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Rotational Correlation Functions in Neutron Scattering by Molecular Gases*

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The incoherent neutron scattering cross section of molecular gases is evaluated in terms of classical rotational time correlation functions. The calculation emphasizes the Gaussian behavior of the intermediate scattering function but also treats non-Gaussian effects. Explicit expressions applicable to spherical, linear, and symmetric molecules are given and applied to CH_4, HCl, and NH_3. Comparisons with exact quantum-mechanical calculations and experimental data show the Gaussian approximation to be reasonably accurate. In the case of CH_4, the inclusion of the leading non-Gaussian term brings the agreement to within about 1% of the exact results. The present approach considerably reduces the amount of computation relative to exact calculations; moreover, it permits a physically intuitive and potentially tractable extension to liquids and solids.

I. INTRODUCTION

THE dynamics of molecular gases associated with translations, rotations, and intramolecular vibrations can be observed by means of inelastic neutron scattering.[1] In computing the angular and energy differential cross section, there is no difficulty in treating the effects of translations and vibrations.[2] If rotation-vibration interactions are ignored, the rotational effects also can be calculated rigorously.[3–5] The exact expressions for scattering by rigid rotators contain a number of summations which make actual computation quite involved and time consuming, particularly if the molecules are not spherically symmetric. For this reason the most extensive experimental[6,7] and theoretical studies[5,8] thus far have been directed at methane, a spherical molecule. Theoretical results for linear molecules have been obtained by Lurie,[9] but no experimental data are available for comparison. Measurements on ammonia, a symmetric molecule, are available,[6,10] and recently the cold-neutron data were analyzed by Venkataraman and co-workers.[11] The symmetric-molecule computations are sufficiently complicated that it seems questionable whether similar exact calculations for the asymmetric molecule will be attempted.

Approximate classical calculations have been considered, notably by Kreiger and Nelkin.[12] Although Kreiger and Nelkin originally applied their method to total and angular differential cross sections, others have used the approximation to interpret inelastic scattering experiments.[1] In the latter application, there has been considerable discussion of the validity of the method[5,8]; recently, the nature of the approximations involved was further clarified by Summerfield and Zweifel.[13]

In this paper, we propose a new method for the analysis of neutron scattering by molecular gases. The approach, which is based on the use of classical rotational correlation functions, is considerably simpler than the quantum-mechanical (QM) treatment, and gives quite reasonable results when compared with experiments and exact calculations. The correlation functions describe the time development of the molecule's angular correlations, which, as such, are appropriate quantities for the study of dynamical properties of molecular reorientations.[14–16]

Inelastic scattering of neutrons by gases at normal densities can be quite accurately described in terms of the scattering from each individual molecule. The double differential cross section per molecule is[2,17]

$$\sigma(E_0,E,\theta)=\left(\frac{E}{E_0}\right)^{1/2}\sum_{\nu\nu'}^{n} A_{\nu\nu'}S^{\nu\nu'}(\boldsymbol{\kappa},\omega)\,, \tag{1}$$

where

$$S^{\nu\nu'}(\boldsymbol{\kappa},\omega)=\frac{1}{2\pi}\int_{-\infty}^{\infty}dt\, e^{-i\omega t}\chi^{\nu\nu'}(\boldsymbol{\kappa},t)\,, \tag{2}$$

$$\chi^{\nu\nu'}(\boldsymbol{\kappa},t)=\langle e^{i\boldsymbol{\kappa}\cdot\mathbf{r}_\nu(t)}e^{-i\boldsymbol{\kappa}\cdot\mathbf{r}_{\nu'}(0)}\rangle\,, \tag{3}$$

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and

$$A_{\nu\nu'}=a_{\mathrm{coh}}{}^{\nu}a_{\mathrm{coh}}{}^{\nu'}+(a_{\mathrm{inc}}{}^{\nu})^2\delta_{\nu\nu'}\,. \tag{4}$$

In these expressions the incident and scattered neutron energies are E_0 and E, θ is the scattering angle, $\boldsymbol{\kappa}=\mathbf{k}-\mathbf{k}_0$ and $\omega=E-E_0$ are the momentum and energy transfers, $\mathbf{r}_\nu(t)$ is the position of the ν atom at time t, n is the number of atoms per molecule, and a_{coh} and a_{inc} are the bound-atom coherent and incoherent scattering lengths, respectively. In almost all existing calculations it is assumed that couplings between the different degrees of freedom can be neglected. Then

$$S^{\nu\nu'}(\boldsymbol{\kappa},\omega)=\int\int d\omega' d\omega''$$
$$\times S_t{}^{\nu\nu'}(\boldsymbol{\kappa},\,\omega-\omega')S_r{}^{\nu\nu'}(\boldsymbol{\kappa},\,\omega'-\omega'')S_v{}^{\nu\nu'}(\kappa,\omega'')\,, \tag{5}$$

where the subscripts denote translational (t), rotational (r), and vibrational (v) contributions.

The evaluation of S_t and S_v is well known[2] and requires no discussion. For most inelastic scattering experiments in which low energy ($E_0\sim 5$ meV) incident neutrons are used, it is sufficient to replace S_v by its zero-point vibration expression. Exact QM expressions for S_r are available; in the case of spherical and linear molecules, the intermediate scattering function can be written as[18]

$$\chi_r{}^{\nu\nu'}(\kappa,t)=\sum_{l=0}^{\infty}(2l+1)j_l(\kappa b_\nu)j_l(\kappa b_{\nu'})P_l(\cos\theta_{\nu\nu'})f_l(t)\,. \tag{6}$$

This form shows clearly that the functions $f_l(t)$, to be defined in the Appendices, are the basic quantities in the dynamical calculation. In Sec. II we discuss the classical time correlation functions $F_l(t)$ to be used in place of $f_l(t)$. A method used earlier by Sears[18] is extended to linear and symmetric molecules. In Sec. III a Gaussian approximation (GA) is formulated which enables us to compute $\sigma(E_0,E,\theta)$ with only a knowledge of $F_1(t)$. The approximation is analogous to that used in treating monatomic liquids and gases,[19,20] and we can discuss the non-Gaussian corrections in the rotational problem in a similar way. Numerical results are presented in Sec. IV and comparison is made with experimental data on methane and ammonia. The agreement obtained is very good. Comparison is also made with previous QM calculations for HCl. In Sec. V some concluding remarks are given.

II. ROTATIONAL CORRELATION FUNCTIONS

The connection between $f_l(t)$ and the classical correlation function $F_l(t)$ has been discussed by Sears in the case of spherical molecules.[18] Sears showed that $F(t)$ can be deduced from $f(t)$ provided $B\ll T$, where B is the rotational constant $(1/2I)$, I is the moment of inertia, and T is the temperature.[21] In dimensionless time $t^*=(T/I)^{1/2}t$, the result is

$$F_l(t^*)=\frac{1}{2l+1}\Big[1+2\sum_{\mu=1}^{l}(1-\mu^2t^{*2})e^{-\mu^2t^{*2}/2}\Big]. \tag{7}$$

In general F and f are expected to have the following properties:

$$F_0(t)=1,\quad \text{for all } t \tag{8}$$
$$F_l(0)=1,\quad \text{for any } l.$$

A direct comparison of $F_l(t)$ and $f_l(t)$ is not feasible because the latter is, in general, complex. Following Schofield[22] we may consider the time-displaced function $f_l(t-i/2T)$ as the classical limit of $f_l(t)$. Comparison of $f_1[t^*-i\surd(\frac{1}{2}\tau)]$, $\tau=B/T$, with $F_1(t^*)$ shows that the former gives a somewhat lower value at small times and the deviation decreases with increasing t^*. At $t^*=0$ the ratio is 0.986 at $\tau=0.026$, whereas it is 0.925 at $\tau=0.152$. It is to be expected that $f_l[t^*-i\surd(\frac{1}{2}\tau)]$ will approach $F_l(t^*)$ in the limit of high temperature. The same general tendency holds for higher l, but the discrepancies are somewhat larger.

A similar procedure can be used to derive correlation function $F_l(t)$ for linear and symmetric molecules. It is shown in Appendix A that for linear molecules the result is

$$F_l(t)=\frac{1}{\pi}\left[\frac{\Gamma[\frac{1}{2}(l+1)]}{(\frac{1}{2}l)!}\right]^2E_l$$
$$+2\sum_{n}{}^{\prime}\,\frac{1}{\pi}\,\frac{\Gamma[\frac{1}{2}(l-n+1)]\Gamma[\frac{1}{2}(l+n+1)]}{[\frac{1}{2}(l-n)]![\frac{1}{2}(l+n)]!}$$
$$\times e^{-n^2t^{*2}/2}M(-\tfrac{1}{2},\tfrac{1}{2},\tfrac{1}{2}n^2t^{*2})\,, \tag{9}$$

where E_l is 1 or 0 depending upon whether l is even or odd and $M(a,b,x)$ is the Krummer's confluent hypergeometric function.[23] The prime over the summation indicates that if l is odd, only odd values of n should be taken, whereas if l is even, then only even values (starting with 2) should be used. By direct substitution we find that the properties in Eq. (8) are satisfied. At long times we see that the second term in Eq. (9) vanishes, thus $F_l(t^*)$ approaches zero (l odd) or a positive value (l even) in the limit. The behavior of $F_1(t)$ is shown in Fig. 1 along with similar functions for other types of molecules. Note that for linear molecules $F_1(t)$ can become negative, whereas the spherical-molecule result always remains positive. In Appendix B an approximate expression for $F_1(t)$ is derived for symmetric molecules.

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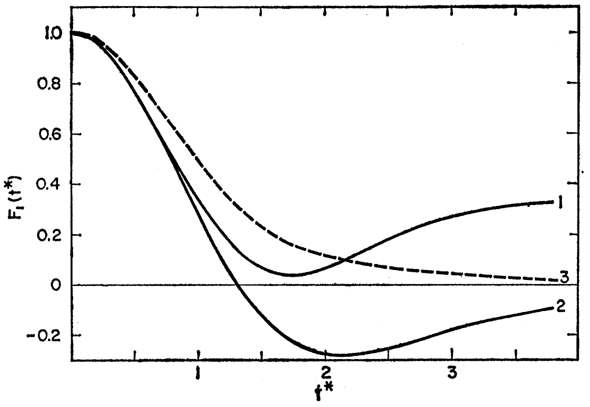

FIG. 1. Rotational time correlation function $F_1(t^*)$ as a function of $t^*=(I/T)^{1/2}t$ for spherical (1), linear (2), and symmetric (3) molecules. Curve (3) corresponds to $c=0.365$ and $\phi=68°$.

The result is

$$F_1(t)=g(t^*)\cos^2\phi+\tfrac{1}{2}[1+g(t^*)]e^{-(c/2)t^{*2}}\sin^2\phi\,, \tag{10}$$

where $c=(I_z-I)/I_z$, ϕ is the angle between the nuclear position vector and the symmetry axis, and $g(t^*)$ is $F_1(t^*)$ from Eq. (9). Depending on the value of ϕ, the correlation function for symmetric molecules can remain positive or display a negative region. As expected, it reduces to the linear-molecule result when $\phi=0$.

III. GAUSSIAN APPROXIMATION

In order to employ the classical functions $F(t)$ in neutron scattering calculations, one needs to express $\chi_r^{\nu\nu'}(\boldsymbol{\kappa},t)$ in terms of the displaced time variable, $t-i/2T$. The intermediate scattering function Eq. (6) then becomes real and can be approximated by the expression

$$\chi_r^{\nu\nu'}(\boldsymbol{\kappa},t)\cong\sum_l(2l+1)j_l(\kappa,b_\nu)j_l(\kappa,b_{\nu'})P_l(\cos\theta_{\nu\nu'})F_l(t) \tag{11}$$

at sufficiently high-temperatures and low-momentum transfers (HTLK). In this case the cross section for spherical molecules becomes a product of the monatomic gas cross section and a rotational factor, $\Gamma_{\nu\nu'}(\boldsymbol{\kappa},\omega)$;

$$S^{\nu\nu'}(\boldsymbol{\kappa},\omega)=S_t(\boldsymbol{\kappa},\omega)\Gamma_{\nu\nu'}(\boldsymbol{\kappa},\omega)\,, \tag{12}$$

where

$$\Gamma_{\nu\nu'}(\boldsymbol{\kappa},\omega)=\sum_l j_l(\kappa b_\nu)j_l(\kappa b_{\nu'})P_l(\cos\theta_{\nu\nu'})$$
$$\times\left[1+2\sum_{\mu=1}^{l}(1+c_\mu)^{-3/2}\left(1+\frac{2c_\mu}{1+c_\mu}\frac{M\omega^2}{2T\kappa^2}\right)e^{[c_\mu/(1+c_\mu)]M\omega^2/2T\kappa^2}\right] \tag{13}$$

with $c_\mu=M\mu^2/I\kappa^2$. In Eq. (12), $S_t(\boldsymbol{\kappa},\omega)$ is the exact QM expression for a monatomic gas of mass M. When $b_\nu=b_{\nu'}=0$, $\Gamma_{\nu\nu'}$ reduces to unity as expected. We have examined the accuracy of this approximation numerically, and some results will be discussed. However, the evaluation of Eq. (13) is still rather involved, and extensions to linear and symmetric molecules are even more complicated. It therefore becomes worthwhile to seek a simpler approximation.

We now describe a GA for $\chi_r(\boldsymbol{\kappa},t)$ applicable to spherical, linear, and symmetric molecules. The approach is closely analogous to that commonly employed in the theory of neutron scattering by monatomic liquids and gases.[19,20] In the liquid problem the GA simplifies the analysis and also greatly facilitates the physical interpretation of the results. For molecular systems one can anticipate similar advantages in the treatment of rotational dynamics. In particular, we will show that, for gaseous systems, the approximation results in a simple and quite accurate calculational procedure requiring only a knowledge of $F_1(t)$.

The GA is inherently an approximation pertaining to the "self" part of the scattering (the $\nu=\nu'$ terms in the cross section), and is usually applied to the calculation of the incoherent cross section. This is not a particularly severe restriction in molecular studies since many of the substances investigated contain hydrogen. We shall therefore restrict our attention to the case of $\nu=\nu'$ and will suppress the atom index ν. From Eq. (11), if we expand the spherical Bessel functions in a power series, the intermediate scattering function is cast into the form

$$\chi_r(\boldsymbol{\kappa},t)=e^{-(\kappa^2/2)W_r(t)}G(\boldsymbol{\kappa},t)\,, \tag{14}$$

$$W_r(t)=\tfrac{2}{3}b^2[1-F_1(t)]\,, \tag{15}$$

$$G(\boldsymbol{\kappa},t)=1+\sum_{n=1}^{\infty}a_n(t)(\kappa b)^{2n}\,. \tag{16}$$

The GA consists of replacing $G(\boldsymbol{\kappa},t)$ by unity. The remainder in Eq. (16) constitutes the non-Gaussian corrections, and the coefficients $a_n(t)$ can be found from the series expansion. For example, one obtains

$$a_1(t)=0\,, \tag{17}$$

$$a_2(t)=(1/18)[-\tfrac{1}{5}+\tfrac{4}{5}F_1(t)-F_1^2(t)+\tfrac{2}{5}F_2(t)]\,, \tag{18}$$

$$a_3(t)=-(1/162)\{18/35-(162/175)F_1(t)$$
$$+(18/35)F_2(t)-(18/175)F_3(t)$$
$$+[1-F_1(t)]^2+54[1-F_1(t)]a_2(t)\}\,. \tag{19}$$

The behavior of $a_2(t)$ and $a_3(t)$ for spherical molecules is shown in Fig. 2. At short times one can show that they increase like t^{*4} and t^{*6}, respectively, and asymptotically they approach the values 0.002 and 0.00045. The region where non-Gaussian effects are expected to be most significant is seen to be t^* from 1 to 3. The general behavior is not unlike that found in monatomic liquids and gases; however, in contrast to the translation problem, the present coefficients approach finite though small values at long times.

The GA reduces the calculation of the intermediate scattering function to a determination of the mean-square displacement function $W(t)$. Our result is equivalent to taking for $W_r(t)=\tfrac{1}{3}\langle[\mathbf{b}(t)-\mathbf{b}(0)]^2\rangle$, where $\mathbf{b}$ is

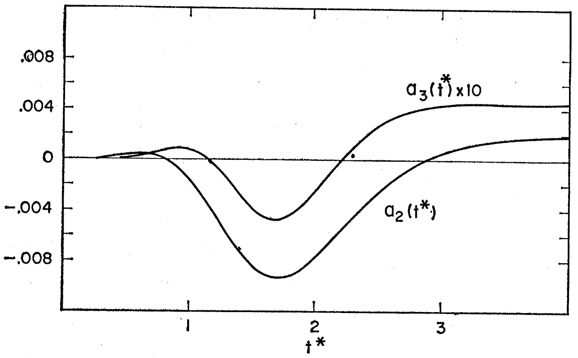

FIG. 2. Non-Gaussian corrections to the rotational intermediate scattering function for a spherical molecule.

the proton position from c.m., the expression given in Eq. (15). In using this classical result in cross-section calculations, it is known that some modifications are necessary.[24] This is a familiar procedure in the treatment of neutron scattering by liquids, and basically the same arguments apply here. Suppose we begin with a Gaussian form for the QM $\chi(\boldsymbol{\kappa},t)$,[25]

$$S(\boldsymbol{\kappa},\omega)=\frac{1}{2\pi}\int_{-\infty}^{\infty}dt\,e^{-i\omega t}e^{-(\kappa^2/2)\gamma(t)}\,, \tag{20}$$

where $\gamma(t)$ is a complex "width" function

$$\gamma(t)=\frac{1}{M}\int_0^\infty d\omega\frac{f(\omega)}{\omega}\left[\coth\frac{\omega}{2T}(1-\cos\omega t)+i\sin\omega t\right] \tag{21}$$

and $f(\omega)$ is the spectral density related to the velocity autocorrelation function. By using a time-displaced variable, one obtains a real function $\gamma(t-i/2T)$ which, as we have seen in Sec. II, is still not a classical quantity in the sense of $F_1(t)$. The difference between $\gamma(t-i/2T)$ and $W(t)$ is that $\gamma(-i/2T)$ does not vanish. (This is in fact the term that accounts for recoil effects.) Thus (20) can be rewritten as

$$S(\boldsymbol{\kappa},\omega)=e^{-\omega/2T}\exp\left[-\frac{\kappa^2}{2}\gamma\left(-\frac{i}{2T}\right)\right]\times\frac{1}{2\pi}\int_{-\infty}^{\infty}e^{-(\kappa^2/2)W(t)}e^{-i\omega t}dt\,, \tag{22}$$

where

$$\gamma\left(-\frac{i}{2T}\right)=\frac{1}{M}\int_0^\infty d\omega\frac{f(\omega)}{\omega}\frac{(\cosh\omega/2T)-1}{\sinh\omega/2T} \tag{23}$$

and

$$W(t)=\frac{1}{M}\int_0^\infty d\omega\frac{f(\omega)}{\omega}\frac{1-\cos\omega t}{\sinh\omega/2T}. \tag{24}$$

The "recoil" factor $e^{-(\kappa^2/2)\gamma(-i/2T)}$ can be rewritten in a more familiar form so that (22) becomes

$$S(\boldsymbol{\kappa},\omega)=e^{-\omega/2T}e^{-(\kappa^2/8MT)G(T)}\frac{1}{2\pi}\int_{-\infty}^{\infty}e^{-(\kappa^2/2)W(t)}e^{-i\omega t}dt, \tag{25}$$

where

$$G(T)=2\int_0^\infty f(\omega)\frac{(\cosh\omega/2T)-1}{\omega/2T\,\sinh\omega/2T}d\omega\,. \tag{26}$$

For a monatomic gas, $f(\omega)=\delta(\omega)$, $G(T)$ becomes unity and Eq. (24) gives $W(t)=(T/M)t^2$. For polyatomic systems at low temperatures, $G(T)$ can deviate considerably from unity, in which case Eq. (26) should be used.

In the present approach the mean-square displacement function has contributions from translations and rotations,

$$W(t)=(T/M)t^2+\tfrac{2}{3}b^2[1-F_1(t)]\,. \tag{27}$$

The translational contribution to $f(\omega)$ is just a δ function, and we will not discuss it any further. Denoting the rotational contribution by $f_r(\omega)$, we obtain

$$p_r(\omega)=\frac{\omega}{2M\sinh\omega/2T}f_r(\omega)=\tfrac{2}{3}b^2\omega^2\frac{1}{\pi}\int_0^\infty dt\,\cos\omega t\,F_1(t)\,. \tag{28}$$

Using the results of Sec. II, we have for spherical molecules

$$p_r(\omega)=(8/9\sqrt{\pi})(I/2T)^{3/2}(\omega^2b)^2e^{-I\omega^2/2T}\,, \tag{29}$$

for linear molecules

$$p_r(\omega)=\tfrac{2}{3}(I/2T)\omega^3b^2e^{-I\omega^2/2T}\,, \tag{30}$$

and for symmetric molecules

$$p_r(\omega)=\tfrac{2}{3}b^2[\cos^2\varphi(I/2T)\omega^3p_1(\omega)+\sin^2\phi\,\omega^2(c_1p_1(\omega)+c_2p_2(\omega))]\,, \tag{31}$$

where

$$p_1(\omega)=e^{-I\omega^2/2T},\qquad p_2(\omega)=\omega e^{-I\omega^2/2T(1+c)}\Phi(c_3\omega)\,,$$
$$\Phi(x)=\frac{2}{\sqrt{\pi}}\int_0^x dte^{-t^2},\qquad c_1=\frac{1}{4}\left(\frac{2I}{\pi cT}\right)^{1/2}\left(1+\frac{c}{1+c}\right),$$
$$c_2=\tfrac{1}{4}(I/T)(1+c)^{-3/2},\qquad c_3=[I/2Tc(1+c)]^{1/2}. \tag{32}$$

Equations (29) and (30) are essentially the results quoted by Schofield.[26] Note that (31) reduces to (30) when $\phi=0$.

It is possible, from Eq. (11), to apply the GA to the interference terms ($\nu\neq\nu'$) as well. Since these are most important for small κ near the elastic peak, as can be seen from Table II, we can obtain a reasonable estimate of the effect with this procedure. However, the approxi-

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[24] See, for example, Rahman, Singwi, and Sjolander, Ref. 19; and M. Rosenbaum and P. F. Zweifel, Phys. Rev. **137**, B271 (1965).

[25] See Schofield, Ref. 22; also, P. A. Egelstaff and P. Schofield, Nucl. Sci. Eng. **12**, 260 (1962).

[26] P. Schofield, Brookhaven National Laboratory Report No. 719, 1962, Vol. 1, p. RB1 (unpublished).

TABLE I. HWHM, $(\Delta\omega)_{1/2}/T$, of $S^{pp}(\kappa,\omega)$ for methane gas.

	$T=125$°K		$T=295$°K	
κ (Å^{-1})	QM	GA	QM	GA
1	0.17	0.17	0.12	0.12
2	0.46	0.46	0.32	0.32
3	0.72	0.72	0.54	0.54
4	0.84	0.92	0.64	0.68
5	0.95	1.05	0.75	0.80
6	1.02	1.14	0.84	0.90

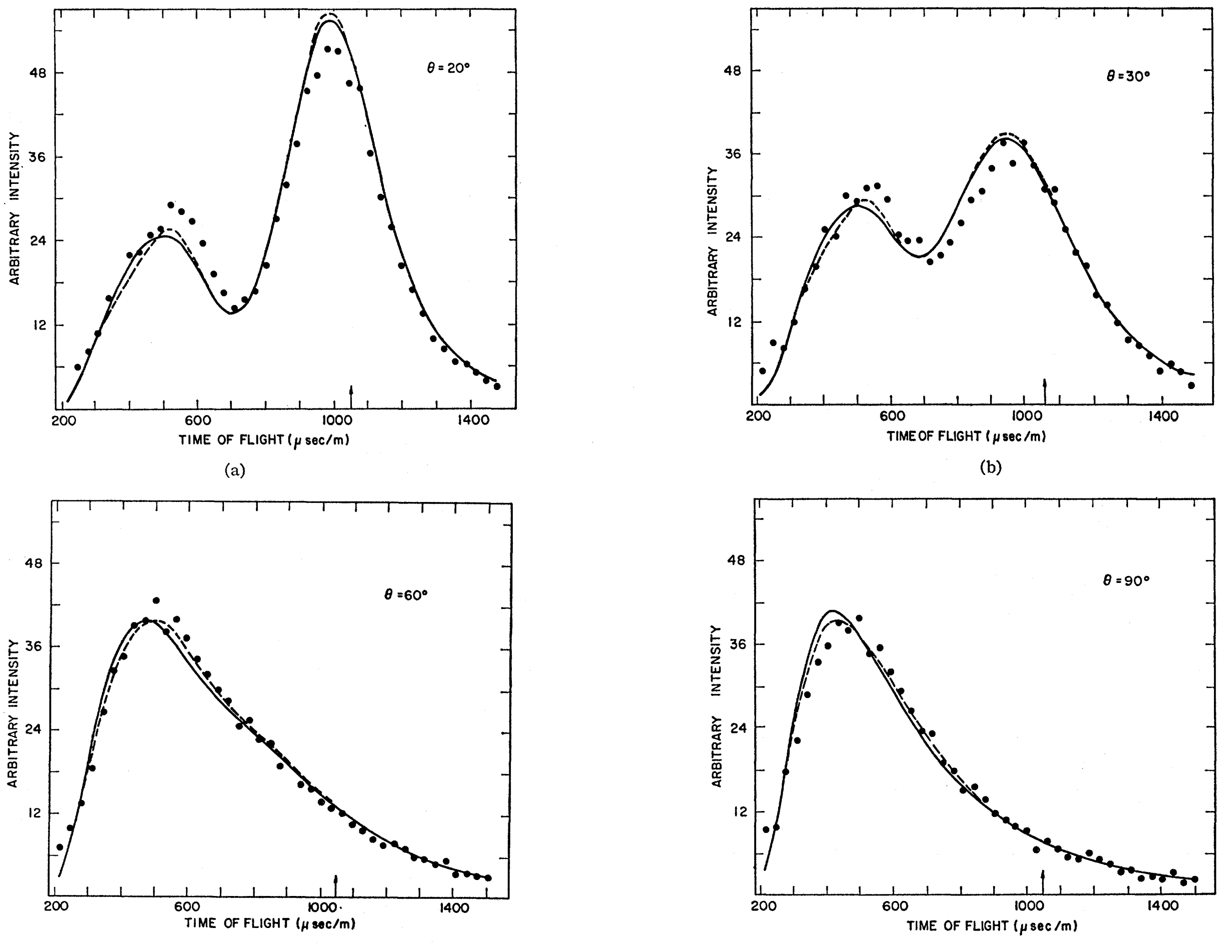
mation breaks down for $\kappa b \gtrsim 1$, as can be seen from the second frequency moment of $S^{vv'}$.

IV. RESULTS AND COMPARISON WITH EXPERIMENTS

The incoherent scattering law,[27] Eq. (25), has been calculated for methane at $T=125$ and 295°K, and compared with exact QM results. It is found that the GA generally underestimates S^{pp} by less than 5% in the range of momentum and energy transfers of experimental interest. Since the general shape of S^{pp} is the same, the comparison is best presented in terms of the

TABLE II. Percentage correction to the pp contribution to cross section of methane gas ($T=295$°K).

κ (Å^{-1}) \ ω/T	0.0	0.1	0.2	0.3	0.4	0.6	1.0
1	14.5	14.0	9.8	0.2	−2.0	−2.1	−1.9
2	8.3	7.8	6.0	3.6	1.0	−1.4	−1.4
3	1.5	1.4	1.1	0.7	0.3	−0.4	−0.5
4	0.9	0.8	0.8	0.8	0.7	0.6	0.6
5	1.9	1.9	1.8	1.8	1.6	1.3	0.8
6	3.8	3.8	3.6	3.5	3.2	2.5	1.9
8	6.3	6.2	6.2	6.1	5.9	5.3	4.0
10	2.5	2.5	2.4	2.4	2.3	2.1	1.7



(a) (b) (c) (d)

FIG. 3. Time-of-flight spectra of neutrons scattered by methane gas at $T=295$°K at various scattering angles θ. Experimental points are given as closed circles and theoretical results are shown as solid (Gaussian approximation) and dashed [including non-Gaussian term $a_2(t)$] lines, respectively. Calculated spectra have been averaged over an incident spectrum (mean energy 4.87 meV is indicated by the arrow) and are area-normalized.

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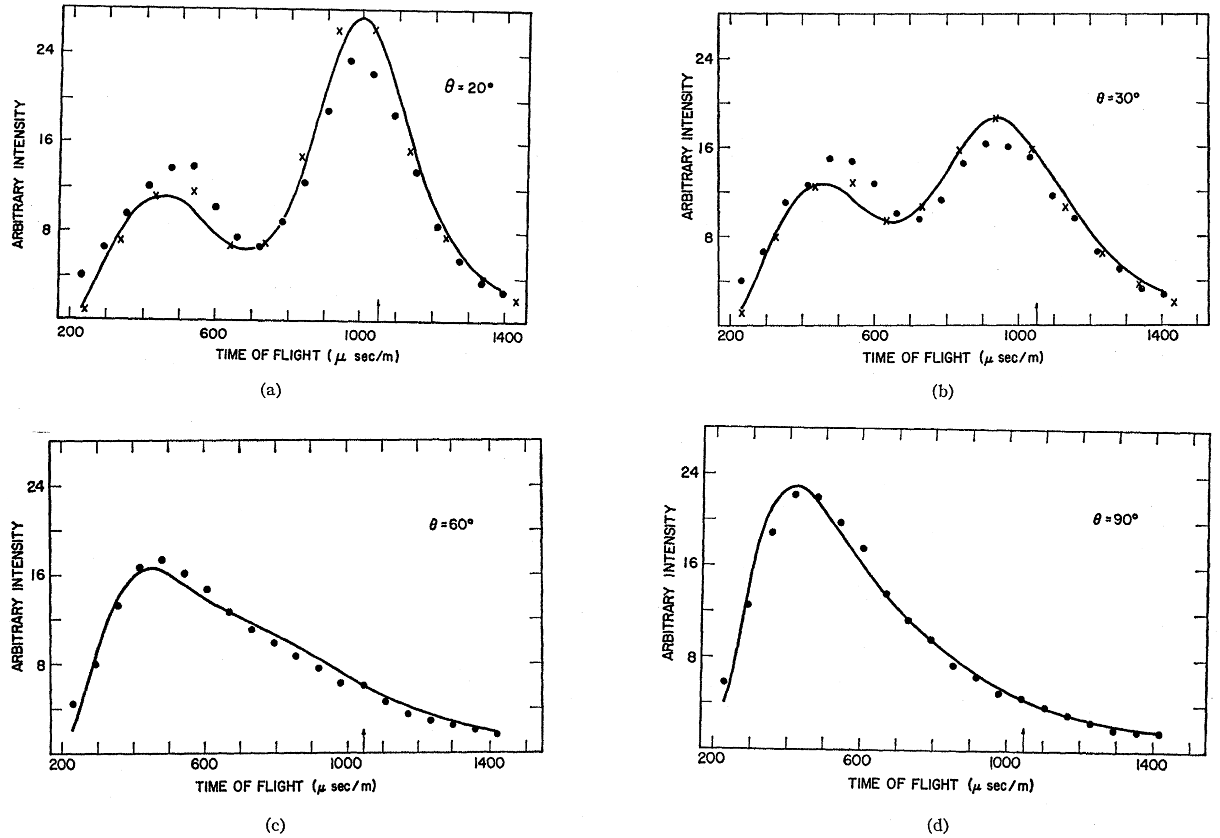
[27] The physical and neutronic properties used are taken from G. Herzberg, *Molecular Spectra and Molecular Structure, Spectra of Diatomic Molecules* (D. Van Nostrand Co., Inc., New York, 1950), 2nd ed., Vol. 1; and D. J. Hughes and J. A. Harvey, Brookhaven National Laboratory Report No. 325, 1958, 2nd ed. (unpublished) (see also supplements 1960, 1964, 1965).



(a) (b) (c) (d)

FIG. 4. Time-of-flight spectra of neutrons scattered by ammonia gas at $T=295$°K at various scattering angles θ. Experimental points are given as closed circles and the Gaussian approximation is shown by the solid line. Exact results are indicated by crosses. Theoretical spectra are computed for incident energy of 4.87 meV, indicated by the arrow, and are area-normalized.

half-width at half-maximum (HWHM) at constant κ. The various values are shown in Table I. We have also examined the HTLK approximation at $T=295$°K. Although the HTLK widths are also reasonable, this approximation results in greater deviations in the intensities of S^{pp}.

In most calculations of neutron spectra of hydrogenous substances, it is conventional to consider only the incoherent scattering due to the hydrogens. Since the expressions for all the contributions in the case of methane are known,[5] it is of interest to estimate the uncertainties introduced by this assumption. In Table II we show the percentage corrections due to all the other terms in Eq. (1) at various κ, and $\epsilon=\omega/T$ values. The correction is seen to be most important in the region of the elastic peak, and is generally quite small in the κ range of 2–5 Å^{-1}. Similar estimates for HCl show that the contribution from the chlorine atom is about 10–20% near the elastic peak and decreases rapidly away from this region. Even though we have not studied the corrections in the case of ammonia, the same type of behavior is expected.

Using Eqs. (1), (25)–(27), and the correlation functions $F_1(t)$ shown in Fig. 1, we have computed the differential cross sections for spherical, linear, and symmetric molecules. In order to be compared with experimental data, the results have to be transformed to time-of-flight cross sections:

$$\sigma(f_0,f,\theta)=2(2/m)^{1/2}E^{3/2}\sigma(E_0,E,\theta)\,, \qquad (33)$$

where f is the time-of-flight and m is the neutron mass. Comparisons with the methane and ammonia measurements[6] are shown in Figs. 3 and 4, respectively. The theoretical spectra consist of only the hydrogen contribution to the cross section. They are area-normalized with respect to the experimental points, and have been averaged over an incident spectrum.[6] The effect of the incident spectrum is found to be quite small.

The observed discrepancy in the GA results with experiment is partly due to non-Gaussian effects. We expect the major contribution to come from the $a_2(t)$ term in Eq. (16). The inclusion of this correction, if $F_2(t)$ is known, does not impose any computational problem. The dashed curves in Fig. 3 show the results obtained when the $a_2(t)$ is included; these agree with the exact QM calculations[28] to within about 1%. The

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[28] These are essentially the results of Venkataraman and coworkers (Ref. 11) except that for methane gas we have extended their calculations to include summations over initial and final rotational states up to quantum number 20.

effects of the non-Gaussian correction in shifting the inelastic peak and changing the elastic-peak intensity are clearly observed in this case.

Even though the non-Gaussian effects for ammonia gas have not been calculated, a trend similar to the methane problem is expected. It can be seen from the comparison of GA with the QM results[11] in Fig. 4 that this is indeed the case. Since some discrepancy still remains between the exact calculation and experiment, the accuracy of our approximate results is considered to be quite good. In this connection we should also note that the theoretical results include only the contribution from the hydrogen atoms.

The spectral density $p_r(\omega)$ introduced in Sec. III is also a useful quantity because it can be obtained, in principle, directly from the experimental data. Webb[6] has extracted such a frequency spectrum from his measurement on ammonia gas. Applying Eq. (31), we find a value of $\beta=\omega/T=0.50$ for the peak position in $p_r(\omega)$ which is in agreement with experiment. At higher frequencies our result shows a slower decay than the expressions suggested by others,[6] but the decay is still more rapid than the experimental extrapolation values.

The numerical results for linear molecule (HCl) are compared, on an absolute scale, with the spectra computed by Lurie[9] in Fig. 5. Here both GA and exact calculations include the contribution due to the chlorine atom but not the interference term. The non-Gaussian effects to the cross section have been treated, as in the methane case, by including the $a_2(t)$ term. The results thus obtained are almost indistinguishable from the exact QM calculation at $\theta=20°$. At $\theta=45°$ the non-Gaussian effects cause only a decrease in the elastic-peak intensity.

Note that a typical calculation of $\sigma(E_0,E,\theta)$ on an IBM 360/65 computer, for a set of (E_0,θ) values, and any molecule, requires about 15–20 sec. For symmetric molecules the time-saving factor is about 200–300 relative to an exact calculation.

V. REMARKS

In this paper we have examined the use of classical rotational correlation functions in the analysis of inelastic neutron scattering experiments. This approach has distinct interpretive and calculational advantages over a QM treatment. It is evident that the GA and the modification to include a non-Gaussian correction represent a considerable computational simplification. From the results and comparisons presented in Sec. IV we see that the procedure is quite accurate for calculations of the double differential cross section. The fact that neutron data inherently have a band-type structure suggests that perhaps it is more physical to interpret the measurements in terms of the time behavior of molecular reorientations rather than the stationary energy levels and transition matrix elements. Indeed, our calculations show that it is not necessary to consider explicitly the discrete nature of the rotational levels in order to explain the data, and that a classical description of the molecular motions gives quite good results.

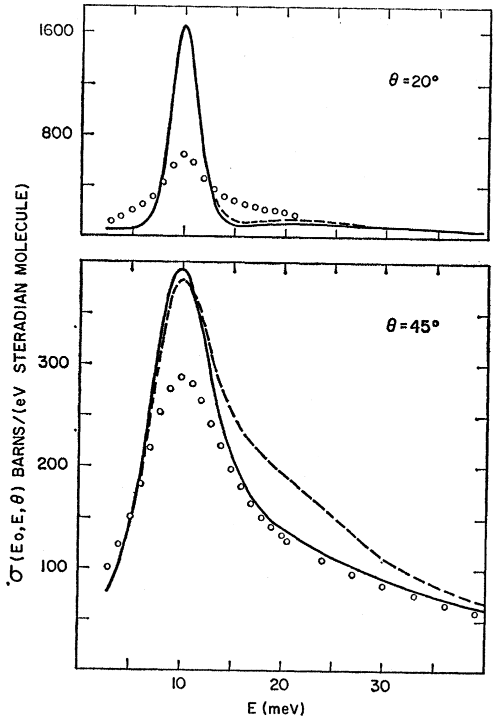

FIG. 5. Absolute neutron scattering cross section of HCl gas at $T=30$ meV for monoenergetic neutrons at $E_0=10$ meV. Gaussian approximation (solid curve) results are compared with exact (dashed curve) and Kreiger-Nelkin (circles) calculations. Interference terms are not included.

Note that since the correlation-function approach is equally applicable to liquids and solids, one therefore has a systematic means of studying rotational phenomena in a bulk medium. By comparing a free-rotation calculation with the measured spectrum one can hope to delineate the effects of angular-dependent forces. For condensed systems it has not been feasible to directly calculate $F_l(t)$; however, they can be obtained from optical measurements. Gordon has shown that $F_1(t)$ and $F_2(t)$ can be obtained from the Fourier transforms of infrared and Raman band shapes, and that the short- and long-time behavior can be separately analyzed.[16] For example, one can discuss the onset of intermolecular torque effects at short times and rotational diffusion processes at long times. Recently several attempts have been made to correlate optical and neutron spectra of liquid and solid methane.[18,29–31] The initial results are quite encouraging, but additional work is still needed to fully establish the utility of this procedure.

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[29] A. K. Agrawal and S. Yip, in *Proceedings of the Symposium on Molecular Dynamics and Structure of Solids* (National Bureau of Standards, Washington, D. C., to be published).

[30] A. K. Agrawal and S. Yip, J. Chem. Phys. **46**, 1999 (1967).

[31] G. Venkataraman, B. A. Dasannacharya, and K. R. Rao, Phys. Rev. **161**, 133 (1967).

Finally we remark that our GA is similar to the Kreiger-Nelkin (KN) calculation only to the extent that the intermediate scattering function in both cases has a Gaussian dependence on κ. The essential difference lies in the treatment of $W_r(t)$. The KN procedure is equivalent to taking the first term in a power-series expansion of $W_r(t)$. This approximation is reasonable at large momentum transfers, but is not expected to hold in the region of the experiments considered here. The failure of KN approximation at low incident energies is therefore to be attributed to its treatment of time dependence and not to the classical nature of the calculation.

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APPENDIX A

We will derive, following a method used by Sears,[18] an expression for the classical time correlation function $F_l(t)$ for linear molecules. The scattering law, considering only translational and rotational motions, is given by

$$S(\kappa,\omega)=\int_{-\infty}^{\infty} S_t(\boldsymbol{\kappa},\omega-\omega')S_r(\boldsymbol{\kappa},\omega')d\omega', \qquad \text{(A1)}$$

where

$$S_r(\boldsymbol{\kappa},\omega)=\sum_{l=0}^{\infty}(2l+1)j_l^2(\kappa b)\mathcal{S}_l(\omega) \qquad \text{(A2)}$$

and

$$\mathcal{S}_l(\omega)=\frac{1}{2\pi}\int_{-\infty}^{\infty} f_l(t)e^{-i\omega t}dt. \qquad \text{(A3)}$$

For spherical molecules we have

$$f_l(t)=\sum_{JJ'}{}'\frac{(2J+1)(2J'+1)}{2l+1}P_J(T)e^{it(E_J-E_{J'})}, \qquad \text{(A4)}$$

where $P_J(T)$ is the Boltzmann's distribution function and the prime over summation indicates that the sum over J' runs from $|J-l|$ to $J+l$. In this case, Sears has obtained an expression for $F_l(t)$, the classical time correlation function.

For a linear molecule, $f_l(t)$ is given by[3,4]

$$f_l(t)=\sum_{JJ'}{}'(2J+1)P_J(T)e^{it(E_J-E_{J'})}\begin{bmatrix} J & l & J' \\ 0 & 0 & 0 \end{bmatrix}^2, \qquad \text{(A5)}$$

where

$$\begin{bmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{bmatrix}$$

denotes a Clebsch-Gordan coefficient. The classical $F_l(t)$ is obtained by approximating the summation over J' and integrating over J in the following way. For $B \ll T$, the most important contribution to $\mathcal{S}_l(\omega)$ comes from values of J very much larger than unity. Thus, $P_J(T) \rightarrow (B/T)e^{-BJ^2/T}$ and the square of the Clebsch-Gordan coefficient is approximated by[32,33]

$$\begin{bmatrix} J & l & J+m \\ 0 & 0 & 0 \end{bmatrix}^2=\frac{1}{\pi}\frac{\Gamma(\frac{1}{2}(l-m+1))\Gamma(\frac{1}{2}(l+m+1))}{[\frac{1}{2}(l-m)]![\frac{1}{2}(l+m)]!}\equiv a_{lm}$$

$$\text{if } l+m \text{ is even,} \qquad \text{(A6)}$$

$$=0 \text{ otherwise.}$$

A test of the classical approximation is obtained by computing

$$\sum_{J=0}^{\infty}(2J+1)e^{-BJ(J+1)/T}.$$

For $T/B=40$ the exact result is 40.128, whereas the classical result is 40. The discrepancy becomes larger as temperature decreases. Combining Eqs. (A3), (A5), and (A6) and using the approximate form for $P_J(T)$, we get

$$\mathcal{S}_l(\omega)\cong\frac{B}{T}\sum_{J=0}^{\infty}2Je^{-BJ^2/T}\sum_{m}^{l}{}'a_{lm}$$
$$\times[\delta(\omega-2BmJ)+\delta(\omega+2BmJ)], \qquad \text{(A7)}$$

where the prime indicates that the summation over m is carried out for all odd values to l if l is odd, and for all even values (starting with 0) if l is even. Equations (A1), (A2), and (A7) can be combined to give an expression for $S(\boldsymbol{\kappa},\omega)$ as a summation over J involving terms like $S_t(\boldsymbol{\kappa},\omega\pm 2BmJ)$. The summation over J is then replaced by an integral, and the result is expressed in the form of (A1) from which one can identify $S_r^{Cl}(\kappa,\omega)$. This procedure reduces $\mathcal{S}_l(\omega)$ to its classical limit $S_l(\omega)$:

$$S_l(\omega)=a_{l0}E_l\delta(\omega)+2\sum_{m}^{l}{}'\frac{I}{T}\frac{1}{m^2}a_{lm}|\omega|e^{-I\omega^2/2m^2T}, \qquad \text{(A8)}$$

where E_l is unity if l is even and zero otherwise. The prime over the summation means sum over all odd m's when l is odd and over all even m's (starting with 2) when l is even. Our result for $S_1(\omega)$ is in agreement with the expression noted by Shimizu.[15] An expression for $F_l(t)$ is obtained by taking the Fourier transform of $S_l(\omega)$. Thus we get

$$F_l(t)=a_{l0}E_l+2\sum_{m}^{l}{}'a_{lm}\sum_{p=0}^{\infty}(-)^p\frac{2^p p!}{(2p)!}(mt^*)^{2p}, \qquad \text{(A9)}$$

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[32] M. E. Rose, *Elementary Theory of Angular Momentum* (John Wiley & Sons, Inc., New York, 1957).

[33] M. A. Preston, *Physics of the Nucleus* (Addison-Wesley Publishing Co., Inc., Reading, Mass., 1962).

where $t^* = (T/I)^{1/2}t$. The summation over p can be expressed in terms of Krummer's confluent hypergeometric function $M(a,b,x)$ [23] as

$$F_l(t) = a_{l0}E_l + 2\sum_{m}^{l}{}' a_{lm}e^{-m^2t^{*2}/2}M(-\tfrac{1}{2}, \tfrac{1}{2}, \tfrac{1}{2}m^2t^{*2}). \quad \text{(A10)}$$

In the following we give the first few $F_l(t)$ for a linear molecule:

$$F_1(t) = M(-\tfrac{1}{2}, \tfrac{1}{2}, \tfrac{1}{2}t^{*2})e^{-t^{*2}/2}, \quad \text{(A11)}$$

$$F_2(t) = \tfrac{1}{4} + \tfrac{3}{4}M(-\tfrac{1}{2}, \tfrac{1}{2}, 2t^{*2})e^{-2t^{*2}}, \quad \text{(A12)}$$

$$F_3(t) = \tfrac{3}{8}M(-\tfrac{1}{2}, \tfrac{1}{2}, \tfrac{1}{2}t^{*2})e^{-t^{*2}/2} + \tfrac{5}{8}M(-\tfrac{1}{2}, \tfrac{1}{2}, \tfrac{9}{2}qt^{*2})e^{-9t^{*2}/2}, \quad \text{(A13)}$$

and

$$F_4(t) = 9/64 + (20/64)M(-\tfrac{1}{2}, \tfrac{1}{2}, 2t^{*2})e^{-2t^{*2}} + (35/64)M(-\tfrac{1}{2}, \tfrac{1}{2}, 8t^{*2})e^{-8t^{*2}}. \quad \text{(A14)}$$

Note that $F_l(t)$ as given by (A10) have the properties given in Eq. (8).

APPENDIX B

An expression for $F_l(t)$ for symmetric molecules can also be obtained by following the method described in Appendix A. The mathematics is more complicated because the energy levels now depend on the projection quantum number K. For this reason we restrict our derivation only to $F_1(t)$.

The QM correlation function $f_l(t)$ can be written

$$f_l(t) = \sum_{JK}(2J+1)P_{JK}(T) \times \sum_{J'K'}{}' e^{i(E_{JK}-E_{J'K'})t}\frac{(l-|K-K'|)!}{(l+|K-K'|)!} \times |P_l^{K-K'}(\cos\phi)|^2\begin{bmatrix} J & l & J' \\ K & K'-K & K' \end{bmatrix}^2, \quad \text{(B1)}$$

where the prime over the summation indicates that J' runs from $|J-l|$ to $J+l$ and ϕ is the angle made by the rotating vector with the symmetry axis. In the classical limit ($B \ll T$), $P_{JK}(T)$ takes the following form:

$$P_{JK}(T) = (c/8\pi)^{1/2}(IT)^{-3/2}e^{-(1/2IT)J^2-(c/2IT)K^2}, \quad \text{(B2)}$$

where $c = (I_z - I)/I_z$. We will make use of the fact that a large contribution to $f_l(t)$ comes from large J [because of the factor $(2J+1)$] but small K values. The nine Clebsch-Gordan coefficients occurring in $f_1(t)$ will be replaced by their asymptotic values. For example,

$$\begin{bmatrix} J & 1 & J \\ K & 0 & K \end{bmatrix}^2 = 0, \quad \begin{bmatrix} J & 1 & J \\ K & 1 & K+1 \end{bmatrix}^2 = \begin{bmatrix} J & 1 & J \\ K & -1 & K-1 \end{bmatrix}^2 = \begin{bmatrix} J & 1 & J+1 \\ K & 0 & K \end{bmatrix}^2 = \begin{bmatrix} J & 1 & J-1 \\ K & 0 & K \end{bmatrix}^2 = \tfrac{1}{2}$$

and

$$\begin{bmatrix} J & 1 & J+1 \\ K & 1 & K+1 \end{bmatrix}^2 = \begin{bmatrix} J & 1 & J+1 \\ K & -1 & K-1 \end{bmatrix}^2 = \begin{bmatrix} J & 1 & J-1 \\ K & 1 & K+1 \end{bmatrix}^2 = \begin{bmatrix} J & 1 & J-1 \\ K & -1 & K-1 \end{bmatrix}^2 = \tfrac{1}{4}. \quad \text{(B3)}$$

Combining Eqs. (A3), (B1), and (B3), we have

$$\mathcal{S}_1(\omega) = \sum_{JK}(2J+1)P_{JK}(T) \times \Bigg(\tfrac{1}{4}\sin^2\phi\bigg\{\Big[\delta\Big(\omega - \frac{c}{I}K\Big) + \delta\Big(\omega + \frac{c}{I}K\Big)\Big] + \frac{1}{2}\Big[\delta\Big(\omega - \frac{J}{I} - \frac{c}{I}K\Big) + \delta\Big(\omega + \frac{J}{I} + \frac{c}{I}K\Big)\Big] + \frac{1}{2}\Big[\delta\Big(\omega - \frac{J}{I} + \frac{c}{I}K\Big) + \delta\Big(\omega + \frac{J}{I} - \frac{c}{I}K\Big)\Big]\bigg\} + \tfrac{1}{2}\cos^2\phi\Big[\delta\Big(\omega - \frac{J}{I}\Big) + \delta\Big(\omega + \frac{J}{I}\Big)\Big]\Bigg). \quad \text{(B4)}$$

An expression for $S(\boldsymbol{\kappa},\omega)$ can be obtained by substituting (B4) into (A2) and combining it with (A1). The result is a sum over l with each term involving a sum over J and K. The latter sums are next replaced by integrals; after some manipulation, the classical limit of $\mathcal{S}_1(\omega)$ is obtained as

$$S_1(\omega) = (I/2T)\cos^2\phi|\omega|p_1(\omega) + \sin^2\phi[c_1p_1(\omega) + c_2p_2(\omega)], \quad \text{(B5)}$$

where

$$\begin{aligned} p_1(\omega) &= e^{-I\omega^2/2T}, \\ p_2(\omega) &= |\omega|e^{-I\omega^2/2T(1+c)}\Phi(c_3\omega), \\ \Phi(x) &= \frac{2}{\sqrt{\pi}}\int_0^x e^{-t^2}dt, \\ c_1 &= \tfrac{1}{4}(2I/\pi cT)^{1/2}(1+c/1+c), \\ c_2 &= \tfrac{1}{4}(I/T)(1+c)^{-3/2}, \\ c_3 &= [I/2Tc(1+c)]^{1/2}. \end{aligned} \quad \text{(B6)}$$

Now, $F_1(t)$ is obtained by a Fourier transform of $S_1(\omega)$. We find

$$F_1(t) = g(t)\cos^2\phi + \tfrac{1}{2}\sin^2\phi e^{-c(T/I)t^2/2}[1 + g(t)], \quad \text{(B7)}$$

where $g(t)$ is the classical correlation function for a linear molecule and is given by Eq. (A11).