

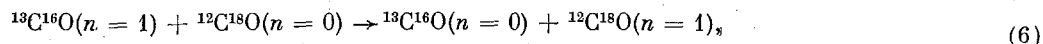
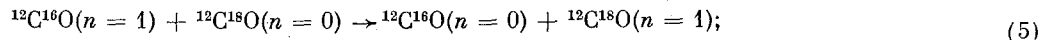
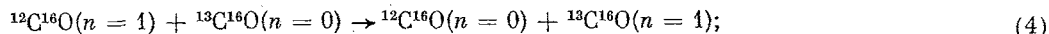
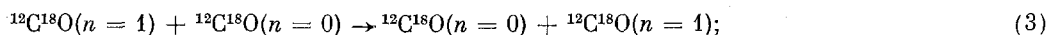
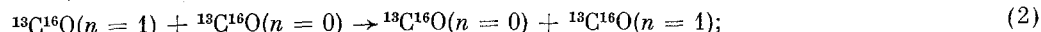
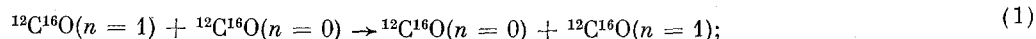
CALCULATION OF PROBABILITIES OF
VIBRATIONAL-VIBRATIONAL EXCHANGE
BETWEEN ISOTOPIC MODIFICATIONS OF
CO MOLECULES

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In recent years, in connection with intense development of different types of CO lasers, the number of papers concerning numerical modeling of relaxation kinetics of vibrationally excited CO molecules at low translational temperatures has increased considerably (see, for example, [1]). As demonstrated in [2], to describe the characteristics of CO lasers correctly it is necessary to include the isotopic composition of carbon monoxide. To perform correct numerical calculations it is necessary to know the probabilities of vibrational-vibrational exchange between isotopic modifications of CO molecules ($^{12}\text{C}^{16}\text{O}$, $^{13}\text{C}^{16}\text{O}$, $^{12}\text{C}^{18}\text{O}$), data on which are extremely sparse in the literature.

The purpose of this paper is to calculate the temperature dependences of the rate constants of vibrational-vibrational exchange $K_{10}^{01}(T)$ for the following processes:



where n is the vibrational quantum number.

The rate constants $K_{10}^{01}(T)$ were calculated in the temperature range 100–500°K, which is of greater interest for operation of CO lasers. In the calculation, we used the theory of near-resonant transfer of vibrational energy, owing to transitions induced by dipole-dipole interactions. This theory was first proposed in [3, 4], modified in [5, 6], and was used successfully to calculate the probabilities of V-V exchange between dipole molecules (see [7]).

The main working equations, used in this paper, are analogous to those presented in [6]. The spectroscopic constants were taken from [8], the collision diameter according to the hard sphere model was taken as equal to $d = 3.7 \cdot 10^{-8}$ m, and in averaging the probabilities over the rotational quantum numbers, it was sufficient to include 40 rotational levels of the CO molecule. The calculation was performed on a ES-1033 computer. The average time for calculating probabilities for a single fixed temperature was 10 min [9]. Figure 1 presents the values of the rate constants $K_{n,n-1}^{01}$ at temperatures $T = 100, 300,$ and 500°K (points 1-3, respectively) calculated in this work (continuous lines) and the experimentally measured values taken from [10]. The difference between the computed and experimental values did not exceed 30%.

Figure 2 illustrates the temperature dependences of the probabilities of V-V exchange $Q_{10}^{01}(T)$ for processes (1)–(6) (the number of the curve corresponds to the order number of the process). The point indicates the probability of V-V exchange measured in [11] for the process (4) at $T = 293^\circ\text{K}$. For processes (5) and (6), no experimental data were found in the literature. Satisfactory agreement between experimental and computed values of the rate constant for processes (1) and (4) gives a basis for assuming that the quantities $K_{10}^{01}(T)$ obtained in this work for processes (2), (3), (5), and (6) are close to the true values as well.

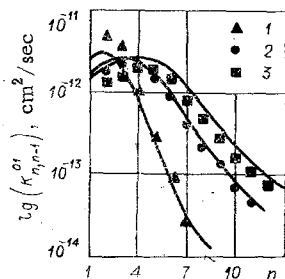


Fig. 1

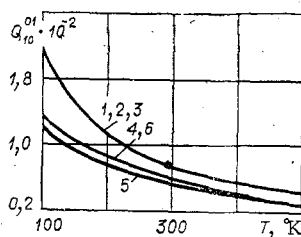


Fig. 2

TABLE 1

i	A_i	B_i	C_i
1	$1,080 \cdot 10^{-5}$	2,2453591	-6,438503
2	$-2,358 \cdot 10^{-7}$	2,3391946	-6,827575
3	$9,788 \cdot 10^{-7}$	2,3912797	-6,969898
4	$4,909 \cdot 10^{-5}$	1,8891169	-47,499114
5	$-1,266 \cdot 10^{-4}$	2,0035623	-71,728275
6	$1,783 \cdot 10^{-6}$	2,3636049	-4,816806

As expected, the values of the rate constants for processes (1)-(3) differ insignificantly from one another and in performing the kinetic calculations, they can evidently be assumed to be equal to one another.

For convenience in using the computed temperature dependences of probabilities of V-V exchange $Q_{10}^{01}(T)$ on a computer, they were approximated by the dependence

$$Q_{10}^{01}(T) = A_i + B_i/T + C_i/T^2.$$

The values of the coefficients are presented in Table 1. The index i corresponds to the number of the process in system (1)-(6).

In conclusion, we note that in the calculations the multipole interaction of higher order than dipolar was neglected. As demonstrated in [11], at temperatures $T \lesssim 500^\circ\text{K}$ and energy defect $\Delta E \lesssim 183 \text{ cm}^{-1}$, the contribution of dipole-quadrupole, quadrupole-quadrupole, etc. interactions can be neglected in the probability of V-V exchange between CO molecules.

The results obtained can be used both in calculating the characteristics of CO lasers and in calculating the parameters of separation of carbon isotopes in chemical reactions, occurring under thermodynamically nonequilibrium conditions [12].

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EQUILIBRIUM CONSTANT IN THE DIFFUSION THEORY OF CHEMICAL REACTIONS

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UDC 530.16

The correct determination of the domains in the phase plane that correspond to the initial and final stages is important to the construction of a diffusion model of a chemical reaction. In case [1] the system state passes a potential barrier with a maximum considerably exceeding the temperature of the medium, the reaction between the particles can be considered complete if the spacing between them is greater than the coordinate corresponding to the position of the maximum of the potential function. The reaction rate is determined here by the probability flux density through a "narrow place," the vertex of the potential barrier. In the problem of dissociation of a diatomic molecule, the situation is rather different. The potential function $U(x)$ of atom interaction in the molecule (its main electronic term) takes on a constant value equal to the dissociation energy, starting with a certain spacing x_1 . Although the atom interaction force vanishes for $x \geq x_1$ and the atoms can be considered free, it would be erroneous to assert that the dissociation reaction is completed upon removal of the atoms to a distance equal to x_1 , and its rate is given by the flux at the point $x = x_1$. The Kramers model to compute the dissociation rates of diatomic molecules was first applied in [2] and it was shown that the values of the rate constants, which agreed correctly with experimental values, are not determined by the flux at the point $x = x_1$ but by the flux at the point $x = l$, where l is a certain parameter equal, in order of magnitude, to the particle mean free path in the medium. However, the parameter l was not defined rigorously in [2].

The purpose of this paper is to consider the problem of atom association in a diatomic molecule and to determine the equilibrium constants for direct and reverse reactions, from which the parameter l is found single-valuedly.

Since the build-up process for a Maxwell equilibrium velocity distribution for reacting particles is more rapid as compared with the process of Boltzmann coordinate distribution formation [2], we consider the Smoluchowski equation in the segment $[0, l]$:

$$\partial M_0 / \partial t + \partial M_1 / \partial x = 0, \quad M_1 = (\mu\gamma)^{-1}(KM_0 - T\partial M_0 / \partial x)_x \quad (1)$$

where $M_0(x, t)$ is the probability density of detecting an atom at the distance x at the time t ; $M_1(x, t)$, probability flux density; $K(x) = -\partial U / \partial x$, force of reacting atoms interaction; μ , their reduced mass; and γ and T , friction coefficient and the temperature of the surrounding medium.

Let us supplement (1) with the initial and boundary conditions

$$M_0(x, 0) = \delta(x - l); \quad (2)$$

$$M_1(0, t) = M_1(l, t) = 0, \quad (3)$$