"Physics of Auroral Phenomena", Proc. XLI Annual Seminar, Apatity, pp. 110-113, 2018

Polar Geophysical Institute

DOI: 10.25702/KSC.2588-0039.2018.41.110-113

INTERMOLECULAR ELECTRON ENERGY TRANSFER PROCESSES IN UPPER ATMOSPHERES OF TITAN, TRITON, PLUTO

A.S. Kirillov[1], R. Werner[2], V. Guineva[2]

[1]*Polar Geophysical Institute, Apatity, Murmansk region, Russia*
[2]*Space Research and Technology Institute of Bulgarian Academy of Sciences, Stara Zagora Department, Stara Zagora, Bulgaria*

Abstract. The simulation of $N_2(A^3\Sigma_u^+)$ and $CO(a^3\Pi)$ vibrational populations at the altitudes of upper atmospheres of Titan, Triton, Pluto is made. The simulation includes the consideration of the electronic excitation of N_2 and CO triplet states by photoelectrons and the quenching processes in spontaneous radiation and in inelastic molecular collisions. Upper atmospheres of the planets are considered as mixtures of molecular nitrogen N_2, methane CH_4, carbon monoxide CO. The influence of metastable molecular nitrogen $N_2(A^3\Sigma_u^+)$ on the electronic excitation of CO molecules in inelastic collisions is studied. The role of molecular inelastic collisions in intermolecular electron energy transfer processes is investigated. It is shown that the increase in the density of upper atmospheres of the planets leads to more significant excitation of lowest vibrational levels of $CO(a^3\Pi)$ by intermolecular electron energy transfers from $N_2(A^3\Sigma_u^+)$ in comparison with direct excitation of the $a^3\Pi$ state by photoelectrons.

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

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

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, 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 $CO(a^3\Pi)$ vibrational populations in an N_2-rich atmospheres of planets with the admixture of CO and CH_4 gases. We simulate the populations at the altitudes of upper atmospheres of Titan, Triton, Pluto for conditions of the interaction with photoelectrons. Special attention is paid to the study of the contribution of the $B^3\Pi_g$, $W^3\Delta_u$, $B'^3\Sigma_u^-$, $C^3\Pi_u$ triplet states of N_2 in the vibrational populations.

The quenching rate coefficients

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 N_2 and CO molecules. Good agreement of the calculated rate coefficients with a few available experimental data was obtained in that paper. Here in the simulation of $N_2(A^3\Sigma_u^+)$ and $CO(a^3\Pi)$ vibrational populations we consider the contributions of intermolecular

$$N_2(A^3\Sigma_u^+, v=0\text{-}23) + CO(X^1\Sigma^+, v=0) \rightarrow N_2(X^1\Sigma_g^+, v''\geq 0) + CO(a^3\Pi, v') \quad , \quad (4)$$
$$N_2(A^3\Sigma_u^+, v=2\text{-}23) + N_2(X^1\Sigma_g^+, v=0) \rightarrow N_2(X^1\Sigma_g^+, v''\geq 0) + N_2(A^3\Sigma_u^+, v') \quad , \quad (5)$$
$$N_2(A^3\Sigma_u^+, v=7\text{-}23) + N_2(X^1\Sigma_g^+, v=0) \rightarrow N_2(X^1\Sigma_g^+, v''\geq 0) + N_2(B^3\Pi_g, v') \quad (6a)$$

and intramolecular

$$N_2(A^3\Sigma_u^+, v=7\text{-}23) + N_2(X^1\Sigma_g^+, v=0) \rightarrow N_2(B^3\Pi_g, v') + N_2(X^1\Sigma_g^+, v=0) \quad (6b)$$

electron energy transfer processes in the removal of metastable nitrogen by inelastic collisions with CO and N_2 molecules. The quenching rate constants of the processes (4, 5, 6a,b) calculated according to analytical formula of [*Kirillov*, 2016] at room temperature have been presented in [*Kirillov*, 2016; *Kirillov et al*., 2017]. Also we suggest to consider the quenching of vibrational levels v=0,1 of the $A^3\Sigma_u^+$ state in the collisions with N_2 molecules as intramolecular quasi-resonant energetic transitions to the $X^1\Sigma_g^+$ state [*Kirillov*, 2012]

$$N_2(A^3\Sigma_u^+,v=0,1) + N_2(X^1\Sigma_g^+,v=0) \rightarrow N_2(X^1\Sigma_g^+,v''=25,26) + N_2(X^1\Sigma_g^+,v=0) \quad . \tag{7}$$

The values $k_7(v=0)=3.7\times10^{-16}$ and $k_7(v=1)=3.4\times10^{-16}$ cm^{3}s^{-1} of the quenching constants of the process (7) for the two vibrational levels are taken according to experimental data by *Dreyer and Perner* [1973].

The calculations of the rate constants $k_4(v)$ for the process (4) by *Kirillov* [2016] have shown a disagreement with experimental data by *Dreyer et al.* [1974] and by *Thomas et al.* [1987] for vibrational level v=0 of metastable nitrogen. Here in our calculations we use the experimental value $k_4(v=0)=1.8\times10^{-12}$ cm^{3}s^{-1} measured by *Dreyer et al*. [1974] with the quantum exits $f_4(v=0\rightarrow v'=0)/f_4(v=0\rightarrow v'=1)\approx5:1$ in agreement with theoretical estimations by *Kirillov* [2016]. Also, the removal rates for the process

$$N_2(A^3\Sigma_u^+,v=1\text{-}6) + CH_4 \rightarrow \text{products} \tag{8}$$

from [*Golde et al*., 1989; *Herron*, 1999] are used in the calculations. Comprehensive quantum chemical analysis by *Sharipov et al.* [2016] was carried out to study the processes (8). 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. Also *Golde et al.* [1989] detected H atoms as a product, but were not able to make a quantitative measurement. By studying the reaction with added CF_3H to relax the upper vibrational levels of $N_2(A^3\Sigma_u^+)$, *Golde et al.* [1989] deduced that vibrational relaxation was the principal deactivation process for v>0, in agreement with *Thomas et al*. [1987], but may be with 12% going by electronic quenching.

Vibrational populations of $N_2(A^3\Sigma_u^+)$ and $CO(a^3\Pi)$ in upper atmospheres of Titan, Triton, Pluto

Vibrational populations of the $W^3\Delta_u$, $B'^3\Sigma_u^-$, $C^3\Pi_u$ states are determined using the equilibrium equations

$$V_i(h)\,q_v^i = \sum_{v'} A_{vv'}^{iB}\, n_v^i(h) \quad , \tag{9}$$

where q_v^i is Franck-Condon factor for the excitation (1) of $N_2(X^1\Sigma_g^+,v=0)$ to the vth level of the ith state with the population n_v^i, $A_{vv'}^{iB}$ are Einstein probabilities for spontaneous radiational transitions (2a-c). To calculate vibrational populations $n_{v'}^B$ and n_v^A for the $B^3\Pi_g$ and $A^3\Sigma_u^+$ states we apply the following equations

$$V_B(h)\,q_{v'}^B + \sum_{i=W,B',C,A}\ \sum_v A_{vv'}^{iB}\, n_v^i(h) + \sum_v \{k_{6a}(v,v') + k_{6b}(v,v')\}[N_2]\,n_v^A(h) = \sum_v A_{v'v}^{BA}\, n_{v'}^B(h) \quad , \tag{10}$$

$$\begin{aligned} &V_A(h)\,q_v^A + \sum_{v'} A_{v'v}^{BA}\, n_{v'}^B(h) + \sum_{v'>v} k_5(v',v)[N_2]\,n_{v'}^A(h) = \\ &= \{[k_5(v) + k_{6a}(v) + k_{6b}(v) + k_7(v)][N_2] + k_8(v)[CH_4] + k_4(v)[CO] + \sum_{v'} A_{vv'}^{AB} + \sum_{v''} A_{vv''}^{AX}\ \}\,n_v^A(h) \end{aligned} \quad , \tag{11}$$

where we take into account not only radiational processes (2a-c,3) but reverse First Positive bands $A^3\Sigma_u^+,v\rightarrow B^3\Pi_g,v'$ [*Gilmore et al.*, 1992]. The quenching rate constants in the equations (10) and (11) are taken according to calculated or measured values at room temperature presented in [*Kirillov*, 2016; *Kirillov et al*., 2017]. It is suggested $k_8(v\geq7)=k_8(v=6)$ in the calculations.

The calculated population of $N_2(A^3\Sigma_u^+,v)$ includes the contributions of the channels:

(a) direct excitation of the $A^3\Sigma_u^+$ state by electron impact (1),

(b) direct excitation of the $B^3\Pi_g$, $W^3\Delta_u$, $B'^3\Sigma_u^-$, $C^3\Pi_u$ states by electron impact (1) and following radiational transitions (2a-c) and (3).

The calculated population of $CO(a^3\Pi,v)$ includes the contributions of the channels:

(c) the processes (a), (b) and (4),

(d) the process

$$e + CO(X^1\Sigma^+,v=0) \rightarrow CO^*(a^3\Pi,v'\geq0) + e \quad . \tag{12}$$

To calculate the concentrations of metastable carbon monoxide we use the measured by *Wysong* [2000] rate coefficients for the deexcitation processes

$$CO(a^3\Pi,v'=0) + N_2 \rightarrow \text{products} \quad , \tag{13}$$

$$CO(a^3\Pi,v'=0) + CO \rightarrow \text{products} \quad . \tag{14}$$

The measured in [*Wysong*, 2000] values of removal rates $k_{13}(v=0)=1.4\times10^{-11}$ cm^{3}s^{-1} and $k_{14}(v=0)=5.7\times10^{-11}$ cm^{3}s^{-1} are suggested in our calculations for all vibrational levels of the $a^3\Pi$ state in the inelastic collisions (13) and (14) with N_2 and CO molecules. The radiative lifetimes of all vibrational levels of metastable carbon monoxide CO($a^3\Pi$) are believed to be equal to 3 ms according to estimations by *Sykora and Vidal* [1999] for v=0. Therefore, the vibrational populations $n_{v'}^a$ of the $a^3\Pi$ state are determined using the equilibrium equations

$$V_a(h)\,q_v^a + \sum_v A_{vv'}^{Aa}[CO]\,n_v^A(h) = (1.4\times10^{-11}\times[N_2] + 5.7\times10^{-11}\times[CO] + \sum_{v''} A_{v'v''}^{aX})\,n_{v'}^a(h) \quad , \qquad (15)$$

where $\sum_{v''} A_{vv''}^{aX} \approx 330$ s^{-1} for radiational processes

$$CO(a^3\Pi, v') \rightarrow CO(X^1\Sigma^+, v'') + h\nu_{Cam} \qquad (16)$$

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 shown in Figs. 1 and 2, respectively. 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.

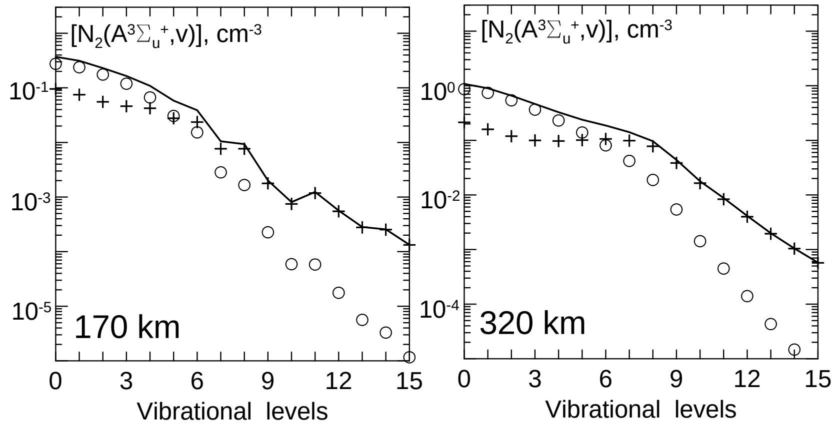

Figure 1. The calculated vibrational populations of $N_2(A^3\Sigma_u^+, v=0\text{-}15)$ at the altitudes of 170 and 320 km in Triton's upper atmosphere (*solid lines*), the contribution of the processes (1) and (2a-c,3) are *crosses* and *circles*, respectively.

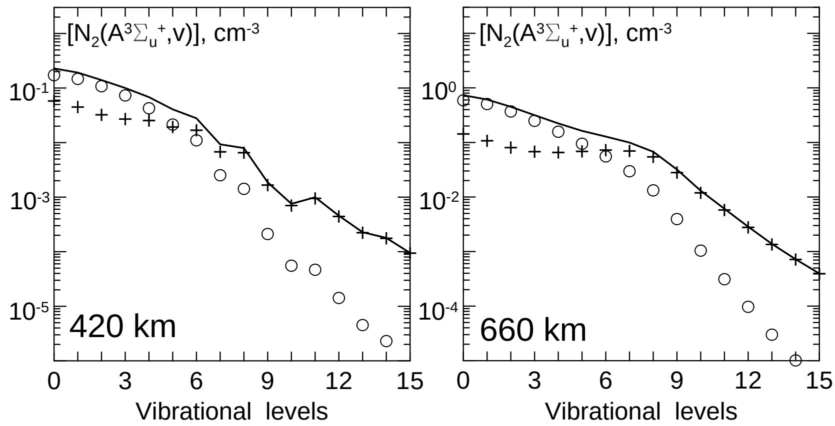

Figure 2. The calculated vibrational populations of $N_2(A^3\Sigma_u^+, v=0\text{-}15)$ at the altitudes of 420 and 660 km in Pluto's upper atmosphere (*solid lines*), the contribution of the processes (1) and (2a-c,3) are *crosses* and *circles*, respectively.

The results of our calculations show that other triplet states $B^3\Pi_g$, $W^3\Delta_u$, $B'^3\Sigma_u^-$, $C^3\Pi_u$ play very important role in vibrational excitation of the $A^3\Sigma_u^+$ and $a^3\Pi$ states. The contributions of the triplet states by radiational cascades (2a-b) and (3) dominates in the excitation at lowest vibrational levels of the $A^3\Sigma_u^+$ state.

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 (4). The exceeding of the contribution by intermolecular energy transfer process (4) over the contribution by direct electron impact (16) 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.

Conclusion

Here we have studied the role of molecular inelastic collisions in intermolecular electron energy transfer processes. It is shown that the increase in the density of upper atmospheres of Titan, Triton, Pluto leads to more significant excitation of lowest vibrational levels of CO($a^3\Pi$) by intermolecular electron energy transfers from $N_2(A^3\Sigma_u^+)$ in comparison with direct excitation of the $a^3\Pi$ state by photoelectrons.

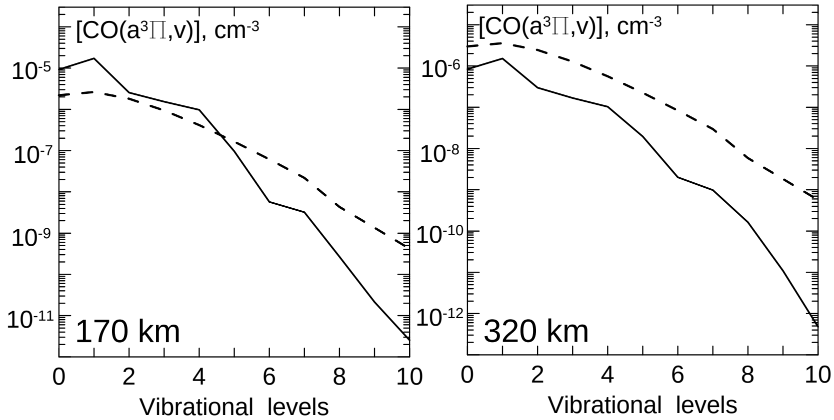

Figure 3. The calculated vibrational populations of CO($a^3\Pi$,*v*=0-10) at the altitudes of 170 and 320 km in Triton's upper atmosphere: the contributions of the processes (4) and (16) are *solid* and *dashed lines*, respectively.

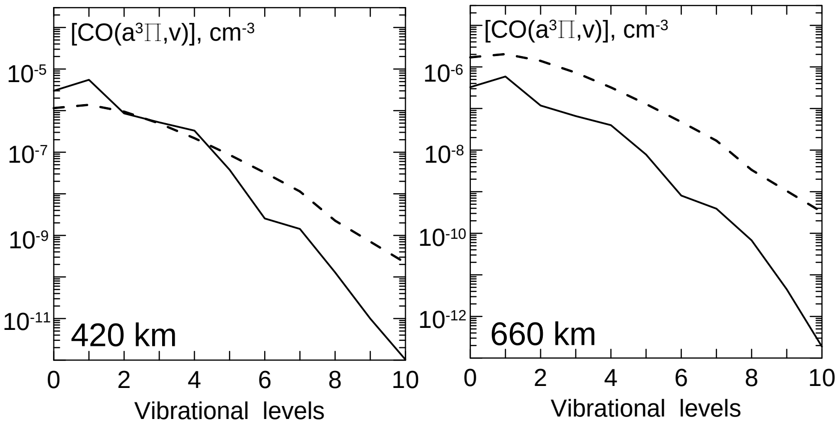

Figure 4. The calculated vibrational populations of CO($a^3\Pi$,*v*=0-10) at the altitudes of 420 and 660 km in Pluto's upper atmosphere: the contributions of the processes (4) and (16) are *solid* and *dashed lines*, respectively.

References

Campbell L., Brunger M.J., Electron collisions in atmospheres, 2016, Inter. Rev. Phys. Chem., v.35, №2, p.297-351.

Dreyer J.W., Perner D., Deactivation of $N_2(A^3\Sigma_u^+$,v=0-7) by ground state nitrogen, ethane, and ethylene measured by kinetic absorption spectroscopy, 1973, J. Chem. Phys., v.58, №3, p.1195-1201.

Dreyer J.W., Perner D., Roy C.R., Rate constants for the quenching of $N_2(A^3\Sigma_u^+$,v_A=0-8) by CO, CO_2, NH_3, NO, and O_2, 1974, J. Chem. Phys., v.61, №8, p.3164-3169.

Gilmore F.R., Laher R.R., Espy P.J., Franck-Condon factors, r-centroids, electronic transition moments, and Einstein coefficients for many nitrogen and oxygen band systems, 1992, J. Phys. Chem. Ref. Data, v.21, №5, p.1005-1107.

Golde M.F., Ho G.H., Tao W., Thomas J.M., Collisional deactivation of $N_2(A^3\Sigma_u^+$,v=0-6) by CH_4, CF_4, H_2, H_2O, CF_3Cl, and CF_2HCl, 1989, J. Phys. Chem., v.93, №3, p.1112-1118.

Herron J.T., Evaluated chemical kinetics data for reactions of N(^{2}D), N(^{2}P), and $N_2(A^3\Sigma_u^+)$ in the gas phase, 1999, J. Phys. Chem. Ref. Data, v.28, №5, p.1453-1483.

Kirillov A.S., Influence of electronically excited N_2 and O_2 on vibrational kinetics of these molecules in the lower thermosphere and mesosphere during auroral electron precipitation, 2012, J. Atmos. Solar Terr. Phys., v.81-82, p.9-19.

Kirillov A.S., Intermolecular electron energy transfer processes in the collisions of $N_2(A^3\Sigma_u^+$,v=0-10) with CO and N_2 molecules, 2016, Chem. Phys. Lett., v.643, p.131-136.

Kirillov A.S., Werner R., Guineva V., The influence of metastable molecular nitrogen $N_2(A^3\Sigma_u^+)$ on the electronic kinetics of CO molecules, 2017, Chem. Phys. Lett., v.685, p.95-102.

Sharipov A.S., Loukhovitski B.I., Starik A.M., Theoretical study of the reactions of methane and ethane with electronically excited $N_2(A^3\Sigma_u^+)$, 2016, J. Phys. Chem. A, v.120, №25, p.4349-4359.

Sykora T., Vidal C.R., Lifetimes of the CO metastable $a^3\Pi(v\leq3,\Omega,J)$ levels, 1999, J. Chem. Phys., v.110, №13, p.6319-6328.

Thomas J.M., Kaufman F., Golde M.F., Rate constants for electronic quenching of $N_2(A^3\Sigma_u^+$,v=0-6) by O_2, NO, CO, N_2O, and C_2H_4, 1987, J. Chem. Phys., v.86, №12, p.6885-6892.

Wysong I.J., Measurement of quenching rates of CO($a^3\Pi$,v=0) using laser pump-and-probe technique, 2000, Chem. Phys. Lett., v.329, №1-2, p.42-46.