

INTERACTION OF NEUTRONS WITH MOLECULES

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MOST experimental investigations of the interaction of neutrons with nuclei contained in molecules refer to the region of relatively low energies E_n of the neutrons, less than say one eV ("slow" neutrons). The reason for this is primarily the relative simplicity of obtaining a beam of slow (i.e., thermal) monoenergetic neutrons, and the ease of counting scattered neutrons having low velocities (for example, by time of flight). This also is why most theoretical work has been on thermal neutrons. Nevertheless, the region of higher neutron energies, for example energies of one eV and above, (we shall call such neutrons fast) is of no less interest than the thermal region, for the following reasons: 1) the analysis of molecular properties from the spectra of scattered fast neutrons is very much simpler and therefore enables one to explain many fine features of molecular structure that are practically impossible to decipher in the spectra of slow neutrons. We note that these considerations were the basis of the proposal of V. I. Gol'danskiĭ in 1956^[1] of the method of molecular "neutronoscopy," i.e., the investigation of properties of molecules from the spectra of scattered fast neutrons; 2) in the scattering by molecules of fast neutrons having an energy of the order of the chemical binding, a variety of chemical transformations are possible whose investigation is of intrinsic interest for radiation chemistry and biology.

A systematic presentation of the theory of scattering of fast neutrons by molecules, based mainly on^[2-9] is the main purpose of this survey.

In doing this we have limited ourselves to that class of problem which is related to the study of spectra of neutrons scattered by molecules, and have not included phenomena of chemical transformation under the influence of neutrons (whose theory is given in our paper^[9]), which require the use of methods of radiation chemistry for their investigation.

Since for many nuclei the scattering amplitudes for fast neutrons are strongly energy dependent (in particular, show resonances) the theory is given right from the start for the general case of variable amplitudes for neutron-nucleus scattering.

The survey also presents the theory of scattering of slow neutrons by molecules, insofar as it can be formulated using a classical description of the molecular rotation, so that one can use the mass tensor method and replace integration over the rotation

variables by an average over molecular orientations in the formulas for the neutron scattering cross section (Chap. II). Our development of this theory, which is widely used by experimenters, but has not been covered well in the survey literature, is based mainly on^[10]. However, the effective mass approximation used in^[10] is subjected to a critical examination, which shows that in many cases it leads to serious errors; a procedure is described for computing scattering cross sections by a rigorous averaging over molecular orientations.

The content of the monograph is more completely described in terms of the following classification of the processes of scattering of neutrons by chemically bound nuclei as they depend on the nature of the neutron-nucleus interaction and the energy of the neutrons.

The neutron-nucleus interaction can be characterized by an effective time of collision of the neutron with the nucleus. If the scattering of the neutron is potential scattering, the effective time of scattering is A/v (A is the amplitude for neutron-nucleus potential scattering, v is the neutron velocity). The fact that this quantity is very much smaller than the period of vibration of atoms in a molecule $1/\omega = \hbar/\Delta E_V$ (where ΔE_V is the difference in energy of vibrational levels in the molecule), is the essential reason why the pseudopotential method of Fermi^[23] is applicable. This method enables one formally to compute the cross section for scattering of neutrons by chemically bound nuclei using matrix elements of the Born type, even though the neutron-nucleus interaction is not weak. The method of the pseudopotential in its usual formulation becomes invalid for the case of varying (in particular, resonant) scattering amplitudes $F(E_n)$ for the neutron-nucleus system. Nevertheless, if this dependence is sufficiently smooth, or the resonance is sufficiently broad, so that the effective time of the neutron-nucleus interaction $\hbar d(\ln F)/dE_n \approx \hbar/\Gamma$ (where Γ is the resonance width) is small compared to the period $1/\omega$ of the molecular vibrations:*

*This condition is satisfied in the overwhelming majority of cases, since the widths of resonances usually exceed 0.1 eV, while the separations of vibrational levels for sufficiently heavy nuclei, which are the only ones for which resonance phenomena can occur, do not exceed hundredths of an eV.

$$\frac{\hbar}{\Gamma} \ll \frac{1}{\omega}, \quad (1)$$

the scattering of neutrons by chemically bound nuclei can be treated in the impulse approximation, which enables one to picture the process in a relatively simple form which is a kind of generalization of the pseudopotential approximation of Fermi. We note that in the case of (1), if the additional condition

$\sqrt{E_m \Delta E_V} / \Gamma \approx 1$ is satisfied, taking account of the energy dependence $F(E_N)$ is important, despite the large resonance width, and leads to the appearance of qualitatively new phenomena, similar to the Doppler effect, that are associated with the intramolecular motions of the nuclei. (The quantity $E_m = 4m\nu E_N / (m\nu + m)^2$ represents the maximum energy that can be transferred from the neutron to the nucleus at rest; m is the neutron mass, and $m\nu$, the mass of the nucleus.) In addition to the effective time for the neutron-nucleus interaction, another important characteristic of the interaction of neutrons with chemically bound nuclei is the effective time for transfer of energy from the neutron to a nucleus of a molecule of mass $m\nu$, which according to the uncertainty relation for the energy is of the order of \hbar/R (where $R = (\hbar k^2 / 2m\nu)$ is the recoil energy, and $\hbar k = \hbar(\mathbf{k} - \mathbf{k}')$ is the momentum transferred to the nucleus, i.e.,

$$R = \frac{\hbar^2}{2m\nu} (k^2 + k'^2 - 2kk' \cos \vartheta),$$

$\hbar k$ and $\hbar k'$ are the neutron momenta before and after scattering, ϑ is the angle of scattering of the neutron in the laboratory coordinate system). On the other hand it is meaningful to introduce several times for changes of the state of the molecule: the time for change in orientation of the molecule $\hbar/\Delta E_r$ (where ΔE_r is the distance between rotational levels of the molecule) and the time for a significant change of separation of nuclei $\hbar/\Delta E_V$. In the region of low (subthermal) neutron energies, the time \hbar/R for transfer of energy R to the nucleus is comparable with or less than the time for change of molecular orientation $\hbar/\Delta E_r$, and in this case the theoretical treatment is extremely complicated (cf. in particular the papers of Zemach and Glauber,^[11,12] and also^[13-22]), since it requires numerical computations for each individual molecule.

If the neutron energy is sufficiently high, so that the condition

$$\frac{\hbar}{R} \ll \frac{\hbar}{\Delta E_r}, \quad (2)$$

is satisfied, one can assume that the molecule does not change its orientation during the time of transfer of energy to the nucleus. This means that the rotation of the nucleus can be treated classically, i.e., one can use the approximation of a classical rotator with simultaneously given angular momentum and orientation. This greatly simplifies all the computations and enables one to write the formulas for the scattering

cross section in a universal form, valid for molecules of any type.

Within the framework of condition (2), the processes of interaction of neutrons with nuclei in molecules can be divided into two regions: a) the slow neutron region, where the condition

$$\frac{\hbar}{R} \gg \frac{1}{\omega}, \quad (3)$$

is satisfied, i.e., the time for transfer to the nucleus of the energy R is greater than, or of the order of, the period of atomic vibration $1/\omega$, so that the distance between the atoms in the molecule can change significantly during the time of the collision, so that the vibration of the atoms during the scattering appears as a quantum mechanical effect. Chapter II is devoted to the description of phenomena that occur when conditions (2) and (3) are satisfied, so that the molecular rotation is treated classically and the molecular vibration quantum mechanically; b) the region of fast neutrons, where the condition

$$\frac{\hbar}{R} \ll \frac{1}{\omega}, \quad (4)$$

is satisfied, i.e., the time for transfer of energy from the neutron to the nucleus is much smaller than the period of molecular vibrations. Together with conditions (2) and (3), this means that all the effective times characterizing the interaction of the neutron with the nucleus are small compared with the effective time for the change of state of the molecule. Consequently, under these conditions the scattering nucleus behaves as if it were free at the time of collision with the neutron, and the molecular binding manifests itself only through the spread in momentum determined by the wave function of the initial state of the molecule. Naturally the total cross section for scattering of neutrons with these energies is close to the cross section for free nuclei, so that these measurements can give no useful information about molecular properties. The features of the molecular structure do, however, have a strong effect on the double differential cross sections for scattering of fast neutrons, $d^2\sigma/d\epsilon d\Omega$, which give the probability for scattering of a neutron by the molecule into the solid angle $d\Omega$ with a given energy change ϵ . Here the theoretical description of the various features of molecular structure that appear in the formulas for $d^2\sigma/d\epsilon d\Omega$, and the unraveling of molecular properties from the spectra of scattered fast neutrons (i.e., from the measured values of $d^2\sigma/d\epsilon d\Omega$) is incomparably simpler than for slow neutrons, since it reduces simply to a correct treatment of the momentum distributions in the scattering nuclei, which can be regarded as free. On the basis of these arguments we believe that fast neutrons, despite difficulties in getting and recording them, are much more attractive for investigations of molecular properties than slow neutrons. The theory of the scattering of fast neutrons is presented in Chapter III. As already mentioned, in-

cluding the energy dependence of the neutron-nucleus scattering amplitude, as is done in this survey, requires the use of the impulse approximation. For this reason Chapter I, preceding the main body of the survey, gives the essentials of this method. The presentation is based on^[4], in a form convenient for treating the scattering of neutrons by chemically bound nuclei.

I. THE IMPULSE APPROXIMATION METHOD AS APPLIED TO SCATTERING OF NEUTRONS BY CHEMICALLY BOUND NUCLEI

1. Cross Sections for Molecular Transitions under the Influence of Neutrons, in the Impulse Approximation.

The impulse approximation in scattering theory, which was first introduced in^[24-27], is based on a series of assumptions. The main assumption is that one requires that the time of interaction of the incident particle with one of the particles making up the scattering system be small. In the case of the scattering of neutrons by chemically bound nuclei this condition coincides with the condition (1) in the introduction. Let us enumerate the main assumptions of the impulse approximation method in this case, starting from the Schroedinger equation for the neutron-molecule system:

$$H'\Psi = E_i\Psi, \quad H' = K + U + V, \quad (1.1)$$

where K is the kinetic energy operator for the system of N atoms making up the molecule and for the neutron, $U(\mathbf{r}_1, \dots, \mathbf{r}_N)$ is the interaction potential of the atoms in the molecule, V is the potential for the interaction of the neutron with the nuclei in the molecule, which is a sum of the potentials for the interaction of the neutron with each of the nuclei in the molecule $V = \sum_{\nu=1}^N V_{\nu}(\mathbf{r} - \mathbf{r}_{\nu})$ (where \mathbf{r} is the radius vector of the neutron and \mathbf{r}_{ν} are the radii vectors of the nuclei). The potentials V_{ν} can be complex, so Eq. (1.1) takes account of the possible capture of the neutron by a nucleus. Obviously, writing the Schrödinger equation in the form (1.1) assumes that the molecule is in its ground electronic state, which does not change as a result of the collision with the neutron. (The interaction between different electronic states can be important only if the corresponding energy terms overlap.) We note that Eq. (1.1) is written in the laboratory system of coordinates, to which we shall refer all our arguments, i.e., in (1.1) E_i is equal to the sum of the kinetic energy of the neutron and the total energy of the molecule in the laboratory coordinate system.

We shall make use of the apparatus of the formal

theory of scattering,^[28] according to which (1.1) can be rewritten in the form*

$$\Psi = \Phi_i + (E_i - H' + i\eta)^{-1} \Psi_i^+, \quad (1.2)$$

where Ψ_i^+ is the wave function describing the transition from the initial state $\Phi_i = \varphi_i(\mathbf{r}_1, \dots, \mathbf{r}_N) e^{i\mathbf{k}\cdot\mathbf{r}}$ (we shall assume that the final state is fixed: $\Phi_f = \varphi_f(\mathbf{r}_1, \dots, \mathbf{r}_N) e^{i\mathbf{k}'\cdot\mathbf{r}}$), and φ_i and φ_f are the wave functions of the molecule in the initial and final states. The neutron wave vectors \mathbf{k} , \mathbf{k}' , before and after scattering, satisfy energy conservation

$$E_i = E_f, \quad \text{i.e.} \quad \varepsilon_i + \frac{\mathbf{k}^2}{2m} = \varepsilon_f + \frac{\mathbf{k}'^2}{2m} \quad (1.3)$$

(ε_i and ε_f are the energies of the molecule before and after scattering of the neutron). Using (1.2) one can write the double differential cross section for scattering of the neutron by the nucleus into an element of solid angle $d\Omega$, accompanied by a transfer to the molecule of energy

$$\varepsilon = \frac{\mathbf{k}^2}{2m} - \frac{\mathbf{k}'^2}{2m}$$

and its transition to some final state φ_f in the form

$$\frac{d^2\sigma}{d\varepsilon d\Omega} = \frac{k'}{k} \left(\frac{m}{2\pi}\right)^2 |T_{if}|^2 \delta(\varepsilon + \varepsilon_i - \varepsilon_f), \quad (1.4)$$

where

$$T_{if} = (\Phi_f, T\Phi_i) = \int \Phi_f^* T\Phi_i d\mathbf{r} d\mathbf{r}_1 \dots d\mathbf{r}_N,$$

and T is the operator defined by the equation

$$T = V\Omega^+ = V + V(E_i - H' + i\eta)^{-1}V,$$

where $\mathbf{r}_1, \dots, \mathbf{r}_N$ are the coordinates of the nuclei in the molecule and \mathbf{r} is the coordinate of the neutron.

The impulse approximation consists in replacing the operator T by the operator $T^{(0)} = \sum_{\nu=1}^N t_{\nu}$, where t_{ν} is defined by the expression

$$t_{\nu} = V_{\nu} \hat{\omega}_{\nu}^+ = V_{\nu} + V_{\nu}(E_K - K - V_{\nu} + i\eta)^{-1}V_{\nu}, \quad (1.5)$$

and E_K is the kinetic energy of all the atoms in the molecule (characterized by a definite set of momenta $\mathbf{p}(\mathbf{p}_1, \dots, \mathbf{p}_N)$ and of the neutron. As is easily seen, $T^{(0)}$ is the leading term in a certain operator expansion, for which the correction characterizing the influence of the molecular binding on the scattering of the neutron has the form

$$T^{(1)} = \sum_{\nu=1}^N t_{\nu\nu},$$

$$t_{\nu\nu} = t_{\nu}(E_K - K + i\eta)^{-1}(E_K - E_i + U)(E_K - K + i\eta)^{-1}t_{\nu}. \quad (1.6)$$

We go over to the momentum representation for the molecular wave functions:

*For convenience we shall use the system of units in which Planck's constant \hbar is unity, and the Boltzmann constant is also one.

$$\varphi_i = (2\pi)^{-\frac{3N}{2}} \int \varphi_i(\mathbf{p}) e^{i\sum p_\lambda r_\lambda} d\mathbf{p},$$

$$\varphi_f = (2\pi)^{-\frac{3N}{2}} \int \varphi_f(\mathbf{p}') e^{i\sum p'_\lambda r_\lambda} d\mathbf{p}'.$$

Then the contribution to the matrix element T_{if} associated with the operator t_ν can be written in the form

$$t_{if}^{\nu} = (\Phi_f, t_\nu, \Phi_i) = \int \varphi_f^*(\mathbf{p}') \chi_{k_p'} t_\nu \chi_{k_p} \varphi_i(\mathbf{p}) d\mathbf{p} d\mathbf{p}' d\mathbf{r} d\mathbf{r}_1 \dots d\mathbf{r}_N. \quad (1.7)$$

Integration over the variables \mathbf{p}' and \mathbf{r} and some elementary transformations (cf. [4]) gives the following expression:

$$t_{if}^{\nu} = \frac{2\pi}{\mu_\nu} \int \varphi_f^* F(\mathbf{k}'_\nu, \mathbf{k}_\nu) e^{i\mathbf{r}_\nu} \varphi_i d\mathbf{r}_1 \dots d\mathbf{r}_N, \quad (1.8)$$

where

$$F_\nu(\mathbf{k}'_\nu, \mathbf{k}_\nu) = \frac{\mu_\nu}{2\pi} \int e^{-i\mathbf{k}'_\nu \mathbf{q}} V_\nu(\mathbf{q}) \psi_{\mathbf{k}'_\nu}(\mathbf{q}) d\mathbf{q},$$

$$\mathbf{q} = \mathbf{r} - \mathbf{r}_\nu, \quad \mathbf{k}_\nu = \frac{m_\nu \mathbf{k} - m \hat{\mathbf{p}}_\nu}{m_\nu + m}, \quad \mathbf{k}'_\nu = \frac{m_\nu \mathbf{k}' - m(\boldsymbol{\alpha} + \hat{\mathbf{p}}_\nu)}{m_\nu + m}. \quad (1.9)$$

In the special case when F_ν depends weakly on \mathbf{p}_ν , we have

$$t_{if}^{\nu} = \frac{2\pi}{\mu_\nu} F_\nu(\mathbf{k}'_{\nu 0}, \mathbf{k}_{\nu 0}) \int \varphi_f^* e^{i\mathbf{r}_\nu} \varphi_i d\mathbf{r}_1 \dots d\mathbf{r}_N, \quad (1.10)$$

where $\mathbf{k}_{\nu 0}$ and $\mathbf{k}'_{\nu 0}$ differ from \mathbf{k}_ν and \mathbf{k}'_ν in having $\hat{\mathbf{p}}_\nu = 0$. If the changes in the neutron-nucleus scattering are potential, i.e., if the F_ν are independent of energy, (1.10) coincides with the pseudopotential method. The quantity F_ν appearing in (1.8) coincides with the elastic scattering amplitude only if $|\mathbf{k}_\nu| = |\mathbf{k}'_\nu|$. However, in the special case of s-scattering, if the condition $k'_\nu d_\nu \ll 1$ is satisfied (where d_ν is the effective radius of the potential V_ν), which will always be the case for us, we can set $e^{-i\mathbf{k}'_\nu \cdot \mathbf{p}} = 1$ in (1.9). Consequently, F_ν is actually independent of \mathbf{k}'_ν , and thus this quantity (up to terms of order $(k'_\nu d_\nu)^2$) coincides with the amplitude for elastic scattering corresponding to the relative momentum \mathbf{k}_ν of neutron and nucleus. In other words, in the case of potential neutron-nucleus scattering we shall have (cf. [29], p. 478)

$$F_\nu = \frac{1}{g_0 - ik_\nu} \approx A_\nu (1 + iA_\nu k_\nu), \quad A_\nu = \frac{1}{g_0} = \text{const}, \quad (1.11)$$

while in the case of resonant neutron-nucleus scattering (cf. [29], p. 513)

$$F_\nu = \frac{1}{2k_\nu} \frac{\Gamma_e}{E - E_0 + \frac{i\Gamma}{2}}, \quad E = \frac{k_\nu^2}{2\mu_\nu}. \quad (1.12)$$

Using the definition of the operator t_ν in (1.5) and the usual definition of the operator $(E_K - K + i\eta)^{-1}$, one can also easily find the correction associated with the operator $t_{\nu\nu}$ of (1.6) which characterizes the effect of the chemical binding. For the most important case of a potential $U(\mathbf{r}_1, \dots, \mathbf{r}_N)$ of the oscil-

lator type the matrix element $t_{\nu\nu}^{if}$ can be written in the form

$$t_{\nu\nu}^{if} = (\Phi_f, \mathcal{F}_\nu e^{i\mathbf{r}_\nu} \Phi_i), \quad (1.13)$$

where $\mathcal{F}_\nu \approx \frac{p_\nu^2}{2m_\nu} \frac{dF_\nu}{dE}$, $E = \frac{k_\nu^2}{2\mu_\nu}$. Using (1.13) one can easily explain in the conditions for validity of the impulse approximation and also, for the special case of potential scattering, obtain the corrections to the Fermi pseudopotential approximation. These corrections have been studied in [30-34], where, however they were obtained in a much more complicated form than that given by (1.13). It is easy to see from (1.10) and (1.13) that the ratio $t_{\nu\nu}^{if}/t_{\nu\nu}^{if}$ is of the same order of magnitude, in general, as the quantity $\bar{\omega}_\nu d \ln F_\nu/dE$, i.e., in the special case of neutron-nucleus potential scattering, $A_\nu \bar{\omega}_\nu/v_\nu$, while for the case of resonance scattering it is $\bar{\omega}_\nu/\Gamma$ (where $\bar{\omega}_\nu$ is the mean vibrational energy of the ν -the atom, and v_ν is the relative velocity of the neutron and nucleus). This is in agreement with condition (1) given in the introduction. Using the matrix element (1.13), one can easily find these corrections explicitly.

It is also easy to get the corrections to formula (1.10), taking account of the dependence of the amplitude F_ν on \mathbf{p}_ν . To do this we expand F_ν in a series in powers of \mathbf{p}_ν . In the lowest approximation we have

$$F_\nu = F_{\nu 0} + \frac{m}{m_\nu + m} \mathbf{p}_\nu \nabla F_\nu \quad (\mathbf{p}_\nu = 0).$$

Then from (1.11) we conclude that the correction to (1.10) when we take account of the dependence of the amplitude F_ν on the momenta of the bound atoms is

$$\frac{m}{m_\nu + m} \int \varphi_f^*(\mathbf{p}) \mathbf{p}_\nu \nabla F_\nu e^{i\mathbf{r}_\nu} \varphi_i(\mathbf{p}) d\mathbf{p}. \quad (1.14)$$

This expression is of order $p_\nu^0 d \ln F_\nu/dk_\nu$ (where p_ν^0 is the characteristic momentum of an atom in the molecule, $1/p_\nu^0$ is the amplitude of vibration of the atoms in the molecule), i.e., is of order $A_\nu p_\nu^0$ in the case of potential scattering and of order $\sqrt{E_m \bar{\omega}_\nu}/\Gamma$ in the case of resonant scattering. It is obvious that for sufficiently high neutron energies the quantity $\sqrt{E_m \bar{\omega}_\nu}/\Gamma$ cannot be small. This means that in such cases one cannot use the approximation (1.10) but must use the general formula (1.8) which includes phenomena similar to the Doppler effect that are associated with intramolecular vibrations.

2. Representation of the Cross Sections for Scattering and Absorption of Neutrons as Averages over the Initial State of the Molecule.

In experiments on the scattering of neutrons by a molecule one does not measure the cross section for a transition of the molecule to some definite final state (1.4), but rather the cross section for scattering of the neutron that corresponds to a transition of the molecule to any of the energetically admissible states.

Using the expression (1.8) for the matrix elements for transition of the molecule to definite final states, and the fact that the wave functions of the final states form a complete set, one easily gets a convenient expression for the cross section that is actually measured experimentally, which is the sum of the cross sections $d^2\sigma_{if}/d\epsilon d\Omega$ for transitions to all energetically allowed final states. According to (1.8)

$$\frac{d^2\sigma}{d\epsilon d\Omega} = \frac{k'}{k} \sum_f \sum_{\nu\nu'} \frac{m^2}{\mu_\nu\mu_{\nu'}} (\varphi_i(\mathbf{p}'), F_{\nu\nu'}^* e^{-i\kappa\mathbf{r}_{\nu'}} \varphi_f(\mathbf{p}')) (\varphi_f(\mathbf{p}), e^{i\kappa\mathbf{r}_\nu} F_{\nu\nu'} \varphi_i(\mathbf{p})) \delta(\epsilon + \epsilon_i - \epsilon_f).$$

Using the completeness relation for the system of functions φ_f , $\sum_f \varphi_f^*(\mathbf{p}') \varphi_f(\mathbf{p}) = \delta(\mathbf{p} - \mathbf{p}')$, the relations

$$e^{iHt} \varphi_i = e^{i\epsilon_i t} \varphi_i, \quad e^{iHt} \varphi_f = e^{i\epsilon_f t} \varphi_f$$

(H is the Hamiltonian of the molecule) and the integral representation for the delta function, we find

$$\frac{d^2\sigma}{d\epsilon d\Omega} = (\varphi_i, \mathfrak{X} \varphi_i),$$

$$\mathfrak{X} = \frac{1}{2\pi} \frac{k'}{k} \sum_{\nu\nu'} \frac{m^2}{\mu_\nu\mu_{\nu'}} \int_{-\infty}^{\infty} e^{-i\epsilon t} F_{\nu\nu'}^* e^{-i\kappa\mathbf{r}_{\nu'}} e^{iHt} e^{i\kappa\mathbf{r}_\nu} F_{\nu\nu'} e^{-iHt} dt. \quad (2.1)$$

Formula (2.1) is the analog of the familiar Zemach-Glauber formula derived^[11] for the case of $F_\nu = \text{const}$. Thus, the double differential cross section for scattering of neutrons can be written as an average over the initial state of the molecule of a set of operators determined by the Hamiltonian of the molecule and the amplitudes for two-particle scattering. The fact that the wave functions φ_f of the final states of the molecule do not appear explicitly in (2.1) is of particular importance in treating the scattering of fast neutrons, which is accompanied by a large energy transfer, so that these wave functions are very complicated and cannot be found practically in explicit form. Expression (2.1) can be somewhat simplified by using the fact that in a classical description of the rotation of the molecule (which we shall always use) the interference terms, which correspond to $\nu \neq \nu'$, are usually unimportant. So for our purposes we may set $\nu = \nu'$ in (2.1).

We make the further transformation^[11]

$$e^{-i\kappa\mathbf{r}_{\nu}} e^{iHt} e^{i\kappa\mathbf{r}_\nu} = e^{iH_\nu t},$$

$$H_\nu = H(\mathbf{p}_1, \dots, \mathbf{p}_\nu + \kappa, \dots, \mathbf{p}_N) = H + R_\nu + L_\nu, \quad R_\nu = \frac{\kappa^2}{2m_\nu},$$

$$L_\nu = \frac{\kappa \mathbf{p}_\nu}{m_\nu}; \quad (2.2)$$

this comes from the familiar commutation rules for the operators \mathbf{p}_ν and \mathbf{r}_ν (cf. [29] p. 46), which allow one to get the relation $e^{-i\kappa \cdot \mathbf{r}_\nu} \mathbf{p}_\nu e^{i\kappa \cdot \mathbf{r}_\nu} = \mathbf{p}_\nu + \kappa$ (and consequently, $e^{-i\kappa \cdot \mathbf{r}_\nu} H e^{i\kappa \cdot \mathbf{r}_\nu} = H_\nu$). Then we can write the operator \mathfrak{X} in (2.1) in the form

$$\mathfrak{X} = \frac{1}{2\pi} \frac{k'}{k} \sum_{\nu} \left(\frac{m}{\mu_\nu} \right)^2 \int_{-\infty}^{\infty} e^{-i\epsilon t} F_{\nu\nu}^* e^{iH_\nu t} F_{\nu\nu} e^{-iHt} dt. \quad (2.3)$$

We shall make extensive use of (2.3).^{*} Since all the formulas we shall give for the cross sections for scattering of neutrons by molecules are made up additively from the cross sections for scattering by individual nuclei, we shall from now on refer all our arguments to an individual nucleus. This means, in particular, that we are not concerned with the spin dependence of the amplitudes F_ν (which is taken into account by a trivial summation over spin projections of the quantities $|F_\nu|^2$ in the final formulas).

By integrating the cross section $d^2\sigma/d\epsilon d\Omega$ given by (2.1) and (2.3) over angles one can obtain the cross section $d\sigma/d\epsilon$ for energy transfer, which is of great interest for the theory of neutron moderation, while by integrating $d\sigma/d\epsilon$ over the energy transfer ϵ using the conservation law (1.3) one gets the total scattering cross section $\sigma(E_n)$.

In addition to the cross sections $d^2\sigma/d\epsilon d\Omega$ described above, for applications to heavy nuclei one is very much interested in the cross section for absorption of neutrons $\sigma_r(E_n)$. In the impulse approximation the chemical binding manifests itself in the absorption of neutrons mainly through the Doppler effect associated with motion of the nuclei in the molecule, so the expression for $\sigma_r(E_n)$ can be obtained in a simple and general form in this case.

The cross section for absorption of neutrons by the ν -the nucleus can be written in the general case in terms of the flux of neutrons incident on this nucleus, in the form

$$\sigma_r = \frac{\pi}{k_\nu^2} \lim_{\rho \rightarrow 0} \rho^2 \int (\Psi_i^* \nabla_{\mathbf{Q}} \Psi_i - \Psi_i \nabla_{\mathbf{Q}} \Psi_i^*) d\mathbf{O}_\nu d\mathbf{r}' \quad (2.4)$$

where the quantities ρ and k_ν are defined in Section 1. Using the expression for the total wave function Ψ_i obtained in the impulse approximation (cf. (1.5)):

$$\Psi_i = \Omega^+ \Phi_i \approx \sum_{\nu} \hat{\omega}_\nu \int \chi_{\mathbf{k}\mathbf{p}} \varphi_i(\mathbf{p}) d\mathbf{p} = \sum_{\nu} \int \psi_{\mathbf{k}\nu}(\mathbf{Q}) e^{i\mathbf{k} \cdot \mathbf{r}_\nu} \chi_{\mathbf{k}\mathbf{p}} \varphi_i(\mathbf{p}) d\mathbf{p},$$

we easily find using (2.4)

$$\sigma_r = \int \sigma_r^{(0)}(\mathbf{p}_\nu) \varphi_i^2(\mathbf{p}) d\mathbf{p}, \quad (2.5)$$

where

$$\sigma_r^{(0)} = \frac{\pi}{k_\nu^2} \lim_{\rho \rightarrow 0} \rho^2 \int (\psi_{\mathbf{k}\nu} \nabla \psi_{\mathbf{k}\nu}^* - \psi_{\mathbf{k}\nu}^* \nabla \psi_{\mathbf{k}\nu}) d\mathbf{O}_\nu = \frac{\pi}{k_\nu^2} (1 - |s_0|^2),$$

$$s_0 = 1 + 2ik_\nu F_\nu(\mathbf{p}_\nu)$$

is the cross section for absorption of the neutron by a free nucleus having momentum \mathbf{p}_ν . In the special case of resonant Breit-Wigner absorption

^{*}As is easily shown, the operators F_ν and $e^{iH_\nu t}$ can be regarded as commuting to an accuracy sufficient for all our further calculations.

$$\sigma_r^{(0)} = \frac{\pi}{k^2} \frac{\Gamma_e \Gamma_r}{E - E_0 + \frac{\Gamma}{4}}, \quad \Gamma_r = \Gamma - \Gamma_e. \quad (2.6)$$

Thus, in the impulse approximation the cross section for absorption is simply the average over the initial state of the molecule $\varphi_i(\mathbf{p})$ of the cross section for two-particle absorption of the neutron by the free nucleus $\sigma_r^{(0)}(\mathbf{p}_\nu)$. The correction to this approximation (analogous to the correction $t_{\nu\nu}^{if}$) is of order $\bar{\omega}_\nu/\Gamma$ and, consequently, the simple formula (2.5) is valid when we satisfy the condition $\omega_\nu \ll \Gamma$, which, as already pointed out, is satisfied in most cases.

If the condition $\omega_\nu \ll \Gamma$ is violated, investigation of the resonance absorption requires the use of the general formalism of the theory of resonance absorption (cf., for example, [69]), according to which, for an isolated resonance, the total cross section for removal of neutrons from the beam, $\sigma_t = \sigma_r + \sigma_e$, can be written, using the optical theorem, in the form $\sigma_t = (4\pi/k) \text{Im } A$, where A is the amplitude for forward resonant scattering, which, according to [75] has the form

$$A = \frac{1}{2k} \int_0^\infty e^{-i(E_n - E_0 - \frac{i}{2}\Gamma)t} (\varphi_i, e^{iH_\nu t} e^{-iHt} \varphi_i) dt, \quad (2.7)$$

where $H_\nu = H(\mathbf{p}_1, \dots, \mathbf{p}_\nu + \mathbf{k}, \dots, \mathbf{p}_N)$. Formula (2.7) is analogous to formula (2.1) for the double differential cross section for potential scattering of neutrons (i.e., with $F_\nu = \text{const}$) if we set

$$\varepsilon = \varepsilon' = E_n - E_0 - \frac{i}{2}\Gamma \quad \text{and} \quad \mathbf{z} = \mathbf{k}.$$

But this analogy is not complete: because ε' is complex the calculations based on (2.7) lead in general to much more complicated formulas than those found for the double differential cross sections for potential scattering.

We shall therefore limit ourselves to investigating formula (2.5), which follows from the impulse approximation, whose advantage (aside from simplicity) is that it is valid for an arbitrary (and not just Breit-Wigner) energy dependence of the amplitude for two-particle neutron-nucleus scattering.

We note that in all the expressions for $d^2\sigma/d\epsilon d\omega$ given above we must average σ_r not only over the momentum distribution in $\varphi_i(\mathbf{p})$ but also take a statistical average (which we shall denote by the symbol $\langle \dots \rangle_T^*$) over the vibration-rotation states of the molecule, which we shall assume to be distributed according to the equilibrium, i.e., Boltzmann, law. In principle, one could avoid this assumption, which is violated in some cases that are of great interest (when there are chemical reactions in a material irradiated with neutrons).

Further simplifications of the general formulas given here for the scattering cross section are based

on special transformations of the operator $e^{iH_\nu t} e^{-iHt}$, which for small energy transfers ϵ are based on certain special assumptions about the wave functions of the initial and final states of the molecule, while in the case of large energy transfers they depend on expansions of this operator in powers of the Hamiltonian H of the molecule.

II. SCATTERING OF SLOW NEUTRONS

3. General Formulas for Slow Neutron Scattering Cross Sections with Classical Treatment of the Molecule.

As already mentioned, for sufficiently low energies of the incident neutrons, satisfying the condition $\sqrt{E_m \bar{\omega}}/\Gamma \ll 1$ (cf. Chap. I, Sec. 1), the neutron-nucleus scattering amplitude may be assumed to be independent of the momenta of the atoms; in this case in the fundamental formula (2.1) for $d^2\sigma/d\epsilon d\omega$ the operator \mathfrak{X} simplifies as follows:

$$\mathfrak{X} = \frac{1}{2\pi} \frac{k'}{k} \sum_\nu |F_\nu|^2 \left(\frac{m}{\mu_\nu}\right)^2 \int_{-\infty}^\infty e^{-i\epsilon t} e^{iH_\nu t} e^{-iHt} dt, \quad (3.1)$$

and the further treatment can be done as for $F_\nu = \text{const}$. For the same reasons the absorption cross section given by the general formula (2.5) coincides with the cross section for absorption by a free nucleus if the neutron resonance E_0 lies at low energies. In the following we investigate the scattering cross sections $d^2\sigma/d\epsilon d\omega$, $d\sigma/d\epsilon$ and $d\sigma/d\omega$ for the case where the operator \mathfrak{X} is given by (3.1).

In carrying out specific computations using this formula, the character of the excitation of the molecules is extremely important. For moderate energy transfers ϵ , much lower than the chemical binding energy D , one can use simplifications based on the properties of the internal motion of the molecule. By this we mean the requirement (usually well satisfied) of low velocities of the nuclei as compared to the electrons, and furthermore, the requirement of absence of crossings of the ground electronic term with other electronic terms in the classically accessible region of the nuclear motion.

Another type of simplification is based on the properties of the motions of the nuclei in the molecule, namely on the assumption that vibrational, rotational and translational motions of the nuclei are independent. This assumption allows us to represent the operators \mathbf{r}_ν , \mathbf{p}_ν and the molecular Hamiltonian H as a sum of independent terms, and the wave functions as products of factors corresponding to the various independent degrees of freedom of the molecule, i.e.,

$$\begin{aligned} \mathbf{r}_\nu &= \mathbf{R}_0 + \mathbf{b}_\nu + \mathbf{u}_\nu, \quad \frac{\mathbf{p}_\nu}{m_\nu} = \mathbf{V}_m + [\Omega \mathbf{b}_\nu] + \dot{\mathbf{u}}_\nu, \\ H &= H_t + H_r + H_v, \quad \varphi = \psi_t \psi_r \psi_v. \end{aligned} \quad (3.2)^*$$

*In addition to $\langle \dots \rangle_T$ we shall use the symbol $\langle \dots \rangle$, denoting both a quantum mechanical and a statistical average.

* $[\Omega \mathbf{b}_\nu] \equiv \Omega \times \mathbf{b}_\nu$.

Here \mathbf{R}_0 , \mathbf{V}_m , H_t , $\psi_t = \frac{1}{V^{3/2}} e^{i\mathbf{M}_\nu \mathbf{V}_M \cdot \mathbf{R}_0}$ are the coordinates, velocity, energy operator and wave function for translational motion of the molecule (ψ translation is normalized to unit volume V), b_ν is the coordinate of the atom relative to the center of gravity of the molecule, Ω is the angular velocity, H_R and ψ_R are the energy operator and wave function for the molecular rotation; \mathbf{u}_ν , $\dot{\mathbf{u}}_\nu$, H_V and ψ_V are the vector displacement of the atom from its equilibrium position, its velocity, the energy operator and wave function for the vibrational motion of the molecule.

A necessary condition for independence of rotation and vibrations of the molecule, i.e., the condition for validity of (3.2), is the inequality

$$\Delta E_R^i, \Delta E_R^f \ll \Delta E_V, \quad (3.3)$$

where ΔE_R^i , ΔE_R^f are the average separations of rotational levels in the initial and final states of the molecule, respectively. If B is the separation of the ground and first excited rotational levels, $\Delta E_R^i \sim \sqrt{BT}$. After transfer to the molecule of an energy ϵ exceeding T , the average distance between levels becomes of the order of $\sqrt{B\epsilon}$. Thus, condition (3.3) may be violated at high temperatures or for high energy transfers. One therefore usually assumes in computations that

$$T \ll \frac{(\Delta E_V)^2}{B}, \quad \epsilon \ll \frac{(\Delta E_V)^2}{B}. \quad (3.4)$$

In accordance with condition (2) of the Introduction we also require that

$$\epsilon \gg \Delta E_R. \quad (3.5)$$

For most molecules ΔE_R is usually some thousandths of an eV, i.e., two orders of magnitude smaller than the separation of vibrational levels. Thus both at normal and low temperatures, but for energies of the incident neutron large compared to ΔE_R , when condition (3.5) holds, high angular momenta are excited in the ground state in the scattering, and these can be described quasiclassically. These arguments are the basis for the mass tensor approximation, which permits a very great simplification of all cross section calculations both at high and low temperatures. This approximation has been used in a whole series of papers,^[10,35-39] mainly applied to the scattering of neutrons by rigid molecules. By the term "scattering by rigid molecules" we mean the situation where the vibrational motion of the molecule does not manifest itself in the collision. We shall begin our discussion with a treatment of this simplest case.

As one knows, the rotational part of the Hamiltonian of a rigid molecule can be written in the following form:

$$H = \frac{1}{2} \mathbf{L} I^{-1} \mathbf{L}, \quad (3.6)$$

where I is the moment of inertia of the molecule, \mathbf{L} is the angular momentum vector.

In the case of a rigid molecule, the expression for the transformed Hamiltonian H_ν in (3.1) is

$$H_\nu = H + \frac{1}{2} [\mathbf{b}_\nu \boldsymbol{\kappa}] I^{-1} [\mathbf{b}_\nu \boldsymbol{\kappa}] + \frac{1}{2} \mathbf{L} I^{-1} [\mathbf{b}_\nu \boldsymbol{\kappa}] + \frac{1}{2} [\mathbf{b}_\nu \boldsymbol{\kappa}] I^{-1} \mathbf{L}.$$

The probability for a rotational transition is given by the expression

$$w = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-i\epsilon t} \langle \psi_R | e^{iH_\nu t} e^{-iHt} | \psi_R \rangle dt. \quad (3.7)$$

Under the condition $\epsilon \gg \Delta E_R$ the noncommutativity of the operators plays no role; thus the probability (3.7) can be taken equal to

$$w = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-i\epsilon t} \langle \psi_R | e^{it \frac{\boldsymbol{\kappa} \hat{R}_\nu \boldsymbol{\kappa}}{2} + it i \mathbf{R}_\nu^{1/2} \boldsymbol{\kappa}} | \psi_R \rangle dt. \quad (3.8)$$

We have introduced a new tensor \hat{R}_ν according to the equation

$$[\mathbf{b}_\nu \boldsymbol{\kappa}] I^{-1} [\mathbf{b}_\nu \boldsymbol{\kappa}] = \boldsymbol{\kappa} \hat{R}_\nu \boldsymbol{\kappa} \quad (3.9)$$

where the vector $\mathbf{L} I^{-1/2} = \mathbf{I}$.

The tensor \hat{R}_ν , having the dimensions of inverse mass, characterizes the motion of the atom in a rigid molecule, its principal components ($R_\nu^{(1)}$, $R_\nu^{(2)}$) are related to the components of the inertia tensor I_i and the position of the scattering atom relative to the principal axes of the molecule, $b_{\nu i}$, as follows:^[38]

$$\begin{aligned} R_\nu^{(1)} &= \frac{1}{2I_1 I_2 I_3} \left\{ \sum_i I_i b_{\nu i}^2 I_i^{(+)} + \left[\left(\sum_i I_i b_{\nu i}^2 I_i^{(-)} \right)^2 \right. \right. \\ &\quad \left. \left. - 4I_1 I_3 b_{\nu 1}^2 b_{\nu 3}^2 I_1^{(-)} I_3^{(-)} \right]^{1/2} \right\}, \\ R_\nu^{(2)} &= \frac{1}{2I_1 I_2 I_3} \left\{ \sum_i I_i b_{\nu i}^2 I_i^{(-)} - \left[\left(\sum_i I_i b_{\nu i}^2 I_i^{(-)} \right)^2 \right. \right. \\ &\quad \left. \left. - 4I_1 I_3 b_{\nu 1}^2 b_{\nu 3}^2 I_1^{(-)} I_3^{(-)} \right]^{1/2} \right\}, \end{aligned} \quad (3.10)$$

where

$$I_i^{(\pm)} = I_2 \pm I_3, \quad I_2^{(\pm)} = I_1 \pm I_3, \quad I_3^{(\pm)} = I_1 \pm I_2, \quad i = 1, 2, 3.$$

The component $R_\nu^{(3)}$, corresponding to motion of the atom along the line joining this atom to the center of gravity of the molecule, is always equal to zero, i.e., $R_\nu^{(3)} = 0$. If the temperature is not high ($T \approx \Delta E_R$), the internal motion of the molecule plays no part, since in this case $\boldsymbol{\kappa} R_\nu \boldsymbol{\kappa} \gg I R_\nu^{1/2} \boldsymbol{\kappa}$, and the second term in the exponent in (3.8) need not be taken into account. In other words, for $T \lesssim \Delta E_R$ and $\boldsymbol{\kappa} R_\nu \boldsymbol{\kappa} \gg \Delta E_R$, the scattering is described by the simple formula

$$w = \left\langle \delta \left(\epsilon - \frac{1}{2} \boldsymbol{\kappa} R_\nu \boldsymbol{\kappa} \right) \right\rangle_\Omega. \quad (3.11)$$

This result is especially easy to see if the rotation of the molecule is described the spherical rotator functions Y_{LM} . In this case we have from (3.8)

$$w = \frac{1}{2L+1} \sum_{M=-L}^L \int Y_{LM}^* \delta \left(\epsilon - \frac{1}{2} \boldsymbol{\kappa} R_\nu \boldsymbol{\kappa} \right) Y_{LM} d\Omega, \quad (3.12)$$

but, since

$$\sum_{M=-L}^L Y_{LM}^* Y_{LM} = \frac{2L+1}{4\pi},$$

we immediately get formula (3.11). The bracket $\langle \dots \rangle_\Omega$ denotes an average over molecular orientations, which, as shown in [38], gives rise to complete elliptic integrals.

Zemach and Glauber [11, 12] have also calculated corrections to formula (3.11) (for the cases of the simplest rotators—spherical and linear). Volkin [38] has made similar calculations for rotators of arbitrary type.

The corrections depend on the specific rotational state of the molecule and are of order $\Delta E_r / \kappa \hat{R}_\nu \kappa$.

For high temperatures $T \gg \Delta E_r$, the treatment given above becomes invalid because the second term in the exponent in (3.8) cannot be regarded as small compared to the first. But in this case one can use the fact that at sufficiently high temperatures the important states of the molecule are those with large angular momenta L , whose wave functions are described by the quasi-classical approximation. Using the fact that in the quasiclassical approximation all the operators appearing in (3.8) commute (cf. [29], p. 49), we write the quantum mechanical average in (3.8) as follows:

$$\frac{1}{2L+1} \int_K \psi_r^* \psi_r e^{iH\nu t} e^{-iHt} d\Omega$$

(K is the projection of the angular momentum L on some selected axis). Since in the general case of an asymmetric rotator, $\sum_K \psi_r^* \psi_r = \frac{2L+1}{4\pi}$ (cf. [38]), in

complete analogy with (3.12), for the case of high temperatures, if we explicitly write the average over the rotational states, including the factor $\exp(-l^2/2T)$, we get

$$w = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-i\epsilon t} dt \int \frac{1}{N_r} e^{-l^2/2T} e^{it \left(\frac{1}{2} \kappa R_\nu \kappa + l R_\nu^{1/2} \kappa \right)} dl \frac{d\Omega}{4\pi},$$

$$N_r = \int e^{-l^2/2T} dl. \quad (3.13)$$

Integration over dl in (3.13) gives the following expression:

$$w = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-i\epsilon t} W_r(t) dt, \quad W_r = \left\langle \exp \left[\frac{1}{2} \kappa R_\nu \kappa (it - l^2 T) \right] \right\rangle_\Omega. \quad (3.14)$$

The validity of the quasiclassical approximation is determined by the two conditions:

$$\kappa R_\nu \kappa \gg \Delta E_r, \quad T \gg \Delta E_r. \quad (3.15)$$

Nevertheless the region of validity of (3.14) is actually much greater, since for $T \rightarrow 0$ formula (3.14) goes over into (3.11) and, consequently, at any temperature it gives correctly the main features of the

process of scattering of neutrons by molecules.* This is related to the fact that at low temperatures the thermal motion is unimportant.

Having at our disposal a simple method for handling rotational transitions of the molecule, it is now no longer difficult to make detailed calculations of the scattering of slow neutrons in the general case, when the cross section is given by formula (3.1), which, in accordance with the assumption that the ψ used above in deriving (3.14) is quasiclassical, can be written in the form

$$\frac{d^2\sigma_v}{d\epsilon d\Omega} = \frac{1}{2\pi} |F_\nu|^2 \left(\frac{m}{\mu_\nu} \right)^2 \frac{k'}{k} \int_{-\infty}^{\infty} e^{-i\epsilon t} W(t) dt, \quad (3.16)$$

where

$$W(t) = \langle W_t W_r W_\nu \rangle_\Omega,$$

W_r coincides with (3.14),

$$W_t = \langle \psi_t | e^{it \left(\frac{\kappa^2}{2M} + \kappa \mathbf{v}_m \right)} | \psi_t \rangle,$$

i.e.,

$$W_t = \int e^{-M\mathbf{v}_m^2/2T} e^{it \left(\frac{\kappa^2}{2M} + \kappa \mathbf{v}_m \right)} d\mathbf{V}_m / \int e^{-M\mathbf{v}_m^2/2T} d\mathbf{V}_m. \quad (3.17)$$

After further integrations over \mathbf{V}_m in (3.17) and over t in (3.16) we arrive at the following expression for the cross section for the process:

$$\frac{d^2\sigma_v}{d\epsilon d\Omega} = |F_\nu|^2 \left(\frac{m}{\mu_\nu} \right)^2 \frac{v'}{v} \left\langle (2kT \kappa \hat{m}_\nu^{-1} \kappa)^{-\frac{1}{2}} \right.$$

$$\left. \times \exp \left[- \frac{\left(\epsilon' - \frac{1}{2} \kappa \hat{m}_\nu^{-1} \kappa \right)^2}{2T \kappa \hat{m}_\nu^{-1} \kappa} \right] W_\nu(\epsilon_\nu) \right\rangle_\Omega, \quad (3.18)$$

where $\hat{m}_\nu^{-1} = \hat{R}_\nu + \frac{1}{M} \hat{1}$, where $\hat{1}$ is the unit tensor.

The quantity \hat{m}_ν is the mass tensor for the atom in the molecule, ϵ' is the energy transferred to the rotation-vibration degrees of freedom of the molecule, ϵ_ν is the energy going into vibrational excitation of the molecule. The total energy transferred by the neutron is $\epsilon = \epsilon' + \epsilon_\nu$. The calculation of the factor

$$W_\nu(\epsilon_\nu) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-i\epsilon_\nu t} \langle e^{-i\kappa \mathbf{u}_\nu e^{iHt}} e^{i\kappa \mathbf{u}_\nu e^{-iHt}} \rangle dt \quad (3.19)$$

is done in the harmonic approximation. To do this we expand the vector for the vibrational displacement of the atom in normal coordinates:

$$\mathbf{u}_\nu = \sum_i c_{\nu i}^i q_i, \quad (3.20)$$

where $C_{\nu i}^i$ is the amplitude vector which describes the intensity with which the atom participates in vibrations of the particular type.

*It should, however, be mentioned that the corrections to formula (3.11) that depend on the temperature are given incorrectly by formula (3.14) in the region $T \leq \Delta E_r$.

The determination of the quantities C_{ν}^i requires, in general, a knowledge of all the elements of the force constant matrix for the molecule, $F_{tt'}$, which are the coefficients in the expansion of the potential in internal valence coordinates:^[40]

$$2V = \sum F_{tt'} S_t S_{t'}, \quad S_t = \sum_i (c_v^i - c_{v'}^i) n_s. \quad (3.21)$$

In the case of diatomic and linear triatomic molecules, to determine them it is sufficient to use the normalization relation

$$\sum_i (c_v^i n)^2 + n m_{\nu}^{-1} n = \frac{1}{m_{\nu}} \quad (3.22)$$

(where n is an arbitrary unit vector), which states the invariance of the kinetic energy when written in normal and natural coordinates. From (3.22) for a diatomic molecule we get, for example,

$$(c_v)^2 = \frac{1}{m_{\nu}} \frac{M - m_{\nu}}{M},$$

where M is the mass of the molecule.

For the case of the water molecule, for which the force constants have been calculated theoretically,^[62] the geometry of the vibrations is shown in Fig. 1. One can approximately combine the vibrations with frequencies $\omega_1 = 0.466$ eV and $\omega_3 = 0.446$ eV and assume that the amplitude vector $c_H^{(1)}$ that characterizes them is directed along the line joining the hydrogen atom to the center of gravity of the molecule. One can also assume that the vector $c_H^{(2)}$, corresponding to the deformation vibration with frequency $\omega_2 = 0.20$ eV, is perpendicular to this direction. According to this model the force constants and the vector amplitudes corresponding to these types of oscillation are uniquely related to their frequencies, namely,

$$[c_H^{(1)}]^2 = 0.945 \frac{1}{m_H}, \quad [c_H^{(2)}]^2 = 0.463 \frac{1}{m_H}. \quad (3.23)$$

We note that a similar model can be used for studying a number of other molecules, for example H_2S and D_2O . In calculations with formulas (3.19) and (3.20) one usually uses second quantization for the coordinate operators and some general theorems about oscillators. These calculations are given in detail in a number of papers and monographs.^[11,41,42,43] The result for $W_{\nu}(\epsilon_{\nu})$ can be written in the form

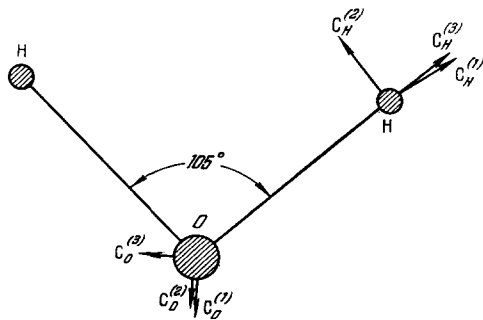


FIG. 1. Geometry of vibrations of the water molecule.

$$W_{\nu} \left(\epsilon_{\nu} = \sum_1^s n_{\lambda} \omega_{\lambda} \right) = \prod_{\lambda} \exp \left[-\frac{(\kappa c_{\nu}^{\lambda})^2}{2\omega_{\lambda}} \operatorname{cth} \frac{\omega_{\lambda}}{2T} \right] \times \exp \left[-\frac{n_{\lambda} \omega_{\lambda}}{T} \right] I_{n_{\lambda}} \left[\frac{(\kappa c_{\nu}^{\lambda})^2}{2\omega_{\lambda} \operatorname{sh} \left(\frac{\omega_{\lambda}}{2T} \right)} \right], \quad (3.24)^*$$

where $I_{n_{\lambda}}$ is the Bessel function of imaginary argument.

4. Scattering of Neutrons with Energies Less than the Energy for Excitation of Molecular Vibrations.

For most molecules the scattering of thermal energy neutrons leads only to rotational excitation, where the chemical binding appears either not at all or only through the zero point vibrations of the molecule. The formula describing this case of scattering has the form

$$\frac{d^2 \sigma_{\nu}}{d\epsilon d\Omega} = |F_{\nu}|^2 \frac{k'}{k} \left\langle (2\pi T \kappa \hat{m}_{\nu}^{-1} \kappa)^{-1/2} \times \exp \left[-\frac{\left(\epsilon - \frac{1}{2} \kappa m_{\nu}^{-1} \kappa \right)^2}{2T \kappa m_{\nu}^{-1} \kappa} \right] e^{-W_T} \right\rangle_{\Omega}, \quad (4.1)$$

$$W_T = \sum_i \frac{(\kappa c_{\nu}^i)^2}{2\omega_i} \operatorname{cth} \frac{\omega_i}{2T}, \quad (4.2)$$

W_T is the Debye-Waller factor. For rigid molecules, when $e^{-W_T} \approx 1$, the problem reduces, as already stated, to the scattering by a free particle with a mass having tensor properties. This approximation, which is called the mass tensor approximation, was first introduced by Sachs and Teller^[35] and used to find total scattering cross sections.

The result of Sachs and Teller is obtained by double integration of formula (4.1) (with $e^{-W_T} = 1$) over energy and angle. A single integration of (4.1) over angles gives the cross section for energy transfer $d\sigma/d\epsilon$. This cross section is used in direct calculations of slowing down and thermalization of neutrons.^[37] Formula (4.1) also has intrinsic importance, since it describes the double differential cross section, which is of paramount interest from the point of view of experimental studies of molecular properties. We shall convert this expression to a form suitable for numerical computation. In the diagonal representation of the tensor \hat{m}_{ν}^{-1} we have for the quantity $\kappa \hat{m}_{\nu}^{-1} \kappa$

$$\kappa \hat{m}_{\nu}^{-1} \kappa = \kappa^2 (r_1 \sin^2 \theta \cos^2 \varphi + r_2 \sin^2 \theta \sin^2 \varphi + r_3 \cos^2 \theta), \quad (4.3)$$

where the symbols r_1, r_2, r_3 denote the components of the tensor \hat{m}_{ν}^{-1} .^[38] The component r_3 corresponds to transfer of momentum directed along the vector joining the scattering atom with the center of gravity of the molecule (θ is the angle between this direction and the vector κ); thus $r_3 = 1/M$, where M is the

* $\operatorname{cth} \equiv \operatorname{coth}$, $\operatorname{sh} \equiv \operatorname{sinh}$.

Values of components of the tensor \hat{m}_ν^{-1} the effective mass for atoms of hydrogen in certain molecules (in units of m , the mass of the hydrogen atom)

Molecule	Component of tensor \hat{m}_ν^{-1}			Effective mass	
	r_1	r_2	r_3	according to Kogen $M_\nu^{(0)}$	according to Krieger and Nelkin \bar{M}_ν
CH ₄	0.438	0.438	0.0625	3.20	3.40
NH ₃	0.604	0.436	0.059	2.72	2.85
H ₂ O	1	0.535	0.0555	1.85	2.06
C ₂ H ₄	0.39	0.151	0.036	5.2	5.81

mass of the molecule. The components of the tensor \hat{m}_ν^{-1} are given in the Table for a number of molecules.

For any diatomic molecule, $r_1 = r_2 = 1/m_\nu$ ($\nu = 1, 2$), for linear and spherical molecules, $r_1 = r_2 = I^{-1}b_\nu^2 + 1/M$ (b_ν is the distance of the atom from the center of gravity of the molecule). The third tensor component r_3 , equal to $1/M$, is usually much smaller than the first two for light atoms. In such cases one may therefore regard only two components of the tensor \hat{m}_ν^{-1} as different from zero. There is, however, a class of molecules and molecular groups (molecules CH₃I, NH₄Br, the groups CH₃, NH₄⁺, H₃O⁺; which enter into the structure of more complex molecules, etc), characterizable by a single axis of rotation to which there corresponds a small moment of inertia; for these we may consider that only one of the components of \hat{m}_ν^{-1} is different from zero; it is $r_1 = I^{-1}b_\nu^2$ (where I is the moment of inertia and b_ν the distance from the special axis). The spectrum of the scattered neutrons depends essentially on the relation between the components of the tensor \hat{m}_ν^{-1} .

Using (4.3), we get the formula

$$\frac{d^2\sigma_\nu}{d\epsilon d\omega} = |F_\nu|^2 \frac{k'}{k} \left(\frac{m}{2\pi T \chi^2}\right)^{1/2} f(\chi, \epsilon). \tag{4.4}$$

For rigid molecules (i.e., for $WT = 0$),

$$f(\chi, \epsilon) = \frac{1}{2\pi} \int_{r_1^*}^1 \int_{r_2^*}^1 \int_{r_3^*}^1 [(x+y) \left(\chi^2 - \frac{x}{r_1^*} - \frac{y}{r_2^*}\right) \times (x - \chi^2 r_3)(y - \chi^2 r_3)]^{-1/2} \exp\left[-\frac{1}{2T} \frac{\left(\epsilon - \frac{1}{2}(x+y)\right)^2}{(x+y)}\right] dx dy \tag{4.5}$$

$$r_1^* = r_1 \left(1 + \frac{r_3}{r_2}\right), \quad r_2^* = r_2 \left(1 + \frac{r_3}{r_1}\right).$$

The region of integration is determined by the inequalities

$$x, y \geq \chi^2 r_3, \quad \frac{x}{r_1^*} + \frac{y}{r_2^*} \leq \chi^2.$$

Formula (4.5) is valid for rigid molecules of any type.

When we include the zero point vibrations in the integrand of (4.5) we get an additional factor depending on the shape and vibration frequency of the molecule. For molecules like H₂O and H₂S this factor has the form

$$I = \exp\left\{-\frac{1}{2m\omega_1} \left(\chi^2 - \frac{x}{r_1} - \frac{y}{r_2}\right) - \frac{1}{2m\omega_2} \frac{y}{r_2}\right\}. \tag{4.6}$$

Formula (4.5) for $d^2\sigma/d\epsilon d\omega$ and the resulting formulas for the cross sections $d\sigma/d\epsilon$ and $\sigma(E_n)$ are quite complicated for practical use. For this reason the different approximations obtainable from (4.1) are of great value.

In recent years, within the framework of the classical approximation for a rotator, there has been extensive use of the effective mass method, the essence of which is the following. In considering rotational transitions of the molecule, we introduce for each of its atoms, in place of the mass tensor \hat{m}_ν , an effective mass $M_\nu^{(0)}$ depending on the rotational properties of the molecule, but independent of the orientation of the molecule relative to κ .

The introduction of an effective mass is obviously equivalent to an approximate averaging of (4.1) over molecular orientations, which gives rise to the so-called monatomic gas approximation. The formulas in this approximation for the cross sections $d^2\sigma/d\epsilon d\omega$ and $d\sigma/d\epsilon$ have the form

$$\left(\frac{d^2\sigma_\nu}{d\epsilon d\omega}\right)^{\text{mon}} = |F_\nu|^2 \frac{m^2}{\mu_\nu^2} \frac{k'}{k} \left(\frac{M_\nu^{(0)}}{2\pi T \chi^2}\right)^{1/2} \exp\left[-\frac{M_\nu^{(0)}}{2T \chi^2} \times \left(\epsilon - \frac{\chi^2}{2M_\nu^{(0)}}\right)^2\right], \quad \frac{d\sigma}{d\epsilon} = \frac{m}{p} \frac{d\sigma}{dp}, \tag{4.7}$$

$$\left(\frac{d\sigma}{dp}\right)^{\text{mon}} = \sigma_{\nu\infty} \frac{M_\nu^{(0)}}{4m} \frac{p}{p_0^2} \left\{ \text{erf}(\theta p - \zeta p_0) \pm \text{erf}(\theta p + \zeta p_0) \right. \\ \left. + e^{\theta^2 p_0^2 - \zeta^2} [\text{erf}(\theta p_0 - \zeta p) \mp \text{erf}(\theta p_0 + \zeta p)] \right\}. \tag{4.8}$$

In formula (4.8), p_0 and p are expressed in units of $\sqrt{2MT}$; the upper sign is for $p_0 > p$, the lower for $p_0 < p$; $\sigma_{\nu\infty} = 4\pi |F_\nu|^2 m/\mu_\nu^2$,

$$\theta = \frac{M_\nu^{(0)} + m}{2\sqrt{M_\nu^{(0)}m}}, \quad \zeta = \frac{M_\nu^{(0)} - m}{2\sqrt{M_\nu^{(0)}m}}, \quad \text{erf } x = \frac{2}{\sqrt{\pi}} \int_0^x e^{-t^2} dt, \\ \sigma = \sigma_{\nu\infty} \left[\frac{M_\nu^{(0)}}{M_\nu^{(0)} + m} \right]^2 \frac{1}{\chi^2 \pi \beta^2} \left[\beta e^{-\beta^2} + (2\beta^2 + 1) \frac{1}{2} \frac{\sqrt{\pi}}{\beta} \text{erf } \beta \right], \\ \beta = \left(\frac{M_\nu^{(0)} E_n}{mT}\right)^{1/2}. \tag{4.9}$$

When $\beta \gg 1$, i.e., when $E_n \gg T$, we get from (4.9)

$$\sigma = \sigma_{\nu\infty} \left[\left(\frac{M_\nu^{(0)}}{M_\nu^{(0)} + m}\right)^2 + \frac{1}{2} \frac{m}{M_\nu^{(0)}} \left(\frac{M_\nu^{(0)}}{M_\nu^{(0)} + m}\right)^2 \frac{T}{E_n} + \dots \right]. \tag{4.10}$$

There are two ways of choosing the effective mass,

proposed respectively by Kogen^[37] and Krieger and Nelkin.^[10] According to Kogen's definition the effective mass is

$$[M_v^{(0)}]^{-1} = \langle n \hat{m}_v^{-1} n \rangle_\Omega \quad (4.11)$$

(n is an arbitrary unit vector). Such a choice for $M_v^{(0)}$ in many cases does not give good agreement with the rigorous formula of Sachs and Teller^[35] for the total cross section, which is obtained directly from the fundamental formula (4.1) by integration over $d\epsilon$ and $d\omega$ and which, when $E_n \gg T$ and $WT = 0$, has the following simple form:

$$\frac{\sigma}{\sigma_{v\infty}} = a + \frac{bT}{E_n}, \quad (4.12)$$

where

$$a = \langle (1 + n \hat{m}_v^{-1} n)^{-2} \rangle_\Omega, \quad \frac{b}{a} = \frac{1}{2} \langle n \hat{m}_v^{-1} n (1 + n \hat{m}_v^{-1} n)^{-2} \rangle_\Omega.$$

Because of this Krieger and Nelkin^[10] propose that one choose the effective mass by an adjustment method, taking as the effective mass in formulas (4.7), (4.8) and (4.10) not (4.11), but another quantity \bar{M}_v , which is defined so that formula (4.10) coincides with (4.12). Comparing (4.10) with (4.12) we find

$$[\bar{M}_v]^{-1} = \frac{1}{2} \left[\frac{1}{M_v^{(1)}} + \frac{1}{M_v^{(2)}} \right], \quad (4.13)$$

where

$$a = \left(1 + \frac{1}{M_v^{(1)}} \right)^{-2}, \quad \frac{b}{a} = \frac{1}{2} M_v^{(2)}.$$

As we see from the table, the effective masses M_v^0 differ considerably.

The effect of the zero point vibrations on neutron scattering can also be taken into account by introducing into (4.1) an average over molecular orientations of the Debye-Waller factor:

$$\langle W_T \rangle_\Omega = \kappa^2 \sum_i \frac{(c_i^z)^2}{6\omega_i} \coth \frac{\omega_i}{2T} = \kappa^2 \gamma. \quad (4.14)$$

Then, as can be shown by simple transformations, to include the zero point vibrations in formula (4.1) it is sufficient to replace the temperature T and the mass \bar{M}_v by T' and \bar{M}'_v :

$$T' = \zeta T, \quad \bar{M}'_v = \zeta \bar{M}_v, \quad (4.15)$$

and add a factor $e^{-\rho\epsilon}$ to formula (4.7) and a factor $e^{\rho(p^2 - p_0^2)}$ in formula (4.8). Here

$$\zeta = (1 + 8\gamma \bar{M}_v T)^{-1/2}, \quad \rho = \frac{1 - \zeta}{2\zeta}.$$

Experimental measurements of total scattering cross sections, made by the method of thermal neutron spectroscopy are in good agreement with the Krieger-Nelkin theory for most molecules.^[44,45] These include experiments for methane CH_4 (Melkonian^[46]), ethylene C_2H_4 (Melkonian,^[46] Janik et al.^[47]), ammonia NH_3 (Janik et al.,^[48] Rush et al.^[49]), for the molecules O_2 , CO_2 , N_2 and CF_4 (Melkonian,^[46] Fermi and Marshall^[51]). Small deviations from the theory were observed for the ethylene

molecule (they were, however, attributed to the uncertainty in the frequencies of the bending vibrations) and the H_2S molecule. More significant differences (in the range of 20–30%) were found for the water molecule.^[50] Even though the experiments on water are considered doubtful by various authors,^[43] the observed deviations from experiment serve as an indication that the Krieger-Nelkin model is not always applicable even for getting the total scattering cross section. This is not an accident. The principal defect of the effective mass method (independent of how one chooses the mass) is the incorrect averaging of the scattering effect over molecular orientations, which manifests itself most clearly when the components of the mass tensor m_{ij} are very different, since in this case the quantity $n \hat{m}_v^{-1} n$ appearing in (4.1) changes considerably with a change in orientation of the molecule. As we see from the Table, among the molecules enumerated this situation is most clearly shown for the H_2O molecule (similarly for H_2S).

Figure 2 shows curves obtained by the Krieger-Nelkin method (curve 1) and by an exact averaging over the molecular orientations (curve 2). As we see from Fig. 2, the difference between these curves when $E_n < T$ is about 10%. Curve 2 lies closer to the experimental points,^[50] but there is still not complete agreement with it. Thus the discrepancy between theory and experiment that was pointed out in^[43,44] is only partially eliminated by the more exact computations. It should be mentioned that the experiments described in^[43,44] contain a small systematic error,^[43] which apparently explains the incomplete agreement of our exact computations with the results.^[50] It seems to us that the effect noted for the example of H_2O (the difference between the total cross section and the Krieger-Nelkin result) may be

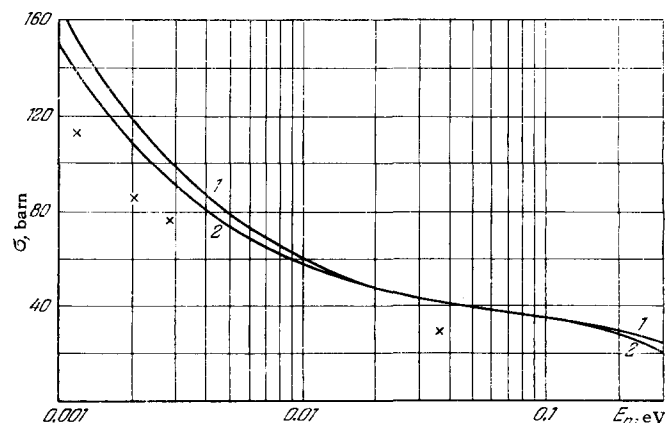


FIG. 2. Energy dependence of total cross section for scattering of neutrons by hydrogen atoms in the water molecule, computed per atom of hydrogen. Curve 1 is obtained by the Krieger-Nelkin method,^[43] curve 2 is obtained by rigorous averaging over molecular orientations in formula (4.1); x – experimental points of Heinoth.^[50]

typical for molecules with a sufficiently large difference in the components r_1 and r_2 of the mass tensor \hat{m}_ν^{-1} .

When applied to the differential scattering characteristics, such as $d\sigma/d\epsilon$, $d\sigma/d\omega$, and $d^2\sigma/d\epsilon d\omega$, the defects of the effective mass method appear even more clearly. This can be seen by a simple comparison of formulas (4.7) and (4.8) with the formulas obtained by rigorous averaging over molecular orientations, i.e., with formula (4.4) and the formulas for $d\sigma/d\epsilon$ that follow from it.

We may assert that in general the effective mass method cannot give the correct result for the cross section $d^2\sigma/d\epsilon d\omega$. This follows in particular from a comparison of (4.7) with (4.4) as $T \rightarrow 0$. From (4.7) it follows that the scattering cross section in this case is proportional to a delta function whose argument is $\epsilon - \kappa^2/2M_\nu^{(0)}$, whereas the true cross section, as we see from (3.11) is "smeared out" over the whole region $\epsilon < \kappa^2 r_1/2$. When $E_n \sim T$, (3.11) and (4.7) approach one another to some extent, but formula (4.7) is quantitatively accurate only when the components of \hat{m}_ν^{-1} are almost equal. The question of the validity of the Krieger-Nelkin approximation for the cross section $d^2\sigma/d\epsilon d\omega$ is discussed in the paper of McMurry et al.^[63] for the example of the methane and propane molecules and OH. They show that this method gives a fair result for the methane and propane molecules (for CH_4 the error seems to be no more than 10%). But for OH the approximation is much cruder.

The cross sections $d\sigma/d\epsilon$ and $d\sigma/d\omega$ are less sensitive to the procedure of averaging over molecular orientations. Figure 3 shows curves of $d\sigma/dp$ computed with the Krieger-Nelkin formula (4.8) and by rigorous averaging over molecular orientations using formula (4.1) (curve 2) for the water molecule H_2O , i.e., for a molecule with markedly different components of the mass tensor. The resulting errors in the determination of the cross section $d\sigma/d\epsilon$ by the effective mass method are about 10–20%. Similar conclusions hold for a number of other molecules (cf.^[9]). This method can therefore not be used for determining the cross sections $d\sigma/d\epsilon$ and $d\sigma/d\omega$ if one requires very high accuracy of the results.

Among the molecular properties that it would be desirable to study experimentally are: the waveform of the molecular vibrations, which is unknown for most molecules, certain features of the internal structure of molecules (Fermi resonance, bending vibrations, hindered rotation), features related to the presence of more than one equilibrium position, and also molecular interactions in liquids and crystals.

The molecular vibrations have only a slight effect on the scattering of thermal neutrons. The effects associated with them are contained in the function W_T (cf. (4.2), (4.1)), which, in the energy region $\epsilon < \omega$ treated here should be less than unity, since in

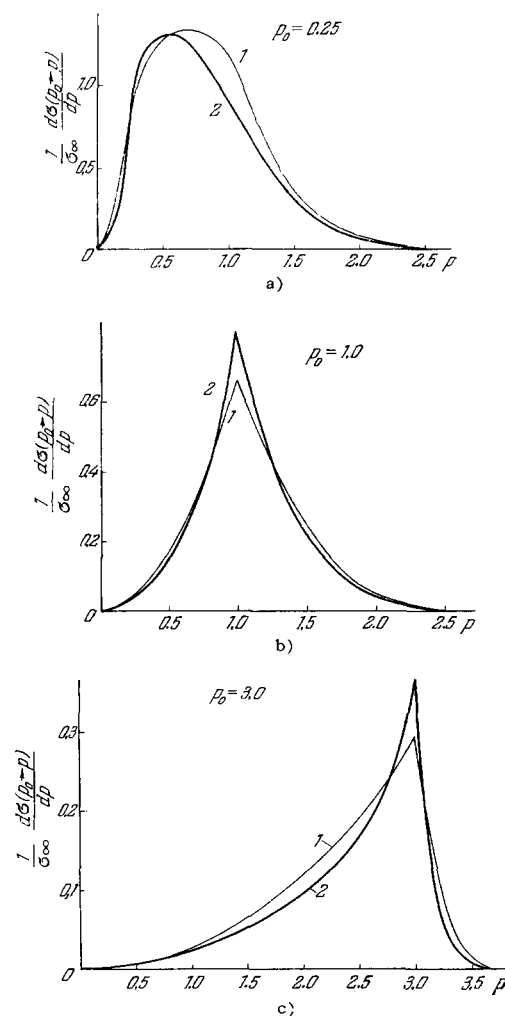


FIG. 3. Cross section $d\sigma/dp$ ($p = \sqrt{(E_n - \epsilon)/T}$), for scattering of neutrons by the hydrogen atoms in the water molecule, for different incident neutron energies $E_n = p^2/2m$. Curve 1 is obtained from formula (4.8); curve 2 is gotten by a rigorous averaging over molecular orientations in formula (4.1). p_0 and p are expressed in units of $\sqrt{2mT}$.

order of magnitude $W_T \sim \epsilon/\omega$. Thus, among the class of problems discussed in this Section are included only the features of the motion of molecular groups and the effect of the aggregate state of the material.

The simplest experiments are those that measure the total scattering cross section and angular distribution of the scattered neutrons. We have already spoken about experiments for simple gaseous molecules. But there is undoubtedly great interest in measurements for molecules in the liquid and solid states. Such measurements have been carried out, for example, for water (Melkonian,^[46] Heinloth^[50]), liquid ammonia NH_3 (Wanic^[52]), for the HCOOH molecule and benzene in the liquid state (Heinloth^[50]), and also for the molecular groups NH_3I and NH_3Br in polycrystalline materials.^[55] The most interesting of these experiments are those done on the temperature dependence of cross sections near a phase tran-

sition of the first kind.^[50,53] At these points one sees a sharp discontinuous change in cross section which indicates a marked change in the character of the intermolecular interactions at the phase transition.

More useful information about molecular properties comes from experiments on the double differential cross sections $d^2\sigma/d\epsilon d\Omega$. Such measurements have been made very recently, and are still few in number. These include the experiments of Randolf et al.^[56] on gaseous methane and a series of papers on water.^[57-60] On the basis of experiments on neutron scattering by water, Larsson and Dahlborg^[60] have calculated the spectra of quasiphonons assuming a quasicrystalline structure for the liquid. These spectra seem to be strongly temperature dependent.

There have recently been studies (made through measurements of the cross sections $d^2\sigma/d\epsilon d\Omega$) of the dynamics of molecular groups like CH_3 , NH_4^+ , and H_3O^+ in different molecules and different molecular media.^[61] From the special features of these cross sections (presence or absence of peaks, kinks) the authors of^[61] draw definite conclusions about the degree of freedom of rotation of individual groups of atoms. We emphasize that the list of experimental papers given here is by no means complete. An exhaustive list (to 1964) is given by Janik in a survey contained in the collection^[43].

5. Scattering of Neutrons Accompanied by Vibrational Excitation of the Molecule.

The general formula describing this case of scattering has the form (3.18), where $W_V(\epsilon_V)$ is given by (3.24). This formula can be simplified in the following two important cases.

For a molecule with a large moment of inertia, so that $Ib_V^2 \gg m_V$ (where b_V is the distance of the atom from the center of gravity of the molecule) rotational transitions are unimportant and the problem reduces to the case of scattering of the neutrons by a system of independent harmonic oscillators, i.e.,

$$\frac{d^2\sigma_V}{d\epsilon d\Omega} = |F_V|^2 \frac{m^2}{\mu_V^2} \frac{k'}{k} \langle W_V(\epsilon) \rangle_\Omega; \quad (5.1)$$

W_V is given by (3.24).

A special case of (5.1) is the model of an isotropic or anisotropic oscillator, which was already studied in the first papers of Fermi^[23] and others.^[30,31] If the inequality $Ib_V^2 \gg m_V$ is not satisfied, the processes of vibrational and rotational excitation of molecules occur simultaneously. One must therefore treat them together. We consider this case for ω , $\epsilon \gg T$. This condition, which is quite typical for most molecules, permits us to neglect the thermal motion of the molecules. In this case we find from (3.18)

$$\left(\frac{d^2\sigma_V}{d\epsilon d\Omega}\right)_{n_\lambda} = |F_V|^2 \left(\frac{m}{\mu_V}\right)^2 \frac{k'}{k} \left\langle \delta \left(\epsilon - \sum n_\lambda \omega_\lambda - \frac{1}{2} \kappa \hat{m}_V^{-1} \kappa \right) \times \prod_\lambda \frac{1}{n_\lambda!} \left[\frac{\langle \kappa c_V^\lambda \rangle^2}{2\omega_\lambda} \right]^{n_\lambda} e^{-\sum \frac{\langle \kappa c_V^\lambda \rangle^2}{2\omega_\lambda}} \right\rangle_\Omega. \quad (5.2)$$

The simplest recipe for further simplification of the calculations is to introduce averages of quantities over molecular orientations:

$$[M_V^{(0)}]^{-1} = \langle n \hat{m}_V^{-1} n \rangle_\Omega, \quad [M_V^\lambda] = \langle (n c_V^\lambda)^2 \rangle_\Omega$$

(n is an arbitrary unit vector). Such an approach was proposed by Nelkin^[65] for calculating excitations of vibrations of molecules of water (taking account of the thermal motion). One can then obtain the cross section $d\sigma/d\epsilon$ and the total cross section for vibration excitation $\sigma_{n_1, \dots, n_\lambda}$, from (5.2) in analytic form. The behavior of the cross section σ_n as a function of incident neutron energy is characterized by the following law: as the energy is increased,

$\sigma(E_n)$ increases (starting from $E_n \gtrsim \frac{M+m}{M} \sum_\lambda n_\lambda \omega_\lambda$), reaches a maximum at approximately the value

$$E_m = \frac{4mm_V}{(m+m_V)^2} E_n \sim \left(m_V \sum_\lambda \frac{1}{M_V^\lambda \omega_\lambda} \right)^{-1} \sum_\lambda n_\lambda$$

and then falls off smoothly to zero as $E_n \rightarrow \infty$.

The errors associated with the use of this procedure are significant even for finding total cross sections for vibration excitation. Such an approach is therefore not applicable for analyzing experiments on neutron scattering. The fact that the cross section for scattering of neutrons by water, calculated using this method, is in fair agreement with experiment^[54,43] in no way contradicts this statement, since in the total cross section one does not observe individual transitions, but rather a collection of them, and furthermore, in the region studied ($E_n < 1$ eV) these transitions still do not play an important role.*

In contrast to the case for the thermal region, the vibrational characteristics of the molecule (frequency and vibration shape) are directly manifested in the scattering cross sections in the region of excitation of vibrational transitions. But the analysis of the cross sections on the basis of formulas (3.18) and (5.2) is very complicated, since each individual molecule requires involved numerical computations, or more precisely, a whole series of such computations.†

Thus the spectroscopy of slow neutrons (energies $E_n < 1$ eV) has limited possibilities as a method for experimental investigation of vibrational characteristics of molecules.

As we shall see, a much simpler connection with

*Some simplifications are also possible in the classical treatment of individual types of molecular excitation (McMurry^[62]), namely those for which we have the inequality $(\kappa \cdot c_V^j)^2 \gg \omega_j$. But this is a very strict condition, since for vibrations with low frequencies the coefficients $(c_V^j)^2$ are usually small.

†In this connection we note that the scheme for numerical computation of cross sections for vibrational excitation was suggested by Massey^[36] even before the appearance of the general formalism of the theory presented here.

the vibrational characteristics is established from spectra of scattering of fast neutrons.

III. SCATTERING OF FAST NEUTRONS

6. Approximation by Free Particles with a Momentum Spread.

As already indicated, for large energy transfers the interaction time of neutron and nucleus is small compared to the period of vibration of the molecule and, consequently, under these conditions the chemical binding can appear only kinematically, through the momentum spread of the atoms in the molecule. The smallness of the time for energy transfer can be formulated mathematically in two ways. The first of these, developed in [66,67], consists of the following. In accordance with the assumption of small time for energy transfer, the operator $e^{iH\nu t} e^{-iHt}$ of (2.3) is expanded in powers of t , and only the leading terms in the expansion are kept. The expansion [67] has the form

$$e^{iH\nu t} e^{-iHt} = e^{iR\nu t} \sum_{n=0}^{\infty} \frac{(it)^n}{n!} g_n, \quad g_0 = 1, \quad g_1 = L\nu, \\ g_2 = \frac{1}{2} (L\nu^2 + [H, L\nu]). \tag{6.1}$$

As has already been noted, [42] formula (6.1) cannot be used for finding the double differential cross section, defined by (2.1) and (2.3), because when we substitute (6.1) in (2.3) singularities appear (the delta function $\delta(\epsilon - R\nu)$ and its derivatives). Thus the expressions given by (6.1) and (2.3) for the double differential cross section can be used only as an intermediate formula for calculating the total scattering cross section $\sigma(E_n)$. In lowest approximation, keeping only the first term of the series (6.1), we find

$$\sigma_\nu = \left\langle \int \sigma_{\nu 0}(\mathbf{p}_\nu) \varphi_i^2(\mathbf{p}) d\mathbf{p} \right\rangle_T, \tag{6.2}$$

where $\sigma_{\nu 0} = 4\pi |F_\nu|^2$ is the cross section for scattering of the neutron by a free nucleus with momentum \mathbf{p}_ν . The formula (6.2) for the scattering cross section obviously has the same meaning as (2.5) for the absorption cross section,—in both cases we are dealing with an average of the cross section for neutron-nucleus interaction over the initial state of the molecule.

A consistent derivation of the formulas for the double differential cross section under these conditions can be given by expanding the operator $e^{iH\nu t} e^{-iHt}$ not in powers of t but in powers of the molecular Hamiltonian H , i.e., roughly speaking, in the reciprocal of the period for molecular vibration (which, we recall is here assumed to be large compared to the effective time for energy transfer). This expansion, including all terms of first order in H , has the form [3,76]

$$e^{iH\nu t} e^{-iHt} = e^{i(R\nu + L\nu)t} \left\{ 1 + \frac{1}{2!} [H, L\nu] (it)^2 + \frac{1}{3!} [[H, L\nu], L\nu] (it)^3 + \dots \right\}.$$

Substituting this expression in (2.3) and integrating over t , we find

$$\frac{d^2\sigma_\nu}{d\epsilon d\Omega} = \frac{k'}{k} \left(\frac{m}{m_\nu} \right)^2 \left\{ |F_\nu(\mathbf{p}_\nu)|^2 \delta(\epsilon - R\nu - L\nu) + \langle |F_\nu(\mathbf{p}_\nu)|^2 h(\epsilon - R\nu - L\nu) \right\rangle, \tag{6.3}$$

where h denotes the operator

$$h(z) = \frac{1}{2!} \delta^{(2)}(z) [H, L\nu] - \frac{1}{3!} \delta^{(3)}(z) [[H, L\nu], L\nu] \\ \dots + (-1)^s \frac{1}{s!} \delta^{(s)}(z) \cdot \underbrace{[\dots [H, L\nu] \dots L\nu]}_s + \dots, \\ \delta^{(s)}(z) = \frac{d^s}{dz^s} \delta(z).$$

The first term in (6.3) has a clear physical meaning: the double differential cross section for scattering of a neutron by a chemically bound nucleus is the result of averaging the differential cross section for scattering of a neutron by a free nucleus, $|F_\nu(\mathbf{p}_\nu)|^2$, over the momentum spread which the nucleus has in the molecule. (The energy and momentum conservation in the collision are taken into account through the argument $(\epsilon - R\nu - L\nu)$ of the delta function.) It is natural to call the resulting expression the approximation by a free particle with a momentum spread. The second term in (6.3) characterizes the finite nature of the time for energy transfer. Including it greatly improves the accuracy of the approximation in some cases.

We note that, according to (6.3), averaging over the momentum spread is equivalent to introducing some effective momentum appearing in the collision, determined by the relation $\epsilon - R\nu - L\nu = 0$, i.e., having order of magnitude $\bar{p}_\nu = \sqrt{m_\nu} (\epsilon - R\nu) / \sqrt{R\nu}$. It then follows that in cases of large energy transfer all the estimates made earlier concerning the role of binding in the scattering and of the role of the variability of the amplitudes F_ν (cf. Sec. 1) must be modified as follows. The correction to (1.13) to take account of the finite time for interaction of neutron and nucleus is equal in order of magnitude to

$$\frac{\bar{p}_\nu^2}{m_\nu} \frac{d \ln F}{dE} \sim \zeta^2 \frac{\bar{\omega}_\nu}{\Gamma}, \quad \zeta = \frac{\epsilon - R\nu}{\sqrt{\omega_\nu R\nu}};$$

the correction for the finite time of energy transfer (second term in (6.3)) is approximately $\sqrt{\bar{p}_\nu^2 / R\nu m_\nu} \sim \zeta \sqrt{\bar{\omega}_\nu / R\nu}$, while the correction for variability of the amplitude (1.14) is

$$(\epsilon - R\nu) \frac{d \ln F_\nu}{dE} \sim \zeta \frac{\sqrt{R\nu \bar{\omega}_\nu}}{\Gamma}.$$

It is easy to see that all these corrections are small for scattering angles close to the angle ϑ_0 corresponding to collision of the neutron with a nucleus initially at rest, and given by the relation $\epsilon = R\nu(\vartheta_0)$.

They increase with increasing $|\vartheta - \vartheta_0|$, since then the factor ζ increases. One may then say that the conditions for validity of all formulas derived on the basis of (6.3) become worse for large deviations of ϑ from ϑ_0 . This fact is, however, unimportant, since, as we shall see, for large $|\vartheta - \vartheta_0|$ the cross section $d^2\sigma/d\epsilon d\Omega$ is exponentially small.

7. The Case of Potential Neutron-nucleus Scattering

a) General formulas for the double differential cross sections. For not too heavy nuclei, the neutron-nucleus scattering in the energy region considered here is potential scattering, and consequently the amplitudes F_ν may be taken to be constant. Thus this case deserves special treatment.

So we set $F_\nu = \text{const}$ and consider the leading term in (6.3). We shall again determine the wave function of the initial state from formula (3.2), but without the assumption that ψ_ν necessarily corresponds to a system of independent harmonic oscillators. The quantum mechanical average in (6.3) can now be written as

$$\int \psi_\nu^* \psi_\nu^* \delta(\epsilon - R_\nu - L_\nu) \psi_\nu \psi_\nu d\mathbf{R}_0 d\Omega d\mathbf{u}, \quad (7.1)$$

where \mathbf{R}_0 is the radius vector to the center of inertia of the molecule, \mathbf{u} is the set of vibrational coordinates, and Ω is the set of angles determining the orientation of the molecule. The further arguments are similar to those made in deriving formulas (3.13) and (3.17). Assuming that the temperature is sufficiently high so that we can use the quasiclassical picture for ψ_ν , we reduce the matrix element (7.1) to $\int \psi_\nu^* \delta(\epsilon - R_\nu - L_\nu) \psi_\nu d\mathbf{u} (d\Omega/4\pi)$, i.e., we are left only with the integration over \mathbf{u} and the averaging over molecular orientations. We write the velocity of the ν -th atom in the molecule as $\mathbf{v}_\nu = \mathbf{V}_m + \Omega \mathbf{b}_\nu + \dot{\mathbf{u}}_\nu$ (cf. (3.2)). The delta function appearing in (6.3) can then be written in the form

$$\delta(\epsilon - R_\nu - L_\nu) = \int \delta(E_t - \kappa \mathbf{V}_m) \delta(E_r - [\Omega \mathbf{b}_\nu] \kappa) \delta(E_\nu - \kappa \dot{\mathbf{u}}_\nu) \times \delta(\epsilon - R_\nu - E_t - E_r - E_\nu) dE_t dE_r dE_\nu. \quad (7.2)$$

Thus,

$$\langle \delta(\epsilon - R_\nu - L_\nu) \rangle = \left\langle \int W_t(E_t) W_r(E_r) W_\nu(E_\nu) \times \delta(\epsilon - R_\nu - E_t - E_r - E_\nu) dE_t dE_r dE_\nu \right\rangle;$$

the factors $W_t W_r W_\nu$ contain an average over the translational, rotational, and vibrational degrees of freedom:

$$W_t = N_t^{-1} \int e^{-\frac{M \mathbf{V}_m^2}{2T}} \delta(E_t - \kappa \mathbf{V}_m) d\mathbf{V}_m = \left(\frac{M}{2\pi T \kappa^2} \right)^{1/2} e^{-E_t^2/a_t^2}, \quad (7.3)$$

$$a_t^2 = \frac{2T \kappa^2}{M}, \quad N_t = \int e^{-M \mathbf{V}_m^2/2T} d\mathbf{V}_m,$$

$$W_r = N_r^{-1} \int e^{-\frac{L \mathbf{L}^2}{2T}} \delta(E_r - \kappa [\Omega \mathbf{b}_\nu]) d\mathbf{L} = (\pi a_r^2)^{-1/2} e^{-E_r^2/a_r^2},$$

$$a_r^2 = 2T \kappa \hat{R}_\nu \kappa, \quad N_r = \int e^{-\frac{L \mathbf{L}^2}{2T}} d\mathbf{L} \quad (7.4)$$

(\mathbf{R}_ν is the mass tensor introduced earlier in Sec. 3),

$$W_\nu = \langle \delta(E_\nu - \kappa \dot{\mathbf{u}}_\nu) \rangle.$$

It then follows that

$$\langle \delta(\epsilon - R_\nu - L_\nu) \rangle = \left\langle \frac{1}{\sqrt{\pi(a_t^2 + a_r^2)}} \int_{-\infty}^{\infty} e^{-\frac{(\epsilon - R_\nu - E_\nu)^2}{a_t^2 + a_r^2}} W_\nu(E_\nu) dE_\nu \right\rangle. \quad (7.5)$$

b) The case of harmonic vibrations. Further specification of (7.5) requires the use of assumptions about the nature of the vibrational motions. If the vibrations of all the atoms are harmonic in the ground and excited states, then one may assume (cf. Sec. 3) that

$$u_\nu = \sum_{i=1}^s c_\nu^i q_i, \quad \dot{u}_\nu = \sum_{i=1}^s c_\nu^i P_i, \quad \psi_\nu = \prod_{i=1}^s \varphi_i(P_i),$$

where q_i, P_i are the normal coordinates and momenta, s is the number of vibrational degrees of freedom, and consequently

$$W_\nu = \int \prod_{i=1}^s W_\nu^{(i)}(E_\nu^{(i)}) \delta\left(E_\nu - \sum_i E_\nu^{(i)}\right) dE_\nu^{(i)},$$

$$W_\nu^{(i)} = \sum_{n=0}^{\infty} (N_t^i)^{-1} e^{-\frac{n\omega_i}{T}} \int |\varphi_t^{(i)}(P_i)|^2 \delta(E_\nu^{(i)} - \kappa c_\nu^i P_i) dP_i$$

$$= \int \Phi_B^i \delta(E_\nu^{(i)} - \kappa c_\nu^i P_i) dP_i,$$

where

$$\Phi_B^i = \sum_{n=0}^{\infty} (N_t^i)^{-1} e^{-\frac{n\omega_i}{T}} |\varphi_t^{(i)}(P_i)|^2 = \left(\pi \omega_i \text{cth} \frac{\omega_i}{2T} \right)^{-1/2}$$

$$\times \exp\left(-\frac{P_i^2}{\omega_i \text{cth} \frac{\omega_i}{2T}} \right)$$

is the Bloch distribution of the momenta of a harmonic oscillator.^[68]

We thus find that

$$W_\nu^{(i)} = \frac{1}{\sqrt{\pi a_\nu^{(i)}}} \exp\left(-\frac{E_\nu^{(i)}}{a_\nu^{(i)2}} \right), \quad (a_\nu^{(i)})^2 = (\kappa c_\nu^i)^2 \text{cth} \frac{\omega_i}{2T}.$$

Substituting these definitions in (7.5) and integrating over $dE_\nu = \prod_{i=1}^s dE_\nu^{(i)}$ we finally get

$$\frac{d^2\sigma_\nu}{d\epsilon d\Omega} = |F_\nu|^2 \left(\frac{m}{\mu_\nu} \right)^2 \frac{k'}{k} \left\langle \frac{1}{\sqrt{\pi a^2}} e^{-\frac{(\epsilon - R_\nu)^2}{a^2}} \right\rangle, \quad (7.6)$$

where

$$a^2 = a_t^2 + a_r^2 + a_\nu^2 = \sum_{i=1}^s (\kappa c_\nu^i)^2 \omega_i \text{cth} \frac{\omega_i}{2T} + 2T \kappa \hat{m}_\nu^{-1} \kappa. \quad (7.6')$$

Introducing the unit vector $\mathbf{n} = \kappa/\kappa$, we can write the quantity a^2 in the form

$$a^2 = 2R_\nu \omega_\nu(\mathbf{n}), \quad \omega(\mathbf{n}) = m_\nu \left[\sum_i (c_\nu^i \mathbf{n})^2 \omega_i \text{cth} \frac{\omega_i}{2T} + 2T \mathbf{n} \hat{m}_\nu^{-1} \mathbf{n} \right].$$

We note that when $T \gg \omega_i$ ($i = 1, \dots, s$), $\omega_\nu(\mathbf{n}) = 2T$. The unit vector \mathbf{n} , which takes on an arbitrary direc-

tion in space, determines the orientation of the molecule. Thus, averaging over orientations of the molecule is equivalent to integrating over the components of the vector \mathbf{n} .

It should be noted that formula (7.6), derived on the assumption that the temperature is sufficiently high, is actually also valid for low temperatures, lower than the rotational energies. The reason is that at low temperatures the rotation of the molecule plays no part in the neutron scattering, i.e., for $T \rightarrow 0$ we can simply set $\alpha_t^2 = \alpha_r^2 = 0$ in (7.6'). The only exception in this respect is the case of diatomic molecules, for which, as $T \rightarrow 0$ a special anomaly appears (cf. below).

Formula (7.6) is also easily modified for the case where the rotations and translational motion of the molecules are not free, as assumed in its derivation, but are frozen (this situation occurs in liquids and molecular crystals). If we assume that the frozen rotation and translational motion are characterized by harmonic oscillations, then, repeating the arguments given earlier, we obtain the earlier expression for $d^2\sigma/d\epsilon d\omega$, i.e., formula (7.6), with the one difference that α_r^2 now has the form $\alpha_r^2 = \omega_t \text{cth}(\omega_t/2T) \times \kappa \hat{R}_\nu \kappa$, where ω_t is the frequency of the orientational vibrations, while $\alpha_t^2 = \omega_n \text{cth}(\omega_n/2T) \kappa^2/M$, where ω_n is the frequency of the translational vibrations. When $\omega_t \gg T$, $\alpha_t^2 = \omega_t \kappa \hat{R}_\nu \kappa$, while for $\omega_t \ll T$ we get the earlier expression (7.4) for α_r^2 (and similarly for α_t^2). We also note that the corrections to formula (7.6) associated with the operator $h(\epsilon - R_\nu - L_\nu)$ in (6.3) also have a relatively simple form in the case where the vibrations in the molecule are completely harmonic. Their detailed computation is given in [3].

Let us discuss formula (7.6) in more detail. Let us introduce a system of coordinates with its center on the ν -th atom, in which the quantity $\omega_\nu(\mathbf{n})$ given by (7.6), which is a quadratic function of the projections of the unit vector, has a canonical form (i.e., if we write the projections as $\cos \theta$, $\sin \theta \sin \varphi$, $\sin \theta \cos \varphi$, where θ and φ are spherical angles, then in the general case

$$\omega = \omega^{(1)} \cos^2 \theta + \omega^{(2)} \sin^2 \theta \sin^2 \varphi + \omega^{(3)} \sin^2 \theta \cos^2 \varphi,$$

where $\omega^{(1)}$, $\omega^{(2)}$, $\omega^{(3)}$ are complicated functions of the components of the amplitude vectors and the components of the mass tensor). The result of integrating in (7.6) over $d\Omega = \sin \theta d\theta d\varphi$ can be expressed in terms of a universal function (ρ^2 , p , q):

$$\frac{d^2\sigma_\nu}{d\epsilon d\omega} = |F_\nu|^2 \left(\frac{m}{\mu_\nu}\right)^2 \frac{k'}{k} \frac{1}{\sqrt{2\pi R_{\nu\omega^{(1)}}}} f(\rho^2, p, q),$$

$$\rho^2 = \frac{(\epsilon - R_\nu)^2}{2R_{\nu\omega^{(1)}}}, \quad p = \frac{\omega^{(2)}}{\omega^{(1)}}, \quad q = \frac{\omega^{(3)}}{\omega^{(1)}} \quad (7.7)$$

(where it is assumed that $\omega^{(1)} > \omega^{(2)} > \omega^{(3)}$), where

$$f(\rho^2, p, q) = \frac{1}{\pi} \int_0^{1/q} dt \frac{e^{-\rho^2 t}}{t}$$

$$\begin{cases} \frac{1}{\sqrt{(1-p)(1-qt)}} K\left(\sqrt{\frac{(p-q)(t-1)}{(1-p)(1-qt)}}\right), & 1 \leq t \leq \frac{1}{p}, \\ \frac{1}{\sqrt{(p-q)(t-1)}} K\left(\sqrt{\frac{(1-p)(1-qt)}{(p-q)(t-1)}}\right), & \frac{1}{p} \leq t \leq \frac{1}{q}. \end{cases}$$

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

In the case of linear molecules there are only two preferred directions in the molecule—along and perpendicular to the molecular axis. Thus, in this case $\omega_\nu = \omega^{(1)} \cos^2 \theta + \omega^{(2)} \sin^2 \theta$. For diatomic molecules the quantities $\omega^{(1)}$, $\omega^{(2)}$ have the meaning

$$\omega_{1,2}^{(1)} = \frac{m_{2,1}}{M} \omega \text{cth} \frac{\omega}{2T} + 2 \frac{m_{1,2}}{M} T, \quad \omega_{1,2}^{(2)} = 2T.$$

Correspondingly, for linear molecules the function f in (7.7) is replaced by

$$f(\rho^2, p) = \frac{1}{\sqrt{2(1-p)}} \int_0^{1/p} dt \frac{e^{-\rho^2 t}}{t \sqrt{1-pt}}, \quad p = \frac{\omega^{(2)}}{\omega^{(1)}}. \quad (7.8)$$

For $\rho = 0$ (scattering at the angle ϑ_0 corresponding to scattering of the neutron by a nucleus at rest) the function $f(0, p)$ has a maximum equal to

$$f(0, p) = \frac{1}{2\sqrt{1-p}} \ln \left(\frac{1+\sqrt{1-p}}{1-\sqrt{1-p}} \right) \approx \frac{1}{2} \ln \frac{2}{p} \quad \text{as } p \rightarrow 0; \quad (7.9)$$

in the case of diatomic molecules, at sufficiently low temperatures

$$p = \frac{m_{1,2}}{M} \frac{2T}{\omega} \ll 1.$$

Consequently the scattering cross section at angle ϑ_0 may reach large values as $T \rightarrow 0$:

$$\frac{d^2\sigma_{1,2}(\vartheta_0)}{d\epsilon d\omega} = |F_{1,2}|^2 \left(\frac{m}{\mu_{1,2}}\right)^2 \frac{1}{\sqrt{2\pi R_{1,2\omega^{(1)}}}} \ln \left(\frac{\omega}{2T} \frac{M}{m_{2,1}} \right). \quad (7.10)$$

The anomaly mentioned occurs in the region of angles of order $|\vartheta - \vartheta_0| \sim \left(\frac{m\omega}{\kappa^2} p \ln \frac{1}{p}\right)^{1/2}$. Formula (7.10)

becomes invalid for very low temperatures, lower than the rotational energies. On the other hand, in liquids the inclusion of frozen rotation by the same method as in Sec. 7a leads to replacing the argument of the logarithm in formula (7.10) by ω/ω_t , where ω_t is the frequency of orientational vibrations. An example of a calculation of the angular distribution of neutrons scattered by the hydrogen atoms of the water molecule, done using formula (7.6)* is shown in Fig. 4. We note that the spread in angle is quite large, i.e., is easily observable, and depends strongly on the temperature.

The differential cross section (7.6) for scattering

*The graph in Fig. 4 was constructed to include the correction $h(\epsilon - R_\nu - L_\nu)$ in (6.3).

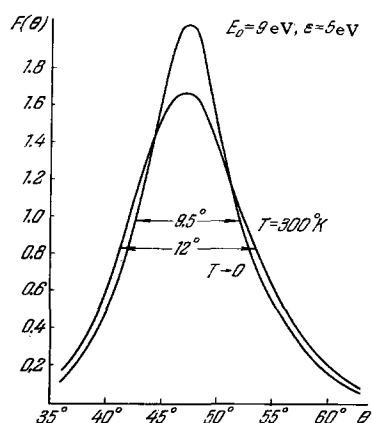


FIG. 4. Angular distribution of cross section $d^2\sigma/d\epsilon do$ for scattering of fast neutrons by hydrogen atoms of the water molecule for two different temperatures. The cross section is computed using (7.6) and is given in units of $4 |F_H|^2 \frac{k'}{k} \left(\frac{1}{4\pi T\epsilon}\right)^{1/2}$; E_0 is the initial neutron energy.

of fast neutrons contains the most important properties of the molecule: the frequencies ω_i of the molecule and the amplitude vectors c_i^j , which are directly related to the force constants (cf. Sec. 3). We shall discuss the question of possible determination of the components of the amplitude vectors from the spectrum of scattered fast neutrons (assuming that the frequencies of the molecule and its geometry are given) for the general case of a molecule consisting of N different atoms. The experiment enables one to determine the spectra for scattering of the neutron from each individual atom, since the angles which correspond to maxima of the angular distributions of the scattered neutrons, and are given by relations $\epsilon = R_\nu(\vartheta_0)$ depend critically on the mass of the scattering atoms and are therefore well separated. Using formula (7.7) we can, from the spectra of scattered neutrons, determine for each atom the quantities $\omega^{(1)}$, $\omega^{(2)}$, $\omega^{(3)}$, i.e., we can get $3N$ relations connecting the components of the amplitude vectors, of which there are $3N$ s. Considering that the components of the amplitude vectors are connected by the relations (3.22) and the relations that follow from conservation of momentum and angular momentum (cf. Sec. 3 and [40] p. 11), the number of which, in general, is $3N + 6$ s, we arrive at the conclusion that the use of the additional relations among the components of the amplitude vectors that are obtained from neutron measurements is sufficient for a complete determination of all the components of the amplitude vectors and, consequently, of the complete set of force constants for the general case of a triatomic molecule. For more complex molecules one must make measurements at several temperatures corresponding essentially to the different values of $\omega^{(1)}$, $\omega^{(2)}$, and $\omega^{(3)}$. The use of molecular symmetry elements usually greatly simplifies the analysis. For example, for linear triatomic molecules $X_1X_2X_3$ it is sufficient to

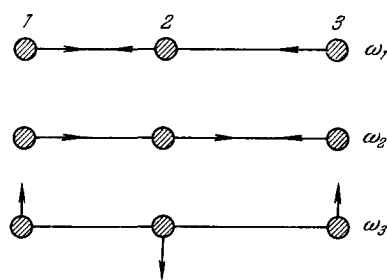


FIG. 5. Geometry of vibrations of linear triatomic molecules.

measure the maximum of the angular distribution (for a given energy transfer ϵ) described by formula (7.9), in order to determine the values of the three force constants F_1 , F_2 , F_3 characterizing respectively the longitudinal vibrations along the bonds X_1X_2 and X_2X_3 and the interaction of these two vibrations (Fig. 5). Assuming that $\omega^{(2)}$ is known (it is the uniquely determinable frequency of transverse vibrations) one can from the measured $d^2\sigma(\vartheta_0)/d\epsilon do$ for scattering by one of the atoms (for example, X_1) find the frequency $\omega^{(1)}$ by means of the formula (7.6):

$$\omega^{(1)} = \omega_1 \operatorname{cth} \frac{\omega_1}{2T} [c_1^{(1)}]^2 + \omega_2 \operatorname{cth} \frac{\omega_2}{2T} [c_1^{(2)}]^2,$$

where ω_1 , ω_2 , $C_1^{(1)}$, $C_1^{(2)}$ are the frequencies of longitudinal vibrations and the amplitude vectors corresponding to the two types of longitudinal vibrations. Now, using (3.22),

$$[c_1^{(1)}]^2 + [c_1^{(2)}]^2 = \frac{1}{m_1} - \frac{1}{M}$$

and the relations following from momentum conservation ([40] p. 23),

$$m_1 c_1^{(1)} - m_2 c_2^{(1)} - m_3 c_3^{(1)} = 0, \quad m_1 c_1^{(2)} + m_2 c_2^{(2)} - m_3 c_3^{(2)} = 0,$$

we find $C_1^{(1)}$, $C_1^{(2)}$, $C_2^{(1)}$, $C_2^{(2)}$, $C_3^{(1)}$, $C_3^{(2)}$, and from them, by using (3.21), we get the force constants. A good example of this type of molecule is OCS, for which the force constants F_1 , F_2 , F_3 are unknown. In the case of a molecule of the type $X_1X_2X_1$ (for example, CO_2) the analysis is even simpler, but in this case there are only two force constants for longitudinal vibrations, which are uniquely determined by the longitudinal frequencies. It should be emphasized that at present there is no general experimental method for determining molecular force constants, and they are usually found by incomplete theoretical calculations, or from molecular frequencies by using the crude valence force approximation ([40] p. 174). The development of methods for determining them by means of neutron spectroscopy would therefore be of great importance for quantum chemistry.

c) Effects of anharmonicity of intramolecular vibrations. In certain cases that are of great interest the vibrations of the atom corresponding to one or more degrees of freedom are strongly anharmonic. This is the case, in particular, for NH_3 and PH_3 ,

characterized by an inversion doubling of levels. In such molecules the vibration of the N or P atom relative to the H_3 plane occurs in a complicated potential obtained by superposing two parabolas separated by a potential barrier, whose height in the case of NH_3 is $D = 2076 \text{ cm}^{-1}$ (cf. Fig. 8.4 of [40]). At low temperatures $T \ll D$ the vibrations of the N atom are harmonic and the cross section for scattering of neutrons by the N atom is given by our earlier formula (7.6). On the other hand, at temperatures of the order of thousands of degrees the N atom carries out a complicated motion, shifting from one equilibrium position to the other. Approximately, such an intramolecular motion of the atoms can be described by using a simplified model, according to which one of the normal vibrations of the N atom (perpendicular to the H plane) occurs in this complex potential, while the other normal vibrations remain harmonic.

Another example of partially harmonic intramolecular vibrations is the freezing in of the rotation of groups of atoms within the molecule. The simplest example of this phenomenon occurs for the CH_3OH molecule (cf. [43]). In this molecule the H atom of the hydroxyl group moves relative to the CO bond in a complex potential having three minima. If the temperature is low, we may assume that the H atom of the hydroxyl group vibrates harmonically near one of the three equilibrium positions. But if the temperature is sufficiently high (of the order of several thousand °C), this atom performs a complicated periodic motion, rotating around the CO bond. Under these conditions we may again use a simplified model in which all the vibrations are taken to be harmonic, except for the one in which the H atom of the hydroxyl group moves in the plane perpendicular to the CO bond. It is easy to get a formula for $d^2\sigma/d\epsilon d\Omega$ for these molecular models which are characterized by one anharmonic degree of freedom.

Repeating the arguments used in deriving (7.3), and assuming that one degree of freedom (the j -th) is anharmonic, we get a formula that includes both the cases discussed:

$$\frac{d^2\sigma_v}{d\epsilon d\Omega} = |F_v|^2 \left(\frac{m}{\mu_v}\right)^2 \frac{k'}{k} \left\langle \frac{1}{\sqrt{\pi a^2}} \int_{-\infty}^{\infty} \exp\left[-\frac{(\epsilon - R_v - E_v^{(j)})^2}{a^2}\right] \times W_j(E_v^j) dE_v^j \right\rangle_{\Omega}, \quad (7.11)$$

where

$$a^2 = \sum_{i=1}^s (\kappa c_v)^2 \omega_i \operatorname{cth}\left(\frac{\omega_i}{T}\right) + 2T\kappa \dot{m}_v^2 \kappa$$

(the prime means that the j -th term of the sum is omitted)

$$W_j(E_v^j) = \left\langle \int \varphi_j^*(\mathbf{p}_j) \delta\left(E_v^j - \frac{\mathbf{p}_j^2}{m_v}\right) \varphi_j(\mathbf{p}_j) d\mathbf{p}_j \right\rangle_T,$$

$\varphi(\mathbf{p}_j)$ is the momentum distribution corresponding to the motion in the j -th ("anharmonic") coordinate.

Formula (7.11) can be used for determining the characteristics of the anharmonic potentials discussed above from the spectra of scattered fast neutrons.

Anharmonicity of the intramolecular vibrations also manifests itself in the peculiar phenomenon of Fermi resonance, which lifts the degeneracy of two neighboring vibrational energy states of a polyatomic molecule to which there correspond harmonic vibrational wave functions ψ_1 and ψ_2 . The lifting of the degeneracy gives a mixture of these states $\psi^1 = a\psi_1 + b\psi_2$, $\psi^2 = b\psi_1 - a\psi_2$, where a and b are parameters determined by the anharmonicity. The calculation [6] of the cross section for scattering of fast neutrons taking account of Fermi resonances reduces to replacing ψ_1, ψ_2 by ψ^1, ψ^2 in the summation (Sec. 7a) over vibrational states of the molecule, and leads to the appearance in formula (7.6), which can be written in the form

$$\frac{d^2\sigma_v}{d\epsilon d\Omega} = |F_v|^2 \left(\frac{m}{\mu_v}\right)^2 \frac{k'}{k} \langle W \rangle_{\Omega},$$

of an additional term ΔW , i.e.,

$$\frac{d^2\sigma_v}{d\epsilon d\Omega} = |F_v|^2 \left(\frac{m}{\mu_v}\right)^2 \frac{k'}{k} \langle W + \Delta W \rangle_{\Omega}.$$

As one can show, [6] in order of magnitude,

$$\frac{\Delta W}{W} \sim (1 - e^{-\frac{E_1}{T}}) e^{-\frac{E_1}{T}} b^2,$$

where E_1 is the excitation energy of the molecule corresponding to the unsplit vibrational level. The presence of the additional term ΔW leads to the appearance of an easily observable asymmetry in the angular distribution of scattered neutrons with respect to the angle ϑ_0 , as given by $\epsilon = R_v(\vartheta)$. In the case of Fermi resonance for the CO_2 molecule (lifting of degeneracy of the 100 and 020 levels), the estimates [6] show that for $T \approx E_1 = 0.16 \text{ eV}$, $\Delta W/W \approx 0.1$, i.e., the effect is surely observable.

d) Cross section for energy transfer. In connection with the important part of the energy transfer cross section $d\sigma/d\epsilon$ in the theory of neutron moderation, we study its behavior in the region of high initial neutron energies. On the basis of (7.6), integrating over all scattering angles, we find, to within exponentially small quantities,

$$\frac{d\sigma_v}{d\epsilon} = \frac{\sigma_{v0}}{E_m} w(\epsilon), \quad w(\epsilon) = \frac{1}{2} \left\langle 1 + \operatorname{erf}\left[a\left(\frac{k'}{k} - \delta\right)\right] \right\rangle_{\Omega}, \quad (7.12)$$

where

$$a = \frac{k}{2\sqrt{m\omega_v(n)}} \left(1 + \frac{m}{m_v}\right), \quad \delta = \frac{m_v - m}{m_v + m}, \quad \sigma_{v0} = 4\pi |F_v|^2;$$

the quantity $w(\epsilon)$ has the meaning of the probability for transfer of energy ϵ to the nucleus. In the special case of scattering by a hydrogen atom,

$$\frac{d\sigma_v}{d\epsilon} = \frac{\sigma_{v0}}{k_m} w(\epsilon), \quad w(\epsilon) = \left\langle \operatorname{erf}\left[\frac{k'}{\sqrt{2m\omega_v(n)}}\right] \right\rangle_{\Omega}. \quad (7.13)$$

An interesting feature of this last formula is that the probability w appearing in it is independent of the initial neutron energy E_n .

Formulas (7.12) and (7.13) can be simplified considerably by replacing the averages over molecular orientations by the averaged quantity $\bar{\omega}_\nu$

$= \int \omega_\nu(\mathbf{n}) \frac{d\Omega}{4\pi}$. As the results of an exact averaging over molecular orientations show for the case of neutron scattering by the hydrogen atoms in the water molecule, this procedure does not lead to serious errors, i.e., in all cases one can use formulas (7.12) and (7.13), simplified by introducing the average quantity $\bar{\omega}_\nu$ in this way. Then the formulas acquire a clear physical meaning. According to (7.12) the probability for energy transfer is $w(\epsilon) = 1$ if the final neutron energy $E'_n = k'^2/2m$ exceeds the minimum energy $\delta^2 E'_n$ that it would have on the basis of the conservation laws after scattering by a free nucleus of mass m_ν at rest. On the other hand, when $E'_n < \delta^2 E_n$ the probability for energy transfer is exponentially small. The width of the region in which the smearing of the step function with $w(\epsilon) = 1$ for $E'_n \geq \delta^2 E_n$, $w = 0$ for $E'_n \leq \delta^2 E_n$ occurs is given, according to (7.12), by a quantity of order of magnitude $\sqrt{E_m \bar{\omega}}$ (in energy units).

We note that formulas (7.12) and (7.13) are not valid for quasielastic scattering of fast neutrons, i.e., for $\epsilon \lesssim \bar{\omega}_\nu$, since in that case the approximation by a free particle having a momentum spread is invalid (cf. Sec. 6). In this case we can, however, use the general formula (4.1), which is also valid, as follows from its derivation, for describing the scattering of fast neutrons accompanied by small energy transfers.

Assuming that the auxiliary condition $\frac{(k+k')^2}{2m_\nu} >> 4T(m_\nu \cdot n \hat{m}_\nu^{-1} n)^{-1}$ is satisfied, by integrating formula (4.1) over angle one can obtain a cross section $d\sigma/d\epsilon$ valid for $\epsilon < \bar{\omega}_\nu$:

$$\frac{d\sigma_\nu}{d\epsilon} = \frac{\sigma_{\nu 0}}{E_m} w(\epsilon), \quad w(\epsilon) = \left\langle \frac{1}{\mu s} e^{-\frac{\epsilon}{2T}(s \pm 1)} \right\rangle_\Omega, \quad (7.14)$$

where

$$\mu = m_\nu n \hat{m}_\nu^{-1} n, \quad s = \sqrt{1 + \frac{4T}{\mu \beta}}, \quad \beta = \sum_{i=1}^s \frac{(nc_i^i)}{\omega_i} \operatorname{cth} \frac{\omega_i}{2T}$$

(the minus sign refers to processes in which the neutron loses energy, the plus to those in which it gains energy in collision with the molecule). Just as in formulas (7.12) and (7.14), we can replace the averaging in (7.14) over molecular orientations by introducing averaged quantities

$$\bar{\mu} = \int \mu \frac{d\Omega}{4\pi}, \quad \bar{\beta} = \int \beta \frac{d\Omega}{4\pi}.$$

Figures 6 and 7 show graphs of the dependence of $w(E'_n)$, constructed using formulas (7.12)–(7.14), for the case of scattering of neutrons by H and D atoms in the H_2O and D_2O molecules. As we see from the graphs, the region of quasielastic scattering $\epsilon \lesssim \bar{\omega}_\nu$ is characterized by a "spike," which is related to the fact that for small energy transfers the

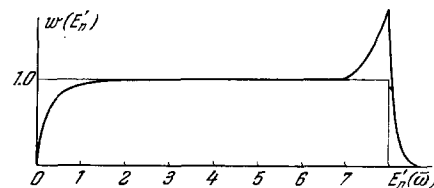


FIG. 6. Probability of energy loss $w(E'_n)$, $E'_n = K'^2/2m$, for scattering of neutrons by H atoms in H_2O . Computations for $E_n - E'_n \gg \bar{\omega}$ done using formula (7.13) and those for $E_n - E'_n \leq \bar{\omega}$ using formula (7.14). E'_n is expressed in units of $\bar{\omega}$.

nucleus does not behave as if it were free and the scattering of the neutron is markedly affected by the chemical binding and the inertia of the molecule.

8. Case of Variable Amplitudes for Neutron-nucleus Scattering

a) Absorption cross section. One can write the general formula (2.5) for the absorption cross section in a more detailed form, assuming, as usual, that the wave function for the initial state of the molecule is given by the adiabatic approximation $\varphi_i = \psi_t \psi_r \psi_v$. We write the cross section for absorption of a neutron by a free nucleus, which depends on the energy of relative motion of the neutron and nucleus, for $m_\nu \gg m$,

$$E = \frac{k_v^2}{2m_\nu} \approx \frac{m_\nu}{m_\nu + m} E_n - \mathbf{k} \mathbf{v}_\nu,$$

as follows:

$$\sigma_r^{(0)} = \int \sigma_r^{(0)} \left(\frac{m_\nu}{m_\nu + m} E_n - E_{\text{trans}} - E_r - E_v \right) \delta(E_t - \mathbf{k} \mathbf{V}_m) \delta(E_r - \mathbf{k} \{\mathbf{\Omega} \mathbf{h}_\nu\}) \delta(E_v - \mathbf{k} \mathbf{u}_\nu) dE_{\text{trans}} dE_r dE_v.$$

Arguing in the same way as in the derivation of (7.6), we have

$$\sigma_r = \left\langle \int W_t W_r W_v \sigma_r^{(0)} \left(\frac{m_\nu}{m_\nu + m} E_n - E_t - E_r - E_v \right) \times dE_t dE_r dE_v \right\rangle_\Omega, \quad (8.2)$$

where the factors W_t , W_r , W_v differ from those defined earlier in (7.3) and (7.4) in having κ replaced by \mathbf{k} . If we assume that all the molecular vibrations are harmonic, (8.1) can be written as follows:

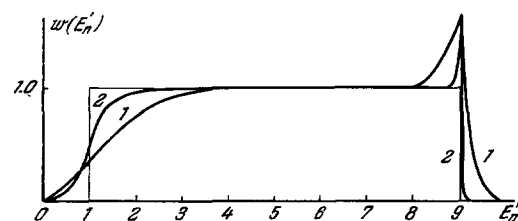


FIG. 7. Probability of energy loss $w(E'_n)$ for scattering of neutrons by D atoms in D_2O . Curve 1 corresponds to $E_n = 9\text{eV}$. Curve 2 is for $E_n = 9\bar{\omega}$ (where $\bar{\omega}$ is the effective "frequency" of vibration of the D atom in D_2O , equal to 0.14 eV at $T = 300^\circ\text{K}$). In both cases the energy scale is expressed in units of $\bar{\omega}$.

$$\sigma_r = \left\langle \int e^{-\frac{1}{\Delta^2} \left(\frac{m_\nu}{m_\nu+m} E_n - \eta \right)^2} \sigma_r^{(0)} \left(\frac{m_\nu}{m_\nu+m} E_n - \eta \right) d\eta \right\rangle_\Omega, \quad (8.3)$$

where

$$\Delta^2 = E_m \cdot \frac{1}{2} \omega(\mathbf{n}),$$

and $\omega(\mathbf{n})$ is defined in (7.6). In the special case of resonant Breit-Wigner scattering, when $\sigma_r^{(0)}$ is given by formula (2.6), we have from (8.3)

$$\sigma_r = \frac{4\pi\Gamma_e\Gamma_r}{k^2\Gamma^2} \int \psi(\xi, x) \frac{d\Omega}{4\pi},$$

$$\psi(\xi, x) = \int_{-\infty}^{\infty} e^{-\frac{1}{4}\xi^2(x-y)^2} \frac{dy}{1+y^2}, \quad x = 2 \frac{\frac{m_\nu}{m_\nu+m} E_n - E_0}{\Gamma}, \quad \xi = \frac{\Gamma}{\Delta}. \quad (8.4)$$

If in (8.4) we replace the average over orientations by introducing the average quantity

$$\bar{\omega}_\nu = \int \frac{\omega_\nu(\mathbf{n})}{4\pi} d\Omega = \frac{\omega^{(1)} + \omega^{(2)} + \omega^{(3)}}{3},$$

then

$$\sigma_r = \frac{4\pi\Gamma_e\Gamma_r}{k^2\Gamma^2} \psi(\bar{\xi}, x), \quad \bar{\xi} = \frac{\Gamma}{\sqrt{2 \frac{m}{m_\nu} E_n \bar{\omega}}} \quad (8.5)$$

(where $\bar{\omega}/2 \approx T$ when $T \gg \omega_i$) and, consequently, the resonant absorption of the neutron by a nucleus contained in a molecule is described by the same formula as in the case of the thermal Doppler effect on free nuclei, with the one difference that (8.5) contains, not the thermal energy T , but the effective quantity $\bar{\omega}/2$, which takes account of the momentum spread of the nuclei which is associated simultaneously with the vibrational, translational and rotational motion of the molecule.

As the results of numerical computations show, replacing the rigorous averaging in (8.4) by introducing the averaged quantity $\bar{\omega}_\nu$ is possible only if the effective frequencies $\omega_i^{(1)}, \omega_i^{(2)}, \omega_i^{(3)}$ do not differ too markedly, namely if

$$\frac{\omega^{(2)}}{\omega^{(1)}}, \frac{\omega^{(3)}}{\omega^{(1)}} \gtrsim \frac{1}{2}.$$

In the opposite case one must carry out the rigorous averaging over molecular orientations, which leads to formulas considerably different from those for the thermal Doppler effect. In the most interesting case of $\xi = \Gamma/\Delta < 1$, when the function $\psi(\xi, x)$ can be written as the asymptotic expression

$$\psi(\xi, x) = \sqrt{\pi} \xi \exp\left(-\frac{1}{\pi} \xi^2 x^2\right),$$

we find from the angular integration in (8.4)

$$\sigma_r = \frac{4\pi\Gamma_e\Gamma_r}{k^2\Gamma^2} \sqrt{\pi} \xi_1 f(\rho^2, p, q),$$

$$\xi_1 = \frac{\Gamma}{\Delta_1}, \quad \rho^2 = \frac{x^2}{\Delta_1^2}, \quad \Delta_1 = \sqrt{2 \frac{m}{m_\nu} E_n \omega^{(1)}},$$

$$p = \frac{\omega^{(2)}}{\omega^{(1)}}, \quad q = \frac{\omega^{(3)}}{\omega^{(1)}}, \quad (8.6)$$

where the function $f(\rho^2, p, q)$ is defined by formula (7.7).

We give the results of a specific calculation on the example of resonance absorption of neutrons by Cl atoms in the CCl_4 molecule. In this case we may assume that vibrations of the Cl atoms occur only along the C-Cl bond and perpendicular to it. Using the frequencies of vibration and force constants for the C-Cl and Cl-Cl bonds taken from [70], we get for the effective frequency of vibration along the C-Cl bond (in eV)

$$\omega^{(1)} = 0.0153 \operatorname{cth} \left(\frac{0.0284}{T} \right) + 0.0466 \operatorname{cth} \left(\frac{0.0466}{T} \right) + 0.46T \quad (8.7)$$

and for the effective frequency of vibration along the Cl-Cl bond (in eV)

$$\omega^{(2)} = \omega^{(3)} = 2.7 \cdot 10^{-3} \operatorname{cth} \left(\frac{1.34 \cdot 10^{-2}}{T} \right) + 1.62 \cdot 10^{-2} \operatorname{cth} \left(\frac{1.93 \cdot 10^{-2}}{T} \right) + 1.32T. \quad (8.8)$$

Using (8.7) and (8.8) we get at 300°K, $\omega^{(1)} = 0.055$ eV, $\omega^{(2)} = 0.078$ eV, i.e., $\bar{\omega} = 0.063$ eV and $\bar{\omega}/2T = 1.1$. Thus, in this case the energy dependence of the absorption cross section as given by (8.5) agrees closely with the analogous dependence for the thermal Doppler effect. On the other hand, when $T = 100^\circ\text{K}$, $\omega^{(1)} = 0.066$ eV, $\omega^{(2)} = 0.027$ eV, i.e., $\bar{\omega} = 0.04$ eV and $\bar{\omega}/2T = 2.3$. Thus, at low temperatures the difference from the thermal Doppler effect is very great. One may expect the molecular bonds to show up more clearly at room temperature in the case of the molecules NOCl and CH_3Cl , for which $\bar{\omega} \approx 0.1$ eV at 300°K.

Formulas (8.5) and (8.6) may find application to analysis of results of measurements of parameters of nuclear resonances for nuclei contained in a molecule. At the same time it should be mentioned that measurement of the energy dependence $\sigma_r(E_n)$ (in those cases where it is sufficiently clear) can be used for determining some of the characteristics of molecules. One should be guided by the arguments that molecular properties manifest themselves significantly in neutron absorption when the parameter $\Gamma/\sqrt{2(m/m_\nu)E_0\bar{\omega}}$ is small (where E_0 is the resonance energy). This is the situation, for example, in the case of the chlorine nucleus (resonance with parameters $E_0 = 400$ eV, $\Gamma = 0.06$ eV [71]) and the iron nucleus (resonance with parameters $E_0 = 200$ eV, $\Gamma = 0.6$ eV [72]). Thus we may hope that observation of the energy dependence of the cross section for resonant absorption of neutrons by iron nuclei may be used, in particular, for studying biological objects of interest, for example hemin, which is contained in hemoglobin, [73] and which contains iron.

It should also be noted that in some cases, when the vibrational motion of the resonantly absorbing nucleus is strongly anharmonic, the dependence of the

neutron absorption cross section should show a peculiar behavior. Such is the case, for example, for the AsCl_3 molecule, in which the As nucleus (having a convenient resonance with parameters $E_0 = 47$ eV, $\Gamma = 0.34$ eV^[74]) can occupy two equilibrium positions, as does N in NH_3 .

b) Neutron scattering cross sections. It follows from (6.2) that the formula for the total cross section for resonant scattering of neutrons should differ from (8.4) only in the replacement of the factor $\Gamma_e \Gamma_p / \Gamma^2$ by Γ_e^2 / Γ^2 (i.e., the whole derivation of a) remains valid also for the scattering cross sections). It is also of interest to discuss the regularities associated with the double differential cross section for resonant scattering of neutrons, since one can obtain additional information about molecular structure by measuring them. When all the vibrations of the molecule are harmonic, we easily find, using (6.3),

$$\frac{d^2\sigma_v}{d\epsilon d\Omega} = \langle |F_v(\mathbf{p}_v)|^2 \delta(\epsilon - R_v - L_v) \rangle_\Omega$$

$$= \frac{4\pi}{k^2} \frac{\Gamma_e^2}{\Gamma^2} \left\langle \psi(\xi, x) \frac{1}{\sqrt{2\pi R_v \omega_v(n)}} e^{-\frac{(\epsilon - R_v)^2}{2R_v \omega_v(n)}} \right\rangle_\Omega, \quad (8.9)$$

where

$$\xi = \frac{\Gamma}{\sqrt{k^2 - \frac{1}{4}x^2}}, \quad x = \frac{2}{\Gamma} \left(\frac{m_v}{m_v + m} E_n - E_0 - \frac{1}{2}(\epsilon - R_v) \right).$$

In the general case the angular distributions of the scattered neutrons described by (8.9) are characterized (for a given energy transfer ϵ) by having two maxima, of which one is determined by the condition $x = 0$, and the other by the condition $\epsilon = R_v$. In scattering into the backward hemisphere one may usually take $\xi \gg 1$, and then on the basis of (8.9) we arrive at the conclusion that in this case

$$\frac{d^2\sigma_v}{d\epsilon d\Omega} = \left| F_v \left(\frac{m_v}{m_v + m} E_n - E_0 - \frac{1}{2}(\epsilon - R_v) \right) \right|^2$$

$$\times \langle (2\pi R_v \omega_v(n))^{-1/2} e^{-\frac{(\epsilon - R_v)^2}{2R_v \omega_v(n)}} \rangle_\Omega. \quad (8.10)$$

we recall that formulas (8.9) and (8.10) are valid under the conditions $\Gamma, \epsilon \gg \bar{\omega}$. When the energy transfer is low, $\epsilon \lesssim \bar{\omega}$ and $\Gamma \gg \bar{\omega}$, the cross sections for resonant scattering are described by the formulas found in^[14].*

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