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THE STUDY OF THE ROLE OF INTERMOLECULAR PROCESSES IN THE KINETICS OF $N_2(A^3\Sigma_U^+)$ IN UPPER ATMOSPHERES OF PLANETS OF SOLAR SYSTEM

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Abstract. We study the electronic kinetics of metastable molecular nitrogen $N_2(A^3\Sigma_u^+)$ in upper atmospheres of N_2-rich planets. The simulation of $N_2(A^3\Sigma_u^+)$ vibrational populations at the altitudes of upper atmospheres of the planets is made. The mixtures of N_2-O_2 gases and N_2-CH_4-CO gases are considered for the atmospheres of Earth and Titan-Triton-Pluto, respectively. The role of molecular inelastic collisions in intermolecular electron energy transfer processes is investigated. The influence of metastable molecular nitrogen $N_2(A^3\Sigma_u^+)$ on the electronic excitation of O_2 and CO molecules in inelastic collisions is studied. It is shown that the increase in the density of upper atmospheres of the planets leads to more significant excitation of electronically excited O_2 and CO by intermolecular electron energy transfers from $N_2(A^3\Sigma_u^+)$.

1. 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:

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

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

$$N_2(W^3\Delta_u, v) \rightarrow N_2(B^3\Pi_g, v') + h\nu_{WB} \quad , \qquad (2a)$$
$$N_2(B'^3\Sigma_u^-, v) \rightarrow N_2(B^3\Pi_g, v') + h\nu_{AG} \quad , \qquad (2b)$$
$$N_2(C^3\Pi_u, v) \rightarrow N_2(B^3\Pi_g, v') + h\nu_{2PG} \quad , \qquad (2c)$$
$$N_2(B^3\Pi_g, v') \rightarrow N_2(A^3\Sigma_u^+, v) + h\nu_{1PG} \qquad (3)$$

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,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 mixture of N_2 and CO gases is applied in active media of infrared CO lasers. The presence of other molecular gases in the gas mixture with carbon monoxide leads to a redistribution of energies of vibrational quanta between molecules and affects the temporal dependence of small-signal gain dynamics [*Vetoshkin et al.*, 2007]. Results of the investigation of the effect of N_2, on the small-signal gain and the lasing characteristics of a CO laser operating on CO high vibrational transitions, by *Basov et al.* [2002] have pointed out that the interaction of N_2 molecules with highly excited CO plays a significant part in the production of population inversion on high vibrational levels.

Recent investigations of *Seppälä 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. 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; *Zipf and Prasad*, 1980].

Here we consider the influence of intermolecular electron energy transfer processes from $N_2(A^3\Sigma_u^+)$ on electronic and vibrational kinetics molecules in the mixtures of N_2-O_2 and N_2-CH_4-CO gases.

2. The mixtures of N_2-O_2 gases in the atmosphere of the Earth

The calculation of the rate coefficients for the production of vibrationally excited $N_2(X^1\Sigma_g^+, v'>0)$ molecules in the processes of electronic quenching is made for the collisions of triplet nitrogen $N_2(A^3\Sigma_u^+)$ with N_2 and O_2 molecules.

Here we take into account only spin-allowed processes. Estimations of quenching rate constants for spin-forbidden processes by *Kirillov* [2011] pointed out on about two orders lower values of the coefficients in comparison with ones for spin-allowed processes.

The calculated rate coefficients for the quenching of four triplet states

$$N_2(A^3\Sigma_u^+,v=2\text{–}23) + N_2(X^1\Sigma_g^+,v=0) \rightarrow N_2(X^1\Sigma_g^+,v') + N_2(Y,v'') \,, \tag{4a}$$

$$N_2(A^3\Sigma_u^+,v=0\text{–}23) + O_2(X^3\Sigma_g^-,v=0) \rightarrow N_2(X^1\Sigma_g^+,v') + O_2(Z,v'')\ (O + O) \,, \tag{4b}$$

with $v'\geq1$ are presented by *Kirillov* [2012]. Here *Y,Z* in the process (4a, 4b) means the consideration of $A^3\Sigma_u^+$, $B^3\Pi_g$, $W^3\Delta_u$, $B'^3\Sigma_u^-$ triplet states of N_2 and $a^1\Delta_g$, $b^1\Sigma_g^+$, $c^1\Sigma_u^-$, $A'^3\Delta_u$, $A^3\Sigma_u^+$ states of O_2.

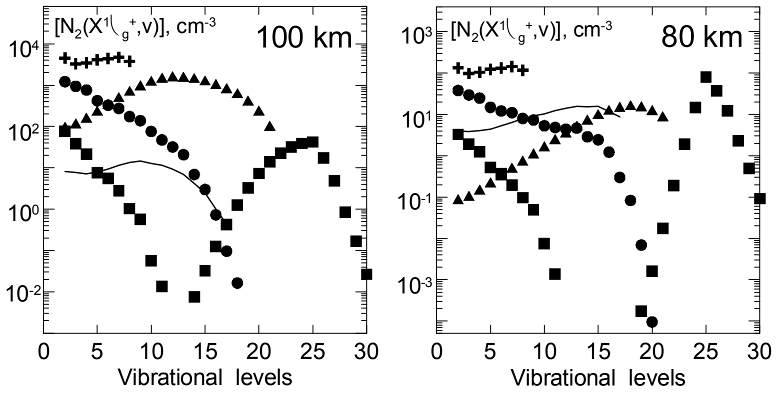

Figure 1. The calculated vibrational populations of the ground-state $N_2(X^1\Sigma_g^+)$ molecule corresponding to the contributions of different sources: from $N_2(A^3\Sigma_u^+)$ through collisions with N_2 and O_2 (*squares* and *circles*, respectively) and spontaneous radiational processes (*triangles*), from triplet states $B^3\Pi_g$, $W^3\Delta_u$, $B'^3\Sigma_u^-$ (*solid lines*) and direct vibrational excitation by auroral electrons (*crosses*) at the altitudes of 100 km (*left*) and 80 km (*right*).

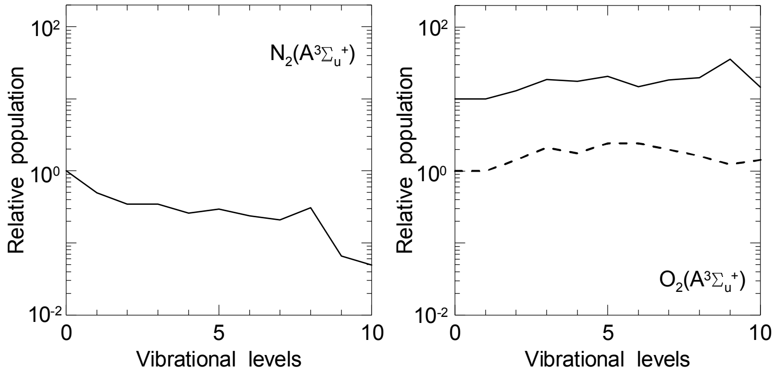

Figure 2. The calculated relative vibrational population of $N_2(A^3\Sigma_u^+)$ (left) at the altitude of 50 km of Earth (*solid line*) and of $O_2(A^3\Sigma_u^+)$ (*right*) without and with inclusion (4b) process (*dashed and solid lines*, respectively).

Contributions of electronically excited nitrogen molecules $N_2(A^3\Sigma_u^+)$, $N_2(B^3\Pi_g$, $W^3\Delta_u$, $B'^3\Sigma_u^-)$ and of direct excitation by auroral electron impact (1) in vibrational population of the ground state $X^1\Sigma_g^+$ of N_2 at the altitudes of 100 and 80 km of auroral lower thermosphere and mesosphere of the Earth are presented in Fig. 1. It is seen from Fig. 1 that metastable nitrogen $N_2(A^3\Sigma_u^+)$ plays very important role in vibrational kinetics of $N_2(X^1\Sigma_g^+)$. The contribution of metastable nitrogen $N_2(A^3\Sigma_u^+)$ in the vibrational excitation of $N_2(X^1\Sigma_g^+,v>0)$ dominates for high considered vibrational levels $v>22$. Moreover, it is seen from Fig. 1 that the increase in the density of the upper atmosphere of the Earth leads to the higher contribution of molecular inelastic collisions in the vibrational excitation of the ground-state molecular nitrogen $N_2(X^1\Sigma_g^+)$ in the upper atmosphere during auroral electron precipitations. Similar results should be in the case of the penetration of high-energetic electrons for conditions of a laboratory discharge.

Fig. 2 is a plot of the calculated relative vibrational populations of the $A^3\Sigma_u^+$ state of molecular nitrogen N_2 ($[N_2(A^3\Sigma_u^+,v=0\text{-}10)]/[N_2(A^3\Sigma_u^+,v=0)]$) at the altitude of 50 km for the case of solar proton precipitations taking into account all intramolecular and intermolecular electron energy transfer process by inelastic molecular collisions. Concentrations of main atmospheric components are taken as $[N_2]=1.2\times10^{16}$ cm^{-3}, $[O_2]=3.1\times10^{15}$ cm^{-3}. Also we consider the vibrational populations of the $A^3\Sigma_u^+$ state of molecular oxygen O_2 ($[O_2(A^3\Sigma_u^+,v=0\text{-}10)]/[O_2(A^3\Sigma_u^+,v=0)]$) at the altitude of 50 km without and with inclusion (4b) process. It is seen from Fig.2 that the process (4b) of electron energy transfer by inelastic molecular collisions plays very important role in electronic excitation of the $A^3\Sigma_u^+$ state of molecular oxygen O_2. The contribution of the intermolecular process of electron energy transfer dominates in the excitation of $O_2(A^3\Sigma_u^+,v=0\text{-}10)$ and it exceeds the contribution of the electronic excitation related with the impact of O_2 molecules by high-energetic particles.

3. The mixtures of N_2-CH_4-CO gases in the atmospheres of Titan, Triton, Pluto

Kirillov [2016] has shown that intermolecular electron energy transfers play a very important role in the processes of electronic quenching of metastable nitrogen $N_2(A^3\Sigma_u^+)$ in collisions with CO molecules.

$N_2(A^3\Sigma_u^+,v=0\text{-}23) + CO(X^1\Sigma^+,v=0) \rightarrow N_2(X^1\Sigma_g^+,v''\geq 0) + CO(a^3\Pi,v')$, (5)

Good agreement of the calculated rate coefficients with a few available experimental data was obtained in that paper. Also, the removal rates for the process

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

from [*Herron*, 1999] are used in the calculations. Comprehensive quantum chemical analysis by *Sharipov et al.* [2016] was carried out to study the processes (6). They have shown that the reaction of $N_2(A^3\Sigma_u^+)$ with CH_4 can lead to the dissociative quenching of $N_2(A^3\Sigma_u^+)$ and the production of H and CH_3.

The calculated vibrational populations of $N_2(A^3\Sigma_u^+,v=0\text{-}15)$ and $CO(a^3\Pi,v=0\text{-}10)$ at the altitudes of 1200, 1000, 800 and 724 km in Titan's upper atmosphere are presented by *Kirillov et al.* [2017]. The calculated vibrational populations of $N_2(A^3\Sigma_u^+,v=0\text{-}15)$ at the altitudes of 170 and 320 km in Triton's upper atmosphere and at the altitudes of 420 and 660 km in Pluto's upper atmosphere are presented by *Kirillov et al.* [2018].

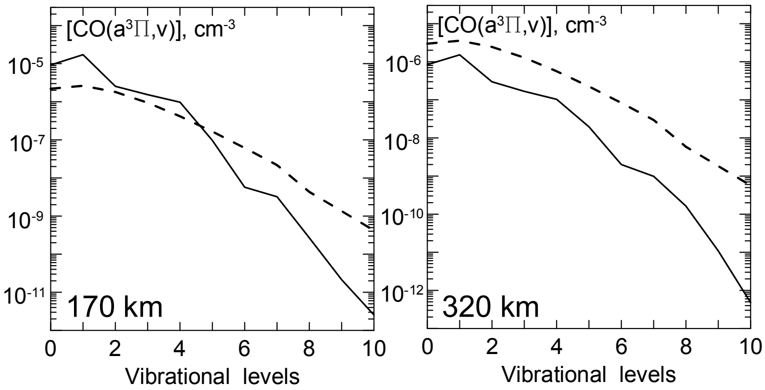

Figure 3. The calculated vibrational populations of $CO(a^3\Pi,v=0\text{-}10)$ at the altitudes of 170 and 320 km in Triton's upper atmosphere: the contributions of the processes (5) and (7) are solid and dashed lines, respectively [*Kirillov et al.*, 2018].

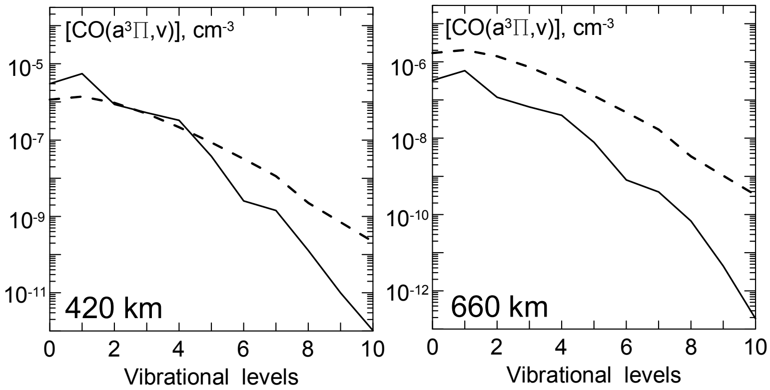

Figure 4. The calculated vibrational populations of $CO(a^3\Pi,v=0\text{-}10)$ at the altitudes of 420 and 660 km in Pluto's upper atmosphere: the contributions of the processes (5) and (7) are solid and dashed lines, respectively [*Kirillov et al.*, 2018].

The calculated vibrational populations of $CO(a^3\Pi,v=0\text{-}10)$ at the altitudes of 170 and 320 km in Triton's upper atmosphere and at the altitudes of 420 and 660 km in Pluto's upper atmosphere are shown in Figs. 3 and 4, respectively. The calculated populations of $CO(a^3\Pi,v)$ includes the contributions of direct excitation by electrons:

$e + CO(X^1\Sigma^+,v=0) \rightarrow CO^*(a^3\Pi,v'\geq 0) + e$. (7)

Also, the calculations show that the increase in the density of upper atmospheres of the planets leads to the more effective excitation of lowest vibrational levels of $CO(a^3\Pi)$ by the intermolecular process (5). The exceeding of the contribution by intermolecular energy transfer process (5) over the contribution by direct electron impact (7) is seen at the altitudes of 170 (Triton) and 420 (Pluto) km. Therefore, there is a possibility of effective pumping of electronic excitation of CO molecules by metastable molecular nitrogen in N_2-rich atmospheres and the rates of the pumping increase with the enhancement in the density of the atmosphere. Similar results should be in the case of the penetration of high-energetic electrons for conditions of a laboratory discharge in the mixture of N_2 and CO gases.

4. Conclusions

We have studied the electronic kinetics of metastable molecular nitrogen $N_2(A^3\Sigma_u^+)$ in upper atmospheres of the planets. The mixtures of N_2-O_2 and N_2-CH_4-CO was considered for the atmospheres of Earth and Titan-Triton-Pluto, respectively. It is shown that the increase in the density of upper atmospheres of the planets leads to more significant excitation of electronically excited O_2 and CO by intermolecular electron energy transfers from metastable nitrogen $N_2(A^3\Sigma_u^+)$. Also electronically excited N_2 plays very important role in vibrational excitation of $N_2(X^1\Sigma_g^+,v>0)$ at the altitudes of lower thermosphere and mesosphere.

1. There is the influence of metastable nitrogen $N_2(A^3\Sigma_u^+)$ on N_2 vibrational kinetics and O_2 electronic kinetics in the atmosphere of Earth (N_2-O_2 mixture).
2. There is the influence of metastable nitrogen $N_2(A^3\Sigma_u^+)$ on electronic excitation of $CO(a^3\Pi)$ in inelastic molecular collisions in the atmospheres of Titan, Triton, Pluto (N_2-CH_4-CO mixture).

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