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THE SIMULATION OF VIBRATIONAL POPULATIONS OF ELECTRONICALLY EXCITED N_2 IN TITAN'S UPPER ATMOSPHERE DURING PRECIPITATIONS OF HIGH-ENERGETIC PARTICLES

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Abstract. We study the electronic kinetics of singlet molecular nitrogen in Titan's upper atmosphere during precipitations of high-energetic particles. Both radiative processes and processes of electron excitation energy transfer during inelastic collisions with N_2 and CH_4 molecules were considered in the calculation of vibrational populations of electronically excited singlet states $a'^1\Sigma_u^-$, $a^1\Pi_g$, $w^1\Delta_u$ of molecular nitrogen in the upper atmosphere of Titan. It is shown that the calculated volume emission intensities of the Lyman-Birge-Hopfield bands correlate with the profiles of the ion production rate in the atmosphere of Titan during the considered cases of electron precipitation for considered interval of the energies 30-1000 eV of magnetospheric electrons. This fact is explained by the negligible contribution of collisional processes to the vibrational populations $a^1\Pi_g(v'=0\text{-}6)$ in the considered range of heights above 900 km.

Introduction

Molecular nitrogen N_2 is the major molecular gas in the atmospheres of Titan, Triton and Pluto. The interaction of high-energetic solar UV photons, magnetospheric particles and cosmic rays with atmospheric molecules causes the production of fluxes of free electrons in their atmospheres during processes of ionisation [*Campbell and Brunger*, 2016]. Produced free electrons excite different singlet states of N_2 in the inelastic collisions:

$$e + N_2(X^1\Sigma_g^+, v=0) \rightarrow N_2(a'^1\Sigma_u^-,\ a^1\Pi_g,\ w^1\Delta_u;\ v\geq 0) + e. \tag{1}$$

Spontaneous radiative transitions from the excited state $a^1\Pi_g$ to the ground state $X^1\Sigma_g^+$ in the nitrogen molecule

$$N_2(a^1\Pi_g, v') \rightarrow N_2(X^1\Sigma_g^+, v'') + h\nu_{LBH} \tag{2}$$

cause the emission of the Lyman-Birge-Hopfield (LBH) bands, which are located in the far ultraviolet region (120-200 nm) of the emission spectrum of Titan's atmosphere. Experimental measurements of the emission spectra of the upper atmosphere of Titan [*Ajello et al.*, 2008; *Stevens et al.*, 2011; *Ajello et al.*, 2012; *Weat et al.*, 2012] have shown the presence of Lyman-Birge-Hopfield bands in the far ultraviolet region.

The main aim of this work is to study the main processes related with the kinetics of singlet electronically excited states $a'^1\Sigma_u^-$, $a^1\Pi_g$, $w^1\Delta_u$ of molecular nitrogen in the upper atmosphere of Titan, as well as to calculate the volume and column intensities of the Lyman-Birge-Hopfield bands 146.4, 138.4, 135.4, 132.5 nm of molecular nitrogen during the precipitation of electrons with energies of 30-1000 eV from the magnetosphere of Saturn into the atmosphere of Titan.

The electronic kinetics of singlet electronically excited N_2 in Titan's atmosphere

In addition to spontaneous transitions (2) with emission of LBH bands it is also necessary to take into account the emission of infrared bands of two McFarlane (McF) systems [*Gilmore et al.*, 1992]

$$N_2(w^1\Delta_u, v') \leftrightarrow N_2(a^1\Pi_g, v'') + h\nu_{McF}\ , \tag{3a}$$

$$N_2(a'^1\Sigma_u^-, v') \leftrightarrow N_2(a^1\Pi_g, v'') + h\nu_{McF}\ , \tag{3b}$$

as well as spontaneous transitions (with the emissions of the Ogawa-Tanaka-Wilkinson-Mulliken (OTWM) bands) [*Casassa and Golde*, 1979]

$$N_2(a^1\Pi_g, v') \rightarrow N_2(X^1\Sigma_g^+, v'') + h\nu_{OTWM}\ . \tag{4}$$

When we calculate the vibrational populations of electronically excited singlet states of molecular nitrogen in the atmosphere of Titan at altitudes where the radiative and collisional lifetimes of the states are comparable, it is necessary to take into account both intramolecular and intermolecular processes of the transfer of electronic excitation energy in inelastic molecular collisions with N_2 molecules:

$$N_2(a'^1\Sigma_u^-,\ w^1\Delta_u; v') + N_2 \rightarrow N_2(a^1\Pi_g, v'') + N_2\ , \tag{5a}$$

$$N_2(a^1\Pi_g, v') + N_2 \rightarrow N_2(a'^1\Sigma_u^-,\ w^1\Delta_u; v'') + N_2\ , \tag{5b}$$

$$N_2(Y, v') + N_2(X^1\Sigma_g^+, v=0) \rightarrow N_2(X^1\Sigma_g^+, v^*\geq 0) + N_2(Z, v'')\ , \tag{6}$$

where Y and Z mean any singlet state from the $a'^1\Sigma_u^-$, $a^1\Pi_g$, $w^1\Delta_u$ states. The results of the calculation of the quenching constants for different vibrational levels of the singlet states in inelastic interactions with N_2 molecules (5a, 5b, 6) was presented in [*Kirillov*, 2011a; *Kirillov*, 2011b] where Landau-Zener and Rosen-Zener quantum chemical approximations were applied.

In addition to the collisions with nitrogen molecules (5a, 5b, 6), it is necessary to take into account the inelastic interaction with CH_4 methane molecules, since the relative concentrations of methane at altitudes in the upper and middle atmosphere of Titan is about 1.5% [*Vuitton et al.*, 2019]. Therefore, when we consider the electronic kinetics of the singlet states, it is necessary to take into account the quenching in collisions with CH_4 molecules

$$N_2(a'^1\Sigma_u^-,\ a^1\Pi_g,\ w^1\Delta_u; v') + CH_4 \rightarrow \text{products}\ . \tag{7}$$

Moreover, as shown by measurements in [*Umemoto et al.*, 2002], the dominant channel of inelastic interaction (7) is the process of dissociation of the CH_4 molecule with the formation of H atoms. In this case, the rates of interaction of singlet molecular nitrogen with methane molecules are close to gas kinetic values. In the calculations, we assume for an even ("gerade") state the constant $k_7(a^1\Pi_g)=5.2\cdot10^{-10}$ cm^{3}s^{-1}, measured in [*Marinelli et al.*, 1989] for $N_2(a^1\Pi_g, v'=0)$, for odd ("ungerade") states $a'^1\Sigma_u^-$ and $w^1\Delta_u$ constants $k_7(a'^1\Sigma_u^-)=k_7(w^1\Delta_u)=2.4\cdot10^{-10}$ cm^{3}s^{-1}, similarly measured in [*Umemoto et al.*, 2002] for $N_2(a'^1\Sigma_u^-, v'=0)$ and consistent with the results of measurements in [*Piper*, 1987] $3.0\cdot10^{-10}$ cm^{3}s^{-1}. Interaction with other small components as H_2 and CO can be neglected, since their concentrations are much lower than the concentrations of methane CH_4. Moreover, the rates of the interaction of the minor components are less than gas-kinetic values.

The calculation of the emission intensities of the Lyman-Birge-Hopfield bands

To calculate the emission intensities of the Lyman-Birge-Hopfield bands in the Titan's atmosphere, we apply the solution of the system of equations:

$$\begin{aligned} &Q^Y q_{0v'}^{XY} + \sum_{v''} A_{v''v'}^{aY} N_{v''}^a + \sum_{v''} k^{*aY}_{v''v'} N_{v''}^a [N_2] + \sum_{Z,v''} k^{**ZY}_{v''v'} N_{v''}^Z [N_2] + \sum_{v''} k^{**aY}_{v''v'} N_{v''}^a [N_2] \\ &= \left\{ \sum_{v''} A_{v'v''}^{Ya} + A^{*Y}_{v'} + \sum_{v''} k^{*Ya}_{v'v''} [N_2] + \sum_{Z,v''} k^{**YZ}_{v'v''} [N_2] + \sum_{v''} k^{**Ya}_{v'v''} [N_2] + 2.8\cdot10^{-10}[CH_4] \right\} N_{v'}^Y \end{aligned} , \tag{8a}$$

$$\begin{aligned} &Q^a q_{0v'}^{Xa} + \sum_{Y,v''} A_{v''v'}^{Ya} N_{v''}^Y + \sum_{Y,v''} k^{*Ya}_{v''v'} N_{v''}^Y [N_2] + \sum_{Y,v''} k^{**Ya}_{v''v'} N_{v''}^Y [N_2] + \sum_{v''} k^{**aa}_{v''v'} N_{v''}^a [N_2] = \\ &= \left\{ \sum_{Y,v''} A_{v'v''}^{aY} + \sum_{Y,v''} k^{*aY}_{v'v''} [N_2] + \sum_{Y,v''} k^{**aY}_{v'v''} [N_2] + \sum_{v''} k^{**aa}_{v'v''} [N_2] + 5.2\cdot10^{-10}[CH_4] \right\} N_{v'}^a \end{aligned} , \tag{8b}$$

where Y and Z mean the odd states $a'^1\Sigma_u^-$ and $w^1\Delta_u$; Q^Y, Q^a are the rates of the excitation of Y, $a^1\Pi_g$ states, respectively; A is the Einstein coefficient for all mentioned spontaneous transitions; k^* and k^{**} mean the rate constants of intramolecular (5a, 5b) and intermolecular (6) energy transfer processes, respectively; $A^{*Y}_{v'}$ is equal to the emission probability for transitions with emission of the Ogawa-Tanaka-Wilkinson-Mulliken bands in the case of the $a'^1\Sigma_u^-$ state [*Casassa and Golde*, 1979] and $A^{*Y}_{v'}=0$ for the $w^1\Delta_u$ state. In addition, for the lower vibrational level $v'=0$ of the $a'^1\Sigma_u^-$ state, it is necessary to take into account the quenching in collisions with N_2 molecules with the formation of the $B^3\Pi_g$ triplet state and the interaction rate constant equal to $2.0\cdot10^{-13}$ cm^{3}s^{-1} [*Kirillov*, 2011b; *Umemoto et al.*, 2002].

The data of the Titan's ionosphere obtained from the Cassini spacecraft on October 26, 2004 and April 16, 2005 are analyzed in [*Cravens et al.*, 2005; *Agren et al.*, 2007]. The authors of [*Cravens et al.*, 2005; *Agren et al.*, 2007] have presented the rates of ion production in the atmosphere of Titan during the precipitation of electrons from the Saturn's magnetosphere. We use the data from [*Cravens et al.*, 2005; *Agren et al.*, 2007] for electron energies of 30 eV - 1000 eV. To calculate the rates of the excitation of electronically excited states of molecular nitrogen during the precipitation of high-energy electrons from the magnetosphere of Saturn, we will use the method of degradation spectra of electrons in molecular nitrogen N_2 [*Konovalov*, 1993].

Figure 1 shows profiles of volume emission intensities of the Lyman-Birge-Hopfield bands at 146.4, 138.4, 135.4, and 132.5 nm calculated according to (8b) for electrons with energies E=30 eV and flux $F=7.9\cdot10^5$ el/cm$^2\cdot$s. The emission of these four bands is associated with spontaneous radiative transitions (2) $v'=1\rightarrow v''=1$, $v'=2\rightarrow v''=0$, $v'=3\rightarrow v''=0$ and $v'=4\rightarrow v''=0$, respectively. The results of similar calculations for E=200 eV, $F=1.3\cdot10^5$ el/cm$^2\cdot$s and E=1000 eV, $F=2.4\cdot10^4$ el/cm$^2\cdot$s are shown in Figures 2 and 3, respectively.

It is seen from the presented figures, the energy losses of electrons precipitating into the Titan's atmosphere are mainly at altitudes above 900 km, where concentrations of molecular nitrogen $[N_2]<10^{11}$ cm^{-3}. Since the radiative lifetimes of all vibrational levels v'=0-6 of the $a^1\Pi_g$ state are of the order of 60 microseconds [*Gilmore et al.*, 1992], collisional processes can be neglected at the altitudes of the upper atmosphere of Titan in the calculations of the concentrations $a^1\Pi_g(v'=0\text{-}6)$. Similarly, for all the considered levels of the $w^1\Delta_u$ state, the radiative lifetimes are less than 1 millisecond [*Gilmore et al.*, 1992]. Therefore, collisional processes in the considered interval of heights can also be neglected for the $w^1\Delta_u$ state. For the lower two vibrational levels v'=0,1 of the $a'^1\Sigma_u^-$ state, the radiative lifetimes are of the order of 20 milliseconds [*Casassa and Golde*, 1979; *Gilmore et al.*, 1992], but the quenching rate constants have low values [*Kirillov*, 2011a, 2011b]. Therefore, the quenching processes become effective at altitudes less than 800 km, this means for the precipitation of more energetic electrons or other charged particles. It is seen from Figures 1-3, the profiles of volume emission intensities of all four Lyman-Birge-Hopfield bands practically correlate with the profiles of the ion production rate in the atmosphere of Titan for all considered cases of electron precipitation [*Cravens et al.*, 2005; *Agren et al.*, 2007].

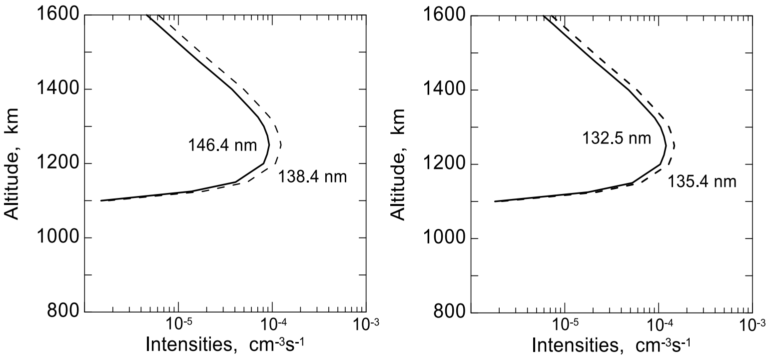

Figure 1. Profiles of volume emission intensities of the Lyman-Birge-Hopfield bands at 146.4, 138.4, 135.4, 132.5 nm calculated according to (8b) for electrons with energies E=30 eV and flux F=7.9·10^5 el/cm^2·s.

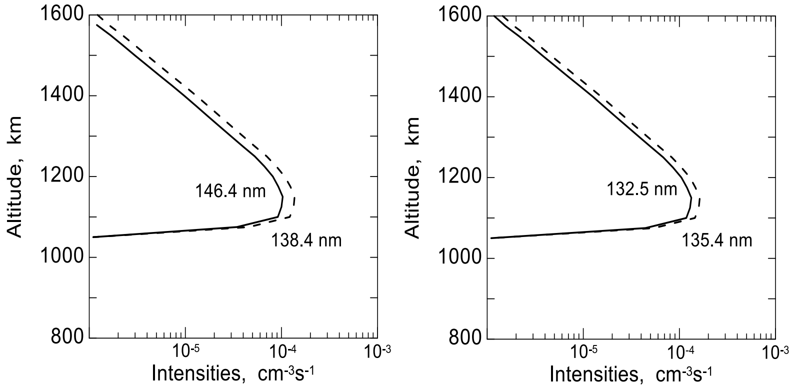

Figure 2. Profiles of volume emission intensities of the Lyman-Birge-Hopfield bands at 146.4, 138.4, 135.4, 132.5 nm calculated according to (8b) for electrons with energies E=200 eV and flux F=1.3·10^5 el/cm^2·s.

Conclusions

Calculations of the volume and integral emission intensities of the Lyman-Birge-Hopfield bands at 146.4, 138.4, 135.4, and 132.5 nm of molecular nitrogen in the upper atmosphere of Titan during the precipitation of electrons with an energy of 30-1000 eV from the magnetosphere of Saturn have been made. Both radiative processes and processes of electron excitation energy transfer during inelastic collisions with N_2 and CH_4 molecules were considered in the calculation of vibrational populations of electronically excited singlet states $a'^1\Sigma_u^-$, $a^1\Pi_g$, $w^1\Delta_u$ of molecular nitrogen in the upper atmosphere of Titan. It is shown that the calculated volume emission intensities of the Lyman-Birge-Hopfield bands correlate with the profiles of the ion production rate in the atmosphere of Titan during the considered cases of electron precipitation [*Cravens et al.*, 2005; *Agren et al.*, 2007] for considered interval of the energies 30-1000 eV of magnetospheric electrons. This fact is explained by the negligible contribution of collisional processes to the vibrational populations $a^1\Pi_g(v'=0\text{-}6)$ in the considered range of heights above 900 km.

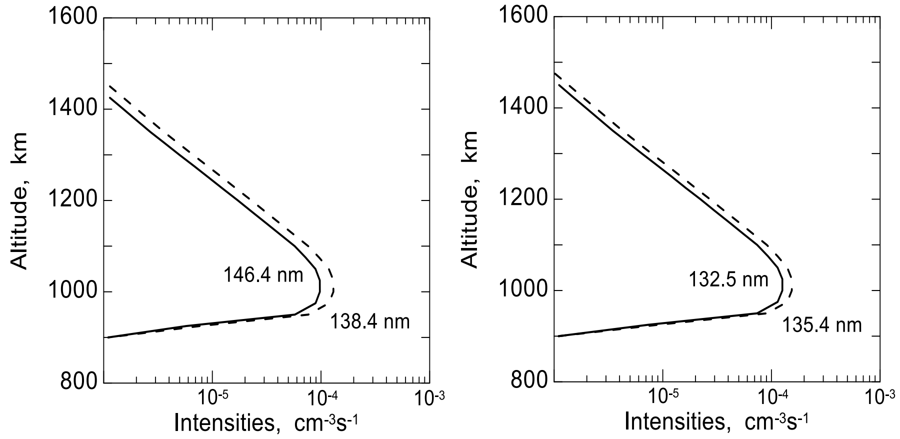

Figure 3. Profiles of volume emission intensities of the Lyman-Birge-Hopfield bands at 146.4, 138.4, 135.4, 132.5 nm calculated according to (8b) for electrons with energies E=1000 eV and flux F=2.4·10^4 el/cm^2·s.

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