Model Calculation of N$_2$ Vegard-Kaplan band emissions in Martian dayglow

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Abstract

A model for N$_2$ Vegard-Kaplan band ($A^3\Sigma_u^+ - X^1\Sigma_g^+$) emissions in Martian dayglow has been developed to explain the recent observations made by the SPICAM ultraviolet spectrograph aboard Mars Express. Steady state photoelectron fluxes and volume excitation rates have been calculated using the Analytical Yield Spectra (AYS) technique. Since inter-state cascading is important for triplet states of N$_2$, the population of any given level of N$_2$ triplet states is calculated under statistical equilibrium considering direct excitation, cascading, and quenching effects. Relative population of all vibrational levels of each triplet state is calculated in the model. Line of sight intensities and height-integrated overhead intensities have been calculated for Vegard-Kaplan (VK), First Positive ($B^3\Pi_g - A^3\Sigma_u^+$), Second Positive ($C^3\Pi_u - B^3\Pi_g$), and Wu-Benesch ($W^3\Delta_u - B^3\Pi_g$) bands of N$_2$. A reduction in the N$_2$ density by a factor of 3 in the Mars Thermospheric General Circulation Model is required to obtain agreement between calculated limb profiles of VK (0-6) and SPICAM observation. Calculations are carried out to assess the impact of model parameters, viz., electron impact cross sections, solar EUV flux, and model atmosphere, on the emission intensities. Constraining the N$_2$/CO$_2$ ratio by SPICAM observations, we suggest the N$_2$/CO$_2$ ratios to be in the range 1.1 to 1.4% at 120 km, 1.8 to 3.2% at 140 km, and 4 to 7% at 170 km. During high solar activity the overhead intensity of N$_2$ VK band emissions would be $\sim$2.5 times higher than that during low solar activity.

1 Introduction

Emissions from excited states of N$_2$ have been studied extensively in the terrestrial airglow and aurora (e.g., Sharp, 1971; Conway and Christensen, 1985; Meier, 1991; Morrill and Benesch, 1996; Broadfoot et al., 1997). But the absence of any emission feature of N$_2$ during Mariner observations of Mars (Barth et al., 1971) surprised the planetary scientists who attributed it to the low fractional abundance by volume of molecular nitrogen on Mars (Dalgarno and McElroy, 1970). Earlier, N$_2$ emissions on Mars were predicted by Fox and co-workers (Fox et al., 1977; Fox and Dalgarno, 1979), who suggested that a high resolution UV spectrometer could detect the N$_2$ UV emissions on Mars. Fox and Dalgarno (1979) have predicted the intensity of various N$_2$ triplet state emissions (Vegard-Kaplan, First positive, Second Positive, W – B), along with LBH band of N$_2$ and First Negative band of N$_2$'. In the terrestrial atmosphere emission from Vegard-Kaplan (VK) bands are weak due to efficient quenching by atomic oxygen, but CO$_2$ is not good at quenching VK bands (Fox and Dalgarno, 1979; Dreyer et al., 1974), so the intensity of these band should be appreciable in Martian airglow.

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Recent observations by SPICAM (Spectroscopy for Investigation of Characteristics of the Atmosphere of Mars) onboard Mars Express (MEX) have, for the first time, observed \( \text{N}_2 \) emissions in the dayglow of Mars (Leblanc et al., 2006, 2007). The main emissions observed are (0, 5), (0, 6), and (0, 7) bands of VK system, which originate from triplet \( \text{A}^3\Sigma_u^+ \) state of excited \( \text{N}_2 \) molecule. The overhead intensity of the \( \text{N}_2 \) VK (0, 6) band derived from the intensity observed by the SPICAM is found to be \( \sim 3 \) times smaller than the intensity calculated by Fox and Dalgarno (1979).

There have been several measurements of electron impact cross sections of triplet states of \( \text{N}_2 \) since Fox and Dalgarno (1979) carried out their calculations. With new cross sections and updated molecular parameters (transition probability and Franck-Condon factor) a model of \( \text{N}_2 \) dayglow emission on Mars is necessary for a better understanding of the recent SPICAM observations. In the present work, a model has been developed to calculate the \( \text{N}_2 \) dayglow emissions on Mars using the Analytical Yield Spectra approach. While calculating the emission of VK bands of \( \text{N}_2 \), cascading from the higher lying states and quenching by atmospheric constituents are considered and the population of any given vibrational level of a state is calculated under statistical equilibrium. Height-integrated overhead intensities are reported for major vibrational bands of \( \text{N}_2 \) VK, First Positive (\( \text{B}^3\Pi_g - \text{A}^3\Sigma_u^+ \)), Second Positive (\( \text{C}^3\Pi_u - \text{B}^3\Pi_g \)), and Wu-Benesch (\( \text{W}^3\Delta_u - \text{B}^3\Pi_g \)) bands. Limb profiles of VK (0, 5), (0, 6), and (0, 7) bands are calculated. The limb profile of VK (0, 6) band is compared with that reported by the SPICAM observations. The present model has been used recently to estimate the \( \text{N}_2 \) triplet band intensities on the Venus (Bhardwaj and Jain, 2011).

2  Vegard-Kaplan Band \( (\text{A}^3\Sigma_u^+ \to \text{X}^1\Sigma_g^+) \)

Figure 1 shows schematic diagram of \( \text{N}_2 \) triplet states energy level with excitation and subsequent cascading processes. The transition from the ground state \( (\text{X}^1\Sigma_g^+) \) to the \( \text{A}^3\Sigma_u^+ \) state is dipole forbidden, so photoelectron impact is the primary excitation source for this state. In addition to the direct excitation from the ground state, cascade from higher triplet states \( \text{C}, \text{B}, \text{W}, \) and \( \text{B}' \) are also important. All excitations of higher triplet states will eventually cascade into the \( \text{A}^3\Sigma_u^+ \) state (Cartwright et al., 1971; Cartwright, 1978). The width and shape of VK bands are quite sensitive to the rotational temperature, making them useful as a monitor of the neutral temperature of the upper atmosphere (Broadfoot et al., 1997).

All transitions between the triplet states of \( \text{N}_2 \) and the ground state are spin forbidden, therefore excitation of these states is primarily due to the electron impact. The higher lying states \( \text{C}, \text{W}, \) and \( \text{B}' \) populate the \( \text{B} \) state, which in turn radiates to the \( \text{A} \) state. Inter-system cascading \( \text{B}^3\Pi_g \Rightarrow \text{A}^3\Sigma_u^+ \) and \( \text{B}^3\Pi_g \Rightarrow \text{W}^3\Delta_u \) is important in populating the \( \text{B} \) state (Cartwright et al., 1971; Cartwright, 1978).

Direct excitation of the \( \nu' = 0 \) vibrational level of the \( \text{A}^3\Sigma_u^+ \) state by electron impact is extremely small, because Frank-Condon factor to the \( \nu'' = 0 \) level of the ground electronic state, \( q_{00} \), is only \( 9.77 \times 10^{-4} \) (Gilmore et al., 1992; Piper, 1993). Contributions to \( \nu' = 0 \) level of \( \text{A} \) state come from the higher states cascading. We have also included \( \text{E} \rightarrow \text{B}, \text{E} \rightarrow \text{C}, \text{E} \rightarrow \text{A}, \text{B} \rightarrow \text{W}, \) and reverse first positive \( \text{A} \rightarrow \text{B} \) cascading in our calculation. The effect of reverse first positive transition is important in populating the lower vibrational levels of \( \text{B} \) state, which in turn populate the lower vibrational levels of the \( \text{A} \) state (Sharp, 1971; Cartwright et al., 1971; Cartwright, 1978). Thus, to calculate the production rate of any vibrational level of triplet state of \( \text{N}_2 \), one must take into account direct excitation as well as inter-state cascading effects.

3  Model Input Parameters

The model atmosphere considering five gases (\( \text{CO}_2, \text{CO}, \text{N}_2, \text{O}, \) and \( \text{O}_2 \)) is taken from the Mars Thermospheric General Circulation Model (MTGCM) of Bougher et al. (1990, 1999, 2000) for a solar longi-
tude of 180°, latitude of 47.5°N, and at 1200 LT; and is same as used in the study of Shematovich et al. (2008). The EUVAC model of Richards et al. (1994) has been used to calculate the 37-bin solar EUV flux for the day of observation, which is based on the F10.7 and F10.7A (81-day average) solar index. The F10.7 flux as seen by Mars (by accounting for the Mars-Sun-Earth angle) is used to derive the 37-bin solar EUV flux. The EUVAC solar spectrum thus obtained is then scaled for the heliocentric distance of Mars for flux. The EUVAC solar spectrum is used to derive the 37-bin solar EUV flux as seen by Mars (by accounting for the Mars-Sun-Earth angle) is used to derive the 37-bin solar EUV flux. The EUVAC model of Tobiska (2004).

Photoionization and photoabsorption cross sections for the gases considered in the present study are taken from Schunk and Nagy (2000). The branching ratios for excited states of CO$_2^+$, CO$^+$, N$_2^+$, O$^+$, and O$_2^+$ have been taken from Avakyan et al. (1998). For calculating the intensity of a specific band $\nu' - \nu''$, Franck-Condon factors and transition probabilities are required. For N$_2$ these are taken from Gilmore et al. (1992). Electron impact cross sections for N$_2$ triplet excited states (A, B, C, W, B', and E) were measured by Cartwright et al. (1977) up to 50 eV. These cross sections were renormalized later by Trajmar et al. (1983) with the use of improved data on elastic cross sections. More recently, N$_2$ triplet state cross sections have been measured by Campbell et al. (2001) and Johnson et al. (2005). Itikawa (2006) reviewed the cross sections of the N$_2$ triplet excited states and recommended the best values determined by Brunger et al. (2003). We have taken the N$_2$ triplet states cross sections from Itikawa (2006), which have been fitted analytically using equation (cf. Jackman et al., 1977; Bhardwaj and Jain, 2009)

$$\sigma(E) = \frac{(q_0 F)}{W^2} \left[ 1 - \left( \frac{W}{E} \right)^{\alpha} \right] \left[ \frac{W}{E} \right]^{\Omega},$$

(1)

where $q_0 = 4\pi a_0 R^2$ and has the value $6.512 \times 10^{-14}$ eV$^2$ cm$^2$. Table 1 shows the corresponding parameters. Fig. 2 shows the fitted cross sections of the N$_2$ triplet A, B, C, and W states along with the recommended cross sections of Itikawa (2006). For other gases electron impact cross sections have been taken from Jackman et al. (1977), except for CO$_2$, which are from Bhardwaj and Jain (2009).

We have run our model for the Mars Express observation on 16 Dec. 2004 (Sun-Mars distance = 1.59 AU, and F10.7 at Mars = 35.6), taking solar zenith angle as 45°, solar EUV flux from the EUVAC model, and MTGCM model atmosphere. Hereafter we refer it as the “standard case”. We have also studied the effects of various input parameters (like solar EUV flux, N$_2$ triplet state cross sections, model atmosphere, solar cycle) on the emission intensity, which are discussed in Section 6.

4 Model Calculation

4.1 Photoelectron Production Rate

Primary photoelectron production rate is calculated using

$$Q(Z, E) = \sum_{l} n_l(Z) \sum_{j,\lambda} \sigma_{l}^{A}(j, \lambda) I(Z, \lambda) \delta \left( \frac{hc}{\lambda} - E - W_{jl} \right)$$

(2)

$$I(Z, \lambda) = I(\infty, \lambda) \exp \left[ -\sec(\chi) \sum_{l} \sigma_{l}^{A}(\lambda) \int_{Z}^{\infty} n_l(Z') dZ' \right]$$

(3)

where $\sigma_{l}^{A}$ and $\sigma_{l}^{A}(j, \lambda)$ are the total photoabsorption cross section and the photoionization cross section of the jth ion state of the constituent l at wavelength $\lambda$, respectively; $I(\infty, \lambda)$ is the unattenuated solar flux at wavelength $\lambda$, $n_l$ is the neutral density of constituent l at altitude Z; $\sec(\chi)$ is the Chapman function, $\chi$ is the solar zenith angle (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 jth ion state of the lth constituent, and $E$ is the energy of ejected electron. We have used $\sec(\chi)$ in place of $\sinh(\chi)$, which is valid for $\chi$ values up to 80°. Figure 3 shows the primary photoelectron energy spectrum at three different altitudes. There is a sharp peak at 27...
eV due to the ionization of CO$_2$ in the ground state by the He II solar 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. The individual peaks structure shown in the figure are different from that of Mantas and Hanson (1979), which is due to revisions in the branching ratios (Avakyan et al., 1998) used in the present study.

4.2 Photoelectron Flux

To calculate the photoelectron flux we have adopted the Analytical Yield Spectra (AYS) technique (cf. Singhal and Haider, 1984; Bhardwaj and Singhal, 1990; Bhardwaj et al., 1990, 1996; Singhal and Bhardwaj, 1991; Bhardwaj, 1999, 2003; Bhardwaj and Michael, 1999a,b). The AYS is the analytical representation of numerical yield spectra obtained using the Monte Carlo model (cf. Singhal et al., 1980; Bhardwaj and Michael, 1999a,b; Bhardwaj and Jain, 2009). Recently, the AYS model for electron degradation in CO$_2$ has been developed by Bhardwaj and Jain (2009). Further details of the AYS technique are given in Bhardwaj and Michael (1999a), Bhardwaj and Jain (2009), and references therein. Using AYS the photoelectron flux has been calculated as (e.g. Singhal and Haider, 1984; Bhardwaj and Michael, 1999b)

$$\phi(Z,E) = \int_{W_{kl}}^{100} \frac{Q(Z,E)U(E,E_0)}{\sum_i n_i(Z)\sigma_{IT}(E)} dE_0 \quad (4)$$

where $\sigma_{IT}(E)$ is the total inelastic cross section for the $l$th gas, $n_i$ is its density, and $U(E,E_0)$ is the two-dimensional AYS, which embodies the non-spatial information of degradation process. It represents the equilibrium number of electrons per unit energy at an energy $E$ resulting from the local energy degradation of an incident electron of energy $E_0$. For the CO$_2$ gas it is given as (Bhardwaj and Jain, 2009)

$$U(E,E_0) = A_1E^s_k + A_2(E_k^{1-t}/e^{3/2+r}) + \frac{E_0B_0e^x/B_1}{(1 + e^x)^2} \quad (5)$$

Here $E_k = E_0/1000$, $e = E/I$ ($I$ is the lowest ionization threshold), and $x = (E - B_2)/B_1$. $A_1 = 0.027$, $A_2 = 1.20$, $t = 0$, $r = 0$, $s = -0.0536$, $B_0 = 10.095$, $B_1 = 5.5$, and $B_2 = 0.9$ are the best fit parameters.

For other gases, viz., O$_2$, N$_2$, O, and CO, we have used the AYS given in Singhal et al. (1980)

$$U(E,E_0) = C_0 + C_1(E_k + K)/[(E - M)^2 + L^2]. \quad (6)$$

Here $C_0$, $C_1$, $K$, $M$, and $L$ are the fitted parameters which are independent of the energy, and whose values are given by Singhal et al. (1980).

The calculated photoelectron flux at 130 km altitude is shown in Figure 4 for the standard case as well as for conditions similar to those of Viking 1 (see Section 5.2). The photoelectron flux calculated by Simon et al. (2009) and Fox and Dalgarno (1979) are also shown in Figure 4 at same altitude. Overall important peak structures are similar in all the three calculated fluxes, e.g., the peak at 27 eV and broad peak at 21-23 eV. A sharp dip at around 3 eV is prominent in all three photoelectron fluxes, which is due to large vibrational cross sections at 3.8 eV for electron impact on CO$_2$. The calculated fluxes decrease exponentially with increasing energy. The sudden decrease in the photoelectron flux at higher energies is due to the presence of these features in the primary photoelectron energy spectrum (cf. Figure 3).

5 Results and discussion

5.1 Volume excitation rates

We have calculated volume excitation rate $V_{il}(Z,E)$ for the $i$th state of the $l$th gas at altitude $Z$ and energy $E$ using the equation (Singhal and Bhardwaj, 1991; Bhardwaj, 1999, 2003; Bhardwaj and Michael, 1999b)
\[ V_{il}(Z, E) = n_l(Z) \int_{E_{th}}^{E} \phi(Z, E) \sigma_{il}(E) dE, \] (7)

where \( n_l(Z) \) is the density of the \( l \)th gas at altitude \( Z \) and \( \sigma_{il}(E) \) is the electron impact cross section for the \( i \)th state of the \( l \)th gas, for which the threshold is \( E_{th} \). Figure 5 (upper panel) shows the volume excitation rates of the \( \text{N}_2 \) triplet states (\( A, B, C, W, B', \) and \( E \)) excited by photoelectron impact. The altitude of peak production for all states is \( \sim 126 \) km for the standard case. The volume excitation rate of \( \text{N}_2(\text{A}) \) state calculated using the S2K solar flux model is also shown in the upper panel of Figure 5. The peak of excitation rate occurs at the same altitude for both solar EUV flux models but the magnitude of excitation rate is slightly higher when the S2K model is used. More discussion about the effect of solar EUV flux model on emission intensities is given in Section 6.2.

To calculate the contribution of cascading from higher triplet states and interstate cascading between different states, we solve the equations for statistical equilibrium based on the formulation of Cartwright (1978) and assumed that only excitation from the lowest vibrational level of the electronic ground state is important. At a specified altitude, for a vibrational level \( \nu \) of a state \( \alpha \), the population is determined using statistical equilibrium

\[ V^\alpha_{q_{0\nu}} + \sum_\beta \sum_s A^\beta\alpha_{s\nu} n^\beta_s = \{ K^\alpha_{q\nu} + \sum_\gamma \sum_r A^\gamma\nu_{r\nu} \} n^\alpha_\nu \] (8)

where

\( V^\alpha_{q_{0\nu}} \) electron impact volume excitation rate (\( \text{cm}^{-3} \text{s}^{-1} \)) of state \( \alpha \);

\( q_{0\nu} \) Franck-Condon factor for the excitation from ground level to \( \nu \) level of state \( \alpha \);

\( A^\beta\alpha_{s\nu} \) transition probability (\( s^{-1} \)) from state \( \beta(s) \) to \( \alpha(\nu) \);

\( K^\alpha_{q\nu} \) total electronic quenching frequency (\( s^{-1} \)) of level \( \nu \) of state \( \alpha \) by the all gases defined as: \( \sum_l K^\alpha_{q(l)\nu} \times n_l \); where,

\( K^\alpha_{q(l)\nu} \) is the quenching rate coefficient of level \( \nu \) of gas \( l \) of density \( n_l \);

\( A^\alpha_{\gamma\nu} \) transition from level \( \nu \) of state \( \alpha \) to vibrational level \( r \) of state \( \gamma \);

\( n \) density (\( \text{cm}^{-3} \));

\( \alpha, \beta, \gamma \) electronic states;

\( s, r \) source and sink vibrational levels, respectively.

While calculating the cascading from \( C \) state, we have taken predissociation also into account. The \( C \) state predissociates approximately half the time (this is an average value for all vibrational levels of the \( C \) state; 0 and 1 levels do not predissociate at all) (cf. Daniell and Strickland, 1986). In the terrestrial thermosphere, the \( \text{N}_2(A) \) state is effectively quenched by atomic oxygen. In the case of Mars the main constituent \( \text{CO}_2 \) does not quench \( \text{N}_2(A) \) level that efficiently, but still there will be some collisional deactivation by other atmospheric constituents of Mars. The electronic quenching rates for vibrational levels of \( \text{N}_2 \) triplet states by \( \text{O}, \text{O}_2 \), and \( \text{N}_2 \) are adopted from Morrill and Benesch (1996) and Cartwright (1978) and by \( \text{CO}_2 \) and \( \text{CO} \) are taken from Dreyer et al. (1974).

Figure 6 shows the population of different vibrational levels of triplet states of \( \text{N}_2 \) relative to the ground state at 130 km. The relative population of \( \text{N}_2(A) \) at 110 km is also shown in the figure. Our calculated relative vibrational populations agree well with the earlier calculations (Morrill and Benesch, 1996; Cartwright, 1978). To show the effect of quenching the relative vibrational populations of \( \text{N}_2(A) \) state calculated without quenching at 110 and 130 km are also shown in Figure 6. The quenching does affect the vibrational population of \( \text{N}_2(A) \) state mainly for vibrational levels between 5 and 10 at lower altitudes (<130 km), as the altitude increases the effect of quenching decreases. Figure 7 shows the steady state fractional population altitude profiles of a few vibrational levels of \( A \) state and \( \nu' = 0 \) level of \( B, C, W, \) and \( B' \) excited states of \( \text{N}_2 \).

After calculating the steady state density of different vibrational levels of excited states of \( \text{N}_2 \), the volume emission rate \( V^{\alpha\beta}_{\nu'\nu''} \) of a vibration band \( \nu' \rightarrow \nu'' \)
can be obtained using

\[ V_{\nu',\nu}^{\alpha\beta} = n_{\nu'}^\alpha \times A_{\nu',\nu}^{\alpha\beta} \text{ (cm}^{-3} \text{ s}^{-1}) \]  

(9)

where \( n_{\nu'}^\alpha \) is the density of vibrational level \( \nu' \) of state \( \alpha \), and \( A_{\nu',\nu}^{\alpha\beta} \) is the transition probability \( (\text{s}^{-1}) \) for the transition from the \( \nu' \) level of the \( \alpha \) state to the \( \nu'' \) level of the \( \beta \) state. Figure 5 (bottom panel) shows the volume emission rates for the VK (0, 4), (0, 5), (0, 6), and (0, 7) bands. We have integrated the volume emission rates over the altitudes 80 – 400 km to obtain the overhead intensity for various VK bands of N\(_2\), which are tabulated in Table 2 (standard case). Table 3 shows the calculated height-integrated overhead intensities for a few of the prominent bands of First Positive (B \( \rightarrow \) A), Second Positive (C \( \rightarrow \) B), and Wu-Benesch (W \( \rightarrow \) B) emissions.

### 5.2 Line of sight intensity

For comparison of the calculated intensity with SPICAM observation we have integrated the calculated emission rate along the line of sight and expressed the results in kR \( (1 \text{ Rayleigh} = 10^6 \text{ photon cm}^{-2} \text{ s}^{-1}) \)

\[ I = \int V(r) dr, \]  

(10)

where \( V(r) \) is the volume emission rate \( (\text{cm}^{-3} \text{ s}^{-1}) \) for a particular emission, calculated using equation (9) and \( r \) is abscissa along the horizontal line of sight. The upper limit of the atmosphere in our model is taken as 400 km. While calculating limb intensity we assume that the emission rate is constant along local longitude/latitude. For the emissions considered in the present study, the effect of absorption in the atmosphere is found to be negligible. As mentioned earlier (cf. Leblanc et al., 2007), the main N\(_2\) emission features observed by SPICAM are (0, 5) and (0, 6) transitions of the Vegard-Kaplan \( (A^3\Sigma_u^+ - X^1\Sigma_g^+) \) band. Leblanc et al. (2006) also reported the detection of VK (0, 7) band, but it was characterized by a large uncertainty because it falls between two intense emissions at 289 nm and 297.2 nm of CO\(_2\) UV doublet and oxygen line emission, respectively. Otherwise, as shown in Table 2, VK(0, 7) band would have been more intense than the (0, 5) band. The ratio between calculated intensity of the VK (0, 6) and (0, 5) bands is 1.3, which is in good agreement with the results of Leblanc et al. (2007) and Fox and Dalgarno (1979).

Figure 8 shows the limb profiles of the VK (0, 6) band at different solar zenith angles along with the SPICAM observed profiles averaged over the solar longitude L\(_s\) 100°–171° and SZA 8°–36° and 36°–64°, taken from Leblanc et al. (2007). The effect of SZA on the calculated profiles is clearly visible in Figure 8; the peak of the altitude profile rises while the intensity decreases with increasing SZA. The limb profiles of the VK (0, 5) and (0, 6) bands at SZA = 45° are also plotted in Figure 8. For the standard case (SZA = 45°), the peak intensities of the VK (0, 5), (0, 6), and (0, 7) bands are \( \sim \) 0.9, 1.1, and 1 kR, respectively, at 120 km. For SZA values of 20° and 60°, the N\(_2\) VK (0, 6) band peaks at 118 and 124 km with a value of 1.4 and 0.9 kR, respectively.

The shape of calculated and observed limb intensities are in agreement with each other but the magnitude of calculated intensities are larger by a factor of \( \sim 3 \) at SZA = 20°. This difference could be due to the larger abundance of N\(_2\) in the model atmosphere used in the present study. Other factors can also affect the calculated intensities, but their combined uncertainties also cannot account for the difference by a factor of 3 in the calculated and observed intensities (effect of other input parameters, viz., electron impact cross section, and solar EUV flux model is described in Sections 6.1 and 6.2, respectively). Figure 8 also shows the computed limb intensity of the VK (0, 6) emission at SZA 20°, 45°, and 60° obtained after reducing the density of N\(_2\) by a factor of 3, which compares favourably in both shape and magnitude with the observed emission. The N\(_2\)/CO\(_2\) ratio, after reducing the N\(_2\) density by a factor of 3 is to 0.9, 2.1, and 7.1% at altitudes of 120, 140, and 170 km, respectively. The calculated overhead intensities of VK bands after reducing N\(_2\) density by a factor of 3 (for the standard case) are depicted in column 3 of Table 2. It may however be noted that the observed limb profiles (Leblanc...
et al., 2007) are averaged over several days of observation (Ls=101°-171°) and range of SZA values, while the model profile is for a single day (16 Dec. 2004) at Ls = 130° and SZA = 20°.

We have also calculated the nadir intensity for the condition similar to that of Viking landing (Sun-Mars distance = 1.65 AU and F10.7 = 68). The model atmosphere was taken from Fox (2004) for the low solar activity condition and a SZA of 45°. For the VK (0, 6) band our calculated intensity is 26 R, which is consistent with results (20 R) of Fox and Dalgarno (1979) for the similar condition. The minor difference may be due to the updated cross sections and transition probabilities. For the condition similar to that of Viking, Leblanc et al. (2007) have measured an intensity of ~180 R for the VK (0, 6) band, which corresponds to a nadir intensity of ~6 R. The measured value is about 4 times smaller than our calculated intensity. Such a difference by a factor of 4 between observed and calculated intensities might be due to the higher density of N2 taken in our model atmosphere. Leblanc et al. (2007) have suggested that ratio of the integrated column densities of N2 and CO2 between 120 and 170 km, that is the mixing ratio between N2 and CO2 for a uniformly mixed atmosphere, would be 0.9% for an overhead intensity of 6 R. For the same altitude range, the ratio of N2/CO2 density is 3.5% and 3.7% in model atmosphere used in the work of Fox (2004) and Bougher’s MTGCM, respectively, which is a factor of 4 higher than that suggested by Leblanc et al. (2007).

To summarize, the above results indicate that the N2 density in the MTGCM atmosphere, as well as in the model atmosphere of Fox (2004), has to be reduced by a factor of ~3 to obtain agreement between the SPICAM observation and the calculated intensity.

5.3 Variation with Solar Zenith Angle and Solar 10.7 flux

Figure 9 shows the variation of the VK (0, 6) band intensity, averaged between 120 and 170 km, with SZA and its comparison with SPICAM observations. Calculated intensities are for standard case obtained after reducing the N2 density profile in the MTGCM atmosphere by a factor of 3 (see discussion in the previous section). Model intensity shows a cosine SZA dependence, with larger attenuation of solar EUV flux at higher SZA, resulting in decrease in the intensity at higher SZA. Calculated intensities are in agreement with the observed values, within observational and model uncertainties.

Another important model parameter, which affects the emission intensities is the solar EUV flux, whose variation is assumed to be given by the F10.7 index. Solar EUV flux has been calculated using the F10.7 flux for the day of observation and scaled to the Mars according to its heliocentric distance. For the observations reported by Leblanc et al. (2007) the solar longitude of Mars varied between 101° and 171°, which corresponds to change in the heliocentric distance of Mars form 1.64 to 1.49 AU. Figure 10 shows the variation of VK (0, 6) band intensity with respect to the F10.7 solar index at Mars. Calculations are made for the standard case with the N2 density in the MTGCM model reduced by a factor 3. Model calculated intensities are consistent with the observed values within the uncertainties of observation and model.

6 Effect of various model parameters on Intensity

To evaluate the effect of various model input parameters, such as solar flux, cross sections, and model atmosphere, on the VK band emissions, we have conducted a series of test studies by changing one parameter at a time and compare the results with those of the standard case. The results are presented in Table 2 and discussed below.
6.1 Electron impact cross sections for the triplet states

Since electron impact on N\textsubscript{2} is the source of excitation of forbidden triplet states of N\textsubscript{2}, any change in electron impact cross sections will directly affect the VK band emission intensities. Various measurements of the N\textsubscript{2} triplet state cross sections were discussed in Section 3. In the standard case we have taken the recommended cross sections of Itikawa (2006), which are fitted using the semiempirical relation given in equation (1) (cf. Table 1 and Figure 2). Instead of analytically fitted cross sections, if the triplet state cross sections of Itikawa (2006) are used in the model, the calculated triplet band intensities differ from the standard case by less than 10%.

Itikawa’s recommended cross sections are based on the best values determined by the Brunger et al. (2003). For the triplet states cross section, Brunger et al. (2003) have estimated the uncertainty of the recommended cross sections as ±35% (±40% at energies below 15 eV) for A\textsuperscript{3}Σ\textsuperscript{u}+, ±35% for B\textsuperscript{3}Π\textsuperscript{g} and W\textsuperscript{3}Δ\textsubscript{u}, ±40% for B\textsuperscript{2}Π\textsuperscript{g}, ±30% for C\textsuperscript{3}Π\textsubscript{u} and ±40% for E\textsuperscript{3}Σ\textsuperscript{g} state. The integral cross sections (ICS) of Johnson et al. (2005) are derived from the differential cross sections (DCS) of Khakoo et al. (2005). Johnson et al. (2005) have given the ICS at 8 energies between 10 and 100 eV, with uncertainty for all states cross sections varying between ±20% to ±22%; at a few energy points it is as high as ±35%.

To evaluate the effect of electron impact cross sections on the VK band emissions we have taken two sets of cross sections; one from Cartwright et al. (1977), which were renormalized by Trajmar et al. (1983), and second from the recent cross sections given by Johnson et al. (2005). The resulting VK band intensities are shown in Table 2. The intensities calculated with the cross sections of Trajmar et al. (1983) are almost the same as in the standard case. However, when the cross sections of Johnson et al. (2005) are used, the VK band intensities are reduces by 45%, compared to the intensities computed for the standard case, which is due to smaller cross sections of Johnson et al. (2005). The effect of the smaller triplet state cross sections of Johnson et al. (2005) is also seen on the limb intensities shown in the Figure 11 where a reduction in N\textsubscript{2} density by a factor 2 is sufficient to fit the SPICAM observed profile. Thus, the electron impact triplet state excitation cross sections of N\textsubscript{2} also help in constraining the N\textsubscript{2} density in the model atmosphere.

6.2 Input solar EUV flux model

SOLAR2000 model of Tobiska (2004) and EUVAC model of Richards et al. (1994) are the two widely used solar flux models in the aeronomical calculations. In the standard case we have used EUVAC model. To see the effect of input solar flux on the VK emissions, we conducted a test study by taking the solar EUV flux from SOLAR2000 v.2.36 (S2K) model of Tobiska (2004) at 37 wavelength bins; the other input parameters remain the same as in the standard case. The calculated integrated overhead intensities are shown in the Table 2. The calculated intensities of VK bands using S2K model are ∼15% larger than those calculated by using the EUVAC model. This results in the requirement of a larger reduction in the N\textsubscript{2} density, that is, a factor of 3.4 compared to 3.0 for the standard case to fit the observed limb profile of the VK (0, 6) band.

6.3 Model atmosphere

The importance of model atmosphere on the calculated intensities has been demonstrated in Section 5.2. The N\textsubscript{2}/CO\textsubscript{2} ratio, which describes the abundance of molecular nitrogen in the atmosphere of Mars, is different in different model atmospheres. For the present study we have taken the atmosphere from Bougher’s MTGCM (Bougher et al., 1990, 1999, 2000) as used in study of Shematovich et al. (2008) where the N\textsubscript{2}/CO\textsubscript{2} ratio is 2.8, 6.4 and 21% at 120, 140 and 170 km, respectively. Leblanc et al. (2007) suggested that N\textsubscript{2}/CO\textsubscript{2} ratio is higher in the model atmosphere used by Fox and Dalgarno (1979). The recent models of Krasnopolsky (2002) are characterized by smaller
abundances of N$_2$ than that of Fox and Dalgarno (1979). The N$_2$/CO$_2$ ratios are 2.6, 3.8, and 8.6% at 120, 140, and 170 km, respectively in Krasnopolsky’s model.

We have used the model atmospheres of Krasnopolsky (2002) and Fox (2004) to study the effect of model atmosphere on the VK emission intensities. Figure 11 shows the calculated limb intensity of the VK (0, 6) band for both model atmospheres at SZA 20° (all other conditions are similar to the standard case). The emission peaks at ~116 km in the case of Krasnopolsky (2002), which is almost similar to standard case (~118 km). But the emission peaks at higher altitude (~123 km) when the model atmosphere of Fox (2004) is used, which is due to higher CO$_2$ abundance in her model. The intensities calculated using both models are found to be larger than the observed values. To fit the observed limb profile, the N$_2$ density in the Krasnopolsky (2002) model has to be reduced by a factor of 2.1, the N$_2$/CO$_2$ ratios thus become 1.3, 1.8, and 4.4% at 120, 140, and 170 km, respectively. In the case of Fox (2004) model atmosphere, the required decrease in N$_2$ density is a factor of 2.5, which corresponds to the N$_2$/CO$_2$ ratios of 1.1, 1.9, and 5.3% at 120, 140, and 170 km, respectively.

6.4 Solar Cycle

The solar cycle is approaching higher solar activity, and MEX is currently orbiting Mars. We therefore hope to observe the effects of higher solar activity on the Martian dayglow emissions. Using the EUVAC model we have calculated the various N$_2$ triplet band emissions for high solar activity conditions similar to that of Mariner 6 and 7 flybys when the F10.7 index was $\simeq 190$ at 1 AU. The model atmosphere for solar maximum conditions was taken from Fox (2004); other model parameters are same as in the standard case. The calculated height-integrated overhead intensities for the VK bands are presented in the Table 2, and those for the other triplet bands in Table 3. The calculated solar maximum intensities are larger by a factor of $\sim 1.5$ than those of the standard case, and $\sim 2.5$ times larger than those for Viking conditions. As mentioned in section 5.2, the calculated and observed limb profiles are consistent with each other when the N$_2$ density in the atmosphere is reduced by a factor of 3. If a similar situation prevails during high solar activity conditions, then the calculated intensity of N$_2$ VK band system would be smaller by a factor of 2 to 3.

7 Summary

We have presented models for the intensities of the N$_2$ triplet band systems in the Martian dayglow. We have used the analytical yield spectra technique to calculate the steady state photoelectron flux, which in turn is used to calculate volume excitation rates of N$_2$ VK bands and other triplet states. The populations of various vibrational levels of the triplet states of N$_2$ have been calculated considering direct excitation as well as cascading from higher triplet states in statistical equilibrium conditions. Using calculated emission rates the limb profiles of the VK (0, 5), (0, 6), and (0, 7) bands have been calculated and compared with the SPICAM observed limb profile reported by Leblanc et al. (2007). The observed and calculated limb profiles of the VK (0, 6) band are in good agreement when the N$_2$ density is reduced by a factor of 3 from those given by the MTGCM model of Bougher et al. (1990, 1999, 2000). Overhead intensities of prominent transitions in VK, First Positive, Second Positive, and $W \rightarrow B$ bands have been calculated.

The effect of important model parameters, viz., electron impact N$_2$ triplet state excitation cross sections, solar flux, solar activity, and model atmosphere, on emissions have been studied. Changes in cross sections of N$_2$ triplet states can alter the calculated intensity by a factor of $\sim 2$. On the other hand, the calculated intensities are $\sim 15\%$ larger when the SOLAR2000 v.2.36 solar EUV flux model of Tobiska (2004) is used instead of the EUVAC model of Richards et al. (1994). During high solar activity, when the F10.7 is similar to those at the times of the Mariner 6 and 7 flybys, the calculated intensities
are about a factor of 2.5 larger than those calculated for the low solar activity conditions of the Viking mission. On using the model atmospheres of Fox (2004) and Krasnopolsky (2002), a decrease in N\textsubscript{2} density in their atmospheric model by a factor of 2.5 and 2.1, respectively, is required to reconcile the calculated VK (0, 6) band limb profile with the observed profile.

The most important parameter that governs the limb intensity of VK band is the N\textsubscript{2}/CO\textsubscript{2} ratio. Constraining the N\textsubscript{2}/CO\textsubscript{2} ratio by SPICAM observations, for different cases of model input parameters, we suggest that the N\textsubscript{2}/CO\textsubscript{2} ratio would be in the range of 1.1 to 1.4% at 120 km, 1.8 to 3.2% at 140 km, and 4 to 7% at 170 km. Our study suggests that most of the atmospheric models have N\textsubscript{2} abundances that are larger than our derived values by factors of 2 to 4. Clearly there is a need for improved understanding of the Martian atmosphere, and the SPICAM observations help to constrain the N\textsubscript{2} relative abundances. A decrease in the N\textsubscript{2} densities in the atmospheric models, as suggested by our calculations, would affect the chemistry and other aeronomical processes in the Martian upper atmosphere and ionosphere.

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Table 1: Fitting parameters (equation 1) for N$_2$ triplet state cross sections.

| Parameter | A$^3\Sigma^+_u$ | B$^3\Pi_g$ | C$^3\Pi_u$ | W$^3\Delta_u$ | B$^3\Sigma^-_u$ | E$^3\Sigma^+_g$ |
|-----------|-----------------|-------------|-------------|--------------|----------------|----------------|
| Th$^*$    | 6.17            | 7.35        | 11.03       | 7.36         | 8.16           | 11.9           |
| $\alpha$  | 1.00            | 3.00        | 3.20        | 1.50         | 1.70           | 1.70           |
| $\beta$   | 1.55            | 2.33        | 1.00        | 2.30         | 1.50           | 3.00           |
| $\Omega$  | 2.13            | 2.50        | 2.70        | 2.60         | 2.12           | 3.00           |
| F         | 0.20            | 0.178       | 0.248       | 0.378        | 0.08           | 0.03           |
| W         | 6.99            | 7.50        | 11.05       | 8.50         | 8.99           | 12.0           |

$^*$Threshold in eV.
Table 2: \( \text{N}_2 \) Vegard-Kaplan Band \( (A^3\Sigma_u^+ \rightarrow X^1\Sigma_g^+) \) height-integrated overhead intensity for different cases.

| Band \( \nu' - \nu'' \) | Band Origin (Å) | Std.* | \( \rho[\text{N}_2] \) \(/3.0\) | Viking Cond. | Overhead Intensity (R) | Cross section CS-A† | CS-B‡ | Flux Max.* |
|--------------------------|-----------------|-------|-----------------|-------------|------------------------|---------------------|-------|------------|
| 0-2                      | 2216            | 1.5   | 0.5             | 0.9         | 1                      | 1.4                 | 1.7   | 2.3        |
| 0-3                      | 2334            | 7.2   | 2.5             | 4.4         | 5                      | 6.8                 | 8.3   | 10.9       |
| 0-4                      | 2463            | 19.4  | 6.8             | 11.7        | 13.3                   | 18.3                | 22.2  | 29.3       |
| 0-5                      | 2605            | 34.3  | 12.1            | 20.7        | 23.5                   | 32.4                | 39.4  | 51.8       |
| 0-6                      | 2762            | 43.7  | 15.4            | 26.3        | 30                     | 41.3                | 50.1  | 66.0       |
| 0-7                      | 2937            | 41.5  | 14.6            | 25.0        | 28.5                   | 39.2                | 47.6  | 62.7       |
| 0-8                      | 3133            | 30.7  | 10.8            | 18.5        | 21                     | 29                  | 35.2  | 46.4       |
| 0-9                      | 3354            | 18    | 6.3             | 10.8        | 12.3                   | 17                  | 20.6  | 27.0       |
| 1-8                      | 2998            | 25.9  | 9.1             | 15.5        | 18.8                   | 25.3                | 29.6  | 38.4       |
| 1-9                      | 3200            | 38    | 13.4            | 22.8        | 27.8                   | 37.4                | 43.7  | 56.6       |
| 1-10                     | 3427            | 35.9  | 12.7            | 21.5        | 26                     | 35.1                | 41    | 53.2       |
| 1-11                     | 3685            | 24    | 8.5             | 14.4        | 17.5                   | 23.5                | 27.5  | 35.6       |
| 2-10                     | 3270            | 12    | 4.2             | 7.1         | 8.8                    | 11.9                | 13.6  | 17.3       |
| 2-11                     | 3503            | 24.9  | 8.8             | 14.8        | 18.5                   | 24.9                | 28.5  | 36.3       |
| 2-12                     | 3769            | 26.9  | 9.5             | 16.0        | 20                     | 26.9                | 30.8  | 39.3       |
| 2-13                     | 4074            | 18.9  | 6.7             | 11.3        | 14                     | 18.9                | 21.7  | 27.6       |
| 3-13                     | 3857            | 16.3  | 5.7             | 9.7         | 12.3                   | 16.5                | 18.7  | 24.0       |
| 3-14                     | 4171            | 18.1  | 6.4             | 10.8        | 13.7                   | 18.3                | 20.7  | 26.7       |

*Standard case. See text for details
†Cross sections taken from Johnson et al. (2005).
‡Cross sections taken from Trajmar et al. (1983).
§SOLAR2000 model of Tobiska (2004).
¶Solar maximum flux for condition similar to Mariner 6 flyby (F10.7 ≃ 190).
Table 3: Calculated height-integrated overhead intensity of N$_2$ triplet emissions.

| Band Origin (ν' − ν'') Å | Intensity (R) Std. Max.* |
|---------------------------|--------------------------|
| | First Positive $B^3\Pi_g - A^3\Sigma_u^+$ |
| 0-0 | 10469 | 60.9 | 95.4 |
| 0-1 | 12317 | 32.7 | 51.2 |
| 0-2 | 14895 | 9.8 | 15.3 |
| 1-0 | 8883 | 96 | 149.7 |
| 1-2 | 11878 | 17.8 | 27.8 |
| 1-3 | 14201 | 13.6 | 21.2 |
| 2-0 | 7732 | 46.9 | 72.9 |
| 2-1 | 8695 | 60.6 | 94.2 |
| 2-2 | 9905 | 11.2 | 17.5 |
| 3-0 | 7606 | 64.3 | 100 |
| 3-1 | 8516 | 16.8 | 26.1 |
| 3-2 | 9648 | 20.3 | 31.5 |
| 3-3 | 6772 | 19.6 | 30.5 |
| 4-0 | 7484 | 49.2 | 76.4 |
| 4-1 | 9404 | 14.8 | 22.9 |
| 5-0 | 6689 | 22.1 | 34.4 |
| 5-1 | 7368 | 26.2 | 40.7 |
| 6-0 | 6808 | 18 | 28 |
| 7-4 | 6530 | 12 | 18.5 |
| | Second Positive $C^3\Pi_u - B^3\Pi_g$ |
| 0-0 | 3370 | 32.1 | 51 |
| 0-1 | 3576 | 21.7 | 34.5 |
| 0-2 | 3804 | 8.7 | 13.9 |
| 1-0 | 3158 | 8.3 | 13.2 |
| | Wu-Benesch ($W^3\Delta_u - B^3\Pi_g$) |
| 2-0 | 33206 | 4 | 6.4 |
| 3-0 | 22505 | 3.4 | 5.4 |
| 3-1 | 36522 | 3 | 4.7 |
| 4-1 | 24124 | 5.1 | 8 |
| 5-0 | 18090 | 4.7 | 7.4 |
| 5-1 | 25962 | 4.5 | 7.0 |
| 6-0 | 19193 | 5.8 | 9.0 |
| 7-2 | 15281 | 4.7 | 7.3 |
| 7-3 | 20421 | 5.1 | 8.0 |
| 8-3 | 16112 | 5.1 | 8.0 |
| 9-4 | 17024 | 4.4 | 6.9 |

*Standard Case. See text for details.
†Solar maximum flux for condition similar to Mariner 6 flyby.
Figure 1: Energy level diagram for the excitation of N$_2$ triplet states and subsequent inter-state cascading processes. Solid arrows show the excitation from ground state to higher states, and dashed arrows represent the transitions between different states (HK: Herman-Kaplan; 1P: First Positive; R1P: Reverse First Positive; 2P: Second Positive; VK: Vegard-Kaplan band system). Excitation thresholds for all the triplet states are given Table 1.
Figure 2: The triple states cross sections due to electron impact on N\textsubscript{2}. Symbols represent the values of Itikawa (2006) and the solid curve represents the analytical fits using equation 1. Cross sections of \textit{B} and \textit{W} have been plotted after multiplying by a factor of 10 and 5, respectively.

Figure 3: Primary photoelectron energy distribution at three different altitudes for the standard case.
Figure 4: Model steady-state photoelectron flux calculated at 130 km for standard case and for Viking condition. Flux calculated by Simon et al. (2009) and Fox and Dalgarno (1979) at 130 km are also shown for comparison.
Figure 5: (Upper panel) The volume excitation rates of various triplet states of N$_2$ by direct electron impact excitation for the standard case. Dashed curve shows the excitation rate of A state calculated using S2K model. The excitation rate of the E state has been multiplied by a factor of 10. (Bottom panel) The volume emission rates of the VK (0, 4), (0, 5), (0, 6), and (0, 7) bands.
Figure 6: The relative populations of vibrational levels of different triplet states of N$_2$ with respect to the N$_2$ density at 130 km. Dashed line with triangle shows the relative vibrational populations of A at 110 and 130 km, respectively, without considering the quenching.

Figure 7: Altitude profiles of the relative populations of selected vibrational levels of the N$_2$(A) state, and 0 level of the B, B', C, and W states with respect to those of N$_2$(X). Population of B, B', and C have been plotted after multiplying by a factor of 10$^4$, 10$^5$, and 10$^6$, respectively.
Figure 8: Calculated limb intensity of the N\textsubscript{2} VK (0, 6) band at different solar zenith angles and for the VK (0, 5) and (0, 7) at SZA = 45° for the standard case. Lines with symbols (open squares, SZA = 8°–36°; open circles, SZA = 36°–64°) represent the averaged observed value of the VK (0, 6) band for solar longitude (Ls) between 100° and 171° taken from Leblanc et al. (2007). The calculated intensities, when the N\textsubscript{2} density is reduced by a factor of 3, are also shown.

Figure 9: The variation of the intensity of the N\textsubscript{2} VK (0, 6) emission with respect to solar zenith angle. The observed intensity of the VK (0, 6) band is taken from Figure 2 of Leblanc et al. (2007). The calculated intensity is averaged-value between 120 and 170 km for the standard case with N\textsubscript{2} density in the atmosphere reduced by a factor of 3.
Figure 10: Intensity variation of the N$_2$ VK (0, 6) band with respect to solar index F10.7 (W/m$^2$/Hz) at Mars (scaled from the measured value at Earth). The observed intensity of the VK (0, 6) band is taken from Figure 3 of Leblanc et al. (2007). The calculated intensity is averaged-value between 120 and 170 km for the standard case with N$_2$ density in the atmosphere reduced by a factor of 3.

Figure 11: The calculated limb intensity of the N$_2$ VK (0, 6) band at SZA = 20°. The observed values are taken from Leblanc et al. (2007). The calculated intensities are shown for the model atmospheres of Fox (2004) (when the density of N$_2$ is reduced by a factor of 2.5) and Krasnopolsky (2002) (the N$_2$ density reduced by a factor of 2.1). The intensity calculated by using the electron impact cross sections of Johnson et al. (2005) is shown when the N$_2$ density is reduced by a factor of 2.