Model for Nitric oxide and its dayglow emission in the Martian upper atmosphere using NGIMS/MAVEN measured neutral and ion densities

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1. Introduction

Many in-situ and remote observations along with theoretical studies were carried out to understand the composition and energetics of the Martian upper atmosphere (Nier and McElroy, 1977; Krasnopolsky, 1993; Bertaux et al., 2005b; Withers, 2006; González-Galindo et al., 2009; Bouger et al., 2015a; Mahaffy et al., 2015; Bhardwaj et al., 2016, 2017). However, the study of minor neutrals in Martian upper atmosphere is still sparse due to lack of several key chemical reaction parameters and insufficient measurements from remote and in-situ observations. Nitric oxide (hereafter NO) is a minor species and its density in the dayside of Martian upper atmosphere is not well constrained. Several studies have shown that though the abundance of this species is in parts per million by volume in the thermosphere of Earth, but can play a significant role in driving the chemistry and thermal balance of the upper atmosphere (Barth, 1964; Norton and Barth, 1970; Eparvier and Barth, 1992; Barth et al., 2003; Bharti et al., 2019). Due to its lowest ionization potential (9.26 eV) compared to any other atmospheric species, NO quickly does exchange the charge with O$_2^+$ and causes NO$^+$ as the dominant ion at the lower altitudes around 80 km in the Martian ionosphere (Fox, 2004). Hence, this species plays a significant role in the thermospheric energy budget and also in determining the ionospheric composition in the Martian atmosphere. But the study of NO global distribution and its role in the energy budget of Martian thermosphere is limited due to the lack of adequate in-situ and remote observations.

The global distribution of NO in the Martian upper atmosphere can be studied from the remote observations of its $\gamma$ band emissions in the ultraviolet region. But the observation of these band emissions and the derivation of NO density in sunlit Martian upper atmosphere is challenging due to the presence of intense CO Cameron bands in the same emitting wavelength region. Spectroscopy for the Investigation of the Characteristics of the Atmosphere of Mars (SPICAM) experiment on-board Mars Express (MEx) spacecraft (SPICAM/MEx) and Imaging Ultraviolet Spectrograph (IUVS) onboard MAVEN observations and also with other modelling studies. We found that the local CO$_2$ and N$_2$ density variations can lead to a change in NO density and consequently its dayglow intensity by a factor of 2 to 5. Since NO is a trace constituent and also its dayglow emissions are strongly obscured by CO Cameron band emissions, we suggest that the derivation of NO number density based on our approach can constrain its abundance in the dayside upper atmosphere of Mars. More observations of (1-0) $\gamma$ band emission along with modelling will help to study the global distribution of NO in the Martian atmosphere.
Regarding in-situ measurements, Upper Atmosphere Mass Spectrometer (UAMS) instruments on-board Viking 1 and 2 landers made first-ever in-situ NO number density measurements in the dayside Martian upper atmosphere on 20 July 1976 (solar longitude, Ls = 97°) and 3 September 1976 (Ls = 118°), respectively, at three to four different altitudes between 110 and 150 km. (McElroy et al., 1976; Nier and McElroy, 1977). By accounting for the important photochemical reaction network, Fox (1993) modelled NO number density and found that their calculated density is smaller by a factor of 2–3 compared to the Viking measurement at an altitude around 115 km. The reason for the discrepancy between the Fox (1993) modelled and Viking observed NO densities has not been understood and remained as a long-standing issue due to the lack of adequate measurements. After nearly four decades, since the Viking landers experiments, the Neutral Gas and Ion Mass Spectrometer (NGIMS) on-board MAVEN mission (NGIMS/MAVEN) measured NO number densities in the Martian upper atmosphere (Mahaffy et al., 2015; Vogt et al., 2017). However, the NGIMS/MAVEN measured NO densities are an order of magnitude higher than those predicted by earlier theoretical models. As pointed by Stevens et al. (2019), the contamination in the measurement, which arises due to the recombination of atomic nitrogen and atomic oxygen within the instrument, could be a reason for the higher reported NO densities.

As discussed before, there are several constraints to study NO number density in the dayside Martian upper atmosphere for the both in-situ (Viking 1, 2, and NGIMS/MAVEN) and remote (SPICAM/MEx and IUVS/MAVEN) observations. In this paper, we present an approach of calculating the NO number density in the dayside Martian upper atmosphere by incorporating NGIMS/MAVEN measured neutral (CO₂, N₂, and O) and ion (NO⁺, O₂⁺ and CO₂⁺) number densities in the photochemical network. We show that our approach can be used to constrain the NO density in the altitude range between 120 and 200 km based on the MAVEN measurements during deep dip 8 and 9 campaigns. We have also calculated dayside NO (1-0) γ limb intensity profiles from our modelled NO densities and compared them with the IUVS/MAVEN observations. The methodology adopted in this work is explained in Section 2. The results obtained analysis are presented in Section 3. We have discussed various factors which can influence our modelled NO density profiles in Section 4. This work has been summarized and conclusions are drawn in Section 5.

2. Methodology

The neutral and ion number densities are taken from the dayside NGIMS/MAVEN inbound measurements for SZA smaller than 60° during deep dip 8 and 9 campaigns. To extract the neutral and ion density profiles, we utilized level 2 data (L2), version 7 (8), revision 3 (1) data for deep dip 8 (9) campaign. Additional 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 chose only those orbits of MAVEN deep dip 8 and 9 campaigns where both neutral and ion densities are measured. The obtained densities are interpolated over a uniform grid of 1 km from MAVEN’s periapsis altitude to 200 km. Table 1 summarizes the MAVEN observational conditions, such as observation period, orbit numbers, Ls, and the variation in SZA and latitude during orbits, during deep dip 8 and 9 campaigns.

The chemical network considered in this work is based on the compilation of Fox and Sung (2001) with updated rate coefficients from McElroy et al. (2013). These chemical reactions are tabulated in Table 2. The electron temperature, which determines the dissociative recombination rate of ions, is taken from Ergun et al. (2015). Using the Analytical yield spectrum (AYS) approach, we calculated the suprathermal electron flux and electron impact dissociation rate of N₂ in the Martian upper atmosphere. More details of degradation of solar flux and the calculation of suprathermal electron flux using AYS method can be found in our earlier work (Bhardwaj et al., 1990; Bhardwaj et al., 1996; Bhardwaj, 1999; Jain and Bhardwaj, 2011; Jain and Bhardwaj, 2012; Bhardwaj and Jain, 2013; Raghuram and Bhardwaj, 2020). By assuming photochemical equilibrium condition and accounting for various production and loss mechanisms, we determined the NO, N(⁴S) and N(⁵D) number densities for the altitudes between 120 and 200 km. The effect of transport in calculating the number densities of these species is discussed in Section 4.

We have taken the fluorescence efficiency (g-factor) for NO (1,0) γ band emission as 2.68 × 10⁻⁶ photons s⁻¹ molecule⁻¹ and all the photorates are scaled to heliocentric distance of 1.57 AU (Stevens et al., 2019). The Volume Emission Rate (VER), which is the number of photons scattered per unit volume per unit time, is calculated by multiplying the modelled NO number density with the g-factor. The limb emission intensity of this band is obtained by integrating the volume emission rate along the line of sight and converted into brightness in Rayleigh (1 Rayleigh = 10⁶/4π photons cm⁻² sec⁻¹ sr⁻¹) using the following equation.

\[
I = 2 \times 10^{-6} \int_{0}^{\infty} V E R(r) \, dr
\]
3. Results

The NGIMS/MAVEN measured neutral and ions densities profiles for orbit #5947 of deep dip 8 campaign are presented in Figure 1. In this Figure, we compared the NGIMS/MAVEN measured CO$_2$, N$_2$, and O density profiles with Fox (2004) modelled density profiles, which are constructed based on the Viking observations for solar minimum condition. It can be noticed in this figure that Fox (2004) modelled neutral density profiles are higher by a factor of 2 to 4 compared to NGIMS/MAVEN measured values.

Using the NGIMS/MAVEN measurements for orbit #5947, the modelled production and loss profiles of N($^4$S), N($^2$D), and NO are presented in the top and bottom panels of Figure 2, respectively. The calculated production rate profiles in the top panels of this Figure show that photodissociation of N$_2$ is the major source of N($^4$S) and N($^2$D) production, whereas the collisional reaction between N($^2$D) and CO$_2$ leads to the formation of NO. For the altitudes above 180 km, radiative decay of N($^2$D) also contributes significantly to the total formation of N($^4$S), whereas the collisional reaction between CO$_2^+$ and N($^4$S) is also an important source mechanism in the total NO formation. It can be noticed in this Figure that the role of other chemical processes is small in the formation of N($^4$S), N($^2$D) and NO when compared to previously discussed major production mechanisms.

The modelled loss frequency profiles in the bottom panels of Figure 2 show that for the altitudes below 160 km, the total loss of N($^4$S) is mainly due to the collisions with NO, and above this distance it is removed by the collisions of O$_2^+$ in the Martian upper atmosphere. The loss frequency of N($^4$S) by CO$_2$ collision is smaller by an order of magnitude or more compared to that of the previously discussed loss mechanisms which is due to small collisional rate coefficient (more than five order of magnitude smaller, see reactions R7, R8, and R10 in Table 2). For the altitudes below 180 km, the total loss of N($^2$D) is mainly due to the collisions with CO$_2$, which leads to the formation of NO, and above this altitude the radiative decay is the dominant loss mechanism that causes N($^2$S) formation. The loss of NO is mainly due to the collisions with N($^2$S) which leads to the formation of N$_2$. Several other reactions are also involved in the loss of these species but their contribution to the total loss frequency is small.

The modelled number density profiles of N($^4$S), N($^2$D) and NO for orbit #5947 of MAVEN deep dip 8 campaign are presented in Figure 3. Our modelled NO and N($^4$S) density profiles are lower and higher by a factor of 2 to 3, respectively, compared those of Fox (2004). Our modelled N($^2$D) density profile is closer to Fox (2004) calculated value for the altitude above 130 km. The reason for differences between these density profiles is discussed in Section 4.

We have employed the same approach in calculating the NO number density profiles for all the orbits of MAVEN deep dip 8 and 9 campaigns. Using the NGIMS/MAVEN measured neutral and ion number density for the orbits of deep dip 8 campaign (#5909 to #5947) and accounting for the previously discussed photochemical network of reactions, the modelled NO number density profiles are presented in Figure 4. We find that our modelled NO number density is varying over different orbits and this is mainly associated with the variability in the NGIMS/MAVEN measured neutral and ions density measurements. The variation in the calculated NO number density for different orbits is found to be small (by a factor of 2) at lower altitudes (around 120 km) and it is increasing with altitude (more than a factor of 2, see the gray shaded area in Figure 4). The calculated NO number density profiles for all the 32 orbits, i.e., from #6936 to #6973, of MAVEN deep dip 9 campaign are presented in Figure 5. In this case, the calculated NO density around 120 km altitude is about 10$^6$ cm$^{-3}$ and comparable to the derived value for the deep dip 8 campaign.

In Figure 6, we compared the calculated NO number density profiles during MAVEN deep dip 8 and 9 campaigns with IUVS/MAVEN retrieved value. The modelled average NO number density profile for deep dip 8 campaign is consistent with the IUVS/MAVEN retrieved value at around 125 km altitude. Stevens et al. (2019) modelled NO density profiles in the altitude range 80 and 160 km at SZA 44$^\circ$ and 75$^\circ$ for IUVS and Viking observational conditions, respectively (see dashed red and blue curves in Figure 6). Our modelled NO number density profiles are also consistent with the
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| No. | Reaction | Rate coefficient \( \text{\( \text{cm}^2\text{s}^{-1}\) or sec}^{-1} \) | Reference |
|-----|----------|---------------------------------|------------|
| R1 | \( \text{N}^{(2)}\text{D} + \text{CO}_2 \rightarrow \text{NO} + \text{CO} \) | \( 3.6 \times 10^{-15} \) | Herron (1999) |
| R2 | \( \text{N}^{(2)}\text{D} + \text{O} \rightarrow \text{N}^{(5)}\text{S} + \text{O} \) | \( 6.9 \times 10^{-13} \) | Fell et al. (1990) |
| R3 | \( \text{N}^{(2)}\text{D} + \text{N}_2 \rightarrow \text{N}^{(5)}\text{S} + \text{N}_2 \) | \( 1.7 \times 10^{-14} \) | Herron (1999) |
| R4 | \( \text{N}^{(2)}\text{D} + \text{NO} \rightarrow \text{N}^{(5)}\text{S} + \text{NO} \) | \( 6.7 \times 10^{-11} \) | Fell et al. (1990) |
| R5 | \( \text{N}^{(2)}\text{D} + \text{O}_2^+ \rightarrow \text{NO}^+ + \text{O} \) | \( 1.8 \times 10^{-10} \) | Goldan et al. (1966) |
| R6 | \( \text{N}^{(2)}\text{D} + \text{e}_{\text{ph}} \rightarrow \text{N}^{(5)}\text{S} + \text{O} \) | \( 3.86 \times 10^{-10} \left( T_e/300 \right)^{0.81} \) | Berrington and Burke (1981) |
| R7 | \( \text{N}^{(2)}\text{S} + \text{CO} \rightarrow \text{NO} + \text{CO} \) | \( 1.7 \times 10^{-16} \) | Fox and Sung (2001) |
| R8 | \( \text{N}^{(4)}\text{S} + \text{NO} \rightarrow \text{N}_2 + \text{O} \) | \( 3.38 \times 10^{-11} \left( 300/T_e \right)^{0.17} \text{exp}(-2.8/T_e) \) | McElroy et al. (2013) |
| R9 | \( \text{N}^{(4)}\text{S} + \text{CO}_2 \rightarrow \text{NO} + \text{CO}^+ \) | \( 3.4 \times 10^{-10} \) | Scott et al. (1998) |
| R10 | \( \text{N}^{(2)}\text{O} + \text{O}_2^+ \rightarrow \text{NO}^+ + \text{O} \) | \( 1.8 \times 10^{-10} \) | McElroy et al. (2013) |
| R11 | \( \text{NO}^+ + \text{e}_{\text{ph}} \rightarrow \text{N}^{(5)}\text{S} + \text{O} \) | \( 0.60 \times 10^{-17} \left( 300/T_e \right)^{0.5} \) | Vejby-Christensen et al. (1998) |
| R12 | \( \text{NO}^+ + \text{e}_{\text{ph}} \rightarrow \text{N}^{(2)}\text{D} + \text{O} \) | \( 3.4 \times 10^{-17} \left( 300/T_e \right)^{0.5} \) | Vejby-Christensen et al. (1998) |
| R13 | \( \text{NO} + \text{CO}_2^+ \rightarrow \text{NO}^+ + \text{CO}_2 \) | \( 1.2 \times 10^{-10} \) | McElroy et al. (2013) |
| R14 | \( \text{NO} + \text{O}_2^+ \rightarrow \text{NO}^+ + \text{O}_2 \) | \( 4.6 \times 10^{-10} \) | McElroy et al. (2013) |
| R15 | \( \text{N}_2 + \text{hv} \rightarrow \text{N}^{(5)}\text{S} + \text{N}^{(5)}\text{S} \) | Calculated | This work |
| R16 | \( \text{N}_2 + \text{hv} \rightarrow \text{N}^{(2)}\text{D} + \text{N}^{(5)}\text{S} \) | Calculated | This work |
| R17 | \( \text{N}_2 + \text{e}_{\text{ph}} \rightarrow \text{N}^{(5)}\text{S} + \text{N}^{(5)}\text{S} \) | Calculated | This work |
| R18 | \( \text{N}_2 + \text{e}_{\text{ph}} \rightarrow \text{N}^{(2)}\text{D} + \text{N}^{(5)}\text{S} \) | Calculated | This work |
| R19 | \( \text{N}_2 + \text{O}_2^+ \rightarrow \text{NO}^+ + \text{NO} \) | \( 2.0 \times 10^{-18} \) | Matsuoka et al. (1981) |
| R20 | \( \text{N}^{(2)}\text{D} \rightarrow \text{N}^{(4)}\text{S} + \text{hv} \) | \( 2.78 \times 10^{-5} \) | Tachiev and Froese Fischer (2002) |

\( \text{hv} \) is photon, \( \text{e}_{\text{ph}} \) is photoelectron and \( \text{e}_{\text{th}} \) is thermal electron; \( T_n \) and \( T_e \) are neutral and electron temperatures, respectively.

Stevens et al. (2019) modelled profiles in the altitude range 120 to 160 km.

Our calculations in Figure 2 show that \( \text{N}_2 \) and \( \text{CO}_2 \) play a crucial role in determining the NO density in the Martian upper atmosphere. Hence, we studied the variation in our modelled NO density with respect to the changes in MAVEN measured \( \text{CO}_2 \) and \( \text{N}_2 \) densities. It can be noticed in Figure 7 that both the \( \text{CO}_2 \) and \( \text{N}_2 \) densities locally vary about a factor of 2 to 5 during deep dip 8 and 9 campaigns in the altitude range 120 to 200 km (see the shaded areas in figure 7). Due to significant variability in the measured densities, it is difficult to describe the impact of \( \text{CO}_2 \) and \( \text{N}_2 \) on NO for each orbit of both deep dip 8 and 9 campaigns. Hence, we chose two orbits for each campaign to demonstrate the impact of MAVEN measurements on the modelled NO density. As shown in the top panel of Figure 7, the MAVEN measured \( \text{CO}_2 \) and \( \text{N}_2 \) densities for orbit #5943 are higher compared to those for #5947 at the altitudes below 165 km and above this radial distance it is opposite. This cross over in the measured \( \text{CO}_2 \) and \( \text{N}_2 \) density profiles is also reflected in our modelled NO profiles for the corresponding orbits at 165 km altitude (see solid and dashed purple lines in the top panel of Figure 7). Similarly, as shown in the bottom panel of this figure, the MAVEN measured \( \text{CO}_2 \) and \( \text{N}_2 \) densities for orbits #6937 are higher compared to those for #6949 for deep dip 9 campaign in the altitude range 120 to 200 km. The higher densities of \( \text{CO}_2 \) and \( \text{N}_2 \) lead to larger production of NO which is reflected in the modelled NO density for orbit #6937. These calculations suggest that the change in \( \text{CO}_2 \) and \( \text{N}_2 \) densities directly can influence the NO density in the Martian upper atmosphere.

By utilizing the corresponding modelled NO number densities, the calculated limb intensity profiles for NO (1,0) \( \gamma \) band for the MAVEN deep dip 8 and 9 campaigns are presented in Figures 8 and 9, respectively. The calculated NO (1,0) \( \gamma \) band limb intensity is found to vary between 90 and 200 R (between 100 and 300 R) at the MAVEN periapsis altitude around 120 km during MAVEN deep dip 8 (9) campaign. We compared our calculated NO (1, 0) \( \gamma \) limb intensity profiles with and IUVS/MAVEN observation in Figure 10. Our calculated mean limb intensities for deep dip 8 and 9 campaigns around 120 km altitude are found to be consistent with the IUVS/MAVEN observation.

4. Discussion

During the deep dip campaigns, NGIMS/MAVEN measured both neutral and ion densities at the altitudes as low as 125 km, whereas the regular measurements cover the altitudes above 150 km. This possibility enabled us to calculate NO number density at the lower altitudes which is not possible for other measurements. Out of the total nine MAVEN deep dip campaigns so far, deep dip 2, 8, and 9 campaigns are occurred on the dayside. Recently, Cui et al. (2020) also used the NGIMS neutral and ion density measurements to constrain the NO density in the dayside Martian upper atmosphere, specifically for the deep dip 2 campaign during 17-22 April 2015 with a periapsis altitude of 130 km and appropriate for the subsolar condition. By neglecting transport, these authors carried out time-dependent calculations at a fixed altitude of 160 km to investigate the diurnal variation under the influences of both dayside solar radiation and
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![Figure 2: Various modelled formation (top panels) and destruction (bottom panels) processes for N(4S), N(2D) and NO in the Martian upper atmosphere for orbit #5947 during MAVEN deep dip 8 campaign. hv, e
ph, and e
th represent the solar photon, photoelectron, and thermal electron, respectively. Production rate of NO via N2 and O2+ is plotted after multiplying by a factor of 10^5. The reaction profile CO2 and NO, which is a loss frequency profile of NO, is plotted after multiplying by a factor of 10.](image)

The present study has several advances over Cui et al. (2020) in that (1) our calculations are made over a broad altitude range of 120 - 200 km to provide the vertical distribution of NO for deep dip 8 and 9 campaigns; (2) we emphasize the dayside variability in NO density driven by the variability of the background atmosphere, especially in terms of the CO2 and N2 densities, rather than the mean diurnal variability focused by Cui et al. (2020); (3) we also estimate the NO (1,0) gamma band emission such that our results could be directly compared to the MAVEN IUVS limb observations. By comparing our modelled NO density profiles with Cui et al. (2020) calculations, we find that our calculated densities are smaller by a factor 2 to 3. This difference could be due to the different prevailing conditions in the Martian upper atmosphere during deep dip 2, 8 and 9 campaigns. Moreover, Cui et al. (2020) account for local time variability of neutral species in their calculations which is not the case in this work.

The calculations presented in Figure 2 show that the odd nitrogen species, which are primarily produced from the photodissociation of N2, initiate the formation of NO via collisions with CO2, and further interaction of these species with NO subsequently recycles the N2 in the Martian upper atmosphere (see chemical reactions R1, R8, R15 and R16 in Table 2). So it should be noticed that besides variation in CO2 and N2 densities, the NO density in the Martian upper atmosphere depends significantly on chemical reactions particularly R1 and R8, which are respective major production and loss channels initiated by photodissociation of N2. However, the calculations presented in figure 2 suggest that the NGIMS/MAVEN measured major neutral and ion densities (CO2, N2, and O2+) along with a few major chemical reactions are sufficient to determine the NO density in the altitude range 120 to 200 km, rather than using a complex chemical network.

The difference between our calculated odd nitrogen species density profiles and Fox (2004) modelled values, which is about a factor of 2 to 5, is mainly due to the change in input CO2 and N2 densities (see Figures 1 and 3). But our modelled NO density profile in the altitude range 120 to 200 km is closer to the Fox (2004) calculation (with a factor of 2 difference), which suggests that NO is strongly controlled by photochemical reactions rather than transport in the upper atmosphere. Time scales of odd nitrogen
Nitric oxide in the dayside of Martian upper atmosphere

Figure 3: Modelled N(4S), N(2D), and NO densities in the Martian upper atmosphere for orbit #5947 of MAVEN deep dip 8 campaign. The dashed curves with corresponding colours represent the modelled density profiles from Fox (2004) for solar minimum condition.

species as determined by Cui et al. (2020) also suggest that NO is under photochemical equilibrium for the altitudes up to 180 km and above which chemical diffusion significantly controls its density (see Fig. 1d in Cui et al., 2020). Moreover, the agreement between our calculated NO densities for different orbits of deep dip 8 and 9 campaigns with the Stevens et al. (2019) modelled values for IUVS/MAVEN observation condition in the altitude range 120 to 160 km also supports our approach that NO can be derived from the NGIMS/MAVEN measured CO₂ and N₂ densities and also by considering the major photochemical reactions (see Figure 6).

NO density in the Martian upper atmosphere is significantly driven by photochemical reactions as well as local neutral densities of CO₂ and N₂. Our calculations in Figure 2 show that below 170 km, the chemical cycle of NO mainly depends on density distribution of N₂ and CO₂ in the Martian upper atmosphere. Hence, the variation in the measured densities of these species directly can impact the modelled NO number density. As explained before, the variability in the MAVEN measured CO₂ and N₂ densities is directly linked to the NO density in the Martian upper atmosphere (see solid and dashed curves in Fig. 7). The higher volume mixing ratios of N₂ leads to the larger formation rate of dissociative products N(4S) and N(2D) and eventually can produce more NO. Since the major production source of NO is via collisional reactions between N(2D) with CO₂, the variation in local CO₂ density can also control the NO density. The ambient density variation presented in the Figure 7 show that during deep dip 8 and 9 campaigns both CO₂ and N₂ densities varied by a factor of 5 or more in the Martian upper atmosphere which results in the variation in our calculated NO densities. The calculations done by Cui et al. (2020) for deep dip 2 campaign show that the diurnal variation in NO, N(4S) and N(2D) at the reference altitude 160 km is due to ambient N₂ mixing ratio at 160 km. But the calculations presented in this work show that besides the variation in N₂ volume mixing ratio, the change in CO₂ density also plays an important role in determining the NO density in the Martian upper atmosphere.

As shown in Figure 6, our calculated NO number densities around 125 km, for deep dip 8 and dip 9 campaigns, are consistent with the IUVS/MAVEN measurements and also with the modelled density profiles in the altitude range 120–160 km. It can be noticed in this figure that at 125 km altitude, the calculated NO number density varies by a factor of about 5 over the both deep dip campaigns, which is mainly due to the local variation in the measured CO₂ and N₂ densities. The earlier MAVEN deep dip campaigns also reveal that there is a variability in the measured neutrals and ions in the Martian upper atmosphere (Bougher et al., 2015). Small scale structures in the NGIMS/MAVEN observed neutral and ion densities are linked to wave activity in the upper atmosphere or solar wind interaction with ionosphere (England et al., 2017; Kopf et al., 2008). Williamson et al. (2019) also observed large scale amplitude perturbations in the measured densities of different species, which could be due to gravity waves. These observations suggest that dynamics in the upper atmosphere could significantly influence the neutral densities of N₂ and CO₂, and subsequently affect the NO density in the Martian upper atmosphere.

Stevens et al. (2019) were able to analyze the IUVS/MAVEN observed NO γ limb intensity profiles for a small period of observation i.e., 6–8 April 2016. Based on the observed limb intensity, the NO number densities were retrieved from the observed spectra between the altitudes 80 to 128 km, above which the retrieval becomes very difficult due to the presence of intense CO Cameron band emissions. But our method of calculation is able to determine the NO number density profile from 120 to 200 km. Since the derivation of NO density at higher altitudes is difficult, we suggest that our approach can be used as a baseline to constrain the NO abundance in the sunlit Martian upper atmosphere for different MAVEN observational conditions. However, the MAVEN observations are limited up to periapsis altitude and it is difficult to compute the NO densities lower than 120 km altitude using this approach.

Stevens et al. (2019) modelled NO density for the IUVS/MAVEN observation period and found that their derived density is smaller by a factor of 5 compared to the earlier Viking observations for the altitudes below 100 km. They ascribed this discrepancy to the assumed collisional rate coefficient for the reaction between N(4S) and CO₂, which is 1 × 10⁻¹⁸ cm³ s⁻¹ instead of earlier Fox (2004) assumed value of 1 × 10⁻¹⁶ cm³ s⁻¹. By using the rate coefficient as used by Fox (2004), our calculations in Figure 2 show that the contribution from N(4S) and CO₂ collisions is negligible to the total formation of NO for the altitudes above 120 km. By considering Stevens et al. (2019) assumed rate coefficient in our calculations, which is two orders of magnitude smaller compared to the value used in the present work, we find no change in the modelled
Figure 4: The modelled NO number density profiles for the various orbits of MAVEN deep dip 8 campaign. The Gray shaded area represents the variability in the calculated NO number density.

NO density profile. Thus, this calculation suggests that the contribution of N(^4S) and CO₂ collisional reaction in the formation of NO can be neglected for the altitudes above 120 km.

Besides the observations of major neutral species, NGIMS/MAVEN also provides NO density measurements in the Martian upper atmosphere. But various observations show that the NGIMS/MAVEN measured NO densities are higher by an order of magnitude compared to IUVS/MAVEN derived values. This higher density is attributed to the recombination of N and O atoms inside the walls of mass spectrometer which produces additional NO. As Stevens et al. (2019) noticed, the effect of contamination in measuring the NO number density due to recombination of atomic oxygen and nitrogen cannot be neglected. By studying various factors associated in the calculation of NO density, Fox (2004) concluded that Viking 2 measurements may not be accurate. Hence, the instrumental bias during Viking 2 measurements could be the main reason for the discrepancy between the modelled and observation of NO densities. Thus, there remains a compelling need of new measurements of NO densities in the Martian upper atmosphere to reconcile this long-standing problem.

The high emission rate factor makes NO (1,0) transition as the brightest feature of γ band emission at the wavelength 214.9 nm compared to other transitions in the ultraviolet region. But this band emission is strongly obscured by CO (0,1) Cameron band emission (215.5 nm) due to proximity in the wavelength and also due to its intensity. Using the derived NO densities, our calculated limb intensities during deep dip 8 and 9 campaigns are consistent with the mean value of IUVS/MAVEN measurement around 120 km (see Figure 10). However, it should be cautioned that the uncertainty in the measured limb radiance is large for the altitudes above 120 km (Stevens et al., 2019).

Fox (2004) has modelled NO number density for low solar activity condition, by assuming a downward flux of -2 × 10⁷ cm⁻² s⁻¹ at lower boundary i.e., 80 km. Stevens et al. (2019) have reduced this downward flux value by two orders of magnitude to fit the IUVS/MAVEN retrieved NO density profiles. They also noticed that assumed transport flux can affect the shape of fitted profile only for altitudes below 100 km. But our calculated NO number densities around 120 km altitude are consistent with IUVS modelled profiles also supports the assumption that the transport has a minor role in determining NO number density in the altitude range 120–160 km (see Figure 6). Hence, we suggest that the NGIMS/MAVEN measured neutral and ion densities are suitable to study NO density and also its dayglow emission intensity for different seasonal conditions in the dayside upper atmosphere of Mars in this altitude range.

As earlier discussed, the intense CO Cameron band inhibits the measurement of NO emission intensity in the dayglow spectra. Our calculation in Figure 10 suggests that the emission intensity falls by an order of magnitude beyond 150 km, hence it is difficult to extract NO number density.
from the faint NO $\gamma$ band emission in the background of intense CO Cameron band emission. Hence, we suggest that the derivation of NO number density based on photochemistry and subsequently calculating its dayglow emission intensity can serve as a baseline while analysing the ongoing and upcoming IUVS/MAVEN observations. More such observations of NO dayglow emissions along with modelling studies are necessary to constrain its variability in the Martian upper atmosphere.

5. Summary and Conclusions

The in-situ NO density measurements are difficult to make in the Martian upper atmosphere because of its low abundance (more than 3 orders of magnitude compared to CO$_2$) and also highly reactive in nature. Moreover, the thermal recombination of atomic nitrogen and atomic oxygen inside the mass spectrometer also inhibits the accurate determination of NO density. Measurement of NO density from the remote dayglow observations is also difficult since its strongest ultraviolet emission feature, i.e., (1,0) gamma band, is severely obscured by the intense CO Cameron band (50 times higher in magnitude). By accounting for major chemical reactions and using the NGIMS/MAVEN measured neutral and ion densities, we developed a photochemical model to study the photochemistry of NO in the Martian upper atmosphere. MAVEN’s deep dip campaigns provide a unique opportunity to study NO photochemistry in the dayside Martian upper atmosphere at the altitudes as low as 120 km. By utilizing the NGIMS/MAVEN measured neutral and ion densities during MAVEN deep dip 8 and 9 campaigns in our model, we present a method to calculate NO number density in the dayside upper atmosphere of Mars. Using the modelled NO number density profiles we also calculated NO dayglow (1,0) $\gamma$ band emission intensity. Our calculated NO number density profiles are consistent with the IUVS/MAVEN retrieved profile and also with the modelled values for IUVS observation conditions. We found that the calculated NO number density varies by a factor of 2–5 and consequently its dayglow intensity due to the variation in CO$_2$ and N$_2$ densities at around 120 km. Hence, we suggest that the present method of calculation serves as a baseline to estimate the NO number density and also its $\gamma$ bands emission intensity under different seasonal and solar conditions in the dayside Martian upper atmosphere. Based on our calculations we suggest that future MAVEN deep dip and remote IUVS/MAVEN observations should be focused in the altitude region 120 and 130 km to
constrain the NO density in the Martian upper atmosphere. More observations of NO emissions along with modelling studies are necessary to fully comprehend the NO density distribution on the dayside upper atmosphere of Mars.

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Data Availability

This paper make use of NGIMS/MAVEN measured neutral and ion number densities L2 data for deep dip 8 and 9 campaigns which has been accessed through the web link https://pds-atmospheres.nmsu.edu. The derived data generated in this research will be shared on reasonable request to the corresponding author.

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Figure 8: Modelled limb radiance profiles for Nitric oxide (NO) 1-0 $\gamma$ emission for the MAVEN Deep dip 8 campaign. The Gray shaded area represents the variability in the calculated NO (1-0) $\gamma$ intensity.

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**Figure 9**: Modelled limb radiance profile of Nitric oxide (NO) emission for the MAVEN deep dip 9 campaign. The Gray shaded area represents the variability in the calculated NO (1-0) intensity.

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Figure 10: Comparison between the modelled and the IUVS/MAVEN observed NO (1,0) γ band limb intensity profiles. The black and red curves represent the calculated average NO (1,0) γ band limb intensity for deep dip 8 and 9 missions respectively. Blue curve and gray errors bars represents the observed average IUVS/MAVEN dayglow profile and 1-σ uncertainty associated with observation, respectively (taken from Stevens et al., 2019). Green and yellow shaded areas represent the variability in the calculated NO (1,0) γ band limb intensity for deep dip 8 and 9 missions, respectively.