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The Molecular Motion of Phenyl Groups in Toluene, Diphenylmethane and Triphenylmethane in Solutions of Carbon Tetrachloride by Raman Line Shape Analysis

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Synopsis. The reorientational correlation times of phenyl groups in the molecules of toluene, diphenylmethane, and triphenylmethane in carbon tetrachloride solutions were measured by the Raman-line-shape analysis. The reorientational relaxation times of the phenyl groups obtained increased in this order: toluene<diphenylmethane<triphenylmethane as a result of the increase in the mutual interaction among phenyl groups themselves in the molecule.

In the Raman spectroscopic study of the molecular dynamics in the liquid state, the most important model-independent quantity obtainable is the reorientational correlation time, τ(OR). When a molecule has a symmetric top, the analysis of the isotropic and anisotropic Raman-line shapes of the nondegenerate vibrations uniquely determines the reorientational correlation time for the tumbling motion of the molecule.

In our previous papers[1-3] it has been shown that the reorientational correlation time of a molecule obtained is an important quantity intimately related to the inter- and intramolecular interaction.

In the present note, the reorientational correlation times of phenyl groups in the molecules of toluene, diphenylmethane, and triphenylmethane dissolved in carbon tetrachloride were determined by Raman-line shape analysis, and the mutual interaction among phenyl groups in the molecule was discussed.

The apparatus used consisted of an argon ion laser (800 mW at 4880 Å) produced by the Coherent Radiation Co. Ltd., and a laser Raman spectrometer of the JRS-Ul type of JEOL, Ltd., Japan. The toluene and carbon tetrachloride used were commercial products of spectra-grade reagents, while the diphenylmethane and triphenylmethane were extra-pure-grade reagents supplied by the Tokyo Kasei (Chemical) Industrial Co., Ltd. The solutions used for the measurements contained such amounts of the solutes that the concentration of phenyl groups was 2 mol per liter of solution.

In order to obtain the orientational correlation times, the Raman-line shape of the ν_2 fundamental of the phenyl group was analyzed. The Raman spectrum was observed at 90 °C with respect to the 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,

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

$$I_{\perp}(\omega) = I_{\mathrm{anis}}(\omega) \quad (2)$$

$$\rho_s = \frac{I_{\perp}(\omega)}{I_{\parallel}(\omega)} \quad (3)$$

where ρ_s is the depolarization ratio. $I_{\mathrm{isot}}(\omega)$ represents the intrinsic vibrational line shape, and $I_{\mathrm{anis}}(\omega)$, a convolution of the vibrational line shape and the orientational spectrum.

The line shape of $I_{\parallel}(\omega)$ and $I_{\perp}(\omega)$ of the ν_2 (a_{1g}) fundamental (1002 cm^{-1}) obtained showed Lorentz-type cruves. This fact shows that the vibrational and the rotational motions of the phenyl group are not coupled. We can write;

$$\omega_{1/2}(\mathrm{anis}) = \omega_{1/2}(\mathrm{isot}) + \omega(\mathrm{or}) \quad (4)$$

where the $\omega_{1/2}$ terms are the half-width of the respective line shapes.

In order to eliminate the effect of the slit-width on the shape of the spectrum, the half-width of the spectrum was plotted against the slit-width, the true half-width was then obtained by extrapolating to zero slit-width.

The reorientational correlation time is obtained by means of;

$$\tau(\mathrm{OR})^{-1} = 2\pi c\omega(\mathrm{or}) \quad (5)$$

where τ(OR) is the reorientational correlation time, and c, the velocity of light. The details of the experimental procedures and the data reductions have been reported previously.[1-2]

TABLE 1.

	$\rho_s \times 10^{-2}$	$\omega_{1/2}$ (isot) cm^{-1}	$\omega_{1/2}$ (anis) cm^{-1}	ω (or) cm^{-1}	τ (OR) $\times 10^{-12} s^{-1}$
Toluene	1.13	1.72	3.56	1.84	2.88
Diphenylmethane	2.32	1.52	2.47	0.95	5.58
Triphenylmethane	3.15	2.37	2.66	0.29	18.6

The experimental results obtained are summarized in Table 1, where the half-width and the correlation time of the reorientational motion are listed in the last two columns. As may be seen in Table 1, the reorientational correlation time increase with an increase in the number of phenyl groups in a molecule; one in toluene, two in diphenylmethane, and three in triphenylmethane. Since the concentration of phenyl groups in the solutions was kept constant, this change in correlation time can be ascribed to the change in the degree of mutual interaction among phenyl groups themselves in a molecule.

The reorientational correlation time of phenyl groups in the dibenzyl molecules dissolved in carbon tetrachloride was 3.80×10^{-12} s^{-1},[2] as has been reported previously. The reorientational correlation time of the phenyl groups in the diphenylmethane molecules is a little larger than that in the dibenzyl molecules. This shows the existence of some interaction between the

phenyl groups themselves in the diphenylmethane molecules, which hinders the orientational motion of the phenyl groups to some extent.

In the triphenylmethane molecules, the rotational motion of phenyl groups are much more strongly hindered by the strong interaction among phenyl groups themselves, such as the steric hinderance and π-coupling. For this reason, the value of the reorientational correlation time of triphenylmethane increased to as much as three times that of free toluene molecules in the solution.

References

1) H. Nomura and Y. Miyahara, This Bulletin, **48**, 2779 (1975).
2) H. Nomura and Y. Miyahara, *Polmer J.*, **8**, 30 (1976).
3) H. Nomura, S. Koda, and Y. Miyahara, *J. Chem. Phys.*, in printing.