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THE STUDY OF KINETICS OF MOLECULAR NITROGEN IN THE STRATOSPHERE OF TITAN DURING PRECIPITATION OF GALACTIC COSMIC RAYS

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Abstract. We study the electronic kinetics of molecular nitrogen in the stratosphere of Titan during precipitation of galactic cosmic rays. The composition of Titan's atmosphere at the altitudes is considered as the mixture of N_2-CH_4-H_2-CO gases with admixtures of hydrocarbons. Special attention is paid to the investigation of the role of inelastic molecular collisions in the redistribution of the excitation energy between different molecular degrees of freedom. The inelastic intramolecular and intermolecular electron energy transfers during molecular collisions are taken into account in the calculation of vibrational populations of electronically excited states of N_2 at the altitudes of the stratosphere. The important role of electronically excited molecular nitrogen in the production of CH_3 radicals and H atoms is discussed.

1. Introduction

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. The radiation is the main mechanism of ionization and dissociation processes in the middle and lower atmosphere of Titan (*Molina-Cuberos et al.*, 1999). Galactic cosmic rays are the source of ionization of the atmosphere at lower altitudes and produce fluxes of secondary electrons in the ionization processes. *Kirillov et al.* (2023) have considered the excitation of triplet electronically excited states of molecular nitrogen by produced secondary electrons at the altitudes of the Titan's middle atmosphere and the influence of electronically excited N_2 on the production of C_2H and C_2H_3 radicals during inelastic collisions with C_2H_2 and C_2H_4 molecules.

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 $CO(a^3\Pi)$. Therefore there is very important role of electronically excited N_2 on the electronic kinetics of minor component CO and on chemical kinetics in the upper and middle atmosphere of Titan.

Main aim of the paper is the study of electronic kinetics of N_2 triplet and singlet 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. Also we will show the influence of the inelastic collisions of electronically excited N_2 molecules with methane molecules on the production of H atoms and CH_3 radicals.

2. The production and quenching mechanisms of N_2 triplet and singlet states

We consider here the excitation of five triplet electronic states

$$e + N_2(X^1\Sigma_g^+,v=0) \rightarrow N_2(A^3\Sigma_u^+,v'=0\text{-}29) + e \qquad (1a)$$
$$\rightarrow N_2(B^3\Pi_g,v'=0\text{-}12) + e \qquad (1b)$$
$$\rightarrow N_2(W^3\Delta_u,v'=0\text{-}21) + e \qquad (1c)$$
$$\rightarrow N_2(B'^3\Sigma_u^-,v'=0\text{-}15) + e \qquad (1d)$$
$$\rightarrow N_2(C^3\Pi_u,v'=0\text{-}4) + e \qquad (1e)$$

and the excitation of three singlet electronic states of molecular nitrogen

$$e + N_2(X^1\Sigma_g^+,v=0) \rightarrow N_2(a'^1\Sigma_u^-,v'=0\text{-}17) + e \qquad (2a)$$
$$\rightarrow N_2(a^1\Pi_g,v'=0\text{-}6) + e \qquad (2b)$$
$$\rightarrow N_2(w^1\Delta_u,v'=0\text{-}13) + e \qquad (2c)$$

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 $Y=A^3\Sigma_u^+$, $B^3\Pi_g$, $W^3\Delta_u$, $B'^3\Sigma_u^-$, $C^3\Pi_u$ and $Y=a'^1\Sigma_u^-$, $a^1\Pi_g$, $w^1\Delta_u$ is proportional to the Franck-Condon factor $q^{XY}_{0v'}$of the transition $X^1\Sigma_g^+,v=0 \rightarrow Y,v'$. The scheme of vibrational levels of triplet and singlet states of molecular nitrogen is presented in Figure 1.

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:

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

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

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

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

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

Einstein coefficients for the radiational transitions (3a-3e) are taken according to (*Gilmore et al.*, 1992) in this paper. The electronically excited singlet nitrogen molecules radiate the bands of Ogawa-Tanaka-Wilkinson-Mulliken (OTWM), Lyman-Birge-Hopfield (LBH) and MacFarlane (MF) systems:

$$N_2(a'^1\Sigma_u^-,v') \rightarrow N_2(X^1\Sigma_g^+,v'') + h\nu_{OTWM} \ , \quad (4a)$$

$$N_2(a^1\Pi_g,v') \rightarrow N_2(X^1\Sigma_g^+,v'') + h\nu_{LBH} \ , \quad (4b)$$

$$N_2(a^1\Pi_g,v') \leftrightarrow N_2(a'^1\Sigma_u^-,v'') + h\nu_{MF} \ , \quad (4c)$$

$$N_2(a^1\Pi_g,v') \leftrightarrow N_2(w^1\Delta_u,v'') + h\nu_{MF} \ . \quad (4d)$$

Einstein coefficients and radiational lifetimes for the radiational transitions (4a) and (4b-4d) are taken according to (*Casassa and Golde*, 1979) and (*Gilmore et al.*, 1992), respectively.

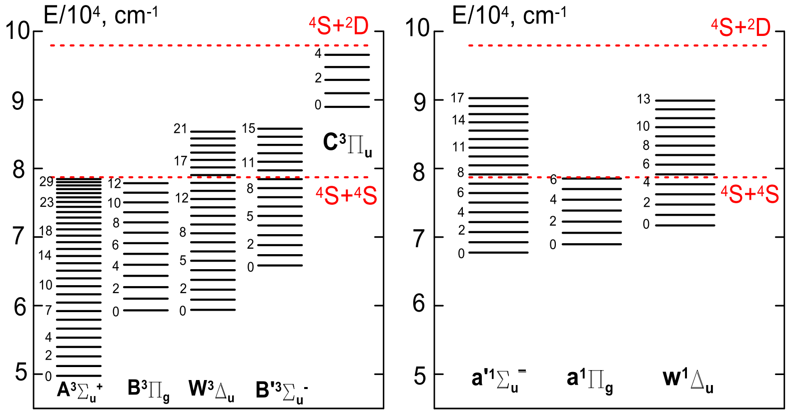

Figure1. The scheme of vibrational levels of N_2 triplet and singlet states.

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 and singlet states in molecular collisions. In the case of the triplet states of molecular nitrogen we consider the following intramolecular processes:

$$N_2(Y,v') + N_2 \rightarrow N_2(B^3\Pi_g,v'') + N_2 \ , \quad (5a)$$

$$N_2(B^3\Pi_g,v') + N_2 \rightarrow N_2(Y;v'') + N_2 \quad (5b)$$

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

$$N_2(Y,v') + N_2(X^1\Sigma_g^+,v=0) \rightarrow N_2(X^1\Sigma_g^+,v^*\geq 0) + N_2(Z,B^3\Pi_g;v'') \ , \quad (6a)$$

$$N_2(B^3\Pi_g,v') + N_2(X^1\Sigma_g^+,v=0) \rightarrow N_2(X^1\Sigma_g^+,v^*\geq 0) + N_2(Z,B^3\Pi_g;v'') \ . \quad (6b)$$

$$N_2(C^3\Pi_u,v') + N_2(X^1\Sigma_g^+,v=0) \rightarrow N_2(X^1\Sigma_g^+,v^*\geq 0) + N_2(Z,B^3\Pi_g,C^3\Pi_u;v'') \quad (6c)$$

with Y and $Z = A^3\Sigma_u^+$, $W^3\Delta_u$, $B'^3\Sigma_u^-$ for the inelastic collisions with N_2 molecules (*Kirillov*, 2023). In the case of the singlet states of molecular nitrogen we consider the following intramolecular processes:

$$N_2(Y,v') + N_2 \rightarrow N_2(a^1\Pi_g,v'') + N_2 \ , \quad (7a)$$

$$N_2(a^1\Pi_g,v') + N_2 \rightarrow N_2(Y;v'') + N_2 \quad (7b)$$

with Y = $a'^1\Sigma_u^-$, $w^1\Delta_u$ and intermolecular processes:

$$N_2(Y,v') + N_2(X^1\Sigma_g^+,v=0) \rightarrow N_2(X^1\Sigma_g^+,v^*\geq 0) + N_2(Z,a^1\Pi_g;v'') , \quad (8a)$$

$$N_2(a^1\Pi_g,v') + N_2(X^1\Sigma_g^+,v=0) \rightarrow N_2(X^1\Sigma_g^+,v^*\geq 0) + N_2(Z,a^1\Pi_g;v'') . \quad (8b)$$

with Y and Z = $a'^1\Sigma_u^-$, $w^1\Delta_u$ for the inelastic collisions with N_2 molecules. The quenching rate coefficients for the processes (5a,5b,6a-6c) and (7a,7b,8a,8b) have been calculated by *Kirillov* (2016, 2019) and by *Kirillov* (2011a, 2011b), respectively. We apply here the calculated constants in those papers.

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. The interaction

$$N_2(A^3\Sigma_u^+,v'=1\text{-}6) + CH_4 \rightarrow N_2(A^3\Sigma_u^+,v''=v'-1) + CH_4 \quad (9a)$$

is the dominating mechanism of the inelastic interaction for vibrational levels $v'>0$ (*Kirillov et al.*, 2023). The electronic quenching by CH_4 with the transfer of the excitation energy on the methane molecule with the dissociation (*Sharipov et al.*, 2016)

$$N_2(A^3\Sigma_u^+,v'=0) + CH_4 \rightarrow N_2(X^1\Sigma_g^+,v'') + CH_3 + H \text{ , products} \quad (9b)$$

is considered here as the quenching mechanism for vibrational level $v'=0$.

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

$$N_2(B^3\Pi_g,v') + CH_4 \rightarrow N_2(X^1\Sigma_g^+,v'') + CH_3 + H \text{ , products} \quad (10)$$

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

$$N_2(Y,v') + CH_4 \rightarrow N_2^* + CH_3 + H \text{ , products} \quad (11)$$

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 $k_{11}=k_{10}$. The quenching rate coefficients $k_{10}=k_{11}=2.0\cdot 10^{-11}$ cm^{3}s^{-1} of the processes (10) and (11) 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).

Piper (1987) and *Umemoto et al.* (2002) have studied the quenching of $N_2(a'^1\Sigma_u^-,v'=0)$ by CH_4 molecules. Both results of measured rate constant showed good agreement, therefore we suggest to take $k_{12}=2.9\cdot 10^{-10}$ cm^{3}s^{-1} according to (*Umemoto et al.*, 2002) for the collisions of "ungerade" electronically excited states

$$N_2(a'^1\Sigma_u^-, w^1\Delta_u,v'\geq 0) + CH_4 \rightarrow N_2(X^1\Sigma_g^+,v'') + CH_3 + H \text{ , products.} \quad (12)$$

Marinelli et al. (1989) have studied the quenching of $N_2(a^1\Pi_g,v'=0)$ by CH_4 molecules. We suggest to take $k_{13}=5.2\cdot 10^{-10}$ cm^{3}s^{-1} according to (*Marinelli et al.*, 1989) for the collisions

$$N_2(a^1\Pi_g,v'\geq 0) + CH_4 \rightarrow N_2(X^1\Sigma_g^+,v'') + CH_3 + H \text{ , products.} \quad (13)$$

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

$$N_2(A^3\Sigma_u^+,v') + CO(X^1\Sigma^+,v=0) \rightarrow N_2(X^1\Sigma_g^+,v^*\geq 0) + CO(a^3\Pi,v'') \quad (14)$$

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 (14) 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.

3. Vibrational populations of electronically excited N_2 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 equations from (*Kirillov et al.*, 2023). To calculate vibrational populations N of the $a'^1\Sigma_u^-$, $a^1\Pi_g$, $w^1\Delta_u$ singlet states we apply the following equations

$$Q^{Y} q_{0v'}^{XY} + \sum_{v''} A_{v''v'}^{aY} N_{v''}^{a} + \sum_{v''} k^{*aY}_{v''v'} N_{v''}^{a}[N_2] + \sum_{Z=a',a,w;v''} k^{**ZY}_{v''v'} N_{v''}^{Z}[N_2] =$$
$$= \left\{ \sum_{v''} A_{v'v''}^{Ya} + A^{*Y}_{v'} + \sum_{v''} k^{*Ya}_{v'v''}[N_2] + \sum_{Z=a',a,w;v''} k^{**YZ}_{v'v''}[N_2] + 2.8 \cdot 10^{-10}[CH_4] \right\} N_{v'}^{Y} \tag{15a}$$

$$Q^{a} q_{0v'}^{Xa} + \sum_{Y,v''} A_{v''v'}^{Ya} N_{v''}^{Y} + \sum_{Y,v''} k^{*Ya}_{v''v'} N_{v''}^{Y}[N_2] + \sum_{Y,v''} k^{**Ya}_{v''v'} N_{v''}^{Y}[N_2] + \sum_{v''} k^{**aa}_{v''v'} N_{v''}^{a}[N_2] =$$
$$= \left\{ \sum_{Y,v''} A_{v'v''}^{aY} + \sum_{Y,v''} k^{*aY}_{v'v''}[N_2] + \sum_{Y,v''} k^{**aY}_{v'v''}[N_2] + \sum_{v''} k^{**aa}_{v'v''}[N_2] + 5.2 \cdot 10^{-10}[CH_4] \right\} N_{v'}^{a} \tag{15b}$$

where $Y = a'^1\Sigma_u^-$, $w^1\Delta_u$; Q^Y, Q^a are production rates of the Y-th, $a^1\Pi_g$ states, respectively; A are spontaneous radiational probabilities for the transitions (4a-4d); k^* and k^{**} mean the constants of intramolecular and intermolecular electron energy transfer processes, respectively; $A^{*Y}_{v'}$ is equal to radiational probability for 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.

We assume in our calculations that methane and carbon monoxide concentrations are related with N_2 concentrations by the ratios $[CH_4] = 1.5 \cdot 10^{-2} \cdot [N_2]$ and $[CO] = 5 \cdot 10^{-5} \cdot [N_2]$ (*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

$$I(h) = \frac{1}{\varepsilon} \frac{\partial E}{\partial x}(h) \tag{16}$$

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).

4. The calculated contribution rates of electronically excited N$_2$ in the production of CH$_3$ radicals

We will consider here the influence of the interaction of electronically excited nitrogen molecules with methane molecules on the dissociation of the target molecules and the production of the CH_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

$$\left(\frac{\partial E}{\partial x}\right)_{MAC}(h) = \frac{\partial E}{\partial x}(h) \cdot \frac{[MAC](h)}{[N_2](h)}, \tag{17}$$

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

The results of the calculations of CH_3 and H production rates at the altitudes 50-250 km are shown in Figure 2. Contributions of the $A^3\Sigma_u^+$, $B^3\Pi_g$, $W^3\Delta_u$, $B'^3\Sigma_u^-$, $C^3\Pi_u$ triplet states and the singlet $a'^1\Sigma_u^-$, $a^1\Pi_g$, $w^1\Delta_u$ states in inelastic molecular collisions (9b, 10-13) and the contribution of direct production by energetic secondary electrons

$$e + CH_4 \rightarrow CH_3 + H + e \tag{18}$$

according to (*Vuitton et al.*, 2019, Fig.18) are presented in Figure 2. The yield for the production of H atom and CH_3 radical for the collisions of $N_2(a'^1\Sigma_u^-, v=0)$ metastable nitrogen with CH_4 molecule was determined to be 0.7±0.2 by *Umemoto et al.* (2002). We have taken the value f=0.7 for the production yield of CH_3+H in the reactions (9b, 10-13).

To estimate the average energy necessary for dissociation of methane molecules we can use the averaged energy for production of an ion pair in methane ε_{CH4}^{ion}=31 eV (*Fox et al.*, 2008). We apply the relation $\sigma^{diss}/\sigma^{ion}$ ~1.1 from the data for the electron energy E=100 eV by *Erwin and Kunc* (2008), therefore we suggest ε_{CH4}^{diss}=28 eV in our calculations. If to suggest in the calculations that the production of CH_3 radical and H atom is the main exit in the dissociation process (18) so we receive good agreement with the profile by *Vuitton et al.* (2019) presented in Figure 2. In fact the authors of (*Erwin and Kunc*, 2008) have shown that other production channels are significant in the inelastic interaction of high-energetic electrons and methane molecules, so we consider the calculated production rate of the process (18) as an upper limit.

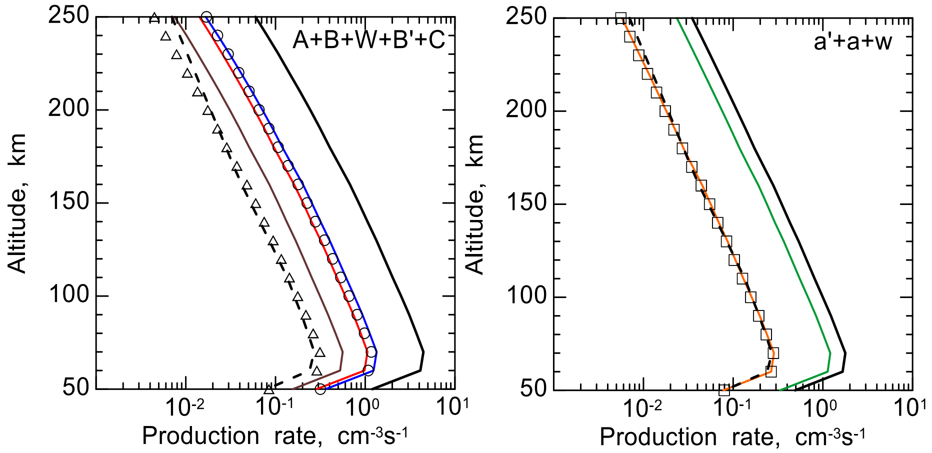

Figure 2. The calculated CH_3 and H production rates at the altitudes 50-250 km. Left panel: contributions of the $A^3\Sigma_u^+$, $B^3\Pi_g$, $W^3\Delta_u$, $B'^3\Sigma_u^-$, $C^3\Pi_u$ states are shown as red, blue lines, circles, triangles and brown line, respectively; the sum of the contributions is black line. Right panel: contributions of the $a'^1\Sigma_u^-$, $a^1\Pi_g$, $w^1\Delta_u$ states are shown as orange, green lines, squares, respectively; the sum of the contributions is black line. The production in the process (18) according to *Vuitton et al.* (2019) is dashed line in left and right panels.

We see very important role of the considered processes (9b, 10-13) in the production of H atom and CH_3 radical at all considered altitudes from 50 km to 250 km of the Titan's middle atmosphere. The contributions of N_2 triplet and singlet states exceed the contribution of the process (18) according to (*Vuitton et al.*, 2019) at the maximum of N_2 ion production at the altitude h~70 km by 16 and 6 times, respectively. Nevertheless, it must be emphasized that in the our calculations we have applied the results by *Umemoto et al.* (2002) for the $N_2(a'^1\Sigma_u^-,v=0)$ molecule to other triplet and singlet states assuming the transition of the CH_4 molecule in an excited repulsive state followed by the dissociation of the target molecule.

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 and $a'^1\Sigma_u^-$, $a^1\Pi_g$, $w^1\Delta_u$ singlet 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. The interaction of electronically excited N_2 molecules with methane molecules in the Titan's middle atmosphere at the altitudes of 50-250 km is studied. The calculations indicate very important role of the considered processes (9b, 10-13) in the production of H atom and CH_3 radical at all considered altitudes from 50 km to 250 km of the Titan's middle atmosphere. The contributions of N_2 triplet and singlet states exceed the contribution of the process (18) according to (*Vuitton et al.*, 2019) at the maximum of N_2 ion production at the altitude h~70 km by 16 and 6 times, respectively.

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