

Theoretical study of electron scattering from carbon dioxide: excitation of bending vibration

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Abstract. The electron-impact excitation of a bending-mode vibration of CO₂ is studied theoretically. Differential and integral cross sections are calculated for the vibrational excitation in the range 2.0–50.0 eV. The calculation is based on the fixed-nuclear orientation approximation. A vibrational two-state close-coupling method is employed with an *ab initio* electrostatic potential and local model potentials for exchange and correlation–polarization interaction. The calculated differential cross sections are found to be satisfactory when compared with experimental data. The resulting integral cross section does not decay quickly at energies above 10 eV, unlike the result of a swarm analysis.

1. Introduction

Carbon dioxide (CO₂), which is a typical linear polyatomic molecule, is one of the main target molecules for electron scattering studies. Although there are many (theoretical and experimental) reports dealing with electron scattering from CO₂, studies taking into account the motion of the nuclei have rarely been performed. Vibrational excitation is the dominant energy-loss process of the incident electron in the low-energy region and cross sectional data for the vibrational excitation of CO₂ are important for various applications, such as atmospheric processes, gas lasers and astrophysics (Trajmar and Cartwright 1984). In a previous paper (Takekawa and Itikawa 1998), vibrational excitations of two stretching modes of CO₂ were theoretically studied. A vibrational excitation of the bending mode is investigated in the present paper as a continuation of the previous study.

The CO₂ molecule has three normal modes of vibration: symmetric stretching, bending (which is doubly degenerate) and antisymmetric stretching. The vibrational excitation energy of CO₂ for the bending mode, $(n_1, n_2, n_3) = (000) \rightarrow (010)$, is 0.0827 eV (Shimanouchi 1972) where n_1, n_2 and n_3 denote the vibrational quantum numbers for symmetric stretching, bending and antisymmetric stretching. In an electron energy-loss spectrum, a peak corresponding to the excitation of the (010) bending mode is located close to the very strong peak of elastic scattering. It is, therefore, difficult to investigate the excitation of the (010) state of CO₂ experimentally.

Several beam-type measurements have been carried out to obtain differential cross sections (DCSs) and integral cross sections (ICSs) for the vibrational excitation of the bending mode of CO₂ by electron impact. Andrick *et al* (1969) obtained DCSs in a relative scale in the

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forward scattering region at an impact energy of 1.9 eV. Register *et al* (1980) reported DCSs for the scattering angle region from 10° to 140° at the incident energies of 4, 10, 20 and 50 eV. They also obtained ICSs by extrapolating their DCSs at the forward and backward scattering angles, with the only exception at 50 eV. Kochem *et al* (1985) measured DCSs in the energy region from threshold to 1.5 eV. Antoni *et al* (1986) obtained DCSs and ICSs at the incident energies of 2 and 3.8 eV. Field *et al* (1991) measured ICSs in the energy region below 1.0 eV. Johnstone *et al* (1995) reported absolute values of DCSs measured at a scattering angle of 20° in the energy region from 1 to 7.5 eV. A beam-type measurement was recently made by Tanaka (1998) to obtain DCSs in the low to intermediate energy region. A swarm-type experiment was carried out by Nakamura (1995). He provided ICSs over the energy range from threshold to 100 eV. His cross sections were obtained as an improvement over the data given by Bulos and Phelps (1976).

Among the three normal modes of vibration, the bending mode is especially difficult to deal with theoretically, because the symmetry is not conserved throughout the collision. For the bending vibration, an elaborate calculation was performed by Whitten and Lane (1982). They reported their theoretical ICS for the $(000) \rightarrow (010)$ excitation near its threshold. Their calculation was made in the vibrational close-coupling approximation with a simple interaction potential. The short-range part of the interaction is the sum of the central 'carbon potential' and a spherical average of the two oxygen potentials. The long-range part of the potential is represented by an electric dipole interaction with a cutoff parameter. The wavefunction for the scattered electron is expanded in terms of partial waves, but only the term of σ symmetry is taken into account.

In the present paper, DCSs and ICSs for the bending mode of CO_2 are obtained theoretically to present comprehensive cross sectional data for a wide range of collisional energies and scattering angles, which have been available until now. Together with the previous study of stretching vibrations, the present work provides a systematic insight into the vibrational excitation of CO_2 . The present calculation focuses on the energy range 2.0–50.0 eV, so that the resulting cross section can be compared with the data obtained by Nakamura (1995). A vibrational two-state (i.e., the vibrational ground state and the first excited state for bending mode) close-coupling calculation in the fixed-nuclear orientation (FNO) approximation is employed in the present study.

2. Theory

In the present study, the problem of an electron scattering from a CO_2 molecule is treated in a manner similar to that used in our previous study of stretching modes (Takekawa and Itikawa 1998). In the bending vibration of a CO_2 molecule, however, the linear symmetry of the molecule is not conserved, unlike in the case of stretching modes. Special care should be taken in the construction of a vibrational wavefunction in the present case. Atomic units are used throughout the present paper unless otherwise stated.

The present calculation is made in the FNO approximation. The bending mode is treated as harmonic and uncoupled with other normal modes of vibration. The electronic state of the target molecule is assumed to be in its ground state throughout the collision. The normal coordinates of a bending vibration are denoted by ξ_{2a} and ξ_{2b} (Herzberg 1964). They are orthogonal with each other and perpendicular to the z -axis (the z -axis in the body-fixed frame is chosen to be the internuclear axis of the molecule in its vibrational ground state). These normal coordinates are transformed into cylindrical coordinates (ρ, δ) ,

$$\xi_{2a} = \rho \cos \delta, \quad \xi_{2b} = \rho \sin \delta. \quad (1)$$

We replace ρ with its dimensionless form q_2 , where $q_2 = \sqrt{\alpha_2}\rho$ and $\alpha_2 = 2\pi\nu_2/\hbar$. Here ν_2 is the frequency of the bending vibration and $\hbar = h/2\pi$, where h is Planck's constant. The wavefunction for the bending mode is specified by the quantum number (n_2, p) , where p distinguishes the two degenerate vibrations. Assuming a harmonic oscillator, the vibrational wavefunctions of the lowest two states of the bending vibration $\chi_{n_2 p}$ can be described as,

$$\chi_{00}(q_2, \delta) = \sqrt{2} \exp\left[-\frac{1}{2}q_2^2\right] \left(\frac{1}{\sqrt{2\pi}}\right) \quad (2a)$$

$$\chi_{1e}(q_2, \delta) = \sqrt{2}(-q_2) \exp\left[-\frac{1}{2}q_2^2\right] \left(\frac{1}{\sqrt{\pi}} \cos \delta\right) \quad (2b)$$

$$\chi_{1o}(q_2, \delta) = \sqrt{2}(-q_2) \exp\left[-\frac{1}{2}q_2^2\right] \left(\frac{i}{\sqrt{\pi}} \sin \delta\right). \quad (2c)$$

The two degenerate vibrations, denoted by $(n_2, p) = (1, e)$ and $(1, o)$ are equivalent. On the assumption (see the statement at the end of the present section) that the transition between the degenerate two states is small, a two-state close-coupling method is applied for the transition between the ground state and one of the degenerate excited states, say $(1, e)$. The cross sections obtained are then multiplied by two to take the effect of the degeneracy into account. In the following formulation the index p in the vibrational wavefunction is omitted for brevity.

The total wavefunction in the body-fixed frame is expanded as,

$$\Psi(q_2, \delta|r) = \sum_{n_2 l \mu} r^{-1} f_{n_2 l \mu}(r) \chi_{n_2}(q_2, \delta) Y_{l \mu}(\hat{r}), \quad (3)$$

where $f_{n_2 l \mu}(r)$ is the radial part of the wavefunction for the incident electron and $Y_{l \mu}(\hat{r})$ represents the spherical harmonics. Here l is the angular momentum quantum number of the incident electron and μ represents the projection of the angular momentum on the z -axis in the body-fixed frame. A set of coupled differential equations for the radial part of the incident electron wavefunction are obtained in the form,

$$\left(\frac{d^2}{dr^2} - \frac{l(l+1)}{r^2} + k_{n_2}^2\right) f_{n_2 l \mu}(r) = 2 \sum_{n_2' l' \mu'} \langle n_2 l \mu | V | n_2' l' \mu' \rangle f_{n_2' l' \mu'}(r), \quad (4)$$

where V is the interaction potential and the wavenumber k_{n_2} is defined as,

$$k_{n_2}^2 = 2[E - E_{n_2}]. \quad (5)$$

Here E is the total energy and E_{n_2} is the excitation energy for the bending mode of vibration. The interaction matrix element appearing in equation (4) is defined by,

$$\langle n_2 l \mu | V | n_2' l' \mu' \rangle = \int d\hat{r} Y_{l \mu}^*(\hat{r}) \langle n_2 | V | n_2' \rangle Y_{l' \mu'}(\hat{r}), \quad (6)$$

where

$$\langle n_2 | V | n_2' \rangle = \int d\delta \int dq_2 q_2 \chi_{n_2}^*(q_2, \delta) V \chi_{n_2'}(q_2, \delta). \quad (7)$$

We solve equation (4) with the boundary condition

$$f_{n_2' l' \mu'}^{n_2 l \mu}(r) \underset{r \rightarrow \infty}{\sim} k_{n_2'}^{-1/2} \left\{ \delta_{n_2 n_2'} \delta_{l l'} \delta_{\mu \mu'} \exp\left[-i\left(k_{n_2'} r - \frac{l'}{2}\pi\right)\right] - S_{n_2' l' \mu'}^{n_2 l \mu} \exp\left[+i\left(k_{n_2'} r - \frac{l'}{2}\pi\right)\right] \right\}, \quad (8)$$

to evaluate the S -matrix element ($S_{n_2 l' \mu'}^{n_2 l \mu}$) in the body-fixed frame. The DCS (denoted as q) for the vibrational excitation of the bending mode can be obtained in the form,

$$q_{(000) \rightarrow (010)}(\theta) = \sum_L A_L P_L(\cos \theta), \quad (9)$$

where θ is the scattering angle in the space-fixed frame and P_L is the Legendre polynomial. In equation (9), A_L is given by,

$$\begin{aligned} A_L = & \frac{1}{4k_0^2} (2L+1) \sum_{\bar{l}} \sum_{l'} \sum_{\bar{\mu}} \sum_{\mu'} i^{l-l'-\bar{l}+\bar{\mu}} [(2l+1)(2l'+1)(2\bar{l}+1)(2\bar{\mu}+1)]^{1/2} (-1)^{\mu-\mu'} \\ & \times \begin{pmatrix} l & \bar{l} & L \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l' & \bar{l}' & L \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l & \bar{l} & L \\ \mu & -\bar{\mu} & -m_L \end{pmatrix} \begin{pmatrix} l' & \bar{l}' & L \\ \mu' & -\bar{\mu}' & -m_L \end{pmatrix} \\ & \times (T_{0l'\mu'}^{1l\mu})(T_{0\bar{l}'\bar{\mu}'}^{1\bar{l}\bar{\mu}})^*. \end{aligned} \quad (10)$$

Here the T -matrix element is defined by,

$$T_{0l'\mu'}^{1l\mu} = \delta_{ll'} \delta_{\mu\mu'} - S_{0l'\mu'}^{1l\mu}. \quad (11)$$

The integral cross section (denoted as Q) is evaluated by,

$$\begin{aligned} Q_{(000) \rightarrow (010)} &= 4\pi A_0 \\ &= \frac{\pi}{k_0^2} \sum_{l'} \sum_{\mu'} |T_{0l'\mu'}^{1l\mu}|^2. \end{aligned} \quad (12)$$

Due to the long-range dipole interaction, the DCS for the vibrational excitation converges very slowly with respect to the partial wave expansion. To remedy the difficulty, the scattering due to the long-range interaction is treated with the Born approximation, i.e., the T -matrix elements for large l and μ are replaced by the corresponding values obtained by the Born approximation with the dipole interaction. We then adopt a closure approximation such as (Gianturco and Scialla 1987),

$$q = q^B + \sum_L^{L_B} (A_L - A_L^B) P_L(\cos \theta), \quad (13)$$

where the superscript B denotes the quantity calculated by the Born approximation with the dipole interaction. The upper limits of summations for l and μ in (10) are determined in such a way that, above the limit, the T -matrix elements calculated by the coupled differential equations (4) can be safely replaced with those calculated by the Born approximation. The upper limit of the summation in (13), L_B , is set to twice the upper limit of l (see section 3). In the same way, the ICS is calculated by

$$Q = Q^B + 4\pi(A_0 - A_0^B). \quad (14)$$

All the terms in equations (13) and (14) are multiplied by two in order to take the effect of degeneracy into account. The expressions of the T -matrix element and the cross sections in the dipole Born approximation are given in the appendix.

The interaction matrix element (6) is necessary to solve the coupled differential equations (4). The interaction potential can be expanded as follows (Clary 1981):

$$V(q_2, \delta|r) = \sum_{m \geq 0} h_m(q_2|r, \vartheta) \cos[m(\varphi - \delta)], \quad (15)$$

where $\hat{r} = (\vartheta, \varphi)$. The vibrational interaction matrix element (7) for the (000) \rightarrow (010) transition is obtained as,

$$\langle n_2 = 1 | V | n_2' = 0 \rangle = \frac{1}{\sqrt{2}} \cos \varphi \int dq_2 q_2 \Gamma_1^*(q_2) h_1(q_2|r, \vartheta) \Gamma_0(q_2), \quad (16)$$

where

$$\begin{aligned}\Gamma_0(q_2) &= \sqrt{2} \exp[-\frac{1}{2}q_2^2], \\ \Gamma_1(q_2) &= \sqrt{2}(-q_2) \exp[-\frac{1}{2}q_2^2].\end{aligned}$$

The interaction potential can be expanded in another form,

$$V(q_2, \delta|r) = \sum_{\lambda\nu} v_{\lambda\nu}(q_2, \delta|r) Y_{\lambda\nu}(\hat{r}). \quad (17)$$

From (15) and (17), the following relation is obtained for $n \geq 0$:

$$h_n(q_2|r, \vartheta) \cos(n\delta) = (2 - \delta_{n0}) \sum_{\lambda \geq n} \text{Re } v_{\lambda n}(q_2, \delta|r) C_{\lambda n} P_\lambda^n(\cos \vartheta). \quad (18)$$

Here the relation

$$Y_{\lambda\nu}(\hat{r}) = C_{\lambda\nu} P_\lambda^\nu(\cos \vartheta) \exp[i\nu\varphi] \quad (19)$$

is used ($P_\lambda^\nu(\cos \vartheta)$ is the associated Legendre polynomial) and $\text{Re } v_{\lambda n}(q_2, \delta|r)$ denotes the real part of $v_{\lambda n}(q_2, \delta|r)$. Equation (18) holds for any δ . When we take $\delta = 0$, $v_{\lambda n}(q_2, \delta|r)$ is shown to be real. From equation (18) with $\delta = 0$, the following relation is obtained for $n = 1$:

$$h_1(q_2|r, \vartheta) = 2 \sum_{\lambda=1} v_{\lambda 1}(q_2, \delta = 0|r) C_{\lambda 1} P_\lambda^1(\cos \vartheta). \quad (20)$$

From (6), (16) and (20), finally, the interaction matrix element for $(n_2, n'_2) = (1, 0)$ is obtained as follows:

$$\begin{aligned}\langle 1l\mu|V|0l'\mu'\rangle &= \frac{1}{\sqrt{2}}(-1)^\mu \sum_{\lambda=1} \langle 1|v_{\lambda 1}(q_2, \delta = 0|r)|0\rangle \left[\frac{(2l+1)(2l'+1)(2\lambda+1)}{4\pi} \right]^{1/2} \\ &\times \begin{pmatrix} l & l' & \lambda \\ 0 & 0 & 0 \end{pmatrix} \left[\begin{pmatrix} l & l' & \lambda \\ -\mu & \mu' & 1 \end{pmatrix} - \begin{pmatrix} l & l' & \lambda \\ -\mu & \mu' & -1 \end{pmatrix} \right].\end{aligned} \quad (21)$$

Furthermore, $v_{\lambda 1}(q_2, \delta = 0|r)$ is expanded in terms of the dimensionless normal coordinate q_2 around its equilibrium position, i.e.,

$$v_{\lambda 1}(q_2, \delta = 0|r) = v_{\lambda 1}(q_2 = 0, \delta = 0|r) + \left(\frac{\partial v_{\lambda 1}(q_2, \delta = 0|r)}{\partial q_2} \right)_{q_2=0} q_2 + (\text{higher-order terms}), \quad (22)$$

and only the first two terms are retained. The vibrational interaction matrix in equation (21) is obtained as follows:

$$\begin{aligned}\langle 1|v_{\lambda 1}(q_2, \delta = 0|r)|0\rangle &= \int dq_2 q_2 \Gamma_1^*(q_2) v_{\lambda 1}(q_2, \delta = 0|r) \Gamma_0(q_2) \\ &= - \left(\frac{\partial v_{\lambda 1}(q_2, \delta = 0|r)}{\partial q_2} \right)_{q_2=0}.\end{aligned} \quad (23)$$

When the incident electron is located at a large distance from the target molecule, the term of $v_{\lambda 1}(q_2, \delta = 0|r)$ can be expressed in terms of the electron interaction with the electric multipole moment. The term $v_{11}(q_2, \delta = 0|r)$ is, for example, expressed by the x -component of the dipole moment and we have,

$$\left(\frac{\partial v_{11}(q_2, \delta = 0|r)}{\partial q_2} \right)_{q_2=0} \underset{r \rightarrow \infty}{\sim} \frac{1}{r^2} \sqrt{\frac{2\pi}{3}} \left(\frac{\partial \mu_x}{\partial q_2} \right)_{q_2=0}. \quad (24)$$

The interaction matrix elements for the vibrationally elastic scattering, i.e., $(n_2, n'_2) = (0, 0)$, have already been given in a previous paper (Takekawa and Itikawa 1996). The interaction

Table 1. The dipole moment derivative of CO₂ for bending mode (in au).

	Experiment		Theory			
	Bishop ^a	Johns ^b	Morrison ^c	Amos ^d	Rakauskas ^e	Present
$(\partial\mu_x/\partial q_2)_{q_2=0}$	0.0665	0.0681	0.1054	0.1053	0.1004	0.1048

^a Bishop and Cheung (1982).

^b Johns *et al* (1990).

^c Morrison and Hay (1979).

^d Amos *et al* (1980).

^e Rakauskas *et al* (1989).

matrix elements for $(n_2, n'_2) = (1, 1)$ are the same as those for $(n_2, n'_2) = (0, 0)$ in the present approximation.

It should be noted here that, with the present model of interaction potential, no transition occurs between the two degenerate members of the first excited state of the bending vibration. That is, the interaction matrix element between the states $(1, e)$ and $(1, o)$ becomes zero, if we retain only the first two terms in (22).

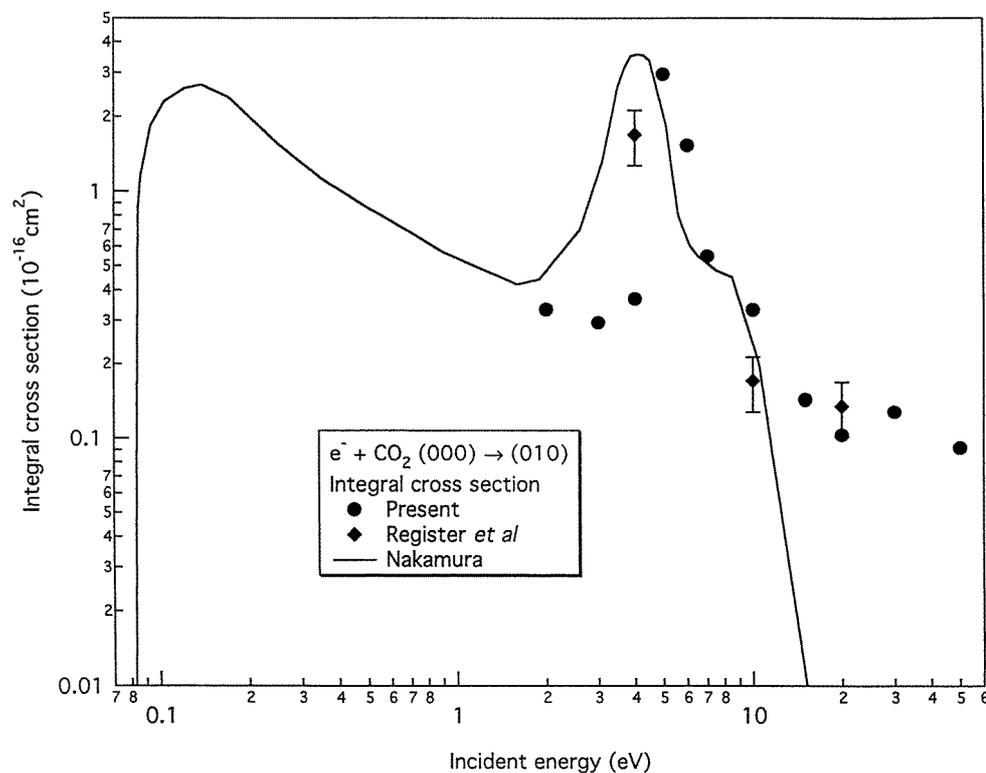


Figure 1. ICSs (in 10^{-16} cm²) for the (000) \rightarrow (010) excitation of CO₂ by electron impact. The present calculation is compared with the experimental data obtained by Register *et al* (1980) (beam-type measurements) and Nakamura (1995) (swarm experiment).

3. Numerical calculation

The interaction potential (V) in equation (4) is composed of three terms, i.e., static, exchange and correlation–polarization potentials. The electrostatic potential is evaluated with an *ab initio* self-consistent field (SCF) multicentred wavefunction. The target wavefunction is constructed by using the quantum chemistry molecular orbital code, GAMESS (the North Dakota State University version, see Schmidt *et al* (1993)). The exchange and the correlation–polarization interactions are approximately taken into consideration with a free–electron gas model (see Takekawa and Itikawa 1996 for details). The exchange interaction is adopted by using the Hara version of the free–electron gas exchange model (Hara 1967). The correlation–polarization potential is constructed by matching the short-range correlation potential (see Padial and Norcross 1984) and the long-range polarization potential. The internuclear distance of equilibrium geometry is taken as 2.191 69 au. As stated in section 2, the asymptotic form of the potential derivative $(\partial v_{11}/\partial q_2)_{q_2=0}$ can be given by the derivative of the dipole moment, i.e., $(\partial \mu_x/\partial q_2)_{q_2=0}$. Table 1 shows the present derivative of the x -component of the dipole moment with experimental and other theoretical results. Although the present value is consistent with the other theoretical values, a rather large disagreement is found when compared with the experimental values. This disagreement affects the DCS in the forward scattering region. To obtain cross sections properly, the derivative of the static potential for $\lambda = 1$ is adjusted to have an asymptotic form (24) with the derivative of the dipole moment recommended by Bishop and Cheung (1982), i.e., 0.0665 au.

We take the terms up to $l = 24$ and $\mu = 2$ in equation (10) and up to $\lambda = 48$ in equation (21) and $L = 48$ (i.e., $L_B = 48$) in (13). The T -matrix elements for $l \geq 24$ or $\mu \geq 2$ obtained by solving equation (4) are confirmed to be in good agreement with the corresponding values calculated by the Born approximation.

4. Results and discussion

Figure 1 shows the ICSs for the vibrational excitation of the bending mode at the energies from the threshold to 50.0 eV. In this figure the present result is compared with the experimental data obtained by Register *et al* (1980) and Nakamura (1995). The strong Π_u resonance peak is shown at around 5.0 eV in the present ICS. This is located at the energy slightly higher than the peak position given by Nakamura. A similar difference in the energy of the resonance peak was found in the previous study of elastic scattering and excitation of symmetric stretching mode of vibration in electron– CO_2 scattering (Takekawa and Itikawa 1996, 1998). The difference between the present theoretical and the experimental results is, therefore, considered to be due to the intrinsic behaviour of the interaction potential adopted in the present calculation. In the energy region $E \geq 10.0$ eV, the present calculation shows a different energy dependence from the swarm experiment. The swarm data decrease rapidly with increasing energy at $E \geq 8.0$ eV. On the other hand, the present cross section at $E = 20.0$ eV has a considerable magnitude, being consistent with the result obtained by the beam-type measurement of Register *et al* within the limit of its error. The swarm analysis by Nakamura was based on a simple extrapolation of the cross section previously determined at the energies up to 10.0 eV (Bulos and Phelps 1976). In the energy region above 10.0 eV, other inelastic processes dominate so much that the swarm analysis is less sensitive to the vibrational excitation to determine reliable cross sections for the process. The present calculation shows a small resonance-like peak around the incident energy of 30.0 eV. A similar structure has been seen in our cross sections for vibrational excitation of stretching modes (Takekawa and Itikawa 1998). The energy dependence of the DCS at 30° and 90° are presented in figure 2. A peak at 30 eV is clearly shown in the DCSs at 90° . The

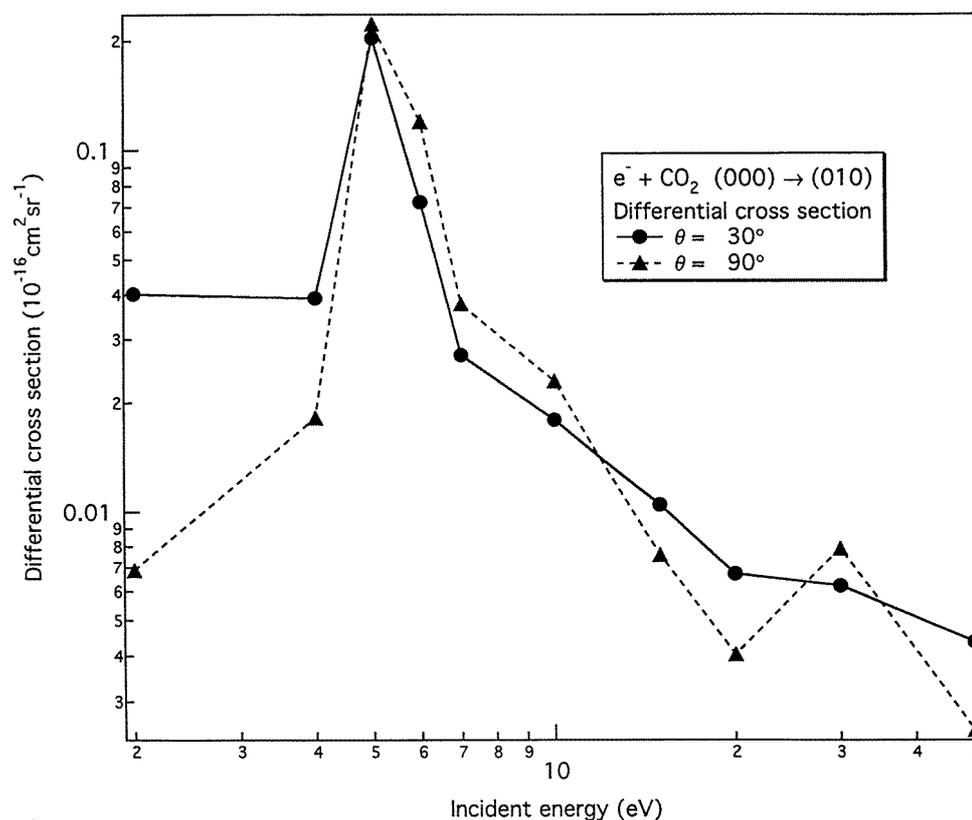


Figure 2. DCSs (in $10^{-16} \text{ cm}^2 \text{ sr}^{-1}$) for the (000) \rightarrow (010) excitation of CO_2 by electron impact at $\theta = 30^\circ$ and 90° as a function of electron energy.

disappearance of the peak in the DCS at 30° can be interpreted by the influence of the long-range dipole interaction. Figure 3 shows the DCSs for the vibrational excitation of bending mode at $\theta = 20^\circ$ in the energy range from 1.0 to 7.0 eV with the experimental data obtained by Johnstone *et al* (1995). In this figure, the present results are quantitatively consistent with the experimental data, except at around 5.0 eV. The peak at 5.0 eV in the present calculation is due to the resonance effect. In the data obtained by Johnstone *et al*, no explicit resonance peak exists though it is generally detected at around 3.8 eV in experimental study.

Figure 4 shows the DCSs for the vibrational excitation of bending mode at 2.0 eV. The DCS calculated by the Born approximation with a dipole interaction is also included in this figure. The Born approximation reproduces very well the result obtained by the close-coupling method. From a comparison of the measurement with the Born result at the energies less than 1.0 eV (Kochem *et al* 1985), the Born approximation is expected to work well in the low-energy region. The present result at 2.0 eV confirms this expectation. (This has also been recently confirmed by experiment (Tanaka 1998).) At the collision energies above 2.0 eV, however, the present result deviates from the Born values even in the non-resonant region.

Figure 5 shows the DCSs for the vibrational excitation of bending mode at 4.0 eV. The DCS obtained by Register *et al* (1980) and the present DCS at 5.0 eV are also included in figure 5. Since the incident energy is in the resonance region (see figure 1), the scattering dynamics around 4.0 eV should be very complicated. The present DCS in the forward scattering region

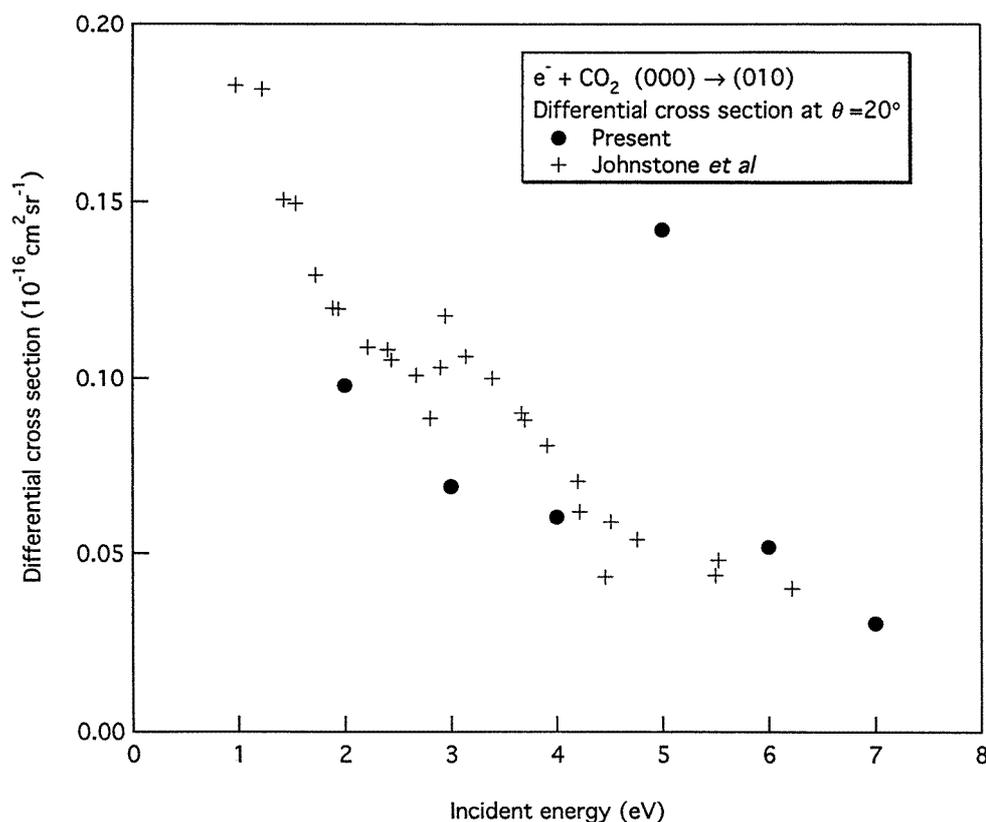


Figure 3. DCSs (in $10^{-16} \text{ cm}^2 \text{ sr}^{-1}$) for the (000) \rightarrow (010) excitation of CO_2 by electron impact at $\theta = 20^\circ$ as a function of electron energy. The present calculation is compared with the experimental data obtained by Johnstone *et al.* (1995).

is consistent with the experimental result. This is because the long-range dipole interaction dominates in the forward scattering. As stated before, the present Π_u resonance is located at an energy of about 1.0 eV higher than the value found by swarm experiment. This suggests that the present DCS at 5.0 eV would have a resonance feature. This is clearly seen in figure 5, when a comparison is made between the present DCSs at 4.0 and 5.0 eV. The present result at 5.0 eV is qualitatively consistent with the result of the beam-type experiment at 4.0 eV.

Figures 6–8 compare the present DCSs for (000) \rightarrow (010) at 10.0, 20.0 and 50.0 eV with the experimental results by Register *et al.* (1980). The present calculation reproduces fairly well the experimental DCSs at these energies. A small difference is found at 10.0 eV between the present result and the experimental one. The present DCS in the scattering region $\theta > 20^\circ$ at 10.0 eV seems to have slight angular dependence. A similar feature is shown in the present DCS at 5.0 eV (see figure 5). The resonance process at around 5.0 eV might still have an influence on the scattering at 10.0 eV in the present scattering model.

In a beam-type experiment, DCSs are difficult to measure in the regions of forward and backward scattering. The open circles in the figures 5–8 are the DCSs extrapolated by Register *et al.* It should be noted that no reliable method of extrapolation has been established yet. In the experimental result at 50.0 eV (figure 8), no extrapolated DCSs have been actually given for the scattering angles $\theta < 40^\circ$ and the extrapolated values of DCS at $\theta \geq 160^\circ$ seem to

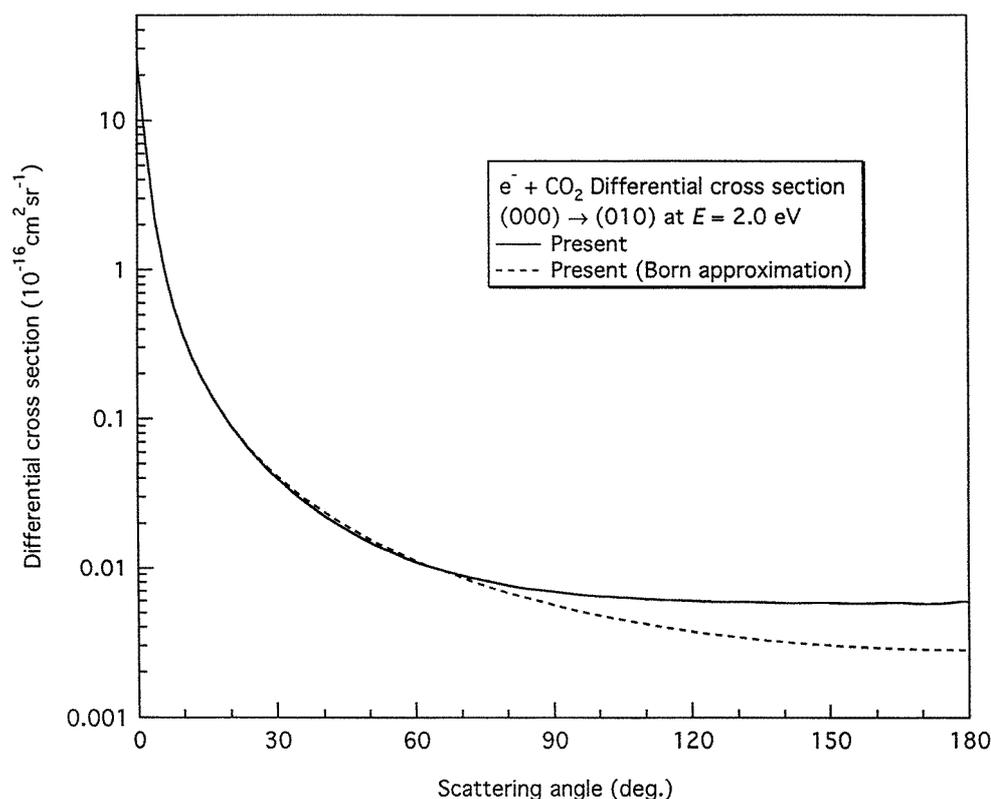


Figure 4. DCSs (in $10^{-16} \text{ cm}^2 \text{ sr}^{-1}$) for the (000) \rightarrow (010) excitation of CO_2 by electron impact at 2.0 eV. The present calculation is compared with the result obtained by the Born approximation.

be overestimated compared with the present calculation. The present calculation would be helpful to evaluate the extrapolated DCSs in beam-type experiments.

5. Conclusion

The vibrational excitation of the bending mode of CO_2 by electron impact has been studied at the collision energies in the range 2.0–50.0 eV. DCSs and ICSs for the vibrational excitation from the ground to the lowest excited state of the bending mode have been evaluated theoretically. The calculation is based on the FNO approximation. In order to take into account the degeneracy of the excited state of the bending vibration, only one of the states is taken coupled to the ground state and then the resulting cross section is multiplied by two. A closure formula is adopted to get rid of the slow convergence of cross sections with respect to the partial wave expansion.

The present ICS at energies above 10.0 eV shows an energy dependence considerably different from the experimental ICS obtained by Nakamura (1995) with the swarm technique. A resonance-like peak appears at around 30.0 eV. It is found that the present DCS at 2.0 eV is well reproduced by the Born approximation with a dipole interaction. This is a confirmation of the previous study near threshold (Kochem *et al* 1985), where the Born approximation with a dipole interaction reproduces very well the data measured in the energy region below about 1.0 eV. The theoretical DCS at the energy of Π_u resonance peak, i.e., $E = 5.0$ eV,

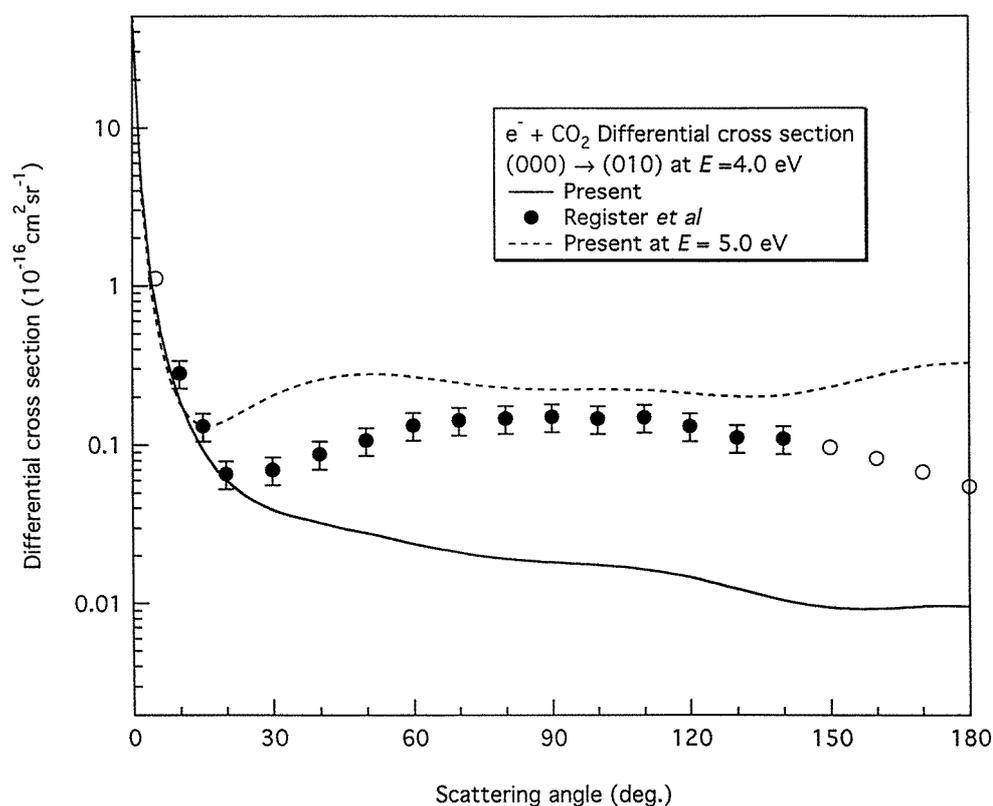


Figure 5. DCSs (in $10^{-16} \text{ cm}^2 \text{ sr}^{-1}$) for the (000) \rightarrow (010) excitation of CO₂ by electron impact at 4.0 eV and at 5.0 eV. The present calculations are compared with the experimental data at 4.0 eV obtained by Register *et al* (1980) (The data denoted by open circles show their extrapolation.)

is qualitatively consistent with the experimental DCS (Register *et al*) at the resonance peak (4.0 eV) experimentally found by Nakamura. The DCSs at 20.0 and 50.0 eV are quantitatively consistent with the results of the beam-type experiment though the DCS at 10.0 eV is slightly inconsistent with the corresponding experimental result.

The present method of the calculation of the cross section is thus found useful over a wide energy region, when compared with experimental data. To provide a quantitatively accurate result, however, a more rigorous treatment would be needed. The present wavefunction for the target molecule is less reliable for representing the effect of the nuclear motion exactly. More accurate molecular wavefunctions, such as those which include electron correlation, should be adopted. The present calculation is based on the vibrational two-state close-coupling method. The coupling effect with other vibrational states should be included to obtain more reliable cross sections of vibrational excitation.

The vibrational excitation of the bending mode is investigated in the present paper. A similar study of the other normal modes (symmetric and antisymmetric stretching) has already been carried out in our previous paper (Takekawa and Itikawa 1998). The present paper, together with the previous one, systematically gives an insight into the vibrational excitation of CO₂. The present method can be applied to any other polyatomic molecule to perform a similar systematic study of the vibrational excitation process.

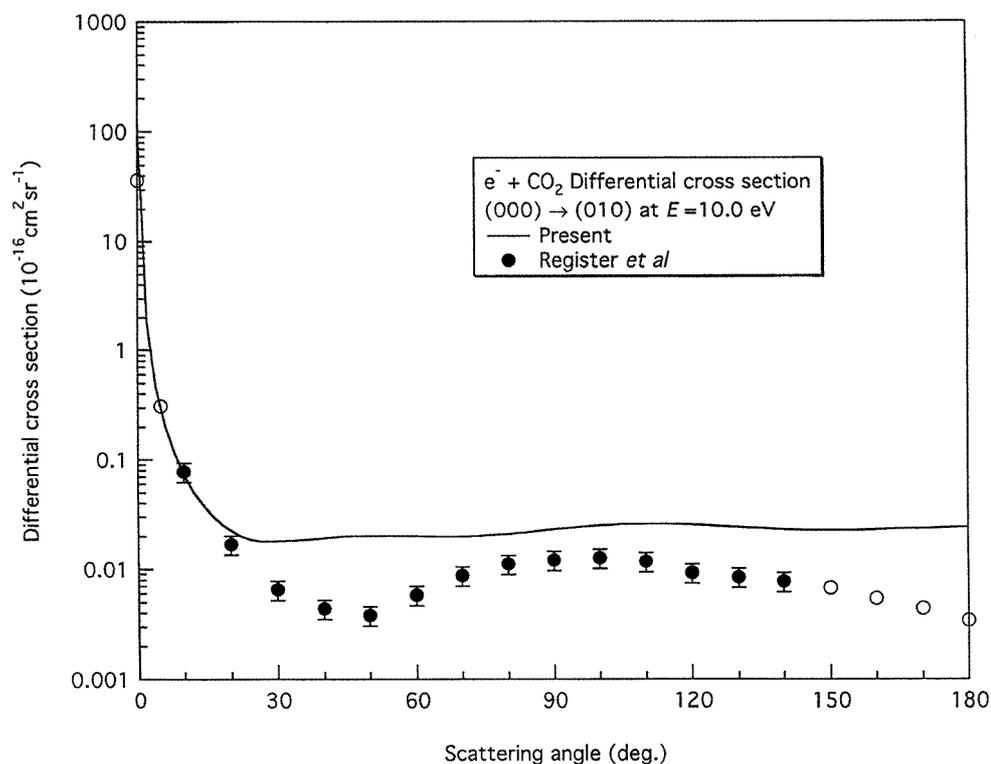


Figure 6. DCSs (in $10^{-16} \text{ cm}^2 \text{ sr}^{-1}$) for the $(000) \rightarrow (010)$ excitation of CO_2 by electron impact at 10.0 eV. The present calculation is compared with the experimental data obtained by Register *et al* (1980) (The data denoted by open circles show their extrapolation.)

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Appendix

The Born T -matrix (denoted as T^{B}) is evaluated with the Born K -matrix (denoted as K^{B}). The Born K -matrix element for $(000) \rightarrow (010)$ can be given as (Morrison and Sun 1995),

$$(K_{0l'\mu'}^{1l\mu})^{\text{B}} = -2\sqrt{k_0 k_1} \int dr r^2 j_l(k_0 r) j_{l'}(k_1 r) \langle 1l\mu | V | 0l'\mu' \rangle. \quad (25)$$

If one only takes the dipole interaction into account, the Born K -matrix element without taking account of the degeneracy of vibration is obtained as follows:

$$(K_{0l'\mu'}^{1l\mu})^{\text{B}} = \sqrt{\frac{\pi^3}{3}} \left(\frac{\partial \mu_x}{\partial q_2} \right)_{q_2=0} (-1)^{\mu'} \left[\frac{3(2l+1)(2l'+1)}{4\pi} \right]^{1/2} \begin{pmatrix} l & l' & 1 \\ 0 & 0 & 0 \end{pmatrix} \\ \times \left[\begin{pmatrix} l & l' & 1 \\ \mu & -\mu' & 1 \end{pmatrix} - \begin{pmatrix} l & l' & 1 \\ \mu & -\mu' & -1 \end{pmatrix} \right] \mathcal{J}_1. \quad (26)$$

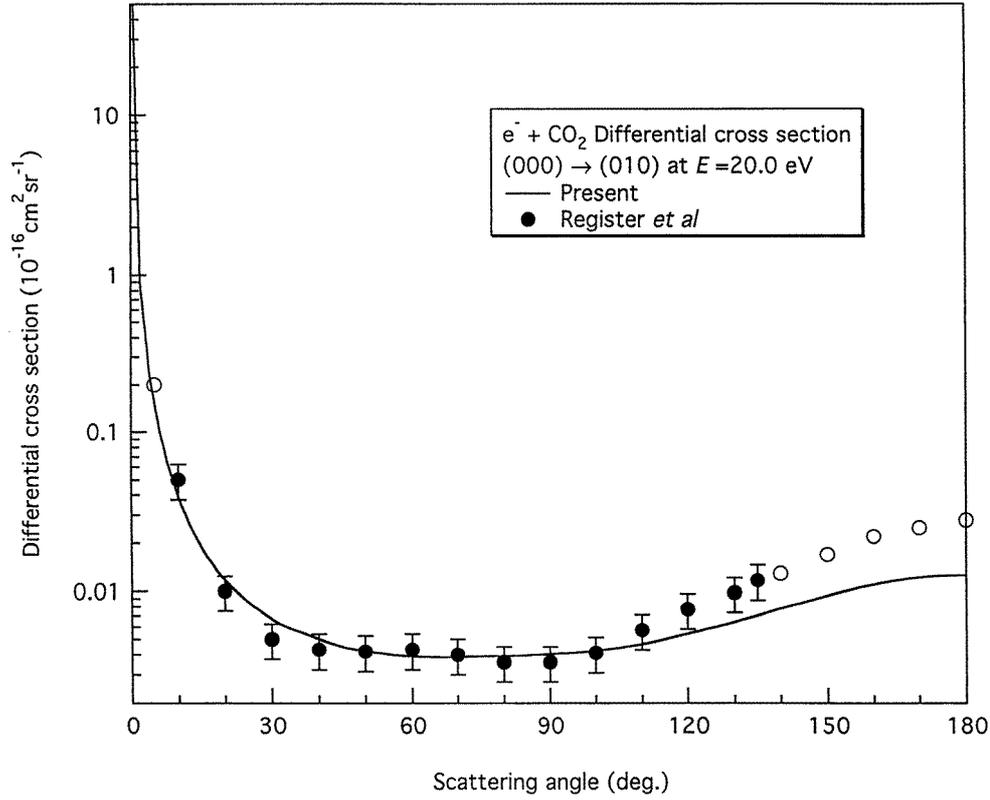


Figure 7. Same as figure 6, but at 20.0 eV.

Here $j_l(kr)$ is the spherical Bessel function, $(\partial\mu_x/\partial q_2)_{q_2=0}$ is the derivative of the x -component of the dipole moment. Similarly, the Born K -matrix element for elastic scattering is given by,

$$\begin{aligned}
 (K_{0l'\mu'}^{0l\mu})^B = (K_{l'l'\mu'}^{ll\mu})^B = & \sqrt{\pi^3} \alpha_0 (-1)^{\mu'} \left[\frac{(2l+1)(2l'+1)}{4\pi} \right]^{1/2} \begin{pmatrix} l & l' & 0 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l & l' & 0 \\ \mu & -\mu' & 0 \end{pmatrix} \mathcal{J}_3 \\
 & + \pi (-1)^{\mu'} \left[\frac{5(2l+1)(2l'+1)}{4\pi} \right]^{1/2} \begin{pmatrix} l & l' & 2 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l & l' & 2 \\ \mu & -\mu' & 0 \end{pmatrix} \\
 & \times \left[\sqrt{\frac{4\pi}{5}} \theta_{zz} \mathcal{J}_2 + \sqrt{\frac{\pi}{5}} \alpha' \mathcal{J}_3 \right]. \quad (27)
 \end{aligned}$$

In equation (27), θ_{zz} is the quadrupole moment and α_0 (α') is the spherical (non-spherical) part of polarizability (see Takekawa and Itikawa 1996 for details).

In equations (26) and (27), \mathcal{J}_ν ($\nu = 1, 2$ or 3) denotes the integration of the product of the Bessel functions and is defined as,

$$\mathcal{J}_\nu = \int_0^\infty dr r^{-\nu} J_{l+1/2}(k_0 r) J_{l'+1/2}(k_1 r). \quad (28)$$

Here k_0 (k_1) is the wavenumber for an incoming (outgoing) electron ($k_1 = k_0$ in the case of elastic scattering).

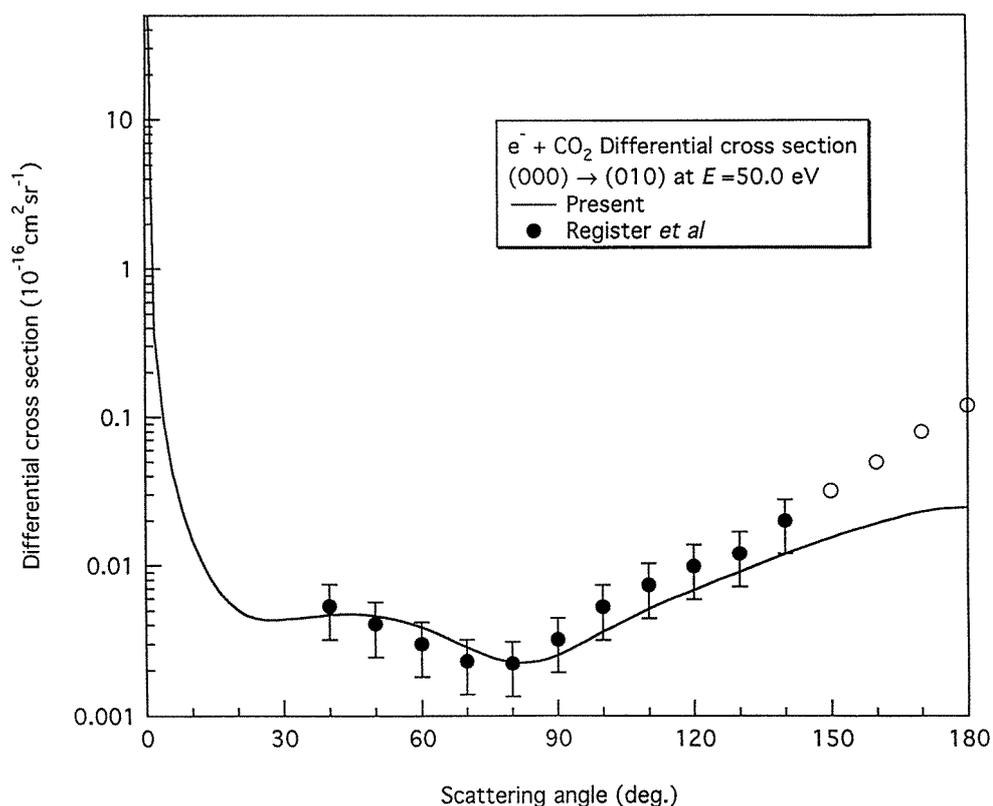


Figure 8. Same as figure 6, but at 50.0 eV.

After evaluating the K -matrix elements by the Born approximation, the Born T -matrix can be obtained as follows:

$$T^B = \frac{2(K^B)^2}{(K^B)^2 + I} - \frac{2K^B}{(K^B)^2 + I}i, \quad (29)$$

where I denotes the unit matrix.

The DCS (ICS) by the dipole Born approximation denoted as q^B (Q^B) is given by (Itikawa 1997),

$$q_{(000) \rightarrow (010)}^B(\theta) = \frac{4}{3} \frac{k_1}{k_0} \frac{1}{K^2} \left[\frac{1}{\sqrt{2}} \left(\frac{\partial \mu_x}{\partial q_2} \right)_{q_2=0} \right]^2, \quad (30)$$

$$Q_{(000) \rightarrow (010)}^B = \frac{8\pi}{3} \frac{1}{k_0^2} \ln \left| \frac{k_0 + k_1}{k_0 - k_1} \right| \left[\frac{1}{\sqrt{2}} \left(\frac{\partial \mu_x}{\partial q_2} \right)_{q_2=0} \right]^2, \quad (31)$$

where

$$K^2 = k_0^2 + k_1^2 - 2k_0k_1 \cos \theta. \quad (32)$$

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