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THE SIMULATION OF VIBRATIONAL POPULATIONS OF ELECTRONICALLY EXCITED N_2 AND O_2 MOLECULES IN THE MIDDLE ATMOSPHERE OF THE EARTH DURING PRECIPITATIONS OF HIGH-ENERGETIC PARTICLES

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Abstract. We study the electronic kinetics of molecular nitrogen and molecular oxygen in the middle atmosphere of the Earth during precipitations of high-energetic protons and electrons. The role of molecular inelastic collisions in intermolecular electron energy transfer processes is investigated. It is shown that inelastic molecular collisions influence on vibrational populations of electronically excited molecular oxygen. It is pointed out on very important role of the collisions of $N_2(A^3\Sigma_u^+)$ with O_2 molecules on the electronic excitation of Herzberg states of molecular oxygen at the altitudes of the middle atmosphere.

Introduction

Molecular nitrogen N_2 is the major molecular gas in the atmospheres of Earth, Titan, Triton and Pluto. The interaction of high-energetic solar UV photons, magnetospheric particles and cosmic rays with atmospheric molecules causes the production of fluxes of free electrons in their atmospheres during processes of ionisation [*Campbell and Brunger*, 2016]. Produced free electrons excite different triplet states of N_2 in the inelastic collisions:

$$e + N_2(X^1\Sigma_g^+,v=0) \rightarrow N_2(A^3\Sigma_u^+, B^3\Pi_g, W^3\Delta_u, B'^3\Sigma_u^-, C^3\Pi_u, v\geq 0) + e. \quad (1)$$

Emissions of Wu-Benesch, Afterglow, Second Positive (2PG) and First Positive (1PG) bands during spontaneous radiational transitions

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

$$N_2(B'^3\Sigma_u^-,v) \rightarrow N_2(B^3\Pi_g,v') + h\nu_{AG}\,, \quad (2b)$$

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

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

lead to the accumulation of the energy of electronic excitation on vibrational levels of the lowest triplet state $A^3\Sigma_u^+$. Einstein coefficients of the dipole-allowed transitions (2a-c) and (3) are of high magnitudes [*Gilmore et al.*, 1992] and the emissions of the bands play a very important role in the electronic kinetics and in a redistribution of excitation energy between the triplet states of N_2 on the altitudes of upper atmospheres of the planets and/or their moons.

The main aim of this study is the simulation of $N_2(A^3\Sigma_u^+)$ and $O_2(c^1\Sigma_u^-, A'^3\Delta_u, A^3\Sigma_u^+)$ vibrational populations in an N_2-rich mixture with the admixture of O_2 (the Earth's atmosphere). The simulation of N_2 and O_2 vibrational populations at the altitudes of the Earth's atmosphere is made taking into account the 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 in vibrational populations of O_2.

The quenching constants of $N_2(A^3\Sigma_u^+)$ in the collisions with O_2 molecules

The calculation of the quenching rate constants during inelastic molecular collisions [*Kirillov*, 2010] has shown, that the interaction of metastable molecular nitrogen $N_2(A^3\Sigma_u^+,v'=0)$ with O_2 molecules leads to the excitation of O_2 Herzberg states $c^1\Sigma_u^-$, $A'^3\Delta_u$, $A^3\Sigma_u^+$

$$N_2(A^3\Sigma_u^+,v'=0) + O_2(X^3\Sigma_g^-,v=0) \rightarrow N_2(X^1\Sigma_g^+,v^*\geq 0) + O_2(c^1\Sigma_u^-,v''=4,5,6)\,, \quad (4a)$$

$$N_2(A^3\Sigma_u^+,v'=0) + O_2(X^3\Sigma_g^-,v=0) \rightarrow N_2(X^1\Sigma_g^+,v^*\geq 0) + O_2(A'^3\Delta_u,v''=4,5)\,, \quad (4b)$$

$$N_2(A^3\Sigma_u^+,v'=0) + O_2(X^3\Sigma_g^-,v=0) \rightarrow N_2(X^1\Sigma_g^+,v^*\geq 0) + O_2(A^3\Sigma_u^+,v''=4)\,. \quad (4c)$$

The total constant of the processes (4a-4c) is $k_{4a}+k_{4b}+k_{4c} = 1.1\cdot 10^{-12}$ cm^{3}s^{-1}. Also there is the dissociative process

$$N_2(A^3\Sigma_u^+,v'=0) + O_2(X^3\Sigma_g^-,v=0) \rightarrow N_2(X^1\Sigma_g^+,v^*\geq 0) + O + O \quad (4d)$$

with the constant of the interaction $k_{4d}=1.0\cdot10^{-12}$ cm^3s^{-1}. The calculated total constant $k_4=2.1\cdot10^{-12}$ cm^3s^{-1} for the processes (4a-4d) is in good agreement with experimental data $(1.9\pm0.3)\cdot10^{-12}$ cm^3s^{-1} [*Dreyer et al.*, 1974], $(2.3\pm0.4)\cdot10^{-12}$ cm^3s^{-1} [*Piper et al.*, 1981] and $(2.5\pm0.4)\cdot10^{-12}$ cm^3s^{-1} [*Thomas and Kaufman*, 1985]. In the case of the interaction of vibrationally excited metastable nitrogen $N_2(A^3\Sigma_u^+,v'>0)$ with O_2 molecules there is the transfer of electronic energy on the excitation of repulsive states with the production of two oxygen atoms [*Kirillov*, 2010, 2011].

After the excitation of the Herzberg states $Y=c^1\Sigma_u^-$, $A'^3\Delta_u$, $A^3\Sigma_u^+$ inelastic collisions with N_2 and O_2 molecules in the Earth's atmosphere cause the transformation of the excitation energy into singlet states $a^1\Delta_u$ and $b^1\Sigma_g^+$ during inelastic intramolecular and intermolecular transfer processes:

$$O_2(Y,v') + N_2, O_2 \rightarrow O_2(a^1\Delta_g,v'') + N_2, O_2 , \quad (5a)$$

$$O_2(Y,v') + N_2, O_2 \rightarrow O_2(b^1\Sigma_g^+,v'') + N_2, O_2 , \quad (5b)$$

$$O_2(Y,v') + O_2(X^3\Sigma_g^-,v=0) \rightarrow O_2(X^3\Sigma_g^-,v^*\geq0) + O_2(a^1\Delta_g,v'') , \quad (5c)$$

$$O_2(Y,v') + O_2(X^3\Sigma_g^-,v=0) \rightarrow O_2(X^3\Sigma_g^-,v^*\geq0) + O_2(b^1\Sigma_g^+,v'') , \quad (5d)$$

with the excitation of high vibrational levels of the $a^1\Delta_u$ and $b^1\Sigma_g^+$ singlet states in the intramolecular processes (5a,b) and low v''=0-2 vibrational levels in the intermolecular energy transfer processes (5c, d).

The electron energy transfer from metastable nitrogen $N_2(A^3\Sigma_u^+)$ to O_2 molecules in the Earth's atmosphere

When high-energy protons (energies of several hundred MeV) or electrons (energies of several MeV) precipitate into the Earth's atmosphere, their inelastic interaction with atmospheric molecules leads to the production of the energy spectrum of secondary electrons formed during ionization processes. Secondary electrons excite various triplet states of N_2 in inelastic collisions (1), and also lead to the formation of electronically excited Herzberg states of the O_2 molecule

$$e + O_2(X^3\Sigma_g^-,v=0) \rightarrow O_2(c^1\Sigma_u^-, A'^3\Delta_u, A^3\Sigma_u^+;v\geq0) + e . \quad (6)$$

The calculation the excitation rates of triplet states of N_2 molecules and the Herzberg states of O_2 molecules by secondary electrons at altitudes of the Earth's middle atmosphere is made using the method of electron degradation spectra in air [*Konovalov*, 1993]. This method takes into account all the processes of an excitation of vibrational levels of the ground state, various electronically excited states, processes of ionization and dissociation. In this case, we consider both the processes of direct excitation by secondary electrons (6) of the Herzberg states $c^1\Sigma_u^-$, $A'^3\Delta_u$, $A^3\Sigma_u^+$, and the processes of excitation in molecular collisions (4a-4c) (see Fig.1).

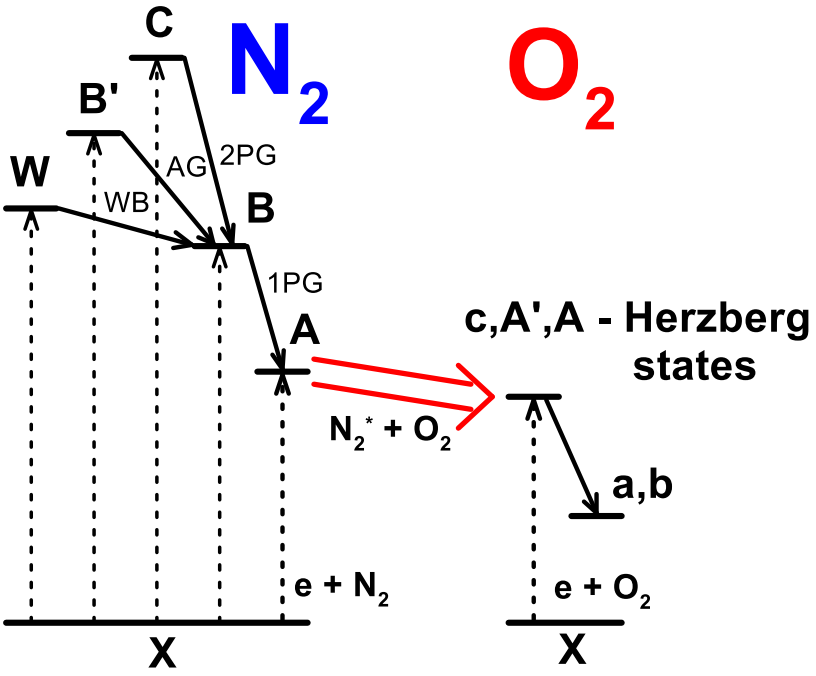

Figure 1. The scheme of processes of the excitation and the quenching of electronically excited states of molecular nitrogen and molecular oxygen in the Earth's atmosphere.

Figures 2-4 show the results of the calculated concentrations for the $c^1\Sigma_u^-$, $A'^3\Delta_u$, $A^3\Sigma_u^+$ Herzberg states of molecular oxygen at the altitudes of 70 and 50 km with an energy $W=10^6$ eV/cm^{3}s dissipated in 1 cm^3. Here, the contributions of secondary electrons are also presented (process (6)). In addition, the contributions of the processes (4a-4c) are shown for two cases: (a) upon excitation of only the $N_2(A^3\Sigma_u^+)$ state by secondary electrons, (b) upon excitation of the states $N_2(B^3\Pi_g, W^3\Delta_u, B'^3\Sigma_u^-, C^3\Pi_u)$ and the energy transfer from these four states to the $A^3\Sigma_u^+$ state during spontaneous transitions (2a-2c, 3) and in molecular collisions [*Kirillov*, 2010, 2011; *Kirillov et al.*, 2017].

The presented results demonstrate the influence of intermolecular processes of energy transfer from metastable nitrogen $N_2(A^3\Sigma_u^+)$ (process (4a-4c)) on the $c^1\Sigma_u^-$, $A'^3\Delta_u$, $A^3\Sigma_u^+$ Herzberg states of molecular oxygen at the altitudes of 70 and 50 km of the middle atmosphere. This fact indicates the need to take into account the electronic kinetics of N_2 in the calculation the concentrations of electronically excited oxygen molecules in the Earth's middle atmosphere, as well as in laboratory conditions (active media of discharges, lasers, etc.).

Conclusions

The electronic kinetics of molecular nitrogen and molecular oxygen in the middle atmosphere of the Earth during precipitations of high-energetic protons and electrons is studied. We consider the processes of the excitation of various triplet states of N_2 and of the formation of electronically excited Herzberg states of the O_2 molecule in inelastic collisions (1) and (6) by secondary electrons. Also molecular inelastic collisions in intermolecular electron energy transfer processes (4a-4c) are considered. For the first time it is shown that inelastic molecular collisions influence on vibrational populations of electronically excited molecular oxygen. It is pointed out on very important role of the collisions of $N_2(A^3\Sigma_u^+)$ with O_2 molecules on the electronic excitation of O_2 at the altitudes of the middle atmosphere.

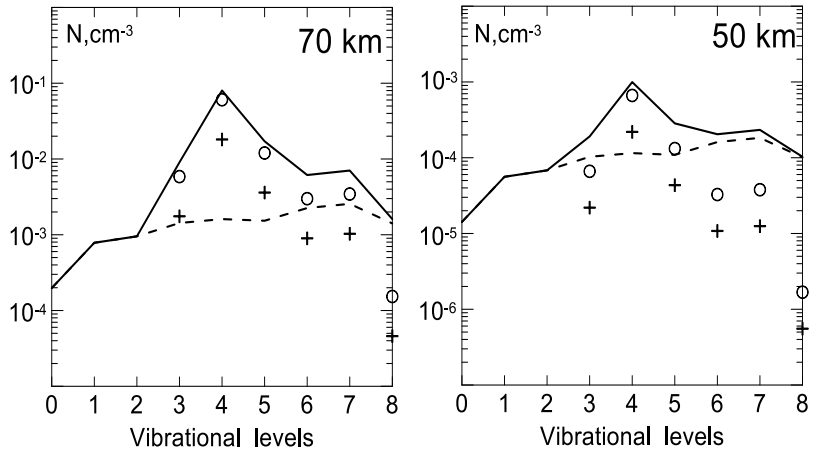

Figure 2. The calculated concentrations of $O_2(c^1\Sigma_u^-, v=0\text{-}8)$ at the altitudes of 70 and 50 km: dashed lines are the contribution of the process (6), crosses are the contribution of the $A^3\Sigma_u$ state of molecular nitrogen excited by secondary electrons, circles are the contribution of the states $B^3\Pi_g$, $W^3\Delta_u$, $B'^3\Sigma_u^-$, $C^3\Pi_u$ of molecular nitrogen excited by secondary electrons, the solid line is the sum of all processes.

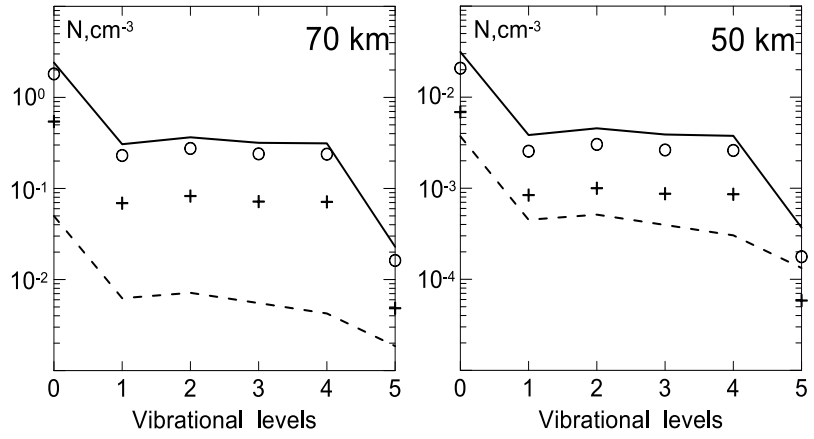

Figure 3. The calculated concentrations of $O_2(A'^3\Delta_u, v=0\text{-}5)$ at the altitudes of 70 and 50 km (designations as in Fig. 2).

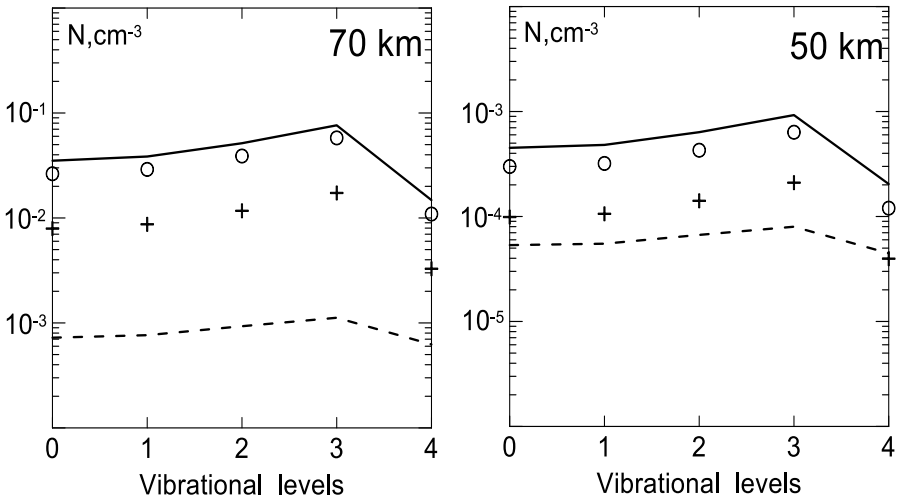

Figure 4. The calculated concentrations of $O_2(A^3\Sigma_u^+,v=0\text{-}4)$ at the altitudes of 70 and 50 km (designations as in Fig. 2).

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