Calculation of rate coefficients of electron energy transfer processes for molecular nitrogen and molecular oxygen

1 AUTHOR:

Andrey S. Kirillov

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Calculation of rate coefficients of electron energy transfer processes for molecular nitrogen and molecular oxygen

A.S. Kirillov

Polar Geophysical Institute, Apatity, Murmansk region 184200, Russia

Abstract

Cross sections and rate coefficients of electronic quenching for triplet and singlet states of molecular nitrogen and molecular oxygen in molecular inelastic collisions N_2–N_2 and O_2–O_2 were calculated from analytical expressions. Electronic quenching is considered as a sum of quasi-resonant intramolecular and intermolecular electron energy transfer processes in inelastic interactions. In most conditions good agreement with experimental data is obtained.
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Keywords: Ionosphere; Molecular nitrogen; Molecular oxygen; Electron energy transfer processes
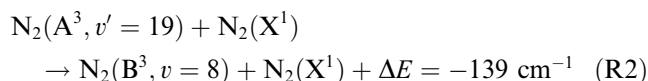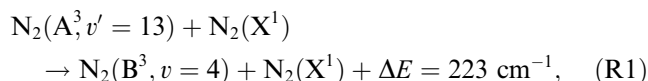
1. Introduction

The total rate of the excitation of triplet and singlet states of molecular nitrogen and molecular oxygen in low temperature plasma (Konovalov and Son, 1987) and in auroral ionosphere (Sergienko and Ivanov, 1993) is comparable with the rate of ion–electron pair production. The spontaneous transitions between the states of N_2 cause emission of Vegard–Kaplan (transition $A^3\Sigma_u^+ \to X^1\Sigma_g^+$), first positive ($B^3\Pi_g \to A^3\Sigma_u^+$), second positive ($C^3\Pi_u \to B^3\Pi_g$), Wu–Benesch ($W^3\Delta_u \to B^3\Pi_g$), Lyman–Birge–Hopfield ($a^1\Pi_g \to X^1\Sigma_g^+$), etc. bands. The spontaneous transitions between the states of O_2 cause the radiation of infrared atmospheric, atmospheric, Herzberg I, II, III, etc. bands (transitions from $a^1\Delta_g$, $b^1\Sigma_g^+$, $A^3\Sigma_u^+$, $c^1\Sigma_u^-$, $A'^3\Delta_u$ states to $X^3\Sigma_g^-$, respectively).

Electronic and vibrational excitation of N_2 and O_2 could increase the rate coefficients of chemical reactions with ions and neutrals influencing atmospheric chemical kinetics. The collisional quenching rates of some triplet and singlet states are comparable with radiational ones in the region of the lower thermosphere–mesosphere.

Main purpose of the paper is the calculation of cross sections and rate coefficients of electron energy transfers and quenching processes for triplet and singlet states of molecular nitrogen and molecular oxygen in molecular inelastic collisions N_2–N_2 and O_2–O_2. To this end we apply the set of formulas derived by Kirillov (2003).
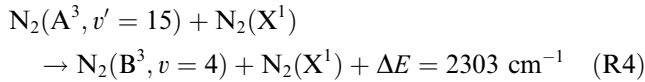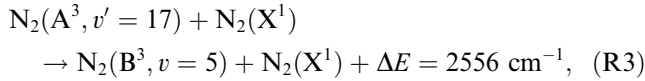
2. Electron energy transfers between triplet states of N_2

Collision-induced coupling within the triplet manifold of N_2 has been studied in Bachmann et al. (1992, 1993), Ottinger et al. (1995). The investigations have shown that the processes

$$N_2(A^3, v' = 13) + N_2(X^1)$$
$$\to N_2(B^3, v = 4) + N_2(X^1) + \Delta E = 223 \text{ cm}^{-1}, \quad \text{(R1)}$$

$$N_2(A^3, v' = 19) + N_2(X^1)$$
$$\to N_2(B^3, v = 8) + N_2(X^1) + \Delta E = -139 \text{ cm}^{-1} \quad \text{(R2)}$$
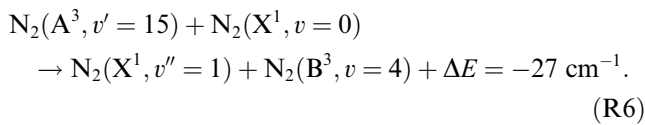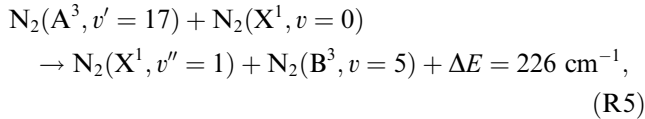
have large cross sections due to energy resonance between the reactant and product vibrational levels. Moreover, it was obtained that in the experiments the off-resonance processes

$$N_2(A^3, v' = 17) + N_2(X^1)$$
$$\rightarrow N_2(B^3, v = 5) + N_2(X^1) + \Delta E = 2556 \text{ cm}^{-1}, \quad (R3)$$

$$N_2(A^3, v' = 15) + N_2(X^1)$$
$$\rightarrow N_2(B^3, v = 4) + N_2(X^1) + \Delta E = 2303 \text{ cm}^{-1} \quad (R4)$$

were found rather important. Bachmann et al. (1993) attributed this to absorption of excess energy by target vibration as an additional degree of freedom. We, however, feel the processes (R3) and (R4) are intermolecular electron energy transfers to target molecule, namely:

$$N_2(A^3, v' = 17) + N_2(X^1, v = 0)$$
$$\rightarrow N_2(X^1, v'' = 1) + N_2(B^3, v = 5) + \Delta E = 226 \text{ cm}^{-1},$$
$$(R5)$$

$$N_2(A^3, v' = 15) + N_2(X^1, v = 0)$$
$$\rightarrow N_2(X^1, v'' = 1) + N_2(B^3, v = 4) + \Delta E = -27 \text{ cm}^{-1}.$$
$$(R6)$$

Moreover, an isotopic study of electron energy transfer processes (Ottinger et al., 1995) by separating of intermolecular from competing intramolecular collisional coupling has shown that intermolecular coupling of triplet states in N_2–N_2 collisions occurs with cross sections of similar magnitudes as the intramolecular processes.

We suggest to calculate the quenching coefficients of intramolecular (Eqs. (R1) and (R2)) and intermolecular (Eqs. (R5) and (R6)) processes according to analytical formulas obtained by Kirillov (2003) applying Landau–Zener and Rosen–Zener approximations. In this approach the processes (R3) and (R4) are unimportant because the Franck–Condon factor for the molecule disappears in Eq. (27) of Kirillov (2003).

By the way, here we use conclusions of Bachmann et al. (1993) that a large cross section of the exothermic process equation (R1) compared to the one of endothermic process equation (R2) points to a crossing of exchange potentials in the case of $A^3\Sigma_u^+, v' \rightarrow B^3\Pi_g, v$ exothermic transfer. Suggested rate coefficients for $A^3\Sigma_u^+, v' \rightarrow B^3\Pi_g, v$, $W^3\Delta_u, v' \rightarrow B^3\Pi_g, v$, $B'^3\Sigma_u^-, v' \rightarrow B^3\Pi_g, v$ transitions are

$$k = k_{LZ}q_{v'v}, \quad (1)$$

$$k = k_{RZ}q_{v'v} \quad (2)$$

for intramolecular exothermic and endothermic energy transfer processes, respectively, and

$$k = k_{LZ}q_{v'v''}q_{0v}, \quad (3)$$

$$k = k_{RZ}q_{v'v''}q_{0v} \quad (4)$$

for intermolecular exothermic and endothermic energy transfer processes, respectively. k_{RZ} and k_{LZ} have to be calculated according to Eqs. (20) and (22) of Kirillov

(2003). Franck–Condon factors q were taken according to Gilmore et al. (1992).

We took also account of the fact that $A^3\Sigma_u^+$, $W^3\Delta_u$, $B'^3\Sigma_u^-$ states have 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 there is the $\sigma_g \rightarrow \pi_u$ change in the transitions to $B^3\Pi_g$ state. Moreover, it is suggested that all three states have similar repulsive exchange potentials and the parameters γ and β in Eqs. (20) and (22) of Kirillov (2003) have the same magnitudes for $A^3\Sigma_u^+, v' \rightarrow B^3\Pi_g, v$, $W^3\Delta_u, v' \rightarrow B^3\Pi_g, v$ and $B'^3\Sigma_u^-, v' \rightarrow B^3\Pi_g, v$ electron energy transfers. Only the parameter k_0 is two times greater for transitions from the $W^3\Delta_u$ state because of Λ-doubling of this initial state.

Experimental data of Bachmann et al. (1992, 1993) for 14 $A^3\Sigma_u^+, v' \rightarrow B^3\Pi_g, v$ and seven $W^3\Delta_u, v' \rightarrow B^3\Pi_g, v$ electron transitions were normalized on the expressions (1)–(4) to obtain the mentioned parameters. The method of least squares was used in the normalizing. Corre-
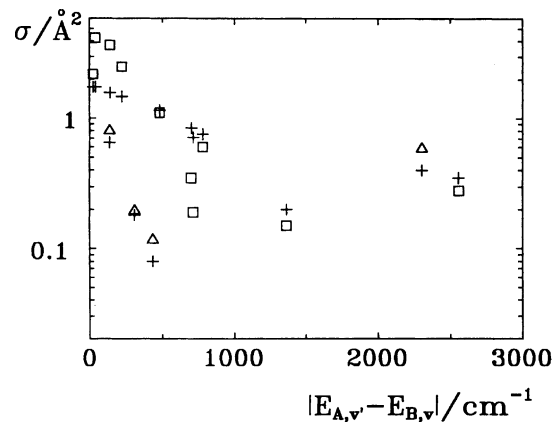

Fig. 1. Calculated cross sections (crosses) for $A^3\Sigma_u^+, v' \rightarrow B^3\Pi_g, v$ transitions are compared with experimental data of Bachmann et al. (1993, squares and triangles for exothermic and endothermic processes, respectively).

Fig. 2. Calculated cross sections (crosses) for $W^3\Delta_u, v' \rightarrow B^3\Pi_g, v$ transitions are compared with experimental data of Bachmann et al. (1992, 1993, squares and triangles for exothermic and endothermic processes, respectively).
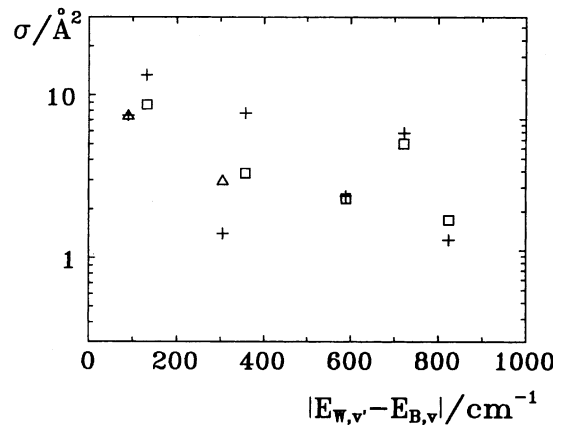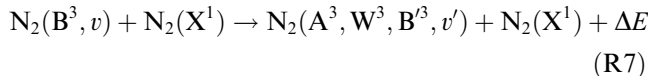
sponding to experimental conditions of Bachmann et al. (1992, 1993) temperature T was taken equal to 657 K. Every energy transfer process was considered as a sum of possible intramolecular and intermolecular processes. The normalization has given $\gamma = 106$ cm^{-1} and $\beta = 0.446$ cm^{-1}/K. k_0 is equal to 5.1×10^{-10} cm^3 s^{-1} for the transitions from the $A^3\Sigma_u^+$ state (also from the $B'^3\Sigma_u^-$ state) and 10.2×10^{-10} cm^3 s^{-1} for the transitions from the $W^3\Delta_u$ state. Results of our calculations for cross sections are compared with experimental data of Bachmann et al. (1992, 1993) for 14 $A^3\Sigma_u^+, v' \rightarrow B^3\Pi_g, v$ transitions in Fig. 1 and for seven $W^3\Delta_u, v' \rightarrow B^3\Pi_g, v$ transitions in Fig. 2.
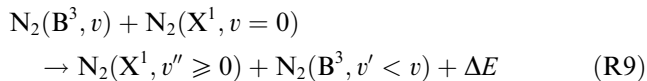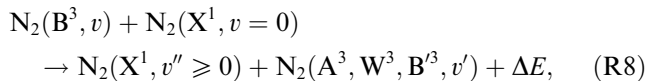
3. Quenching rate coefficients of triplet and singlet states of molecular nitrogen in inelastic collisions N_2–N_2

Applying Kirillov (2003) here we consider every inelastic quenching of electronically excited triplet and singlet states of molecular nitrogen as a sum of all possible effective intramolecular and intermolecular energy transfer processes.

For the $B^3\Pi_g$ state we took account of the intramolecular

$$N_2(B^3, v) + N_2(X^1) \rightarrow N_2(A^3, W^3, B'^3, v') + N_2(X^1) + \Delta E \quad (R7)$$

and intermolecular

$$N_2(B^3, v) + N_2(X^1, v = 0)$$
$$\rightarrow N_2(X^1, v'' \geqslant 0) + N_2(A^3, W^3, B'^3, v') + \Delta E, \quad (R8)$$

$$N_2(B^3, v) + N_2(X^1, v = 0)$$
$$\rightarrow N_2(X^1, v'' \geqslant 0) + N_2(B^3, v' < v) + \Delta E \quad (R9)$$

processes. The summation includes all possible v' in the case of intramolecular transfers and all possible v', v'' in the case of intermolecular transfers. Contributions of energetic non-resonant processes in the summation are negligible due to exponential dependence on $|\Delta E|$. The rates of exothermic and endothermic processes were calculated according to Eqs. (2), (4) and Eqs. (1), (3), respectively. The results of our calculation at temperature $T = 300$ K are compared in Fig. 3 with experimental data of Piper (1988) and Shemansky (1976). Good agreement was found with experimental data. Note that the calculation is made with parameters $k_0 = 10.2 \times 10^{-10}$ cm^3 s^{-1}, β and γ obtained by normalizing the analytical expressions with experimental data (Bachmann et al., 1992, 1993).

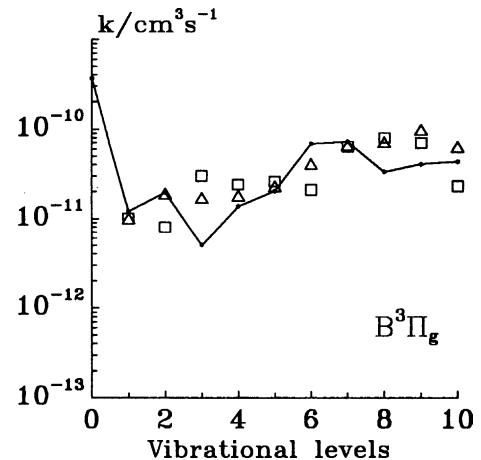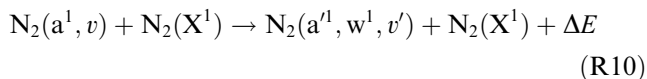For the $a^1\Pi_g$ state we took account of the intramolecular

$$N_2(a^1, v) + N_2(X^1) \rightarrow N_2(a'^1, w^1, v') + N_2(X^1) + \Delta E \quad (R10)$$

Fig. 3. Calculated quenching rate coefficients for the $B^3\Pi_g$ state of N_2 at temperature $T = 300$ K are compared with experimental data of Piper (1988, squares) and Shemansky (1976, triangles).
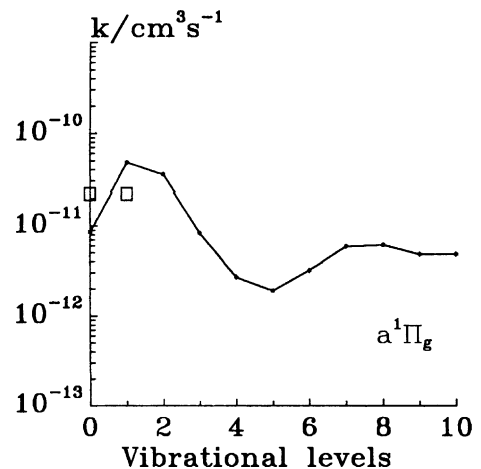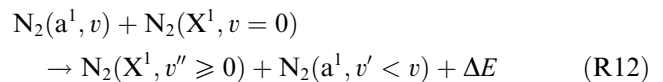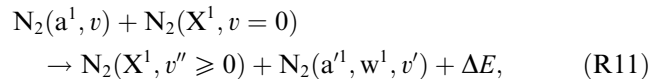

Fig. 4. Calculated quenching rate coefficients for the $a^1\Pi_g$ state of N_2 at temperature $T = 300$ K are compared with experimental data of van Veen et al. (1982, squares).

and intermolecular

$$N_2(a^1, v) + N_2(X^1, v = 0)$$
$$\rightarrow N_2(X^1, v'' \geqslant 0) + N_2(a'^1, w^1, v') + \Delta E, \quad (R11)$$

$$N_2(a^1, v) + N_2(X^1, v = 0)$$
$$\rightarrow N_2(X^1, v'' \geqslant 0) + N_2(a^1, v' < v) + \Delta E \quad (R12)$$

processes. The value of $k_0 = 3.4 \times 10^{-10}$ cm^3 s^{-1} was taken three times lower than for the $B^3\Pi_g$ state because of the multiplicity $2S + 1 = 1$. Values of β and γ were taken as for the $B^3\Pi_g$ state. The rates of exothermic and endothermic processes were calculated according to Eqs. (2), (4) and Eqs. (1), (3), respectively. The similarity of the calculations for $a^1\Pi_g$ and $B^3\Pi_g$ states is explained by configuration similarity of their electron orbitals. Also all five $A^3\Sigma_u^+$, $W^3\Delta_u$, $B'^3\Sigma_u^-$, $a'^1\Sigma_u^-$, $w^1\Delta_u$, states are identical. The results of our calculation at temperature

$T = 300$ K are compared in Fig. 4 with experimental data of van Veen et al. (1982).

4. Franck–Condon factors for O_2

Our calculations differ from similar ones for molecular nitrogen in applying Franck–Condon factors obtained by Morse approximation. The Morse potential U is expressed as

$$U(r) = D_e\{1 - \exp[-a(r - r_e)]\}^2, \tag{5}$$

where r_e is the equilibrium value of internuclear distance r, D_e and a are parameters. Eq. (5) is a very good approximation for real potentials in most cases (Kuzmenko et al., 1984). Moreover, the Schroedinger equation with the potential has an exact solution for nuclear wavefunctions:

$$\psi_v(r) = N_v e^{-z/2} z^{\beta/2} L_v^\beta(z), \tag{6}$$
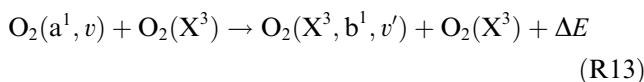
where $z = \exp[-a(r - r_e)]/x_e$, $\beta = 1/x_e - 2v - 1$, x_e is anharmonic constant, L_v^β are Laguerre polynomials.

Spectroscopic constants for $X^3\Sigma_g^-$, $a^1\Delta_g$, $b^1\Sigma_g^+$ states were taken according to Huber and Herzberg (1979) and for $c^1\Sigma_u^-$, $A'^3\Delta_u$, $A^3\Sigma_u^+$ states according to Slanger and Cosby (1988). Franck–Condon factors were calculated for all considered electron transitions.
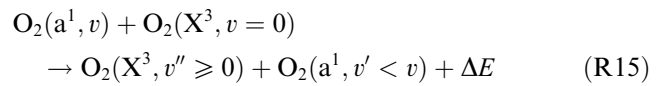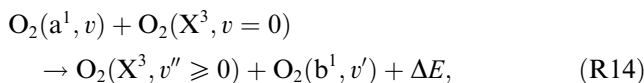
5. Quenching rate coefficients of $a^1\Delta_g$ and $b^1\Sigma_g^+$ states of molecular oxygen in inelastic collisions O_2–O_2

A lot of vibrational levels of $X^3\Sigma_g^-$, $a^1\Delta_g$, $b^1\Sigma_g^+$ states are in good energetic resonance. Moreover, since all three $X^3\Sigma_g^-$, $a^1\Delta_g$, $b^1\Sigma_g^+$ states have same configuration of electron orbitals $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 3\sigma_g^2 1\pi_u^4 1\pi_g^2$, we believe that all exchange potentials are parallel and apply only Eqs. (2) and (4) for the calculation of quenching rate coefficients of the states. Distinct from the calculations for states of N_2 we have no any information about parameter γ. γ was taken equal to 106 cm^{-1} in the calculations for triplet and singlet states on N_2. So similar values were adopted for O_2 and we have made our calculations for states of O_2 at $\gamma = 90$ and 120 cm^{-1}. Parameter k_0 was taken 3 and 6 times smaller for $a^1\Delta_g$ and $b^1\Sigma_g^+$ states, respectively, than for the $B^3\Pi_g$ state of N_2 because of degeneration of these states.
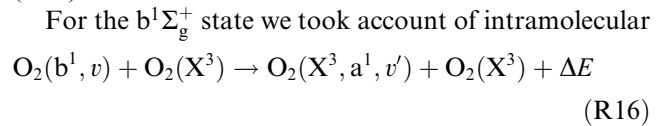
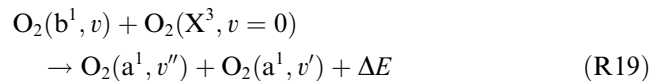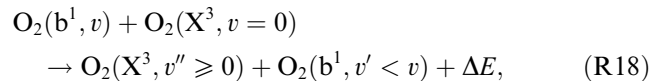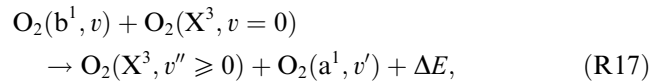For the $a^1\Delta_g$ state we took account of intramolecular

$$O_2(a^1, v) + O_2(X^3) \rightarrow O_2(X^3, b^1, v') + O_2(X^3) + \Delta E \tag{R13}$$

and intermolecular

$$O_2(a^1, v) + O_2(X^3, v = 0)$$
$$\rightarrow O_2(X^3, v'' \geqslant 0) + O_2(b^1, v') + \Delta E, \tag{R14}$$

$$O_2(a^1, v) + O_2(X^3, v = 0)$$
$$\rightarrow O_2(X^3, v'' \geqslant 0) + O_2(a^1, v' < v) + \Delta E \tag{R15}$$

processes. The summation includes all possible v' in the case of intramolecular transfers and all possible v', v'' in the case of intermolecular transfers. Results of the calculation have shown that processes (R15) with $v' = 0$ and $v'' = v$ or $v'' = v - 1$ dominate. Calculated quenching rate coefficients with $k_0 = 3.4 \times 10^{-10}$ cm^3 s^{-1} are presented in Fig. 5. As it is seen from this figure there appears a local dip in the calculated rate coefficients at $v = 7$–8. The presence of the dip could be explained by greatest mismatch $|\Delta E| \sim 700$–800 cm^{-1} in processes (R15) for the vibrational levels.

For the $b^1\Sigma_g^+$ state we took account of intramolecular

$$O_2(b^1, v) + O_2(X^3) \rightarrow O_2(X^3, a^1, v') + O_2(X^3) + \Delta E \tag{R16}$$

and intermolecular

$$O_2(b^1, v) + O_2(X^3, v = 0)$$
$$\rightarrow O_2(X^3, v'' \geqslant 0) + O_2(a^1, v') + \Delta E, \tag{R17}$$

$$O_2(b^1, v) + O_2(X^3, v = 0)$$
$$\rightarrow O_2(X^3, v'' \geqslant 0) + O_2(b^1, v' < v) + \Delta E, \tag{R18}$$

$$O_2(b^1, v) + O_2(X^3, v = 0)$$
$$\rightarrow O_2(a^1, v'') + O_2(a^1, v') + \Delta E \tag{R19}$$

processes. Results of the calculation have shown that processes (R18) with $v' = 0$ and $v'' = v$ or $v'' = v - 1$ dominate for low values of v. But the contribution of processes (R17) with $v' = 0$, 1 and $v'' = v + 2$ or $v'' = v + 3$ increases for higher values of v. Calculated quenching rate coefficients with $k_0 = 1.7 \times 10^{-10}$ cm^3 s^{-1} are compared in Fig. 6 with experimental data of Bloemink et al. (1998), Kalogerakis et al. (2002), Yan-
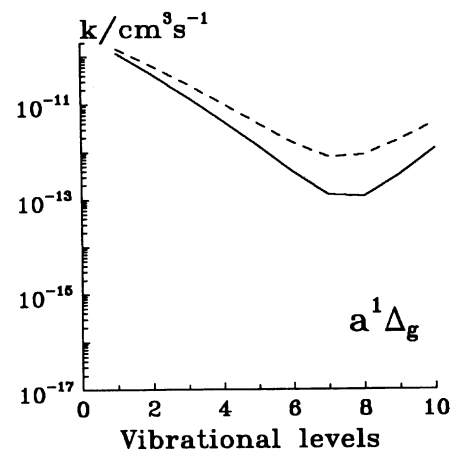

Fig. 5. Calculated quenching rate coefficients for the $a^1\Delta_g$ state of O_2 (solid and dashed lines are for $\gamma = 90$ and 120 cm^{-1}, respectively).
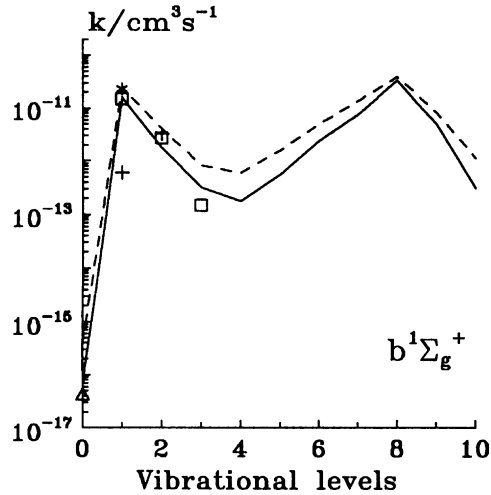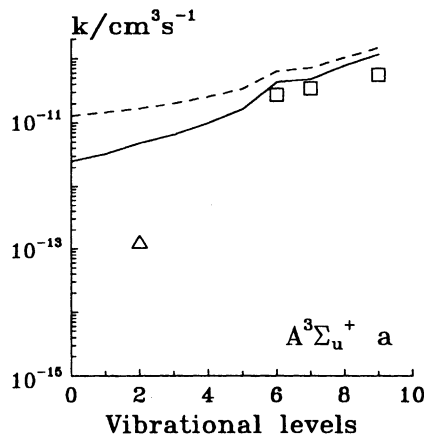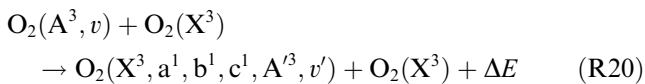
Fig. 6. Calculated quenching rate coefficients for the $b^1\Sigma_g^+$ state of O_2 are compared with experimental data of Bloemink et al. (1998, squares), Kalogerakis et al. (2002, squares), Yankovskii (1991, crosses), Kebabian and Freedman (1997, triangle), Lee and Slanger (1978, star). Solid and dashed lines are for $\gamma = 90$ and 120 cm^{-1}, respectively.
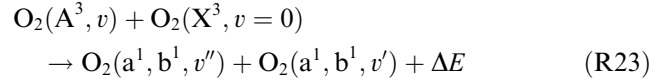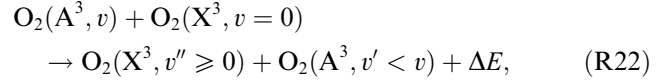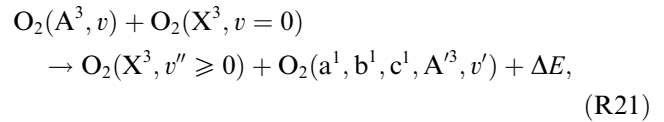
kovskii (1991), Kebabian and Freedman (1997) and Lee and Slanger (1978). As in the case of the $a^1\Delta_g$ state the calculated rate coefficients (Fig. 6) are decreasing from $v = 1$ to $v = 4$ with a local dip at $v = 4$ and an increase thereafter up to $v = 8$. The decrease is in agreement with experimental data and also could be explained by greatest mismatch $|\Delta E|$ in processes (R19) for $v = 4$.

6. Quenching rate coefficients of $A^3\Sigma_u^+$ and $c^1\Sigma_u^-$ states of molecular oxygen in inelastic collisions O_2–O_2
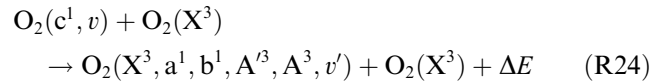
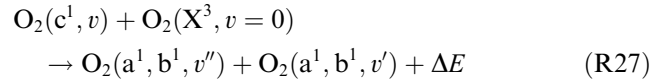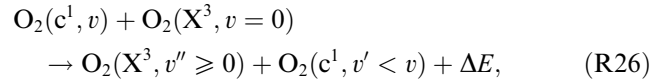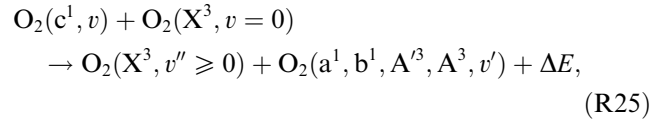For the $A^3\Sigma_u^+$ state we took account of intramolecular

$$O_2(A^3, v) + O_2(X^3)$$
$$\rightarrow O_2(X^3, a^1, b^1, c^1, A'^3, v') + O_2(X^3) + \Delta E \quad \text{(R20)}$$

and intermolecular

$$O_2(A^3, v) + O_2(X^3, v = 0)$$
$$\rightarrow O_2(X^3, v'' \geqslant 0) + O_2(a^1, b^1, c^1, A'^3, v') + \Delta E, \quad \text{(R21)}$$

$$O_2(A^3, v) + O_2(X^3, v = 0)$$
$$\rightarrow O_2(X^3, v'' \geqslant 0) + O_2(A^3, v' < v) + \Delta E, \quad \text{(R22)}$$

$$O_2(A^3, v) + O_2(X^3, v = 0)$$
$$\rightarrow O_2(a^1, b^1, v'') + O_2(a^1, b^1, v') + \Delta E \quad \text{(R23)}$$

processes. For the $c^1\Sigma_u^-$ state we took account of intramolecular

$$O_2(c^1, v) + O_2(X^3)$$
$$\rightarrow O_2(X^3, a^1, b^1, A'^3, A^3, v') + O_2(X^3) + \Delta E \quad \text{(R24)}$$

and intermolecular

$$O_2(c^1, v) + O_2(X^3, v = 0)$$
$$\rightarrow O_2(X^3, v'' \geqslant 0) + O_2(a^1, b^1, A'^3, A^3, v') + \Delta E, \quad \text{(R25)}$$

$$O_2(c^1, v) + O_2(X^3, v = 0)$$
$$\rightarrow O_2(X^3, v'' \geqslant 0) + O_2(c^1, v' < v) + \Delta E, \quad \text{(R26)}$$

$$O_2(c^1, v) + O_2(X^3, v = 0)$$
$$\rightarrow O_2(a^1, b^1, v'') + O_2(a^1, b^1, v') + \Delta E \quad \text{(R27)}$$

processes.

Since $c^1\Sigma_u^-$, $A'^3\Delta_u$, $A^3\Sigma_u^+$ states have the same configuration of electron orbitals $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 3\sigma_g^2 1\pi_u^3 1\pi_g^3$, so transitions to lower $X^3\Sigma_g^-$, $a^1\Delta_g$, $b^1\Sigma_g^+$ states cause the *"gerade"* π-orbital to change into *"ungerade"* one. Therefore we suggest parallel exchange potentials and apply Eqs. (2) and (4) in all calculations for the states.

Fig. 7. Calculated quenching rate coefficients for the $A^3\Sigma_u^+$ state of O_2 in processes (R20) and (R23) (a and b, respectively) are compared with experimental data of Knutsen et al. (1994, squares) and Kenner and Ogryzlo (1983, triangle). Solid and dashed lines are for $\gamma = 90$ and 120 cm^{-1}, respectively.
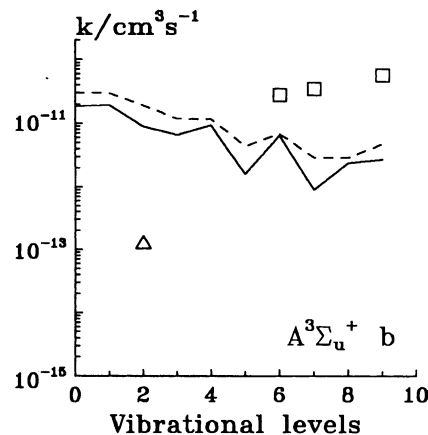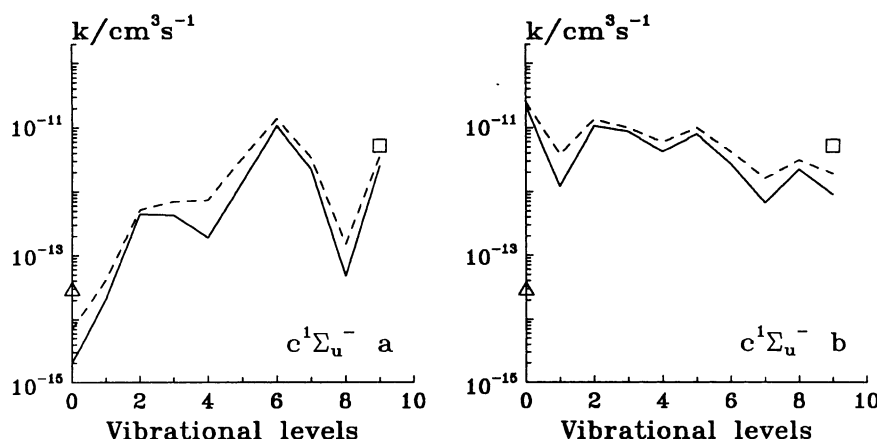
Fig. 8. Calculated quenching rate coefficients for the $c^1\Sigma_u^-$ state of O_2 in processes (R24) and (R27) (a and b, respectively) are compared with experimental data of Copeland et al. (1996, square) and Kenner and Ogryzlo (1983, triangle). Solid and dashed lines are for $\gamma = 90$ and 120 cm^{-1}, respectively.

The calculations of quenching rate coefficients for the $A^3\Sigma_u^+$ state have shown that intermolecular processes (R21) and (R22) can be neglected. Calculated values for processes (R20) and (R23) with $k_0 = 5.1 \times 10^{-10}$ cm^3 s^{-1} are presented in Fig. 7(a) and (b), respectively. Experimental data of Knutsen et al. (1994) and Kenner and Ogryzlo (1983) have been compared with the results of the calculation. Similar results are obtained for the $c^1\Sigma_u^-$ state. Calculated values for Eqs. (R24) and (R27) with $k_0 = 1.7 \times 10^{-10}$ cm^3 s^{-1} are presented in Fig. 8(a) and (b), respectively. Experimental data of Copeland et al. (1996) and Kenner and Ogryzlo (1983) have been compared with our calculation. It is seen from Figs. 7 and 8 that our calculations of quenching rate coefficients correlate with experimental data only for intramolecular processes.

7. Conclusions

1. Analytical expressions obtained by Kirillov (2003) were applied to calculate rate coefficients of intramolecular and intermolecular energy transfer processes between triplet states of molecular nitrogen in molecular inelastic collisions N_2–N_2. Experimental data of Bachmann et al. (1992, 1993) were normalized on the expressions to obtain all necessary parameters for the calculation. Every energy transfer process between triplet states were considered as a sum of possible intramolecular and intermolecular processes. Results of our calculations for cross sections were compared with experimental data of Bachmann et al. (1992, 1993) for 14 $A^3\Sigma_u^+, v' \rightarrow B^3\Pi_g, v$ and for seven $W^3\Delta_u, v' \rightarrow B^3\Pi_g, v$ transitions.
2. Rate coefficients of electronic quenching in molecular collisions N_2–N_2 were calculated for $B^3\Pi_g$ and $a^1\Pi_g$ states of N_2 and compared with experimental data. Good agreement of calculated rate coefficients with experimental data was obtained for the $B^3\Pi_g$ state.
3. Rate coefficients of electronic quenching in molecular collisions O_2–O_2 were calculated for $a^1\Delta_g$ and $b^1\Sigma_g^+$ states of O_2 and were compared with experimental data for the $b^1\Sigma_g^+$ state. Dips found in the results of the calculation and in experimental data are explained by energy mismatch for some vibrational levels of the states. It is pointed that intermolecular energy transfer processes are giving the main contribution to the electronic quenching.
4. Rate coefficients of electronic quenching in molecular collisions O_2–O_2 were calculated for $A^3\Sigma_u^+$ and $c^1\Sigma_u^-$ states of O_2 and compared with experimental data. It was shown that a correlation of the results of the calculation with experimental data could be obtained only when intramolecular energy transfer processes were dominant.

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