

# Calculation of rate coefficients for the interaction of singlet and triplet vibrationally excited oxygen

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**Abstract.** Using the experimental rates of  $O_2(b^1\Sigma_g^+, v = 1-3)$  quenching by oxygen molecules at different temperatures available from the literature, estimates were made of the parameters for analytical formulas which permit calculating the quenching constants for singlet oxygen. The calculated  $O_2(b^1\Sigma_g^+, v = 1-15)$  and  $O_2(a^1\Delta_g, v = 1-20)$  constants of quenching by unexcited oxygen molecules for temperatures  $T = 300$  and  $155$  K are in good agreement with experimental data. The main channels of  $O_2(a^1\Delta_g, v = 0-20)$  and  $O_2(b^1\Sigma_g^+, v = 0-15)$  quenching by vibrationally excited  $O_2(X^3\Sigma_g^-, v = 1-4)$  oxygen molecules were investigated.

**Keywords:** molecular oxygen, vibronic excitation, quenching constants, Rosen–Zener approximation.

## 1. Introduction

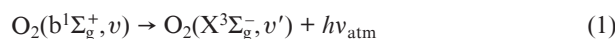
Molecular oxygen in the first and second electronically excited states  $a^1\Delta_g$  and  $b^1\Sigma_g^+$  (singlet oxygen) is an important component in the active medium of an oxygen–iodine laser (OIL). The excitation energy transfer from an oxygen molecule to the ground state of atomic iodine  $I(^2P_{3/2})$  in inelastic collisions provides efficient pumping of the upper laser level  $I(^2P_{1/2})$ , and a spontaneous transition from the upper iodine level to the ground one results in the emission of a photon with a wavelength  $\lambda = 1.315$  nm. The source of singlet oxygen delivered to the active medium of an OIL may be a chemical generator in which chlorine reacts with an alkaline solution of hydrogen peroxide [1], the low-temperature plasma of an RF discharge in an oxygen medium [2, 3], or an optical boiler containing molecular oxygen and the radiation with a wavelength of  $\sim 762$  nm [4].

The emission technique for the investigation of singlet oxygen in the active medium of a chemical OIL proposed in Refs [5–7] enabled determining that about 22% of the total number of the  $O_2(b^1\Sigma_g^+)$  molecules are in the first vibrational level ( $v = 1$ ) and about 10% are in the second one ( $v = 2$ ). Owing to a fast EE energy exchange, the degree of vibrational excitation of the  $O_2(X^3\Sigma_g^-)$ ,  $O_2(a^1\Delta_g)$ , and  $O_2(b^1\Sigma_g^+)$  oxygen molecules is practically the same [5–7]. That is why further investigations in the kinetics of the OIL active medium necessitates knowing the interaction constants for singlet and triplet oxygen in inelastic collisions as well as the quantum yields of

these interactions. Furthermore, the investigations performed in Ref. [8] showed that the temperature growth of the solution in the generator of singlet oxygen leads to changes in gas-dynamic properties of the OIL active medium. The increase in the solution temperature in the generator from  $-20$  to  $-4^\circ\text{C}$  was accompanied by an increase in the temperature of the active medium from 205 to 241 K [8]. This signifies that correct simulations of the chemical composition of the OIL active medium necessitate knowing the temperature dependence of inelastic interaction rate coefficients.

The kinetics of vibrationally excited singlet oxygen is also of interest for the problems of upper atmospheric glow. In experimental investigations of auroral ionospheric emissions [9, 10] it was found that the precipitation of auroral particles into the upper atmosphere is attended with the production of  $O_2(b^1\Sigma_g^+, v = 1-5)$  molecules in the ionosphere. The authors of Ref. [11] proposed a possible mechanism of  $O_2(b^1\Sigma_g^+, v = 1-5)$  production involving the reaction of vibrationally excited oxygen ions  $O_2^+(X^2\Sigma_g^+, v > 0)$  with nitric oxide NO; however, more recent theoretical investigations [12] cast doubt on the efficiency of the proposed  $O_2(b^1\Sigma_g^+, v = 1-5)$  production mechanism. Therefore, the question of  $O_2(b^1\Sigma_g^+, v = 1-5)$  kinetics in the auroral ionosphere is still an open question.

In Ref. [13], the first data were presented about the intensities of the nightglow (at altitudes from 80 to 110 km) in the bands of the atmospheric system of molecular oxygen



with 15 vibrationally excited levels ( $v = 1-15$ ); these data were obtained by spectrometric measurements on the Keck I telescope. It was shown that the  $O_2(b^1\Sigma_g^+, v = 1-15)$  nightglow intensity distribution measured in Ref. [13] is bimodal in character, with two peaks for  $v = 3, 4$  and  $v = 12$  and a sharp minimum for  $v = 8$ . To explain this property of intensity distribution, the authors of Ref. [13] suggested two hypotheses. In the first case they considered different production mechanisms of vibrationally excited  $O_2(b^1\Sigma_g^+, v > 0)$  in reactions like  $H + O_3$  and  $NaO + O(^3P)$ . In the second case, they assumed that this character of the measured distribution is attributable to the properties of  $O_2(b^1\Sigma_g^+, v > 0)$  quenching by oxygen molecules. Recently it was shown [14] that the measurement data of Ref. [13] may be explained by precisely the properties of quenching of electronically excited  $O_2(b^1\Sigma_g^+, v > 0)$  by oxygen molecules. However, like in the case of auroral ionosphere, the question of  $O_2(b^1\Sigma_g^+)$  production mechanisms at altitudes of the nightglow is still an open question.

In the present work we calculated the rate coefficients for the inelastic interaction of electronically excited  $O_2(b^1\Sigma_g^+, v = 0-15)$  and  $O_2(a^1\Delta_g, v = 0-20)$  molecules in collisions with

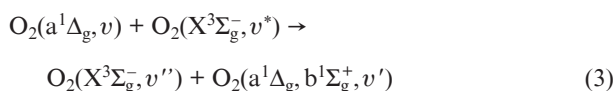
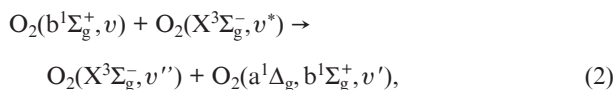
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Received 23 September 2011; revision received 27 March 2012  
Kvantovaya Elektronika 42 (7) 653–658 (2012)  
Translated by E.N. Ragozin

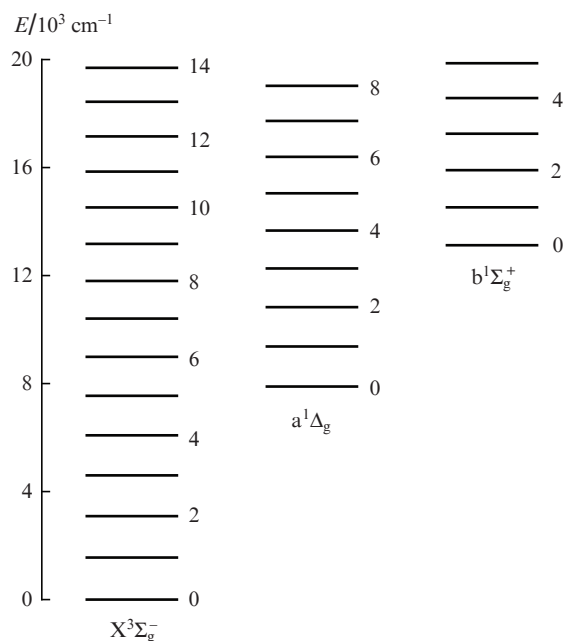
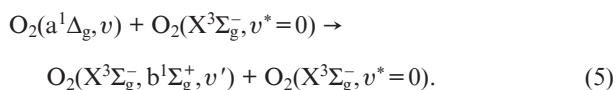
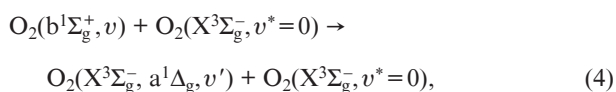
$O_2(X^3\Sigma_g^-, v=0-4)$  molecules. The calculated constants may be used in the simulations of the vibrational distribution of singlet  $O_2(a^1\Delta_g, v \geq 0)$ ,  $O_2(b^1\Sigma_g^+, v \geq 0)$  and triplet  $O_2(X^3\Sigma_g^-, v \geq 0)$  molecular oxygen in the active medium of an OIL.

## 2. Quenching rate coefficients of $b^1\Sigma_g^+$ and $a^1\Delta_g$ singlet states by $O_2(X^3\Sigma_g^-, v=0)$ molecules

Figure 1 shows the diagram of the vibrational energy levels for the three oxygen states  $X^3\Sigma_g^-(v \geq 0)$ ,  $a^1\Delta_g(v \geq 0)$ ,  $b^1\Sigma_g^+(v \geq 0)$  considered in the present work whose energies do not exceed  $20000 \text{ cm}^{-1}$ . The quenching rate coefficients of the electronically excited states  $b^1\Sigma_g^+, v=1-15$  and  $a^1\Delta_g, v=1-20$  of molecular oxygen in collisions with unexcited  $O_2(X^3\Sigma_g^-, v=0)$  molecules were calculated in Refs [14–16]. The calculations were performed using analytical formulas [15, 17] based on the Rosen–Zener approximation [18], and for the indicated intervals of vibrational energy levels of the  $b^1\Sigma_g^+$  and  $a^1\Delta_g$  states we considered molecular processes of electronic excitation transfer



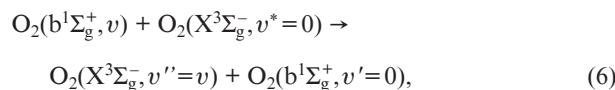
and intramolecular processes



**Figure 1.** Vibrational energy level diagram of the  $X^3\Sigma_g^-$ ,  $a^1\Delta_g$  and  $b^1\Sigma_g^+$  molecular oxygen states.

The states  $c^1\Sigma_u^-$ ,  $A^3\Delta_u$ , and  $A^3\Sigma_u^+$  are not considered here, because the energies of the zero vibrational levels of these states are greater than the energies of  $b^1\Sigma_g^+, v=15$  and  $a^1\Delta_g, v=20$ . The calculations of Refs [14–16] suggest that the prevalent quenching channels for the  $b^1\Sigma_g^+$  state are reactions (2) involving the excitation of both  $a^1\Delta_g$  and  $b^1\Sigma_g^+$  states, while the quenching of  $a^1\Delta_g$  is dominated by reactions (3) with the excitation of only  $a^1\Delta_g$ .

In this work we take advantage of the data of experimental works [19–21], in which the method of resonance-enhanced multiphoton ionisation (REMPI) 2+1 was employed to determine the constants of  $O_2(b^1\Sigma_g^+, v=1, 2, 3)$  quenching by oxygen molecules in the 110–298 K temperature range. In these papers the authors presented by four constant values (for different temperatures) for the levels  $v=1, 2$  and three constant values for  $v=3$ . Proceeding from their analysis of the resultant data the authors of Ref. [21] draw a conclusion that the prevalent channel of  $O_2(b^1\Sigma_g^+, v=1, 2, 3)$  quenching by oxygen molecules is the EE process



which is in perfect agreement with the results of our theoretical calculations [14–16].

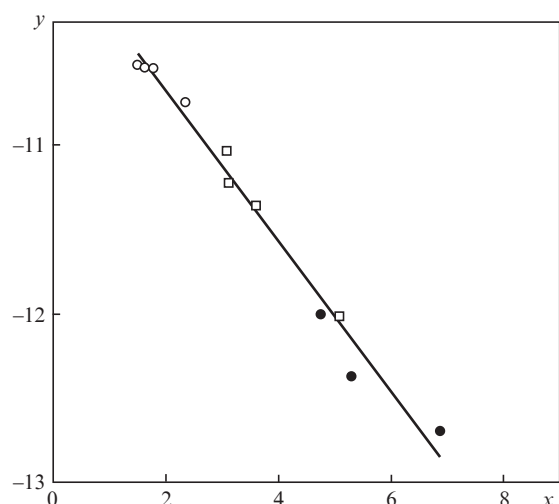
It is noteworthy that the calculations of Refs [14–16] were performed on the basis of analytical approximation parameters from Refs [14, 16] derived from the experimental  $O_2(b^1\Sigma_g^+, v=1-3)$  quenching constants at room temperature. In the present work we take advantage of the data of Refs [19–21] for different temperatures for the purpose of determining the parameters in use.

Following Refs [15, 17], the rate coefficients of EE reactions (6) may be calculated by the formula

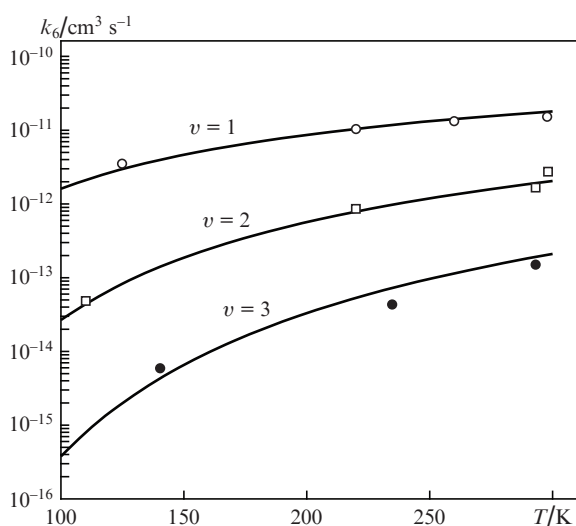
$$k_6(v=i) = k_0 \sqrt{\frac{T}{300}} \exp\left(-\frac{|\Delta E|}{\gamma \sqrt{T/300}} + \frac{\Delta E}{2k_B T}\right) q_{0,0} q_{i,i}, \quad (7)$$

where  $k_0$  and  $\gamma$  are parameters;  $q_{i,i}$  is the Franck–Condon factor for the  $b^1\Sigma_g^+, v=i \leftrightarrow X^3\Sigma_g^-, v=i$  transition;  $T$  is the temperature;  $k_B$  is the Boltzmann constant; and  $\Delta E$  is the energy difference of the final and initial vibronic states. The exponent in formula (7) consists of two terms. The first term is related to the integration of Rosen–Zener inelastic transition probabilities [18] over velocity distribution and the second one is due to a quasiclassical correction [22, 23]. In our calculations we take into account the values of the Franck–Condon factors  $q_{0,0} = 0.930$ ,  $q_{1,1} = 0.792$ ,  $q_{2,2} = 0.651$ , and  $q_{3,3} = 0.512$ , which can be easily calculated using the Morse approximation with the help of spectroscopic constants from [24].

Figure 2 shows the dependence of  $y = \lg([k_6(v, T)/q_{0,0} q_{i,i}] \times \sqrt{300/T} \exp[-\Delta E/2k_B T])$  on  $x = |\Delta E|/(100 \sqrt{T/300})$  calculated from the experimental data of Refs [19–21]. Also plotted in the figure is the straight line  $y = ax + b$  obtained by a least square technique, which provides the best approximation for the  $y(x)$  dependence, where  $a = -0.446$  and  $b = -9.78$ . One can see from Fig. 2 that all eleven points are located sufficiently close to the straight line. Using the values of  $a$  and  $b$  we obtain  $k_0 = 1.66 \times 10^{-10} \text{ cm}^{-3} \text{ s}^{-1}$  and  $\gamma = 97.4$ . The temperature dependences of the constants  $k_6$  calculated for three vibrational levels  $v=1-3$  for the parameters  $k_0$  and  $\gamma$  specified above are plotted in Fig. 3 along with the experimental values given in Refs [19–21].



**Figure 2.** Dependence  $y(x)$  for  $v = 1$  ( $\circ$ ),  $v = 2$  ( $\square$ ),  $v = 3$  ( $\bullet$ ) calculated from the experimental data of Refs [19–21];  $y = \lg([k_6(v, T)/q_{\text{O}_2, \text{O}}] \times (300/T)^{1/2} \exp[-\Delta E/2k_B T])$ ;  $x = |\Delta E|/[100(T/300)^{1/2}]$ ; the solid line stands for  $y = ax + b$ , where  $a = -0.446$  and  $b = -9.78$ .

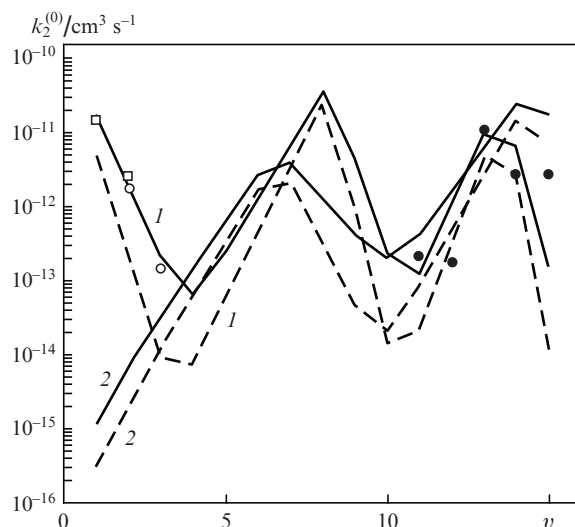


**Figure 3.** Temperature dependences of the constants  $k_6$  for  $v = 1-3$  (solid curves). The points stand for experimental values [19–21] for  $v = 1$  ( $\circ$ ),  $v = 2$  ( $\square$ ), and  $v = 3$  ( $\bullet$ ).

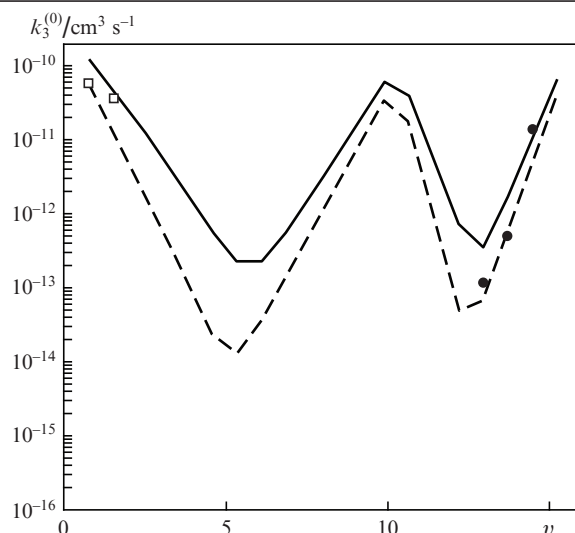
Figure 4 shows the  $\text{O}_2(\text{b}^1\Sigma_g^+, v=1-15)$  quenching constants for temperatures  $T = 300$  and  $155$  K calculated by the formulas of Refs [15, 17] for reactions (2) and  $v^* = 0$ . In this calculation, in the case of  $\text{a}^1\Delta_g$  production the parameter  $k_0$  was taken equal to  $3.32 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ , because the statistical weight of the  $\text{a}^1\Delta_g$  state is two times the statistical weight of the  $\text{b}^1\Sigma_g^+$  state. Figure 4 also shows the experimental estimates of  $k_2^{(0)}$  for room temperature taken from Refs [19, 21] and for  $T = 155$  K borrowed from Refs [25, 26].

As is evident from Fig. 4, the results of calculations agree reasonably well with experimental data. For small values  $v = 1, 2$ , the quenching of  $\text{O}_2(\text{b}^1\Sigma_g^+, v)$  molecules is dominated by the intermolecular reaction (2) with the production of the  $\text{b}^1\Sigma_g^+$  state; with increasing  $v$ , the contribution of reaction (2) with the formation of the  $\text{a}^1\Delta_g$  state is increased.

Similar calculations were made for  $\text{O}_2(\text{a}^1\Delta_g, v=1-20)$  quenching constants. In the calculation it was assumed that



**Figure 4.** Quenching constants  $k_2^{(0)}$  for  $\text{O}_2(\text{b}^1\Sigma_g^+, v = 1-15)$  molecules calculated for temperatures  $T = 300$  and  $155$  K (solid and dashed lines, respectively) for reactions (2) with the production of the states  $\text{b}^1\Sigma_g^+$  (1) and  $\text{a}^1\Delta_g$  (2), as well as experimental values of  $k_2^{(0)}$  taken from Refs [19] ( $\square$ ), [21] ( $\circ$ ), and [25, 26] ( $\bullet$ ).



**Figure 5.** Quenching constants  $k_3^{(0)}$  for  $\text{O}_2(\text{a}^1\Delta_g, v = 1-20)$  molecules calculated for temperatures  $T = 300$  and  $155$  K (solid and dashed lines, respectively) for reactions (3), as well as the experimental  $k_3^{(0)}$  values taken from Ref. [27] ( $\square$ ) and Refs [25, 26] ( $\bullet$ ) (see the text).

$k_0 = 3.32 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$  and  $\gamma = 97.4$ . In Fig. 5, the constants calculated for temperatures  $T = 300$  and  $155$  K for reactions (3) and  $v^* = 0$  are compared with the experimental estimates of Ref. [27] for  $v = 1, 2$  at room temperature and with those of Refs [25, 26] for  $v = 17-19$  at a temperature  $T = 155$  K. Observed in both intervals of vibrational quantum numbers is a correlation between the calculated and experimental values: a decrease in the absolute values of  $k_3^{(0)}$  with increasing  $v$  for low vibrational quantum numbers and an increase in  $k_3^{(0)}$  with  $v$  for  $v = 17-19$ .

### 3. Rate coefficients for $\text{a}^1\Delta_g$ and $\text{b}^1\Sigma_g^+$ state quenching by $\text{O}_2(\text{X}^3\Sigma_g^-, v = 1-4)$ molecules

As shown by the calculations of the constants of quenching by  $\text{O}_2(\text{X}^3\Sigma_g^-, v^* = 0)$  molecules, for the considered intervals of

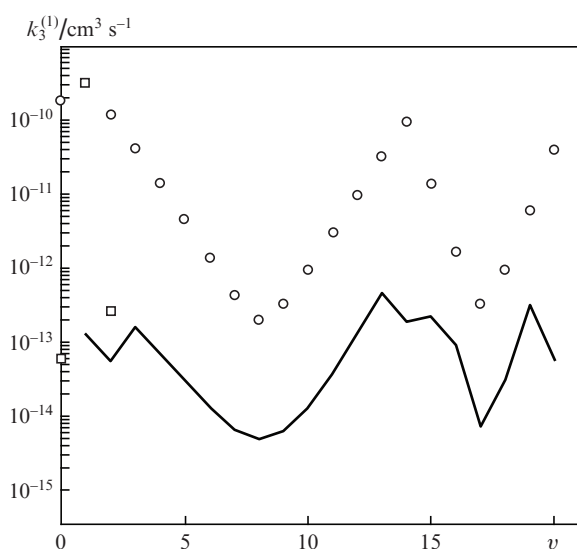
vibrational levels of the  $a^1\Delta_g$  and  $b^1\Sigma_g^+$  states the main quenching channel is the intermolecular electronic excitation transfer with the production of  $O_2(a^1\Delta_g, v'=0)$  and  $O_2(b^1\Sigma_g^+, v'=0)$ . This is due to the large values of Franck–Condon factors for the transitions  $X^3\Sigma_g^-, v^*=0 \rightarrow a^1\Delta_g, v'=0$  and  $X^3\Sigma_g^-, v^*=0 \rightarrow b^1\Sigma_g^+, v'=0$  as well as to their sharp decrease with increasing  $v'$ .

In the collision of singlet oxygen molecules with vibrationally excited  $O_2(X^3\Sigma_g^-, v^* > 0)$  molecules, the  $X^3\Sigma_g^-, v^* > 0 \rightarrow a^1\Delta_g, v'=v^*$  and  $X^3\Sigma_g^-, v^* > 0 \rightarrow b^1\Sigma_g^+, v'=v^*$  transitions may turn out to be most efficient, because the values of the elements of the Franck–Condon factor matrix for these electron transitions are maximal on the diagonal. In this connection we calculated the quenching rate constants for reactions (2) and (3) with the initially vibrationally excited  $O_2(X^3\Sigma_g^-, v^* = 1-4)$

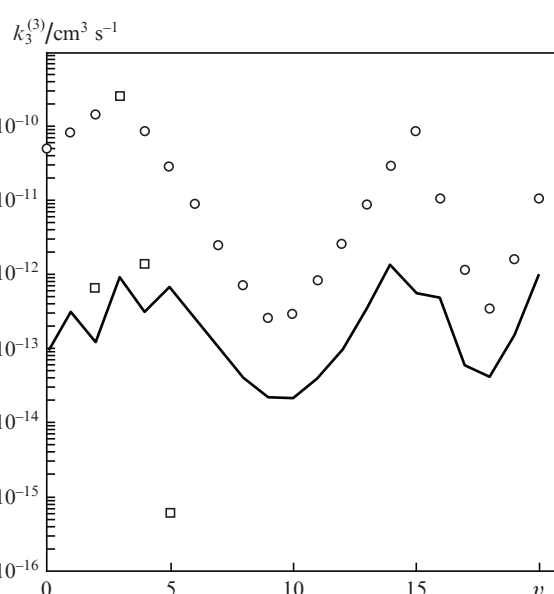
molecule and extracted the production rates of singlet oxygen with  $v'=v^*$ .

Figures 6–9 show the calculated rate coefficients for the quenching of singlet oxygen  $O_2(a^1\Delta_g, v=0-20)$  in collisions with  $O_2(X^3\Sigma_g^-, v^*=1-4)$  in the intermolecular reactions (3) at a temperature  $T = 300$  K. The contribution of reactions with  $v'=v^*$  and the total contribution of reactions with  $v' \neq v^*$  to the quenching are separated out in these figures. Furthermore, also given there are the contributions of reactions with  $v'=v$ , whose rates can be measured only in experiments with isotopes.

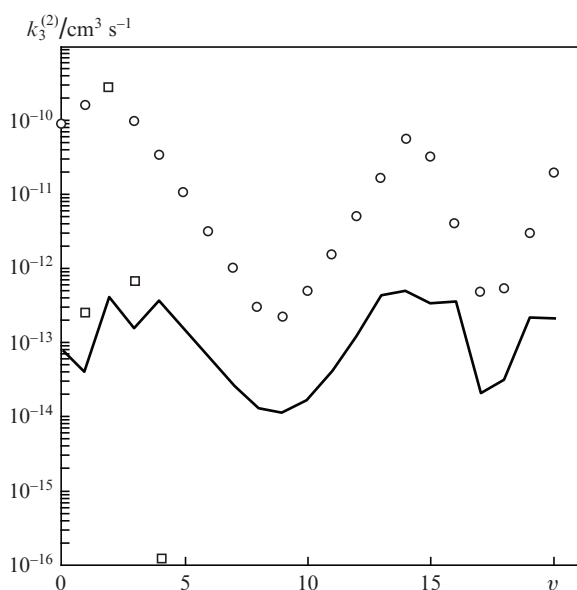
As is evident from Figs 6–9, in the four cases considered the main contribution to the quenching of singlet oxygen in the  $v = 0-20$  interval is caused by the EE exchange



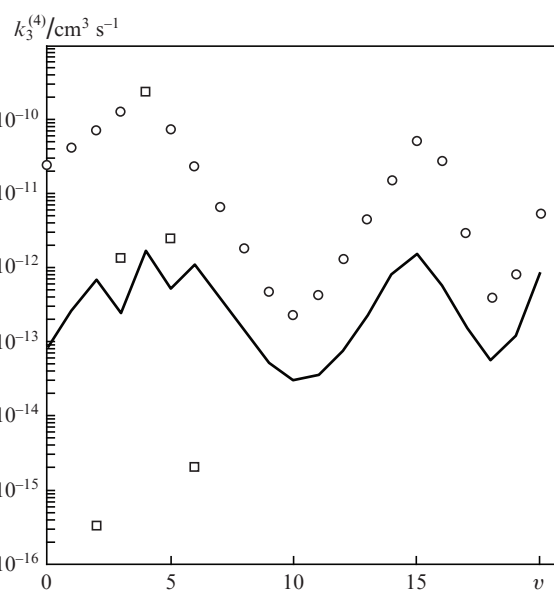
**Figure 6.** Calculated quenching rate constants  $k_3^{(1)}$  of the  $O_2(a^1\Delta_g, v=0-20)$  molecules in the EE exchange (3) in collisions with  $O_2(X^3\Sigma_g^-, v^*=1)$ :  $v'=v^*$  (○),  $v'=v$  (□),  $v' \neq v^*$  (solid curve).



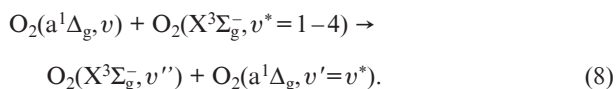
**Figure 8.** The same as in Fig. 6 for  $O_2(X^3\Sigma_g^-, v^*=3)$ .



**Figure 7.** The same as in Fig. 6 for  $O_2(X^3\Sigma_g^-, v^*=2)$ .



**Figure 9.** The same as in Fig. 6 for  $O_2(X^3\Sigma_g^-, v^*=4)$ .

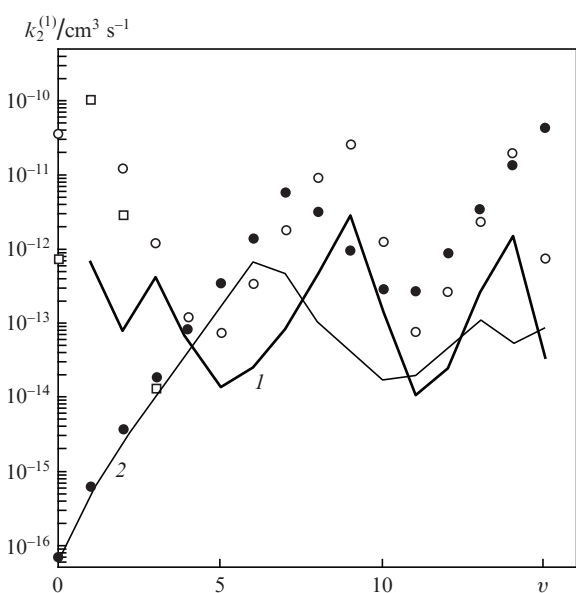
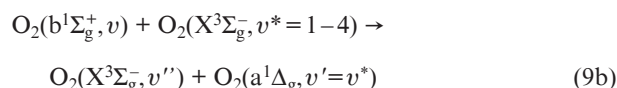
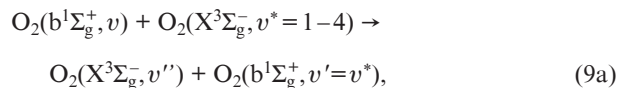


In this case, up to the first minimal value of the constants in Figs 6–9, which corresponds to  $v = 8-10$ , the vibrational number  $v'' = v$ ; and then  $v''$  gradually decreases to reach, for  $v = 20$ , values of 17 and 18 for  $v^* = 1$  and 4, respectively.

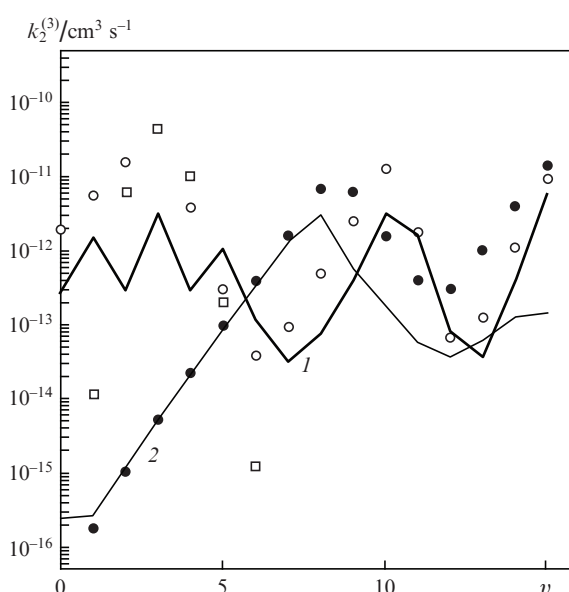
The results of similar calculation of the constants for the collisions of  $\text{O}_2(b^1\Sigma_g^+, v=0-15)$  with  $\text{O}_2(X^3\Sigma_g^-, v^* = 1-4)$  are presented in Figs 10–13. The calculations were made for the intermolecular reactions (2) in the case of  $b^1\Sigma_g^+$  state as well of the  $a^1\Delta_g$  state production. Like in Figs 6–9, in Figs 10–13 the

contributions to the quenching made by reactions with  $v' = v^*$ , and  $v' \neq v^*$  are also separated out, and given are the contributions of reactions (2) with the production of the state  $b^1\Sigma_g^+$  and  $v' = v$ , which may be measured only in experiments with isotopes.

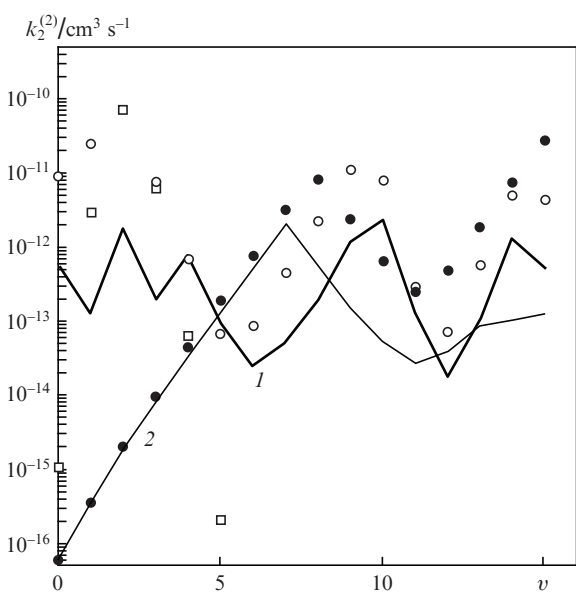
As follows from Figs 10–13, the EE exchange reactions



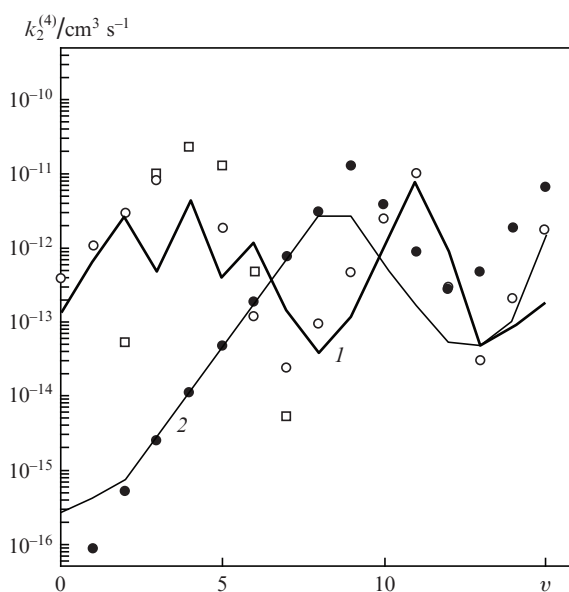
**Figure 10.** Calculated quenching rate constants  $k_2^{(1)}$  of the  $\text{O}_2(b^1\Sigma_g^+, v=0-15)$  molecules in the EE exchange (2) in collisions with  $\text{O}_2(X^3\Sigma_g^-, v^* = 1)$  with the production of the  $b^1\Sigma_g^+$  state [ $v' = v^*$  (○),  $v' \neq v^*$  (1),  $v' = v$  (□)] and the  $a^1\Delta_g$  state [ $v' = v^*$  (●),  $v' \neq v^*$  (2)].



**Figure 12.** The same as in Fig. 10 for  $\text{O}_2(X^3\Sigma_g^-, v^* = 3)$ .



**Figure 11.** The same as in Fig. 10 for  $\text{O}_2(X^3\Sigma_g^-, v^* = 2)$ .



**Figure 13.** The same as in Fig. 10 for  $\text{O}_2(X^3\Sigma_g^-, v^* = 4)$ .

are dominant not for all vibrational levels. For instance, for  $v = 0-4$  the contribution of reactions with  $v' = v^*$  becomes comparable to that of reactions with  $v' \neq v^*$  with increase in the vibration excitation of  $O_2(X^3\Sigma_g^-, v^*)$ .

#### 4. Conclusions

The main results of the present work reduce to the following:

(i) Using the experimental values of  $O_2(b^1\Sigma_g^+, v=1-3)$  quenching rate coefficients for the  $T = 110-298$  K temperature interval taken from Refs [19–21], estimates were made of the parameters in formula (7), which was proposed in Refs [15, 17] for the calculation of the quenching constants and is based on the Rosen–Zener approximation [18]. The constants calculated for  $v = 1-3$  are in good agreement with experimental data of Refs [19, 21] in the specified temperature interval.

(ii) The calculated  $O_2(b^1\Sigma_g^+, v=1-15)$  and  $O_2(a^1\Delta_g, v=1-20)$  constants for the quenching by unexcited oxygen molecules at temperatures  $T = 300$  and  $155$  K exhibit good agreement with the experimental data available in the literature [19, 21, 25–27].

(iii) The  $O_2(a^1\Delta_g, v=0-20)$  and  $O_2(b^1\Sigma_g^+, v=0-15)$  constants of quenching by vibrationally excited  $O_2(X^3\Sigma_g^-, v^* = 1-4)$  oxygen molecules were calculated for a temperature  $T = 300$  K. The calculations suggest that the main contribution to the quenching of  $O_2(a^1\Delta_g, v)$  throughout the  $v = 0-20$  interval is made by the intermolecular EE exchange (8) with the production of  $O_2(a^1\Delta_g, v' = v^*)$ . In the case of  $O_2(b^1\Sigma_g^+, v)$  quenching, also observed is a high efficiency of  $O_2(b^1\Sigma_g^+, v' = v^*)$  and  $O_2(a^1\Delta_g, v' = v^*)$  production in reactions (9a) and (9b); however, with increase in the vibrational excitation of  $O_2(X^3\Sigma_g^-, v^*)$  this efficiency becomes lower.

The rate coefficients for the quenching of  $O_2(a^1\Delta_g, v = 0-20)$  and  $O_2(b^1\Sigma_g^+, v = 0-15)$  singlet oxygen by  $O_2(X^3\Sigma_g^-, v^* = 0-4)$  molecules may be used in the investigation of the kinetics of electronically excited molecular oxygen and the calculation of unexcited  $O_2(X^3\Sigma_g^-)$  and singlet  $O_2(a^1\Delta_g)$  and  $O_2(b^1\Sigma_g^+)$  molecular oxygen distribution over vibrational levels in the active medium of an OIL under different temperature modes.

**Acknowledgements.** This work was supported by the Physical Sciences Division Programme ‘Plasma Processes in the Solar System’ and the Programmes of the Presidium of the Russian Academy of Sciences No. 4, 22.

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