Vibrational kinetics of NO and N_2 in the Earth's middle atmosphere during GLE69 on January 20, 2005

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Key Points:

Vibrational kinetics of NO and N_2 in the middle atmosphere during high-energetic proton precipitation is considered.

Intramolecular and intermolecular electron energy transfers are taken into account in calculations of vibrational populations of molecules.

It is shown that there is a dependence of calculated vibrational populations on the altitude of the atmosphere.

Abstract

The mechanisms of the production of vibrationally excited NO and N_2 molecules at the altitudes of the middle atmosphere of the Earth during high-energetic proton precipitation are considered. The study of vibrational populations $N_2(X^1\Sigma_g^+,v'>0)$ during high-energetic proton precipitation has shown different principal mechanisms in the $N_2(X^1\Sigma_g^+,v'>0)$ excitation. Firstly, the excitation by secondary electrons is principal for vibrational levels $v'=1–10$. Secondly, it is obtained that intramolecular electron energy transfer process in $N_2(A^3\Sigma_u^+)+N_2$ collisions dominates in vibrational excitation of high vibrational levels $v'=20–30$. It is shown that the chemical reaction of metastable atomic nitrogen with molecular oxygen is the main production mechanism of vibrationally excited $NO(X^2\Pi,v>0)$ and of the radiation of 5.3 μm and 2.7 μm infrared emissions at the altitudes. The role of VV'-processes in the radiation of the 5.3 μm infrared emission is discussed.

1. Introduction

Solar protons play significant role in the atmosphere of Earth. The particles are usually characterized by soft energy spectra (energies of the order of several hundred MeV) but sometimes relativistic energetic protons are observed. They are detected as ground level enhancements (GLEs) by the terrestrial neutron monitors placed in polar areas. The use of data from a network of neutron monitors makes it possible to determine the spectra of high-energetic protons precipitated into the Earth's atmosphere.

The energetic particle precipitation causes an increase in odd nitrogen NO_x and odd hydrogen HO_x at the altitudes of high-latitude atmosphere via a cascade of dissociation, ionization, and recombination processes. During solar proton events (SPE) the particle precipitation into the atmosphere can produce ozone depletion in the middle atmosphere. Seppälä et al. (2006, 2008), Verronen et al. (2007), Jackman et al. (2011), Damiani et al. (2012), Mironova et al. (2012) have analyzed the influence of very large solar proton events in January 2005 over the long-term middle atmosphere, indicating that the impact of energetic particle precipitations was in the production of odd nitrogen (NO_x) and odd hydrogen (HO_x), in the changes of ozone content profiles, in enhancement of chlorine compounds.

Nitric oxide molecules NO have a valent electron and take an active part in the chemistry and vibrational kinetics of the atmosphere. In particular the cross sections of the inelastic

collision of NO molecule have high magnitudes in their interaction with other radicals. The rate coefficient of the interaction may be of the order of the gas-kinetic value (Smith, 1986). Since odd nitrogen is efficiently produced in the upper atmosphere during auroral precipitation and in the middle atmosphere during the precipitation of high-energetic protons, the concentrations of nitric oxide can be increased sufficiently influencing the chemical balance of the polar upper and middle atmosphere. Moreover, Kockarts (1980), Caledonia and Kennealy (1982), Gordiets et al. (1982), Gordiets (1986), Sharma et al. (1996), Kirillov and Aladjev (1998), Cartwright et al. (2000), Campbell and Brunger (2007), Venkataramani et al. (2016), Bouziane et al. (2021) have shown that nitric oxide plays a significant role in infrared balance of the upper atmosphere and have studied production and loss mechanisms of vibrationally excited NO molecules. Special attention in the papers was devoted to the infrared 5.3 μm and 2.7 μm emissions of nitric oxide molecules radiated in the spontaneous transitions

$$NO(X^2\Pi, v>0) \rightarrow NO(X^2\Pi, v'=v-1) + h\nu_{5.3} \ , \quad (1a)$$

$$NO(X^2\Pi, v>1) \rightarrow NO(X^2\Pi, v'=v-2) + h\nu_{2.7} \ , \quad (1b)$$

where $X^2\Pi$ is the ground sate of nitric oxide molecule. Therefore these infrared emissions are characteristic features in the atmospheric spectrum when the atmosphere is disturbed by high-energetic particles.

Moreover, important role of electronically and vibrationally excited atmospheric molecules in chemical balance of disturbed atmosphere is known. Mrazkova et al. (2009) have concluded that a certain amount of energy is needed for the dissociation, the production must be caused by some long-lived energy carrying species, such as N_2 metastables or vibrationally excited states. Fraser et al. (1990) have postulated from their experimental measurements that the interaction of vibrationally excited nitrogen $N_2(X^1\Sigma_g^+, v\geq 15)$ with singlet oxygen $O_2(a^1\Delta_g, b^1\Sigma_g^+)$ can be considered as possible effective mechanism of the production of greenhouse gas N_2O during atmospheric disturbances related with precipitations of high-energetic particles. Gordiets et al. (1982) have presented a theory of infrared radiation (2-20 μm) of the Earth's upper atmosphere. They have considered physical processes leading to vibrational excitation of minor components in the atmosphere. One of the processes is the energy exchange in the collisions with vibrationally excited $N_2(X^1\Sigma_g^+, v>0)$ molecules. Good energy quasi-resonance in vibrational modes causes effective transfer of vibrational excitation from N_2 molecules to minor atmospheric components.

Richards et al. (1986) have firstly recognized the potential importance of cascade from $A^3\Sigma_u^+$ triplet state of N_2 on vibrational excitation of the molecules in the ionosphere. Richards et al. (1986) have not presented any quantitative study of the cascade, but they concluded that it could be very important. Aladjev and Kirillov (1995) have numerically studied the contribution of radiational spontaneous transitions from electronically excited molecules $N_2(A^3\Sigma_u^+, v)$ in vibrational excitation of N_2 molecules in the high-latitude ionosphere. They have shown that an increase in the density of the atmosphere causes the rise of relative contribution from these cascade processes during inelastic molecular collisions in vibrational excitation of N_2. Campbell et al. (2006) presented an extensive study of the role of electronically excited N_2 in vibrational excitation of the N_2 $X^1\Sigma_g^+$ ground state at high latitudes. Kirillov (2012) has shown significant contributions of cascade processes in molecular collisions on vibrational population of the $X^1\Sigma_g^+$ state at altitudes of the lower thermosphere and mesosphere during auroral electron precipitation.

Kirillov et al. (2021) have considered electronic kinetics of five triplet $A^3\Sigma_u^+$, $B^3\Pi_g$, $W^3\Delta_u$, $B'^3\Sigma_u^-$, $C^3\Pi_u$ of molecular nitrogen N_2 in the middle atmosphere during precipitation of high-energetic protons during GLE69 taking into account intermolecular and intramolecular electron energy transfer processes. The results of the calculations by Kirillov et al. (2021) have shown high efficiencies of intermolecular and intramolecular electron energy transfers in the quenching of N_2 triplet states and redistribution of dissipated energy of protons between electronically excited states of molecular nitrogen. As one might expect similar high excitation rates for vibrational levels of ground-state molecules $N_2(X^1\Sigma_g^+)$ can be at the altitudes of the middle

atmosphere where collisional lifetimes of electronically excited molecules are less than radiational ones and intermolecular and intramolecular energy transfer processes could contribute to this vibrational excitation.

The purpose of the present work is to study the vibrational populations of nitric oxide $NO(X^2\Pi,v>0)$ and molecular nitrogen $N_2(X^1\Sigma_g^+,v>0)$ taking into account cascade processes from electronically excited N_2 in the middle atmosphere during GLE69 event. The study will include the calculations of intensities of infrared 5.3 μm and 2.7 μm emissions at the altitudes of the middle atmosphere with the inclusion of the excitation by secondary electrons and intermolecular and intramolecular electron energy transfers in inelastic molecular collisions.

2. The production and loss mechanisms of vibrationally excited nitric oxide in the middle atmosphere during proton precipitations

Vibrationally excited NO molecules radiates effectively the 5.3 μm and 2.7 μm emissions and the calculation of intensities of infrared nitric oxide radiation in the atmosphere requires knowledge of main production mechanisms of $NO(X^2\Pi,v>0)$ and quantum efficiencies of vibrational excitation to different levels in the processes of the excitation. Also it is necessary to take into account all loss processes including spontaneous radiative transitions and vibrational relaxation in inelastic molecular collisions with other atmospheric components.

The primary sources of vibrationally excited NO in auroral ionosphere have been discussed by Kockarts (1980), Caledonia and Kennealy (1982), Gordiets et al. (1982), Gordiets (1986), Sharma et al. (1996), Kirillov and Aladjev (1998), Cartwright et al. (2000), Campbell and Brunger (2007), Venkataramani et al. (2016), Bouziane et al. (2021). The main production mechanisms of $NO(X^2\Pi,v)$ in the mixture N_2 and O_2 with high translational temperature and during the penetration of high-energetic particles in the upper atmosphere are the chemical reactions of unexcited and metastable atomic nitrogen with molecular oxygen

$$N(^4S) + O_2 \rightarrow NO(X^2\Pi,v) + O \quad , \qquad (2a)$$
$$N(^2D) + O_2 \rightarrow NO(X^2\Pi,v) + O \quad , \qquad (2b)$$
$$N(^2P) + O_2 \rightarrow NO(X^2\Pi,v) + O \quad , \qquad (2c)$$

where atoms $N(^4S,^2D,^2P)$ are mainly produced in N_2 dissociation and dissociative ionization by auroral electron impact or in ionic cycle of the auroral ionosphere, and TV-energy transfer in thermal collisions

$$NO(X^2\Pi,v=0) + O \rightarrow NO(X^2\Pi,v>0) + O \quad . \qquad (3).$$

Since the concentrations of atomic oxygen and temperature in the middle atmosphere have low values, the processes (2a) and (3) can be neglected in the production of vibrationally excited $NO(X^2\Pi)$ at the altitudes.

Cartwright et al. (2000) have paid special attention to electron impact excitation of vibrational levels in the ground electronic state $X^2\Pi$ and nine electronically excited states of NO molecules in the upper atmosphere. They have simulated vibrational populations of the states for an IBC II aurora in order to predict NO excited state number densities and band emission intensities. The vibrational populations of 10 NO electronic states in auroral ionosphere were determined under conditions of statistical equilibrium. The model has taken into account an extended vibrational distribution in the NO ground electronic state $X^2\Pi$ produced in the processes of direct excitation by secondary auroral electrons and in radiative cascades from seven doublet and two quartet higher-lying excited electronic states populated by electron impact

$$e + NO(X^2\Pi,v=0) \rightarrow NO(X^2\Pi,v'>0) + e \qquad (4a)$$
$$e + NO(X^2\Pi,v=0) \rightarrow NO(A^2\Sigma^+, B^2\Pi, C^2\Pi, D^2\Sigma^+, L^2\Pi, B'^2\Delta, L'^2\Phi;v') + e \qquad (4b)$$
$$e + NO(X^2\Pi,v=0) \rightarrow NO(a^4\Pi, b^4\Sigma^-;v') + e \qquad (4c)$$

Therefore Cartwright et al. (2000) have calculated fractional population rates for $X^2\Pi,v'>0$ by direct excitation and various radiative processes as a function of the vibrational quantum number v'. Nevertheless they have not included inelastic molecular processes in their study because the concentrations of atmospheric components at the altitudes of the upper atmosphere are small and the collisional lifetimes are large in comparison with radiational lifetimes.

Clark and Setser (1980), Golde and Moyle (1985), Piper et al. (1986), Thomas and Katayama (1993), De Benedictis et al. (1997) have studied in experimental studies that the interaction of metastable molecular nitrogen $N_2(A^3\Sigma_u^+)$ with NO molecules proceeds effectively through the production of electronically excited nitric oxide

$$N_2(A^3\Sigma_u^+,v\geq0) + NO(X^2\Pi,v=0) \rightarrow N_2(X^1\Sigma_g^+,v^*) + NO(A^2\Sigma^+,v'\geq0) \quad (5)$$

The study of calculated relative vibrational populations of the $A^3\Sigma_u^+$ state of N_2 for conditions of laboratory discharge at O_2 admixture 20% for pressures 1-1000 Pa by Kirillov (2011) has shown that there is a accumulation of the energy of electronic excitation on the $A^3\Sigma_u^+$ state and a dependence of the population on the density of the atmosphere. Piper et al. (1986) have determined the rate coefficients for the state-to-state excitation of $NO(A^2\Sigma^+,v'=0\text{-}2)$ by $N_2(A^3\Sigma_u^+,v=0\text{-}2)$ in inelastic collisions (5). Therefore we apply here the rate constants for the process (5) presented by Piper et al. (1986).

The quenching of electronically excited nitric oxide $NO(A^2\Sigma^+)$ at the altitudes of the middle atmosphere can be through the radiation of γ bands (Piper and Cowles, 1986; Settersten et al., 2009a)

$$NO(A^2\Sigma^+,v\geq0) \rightarrow NO(X^2\Pi,v'\geq0) + h\nu_\gamma \quad (6)$$

with the production of vibrationally excited $NO(X^2\Pi)$ or through the inelastic collisions with O_2 molecules (Settersten et al., 2009b; Few et al., 2017; Blackshaw et al., 2019)

$$NO(A^2\Sigma^+,v\geq0) + O_2 \rightarrow NO(X^2\Pi,v'\geq0) + O_2^* \ (O+O) \quad (7)$$

with the electronic transition from the $A^2\Sigma^+$ state to the $X^2\Pi$ state and the electronic excitation of O_2^* molecules or the transition of O_2 molecules in repulsive states with the dissociation of the molecule. Results of experimental measurements by Settersten et al. (2009b) show clearly that collisions of $NO(A^2\Sigma^+,v\geq0)$ with nitrogen molecules can be neglected in comparison with the process (7). Therefore we apply here transition probabilities by Settersten et al. (2009a) for the radiation of γ bands (6) and the quantum yields of $NO(X^2\Pi,v'\geq0)$ in the process (7) according to Few et al. (2017).

The quenching of vibrationally excited nitric oxide $NO(X^2\Pi)$ at the altitudes of the middle atmosphere proceed through the radiation of infrared 5.3 and 2.7 μm bands (1a,b) (Billingsley, 1976; Rawlins et al., 1998) or through the inelastic collisions with O_2 molecules (Green et al., 1982; Hancock et al., 2006)

$$NO(X^2\Pi,v>0) + O_2 \rightarrow NO(X^2\Pi,v'=v\text{-}1) + O_2(v=1) \quad (8)$$

with the excitation of $O_2(X^3\Sigma_g^-)$ molecule in vibrational level $v=1$. We apply here transition probabilities by Rawlins et al. (1998) for the radiation of infrared 5.3 μm and 2.7 μm bands (1a,b) and the rate coefficients of $NO(X^2\Pi,v'\geq0)$ quenching in the process (8) according to Hancock et al. et al. (2006).

3. The production of vibrationally excited molecular nitrogen in the middle atmosphere during proton precipitations

As in our previous papers (Kirillov and Belakhovsky, 2019, 2020a, 2020b) here we similarly consider the excitation of five triplet states of molecular nitrogen in the collisions of $N_2(X^1\Sigma_g^+,v=0)$ molecules with produced in ionization processes secondary electrons at the altitudes of the middle atmosphere

200 $e + N_2(X^1\Sigma_g^+,v=0) \rightarrow N_2(A^3\Sigma_u^+, B^3\Pi_g, W^3\Delta_u, B'^3\Sigma_u^-, C^3\Pi_u;v) + e$ (9)

201 and the excitation of three singlet states of N_2

202 $e + N_2(X^1\Sigma_g^+,v=0) \rightarrow N_2(a'^1\Sigma_u^-, a^1\Pi_g, w^1\Delta_u;v) + e$. (10)

203 The quenching of the triplet states can be through radiational emissions of First and Second
204 Positive (1PG and 2PG), Wu-Benesch (WB), Infrared Afterglow (IRAG), Vegard-Kaplan (VK)
205 band systems and the quenching of the singlet states can be through the radiational emissions of
206 MacFarlane (MF) band systems, Lyman-Birge-Hopfield (LBH) and Ogawa-Tanaka-Wilkinson-
207 Mulliken (OTWM) (Gilmore et al., 1992; Cassasa and Golde, 1979) bands of N_2. Electronic
208 kinetics of the triplet and singlet N_2 states for the altitudes of the middle atmosphere during
209 precipitations of high-energetic particles is described in (Kirillov and Belakhovsky, 2019, 2020a,
210 2000b; Kirillov et al., 2021).

211 Intermolecular electron energy transfers in inelastic molecular collisions at the altitudes of
212 the middle atmosphere lead to both the electronic excitation of target molecule and vibrational
213 excitation in the ground state of primary excited molecule. Intramolecular transfers contribute to
214 the production of vibrationally excited molecule when there are transitions from electronically
215 excited state to the $X^1\Sigma_g^+$ ground state during inelastic collisions. The rate coefficients for the
216 quenching of four triplet states

217 $N_2(A^3\Sigma_u^+,v\geq2) + N_2(X^1\Sigma_g^+,v=0) \rightarrow N_2(X^1\Sigma_g^+,v') + N_2(Y,v^*)$, (11a)
218 $N_2(B^3\Pi_g,v\geq0) + N_2(X^1\Sigma_g^+,v=0) \rightarrow N_2(X^1\Sigma_g^+,v') + N_2(Y,v^*)$, (11b)
219 $N_2(W^3\Delta_u,v\geq0) + N_2(X^1\Sigma_g^+,v=0) \rightarrow N_2(X^1\Sigma_g^+,v') + N_2(Y,v^*)$, (11c)
220 $N_2(B'^3\Sigma_u^-,v\geq0) + N_2(X^1\Sigma_g^+,v=0) \rightarrow N_2(X^1\Sigma_g^+,v') + N_2(Y,v^*)$, (11d)

221 where in the processes (11a–d) Y means the consideration of all four $A^3\Sigma_u^+$, $B^3\Pi_g$, $W^3\Delta_u$, $B'^3\Sigma_u^-$
222 triplet states of N_2, and the rate coefficients for the quenching of three singlet states

223 $N_2(a'^1\Sigma_u^-,v\geq2) + N_2(X^1\Sigma_g^+,v=0) \rightarrow N_2(X^1\Sigma_g^+,v') + N_2(Y,v^*)$, (12a)
224 $N_2(a^1\Pi_g,v\geq1) + N_2(X^1\Sigma_g^+,v=0) \rightarrow N_2(X^1\Sigma_g^+,v') + N_2(Y,v^*)$, (12b)
225 $N_2(w^1\Delta_u,v\geq0) + N_2(X^1\Sigma_g^+,v=0) \rightarrow N_2(X^1\Sigma_g^+,v') + N_2(Y,v^*)$, (12c)

226 where in the processes (12a–c) Y means the consideration of all three $a'^1\Sigma_u^-$, $a^1\Pi_g$, $w^1\Delta_u$ singlet
227 states of N_2, have been calculated by Kirillov (2012). We apply here the calculated rate
228 coefficients in (Kirillov, 2012), but the exception is made for the process (11a). We have
229 recalculated the constants taking into account new results for the intermolecular electron energy
230 by Kirillov (2016).

231 The processes of the quenching of four triplet states of N_2 in collisions with molecular
232 oxygen

233 $N_2(A^3\Sigma_u^+,v\geq0) + O_2(X^3\Sigma_g^-,v=0) \rightarrow N_2(X^1\Sigma_g^+,v') + O_2(Z,v^*)$ or $O + O$, (13a)
234 $N_2(Y,v\geq0) + O_2(X^3\Sigma_g^-,v=0) \rightarrow N_2(X^1\Sigma_g^+,v') + O_2(Z,v^*)$ or $O + O$, (13b)

235 where Y are the triplet $B^3\Pi_g$, $W^3\Delta_u$, $B'^3\Sigma_u^-$ and singlet $a'^1\Sigma_u^-$, $a^1\Pi_g$, $w^1\Delta_u$ states, Z means the
236 consideration of four $c^1\Sigma_u^-$, $A'^3\Delta_u$, $A^3\Sigma_u^+$, $B^3\Sigma_u^-$ states of O_2 and the electronic transitions in
237 Herzberg or Schumann-Runge continuums or excitations of repulsive $1^1\Pi_g$ or $1^3\Pi_g$ states of O_2
238 are included in the consideration for the dissociation channel O+O (Kirillov, 2011). We apply
239 here the calculated by Kirillov (2012) rate coefficients for the processes (13a) and (13b).

240 Also we consider here intramolecular electron energy transfer process

241 $N_2(A^3\Sigma_u^+,v) + N_2(X^1\Sigma_g^+,v=0) \rightarrow N_2(X^1\Sigma_g^+,v'=v+25) + N_2(X^1\Sigma_g^+,v=0)$ (14)

242 for lowest levels v=0–5 of the $A^3\Sigma_u^+$ state. The rate coefficients $k_{14}(v=0)=3.7\times10^{-16}$ and
243 $k_{14}(v=1)=3.4\times10^{-16}$ $cm^{-3}s^{-1}$ of the process (14) for two vibrational levels v=0,1 are taken
244 according to experimental data of Dreyer and Perner (1973). The rate coefficients for v=2–5 are
245 estimated according to the expression $k_{14}(v)=3.3\times10^{-16}\cdot\exp(-|\Delta E|/105)$ $cm^{-3}s^{-1}$, where ΔE (in

cm^{-1}) is the energy defect of the transition $A^3\Sigma_u^+,v \rightarrow X^1\Sigma_g^+,v'=v+25$, assuming the Landau-Zener approximation for exothermic transitions from v=0,1 levels and the Rosen-Zener approximation for endothermic ones from v=2–5 levels (Kirillov, 2012).

Here we consider the processes of production and quenching for vibrationally excited $N_2(X^1\Sigma_g^+,v'>0)$ molecules. The same method applied by Kirillov and Belakhovsky (2019, 2020a, 2020b) for electronic excitation of molecular nitrogen is used in the calculation of rates of vibrational excitation of N_2 molecules by secondary electrons in the process

$$e + N_2(X^1\Sigma_g^+,v=0) \rightarrow e + N_2(X^1\Sigma_g^+,v'>0) . \quad (15)$$

Since Konovalov (1993) has presented values of "excitation energy costs" for v'=1–8, we consider here the excitation of eight vibrational levels in the process (15) according to (Konovalov, 1993). The excitation of vibrational levels $v'>8$ is calculated according (Simek, 2002).

One of the fundamental features of N_2 vibrational kinetics is the inclusion of VV-processes

$$N_2(X^1\Sigma_g^+,v') + N_2(X^1\Sigma_g^+,v=0) \rightarrow N_2(X^1\Sigma_g^+,v'-1) + N_2(X^1\Sigma_g^+,v=1) , \quad (16)$$

VV'-processes

$$N_2(X^1\Sigma_g^+,v') + O_2(X^3\Sigma_g^-,v=0) \rightarrow N_2(X^1\Sigma_g^+,v'-1) + O_2(X^3\Sigma_g^-,v=1) , \quad (17a)$$
$$N_2(X^1\Sigma_g^+,v') + CO_2(^1\Sigma_g^+,0,0,v_3=0) \rightarrow N_2(X^1\Sigma_g^+,v'-1) + CO_2(^1\Sigma_g^+,0,0,v_3=1) , \quad (17b)$$
$$N_2(X^1\Sigma_g^+,v') + NO(X^2\Pi,v=0) \rightarrow N_2(X^1\Sigma_g^+,v'-1) + NO(X^2\Pi,v=1) , \quad (17c)$$

and VT-processes

$$N_2(X^1\Sigma_g^+,v') + N_2 \rightarrow N_2(X^1\Sigma_g^+,v'-1) + N_2 , \quad (18a)$$
$$N_2(X^1\Sigma_g^+,v') + O_2 \rightarrow N_2(X^1\Sigma_g^+,v'-1) + O_2 \quad (18b)$$

with a redistribution of vibrational excitation within the $X^1\Sigma_g^+$ ground state. The rate coefficients for the processes (16,17a) and (18a,b) can be calculated according to estimations by Kirillov (1998) made according to first-order perturbation approximation taking into account factors of molecular attraction, oscillator frequency change, anharmonicity, 3-dimensionality and quasiclassical motion during collisions.

4. The calculated vibrational populations of $N_2(X^1\Sigma_g^+)$ and $NO(X^2\Pi)$ molecules during GLE69 event

On January 20, 2005, the worldwide network of neutron monitors (NM) registered increases (it was given the number GLE69) caused by solar cosmic rays (SCR). It turned out to be the second in terms of the recorded amplitude. Only GLE05 (on February 23, 1956) was more powerful than the event. The maximum increase on NM was observed at the south polar stations: South Pole (5000%), McMurdo (3000%) and Terre Adélie (4500%) according to one-minute data.

The GLE69 event occurred from the 2B/X7.1 flare with coordinates N14W61. The flare was accompanied by type II and IV radio bursts, which are tracers of particle acceleration. The onset of the type II radio emission (probable instant of the generation of relativistic SCR) was recorded at 0644 UT and SCRs have reached the Earth at ~06:53 UT. The GLE69 event was characterized at its initial phase by a very large enhancement amplitude and strong north–south anisotropy effect in the relativistic SCR flux (Vashenyuk et al., 2006).

In this paper, we consider the GLE69 event, which was accompanied by an increase in the rate of formation of ion pairs at altitudes from 0 to 80 km. To calculate the penetration of SCR through the Earth's atmosphere, the GEANT4 software development package [Agostinelli et al., 2003] is used, with the help of which the corresponding models are created. The RUSCOSMICS software package was developed at the Polar Geophysical Institute [Maurchev et al., 2015, 2019; Maurchev and Balabin, 2016]. This method is as a more modern tool for replacing

PLANETOCOSMICS package. A description of the method for obtaining data on primary SCR spectra used in our modeling is presented in (Vashenyuk et al., 2011). The calculated ion production rates at 0800 UT on January 20, 2005 at the altitudes of 20-80 km according to [Kirillov et al., 2021] are shown in Figure 1. The temperature profile of the middle atmosphere0 according to MSIS-90 model at the same time is also presented in Figure 1.

It is seen from Figure 1 that the temperature at these altitudes of the middle atmosphere is in the range of 200-260 K. Therefore we have calculated the rate coefficients for the processes (16) and (17b) for temperatures 200-260 K. The rate coefficient for the process (17b) with v'=1 is taken according to (Taylor and Bitterman, 1969). Also we apply the theory of anharmonic oscillator (Kirillov, 1998) to calculate the rate coefficients of the process (17b) with v'>1. The calculated rate coefficients for the processes (16) and (17b) at temperatures T=200, 230 and 260 K are shown in Figure 2.

To calculate the population $N_{v'}^{X}$ of the v'-th vibrational level of the $X^1\Sigma_g^+$ state of N_2 we use the equation:

$$\begin{aligned} &Q_{v'}^{X} + \sum_{Y;v} A_{vv'}^{YX} \cdot N_v^Y + \sum_{Y;v} k^{*YX}_{vv'} \cdot [N_2] \cdot N_v^Y + \sum_{Y;v} k^{**YX}_{vv'} \cdot [O_2] \cdot N_v^Y + \\ &+ k_{14}(v) \cdot ([N_2]+[O_2]) \cdot N_v^A + \{ f_{VV}(v'+1) + f_{VT}(v'+1) \} \cdot N_{v'+1}^{X} = \\ &= \{ f_{VV}(v') + f_{VT}(v') \} \cdot N_{v'}^{X} \end{aligned} \quad . \qquad (19)$$

Here $Q_{v'}^{X}$ is the production rate of v'-th vibrational level of this state by secondary electrons, $A_{vv'}^{YX}$ are Einstein probabilities for the spontaneous transitions $Y,v \rightarrow X^1\Sigma_g^+,v'$ (Y=$A^3\Sigma_u^+$, $a'^1\Sigma_u^-$, $a^1\Pi_g$), $k^{*YX}_{vv'}$ and $k^{**YX}_{vv'}$ are the rate coefficients for intermolecular electron energy transfer processes with the quenching of Y,v and the excitation of $X^1\Sigma_g^+,v'$ in collisions with N_2 (processes 11a–d;12a–c) and O_2 (processes 13a,b) molecules, respectively, $k_{14}(v)$ is the rate coefficient for intramolecular process (14), $f_{VV}(v') = k_{16}(v')[N_2] + k_{17a}(v')[O_2] + k_{17b}(v')[CO_2]$, $f_{VT}(v') = k_{18a}(v')[N_2] + k_{18b}(v')[O_2]$. We consider the rates of intramolecular processes (14) independent on the kind of the collision with N_2 or O_2, therefore the sum of concentrations $[N_2]+[O_2]$ is included in Equation (19) for contributions of the processes. The electronic kinetics of all electronically excited states and the concentrations N_v^Y of the states are taken according to results by Kirillov et al. (2021).

Contributions of metastable molecular nitrogen $N_2(A^3\Sigma_u^+)$ (processes (11a), (13a), (14), of electronically excited nitrogen molecules $N_2(Y$=$B^3\Pi_g$, $W^3\Delta_u$, $B'^3\Sigma_u^-$, $C^3\Pi_u$, $a'^1\Sigma_u^-$, $a^1\Pi_g$, $w^1\Delta_u)$ (processes (11b-d), (12a-c), (13b)) and of direct excitation by secondary electron impact (15) in vibrational population of the ground state $X^1\Sigma_g^+$ of N_2 at the altitudes of 20, 40, 60 and 80 km during GLE69 event are presented in Figure 3. Since concentrations of vibrational level v'=1 of the $X^1\Sigma_g^+$ state has very high values in comparison with the concentrations of v'>1 we do not present here results of the calculation for the level. Concentrations of N_2, O_2 components are taken according to MSIS-90 model. We believe in the calculations that CO_2 concentrations are $3 \cdot 10^3$ times lower than corresponding N_2 concentrations. The results of the calculations are presented in Figure 3 for temperature T=230 K.

The results of the calculation show very important role of all considered mechanisms of the vibrational excitation $N_2(X^1\Sigma_g^+,v'$=2-30) during GLE69 event. Our calculations have pointed out on significant contributions of cascades from electronically excited states in vibrational excitation of the ground state of N_2. Moreover it is seen from Figure 3 that the contribution of intramolecular process (14) dominates in vibrational population of $N_2(X^1\Sigma_g^+)$ for v'=20–30. The excitation by secondary electrons is principal for v'=2-10 levels but it can be neglected for v'>10.

To calculate the population $N_{v'}^{X}$ of the v'-th vibrational level of the $X^2\Pi$ state of NO we use the equation:

$$Q_{v'}^{X} + k_{2b}\, f_{2b}(v')[N(^2D)][O_2] + \sum_{v=0-2}(k_7[O_2] + A_{vv'}^{AX}) \cdot [NO(A^2\Sigma^+, v] + \\ + A_{v'+1v'}^{XX} N_{v'+1}^{X} + A_{v'+2v'}^{XX} N_{v'+2}^{X} = \{A_{v'v'-1}^{XX} + A_{v'v'-2}^{XX} + k_8(v')[O_2]\} \cdot N_{v'}^{X} \quad . \quad (20)$$

Here $Q_{v'}^{X}$ is the production rate of v'-th vibrational level of the $X^2\Pi$ state by secondary electrons, $A_{vv'}^{AX}$ are Einstein probabilities for the spontaneous transitions $A^2\Sigma^+,v \rightarrow X^2\Pi,v'$ (taken according to (Settersten et al., 2009a)), $A_{vv'}^{XX}$ are Einstein probabilities for the spontaneous transitions (1a) and (1b) (taken according to (Hancock et al., 2006)). It is to note that in comparison with results by Cartwright et al. (2000) we consider here only one $A^2\Sigma^+$ electronically excited state of NO molecule excited by direct electronic impact (4b) and in electron energy transfer process (5) during inelastic molecular collisions. Also for first vibrational level $v'=1$ we take into account the contribution of the VV'-process (17c).

The branching ratios $f_{2b}(v')$ in the process (2b) have been calculated by Kirillov and Aladjev (1998) with the aid of surprisal theory (Bernstein and Levine, 1976; Nesbet, 1981) for surprisal parameter λ=-7 – -2. The vibrational distribution of nitric oxide in polar ionosphere computed by Kirillov (1998) according to one-dimensional non-steady model of chemical and vibrational kinetics of upper atmosphere has been compared with experimental data from rocket measurements of Rawlins et al. (1981). It was determined that the best agreement for MSIS-83 profile of atomic oxygen concentrations was obtained for λ=-6. The value of the surprisal parameter was in better agreement with laboratory estimations of Rawlins et al. (1989). Therefore we apply here the values of the branching ratios $f_{2b}(v')$ in the process (2b) calculated by Kirillov and Aladjev (1998) for surprisal parameter λ=-6.

To calculate the contributions of the processes (4a), (4b), (5), (17c) in the vibrational populations of $NO(X^2\Pi,v')$ it is necessary to estimate nitric oxide concentrations in the middle atmosphere during proton precipitations. The determination of the NO concentrations is made according to Zadodozhny et al. (1992, 1994). They have estimated the nitric oxide quantity produced at the altitudes of the middle atmosphere from the beginning of the SPE (Solar Proton Event) until the time of measurements. It is well known that the ionization of the atmosphere by high-energy particles produces ~1.2-1.6 molecules of NO per ion pair production [Porter et al., 1976]. Since the nitric oxide photochemical lifetime in the middle atmosphere is many times more than SPE duration, the NO concentration is determined by the total quantity of ion pairs produced at this height during the particle precipitation:

$$[NO]\,(h) = (1.2 \div 1.6) \int_0^t P_i(h)\, dt \quad (21)$$

Therefore we apply the formula (21) to receive the [NO](h) altitude profile taking rates of ion production according to [Kirillov et al., 2021] (Figure 1). We assumed that the duration of the proton precipitation was about 3 hours (approximately 10^4 sec) and the factor 1.4 was applied in the formula (21). The calculation has shown that $[NO] \sim 2\times10^{-8}[N_2]$ at the altitudes 25-80 km after the precipitation.

The calculated intensities of NO infrared 5.3 μm emission (radiational process (1a)) at the altitudes of 20-80 km of the middle atmosphere are shown in Figure 4. Contributions of the processes (2b), (4a), (4b), (5), (17c) are presented in this figure. To calculate the rates of the process (17c) we have taken the constant $k_{17c}=2.2\times10^{-15}$ cm^3s^{-1} according to (Whitsen and McNeal, 1977). The contribution of the process (17c) in Figure 4 is multiplied by factor of 10^4, the contributions of the processes (4a), (4b), (5) are multiplied by factor of 10^6. It seen from Figure 4 that the chemical reaction (2b) dominates in the excitation of $NO(X^2\Pi,v')$ and in the

radiation of NO infrared 5.3 μm emission. Nevertheless the negligible values of contributions of other processes are related with small concentrations of nitric oxide. An increase in nitric oxide concentrations by 4-5 orders of magnitude will lead to the fact that the contribution of the process (17c) will be comparable to the contribution of the process (2b). The situation can be realized in laboratory conditions as for example in (Simek, 2002). Also the contributions of the processes (4a), (4b), (5) can be significantly increased in the case $[NO]\sim[N_2]$ and in laboratory discharge.

The calculated intensities of NO infrared 2.7 μm emission (radiational process (1b)) at the altitudes of 20-80 km of the middle atmosphere are shown in Figure 5. Contributions of the processes (2b), (4a), (4b), (5) multiplied by the factor 10^6 are presented in this figure. As in the case of the radiation of the 5.3 μm emission there is a domination of chemical reaction (2b) in the excitation of $NO(X^2\Pi,v')$ and in the radiation of NO infrared 2.7 μm emission. Contributions of the processes (2b), (4a), (4b), (5), (17) in vibrational population of $NO(X^2\Pi)$ at the altitudes of 20, 40, 60 and 80 km during GLE69 event are presented in Figure 6. Also we see the domination of the process (2b) in the excitation of $NO(X^2\Pi,v>0)$ at the altitudes of the middle atmosphere.

The calculated intensities of NO infrared 5.3 μm emission by the process (17c) and concentrations $[N_2(X^1\Sigma_g^+,v=1)]$ at the altitudes of 20-80 km of the middle atmosphere at temperatures T=200 K, 230 K and 260 K. It is seen the dependence of the altitude profiles on temperature. This fact can be explained by different rates of VV-processes (16) and VV'-process (17b) at the temperature interval T=200-260 K (Figure 2). Therefore the contribution of the process (17c) in the intensities of NO infrared 5.3 μm emission depends on temperature of the atmosphere and on NO concentrations in the mixture of N_2 and O_2 molecules.

5. Conclusions

We have considered the mechanisms of the production of vibrationally excited NO and N_2 molecules at the altitudes of the middle atmosphere during high-energetic proton precipitation. The calculations are made for GLE69 event.

The main results of these calculations are as follows.

1. The study of vibrational populations $N_2(X^1\Sigma_g^+,v'=2\text{-}30)$ during GLE69 event at the altitudes of the middle atmosphere has shown different principal mechanisms in the $N_2(X^1\Sigma_g^+,v'>0)$ excitation. Firstly, the excitation by secondary electrons is principal for all v'=1–10 levels. Secondly, it is obtained that intramolecular electron energy transfer process in $N_2(A^3\Sigma_u^+,v=0–5)+N_2$ collisions (the process (14)) dominates in vibrational excitation of high vibrational levels v'=20–30. The vibrationally excited nitrogen molecules could play very important role in vibrational excitation of greenhouse gases and in infrared radiational balance of the Earth's middle atmosphere during disturbances.
2. The study of vibrational populations $NO(X^2\Pi,v'=1\text{-}20)$ during GLE69 event at the altitudes of the middle atmosphere has shown that the chemical reaction of metastable atomic nitrogen with molecular oxygen is the main production mechanism of vibrationally excited $NO(X^2\Pi,v>0)$ and of the radiation of 5.3 μm and 2.7 μm infrared emissions at the altitudes. It is presented that the relative contribution of VV'-process (17c) can be significantly increased when concentrations of nitric oxide [NO] is comparable with the concentrations of molecular nitrogen $[N_2]$ in the atmospheric mixture.

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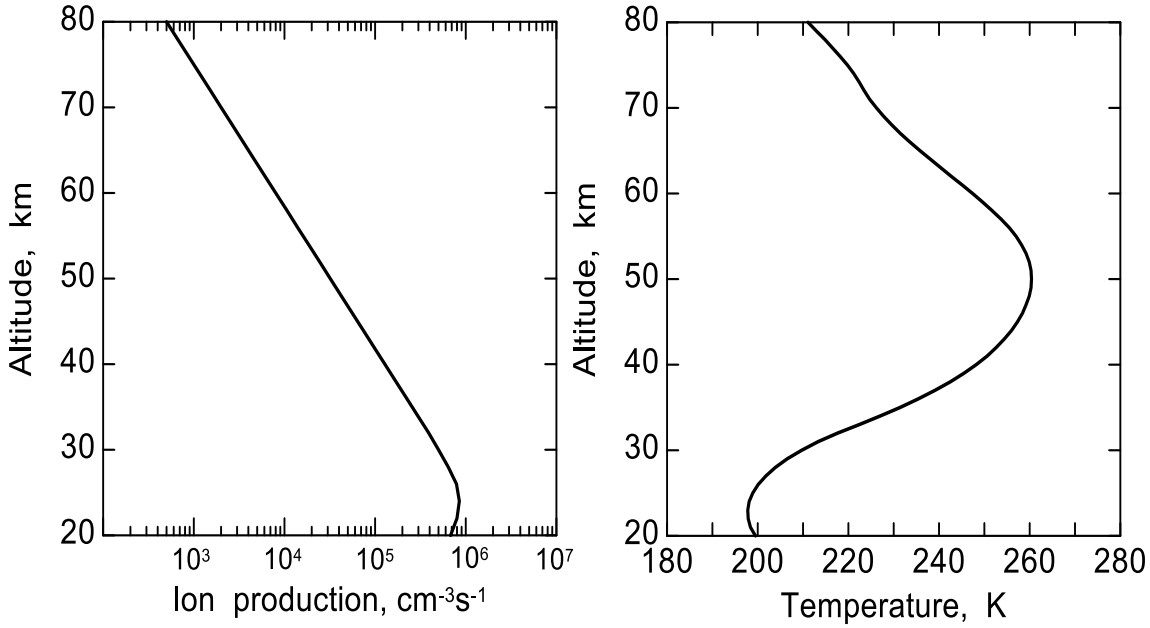

Figure 1. The calculated ion production rates at the altitudes of 20-80 km according to [Kirillov et al., 2021] and the temperature profile according to MSIS-90 model.

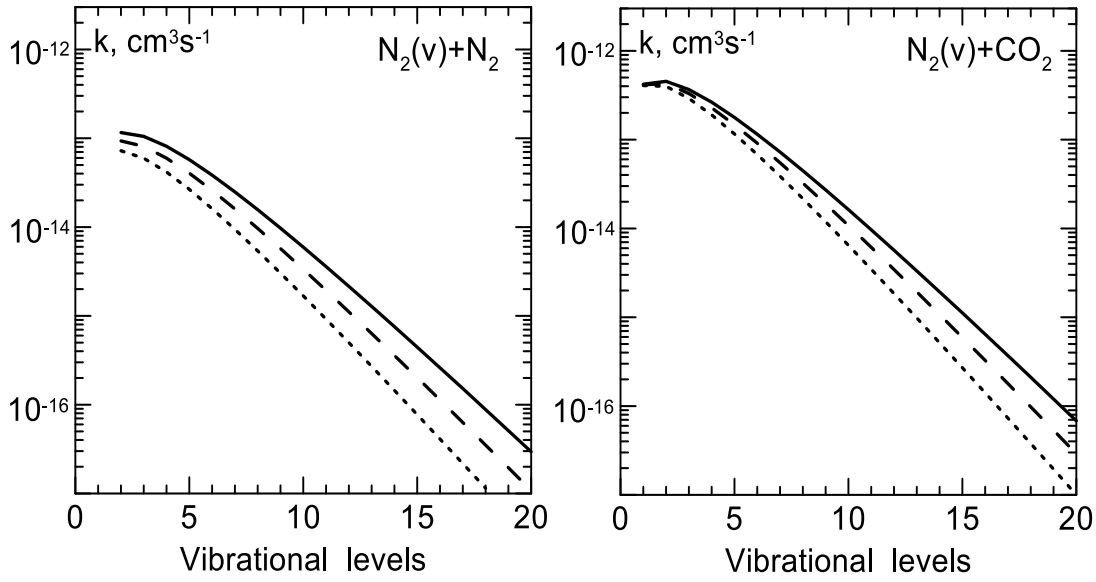

Figure 2. The calculated rate coefficients for the processes (16) and (17b) at temperatures T=200 K (short dashed lines), T=230 K (long dashed lines) and T=260 K (solid lines).

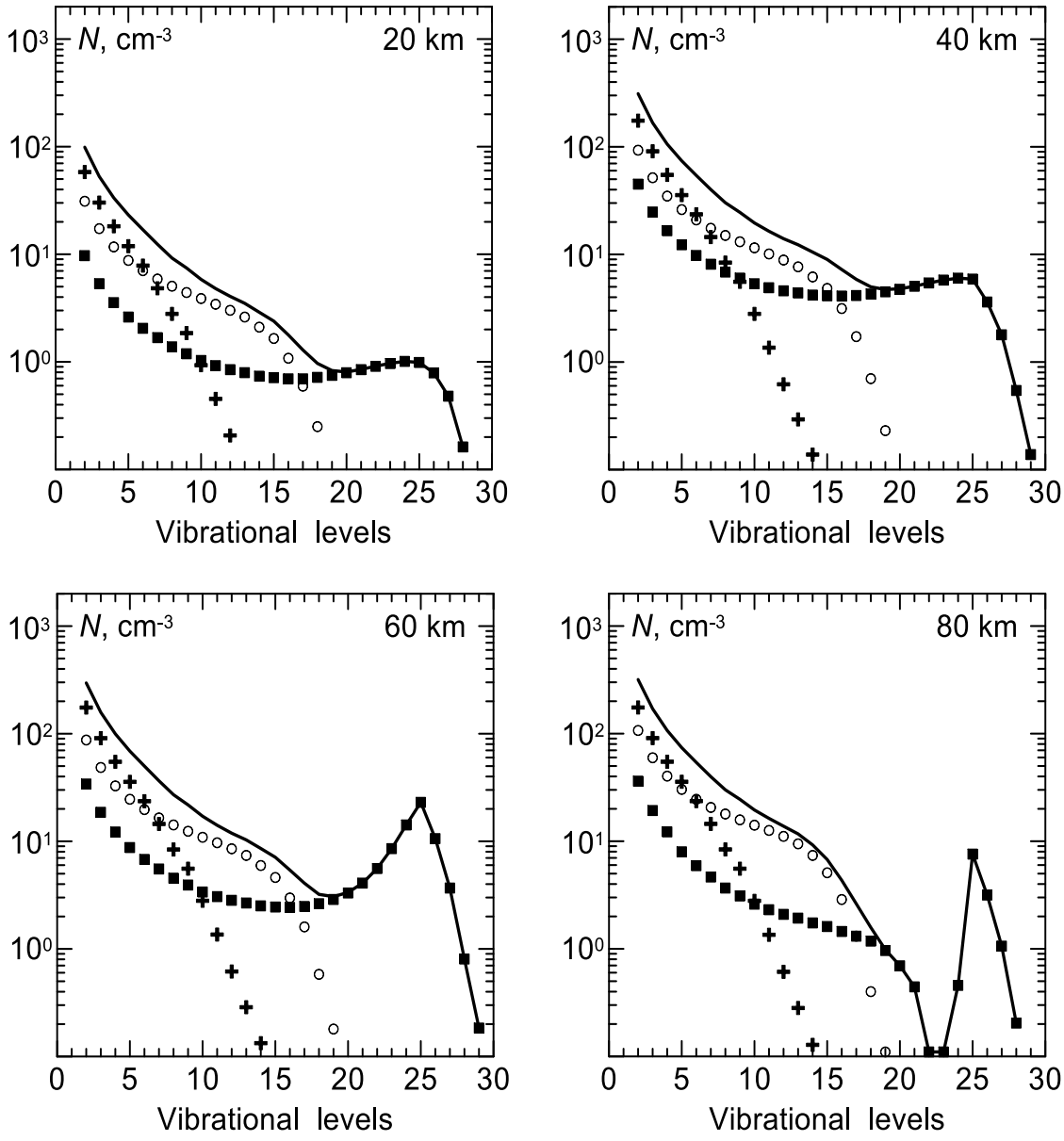

Figure 3. Contributions of metastable molecular nitrogen $N_2(A^3\Sigma_u^+)$ (squares), of electronically excited nitrogen molecules $N_2(Y=B^3\Pi_g, W^3\Delta_u, B'^3\Sigma_u^-, C^3\Pi_u, a'^1\Sigma_u^-, a^1\Pi_g, w^1\Delta_u)$ (circles), of direct excitation by secondary electron impact (crosses) in vibrational population of $N_2(X^1\Sigma_g^+)$ at the altitudes of 20, 40, 60 and 80 km during GLE69 event. Solid lines are the sums of all processes.

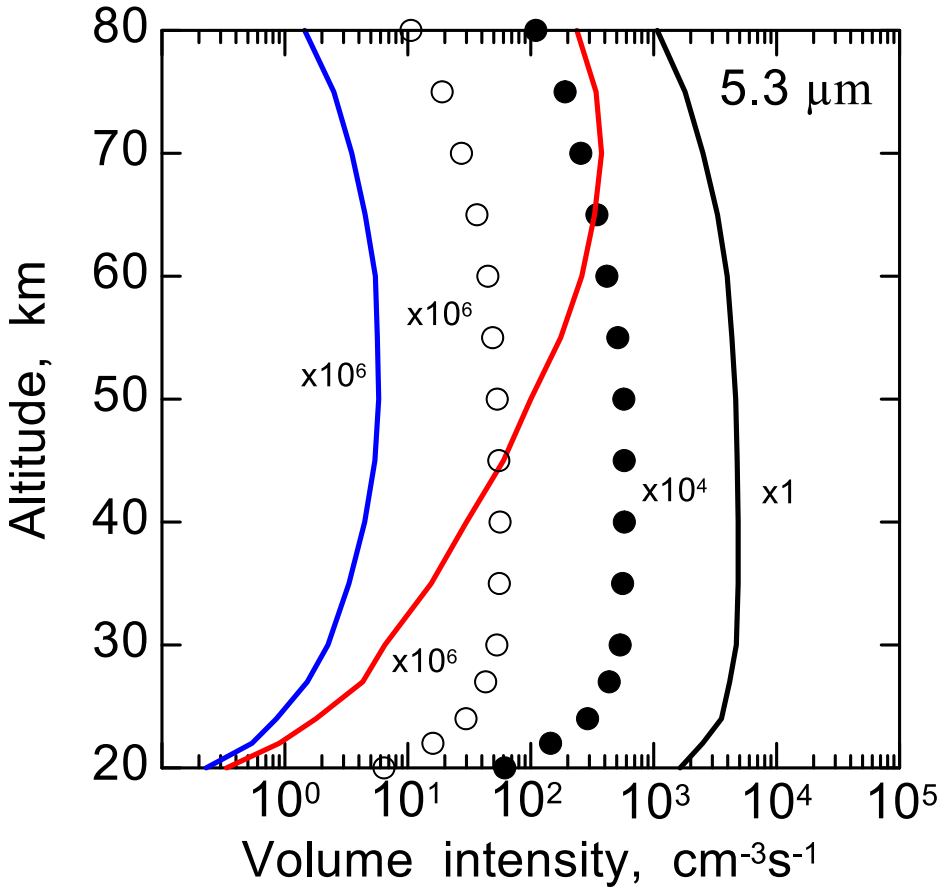

Figure 4. The calculated intensities of NO infrared 5.3 μm emission at the altitudes of 20-80 km of the middle atmosphere. Contributions of the processes (2b), (4b), (5) are presented as black, blue and red lines, respectively, contributions of the processes (4a), (17) are presented as open and solid circles, respectively.

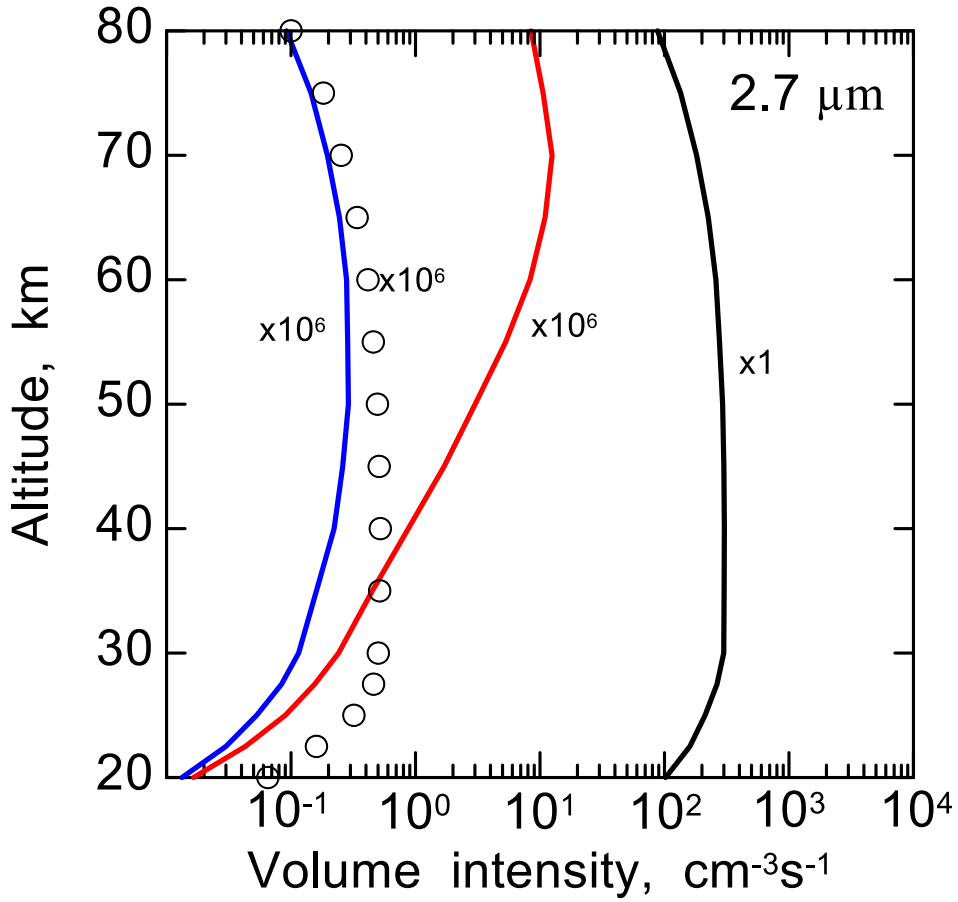

Figure 5. The calculated intensities of NO infrared 2.7 μm emission at the altitudes of 20-80 km of the middle atmosphere. Contributions of the processes (2b), (4b), (5) are presented as black, blue and red lines, respectively, contribution of the process (4a) is presented as open circles.

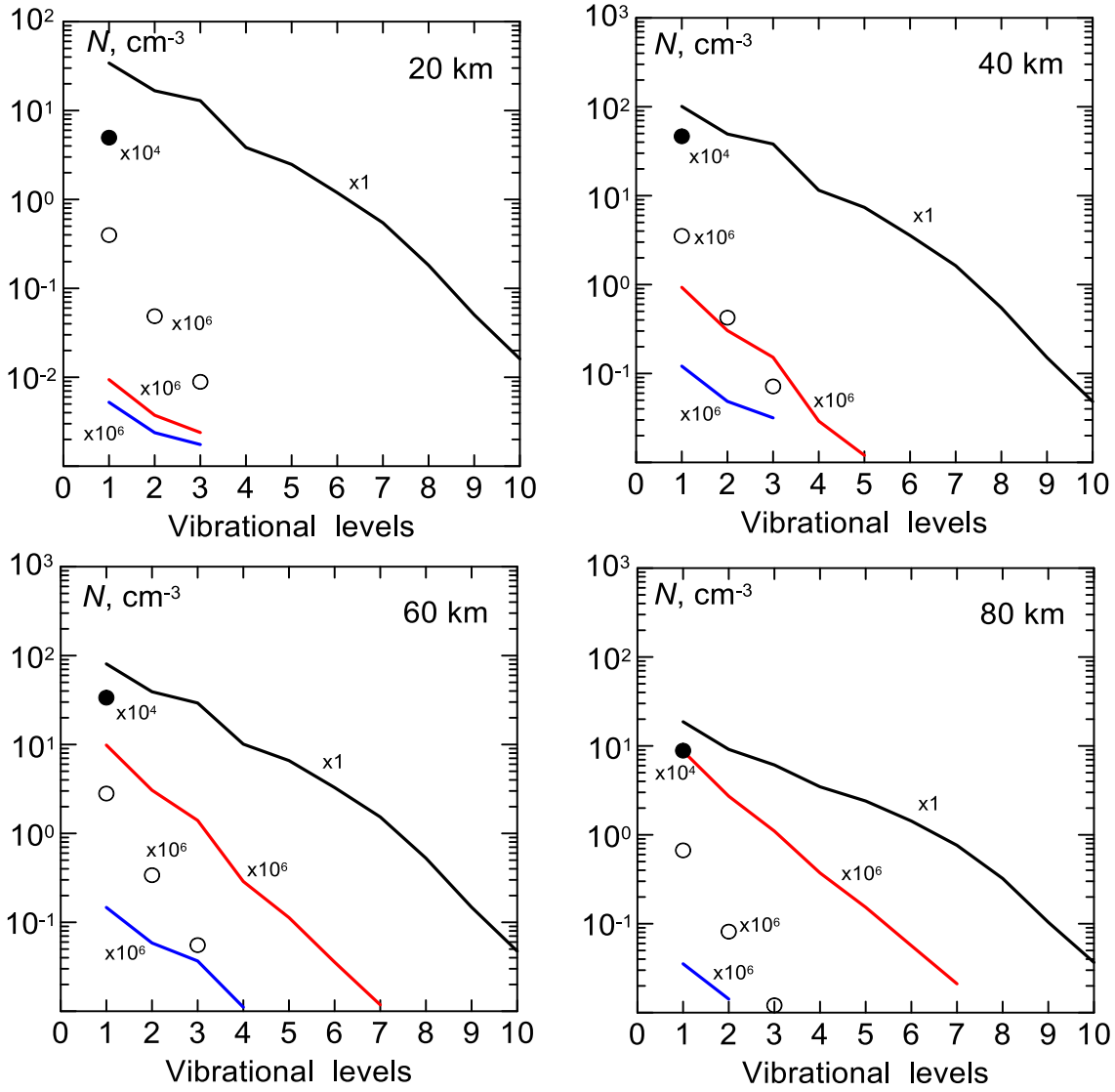

Figure 6. Contributions of the processes (2b), (4a), (4b), (5), (17) in vibrational population of $NO(X^2\Pi)$ at the altitudes of 20, 40, 60 and 80 km during GLE69 event. Contributions of the processes (2b), (4b), (5) are presented as black, blue and red lines, respectively, contributions of the processes (4a), (17) are presented as open and solid circles, respectively.

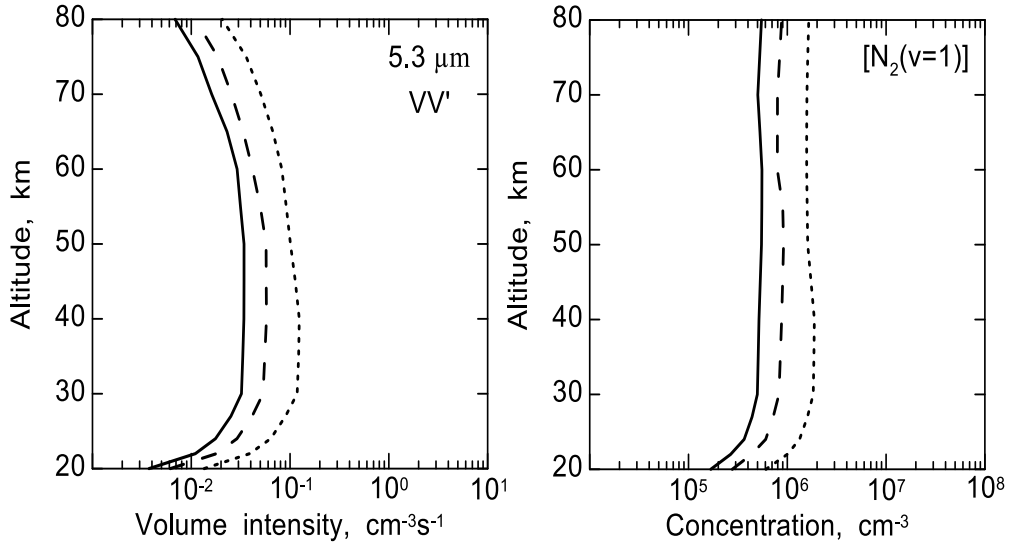

Figure 7. The calculated intensities of NO infrared 5.3 μm emission by the process (17) and concentrations $[N_2(X^1\Sigma_g^+, v=1)]$ at the altitudes of 20-80 km of the middle atmosphere at temperatures T=200 K (short dashed lines), T=230 K (long dashed lines) and T=260 K (solid lines).