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Molecular Reorientational Motion of the Benzene Molecule in a Mixture of Benzene with Carbon Tetrachloride by Raman Band Spape Analysis

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The reorientational correlation times of the benzene molecule in mixtures of benzene with carbon tetrachloride were measured by the method of the Raman line shape analysis. The reorientational relaxation times τ_{OR} of C_6H_6 in solutions increased with increasing mole fraction of CCl_4. Information was also obtained on an intermolecular vibration-vibration energy transfer process which primarily affects the mean life time of the first excited vibrational state ν_2 (a_{1g}) in benzene in solutions.

Numerous investigations have been made to determine the nature of the interaction which affects the Raman spectra of molecules in solution. The measured linewidth of the Raman line provides new information about the mechanisms of intermolecular interaction in solutions.

The most accessible experimental quantity in studies of rotational molecular motion in liquids and/or solutions is the rotational correlation time τ. This value is the zero Fourier transform of the orientational time correlation function. Values of τ can be estimated from a variety of experimental techniques, for example Rayleigh-wing scattering and Raman line shape analysis.[1-4)]

We estimated the reorientational correlation times of the benzene molecule in a mixture of benzene with carbon tetrachloride from the Raman line shape analysis. As a result, information has been obtained on an intermolecular vibration to vibration energy transfer process which primarily affects the mean life time of the first excited vibrational state $\nu_2(a_{1g})$ in benzene.

Experimental

We have used an argon ion laser (Coherent Radiation Co. Ltd. 2W) for the light source. The scattered light was analyzed with a double monochromator (JRS-Ul Laser Raman Spectrometer).

Raman theory and analysis

Analysis of the Raman line shape of the $\nu_2(a_{1g})$ fundamental in benzene yields information about the diffusion constant $D_\perp$. The theory has recently been summarized[5)] and needs only a cursory introduction here. The mechanics of the data aquisition and analysis requires clarification, however.

All experiments were done using 90° scattering and linearly polarized incident light. With $I_\parallel(\omega)$ and $I_\perp(\omega)$ representing the strong and weak components of the scattered light, one can write

$$I_\parallel(\omega) = I_{\text{isot}}(\omega) + 4/3 I_{\text{anis}}(\omega) \tag{1}$$

$$I_\perp(\omega) = I_{\text{anis}}(\omega) \tag{2}$$

$$\rho_s = \frac{I_\perp(\omega)}{I_\parallel(\omega)} = \frac{I_{\text{anis}}(\omega)}{I_{\text{isot}}(\omega) + 4/3\, I_{\text{anis}}(\omega)} \tag{3}$$

where ρ_s is the depolarization ratio. $I_{\text{isot}}(\omega)$ represents the intrinsic vibrational line shape, whereas $I_{\text{anis}}(\omega)$ is a convolution of the vibrational line shape and the orientational spectrum. The problem is to separate the two accurately.

$I_{\text{isot}}(\omega)$ can be extracted directly from measurements of $I_\parallel(\omega)$ and $I_\perp(\omega)$. But since the depolarization ratio is very small for the band under consideration (ρ_s (991 cm^{-1})$=0.00986\pm0.0005$) the intrinsic vibration line shape $I_{\text{isot}}(\omega)$ and the measured line shapes $I_\parallel(\omega)$ can be considered to be the same without introducing significant errors ($I_{\text{isot}}(\omega)\simeq 0.991\ I_\parallel(\omega)$). Generally, however, the measured spectrum is a convolution of the true spectrum and the Gaussian slit function $S(\nu_i, \omega)$. One can write

$$I'_{\text{anis}}(\omega) = \int_{-\infty}^{\infty} I_{\text{or}}(\omega) I_{\text{isot}}(\omega) S(\nu_i, \omega)\,\mathrm{d}\omega \tag{4}$$

and

$$I'_{\text{isot}}(\omega) = \int_{-\infty}^{\infty} I_{\text{isot}}(\omega) S(\nu_i, \omega)\,\mathrm{d}\omega \tag{5}$$

where the primed and unprimed functions denote the measured and true shapes respectively. At first sight, it would appear that the order of convolution is not important and hence the slit function would cancel. This is not the case except when the line widths are very similar in magnitude. To obviate the large errors associated with this assumption, true line widths were determined directly as a function of slit width; a plot is shown in Fig. 1. For the 991 cm^{-1} line of benzene, $I_\parallel(\omega)$ can be determined directly by setting the slit 20 μ or less. In order to obtain

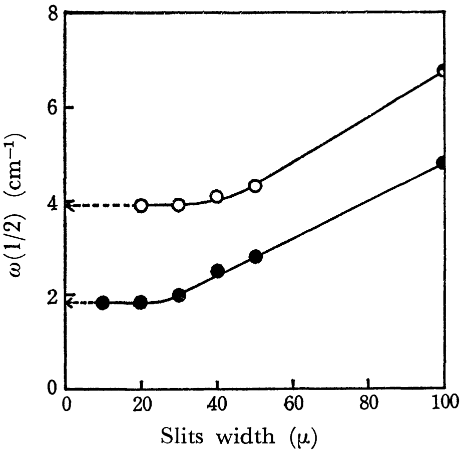

Fig. 1. Linewidth of $\nu_2(a_{1g})$ of C_6H_6 in carbon tetrachloride as a function of slit width. (37.6 mol% of benzene)

○: $\omega_{\text{anis}}(1/2)$, ●: $\omega_{\text{isot}}(1/2)$

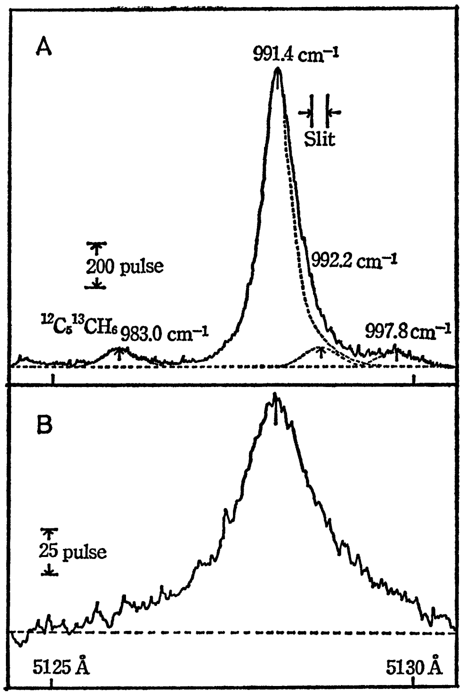

Fig. 2. A; Polarized Raman spectrum, $I_{\parallel}(\omega)$, of $\nu_2(a_{1g})$ of C_6H_6 (slit=20 μ×10 mm high, scan rate=0.5 Å/min), B; Depolarized spectrum $I_{\perp}(\omega)$(slit=25 μ×10 mm high, scan rate=0.5 Å/min) (20.0 mol% of benzene in mixtures).

$I_{isot}(\omega)$, $I_{\perp}(\omega)$ must be evaluated at the same slit width. Examples of measured $I_{\parallel}(\omega)$ and $I_{\perp}(\omega)$ are shown in Fig. 2. Errors arising from monochromator polarization response, beam convergence, light collection angles, analyzer light leak, ellipticity of the exciting light polarization, laser power fluctuations, and stray light have been minimized.

Implicit in the treatment of the data are the assumptions that $I_{isot}(\omega)$ and $I_{anis}(\omega)$ are Lorentzian and that vibrational and reorientational motions are not coupled. A test of these assumptions is shown in Fig. 3, in which $I_{isot}(\omega)$ and $I_{anis}(\omega)$, normalized to unit height, are displayed (pionts). The solid lines are calculated Lorentz functions based on the observed line width. Because $I_{anis}(\omega)$ is a convolution of $I_{isot}(\omega)$ with $I_{or}(\omega)$, the $I_{or}(\omega)$ is also Lorentzian. Accordingly,

$$\omega_{1/2}(\text{anis}) = \omega_{1/2}(\text{isot}) + \omega_{1/2}(\text{or}) \tag{6}$$

where the $\omega_{1/2}$ terms are half widths. Furthermore, the reorientational correlation time is obtained as follows:

$$\tau^{-1}(\text{or}) = 2\pi c\omega_{1/2}(\text{or}) \tag{7}$$

where c is the velocity of light.

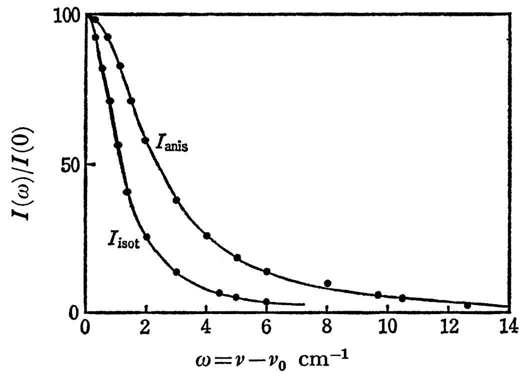

Fig. 3. Normalized line shapes of $I_{isot}(\omega)$(●) and $I_{anis}(\omega)$(○) of the $\nu_2(a_{1g})$ band of C_6H_6 in carbon tetrachloride (20.0 mol% of benzene).

Results and Discussion

Before the measurements of the benzene–carbon tetrachloride solution were made, we measured the reorientational correlation time of pure liquid benzene together with a calibration of the Raman Spectrometer used. The values obtained by the excitation light of 4880 Å and 5145 Å wavelengths are summarized in Table 1. As is seen there, the reorientational correlation time τ from these values was in very good agreement with that obtained by Litovitz *et al.*[5] and also the values of $\omega_{1/2}$ (isot) were in good agreement with those of Griffith *et al.*[6] The line shapes of the 991 cm^{-1} Raman active fundamental of C_6H_6 are shown in Fig. 2(a). This line shape is also the same as that obtained by Griffith *et al.*[6] Several prominent features are observed. Important hot bands cause the observed bands to be skewed. The most interesting feature is that the hot band in C_6H_6 occurs on the high frequency side of ν_2. Additional Raman bands also occur in the far wings of the bands under study but they do not interfere significantly.

The dependence of the linewidth of the 991 cm^{-1} band on the mole fraction of CCl_4 is shown in Fig. 4. The reported linewidths are those obtained after

TABLE 1. LINE WIDTH OF $\nu_2(a_{1g})$ OF C_6H_6 AT VARIOUS LIGHTS

	$\omega_{1/2}$(aniso)	$\omega_{1/2}$(isot)	$\omega_{1/2}$(or)
5145 Å	4.54 cm^{-1}	2.45 cm^{-1}	2.09 cm^{-1}
4880 Å	4.52 cm^{-1}	2.49 cm^{-1}	2.03 cm^{-1}
* Litovitz *et al.*[5]			2.0±0.5 cm^{-1}

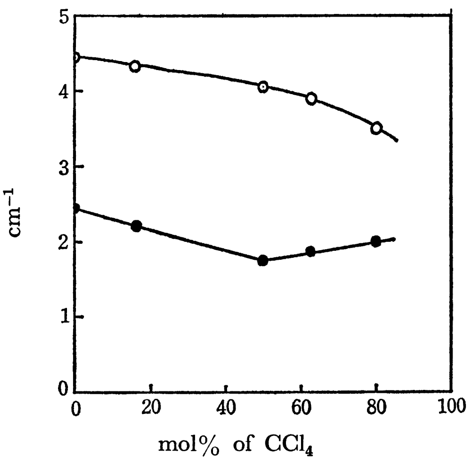

Fig. 4. Relationship between $\omega_{1/2}$(isot), $\omega_{1/2}$(anis) and the mole fraction of carbon tetrachloride.

graphical resolution of the over-all contour into the constituent $v=0\rightarrow 1$ and hot band components. As is seen in Fig. 4, the $\omega_1/_2$ (anis)'s decreased monotonously with increasing CCl_4 mole fraction. However, the $\omega_{1/2}$ (isot)'s decreased with increasing concentration of CCl_4 up to about the equimolar point and after this minimum point increased with increasing concentration of CCl_4.

Recently, the linewidths of the 991 cm^{-1} and 945 cm^{-1} bands for several mixtures of C_6H_6 and C_6D_6 were measured by Griffith *et al.*[6] They have explained their results as follows: the linewidth of the 954 cm^{-1} band of C_6D_6 is independent of the concentration, thereby supporting the initial supposition that the lack of close lying energy levels would preclude an intermolecular vibration to vibration energy transfer process from affecting the lifetime of the ν'_2 state in that molecule. In C_6H_6, however, where two close lying energy levels are available, at 985 cm^{-1} and 970 cm^{-1}, the linewidth of the 991 cm^{-1} line is linearly dependent upon the concentration. As the C_6H_6 concentration decreases, the frequency of collisions between C_6H_6 molecules decreases to the same extent. If the life time of ν_2 becomes longer by the mechanism for the energy dissipating process, the linewidth will be narrow and continue narrowing untill no more collisions between C_6H_6 molecules occur.

For the C_6H_6–CCl_4 mixtures, the energy dissipating process can be considered as the same mechanism. In CCl_4, there is a vibrational combination band of benzene near 991 cm^{-1} of $\nu_2(a_{1g})$; it is measured by infrared absorption spectra. We consider the following energy transfer mechanism:

$$C_6H_6(\nu_2') + CCl_4(\nu_2, \nu_3) \rightarrow$$
$$C_6H_6(\nu_2) + CCl_4(\nu_2', \nu_3') + E\ (9\ cm^{-1})$$

But the linewidth broadenings by such collisions are smaller than those by C_6H_6–C_6H_6 collisions in solutions.

We consider the line broadening or narrowing mechanism of $\nu_2(a_{1g})$ of benzene in C_6H_6–CCl_4 mixtures to be that the line narrowing occurs due to the energy transfer by the collision process of C_6H_6–C_6H_6 upon increasing the mole fraction of CCl_4, but after the equimolar point the collisions between C_6H_6 and CCl_4 are predominant and then line broadening occurs due to the energy transfer in C_6H_6–CCl_4 collisions.

Following Griffith *et al.*,[6] we take the value of 1.62 cm^{-1} for the mean intrinsic linewidth of ν_2 in the absence of energy transfer collisions and we can obtain the reorientational relaxation time (τ) of C_6H_6 in solutions. We show the relationship between the τ (or) of C_6H_6 and the mole fraction of CCl_4 in Fig. 5. As is seen in Fig. 5, the τ (or) of C_6H_6 in solutions increased with increasing mole fraction of CCl_4. The reorientational relaxation times are related to the "micro-viscosity" of solution η_m as follows:

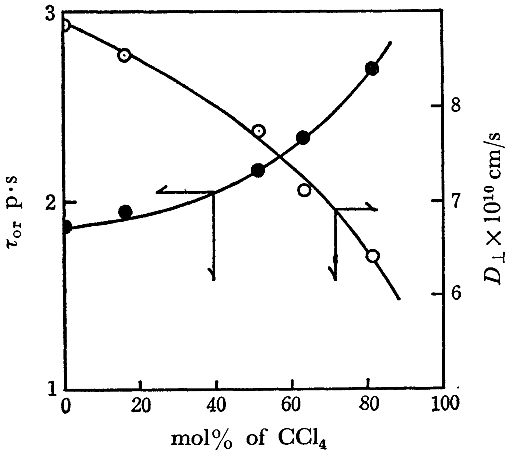

Fig. 5. Dependence of reorietntational correlation times with the mole fraction of carbon tetrachloride.

$$\tau_D = \frac{4\pi a^3}{kT}\eta_m \qquad (8)$$

where a is the radius of the molecules in solution. Now assuming the micro-viscosity η_m to be equal to the viscosity η, τ_D/η should be constant. The value of τ_D/η at various mole fractions of CCl_4 is $2.96\pm 0.20\times 10^{-9}$ and independent of the mole fraction of CCl_4. The radius of the C_6H_6 molecules in solutions is found to be about 4.6 Å. This value is a very reasonable one.

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