

THE DISTRIBUTION OF SOLAR PROTON ENERGY ON ELECTRONIC STATES OF MOLECULES IN THE MIXTURE OF N₂, O₂, CO, CO₂ GASES

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Abstract: Precipitations of intensive fluxes of high-energy solar protons in the atmospheres of terrestrial planets cause electronic excitation of main molecular components of the atmospheres. Electronically excited molecules play very important role in chemical balances of the atmospheres. Recent investigations of Seppala et al. [2008] and Lillis et al. [2012] consider the precipitations of solar energetic particles in the atmospheres of Earth and Mars, consequently. The main aim of our studies is the development of a model of electronic and vibrational kinetics of molecular components in the atmospheres of terrestrial planets. The calculated quenching rate coefficients of electronically excited molecules are applied in the simulations of vibrational populations of N₂, CO, O₂ electronic states in the mixture of N₂, O₂, CO, CO₂ gases. We consider electronic kinetics of triplet states of N₂ and CO and the kinetics of Herzberg states of O₂. The calculations are made for the altitudes of middle atmospheres of Earth and Mars. **(The paper is prepared for the publishing in Advances in Space Research).**

Introduction

In order to consider correctly the chemical balance of middle atmospheres of terrestrial planets including ozone component, it is necessary to calculate the contents of numerous minor atmospheric components produced during solar proton events on the planets. Recent investigations of Seppala et al. [2008] and Lillis et al. [2012] consider the precipitations of solar energetic particles in the atmospheres of Earth and Mars, consequently. The inelastic interaction of solar particles with atomic and molecular components of the atmospheres causes electronic (and vibrational) excitation of the atoms and molecules. Few papers related with chemical reactions with the participation of electronically and vibrationally excited molecules in the middle atmosphere of Earth were published in NATURE and journals of AGU.

It is known the odd-nitrogen compounds (NO_y) and the odd hydrogen compounds (including the hydroxyl radical OH) are important components. Toumi (1993,GRL), Siskind et al. (1993,GRL) have proposed that the reactions of singlet molecular oxygen O₂(b¹Σ_g⁺) with either molecular hydrogen H₂ or nitrous oxide N₂O could be sources of OH and NO_y, respectively.

Moreover, sometimes the interaction of metastable molecular nitrogen N₂(A³Σ_u⁺) with molecular oxygen O₂ is considered as possible source of nitrous oxide at altitudes of the middle atmosphere [Zipf, 1980, Nature; Zipf and Prasad, 1980, Nature]. Also Prasad and Zipf [1981, Nature] have studied the influence of nitrous oxide formed in the interaction of N₂⁺ in the atmosphere during solar proton events on atmospheric chemical balance.

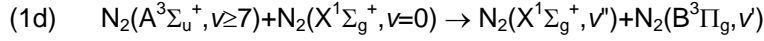
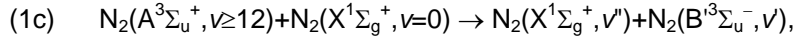
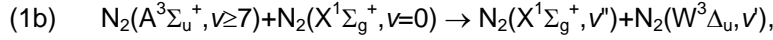
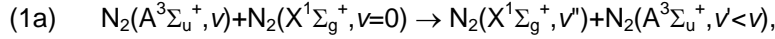
Solar protons precipitating in the middle atmospheres of terrestrial planets produce effectively secondary electrons in collisions with N₂, O₂ molecules in the atmosphere of Earth and with CO₂ molecules in the atmosphere of Mars. The electrons take active part in the production of different electronically excited states of main atmospheric components N₂, O₂, CO, CO₂ [Konovalov and Son, 1987, Bhardwaj and Jain, 2009]. When collisional lifetimes of the states are less or comparable with radiational ones at the altitudes of the middle atmosphere so the collisional processes influence the electronic kinetics of the components. Therefore the energy of solar protons is accumulated on electronic states of molecules in radiational and collisional processes.

Electronic Quenching

We use analytical expressions for the rate coefficients of electronic quenching in molecular collisions based on quantum-mechanical Landau-Zener and Rosen-Zener approximations and presented by Kirillov [2004a,b]. Franck-Condon factors for the calculations related with transitions in

N_2 molecule are taken from [Gilmore et al., 1992]. Franck-Condon factors for the transitions in O_2 molecule are calculated applying Morse approximation [Kirillov, 2004b].

Here we present the results of our calculations for the quenching constants of the collisions $N_2(A^3\Sigma_u^+, v=2-23)+N_2$. The calculations include the consideration of intermolecular electron energy transfer processes



and intramolecular process

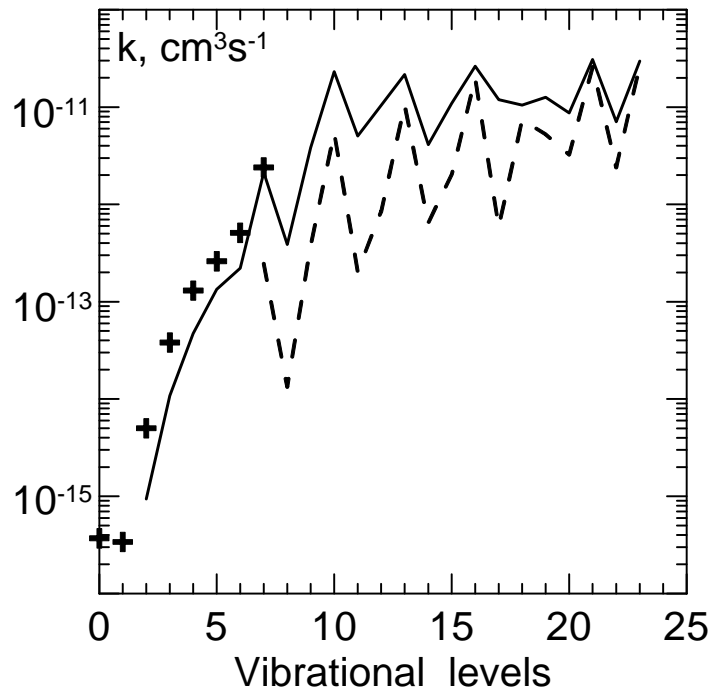
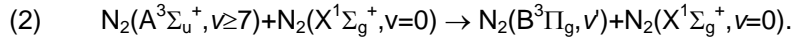
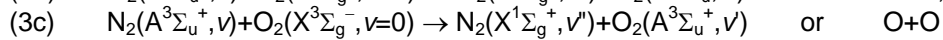
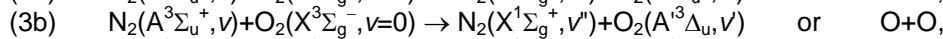
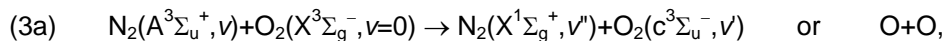


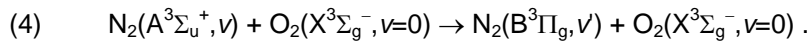
Fig. 1. The calculated quenching constants for the collisions $N_2(A^3\Sigma_u^+, v=2-23)+N_2$ (solid line) are compared with experimental data of [Dreyer and Perner, 1973] (crosses); the contribution of intramolecular process (2) – dashed line

The calculated quenching constants for the collisions $N_2(A^3\Sigma_u^+, v=2-23)+N_2$ at room temperature are compared with experimental data of [Dreyer and Perner, 1973] in Fig.1. Also we show here the contribution of intramolecular process (2). It is seen good agreement of our results with the data.

Here we present the results of our calculations for the quenching constants of the collisions $N_2(A^3\Sigma_u^+, v=0-23)+O_2$. The calculations include the consideration of intermolecular electron energy transfer processes



and intramolecular process



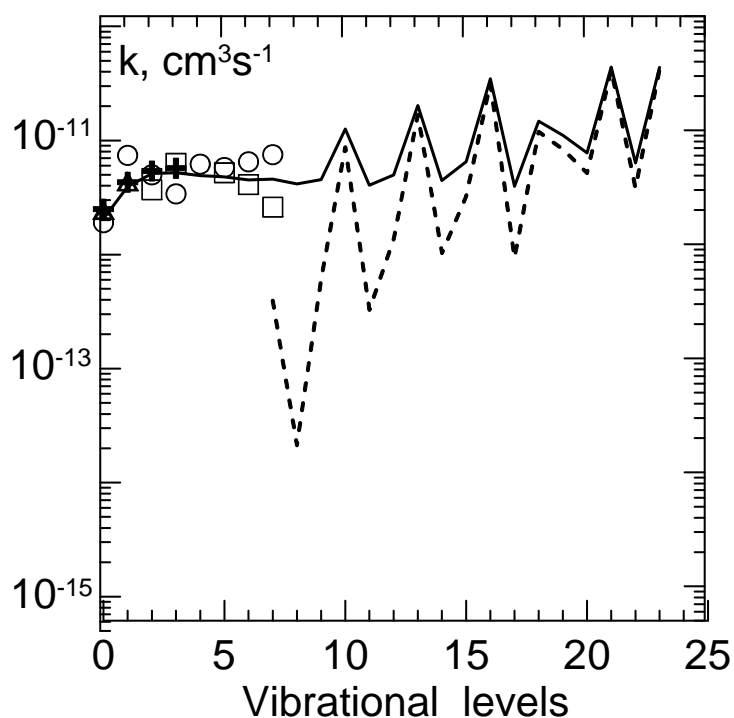


Fig. 2. The calculated quenching constants for the collisions $N_2(A^3\Sigma_u^+, v=0-23)+O_2$ (solid line) are compared with experimental data of [Dreyer et al., 1974] (circles), [Piper et al., 1981] (triangles), [Thomas and Kaufman, 1985] (crosses), [De Benedictis and Dilecce, 1997] (squares); contribution of intramolecular process (4) – dashed line

The calculated quenching constants for the collisions $N_2(A^3\Sigma_u^+, v=0-23)+O_2$ at room temperature are compared with experimental data of [Dreyer et al., 1974], [Piper et al., 1981], [Thomas and Kaufman, 1985], [De Benedictis and Dilecce, 1997] in Fig.2. Also we show here the contribution of intramolecular process (4). It is seen good agreement of our results with the data.

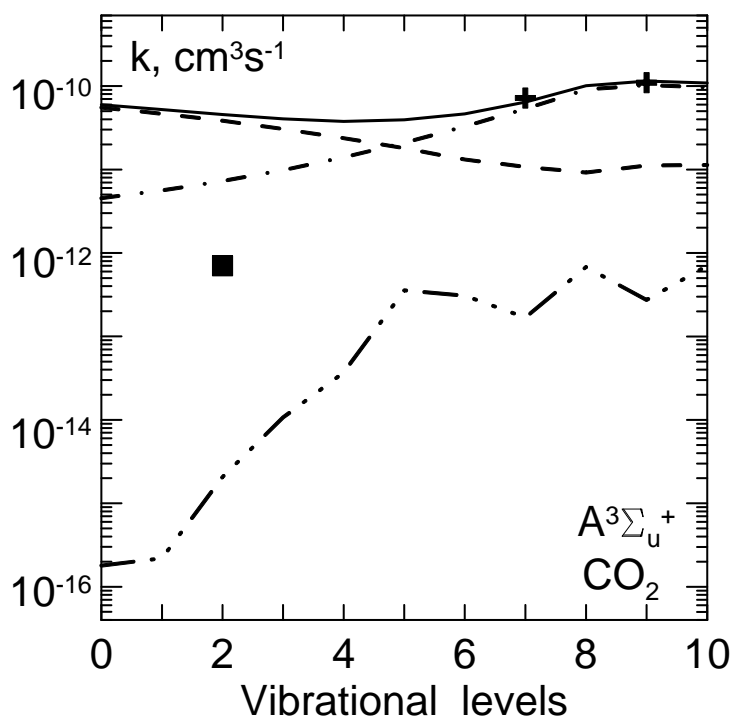
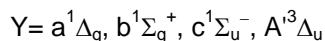
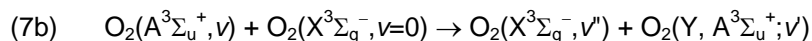
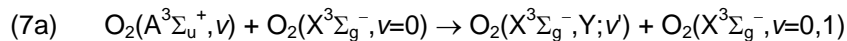
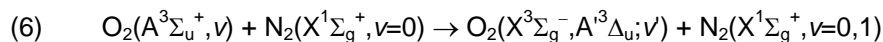
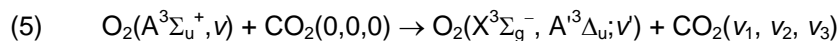


Fig. 3. The calculated quenching rate coefficients of the $A^3\Sigma_u^+$ state by CO_2 molecule (solid line) are compared with experimental data by Knutsen et al. [1994] (crosses) and Kenner and Ogryzlo [1983a] (square). The calculated contributions of E- and EV-processes with the excitation of one or two vibrational quanta of CO_2 are dash-dotted, dashed, dash and three dotted lines, respectively

Here we design to make the calculations of removal rates for O₂ Herzberg states for the collisions with CO₂, N₂, O₂ molecules and consider only spin-allowed processes in the quenching of the states with vibrational excitation of target molecules



The processes (5,6,7a) include both intramolecular electron energy transfers without any vibrational excitation of target molecules (E-processes) and intramolecular electron energy transfers with vibrational excitation $v=0 \rightarrow v=1$ of ones (EV-processes). The intermolecular process (7b) is related with the changes of electronic configurations in both collided molecules (EE-processes).

The results of our calculations for $A^3\Sigma_u^+$ ($v=0-10$) removal constants in the processes (5), (6), (7a,b) at room temperature are plotted in Figs.3-5, respectively. We compare our results with experimental data of [Kenner and Ogryzlo, 1983a,b; Knutsen et al., 1994; Copeland, 1994] for collisions with CO₂, N₂ and O₂ molecules in Figs.3-5.

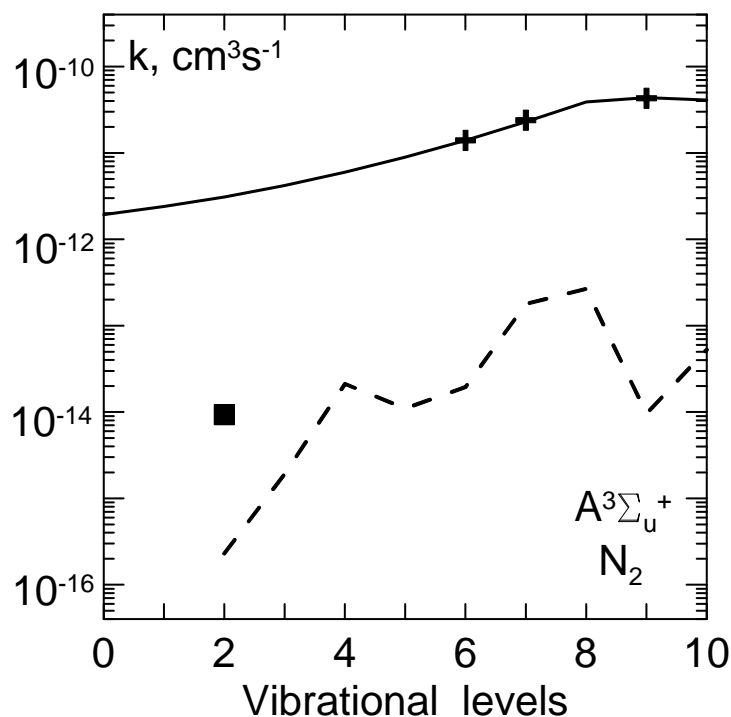


Fig. 4. The calculated quenching rate coefficients of the $A^3\Sigma_u^+$ state of molecular oxygen by N₂ molecules (solid line) are compared with experimental data by Knutsen et al. [1994] (crosses), Kenner and Ogryzlo [1983b] (square). The calculated contributions of EV-processes with the excitation of one vibrational quantum of N₂ is dashed line

Good agreement of calculated coefficients with the results of laser experimental measurements by Knutsen et al. [1994] and Copeland [1994] is seen from the comparison. Nevertheless, there is not any agreement with ancient data by Kenner and Ogryzlo [1983a,b] received applying catalytical recombination of oxygen atoms on a nickel surface. The data of [Kenner and Ogryzlo, 1983a,b] are significantly lower than the calculated constants for all three target molecules.

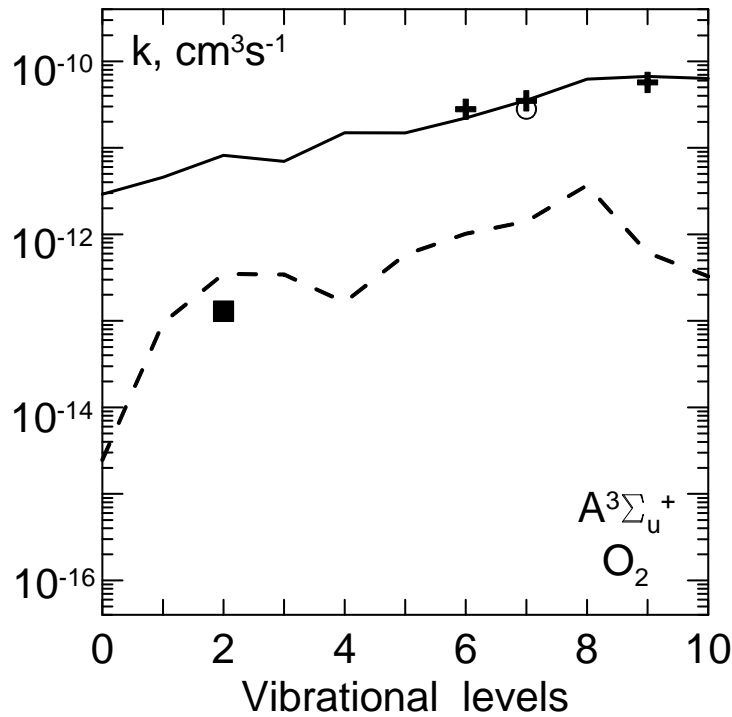


Fig. 5. The calculated quenching rate coefficients of the $A^3\Sigma_u^+$ state of molecular oxygen by O_2 molecules (solid line) are compared with experimental data by Knutsen et al. [1994] (crosses), Kenner and Ogryzlo [1983a] (square), Copeland [1994] (circle). The calculated contributions of EV-processes with the excitation of one vibrational quantum of O_2 is dashed line

Vibrational Populations of Electronically Excited N_2 and O_2 in the Atmosphere of Earth

We pay special attention to the presentation of vibrational populations of triplet $A^3\Sigma_u^+$ state of N_2 and Herzberg $A^3\Sigma_u^+$ state of O_2 for conditions of middle atmosphere of Earth during solar proton precipitation. To calculate the population of the v -th vibrational level of the $A^3\Sigma_u^+$ states we use the steady-state equations with the production rates of the states by solar protons, with applying of the rate constants for intermolecular and intramolecular electron energy transfer processes and with using of Einstein coefficients for spontaneous radiational transitions between electronically excited states of N_2 and O_2 . The quenching and production of electronically excited states in inelastic molecular collisions are taken into account.

To estimate vibrational population of $N_2(A^3\Sigma_u^+, v)$ we calculate the populations of the $B^3\Pi_g$, $W^3\Delta_u$, $B^3\Sigma_u^-$, $C^3\Pi_u$ states of N_2 . The rate coefficients for all intermolecular and intramolecular electron energy transfer processes are calculated as described in previous section. Fig.6 is a plot of the calculated relative vibrational populations of the $A^3\Sigma_u^+$ state of N_2 ($[N_2(A^3\Sigma_u^+, v)]/[N_2(A^3\Sigma_u^+, v=0)]$) at the altitude of 50 km. Concentrations of main atmospheric components are taken as $[N_2]=1.2 \times 10^{16} \text{ cm}^{-3}$, $[O_2]=3.1 \times 10^{15} \text{ cm}^{-3}$.

Results of the calculation of $O_2(A^3\Sigma_u^+, v)$ are given in Fig.7 for two cases. At first we have made the calculation without the inclusion of electronic energy transfer processes from metastable nitrogen $N_2(A^3\Sigma_u^+)$ (3c). In the second instance the contribution of the processes (3c) is taken into consideration. The normalising of presented populations is made on the populations of vibrational level $v=0$ of the Herzberg state for the first instance. Fig.7 indicates obviously that these intermolecular processes are dominant in the population of the Herzberg state at altitudes of middle atmosphere during solar proton precipitation and the inclusion of the processes (3a-c) is very important in the study of electronic kinetics of the Herzberg states of O_2 .

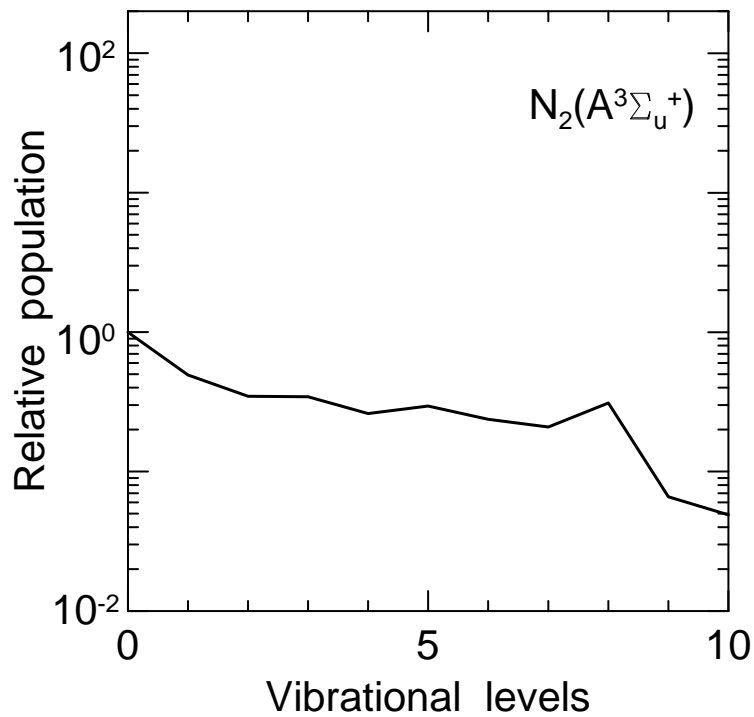


Fig. 6. The calculated relative vibrational population of the $A^3\Sigma_u^+$ state of N_2 at the altitude of 50 km of Earth (solid line)

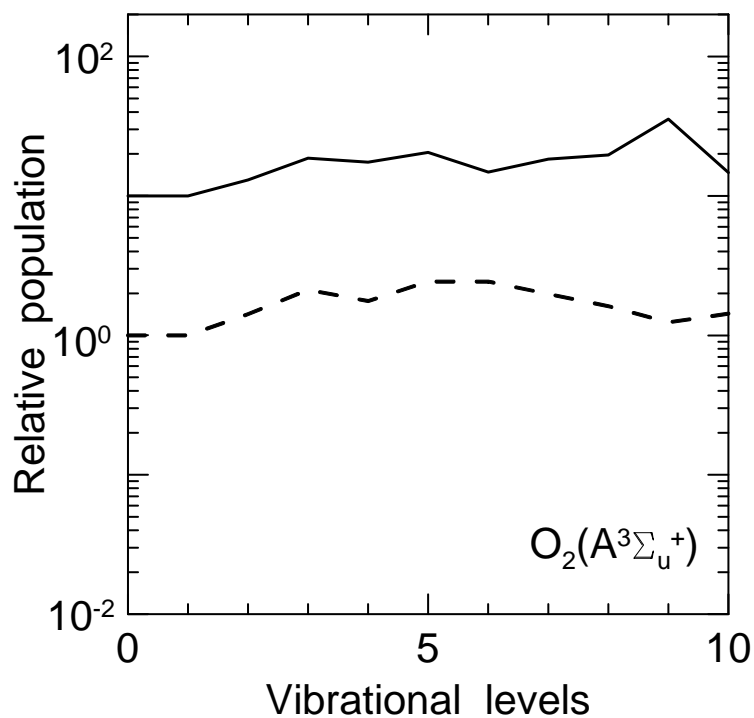


Fig. 7. The calculated relative vibrational populations of the $A^3\Sigma_u^+$ state of O_2 at the altitude of 50 km of Earth: dashed and solid lines – without and with the contribution of the process (3c), respectively

Vibrational Populations of Electronically Excited N_2 and CO in the Atmosphere of Mars

Here we pay special attention to the presentation of vibrational populations of triplet $A^3\Sigma_u^+$ state of N_2 and of triplet $a^3\Pi_r$ state of CO for conditions of middle atmosphere of Mars during solar proton precipitation.

To calculate the population of the v -th vibrational level of the $A^3\Sigma_u^+$ state we use the steady-state equations with the production rates of the states by solar protons, with applying of the rate

constants for intermolecular and intramolecular electron energy transfer processes for collisions with N_2 and O_2 molecules and with using of Einstein coefficients for spontaneous radiational transitions. Only intramolecular electron energy transfer processes are considered for collisions with CO_2 molecules. The quenching and production of electronically excited states of N_2 in inelastic molecular collisions are taken into account.

To estimate vibrational population of $N_2(A^3\Sigma_u^+, \nu)$ we calculate the populations of $B^3\Pi_g$, $W^3\Delta_u$, $B^3\Sigma_u^-$, $C^3\Pi_u$ states of N_2 . Fig.8 is a plot of the calculated relative vibrational populations of the $A^3\Sigma_u^+$ state of N_2 ($[N_2(A^3\Sigma_u^+, \nu)]/[N_2(A^3\Sigma_u^+, \nu=0)]$) at the altitude of 50 km of Mars. Concentrations of main atmospheric components are taken as $[CO_2]=8 \times 10^{14} \text{ cm}^{-3}$, $[N_2]=2.3 \times 10^{13} \text{ cm}^{-3}$, $[O_2]=1.1 \times 10^{12} \text{ cm}^{-3}$. Results of the calculation of $N_2(A^3\Sigma_u^+, \nu)$ are given in Fig.8 for two cases. At first we have made the calculation without the inclusion of electronic energy transfer processes (3a-c). In the second instance the contribution of the processes (3a-c) is taken into consideration. The normalising of presented populations is made on the populations of vibrational level $\nu=0$ of the $A^3\Sigma_u^+$ state for the first instance. Although concentrations of molecular oxygen are one-two orders lower concentrations of CO_2 and N_2 it is seen from Fig.8 that these intermolecular processes are very important in the population of the $A^3\Sigma_u^+$ state at altitudes of middle atmosphere of Mars during solar proton precipitation.

To estimate vibrational population of $CO(a^3\Pi_r, \nu)$ we calculate the populations of $a^3\Sigma^+$, $d^3\Delta_i$, $e^3\Sigma^-$ states of CO . To calculate the population of the ν -th vibrational level of the $a^3\Pi_r$ state we use the steady-state equations with the production rates of the states by solar protons and with using Einstein coefficients for spontaneous radiational transitions. Fig.9 is a plot of the calculated relative vibrational populations of the $a^3\Pi_r$ state of CO ($[CO(a^3\Pi_r, \nu)]/[CO(a^3\Pi_r, \nu=0)]$) at the altitudes of Mars.

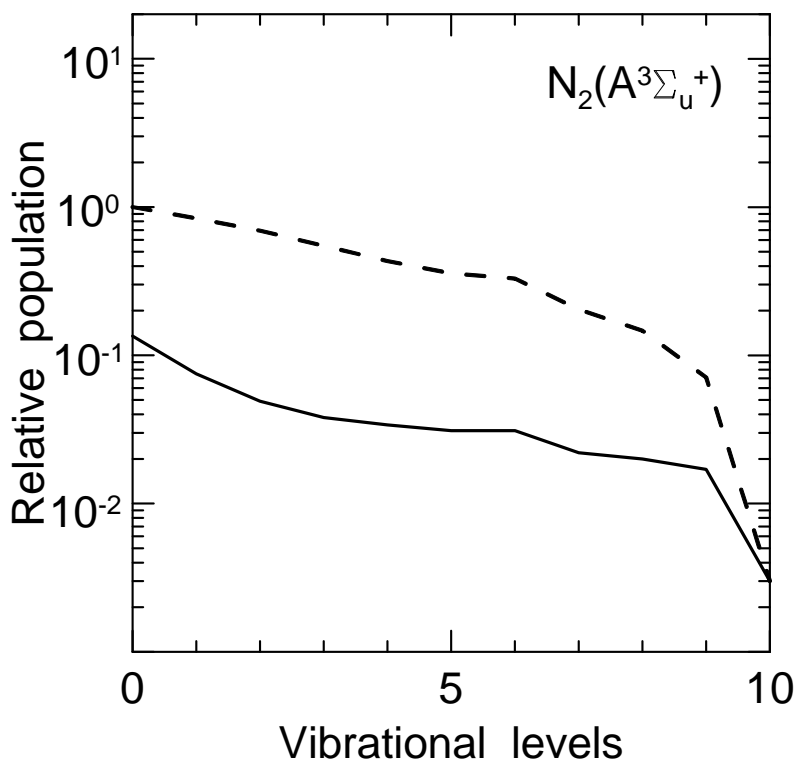


Fig. 8. The calculated relative vibrational populations of the $A^3\Sigma_u^+$ state of N_2 at the altitude of 50 km of Mars: dashed and solid lines – without and with the contribution of the processes (3a-c), respectively

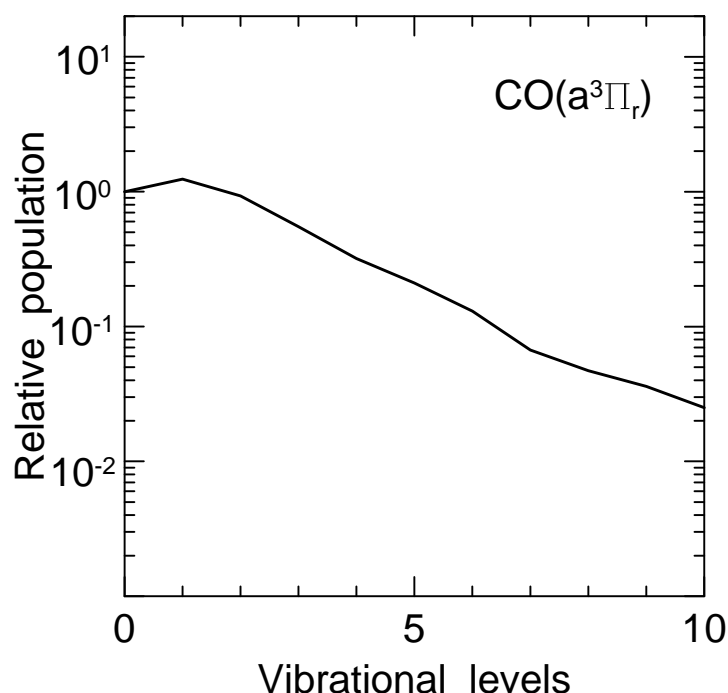


Fig. 9. The calculated relative vibrational population of the $a^3\Pi_r$ state of CO at the altitudes of Mars (solid line)

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