BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 39 2385—2395 (1966)

Non-Debye Reorientation Processes of Molecules. Correlation Functions and Spectral Densities for Spherical Molecules

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(Received May 16, 1966)

The non-Debye reorientation processes in which the Debye equation is inapplicable are studied for spherical molecules by using an equation proposed by the author. The physical meaning of the angular correlation in the non-Debye processes is discussed in detail. It is shown that in the non-Debye processes the non-dissipative decay of the mutual-phase correlation of rotating molecules must be taken into account, in addition to the dissipative decay due to molecular collisions, and that the use of the "microscopic viscosity" in the Debye equation is not plausible. It is also shown that, in contrast to the Debye processes, there is no one-to-one correspondence between the correlation time for molecular reorienation and the mean life time of the rotation, since the contribution from the nondissipative decay should be considered also. The vector and the tensor correlation functions,

$$\langle \cos\theta(0)\cos\theta(t)\rangle \quad \text{and} \quad \langle (1/2)\{3\cos^2\theta(0)-1\}\{(1/2)3\cos^2\theta(t)-1\}\rangle,$$

and the corresponding spectral densities, the band shapes of infrared and Raman spectra respectively, are obtained theoretically for various conditions and are shown graphically. As illustravtie examples of the treatment, methane and deutero methane molecules are studied. Vector correlation functions are obtained from the observed band shapes of the infrared spectra of these molecules. Comparing the theoretical correlation functions with experimental ones, it is shown that a reasonable agreement between theory and experiment is obtained and that methane molecules have a typical non-Debye reorientation process even below the freezing point. Some characteristic features of the non-Debye process are also discussed.

The observed correlation times for the reorientation of molecules are, in general, shorter than those derived from Debye's theory of the reorientation of spherical particles in liquids.(1) In particular, for light molecules such as substituted benzenes or some of the lower ethers or alcohols, the observed correlation times, τ_1 and τ_2, for the vector and the tensor correlation function:

$$\Phi_1(t) = N_1\langle \cos\theta(0)\cos\theta(t)\rangle \tag{1}$$

and

$$\Phi_2(t) = N_2\langle \frac{1}{2}\{3\cos^2\theta\,(0)-1\}\frac{1}{2}\{3\cos^2\theta(t)-1\}\rangle \tag{2}$$

are shorter by a factor of 10—100.(2,3) In these

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1) P. Debye, "Polar Molecules," Chemical Catalog Company, New York (1929).

2) K. Higasi, "Dipole, Molecule and Chemistry," Research Institute of Applied Electricity, Hokkaido University, Sapporo (1965).

3) W. B. Moniz and H. S. Gutowsky, *J. Chem. Phys.*, **38**, 1155 (1963).

equations, for instance in (1), $\langle\ \rangle$ refers to the average of the products, $\cos\theta$ at $t=0$ times $\cos\theta$ at $t=t$, over the ensemble, where θ is the angle between a vector fixed on a molecule and the z-axis of a space-fixed laboratory frame. N_1 is a normalization constant which makes $\Phi_1(0)$ unity.

The serious disagreement between the theoretical and the experimental correlation times may be attributed to the use of the macroscopic viscosity, η, in the Debye equation:[1,4]

$$\tau_j = \frac{4\pi\eta a^3}{3\boldsymbol{k}T}(1+\delta_{1j}) \tag{3}$$

In this equation, a refers to the radius of the molecule; $\delta_{1j}=1$ for $j=1$ and is otherwise zero. Since no medium is continuous or homogeneous on the molecular scale, the effective viscosity for molecular reorientation, the microscopic viscosity, must be, in general, different from the macroscopic one. However, the use of the microscopic viscosity in (3) may not be a sufficient improvement on Debye's theory. As is shown below, the disagreement arises from the basic inapplicability of Debye's scheme to the substances mentioned above.

The Debye equation is derived on the assumption that random reorientations of molecules can be described in terms of a diffusion equation.[1,4] Therefore, a molecular reorientation with a finite and large angle is assumed to appear as a result of many rotations which occur successively in time.[4] This situation may be compared with the translational diffusion of molecules in a three-dimensional space, where a molecule moves step by step, at random and in all directions.[5] The assumption of a continuous medium is consistent with the basic concept of the diffusion: the continuous liquid *constantly* exerts against a rotating molecule. This force leads to two important sequences through *constantly* exerts a resistive force against a rotating molecule. This force leads to two important sequences through the reduction of the angular velocity of the rotating molecule: (1) it reduces the magnitude of a step of the tiny rotation, and (2) fluctuating forces must be supplied constantly from the outside in order to keep the average rotational energy constant against the friction.

On the other hand, the discrete and inhomogeneous nature of the medium may not result in a diffusion process, at least not when the medium molecules move at random at a rate that is comparable with that of the rotation of the solute molecule. A fluctuation in the positions of the medium molecules may temporarily give the solute molecule a vacant space and allow it to rotate relatively freely as in the gas phase. Since the duration of such a "vacant" space is fairly close to the mean period of the rotation of the solute molecule, a step of a single rotation must be so large that the reorientation of the solute molecule cannot be related to a diffusion process. Moreover, the appearance of the nature of the "free" rotation in liquids clearly makes the correlation times very short.

The use of the Debye equation, which is equivalent to the assumption of the existence of a well-defined diffusion process in the liquid, is not appropriate in those many cases where we really use a microscopic viscosity instead of η in order to reduce the large disagreement between theory and experiment. We may call such fast reorientation processes "non-Debye processes."

A further step in the study of the random reorientation of molecules has been made in a paper by Gordon.[6] He showed that a tensor correlation function could be obtained from a Raman spectrum as the Fourier transform of the band-shape function whose structures are originally due to the rotation-vibration interaction. In other words, the band shape itself represents the spectral density of the random reorientation of a molecule. This idea was soon extended by Gordon[7] to the infrared case: vector correlation functions were obtained similarly from infrared spectra. He discussed briefly the form of the correlation functions corresponding to a non-Debye process. The correlation functions for CO and CH_4 molecules clearly showed that the reorientation processes for these molecules are non-Debye, even in solution.

A general theory of the random reorientation of molecules, including non-Debye processes, was proposed by Shimizu[8]; he also obtained vector and tensor correlation functions theoretically. Then, by using the theory of linear response,[9] it was shown that band-shape functions corresponding to various kinds of spectra, including infrared, Raman, and dielectric relaxation, could be obtained in terms of the Fourier transform of the theoretical correlation functions, and vice versa. The theory was found to be reasonable from a comparison with the correlation functions obtained experimentally from the infrared spectrum of *trans*-dichloroethylene.

In the present paper, the nature of the non-Debye reorientation of a spherical rotor will be discussed, using as a typical example the methane molecule. Graphical representations of the correlation functions and the corresponding spectral densities will

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[4] H. Frohlich, "Theory of Dielectrics" Clarendon Press, Oxford, (1958).

[5] S. Chandrasekhar, *Rev. Modern Phys.*, **15**, 1 (1943).

[6] R. G. Gordon, *J. Chem. Phys.*, **42**, 3658 (1965).

[7] R. G. Gordon, ibid., **43**, 1307 (1965).

[8] H. Shimizu, ibid., **43**, 2453 (1965). The terms "the Debye limit" and "the inertial limit" were used there. It was assumed that, in the Debye limit, the correlation function with the correlation time τ_j given by the Debye equation holds. In this paper "the Debye process" means the molecular reorientation process within the Debye limit.

[9] R. Kubo, *J. Phys. Soc. Japan*, **12**, 570 (1957).

be given from the theory. The relations between the band shapes of the infrared and Raman spectra and the random reorientation process of molecules will be automatically discussed in the present paper, since the spectral densities corresponding to a vector correlation function and tensor correlation function are equivalent to the band shape of infrared and Raman spectra respectively.(6-8) No effort will be made to discuss the accurate form of the correlation functions. Our principal aim is to show the properties of non-Debye processes in terms of simple physical concepts and straightforward mathematical expressions.

The Correlation Functions for Non-Debye Processes

Though the general form of the correlation functions for non-Debye reorientation processes have already been discussed,(8) the correlation functions for spherical rotors were only briefly given. Therefore, a detailed discussion of the form of the correlation functions and the spectral densities of spherical molecules will be given in this and the next section in order to illustrate the general features of non-Debye processes.

The correlation function for non-Debye processes, more accurately, for the inertial limit, may be approximately given by(8):

$$\Phi_j(t) = a_j(t)\Phi_j^{(0)}(t) + b_j(t)\Phi_j^{(p)}(t) \qquad (4)$$

$$\text{with } j = \begin{cases} 1 & \text{for the vector correlation function} \\ 2 & \text{for the tensor correlation function,} \end{cases}$$

where $\Phi_j^{(0)}(t)$ is the correlation function for "free" molecules. The perturbed correlation function, $\Phi_j^{(p)}(t)$, is related to the reorientation of the molecule under the perturbation due to the interaction with the neighboring molecules. We may assume that the perturbed correlation function has an exponential form when $t \gg \tau_f$.(8,10) Here the mean period of rotation, τ_f, is a function of the absolute temperature, T, and the moment of inertia, I, of the molecule:

$$\tau_f = (I/kT)^{1/2}$$

For example, we may assume(8,11):

$$\Phi_j^{(2)}(t) = \exp\left\{-\Delta_j^2\int_0^t \mathrm{d}t'(t-t')\exp(-|t|/\tau_{rj})\right\} \qquad (5)$$

as a first-order approximation, where τ_{rj} is the life time of the rotation. The modulation amplitude is a function of the magnitude of the fluctuation of the angular velocities of the rotating molecules, velocities arising from the perturbation from the neighboring molecules. Equation 5 corresponds an assumption that the fluctuation of the angular velocities is a Gaussian process.(10) A strong collision assumption leads to a simple form(8):

$$\Delta_1^2 = 3/\tau_f^2 \qquad (6)$$

The Δ_2^2 quantity was not discussed before. Hence, we will give it here. We may assume that a non-Debye process approaches a Debye process as $\tau_{rj}/\tau_f \rightarrow 0$, where, due to frequent collisions with the neighboring molecules, the (solute) molecules are allowed such small rotations as occur in rotational diffusion. Debye's theory gives:

$$\tau_1/\tau_2 = 3 \qquad (7)$$

On the other hand, the effective correlation time for $\Phi_j^{(2)}(t)$ is given by(8):

$$\tau_j' \cong (\Delta_j^2\tau_{rj})^{-1} \qquad (8)$$

Thus, naively assuming $\tau_{r1} = \tau_{r2}$, we obtain:

$$\Delta_2^2 = 9/\tau_f^2 \qquad (9)$$

from (6)—(8). The modulation amplitude, (6) or (9), was obtained by assuming that the magnitude of the angular momentum was changed at each collision.(8) If only the orientation of the angular momentum is changed by collisions, the correlation function, $\Phi_j^{(2)}(t)$, is improper. A detailed discussion of the correlation function will be presented in the near future. Qualitatively, the nature of the reorientation processes determines the magnitude of the modulation amplitude.

The simplest assumption as to the form of the adjusting functions will be taken as(8):

$$\left.\begin{aligned} b_j(t) &= 1 - \exp(-|t|/\tau_{bj}) \\ a_j(t) &= \exp(-|t|/\tau_{aj}) \end{aligned}\right\} \qquad (10)$$

The time constants, τ_{aj} and τ_{bj}, are roughly the lifetime of rotation.

By using a very simple assumption:

$$\tau_{rj} = \tau_{aj} = \tau_{bj} \equiv \tau_r$$

vector and tensor correlation functions were calculated by varying τ_r/τ_f. The results are shown graphically in Figs. 1 and 2, where the unit of the time scale is τ_f. The correlation functions are not exponential, unless τ_r/τ_f is much smaller than unity. For $\tau_r/\tau_f \gtrsim 1$, the nonexponential contribution of $\Phi_j^{(0)}(t)$ to $\Phi_j(t)$ is appreciable.

An Interpretation of the Form of Correlation Functions

We choose the local frame or the local coordinate system of each molecule in such a way that their

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10) R. Kubo, "Fluctuation, Relaxation, and Resonance in Magnetic System," Oliver and Boyd, Ltd., London (1962).

11) The use of (5) is correct only when the random process of ω-fluctuation is a Gaussian process. Therefore, the physical meaning of Eq. 4 with 5 is that all the molecules start to rotate in phase at $t=0$ and then, regarding the molecules which have had more than one collision since $t=0$, the initial memory of the phases of rotation is randomized. Therefore, after a collision the molecular reorientation process may be regarded as a Gaussian process with random phases. This process is given by (5).

origins are common with that of the laboratory frame. A local frame of a molecule coincides with the corresponding molecular frame at $t=0$, except for the origin. One can thus transform between the two frames by a pure translation. The Eulerian angles between a local frame and the laboratory frame may be written as $\Omega\equiv(\alpha, \theta(0), \gamma)$. By introducing Wigner's rotation matrix, $D_{mm'}^{(1)}(\Omega)$, of the first order, the direction cosines between the z-axes of the molecular and the laboratory frames may be written as:

$$\cos\Theta(t) = \sum D_{mo}^{(1)}(\alpha, \theta(0), \gamma) y_m(\Theta(t), \Psi(t)) \tag{11}$$

where $y_m(\Theta, \Psi)$ are the reduced spherical harmonics relating the spherical coordinates of the z-axis of the molecular frame as observed in the local frame;

$$\left.\begin{aligned} & y_1(\theta(t), \Psi(t)) \\ & \quad = -\frac{1}{\sqrt{2}} \sin\Theta(t) \exp\{i\Psi(t)\} \\ & y_0(\Theta(t), \Psi(t)) = \cos\Theta(t) \\ & y_{-1}(\Theta(t), \Psi(t)) \\ & \quad = \frac{1}{\sqrt{2}} \sin\Theta(t) \exp\{-i\Psi(t)\} \end{aligned}\right\} \tag{12}$$

From (11)—(12), with the assumption $\Theta(0)=\Psi(0)=0$;

$$\begin{aligned} \langle\cos\theta(0)\ \cos\theta(t)\rangle &= \langle\cos\theta(0)\cdot\cos\theta(0)\cos\Theta(t)\rangle \\ &\quad + \langle\cos\theta(0)\cdot\sin\theta(0)\sin\Theta(t)\cos(\Psi(t) \\ &\quad - \alpha(0))\rangle \qquad (13) \\ &= \langle\cos^2\theta(0)\rangle\langle\cos\Theta(t)\rangle \qquad (14) \end{aligned}$$

where the last expression is only when the system is spatially isotropic. In fact, for an isotropic system the statistical average of a physical quantity of an ensemble must be independent of the directions of the coordinate axis of the laboratory frame. From this it follows that the average over the fraction of the molecules, $f(\theta, \varphi)\sin\theta d\theta d\varphi$, is independent of θ and φ, provided that the magnitude of the solid angle, $\sin\theta d\theta d\varphi$, is properly chosen. The $f(\theta, \varphi)$ function is a normalized distribution function of the molecular axis (the z-axis of the molecular frame) in terms of the spherical coordinates defined with respect to the laboratory frame. The ensemble average is, in general, equivalent to the average over the molecules in an arbitrary fraction, $f(\theta, \varphi)\sin\theta d\theta d\varphi$. In Function 13, the averages of $\cos\Theta$ and $\sin\Theta$ are independent of $\theta(0)$. Hence, the functions of $\theta(0)$ and Θ may be averaged independently. Denoting the average over the molecules whose initial orientations are in a small solid angle, $d\Omega$, around $\theta(0)=0$ as $\langle\ \rangle_{\theta(0)=0}$, we may obtain:

$$\Phi_1(t) = \langle\cos\theta(t)\rangle_{\theta(0)=0} \tag{15}$$

since in an isotropic system it is clear that:

$$\begin{aligned} \langle\cos\theta(0)\cos\theta(t)\rangle_{\theta(0)=0} &= \langle\cos\theta(t)\rangle_{\theta(0)=0} \\ = \langle\cos\Theta(t)\rangle_{\theta(0)=0} &= \langle\cos\Theta(t)\rangle = \Phi_1(t) \end{aligned}$$

The definition of the correlation function, 15, was used in a previous paper[8] without explicit proof. The use of the new definition (15) instead of (1) has the great advantage that a correlation function may be discussed in terms of a simple model of molecular motion. For instance, it immediately turns out from (15) that the $\Phi_1(t)$, correlation function, is a periodic function of the time, when all the molecules rotate with a uniform frequency and phase. On the other hand, if the phases of the rotating molecules are random, the correlation function decays in a monotonic manner. The $\Phi_1^{(0)}(t)$ correlation function in Fig. 1 is interesting from this point of view, since it is a hybrid of these two extremes.

As an introductory example, the $\Phi_1^{(0)}(t)$ function for diatomic molecules will be discussed first and then the discussion will be extended to spherical molecules. Molecules whose initial orientations are not in the solid angle, $d\Omega$, around $\theta(0)=0$ will not be explicitly discussed. This does not, however, imply that we assume that all the molecules in the system have the same orientation at $t=0$. In the discussion below the word "molecules" in quotation marks refers to the molecules characterized by $\theta(0)=0$.

The correlation function may be given in terms of two different representations, the orientation representation by Debye and the angular momentum representation by Schwinger.[12] The latter representation was used in the discussion of the nuclear magnetic relaxation of hydrogen molecules in the gas phase. There the Hamiltonian

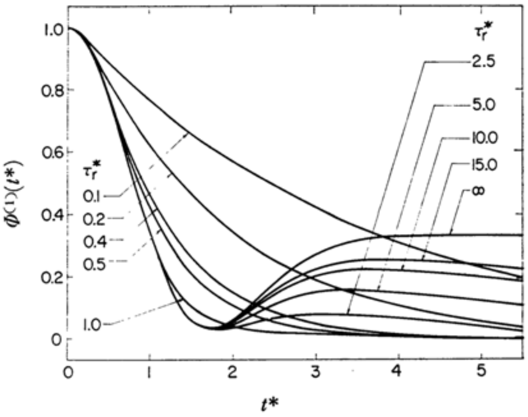

Fig. 1. The vector correlation functions for a spherical rotor obtained by using Eq. 4. The asterisks on t and τ_r indicate that these quantities are measured on the τ_f-scale. Note that $\Phi_1^{(0)}(t^*)=\Phi_1(t^*)$ for $\tau_r^*=\infty$.

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[12] Referred to in N. Bloembergen, E. M. Purcell and R. V. Pound, *Phys. Rev.*, **73**, 679 (1948). Schwinger's theory is cited in this paper.

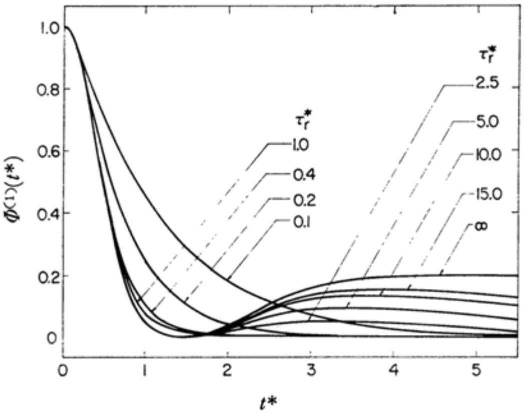

Fig. 2. The tensor correlation fractions, $\Phi_2(t^*)$, for a spherical rotor obtained by using Eq. 4. Note that $\Phi_2^{(0)}(t^*)=\Phi_2(t^*)$ for $\tau_r^*=\infty$.

for the magnetic dipolar coupling between two protons was given in terms of the angular momentum vector of the molecule by replacing the interatomic vector by the angular momentum vector using the Wigner-Eckart theorem.

The vector correlation function in the orientation representation may be given as:

$$\Phi_1^{(0)}(t) = \cos\omega_0 t \tag{16}$$

for the *free* "molecules" with a uniform frequency, ω_0, and a uniform phase. Since the "molecules" have two rotational degrees of freedom, they rotate around the uniformly-distributed axes in the *x*-*y* plane. The 16 function never decays, since the mutual phase correlations among the "molecules" are never randomized. In the angular momentum representation, the abovementioned correlation function should be a constant:

$$\Phi_{1\mathrm{J}}^{(0)}(t) = 1 \tag{17}$$

because the angular momenta of the "molecules" are never changed. In order to get a better image of the angular momentum representation, we will introduce a description of the molecular motion in terms of the rotating coordinate system; each "molecule" is observed from the corresponding rotating frame, where the axis of rotation is the same as that of the observed "molecule." Moreover, the angular frequency, ω_0, of the rotation of the frame is the same as that of the "molecule." Therefore, the "molecules" are fixed on the rotating frames, where the *z*-axes are chosen parallel to the μ vectors on the "molecules." We assume that the fraction of the "molecules" whose axes of rotation are in $\mathrm{d}\varphi$ around φ' can be observed from the same rotating frame, $S_\mathrm{R}(\omega_0;\ \theta,\ \varphi)=S_\mathrm{R}(\omega_0;\ \pi/2,\ \varphi')$. We choose the value of $\mathrm{d}\varphi$ so that the statistical behavior of the "molecules" in such a fraction is independent of φ. It is clear that the description of the motion of molecules in terms of the angular momentum representation is basically equivalent to that in the rotating frames, provided that ω_0 is proportional to the magnitude of angular momentum and provided that the direction specified by θ and φ is parallel to the direction of angular momentum. We thus obtain:

$$\Phi_{1\mathrm{R}}^{(0)}(t) = 1 \tag{18}$$

in a rotating frame, for instance, in $S_\mathrm{R}(\omega_0;\ \pi/2,0)$. For the "molecules" which are fixed in the laboratory frame, we obtain:

$$\left.\begin{aligned} \Phi_1(t) &= 1 \\ \Phi_{1\mathrm{J}}(t) &= \Phi_{1\mathrm{R}}(t) = \cos\omega_0 t \end{aligned}\right\} \tag{19}$$

The relationship between the two representations is not straightforward, as is shown above, if the "molecules" have nonuniform angular velocities. Even in such a case, however, the 17 correlation function is valid for the free "molecules." However, in a rotating frame, $S_\mathrm{R}(\omega_0:\ \pi/2,\ \varphi)$, the correlation function, $\Phi_{1\mathrm{R}}^{(0)}(t)$, is, in general, not so simple as in (18), because there are many "molecules" whose angular frequency is different from ω_0. In general, the "molecule" has the angular frequency of $\omega-\omega_0$ in $S_\mathrm{R}(\omega_0:\ \pi/2,\ \varphi)$. As a result, the "molecules" with $\omega>\omega_0$ and $\omega<\omega_0$ rotate in positive and negative directions respectively. Hence, the directions of the vectors $\boldsymbol{\mu}$ in S_R will gradually be randomized.

To treat this process more explicitly, we will consider a subensemble of the "molecules" whose rotation is to be described in $S_\mathrm{R}(\omega_0:\ \pi/2,\ 0)$. The distribution of ω may be given by the Boltzmann distribution, $\exp(-I\omega^2/2\boldsymbol{k}T)$. If ω_0 is defined by the equation:

$$\int_0^\infty \exp\left(-I\omega^2/2\boldsymbol{k}T\right)\sin\left(\omega-\omega_0\right)\mathrm{d}\omega=0 \tag{20}$$

or, more explicitly, by:

$$\omega_0(t) = \frac{1}{t}\tan^{-1}\left\{\frac{2}{\sqrt{\pi}}E_{rf}(t/\sqrt{2}\,\tau_f)\right\} \tag{21}$$

then the expectation value of the vector sum of each vectors, $\boldsymbol{\mu}$, over the subensemble in the rotating frame, $S_\mathrm{R}(\omega_0:\ \pi/2,0)$, is always parallel to the *z*-axis of $S_\mathrm{R}(\omega_0:\ \pi/2,0)$. The $\omega_0(t)$ frequency is roughly independent of the time:

$$\omega_0(0) = \frac{\tau_f}{\sqrt{2\pi}} \tag{22}$$

for small t values and gradually decreases with time. As has been mentioned before, the phase correlations among the vectors $\boldsymbol{\mu}$ in $S_\mathrm{R}(\omega_0:\ \pi/2,0)$ eventually vanish and the directions of the vectors are eventually randomized. Hence, the $\Phi_{1\mathrm{R}}^{(0)}(t)$ function, which is proportional to the *z*-component of a vector-sum, $\boldsymbol{p}$, of the vectors, $\boldsymbol{\mu}$, on each member of subensemble "molecules," decreases with time. It can be shown that:

$$\Phi_{1\mathrm{R}}^{(0)}(t)=\int_0^\infty \exp\left(-I\omega^2/2\boldsymbol{k}T\right)\cos\left(\omega-\omega_0\right)t\,\mathrm{d}\omega$$
$$=\frac{\sqrt{2}}{\tau_f}\mathrm{e}^{-t^2/2\tau_f{}^2}\{\sqrt{\pi}\cos\omega_0 t$$
$$+E_{rf}(t/\sqrt{2}\,\tau_f)\sin\omega_0 t\} \tag{23}$$

from which $\Phi_{1\mathrm{R}}^{(0)}(t)\rightarrow 0$, as $t\rightarrow\infty$ is clear. Thus, roughly speaking, the mean period of rotation, τ_f, is the relaxation time of $\Phi_{1\mathrm{R}}^{(0)}(t)$, namely, the relaxation time of $\Phi_1^{(0)}(t)$. To facilitate discussion, we will call the vectors on each "molecules" the μ-vectors, and the sum of the $\boldsymbol{\mu}$-vectors on all the "molecules," the $\boldsymbol{P}$-vectors.

The decay of $\Phi_{1\mathrm{R}}^{(0)}(t)$ due to the loss of the phase correlation of the $\boldsymbol{\mu}$-vectors in the rotating frame may be compared to the free-induction decay of a macroscopic magnetization vector, $\boldsymbol{M}$, which was discussed by Hahn,[13] namely, the decay of the magnetization vector after a 90°-pulse. This pulse changes the direction of the magnetization vector by 90°. Then the vector begins to precess in a plane perpendicular to the direction of the magnetic field. In properly-chosen rotating frames, the motion of an ensemble of the $\boldsymbol{\mu}$-vectors with a uniform angular frequency may be compared to that of an ensemble of the noninteracting microscopic magnetization vectors, $\boldsymbol{m}$, in a homogeneous magnetic field. In both cases the $\boldsymbol{P}$ and $\boldsymbol{M}$ vectors are constant in the rotating frames. The motion of the $\boldsymbol{M}$-vector in an inhomogeneous field is similar to that of the $\boldsymbol{P}$-vector when the molecules have nonuniform frequencies; the phase memory among the $\boldsymbol{m}$-vectors is gradually lost as a result of the inhomogeneity of the magnetic field, which gives nonuniform frequencies to the precessing $\boldsymbol{m}$-vectors. It should be noted that no energy exchange process is involved here between the microscopic vectors, or between the microscopic vectors and the external degrees of freedom. In any case, the $\boldsymbol{P}$ vector relaxes or goes to zero, efficiently. Though the existence of this mechanism in the relaxation of the correlation function has not yet been noticed explicitly, it must be one of the important relaxation mechanisms, even when interactions are introduced among the molecules. This decay process may be tentatively called a *non-dissipative process*, though it must be more properly named in the future. The correlation function in the Debye representation is given, in terms of $\Phi_{1\mathrm{R}}(t)$, as:

$$\Phi_1(t)=\Phi_{1\mathrm{R}}(t)\cos\omega_0 t \tag{24}$$

where ω_0 is a function of the time as shown by (21).

The constant term, 1/3, in the correlation function, $\Phi_1^{(0)}(t)$, for spherical molecules results from three rotational degrees of freedom of spherical molecules. In other words, the "molecules" can rotate around any arbitary axes. For example, for the fraction of " molecules " whose axis of rotation is parallel to the z-axis, the $\boldsymbol{\mu}$-vectors are constants of motion. Thus, the $\Phi_1^{(0)}(t)$ function must have a constant term, which is contributed by the "molecules" to be described in the $S_\mathrm{R}(\omega_0\colon\ \theta\neq\pi/2,\ \varphi)$ rotating frames.

Summarizing the discussions given above, we may describe the characteristic features of the $\Phi_1^{(0)}(t)$ correlation function for free spherical molecules as follows: (a) it is a periodic function of time; (b) however, the frequency of the periodicity, ω_0, is a function of time and is inversely proportional to t in a rough sense of the word; and (c) as a result of the existence of a non-dissipative process, the function relaxes, with a relaxation time of the order of τ_f, to a constant value which, qualitatively, arises from the fraction of "molecules" whose axis of rotation is parallel to the z-axis of the laboratory frames. The correlation function, $\Phi_1^{(0)}(t)$, shown in Fig. 1 has all these features.

We may use a similar argument for interacting molecules, or when there are collisions amoung the molecules in the system. The magnitude and the direction of the angular momentum of a "molecule" will be changed when it collides with other molecules. The transition of a $\boldsymbol{\mu}$-vector from one rotating frame to another is involved when the orientation of the angular momentum is changed. Thus, we may assume that the orientation of the $\boldsymbol{\mu}$-vectors after a collision may be randomized in the y-z plane of the rotating frames. As a result, the magnitude of $\boldsymbol{p}$ is reduced. This process of the relaxation of the angular correlation may be called a *dissipative process*, one which gives a non-periodic decay of the correlation function. In general, to $\Phi_1(t)$, correlation function is decreased by two causes which reduce the phase correlations among the rotating "molecules", the dissipative and the non-dissipative processes. Using the analogy of the free induction decay, we may compare these relaxation processes with the phase memory relaxation of the $\boldsymbol{m}$-vectors due to the spin-relaxation and due to the inhomogeneties of the external field.

When $\tau_r\gg\tau_f$, the correlation function has an extra maximum between $t=2\tau_f$ and $5\tau_f$. The decay before the maximum is mainly due to the non-dissipative process, while the one after the maximum is due to the dissipative process, where, qualitatively speaking, the orientation of the vectors which were parallel or nearly parallel to the z-axis at $t=0$ is changed by collisions. Quite similar discussions may be applied to the tensor correlation functions.

The form of the correlation functions near $t=\tau_f$ sharply depends on the τ_r/τ_f ratio when $\tau_r/\tau_f=0.5$—2.5, in other words, when τ_r is of the order of magnitude of τ_f. It is insensitive when

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[13] E. L. Hahn, *Phys. Rev.*, **77**, 297 (1950); **80**, 580 (1950).

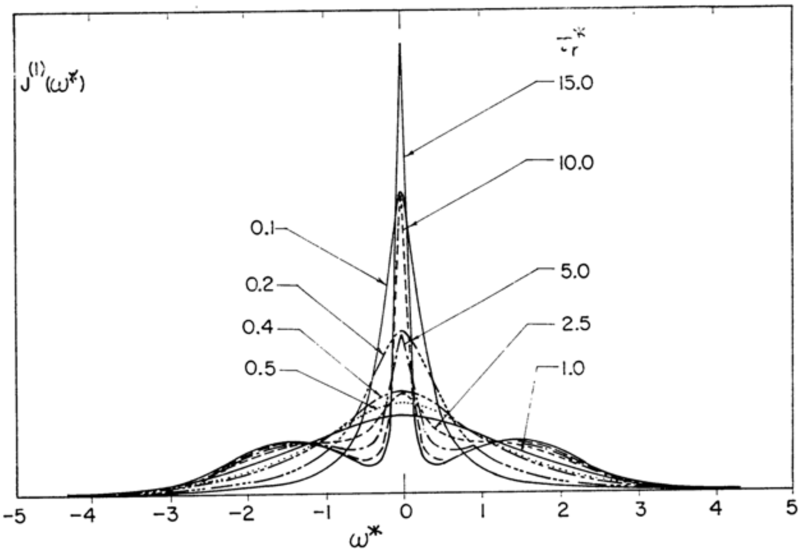

Fig. 3. The spectral densities or the infrared band spectrum for a spherical rotor, $J_1(\omega^*)$, obtained by using Eqs. 4 and 17. The asterisk on ω indicates that it is given in units of $1/\tau_f$. An arbitrary units is used for the ordinate.

$\tau_r/\tau_f \geqslant 10$. There is no bump in the correlation function when $\tau_r/\tau_f \leqslant 1.0$.

The Spectral Density and the Band Shape of Spectra

Spectral Densities.—The spectral densities corresponding to the correlation functions discussed above may be defined by[8]:

$$J_j(\omega) = \frac{1}{2}\int_{-\infty}^{\infty} \Phi_j(t)\mathrm{e}^{-i\omega t}\mathrm{d}t \tag{25}$$

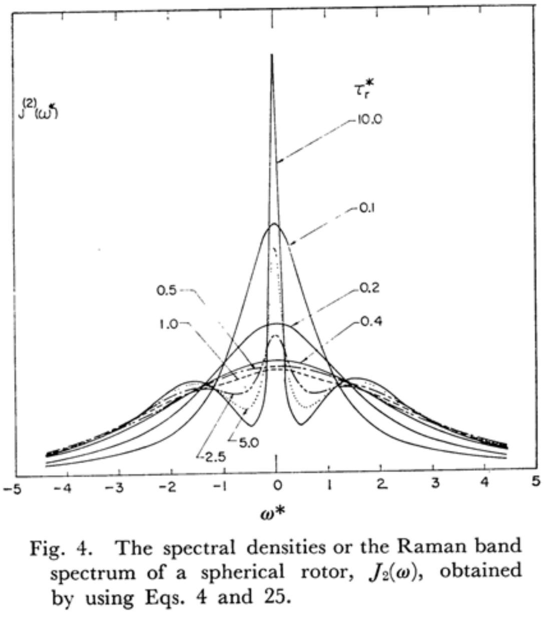

Fig. 4. The spectral densities or the Raman band spectrum of a spherical rotor, $J_2(\omega)$, obtained by using Eqs. 4 and 25.

The forms of the $J_1(\omega)$ and $J_2(\omega)$ functions are given in Figs. 3 and 4 respectively, where $1/\tau_f$ is chosen as the unit of the angular frequency These figures also show the band shapes of respectively, the infrared and Raman spectra of spherical molecules.

For $\tau_r/\tau_f \gg 1$, the spectral density is composed of three distinguishable parts, that is, the so-called P, Q, and R branches.[14] The spectral density, $J_j^{(0)}(\omega)$ for a free rotor has a δ-function-like line at $\omega=0$; this line results from the constant term in the $\Phi_j^{(0)}(t)$ correlation function. Collisions give a finite width to this line. When $\tau_r/\tau_f \gg 1$, the width of the central line is roughly the inverse of the "relaxation time" for the decay of the correlation function after the bump, that is, the relaxation time for the dissipative process. Mathematically, the bump of the correlation function gives bumps in the corresponding spectral density, or vice versa. Hence, when there is no bump in the correlation function, we cannot distinguish the P, Q, and R branches in the spectral density. When $\tau_r/\tau_f \ll 1$, the shape of the spectral density is close to a Lorentz form.

Correlation Times.—The correlation time for a $\Phi_j(t)$ correlation function may be defined as:[6,8,9]

$$\tau_j \equiv \frac{1}{2} J_j(0) = \frac{1}{2}\int_{-\infty}^{\infty} \Phi_j(t)\mathrm{d}t \tag{26}$$

Fig. 6 shows the dependence of the normalized correlation times, $\tau_j^* \equiv \tau_r/\tau_f$, on the normalized

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[14] C. Herzberg, "Molecular Spectra and Molecular Structure. I. The Spectra of Diatomic Molecules," D. Van Nostrand Company, Princeton (1950).

lifetime of the rotation, $\tau_r^* \equiv \tau_r/\tau_f$. On a semilogarithmic scale, τ_i^* is almost symmetric with respect to $\tau_r^*=1$. This is also appproximately true for τ_2^*. In the Debye process there is a one-to-one correspondence between τ_r and τ_j, while in the non-Debye process this is not true, because of contributions from the non-dissipative decay of the angular correlation. Therefore, the reorientation rate cannot be determined by measuring only the correlation times. In particular, it is difficult to determine the value of τ_r^* from τ_2^* when τ_r^* is between 0.3—1.2.

Reorientation of Methane Molecules

It has been shown experimentally[15,16] that methane molecules have a non-Debye reorientation process in the liquid state. To show this clearly, vector correlation functions are obtained from the observed infrared spectra of methane molecules by the relation:[6-8]

$$\Phi_1(t) = \int_{-\infty}^{\infty} \omega^{-1}\sigma_1(\omega) \exp(i\omega t)\mathrm{d}\omega \qquad (27)$$

where $\sigma_1(\omega)$ is the band-shape function. The results are shown in Fig. 5, where τ_f is chosen as the time unit. Clearly, the functions are not exponential; this suggests non-Debye processes in the molecules. The characteristic features of the experimental functions are quite well approximated by Eq. 4, as is shown in Fig. 5. One of the remarkable points of Fig. 5 is that the vector correlation functions for CH_4 and CD_4 in the liquid state of 104°K are fairly close. The molecular structures of CH_4 and CD_4 were studied by Kuchitsu and Bartell[18] by means of the electron diffraction. The values of $r_0=1.0940$ Å and $r_e=1.0850$ Å were reported for the C–H bond, and $r_0=1.0918$ Å and $r_e=1.0850$ Å for the C–D bond, where r_0 and r_e refer to the bond lengths corresponding to the minimum potential and the equilibrium distance respectively. In our calculation we roughly assumed that $r_e(\text{C–H})=r_e(\text{C–D})=1.085$Å at various temperatures, since there were no serious results of this assumption in the final results.

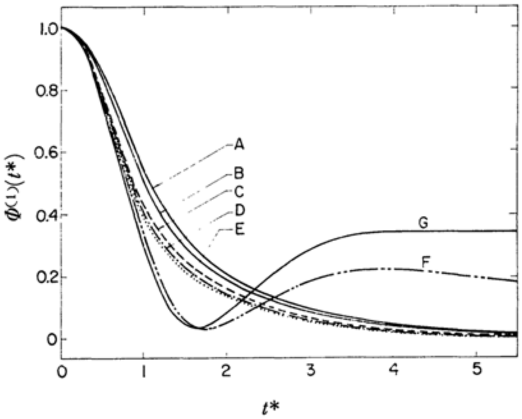

Fig. 5. The vector correlation functions $\Phi_1(t^*)$ for methane or deuteromethane molecules. The functions were obtained from experimental IR spectra by using Eq. 27, where the band shape functions for A—E and for F were, respectively, taken from Ewig's[14] and Armstrong and Welsch's[17] data. A=(CD_4 in CH_4, liquid at 104°K), B=(CD_4 in CD_4, liquid at 104°K), C=(CH_4 in CH_4, liquid at 104°K), D=(CH_4 in CH_4, liquid at 98°K), E=(CH_4 in CH_4, solid at 95°K), F=(CH_4 in He, gas at 294°K, 201 Amag.), and G=$\Phi_1^{(0)}(t)$. In this figure the wiggles which appear after a long time in the correlation functions are properly smoothed out.

It should be noted that the time scale in Fig. 5 has a unit of $\tau_f=(I/\boldsymbol{k}T)^{1/2}$; the length of the time unit in Fig. 5 for the CD_4-function is larger than that for the CH_4-function by about 1.4 times. If we assume that the Debye equation is reasonable for the reorientation processes of methane molecules, there must be no significant difference between the CH_4- and CD_4- correlation functions, and the two functions must be quite different in Fig. 5. In addition, in contrast to Fig. 5, the CD_4-function must be inside the CH_4-function. Hence, it is clear that Debye's picture is entirely inapplicable to methane molecules.

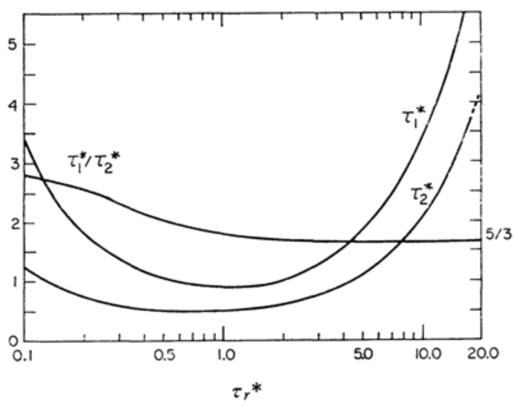

Fig. 6. Dependences of τ_1^*, τ_2^*, and τ_1^*/τ_2^* on τ_r^*. These curves were obtained by using Eq. 4.

The above-mentioned difficulties in Fig. 5 may be interpreted as follows. In Fig. 5, the unperturbed functions, $\Phi_1^{(0)}(t)$, for CH_4 and CD_4 are equivalent. In other words, the contribution from the nondissipative process to the correlation functions, $\Phi_1(t^*)$, of CH_4 and CD_4 are the same in Fig. 5. Hence, the observed small differences

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[15] G. E. Ewing, *J. Chem. Phys.*, **40**, 179 (1964).

[16] G. A. deWit and M. Bloom, *Can. J. Phys.*, **43**, 986 (1965).

[17] R. L. Armstrong and H. L. Welsch, *Spectrochim. Acta*, **16**, 840 (1960).

[18] K. Kuchitsu and L. S. Bartell, *J. Chem. Phys.*, **36**, 2470 (1962).

among the $\Phi_1(t^*)$ correlation functions may be attributed to the differences in $\tau_r^*=\tau_r/\tau_f$, the normalized mean lifetime of the rotation. For the sake of convenience, the notation $\Phi_{\mathrm{CH_4/CD_4}}(t;\ 100°\mathrm{K})$ will be used for the vector correlation function of CH_4 measured at 100°K in a CD_4 solution. The times, τ_f and τ_r, corresponding to this correlation function may be denoted as $\tau_f(\mathrm{CH_4/CD_4};\ 100°\mathrm{K})$ and $\tau_r(\mathrm{CH_4/CD_4};\ 100°\mathrm{K})$. Comparing Fig. 5 with Fig. 1, we have:

$$\tau_r^*(\mathrm{CH_4/CH_4}\colon 104°\mathrm{K})>\tau_r^*(\mathrm{CD_4/CD_4}\colon 104°\mathrm{K}) >\tau_r(\mathrm{CD_4/CH_4}\colon 104°\mathrm{K}) \tag{28}$$

Qualitatively, this relation may be proved as follows. We may assume that the translational energy of a molecule is so much larger than the rotational energy that the rate of the change in the rotation of molecules depends only on the collision frequency. Therefore, $1/\tau_r$, the rate of the change in the rotational motion of molecules, is proportional to the frequency of collisions per second.

The total number of N_{12} collisions occuring per unit volume and per unit of time between pairs of the 1 and 2 gas molecules whose masses are, respectively, m_1 and m_2, is given by[19]:

$$N_{12}=2n_1n_2\sigma_{12}{}^2\left[\frac{2\pi \boldsymbol{k}T(m_1+m_2)}{m_1m_2}\right]^{1/2} \tag{29}$$

where n_1 and n_2 are the number of the 1 and 2 molecules in a unit of volume, and where σ_{12} is the mean diameter of the molecules and is given in terms of the diameters of the 1 and 2 molecules, σ_1 and σ_2, by:

$$\sigma_{12}=\frac{1}{2}\,(\sigma_1+\sigma_2)$$

We may also consider other models of collisions. For example, we may treat molecules as harmonic oscillators which are restricted to their equilibrium positions. The frequencies of oscillators are inversely proportional to the square root of the m_1 or m_2 masses. We may assume that a collision occurs when one of the oscillating molecules is at the maximum deviation from its equilibrium position. Hence, we obtain:

$$N_{12}\propto\left(\frac{1}{\sqrt{m_1}}+\frac{1}{\sqrt{m_2}}\right) \tag{30}$$

In any case, the reduced lifetime of the rotation, τ_r^*, is portional to:

$$\tau_r^*\propto\sqrt{I}\,N_{12} \tag{31}$$

By neglecting the contribution from CD_4–CD_4 collision to $\tau_r^*(\mathrm{CD_4/CH_4})$ and by using (29) or (30), the inequality (28) is obtained. From (29) and (30) we obtain $\tau_r^*(\mathrm{CH_4/CH_4})$: $\tau_r^*(\mathrm{CD_4/CD_4})$: $\tau_r^*(\mathrm{CD_4/CH_4})=1:.79:.72$ and $1:.79:.75$ respectively. The difference between $\tau_r^*(\mathrm{CD_4/CD_4})$ and $\tau_r^*(\mathrm{CD_4/CH_4})$ is very small in the latter case.

Another interesting feature is that the $\Phi_{\mathrm{CH_4/CH_4}}\ (t:95°\mathrm{K})$ correlation function obtained from the infrared spectrum of solid methane is very close to those $\Phi_{\mathrm{CH_4/CH_4}}\ (t:98°\mathrm{K})$ and $\Phi_{\mathrm{CH_4/CH_4}}\ (t:104°\mathrm{K})$. Ewing[14] discussed this point in terms of the infrared spectra. It was also pointed out by deWit and Bloom[16] after their measurement of the nuclear magnetic relaxation of methane and deuteromethane. The latter found that there was no discontinuity in the nuclear magnetic relaxation time, T_1, just before and after the melting point of the solid methane. In addition, the temperature dependence of the relaxation time, T_1, was much weaker than that predicted by Debye's theory. From Fig. 5 we may say that the reorientation process of methane near the melting point is a non-Debye process. The $\Phi_{\mathrm{CH_4/He}}\ (t:294°\mathrm{K})$ correlation function shows very clearly that the decay of the angular correlation is caused by two different effects, the dissipative and the nondissipative processes.

By comparing Figs. 1 and 5, we find that $\tau_r^*(\mathrm{CH_4/CH_4}:\ 95°\mathrm{K})$, $\tau_r^*(\mathrm{CH_4/CH_4};\ 98°\mathrm{K})$ and $\tau_r^*(\mathrm{CH_4/CH_4}\colon\ 104°\mathrm{K})$ are of the order of 0.4—0.5, that $\tau_r^*(\mathrm{CD_4/CD_4}\colon\ 104°\mathrm{K})$ and $\tau_r^*(\mathrm{CD_4/CH_4}\colon\ 104°\mathrm{K})$ are roughly equal to 0.3—0.4, and that $\tau_r^*(\mathrm{CH_4/He_4}\colon\ 294°\mathrm{K})=5.0$—10.0, as is suggested by a rough estimation that the rotational states of methane molecules are changed at each collision.

Discussion

The characteristic differences between the Debye and the non-Debye processes may be observed in the following phenomena: (a) the temperature dependence of the correlation function or of the correlation time, (b) the dependence of these quantities on the moment of inertia of molecules, and (c) the deviation of the form of correlation functions from an exponential one. Of course, it is also clear that the correlation function depends on the macroscopic viscosity, η, quite differently from what is predicted by the Debye equation. However, we do not wish to become involved in a discussion of ways of improving the Debye model by simply introducing the concept of the microscopic viscosity or that of the effective molecular radius.

The Temperature Dependence.—If we use the reduced time, t^*, whose unit is chosen as τ_f, the correlation functions for the free rotor, $\Phi_j^{(0)}(t^*)$, will be independent of the temperature. This is because τ_f is the correlation time corresponding to the $\Phi_j^{(0)}(t)$ function and, in addition, the temperature dependence of this function comes only through τ_f. In the inertial limit the temperature

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[19] S. Chapman and T. G. Cowling, "The Mathematical Theory of Non-Uniform Gases," Cambridge University Press, London (1952).

dependence of the $\Phi_j(t^*)$ function is given only through τ_r^*. For example, when τ_r is proportional to τ_f, that is, when it is proportional to $T^{-1/2}$, the $\Phi_j(t^*)$ correlation function is independent of the temperature. Such a case is given when (29) is satisfied. Then, the spectral density,

$$J_j(\omega^*) \equiv \frac{1}{2}\int_{-\infty}^{\infty} \Phi_j(t^*)\mathrm{e}^{-i\omega^* t^*}\mathrm{d}t^* \qquad (32)$$

must also be independent of the temperature where $\omega^* = |\tau_f|\omega$. The dimensionless quantity, $|\tau_f|$, is used to indicate that ω^* is measured in units of $1/\tau_f$. From (25) and (32) we obtain:

$$J_j(\omega) = |\tau_f| J_j(\omega^*/|\tau_f|) \qquad (33)$$

which gives the temperature dependence of the spectral density. Similarly, we obtain from (33) and (26):

$$\tau_j = \frac{1}{2}|\tau_f| J_j(0^*) \qquad (34)$$

Of course, (32)—(34) are valid only in a limited range of temperature, and a phase transition must not be involved in such a temperature range. Equation 34 gives a weaker temperature dependence of the correlation time than the Debye equation (3). The motional narrowing effect of the anisotropic potential due to the motion of the solvent molecules[8,20] has another effect on τ_j. If this effect is included, the $J_j(0^*)$ quantity becomes a function of the temperature; $J_j(0^*)$ will be increased when the temperature is raised.[8,20] Therefore, the temperature dependence of τ_j through $|\tau_f|$ is partially cancelled by this effect. Hence, we have here a weaker temperature dependence than that obtained from (34).

The Dependence on the Moment of Inertia.—In the Debye process the correlation time depends on the viscosity and on the size of the molecule. Hence, the effect of the isotopic substitution on the correlation time is, in general, so small that we can neglect it for all practical purposes. On the other hand, in the non-Debye process, the isotopic effect must be fairly large, as it is clearly shown in (34). Note that the *reduced* correlation function for the free rotor is independent of the moment of inertia.

The Form of Correlation Functions.—Correlation functions do not have an exponential form when the nondissipative loss of the phase correlation is appreciable. Experimentally, this can be checked by two different methods; from the infrared or Raman spectra, and from the nuclear magnetic relaxation. In the former experiment, the band shape of a spectrum must be quite different from a Lorentz form, provided that the nondissipative loss is appreciable. The measurement of the nuclear magnetic relaxation due to the spin-rotation interaction is also very helpful, because we can estimate the lifetime of the rotation, τ_r directly. If τ_r is comparable with or larger than τ_f, the form of the correlation function must not be exponential.

Effective Viscosities.—It is not accidental that methane shows non-Debye processes. This is because of the highly symmetric structure of this molecule. In general, rotational motions of molecules are perturbed by the anisotorpic part, V_{aniso}, of the intermolecular potential, but not by the isotropic part, V_{iso}, which perturbs the translational motion. Since the macroscopic viscosity for translational diffusions is used in the Debye equation (3), a necessary condition for Debye's theory must be $V_{\mathrm{aniso}} \doteqdot V_{\mathrm{iso}}$. Clearly this is not true for methane molecules. The concept of the effective viscosity for a given effective radius of a molecule or that of the effective radius for a given viscosity is nonsense in the strict sense of the words in non-Debye processes: the correlation times, τ_1 and τ_2, for which the τ_1/τ_2 ratio is not equal to 3 result in different viscosities or in effective radii from those produced by the Debye equation. In other words, these phenomenological quantities depend on the methods of measurement. Note Fig. 6

Conclusion

If the correlation time, τ_j, obtained from the experimental data is quite different from the corresponding one obtained from the Debye equation (3), there is a high possibility that the molecular reorientation is of a non-Debye process, where the nondissipative decay of angular correlation is not negligible. Therefore, the use of the Debye equation with an effective viscosity or microscopic viscosity is physically nonsense in such processes. However, it may not always be true that any non-Debye process gives a very much smaller correlation time than the corresponding Debye process. In the non-Debye processes correlation times may have a weaker temperature dependence than in the Debye processes, and they depend on the moment of inertia of the molecule. Often the forms of the correlation functions are different from the exponential ones as a result of the existence of the nondissipative decay of angular correlation, as we showed in the case of methane.

When the correlation functions of spherical particles for non-Debye processes are needed, we may conveniently use Eq. 4 as an approximate expression. It has been proved that (4) is a reasonably simplified expression for the correlation function of non-Debye processes, being related to the two kinds of decays of angular correlation. Or, experimentally, the vector and the tensor

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20) M. Bloom, to be published.

correlation functions may be obtained from infrared and Raman spectra respectively in terms of the Fourier transform of the band-shape functions. Fourier transform of the band-shape functions. Conversely, the infrared and Raman spectra can be calculated from Function 4 by means of the Fourier transformation. Therefore, the theory of the band shape of the vibrational spectra is basically equivalent with the theory of the angluar correlation of molecules. Information on the reorientation process is obtained through the measurements of the vibrational spectra or of the nuclear magnetic relaxation due to the spin-rotation interaction.

The present work was supported by NIH Grant-GM-13545-01. For priceless 7094 computer time (the problem number N-4210) the author wishes to thank the M. I. T. Computation Center. Without this grant, many of the problems presented here could not have been solved. The author was also partly helped in his calculation by the Stanford University Computation Center, which gave him free 7090 computer time under Account Number F134. Deep thanks are also due Professor Baldeschwieler for his warm hospitality to the author.