

ELASTIC AND QUASIELASTIC SCATTERING OF NEUTRONS BY MOLECULES

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Neutron scattering cross sections of molecules are calculated for the case when the imparted energy is of the order of the mean difference between the rotational energy levels of the molecule and is much smaller than the mean thermal excitation energy of the molecule. The quasiclassical representation of rotational wave functions is employed in the calculations. Freely rotating molecules which possess the properties of a linear or spherical rotator, and arbitrary molecules with a preferred axis of free or hindered rotation, are considered.

THE purpose of this paper is a theoretical study of the scattering of neutrons by molecules in the region of relatively small energy and momentum transfers, where the major role is played by elastic processes or transitions between neighboring rotational energy levels. It is assumed that the average distance $\bar{\epsilon}$ between the rotational energy levels of the molecule are much smaller than the energy T of its thermal excitation. For most molecules this assumption, as is well known, is already satisfied even at normal temperatures.

Let us discuss briefly certain peculiarities of the processes that occur in the energy-transfer region under consideration, that is, when

$$\epsilon \sim \bar{\epsilon}, \quad \bar{\epsilon} \ll T. \quad (1)$$

They are obviously characterized by a small change of the internal energy of the molecule. For this reason, they can naturally be called quasielastic processes. Another peculiarity of the processes in question is that their duration $\tau_{\text{coll}} \sim \hbar/\epsilon$ coincides in order of magnitude with the period of rotation of the molecule $\tau_{\text{rot}} \sim \hbar/\bar{\epsilon}$ (we use throughout a system of units in which the Planck and Boltzmann constants are assumed equal to unity).

Under such conditions of "unique resonance" of the times τ_{coll} and τ_{rot} , we can expect the greatest manifestation of the singularities of the rotational motion of the molecules in the corresponding neutron scattering spectrum, as is confirmed by the concrete calculations presented below for freely rotating molecules, and also for molecules with internal hindered motion.

SCATTERING OF NEUTRONS BY FREELY ROTATING MOLECULES

Under condition (1) there is no need for using the rigorous quantum-mechanical methods developed in the papers of Schwinger and Teller,^[1] Goryunov^[2] and Rahman.^[3] They would call for cumbersome numerical calculation (such as carried out by Griffing^[4] for the methane molecules). It is more convenient to carry out the calculations approximately, using from the very outset the approximations connected with the quasiclassical character of rotation of the molecules in the initial and in the final states. We note that the assumption of classical rotation of the molecules was used by Sachs and Teller^[5] and by Krieger and Nelkin^[6] in calculations of the scattering cross sections under conditions of large transfer of rotational energy $\epsilon \gg \bar{\epsilon}$. The case $\epsilon \gg \bar{\epsilon}$ was investigated also by Zemach and Glauber^[7] and by Volkin.^[8] For $\epsilon \gg \bar{\epsilon}$ the collision process is essentially classical. In contrast, in the case which we are considering ($\epsilon \sim \bar{\epsilon}$), the collision process has essentially a quantum-mechanical character in spite of the quasiclassical character of the rotational motion of the molecule. This is a very important circumstance for the calculations that follow.

We shall assume in the calculation, as usual, that the rotational and vibrational degrees of freedom of the molecule are independent. In accordance with this and also with the circumstance that when $\epsilon \sim \bar{\epsilon}$ the transferred energies are much smaller than the distance between the vibrational energy levels so that vibrational transitions are excluded, the differential cross section for neu-

tron scattering per unit interval of the angles θ and of the energies ϵ can be written in the form

$$\frac{d^2\sigma}{d\epsilon d\theta} = \sum_{\nu\nu'} a_\nu a_{\nu'} \frac{k_1}{k_0} \int w_{\text{rot}}^{\nu\nu'}(\epsilon_r, \kappa) \times w_{\text{tran}}(\epsilon_t, \kappa) \delta(\epsilon - \epsilon_r - \epsilon_t) d\epsilon_r d\epsilon_t, \quad (2)$$

where $a_\nu a_{\nu'}$ is the product of the amplitudes for scattering by nuclei ν and ν' , averaged over the spin variable of the neutron and the nuclei of the molecule, and k_0 and $k_1 = k_0 - \kappa$ are the neutron momenta before and after scattering. In this expression the probability of a process that is elastic with respect to the lattice vibrations is taken equal to unity. It can be shown that in the region of the "single-quantum" transitions this is valid with accuracy $\bar{E}^3/E_{\text{vib}}T \ll 1$, where E_{vib} is the average vibrational energy of the atoms.

The probability w_{tran} in free translational motion of the molecule (its mass is designated by M_0) is given by the well known formula^[7]

$$w_{\text{tran}} = \left(\frac{M_0}{2\pi T \kappa^2} \right)^{1/2} \exp \left[- \frac{(\epsilon_t - \kappa^2/2M_0)^2 M_0}{2T \kappa^2} \right]. \quad (3)$$

To find the probability w_{rot} of the rotational transition, let us consider a molecule possessing the properties of a symmetrical top. The quantum-mechanical state of the symmetrical top is given, as is well known, by the total angular momentum L , its projection M on some stationary axis, and the projection K on the symmetry axis of the molecule. The quasiclassical representation of the wave function can be readily seen from the corresponding Schrödinger equation, and is equal to

$$\psi_{\text{rot}} = \sqrt{\frac{2}{\pi}} \frac{1}{\sin \theta} p^{-1/2} \sin \left[\int_{\theta_0}^{\theta} p d\theta + \frac{\pi}{4} \right] \frac{1}{\sqrt{2\pi}} e^{iM\varphi} \frac{1}{\sqrt{2\pi}} e^{iK\psi},$$

$$p = (L^2 \sin^2 \theta - K^2 - M^2 - 2KM \cos \theta)^{1/2} / \sin \theta,$$

$$p(\theta_0) = 0, \quad (4)$$

θ , φ , and ψ are the Euler angles.

We consider quasielastic scattering, in which the rotational state of the molecules changes insignificantly, that is, the changes in the quantum numbers l (for the momentum L) and k (for the momentum projection K) are small: $l \ll L$, $k \ll K$. The integral $\int p d\theta$ has a large absolute magnitude. Therefore in calculating the matrix elements

$$M_{\text{rot}} = \int \psi_{\text{rot}}'^* e^{i\kappa\rho} \psi_{\text{rot}} d\Omega \quad (d\Omega = \sin \theta d\theta d\varphi d\psi) \quad (5)$$

(ψ_{rot} and ψ_{rot}' are the wave functions for the initial and final states) it is necessary to use the expression

$$M_{\text{rot}} = \frac{1}{\pi} \int \frac{1}{p \sin \theta} \cos \left[\int_{\theta_0}^{\theta} (p' - p) d\theta \right] e^{i\kappa\rho} e^{ik\psi} d\Omega, \quad (6)$$

where

$$p' - p = \frac{Ll}{p} - \frac{K + M \cos \theta}{p \sin^2 \theta} k,$$

$$\kappa\rho = \kappa\rho_z \cos \theta + \kappa\rho_\perp \sin \theta \sin \psi,$$

$$\rho_\perp = \sqrt{\rho^2 - \rho_z^2},$$

ρ_z is the projection of the vector ρ , which joins the center of gravity at the center of the molecule and the scattering atom, on the symmetry axis of the molecule. We note that when using expression (6), we must obviously assume that $\kappa < p$.

If we use the variable

$$y = \arcsin \frac{b+t}{a}; \quad a = \left[\left(1 - \frac{K^2}{L^2} \right) \left(1 - \frac{M^2}{L^2} \right) \right]^{1/2},$$

$$b = \frac{KM}{L^2},$$

we can rewrite the integral in (6) in the form

$$M_{\text{rot}} = e^{-i\kappa\rho_z b} \frac{1}{2\pi^2} \int_{-\pi/2}^{\pi/2} \int_0^{2\pi} e^{i\kappa\rho_z a \sin y} \cos \left[ly - q(t(y)) + \frac{\pi}{2} l \right] \times \exp [i\kappa\rho_\perp \sqrt{1 - [t(y)]^2} \sin \psi + ik\psi] dy d\varphi,$$

$$q(t) = \int_{-a-b}^t \frac{1}{L} \frac{K + Mt}{\sqrt{a^2 - (b+t)^2}} \frac{dt}{1-t^2}. \quad (7)$$

The probability of rotational transition, which is proportional to the square of the matrix element (7) and to the distribution function of the rotational states, can be readily calculated in the following three important particular cases. We consider first incoherent scattering, that is, the terms with $\nu = \nu'$ in the sum (2).¹⁾ The results presented below describe scattering by one of the atoms of the molecule (we omit the index of the atom).

1. Diatomic and linear polyatomic molecules. The symmetry axis of the molecules lies along the line of the atoms. Therefore $K = 0$ and furthermore $\rho_z = \rho$ and $\rho_\perp = 0$. From (7) it follows immediately that

$$|M_{\text{rot}}|^2 = |J_l(\kappa\rho \sqrt{1 - M^2/L^2})|^2,$$

$J_l(z)$ is a Bessel function.

¹⁾For hydrogen-containing molecules, which are presently most intensely investigated, the interference scattering is the fundamental one.

Taking into account the distribution of the molecules over the rotational space.

$$W(L) = \frac{BL}{T} \exp\left(-\frac{BL^2}{2T}\right), \quad B = \frac{1}{I},$$

where I is the moment of inertia of the molecule, we readily obtain for the elastic scattering:

$$w_{\text{rot}}^0 = f_0(\kappa\rho) \quad (8)$$

and for the inelastic scattering with change of the quantum number L by an amount l (l —positive or negative integer):

$$w_{\text{rot}}^l = \frac{|\varepsilon_r|}{BTl^2} \exp\left(-\frac{\varepsilon_r^2}{2BTl^2}\right) f_l(\kappa\rho), \quad (9)$$

where

$$f_l(\kappa\rho) = \int_0^1 |J_l(\kappa\rho\sqrt{1-x^2})|^2 dx. \quad (10)$$

The function $f_l(\kappa\rho)$ for $l = 0, 1$, and 2 is shown in Fig. 1.

When $\kappa\rho \gg 1$ we have $f_l = 1/2\kappa\rho$. In this case the probability of energy transfer is given by the formula

$$w_{\text{rot}} = \frac{1}{2\kappa\rho} \left(\frac{\pi}{2BT}\right)^{1/2}, \quad (11)$$

which coincides with the Krieger-Nelkin formulas^[6] for $B(\kappa\rho)^2 < T$, and $\varepsilon \ll T$,²⁾ made more accurate by a more rigorous averaging of the classical scattering cross section over the molecular orientations.

In the region of greatest interest $\kappa\rho \sim 1$, where the quantum effect comes significantly into play, the experiment that determines energy-transfer probability $w(\varepsilon)$ is in fact represented by only two or three terms of w_{rot}^l in (9). Substituting (9) in (2) we obtain after integration of the following expression for the experimentally observed doubly differential cross section of neutron scattering

$$\begin{aligned} \frac{d^2\sigma}{d\varepsilon d\Omega} &= a^2 \frac{k_1}{k_0} \sum_{l \geq 0} \left[f_l(\kappa\rho) - \frac{1}{2} \delta_{0l} f_0(\kappa\rho) \right] \frac{2}{\sqrt{\pi}} \frac{1}{\alpha^2 + \beta^2} \\ &\times \left\{ \beta \exp\left[-\frac{\alpha_l^2 \tilde{\varepsilon}^2}{\beta^2(\alpha_l^2 + \beta^2)}\right] + \sqrt{\pi} \frac{\alpha_l \tilde{\varepsilon}}{\sqrt{\alpha_l^2 + \beta^2}} \right. \\ &\times \left. \operatorname{erf}\left[\frac{\alpha_l \tilde{\varepsilon}}{\beta \sqrt{\alpha_l^2 + \beta^2}}\right] \right\} \exp\left[-\frac{\tilde{\varepsilon}^2}{\alpha_l^2 + \beta^2}\right]. \quad (12) \end{aligned}$$

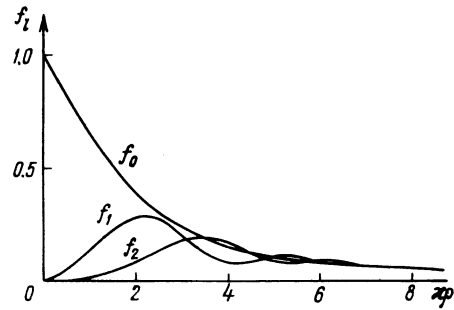


FIG. 1. Neutron scattering cross sections (9) and (18) vs. momentum transfer κ for the elastic process (f_0) and for the inelastic single-quantum (f_1) and two-quanta (f_2) rotational transitions in the molecule.

In this formula

$$\alpha_l = \sqrt{2BTl^2}, \quad \beta = \sqrt{2T\kappa^2/M_0}, \quad \tilde{\varepsilon} = \varepsilon - \frac{\kappa^2}{2M_0},$$

$$\operatorname{erf} x = \frac{2}{\sqrt{\pi}} \int_0^x e^{-t^2} dt, \quad \delta_{0l} = 1 \text{ for } l = 0$$

and $\delta_{0l} = 0$ for $l \neq 0$.

2. Molecules having symmetrical-top properties. This class includes the regular-tetrahedral molecules (CH_4 , CCl_4 , etc.). The distribution function of the molecules relative to the rotational states is in this case

$$W(L) = \frac{4}{\sqrt{\pi}} L^2 \left(\frac{B}{2T}\right)^{3/2} \exp\left(-\frac{BL^2}{2T}\right).$$

The quantization axis connected with the molecules can always be chosen such as to pass through the scattering atom. Therefore, just as in the preceding case, we have $\rho_z = \rho$ and $\rho_{\perp} = 0$. However, the square of the matrix element, which has for the spherical-top molecule the form

$$|M_{\text{rot}}|^2 = \left| J_l \left(\kappa\rho \sqrt{\left(1 - \frac{M^2}{L^2}\right) \left(1 - \frac{K^2}{L^2}\right)} \right) \right|^2, \quad (13)$$

is averaged not only over M but also over K . Taking this into account, we obtain, after simple transformations, for elastic scattering

$$w_{\text{rot}}^0 = \varphi_0(\kappa\rho) \quad (14)$$

and for quasielastic scattering

$$w_{\text{rot}}^l = \frac{4}{\sqrt{\pi}} \frac{\varepsilon_r^2}{(2BTl^2)^{3/2}} \exp\left(-\frac{\varepsilon_r^2}{2BTl^2}\right) \varphi_l(\kappa\rho), \quad (15)$$

where

$$\varphi_l(\kappa\rho) = \int_0^1 J_l^2(\kappa\rho x) x K(\sqrt{1-x^2}) dx, \quad (16)$$

$K(z)$ is the complete elliptic integral of the first kind.

²⁾The condition $B(\kappa\rho)^2 < T$ is equivalent to the condition $\kappa < p$ which we are using.

The functions $\varphi_2(\kappa\rho)$ are essentially analogous to the functions $f_l(\kappa\rho)$ shown in Fig. 1. For large $\kappa\rho$ ($\kappa\rho \gg 1$) we have $\varphi_l = \pi/4\kappa\rho$ and upon summation of the partial contributions the probability of energy transfer goes over into (11). This is as it should be, for in the classical limit the probabilities of the rotational excitation are given by identical formulas for the linear and spherical rotators.

The experimentally observed differential cross section for neutron scattering by the spherical-top molecules is

$$\frac{d^2\sigma}{d\epsilon d\Omega} = a^2 \frac{k_1}{k_0} \sum_{l>0} \left[\varphi_l(\kappa\rho) - \frac{1}{2} \delta_{0l} \varphi_0(\kappa\rho) \right] \frac{4}{\sqrt{\pi}} (\alpha_l^2 + \beta^2)^{-3/2} \times \left[\frac{\beta^2}{2} + \tilde{\epsilon}^2 \frac{\alpha_l^2}{\alpha_l^2 + \beta^2} \right] \exp\left(-\frac{\tilde{\epsilon}^2}{\alpha_l^2 + \beta^2}\right). \quad (17)$$

The notation is the same as for formula (12). We emphasize once more that in the most interesting region ($\kappa\rho \sim 1$) it is sufficient to use in (17), just as in (12), only two or three terms of the series in l . We note that when $(\kappa\rho)^2 \ll 1$, formula (17) coincides with formula (2.7) obtained by Dzyub^[9] by another method.³⁾

3. Molecules and molecular groups having a preferred axis of rotation. We consider here the case when the moment of inertia corresponding to rotation of the molecule about some axis, say z , is much smaller than the other components of the moment of inertia, that is, $I_z \ll I_x, I_y$ or, if we introduce the characteristic distances between levels, $B_z \gg B_x, B_y$. Such a situation arises for molecules which are of great experimental interest, for example, dimethyl acetylene $H_3C-C \equiv C-CH_3$ (preferred axis along the line of the carbon atoms), the CH_3Cl molecules, etc., and also in rotation (if this rotation is free) of individual molecular groups, for example H_3O^+ , NH_4 in the molecules H_3OClO_4 , NH_4PH_6 , NH_4ClO_4 , etc.

If the energy transfers are chosen such that $\epsilon \sim \bar{B}_z$, then it is obvious that when the neutrons are scattered there will be a very limited number of transitions connected with the change in the state of rotation of the molecule about the z axis, and a large number of transitions for other rotation directions. Assume now that we are interested only in transition of the former type; then, summing over l in the square of the matrix element (7), we obtain

$$w_z^h = \left(\frac{2}{\pi B_z T k^2} \right)^{1/2} \exp\left(-\frac{\epsilon_z^2}{2B_z T k^2}\right) f_h(\kappa\rho_\perp). \quad (18)$$

Here ρ_\perp is the shortest distance from the atom to the z axis, and the function $f_h(\kappa\rho_\perp)$ is given by formula (10) (for $k = 0, 1, 2$, see also Fig. 1).

Formula (18), derived for symmetrical-top molecules, has in fact a general character and is valid under the condition $I_z \ll I_x, I_y$ for molecules of arbitrary type.

The dependence of the neutron-scattering cross section on the energy transfer in the region $\epsilon \sim \bar{B}_z$ is given when $\kappa\rho \sim 1$ (ρ is the distance from the center of gravity of the molecule to the scattering atom) by formula (18), since all the unaccounted for effects connected with the quantum structure of rotation of the molecule about the x and y axes are significant only in the region $\epsilon \sim \bar{B}_x, \bar{B}_y \ll \bar{B}_z$, which is very close to the elastic maximum. But if $\kappa\rho \gg 1$, then the contribution of the rotational transitions for the x and y axes must be taken into account. This can obviously be done in classical fashion. Thus, it is necessary to introduce into consideration a molecule that differs from the real one in having an infinite moment of inertia I_z about the z axis. If we now introduce, following Krieger and Nelkin,^[6] the effective masses of the atoms $M^{(0)}$ corresponding to such a molecule, we readily obtain from (2) the following formula for the neutron scattering cross section, which takes into account the quantum character of the excitation of the rotational state for the preferred axis:

$$\frac{d^2\sigma}{d\epsilon d\Omega} = a^2 \frac{k_1}{k_0} \sum_{h \geq 0} \left[f_h(\kappa\rho_\perp) - \frac{1}{2} \delta_{0h} f_0(\kappa\rho_\perp) \right] \times \frac{2}{\sqrt{\pi}} \frac{1}{\sqrt{\alpha_h^2 + \beta^2}} \exp\left(-\frac{\tilde{\epsilon}^2}{\alpha_h^2 + \beta^2}\right), \quad (19)$$

$$\tilde{\epsilon} = \epsilon - \kappa^2/2M^{(0)}, \quad \beta = \sqrt{2T\kappa^2/M^{(0)}}, \quad \alpha_h = \sqrt{2B_z T k^2}.$$

We now discuss the role of the interference determined by the contribution of the scattering of neutrons by different atoms of the molecule. As already mentioned, it is unnecessary to take into account interference for hydrogen atoms. Therefore formulas (12), (17), and (19) proposed above can be used directly for hydrogen-containing molecules. For other molecules, it is necessary to calculate in addition the interference terms $\sigma_{\nu\nu'}$, taking into account only the contributions of those atoms which are separated from one another by a distance such that $\kappa|\rho_\nu - \rho_{\nu'}| \lesssim 1$, since there is practically no interference in the opposite case $\kappa|\rho_\nu - \rho_{\nu'}| \gg 1$.

It is simplest to take into account interference

³⁾In the region $\kappa\rho \sim 1$ there is no agreement with the results of Dzyub^[9]. In our opinion this is due to the fact that his method cannot be used in the given momentum-transfer region.

in the case of diatomic and linear polyatomic molecules. The contribution due to scattering by the atoms ν and ν' is proportional to

$$a_\nu a_{\nu'} \int_0^1 J_l(\kappa \rho_\nu \sqrt{1-x^2}) J_l(\kappa \rho_{\nu'} \sqrt{1-x^2}) dx, \quad (20)$$

in lieu of the quantity $a_\nu^2 \int_0^1 J_l^2(\kappa \rho_\nu \sqrt{1-x^2}) dx$, as in the case of "direct" scattering by the atom ν (of ν'). We see that the character of the energy and the temperature dependences of the cross section remains the same as before when interference is taken into account.

For molecules with a preferred rotation axis, the cross section $\sigma_{\nu\nu'}$ is proportional to

$$a_\nu a_{\nu'} \int_0^1 J_k(\kappa \rho_{\nu\perp} \sqrt{1-x^2}) J_k(\kappa \rho_{\nu'\perp} \sqrt{1-x^2}) \times \cos[\kappa(\rho_{\nu z} - \rho_{\nu' z})x + k\Delta\psi_{\nu\nu'}] dx. \quad (21)$$

Here $\rho_{\nu z}$, $\rho_{\nu' z}$, $\rho_{\nu\perp}$, and $\rho_{\nu'\perp}$ are the projections of the vectors ρ_ν and $\rho_{\nu'}$ on the z axis and on the plane perpendicular to this axis, $\Delta\psi_{\nu\nu'}$ is the angle between the vectors ρ_ν and $\rho_{\nu'}$ and the plane perpendicular to the z axis.

For atoms lying in one plane (frequently only the contributions of these atoms must be taken into account), expression (21) simply becomes

$$a_\nu a_{\nu'} \cos(k\Delta\psi_{\nu\nu'}) f_k(\kappa \rho_\perp), \quad (22)$$

where $f_k(\kappa \rho_\perp)$ is given by (10). In this case, too, the interference can obviously change only the dependence of the cross section on the momentum transfer.

An analysis of neutron-scattering experiments is usually carried out by investigating the dependence of the cross section on the values of ϵ , κ , and T . Formulas (12), (17), and (19), and also the formulas which take into account the interference effect, give this dependence in a simple and very lucid form. It follows from them, in particular, that the most convenient from the point of view of investigation of the features of molecular rotation is the region of "single-quantum" transitions, that is, the region $0.5 < \kappa \rho < 3$. In this momentum-transfer region the cross section for energy transfer has a qualitative singularity (for example, a maximum), which depends essentially on how the molecules (or some other group of atoms of the molecule) rotate: in three, two, or only in one direction, and whether this rotation is free.⁴⁾ If the

rotation is not free, then formulas (12), (17), and (19) cannot be used directly but it is possible to use them, during the interpretation of the experiment, to draw qualitative conclusions concerning the degree of constraint of such a rotation.

DEGREE OF INTERNAL HINDERED ROTATION OF MOLECULES

At the present time, hindered rotation of molecules is the subject of intense experimental investigation (see, for example, the work of Janik et al.^[10, 11]). To this end one uses normally the region of relatively high energies and momentum transfers, in which the theoretical analysis, however, entails great difficulties. In most cases, therefore, conclusions concerning the character of the rotations of the molecules are qualitative in nature.

Let us see what information on the internal motion of the molecules can be extracted from quasi-elastic neutron scattering. We use in our analysis, as an example, a symmetrical-rotator molecule consisting of two parts with common rotation axis z . Their moments of inertia will be denoted I'_z and I''_z ($I'_z + I''_z = I_z$). As regards I_z we assume that $I_z \ll I_x, I_y$.⁵⁾

Let a neutron be scattered by one of the atoms of the molecular group with moment I'_z . In accordance with the usual prescription, we set up an expression for this part of the matrix element, which describes the transitions connected with the rotation of the molecule about the z axis (we recall that if $I_z \ll I_x, I_y$, then transitions along other rotation directions can readily be taken into account classically)

$$M_z = \int \psi_{\text{rot}}'^* e^{i\kappa \rho_\perp \sin \theta \sin \psi_1} \psi_{\text{rot}} d\psi_1 d\psi_2, \quad (23)$$

$$\psi_{\text{rot}} = \frac{1}{\sqrt{2\pi}} e^{iK\Phi} \Psi(\varphi), \quad (24)$$

where $\Psi(\varphi)$ describes the relative motion of two parts of the molecule. Going over in (23) to the variables Φ and φ

$$\psi_1 = \Phi - \frac{I''_z}{I_z} \varphi, \quad \psi_2 = \Phi + \frac{I'_z}{I_z} \varphi,$$

we obtain

$$M_z = J_k(\kappa \rho_\perp \sin \theta) \int \Psi'^*(\varphi) \exp\left(ik \frac{I''_z}{I_z} \varphi\right) \Psi(\varphi) d\varphi, \quad (25)$$

$$k = K' - K.$$

⁴⁾At the same time, in the energy region $\epsilon \sim T \gg \bar{B}$ the spectra for the scattering of neutrons by different molecules differ only quantitatively.

⁵⁾In the case $I'_z \ll I_z, I_x, I_y$ the results are valid for molecules of arbitrary type.

Thus, the dependence of the cross section on the momentum transfer is determined only by the type of transition in the molecule; it is given by the expression $|J_K(\kappa\rho_\perp \sin \theta)|^2$, averaged over the orientations of the z axis of the molecule. This is the function $f_K(\kappa\rho_\perp)$ shown in Fig. 1.

Inasmuch as the single-quantum transition ($k = 1$) is of greatest interest, we confine ourselves only to this case. As can be seen from (25), the probabilities of single-quantum transitions are proportional to the quantities

$$|M_z'|^2 = \left| \int \Psi'^*(\varphi) \exp\left(i\kappa \frac{I_z''}{I_z} \varphi\right) \Psi(\varphi) d\varphi \right|^2, \quad (26)$$

from which we can determine the properties of the wave functions, and from the latter, in turn, the features of the dynamics of the hindered rotations.

We calculate the matrix elements M_z' under the assumption that the internal motion is quasiclassical. We consider for simplicity the case $I_z' \ll I_z$, when the quantum numbers of internal rotation do not depend on K . This case occurs, for example, for the molecules CH_3CCl_3 etc.

The periodic hindering potential is chosen in the usual form

$$V = \frac{1}{2}V_0(1 - \cos n\varphi). \quad (27)$$

For excitation energies $E < V_0$ and $E > V_0$, respectively, the quasiclassical wave function is

$$\Psi(\varphi) = \left(\frac{2}{\pi} \frac{\omega I_z'}{p}\right)^{1/2} \sin \left[\int_{\varphi_0}^{\varphi} p d\varphi + \frac{\pi}{4} \right],$$

$$\Psi(\varphi) = \left(\frac{\omega I_z'}{2\pi p}\right)^{1/2} \exp \left\{ \int_0^{\varphi} p d\varphi \right\}, \quad (28)$$

where

$$p = \{2I_z'[E - \frac{1}{2}V_0(1 - \cos n\varphi)]\}^{1/2},$$

$$p(\varphi_0) = 0 \text{ for } E < V_0,$$

ω is the distance between the neighboring energy levels.

The transition between neighboring energy levels for $E < V_0$ will be calculated by means of the formula

$$\frac{\omega I_z'}{\pi} \int_{\varphi_0}^{\varphi} \cos \left[\int_{\varphi_0}^{\varphi} (p' - p) d\varphi \right] e^{i\varphi} \frac{d\varphi}{p}.$$

We introduce the variable t :

$$\int (p' - p) d\varphi \approx I_z' \omega \int \frac{d\varphi}{p} = \frac{\pi}{2} + \omega t;$$

and obtain for $E < V_0$ and $E > V_0$ respectively

$$M_z' = \frac{\omega}{2\pi} \int_{-\pi}^{\pi} \sin \omega t e^{i\varphi(t)} dt, \quad M_z' = \frac{\omega}{2\pi} \int_{-\pi}^{\pi} e^{-i\omega t + i\varphi(t)} dt. \quad (29)$$

For over-the-barrier motion, when the energy of the excited level E , measured from the minimum of the potential V (27), exceeds V_0 , that is, when $E > V_0$, we obtain $\varphi(t)$ from the relation

$$t = \frac{2}{n} \left(\frac{I_z'}{2E}\right)^{1/2} F\left(\frac{n\varphi}{2}, \sqrt{\frac{V_0}{E}}\right), \quad (30)$$

$F(k, x)$ is an elliptic integral of the first kind. The motion is periodic, with period

$$\tau = \frac{2\pi}{\omega} = \frac{8}{n} \left(\frac{I_z'}{2E}\right)^{1/2} F\left(\frac{\pi}{2}, \sqrt{\frac{V_0}{E}}\right), \quad (31)$$

ω is the difference between the energy levels.

It can be shown that in almost the entire region $E > V_0$ (with the exception of a very narrow energy band adjacent to V_0) the function $\varphi(t)$ can be described with good accuracy by the simple formula

$$\varphi(t) = \omega t + \frac{1}{2n} \frac{V_0}{E} \sin n\omega t. \quad (32)$$

Substituting (32) in (29) we get $|M_z'| = 1$, accurate to terms of order of smallness $(1/n)(V_0/4nE)^{2/n}$.

We now consider sub-barrier motion ($E < V_0$). The dependence of the angle φ on the time t is given by

$$t = \frac{2}{n} \left(\frac{I_z'}{2V_0}\right)^{1/2} F\left(\arcsin \sqrt{\frac{V_0}{E}} \sin \frac{n\varphi}{2}, \sqrt{\frac{E}{V_0}}\right). \quad (33)$$

The function $\varphi(t)$ obtained from (32) is periodic and has a period

$$\tau = \frac{2\pi}{\omega} = \frac{8}{n} \left(\frac{I_z'}{2V_0}\right)^{1/2} F\left(\frac{\pi}{2}, \sqrt{\frac{E}{V_0}}\right). \quad (34)$$

It is convenient to investigate this function by using a Fourier expansion in trigonometric functions. Analysis shows that $\varphi(t)$ can be described with good accuracy, in almost the entire region $E < V_0$, by the first term of the expansion

$$\varphi(t) = \alpha(E) \sin \omega t, \quad (35)$$

where $\alpha(E)$ can be taken to be

$$\alpha(E) = \frac{2}{n} \left[\arcsin \sqrt{\frac{E}{V_0}} + 0.2 \left(\frac{E}{V_0}\right)^4 \right], \quad (36)$$

that is, a quantity close to the classical oscillation amplitude.

Substituting (35) in (29) we obtain for the transitions between the sub-barrier energy levels

$$M_z' = J_1(\alpha(E)), \quad (37)$$

J_1 is a Bessel function.

It follows from (37) that the probability of the sub-barrier transition, which is proportional to $|J_1(\alpha(E))|^2$, depends on the excitation energy of the molecule, and that the dependence increases

with increasing oscillation. Obviously, a molecule in a sub-barrier state is excited with less probability than a molecule in the over-the-barrier state.

It is now easy to obtain the dependence of the neutron scattering cross section on the energy transferred to the neutrons. This dependence is given by the formula

$$w(\epsilon) = \frac{1}{Z} e^{-E(\epsilon)/T} \frac{1}{\epsilon} \frac{dE(\epsilon)}{d\epsilon} A(E(\epsilon)), \quad Z = \int e^{-E/T} \frac{dE}{\epsilon}, \quad (38)$$

where for sub-barrier states $E < V_0$ the quantity $E(\epsilon)$ is determined from (34), where $\omega = \epsilon$. The quantity

$$A(E) = |J_1(\alpha(E))|^2; \quad (39)$$

for $n \geq 3$ we can choose for $A(E)$ approximately

$$A(E) = \frac{\alpha^2}{4} \left(1 - \frac{\alpha^2}{4} \right). \quad (40)$$

For over-the-barrier states $E > V_0$ we have $A(E) = 1$ and we must use (31) to determine $E(\epsilon)$.

Figure 2 shows the dependence of the cross section for the scattering of neutrons by molecules on the energy transfer in the case of free and hindered internal rotation. Curve 2 is calculated for the case $n = 3$ and $T = V_0$. It is important to note that if the constraining potential is chosen in a form other than (27), $E(\epsilon)$ changes in formula (38) and $\alpha(E)$ changes in the expression (39) for $A(E)$ (these functions can be readily calculated for any potential).

We can thus determine the values of the hindering potentials and draw certain conclusions concerning their form from the dependence of the quasielastic-scattering cross section on the energy transfer. To this end it is necessary to use the temperature range $T \sim V_0$ (in a large number of cases of practical interest $V_0 < 1000^\circ \text{K}$).

At the same time, when $T < V_0$ there is a certain additional possibility of investigating the properties of the potential V . In the calculations above we neglected the level splitting connected with the sub-barrier transitions of the molecule from one equilibrium position to another. Such a level splitting always takes place (each of the levels s splits into n sublevels), although it does not manifest itself noticeably in the energy-transfer region considered above, since the small probability of the sub-barrier transitions makes the distance Δ_{S_i} between the sublevels much smaller than the distance between the levels that characterize the motion in an isolated potential well. This effect can become manifest, however, at energies $\epsilon \sim \Delta_S$.

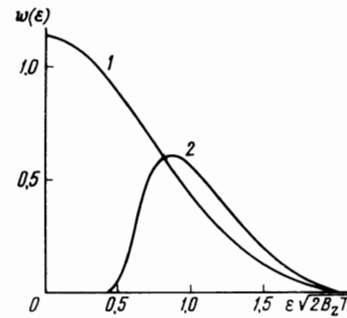


FIG. 2. Cross sections for the transfer of rotational energies (38) vs. $\epsilon/\sqrt{2B_z T}$ in the case of free internal rotation of the molecule (curve 1) or hindered rotation (curve 2). Curve 2 is plotted for the case $n = 3$ and $T = V_0$ in formula (27) for the hindering potential.

The probability of transition between the sublevels s_i and s_j of the level s in the case of neutron scattering is given by the simple formula

$$w_{s_i s_j} = \beta_{s_i s_j} Q_s, \quad (41)$$

where Q_s is a function whose value under classical conditions (for large s) is $|J_0(\alpha(E_s))|^2$ (E_s is the energy of the level s and $\alpha(E)$ is the amplitude of the oscillations), and has a value close to unity for small s . $\beta_{s_i s_j} = 1$ for $n = 2$ and $i \neq j$;

when $n = 3$ we have $\beta_{s_i s_j} = 1/2$ if one of the indices (i or j) belongs to the fully symmetrical state (relative to rotation of the molecule through angles $\varphi = 2\pi/3, 4\pi/3$), and $\beta_{s_i s_j} = 1/4$ if i and j do not pertain to such a state.

Thus, in the temperature region $T < V_0$ there is the possibility of investigating the energy-level splitting determined by the magnitude and form of the hindering potential.

In conclusion, let us discuss practical possibilities of experiments in the region of "single-quantum" rotational transitions of molecules. We note first that the cross sections $d^2\sigma/d\epsilon d\omega$ have at energies $\epsilon \sim \bar{B}$ the same order of magnitude as the cross sections $d^2\sigma/d\epsilon d\omega$ of the customarily investigated inelastic processes when $\epsilon \sim T$. The advantages of the region of measurement at energy $\epsilon \sim \bar{B}$ (compared with the region $\epsilon \sim T$) are the stronger and more detailed dependence of the neutron-scattering spectrum on the singularities of the rotational motion of the molecules, and the relative simplicity and reliability of the theoretical interpretation of the obtained results; a shortcoming is the relative smallness of the region of measurement itself when $\epsilon \sim \bar{B}$: in practice it amounts to 0.002–0.005 eV.

In spite of this fact it can be readily shown that the corresponding neutron spectra can be investi-

gated with sufficient accuracy by using the usual procedure of measuring the double-differential cross sections with the aid of monochromatic beams of incident neutrons, a procedure used, for example, by Randolph et al.^[12] To this end, the monochromaticity of the beam η and the resolution of the recording apparatus (the time of flight selector) δ should be such that $\eta E_0 \lesssim \bar{B}$, $\delta E_0 \ll \bar{B}$ (E_0 is the energy of the incident neutron). The apparatus described in ^[12] has a monochromaticity $\eta = 0.07$ (for $E_0 = 0.015$ eV) and a resolution $\delta = 0.02$. With suitable choice of E_0 ($E_0 \sim 0.005$ – 0.015 eV) and the scattering angle ϑ (for which $\kappa\rho \approx 1$ – 2 , $\kappa \approx \sqrt{2} k_0 \sqrt{1 - \cos \vartheta}$) at the same statistical measurement accuracy ($\sim 5\%$, as in ^[12]), such parameters are certain to insure the necessary accuracy in the investigation of quasielastic scattering of neutrons by molecules.

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¹J. Schwinger and E. Teller, Phys. Rev. **52**, 286 (1937).

²A. F. Goryunov, Atomnaya Énergiya No. 3, 45 (1956).

³A. Rahman, Nucl. Energy, Part A: Reactor Science, **13**, 128 (1956).

⁴G. C. Griffing, Phys. Rev. **124**, 1489 (1961).

⁵R. Sachs and E. Teller, Phys. Rev. **60**, 18 (1941).

⁶T. J. Krieger and M. S. Nelkin, Phys. Rev. **106**, 280 (1957).

⁷A. C. Zemach and R. J. Glauber, Phys. Rev. **101**, 118, 129 (1956).

⁸H. Volkin, Phys. Rev. **113**, 866 (1959); **117**, 1029 (1960).

⁹I. P. Dzyub, JETP **49**, 493 (1965), Soviet Phys. JETP **22**, 347 (1966).

¹⁰J. A. Janik, J. M. Janik, J. Mellor, and H. Pavlevsky, J. Phys. Chem. Solids **25**, 1091 (1964).

¹¹J. A. Janik, J. M. Janik, A. Bajorek, and K. Parlinski, Phys. Stat. Sol. **9**, 905 (1965).

¹²R. G. Randolph, R. M. Brugger, K. A. Strong, and R. E. Schmunk, Phys. Rev. **124**, 460 (1961).

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