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# THE STUDY OF THE INFLUENCE OF METASTABLE NITROGEN ON THE PRODUCTION OF RADICALS IN THE STRATOSPHERE OF TITAN

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**Abstract.** The model of electronic kinetics of molecular nitrogen in the stratosphere of Titan is developed. We consider the collisions of electronically excited molecular nitrogen with $N_2$, $CH_4$, $H_2$, CO, $C_xH_y$ gases. It is shown that inelastic intramolecular and intermolecular electron energy transfers during the collisions influence on vibrational populations of excited electronic states of $N_2$ at the altitudes of the stratosphere. Special attention is paid to the investigation of the role of electronically excited molecular nitrogen in the dissociation processes during collisions with different atmospheric components. We consider the production of $CH_3$ and $C_2H_5$ radicals in the collisions with methane $CH_4$ and ethane $C_2H_6$ gases. It is shown that metastable molecular nitrogen dominates in the production of radical atmospheric components at the altitudes of Titan's stratosphere.

## Introduction

Galactic cosmic rays are the source of ionization and produce fluxes of secondary electrons in the ionization processes in the middle and lower atmosphere of Titan (*Molina-Cuberos et al.*, 1999). *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 $CO(a^3\Pi)$.

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. Also we will show the influence of the inelastic collisions of electronically excited $N_2$ molecules with $CH_4$ and $C_2H_6$ gases on the production of $CH_3$ and $C_2H_5$ radicals.

## The production and quenching of $N_2$ triplet states in the Titan's atmosphere

We consider here the excitation of five triplet electronic states

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

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

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

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

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

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 scheme of vibrational levels of $N_2$ triplet 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:

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

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

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

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

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

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

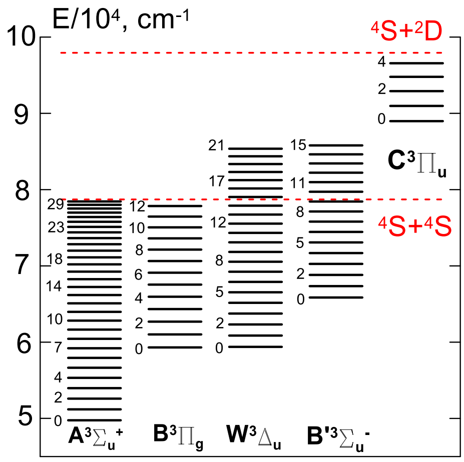


**Figure1.** The scheme of vibrational levels of $N_2$ triplet states.

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

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

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

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

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

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

$N_2(C^3\Pi_u,v') + N_2(X^1\Sigma_g^+,v=0) \rightarrow N_2(X^1\Sigma_g^+,v^*\geq 0) + N_2(Z,B^3\Pi_g,C^3\Pi_u;v'')$ (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 (*Kirillov et al.*, 2023). The quenching rate coefficients for the processes (3a,3b,4a-4c) have been calculated by *Kirillov* (2016, 2019). We apply here the calculated constants in those papers.

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

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

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)

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

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

Also we consider the inelastic interaction

$N_2(A^3\Sigma_u^+,v'=0) + C_2H_6 \rightarrow N_2(X^1\Sigma_g^+,v'') + C_2H_5 + H$ , products (6) according to (*Sharipov et al.*, 2016). Temperature dependence of the rate coefficients for the processes (5b) and (6) calculated according to (*Sharipov et al.*, 2016) is presented in Figure 2. The calculated constants are compared with experimental data available in scientific literature (*Herron*, 1999).

*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

$$N_2(A^3\Sigma_u^+,v') + CO(X^1\Sigma^+,v=0) \rightarrow N_2(X^1\Sigma_g^+,v^*\geq 0) + CO(a^3\Pi,v'') \quad (7)$$

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 (7) 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.

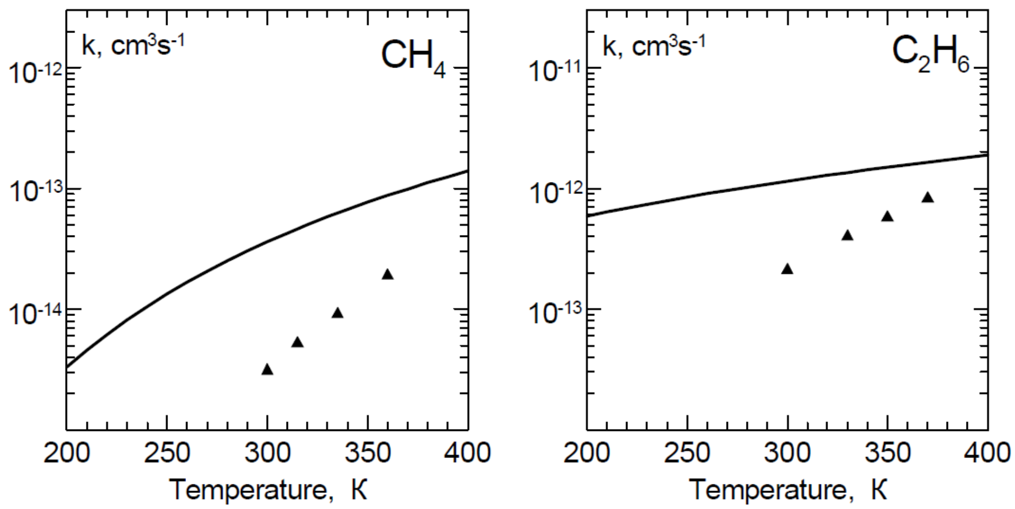


**Figure 2.** Temperature dependence of the rate coefficients for the processes (5b) and (6) calculated according to (*Sharipov et al.*, 2016) (solid lines) is compared with experimental data (*Herron*, 1999) (triangles).

## 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). 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

$$I(h) = \frac{1}{\varepsilon}\frac{\partial E}{\partial x}(h) \quad (8)$$

where $\partial E$ is the mean energy loss in the atmospheric layer $\partial x$ at depth *x* (g·cm$^{-2}$), $\varepsilon_{N2}^{ion}$ = 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 $\varepsilon$ necessary for the excitation of $N_2$ triplet states by produced energetic secondary electrons in pure nitrogen in the processes (1a-1e).

**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 and ethane molecules on the dissociation of the target molecules and the production of the $CH_3$ and $C_2H_5$ 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

$$\left(\frac{\partial E}{\partial x}\right)_{MAC}(h) = \frac{\partial E}{\partial x}(h) \cdot \frac{[MAC](h)}{[N_2](h)} \quad , \qquad (9)$$

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

The results of the calculation for the profiles of production rates of the $CH_3$ and $C_2H_5$ radicals in the inelastic processes

$$N_2(A^3\Sigma_u^+) + CH_4 \rightarrow N_2(X^1\Sigma_g^+) + CH_3 + H \text{ , products ,} \qquad (10)$$

$$N_2(A^3\Sigma_u^+) + C_2H_6 \rightarrow N_2(X^1\Sigma_g^+) + C_2H_5 + H \text{ , products .} \qquad (11)$$

are shown in Figure 3. We have assumed in our calculations that methane and ethane concentrations are related with $N_2$ concentrations by the ratios $[CH_4]=1.5 \cdot 10^{-2} \cdot [N_2]$ and $[C_2H_6]=2 \cdot 10^{-5} \cdot [N_2]$ (*Bezard et al.*, 2014; *Vuitton et al.*, 2019). Also the profiles of production rates in the inelastic processes

$$N_2(Y) + CH_4 \rightarrow N_2(X^1\Sigma_g^+) + CH_3 + H \text{ , products ,} \qquad (12)$$

$$N_2(Y) + C_2H_6 \rightarrow N_2(X^1\Sigma_g^+) + C_2H_5 + H \text{ , products} \qquad (13)$$

are shown in Figure 3, where $Y=B^3\Pi_g$, $W^3\Delta_u$, $B'^3\Sigma_u^-$, $C^3\Pi_u$ .

The results of the influence of electronically excited $N_2$ on the $CH_3$ and $C_2H_5$ production in the processes (10-13) are compared with the production rates in the dissociation by secondary electrons

$$e + CH_4 \rightarrow CH_3 + H + e \text{ ,} \qquad (14)$$

$$e + C_2H_6 \rightarrow C_2H_5 + H + e \text{ .} \qquad (15)$$

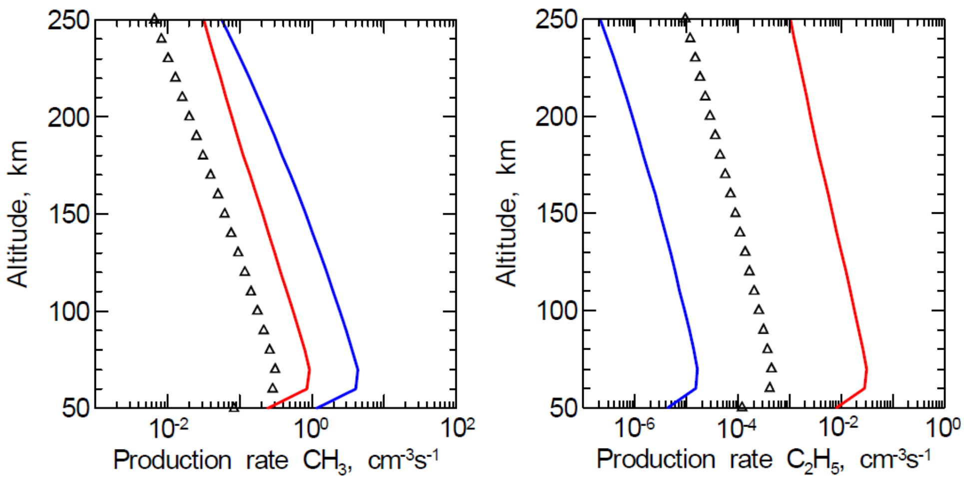


**Figure 3.** The calculated $CH_3$ and $C_2H_5$ production rates at the altitudes 50-250 km: the processes (10), (11) are shown as red lines, the processes (12), (13) as blue lines, the processes (14), (15) as triangles.

The comparison of contribution rates in Figure 3 shows the domination of the reactions (10), (11) and (12) in the productions of the $CH_3$ and $C_2H_5$ radicals. It is seen that the contributions of the processes in the productions of the $CH_3$ and $C_2H_5$ radicals exceed the contributions of the processes (14) and (15). Therefore the processes (10), (11) and (12) have to be taken into account in a study of chemical kinetics in the Titan's middle atmosphere.

## 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. The interaction of metastable electronically excited $N_2$ molecules with methane and ethane 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 (10), (11) and (12) in the productions of the $CH_3$ and $C_2H_5$ radicals. The contributions of the processes (10), (11) and (12) in the productions of the $CH_3$ and $C_2H_5$ radicals exceed the contributions of processes (14) and (15) at all altitude range.

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