

Study of Molecular Reorientation in Liquid with Raman Spectroscopy. Intermolecular Interaction of Hexafluorobenzene with Benzene

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Raman spectroscopy was used to study the reorientational motion of hexafluorobenzene in benzene and also in neutral solvents. From the viscosity dependence of the reorientation time, intermolecular interaction in the systems was investigated. No evidence was found to support the presence of long-lived 1:1 complex of hexafluorobenzene and benzene. The unusual viscosity dependence of the reorientational motion observed in the systems was explained as due to the formation of transient complexes.

Introduction

Patrick and Prosser¹ observed the formation of solid upon mixing hexafluorobenzene (HFB) and benzene. Crystallographic investigation revealed the structure of alternate HFB/benzene molecules in parallel stacks. These facts led to the expectation that complexes would exist in the liquid state also. Thermodynamic² and optical³ measurements were consistent with the presence of 1:1 complex in the solutions of HFB in benzene.

On the other hand, spectroscopic investigation did not produce any evidence supporting the presence of 1:1 complex in solution. Charge-transfer band was missing in ultraviolet spectrum⁴, and there was very little effect on the ¹⁹F spin-lattice relaxation time of HFB in benzene in NMR.⁵ Time correlation function approaches using IR^{6,7} and Raman^{6,8} spectroscopic techniques were not conclusive since the vibrational and reorientational contribution to line shape were not separated.

Bauer *et al.*⁹ used depolarized Rayleigh scattering technique to investigate the effect of concentration and viscosity of solution on the reorientational correlation time of HFB. No significant contribution from a long-lived complex was observed even though the reorientational relaxation was slowed upon mixing HFB with benzene. However, depolarized Rayleigh scattering technique suffers from the difficulty of separating the contributions of HFB and benzene, both of which are anisotropic.

In this work, Raman spectroscopy is used to study the molecular interaction between HFB and benzene. The reorientation time of HFB is obtained by analyzing 560cm⁻¹ band (ν_2) in HFB Raman spectrum. Viscosity dependence of the reorientational motion is measured to investigate the nature of interaction between HFB and benzene. For comparison, the reorientational relaxation of HFB in neutral solvents such as *n*-C₆H₁₄, *c*-C₈H₁₆, CCl₄ and CDCl₃ are also investigated.

Experimental

Details of the apparatus and experimental techniques to determine the Raman band widths have been described previously.¹⁰ Briefly, Raman spectra were recorded with a JASCO Raman spectrometer (Model R300) using 514.5 nm

line of an argon ion laser (Spectra-physics Model 164-09). The DC detection system in the original instrument was replaced by a photon counting system (EG & G PAR Model 1120/1105) to improve *S/N* ratio. The temperature of the capillary sample cell was maintained at 25±1 °C using a homemade temperature controller.¹¹ Parallel (*I*_{||}) and perpendicular (*I*_⊥) components of Raman band were obtained using a polarization analyzer (JASCO Model RDP-PS-OO). Widths of isotropic (*I*_{iso}) and anisotropic (*I*_{aniso}) components,

$$I_{\text{iso}} = I_{\text{||}} - \frac{4}{3}I_{\perp} \quad (1)$$

$$I_{\text{aniso}} = I_{\perp} \quad (2)$$

were determined following the procedure described by Tanabe *et al.*¹² Spectral slit width was determined using the fluorescence lines from the Ar⁺ laser. Viscosities of solutions were measured with a Cannon-Ubbelohed viscometer, and densities were determined using a homemade ~0.5 ml micropipette. All reagents were commercial products and were used without further purification.

Results and Discussion

Raman spectrum of HFB in benzene does not show any additional peak other than those from solute and solvent molecules. Splitting of HFB bands was not observed. Hence, presence of a long-lived complex in the mixture does not seem to be likely.

Table 1 lists the widths of the isotropic (δ_{iso}) and anisotropic (δ_{aniso}) components of HFB ν_2 band in neutral solvents. Peak position and solution viscosity are also listed. Similar data are shown in Table 2 for HFB in (benzene + neutral solvents). From the band widths, the reorientation time (τ_{reor}) in each solution was evaluated using the following relationship.¹³⁻¹⁵

$$\tau_{\text{reor}} = [\pi c (\delta_{\text{aniso}} - \delta_{\text{iso}})]^{-1} \quad (3)$$

The reorientation time of HFB in each solution is listed also in Table 1 and 2.

Temperature (*T*) and viscosity (η) dependence of reorientational motion of HFB molecules in neat liquid was investigated previously.¹¹ The reorientation time in neat liquid

TABLE 1: HFB in Neutral Solvents

$X_{C_6F_6}$	Solvent mole fractions	δ_{iso}^a , cm^{-1}	δ_{aniso}^a , cm^{-1}	$\bar{\nu}_R$, cm^{-1}	τ_{reor}^a , psec	η , cp
0.4	0.6 n-C ₆ H ₁₄	5.10	7.57	559	4.30	0.385
0.4	0.3 n-C ₆ H ₁₄ 0.3 CCl ₄	5.21	7.06	559	5.74	0.506
0.4	0.6 CDCl ₃	5.34	6.96	559	6.55	0.629
0.4	0.6 CCl ₄	5.29	6.72	559	7.42	0.711
0.8	0.2 n-C ₆ H ₁₄	5.27	7.12	560	5.74	0.631
0.8	0.2 CDCl ₃	5.25	6.82	560	6.76	0.777
0.8	0.2 CCl ₄	5.35	6.90	560	6.85	0.785
1.0	—	5.19	6.76	560	6.76	0.854

^a Errors estimated to $\pm 0.9\%$, $\pm 1.2\%$ and $\pm 6.3\%$ for δ_{iso} , δ_{aniso} and τ_{reor} , respectively.

TABLE 2: HFB^a in Benzene with Neutral Solvents

$X_{C_6F_6}$	Solvent mole fractions	δ_{iso}^b , cm^{-1}	δ_{aniso}^b , cm^{-1}	$\bar{\nu}_R$, cm^{-1}	τ_{reor}^b , psec	η , cp
0.4	0.2 n-C ₆ H ₁₄	5.31	6.75	559	7.37	0.516
0.4	0.2 CDCl ₃	5.27	6.58	559	8.10	0.641
0.4	0.2 CCl ₄	5.36	6.63	559	8.35	0.675
0.4	0.2 c-C ₈ H ₁₆	5.47	6.68	559	8.77	0.755

^a $X_{benzene}=0.4$. ^b Errors estimated to be $\pm 1.1\%$, $\pm 1.6\%$ and $\pm 7.6\%$ for δ_{iso} , δ_{aniso} and τ_{reor} , respectively.

was found to display the following relationship which was established for other systems previously.¹⁶⁻¹⁸

$$\tau_{reor} = \left(\frac{\kappa}{T} \right) \eta + \tau_0 \quad (4)$$

where κ is a proportionality constant and τ_0 is a zero-viscosity intercept. τ_0 for HFB in neat liquid was found to be rather similar to the classical free rotor reorientation time, τ_{FR} , given by¹⁹

$$\tau_{FR} = \frac{2\pi}{9} \left(\frac{I}{kT} \right)^{1/2} \quad (5)$$

where I is the moment of inertia related to the tumbling motion of C₆-axis in HFB. When the viscosity-dependent part of the reorientation time was identified with Stokes-Einstein equation,²⁰ κ was found to be similar to the theoretical proportionality constant obtained with "slip" boundary condition (κ_{slip})²¹ rather than that with "stick" condition (κ_{stick}).

$$\kappa_{stick} = f_p \frac{V_m}{k} \quad (6)$$

$$\kappa_{slip} = f_{HZ} f_p \frac{V_m}{k} \quad (7)$$

where k is the Boltzmann constant, V_m is the volume of the molecule. f_p is the Perrin correction factor^{22,23} for the ellipsoidal shape of the molecule, and f_{HZ} is the Hu-Zwanzig correction term²¹ to account for the change of boundary condition from "stick" to "slip".

Figure 1a shows τ_{reor} vs. viscosity plots for solutions of different concentration of HFB in neutral solvents. Curve III in the Figure is drawn with data from the previous work.¹¹ Thus, in neutral solvents as well as in neat liquid, viscosity dependence of the reorientation time of HFB is described by eq. (4). The slopes and intercepts of the curves are listed in

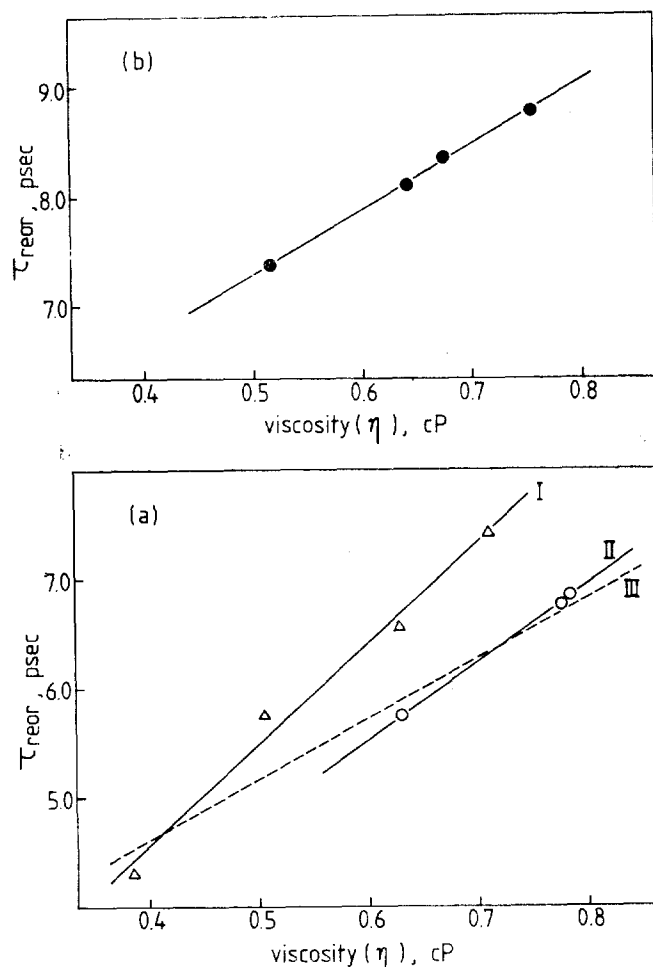


Figure 1. Viscosity dependence of τ_{reor} for tumbling of HFB. In (a), τ_{reor} data in neat liquid (curve III) and in neutral solvents (curves I and II) are shown. HFB mole fractions are 0.4 and 0.8 for curve I and curve II, respectively. Figure (b) is for HFB (0.4 mole fraction) in benzene (0.4 mole fraction) and neutral solvents.

TABLE 3: Viscosity Dependence of Experimental and Theoretical τ_{reor}

Type	Systems or models	Slope (κ/T), psec/cp	Intercept (τ_0), psec
Experimental	$X_{C_6F_6} = 1.0^a$	5.5 ± 2.0	2.4 ± 1.4
	$X_{C_6F_6} = 0.8$ in neutral solvents	7.1 ± 1.9	1.3 ± 1.2
	$X_{C_6F_6} = 0.4$ in neutral solvents	9.2 ± 0.9	0.9 ± 0.4
	HFB in benzene	5.9 ± 2.5	4.3 ± 1.5
Theoretical	Stick model (free HFB)	31.9	1.0
	Slip model (free HFB)	10.9	1.0
	Slip model (HFB-benzene complex)	0.05	1.6

^a Ref. 11.

Table 3. From the Table, it is seen that the viscosity dependence of τ_{reor} gets slightly stronger (slope gets larger) as the solution gets less concentrated while the zero-viscosity intercept gets smaller. Also listed in the Table are theoretical slopes reported previously¹¹ which were calculated using equation (6) and (7). Theoretical intercept shown in the Table is the free rotor reorientation time calculated previously using eq. (5). Hence, viscosity-dependence of τ_{reor} of HFB in neutral solvents gets better and better described by "slip" model as the solution gets less concentrated with HFB. Also, zero-viscosity intercept approaches τ_{FR} in dilute solutions. This is a rather notable result considering the controversy in identifying τ_0 with τ_{FR} .^{16, 18, 24} As far as τ_0 is identified with τ_{FR} , increase of τ_0 in concentrated solutions indicates that interaction between HFB molecules is stronger than between HFB and neutral solvent molecules. Slight but significant difference in slope among solutions of different HFB concentration was not expected. For example, formation of dimers in concentrated solution will not decrease but increase the slope, since the effective volume will be increased in such a case (eq. (7)). This behavior will be discussed further after discussing the HFB-benzene system.

The reorientation time of HFB in solutions containing benzene is plotted in Figure 1(b) as a function of viscosity. Here again, viscosity dependence of τ_{reor} is well described by eq. (4). The slope and intercept of the line is listed in Table 3 also. Zero-viscosity intercept in this system is larger than those for HFB-neutral solvent system indicating even stronger interaction between HFB and benzene. Slope of the viscosity dependence curve is smaller than in neutral solvents, being rather comparable to that in neat liquid.

Other reorientational relaxation models developed for noninteracting system were examined looking for an explanation for weaker viscosity dependence of HFB reorientation time in benzene and in neat liquid than in neutral solvents.²⁵ "Semislip" rotational diffusion model proposed by Hynes *et al.*²⁶ and further refined by Tanabe^{23, 27} resulted in similar viscosity dependence as "slip" model. Estimated viscosity

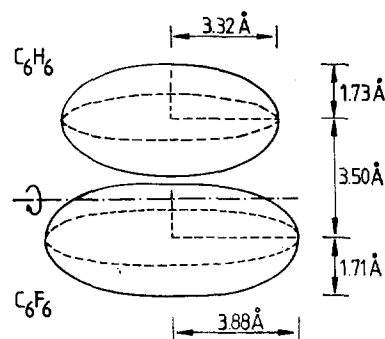


Figure 2. Assumed structure of a long-lived complex used for theoretical calculations.

dependence using "microviscosity theory" proposed by Gierer and Wirtz²⁸ was rather similar to the experimental values for HFB in benzene and in neat liquid. However, the latter model could not account for the stronger viscosity dependence in dilute solutions.

To examine the possibility of 1:1 HFB/benzene complex formation, structure of a possible complex was formulated as shown in Figure 2 based on X-ray crystallographic data.²⁹ Viscosity dependence of the reorientational relaxation of the assumed complex was calculated using "slip" model (eq. (7)). Zero-viscosity intercept was estimated as the free rotor reorientation time (eq. (5)). Results are listed also in Table 3. Theoretical slope of the assumed complex is much smaller than the experimental data obtained for HFB/benzene system. Overall reorientation time of the complex will be a factor of ~ 5 shorter than that of free HFB molecules in the HFB/benzene systems investigated. If the complex is in equilibrium with free molecules, a sharp band due to free HFB would appear superimposed on, and possibly shifted from, broader complex band. Absence of any structure in the Raman band of HFB is an evidence against the formation of a long-lived complex with benzene.

A plausible explanation for the viscosity dependence of the reorientational motion of HFB in the systems investigated may be found through closer inspection of the hydrodynamic models. Under "slip" boundary condition, spinning motion of spheroid experiences no frictional force.²¹ Hence, relaxation time of such motion does not exhibit viscosity dependence.¹¹ Tumbling of a spheroid, which is discussed in this paper, experiences some friction due to the displacement of fluid arising from the motion. Expression in eq. (7) is the reorientational relaxation time derived through such consideration. Strong interaction between HFB molecules and between HFB and benzene may be viewed as the existence of short-lived complex or clusters. Formation of transient complex would slow down the rotation of molecules as indicated by large zero-viscosity intercept for HFB in concentrated solutions or in solutions with benzene. At the same time, molecules forming the complex will exhibit some degree of collective rotation. Hence, less amount of solvent fluid will be displaced, resulting in weaker dependence of relaxation time on viscosity. More simplistically, in the presence of strong interaction, viscosity felt by a molecule will be larger

than the bulk viscosity. Hence, reorientational motion will display less dependence on bulk viscosity. For quantitative explanation, further development in hydrodynamic microviscosity theory for interacting system is needed.

Brown and Swinton³⁰ found that the quadrupole-quadrupole interaction between HFB and benzene was responsible for the solid state structure of HFB/benzene mixture observed with X-ray crystallography. Similar interaction may persist in liquid state, contributing to the formation of transient complex. Even though weaker than in HFB/benzene system, an appreciable interaction was indicated between HFB molecules in the present work. However, nature of such interaction is not known at the moment.

Summary and Conclusion

Viscosity dependence of the reorientational motion of HFB was determined in several solvent systems. For solutions containing 0.4 mole fraction of HFB in neutral solvents, viscosity dependence of τ_{reor} was found to be well described by hydrodynamic "slip" model. Zero-viscosity intercept of the same system agrees very well with the free-rotor correlation time. The present results seem to support identifying the zero-viscosity intercept with free-rotor correlation time when intermolecular interaction is not appreciable. When the solution gets more concentrated, viscosity dependence gets weaker and zero-viscosity intercept gets larger. The same trend was observed when 0.4 mole fraction of benzene was added to the same concentration of HFB. Observation could not be adequately explained assuming the presence of long-lived 1:1 complex of HFB/benzene. Formation of short-lived complex in concentrated solution of HFB and in HFB/benzene system was proposed as a plausible explanation for the experimental findings. Further theoretical works need to be done to clarify the nature of the zero-viscosity intercept and also of the interaction between HFB molecules. Development of microviscosity theory applicable to interacting system is also needed.

In the present work, Raman spectroscopy was found to provide useful information about intermolecular interaction in liquid. Compared to depolarized Rayleigh scattering technique, data analysis was more straightforward and additional information such as change of Raman shift and peak splitting was available.

Acknowledgement. Authors wish to thank Mr. W.I. Lee in the Department of Chemistry, Seoul National University for assistance. This work was supported by a grant from the Ministry of Education, Republic of Korea (Grant No. ED 83-313).

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