December, 1978] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 51 (12), 3475—3481 (1978)

Depolarized Rayleigh Wings of the Liquids and Solutions of Some Symmetric Top Molecules

Keiji KAMOGAWA

Department of Chemistry, Faculty of Science, Tohoku University, Aramaki, Aoba, Sendai 980

(Received July 17, 1978)

Spectra of depolarized Rayleigh wings were observed for the liquids and CCl_4 solutions of C_6H_6, CH_3CN, and $CHCl_3$. The spectral band shape can be reproduced very well by a Lorentz function for the low frequency wing component and a Gauss function for the far wing component. The functions for neat liquids gave the relaxation times for orientational motion, which support free rotation models. The relaxation times of the solutions were found to be independent of concentration, the integrated intensities showing a linear dependence on concentration. The results for the wing component are in marked contrast to those found for the central component of the spectra. The difference is discussed in terms of dynamical structure of the liquids.

The depolarized Rayleigh scattering spectrum of liquids usually appears in the frequency region less than 100 cm^{-1}, consisting of a sharp line at the exciting frequency and a broad wing spread over a wide frequency region. The spectrum is caused by fluctuations in the polarizability anisotropy of the molecules and provides information on the molecular motion and local structure of the liquid. The sharp line arises from the fluctuation caused by rotational diffusion motion of time scale ≈ 1 ps. The broad wing reflects the fluctuation of shorter time scale of 0.1 ps which is probably due to librational motion (rotational oscillation)[1-3] or collisional motion of the molecules.[4,5] Thus, the sharp line and broad wing correspond to the diffusional motion and bounded motion, respectively.

In order to clarify the dynamical behavior of molecules in the usual liquid, it is important to study the concentration (N) dependence of the Rayleigh scattering spectrum. For the liquids of symmetric top molecules, the concentration dependence has been studied theoretically and experimentally for the sharp line component and for the total Rayleigh intensity, the results being interpreted in terms of the rotational diffusion and the pair correlation.[6-13] However, there seems to be no study on the concentration dependence of the broad wing. In the present work, the concentration dependence of the wing components of several symmetric top molecules, C_6H_6, CH_3CN, and $CHCl_3$, was studied in their carbon tetrachloride solutions. The results provide information on the orientational correlation function between the solute molecules of the short time scale of 0.1 ps. By combining the results with the information of the longer time scale motions available from the analysis of the central component, the whole aspect of the dynamical structure of the liquid can be made clear.

Experimental

The experimental arrangement for Rayleigh scattering is almost the same as that for Raman spectral measurements. An argon ion laser operating at 514.5 nm was used as a light source. The incident light was chopped by a rotating sector at 20 Hz to avoid thermal lensing effect. After being passed through a Glan-Thomson prism, the light was focused with a long focusing lens into a sample cell kept at 30.0±0.1 °C. The light scattered at 90° with a small solid angle of 10^{-4} radian was observed along the direction parallel to that of the electric polarization of incident light and collected to a Nalumi double monochromator scanning with instrumental width of 1 cm^{-1}. The signal detected by an HTV R585 or cooled R649 photomultiplier was counted with an ORTEC Model 9315 photoncounter with time constant 5—10 s and digitally recorded with an interval of 0.6—1.2 cm^{-1}. The signals were averaged after several repeated measurements. The whole scattering intensity of solution was determined relative to the intensity of the neat liquid which was taken to be 100. The observed intensities thus obtained were not corrected for spectral sensitivity of the detection system because of the narrow frequency region. The spectra obtained were usually symmetric except for the Boltzmann factor, the intensity maxima being taken as $\omega=0$. The measurements were carried out from the intensity maxima to lower frequency region. The samples were neat liquids of C_6H_6, CH_3CN, $CHCl_3$, and CS_2 and their mixtures with CCl_4. They were of spectral grade and used without further purification. Just before the spectral measurements, the samples were filtered with 0.2 μm millipore membrane filter to remove suspended dusts. The refractive indices of the solutions were measured with an Abbe refractometer.

Results and Band Shape Analysis

The depolarized Rayleigh scattering spectrum of liquid CH_3CN is shown in Fig. 1. The spectrum consists of a sharp component at the center and a broad

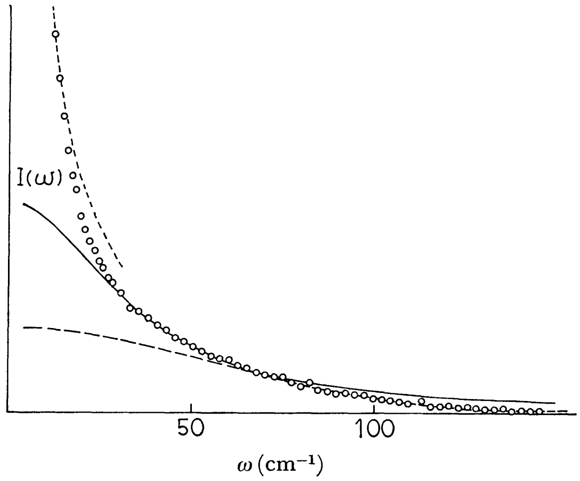

Fig. 1. The observed spectrum of liquid CH_3CN (circles) and analysis of the band shape by wing Lorentzian (full line), wing Lorentzian plus center Lorentzian (dotted line) and far wing Gaussian (broken line).

wing. In order to analyze the band shape, it is useful to assume reasonable analytical function.

Depolarized Rayleigh scattering originates from fluctuation in the local polarizability anisotropy α. Three kinds of fluctuations; rotational diffusion, libration (rotational oscillation in a potential well) and collision of the molecules; seem to contribute to the intensity $I(\omega)$ through the polarizability correlation function $\langle\alpha(t)\alpha(0)\rangle$. According to Keyes and Kivelson[6] and Alms *et al.*,[7] the rotational diffusion of symmetric top molecule gives the spectrum expressed by the Lorentz function

$$I_r(\omega) = \frac{A}{15n^2\pi}\left[\frac{n^2+2}{3}\right]^4 \beta^2 N(1+fN)\frac{6D'}{\omega^2+(6D')^2},$$

$$D' = \left(\frac{(1+gN)}{(1+fN)}\right)D, \tag{1}$$

where n, N, β, and D are the refractive index,[12] density of liquid, optical anisotropy of the molecule and rotational diffusion constant, respectively. f is the static orientational pair correlation function given by

$$f = \frac{\langle\alpha_0^i(0)\alpha_0^j(0)\rangle}{\langle\alpha_0^i(0)\alpha_0^i(0)\rangle}, \tag{2}$$

where $\alpha_0^i(0)$ and $\alpha_0^j(0)$ are the polarizability anisotropies of the rigid rotating molecules i and j at $t=0$. g is the dynamical pair correlation function (Eq. B6, Ref. 6). The integrated intensity of Eq. 1 is given by

$$I_r = \frac{A}{15n^2}\left[\frac{n^2+2}{3}\right]^4 \beta^2 N(1+fN). \tag{3}$$

It is well established that the rotational diffusion contributes to most of the intensities of narrow wave number region around the center of the Rayleigh scattering, giving rise to the sharp band of Lorentzian shape.

On the other hand, based on the librational scattering models, Starunov[1] obtained a modified Lorentzian spectrum expressed by

$$I(\omega) = \frac{I^0}{(1-I_\perp\omega^2/\mu)^2+\zeta^2\omega^2/\mu^2}, \tag{4}$$

while Prorvin[2] and Sechkarev and Nikolaenko[3] gave on nearly the same model a squared Lorentzian

$$I(\omega) = \frac{I^0}{(1+\tau_2^2\omega^2)^2} \qquad \tau_2^2 = \frac{1}{1/\tau_0^2+z^2}. \tag{5}$$

In Eqs. 4 and 5, I^0 is the peak intensity at $\omega=0$, ζ the internal friction constant of the molecule in the liquid, μ the elastic constant, $I_\perp$ the moment of inertia of the molecule perpendicular to the principal axis, τ_0 the average half-period of the libration, and z an average frequency of intermolecular interactions. Although it is assumed in both models that the scattering comes from the librational motion of individual molecules ($f=0$), Starunov's model is based on the stable librators of different sites in the liquid. Thus, different molecules contribute to the central and wing components. On the other hand, Sechkarev and Nikolaenko assumed that the librator is a temporary one appearing and disappearing by jump diffusion from one potential well to another and the two components of the spectrum come from the same molecules in different time periods. Thus, the band shape of the modified Lorentzian (Eq. 4) or the squared Lorentzian (Eq. 5) is expected if the librational fluctuations are predominant.

The collisional motion of the pairing molecules is known to give the spectrum of a modified exponential type[4] of Eq. 6 or a sum or a combination of exponential functions.[5,14]

$$I(\omega) = \omega^{2(m-7)/7}\exp(-\omega/\omega_0). \quad (\omega>\omega_0) \tag{6}$$

ω_0 is an average frequency of translational oscillation and m has the value of 9 or 13 according to whether the fluid is an atomic or molecular fluid. Equation 6 holds on the assumption that collisionally induced polarizability $\Delta\alpha$ depends on the intermolecular distance r as follows:

$$\Delta\alpha \propto r^{-m}. \tag{7}$$

In many liquids the librational and collisional motions give a broad spectrum, the Rayleigh wing, spread over a wide frequency region. In liquids composed of symmetric top molecules, both the modified Lorentzian and the squared Lorentzian reproduce the observed wing better than the modified exponential type.[15,16] We thus start analysis of the observed wing on the basis of the librational models. Both Eqs. 4 and 5 give a Lorentzian in the low frequency region. First we look for the low frequency region of the wing component where the spectrum can be expressed by a Lorentzian $I_L(\omega)$. Second, the central component obtained by subtraction of $I_L(\omega)$ from the observed intensities will be examined by another Lorentzian $I_r(\omega)$ corresponding to Eq. 1. A typical example of the analysis is shown in Fig. 1 for neat CH_3CN liquid. In the low frequency wing region 25—60 cm^{-1}, the spectrum can be reproduced by a Lorentzian $I_L(\omega)$ (called wing Lorentzian in this study). The spectral region less than 20 cm^{-1} can be reproduced by addition

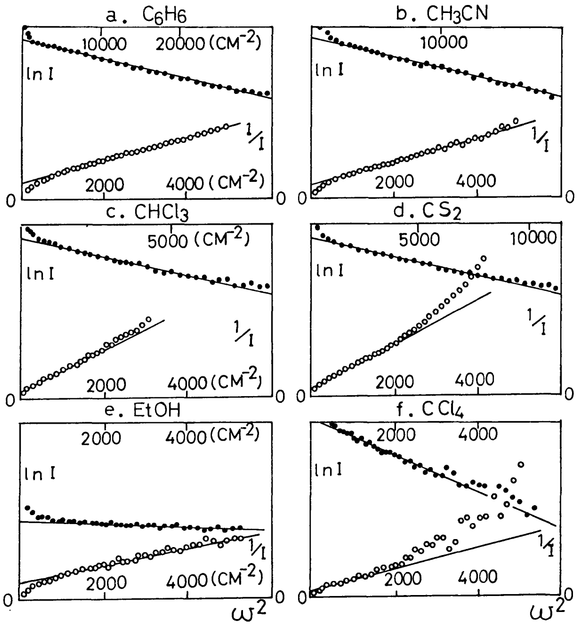

Fig. 2. Band shape analyses for neat liquids. A line drawn for the plots ○ of $1/I$ against ω^2 corresponds to the wing Lorentzian and a line drawn for the plots ● of ln I against ω^2 to the far wing Gaussian.

of the Lorentzian $I_L(\omega)$ plus another Lorentzian $I_r(\omega)$. The observed points for this frequency region are few and $I_r(\omega)$ involves a considerable ambiguity. No attempt was made to deduce physical quantities from $I_r(\omega)$. In this way, for all the liquids except for CCl_4, the spectra over the central and low frequency wing regions can be reproduced by a Lorentzian $I_L(\omega)$ and the central component which has a form close to that of Lorentzian $I_r(\omega)$. The results of the analysis are shown in Fig. 2.

However, the spectrum of the far wing region cannot be reproduced by the above analysis. As seen in Fig. 1, the spectrum deviates appreciably "downward" from the Lorentzian $I_L(\omega)$ in the frequency region higher than 65 cm^{-1}. The "downward" deviation cannot be reproduced by addition of another Lorentzian. As far as the spectral region is concerned, the spectrum can be expressed very well by a Gauss function. The Gauss function changes smoothly to the Lorentzian $I_L(\omega)$. The same is true for the far wing regions of all the liquids studied here (Fig. 2). The Gauss function is called far wing Gaussian $I_g(\omega)$ in this study. The central region of the Rayleigh scattering spectrum is explained by overlapping of the central component lying close to the Lorentzian $I_r(\omega)$ given by Eq. 1 and the wing Lorentzian $I_L(\omega)$. The low frequency wing region is expressed practically by $I_L(\omega)$, since the contribution from the central component is negligibly small in this region. For the far wing region, the spectrum can be reproduced very well by the far wing Gaussian $I_g(\omega)$ only. We assume that $I_L(\omega)$ does not necessarily extend to the far wing region.

Band shape analysis by the above method is successful for the symmetric top molecules, C_6H_6, CH_3CN, $CHCl_3$, and CS_2 (Figs. 2a—2d), and also for EtOH which is an asymmetric top and highly associative molecule (Fig. 2e). For these molecules, the deviation of the observed intensities from the analytical ones were within $\pm 2\%$ for the whole wing region. On the other hand, the Lorentzian analysis for the low frequency wing of CCl_4 shows appreciable deviation from the observed shape while a Gaussian for the far wing gives a good fit (Fig. 2f). The inadequacy of the Lorentzian analysis for the low frequency wing seems to be characteristic of isotropic molecules, for which only the collisional mechanism gives depolarized Rayleigh scattering.

We should compare the present analysis for the wing with the analysis based on the single function of the squared Lorentzian proposed by Prorvin[2] and Sechkarev and Nikolaenko.[3] Figure 3 shows the plots of $I(\omega)^{-1/2}$ *vs.* ω^2 for the wings of C_6H_6 and CH_3CN. The frequency regions where the observed band shape is well described by the squared Lorentzian are summarized in Table 1 together with the regions of the good fit obtained by the present analysis. Although the squared Lorentzian reproduces the observed band shape fairly well over a wide wing region, considerable deviation occurs in the far wing region especially for C_6H_6. Measurements of Rayleigh scattering carried out by many workers are usually limited in the frequency region up to 100 cm^{-1}.[2,3,17] In this frequency region, the spectra can be reproduced fairly well by a single function of the squared Lorentzian. However, it is evident from our data that it is impossible to have a good fit with a single function for wider frequency region. It seems adequate to adopt a combination of a Lorentzian and a Gaussian for the wing in a wide frequency region.

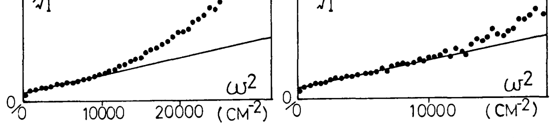

Fig. 3. Band shape analyses for liquid C_6H_6 and CH_3-CN. A line drawn corresponds to the squared Lorentzian.

Table 1. Frequency regions of the wing (cm^{-1}) for which the observed spectrum is reproduced by the assumed functions

	CH_3CN	C_6H_6	CS_2	$CHCl_3$
Lorentzian	27—65	36—73	17—46	15—41
Gaussian	57—146	44—163	46—86	42—76
Squared Lorentzian	32—94	30—105	16—66	20—57

From the slopes and the intercepts of the straight lines (Fig. 2) band widths and integrated intensities can be obtained for the low frequency wing and for the far wing. When the functions are given by

$$I_L(\omega) = \frac{1}{a_L + b_L\omega^2},$$

$$I_g(\omega) = \exp(a_g - b_g\omega^2), \tag{8}$$

the widths and the integrated areas for them are

$$\omega_L = \sqrt{\frac{a_L}{b_L}}, \qquad \omega_g = \sqrt{\frac{1}{b_g}},$$

$$\int_0^{\omega_c} I_L(\omega)\mathrm{d}\omega = \frac{1}{\sqrt{a_L b_L}}\tan^{-1}\left[\frac{\omega_c}{\omega_L}\right],$$

$$\int_{\omega_c}^{\infty} I_g(\omega)\mathrm{d}\omega = \exp[\mathrm{a}]\int_{\omega_c}^{\infty}\exp[-b_g\omega^2]\mathrm{d}\omega, \tag{9}$$

where the two functions are joined at $\omega = \omega_c$. Although ω_c is arbitrary, the value does not affect the total wing intensity as far as $I_L(\omega)$ smoothly changes to $I_g(\omega)$ around the region $\omega \approx \omega_c$ (Fig. 1). Integration of $I_g(\omega)$ can be carried out by use of a numerical table for the error function. The relaxation time τ_L can be calculated from the half band width ω_L of the wing Lorentzian by $\tau_L = 1/2c\pi\omega_L$, while the relaxation time

Table 2. Observed band width and relaxation time for the neat liquids

	CH_3CN	EtOH	C_6H_6	CS_2	$CHCl_3$	CCl_4
ω_g cm^{-1}	74	66	76	48	45	37
τ_2^{-1} cm^{-1}	66	—	76	40	38	—
τ_g ps	0.14	0.16	0.14	0.22	0.24	0.29
ω_L cm^{-1}	34	48	43	18	19	21
τ_L ps	0.16 (0.15)[a]	0.11	0.12	0.30	0.28	0.25

a) Schwarz and Wang.[16]

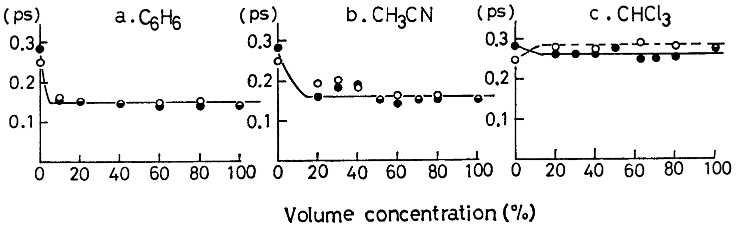

Fig. 4. Experimental relaxation times τ_g (●) and τ_L (○) for carbon tetrachloride solutions of C_6H_6, CH_3CN, and $CHCl_3$ at various volume concentrations.

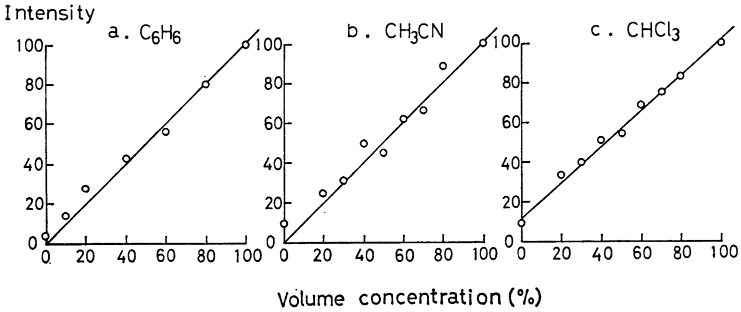

Fig. 5. Concentration dependence of the integrated intensity $\left(I/\frac{1}{n^2}\left(\frac{n^2+2}{3}\right)^4\right)$ for carbon tetrachloride solutions of C_6H_6, CH_3CN, and $CHCl_3$ (I is given by I_L+I_g).

τ_g can be calculated from the band width ω_g of the far wing Gaussian by means of $\tau_g=1/c\pi\omega_g$. The widths and relaxation times obtained are given in Table 2. Both τ_L and τ_g are as short as the order of 0.1 ps for all the liquids. τ_g corresponds to the time in which the correlation function $\langle\alpha(t)\alpha(0)\rangle$ decays to $1/e$ according to

$$\langle\alpha(t)\alpha(0)\rangle \propto 1-t^2/\tau_g{}^2+O(t^4) \approx \exp\left[-t^2/\tau_g{}^2\right]. \quad (10)$$

τ_L is the time in which the correlation function decays exponentially to $1/e$.

The above are the results for the neat liquids. The relaxation times were also obtained from the analysis of the solution spectra at various concentrations. The observed τ_g and τ_L of the carbon tetrachloride solutions of C_6H_6, CH_3CN, and $CHCl_3$ at various concentrations are plotted against the concentrations in Fig. 4. We see that τ_g and τ_L remain unchanged over all the concentrations except for the region less than 10%. The sudden increases for C_6H_6 and CH_3CN at concentrations less than 10% are due to the appearance of CCl_4 spectrum whose relaxation time is 0.29 ps. According to Alms *et al.*,$^{7)}$ in contrast to τ_L and τ_g, the relaxation time for the central component τ_c varies depending on the concentration and kind of the solvent. They found that τ_c varies from 2.91 to 1.79 ps for C_6H_6 in isopentane and from 2.95 to 1.74 ps for $CHCl_3$ in CCl_4 with change in volume concentration from 100 to 20%. They also found that the relaxation time obtained from NMR of $CHCl_3$ in CCl_4 remains constant at 1.5 ps over a wide concentration range, which is also close to the time obtained from NQR. The concentration independence of τ_g and τ_L is similar to the concentration behavior of the relaxation times obtained from NMR and NQR but differs from the concentration dependence of the central component.

The observed integrated intensities of the wing components I_L+I_g at various concentrations are given for the carbon tetrachloride solutions of C_6H_6, CH_3CN, and $CHCl_3$ in Fig. 5. The wing components of C_6H_6 show almost linear dependence on the concentration. The observed points lie near the straight line passing through the origin. This indicates that there is no orientational correlation ($f=0$) among the solute molecules, if Eq. 3 is applied to the wing component, I_L+I_g. The wing components of CH_3CN and $CHCl_3$ also show similar concentration dependence.†

On the other hand, the central component seems to show a concentration dependence differing from that of the wing component. $f=-0.2$ for the central component of C_6H_6 and $f=+0.9$ for that of $CHCl_3$ reported by Bauer *et al.*,$^{12,18)}$ are different from $f\approx 0$ obtained for the wing components.

Discussion

Collisional Scattering. Let us first examine the possibility of the collisional process as a cause of the wing component. The collisional process can be tested by the observed relaxation time, its concentration dependence and the integrated intensity of the spectrum.

---

† In contrast, ethanol solution of CCl_4 shows quite different solute concentration dependence of the integrated intensity, which is non-linear in concentration. The non-linear dependence seems to be expressed by the sum of the part proportional to the square of the CCl_4 concentration and that of linear concentration dependence of EtOH.

The collisional interval time τ_{BC} is considered to be an average time interval between collisions and given by[19]

$$\tau_{BC} = 1/\bar{v}[V_m^{1/3} - \sigma], \tag{11}$$

where V_m is the average molecular volume, σ the collision diameter and $\bar{v}$ the average velocity of the molecules. τ_{BC} is not the exact relaxation time for collisional scattering determined by the correlation function for the intermolecular separation and its orientation of a pair molecule. However, τ_{BC} corresponds to the librational half period of the pair molecules so that it will be a measure of the collisional relaxation time. τ_{BC} given by Bartoli and Litovitz[19] are compared with τ_g obtained in the present study in Table 3. Although qualitative correlation seems to exist between them, τ_{BC} differes from τ_g by a factor of 5. The collisional interval time τ_{BC} should be dependent on the concentration, since τ_{BC} (Eq. 11) changes with the changes in the reduced mass of the colliding pair and $V^{1/3}$. Actually, such a change was experimentally confirmed by Dill *et al.*[20] for the angular velocity correlation time (τ_j) which is a measure of τ_{BC}. However, τ_g as well as τ_L are found to be almost independent of concentration. If the spectrum is caused by the binary collision process, the integrated intensity of the wing should change with the square of the concentration. However, the intensity of the wing component has linear dependence on the concentration for C_6H_6, CH_3CN, and $CHCl_3$.

Thus, the observed relaxation time, its concentration dependence and the integrated intensity do not support the collisional scattering process. It seems that the wing component comes from dynamical process of the single molecule rather than collision process between pairing molecules.

Librational Scattering. The observed spectra of the far wing region are reproduced by a Gauss function. The far wing spectrum corresponds to the motion of short time period which seems to be inertial. There are two types of rotational motions in liquids according to the classification by Atkins,[21] conditional and unconditional free rotations, which give a Lorentzian shape and a Gaussian shape, respectively. The former exists in the first stage of orientational motion of the molecule in homogeneous media having weak intermolecular torque. The correlation function for this process was given by Steel,[22] Gordon,[23] and Atkins[21] as follows.

$$\langle \alpha_0(t)\alpha_0(0)\rangle \propto 1 - \frac{l(l+1)kT}{2I_\perp}t^2 + O(t^4)$$

$$\approx \exp\left[-\frac{l(l+1)kT}{2I_\perp}t^2\right], \tag{12}$$

where $l=2$ for light scattering and NMR process. The relaxation time, τ_{FR}, for Eq. 12, is given by $\sqrt{I_\perp/3kT}$, corresponding to Gaussian relaxation time. Another definition of the relaxation time for the unconditional free rotation was given by Bartoli and Litovitz[19] as the time in which a molecule rotates 41° based on the fact that the correlation function is the second Legendre polynomial. It is given by $41/360 \cdot 2\pi\sqrt{I_\perp/kT}$. Both τ_{FR} should be proportional to $I_\perp^{1/2}$. Figure 6 shows the plot of τ_g *vs.* $I_\perp^{1/2}$, which gives a straight line with zero intercept. This provides strong evidence that the far wing component arises from the unconditional free rotation of the molecule. However, τ_{FR} calculated by $\sqrt{I_\perp/3kT}$ differs from τ_g by a factor of 2 as shown in Table 3.

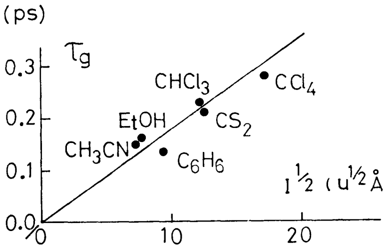

Fig. 6. Correlation between the relaxation time τ_g and $I_\perp^{1/2}$ ($I_\perp$: moment of inertia of the molecule).

TABLE 3. OBSERVED AND CALCULATED RELAXATION TIMES AND MOMENT OF INERTIA OF THE MOLECULES

	CH_3CN	EtOH	C_6H_6	CS_2	$CHCl_3$	CCl_4
τ_g ps	0.14	0.16	0.14	0.22	0.24	0.29
τ_{BC}[a)] ps	0.026	—	0.023	0.074	0.071	0.114
τ_{FR} ps	0.27	0.29	0.34	0.46	0.44	0.63
$I_\perp$ aumA^{2}[c)]	54.9	57.8	88.9	155.9	148.1	295.7
τ_L ps	0.16	0.11	0.12	0.30	0.28	0.25
τ_{LC} ps	0.19	0.19	0.17	0.32	0.22	0.36

a) Bartoli and Litovitz.[19] b) "Landolt-Börnstein," ed by K. H. Hellwege, Springer-Verlag, Berlin (1976), New Series II 7. c) lamu$=1.66056\times10^{-27}$ kg.

The conditional free rotation would be of importance in the media where the intermolecular torques are appreciable. In such circumstances, free rotation occurs only in the local part of the media such as lattice defect, but it is inhibited in other parts of the liquid. The orientational correlation function for such conditional free rotation shows an exponential decay[21] on the assumption that the free rotation is caused by fast formation and destruction of the lattice defects, the rates being proportional to time t. The relaxation time of this model is given by

$$\tau_{LC} = \sqrt{\frac{I_\perp}{3kT}}\left(\frac{\alpha}{1+2\alpha}\right)^{1/2} P_d^{-1}, \tag{13}$$

where α is given by $I_\perp/I_\parallel$, a ratio of the moments of inertia perpendicular and parallel to the principal axis of the related symmetric top molecule, and P_d is the probability of finding the molecule in the lattice defects, being equal to 1 at the limit of weak intermolecular torques. The observed τ_L values obtained from the wing Lorentzian $I_L(\omega)$ are compared with τ_{LC} calculated by means of Eq. 13 at the limit of $P_d=1$, in Table 3. We see that the correlation between τ_L and τ_{LC} is fairly good. It seems that the orientational motions of the molecules are mostly free in the first stage to give the far wing Gaussian, the free rotation undergoing weak intermolecular interactions in the next stage to give the wing Lorentzian. This is the reason why the wing component can be separated into the Lorentzian and Gaussian parts as shown in the band analysis. The concentration independence of τ_g and τ_L is important. In the orientational diffusion process, the concentration dependence of the relaxation time is determined by the pair correlation as shown by Eq. 1. If the process is of single molecular nature, the relaxation time should be independent of the concentration as found in NMR and NQR for the mixture of $CHCl_3$ and CCl_4. Our result confirms the view that the motion corresponding to the broad wing should be of single molecular nature with no correlation between different molecules. The orientational pair correlation f is expressed by[24]

$$f=\frac{1}{2}\langle 3\cos^2\Psi_{ij}(0)-1\rangle, \tag{14}$$

where $\Psi_{ij}(0)$ is the angle between the principal axis of molecule i and that of molecule j at arbitrary instant. From Eq. 14 we see that a negative value of f indicates perpendicular orientation of the two molecules, a positive value of f parallel orientation and $f=0$ random orientation. The concentration dependence of integrated intensities suggests that f is nearly zero in the short time period of 0.1 ps; the random orientation is realized in this short time scale. This is quite in contrast to the appreciable correlation in the long time period ≈ 2 ps known for C_6H_6[25] and $CHCl_3$,[26] showing perpendicular and parallel correlations, respectively.

Origin of Different f Values. We obtained $f\approx 0$ for the wing component from both the relaxation times and the integrated intensity, while $f\neq 0$ is shown by many workers for the central component. We should consider the cause of this difference, since f should be independent of time according to Eq. 2. The orientational pair correlation function f is as follows.[24]

$$\begin{aligned}\langle\alpha_o(t)\alpha_o(0)\rangle &= \sum_{i,j}\langle\alpha_o^i(t)\alpha_o^j(0)\rangle\\ &\propto \sum_i\langle P_2[\cos\theta_i(t)]P_2[\cos\theta_i(0)]\rangle\sum_j\langle 3\cos^2\Psi_{ij}(0)-1\rangle\frac{1}{2},\end{aligned} \tag{15}$$

where $P_2[\cos\theta]$ is the second Legendre polynomial and $\Psi_{ij}(0)$ is given by Eq. 14. The ensemble average $1/2<3\cos^2\Psi_{ij}(0)-1>$ should be replaced by a time average for finite time T as follows.

$$\bar{f}^T=\frac{1}{2}(3\cos^2\Psi_{ij}(0)-1)^T=\frac{\frac{1}{2}\int_0^T(3\cos^2\Psi_{ij}(t)-1)\mathrm{d}t}{T}, \tag{16}$$

where T is the duration time of the motion.

We assume that T can be replaced by relaxation time. The central and the wing component have different relaxation time τ_c and τ_L or τ_g, respectively. The pair correlation function for the central component might differ from that for the wing component. The different pair correlation function (f) indicates that the molecules in the different time scale are in different non-stationary states with regard to orientation. There should be a finite time τ_r in which the molecule has a preferential orientation in average relative to the neighbors. τ_r should be at least the period of libration in a potential well ($2\tau_0$, Eq. 5) and also a few times greater than τ_g (Eq. 5 and Table 2). Since the central component reflects the rotational diffusion, τ_c should be greater than τ_r. Thus, we have

$$\tau_c>\tau_r>\tau_g.$$

The rapid process with the relaxation time τ_g cannot reflect the stationary state, since the stationary state requires a relaxation time greater than τ_r.[27] In other words, the relaxation process for the wing scattering is too rapid for a molecule to follow average orientation of neighboring molecules. Such a rapid process gives random orientation corresponding to non-correlation ($f=0$).

Another interpretation for the different f values is possible when the liquid consists of two different portions, one giving the center spectrum and the other the broad wing spectrum. Transition from one portion to another may be fast or slow depending on the stability of the inhomogeneous liquid structure. The most unstable structure corresponds to the conditional free rotation model. The different orientational pair correlations will be obtained by assuming an inhomogeneous model. For the portion giving the wing scattering, intermolecular torques are weak enough to allow free rotation, the molecules taking random orientation without pair correlation. However, in another portion, the molecules are packed to the extent that they undergo diffusional motion as a whole. The pair correlation function for this portion will be positive or negative depending on the orientation of the pairing molecules. So far we have not sufficient evidence to make a choice from the two models.

The author sincerely thanks Prof. Mitsuo Ito and Dr. Yasuo Udagawa for their valuable advice, and Assist. Prof. Tohru Azumi for his help in the experimental setup.

References

1) V. S. Starunov, *Opt. Spektrosk.*, **18**, 165 (1965).

2) A. I. Prorvin, *Opt. Spektrosk.*, **24**, 380 (1968).

3) A. V. Sechkarev and P. T. Nikolaenko, *Soviet. Phys. DOK.*, **13**, 888 (1969).

4) J. A. Bucaro and T. A. Litovitz, *J. Chem. Phys.*, **54**, 3846 (1971).

5) H. A. Posch and T. A. Litovitz, *Mol. Phys.*, **32**, 1559 (1976).

6) T. Keyes and D. Kivelson, *J. Chem. Phys.*, **56**, 1057 (1972).

7) G. R. Alms, D. R. Bauer, J. I. Brauman, and R. Pecora, *J. Chem. Phys.*, **58**, 5570 (1973); **59**, 5310 (1973).

8) D. J. Coumou, J. Hijmans, and E. L. Mackor, *Trans. Faraday Soc.*, **60**, 2244 (1974).

9) M. S. Malmberg and E. R. Lippincott, *J. Colloid. Interface Sci.*, **27**, 591 (1968).

10) P. Bothorel, C. Such, and C. Clement, *J. Chim. Phys. Phys.-Chim. Biol.*, **69**, 1443 (1972).

11) G. Dezelic and N. Segudovic, *Croat. Chim. Acta*, **45**, 407 (1973).

12) D. R. Bauer, J. I. Brauman, and R. Pecora, *J. Chem. Phys.*, **63**, 53 (1975).

13) G. D. Patterson and J. E. Griffth, *J. Chem. Phys.*, **63**, 2406 (1975).

14) P. A. Fleury, W. B. Daniels, and J. M. Worlock, *Phys. Rev. Lett.*, **27**, 1493 (1971).

15) J. H. K. Ho and G. C. Tabisz, *Can. J. Phys.*, **51**, 2025 (1973).

16) M. Schwarz and C. H. Wang, *Chem. Phys. Lett.*, **29**, 383 (1974).

17) B. Simic-Glavaski and D. A. Jackson, *J. Phys. (Paris)*, **33**, 183 (1972).

18) D. R. Bauer, J. I. Brauman, and R. Pecora, *Ann. Rev. Phys. Chem.*, **27**, 443 (1976).

19) F. J. Bartoli and T. A. Litovitz, *J. Chem. Phys.*, **56**, 413 (1972).

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

21) P. W. Atkins, *Mol. Phys.*, **17**, 321 (1969); **17**, 329 (1969).

22) A. Steel, *J. Chem. Phys.*, **38**, 2411 (1963).

23) R. G. Gordon, *J. Chem. Phys.*, **43**, 1307 (1965).

24) D. A. Pinnow, S. J. Candau, and T. A. Litovitz, *J. Chem. Phys.*, **49**, 347 (1968).

25) A. H. Harten, *J. Chem. Phys.*, **67**, 2102 (1977).

26) P. R. Ireland, R. Mason, and A. I. M. Rae, *Mol. Phys.*, **24**, 17 (1972).

27) K. B. Tolpigo, "Termodinamika i Statisticheskaya Fizika," Kiev Univ., (Japanese translation) (1966).