

# Tumbling and spinning diffusions of acetonitrile in water and organic solvents

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The spin–lattice relaxation times  $T_1$  for  $^2\text{H}$  and  $^{14}\text{N}$  of acetonitrile- $d_3$  ( $\text{CD}_3\text{CN}$ ) are measured in pure liquid, *n*-hexane, carbon tetrachloride, acetone, methanol, water, and heavy water as functions of temperature and concentration. From the  $T_1$  values, the rotational diffusion coefficients for the tumbling and spinning motions are separately obtained. The tumbling motion is strongly dependent on the solvent and temperature and its diffusion coefficient is qualitatively explained by a simple dielectric friction model. The spinning motion is, on the other hand, weakly dependent on the solvent and temperature. The observed large anisotropy ratio ( $\sim 9$ ) of the spinning to the tumbling modes represents the anisotropy of the solvation shell and is explained by neither the free rotor model nor the hydrodynamic continuum model. The tumbling motion is more strongly hindered than the spinning motion due to the dipolar interaction between the solute and solvent. © 2000 American Institute of Physics. [S0021-9606(00)51203-3]

## I. INTRODUCTION

In solution, the rotational dynamics of molecules is sensitive to the molecular environment in the short range and directly probes the solvation shell structure controlled by the solute–solvent interactions.<sup>1–6</sup> A typical and strong molecular interaction is the hydrogen bonding. Temperature<sup>1</sup> and pressure<sup>2</sup> effects have disclosed the important role played by the attractive potential in controlling the rotational dynamics of such a hydrogen bonding solute as water in organic solvents. In this paper, acetonitrile, which is polar but not hydrogen bonding, is studied for comparison with water. Acetonitrile has a large dipole moment (4 D) and is useful for elucidating the effect of dipolar interactions on the solvation shell structure. It is a symmetric top with the two rotational modes; one is the tumbling ( $\perp$ ) and the other the spinning ( $\parallel$ ) motions. The difference in the diffusion coefficient between the two motions is a sensitive measure of the anisotropy in the solvation structure.

The rotational motions of acetonitrile have been investigated by various methods: IR,<sup>7–10</sup> Raman,<sup>9–14</sup> dynamic light scattering,<sup>12–15</sup> NMR,<sup>6,16–25</sup> pulse laser,<sup>26–28</sup> and computer simulation.<sup>23,24,29–31</sup> Most of the studies are, however, confined to neat liquid or in rather concentrated solutions. In order to elucidate the solute–solvent interaction effect on the rotational dynamics, we focus on the solvent effect on the rotational diffusion coefficients of acetonitrile at infinite dilution. Water and various organic solvents including apolar ones are employed to shed light on molecular factors neglected by the hydrodynamic model. While the hydrodynamic continuum models may be applied to such large molecules as dyes,<sup>32–34</sup> their applicability is not assured *a priori* to such a small molecule as acetonitrile due to the neglect of molecular factors in the short range.

The tumbling motion of acetonitrile is the rotation about an axis perpendicular to the symmetry axis and brings about the rotation of the large dipole. The spinning motion is the rotation about the symmetry axis and indistinguishable from the internal rotation of the methyl group. In neat liquid,<sup>6,16–19</sup> the rotational diffusion coefficients for the two modes are not identical and involves a large value of anisotropy ( $\sim 9$ ), which is much larger than the length ratio of the long to the short axes (1.3). In this work, we investigate the anisotropy of the solvation shell formed around acetonitrile by examining the ratio of the diffusion coefficients of the spinning to tumbling motions. For the tumbling motion of acetonitrile, the dipolar interaction effects may be large enough to control the rotational diffusion of the dipole. In a previous work, we elucidated the validity of the dielectric friction theory<sup>35</sup> to the rotation of such an ion as the nitrate ion.<sup>36</sup> The unexpectedly large values of the rotational correlation time of the nitrate ion in alcohols were explained in terms of the dielectric friction coefficient. For the case of such a neutral dipolar molecule as acetonitrile, it has been reported by Kovacs and co-workers that this theory was applicable to the tumbling motion of acetonitrile in water–1-propanol mixture solvent.<sup>22</sup> We test the qualitative applicability of the dielectric friction theory to the tumbling diffusion of the neutral dipolar molecule acetonitrile in various solvents. For the case of the spinning, on the other hand, the direction of the dipole moment does not change and may be independent of the dipolar interaction. On the spinning motion of acetonitrile in dilute solutions, Yuan and Schwartz have investigated the effects of apolar and polar solvents by means of NMR.<sup>25</sup> They have reported that the spinning motion has no correlation with the solvent viscosity. It is then of interest to ask how the rotational diffusion coefficient of the spinning motion is affected by the solvation structure, in particular when the solvent is water. This is indeed motivated by the report from recent computer simulation observations that for such

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polar solutes as methanol and acetonitrile, the hydrophobic hydration shell is formed around the apolar methyl group in the solute molecules.<sup>24,37</sup> For the dilute solution in carbon tetrachloride, it has been reported by Knözinger, Leutloff, and Wittenbeck<sup>7</sup> that monomeric acetonitrile molecules librate. This means that acetonitrile molecules are in a strong solvation shell. One may observe that methyl group can reorient with a small friction in a strong solvation shell made of such immobile molecules as carbon tetrachloride and hydrophobic hydrating water.

In Sec. II, brief review of rotational dynamics of acetonitrile is given. In Sec. III, the experimental procedure is explained. In Sec. IV, the results are shown. In Sec. V, the intermolecular interaction effect on the rotational dynamics are discussed. The paper is concluded in Sec. VI.

## II. A BRIEF REVIEW OF ROTATIONAL DYNAMICS OF ACETONITRILE

In the 1960s and 1970s, the rotational dynamics of acetonitrile was studied by means of IR,<sup>10</sup> Raman,<sup>10–12</sup> and NMR.<sup>16–19</sup> It was then found that for the tumbling motion, the rotational correlation time is  $\sim 1$  ps whereas that of the spinning motion is a much smaller value of  $\sim 0.1$  ps. It was also reported that such small molecules as  $\text{ND}_3$ ,<sup>38</sup>  $\text{NH}_3$ ,<sup>38</sup>  $\text{N}_2$ ,<sup>39</sup>  $\text{CD}_4$ ,<sup>40</sup> and  $\text{CD}_3$  groups in monohalomethanes<sup>41–43</sup> and methyl acetylene<sup>44</sup> involve very small rotational correlation times (0.1–0.4 ps). In this era, however, since the detailed knowledge of the rotational correlation function was still absent, such a method as the “ $\chi$ ” test<sup>45</sup> was used to characterize the rotational dynamics. The  $\chi$  value is defined as the ratio of the rotational correlation time observed ( $\tau_{2R}$ ) to the calculated value for a free rotor<sup>46</sup> ( $\tau_{\text{FR}}$ );

$$\chi = \frac{\tau_{2R}}{\tau_{\text{FR}}}, \quad (1)$$

$$\tau_{\text{FR}} = \frac{\pi}{2\sqrt{3}} \sqrt{\frac{I}{k_B T}} \quad (2)$$

where  $I$  is the moment of inertia,  $T$  is the temperature, and  $k_B$  is the Boltzmann constant. When the  $\chi$  value is smaller than 3, the rotational motion is considered “inertial,” and when the  $\chi$  value is larger than 5, the rotational motion is considered “diffusive.” In pure acetonitrile liquid, for example, the values are 3 and 1 for the tumbling and spinning motions, respectively. When the  $\chi$  value is unity, the rotational motion has been regarded as a free rotor. This characterization was widely used without resorting to the functional form of the rotational correlation functions.<sup>18,45,46</sup>

In the 1980s, molecular dynamics (MD) simulation enabled one to discuss the rotational correlation function itself. Böhm *et al.* investigated the rotational dynamics of acetonitrile in neat liquid using MD simulation.<sup>30</sup> They calculated the rotational correlation functions of Legendre functions  $Y_{lm}$  for  $l=2$  and  $m=0, \pm 1$ , and  $\pm 2$ . Each correlation function is fitted to a single exponential function while a Gaussian-like decay is observed in the short-time region. For  $l=2$  and  $m=0$ , they estimated the rotational correlation times from the integration and from the exponential fitting at

long times where the correlation function is smaller than  $1/e$ . The rotational correlation times calculated from the integral and the slope were found to be 0.96 and 1.16 ps, respectively, and they are close to each other within the precision of our discussion. In addition, these values are in good agreement with the values measured by means of the Raman linewidth<sup>12</sup> and the NMR relaxation measurement,<sup>17</sup> 1.1 and 1.3 ps, respectively. This indicates that the rotational diffusion model is applicable to the tumbling mode of acetonitrile in the pure liquid. They also showed that the rotational diffusion model is semiquantitatively applicable to the spinning mode. In the case of solutions, Laaksonen and Kovacs showed similar results for the solution of chloroform.<sup>24</sup> By means of depolarized Rayleigh scattering<sup>14</sup> and Raman,<sup>9</sup> it was reported that the rotational correlation functions are fitted to single exponential decay functions except for initial Gaussian decay functions, in good agreement with the results of the MD simulations. These also show the applicability of the rotational diffusion model to the tumbling and spinning motions of acetonitrile as a good approximation. According to these results, the spinning motion of acetonitrile is sufficiently diffusive even when the  $\chi$  value is very close to unity.

In this study, our purpose is to elucidate the solute–solvent interaction effects on the tumbling and spinning motions. The rotational correlation times of acetonitrile should then be measured in dilute solutions. For this purpose, NMR is one of the most powerful methods because of its sensitivity and selectivity. In the present study, we will measure the rotational correlation times using NMR and apply the rotational diffusion model to the rotational motions of acetonitrile in its dilute solutions, in order to extract two rotational diffusion coefficients corresponding to the tumbling and spinning motions.

## III. EXPERIMENT

### A. Materials

Acetonitrile- $d_3$  ( $\text{CD}_3\text{CN}$ ) (> 99.6%, CEA) was used after dried by molecular sieves 3A (Nacalai). Deuterated water (99.8%) was supplied from CEA. Acetone, methanol, carbon tetrachloride, and *n*-hexane of spectrograde were obtained from Nacalai and dried several days before use with molecular sieves (3A or 4A, Nacalai). Distilled water ( $\text{H}_2\text{O}$ ) was used after being purified further by a Milli-Q Labo (Millipore) filter system. Solutions of acetonitrile- $d_3$  were prepared by weight. To elucidate the concentration dependence of the tumbling motion of acetonitrile, the concentration of the solution was changed from 0.05 to 1 M ( $\text{M} = \text{mol dm}^{-3}$ ). As shown in Sec. IV A, the association between acetonitrile molecules is considered negligible at concentrations of 0.05, 0.05, 0.5, 0.5, 1, and 1 M for  $\text{CCl}_4$ ,  $\text{C}_6\text{H}_{14}$ ,  $\text{CH}_3\text{OH}$ ,  $(\text{CH}_3)_2\text{CO}$ ,  $\text{H}_2\text{O}$ , and  $\text{D}_2\text{O}$ , respectively. Temperature dependence of the rotational diffusion coefficients was examined at the constant concentration where the rotational diffusion coefficient is considered equal to that in the infinite dilution limit.

## B. Apparatus and experimental procedure

The spin–lattice relaxation times  $T_1$  for  $^2\text{H}$  and  $^{14}\text{N}$  in acetonitrile- $d_3$  were measured by the inversion recovery method using NMR spectrometer (JEOL, EX-270) equipped with a superconductor magnet whose magnetic field is 6.35 T. Free induction decay signals were accumulated 2 times for  $^2\text{H}$  and 2000 times for  $^{14}\text{N}$ . The uncertainty of  $T_1$  was within 2% for all solutions. The temperature was controlled to  $\pm 0.1^\circ\text{C}$ .

## C. Data reduction

The main relaxation mechanism of  $^2\text{H}$  and  $^{14}\text{N}$  is quadrupolar and is controlled by the interaction between the quadrupole of nucleus ( $eQ$ ) and the electric field gradient ( $eq$ ) at the nucleus. Under extreme narrowing conditions, the spin–lattice relaxation time measured is related to the rotational correlation time  $\tau_{2R}$  for the corresponding principal axis of the electric field gradient through

$$\frac{1}{T_1} = \frac{3\pi^2}{2} \left( \frac{e^2Qq}{h} \right)^2 \tau_{2R}, \quad (3)$$

where  $e^2Qq/h$  is the quadrupole coupling constant (QCC): the QCC values are 165 kHz and 3.74 MHz for  $^2\text{H}$  and  $^{14}\text{N}$ , respectively.<sup>18</sup> The rotational correlation time is expressed by the time integration of the rotational time correlation function of second order. By solving the Langevin equation for rotational motion and using the Debye diffusion limit,<sup>3</sup> the rotational correlation time is expressed in terms of the rotational diffusion coefficients for the tumbling ( $D_\perp$ ) and spinning ( $D_\parallel$ ) motions as

$$\tau_{2R} = \frac{3}{2} \left( \frac{(3 \cos^2 \theta - 1)^2}{36D_\perp} + \frac{2 \sin^2 \theta \cos^2 \theta}{5D_\perp + D_\parallel} + \frac{\sin^4 \theta}{4D_\perp + 8D_\parallel} \right), \quad (4)$$

where the angle  $\theta$  between the principal axis of the electric field gradient and the symmetry axis are 0 and  $109.55^\circ$  for  $^{14}\text{N}$  and  $^2\text{H}$ , respectively. Using Eq. (4), the two rotational diffusion coefficients,  $D_\perp$  and  $D_\parallel$ , are obtained from the  $T_1$  of  $^2\text{H}$  and  $^{14}\text{N}$ . In our model, even the rotational relaxation of the spinning motion is assumed to be described by the small step diffusion. The rotational diffusion model is supported by the MD simulation study<sup>30</sup> as mentioned in Sec. II.

In spite of the large value of the spinning diffusion coefficients, nonzero activation energy ( $\sim 3 \text{ kJ mol}^{-1}$ ) is observed and is dependent on solvent as shown in Sec. V A. This value is larger than the value from a simple free rotation ( $\sim 1.3 \text{ kJ mol}^{-1}$  around  $30^\circ\text{C}$ ) and the spinning motion is influenced by the intermolecular interactions. We have also observed nonzero activation volume ( $\sim 0.2 \text{ cm}^3 \text{ mol}^{-1}$ ) for the spinning motion.<sup>47</sup> These results indicate that even the spinning motion is not a simple free rotation, which has almost zero activation energy and zero activation volume. The spinning motion is the reorientational motion influenced from the intermolecular interactions. These experimental results are in favor of the rotational diffusion approximation validated by the MD study.<sup>30</sup>

For each mode of the tumbling and spinning motions, the above-obtained rotational diffusion coefficient  $D_i$  is re-

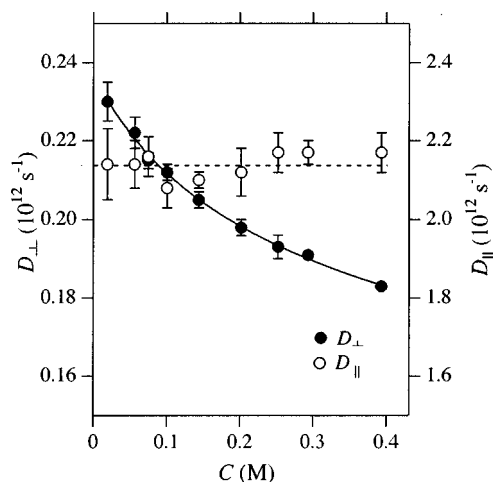


FIG. 1. Concentration dependence of the rotational diffusion coefficients of the tumbling ( $D_\perp$ ) and the spinning ( $D_\parallel$ ) motions of  $\text{CD}_3\text{CN}$  in  $\text{C}_6\text{H}_{14}$  at  $30^\circ\text{C}$ .

lated to the “pure” rotational correlation times  $\tau_{lR}(i)$  for that mode in the rotational diffusion limit as follows:

$$\tau_{lR}(i) = \frac{1}{l(l+1)D_i}, \quad (5)$$

where  $l$  is the rank of the orientational correlation function. The rotational correlation times for  $l=1$  and  $l=2$  are obtained by means of IR and NMR, respectively. For example, in the pure liquid at  $30^\circ\text{C}$ ,  $D_\perp = 1.35 \times 10^{11}$  and  $D_\parallel = 14.8 \times 10^{11} \text{ s}^{-1}$  correspond to  $\tau_{2R}(\perp) = 1.23$  and  $\tau_{2R}(\parallel) = 0.113$  ps, respectively.

## IV. RESULTS

In order to elucidate how the solute–solute and the solute–solvent interactions affect the rotational dynamics of acetonitrile, we have examined the dependence of the rotational diffusion coefficients for the tumbling and spinning motions on the concentration, solvent, and temperature. First, we study the concentration dependence. We will show the association of acetonitrile in apolar solvent and its effects on the tumbling and spinning motions, and determine the concentration at which the solution can be considered dilute. Second, we study the temperature and solvent dependencies of the rotational diffusion coefficients of the tumbling and spinning motions at infinite dilution. The correlations of the rotational diffusion coefficients with solvent viscosity and polarity are shown. We will show that the anisotropy ratio of the spinning to the tumbling diffusion coefficients is also dependent on solvent and temperature.

### A. Dipolar association

In order to see the solute–solute interaction effect on the rotational dynamics for acetonitrile, the concentration dependence of the rotational diffusion coefficients was measured in such apolar solvents as carbon tetrachloride and  $n$ -hexane, and in such polar solvents as acetone and water at  $30^\circ\text{C}$ . In the apolar solvent,  $n$ -hexane, Fig. 1 shows that the  $D_\perp$  exhibits strong nonlinear dependence on the concentration; it gets smaller as the concentration increases. This indicates

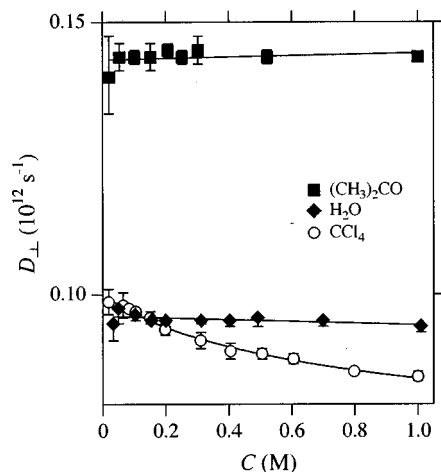


FIG. 2. Concentration dependence of the rotational diffusion coefficient ( $D_{\perp}$ ) of the tumbling motions of  $\text{CH}_3\text{CN}$  in apolar and polar solvents at  $30^\circ\text{C}$ .

that the tumbling motion is hindered by the dipolar association. This result is similar to the results of the solutions in alkanes and carbon tetrachloride by Tiffon and co-workers.<sup>20,21</sup> They have shown that the rotational diffusion coefficient of acetonitrile deviates from the prediction of the hydrodynamic model and have explained the deviation in terms of the association of acetonitrile in apolar solvents. For the spinning motion, on the other hand, the concentration dependence is negligible even in apolar solvents as shown in Fig. 1. This means that the association of dipolar acetonitrile molecules hardly hinder the spinning mode. This result supports that the structure of a dimer is antiparallel, which has been observed by means of computer simulations<sup>48–50</sup> and IR.<sup>7</sup>

In Fig. 2, the  $D_{\perp}$  values of acetonitrile in such an apolar solvent as carbon tetrachloride and in such polar solvents as water and acetone are plotted against concentration. In carbon tetrachloride, the  $D_{\perp}$  depends significantly on the concentration as in *n*-hexane. In polar solvents, on the other hand, no concentration dependence is observed. This means that in polar solvents, the dipolar interaction between the solute molecules is interfered by the solvent molecules which themselves have a large dipole moment. In this study, there is no evidence for the dimerization of acetonitrile in water, in disagreement with the RISM calculation.<sup>51</sup> IR studies show that acetonitrile generates a dimer in apolar solvents and that pivalonitrile [ $(\text{CH}_3)_3\text{CCN}$ ] with the bulky apolar group forms no dimers.<sup>7</sup> This result indicates that the driving force for the dimerization is short ranged and not hydrophobic but dipolar interactions. In polar solvents including water, acetonitrile molecules are solvated by the surrounding solvent molecules which have a large dipole moment and no dimerization of acetonitrile molecules occurs in the whole concentration range studied due to the competition between the solute–solute and solute–solvent interactions.

In the two-state model, the  $D_{\perp}$  value observed is the mean value of the monomer and the dimer states as described by

$$D_{\perp} = x_m D_{\perp}^m + x_d D_{\perp}^d, \quad (6)$$

TABLE I. Association constant  $K$  and rotational diffusion coefficients of the tumbling motions for the monomer ( $D_{\perp}^m$ ) and dimer ( $D_{\perp}^d$ ) states of acetonitrile in solutions at  $30^\circ\text{C}$ .

Solvent	$K$ ( $\text{mol}^{-1} \text{dm}^3$ )	$D_{\perp}^m$ ( $10^{11} \text{s}^{-1}$ )	$D_{\perp}^d$ ( $10^{11} \text{s}^{-1}$ )
$\text{CCl}_4$	$0.57 \pm 0.16$	$1.00 \pm 0.01$	$0.620 \pm 0.046$
$\text{C}_6\text{H}_{14}$	$1.41 \pm 0.29$	$2.37 \pm 0.02$	$1.03 \pm 0.11$

where

$$x_m = \frac{C_m}{C^0}, \quad x_d = \frac{2C_d}{C^0}, \quad C^0 = C_m + 2C_d.$$

Here  $x_m$  and  $x_d$  are the mole fractions of the acetonitrile molecule for the monomer and the dimer states, respectively, and  $C_m$ ,  $C_d$ , and  $C^0$  are the concentrations of the monomer, the dimer, and the total, respectively.  $D_{\perp}^m$  and  $D_{\perp}^d$  are the rotational diffusion coefficients of the tumbling motion for the monomer and the dimer, respectively. The equilibrium constant  $K$  defined as

$$K = \frac{C_d}{C_m^2}. \quad (7)$$

From Eqs. (6) and (7), the three parameters,  $K$ ,  $D_{\perp}^m$ , and  $D_{\perp}^d$ , are obtained by the least-squares method and their results at  $30^\circ\text{C}$  are listed in Table I. The association constant for the dipolar acetonitrile is twice as large in *n*-hexane as in carbon tetrachloride. The rotational diffusion coefficient for the tumbling motion of the dimer,  $D_{\perp}^d$ , is twice as large as that of the monomer,  $D_{\perp}^m$ , as expected from a hydrodynamic point of view: approximately, the solute volume of the dimer is twice as large as that of the monomer. Thus, the concentration dependence of the rotational diffusion coefficient for the tumbling motion is successfully explained in terms of the dipolar association.

Figures 1 and 2 show that the temperature and solvent effects on unassociated acetonitrile can therefore be studied at 50 mM in apolar solvents; at this concentration, the rotational diffusion coefficients of acetonitrile are considered equal to the monomer values, which are obtained at the dilution limit. In Sec. IV B we deal with the diffusion coefficient at infinite dilution.

## B. Temperature and solvent effects

The rotational diffusion coefficients for the tumbling and the spinning motions are determined in apolar and polar solvents including water over a wide range of temperatures. In Table II, the rotational diffusion coefficients for the tumbling  $D_{\perp}$  are summarized. The  $D_{\perp}$  value at  $30^\circ\text{C}$  is in the following sequence:

$$\begin{aligned} \text{C}_6\text{H}_{14}(2.28) > (\text{CH}_3)_2\text{CO}(1.37) > \text{CD}_3\text{CN}(1.35) \\ > \text{CCl}_4(0.985) > \text{H}_2\text{O}(0.930) > \text{CH}_3\text{OH}(0.872) \\ > \text{D}_2\text{O}(0.794), \end{aligned} \quad (8)$$

where the numbers in parentheses indicate the  $D_{\perp}$  values in  $10^{11} \text{s}^{-1}$ . According to the hydrodynamic model, the diffusion coefficient should be proportional to the inverse of the



TABLE II. Limiting rotational diffusion coefficients  $D_{\perp}$  for the tumbling motions of  $\text{CD}_3\text{CN}$  in pure liquid and solutions.<sup>a</sup>

$T$ (°C)	$D_{\perp}$ ( $10^{11}\text{s}^{-1}$ )						
	$\text{C}_6\text{H}_{14}$ (0.285) <sup>b</sup>	$(\text{CH}_3)_2\text{CO}$ (0.292) <sup>b</sup>	$\text{CD}_3\text{CN}$ (0.324) <sup>b</sup>	$\text{CH}_3\text{OH}$ (0.508) <sup>b</sup>	$\text{H}_2\text{O}$ (0.797) <sup>b</sup>	$\text{CCl}_4$ (0.847) <sup>b</sup>	$\text{D}_2\text{O}$ (0.973) <sup>b</sup>
50	...	...	...	...	...	1.24	1.18
40	2.58	...	...	...	...	1.09	0.981
30	2.28	1.37	1.35 <sup>c</sup>	0.872	0.930 <sup>d</sup>	0.985 <sup>e</sup>	0.794
20	2.06	1.24	1.22	0.767	0.727 <sup>d</sup>	0.855	0.614
10	1.86	1.11	1.09	0.665	0.563	0.784	0.452
0	...	0.995	0.974	0.574	0.407	...	0.311
-10	...	0.862	0.856	0.476	...	...	...
-20	...	0.754	0.742	0.411	...	...	...
-30	...	...	0.634	...	...	...	...
-40	...	...	0.532	...	...	...	...

<sup>a</sup>Uncertainty is within  $\pm 2\%$  for  $\text{C}_6\text{H}_{14}$  and  $\text{CCl}_4$ , and  $\pm 1\%$  for the others.

<sup>b</sup>Solvent viscosity in centipoise at 30 °C; from Ref. 61.

<sup>c</sup>This value is comparable with  $1.27 \times 10^{11} \text{ s}^{-1}$  at 23 °C in Ref. 25, and slightly smaller than 1.35 and  $1.40 \times 10^{11} \text{ s}^{-1}$  at 25 °C in Refs. 17 and 18, respectively.

<sup>d</sup>These values are in good agreement with  $0.83 \times 10^{11} \text{ s}^{-1}$  at 25 °C in Ref. 22.

<sup>e</sup>This value is slightly larger than  $0.96 \times 10^{11} \text{ s}^{-1}$  at 39 °C in Ref. 25. This discrepancy would be due to the difference in the concentration: our concentration (50 mM) is one order of magnitude lower than that in Ref. 25. The concentration dependence of the  $D_{\perp}$  is large in apolar solvents due to the competition between the solute-solute and solute-solvent interactions as described in the text.

solvent viscosity  $\eta$ . Figure 3 shows the correlation diagram between the inverse viscosity  $1/\eta$  and the  $D_{\perp}$ . The solvent dependence of the  $D_{\perp}$  is similar to but not in accord with that expected from the hydrodynamic model. The effects of temperature and solvent on the diffusion coefficient are large as a result of drastic perturbation of the solvation shell by the dipolar reorientation.

The rotational diffusion coefficients for the spinning  $D_{\parallel}$  are listed in Table III. The  $D_{\parallel}$  value is an order of magnitude larger than the  $D_{\perp}$  in each solvent and its temperature dependence is smaller. This means that the friction for the spin-

ning motion is much smaller than that of the tumbling. The  $D_{\parallel}$  value at 30 °C is in the following sequence:

$$\text{CCl}_4(22.8) > \text{C}_6\text{H}_{14}(21.3) > \text{H}_2\text{O}(17.1) > \text{D}_2\text{O}(16.1) \\ > \text{CH}_3\text{OH}(15.5) > \text{CD}_3\text{CN}(14.8) > (\text{CH}_3)_2\text{CO}(12.7), \quad (9)$$

where the numbers in parentheses are rotational diffusion coefficients in  $10^{11} \text{ s}^{-1}$ . This sequence has no correlation with solvent viscosity as shown in Fig. 3 in contrast to that of the tumbling.

In order to estimate the solvent effect on the rotational diffusion coefficients, the Stokes-Einstein (SE) product  $T/D\eta$  is also calculated. The SE product represents the effective volume of the solute molecule according to the simple hydrodynamic model. In other words, the smaller the product, the smaller the effective volume. In this simple model, electrostatic solute-solvent interactions are neglected. In Fig. 4, the correlation diagram between the dielectric constant and the SE product is shown. Except for  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$ , the SE product has a good correlation with the dielectric constant. This may imply that the difference in the SE product reflects the difference in the polarity of the solvent. The smallness of the SE products in light and heavy water will be explained in terms of the dielectric friction model in Sec. V.

The rotational anisotropy ratio  $\alpha$  is defined by the ratio of the rotational diffusion coefficient of the spinning motion to that of the tumbling motion,

$$\alpha = \frac{D_{\parallel}}{D_{\perp}}. \quad (10)$$

When  $\alpha > 1$ , the tumbling motion is more prohibited than the spinning motion. In Fig. 5, the anisotropy ratio  $\alpha$  is plotted against temperature. The  $\alpha$  values are larger than 9 at all the

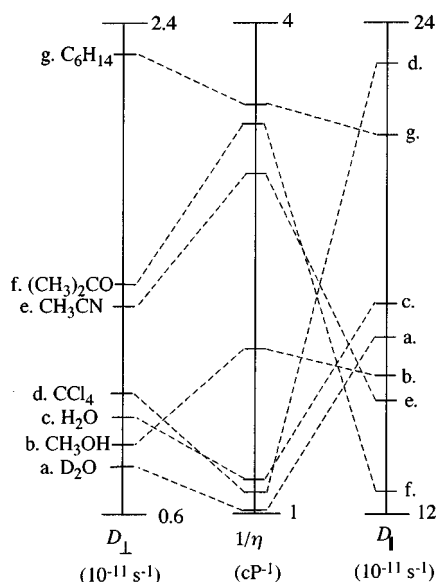


FIG. 3. Correlation diagram among the inverse solvent viscosity ( $1/\eta$ ) and the rotational diffusion coefficients of the tumbling ( $D_{\perp}$ ) and the spinning ( $D_{\parallel}$ ) motions of  $\text{CD}_3\text{CN}$  at 30 °C.

TABLE III. Limiting rotational diffusion coefficients  $D_{\parallel}$  for the spinning motions of  $\text{CD}_3\text{CN}$  in pure liquid and solutions.<sup>a</sup>

$T(^{\circ}\text{C})$	$D_{\parallel}(10^{11}\text{s}^{-1})$						
	$\text{C}_6\text{H}_{14}$ (0.285) <sup>b</sup>	$(\text{CH}_3)_2\text{CO}$ (0.292) <sup>b</sup>	$\text{CD}_3\text{CN}$ (0.324) <sup>b</sup>	$\text{CH}_3\text{OH}$ (0.508) <sup>b</sup>	$\text{H}_2\text{O}$ (0.797) <sup>b</sup>	$\text{CCl}_4$ (0.847) <sup>b</sup>	$\text{D}_2\text{O}$ (0.973) <sup>b</sup>
50	...	...	...	...	...	24.5	...
40	20.4	...	...	...	...	23.7	...
30	21.3	12.7	14.8 <sup>c</sup>	15.5	17.1	22.8 <sup>d</sup>	16.1
20	20.9	12.0	14.7	14.7	17.1	22.4	16.3
10	20.5	11.2	14.0	14.0	16.0	20.3	14.8
0	...	10.2	13.5	13.1	15.2	...	13.8
-10	...	9.83	12.8	12.8	...	...	...
-20	...	9.00	11.9	...	...	...	...
-30	...	...	11.4	...	...	...	...
-40	...	...	10.8	...	...	...	...

<sup>a</sup>Uncertainty is within  $\pm 1\%$ ,  $\pm 2\%$ ,  $\pm 3\%$ ,  $\pm 4\%$ ,  $\pm 4\%$ , and  $\pm 8\%$  for  $\text{CD}_3\text{CN}$ ,  $\text{H}_2\text{O}$ ,  $\text{CH}_3\text{OH}$ ,  $\text{C}_6\text{H}_{14}$ ,  $(\text{CH}_3)_2\text{CO}$ ,  $\text{CCl}_4$ , and  $\text{D}_2\text{O}$ , respectively.

<sup>b</sup>Solvent viscosity in centipoise at 30  $^{\circ}\text{C}$ ; from Ref. 61.

<sup>c</sup>This value is in good agreement with  $13.8$ ,  $12.7$ , and  $12.0 \times 10^{11} \text{ s}^{-1}$  at 25  $^{\circ}\text{C}$  in Refs. 18, 25, and 17, respectively.

<sup>d</sup>This value is in close agreement with  $21.1 \times 10^{11} \text{ s}^{-1}$  at 25  $^{\circ}\text{C}$  in Ref. 25.

conditions examined. The  $\alpha$  value is not constant and strongly dependent on the solvent. At 30  $^{\circ}\text{C}$ , the  $\alpha$  is in the following sequence:

$$\text{D}_2\text{O}(20.3) > \text{CCl}_4(19.7) > \text{H}_2\text{O}(18.4) > \text{CH}_3\text{OH}(17.8)$$

$$> \text{CD}_3\text{CN}(11.0) > (\text{CH}_3)_2\text{CO}(9.3) \approx \text{C}_6\text{H}_{14}(9.3), \quad (11)$$

where the numbers in parentheses are the  $\alpha$  values. This sequence is parallel to that of solvent viscosity, as seen from Fig. 3. The more immobile the solvent, the larger the anisotropy. This is also the case when the solvent viscosity is increased by lowering temperature. The  $\alpha$  value increases with decreasing temperature in each solvent. This implies that the anisotropy of the solvation shell is weaker at a higher temperature. In Fig. 5, solvents are separated into three groups

according to the temperature dependence of the  $\alpha$ . Acetone, acetonitrile, and  $n$ -hexane belong to the first group, in which the  $\alpha$  values and their temperature dependencies are small. Carbon tetrachloride and methanol form the second group, where the  $\alpha$  values and their temperature dependencies are large. Water and heavy water are the third group, for which the  $\alpha$  values are close to those in the second group whereas the temperature dependence is much larger than those in the second group. In particular, the  $\alpha$  in water has the largest temperature dependence.

## V. DISCUSSION

In order to elucidate the solute-solvent interaction effect on the tumbling and spinning motions, the solvent dependence of the activation energies is discussed. For the tumbling motion, we will examine the applicability of the dielectric friction theory based on the hydrodynamic continuum model. By comparing the rotational dynamics of acetonitrile

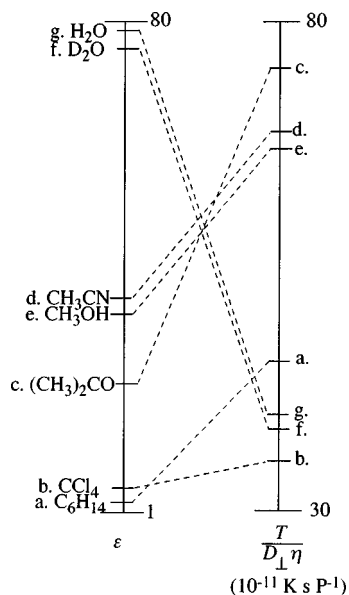


FIG. 4. Correlation diagram between the dielectric constant ( $\epsilon$ ) and the SE product ( $T/D_{\perp}\eta$ ) of the tumbling motion of  $\text{CD}_3\text{CN}$  at 30  $^{\circ}\text{C}$ .

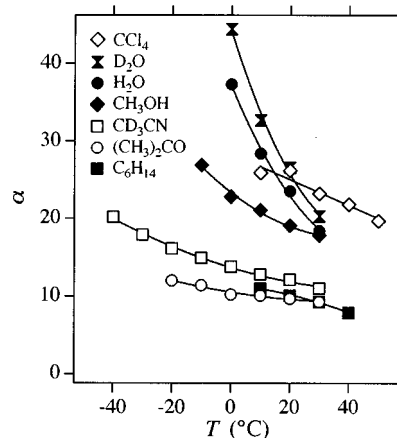


FIG. 5. Anisotropy ratio ( $\alpha$ ) of the rotational diffusion coefficients of the spinning to the tumbling motions of  $\text{CD}_3\text{CN}$  in pure liquid and in solutions as a function of temperature.

TABLE IV. Activation energy  $E_a$  of the diffusion coefficients for the tumbling and spinning motions of acetonitrile, for heavy water, and for benzene, together with the activation energy of the solvent viscosity.

Solvent	$E_a$ (kJ mol <sup>-1</sup> )				
	CD <sub>3</sub> CN (tumbling $D_{\perp}$ )	CD <sub>3</sub> CN (tumbling $D_{\parallel}$ )	D <sub>2</sub> O <sup>a</sup>	C <sub>6</sub> D <sub>6</sub> <sup>b</sup>	Viscosity <sup>c</sup>
C <sub>6</sub> H <sub>14</sub>	7.9±0.4	...	...	5.8	7.4
CCl <sub>4</sub>	8.8±0.5	3.3±0.5	8.6	7.5	10.3
C <sub>6</sub> H <sub>6</sub>	...	...	9.8	6.8	10.7
CHCl <sub>3</sub>	...	...	9.3	7.9	7.3
(CH <sub>3</sub> ) <sub>2</sub> CO	7.6±0.1	4.4±0.2	11	...	6.8
CH <sub>3</sub> OH	9.7±0.2	3.2±0.3	...	6.7	10.1
CD <sub>3</sub> CN	7.8±0.1	2.8±0.1	10 <sup>d</sup>	6.2 <sup>d</sup>	7.6 <sup>d</sup>
H <sub>2</sub> O	18.9±0.5	2.9±0.6	...	15.3	16.5
D <sub>2</sub> O	19.5±0.8	3.9±1.0	19	...	17.6

<sup>a</sup>Data from Ref. 1.<sup>b</sup>Calculated from data in Ref. 3.<sup>c</sup>Calculated from viscosity data at 20, 25, 30, 35, and 40 °C obtained from Ref. 61.<sup>d</sup>For the solvent CH<sub>3</sub>CN.

with that of the nitrate ion, water, and benzene, we will discuss the solute–solvent interaction effects in the short range. For the spinning motion, we will shed light on the solvation shell effect on the rotation.

## A. Molecular tumbling

### 1. Activation energy

To elucidate the solute–solvent interaction effect on the two rotational modes, activation energies  $E_a$  are calculated from the slopes of the Arrhenius plots for the tumbling and spinning diffusion coefficients as follows:

$$D_i = A \exp\left(-\frac{E_a(i)}{RT}\right), \quad (12)$$

where  $A$  is a pre-exponential factor and  $R$  is the gas constant. The  $E_a$  values are listed in Table IV. For the tumbling motion, the  $E_a$  values in organic solvents are 8–9 kJ mol<sup>-1</sup>. In light and heavy waters, the  $E_a$  values are ~19 kJ mol<sup>-1</sup> and two times larger than those in organic solvents. These large activation energies come from the large energy required to break the acetonitrile–water interaction and reorient water molecules in the solvation shell: The  $E_a$  of heavy water in pure liquid is 19 kJ mol<sup>-1</sup>. The activation energy of the solvent viscosity is also listed in Table IV. The  $E_a$  value of the tumbling motion is close to that of the solvent viscosity whereas the  $E_a$  of the spinning motion is much smaller and has no correlation with the activation energy of the solvent viscosity. This means that the  $E_a$  of the tumbling motion is affected not only by the solute–solvent interaction but also by the solvent–solvent interaction due to the exclusion of the solvent molecules.

The effect of the solute–solvent interaction is further appreciated by comparing the  $E_a$  of acetonitrile with the  $E_a$ 's of heavy water and benzene when they are used as solutes. In each solvent, the  $E_a$  is in the following sequence:

$$D_2O > CD_3CN(\perp) > C_6D_6 > CD_3CN(\parallel). \quad (13)$$

The solute–solvent interaction between the solute water and the solvent is mainly the hydrogen bond. This result indi-

cates that the hydrogen bond effect is stronger than the dipolar interaction effect. The dipolar interaction of acetonitrile is stronger than the interaction of such an apolar solute as benzene. For the spinning motion of acetonitrile, the rotational activation is easy because the methyl group is apolar and small.

### 2. Hydrodynamic effect

According to the Einstein relation, the rotational diffusion coefficient  $D_i$  is expressed by the rotational friction coefficient  $\zeta_i$  and the temperature  $T$  as follows:

$$\frac{1}{D_i} = \frac{\zeta_i}{k_B T}, \quad (14)$$

where the symbol  $i$  denotes the tumbling ( $\perp$ ) or the spinning ( $\parallel$ ) motion. In the hydrodynamic model, the solvent is regarded as a viscous continuum and the inverse of the rotational diffusion coefficient  $1/D_i$  is then proportional to solvent viscosity divided by temperature  $\eta/T$ . In order to compare the solvent effect on the rotational dynamics,  $\eta/T$  is used as a parameter to normalize the solvent viscous friction. When  $1/D_i$  is plotted against  $\eta/T$ , the slope reflects the solvent effect on the rotational diffusion coefficient at a fixed  $\eta/T$ . In Fig. 6,  $1/D_{\perp}$  are plotted against  $\eta/T$ . In polar solvents except for water, the plots are within 10% of each other and the slopes are ~1.5 times larger than those in apolar solvents and in water. While  $1/D_{\perp}$  is almost proportional to  $\eta/T$  in each solvent, the slope is different among solvents. The slope can be regarded as a measure of the solute–solvent interaction as in the cases of the solute water<sup>1</sup> and benzene.<sup>3</sup> It is approximately equal to the SE product and represents the effective volume of the solute which is modified by the solute–solvent interaction. The slopes  $S_{\perp}$  of the plot of  $1/D_{\perp}$  against  $\eta/T$  measured are listed in Table V. The slope is in the following sequence:

$$\begin{aligned} (CH_3)_2CO(59) > CD_3CN(49) > CH_3OH(46) > H_2O(36) \\ = D_2O(36) > C_6H_{14}(35) > CCl_4(24), \end{aligned} \quad (15)$$

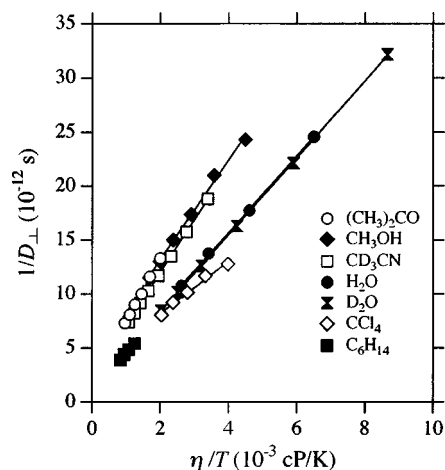


FIG. 6. Plots of the inverse rotational diffusion coefficient ( $1/D_{\perp}$ ) of the tumbling motion of  $\text{CD}_3\text{CN}$  in pure liquid and in solutions against solvent viscosity divided by temperature ( $\eta/T$ ).

where the numbers in parentheses are slopes in  $10^{-8} \text{ s K P}^{-1}$ . A frequently employed approach to correlate the sequence in Eq. (15) with the solvent property is the hydrodynamic model. Since we are concerned with the rotational anisotropy of acetonitrile, it is natural to employ the hydrodynamic model for an ellipsoid.

The rotational friction coefficients of an ellipsoid have been calculated by Perrin under the stick condition.<sup>46,52</sup> We have the rotational friction coefficients

$$\zeta_{\perp} = \frac{32\pi b^2(a^2 - b^2)}{6a - 3b^2s} \eta, \quad (16)$$

$$\zeta_{\parallel} = \frac{32\pi(a^4 - b^4)}{3(2a^2 - b^2)s - 6a} \eta, \quad (17)$$

where

$$s = \frac{2}{(a^2 - b^2)^{1/2}} \ln \left\{ \frac{a + (a^2 - b^2)^{1/2}}{b} \right\}, \quad a > b. \quad (18)$$

TABLE V. The slopes  $S_{\text{diel}}$  calculated from Eq. (22) in terms of the dielectric friction model, the observed slope  $S_{\perp}$ , and its difference  $\Delta S_{\perp}$  between a polar solvent (X) and the reference solvent ( $\text{CCl}_4$ ):  $\Delta S_{\perp} = S_{\perp}(\text{X}) - S_{\perp}(\text{CCl}_4)$ . The dielectric constants  $\epsilon$ , and the Debye dielectric relaxation times  $\tau_D$  are also listed.

Solvent	$\epsilon$	$\tau_D$ (ps)	$S_{\perp}$ ( $10^{-8} \text{ s K P}^{-1}$ )	$S_{\text{diel}}$ ( $10^{-8} \text{ s K P}^{-1}$ )	$\Delta S_{\perp}$ ( $10^{-8} \text{ s K P}^{-1}$ )
$\text{C}_6\text{H}_{14}$	1.9 <sup>a</sup>	...	35	0	11
$\text{CCl}_4$	2.2 <sup>a</sup>	...	24	...	...
$(\text{CH}_3)_2\text{CO}$	20.7 <sup>a</sup>	2.8 <sup>b</sup>	59	28	35
$\text{CH}_3\text{OH}$	31.9 <sup>b</sup>	1.1 <sup>c</sup>	46	4.3	22
		7.1 <sup>c</sup>		28	
		47.0 <sup>c</sup>		180	
$\text{CD}_3\text{CN}$	35.2 <sup>b</sup>	3.6 <sup>b</sup>	49	19	25
$\text{H}_2\text{O}$	76.8 <sup>b</sup>	7.2 <sup>b</sup>	36	7.8	12
$\text{D}_2\text{O}$	76.2 <sup>a</sup>	9.2 <sup>d</sup>	36	8.2	12
Hydrodynamic model <sup>e</sup>	...	...	290	...	...

<sup>a</sup>From Ref. 62.

<sup>b</sup>From Ref. 36.

<sup>c</sup>From Ref. 56.

<sup>d</sup>Interpolated from the data obtained from Ref. 63.

<sup>e</sup>The rotational friction coefficient of an ellipsoid under stick condition is calculated; from Eqs. (16), (18), and (19) according to Ref. 52.

Here,  $a$  and  $b$  are the lengths of the longer and shorter axes, respectively, and for acetonitrile,<sup>53</sup>

$$a = 0.291 \text{ nm}, \quad b = 0.224 \text{ nm}. \quad (19)$$

From Eqs. (16) to (19) we can obtain the slope of the plot of  $1/D_i$  against  $\eta/T$  for the tumbling and the spinning motions  $S_{\perp} = 290 \times 10^{-8}$ ,  $S_{\parallel} = 240 \times 10^{-8} \text{ s K P}^{-1}$ , respectively. The value to be employed here is  $S_{\perp} = 290 \times 10^{-8} \text{ s K P}^{-1}$ . This value is larger by an order of magnitude than the values in Eq. (15). Therefore, the tumbling motion is much less restricted than the value predicted by the hydrodynamic model in which the molecular structure is neglected.

### 3. Dielectric friction effect

In order to explain the solvent dependence of the slope of the plot of  $1/D_{\perp}$  against  $\eta/T$  in Fig. 6, we will examine the dielectric friction model. In polar solvents, the interaction between a dipole moment and its reaction field may make an excess contribution to the friction coefficient of the tumbling motion. This long-range effect is called the dielectric friction.<sup>35</sup> This effect on the rotational diffusion coefficient may be expressed as

$$\frac{1}{D} = \frac{1}{D_0} + S_{\text{hyd}} \frac{\eta}{T} + \frac{6\mu^2}{k_B T R^3} \frac{\epsilon_0 - 1}{(2\epsilon_0 + 1)^2} \tau_D. \quad (20)$$

Here,  $1/D_0$  is the intercept obtained by plotting  $1/D$  against  $\eta/T$ ,  $S_{\text{hyd}}$  is the slope due to the viscous friction of the solvent,  $\tau_D$  is Debye's dielectric relaxation time of solvent,  $\epsilon_0$  is the static dielectric constant of the solvent,  $R$  is the radius of the solute (0.291 nm used),  $\mu$  is the dipole moment of the solute. According to the temperature-variable measurements of the dielectric relaxation times of water<sup>54</sup> and methanol,<sup>55</sup>  $\tau_D$  is almost proportional to  $\eta/T$ . When  $\tau_D$  is assumed to be proportional to  $\eta/T$  in the temperature variation for a fixed solvent, Eq. (20) is rewritten as

$$\frac{1}{D} = \frac{1}{D_0} + (S_{\text{hyd}} + S_{\text{diel}}) \frac{\eta}{T}, \quad (21)$$



where

$$S_{\text{diel}} = \frac{6\mu^2}{k_B T_r R^3} \frac{\epsilon_0 - 1}{(2\epsilon_0 + 1)^2} \frac{\tau_D(T_r)}{\eta(T_r)} \cdot \quad (22)$$

The reference temperature  $T_r$  may be taken here as 30 °C. Using Eqs. (21) and (22) we have estimated the dielectric friction effect on the rotational diffusion coefficients; the results are shown in Table V. When we attribute the effect of the dielectric friction to the difference in the  $S_{\perp}$  between a polar solvent ( $X$ ) and carbon tetrachloride, the theoretical slope due to the dielectric friction,  $S_{\text{diel}}$ , is to be compared with the experimental value  $\Delta S_{\perp} = S_{\perp}(X) - S_{\perp}(\text{CCl}_4)$ . The value of  $\Delta S_{\perp}$  is in the following sequence:

$$(\text{CH}_3)_2\text{CO}(35) > \text{CD}_3\text{CN}(25) > \text{CH}_3\text{OH}(22) > \text{H}_2\text{O}(12), \quad (23)$$

where the numbers in parentheses are in  $10^{-8} \text{ s KP}^{-1}$ . The value of  $S_{\text{diel}}$  calculated by Eq. (22) is in the sequence,

$$(\text{CH}_3)_2\text{CO}(28) > \text{CD}_3\text{CN}(19) > \text{H}_2\text{O}(7.7), \quad (24)$$

where the numbers in parentheses are in  $10^{-8} \text{ s KP}^{-1}$ . Except for methanol, the calculated slope  $S_{\text{diel}}$  is comparable to the observed slope  $\Delta S_{\perp}$  for each solvent. For the case of methanol, it has been observed that there are three dielectric relaxation times, 1.1, 7.1, and 47.0 ps.<sup>56</sup> The solvent dynamics with a shorter time scale than the tumbling ( $\sim 2$  ps) is averaged out and the solvent dynamics with a sufficiently larger time scale can be regarded to be almost static or frozen. As in the case of the solvation dynamics,<sup>57</sup> we consider that only the solvent dynamics with the comparable time scale ( $\sim 1$  ps) is involved in the energy dissipation or the friction of our interest. The slope due to the dielectric friction model may be in the region from 4.3 to  $28 \times 10^{-8} \text{ s KP}^{-1}$  corresponding to the dielectric relaxation times of 1.1 and 7.1 ps. The  $S_{\text{diel}}$  thus calculated is comparable to the observed value as in the other solvents. This result indicates that the dielectric friction model is qualitatively valid for the tumbling motion of acetonitrile. In such an apolar solvent as *n*-hexane, however, the  $\Delta S_{\perp}$  value is  $11 \times 10^{-8} \text{ s KP}^{-1}$  and close to the  $\Delta S_{\perp}$  in water whereas the dielectric friction coefficient should be equal to zero. The difference in slope between *n*-hexane and carbon tetrachloride is not explained by the dielectric friction model. The solute–solvent interaction in the short range is also needed for the explanation of the solvation dependence of the slopes.

#### 4. Solute–solvent interaction in the short range

In order to investigate how the solute–solvent interactions affect the rotational dynamics of the solute, we compare the slopes of the rotational correlation times against  $\eta/T$  for acetonitrile with those of the nitrate ion, water, and benzene, which are a typical ion, a polar and hydrogen-bonding solute, and an apolar solute, respectively. The rotational correlation times for the pure tumbling motion of acetonitrile is calculated from Eq. (5). The slopes of the rotational correlation time against  $\eta/T$  are summarized in Table VI.

For such an ion as the nitrate ion, the slope in methanol is  $\sim 9$  times larger than those in acetonitrile and in water

TABLE VI. Slopes of the plots of the rotational correlation times against  $\eta/T$  for nitrate ion, acetonitrile, heavy water, and benzene in various solvents.

Solvent	Slopes ( $10^{-8} \text{ s KP}^{-1}$ )			
	$\text{NO}_3^-$ <sup>a</sup> (0.15–0.26) <sup>d</sup>	$\text{CD}_3\text{CN}$ (tumbling $D_{\perp}$ ) (0.22–0.29) <sup>d</sup>	$\text{D}_2\text{O}$ <sup>b</sup> (0.14) <sup>e</sup>	$\text{C}_6\text{D}_6$ <sup>c</sup> (0.17–0.36) <sup>d</sup>
$\text{C}_6\text{H}_{14}$	...	5.8	...	3.1
$\text{CCl}_4$	...	4.0	0.22	2.5
$\text{C}_6\text{H}_6$	...	...	1.1	3.4
$\text{CHCl}_3$	...	...	1.2	6.9
$(\text{CH}_3)_2\text{CO}$	...	9.8	12	...
$\text{CH}_3\text{OH}$	27	7.7	...	2.2
$\text{CD}_3\text{CN}$	3.3 <sup>f</sup>	8.1	6.5 <sup>f</sup>	4.7 <sup>f</sup>
$\text{H}_2\text{O}$	3.0	6.0	...	3.5
$\text{D}_2\text{O}$	...	6.0	6.5	...

<sup>a</sup>From Ref. 36 and unpublished data on the temperature effect.

<sup>b</sup>From Ref. 1

<sup>c</sup>From Ref. 3.

<sup>d</sup>The lengths of the shorter and the longer axes in nanometers.

<sup>e</sup>Commonly used radius in nanometers.

<sup>f</sup>In  $\text{CH}_3\text{CN}$ .

whereas for the solute acetonitrile the slopes are close to each other. In such alcohols as methanol, ethanol, and 1-propanol, the rotational correlation times of the nitrate ion are an order of magnitude larger than those in other polar solvents.<sup>36</sup> The slope of the nitrate ion in methanol is 3 times larger than that of acetonitrile though the size is smaller. These large solvent dependencies can be expressed in terms of the dielectric friction model when the largest dielectric relaxation time (cf. 47.0 ps for methanol) in the three relaxation times is used in contrast to the case of acetonitrile. This result implies that the time scale of the solvation dynamics which affects the rotational motion is larger for such an ion as the nitrate ion than for such a dipolar molecule as acetonitrile.

For the solute water, the difference in the slope among solvents is much larger than that of acetonitrile. For example, the ratio of the slope in acetone to that in carbon tetrachloride is  $\sim 50$  whereas the ratio for the solute acetonitrile is only 2.5. This large solvent dependence is not explained in terms of the dielectric friction model. It has been explained that the sequence of the slopes is strongly correlated with the strength of the hydrogen bonding between water and solvent molecules.<sup>1</sup> It is noted that the interaction between water (solute) and acetone (solvent) is very strong. This trend is also observed in the case of the solute acetonitrile, which is also an example of the solvent specificity.

For the solute benzene, which has no dipole moment, the slope is controlled not by the dipolar interaction but by other short-range solute–solvent interactions, van der Waals, and quadrupolar interactions. As seen in Table VI, the slope in methanol is smaller than that in carbon tetrachloride in contrast to the case of the dipolar solute acetonitrile. The slope in chloroform is the largest among the solvents studied. We have shown that the experimentally determined slope of benzene has a positive correlation with the solvation enthalpy, which reflects the strength of the solute–solvent interaction.<sup>3</sup> Even for such an apolar solute, the rotational dynamics is

controlled not by the solvent viscosity but by the short-range solute–solvent interaction.

## B. Spinning diffusion

### 1. Solute–solvent interaction

In the spinning motion, the direction of the dipole moment does not change. The problem is then to identify the factor to influence the spinning motion. In order to elucidate the solvent dependence of the rotational diffusion coefficients for the spinning, the activation energy  $E_a$  for the spinning is calculated from the Arrhenius plots of the  $D_{\parallel}$ . The observed  $E_a$  values are shown in Table IV. For the spinning motion, the  $E_a$  values are  $\sim 3$  kJ mol $^{-1}$  and much smaller than that for the tumbling motion. This result indicates that the spinning motion is not strongly affected by the solvent molecules. However, the methyl group cannot rotate freely because the  $E_a$  values are two or three times larger than that of a free rotor (1.3 kJ mol $^{-1}$ ). The methyl group reorients in the solute–solvent interaction potential. The  $E_a$  in water is close to those in other organic solvents in contrast to the tumbling motion. This indicates that the spinning motion does not exclude the solvent water molecules around a methyl group and that the solute–solvent interaction is not strong. On the other hand, the  $E_a$  in acetone is larger than that in water. The spinning motion is more hindered in acetone than in other organic solvents.

Here, the solute–solvent interaction effects on the spinning motion are elucidated from the solvent dependence of the  $D_{\parallel}$ . As seen in Eq. (9), the  $D_{\parallel}$  value is larger in water than in the other polar solvents in spite of the large difference in the solvent viscosity. In contrast to the case of the tumbling motion, this largeness cannot be explained in terms of the dielectric friction model because the spinning motion does not change the direction of the dipole moment. Such weak hindrance in the solvent water has been observed for the rotational mobility of the solute benzene.<sup>4</sup> The hydrophobic hydration shell around such a hydrophobic solute as benzene makes the friction weaker. It has also been reported that for such polar solutes as acetonitrile and methanol, the hydrophobic hydration shell is formed around the methyl groups.<sup>24,37</sup> Our result indicates that the rotational friction of the spinning motion is reduced by the hydrophobic hydration shell around the methyl group. In water, the rotational correlation time for the spinning of acetonitrile is 0.10 ps. It is comparable to the rotational correlation time of methane (0.12 ps) measured in water by Laaksonen and Stilbs.<sup>58</sup> This result also indicates that the rotational motion is less hindered when a cage is formed by more heavy solvent molecules.

We will compare the  $D_{\parallel}$  value in carbon tetrachloride with  $n$ -hexane. In carbon tetrachloride at 30 °C, the  $D_{\parallel}$  value is larger than that in  $n$ -hexane though the viscosity of carbon tetrachloride is  $\sim 3$  times larger than that of  $n$ -hexane as shown in Table III. Since a carbon tetrachloride molecule is a heavy and rather sphere molecule, the methyl group can reorient more freely in its solvation shell formed by heavy molecules because the collision frequency is smaller.

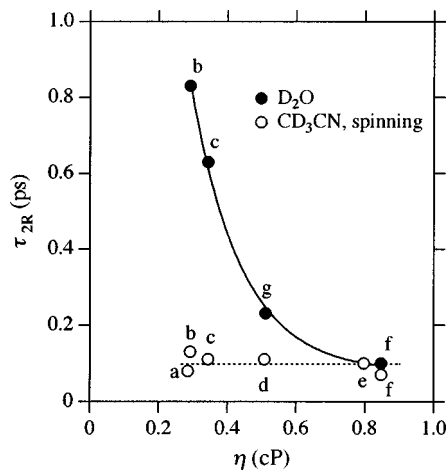


FIG. 7. Solvent dependence of the rotational correlation times ( $\tau_{2R}$ ) for  $D_2O$  and the spinning motion of  $CD_3CN$ . (a)  $C_6H_{14}$ ; (b)  $(CH_3)_2CO$ ; (c)  $CD_3CN$ ; (d)  $CH_3OH$ ; (e)  $H_2O$ ; (f)  $CCl_4$ ; (g)  $CHCl_3$ .

In contrast to water and carbon tetrachloride, the  $D_{\parallel}$  value in acetone is unexpectedly small and the friction coefficient is large. The large activation energy is also observed in acetone as seen in Table IV. A similar phenomenon has been observed in dimethyl sulfoxide by Yuan and Schwartz.<sup>25</sup> They measured the rotational diffusion coefficients of the tumbling and the spinning motions of acetonitrile- $d_3$  in pure liquid, carbon tetrachloride, dimethyl sulfoxide, and butanol. The sequence of the  $D_{\perp}$  value is

$$CD_3CN(1.27) > CCl_4(0.710) > (CH_3)_2SO(0.359) > C_4H_9OH(0.240), \quad (25)$$

where the numbers in parentheses are the  $D_{\perp}$  values in  $10^{11} s^{-1}$ . This sequence is the same as the sequence of viscosity increasing. The tumbling motion is controlled mainly by the solvent viscosity due to the hydrodynamic friction coefficient. For the spinning motion, on the other hand, the sequence of the  $D_{\parallel}$  value has no correlation with that of the solvent viscosity in the following:

$$CCl_4(21.1) > C_4H_9OH(13.8) > CD_3CN(12.7) > (CH_3)_2SO(7.3), \quad (26)$$

where the numbers in parentheses are the  $D_{\parallel}$  values in  $10^{11} s^{-1}$ . This trend is just the same as our observation. In acetone and dimethyl sulfoxide, the spinning motion of methyl group of acetonitrile is strongly hindered by such polar groups as CO and SO or by methyl groups in solvent molecules but the details of the solvation shell structure are not known yet.

### 2. Comparison of acetonitrile spinning and water rotation

Both solutes, water and methyl group, have very small moments of inertia; the moments of inertia are 3.8 and  $10.9 \times 10^{-47}$  kg m $^{-2}$  for  $D_2O$ <sup>59,60</sup> and  $CD_3$  group,<sup>30</sup> respectively. In Fig. 7, the  $\tau_{2R}$  values for these small atomic groups at 30 °C are plotted against solvent viscosity. For the methyl group in acetonitrile, the  $\tau_{2R}$  is very small ( $\sim 0.1$  ps) and

almost independent of the solvent viscosity. This means that the spinning motion is almost insensitive to the nature of solvent shell. For the solute water, on the other hand, the  $\tau_{2R}$  steeply decreases with increasing viscosity in contrast to the hydrodynamic prediction. The solvents we used for the study of the rotational dynamics of water are acetone, acetonitrile, chloroform, and carbon tetrachloride. The sequence of the  $\tau_{2R}$  value can be explained simply in terms of weakened or broken hydrogen bonds between the solute and solvent. Concerning the activation energy, a similar solvent dependence is observed. As shown in Table IV, the activation energy  $E_a$  for the solute water is larger than that for the spinning motion of acetonitrile in each solvent by a factor of more than 2. The  $E_a$  value for the solute water increases with increasing hydrogen-bonding ability of the solvent, whereas the  $E_a$  value for the spinning motion of acetonitrile has no correlation with the polarity of the solvent. These results indicate that the solute–solvent interaction is stronger for the solute water than for the solute methyl group. We should note the following difference: the C–H bond is almost nonpolar, whereas the O–H bond is strongly polar and can form a hydrogen bond. For such small solutes as methyl group and water, reorientational motion depends not on the solvent viscosity but on the solute–solvent interactions in the short-range.

### C. Anisotropy

In this section, we will compare the observed rotational anisotropy ratio  $\alpha$  with the predicted values calculated by the free rotation model and the hydrodynamic model. The  $\alpha$  is defined by Eq. (10) and is equal to the ratio of the rotational correlation times  $\tau_{2R}$  for the tumbling motion to that for the spinning.

For an isolated molecule in dilute gas, the rotational correlation time  $\tau_{FR}(i)$  for  $l=2$  is calculated from the moment of inertia  $I_i$  and the temperature  $T$ ,<sup>46</sup>

$$\tau_{FR}(i) = \frac{\pi}{2\sqrt{3}} \sqrt{\frac{I_i}{k_B T}}, \quad (27)$$

where  $i$  denotes the tumbling and the spinning motions and  $k_B$  is the Boltzmann constant. The moments of inertia of the tumbling and spinning modes for CD<sub>3</sub>CN are 106.8 and  $91.2 \times 10^{-47}$  kg m<sup>2</sup>, respectively, and the  $\alpha$  predicted from Eq. (27) is  $\sim 3.3$ , in disagreement with the experimental value  $\sim 9$ . This large discrepancy indicates that the tumbling motion is damped more strongly than the spinning motion due to the interaction with the surrounding molecules.

According to the hydrodynamic model, the rotational correlation time is proportional to the rotational friction coefficient. In this case, as calculated from Eqs. (16) to (19), the ratio of the friction coefficients of the tumbling to the spinning motions is about 1.2. Even if the dielectric friction coefficient is considered, the effect is no more than a factor of 2.5. This shows that the hydrodynamic model predicts almost isotropic rotation, in clear disagreement with our observation.

These two models cannot explain the large rotational anisotropy ratio observed in this study. They cannot explain

the temperature dependence of the  $\alpha$  values, either, because the ratio calculated from these two models is independent of the temperature. The tumbling motion is strongly restricted by the solvent molecules due to the dipolar interaction, so that the anisotropy ratio is much larger than those predicted by the simple models which neglect the details of short-range interactions.

### VI. CONCLUSIONS

We have measured the spin–lattice relaxation times for <sup>2</sup>H and <sup>14</sup>N in CD<sub>3</sub>CN in various organic solvents and calculated two modes of rotational diffusion coefficients; one is for the spinning and the other is for the tumbling. The rotational diffusion coefficients are obtained at various concentrations, temperatures, and solvents.

In order to elucidate the solvent effects on the two rotational motions, we used such polar solvents as acetone, acetonitrile, methanol, water, and heavy water and such apolar solvents as carbon tetrachloride and hexane. In each solvent, the rotational diffusion coefficient of the tumbling motion is an order of magnitude smaller than that of the spinning. The rotational anisotropy ratio is more than 9. This large anisotropy cannot be explained either by the free rotor model or by the hydrodynamic model. The activation energy of the spinning motion is  $\sim 3$  times smaller than that of the tumbling motion.

For the tumbling motion, the solvent dependence is discussed in terms of the slopes of the inverse rotational diffusion coefficient  $1/D_{\perp}$  against solvent viscosity divided by temperature  $\eta/T$ : the slope is approximately equal to the SE product and represents the effective volume of the solute which is modified by the solute–solvent interaction. The slopes in polar solvents are twice as large as that in such an apolar solvent as carbon tetrachloride. The difference in the slope is qualitatively explained in terms of the dielectric friction model based on the hydrodynamic continuum model. The slope for acetonitrile is compared with those for such an ion as the nitrate ion, such a hydrogen bonding molecule as water, and such an apolar molecule as benzene. The dielectric friction effect of the nitrate ion in methanol is much larger than that of the dipolar and neutral molecule acetonitrile. The hydrogen-bonding effect on the rotational motion is larger than the dipolar interaction. The apolar solute benzene has a different solvent dependence. The solvent effect is strongly dependent on the type of solute–solvent interactions.

For the spinning motion, the large diffusion coefficient in water is explained by the hydrophobic hydration shell around the methyl group. In such apolar and heavy solvent as carbon tetrachloride, a large diffusion coefficient is observed too. These two results indicate that a molecule in the solvation shell which is formed by heavy molecules or is relatively rigid can reorient with a weak friction.

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