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The study of intermolecular energy transfers in electronic energy quenching for molecular collisions N$_2$-N$_2$, N$_2$-O$_2$, O$_2$-O$_2$

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Abstract. Contributions of intermolecular electron energy transfers in the electronic quenching are calculated for molecular collisions N$_2$(A$^3\Sigma_u^+$, W$^3\Delta_u$)+N$_2$(X$^1\Sigma_g^+$, v=0), N$_2$(A$^3\Sigma_u^+$)+N$_2$(X$^1\Sigma_g^+$, v≥0), N$_2$(A$^3\Sigma_u^+$)+O$_2$(X$^3\Sigma_g^-$, v=0–2), O$_2$(a$^1\Delta_g$, b$^1\Sigma_g^+$)+O$_2$(X$^3\Sigma_g^-$, v=0–2). The calculation has allowed one to estimate the product branching ratios. It is shown that there is a dependence of the calculated rate coefficients on the vibrational excitation of N$_2$(X$^1\Sigma_g^+$) and O$_2$(X$^3\Sigma_g^-$) molecules. In many cases, the calculated rate coefficients have a good agreement with available experimental data.

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

1 Introduction

The auroral electrons and protons interact inelastically with atmospheric N$_2$ and O$_2$ molecules, causing the electronic excitation of the molecules. Spontaneous radiational and collisional cascade processes in these molecules decrease the level of the electronic excitation. By these processes, the excitation energy is finally accumulated in the vibrational levels of the lowest metastable states A$^3\Sigma_u^+$ of N$_2$ and a$^1\Delta_g$ and b$^1\Sigma_g^+$ of O$_2$.

The application of Landau-Zener and Rosen-Zener approximations by Kirillov (2004a) allowed us to obtain analytical formulas for the calculation of electronic energy quenching rate coefficients in molecular collisions. The calculation of the rate coefficients for collisions N$_2$-N$_2$ and O$_2$-O$_2$ by Kirillov (2004b) showed a good agreement with laboratory experimental data for a few states of molecular nitrogen and molecular oxygen. Moreover, the analysis of temperature

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dependence of the calculated rate coefficients for the b$^1\Sigma_g^+$ state of O$_2$ by Kirillov (2004c) showed a good agreement of the theoretical results with experimental data for vibrational levels v=1–3.

In isotopic studies of collisional processes in N$_2$ (Pravilov et al., 1988; Piper, 1994; Ottinger et al., 1995) the important role of intermolecular electron energy transfers during inelastic molecular interaction was emphasized. The suggestion of Kirillov (2004a) to consider the electronic quenching processes as a sum of intramolecular and intermolecular quasi-resonant energy transfers assumes a possible sufficient contribution of both kinds of these transfers in the quenching rate coefficients, as well.

The main aim of the paper is a new calculation of quenching rate coefficients for the lowest metastable and long-lived electronically excited states of N$_2$ and O$_2$. Special attention shall be paid namely to the study of the important role of intermolecular electron energy transfer processes related to the A$^3\Sigma_u^+$ state of N$_2$ and a$^1\Delta_g$ and b$^1\Sigma_g^+$ states of O$_2$ in molecular collisions N$_2$-N$_2$, N$_2$-O$_2$, O$_2$-O$_2$.

2 Collisions N$_2$(A$^3\Sigma_u^+$, W$^3\Delta_u$)+N$_2$(X$^1\Sigma_g^+$)

Collision-induced energy transfers among metastable A$^3\Sigma_u^+$ with long-lived W$^3\Delta_u$ states and the radiating B$^3\Pi_g$ state of N$_2$ were studied by Bachmann et al. (1992, 1993). Our analysis in Kirillov (2004a, b) of their experimental data led us to consider any quenching of an electronically excited state in a molecular collision as a sum of energetically quasi-resonant intramolecular and intermolecular energy transfer processes. Moreover, isotopic study of the considered collisions by Ottinger et al. (1995) on the basis of well-resolved 1PG emission spectrum allowed us to distinguish between intramolecular and intermolecular mechanisms. Hereby, we would like to compare our calculations of the contributions of the considered metastable A$^3\Sigma_u^+$ with long-lived W$^3\Delta_u$ states in the
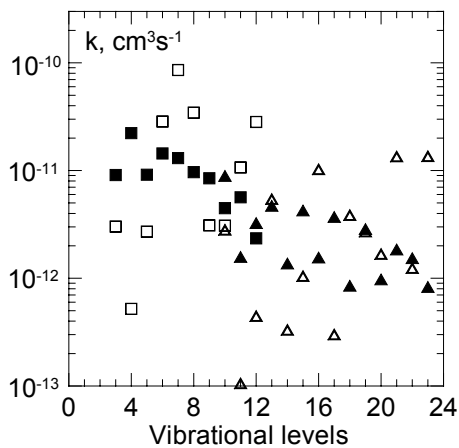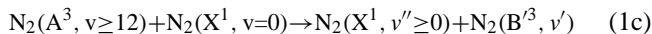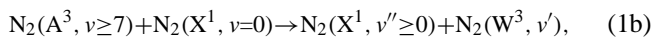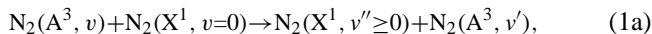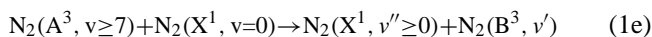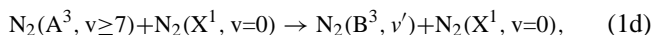
Fig. 1. The calculated rate coefficients of processes: (1d) – solid triangles, (1e) – open triangles, (2d) – solid squares, (2e) – open squares.

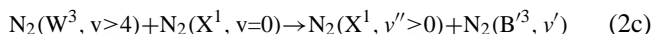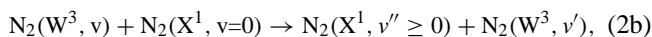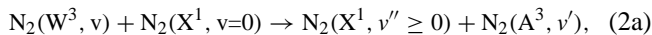vibrational population of the $B^3\Pi_g$ state with quantitative estimations of Ottinger et al. (1995).

The results of the calculations for quenching rate coefficients in $N_2(A^3\Sigma_u^+,\ v=2\text{--}23)+N_2$ and $N_2(W^3\Delta_u,\ v=0\text{--}18)+N_2$ collisions are made by Kirillov (2008)[1]. The calculations have included contributions of intermolecular electron energy transfer processes

$$N_2(A^3, v)+N_2(X^1, v=0)\rightarrow N_2(X^1, v''\geq 0)+N_2(A^3, v'), \qquad (1a)$$

$$N_2(A^3, v\geq 7)+N_2(X^1, v=0)\rightarrow N_2(X^1, v''\geq 0)+N_2(W^3, v'), \qquad (1b)$$

$$N_2(A^3, v\geq 12)+N_2(X^1, v=0)\rightarrow N_2(X^1, v''\geq 0)+N_2(B'^3, v') \qquad (1c)$$

with the excitation of more lower vibrational levels of the same state and $W^3\Delta_u$, $B'^3\Sigma_u^-$ states with similar configuration of electron orbitals $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\pi_u^3 3\sigma_g^2 1\pi_g$ and the sum of intramolecular and intermolecular electron energy transfer processes
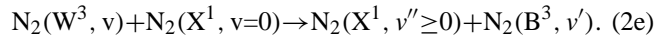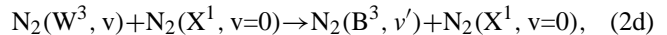
$$N_2(A^3, v\geq 7)+N_2(X^1, v=0) \rightarrow N_2(B^3, v')+N_2(X^1, v=0), \qquad (1d)$$

$$N_2(A^3, v\geq 7)+N_2(X^1, v=0)\rightarrow N_2(X^1, v''\geq 0)+N_2(B^3, v') \qquad (1e)$$

with the $\sigma_g\rightarrow\pi_u$ change in electronic configurations. Similarly for the $W^3\Delta_u$ state the electronic quenching includes intermolecular electron energy transfer processes

$$N_2(W^3, v) + N_2(X^1, v=0) \rightarrow N_2(X^1, v'' \geq 0) + N_2(A^3, v'), \qquad (2a)$$

$$N_2(W^3, v) + N_2(X^1, v=0) \rightarrow N_2(X^1, v'' \geq 0) + N_2(W^3, v'), \qquad (2b)$$

$$N_2(W^3, v\geq 4)+N_2(X^1, v=0)\rightarrow N_2(X^1, v''\geq 0)+N_2(B'^3, v') \qquad (2c)$$

and the sum of the intramolecular and intermolecular ones

$$N_2(W^3, v)+N_2(X^1, v=0)\rightarrow N_2(B^3, v')+N_2(X^1, v=0), \qquad (2d)$$

$$N_2(W^3, v)+N_2(X^1, v=0)\rightarrow N_2(X^1, v''\geq 0)+N_2(B^3, v'). \qquad (2e)$$

The existence of intermolecular energy transfers (1e) and (2e) between two nitrogen molecules was demonstrated by Ottinger et al. (1995) by means of isotopic labeling. A beam of electronically excited $^{14}N_2(A^3\Sigma_u^+)$ and $^{14}N_2(W^3\Delta_u)$ molecules was generated by means of a dc discharge. The beam was passed through a collision cell where both $^{14}N_2(X^1\Sigma_g^+)$ and $^{15}N_2(X^1\Sigma_g^+)$ were used as target molecules and the collisions were taking place. High-resolution spectral detection allowed one to distinguish between the $^{14}N_2(B^3\Pi_g)$ and $^{15}N_2(B^3\Pi_g)$ product emission from many well-specified vibrational levels. An inspection of the obtained spectrums of the $\Delta v=2$ and $\Delta v=3$ sequences of $B^3\Pi_g$, $v'\rightarrow A^3\Sigma_u^+$, v'' emissions by Ottinger et al. (1995) proved that intermolecular energy transfers do occur in agreement with the conclusions by Pravilov et al. (1988).

It should be noted that Ottinger et al. (1995) considered the vibrational population of $^{14}N_2(B^3\Pi_g)$ and $^{15}N_2(B^3\Pi_g)$ molecules in v=2-10 vibrational levels (energies $E=62\,688\text{--}75\,051$ cm^{-1} for the $^{14}N_2$ molecule), so, hereby, we shall deal with energetically close $v=10\text{--}23$ levels ($E=62\,823\text{--}75\,092$ cm^{-1}) of $N_2(A^3\Sigma_u^+)$ and $v=3\text{--}12$ levels ($E=63\,750\text{--}75\,540$ cm^{-1}) of $N_2(W^3\Delta_u)$. Calculated rate coefficients of intramolecular (1d) and (2d) and intermolecular (1e) and (2e) processes for the mentioned vibrational levels of $A^3\Sigma_u^+$ and $W^3\Delta_u$ states, according to analytical formulas by Kirillov (2004a), shown in Fig. 1. The results are indicative of an effective production of the $B^3\Pi_g$ state, both in the electronically excited nitrogen molecule and in the target molecule during these collisions. Using the vibrational population of the $B^3\Pi_g$ state ($v=2\text{--}10$) related to the intramolecular energy transfers (Fig. 5 of Ottinger et al., 1995) we have calculated the populations of $A^3\Sigma_u^+$, $v=10\text{--}23$ and $W^3\Delta_u$, $v=3\text{--}12$, suggesting that every state has the only contribution in the $B^3\Pi_g$ excitation. Since the amount of the considered vibrational levels of the $A^3\Sigma_u^+$ and $W^3\Delta_u$ states exceeds the one for the $B^3\Pi_g$ state we have proposed equal populations $f(v_i)=f(v_{i+1})$ for the $i=11, 14, 17, 19, 21$ of the $A^3\Sigma_u^+$ state and $i=9$ of the $W^3\Delta_u$ state. The calculated vibrational populations of $A^3\Sigma_u^+$ and $W^3\Delta_u$ states are shown in Fig. 2. Any tendency of the decrease in vibrational populations with the increasing number of vibrational levels in the considered v intervals is seen for both states.

Applying the calculated rate coefficients for processes (1e) and (2e) and the obtained vibrational populations of $A^3\Sigma_u^+$ ($v=10\text{--}23$) and $W^3\Delta_u$ ($v=3\text{--}12$) states we have completed the estimation of the vibrational population of the $B^3\Pi_g$ ($v=2\text{--}10$) state related to the intermolecular energy transfers. The results of the calculation for both states are compared in Fig. 3 with experimental estimations by Ottinger et

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[1]Kirillov, A. S.: Electronic kinetics of main atmospheric components in high-latitude lower thermosphere and mesosphere, Ann. Geophys., to be submitted, 2008.
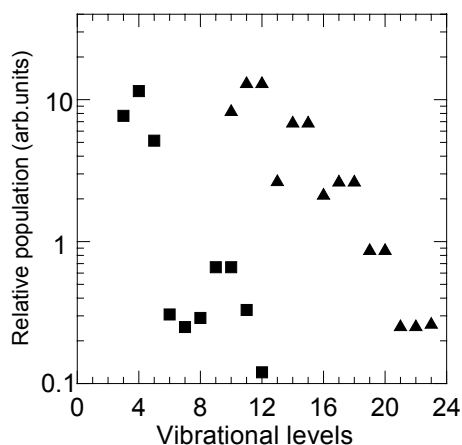
Fig. 2. The calculated populations of $A^3\Sigma_u^+$ and $W^3\Delta_u$ states – triangles and squares, respectively.

Fig. 3. The vibrational population of the $B^3\Pi_g$ state: calculated from the $A^3\Sigma_u^+$ distribution – triangles, from the $W^3\Delta_u$ distibution – squares, experimental data by Ottinger et al. (1995) – solid and open circles, for intramolecular and intermolecular electron energy transfers, respectively.

al. (1995). It is seen from Fig. 3 that there is a good qualitative agreement of theoretical estimations with experimental ones in the predominance of the population for low vibrational levels. In accordance with the data by Ottinger et al. (1995) the contribution of processes (1e) and (2e) in the excitation of high levels of the $B^3\Pi_g$ state is negligible.

3   Orange afterglow of molecular nitrogen

Hays and Oskam (1973) studied a spectral distribution of 1PG bands during an afterglow period of nitrogen plasma. They found that at least three processes populate the $B^3\Pi_g$ state of N_2 during afterglow long and short periods.

The first process is related to the recombination of nitrogen atoms. The well-known, long-duration Lewis-Rayleigh (yellow) afterglow is caused by this recombination (Brown, 1970). The pink short-duration afterglow is related to similar recombination processes and collisions of excited molecules (Oldenberg, 1971). The reduction in the discharge to the weakest current changes its colour to blue (Bryan et al., 1957). The cooling of the nitrogen to low temperature changes the colour of the short-duration afterglow from pink to green (auroral) (Tanaka and Jursa, 1961). This recombination of atomic nitrogen mainly populates the upper vibrational levels v=10–12 of the $B^3\Pi_g$ state of the nitrogen molecule.

Hays and Oskam (1973) also showed that the emission of 1PG bands during the early afterglow period is governed mainly by the annihilation of two metastable molecules $N_2(A^3\Sigma_u^+)$ with the production of the $N_2(B^3\Pi_g)$ molecule. This pooling mechanism was studied later by Piper (1988). In all cases it was obtained that the intensity of 1PG bands varied quadratically with the intensity of Vegard-Kaplan (VK) bands.
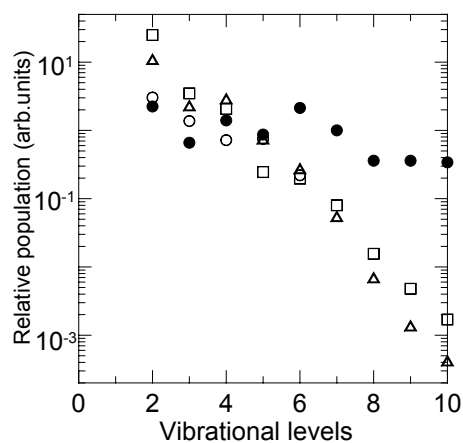
The last mechanism of the $N_2(B^3\Pi_g)$ production in the afterglow, suggested by Hays and Oskam (1973), is the population of the $B^3\Pi_g$ state by radiationless transitions from highly vibrationally excited $A^3\Sigma_u^+$ state molecules which are produced in the interaction of $N_2(A^3\Sigma_u^+)$ with vibrationally excited ground state $N_2(X^1\Sigma_g^+)$. Piper (1989, 1994) continued the study of the afterglow spectrum produced in the interaction of these molecules. It was found in those papers that the nitrogen orange afterglow results from the production of $N_2(B^3\Pi_g, v$=1–12) in the energy transfer reaction between $N_2(A^3\Sigma_u^+)$ and $N_2(X^1\Sigma_g^+, v{\geq}4)$ molecules. Estimations of the vibrational population of the $B^3\Pi_g$ state in the orange afterglow by Piper (1989, 1994) showed a monotonic decrease with increasing vibrational levels, in contrast to yellow, pink, blue and green afterglows. Piper (1994) also has obtained that the mixing of $^{15}N_2(X^1\Sigma_g^+, v)$ and $^{14}N_2(A^3\Sigma_u^+)$ molecules generated the orange afterglow with the predominance of emissions from $^{15}N_2(B^3\Pi_g)$, emphasizing the dominance of intermolecular electron energy transfers.

Hereby, we complete our calculations for the intermolecular electron energy transfer process from the $A^3\Sigma_u^+$ state

$$N_2(A^3, v)+N_2(X^1, v{\geq}0){\rightarrow}N_2(X^1, v''{\geq}0)+N_2(B^3, v'), \quad (3)$$
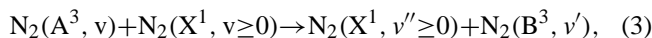
taking into account the "hot" vibrational excitation of the $N_2(X^1\Sigma_g^+)$ molecule. Piper and Marinelli (1988) demonstrated that the vibrational distribution of $N_2(X^1\Sigma_g^+)$ molecules in microwave-discharge did not follow the Boltzmann distribution, but rather the modified Treanor distribution (Treanor et al., 1968). Therefore, in this paper we use Eqs. (2–5) from their paper to calculate the vibrational distribution of $N_2(X^1\Sigma_g^+)$ molecules for vibrational levels v=0–17. The Boltzmann vibrational temperature (see Eq. (3) of Piper and Marinelli, 1988) is taken to equal 5000 K, in
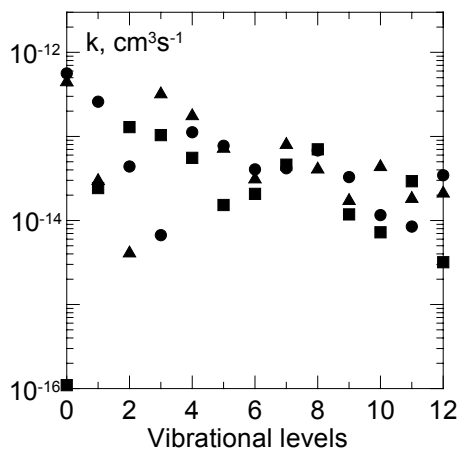
Fig. 4. The calculated rate coefficients of the excitation of the $B^3\Pi_g$ state in the process (3) for vibrational levels v=0, 2, 4 of the $A^3\Sigma_u^+$ state – squares, circles, triangles, respectively.
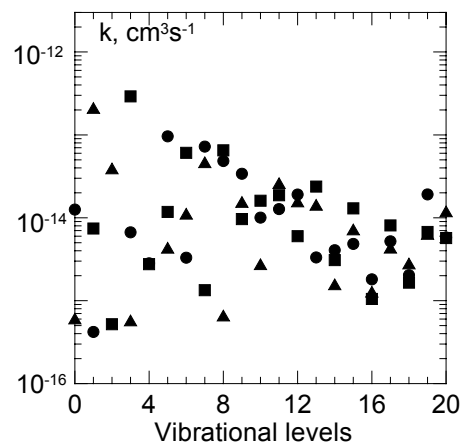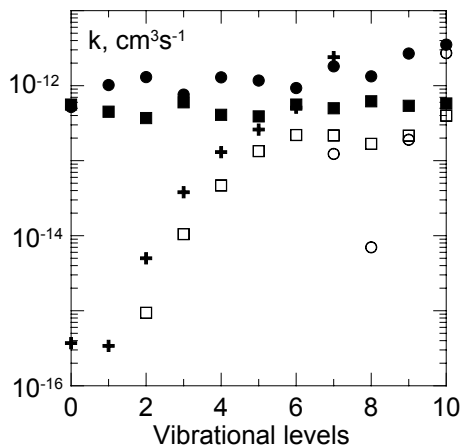

Fig. 5. The calculated rate coefficients of the excitation of the $A^3\Sigma_u^+$ state in the process (4) for vibrational levels v=0, 2, 4 of the $A^3\Sigma_u^+$ state – squares, circles, triangles, respectively.

agreement with similar estimations of Piper (1994). The results of our calculations of the excitation of the $B^3\Pi_g$ state (v'=0–12) for vibrational levels v=0, 2, 4 of the $A^3\Sigma_u^+$ state are shown in Fig. 4. It is seen from Fig. 4 that overall there is a tendency of a decrease in the rate coefficients with the increasing vibrational level v', in some accordance with the vibrational distribution of the $B^3\Pi_g$ state registered by Piper (1989, 1994).

Also in the study of the orange afterglow by Piper (1989) it was directly evidenced that there was a regeneration of $N_2(A^3\Sigma_u^+)$ molecules with vibrational levels exceeding v=0. Since intermolecular electron energy transfer processes (1e) and (3) are distinguished only by "cold" and "hot" vibrational distributions of the ground state nitrogen molecule, we propose, in a similar way, the alternative process for the energy transfer in (1a). The results of our calculation for the intermolecular electron energy transfer process from $A^3\Sigma_u^+$ (v=0, 2, 4) to $A^3\Sigma_u^+$ (v'=0–20) states

$$N_2(A^3, v)+N_2(X^1, v\geq0)\rightarrow N_2(X^1, v''\geq0)+N_2(A^3, v')\quad(4)$$
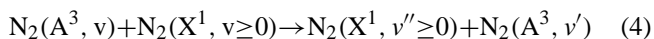
are shown in Fig. 5. The calculation is completed for the modified Treanor distribution of $N_2(X^1\Sigma_g^+)$ molecules on vibrational levels, as for process (3). The results show that there is an effective excitation of the lowest vibrational levels of the $A^3\Sigma_u^+$ state for conditions of the orange afterglow. Therefore, the regeneration of $N_2(A^3\Sigma_u^+, v>0)$ evidenced by Piper (1989) may be related to intermolecular electron energy transfers (4).

Dependencies of the quenching rate coefficients on the vibrational level v for processes (1a), (1e), (3), (4) are shown in Fig. 6. The rate coefficients are calculated by the sum on v'=0–20 for (1a) and (4) processes and v'=0–12 for (1e) and (3) processes. Experimental data by Dreyer and Perner (1973) are also presented in Fig. 6. It is seen that there

is a good agreement of theoretical estimations for the process (1a) and experimental results in the magnitude and in the increase with the increasing number for vibrational levels v=2–7. It was found by Kirillov (2008)[1] that the main contribution in rate coefficients for vibrational levels v=2–6 comes from intermolecular process (1a) and for $v\geq7$ from the sum of processes (1d) and (1e). Therefore, the results of this paper emphasise that the vibrational excitation of $N_2(X^1\Sigma_g^+)$ molecules increases sufficiently the rates of intermolecular electron energy transfer processes in collisions with metastable molecules $N_2(A^3\Sigma_u^+)$, especially for low vibrational levels of metastable molecule.

4 Processes of electronic energy transfer and dissociation in collisions $N_2(A^3\Sigma_u^+)$+$O_2(X^3\Sigma_g^-)$

Experimental measurements of the overall rate coefficients for the title reaction have been performed by several groups (Dreyer et al., 1974; Thomas and Kaufman, 1985; De Benedictis and Dilecce, 1997). One of the problems related to the reaction is the estimation of product branching ratios. A laboratory study by Zipf (1980) gave a very high effective yield of 0.6 for the production of the nitrous oxide molecule in the interaction. This high value has allowed one to speculate considerably about the effective production of N_2O by the reaction in the auroral D and E regions (Zipf and Prasad, 1980), in the quiet mesosphere, as well as the mesosphere disturbed by solar protons and relativistic electrons (Prasad and Zipf, 1981; Zipf and Prasad, 1982), and in the troposphere during a thunderstorm lightning (Levine and Shaw, 1983).
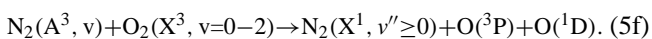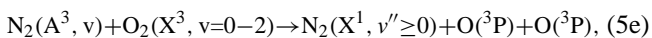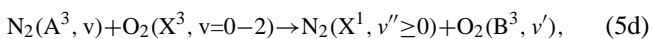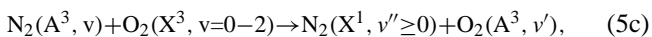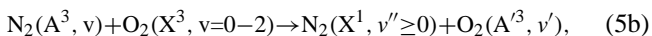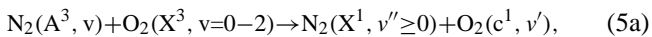
However, a variety of other laboratory investigations of the N_2O formation of Iannuzzi et al. (1982); De Souza et al. (1985); Fraser and Piper (1989) has led to the conclusion about the negligible role of the reaction as a source of atmospheric nitrous oxide. Moreover, Fraser et al. (1990),

Fig. 6. The calculated rate coefficients for processes (1a) and (4) – open and solid squares, respectively, for processes (1e) and (3) – open and solid circles, respectively; experimental data by Dreyer and Perner (1973) – crosses.
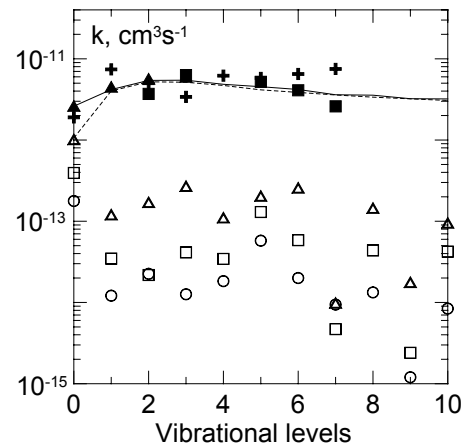

Fig. 7. The calculated total quenching rate coefficients of $N_2(A^3\Sigma_u^+, v) + O_2(X^3\Sigma_g^-, v=0)$ (solid line) are compared with experimental data by Dreyer et al. (1974) (crosses), Thomas and Kaufman (1985) (solid triangles), De Benedictis and Dilecce (1997) (solid squares). The calculated contributions of Eqs. (5a), (5b), (5c) processes, molecular oxygen dissociation – open triangles, open squares, circles and dotted line, respectively.

Fig. 8. The same as in Fig. 7, but for the vibrational level $v=1$ of $O_2(X^3\Sigma_g^-)$.

using their results of an experimental study, postulated that the principal N_2O production mechanism in the atmosphere during the discharge is the interaction of highly vibrationally excited ground state N_2 with electronically excited $O_2(a^1\Delta_g$ or $b^1\Sigma_g^+)$.

Therefore, hereby, we consider the processes of the interaction of metastable molecular nitrogen with a ground state O_2 molecule as a sum of the processes of intermolecular electronic energy transfers and the dissociation

$$N_2(A^3, v) + O_2(X^3, v=0-2) \rightarrow N_2(X^1, v''\geq0) + O_2(c^1, v'), \quad (5a)$$

$$N_2(A^3, v) + O_2(X^3, v=0-2) \rightarrow N_2(X^1, v''\geq0) + O_2(A'^3, v'), \quad (5b)$$

$$N_2(A^3, v) + O_2(X^3, v=0-2) \rightarrow N_2(X^1, v''\geq0) + O_2(A^3, v'), \quad (5c)$$

$$N_2(A^3, v) + O_2(X^3, v=0-2) \rightarrow N_2(X^1, v''\geq0) + O_2(B^3, v'), \quad (5d)$$

$$N_2(A^3, v) + O_2(X^3, v=0-2) \rightarrow N_2(X^1, v''\geq0) + O(^3P) + O(^3P), \quad (5e)$$

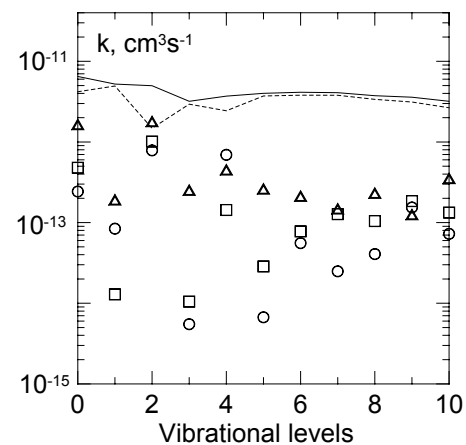$$N_2(A^3, v) + O_2(X^3, v=0-2) \rightarrow N_2(X^1, v''\geq0) + O(^3P) + O(^1D). \quad (5f)$$

We do not take into account the processes of the excitation of singlet $a^1\Delta_g$ and $b^1\Sigma_g^+$ states of molecular oxygen since the probabilities of the excitation calculated according to Kirillov (2004a) are negligible. To calculate the rates of processes (5e) and (5f) through continuums of $c^1\Sigma_u^-$, $A'^3\Delta_u$, $A^3\Sigma_u^+$ and $B^3\Sigma_u^-$ states we use Franck-Condon densities, taken according to Jarmain and Nicholls (1964, 1967).

The calculated rate coefficients of (5a), (5b), (5c) processes, molecular oxygen dissociation and total quenching of $N_2(A^3\Sigma_u^+, v=0-10)$ in (5a–f) processes are presented in Figs. 7–9 for vibrational levels 0, 1, 2 of the $X^3\Sigma_g^-$ ground state of O_2, respectively. Since the $B^3\Sigma_u^-$ state is mainly predissociated, we have included process (5d) in the channel of the dissociation. Experimental data of Dreyer et al. (1974),

Thomas and Kaufman (1985), De Benedictis and Dilecce (1997) are compared with the results of our calculation for vibrational level $v=0$ in Fig. 7. It is seen from Fig. 7 that there is a good agreement of experimental estimations with theoretical results. The considered intermolecular processes (5a–f) are principal in electronic quenching of $N_2(A^3\Sigma_u^+)$ for the lowest vibrational levels. Only for $v\geq10$ was it necessary to include intramolecular electron energy transfer from the $A^3\Sigma_u^+$ state to the $B^3\Pi_g$ state (Kirillov, 2008[1]).

The results of this calculation have shown that there is an increase in the total quenching rate coefficient for the $N_2(A^3\Sigma_u^+, v=0)$ molecule with the rise in the vibrational level of $O_2(X^3\Sigma_g^-)$. Moreover, there is an increase in
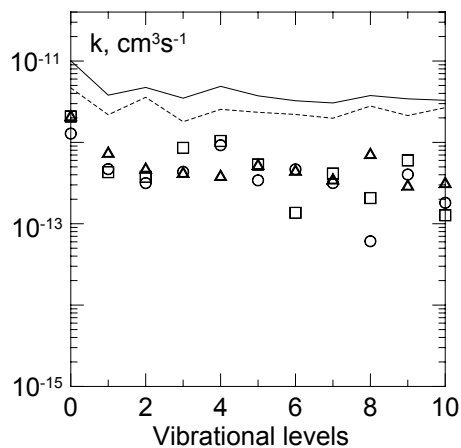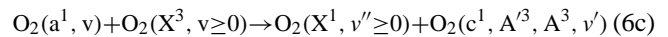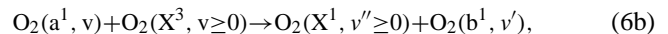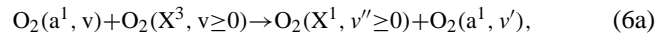
Fig. 9. The same as in Fig. 7, but for the vibrational level v=2 of $O_2(X^3\Sigma_g^-)$.

the partial contribution of electronic excitation of the O_2 molecule for v=1–10 vibrational levels of $N_2(A^3\Sigma_u^+)$ with the vibrational excitation of the O_2 molecule. High branching ratios of the dissociation for all vibrational levels of the $A^3\Sigma_u^+$ state are in good agreement with the experimental conclusions by Iannuzzi et al. (1982), Fraser and Piper (1989).
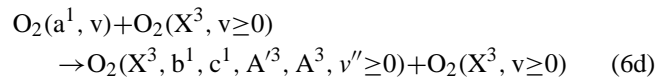
5 Electronic quenching of the singlet oxygen in collisions $O_2(a^1\Delta_g, b^1\Sigma_g^+)$+$O_2(X^3\Sigma_g^-)$

The processes with participation of metastable singlet oxygen $O_2(a^1\Delta_g, b^1\Sigma_g^+)$ are a subject of great interest, mainly due to the radiational and chemical activity of the molecule in various atmospheric and biological processes. Six vibrational levels of the $b^1\Sigma_g^+$ state are effectively excited in the aurora with the subsequent emission of atmospheric bands (Vallance Jones and Gattinger, 1974; Henriksen and Sivjee, 1990; Witt, 2006). There is also a large enhancement of intensities of the infrared atmospheric band 1.27 μm in the aurora (Noxon, 1970; Gattinger and Vallance Jones, 1973; Baker et al., 1978). The mechanisms of the production of the singlet oxygen in the mesosphere and lower thermosphere and the emission in the infrared atmospheric and atmospheric band nightglow have been studied during a few decades (Llewellyn and Solheim, 1978; Witt et al., 1979; McDade et al., 1986, 1987; Kita et al., 1992; Slanger et al., 2000, 2003). It is known that the singlet oxygen is very active in the interaction with organic molecules and processes of chemiluminescence (Kearns, 1971; Lissi et al., 1993). The very important role of the singlet oxygen in oncological issues, photodynamic therapy, including the mechanisms of certain human diseases, cell aging and laser cancer treatment was studied by Gomer (1991); Pass (1993); Gal (1994).
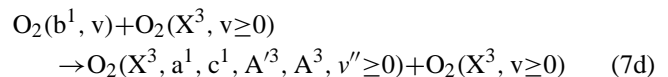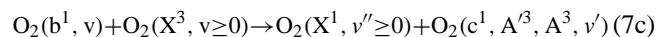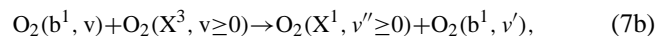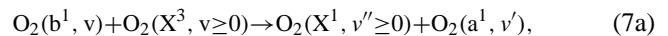
The first calculation of quenching rate coefficients for $a^1\Delta_g$ and $b^1\Sigma_g^+$ states of molecular oxygen was completed by Kirillov (2004b) for vibrational levels v=0–10. Hereby, we continue the calculation for higher levels of these states. The calculation includes the following intermolecular electron energy transfer processes

$$O_2(a^1, v)+O_2(X^3, v\geq0)\rightarrow O_2(X^1, v''\geq0)+O_2(a^1, v'), \quad (6a)$$

$$O_2(a^1, v)+O_2(X^3, v\geq0)\rightarrow O_2(X^1, v''\geq0)+O_2(b^1, v'), \quad (6b)$$

$$O_2(a^1, v)+O_2(X^3, v\geq0)\rightarrow O_2(X^1, v''\geq0)+O_2(c^1, A'^3, A^3, v') \quad (6c)$$

and intramolecular processes

$$O_2(a^1, v)+O_2(X^3, v\geq0)$$
$$\rightarrow O_2(X^3, b^1, c^1, A'^3, A^3, v''\geq0)+O_2(X^3, v\geq0) \quad (6d)$$

for the $a^1\Delta_g$ state and a similar set of processes

$$O_2(b^1, v)+O_2(X^3, v\geq0)\rightarrow O_2(X^1, v''\geq0)+O_2(a^1, v'), \quad (7a)$$

$$O_2(b^1, v)+O_2(X^3, v\geq0)\rightarrow O_2(X^1, v''\geq0)+O_2(b^1, v'), \quad (7b)$$

$$O_2(b^1, v)+O_2(X^3, v\geq0)\rightarrow O_2(X^1, v''\geq0)+O_2(c^1, A'^3, A^3, v') \quad (7c)$$

$$O_2(b^1, v)+O_2(X^3, v\geq0)$$
$$\rightarrow O_2(X^3, a^1, c^1, A'^3, A^3, v''\geq0)+O_2(X^3, v\geq0) \quad (7d)$$

for the $b^1\Sigma_g^+$ state. The results of our calculation for vibrational levels v=1–25 of the $a^1\Delta_g$ state and v=1–20 of the $b^1\Sigma_g^+$ state at temperatures of 155 and 300 K are compared in Figs. 10 and 11 with the experimental data by Hwang et al. (1998), Bloemink et al. (1998), Kalogerakis et al. (2002), Slanger and Copeland (2003) obtained at room temperature and the experimental data by Amaral et al. (2002), Slanger and Copeland (2003) obtained at a temperature of 155 K. It is seen from Figs. 10 and 11 that there is good agreement between the calculated rate coefficients and experimental data for low and high vibrational levels for both states. The calculation has shown that intermolecular energy transfers (6a), (7a), (7b) are dominant in the quenching of these states for the considered intervals of vibrational levels. The contributions of (6c) and (7c) are negligible and there is an increase in the contribution of intramolecular processes (6d) and (7d) with the excitation of the ground and Herzberg states for $v\sim$30.

The calculated quenching rate coefficients for $a^1\Delta_g$ and $b^1\Sigma_g^+$ states in collisions with $O_2(X^3\Sigma_g^-$, v=0–2) are compared in Figs. 12 and 13. It is seen from these figures that there is a movement of positions of maximal and minimal values in the side of higher v with the increase in the vibrational excitation of $O_2(X^3\Sigma_g^-)$.
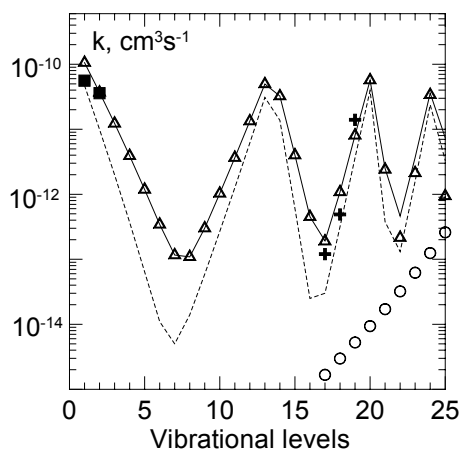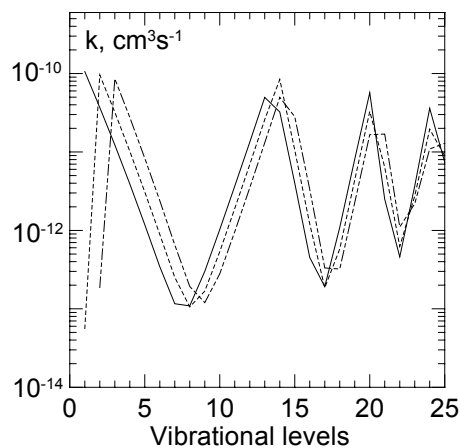
Fig. 10. The calculated total quenching rate coefficients of $O_2(a^1\Delta_g, v)+O_2(X^3\Sigma_g^-, v=0)$ at temperatures of 155 and 300 K (dotted and solid lines, respectively) are compared with experimental data by Hwang et al. (1998) (squares) and Amaral et al. (2002), Slanger and Copeland (2003) (crosses). The calculated contributions of processes (6a) and (6b) at room temperature – triangles and circles, respectively.
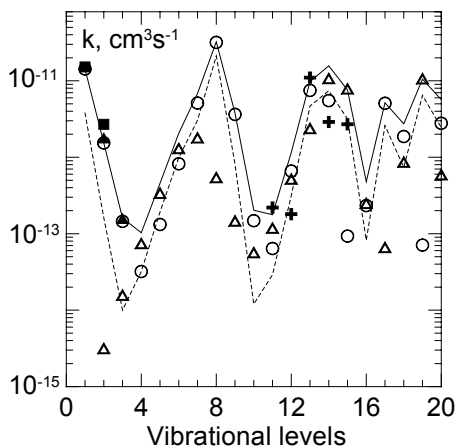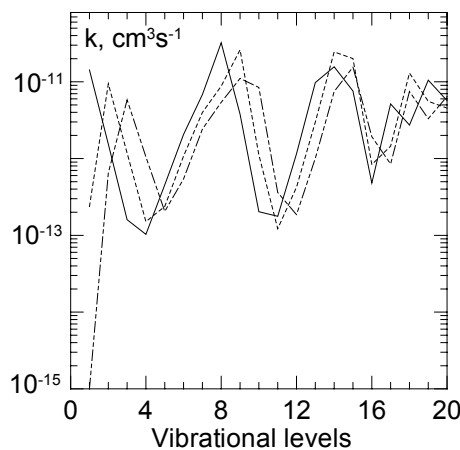

Fig. 11. The calculated total quenching rate coefficients of $O_2(b^1\Sigma_g^+, v)+O_2(X^3\Sigma_g^-, v=0)$ at temperatures of 155 and 300 K (dotted and solid lines, respectively) are compared with experimental data by Bloemink et al. (1998) (squares), Kalogerakis et al. (2002) (solid triangles) and Amaral et al. (2002), Slanger and Copeland (2003) (crosses). The calculated contributions of processes (7a) and (7b) at room temperature – open triangles and circles, respectively.

6 Conclusions

Hereby, we have continued our calculation of quenching rate coefficients for various vibrational levels of electronically excited states of N_2 and O_2 in collisions N_2-N_2, N_2-O_2, O_2-O_2, started in Kirillov (2004b, 2008[1]). This paper has shown that intermolecular electron energy transfers play a very important role in processes of electronic quenching of metastable

Fig. 12. The calculated total quenching rate coefficients of $O_2(a^1\Delta_g, v)+O_2(X^3\Sigma_g^-, v=0, 1, 2)$ at a temperature of 300 K (solid, dotted and dotted-dashed lines, respectively).

Fig. 13. The calculated total quenching rate coefficients of $O_2(b^1\Sigma_g^+, v)+O_2(X^3\Sigma_g^-, v=0, 1, 2)$ at a temperature of 300 K (solid, dotted and dotted-dashed lines, respectively).

molecular nitrogen $N_2(A^3\Sigma_u^+)$ and singlet oxygen $O_2(a^1\Delta_g, b^1\Sigma_g^+)$. These transfers are dominant for many vibrational levels of the considered states of N_2 and O_2. Moreover, we have obtained good agreement between the calculated rate coefficients with a few available experimental data.

The main results of these calculations are as follows:

1. Using a vibrational population of the $N_2(B^3\Pi_g)$ molecules obtained in the experimental arrangement by Ottinger et al. (1995) for intramolecular electron energy transfers, we have estimated the possible vibrational populations of $N_2(A^3\Sigma_u^+)$ and $N_2(W^3\Delta_u)$ in the experiment. The populations were used to calculate the vibrational population of $N_2(B^3\Pi_g)$ molecules for intermolecular transfers. The results of the calculation are in good qualitative agreement with the similar estimation

by Ottinger et al. (1995), showing a sufficient population at low vibrational levels and a monotonic decrease in the region of high v.

2. The analysis of the interaction of metastable $N_2(A^3\Sigma_u^+, v=0, 2, 4)$ molecules with vibrationally excited ground state $N_2(X^1\Sigma_g^+)$ molecules for conditions of orange afterglow by Piper (1989, 1994) has shown that the molecular collisions caused effective production of $N_2(B^3\Pi_g, v=0-12)$ and $N_2(A^3\Sigma_u^+, v=0-20)$ electronically excited molecules in intermolecular electron energy transfers. A comparison of the rate coefficients of the interaction of $N_2(A^3\Sigma_u^+, v)$ with vibrationally "cold" and "hot" $N_2(X^1\Sigma_g^+)$ molecules is indicative of the sufficient increase with the rise in vibrational temperature, especially for low vibrational levels of metastable nitrogen.

3. Our calculation of rate coefficients for the interaction $N_2(A^3\Sigma_u^+)+O_2(X^3\Sigma_g^-, v=0-2)$ shows a very high branching ratio of the process of the O_2 dissociation in good agreement with the experimental results by Iannuzzi et al. (1982), Fraser and Piper (1989). The partial contribution of the electronic excitation of molecular oxygen (namely in Herzberg states) during this molecular collision rises with the increase in vibrational excitation of the ground state of oxygen molecule.

4. We have continued the calculation of quenching rate coefficients for $a^1\Delta_g$ and $b^1\Sigma_g^+$ states in collisions with $O_2(X^3\Sigma_g^-)$, started in Kirillov (2004b) for high vibrational levels of these states. The results of the calculation have shown an excellent agreement with all experimental data available in a review by Slanger and Copeland (2003). It is indicative of the fact that intermolecular transfers with the production of singlet oxygen (processes 6a, 7a, 7b) are dominant in the electronic quenching for considered intervals of vibrational levels of the metastable states. It was shown that the vibrational excitation of the $O_2(X^3\Sigma_g^-)$ molecule causes changes in the rates of the electronic quenching of singlet oxygen.

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