On the theory of vibration-rotation excitation of molecules

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The transition of translational energy into rotation and vibration excitation in molecular collisions is considered. A modification of the sudden perturbation method is employed, it being assumed that the transition-inducing interaction is not small. In this way it is possible to increase considerably the range of collision velocities for which the transition probability and cross section can be calculated explicitly. The probability for rotational excitation of molecules under the action of a short light pulse is also calculated.

A semiclassical approach, first suggested by Zener[1], can be used in many problems of inelastic collision theory. The relative motion of the colliding particles is considered classically, while their internal degrees of freedom are described quantum-mechanically, The problem of inelastic collisions is thus reduced to a problem of quantum transitions under the action of nonstationary perturbations. The probabilities for these transitions can be calculated only for a few cases. One of them occurs when perturbation theory is applicable, for which it is necessary that the condition $V\tau \ll 1$ be satisfied, where V is the characteristic magnitude of the perturbation and τ is its duration (the collision time). Another example is the adiabatic situation, when the condition $\omega\tau \gg 1$ (the Massey criterion) is satisfied, where ω is a characteristic frequency corresponding to the internal motion of the colliding particles.

In the adiabatic approximation, however, the problem cannot be solved in general form (unlike perturbation theory) and it is necessary to introduce additional simplifications, such as strong coupling between two states, simulation of the functional dependence of the quasi-molecular terms on the internuclear distances, etc. At the same time physical situations occur in which neither the Massey criterion nor the applicability condition of perturbation theory are satisfied. Most sensitive in this sense are inelastic collisions with excitation of vibrational and rotational molecular degrees of freedom or transitions between highly excited atomic states.

We consider one concrete example in detail. In collisions of charged particles with molecular dipoles, an important role is played by the long-range part of the interaction potential, which in atomic units is of the form

$$V = \mathbf{dR}(t)/R^3(t), \tag{1}$$

where d is the dipole moment and $\mathbf{R}(t)$ is the vector of relative motion. In the straight-line trajectory approximation $\mathbf{R} = \boldsymbol{\rho} + \mathbf{v}t$ (ρ is the impact parameter and v is the collision velocity). The probability of rotational-level excitation can then be calculated by perturbation theory if $\int V dt \ll 1$, i.e., $\rho \gg d/v$. The adiabatic approximation is satisfied for $\rho \gg Mv$ since $\omega_{\text{rot}} \sim 1/M$ where M is the reduced mass of the molecule. Thus, for velocities satisfying the condition $1/M \ll v \ll d$ a wide range of impact parameters is excluded from consideration.

In this paper we use a modified sudden-perturbation method, which is valid for $\omega\tau \ll 1$ independently of the value of the interaction, i.e., $v\tau$ is not necessarily small. As will be shown, this allows us to extend considerably the range of velocities in which the transition probability between rotational levels can be calculated explicity. The method proposed is similar to the impulse approximation in scattering theory[2,3].

We start from the nonstationary Schrödinger equation

$$i\dot{\Psi} = \hat{H}_0\Psi + \hat{V}(t)\Psi \tag{2}$$

and introduce a new unknown function defined by

$$\Psi = T\exp\left(-i\int_{t_0}^{t}\hat{V}\,dt\right)\varphi,$$

where T is the time-ordering symbol. For the function φ we obtain the equation

$$i\dot{\varphi} = \left[T\exp\left(-i\int_{t_0}^{t}\hat{V}\,dt\right)\right]^{+}\hat{H}_0 T\exp\left(-i\int_{t_0}^{t}\hat{V}\,dt\right)\varphi. \tag{3}$$

We assume that the perturbation $\hat{V}(t)$ has the form of a short pulse, so that as $\omega\tau \to 0$ we obtain in fact in the right-hand side of (2) a term proportional to $\hat{P}\delta(t)$:

$$\hat{P} = \int_{-\infty}^{+\infty}\hat{V}\,dt.$$

In Eq. (3) for the function φ, however, the coefficients are finite despite the discontinuity at $t = 0$, and therefore the function φ itself is discontinuous at this point. The relation between the values of the wave function Ψ before and after the perturbation is hence easily obtained:

$$\Psi(t \to +0) = e^{-i\hat{P}}\Psi(t \to -0). \tag{4}$$

Thus, if the system was in state Ψ_i prior to the collisions, the probability amplitude of exciting the n-th level equals

$$a_n = \int \Psi_n^*(q)\, e^{-i\hat{P}(q)}\Psi_i(q)\,dq, \tag{5}$$

where q is the set of internal coordinates of the colliding particles.

A function similar to (4) was used by Mizushima[4] to calculate collision widths of spectral lines. Mizushima's derivation, however, seems to us unsatisfactory, as it is based on assuming that $\hat{H}_0$ and $\hat{V}$ commute.

Several cases are known when the time-dependent Schrödinger equation has an accurate solution, for example, an oscillator acted upon by a variable external force and a two-level system, if the time dependence of the nondiagonal matrix element has the form of a rectangular pulse[1)]. In all these cases Eq. (5) coincides with the limiting values of the exact expressions as $\omega\tau \to 0$. The order of magnitude of the corrections depends on the pulse shape: for an oscillator acted upon by an external force this correction is of order $(\omega\tau)^2$ for a Gaussian pulse shape and of order $\omega\tau$ for a Lorentzian shape. The model of an oscillator acted upon by an external force pulse f(t) was used by Osipov and Stupochenko[5] to calculate the probability of molecular vibrational excitation in head-on collisions. In this case $\hat{P}$ in (5) equals

$$x\int_{-\infty}^{+\infty} f\,dt$$

(x is the vibrational coordinate), and Eq. (5) gives then the result of ref. 5. As mentioned already, however, this model permits an accurate solution independently of the magnitude of $\omega\tau$.

We consider now specific applications of Eq. (5).

1. Rotational-level excitation of diatomic dipolar molecules in collisions with heavy charged particles.

a) The rigid rotator approximation. As will be seen from the results, the excitation cross section is large in comparison with the atomic cross section, therefore the long-range part of the interaction (Eq. (1)) plays the principal role. The quantity P equals

$$P = \frac{2d}{\rho v}\cos\frac{\mathbf{d}\rho}{d\rho}.$$

Let the initial state correspond to a Σ-term and to a zero rotational number. A selection rule for the azimuthal quantum number, $\Delta M_K = 0$, follows from the expression for P. For the excitation probability of the K-th rotational level we obtain the equation

$$W_{0K} = (2K+1)\frac{\pi}{2\lambda}J^2_{K+1/2}(\lambda), \qquad \lambda \equiv \frac{2d}{\rho v}, \tag{6}$$

where J is a Bessel function.

At large values of λ (the case opposite to the applicability condition of perturbation theory), levels with $K \sim \lambda$ are most effectively excited. This is seen from (6) since W_{0K} has a maximum at $K \sim \lambda$. The total rotational level excitation probability equals

$$\sum_{K=1}^{\infty} W_{0K} = 1 - \frac{\sin^2\lambda}{\lambda^2}.$$

The condition $\omega\tau \ll 1$ implies that Eq. (6) is valid only if K satisfies the inequality $K \ll Mv/\rho$. The integrals determining the excitation cross section of rotational levels converge for $\rho \sim d/v$ if $K \geq 2$. Thus, when the condition $Mv^2/d \gg 1$ is satisfied there exists a large number of rotational states, transitions into which are described by Eq. (6). Integrating over the impact parameter, we find the cross section σ_{0K}:

$$\sigma_{0K} = 2\pi\int_0^{\infty} W_{0K}\rho\,d\rho = \frac{8\pi}{3}\left(\frac{d}{v}\right)^2\frac{(2K+1)}{K(K-1)(K+1)(K+2)}, \quad K = 2, 3, \ldots. \tag{7}$$

As to the excitation cross section of K = 1 levels, the corresponding integral in W_{01} diverges logarithmically at the upper limit. This means that in this case large ρ, for which the suddenness criterion $\omega\tau \ll 1$ is violated, play an essential role. When, however, the already mentioned criterion $Mv^2/d \gg 1$ is satisfied the applicability regions of Eq. (6) and perturbation theory overlap, since the first is applicable at $\rho \ll Mv$ and the second at $\rho \gg d/v$.

The cross section σ_{01} evaluated by perturbation theory diverges logarithmically at the lower limit. To take correct account of all contributions we proceed as follows. We choose R for which the inequalities

$$R \gg d/v, \quad R \ll v/\omega_{rot} \sim Mv$$

are satisfied and in the integral with respect ρ we substitute $W_{01}(\rho)$ from (6) in the interval [0, R], and use the expression obtained for the probability from perturbation theory in the region [R, ∞]. Owing to the overlap of the applicability regions the quantity R drops out from the result. After rather cumbersome calculations we obtain

$$\sigma_{01} = \frac{8\pi}{3}\left(\frac{d}{v}\right)^2\left\{\ln\frac{v^2}{\omega_{rot}d} + C + \frac{7}{4} - \ln 2\right\}. \tag{8}$$

Here C is Euler's constant, and ω_{rot} is the rotational transition frequency between the zeroth and first level.

It is seen from Eqs. (7) and (8) that the cross section is large when $d^2/v^2 \gg 1$. Impact parameters large in comparison with the molecule dimensions play then an important role, and this justifies the asymptotic form of the interaction (1). All conditions used above are, thus, compatible in the velocity range $d/M \ll v^2 \ll d^2$.

b) Rotating harmonic oscillator. If the condition $\omega\tau \ll 1$ is also satisfied with respect to the vibrational frequencies, Eq. (5) can be used to obtain rotational-vibrational molecule excitations. In this case the quantity P is of the form

$$P = \frac{2d_e}{\rho v}\left(1 + \frac{x}{r_e}\right)\cos\frac{\mathbf{n}\rho}{\rho}, \tag{9}$$

where x is the vibrational coordinate, d_e is the dipole moment at the equilibrium internuclear distance denoted by r_e, and n is a unit vector along the molecular axis.

The probability amplitude of the (0, 0) → (K, n) transition integrated with respect to the vibrational coordinate is of the form

$$a_{00}^{Kn} = \frac{1}{2}\left[\frac{(2K+1)2^n}{n!}\right]^{1/2}\int_{-1}^{+1} P_K(z)\left(\frac{z}{\nu}\right)^n \exp\left\{-i\lambda_e z - \frac{z^2}{\nu^2}\right\}dz. \tag{10}$$

Here $\lambda_e \equiv 2d_e/\rho v$, $\nu \equiv r_e(M\omega_e)^{1/2}\rho v/d_e$, n is the vibrational quantum number, ω_e is the vibrational frequency, and $P_K(z)$ is a Legendre polynomial. The general analysis of Eq. (10) is quite difficult, therefore we investigate below some special cases.

If n = 0, we deal with purely rotational transitions. In this case expression (10) differs from the corresponding equation for a rigid rotator by the factor $\exp(-z^2/\nu^2)$ under the integral sign. For $\rho \sim d_e/v$ (exactly such ρ are significant in the integral that determines the cross section), however, the argument of this exponential is of order $1/\nu^2 \sim 1/M\omega_e^2 \sim 1/M^{1/2}$. Thus, the results of the preceding section are reproduced with relative accuracy $1/M^{1/2}$.

Let now $n \neq 0$. Two characteristic dimensions relative to the parameter ρ compete in Eq. (10):

$$\rho_1 \sim d_e/v, \quad \rho_2 \sim d_e/r_e v M^{1/4}.$$

They are found from the relationships $\lambda_e \sim 1$ and $\nu_e \sim 1$. If ρ of the order of ρ_1 are significant, one can put in (10) $\exp(-z^2/\nu^2) \approx 1$ and obtain

$$|a_{00}^{Kn}|^2 = \frac{2^n\pi}{n!}\left(\frac{d_e^2}{M\omega_e\rho^2 v^2 r_e^2}\right)^n\left(K + \frac{1}{2}\right)\left[\frac{\partial^n}{\partial\lambda_e^n}\frac{J_{K+1/2}(\lambda_e)}{\lambda_e^{1/2}}\right]^2. \tag{11}$$

It follows from the properties of the asymptotic expansion of the Bessel function if that such an approximation is valid $\rho_1/K \gg \rho_2$, i.e., $K^2 \ll M^{1/2}$. This implies that the rotational energy is much smaller than the distance between vibrational levels. Equations for the cross section then follow from (11):

$$\sigma_{00}{}^{01} = \pi d_e{}^2 / M\omega_e v^2 r_e{}^2,$$

$$\sigma_{00}{}^{K1} = \frac{2\pi}{3} \frac{(2K+1)}{(K-1)(K+2)} \frac{d_e{}^2}{M\omega_e v^2 r_e{}^2}, \quad K = 2, 3 \ldots . \tag{12}$$

The $(0, 0) \rightarrow (1, 1)$ transition is a special case because of the logarithmic divergence of the cross section at large ρ. Proceeding as in the preceding section, one can match Eq. (11) with the expression that follows from perturbation theory. The expression for the cross section σ_{00}^{11} is of the form

$$\sigma_{00}{}^{11} = \frac{4\pi d_e{}^2}{3M\omega_e v^2 r_e{}^2} \left[\ln \frac{v^2}{\Omega d_e} + C + 8 - 6 \ln 2 + \frac{1}{6} \right], \tag{13}$$

where $\Omega = \omega_{et}\, \omega_{rot}$. The matching condition is determined in this case by the inequality $M^{1/2}v^2 \gg 1$. When this condition is fulfilled the cross section determined by Eqs. (12) and (13) is less than unity on the atomic scale. This, however, does not contradict the applicability of Eq. (1), since large ρ ($\rho \sim d_e/v$), as usual, contribute significantly to the cross section. The small cross section is due to the low transition probability $|a_{00}^{K1}|^2 \sim 1/M^{1/2}$. Expressions (12) and (13) are thus asymptotically accurate in the region $d_e^2 \gg v^2 \gg d_e/M^{1/2}$, $K^2 \ll M^{1/2}$.

We find next the total vibrational excitation probability W_0^n, equal to

$$\sum_{K=0}^{\infty} |a_{00}{}^{Kn}|^2.$$

This can be performed at any ratio of ρ_1 and ρ_2, since expression (10) has the form of the function

$$(z/\nu)^n \exp\{-i\lambda_e z - z^2/\nu^2\}$$

expanded in Legendre polynomials:

$$W_0{}^n = \sum_{K=0}^{\infty} |a_{00}{}^{Kn}|^2 = \frac{2^n}{n!} \int_0^1 \frac{z^{2n}}{\nu^{2n}} \exp\left(-\frac{2z^2}{\nu^2}\right) dz. \tag{14}$$

The corresponding total cross section equals

$$\sigma_0{}^n = \frac{2\pi}{3} \frac{1}{n(n-1)} \frac{d_e{}^2}{M\omega_e v^2 r_e{}^2}, \quad n = 2, 3 \ldots . \tag{15}$$

At $n = 1$ the asymptotic form of $W_0^1(\rho)$ as $\rho \rightarrow \infty$ is

$$W_0{}^1 \approx 2d_e{}^2 / 3r_e{}^2 M\omega_e v^2 \rho^2. \tag{16}$$

This coincides with the asymptotic expression for $|a_{00}^{11}|^2$ as $\rho \rightarrow \infty$; consequently, the divergence of σ_0' is due to the divergence of one term of the series

$$2\pi \sum_{K=0}^{\infty} \int |a_{00}{}^{1K}|^2 \rho\, d\rho,$$

corresponding to $K = 1$. Replacing this term with the expression for σ_{00}^{11} in (13), we obtain the correct equation for the total excitation cross section of the first vibrational level

$$\sigma_0{}^1 = \frac{4\pi}{3} \frac{d_e{}^2}{M\omega_e v^2 r_e{}^2} \ln \frac{v^2 (M\omega_e)^{1/4} r_e}{\Omega d_e} + \frac{1}{3} + \frac{C}{2} - \frac{\ln 2}{2} \Big]. \tag{17}$$

The following comments must be made in connection with Eq. (17). $W_0^1(\rho)$ reaches its asymptotic form at $\rho \gtrsim \rho_2$, whereas $|a_{00}^{11}|^2$ can be replaced by its asymptotic expression at $\rho \lesssim \rho_1 \gg \rho_2$. In the region $\rho_1 > \rho > \rho_2$ the relation $W_0^1 \gg |a_{00}^{11}|^2$ holds. These quantities become comparable only at $\rho \sim \rho_1$ and are of the order of $1/M^{1/2}$. It follows therefore that, as usual, large ρ (of the order of $d_e/v \gg 1$) contribute appreciably to the cross section σ_0^1.

2. Rotational-level excitation by an ultrashort light pulse.

At the presently attainable durations of ultrashort pulses, $\tau \sim 10^{-12}$ sec, the criterion $\omega\tau \ll 1$ can be satisfied (with small margin, to be sure) for several molecular rotational transitions. For the CO_2 and I_2 molecules, for example, the transitions between the zeroth and second rotational levels correspond to $\omega_{rot}\tau \approx 0.4$ and 0.04, respectively, Since at realistic temperatures only a small fraction of the molecules is in the state $K = 0$, the process considered is not an effective mechanism for light-energy dissipation. It can, however, be detected in the emission of excited molecules in the frequency region corresponding to transitions between low rotational levels. As to vibrational transitions, the quantity $\omega_{vib}\tau$ can be large because the large ratio of the rotational and vibrational times (of the order of $M^{1/2}$).

The vibrations thus undergo adiabatic perturbations up to $\tau \sim 10^{-13}$–10^{-14} sec and their excitation is therefore of low probability. Since the characteristic wavelength of light is much larger than the dimension of the molecule, the electric field of the wave can be assumed to be quasistationary:

$$\mathbf{E}(t) = \mathbf{e}E_0(t) \cos \omega_0 t,$$

where $\mathbf{e}$ is the polarization vector, E_0 is the amplitude of the wave, and ω_0 is the wave frequency. In reality ω_0 lies in the infrared or visible red region and is, consequently, much smaller than electronic frequencies of the molecule. One can therefore use the expression for the interaction energy of a molecule with an electromagnetic wave, averaged over the electronic state:

$$V = \frac{1}{2} \alpha_{ik} e_i e_k E_0{}^2 \cos^2 \omega_0 t, \tag{18}$$

where α_{ik} is the polarizability tensor of the molecule.

Taking into account dispersion, α_{ik} must be replaced by

$$\frac{\partial}{\partial\omega_0} [\omega_0 \alpha_{ik}(\omega_0)]$$

(see[6]). If the molecule possesses a dipole moment, the corresponding interaction is of the form $\mathbf{d} \cdot \mathbf{e}E_0 \cos \omega_0 t$ and its contribution to the transition is negligibly small because of the fast oscillations (the characteristic dimension of $E_0(t)$ coincides with the pulse duration τ, which is assumed to be much smaller than ω_{rot}^{-1} but much larger than ω_0^{-1}). Only the constant component of (18) is important in the calculation of P.

For a linear or symmetric-top molecule, the tensor α_{ik} expressed in terms of the principal axes has only two independent components: $\alpha_{11} = \alpha_{zz} = \alpha_\perp$ and $\alpha_{33} = \alpha_\parallel$. Converting to the laboratory coordinate system and assuming linearly-polarized light, we obtain

$$P = \frac{1}{4} \alpha_{ik} e_i e_k \int_{-\infty}^{+\infty} E_0{}^2(t)\, dt = \gamma \cos^2 \theta,$$

$$\gamma = \frac{1}{4} (\alpha_\parallel - \alpha_\perp) \int_{-\infty}^{+\infty} E_0{}^2(t)\, dt. \tag{19}$$

(A term independent of ϑ was omitted from (19).) Only transitions satisfying the selection rules $\Delta M_K = 0$,

$\Delta K = \pm 2, \pm 4, \ldots$, are possible. For the transition amplitude we obtain

$$a_{0K} = (2i\gamma)^{K/2}(2K+1)^{1/2}\frac{(K-1)!!}{(2K+1)!!}F\left(\frac{K+1}{2}, K+\frac{3}{2}; i\gamma\right), \qquad (20)$$

where F is a confluent hypergeometric function. Choosing[2] $\tau \sim 10^{-12}$ sec and $|\alpha_{\parallel} - \alpha_{\perp}| \sim 1$ to 10, we obtain $\gamma \gtrsim 1$ for $E_0 \gtrsim (2-5)\times 10^7$ V/cm^2. Since field intensities attained in a pulse can exceed this figure, it is sensible to investigate Eq. (20) for both small and large γ.

If $\gamma \ll 1$, the transition probability equals

$$W_{0K} \approx (2\gamma)^K (2K+1)\left[\frac{(K-1)!!}{(2K+1)!!}\right]^2.$$

For $\gamma \gg 1$ and $K \lesssim \gamma^{1/2}$ we have

$$W_{0K} \approx \frac{\pi}{4}\frac{(2K+1)}{\gamma}\left[\frac{(K-1)!!}{K!!}\right]^2$$

It is seen from the last equation that W_{0K} is practically independent of K up to $K \sim \gamma^{1/2}$. It can be shown that at $K \gg \gamma$ the quantity W_{0K} decreases like $2(\gamma e/2K)^K/K$.

In conclusion we emphasize that the problem considered in this paper is solvable neither by perturbation theory nor in the adiabatic approximation, since it is required to calculate the K-th term of a Born series to find W_{0K}, and in the adiabatic theory one is restricted to a small number of strongly bound states. Obviously, only in the region where (5) is applicable can one obtain an answer in simple analytic form. In several cases one can find asymptotically accurate equations for the cross section by using the overlap of the applicability regions of the sudden-action approximation and perturbation theory.

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[1] In the first case $\hat{P}(q)$ is simply a c-number and in the second case a two-row matrix.

[2] For CO$_2$, for example, $\alpha_{\parallel} - \alpha_{\perp} = 16.8$ a.u.

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