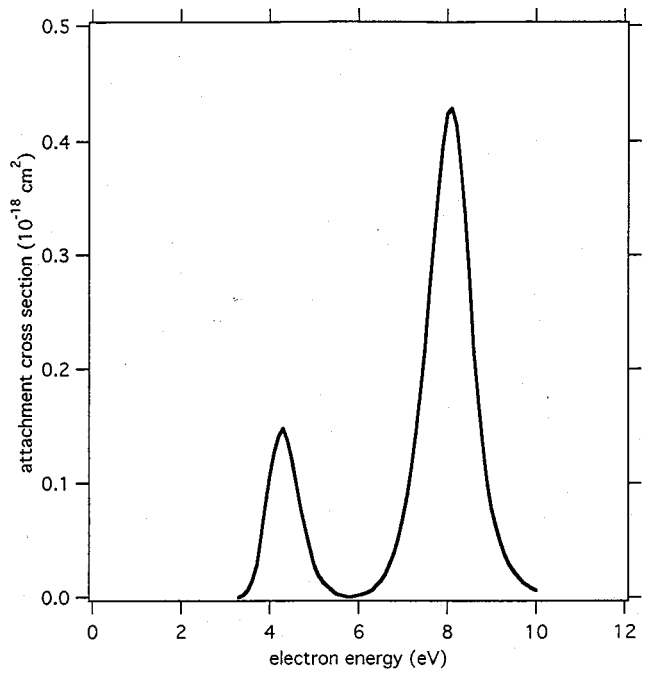

FIG. 18. Recommended values of electron attachment cross section for the electron collision with CO_2.

data. Measuring TOF spectra of O (^1S), they determined the kinetic energy distribution of the fragment atom. On the basis of an analysis of the distribution, they discussed possible dissociation channels for the production of O (^1S).

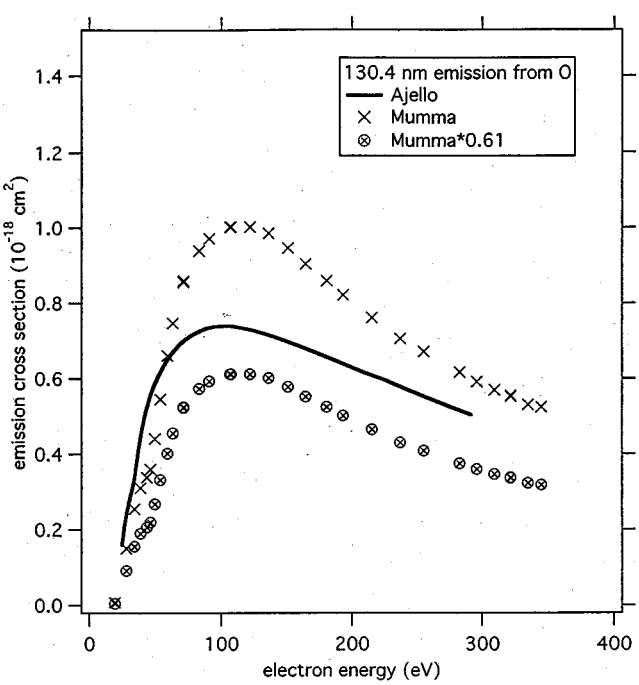

FIG. 17. Cross sections for the emission of 130.4 nm radiation from O upon electron collision with CO_2, measured by Ajello[63] and Mumma *et al.*[67] Renormalized cross section of Mumma *et al.* (Ref. 67) are also shown (see text).

They concluded that a part of it definitely comes from

$$e+CO_2 \rightarrow e+CO_2(^1\Sigma_u^+) \rightarrow e+CO(^1\Sigma^+)+O(^1S) \quad (6)$$

but many other channels contribute to the production of O (^1S). A recent measurement of the cross section for the excitation of the $^1\Sigma_u^+$ state of CO_2 by Green *et al.*[48] supports this dissociation channel.

LeClair and McConkey[75] also measured the metastable fragment CO ($a\ ^3\Pi$). Since they have no information on the detection efficiency of their solid Xe detector for CO ($a\ ^3\Pi$), they could not obtain an absolute magnitude of the cross section for the CO ($a\ ^3\Pi$) production. The relative energy dependence of the cross section, however, is somewhat different from the cross section for the emission from CO ($a\ ^3\Pi$) (see Ajello [63]). LeClair and McConkey[75] estimated the detection efficiency of CO to be very small. Furthermore it may be sensitive to the condition of the CO fragment (i.e., both its kinetic and internal energies). In conclusion, no definitely quantitative information is available for the production of CO ($a\ ^3\Pi$).

11. Summary and Conclusion

Figure 20 shows the cross sections for the electron collision with CO_2 recommended in the present paper. They are

(i) total scattering cross section Q_T (Fig. 2 and Table 3);
(ii) elastic scattering cross section Q_{elas} (Fig. 3 and Table 4);

TABLE 14. Electron attachment cross section

Energy (eV)	Cross section (10^{-16} cm^2)
3.3	0
3.4	1.76*e*-05
3.5	6.16*e*-05
3.6	0.000 141
3.7	0.000 273
3.8	0.000 528
3.9	0.000 818
4.0	0.001 06
4.1	0.001 28
4.2	0.001 41
4.3	0.001 48
4.4	0.001 36
4.5	0.001 21
4.6	0.000 976
4.7	0.000 774
4.8	0.000 598
4.9	0.000 440
5.0	0.000 282
5.1	0.000 194
5.2	0.000 132
5.3	9.68*e*-05
5.4	6.16*e*-05
5.5	2.64*e*-05
5.6	1.76*e*-05
5.7	8.80*e*-06
5.8	0
5.9	8.80*e*-06
6.0	1.76*e*-05
6.1	2.64*e*-05
6.2	4.40*e*-05
6.3	6.16*e*-05
6.4	0.000 106
6.5	0.000 141
6.6	0.000 202
6.7	0.000 290
6.8	0.000 387
6.9	0.000 528
7.0	0.000 897
7.1	0.000 897
7.2	0.001 14
7.3	0.001 45
7.4	0.001 78
7.5	0.002 16
7.6	0.002 67
7.7	0.003 12
7.8	0.003 57
7.9	0.003 96
8.0	0.004 24
8.1	0.004 28
8.2	0.004 13
8.3	0.003 80
8.4	0.003 36
8.5	0.002 83
8.6	0.002 15
8.7	0.001 72
8.8	0.001 36
8.9	0.001 02
9.0	0.000 783
9.1	0.000 616
9.2	0.000 484
9.3	0.000 369
9.4	0.000 290
9.5	0.000 229
9.6	0.000 176
9.7	0.000 132
9.8	0.000 106
9.9	7.92*e*-05
10.0	6.16*e*-05

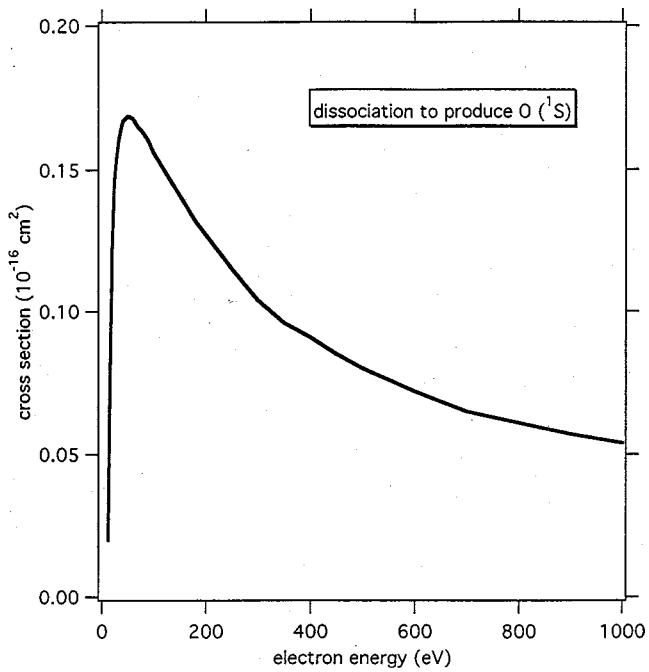

FIG. 19. Recommended values of the electron-impact dissociation cross section of CO_2 for the production of O(^1S).

(iii) momentum-transfer cross section Q_m (Fig. 4 and Table 5);
(iv) total ionization cross section Q_{ion}(tot) (Fig. 12 and Table 8);
(v) dissociative ionization cross section Q_{ion}(dis) (i.e., the sum of the partial ionization cross sections in Table 9);
(vi) cross sections for the emissions from the *A* and *B* states of CO_2^+ (Fig. 14 and Table 12);
(vii) cross section for the production of O (^{1}S) (Fig. 19 and Table 15); and
(viii) vibrational excitation cross sections (Figs. 5–7 and Table 6).

The electron attachment cross section (Fig. 18 and Table 14) is too small to be plotted here.

For the cross sections shown in Fig. 20 to be consistent with each other, the following relation should hold:

$$Q_T = Q_{elas} + Q_{ion}(\text{tot}) + \Sigma Q_{exc}. \tag{7}$$

The last term on the right side of the equation includes all the excitation cross sections of the electronic, as well as vibrational, states. For the electronic excitation of CO_2, only the cross section for the production of O (^1S) is shown in the figure. Other electronic excitation cross sections are either known to be smaller than this or not known quantitatively (see Secs. 6, 8 and 10). Another point which should be noted here is the resonance region at around 3.8 eV. The difference between the Q_T and Q_{elas} in the region seems too large to be

TABLE 15. Cross section for $O(^1S)$ production

Energy (eV)	Cross section (10^{-16} cm^2)
12	0.020
14	0.051
16	0.082
18	0.103
20	0.122
24	0.146
28	0.154
32	0.160
36	0.164
40	0.167
45	0.168
50	0.169
60	0.168
70	0.165
80	0.163
90	0.160
100	0.156
120	0.150
140	0.144
160	0.138
180	0.132
200	0.127
250	0.115
300	0.104
350	0.096
400	0.091
450	0.085
500	0.080
600	0.072
700	0.065
800	0.061
900	0.057
1000	0.054

filled by the vibrational excitation cross sections. As is discussed in Sec. 5, however, overtone bands of the vibrational modes [e.g., (020)] are excited significantly in the resonance region. The overtone excitation can be definitely contributed to the sum of the excitation cross sections in the resonance region, but no quantitative information is available for that. Subject to these conditions, relation (7) holds for the present set of recommended cross sections.

Finally it would be appropriate to mention that further data are needed for the electron collision with CO_2. The most urgent data needed are the cross sections for the excitation of electronic states. There is no definite information available for the excited electronic states of CO_2, except for high-lying Rydberg states. Comprehensive elaborate calculations are probably adequate to provide the necessary information. The low-energy electron collision is also helpful in understanding the structure of the excited states. Furthermore, once electronically excited, the molecule often dissociates into neutral fragments. Those fragments (CO, O, and C) are of practical importance in many application fields. Thus any detailed knowledge about them is necessary. At the collision energy below about 5 eV, vibrational excitation is very important. Even if the absolute magnitude of the excitation cross section is small, the vibrational excitation is the most significant energy loss process of the incident electron in the energy region. In this sense, more accurate cross sections need to be measured, particularly at energies below 1 eV. Also more comprehensive data of the vibrational cross section would be desirable even above 1 eV.

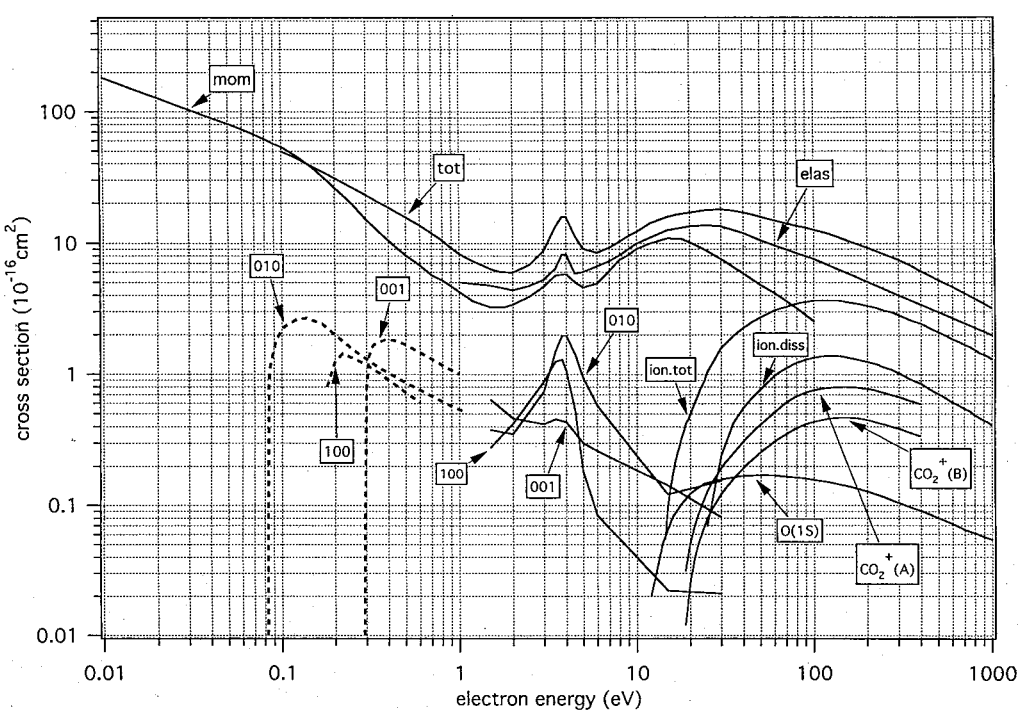

FIG. 20. Summary of the recommended electron collision cross sections for CO_2.

12. Acknowledgments

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