Study of Molecular Reorientation in Liquid with Raman Spectroscopy (III). Temperature Dependence of Molecular Rotation of C₆F₆ in Neat Liquid

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ABSTRACT. The reorientational motion of C₆F₆ in neat liquid is investigated in the temperature range 293~333K by analyzing ν₆ and ν₁₆ bands of its Raman spectrum. Diffusion constants for the tumbling (Dₖ) and spinning (Dₑ) 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 C₆F₆ 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 (Dₖ) and spinning (Dₑ) motions of the figure axis of the molecule were determined from the Raman band widths. And the reorientational motion of C₆F₆ was found to be distinctly anisotropic, spinning motion being much easier than tumbling.

In the present work, the rotational diffusion constants (Dₖ and Dₑ) 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.

ν₂(A₁₂), 560 cm⁻¹ and ν₁₆(F₂₆), 1157 cm⁻¹ modes, correspond to symmetric and asy-
symmetric ring-breathing modes of C₆F₆, respectively, were chosen for the investigation of the recorientational 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. 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 (0~1°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 ±1°C.

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

\[ \delta_i = \delta_a [1 - (s/\delta_a)^{1/2}] \]

where \( \delta_i \) is the true band width (FWHM), \( \delta_a \) 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 relations

\[ I_{iso} = I_1 - \frac{4}{3} I_{\perp} \]
\[ I_{aniso} = I_{\perp} \]

Measured widths (FWHM) of the isotropic \( \delta_{iso} \) and anisotropic \( \delta_{aniso} \) components for \( \nu_2 \) and \( \nu_5 \) vibrational modes of neat liquid C₆F₆ at various temperature are listed in Table 1. It is to be noted that \( \delta_{iso} \) of \( \nu_5 \) \( (E_{2g}) \) mode could not be determined since the depolarization ratios \( \rho = I_{//}/I_1 \) 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 \( D_L \) and spinning \( D_S \) motions of molecules in liquid has been described previously. Briefly, assuming exponential correlation functions for both the vibrational and recorientational relaxation processes, corresponding correlation times \( \tau_{vib} \) and \( \tau_{rec} \) are determined from the widths of the isotropic and anisotropic components of a Raman band, i.e.,

\[ \tau_{vib} = (\pi c \delta_{iso})^{-1} \]
\[ \tau_{rec} = [\pi c (\delta_{aniso} - \delta_{iso})]^{-1} \]

Using the rotational diffusion model for sym-
metric top molecules, \( \tau_{\text{rot}} \) is related to the rotational diffusion constants as

\[
\tau_{\text{rot}} = \left[ n(n+1)D_\perp + m^2(D_\parallel - D_\perp) \right]^{-1},
\]

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 \( \text{C}_6\text{F}_6 \). \( D_\perp \) may be determined directly from \( \tau_{\text{rot}} \) of \( \nu_2 \) mode. To determine \( D_\parallel \), \( \tau_{\text{rot}} \) of a nontotally symmetric \( (m \neq 0) \) mode such as \( \nu_{16}(E_{2g}) \) of \( \text{C}_6\text{F}_6 \) should be known. However, for such a mode, \( \delta_{\text{iso}} \) can not be measured since the isotropic component \( (I_{\text{iso}}) \) vanishes completely for symmetry reason. Tanabe\(^8\) proposed the inverse square relationship between the isotropic band width\( (\delta_{\text{iso}}) \) 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 \( \nu_2 \) and \( \nu_{16} \) modes of \( \text{C}_6\text{F}_6 \) represent ring breathing vibrations, the isotropic band width of \( \nu_{16} \) mode may be estimated from that of \( \nu_2 \) using the following relationship.

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

Diffusion constants thus determined are listed in Table 2. Data indicate a highly anisotropic nature of reorientational motion of \( \text{C}_6\text{F}_6 \) in the temperature range covered in this experiment. Also, notice that the tumbling of figure axis of \( \text{C}_6\text{F}_6 \) displays rather strong temperature dependence, \( D_\perp \) increasing by \( \approx 50\% \) with the temperature increase of \( 40^\circ\text{C} \). On the other hand, the spinning motion hardly shows any temperature dependence.

### Hydrodynamic Models for Reorientational Motion

It was found experimentally by previous investigators\(^11\) that the reorientational correlation time displays the following dependence on viscosity(\( \eta \)) and temperature\( (T) \) of liquid.

\[
\tau_{\text{rot}} = \kappa \left( \frac{\eta}{T} \right) + \tau_0,
\]

where \( \kappa \) is a proportionality constant depending on the properties of the molecule and \( \tau_0 \) is the zero viscosity intercept. \( \tau_0 \) was found to be rather similar to the classical free rotor reorientation time, \( \tau_{\text{FR}}\(^3\),

\[
\tau_{\text{FR}} = \frac{2\pi I}{9} \left( \frac{\eta}{T} \right)^{1/2},
\]

where \( I \) is the moment of inertia related to the particular reorientational motion being investigated. However, interpretation of \( \tau_0 \) 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 \( \tau_0 \) with \( \tau_{\text{FR}} \).

According to Stokes–Einstein equation\(^13\) 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 ($\tau_{\text{theory}}$) is given by

$$\tau_{\text{theory}} = \frac{4 \pi \rho r^3}{3kT} = \frac{\eta V_m}{kT}$$

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

This expression was taken by previous investigators 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 $\tau_{\text{theory}}$, they suggested the following expression for the proportionality constant, $\kappa$, in "stick limit".

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

This relation may be modified using a correction factor derived by Perrin 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 Zwanzig 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.

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

where $f_{\text{HZ}}$ is the correction factor due to the change of boundary condition from "stick" to "slip", $f_{\text{HZ}}$ 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 $\tau_{\text{rew}}$ 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 $\tau_{\text{rew}}$ vs. $\eta/T$ plot for the tumbling motion of $C_6F_6$. The proportionality constant, $\kappa$, 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 ($V_m = 108 \text{Å}^3$, $R = 0.44$) of $C_6F_6$, reported in ref. 16, $\kappa$ 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.

Using the value of moment of inertia ($I_{xx} = I_{yy} = 8.16 \times 10^{-30}$ gm·cm$^2$) of $C_6F_6$, reported by Schlupf and Weber, $\tau_{\text{HZ}}$ is calculated to be $\sim 1.0$ ps in the temperature range covered in

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

<table>
<thead>
<tr>
<th>$T$, °C</th>
<th>Density ($\rho$), g/cm$^3$</th>
<th>Hard sphere diameter ($d$), Å</th>
<th>Viscosity ($\eta$), cP</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>1.616</td>
<td>5.601</td>
<td>0.922</td>
</tr>
<tr>
<td>30</td>
<td>1.594</td>
<td>5.593</td>
<td>0.785</td>
</tr>
<tr>
<td>40</td>
<td>1.571</td>
<td>5.584</td>
<td>0.679</td>
</tr>
<tr>
<td>50</td>
<td>1.549</td>
<td>5.576</td>
<td>0.596</td>
</tr>
<tr>
<td>60</td>
<td>1.526</td>
<td>5.567</td>
<td>0.528</td>
</tr>
</tbody>
</table>

the present work. Therefore, \( \tau_0 \) obtained from the intercept resembles \( \tau_{iB} \) rather closely.

\( \tau_{iB}(=1/6D_3) \) for the spinning motion of C\(_6\)F\(_6\) doesn't show any apparent temperature dependence. In the temperature range covered, \( \tau_{iB} = 0.72 \text{ps} \), which is rather small compared to the calculated (using \( I_{zz} = 2I_{xx} = 1.63 \times 10^{-37} \text{gm} \cdot \text{cm}^2 \)) \( \tau_{iB} \) of 1.4ps. Causes for such discrepancy are not clear. It may not be valid to identify \( \tau_0 \) with \( \tau_{iB} \), as was suggested by Jonas et al.\(^{12} \). Or, the discrepancy may reflect the problem related to the present method for \( D_3 \) determination.

\( \chi \)-Test. Huntress\(^{39} \) has suggested the use of the so-called \( \chi \)-test to determine the nature of a reorientational process. The quantity \( \chi \) is the ratio of the reorientational correlation time in liquid to the theoretical reorientation time of the free rotor, \( I.e., \)

\[
\chi = \frac{5}{18D} \left( \frac{kT}{T} \right)^{1/2}.
\]

Values of \( \chi \) less than 3 usually indicate\(^{21} \) that the reorientational mechanism is largely inertial, while \( \chi \) larger than 5 indicates diffusion mechanism. Table 4 shows the \( \chi \)-values evaluated from the experimental data. Hence, \( \chi \)-test also indicates that the tumbling motion of C\(_6\)F\(_6\) 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 as\(^{22} \)

\[
D = A \exp(-E_a/RT).
\]

**Fig. 3** shows the ln \( D \) vs. 1/T plot for the tumbling motion of C\(_6\)F\(_6\). Activation energy determined from the slope of the curve is \( E_a = (2.1 \pm 0.4) \text{kcal} \cdot \text{mol} \cdot \text{K}^{-1} \). Therefore, the tumbling of C\(_6\)F\(_6\) requires some activation energy, the magnitude of which is comparable to the values\(^{22} \) reported for other molecules which are thought to undergo reorientation by diffusion process. Spinning of C\(_6\)F\(_6\) 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\(_6\)F\(_6\) is largely diffusional while the spinning is mostly inertial.

### 4. SUMMARY AND CONCLUSIONS

The reorientational motion of C\(_6\)F\(_6\) in neat liquid has been investigated with Raman spectroscopy. Based on the rotational diffusion constants determined in this work, the reorientation of C\(_6\)F\(_6\) has been found to be distinctly anisotropic.

Nature of the reorientation mechanism has
been investigated using the hydrodynamic theory in several ways. Temperature dependences of diffusion constants indicate that the tumbling motion of the figure axis of C₆F₆ 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.

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