

용액 중에서의 분자의 재배치 운동에 관한 라만 분광법적  
연구 (제 1 보), 순수 액체상태의  $\text{CDCl}_3$ 에 관한 비등방성 회전

金明洙 · 申蕪朝†

서울대학교 자연과학대학 화학과

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Study of Molecular Reorientation in Liquid  
with Raman Spectroscopy (I). Anisotropic  
Rotation of  $\text{CDCl}_3$  in Neat Liquid

Myung Soo Kim and Kook Joe Shin†

Department of Chemistry, Seoul National University, Seoul 151, Korea

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**요약.** 순수 액체상태의  $\text{CDCl}_3$ 의 비등방성 회전운동을 라만 스펙트럼의  $\nu_1$ -band를 분석하여 조사하였다. 이로부터 분자의  $\text{C}_3$ -대칭축에 수직인 축 주위로의 회전운동에 관계되는 확산상수 ( $D_{\perp}$ )를 구하였다. 대칭축 주위로의 회전운동에 관계되는 확산상수 ( $D_{\parallel}$ )는 위에서 얻은  $D_{\perp}$ 와  $^{35}\text{Cl}$ 의 NQR 이완시간으로부터 구하였다. 이렇게 구한 확산상수들은  $^2\text{H}$ 와  $^{35}\text{Cl}$ 의 NQR 이완시간으로부터 구한 값들과 실험오차 범위내에서 잘 일치하였다. 또한 두 확산상수들의 값들로부터 순수한  $\text{CDCl}_3$ 의 재배치 운동이 상당히 비등방적인 것을 알게 되었다.

**ABSTRACT.** Anisotropic rotation of  $\text{CDCl}_3$  in neat liquid is investigated by the analysis of  $\nu_1$  band of Raman spectrum and the diffusion constant ( $D_{\perp}$ ) for the tumbling motion is obtained. The diffusion constant ( $D_{\parallel}$ ) for the spinning motion is obtained from the above  $D_{\perp}$  value and the chlorine-35 nuclear quadrupole relaxation time. The diffusion constants thus obtained seem to agree very well with the ones obtained from  $^2\text{H}$  and  $^{35}\text{Cl}$  NQR results within experimental errors. The data suggest fairly anisotropic character of reorientational motions in neat  $\text{CDCl}_3$ .

## INTRODUCTION

Study of reorientational motions of molecules in liquid is important in understanding molecular dynamics in liquid and much effort has been paid both theoretically<sup>1</sup> and experimentally<sup>2</sup>.

Raman spectroscopy is one of the widely used techniques which have been employed to investigate molecular reorientations in liquids.

Since the Raman bands are broadened by various processes including vibrational and rotational relaxations of molecules, proper band analyses would produce necessary information. Sometimes it is used as a separate probe but often it is complemented by other methods such as NMR, IR, etc. Combination of different methods is particularly useful when there are certain uncertainties in the analysis of molecular motions using only one technique.

Chloroform ( $\text{CHCl}_3/\text{CDCl}_3$ ) is one of the substances extensively studied by Raman<sup>3-9</sup>, IR<sup>3,10</sup>, depolarized Rayleigh scattering<sup>10-12</sup>, far IR<sup>10-15</sup> and NMR<sup>4,7,11,13,14</sup>. Since chloroform is a symmetric top molecule its rotation in liquid is expected to be anisotropic. This has been investigated by NMR<sup>13,14</sup> some years ago but Raman studies<sup>7,8</sup> have been carried out by assuming isotropic rotation.

In this work we study the anisotropic rotation of  $\text{CDCl}_3$  with Raman spectroscopy complemented by NQR data obtained earlier<sup>13</sup>. In the analysis of Raman spectrum of neat liquid  $\text{CDCl}_3$  one usually investigates the  $\nu_1$  band at  $2255\text{ cm}^{-1}$  which is due to the C-D stretching vibration. This band is chosen because it shows no vibration-rotation coupling<sup>6</sup>. But the analysis of  $\nu_1$  band alone is not enough to investigate the anisotropic rotation and additional information has to be supplied from other bands or from other methods. However, other Raman bands with the same symmetry as the  $\nu_1$  band merely produce the same information and they are not helpful for the study of anisotropic rotation. Moreover, for all the remaining fundamental bands with different symmetry the depolarization ratio ( $\rho$ ) becomes 3/4 which makes it impossible to separate the vibrational relaxation contribution from the anisotropic component of the Raman spectra. Therefore, we must resort to other methods for additional information.

Nuclear quadrupole relaxation technique is an excellent candidate for this purpose because the nuclear quadrupole interaction is a dominating process contributing to the spin-lattice relaxation time. This avoids further complications of separating various relaxation mechanisms due to the dipole-dipole and spin-rotation interactions.

In order to analyze the Raman and NMR

data one needs to have a theoretical basis. Due to complicated molecular dynamics in liquid phase several simplified models are widely used<sup>1</sup>. Among these the rotational diffusion model<sup>22</sup> and the extended rotational diffusion model<sup>23</sup> are extensively used to analyze Raman or NMR measurements. Although the latter is more general in that the inertial effect is properly taken into consideration, it has not been developed to analyze the anisotropic rotations. For this reason we adopt the former model which assumes small step diffusional rotation and is generalized to describe the anisotropic rotation of symmetric top molecules<sup>18</sup>.

In this work we study the anisotropic rotation of  $\text{CDCl}_3$  in neat liquid by analyzing the  $\nu_1$  band of spontaneous Raman spectra. This gives a component of rotational diffusion tensor and the other component is obtained from the chlorine-35 NQR data of Huntress<sup>13</sup>.

## 2. THEORETICAL BACKGROUND

The isotropic and anisotropic Raman scattering spectra can be obtained from the measured parallel ( $I_{\parallel}$ ) and perpendicular ( $I_{\perp}$ ) components by the well known relations<sup>24</sup>

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

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

Since  $I_{\text{iso}}(\omega)$  contains the isotropic component of the polarizability tensor it can be expressed in terms of vibrational correlation function only. On the other hand  $I_{\text{aniso}}(\omega)$  contains the anisotropic component of the polarizability tensor and is sensitive to molecular reorientation and it is given by the convolution of both vibrational and reorientational correlation functions. When vibrational and reorientational motions are uncoupled, such is the case for the  $\nu_1$  band of  $\text{CDCl}_3$ , it can be written as Fourier trans-

form of the product of the vibrational and reorientational correlation functions:

$$I_{\text{iso}}(\omega) = \int_{-\infty}^{\infty} \Phi_{\text{vib}}(t) \exp(i\omega t) dt \quad (3)$$

$$I_{\text{aniso}}(\omega) \approx \int_{-\infty}^{\infty} \Phi_{\text{vib}}(t) \Phi_{\text{reor}}(t) \exp(i\omega t) dt \quad (4)$$

The vibrational correlation function is assumed to have an exponential shape

$$\Phi_{\text{vib}}(t) = \exp(-t/\tau_{\text{vib}}) \quad (5)$$

then the vibrational correlation time,  $\tau_{\text{vib}}$ , is related to the band width (FWHM),  $\delta_{\text{iso}}$ , of the isotropic component by<sup>8</sup>

$$\tau_{\text{vib}}^{-1} = \pi c \delta_{\text{iso}} \quad (6)$$

The reorientational correlation function is usually expressed by Kubo function<sup>17</sup> but it is reduced to an exponential function when the time between successive collisions is very short:

$$\Phi_{\text{reor}}(t) = \exp(-t/\tau_{\text{reor}}) \quad (7)$$

and the reorientational correlation time  $\tau_{\text{reor}}$  is given by<sup>8</sup>

$$\tau_{\text{reor}}^{-1} = \pi c (\delta_{\text{aniso}} - \delta_{\text{iso}}) \quad (8)$$

with the band width (FWHM),  $\delta_{\text{aniso}}$ , of the anisotropic component. For a symmetric top molecule undergoing an anisotropic reorientation,  $\tau_{\text{reor}}$  can be expressed in terms of two different components of the diffusion tensor<sup>18</sup>

$$\tau_{\text{reor}}^{-1} = n(n+1)D_{\perp} + m^2(D_{\parallel} - D_{\perp}) \quad (9)$$

This expression is obtained when the molecular reorientation is governed by rotational diffusion process. The constants  $n$  and  $m$  label the symmetry property of a particular band ( $n=2$ ,  $m=0$  for  $\nu_1$  band). The diffusion constants  $D_{\perp}$  and  $D_{\parallel}$  characterize the tumbling motion of the  $C_3$  symmetry axis and spinning about the symmetry axis, respectively.

### 3. EXPERIMENTAL

Raman spectra were recorded with a Laser

Raman spectrophotometer, Japan Spectroscopic Co. Model R-300. The original DC detection system in the spectrophotometer was replaced by a photon counting system consisting of EMI 9789B alkali PM-tube, EG & G Princeton Applied Research model 1120 amplifier/discriminator and model 1105 data converter to improve the signal to noise ratio of the spectra. 514.5 nm line of Argon ion laser, Spectra Physics model 164-06 was used as the exciting source with 200 mW output power.

The temperature of the sample was maintained at  $20 \pm 0.5$  °C using a homemade temperature controller, which consists of a brass capillary cell holder also working as a heat jacket and a constant temperature circulator, Haake type F 4391.

The slit effect on the Raman band width was corrected using the formula<sup>19</sup>

$$\delta_t = \delta_a [1 - (S/\delta_a)^2] \quad (10)$$

where  $\delta_t$  is the true band width (FWHM),  $\delta_a$  the apparent band width, and  $S$  the spectral slit width. Experiments were performed with 200  $\mu$  slit widths, and the spectral slit width at 2255  $\text{cm}^{-1}$  Raman shift was estimated by measuring the widths of Neon emission lines at several wavelengths and interpolating. Neon emission lines at 17342.99, 16996.61, 16816.67  $\text{cm}^{-1}$ , each corresponding to 2086.92, 2433.3, 2613.24  $\text{cm}^{-1}$  Raman shift respectively, were used as calibration lines in this experiment.

Parallel and perpendicular components of the Raman band were measured with polarization analyzer and polarization scrambler. Isotropic and anisotropic components of the Raman band can be evaluated from Eqs. (1) and (2). Instead of evaluating the full profiles of  $I_{\text{iso}}$  and  $I_{\text{aniso}}$  and then measuring the FWHM's of each profile, band widths of above components were calculated directly from those of  $I_{\perp}$  and  $I_{\parallel}$

and the depolarization ratio following the procedure suggested by Tanabe and Hiraishi<sup>8</sup>.

CDCl<sub>3</sub> was purchased from the Aldrich Chemical Co. and used without further purification.

#### 4. RESULT AND DISCUSSION

Fig. 1 shows the parallel and perpendicular components of the  $\nu_1$  band of CDCl<sub>3</sub> at 2255 cm<sup>-1</sup>. Calibrated band widths of isotropic ( $\delta_{\text{iso}}$ ) and anisotropic ( $\delta_{\text{aniso}}$ ) components averaged over 18 different measurements are listed in Table 1.

The diffusion constant  $D_{\perp}$  obtained from the analysis of the  $\nu_1$  band of CDCl<sub>3</sub> is 1.07 ( $\pm$

Table 1. Widths of  $\nu_1$  Raman band of CDCl<sub>3</sub> at 20°C.<sup>a</sup>

$\delta_{\text{iso}}, \text{cm}^{-1}$	$\delta_{\text{aniso}}, \text{cm}^{-1}$	$(\delta_{\text{aniso}} - \delta_{\text{iso}}), \text{cm}^{-1}$
5.13 $\pm$ 0.16	11.97 $\pm$ 0.21	6.84 $\pm$ 0.37

<sup>a</sup> These values are after slit effect correction.

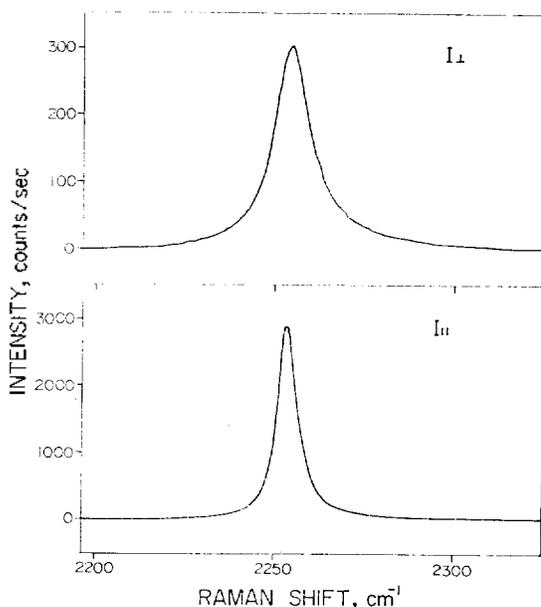


Fig. 1. The parallel ( $I_{\parallel}$ ) and perpendicular ( $I_{\perp}$ ) components of the  $\nu_1$  band. Spectra were recorded with 1 and 10 sec. time constants for  $I_{\parallel}$  and  $I_{\perp}$ , respectively.

$0.06) \times 10^{11} \text{ sec}^{-1}$ . This is the measure of the tumbling motion of the  $C_3$  symmetry axis. This value agrees well with the reorientational correlation time data obtained earlier by Arndt and McClung<sup>7</sup>, and Tanabe and Hiraishi<sup>8</sup>. Although they didn't analyze their data in terms of anisotropic rotational diffusion for a symmetric top molecule, their reorientational correlation times correspond to our  $D_{\perp}$  by the relation  $1/\tau = 6D$ . Their diffusion constants thus obtained were  $1.07 \times 10^{11} \text{ sec}^{-1}$  at 303K and  $0.95 \times 10^{11} \text{ sec}^{-1}$  at room temp., respectively.

To obtain  $D_{\parallel}$  from the Raman spectroscopy a vibrational band with different symmetry (*i. e.*,  $m \neq 0$  in Eq. 9) must be analyzed. Since all the non-totally symmetric Raman bands are depolarized ( $\rho = \frac{3}{4}$ ),  $I_{\text{iso}}(\omega) = 0$  (Eq. 1), and contribution of the vibrational relaxation cannot be rigorously separated from the anisotropic component. Several approximate procedures had been proposed. For example, Tanabe<sup>20</sup> studied reorientational motion of liquid benzene using  $\nu_1$  ( $A_{1g}$ ) and  $\nu_{15}$  ( $E_{2g}$ ) Raman bands, both corresponding to the C-H stretching vibration. Contribution of the vibrational relaxation to  $\nu_{15}$  anisotropic band was removed with the information of  $\nu_1$  vibrational relaxation data and using the isolated binary collision theory of Fischer and Laubereau<sup>21</sup>.

Even such an approximate procedure can not be adopted for CDCl<sub>3</sub> since there is no C-D stretching vibrational mode other than  $\nu_1$ .

In order to obtain  $D_{\parallel}$ , we utilize the nuclear quadrupole relaxation measurements by Huntress<sup>13</sup>. He has developed a theory for the spin-lattice relaxation time due to nuclear quadrupole interaction in terms of anisotropic rotational diffusion model for various types of molecules. For a symmetric top molecule he obtained

$$\frac{1}{T_{1Q}} = \frac{\pi^2}{20} \left[ \frac{2I+3}{I^2(2I-1)} \right] \left( \frac{e^2qQ}{h} \right)^2 \frac{1}{D_{\perp}}$$

$$\times \left[ 1 + \frac{3(D_{\perp} - D_{\parallel})}{(5D_{\perp} + D_{\parallel})} \sin^2 \theta \right. \\ \left. \times \left( 1 + \frac{3(D_{\perp} - D_{\parallel})}{2(D_{\perp} + 2D_{\parallel})} \sin^2 \theta \right) \right] \quad (11)$$

where  $\theta$  is the polar angle of a nucleus with respect to the figure axis. For  $\text{CDCl}_3$ , this formula shows that the deuteron spin relaxation time is dependent only on  $D_{\perp}$  ( $\theta=0^\circ$ ). The  $D_{\perp}$  value thus obtained was  $0.96(\pm 0.19) \times 10^{11} \text{ sec}^{-1}$  (at  $20^\circ\text{C}$ )<sup>13</sup> which is in good agreement with our result. On the other hand, the chlorine-35 spin relaxation time depends on both  $D_{\perp}$  and  $D_{\parallel}$  ( $\theta=110.55^\circ$ ) and the use of  $D_{\perp}$  value from either Raman  $\nu_1$  band analysis or the deuteron relaxation result yields the value of  $D_{\parallel}$ . Our  $D_{\perp}$  value of  $1.07 \times 10^{11} \text{ sec}^{-1}$  is substituted in the expression for the chlorine-35 spin relaxation time to yield the value of  $D_{\parallel} = 1.56(\pm 0.53) \times 10^{11} \text{ sec}^{-1}$  which agrees well with Huntress' result of  $D_{\parallel} = 1.8(\pm 1.1) \times 10^{11} \text{ sec}^{-1}$  using only NQR data. Necessary parameter values and experimental relaxation times are summarized in Table 2 and the final results from two different methods are compared in Table 3.

Comparison of two diffusion constants shows that the reorientation of  $\text{CDCl}_3$  is fairly anisotropic. That is, the rotation about the  $\text{C}_3$

Table 2. Parameters used in NQR<sup>a</sup>.

	I	$\theta$ (deg.)	$\frac{e^2qQ}{h}$ (MHz)	$T_{1Q}$ (sec)
<sup>2</sup> H	1	0	0.170	1.35
<sup>35</sup> Cl	3/2	110.55	79	$31.0 \times 10^{-6}$

<sup>a</sup>Ref. 13

Table 3. Rotational diffusion constants.

	$D_{\perp}$ ( $10^{11} \text{ sec}^{-1}$ )	$D_{\parallel}$ ( $10^{11} \text{ sec}^{-1}$ )
Present work	$1.07 \pm 0.06$ (Raman)	$1.56 \pm 0.53$ (Raman + <sup>35</sup> Cl-NQR)
Huntress <sup>13</sup>	$0.96 \pm 0.19$ ( <sup>2</sup> H-NQR)	$1.8 \pm 1.1$ ( <sup>2</sup> H-NQR + <sup>35</sup> Cl-NQR)

symmetry axis is easier than the tumbling of the symmetry axis.

Good agreements for the diffusion constants in both Raman and NQR measurements also demonstrated the compatibility and complementarity of two techniques.

In summary, anisotropic reorientational motion in neat  $\text{CDCl}_3$  was studied with Raman spectroscopy with the help of <sup>35</sup>Cl-NQR result. Rotational diffusion constants ( $D_{\perp}$ ,  $D_{\parallel}$ ) thus obtained display fairly anisotropic behavior of the reorientational motion. It has been clearly demonstrated that due to the complementary nature of the two techniques, combination of these techniques can be used advantageously for the study of reorientational motions in liquids in favorable cases.

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