"Physics of Auroral Phenomena", Proc. XLV Annual Seminar, Apatity, pp. 130-135, 2022

Polar
Geophysical
Institute

DOI: 10.51981/2588-0039.2022.45.031

ELECTRONIC KINETICS OF MOLECULAR NITROGEN IN THE MIDDLE ATMOSPHERES OF TITAN DURING PRECIPITATIONS OF HIGH-ENERGETIC PARTICLES

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Abstract. We study the electronic kinetics of molecular nitrogen in the middle atmospheres of Titan during precipitations of high-energetic particles. The Titan's atmosphere is considered as the mixture of N_2-CH_4-H_2-CO gases with admixtures of hydrocarbons. The role of molecular inelastic collisions in intramolecular and intermolecular electron energy transfer processes is investigated. It is shown that inelastic molecular collisions influence on vibrational populations of metastable molecular nitrogen at the altitudes of the middle atmospheres of the planet. The important role of metastable molecular nitrogen in the production of radicals is shown.

1. Introduction

Inelastic interaction of high-energy particles and photoelectrons with N_2 molecules in the Titan's atmospheres leads to the excitation of triplet electronically excited states of molecular nitrogen. Cosmic ray radiation is the main mechanism of ionization and dissociation processes in the middle and lower atmosphere of Titan (*Capone et al.*, 1980, 1983; *Molina-Cuberos et al.*, 1999). Cosmic rays having very high penetration power penetrate deep into the Titan's atmosphere in comparison with solar photons and electrons from Saturn's magnetosphere. Therefore galactic cosmic rays are the source of ionization of the atmosphere at lower altitudes and produce fluxes of secondary electrons in the ionization processes. Moreover, produced secondary electrons interact with atmospheric molecular nitrogen exciting different triplet electronic states of N_2 molecules.

Kirillov (2011) has studied vibrational populations of the $A^3\Sigma_u^+$ state of molecular nitrogen in the mixture N_2-O_2 for conditions of laboratory discharge at O_2 admixtures 0-20%. He has shown that the role of inelastic molecular collisions in the kinetics of N_2 triplet and singlet states is enhanced with an increase of N_2 concentrations. Therefore there is strong dependence of the vibrational populations on atmospheric density in pure nitrogen. Moreover an increase in the N_2 density can lead to significant influence of electronically excited nitrogen molecule on radiational balance of N_2-rich atmosphere. *Kirillov et al.* (2017) and *Kirillov* (2020) have considered the processes of energy transfer from metastable molecular nitrogen $N_2(A^3\Sigma_u^+)$ to carbon monoxide in the atmospheres of Titan, Triton, and Pluto (as a mixture of N_2–CH_4–CO gases). It was shown numerically for the first time that the contribution of $N_2(A^3\Sigma_u^+)$ to the formation of electronically excited carbon monoxide $CO(a^3\Pi)$ increases significantly with increasing density in the atmospheres of Titan, Triton, and Pluto, and becomes predominant for the lower vibrational levels of $CO(a^3\Pi)$.

Main aim of the paper is the study of electronic kinetics of N_2 triplet states in the Titan's middle atmosphere (the mixture N_2-CH_4-H_2-CO) during the precipitation of cosmic rays taking into account molecular collision processes at these altitudes. We will consider vibrational populations of N_2 triplet states at different altitudes of the Titan's atmosphere. Also we will show the influence of the inelastic collisions of metastable $N_2(A^3\Sigma_u^+)$ molecules with acetylene, ethylene molecules on the production of H atoms and C_2H, C_2H_3 radicals.

2. The production and quenching mechanisms of N_2 triplet states

Kirillov (2008, 2011, 2016, 2019) has shown that intramolecular and intermolecular electron energy transfers play a very important role in the processes of the electronic quenching of electronically excited nitrogen $N_2(A^3\Sigma_u^+, B^3\Pi_g, W^3\Delta_u, B'^3\Sigma_u^-, C^3\Pi_u)$ in the collisions with N_2 molecules. Good agreement of calculated rate coefficients with a few available experimental data was obtained in those papers.

We consider here the excitation of five triplet electronic states

$$e + N_2(X^1\Sigma_g^+,v=0) \quad N_2(A^3\Sigma_u^+,v'=0\text{-}29) + e \tag{1a}$$

$$N_2(B^3\Pi_g,v'=0\text{-}12) + e \tag{1b}$$

$$N_2(W^3\Delta_u,v'=0\text{-}21) + e \tag{1c}$$

$$N_2(B'^3\Sigma_u^-,v'=0\text{-}15) + e \tag{1d}$$

$$N_2(C^3\Pi_u,v'=0\text{-}4) + e \tag{1e}$$

in the collisions of $N_2(X^1\Sigma_g^+, v=0)$ with high-energetic secondary electrons produced in the lower and middle atmosphere of Titan during cosmic ray precipitation. We believe that the rate of the excitation of any vibrational level v' of the states $Y=A^3\Sigma_u^+$, $B^3\Pi_g$, $W^3\Delta_u$, $B'^3\Sigma_u^-$, $C^3\Pi_u$ is proportional to the Franck-Condon factor $q_{0v'}^{XY}$ of the transition $X^1\Sigma_g^+, v=0 \rightarrow Y, v'$. The sums of the Franck-Condon factors $q_{0v'}^{XY}$ from $v'=0$ to upper considered value of vibrational levels are >0.99 for the $A^3\Sigma_u^+$, $W^3\Delta_u$, $C^3\Pi_u$ states, and >0.92 for the $B'^3\Sigma_u^-$ state (*Gilmore et al.*, 1992). The predissociation processes are related with the $B^3\Pi_g(v'>12)$ molecules.

The electronically excited triplet nitrogen molecules radiate the bands of Vegard-Kaplan (VK), First Positive (1PG), Wu-Benesch (WB), Infrared Afterglow (IRAG), Second Positive (2PG) systems:

$$N_2(A^3\Sigma_u^+, v') \rightarrow N_2(X^1\Sigma_g^+, v'') + h\nu_{VK} \ , \tag{2a}$$

$$N_2(B^3\Pi_g, v') \leftrightarrow N_2(A^3\Sigma_u^+, v'') + h\nu_{1PG} \ , \tag{2b}$$

$$N_2(W^3\Delta_u, v') \leftrightarrow N_2(B^3\Pi_g, v'') + h\nu_{WB} \ , \tag{2c}$$

$$N_2(B'^3\Sigma_u^-, v') \leftrightarrow N_2(B^3\Pi_g, v'') + h\nu_{IRAG} \ , \tag{2d}$$

$$N_2(C^3\Pi_u, v') \rightarrow N_2(B^3\Pi_g, v'') + h\nu_{2PG} \ . \tag{2e}$$

Einstein coefficients for the radiational transitions (2a-2e) are taken according to (*Gilmore et al.*, 1992).

Moreover, for conditions of high pressure at the altitudes of the lower and middle Titan's atmosphere it is necessary to include processes of the electronic quenching of all triplet states in molecular collisions. In the case of the triplet states of molecular nitrogen we consider the following intramolecular processes:

$$N_2(Y, v') + N_2 \rightarrow N_2(B^3\Pi_g, v'') + N_2 \ , \tag{3a}$$

$$N_2(B^3\Pi_g, v') + N_2 \rightarrow N_2(Y; v'') + N_2 \tag{3b}$$

with $Y = A^3\Sigma_u^+$, $W^3\Delta_u$, $B'^3\Sigma_u^-$ and intermolecular processes:

$$N_2(Y, v') + N_2(X^1\Sigma_g^+, v=0) \rightarrow N_2(X^1\Sigma_g^+, v^* \geq 0) + N_2(Z, B^3\Pi_g; v'') \ , \tag{4a}$$

$$N_2(B^3\Pi_g, v') + N_2(X^1\Sigma_g^+, v=0) \rightarrow N_2(X^1\Sigma_g^+, v^* \geq 0) + N_2(Z, B^3\Pi_g; v'') \ , \tag{4b}$$

$$N_2(C^3\Pi_u, v') + N_2(X^1\Sigma_g^+, v=0) \rightarrow N_2(X^1\Sigma_g^+, v^* \geq 0) + N_2(Z, B^3\Pi_g, C^3\Pi_u; v'') \tag{4c}$$

with Y and $Z = A^3\Sigma_u^+$, $W^3\Delta_u$, $B'^3\Sigma_u^-$ for the inelastic collisions with N_2 molecules.

The quenching rate coefficients for the processes (2a,2b,3a-3c) have been calculated by *Kirillov* (2008, 2016, 2019). We apply here the calculated in those papers constants.

Also at the altitudes of the lower and middle Titan's atmosphere it is necessary to take into account molecular collisions with CH_4 molecules. *Golde et al.* (1989) have received the rates for $v'=1$-6 in good agreement with the results by *Thomas et al.* (1983). Therefore we believe the vibrational relaxation of $N_2(A^3\Sigma_u^+, v'=1\text{-}6)$ in inelastic collisions with CH_4 molecule

$$N_2(A^3\Sigma_u^+, v'=1\text{-}6) + CH_4 \rightarrow N_2(A^3\Sigma_u^+, v''=v'-1) + CH_4 \tag{5a}$$

is the dominating mechanism of the inelastic interaction for vibrational levels $v'>0$. The electronic quenching by CH_4 with the transfer of the excitation energy on the methane molecule with the dissociation (*Sharipov et al.*, 2016)

$$N_2(A^3\Sigma_u^+, v'=0) + CH_4 \rightarrow N_2(X^1\Sigma_g^+, v'') + CH_3 + H \ , \ \text{products} \tag{5b}$$

is considered here as the quenching mechanism for vibrational level $v'=0$. The quenching rate coefficients for the processes (5a) and (5b) are taken according to (*Golde et al.*, 1989) and (*Slanger et al.*, 1973), respectively.

Piper (1992) has studied the quenching of $N_2(B^3\Pi_g, v'=1\text{-}12)$ by CH_4 molecules. Therefore we suggest for the quenching

$$N_2(B^3\Pi_g, v') + CH_4 \rightarrow N_2(X^1\Sigma_g^+, v'') + CH_3 + H \ , \ \text{products} \tag{6}$$

with an averaged rate constant $k_6=2.8 \cdot 10^{-10}$ cm^{3}s^{-1} for all $v'=1$-12 vibrational levels of the $B^3\Pi_g$ state and the energy transfer process (6) can cause the excitation of repulsive states of CH_4 with the dissociation of methane molecules. The same is suggested for the inelastic collisions:

$$N_2(Y, v') + CH_4 \rightarrow N_2^* + CH_3 + H \ , \ \text{products} \tag{7}$$

where $Y = W^3\Delta_u(v'=1\text{-}21)$, $B'^3\Sigma_u^-(v'=0\text{-}15)$, $C^3\Pi_u(v'=0\text{-}4)$; N_2^* means electronically and vibrationally excited nitrogen molecules and $k_7=k_6$. The quenching rate coefficients $k_6=k_7=2.0 \cdot 10^{-11}$ cm^{3}s^{-1} of the processes (6) and (7) for the $N_2(B^3\Pi_g, v'=0)$ and $N_2(W^3\Delta_u, v'=0)$ states are taken according to *Umemoto* (2003).

Kirillov et al. (2017) have shown very important role of inelastic collisions with CO molecules in the upper Titan's atmosphere for lowest vibrational levels of the $A^3\Sigma_u^+$ state. Therefore we take into account the collisions

$$N_2(A^3\Sigma_u^+, v') + CO(X^1\Sigma^+, v=0) \rightarrow N_2(X^1\Sigma_g^+, v^* \geq 0) + CO(a^3\Pi, v'') \tag{8}$$

with the rate coefficient according to (*Kirillov*, 2016; *Kirillov et al.*, 2017). We neglect collisions with hydrogen molecules because the concentrations [H_2] are much less than [CH_4] (*Bezard et al.*, 2014; *Vuitton et al.*, 2019) and the quenching rate coefficients for most N_2 states are of the order of gas-kinetic values. The collisions of $N_2(A^3\Sigma_u^+)$ and H_2 have very small values of the quenching rate coefficients (*Herron*, 1999). Therefore we take into account only the collisions (8) with CO molecules.

Since the concentrations of minor atmospheric components at the altitudes of the lower, middle and upper Titan's atmosphere are significantly less than concentrations of N_2, CH_4, H_2 and CO (*Bezard et al.*, 2014; *Vuitton et al.*, 2019), in the first approximation we can be consider the collisional part of electronic kinetics of N_2 molecules in the frames of N_2^*–N_2, N_2^*–CH_4, N_2^*–H_2, N_2^*–CO collisions, where N_2^* means electronically excited nitrogen molecules. Nevertheless, we will make refinements in the model of molecular inelastic collisions influencing on the N_2 electronic kinetics.

3. Vibrational populations of electronically excited $N_2(A^3\Sigma_u^+)$ in the Titan's middle atmosphere

To calculate vibrational populations *N* of the $A^3\Sigma_u^+$, $B^3\Pi_g$, $W^3\Delta_u$, $B'^3\Sigma_u^-$, $C^3\Pi_u$ triplet states we apply the following equations

$$\begin{aligned} &Q^A q_{0v'}^{XA} + \sum_{v''} A_{v''v'}^{BA} N_{v''}^B + \sum_{v''} k^{*BA}_{v''v'} N_{v''}^B [N_2] + \sum_{Z=A,B,W,B',C;v''} k^{**ZA}_{v''v'} N_{v''}^Z [N_2] = \\ &= \left\{ \sum_{v''} A_{v'v''}^{AB} + \sum_{v''} A_{v'v''}^{AX} + \sum_{v''} k^{*AB}_{v'v''}[N_2] + \sum_{Z=A,B,W,B';v''} k^{**AZ}_{v'v''}[N_2] + k^{**A}_{v'}[CH_4] + k_{14}(v')[CO] + k_{MAC}[MAC] \right\} N_{v'}^A \end{aligned} \tag{9a}$$

$$\begin{aligned} &Q^B q_{0v'}^{XB} + \sum_{Z=A,W,B',C;v''} A_{v''v'}^{ZB} N_{v''}^Z + \sum_{Z=A,W,B';v''} k^{*ZB}_{v''v'} N_{v''}^Z [N_2] + \sum_{Z=A,B,W,B',C;v''} k^{**ZB}_{v''v'} N_{v''}^Z [N_2] = \\ &= \left\{ \sum_{Z=A,W,B';v''} A_{v'v''}^{BZ} + \sum_{Z=A,W,B';v''} k^{*BZ}_{v'v''}[N_2] + \sum_{Z=A,B,W,B',C;v''} k^{**BZ}_{v'v''}[N_2] + k_{10}(v')[CH_4] \right\} N_{v'}^B \end{aligned} \tag{9b}$$

$$\begin{aligned} &Q^Y q_{0v'}^{XY} + \sum_{v''} A_{v''v'}^{BY} N_{v''}^B + \sum_{v''} k^{*BY}_{v''v'} N_{v''}^B [N_2] + \sum_{Z=A,B,W,B',C;v''} k^{**ZY}_{v''v'} N_{v''}^Z [N_2] = \\ &= \left\{ \sum_{v''} A_{v'v''}^{YB} + \sum_{v''} k^{*YB}_{v'v''}[N_2] + \sum_{Z=A,B,W,B';v''} k^{**YZ}_{v'v''}[N_2] + k_{11}(v')[CH_4] \right\} N_{v'}^Y \end{aligned} \tag{9c}$$

$$Q^C q_{0v'}^{XC} + \sum_{v''>v'} k^{**CC}_{v''v'} N_{v''}^C [N_2] = \left\{ \sum_{v''} A_{v'v''}^{CB} + \sum_{Z=A,B,W,B';v''} k^{**CZ}_{v'v''}[N_2] + \sum_{v''<v'} k^{**CC}_{v'v''}[N_2] + 2.8 \cdot 10^{-10}[CH_4] \right\} N_{v'}^C \tag{9d}$$

where Y=$W^3\Delta_u$, $B'^3\Sigma_u^-$; Q^A, Q^B, Q^Y, Q^C are production rates of the $A^3\Sigma_u^+$, $B^3\Pi_g$, *Y*-th, $C^3\Pi_u$ states, respectively; *A* are spontaneous radiational probabilities for the transitions (2b-2e); k^* and k^{**} mean the constants of intramolecular and intermolecular electron energy transfer processes, respectively; k_{MAC} means the rate coefficient of an interaction with minor atmospheric components (MAC) and the inclusion of the interaction is necessary when the characteristic collision time is comparable to the times of all components considered above. It should be noted that for the lowest vibrational level v=0 of the $A^3\Sigma_u^+$ state it is necessary to take into account collisions with acetylene C_2H_2 molecules.

We assume in our calculations that methane and carbon monoxide concentrations are related with N_2 concentrations by the ratios $[CH_4]=1.5\cdot10^{-2}\cdot[N_2]$ and $[CO]=5\cdot10^{-5}\cdot[N_2]$ (*Bezard et al.*, 2014; *Vuitton et al.*, 2019). The altitude profiles of calculated ionization rates in the lower and middle Titan's atmosphere during the interaction of cosmic particles with atmospheric components have been presented by *Molina-Cuberos et al.* (1999), *Vuitton et al.* (2019). We choose the altitude profile of N_2 ion production rates according to Fig. 18 by *Vuitton et al.* (2019) in our calculations.

The ionization rate $I(h)$ ($cm^{-3}s^{-1}$) at a given altitude *h* of the Titan's atmosphere can be expressed as

$$I(h) = \frac{1}{\varepsilon}\frac{\partial E}{\partial x}(h) \tag{10}$$

where ∂E is the mean energy loss in the atmospheric layer ∂x at depth *x* ($g\cdot cm^{-2}$), ε_{N2}^{ion} = 37 eV is the average energy necessary for the production of an ion pair in pure nitrogen (*Fox et al.*, 2008). The method of degradation spectra (*Fox and Victor*, 1988) was applied in the calculation of average energies ε necessary for the excitation of N_2 triplet states by produced energetic secondary electrons in pure nitrogen in the processes (1a-1e).

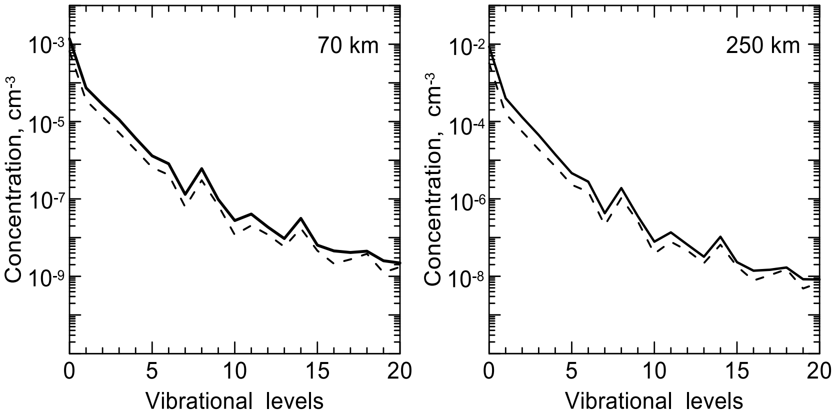

Figure 1. Vibrational populations of the $A^3\Sigma_u^+$ state of N_2 at the altitudes 70 and 250 km (solid lines). Contributions of direct excitation of the $A^3\Sigma_u^+$ state are shown as dashed lines.

The profile of N_2 ion production rates at the altitudes of 50-250 km of the Titan's middle atmosphere during the precipitation of cosmic rays is taken according to *Vuitton et al.* (2019). Vibrational populations of the $A^3\Sigma_u^+$ state of N_2 at the altitudes 70 and 250 km are shown in Fig. 1. Also the contributions of direct excitation of all triplet and singlet states in the vibrational populations are here presented.

4. The calculated contribution rates of $N_2(A^3\Sigma_u^+)$ in the production of C_2H and C_2H_3 radicals

We will consider here the influence of the interaction of electronically excited nitrogen molecules with methane, acetylene, ethylene molecules on the dissociation of the target molecules and the production of the C_2H and C_2H_3 radicals. To compare the contribution by electronically excited nitrogen molecules with the contribution by the cosmic rays we assume in the calculations that the cosmic ray energy loss on some minor atmospheric component (MAC) $\left(\frac{\partial E}{\partial x}\right)_{MAC}$ at the altitude *h* is related to the total energy loss $\frac{\partial E}{\partial x}$ by the ratio

$$\left(\frac{\partial E}{\partial x}\right)_{MAC}(h) = \frac{\partial E}{\partial x}(h) \cdot \frac{[MAC](h)}{[N_2](h)} \quad , \tag{11}$$

where [MAC] and $[N_2]$ are concentrations of minor atmospheric component and molecular nitrogen.

Umemoto (2007) has evaluated production yield of H atoms in the reactions of the $N_2(A^3\Sigma_u^+)$ metastable nitrogen with C_2H_2 and C_2H_4 molecules. He has received that the H-atom yields in the inelastic collisions are 0.52 and 0.30, respectively. It can be assumed that the main component in the active medium of Umemoto's experiment was $N_2(A^3\Sigma_u^+,v'\sim0)$ molecules, since collisional processes could lead to the accumulation of excitation energy at lowest vibrational levels.

We believe in our calculation that the main production channels of the H atoms are the reactions

$$N_2(A^3\Sigma_u^+) + C_2H_2 \rightarrow N_2(X^1\Sigma_g^+) + C_2H + H \ \text{, products} \ , \tag{13}$$

$$N_2(A^3\Sigma_u^+) + C_2H_4 \rightarrow N_2(X^1\Sigma_g^+) + C_2H_3 + H \ \text{, products} \ . \tag{14}$$

Also *Umemoto* (2007) has measured the total quenching rate coefficients for the collisions of $N_2(A^3\Sigma_u^+)$ with acetylene and ethylene molecules and his measured values $k_{13}=1.4\cdot10^{-10}$ cm^{3}s^{-1} and $k_{14}=0.97\cdot10^{-10}$ cm^{3}s^{-1} are in good agreements with all experimental results available in scientific literature (*Dutuit et al.*, 2013).

The results of the calculation for the profiles of production rates of the C_2H and C_2H_3 radicals are shown in Figs. 2 and 3. We assumed in our calculations that acetylene and ethylene concentrations are related with N_2 concentrations by the ratios $[C_2H_2]=4\cdot10^{-6}\cdot[N_2]$ and $[C_2H_4]=1.5\cdot10^{-7}\cdot[N_2]$ (*Bezard et al.*, 2014; *Vuitton et al.*, 2019). It should be noted that at the concentrations of acetylene the rates of the interaction of $N_2(A^3\Sigma_u^+,v'=0,1)$ with C_2H_2 molecules are comparable with the rates of the interaction with N_2, CH_4, CO.

The results of the influence of electronically excited N_2 on the C_2H and C_2H_3 production are compared with the production rates in the dissociation by secondary electrons

$$e + C_2H_2 \rightarrow C_2H + H + e \ , \tag{15}$$

$$e + C_2H_4 \rightarrow C_2H_3 + H + e \ . \tag{16}$$

To estimate the rates of the process (15) according to (11) we have used ε_{C2H2}^{ion} =26 eV (*Fox et al.*, 2008) and similar values of cross sections for ionization and dissociation (*Song et al.*, 2017). Therefore we use $\varepsilon_{C2H2}^{diss} = \varepsilon_{C2H2}^{ion}$ =26 eV. We assume the same for the case of collisions with ethylene molecules (16) and use $\varepsilon_{C2H4}^{diss} = \varepsilon_{C2H4}^{ion}$ =26 eV (*Fox et al.*, 2008) in the equation (11).

The comparison of contribution rates in Figs. 2 and 3 shows the domination of the reactions (13) and (14) in the productions of the C_2H and C_2H_3 radicals. It is seen that the contributions of the processes (13) and (14) in the productions of the C_2H and C_2H_3 radicals exceed on few orders of magnitudes than the contributions of the processes (15) and (16). Therefore the processes (13) and (14) have to be taken into account in a study of chemical kinetics in the Titan's middle atmosphere.

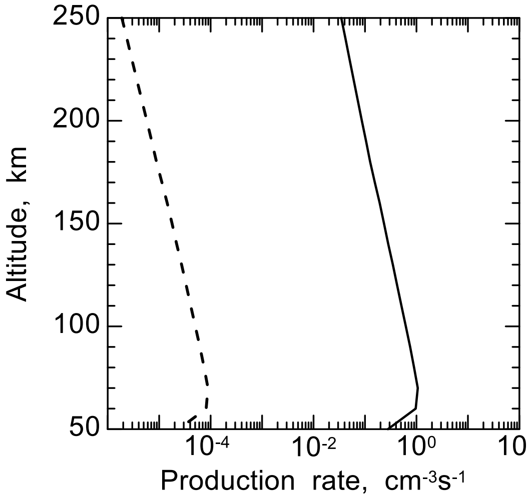

Figure 2. The calculated C_2H and H production rates at the altitudes 50-250 km: processes (13) and (15) are shown as solid and dashed lines, respectively.

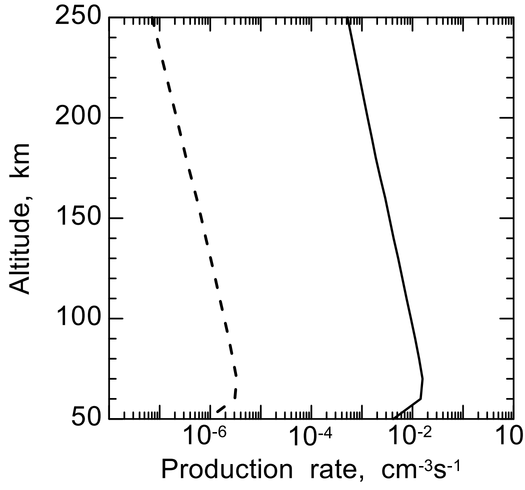

Figure 3. The calculated C_2H_3 and H production rates at the altitudes 50-250 km: processes (14) and (16) are shown as solid and dashed lines, respectively.

5. Conclusions

The electronic kinetics of $A^3\Sigma_u^+$, $B^3\Pi_g$, $W^3\Delta_u$, $B'^3\Sigma_u^-$, $C^3\Pi_u$ triplet states of N_2 in the Titan's middle atmosphere during the precipitation of cosmic rays is considered. Intramolecular and intermolecular electron energy transfers in inelastic collisions of electronically excited molecular nitrogen with N_2, CH_4, CO molecules are taken into account in the calculations. Vibrational populations of metastable electronically excited N_2 states are presented. The interaction of metastable electronically excited N_2 molecules with acetylene, ethylene molecules in the Titan's middle atmosphere at the altitudes of 50-250 km is studied. For the first time it is shown that there is a domination of the reactions (13) and (14) in the productions of the C_2H and C_2H_3 radicals. The contributions of the processes (13) and (14) in the productions of the C_2H and C_2H_3 radicals exceed on few orders of magnitudes than the contributions of processes (15) and (16) at all altitude range.

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