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The Concentration Dependence of the Raman Intensity in Binary Mixtures and the Determination of Polarizability and Hyperpolarizability Derivative Tensors

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Raman intensities were observed at various concentrations. The observed lines were: the ν_8 line of CH_3CN (in CCl_4 and CH_3I), the ν_3 line of CH_3I (in CCl_4), and the ν_2 line of $CHCl_3$ (in CCl_4). Even after the elimination of the local-field effect, the Raman intensities showed concentration dependencies. The observed solvent effects were explained quantitatively by the use of the dipole interaction model. The polarizability and hyperpolarizability derivatives were determined for the ν_8 fundamental of CH_3CN. The criteria for the internal standard method were discussed quantitatively.

In the preceding report,[1] the solvent effects on the absolute infrared intensities have been discussed quantitatively from the viewpoint of dipole-dipole interaction. It has been shown that the interaction of the dipole-dipole type is a quite reasonable model in explaining the spectroscopic information observed in various binary solutions. It has also been shown in the report that the polarizability derivatives can be determined by observing the solvent effects on the infrared-absorption intensities.

The present report will concern itself with the observation of the Raman intensities of acetonitrile, methyl iodide, chloroform, and carbon tetrachloride in their binary mixtures. Our interest lies in:

1) the possibility of determining the magnitude of polarizability and hyperpolarizability derivatives through the observation of the solvent effects on Raman intensities, and

2) the examination of the criteria for the internal-standard method, which is widely used for the representation of Raman intensities.

Experimental

The spectrometer used for the present work was designed and constructed by the authors. The instrument is composed of a He-Ne gas laser source (NEC, GLG-108, 50 mW), a JSG-125 grating monochromator (JEOL), a HTV R-376 photomultiplier (S-20 response), a handmade lock-in amplifier (375 cps modulation), and a recorder.

The linearity of the whole system with respect to an intensity axis was carefully checked. First the output current of the photomultiplier was plotted against the light energy. The linearity was perfect for the output voltage of 20 V with $R_p = 1\ \mathrm{M}\Omega$. Then, the linearity of the amplifier was tested by using attenuators (0.1—120 db for each 0.1 db). Finally, the linearity of the whole system was checked by plotting the final recorder output voltage against the light energy which passes through the entrance slit of the monochromator. The light energy was attenuated by using neutral filters (Kenko, ND). From the standard errors estimated from the linear fitting, the linearity of the whole system was ascertained to be better than 1% of the full scale as long as the output voltage was less than 10 V.

Special attention was paid to the output power of the laser source. The stability of the laser output during the individual spectral measurements was observed by monitoring the light energy which penetrated through the 100-percent reflectance mirror of the laser cavity. When the power of the laser source drifted more than 1 percent during the measurements, the data observed were completely discarded.

All the chemicals were commercial products of a spectroscopic grade. The carbon tetrachloride and methyl iodide were purified by fractional distillation just before the spectral measurement. The chloroform was purified by column chromatography on alumina. The acetonitrile was used without further purification.

The Raman spectra were observed for; the ν_1 band of carbon tetrachloride, the ν_2 band of chloroform, the ν_8 band of acetonitrile, and the ν_3 band of methyl iodide in the binary solutions of $CHCl_3$–CCl_4, CH_3CN–CCl_4, CH_3I–CCl_4, and CH_3CN–CH_3I. All the spectra were recorded at the temperature of 22±1 °C. The band areas were determined by the weight method. The observations were repeated eight times for each concentration. The deviations of the observed band areas from the averaged values were less than 3 percent. The reproducibility of the observed peak frequency was within $\pm 2\ \mathrm{cm}^{-1}$, and no peak frequency shift due to the different concentrations was observed. All the bands observed had intensities strong enough for us to obtain accurate intensity data by the use of our instrument.

Results and Discussion

Concentration Dependence of Relative Intensity. Consider the observation of the relative intensities of two Raman lines arising from two components of a binary solution. The quantities related to the two Raman lines will be distinguished by the suffixes a and b. The observed intensity, I, is proportional to the molar concentration, c_m, the scattering cross section per molecules, Ω, and the corresponding factor for the internal field effect[2]; *i.e.*,

$$I_a = C\cdot c_{ma}\Omega_a \frac{1}{n_s}\left[\frac{n_a^2+2}{(n_a/n_s)^2+2}\right]^4 \tag{1}$$

$$I_b = C\cdot c_{mb}\Omega_b \frac{1}{n_s}\left[\frac{n_b^2+2}{(n_b/n_s)^2}\right]^4 \tag{2}$$

where C is a constant and where n_a, n_b, and n_s are, respectively, the refractive indices of the a component, the b component, and the mixture of the a and b components. It can immediately be concluded from these equations that:

$$\frac{\Omega_a}{\Omega_b} = \frac{I_a}{I_b}\frac{c_{mb}}{c_{ma}}\left[\frac{n_b^2+2}{n_a^2+2}\,\frac{(n_a/n_s)^2+2}{(n_b/n_s)^2+2}\right]^4 \tag{3}$$

Thus, we can obtain the ratio, Ω_a/Ω_b, of the scattering cross sections from the observed intensity ratio, I_a/I_b,

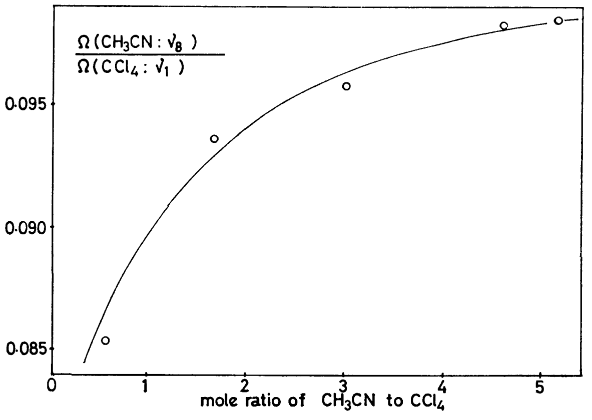

Fig. 1. Concentration dependence of $\Omega(\mathrm{CH_3CN};\ \nu_8)/\Omega(\mathrm{CCl_4};\ \nu_1)$.

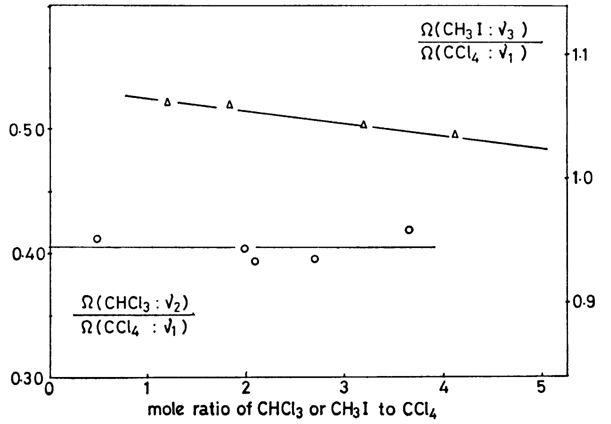

Fig. 2. Concentration dependence of $\Omega(\mathrm{CHCl_3};\ \nu_2)/\Omega(\mathrm{CCl_4};\ \nu_1)$ (circle) and $\Omega(\mathrm{CH_3I};\ \nu_3)/\Omega(\mathrm{CCl_4};\ \nu_1)$ (triangle).

because $c_{\mathrm{ma}}/c_{\mathrm{mb}}$ is known from the experimental conditions and because the refractive indices can be measured by the use of a refractometer.

Figure 1 shows the ratio of the scattering cross section of the ν_8 band of acetonitrile, $\Omega(\mathrm{CH_3CN};\ \nu_8)$, and that of the ν_1 band of carbon tetrachloride, $\Omega(\mathrm{CCl_4};\ \nu_1)$, observed at several concentrations. It may be seen from the figure that the $\Omega(\mathrm{CH_3CN};\ \nu_8)/\Omega(\mathrm{CCl_4};\ \nu_1)$ ratio decreases as the concentration of acetonitrile decreases. Thus, $\Omega(\mathrm{CH_3CN};\ \nu_8)$ and/or $\Omega(\mathrm{CCl_4};\ \nu_1)$ vary with the change in concentration.

Figure 2 shows the $\Omega(\mathrm{CHCl_3};\ \nu_2)/\Omega(\mathrm{CCl_4};\ \nu_1)$ and $\Omega(\mathrm{CH_3I};\ \nu_3)/\Omega(\mathrm{CCl_4};\ \nu_1)$ ratios observed for the $\mathrm{CHCl_3}$–$\mathrm{CCl_4}$ and $\mathrm{CH_3I}$–$\mathrm{CCl_4}$ systems respectively at various concentrations. Obviously, the ratios are not dependent on the concentration. These results probably suggest that $\Omega(\mathrm{CHCl_3};\ \nu_2)$, $\Omega(\mathrm{CH_3I};\ \nu_3)$, and $\Omega(\mathrm{CCl_4};\ \nu_1)$ do not depend on the concentration. Therefore, the concentration dependency of $\Omega(\mathrm{CH_3CN};\ \nu_8)/\Omega(\mathrm{CCl_4};\ \nu_1)$ of Fig. 1 can be ascribed to the concentration dependency of $\Omega(\mathrm{CH_3CN};\ \nu_8)$.

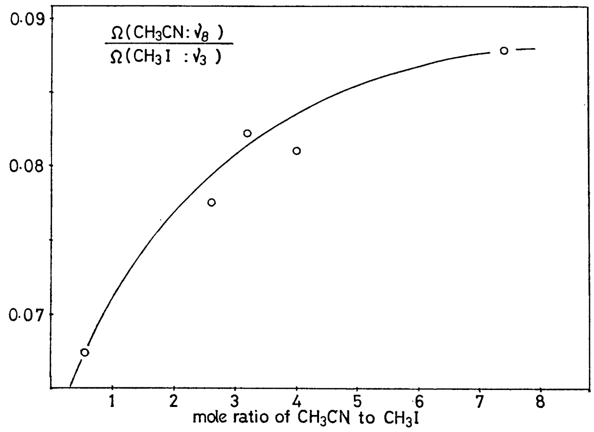

Fig. 3. Concentration dependence of $\Omega(\mathrm{CH_3CN};\ \nu_8)/\Omega(\mathrm{CH_3I};\ \nu_3)$.

Figure 3 shows the $\Omega(\mathrm{CH_3CN};\ \nu_8)/\Omega(\mathrm{CH_3I};\ \nu_3)$ ratio observed for the $\mathrm{CH_3CN}$–$\mathrm{CH_3I}$ system at various concentrations. It may be seen from the figure that the $\Omega(\mathrm{CH_3CN};\ \nu_8)/\Omega(\mathrm{CH_3I};\ \nu_3)$ ratio increases as the concentration of acetonitrile increases. The magnitude of the relative cross-section change due to the concentration is as large as that observed for the $\mathrm{CH_3CN}$–$\mathrm{CCl_4}$ system, which may indicate that the concentration dependence is to be ascribed mostly to the physical property of acetonitrile. In the following discussion, therefore, we will focus our attention on the role of a large dipole moment of acetonitrile.

Hyperpolarizability and Dipole Field. It is known that a scattering cross-section is proportional to the square of a transition polarizability, $\boldsymbol{\alpha}_1$,

$$\Omega \propto (\boldsymbol{\alpha}_1)^2 \tag{4}$$

and:

$$(\boldsymbol{\alpha}_1) = (\partial\boldsymbol{\alpha}/\partial Q)\langle I|Q|F\rangle$$

where $\boldsymbol{\alpha}_1$ is a transition polarizability tensor, Q is a normal coordinate, and $\langle I\,|\,Q\,|F\rangle$ is a matrix element corresponding to the transition between vibrational levels I and F. An i, j-element of a transition polarizability tensor of a molecule changes its magnitide when surrounding molecules produce an electric field, $\langle \boldsymbol{F}_0\rangle_{\mathrm{av}}$, on the position of the molecule. As is illustrated in Appendix I, an i,j-element of a transition polarizability under the influence of $\langle \boldsymbol{F}_0\rangle_{\mathrm{av}}$ is expressed by the following equation:

$$(\alpha_1)_{ij} = (\alpha_1^0)_{ij} + (\beta_1^0)_{ijk}\langle \boldsymbol{F}_{0k}\rangle_{\mathrm{av}} \tag{5}$$

where $(\alpha_1^0)_{ij}$ is an i,j-element of a transition polarizability tensor of an isolated molecule, $(\beta_1^0)_{ijk}$ is an element of a transition hyperpolarizability tensor, and $\langle \boldsymbol{F}_{0k}\rangle_{\mathrm{av}}$ is a k-component of $\langle \boldsymbol{F}_0\rangle_{\mathrm{av}}$ (see Appendix I).

There are many types of intermolecular interactions which produce electric fields at the position of a given molecule in liquids or solutions. The simplest and most important of these is the interaction of a dipole-dipole type. A molecule with a dipole moment affects the orientational distribution of surrounding molecules through dipole-dipole or dipole-induced dipole interactions. This results in the appearance of a non-zero averaged electric field at the position of the central dipole. For a binary solution, this averaged electric field, $\langle \boldsymbol{F}_{0k}\rangle_{\mathrm{av}}$, has been calculated to be[3];

$$\langle \boldsymbol{F}_{0k}\rangle_{\mathrm{av}} = \frac{4\pi^2}{27}N_{\mathrm{a}}^2\mu\left[\left(\frac{\mu^2}{kT}+\alpha\right)\frac{\rho}{W_{\mathrm{m}}}c_{\mathrm{m}} + \left(\frac{\mu_{\mathrm{s}}^2}{kT}+\alpha_{\mathrm{s}}\right)\frac{8}{A}c_{\mathrm{ms}}\right] \tag{6}$$

with

$$A=\left[\left(\frac{W_{\mathrm{m}}}{\rho}\right)^{1/3}+\left(\frac{W_{\mathrm{ms}}}{\rho_{\mathrm{s}}}\right)^{1/3}\right]^3,$$

where μ is a permanent dipole moment, α, the polarizability; c_{m}, the molar concentration: ρ, the density; W_{m}, the molecular weight; T, the temperature; k, the Boltzmann constant, and N_{a}, the Avogadro number. The symbols suffixed by "s" correspond to the solvent molecule.

Symmetry considerations of $(\alpha_1^0)_{ij}$ and $(\beta_1^0)_{ijk}$ are described in Appendix II. Using the results obtained in Appendix II, together with the discussion of Appendix III, we obtain the expression of $\Omega(\mathrm{CH_3CN};\nu_8)/\Omega(\mathrm{CCl_4};\nu_1)$ in temrs of $(\alpha_1^0)_{ij}$, $(\beta_1^0)_{ijk}$, and $\langle \boldsymbol{F}_{0k}\rangle_{\mathrm{av}}$ as:

$$\frac{\Omega(\mathrm{CH_3CN};\nu_8)}{\Omega(\mathrm{CCl_4};\nu_1)}=\left(\frac{14}{15}\right)\frac{1}{{}^{Q_1}(\alpha_1^0)^2}[B+A\langle \boldsymbol{F}_{0z}\rangle_{\mathrm{av}}], \tag{7}$$

with

$$A=2[{}^{Q_8}(\alpha_1^0)_{\mathrm{xy}}{}^{Q_8}(\beta_1^0)_{\mathrm{xyz}}+{}^{Q_8}(\alpha_1^0)_{\mathrm{yz}}{}^{Q_8}(\beta_1^0)_{\mathrm{yzz}}]$$

and

$$B={}^{Q_8}(\alpha_1^0)_{\mathrm{xy}}^2+{}^{Q_8}(\alpha_1^0)_{\mathrm{yz}}^2,$$

where ${}^{Q}(\alpha_1^0)_{ij}$ is the i,j-element of the transition polarizability tensor which is related with the normal coordinate Q, and where $\langle \boldsymbol{F}_{0z}\rangle_{\mathrm{av}}$ is the electric field produced at an acetonitrile molecule in the direction of the molecular axis. No electric field is produced at a carbon tetrachloride molecule, because it has no permanent dipole moment.

Determination of Transition Polarizability and Transition Hyperpolarizability. Equation 7 predicts that a linear relation will hold between $\Omega(\mathrm{CH_3CN};\nu_8)/\Omega(\mathrm{CCl_4};\nu_1)$ and $\langle \boldsymbol{F}_{0z}\rangle_{\mathrm{av}}$ if the dipole interaction model is reasonable. Figure 4 shows the relation between the observed $\Omega(\mathrm{CH_3CN};\nu_8)/\Omega(\mathrm{CCl_4};\nu_1)$ and the calculated $\langle \boldsymbol{F}_{0z}\rangle_{\mathrm{av}}$ values. In the calculation of $\langle \boldsymbol{F}_{0z}\rangle_{\mathrm{av}}$, the permanent dipole moment of acetonitrile was taken to be 3.92 D.[4] Obviously, a linear relation holds between the relative cross-section and the electric dipole field. From the slope, A^*, and the intercept, B^*, of the line, we can determine the corresponding terms of Eq. 7. From the results of Fig. 4, A^* and B^* are given the values of 7.18×10^3 (dyn^{-1} esu) and 0.0776 respectively.

According to the preceding report,[1] the magnitude of ${}^{Q_8}(\alpha_1^0)_{\mathrm{yz}}$ has been observed to be 0.0204 (Å^3) from the measurement of the infrared absorption intensity for the ν_8 fundamental band of acetonitrile in a carbon tetrachloride solution. The ${}^{Q_1}(\alpha_1^0)$ value of carbon tetrachloride, on the other hand, can be determined by the absolute intensity measurement of the ν_1 fundamental line. Kato *et al.* have reported the $|{}^{Q_1}(\alpha_1^0)|^2$ value to be 1.99×10^{-50} (cm^6).[7] Thus, we can obtain the following values and relations for the ν_8 line of methyl cyanide:

$${}^{Q_8}(\alpha_1^0)_{\mathrm{xy}}=0.0352\ (\text{Å}^3),$$

$${}^{Q_8}(\alpha_1^0)_{\mathrm{yz}}=0.0204\ (\text{Å}^3),$$

and:

$$|3.52\,{}^{Q_8}(\beta_1^0)_{\mathrm{xyz}}|+|2.04\,{}^{Q_8}(\beta_1^0)| = 7.654\times10^{-8}(\text{Å}^6\ \mathrm{dyn}^{-1}\ \mathrm{esu}) \tag{8}$$

As is illustrated in Appendix II, all the necessary transition polarizabilities for an e-type fundamental of $\mathrm{C_{3v}}$ symmetry are ${}^{Q}(\alpha_1^0)_{\mathrm{yz}}$ and ${}^{Q}(\alpha_1^0)_{\mathrm{xy}}$. That is to say, the scattering polarizability tensor can be completely determined by observing the solvent effects on the infrared absorption and the Raman spectra. In the case of the infrared absorption spectra, only ${}^{Q}(\alpha_1^0)_{\mathrm{yz}}$ is obtained through this relation:

$$\Gamma_{\mathrm{c}}\propto\left(\frac{\partial\mu_{\mathrm{y}}^0}{\partial Q_8}\right)^2+2\left(\frac{\partial\mu_{\mathrm{y}}^0}{\partial Q_8}\right){}^{Q_8}(\alpha_1^0)_{\mathrm{yz}}\langle \boldsymbol{F}_{0z}\rangle_{\mathrm{av}}$$

where Γ_{c} is an absolute absorption intensity observed in a solution and $(\partial\mu_{\mathrm{y}}^0/\partial Q_8)$ is a dipole moment derivative which can be determined by observing the absolute infrared absorption intensity of the ν_8 fundamental in the gas phase. The sign of the product, $(\partial\mu_{\mathrm{y}}^0/\partial Q_8){}^{Q_8}(\alpha_1^0)_{\mathrm{yz}}$, can be determined from the solvent effect data; therefore, the sign of ${}^{Q_8}(\alpha_1^0)_{\mathrm{yz}}$ can be definitely determined if the sign of $(\partial\mu_{\mathrm{y}}^0/\partial Q_8)$ is known. In the case of the Raman spectra, on the other hand, the sum, ${}^{Q}(\alpha_1^0)_{\mathrm{yz}}^2+{}^{Q}(\alpha_1^0)_{\mathrm{xz}}^2$, can be obtained. Thus, the signs of ${}^{Q}(\alpha_1^0)$'s are ambiguous; that is, only an absolute value, $|{}^{Q}(\alpha_1^0)|$, is obtained by this method.

The ν_3 Line of Methyl Iodide. For an $\mathrm{a_1}$-type line of $\mathrm{C_{3v}}$ symmetry, the relation corresponding to Eq. 7 is obtained. As an example, the ν_3 fundamental line of methyl iodide in a carbon tetrachloride solution is expressed as:

$$\frac{\Omega(\mathrm{CH_3I};\nu_3)}{\Omega(\mathrm{CCl_4};\nu_1)}=\left(\frac{1}{15}\right)\frac{1}{{}^{Q_1}(\alpha_1^0)^2}(B+A\langle \boldsymbol{F}_{0z}\rangle_{\mathrm{av}}) \tag{9}$$

with:

$$A=18\,{}^{Q_3}(\alpha_1^0)_{\mathrm{xx}}{}^{Q_3}(\beta_1^0)_{\mathrm{xxz}}+8\,{}^{Q_3}(\alpha_1^0)_{\mathrm{zz}}{}^{Q_3}(\beta_1^0)_{\mathrm{zzz}}+2\,{}^{Q_3}(\alpha_1^0)_{\mathrm{xx}}{}^{Q_3}(\beta_1^0)_{\mathrm{zzz}}+2\,{}^{Q_3}(\alpha_1^0){}^{Q_3}(\beta_1^0)_{\mathrm{xxz}}$$

and:

$$B=9\,{}^{Q_3}(\alpha_1^0)_{\mathrm{xx}}^2+2\,{}^{Q_3}(\alpha_1^0)_{\mathrm{xx}}{}^{Q_3}(\alpha_1^0)_{\mathrm{zz}}+4\,{}^{Q_3}(\alpha_1^0)_{\mathrm{zz}}^2$$

Although the observed data of Fig. 2 for $\mathrm{CH_3I}$–$\mathrm{CCl_4}$ system are not accurate enough, we tried to determine the necessary transition polarizability and transition hyperpolarizability for the ν_3 line of methyl iodide. From the plotting of $\Omega(\mathrm{CH_3I};\nu_3)/\Omega(\mathrm{CCl_4};\nu_1)$ against $\langle \boldsymbol{F}_{0z}\rangle_{\mathrm{av}}$, the slope, A^*, and the intercept, B^*, were obtained to be:

$$A^*=-0.0309\times10^{-4}\ \mathrm{dyn}^{-1}\ \mathrm{esu},$$

and:

$$B^*=1.104$$

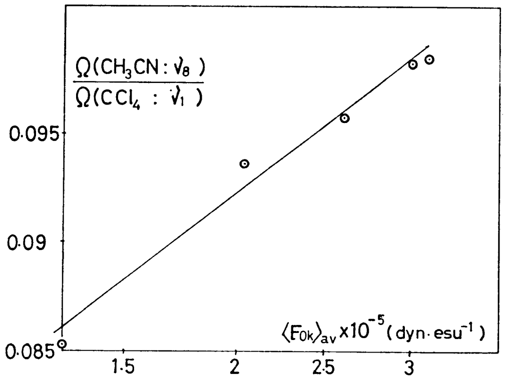

Fig. 4. Plotting of $\Omega(\mathrm{CH_3CN};\nu_8)/\Omega(\mathrm{CCl_4};\nu_1)$ against $\langle \boldsymbol{F}_{0z}\rangle_{\mathrm{av}}$.

TABLE 1. $\langle \boldsymbol{F}_{0z}\rangle_{av}$ VALUES CALCULATED FOR $CHCl_3$, CH_3I, AND CH_3CN IN CCl_4 SOLUTIONS

Mole ratio of $CHCl_3$	$\langle \boldsymbol{F}_{0z}\rangle_{av}$ ($\times 10^{-3}$ dyn esu)	Mole ratio of CH_3I	$\langle \boldsymbol{F}_{0z}\rangle_{av}$ ($\times 10^{-4}$ dyn esu)	Mole ratio of CH_3CN	$\langle \boldsymbol{F}_{0z}\rangle_{av}$ ($\times 10^{-5}$ dyn esu)
0.492	1.007	0.550	0.892	0.540	0.741
1.026	1.498	1.214	1.294	1.679	1.474
1.981	1.966	1.840	1.529	2.990	1.889
2.095	2.004	3.202	1.827	4.580	2.013
2.688	2.165	4.124	1.947	5.217	2.231
3.648	2.341				
$\mu_{CHCl_3}=1.05$ D (Ref. 6)		$\mu_{CH_3I}=1.65$ D (Ref. 5)		$\mu_{CH_3CN}=3.92$ D (Ref. 4)	

Using these values and the previous data[1]; ${}^{Q_3}(\alpha_1^0)_{zz}=-1.13\times 10^{-25}$ (cm^3), we can obtain the following values and relations;

$$ {}^{Q_8}(\alpha_1^0)_{xx} = -1.164 \times 10^{-25} \text{ or } 1.888 \times 10^{-25}\ \mathrm{cm}^3 $$

and:

$$ \begin{aligned} &18\,{}^{Q_3}(\alpha_1^0)_{xx}{}^{Q_3}(\beta_1^0)_{xxz} + 8\,{}^{Q_3}(\alpha_1^0)_{zz}{}^{Q_3}(\beta_1^0)_{zzz} \\ &\quad + 2\,{}^{Q_3}(\alpha_1^0)_{xx}{}^{Q_3}(\beta_1^0)_{zzz} + 2\,{}^{Q_3}(\alpha_1^0)_{zz}{}^{Q_3}(\beta_1^0)_{xxz} \\ &\quad = -9.224 \times 10^{-51}\ \mathrm{cm}^6\,\mathrm{dyn}^{-1}\,\mathrm{esu}. \end{aligned} \tag{10} $$

The A^* and B^* values for the ν_3 line of methyl iodide can be determined in another way. By combining Eqs. 7 and 9, $\Omega(CH_3CN;\ \nu_8)/\Omega(CH_3I;\ \nu_3)$ can be expressed as:

$$ \frac{\Omega(CH_3CN;\nu_8)}{\Omega(CH_3I;\nu_3)} = \frac{\Omega(CH_3CN;\nu_8)}{\Omega(CCl_4;\nu_1)} \bigg/ \frac{\Omega(CH_3I;\nu_3)}{\Omega(CCl_4;\nu_1)} = \frac{(B^*_{CH_3CN}+\langle \boldsymbol{F}_{0z}\rangle_{av}A^*_{CH_3CN})}{(B^*_{CH_3I}+\langle \boldsymbol{F}_{0z}\rangle_{av}A^*_{CH_3I})} \tag{11} $$

As we have the observed $\Omega(CH_3CN;\ \nu_8)/\Omega(CH_3I;\ \nu_3)$ values of Fig. 3, and the $B^*_{CH_3CN}$ and $A^*_{CH_3CN}$ values, we can calculate the $A^*_{CH_3I}$ and $B^*_{CH_3I}$ values for the ν_3 line of methyl iodide in the carbon tetrachloride solution as:

$$ A^* = -0.0305 \times 10^{-4}\ \mathrm{dyn}^{-1}\,\mathrm{esu} $$

and:

$$ B^* = 1.528. $$

These values are not very different from those obtained in the previous way.

Criteria for the Internal Standard Method. The present results afford some useful information about the reliability of a so-called internal standard method for the determination of relative Raman intensities which are mutually comparable. The concentration dependency of a relative intensity of a Raman line arises from the existence of the concentration-dependent term, $A^*\langle \boldsymbol{F}_{0z}\rangle_{av}$, of Eq. 7 or 9.

We have very little knowledge about the magnitude of A^*. Therefore, we first compare the magnitudes of $\langle \boldsymbol{F}_{0z}\rangle_{av}$ of chloroform, methyl iodide, and acetonitrile in carbon tetrachloride solutions. Table 1 shows the $\langle \boldsymbol{F}_{0z}\rangle_{av}$ values of chloroform, methyl iodide, and acetonitrile calculated for carbon tetrachloride solutions. It may be seen from the table that the orders of $\langle \boldsymbol{F}_{0z}\rangle_{av}$ are 10^3 for chloroform, 10^4 for methyl iodide, and 10^5 for acetonitrile, in units of dyn esu^{-1}. The difference arises, of course, from the difference in the magnitude of the dipole moments. The dipole moment of acetonitrile is 3.92 D[4], while those of methyl iodide and chloroform are 1.65 D[5] and 1.05 D[6] respectively. These facts are definitely reflected in the observed Raman intensity changes due to the concentration, as is shown in Figs. 1 and 2. Thus, we can conclude that the concentration dependence of a Raman intensity is more distinct for a molecule with a larger dipole moment.

If A^* is large, on the other hand, the concentration dependence of Raman intensity may be large enough to be observed even though $\langle \boldsymbol{F}_{0z}\rangle_{av}$ is small. It has been shown that $A^*\approx 0.07\times 10^{-5}$ dyn^{-1} esu and $A^*\approx -0.03\times 10^{-4}$ dyn^{-1} esu for the ν_8 of acetonitrile and ν_3 of methyl iodide respectively. The corresponding $\langle \boldsymbol{F}_{0z}\rangle_{av}$ values are, respectively, $\approx 10^5$ dyn esu^{-1} and $\approx 10^4$ dyn esu^{-1}; the result is that the products, $A^*\times\langle \boldsymbol{F}_{0z}\rangle_{av}$, have almost the same magnitudes. In the former case, the main factor which makes the concentration dependence observable is $\langle \boldsymbol{F}_{0z}\rangle_{av}$, while in the latter it is the magnitude of A^*. Detailed discussions of the magnitude of A^* from the viewpoint of the transition polarizability and transition hyperpolarizability are quite difficult at this stage, because A^* is a rather complicated function of the transition polarizability and the transition hyperpolarizability (see Eq. 7 or 9). As there have been reported quite a few number of values for ${}^{Q}(\alpha_1^0)$ and ${}^{Q}(\beta_1^0)$ with their definite signs, except the ${}^{Q}(\alpha_1^0)\approx 10^{-26}$ cm^3 and ${}^{Q}(\beta_1^0)\approx 10^{-32}$ cm^3 dyn^{-1} esu, we can only conclude that the concentration dependence might be observed even for a molecule with a much smaller dipole moment. Incidentally, the plus and minus signs of A^* correspond to the increase and decrease in scattering cross sections with the increase in the concentration (see Figs. 1 and 2).

Appendix I. Definition of an Apparent Transition Polarizability Derivative

The energy, U, of a molecule in an electric field, $\boldsymbol{F}$, is expressed as a function of $\boldsymbol{F}$:

$$ U = U(\boldsymbol{F}) \tag{A1} $$

The Maclaurin expansion of Eq. A1 yields:

$$ U = U(0) - \sum \mu_i^0 F_i - \frac{1}{2!}\sum_{ij}\alpha_{ij}^0 F_i F_j - \frac{1}{3!}\sum_{ijk}\beta_{ijk}^0 F_i F_j F_k - \cdots \tag{A2} $$

and:

$$\mu^0_i = -(\partial U/\partial F_i)_0$$
$$\alpha^0_{ij} = -(\partial^2 U/\partial F_i \partial F_j)_0$$
$$\beta^0_{ijk} = -(\partial^3 U/\partial F_i \partial F_j \partial F_k)_0$$

The coefficients, μ^0_i, α^0_{ij}, and β^0_{ijk} are independent of $\boldsymbol{F}$. They are called, respectively, a permanent dipole moment, a polarizability, and a hyperpolarizability.

Put a molecule which has a permanent dipole moment, $\boldsymbol{\mu}$, polarizability, $\boldsymbol{\alpha}^0$, and hyperpolarizability, $\boldsymbol{\beta}^0$, in an electric field, $\boldsymbol{F}$. Then the total dipole moment, $\boldsymbol{m}$, of the molecule is:

$$\boldsymbol{m} = \boldsymbol{\mu}^0 + \boldsymbol{p} \tag{A3}$$

where $\boldsymbol{p}$ is an dipole moment induced by the electric field, $\boldsymbol{F}$:

$$\boldsymbol{p} = \boldsymbol{\alpha}^0 \cdot \boldsymbol{F} + \frac{1}{2}\boldsymbol{\beta}^0 : \boldsymbol{F}\boldsymbol{F} \tag{A4}$$

In the present problem, $\boldsymbol{F}$ is composed of two different electric fields. One is an electric field, $\boldsymbol{F}_\mathrm{l}$, of radiating light, while the other is an electric field, $\boldsymbol{F}_\mathrm{m}$, produced by molecules in a condensed phase. Thus, an induced moment, $\boldsymbol{p}$, is expressed as:

$$\boldsymbol{p} = \boldsymbol{p}_\mathrm{l} + \boldsymbol{p}_\mathrm{m},$$

where $\boldsymbol{p}_\mathrm{l}$ is a dipole moment induced by $\boldsymbol{F}_\mathrm{l}$ and $\boldsymbol{p}_\mathrm{m}$ is that induced by $\boldsymbol{F}_\mathrm{m}$. Therefore, the induced moment, $\boldsymbol{p}_\mathrm{l}$, is:

$$\begin{aligned}\boldsymbol{p}_\mathrm{l} &= \boldsymbol{p} - \boldsymbol{p}_\mathrm{m} \\ &= \left[\boldsymbol{\alpha}^0 \cdot (\boldsymbol{F}_\mathrm{l} + \boldsymbol{F}_\mathrm{m}) + \frac{1}{2}\boldsymbol{\beta}^0 : (\boldsymbol{F}_\mathrm{l} + \boldsymbol{F}_\mathrm{m})(\boldsymbol{F}_\mathrm{l} + \boldsymbol{F}_\mathrm{m})\right] \\ &\quad - \left[\boldsymbol{\alpha}^0 \cdot \boldsymbol{F}_\mathrm{m} + \frac{1}{2}\boldsymbol{\beta}^0 : \boldsymbol{F}_\mathrm{m}\boldsymbol{F}_\mathrm{m}\right] \\ &= \boldsymbol{\alpha}^0 \cdot \boldsymbol{F}_\mathrm{l} + \boldsymbol{\beta}^0 : \boldsymbol{F}_\mathrm{m}\boldsymbol{F}_\mathrm{l} + \frac{1}{2}\boldsymbol{\beta}^0 : \boldsymbol{F}_\mathrm{l}\boldsymbol{F}_\mathrm{l} \end{aligned} \tag{A5}$$

In the present work, the last term of Eq. A5 may be neglected, because $\boldsymbol{F}_\mathrm{l}$ is small. Thus,

$$\begin{aligned}\boldsymbol{p}_\mathrm{l} &= \boldsymbol{\alpha}^0 \cdot \boldsymbol{F}_\mathrm{l} + \boldsymbol{\beta}^0 : \boldsymbol{F}_\mathrm{m}\boldsymbol{F}_\mathrm{l} \\ &= [\boldsymbol{\alpha}^0 + \boldsymbol{\beta}^0 \cdot \boldsymbol{F}_\mathrm{m}] \cdot \boldsymbol{F}_\mathrm{l}\end{aligned} \tag{A6}$$

Here, we define "an apparent polarizability" as:

$$\boldsymbol{\alpha} = \boldsymbol{\alpha}^0 + \boldsymbol{\beta}^0 \cdot \boldsymbol{F}_\mathrm{m} \tag{A7}$$

Then the induced moment is expressed in this form:

$$\boldsymbol{p}_\mathrm{l} = \boldsymbol{\alpha} \cdot \boldsymbol{F}_\mathrm{l}$$

which formally coincides with usual expression for an induced moment. Therefore, an i,j-element of α becomes:

$$\alpha_{ij} = \alpha^0_{ij} + \sum_k \beta^0_{ijk} F_{mk} \tag{A8}$$

where F_{mk} is a k-component of $\boldsymbol{F}_\mathrm{m}$.

In order to obtain an explicit expression for a Raman scattering cross-section, it is necessary to rewrite Eq. A8 in terms of transition polarizability and transition hyperpolarizability derivatives, which are defined as:

$$^Q(\alpha^0_1)_{ij} = (\alpha^0_1)_{ij}\langle I|Q|F\rangle$$
$$(\alpha^0_1)_{ij} = (\partial\alpha^0_{ij}/\partial Q)_0,$$

and:

$$^Q(\beta^0_1)_{ijk} = (\beta^0_1)_{ijk}\langle I|Q|F\rangle$$
$$(\beta^0_1)_{ijk} = (\partial\beta^0_{ijk}/\partial Q)_0, \tag{A9}$$

where Q is a normal coordinate. Differentiating Eq. A8 with respect to Q, we rewrite Eq. A8 as:

$$\begin{aligned}^Q(\alpha_1)_{ij} &= {}^Q(\alpha^0_1)_{ij} + \sum_k {}^Q(\beta^0_1)_{ijk} F_{mk} \\ &\quad + \sum_k \beta^0_{ijk}(\partial F_{mk}/\partial U)_0\end{aligned} \tag{A10}$$

As $\boldsymbol{F}$ is almost independent of the molecular vibration, we finally obtain:

$$^Q(\alpha_1)_{ij} = {}^Q(\alpha^0_1)_{ij} + \sum_k {}^Q(\beta^0_1)_{ijk} F_{mk} \tag{A11}$$

In the present work, F_{mk} will be replaced by $\langle \boldsymbol{F}_{0k}\rangle_\mathrm{av}$. It is important to add that the k direction should be parallel to the molecular axis under consideration, because the averaged dipole field has a non-zero value only in the direction of the dipole moment. Thus, Eq. A11 can be rewritten as:

$$^Q(\alpha_1)_{ij} = {}^Q(\alpha^0_1)_{ij} + {}^Q(\beta^0_1)_{ijk}\langle \boldsymbol{F}_{0z}\rangle_\mathrm{av}$$

where the molecular axis being chosen is the z-axis.

Appendix II. Symmetry Properties of α and β

The molecules studied in the present study belong to the point groups of C_{3v} and T_d. Thus, we will confine our discussion to C_{3v} and T_d symmetries.

a) Polarizability. If a molecule is in an equilibrium position, the polarizability is invariant with respect to the operations, S, of the symmetry group of the molecule:

$$S(\alpha^0_{ij}) = \alpha^0_{ij} \tag{A12}$$

Eq. A12 requires that some polarizability components, α^0_{ij}, vanish. As an example, let us consider a rotation about the z-axis by an angle of φ. The corresponding symmetry operation, S, is expressed as:

$$S\begin{pmatrix}\alpha^0_{xx}\\ \alpha^0_{yy}\\ \alpha^0_{xy}\\ \alpha^0_{xz}\\ \alpha^0_{yz}\\ \alpha^0_{zz}\end{pmatrix} = \begin{pmatrix} a^2 & b^2 & 2ab & 0 & 0 & 0 \\ b^2 & a^2 & -2ab & 0 & 0 & 0 \\ -ab & ab & a^2-b^2 & 0 & 0 & 0 \\ 0 & 0 & 0 & a & b & 0 \\ 0 & 0 & 0 & -b & a & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix}\begin{pmatrix}\alpha^0_{xx}\\ \alpha^0_{yy}\\ \alpha^0_{xy}\\ \alpha^0_{xz}\\ \alpha^0_{yz}\\ \alpha^0_{zz}\end{pmatrix} \tag{A13}$$

where $a = \cos\varphi$ and $b = \sin\varphi$. From Eqs. A12 and A13,

$$a^2\alpha^0_{xx} + b^2\alpha^0_{yy} + 2ab\alpha^0_{xy} = \alpha^0_{xx}$$

and similar relations for other symmetry operation. Thus, for C_{3v} symmetry, these relations;

$$\alpha^0_{xx} = \alpha^0_{yy} \neq \alpha^0_{zz}$$

and

$$\alpha^0_{xy} = \alpha^0_{xz} = \alpha^0_{yz} \tag{A14}$$

are obtained. Eq. A14 shows that the polarizability tensor has only the diagonal elements and that the polarizability ellipsoid will become a rotation ellipsoid about the z-axis. These are the results obtained for a molecule in an equilibrium position.

For the displacements of nuclei due to vibration, the symmetry of the molecule is destroyed except when the vibrational mode is totally symmetric. Consider a molecule whose nuclei deviate from their equilibrium position according to a particular normal mode. There are two ways of applying symmetry operations, S, for the molecule. One is to apply the symmetry operations to the polarizability directly, while the other is to apply the symmetry operations to the normal coordinate. The results obtained by these two methods should be the same. Thus,

$$\begin{aligned}&S\alpha^0_{ij}(Q_1, Q_2, \ldots\ldots, Q_n) \\ &\quad = \alpha^0_{ij}(S_0Q_1, S_0Q_2, \ldots\ldots, S_0Q_n)\end{aligned} \tag{A15}$$

where the symmetry operations are distinguished as S_0 and S, simply because $\boldsymbol{\alpha}$ is a tensor quantity, while Q_1 is a vector quantity. In order to calculate the right-hand side of Eq. A15, we have to know the transformation property of a normal coordinate due to the symmetry operation.

Consider a molecule with C_{3v} symmetry like acetonitrile. The normal coordinates, Q_8 and $Q_{8'}$, are transformed by the C_3 operation thus:

$$Q_8 \xrightarrow{C_3} -\frac{1}{2}Q_8 - \frac{\sqrt{3}}{2}Q_{8'}$$

and: (A16)

$$Q_{8'} \xrightarrow{C_3} \frac{\sqrt{3}}{2}Q_8 - \frac{1}{2}Q_{8'}$$

The polarizability is expressed in terms of normal coordinates:

$$\alpha^0_{ij} = (\alpha^0_{ij})_0 + \sum_k (\partial\alpha^0_{ij}/\partial Q_k)Q_k \tag{A17}$$

By combining Eqs. A16 and A17, we obtain this relation for α^0_{xx}:

$$\begin{aligned}\frac{\partial(\alpha^0_{\mathrm{xx}})}{\partial(C_3Q_8)} &= -\frac{1}{2}\left(\frac{\partial\alpha^0_{\mathrm{xx}}}{\partial Q_8}\right)+\frac{\sqrt{3}}{2}\left(\frac{\partial\alpha^0_{\mathrm{xx}}}{\partial Q_{8'}}\right)\\ &= -{}^{Q_8}(\alpha^0_1)_{\mathrm{xx}}/2 + \sqrt{3}\,{}^{Q_8'}(\alpha^0_1)_{\mathrm{xx}}/2\end{aligned} \tag{A18}$$

From Eq. A13, on the other hand,

$$\begin{aligned}\frac{\partial(C_3\alpha^0_{\mathrm{xx}})}{\partial Q_8} &= \frac{1}{4}\left(\frac{\partial\alpha^0_{\mathrm{xx}}}{\partial Q_8}\right)+\frac{3}{4}\left(\frac{\partial\alpha^0_{\mathrm{yy}}}{\partial Q_8}\right)-\frac{\sqrt{3}}{2}\left(\frac{\partial\alpha^0_{\mathrm{xy}}}{\partial Q_8}\right)\\ &= {}^{Q_8'}(\alpha^0_1)_{\mathrm{xx}}/4 + 3\,{}^{Q_8}(\alpha^0_1)_{\mathrm{yy}}/4 - \sqrt{3}\,{}^{Q_8}(\alpha^0_1)_{\mathrm{xy}}/2\end{aligned} \tag{A19}$$

By equating Eqs. A18 and A19, we obtain this relation:

$$\begin{aligned}&\frac{3}{4}({}^{Q_8}(\alpha^0_1)_{\mathrm{xx}} + {}^{Q_8}(\alpha^0_1)_{\mathrm{yy}})\\ &\qquad = \frac{\sqrt{3}}{2}({}^{Q_8'}(\alpha^0_1)_{\mathrm{xx}} + {}^{Q_8}(\alpha^0_1)_{\mathrm{xy}})\end{aligned} \tag{A20}$$

Similar but different relations are obtained for other polarizability derivatives and for other normal coordinates by applying the C_3 and σ_v operations. The transformation relations:

$$\begin{aligned}&Q_8 \xrightarrow{\sigma_v} -Q_8\\ &Q_{8'} \xrightarrow{\sigma_v} Q_{8'}\end{aligned} \tag{A21}$$

are used for the σ_v operation. From these results, the following relations between the polarizability derivatives or transition polarizability derivatives are obtained:

$$\begin{aligned}&{}^{Q_8}(\alpha^0_1)_{\mathrm{xx}} = {}^{Q_8}(\alpha^0_1)_{\mathrm{yy}} = {}^{Q_8}(\alpha^0_1)_{\mathrm{zz}} = {}^{Q_8'}(\alpha^0_1)_{\mathrm{zz}} = 0\\ &{}^{Q_8'}(\alpha^0_1)_{\mathrm{xy}} = {}^{Q_8'}(\alpha^0_1)_{\mathrm{yz}} = {}^{Q_8}(\alpha^0_1)_{\mathrm{xz}} = 0\\ &{}^{Q_8}(\alpha^0_1)_{\mathrm{xy}} = {}^{Q_8'}(\alpha^0_1)_{\mathrm{yy}} = -{}^{Q_8'}(\alpha^0_1)_{\mathrm{xx}}\\ &{}^{Q_8}(\alpha^0_1)_{\mathrm{yz}} = {}^{Q_8'}(\alpha^0_1)_{\mathrm{xz}}\end{aligned} \tag{A22}$$

b) Hyperpolarizability. Generally, a hyperpolarizability tensor has ten independent elements because of its symmetry property. These elements are related to each other in accordance with the molecular symmetry. The procedure of finding the relations between the hyperpolarizability derivatives is exactly the same as that discussed in a). For example, consider a rotation about the z-aixs by an angle of φ. The matrix representation for S corresponding to Eq. A13 is:

$$S\begin{pmatrix}\beta^0_{\mathrm{xxx}}\\ \beta^0_{\mathrm{yyy}}\\ \beta^0_{\mathrm{xxy}}\\ \beta^0_{\mathrm{xyy}}\\ \beta^0_{\mathrm{xxz}}\\ \beta^0_{\mathrm{yyz}}\\ \beta^0_{\mathrm{xyz}}\\ \beta^0_{\mathrm{xzz}}\\ \beta^0_{\mathrm{yzz}}\\ \beta^0_{\mathrm{zzz}}\end{pmatrix} = \left(\begin{array}{cccc|cccccc} a^3 & b^3 & 3a^2b & 3ab^2 & 0 & 0 & 0 & 0 & 0 & 0\\ -b^3 & a^3 & 3ab^2 & -3a^2b & 0 & 0 & 0 & 0 & 0 & 0\\ -a^2b & ab^2 & a^3-2ab^2 & 2a^2b-b^3 & 0 & 0 & 0 & 0 & 0 & 0\\ ab^2 & a^2b & b^3-2a^2b & a^3-2ab^2 & 0 & 0 & 0 & 0 & 0 & 0\\ \hline 0 & 0 & 0 & 0 & a^2 & b^2 & 2ab & 0 & 0 & 0\\ 0 & 0 & 0 & 0 & b^2 & a^2 & -2ab & 0 & 0 & 0\\ 0 & 0 & 0 & 0 & -ab & ab & a^2-b^2 & 0 & 0 & 0\\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & a & b & 0\\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -b & a & 0\\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1\end{array}\right) \times \begin{pmatrix}\beta^0_{\mathrm{xxx}}\\ \beta^0_{\mathrm{yyy}}\\ \beta^0_{\mathrm{xxy}}\\ \beta^0_{\mathrm{xyy}}\\ \beta^0_{\mathrm{xxz}}\\ \beta^0_{\mathrm{yyz}}\\ \beta^0_{\mathrm{xyz}}\\ \beta^0_{\mathrm{xzz}}\\ \beta^0_{\mathrm{yzz}}\\ \beta^0_{\mathrm{zzz}}\end{pmatrix} \tag{A23}$$

where $a=\cos\varphi$ and $b=\sin\varphi$. As is shown in Appendix I, the elements on which at least one z is subscribed are important in the present work. In other words, only the submatrix of Eq. A23 enclosed in the square of the dotted line is important for the present discussion. It is necessary, therefore, to know the symmetry property of the submatrix. A comparison of Eqs. A13 and A23 shows that the submatrix is exactly the same as that of Eq. A13.

The transformation of β with respect to a normal coordinate is the same as that described in a), as β_{ijk} is expressed as:

$$\beta^0_{ijk} = (\beta^0_{ijk})_0 + \sum_l\left(\frac{\partial\beta^0_{ijk}}{\partial Q}\right)Q_l \tag{A24}$$

Thus, we ascertain the relations between the hyperpolarizability derivatives or transition hyperpolarizabilities by direct analogy with Eq. A22:

$$\begin{aligned}&{}^{Q_8}(\beta^0_1)_{\mathrm{xxz}} = {}^{Q_8}(\beta^0_1)_{\mathrm{yyz}} = {}^{Q_8}(\beta^0_1)_{\mathrm{zzz}} = {}^{Q_8'}(\beta^0_1)_{\mathrm{zzz}} = 0\\ &{}^{Q_8'}(\beta^0_1)_{\mathrm{xyz}} = {}^{Q_8'}(\beta^0_1)_{\mathrm{yzz}} = {}^{Q_8}(\beta^0_1)_{\mathrm{xzz}} = 0\\ &{}^{Q_8}(\beta^0_1)_{\mathrm{xyz}} = {}^{Q_8'}(\beta^0_1)_{\mathrm{yyz}} = -{}^{Q_8'}(\beta^0_1)_{\mathrm{xxz}}\\ &{}^{Q_8}(\beta^0_1)_{\mathrm{yzz}} = {}^{Q_8'}(\beta^0_1)_{\mathrm{xzz}}\end{aligned} \tag{A25}$$

Appendix III. Reduction to a Scattering Cross-section

In order to calculate a scattering cross-section, it is necessary to know the actual geometric conditions of the Raman spectral measurement. In the present work, the observed Raman intensities are expressed as:

$$\Omega \propto ((\alpha_1)^2_{\mathrm{YZ}} + (\alpha_1)^2_{\mathrm{ZZ}}) \tag{A26}$$

where X, Y, and Z are the spece-fixed Cartesian coordinates. The relations between the polarizability tensors expressed in the molecular-fixed Cartesian coordinates and the space-fixed Cartesian coordinates are:

$$\begin{aligned}\alpha^2_{\mathrm{YZ}} &= \frac{1}{15}\sum_i\alpha^2_{ii} - \frac{1}{15}\sum_{i<j}\alpha_{ii}\alpha_{jj} + \frac{1}{5}\sum_{i<j}\alpha^2_{ij}\\ \alpha^2_{\mathrm{ZZ}} &= \frac{1}{5}\sum_i\alpha^2_{ii} + \frac{2}{15}\sum_{i<j}\alpha_{ii}\alpha_{jj} + \frac{4}{15}\sum_{i<j}\alpha^2_{ij}\end{aligned} \tag{A27}$$

Eqs. A26 and A27, together with Eq. A22, give the cross section, Ω(e), for the e-type line of a molecule with C_{3v}

symmetry:

$$\Omega(\mathrm{e}) \propto \frac{14}{15}({}^{Q}(\alpha_1)^2_{\mathrm{xy}} + {}^{Q}(\alpha_1)^2_{\mathrm{yz}}) \tag{A28}$$

In the case of the a_1-type line of C_{3v} symmetry, the relations corresponding to Eq. A22 are:

$$\begin{aligned} &{}^{Q}(\alpha_1^0)_{\mathrm{xx}} = {}^{Q}(\alpha_1^0)_{\mathrm{yy}},\ {}^{Q}(\alpha_1^0)_{\mathrm{zz}}, \\ &{}^{Q}(\alpha_1^0)_{\mathrm{xy}} = {}^{Q}(\alpha_1^0)_{\mathrm{yz}} = {}^{Q}(\alpha_1^0)_{\mathrm{zx}} = 0 \end{aligned} \tag{A29}$$

Therefore, the cross section, $\Omega(a_1)$, for the a_1-type line of a molecule with C_{3v} symmetry is expressed as:

$$\begin{aligned} \Omega(\alpha_1) \propto 3{}^{Q}(\alpha_1)^2_{\mathrm{xx}}/5 + 2{}^{Q}(\alpha_1)_{\mathrm{xx}}{}^{Q}(\alpha_1)_{\mathrm{zz}}/15 \\ + 4{}^{Q}(\alpha_1)^2_{\mathrm{zz}}/15 \end{aligned} \tag{A30}$$

By inserting Eq. A11 into Eq. A28 or A30, and by neglecting the terms corresponding to $\langle \boldsymbol{F}_{0k} \rangle^2_{\mathrm{av}}$, we can express the Raman scattering cross-section in terms of α_1, β_1, and $\langle \boldsymbol{F}_{0k} \rangle_{\mathrm{av}}$.

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