

EXCITATION AND DEACTIVATION OF MOLECULAR ROTATION IN ATOM - MOLECULE COLLISIONS

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The article deals with the processes of the excitation and deactivation of rotation in diatomic molecules which constitute a small impurity in a monatomic gas.

In some types of flow in a rarefied gas it becomes significant to consider the reduction in the rate of energy exchange between the translational and rotational degrees of freedom of the molecules. The information available today is not yet sufficient for a satisfactory solution of this problem. It is known only [1, 2] that in most cases the characteristic time required for the process of establishing equilibrium with respect to the rotational degrees of freedom of the molecules is of the same order of magnitude as, or somewhat greater than, the time required for establishment of a Maxwellian distribution of molecular velocities in the gas.

1. The collision of a molecule with an atom will be considered within the framework of classical mechanics. Atoms, either in molecules or as free atoms, will be represented by mass points. We shall confine our investigation to the case in which the relative-velocity vectors lie in the plane which contains all three atoms, i.e., confine it to plane problems. Initially the potential of the forces of interaction between atoms within a molecule was specified as in the Morse anharmonic oscillator; however, calculations showed that, under the circumstances we are considering, the molecule is satisfactorily described by the rigid-rotator model. The potential about which the least is known is that of the forces of interaction between molecules; as a rough approximation, we assume that the centers of the repulsion forces coincide with the nuclei of the atoms. The attraction forces were left out of consideration in the problem of individual collisions, their role being taken approximately into account when we determined the results of many collisions by using the increase in the relative velocity of the colliding particles, which is determined from the depth of the potential well.

A diagram representing the collision and indicating the notation used is shown in Fig. 1. The Hamiltonian H of the atom-molecule system in a fixed system of coordinates can be written in the form

$$H = \frac{P_x^2 + P_y^2}{2M} + \frac{P_\xi^2 + P_\eta^2}{2m_a} + V(R_1 R_2) + \frac{P_\phi^2}{2m^* r^2} + \frac{P_r^2}{2m^*} + v(r) \quad (1.1)$$

$(m^* = m_1/2 = m_2/2, M = m_1 + m_2)$

Here the symbol P represents generalized impulses; x, y, ξ , and η are Cartesian coordinates. The first term of the sum is due to the motion of the center of gravity of the molecule, the second term is due to the motion of the impinging atom, the third term represents the potential energy of intermolecular interaction, the next two terms are due to the rotation of the molecule about its center of gravity and to the vibration of the nuclei in the molecule, and the last term represents the potential energy of interaction between these nuclei. In the case of a rigid rotator the last two terms are constant, and $r = r_e$ (where r_e is the equilibrium distance between the nuclei within the molecule). By hypothesis,

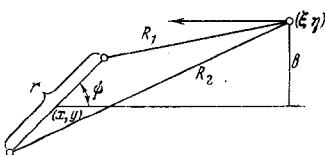


Fig. 1

$$V(R_1 R_2) = V_0 \exp(-\alpha R_1) + V_0 \exp(-\alpha R_2) \quad (1.2)$$

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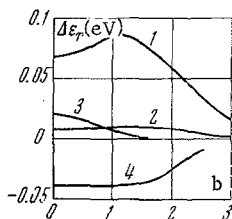


Fig. 2

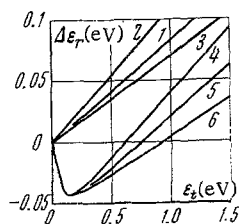


Fig. 3

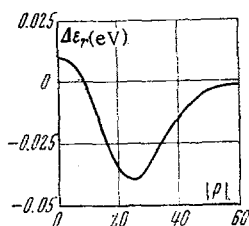


Fig. 4

The Hamiltonian was solved numerically for parameters corresponding to a collision between A and O₂. Experiments on the elastic scattering of molecular beams [3] yielded average values of the interaction potential for this pair, where the average was taken over all possible orientations of the molecule. The parameters V_0 and α in formula (2) were calculated on the basis of this potential, using the procedure proposed in [4]. The results found were that $V_0 = 32,250$ eV and $\alpha = 4.12 \text{ \AA}^{-1}$.

The calculation of each trajectory began at distance $\xi - x = 5r_e$. In our calculations we varied the values of: ψ , the angle of orientation of the molecular axis with respect to the relative-velocity vector; $b = |y - \eta|$, the target distance; the initial velocity of the impinging atom (i.e., the energy of relative motion, ε_t); and P_ψ , the initial rotational angular momentum of the molecule. In each variant of the collision the increment of the rotational energy of the molecule, $\Delta\varepsilon_r$ ($\varepsilon_r = P_\psi^2 / 2m^*r_e^2$), was kept fixed.

The quantities ε_t and ε_r will be expressed in electron-volts (eV), the target-distance parameter b in units equal to r_e ($r_e = 1.207 \text{ \AA}$), and p , the rotational momentum of the O₂ molecule, in units equal to $h/2\pi$ ($p = 2\pi\hbar^{-1}P_\psi$, where h is Planck's constant).

Figures 2-4 show some of the calculation results, averaged over the various initial orientations:

$$\Delta\varepsilon_r(b, \varepsilon_t, p) = \frac{1}{2\pi} \int_0^{2\pi} \Delta\varepsilon_r(b, \varepsilon_t, p, \psi) d\psi \quad (1.3)$$

Figure 2 gives examples showing how $\Delta\varepsilon_r$ varies as a function of the target-distance parameter b for combinations 1-4 of p and ε_t values; the specific values of p and ε_t were those shown in parentheses below:

$$1 (p = 0, \varepsilon_t = 0.8184), \quad 2 (p = 0, \varepsilon_t = 0.102), \\ 3 (|p| = 21, \varepsilon_t = 0.8184), \quad 4 (|p| = 21, \varepsilon_t = 0.102)$$

It can be seen that in cases with no initial rotation ($p=0$), the rotation is most effectively excited when $b \approx 1$.

The variation of $\Delta\varepsilon_r$ as a function of ε_t , the energy of the impinging atoms, is shown in Fig. 3. Here curves 1, ..., 6 correspond to the following combinations of p and b values:

$$1 (p = 0, b = 0), \quad 2 (p = 0, b = 1.2), \quad 3 (p = 0, b = 2.0) \\ 4 (|p| = 21, b = 0), \quad 5 (|p| = 21, b = 1.2), \quad 6 (|p| = 21, b = 2.0)$$

For $p=0$ the function $\Delta\varepsilon_r(\varepsilon_t)$ is almost linear. In this case, which is the simplest of all, the numerical solution described here agrees qualitatively with the results obtained by Parker [5], who used an analytical method. Implicit in [5] was the assumption that the configuration of the colliding particles at the instant of their nearest approach is independent of the initial orientation of the molecules.

This assumption makes it possible to obtain an analytical average over the values of the parameter ψ in an expression of the type (3). The calculation results show that this assumption is acceptable when $p=0$. When $p \neq 0$, the picture becomes more complicated, so that extending Parker's method to cases of this type would yield incorrect results. In Fig. 4 we show, as an example, the variation of $\Delta\varepsilon_r$ as a function of $|p|$ when $b=0$ and $\varepsilon_t=0.102$.

It can be seen that for some value of p the rotational energy remains constant ($\Delta\varepsilon_r=0$). This happens when ε_r^0 is approximately one-fifth of the energy of relative motion of the colliding particles. This result is confirmed by all the calculations carried out for $0.1 \leq \varepsilon_t \leq 1.64$ and $0 \leq p \leq 61$.

For higher initial values of rotational energy we observe a deactivation of the rotational levels, with a conversion of part of the initial rotational energy of the molecule to translational energy. For the case $p \neq 0$, applying Parker's method does not give us the deactivation effect.

TABLE 1

T, °K	p ₀ = 0	5	11	21	31	41	61
300	0.38		-0.18		-0.32		
500	0.74						
1000	1.80	1.44		-0.55		-1.43	
1500	3.05	2.56	1.26	-0.37	-1.27	-2.16	-2.16
2000	4.44	3.82	2.14	-0.02	-1.25	-2.44	-3.64
3000	7.50	6.63	4.16	0.86	-0.95	-2.60	-5.20
4000	10.90	9.75	6.44	1.96	-0.33	-2.35	-6.18
6000	18.40	16.60	11.50	4.57	0	-1.36	-7.04
8000	26.80	24.40	17.30	7.63	3.46	0.24	-6.94
10000	35.60	32.40	23.30	10.90	5.81	2.12	-6.18
12000	44.20	40.40	29.30	14.10	8.22	4.18	-5.08

2. The above results, obtained for the solution of the dynamic problem of collisions, may be used, in principle, when we consider the kinetics of the rotational-energy distribution function for a rigid rotator and find the appropriate relaxation equation. The solution of such a kinetic problem is very complicated and laborious and was not included among the purposes of this study. In the present article we describe estimates for the velocity of rotational relaxation and consider qualitatively how it varies as a function of such physical factors as the direction of the process, the initial energy state of the rotational and translational motions, and the attraction forces acting at long distances.

In the general case the rotational-relaxation time is comparable to the time required for the establishment of equilibrium with respect to the translational degrees of freedom [2, 5], and therefore these processes should be considered jointly, which simplifies the problem to a substantial extent. However, if we assume that the diatomic O₂ molecules constitute only a small impurity in the basic monatomic component A, whose translational degrees of freedom have an equilibrium Maxwell distribution (thermodynamic condition), then the relaxation of the rotational energy of the rigid rotator can be considered separately. This is the case we will consider in the rest of this article.

In order to estimate the rotational-relaxation time in the O₂-A mixture, we shall carry out a static-averaging process on the result of the solution of the dynamic problem of collisions involving the variation of $\Delta \varepsilon_r$ with b , ε_t , and p . We assume that the distribution function with respect to the rotational degrees of freedom is Maxwellian. In that case the frequency of collisions (sec⁻¹) of O₂ molecules with A atoms for relative velocities lying between v and $v+dv$ (cm/sec), target distances lying between b and $b+db$ (cm), and azimuth angles lying between χ and $\chi+d\chi$ will be

$$2n\{A\} \left(\frac{\mu}{2\pi kT} \right)^{3/2} \exp \frac{-\mu v^2}{2kT} v^3 b db dv d\chi \quad (2.1)$$

$$\mu = \frac{m_1 m_2}{m_1 + m_2}, \quad k = 1.38 \cdot 10^{-16} \frac{\text{erg}}{^\circ\text{K}}$$

Here μ is the reduced mass, k is the Boltzmann constant, T is the temperature (°K), and $n\{A\}$ is the density of A atoms (cm⁻³). For the average change per unit time in the rotational energy of molecules with a given initial value p_0 , in a calculation involving one molecule for one collision, we have

$$\frac{dE_r(T, p_0)}{dt} = 2 \left(\frac{\mu}{2\pi kT} \right)^{3/2} \int_0^{2\pi} \int_0^\infty \Delta \varepsilon_r[b, \varepsilon_t(v), p_0] \exp \frac{-\mu v^2}{2kT} v^3 b db dv d\chi \quad (2.2)$$

When we integrated in (2.2), we used for $\Delta \varepsilon_r(b, \varepsilon_t, p_0)$ an analytic approximation to the results of the solution of all variants of the dynamic problem. Since we disregarded the variation of $\Delta \varepsilon_r$ as a function of χ , the calculation of the integral with respect to χ is trivial. The integral with respect to b was obtained analytically, and the integral with respect to ε_t (i.e., with respect to v) was obtained numerically. The values of dE_r/dt (10¹² eV · cm³/sec) for various thermostat temperatures and for an initial rotational momentum p_0 are shown in Table 1. It should be noted that in (2.2) the distribution function of the molecules with respect to p is "monochromatic," $f(p) = \delta(p - p_0)$, i.e., the rotational temperature is $T_r = 0$.

We may mention in passing that when we have the relation $p_0^2 = 0.22 T$ there is no exchange of energy at all between rotational and translational degrees of freedom. In this case, relaxation begins with a redistribution of rotational energy with respect to direction, until a Boltzmann equilibrium distribution is established.

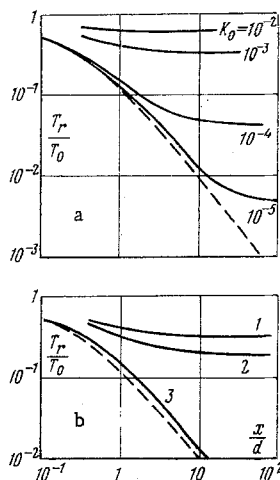


Fig. 5

An approximation of the calculation results for $p_0=0$ (the first column of dE_r/dt values in Table 1) yields

$$\frac{dE_r(T)}{dt} \Big|_{T_r=0} = 3.6 \cdot 10^{-28} n \{A\} T^{1.3} \left(\frac{\text{eV}}{\text{sec}} \right) \quad (2.3)$$

The effect of long-distance attraction forces can be taken into consideration by increasing the relative velocity of the colliding particles. This should increase the dE_r/dt values obtained here. An analytic solution of the problem for $p_0=0$, carried out for the A-O₂ system, like Parker's method [5], yields a correction for attraction forces in the form of a factor g by which the right side of (2.3) should be multiplied:

$$g = 1 + \frac{\pi^{3/2}}{2} \left(\frac{T^*}{T} \right)^{1/2} + \left(\frac{\pi^2}{4} + \pi \right) \frac{T^*}{T} \quad (2.4)$$

Here T^* is the depth of the potential well; for an A-O₂ system, $T^* = 101^\circ\text{K}$. The value of the factor for high temperatures is close to unity; for example, when $T = 10,000^\circ\text{K}$, we have $g = 1.337$. As the temperature is reduced, the value of g increases markedly. Thus, $g = 1.91$ for $2,000^\circ\text{K}$, and $g = 4.5$ for $T = 300^\circ\text{K}$.

The result (2.3) enables us to estimate τ (the rotational-relaxation time for O₂ present as a small impurity in A under thermostatic conditions) at high temperatures. We can determine τ by using the equation

$$\tau = E_r^\circ(T) / (dE_r/dt)_{T_r=0}. \quad (2.5)$$

where $E_r^\circ(T) = kT$ is the equilibrium rotational energy per molecule, and the derivative is the rate of increase of this energy for an initially nonrotating molecule. If the rotational energy satisfies a relaxation equation of the form

$$dE_r/dt = [E_r^\circ(T) - E_r(t)]\tau^{-1} \quad (2.6)$$

then τ has the usual meaning. From (2.3), (2.5), and the equation of state of the gas under thermostatic conditions, we find

$$\tau p = 4.25 \cdot 10^{-11} T^{0.7} \quad (2.7)$$

where p is the pressure (atm) and τ is measured in seconds.

The quantity $z = \tau/\tau_0$, where τ_0 is the average time between collisions, gives us an estimate of the number of collisions leading to the establishment of equilibrium with respect to the rotational degrees of freedom. For a Maxwellian distribution of velocities in the case of A-O₂ collisions [6] we have

$$\tau_0 = 9.25 \cdot 10^{-5} T^{1/2} / n \{A\} \sigma^2 \quad (2.8)$$

where σ is the gas-kinetic diameter of the collision (cm). The variation of the square of this quantity as a function of temperature, according to measurements made in experiments on the scattering of a molecular beam [3] for temperatures of $2,000^\circ\text{K} \leq T \leq 10,000^\circ\text{K}$, admits of an approximation of the form

$$\sigma^2(T) = 3.76 \cdot 10^{-15} T^{-0.2} \quad (\text{cm}^2) \quad (2.9)$$

Comparing (2.7)-(2.9), we find that z is practically independent of T and has a value of about 14.

The expression (2.4) shows that even when we take attraction forces into consideration, our conclusion remains true at least for high temperatures. The estimate we have obtained for the rotational relaxation time agrees with the results of [5].

If the initial rotational energy cannot be considered small ($T_r|_{t=0} \neq 0$), our calculations yield a substantially different result. To make the following estimates easier to visualize, we shall make one more assumption. Suppose that in the process of rotational relaxation there exists a Boltzmann distribution with respect to rotational levels, $f(E_r) \sim \exp\{-E_r/kT_r\}$, with a rotational temperature T_r different from the thermostat temperature T . The possibility of realizing such a process was shown in [7] for the case in which the average energy added by one collision to the rotation of the molecule is small in comparison with the kinetic energy of relative motion.

This will be true when a heavy rigid rotator collides with light atoms (for example, in Br₂-He collisions). In the case we have considered in this article, A and O₂ have comparable masses, so that this assumption is not strictly true. However, numerical calculations show (Fig. 3 and Fig. 4) that for $0.4 < \varepsilon_t < 1.6$ (which corresponds to $2,500^\circ\text{K} < T < 15,000^\circ\text{K}$) the $\Delta\varepsilon_r$ value averaged with respect to ψ is less by a factor of 3-5 than ε_t , the energy of relative motion. This gives reason to hope that the assumption of a Boltzmann distribution for the rotational energy of the O₂ molecule will yield a satisfactory qualitative description of the process of rotational relaxation.

We integrate dE_r/dt in the expression (2.2) with respect to p_0 , with a Boltzmann weighting factor, by numerical methods, using values from Table 1:

$$\frac{dE_r(T, T_r)}{dt} = \left\{ \int_0^\infty \exp \frac{-\varepsilon_r}{kT_r} d\varepsilon_r \right\}^{-1} \int_0^\infty \frac{dE_r(T, p_0(\varepsilon_r))}{dt} \exp \frac{-\varepsilon_r}{kT_r} d\varepsilon_r \quad (2.10)$$

By approximating the integration in (2.10), we obtain

$$\frac{dE_r(T, T_r)}{dt} = \frac{dE_r(T, 0)}{dt} \left[1 - \left(\frac{T_r}{T} \right)^{0.3} \right] \quad (2.11)$$

where the first factor is given by the expression (2.3). For $T_r = 0$ the value of dE_r/dt is found to be the same as before. In the equilibrium condition $T_r = T$, and naturally we also have $dE_r(T, T_r)/dt = 0$. In the general case the rate of excitation or deactivation depends both on the temperature of the translational degrees of freedom and on the rotational temperature.

3. As an example of the application of formula (2.11), we consider the distribution of the rotational temperature of O₂ molecules along the axis of a jet emerging into a vacuum. At a sufficiently long distance from the source, i.e., at a point where the density of the gas becomes small, we can observe a deviation of the rotational temperature from the temperature of the translational degrees of freedom. A little further downstream, there is complete freezing first of the rotational temperature and then of the translational temperature as well [8]. The discussion of this problem in [9] made use of a relaxation equation of the form (2.6).

Suppose that the jet emerges from a reservoir through an orifice of diameter d . The main component of the jet is argon, which determines its gas-dynamic and thermodynamic properties, in particular the adiabatic exponent $\gamma = 5/3$. Let the distance x be measured from the critical cross section, which is situated at the orifice; then for the distribution of the number M along the axis of the jet we can take an approximate function similar to the one proposed by M. Ladyzhenskii:

$$M = 3.64 (x/d)^{1/3} + 1 \quad (3.1)$$

For a value of T_r characterizing a small admixture of molecular oxygen, Eq. (2.11) can be reduced to the form

$$\frac{d}{dx} \left(\frac{T_r}{T_0} \right) = \frac{0.4}{K_0 M (1 + 1/3 M^2)^2} \left[\left(1 + \frac{1}{3} M^2 \right)^{-0.3} - \left(\frac{T_r}{T_0} \right)^{0.3} \right] \quad (3.2)$$

Here T_0 is the stagnation temperature and K_0 is the Knudsen number, which is determined from the free path length of the molecules in the reservoir and the diameter d of the orifice. If we assume that T_r and T are in equilibrium everywhere inside the reservoir up to the critical cross section, we obtain the initial condition

$$(T_r/T_0)|_{x=0} = 3/4 \quad (3.3)$$

The results of numerical calculations using Eq. (3.2), where M is given by Eq. (3.1) with the initial condition (3.3) for various values of the parameter K_0 , are shown by solid curves in Fig. 5a. The dashed curve shows the distribution of the translational temperature. It can be seen that the variation of the rotational temperature along the axis of the jet has a nonequilibrium character. As the jet moves away from the source, the temperature deviates more and more from the equilibrium value, and at a sufficiently distant point it freezes. The degree of nonequilibrium and the level of the frozen rotational temperature increase as K_0 increases.

Similar calculations were carried out for the case in which the correction for long-distance attraction forces between the molecules was taken into consideration. The right side of Eq. (3.2) was multiplied

by the factor g (formula (2.4)). This factor introduces a variation with the absolute temperature value. Figure 5b shows the results of calculations using $K_0 = 10^{-3}$. Curve 1, calculated without taking the attraction forces into consideration, is independent of T_0 ; curve 2 was calculated with the attraction forces taken into consideration for $T_0 = 10,000^\circ\text{K}$, and curve 3 for $T_0 = 300^\circ\text{K}$. It can be clearly seen that in the high-temperature case the attraction forces have little effect on the final result. On the other hand, for $T_0 = 300^\circ\text{K}$ the effect of the attraction forces is that the T_T curve is practically identical with the T curve up to $x/d = 100$.

Marrone [10] found experimentally that for $K_0 \sim 10^{-3}$ and $T_0 = 300^\circ\text{K}$, in a jet of pure nitrogen, freezing of T_T takes place when $x/d \sim 20$. Curve 3 cannot be expected to be in good quantitative agreement with real flow, since the attraction forces were only qualitatively taken into consideration. It should be pointed out that in Marrone's experiments [10] for identical values of x/d the temperature was higher, because of differences in the adiabatic exponent, than in the calculations, and therefore the effect of the attraction forces is less pronounced.

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