4.1 Introduction

First observations of CO Cameron band \((a^3\Pi - X^1\Sigma^+; 180 – 260 \text{ nm})\) and \(\text{CO}_2^+\) ultraviolet doublet \((B^2\Sigma^+ - X^2\Pi; 2883 \text{ and } 2896 \text{ Å})\) emissions in the Martian dayglow were made by the Mariner 6 and 7 flybys in 1969–1970 [Barth et al., 1971; Stewart, 1972]. These observations provided an opportunity to study the Martian upper atmosphere in a greater detail. Figure 4.1 shows the energy level diagram of CO. The CO Cameron band system arises due to the transition from the excited triplet \(a^3\Pi\) state, the lowest of the triplet states, to the ground \(X^1\Sigma^+\) state of CO. The transition from excited \(\text{CO}_2^+\) \((B^2\Sigma_u^+)\) to the ground \(X^2\Pi\) state of \(\text{CO}_2^+\) gives emission in ultraviolet wavelengths at 2883 and 2896 Å. Apart from these emissions, Fox-Duffenback-Berger band of \(\text{CO}_2^+\) \((A^2\Pi_u - X^2\Pi_g)\), fourth positive band of CO, first negative band of \(\text{CO}^+\) \((B - X)\), and several atomic line emissions of carbon and oxygen atoms were also recorded by Mariner 6, 7, and 9 UV spectrometers [Barth et al., 1971; Stewart, 1972; Stewart et al., 1972]. Maximum intensity of CO Cameron band and \(\text{CO}_2^+\) UV doublet emissions observed by Mariner 6 and 7 was 600 kR at \(\sim 131 \text{ km}\) and 35 kR at 148 km, respectively. With the help of theoretical calculations and laboratory measurements, Barth et al. [1971] proposed possible mechanisms for the observed dayglow emissions in the Martian atmosphere. They concluded that most of emissions observed on Mars is the result of photon and electron impact on \(\text{CO}_2\) and its dissociative products.

The CO Cameron band and \(\text{CO}_2^+\) UV doublet emissions were also observed in 1971–1972 by Mariner 9, the first spacecraft to orbit Mars. Stewart et al. [1972] observed a reduction in the intensity of CO Cameron band by a factor of 2.5 compared to Mariner 6 and 7 observations. They attributed this difference to the reduction in the solar activity and better calibration of Mariner 9 instrument. The observed maximum slant intensities of CO Cameron band were between 200 and 300 kR and averaged topside scale height for the same band was 17.5 km. Stewart [1972] also observed a good correlation between
Chapter 4: CO Cameron band and CO$_2^+$ UV doublet emissions

![Energy Level Diagram of CO](image)

**Figure 4.1:** Schematic energy level diagram of Carbon Monoxide showing different spectroscopic transitions.

CO Cameron band intensity and solar F10.7 flux, which suggest that these emissions are controlled by the incident solar photon flux.

The SPectroscopy for the Investigation of the Characteristics of the Atmosphere of Mars (SPICAM) on-board Mars Express (MEx) have carried out airglow observations from Mars orbit more than three decade after the Mariner observations. Emissions observed by SPICAM in UV dayglow include H Lyman-α emission at 121.6 nm, the atomic oxygen emissions at 130.4 and 297.2 nm, the Cameron and fourth positive bands ($A^1\Pi - X^1\Sigma^+$) of CO, and CO$_2^+$ UV doublet emissions [cf. Leblanc et al., 2006; Chaufray et al., 2008b; Gronoff et al., 2012a]. SPICAM has observed dayglow on Mars throughout the Martian year. The effect of Solar Zenith Angle (SZA), seasonal variation, and Martian dust storms on the dayglow emissions has been studied with the help of SPICAM-observations [cf. Leblanc et al., 2006, 2007; Shematovich et al., 2008; Simon et al., 2009; Forget et al., 2009; Cox et al., 2010].

Several theoretical studies have been made for the dayglow emissions on Mars [McConnell and McElroy, 1970; Barth et al., 1971; Fox and Dalgarno, 1979a; Mantas and Hanson, 1979; Conway, 1981; Shematovich et al., 2008; Simon et al., 2009; Cox et al., 2010; Gronoff et al., 2012a, b]. First detailed calculation of dayglow emission on Mars was carried out by Fox and Dalgarno [1979a]. Their calculated overhead intensities of CO Cameron band and CO$_2^+$ UV doublet emissions were 49 kR and 12 kR, respectively, for the low solar activity condition similar to Viking landing [Fox and Dalgarno, 1979a]. Simon et al. [2009] used Trans-Mars model to calculate limb intensities of CO Cameron
band and CO\textsuperscript{+} \textsuperscript{2} UV doublet emissions for low solar activity (condition similar to Viking landing) and compared them with SPICAM-observation. Shematovich et al. [2008] have used Direct Simulation Monte Carlo (DSMC) method for electron transport and calculated intensities of CO Cameron band and CO\textsuperscript{+} \textsuperscript{2} UV doublet emissions in the Martian atmosphere. Cox et al. [2010] have presented a statistical analysis of Cameron band and UV doublet emissions, peak altitude of emissions, and ratio between UV doublet and Cameron band. They reported SPICAM-observations for one particular season, solar longitude (Ls) = 90 to 180°, and compared observational data with model calculations based on Monte Carlo method, which has also been used by Shematovich et al. [2008] for the Martian dayglow studies.

Recently, Gronoff et al. [2012a, b] have calculated the production of excited species and brightness profiles of CO Cameron band, CO\textsuperscript{+} \textsuperscript{2} UV doublet, and OI 2972 Å emissions on Mars. They have used Aeroplanet model for dayglow calculation on Mars. Aeroplanet model is restructured and enhanced version of the Trans-* model series (e.g., Trans-Mars, Trans-Venus) [Lummerzheim and Lilensten, 1994], which have been used by Gronoff and Co-workers to calculate the excited species production in the atmospheres of Mars and Venus [Gronoff et al., 2008; Simon et al., 2009; Nicholson et al., 2009]. Gronoff et al. have used Monte Carlo model to calculate the model uncertainties due to different model input parameters in calculating the excited species production in the atmosphere of Mars.

Prior to Venus Express (VEx), Venus has been visited by several spacecraft (see Chapter 1), but none of them observed CO Cameron band and CO\textsuperscript{+} \textsuperscript{2} UV doublet emissions in the dayglow of Venus. Very recently, the first observation of CO Cameron band and CO\textsuperscript{+} \textsuperscript{2} UV doublet emissions made by SPectroscopy for the Investigation of the Characteristics of the Atmosphere of Venus (SPICAV) onboard VEx in the dayglow of Venus is reported by Chaufray et al. [2012]. The Cameron band brightness peaks at 137.5 ± 1.5 km with a peak brightness of 2000 ± 100 kR and the CO\textsuperscript{+} \textsuperscript{2} doublet peaks at 135.5 ± 2.5 km with a peak brightness of 270 ± 20 kR [Chaufray et al., 2012]. The spectral shape of the Cameron bands observed on Mars and Venus (see Figure 1.12) is very similar indicating that similar mechanisms are responsible for these emissions on the two planets. The above mentioned brightness of CO Cameron band and CO\textsuperscript{+} \textsuperscript{2} UV doublet emissions on Venus is about 10 times higher than that reported on Mars for SZA <40° [Leblanc et al., 2006].

This chapter provides a detailed calculation of various production sources of CO(a\textsuperscript{3}Π) and CO\textsuperscript{+} \textsuperscript{2}(B) in the dayglow of Venus and Mars. The study carried out in this chapter also aims to assess the impact of solar EUV flux models on CO Cameron band and CO\textsuperscript{+} \textsuperscript{2} doublet emission intensities on Mars and Venus. Photoelectron flux, volume excitation rates, and overhead intensities are calculated on Mars and Venus using the two solar EUV flux models, viz., EUVAC [Richards et al., 1994] and S2K [Tobiska, 2004], for
low, moderate, and high solar activity conditions. Line of sight intensities for CO Cameron band and CO$_2^+$ doublet emissions are calculated and compared with the latest observations by SPICAM and SPICAV on Mars and Venus, respectively.

### 4.2 Development of the model

The neutral species considered in the model are CO$_2$, N$_2$, CO, O, and O$_2$. Model atmospheres for solar minimum and maximum conditions are taken from Fox [2004]. For the SPICAM observation conditions model atmosphere is taken from the Mars Thermospheric General Circulation Model (MTGCM) [Bougher et al., 1999, 2000, 2004] as used in the study of Shematovich et al. [2008]. Model atmospheres for both low and high solar activity condition are shown in Figure 4.2 (top panel). Below 180 (200 km), CO$_2$ is the dominant gas in solar minimum (maximum) condition. Above this altitude atomic oxygen takes over CO$_2$ and becomes the dominant gas, which is similar to that in Earth’s atmosphere where atomic oxygen becomes the dominant gas at higher altitudes (>250 km).

Neutral density (CO$_2$, N$_2$, CO, and O) profiles on Venus is taken from the VTS3 model of Hedin et al. [1983] for solar minimum (F10.7 = 60) and maximum (F10.7 = 200) conditions, for equatorial region and local time of 1500 hrs, which corresponds to SZA of around 45°. Density of O$_2$ is taken as $3 \times 10^{-3}$ that of CO$_2$ based on the study of Fox and Bougher [1991]. Figure 4.2 (bottom panel) shows the model atmospheres of Venus for low and high solar activity conditions. Below 160 km (150 km in the case of high solar activity) CO$_2$ is the major species but above that altitude atomic oxygen becomes the dominant neutral in the atmosphere of Venus. Due to the higher gravity of Venus the fall in CO$_2$ density with altitude is much more rapid than that on Mars.

Production mechanisms for CO($a^3\Pi$) are photon and electron impact dissociative excitation of CO$_2$, electron dissociative recombination of CO$_2^+$, and electron impact excitation of CO. Since $X^1\Sigma^+ \rightarrow a^3\Pi$ is a forbidden transition, resonance fluorescence of CO is not an effective excitation mechanism. The CO($a^3\Pi$) is a metastable state; Lawrence [1972a] had measured its lifetime as $7.5 \pm 1$ ms, which is consistent with the the value of 9 ms measured by Johnson [1972]. Due to its long lifetime, cross section for the production of CO($a^3\Pi$) state due to electron impact dissociation of CO$_2$ (e-CO$_2$) is difficult to measure in the laboratory. Ajello [1971b] reported relative magnitudes of the cross section for the (0, 1) transition of CO Cameron band at 215.8 nm and reported a value of $7.1 \times 10^{-17}$ cm$^2$ at 80 eV. This cross section value was later re-evaluated by Erdman and Zipf [1983]. Based on the radiative lifetime of 9 ms [Johnson, 1972], Erdman and Zipf [1983] evaluated the cross section given by Ajello [1971a] and reported a value of $9 \times 10^{-17}$ cm$^2$ at 80 eV, which was subsequently multiplied by a factor of 2.7 to account for higher mean velocity of CO($a^3\Pi$) fragments, which might have escaped detection [Wells et al., 1972]. Therefore, Erdman and Zipf [1983] have reported a value
Avakyan et al. [1998] have estimated the CO Cameron band cross section based on the cross section of Ajello [1971b] with the correction of Erdman and Zipf [1983]. Bhardwaj and Jain [2009] have analytically fitted the cross section of CO($a^3\Pi$) production due to electron impact on CO$_2$ using the suggested value of Erdman and Zipf [1983].

Based on theoretical and experimental work, Gilijamse et al. [2007] have re-analysed the radiative lifetime of CO($a^3\Pi$), and found a value of $\sim$3.16 ms, which is around 3 times less than the value of Johnson [1972]. Conway [1981] constructed a synthetic spectrum of Martian dayglow between 1800 and 2600 Å. Based on the comparison of theoretical
zenith intensity of CO Cameron band with the Mariner observations, Conway [1981] suggested a peak cross section value of $7 \times 10^{-17}$ cm$^2$ for electron impact dissociative excitation of CO$_2$. The value suggested by Conway [1981] is around a factor of 3 smaller than that of Erdman and Zipf [1983].

Recent comparison between calculations and observations of dayglow emission on Mars suggests a lower value of e-CO$_2$ cross section for the CO Cameron band production [Simon et al., 2009; Jain and Bhardwaj, 2012; Gronoff et al., 2012a]. Jain and Bhardwaj [2012] and Gronoff et al. [2012a] have shown that Cameron band cross sections of Erdman and Zipf [1983] should be reduced by a factor of 2 to 3, to bring the calculated CO Cameron band intensities in agreement with the Mars Express observation. In the present study the cross section for Cameron band production due to electron impact on CO$_2$ is taken from Bhardwaj and Jain [2009] after dividing it by a factor of 3, which is shown in Figure 4.3 along with the recommended cross section of Avakyan et al. [1998].

Electron impact on CO (e-CO) is also a source of CO Cameron band. On Mars, due to less abundance of CO, it does not contribute significantly to the total Cameron band emission [Fox and Dalgarno, 1979a; Simon et al., 2009; Jain and Bhardwaj, 2012; Gronoff et al., 2012a]. However, on Venus, CO contribution can not be neglected due to its relatively larger abundance above 150 km (cf. Figure 4.2). In comets where the CO
abundance is larger or equal to that of the CO$_2$, the major contribution to CO Cameron band emission comes from electron impact on CO [Bhardwaj and Raghuram, 2011; Raghuram and Bhardwaj, 2012]. Ajello [1971b] reported the Cameron band emission cross section following the electron impact on CO. Ajello used the (1,4) Cameron band at 2389 Å to normalize the entire band system cross section in electron impact excitation of CO. However, according to Erdman and Zipf [1983], the (1,4) Cameron band was contaminated by (6,16) CO fourth positive band. Erdman and Zipf [1983] repeated and re-analysed the Ajello’s experiment with higher sensitivity and concluded that total cross section value ($1.1 \times 10^{-16}$ cm$^2$ at 11 eV) measured by Ajello [1971b] should be reduced by a factor of 8 to an apparent value of $1.4 \times 10^{-17}$ cm$^2$ at 11 eV. In addition to the contamination problem, Ajello’s total Cameron band emission cross section was based on the assumption of radiation lifetime of 1 ms for a$^3$Π state. Erdman and Zipf [1983], used the radiative life of 9 ms [Johnson, 1972] and multiply the cross section (already corrected for contamination) by a factor of 9 and gave a cross section value of $1.5 \times 10^{-16}$ cm$^2$ at 11 eV.

After accounting for corrections, the cross section value suggested by Erdman and Zipf [1983] is very close to the cross section of Ajello [1971b]. However, based on recent measurements on radiative lifetime of ~3 ms [Gilijamse et al., 2007], the Cameron band cross section in e-CO process should be reduced by a factor of 3. Similar correction is applied to Cameron band cross section in e-CO$_2$ process.

LeClair et al. [1994] have measured the e-CO cross section for CO(a$^3$Π) production using solid xenon detector and time of flight (TOF) technique. LeClair et al. [1994] have given the integral cross section (ICS) of CO(a$^3$Π)—that include cascading contributions from higher triplet states—by normalizing their excitation function to the maximum absolute cross section ($1.5 \times 10^{-16}$ cm$^2$ at 11 eV) obtained by Erdman and Zipf [1983]. The shape of normalized CO(a$^3$Π) cross section measured by LeClair et al. [1994] is identical to the one recorded by Ajello [1971b]. However, maximum cross section is at 9.4 eV in LeClair et al. [1994] measurements compared to 11 eV in Ajello [1971b] experiment. LeClair et al. [1994] attributed this difference in peak position to the electron beam characteristic in the two experiment.

Furlong and Newell [1996] measured the absolute integral cross section for CO(a$^3$Π) production in the e-CO collision by normalizing their measurements to maximum cross section value ($1.698 \times 10^{-16}$ cm$^2$ at 8.5 eV) of Morgan and Tennyson [1993]. Below 10 eV, their cross section is in good agreement with that of LeClair et al. [1994]. Above 10 eV, Furlong and Newell [1996] reported an increase in cross section due to the contribution from cascading into a$^3$Π state. The cross sections obtained by Furlong and Newell [1996] are about a factor of 2 higher between 10 and 35 eV compared to that of LeClair et al. [1994].

The above mentioned discussion clearly points out the difference in the cross sections
of CO($a^3\Pi$) in electron impact excitation of CO. In the present study, cross section of Furlong and Newell [1996] is used for CO($a^3\Pi$) production in e-CO collision. The cross section of LeClair et al. [1994] is also used to assess the effect of cross section in Cameron band intensity. The reason for using these two cross sections over the one measured by Ajello [1971b] is due to the fact that Ajello’s measured cross section have been shown to be flawed by Erdman and Zipf [1983]. However, the correction factor of radiative lifetime of 9 ms [Johnson, 1972] that Erdman and Zipf [1983] used to correct the $a^3\Pi$ state cross section in electron impact on CO$_2$ and CO is about a factor of 3 higher based on the recent radiative lifetime value of 3 ms. Since, LeClair et al. [1994] have normalized their measured cross section to maximum absolute cross section of CO($a^3\Pi$) obtained by Erdman and Zipf [1983], the cross section values given by LeClair et al. [1994] might be overestimated. The cross section measured by Furlong and Newell [1996] shows a broad shoulder above 10 eV, which they attributed to the cascade contribution from higher triplet states. The effect of the two set of CO($a^3\Pi$) cross section used in the present study will be discussed in later sections along with the importance of CO($a^3\Pi$) cross section in determining the role of CO in Cameron band production. Figure 4.3 depicts the CO($a^3\Pi$) cross sections for electron impact on CO used in the present study along with the cross section of Ajello [1971b].

Cross section for photodissociation of CO$_2$ producing CO($a^3\Pi$) is taken from Lawrence [1972a], which is shown in Figure 4.4. The cross section is averaged at 37 wavelength bin according to solar flux input. A discussion on various photodissociative channels
CO$_2$ + h$\nu$ $\rightarrow$ CO(a$^3\Pi$) + O($^3\P$) Model ($K_1$) Lawrence [1972a]
CO$_2$ + e$^-_{ph}$ $\rightarrow$ CO(a$^3\Pi$) + O + e$^-$ Model ($K_2$) Present work
CO + e$^-_{ph}$ $\rightarrow$ CO(a$^3\Pi$) + e$^-$ Model ($K_3$) Present work
CO$_2^+$ + e$^-$ $\rightarrow$ CO(a$^3\Pi$) + O $K_4$ Viggiano et al. [2005]; Rosati et al. [2003]
CO(a$^3\Pi$) + CO$_2$ $\rightarrow$ CO + CO$_2$ 1.0 $\times$ 10$^{-11}$ Skrzypkowski et al. [1998]
CO(a$^3\Pi$) + CO $\rightarrow$ CO + CO 5.7 $\times$ 10$^{-11}$ Wysong [2000]
CO(a$^3\Pi$) $\rightarrow$ CO + h$\nu$ $K_5$ = 1.26 $\times$ 10$^2$ Lawrence [1971]

\(e_{ph} = \) photoelectron.

\(K_4 = 4.2 \times 10^{-7}(300/T_e)^{0.75} \times 0.29 \text{ cm}^3\text{s}^{-1}; \) here, 0.29 is the yield of CO(a$^3\Pi$) production. $K_1$, $K_2$, $K_3$, $K_4$, and $K_5$ are described in Eq. 4.10.

Major reactions for the production and loss of CO(a$^3\Pi$).

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate (cm$^3$ s$^{-1}$ or s$^{-1}$)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$ + h$\nu$ $\rightarrow$ CO(a$^3\Pi$) + O($^3\P$)</td>
<td>Model ($K_1$)</td>
<td>Lawrence [1972a]</td>
</tr>
<tr>
<td>CO$<em>2$ + e$^-</em>{ph}$ $\rightarrow$ CO(a$^3\Pi$) + O + e$^-$</td>
<td>Model ($K_2$)</td>
<td>Present work</td>
</tr>
<tr>
<td>CO + e$^-_{ph}$ $\rightarrow$ CO(a$^3\Pi$) + e$^-$</td>
<td>Model ($K_3$)</td>
<td>Present work</td>
</tr>
<tr>
<td>CO$_2^+$ + e$^-$ $\rightarrow$ CO(a$^3\Pi$) + O</td>
<td>$K_4$</td>
<td>Viggiano et al. [2005]; Rosati et al. [2003]</td>
</tr>
<tr>
<td>CO(a$^3\Pi$) + CO$_2$ $\rightarrow$ CO + CO$_2$</td>
<td>1.0 $\times$ 10$^{-11}$</td>
<td>Skrzypkowski et al. [1998]</td>
</tr>
<tr>
<td>CO(a$^3\Pi$) + CO $\rightarrow$ CO + CO</td>
<td>5.7 $\times$ 10$^{-11}$</td>
<td>Wysong [2000]</td>
</tr>
<tr>
<td>CO(a$^3\Pi$) $\rightarrow$ CO + h$\nu$</td>
<td>$K_5$ = 1.26 $\times$ 10$^2$</td>
<td>Lawrence [1971]</td>
</tr>
</tbody>
</table>

Minor production sources of CO$_2$(B$^2\Sigma_u^+$) are photon and electron impact ionization of CO$_2$. Cross section for the formation of CO$_2^+$(B$^2\Sigma_u^+$) in electron impact ionization of CO$_2$ is taken from Itikawa [2002], and cross section for photoionization of CO$_2$ is based on the branching ratio given by Avakyan et al. [1998] (see Chapter 2). In the present study contribution of fluorescence scattering by CO$_2^+$ is included in the model calculation by taking $g$ values of 5.3 $\times$ 10$^{-3}$ and 1.2 $\times$ 10$^{-3}$ for Venus and Mars, respectively, [Dalgarno and Degges, 1971]. While calculating the emission from $B$ state of CO$_2^+$, we have taken the branching ratio of 0.5 from the CO$_2^+$(B) to (A) based on the study of Fox and Dalgarno [1979a].

The 37 bin EUVAC model of Richards et al. [1994] and S2K version 2.36 of Tobiska [2004] solar EUV flux are used in the study. In these models, bins consist of band of 50
Figure 4.5: Solar photon flux at 1 AU, in bands and at lines, as a function of wavelength in EUVAC and S2K solar EUV flux models. (a) for the low solar activity condition on 20 July 1976 (similar to Viking landing, F10.7 = 70), and (b) for high solar activity condition on 2 August 1969 (similar to Mariner 6 and 7 observations period, F10.7 = 186).

Å width each and few prominent solar EUV lines, and are sufficient for the modelling of photoionization and photoelectron flux calculations [Richards et al., 1994; Simon et al., 2009]. Solar EUV flux has been taken at 1 AU and then scaled to the Sun-Mars (as seen from the Mars, taking the Sun-Earth-Mars angle into consideration) and Sun-Venus
distances. Figure 4.5 shows the output of EUVAC and S2K solar EUV flux models for both solar minimum (20 July 1976) and solar maximum (2 August 1969) conditions at 1 AU. There are substantial differences in the solar EUV fluxes of EUVAC and S2K models; moreover, these differences are not similar in solar minimum and maximum conditions. In both, solar minimum and maximum conditions, the solar flux in bands is higher in S2K than in EUVAC, except for bins below 250 Å (150 Å for solar minimum condition), whereas the solar flux at lines is higher in EUVAC model at all wavelengths. A major difference between solar EUV fluxes of S2K and EUVAC models is the solar flux at bin containing 1026 Å H Ly-β line, which, in both solar minimum and maximum conditions, is about an order of magnitude higher in S2K compare to EUVAC solar flux model (cf. Figure 4.5). Flux at these wavelengths does not contribute to the photoionization, but are very important for dissociative excitation processes. The CO(a^3Π) cross section in photodissociation of CO_2 lies in longer (700–1080 Å) wavelength regime [Lawrence, 1972a]. Hence, the excitation rate of CO in a^3Π state followed by photodissociation of CO_2 would be larger when S2K solar EUV flux model is used.

Primary photoelectron production energy spectrum at altitude Z is calculated using

\[ Q(Z, E) = \sum_l n_l(Z) \sum_{j, \lambda} \sigma^A_l(j, \lambda) I(Z, \lambda) \delta \left( \frac{hc}{\lambda} - E - W_{jl} \right) \]  \hspace{1cm} (4.1)

\[ I(Z, \lambda) = I(\infty, \lambda) \exp[-\tau] \]  \hspace{1cm} (4.2)

where,

\[ \tau(\lambda, Z) = \sec(\chi) \sum_l \sigma^A_l(\lambda) \int_Z^\infty n_l(Z') dZ' \]  \hspace{1cm} (4.3)

is the optical depth at wavelength \( \lambda \) and altitude \( Z \), \( \sigma^A_l \) and \( \sigma^I_l(j, \lambda) \) are the total photoabsorption and photoionization cross sections of the \( j \)th ion state of the constituent \( l \) at wavelength \( \lambda \), respectively; \( I(\infty, \lambda) \) is the unattenuated solar flux at wavelength \( \lambda \), \( n_l(Z) \) is the neutral density of constituent \( l \) at altitude \( Z \); \( \chi \) is the SZA; \( \delta(hc/\lambda - E - W_{jl}) \) is the delta function, in which \( hc/\lambda \) is the incident photon energy, \( W_{jl} \) is the ionization potential of the \( j \)th ion state of the \( l \)th constituent, and \( E \) is the energy of ejected electron. The \( \sec(\chi) \) is used in model calculation in place of Chapman function \( \chi(\chi) \), which is valid for \( \chi \) values upto 80°. The details of photoabsorption and photoionization cross sections used in the present study have been presented in Chapter 2.

In an atmosphere the absorption of photons maximizes where \( \tau(\lambda, Z) = 1 \). The altitude of unit optical depth is shown in Figure 4.6 for wavelengths from XUV to FUV for SZA = 45° in the atmospheres of Mars and Venus for low and high solar activity conditions. CO_2 is the main absorber of FUV and EUV photons on Mars and Venus, although at wavelengths less than 1000 Å, other species namely, N_2, CO, and O also attenuate incoming solar radiation (see absorption cross sections in Figure 2.2). High energy photons (<100 Å) deposit their maximum energy below 120 km on Mars.
Figure 4.6: The altitude where optical depth $\tau$ becomes unity for SZA = 45°, at various wavelengths, on Mars and Venus for low and high solar activity conditions.

On Mars, maximum absorption of photons in wavelength range 200–1000 Å occurs at altitudes between 130 and 135 km in solar minimum condition. During solar maximum condition the altitude of maximum absorption of photons (between 200–1000 Å) is $\sim$140 km, an upward shift of 5 km compared to solar minimum condition. For few wavelengths altitude of unit optical depth is as high as 150 km. In general, on Mars maximum absorption of ionizing photons takes place at an altitude of around 135 km, which coincide with the altitude of maximum photoionization. For photons of wavelength $>1200$ Å, the maximum absorption occurs below 100 (110) km during solar minimum (maximum) condition. These photons do not have enough energy to ionize the gases but can dissociate atmospheric constituents, e.g., the production of O($^1$S) and O($^1$D) on Mars maximizes around 90 km, which is mainly because of solar photons at wavelengths higher than 1200 Å.

On Venus maximum deposition (for photons $<100$ Å) takes place below 130 km, while solar photons in wavelength range 200–1000 Å suffer maximum absorption at $\sim$140 km for both solar minimum and maximum conditions. On Venus, the difference in the altitude of unit optical depth for low and high solar activity conditions is small compared to that on Mars. Solar photons having wavelength between 1200 and 1600 Å deposit their maximum energy around 120 km.
4.3 CO Cameron band and CO$_2^+$ doublet emissions on Mars

A model for CO Cameron band and CO$_2^+$ UV doublet emission in dayglow of Mars is developed using the input parameters described in the previous section. The results are presented in the following sections.

4.3.1 Photoelectron production rate and photoelectron flux

Figure 4.7 shows the primary photoelectron energy spectrum at three different altitudes calculated using Eq. 4.1. There is a sharp peak at 27 eV due to the ionization of CO$_2$ in the ground state by the solar He II Lyman $\alpha$ line at 303.78 Å. The peaks at 21 and 23 eV are due to ionization of CO$_2$ in the $A^2\Pi_u$ and $B^2\Sigma^+_u$ states of CO$_2^+$, respectively, by the 303.78 Å solar photons. To calculate the photoelectron flux the AYS technique is used, which has been described in Chapter 3. Using AYS the photoelectron flux has been calculated as [e.g. Singhal and Haider, 1984; Bhardwaj and Michael, 1999b; Michael, 2000]

$$\phi(Z,E) = \int_{W_{zt}}^{100} Q(Z,E)U(E,E_0) \sum_l n_l(Z)\sigma_{IT}(E) \, dE_0$$  \hspace{1cm} (4.4)

where $\sigma_{IT}(E)$ is the total inelastic cross section for the $l$th gas, $n_l$ is its density, $Q(Z,E)$ is the photoelectron production as described in Section 4.2, and $U(E,E_0)$ is the two-dimensional AYS, which embodies the non-spatial information of degradation process. It
Table 4.2: Amplitude parameters for the two-dimensional yield spectra (Eq. 4.5) for CO, N\(_2\), O, and O\(_2\) taken from Singhal et al. [1980].

<table>
<thead>
<tr>
<th>Gas</th>
<th>(C_0)</th>
<th>(C_1)</th>
<th>(C_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>0.0204</td>
<td>5.29</td>
<td>176.9</td>
</tr>
<tr>
<td>N(_2)</td>
<td>0.0166</td>
<td>5.04</td>
<td>169.0</td>
</tr>
<tr>
<td>O</td>
<td>0.0140</td>
<td>5.02</td>
<td>246.9</td>
</tr>
<tr>
<td>O(_2)</td>
<td>0.0108</td>
<td>6.15</td>
<td>177.0</td>
</tr>
</tbody>
</table>

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 \(E_0\) (details are given Chapter 3).

For CO\(_2\) the AYS is described in Chapter 3. For O\(_2\), N\(_2\), O, and CO, the AYS is taken from the work of Singhal et al. [1980] as

\[
U(E, E_0) = C_0 + C_1\chi + C_2\chi^2
\]  \hspace{1cm} (4.5)

Here \(C_0\), \(C_1\), and \(C_2\) are external parameters which are independent of the energy, whose values are presented in Table 4.2 [Singhal et al., 1980] and

\[
\chi = \frac{E_\Omega}{E + L}
\]  \hspace{1cm} (4.6)

where \(\Omega\) and \(L\) are intrinsic parameter having a value of 0.585 and 1 eV, respectively. \(E_k\) is the incident electron energy (in keV) and \(E\) is the spectral variable (in eV). The values of \(\Omega\) and \(L\) are 0.585 and 1 eV, respective, for all gases [Singhal et al., 1980].

Figure 4.8 shows the photoelectron fluxes in the atmosphere of Mars calculated using EUVAC and S2K solar flux models. Below 70 eV, photoelectron flux calculated using S2K is higher compared to that calculated using EUVAC model for low solar activity condition (Figure 4.8). Above 70 eV, photoelectron flux calculated using EUVAC model is higher than that calculated using S2K model, which is due to the larger solar EUV flux at shorter wavelengths (<250 Å) in EUVAC model (cf. Figure 4.5). During solar maximum condition, due to higher solar EUV flux at wavelength below 250 Å in EUVAC model, the photoelectron flux calculated by using EUVAC model is higher than that calculated using S2K model. Photoelectron fluxes calculated using both solar EUV flux models are similar in shape but peaks around 20–30 eV are more prominent when EUVAC model is used, which is due to the higher solar EUV flux at lines (e.g., He II Lyman-\(\alpha\) line at 303.78 Å) (Figure 4.5).

The calculated photoelectron flux are employed to compute the volume excitation rate of CO(a\(^3\)\(\Pi\)) and CO\(_2^+\)(B\(^2\Sigma_u^+\)) molecules in electron impact processes as,

\[
V_i(Z) = n(Z) \int_{E_{th}}^{E} \phi(Z, E)\sigma_i(E) dE,
\]  \hspace{1cm} (4.7)

where \(n(Z)\) is the density at altitude \(Z\), \(\sigma_i(E)\) is the electron impact cross section for \(i^{th}\) process, for which the threshold is \(E_{th}\), and \(\phi(Z, E)\) is the photoelectron flux. Following
Figure 4.8: Calculated photoelectron fluxes on Mars for low (upper panel) and high (lower panel) solar activity conditions at SZA = 45°. The ratio of the photoelectron flux at 130 km calculated using the two solar flux models is also shown with magnitude on right side Y-axis. Thin dotted horizontal line is drawn for the ratio = 1.

sections describe the production of CO(\(a^3\Pi\)) and \(CO_2^+ (B^3\Sigma_u^+)\) molecules and subsequent Cameron band and UV doublet emissions, respectively, in the atmosphere of Mars for different solar activity conditions.
4.3.2 Low solar activity condition

The model calculation is carried out for low solar activity condition (similar to Viking landing). The Sun-Mars distance $D_{S-M} = 1.64$ AU and solar zenith angle is taken as 45°.

![Figure 4.9](#)

Figure 4.9: Densities of $\text{CO}_2^+$ and $\text{O}_2^+$ ions and CO($a^3\Pi$) molecule on Mars for solar minimum condition calculated using EUVAC (solid curve) and S2K (dashed curve) solar EUV flux models. Density of CO($a^3\Pi$) molecule is plotted after multiplying by a factor of 100. Dotted curves show the densities of $\text{CO}_2^+$ and $\text{O}_2^+$ ions for first case ($L_s < 130^\circ$) using EUVAC solar flux.

Figure 4.9 shows the calculated densities of $\text{CO}_2^+$ and $\text{O}_2^+$ ions in the Martian upper atmosphere. The peak density of $\text{CO}_2^+$ calculated using S2K model is $\sim 20\%$ higher than that calculated using EUVAC, which is due to higher production rate of $\text{CO}_2^+$ when S2K model is used. Below 120 km, ion densities calculated by using EUVAC model are higher than that calculated using S2K model due to higher photon fluxes below 250 Å in EUVAC model (cf. Figure 4.5). There is a small discontinuity in the $\text{O}_2^+$ ion density around 180 km, which is due to the sudden change in the electron temperature at 180 km [see Figure 2 of Fox, 2009]. The calculated ion densities are consistent with calculations of Fox [2004].

Figure 4.10 (upper panel) shows the excitation rate profiles CO($a^3\Pi$) molecule calculated using EUVAC and S2K solar EUV flux models. Around the peak of CO($a^3\Pi$) production, the major source is photoelectron impact dissociation of CO$_2$, while at higher altitudes photodissociation excitation of CO$_2$ takes over. Contribution of dissociative recombination is about 20%, while photoelectron impact excitation of CO contributes $\sim 13\%$ to the CO($a^3\Pi$) production at the peak [when cross section measured by Furlong...
Figure 4.10: Calculated production rates of the CO($a^3\Pi$) (upper panel) and CO$_2^+$($B^2\Sigma_u^+$) (bottom panel) on Mars for low solar activity condition ($Ls\sim 100–140^\circ$). DR stands for dissociative recombination. Blue curves show the production rates calculated using EUVAC model while red curves show them for S2K solar flux model.

and Newell, 1996, are used]. The altitude of peak CO($a^3\Pi$) production remains the same for the two solar flux models. However, the magnitude of VERs calculated using S2K model are about 40% higher than those calculated using EUVAC model. Due to larger photon flux at longer (700–1050 Å) wavelengths (region where photodissociation of CO$_2$ becomes important) in S2K model compared to EUVAC model (cf. Figure 4.5), the CO($a^3\Pi$) production in photodissociative excitation of CO$_2$ is $\sim 50\%$ higher when S2K model is used. It is also clear from the upper panel of Figure 4.10 that the altitude
where the photodissociation of CO\textsubscript{2} takes over electron impact dissociation of CO\textsubscript{2} in CO(a\textsuperscript{3}Π) formation is slightly higher when EUVAC model is used. In the present model calculations, CO\textsubscript{2} photodissociation is the major source of CO(a\textsuperscript{3}Π) at higher altitudes (> 160 km) and is a factor of 2 higher than the electron impact dissociation of CO\textsubscript{2}.

Figure 4.10 (bottom panel) shows the calculated production rates of CO\textsubscript{2}\textsuperscript{+} in B\textsuperscript{2}Σ\textsuperscript{u}\textsuperscript{+} state. Production of CO\textsubscript{2}\textsuperscript{+}(B\textsuperscript{2}Σ\textsuperscript{u}\textsuperscript{+}) due to photoionization of CO\textsubscript{2} is about a factor of ∼3 higher than due to photoelectron impact ionization. The CO\textsubscript{2}\textsuperscript{+}(B\textsuperscript{2}Σ\textsuperscript{u}\textsuperscript{+}) production rate calculated using S2K is higher than that calculated using EUVAC flux by about 33%, but peak altitude remains the same in both cases.

Volume emission rates are height-integrated to calculate overhead intensities, which are presented in Table 4.3 for CO Cameron band and CO\textsubscript{2}\textsuperscript{+} UV doublet emissions. For CO Cameron band, the contribution of e-CO\textsubscript{2} process is maximum (38%) followed by photodissociation of CO\textsubscript{2} (28%). Contribution of both dissociative recombination and e-CO processes is ∼15%. For CO\textsubscript{2}\textsuperscript{+} doublet, the major (73%) contribution is from photoionization of CO\textsubscript{2}, the rest is due to electron impact ionization of CO\textsubscript{2}. Contribution of fluorescence scattering by CO\textsubscript{2}\textsuperscript{+} is very small (∼4%).

For comparing the model output with observed emission the volume emission rates are integrated along the line of sight. The abscissa \(r\) along the horizontal line of sight is calculated as

\[
    r = \sqrt{(R + z)^2 - (R + h)^2}
\]

(4.8)

Where \(R\) is the radius of planet, \(z\) the local altitude of the emission, and \(h\) is the altitude of nearest tangent point (see Figure 4.11). Limb intensity at each tangent point is calculated as

\[
    I = 2 \int \limits_0^\infty V(r)dr,
\]

(4.9)

where \(V(r)\) is the volume emission rate (in cm\textsuperscript{-3} s\textsuperscript{-1}) at a particular emission point \(r\). Multiplication by a factor of 2 is due to symmetry along the line of sight with respect to the tangent point. While calculating limb intensity it is assumed that the emission rate is constant along local longitude/latitude. For emissions considered in the present study the effect of absorption in the atmosphere is found to be negligible.

Figure 4.12 shows the calculated brightness profiles of the CO Cameron band and CO\textsubscript{2}\textsuperscript{+} UV doublet emissions along with the SPICAM-observed limb intensity taken from Simon \textit{et al.} [2009]. Observed values are averaged over the orbits close to Viking 1 condition (Ls\sim100–140°), low solar activity, and for SZA=45°. Below 100 km there is a sudden increase in the observed CO\textsubscript{2}\textsuperscript{+} doublet intensity, which is due to the significant solar contamination below 100 km [Simon \textit{et al.}, 2009]. The limb intensities calculated using S2K flux are ∼40–50% higher than those calculated using EUVAC: depicting the effect of input solar EUV flux on the calculated intensities. The limb intensities of CO Cameron band and CO\textsubscript{2}\textsuperscript{+} doublet emissions calculated using EUVAC model are in
Table 4.3: Overhead intensities (in kR) of CO Cameron band and CO$_2^+$ UV doublet emissions on Mars.

<table>
<thead>
<tr>
<th>Emissions</th>
<th>EUVAC</th>
<th>SOLAR2000</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\nu$+CO$_2$</td>
<td>e+CO$_2$</td>
</tr>
<tr>
<td>-----------------</td>
<td>------------------</td>
<td>-------------</td>
</tr>
<tr>
<td>CO Cameron band</td>
<td>1.2</td>
<td>1.6</td>
</tr>
<tr>
<td>CO$_2^+$ UV doublet</td>
<td>1.1</td>
<td>0.3</td>
</tr>
</tbody>
</table>

SPICAM/Mars-Express, First Case (Ls <130°)

| CO Cameron band | 1.4              | 2.4         | 0.8  | 0.5 | 1.7 | 6.4  | 2.2              | 2.6         | 0.9 | 0.6 | 2  | -  | 7.6  |
| CO$_2^+$ UV doublet | 1.5            | 0.5         | -    | -   | 0.1 | 2.1  | 1.6             | 0.5         | -   | -   | 0.2 | 2.3 {1.2} |

SPICAM/Mars-Express, Second Case (Ls >130°)

| CO Cameron band | 1.6              | 2.7         | 2.1  | 1.4 | 1.1 | 7.5  | 2.6              | 2.9         | 2.4 | 1.6 | 1.3 | -  | 9.3  |
| CO$_2^+$ UV doublet | 1.7            | 0.5         | -    | -   | 0.1 | 2.3  | 1.9             | 0.6         | -   | -   | 0.1 | 2.6 {1.3} |

Higher solar activity (Mariner observations)

| CO Cameron band | 2.3              | 5.2         | 4    | 2.7 | 2.5 | 14   | 3.6              | 4.5         | 3.7 | 2.5 | 2.3 | -  | 14.1 |
| CO$_2^+$ UV doublet | 3.1            | 1.1         | -    | -   | 0.2 | 4.4  | 2.8             | 0.9         | -   | -   | 0.2 | 3.9 {2} |

1) Dissociative recombination ($e + CO_2^+$).
2) Fluorescent Scattering ($\nu + CO_2^+$).
3) Calculate values in parenthesis are for CO($\pi^3\Pi$) cross section obtained by LeClair et al. [1994].
4) Values in braces are calculated by taking the 50% cross over from B to A before radiating.
Figure 4.11: Schematic diagram of line of sight configuration for a typical limb measurement. The altitude of nearest point is $h$. $R$ is the radius of the planet and $r$ is the abscissa along the line of sight along which the intensities must be integrated.

Figure 4.12: Calculated limb profiles of CO$_2^+$ UV doublet bands (left panel) and CO Cameron (right panel) on Mars for low solar activity condition. Solid squares with error bars represents the SPICAM-observed values taken from Simon et al. [2009]. Dashed curves show the calculated intensity (using EUVAC model) after reducing the density of CO$_2$ by a factor of 1.5.

agreement with the observation within the uncertainty of observation and model. For both emissions, the calculated intensity profile peaks at higher ($\sim$5 km) altitude in comparison with the observation—indicating a denser neutral atmosphere in the model. The dashed curves in Figure 4.12 show the calculated intensities after reducing the CO$_2$
density by a factor of 1.5; a good agreement in the altitude of peak emission is seen between calculated and observed limb profiles.

### 4.3.3 SPICAM observations

Leblanc et al. [2006] have presented detailed analysis of SPICAM data during the period October 2004 to March 2005, spanning the solar longitude (Ls) from 101° to 171°. They divided the total data set into two periods of solar longitude: first, Ls = 101° to 130°, and second, Ls = 139° to 171° [cf. Table 2 of Leblanc et al., 2006]. Leblanc et al. [2006] found that the altitude of peak emission for CO\textsuperscript{2+} UV doublet and CO Cameron band is around 10 km higher for Ls > 138° (122.5 km and 132.5 km for UV doublet and Cameron bands, respectively) compared to Ls < 130° (112.5 km and 117.5 km, for the same emissions). Leblanc et al. [2006] could not provide the reason for the higher altitude of peak emission for Ls > 130° observations. Later, Forget et al. [2009] derived neutral densities in Martian upper atmosphere using the SPICAM instrument in stellar occultation mode for the same observation period. Forget et al. [2009] found that there is a sudden increase in the CO\textsuperscript{2+} density in the Martian upper atmosphere for Ls ∼ 130°–140°, which they attributed to a dust storm. Dust storm can heat the lower atmosphere and thus increase the densities at higher altitudes, which could explain the higher altitude for peak emission observed by the SPICAM for Ls > 130° observations. Thus, the increase in the altitude of peak intensity of dayglow emissions clearly shows the effect of dust storms on Martian dayglow emissions.

**First case (Ls < 130°)**

To model the SPICAM observations for Ls < 130° the model atmosphere is based on MTGCM of Boughe et al. [1999] [taken from Shematovich et al., 2008]. Calculations are made for MEx orbit 983 (24 Oct. 2004) when Mars is at heliocentric distance of 1.64 AU and F10.7 = 87.7 (F10.7A = 107.3).

Figure 4.13 (upper panel) shows the volume excitation rate of CO(a\textsuperscript{3}Π). The total VER calculated using S2K flux is slightly higher (∼15%) than that obtained using EU-VAC flux. However, the CO(a\textsuperscript{3}Π) production rate due to photodissociative excitation of CO\textsubscript{2} is around 50% higher when S2K model is used. The CO\textsuperscript{2+} dissociative recombination (DR) contributes ∼26% to the production of CO(a\textsuperscript{3}Π). This value is higher than the CO\textsubscript{2} photodissociative excitation (∼22%) and it is higher than that compared to the contribution of CO\textsuperscript{2+} DR in low solar activity (Viking condition) (see Table 4.3). Leblanc et al. [2006] mentioned that higher values of CO\textsuperscript{2+} can contribute up to 30% to the CO Cameron band production depending on the solar zenith angle. To account for DR in CO(a\textsuperscript{3}Π) production, Shematovich et al. [2008] and Cox et al. [2010] have taken CO\textsuperscript{2+} and electron densities from Fox [2004] for low solar activity condition. Since SPICAM observations are made during moderate solar activity condition, the contribution of
Figure 4.13: Calculated production rates of the CO(a^3Π) (upper panel) and CO_2^+ (B^2Σ_u^+) (bottom panel) on Mars for solar longitude Ls <130°. DR stands for dissociative recombination. Blue curves show the calculated production rates using EUVAC model, while red curves show them for S2K solar flux model.

DR in CO(a^3Π) production would be lower in their calculations. Figure 4.13 (bottom panel) shows the calculated production rate of CO_2^+ (B^2Σ_u^+) molecule. Total excitation rate calculated using both solar flux models peaks at same altitude (∼125 km), but total rate calculated using S2K model is higher (around 10%) than that calculated using EUVAC model. Table 4.3 shows the overhead intensities of CO Cameron band and CO_2^+ doublet emissions calculated using EUVAC and S2K models. For CO_2^+ UV doublet, photoionization of CO_2 is the dominant process contributing around 70% to
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the total overhead intensity.

Figure 4.14: Calculated limb profiles of CO$_2^+$ UV doublet (left panel) and CO Cameron band emissions (right panel) on Mars for Ls < 130°. Symbols represent the SPICAM-observed intensities taken from Leblanc et al. [2006].

Figure 4.14 shows the calculated limb intensities of CO Cameron and CO$_2^+$ UV doublet emissions. SPICAM-observed intensities of CO Cameron and CO$_2^+$ UV doublet emissions (for Ls = 100–130° with 10 orbit) taken from Leblanc et al. [2006] are also shown in Figure 4.14. Limb intensities of CO$_2^+$ UV doublet and Cameron bands calculated using the S2K model are ~6% and ~19%, respectively, higher compared to those obtained using EUVAC model. Calculated intensities of CO Cameron band and CO$_2^+$ UV doublet emissions for both solar flux models are higher than the SPICAM-observed values. The reason for the discrepancy between observed and calculated intensities might be that observations are averaged over several solar longitudes and solar zenith angles while model calculation is made for a single day and for a SZA. Altitude of the calculated intensity for both CO Cameron band and CO$_2^+$ UV doublet peaks ~2 to 3 km higher than the observation, which is well within the observational uncertainties.

Figure 4.15 shows the calculated intensity ratio of CO$_2^+$ UV doublet to CO Cameron band along with the observed ratio derived from SPICAM observations [Leblanc et al., 2006]. At lower altitudes the calculated ratio is in agreement with the observation. The calculated ratio remains almost constant up to ~120 km (where Cameron band and UV doublet emission peaks), then starts to decrease with altitude and becomes gradually flat at higher altitudes. The observed ratio decreases almost monotonically from 100 km to 160 km. Leblanc et al. [2006] have not found any dependence of SZA on the UV doublet to Cameron band intensity ratio, though they have observed a weak dependence.
of this intensity ratio on the solar activity. From the observed intensity ratio profile it is clear that in upper atmosphere CO Cameron band intensity is increasing steadily compare to CO$_2^+$ UV doublet, which indicates source other than photon and electron impact on CO$_2$ is involved in the production of CO($a^3\Pi$) and CO$_2^+$($B^2\Sigma_u^+$). That source could be the dissociative recombination process which is sensitive to the density of CO$_2^+$ ion (as shown in the Figure 4.9).

Second case (Ls $>$130$^\circ$)

As discussed earlier, due to dust storm during SPICAM observations for Ls greater than 130$^\circ$, atmospheric densities were higher resulting in upward shift in the altitude of peak emission ($\sim$132.5 km for CO Cameron band emission). For Mariner 6 and 7 observations the intensity of CO Cameron band peaked at altitude of $\sim$133 km. Mariner observations were carried out during solar maximum condition (F10.7 $\simeq$ 180), whereas SPICAM observations are made during moderate solar activity condition. To model dayglow emissions for Ls $>$130$^\circ$, the calculation is carried out for MEx orbit 1426 (26 Feb. 2005), taking model atmosphere from Fox [2004] for high solar activity condition. Sun-Mars distance is 1.5 AU, F10.7 = 98 (F10.7A = 97). The EUV flux at 1 AU calculated using EUVAC model remains same for first (Ls $<$130$^\circ$) and second (Ls $>$130$^\circ$) cases. This is because in EUVAC model the average of F10.7 and F10.7A (81-day average) is used to scale the solar flux, and in both cases average of F10.7 and F10.7A does not change (it is 97.5 in both cases), although the F10.7 flux increased by 10 unit (see Eq. 2.1

Figure 4.15: Altitude variation of intensity ratio of CO$_2^+$ UV doublet and CO Cameron band emissions on Mars. Model calculated ratio is shown for EUVAC solar flux model. SPICAM-observed ratio is from Figure 9(a) of Leblanc et al. [2006].
for detail). The solar EUV flux in S2K model depends not only on the F10.7, but also on other proxies (see Section 2.2) [Tobiska, 2004], hence flux calculated using S2K model is different on the two days.

Figure 4.16: The calculated production rates of the CO\(^{a^3\Pi}\) (upper panel) and CO\(_2^+\)(B\(^2\Sigma_u^+\)) (bottom panel) on Mars for solar longitude \(L_s > 130^\circ\). DR stands for dissociative recombination. Blue curves show calculated production rates using EUVAC model, while red curves show them for S2K solar flux model.

Figure 4.16 (upper panel) shows the VER of CO\(^{a^3\Pi}\) calculated using S2K and EUVAC models. Total VER calculated using S2K is about 22% higher than that calculated using EUVAC model. Total CO\(^{a^3\Pi}\) production rate (calculated using EUVAC model) maximises at an altitude of 134 km with a value of about 2483 cm\(^{-3}\) s\(^{-1}\), which is around 10 km higher than that in the first case (\(L_s < 130^\circ\)). Although
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Figure 4.17: Calculated limb profiles of CO$_2^+$ UV doublet (left panel) and CO Cameron band emissions (right panel) on Mars for Ls > 130°. Open circles with error bars represent the SPICAM-observed intensity taken from Shematovich et al. [2008].

The contribution of electron impact on CO at the peak CO($a^3\Pi$) production is about 28% higher than that due to PD of CO$_2$ when the EUVAC model is used. The contribution of e-CO process in Cameron band production depends on the cross section for this process used in the model calculation. The effect of different e-CO cross sections on CO($a^3\Pi$) production will be discussed later. In both, first and second cases, for EUVAC model, the altitude where photodissociation of CO$_2$ takes over electron impact dissociation of CO$_2$ is slightly higher than that for S2K model.

Bottom panel of Figure 4.16 shows production rates of CO$_2^+$($B^2\Sigma_u^+$). Total excitation rate calculated using the S2K model is 12% higher than that calculated using EUVAC model. Similar to the CO($a^3\Pi$) production rate, CO$_2^+$($B^2\Sigma_u^+$) production rate at peak is lower than that in the first case, but at higher altitudes CO$_2^+$($B^2\Sigma_u^+$) production rate becomes higher in the second case. Table 4.3 shows the overhead intensities of CO Cameron and CO$_2^+$ UV doublet emissions. Contributions of photodissociation of CO$_2$, e-CO$_2$, e-CO, and CO$_2^+$ DR to the CO Cameron band emission are 21 (28%), 36 (31%), 28 (26%), and 14 (14%), respectively, when EUVAC (S2K) model is used.

Figure 4.17 shows the calculated limb intensity of CO$_2^+$ doublet and CO Cameron band emissions along with SPICAM-observed intensity (MEx orbit 1426 on 26 Feb.
2005) taken from the study of Shematovich et al. [2008]. Intensities calculated using S2K model are higher by ∼10–20% than those calculated using EUVAC model. The altitude of peak emission of calculated and observed intensity profiles is in good agreement (e.g., ∼128 km for Cameron band) within the uncertainties of observations and model calculations. Calculated intensities of CO Cameron band and \( \text{CO}_2^+ \) doublet emissions are in agreement with the observations.

### 4.3.4 Solar maximum (Mariner observations)

The observations by Mariner 6 and 7 were carried during the solar maximum conditions (July-August 1969; \( \text{F}10.7 = 186 \) at 1 AU). Mars was also at perihelion (distance between Sun and Mars was around 1.42 AU) during Mariner observations. The model calculations are carried out for the condition similar to the Mariner observation. Model atmosphere for solar maximum condition is taken from Fox [2004] which is shown in Figure 4.2.

Figure 4.18 (upper panel) shows the production rate of \( \text{CO}(a^3\Pi) \) for higher solar activity condition, calculated using EUVAC and S2K solar flux models. Due to the higher photoelectron flux, \( \text{CO}(a^3\Pi) \) production due to \( \text{e-CO}_2 \) and \( \text{e-CO} \) processes are higher when EUVAC model is used. \( \text{CO}(a^3\Pi) \) production in PD of \( \text{CO}_2 \) is still 50% higher when S2K model is used, which is due to the higher EUV fluxes at longer wavelengths in the S2K model. Similar to that in the previous cases, the cross over point between photodissociation and electron impact dissociation of \( \text{CO}_2 \) forming \( \text{CO}(a^3\Pi) \) occurs at higher altitude when EUVAC model is used. Bottom panel of Figure 4.18 shows the production rates of \( \text{CO}_2^+ (B^2\Sigma_u^+) \) molecule. The excitation rate calculated using EUVAC model is slightly higher than that calculated using S2K model. During solar minimum condition, volume production rate of \( \text{CO}(a^3\Pi) \) and \( \text{CO}_2^+ (B^2\Sigma_u^+) \) calculated using S2K model is higher than that calculated using EUVAC model, whereas in solar maximum it is vice-versa. Except photodissociation excitation process, production rates of \( \text{CO}(a^3\Pi) \) due to other mechanisms calculated using EUVAC model are higher than that calculated by using S2K model. In both, solar minimum and maximum conditions, \( \text{CO}(a^3\Pi) \) production rate due to PD of \( \text{CO}_2 \) is about 50% higher, when S2K model is used.

Table 4.3 shows the overhead intensities of CO Cameron band and \( \text{CO}_2^+ \) doublet emissions. The PD of \( \text{CO}_2 \), electron impact on \( \text{CO}_2 \) and \( \text{CO} \), and DR of \( \text{CO}_2^+ \) contribute 16 (25), 37 (32), 28 (26), and 18 (16)% to the Cameron band production when EUVAC (S2K) model is used. For solar maximum condition as well as for the second case (see Section 4.3.3), the present calculation shows that the \( \text{e-CO} \) and \( \text{CO}_2^+ \) dissociative recombination processes contribute significantly to the CO Cameron band emission. For \( \text{CO}_2^+ \) doublet emission, photoionization of \( \text{CO}_2 \) is the major contributor (70%) followed by electron impact ionization of \( \text{CO}_2 \) (25%). Contribution of fluorescence scattering by \( \text{CO}_2^+ \) is ∼5% only.
Figure 4.18: The calculated production rates of the CO(a^3Π) (upper panel) and CO$_2^+$ (B$^2\Sigma_u^+$) (bottom panel) on Mars for solar maximum condition. DR stands for dissociative recombination. Blue curves show calculated production rates using EUVAC model, while red curves show them for S2K solar flux model.

Figure 4.19 shows model intensities of CO Cameron band and CO$_2^+$ (B - X) UV doublet emissions calculated using both EUVAC and S2K models at SZA = 45° along with intensities observed by Mariner 6 and 7. Limb intensities measured by Mariner 6 and 7 on Mars are at SZA = 27° and 0°, and at SZA = 44° and 0°, respectively. Calculated limb intensities using EUVAC model at SZA = 0° are also shown in the Figure 4.19. Limb intensities calculated using EUVAC model are only slightly higher than those calculated using S2K model. Solar zenith angle effect is clearly visible at altitudes below 150 km, where intensity is larger and emission peak shift deeper in the
atmosphere for lower SZA. Calculated intensities of CO Cameron and \( \text{CO}^+_2 \) doublet emissions are lower than the observed values. \cite{Stewart1972} have pointed out that due to calibration problem in Mariner 6 and 7 instrument the observed values might be higher. This may be the reason for the discrepancy between the calculated and observed brightness profiles of CO Cameron band and \( \text{CO}^+_2 \) doublet emissions.

### 4.3.5 \( \text{CO}(a^3\Pi) \) density

The density of \( \text{CO}(a^3\Pi) \) is calculated under photochemical equilibrium condition. Radiative decay is the dominant loss process of \( \text{CO}(a^3\Pi) \), the loss from other processes is negligible \cite{BhardwajRaghuram2011}. Figure 4.9 shows the calculated \( \text{CO}(a^3\Pi) \) density using EUVAC and S2K EUV flux models for low solar activity condition. The calculated column density of \( \text{CO}(a^3\Pi) \) molecule is \( 3.3 \times 10^7 \, (1.3 \times 10^8) \, \text{cm}^{-2} \) for the solar minimum condition using EUVAC (S2K) model. Except in the solar maximum condition, density of \( \text{CO}(a^3\Pi) \) molecule calculated using S2K model is higher than that calculated using EUVAC model. During solar maximum condition, \( \text{CO}(a^3\Pi) \) density
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calculated using EUVAC model is slightly higher at peak (around 5%), but at altitudes above 140 km, density calculated using S2K model becomes higher (∼10% at 200 km).

The shape of the density of CO($a_3^\Pi$) is similar to that of its production rate (cf. Figure 4.10) since the main loss mechanism of CO($a_3^\Pi$) is radiative decay whose value is independent of altitude. Hence, the density of CO($a_3^\Pi$) in the Martian atmosphere can be represented by

$$\left[CO(a_3^\Pi)\right] = \frac{[CO_2] (K_1 + K_2) + [CO] K_3 + [CO_2^+] [n_e] K_4}{K_5}$$  \hspace{1cm} (4.10)

$K_1$ and $K_2$ are photodissociation rate and electron impact dissociation rate of CO$_2$, respectively, $K_3$ is electron impact excitation rate of CO, $K_4$ is CO$_2^+$ dissociative recombination rate, $K_5$ is radiative decay loss frequency, and $n_e$ is the electron density. The values of $K_1$ (photodissociation rate) in units of s$^{-1}$ at the top of atmosphere in case of EUVAC (S2K) model are $7.5 \times 10^{-8}$ ($1.1 \times 10^{-7}$), $8.7 \times 10^{-8}$ ($1.3 \times 10^{-7}$), $1.03 \times 10^{-7}$ ($1.6 \times 10^{-7}$), and $1.5 \times 10^{-7}$ ($2.25 \times 10^{-7}$) in the solar minimum, first case, second case, and solar maximum, respectively.

4.3.6 Effect of e-CO cross section on CO Cameron band

The cross section of CO($a_3^\Pi$) in electron impact excitation of CO plays an important role in determining the role of CO in the CO Cameron band production. To assess the effect of e-CO cross section on CO Cameron band emission, CO($a_3^\Pi$) excitation rate calculations are made using the e-CO cross section (for CO($a_3^\Pi$) production) measured by LeClair et al. [1994] (see Table 4.3).

In all cases, the contribution of electron impact excitation of CO in Cameron band emission reduces by ∼50% when e-CO cross section measured by LeClair et al. [1994] is used in the model calculations instead of cross sections obtained by Furlong and Newell [1996]. In first two cases (low solar activity and ‘First case’) the e-CO process contributes ∼10% to the CO Cameron band emission. While in later two cases (solar maximum and ‘Second case’) its contribution is about 20%, (roughly equal to the contribution of PD of CO$_2$, when EUVAC model is used).

The present calculation shows that contribution of e-CO process in CO Cameron band emission is significant for moderate and high solar activity conditions, and it is important to constrain the cross section for CO($a_3^\Pi$) production in e-CO process for better understanding the role of CO in Cameron band emission.
4.4 CO Cameron band and CO\textsubscript{2} UV doublet emissions on Venus

Having calculated the Cameron and UV doublet dayglow emissions on Mars, the model is applied on Venus to calculate various production sources of CO Cameron and CO\textsubscript{2} UV doublet band emissions in the dayglow of Venus for low and high solar activity conditions. Results and discussion are presented in the following sections. The various input parameters in the model have been discussed in Section 4.2. The heliocentric distance of Venus is taken as 0.72 AU and solar zenith angle 45°. As mentioned in Section 4.1, the observation of CO Cameron band and CO\textsubscript{2} UV doublet emissions have very recently been reported for the first time in the dayglow of Venus [Chaufray et al., 2012]. The model calculation is carried out for the condition similar to recent SPICAV observation and the calculated brightness profiles are compared with the observed profiles.

4.4.1 Results

4.4.1.1 Solar minimum condition

Figure 4.20 shows the calculated photoelectron flux on Venus at 150 km altitude for low (top panel) and high (bottom panel) solar activity conditions. On Venus, calculated photoelectron fluxes for low and high solar activity conditions show similar behaviour as in the case of Mars. In solar minimum condition, photoelectron flux calculated using S2K model is higher (below 70 eV) than that calculated using EUVAC model. While during solar maximum condition photoelectron flux calculated using S2K model is slightly lower than that calculated using EUVAC model. The cause for these differences in photoelectron fluxes has been discussed in Section 4.3.1.

Figure 4.21 shows the calculated volume excitation rates of CO(a\textsuperscript{3}Π) and CO\textsubscript{2}(B\textsuperscript{2}Σ\textsuperscript{u}+) on Venus for low solar activity condition. The altitude of peak production is at \(~140\) km, which is \(~10\) km higher than that on Mars (see Section 4.3). Major production of Cameron band at the peak is due to the e-CO process, whose contribution is about 44%; unlike on Mars, where electron impact on CO\textsubscript{2} is the major Cameron band production mechanism. Table 4.4 shows the height-integrated overhead intensity of CO Cameron band with contributions of different sources. The e-CO is the major source of Cameron band production with contribution of around 45%, followed by e-CO\textsubscript{2}, photodissociation of CO\textsubscript{2}, and dissociative recombination (DR) of CO\textsubscript{2}+, whose contributions are around 25, 23, and 7%, respectively.

Bottom panel of Figure 4.21 shows the volume production rate of CO\textsubscript{2}+(B\textsuperscript{2}Σ\textsuperscript{u}+) in the atmosphere of Venus. Photoionization of CO\textsubscript{2} is the dominant source (75%) of production of CO\textsubscript{2}+(B\textsuperscript{2}Σ\textsuperscript{u}+), followed by the electron impact ionization of CO\textsubscript{2} (21%). Con-
Figure 4.20: Calculated photoelectron fluxes on Venus for low (upper panel) and high (lower panel) solar activity conditions at SZA = 45°. The calculated ratio of the photoelectron flux at 150 km using the two solar flux models is also shown with magnitude on right side Y-axis. Thin dotted horizontal line depicts the S2K/EUVAC ratio = 1.

The distribution of fluorescent scattering of CO$_2^+$ is negligible (∼4%) to the total CO$_2^+$(B$^2\Sigma_u^+$) production. The height-integrated overhead intensity of CO$_2^+$ UV doublet band emission is given in Table 4.4. The overhead intensity of CO$_2^+$ UV doublet band is about a factor of 4.6 higher on Venus than that on Mars, while the intensity of Cameron band on Venus is about a factor of 6 larger compared to that on Mars (see Section 4.3).
Figure 4.21: Calculated production rates of the CO($a^3\Pi$) (upper panel) and CO$_2^+$($B^2\Sigma_u^+$) (bottom panel) on Venus for low solar activity condition. Blue curves show calculated production rates using EUVAC model while red curves show them for S2K solar flux model.

Figure 4.22 shows the volume production rate of CO($a^3\Pi$) for low and high solar activity conditions calculated by using the $e + CO \rightarrow CO(a^3\Pi)$ cross section measured by LeClair et al. [1994]. The height-integrated intensity of Cameron band is given in Table 4.4. The $e$-CO process is still the dominant source of Cameron band production, though its contribution in Cameron band production is reduced compared to the case when CO($a^3\Pi$) production cross section is taken from Furlong and Newell [1996].

The volume excitation rates are integrated along the line of sight to calculate the limb intensities of CO$_2^+$ UV doublet and CO Cameron band emissions in the dayglow.
Chapter 4: CO Cameron band and $CO_2^+$ UV doublet emissions

Figure 4.22: Calculated production rates of the $CO(a^3\Pi)$ on Venus for low (left panel) and high (right panel) solar activity conditions. Black curves show calculated production rates using EUVAC model and the $CO(a^3\Pi)$ cross section in e-CO process from LeClair et al. [1994], while blue curves show the production rate of $CO(a^3\Pi)$ in e-CO process and total production rate when $CO(a^3\Pi)$ cross section are taken from Furlong and Newell [1996].

Figure 4.23: Calculated limb profiles of $CO_2^+$ UV doublet (left panel) and CO Cameron band (right panel) emissions on Venus for low solar activity condition.

of Venus. Figure 4.23 shows the limb intensities of $CO_2^+$ UV doublet and CO Cameron band emissions on Venus. The calculated limb intensity of Cameron band peaks at 137 km with a value of $\sim$1200 kR, while maximum limb intensity of $CO_2^+$ UV doublet is 183 kR at an altitude of 136 km.
Table 4.4: Overhead intensities (in kR) of CO Cameron band and $\text{CO}_2^+$ UV doublet emissions on Venus for low and high solar activity conditions.

<table>
<thead>
<tr>
<th>Source</th>
<th>Intensity (kR)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CO Cameron Band</td>
</tr>
<tr>
<td></td>
<td>Low SA*</td>
</tr>
<tr>
<td></td>
<td>Low SA</td>
</tr>
<tr>
<td>EUVAC</td>
<td></td>
</tr>
<tr>
<td>$\text{CO}_2 + h\nu$</td>
<td>5.7 (6.2)§</td>
</tr>
<tr>
<td>e + $\text{CO}_2$</td>
<td>6.6 (7.8)</td>
</tr>
<tr>
<td>e + CO</td>
<td>11.4 [7.8]¶</td>
</tr>
<tr>
<td>e + $\text{CO}_2^+$</td>
<td>1.7 (2)</td>
</tr>
<tr>
<td>FS§</td>
<td>-</td>
</tr>
<tr>
<td>Total</td>
<td>25.3 [22] (18)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Source</th>
<th>Intensity (kR)</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>CO Cameron Band</td>
</tr>
<tr>
<td></td>
<td>Low SA</td>
</tr>
<tr>
<td>S2K</td>
<td></td>
</tr>
<tr>
<td>$\text{CO}_2 + h\nu$</td>
<td>8.6</td>
</tr>
<tr>
<td>e + $\text{CO}_2$</td>
<td>9.2</td>
</tr>
<tr>
<td>e + CO</td>
<td>16.2</td>
</tr>
<tr>
<td>e + $\text{CO}_2^+$</td>
<td>2.6</td>
</tr>
<tr>
<td>FS</td>
<td>-</td>
</tr>
<tr>
<td>Total</td>
<td>36.3</td>
</tr>
</tbody>
</table>

*Low solar activity. †High solar activity. §Fluoresence scattering $\text{CO}_2^+ + h\nu$.

§Values in parenthesis are calculated by using the model atmosphere of Fox and Dalgarno [1981] and e-CO cross section from Ajello [1971b]. ¶Calculated values in square brackets are for the $\text{CO}(a^3\Pi)$ cross section of LeClair et al. [1994]. ‖Values in braces are calculated by taking the 50% cross over from $B$ to $A$ before radiating.

4.4.1.2 Solar maximum condition

Figure 4.20 (bottom panel) shows the calculated photoelectron flux on Venus at 150 km for solar maximum condition. As in the case of Mars, the photoelectron flux calculated using EUVAC model is higher than that calculated using S2K model. The solar EUV flux below 250 Å is higher in the EUVAC model which produces high energy photoelectrons. These high energy electron causes further ionization and compensate for higher EUV flux in S2K model at wavelengths >250 Å (cf. Figure 4.5).

Figure 4.24 shows the calculated volume excitation rates of $\text{CO}(a^3\Pi)$ (upper panel) and $\text{CO}_2^+ (B^2\Sigma_u^+)$ (lower panel) for solar maximum condition. The production rate of Cameron band attains a maximum value of $3.8 \times 10^4 \text{ cm}^{-3} \text{ s}^{-1}$ at an altitude of 137 km. The height-integrated overhead intensity is presented in Table 4.4. Electron impact on CO is by far the dominant mechanism of Cameron band production contributing about 60%, followed by electron impact on $\text{CO}_2$ (23%), photodissociation of $\text{CO}_2$ (12%), and dissociative recombination of $\text{CO}_2^+$ (4%). The $\text{CO}(a^3\Pi)$ production rate calculated using e-CO cross section from LeClair et al. [1994] is shown in Figure 4.22 and corresponding
height-integrating intensities in Table 4.4.

For the CO$_2^+$ (B$^2\Sigma_u^+$), maximum production rate occurs at an altitude of 135 km with a value of $\sim 8.7 \times 10^3$ cm$^{-3}$ s$^{-1}$. The overhead intensity of CO$_2^+$ UV doublet band is presented in Table 4.4. The photodissociation of CO$_2$ is the dominant (74%) production source of UV doublet band emission followed by electron impact on CO$_2$ (23%) and fluorescent scattering by CO$_2^+$ (3%). Figure 4.25 shows the calculated line of sight intensities of CO Cameron band and CO$_2^+$ UV doublet emissions. The intensity of Cameron band peaks near 135 km with a value of 2700 kR, while the intensity of UV doublet band attains a maximum value of around 350 kR at an altitude of 132 km.
4.4.2 Discussion

The present model calculation shows that the electron impact on CO is the dominant source of CO Cameron band production in the atmosphere of Venus for low, moderate, and high solar activity conditions using the CO($a^3\Pi$) cross sections of Bhardwaj and Jain [2009] and Furlong and Newell [1996] in electron impact on CO$_2$ and CO, respectively. For solar minimum condition Fox and Dalgarno [1981] and Gronoff et al. [2008] reported e-CO$_2$ process to be the major production source of Cameron band. Gronoff et al. [2008] have calculated CO Cameron band intensity of 17.3 kR; with 7 kR from electron impact on CO$_2$, 5.3 kR from PD of CO$_2$, 4 kR from electron impact on CO, and 1 kR from DR of CO$_2^+$. Gronoff et al. [2008] have used the cross section of Ajello [1971a] for electron impact on CO, while in the present study the cross section of Furlong and Newell [1996] has been used. Using the cross section of Ajello [1971a], our model calculated overhead Cameron band intensity is 18.6 kR, with contributions from PD of CO$_2$, e-CO$_2$, e-CO, and DR of CO$_2^+$ processes being 5.6, 6.7, 4.6, and 1.7 kR, respectively. The model calculated total CO Cameron band intensity is in good agreement with that of Gronoff et al. [2008]. Fox and Dalgarno [1981] reported the Cameron band intensity of about 20 kR, with contribution of $\sim$25% from DR of CO$_2^+$ and 6% from e-CO process. The present calculation, as well as that of Gronoff et al. [2008], show that the contribution of DR of CO$_2^+$ (which depends on electron density and temperature) is smallest among the...
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processes considered in the model (see Table 4.4). Fox and Bougher [1991] suggested that the source of DR was overestimated in the pre-Pioneer Venus model of Fox and Dalgarno [1981] because of low density of atomic oxygen, which led to larger densities of CO$_2^+$ ion. The mixing ratio of CO was lower in the model atmosphere used by Fox and Dalgarno [1981], whereas in the present calculation, as well as in the model of Gronoff et al. [2008], the VTS3 model atmosphere is used, which has larger CO mixing ratio. To evaluate the effect of low CO mixing ratio, the model calculation is also carried out by taking model atmosphere of Fox and Dalgarno [1981]; the results are shown in Table 4.4. The Cameron band intensity is 18 kR when the model atmosphere of Fox and Dalgarno [1981] and e-CO cross section of Ajello [1971a] are used, which is in agreement with the model result of Fox and Dalgarno [1981]. However, in the present calculation the contribution of DR is about 11%, which is lower than that reported by Fox and Dalgarno [1981]; this might be due to the difference in DR rate coefficient for CO(a$^3\Pi$) production in the two calculations.

For solar maximum condition, Fox and Bougher [1991] have reported total Cameron band intensity of 57 kR, which is in agreement with the calculated value of 60 kR in the present study. However, the contribution of individual processes is different in the two studies. In the present study the e-CO is the dominant process; whereas in the model calculation of Fox and Bougher [1991] the photon and electron impact on CO$_2$ played the dominant role with contribution of about 36% from each, while the contributions of electron impact on CO and DR of CO$_2^+$ were 20 and 8%, respectively.

The present study shows that the contribution of e-CO process in CO(a$^3\Pi$) production is directly related to the cross section used in the calculation. For CO(a$^3\Pi$) cross section of LeClair et al. [1994], the model calculations demonstrate that the e-CO process is the dominant source of CO Cameron band (see Figure 4.22 and Table 4.4). Thus, the role of electron impact on CO in the Cameron band production might have been underestimated in the earlier calculations [Fox and Dalgarno, 1981; Gronoff et al., 2008] due to the choice of e-CO cross section for CO(a$^3\Pi$) production.

4.4.2.1 Effect of solar EUV flux models

During the solar minimum condition, the CO Cameron band excitation rate calculated using the S2K model is about 45% larger than that calculated using the EUVAC model, while the production in the photodissociation of CO$_2$ is about 50% higher when S2K model is used. However, the altitude of peak production is same for both solar EUV flux models (see Figure 4.21). The limb intensities calculated using the S2K model are about 40% larger than those calculated using the EUVAC model (see Figure 4.23).

For solar maximum condition, the calculated intensity of CO Cameron and CO$_2^+$ UV doublet band emissions using the EUVAC model is about 2% and 10%, respectively, higher than those calculated using the S2K model. This is due to the higher solar EUV
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flux in EUVAC model at wavelengths $\leq$ 250 Å that produces energetic photoelectrons which further ionize the medium and compensate for the higher photoionization by solar EUV flux at wavelengths $>$ 250 Å in the S2K model. Similar variation in the emission intensities due to the change in EUV flux models for solar minimum and maximum conditions have been found on Mars (see Section 4.3).

For both, low and high solar activity conditions, the contribution of photodissociation of CO$_2$ to the Cameron band production is 50% higher when the S2K solar flux model is used. This is because of an order of magnitude higher solar EUV flux in the 1000–1050 Å bin in the S2K model compared to that in the EUVAC model. Solar EUV flux in the 1000-1050 Å bin does not significantly contribute to the photoionization, but significantly affects the photodissociation of CO$_2$: thus affecting the Cameron band production in the photodissociation of CO$_2$.

For solar maximum condition, the calculated intensities using the EUVAC model are about two times higher than those calculated for solar minimum. When S2K model is used, the calculated intensities of UV doublet and Cameron band emissions are 1.3 and 1.6, respectively, times larger in high solar activity that those in low solar activity condition. For the EUVAC solar flux model, the variation in contribution of electron impact processes are more prominent for change in solar activity from low to high due to a change of more than a factor of 2 in the solar EUV flux below 250 Å, whereas solar EUV flux in the S2K model varies by less than a factor of 2 from solar minimum to maximum condition (see Figure 4.5).

4.4.3 Comparison of model calculations with SPICAV observation

Very recently Chaufray et al. [2012] have reported the first Venusian dayglow observation of CO Cameron band and CO$_2^+$ UV doublet emissions using the SPICAV aboard Venus Express. The SPICAV observations were made between October and December 2011, with solar zenith angles vary between 20$^\circ$ and 30$^\circ$. We have carried out calculation for the similar condition as reported by Chaufray et al. [2012] by taking SZA of 25$^\circ$ and VTS3 model atmosphere for 15 November 2011 (F10.7 = 148 and F10.7-81 day average = 144). Figure 4.26 shows the calculated CO Cameron band and CO$_2^+$ UV doublet brightness profiles along with the SPICAV-observed profiles taken from Chaufray et al. [2012].

The model calculated brightness of CO Cameron band peaks at 134 km with a value of 3200 kR. The SPICAV-observed peak of Cameron band brightness is situated at 137±1.5 km and the magnitude of limb intensity at this altitude is $\sim$2000 kR [Chaufray et al., 2012]. The calculated intensity at the peak is about 50% higher than the observed value. When the CO(a$^3\Pi$) production cross section in e-CO collision of LeClair et al. [1994] is used, the limb intensity of Cameron band at the peak altitude is 2700 kR. As mentioned
earlier, the cross section obtained by LeClair et al. [1994] might be overestimated by a factor of 3 (see Section 4.2). On deceasing the LeClair et al.’s measured cross section by a factor of 3, the calculated CO Cameron band brightness at the peak is $\sim$2000 kR. For CO$_2^+$ ultraviolet doublet emission, maximum limb intensity of $\sim$370 kR is obtained at an altitude of 133 km, which is about 30% higher than the SPICAV-observed value of 270 kR (at 135.5 ± 2.5 km) [Chaufray et al., 2012].

Chaufray et al. [2012] have derived the overhead intensity of 25.3 kR and 3.2 kR for Cameron band and CO$_2^+$ UV doublet emissions, respectively, by converting the limb intensity to zenith brightness above sub-solar point. These values are significantly lower than our model calculated high-integrated overhead intensities of of 70 and 8 kR (at SZA = 25°) for Cameron band and CO$_2^+$ UV doublet emissions, respectively. This discrepancy in the calculated and observation-derived overhead intensity is significant and it is difficult to comment on the cause for this difference at present, since it is not clear to us the methodology used by Chaufray et al. [2012] for calculating zenith intensity.
The calculated altitude of peak brightness of both CO Cameron band and CO$_2^+$ UV doublet emissions is lower by $\sim 5$ km than the observation. The difference in peak altitude of observed and calculated emissions shows that the neutral density in Venus model atmosphere is lower in the present calculation. Recent, Venus Thermospheric General Circulation Model (VTGCM) also suggests that VTS3 empirical model is inadequate to properly represent lower thermosphere thermal structure [Brecht and Bougher, 2012]. Density profile of CO$_2$ calculated by VTGCM differs from that calculated by VTS3 model above 100 km.

The profile of observed CO$_2^+$ UV doublet emission may contain small portion of OI 2972 Å emission [Chaufray et al., 2012], which makes the shape of observed profile different than the calculated emission profile at lower altitudes. The calculated CO$_2^+$ UV doublet emission profile with 15% OI 2972 Å emission is also shown in Figure 4.26.

A more detailed study of these emissions with VTGCM needs to be carried out to understand the recent SPICAV observations.

### 4.5 CO($a'$, $d$, $e$) triplet emissions on Mars and Venus

The photodissociation of CO$_2$ below 1080 Å leads to the formation of CO($a^3\Pi$), but at photon energies greater than 12.4 eV (wavelength < 1000 Å) other channels open up. The photodissociation of CO$_2$ in the 10.3-13.8 eV (1200–900 Å) region leads to the channel CO* + O($^3\Pi$), where CO* corresponds to four triplet levels $a^3\Pi$, $a^3\Sigma^+$, $d^3\Delta$, and $e^3\Sigma^−$ (see Figure 4.1). Emissions arising due to the transition from the $a'$, $d$, and $e$ states down to $a^3\Pi$ state are called Asundi, Triplet, and Herman bands, respectively. Conway [1981] has reported that the CO Cameron band spectra observed by Mariner showed a very hot rotational distribution. His analysis showed a bimodal fit with temperatures 1600 K and 10,000 K. Analysis of SPICAM/MEx data also showed similar hot distribution [Kalogerakis et al., 2012]. Recently, Kalogerakis et al. [2012] studied the EUV photodissociation of CO$_2$ in laboratory and found strong emissions in the visible and near-IR region arising from the CO($a'$, $d$, $e$) triplet states. They attributed these triplet band emissions to be the primary source for the CO($a$–X) Cameron bands. Kalogerakis et al. concluded that most of the observed Cameron band arising from photodissociation of CO$_2$ is preceded by the cascading from the CO($a'$, $d$, $e$) triplet states, and predicted that the visible and near-IR (6000 to >14000 Å) emissions from these triplet states is of the same magnitude as the CO Cameron band.

Based on the study of Kalogerakis et al. [2012], one can predict the lower limit of Asundi, triplet, and Herman bands in the atmospheres of Mars and Venus, if only photodissociation of CO$_2$ is considered as the primary source of these CO($a'$, $d$, $e$) triplet states. Results from the present study show that for solar minimum condition the contribution of photodissociation of CO$_2$ to the CO Cameron band production on Mars and Venus is 1.2 and 5.7 kR, respectively (see Tables 4.3 and 4.4). Thus, the CO($a'$, $d$, $e$)
triplet band emissions would be about 1.2 and 5.7 kR on Mars and Venus, respectively, spread over the 6000 to >14000 Å range. The Asundi $a' - a$ (5-0) band at 7830 Å is about 10% of the total triplet band emissions [Kalogerakis et al., 2012], thus its overhead intensity on Mars and Venus would be $\sim$120 and 570 R, respectively. Similarly, during solar maximum condition the intensity of CO($a', d, e$) triplet and Asundi $a' - a$ (5-0) bands on Mars (Venus) would be 3.1 (7.5) kR and 310 (750) R, respectively. The maximum fraction of Cameron band originate from electron impact on CO$_2$ and CO on Mars and Venus and these processes do not exclude similar CO product [Kalogerakis et al., 2012]. The magnitude of CO($a', d, e$) triplet bands on Venus reported above would be a lower limit: an upper limit could be larger by a factor of 2 to 4.

### 4.6 Summary and conclusion

The present study deals with the calculations of CO Cameron band and CO$_2^+$ doublet ultraviolet emissions in the dayglow of Mars and Venus and the impact of solar EUV flux on the calculated intensities. Emission rates of CO Cameron band and CO$_2^+$ UV doublet emissions due to photon and electron impact on CO$_2$ have been calculated using EUVAC and S2K solar EUV flux models. The excitation rates of CO($a^3Π$) and CO$_2^+$($B^2Σ_u^+$) are height-integrated to calculate the overhead intensity and along the line of sight to obtain the limb intensities. The intensities of CO($a', d, e$) triplet band emissions on Mars and Venus are predicted. Calculated limb intensities on Mars are compared with the SPICAM and UV spectrometer/Mariner observed intensities. The calculated brightness profiles of CO Cameron band and CO$_2^+$ doublet emissions are in agreement with the SPICAM-observations, however, in solar maximum condition the calculated intensities are lower than that observed by Mariner 6 and 7 ultraviolet spectrometers.

On Venus, the calculated brightness of CO Cameron band and CO$_2^+$ doublet emissions is compared with the recent SPICAV-observation. The calculated intensity of CO Cameron band at the peak altitude is about 50% higher than the observation. However, when the CO($a^3Π$) production cross section in e-CO collision measured by LeClair et al. [1994] is used in the model calculation this difference reduces to 30%, and with a correction by a factor of 3 in cross section, the magnitude of calculated brightness at peak is in good agreement with the observation. The calculated limb intensity of CO$_2^+$ doublet emission is 30% higher than the SPICAV-observation. The calculated overhead intensities of the two emissions is significantly higher than those derived from the observations. Presently, it is difficult to comment on this discrepancy and further investigation is needed. The model calculated peak altitude of CO Cameron band and CO$_2^+$ UV doublet emission profiles is lower than that observed by SPICAV, indicating lower neutral density in the VTS3 model atmosphere for Venus.

Following conclusion can be drawn from the present study:
1. On Mars, photoelectron impact on CO\textsubscript{2} is the dominant process for the production of Cameron band. The PD of CO\textsubscript{2} is the second most important source of Cameron band in low solar activity condition, while photoelectron impact on CO becomes an important processes in moderate and high solar activity.

2. On Venus, electron impact on CO is the major process of Cameron band production, followed by photoelectron impact on CO\textsubscript{2} and PD of CO\textsubscript{2}. Thus, the situation on Venus is quite different than that on Mars.

3. For CO\textsuperscript{2} UV doublet emissions on Mars and Venus, photoionization of CO\textsubscript{2} is the dominant process followed by electron impact on CO\textsubscript{2}.

4. Generally, solar EUV fluxes in bands are higher in S2K model compared to EUVAC model except at few bands at shorter wavelength range (\(<\) 250 Å). Solar EUV fluxes at longer wavelengths are higher in the S2K model, specially in the 1000-1050 Å bin, where the flux is around an order of magnitude higher than the corresponding flux in the EUVAC model. Solar EUV flux at lines is smaller in the S2K model compared to that in the EUVAC model.

5. Due to higher EUV flux at lines in the EUVAC model, the peaks in the 20–30 eV range in the photoelectron flux are more prominent when EUVAC model is used.

6. During the high solar activity condition, calculated photoelectron fluxes are higher for EUVAC model due to higher EUV fluxes below 250 Å in the EUVAC model. Hence, intensities calculated using the EUVAC model are higher by 5–10\% than those calculated using the S2K model.

7. During both solar conditions, the Cameron band production due to photodissociative excitation of CO\textsubscript{2} is about 50\% higher when the S2K solar EUV flux model is used.

8. The altitude of peak production rate of Cameron and CO\textsuperscript{2} UV doublet bands is independent of the solar EUV flux model used in the calculations.

The present study clearly demonstrates that the cross section of a\textsuperscript{3}Π state in e-CO process is important in modelling CO Cameron band emission on Mars and Venus. The contribution of e-CO process in CO Cameron band production also depends on the density of CO in the atmosphere. Hence, it is difficult to constrain the former without fixing the later. However, the calculations carried out in this chapter suggest that the role of electron impact on CO in Cameron band production on Mars and Venus needs to be reconsidered.

Recently, SPICAM/Mars Express observed N\textsubscript{2} VK band emission on Mars. Since, N\textsubscript{2} is second most abundant gas on Venus, the N\textsubscript{2} triplet band features are expected
on Venus also. The application of AYS to the calculation of N$_2$ triplet dayglow band emissions on Mars and Venus is presented in the next Chapter.