

액체분자의 재배치 운동에 관한 라만 분광법적 연구 (제 3 보).
순수한 C_6F_6 액체분자의 회전운동에 대한 온도의 영향

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(1983. 10. 19 접수)

Study of Molecular Reorientation in Liquid with Raman
Spectroscopy (III). Temperature Dependence of
Molecular Rotation of C_6F_6 in Neat Liquid

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(Received October 19, 1983)

요 약. 라만분광법을 사용하여 순수한 액체 상태의 C_6F_6 의 재배치 운동을 연구하였다. 라만스펙트럼 중 ν_2 와 ν_{16} 밴드를 선정하여 그 모습을 293~333 K 온도 범위에서 측정하였다. 분자의 주대칭축(C_6 -축)의 회전 및 스핀운동에 관한 회전 확산 상수(D_{\perp} , D_{\parallel})가 온도의 함수로써 결정되었으며 이로부터 C_6F_6 의 재배치운동은 명백히 비등방적임을 알게 되었다. 실험 결과를 유체역학적 모델로 분석하여 본 결과 주대칭축의 회전운동은 확산적이며 스핀운동은 관성적이라는 것이 밝혀졌다.

ABSTRACT. The reorientational motion of C_6F_6 in neat liquid is investigated in the temperature range 293~333K by analyzing ν_2 and ν_{16} bands of its Raman spectrum. Diffusion constants for the tumbling (D_{\perp}) and spinning (D_{\parallel}) motions are determined. The reorientation of the molecule seems to be distinctly anisotropic. Based on the hydrodynamic model, the tumbling motion of the figure axis of C_6F_6 is largely diffusional. On the other hand, the spinning motion of the same axis looks mostly inertial.

1. INTRODUCTION

Raman spectroscopy has been widely used to study molecular motion in liquid.¹⁻³ Recently, we reported the room temperature investigation of the molecular reorientational motion of hexafluorobenzene in neat liquid with Raman spectroscopy.⁴ Using the rotational diffusion model, diffusion constants related to the tumbling (D_{\perp}) and spinning (D_{\parallel}) motions of the figure axis of the molecule were determined from the Raman band widths. And the reorien-

tational motion of C_6F_6 was found to be distinctly anisotropic, spinning motion being much easier than tumbling.

In the present work, the rotational diffusion constants (D_{\perp} and D_{\parallel}) of the same molecule have been determined as a function of temperature with Raman spectroscopy. Nature of the reorientational mechanism will be analyzed based on the hydrodynamic models for the reorientation of spheroid.

$\nu_2(A_{1g}, 560\text{cm}^{-1})$ and $\nu_{16}(E_{2g}, 1157\text{cm}^{-1})$ modes, corresponding to symmetric and asy-

mmetric ring-breathing modes of C_6F_6 , respectively, were chosen for the investigation of the reorientational motion of the molecule in neat liquid.

2. EXPERIMENTAL

Details of the apparatus and experimental techniques to determine the Raman band widths have been described previously.⁵ To record a Raman band at various temperature, a capillary sample cell was inserted into a capillary cell holder made of brass shown in Fig. 1. Water at constant temperature was circulated through the cell holder using a constant temperature circulator (Haake type F4391). To check the sample temperature, a chromel-alomel thermocouple was inserted within a few millimeters from the Raman scattering volume. Temperature difference ($0\sim 1^\circ C$) between the sample and the bath was measured and used for temperature calibration in subsequent experiments. With this technique, temperature of the sample is thought to be controlled better than within $\pm 1^\circ C$.

The slit effect on the Raman band width was corrected using the formula proposed by Tanabe⁶,

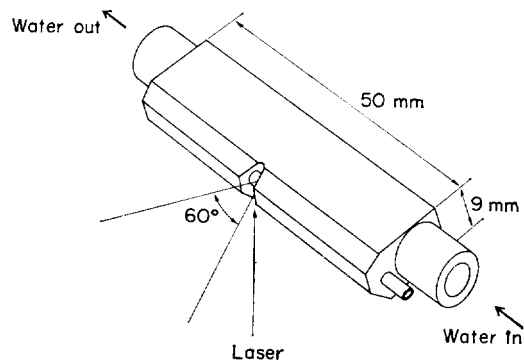


Fig. 1. Constant temperature capillary cell holder.

$$\delta_t = \delta_a [1 - (s/\delta_a)^2],$$

where δ_t is the true band width (FWHM), δ_a is the apparent band width, and s is the spectral slit width determined by the width of neon emission lines.

Hexafluorobenzene with the minimum purity of 99% was purchased from Aldrich Chemical Company and used without further purification.

3. RESULTS AND DISCUSSIONS

Isotropic (I_{iso}) and anisotropic (I_{aniso}) components of a Raman band are obtained from the experimental parallel ($I_{||}$) and perpendicular (I_{\perp}) components using the relations⁷

$$I_{iso} = I_{||} - \frac{4}{3} I_{\perp}$$

$$I_{aniso} = I_{\perp}$$

Measured widths (FWHM) of the isotropic (δ_{iso}) and anisotropic (δ_{aniso}) components for ν_2 and ν_{16} vibrational modes of neat liquid C_6F_6 at various temperature are listed in Table 1. It is to be noted that δ_{iso} of ν_{16} (E_{2g}) mode could not be determined since the depolarization ratios ($\rho = I_{\perp}/I_{||}$) are 3/4 for nontotally symmetric Raman bands.

Determination of Diffusion Constants. A detailed description of the procedure employed to determine the diffusion constants for the tumbling (D_{\perp}) and spinning ($D_{||}$) motions of molecules in liquid has been described previously.^{4,5} Briefly, assuming exponential correlation functions for both the vibrational and reorientational relaxation processes, corresponding correlation times (τ_{vib} and τ_{reor}) are determined from the widths of the isotropic and anisotropic components of a Raman band, *i. e.*,

$$\tau_{vib} = (\pi c \delta_{iso})^{-1}$$

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

Using the rotational diffusion model⁸ for sym-

Table 1. Widths^{a,b} of ν_2 and ν_{16} Raman bands of C_6F_6 at several temperatures.

Temperature, °C	ν_2		ν_{16}
	δ_{iso} , cm ⁻¹	δ_{aniso} , cm ⁻¹	δ_{aniso} , cm ⁻¹
20	5.36	6.80	11.73
30	5.53	7.08	11.73
40	5.69	7.40	11.79
50	5.77	7.77	11.82
60	5.93	8.10	11.87

^aAverages of 27 measurements. ^bErrors estimated to be $\pm 1.2\%$, $\pm 1.9\%$, and $\pm 1.0\%$, for $\delta_{iso}(\nu_2)$, $\delta_{aniso}(\nu_2)$, and $\delta_{aniso}(\nu_{16})$, respectively.

metric top molecules, τ_{reor} is related to the rotational diffusion constants as

$$\tau_{reor} = [n(n+1)D_{\perp} + m^2(D_{\parallel} - D_{\perp})]^{-1},$$

where n and m are integers determined by the symmetry of the Raman band ($n=2$, $m=0$ for $\nu_2(A_{1g})$ mode, and $n=2$, $m=\pm 2$ for $\nu_{16}(E_{2g})$ mode of C_6F_6). D_{\perp} may be determined directly from τ_{reor} of ν_2 mode. To determine D_{\parallel} , τ_{reor} of a nontotally symmetric ($m \neq 0$) mode such as $\nu_{16}(E_{2g})$ of C_6F_6 should be known. However, for such a mode, δ_{iso} can not be measured since the isotropic component (I_{iso}) vanishes completely for symmetry reason. Tanabe⁸ proposed the inverse square relationship between the isotropic band widths (δ_{iso}) and the vibrational frequencies for the vibrational modes of the similar type assuming that the vibrational relaxation is mostly due to dephasing^{9,10} process. Since both ν_2 and ν_{16} modes of C_6F_6 represent ring breathing vibrations, the isotropic band width of ν_{16} mode may be estimated from that of ν_2 using the following relationship.

$$\delta_{iso}(\nu_{16}) = \left(\frac{\nu_2}{\nu_{16}}\right)^2 \delta_{iso}(\nu_2).$$

Diffusion constants thus determined are listed in Table 2. Data indicate a highly anisotropic nature of reorientational motion of C_6F_6 in the

Table 2. Rotational diffusion constants of C_6F_6 at several temperatures.

T , °C	D_{\perp} , 10 ¹¹ sec ⁻¹	D_{\parallel} , 10 ¹¹ sec ⁻¹
20	0.225	2.35
30	0.245	2.34
40	0.269	2.33
50	0.313	2.31
60	0.341	2.30

^aErrors estimated to be $\pm 8\%$ and $\pm 2\%$ for D_{\perp} and D_{\parallel} , respectively.

temperature range covered in this experiment. Also, notice that the tumbling of figure axis of C_6F_6 displays rather strong temperature dependence, D_{\perp} increasing by $\sim 50\%$ with the temperature increase of 40°C. On the other hand, the spinning motion hardly shows any temperature dependence.

Hydrodynamic Models for Reorientational Motion. It was found experimentally by previous investigators¹¹ that the reorientational correlation time displays the following dependence on viscosity (η) and temperature (T) of liquid.

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

where κ is a proportionality constant depending on the properties of the molecule and τ_0 is the zero viscosity intercept. τ_0 was found to be rather similar to the classical free rotor reorientation time, τ_{FR} ³,

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

where I is the moment of inertia related to the particular reorientational motion being investigated. However, interpretation of τ_0 as the free rotor reorientation time may be valid only over a limited range of temperature. Jonas *et al.*¹² questioned the validity of identifying τ_0 with τ_{FR} .

According to Stokes-Einstein equation¹² deri-

ved for the reorientation of a hard sphere under "stick" boundary condition, where the sphere carries the layer of fluid in contact with it, reorientation time (τ_{theory}) is given by

$$\begin{aligned}\tau_{\text{theory}} &= \frac{4\pi\eta r^3}{3kT} \\ &= \frac{\eta V_m}{kT}\end{aligned}$$

where r and V_m are the radius and the volume of the sphere, respectively.

This expression was taken by previous investigators¹¹ as an explanation for the viscosity dependence of the experimental reorientation time. Thus, by identifying the viscosity-dependent part of the experimental reorientation time with τ_{theory} , they suggested the following expression for the proportionality constant, κ , in "stick limit".

$$\kappa = \frac{V_m}{k}$$

This relation may be modified using a correction factor derived by Perrin¹⁴ to describe the reorientation of an ellipsoid in "stick" limit. Then,

$$\tau_{\text{theory}} = f_P \frac{\eta V_m}{kT},$$

and

$$\kappa = f_P \frac{V_m}{k}$$

Hu and Zwanzig¹⁵ have reported that the hydrodynamic theory in "stick" limit predicts too much friction for particles of molecular size and have introduced the so-called "slip" boundary condition. In this limit, the rotating molecule doesn't carry any of fluid along with it, and the reorientation time needs further modification.

$$\tau_{\text{theory}} = f_{\text{HZ}} f_P \frac{\eta V_m}{kT},$$

where f_{HZ} is the correction factor due to the

change of boundary condition from "stick" to "slip". f_{HZ} for the tumbling motion of spheroid is tabulated as a function of R (ratio of the length of shorter axis to longer axis) by Hu and Zwanzig.

Spinning motion of a spheroid in this limit doesn't displace any of fluid, hence, $f_{\text{HZ}}=0$.

Using the temperature-dependent τ_{reor} data obtained in the present work, one may analyze the nature of the reorientational motion of C_6F_6 in relation to the hydrodynamic models described above. Temperature-dependent values for some relevant molecular parameters are listed in Table 3.

Fig. 2 shows the τ_{reor} vs. η/T plot for the tumbling motion of C_6F_6 . The proportionality constant, κ , determined from the slope, is $\kappa = (1.6 \pm 0.6) \times 10^{-7}$ sKP⁻¹, and the zero viscosity intercept is $\tau_0 = (2.4 \pm 1.4)$ ps. Using molecular parameters ($V_m = 108 \text{ \AA}^3$, $R = 0.44$) of C_6F_6 reported in ref. 16, κ may be evaluated with the hydrodynamic models, resulting in $\kappa = 9.7 \times 10^{-7}$ sKP⁻¹ in "stick" limit, and $\kappa = 3.3 \times 10^{-7}$ sKP⁻¹ in "slip" limit. Thus, the tumbling motion of C_6F_6 is better described by "slip" boundary condition than "stick", as were found for the tumbling of benzene and other molecules.^{17,18} Using the value of moment of inertia ($I_{xx} = I_{yy} = 8.16 \times 10^{-38}$ gm·cm²) of C_6F_6 reported by Schlupf and Weber¹⁸, τ_{FR} is calculated to be ~ 1.0 ps in the temperature range covered in

Table 3. Some relevant molecular parameters of C_6F_6 at several temperatures

$T, ^\circ\text{C}$	Density (d) ^a , gcm ⁻³	Hard sphere diameter (σ) ^a , Å	Viscosity (η) ^b , cP
20	1.616	5.601	0.922
30	1.594	5.593	0.785
40	1.571	5.584	0.679
50	1.549	5.576	0.596
60	1.526	5.567	0.528

^a Ref. 23, ^b Ref. 24.

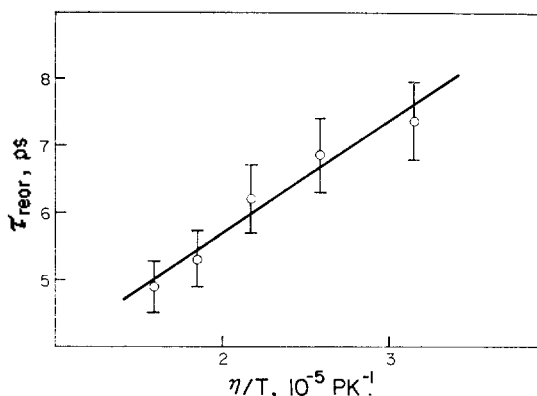


Fig. 2. τ_{reor} vs η/T plot for the tumbling motion of hexafluorobenzene.

the present work. Therefore, τ_0 obtained from the intercept resembles τ_{FR} rather closely.

τ_{reor} ($\equiv 1/6D_{\parallel}$) for the spinning motion of C_6F_6 doesn't show any apparent temperature dependence. In the temperature range covered, $\tau_{reor, \parallel} = 0.72 \text{ ps}$, which is rather small compared to the calculated (using $I_{zz} = 2I_{xx} = 1.63 \times 10^{-27} \text{ gm} \cdot \text{cm}^2$) $\tau_{FR, \parallel}$ of 1.4 ps. Causes for such discrepancy are not clear. It may not be valid to identify τ_0 with τ_{FR} , as was suggested by Jonas *et al.*¹² Or, the discrepancy may reflect the problem related to the present method for D_{\parallel} determination.

χ -Test. Huntress²⁰ has suggested the use of the so-called χ -test to determine the nature of a reorientational process. The quantity χ is the ratio of the reorientational correlation time in liquid to the theoretical reorientation time of the free rotor, *i. e.*,

$$\chi = \frac{5}{18D} \left(\frac{kT}{I} \right)^{1/2}$$

Values of χ less than 3 usually indicate²¹ that the reorientational mechanism is largely inertial, while χ larger than 5 indicates diffusion mechanism. Table 4 shows the χ -values evaluated from the experimental data. Hence, χ -test also indicates that the tumbling motion of C_6F_6

Table 4. χ values for tumbling (χ_L) and spinning (χ_n) motions of C_6F_6

Temperature °C	χ_L	χ_n
20	8.7	0.59
30	8.1	0.60
40	7.5	0.61
50	6.6	0.63
60	6.1	0.64

is largely diffusional while the spinning is mostly inertial.

Activation Energy of Reorientation. The activation energy of reorientation, which is usually a sensitive function of the model, is expressed as²²

$$D = A \exp(-E_a/RT)$$

Fig. 3 shows the $\ln D$ vs. $1/T$ plot for the tumbling motion of C_6F_6 . Activation energy determined from the slope of the curve is $E_a = (2.1 \pm 0.4) \text{ kcal} \cdot \text{mol}^{-1} \text{K}^{-1}$. Therefore, the tumbling of C_6F_6 requires some activation energy, the magnitude of which is comparable to the values²² reported for other molecules which are thought to undergo reorientation by diffusion process. Spinning of C_6F_6 doesn't show any apparent temperature dependence.

Hence, in agreement with the analysis based on hydrodynamic models, activation energy analysis also indicates that the tumbling of C_6F_6 is largely diffusional while the spinning is mostly inertial.

4. SUMMARY AND CONCLUSIONS

The reorientational motion of C_6F_6 in neat liquid has been investigated with Raman spectroscopy. Based on the rotational diffusion constants determined in this work, the reorientation of C_6F_6 has been found to be distinctly anisotropic.

Nature of the reorientation mechanism has

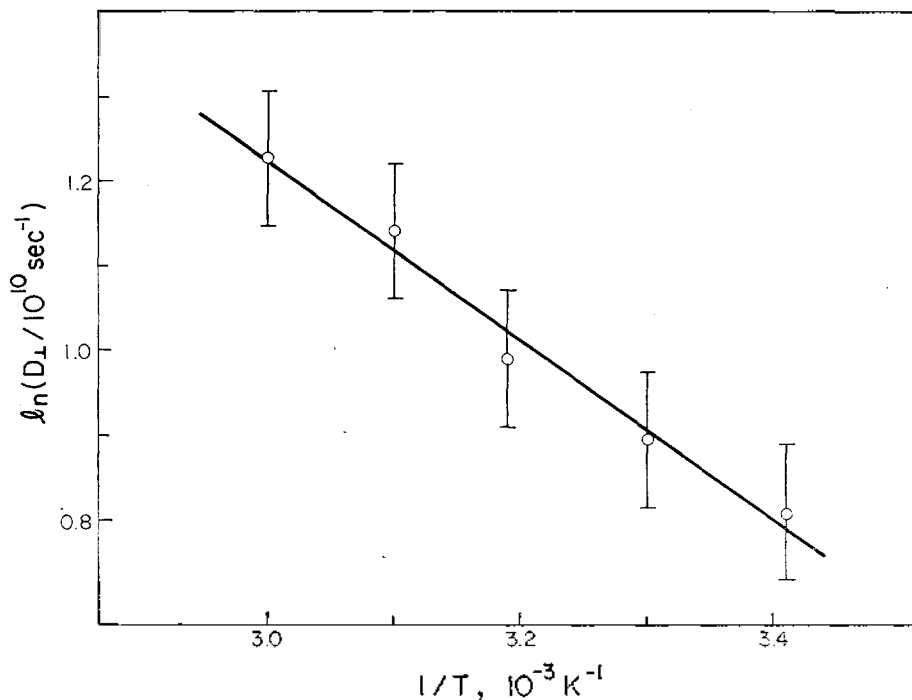


Fig. 3. $\ln D$ vs. $1/T$ plot for the tumbling motion of hexafluorobenzene.

been investigated using the hydrodynamic theory in several ways. Temperature dependences of diffusion constants indicate that the tumbling motion of the figure axis of C_6F_6 is largely diffusional, being describable with "slip" boundary condition. The spinning of the same axis, on the other hand, has been found to be mostly inertial. These are supported further by the activation energy analysis and χ -test on the magnitudes of the diffusion constants.¹

ACKNOWLEDGEMENTS

The author wishes to thank Prof. K. J. Shin in the Department of Chemistry, Seoul National University, for helpful discussions. This work was supported by a grant from the Ministry of Education, Republic of Korea (Grant No. ED83-313).

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