Monte Carlo model of electron energy degradation in a CO$_2$ atmosphere

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Abstract. A Monte Carlo model has been developed to study the degradation of $\leq$1000 eV electrons in an atmosphere of CO$_2$, which is one of the most abundant species in Mars’ and Venus’ atmospheres. The e-CO$_2$ cross sections are presented in an assembled set along with their analytical representations. Monte Carlo simulations are carried out at several energies to calculate the “yield spectra”, which embodied all the information related to electron degradation process and can be used to calculate “yield” (or population) for any inelastic process. The numerical yield spectra have been fitted analytically resulting in an analytical yield spectra (AYS). We have calculated the mean energy per ion pair and efficiencies for various inelastic processes, including the double and dissociative double ionization of CO$_2$ and negative ion formation. The energy distribution of the secondary electrons produced per incident electron is also presented at few incident energies. The mean energy per ion pair for CO$_2$ is 37.5 (35.8) eV at 200 (1000) eV, compared to experimental value 32.7 eV at high energies. Ionization is the dominant loss process at energies above 50 eV with contribution of ~50%. Among the excitation processes, 13.6 eV and 12.4 eV states are the dominant loss processes consuming ~28% energy above 200 eV. Around and below ionization threshold, 13.6 eV, 12.4 eV, and 11.1 eV, followed by 8.6 eV and 9.3 eV excitation states are important loss processes, while below 10 eV vibrational excitation dominates.
1. Introduction

Photoionization is the main source of electrons and ions in the dayside upper atmosphere of planets. Photoelectrons, generated due to photoionization process, can have enough kinetic energy to ionize the atmospheric constituents and produce secondary electrons. Similarly, energetic electrons precipitating along the magnetic field lines into the auroral atmosphere of planets can ionize the medium producing secondary electrons. Besides ionization, the electron energy is lost in excitation, attachment, and dissociation. Hence, the study of electron energy deposition in atmosphere is an important aspect in understanding processes like aurora, dayglow, nightglow [e.g., Bhardwaj and Gladstone, 2000; Fox et al., 2008]. To model the electron energy degradation in an atmosphere one has to first compile cross sections for various loss processes, and then develop an electron energy apportionment method, which will distribute the electron energy among different loss channels.

The study of the electron energy degradation in CO$_2$ is of fundamental interest in various fields of science. CO$_2$ is one of the most important molecules in our solar system. It comprise more than 90% of the atmospheres of Venus and Mars. It is also used in lasers, gaseous discharge or low power plasma device. Electron energy degradation in CO$_2$ gas has important applications to Mars and Venus. Earlier results from Mariner satellites and Mars 3 and Mars 4 spacecrafts have confirmed the presence of an ionosphere on Mars, and also detected various emission features on Mars [e.g., Barth et al., 1971; Dementyeva et al., 1972], which have been studied in detail by recent SPICAM ultraviolet spectrometer observations aboard Mars Express [e.g., Bertaux et al., 2006; Leblanc et al., 2006]. Emissions from Venus have been studied quite extensively by Pioneer Venus [e.g., Fox and Bougher, 1991] and by the ongoing Venus Express [e.g., Bertaux et al, 2007]. Electron impact excitation and dissociative excitation of CO$_2$ are the key processes in the production of several emissions on Mars and Venus.

In this paper we present a Monte Carlo model which describes the energy degradation of ≤1000 eV electrons in an atmosphere of CO$_2$. Earlier studies of electron degradation in CO$_2$ have been carried out by Sawada et al. [1972], Green et al. [1977], and Fox and Dalgarno [1979]. Monte Carlo methods are class of numerical methods based on stochastic technique. Though it is time consuming, but due to its probabilistic nature, it is an excellent technique for studying the energy degradation of particles, provided sufficient sample size is taken. Hence, Monte Carlo methods have been widely used in problems dealing with energetic particle degradation in gases and in applications to the planetary atmospheres [e.g., Cicerone and Bowhill, 1971; Ashihara, 1978; Green et al., 1977, 1985; Singhal et al., 1980; Singhal and Green, 1981; Singhal and Bhardwaj, 1991; Bhardwaj and Singhal, 1993; Michael and Bhardwaj, 2000; Bhardwaj and Michael, 1999a, b; Shematovich et al., 2008].

In section 2, we present a compilation of all the e-CO$_2$ loss processes cross sections available up to the present date and fitted them with a simple analytical form. These analytically fitted cross sections can be easily used in the Monte Carlo model, which is presented in section 3. The output of the Monte Carlo simulation is employed to generate a “yield spectrum,” which is presented in section 4. The concept of the yield spectrum was first introduced by Green et al. [1977] and further developed by many workers [e.g., Green and Singhal, 1979; Singhal and Green, 1981; Singhal and Haider, 1984; Green et al., 1985;
Singhal and Bhardwaj, 1991; Bhardwaj and Singhal, 1993; Bhardwaj and Michael, 1999a]. The yield spectra embodied the information about the electron degradation processes and can be used to calculate “yield” for any inelastic event. The numerical yield spectrum is represented in an analytical form resulting in an analytical yield spectrum (AYS). The AYS and its comparison with the numerical yield spectrum is also presented in the section 4. In sections 5 and 7, we present the calculated mean energy per ion pair and efficiencies for inelastic processes, respectively, using AYS and compare them with that obtained by using numerical yield spectra. The energy distribution of secondary and tertiary electrons produced during ionization events is presented in section 6. Summary of the paper is presented in section 8.

2. Cross sections
2.1. Total

The laboratory measured total scattering cross section (TCS) is available between 0.1 eV and 5000 eV. The TCS for e-CO$_2$ collision has been measured by several authors in different energy ranges – Ferch et al. [1981] in the energy range 0.007-4.5 eV, Buckman et al. [1987] 0.1-5 eV, Szmytkowski et al. [1987] 0.5-3000 eV, Kimura et al. [1997] 0.8-500 eV, Kwan et al. [1983] 1-500 eV, and Garcia and Manero [1996] 400-5000 eV. At low energies, the TCS of Szmytkowski et al. [1987], Buckman et al. [1987], and Ferch et al. [1981] are in agreement to within 10%. Recently, Zecca et al. [2002] have determined the best value of TCS. In the lowest energy range (<1 eV) Zecca et al. [2002] adopted the experimental data of Ferch et al. [1981] and Buckman et al. [1987], which are in good agreement with each other. In the 1-1000 eV energy range, Zecca et al. [2002] averaged the cross sections obtained by Szmytkowski et al. [1987], Kimura et al., [1997] and Kwan et al. [1983], with equal weight, to obtain the recommended values, which are in good agreement with each other. In the 1-1000 eV energy range, Zecca et al. [2002] averaged the cross sections obtained by Szmytkowski et al. [1987], Kimura et al., [1997] and Kwan et al. [1983], with equal weight, to obtain the recommended values, which are in good agreement with Garcia and Manero [1996] at higher (>400 eV) energies. In his review, Itikawa [2002] has recommended the TCS of Zecca et al. [2002]. The TCS reaches a maximum value of $60 \times 10^{-16}$ cm$^2$ at 0.1 eV [Ferch et al., 1981; Buckman et al., 1987], it then goes through a minimum of $5.5 \times 10^{-16}$ cm$^2$ at 1.9 eV [Szmytkowski et al. 1987]. At lower energies a resonant structure is present ~3.8 eV.

2.2. Elastic
2.2.1. Differential elastic

The differential elastic scattering cross section (DCS) for e-CO$_2$ collision has been measured by many authors [cf. review by Itikawa, 2002; Karwasz et al., 2001].

In the 1-4 eV energy, the DCS values of Gibson et al. [1999] and Tanaka et al. [1998] are in good agreement at forward angles ($\leq 50^\circ$), however at larger angles they differ by 20-30%. Overall, at most of the energies there are good agreement in shape between these two DCS. At 30, 40, and 50 eV, the DCS measurements of Gibson et al. [1999], Kanik et al. [1989], and Tanaka et al. [1998] are in reasonable accord, within the uncertainties of each measurement, and at 50 eV the DCS of Gibson et al. [1999] and Register et al. [1980] are consistent. At 100 eV, the measured DCS values of Iga et al. [1999] are in good agreement with Kanik et al. [1989] and Tanaka et al. [1998].

We have taken the DCS values from Tanaka et al. [1998] in the 1-100 eV range, however values at 40, 50, 70, 80, and 90 eV are taken from Kanik et al. [1989] which agree well with the cross section of Tanaka et al. [1998] in the entire energy range. The DCS values
in 200-400 eV range are taken from Iga et al. [1999], and those in 500-1000 eV are taken from Iga et al. [1984]. In Table 1, we present the DCS values used in this work.

2.2.2. Total elastic

Based on the DCS measured by Register et al. [1980], Tanaka et al. [1998] and Gibson et al. [1999], Buckman et al. [2002] have determined the total elastic cross section in 1-100 eV range with an estimated uncertainty of ±30%. Shirai et al. [2001] have reported the recommended elastic cross section up to 100 eV by considering the beam data of Iga et al. [1999]. Itikawa [2002] has recommended the elastic cross section of Buckman et al. [2002] in the energy range 1-60 eV, and Shirai et al. [2001] in the energy range 100-1000 eV. The two data sets merge smoothly.

We have taken total elastic cross section as recommended by Itikawa [2002]. The total elastic cross section is fitted using the semi-empirical formula [Bhardwaj and Michael, 1999a]:

\[ \sigma(\epsilon) = \frac{1}{A_1 + B_1 \epsilon} + \frac{1}{A_2 + B_2 \epsilon} + \frac{2}{E \ A_2 B_1 - A_1 B_2} \sqrt{A_1 A_2} \ln \left( \frac{1 + B_1 \epsilon/A_1}{1 + B_2 \epsilon/A_2} \right), \]  

(1)

where \( A_1, B_1, A_2, \) and \( B_2 \) are the fitting parameters, whose values are \( 8.090 \times 10^{-16} \) Å\(^{-2} \), \( 2.184 \times 10^{-2} \) Å\(^{-2} \) keV, 0.92 Å\(^{-2} \) and \( 5.0 \times 10^{-4} \) Å\(^{-2} \) keV, respectively, and \( \epsilon \) is the energy of the electron in eV. Lower limit of fit is 30 eV, and fitted cross section is shown in Figure 1. At energies below 30 eV it is difficult to fit the cross section using above equation due to resonance structure present at low energies (\( \sim 4 \) eV), and hence these values are fed numerically in the Monte Carlo model.

2.3. Dissociative electron attachment

The dissociative attachment process in e-CO\(_2\) collisions, which mainly occurs at energies <12 eV, leads to the formation of negative ions O\(^-\), O\(^-\)\(_2\), and C\(^-\). Rapp and Briglia [1965] measured absolute values of the total cross section for the production of negative ions from CO\(_2\). Orient and Srivastava [1983] obtained the cross section for the production of O\(^-\) ions and showed that it is the dominant anion. Their values are in agreement with those of Rapp and Briglia [1965] within the uncertainty of the cross sections (±20%) and the energy scale (±0.1 eV). Spence and Schulz [1974] measured the cross sections for the production of C\(^-\) and O\(^-\)\(_2\) ions. The cross section for O\(^-\)\(_2\) production has two peaks of the order of \( 10^{-24} \) cm\(^2\) at 11.3 and 12.9 eV, while cross section for C\(^-\) production has three peaks with the largest value of \( \sim 2 \times 10^{-21} \) cm\(^2\). The cross sections for O\(^-\)\(_2\) and C\(^-\) are small compared to that of O\(^-\), and hence are not considered in our study.

We have adopted the cross section values of Rapp and Briglia [1965] for the production of O\(^-\) ions from CO\(_2\). The cross section shows a double-peak structure – peaks at 4.1 and 8.3 eV, with the later peak value \( (4.28 \times 10^{-19} \) cm\(^2\)\) about 2.5 times the value of the former peak. The cross section for each peak has been fitted with the following analytical form [Bhardwaj and Michael, 1999a]:

\[ \sigma(\epsilon) = \frac{Ae^t/\epsilon}{(1 + e^t)^2}, \]  

(2)

Here \( t = (\epsilon - W_p)/U \), where \( W_p \) is the energy at the peak. The values of the overall normalization parameter \( A \) and the effective width parameter \( U \) for each of the peaks...
along with the parameter $W_p$ and threshold energy $W_{th}$ are presented in Table 2. The fitted cross sections along with laboratory measurements are given in Figure 2.

### 2.4. Ionization

The ionization and dissociative ionization of CO$_2$ by electron impact produce singly and doubly ionized ions (CO$_2^+$, CO$^+$, C$^+$, O$^+$, C$^{++}$, O$^{++}$, and CO$_2^{++}$). The cross sections for these processes have been reported by Rapp and Englander-Golden [1965], Shyn and Sharp [1979], Orient and Srivastava [1987], Tian and Vidal [1998], and Straub et al. [1996]. Recently, McConkey et al. [2008] have reviewed the electron impact dissociation cross sections for CO$_2$. For the total ionization cross section, measurements of Orient and Srivastava [1987], Tian and Vidal [1998], and Straub et al. [1996] are within the error limits with values of Rapp and Englander-Golden [1965] up to 1000 eV, and with the data of Shyn and Sharp [1979] in the energy range 50-400 eV. Tian and Vidal [1998] have also measured the cross sections for double and triple ionization of CO$_2$ due to electron impact. After a survey of the available experimental data, Lindsay and Mangan [2002] suggested recommended values of ionization cross section. Their partial cross sections are based on measurement of Straub et al. [1996]. For total ionization cross section below 25 eV, Lindsay and Mangan [2002] adopted the values of Rapp and Englander-Golden [1965]. At energies above 25 eV, they reported uncertainties of 5% for the partial cross sections for the production of CO$_2^+$, CO$^+$, C$^+$, O$^+$, and the total ionization cross section. The cross sections at energies below 25 eV have uncertainties of 7%. There are also uncertainties in appearance energies of fragmented ions CO$^+$, C$^+$, O$^+$, C$^{++}$, and O$^{++}$. We have taken the appearance energies for the fragmented ions from Itikawa [2002].

We have used the dissociative and direct ionization cross sections recommended by Lindsay and Mangan [2002] [cf. Itikawa, 2002; McConkey et al., 2008]. The CO$_2^+$ ion can be produced in four excited states, viz., $X^2\Pi_g$, $A^2\Pi_u$, $B^2\Sigma_u^+$, and $C^2\Sigma_g^+$. Cross sections for $A^2\Pi_u$ and $B^2\Sigma_u^+$ states have been taken from Itikawa [2002], while the cross sections for $X^2\Pi_g$ and $C^2\Sigma_g^+$ states have been taken from Jackman et al. [1977]. For double ionization, cross sections of (CO$^+$,O$^+$), (C$^+$,O$^+$), and (O$^+$,O$^+$) production have been taken from Tian and Vidal [1998] up to 600 eV; these cross sections have not been added in the total ionization cross section because they are already accounted in the cross sections for the formation of CO$^+$, C$^+$, and O$^+$ ions. All these cross sections have been fitted using the analytical expression [Jackman et al., 1977; Bhardwaj and Michael, 1999a].

\[
\sigma(E) = A\Gamma \left[ \arctan \left( \frac{T_M - T_0}{\Gamma} \right) + \arctan \left( \frac{T_0}{\Gamma} \right) \right],
\]

where

\[
A(E) = \left[ \frac{K}{E + K_B} \right] \ln \left[ \frac{E}{J} + J_B + J_C \right];
\]

\[
\Gamma(E) = \Gamma_S \left[ \frac{E}{E + \Gamma_B} \right];
\]

\[
T_0(E) = T_S - \left[ \frac{T_A}{E + T_B} \right]; T_M = \frac{E - I}{2}.
\]

Here $E$ is the incident energy in eV, $I$ is the fitting ionization potential in the eV, which is generally close to the threshold potential ($W_{th}$), and $\sigma$ is in units of $10^{-16}$ cm$^2$. This form
gives the asymptotic behavior $\sigma(E) \propto E^{-1} \ln E$ at high energies, which is expected from the Born approximation. The fitting parameters are presented in the Table 3. The fitted cross sections for single and double ionization are shown in Figures 3 and 4, respectively.

2.5. Excitation cross sections

2.5.1. Vibrational excitation

CO$_2$ is a linear triatomic molecule, which has three normal modes of vibration, i.e., a bending mode (0 n 0), a symmetric stretching mode (n 0 0), and an asymmetric stretching mode (0 0 n), with excitation energy 83 meV, 172 meV, and 291 meV, respectively [Kochem et al., 1985]. Infrared active (010) bending and (001) asymmetric stretching modes in the near-to-threshold region follow the Born approximation. Moreover, the structure near the threshold of vibration excitation in CO$_2$ has been investigated by Kochem et al. [1985], vibrationally inelastic DCS above 4 eV impact energies have been measured by Register et al. [1980] for scattering angles $10^\circ - 140^\circ$ and impact energies of 4, 10, 20, and 50 eV, and by Johnstone et al. [1995] for only one scattering angle ($20^\circ$) in the energy region 1 to 7.5 eV. Nakamura [1995] determined the vibrational cross section using swarm experiment. Kitajima et al. [2001] made measurements of DCS for the electron impact excitation of CO$_2$ for (010), (100), (001), and (020) vibrational modes over the scattering angles $20^\circ - 130^\circ$ and energy range 1.5-30 eV (except at 4 eV where the smallest angle was extended upto $10^\circ$), and assigned an uncertainty of 30% to their measurements. Their DCS is consistent with the results of previous beam-type measurements. Itikawa [2002] has extrapolated the DCS of Kitajima et al. [2001] to obtain the total vibration cross sections for three modes, which are presented in Figure 1.

In our studies we have taken cross sections for the three fundamental vibrational modes (010), (100), and (001) from Itikawa [2002]. There are other modes also but their cross sections are small compare to these three fundamental modes.

2.5.2. Electronic excitation

There are several features in the optical and electron scattering spectrum of CO$_2$ in the energy loss range between 7 and 11 eV (Herzberg, 1966; Rabalais et al., 1971; Hall et al., 1973). Except for Rydberg states, there is still no definite consensus about structure and assignment of the excited electronic states of CO$_2$. In the energy loss spectra of CO$_2$, Green et al. [2002] have found four clearly distinct peaks at 10.98, 11.05, 11.16, and 11.40 eV, with an uncertainty of 30% in their results. Itikawa [2002] in his review paper has recommended the DCS of Green et al. [2002], for the excitation of the 10.8-11.5 eV energy loss states. Recently, Kawahara et al. [2008] have given the integral cross section for electronic states $^1\Sigma_u^+$ and $^1\Pi_u$ of CO$_2$, based on the DCS measurement of Green et al. [2002] in the energy range 20-200 eV.

Theoretical calculations of electronic structure have also been made by several authors [Nakatsuji, 1983; Spielfiedel et al., 1992; Buenker et al., 2000; Lee et al., 1999]. Using distorted-wave method, Lee and McKoy [1983] calculated the cross section for the excitation of eight low lying-states. But there is not much agreement among these calculations. In summary, there is still a need for a detailed study of excitation of electronic states of CO$_2$ by electron impact.

We have taken the empirical cross sections of Jackman et al. [1977] for the electronic states of CO$_2$. These cross sections have been obtained using equation:
σ(E) = \frac{(q_0 F)}{W^2} \left[ 1 - \left( \frac{W}{E} \right)^\alpha \right] \left[ \frac{W}{E} \right]^\beta \Omega \tag{4}

where \( q_0 = 4\pi a_0 R^2 \) and has the value \( 6.512 \times 10^{-14} \) eV\(^2\) cm\(^2\). The fitting parameter are given in Table 4. The parameters for the two states 12.4 and 13.6 eV, that corresponds to Cameron band of CO [cf. Sawada et al., 1972] have been modified. The peak cross section of their sum is \( 2.40 \times 10^{-16} \) cm\(^2\) at 80 eV [Erdman and Zipf, 1983].

2.6. Emission

Electron impact dissociation and ionization of CO\(_2\) can result in the production of excited fragments of CO, O, and CO\(_2\) in the neutral and ionized states, resulting in the emissions in the ultraviolet region. These emissions are important for understanding phenomena like aurora, dayglow that occur in the atmospheres of Mars, Venus, and CO\(_2\)-containing atmospheres. The strong band systems observed on Mars are Fox-Duffendack-Barker bands (\( A^2\Pi_u \rightarrow X^2\Pi_g \)) and ultraviolet doublet (\( B^2\Sigma^+_u \rightarrow X^2\Pi_g \)) of CO\(_2^+\), and Cameron bands (\( a^3\Pi \rightarrow X^1\Sigma^+ \)) of CO [Ajello, 1971; Barth et al., 1971; Bertaux et al., 2006; Leblanc et al., 2006]. Ajello [1971] measured the emission cross sections for the \( A^2\Pi_u \rightarrow X^2\Pi_g \) and \( B^2\Sigma^+_u \rightarrow X^2\Pi_g \) bands of CO\(_2^+\) from threshold to 300 eV. He also measured cross sections for the excitation of the fourth positive system of CO (\( A^1\Pi \rightarrow X^1\Sigma^+ \)), the first negative system of CO\(^+\) (\( B^2\Sigma^+ \rightarrow X^2\Sigma^+ \)) and several atomic multipletes of carbon and oxygen produced from dissociative excitation of CO\(_2\).

2.6.1. Emission from CO\(_2^+\)

McConkey et al. [1968], Ajello [1971], and Tsurubuchi and Iwai [1974] have detected emissions corresponding to the following transitions:

\[ A^2\Pi_u \rightarrow X^2\Pi_g \quad \text{at} \quad 293.6 - 438.4 \ \text{nm} \]

and

\[ B^2\Sigma^+_u \rightarrow X^2\Pi_g \quad \text{at} \quad 218.9 - 226.8 \ \text{nm} \]

The peak value of cross sections measured by the three groups for the above transitions are in good agreement with each other. These emissions are well known in the Mars upper atmosphere. Both the ground and excited states of CO\(_2^+\) are known to be linear [Herzberg, 1966]. The cross section of Ajello [1971] has too steep an energy dependence near threshold compared to McConkey et al. [1968] and Tsurubuchi and Iwai [1974]. In his review, Itikawa [2002] recommended the cross sections of Tsurubuchi and Iwai [1974], for which the peak values are \((8.0 \pm 2.0) \times 10^{-17} \) cm\(^2\) at 160 eV for the \( A - X \) transition, and \((4.7 \pm 1.2) \times 10^{-17} \) cm\(^2\) for the \( B - X \) transition. We have taken the cross sections for \( A - X \) and \( B - X \) emissions of CO\(_2^+\) from Itikawa [2002]. These cross sections have been fitted using equation (3). The fitting parameters are given in Table 3, and fitted cross sections in Figure 3.

2.6.2. Emission from CO\(^+\)

Only Ajello [1971] has measured the cross section for the emission of first negative system (\( B^2\Sigma^+ \rightarrow X^2\Sigma^+ \)) of CO\(^+\). The cross section exhibits an appearance potential of 25.11 eV, and the peak value of cross section is \( 1.9 \times 10^{-18} \) cm\(^2\) around 100 eV. The cross section for the excitation of the first negative system of CO\(^+\) from electron impact on CO\(_2\)
is about a factor of 25 less than for excitation of the same system from CO [Ajello, 1971]. We have adopted the cross section of Ajello [1971], which has been fitted analytically using equation (4); the fitting parameters are given in Table 4. Figure 3 shows the fitted cross section along with experimental cross section.

### 2.6.3. Emission from CO

Cross sections for the production of Cameron band system ($a^3\Pi \rightarrow X^1\Sigma^+$) and fourth positive system ($A^1\Pi \rightarrow X^1\Sigma^+$) of CO have been measured by Ajello [1971]. The emission cross section for the fourth positive system is very weak and Ajello could not measure the cross section near threshold (13.48 eV). For the Cameron band system, Ajello [1971] reported relative magnitudes of the cross section for the (0, 1) band at 215.8 nm. The upper state ($a^3\Pi$) of Cameron emission is metastable and has a long radiative lifetime (∼3 ms) [Gilijamse et al., 2007], and kinetic energies of the CO($a^3\Pi$) fragments are in the range of 0–1.2 eV [Freund, 1971]. Erdman and Zipf [1983] measured the total cross section for CO ($a^3\Pi \rightarrow X^1\Sigma^+$) electronic transition. They estimated the absolute magnitude of total Cameron band emission cross section of $2.4 \times 10^{-16}$ cm$^2$ at 80 eV. The Cameron band is the brightest emission feature in the UV dayglows of both Mars and Venus as well as an important emission in CO$_2$-containing atmospheres, e.g. comets.

### 2.6.4. Emission from O and C

Both Ajello [1971] and Mumma et al. [1972] have reported cross section for the emission of the O 130.4 nm triplet from electron impact on CO$_2$, but the measurements are not consistent with each other. There are many other atomic emissions produced in e-CO$_2$ collisions, but they have very small cross sections [cf. van der Burgt et al., 1989]. Kanik et al. [1993] have reported the emission cross sections for O, O $^+$, C, C $^+$, CO, and CO $^+$ in the wavelength region 40 - 125 nm. All the cross sections of Kanik et al. [1993] are less than $10^{-18}$ cm$^2$. We have adopted the O I and C I production cross sections of Jackman et al. [1977].

### 3. Monte Carlo Model

The transport of radiation is a natural stochastic process that is amenable to the Monte Carlo method due to its probabilistic nature. In the Monte Carlo simulation, modeling of an inherently stochastic system is carried out by artificial random sampling. In the present work we have developed a Monte Carlo model to simulate the local degradation of 1-1000 eV electrons in an atmosphere of CO$_2$ gas. The energy bin size is taken as 1 eV throughout the energy range. In the simulation we have considered elastic scattering between electrons and neutral CO$_2$ molecules, and various inelastic processes like ionization, excitation, attachment, dissociation, etc; the cross sections for these processes are described in section 2. Figure 5 illustrates how an individual electron is treated in the Monte Carlo simulation.

The initial energy $E_0$ of the electron is fixed at the beginning of the simulation and the direction of movement of the electron ($\theta$, $\phi$) is decided with the help of two random numbers $R_1$ and $R_2$ [random numbers are uniformly distributed in the range (0, 1)] as

$$\theta = \cos^{-1}(1 - 2R_1), \quad (5)$$

$$\phi = 2\pi R_2. \quad (6)$$
The distance to next collision is calculated from

\[ S = -\log(1 - R_3)/n\sigma_T, \quad (7) \]

where \( R_3 \) is a random number, \( n \) is the number density of the neutral target species (taken as \( 1 \times 10^{10} \text{ cm}^{-3} \)), and \( \sigma_T \) is the total (elastic + inelastic) electron impact collision cross section. After generating a new random number \( R_4 \), the probability of elastic collision \( P_{el} = \sigma_{el}/\sigma_T \) is calculated. If \( P_{el} > R_4 \), elastic collision takes place. If \( P_{el} \leq R_4 \), the inelastic event takes place, and in this case we further test for the type of inelastic event that has taken place with the help of another random number.

For elastic scattering the energy loss is calculated as

\[ \Delta E = \frac{m^2v^2}{m+M} - \frac{m^2vV_1 \cos \delta}{m+M}, \quad (8) \]

\[ V_1 = v \left[ \frac{m \cos \delta + [M^2 + m^2(\cos \delta - 1)]^{1/2}}{m+M} \right]. \]

Here \( \delta \) is the scattering angle in the laboratory frame, \( v \) and \( m \) are the velocity and mass, respectively, of the electron, and \( M \) is the mass of the target particle. Differential elastic cross sections (discussed in section 2.2.1) are used to obtain the scattering angle \( \delta \). Differential cross sections are fed numerically in the Monte Carlo model at 28 unequally spaced energy points (1.5, 2, 3, 3.8, 4, 5, 6, 6.5, 7, 8, 9, 10, 15, 20, 30, 40, 50, 60, 70, 80, 90, 100, 200, 300, 400, 500, 800, and 1000 eV) and at 20 scattering angles (0°, 5°, 10°, 15°, 20°, 30°, 40°, 50°, 60°, 70°, 80°, 90°, 100°, 110°, 120°, 130°, 135°, 150°, 165°, and 180°). At intermediate energies and angular points the values are obtained through linear interpolation. The energy \( \Delta E \) is subtracted from the energy of the test particle. After the collision, the deflection angle relative to the direction \((\theta, \phi)\) is obtained as

\[ \cos \theta'' = \cos \theta \cos \theta' - \sin \theta \sin \theta' \cos \phi', \]

\[ \cos \phi'' = (\cos \theta \cos \phi \sin \theta' \sin \phi' - \sin \phi \sin \theta' \sin \phi' + \sin \theta \cos \phi \cos \theta')/ \sin \theta'', \]

\[ \sin \phi'' = (\cos \theta \cos \phi \sin \theta' \cos \phi' - \cos \phi \sin \theta' \sin \phi' + \sin \theta \sin \phi \cos \theta')/ \sin \theta''. \]

Here \( \theta', \phi' \) are the scattering angles.

In the case of an inelastic collision, the next step is to find whether the event is ionization or any of the other type of inelastic collision. If the collision is an ionization event, a secondary electron is produced. The energy of the secondary electron \( T \) is calculated with the help of a random number \( R \) as [Bhardwaj and Michael, 1999a]

\[ T = \frac{\Gamma_S E_v}{E_v + \Gamma_B} \left[ \tan(RK_1 + (R - 1)K_2) \right] + T_S - \left[ \frac{T_A}{E_v + T_B} \right], \quad (10) \]

where

\[ K_1 = \tan^{-1} \left\{ \left[ \frac{(E_v - I)}{2} - T_S + \frac{T_A}{(E_v + T_B)} \right] / \frac{\Gamma_S E_v}{(E_v + \Gamma_B)} \right\}, \]
\[ K_2 = \tan^{-1} \left\{ \frac{T_S - T_A}{(E_v + T_B)} \right\} \left/ \left( \frac{\Gamma_S E_v}{(E_v + \Gamma_B)} \right) \right. \]

Here \( E_v \) is the energy of the incident primary electron before the ionization event. \( \Gamma_S \), \( \Gamma_A \), \( T_A \), \( T_B \), and \( T_S \) are the fitting parameters, and \( I \) is the ionization threshold. The values of these parameters are given in Table 3. If the energy of secondary electron, produced in the ionization event, is more than the lowest cutoff energy (which is 1 eV in our simulation) then it is also tracked in a similar manner as the primary electron (cf. Figure 5). The secondary electrons can also cause ionization, producing tertiary electrons, which are treated in a similar way as secondary electrons. In the Monte Carlo simulation we also follow tertiary and subsequent electrons. The number of secondary, tertiary, and subsequent electrons produced during the ionization events are stored in the appropriate energy bins. After the type of collision event has been decided, the appropriate energy is subtracted from the energy of the particle. All the collision events are recorded in the appropriate energy bins corresponding to the energy of the electron at the time of collision. The history (track view) of a particle with each interaction event is traced until the electron energy falls below an assigned cutoff value, which is 1 eV. The sample size in the present study is \( 10^6 \) particles for each simulation.

4. Yield Spectra

When all the sampled electrons have been degraded, we get a two dimensional yield spectrum, which is a function of the spectral energy \( E \) and incident primary electron energy \( E_0 \), defined as \( \text{[Green et al., 1977]} \):

\[
U(E, E_0) = \frac{N(E)}{\triangle E}, \tag{11}
\]

where \( N(E) \) is the number of inelastic collision events for which the spectral energy of the electron is between \( E \) and \( E + \triangle E \), where \( \triangle E \) is the energy bin width, which is 1 eV in our model. This yield spectrum is related to the degradation spectrum or equilibrium flux \( f(E, E_0) \) of \( \text{Spencer and Fano [1954]} \) by the equation

\[
U(E, E_0) = \sigma_T(E) f(E, E_0), \tag{12}
\]

where \( \sigma_T \) is the total inelastic collision cross section.

The analytical yield spectrum \( U(E, E_0) \) embodies the nonspatial information of the degradation process. It represents the equilibrium number of electrons per unit energy at an energy \( E \) resulting from the local energy degradation of an incident electron of energy \( E_0 \), and can be used to calculate the yield \( J_j \) of any state \( j \) at energy \( E_0 \) with the help of following equation:

\[
J_j(E_0) = \int_{W_{th}}^{E_0} U(E, E_0) P_j(E) dE \tag{13}
\]

where \( P_j(E) = \sigma_j(E)/\sigma_T(E) \) is the probability of occurrence of the \( j \)th process whose threshold potential is \( W_{th} \). The yield for a particular process obtained by using the above
equation is used in the following sections to calculate the mean energy per ion pair and efficiencies for various loss processes. Except at very low energies, yield spectrum $U(E, E_0)$ and probability of excitation $P_j(E)$ both vary with $E$ in a much simpler manner than do $f(E, E_0)$ and $\sigma_j(E)$.

For many application purposes yield spectrum obtained by equation (11) is represented in the following form:

$$U(E, E_0) = U_a(E, E_0)\ H(E_0 - E - E_m) + \delta(E_0 - E).$$  \hspace{1cm} (14)

Here $H$ is the Heavyside function, with $E_m$ being the minimum threshold of the processes considered, and $\delta(E_0 - E)$ is the Dirac delta function which allows for the contribution of the source itself. In atmospheric and astrophysical applications it is convenient to represent $U_a(E, E_0)$ in an analytical form [Green et al., 1977]:

$$U_a(E, E_0) = A_1 \xi_0^s + A_2 (\xi_1^t/\epsilon^{3/2+r})$$  \hspace{1cm} (15)

Here $\xi = E_0/1000$ and $\epsilon = E/I$ ($I$ is equal to lowest ionization threshold). $A_1 = 0.027$, $A_2 = 1.20$, $t = 0$, $r = 0$, and $s = -0.0536$ are the best fit parameters.

We have also tried two other analytical forms given by Singhal et al. [1980] and Green et al. [1985]. The form given by Singhal et al. [1980] is:

$$U_a(E, E_0) = C_0 + C_1 \chi + C_2 \chi^2$$  \hspace{1cm} (16)

Here $\chi = E_0^\Omega/(E + L)$; where $\Omega = 0.585$ and $L = 1.0$ and $E_0$ is in keV, $C_0 = 0.0185$, $C_1 = 5.98$, and $C_2 = 210.4$ are fitted parameters. The analytical form given by Green et al. [1985] is:

$$U_a(E, E_0) = C_0 + C_1 (E_k + K)/[(E - M)^2 + L^2].$$  \hspace{1cm} (17)

Here $E_k = E_0/1000$, and $C_0$, $C_1$, $K$, $M$, and $L$ are the fitted parameters which are independent of the energy. The values of these constant parameters are $C_0 = 0.0299$, $C_1 = 430$, $K = 0.0041$ keV, $M = 0.31$ eV, and $L = 1.9$ eV.

In obtaining our analytical fits we did not include values of the yield spectra very close to $E_0$ because in this regime yield spectra contain the rapid oscillations known as “Lewis effect” [cf. Douthat, 1975]. These oscillations are channels with a finite number of threshold energies, so that there are only certain energies near $E_0$ which an electron can acquire. Obviously, no electron can acquire an energy between $E_0$ and $E_0 - E_m$, and that is why the Heavyside function $H$ is inserted in the first term on the right-hand side of equation (14). The numerical yield spectrum represented analytically using equations (15), (16), and (17) is the two-dimensional analytical yield spectrum (AYS). In our studies, we have used the AYS obtained using equation (15), which is presented in Figure 6 along with the numerical yield spectra obtained by using (14). It is clear from Figure 6 that the analytical spectra represents quite well the numerical yield spectra above the ionization threshold; however, at lower energies (below 15 eV) the AYS departs from the numerical yield spectra. Similar behavior is seen in the AYS of Green et al. [1977].
To overcome this deficiency we introduce an additional function to modify the lower energy part of the AYS:

\[ U_b(E, E_0) = \frac{E_0 A_0 e^x/A_1}{(1 + e^x)^2}, \]  

(18)

Here \( x = (E - A_2)/A_1 \), and \( A_0, A_1, \) and \( A_2 \) are the fitting parameters. The values of parameters are \( A_0 = 10.095, A_1 = 5.5, \) and \( A_2 = 0.9 \). Equation (18) only affects the lower energy (\( \leq 15 \) eV) part of the fit. The final AYS is the sum of equations (15) and (18) which is shown in Figure 6 at several incident energies: depicting a better fit at lower energies (\( > 5 \) eV) as well as at higher energies.

Because of the simplicity of function and cost effective computational advantage, the AYS technique has been widely used in different planetary atmospheres for various aeronomical calculations, like steady state electron fluxes and volume production rates for any ionization or excitation state; the details of the computational technique are described in earlier papers [e.g., Singhal and Haider, 1984; Bhardwaj and Singhal, 1993; Singhal and Bhardwaj, 1991; Bhardwaj et al., 1990, 1996; Bhardwaj, 1999, 2003; Bhardwaj and Michael, 1999a, b; Michael and Bhardwaj, 2000; Haider and Bhardwaj, 2005].

5. Mean Energy per Ion Pair

The mean energy per ion pair, \( \mu_j \), is defined as the incident energy \( E_0 \) divided by the number of ion pairs produced. It can be expressed as

\[ \mu_j(E_0) = E_0/J_j(E_0), \]  

(19)

where \( J_j(E_0) \) is the population of the \( j \)th ionization process obtained by equation (13). The quantity mean energy per ion pair is known to approach a constant value at higher energies.

Figure 7 shows the mean energy per ion pair for the ions CO\(_2^+\) (including the ground and excited states), CO\(^+\), O\(^+\), C\(^+\), CO\(^{2+}\), O\(^{2+}\) and C\(^{2+}\) along with the mean energy per ion pair for neutral CO\(_2\), solid symbol represents the mean energy per ion pair for neutral CO\(_2\) obtained directly from the Monte Carlo simulation at few energy points.

Mean energy for all the ions decreases very rapidly above their threshold value, but after \( \sim 100 \) eV \( \mu \) declines slowly and at higher energies it becomes almost constant. The values of \( \mu \) for CO\(_2^+\), CO\(^+\), O\(^+\), and C\(^+\) at 200 (1000) eV are 53.6 (51.2), 403 (415), 263.1 (247.8), and 626.7 eV (576.2) eV, respectively. The mean energy per ion pair for neutral CO\(_2\) gas is 37.5 (35.8) eV at 200 (1000) eV. Fox and Dalgarno [1979] reported a value of 33.1 eV at 200 eV for the \( \mu \), while Green et al. [1977] obtained a value of 34.7 eV at 200 eV from their MDEB method. The measured value of the mean energy per ion pair in neutral CO\(_2\) is 32.7 at high energies [Klots, 1968]. Mean energy per ion pair for \( X^2\Pi_g, A^2\Pi_u, B^2\Sigma^+_u, \) and \( C^2\Sigma^+_g \) states of CO\(_2\) at 200 (1000) eV are 112.3 (118.4), 180.3 (156), 301.5 (266.4), and 1999 (1222) eV, respectively.

6. Secondary Electron Distribution

During the degradation process, every time the electron undergoes an ionization collision event, a secondary electron is produced. The energy of the secondary electron produced
is calculated using (10). The maximum energy of the secondary electron produced can be \((E - I)/2\), where \(E\) is the energy of the colliding electron and \(I\) is the ionization potential. As mentioned before, secondary and tertiary electrons are also treated in the same manner as the primary electrons in the Monte Carlo model. The energy distribution of secondary electrons is presented in Figure 8 at several incident energies showing the number of secondary electrons produced per incident primary electron. The energy distributions of tertiary and quaternary electrons, which are presented only at \(E_0 = 1000\) eV, are much steeper than that of secondary electrons. Each incident electron of \(E_0 = 1000\) eV, at some point of its energy degradation process, produces at least one secondary or tertiary or quaternary electron, whose energy is \(< 7\) eV.

7. Efficiency

As the electron collide with the atmospheric particles, they lose their energy and finally become thermalized. The energy of the colliding electron is divided among the various inelastic loss processes. Efficiency means the fraction of incident energy of the electron which is eventually deposited in a particular loss channel after the completion of the entire degradation process. The efficiency, \(\eta_j(E_0)\), of the \(j\)th process at incident energy \(E_0\) can be obtained as

\[
\eta_j(E_0) = \frac{W_{th}}{E_0} J_j(E_0)
\]

We have calculated the efficiencies for all inelastic collisions using numerical yield spectra obtained from equation (14) and the AYS [sum of equations (15) and (18)].

Figure 9 presents efficiencies of various single ionization events producing \(\text{CO}_2^+\), \(\text{CO}^+\), \(\text{O}^+\), and \(\text{C}^+\). The \(\text{CO}_2^+\) has the maximum efficiency throughout the energy region due its higher ionization cross section. At 1000 eV, \(~31\)% energy of the incident electron goes into \(\text{CO}_2^+\) formation, while 5.9\%, 9.8\%, and 5.0\% energy goes into the production of \(\text{CO}^+\), \(\text{O}^+\), and \(\text{C}^+\), respectively. At higher energies (>100 eV), increase in the efficiencies for all ions is small, but near threshold it falls very rapidly. At threshold, efficiencies for \(\text{CO}_2^+\), \(\text{CO}^+\), \(\text{O}^+\), and \(\text{C}^+\) are 5.1\%, 1.1\%, 0.16\% and 0.19\%, respectively, while at 200 eV these are 29\%, 6.0\%, 9.2\%, and 4.6\%, respectively. Efficiencies for \(\text{CO}_2^+\) (A-X), \(\text{CO}_2^+(\text{B-X})\), and first negative band of \(\text{CO}^+\) (B-X) are also shown in Figure 9. At 200 (1000) eV, 12.2 (11.6)\% of incident electron energy goes in to the emission \(\text{CO}_2^+(\text{A-X})\), while 9.8 (11.4)\% and 3.0 (3.3)\% goes in to the emissions \(\text{CO}_2^+(\text{B-X})\) and \(\text{CO}^+(\text{B-X})\), respectively.

Figure 10 shows the efficiencies for double ionization of \(\text{CO}_2\). At 200 (1000) eV, efficiencies for \(\text{CO}_2^{++}\), \(\text{O}^{++}\), and \(\text{C}^{++}\) are 0.56 (0.67)\%, 0.052 (0.12)\%, and 0.092 (0.14)\%, respectively. We have also calculated the efficiencies for \((\text{CO}^+,\text{O}^+)\), \((\text{C}^+,\text{O}^+)\), and \((\text{O}^+,\text{O}^+)\), based on cross sections of Tian and Vidal [1998], whose values are 2.7 (3.1)\%, 1.8 (2.4)\%, and 0.96 (1.1)\% at 200 (1000) eV. It is clear from Figures 9 and 10, that efficiencies calculated from the model and those obtained by using AYS are in good agreement.

Efficiencies for various excitation processes are presented in Figure 11. The 13.6, 12.4, and 11.1 eV states dominate the excitation events having efficiencies 16 (15)\%, 12 (13)\%, and 4.7 (4.2)\% at 200 (1000) eV, respectively. Efficiencies of various line emissions of atomic oxygen and carbon are shown in Figure 12. Efficiencies for O I (1304), O I (1356), C I (1279), C I (1329), C I (1561), and C I (1657), are 0.12 (0.13)\%, 0.27 (0.28)\%, 0.084
(0.089)%, 0.035 (0.030)%, 0.10 (0.093)%, and 0.19 (0.18)%, respectively, at 200 (1000) eV. Overall efficiencies calculated from numerical yield spectra and AYS for various emission and excitation events are in good agreement.

In Figure 13, we present a summary picture of the electron energy distribution in CO$_2$ for all the loss processes grouped into important loss channels. At higher (>50 eV) energies ionization is the dominant loss process with energy consumption of ~50%. At lower energies (<15 eV), 11.1, 12.4, 8.6, and 9.3 eV loss channels are more important. At energies below 10 eV, vibration becomes the main loss channel. We have also shown the efficiency for total attachment process, which produces negative ion O$^-$. The efficiency for anion O$^-$ production peaks around 8 eV with a value of 0.8%, while it is 0.15 (0.13)% at 200 (1000) eV. The total efficiency for double ionization, which results in the production of CO$_2^{++}$, O$^{++}$, and C$^{++}$ ions, is also depicted in the figure. The double ionization efficiency raises sharply above 40 eV, having value of 0.4 (0.7)% at 100 (200) eV. Around 1000 eV, double ionization efficiency is 0.9%, which is higher than that of 8.6 and 9.3 eV excitation states. On the other hand, at energies >100 eV efficiency for dissociative ionization is higher than that of the 13.6 and 12.4 eV states.

8. Summary

In this paper we have presented a Monte Carlo model for ≤1000 eV electron degradation in CO$_2$ gas. All the e-CO$_2$ collision cross sections are compiled and fitted analytically. The analytical cross sections are presented in figures along with the laboratory measured cross sections for direct comparison, and the fitting parameters are provided in tables. The output of the Monte Carlo model is used to calculate the numerical “yield spectra”, which is represented by an analytical form. This analytical yield spectra (AYS) can be used in planetary atmospheres to determine various aeronomical quantities. We have modified and improved the AYS presented by Green et al. [1977] and Singhal et al. [1980] by adding a term that provides a better analytical representation of yield spectra at lower (<15 eV) energies. The yield spectra is employed to compute the mean energy per ion pair and efficiency of various inelastic processes. The mean energy per ion pair for CO$_2$ is found to be 37.5 (35.8) at 200 (1000) eV. The energy distribution of secondary electrons produced per incident electron is presented at few incident energies.

Efficiency is an effective measure to know what fraction of the incoming particle energy goes into a particular loss channel. We have presented efficiencies for various inelastic events calculated by using the AYS as well as by using the numerical yield spectra obtained from the Monte Carlo model. Efficiencies obtained by the two methods are in good agreement. In addition to major inelastic processes, efficiencies are presented for the formation of negative ions, double and dissociative double ionization of CO$_2$, and total vibrational excitation in the (100), (010), and (001) states. Since the AYS do not represent well the numerical yield spectra at very low (<5 eV) energies, the yield for vibrational excitation and attachment processes calculated by the AYS would be approximate. Ionization is the dominant loss process at higher energies, above 100 eV ~50% energy goes into ionization. At energies around and below ionization threshold excitation processes become important, and at energy below 10 eV, vibration is the dominant loss channel consuming more than 70% energy. The 13.6 and 12.4 eV loss channels are also important, at 1000 eV, around 28% of incident particle energy goes in to these states. A part of these
states represents the emissions of Cameron band system, which is an important emission in atmospheres of Mars and Venus as well as on comets (Bhardwaj and Raghuram, 2009, in preparation).

Efficiencies presented in this paper can be applied to planetary atmospheres by folding them with electron production rate and integrating over the energy. These results will be useful in the modeling of aeronomical processes in atmospheres of Mars, Venus, and CO$_2$-containing atmospheres.

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| Energy (eV) | Angle (degree) | 0   | 5   | 10  | 15  | 20  | 30  | 40  | 50  | 60  | 70  |
|------------|----------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| 1.5        | (1.350)        | (1.252) | (1.154) | (1.056) | 0.9580 | 0.7620 | 0.5410 | 0.4050 | 0.3289 | 0.2957 |
| 2.0        | (1.157)        | (1.055) | (0.954) | (0.852) | 0.7505 | 0.5472 | 0.3896 | 0.2455 | 0.2368 | 0.2489 |
| 3.0        | (1.174)        | (1.060) | (0.945) | (0.831) | 0.7160 | 0.4868 | 0.3069 | 0.3118 | 0.3386 | 0.3779 |
| 3.8        | (2.295)        | (2.059) | (1.824) | (1.589) | 1.3536 | 0.8831 | 0.6294 | 0.5897 | 0.5715 | 0.5367 |
| 4.0        | (2.007)        | (1.844) | (1.681) | (1.517) | 1.3536 | 1.0269 | 0.7770 | 0.6857 | 0.6472 | 0.5834 |
| 5.0        | (0.250)        | (0.333) | (0.416) | (0.499) | 0.5824 | 0.7486 | 0.8076 | 0.8994 | 0.8079 | 0.7272 |
| 6.0        | (0.501)        | (0.546) | (0.592) | (0.637) | 0.6823 | 0.7730 | 0.8244 | 0.8383 | 0.8373 | 0.7644 |
| 6.5        | (0.933)        | (0.914) | (0.896) | (0.878) | 0.8599 | 0.8236 | 0.9132 | 0.9286 | 0.8950 | 0.6978 |
| 7.0        | (0.986)        | (0.960) | (0.934) | (0.909) | 0.8828 | 0.8313 | 0.9039 | 0.9391 | 0.8025 | 0.7558 |
| 8.0        | (16.88)        | (12.95) | (9.02)  | 5.0890 | 1.1590 | 1.0020 | 0.9640 | 0.8542 | 0.7214 | 0.6755 |
| 9.0        | (24.24)        | (18.56) | (12.87) | 7.1830 | 1.4960 | 1.5880 | 1.0870 | 0.9487 | 0.8375 | 0.6622 |
| 10.0       | (39.19)        | (29.96) | (20.74) | 11.520 | 2.2977 | 1.5342 | 1.2136 | 0.9926 | 0.7430 | 0.6260 |
| 15.0       | (31.84)        | (24.84) | (17.84) | 10.843 | 3.8430 | 2.7180 | 1.7789 | 1.1756 | 0.7997 | 0.5777 |
| 20.0       | (13.80)        | (11.77) | (9.743) | 7.7149 | 5.6871 | 3.2623 | 1.8542 | 1.2248 | 0.7475 | 0.4324 |
| 30.0       | (19.89)        | (17.10) | (14.31) | (11.52) | 8.7310 | 3.1540 | 1.4363 | 0.7430 | 0.4678 | 0.3060 |
| 40.0       | (15.70)        | (13.51) | (11.31) | (9.115) | 6.9200 | 2.5300 | 1.0400 | 0.5300 | 0.3100 | 0.1800 |
| 50.0       | 14.820         | 12.690 | 10.560 | 8.4300 | 6.3000 | 2.0400 | 0.8100 | 0.4000 | 0.2100 | 0.1440 |
| 60.0       | (13.44)        | (11.50) | (9.556) | (7.614) | 5.6710 | 1.7860 | 0.6597 | 0.3412 | 0.1683 | 0.1109 |
| 70.0       | (10.61)        | (9.055) | (7.50)  | (5.945) | 4.3900 | 1.2800 | 0.5200 | 0.2500 | 0.1420 | 0.1130 |
| 80.0       | (9.79)         | (8.35)  | (6.91)  | (5.470) | 4.0300 | 1.1500 | 0.4700 | 0.2200 | 0.1360 | 0.1090 |
| 90.0       | (8.50)         | (7.24)  | (5.98)  | (4.72)  | 3.4600 | 0.9400 | 0.3800 | 0.2000 | 0.1450 | 0.1120 |
| 100.0      | (9.273)        | (7.893) | (6.514) | (5.134) | 3.7543 | 0.9950 | 0.3969 | 0.2026 | 0.1502 | 0.1124 |
| 200.0      | (31.75)        | (22.68) | 13.610 | 4.5390 | 2.4170 | 0.6160 | 0.3380 | 0.2230 | 0.1270 | 0.0952 |
| 300.0      | (19.35)        | (13.86) | 8.3720 | 2.8850 | 1.2350 | 0.3880 | 0.2670 | 0.1290 | 0.0716 | 0.0539 |
| 400.0      | (16.82)        | (12.00) | 7.1900 | 2.3770 | 1.0400 | 0.4550 | 0.2150 | 0.0968 | 0.0624 | 0.0523 |
| 500.0      | (132.80)       | 77.22  | 21.600 | 6.6100 | 2.7800 | 1.5600 | 0.7130 | 0.3140 | 0.2190 | 0.1620 |
| 800.0      | (138.20)       | 75.020 | 11.810 | 4.1800 | 2.6500 | 0.9050 | 0.3280 | 0.1900 | 0.0920 | 0.0673 |
| 1000.0     | (113.0)        | 62.100 | 11.200 | 3.5500 | 2.3500 | 0.6600 | 0.2820 | 0.1430 | 0.0925 | 0.0640 |
Table 1.  Contd.

| Energy (eV) | 80   | 90   | 100  | 110  | 120  | 130  | 135  | 150  | 165  | 180  |
|------------|------|------|------|------|------|------|------|------|------|------|
| 1.5        | 0.2700 | 0.2405 | 0.3080 | 0.3040 | 0.3567 | (0.3629) | (0.3816) | (0.3941) | (0.4065) |
| 2.0        | 0.2765 | 0.2845 | 0.3021 | 0.3276 | 0.3776 | 0.3992 | (0.4100) | (0.4424) | (0.4748) | (0.5072) |
| 3.0        | 0.3876 | 0.3937 | 0.3950 | 0.4380 | 0.4830 | 0.5173 | (0.5345) | (0.5859) | (0.6374) | (0.6888) |
| 3.8        | 0.5539 | 0.5739 | 0.5096 | 0.5187 | 0.5280 | 0.5475 | (0.5573) | (0.5865) | (0.6158) | (0.6450) |
| 4.0        | 0.5595 | 0.5037 | 0.4431 | 0.4217 | 0.4258 | 0.4803 | (0.5076) | (0.5893) | (0.6711) | (0.7528) |
| 5.0        | 0.6026 | 0.4794 | 0.3910 | 0.3647 | 0.3136 | 0.3724 | (0.3687) | (0.3576) | (0.3465) | (0.3354) |
| 6.0        | 0.6225 | 0.5258 | 0.4518 | 0.4376 | 0.4316 | 0.4803 | (0.5076) | (0.5893) | (0.6711) | (0.7528) |
| 6.5        | 0.6616 | 0.5300 | 0.4252 | 0.3390 | 0.3201 | 0.3520 | (0.3680) | (0.4158) | (0.4637) | (0.5115) |
| 7.0        | 0.6258 | 0.5273 | 0.4333 | 0.3766 | 0.3798 | 0.3724 | (0.3687) | (0.3576) | (0.3465) | (0.3354) |
| 8.0        | 0.6761 | 0.5343 | 0.4596 | 0.4263 | 0.4058 | 0.5183 | (0.5746) | (0.7433) | (0.9121) | (1.0810) |
| 9.0        | 0.5799 | 0.5394 | 0.4811 | 0.4381 | 0.4816 | 0.6006 | (0.6601) | (0.8386) | (1.0170) | (1.1960) |
| 10.0       | 0.5468 | 0.4856 | 0.4478 | 0.4319 | 0.5304 | 0.7077 | (0.7964) | (1.0620) | (1.3280) | (1.5940) |
| 15.0       | 0.4471 | 0.3596 | 0.3673 | 0.4046 | 0.5445 | 0.7832 | (0.9026) | (1.2610) | (1.6190) | (1.9770) |
| 20.0       | 0.3516 | 0.3041 | 0.3071 | 0.3887 | 0.5493 | 0.6738 | (0.7361) | (0.9228) | (1.1100) | (1.2960) |
| 30.0       | 0.1896 | 0.1882 | 0.2391 | 0.2536 | 0.3195 | 0.4441 | (0.5064) | (0.6933) | (0.8802) | (1.0670) |
| 40.0       | 0.1330 | 0.1190 | 0.1130 | 0.1500 | 0.2400 | (0.330) | (0.3750) | (0.5100) | (0.6450) | (0.7800) |
| 50.0       | 0.1180 | 0.0920 | 0.0810 | 0.1300 | 0.2500 | (0.370) | (0.4300) | (0.6100) | (0.7900) | (0.9700) |
| 60.0       | 0.0936 | 0.0911 | 0.0812 | 0.01175 | 0.1805 | 0.2748 | (0.3220) | (0.4634) | (0.6049) | (0.7463) |
| 70.0       | 0.1040 | 0.0850 | 0.0910 | 0.1400 | 0.2100 | (0.280) | (0.3150) | (0.4200) | (0.5250) | (0.6300) |
| 80.0       | 0.0900 | 0.0850 | 0.0900 | 0.1200 | 0.1800 | (0.240) | (0.2700) | (0.3600) | (0.4500) | (0.5400) |
| 90.0       | 0.0804 | 0.0890 | 0.0920 | 0.1200 | 0.1600 | (0.200) | (0.2200) | (0.2800) | (0.3400) | (0.4000) |
| 100.0      | 0.0840 | 0.0697 | 0.0754 | 0.0880 | 0.1076 | 0.1373 | (0.1522) | (0.1967) | (0.2413) | (0.2858) |
| 200.0      | 0.0756 | 0.0646 | 0.0709 | 0.0770 | 0.0804 | 0.0878 | (0.0944) | (0.1142) | (0.1340) | (0.1538) |
| 300.0      | 0.0505 | 0.0376 | 0.0337 | 0.0314 | 0.0272 | 0.0233 | (0.0217) | (0.0169) | (0.0121) | (0.0073) |
| 400.0      | 0.0376 | 0.0305 | 0.0256 | 0.0255 | 0.0236 | 0.0223 | (0.0202) | (0.0139) | (0.0076) | (0.0013) |
| 500.0      | 0.1080 | 0.0843 | 0.0752 | 0.0658 | 0.0548 | (0.0438) | (0.0383) | (0.0218) | (0.0053) | (0.00012) |
| 800.0      | 0.0523 | 0.0319 | 0.0283 | 0.0238 | 0.0221 | (0.0204) | (0.0195) | (0.0170) | (0.0145) | (0.01190) |
| 1000.0     | 0.0360 | 0.0275 | 0.0220 | 0.0165 | 0.0149 | (0.0133) | (0.0125) | (0.0101) | (0.0077) | (0.0053) |

1Values inside the bracket indicates a linearly extrapolated value.
| Table 2. Parameters for Electron attachment process |
|---------------------------------------------------|
| $W_P$   | $A$     | $U$ | $W_{th}$ |
| $O^-I$  | 4.3     | $0.0013 \times 10^{-16}$ | 0.22 | 3.4   |
| $O^-II$ | 8.1     | $0.0056 \times 10^{-16}$ | 0.33 | 5.9   |

| Table 3. Parameters for various ionization processes |
|-----------------------------------------------------|
| $W_{th}$  | $I$  | $K$ | $K_B$ | $J$   | $J_B$  | $\Gamma_S$ | $\Gamma_B$ | $T_S$ | $T_A$ | $T_B$ |
| $\text{CO}_2^+$ (Total) | 13.76 | 13.76 | 9.83 | 0.0 | 40.59 | 1.050 | 18.61 | -13.23 | -0.847 | 875 | 44.52 |
| $\text{CO}_2^+$ ($X^2\Pi_g$) | 13.76 | 13.76 | 3.480 | 0.0 | 4.099 | -2.35 | 11.11 | -13.26 | -0.847 | 1000 | 27.52 |
| $\text{CO}_2^+$ ($A^2\Pi_u$) | 17.8 | 17.8 | 8.632 | 6.0 | 86.36 | 1.004 | 12.00 | -18.80 | -1.996 | 550 | 10.20 |
| $\text{CO}_2^+$ ($B^2\Sigma^+_g$) | 18.1 | 18.1 | 4.632 | 5.0 | 85.36 | 1.004 | 12.00 | -18.5 | -0.978 | 450 | 10.20 |
| $\text{CO}_2^+$ ($C^2\Sigma^+_g$) | 19.4 | 19.4 | 0.580 | 0.0 | 21.19 | 1.270 | 10.98 | -19.00 | -0.887 | 1000 | 38.80 |
| $\text{CO}^+$ | 24.76 | 24.76 | 1.347 | 15.00 | 6.650 | 1.256 | 9.556 | -24.0 | 1.887 | 800 | 25.52 |
| $O^+$ | 24.5 | 24.5 | 2.399 | 40.00 | 11.34 | -1.10 | 13.42 | -24.0 | -0.587 | 0.0 | 0.0 |
| $C^+$ | 29.5 | 29.5 | 1.659 | 0.0 | 53.54 | 0.625 | 10.62 | -29.0 | 2.800 | 21.8 | 44.00 |
| $C^{++}$ | 79.94 | 79.94 | 0.0012 | 25.00 | 0.100 | 0.656 | 79.11 | 0.0 | 0.8473 | 0.0 | 0.0 |
| $O^{++}$ | 94 | 94 | 0.0055 | 10.00 | 1.700 | -3.156 | 20.11 | 0.0 | -0.8473 | 0.0 | 0.0 |
| $\text{CO}_2^{++}$ | 37.6 | 44.75 | 0.0583 | 1.20 | 0.250 | 0.0 | 11.57 | 35.26 | 1.548 | 800 | 30.52 |
| $(\text{CO}^+,O^+)$ | 44.7 | 44.7 | 0.285 | 1.200 | 0.550 | 0.0 | 11.97 | 35.26 | 1.547 | 650 | 30.52 |
| $(C^+,O^+)$ | 44.7 | 44.7 | 0.288 | 1.200 | 0.550 | 0.0 | 10.40 | 45.00 | 1.547 | 750 | 0.0 |
| $(O^+,O^+)$ | 44.7 | 44.7 | 0.158 | 1.200 | 0.450 | 0.0 | 5.400 | 15.00 | 5.547 | 750 | 0.0 |
Table 4. Parameters for various excitation and emission processes

| Excitation states | $W$  | $\alpha$ | $\beta$ | $W_J$ | $\Omega$ | $F$  | A.F. |
|-------------------|------|----------|--------|-------|---------|-----|------|
| [Vibration, (010)]$^1$ | 0.080 | 2.750    | 1.000  | 0.080 | 0.750   | 0.000 060 | 0.0 |
| [Vibration, (100)] | 0.180 | 1.070    | 1.000  | 0.180 | 0.750   | 0.000 031 | 0.0 |
| [Vibration, (001)] | 0.290 | 2.910    | 0.500  | 0.300 | 0.810   | 0.000 045 | 0.0 |
| 8.6 eV state      | 8.600 | 0.556    | 2.000  | 8.600 | 0.936   | 0.060 060 | 0.0 |
| 9.3 eV state      | 9.300 | 0.603    | 2.000  | 9.300 | 0.909   | 0.064 000 | 0.0 |
| 11.1 eV state     | 7.760 | 0.246    | 3.000  | 11.100| 1.110   | 4.420 000 | 0.0 |
| [12.4 eV state]   | 9.610 | 0.338    | 3.000  | 12.400| 0.830   | 6.700 000 | 0.0 |
| [13.6 eV state]   | 10.50 | 0.625    | 3.000  | 13.600| 0.849   | 3.350 000 | 0.0 |
| 15.5 eV state     | 15.50 | 0.739    | 2.000  | 15.500| 0.793   | 0.139 000 | 0.750|
| 16.3 eV state     | 12.30 | 0.605    | 3.000  | 16.300| 0.911   | 0.716 000 | 0.750|
| 17.0 eV state     | 13.00 | 0.649    | 3.000  | 17.000| 0.878   | 0.114 000 | 0.750|
| 17.8 eV state     | 14.00 | 0.977    | 3.000  | 17.800| 0.725   | 0.051 100 | 0.750|
| OI (1304)         | 20.10 | 0.599    | 3.000  | 22.000| 1.000   | 0.127 000 | 0.750|
| OI (1356)         | 16.40 | 0.600    | 3.000  | 20.400| 0.944   | 0.168 000 | 0.500|
| CI (1279)         | 15.70 | 1.000    | 3.000  | 26.200| 0.643   | 0.010 400 | 0.500|
| CI (1329)         | 21.80 | 1.000    | 3.000  | 20.900| 1.040   | 0.020 200 | 0.500|
| CI (1561)         | 22.40 | 1.000    | 3.000  | 24.500| 0.982   | 0.053 800 | 0.500|
| CI (1657)         | 21.10 | 1.000    | 3.000  | 24.100| 0.947   | 0.872 000 | 0.500|
| [CO$^+$ (first negative)] | 18.13 | 0.656    | 2.54   | 25.11 | 0.804   | 1.055 | 0.0  |

$^1$Parameters are taken from *Jackman et al.* [1977], except for the states which are inside the square brackets whose parameters have been modified.
Figure 1. The e-CO$_2$ total elastic cross section and vibrational excitation cross sections for three modes. For elastic cross section, symbol represents the cross section values of Itikawa [2002], and solid curve represents the analytical fit using equation (1). Dashed curve represents the vibrational excitation cross sections taken from Itikawa [2002].

Figure 2. Dissociative electron attachment cross section for the formation of O$^-$ ion. Symbol represents the values of Itikawa [2002] based on Rapp and Briglia [1965]; solid curve represents analytical fit of O$^-$ cross section using equation(2). I and II denotes the first and second peak.
Figure 3. Ionization and emission cross sections of CO$_2$. Symbol represents the values of Itikawa [2002], and solid curve represents the analytical fits using equation (3) except for CO$^+$ (B-X) state, which is fitted using equation (4). Note that the cross section for CO$_2^+$ (B$^2\Sigma^+_u$) state has been plotted after multiplying by a factor of 3.

Figure 4. Cross sections for electron impact double ionization of CO$_2$. Symbol represents the measured cross section values and solid curve represents the analytical fit using equation (3). Cross sections for (CO$^+$,O$^+$), (C$^+$,O$^+$), and (O$^+$,O$^+$) have been taken from Tian and Vidal [1998], and that for CO$_2^{++}$, O$^{++}$, and C$^{++}$ from Itikawa [2002]. Cross section for O$^{++}$ has been plotted after multiplying by a factor of 2.
**Figure 5.** A simplified flow diagram of the Monte Carlo simulation. The diagram shows flow up to secondary electron, but tertiary and subsequent electrons are also treated in a similar manner in the simulation.

**Figure 6.** The numerical yield spectra from the Monte Carlo model (solid curve) and AYS using equation (15) (dotted curve) at incident energies ($E_0$) 30, 100, 200, 500, and 1000 eV. Dashed curve represents the improved AYS calculated by summing equations (15) and (18). The yield spectra at 100, 200, 500, and 1000 eV are plotted after multiplying by a factor of 10, 80, 600, and 5000, respectively.
Figure 7. The mean energy per ion pair for ions CO$_2^+$ (CO$_2^+$ is the sum of four states X$^2\Pi_g$, A$^2\Pi_u$, B$^2\Sigma_u^+$, and C$^2\Sigma_g^+$), CO$^+$, O$^+$, C$^+$, CO$_2^{++}$, O$^{++}$, and C$^{++}$, and the neutral CO$_2$ gas (total), symbol represents the $\mu$ calculated using numerical yield spectra for the CO$_2^+$ and neutral CO$_2$.

Figure 8. The energy distribution of secondary electrons at six incident energies ($E_0$): 50, 100, 200, 500, 700, and 1000 eV. $N_e$ represents the number of secondary, tertiary, or quaternary electrons produced per incident primary electron. Dotted curve and dashed curve represent energy distribution of tertiary and quaternary electrons, respectively at $E_0 = 1000$ eV.
Figure 9. Efficiencies of various ionization and emission processes. Symbol represents the efficiency calculated by numerical yield spectra and curves represent the efficiency calculated by the AYS. $\text{CO}_2^+(\text{A}^2\Pi_u)$ and $\text{CO}_2^+(\text{B}^2\Sigma^+_u)$ represent FDB ($\text{A}^2\Pi_u \rightarrow \text{X}^2\Pi_g$) and ultraviolet doublet ($\text{B}^2\Sigma^+_u \rightarrow \text{X}^2\Pi_g$) emissions, respectively, and $\text{CO}^+(\text{B-X})$ represents first negative band emission of $\text{CO}^+$ ion.

Figure 10. Efficiencies for double ionization of $\text{CO}_2$ due to electron impact. Symbol represents the efficiency calculated by numerical yield spectra and curves represent the efficiency calculated by the AYS.
Figure 11. Efficiencies of various excited states. Symbol represents the efficiency calculated by numerical yield spectra and curves represent efficiency calculated by the AYS.

Figure 12. Efficiencies of various oxygen and carbon line emissions. Symbol represents the efficiency calculated by numerical yield spectra and curves represent the efficiency calculated by the AYS.
Figure 13. Efficiencies for various important loss channels calculated using numerical yield spectra. Dissociative ionization includes the production of $O^+$, $C^+$, and $CO^+$ ions; double ionization includes the production of $CO_2^{++}$, $O^{++}$, and $C^{++}$ ions; and attachment denotes the production of $O^-$ ion.