Kinetics of electronically excited O_2 molecules in the mixture of CO_2, CO, N_2, O_2 gases

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Introduction (1)

CO_2, CO, N_2, O_2 gases are the main components in the atmospheres of terrestrial planets. Electronically excited molecules play very important role in chemical kinetics of a mixture of atmospheric gases. It has been proposed by Toumi [1993], Siskind et al. [1993], Prasad [1997] that the interaction of $O_2(b^1\Sigma_g^+)$ with H_2 and N_2O molecules may significantly influence the chemistry of the stratosphere and upper troposphere of the Earth as a source of odd-hydrogen (HO_x) or odd-nitrogen (NO_x).

$O_2(b^1\Sigma_g^+)$ molecules are effectively produced in the atmosphere of the Earth at altitudes between 80 and 110 km. Three-body collisions

$$O + O + M \rightarrow O_2^* + M \qquad (1)$$

are main production mechanism of electronically excited molecular oxygen at the altitudes of the nightglow in the atmosphere of the Earth [Slanger and Copeland, 2003].

Introduction (2)

Spontaneous radiative transitions from the $b^1\Sigma_g^+$ state to the ground $X^3\Sigma_g^-$ state lead to emissions of Atmospheric bands in the nightglow of the atmosphere.

$$O_2(b^1\Sigma_g^+,v) \rightarrow O_2(X^3\Sigma_g^-,v') + h\nu_{Atm}. \quad (2)$$

A study of excitation, quenching, and energy transfer processes in the oxygen nightglow on Venus and Mars by Krasnopolsky [2011] has considered altitude profiles of $[O_2(b^1\Sigma_g^+)]$ in atmospheres of the planets. The study was based on the observed nightglow intensities and vertical profiles, measured reaction rate coefficients, and photochemical models of the nighttime atmospheres of the Venus and Mars. Krasnopolsky [2011] has analysed mainly the kinetics of $O_2(b_1\Sigma_g^+,v=0)$, but detailed study of $O_2(b^1\Sigma_g^+,v\geq 0)$ needs a set of the quenching constants for collisions with molecules of main gases in atmospheres of the planets.

The quenching rate coefficients (1)

We apply the Rosen-Zener approximation to calculate the removal rates of O_2^* in inelastic collisions with CO_2, CO, N_2, O_2 molecules [Kirillov, 2004a,b]. The quenching rates of the $b^1\Sigma_g^+, v$=1-15 state by O_2 molecules are calculated with the consideration of intermolecular (EE-processes) transfers of electronic excitation [Kirillov, 2012]

$$O_2(b^1\Sigma_g^+, v) + O_2(X^3\Sigma_g^-, v=0) \rightarrow O_2(X^3\Sigma_g^-, v') + O_2(a^1\Delta_g, b^1\Sigma_g^+, v''). \quad (3)$$

Also we consider EV-processes of removal in the collisions with N_2, CO, CO_2, O_2 molecules

$$O_2(b^1\Sigma_g^+, v) + N_2(X^1\Sigma_g^+, v=0) \rightarrow O_2(a^1\Delta_g, v') + N_2(X^1\Sigma_g^+, v=1), \quad (4)$$

$$O_2(b^1\Sigma_g^+, v) + CO(X^1\Sigma^+, v=0) \rightarrow O2(a^1\Delta_g, v') + CO(X^1\Sigma^+, v=1), \quad (5)$$

$$O_2(b^1\Sigma_g^+, v) + CO_2(X^1\Sigma_g^+, 0,0,0) \rightarrow O_2(a^1\Delta_g, v') + CO_2(X^1\Sigma_g^+, 1,0,1), \quad (6)$$

$$O_2(b^1\Sigma_g^+, v) + O_2(X^3\Sigma_g^-, v=0) \rightarrow O_2(a^1\Delta_g, v') + O_2(X^3\Sigma g^-, v=1). \quad (7)$$

Here there are the transitions of electronically excited O2* molecules in another excited state with vibrational excitation of the ground state of target molecules.

The quenching rate coefficients (2)

Moreover, we take into account the processes of VV-processes of energy exchange in the collisions with carbon dioxide molecules

$$O_2(b^1\Sigma_g^+,v) + CO_2(X^1\Sigma_g^+,0,0,0) \rightarrow O_2(b^1\Sigma_g^+,v\text{-}1) + CO_2(X^1\Sigma_g^+,1,0,0). \quad (8)$$

The process (8) means that the $O_2(b^1\Sigma_g^+,v)$ molecule losses one vibrational quantum of the $b^1\Sigma_g^+$ state and the energy transforms in vibrational quantum of symmetric stretch mode of CO_2 molecule.

The calculated quenching rate coefficients for the $b^1\Sigma_g^+,v$=1-15 state in the collisions (3-8) with O_2, N_2, CO, CO_2 molecules are presented in Fig.1. The calculations have shown that the quenching is very efficient in the collisions with O_2 molecules for high vibrational levels of this singlet state.

More effective quenching by carbon dioxide molecules is seen for lower vibrational states of the $b^1\Sigma_g^+$ state. The calculated quenching rate coefficients of electronically excited O_2 molecules are used in the simulations of vibrational populations of O_2 electronic states in the mixture of gases.

The quenching rate coefficients (3)

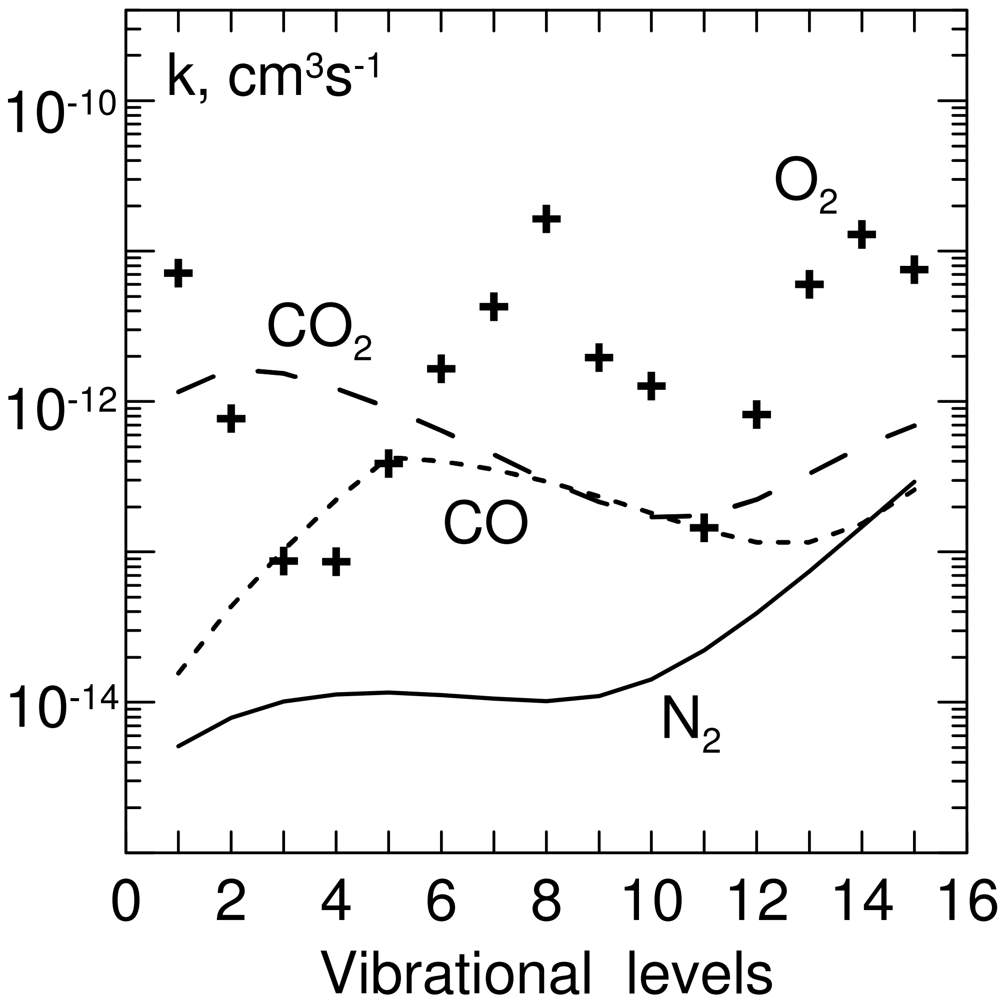

Fig.1. The calculated quenching rate coefficients for the $b^1\Sigma_g^+, v$=1-15 state in the collisions with O_2, N_2, CO, CO_2 molecules (crosses; solid, short-dashed, long-dashed lines, respectively).

Vibrational populations of $O_2(b^1\Sigma_g^+)$ in the mixture (1)

It is suggested that three-body collisions (1) are the production mechanism of initially excited O_2. Vibrational populations of singlet oxygen are calculated at mixture pressures of 10-1-100 Pa. The removal rates are taken according to the data presented in Fig.1.

The calculated vibrational populations of singlet $b^1\Sigma_g^+, v$=1-15 state of molecular oxygen in the mixture of O_2^* with the gases N2, CO, CO_2 at pressures of 10-1-100 Pa are shown in Fig.2. Also the experimental data of populations estimated from spectrometric observations from Keck-I telescope [Slanger et al., 2000] are presented in Fig.2. Slanger et al. [2000] have observed the intenities of Atmospheric bands (2) emitted from fifteen vibrational levels of the singlet state in the nightglow of the Earth.

It is seen from this figure that the behaviour of the populations in the cases of N_2-O_2 and CO-O_2 mixtures are similar. The principal influence of carbon dioxide molecules is seen in the case of CO_2-O_2 mixture. This mixture is an analogue of Venus and Mars atmosphere at the altitudes of the nightglow. It is seen from Fig.2 that there is an increase of relative populations of highest vibrational levels in comparison with ones of lowest levels. The difference in the behaviour of the populations for the mixtures can be explained by the removal rates presented in Fig.1.

Vibrational populations of $O_2(b^1\Sigma_g^+)$ in the mixture (2)

The results of the calculations can be applied in the study of electronic kinetics of O_2^* at the altitudes of nightglows in the atmospheres of terrestrial planets and in active mediums of laboratory discharges and lasers.

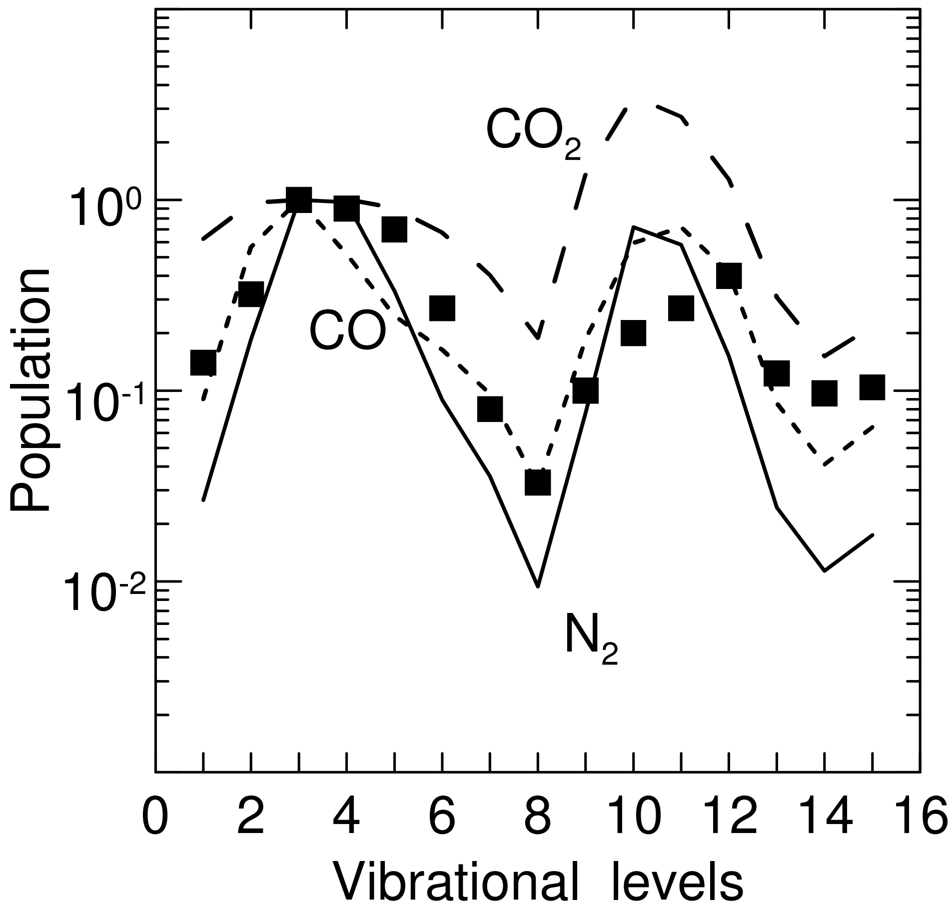

Fig.2. The calculated vibrational populations of singlet $b^1\Sigma_g^+, v$=1-15 state of molecular oxygen in the mixture of O_2^* with the gases N2 (solid line), CO (short-dashed line), CO_2 (long-dashed line); experimental data by Slanger et al . [2000] – squares.

Conclusions

The main results of this presentation are as follows:

1. Applying the Rosen-Zener approximation we have calculated the removal rates of $O_2(b^1\Sigma_g+,v)$ in inelastic collisions with CO_2, CO, N_2, O_2 molecules. The calculation has taken into account EE (3), EV (4-7) and VV (8) electron energy transfer processes.
2. Using the calculated removal rate constants we have simulated vibrational populations of singlet $b^1\Sigma_g^+,v$=1-15 state of molecular oxygen in the mixture of O_2^* with the gases N_2, CO, CO_2 at pressures of 10-1-100 Pa. The results of the calculation show the principal dependence of the populations on the kind of admixture gas. The dependence can be explained by peculiarities of removal rates of $O_2(b^1\Sigma_g^+)$ in inelastic collisions with another molecules.

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Thank you very much for your attention