Vibrational exchange and its effect on the transport properties of spherical-top molecules

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(Submitted 5 March 1985)
Zh. Eksp. Teor. Fiz. **89**, 1941–1950 (December 1985)

The effect of a vibrational level degeneracy on excitation and momentum transfers between nonpolar spherical-top molecules, caused by a dipole-dipole interaction, is analyzed in the approximation of rectilinear trajectories. The V-V exchange constants and the increments to the transport scattering cross sections are calculated.

A number of various problems involving the effect of radiation on molecules, some which are of considerable interest, involve collisions between molecules excited by a laser beam. Interest in these questions stems from both conventional problems [research on collisional line shapes,[1,2] on collisional relaxation (*V-T* and R-T processes),[3,4] and on resonant exchange (V-V and R-R processes)[4,5]] and problems which have arisen with the advent of lasers, e.g., photoinduced collisions (i.e., collisions of molecules in the presence of an intense laser field[6,7]), photoinduced drift,[8,11] laser thermodiffusion,[12,14] and their analogs.[15]

In the present paper we study the effect of a level degeneracy on collision processes in molecules. We consider collisions which occur at distances greater than the gas-kinetics distances and in which one of the molecules is vibrationally excited. The trajectories of these molecules differ slightly from those of molecules which are not excited by a change in the dipole-dipole interaction.

The total rotational angular momentum ($\mathbf{J}_\Sigma$) of the system of two molecules and its projection M_Σ are conserved in the scattering. Since the interaction between the molecules is weak, the absolute values of the rotational angular momenta of each of the colliding molecules, $|\mathbf{J}_0|$ and $|\mathbf{J}_1|$, are also conserved. As a result, the angular-momentum difference $\mathbf{J}_p = \mathbf{J}_0 - \mathbf{J}_1$ is conserved in absolute value, while its projection onto the coordinate axis before the collision ($m = M_0 - M_1$) will generally differ from that ($m' = M_0' - M_1'$) after the collision.

The dipole-dipole interaction is weak at long range, and its energy is smaller than the difference between the energy of the state of the molecules with the rotational quantum numbers J_0 and J_1 and the energies of their states with quantum numbers differing by unity, $J_0 \pm 1$, $J_1 \mp 1$. Nevertheless, this interaction basically determines the probability for *V-V* exchange, and for molecules with inversion symmetry it may even play the decisive role in the change in the scattering cross section upon vibrational excitation. In other words, in a collision of molecules there is an interaction between two levels which are $(2J_p + 1)$-fold degenerate in m,

$$|0, J_0, M_0;\ 1, J_1, M_1\rangle \rightleftharpoons |1, J_0, M_0';\ 0, J_1, M_1'\rangle,$$
$$M_1 + M_0 = M_1' + M_0' = M_\Sigma,$$

with energies which are equal or approximately equal (when the vibrational-rotational interaction is taken into account). This interaction might be called a "Q-Q encounter transition" in the course of which there is a change in the projection of the difference between rotational angular momenta. In this situation, the relaxation-time model which is ordinarily used must be rejected since it is derived under the assumption that the quantum states are isolated.[16] It thus becomes necessary to use a dynamic description of the processes of interest which occur in systems with degenerate levels. Our purpose in the present paper is thus to describe the effect of spectrum degeneracy on V-V exchange and on the change in the transport cross section upon excitation of one of the colliding molecules.

After an average is taken over the rotational states, this problem becomes equivalent to that of finding four of the 2^8 matrix elements (in the two-level model) of the collision operator $\hat{R}(\mathbf{v}, \mathbf{v}', \mathbf{v}'', \mathbf{v}''')$ in the Boltzmann equation of motion for the velocity-dependent vibrational density matrix of the molecule, $\rho_{n,p}$:

$$(\mathbf{v}\nabla\rho_{n,p}) + \frac{\partial\rho_{n,p}}{\partial t} = -\frac{i}{\hbar}[\hat{H}, \hat{\rho}] + \sum_{k',s'}\Big\{\int R^{k,s,l,f}_{k',s',n,p}\rho_{k,s}(\mathbf{v}'')\rho_{l,f}(\mathbf{v}''')\,d\mathbf{v}''d\mathbf{v}''' - \sum_{k,l,s,f}\int R^{k',s',n,p}_{k,s,l,f}\rho_{k',s'}(\mathbf{v}')\rho_{n,p}(\mathbf{v})\,d\mathbf{v}'\Big\}, \tag{1}$$

where $\hat{H}$ is the Hamiltonian of the molecule. Specifically, we are interested in the matrix elements

$$R^{1100}_{1100}, R^{0011}_{0011}, R^{1100}_{0011}, R^{0011}_{1100}.$$

Two of them,

$$R^{0011}_{0011}(\mathbf{v}, \mathbf{v}', \mathbf{v}'', \mathbf{v}'''), \quad R^{1100}_{1100}(\mathbf{v}, \mathbf{v}', \mathbf{v}'', \mathbf{v}'''),$$

determine the probability for changes in the velocities $\mathbf{v}''$ and $\mathbf{v}'''$ of the colliding molecules by $\mathbf{v}'$ and $\mathbf{v}$ while the level of excitation of each of the molecules is conserved. These probabilities give for the scattering cross sections of the excited molecules expressions which differ from the unexcited-molecules scattering cross section defined by the quantity

$$R^{0000}_{0000}(\mathbf{v}, \mathbf{v}', \mathbf{v}'', \mathbf{v}'''),$$

because of the change in the dipole-dipole interaction upon excitation of one of the molecules. It is this difference in

0038-5646/85/121119-06$04.00

transport cross sections which is the object of our study. The probability for vibrational exchange is described by two other matrix elements:

$$R_{0011}^{1100},\ R_{1100}^{0011}.$$

As we have already mentioned, in a collision of an excited molecule with an unexcited molecule there is an interaction only between a pair of levels,

$$|0, J_0, M_0; 1, J_1, M_1\rangle, \quad |1, J_0, M_0'; 0, J_1, M_1'\rangle.$$

These levels are degenerate in the projection of the difference between the angular momenta of the molecules, so that for a description of the collision process it is more convenient to use quantum numbers corresponding to the sum of the angular momenta (J_Σ, M_Σ) and the difference between the angular momenta (J_p, m) rather than the quantum numbers corresponding to the rotational states of each of the molecules. In the basis of the quantum numbers J_Σ, J_p, M_Σ, m the interaction occurs between states

$$|0, 1, J_\Sigma, J_p, M_\Sigma, m\rangle, \quad |1, 0, J_\Sigma, J_p, M_\Sigma, m'\rangle.$$

We denote the first of these states by $|m\rangle$, the second by $|m'\rangle$, and their wave functions by $\tilde{\psi}_m(t)$ and $\tilde{\psi}_{m'}(t)$, respectively. For these states we can write a Schrödinger equation

$$i\dot{\tilde{\psi}}_m=\Delta_m\tilde{\psi}_m+\sum_{m'} V_m{}^{m'}(t)\,\tilde{\psi}_{m'},$$

$$i\dot{\tilde{\psi}}_{m'}=\Delta_{m'}\tilde{\psi}_{m'}+\sum_{m} V_{m'}{}^{m}(t)\,\tilde{\psi}_m, \quad \hbar=1. \tag{2}$$

Here Δ_m and Δ_m' are the energies of the $2(2J_p+1)$-fold degenerate states $|m\rangle$ and $|m'\rangle$ in the case of noninteracting molecules which are separated by a large enough distance.

The energies $\Delta_{m'}$ and Δ_m may differ in origin. For molecules of a common isotopic composition, all the Δ_m and $\Delta_{m'}$ are equal if the vibrational-rotational interaction is ignored. Allowance for centrifugal elongation in spherical symmetric molecules causes the values of Δ_m, which are equal to each other, to begin to differ from the values of $\Delta_{m'}$, which are also equal to each other. An external field may lift the degeneracy in m and in m'. In a collision of molecules of different isotopic composition, the absolute value of the difference between Δ_m and $\Delta_{m'}$ may be one or two orders of magnitude greater than the vibrational-rotational interaction.

The interaction between molecules is described by the dipole-dipole interaction operator $\hat{V}(R(t))$, which depends on the distance $R(t)=(b^2+v^2t^2)^{1/2}$ and whose matrix elements can be written

$$V_m{}^{m'}(t)=\left\langle m\,\middle|\,\frac{\hat{\boldsymbol{\mu}}_0\hat{\boldsymbol{\mu}}_1-3(\mathbf{n}(t)\hat{\boldsymbol{\mu}}_0)(\mathbf{n}(t)\hat{\boldsymbol{\mu}}_1)}{R^3(t)}\,\middle|\,m'\right\rangle, \tag{3}$$

where $\mathbf{n}(t)$ is the unit vector along the direction between the molecules, $\hat{\mu}_0$ and μ_1 are the dipole-moment operators, v is the relative-approach velocity of the molecules, and b in the minimum distance between the colliding molecules (the impact parameter). Expression (3) means that the transition matrix element can be written in the form

$$\begin{aligned}
&V_m{}^{m'}(t)\\
&=R^{-3}(t)\{\langle 0, J_0, M_0|\mu_0{}^x|1, J_0M_0'\rangle\langle 1, J_1, M_1|\mu_1{}^x|0, J_1, M_1'\rangle\\
&+\langle 0, J_0, M_0|\mu_0{}^y|1, J_0, M_0'\rangle\langle 1, J_1, M_1|\mu_1{}^y|0, J_1, M_1'\rangle\\
&+\langle 0, J_0, M_0|\mu_0{}^z|1, J_0, M_0'\rangle\langle 1, J_1M_1|\mu_1{}^z|0, J_1\, M_1'\rangle\\
&-3[\langle 0, J_0, M_0|\mu_0{}^x|1, J_0, M_0'\rangle\langle 1, J_1, M_1|\mu_1{}^x|0, J_1, M_1'\rangle\cos^2\chi_1\\
&+\langle 0, J_0, M_0|\mu_0{}^y|1, J_0, M_0'\rangle\langle 1, J_1, M_1|\mu_1{}^y|0, J_1, M_1'\rangle\sin^2\chi_1\\
&+(\langle 0, J_0, M_0|\mu_0{}^x|1, J_0, M_0'\rangle\langle 1, J_1, M_1|\mu_1{}^y|0, J_1, M_1'\rangle\\
&+\langle 0, J_0, M_0|\mu_0{}^y|1, J_0, M_0'\rangle\\
&\times\langle 1, J_1, M_1|\mu_1{}^x|0, J_1, M_1'\rangle)\sin\chi_1\cos\chi_1]\},
\end{aligned} \tag{4}$$

where the x axis is directed along the relative-velocity vector of the particles, the y axis is perpendicular to x in the plane of the collision, and χ_1 is the angle between the x axis and the line joining the centers of the molecules. Expression (4) relates the matrix elements of the probabilities for collisional transitions in a system of two molecules with the matrix elements of the dipole-moment operator, which is responsible for the vibrational-rotational transitions of the molecules upon irradiation.

If the matrix elements in (4) are averaged over the collision directions, i.e., if it is assumed that the vector connecting the centers of the molecules at the time of their closest approach is oriented in a random way in space, and if we also average over the directions of the total angular momentum $\mathbf{j}_\Sigma$, i.e., over M_Σ, we find that the expectation value of each matrix element is zero. We can thus use statistical methods similar to those of Refs. 17 and 18 to solve our problem. When we take this approach, we find that the leading role is played by the mean square interaction matrix element $\langle[V_m^{m'}(R)]^2\rangle^{1/2}$, which depends on only the distance between molecuiles.

If the number of exchanges of quanta during the collision is much smaller than $2(2J_p+1)$, the statistics of the matrix elements does not play an important role, and the calculations can be simplified by using the Wigner distribution function of matrix elements.[17,18] It should be noted that Eq. (2) is a system of linear differential equations with time-dependent coefficients. For convenience in solving our problem we assume that the interaction $V(t)$ is nonzero for only a certain bounded time interval T. We introduce a frequency corresponding to T: $\Omega=2\pi/T$. This assumption allows us to use the method of quasienergy states[19,20] to solve Eq. (2), without any loss of generality[1)]; i.e., we can write the functions $\tilde{\psi}$ and the interaction as Fourier series,[2)]

$$\tilde{\psi}_m=\sum_k \psi_m{}^k(t)\,e^{ik\Omega t}, \quad \tilde{\psi}_{m'}=\sum_{k'} \psi_{m'}{}^{k'}e^{ik'\Omega t}, \tag{5}$$

$$V_m{}^{m'}(t)=g_m{}^{m'}\sum_{k''} G_{k''}e^{ik''\Omega t}, \tag{6}$$

and reduce Eq. (2) to a system of equations which is of large dimensionality but whose coefficients are independent of the time. The initial conditions on Eq. (2) are taken into account:

$$\tilde{\psi}_0|_{t=t_0}=1; \quad \tilde{\psi}_m|_{t=t_0}=0, \quad m\neq 0; \quad \psi_{m'}|_{t=t_0}=0. \tag{7}$$

We take Fourier transforms for the resulting system of equations:

$$\varphi_m{}^k(\varepsilon)=\int_{-\infty}^{+\infty} e^{i\varepsilon t}\psi_m{}^k(t)\,dt, \qquad \overline{\varphi}_m{}^k(\xi)=\int_{-\infty}^{+\infty} e^{-i\xi t}\overline{\psi}_m{}^k(t)\,dt, \tag{8}$$

where the superior bar means complex conjugation.

We introduce the notation

$$\langle n|\hat{I}|n'\rangle=\delta_{n,\,n'}, \quad \langle n|\hat{B}|n'\rangle=n\delta_{n,\,n'}, \quad \langle n|\hat{G}|n'\rangle=G_{n-n'} \tag{9}$$

with corresponding notation for the adjoint operators. After the Fourier transformation (8) the set of equations, with the initial conditions and the definitions in (9), reduces to a system of equations whose solution can be written as a power series in the interaction $\hat{g}\hat{G}$ (Refs. 17–20), where the operator $\hat{g}$ acts on the state of the system ($|m\rangle$, $|m'\rangle$), while $\hat{G}$ acts on the quasienergy variables.

Corresponding to each matrix $L_m^{m'}$ of the operator $\hat{L}$ upon the transformation to a quasienergy representation there is a large-dimensionality matrix: $L_m^{m'}\leftrightarrow L_{m,k}^{m',k'}$. The expression for L can be found by a method like that of Refs. 19 and 20, which allows us to ignore in the averaging operations all terms of the series except those which are quadratic in the interaction $\hat{g}\hat{G}$. To find the expectation value of the operator $\hat{L}$ it is necessary to follow the averaging operations with a multiplication of the matrix $L_{m,k}^{m',k'}$ from the left and the right by vectors $(\ldots, e^{ik\Omega t}\ldots)$ and $(\ldots, e^{-ik\Omega t}\ldots)$, to sum the resulting expressions over the system variables m and m′, and to take the inverse Fourier transforms subject to the initial conditions.

We seek the probability (ρ_{11}) that a molecule which is initially unexcited will be in a vibrationally excited state at the time t. Corresponding to the excitation probability ρ_{11} is the matrix

$$\hat{\Sigma}_1=\sum_{m'}\overline{\varphi}_{m'}{}^{k'}(\xi)\varphi_{m'}{}^{k'}(\varepsilon), \tag{10}$$

which could hardly be derived for the general case, but which can be derived in the two limiting cases: 1) The distance between the levels of the colliding molecules, or the characteristic frequency $\Omega_0\approx v/b$, is much greater than the interaction between molecules, $U\sim\mu^2/b^3$, i.e., the case $\Delta\gg U$ or $\Omega_0\gg U$. 2) The interaction between the molecules is much greater than the distance between levels, $U\gg\Delta$.

Under the condition $\Delta\gg U$ or $\Omega_0\gg U$, we need consider only the first nonvanishing term of the series

$$\hat{\Sigma}_{11}=\sum_{m'}\langle(g_0{}^{m'})^2\rangle\hat{H}_{m'}{}^{-1}(\varepsilon)\overline{\hat{H}}_{m'}(\xi)\hat{G}\overline{\hat{G}}\hat{H}_0{}^{-1}(\varepsilon)\overline{\hat{H}}_0{}^{-1}(\xi), \tag{11}$$

where

$$\begin{gathered}\hat{H}_{m'}(\varepsilon)=(\varepsilon-\Delta_{m'})\hat{I}+\Omega\hat{B}, \qquad \overline{\hat{H}}_{m'}(\xi)=(\xi-\Delta_{m'})\overline{\hat{I}}+\Omega\overline{\hat{B}},\\ \hat{H}_0(\varepsilon)=\varepsilon\hat{I}+\Omega\hat{B}, \qquad \overline{\hat{H}}_0(\xi)=\xi\overline{\hat{I}}+\Omega\overline{\hat{B}}.\end{gathered} \tag{12}$$

After taking inverse Fourier transforms and summing over the quasienergy variables, using

$$\langle(g_0{}^{m'})^2\rangle=4\langle(\mu_0{}^{m'})^4\rangle/3b^6, \tag{13}$$

and taking the limits $t_0\to-\infty$ and $t\to+\infty$, we find

$$\rho_{11}=\frac{16}{3v^4b^2}\sum_{m'}\langle(\mu_0{}^{m'})^4\rangle\Delta_{m'}{}^2K_1\left(\frac{\Delta_{m'}b}{v}\right), \tag{14}$$

where $K_j(z)$ is a modified Bessel function. Integrating (14) over $2\pi bdb$, we find the cross section for the transfer of a vibrational quantum:

$$\sigma_{0,1}=\frac{16\pi}{3v^4}\sum_{m'}\langle(\mu_0{}^{m'})^4\rangle\Delta_{m'}{}^2\left[K_1{}^2\left(\frac{\Delta_{m'}b_1}{v}\right)+K_0{}^2\left(\frac{\Delta_{m'}b_1}{v}\right)\right] \tag{15}$$

where b_1 is the minimum possible impact parameter. It is found from the condition for the applicability of perturbation theory, but it cannot be smaller than the gas-kinetics diameter of the colliding molecules.

In the limit $\Omega_0\gg\Delta$ in which the reciprocal of the flyby time of the molecules past each other is greater than the distance between levels, we find

$$\sigma_{0,1}\approx\frac{16\pi}{3b_1{}^2v^2}\sum_{m'}\langle(\mu_0{}^{m'})^4\rangle. \tag{16}$$

If the distance between levels exceeds the reciprocal of the flyby time, $\Delta\gg\Omega_0$, we have

$$\sigma_{01}\approx\frac{16\pi}{3b_1v^3}\sum_{m'}\Delta_{m'}\langle(\mu_0{}^{m'})^4\rangle\exp\left(-\frac{2\Delta_{m'}b_1}{v}\right). \tag{17}$$

We recall that the subscript 0 labels one of the $2J_p=1$ possible initial states over which the averaging is to be carried out. For convenience we introduce the notation

$$\sum_{m'}\langle(\mu_0{}^{m'})^2\rangle=\langle(\mu_0{}^1)^2\rangle.$$

In both cases, (16) and (17), the cross section for the transfer of a quantum is proportional to the square of the interaction. This is a perfectly natural result, since in this limiting case we are considering only the first nonvanishing pertubation-theory term.

For the typical molecular parameter values $b_1=5$ Å, $\langle(\mu_0^1)\rangle=(0.3D)^2$, and $v=10^5$ cm/s, we find $\sigma_{01}=51.6$ Å^2 from (16). An estimate of the transfer cross section from (17) for quasiresonant vibrational exchange in a collision of molecules of different isotopic composition, for the case $\Delta_{m'}=\Delta=20$ cm^{-1}, $b_1=5$ Å, $\langle(\mu_0{}^1)^2\rangle=(0.3D)^2$, and $v=3\cdot10^4$ cm/s, yields $\sigma_{01}=9.2\cdot10^{-3}$ Å^2. In order to calculate the total cross section for the transfer of a vibrational quantum with $\Delta\approx20$ cm^{-1} and at small impact parameters, we need consider only Q-Q encounter transitions.

Up to this point we have been dealing with the case of a weak interaction. In the case in which the interaction between the molecules is substantially greater than the distance between levels ($U\gg\Delta$), we can simplify the original Schrödinger equation in order to find the probability for a transfer of excitation. Ignoring the terms $\Delta_m\tilde{\psi}_m$ and $\Delta_{m'}\tilde{\psi}_{m'}$, and noting that the system variables and the time variables are separated, we find

$$i\dot{\tilde{\psi}}_m=V(t)\sum_{m'}g_m{}^{m'}\tilde{\psi}_{m'}(t), \qquad i\dot{\tilde{\psi}}_{m'}=V(t)\sum_{m}g_{m'}{}^{m}\tilde{\psi}_m(t). \tag{18}$$

Transforming to the reduced time

$$\tau=\int_{-\infty}^{t} V(t_1)\,dt_1 \tag{19}$$

and using the solution methods described in Ref. 19, we find explicit expressions for ρ_{00} and ρ_{11}:

$$\rho_{00}={}^1/_2+J_1(z)/z,\ \ \rho_{11}={}^1/_2-J_1(z)/z,\ \ z=8\,({}^2/_3)^{1/2}\langle(\mu_m{}^{m'})^2\rangle\tau/b^3, \tag{20}$$

where $J_j(z)$ is a Bessel function. In the limit $t\to\infty$ we have $\tau\to 2b/v$ and

$$z(t\to\infty)=16\,({}^2/_3)^{1/2}\langle(\mu_m{}^{m'})^2\rangle/b^2v. \tag{21}$$

Expressions (20) and (21) reflect the circumstance that in the case of a strong interaction (small impact parameters and large matrix elements of the transition dipole moments) the probability for the transfer of a vibrational quantum is large. It follows from (20) that the cross section for the transfer of a quantum is given by

$$\delta\sigma_{01}=\pi\int_{b_1}^{b_2}[1-J_2(z)-J_0(z)]\,b\,db, \tag{22}$$

where the impact parameter b_1 is on the order of the gas-kinetics size of the molecule, and b_2 is the impact parameter at which the interaction between the molecules is comparable to the distance between levels, which we have ignored in Eq. (2):

$$({}^8/_3)^{1/2}\langle(\mu_m{}^{m'})^2\rangle/b_2{}^3=\Delta. \tag{23}$$

If the differences between Δ_m and $\Delta_{m'}$ are zero, the integration in (22) can be extended to $-\infty$. Noting that the probability for a transfer of excitation during the collision cannot exceed unity, we can set the lower limit of the integration in (23) equal to zero; we then find the following expression for the total cross section for a resonant transfer of a vibrational quantum:

$$\sigma_{01}=32\,({}^2/_3)^{1/2}\pi\langle(\mu_m{}^{m'})^2\rangle/3\hbar v. \tag{24}$$

It follows from (24) that the cross section for the resonant transfer of a vibrational quantum does not depend on the size of this quantum. We put (24) in the form

$$\sigma_{01}=64\left(\frac{2}{3}\right)^{1/2}\frac{\pi}{3}\pi\lambda^2\frac{\langle(\mu_m{}^{m'})^2\rangle/\lambda^3}{\hbar\omega v/c}, \tag{25}$$

where λ is the radiation wavelength corresponding to this vibrational transition, of frequency ω. The cross section for the transfer of a vibrational quantum is proportional to the product of the square of the corresponding wavelength and the ratio of the interaction between molecules at a distance equal to this wavelength to the Doppler broadening.

In the case of an interaction of a vibrationally excited molecule having a rotational quantum number J_1 and an unexcited molecule having a rotational quantum number J_0, the distance between levels is determined by the vibrational-rotational interaction:

$$\Delta(J_1,\ J_0)=\alpha B(J_1-J_0)(J_1+J_0-1), \tag{26}$$

where αB is the constant of the vibrational-rotational interaction.

If the square of the distance b_2 in (23), over which the interaction between the molecules is equal to the distance Δ in (26), is substantially smaller than the cross section for the transfer of excitation in the purely resonant case, the cross section for the transfer of excitation is

$$\sigma_{01}\approx\pi b_2{}^2/2. \tag{27}$$

The rate constant K, for the transfer of a quantum, if given by

$$K(T_t,T_r)=\int_0^\infty dv\int_0^\infty dJ_0\int_0^\infty dJ_1\sigma(J_0,J_1,v)\,vf(v,T_t)f_1(J_1T_r)f_1(J_0,T_r), \tag{28}$$

were $f(v,\ T_t)$ is the velocity distribution of the molecules: $f_1(J_j,T_r)$ is the distribution of molecules in rotational states; $J=0,1$; and T_t and T_r are the translational and rotational temperatures.

For an ideal gas at thermodynamic equailibrium in terms of the rotational and translational degrees of freedom at $kT_r\gg B$, where B is the rotational constant, and using the relation

$$\frac{[\langle(\mu_m{}^{m'})^2\rangle(\alpha B)^2]^{1/3}}{v}\left(\frac{2kT_r}{B}\right)^{2/3}\gg 1,$$

which holds for molecules with characteristic parameter values $B=0.1\ \text{cm}^{-1}$, $\alpha B=0.001\ \text{cm}^{-1}$, $\langle(\mu_m^{m'})^2\rangle=(0.3D)^2$ and $T_r=T_t=300$ K, we find from (28)

$$K(T_t,T_r)\approx\frac{9\pi^2\cdot 3^{1/6}e^{-5/2}}{2}\left(\frac{8kT_t}{\pi m_1}\right)^{1/2}\left[\frac{\langle(\mu_m{}^{m'})^2\rangle B}{kT_r(\alpha B)}\right]^{2/3}, \tag{29}$$

where m_1 is the reduced mass of the colliding molecules, and k is the Boltzmann constant. If $T_r=T_t=T$, then we have $K\propto T^{-1/6}$, and for $m_1=50$ a.u. we have

$$K(T)=5{,}3\cdot 10^{-10}(300/T)^{1/6}\ \text{cm}^3/\text{s}\,.$$

The average cross section for the transfer of a quantum is

$$\sigma_{01}{}^c=K(T)\,(8kT/\pi m_1)^{-1/2}=150\,(300\,T)^{2/3}[\text{Å}^2].$$

At $T=300$ K, the cross section $\sigma_{01}{}^c$ is nearly four times smaller than the cross section for the purely resonant case.

It follows from the condition for the applicability of the semiclassical approach that under the condition $U>\Omega_0$ we can use equations from classical mechanics to find the increment in the transport cross section, $\delta\sigma_{\text{tr}}$:

$$\delta\sigma_{\text{tr}}=2\pi\int_{b_1}^{b_3}[1-\cos\chi(b)]\,b\,db, \tag{30}$$

where b_3 is the impact parameter at which we have $U(b_3)=v/b_3$, and χ is the angle made with the x axis. Noting that χ is small, we can write $\chi=\delta P_{\text{cl}}/P_0$ where δP_{cl} is the classical momentum which is acquired (the momentum transfer) in the direction perpendicular to the initial relative velocity (along the y axis), and P_0 is the momentum of the particle with respect to the scattering center. For small values of χ, the expression for $\delta\sigma_{\text{tr}}$ simplifies:

$$\delta\sigma_{\mathrm{tr}}\approx\pi\int_{b_1}^{b_3}\left(\frac{\delta P_{\mathrm{cl}}}{P_0}\right)^2 b\,db. \tag{31}$$

At small values of δP_{cl} we can also assume

$$(\delta P_{\mathrm{cl}})^2\approx\langle(\delta M/b)^2\rangle\approx\langle(\delta S_0/b)^2\rangle, \tag{32}$$

where δS_0 is the change in the action.

Let us consider the case in which the condition $U>\Omega_0$ holds and the distance between levels is greater than the interaction: $\Delta > U$. In this case we can write

$$\langle(\delta S_0)^2\rangle\approx\langle\delta S_0\rangle^2,\qquad \delta S_0\approx\int_{-\infty}^{t}\langle U(t_1)\rangle dt_1. \tag{33}$$

The quantity $\langle U(t)\rangle$ corresponds to the operator in the quasienergy representation, written as the sum $\hat{\Sigma}_{\langle U\rangle}$, for which the first nonvanishing term of the series in the magnitude of the $\hat{g}\hat{G}$, is written

$$\hat{\Sigma}^{1}_{\langle U\rangle}=\sum_{m'}\langle(g_0{}^{m'})^2\rangle[\hat{H}_{m'}^{-1}(\varepsilon)+\overline{\hat{H}}_{m'}^{-1}(\xi)]\hat{G}\overline{\hat{G}}\hat{H}_0{}^{-1}(\varepsilon)\overline{\hat{H}}_0{}^{-1}(\xi). \tag{34}$$

We carry out the same operations with $\hat{\Sigma}^{1}_{\langle U\rangle}$ as we did with $\hat{\Sigma}_{11}$; we find

$$\langle U(t)\rangle=4\langle(g_0{}^{m'})^2\rangle V(t)\int_{-\infty}^{t}V(t_1)\sin\Delta(t-t_1)dt_1. \tag{35}$$

With $\Delta=0$ we have $\langle U(t)\rangle=0$; the expectation value of the momentum transfer is zero in the case of an exact resonance. This result reflects the fact that in a single interaction between molecules having a random distribution of vibration phases the momentum transfer can be of either sign. From (32), (33), and (35) we find

$$\delta P_{\mathrm{cl}}(t\to\infty)=\frac{4\langle(g_0{}^{m'})^2\rangle}{h}\int_{-\infty}^{\infty}dt\,V(t)\int_{-\infty}^{t}dt_1V(t_1)\sin\Delta(t-t_1). \tag{36}$$

From (31) and (36) we find an estimate of the increment in the transport scattering cross section:

$$\pi b^2\frac{64[\langle(\mu_0{}^{m'})^2\rangle]^4}{45E^2\Delta^2b_1{}^{12}}\left[1-\left(\frac{b_1}{b_3}\right)^{10}\right]>\delta\sigma_{\mathrm{tr}}\geqslant\pi b_1{}^2\frac{\pi^2[\langle(\mu_0{}^{m'})^2\rangle]^4}{40E^2\Delta^2b_1{}^{12}}\left[1-\left(\frac{b_1}{b_3}\right)^{10}\right] \tag{37}$$

where E is the kinetic energy of the molecule with respect to the center of mass.

If we are interested in the change in the transport properties of the molecules in a mixture of isotopes, we can substitute some typical molecular parameter values [$b_1=4$ Å, $E_0=10^{-13}$ erg, $(\mu_0^{m'})^2=(0.3D)^2$, and $\Delta=20\ \mathrm{cm}^{-1}$] into (37); we find $b_3=5.8$ Å, and $\pi b_1^2\cdot 3.3\cdot 10^{-5}>\delta\sigma_{\mathrm{tr}}\geqslant\pi b_1^2\cdot 5.7\cdot 10^{-6}$. In other words, the change in the transport cross section due to the vibrational excitation of one of the molecules is exceedingly small.

As we mentioned earlier, the expectation value of the momentum transfer is zero in the case $\Delta=0$. The physical meaning of this result is that there are equal probabilities for the acquisition of momenta in the positive and negative directions along the y axis. In other words, in calculating the increments in the transport cross sections in this case it is necessary to consider only those terms which correspond to even powers of the momentum.

If the condition $U>\Omega_0$ holds and the distance between levels is substantially smaller than the interaction, we have

$$\langle(\delta S_0)^2\rangle\approx\langle(U)^2\rangle\tau^2, \tag{38}$$

where τ is the reduced time given in (19). To find the expectation value of the square of the interaction, we sum all orders of perturbation theory in $\hat{g}$ (Ref. 19). Since the vibrational phases of the molecules, the directions of their dipole moments, and the directions of the line connecting the centers of the molecules are all random, the summation leaves only the even-powered terms of the Fourier transforms of the interaction operators, as we just mentioned. The set of these terms transforms into a finite algebraic expression for the Fourier transform of the quantity corresponding to $\langle(U)_2\rangle$. Taking the inverse Fourier transforms with the help of the expression corresponding to $\langle(U)^2\rangle$, as we did in finding ρ_{11} and ρ_{00}, we find

$$\langle(U)^2\rangle=2\langle(g_m{}^{m'})^2\rangle. \tag{39}$$

From (31), (32), and (39) we find

$$\delta\sigma_{\mathrm{tr}}\approx\frac{2\pi b_1{}^2}{3}\frac{[\langle(\mu_m{}^{m'})^2\rangle]^2}{E^2b_1{}^6}\left[1-\left(\frac{b_1}{b_3}\right)^4\right]. \tag{40}$$

The increment in the transport scattering cross section is thus directly proportional to the gas-kinetics scattering cross section multiplied by the ratio of the squares of the energy of the dipole-dipole interaction at the distance b_1 to the energy of the kinetic motion of the colliding particles. Expression (40) holds for both $\Omega_0>\Delta$ and $\Omega_0<\Delta$. With $E=10^{-3}$ erg, $\langle(\mu_m^{m'})^2\rangle=(0.3D)^2$, $b_1=4$ Å, and $v=3\cdot 10^4$ cm/s, we find $b_1/b_3=0.22$, and the change in the transport cross section for these parameter values is $\delta\sigma_{\mathrm{tr}}\approx 10^{-4}\pi b_1^2$. In our case we have $b_1=4$ Å and $\delta\sigma_{\mathrm{tr}}\approx 5.1\cdot 10^{-3}$ Å^2, which is substantially smaller than the gas-kinetics cross section.

These results show that the transfer of a vibrational quantum is a very efficient process in the resonant case. At velocities $\sim 10^4$ cm/s the cross section for the transfer of a quantum is more than several hundred square angstroms.

Averaging the cross section (24), for the resonant transfer of a quantum over the velocities, we find the quantum transfer constant to be

$$K=32(2/3)^{1/2}\pi\langle(\mu_m{}^{m'})^2\rangle/3\hbar v,$$

and independent of T. Allowance for the vibrational-rotational interaction makes the constant of the resonant transfer of a quantum slightly dependent on the temperature: $K\propto T^{-1/6}$. The reason for this behavior is that the rotational numbers of the colliding molecules become progressively more different as T increases, and the resonant nature of the vibrational transition is disrupted.

If the distance between levels exceeds the dipole-dipole interaction, the increment to the cross section for the transfer of a quantum is substantially smaller than the gas-kinetics dimensions of the molecules. At $E \gg \Delta > U$, this process is dominated by collisions with impact parameters on the order of or smaller than the gas-kinetics dimensions of the molecules. In calculating the cross sections for the transfer of a quantum at $b < b_1$ we need to consider transitions other than $Q \leftrightarrow Q$ encounter transitions.

Significantly, the increments in the transport scattering cross sections are small even for the purely resonant case. The reason for this result is that the dipole-dipole interaction of nonpolar molecules, one of which is excited, is small in comparison with the kinetic energy of these molecules at room temperature. The existence of a level spacing greater than the interaction causes the increment in the transport cross section to become even smaller [see (37)]. If the level spacing is a few reciprocal centimeters, the increment in the transport cross section will not exceed a few hundredths of 1% at typical values of the molecular parameters

We wish to thank N. V. Karlov and Yu. N. Petrov for a discussion of this study.

[1)] Since the time interval T is arbitrary, as are the derivatives of arbitrary order of the interaction at the ends of this interval.

[2)] In writing expression (6) we have taken into account the circumstance that the variables of the system (m and m') and the variables of the harmonics (k'') have been separated. This separation is a consequence of the dependence of the effect on the mean square matrix element of the interaction operator.

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Translated by Dave Parsons