Solvent Effects on Raman Intensity and the Determination of Transition Hyperpolarizability Tensor Element

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Raman intensities of methyl iodide were observed in carbon tetrachloride solution at various concentrations. The observed lines were ν_1, ν_2, ν_3, ν_5, and ν_6. From the observed data, the transition polarizabilities were determined for the ν_1, ν_2, and ν_3 fundamentals of methyl iodide and the transition hyperpolarizabilities were obtained for the ν_3 fundamental of methyl iodide in the form of tensor elements.

In preceding reports,[1,2] the solvent effects on the absolute infrared intensities and on the absolute Raman scattering cross-sections have been discussed quantitatively from the view-point of dipole-dipole interaction. It has been shown that the interaction of the dipole-dipole type is quite a reasonable model for explaining the spectroscopic information observed in various binary solutions. It has also been shown in these reports that the polarizability derivatives can be determined by observing the solvent effects on the infrared-absorption intensities and that the hyperpolarizability derivatives can be determined by observing the solvent effects on the Raman scattering cross-sections. In the report,[2] however, we could not obtain the hyperpolarizability derivatives in the form of a tensor element, but in the form of a linear combination of the products of polarizability and hyperpolarizability derivatives.

The present report will concern itself with the observation of the Raman intensities of methyl iodide in carbon tetrachloride solutions. Our interest lies in the possibility of determining the magnitude of polarizability and hyperpolarizability derivatives in the form of tensor elements through the observation of solvent effects on 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, GLF-105, 15 mW), a JSG-125 grating monochromator (JEOL), a HTV R-374 photomultiplier (S-20 response), a lock-in amplifier (LI-573, NF), and a recorder. The linearity of the whole system with respect to an intensity axis was ascertained to be better than 1 percent of the full scale, as long as the output voltage was less than 10 V.

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.

The light scattered at 90° within a solid angle of 8×10^{-3} steradians was observed. The electric polarization of the incident light was rotated by the use of a half-wave plate (1419PA polarization rotator, Spex). The polarization characteristics of the monochromator and the frequency dependence of the photomultiplier sensitivity were calibrated by the use of a standard halogen lamp.

All the chemicals were commercial products of spectroscopic grade. Carbon tetrachloride and methyl iodide were doubly distilled following the directions given in the literature.[3]

The Raman intensities were observed for the ν_1, ν_2, ν_3, ν_5, and ν_6 bands of methyl iodide relative to the intensity of the ν_1 band of carbon tetrachloride for various concentrations.

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 two Raman lines will be distinguished by the suffixes a and b. The observed intensity area I is proportional to the molar concentration c_m, the scattering cross section per molecules Ω, the instrumental factors $S\beta$, and the factor for the internal field effect:[4)]

$$I_\mathrm{a} = C\cdot c_\mathrm{ma}\Omega_\mathrm{a}\frac{1}{n_\mathrm{s}}\left(\frac{n_\mathrm{a}{}^2+2}{(n_\mathrm{a}/n_\mathrm{s})^2+2}\right)^4 S_\mathrm{a}\beta_\mathrm{a} \tag{1}$$

$$I_\mathrm{b} = C\cdot c_\mathrm{mb}\Omega_\mathrm{b}\frac{1}{n_\mathrm{s}}\left(\frac{n_\mathrm{b}{}^2+2}{(n_\mathrm{b}/n_\mathrm{s})^2+2}\right)^4 S_\mathrm{b}\beta_\mathrm{b} \tag{2}$$

where C is a constant, S the relative sensitivity of the photomultiplier, β the transmittance of the monochromator for the light whose electric vector is polarized perpendicularly to the slit, 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:

$$\frac{\Omega_\mathrm{a}}{\Omega_\mathrm{b}} = \frac{I_\mathrm{a}}{I_\mathrm{b}}\cdot\frac{c_\mathrm{mb}}{c_\mathrm{ma}}\left(\frac{n_\mathrm{b}{}^2+2}{n_\mathrm{a}{}^2+2}\ \frac{(n_\mathrm{a}/n_\mathrm{s})^2+2}{(n_\mathrm{b}/n_\mathrm{s})^2+2}\right)^4\cdot\frac{S_\mathrm{b}\beta_\mathrm{b}}{S_\mathrm{a}\beta_\mathrm{a}} \tag{3}$$

Thus we can obtain the ratio, $\Omega_\mathrm{a}/\Omega_\mathrm{b}$, of the scattering cross sections from the observed intensity ratio, $I_\mathrm{a}/I_\mathrm{b}$, because c_m, S, and β are known from the experimental conditions and because the refractive indices can be measured by the use of a refractometer.

In the previous report,[2)] the expression for Raman intensity has been given for the case where the existence of the non-zero averaged molecular field introduces non-linear effects to the molecular polarizability. For the binary mixture of methyl iodide and carbon tetrachloride, the ratio of the scattering cross section of the ν_i band of methyl iodide, $\Omega(\mathrm{CH_3I};\nu_\mathrm{i})$, can be expressed by the equation:

$$\frac{\Omega(\mathrm{CH_3I};\nu_\mathrm{i})}{\Omega(\mathrm{CCl_4};\nu_1)} = \left(\frac{\lambda_1{}^4}{\lambda_\mathrm{i}{}^4}\right)\frac{B+A\langle \boldsymbol{F}_{0z}\rangle_\mathrm{av}}{{}^{Q_1}(\alpha_1^\circ)^2_{\mathrm{CCl_4}}} \tag{4}$$

where λ_1 is the wavelength of the ν_1 line of carbon tetrachloride, λ_i the wavelength of the ν_i line of methyl iodide, and ${}^{Q_1}(\alpha_1^\circ)_{CCl_4}$ the transition polarizability of carbon tetrachloride related to the normal coordinate, Q_1.

$\langle \boldsymbol{F}_{0z}\rangle_{av}$ of Eq. 4 is an averaged molecular field which is produced at the position of a methyl iodide molecule by the surrounding molecules. 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. Taking into account this type of interaction, $\langle \boldsymbol{F}_{0z}\rangle_{av}$ for a binary solution has been calculated to be[5)]

$$\langle \boldsymbol{F}_{0z}\rangle_{av} = \frac{4\pi^2}{27}N_A{}^2\mu_0\left(\left(\frac{\mu_0{}^2}{kT}+3\bar{\alpha}\right)\frac{\rho c_m}{W_m}+\left(\frac{\mu_{0s}^2}{kT}+3\bar{\alpha}_s\right)\frac{8}{K}c_{ms}\right)$$
$$+\frac{2\pi^4}{25\times 243}N_A{}^4\frac{\mu_0{}^3}{(kT)^3}\left(\mu_0{}^4\left(\frac{\rho}{W_m}\right)^3 c_m+\mu_{0s}^4\left(\frac{8}{K}\right)^3 c_{ms}\right)$$

with

$$K=\left(\left(\frac{W_m}{\rho}\right)^{1/3}+\left(\frac{W_{ms}}{\rho_s}\right)^{1/3}\right)^3 \tag{5}$$

where μ_0 is a permanent dipole moment; $\bar{\alpha}$, the averaged polarizability defined by $3\bar{\alpha}=(\alpha_{xx}+\alpha_{yy}+\alpha_{zz})$; c_m, the molar concentration; ρ, the density; W_m, the molecular weight; T, the absolute temperature; k, the Boltzmann constant; and N_A, Avogadro number. The symbols suffixed by "s" correspond to the solvent molecule. As the $\langle \boldsymbol{F}_{0z}\rangle_{av}$ is concentration dependent, we can determine the A and B values by plotting the observed $\Omega(CH_3I;\ \nu_i)/\Omega(CCl_4;\ \nu_1)$ values against the calculated $\langle \boldsymbol{F}_{0z}\rangle_{av}$ values. In Table 1, the A and B values thus obtained are summarized. The value of 1.99×10^{-50} cm^6 observed by Kato *et al.*[6)] was used for the ${}^{Q_1}(\alpha_1^\circ)^2$ of carbon tetrachloride. As for the ν_1 and ν_2 lines of methyl iodide, accurate A values could not be obtained because their intensities were not strong enough for our instrument.

TABLE 1. THE OBSERVED A AND B VALUES FOR METHYL IODIDE IN CARBON TETRACHLORIDE SOLUTION

Line	$B_{//}$ 10^{-50} cm^6	$A_{//}$ 10^{-55} cm^6 dyn esu^{-1}	$B_\perp$ 10^{-51} cm^6	$A_\perp$ 10^{-55} cm^6 dyn esu^{-1}
ν_1	2.31	—	1.50	—
ν_2	0.16	—	0.23	—
ν_3	2.38	−1.97	7.84	−1.61
ν_5	0.10	—	—	—
ν_6	0.27	—	—	—

Calculation of Transition Polarizabilities. The parameters A and B of Eq. 4 can be expressed in terms of transition polarizability and transition hyperpolarizability.[2)] In the case of a molecule belonging to a C$_{3v}$ symmetry, A and B are expressed as:

1) an a$_1$-type vibration

1-a) for a parallel component,

$$A_{//}=\frac{1}{15\gamma(\lambda_i)}[(16\gamma(\lambda_i)+2)^{Q_i}(\alpha_1^\circ)_{xx}{}^{Q_i}(\beta_1^\circ)_{xxz}$$
$$+(6\gamma(\lambda_i)+2)^{Q_i}(\alpha_1^\circ)_{zz}{}^{Q_i}(\beta_1^\circ)_{zzz}$$
$$+(4\gamma(\lambda_i)-2)^{Q_i}(\alpha_1^\circ)_{xx}{}^{Q_i}(\beta_1^\circ)_{zzz}$$
$$+(4\gamma(\lambda_i)-2)^{Q_i}(\alpha_1^\circ)_{zz}{}^{Q_i}(\beta_1^\circ)_{xxz}] \tag{6a}$$

$$B_{//}=\frac{1}{15\gamma(\lambda_i)}[(8\gamma(\lambda_i)+1)^{Q_i}(\alpha_1^\circ)^2_{xx}$$
$$+(3\gamma(\lambda_i)+1)^{Q_i}(\alpha_1^\circ)^2_{zz}$$
$$+(4\gamma(\lambda_i)-2)^{Q_i}(\alpha_1^\circ)_{xx}{}^{Q_i}(\alpha_1^\circ)_{zz}] \tag{6b}$$

1-b) for a perpendicular component,

$$A_\perp=\frac{2(15\gamma(\lambda_i)+15)}{15\gamma(\lambda_i)}({}^{Q_i}(\alpha_1^\circ)_{xx}-{}^{Q_i}(\alpha_1^\circ)_{zz})$$
$$\times({}^{Q_i}(\beta_1^\circ)_{xxz}-{}^{Q_i}(\beta_1^\circ)_{zzz}) \tag{7a}$$

$$B_\perp=\frac{1+\gamma(\lambda_i)}{15\gamma(\lambda_i)}({}^{Q_i}(\alpha_1^\circ)_{xx}-{}^{Q_i}(\alpha_1^\circ)_{zz})^2 \tag{7b}$$

2) for an e-type vibration, and for a parallel component

$$A_{//}=\frac{4\gamma(\lambda_i)+3}{15\gamma(\lambda_i)}\cdot 4({}^{Q_i}(\alpha_1^\circ)_{xy}{}^{Q_i}(\beta_1^\circ)_{xyz}+{}^{Q_i}(\alpha_1^\circ)_{yz}{}^{Q_i}(\beta_1^\circ)_{yzz}) \tag{8a}$$

$$B_{//}=\frac{4\gamma(\lambda_i)+3}{15\gamma(\lambda_i)}\cdot 2({}^{Q_i}(\alpha_1^\circ)^2_{xy}+{}^{Q_i}(\alpha_1^\circ)^2_{yz}) \tag{8b}$$

where the molecular fixed Cartesian coordinates, x, y, and z, are defined so that the z-axis coincides with the molecular axis. For e-type lines, $A_\perp$ and $B_\perp$, which correspond to the perpendicular components, are: $A_\perp=(3/4)A_{//}$ and $B_\perp=(3/4)B_{//}$. In the above equations, $\gamma(\lambda_i)=\beta_\perp(\lambda_i)/\beta_{//}(\lambda_i)$, represents the ratio of the transmittances of the monochromator for the light whose electric vector is being polarized perpendicular to the slit, $\beta_\perp(\lambda_i)$, and that parallel to the slit, $\beta_{//}(\lambda_i)$, at the wavelength λ_i. In the case of an a$_1$-type vibration of a molecule belonging to a C$_{3v}$ symmetry, the transition polarizability tensor can be completely determined if we know the elements ${}^{Q}(\alpha_1^\circ)_{zz}$ and ${}^{Q}(\alpha_1^\circ)_{xx}$, because the relations between the tensor elements are:

$$ {}^{Q_1}(\alpha_1^\circ)_{xx}={}^{Q_1}(\alpha_1^\circ)_{yy}\mp 0,\quad {}^{Q_1}(\alpha_1^\circ)_{zz}\mp 0,$$
$$ {}^{Q_1}(\alpha_1^\circ)_{xy}={}^{Q_1}(\alpha_1^\circ)_{xz}={}^{Q_1}(\alpha_1^\circ)_{yz}=0.$$

For an e-type vibration, it is necessary to know the elements ${}^{Q}(\alpha_1^\circ)_{xy}$ and ${}^{Q}(\alpha_1^\circ)_{yz}$, because the relations which hold in this case are:[7)]

$$ {}^{Q_i}(\alpha_1^\circ)_{xx}={}^{Q_i}(\alpha_1^\circ)_{yy}={}^{Q_i}(\alpha_1^\circ)_{zz}={}^{Q_i'}(\alpha_1^\circ)_{zz}=0,$$
$$ {}^{Q_i'}(\alpha_1^\circ)_{xy}={}^{Q_i'}(\alpha_1^\circ)_{yz}={}^{Q_i}(\alpha_1^\circ)_{xz}=0,$$
$$ {}^{Q_i}(\alpha_1^\circ)_{xy}=-{}^{Q_i'}(\alpha_1^\circ)_{yy}={}^{Q_i'}(\alpha_1^\circ)_{xx},$$
$$ {}^{Q_i}(\alpha_1^\circ)_{yz}=-{}^{Q_i'}(\alpha_1^\circ)_{xz}.$$

where Q_i and Q_i' refer to the doubly degenerated normal coordinate pair. Similar relations hold between transition hyperpolarizabilities, as has been shown in the previous report.[7)]

Using the A and B values obtained for the a$_1$-type vibrations, we can obtain the transition polarizabilities and hyperpolarizabilities, ${}^{Q}(\alpha_1^\circ)_{xx}$, ${}^{Q}(\alpha_1^\circ)_{zz}$, ${}^{Q}(\beta_1^\circ)_{xxz}$, and ${}^{Q}(\beta_1^\circ)_{zzz}$. First, we can determine ${}^{Q}(\alpha_1^\circ)_{xx}$ and ${}^{Q}(\alpha_1^\circ)_{zz}$ by solving the simultaneous equation which is composed from Eqs. 6b and 7b. Then, the ${}^{Q}(\beta_1^\circ)_{xxz}$ and ${}^{Q}(\beta_1^\circ)_{zzz}$ values can be determined by putting the ${}^{Q}(\alpha_1^\circ)_{xx}$ and ${}^{Q}(\alpha_1^\circ)_{zz}$ values into Eqs. 6a and 7a and by solving the resultant simultaneous equation composed from Eqs. 6a and 7a. The polarizability derivative, $\partial\alpha^\circ/\partial Q$, is related to the transition polarizability, ${}^{Q}(\alpha_1^\circ)$, as

$$ {}^{Q}(\alpha_1^\circ)_{ij}=\left(\frac{\partial\alpha_{ij}^\circ}{\partial Q}\right)\langle I|Q|F\rangle$$

Table 2. Plausible sets of polarizability derivatives for a_1-type lines of methyl iodide (10^{-6} $g^{-1/2}$ cm^2)

#	$\partial\alpha_{xx}/\partial Q_1$	$\partial\alpha_{zz}/\partial Q_1$	$\partial\alpha_{xx}/\partial Q_2$	$\partial\alpha_{zz}/\partial Q_2$	$\partial\alpha_{xx}/\partial Q_3$	$\partial\alpha_{zz}/\partial Q_3$
1	10.74	23.42	3.49	0.36	9.02	−2.46
2	10.74	23.42	3.49	0.36	1.37	12.84
3	10.74	23.42	3.49	0.36	−9.02	2.46
4	10.74	23.42	3.49	0.36	−1.37	−12.84
5	10.74	23.42	1.41	4.54	9.02	−2.46
6	10.74	23.42	1.41	4.54	1.37	12.84
7	10.74	23.42	1.41	4.54	−9.02	2.46
8	10.74	23.42	1.41	4.54	−1.37	−12.84
9	10.74	23.42	−3.49	−0.36	9.02	−2.46
10	10.74	23.42	−3.49	−0.36	1.37	12.84
11	10.74	23.42	−3.49	−0.36	−9.02	2.46
12	10.74	23.42	−3.49	−0.36	−1.37	−12.84
13	10.74	23.42	−1.41	−4.54	9.02	−2.46
14	10.74	23.42	−1.41	−4.54	1.37	12.84
15	10.74	23.42	−1.41	−4.54	−9.02	2.46
16	10.74	23.42	−1.41	−4.54	−1.37	−12.84
17	19.19	6.51	3.49	0.36	9.02	−2.46
18	19.19	6.51	3.49	0.36	1.37	12.84
19	19.19	6.51	3.49	0.36	−9.02	2.46
20	19.19	6.51	3.49	0.36	−1.37	−12.84
21	19.19	6.51	1.41	4.54	9.02	−2.46
22	19.19	6.51	1.41	4.54	1.37	12.84
23	19.19	6.51	1.41	4.54	−9.02	2.46
24	19.19	6.51	1.41	4.54	−1.37	−12.84
25	19.19	6.51	−3.49	−0.36	9.02	−2.46
26	19.19	6.51	−3.49	−0.36	1.37	12.84
27	19.19	6.51	−3.49	−0.36	−9.02	2.46
28	19.19	6.51	−3.49	−0.36	−1.37	−12.84
29	19.19	6.51	−1.41	−4.54	9.02	−2.46
30	19.19	6.51	−1.41	−4.54	1.37	12.84
31	19.19	6.51	−1.41	−4.54	−9.02	2.46
32	19.19	6.51	−1.41	−4.54	−1.37	−12.84

where $\langle I|Q|F\rangle$ is a transition matrix element corresponding to the transition between the vibrational levels I and F.

As the Eqs. 6b and 7b are quadratic with respect to the polarizability derivatives, there are four possible sets of polarizability derivative values for each normal mode, Q_1, Q_2, and Q_3. Therefore, there can be obtained $4^3=64$ possible combinations of polarizability derivatives, which are summarized in Table 2. The sixty-four sets of polarizability derivatives can be classified into two groups whose polarizability derivatives have exactly the same absolute values with an opposite sign. As we have no way to distinguish these two groups at present, we assume that all the polarizability derivatives related with the normal mode Q_1 are positive.[8] Therefore, we consider only thirty-two sets of polarizability derivatives hereafter.

Determination of Transition Polarizability. In order to select the most reliable set of polarizability derivatives out of the thirty-two, we introduce the so-called bond polarizability theory which was proposed first by Wolkenstein[9] and Eliashevich[10] and was modified later by Long.[11] The basic idea of this theory is the assignment of a characteristic bond polarizability to each bond in the molecule. This bond polarizability is then defined completely in terms of a polarizability ellipsoid having the major axis coincident with the bond direction. Instead of an irreducible tensor expression which is used in Long's theory, we focus our attention on a reducible tensor, simply because it is more convenient for determining the elements of a transition polarizability tensor. The polarizability derivative, $\partial\alpha/\partial Q$, is expressed as a linear combination of the bond polarizability parameters:[12]

$$\begin{aligned}\frac{\partial\alpha}{\partial Q} &= (J(\gamma_1')K^*L_x)\gamma_1' + (J(\delta_1')K^*L_x)\delta_1' \\ &\quad + (J(\varepsilon_1)K^*L_x)\frac{\varepsilon_1}{r_{CI}} + (J(\gamma_2')K^*L_x)\gamma_2' \\ &\quad + (J(\delta_2')K^*L_x)\delta_2' + (J(\varepsilon_2)K^*L_x)\frac{\varepsilon_2}{r_{CH}} \qquad (9)\end{aligned}$$

where $(\gamma_1', \delta_1', \varepsilon_1/r_{CI})$ and $(\gamma_2', \delta_2', \varepsilon_2/r_{CH})$ are the bond polarizability parameters related with the C–I and C–H bonds, respectively. The matrices J and K are determined only from the molecular geometry. The matrix L_x is the transformation matrix between the Cartesian displacement coordinates fixed in the molecule and the normal coordinates, and therefore can be calculated from the molecular force field. In the case of the a_1-type vibrations of methyl iodide, the transformation matrix (JKL_x) is 6×6, because the number of the bond polarizability parameters is six, while the six elements of the bond polarizability derivative contribute to the scattering cross-section of the a_1-type vibrations. Therefore, we can in principle calculate the bond polarizability parameters by the use of the polarizability derivative values of Table 2. The transformation matrix (JKL_x), which was calculated by the use of the force constants reported by Crawford *et al.*,[8] relates the polarizability derivatives and the bond polarizability parameters:

$$\begin{bmatrix} \partial\alpha^\circ_{xx}/\partial Q_1 \\ \partial\alpha^\circ_{zz}/\partial Q_1 \\ \partial\alpha^\circ_{xx}/\partial Q_2 \\ \partial\alpha^\circ_{zz}/\partial Q_2 \\ \partial\alpha^\circ_{xx}/\partial Q_3 \\ \partial\alpha^\circ_{zz}/\partial Q_3 \end{bmatrix} = \begin{bmatrix} 0 & a & 0 & d & i & m \\ a & a & 0 & e & j & n \\ 0 & b & 0 & f & k & p \\ b & b & 0 & g & k & q \\ 0 & c & 0 & h & l & r \\ c & c & 0 & i & l & s \end{bmatrix} \begin{bmatrix} \gamma_1' \\ \delta_1' \\ \varepsilon_1/r_{CI} \\ \gamma_2' \\ \delta_2' \\ \varepsilon_2/r_{CH} \end{bmatrix} \tag{10}$$

Eq. 10 shows that the parameter ν_1 does not contribute to any polarizability derivatives and, therefore, the inverse matrix $(JKL_x)^{-1}$ does not exist. However, we can reduce the transformation matrix of Eq. 10 into:

$$\begin{bmatrix} \partial\alpha^\circ_{xx}/\partial Q_1-\partial\alpha^\circ_{zz}/\partial Q_1 \\ \partial\alpha^\circ_{xx}/\partial Q_2-\partial\alpha^\circ_{zz}/\partial Q_2 \\ \partial\alpha^\circ_{xx}/\partial Q_3-\partial\alpha^\circ_{zz}/\partial Q_3 \end{bmatrix} = \begin{bmatrix} -a & d-l & m-n \\ -b & f-g & p-q \\ -c & h-i & r-s \end{bmatrix} \begin{bmatrix} \gamma_1' \\ \delta_2' \\ \varepsilon_2/r_{CH} \end{bmatrix} \tag{11}$$

Thus we can calculate the bond polarizability parameters, γ_1', γ_2', and ε_2/r_{CH}, by solving Eq. 11. By putting back the calculated bond polarizability parameters into Eq. 10 and by solving the linear equations composed from the first and the third columns of Eq. 10, we can obtain the remaining bond polarizability parameters, δ_1' and δ_2'. In other words, we can calculate the thirty-two sets of bond polarizability parameters, γ_1', γ_2', δ_1', δ_2', and ε_2/r_{CH}, which correspond to the thirty-two sets of polarizability derivatives. Finally, we calculate the polarizability derivatives, $\partial\alpha^\circ_{xx}/\partial Q_3$ and $\partial\alpha^\circ_{zz}/\partial Q_3$, using the fifth and sixth columns of Eq. 10: the results are summarized in Table 3. By comparing the calculated values of $\partial\alpha^\circ_{xx}/\partial Q_3$ and $\partial\alpha^\circ_{zz}/\partial Q_3$ with the observed values of Table 2, we can select the eight possible sets of molecular polarizability derivatives (#11, 12, 15, 16, 27, 28, 31, and 32) out of the thirty-two sets of Table 2.

The next step is to select more reliable sets of polarizability derivatives out of the eight sets. This can be done by calculating the remaining undetermined bond polarizability parameter, ε_1/r_{CH}, from the observed intensities related with the e-species Raman lines. For the e-type vibrations, the transformation matrix (JKL_x), which was calculated by the use of the force constants of Crawford,[8] relates the polarizability derivatives and the bond polarizability parameters:

$$\begin{bmatrix} \partial\alpha^\circ_{xy}/\partial Q_i \\ \partial\alpha^\circ_{yz}/\partial Q_i \end{bmatrix} = \begin{bmatrix} 0 & a & b \\ c & d & e \end{bmatrix} \begin{bmatrix} \varepsilon_1/r_{CI} \\ \gamma_2' \\ \varepsilon_2/r_{CH} \end{bmatrix} \tag{12}$$

By putting the eight possible sets of polarizability parameters previously calculated, γ_2' and ε_2/r_{CH}, into Eq. 12 and by putting Eq. 12 into Eq. 8b, we can derive the quadratic equation with respect to the remaining bond polarizability parameter, ε_1/r_{CI}. Thus the remaining bond polarizability parameter, ε_1/r_{CI}, can be calculated for both ν_5 and ν_6 lines corresponding to the eight possible sets of bond polarizability parameters. The results are summarized in Table 4. As the bond polarizability parameters should be real, the sets #11, 12, 15, 28, 31, and 32, can be discarded, because the calculated ε_1/r_{CI} values are imaginary. The remaining sets #16 and 27 are considered to be reasonable, because the ε_1/r_{CI} values which have been obtained are similar in magnitude for ν_5 and ν_6: 2.54×10^{-16} cm^2 (ν_5) and 2.24×10^{-16} cm^2 (ν_6) for #16, and -2.54×10^{-16} cm^2 (ν_5) and -2.24×10^{-16} cm^2 (ν_6) for #27. There is no way to distinguish these two sets of polarizability derivatives within the bond polarizability hypothesis. Fortunately, however, we can choose sets #16 as the most reliable set of molecular polarizability derivatives, because of the following reason.

In the preceding discussion, the transition polarizability related with the Q_3 normal mode, $^{Q_3}(\alpha_1^\circ)_{zz}$, was obtained to be 2.94×10^{-25} cm^3 (for #16) or -2.94×10^{-25} cm^3 (for #27). According to our previous work

TABLE 3. POLARIZABILITY DERIVATIVES FOR Q_3 OF METHYLIODIDE CALCULATED FROM BOND POLARIZABILITY PARAMETERS (10^{-5}g$^{-1/2}$ cm^2)

#	$\partial\alpha_{xx}/\partial Q_3$	$\partial\alpha_{zz}/\partial Q_3$	#	$\partial\alpha_{xx}/\partial Q_3$	$\partial\alpha_{zz}/\partial Q_3$
1	6.14	−5.33	17	6.11	−5.36
2	−1.50	9.97	18	−1.53	9.94
3	−1.50	9.97	19	−1.53	9.94
4	6.14	−5.33	20	6.11	−5.36
5	6.14	−5.33	21	6.12	−5.35
6	−1.50	9.97	22	−1.52	9.94
7	−1.50	9.97	23	−1.52	9.94
8	6.14	−5.33	24	6.12	−5.35
9	−1.87	−13.34	25	−1.89	−13.36
10	−9.51	1.96	26	−9.53	1.94
11	−9.51	1.96	27	−9.53	1.94
12	−1.87	−13.34	28	−1.89	−13.34
13	−1.87	−13.34	29	−1.89	−13.37
14	−10.00	1.48	30	−9.54	1.93
15	−10.00	1.48	31	−9.54	1.93
16	**−1.87**	−13.34	32	−1.89	−13.37

Table 4. ε_2/r_{CH} values calculated for ν_5 and ν_6 lines (10^{-16} cm^2)

♯	11	12	15	16
ν_5	3.61±1.96i	7.93±10.2i	8.12±13.0i	2.54 −7.98
ν_6	−0.67 −2.70	3.35±9.39i	3.93±1.26i	2.24 −0.05
♯	27	28	31	32
ν_5	−2.54 7.98	8.12±13.0i	7.93±10.2i	3.61±1.96i
ν_6	−2.24 0.05	3.93±1.26i	3.35±9.39i	−0.67 −2.70

on the solvent effect on the infrared absorption intensity for the ν_3 band of methyl iodide,[1] the $^{Q_3}(\alpha_1^\circ)_{zz}$ has been obtained to be -1.1×10^{-25} cm^3. We should not attach too much importance to the absolute values of these results, because the frequency region of the infrared measurement belongs to the resonant region, while that of the Raman measurement belongs to the off-resonant region. However, the minus sign attached to the $^{Q_3}(\alpha_1^\circ)_{zz}$ value is of much importance, because the signs attached to the $^{Q_3}(\alpha_1^\circ)_{zz}$ values of the Raman and infrared results should be the same. Thus we can say that set ♯16 is more reliable than set ♯27.

Determintaion of Transition Hyperpolarizability. Using the finally determined set of polarizability derivatives, that is,

$$^{Q_1}(\alpha_1^\circ)_{xx} = 1.05\times10^{-25} \quad (\mathrm{cm}^3)$$
$$^{Q_1}(\alpha_1^\circ)_{zz} = 2.28\times10^{-25} \quad (\mathrm{cm}^3)$$
$$^{Q_2}(\alpha_1^\circ)_{xx} = -2.10\times10^{-26} \quad (\mathrm{cm}^3)$$
$$^{Q_2}(\alpha_1^\circ)_{zz} = -6.76\times10^{-26} \quad (\mathrm{cm}^3)$$
$$^{Q_3}(\alpha_1^\circ)_{xx} = -3.14\times10^{-26} \quad (\mathrm{cm}^3)$$
$$^{Q_3}(\alpha_1^\circ)_{zz} = -2.94\times10^{-25} \quad (\mathrm{cm}^3)$$

and using Eqs. 6a and 7a, we can calculate the transition hyperpolarizability elements for Q_3:

$$^{Q_3}(\beta_1^\circ)_{xxz} = 7.07\times10^{-31} \quad (\mathrm{cm^3\,dyn^{-1}\,esu})$$
$$^{Q_3}(\beta_1^\circ)_{zzz} = 8.88\times10^{-31} \quad (\mathrm{cm^3\,dyn^{-1}\,esu})$$

which are certainly of the correct order of magnitude. The magnitude of the transition hyperpolarizability has been considered to be of the order of 10^{-31}—10^{-32} (cm^3 dyn^{-1} esu), although no direct measurement of transition hyperpolarizability has actually been reported yet.

Concluding Discussion. From the discussion of the previous paragraphs, a few important conclusions can be drawn.

1) It was shown that the hyperpolarizability, which is a higher order term of the polarizability, does change the Raman intensities through the existence of the averaged molecular field, $\langle F_{0z}\rangle_{av}$, in solution. If the averaged molecular field is properly estimated, the transition polarizability and transition hyperpolarizability can be determined simultaneously in the form of tensor elements by observing the solvent effect on Raman intensity.

2) For determining the sign of the transition polarizability, the bond polarizability theory has been shown to be quite helpful. At the same time, the information about the sign of the transition polarizability which is observed in the solvent effect on infrared intensity is very important and convincing.

3) Incidentally, this seems to be the first work in which the transition hyperpolarizability is obtained in the form of a tensor element. The examination of the reliability of the resultant transition hyperpolarizability, however, will be left for future studies in which the transition hyperpolarizability will be directly observed by, for example, the intensity measurement of a hyper-Raman line.

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5) In our previous reports (Ref. 1 and Ref. 2), the terms corresponding to the dipole-induced dipole interaction have been under-estimated. Readers are invited to have more confidence in Eq. 5 of the present report.

6) Y. Kato, Thesis submitted to the University of Tokyo (1969).

7) These relations have been mis-printed in Appendix II of Ref. 2. Readers are invited to read Eq. A25 and Eq. A22 of Ref. 2 as:

$$^{Q_s}(\beta_1^\circ)_{xyz} = -^{Q_s'}(\beta_1^\circ)_{yyz} = {}^{Q_s'}(\beta_1^\circ)_{xxz}$$
$$^{Q_s}(\beta_1^\circ)_{yzz} = -^{Q_s'}(\beta_1^\circ)_{xzz} \qquad \text{(A25)}$$
$$^{Q_s}(\alpha_1^\circ)_{xy} = -^{Q_s'}(\alpha_1^\circ)_{yy} = {}^{Q_s'}(\alpha_1^\circ)_{xx}$$
$$^{Q_s}(\alpha_1^\circ)_{yz} = -^{Q_s'}(\alpha_1^\circ)_{xz} \qquad \text{(A22)}$$

8) This assumption has been widely accepted in previous works: A. D. Dickson, I. M. Mills, and B. L. Crawford, Jr., *J. Chem. Phys.*, **27**, 445 (1957); D. A. Long, *Trans. Faraday Soc.*, **59**, 43 (1963).

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12) For the detailed notations, see R. E. Hester in: "Raman Spectroscopy," ed by Szymanski, Plenum Press, New York (1967), Chap. 4.