Orientation-Averaged Amplitude of the One-Quantum Term in the Neutron Scattering Law for Molecular Gases

JOHN M. CARPENTER

Department of Nuclear Engineering, The University of Michigan, Ann Arbor, Michigan

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The amplitude of the one-quantum term in the scattering law for coherent scattering of neutrons by molecular gases is calculated using a generating-function approach. The phase factor $\exp(i\kappa\cdot\mathbf{b})$ is averaged jointly with the amplitude factor $(\kappa\cdot\gamma_\nu)(\kappa\cdot\gamma_{\nu'})$, as opposed to the more common technique of approximating the joint average by the product of the average of each factor. Results of example calculations show that the correction is of the same magnitude as the result of the conventional calculation.

THE differential cross section for thermal neutron scattering by molecular gases is conveniently calculated in terms of the scattering law[1–3]

$$\partial^2\sigma/\partial\Omega\partial\epsilon = (k_f/k_0)\exp(-\epsilon/2k_BT)\tilde{S}(\kappa,\epsilon), \quad (1)$$

which is written here in symmetric form,

$$\tilde{S}(\kappa,\epsilon) = \tilde{S}(\kappa,-\epsilon), \quad (2)$$

where $\hbar k_0$ and $\hbar k_f$ are neutron initial and final momenta, $\hbar\kappa = \hbar|\mathbf{k}_f - \mathbf{k}_0|$ and $\epsilon = (\hbar^2/2m)(k_f^2 - k_0^2)$ are neutron momentum and energy gain. When the scatterer is a molecular gas, it is further convenient to express $\tilde{S}$ as a weighted sum,

$$\tilde{S} = (4\pi)^{-1}\sum_{\nu,\nu'}\sigma_{\nu\nu'}\tilde{S}_{\nu\nu'} \quad (3)$$

in which the sum is taken twice over all atoms ν of the molecule. The $\sigma_{\nu\nu'}$ are the direct or interference cross sections, respectively, for $\nu=\nu'$ or $\nu\neq\nu'$,

$$(4\pi)^{-1}\sigma_{\nu\nu'} = A_\nu A_{\nu'} + C_\nu^2\delta_{\nu\nu'} \quad (4)$$

and A_ν and C_ν are the coherent and incoherent bound atom scattering lengths of the νth atom.

The scattering law may be discussed in terms of the intermediate scattering function $\tilde{\chi}(\kappa,t)$[2,3]

$$\tilde{S}_{\nu\nu'}(\kappa,\epsilon) = (2\pi\hbar)^{-1}\int_{-\infty}^{\infty}\exp\left(\frac{i\epsilon t}{\hbar}\right)\tilde{\chi}_{\nu\nu'}(\kappa,t)dt, \quad (5a)$$

$$\tilde{\chi}_{\nu\nu'}(\kappa,t) = \int_{-\infty}^{\infty}\exp\left(\frac{-i\epsilon t}{\hbar}\right)\tilde{S}_{\nu\nu'}(\kappa,\epsilon)d\epsilon. \quad (5b)$$

The intermediate functions $\tilde{\chi}_{\nu\nu'}$ for scattering by molecular gases are products of intermediate functions describing the effect of center-of-mass translation and the joint effect of rotation about the center of mass and internal vibration,

$$\tilde{\chi}_{\nu\nu'} = \tilde{\chi}^{\text{trans}}\tilde{\chi}_{\nu\nu'}^{\text{rot-vib}}. \quad (6)$$

The translational intermediate function is rigorously separable.[2] For calculation of the direct scattering terms $\nu=\nu'$, the approximation that rotation and vibration are separable in $\tilde{\chi}$ has been frequently used[3–5] and the rotational direct scattering has been calculated using the mass–tensor approach.[2,4] The vibrational part has been approximated as an average over molecular orientations[5,6]

$$\tilde{\chi}_{\nu\nu'}^{\text{rot-vib}}\approx\tilde{\chi}_{\nu\nu'}^{\text{rot}}\langle\tilde{\chi}_{\nu\nu'}^{\text{vib}}\rangle_\Omega \quad (7)$$

separating the rotational function; problems of calculating the rotational function are not to be discussed here. These procedures lead to calculated cross sections which compare well with experiment at larger values of neutron momentum transfer, for scattering by hydrogenous molecules, in which direct terms $\nu=\nu'$ are of greatest importance.

Recently, several authors[7,8] have applied similar approximations in cases where interference scattering is important. The effects of interference scattering are contained in the terms $\nu\neq\nu'$ of Eq. (3).

Within the approximation of Eq. (7),[2,3]

$$\langle\tilde{\chi}_{\nu\nu'}^{\text{vib}}\rangle_\Omega = \langle\exp(i\kappa\cdot\mathbf{b}_{\nu\nu'})\exp(-2W_{\nu\nu'})$$

$$\times\prod_\lambda\left[\sum_{n_\lambda=-\infty}^{\infty}\exp(in_\lambda\omega^\lambda t)I_{n_\lambda}(g^\lambda_{\nu\nu'})\right]\rangle_\Omega, \quad (8)$$

$$2W_{\nu\nu'} = \sum_\lambda h^\lambda_{\nu\nu'}, \quad (8a)$$

$$h^\lambda_{\nu\nu'} = \hbar[(\kappa\cdot\gamma_\nu^\lambda)^2 + (\kappa\cdot\gamma_{\nu'}^\lambda)^2]$$
$$\times(4\omega^\lambda)^{-1}\coth(\hbar\omega^\lambda/2k_BT), \quad (8b)$$

$$g^\lambda_{\nu\nu'} = \hbar(\kappa\cdot\gamma_\nu^\lambda)(\kappa\cdot\gamma_{\nu'}^\lambda)(2\omega^\lambda)^{-1}\text{csch}(\hbar\omega^\lambda/2k_BT). \quad (8c)$$

[1] L. Van Hove, Phys. Rev. **95**, 111 (1954).
[2] J. A. Janik and A. Kowalska, in *Thermal Neutron Scattering*, P. A. Egelstaff, Ed. (Academic Press Inc., New York, 1965).
[3] A. C. Zemach and R. J. Glauber, Phys. Rev. **101**, 118, 129 (1956).
[4] R. J. Krieger and M. S. Nelkin, Phys. Rev. **106**, 290 (1957).
[5] H. L. McMurry, Nucl. Sci. Eng. **15**, 429 (1963); H. L. McMurry, L. J. Gannon, and W. A. Hestir, *ibid.* **15**, 438 (1963).
[6] Several approximate schemes are compared in Ref. 5 for calculation of the direct scattering; one of these numerically computes the orientation averages.
[7] M. Antonini, P. Ascarelli, and G. Cagliotti, Phys. Rev. **136**, A1280 (1964).
[8] R. E. West, R. M. Brugger, and G. W. Griffing, Phys. Rev. **148**, 163 (1966).

The normal-mode displacements γ are normalized

$$\sum_{\nu} m_\nu (\gamma_\nu^\lambda)^2 = 1. \tag{9}$$

Subscript Ω indicates an orientation average.

In the average computed term by term in the summation on n_λ, the "one-quantum" terms $n_\lambda = \pm 1$ are

$$\langle \tilde{\chi}_{\nu\nu'}^{\lambda(1)} \rangle_\Omega$$
$$= \langle \exp(i\kappa \cdot \mathbf{b}_{\nu\nu'}) \exp(-2W_{\nu\nu'}) g_{\nu\nu'}^\lambda / 2 \rangle_\Omega \exp(\pm i\omega^\lambda t), \tag{10}$$

in which only the leading term in the Bessel function is retained.

The essence of the approximations of Refs. 7 and 8 is that the phase factor $\exp(i\kappa \cdot \mathbf{b}_{\nu\nu'})$ is averaged separately from the other factors in Eq. (10):

$$\langle \chi \rangle_\Omega \approx \langle \exp(i\kappa \cdot \mathbf{b}) \rangle_\Omega \langle \exp(-2W) g/2 \rangle_\Omega \exp(\pm i\omega t). \tag{11}$$

It is the purpose here to improve on this approximation by averaging jointly the factors

$$F_{\nu\nu'}^\lambda = \exp(i\kappa \cdot \mathbf{b}_{\nu\nu'}) (\kappa \cdot \gamma_\nu^\lambda) (\kappa \cdot \gamma_{\nu'}^\lambda). \tag{12}$$

Under many circumstances the Debye–Waller factor $\exp(-2W_{\nu\nu'})$ is slowly varying and may justifiably be averaged separately; the phase factor $\exp(i\kappa \cdot \mathbf{b}_{\nu\nu'})$ varies more rapidly for κ's encountered in experiment. To perform the average in (12) consider

$$G_{\nu\nu'}^\lambda = \exp[i\kappa \cdot (\mathbf{b}_{\nu\nu'} + \alpha\gamma_\nu^\lambda + \beta\gamma_{\nu'}^\lambda)]. \tag{13}$$

Then

$$F_{\nu\nu'} = -\partial^2 G_{\nu\nu'} / \partial\alpha\partial\beta \big|_{\alpha=\beta=0}. \tag{14}$$

Exponential functions such as those in (13) serve as generating functions not only for (12) but also for higher-than-one-quantum terms in (8). The average (9) is then

$$\langle F_{\nu\nu'} \rangle_\Omega = -\partial^2 \langle G_{\nu\nu'} \rangle_\Omega / \partial\alpha\partial\beta \big|_{\alpha=\beta=0}. \tag{15}$$

The average may be taken over orientations of the unit vector $\hat{\kappa}$:

$$\langle G_{\nu\nu'} \rangle_\Omega = (4\pi)^{-1} \int \exp(i\kappa \cdot \mathbf{b}) d^2\hat{\kappa}$$
$$= j_0(\kappa b) \tag{16}$$

(where the integral is taken over all orientations of $\hat{\kappa}$)

$$\langle F_{\nu\nu'} \rangle_\Omega = [\kappa^2 j_0''(\kappa b) (\partial b/\partial\alpha) (\partial b/\partial\beta)$$
$$+ \kappa j_0'(\kappa b) (\partial^2 b/\partial\alpha\partial\beta)]_{\alpha=\beta=0}, \tag{17}$$

where primes denote differentiation with respect to

argument, the j_l are spherical Bessel functions,

$$b = | \mathbf{b}_{\nu\nu'} + \alpha\gamma_\nu + \beta\gamma_{\nu'} | \text{ and } b_{\nu\nu'} = | \mathbf{b}_{\nu\nu'} |. \tag{18}$$

Forming the functions in (17) and applying recurrence relations for the j_l, the result is obtained after a brief calculation:

$$\langle F_{\nu\nu'} \rangle_\Omega = \kappa^2 \{ \tfrac{1}{3} (\gamma_\nu \cdot \gamma_{\nu'}) j_0(\kappa b)$$
$$+ [\tfrac{1}{3}(\gamma_\nu \cdot \gamma_{\nu'}) - (1/b^2) (\mathbf{b} \cdot \gamma_\nu) (\mathbf{b} \cdot \gamma_{\nu'})] j_2(\kappa b) \}, \tag{19}$$

in which the subscripts on $b_{\nu\nu'}$ have been dropped for brevity. The first term is just what would be obtained by the approximate technique of Eq. (11); the second term in (19) is the entire correction to (11), obtained by averaging jointly. Further, under realistic circumstances, the second term is of comparable magnitude to the first. Direct terms $\nu = \nu'$ are correctly calculated from (11) or (19) by using the limiting form $b \rightarrow 0$.
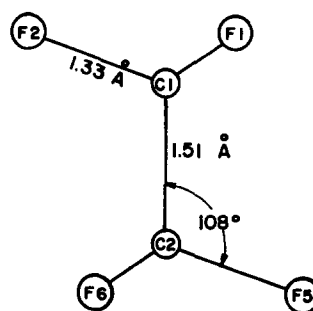
Using (19), (10), and (5),

$$\tilde{S}_{\nu\nu'}^{\lambda(1)}(\kappa, \epsilon) = \exp(-2\langle W_{\nu\nu'} \rangle_\Omega) \hbar \langle F_{\nu\nu'}^\lambda \rangle_\Omega$$
$$\times (4\omega^\lambda)^{-1} \operatorname{csch}(\hbar\omega^\lambda / 2k_B T) \delta(\epsilon \pm \hbar\omega^\lambda). \tag{20}$$

It is convenient for calculation to rewrite the sum in
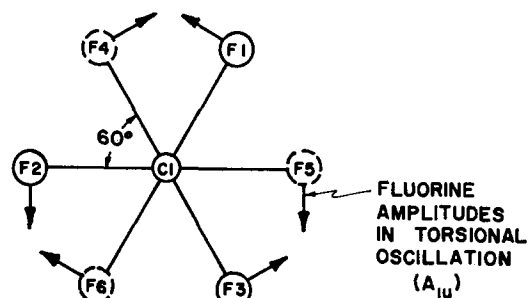
(a) TOP VIEW

(b) SIDE VIEW

FIG. 1. Structure of C_2F_6 (from Ref. 7) showing directions of fluorine motion in the torsional mode.

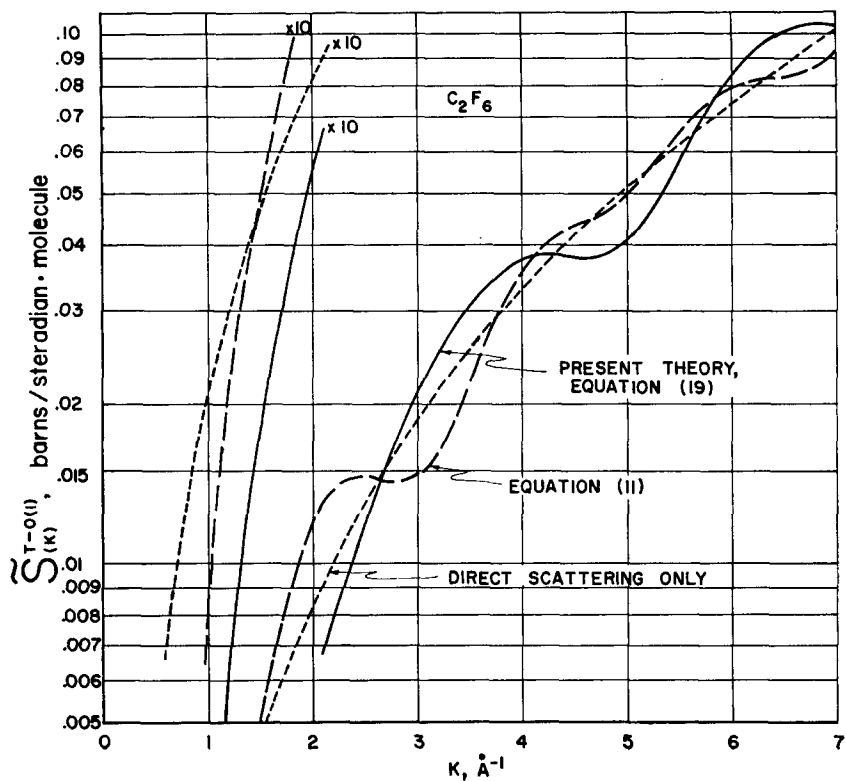FIG. 2. Amplitude of the one-quantum term in the scattering law, for the torsional oscillation of C_2F_6.

FIG. 3. Amplitude of the one-quantum term in the scattering law, for the vibration of Br_2.
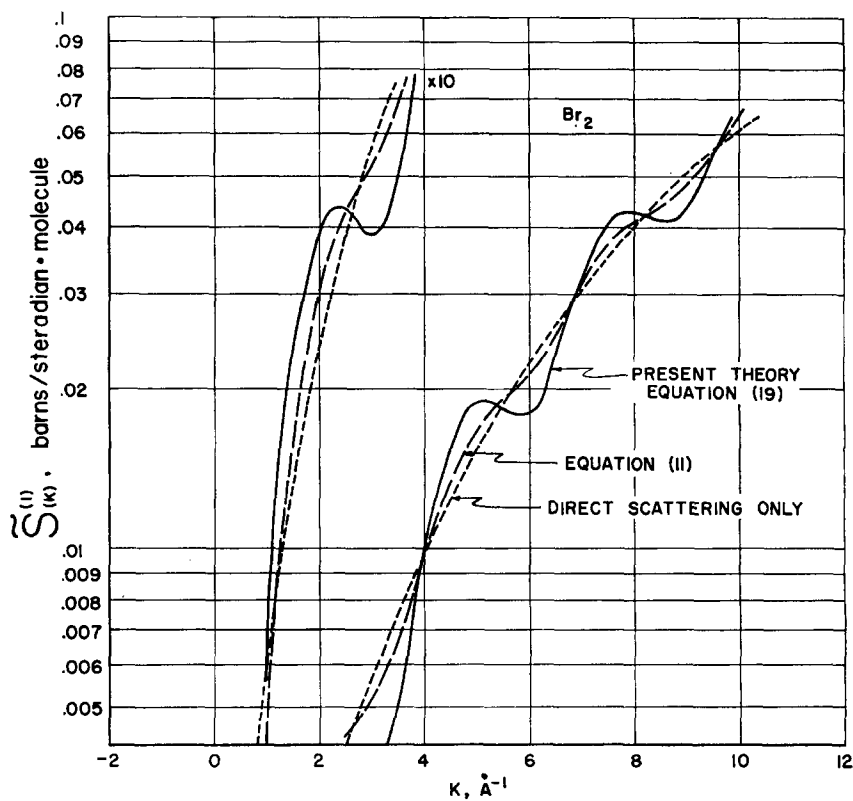
TABLE I. Parameters for C_2F_6 torsion.

Type of term	Number of terms	b (Å)	$\frac{1}{3}\gamma_\nu \cdot \gamma_{\nu'}$ (amu^{-1})	$(1/b^2)(b\cdot\gamma_\nu)(b\cdot\gamma_{\nu'})$ (amu^{-1})
F direct	6	0	0.002924	...
C direct	2	0		No contribution
F$\cdots$F interference	12	2.15	−0.001462	0.002213
F$\cdots$F$_{gauche}$ interference	12	2.76	−0.001462	−0.001393
F$\cdots$F$_{trans}$ interference	6	3.49	0.002924	0
C–C interference	2	1.51		No contribution
C–F interference	12	1.33		No contribution
C$\cdots$F interference	12	2.34		No contribution

Eq. (3), accumulating all like terms, as

$$\tilde{S}^{\lambda(1)} = (4\pi)^{-1}\left(\sum_s n_s{}^d\sigma_s{}^d\tilde{S}_s{}^{d\lambda(1)} + \sum_p n_p{}^i\sigma_p{}^i\tilde{S}_p{}^{i\lambda(1)}\right), \quad (21)$$

where $n_s{}^d$ is the number of nuclei of type s, $\sigma_s{}^d$ is their direct cross section, $n_p{}^i$ is the number of ordered pairs (equal to 2× number of pairs) of type p, $\sigma_p{}^i$ their interference cross section. Nuclei or pairs are classified as to environment as well as with respect to nuclear species.

The final expression for the one-quantum term for the λth mode is then

$$\tilde{S}_{(\kappa,\epsilon)}{}^{\lambda(1)} = \left[\sum_s n_s{}^d\sigma_s{}^d \exp(-2\langle W_s\rangle_\Omega)\langle F_s{}^\lambda\rangle_\Omega\right.$$

$$+ \sum_p n_p{}^i\sigma_p{}^i \exp(-2\langle W_p\rangle_\Omega)\langle F_p{}^\lambda\rangle_\Omega\bigg]$$

$$\times (4\omega^\lambda)^{-1}\operatorname{csch}(\hbar\omega^\lambda/2k_BT)\hbar\delta(\epsilon\pm\hbar\omega^\lambda). \quad (22)$$

The coefficient of the δ function is the amplitude of the one-quantum transition which we denote $\tilde{S}^{\lambda(1)}(\kappa)$.

As an example, the amplitude of the scattering law for exchange of one quantum with the torsional oscillator in C_2F_6 has been calculated according to Eq. (16). A frequency of 12 meV ($=97$ cm^{-1}) was assumed[9] with absolute temperature 300°K, and other data given in Fig. 1 and Table I. The structural data are from Ref. 11. The displacements γ are easily calculated for this mode since it mixes with no others; they are directed as in Fig. 1(a), while the amplitudes are easily computed from the normalizing condition, Eq. (9). Since only fluorines move in the torsional mode, and the amplitudes of the six fluorines are identical, this gives

$$\gamma_F{}^2 = 1/(6m_F). \quad (23)$$

A fluorine cross section of 4.0 b, assumed completely coherent, and a fluorine mass of 19 amu were used.

Several terms contribute to the amplitude; F direct terms and interference terms between F$\cdots$F, F$\cdots$F$_{gauche}$, and F$\cdots$F$_{trans}$. No carbon terms enter because carbons do not move (i.e., $\gamma_c = 0$) in the torsional mode.

The amplitude of the one-quantum term for the vibrational mode of Br_2 has also been calculated. A frequency of 40 meV ($=323$ cm^{-1}), and internuclear spacing 2.28 A[12] were used, with incoherent and coherent cross sections 6.1 and 5.7 b, respectively. The displacements γ, which are equal, oppositely directed, and colinear with b, are calculated from Eq. (9):

$$\gamma^2 = 1/(2m_{Br}). \quad (24)$$

Thus, using a bromine mass of 80 amu,

$$\tfrac{1}{3}\gamma^2 = 0.002083,$$

$$\tfrac{1}{3}\gamma_1\cdot\gamma_2 = -0.002083,$$

$$\tfrac{1}{3}\gamma_1\cdot\gamma_2 - (1/b^2)(b\cdot\gamma_1)(b\cdot\gamma_2) = 0.004166 \text{ amu}^{-1},$$

where a temperature of 300°K was used.

The calculations were performed using The University of Michigan IBM 7090, and the results are shown as a function of κ in Figs. 2 and 3. Also shown are calculations for the approximation of Eq. (11), and the direct part only.

We conclude that within the approximation of averaging the vibrational part of the scattering over orientation, the correction represented by Eq. (19) is an improvement over the usual averaging procedure, and that differences in results are significant. The correction is nearly as easily calculated as the approximation. The generating function approach to the calculation of vibrational intensities is easily generalized to calculate higher-than-one-quantum amplitudes.

ACKNOWLEDGMENTS

[9] As of quite recently, this frequency was not well known.[10] The choice of 12 meV arises in connection with the analysis of a recent experiment which suggests this value.

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