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Dipole Correlation Functions of Non-interacting Symmetric Vib-rotors

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Dipolar correlation functions of non-interacting symmetric top molecules were obtained by quantum mechanical calculation. The effect of the rotation-vibration interaction on the correlation function is discussed, taking the constant ζ of the Coriolis coupling and the asymmetry I_x/I_z as parameters. It is shown that the decay of the correlation function for perpendicular vibrations very much depends on the sign and the magnitude of ζ. Some relationships between the shape of the correlation function and the value of the parameters are given.

Detailed information on the reorientational motion of molecules in the liquid state is obtained by infrared spectroscopy; the dipolar correlation function $\Xi(t)$ is given[1,2] from infrared spectrum $I(\omega)$ according to the Fourier transform

$$\Xi(t) = \int_{-\infty}^{+\infty} I(\omega) \exp(i\omega t) d\omega.$$

A number of studies[1-13] have shown that molecular reorientation of small molecules is not of rotational diffusion as described by Debye[14] but to some extent of free rotation. Contribution from this deviates the form of correlation function $\Xi(t)$ from exponential decay curves. Qualitatively, the function $\Xi(t)$ is represented by that of free rotors followed by an exponential curve.[2,5] The molecular motion can be treated more quantitatively, considering the effect of free rotation rigorously.[3,14-19] The form and the relaxation time of $\Xi(t)$ for non-interacting molecules give useful information for the study of observed functions. Thus, $\Xi(t)$ has been calculated for free diatomic,[1,2] spherical[5,20] and symmetric top[21] molecules.

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The most important merit of the IR method may be that detailed and quantitative information is obtained on the anisotropy in molecular reorientation as predicted by theories.[1,2] Shimozawa and Wilson[4] first reported the observation of the anisotropic rotation in liquids by the IR method by using *trans*-dichloroethylene. The reorientational motion of acetone in various polar and non-polar solution was recently studied by Koga *et al.*[22] They found that the anisotropy was influenced by the density and polarizability of the solvent.

Observation of the anisotropy is difficult, however, because observed functions often differ much from theoretical ones.[14,22] The most significant contribution to the difference seems to result from the Coriolis' coupling as pointed out by Rothschild.[23] In the present paper we will show how the function $\Xi(t)$ of free symmetric top molecules is influenced by the Coriolis' coupling, taking the coupling constant ζ and the ratio of the moments of inertia, I_x/I_z, as parameters.

Methods of Calculation

In order to take into account the Coriolis' coupling at full length, we may write the Hamiltonian of a vib-rotor[24] as

$$H = H_v + H_r + H', \tag{1}$$

where

$$H_v = (1/2)\sum_i p_i^2 + V_0 + (1/2)l_z^2/I_z, \tag{2}$$

$$H_r = (1/2)(J_x^2/I_x + J_y^2/I_y + J_z^2/I_z) \tag{3}$$

and

$$H' = -J_z l_z/I_z. \tag{4}$$

x, y, and z in (2)—(4) refer to the principal inertial axes of molecule with components of the moment of inertia I_x, I_y, and I_z, respectively; J_x, J_y, and J_z are the components of the total angular momentum $\boldsymbol{J}$ onto the same axes; l_z is the z component of the vibrational angular momentum $\boldsymbol{l}$; p_i is the momentum conjugate to the i-th normal coordinate; and V_0 is the intra-molecular potential. We neglect anharmonicity in vibrations as well as vibration-rotation interactions higher than the first order one H'. We are interested only in the relative frequency of component lines to the center of vibration-rotation bands and not in absolute value. The anharmonicity can therefore be neglected, since it contributes mainly to shifting the whole band spectrum with band center. Vibration-rotation interactions of higher order shift energy levels of vibrationally excited states in the wave number of the order of the rotational constant B $(=\hbar/4\pi c I_x$, where c is the light velocity). The energy change in wave number is of the order of 10^{-2} cm^{-1} for an ordinary molecule. Displacements of the component line of the order of 10^{-2} cm^{-1} can be safely neglected, since neighboring lines are generally separated from each other about the wave number of the order of 1 cm^{-1}.

The eigenfunctions and eigenvalues for the Hamiltonian H may be rewritten in terms of conventional notation corresponding to (1) as follows.

$$H|v, l, k, M) = \hbar\omega(v, l, J, k)|v, l, k, M) \tag{5}$$

with

$$\omega(v, l, J, k) = \omega_v(v, l) + \omega_r(J, k) + \omega'(k, l) \tag{6}$$

$$\omega_v(v, l) = \begin{cases} (v+1/2)\omega_v & \\ \qquad \text{for non-degenerate vibrations} & (7\text{a}) \\ (v+1)\omega_v + \hbar\zeta^2 l^2/2I_z & \\ \qquad \text{for degenerate vibrations} & (7\text{b}) \end{cases}$$

$$\left.\begin{aligned} \omega_r(J, k) &= \hbar J(J+1)/2I_x + \hbar k^2/[2(1/I_z - 1/I_x)] \\ \omega'(k, l) &= \hbar\zeta k l/I_z, \end{aligned}\right\} \tag{8}$$

where $l = \pm 1$ is the quantum number for l_z, *viz.*, the projection of vibrational angular momentum $\boldsymbol{l}$ onto the molecular axis. The Coriolis' coupling appears only when vibrational states are degenerated. Such degenerate vibrations have an induced dipole moment in the x-y plane perpendicular to the molecular axis. In the following treatment the set of quantum numbers v, l, J, k, and M may be concisely represented in a symbolic way by a single letter n. In other words, all the possible quantum states are properly numbered from $n=1$ to infinity. The Schrödinger equation (4) is briefly rewritten as

$$H|n) = \hbar\omega_n|n) \tag{9}$$

with

$$|n) = |n_v)|n_r) \equiv |v, l)|J, k, M).$$

The dipole correlation function $\Xi(t)$, a normalized and dimensionless quantity, may be defined by

$$\Xi(t) = N\langle\mu_z(0), \mu_z(t)\rangle, \tag{10}$$

where μ_z refers to the projection of the induced moment μ onto the space fixed Z-axis which is taken arbitrarily in a plane perpendicular to the direction of propagation of the IR light; $<A, B>$ represents the canonical average between variables A and B; and $N = <\mu_z(0), \mu_z(0)>^{-1}$ is the normalization constant which makes $\Xi(0) = 1$. When molecules are free from intermolecular interactions, energy H is a constant of motion. The correlation function is then conveniently expressed in terms of eigenfunctions $|n)$ and eigenvalues ω_n as follows.[25]

$$\begin{aligned} \Xi(t) = N\sum_{n,n'}(\beta\hbar\omega_{nn'})^{-1}\exp(-\beta\hbar\omega_n)\{\exp(\beta\hbar\omega_{nn'}) - 1\} \\ \times \exp(i\omega_{nn'}t)(n|\mu_z|n')(n'|\mu_z|n), \end{aligned} \tag{11}$$

where

$$\omega_{nn'} \equiv \omega_n - \omega_{n'}$$

and $\beta \equiv 1/kT$ with Boltzmann constant k and absolute temperature T. The angular frequency $\omega_{nn'}$ may be given by

$$\omega_{nn'} = \omega_{nn'}{}^c + \omega_{nn'}^* \tag{12}$$

where $\omega^c(n;\ n') \equiv \omega_{nn'}{}^c$, the angular frequency of the center of fundamental band $\{n \to n'\}$, is independent of the sets of rotational quantum numbers n_r and $n_{r'}$ in the present approximation; namely,

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[22] K. Koga, Y. Kanazawa, and H. Shimizu, *J. Molec. Spectrosc.* (in press).

[23] W. G. Rothschild, *J. Chem. Phys.*, **57**, 991 (1972).

[24] H. H. Nielsen, *Phys. Rev.*, **60**, 794 (1941).

[25] R. Kubo and K. Tomita, *J. Phys. Soc. Jap.*, **9**, 45 (1954).

$$\omega^c(n, n') = \omega^c(n_v; n_{v'}) \tag{13}$$

with $v=0$ and $v'=1$. By utilizing (12) the correlation function (11) may be rewritten as

$$\Xi(t) = \Xi^*(t) \exp[i\omega^c(n_v; n_{v'})t]$$

with

$$\Xi^*(t) = N'\sum_{n,n'}(\beta\hbar\omega_{nn'})^{-1}\exp(-\beta\hbar\omega_{n_r})[\exp(\beta\hbar\omega_{nn'})-1] \times \exp(i\omega^*_{nn'}t)(n|\mu_z|n')(n'|\mu_z|n), \tag{14}$$

where N' is the normalization factor of $\Xi^*(t)$. The Fourier transform of $\Xi^*(t)$ gives the "normalized" and dimensionless rotation-vibration spectrum $S^*(\omega)$ relative to the band center ω^c. The inverse Fourier transformation of $S^*(\omega)$ results in $\Xi^*(t)$. In classical limit $\beta\hbar\omega_{nn'}\ll 1$, (14) is reduced to

$$\Xi^*_{cl}(t) = N'\sum_{n,n'}\exp(-\beta\hbar\omega_{n_r}) \times \exp(i\omega^*_{nn'}t)(n|\mu_z|n')(n'|\mu_z|n). \tag{15}$$

Further calculation of $\Xi(t)$ is possible when μ_z in the matrix elements of (11) is given in terms of variables defined in molecular-fixed coordinate systems. Wigner's rotation matrix $A_{mm'}{}^{(1)}(\Omega)$ can be most conveniently used for this purpose:[26]

$$\mu_z = \sum_{m=-1}^{1} A^{(1)}_{m0}(\Omega)\mu_m \tag{16}$$

with

$$\begin{pmatrix} \mu_{+1} \\ \mu_0 \\ \mu_{-1} \end{pmatrix} = \begin{pmatrix} -1/\sqrt{2}(\mu_x+i\mu_y) \\ \mu_z \\ 1/\sqrt{2}(\mu_x-i\mu_y) \end{pmatrix} \tag{17}$$

and Ω refers to Eulerian angles between the space-fixed and molecule-fixed coordinate systems. We obtain

$$(n'|\mu_z|n) = \sum_{m=-1}^{1}(n_r'|A^{(1)}_{m0}(\Omega)|n_r)(n_v'|\mu_m|n_v), \tag{18}$$

where $(n_v'|\mu_m|n_v)$ have non-vanishing values only when $v'=v\pm 1$ and $l'=l+m$.

We obtain the function $\Xi(t)$ corresponding to fundamental bands from (11) by confining ourselves to states $|n)$ with $v=0$ and $l=0$, or such states where $|n_v)=|n_0)$. Hence, non-vanishing elements appear when $v'=1$ and $l'=m$. Since the induced moment μ_m is given in terms of the normal coordinate Q_i by

$$\mu_m \simeq Q_i(\partial\mu_m/\partial Q_i)_e, \tag{19}$$

nonvanishing elements become

$$\begin{aligned} (1, 0|\mu_0|0, 0) &= [\hbar/2\omega_v]^{1/2}(\partial\mu_0/\partial Q_i)_e \\ (1, \pm 1|\mu_{\pm 1}|0, 0) &= \mp[\hbar/\omega_v]^{1/2}(\partial\mu_{\pm 1}/\partial Q_i)_e. \end{aligned} \tag{20}$$

Matrix elements $(n_{r'}|A_{m0}{}^{(1)}|n_r)$ may be conveniently given in terms of Clebsch-Gordan coefficients[15] as

$$(J', K', M'|A^{(1)}_{m0}|J, K, M) = [J+1]^{1/2}C(J, 1, J'; K, m), \tag{21}$$

which have non-vanishing values only when

$$\Delta J \equiv J' - J = 0, \pm 1 \tag{22}$$

and

$$\Delta K \equiv K' - K = m.$$

Results and Discussion

Parallel Bands. The excited states in the present case have no vibrational angular momentum, *i.e.* $l'=0$. Thus (18) is transformed into

$$(n'|\mu_z|n) = (n_r'|A^{(1)}_{00}(\Omega)|n_r)(n_v'|\mu_0|n_v) \tag{23a}$$

$$\begin{aligned} &= (J', K, M'|A^{(1)}_{00}(\Omega)|J, K, M)(1, 0|\mu_0|0, 0) \\ &= C(J, 1, J'; K, 0)[\hbar(J+1)/2\omega_v]^{1/2}(\partial\mu_0/\partial Q_i)_e \end{aligned} \tag{23b}$$

by utilizing (20), (21) and (22). The quantity C in (23b) is non-vanishing only when $J'=J-1$, J, and $J+1$:

$$\begin{aligned} C(J, 1, J-1; K, 0) &= [J^2-K^2]^{1/2}/[J(2J+1)]^{1/2} \\ C(J, 1, J; K, 0) &= K/[J(J+1)]^{1/2} \\ C(J, 1, J+1; K, 0) &= [(J+1)^2-K^2]^{1/2}/[(J+1)(2J+1)]^{1/2}. \end{aligned} \tag{24}$$

We have

$$\omega^*_{nn'} = \begin{cases} -2BJ & \text{for } J' = J-1 \\ 0 & J' = J \\ +2BJ & J' = J+1. \end{cases} \tag{25}$$

The reduced correlation function $\Xi^*(t)$ is easily obtained from (7), (14), (23b), (24), and (25).

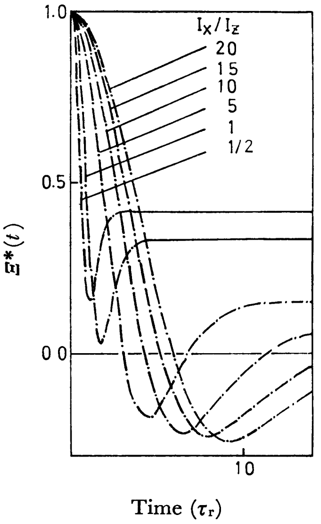

Fig. 1. Time correlation functions $\Xi^*(t)$ for parallel band obtained at $T=300$ K and $\omega_{nn'}{}^c=2{,}000$ cm^{-1} in units of $\tau_r\equiv(I_z/kT)^{1/2}$, the mean period of rotation.

The functions $\Xi^*(t)$ at 300 K and $\omega_{nn'}{}^c=2000$ cm^{-1} are shown in Fig. 1, taking the ratio I_x/I_z as a parameter. The value of I_z is assumed to be 5×10^{-40} g·cm^2, which is nearly the same with the moment of inertia of CH$_3$X. The calculated functions are clearly of non-exponential form with non-vanishing limiting value $\Xi^*(\infty)$, which results from the Q branch of spectrum. The limiting value $\Xi^*(\infty)$ is directly related to the relative intensity the Q branch. The proof is very simple. The spectrum $S^*(\omega^*)$ may be composed of the sum of the P and R branches, $S_1^*(\omega^*)$, and the Q branch, $S_2^*(0)\delta(\omega^*)$. The Fourier transform of $S^*(\omega^*)$ gives

$$\Xi^*(t) = \int_{-\infty}^{\infty} S_1^*(\omega^*)e^{i\omega^*t}d\omega^* + S_2^*(0)\int_{-\infty}^{\infty}\delta(\omega^*)e^{i\omega^*t}d\omega^*,$$

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[26] M. E. Rose, "Elementary Theory of Angular Momentum," John Wiley & Sons, Inc., N. Y. (1957), p. 52.

where the first term in the RHS vanishes when $t \rightarrow \infty$. Hence, $\Xi^*(\infty) = S_2^*(\omega_{nn'}{}^c)$.

It is noted that the magnitude of the transition moment $(n|\mu_z|n')$ is independent of the moment of inertia of molecule as indicated by (23) and (24). This means that the relative intensity S_2^* of the Q branch is varied only by the statistical factor, the Boltzmann distribution factor $\exp(-\hbar\omega_n/kT)$, which is a function of the ratio of ω_n and temperature T. The eigenvalues (6)—(8) lead to the result that an increase in the moment of inertia I_x decreases the magnitude of ω_n/T and, hence, the relative intensity S_2^*. A similar effect is expected by increasing temperature T instead of I_x. On the other hand, there is the relation $\Xi^*(\infty) = S_2^*$ as shown above. Therefore, $\Xi^*(\infty)$ is a decreasing function of I_x as well as T.

It was shown by one of us (H.S.)[5] that the non-dissipative relaxation of the dipolar correlation $\Xi^*(t)$ is characterized by two dynamical factors, the mean period τ_f of rotation and the relaxation time τ_p of the phase coherence among dipole moments which are in phase at initial time $t=0$. The rate of the initial decay of the correlation function $\Xi^*(t)$ for non-interacting molecules is inversely proportional to τ_f, or estimated qualitatively by $<|\hbar/\omega_{nn'}{}^*|>$, where $< >$ refers to the ensemble average. In other words, the rate of the initial decay of the function $\Xi^*(t)$ is proportional to $<|\omega_{nn'}{}^*|>$ in a qualitative sense. The results (25) leads to $<|\omega_{nn'}{}^*|> \propto B \propto 1/I_x$, indicating that the smaller the moment of inertia I_x for a fixed value of I_z, the larger the rate of initial decay. The tendency is demonstrated in Fig. 1. The relaxation of the phase coherence gives rise to the disappearance of the oscillatory behavior of the correlation function and makes the function approach zero. The depth of the minimum $\Xi_m{}^*$ of the correlation function is, therefore, an increasing function of τ_p, or the relaxation time of the phase coherence and is inversely proportional to $<|\Delta\omega_{nn'}{}^*|> \equiv <|\omega_{nn'}{}^* - <\omega_{nn'}{}^*>|>$. The rates of reorientation of molecular frame, (25), indicate that $<|\Delta\omega_{nn'}{}^*|>$ is further proportional to B or $1/I_x$. Thus, the larger the ratio I_x/I_z in Fig. 1 the deeper the minimum of the correlation function. The time t_m where the correlation function takes the minimum value $\Xi_m{}^*$ is linearly proportional to $[I_z/I_x]^{1/2}$ as shown in Fig. 2. t_m is given in Fig. 3 as a function of $[I_z/I_x]^{1/2}$, indicating that it is proportional to $[I_z/I_x]^{1/2}$. In other words, t_m multiplied by $\Xi_m{}^*$ is constant.

In classical limit, $\beta\hbar\omega_{nn'} \ll 1$, no vibrational effect exists in the correlation function $\Xi^*(t)$, because matrix elements $(n'|\mu_z|n)$ in (15) can be replaced by $(n_r'|A_{00}{}^{(1)}|n_r)$ and, the vibrational contributions, $(n_v'|\mu_0|n_v)$, can be included in the normalization factor N'. Hence, the correlation function in classical limit $\Xi_{\mathrm{cl}}{}^*(t)$ represents the dipole correlation of rotor but not of vib-rotor. On the other hand, $\Xi^*(t)$ describes that of free vib-rotor.

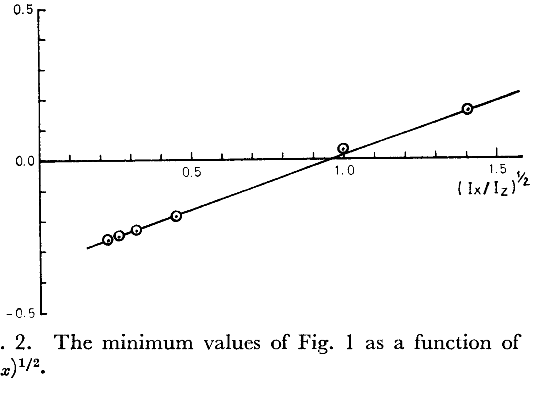

Fig. 2. The minimum values of Fig. 1 as a function of $(I_z/I_x)^{1/2}$.

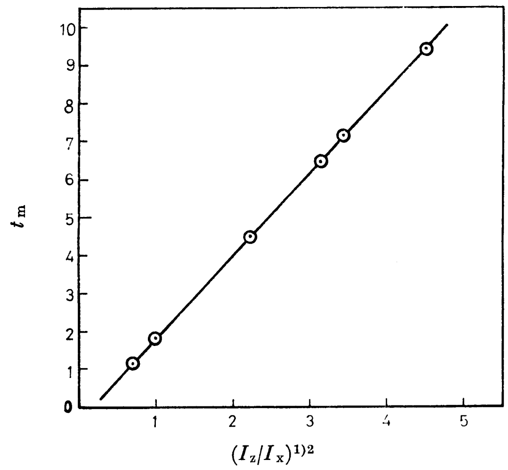

Fig. 3. The position of the minimum of $\Xi^*(t)$ in units of $t_m = t(I_z/kT)^{1/2}$ as a function of $(I_x/I_z)^{1/2}$.

Perpendicular Bands. In the present case where $l' \geq 1$, vibrations interact with molecular rotation through the Coriolis' coupling and vibration and rotation are often influenced substantially. From (20), (21) and (22), (18) becomes

$$(n'|\mu_z|n) = (n_r'|A^{(1)}_{\pm 10}(\Omega)|n_r)(n_v'|\mu_{\pm 1}|n_v) \tag{26a}$$

$$= (J', K', M|A^{(1)}_{\pm 10}(\Omega)|J, K, M)(1, \pm 1|\mu_{\pm 1}|0, 0)$$

$$= C(J, 1, J'; K, \pm 1)[\hbar(2J+1)/\omega_v]^{1/2}(\partial\mu_{\pm 1}/\partial Q)_e. \tag{26b}$$

The coefficients C in (26b) have non-vanishing values only when $J'=J-1$, J, and $J+1$ and $K'=K-1$, and $K+1$:

$$\begin{aligned} &C(J, 1, J-1; K, \pm 1) \\ &\qquad = [(J \mp K+1)(J \mp K)]^{1/2}/[2J(2J+1)]^{1/2} \\ &C(J, 1, J; K, \mp 1) \\ &\qquad = -[(J \mp K+1)(J \pm K)]^{1/2}/[2J(J+1)]^{1/2} \\ &C(J, 1, J+1; K, \pm 1) \\ &\qquad = [(J \pm K+1)(J \pm K)]^{1/2}/[2(J+1)(2J+1)]^{1/2}. \end{aligned} \tag{27}$$

We have[27]

$$\omega_{nn'} = \omega_v - B + \zeta(\zeta-2)A \pm 2K[(1-\zeta)A-B] \mp 2BJ, \tag{28a}$$

where the upper sign refers to $J'=J+1$, $K'=K-1$ and $l'=l-1$, and the lower one to $J'=J-1$, $K'=K+1$ and $l'=l+1$, and $A=\hbar/4\pi c I_z$. Similarly, we have

$$\omega_{nn'} = \omega_v - B + \zeta(\zeta-2)A \pm 2K[(1-\zeta)A-B], \tag{28b}$$

where the upper sign refers to $J'=J$, $K'=K+1$ and $l'=l+1$, and the lower $J'=J$, $K'=K-1$ and $l'=l-1$. For $J'=J+1$, $K'=K+1$ and $l'=l+1$ and for $J'=$

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27) H. H. Nielsen, "Handbuch der Physik," Band 37–1, Atom 3-Molekül 1, Springer-Verlag Berlin, Göttingen, Heidelberg (1959), p. 254.

$J-1$, $K'=K-1$ and $l'=l-1$ we write

$$\omega_{nn'} = \omega_v - B + \zeta(\zeta-2)A \\ \pm 2K[(1-\zeta)A-B] \pm 2BJ. \qquad (28c)$$

From (7), (14), (26b), (27), (28a), (28b), and (28c), the reduced correlation function $\Xi^*(t)$ is easily calculated. In Figs. 4—9 are shown the dipole correlation functions at $T=300$ K and $\omega_{nn'}{}^c=2000$ cm^{-1}, regarding the Coriolis' coupling constant ζ as a parameter. When $\zeta \neq 0$, correlation function is affected not only by rotational state but also by interactions of the vibration and the rotation. Generally, the correlation function of degenerate vibrations obtained from infrared spectrum significantly differs from the dipole correlation functions of rotors as shown in Figs. 4—9.

Symmetric top molecules are classified into two groups, the oblate symmetric top (in the case of $I_z>I_x$)

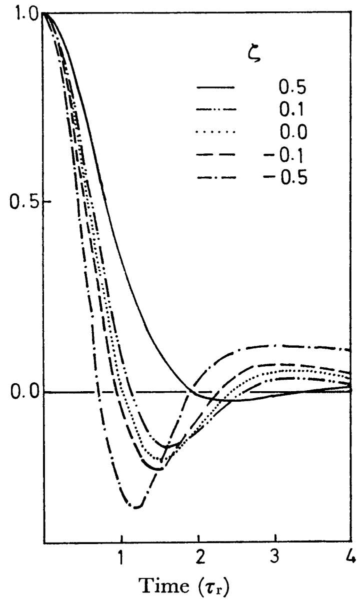

Fig. 4. Time correlation fuctions $\Xi^*(t)$ for perpendicular band at $I_x/I_z=1/2$, $T=300$ K and $\omega_{nn'}{}^c=2{,}000$ cm^{-1} in units of $(I_z/kT)^{1/2}$.

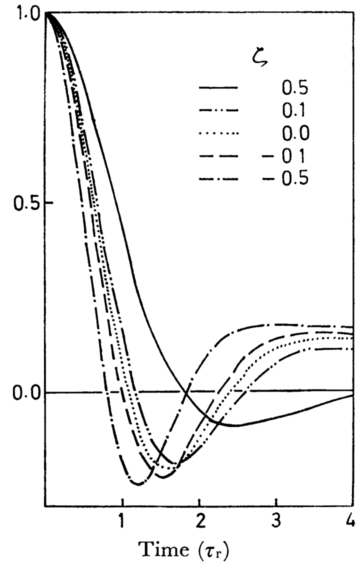

Fig. 5. Time correlation fuctions $\Xi^*(t)$ for perpendicular band at $I_x/I_z=3/4$, $T=300$ K and $\omega_{nn'}{}^c=2{,}000$ cm^{-1}.

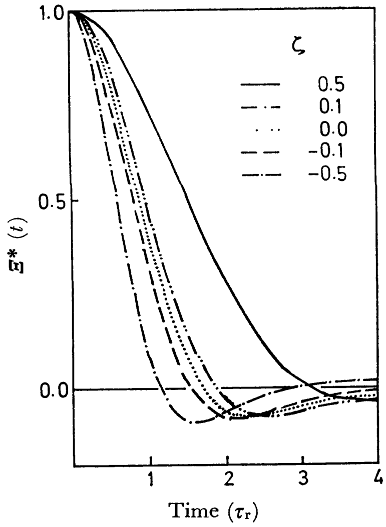

Fig. 6. Time correlation functions $\Xi^*(t)$ for perpendicular band at $I_x/I_z=5$, $T=300$ K and $\omega_{xx'}{}^c=2{,}000$ cm^{-1}.

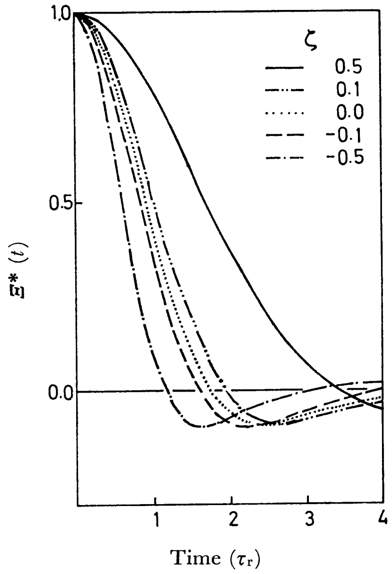

Fig. 7. Time correlation functions $\Xi^*(t)$ for perpendicular band at $I_x/I_z=10$, $T=300$ K and $\omega_{nn'}{}^c=2{,}000$ cm^{-1}.

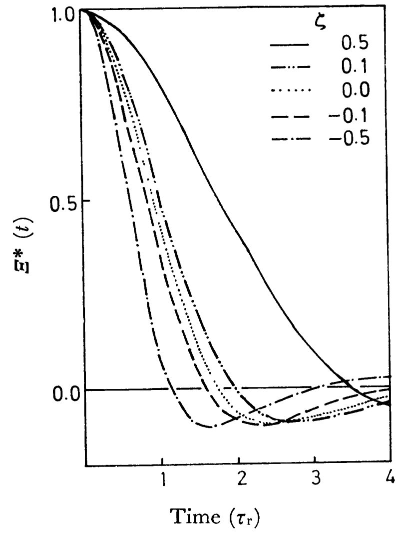

Fig. 8. Time corrlation functions $\Xi^*(t)$ for perpendicular band at $I_x/I_z=15$, $T=300$ K and $\omega_{nn'}{}^c=2{,}000$ cm^{-1}.

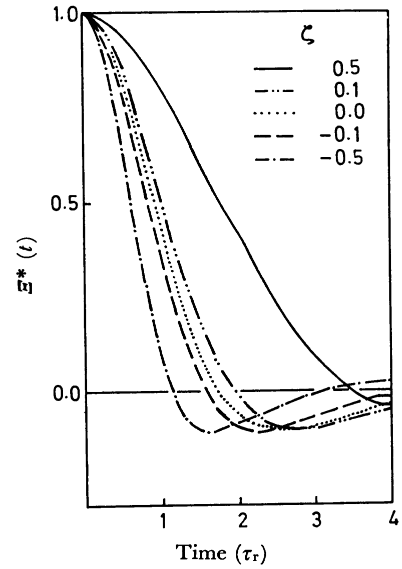

Fig. 9. Time correlation functions $\Xi^*(t)$ for perpendicular band at $I_x/I_z=20$, $T=300$ K and $\omega_{nn'}{}^c=2{,}000$ cm^{-1}.

and prolate symmetric top ($I_z<I_x$), the functions $\Xi^*(t)$ for the oblate and prolate molecules being shown in Figs. 4—5 and in Figs. 6—9, respectively. The dependence of the correlation function on I_x/I_z is more pronounced in oblate molecules than in prolate ones.

We will discuss the form of the correlation function more in detail by considering the two dynamical factors as in the case of parallel bands. In the present case the orientation of the dipole moment is changed by molecular vibrations with non-vanishing angular momentum as well as by molecular rotations. When $\zeta<0$ vibration and rotation change the orientation of the dipole moment in the same direction whereas in opposite directions for $\zeta>0$. Therefore, the rate of the initial decay of the function $\Xi^*(t)$ is evidently larger when $\zeta<0$ than when $\zeta>0$. Relations (28) demonstrate that $\omega_{nn'}{}^*\equiv\omega_{nn'}-\omega_v$ decreases as Ξ is increased for constant A and B from -1 to $+1$. This means that $\langle|\omega_{nn'}{}^*|\rangle$ or the rate of the initial decay is also a decreasing function of ζ when the values of I_x and I_z are fixed. On the other hand, when I_x changes with constant I_z and ζ, the variable part of $\omega_{nn'}{}^*$ is $\mp 2(J+K)B$. This indicates that $\langle|\omega_{nn'}{}^*|\rangle$ or the rate of the initial decay of the correlation function decreases as B is decreased, *i.e.*, as I_x/I_z is increased. Equations (28) show that the ζ-dependence of the rate of the initial decay becomes sharper as the ratio $I_x/I_z=A/B$ is increased.

In contrast to the case of parallel bands, the larger the rate of the initial decay of the function $\Xi^*(t)$ the deeper the minimum $\Xi_m{}^*$ as seen in Figs. 4—9. The tendency may be explained as follows in terms of the relaxation of the phase coherence among dipole moments.

The rate of the change of the orientation of induced moments depends not only on the rotational quantum number J but also on the quantum number K of component of angular momentum along molecular axis. To estimate the effect caused by the K-dependence of molecular reorientation on τ_p, it will be convenient to utilize the relation $\tau_p \simeq \hbar/\langle\Delta\omega^*\rangle$, where $\langle\Delta\omega^*\rangle$ is the width of band spectrum in angular frequency units. Equations (28) together with (27) give an inhomogenous distribution of component lines and the spectrum is made from a subband structure. The wings of the whole spectrum are mainly contributed from P and Q branches of sub-bands, respectively, and give rapidly relaxing components in the phase correlation, since separations from the band center are large. The relaxation time τ_p is, therefore, contributed most effectively by Q branches which gather rather closely in the central part of the spectrum and gives a slowly relaxing component. In other words, the width of the spectrum is contributed most effectively from the Q branches as far as the phase relaxation is concerned. Hence, we have in a rough measure

$$\tau_p \simeq \hbar/\langle|\Delta\omega^*_{nn'}(Q)|\rangle, \qquad (29)$$

where $\Delta\omega_{nn'}{}^*(Q)$ is the position of the Q branches relative to the center of the spectrum, namely,

$$\Delta\omega^*_{nn'}(Q) = 2AK[(1-\zeta)-I_z/I_x], \qquad (30)$$

from (28) for a fixed value of I_z.

When the ratio I_x/I_z is increased from zero, we obtain a decrease in the value of $\langle|\Delta\omega_{nn'}{}^*(Q)|\rangle$ and its minimum value, *i.e.* the maximum value of τ_p, at

$$I_x/I_z = 1/(1-\zeta). \qquad (31)$$

Further increase of I_x/I_z leads to an increase of $\langle|\Delta\omega_{nn'}{}^*(Q)|\rangle$ or a decrease of τ_p. Equation (30) indicates that the main contribution to τ_p results from the term $1-\zeta$, provided that

$$I_x/I_z \gg 1/(1-\zeta). \qquad (32)$$

Equation (31) leads to the result that the larger the Coriolis' coupling constant ζ the larger the ratio I_x/I_z which gives the maximum τ_p. Comparison of the correlation functions for $=-0.5$ and $=0.5$ in Figs. 4—9 support the above discussion.

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