Forbidden atomic oxygen emissions in the Martian dayside upper atmosphere

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ABSTRACT

Recently, Nadir and Occultation for Mars Discovery (NOMAD) ultraviolet and visible spectrometer instrument on board the European Space Agency’s ExoMars Trace Gas Orbiter (TGO) simultaneously measured the limb emission intensities for both [OI] 2972 and 5577 Å (green) emissions in the dayside of Martian upper atmosphere. But the atomic oxygen red-doublet emission lines ([OI] 6300 and 6364 Å), which are expected to be observed along with [OI] 5577 and 2972 Å emissions, are found to be absent in the NOMAD-TGO dayside observed spectra. We aim to explore the photochemistry of all these forbidden atomic oxygen emissions ([OI] 2972, 5577, 6300, 6464 Å) in the Martian daylight upper atmosphere and suitable conditions for the simultaneous detection of these emissions lines in the dayside visible spectra. A photochemical model is developed to study the production and loss processes of O(1\textsuperscript{S}) and O(1\textsuperscript{D}), which are the respective excited states of green and red-doublet emissions, by incorporating various chemical reactions of different O-bearing species in the upper atmosphere of Mars. By reducing Fox (2004) modelled neutral density profiles by a factor of 2, the calculated limb intensity profiles for [OI] 5577 and 2972 Å emissions are found to be consistent with the NOMAD-TGO observations. In this case, at altitudes below 120 km, our modelled limb intensity for [OI] 6300 Å emission is smaller by a factor 2 to 5 compared to that of NOMAD-TGO observation for [OI] 2972 Å emission, and above this distance it is comparable with the upper limit of the observation. We studied various parameters which can influence the limb intensities of these atomic oxygen forbidden emission lines. Our calculated limb intensity for [OI] 6300 Å emission, when the Mars is at near perihelion and for solar maximum condition, suggests that all these forbidden emissions should be observable in the NOMAD-TGO visible spectra taken on the dayside of Martian upper atmosphere. More simultaneous observations of forbidden atomic oxygen emission lines will help to understand the photochemical processes of oxygen-bearing species in the dayside Martian upper atmosphere.

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1. Introduction

Forbidden atomic oxygen emissions are the prominent features in the visible spectra of terrestrial atmospheres. These emissions have been studied extensively from various ground- and space-based observatories. Observation of these emissions provides valuable information about the energy deposition and chemical processes in the upper atmospheres of terrestrial planets. About 5% of excited atomic oxygen atoms produced in $^1S$ state decay directly to the ground state ($^3P$) and produce $[\text{OI}] 2972 \, \text{Å}$ emission, and the rest decay via $^1D$ state that results in the emission at wavelength 5577 Å (green line). Radiative decay of $\text{O}(^1\text{D})$ to the ground state produces the red-doublet emissions at wavelengths 6300 and 6364 Å, provided it is not collisionally quenched by other species. Since both $[\text{OI}] 2972$ and 5577 Å emissions are produced due to de-excitation of same electronic excited state ($^1S$), detection of one of these lines confirms the presence of other. Similarly, the observation of green line also indicates the presence of red-doublet emissions but the opposite is not always true in case the $\text{O}(^1\text{S})$ state is not produced in the atmosphere or totally deactivated by collisions.

Several theoretical works were carried out to study the photochemistry of metastable atomic oxygen atoms in the Martian upper atmosphere. About 40 years ago, Fox and Dalgarno (1979) predicted the forbidden emissions of atomic oxygen in the upper atmosphere of Mars. Simon et al. (2009) developed a kinetic model to study the seasonal variation of the dayside $[\text{OI}] 2972 \, \text{Å}$ emission intensity along with other important emissions, such as $\text{CO}_2^+$ UV-doublet and $\text{CO}$ Cameron bands. These modelling studies show that photodissociative excitation of $\text{CO}_2$ is the major source of $\text{O}(^1\text{S})$ in the upper atmosphere of Mars. But the study of these emissions by Huestis et al. (2010) shows that dissociative recombination of $\text{O}_2^+$ also plays an important role in producing $\text{O}(^1\text{S})$ and determining the $[\text{OI}] 2972$ and 5577 Å emission intensities. Hence, it is suggested that the observed $[\text{OI}] 2972 \, \text{Å}$ emission intensity should be used to monitor the Martian ionosphere and not the ambient neutral temperature. The calculations made by Gronoff et al. (2012a) and Gronoff et al. (2012b) showed that the uncertainties associated with modelling parameters can influence the calculated limb intensities of spectroscopic emissions. To understand the photochemistry of these forbidden emissions, Jain (2013) accounted for several production and loss mechanisms of $\text{O}(^1\text{S})$ and $\text{O}(^1\text{D})$ in the Martian upper atmosphere and modelled the atomic oxygen emission intensities for both solar maximum and minimum conditions. Recently, Gkouvelis et al. (2018) have reported observations of $[\text{OI}] 2972 \, \text{Å}$ emission in the Imaging Ultraviolet Spectrograph (IUVS) onboard Mars Atmosphere and Volatile Evolution (MAVEN) satellite observed ultraviolet spectra and constrained the quantum yield for photodissociation of $\text{CO}_2$ producing $\text{O}(^1\text{S})$ at Ly-α wavelength (1216 Å) as about 8%.

The observation of $[\text{OI}] 2972 \, \text{Å}$ emission has been done in the Martian upper atmosphere by several spacecraft-borne ultraviolet spectrometers starting from Mariner 6 to the recent MAVEN mission (Stewart, 1972; Leblanc et al., 2006; Jain et al., 2015). But the observation of $[\text{OI}] 5577 \, \text{Å}$ emission had never been reported in the dayside of Martian upper atmosphere until the recent detection from Nadir and Occultation for Mars Discovery ultraviolet and visible spectrometer instrument on board the European Space Agency’s ExoMars Trace Gas Orbiter (NOMAD-TGO) by Gérard et al. (2020). Owing to its wide detection range (2000–6500 Å), this spectrometer is capable of observing the four forbidden atomic oxygen emissions ($[\text{OI}] 2972$, 5577, 6300, and 6364 Å) simultaneously in the Martian upper atmosphere. NOMAD-TGO could observe both $[\text{OI}] 2972$ and 5577 Å emissions simultaneously and the observed intensity ratio is used to determine the corresponding transition probabilities ratio of $\text{O}(^1\text{S})$. However, the emission features at $[\text{OI}]$ red-doublet wavelengths were found to be absent in the NOMAD-TGO observed dayside spectra (at the 1σ level, Gérard et al., 2020). We aim to study the photochemistry of these forbidden emission lines in the dayside of Martian upper atmospheres and explore suitable conditions to observe all these emissions simultaneously in the NOMAD-TGO spectra. By accounting for the important production and loss mechanism of $\text{O}(^1\text{S})$ and $\text{O}(^1\text{D})$ in our well utilized photochemical model, we studied the emission processes of forbidden atomic oxygen emission lines in the dayside Martian upper atmosphere. The model inputs and calculations are presented in Section 2. We present the results of our model calculations and discussion in Section 3. In Section 4, this work is summarized and conclusions are drawn.

2. Model inputs and calculations

A detailed description of the model calculations is provided in our earlier work (Jain, 2013; Jain and Bhardwaj, 2012; Raghuram and Bhardwaj, 2012; Bhardwaj and Raghuram, 2012; Raghuram and Bhardwaj, 2020). Here we briefly
describe the model inputs that are used for the present calculations. The neutral density profiles for the primary species (CO$_2$, CO, N$_2$, O$_2$, and O) of Martian upper atmosphere are considered from Fox (2004), which are based on the Viking measurements and for solar minimum condition. To compare these density profiles with the ongoing Neutral Gas and Ion Mass Spectrometer (NGIMS) on-board MAVEN mission measurements, we analysed NGIMS/MAVEN level 2 (L2) version 1 data for the period April to December 2019, during which NOMAD-TGO measured the limb emission intensities of forbidden oxygen emission lines in the Martian upper atmosphere. More details of the L2 data product are available in Benna and Elrod (2018) and the data can be accessed from a web link (https://pds-atmospheres.nmsu.edu). We noticed that most of the NGIMS/MAVEN measurements from April to December 2019 were on the night side of the Mars. Due to the MAVEN being on the night side, we do not have NGIMS/MAVEN measured neutral atmospheric densities at the time of NOMAD-TGO dayside observations. During September 2019, observations were on the dayside Martian upper atmosphere for solar zenith angle (SZA) <40$^\circ$ and similar to the NOMAD-TGO observational conditions on 28 April 2019 (SZA = 30$^\circ$) but at different Martian solar longitudes ($L_s$). We plotted neutral density profiles of Fox (2004) along with variability in the NGIMS/MAVEN measured CO$_2$ and O density profiles in Figure 1. The input solar radiation flux, which is a daily-averaged flux generated based upon on the Flare Irradiance Spectra Model-Mars (FISM-M) using the EUV calibrated band irradiance measured by Solar Extreme Ultraviolet Monitor (EUVM) instrument onboard MAVEN and interpolated Earth-based solar indices, in the wavelength region of 5–1900 Å is taken on 28 April 2019 (Eparvier et al., 2015; Thiemann et al., 2017, https://pds-ppi.jgpp.ucla.edu). As a case study, we also calculated the limb intensity profiles for forbidden atomic oxygen emissions for solar maximum condition by considering the neutral atmospheric model from Fox (2004). For this calculation, we used EUVM onboard MAVEN measured solar flux on 12 December 2014 during which Mars was at perihelion.

The input photon and electron impact cross sections are described in Jain (2013). Here we considered the total absorption cross section of CO$_2$ and the yield for the photodissociative excitation of CO$_2$ producing O($^1$S) from Gkouvelis et al. (2018). Based on the discussion of Gkouvelis et al. (2018), we have taken a quantum yield of 0.09 for the dissociative recombination of O$_2^+$ producing O($^1$S). Following the assumptions of Gkouvelis et al. (2018) and Jain (2013), we considered the quantum yields for the thermal recombination of CO$_2^+$ producing O($^1$S) and O($^1$D) as 0.05 and 0.59, respectively. However, we vary these assumed yields to study the impact of dissociative recombination of CO$_2^+$ on the modelled limb intensities. The photochemical reaction network used for calculating various production and loss rates of O($^1$S) and O($^1$D) is presented in Table 1. Electron and neutrals temperature profiles are taken from Fox and Hać (2009) for solar minimum and maximum conditions.

3. Results and Discussion

The modelled production rate and loss frequency profiles of O($^1$S) and O($^1$D) for various photochemical processes in the Martian upper atmosphere are presented in Figure 2. The calculated volume production rate profiles in Figure 2 (a) show that the total O($^1$S) formation rate, which is majorly due to photodissociative excitation of CO$_2$, has a double peak structure with lower and upper peaks at altitudes of 85 and 135 km, respectively. Photodissociative excitation of CO$_2$ by the solar radiation flux at HI Lyman-α wavelength causes the lower production peak, whereas the upper production peak is controlled by the flux mainly in wavelength region 860–1160 Å. The formation rate of O($^1$S) due to other excitation mechanisms is smaller by a factor of 3 or more compared to that from photodissociative excitation of CO$_2$. 

![Figure 1: Neutral density distribution in the Martian upper atmosphere. The density profiles of major species are taken from Fox (2004) for solar minimum condition. Green and yellow shaded areas represent the variability in the NGIMS measured CO$_2$ and O densities during September 2019 for solar zenith angle less than 40$^\circ$](image-url)
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Table 1
Photochemical reactions for the formation and destruction of O(1D) and O(1S) in the Martian upper atmosphere

| No. | Reaction | Rate Coefficient | Reference |
|-----|----------|------------------|-----------|
| R1  | hν + CO₂ → O(1S) + CO | 1.63 × 10⁻⁷     | This work |
| R2  | hν + CO → O(1S) + C | 1.43 × 10⁻⁸     | This work |
| R3  | hν + O₂ → O(1S) + O | 1.28 × 10⁻⁸     | This work |
| R4  | e_th + CO₂ → O(1S) + CO | Calculated | This work |
| R5  | e_th + CO → O(1S) + C | Calculated | This work |
| R6  | e_th + O → O(1S) + O | Calculated | This work |
| R7  | e_th + O → O(1S) + O | Calculated | This work |
| R8  | CO₂ + e_h → O(1S) + CO | 4.2 × 10⁻⁷ (300/T_e)⁰.⁷⁸ | Gkouvelis et al. (2020) |
| R9  | O⁺ + e_h → O(1S) + CO | 1.95 × 10⁻⁷ (300/T_e)⁰.⁷ | Gkouvelis et al. (2020) |
| R10 | hν + CO₂ → O(1D) + CO | 2.72 × 10⁻⁷     | This work |
| R11 | hν + CO → O(1D) + C | 1.43 × 10⁻⁸     | This work |
| R12 | hν + O₂ → O(1D) + O | 6.8 × 10⁻⁷       | This work |
| R13 | e_th + CO₂ → O(1D) + CO | Calculated | This work |
| R14 | e_th + CO → O(1D) + C | Calculated | This work |
| R15 | e_th + O → O(1D) + O | Calculated | This work |
| R16 | e_th + O → e + O | Calculated | This work |
| R17 | CO₂ + e_h → O(1D) + CO | 4.2 × 10⁻⁷ (300/T_e)⁰.⁷⁸ | Viggiano et al. (2005) ² |
| R18 | CO⁺ + e_h → O(1D) + CO | 2.5 × 10⁻⁸ (300/T_e)⁰.⁵⁵ | Rosén et al. (1998) |
| R19 | O⁺ + e_h → O(1D) + O | 2.21 × 10⁻⁷ (300/T_e)⁰.⁴⁶ | Guberman (1988) |
| R20 | O(1S) + e_h → O(1D) + e_th | 8.5 × 10⁻⁹ | Berrington and Burke (1981) |
| R21 | O(1S) + CO₂ → O⁺(P) + CO₂ | 3.21 × 10⁻¹¹ exp(-1323/Tn) | Capetanakis et al. (1993) |
| R22 | O(1S) + CO → O⁺(P) + CO | 7.4 × 10⁻¹⁴ exp(-957/Tn) | Capetanakis et al. (1993) |
| R23 | O(1S) + O₂ → O⁺(P) + O₂ | 2.32 × 10⁻¹² exp(-812/Tn) | Capetanakis et al. (1993) |
| R24 | O(1S) + N₂ → O⁺(P) + N₂ | 5 × 10⁻¹⁰ | Atkinson and Welge (1972) |
| R25 | O(1S) + O(3P) → 2 O⁺(D) | 2 × 10⁻¹⁴ | Krauss and Neumann (1975) |
| R26 | O(1S) + e_h → O⁺(P) + e_h | 7.3 × 10⁻¹³ T_e⁻⁹⁴ | Berrington and Burke (1981) |
| R27 | O(1S) → O⁺(D) + hν₁₆₅₇₇₅ | 1.26 | Wiese et al. (1996) |
| R28 | O(1S) → O⁺(P) + hν₂₉₅₇₂ | 0.075 | Wiese et al. (1996) |
| R29 | O⁺(D) + CO₂ → O⁺(P) + CO₂ | 6.8 × 10⁻¹¹ exp(117/T_e) | Streit et al. (1976) |
| R30 | O⁺(D) + N₂ → O⁺(P) + N₂ | 1.8 × 10⁻¹¹ exp(107/T_e) | Atkinson et al. (1997) |
| R31 | O⁺(D) + CO → O⁺(P) + CO | 1 × 10⁻¹¹ | Schofield (1978) |
| R32 | O⁺(D) + O₂ → O⁺(P) + O₂ | 3.2 × 10⁻¹¹ exp(67/T_e) | Atkinson et al. (1997) |
| R33 | O⁺(D) + O⁺(P) → 2 O⁺(P) | 2.13 × 10⁻¹² + 2.60 × 10⁻¹³ T_e⁻⁵ | Yee et al. (1990) |
| R34 | O⁺(D) → O⁺(P) + hν₆₃₆₅₀ | 6.478 × 10⁻³ | Froese Fischer and Tachiev (2004) |
| R35 | O⁺(D) → O⁺(P) + hν₆₃₆₃₄ | 2.097 × 10⁻³ | Froese Fischer and Tachiev (2004) |
| R36 | O⁺(D) + e_h → O⁺(P) + e_h | 1.6 × 10⁻¹₂ T_e⁻⁹¹ | Berrington and Burke (1981) |

The unattenuated photodissociative excitation frequencies for reactions R1, R2, R3, R10, R11, & R12 are calculated at heliocentric distance of 1.57 AU; * This value is multiplied by 0.05, see Gkouvelis et al. (2020); † This rate coefficient is multiplied with a factor 0.59, see Jain (2013) and the main text; ‡ This rate coefficient is multiplied by a factor 0.09, see Gkouvelis et al. (2020) for more details; hν, e_th, e_h, T_e, and T_n represent solar photon, photoelectron, thermal electron, electron and neutral temperatures, respectively.

Various modelled volume production rate profiles presented in Figure 2 (b) show that the total formation rate of O(1D) is controlled by different excitation sources. The lower volume production peak of O(1D) at altitude of 90 km is mainly due to the photodissociative excitation of CO₂, whereas the upper peak (at an altitude of 130 km) is controlled by photodissociative excitation of CO₂, dissociative recombination of O₂⁺, and radiative decay of O(1S). Electron impact excitation of atomic oxygen and dissociative recombination of O₂⁺ contribute equally to the total O(1D) formation at altitudes above 170 km. Four excitation sources, viz., photodissociative excitation of CO₂, radiative decay of O(1S), electron impact on atomic oxygen, and dissociative recombination of O₂⁺ together produce more than 95% of total O(1D) in the altitude range of 60 to 220 km, whereas the other excitation sources play a minor role in the O(1D) formation. We also determined the relative contributions of these excitation sources to the total formation of O(1D) and found that the photodissociative excitation of CO₂ and radiative decay of O(1S) together produce about 50% of total O(1D) in the
Figure 2: Modeled volume production rate (top panels) and loss frequency profiles (bottom panels) of O(1S) and O(1D) for different photothermal processes in the Martian upper atmosphere for solar zenith angle 30° using EUVM/MAVEN measured solar flux on 28 April 2019.

The altitude range of 130 to 160 km and rest is majorly via electron impact on atomic oxygen and dissociative recombination of O2+. Above 170 km altitude, the electron impact on atomic oxygen and dissociative recombination of O2+ gradually takes over as major production sources of O(1D) (see Figure 2 (b)).

The modelled loss frequency profiles presented in Figure 2 (c) show that radiative decay is the dominant loss mechanism for O(1S) in the Martian upper atmosphere. Owing to a short radiative lifetime (0.75 s), the collisional quenching with Martian neutral species has no impact on total loss frequency of O(1S). As shown in Figure 2 (d), due to the long radiative lifetime (∼120 s), the collisional quenching of O(1D) by CO2 is significant at altitudes up to 190 km, and above this distance radiative decay takes over as the dominant loss mechanism.

By incorporating the previously discussed different production and loss processes, the modelled density and volume emission rate profiles for O(1S) and O(1D) are presented in Figure 3. The calculated density profile for O(1S) has a double peak structure with respective upper and lower peaks at altitudes around 85 and 135 km (see solid green curve in Figure 3). These peaks are mainly due to the formation of O(1S) via photodissociative excitation of CO2 by solar radiation flux in different wavelength regions (see Figure 2 (a)). The modelled O(1D) density profile has a broad peak in the altitude range of 150 to 200 km, which is determined by various production processes and the collisional quenching of O(1D) by CO2 (see solid red curve in Figure 3). This calculation shows that strong collisional quenching of O(1D) substantially reduces its density at altitudes below 150 km. We calculated volume emission rates of these metastable species by multiplying the modelled density profiles with corresponding transition probabilities (see dashed curves in Figure 3). The radiative lifetime of O(1S) is smaller by more than two orders of magnitude compared to that of O(1D), which re-
results in faster spontaneous decay compared to that of O(1D). Our modelled volume emission rates profiles show that radiative decay of O(1D) and O(1S) produce corresponding forbidden oxygen emissions with maximum intensities at altitudes above and below 140 km in the Martian upper atmosphere, respectively.

A comparison between the modelled limb emission intensity profiles and NOMAD-TGO observations for [OI] 2972 and 5577 Å emissions is presented in Figure 4. By decreasing the neutral density profiles of Fox (2004) model by a factor of 2, which we call a standard case, the calculated limb emission intensity profiles for [OI] 2972 and 5577 Å emissions are found to be consistent with NOMAD-TGO observations at altitudes below 150 km (see solid blue and green curves in Figure 4). This agreement suggests that photodissociative excitation of CO\textsubscript{2} is sufficient to explain the NOMAD-TGO observed limb intensities for [OI] 2972 and 5577 Å emissions. At altitudes above 140 km, our modelled limb intensities are decreasing rapidly and smaller by an order of magnitude compared to NOMAD-TGO observation. However, it should be noted that the uncertainties in the NOMAD-TGO measured limb intensities for [OI] 2972 and 5577 Å emissions are larger at altitudes above 140 km compared to those at lower altitudes.

We have considered Fox (2004) modelled neutral density profiles, which are based on the Viking measurements and for solar minimum condition, to calculate the limb intensities of forbidden atomic oxygen emission lines. As shown in Figure 1, the in-situ measured CO\textsubscript{2} and O densities vary about an order of magnitude at altitudes around 200 km. Considering this variability into account, a reduction in the neutral density of Fox (2004) model by a factor of 2 is necessary to explain the observed limb intensity profiles. We compared the Fox (2004) neutral density profiles for solar minimum condition with Mars Climate Database (MCD) modelled neutral densities for NOMAD-TGO observational condition and found that they are nearly consistent. By reducing the neutral density profiles of MCD by a factor of 2, Gérard et al. (2020) also explained the observed emission limb intensity profiles of [OI] 2972 and 5577 Å emissions. Our calculations and Gérard et al. (2020) study showed that the observed limb intensity profiles of forbidden oxygen emission (5577 & 2972 Å) lines can be used to constrain the neutral abundances, particularly CO\textsubscript{2}, in the Martian upper atmosphere.

For our standard case, the modelled intensity profiles of [OI] 5577 and 6300 Å emissions via major production processes are presented in Figure 5. The calculated limb intensity profiles in the left panel of this figure show that most
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of the [OI] 5577 Å emission produces via photodissociative excitation of CO$_2$ in the limb viewing geometry with a contribution more than 80% in the altitude range 60 to 200 km. The remaining significant contributions are from the thermal recombination of O$_2^+$ and electron impact excitation of atomic oxygen and CO$_2$. Thus, the observed limb intensity of this emission can be used to constrain the CO$_2$ density in the upper atmosphere of Mars.

In the case of [OI] 6300 Å emission, for the altitudes below 170 km, we determined that the total limb intensity is controlled by photodissociation of CO$_2$, thermal recombination of O$_2^+$, electron impact on atomic oxygen, and radiative decay of O(1S), with a relative contribution of about 35%, 30%, 10% and 15%, respectively (see the right panel of Figure 5). The remaining 10% of emission intensity is determined by several excitation sources as shown in Figure 2 (b). It can be noticed in this figure that above 170 km altitude, electron impact on atomic oxygen and thermal recombination of O$_2^+$ significantly contribute to the total limb intensity of [OI] 6300 Å emission. In the following section we discuss the role of various parameters which can influence the observed [OI] red-doublet limb intensities in the Martian upper atmosphere.

3.1. Effect of input parameters on the modelled red-doublet limb intensities

The branching ratios for O(1D) radiative decay transitions show that the emission intensity of [OI] 6364 Å line should be about one third that of [OI] 6300 Å (see emission rates for reactions R34 and R35 in Table 1 and Wiese et al., 1996). Hence, we present the calculated limb intensity profile only for [OI] 6300 Å emission and compare its magnitude with those of [OI] 2972 and 5577 Å emissions in Figure 4 (see red curves in this Figure).

The modelled limb intensity profile for [OI] 6300 Å emission, which is calculated for our standard case, has a broad peak in the altitude range of 120 to 170 km and comparable with the upper limit of [OI] 2972 Å observation (see solid red curve in Figure 4). At altitudes below 120 km, the modelled limb intensity of [OI] 6300 Å emission is smaller by a factor of 2 to 5 compared to that of NOMAD-TGO observation for [OI] 2972 Å emission (see solid red and magenta curves in Figure 4). This calculation shows that the modelled limb intensity for [OI] 6300 Å emission is significant compared to that of [OI] 2972 Å and should be observable in NOMAG-TGO dayside spectra taken in the altitude region of 120 to 170 km, provided sufficient signal-to-noise ratio in the measurement during the observation period.

As pointed out by Huestis and Slanger (2006), the photodissociative cross section of CO$_2$ producing O(1D) was not experimentally determined before. But there are several recent developments in measuring the cross section for this excitation processes (Sutradhar et al., 2017; Lu et al., 2015; Song et al., 2014; Gao and Ng, 2019). However, these measured cross sections are limited to a small wavelength range from threshold to 1000 Å. Recently, Raghuram et al. (2020) modelled atomic oxygen green and red-doublet emissions in CO-dominated and water-poor comet C/2016 R2 (Pan-STARRS). By accounting for various photochemical processes, it was found that both green and red-doublet atomic
oxygen emissions are controlled by photodissociative excitation of CO$_2$ in the cometary coma of this comet. They also showed that the uncertainties associated with the photon cross section of CO$_2$ producing O($^1$D) play an important role in determining the observed atomic oxygen green to red-doublet emission intensity ratio in comet C/2016 R2 (Pan-STARRS). By comparing the modelled and observed atomic oxygen green to red-doublet emission intensity ratios, Raghuram et al. (2020) suggested that the photodissociative excitation cross section of CO$_2$ producing O($^1$D) should be increased by a factor of 3. Considering the uncertainty associated with this excitation process, when we increase the cross section for photodissociative excitation of CO$_2$ by a factor of 3, the modelled total [OI] 6300 Å limb intensity is found to be 60% higher compared to that of our standard case. This calculation suggests that the role of uncertainty associated with photodissociative excitation of CO$_2$ lead to higher [OI] red-doublet limb intensities than our standard case. 

Due to lack of experimentally determined value, following the assumption of Jain (2013), we incorporated branching ratio for dissociative recombination of CO$_2^+$ producing O($^1$D) as 0.59. Our calculations in Figure 2 (b) show that the dissociative recombination of CO$_2^+$ plays a minor role in the total production of O($^1$D). Even with the assumed higher branching ratio, we find that this excitation process contributes little (<10%) to the total formation of O($^1$D) when compared to that from other excitation sources in the Martian upper atmosphere. Hence, our assumed branching ratio has no impact on the modelled [OI] red-doublet limb intensities. Similarly, considering branching ratio from Gkouvelis et al. (2018) for dissociative recombination of CO$_2^+$, our modelled production rate of O($^1$S) is smaller by an order of magnitude or more compared to that from photodissociation of CO$_2$. Thus, the assumed branching ratio for dissociative recombination of CO$_2^+$ has no impact on the modelled [OI] 2972 and 5577 Å limb intensities.

Collisional quenching of O($^1$D) has an important role in determining the limb intensities of [OI] red-doublet emissions in the Martian upper atmosphere. By comparing the modelled total production rate and loss frequency profiles in Figure 2 we can understand that though O($^1$D) is produced by an order magnitude higher than that of O($^1$S) for the altitudes below 140 km, the strong collisional quenching by CO$_2$ substantially reduces its density at lower altitudes (see Figure 3). We evaluated that about 30% of the total O($^1$D) production is due to photodissociative excitation of CO$_2$ at altitudes above 140 km, and remaining is due to other excitation sources. Hence, larger amount of CO$_2$ significantly leads to strong collisional quenching of O($^1$D) rather than its production. But it should be noted that the large amount CO$_2$ density in the Martian upper atmosphere also leads to an increase in the [OI] 2972 and 5577 Å limb emission intensities. The compilation of various experimentally determined O($^1$D) quenching rates by Burkholder et al. (2015) and recent measurements by Nuñez-Reyes and Hickson (2018) showed that the uncertainty in measuring the rate coefficient of collisional reaction between CO$_2$ and O($^1$D) is only about 20%, which suggests larger quenching of O($^1$D) in the Martian upper atmosphere is unlikely.

As discussed earlier, at altitudes above 170 km, the contribution from dissociative recombination of O$_2^+$ and electron impact excitation of atomic oxygen is significant to the total formation of O($^1$D) (see Figure 2 and also the right panel of Figure 5). The formation of O$_2^+$ ion is mainly due the collisions between CO$_2^+$ and atomic oxygen. Hence, the change in neutral density profile of atomic oxygen can influence O$_2^+$ ion density and also total volume production of O($^1$D) in the Martian upper atmosphere. As shown in Figure 1, the NGIMS/MAVEN measured atomic oxygen and CO$_2$ densities during September 2019 are varying by an order of magnitude at altitudes above 170 km. Using NGIMS/MAVEN measurements, we find that the measured volume mixing ratios of O/CO$_2$ are smaller by a factor of 2 to 10 compared to that of Fox (2004) in the altitude range of 150 to 200 km. Considering the variability in NGIMS/MAVEN measured densities into account, we decreased the Fox (2004) atomic oxygen density by an order of magnitude to study its impact on the modelled [OI] 6300 Å limb intensity. By decreasing the atomic oxygen density, we found that the modelled [OI] 6300 Å limb intensity is smaller by maximum factor of 2 compared to our standard case (see dashed red-curve in Figure 4). In this case, the contributions from both electron impact on atomic oxygen and thermal recombination of O$_2^+$ to the total O($^1$D) production significantly decrease in the altitude range 60 to 200 km, whereas the radiative decay of O($^1$S) and photodissociation of CO$_2$ majorly produce O($^1$D) and cause the [OI] red-doublet emissions (see the right panel of Figure 5). This calculation shows that the variation in atomic oxygen density in the Martian upper atmosphere can lead to a significant change in the observed limb intensities of [OI] red-doublet emissions.
The NGIMS/MAVEN measurements in the altitude range of 150 to 200 km shows that the CO₂ and O densities can vary by an order magnitude and are also smaller than those of Fox (2004) model (see Figure 1). When we scaled the neutral densities of Fox (2004) model to the lower limit of NGIMS/MAVEN measurements, the calculated limb intensity for [OI] 6300 Å is closer to our standard case at altitudes below 120 km. This calculation shows that in spite of lower neutral densities than those of Fox (2004), the observed [OI] 6300 Å is not expected to change significantly compared to our standard case at altitudes below 120 km. Thus, the modelled limb intensity profile of [OI] 6300 Å for our standard case serves as an upper limit during NOMAD-TGO observation period.

The thermal structure of Martian upper atmosphere also plays an important role in determining the neutral densities and subsequently the emission intensities of forbidden atomic oxygen emission lines. During solar active condition, the densities of atomic oxygen and CO₂ increase in the upper atmosphere of Mars. We noticed in our calculations that the larger volume mixing ratio of atomic oxygen leads to higher limb intensities of [OI] 2972 and 5577 Å emissions only for altitudes above 150 km. But when we increase the atomic oxygen density in the model, the calculated limb intensity for [OI] 6300 Å emission also increased in the altitude range of 60 to 200 km. Hence, for higher thermospheric temperature all these emission lines are expected to be observed in the NOMAG-TGO dayside spectra. However, it should be noted that the NOMAD-TGO observations were carried out on Mars for solar longitudes between 16° and 115° when it was crossing the aphelion and the solar activity during this period was also low. Thus, larger neutral densities are not expected in the Martian upper atmosphere during NOMAD-TGO observation period.

During the NOMAD-TGO observation period, the background intensity level around wavelength 6300 Å is equivalent to more than 10 kR. Moreover, the [OI] red-doublet emission lines are closer to the longer wavelength limit of the NOMAD-TGO instrument and the detector has a reduced sensitivity in this region, which is the main reason for the absence of these emissions in the observed dayside spectra (personal communication, Gérard et al., 2020). Furthermore, most of the NOMAD-TGO observations took place when Mars was moving away from the Sun. But when Mars reaches perihelion, due to proximity of the Sun, the neutral densities of Martian upper atmosphere increases due to large thermospheric temperature. We evaluated the limb intensity of [OI] 6300 Å emission during high solar activity and when Mars is at perihelion. For this case, we accounted for neutral atmosphere from Fox (2004) for solar maximum condition and used the EUVM/MAVEN measured solar flux on 12 December 2014 (during which Mars was at perihelion and solar activity was also high, F₁₀,7 = 152 × 10⁻²² W m⁻² Hz⁻¹). We find that the modelled limb intensity [OI] 6300 Å emission is higher by a more than a factor of 3 than our standard case (see dash double-dotted red curve in Figure 4). In this case, the modelled [OI] 6300 Å peak emission limb intensity is about 30 kR at altitudes above 140 km and this emission line would have be seen in NOMAD-TGO spectra, provided that the background intensity is smaller compared to the modelled limb emission intensity. Thus, we suggest that the simultaneous detection of [OI] red-doublet emission along with other atomic forbidden emissions on the dayside Martian upper atmosphere by NOMAD-TGO would be possible when Mars is at perihelion.

Our calculations showed that there are a few parameters which determine the limb intensities of [OI] red-doublet emissions in the Martian upper atmosphere. In spite of variability in the neutral densities in the Martian upper atmosphere, we find that the modelled limb intensity of [OI] 6300 Å emission should be smaller than that of [OI] 2972 Å emission by a factor of 2 to 5 at altitudes below 120 km and it is higher above this altitude (see Figure 4). NOMAD-TGO should be able to detect these emissions in the dayside spectra provided sufficient signal-to-noise ratio during the observation. Instrument sensitivity coupled with uncertainties in the neutral atmosphere (given the large variability in atomic oxygen and CO₂ as shown Figure 1) may explain the absence of [OI] red-doublet emission lines in the dayside spectra taken during NOMAD-TGO observation period. However, when Mars gets closer to the Sun, the seasonal and solar cycle variations significantly affect the neutral densities of Martian upper atmosphere and result in the [OI] 6300 Å limb emission intensity within the observation limit of NOMAD-TGO. More simultaneous observations of forbidden atomic oxygen emissions are required to study the photochemistry of these emissions in the Martian upper atmosphere.

4. Summary and Conclusions

Recently, Nadir and Occultation for Mars Discovery ultraviolet and visible spectrometer instrument on board the European Space Agency’s ExoMars Trace Gas Orbiter made
simultaneous detection of forbidden atomic oxygen emissions at wavelengths 2972 and 5577 Å in the spectra observed between 24 April and 1 December 2019 on the dayside Martian upper atmosphere. Thanks to the wide detection wavelength range of this instrument, it can measure the limb emission intensities of four forbidden atomic oxygen emissions at wavelengths 2972, 5577, 6300, and 6364 Å simultaneously. Since both [OI] 2972 and 5577 Å emissions originate from the same excited state of atomic oxygen, detection of any one of these emissions confirms the presence of other. Similarly, detection of [OI] 5577 Å emission line also indicates the presence of [OI] red-doublet emissions at wavelengths 6300 and 6364 Å, but the opposite is not true. However, these [OI] red-doublet emissions were not observed in the visible spectra taken during the NOMAD-TGO observation period due to the reduced sensitivity of the detector. By accounting for the important chemical pathways of O(1S) and O(1D), which are the excited states of these forbidden atomic oxygen emissions, we developed a model to study the photochemistry of these forbidden emissions in the Martian upper atmosphere and aimed to explore the suitable conditions to observe [OI] red-doublet emissions along with other atomic oxygen forbidden emissions. Our calculations show that NOMAD-TGO observed limb intensities for [OI] 2972 and 5577 Å emissions are mainly controlled by photodissociative excitation of CO2. On reducing neutral density profiles of Fox (2004) model for solar minimum condition by a factor of 2, our modelled limb intensities of [OI] 2972 and 5577 Å emissions are found to be in agreement with NOMAD-TGO observations.

We studied the role of different parameters which can influence the observation of [OI] red-doublet emissions in the dayside Martian upper atmosphere. The limb emission intensities of these emissions are found to be controlled by photodissociative excitation of CO2, radiative decay of O(1S), dissociative recombination of O2+, and electron impact on atomic oxygen. Our modelled limb intensity profile of [OI] 6300 Å emission is comparable and higher than that of NOMAD-TGO observation for [OI] 2972 Å emission in the altitude range of 60 to 200 km. We find that the peak limb emission intensity for [OI] 6300 Å emission occurs at altitudes above 120 km and higher than the upper limit of NOMAD-TGO observation for [OI] 2972 Å emission. But at altitudes below 120 km, the modelled limb intensity for [OI] 6300 Å emission is smaller by a factor of 2 to 5 compared to that of NOMAD-TGO observation for [OI] 2972 Å emission. Hence, [OI] 6300 Å emission line is expected to be observed in the dayside spectra of NOMAD-TGO at altitudes above 140 km provided that the signal-to-noise ratio is sufficient during the observation period. Due to the reduced detector sensitivity around the wavelength 6300 Å, NOMAD-TGO could not observe the [OI] red-doublet emission lines in the dayside of Mars. Moreover, most of the NOMAD-TGO observations took place when the Mars was travelling away from the Sun (LS is varying from 16° to 115°), during which the neutral densities in the Martian upper atmosphere are smaller compared to those at near perihelion. Based on our modelling we suggest that all these atomic forbidden emissions should be observable in the dayside NOMAD-TGO spectra taken over the southern hemisphere, when Mars is at perihelion. More simultaneous observations of forbidden atomic oxygen emission lines are required to study the photochemistry of Martian upper atmosphere.

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Data Availability

This paper make use of NGIMS/MAVEN measured neutral and ion number densities L2 data which has been accessed through the web link (https://pds-atmospheres.nmsu.edu) The modelled data in this research will be shared on reasonable request to the corresponding author.

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