Slow-Neutron Scattering by Molecules

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The operator formalism in slow-neutron scattering theory introduced by Wick and by Zemach and Glauber is considered in an approximation in which molecular rotational and vibrational effects are explicitly separated. The combined effects of rotation and translation are treated in terms of the Sachs-Teller "mass-tensor" concept, which is rederived on the basis of a rigid molecule Hamiltonian and extended to include interference effects. Only elastic vibrational transitions from the ground vibrational state are considered. The applicable neutron energy range is restricted to values large compared to the rotational level separation but below the vibrational threshold.

The method is applicable to the calculation of differential as well as total scattering cross sections and to molecules of arbitrary structure. Expressions in closed form for these cross sections are obtained through use of an approximate procedure for averaging over molecular orientations. In the case of hydrogenous molecules, where direct scattering is dominant, the scattering by a given nucleus is described in terms of two parameters, viz., an effective nuclear mass for rotation and translation, and a vibrational constant. The relative simplicity of the method is illustrated in the calculation of the differential and total cross sections of CH_4 and the total cross section of H_2. Agreement of these calculations with experiment and with other calculations is good.

I. INTRODUCTION

IN the Fermi pseudopotential approximation,[1] the problem of slow-neutron scattering by nuclei of chemically bound atoms can be formulated very concisely by the introduction of the Fourier representation for the energy-conserving δ-function, which permits an implicit summation over final molecular states. This formulation has been used for molecular scattering by Wick[2] and by Zemach and Glauber.[3] The work of Wick is concerned mainly with the asymptotic behavior of the total cross section at high energy while that of Zemach and Glauber is directed toward the more formidable problem of calculating the differential cross section at arbitrary energy. The results obtained by Z.G. for CH_4 are in much better agreement with experiment than are the calculations of Pope.[4]

Another, and much earlier, approach to the problem of slow-neutron scattering by molecules, is that of Sachs and Teller,[5] in which only the total cross section is considered and interference and vibrational effects are neglected. The basis of the S.T. method is the concept of a nuclear mass tensor whose properties replace the effects of chemical binding. The S.T. method has been extended by Messiah[6] to include molecular vibrations.

In this paper, the mass tensor approximation is rederived by use of the formalism of Z.G., and is extended to include interference effects and the calculation of the differential cross section. This reformulation is quite concise, and demonstrates clearly the origin of the mass tensor approximation, which is somewhat obscured

in the original S.T. paper. The expression from which the cross section is calculated can be averaged over the thermal equilibrium distribution of initial molecular states, but the evaluation of the average over molecular orientations is much more difficult. The use of the Z.G. formalism suggests a mathematical approximation for averaging over orientations. When this approximation is used, an expression in closed form for the total cross section for direct scattering is obtained. The differential cross section is then found by simple numerical integration. The results are compared with experiment in the cases of CH_4 and H_2, and the agreement is found to be good.

II. FORMAL RESULTS

In the Z.G. formalism, $\sigma(\theta,\epsilon)$, the differential cross section for molecular scattering through an angle θ with energy gain ϵ, is given by

$$\sigma(\theta,\epsilon) = \sum_{\nu,\nu'} \sigma_{\nu\nu'}(\theta,\epsilon), \qquad (1)$$

with

$$\sigma_{\nu\nu'}(\theta,\epsilon) = a_{\nu\nu'}(k/2\pi k_0) \int_{-\infty}^{+\infty} e^{-i\epsilon t} \langle \chi_{\nu\nu'} \rangle_T dt. \qquad (2)$$

Here $\sigma_{\nu\nu'}(\theta,\epsilon)$ is the contribution to the cross section from the ordered pair of nuclei ν and ν'; $\mathbf{k}_0$ is the initial neutron momentum; $\mathbf{k}$ is the final neutron momentum;

$$\langle \chi_{\nu\nu'} \rangle_T = [\sum_i \chi_{\nu\nu'}{}^i \exp(-E_i/T)]$$
$$\times [\sum_i \exp(-E_i/T)]^{-1}, \qquad (3)$$

$$\chi_{\nu\nu'}{}^i = \langle \psi_i | \exp\{i\boldsymbol{\kappa}\cdot\mathbf{r}_\nu(t)\} \exp\{-i\boldsymbol{\kappa}\cdot\mathbf{r}_{\nu'}(0)\} | \psi_i \rangle;$$

T is the absolute temperature in energy units, ψ_i the initial molecular wave function, $\boldsymbol{\kappa}$ the momentum gained by the neutron, and $\mathbf{r}_\nu(t)$ the Heisenberg position-vector operator of the νth nucleus. Natural units with $\hbar=1$ are used, and all quantities refer to the laboratory system. The terms in (1) with $\nu=\nu'$ give the direct scattering

* Operated by the General Electric Company for the U. S. Atomic Energy Commission.
[1] E. Fermi, Ricerca Sci. **1**, 13 (1936).
[2] G. C. Wick, Phys. Rev. **94**, 1228 (1954).
[3] A. C. Zemach and R. J. Glauber, Phys. Rev. **101**, 118, 129 (1956). These papers will be referred to as Z.G.
[4] N. K. Pope, Can. J. Phys. **30**, 597 (1952).
[5] R. G. Sachs and E. Teller, Phys. Rev. **60**, 18 (1941). This paper will be referred to as S.T.
[6] A. M. L. Messiah, Phys. Rev. **84**, 204 (1951).

contributions; for these $a_{\nu\nu'}$ in (2) has the value

$$a_{\nu\nu} = A_\nu^2 + C_\nu^2, \qquad (4)$$

where A_ν and C_ν are the bound coherent and incoherent scattering lengths, respectively. For the interference terms, on the other hand,

$$a_{\nu\nu'} = A_\nu A_{\nu'}, \quad (\nu \neq \nu'). \qquad (5)$$

In (4) and (5), the effects of nuclear spin correlation have been neglected.

We shall be interested in neutron energies large compared to the spacing of the molecular rotational levels. At these energies, and provided T is much larger than the rotational constant, the rotations may be treated in a "quasiclassical" approximation which permits the evaluation of $\chi_{\nu\nu'}$ at a fixed molecular orientation Ω. A further implication of this quasi-classical approximation[7] for the rotations is that (neglecting rotation-vibration interactions) $\chi_{\nu\nu'}$, and hence $\langle \chi_{\nu\nu'} \rangle_T$, may be separated into factors corresponding to translation, rotation, and vibration, respectively,

$$\langle \chi_{\nu\nu'} \rangle_T = \langle \chi_{\nu\nu'}{}^t \rangle_T \langle \chi_{\nu\nu'}{}^r \rangle_T \langle \chi_{\nu\nu'}{}^v \rangle_T. \qquad (6)$$

The dependence of (6) on Ω is contained in the rotational and vibrational factors. When vibrations are completely neglected, the vibrational factor disappears, and the result then leads to a generalization of the S.T. approximation which includes interference effects. As is shown in the appendix, the present approximation yields

$$\langle \chi_{\nu\nu'}{}^t \rangle_T \langle \chi_{\nu\nu'}{}^r \rangle_T = \exp\{-\tfrac{1}{2}(\mathbf{\kappa} \cdot \mathfrak{M}_\nu^{-1} \cdot \mathbf{\kappa})(it + Tt^2)\}$$
$$\times \exp\{i\mathbf{\kappa} \cdot [\mathbf{b}_\nu(0) - \mathbf{b}_{\nu'}(0)]\}, \qquad (7)$$

where $\mathbf{b}_\nu(0)$ and $\mathbf{b}_{\nu'}(0)$ are the equilibrium position vectors of the νth and ν'th nuclei with respect to the molecular center of mass, and $\mathfrak{M}_\nu$ is the S.T. mass tensor corresponding to the νth nucleus.

The vibrational factor $\langle \chi_{\nu\nu'}{}^v \rangle_T$ is evaluated in Z.G. If we restrict attention to neutron energies below the vibrational threshold, and assume, moreover, that all molecules are initially in their ground vibrational states (i.e., that $T = 0$ for vibrations), then $\langle \chi_{\nu\nu'}{}^v \rangle_T$ reduces to the time-independent form

$$\langle \chi_{\nu\nu'}{}^v \rangle_{T=0} = \prod_\lambda \exp\{-(4\omega_\lambda)^{-1}[(\mathbf{\kappa} \cdot \mathbf{c}_\nu^{(\lambda)})^2 + (\mathbf{\kappa} \cdot \mathbf{c}_{\nu'}^{(\lambda)})^2]\}, \qquad (8)$$

where $\mathbf{c}_\nu^{(\lambda)}$ is the amplitude vector corresponding to the νth nucleus and the λth vibrational mode, and ω_λ is the angular frequency of the λth mode. For each value of λ, the amplitude vectors are normalized via the condition

$$\sum_\nu M_\nu [c_\nu^{(\lambda)}]^2 = 1, \qquad (9)$$

M_ν being the mass of the νth nucleus. The dependence of $\langle \chi_{\nu\nu'}{}^v \rangle_T$ on the molecular orientation Ω is contained in the

quantities $\mathbf{c}_\nu^{(\lambda)}$. The function $\langle \chi_{\nu\nu'} \rangle_T$ is obtained by substituting (7) and (8) into (6).

To perform the averaging over molecular orientations, we note that $\langle \chi_{\nu\nu'} \rangle_T$ appears as a product of factors. The first of these, $\exp\{i\mathbf{\kappa} \cdot [\mathbf{b}_\nu(0) - \mathbf{b}_{\nu'}(0)]\}$, is a static interference term which can be a rapidly varying function of orientation. The second factor,

$$\chi_\nu{}^{ST} = \exp\{-\tfrac{1}{2}(\mathbf{\kappa} \cdot \mathfrak{M}_\nu^{-1} \cdot \mathbf{\kappa})(it + Tt^2)\}, \qquad (10)$$

represents, in the S.T. approximation, the combined dynamical effects of molecular rotation and translation on the scattering from the νth nucleus. The final factor is given by (8) and represents the dynamical effects of zero-point vibrations. The dependence of this factor on orientation depends on the degree of anisotropy of the vibrations. We now make the approximation that the average of the product of these three factors is equal to the product of their averages. The accuracy of this approximation can be judged by comparison with the results of Messiah[6] for H_2 and CH_4 obtained by a rigorous averaging over orientations. This comparison will be made in the next section.

The static interference factor in (7) is easily averaged, giving

$$\langle \exp\{i\mathbf{\kappa} \cdot [\mathbf{b}_\nu(0) - \mathbf{b}_{\nu'}(0)]\} \rangle_\Omega = j_0(\kappa b_{\nu\nu'}), \qquad (11)$$

where $b_{\nu\nu'} = |\mathbf{b}_\nu(0) - \mathbf{b}_{\nu'}(0)|$, and $j_0(x) = x^{-1} \sin x$. An approximate average of the S.T. factor (10) can be obtained by averaging in the exponent:

$$\langle \chi_\nu{}^{ST} \rangle_\Omega \approx \exp\{-\kappa^2 (2M_\nu^{(0)})^{-1}(it + Tt^2)\}, \qquad (12)$$

where

$$[M_\nu^{(0)}]^{-1} = \tfrac{1}{3} Spur[\mathfrak{M}_\nu^{-1}]. \qquad (13)$$

Equation (12) gives the $\langle \chi \rangle_T$-function corresponding to the scattering by a monatomic gas of mass $M_\nu^{(0)}$ at temperature T.[3] The effects on slow-neutron scattering of the dynamics of the rotational and translational motions of the νth nucleus have thus been reproduced by the use of an equivalent free translation with a modified nuclear mass.[8]

The accuracy of this approximation can be gauged by comparing the total cross section for direct scattering in the S.T. approximation with that for a monatomic gas in the high energy limit $(\lambda T/E_0) \ll 1$, $\lambda = (m/M_\nu)$ being the ratio of neutron mass to nuclear mass. In this energy range, the monatomic gas cross section has the well-known form

$$(\sigma_{tot}/\sigma_{bound}) = (1+\lambda)^{-2}[1 + \tfrac{1}{2}\lambda(T/E_0)]. \qquad (14)$$

On the other hand, it follows from (7) and (14) that the Sachs-Teller result for the rigid rotator is

$$(\sigma_{tot}/\sigma_{bound}) = a + b(T/E_0), \qquad (15)$$

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[7] The "quasiclassical" approximation employed in this paper is not to be confused with the semiclassical or static approximation used, for example, by N. K. Pope, reference 4.

[8] The device of replacing a gas of rigid rotators by a monatomic gas with effective mass given by (13) was first used in a study of neutron thermalization by H. D. Brown and D. S. St. John, Atomic Energy Commission Report DP-33 (unpublished).
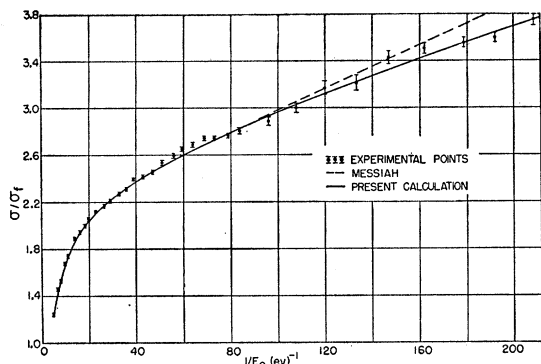
FIG. 1. Total slow-neutron scattering cross section per proton of CH_4 as a function of E_0^{-1} at room temperature. $\sigma_f = 20.36$ barns is the free-proton cross section.

where

$$a = \langle (1 + m\mathbf{u} \cdot \mathfrak{M}^{-1} \cdot \mathbf{u})^{-2} \rangle_\Omega, \tag{16}$$

$$b = \langle \tfrac{1}{2} m (\mathbf{u} \cdot \mathfrak{M}^{-1} \cdot \mathbf{u})(1 + m\mathbf{u} \cdot \mathfrak{M}^{-1} \cdot \mathbf{u})^{-2} \rangle_\Omega, \tag{17}$$

and $\mathbf{u}$ is an arbitrary unit vector. The expressions (16) and (17) may be evaluated, for a given molecule, in terms of the components of the mass tensor, and are easily shown to agree with the results of Messiah[6] for spherical top or linear molecules.[9] We now define two effective masses $M_\nu^{(1)} = (m/\lambda_1)$ and $M_\nu^{(2)} = (m/\lambda_2)$, where

$$a = (1+\lambda_1)^{-2}, \quad (b/a) = (\lambda_2/2). \tag{18}$$

If, for a particular molecule, λ_1 and λ_2 are nearly equal, it can be assumed that the form (12) for the rigid rotator scattering, with $M_\nu^{(0)}$ replaced by an average

$$\bar{M}_\nu = (2m)(\lambda_1 + \lambda_2)^{-1}, \tag{19}$$

can be used with good accuracy. Although the discussion of this and the preceding paragraph is primarily a justification for (12), a slight improvement in accuracy results when (19) is used. In most cases λ_1 and λ_2 are very nearly equal, neither differing much from $\lambda_0 = (m/M_\nu^{(0)})$. This is illustrated in Table I for protons in CH_4, H_2, and H_2O.

Finally, it is necessary to average the vibrational factor (8) over orientations. Again, this can be done conveniently by the approximation of averaging in the exponent, which gives

$$\langle \chi_{\nu\nu'}{}^\nu \rangle_{T=0} \approx \exp(-\kappa^2 \gamma_{\nu\nu'}), \tag{20}$$

where

$$\gamma_{\nu\nu'} = \sum_\lambda (12\omega_\lambda)^{-1} [(c_\nu^{(\lambda)})^2 + (c_{\nu'}^{(\lambda)})^2] = \tfrac{1}{2}[\gamma_{\nu\nu} + \gamma_{\nu'\nu'}].$$

In general, the argument of the exponential in (8) will contain a term of the form $(\kappa^2\gamma)$ plus a term dependent on orientation. The accuracy of the approximation (20) depends on the magnitude of the orientation-dependent term. If this term is small compared to unity for the

values of $(\kappa^2\gamma)$ which are of interest, the approximation (20) will be accurate.

The final expression for $\langle \chi_{\nu\nu'} \rangle_T$, obtained by combining (20), (12), (11) and (7), is

$$\langle \chi_{\nu\nu'} \rangle_T = j_0(\kappa b_{\nu\nu'}) \exp(-\kappa^2 \gamma_{\nu\nu'})$$
$$\times \exp\{ -\kappa^2 (2\bar{M}_\nu)^{-1}(it + Tt^2) \}, \tag{21}$$

where $\bar{M}_\nu$ is defined by (19). Specific examples of the application of (21) will be discussed in the next section.

III. CALCULATION OF CROSS SECTIONS

In order to estimate the accuracy of the mathematical approximations employed above in averaging over molecular orientations, we shall compare the total molecular direct scattering cross sections of CH_4 and H_2 as calculated by the method outlined above with those obtained by the method of Messiah[6] in which the averaging over orientations is performed exactly. It is most convenient to start from the relation obtained by integrating (2) over the momentum transfer:

$$\sigma_{tot}{}^{(\nu)}(E_0) = (a_{\nu\nu}/2\pi mk_0) \int\int d^3\kappa\, dt\, e^{-i\epsilon t} \langle \chi_{\nu\nu} \rangle_T, \tag{22}$$

where

$$\langle \chi_{\nu\nu} \rangle_T = \exp(-\kappa^2 \gamma_{\nu\nu}) \exp\{ -\kappa^2 (2\bar{M}_\nu)^{-1}(it + Tt^2) \}. \tag{23}$$

If in (22) the κ integration is performed by a transformation to polar variables with polar axis along $\mathbf{k}_0$, one obtains

$$\sigma_{tot}{}^{(\nu)}(E_0) = (2\pi)^{\frac{1}{2}} a_{\nu\nu} k_0^{-1} (\bar{M}_\nu/T)^{\frac{3}{2}} \int_{-\infty}^{+\infty} \frac{dt}{t^3} u^{\frac{3}{2}} e^{-Cu}, \tag{24}$$

where $C \equiv (\bar{M}_\nu E_0/Tm)$ and $u \equiv (1 - i\alpha t^{-1} + \beta t^{-2})^{-1}$, in which $\alpha \equiv (m + \bar{M}_\nu)/mT$ and $\beta \equiv (2\bar{M}_\nu \gamma_{\nu\nu}/T)$. The integral in (24) may be evaluated by means of contour integration in the u plane.[10] The final result is

$$\sigma_{tot}{}^{(\nu)}(E_0) = \pi a_{\nu\nu}(2\bar{\omega}/E_0)\{ \mathrm{erf}[C^{\frac{1}{2}}]$$
$$- (1-p)^{\frac{1}{2}} e^{-Cp}\, \mathrm{erf}[C^{\frac{1}{2}}(1-p)^{\frac{1}{2}}] \}, \tag{25}$$

where

$$\bar{\omega} \equiv (4m\gamma_{\nu\nu})^{-1},$$

$\mathrm{erf}\, z$ is the error function

$$\mathrm{erf}\, z \equiv \frac{2}{\sqrt{\pi}} \int_0^z \exp(-t^2) dt,$$

TABLE I. Effective inverse rotational masses for the protons in several molecules, as defined in Eqs. (13) and (18).

	λ_0	λ_1	λ_2
CH_4	0.313	0.297	0.292
H_2	0.833	0.814	0.808
H_2O	0.531	0.482	0.491

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[9] This point is discussed in more detail in the Atomic Energy Commission Report KAPL-1597 (unpublished) by the authors.

[10] This integral has been evaluated in another connection by H. Hurwitz and P. F. Zweifel (private communication).

and

$$p = [1 + (\alpha^2/4\beta)]^{-1}. \qquad (26)$$

Following Messiah,[6] we shall calculate only the direct scattering by hydrogen nuclei. Considering the CH_4 molecule first, we note that here, owing to the small rotational constant ($B = 0.0006$ ev), the mass-tensor approximation should give good results. Furthermore, the use of the other approximations introduced by the present method is seen to be well justified in view of the near equality of λ_1 and λ_2 (see Table I) and of the small anisotropy of the equivalent vibrators.[4]

Using Messiah's molecular data, Eq. (26), and Table I, we find

$$(m/\bar{M}_H) = 0.2944,$$

$$\bar{\omega} = (4m\gamma_{HH})^{-1} = 0.1656 \text{ ev},$$

and, for $T = 294°K$,[11]

$$p = 0.0510.$$

With these values, the cross section per proton may now be calculated from Eq. (25). In Fig. 1, the results of this calculation are compared with those of Messiah and with Melkonian's experimental data.[12] (For convenience, the ratio of the cross section to the free-proton cross section $\sigma_f = \pi a_{HH} = 20.36$ barns is used as ordinate.) We note that above 0.01 ev the two theoretical curves are in good agreement with each other and with the experimental curve. Below 0.01 ev the present calculation is in better agreement with experiment, which may be attributed to the inadequacy of Messiah's $1/E_0$ expansion at these low energies. However, as was pointed out by Messiah, the mass-tensor approximation breaks down below about 0.01 ev in the case of CH_4. The improved agreement of the present calculation with experiment indicates only that the $1/E_0$ expansion in that energy region introduces greater inaccuracies than does the mass-tensor approximation.

For the H_2 molecule, the applicability of the mass-tensor approximation is of more restricted validity since the rotational constant is larger ($B = 0.007356$ ev).[6] The mass-tensor approximation, therefore, should break down at a higher energy than in the case of CH_4. Moreover, the rotations of an H_2 molecule at room temperature are not well described by a Maxwellian distribution. To meet this difficulty we define an effective temperature T', by means of $T' = (3/5)T + (2/5)\langle E_R \rangle_T$. For $T = 300°K$, $\langle E_R \rangle = 0.0235$ ev,[6] we find $T' = 0.0249$ ev $= 289°K$. This 4% correction is similar in magnitude to the one applied by Messiah for the incompleteness of rotational excitations. In order to make the comparison with Messiah's results more precise, the H_2 calculations were performed for $T = 300°K$. The input parameters for (25) are

$$(m/\bar{M}_H) = 0.8107, \quad \bar{\omega} = 1.6385 \text{ ev}, \quad p = 0.00751.$$

[11] Messiah uses $T = 300°K$, which makes precise comparison with our calculations difficult.
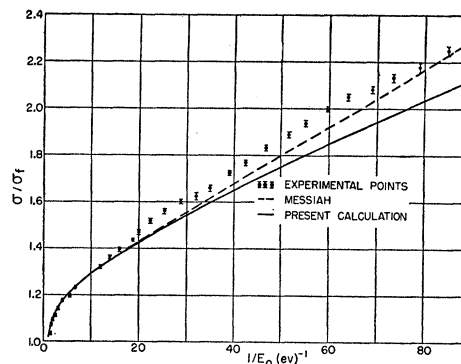
[12] E. Melkonian, Phys. Rev. **76**, 1744 (1949).

FIG. 2. Total slow-neutron scattering cross section per proton of H_2 at $T = 300°K$. Interference terms are neglected.

The present approximation for averaging over orientations in (10) should be a good one in this case also, since $\lambda_1 \approx \lambda_2$. Although the vibrations are quite anisotropic, the vibrational factor

$$\kappa^2\gamma = (k/k_0)^2 (E_0/2\bar{\omega})$$

is much smaller than unity over the energy range of interest, so that averaging in the exponent in (8) is reasonably accurate. In Fig. 2, the cross section of H_2 as calculated from (25) is compared with Messiah's curve and with experiment.[12] The two theoretical curves differ in the same way as in the case of CH_4. The agreement of the present calculation with experiment is not so good because of the greater inaccuracy of the mass-tensor approximation when applied to H_2. The omission of interference effects in the total cross section calculations is justified by the smallness of the hydrogen coherent scattering length.

As a further check on the accuracy of the method of calculation presented in this paper, the differential cross section for the CH_4 molecule was calculated and the results compared with the calculations of Z.G.,[3] who, while not using a mass-tensor approximation, made expansions in inverse powers of neutron energy and rotational mass. To obtain an expression for the differential cross section, we combine (2) and (21) and integrate over ϵ. The integration over t is performed first, being the same as that for a monatomic gas. It is easily carried out[3] to give

$$\sigma_{\nu\nu'}(\theta) = a_{\nu\nu'}\left(\frac{\bar{M}_\nu}{2\pi T}\right)^{\frac{1}{2}} \int_{-E_0}^{\infty} d\epsilon \frac{k}{k_0} j_0(\kappa b_{\nu\nu'}) \left\{ \exp(-\kappa^2\gamma_{\nu\nu'}) \right.$$

$$\left. \times \exp\left[-\frac{\bar{M}_\nu}{2T\kappa^2}\left(\epsilon + \frac{\kappa^2}{2\bar{M}_\nu}\right)^2\right]\right\}. \qquad (27)$$

If we set $\zeta_{\nu\nu'} = (1 + 8\gamma_{\nu\nu'}\bar{M}_\nu T)^{-\frac{1}{2}}$, $\rho_{\nu\nu'} = (1 - \zeta_{\nu\nu'})(2T\zeta_{\nu\nu'})^{-1}$, $T' = \zeta_{\nu\nu'}T$, and $\bar{M}_\nu' = \zeta_{\nu\nu'}\bar{M}_\nu$, the factor in curly brackets in (27) becomes

$$\exp(\rho_{\nu\nu'}\epsilon) \exp\left[-\frac{\bar{M}_\nu'}{2T'\kappa^2}\left(\epsilon + \frac{\kappa^2}{2\bar{M}_\nu'}\right)^2\right], \qquad (28)$$
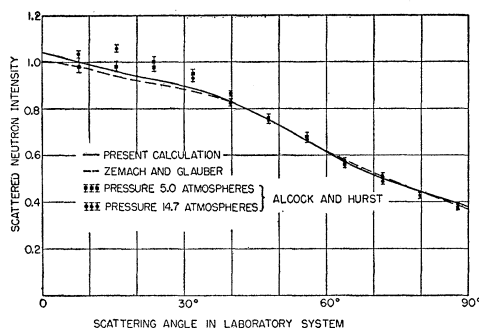
FIG. 3. Differential cross section of CH_4 for slow neutron scattering at $E_0=0.0732$ ev and $T=0.0255$ ev. Normalization of the present calculation is such as to agree with curve of Z.G. in the range 40°–50°. Normalization of experimental data is that of Z.G.

from which, incidentally, it can be seen that, in the case of direct scattering from the νth nucleus,

$$\sigma_{\nu\nu}(\theta,\epsilon) = \exp(\rho_{\nu\nu}\epsilon)\sigma_{\nu\nu}'(\theta,\epsilon), \qquad (29)$$

where $\sigma_{\nu\nu}'(\theta,\epsilon)$ is the differential cross section corresponding to a monatomic gas of νth nuclei at a fictitious temperature T' and of fictitious mass $\bar{M}_{\nu}'$.[13]

The differential cross section $\sigma(\theta)=\sum_{\nu,\,\nu'}\sigma_{\nu\nu'}(\theta)$ of CH_4 was calculated from (27) by numerical integration, after a transformation of the variable of integration to $z=(k/k_0)$. The following values of the parameters were used[4]: $T=0.0255$ ev, $E_0=0.0732$ ev, $C_C=0$, $A_C=0.64$ $\times 10^{-12}$ cm, $C_H=2.52\times 10^{-12}$ cm, $A_H=-0.42\times 10^{-12}$ cm, $b_{CH}=1.093\times 10^{-8}$ cm, $b_{HH}=1.7848\times 10^{-8}$ cm, $\bar{M}_H = (m/0.2944)$, $\bar{M}_C=16$ m, $\gamma_{HH}=6.266\times 10^{-19}$ cm^2, $\gamma_{CC} =2.1375\times 10^{-20}$ cm^2. The interference terms in $\sigma(\theta)$ $(\nu\neq\nu')$ were found to be very small since $A_H^2\ll C_H^2$. Moreover they tend to cancel since A_C and A_H are of opposite sign. The results of the calculation are shown plotted in Fig. 3, together with the data of Alcock and Hurst[14] and the calculation of Z.G. The normalization of the present calculation is such as to produce best fit with the data in the region $\theta=40°-50°$. It will be observed that the present calculation fits the data very well for $\theta>30°$. For $\theta\leq 30°$ there is some doubt concerning the accuracy of the experimental data, as can be seen from the inconsistencies in the high- and low-pressure values. In general, however, it appears that the present calculation gives a somewhat better fit at small scattering angles than does the Z.G. curve.[15]

IV. SUMMARY AND CONCLUSIONS

A simplified model for calculating the slow-neutron scattering cross section of free polyatomic molecules has been developed on the basis of an extended mass-tensor concept. The model, which is valid for neutron energies large compared to the rotational constant but below the vibrational threshold, includes the effects of zero-point molecular vibrations, and permits the calculation of both the interference and direct scattering terms without resort to expansions in inverse powers of the nuclear mass or neutron energy. In the application of the method to the slow-neutron scattering by hydrogenous molecules, in which case chemical binding effects are greatest, there is the simplifying feature that the scattering is predominantly direct, with interference terms making only a small contribution to the total scattering. Here the model essentially reduces the description of the scattering to the consideration of two molecular parameters: $\bar{M}_H$, an effective proton mass for translation and rotation, and γ_{HH}, a vibrational constant equal to the mean square zero-point vibrational displacement of the proton. The method thus represents a considerable simplification over the more rigorous Z.G. method, which, despite its powerful techniques, does not yield an exact solution to the rotator problem. Moreover, it gives approximate solutions only in the cases of spherical top or linear molecules, whereas the present method applies to molecules of arbitrary structure. Of course, the simplifications described here have been achieved at the expense of a considerable restriction in the applicable energy range, dictated by the use of the mass-tensor concept. Though small, this energy range is nevertheless of considerable interest.

The utility and relative simplicity of the method is demonstrated by the calculations of the cross sections of CH_4 and H_2, which are in quite good agreement with experiment, and with the results obtained by more complex methods.

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APPENDIX

In this appendix, it will be shown that, in the "quasi-classical" approximation introduced in the text,

$$\langle\chi_{\nu\nu'}{}^t\rangle_T\langle\chi_{\nu\nu'}{}^r\rangle_T = \exp\{i\kappa\cdot[\mathbf{b}_{\nu}(0)-\mathbf{b}_{\nu'}(0)]\}$$
$$\times\exp\{-\tfrac{1}{2}(\kappa\cdot\mathfrak{M}_{\nu}^{-1}\cdot\kappa)(it+T t^2)\}, \quad (A1)$$

where $\mathfrak{M}_{\nu}$ is the usual S.T. mass tensor.

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[13] The form of $\sigma_{\nu\nu}(\theta,\epsilon)$ given by (29) is convenient for calculations of neutron thermalization, where the monatomic gas kernels have already been programmed for machine calculation. This point is amplified in reference 9.

[14] N. Z. Alcock and P. G. Hurst, Phys. Rev. 83, 1100 (1951).

[15] A weak logarithmic singularity in the differential cross section at $\theta=0°$, which occurs in the present calculation and in the Z.G. rigorous monatomic gas scattering analysis, is not shown. It is absent in the Z.G. CH_4 calculation because of the approximate expansions employed. The numerical work of the present calculation indicates that the singularity is confined to very small scattering angles and is already completely negligible at $\theta=5°$ for $E_0=0.0732$ ev. The origin of the singularity is discussed by Z.G.

We start with a form analogous to (3):

$$\langle \chi_{\nu\nu'}{}^{r} \rangle_{T} = \langle \psi^{r} | \exp\{i\boldsymbol{\kappa} \cdot \mathbf{b}_{\nu}(t)\} \exp\{-i\boldsymbol{\kappa} \cdot \mathbf{b}_{\nu'}(0)\} | \psi^{r} \rangle_{T}$$
$$= \langle \psi^{r} | \exp(iHt) \exp(-iH_{\nu}t) \exp[i\boldsymbol{\kappa} \cdot \mathbf{b}_{\nu}(0)]$$
$$\times \exp[-i\boldsymbol{\kappa} \cdot \mathbf{b}_{\nu'}(0)] | \psi^{r} \rangle_{T}, \quad (A2)$$

where H is the Hamiltonian for the rotating rigid molecule, and H_{ν} is H with $\mathbf{p}_{\nu}$ replaced by $(\mathbf{p}_{\nu}-\boldsymbol{\kappa})$. An expression for H in terms of the $\mathbf{p}_{i}$'s is obtained on writing the total rotational energy of the molecule in terms of the total angular momentum $\mathbf{L}=\sum_{i} \mathbf{b}_{i} \times \mathbf{p}_{i}$, and the moment of inertia tensor $\mathfrak{J}$,

$$H = \tfrac{1}{2} \mathbf{L} \cdot \mathfrak{J}^{-1} \cdot \mathbf{L}$$
$$= \tfrac{1}{2}(\sum_{i} \mathbf{b}_{i} \times \mathbf{p}_{i}) \cdot \mathfrak{J}^{-1} \cdot (\sum_{j} \mathbf{b}_{j} \times \mathbf{p}_{j}) \quad (A3)$$
$$= \tfrac{1}{2} \sum_{i,j} \mathbf{p}_{i} \cdot \mathfrak{K}_{ij} \cdot \mathbf{p}_{j},$$

where

$$\mathfrak{K}_{ij} = \mathfrak{B}_{i}{}^{\dagger} \cdot \mathfrak{J}^{-1} \cdot \mathfrak{B}_{j} = \mathfrak{K}_{ji}{}^{\dagger}, \quad (A4)$$

with

$$-\mathfrak{B}^{\dagger} = \mathfrak{B} = \begin{bmatrix} 0 & -b_{z} & b_{y} \\ b_{z} & 0 & -b_{x} \\ -b_{y} & b_{x} & 0 \end{bmatrix}. \quad (A5)$$

From (A3),

$$H_{\nu} = H - \tfrac{1}{2} \mathbf{L} \cdot \mathfrak{J}^{-1} \cdot \mathfrak{B}_{\nu} \cdot \boldsymbol{\kappa}$$
$$- \tfrac{1}{2} \boldsymbol{\kappa} \cdot \mathfrak{B}_{\nu}{}^{\dagger} \cdot \mathfrak{J}^{-1} \cdot \mathbf{L} + \tfrac{1}{2} \boldsymbol{\kappa} \cdot \mathfrak{K}_{\nu\nu} \cdot \boldsymbol{\kappa}. \quad (A6)$$

Direct substitution of (A3) and (A6) into (A2) is not a useful procedure owing to the noncommutativity of the various operators appearing in (A3) and (A6). This difficulty is not the result of the complexity of the scattering system, as may be seen from the fact that the same difficulty arises in calculations with the greatly simplified rigid rotator model employed by Z.G.

The quasiclassical approximation introduced here consists essentially in treating the operators in (A2) as classical, commuting variables and replacing the rigid rotator wave functions ψ^{r} by rotational wave packets characterized by simultaneously well-defined values of orientation and angular momentum. Such wave packets will exist when the rotator is sufficiently excited, i.e., when $T \gg B$, and when the collision time is small compared to the rotational period, i.e., when $E_{0} \gg (BT)^{\frac{1}{2}}$, where $(BT)^{\frac{1}{2}}$ is the level spacing in the neighborhood of the most probable level. These are the usual conditions for the validity of the S.T. mass-tensor approximation. The thermal average in this approximation involves, in general, an average over molecular orientations together with an average over a Boltzmann distribution of $\mathbf{L}$ values. However, since ψ^{ν} also depends on orientation, it is necessary to reserve the averaging over orientations

for a later stage in the calculation. The symbol $\langle \ \rangle_{T}$ will thus refer, from this point on, to merely an average over $\mathbf{L}$ values. Hence, from (A2), in the quasi-classical approximation,

$$\langle \chi_{\nu\nu'}{}^{r} \rangle_{T} = \langle \exp\{-[\boldsymbol{\kappa} \cdot \mathfrak{B}_{\nu} \cdot \mathfrak{J}^{-1} \cdot \mathbf{L} + \tfrac{1}{2} \boldsymbol{\kappa} \cdot \mathfrak{K}_{\nu\nu} \cdot \boldsymbol{\kappa}]it\} \rangle_{T}$$
$$\times \exp\{i\boldsymbol{\kappa} \cdot [\mathbf{b}_{\nu}(0) - \mathbf{b}_{\nu'}(0)]\}. \quad (A7)$$

The thermal average is effected by integrating over an $\mathbf{L}$ distribution determined by the Boltzmann weighting factor $\exp\{-(2T)^{-1}(\mathbf{L} \cdot \mathfrak{J}^{-1} \cdot \mathbf{L})\}$. The resulting integrals may be evaluated by setting $\mathbf{L} = \mathbf{l} \cdot \mathfrak{J}^{\frac{1}{2}} = \mathfrak{J}^{\frac{1}{2}} \cdot \mathbf{l}$, and $d^{3}\mathbf{L} = (\text{Det}\mathfrak{J}^{\frac{1}{2}})d^{3}\mathbf{l}$. The thermal average (A7) then becomes

$$\langle \chi_{\nu\nu'}{}^{r} \rangle_{T} = \exp\{i\boldsymbol{\kappa} \cdot [\mathbf{b}_{\nu}(0) - \mathbf{b}_{\nu'}(0)]\} \exp\{-\tfrac{1}{2}it\boldsymbol{\kappa} \cdot \mathfrak{K}_{\nu\nu} \cdot \boldsymbol{\kappa}\}$$

$$\times \left[\int \exp(-l^{2}/2T)d^{3}\mathbf{l} \right]^{-1}$$

$$\times \left[\int \exp(-l^{2}/2T) \right.$$

$$\left. \times \exp\{(it\boldsymbol{\kappa} \cdot \mathfrak{B}_{\nu}{}^{\dagger} \cdot \mathfrak{J}^{-\frac{1}{2}} \cdot \mathbf{l})\}d^{3}\mathbf{l} \right]. \quad (A8)$$

The integrals (A8) are easily evaluated, yielding

$$\langle \chi_{\nu\nu'}{}^{r} \rangle_{T} = \exp\{i\boldsymbol{\kappa} \cdot [\mathbf{b}_{\nu}(0) - \mathbf{b}_{\nu'}(0)]\}$$
$$\times \exp\{-\tfrac{1}{2}(\boldsymbol{\kappa} \cdot \mathfrak{K}_{\nu\nu} \cdot \boldsymbol{\kappa})(it + Tt^{2})\}. \quad (A9)$$

The translational function is given by Z.G.:

$$\langle \chi_{\nu\nu'}{}^{t} \rangle_{T} = \exp\{-\kappa^{2}(2M)^{-1}(it + Tt^{2})\}, \quad (A10)$$

where M is the molecular mass. Combining (A9) and (A10) gives the desired result (A1), with

$$\mathfrak{M}_{\nu}^{-1} = \mathfrak{K}_{\nu\nu} + M^{-1}\mathbf{1}, \quad (A11)$$

where $\mathbf{1}$ is the unit tensor and $\mathfrak{M}_{\nu}$, by comparison of components, is seen to be identical with the S.T. mass tensor corresponding to the νth nucleus.

It may be verified on a more rigorous basis that the present model gives the correct result for a rigid rotator in the limit of very large neutron energies. For in this case, all initial molecular motion may be ignored, with the result that

$$\exp(iHt) \exp(-iH_{\nu}t) \rightarrow \exp\{-\tfrac{1}{2}it\boldsymbol{\kappa} \cdot \mathfrak{K}_{\nu\nu} \cdot \boldsymbol{\kappa}\}, \quad (A12)$$

a form dependent only on the molecular orientational coordinates. The thermal average defined in the text then reduces rigorously to an average over these coordinates, independent of the molecular energy levels or wave functions. The form (A12) represents a generalization of the "classical limit" introduced by Z.G. to arbitrary molecular structure.