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Use of the memory function to predict microwave/far i.r. rotational bandshapes

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Abstract—The Mori continued fraction representation of the memory function is used to predict the bandshape of rotational type absorptions in the microwave and far i.r. (0.1–250 cm^{-1}) for *t*-butyl chloride (rotator phase I) at 238 K and for 2 chloro 2 nitropropane (liquid) at 293 K. These curves are fitted to the experimental data of LASSIER *et al.* [15] and of CLEMMETT *et al.* [16] and HAFFMANNS *et al.* [17] over a total of three decades of frequency. The theoretical and experimental curves superimpose satisfactorily, in contrast to a model of librational motion based on the hard-core *m*-diffusion mechanism which corresponds to a truncation of the Mori series one level before the one used here.

INTRODUCTION

The memory function [1] representation of time-auto-correlation functions [2] is proving useful [3] in inter-relating experimental data and theories of molecular motion and interaction in the condensed state. In particular, the Mori continued fraction representation [4] of the memory function, truncated at convenient levels, can generate spectral functions which are directly comparable with experimental data. Such data is available from, for example, microwave and far i.r. absorption [5], depolarized Rayleigh scattering [6], NMR spin-rotation relaxation [7], isotope mass-diffusion etc., and can be cast into the form of time correlation-functions using the fluctuation-dissipation theorem [8] of non-equilibrium statistical mechanics.

This note intends to show how the autocorrelation function $\langle u(o) \cdot u(t) \rangle$, where u is a unit vector fixed in the molecular frame (usually along the dipole moment, if this exists), available [5] from microwave and far i.r. (0.1–200 cm^{-1}) absorption measurements [9], can be usefully approximated by particular truncations of the Mori series. The resulting spectral intensity, expressed as $\alpha(w)$, where w is the angular frequency (rad s^{-1}) and α the power absorption coefficient per unit path length of absorber (neper cm^{-1}) is compared with experimental data over three and more decades of frequency for $(CH_3)_3CCl$ in the rotator phase [10] at 238 K, and for 2 chloro 2 nitropropane in the liquid phase at 293 K.

These two compounds are chosen because of the following reasons.

(i) The translational contribution [11] to $\langle u(o) \cdot u(t) \rangle$ is eliminated in the rotator phase of $(CH_3)_3CCl$ so that the molecular motion can be described in terms of a modified rotational Langevin type equation [1, 5, 8]. Any induced absorption [9, 11, 12] caused by the electrostatic fields of neighbouring molecules will be minimized by their symmetric arrangement [11] with respect to a given central molecule.

(ii) Induced dipolar absorption [12–14] will be present in the spectrum of liquid 2 chloro 2 nitropropane in the region 0.1–250 cm^{-1}, but will be negligible compared with the intense permanent dipolar absorption of this molecule. A pure translational mode will be present but again of the order of magnitude in intensity of the induced absorption [11], so that this strongly dipolar, rigid, pseudo-spherical molecule is well-suited for comparison with a model of rotational type molecular motion of the permanent dipole.

(iii) Good microwave [15, 16] and acceptable far i.r. data are available over most of the frequency range of interest.

(iv) These spectra have been compared [17] previously with bandshapes predicted by a model of molecular torsional oscillation [18] based on the well-known M-diffusion model [2, 5, 7] of the motion of vibrators interrupted by collisions taking place at random times which randomize the molecular angular momentum in direction but not in magnitude. It will be shown below that this model corresponds to a truncation of the Mori series one level below the one used in the present paper, which describes the experimental data more accurately.

THEORY

The fluctuation–dissipation theorem of linear response theory [1] relates the energy dissipated by a system when it is exposed to an external field to a time correlation function which describes the detailed way in which spontaneous fluctuations regress in the equilibrium state. Quite generally, it is possible to use projection operators to show that any autocorrelation function $C(t)$ can be written as:

$$\frac{\partial}{\partial t} C(t) = -\int_0^t K(t-\tau)C(\tau)\,d\tau \tag{1}$$

where K is a response function which is even in time (as is the equilibrium property $C(t)$), and whose Fourier transform is a frequency dependent Langevin type [8] "friction coefficient." In the simple case where K has no memory of past events, i.e. is given by $\gamma\delta(t)$ where $\delta(t)$ is a delta function, then the correlation function is a simple exponential, $\exp(-\gamma t)$, i.e., is not even and is always positive. Therefore K must be time dependent in general, and is by causality known as the memory function. The experimental autocorrelation function is observed [5, 6, 12] to be even at short times (zero slope as $t \to 0$) and pseudo-exponential at long times, so that the theoretical K must behave accordingly.

The Mori theorem [4, 1] allows one to write K as:

$$\frac{\partial}{\partial t}(K_{n-1}(t)) = -\int_0^t K_n(t-\tau)K_{n-1}(\tau)\,d\tau \tag{2}$$

with $n = o, \ldots, N$, and where $K_{-1}(t) = C(t)$. Taking Laplace transforms of Equations (2) gives:

$$C(p) = \frac{C(o)}{p + K_0(p)} = \frac{C(o)}{p + \dfrac{K_0(o)}{p + K_1(p)}} = \ldots\ldots(3)$$

with $C(o) = 1$ by definition. This is a continued fraction representation of the Laplace transform of $C(t)$. It is straightforward to show that the equilibrium averages $K_o(o), \ldots, K_n(o)$ are related to the coefficients a_n in the expansion:

$$C(t) = \sum_{n=0} a_n \frac{t^{2n}}{(2n)!}, \tag{4}$$

so that, for example,

$$K_0(o) = -a_1; \quad K_1(o) = a_1 - \frac{a_2}{a_1}.$$

It is a useful property of Equations (3) that a general complex spectral intensity $\tilde{C}(-iw)$ can be defined as being the Fourier/Laplace transform of $C(p)$, and may be obtained by replacing p by $-iw$ in Equations (3). Thus, with the memoryless $K_o(p)$ a simple constant, the real part (absorption) of $\tilde{C}(-iw)$ is a Lorentzian, (and $C(t)$ an exponential).

As an illustration of the physical significance of the series of Equations (3) it is instructive to consider the truncation:

$$K_0(t) = K_0(o)\exp(-\gamma_0 t), \tag{5}$$

so that:

$$K_0(p) = \frac{K_0(o)}{(p + \gamma_0)},$$

and

$$C(p) = \frac{p + \gamma_0}{p^2 + p\gamma_0 + K_0(o)} \tag{6}$$

The absorption coefficient is given as [19]:

$$\alpha(w) \propto w^2\,\text{Real}\,[\tilde{C}(-iw)] = \frac{w^2\gamma_0 K_0(o)}{[K_0(o) - w^2]^2 + w^2\gamma_0^2} \tag{7}$$

which is asymptotic as w^{-2} at high frequencies, in contrast with $\alpha(w)$ derived from a memoryless $K_o(t)$, which is asymptotic as w^o, i.e., does not predict the observed [9] return to spectral transparency which takes place typically at *ca.* 100–300 cm^{-1} in rotator and liquid phases of dipolar molecules (see Figs. 1 and 3).

Inverting Equation (6) gives the autocorrelation function $C(t)$ as:

$$\begin{aligned} C(t) &= \exp(-\gamma_0 t)[\cos([K_0(o) - \gamma_0^2/4]^{1/2} t) \\ &\quad k_0(o) + \frac{\gamma_0}{2}\left[-\frac{\gamma_0^2}{4}\right]^{-1/2} \sin\left(\left[K_0(o) - \frac{\gamma_0^2}{4}\right]^{1/2} t\right)\Bigg] \\ &\quad \text{for } K_0(o) > \gamma_0^2/4 \\ &= \exp(-\gamma_0 t)[1 + \gamma_0 t/4] \quad \text{for} \quad K_0(o) = \gamma_0^2/4 \\ &= \exp(-\gamma_0 t)[\cosh([\gamma_0^2/4 - K_0(o)]^{1/2} t) \\ &\quad + \frac{\gamma_0}{2}\left[\frac{\gamma_0^2}{4} - K_0(o)\right]^{-1/2} \sinh\left(\left[\frac{\gamma_0^2}{4} - K_0(o)\right]^{1/2} t\right) \\ &\quad \text{for } K_0(o) < \gamma_0^2/4 \end{aligned} \tag{8}$$

whose Maclaurin time expansion is even up to t^2, but has a term in t^3. Its physical significance is clear because it is the time autocorrelation function derivable from solving the Langevin type equation [8] of a vibrator of natural frequency w_o randomly perturbed by collisions separated by a mean interval τ_c

$$\ddot{\mathbf{x}} + \dot{\mathbf{x}}/\tau_c + w_0^2\mathbf{x} = \mathbf{A}(t) \tag{9}$$

Here, $\dot{\mathbf{x}}$ has the units of angular velocity, and $\langle \mathbf{x}(o) \cdot \mathbf{x}(t)\rangle / \langle \mathbf{x}^2(o)\rangle$ is given by Equation (8) with γ_o replaced by $1/\tau_c$ and $K_o(o)$ by w_o^2. $\mathbf{A}(t)$ is a stochastic torque per unit mass, uncorrelated with $\mathbf{x}$, so that:

$$\langle \mathbf{A}(t)\rangle = 0; \quad \langle \mathbf{A}(o) \cdot \mathbf{x}(t)\rangle = 0.$$

The situation is identical with that where hard-core collisions between molecules are envisaged to take place at random times so that the molecular angular velocity vector is randomized in direction. Its macroscopic value is then the root mean square, w_o. Therefore the M diffusion model envisages the case where $K(t)$ is a single exponential, given at $t=0$ by $K_0(o) = w_0{}^2 = 2kT/I_B$ for a linear molecule or a symmetric top. Bliot *et al.* [20] have demonstrated that if the collisions were to randomize the angular velocity in both direction and magnitude, the J-diffusion model, then:

$$K(t) = K_{FR}(t)\exp(-\gamma_0|t|)$$

would be the equivalent response function, with $K_{FR}(t)$ that corresponding to a Gaussian distribution of freely rotating molecules.

The hard-core M diffusion model was extended by Brot *et al.* [18] and by Larkin *et al.* [17] to describe librational reorientation in energy wells of rotator phases and liquids where the duration of the local structure lasts longer than the mean waiting time for a reorientation of the reference molecule. The contact with the thermal bath is now provided by both weak collisions, which change only the librational state in the well, and by strong ones which induce a change of wells. The theoretical $\alpha(w)$ of this model has been compared with experimental data by Larkin *et al.* [17], and the behaviour of the related correlation function has been investigated by Evans [21] for about thirty molecules.

As would be expected from a model involving instantaneous reorientations of angular velocity, the correlation function is badly behaved at short times, and the spectral intensity distribution at high frequencies is such that transparency is regained too slowly (the w^{-2} dependence of Equation (7)). Equation (5), and the $C(t)$ of Equation (8) do not take account of any coefficient in Equation (4) other than a_1, which Gordon [22] has shown to be a *single* molecule property ($a_1 = -2kT/I_B$). The first term specific to molecular interaction is a_2, which for a vectorial time autocorrelation function derived from a rotational type i.r./microwave band is given for a linear molecule by [22]:

$$a_2 = \frac{1}{3}\left(\frac{kT}{I}\right)^2 + \frac{1}{24I^2}\langle o^2(V)\rangle$$

where $\langle o^2(V)\rangle$ is the intermolecular mean square torque. This term becomes instantaneously infinite in any hard-core model of molecular interaction. Therefore any analytical expression for $C(t)$ (and thus for $\tilde{C}(-iw)$) that invokes a well-defined $\langle o^2(V)\rangle$ with no singularities must be derived from a truncation of the series of Equations (3) inclusive of the equilibrium average $K_1(o)$. This can be achieved [3] with the approximation:

$$K_1(t) = K_1(o)\exp(-\gamma_1 t) \qquad (10)$$

so that the *overall* response function K of Equation (1) is given by:

$$K(t) = K(o)f(t)$$

where $f(t)$ is defined by Equation (8) with $K_0(o)$ replaced by $K_1(o)$, and γ_0 by γ_1. Therefore the function K is even up to t^2, and $C(t)$ therefore up to t^4. To extract the physical implication of Equation (10) it is useful to see that the overall K is exactly the same in form as the $C(t)$ of the m-diffusion model. By Kubo's second fluctuation–dissipation theorem [23]:

$$K(t) \propto \langle \mathbf{F}(o)\cdot\mathbf{F}(t)\rangle \qquad (11)$$

i.e., K is the correlation over time of the Langevin type of random force $\mathbf{F}(t)$ exerted on a Brownian particle by its surroundings. If this fluctuates so rapidly that the particle experiences only a steady, overall frictional retardation, then K is a delta function. The Debye model of dielectric relaxation, which invokes this concept, works well at low frequencies, but absorptions in the far i.r. of the Brownian particle (or molecule) fluctuating as rapidly as the neighbouring ones which make up $\mathbf{F}(t)$ have to be described by a finite K, dependent on past time and past events.

So a M-diffusion type memory function (or force-correlation) implies that the derivative of the related angular acceleration is randomized in direction by events separated by a correlation time $\gamma_1{}^{-1}$, in a way exactly analagous to that where the derivative of position (the angular velocity) is randomized in direction by events separated by the critical time τ_c of M-diffusion.

Using Equations (3) and (10), we have:

$$\alpha(w) \propto \frac{w^2K_0(o)K_1(o)\gamma_1}{\gamma_1{}^2(K_0(o)-w^2)^2 + w^2(w^2-(K_0(o)+K_1(o)))^2}, \qquad (12)$$

the correlation function being now of the form:

$$C(t) = (\Gamma_0\cos\beta t + \Gamma_1\sin\beta t)\times\exp(-\alpha_1 t) + \Gamma_2\exp(-\alpha_2 t)$$

where Γ_0, Γ_1, Γ_2, α_1, α_2 and β are functions of $K_0(o)$, $K_1(o)$ and γ_1 such that $C(t)$ is even up to t^4 in its Maclaurin expansion. The proportionality constant in Equation (12) is given [19] by $\Lambda(\epsilon_0 - \epsilon_\infty)/n(w)c$, where $n(w)$ is the refractive index. The problem of the internal field [9] correction (Λ) has been discussed by many authors in the past [19, 24–28], but a recent study [29] leads to the conclusion that such an involved correction might be often overestimated in importance. Certainly in the far i.r. it is almost bandshape independent, and can be roughly approximated by the POLO/WILSON factor [30] of $\Lambda = 9n_D^2/(n_D^2+2)^2$, where n_D is the D line refractive index.

DISCUSSION

In applying Equation (12) to the experimental data, the coefficients $K_1(o)$ and γ_1 are regarded as phenomenological with $K_0(o)$ fixed at $2kT/I_B$. The data is then fitted by minimization of squared deviations from the analytical curve $\alpha(w)$, or for microwave regions, $\epsilon''(w)$ (the loss factor, given by $\epsilon'' = n(w)\alpha/w$). The theoretical microwave absorption was generated from the far i.r. analysis. The results are illustrated in Figs. 1–4, and the parameters used are listed in Table 1.

At low frequencies (where w^4 is negligible compared with w^2) Equation (12) reduces to a Debye type loss curve ($\epsilon''(w) \propto w/(A+Bw^2)$) as is seen in Figs. 2 and 4. In the far i.r., the overall absorption is reproduced satisfactorily (Figs. 1 and 3), the predicted return to transparency being much more rapid ($\alpha(w) \rightarrow w^{-4}$) than that of the extended M diffusion mechanism of BROT [18] and LARKIN [17, 21]. The fit is arguably better for $(CH_3)_3CCl$ in the rotator phase than for the liquid phase of 2 chloro 2 nitropropane, although the theoretical band is always inside the far i.r. experimental uncertainty for both cases. The torque term $K_1(o)$ is fractionally lower for $(CH_3)_3CCl$ in the rotator phase, which may be a reflection of the increased intra-molecular and inter-molecular symmetry of this compound. More and better quality data are needed, especially in the interesting region from

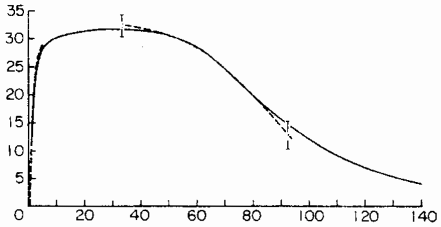

Fig. 1. Far i.r. absorption of $(CH_3)_3CCl$ (rotator I) at 238 K. --I-- Experimental [15] with uncertainty limits. — Equation (12). Ordinate: $\alpha(w)$/neper cm^{-1}; abscissa: $\bar{\nu}$/cm^{-1}.

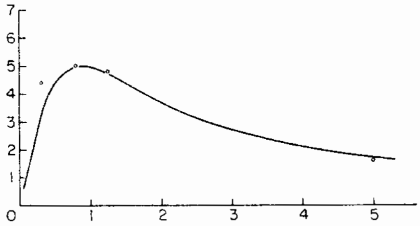

Fig. 2. Microwave absorption of $(CH_3)_3CCl$ at 238 K. ○ Experimental [15], (klystrons at 32.5, 12.5, 8 and 2 mm). — Equation (12), function as predicted from the far i.r. fitting. Ordinate: $\epsilon''(w)$; absicissa: $\bar{\nu}$/cm^{-1}.

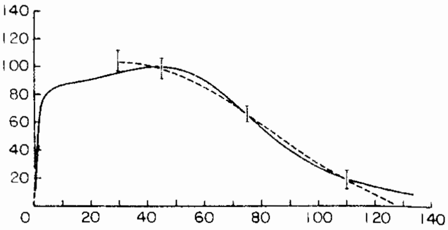

Fig. 3. Far i.r. absorption of 2 chloro 2 nitropropane (liquid) at 293 K. --I-- Experimental, [10, 17] with uncertainty limits. — Equation (12). Ordinate: $\alpha(w)$/neper cm^{-1}; abscissa: $\bar{\nu}$/cm^{-1}.

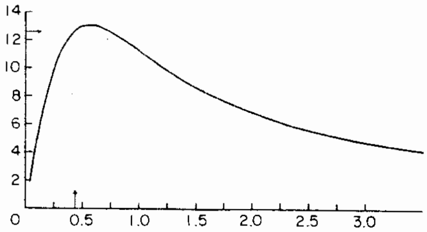

Fig. 4. Microwave curve predicted from the far i.r. fitting of Fig. 3. Ordinate: $\epsilon''(w)$; abscissa: $\bar{\nu}$/cm^{-1}. The arrows show the positions of the observed [10, 17] maximum loss and microwave critical frequency.

Table 1. Parameters of Equation (12) used in the curve fitting

Molecule	Phase	T/K	$\left[\frac{I_B}{2kT}\right]^{1/2v}$	$\frac{I_B}{2kT} \cdot K_1(o)$	$10^{40} I_B$ /g cm^2
t butyl chloride	Rotator(I)	238	13.8	103.5	269
2 chloro 2 nitro-propane	Liquid	293	12.2	115.6	494

2–15 cm^{-1} and over an extended range of temperature and/or pressure before the usefulness of Equation (12) may be fully ascertained. Nevertheless, this is an encouraging start.

APPENDIX

Since $K_1(t)$ is an even, equilibrium function of time, the truncation in Equation (10) is not satisfactory, although the predicted $C(t)$ is even up to t^4, and the spectral function calculated therefrom lies close to the experimental. The form:

$$K_1(t) = K_1(o)\exp[1-(1+(t/\tau)^2)^{1/2}]$$

first used by Birnbaum and Cohen [31], is even in time and well defined at $t = o$.

The corresponding spectral function is:

$$\alpha(w) \propto \tau e Z^3 K_1(Z) K_1(o) K_o(0) w^2/D(w)$$

where

$$D(w) = [Z^2(K_0(o) - w^2) + w^2\tau^2 K_1(o) \times (1+\psi(w))]^2 + [K_1(o) w\tau e Z K_1(Z)]^2$$

where $Z = (1+w^2\tau^2)^{1/2}$; $K_1(Z)$ is a modified [32] Bessel function (first order) of the second kind; and:

$$\psi(w) = e\int_0^1 \exp(-(1+\mathrm{w}^2\tau^2(1-\eta^2))^{1/2})\,\mathrm{d}\eta.$$

This is a function that fulfills the requirement that $K_1(t)$ be even, and which also has the advantage of including the torque term $K_1(o)$, so that a measure of intermolecular effect is attainable. It reduces to the Debye type:

$$\alpha(w) \propto \frac{w^2\tau e K_1(Z) K_1(o) K_0(o)}{K_0{}^2(o) + w^2[\tau^2(2K_1(o)K_0(o)(1+\psi) - K_1{}^2(o)e^2K_1{}^2(Z)) - 2K_0(o)]}$$

at microwave frequencies.

REFERENCES

[1] B. J. Berne and G. D. Harp, *Advances in Chemical Physics*, Vol. XVII, p. 63, (Eds. I. Prigogine and S. A. Rice) Wiley-Interscience; B. J. Berne, *Physical Chemistry—an advanced treatise*, Vol. VIIIB, (Liquid state), Chapt 9, (Eds. H. Eyring, D. Henderson and W. Jost), Academic Press, N.Y., London.

[2] R. G. Gordon, *Advan. Mag. Resonance*, **3,** 1 (1968).

[3] B. Quentrec and P. Bezot, *Molec. Phys.*, **27,** 879 (1974).

[4] H. Mori, *Progr. Theoret. Phys.*, **33** 423 (1965).

[5] C. Brot, *Dielectric and Related Molecular Processes*, Vol. II, p. 1, Chem. Soc. Specialist Per. Rep., (senior reporter—Mansel Davies) (1975).

[6] J. F. Dill, T. A. Litovitz, and J. A. Bucaro, *J. Chem. Phys.*, **62,** 3839 (1975).

[7] N. Boden, *Nuclear Magnetic Resonance*, Vol. I, p. 115, Chem. Soc. Specialist Per. Rep., (senior reporter—R. K. Harris) (1972) J. Jonas, J. Dezwaan and J. H. Campbell, in *Molecular Motions in Liquids*, (Ed. J. Lascombe) pp. 359–369 Reidel, Dordrecht, 1974.

[8] G. Wyllie, *Dielectric and Related Molecular Processes*, Vol. I, p. 21, Chem. Soc. Specialist Per. Rep., (senior reporter—Mansel Davies) (1973).

[9] M. Davies, *Rept. Chem. Soc.*, **71,** 69 (1971); N. E. Hill, A. H. Price, W. E. Vaughan, and M. Davies, *Dielectric Properties and Molecular Behaviour*, van Nostrand, London, 1969.

[10] I. W. Larkin, *Faraday Symp.*, **6,** 112 (1972).

[11] W. Ho, G. Birnbaum and A. Rosenberg, *J. Chem. Phys.*, **55,** 1028 (1971).

[12] G. J. Davies and M. Evans, *J. Chem. Soc. Faraday II*, **71,** 1275 (1975); G. J. Davies, J. Chamberlain and M. Davies, *J. Chem. Soc. Faraday II*, **69,** 1223 (1973); G. J. Davies and J. Chamberlain, *J. Chem. Soc. Faraday II*, **69,** 1739 (1973).

[13] M. Evans, *Molec. Phys.*, **29,** 1345 (1975); *J. Chem. Soc. Faraday II*, **71,** 71 (1975).

[14] A. I. Baise, *J. Chem. Soc. Faraday II*, **68,** 1904 (1972).

[15] B. Lassier and C. Brot, *J. Chim. Physique*, **48,** 39 (1969).

[16] C. Clemmett and M. Davies, *Trans. Faraday Soc.*, **58,** 1705 (1962).

[17] R. Haffmanns and I. W. Larkin, *J. Chem. Soc. Faraday II*, **68,** 1729 (1972); I. W. Larkin, *J. Chem. Soc. Faraday II*, **69,** 1278 (1973); **70,** 1457 (1974).

[18] C. Brot *J. Phys. Rad.*, **28,** 789 (1967); B. Lassier and C. Brot, *Chem. Phys. Lett.* **1,** 581 (1968); *Disc. Faraday Soc.*, **48,** 39 (1969).

[19] R. H. Cole, *J. Chem. Phys.*, **42,** 637 (1965).

[20] F. Bliot and E. Constant, *Chem. Phys. Lett.* **29,** 618 (1974); **18,** 253 (1973); F. Bliot, C. Abbar and E. Constant, *Molec. Phys.*, **24,** 241 (1972).

[21] M. Evans, *J. Chem. Soc. Faraday II*, **71,** 1255 (1975).

[22] R. G. Gordon, *J. Chem. Phys.*, **43,** 1307 (1965); **44,** 1830 (1966); **38,** 1724 (1963).

[23] R. Kubo, *Lectures in Theoretical Physics, Vol. I*, p. 120, Interscience N.Y.; *Statistical Mechanics of Equilibrium and non-Equilibrium*, North Holland., Amsterdam.

[24] P. Debye, *Polar Molecules*, Chapt V, Dover, N.Y., 1929.

[25] J. L. Rivail, *J. Chim. Phys.*, **66,** 981 (1969).

[26] D. D. Klug, D. E. Kranbuehl and W. E. Vaughan, *J. Chem. Phys.*, **50,** 3904 (1969).

[27] T. W. Nee and R. Zwanzig, *J. Chem. Phys.*, **52,** 6353 (1970).

[28] M. Titulaer and J. M. Deutch, *J. Chem. Phys.*, **60,** 1502 (1974).

[29] J. L. Greffe, J. Goulon, J. Brondeau, and J. L. Rivail, *Molecular Motions in Liquids* (Ed. J. Lascombe) p. 151, Reidel, Dordrecht, 1973.

[30] S. R. Polo and M. K. Wilson, *J. Chem. Phys.*, **23,** 2376 (1955).

[31] G. Birnbaum and E. R. Cohen, *J. Chem. Phys.*, **53,** 2885 (1970).

[32] A. Erdelyi, W. Magnus, F. Oberhettinger and F. G. Triconi, *Tables of Integral Transforms* Vol. 1, p. 16, No. 26 McGraw-Hill, N.Y., 1954.