Rotational Isomerism and Intermolecular Interaction in the Liquid Phase

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The Raman intensities of some fundamental lines of 1,2-dichloroethane and 1,2-dibromoethane and related molecules with internal rotation axes were observed at various temperatures. The observed relative intensities were corrected for some systematic errors expected in the intensity measurement. The importance of a local-field effect was emphasized. The van't Hoff plot of the observed intensity ratios of the *trans* and *gauche* isomers showed the existence of strong intermolecular interactions in the liquid phase. The intermolecular interaction energy in the liquid phase was theoretically estimated from both the macroscopic and microscopic points of view. The usefulness of a dipole-dipole interaction model was emphasized.

Rotational isomerism has been one of the major subjects in the field of physical chemistry. Many investigations have been concerned with the determination of the energy difference between rotational isomers, ΔE. In doing so, one uses the van't Hoff relation and plots the logarithms of the intensity ratio of the vibration spectra of two isomers against $1/T$, where T is the absolute temperature, and thus obtains ΔE from the slope of the plot. This method may be reasonable for the study of ΔE in the gas phase. In the case of a liquid, however, ΔE may be dependent on the temperature because of the existence of intermolecular interactions.

The present report will be concerned with the accurate measurement of the relative intensities of the Raman lines corresponding to the rotational isomers and with the determination of the interaction terms which mainly contribute to ΔE. In order to estimate the interaction energy from the microscopic point of view, it is necessary to know the relative population of the rotational isomers coexisting in the liquid phase. Detailed discussions will also be given for some experimental problems in determining relative populations from the observed Raman intensities.

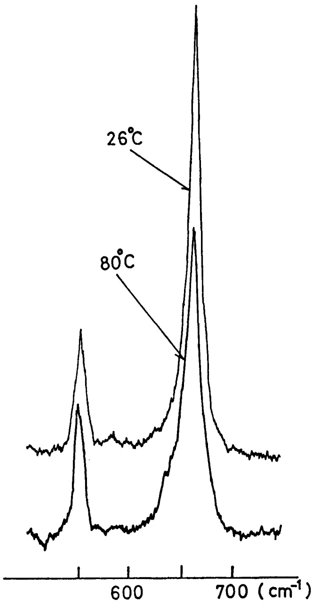

Fig. 1. Raman spectra of 1,2-dibromoethane in the region of 700—500 cm^{-1}.

Experimental

The samples used in the present work were commercial products. After fractional distillation, the purity was checked by gas chromatography.

The Raman spectra were recorded using a laser Raman spectrometer designed and constructed by the authors.[1] The instrument is composed of a He–Ne gas laser source (NEC, GLC 108, 50 mW), a Spex 1401 double monochromator, a HTV R-376 photomultiplier (S-20 response), a handmade lock-in amplifier (375 cps modulation), and a recorder. The linearity of the whole electronic system has been carefully tested. From the standard errors estimated by a linear fitting of the final output voltage against the light energy, the linearity of the whole system was claimed to be better than 1% of the full scale as long as the full scale output voltage was within 10—0.3 V[1]. Special attention was paid to the stability of the laser source.

The stability of the laser output during the spectral measurement was observed by monitoring the light energy which penetrated through the 100% reflectance mirror of the laser cavity. When the output power of the laser source drifted more than 1% during the intensity measurements, the data observed were completely discarded.

The high-temperature cell used for the measurement has been described previously.[2] The accuracy of the observed temperature is within ±1 °C.

The 754 and 654 cm^{-1} lines of 1,2-dichloroethane were used for the relative intensity measurements. These two lines correspond to the C–Cl stretching vibrations of the *trans* and *gauche* isomers respectively. As for 1,2-dibromoethane, the, 660 cm^{-1} (of *trans*) and the 551 cm^{-1} (of *gauche*) lines were used. Those four lines have scattering cross sections large enough for their relative intensities to be observed with a high accuracy. Relative intensity measurements were repeated eight times at each temperature, the reproducibility of the observed integrated intensities was more than 99%. A typical trace of the observed spectra of 1,2-dibromoethane is illustrated in Fig. 1, which may demonstrate the actual S/N ratio of the observation. The relative intensity areas were determined by a weight method. The averaged value of the eight intensity data was taken as the observed Raman intensity. The maximum deviation of the observed intensity from the averaged value was less than 2%.

Results and Discussion

Correction of the Intensity Data for Systematic Errors. In a previous report, the apparent intensity change due to the temperature has been throughly discussed for typical liquid systems, where the importance of a local-field effect and a density effect have been emphasized.[2] According to the conclusion of the report, an appropriate factor or local-field correction for Raman scattering, L, may be expressed as:

$$L=\frac{(n^2+2)^4}{81}, \tag{1}$$

if the variation in the refractive index over the frequency range of the Raman shift can be ignored. The refractive indices for different temperatures may be estimated from the empirical Eykman equation:

$$\frac{n^2-1}{n+0.4}=\frac{d}{M}\times C, \tag{2}$$

where C is a constant characteristic for a molecule; M the molecular weight, and d, the density.[3] The density, d, as a function of temperature may be found in the International Critical Tables.[4]

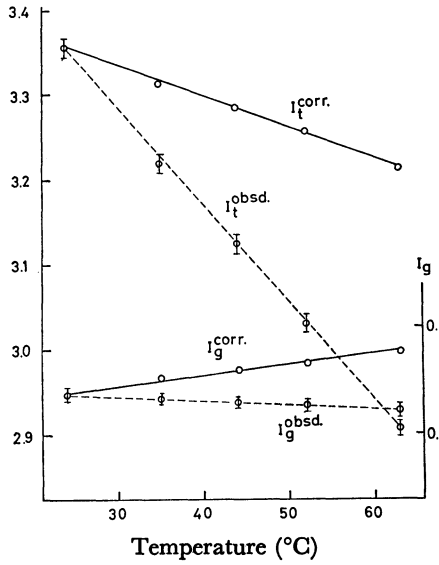

Fig. 2. Raman intensity changes due to temperature for 1,2-dibromoethane.
Observed value; ······, corrected value; ——.

The observed relative intensities were corrected for the above two factors. The importance and the validity of those corrections are most obvious for 1,2-dibromoethane. In Fig. 2, the observed (denoted as I^{obsd}) and corrected (denoted as I^{corr}) intensities are plotted against the temperature in arbitrary units. It may be seen from the figure that both I_t^{obsd} (of the *trans* isomer) and I_g^{obsd} (of the *gauche* isomer) decrease in magnitude as the temperature increases. If the scattering cross section of the *trans* and *gauche* bands do not change in magnitude within the temperature range of the present experiment, this result is obviously strange because the *trans* and *gauche* isomers are in a thermal equilibrium. After being corrected for the effects of the density and a local-field, however, I_t^{corr} decreases in magnitude as the temperature increases, while I_g^{corr} increases in magnitude within the same temperature range.

Determination of the Relative Population of Rotational Isomers. If we know a scattering cross section of individual Raman lines, the relative population of rotational isomers can be determined from the observed intensity data. Haltman *et al.*[5] have discussed this problem in the case of an infrared absorption and proposed this relation:

$$\frac{A_1}{\alpha_1}+\frac{A_2}{\alpha_2}=C_{\mathrm{T}}, \tag{3}$$

if components 1 and 2 are in thermal equilibrium. In Eq. 3, C_{T} is the total concentration of components 1 and 2; A, the band area, and α, the absorption coefficient. A similar relation holds for the case of a Raman scattering;

$$\frac{I_t^{\mathrm{obsd}}}{\Omega_t}+\frac{I_g^{\mathrm{obsd}}}{\Omega_g}=C, \tag{4}$$

or

$$I_g^{\mathrm{obsd}}=-(\Omega_g/\Omega_t)I_t^{\mathrm{obsd}}+\Omega_g C \tag{4'}$$

where Ω is an absolute scattering cross section, and C, a constant determined by the experimental conditions. By plotting I_g^{obsd} against I_t^{obsd} at series of temperatures, a straight line with a slope of $-(\Omega_g/\Omega_t)$ is generated as long as the scattering cross sections, Ω_g and Ω_t, are constant over the temperature range. As was emphasized in the preceding section, however, the correction of the intensity data for the systematic errors is a pivotal point for the determination of (Ω_g/Ω_t) by the use of Eq. 4.[6] Therefore, Eq. 4 should be modified to:

$$\frac{I_t^{\mathrm{corr}}}{\Omega_t}+\frac{I_g^{\mathrm{corr}}}{\Omega_g}=C. \tag{5}$$

The same intensity correction is also important in the case of infrared absorption, because the observed band area, A, should be corrected for the same types of systematic errors.[7,8]

Figure 3 shows the plotting of I_g^{corr} against I_t^{corr} at a series of temperatures for 1,2-dibromoethane. As is to be expected from Eq. 5, the plot gives a straight

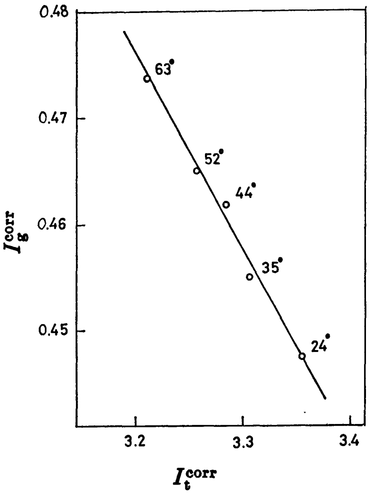

Fig. 3. $I_g^{\mathrm{corr}}-I_t^{\mathrm{corr}}$ plot for 1,2-dibromoethane.

line with a slope of $-(\Omega_g/\Omega_t) = -0.18$ for 1,2-dibromoethane. The number ratio of the *trans* and *gauche* isomers can, then, be calculated from this relation:

$$\frac{n_t}{n_g} = \frac{I_t^{\mathrm{corr}}}{I_g^{\mathrm{corr}}}\frac{\Omega_g}{\Omega_t}. \qquad (6)$$

In the case of 1,2-dichloroethane, the $I_g^{\mathrm{corr}} - I_t^{\mathrm{corr}}$ plot was not successful, because the temperature dependence of the relative intensities of the *trans* and *gauche* bands was very small.

van't Hoff Plot and Energy Difference between Rotational Isomers. It has been widely accepted that the energy difference between the *trans* and *gauche* isomers, $\Delta E = E_g - E_t$, can be obtained by the use of the van't Hoff relation:

$$\ln\left(\frac{n_t}{n_g}\right) = A^\circ + \left(\frac{\Delta E}{kT}\right) \qquad (7)$$

where A° is a constant; k, the Boltzmann constant, and T, the absolute temperature. Equation 7 claims that a straight line relation should hold between $\ln(n_t/n_g)$ and $(1/T)$. Actually, the observed $\ln(n_t/n_g)$ is plotted against $(1/T)$ in Fig. 4. We see from the figure that a straight line relation does not hold for the present results. This probably means that ΔE depends on the temperature in the case of liquid 1,2-dibromoethane. The effects of the entropy changes due to the temperature are included in the constant term, A°, of Eq. 7. These effects are ascertained to be negligible in the present discussion if we take into account the frequency changes in the torsional vibrations due to the temperature, and if we assume that the molecular structure is independent of the temperature within the temperature range of the present experiment. It is important to add that the absolute scattering cross sections of the *trans* and *gauche* bands are verified to be independent of the temperature from the plotting of Fig. 3.

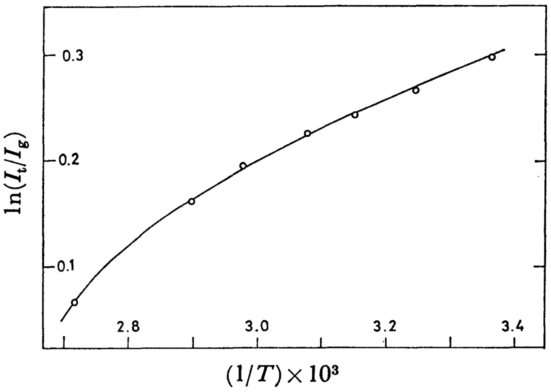

Fig. 4. Relation between $\ln(n_t/n_g)$ and $(1/T)$ for 1,2-dibromoethane.

From the $\ln(n_t/n_g)$ against $(1/T)$ plot, the ΔE values of 650—900 cal/mol are obtained according to the temperature range under consideration. If we fit the observed points to a linear function, the value of 750 cal/mol is obtained for ΔE of liquid 1,2-dibromoethane. Similar anomalous behavior for van't Hoff plot has been observed for the molecules whose *gauche* forms have large dipole moments, such as 1,2-dichloroethane and 1,1,2,2-tetrabromoethane. In the case of non-polar molecules, on the other hand, beautiful straight lines have been obtained for the van't Hoff plot. A typical example observed for the TT- and TG-form bands of pentane is illustrated in Fig. 5.[9] These results indicate that ΔE is dependent on the temperature and that the temperature dependency may arise from intermolecular interactions related with a dipole moment. As the *trans* isomer has no dipole moment, only the interaction between the *gauche* isomers will be considered.

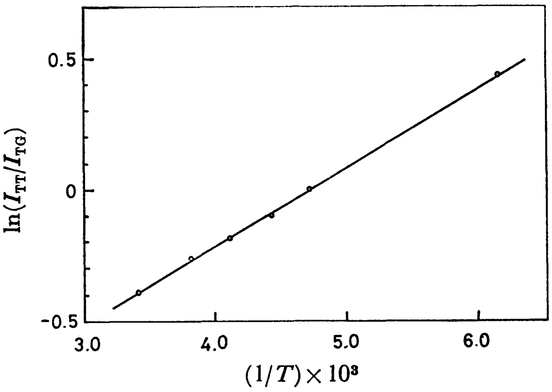

Fig. 5. van't Hoff plot for the TT- and TG-bands of pentane.

Taking into account the intermolecular interactions expected in the liquid phase, we may rewrite Eq. 7 as:

$$\ln\left(\frac{n_t}{n_g}\right) = A^\circ + \left(\frac{\Delta E^\circ}{kT}\right) + \left(\frac{H}{kT}\right) \qquad (8)$$

where H represents the stabilization energy of the *gauche* isomer due to the intermolecular interaction of the dipole type, and where ΔE° menas the intrinsic energy difference between rotational isomers or the energy difference in the rotational isomers when they are well isolated from other molecules. In other words, ΔE° is to be compared with the energy difference observed in the gas phase. If an interaction term, H/kT, be estimated, the $\ln(n_t/n_g)$ values for the gas phase can be estimated from those observed in the liquid phase:

$$\ln\left(\frac{n_t}{n_g}\right)_{\mathrm{gas}} = \ln\left(\frac{n_t}{n_g}\right)_{\mathrm{liquid}} - \left(\frac{H}{kT}\right) \qquad (9)$$

Estimation of the Interaction Energy: Macroscopic.

The simplest way of estimating the interaction energy, H, has been proposed by Watanabe.[10] The idea is based upon the reaction field of Onsager in a dilectric field.[11]

If we consider the dielectric field of Onsager, and consider a small cavity with a radius, a, in a continuous medium of the dielectric constant, ε, a dipole moment, μ, at the center of this cavity should cause dielectric polarization in the continuous medium. The polarization in turn exerts a field, F, upon the original dipole:

$$F = \frac{2(\varepsilon-1)}{2\varepsilon+1}\frac{\mu}{a^3} \qquad (10)$$

In the present case, the *gauche* isomer can be represented by the sphere, because the *trans* isomer has no dipole moment. The *gauche* isomer in the liquid phase will then possess an excess of electrostatic energy by an amount of:

$$H = \frac{(\varepsilon - 1)}{2\varepsilon + 1} \frac{\mu_g}{a^3} \tag{11}$$

as compared with that of the free molecule, where, in the present case, μ_g, is the permanent dipole moment of the *gauche* isomer. The corresponding energy change in the *trans* isomer with no dipole moment is negligible. By introducing the observed μ_g, and ε values of Morino *et al.*[12] into Eq. 11, the (H/kT) values were obtained. Then the expected values of $\ln(n_t/n_g)_{\mathrm{gas}}$ were calculated by the use of Eq. 9. The results are given in the last column of Table 1 and are illustrated on Fig. 6 (denoted as the Onsager Field). Obviously, the calculated points of $\ln(n_t/n_g)$ for different temperatures fall on a straight line, from which the $\Delta E°$ value expected for the gas phase is calculated to be 1.6 kcal/mol and the $\ln(n_t/n_g)$ value, to be 1.53 at 20 °C. The experimental $\Delta E°$ values observed by the dielectric constant measurement,[13] and the vibration spectra[14—16] are 1.4—1.78 kcal/mol. These values agree well with the calculated value of 1.6 kcal/mol. The logarithmic relative population, $\ln(n_t/n_g)$, as observed by a gas-phase electron-diffraction method, has been reported to be 1.38—1.7 at 20 °C.[17] The agreements between the expected and observed values are quite satisfactory; this indicates the validity of the way of estimating the interaction term, H, on a macroscopic base.

TABLE 1. OBSERVED AND CALCULATED $\ln(n_t/n_g)$-VALUES AT VARIOUS TEMPERATURES

(I) Dipole-dipole interaction, (II) dipole-dipole interaction+dipole-induced dipole interaction, (III) reaction field of Onsager.

Temperature (°C)	Observed (Liquid)	Calculated		
		(I)	(II)	(III)
24	0.300	0.755	0.951	1.534
35	0.269	0.690	0.878	1.444
44	0.245	0.640	0.822	1.372
52	0.232	0.603	0.779	1.318
63	0.199	0.544	0.713	1.233
72	0.164	0.490[a]	0.654[a]	1.157[a]
97	0.071	0.362[a]	0.522[a]	1.018[a]

a) Density as a function of the temperature is not given in these temperature ranges (see Ref. 4).

Estimation of the Interaction Energy: *Microscopic.* The preceding discussion has been based upon a macroscopic point of view. As the macroscopic estimation of H was quite successful, it is of much importance to calculate the interaction term, H, on a microscopic base, also.

Consider the environments to be built up of gas-like molecules dispersed in a vacuum to give the actual density of the liquid phase, instead of looking on them as continuous dielectrics. Only the interactions between the *gauche* isomers are considered in the estimation of H, because the *gauche* isomer has a large dipole moment. Then, H is expressed as:[18,19]

$$H = H_1 + H_2 \tag{12}$$

where

$$H_1 = -\frac{4\pi^2}{27} \frac{\mu_g^4}{kT} \left(\frac{\rho}{W_m}\right)^2 \frac{N_a^2}{1 + (n_t/n_g)} \tag{12a}$$

$$H_2 = -\frac{4\pi^2}{27} \alpha m^2 \left(\frac{\rho}{W_m}\right)^2 N_a^2 \tag{12b}$$

and

$$m = \frac{\mu_g}{1 - \dfrac{4\pi^2}{27}\left(\dfrac{\rho}{W_m}\right) N_a^2 \alpha \left[\dfrac{\mu_g^2}{kT} \dfrac{1}{1+(n_t/n_g)} + \alpha\right]} \tag{12c}$$

In Eqs. 12, μ_g is a dipole moment of the *gauche* isomer; ρ, the density; W_m, the molecular weight; α, the averaged polarizability of a *trans-gauche* mixture; N_a, Avogadro's number, and k, the Boltzmann constant. H_1 corresponds to the dipole-dipole interaction between the *gauche* isomers, and H_2, the dipole-induced dipole interaction. By introducing the observed values of μ_g,[12] ρ, and α[20] into Eqs. 12, we obtained the expected values, $\ln(n_t/n_g)$, by the use of Eq. 9. The results are summarized in Table 1 and are illustrated in Fig. 6. The results show that the value of 1.2 kcal/mol is obtained for $\Delta E°$ if we consider only the dipole-dipole interaction in the estimation of H (see Fig. 6, denoted as Dipole-Dipole). If we add the dipole-induced dipole interaction term, the value of 1.4 kcal/mol, is obtained for $\Delta E°$ (see Fig. 6, denoted as Dipole-Induced Dipole). As the observed $\Delta E°$'s are 1.4—1.78 kcal/mol, the agreement between the calculated and observed values seems satisfactory. On the other hand, Table 1 and Fig. 6 show that the agreement between the calculated and observed $\ln(n_t/n_g)$'s is less satisfactory than that obtained by the preceding macroscopic estimation.

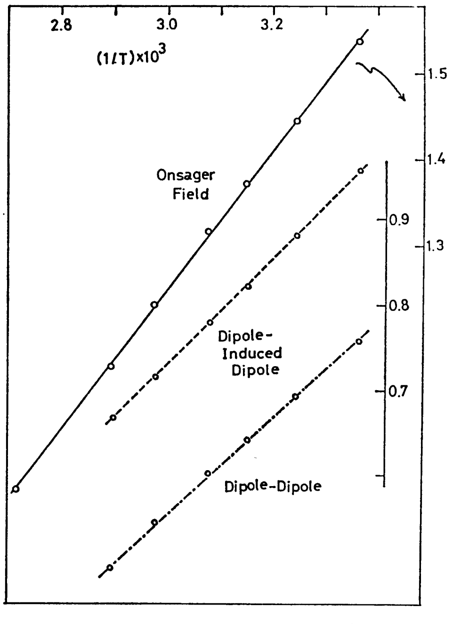

Fig. 6. Expected values for $\ln(n_t/n_g)_{\mathrm{gas}}$ for 1,2-dibromoethane (as for the notations, see the text).

The present theoretical approach to estimating the interaction term, H, is based upon an extremely simple model. As has been described in a reference,[19] we first estimated the total interaction energy using a dipole interaction model, and then we averaged it over all possible orientations and distances of the interacting pair. In the averaging process, we assumed a distribution function of the simple Boltzmann type, and we truncated the Taylor expansion of the distribution function at the first-order term with respect to $(1/T)$. These treatments are certainly over-simplified. The numerical results, however, suggest the possibility of estimating the thermodynamic quantities of the liquid phase by such a purely microscopic approach. Attention must be paid to the fact that the interaction term obtained by the present calculation is expressed in terms of purely molecular quantities, such as a dipole moment and polarizability, instead of a dielectric constans, a very macroscopic quantity, although the polarizability and the molecular radius are *practically* calculated from such macroscopic quantities as the refractive index and the density.

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