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Elastic and inelastic scattering of atomic oxygen on molecular oxygen for relative kinetic energies of 10−6000 cm^{-1}

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The elastic and inelastic scattering cross sections of the O(^3P_g) + O$_2$($^3\Sigma_g^-$) system for the first vibrational levels of the O$_2$ molecule were calculated quantum-mechanically on the ground O$_3$($^1A'$), surface obtained using the multi-reference configurational interaction method (MRCI/AVQZ-F12). The obtained scattering cross sections can be used for excitation and relaxation rates calculations of O$_2$ molecule ro-vibrational levels by atomic oxygen, which are necessary for modeling low-temperature plasma containing oxygen, for example, in gas discharge lasers and etching chambers.

Keywords: elastic and inelastic scattering, atom-diatom collision, oxygen, potential energy surface.

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Oxygen-containing non-equilibrium plasma has been the subject of many years of experimental and theoretical research because of its wide applications in various fields, including diverse technological applications [1] such as etching of various materials and resist stripping in microelectronics [2,3], gas-discharge lasers [4] and plasma-stimulated combustion [5]. The growing interest in discharges in oxygen leads to a constant demand for further experimental and theoretical studies of such discharges in order to improve the understanding of the complex plasma-chemical processes occurring in them.

Thus, recent experimental data on the measurement of the vibration distribution function in the discharge in pure low-pressure oxygen [6] have shown that, unlike other molecules, the vibration distribution function in oxygen is determined by the excitation by electron impact of vibrational levels (υ) and vibrational relaxation O$_2$(υ) on O atoms, and the processes of $\upsilon-\upsilon$-exchange and relaxation of vibrations on O_2 are insignificant. In [7] the theoretical calculations of the cross sections of O$_2$ excitation by electron impact up to $\upsilon = 41$ are presented. The existing approaches to the determination of the relaxation constants of vibrational excitation O$_2$(υ) on O atoms still need to be further analyzed. Although calculations of vibrational-rotational cross sections of the O + O$_2$ system on the basis of quasiclassical methods, which work well in the high energy region, have already been carried out [8], only the rate constants of excitation and relaxation can be found in the publications, and there are no sets of excitation and relaxation cross sections (even quasi-classical ones).

The purpose of the present work — to calculate for the first time the quantum mechanical elastic and inelastic scattering cross sections of the system O(^3P_g) + O$_2$($^3\Sigma_g^-$), in which both the oxygen atom and molecule are in the ground state. To describe the inelastic scattering of an atom on a two-atomic molecule, there are many quantum mechanical methods and approximations [9], among which we have chosen the hybrid method (VCC-IOS) [10], based on the use of a strong coupling method to describe vibrations and an analytical approach to describe rotations, primarily because of its cost-effectiveness.

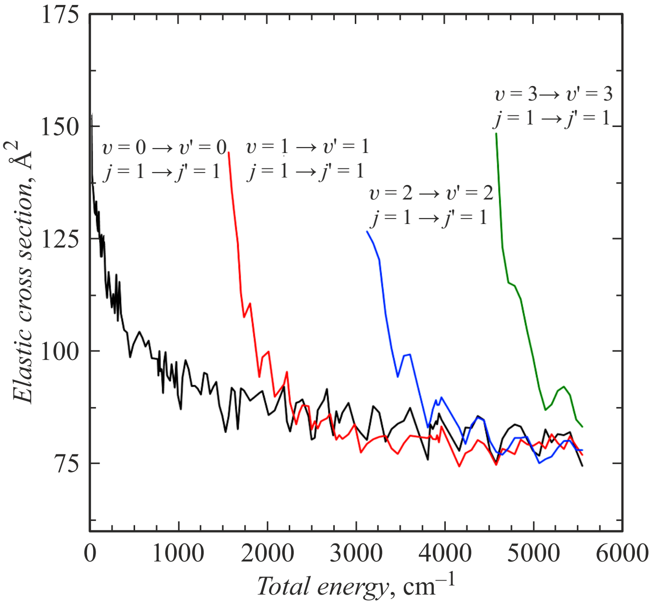

Figure 1. Elastic scattering cross sections for the O+ system O$_2$ as a function of total energy for different states of the oxygen molecule $\upsilon = 0-3$ and $j = j' = 1$.

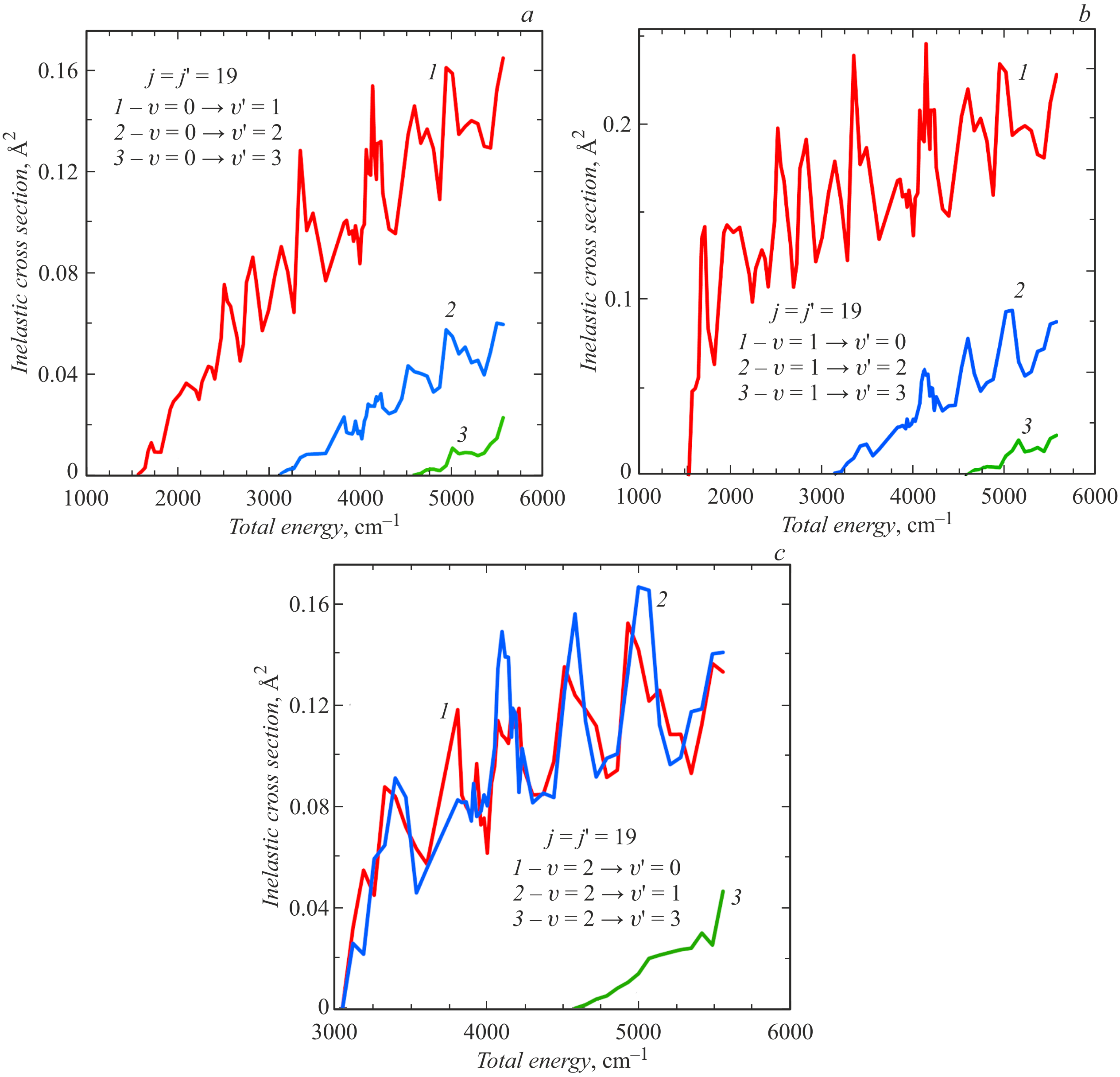

Figure 2. Oscillatory-rotational scattering cross sections of an O atom on an O_2 molecule as a function of total collision energy for rotational quantum number $j = 19$ and vibrational transitions $v = 0 \to v' = 1$, $v = 0 \to v' = 2$, $v = 0 \to v' = 3$ (*a*), $v = 1 \to v' = 0$, $v = 1 \to v' = 2$, $v = 1 \to v' = 3$ (*b*) and $v = 2 \to v' = 0$, $v = 2 \to v' = 1$, $v = 2 \to v' = 3$ (*c*).

To solve our problem, we need to choose a three-dimensional potential surface $V(R, r, \theta)$, correct in the region of interatomic distances O_2 $r = 1-1.7$ Å, for a large number of Jacobi angles and in a wide range of distances (1–25 Å) along the scattering coordinate R. In the present work, the most accurate [11] ground state surface of ozone $O_3(^1A')$, calculated using the multi-configuration interaction method MRCI/AVQZ-F12 [12] and successfully tested on the calculations of the reactive scattering cross sections of the investigated system, is used. We calculated the inelastic scattering cross sections in Jacobi coordinates using the MOLSCAT [13] programme, in which the hybrid VCC-IOS method is implemented as an option.

The program required the calculation of the matrix elements of the potential $V_{v\to v'}(R, \theta)$ between the vibrational levels of the molecule O_2 v and v' for fixed values of the Jacobi scattering angle and the full set of values of the scattering coordinate R of the atom O relative to the center of mass of the molecule O_2:

$$V_{v\to v'}(R, \theta) = \int_0^\infty \psi_v(r) V(R, r, \theta) \psi_{v'}(r) dr, \tag{1}$$

where ψ_v and $\psi_{v'}$ — the wave functions of the vibrational states O_2 v and v'. The matrix elements of (1) were calculated using the modified discrete variable method

(DVR) [14,15], in which $M = 14$ of the calculated exact vibrational eigen-functions $\psi_v(r)$ of the ground state of the molecule O $_2$ were used as basis functions:

$$V_{v\to v'}(R,\theta) = \sum_{i=1}^{M} C_{v,i} V(R, r_i, \theta) C_{v',i}. \tag{2}$$

Here, the DVR points r_i are eigenvalues and $C_{v,j}$ — eigenvectors of the symmetric (14×14) matrix

$$[r]_{v\to v'} = \int_0^\infty \psi_v(r) r \psi_{v'}(r) dr. \tag{3}$$

.The matrix potential element values vv' were calculated using formula (2) for 14 vibrational levels, 256 Jacobi angles and 200 scattering coordinate points, then analytical approximations for 105 two-dimensional surfaces were obtained, which were further used to jointly solve the 14 Schrödinger equations. Unfortunately, the three-dimensional ozone surface used could not be applied to energies $O + O_2$ collisions higher than the energy of the 14 vibrational level of the O_2 molecule.

The use of the MOLSCAT program leads to the calculation of the coefficients Q_L, which are the result of decomposition by L Legendre polynomials of the angular dependence of the S-scattering matrix. The resulting Q_Ls are used to calculate vibrational-rotational inelastic scattering cross sections [16]:

$$\sigma_{v,j\to v',j'}(E) = (2j'+1) \sum_{L=|j-j'|}^{j+j'} \begin{pmatrix} j & j' & L \\ 0 & 0 & 0 \end{pmatrix} Q_L^{v\to v'}(E), \tag{4}$$

where j, j' — the initial and final rotational quantum numbers, and the expression in brackets — $3j$ is a symbol.

In the absence of published sets of cross sections for the system under study, it is first useful to analyze the behavior of specifically elastic scattering cross sections obtained from the diagonal elements of the S-matrix at $v = v' = 0-3$. They should have characteristic features of atom-atom elastic scattering cross sections, such as Glory maxima, whose number is equal to the number of bound states of the potential under study, and shape resonances observed for interatomic potentials with an attraction region [17]. Fig. 1 shows our calculated elastic scattering cross sections for the system $O + O_2$ as a function of total energy for the oxygen molecule with quantum numbers $v = 0-3$ and $j = j' = 1$. Both the Glori wave-like structure at all four cross sections and the numerous shape resonances in the low energy region for the $v = v' = 0$ case are clearly visible. The resolution of these resonances is of academic interest only, so in the following we discuss only the vibrational-rotational cross sections of inelastic scattering. Note that, since we consider a system of ^{16}O atoms, here and further states only with odd initial and finite rotational quantum numbers are considered.

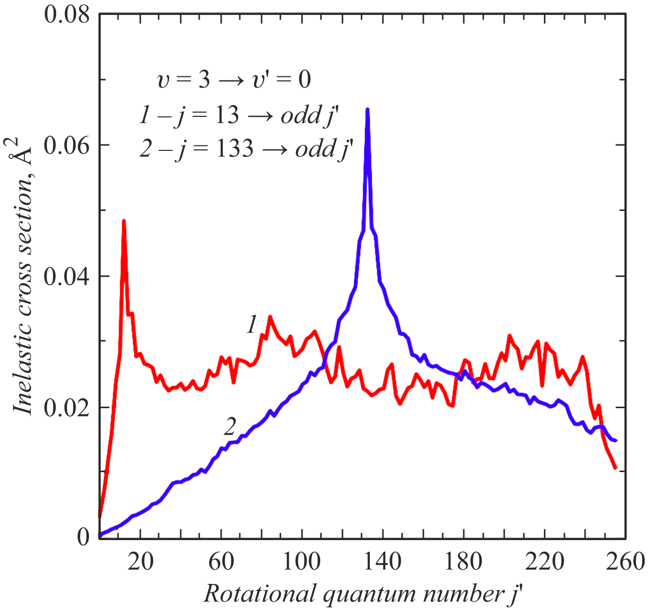

Figure 3. Excitation cross sections of rotational transitions of molecule O_2 in collisions with atom O for energy 4935 cm^{-1} and vibrational transition $v = 3 \to v' = 0$ from rotational levels $j = 13$ and 133 to odd levels j'.

Fig. 2, $a-c$ demonstrates the energy dependence of the calculated vibrational-rotational cross sections for different vibrational transitions and fixed initial and final rotational quantum numbers $j = j' = 19$. All cross sections behave similarly: growing with increasing energy and markedly modulated by Glori waves. The calculated excitation cross sections start at energies corresponding to the energy thresholds of opening of vibrational channels $E_i = 1549.6$, 3075.4 and 4577 cm^{-1} for $i = 1-3$, respectively. The obtained deexcitation cross sections can be used to describe the relaxation of the O_2 molecule in low-temperature plasma as well.

It is also interesting to see that the dependence of the inelastic cross sections on the final rotational number behaves similarly to the cross section dependence obtained in the Born approximation.

Thus, Fig. 3 shows excitation cross sections of rotational transitions of molecule O_2 in collisions with atom O for energy 4935 cm^{-1}and vibrational transition $v = 3 \to v' = 0$ from initial rotational levels $j = 13$ and 133 to odd levels j'. It can be seen that the cross sections have similar maxima at $j' = j$ and differ in behavior at j', greater than j. „The tail“ of the cross section with $j = 133$ decreases noticeably faster than for $j = 13$. In general, the dependence of the cross section on the rotational quantum number is as expected.

The authors expect that the quantum mechanical cross sections calculated for the first time will prove useful in modelling oxygen-containing low-temperature plasma in gas-discharge lasers, combustion and etching chambers. The entire resulting set of $Q_L(E, v, v')$values and the Fortran program needed to calculate the cross sections can be obtained directly from the authors by email.

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Conflict of interest

The authors declare that they have no conflict of interest.

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