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Abstract

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On the Probability of Conversion of the Vibrational Energy of Oxygen upon Collision with a Nitrogen Dioxide Molecule

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At present, one of the most promising methods for studying processes of energy exchange in collisions of molecules situated at high vibrational levels is the method of flash photolysis, developed by Norrish and co-workers ($^{1-3}$). In particular, in the experiments described in (^{3}), vibrationally excited oxygen molecules, predominantly distributed on the 8th level, were obtained by flash photolysis of chlorine dioxide, and also of nitrogen dioxide in the presence of large amounts of nitrogen and other gases. By measuring the intensity of oxygen absorption bands corresponding to $n = 6$ at different instants of time after the cessation of irradiation, Norrish and co-workers determined the half-life of the population of oxygen molecules on the 6th vibrational level and estimated the efficiency of conversion of an oxygen vibrational quantum upon collision with other molecules.

A theoretical consideration of the processes leading to deactivation of vibrationally excited oxygen molecules formed in the flash photolysis of chlorine dioxide was carried out in (^{4,5}). In the case of deactivation of oxygen formed in the flash photolysis of nitrogen dioxide, the elementary process leading to deactivation is known. It has been established experimentally that an excited oxygen molecule loses its vibrational energy upon collision with undecomposed nitrogen dioxide molecules. In this connection the following problem arises: on the basis of the experimentally known values of the half-life of oxygen molecules situated on the 6th vibrational level, to determine the probability of conversion of the vibrational energy of oxygen upon collision with a nitrogen dioxide molecule. The present work is devoted to the solution of this problem.

The experimental data relating to the deactivation of oxygen formed in the flash photolysis of nitrogen dioxide are as follows (^{3}). Composition of the mixture subjected to flash photolysis: NO_2 (1 mm Hg), N_2 (580 mm Hg). Duration of the flash ~ 10 μsec; maximum fraction of decomposed nitrogen dioxide molecules 60%; half-life of the population of oxygen molecules on the 6th vibrational level 75 μsec; time interval between the beginning of the flash and the beginning of observation 150 μsec, temperature room temperature. In what follows we shall take $T = 288^\circ$ K.

The system of equations describing the process of vibrational relaxation of O_2

molecules situated on the 6th vibrational level has the form

$$
\begin{aligned}
\frac{dx_8}{dt} &= -ZP_{8,7}x_8, \\
\frac{dx_7}{dt} &= Z\left(P_{8,7}x_8 - P_{7,6}x_7\right), \\
\frac{dx_6}{dt} &= Z\left(P_{7,6}x_7 - P_{6,5}x_6\right),
\end{aligned}
\tag{1}
$$

where $x_n(t)$ is the concentration of O_2 molecules at the n-th level; Z is the number of collisions of an O_2 molecule with NO_2 molecules per second. $P_{n,n-1}$ is the probability of transition of an oxygen molecule from the n-th vibrational state to the $(n-1)$-st, calculated per one collision.

The system of equations (1) describes transitions between levels which, in the first approximation, may be regarded as equidistant. In this case, to determine $P_{n,n-1}$, one may use the harmonic-oscillator model, i.e., assume that $P_{n,n-1} = nP_{10}$. The quantity P_{10} characterizes the probability of the transition $1 \to 0$ for an oscillator whose vibrational quantum is equal to the mean vibrational quantum of an O_2 molecule for the levels under consideration. In writing system (1), only the deactivation processes of O_2 molecules were taken into account; the processes of excitation of O_2 upon collisions were neglected. This neglect is justified. Under the conditions considered, the excitation probability $P_{n,n+1}$ is smaller than the deactivation probability by $\exp\frac{\hbar\omega}{kT} \sim 10^3$ times; therefore, during the half-life time the excitation processes will not play an appreciable role, and they may be neglected. This latter circumstance considerably simplifies the problem, since it makes it possible to reduce the infinite system of equations describing the process of vibrational relaxation in the general case to a closed system of 3 equations.

The initial conditions for equations (1) are written in the form

$$
x_n\big|_{t=0} = x_n(0), \tag{2}
$$

where $x_n(0)$ gives the distribution of oxygen molecules over vibrational levels at the moment the pulse ends.

The distribution of O_2 molecules at the 6th vibrational level at any instant of time is found from the solution of system (1) with the initial conditions (2) and has the form

$$
x_6(t) = x_8(0)\,28(1-e^{-\tau})^2e^{-6\tau} + x_7(0)\,7(1-e^{-\tau})e^{-6\tau} + x_6(0)e^{-6t}, \tag{3}
$$

where $\tau = tZP_{10}$.

To determine the half-life time of the population $x_6(t)$, it is necessary to know the explicit form of $x_n(0)$. Since in the case considered the value of $x_n(0)$ is unknown, let us consider two limiting cases: the relaxation time is much greater, and the relaxation time is much smaller, than the pulse duration (by relaxation time we mean the quantity $\sim 1/ZP_{6,5}$). We shall determine the explicit form of $x_n(0)$ for both cases and find the corresponding half-life times. The half-life times calculated in this way will determine the upper and lower limits of $P_{6,5}$.

In the first limiting case the relaxation time is much greater than the pulse duration; therefore, during the pulse the distribution of O_2 molecules over vibrational levels will not change, and at the moment the pulse ends the molecules will remain at those levels at which they were formed. In the experiments considered, the excited O_2 molecules are formed predominantly at the 6th vibrational level; therefore,

$$x_8\big|_{t=0} = x_8(0); \quad x_n = 0 \text{ for the remaining } n. \tag{4}$$

In the second limiting case the relaxation time is much smaller than the pulse duration; therefore, during the pulse the molecules have time to pass to other vibrational levels. The distribution of molecules over vibrational levels at the moment the pulse ends can in this case be found from the solution of the system of equations describing the process of vibrational relaxation in the presence of a continuously acting source. This system has the form

$$\frac{dx_n}{dt} = Z(P_{n+1,n}x_{n+1} - P_{n,n+1}x_n + P_{n-1,n}x_{n-1} - P_{n,n-1}x_n) + N\delta_{n8},$$

$$n = 0, 1, 2, \dots, \tag{5}$$

where N is the power of the source, $P_{n,n-1} = nP_{10}$.

From the simplest physical considerations (6) it is clear that the solution of system (5), describing the behavior of the distribution function $x_n(t)$ at times greatly exceeding the relaxation time, must have the form

$$x_n(t) = tNx_n^{(0)} + f_n, \tag{6}$$

where $x_n^{(0)}$ is the Boltzmann function normalized to unity, and f_n is an unknown function assumed to be independent of time.

Substituting (6) into (5), we obtain, for determining f_n, an algebraic system of inhomogeneous equations; moreover, the solution of the corresponding homogeneous adjoint system of equations is orthogonal to the right-hand side. The solution of the inhomogeneous system of equations is found by double summation of the equations. In the case under consideration $\left(\exp \frac{\hbar\omega}{kT} \gg 1\right)$ the solution has the form

$$\begin{aligned} f_n &= B(n)e^{-n\theta}, \quad n \leq 8, \\ f_n &= B(8)e^{-n\theta}, \quad n > 8, \end{aligned} \tag{7}$$

$$B(n) = \frac{N}{ZP_{10}} \frac{e^{n\theta}}{n}, \qquad \theta = \frac{\hbar\omega}{kT}, \qquad f_0 = 0.$$

From (7) it is seen that

$$f_n \ll f_8, \qquad n \geq 9.$$

Thus, in the second limiting case

$$x_n\Big|_{t=0} = \frac{N}{ZP_{10}} \frac{1}{n} \qquad \text{for } n \leq 8, \tag{8}$$

$$x_n = 0 \qquad \text{for } n \geq 9.$$

The additive Boltzmann part $t_1 N x_n^{(0)}$, where t_1 is the pulse duration, is not considered, since it is insignificant in the relaxation process. Knowing the explicit form of $x_n(0)$ and the experimental value of the half-life time, one can determine P_{10}.

In the first limiting case (condition (4))

$$P_{10} = \frac{3.2 \cdot 10^3}{Z}.$$

In the second limiting case (condition (8))

$$P_{10} = \frac{2.5 \cdot 10^3}{Z}.$$

From a practical point of view the difference between these quantities is insignificant. Assuming that the collision cross sections of $O_2 - N_2$ and $O_2 - NO_2$ are approximately equal, and that the fraction of decomposed molecules is 50%, we obtain for Z the value $0.4 \cdot 10^7$. Thus, $P_{6,5} = 6(0.8 - 0.6) \cdot 10^{-3} \sim 5 \cdot 10^{-3}$. According to the estimates of Norrish (3), $P_{6,5} > 2 \cdot 10^{-3}$. The value found for $P_{6,5}$ makes it possible to draw some conclusions about the mechanism of conversion of the vibrational quantum of O_2.

Let us consider three possible mechanisms of conversion of vibrational energy in a collision of O_2 and NO_2 molecules: adiabatic transition of the vibrational energy of O_2 into translational energy, which occurs without the participation of the electron shells of the incident molecules; nonadiabatic transition of the vibrational energy of O_2 into translational energy; adiabatic transition of the vibrational energy of O_2 into the vibrational energy of NO_2. The probability $P_{6,5}$ in the first process is approximately equal to the probability of the analogous process in the collision of O_2 and N_2 molecules and is of the order of 10^{-6} ([5]). To estimate the probability $P_{6,5}$ in the nonadiabatic transition of energy one may use the known values of the probability for NO ([7,8]). In this case $P_{6,5} \sim 10^{-3}$. An estimate of the probability $P_{6,5}$ for the third process gives a value $\sim 10^{-2}$.

Thus, the possible processes for the transformation of the vibrational energy of O_2 upon collision with an NO_2 molecule are the nonadiabatic transition of the vibrational energy of O_2 into translational energy and the adiabatic exchange of vibrational quanta between O_2 and NO_2. A choice between the two indicated processes can be made if the temperature dependence of $P_{6,5}$ is investigated. In the first case $\ln P_{6,5} \sim -1/T$, and in the second $\ln P_{6,5} \sim -1/T^{1/3}$.

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Note: Figure translations are in progress. See original paper for figures.