ELECTRONIC KINETICS OF MOLECULES IN UPPER ATMOSPHERES OF EARTH AND MARS DURING SOLAR PROTON PRECIPITATIONS

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Abstract: Electronically excited molecules play very important role in chemical kinetics in a mixture of atmospheric gases. It is known that the excitation decreases activation barriers of chemical reactions and increases the rates of chemical processes. The precipitation of energetic protons in the atmospheres of terrestrial planets causes the electronic excitation of molecules. Recent investigations of Seppala et al. [2008, J. Geophys. Res., v.113, A11311] and Lillis et al. [2012, J. Geophys. Res., v.117, E03004] consider the precipitations of solar energetic particles in the atmospheres of Earth and Mars, consequently. We suggest 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 CO, N_2, O_2 electronic states in the mixture of N_2, O_2, CO, CO_2 gases. We consider triplet states $a^3\Pi$, $a'^3\Sigma^+$, $d^3\Delta$, $e^3\Sigma^-$ of CO; triplet states $A^3\Sigma_u^+$, $B^3\Pi_g$, $W^3\Delta_u$, $B'^3\Sigma_u^-$ of N_2; Herzberg states $c^1\Sigma_u^-$, $A'^3\Delta_u$, $A^3\Sigma_u^+$ of O_2. Vibrational populations of the excited molecules are calculated for the atmospheres of Earth and Mars.

Introduction

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.

It is known the odd-nitrogen compounds (NO_y) and the odd hydrogen compounds (including the hydroxyl radical OH) are important components. Toumi (1993), Siskind et al. (1993) have proposed that the reactions of singlet molecular oxygen $O_2(b^1\Sigma_g^+)$ with either molecular hydrogen H_2 or nitrous oxide N_2O could be sources of OH and NO_y, respectively.

Moreover, sometimes the interaction of metastable molecular nitrogen $N_2(A^3\Sigma_u^+)$ with molecular oxygen O_2 is considered as possible source of nitrous oxide at altitudes of the middle atmosphere [Zipf, 1980, Nature; Zipf and Prasad, 1980]. Also Prasad and Zipf [1981] have studied the influence of nitrous oxide formed in the interaction of N_2^* 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 N_2, O_2 molecules in the atmosphere of Earth and with CO_2 molecules in the atmosphere of Mars. The electrons take active part in the production of different electronically excited states of main atmospheric components N_2, O_2, CO, CO_2 [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.

The main aim of our study is the calculation of the quenching rate coefficients for electronically excited molecules in collisions with CO_2, CO, N_2, O_2 ground-state molecules and the application of the removal rates in the study of electronic kinetics of main components in upper and middle atmospheres of terrestrial planets disturbed by precipitation of energetic solar protons.

Electronic Quenching

One year ago Kirillov, Werner, Guineva (2013) have presented the quenching rate coefficients for electronically excited N_2 and O_2 molecules. They have used 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].
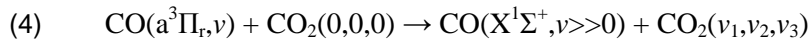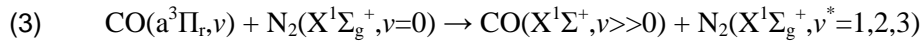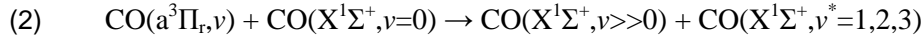
Franck-Condon factors for the transitions in O_2 molecule are calculated applying Morse approximation [Kirillov, 2004b].

Here we present the results of our new investigations for $CO(a^3\Pi_r)$ molecules effectively produced in dissociative processes

(1) $\qquad p(e_{sec}) + CO_2(X^1\Sigma_g^+) \rightarrow CO(a^3\Pi_r) + O(^3P)$
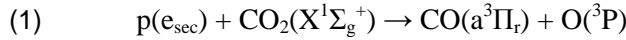
related with the collisions of protons and secondary electrons with main component CO_2 of Mars atmosphere. Since the concentrations of CO_2 in Mars atmosphere are significantly higher than the concentrations of CO, N_2, O_2 components so the consideration of the quenching processes of $CO(a^3\Pi_r)$ can be limited by collisions with CO_2 molecules.

To estimate the quenching rate coefficients of $CO(a^3\Pi_r)$ in collisions with CO, N_2, CO_2 molecules we follow the results published by Kirillov (2013, 2014) for EV-processes in collisions of $O_2(b^1\Sigma_g^+)$ and $O_2(c^1\Sigma_u^-, A'^3\Delta_u, A^3\Sigma_u^+)$ with CO_2, CO, N_2, O_2 molecules. Therefore we consider the processes

(2) $\qquad CO(a^3\Pi_r,v) + CO(X^1\Sigma^+,v=0) \rightarrow CO(X^1\Sigma^+,v>>0) + CO(X^1\Sigma^+,v^*=1,2,3)$

(3) $\qquad CO(a^3\Pi_r,v) + N_2(X^1\Sigma_g^+,v=0) \rightarrow CO(X^1\Sigma^+,v>>0) + N_2(X^1\Sigma_g^+,v^*=1,2,3)$

(4) $\qquad CO(a^3\Pi_r,v) + CO_2(0,0,0) \rightarrow CO(X^1\Sigma^+,v>>0) + CO_2(v_1,v_2,v_3)$

Here we apply in the calculations of the removal rates for the EV-processes the following formula

(5) $\qquad k(v) = k_o\, \alpha\, \beta\, \sqrt{\dfrac{T}{300}}\, \exp\left(-\dfrac{|\Delta E|}{\gamma\sqrt{T/300}} + \dfrac{\Delta E}{2k_BT}\right),$

where k_o, α, β and γ are parameters, ΔE is the energy defect of the interaction, k_B and T are the Boltzmann constant and temperature. The parameter $\gamma = 105$ cm^{-1} is taken according to collisions of isoelectronic excited N_2 [Kirillov, 2004a,b].

We believe the parameter α is related with gas-kinetic radius of a collision. According to Kirillov [2013, 2014] we have put α equal to 1.69, 0.72, 1 for the collisions CO–CO_2, CO–N_2, CO–CO, respectively. We believe $\beta \approx 0.17$ for EV-processes in CO^*–CO, CO^*–CO_2 collisions and $\beta \approx 0.07$ for EV-processes in CO^*–N_2 collisions with the excitation of one vibrational quantum of target-molecule. We suggest $\beta \approx 0.17^2 \approx 0.029$ for the collisions CO^*–CO_2 with the excitation of (110), (101), (011) modes and for the collisions CO^*–CO with the excitation of two vibrational quanta of CO. $\beta \approx 0.07^2 \approx 0.005$ for the collisions CO^*–N_2 with the excitation of two vibrational quanta of N_2. Respectively, we apply $\beta \approx 0.17^3$ and $\beta \approx 0.07^3$ in the cases of the excitation of three vibrational quanta of target-molecules CO and N_2.
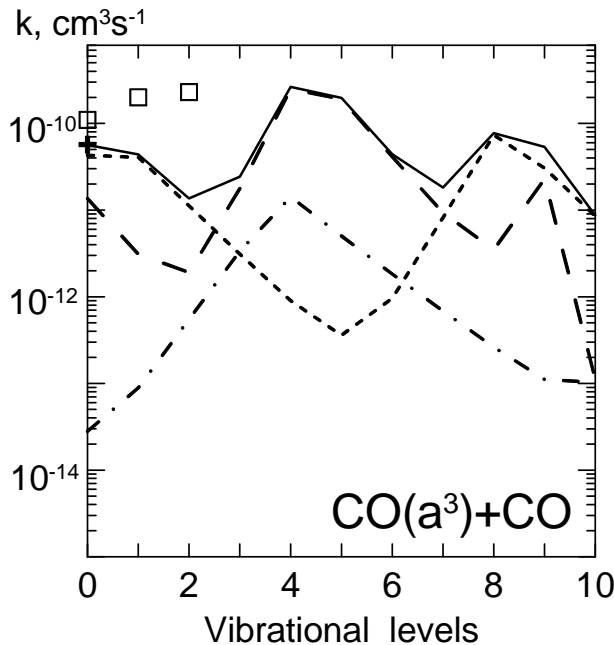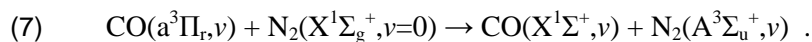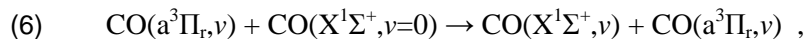

Fig. 1. The calculated quenching rate constants for the collisions $CO(a^3\Pi_r,v=0–10)$+CO (solid line) are compared with experimental data of [Taylor and Setser, 1973] (squares) and [Wysong, 2000] (cross). The contributions of the EV-processes with v^*=1,2,3 are shown as long-dashed, short-dashed, dash-dotted lines, respectively

In Figs.1-3 we compare the results of our calculations with experimental data of [Taylor and Setser, 1973] and [Wysong, 2000]. The calculations are made only for the EV-processes (2-4). The exceeding of experimental values over the results of the calculations for v=1,2 of $CO(a^3\Pi_r)$ in collisions with CO and N_2 molecules could be related with the contributions of EE-processes

(6) $\qquad CO(a^3\Pi_r,v) + CO(X^1\Sigma^+,v=0) \rightarrow CO(X^1\Sigma^+,v) + CO(a^3\Pi_r,v)$,

(7) $\qquad CO(a^3\Pi_r,v) + N_2(X^1\Sigma_g^+,v=0) \rightarrow CO(X^1\Sigma^+,v) + N_2(A^3\Sigma_u^+,v)$.

Here we do not consider the EE-processes (6) and (7).
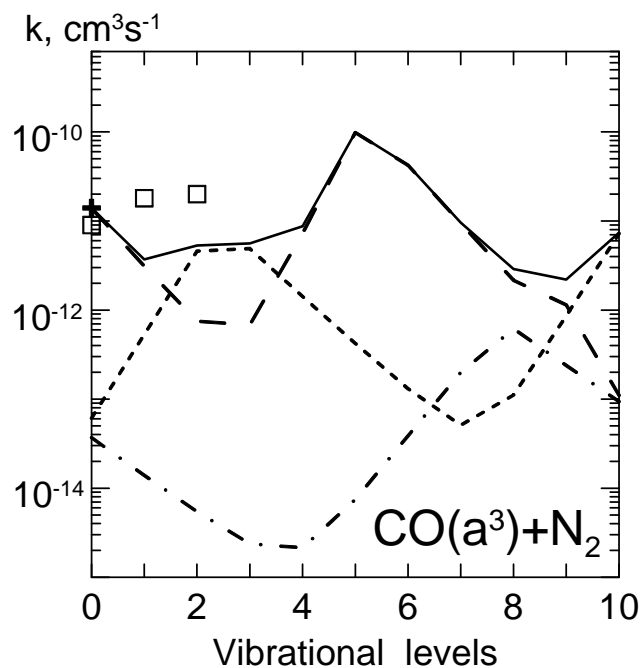

Fig. 2. The calculated quenching rate constants for the collisions $CO(a^3\Pi_r,v$=0–10)+N_2 (solid line) are compared with experimental data of [Taylor and Setser, 1973] (squares) and [Wysong, 2000] (cross). The contributions of the EV-processes with v^*=1,2,3 are shown as long-dashed, short-dashed, dash-dotted lines, respectively
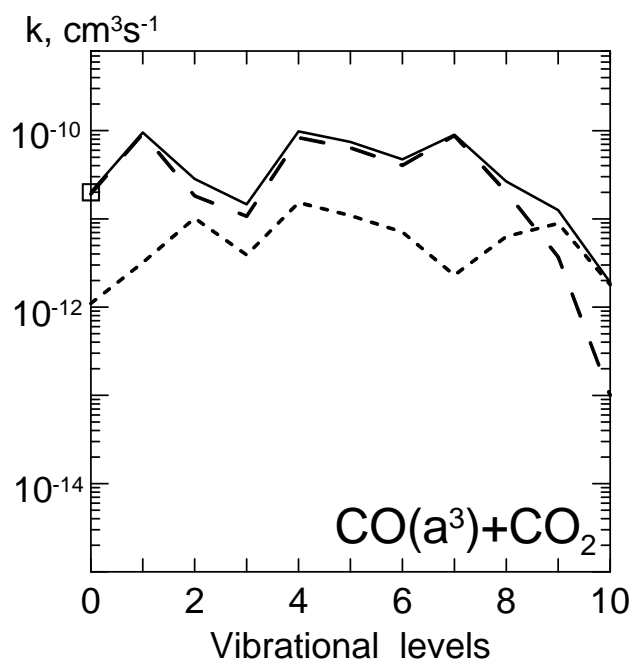

Fig. 3. The calculated quenching rate constants for the collisions $CO(a^3\Pi_r,v$=0–10)+CO_2 (solid line) are compared with experimental data of [Taylor and Setser, 1973] (square). The contributions of the EV-processes with one and two vibrational quanta of CO_2 are shown as long-dashed, short-dashed lines, respectively

Vibrational Populations of Electronically Excited N_2 and Co in the Atmospheres of Earth and Mars

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 by Kirillov, Werner, Guineva (2013). Fig.4 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 $[N_2]=1.2\times10^{16}$ cm^{-3}, $[O_2]=3.1\times10^{15}$ cm^{-3}.

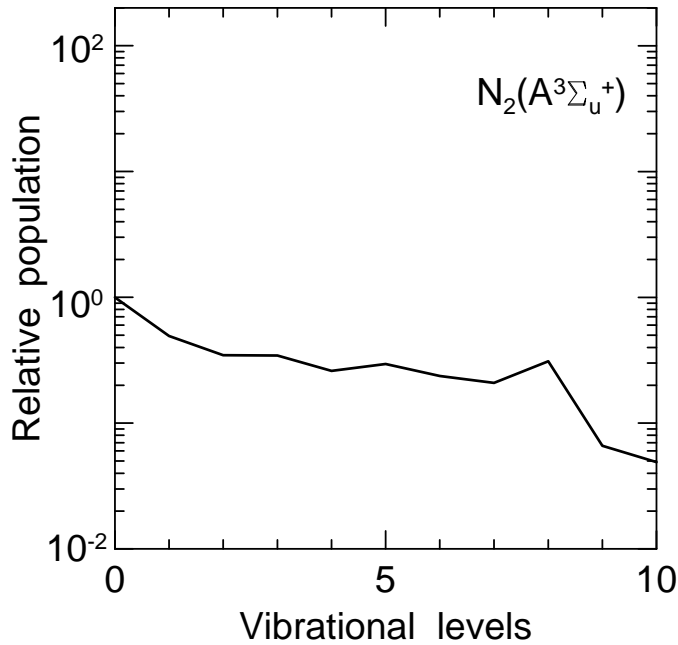Fig. 4. The calculated relative vibrational population of the $A^3\Sigma_u^+$ state of N_2 at the altitude of 50 km of Earth (solid line)
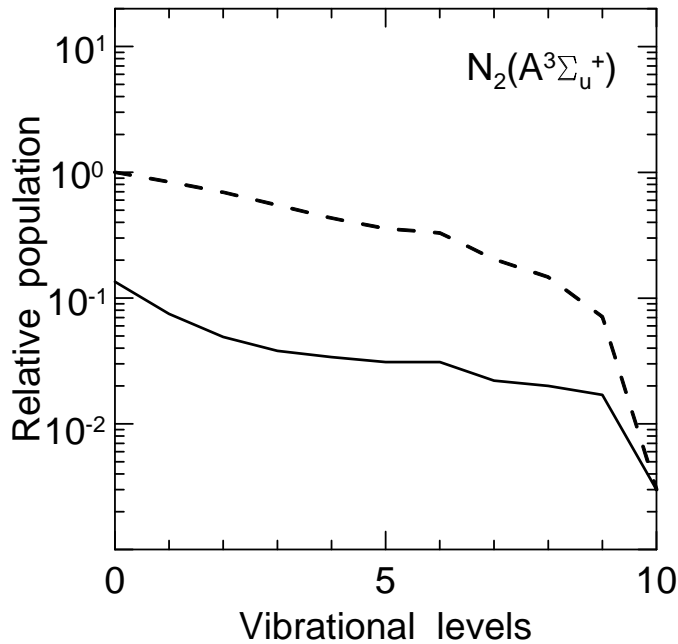

Fig. 5. The calculated relative vibrational populations of the $A^3\Sigma_u^+$ state of N_2 at the altitude of 50 km of Mars: dashed and solid lines – without and with the contribution of intermolecular processes in collisions with O_2

To calculate the population of the v-th vibrational level of the $A^3\Sigma_u^+$ state in the atmosphere of Mars 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 $N_2(A^3\Sigma_u^+,v)$ 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.5 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 of Mars. Concentrations of main atmospheric components are taken as $[CO_2]= 8\times10^{14}$ cm^{-3}, $[N_2]=2.3\times10^{13}$ cm^{-3}, $[O_2]=1.1\times10^{12}$ cm^{-3}. Results of the calculation of $N_2(A^3\Sigma_u^+,v)$ are given in Fig.5 for two cases. At first we have made the calculation without the inclusion of intermolecular electronic energy transfer processes in collisions with O_2 molecules. In the second instance the contribution of the processes is taken into consideration. The normalising of presented populations is made on the populations of vibrational level $v=0$ 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.5 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.
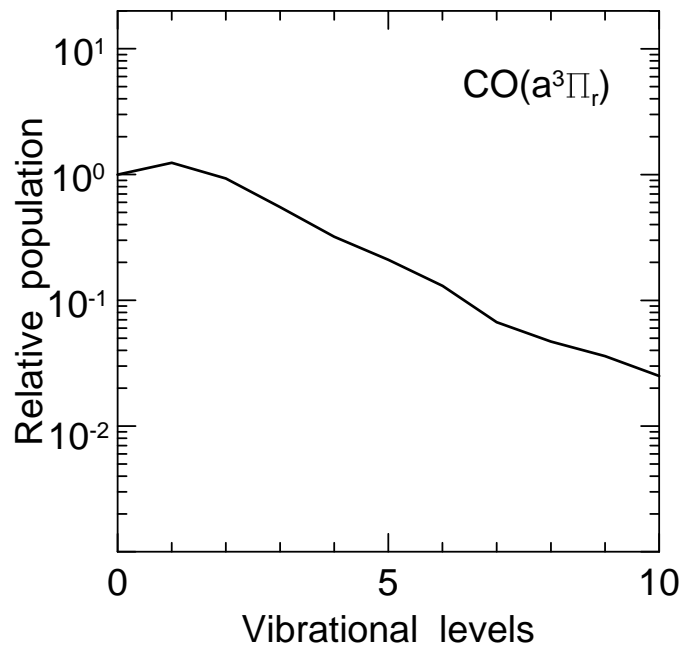

Fig. 6. The calculated relative vibrational population of the $a^3\Pi_r$ state of CO at the altitudes of Mars (solid line)

To estimate vibrational population of $CO(a^3\Pi_r,v)$ we calculate the populations of $a'^3\Sigma^+$, $d^3\Delta_i$, $e^3\Sigma^-$ states of CO. To calculate the population of the v-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.6 is a plot of the calculated relative vibrational populations of the $a^3\Pi_r$ state of CO ($[CO(a^3\Pi_r,v)]/[CO(a^3\Pi_r,v=0)]$) at the altitudes of Mars.

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