CALCULATION OF THE ROTATIONAL TRANSITION PROBABILITIES OF DIATOMIC MOLECULES WHEN THEY COLLIDE WITH HEAVY PARTICLES

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The collisional rotational transition probabilities for molecule–molecule and molecule–atom interactions in three-dimensional space are calculated. The quasiclassical approach developed in [1] is used. Expressions are obtained that are suitable for practical calculations of single-quantum and double-quantum rotational transitions in diatomic molecules. The collisional rotational transition probabilities are averaged over the Maxwell velocity distribution and their dependence on the gas temperature is obtained. To illustrate the method the results of a calculation of the probabilities for HCl–HCl, HCl–He, CO–CO interaction are presented.

To give a rigorous quantitative description of rotational relaxation it is necessary to solve the kinetic equations of a multilevel system, to solve which, in turn, it is necessary to know the excitation (de-excitation) probabilities of the rotational states of the molecules when they collide with one another and with atoms of the inert gases in the case of a mixture. Various methods can be used to calculate the collisional rotational transition probabilities. The classical method does not give the required accuracy and only provides a fairly rough estimate of the number of collisions Z_{rot} necessary to establish rotational equilibrium [2]. A number of papers which have recently appeared [3] are based on a rigorous quantum-mechanical approach to the solution of the rotational excitation problem. However, a rigorous quantum-mechanical calculation cannot, in practice, give numerical values of the collisional rotational transition probabilities averaged over the velocities of the colliding particles for the numerous rotational levels of complex molecules when there is a sharp change in the gas temperature. In this case it is better to use the quasiclassical approach developed by Takayanagi [1]. In his papers he solved the model problem in a plane and gave numerical results for the collisional rotational transition probabilities for the N_2–Ar interaction for fixed velocities of the incident particles. Similar calculations were also made in [4]. However, they also did not average the rotational transition probabilities over the projections of the rotational numbers and the velocities of relative motion of the colliding molecules.

The essence of the method is as follows. The trajectory of motion of a particle is calculated using the classical approach, and the time dependence of the perturbation operator is obtained, by averaging which over the wave functions of the initial and final states the collisional rotational transition probabilities are obtained. A classical calculation of the trajectory of molecular motion is justified by the smallness of the de Broglie wavelength compared with the characteristic atomic distances and the smallness of the transferred rotational quantum compared with the energy of translational motion of the particles. The results will obviously depend to a considerable extent on the chosen interaction potential between the colliding particles. It follows from the Massey criterion that the nonadiabatic interaction region is comparable with the internuclear distances of the molecule. We must therefore choose the short-range potential to describe the interaction. It is usual in such cases [1] to employ the potential in the form of the sum of the potential of the repulsive forces between the individual atoms of the molecules. The additivity of the potential is to some extent confirmed by experimental data on the scattering of molecular beams [5]. In our investigation we chose the interaction potential in the form

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$$V=\sum_{k=3}^{4}\sum_{i=1}^{2}A_{ik}\exp(-\alpha_{ik}r_{ik}), \tag{1}$$

where $r_{ik}=[(x'-x-R)^2+(y'-y)^2+(z'-z)^2]^{1/2}$ is the distance between the two atoms of the colliding molecules (Fig. 1). Assuming α_{ik} to be the same for all pairs of atoms, expanding the potential in terms of the parameter ξ/R, and expressing the cosines of the angles in terms of first- and second-degree Legendre polynomials, we obtain

$$\begin{gathered}
V(R,\ \chi_1,\chi_2)=Be^{-\alpha R}\Big\{1+\frac{D_1}{B}[\mathrm{P}_1(\cos\chi_1)+\mathrm{P}_1(\cos\chi_2)]+\\
+\frac{D_2}{B}[\mathrm{P}_2(\cos\chi_1)+\mathrm{P}_2(\cos\chi_2)]+\frac{D_3}{B}[\mathrm{P}_1(\cos\chi_1)\,\mathrm{P}_1(\cos\chi_2)]+\dots\Big\};\\
B=\sum_{i,k=1}^{2}A_{ik}+\frac{1}{6}(\xi\alpha)^2\frac{m_1^2(A_{12}+A_{22})+m_2^2(A_{12}+A_{11})}{(m_1+m_2)^2};\\
D_1=\xi\alpha\frac{m_2(A_{12}+A_{11})-m_1(A_{12}+A_{22})}{m_1+m_2};\\
D_2=\frac{1}{3}(\xi\alpha)^2\frac{m_1^2(A_{12}+A_{22})+m_2^2(A_{12}+A_{11})}{(m_1+m_2)^2};\\
D_3=(\xi\alpha)^2\frac{m_1^2A_{22}-m_2^2A_{11}}{(m_1+m_2)^2}
\end{gathered} \tag{2}$$

for the interaction of two molecules, and

$$\begin{gathered}
V(R,\chi_1)=Be^{-\alpha R}\left[1+\frac{D_1}{B}\mathrm{P}_1(\cos\chi_1)+\frac{D_2}{B}\mathrm{P}_2(\cos\chi_1)+\dots\right];\\
B=A_{13}+A_{23}+\frac{1}{6}(\xi\alpha)^2\frac{m_2^2A_{13}+m_1^2A_{23}}{(m_1+m_2)^2};\\
D_1=\xi\alpha\frac{m_2A_{13}-m_1A_{23}}{m_1+m_2};\qquad D_2=\frac{1}{3}(\xi\alpha)^2\frac{m_2^2A_{13}+m_1^2A_{23}}{(m_1+m_2)^2}
\end{gathered} \tag{3}$$

for the interaction between a molecule and an atom. In both cases the potential is split into the product of a radial and an angular part. The spherically symmetrical part of the potential is used to calculate the trajectory of motion of the particles, and the angular part defines the selection rule for the rotational transitions. We will consider the choice of the numerical values of α and A_{ik} below.

To calculate the trajectory of motion of the colliding particles in the center of inertia system we used the equation of conservation of energy

$$\frac{1}{2}M\left(\frac{dR}{dt}\right)^2=E-V(R)-\frac{J^2\hbar^2}{2MR^2}, \tag{4}$$

where M is the reduced mass of the two particles, E is the total energy of the system V(R) is the interaction potential of the molecule with the incident particle, and $J\hbar$ is the angular moment of relative rotation of the two particles. Note that in view of the law of conservation of moment the quantum number J must change when j (the rotational quantum number of the molecule) changes. However, the error due to ignoring the change in J is negligible for single-quantum and double-quantum transitions ($\Delta j=\pm 1.2$) for large J, and for small J the value of the energy of relative rotation itself is small compared with the total energy of the system of particles. We made the following approximations when solving Eq. (4): we ignored the change in J, the quantity R was replaced by R_c (the distance at which effective interaction between the particles occurs), and we used as the interaction potential the spherically symmetrical part, namely, the main term in the expansions (2) and (3). Taking these simplifications into account the solution of Eq. (4) takes the form

$$Be^{-\alpha R(t)}=\left(E-\frac{J^2\hbar^2}{2MR_c^2}\right)\mathrm{ch}^{-2}\left[\frac{\alpha}{\sqrt{2M}}\left(E-\frac{J^2\hbar^2}{2MR_c^2}\right)^{1/2}t\right]. \tag{5}$$

The rotational motion of a system of two molecules is described by the Schrödinger equation

$$\{H_r^{(1)}+H_r^{(2)}+V[R(t)]\,\Psi=i\hbar\frac{\partial\Psi}{\partial t}, \tag{6}$$

where $H_r^{(i)}$ is the Hamiltonian operator for free rotation of the i-molecule, V[R(t)] is the perturbation operator, and Ψ is the angular part of the wave function of a system of two molecules (or a molecule–atom).

Using the model of a rigid rotator to describe the rotation, the angular part of the wave function of a system of two molecules can be represented in the form of an expansion in spherical functions,

$$\Psi = \sum_{j_1 m_1 j_2 m_2 J m} C(j_1 m_1 j_2 m_2 J m|t)\, Y(j_1 m_1|\Theta_1 \varphi_1)\, Y(j_2 m_2|\Theta_2 \varphi_2) \times$$

$$\times Y(Jm|\Theta\varphi) \exp\left\{-\frac{it}{\hbar}[w_1(j_1) + w_2(j_2) + w_3(J)]\right\}, \tag{7}$$

where j_k and m_k are the rotational quantum number and its projection on the z axis for the k-molecules, J and m are the quantum number and its projection characterizing the rotation of the system as a whole, $w_k(j_k)$ is the energy of free rotation of the k-molecule, and $w_3(J)$ is the energy of relative rotation of the two molecules.

Substituting the wave function (7) into Eq. (6), and solving it by the method of perturbation theory, we obtain to a first approximation the matrix element of the rotational transition. Then, averaging over the projections of the quantum numbers m_1, m_2, and m, we obtain the collisional rotational transition probabilities

$$P_1(J, j, E) = f(E)\left(\frac{D_1}{B}\right)^2 \frac{j}{2j+1}; \tag{8}$$

$$P_2(J, j, E) = f(E)\left(\frac{D_2}{B}\right)^2 \frac{9}{10} \cdot \frac{J^2 + J - 1}{(2J+3)(2J-1)} \frac{j(j-1)}{(2j+1)(2j-1)}; \tag{9}$$

$$P_{11}(j_1, j_2, J, E) = f(E)\left(\frac{D_3}{B}\right)^2 \frac{201}{405} \frac{j_1 j_2}{(2j_1+1)(2j_2+1)}, \tag{10}$$

where $f(E) = \frac{8M}{\alpha^2\hbar^2}\left(E - \frac{J^2\hbar^2}{2MR_c^2}\right)\frac{\beta^2}{\mathrm{sh}^2\beta}$; $\beta = j\beta_0$, $\beta = (2j-1)\beta_0$, and $\beta = (j_1 + j_2)\beta_0$, respectively, for Eqs. (8), (9), and (10);

$$\beta_0 = \frac{\pi B_0 \sqrt{2M}}{\alpha\hbar}\left(E - \frac{J^2\hbar^2}{2MR_c^2}\right)^{-1/2};$$

B, D_1, D_2, and D_3 are the corresponding expressions for the interaction potentials of the molecule–molecule (2), or molecule–atom (3); B_0 is the rotational constant of the molecule.

Expression (8) corresponds to a single-quantum transition $j \to j-1$; expression (9) corresponds to a double-quantum transition $j \to j-2$; expression (10) corresponds to the exchange of a quantum between the molecules $j_1 \to j_1 - 1$, $j_2 \to j_2 + 1$, and vice versa. The first two expressions hold for collisions between a molecule and a molecule, and between a molecule and an atom.

To calculate the kinetics of rotational relaxation we need not the elementary collision probability but the probability as a function of the gas temperature, since in the overwhelming majority of cases of practical interest a Maxwell velocity distribution becomes established. We therefore averaged the collisional rotational transition probabilities over the quantum number of the relative system rotation, and over the energies of relative motion. Averaging over J was carried out assuming a Boltzmann distribution

$$P(j, E) = \frac{\sum_{J=0}^{\infty} P(j, J, E)(2J+1)\exp\left[-\frac{w_3(J)}{kT}\right]}{\sum_{J=0}^{\infty} (2J+1)\exp\left[-\frac{w_3(J)}{kT}\right]},$$

and then averaging over the energies

$$P(j, T) = \frac{1}{Z_0(T)}\int_0^{\infty} P(j, E)\, Z(E, T)\, dE,$$

where Z(E, T)dE is the number of collisions in unit time in the energy range from E to E+dE, and $Z_0(T)$ is the total number of collisions in unit time at a temperature T. Carrying out these averagings we obtain for single-quantum transitions

$$P_1(j, T) = \frac{64}{\sqrt{3}} \frac{Nd^2}{Z_0(T)} \frac{a^4}{\alpha B_0 \hbar}\left(\frac{D_1}{B}\right)^2 \frac{j^4}{2j-1} \exp\left[-\frac{3(aj)^{2/3}}{(kT)^{1/3}}\right], \tag{11}$$

and for double-quantum transitions

$$P_2(j, T) = \frac{72}{5\sqrt{3}} \frac{Nd^2}{Z_0(T)} \frac{a^4}{\alpha B_0 \hbar}\left(\frac{D_2}{B}\right)^2 \frac{j(j-1)(2j-1)^2}{2j+1} \exp\left[-\frac{3[a(2j-1)]^{2/3}}{(kT)^{1/3}}\right] \tag{12}$$

and for the change in the internal energy of both molecules (for a single quantum)

$$P_{11}(j_1, j_2, T) = \frac{64 \cdot 201}{\sqrt{3} \cdot 405} \frac{N_{j_2} d^2}{Z_0(T)} \frac{a^4}{\alpha B_0 \hbar}\left(\frac{D_3}{B}\right)^2 \frac{j_1 j_2 (j_1 - j_2 - 1)^3 (2j_2 + 1)}{(2j_1+1)(2j_2+1)(2j_2-1)} \exp\left\{-\frac{3[a|j_1 - j_2 - 1|]^{2/3}}{(kT)^{1/3}}\right\} \exp\left[-\frac{2B_0(j_2+1)}{kT}\right]. \tag{13}$$

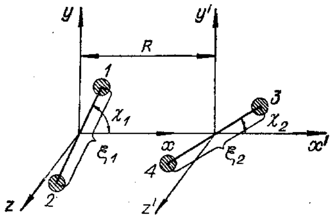

Fig. 1

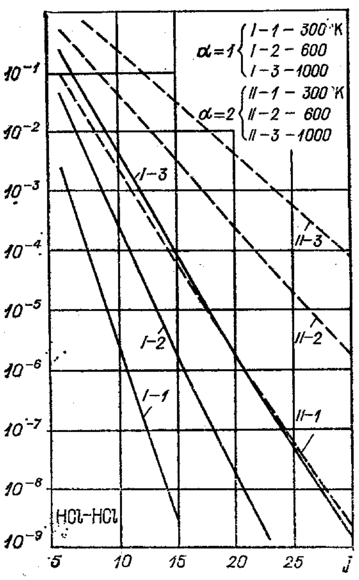

Fig. 2

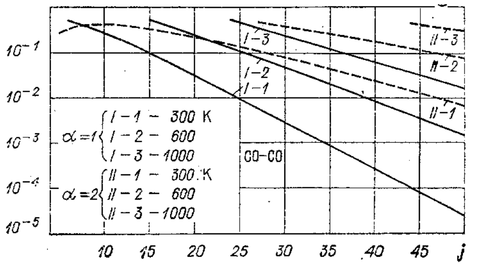

Fig. 3

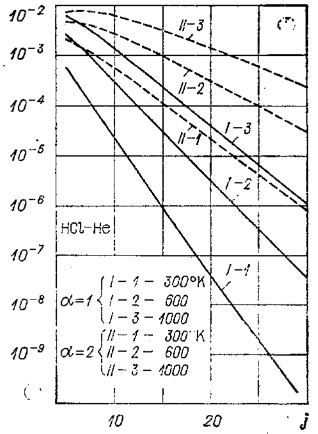

Fig. 4

In expressions (11)-(13) M, B_0B, D_1, D_2, D_3 have their previous meanings, N is the particle density, d is the diameter of the gas-kinetic cross section of the molecule, and $a = \pi\beta_0\sqrt{2M}/\alpha\hbar$.

Equation (13) corresponds to the case $\Delta j_1 = -1$, $\Delta j_2 = +1$. It is obvious that the probability of this transition will be a maximum when $j_2 + 1 = j_1$. In this case Eq. (13) is inapplicable and the probabilities must be calculated directly from Eq. (10).

Let us consider the choice of the parameters A_{ik} and α in the expression for the potential, since they largely determine the values of the probabilities. The numerical values of A_{ik} were taken from experimental data on the scattering of molecular beams [5]. One is not justified in choosing α from these experiments because of the large difference in the energy of relative motion of the particles in the experiments with beams, and in gas relaxation. We consider that the most reliable method of choosing α is by comparing the number of collisions calculated using the collisional rotational transition probabilities with experimental data on the number of collisions Z_{rot} necessary to establish equilibrium with respect to the rotational degrees of freedom. Such a comparison between the experimental and theoretical number of collisions Z_{rot} at different temperatures makes the choice of the values of α and A_{ik} more definite. The present lack of experimental data on the temperature dependence of Z_{rot} in mixtures of diatomic polar dipole molecules with inert gases makes such an analysis impossible without carrying out additional experiments.

To illustrate the method we made numerical calculations of the collisional rotational transition probabilities for the interaction of HCl–HCl, HCl–He, and CO–CO at temperatures of 300, 600, and 1000°K for the two values $\alpha = 1$ and 2 Å^{-1} The results are shown in the form of graphs in Figs. 2-4. We used the following numerical values of the quantities in the calculations: $B_0 = 21 \cdot 10^{-16}$ and $3.83 \cdot 10^{-16}$ erg, $\xi = 1.27 \cdot 10^{-8}$, and $1.13 \cdot 10^{-8}$ cm for HCl and CO; for the mixture HCl−HCl we took $A_{11} = 10^{-10}$, $A_{12} = 10^{-9}$, and $A_{22} = 10^{-8}$ erg; for HCl−He we took $A_{13} = 1.4 \cdot 10^{-10}$ and $A_{23} = 7 \cdot 10^{-9}$ erg; and for CO−CO we took $A_{11} = A_{12} = A_{22} = 10^{-8}$ erg. Since all the equations were obtained in the first approximation of perturbation theory, i.e., they only hold when the square of the modulus of the matrix element is less than unity, this imposes limitations on the energy of relative motion of the colliding particles, and on the number of rotational levels.

The curves shown in the figures terminate at values of the collisional rotational transition probabilities of the order of $^1/_2$. The calculation of probabilities close to unity is a strong-coupling problem and requires a more rigorous calculation as described in [3]. The almost exponentially falling curves as a function of the number of the rotational level is common to all the collisional rotational transition probabilities; it is due to the increase in the energy gap between the rotational levels. The value of this gap is determined by the rotational constant B_0, so that for CO which has a smaller rotational constant, the slope of the curves is less than for HCl and for mixtures of HCl−He. When the temperature is increased the collisions become more effective in the sense of energy transfer from the rotational degrees of freedom to translational degrees of freedom, which agrees with the temperature dependence of the probabilities of vibrational transitions obtained by Landau and Teller.

We will briefly consider the accuracy of the results obtained for the collisional vibrational transition probabilities using this method. As already noted, the values of the probabilities depend to a considerable extent on the interaction potential, and the final result depends not so much on the form of the potential as on the value of the constants A_{ik} and α. It is best to improve the accuracy of the method with respect to the form of the potential, the averaging method, etc. after reliable experimental data becomes available on the temperature dependence of Z_{rot}.

It is clear that any further improvement in the method will not lead to any appreciable change in the dependence of the collisional vibrational transition probabilities on the rotational quantum number j first obtained in this paper.

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