

Electronically excited molecular nitrogen and molecular oxygen in the high-latitude upper atmosphere

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Abstract. Relative vibrational populations of triplet $B^3\Pi_g$, $W^3\Delta_u$, $B'^3\Sigma_u^-$ states of N_2 and the $b^1\Sigma_g^+$ state of O_2 are calculated for different altitudes of the high-latitude upper atmosphere during auroral electron precipitation. It is shown that collisional processes cause a wavelength shift in the distribution of relative intensities for 1PG $\Delta v=3$ sequence of N_2 . The calculation of relative populations for vibrational levels $v=1-5$ of the $b^1\Sigma_g^+$ state in the auroral ionosphere has not given an agreement with experimental results. Preliminary estimation of the contribution of the reaction $O_2^+ + NO$ to the production of $O_2(b^1\Sigma_g^+)$ on the basis of a quantum-chemical approximation does not allow for an explanation of the observable vibrational population of the $b^1\Sigma_g^+$ state in the aurora.

Keywords. Atmospheric composition and structure (Airglow and aurora) – Ionosphere (Auroral ionosphere)

1 Introduction

Electronically excited N_2 and O_2 molecules are the subject of intensive theoretical and experimental studies related to radiational processes in the auroral upper atmosphere (Cartwright et al., 1972; Vallance Jones, 1974; Cartwright, 1978; Morrill and Benesch, 1996), the airglow in the region of lower thermosphere – mesosphere (Broadfoot and Kendall, 1968; Shefov et al., 2006), sprites in the middle atmosphere above large thunderstorm systems (Morrill et al., 1998; Bucselia et al., 2003), laser plasmas and gas discharges (Delcroix et al., 1976; Kamaratos, 1997, 2005a, b, 2006), etc. One of the motivations for the studies was to investigate the role of collisional molecular processes in the electronic excitation and deexcitation of molecules of main atmospheric gases. The collisional lifetime of an electronically

excited molecule decreases with the increase in atmospheric density and therefore intermolecular and intramolecular electron energy transfers should be dominant in the redistribution of excitation energies between various states of N_2 and O_2 molecules.

The emissions of first positive group (the transition $B^3\Pi_g \rightarrow A^3\Sigma_u^+$ in molecular nitrogen) and atmospheric bands (the transition $b^1\Sigma_g^+ \rightarrow X^3\Sigma_g^-$ in molecular oxygen) are especially pronounced in the spectra of the aurora (Vallance Jones, 1974), the nightglow (Broadfoot and Kendall, 1968; Shefov et al., 2006), sprites (Morrill et al., 1998), and the laboratory afterglow (Hays and Oskam, 1973; Piper, 1994; Kamaratos, 1997, 2005a, b, 2006).

The kinetics of the electronically excited state $B^3\Pi_g$ is related to the excitation and deexcitation of other triplet states of N_2 . In several papers (Rotem et al., 1981, 1982; Sadeghi and Setser, 1981; Bachmann et al., 1992, 1993) it was shown for laboratory conditions that there is a collisional coupling between the $B^3\Pi_g$ state and triplet $A^3\Sigma_u^+$, $W^3\Delta_u$, $B'^3\Sigma_u^-$ states. A similar coupling between the $b^1\Sigma_g^+$ state and Herzberg states of O_2 was studied in (Bednarek et al., 1994, 1997; Shiao et al., 1998; Kalogerakis et al., 2000; Pejakovic et al., 2003). Moreover, Kamaratos (1997, 2005a, b, 2006) has established the enhancement of $N_2(B^3\Pi_g, v)$ production in flowing nitrogen afterglows in the case of the addition of discharged O_2 . He suggested the energy transfer reaction of the metastable singlet oxygen $O_2(a^1\Delta_g)$ with metastable triplet nitrogen $N_2(A^3\Sigma_u^+)$ as a possible mechanism of the enhancement. Piper (1988) and Schurath (1975) have studied the formation of $N_2(B^3\Pi_g, v)$ and $O_2(b^1\Sigma_g^+, v)$ molecules in energy pooling reactions between $N_2(A^3\Sigma_u^+, v)$ and between $O_2(a^1\Delta_g, v)$ molecules, respectively.

The main aim of this work is the study of the influence of collisional processes on vibrational populations of triplet states of N_2 and the $b^1\Sigma_g^+$ state of O_2 at altitudes of the high-latitude upper atmosphere. Our study is based on the results of calculations of rate coefficients for the electronic

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quenching in collisions with the participation of N₂ and O₂ molecules made by Kirillov (2004a, 2008a, b¹). A principal advantage of those papers was a suggested method allowing for the calculation of branching ratios for products of the interaction of electronically excited molecules. Therefore, this study is devoted to the model of electronic kinetics of N₂ and O₂, taking into account detailed consideration of product branching ratios for collisions of electronically excited nitrogen and oxygen molecules.

2 Model

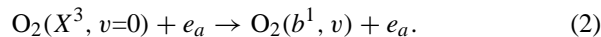
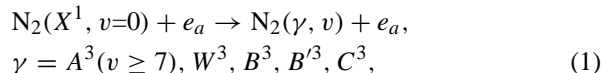
The model of the electronic kinetics of N₂ and O₂ in the auroral upper atmosphere in this work is similar to that of Cartwright et al. (1972), Cartwright (1978), Morrill and Benesch (1996). A main difference in this work consists of a more detailed consideration of product channels in collisions of excited molecules. Since here the main attention is paid to the B³Π_g state from electronically excited states of molecular nitrogen, we have therefore not included in our consideration the lowest vibrational levels (v ≤ 6) of the A³Σ_u⁺ state. Also in the study of electronic kinetics of O₂ for high-latitude lower thermosphere and mesosphere by Kirillov (2008b)¹, it was found that the influence of Herzberg c¹Σ_u⁻, A³Δ_u, A³Σ_u⁺ states on the vibrational population of the b¹Σ_g⁺ state is negligible. Therefore, we neglect the influence of the Herzberg states on the production of O₂(b¹Σ_g⁺) in the auroral ionosphere and don't take into account the production of these three states in this model.

Here we do not consider the energy transfer reactions O₂(a¹Δ_g)+O₂(a¹Δ_g) and O₂(a¹Δ_g)+N₂(A³Σ_u⁺). Firstly, we have no branching ratios for the reactions needed to take into account the interactions in our detailed model of electronic kinetics of N₂ and O₂. Secondly, Gattinger and Vallance Jones (1973) have presented ratios of the rates of the production of O₂(a¹Δ_g) and N₂(A³Σ_u⁺) to the values of intensities of the 427.8 nm emission in the IBC III aurora. The ratios show that the concentration of metastable oxygen can be increased to the value of 10⁷–10⁸ cm⁻³ only after a few tens of minutes of auroral precipitation. One of the aims of this work is the consideration of collisions of electronically excited N₂ and O₂ with the ground state molecules. So we have limited this study to the first minutes of auroral precipitation, where we can apply steady-state balance equations for the calculation of concentrations of electronically excited molecules. The estimation of the contribution of singlet oxygen in electronic kinetics of N₂ and O₂ in the auroral ionosphere during an intensive aurora is the subject of our future studies.

¹Kirillov, A. S.: Electronic kinetics of main atmospheric components in high-latitude lower thermosphere and mesosphere, Ann. Geophys., to be submitted, 2008b.

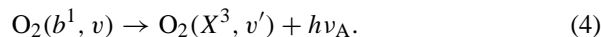
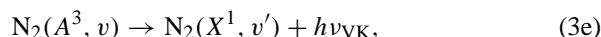
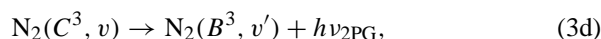
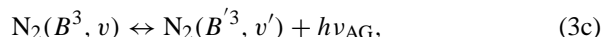
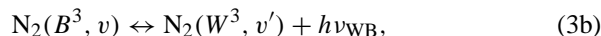
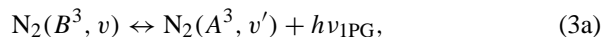
Therefore here we have included the following processes of the excitation and quenching of electronically excited N₂ and O₂ molecules.

1. The electronic excitation by auroral electron impact



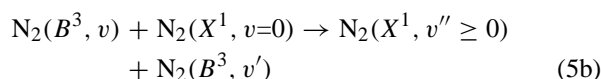
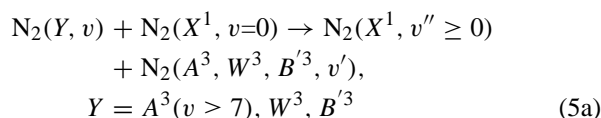
The effective method of “excitation energy costs” was suggested by Gordiets and Konovalov (1991); Sergienko and Ivanov (1993); Kozelov et al. (1995), where rates of the processes (1), (2) can be calculated using the value of the energy dissipated by auroral electrons in 1 cm³. Here we apply the data presented by Kozelov et al. (1995).

2. The spontaneous radiative transitions with the emission of bands of the first positive group (1PG), the Wu-Benesch system (WB), the afterglow system (AG), the second positive group (2PG), the Vegard-Kaplan system (VK) for N₂ and atmospheric system (A) for O₂:

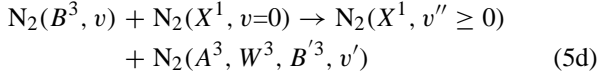
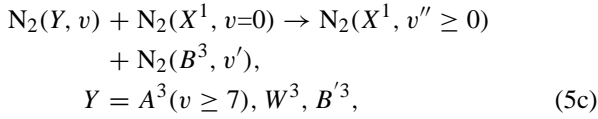


Einstein coefficients for radiational spontaneous transitions are taken according to Gilmore et al. (1992) for processes (3a–e) and according to Vallance Jones (1974) for the process (4).

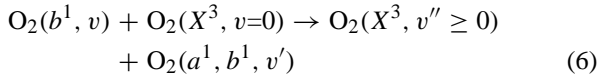
3. Intermolecular electron energy transfers in molecular collisions



with an exchange of electron configurations,

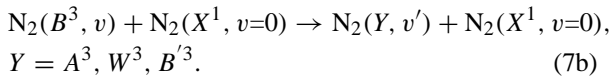
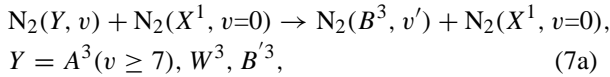


with the exchange and the $\sigma_g \rightarrow \pi_u$ and $\pi_u \rightarrow \sigma_g$ changes in electronic configurations, respectively, and



with the exchange. Here we use the results of the calculations for rate coefficients made by Kirillov (2004a, 2008a, b¹). Electron energy transfers in collisions of $\text{N}_2(A^3\Sigma_u^+, v \geq 7)$ with O_2 with both the production of $\text{O}_2(c^1\Sigma_u^-, A'^3\Delta_u, A^3\Sigma_u^+)$ and the dissociation of O_2 molecule are considered according to Kirillov (2008a, b¹).

4. Intramolecular electron energy transfers in molecular collisions



In a case of similar collisions of an electronically excited nitrogen molecule with oxygen molecule or atom we propose similar magnitudes of rate coefficients.

Intramolecular processes for the $b^1\Sigma_g^+$ state in a collision with an O_2 molecule are negligible according to Kirillov (2008a). Rate coefficients for the quenching by N_2 and O were measured by Bloemink et al. (1998), Kalogerakis et al. (2002, 2004). The results of their measurements are sometimes uncertain and limited to separate vibrational levels of the state. Moreover, now we do not have any estimation of branching ratios for the products of the collision processes; therefore, we have not taken into consideration the quenching by N_2 and O in our model calculations and believe that the processes do not principally change relative vibrational populations in $\text{O}_2(b^1\Sigma_g^+)$.

5. An interaction of metastable $\text{O}(^1\text{D})$ atom with O_2 molecule will be described in Sect. 4.

3 Electronically excited N_2

The $C^3\Pi_u$ state of N_2 is only in the model which has the radiational lifetime sufficiently less than the collisional one for altitudes of the upper atmosphere. Since rate coefficients for the electronic quenching for vibrational levels $v=0-4$ of the state are about $(1-10) \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ by N_2 molecules and $(3-5) \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ by O_2 molecules (Pancheshnyi et al., 2000; Dilecce et al., 2006), so the collisional lifetime at the altitude of 80 km is about 10^{-4} s in comparison with the value $4 \times 10^{-8} \text{ s}$ for the radiational lifetime (Gilmore et al., 1992). Therefore, in our model we do not consider collisional molecular processes for the $C^3\Pi_u$ state. This means that the shape of the vibrational population for the state is universal for all considered altitudes of the upper atmosphere. Rates of the excitation and quenching for vibrational levels of the state are calculated by taking into account processes (1) and (3d), respectively. Other considered triplet $A^3\Sigma_u^+(v \geq 7)$, $B^3\Pi_g$, $W^3\Delta_u$, $B'^3\Sigma_u^-$ states have longer radiational lifetimes and the influence of collisional processes on vibrational distributions of the states at altitudes of the lower thermosphere has to be important.

To calculate the population N_v^Y of the v -th vibrational level of the Y -th electronic state we need a system of steady-state equations for all considered vibrational levels of $A^3\Sigma_u^+$, $B^3\Pi_g$, $W^3\Delta_u$, $B'^3\Sigma_u^-$, $C^3\Pi_u$ states. So we used in our calculations the following steady-state equations for the five electronic states of N_2 :

$$\begin{aligned} Q^A \cdot q_v^A + \sum_{v'} A_{v'v}^{BA} \cdot N_{v'}^B + \sum_{Y=A, W, B, B'; v'} k_{v'v}^{*YA} [\text{N}_2] \cdot N_{v'}^Y + \\ + \sum_{v'} k_{v'v}^{\dagger BA} ([\text{N}_2] + [\text{O}_2] + [\text{O}]) \cdot N_{v'}^B = \{ \sum_{v'} A_{vv'}^{AB} \\ + \sum_{v'} A_{vv'}^{AX} + \sum_{Y=A, W, B, B'; v'} k_{vv'}^{*AY} [\text{N}_2] + \\ + \sum_{v'} k_{vv'}^{\dagger AB} ([\text{N}_2] + [\text{O}_2] + [\text{O}]) \\ + k_v^{*AO_2} [\text{O}_2] \} \cdot N_v^A, \end{aligned} \quad (8a)$$

$$\begin{aligned} Q^B \cdot q_v^B + \sum_{Y=A, W, B', C; v'} A_{v'v}^{YB} \cdot N_{v'}^Y \\ + \sum_{Y=A, W, B, B'; v'} k_{v'v}^{*YB} [\text{N}_2] \cdot N_{v'}^Y + \\ + \sum_{Y=A, W, B'; v'} k_{v'v}^{\dagger YB} ([\text{N}_2] + [\text{O}_2] + [\text{O}]) \cdot N_{v'}^Y \\ = \{ \sum_{Y=A, W, B'; v'} A_{vv'}^{BY} + \\ + \sum_{Y=A, W, B, B'; v'} k_{vv'}^{*BY} [\text{N}_2] \\ + \sum_{Y=A, W, B'; v'} k_{vv'}^{\dagger BY} ([\text{N}_2] + [\text{O}_2] + [\text{O}]) \} \cdot N_v^B \end{aligned} \quad (8b)$$

$$Q^W \cdot q_v^W + \sum_{v'} A_{v'v}^{BW} \cdot N_{v'}^B$$

Table 1. Applied rate coefficients in Eq. (8a).

v	k_v^{*AA}	k_v^{*AB}	k_v^{*AW}	$k_v^{*AB'}$	k_v^{*AO2}	$k_v^{\dagger AB}$
7	2.2(-13) ^(*)	8.2(-13)	8.3(-15)	–	3.6(-12)	1.2(-13)
8	1.7(-13)	9.9(-14)	2.4(-15)	–	3.6(-12)	6.7(-15)
9	2.2(-13)	1.6(-12)	2.0(-15)	–	3.2(-12)	1.9(-13)
10	4.0(-13)	8.6(-12)	2.6(-14)	–	3.2(-12)	2.7(-12)
11	1.1(-12)	1.5(-12)	3.4(-13)	–	3.0(-12)	1.0(-13)
12	1.4(-12)	3.1(-12)	9.2(-13)	–	2.9(-12)	4.3(-13)
13	1.3(-12)	4.5(-12)	3.6(-13)	4.4(-15)	2.8(-12)	5.2(-12)
14	6.2(-13)	1.3(-12)	7.7(-14)	4.8(-14)	2.6(-12)	3.2(-13)
15	3.6(-13)	4.1(-12)	1.5(-13)	2.1(-14)	2.5(-12)	1.0(-12)
16	2.7(-13)	1.5(-12)	1.6(-12)	1.6(-14)	2.3(-12)	9.9(-12)
17	8.2(-13)	3.6(-12)	1.6(-12)	2.4(-13)	2.2(-12)	2.9(-13)
18	3.3(-13)	8.2(-13)	3.5(-13)	3.4(-13)	2.1(-12)	3.7(-12)
19	1.1(-12)	2.8(-12)	3.1(-13)	1.2(-13)	2.0(-12)	2.6(-12)
20	5.3(-13)	9.4(-13)	1.4(-12)	1.5(-13)	1.8(-12)	1.6(-12)
21	7.6(-13)	1.8(-12)	1.9(-13)	9.3(-14)	1.7(-12)	1.3(-11)
22	5.6(-13)	1.5(-12)	4.7(-13)	1.9(-13)	1.8(-12)	1.2(-12)
23	3.4(-13)	8.0(-13)	7.1(-13)	1.1(-13)	1.3(-12)	1.3(-11)

(*)2.2(-13) means $2.2 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$.

Table 2. Applied rate coefficients in Eq. (8b).

v	k_v^{*BA}	k_v^{*BB}	k_v^{*BW}	$k_v^{*BB'}$	$k_v^{\dagger BA}$	$k_v^{\dagger BW}$	$k_v^{\dagger BB'}$
0	5.6(-12)	–	6.9(-14)	–	4.1(-13)	3.6(-10)	–
1	2.1(-12)	7.7(-15)	4.0(-13)	–	9.7(-14)	9.9(-12)	–
2	1.5(-11)	7.2(-15)	3.3(-13)	–	2.9(-12)	1.9(-12)	–
3	2.6(-12)	4.1(-13)	1.7(-13)	–	1.0(-12)	1.8(-12)	7.0(-17)
4	6.6(-12)	1.5(-12)	8.7(-13)	1.2(-13)	3.7(-12)	7.6(-13)	6.2(-13)
5	7.2(-12)	1.0(-12)	4.6(-12)	2.2(-13)	2.5(-12)	5.3(-12)	1.3(-12)
6	3.8(-12)	1.5(-13)	6.5(-12)	2.1(-13)	1.0(-11)	4.6(-11)	1.7(-12)
7	7.4(-12)	3.8(-12)	4.1(-12)	2.1(-13)	2.1(-12)	5.4(-11)	1.8(-12)
8	2.9(-12)	5.7(-12)	1.0(-12)	4.0(-13)	1.0(-11)	1.1(-11)	1.8(-12)
9	5.0(-12)	4.4(-12)	2.9(-12)	8.9(-13)	2.3(-11)	2.4(-12)	1.9(-12)
10	4.6(-12)	3.2(-12)	7.3(-12)	1.5(-12)	2.2(-11)	3.1(-12)	2.5(-12)

$$\begin{aligned}
& + \sum_{Y=A,W,B,B';v'} k_{vv'}^{*YW} [\text{N}_2] \cdot N_{v'}^Y + \\
& + \sum_{v'} k_{vv'}^{\dagger BW} ([\text{N}_2] + [\text{O}_2] + [\text{O}]) \cdot N_{v'}^B \\
= & \left\{ \sum_{v'} A_{vv'}^{WB} + \sum_{Y=A,W,B,B';v'} k_{vv'}^{*WY} [\text{N}_2] + \right. \\
& \left. + \sum_{v'} k_{vv'}^{\dagger WB} ([\text{N}_2] + [\text{O}_2] + [\text{O}]) \right\} \cdot N_v^W, \quad (8c)
\end{aligned}$$

$$\begin{aligned}
& + \sum_{v'} k_{vv'}^{\dagger BB'} ([\text{N}_2] + [\text{O}_2] + [\text{O}]) \cdot N_{v'}^B \\
= & \left\{ \sum_{v'} A_{vv'}^{B'B} + \sum_{Y=A,W,B,B';v'} k_{vv'}^{*B'Y} [\text{N}_2] + \right. \\
& \left. + \sum_{v'} k_{vv'}^{\dagger B'B} ([\text{N}_2] + [\text{O}_2] + [\text{O}]) \right\} \cdot N_{v'}^{B'}, \quad (8d)
\end{aligned}$$

$$Q^C \cdot q_v^C = \sum_{v'} A_{vv'}^{CB} \cdot N_v^C, \quad (8e)$$

$$\begin{aligned}
Q^{B'} \cdot q_v^{B'} + \sum_{v'} A_{vv'}^{BB'} \cdot N_{v'}^B + \sum_{Y=A,W,B,B';v'} \\
k_{vv'}^{*YB'} [\text{N}_2] \cdot N_{v'}^Y +
\end{aligned}$$

where Q^Y is the production rate of the Y -th state by auroral electrons (in $\text{cm}^{-3} \text{ s}^{-1}$), q_v^Y is the Franck-Condon factor for the transition $X^1\Sigma_g^+, v=0 \rightarrow Y, v$, $A_{vv'}^{YZ}$ is the spontaneous transition probability for the transition $Y, v \rightarrow Z, v'$, $k_{vv'}^{*YZ}$ and $k_{vv'}^{\dagger YZ}$ are rate coefficients for intermolecular and

Table 3. Applied rate coefficients in Eq. (8c).

v	k_v^{*WA}	k_v^{*WB}	k_v^{*WW}	$k_v^{*WB'}$	$k_v^{\dagger WB}$
0	4.8(-13)	9.8(-14)	–	–	5.1(-10)
1	3.9(-12)	2.0(-13)	–	–	6.4(-12)
2	2.3(-12)	1.1(-12)	1.7(-15)	–	3.4(-12)
3	3.9(-12)	9.1(-12)	2.2(-14)	–	3.0(-12)
4	1.3(-11)	2.2(-11)	6.5(-14)	3.0(-17)	5.2(-13)
5	1.8(-12)	9.2(-12)	1.4(-13)	1.1(-15)	2.7(-12)
6	1.2(-12)	1.4(-11)	3.3(-13)	1.9(-14)	2.9(-11)
7	4.5(-12)	1.3(-11)	7.8(-13)	1.2(-13)	8.6(-11)
8	2.2(-12)	9.7(-12)	1.3(-13)	6.5(-13)	3.4(-11)
9	3.5(-12)	8.5(-12)	1.5(-13)	2.3(-12)	3.1(-12)
10	4.3(-12)	4.5(-12)	7.1(-13)	6.8(-12)	3.1(-12)
11	2.5(-12)	5.7(-12)	1.5(-12)	2.0(-12)	1.1(-11)
12	1.0(-12)	2.3(-12)	1.6(-12)	1.7(-12)	2.8(-11)
13	1.2(-12)	5.2(-12)	2.6(-12)	2.7(-12)	5.5(-11)
14	6.0(-13)	6.0(-12)	3.9(-12)	5.6(-13)	6.4(-11)
15	4.7(-13)	4.8(-12)	2.7(-12)	6.6(-13)	7.4(-12)
16	5.1(-13)	3.2(-12)	3.6(-12)	3.8(-13)	3.9(-12)
17	3.2(-13)	4.7(-12)	1.3(-12)	4.8(-13)	8.7(-12)
18	2.6(-13)	1.5(-12)	3.0(-12)	2.0(-12)	1.7(-11)

Table 4. Applied rate coefficients in Eq. (8d).

v	$k_v^{*B'A}$	$k_v^{*B'B}$	$k_v^{*B'W}$	$k_v^{*B'B'}$	$k_v^{\dagger B'B}$
0	4.1(-12)	3.2(-12)	3.2(-14)	–	2.4(-13)
1	9.1(-12)	1.2(-11)	3.4(-13)	–	5.2(-13)
2	3.0(-12)	4.7(-12)	2.0(-12)	8.4(-16)	1.1(-12)
3	1.0(-12)	6.8(-12)	4.5(-12)	1.2(-14)	2.3(-12)
4	1.4(-12)	5.0(-12)	3.1(-12)	3.0(-14)	4.7(-12)
5	3.0(-12)	7.2(-12)	4.4(-12)	5.8(-14)	8.7(-12)
6	2.2(-12)	6.6(-12)	1.9(-12)	1.2(-13)	1.5(-11)
7	1.1(-12)	5.5(-12)	8.2(-13)	2.7(-13)	2.3(-11)
8	3.4(-13)	3.0(-12)	1.3(-12)	9.4(-14)	3.4(-11)
9	1.2(-12)	3.4(-12)	1.7(-12)	6.0(-14)	4.7(-11)
10	1.6(-12)	2.8(-12)	1.3(-12)	2.5(-13)	6.1(-11)
11	4.5(-13)	3.0(-12)	1.0(-12)	4.7(-13)	7.6(-11)
12	1.4(-13)	1.6(-12)	1.6(-12)	5.9(-13)	9.0(-11)
13	2.0(-13)	1.9(-12)	6.6(-13)	8.8(-13)	1.0(-10)

intramolecular electron energy transfer processes with the quenching of Y, v and the excitation of Z, v' , respectively. Here we suggest to consider the rate of an intramolecular process independent of the kind of the collision with N_2, O_2 or O . So the sum of the concentrations $[N_2]+[O_2]+[O]$ is included in steady-state Eqs. (8a–d) for the contributions of intramolecular processes. Contributions of intermolecular electron energy transfer processes in collisions of $N_2(A^3\Sigma_u^+, v \geq 7)$ with O_2 , with both the production of $O_2(c^1\Sigma_u^-, A'^3\Delta_u, A^3\Sigma_u^+)$ and the dissociation of O_2 molecule, are included in Eq. (8a) and rate coefficients are denoted by $k_v^{*AO_2}$. Applied rate coefficients $k_v^{*AA}, k_v^{*AB}, k_v^{*AW}, k_v^{*AB'}, k_v^{*AO_2}$ and $k_v^{\dagger AB}$

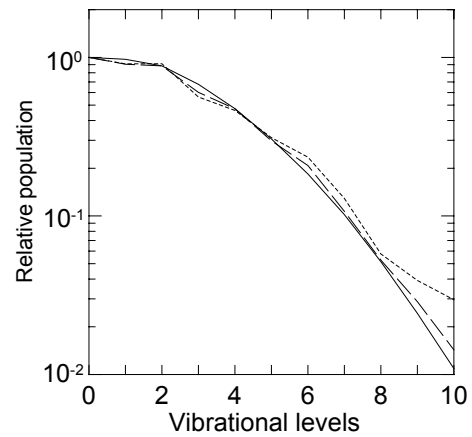


Fig. 1. Calculated relative vibrational populations $[N_2(B^3\Pi_g, v)]/[N_2(B^3\Pi_g, v=0)]$ at altitudes 80, 95 and 150 km (dotted, dashed and solid lines, respectively).

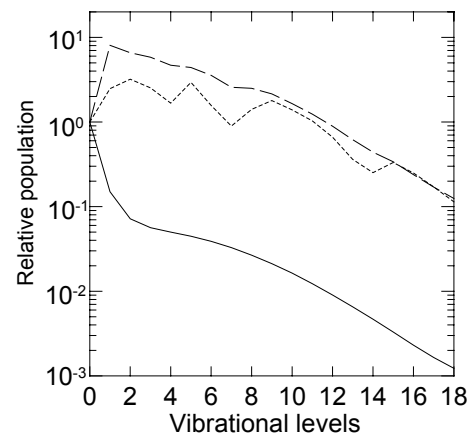


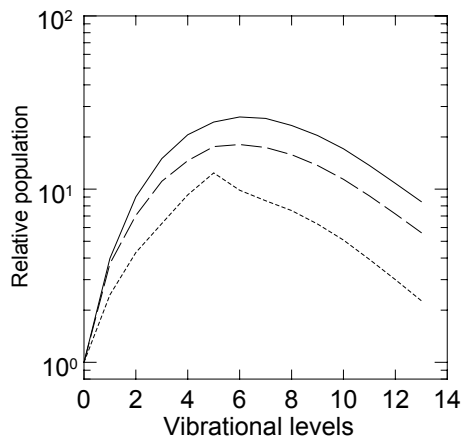
Fig. 2. The same as in Fig. 1 but for the $W^3\Delta_u$ state of N_2 .

for intermolecular and intramolecular processes in Eq. (8a) are shown in Table 1. The rate coefficients k_v^{*YZ} and $k_v^{\dagger YZ}$ mean sums of $k_{vv'}^{*YZ}$ and $k_{vv'}^{\dagger YZ}$ on quantum number v' . Similar rate coefficients for $B^3\Pi_g, W^3\Delta_u, B'^3\Sigma_u^-$ states of N_2 applied in Eqs. (8b–d) are shown in Tables 2–4, respectively.

Results of our calculation of relative vibrational populations ($[N_2(B^3\Pi_g, v)]/[N_2(B^3\Pi_g, v=0)]$, $[N_2(W^3\Delta_u, v)]/[N_2(W^3\Delta_u, v=0)]$, $[N_2(B'^3\Sigma_u^-, v)]/[N_2(B'^3\Sigma_u^-, v=0)]$) at altitudes of 80, 95 and 150 km of auroral upper atmosphere are shown in Figs. 1–3, respectively. It is seen from Figs. 2 and 3 that there is the influence of collisional processes on the distributions of $W^3\Delta_u$ and $B'^3\Sigma_u^-$ states. For the $W^3\Delta_u$ state the increase in the density of the atmosphere causes the rise of the population for the vibrational levels $v \geq 1$. For the $B'^3\Sigma_u^-$ state the similar increase causes the rise in the population of the lowest $v=0-2$ vibrational levels in comparison with the maximum in the distributions.

Table 5. Relative intensities of bands for IPG $\Delta v=3$ sequence.

Experimental data or results of the calculation	$v' (B^3\Pi_g) \rightarrow v'' (A^3\Sigma_u^+), \lambda$ (nm)							
	3→0	4→1	5→2	6→3	7→4	8→5	9→6	10→7
	687.5	678.9	670.5	662.4	654.5	646.9	639.5	632.3
Vallance Jones (1974)	0.46	0.96	1	0.73	0.48	0.25	0.12	0.045
130–200 km	0.43	0.87	1	0.83	0.54	0.28	0.12	0.045
110 km	0.42	0.91	1	0.87	0.55	0.28	0.13	0.05
95 km	0.39	0.89	1	0.97	0.58	0.30	0.15	0.06
80 km	0.34	0.79	0.95	1	0.63	0.29	0.18	0.12
45 km (the pressure ~ 1 Torr)	0.50	0.86	0.71	1	0.46	0.24	0.22	0.18

**Fig. 3.** The same as in Fig. 1 but for the $B^3\Sigma_u^-$ state of N_2 .

The $B^3\Pi_g$ state does not show sufficient variations in the relative population (see Fig. 1). We see an evident increase in the population only for $v=9, 10$ in the region of high densities. However, a dependence of IPG emission intensities on atmospheric density is important in problems related to the production of red lower border of auroral arcs (Benesch, 1981, 1983; Morrill and Benesch, 1996), a movement of the electronic excitation to the lowest vibrational levels of the $B^3\Pi_g$ state in laboratory afterglow (Pravilov et al., 1988; Piper, 1994), a change in relative population of the $B^3\Pi_g$ state at different altitudes in sprites (Morrill et al., 1998; Bucselja et al., 2003).

Benesch (1981, 1983) has suggested that the change in the colour of the lower border in the type B aurora from red to deep crimson could be related to an increased collision frequency in lower thermosphere. He has considered a wavelength shift of the relative intensities of the IPG $\Delta v=3$ sequence from normal auroral observations to results of laboratory measurements made at the pressure of ~ 1 Torr. A comparison of calculated relative intensities of the bands for the IPG $\Delta v=3$ sequence with data of Vallance Jones (1974) is presented in Table 5. The comparison shows a dependence

of the band intensities on the density of the atmosphere. So there is a movement of the band of maximal intensity from the infrared to the red region with the increase in the density of the atmosphere. This fact is in good agreement with the conclusions of Benesch (1981, 1983).

4 Electronically excited O_2

Vallance Jones and Gattinger (1974) and Gattinger and Vallance Jones (1976) in their observations of the auroral ionosphere at Fort Churchill have measured intensities of atmospheric bands of O_2 originated during spontaneous radiational transitions from vibrational levels $v=0-5$ of the $b^1\Sigma_g^+$ state. They emphasised an enhancement as a function of the height in the relative strength of the 1-1 band in comparison with bands both from $v=0$ and from $v>1$. The former behaviour was observed by Omholt (1957). The observation of intensities for normal and high auroras by Gattinger and Vallance Jones (1976) has confirmed that the 1-1 atmospheric band shows a strong enhancement with the height of the aurora but, however, for bands with $2 \leq v \leq 5$ there is very little change with the height relative to bands of the IPG system of N_2 . Moreover, authors of those papers discussed possible mechanisms of high rates of the excitation of $O_2(b^1\Sigma_g^+, v=3-5)$ in auroral ionosphere.

Henriksen and Sivjee (1990) during spectrophotometric observations at Spitsbergen have estimated the vibrational population of the $b^1\Sigma_g^+$ state of molecular oxygen in the auroral ionosphere. For their estimation they have used measured intensities of five oxygen atmospheric bands ($v=v'=1-5$). In a similar way the measurements have shown an anomalous high population of vibrational levels $v=3-5$ and confirmed the dependence of the relative intensity of the (1-1) bands on the height.

Relative vibrational populations $[O_2(b^1\Sigma_g^+, v=1-5)]/[O_2(b^1\Sigma_g^+, v=1)]$ obtained by Vallance Jones and Gattinger (1974), Gattinger and Vallance Jones (1976), Henriksen and Sivjee (1990) for normal and high auroras are shown in Fig. 4. Also, we have presented here results of the theoretical calculation according to our model for the

Table 6. Applied rate coefficients in Eq. (9).

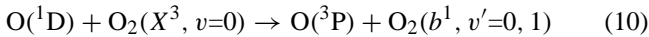
v	k_v^{*ba}	k_v^{*bb}
1	–	1.4(–11)
2	3.0(–15)	1.5(–12)
3	1.5(–14)	1.5(–13)
4	7.1(–14)	3.2(–14)
5	3.2(–13)	1.3(–13)
6	1.2(–12)	8.2(–13)
7	1.7(–12)	5.1(–12)
8	5.2(–13)	3.2(–11)
9	1.4(–13)	3.6(–12)
10	5.4(–14)	1.5(–13)

altitude 80 km. To calculate the population N_v^b of the v -th vibrational level of the $b^1\Sigma_g^+$ state of molecular oxygen we used the following steady-state equation:

$$Q^b \cdot q_v^b + \sum_{v'} k_{v'v}^{*bb} [O_2] \cdot N_{v'}^b = \left\{ \sum_{v'} A_{vv'}^{bX} + \sum_{Y=a,b;v'} k_{vv'}^{*bY} [O_2] \right\} \cdot N_v^b, \quad (9)$$

where Q^b is the production rate of the $b^1\Sigma_g^+$ state by auroral electrons, q_v^b is the Franck-Condon factor for the transition $X^3\Sigma_g^-, v=0 \rightarrow b^1\Sigma_g^+, v$, $A_{vv'}^{bX}$ is the spontaneous transition probability for the transition $b^1\Sigma_g^+, v \rightarrow X^3\Sigma_g^-, v'$, $k_{vv'}^{*bY}$ is a rate coefficient for the intermolecular electron energy transfer process with the quenching of $b^1\Sigma_g^+, v$ and the excitation of Y, v' , respectively. We emphasise that it is here assumed that the quenching of $O_2(b^1\Sigma_g^+, v)$ in collisions with N_2 molecules does not principally change the relative distribution of singlet oxygen shown in Fig. 4. Applied rate coefficients k_v^{*ba} , k_v^{*bb} for intermolecular processes in Eq. (9) are shown in Table 6.

For the altitude 150 km we made a similar calculation but the contribution of the process



is taken into account. According to Green et al. (2000) we believe the yield of the process (10) in inelastic quenching of metastable atomic oxygen by an oxygen molecule is equal to 0.95. Branching ratios for the production of $v'=0$ and 1 are measured by Kalogerakis et al. (2005). They have obtained $k_{v=1}/k_{v=0}=3-4$ in contrast to earlier estimations of Gauthier and Snelling (1974), Lee and Slanger (1978) having values in the interval 0.3–1. Therefore we adopt $k_{v=1}/k_{v=0}=3.5$ in our calculation.

Metastable atomic oxygen is produced in auroral ionosphere mainly in processes of auroral electron impact with $O(^3P)$ atoms and a dissociative recombination of O_2^+ ions. We make the calculation with the energy 10^5 eV dissipated by auroral electrons in 1 cm^3 in one second. The rate of the

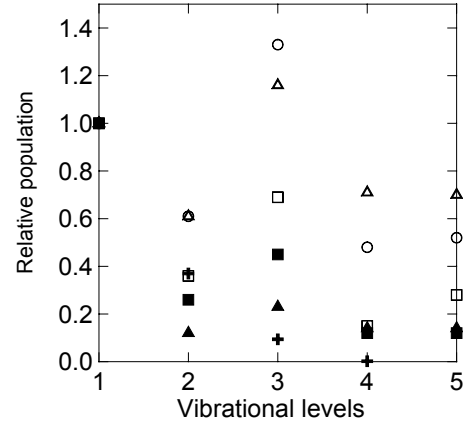


Fig. 4. Relative vibrational populations $[O_2(b^1\Sigma_g^+, v=1-5)]/[O_2(b^1\Sigma_g^+, v=1)]$: results of our calculation for $h=80$ km – crosses; experimental data of Vallance Jones and Gattinger (1974) – circles, Gattinger and Vallance Jones (1976) for normal and high aurora – open and solid triangles, respectively, Henriksen and Sivjee (1990) for normal and high aurora – open and solid squares, respectively.

$O(^1D)$ production by electron impact is estimated according to the method of “excitation energy costs” (Kozelov et al., 1995). For the estimation of the contribution of O_2^+ dissociative recombination it is necessary to know the concentrations of the ion and ionospheric electrons at the considered altitude. Swider and Narcisi (1977) have analysed eight auroral ion composition measurements and according to their data the concentration of O_2^+ at the altitude 150 km is about 0.1–0.3 from the total ion concentration. So we believe in our calculation $[O_2^+]=0.2 \cdot n_e$, where n_e means the ionospheric electron concentration. The value $n_e \sim 1.2 \times 10^5 \text{ cm}^{-3}$ is obtained from the suggestion of 36 eV for the production of one ion-electron pair in auroral electron interaction with main atmospheric components. Petrigiani et al. (2005a, b) have measured quantum exits of $O(^3P)$, $O(^1D)$, $O(^1S)$ atoms for vibrational levels $v=0-2$ of the $O_2^+(X^2\Pi_g)$ ion in the dissociative recombination. We use here the value 0.94 for the $O(^1D)$ production in the case of $v=0$ according to their measurements. Therefore we found that the total rate of the $O(^1D)$ production by auroral electron impact and the dissociative recombination is equal to $\sim 2 \times 10^3 \text{ s}^{-1}$.

Taking into account rate coefficients of the inelastic interaction of $O(^1D)$ atoms with N_2 and O_2 molecules (Sander et al., 2003; Takahashi et al., 2005) and $O(^3P)$ atom (Closser et al., 2005) we have finally obtained the production rates for $O_2(b^1\Sigma_g^+)$ and $O_2(b^1\Sigma_g^+, v=1)$ as 1.6×10^2 and $1.25 \times 10^2 \text{ s}^{-1}$, respectively, at the altitude 150 km. The last value is about 60 times more than the excitation rate of $O_2(b^1\Sigma_g^+, v=1)$ by the auroral electron impact on O_2 (process 2). So we do not show the calculated vibrational population of the $b^1\Sigma_g^+$ state at the altitude 150 km since

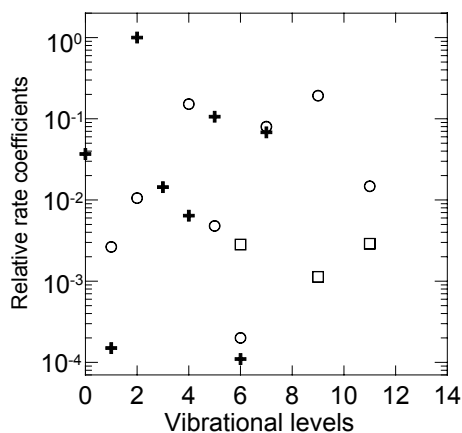


Fig. 5. Calculated relative rate coefficients for the process (11) for vibrational level $v=0$ of the $O_2^+(X^2\Pi_g)$ ion with $O_2(X^3\Sigma_g^-, v)$, $O_2(a^1\Delta_g, v)$, $O_2(b^1\Sigma_g^+, v)$ productions – squares, circles and crosses, respectively.

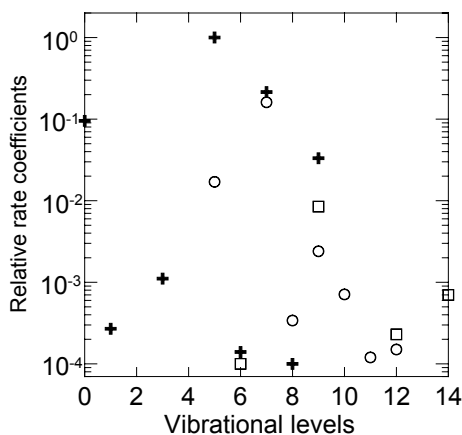
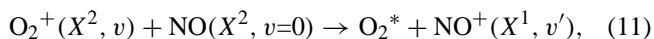


Fig. 6. The same as in Fig. 5 but for vibrational level $v=1$ of the $O_2^+(X^2\Pi_g)$ ion.

concentrations of $O_2(b^1\Sigma_g^+, v>1)$ are negligible in comparison with the one of $v=1$.

Henriksen and Sivjee (1990) have mentioned, originally suggested by Slanger (1986), chemical ion-molecular reaction



as a possible explanation of the high population of vibrational levels $v=3-5$ of $O_2(b^1\Sigma_g^+)$ in aurora. It is to note that Gattinger and Vallance Jones (1976) have also considered this reaction as a possible mechanism of the effective production of $O_2(b^1\Sigma_g^+)$ in the auroral ionosphere. To verify this suggestion we try in this work to calculate the quantum efficiencies of all possible channels of the process (11). We use formulas of Kirillov (2004b) received on the basis of the Rosen-Zener approximation. Calculations are made

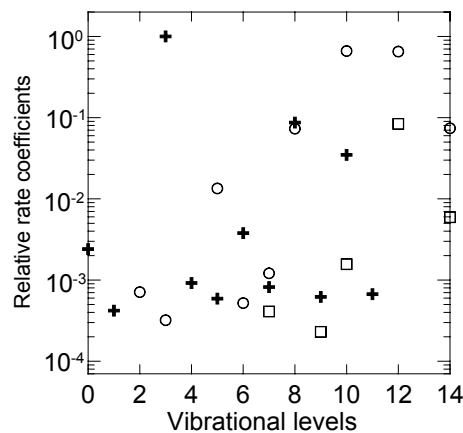


Fig. 7. The same as in Fig. 5 but for vibrational level $v=2$ of the $O_2^+(X^2\Pi_g)$ ion.

for vibrational levels $v=0-5$ of the ground state $X^2\Pi_g$ of the molecular oxygen ion. As possible channels of the reaction we consider the production of the molecule O_2 in $X^3\Sigma_g^-$, $a^1\Delta_g$, $b^1\Sigma_g^+$ states. For nitric oxide ion we take into account the production of the only $X^1\Sigma^+$ state since the energy of the first excited $a^3\Sigma^+$ state is more than the allowed exothermic one, according to the reaction.

Calculated relative rate coefficients for the vibrational levels $v=0-2$ of the ground $X^2\Pi_g$ state of O_2^+ with three exit channels are shown in Figs. 5–7. The normalising is made on partial rate coefficients of vibrational levels $v=2$, $v=5$ and $v=3$ of the $b^1\Sigma_g^+$ state of O_2 , respectively. It is seen from Fig. 5 that the calculation of the rate coefficients for the process (11) (originally suggested by Slanger, 1986) with the lowest vibrational level $v=0$ of the ground state ion of molecular oxygen points out the dominance of $v=2$ in the production of $O_2(b^1\Sigma_g^+)$. The exits for levels $v=3-5$ are 1–2 orders of magnitude lower than the one for $v=2$. The results of the calculation for $v=0$ of $O_2^+(X^2\Pi_g)$ do not allow one to obtain a higher vibrational population for $v=3$ of the state than for $v=2$ observed by Henriksen and Sivjee (1990), since the quenching rate coefficient for $v=3$ is on one order of magnitude lower than the one for $v=2$ (Kalogerakis et al., 2002; Kirillov, 2008a).

Calculations for $v=1$ and 2 of the ground $X^2\Pi_g$ state of O_2^+ , shown in Figs. 6 and 7, point out an effective production of $v=5$ and 3 of $O_2(b^1\Sigma_g^+)$. Similar estimations for $v=3-5$ have given maximal rate coefficients for $v=9-11$ of $O_2(b^1\Sigma_g^+)$. So for the correct calculation of the production of $O_2(b^1\Sigma_g^+, v)$ in the auroral ionosphere we need a full model of vibrational kinetics of molecular oxygen ion. Nevertheless, our preliminary calculation of the rate coefficients for the production of electronically excited O_2 in the process (11) have not shown any pronounced high magnitudes for levels $v=3-5$. Therefore we believe that it is necessary

to consider other mechanisms of the $O_2(b^1\Sigma_g^+)$ production in auroral ionosphere to explain this high vibrational population of $v=3-5$. Maybe the high vibrational population of the $v=3-5$ levels is related to the energy transfer in the collision of metastable atomic nitrogen $N(^2D)$ with molecular oxygen O_2 (Gattinger and Vallance Jones, 1976).

5 Conclusions

Here we have presented the results of the calculation for vibrational populations of triplet states of molecular nitrogen and the $b^1\Sigma_g^+$ state of molecular oxygen in the high-latitude upper atmosphere. Main distinction of our results from similar model calculations of Cartwright et al. (1972); Cartwright (1978); Morrill and Benesch (1996) is the inclusion of intermolecular and intramolecular electron energy transfers related to collisions of electronically excited N_2 and O_2 molecules. Moreover, quantum efficiencies of product channels for the processes are taken according to estimations of Kirillov (2004a, 2008a, b^1) based on an application of the Landau-Zener and Rosen-Zener approximations for the theory of molecular collisions (Kirillov, 2004b).

The main results of these calculations are as follows:

1. It is shown that the vibrational populations of $W^3\Delta_u$ and $B^3\Sigma_u^-$ states of molecular nitrogen have a strong dependence on the altitude for auroral ionosphere. The dependence is related to an important role of collisional processes in the redistribution of the electronic excitation between triplet states of N_2 during molecular inelastic interaction. The increase in the density of the atmosphere causes the rise of relative population of the lowest vibrational level $v=0$ for the $B^3\Sigma_u^-$ state and on the contrary the depletion for the same level of the $W^3\Delta_u$ state.
2. Our estimation of relative band intensities for the 1PG $\Delta v=3$ sequence for different altitudes of the atmosphere shows a dependence on the atmospheric density. There is a pronounced wavelength shift of maximal intensity in the region of lower wavelengths. This result is in good agreement with conclusions of Benesch (1981, 1983) that collisional processes could be responsible for the change in the colour in the lower border of the type B aurora.
3. The theoretical calculation of the vibrational population of the $b^1\Sigma_g^+$ state of molecular oxygen in the auroral ionosphere has shown some disagreement with experimental data of Vallance Jones and Gattinger (1974), Gattinger and Vallance Jones (1976), Henriksen and Sivjee (1990). Using theoretical formulas based on the Rosen-Zener approximation according to Kirillov (2004b) we have calculated the quantum efficiencies of product channels for the process (11) suggested by

Slanger (1986), for the explanation of the experimentally observed distribution. It was found in the calculation that the quantum exits of the production of $O_2(b^1\Sigma_g^+, v=3-5)$ in the reaction of $O_2^+(X^2\Pi_g, v=0)$ ion with NO molecule are insufficient to explain the high vibrational populations of the levels $v=3-5$ estimated from measurements of atmospheric band intensities.

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