Fluctuation of Local Field and Depolarization Ratio of the ν_1 Raman Line of Carbon Tetrachloride in Carbon Disulfide Solution

Shi-aki HYODO
Toyota Central Research and Development Labs., Inc., Nagakute-cho, Aichi-gun, Aichi 480-11

(Received March 3, 1990)

The depolarization ratio of a molecule having T_d symmetry has been expressed in terms of the mean-square fluctuation of the local field which is felt by a molecule in the condensed phase. The fluctuation of the polarizability at each position in the scattering volume was found to dominantly affect local-field fluctuation. The concentration dependence of the depolarization ratio for the ν_1 Raman line of carbon tetrachloride in a carbon disulfide solution could be well described by this expression.

The depolarization ratio of Raman spectra, ρ, for linear polarized incident light sources is defined as

$$\rho=\frac{3\gamma^2}{45\bar{\alpha}^2+\gamma^2}, \tag{1}$$

where

$$\bar{\alpha}\equiv\frac{1}{3}(\alpha'_{xx}+\alpha'_{yy}+\alpha'_{zz})$$

and

$$\gamma^2\equiv[(\alpha'_{xx}-\alpha'_{yy})^2+(\alpha'_{yy}-\alpha'_{zz})^2+(\alpha'_{zz}-\alpha'_{xx})^2].$$

Here, $\alpha'_{\sigma\rho}$ is the $\sigma\rho$-component of the Raman scattering tensor. Using this relation, ρ can supply much useful information concerning molecular structure. It is easy to imagine that ρ also includes information about intermolecular interactions and/or the aggregation structure of molecules in condensed phases. The depolarization ratio of the ν_1 Raman line of liquid carbon tetrachloride is an example of such phenomena. This depolarization ratio should be exactly zero in an isolated molecule, since the relation $\alpha'_{xx}=\alpha'_{yy}=\alpha'_{zz}$ is satisfied. However, it has been reported by many authors[1-6] that the depolarization ratio has an experimental value that is not exactly zero. The isotropic effects of chlorine atoms were quantitatively analyzed and were found to contradict information regarding the origin of this finite value of ρ.[7,8] This ρ value came to be considered to originate from some intermolecular interactions. Its detailed mechanism, however, had not been discussed until a report concerning the fluctuation of the local field[9] appeared.

Hyodo and Fujiyama proposed a model for explaining this finite value of the depolarization ratio.[9] They considered that a molecule is subjected to both the direct field of a light wave and to an indirect field caused by the dipoles of surrounding molecules induced by the light wave field. Such a field as the latter is a so-called "local field." In this case, it depends only on the relative positions of the molecules surrounding the central molecule, because both the polarizability tensor and its derivative with respect to the ν_1 normal coordinate have spherical symmetry. The local field fluctuates by some magnitudes and directions because of the thermal motion of molecules, therefore causing finite depolarized scattering. Nishikawa and Iijima[10] calculated this depolarization ratio based on the formula of Hyodo and Fujiyama. Their own local-lattice structure model for liquid carbon tetrachloride was found to be quantitatively describable as the observed depolarization ratio. The pressure dependence of this depolarization ratio could be explained by a local field fluctuation up to 10^8 Pa by Ikawa and Whalley.[5] This fluctuation was also found to significantly affect the solvent-mixing fraction dependence of the depolarization ratio for the ν_1 Raman line of the perchlorate anion in mixed-solvent solutions of lithium perchlorate.[11]

On the other hand, Murphy et al. reported the concentration dependence of the depolarization ratio of the ν_1 Raman line of carbon tetrachloride in various binary solutions.[3] Unfortunately, however, the formula of Hyodo and Fujiyama was derived under the assumption that explicit information of the local structure is known. Since the proposed explicit structure models are based on X-ray diffraction data for pure liquid carbon tetrachloride,[12-14] this formula is numerically calculable. The local structure in a solution, on the other hand, seems to be very complicated because of the many possible combinations of multicomponent species. The formula of Hyodo and Fujiyama may be too hard to apply solutions.

One possible idea regarding its formulation has a similar basis as work undertaken by Ladanyi and Keyes[15-18] just before the local lattice model[9] was proposed. Their work concerned the local field effect on the Rayleigh scattering intensity. They explained and averaged from the standpoint of statistical mechanics the effect of induced polarization on each molecule, as well as the treated electric field induced from the dielectric continuum, and obtained a detailed, accurate expression of the local field effect on the light scattering intensities. The local field effect on the Raman scattering intensity seems to be explained in a similar way. However, the local field effect of Ladanyi and Keyes cannot be expected on

Raman lines in usual liquids or solutions, since the term of intermolecular interaction among permanent dipoles has significant effects on the intensity of Raman scattering in such cases. Computer simulation is an indispensable process because it gives terms which cannot be extracted from experiments.[19] In the present article, a formulation similar to that of Ladanyi and Keyes is applied to the expression of the fluctuation of the local field on the Raman scattering intensity. An equation with only experimentally observable quantities can be derived by transforming their expression into an expression that is slightly rougher.

The effect of the local field was first introduced by Kakimoto et al. in order to explain the depolarization ratio of the ν_1 Raman line of a T_d molecule with concentration dependence.[20] However, their idea included no consideration of the fluctuation in a medium. Their work caused some confusion because of its failure to consider fluctuation effects. Although the formulation of the present work is essentially different from theirs, it is much indebted to their preliminary work which established the problem.

In the present article, we have tried to express the fluctuation of the local field in a binary solution without any detailed information concerning the local structure. The local field fluctuation was formulated by including terms involving the fluctuation of the polarizability at each position in the scattering volume. A solution consisting of carbon tetrachloride and carbon disulfide was considered to be an ideal mixing solution. This is the reason why the solution was chosen in the present study.

Experimental

All of the chemicals used in the present study were commercially available products without further purifications. The concentrations of involved solutions were $x_{CCl_4}=1.0$, 0.8, 0.6, 0.4, and 0.2, where x_{CCl_4} is the mole fraction of carbon tetrachloride in a carbon disulfide solution.

The polarized and depolarized components of the ν_1 Raman line of carbon tetrachloride were measured with an NR-1000 system (Japan Spectroscopic Co., Ltd.). The 488 nm line of an Ar^+ laser (NEC, GLG 3300) was used as the excitation light source at 700 mW power. Polarization measurements were made using a Kenko PL filter mounted in the pathway of the scattered light. The slit widths of the double monochromator were chosen to be 250, 500 (with two slits), and 250 μm for the incident, middle and exit slits, respectively. The slit height was set at 1 mm. The Raman spectra were recorded at 25 °C.

The extinction coefficient of the polarization filter, β, and the transmittance ratio of the spectrometer for the polarized and depolarized components, γ, were simultaneously determined using a W-X lamp (The Eppley Lab., Inc.) at the peak position of a ν_1 Raman line (ca. 460 cm^{-1}) with 488 nm excitation. These instrumental factors were determined by a method which used a relation among the expected intensities from different polarization configurations. This relation with two polarization filters completely identical with each other is presented in Ref. 21 (also see Appendix). The instrumental factors, β and γ, thus obtained, were used for an intensity data correction. The depolarization ratio of a Raman line, ρ, is determined with β and γ, as

$$\rho=\frac{1}{\gamma}\frac{I_{\perp}-\beta I_{/\!/}}{I_{/\!/}-\beta I_{\perp}}, \tag{2}$$

where $I_{\perp}$ and $I_{/\!/}$ are the integrated depolarized and polarized intensities for this Raman line, respectively.

Theoretical

The intensity of Raman scattering is proportional to the mean-square polarization induced on molecules with a respective Raman frequency. Polarization measurements decompose this intensity to the components of a laboratory-fixed Cartesian coordinate system (X, Y, Z). When linear polarized incident light is used, the polarized and depolarized components of the scattering light are parallel and perpendicular, respectively, to the direction of the incident light polarization. For the ν_1 Raman line of a T_d molecule, the symmetry of the molecular vibration shows no intensity for the depolarized components, as can be seen from eq. 1. The possible depolarized intensity of this Raman line is produced by symmetry degradation due to some kind of intermolecular interaction or local field and its fluctuation. In order to estimate the effect of the local field on the depolarized intensity, the mean-square value of the local field is given in this section.

Consider a molecule i at a position $\boldsymbol{R}_i$ in a scattering volume v. This molecule feels a local field originating from induced polarization at each position $\boldsymbol{R}$ in v. The local field fluctuates in both magnitude and direction, depending on the molecular arrangement around $\boldsymbol{R}_i$. If we choose the incident light beam as being Z-polarized, the depolarized components of the Raman intensity are X- and Y-polarized. A component of the coordinate (X, Y, or Z) is denoted here as g. Assuming isotropic polarizability for all positions, the g-component of the local field, $F_g(\boldsymbol{R}_i)$, is expressed as

$$F_g(\boldsymbol{R}_i)=\int_v \alpha(\boldsymbol{R})\, l_{gZ}(\boldsymbol{R}-\boldsymbol{R}_i)\, \mathrm{d}\boldsymbol{R}. \tag{3}$$

For this simplified expression, the component of the dipole operator tensor, $l_{gg'}(\boldsymbol{r})$, is defined by

$$l_{gg'}(\boldsymbol{r})=\frac{3\, r_g r_{g'}-\delta_{gg'}r^2}{r^5}, \tag{4}$$

where

$$r\equiv|\boldsymbol{r}|=\sqrt{r_X{}^2+r_Y{}^2+r_Z{}^2}.$$

Here, $\delta_{gg'}$ is the Kronecker delta. Equation 3 is integrated in order to consider the contribution of the polarizabilities on all positions. If we take the molecular viewpoint, this integration must be substituted by a summation over all positions of the molecules. However, to actually carry out this summation, detailed information is necessary concerning the molecular arrangement. Integration over all positions, including the no-molecule point, is carried out for the expression of the local field in Eq. 3. In the case of isotropic polarizability, the depolarization ratio, ρ, of the Raman line noticed here can be calculated as

$$\rho=\frac{4\langle F_{g'}^2\rangle}{1+4\langle F_Z^2\rangle}, \tag{5}$$

where g' is X or Y and the brackets $\langle\cdots\rangle$ denote the averaging value over all possible arrangements of the molecules. Factor 4 in Eq. 5 arises from the fact that the two frequency components, Rayleigh and Raman parts, of both $F_{g'}$ and F_Z contribute to the intensity of this Raman line in apparently the same way,[9] as shown in Eq. 5. Here, $\alpha(\boldsymbol{R})$ is decomposed into two parts: an invariable part, $\bar{\alpha}$, and a fluctuating part, $\Delta\alpha(\boldsymbol{R})$. $F_g(\boldsymbol{R}_i)$ can be rewritten as

$$\begin{aligned}F_g(\boldsymbol{R}_i)&=\bar{\alpha}\int_v l_{gZ}(\boldsymbol{R}-\boldsymbol{R}_i)\mathrm{d}\boldsymbol{R}+\int_v \Delta\alpha(\boldsymbol{R})\, l_{gZ}(\boldsymbol{R}-\boldsymbol{R}_i)\mathrm{d}\boldsymbol{R}\\&=\int_v \Delta\alpha(\boldsymbol{R}) l_{gZ}(\boldsymbol{R}-\boldsymbol{R}_i)\mathrm{d}\boldsymbol{R},\end{aligned} \tag{6}$$

where the integral of $l_{gZ}(\boldsymbol{R}-\boldsymbol{R}_i)$ is zero when the explicit expression of Eq. 4 is considered. If the correlation of the space dependence of $\Delta\alpha(\boldsymbol{R})$ is neglected, the mean-square value of $F_g(\boldsymbol{R}_i)$ is

$$\begin{aligned}\langle\{F_g(\boldsymbol{R}_i)\}^2\rangle&=w\int_v \mathrm{d}\boldsymbol{R}'\int_v \langle\{\Delta\alpha(\boldsymbol{R})\, l_{gZ}(\boldsymbol{R}-\boldsymbol{R}_i)\}^2\rangle\, \mathrm{d}\boldsymbol{R}\\&\quad+w\iint_{\boldsymbol{R}'\neq\boldsymbol{R}} \langle\Delta\alpha(\boldsymbol{R})\, \Delta\alpha(\boldsymbol{R}')\, l_{gZ}(\boldsymbol{R}-\boldsymbol{R}_i)\, l_{gZ}(\boldsymbol{R}'-\boldsymbol{R}_i)\rangle\, \mathrm{d}\boldsymbol{R}\, \mathrm{d}\boldsymbol{R}'\\&=w\int_v \mathrm{d}\boldsymbol{R}'\int_v \langle\{\Delta\alpha(\boldsymbol{R})\}^2\rangle\, \{l_{gZ}(\boldsymbol{R}-\boldsymbol{R}_i)\}^2\, \mathrm{d}\boldsymbol{R},\end{aligned} \tag{7}$$

where w is a statistical weight. Since the dipole operator tensor, of course, does not depend on the molecular arrangement, the averaging procedure affects only $\{\Delta\alpha(\boldsymbol{R})\}^2$ in Eq. 7. The last expression of Eq. 7 is derived from this fact. On the other hand, the homogeneity of the medium allows one to replace $\langle\{\Delta\alpha(\boldsymbol{R})\}^2\rangle$ with $\langle(\Delta\alpha)^2\rangle$, a position-independent mean-square quantity of $\Delta\alpha$. Equation 7 can be expressed by

$$\langle\{F_g(\boldsymbol{R}_i)\}^2\rangle=w\langle(\Delta\alpha)^2\rangle\int_v \mathrm{d}\boldsymbol{R}'\int_v \{l_{gZ}(\boldsymbol{R}-\boldsymbol{R}_i)\}^2\, \mathrm{d}\boldsymbol{R}. \tag{7'}$$

If the assumption of the space-independence of the $\Delta\alpha(\boldsymbol{R})$ correlation in Eq. 7 is rejected, details concerning the distribution functions are required. The contribution of the pair-distribution function is considered in Ref. 9 and that of the triplet-distribution function is discussed in Ref. 6. Equation 7′ can be calculated numerically using the formula $l_{gZ}(\boldsymbol{R}-\boldsymbol{R}_i)$. For multi-component systems, however, the integration ranges for each component are different from each other, since the radial part of this integral is restricted by the smallest distance between pairing molecules. The correlation between $\langle\{\Delta\alpha(\boldsymbol{R})\}^2\rangle$ and the integration range, therefore, still holds for multi-component systems. For one-component systems, the problem concerning the integration range is not very complicated. Equation 7′ is rewritten here for one-component systems. In order to consider the discreteness of molecules, the polarizability, α_ϕ, at a no-molecule point is introduced. At that point, α_ϕ is obviously zero. When the probability of finding a molecule at the position is denoted as P, $\bar{\alpha}$, and $\langle(\Delta\alpha)^2\rangle$ are expressed as

$$\bar{\alpha}=P\alpha_M+(1-P)\alpha_\phi=P\alpha_M \tag{8}$$

and

$$\begin{aligned}\langle(\Delta\alpha)^2\rangle&=P\,(\bar{\alpha}-\alpha_M)^2+(1-P)\,(\bar{\alpha}-\alpha_\phi)^2\\&=P\,(\bar{\alpha}-\alpha_M)^2+(1-P)\,(P\alpha_M)^2\\&=P\,(1-P)\,\alpha_M{}^2.\end{aligned} \tag{9}$$

Here, α_M is the polarizability of the molecule in this one-component system. By inserting Eq. 9 into Eq. 7′ and integrating Eq. 7′, the mean-square value of $F_g(\boldsymbol{R}_i)$ for one-component systems can be written as

$$\langle\{F_g(\boldsymbol{R}_i)\}^2\rangle=CP\,(1-P)\alpha_M{}^2N_A{}^2(d/M)^2, \tag{10}$$

where

$$C=\begin{cases}2\,\pi^2/15 & \text{for } g=x \text{ or } y.\\ 8\,\pi^2/45 & \text{for } g=z\end{cases}$$

Further, N_A, d, and M are Avogadro's number, the density of this system, and the molecular weight of the component molecule, respectively. In the derivation of Eq. 10, the following relations were used:

$$\frac{4\pi}{3}a^3 N_A=\frac{M}{d}$$

and

$$w=\frac{\langle n\rangle}{v}=N_\mathrm{A}\frac{d}{M}=\left(\frac{4\pi}{3}a\right)^{-1},$$

where a and $\langle n\rangle$ are the molecular radius and the mean-number of molecules in volume v. The range of integration, as well as the radial part of the integral in Eq. 7′, was taken from $2a$ to infinity.

The quantities of molecules are included in Eq. 10 as α_M, d, and M. A new variable, Q, is introduced in Eq. 11 in order to calculate Eq. 7′ for multi-component systems, although the problem concerning the range of integration cannot be determined yet.

$$Q\equiv\alpha_M\, N_\mathrm{A}\, d/M. \tag{11}$$

Using this variable, Q, we can assume that Eq. 7 is transformed into

$$\langle\{F_g(\boldsymbol{R}_i)\}^2\rangle=C\,\langle(\Delta Q)^2\rangle. \tag{12}$$

Equation 12 is similar to Eq. 10 derived from Eqs. 8 and 9 in the relation between $\bar{Q}$ and $\langle(\Delta Q)^2\rangle$. The use of Q for each component makes it possible to express the complicated relation of Eq. 7′ without any knowledge of the correlation between $\langle(\Delta\alpha)^2\rangle$ and the range of integration in this equation. Therefore, the following relations are expected to hold for a binary solution with A and B components:

$$\overline{Q}=P\{x_{\mathrm{A}}Q_{\mathrm{A}}+(1-x_{\mathrm{A}})Q_{\mathrm{B}}\}+(1-P)\,Q_{\phi} \tag{13}$$

and

$$\langle(\Delta Q)^2\rangle=P\,\{x_{\mathrm{A}}(\overline{Q}-Q_{\mathrm{A}})^2+(1-x_{\mathrm{A}})(\overline{Q}-Q_{\mathrm{B}})^2\}+(1-P)(\overline{Q}-Q_{\phi})^2, \tag{14}$$

where $Q_{\phi}=0$ because $\alpha_{\phi}=0$. x_{A} is the mole fraction of component A. If analytical transformations are made for Eq. 14, the following relation is derived:

$$\langle\{F_g(\boldsymbol{R}_i)\}^2\rangle=C[P^2(Q_{\mathrm{A}}-Q_{\mathrm{B}})^2\,x_{\mathrm{A}}\,(1-x_{\mathrm{A}})+P\,(1-P)\,\{(Q_{\mathrm{A}}^2-Q_{\mathrm{B}}^2)\,x_{\mathrm{A}}+Q_{\mathrm{B}}^2\}]. \tag{15}$$

The equality between Eqs. 15 and 10 is confirmed again when $x_{\mathrm{A}}=1$.

A simpler formulation can be taken if the range of integration is ignored. However, the lower limit of the integration range as well as the radial part of the integral in Eq. 7′ must be given as the mean-value of the nearest-neighbor distances in this case. Since $l_{gZ}(\boldsymbol{R}-\boldsymbol{R}_i)$ takes a large value at short distances, the contribution of a component molecule of smaller size cannot be satisfactorily considered in this treatment. A schematic view of this problem is given in Fig. 1. As a possible formula based on the above simpler formulation, the following expression can be derived:

$$\langle\{F_g(\boldsymbol{R}_i)\}^2\rangle=C[P^2(\alpha_{\mathrm{A}}-\alpha_{\mathrm{B}})^2\,x_{\mathrm{A}}\,(1-x_{\mathrm{A}})+P\,(1-P)\,\{(\alpha_{\mathrm{A}}^2-\alpha_{\mathrm{B}}^2)\,x_{\mathrm{A}}+\alpha_{\mathrm{B}}^2\}]\times N_A\,[\overline{d}/\{M_{\mathrm{A}}\,x_{\mathrm{A}}+M_{\mathrm{B}}\,(1-x_{\mathrm{A}})\}]^2, \tag{16}$$

where $\overline{d}$ is the system density. The error originating from adopting the mean nearest-neighbor distance is not thought to be very large when $x_{\mathrm{A}}\approx1$ and 0, since $\overline{d}\approx d_{\mathrm{A}}$ when $x_{\mathrm{A}}\approx1$ and $\overline{d}\approx d_{\mathrm{B}}$ when $x_{\mathrm{A}}\approx0$. On the other hand, Eq. 16 can be underestimated when $0<x_{\mathrm{A}}<1$, since this equation omits part of the contribution of $l_{gZ}(\boldsymbol{R}-\boldsymbol{R}_i)$ at short distances (The shaded

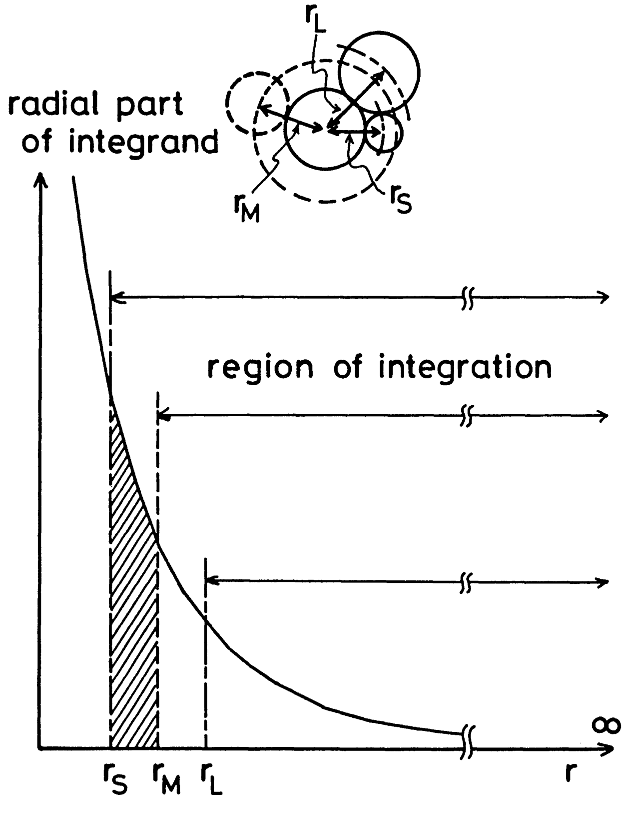

Fig. 1. Schematic view of the problem on the lower limit of the integration range along with the radial part of the integral in Eq. 7. r_M: mean-value of nearest-neighbor distances. r_S:. nearest-neighbor distance between the T_{d} molecule and a component molecule of smaller size. r_L: nearest-neighbor distance between the T_{d} molecule and a component molecule of larger size. Shaded regions were parts omitting the contribution of integrand for the formulation with the mean-value of nearest-neighbor distances.

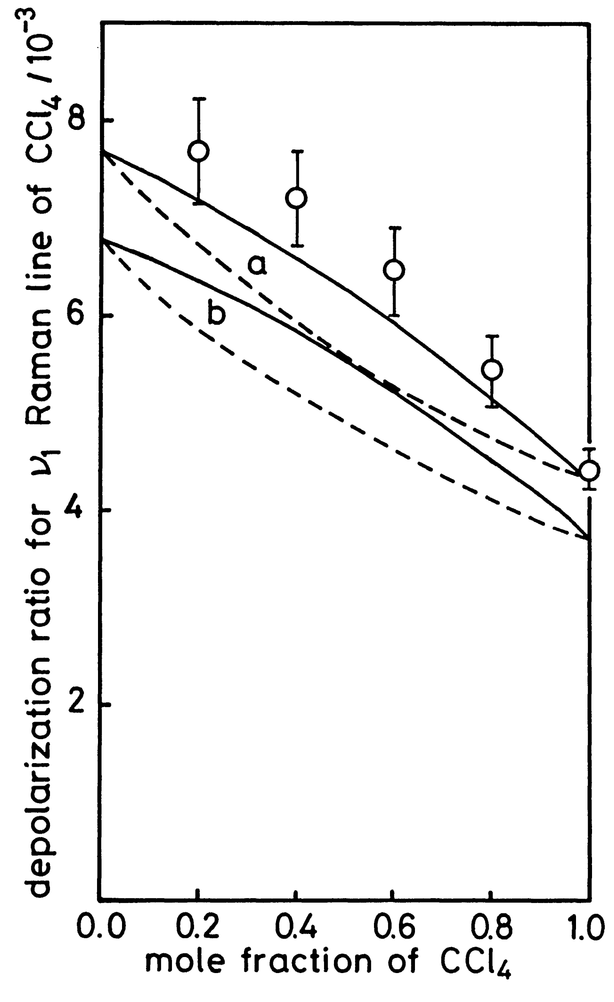

Fig. 2. Observed and calculated depolarization ratios of the ν_1 Raman line of carbon tetrachloride in carbon disulfide solution. Circles with error bars are observed values. Straight and broken lines are curves calculated by Eqs. 15 and 16, respectively. Lines marked "a" are the values for P=0.74, while those marked "b" are the values for P=0.68.

region in Fig. 1). Therefore, we must notice that Eq. 16 possibly gives less quantitative results, except for a system constructed using components of similar size.

The use of distribution functions can result in another explicit formulation of $\langle\{F_g(\boldsymbol{R}_i)\}^2\rangle$ based on some fundamentals from statistical mechanics. Equation 15 is substituted for that derived from this formulation. One example of the use of distribution functions for a pure liquid was given in a previous report.[9] However, numerical calculations using this formulation are impossible if explicit information concerning the distribution functions is not given for an object system. This proves that Eq. 15 is useful.

Results and Discussion

Figure 2 shows the depolarization ratio, ρ, of the ν_1 Raman line of carbon tetrachloride against the mole fraction, x_{CCl_4}, of carbon tetrachloride in carbon disulfide solutions. The instrumental factors of Eq. 2 for deriving the depolarization ratios, β and γ, resulted in 0.0021 and 0.360, respectively, at the wavelength of this Raman line with 488 nm excitation. The observed depolarization ratios are indicated by open circles with a vertical bar through them. These vertical bars indicate the statistic errors, which include the uncertainties of the β and γ values. The observed depolarization ratios increase with the carbon tetrachloride diluted with carbon disulfide along with a curve opening downwards. The extrapolation of this curve to infinite dilution almost duplicates the depolarization ratio of neat carbon tetrachloride. These depolarization ratios agreed fairly well with the previously reported data.[3,22]

The depolarization ratios calculated using Eqs. 15 and 5 are also shown in Fig. 2 as straight lines. The parameters used for these calculations are listed in Table 1. The density data were obtained from Ref. 24. The probability of finding a molecule, P, was defined by simple geometrical calculations for the occupation volume of hard spheres in three types of packing. Calculations regarding two cases of the P value are shown in Fig. 2. The cases for *fcc* and *hcp* are indicated as a, while that for *bcc* is indicated as b. The results obtained by using Eq. 16 are also shown in Fig. 2, as indicated by broken lines in the same manner as those from Eq. 15. The density data were interpolated between each pair of neighboring data points for calculations using Eq. 16.

The observed relation between the depolarization ratio and the mole fraction, ρ-x_{CCl_4}, can be well explained by Eq. 15, because the factor of x_A $(1-x_A)$ must have a positive value. Putting the parameters listed in Table 1 into Eq. 15, the depolarization ratio when $x_{CCl_4}\approx0$ is found to be almost twice as large as that when $x_{CCl_4}\approx1$. The calculated curves of Eq. 15 satisfy the experimental ρ-x_{CCl_4} relation for both the P values adopted here. An X-ray diffraction study[10] confirmed that the local structure of pure liquid carbon tetrachloride ($x_A=1$) is *bcc*. A more explicit expression for the depolarization ratio than that given in the present article resulted in 0.0042, supporting the local *bcc* model.[6,10] The calculated value for $P=0.74$ (*fcc* and *hcp* cases) at $x_A=1$ must be considered to accidentally agree with the observed value. It is not known why these two P values are adopted quantitatively. However, Eq. 15 is sufficiently qualitative to express the observed concentration dependence of the depolarization ratio.

The calculated depolarization ratios of Eq. 16 with both two P values show curves opening upwards, although those of Eq. 15 are curves opening downwards. Since the polarizability fluctuation term in Eq. 16 shows a curve opening downwards, the figured tendency that Eq. 16 shows must be dominantly described by the term involving the mean density of these solutions. The use of the mean density of the solution omits the contribution of a component at short distances, as was stated in the previous section. A qualitative disagreement of Eq. 16 with the observed data, therefore, occurs. This fact seems to stress the necessity for considering the nearest-neighbor distances in binary solutions.

It was found that Eq. 15 qualitatively predicts the fluctuation of the local field by comparing the observed and calculated depolarization ratios of the ν_1 Raman line of carbon tetrachloride in carbon disulfide solution. Also, the agreement between those values was observed within about 10% each for the cases of the different P values, although no quantita-

Table 1. Parameters in Eqs. 15 and 16 for Binary Solution of Carbon Tetrachloride and Carbon Disulfide

			CCl_4		CS_2
Polarizability[a] (α_M/Å^3)			10.5		8.74
Molecular weight (M/g mole^{-1})			154		76
Mole fraction (x_{CCl_4})	1.00	0.75	0.40	0.16	0.00
Density[b] ($\bar{d}$/g cm^{-3})	1.5845	1.5237	1.4197	1.3310	1.2558
P		0.74 for *fcc* and *hcp* packing 0.68 for *bcc* packing			

a) Ref. 23. The trace of the polarizability tensor was taken for carbon disulfide. b) Ref. 24.

tiveness of the theoretical accuracies was guaranteed. As a result, the sufficiency of Eq. 15 was not very bad regarding quantitativeness. The derivation of Eq. 15 was made for completely random mixing. Fortunately, this equation can easily be expanded to involve solutions containing an ideal associated complex[25] by redefining the concentration of the respective species under consideration in which the associating species are treated as being different ones from the individual component. This fact shows that the concentration dependences of the depolarization ratio are different, depending on the system with different association numbers. The determination of the association number must be made experimentally using Eq. 15. This determination is one of the most difficult problems to be solved, because of the insufficient experimental accuracies of our instrumental set-up.

Concluding Discussion

The fluctuation of the local field was expressed in terms of the fluctuation of the polarizability at each position in the scattering volume. The formulation was made by distinguishing the positions with the polarizabilities of molecules from that of a vacancy, in order to take the discreteness of molecules into account. This expression was found to explain well the concentration dependence of the depolarization ratio of the ν_1 Raman line for carbon tetrachloride in carbon disulfide solutions. This concentration dependence cannot be analyzed using the previously proposed local lattice model,[9] without any explicit information concerning the local structure in each solution. The shape of carbon disulfide was assumed to be spherical, and the probability of finding molecules was considered to have no concentration dependence in this formulation. Therefore, the estimation with this expression seems to be very rough. However, the result of the estimation agreed well with the observed concentration dependence of this depolarization ratio. This result indicated that the finite size of a molecule essentially affects the magnitude of the fluctuation of the local field.

The fluctuation of the local field is affected mainly by the region including the first and second nearest-neighbor molecules around each molecule, because this can be calculated using the mean-square values of the dipolar field created by surrounding molecules. Therefore, the fluctuation of the local field suggests the structure of local molecular arrangements. In the present states, the fluctuation of the local field is found to be reflected only in the depolarization ratio of the ν_1 Raman line for T_d molecules. Consequently, the present study indicates that, regardless of the above-mentioned restriction, studies concerning the local field fluctuation are useful for evaluating model systems for discussions concerning the local structure of solution states.

The author is indebted to Dr. Tomohiko Yamazaki of Toyota Central Research and Development Laboratories, Inc. (TCRDL) for his invaluable assistance with the REDUCE operations, of which results are summarized in the Appendix. The author wishes to thank Professor Tadashi Kato of Tokyo Metropolitan University for directing his attention to the papers on the Rayleigh light scattering intensity. The author also thanks Dr. S. Noda and Dr. A. Isogai of TCRDL for their encouragement of this work, and the director of TCRDL for permission to publish this work.

Appendix

This Appendix presents a determination method of the extinction coefficient of the polarization filter, β, and the transmittance ratio of the spectrometer for polarized and depolarized components, γ.

The transmittance ratio, γ, is defined by

$$\gamma \equiv \tau_\perp / \tau_{\parallel}, \tag{A1}$$

where $\tau_\perp$and $\tau_{\parallel}$ are the transmittances of linear polarized lights which are perpendicular and parallel to the slit of the spectrometer. The observed intensities of these two linear polarized components, $I_\perp^{\text{obsd}}$ and $I_{\parallel}^{\text{obsd}}$, are expressed as

$$I_\perp^{\text{obsd}} = t\,\beta\, I_{\parallel}^{\circ}\,\tau_{\parallel} + t\, I_\perp^{\circ}\,\tau_\perp \tag{A2-a}$$

and

$$I_{\parallel}^{\text{obsd}} = t\, I_{\parallel}^{\circ}\,\tau_{\parallel} + t\,\beta\, I_\perp^{\circ}\,\tau_\perp, \tag{A2-b}$$

where t is the transmittance of the polarization filter and superscript $^\circ$ denotes the true intensities. Moreover, the conditions with two polarization filters are considered. The observed intensity is denoted as $I_{\perp\parallel}^{\text{obsd}}$ when one filter is set perpendicular and the other parallel to the slit; it is denoted as $I_{\perp\perp}^{\text{obsd}}$ when both filters are set perpendicular to the slit. These two intensities are expressed as

$$I_{\perp\parallel}^{\text{obsd}} = t_1 t_2 (\beta_1\, I_{\parallel}^{\circ}\,\tau_{\parallel} + \beta_2\, I_\perp^{\circ}\,\tau_\perp) \tag{A3-a}$$

and

$$I_{\perp\perp}^{\text{obsd}} = t_1 t_2 (\beta_1\,\beta_2\, I_{\parallel}^{\circ}\,\tau_{\parallel} + \beta_2\, I_\perp^{\circ}\,\tau_\perp) \tag{A3-b}$$

where subscript 1 and 2 denote the two different polarization filters.

If these two polarization filters are completely identical, the following relations are satisfied:

$$t_1 = t_2 \equiv t \text{ and } \beta_1 = \beta_2 \equiv \beta. \tag{A4}$$

For this condition, the extinction coefficient of the polarization filter, β, can be expressed as

$$\beta = \frac{(1-u+v+uv) \pm \sqrt{(1-u+v+uv)^2 - 4u^2}}{2u}, \tag{A5}$$

where

$$u \equiv \frac{I_\perp^{\text{obsd}}}{I_{\parallel}^{\text{obsd}}} = \frac{\beta+\gamma}{1+\beta\gamma} \tag{A6-a}$$

and

$$v \equiv \frac{I_{\perp\perp}{}^{\mathrm{obsd}}}{I_{\perp /\!/}{}^{\mathrm{obsd}}} = \frac{\beta^2+\gamma}{\beta+\beta\gamma} \tag{A6-b}$$

Simultaneously, γ and t are

$$\gamma = \frac{u-\beta}{1-u\beta} \tag{A7}$$

and

$$\gamma = \frac{I_{/\!/}{}^{\mathrm{obsd}}+\tau_{\perp}{}^{\mathrm{obsd}}}{(1+\beta)I^{\mathrm{obsd}}}, \tag{A8}$$

where I^{obsd} is the observed intensity with no polarization filter. Equations A5-A8 were previously described in Ref. 21.

However, since it is very difficult to obtain two completely identical polarization filters, we analyzed expressions of the observed intensitites without the relations A4. An analysis of the expressions was made using the following definitions:

$$u_i = \frac{\beta_i+\gamma}{1+\beta_i\gamma}, \quad (i=1, 2) \tag{A9}$$

$$v_{12} = \frac{\beta_1\beta_2+\gamma}{\beta_1+\beta_2\gamma}, \tag{A10}$$

$$\beta_1 \equiv \beta, \tag{A11}$$

and

$$\beta_2 \equiv \beta+\beta'. \tag{A12}$$

REDUCE ver. 3.0, a computer language for mathematical analysis, was operated on a computer, IBM 3083. Equations All and A12 are essential for solving the expressions, because of the complexity of the relations. The results of the analysis are

$$\begin{aligned}\beta = [&(u_1^2u_2v_{12}-u_1^2u_2+2u_1u_2+u_2v_{12}+u_2+u_1^2v_{12}-u_1^2-2u_1v_{12}-v_{12}-1)\\ &\pm(u_1+1)\{(v_{12}+1)(u_1-1)\\ &\times(u_1u_2^2v_{12}-3u_1u_2^2-u_2^2v_{12}-u_2^2+2u_1u_2v_{12}+2u_1u_2\\ &+2u_2v_{12}+2u_2-3u_1v_{12}+u_1-v_{12}-1)\}^{1/2}]\\ &\div\{2u_1(u_1u_2+u_2v_{12}-u_1v_{12}-1)\},\end{aligned} \tag{A13}$$

$$\beta' = \frac{(1+\beta\gamma)u_2-(\beta+\gamma)}{1-\gamma u_2}, \tag{A14}$$

and

$$\gamma = \frac{u_1-\beta}{1-u_1\beta} = \frac{u_2-(\beta+\beta')}{1-u_2(\beta+\beta')}. \tag{A15}$$

Usually, $u_i \approx \gamma \approx 1$, $\beta \ll 1$, and $v_{12} \gg 1$. Therefore, sufficient care concerning the experimental accuracy must be taken when determinating these equations.

References

1) A. E. Douglas and D. H. Rank, *J. Opt. Soc. Am.*, **38**, 281 (1948).

2) J. Brandmüller, K. Burchardi, H. Hacker, and H. W. Schrötter, *Z. Angew. Phys.*, **22**, 177 (1967).

3) W. F. Murphy, M. W. Evans, and P. Bender, *J. Chem. Phys.*, **47**, 1836 (1967).

4) K. Fukushi and M. Kimura, *J. Raman Spectrosc.*, **8**, 125 (1979).

5) S. Ikawa and E. Whalley, *J. Chem. Phys.*, **89**, 51 (1988).

6) S. Hyodo, N. Tatsuta, and T. Okamoto, *J. Chem. Phys.*, **92**, 882 (1990).

7) G. W. Chantry, *Spectrochim. Acta*, **21**, 1007 (1965).

8) A. E. Douglas and D. H. Rank, *Nature*, **162**, 453 (1948).

9) S. Hyodo and T. Fujiyama, *Bull. Chem. Soc. Jpn.*, **53**, 2456 (1980).

10) K. Nishikawa and T. Iijima, *Bull. Chem. Soc. Jpn.*, **58**, 1220 (1985).

11) S. Hyodo, *Chem. Phys. Lett.*, **161**, 245 (1989).

12) A. H. Narten, M. D. Danford, and H. A. Levy, *J. Chem. Phys.*, **46**, 4875 (1967).

13) G. Reichelt, J-U. Weidner, and H. W. Zimmermann, *Ber. Bunsen-Ges. Phys. Chem.*, **78**, 1050 (1974).

14) K. Nishikawa and Y. Murata, *Bull. Chem. Soc. Jpn.*, **52**, 293 (1979).

15) B. M. Ladanyi and T. Keyes, *Mol. Phys.*, **33**, 1063 (1977).

16) T. Keyes and B. M. Ladanyi, *Mol. Phys.*, **33**, 1099 (1977).

17) B. M. Ladanyi and T. Keyes, *Mol. Phys.*, **33**, 1247 (1977).

18) T. Keyes and B. M. Ladanyi, *Mol. Phys.*, **33**, 1271 (1977).

19) B. M. Ladanyi and T. Keyes, *J. Chem. Phys.*, **68**, 3217 (1978).

20) M. Kakimoto, T. Fujiyama, and T. Shimanouchi, unpublished results. Bunshikōzō Sōgō Tōronkai, Nagoya, 1973.

21) T. Fujiyama and M. Tasumi, *Bunkou Kenkyu*, **20**, 28 (1971).

22) F. Iida, S. Hyodo, and T. Fujiyama, unpublished results. Bunshikōzō Sōgō Tōronkai, Fukuoka, 1980.

23) Landolt-Börnstein, "Atom und Molekül Physik," 3 Teil, Molekulen II, Springer, Berlin (1951).

24) "International Critical Tables," McGraw-Hill, New York (1928), Vol. III.

25) See for example, I. Prigofine and R. Defay, "Chemical Thermodynamics," Longmans Green and Co., London (1954). Chap. 26.