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Proton Motions in Complex Hydrogenous Liquids. I. A Cross Section for Quasi-Elastic Scattering of Slow Neutrons

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The present work deals with the derivation of a neutron-scattering cross section for quasi-elastic scattering from a complex hydrogenous liquid. The internal motions of the proton within the molecule and possibly the motions of the protons between molecules have to be taken into account in a full description of the dynamical picture, and consequently also have to be included in the interpretation of scattered neutron spectra. The motion of the scattering protons is described as a superposition of the motion of the proton with respect of the center of gravity of the molecule on the motion of the center of gravity itself. A rapid jump motion of the proton during the time τ_1 is considered; the origin of the jump might be an isomeric rotation or a change of proton position due to jumps in a hydrogen bond. In between the jumps, the proton is supposed to vibrate for a time τ_0. The motion of the center of gravity of the molecule is supposed to be either a diffusive motion for a time τ_1', if the molecule is free to move, or a vibration for a time τ_0', if the molecule is bound, for instance via hydrogen bonds to neighbors.

1. INTRODUCTION

DURING the last few years a considerable amount of experimental information has been obtained in various laboratories on the molecular and atomic motions of complex hydrogenous liquids by means of the slow-neutron scattering technique.[1,2] For water, experimental data[3-5] have been compared with very detailed predictions of the diffusive part of the molecular motions worked out by Singwi and Sjölander,[6] Chudley and Elliot,[7] Oskotskii,[8] and Rahman *et al.*[9] In all these cases the motion of a point-like molecule was considered and no investigation was made of the effect of proton motions within the molecule on the neutron-scattering picture obtained.

The quantum-mechanical formulation of Zemach and Glauber,[10] which takes into account the translational, rotational, and vibrational degrees of freedom, was used by Dasannacharya *et al.*[11] to explain the neutron-scattering result on liquid methane. They pictured the translational part as a simple diffusive motion, but the predicted intensity of the quasi-elastic line did not agree with the observed intensity, verified also by other experiments (Janik *et al.*[12]).

There are strong experimental evidences that the hindrance of molecular rotations in the field of neighbors and also the possible change of energy barriers to internal hindered rotations in going from the free gaseous state to the condensed state play a rather important role in quasi-elastic scattering from complex hydrogenous liquids. It seems proved beyond doubt that the picture of simple diffusion for the translational part of the proton motion is insufficient to explain the facts.

In view of the moderate success of the various models in explaining the atomic motions even in simple liquids, it is quite understandable that no effort has been made to establish any model or useful theory by which the apparently complex neutron-scattering results obtained on liquids like glycerol, the alcohols, pentane, etc. could be even qualitatively understood. The experimental results obtained on liquids like glycerol, propyl alcohol, and pentane indicate, however, certain striking facts which might make the understanding of these neutron spectra simpler than the very complex water results. In several cases[13] it was found that the apparent self-diffusion coefficient derived from studies of quasi-elastic linewidths was larger, and in cases like glycerol at low temperature much larger, than the directly measured or calculated real self-diffusion coefficient. The obvious conclusion was that the neutron in such cases observes a mixture of the protonic and molecular motions or only the protonic motions. Under such circumstances the comparison of models created to describe the motion of monatomic liquids with the experimental results obtained on complex liquids seems generally quite meaningless. This is particularly true for strongly associated liquids like propyl alcohol, $C_3H_7(OH)$, with one hydro-

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[1] *Inelastic Scattering of Neutrons in Solids and Liquids* (International Atomic Energy Agency, Vienna, 1961); *Proceedings of the Chalk River Symposium on Inelastic Scattering of Neutrons in Solids and Liquids* (International Atomic Energy Agency, Vienna, 1963); *Inelastic Scattering of Neutrons in Solids and Liquids* (International Atomic Energy Agency, Vienna, 1965).

[2] *Thermal Neutron Scattering*, edited by P. A. Egelstaff (Academic Press Inc., New York, 1965), Chaps. 7, 8.

[3] B. N. Brockhouse, Nuovo Cimento Suppl. **9**, 45 (1958).

[4] D. J. Hughes, H. Palevsky, W. Kley, and E. Tunkelo, Phys. Rev. **119**, 872 (1960).

[5] K. E. Larsson, S. Holmryd, and K. Otnes, in *Inelastic Scattering of Neutrons in Solids and Liquids* (International Atomic Energy Agency, Vienna, 1961), p. 329.

[6] K. S. Singwi and A. Sjölander, Phys. Rev. **119**, 863 (1960). In our derivation we shall follow closely the mathematical procedure of these authors.

[7] C. T. Chudley and R. J. Elliot, Proc. Phys. Soc. (London) **77**, 353 (1961).

[8] V. S. Oskotskii, Fiz. Tverd. Tela **5**, 1082 (1963) [English transl.: Soviet Phys.—Solid State **5**, 789 (1963)].

[9] A. Rahman, K. S. Singwi, and A. Sjölander, Phys. Rev. **126**, 986 (1962); **126**, 997 (1962).

[10] A. C. Zemach and R. J. Glauber, Phys. Rev. **101**, 118 (1956); **101**, 129 (1956).

[11] B. A. Dasannacharya, G. Venkataraman, and K. Usha Deniz, in *Inelastic Scattering of Neutrons in Solids and Liquids*, (International Atomic Energy Agency, Vienna, 1965), Vol. II, p. 157.

[12] J. A. Janik and A. Kowalska, in *Thermal Neutron Scattering* (Academic Press Inc., New York, 1965), p. 474.

[13] K. E. Larsson and U. Dahlborg, Physica **30**, 1561 (1964).

gen bond between a given molecule and one of its neighbors. Also, for long molecules like pentane, C_5H_{12}, or still longer ones, the hindrances for diffusion should be expected to be considerable. On the other hand, internal molecular hindered or partial rotations are known to be possible, so that for instance a CH_3 group or a CH_3CH_2 group may perform a partial rotation over an angle of the order of 120° round a C-C bond to create a rotational isomer. The possibility that such mechanisms might be the cause of the so-called diffusive broadening of a neutron line has been pointed out for the case of glycerol[14] in which a CH_2OH group would have to perform a partial rotation after one hydrogen bond is broken. No cross section was, however, calculated for such a possible and simple cause for the scattering mechanism.

The first of the two present papers will deal with the derivation of a neutron-scattering cross section for a proton bound within a molecule. The proton is supposed to be free to perform jumps from one position to another within the same molecule. Independent of the internal protonic jump motion—which might be caused by rotational jumps as described above—the molecule is supposed to exist in two phases of motion: Either it might be bound to neighbors, for instance by hydrogen bonds, or it might be free to move. It is obvious that the proton motion will appear as a superposition of the two independent motions thus defined.

The second paper will deal with a comparison of the theoretical and experimental results on relaxation times and apparant self-diffusion coefficients for propyl alcohol and pentane.

2. FORMULATION OF THE NEUTRON-SCATTERING CROSS SECTION

Use will be made of the formulation of the incoherent differential scattering cross section per atom, per unit solid angle, and per unit energy $\hbar\omega$ given by van Hove[15]:

$$\frac{d^2\sigma}{d\Omega d\omega}=\frac{a^2}{2\pi}\frac{k}{k_0}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\exp i(\boldsymbol{\kappa}\mathbf{r}-\omega t)G_s(\mathbf{r},t)d\mathbf{r}dt, \quad (1)$$

where a is the bound incoherent scattering length, and $\mathbf{k}$ and $\mathbf{k}_0$ denote, respectively, the final and initial wave vectors of the neutron. The energy and momentum transfers in the scattering process are

$$\hbar\omega=(\hbar^2/2m)(k^2-k_0^2) \quad \text{and} \quad \hbar\boldsymbol{\kappa}=\hbar(\mathbf{k}-\mathbf{k}_0), \quad (2)$$

m being the neutron mass.

The central problem is to formulate the self-correlation function $G_s(\mathbf{r},t)$. To do this we shall make use of the ideas already developed by Singwi and Sjölander[6] and Oskotskii.[8] Four different types of probability density functions contribute in building up $G_s(r,t)$ according to our assumptions, namely:

(a) *to define the internal proton motion:*

$g_i(\mathbf{r},t)$ is the probability of finding the proton vibrating stationary at the position $\mathbf{r}$ within the molecule at time t if it starts at the origin at time 0.

$h_i(\mathbf{r},t)$ is the probability of finding the proton jumping at the position $\mathbf{r}$ within the molecule at time t if it starts at the origin at time 0.

(b) *to define the motion of the molecule:*

$g_e(\mathbf{r},t)$ is the probability of finding the center of gravity of the molecule in a bound state at $\mathbf{r}$ and t if it starts at the origin at time 0.

$h_e(\mathbf{r},t)$ is the probability of finding the center of gravity of the molecule in an unbound state at $\mathbf{r}$ and t if it starts at the origin at time 0.

In an analogous way we define $p_i(t)$ as the probability that the proton remains in a bound vibrating state at time t if it was vibrating at time $t=0$. Furthermore $q_i(t)$ is defined as the probability of finding the proton remaining in a jumping state at time t if it was jumping at $t=0$. Exactly in the same way $p_e(t)$ is defined as the probability of finding the molecule remaining bound to its neighbors at time t if it was bound at time 0. Finally $q_e(t)$ is the probability of finding the molecule free to move (unbound) at time t if it was free at time 0. For all these functions we have that $-p'(t)dt$ or $-q'(t)dt$ gives the probability that a certain state is left between t and $t+dt$.

With these functions defined we divide the molecular motion into steps numbered 0, 1, $2,\cdots, 2m,\cdots$. We assume that during one step for the molecule the proton performs a motion in 1 or 2 or 3 or $\cdots$ or n steps.

Then

$$H_0(\mathbf{r},t)=\int g_e(\mathbf{r}',t)p_e(t)\sum_{n=0}^{\infty}F_n(\mathbf{r}-\mathbf{r}',t)d\mathbf{r}' \quad (3)$$

describes the probability of finding the proton at $\mathbf{r}$ and t if the molecule remains in a bound state. $F_n(\mathbf{r}-\mathbf{r}',t)$ describes the displacement of the proton made in n steps. Here primed quantities describe the coordinates of the center of gravity and unprimed describe the coordinates of the proton. Already in this first step of the final proton motion described by $H_0(\mathbf{r},t)$ it appears as a folding of all possible internal proton motions with the motion of the center of gravity. $\mathbf{r}-\mathbf{r}'$ is the position of the proton with respect to the center of gravity of the molecule.

Step number two will be a free state of the molecule at $\mathbf{r}$ and t with probability

$$H_1(\mathbf{r},t)=-\int_0^t dt_1\int d\mathbf{r}_1 q_e(t-t_1)\int d\mathbf{r}'h_e(\mathbf{r}'-\mathbf{r}_1',t-t_1)\sum_{n=0}^{\infty}F_n[\mathbf{r}-\mathbf{r}_1-(\mathbf{r}'-\mathbf{r}_1'),t-t_1]$$
$$\times\int g_e(\mathbf{r}_1',t_1)p_e'(t_1)\sum_{n=0}^{\infty}F_n(\mathbf{r}_1-\mathbf{r}_1',t_1)d\mathbf{r}_1'. \quad (4)$$

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[14] K. E. Larsson and K. S. Singwi, Phys. Letters **3**, 145 (1962).
[15] L. Van Hove, Phys. Rev. **95**, 249 (1954).

In general it is easy to see that the probability that step number $2m$ of the molecule corresponding to a bound state of the molecule at $\mathbf{r}$ and t will be described by

$$\begin{aligned}H_{2m}(\mathbf{r},t)=(-1)^{2m}\int_0^t dt_{2m}\int_0^{t_{2m}} dt_{2m-1}\cdots\int_0^{t_2} dt_1\int\cdots\int d\mathbf{r}_{2m}\cdots d\mathbf{r}_1 p_e(t-t_{2m})q_e'(t_{2m}-t_{2m-1})\cdots p_e'(t_1)\\ \times\int g_e(\mathbf{r}'-\mathbf{r}_{2m-1}', t-t_{2m})\sum_{n=0}^{\infty} F_n[\mathbf{r}-\mathbf{r}_{2m}-(\mathbf{r}'-\mathbf{r}_{2m}'), t-t_{2m}]d\mathbf{r}'\\ \times\int h_e(\mathbf{r}_{2m}'-\mathbf{r}_{2m-1}', t_{2m}-t_{2m-1})\sum_{n=0}^{\infty} F_n[\mathbf{r}_{2m}-\mathbf{r}_{2m-1}-(2\mathbf{r}_m'-\mathbf{r}_{2m-1}'), t_{2m}-t_{2m-1}]d\mathbf{r}_{2m}'\\ \cdots\\ \times\int g_e(\mathbf{r}_1',t_1)\sum_{n=0}^{\infty} F_n(\mathbf{r}_1-\mathbf{r}_1', t_1)d\mathbf{r}_1'.\end{aligned}\tag{5}$$

But according to definition we have that $G_s(\mathbf{r},t)$ is the probability of finding the proton at $\mathbf{r}$ at time t, if it was at the origin at $t=0$. If we sum up all steps $H_m(\mathbf{r},t)$ we find for the self-correlation function

$$G_s(\mathbf{r},t)=\sum_{m=0}^{\infty}[H_{2m}(\mathbf{r},t)+H_{2m+1}(\mathbf{r},t)],\tag{6}$$

where we always have $t>0$.

Instead of trying to calculate $G_s(\mathbf{r},t)$ we consider the integrals

$$\int_0^{\infty} dt\int d\mathbf{r}\exp[i(\boldsymbol{\kappa}\cdot\mathbf{r}-\omega t)]H_{2m}(\mathbf{r},t).\tag{7}$$

This integral reduces to a simpler expression if the following variables are defined:

$$t-t_{2m}=\tau_{2m+1},\qquad t_{2m}-t_{2m-1}=\tau_{2m}\cdots t_1=\tau_1,\tag{8a}$$

$$\mathbf{r}'-\mathbf{r}_{2m}'=\boldsymbol{\eta}_{2m+1}',\quad \mathbf{r}_{2m}'-\mathbf{r}_{2m-1}'=\boldsymbol{\eta}_{2m}'\cdots\mathbf{r}_1'=\boldsymbol{\eta}_1',\tag{8b}$$

$$\mathbf{r}-\mathbf{r}_{2m}=\boldsymbol{\eta}_{2m+1},\qquad \mathbf{r}_{2m}-\mathbf{r}_{2m-1}=\boldsymbol{\eta}_{2m}\cdots\mathbf{r}_1=\boldsymbol{\eta}_1.\tag{8c}$$

From this substitution it follows that

$$\begin{aligned}\mathbf{r}&=\boldsymbol{\eta}_{2m+1}+\boldsymbol{\eta}_{2m}+\cdots+\boldsymbol{\eta}_1,\\ \mathbf{r}'&=\boldsymbol{\eta}_{2m+1}'+\boldsymbol{\eta}_{2m}'+\cdots+\boldsymbol{\eta}_1',\\ t&=\tau_{2m+1}+\tau_{2m}+\cdots+\tau_1.\end{aligned}\tag{8d}$$

The complex integral (7) then reduces to a product of independent and similar integrals

$$\begin{aligned}&\int_0^{\infty} dt\int d\mathbf{r}\exp[i(\boldsymbol{\kappa}\cdot\mathbf{r}-\omega t)]H_{2m}(\mathbf{r},t)\\ &=\int_0^{\infty} d\tau_{2m+1}\int \exp[i(\boldsymbol{\kappa}\cdot\boldsymbol{\eta}_{2m+1}-\omega\tau_{2m+1})]p_e(\tau_{2m+1})d\boldsymbol{\eta}_{2m+1}\int g_e(\boldsymbol{\eta}_{2m+1}',\tau_{2m+1})\sum_{n=0}^{\infty} F_n(\boldsymbol{\eta}_{2m+1}-\boldsymbol{\eta}_{2m+1}', \tau_{2m+1})d\boldsymbol{\eta}_{2m+1}'\\ &\quad\times(-1)\int_0^{\infty} d\tau_{2m}\int \exp[i(\boldsymbol{\kappa}\boldsymbol{\eta}_{2m}-\omega\tau_{2m})]q_e'(\tau_{2m})d\boldsymbol{\eta}_{2m}\int h_e(\boldsymbol{\eta}_{2m}',\tau_{2m})\sum_{n=0}^{\infty} F_n(\boldsymbol{\eta}_{2m}-\boldsymbol{\eta}_{2m}', \tau_{2m})d\boldsymbol{\eta}_{2m}'\\ &\quad\cdots\\ &\quad\times(-1)\int d\tau_1\int \exp[i(\boldsymbol{\kappa}\cdot\boldsymbol{\eta}-\omega\tau_1)]p_e'(\tau_1)d\boldsymbol{\eta}\int g_e(\boldsymbol{\eta}_1',\tau_1)\sum_{n=0}^{\infty} F_n(\boldsymbol{\eta}_1-\boldsymbol{\eta}_1',\tau_1)d\boldsymbol{\eta}_1'=AC^mD^m.\end{aligned}\tag{9a}$$

Similarly one obtains for the step H_{2m+1} the following result:

$$\int_0^{\infty} dt\int d\mathbf{r}\exp[i(\boldsymbol{\kappa}\mathbf{r}-\omega t)]H_{2m+1}(\mathbf{r},t)=BC^{m+1}D^m.\tag{9b}$$

In the integrals (9a) and (9b) the functions A, B, C, and D are defined by

$$\begin{aligned}
A&=\int_0^\infty dt\int d\mathbf{r}\,\exp[i(\boldsymbol{\kappa}\mathbf{r}-\omega t)]p_e(t)\int g_e(\mathbf{r}',t)\sum_{n=0}^{\infty}F_n(\mathbf{r}-\mathbf{r}',t)d\mathbf{r}',\\
B&=\int_0^\infty dt\int d\mathbf{r}\,\exp[i(\boldsymbol{\kappa}\mathbf{r}-\omega t)]q_e(t)\int h_e(\mathbf{r}',t)\sum_{n=0}^{\infty}F_n(\mathbf{r}-\mathbf{r}'t)d\mathbf{r}',\\
C&=(-1)\int_0^\infty dt\int d\mathbf{r}\,\exp[i(\boldsymbol{\kappa}\mathbf{r}-\omega t)]p_e'(t)\int g_e(\mathbf{r}',t)\sum_{n=0}^{\infty}F_n(\mathbf{r}-\mathbf{r}',t)d\mathbf{r}',\\
D&=(-1)\int_0^\infty dt\int d\mathbf{r}\,\exp[i(\boldsymbol{\kappa}\mathbf{r}-\omega t)]q_e'(t)\int h_e(\mathbf{r}',t)\sum_{n=0}^{\infty}F_n(\mathbf{r}-\mathbf{r}',t)dr'.
\end{aligned}\tag{9c}$$

By summing up all the contributions from the various steps of the molecular motion one obtains

$$\int_{-\infty}^{+\infty}dt\int_{-\infty}^{+\infty}d\mathbf{r}\,\exp[i(\boldsymbol{\kappa}\mathbf{r}-\omega t)]\sum_{m=0}^{\infty}H_m(\mathbf{r},t)=\frac{A+BC}{1-CD}+\text{c.c.}\tag{10a}$$

Here use has been made of the fact that $G_s(\mathbf{r},t)=G_s^*(-\mathbf{r}-t)$. Instead of starting the molecular motion with a bound state the series of steps may start with an unbound molecular state. A calculation for this case carried out in exactly the same way as given above results in an expression:

$$\int_{-\infty}^{+\infty}dt\int_{-\infty}^{+\infty}d\mathbf{r}\,\exp[i(\boldsymbol{\kappa}\mathbf{r}-\omega t)]\sum_{m=0}^{\infty}H_m(\mathbf{r},t)=\frac{B+AD}{1-CD}+\text{c.c.}\tag{10b}$$

If one now defines two average characteristic times for the molecular motion, namely τ_0' during which the molecule is bound to neighbors and τ_1' during which the molecule is unbound, one can easily formulate the cross section by the aid of Eqs. (10a) and (10b). These two contributions to the cross section should be weighted with the respective probabilities $\tau_0'/(\tau_0'+\tau_1')$ and $\tau_1'/(\tau_0'+\tau_1')$ so that the series of steps of molecular motions starts in a bound and an unbound state. One then obtains

$$\frac{d^2\sigma}{d\Omega d\omega}=\frac{a^2}{2\pi}\frac{k}{k_0}\left[\frac{\tau_0'}{\tau_0'+\tau_1'}\frac{A+BC}{1-CD}+\frac{\tau_1'}{\tau_0'+\tau_1'}\frac{B+AD}{1-CD}+\text{c.c.}\right]\tag{11}$$

So far the problem of the internal molecular proton motions described by the sum $\sum F_n(\mathbf{r},t)$ appearing in A, B, C, and D has not been touched. The internal dynamical behavior of the proton within a given molecule is now treated in steps, as the molecular motion was. The proton may be stationary, vibrating for a mean time τ_0 round an equilibrium position, or jumping for a mean time τ_1. The functions $F_n(\mathbf{r},t)$ describe the steps. The evaluation of $F_n(\mathbf{r},t)$ may be made in exactly the same way as for the molecular steps $H_m(\mathbf{r},t)$. Let us consider proton step number $2n$, the first step having index zero and corresponding to a vibratory state. This step will be given by

$$\begin{aligned}
F_{2n}(\mathbf{r},t)=(-1)^{2n}\int_0^t dt_{2n}\int_0^{t_{2n}}dt_{2n-1}\cdots\int_0^{t_2}dt_2\int\cdots\int d\mathbf{r}_{2n}d\mathbf{r}_{2n-1}\cdots d\mathbf{r}_1&\\
\times p_i(t-t_{2n})q_i'(t_{2n}-t_{2n-1})p_i'(t_{2n-1}-t_{2n-2})\cdots p_i'(t)&\\
\times g_i(\mathbf{r}-\mathbf{r}_{2n},\,t-t_{2n})h_i(\mathbf{r}_{2n}-\mathbf{r}_{2n-1},\,t_{2n}-t_{2n-1})\cdots g_i(\mathbf{r}_1,t_1).&
\end{aligned}\tag{12}$$

Here we have written $\mathbf{r}_i$ as an abbreviation instead of $\mathbf{r}_i-\mathbf{r}_i'$, which is the relative coordinate of the proton and which is seen for instance in Eq. (9a) and (9c). As will be seen from Eq. (9c), all steps have to be added and after the folding of each function F_n with a molecular distribution $g_e(\mathbf{r},t)$ or $h_e(\mathbf{r},t)$ the integrals over space and time have to be performed. In order to perform these computations definite forms have to be given to the eight functions g_i, h_i, g_e, h_e, p_i, q_i, p_e, and q_e. We now make the assumption that the four distribution functions $g_{i,e}$ and $h_{i,e}$ are Gaussian in shape:

$$g_{i,e}(\mathbf{r},t)=\frac{1}{[4\pi\rho_{g_i,g_e}(t)]^{3/2}}\exp\left(-\frac{r^2}{4\rho_{g_i,g_e}(t)}\right),$$

and

$$h_{i,e}(\mathbf{r},t)=\frac{1}{[4\pi\rho_{h_i,h_e}(t)]^{3/2}}\exp\left(-\frac{r^2}{4\rho_{h_i,h_e}(t)}\right).\tag{13}$$

To make the computations easy, it is further necessary that the width functions $\rho_{g_e}(t)$ and $\rho_{h_e}(t)$ describing the spreading out in space and time of the molecular center of mass should be linear functions of time such that

$$\rho_{g_e}(t)=\rho_{g_e}(\tau_1+\tau_2+\cdots+\tau_{2m+1})=\sum_{i=1}^{2m+1}\rho_{g_e}(\tau_i),$$

and (14)

$$\rho_{h_e}(t)=\rho_{h_e}(\tau_1+\tau_2+\cdots+\tau_{2m+1})=\sum_{i=1}^{2m+1}\rho_{h_e}(\tau_i).$$

With these simplifications the integrals appearing in Eq. (9c) are evaluated to give for A

$$\int_0^\infty dt\, e^{-i\omega t}p_e(t)\int \exp(i\boldsymbol{\kappa}\cdot\mathbf{r})d\mathbf{r}\int g_e(\mathbf{r}',t) \times F_{2n}(\mathbf{r}-\mathbf{r}',t)d\mathbf{r}'=a_Ac_A{}^nd_A{}^n. \tag{15a}$$

Similarly for step number $2n+1$ for the proton one finds

$$\int_0^\infty dt\, e^{-i\omega t}p_e(t)\int \exp(i\boldsymbol{\kappa}\cdot\mathbf{r})d\mathbf{r}\int g_e(\mathbf{r}',t) \times F_{2n+1}(\mathbf{r}-\mathbf{r}',t)d\mathbf{r}'=b_Ac_A{}^{n+1}d_A{}^n. \tag{15b}$$

If these two expressions are added one finds that the sum over all values of n is given by

$$(a_A+b_Ac_A)/(1-c_Ad_A). \tag{16a}$$

We have not yet made the full determination of A in (9c) because in obtaining (16a) we assumed that the proton started in a vibratory state. The probability of finding this state is $\tau_0/(\tau_0+\tau_1)$. There is, however, a probability $\tau_1/(\tau_0+\tau_1)$ that the proton is found in a jumping state at the start. If this contribution to A is evaluated one finds an expression analogous to (16a), namely

$$(b_A+a_Ad_A)/(1-c_Ad_A). \tag{16b}$$

The value of A thus is

$$A=\frac{\tau_0}{\tau_0+\tau_1}\frac{a_A+b_Ac_A}{1-c_Ad_A}+\frac{\tau_1}{\tau_0+\tau_1}\frac{b_A+a_Ad_A}{1-c_Ad_A}. \tag{17a}$$

In this expression the four functions a_A, b_A, c_A, and d_A are found from

$$a_A=\int_0^\infty dt\, e^{-i\omega t}p_e(t)p_i(t) \times\exp\{-\kappa^2[\rho_{g_i}(t)+\rho_{g_e}(t)]\},$$

and (18a)

$$b_A=\int_0^\infty dt\, e^{-i\omega t}p_e(t)q_i(t) \times\exp\{-\kappa^2[\rho_{h_i}(t)+\rho_{g_e}(t)]\}.$$

If we further assume that the four functions p_i, p_e, q_i, and q_e are given by

$$\begin{aligned} p_i&=e^{-t/\tau_0},\\ p_e&=e^{-t/\tau_0'},\\ q_i&=e^{-t/\tau_1},\\ q_e&=e^{-t/\tau_1'}, \end{aligned} \tag{19}$$

we directly see that

$$\begin{aligned} c_A&=-a_A/\tau_0,\\ d_A&=-b_A/\tau_1. \end{aligned} \tag{18b}$$

In a completely analogous way we now find for the magnitude B:

$$B=\frac{\tau_\theta}{\tau_0+\tau_1}\frac{a_B+b_Bc_B}{1-c_Bd_B}+\frac{\tau_1}{\tau_0+\tau_1}\frac{b_B+a_Bd_B}{1-c_Bd_B}. \tag{17b}$$

The four functions a_B, b_B, c_B, and d_B are given by

$$\begin{aligned} a_B&=\int_0^\infty dt\, e^{-i\omega t}q_e(t)p_i(t) \times\exp\{-\kappa^2[\rho_{g_i}(t)+\rho_{h_e}(t)]\},\\ b_B&=\int_0^\infty dt\, {}^-e^{i\omega t}q_e(t)q_i(t) \times\exp\{-\kappa^2[\rho_{h_i}(t)+\rho_{h_e}(t)]\},\\ c_B&=-a_B/\tau_0,\\ d_B&=-b_B/\tau_1. \end{aligned} \tag{20}$$

Further, the functions C and D are determined by

$$\begin{aligned} C&=-A/\tau_0',\\ D&=-B/\tau_1'. \end{aligned} \tag{21}$$

In order to be able to evaluate A, B, C, and D, which enter into the cross section (11), it is necessary to assume explicit forms for the four width functions $\rho_{h_ih_e}(t)$ and $\rho_{g_ig_e}(t)$. We will assume the following forms with corresponding physical consequences:

When the proton is in a vibratory, bound state with a mean lifetime of τ_0 sec, we assume that it just develops a thermal cloud and consequently

$$\rho_{g_i}(t)\cong\rho_{g_i}(\infty)=\tfrac{1}{6}\langle r_i{}^2\rangle. \tag{22}$$

Here $\langle r_i{}^2\rangle$ is the mean-square radius of the thermal cloud set up by the proton. $\frac{1}{6}\langle r_i{}^2\rangle\kappa^2=2W_i$, which is the Debye-Waller factor for the internal proton motion. We have put $\rho(t)=\rho(\infty)$ because in this work we are interested only in the quasi-elastic scattering. The higher terms in the expansion of the difference $\rho(\infty)-\rho(t)$, which give rise to the phonon terms, are neglected.

When the proton is performing a jump (of mean duration of τ_1 secs) we assume that this occurs during such a short time that the whole motion is gas-like, i.e.

$$\rho_{h_i}(t)=(\tfrac{1}{2}vt)^2. \tag{23}$$

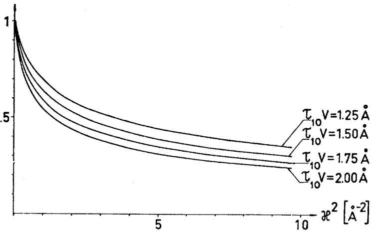

FIG. 1. Computed values of the integrals

$$\frac{\rho_A}{\tau_{10}}\simeq\frac{2}{\tau_{10}v\kappa}\int_0^\infty e^{-x^2-2x/\tau_{10}v\kappa}dx\left(\simeq\frac{\rho_B}{\tau_{11}}\quad\text{if}\quad\begin{array}{c}D_e\kappa^2\tau_{11}\ll1\\ \tau_1\ll\tau_0v\ \text{ and }\ \tau_1'\end{array}\right)$$

in the expressions b_A and b_B for various assumptions regarding the jump length $\tau_1v=l$.

Here v is the average velocity with which the proton performs its jump.

When the molecule is in a bound state of mean lifetime τ_0' sec we assume that the only possible motion for the center of mass is a vibration, i.e.,

$$\rho_{g_e}(t)=\rho_{g_e}(\infty)=\tfrac{1}{6}\langle r_e^2\rangle. \tag{24}$$

Here $\langle r_e^2\rangle$ is the mean-square radius of the thermal cloud set up by the center of mass of the molecule. $(\frac{1}{6}\langle r_e^2\rangle)\kappa^2=2W_e$, which is the Debye-Waller factor for the motion of the molecular center of mass. The phonon terms in the expansion of $\rho(\infty)-\rho(t)$ are neglected.

Finally, we assume that when the molecule is in a free state of mean duration of τ_1' sec, it will diffuse. If we define a diffusion coefficient D_e for this period of τ_1', one may write

$$\rho_{h_e}(t)=D_et. \tag{25}$$

Here the fact that this form of $\rho(t)$ gives a wrong behavior at very short times—when it should generally vary as t^2, not as t—is neglected, because we are not interested in the very small times for which the t^2 variation is of importance ($t<10^{-13}$ sec) when we consider this phase of the molecular motion.

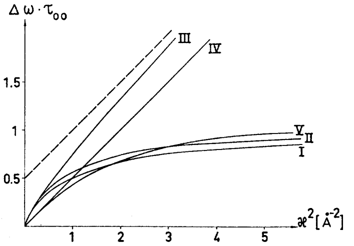

FIG. 2. Predicted widths of the quasi-elastic peak given as a function of κ^2 for various relative magnitudes of the relaxation times. Curves I and II correspond to a case for which the molecule is bound most of the time; curves III and IV illustrate cases for which the molecule is free to diffuse most of the time, and curve V corresponds to the intermediate case. Curve I: $\tau_0'\gg\tau_1'$, τ_0; Curve II: τ_0', $\tau_0\gg\tau_1'$; Curve III: $\tau_1'\gg\tau_0'$, τ_0; Curve IV: τ_1', $\tau_0\gg\tau_0'$; Curve V: $\tau_0'=\tau_1'=\tau_0$.

If we furthermore define a new relaxation time according to

$$\frac{1}{\tau_{kl}}=\frac{1}{\tau_k}+\frac{1}{\tau_l'}\quad\text{with}\quad k,l=0\text{ or }1 \tag{26}$$

we find the explicit forms for the functions a_A, b_A, a_B, and b_B. These are

$$\begin{aligned}
a_A&=\frac{\tau_{00}e^{-2W_i-2W_e}}{1+i\omega\tau_{00}},\\
b_A&=e^{-2W_e}\tau_{10}\frac{2}{v\kappa\tau_{10}}\int_0^\infty\exp\left[-x^2-\frac{2x}{v\kappa\tau_{10}}\right]\\
&\qquad\times\exp\left[-i\frac{2\omega x}{v\kappa}\right]dx=e^{-2W_e}\rho_Ae^{-i\varphi_A},\\
a_B&=\frac{\tau_{01}e^{-2W_i}}{1+i\omega\tau_{01}+D_e\kappa^2\tau_{01}},\\
b_B&=\tau_{11}\frac{2}{v\kappa\tau_{11}}\int_0^\infty\exp\left[-x^2-\frac{2x(1+D_e\kappa^2\tau_{11})}{v\kappa\tau_{11}}\right]\\
&\qquad\times\exp\left[-i\frac{2\omega x}{v\kappa}\right]dx=\rho_Be^{i\varphi_B}.
\end{aligned}\tag{27}$$

It is interesting to note the behavior of the integrals in b_A and b_B for the limits of small and large κ values:

$$\begin{aligned}
\rho_A&\underset{\kappa\to0}{\sim}\tau_{10}(1-\tfrac{1}{2}(\tau_{10}v\kappa)^2)\to\tau_{10},\\
\rho_B&\underset{\kappa\to0}{\sim}\tau_{11}(1-\tfrac{1}{2}(\tau_{11}v\kappa)^2)\to\tau_{11},\\
\rho_A&\underset{\kappa\to\infty}{\sim}\frac{\sqrt{\pi}}{v\kappa}\to0,\\
\rho_B&\underset{\kappa\to\infty}{\sim}\frac{1}{D_e\kappa^2}\to0.
\end{aligned}\tag{28}$$

The general values of the integrals are given in the curves in Fig. 1.

Everything is now known, so that the cross section given in Eq. (11) may be evaluated. Its general form is very complex. Great simplifications are, however, possible under certain assumptions regarding the relative magnitudes of the four relaxation times entering into the formulation. A general and quite obvious assumption is that $\tau_0\gg\tau_1$, i.e., that the jump time of the proton within the molecule, which should be equal to l/v, where l is the jump length, is much smaller than the vibrational time τ_0. If $l\sim10^{-8}$ cm and if $v\sim10^5$ cm/sec, one finds $\tau_1\sim10^{-13}$ sec, which ought to be short compared to the mean life of a vibrational state within the molecule. If it is not, the proton performs practically a free rotation, jumping from position to position without ever really staying at a definite location.

In the cross-section formulas[16] we arrive at in cases I, II, III, and IV below, we have assumed $\tau_1 \ll \tau_0$, τ_0' and τ_1'. As a consequence both τ_{11} and $\tau_{10} \simeq \tau_1$ and therefore $\tau_{10}v$ and $\tau_{11}v$ are both $\simeq \tau_1 v$ which is the jump length l. With this general simplifying assumption as a base, it is possible to study various cases of physical interest of which we shall consider four.

Case I. $\tau_0' \gg \tau_1'$ *and* τ_0. This corresponds to a case of low sample temperature such that the molecule stays bonded to its neighbors most of the time. The viscosity of the liquid must be high—of the order 1–100 poise or more—and the self-diffusion coefficient very small. In this case the cross section reduces to

$$\frac{d^2\sigma}{d\Omega d\omega} = \frac{a^2}{\pi}\frac{k}{k_0}\tau_{00} \times e^{-2W_i-2W_e} \frac{1-(\rho_A/\tau_1)e^{-2W_i-4W_e}}{(\omega\tau_{00})^2+(1-(\rho_A/\tau_1)e^{-2W_i-4W_e})^2}. \tag{29}$$

The quasi-elastic line has a Lorentzian shape and the full width at half-maximum of the line is

$$\Delta E = \frac{2\hbar}{\tau_{00}}\left(1-\frac{\rho_A}{\tau_1}e^{-2W_i-4W_e}\right). \tag{30a}$$

When κ tends to small values and considering that $\tau_{00} \simeq \tau_0$ for this case, one finds

$$\Delta E \underset{\kappa\to 0}{\sim} \frac{2\hbar}{\tau_0}\left(\frac{l^2}{2}+\frac{\langle r_i^2\rangle}{6}\right)\kappa^2. \tag{30b}$$

Here $\langle r_e^2\rangle$ has been assumed $\ll \langle r_i^2\rangle$, because the vibrating mass determining r_i is the proton mass and the mass determining r_e is the much larger molecular mass. It is to be noticed that the slope at the origin of this curve does not give a diffusion coefficient but rather a jump length l, if one assumes $l^2 \gg \frac{1}{3}\langle r_i^2\rangle$. Also the limiting value of the linewidth as $\kappa \to \infty$ is found to be

$$\Delta E \underset{\kappa\to\infty}{\sim} \frac{2\hbar}{\tau_0}. \tag{30c}$$

The linewidth saturates at a value which is determined by the residence time of the proton in a fixed position within the molecule. The general shape of the linewidth curve is given by curve 1 of Fig. 2. To make the numerical computations of ΔE we have assumed in all cases that $D = 10^{-5}$ cm^2/sec, $l = 1.75\times 10^{-8}$ cm, $\langle r_i^2\rangle = 10^{-16}$ cm^2, $\langle r_e^2\rangle = 0$, and $\tau_{00} = 5\times 10^{-12}$ sec. In cases where two relaxation times are supposed to be of the same order of magnitude we have set them equal, with $\tau_0' = \tau_0$ in case II and $\tau_1' = \tau_0$ in case IV.

Case II. τ_0' *and* $\tau_0 \gg \tau_1'$. This is a case very much related to case I. This situation is probably found at fairly high temperatures in associated liquids whose viscosities are in a range of 10–100 centipoise. The cross section is given by

$$\frac{d^2\sigma}{d\Omega d\omega} = \frac{a^2}{\pi}\frac{k}{k_0}\tau_{00} \, e^{-2W_i-2W_e} \frac{(1+D_e\kappa^2\tau_{01})(1-(\tau_{00}/\tau_0)(\rho_A/\tau_1)e^{-2W_i-4W_e})-(\tau_{00}/\tau_0)e^{-4W_i-2W_e}}{[(1+D_e\kappa^2\tau_{01})(1-(\tau_{00}/\tau_0)(\rho_A/\tau_1)e^{-2W_i-4W_e})-(\tau_{00}/\tau_0)e^{-4W_i-2W_e}]^2+(\omega\tau_{00})^2(1+D_e\kappa^2\tau_{01})^2}. \tag{31}$$

The cross section is still of Lorentzian shape and has a full width at half-maximum given by

$$\Delta E = \frac{2\hbar}{\tau_{00}}\left(1-\frac{\tau_{00}}{\tau_0}\frac{\rho_A}{\tau_1}e^{-2W_i-4W_e}-\frac{(\tau_{00}/\tau_0')e^{-4W_i-2W_e}}{1+D_e\kappa^2\tau_{01}}\right) \tag{32a}$$

The behavior of ΔE for small values of κ is given [if Eq. (28) is considered] by

$$\Delta E \underset{\kappa\to 0}{\sim} 2\hbar\left[D+\frac{l^2}{2\tau_0}+\frac{\langle r_i^2\rangle}{6}\left(\frac{1}{\tau_0}+\frac{2}{\tau_0'}\right)\right]\kappa^2. \tag{32b}$$

It is to be observed that D_e is not in general the true self-diffusion coefficient D. This may be defined by

$$D = [\tau_1'/(\tau_0'+\tau_1')]D_e. \tag{33}$$

In the present case, when $\tau_1' \ll \tau_0'$, one has $D \simeq (\tau_1'/\tau_0')D_e$. If again $l^2 \gg \langle r_i^2\rangle$, and if τ_0 is of the same order of magnitude as τ_0', it is seen that the shape of the linewidth curve at the origin is mainly given by the true self-diffusion

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[16] In all our cross-section formulas the detailed-balance factor, $e^{\kappa\hbar\omega/2k_BT}$, has been omitted because it is practically constant and $\simeq 1$ over the quasi-elastic peak.

coefficient taken together with the combination $l^2/2\tau_0$, which may be considered as an internal protonic diffusion coefficient. Since in this case the mobility of the molecules cannot be very high, it is probable that D and $l^2/2\tau_0$ contribute about equal amounts to the slope at the origin.

From (32a) it is also seen that the limiting value of ΔE for large κ values is given by

$$\Delta E \underset{\kappa\to\infty}{\sim} \frac{2\hbar}{\tau_{00}}. \tag{32c}$$

In this case τ_0 and τ_0' are of the same order of magnitude, so that the full value of τ_{00} given by $\tau_{00}^{-1}=\tau_0^{-1}+\tau_0'^{-1}$ has to be used. This case is illustrated as curve II of Fig. 2.

Case III. $\tau_1' \gg \tau_0'$ *and* τ_0. This case corresponds to the extreme opposite of the previous cases. It corresponds to a very high temperature; perhaps it is not possible to reach this state in an associated liquid. The viscosity ought to be very low, <1 centipoise and the self-diffusion rate very high. In this case one finds for the cross section

$$\frac{d^2\sigma}{d\Omega d\omega}=\frac{a^2}{\pi}\frac{k}{k_0}\tau_{01}e^{-2W_i}\frac{1+D_e\kappa^2\tau_{01}-(\rho_B/\tau_1)e^{-2W_i}}{(\omega\tau_{01})^2+(1+D_e\kappa^2\tau_{01}-(\rho_B/\tau_1)e^{-2W_i})^2}. \tag{34}$$

Again the line shape is Lorentzian and has a full width at half-maximum of

$$\Delta E=(2\hbar/\tau_{01})(1+D_e\kappa^2\tau_{01}-(\rho_B/\tau_1)e^{-2W_i}). \tag{35a}$$

Considering that $\tau_{01}\simeq\tau_0$, it is found by use of (28) that the limiting value of ΔE for small κ values is

$$\Delta E \underset{\kappa\to 0}{\sim} 2\hbar[D+(1/\tau_0)(\tfrac{1}{2}l^2+\tfrac{1}{6}\langle r_i^2\rangle)]\kappa^2. \tag{35b}$$

Here use has been made of (33). The slope at the origin is given as a sum of D and $l^2/2\tau_0$, if again $l^2 \gg \frac{1}{3}\langle r_i^2\rangle$. Not even in this case, most similar to a simple diffusion case, is the slope at the origin given by the self-diffusion coefficient.

On the other hand, when κ tends to large values, one finds from (28) that

$$\Delta E \underset{\kappa\to\infty}{\sim} 2\hbar(D\kappa^2+1/\tau_0). \tag{35c}$$

The expected diffusive behavior is reached, but it should be noticed that the line width only asymptotically approaches the simple diffusion value $2\hbar D\kappa^2$. The asymptote intersects the ΔE axis at $2\hbar/\tau_0$. This case is illustrated in curve III on Fig. 2.

Case IV. τ_1' *and* $\tau_0 \gg \tau_0'$. In this case τ_1' is supposed to be of the same order of magnitude as τ_0. The molecule is bound to its neighbors only a small fraction of the time. This case probably does not exist in strongly associated liquids because the requirement that $\tau_1' \gg \tau_0'$ is probably not fulfilled in the liquid state for such molecules. It could possibly be so for van der Waals liquid like methane for which $\tau_0\to\infty$, ethane, propane, etc. but probably not for alcohols, glycerol, etc. In this case the cross section is given by

$$\frac{d^2\sigma}{d\Omega d\omega}=\frac{a^2}{\pi}\frac{k}{k_0}\tau_{01}e^{-2W_i}\frac{1+D_e\kappa^2\tau_{01}-(\tau_{01}/\tau_0)(\rho_B/\tau_1)e^{-2W_i}-(\tau_{01}/\tau_1)e^{-2W_e-4W_i}}{(\omega\tau_{01})^2+(1+D_e\kappa^2\tau_{01}-(\tau_{01}/\tau_0)(\rho_B/\tau_1)e^{-2W_i}-(\tau_{01}/\tau_1)e^{-2W_e-4W_i})^2}. \tag{36}$$

Again the cross section is of Lorentzian shape and has a full width at half-maximum which is

$$\Delta E=\frac{2\hbar}{\tau_{01}}\left[1+D_e\kappa^2\tau_{01}-\frac{\tau_{01}}{\tau_0}\frac{\rho_B}{\tau_1}e^{-2W_i}-\frac{\tau_{01}}{\tau_1'}e^{-2W_i-4W_e}\right]. \tag{37a}$$

The behavior of ΔE at small values of κ is given by use of (28) and (33)

$$\Delta E \underset{\kappa\to 0}{\sim} 2\hbar\left[D+\frac{l^2}{2\tau_0}+\frac{\langle r_i^2\rangle}{6}\left(\frac{1}{\tau_0}+\frac{2}{\tau_1'}\right)\right]\kappa^2. \tag{37b}$$

It has again been assumed that $\langle r_e^2\rangle \ll \langle r_i^2\rangle$. As in cases II and III it is seen that the slope at the origin has three components, namely those from the self-diffusion coefficient, the proton jump length, and the radius of the thermal cloud. As τ_1' and τ_0 are of the same order of magnitude, it is expected that the contributions to the slope at the origin from the first two terms should be comparable in the present case as in the previous one.

For large κ values on the other hand it is seen from (37a) that the linewidth is given by

$$\Delta E \underset{\kappa\to\infty}{\sim} 2\hbar(D\kappa^2+1/\tau_{01}). \tag{37c}$$

This is quite similar to case III and shows that the behavior of ΔE typical for the simple diffusive motion is asymptotically reached. The asymptote intersects the ΔE axis at $2\hbar/\tau_{01}$, where $\tau_{01}^{-1}=\tau_0^{-1}+\tau_1'^{-1}$.

This case is illustrated in curve IV of Fig. 2. The fact that curves III and IV look different originates from the quantity $(\Delta\omega)\ \tau_{00}$ used as ordinate. In the present case we have $\tau_{00}/\tau_{01}\simeq\tau_0'/\tau_{01}$, which is $\ll 1$ according to the assumption. In case III one finds that $\tau_{00}/\tau_{01}\simeq\tau_{00}/\tau_0$, which is of the order of 1 if $\tau_1'\gg\tau_0'$ and τ_0.

In all the simplified cases I–IV it is found that the cross section is of Lorentzian shape. A consequence of this is that the integration over energy is easily performed thus giving the angular distribution, $d\sigma/d\Omega$. One finds:

$$\text{Case I and II:}\quad \frac{d\sigma}{d\Omega}=a^2\frac{k}{k_0}e^{-2W_i-2W_e}.$$

In case II it has been assumed that $D\kappa^2\tau_1'\ll 1$.

$$\text{Case III and IV:}\quad \frac{d\sigma}{d\Omega}=a^2\frac{k}{k_0}e^{-2W_i}.$$

It is seen that in all cases the Debye-Waller factor governs the angular intensity variation. In all cases the factor $2W_i$, the origin of which is the internal proton cloud, enters. It is to be noted also that when the molecule as such diffuses in a simple way (cases III and IV) a Debye-Waller factor determines $d\sigma/d\Omega$. This variation with angle is in sharp contrast to the variation predicted by applying a simple diffusion model for the translational part of the molecular motion, treating the molecule as a mass point, as has for instance been done for methane.[11] This model predicts a constant angular distribution which is not in agreement with observed facts for methane or any other hydrogenous liquid.

If none of the simplifying assumptions given above may be expected to be valid for a particular case, the full cross-section form defined by (11), (17), (21), (27), and (18b) has to be used. However, the cross-section formula thus obtained is quite unsurveyable, though its computation includes only straightforward algebra; therefore, we do not give it here. In the general case the line shape is not Lorentzian. We have used the full formula to compute the linewidth ΔE for the case $\tau_0'=\tau_1'=\tau_0\gg\tau_1$. The result is given as curve V in Fig. 2. The main difference between this curve and the similar curves I and II corresponding to cases I and II discussed above, is that its saturation value is reached more slowly.

In Paper II of this work we will apply the present theory to neutron-scattering data.