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Fluctuation of Local Field and Depolarization Degree of the ν_1 Line of Carbon Tetrachloride

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The depolarization degree of a molecule having a T_d symmetry was expressed in terms of the mean square fluctuation of the local field which is felt by a molecule in the condensed phase. By the use of the mean square amplitude values observed by the X-ray diffraction method, the depolarization degree of liquid carbon tetrachloride was calculated to be 0.0021, which agrees well with the observed value of 0.0039±0.0002.

The depolarization degree of Raman scattering, ρ, can be expressed in terms of a Raman scattering tensor, $\alpha'_{\rho\sigma}$, as

$$\rho = \frac{3\gamma^2}{45\bar{\alpha}^2+4\gamma^2} \tag{1}$$

where

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

$$\gamma^2 = \frac{1}{2}[(\alpha'_{yy}-\alpha'_{zz})^2+(\alpha'_{zz}-\alpha'_{xx})^2+(\alpha'_{xx}-\alpha'_{yy})^2].$$

Therefore, the depolarization degree ρ should be exactly zero if the relation $\alpha'_{xx}=\alpha'_{yy}=\alpha'_{zz}$ is satisfied. The ν_1 Raman line of carbon tetrachloride is just such a case, because the vibration belongs to an a_1 symmetry of a tetrahedral molecule. The depolarization degree for the ν_1 line of liquid carbon tetrachloride, however, is not observed to be zero. With the improvement of Raman spectrometers and related attachements, the depolarization degree for this line has been observed at smaller and smaller values. But it was never observed to be zero. The most reliable value at present is $\rho=0.0039\pm0.0002$ which is reported by Murphy *et al.*1) The finite ρ-value for the ν_1 line is believed to be real, in other words, it cannot be ascribed to any experimental errors.

There were several reports which emphasized the effect of the symmetry degradation due to the existence of the natural abundant Cl^{37}. According to the theoretical estimation of Chantry,2) however, this effect is too small to explain the observed finite value of ρ. Douglas and Rank observed the depolarization degree of the ν_1 line of tin tetrachloride and the related isotope species and concluded that the ρ values for the three isotopic species ($SnCl_4{}^{35}$, $SnCl_3{}^{35}Cl^{37}$, $SnCl_2{}^{35}$-$Cl_2{}^{37}$) agreed with each other within the experimental error.3) This finite magnitude of depolarization degree has been thought to originate from some kinds of intermolecular interactions in the condensed phase, although no detailed mechanisms have been established yet. It will be shown in the present report that the fluctuation of local field is the main cause of the finite magnitude of depolarization degree observed for the ν_1 line of liquid carbon tetrachloride.

Intensity Expression for Raman Scattering. Consider a molecule irradiated by an incident light beam. In the condensed system, the electric field which is felt by the molecule is not the same as that of the incident light, because of the existence of the electric field produced on the surrounding molecuoes. Taking into account this situation, we first derive the Raman intensity expression for the liquid sample.

Imagine a space-fixed Cartesian coordinate system (x, y, z). A z-polarized incident light beam irradiates molecules along the negative x-direction (see Fig. 1). The electric vector of the incident light is expressed by $\boldsymbol{E}=\boldsymbol{E}_0\cos\omega_0 t$ ($\boldsymbol{E}_0=(0,\ 0,\ E_{0z})$). Consider now the scattering in the positive y-direction. The position vector of a molecule (i) is expressed by $\boldsymbol{r}_i$.

Generally, a polarizability $\boldsymbol{\alpha}$ is expanded as a power series of a normal coordinate Q_k as:

$$\boldsymbol{\alpha} = \boldsymbol{\alpha}^\circ + \sum_k\left(\frac{\partial\boldsymbol{\alpha}}{\partial Q_k}\right)_0 Q_k + \text{higher terms} \tag{2}$$

where Q_k is a normal coordinate corresponding to the k-th vibrational mode whose frequency is ω_v^k, *viz.*,

$$Q_k = Q_0{}^k\cos\omega_v^k t.$$

If we focus our attention on a particular vibrational mode and neglect the terms higher than quadratic,

$$\boldsymbol{\alpha} = \boldsymbol{\alpha}^\circ + \boldsymbol{\alpha}'\cos\omega_v t \tag{2'}$$

where

$$\boldsymbol{\alpha}' = \left(\frac{\partial\boldsymbol{\alpha}}{\partial Q}\right)_0 Q_0.$$

In the case of the ν_1 vibration of carbon tetrachloride, the tensors $\boldsymbol{\alpha}^\circ$ and $\boldsymbol{\alpha}'$ have a spherical symmetry. Therefore, we can use the scalar expressions α° and α' instead of the tensors $\boldsymbol{\alpha}^\circ$ and $\boldsymbol{\alpha}'$.

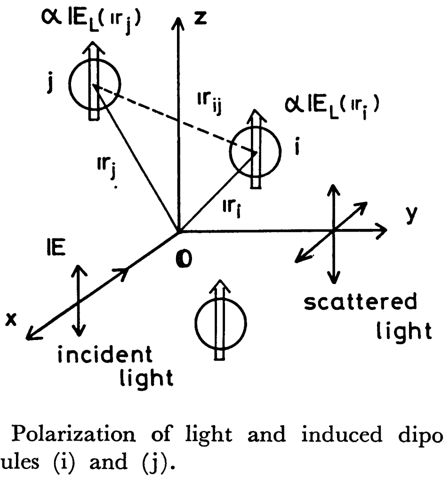


Fig. 1. Polarization of light and induced dipoles on molecules (i) and (j).

Consider a molecule (j) at $\boldsymbol{r}_j$ in the liquid phase. This molecule (j) feels the electric field $\boldsymbol{E}_L(\boldsymbol{r}_j)=\boldsymbol{E}_{L0}(\boldsymbol{r}_j)\cos\omega t$ whose frequency is the same as that of the incident light. The induced dipole, $\alpha^\circ\boldsymbol{E}_L(\boldsymbol{r}_j)$, then produces an electric field $\boldsymbol{f}(\boldsymbol{r}_i,\boldsymbol{r}_j)$ on the molecule (i) at $\boldsymbol{r}_i$. The $\boldsymbol{f}(\boldsymbol{r}_i,\boldsymbol{r}_j)$ is expressed as;

$$\begin{aligned}\boldsymbol{f}(\boldsymbol{r}_i,\boldsymbol{r}_j) &= -\frac{\alpha^\circ\boldsymbol{E}_L(\boldsymbol{r}_j)}{r_{ij}^2}+\frac{3\{(\alpha^\circ\boldsymbol{E}_L(\boldsymbol{r}_j))\cdot\boldsymbol{r}_{ij}\}\boldsymbol{r}_{ij}}{r_{ij}^5}\\ &= \alpha^\circ\boldsymbol{E}_L(\boldsymbol{r}_j)\boldsymbol{l}(\boldsymbol{r}_{ij})\end{aligned}\tag{3}$$

where

$$\boldsymbol{r}_i \equiv \boldsymbol{r}_j-\boldsymbol{r}_i$$
$$r_{ij} \equiv |\boldsymbol{r}_{ij}|$$
$$\boldsymbol{l}(\boldsymbol{r}_{ij}) \equiv \frac{3\boldsymbol{r}_{ij}\boldsymbol{r}_{ij}-r_{ij}^2\mathbf{I}}{r_{ij}^5}$$

and $\mathbf{I}$ is an unit tensor. As the molecule (i) is surrounded by many other molecules designated by (j), the electric field, $\boldsymbol{E}_L(\boldsymbol{r}_i)$, which is felt by the molecule (i) is

$$\boldsymbol{E}_L(\boldsymbol{r}_i) = \boldsymbol{E}+\sum_j\boldsymbol{f}(\boldsymbol{r}_i,\boldsymbol{r}_j).\tag{4}$$

As the $\boldsymbol{f}(\boldsymbol{r}_i,\boldsymbol{r}_j)$ of Eq. 4 is also the function of $\boldsymbol{E}_L(\boldsymbol{r}_j)$ which also has an expression like Eq. 4, the detailed expression of Eq. 4 becomes

$$\begin{aligned}\boldsymbol{E}_L(\boldsymbol{r}_i) &= \boldsymbol{E}+\sum_j\alpha^\circ\boldsymbol{E}_L(\boldsymbol{r}_j)\boldsymbol{l}(\boldsymbol{r}_{ij})\\ &= \boldsymbol{E}+\sum_j\{\boldsymbol{E}+\sum_k\alpha^\circ\{\boldsymbol{E}+\ldots\}\ldots\}\ldots\boldsymbol{l}(\boldsymbol{r}_{jk})\boldsymbol{l}(\boldsymbol{r}_{ij}).\end{aligned}\tag{5}$$

If we truncate Eq. 5 at the second term,

$$\boldsymbol{E}_L(\boldsymbol{r}_i) \cong \boldsymbol{E}+\sum_j\alpha^\circ\boldsymbol{E}\boldsymbol{l}(\boldsymbol{r}_{ij})\tag{5'}$$

and

$$\boldsymbol{f}(\boldsymbol{r}_i,\boldsymbol{r}_j) = -\frac{\alpha^\circ\boldsymbol{E}}{r_{ij}^3}+\frac{3\{(\alpha^\circ\boldsymbol{E})\cdot\boldsymbol{r}_{ij}\}\boldsymbol{r}_{ij}}{r_{ij}^5}.\tag{6}$$

We consider that the dipole moment, $\alpha'\boldsymbol{E}_L(\boldsymbol{r}_i)\cos\omega_v t$, induced onto the molecule (i) scatters Raman light following the classical scattering theory. If the phases of the molecular vibrations of component molecules are independent of each other, the Raman scattering intensity from this system is proportional to the mean square amplitude of this oscillating dipole, $\alpha'\boldsymbol{E}_{L0}(\boldsymbol{r}_i)$. It sometimes happens, however, that the oscillating dipoles induced onto different molecules have the same phase; this mechanism will be shown in what follows.

The oscillating dipole induced by the electric field $\boldsymbol{E}_L(\boldsymbol{r}_i)$ onto the molecule (i), in turn, produces the electric field, $\boldsymbol{f}'(\boldsymbol{r}_j,\boldsymbol{r}_i)$, onto the molecule (j). This electric field has the same frequency as the Raman frequencies $((\omega_0+\omega_v)$ and $(\omega_0-\omega_v))$. $\boldsymbol{f}'(\boldsymbol{r}_j,\boldsymbol{r}_i)$ is expressed as

$$\begin{aligned}\boldsymbol{f}'(\boldsymbol{r}_j,\boldsymbol{r}_i) &= \left[-\frac{\alpha'\boldsymbol{E}_L(\boldsymbol{r}_i)}{r_{ij}^3}+\frac{3\{(\alpha'\boldsymbol{E}_L(\boldsymbol{r}_i))\cdot\boldsymbol{r}_{ij}\}\boldsymbol{r}_{ij}}{r_{ij}^5}\right]\cos\omega_v t\\ &\cong \left[-\frac{\alpha'\boldsymbol{E}}{r_{ij}^3}+\frac{3\{(\alpha'\boldsymbol{E})\cdot\boldsymbol{r}_{ij}\}\boldsymbol{r}_{ij}}{r_{ij}^5}\right]\cos\omega_v t\\ &= \alpha'\boldsymbol{E}\boldsymbol{l}(\boldsymbol{r}_{ij})\cos\omega_v t.\end{aligned}\tag{7}$$

The electric field, $\boldsymbol{f}'(\boldsymbol{r}_j,\boldsymbol{r}_i)$, produces an oscillating dipole $\alpha^\circ\boldsymbol{f}'(\boldsymbol{r}_j,\boldsymbol{r}_i)$ on the molecule (j). This oscillating dipole again scatters light. following the classical scattering theory. It is important that the phase of this scattered light coincides with that of the molecular vibration of the molecule (i). This sort of light can be scattered from all the molecules (i). Thus, the observed Raman intensity is proportional to the mean square amplitude of the two kinds of oscillating induced dipoles, namely, $\alpha'\boldsymbol{E}_L(\boldsymbol{r}_i)\cos\omega_v t$ and $\alpha^\circ\boldsymbol{f}'(\boldsymbol{r}_j,\boldsymbol{r}_i)$. The sum of these induced dipoles is

$$\begin{aligned}&\alpha'\boldsymbol{E}_L(\boldsymbol{r}_i)\cos\omega_v t+\alpha^\circ\sum_j\alpha'\boldsymbol{E}\boldsymbol{l}(\boldsymbol{r}_{ij})\cos\omega_v t\\ &= \alpha'\boldsymbol{E}\cos\omega_v t+\sum_j\alpha'\alpha^\circ\boldsymbol{E}\boldsymbol{l}(\boldsymbol{r}_{ij})\cos\omega_v t\\ &\qquad +\sum_j\alpha^\circ\alpha'\boldsymbol{E}\boldsymbol{l}(\boldsymbol{r}_{ij})\cos\omega_v t\\ &= \alpha'\boldsymbol{E}\{1+2\sum_j\alpha^\circ\boldsymbol{l}(\boldsymbol{r}_{ij})\}\cos\omega_v t\\ &= \alpha'\boldsymbol{E}\{1+2\alpha^\circ\mathbf{L}(\boldsymbol{r}_{ij})\}\cos\omega_v t\end{aligned}\tag{8}$$

where

$$\mathbf{L}(\boldsymbol{r}_i) = \sum_j\boldsymbol{l}(\boldsymbol{r}_{ij}).\tag{9}$$

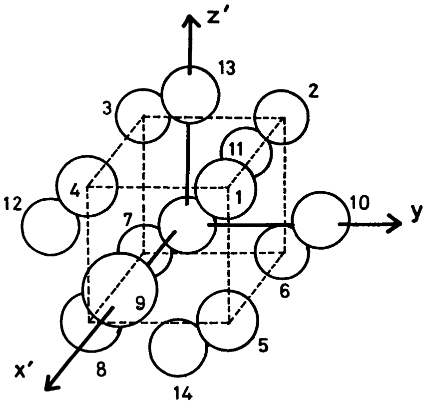
Thus, the polarized and depolarized components, I_z and I_x, of Raman scattering intensity from the liquid system can be expressed as

$$\begin{aligned}I_z &\propto (\alpha')^2\{1+4\alpha^\circ\langle \mathrm{L}_{zz}(\boldsymbol{r}_i)\rangle\\ &\qquad +4(\alpha^\circ)^2\langle(\mathrm{L}_{zz}(\boldsymbol{r}_i))^2\rangle\}E_{0z}^2\end{aligned}\tag{10-a}$$

$$I_x \propto 4(\alpha'\alpha^\circ)^2\langle(\mathrm{L}_{xz}(\boldsymbol{r}_i))^2\rangle E_{0z}^2\tag{10-b}$$

where $\mathrm{L}_{ij}(\boldsymbol{r}_i)$ represents the i,j-element of the tensor $\mathbf{L}(\boldsymbol{r}_i)$ and $\langle\ \rangle$ represents an ensemble averge. The intensity representation of Eqs. 10-a and 10-b shows that the effects of the local field on Raman intensity are completly expressed in terms of the mean and mean square values of the tensor elements, $\mathrm{L}_{ij}(\boldsymbol{r}_i)$. In order to know $\mathrm{L}_{ij}(\boldsymbol{r}_i)$, we have to know the relative molecular configuration of component molecules in the liquid system.

Calculation of $\langle L_{zz}(\boldsymbol{r}_i)\rangle$, $\langle(L_{zz}(\boldsymbol{r}_i))^2\rangle$, $\langle(L_{xz}(\boldsymbol{r}_i))^2\rangle$. The X-ray diffraction study of pure liquid carbon tetrachloride has clarified the existence of a local bcc lattice in the liquid at room temperature, as is shown in Fig. 2.[4] On the basis of this result,



(○ : carbon tetrachloride)

Fig. 2. Local bcc lattice structure of carbon tetrachloride obtained by X-ray diffraction study.[4] (x', y', z') refers to the lattice-fixed coordinate system. The moleucles (1—8) and (9—14) correspond, respectively, to the first and second nearest neighbours.

we calculate $\langle \mathrm{L}_{zz}(\boldsymbol{r}_i)\rangle$, $\langle(\mathrm{L}_{zz}(\boldsymbol{r}_i))^2\rangle$, and $\langle(\mathrm{L}_{xz}(\boldsymbol{r}_i))^2\rangle$ values originating from displacements of component molecules from the bcc structure. Putting the molecule (i) at the center, we express the relative configuration of molecules by a vector group $\{\boldsymbol{r}_{ij}\}$, where $\boldsymbol{r}_{ij}=\boldsymbol{r}_j-\boldsymbol{r}_i$. If the lattice points of the bcc lattice is represented by a vector $\boldsymbol{r}^\circ_{ij}$, the vector $\boldsymbol{r}_{ij}$ can be written as,

$$\boldsymbol{r}_{ij} = \boldsymbol{r}^\circ_{ij} + \Delta\boldsymbol{r}_{ij} \tag{11}$$

where $\Delta\boldsymbol{r}_{ij}$ is a vector which describes the relative displacement of the surrounding molecules (j) due to thermal motion from the individual lattice points.

Now, expression of $\mathrm{L}_{zz}(\boldsymbol{r}_i)$ or $\mathrm{L}_{xz}(\boldsymbol{r}_i)$ with respect to $\Delta\boldsymbol{r}_{ij}$ leads to:

$$\begin{aligned}\mathrm{L}_{zz}(\boldsymbol{r}_i) &= \sum_j l_{zz}(\boldsymbol{r}_{ij})\\ &= \sum_j \left[l_{zz}(\boldsymbol{r}^\circ_{ij}) + \left(\frac{\partial l_{zz}}{\partial \boldsymbol{r}_{ij}}\right)_0 \Delta\boldsymbol{r}_{ij} + \text{higher terms}\right]\\ &= \mathrm{L}^\circ_{zz}(\boldsymbol{r}_i) + \sum_j \left(\frac{\partial l_{zz}}{\partial \boldsymbol{r}_{ij}}\right)_0 \Delta\boldsymbol{r}_{ij} \end{aligned} \tag{12-a}$$

and

$$\mathrm{L}_{xz}(\boldsymbol{r}_i) = \mathrm{L}^\circ_{xz}(\boldsymbol{r}_i) + \sum_j \left(\frac{\partial l_{xz}}{\partial \boldsymbol{r}_{ij}}\right)_0 \Delta\boldsymbol{r}_{ij} \tag{12-b}$$

where

$$\mathrm{L}^\circ_{zz}(\boldsymbol{r}_i) = \sum_j l_{zz}(\boldsymbol{r}^\circ_{ij}) \tag{13-a}$$

$$\mathrm{L}^\circ_{xz}(\boldsymbol{r}_i) = \sum_j l_{xz}(\boldsymbol{r}^\circ_{ij}) \tag{13-b}$$

$$\left(\frac{\partial l_{\sigma\rho}}{\partial \boldsymbol{r}_{ij}}\right)_0 \Delta\boldsymbol{r}_{ij} \equiv \left(\frac{\partial l_{\sigma\rho}}{\partial r^x_{ij}}\right)_0 \Delta r^x_{ij} + \left(\frac{\partial l_{\sigma\rho}}{\partial r^y_{ij}}\right)_0 \Delta r^y_{ij} + \left(\frac{\partial l_{\sigma\rho}}{\partial r^z_{ij}}\right)_0 \Delta r^z_{ij}. \tag{14}$$

In the above equations, $l_{\sigma\rho}$ is a $\sigma\rho$-element of the tensor $\boldsymbol{l}(\boldsymbol{r}_{ij})$, and the shoulder index put on r_{ij} or Δr_{ij} distinguishes among the x, y, or z element of the vector. More detailed expressions of Eqs. 13-a and 13-b are

$$\mathrm{L}^\circ_{zz}(\boldsymbol{r}_i) = \sum_j \frac{3(r^{\circ z}_{ij})^2 - (r^\circ_{ij})^2}{(r^\circ_{ij})^5} \tag{13-a$'$}$$

and

$$\mathrm{L}^\circ_{xz}(\boldsymbol{r}_i) = \sum_j \frac{3(r^{\circ x}_{ij})(r^{\circ z}_{ij})}{(r^\circ_{ij})^5} \tag{13-b$'$}$$

where $r^{\circ x}_{ij}$ and $r^{\circ z}_{ij}$ are the x- and z-elements of a vector $\boldsymbol{r}^\circ_{ij}$.

We assume here that the molecular motions of component molecules are mutually independent and that all the displacement vectors are isotropic. This is equivalent to assuming the relations:

$$\langle\Delta\boldsymbol{r}_{ij}\rangle = 0$$

$$\langle(\Delta r^x_{ij})^2\rangle = \langle(\Delta r^y_{ij})^2\rangle = \langle(\Delta r^z_{ij})^2\rangle = \frac{1}{3}\langle(\Delta\boldsymbol{r}_{ij})^2\rangle$$

and

$$\begin{aligned}\langle\Delta r^x_{ij}\Delta r^y_{ij}\rangle &= \langle\Delta r^y_{ij}\Delta r^z_{ij}\rangle = \langle\Delta r^z_{ij}\Delta r^x_{ij}\rangle = \dots\\ &= \langle\Delta r^x_{ik}\Delta r^x_{ij}\rangle = \langle\Delta r^x_{ik}\Delta r^y_{ij}\rangle = \dots = 0.\end{aligned} \tag{15}$$

Then, the mean values in question can be expressed as:

$$\begin{aligned}\langle\mathrm{L}_{zz}(\boldsymbol{r}_i)\rangle &= \left\langle \mathrm{L}^\circ_{zz}(\boldsymbol{r}_i) + \sum_j \left(\frac{\partial l_{zz}}{\partial \boldsymbol{r}_{ij}}\right)_0 \Delta\boldsymbol{r}_{ij}\right\rangle\\ &= \mathrm{L}^\circ_{zz}(\boldsymbol{r}_i) + \sum_j \left(\frac{\partial l_{zz}}{\partial \boldsymbol{r}_{ij}}\right)_0 \langle\Delta\boldsymbol{r}_{ij}\rangle\\ &= \mathrm{L}^\circ_{zz}(\boldsymbol{r}_i)\end{aligned} \tag{16-a}$$

$$\langle(\mathrm{L}_{zz}(\boldsymbol{r}_i))^2\rangle = \{\mathrm{L}^\circ_{zz}(\boldsymbol{r}_i)\}^2 + \frac{1}{3}\sum_j \left(\frac{\partial l_{zz}}{\partial \boldsymbol{r}_{ij}}\right)_0^2 \langle(\Delta r_{ij})^2\rangle \tag{16-b}$$

and

$$\langle(\mathrm{L}_{xz}(\boldsymbol{r}_i))^2\rangle = \{\mathrm{L}^\circ_{xz}(\boldsymbol{r}_i)\}^2 + \frac{1}{3}\sum_j \left(\frac{\partial l_{xz}}{\partial \boldsymbol{r}_{ij}}\right)_0^2 \langle(\Delta r_{ij})^2\rangle. \tag{16-c}$$

On the other hand, $\langle(\Delta\boldsymbol{r}_{ij})^2\rangle$ for a molecule (j) can be expressed by the use of a polar coordinate system $(\Delta r_{ij}, \theta, \phi)$ whose origin is fixed at the individual lattice point as:

$$\langle(\Delta r_{ij})^2\rangle = \frac{\displaystyle\int_0^{2\pi}\int_0^{\pi}\int_0^{\infty}(\Delta r_{ij})^2 \exp\left(-\frac{\ln 2}{a_j^2}(\Delta r_{ij})^2\right)(\Delta r_{ij})^2 \sin\theta \, d(\Delta r_{ij})\,d\theta\, d\phi}{\displaystyle\int_0^{2\pi}\int_0^{\pi}\int_0^{\infty}\exp\left(-\frac{\ln 2}{a_j^2}(\Delta r_{ij})^2\right)(\Delta r_{ij})^2 \sin\theta \, d(\Delta r_{ij})\,d\theta\, d\phi}. \tag{17}$$

Here we assumed a Gaussian distribution for the distribution of Δr_{ij}. a_j of Eq. 17 is the half-width of the Gaussian distribution for the molecule (j). The integration of those terms related with Δr_{ij} leads to

$$\int_0^{\infty}(\Delta r_{ij})^2 \exp\left(-\frac{\ln 2}{a_j^2}(\Delta r_{ij})^2\right) d(\Delta r_{ij}) = \frac{1}{4}\sqrt{\pi}\left(\frac{\ln 2}{a_j^2}\right)^{-3/2}$$

and

$$\int_0^{\infty}(\Delta r_{ij})^4 \exp\left(-\frac{\ln 2}{a_j^2}(\Delta r_{ij})^2\right) d(\Delta r_{ij}) = \frac{3}{8}\sqrt{\pi}\left(\frac{\ln 2}{a_j^2}\right)^{-5/2}.$$

Therefore, the mean square value of the displacement vector is

$$\langle(\Delta r_{ij})^2\rangle = \frac{3a_j^2}{2\ln 2}. \tag{18}$$

In the liquid carbon tetrachloride, it is hardly possible at room temperature that the orientations of these local bcc lattices coincide with each other. It is more reasonable to assume the random orientation of the local bcc lattices. Therefore Eqs. 16-a, 16-b, and 16-c should be averaged over all the orientations of the local bcc lattices. The terms which should be averaged over all orientations are $\mathrm{L}^\circ_{zz}(\boldsymbol{r}_i)$, $\{\mathrm{L}^\circ_{zz}(\boldsymbol{r}_i)\}^2$, $\{\mathrm{L}^\circ_{xz}(\boldsymbol{r}_i)\}^2$, $(\partial l_{zz}/\partial\boldsymbol{r}_{ij})^2_0$, and $(\partial l_{xz}/\partial\boldsymbol{r}_{ij})^2_0$. It is obvious from Eqs. 13-a′ and 13-b′, however, that $\mathrm{L}^\circ_{zz}(\boldsymbol{r}_i)$, $\{\mathrm{L}^\circ_{zz}(\boldsymbol{r}_i)\}^2$, and $\{\mathrm{L}^\circ_{xz}(\boldsymbol{r}_i)\}^2$ are all zero, because $\mathrm{L}^\circ_{zz}(\boldsymbol{r}_i)$ and $\mathrm{L}^\circ_{xz}(\boldsymbol{r}_i)$ are zero as long as the molecular configuration has a point symmetry with respect to $\boldsymbol{r}_i$. Thus, it is enough to consider $(\partial l_{zz}/\partial \boldsymbol{r}_{ij})_0^2$ and $(\partial l_{xz}/\partial \boldsymbol{r}_{ij})_0^2$.

The more explicit expression of $(\partial l_{zz}/\partial \boldsymbol{r}_{ij})_0^2$ or $(\partial l_{xz}/\partial \boldsymbol{r}_{ij})_0^2$ is

$$\left(\frac{\partial l_{zz}}{\partial \boldsymbol{r}_{ij}}\right)_0^2 = \frac{9}{(r_{ij}^{\circ})^{12}}\{5(r_{ij}^{\circ z})^4 - 2(r_{i}^{\circ z})^2(r_{ij}^{\circ})^2 + (r_{ij}^{\circ})^4\} \tag{19-a}$$

$$\left(\frac{\partial l_{xz}}{\partial \boldsymbol{r}_{ij}}\right)_0^2 = \frac{9}{(r_{ij}^{\circ})^{12}}\{(r_{ij}^{\circ x})^2(r_{ij}^{\circ})^2 + (r_{ij}^{\circ z})^2(r_{ij}^{\circ})^2 + (r_{ij}^{\circ z})^2(r_{ij}^{\circ})^2 + 5(r_{ij}^{\circ x})^2(r_{ij}^{\circ z})^2\}. \tag{19-b}$$

Equetions 19-a and 19-b show that these quantities are proportional to r_{ij}^8, where r_{ij} is an intermolecular distance and, therefore, the effect of the molecules (j) rapidly decreases with the increase of the distance r_{ij}. Therefore, it is enough to consider the contribution from the first nearest neighbors (8 molecules) and the second nearest neighbors (6 molecules) in the bcc lattice. So far the relative configuration of molecules has been described in the lattice-fixed coordinate system. As Eqs. 19-a and 19-b are described in the space-fixed coordinate system, however, we have to transform the coordinates used for the expression of relative configuration from the lattice-fixed to the space-fixed coordinate system. Let the Cartesian coordinates of the molecule (i) be (x_i', y_i', z_i') and (x_i, y_i, z_i) in the lattice-fixed and space-fixed coordinate systems, respectively. If the orientation of the local bcc lattice is specified by the Eulerian angles (α, β, γ) of Fig. 3, the transformation of coordinates from (x′, y′, z′) to (x, y, z) system is given by:

$$\begin{aligned} x &= x'(\cos\alpha\cos\beta\cos\gamma - \sin\beta\sin\gamma) \\ &\quad - y'(\cos\alpha\cos\beta\sin\gamma + \sin\beta\cos\gamma) + z'\sin\alpha\cos\beta \\ y &= x'(\cos\alpha\sin\beta\cos\gamma + \cos\beta\sin\gamma) \\ &\quad - y'(\cos\alpha\sin\beta\sin\gamma - \cos\beta\cos\gamma) + z'\sin\alpha\sin\beta \\ z &= -x'\sin\alpha\cos\gamma + y'\sin\alpha\sin\gamma + z'\cos\alpha. \end{aligned} \tag{20}$$

Let the distances from the center of the molecule (i) and to the centers of its first and second nearest neighbors be d_1 and d_2, respectively. Then, the coordinates of the neighboring molecues (j) in the lattice-fixed system can be calculated easily. Insertion of these coordinate values into the relations, *e.g.*, for the eight nearest neighboring molecules,

$$\begin{aligned} \sum_j (r_{ij}^{\circ x})^2 &= \sum_j x_j^2 = \frac{8}{3}d_1^2 \\ \sum_j (r_{ij}^{\circ z})^2 &= \sum_j z_j^2 = \frac{8}{3}d_1^2 \\ \sum_j (r_{ij}^{\circ z})^4 &= \sum_j z_j^4 = \frac{8}{9}d_1^4\{1 + 4\sin^2\alpha\,(\sin^2\alpha\cos^2\gamma\sin^2\gamma \\ &\qquad + \cos^2\gamma)\} \\ \sum_j (r_{ij}^{\circ x})^2(r_{ij}^{\circ z})^2 &= \sum_j (x_j z_j)^2 \\ &= \frac{8}{9}d_1^4\{4\sin^2\alpha\cos^2\alpha\cos^2\beta(\cos^2\gamma\sin^2\gamma - 1) \\ &\qquad + 1 - 4\sin^2\alpha\sin^2\alpha\cos^2\gamma\sin^2\gamma \\ &\qquad + 4\sin^2\alpha\cos\alpha\sin\beta\cos\beta(\cos^3\gamma\sin\gamma \\ &\qquad - \cos\gamma\sin^3\gamma)\}. \end{aligned} \tag{21}$$

If we assume that the orientation of the local bcc lattice is random, the averaging of a function G(α, β, γ) over all orientations is defined by

$$\overline{G(\alpha, \beta, \gamma)} = \frac{\int G(\alpha, \beta, \gamma)\,d\Omega}{\int d\Omega} \tag{22}$$

where

$$d\Omega = \sin\alpha\, d\alpha\, d\beta\, d\gamma.$$

Inserting Eq. 21 into Eqs. 19-a and 19-b, we obtain, *e.g.*, for the eight nearest neighbors

$$\begin{aligned} \overline{\sum_j \left(\frac{\partial l_{zz}}{\partial \boldsymbol{r}_{ij}}\right)_0^2} &= \frac{9}{d_1^8}\int\left[\frac{40}{9}\{1 + 4\sin^2\alpha(\sin^2\alpha\cos^2\gamma\sin^2\gamma \right. \\ &\qquad \left. + \cos^2\alpha)\} - \frac{16}{3} + 8\right]d\Omega \Big/ \int d\Omega \\ &= 96\frac{1}{d_1^8} \end{aligned} \tag{23-a}$$

$$\overline{\sum_j \left(\frac{\partial l_{xz}}{\partial \boldsymbol{r}_{ij}}\right)_0^2} = 72\frac{1}{d_1^8} \tag{23-b}$$

and for the six second nearest neighbors

$$\overline{\sum_j \left(\frac{\partial l_{zz}}{\partial \boldsymbol{r}_{ij}}\right)_0^2} = 72\frac{1}{d_2^8} \tag{23-c}$$

$$\overline{\sum_j \left(\frac{\partial l_{xz}}{\partial \boldsymbol{r}_{ij}}\right)_0^2} = 54\frac{1}{d_2^8}. \tag{23-d}$$

Putting $a_j = l_1$ (j=1—8) for the first nearest neighbors and $a_j = l_2$ (j=9—14) for the second nearest neighbors and inserting Eqs. 18 and 23 into Eq. 16, we obtain

$$\langle L_{zz}(\boldsymbol{r}_i)\rangle = 0 \tag{24-a}$$

$$\langle (L_{zz}(\boldsymbol{r}_i))^2\rangle = \frac{1}{2\ln 2}\left\{96\frac{l_1^2}{d_1^8} + 72\frac{l_2^2}{d_2^8}\right\} \tag{24-b}$$

$$\langle (L_{xz}(\boldsymbol{r}_i))^2\rangle = \frac{1}{2\ln 2}\left\{72\frac{l_1^2}{d_1^8} + 54\frac{l_2^2}{d_2^8}\right\}. \tag{24-c}$$

Depolarization Degree. We finally obtain the expression for depolarization degree by inserting Eqs. 24-a, 24-b, and 24-c into Eq. 10:

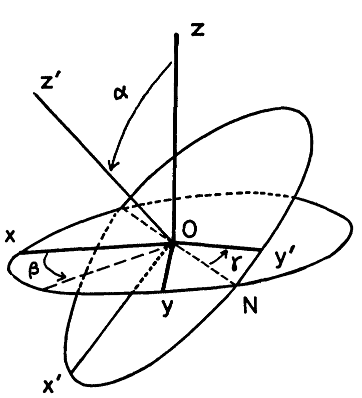


Fig. 3. Definition of Eulerian angles.
ON: Positive direction of line of nodes, the intersection of the xy and x′ y′ planes. α: Angle from Oz to Oz′ ($0 \le \alpha \le \pi$). β: Angle in xy plane from Ox to the projection Oz on the xy plane. Also angle from Oy to ON ($0 \le \beta \le 2\pi$). γ: Angle in x′ y′ plane from ON to Oy′. Also angle from projection of -z on x′ y′ plane to Ox′ ($0 \le \gamma \le 2\pi$).

$$\rho = \frac{I_x}{I_z} = \frac{\dfrac{2(\alpha^\circ)^2}{\ln 2}\left\{72\dfrac{l_1^2}{d_1^8}+54\dfrac{l_2^2}{d_2^8}\right\}}{1+\dfrac{2(\alpha^\circ)^2}{\ln 2}\left\{96\dfrac{l_1^2}{d_1^8}+72\dfrac{l_2^2}{d_2^8}\right\}}. \tag{25}$$

Eq. 25 shows that the depolarization degree ρ can be expressed in terms of the mean intermolecular distances, d_1 and d_2, the mean square amplitudes of the first and second nearest neighbors l_1 and l_2, and the polarizability, α°.

Putting the observed values of $\alpha^\circ = 10.5\ \text{Å}^3$,[5] $l_1 = 0.3\ \text{Å}$, $l_2 = 0.35\ \text{Å}$, $d_1 = 5.77\ \text{Å}$, and $d_2 = 6.77\ \text{Å}$,[4] into Eq. 25, ρ is calculated to be

$$\rho = 0.0021$$

for pure liquid carbon tetrachloride at room temperature. As the observed value is 0.0039±0.0002, the present calculation explains the observed value very well.

Concluding Discussion. The quantities calculated in Eqs. 24-b and 24-c correspond to the magnitude of the mean square fluctuation of the local field. These fluctuations of local field are originating from the thermal displacement of carbon tetrachloride molecules from the mean local bcc structure. In other words, the main cause of the finite ρ value of the ν_1 line of liquid carbon tetrachloride is the fluctuation of local field originating from the thermal displacement of the molecular configuration.

The beautiful agreement between the observed and calculated values of depolarization degree, in turn, suggests the possibility of determining the magnitude of the thermal displacement of component molecules in the condensed system by observing the depolarization degree of liquid samples.

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