

## Research Article

# Comparison of the Molecular Dynamics of C<sub>70</sub> in the Solid and Liquid Phases

R. M. Hughes,<sup>1</sup> P. Mutzenhardt,<sup>2</sup> and A. A. Rodriguez<sup>3</sup>

<sup>1</sup>Department of Biochemistry, NanaLine Duke Building, Duke University Medical Center, Durham, NC 27710, USA

<sup>2</sup>Laboratoire de Méthodologies RMN (UMR 7565 CNRS), Faculté des Sciences et Techniques, Université H. Poincaré, Boulevard des Aigillettes, BP 239, 54506 Vandoeuvre-lès-Nancy Cedex, France

<sup>3</sup>Department of Chemistry, East Carolina University, Greenville, NC 27858, USA

Correspondence should be addressed to A. A. Rodriguez, rodriguez@ecu.edu

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A previous study of C<sub>70</sub> in deuterated benzenes generated evidence suggesting C<sub>70</sub> exhibited unique reorientational behavior depending on its environment. We present a comparison of the dynamic behavior of this fullerene, in the solid and solution phases, to explore any unique features between these two phases. The effective correlation times,  $\tau_C^{\text{eff}}$ , of C<sub>70</sub> in the solid state are 2 to 3 times longer than in solution. In the solid state, a noticeable decrease in all the carbons' correlation times is seen between 293 K to 303 K; suggesting a transition from isotropic to anisotropic reorientational behavior at this temperature change. Although C<sub>70</sub> in solution experiences van der Waals type interactions, these interactions are not strong enough to slow the solution-state motion below what is observed in the solid state. All observed differences in the diffusion constants,  $D_X$  and  $D_Z$ , in solution are smaller than in the solid state suggesting a lower energy of activation between these two modes of reorientation in the liquid phase. A small-step diffusion "like" condition appears to be thermally generated in the solid phase at 323 K.

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## 1. Introduction

Molecular reorientational dynamics are sensitive to several factors including temperature, pressure, free volumes, solute-solvent interactions, and, henceforth, are commonly employed to probe a solute's rotational energetics or the effects of the immediate environment on the rotational motion. While fullerene C<sub>60</sub>'s molecular dynamics have been studied extensively, its close family member C<sub>70</sub> has received limited attention [1–10]. Early solid-state NMR measurements indicated that C<sub>70</sub>'s reorientational motion was anisotropic near room temperature [9]. Later differential scanning calorimetry measurements on solid C<sub>70</sub> indicated that C<sub>70</sub>'s dynamic behavior dependent on the thermally stable solid-phase structure (e.g., fcc, rhombohedral, or monoclinic phase) at a given temperature while zero-field measurements suggested C<sub>70</sub> molecules rotated isotropically [11]. In a later study, Tycko and coworkers found that solid C<sub>70</sub> molecules reorientational motion was anisotropic between 223–330 K (monoclinic and rhombohedral phases)

but became isotropic at temperatures beyond 330 K (face-centered phase) [10]. In terms of molecular dynamics in solution, our recent investigation into the molecular dynamics of C<sub>70</sub> in several deuterated benzenes revealed evidence suggesting C<sub>70</sub>'s reorientational motion oscillated between anisotropic and isotropic behavior depending on the solvent and the temperature [12]. In order to explore any unique features of the dynamic behavior of C<sub>70</sub> in the solid and liquid phase, we present a comparison of our solution measurements to values obtained in the solid state [10].

## 2. Theoretical Background

**2.1. <sup>13</sup>C Spin-Lattice Relaxation.** <sup>13</sup>C spin-lattice relaxation in fullerenes, both in the solid and liquid-phase, is known to be dominated by the chemical shift anisotropy,  $R_1^{\text{CSA}}$  (CSA). The spin-rotation mechanism,  $R_1^{\text{SR}}$  (SR), may also contribute in the liquid phase if the temperature is above 320 K [13–16].

Therefore, the overall  $^{13}\text{C}$  spin-lattice relaxation rate in  $\text{C}_{70}$  can be expressed as sum of these two mechanisms [17]:

$$R_1 = \frac{1}{T_1} = R_1^{\text{CSA}} + R_1^{\text{SR}}. \quad (1)$$

While it is possible for the spin-rotation mechanism to be present in the solid state, (1) can be reduced to  $R_1 = R_1^{\text{CSA}}$  at high magnetic fields and at moderate temperatures. Under extreme narrowing arguments, and assuming axial symmetry of the chemical shift tensor (CST), the CSA relaxation process is described by [18]

$$R_1^{\text{CSA}} = \left(\frac{2}{15}\right) \gamma_C^2 B_0^2 \Delta\sigma^2 \tau_C^{\text{eff}}, \quad (2)$$

where  $\gamma_C$  is the carbon magnetogyric ratio,  $B_0$  represents the field strength,  $\Delta\sigma$  is the CSA, and  $\tau_C^{\text{eff}}$  is the effective reorientational correlation time. The CSA is obtained from the three principal components (i.e.,  $\sigma_{zz} \geq \sigma_{yy} \geq \sigma_{xx}$ ) of the CST as defined by (3):

$$\Delta\sigma = \sigma_{zz} - 0.5(\sigma_{xx} + \sigma_{yy}). \quad (3)$$

Although solid-state NMR measurements can allow the determination of  $\Delta\sigma$ , the approach can be experimentally challenging and is primarily limited to chemical systems with high symmetry. In fact, Tycko and coworkers experienced these challenges when attempting to evaluate the CST for the carbons in  $\text{C}_{70}$  [10]. The relative high noise in their measurements only allowed for an average value of 200 ppm to be determined for each of the carbons in  $\text{C}_{70}$ . Alternatively,  $\Delta\sigma$  can be computed with a high degree of accuracy using standard computational methods [19–26]. The  $\Delta\sigma$  values used in this work were calculated using a Gaussian software package [27], employing the B3LYP exchange-correlation energy density functional, the 6-31G\* basis set [28, 29] and employing the gauge-independent atomic orbital (GIAO) method [30–33]. The calculated  $\Delta\sigma$  values are given in Table 1. It is worth noting the similarity of  $\Delta\sigma$  in  $\text{C}_{70}$  to the value in  $\text{C}_{60}$  (178 ppm) [15], suggesting that anisotropies in fullerenes fall within this range. Substitution of (2) into (1) gives

$$R_1 = \left(\frac{2}{15}\right) \gamma_C^2 B_0^2 (\Delta\sigma)^2 \tau_C^{\text{eff}} + R_1^{\text{SR}}. \quad (4)$$

In the liquid state, a fit of the overall relaxation rate against two or more field strengths ( $B_0^2$ ) allows the separation of the CSA from the SR contribution which then leads to the determination of  $\tau_C^{\text{eff}}$ .

**2.2. Reorientational Dynamics.** Reorientation dynamics in liquids is described by either diffusion constants,  $D_i$ , or reorientational correlation times,  $\tau_C$ , since these two parameters are closely correlated.  $D_i$  is the diffusion rate about a given molecular axis while  $\tau_C$  is the time period required for the angular correlation function to decay to  $1/e$  of its initial value [34, 35]. For symmetric-top molecules, such as  $\text{C}_{70}$ , two diffusion constants,  $D_Z$  and  $D_X$ , are usually required to characterize the overall motion.  $D_Z$

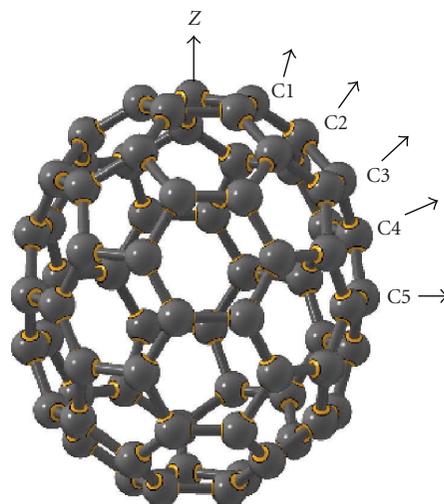


FIGURE 1: Carbon assignments in  $\text{C}_{70}$ . Carbon 1 (151 ppm), carbon 2 (146.5 ppm), carbon 3 (147.5 ppm), carbon 4 (145.5 ppm), and carbon 5 (131 ppm). The approximate carbon CSA tensor orientations ( $\theta$ ), relative to the molecular symmetry axis, are indicated by the various arrows.

and  $D_X$  represent rotational diffusion about and of the top axis, respectively. The overall motion is now characterized by an effective reorientational correlation time,  $\tau_C^{\text{eff}}$ , that, in the limit of small-step diffusion, is given by [36]

$$\tau_C^{\text{eff}} = \frac{0.25(3 \cos^2\theta - 1)^2}{6D_X} + \frac{3 \sin^2\theta \cos^2\theta}{5D_X + D_Z} + \frac{0.75 \sin^4\theta}{2D_X + 4D_Z}. \quad (5)$$

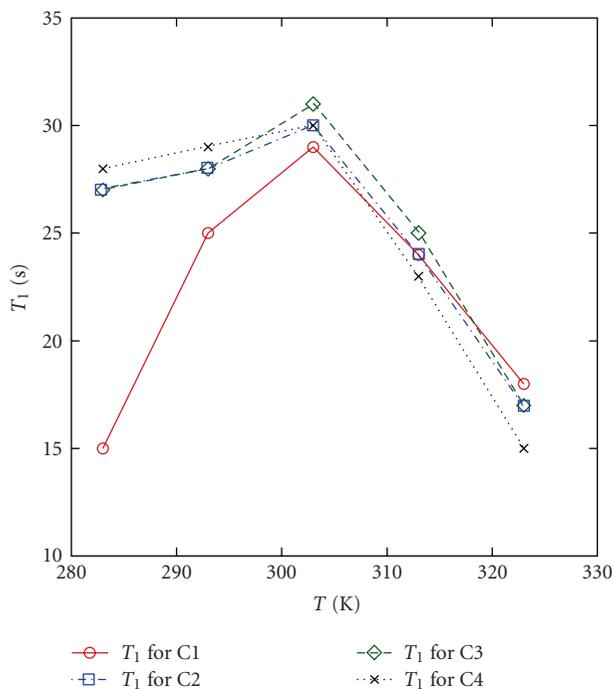
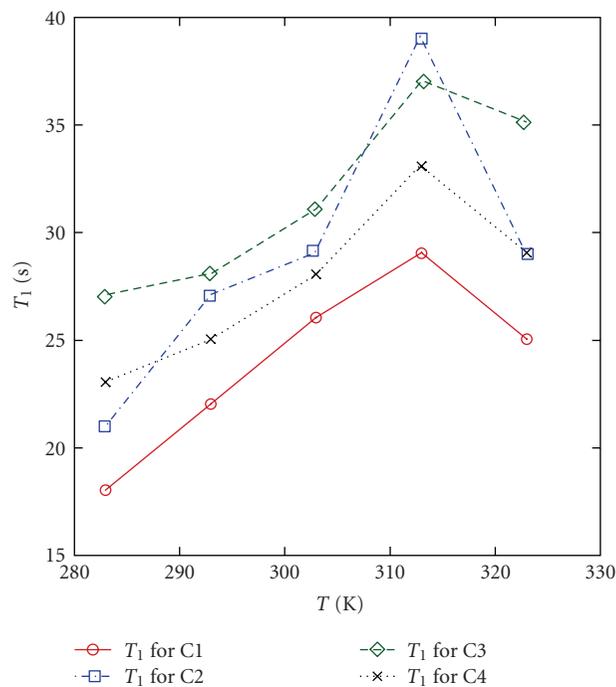
For CSA relaxation,  $\theta$  is the orientation of the CST tensor relative to the molecular symmetry axis. In principle it is possible to determine  $D_Z$  and  $D_X$  for a symmetric-top molecule provided  $\tau_C^{\text{eff}}$  and  $\theta$  values are known for different nuclei in the molecule. We employed the solution and solid-state experimental correlation times, along with the Gaussian generated  $\theta$  values, in (5) to simultaneously solve an equation for each carbon and obtained the best-fit values for  $D_Z$  and  $D_X$  at each temperature. While (5) assumes a small-step diffusion process, one can employ this equation to characterize reorientational motion outside this limit provided the calculated values are viewed as rough or base-line estimates of the diffusion process.

### 3. Experimental Methods

Benzene- $d_6$ , chlorobenzene- $d_5$ , o-dichlorobenzene- $d_4$ , and  $\text{C}_{70}$  were purchased from the Aldrich Chemical Company, USA, and were used as received. Solution and solid-state  $^{13}\text{C}$  NMR spectra of  $\text{C}_{70}$  showed the 5 unique carbon resonances at approximately 151 ppm, 147 ppm, 148 ppm, 146 ppm, and 131 ppm. These carbon resonances correspond to the carbons labeled in Figure 1.

TABLE 1: Average values for the calculated tensor components, chemical shift anisotropies, and the chemical shift tensor (CST) orientation of carbons in  $C_{70}$ .

Carbon	$\sigma_{xx}$ (ppm)	$\sigma_{yy}$ (ppm)	$\sigma_{zz}$ (ppm)	$\Delta\sigma$ (ppm)	$\theta$ (degrees)
1	-33.56	-0.97	162.06	179.32	13.94
2	-24.35	0.04	164.65	176.81	51.99
3	-32.24	3.04	165.95	180.55	62.15
4	-22.30	-2.62	167.19	179.65	72.88
5	-8.62	11.56	181.77	180.30	90.00

FIGURE 2:  $^{13}\text{C}$  relaxation times for  $C_{70}$  carbons at various temperatures in benzene- $d_6$ .FIGURE 3:  $^{13}\text{C}$  relaxation times of  $C_{70}$  carbons at various temperatures in chlorobenzene- $d_5$ .

In solution, resonances for carbons 1–4 were only used for the analysis since slight solvent peak interference and weak peak intensity of the carbon 5 in chlorobenzene- $d_5$  prohibited the inclusion of this peak across all solvents. Optimum room temperature concentrations of  $C_{70}$  in the solvents were calculated from published data [37]. To eliminate the potential for  $C_{70}$  clustering, solutions were prepared with a very low mole fraction of  $1.0 \times 10^{-4}$ . Samples were contained in 5 mm tubes, connected to a vacuum line and thoroughly degassed by several freeze-pump-thaw cycles to remove molecular oxygen. The tubes were then sealed under vacuum.

Solution  $^{13}\text{C}$  spin-lattice relaxation measurements were performed on instruments operating at 11.75 and 7.05 Tesla. Experiments were conducted at five different temperatures (283 K, 293 K, 303 K, 313 K, and 323 K). Temperature accuracy for these measurements is  $\pm 0.1$  K. Relaxation times were obtained using the standard inversion-recovery pulse sequence as described in our earlier work [1–5]. Relaxation

TABLE 2: Experimental  $^{13}\text{C}$  relaxation times for the different carbons at various temperatures for  $C_{70}$  in benzene- $d_6$ . (Relaxation times measured at 11.7 Tesla.)

$T$ (K)	Carbon 1	Carbon 2	Carbon 3	Carbon 4
	$T_1$ (s)	$T_1$ (s)	$T_1$ (s)	$T_1$ (s)
283	15	27	27	28
293	25	28	28	29
303	29	30	31	30
313	24	24	25	23
323	18	17	17	15

times in the various solvents are shown in Tables 2, 3, and 4.

Solid-state relaxation times were obtained from the work of Tycko and coworkers and their temperature-dependent

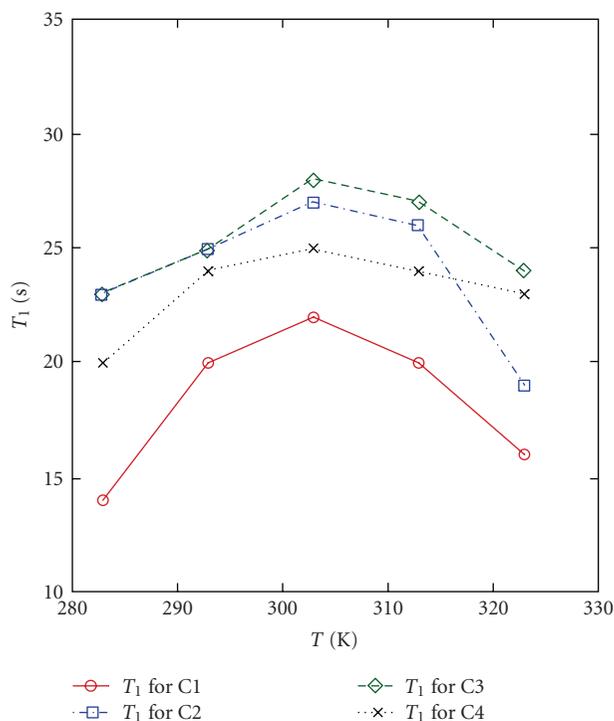


FIGURE 4:  $^{13}\text{C}$  relaxation times of  $\text{C}_{70}$  carbons at various temperatures in dichlorobenzene- $d_4$ .

TABLE 3: Experimental  $^{13}\text{C}$  relaxation times for the different carbons at various temperatures for  $\text{C}_{70}$  in chlorobenzene- $d_5$ . (Relaxation times measured at 11.7 Tesla.)

	Carbon 1	Carbon 2	Carbon 3	Carbon 4
$T$	$T_1$	$T_1$	$T_1$	$T_1$
(K)	(s)	(s)	(s)	(s)
283	18	21	27	23
293	22	27	28	25
303	26	29	31	28
313	29	39	37	33
323	25	29	35	29

TABLE 4: Experimental  $^{13}\text{C}$  relaxation times for the different carbons at various temperatures for  $\text{C}_{70}$  in o-dichlorobenzene- $d_4$ . (Relaxation times measured at 11.7 Tesla.)

	Carbon 1	Carbon 2	Carbon 3	Carbon 4
$T$	$T_1$	$T_1$	$T_1$	$T_1$
(K)	(s)	(s)	(s)	(s)
283	14	23	23	20
293	20	25	25	24
303	22	27	28	25
313	20	26	27	24
323	16	19	24	23

data, ranging from 223 to 342, was interpolated to the corresponding solution phase temperatures to permit the comparisons [10]. These relaxation times are given in Table 5.

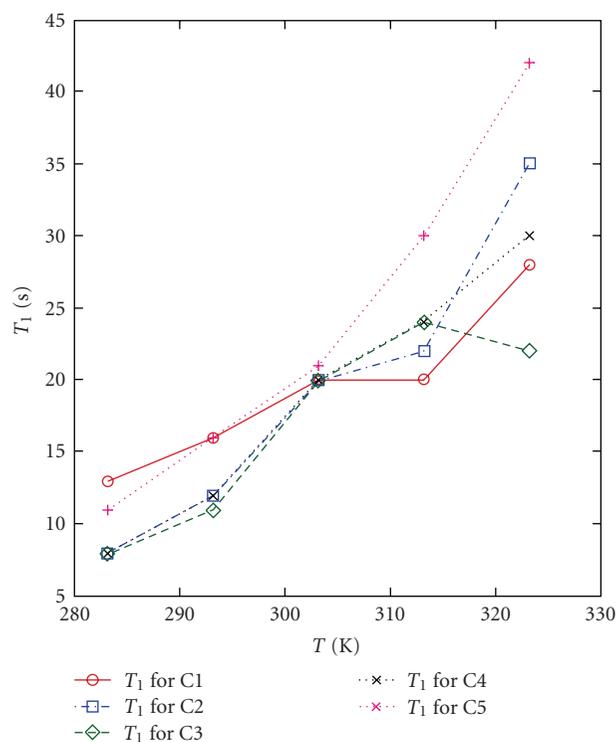


FIGURE 5: Relaxation times of carbons in  $\text{C}_{70}$  in the solid state.

TABLE 5: Experimental  $^{13}\text{C}$  relaxation times for the different carbons at various temperatures for  $\text{C}_{70}$  in the solid state. (Values interpolated from [10].)

	Carbon 1	Carbon 2	Carbon 3	Carbon 4	Carbon 5
$T$	$T_1$	$T_1$	$T_1$	$T_1$	$T_1$
(K)	(s)	(s)	(s)	(s)	(s)
283	13	8	8	8	11
293	16	12	11	12	16
303	20	20	20	20	29
313	20	22	24	24	30
323	28	35	22	30	42

## 4. Discussion

The temperature behavior of the relaxation times of  $\text{C}_{70}$  in benzene- $d_6$ , chlorobenzene- $d_5$ , o-dichlorobenzene- $d_4$  and in the solid-state are illustrated in Figures 2, 3, 4, and 5; respectively. Tables 6, 7, 8, and 9 contain the reorientational correlation times of the various carbons, as well as the calculated diffusion coefficients, of  $\text{C}_{70}$  in the solid state, in benzene, chlorobenzene, and 1,2-dichlorobenzene, respectively.

The reorientational times for all carbons, both in the solid and in solution, are seen to systemically decrease with rising temperature indicating more rapid reorientational motion with escalating temperature. Unlike in  $\text{C}_{60}$ , where faster rapid rotational motion is observed in the solid state than in solution, the  $\tau_C^{\text{eff}}$  values of  $\text{C}_{70}$  in the solid state are found to be from 2 to 3 times longer than in solution [14].

TABLE 6: Experimental correlation times and predicted rotational diffusion constants for the different carbons at various temperatures for  $C_{70}$  in the solid state.

$T$ (K)	Carbon 1	Carbon 2	Carbon 3	Carbon 4	Carbon 5	$D_X \times 10^{-9}$ (1/s)	$D_Z \times 10^{-9}$ (1/s)
	$\tau_C^{\text{eff}}$ (ps)	$\tau_C^{\text{eff}}$ (ps)	$\tau_C^{\text{eff}}$ (ps)	$\tau_C^{\text{eff}}$ (ps)	$\tau_C^{\text{eff}}$ (ps)		
283	45	75	72	73	52	2.2	2.5
293	37	52	50	51	36	3.4	3.6
303	29	30	29	29	20	5.4	7.5
313	29	27	24	24	19	5.5	9.9
323	20	17	26	19	13	8.0	10.5

TABLE 7: Experimental correlation times and predicted rotational diffusion constants for the different carbons at various temperatures for  $C_{70}$  in benzene- $d_6$ .

$T$ (K)	Carbon 1	Carbon 2	Carbon 3	Carbon 4	$D_X \times 10^{-10}$ (1/s)	$D_Z \times 10^{-10}$ (1/s)
	$\tau_C^{\text{eff}}$ (ps)	$\tau_C^{\text{eff}}$ (ps)	$\tau_C^{\text{eff}}$ (ps)	$\tau_C^{\text{eff}}$ (ps)		
283	25	14	13	13	0.6	2.9
293	14	12	12	12	1.2	1.7
303	11	11	10	10	1.5	1.9
313	8	8	7	7	2.0	2.7
323	7	7	5	6	2.4	3.5

The slower rotational dynamics in solid  $C_{70}$ , as compared to solid  $C_{60}$ , can be attributed to differences in the orientational ordering of their lattice structures. Also of interest in the solid state is the noticeable decrease in all the carbons' correlation times in going from 293 K to 303 K. Noting the closeness of the two diffusion constants,  $D_X$  and  $D_Z$ , at the two lowest temperatures, which is indicative of a quasi-isotropic reorientation condition, the observed drastic drop in all the  $\tau_C^{\text{eff}}$  values suggest a definite transition from isotropic to anisotropic reorientational behavior at this temperature change. The enhanced difference between the two diffusion coefficients as temperature rises is particularly interesting since this correlates to the phase transition occurring from rhombohedral to face-centered cubic suggesting an increase in molecular disorder. We must however be cautious in overly interpreting this observation since diffusion values were calculated via (5) which assumes small-step diffusion and, as indicated by Tyco and coworkers, molecular reorientation in this phase is attributed to "thermally activated" orientational jumps rather than to step-wise diffusion. Nonetheless, the calculated diffusion values, and their differences, indicate preferred axial reorientation, becoming more pronounced with rising temperature.

As pointed out above, solution correlation times are significantly shorter than in the solid phase indicating faster reorientational motion in the liquid environment. Unlike the solid-state,  $C_{70}$  in solution is bathed in solvent molecules which, through van der Waals type interaction, experiences solute-solvent interactions which can affect the overall motion. However, these interactions do not appear to be strong enough to slow the solution-state motion

below what is observed in the solid state. Additionally, at any common temperature, one observes that the differences between  $D_X$  and  $D_Z$  in solution are smaller than in the solid state suggesting that, although solvent displacement is needed in solution, the energetic difference between  $D_X$  and  $D_Z$  type motion in solution is lower than in the solid phase. It is interesting to note that diffusion values of solid-state  $C_{70}$  at 323 K are comparable to values observed at 283 K in solution suggesting that, at 323 K, enough thermal energy is present to promote small-step diffusion "like" behavior in the solid phase.

A comparison of the diffusion coefficients,  $D_Z$  and  $D_X$ , for  $C_{70}$  in the various solvents generate some interesting observations. Since the value for  $D_Z$  is slightly lower in the more viscous solvent of 1,2-dichlorobenzene- $d_4$  than in benzene- $d_6$  or chlorobenzene- $d_5$ , this observation suggests that the viscosity parameter is not the dominant factor giving rise to the observed spinning behavior of  $C_{70}$  in these solvents. The data suggest that, in chlorobenzene- $d_5$  and 1,2-dichlorobenzene- $d_4$ , there is a balance between the strength of intermolecular forces and solvent structure which determines the reorientational behavior. Since the free volume is greater in 1,2-dichlorobenzene- $d_4$ , this suggests that the available free space is more important than intermolecular interactions in determining the spinning rate of  $C_{70}$  in these solvents. The tumbling motion,  $D_X$ , is slowest in 1,2-dichlorobenzene- $d_4$ ; consistent with the higher viscosity of this solvent. One must however be cautious of oversimplifying this observation since, as we saw for the other type of motion, other solvent-related factors are also present.

TABLE 8: Experimental correlation times and predicted rotational diffusion constants for the different carbons at various temperatures for  $C_{70}$  in chlorobenzene- $d_5$ .

$T$ (K)	Carbon 1 $\tau_C^{\text{eff}}$ (ps)	Carbon 2 $\tau_C^{\text{eff}}$ (ps)	Carbon 3 $\tau_C^{\text{eff}}$ (ps)	Carbon 4 $\tau_C^{\text{eff}}$ (ps)	$D_X \times 10^{-10}$ (1/s)	$D_Z \times 10^{-10}$ (1/s)
283	20	17	13	15	0.8	1.6
293	13	10	12	13	1.4	1.6
303	9	9	9	10	1.8	1.8
313	7	8	6	7	2.3	2.6
323	6	6	4	5	2.6	3.9

TABLE 9: Experimental correlation times and predicted rotational diffusion constants for the different carbons at various temperatures for  $C_{70}$  in o-dichlorobenzene- $d_4$ .

$T$ (K)	Carbon 1 $\tau_C^{\text{eff}}$ (ps)	Carbon 2 $\tau_C^{\text{eff}}$ (ps)	Carbon 3 $\tau_C^{\text{eff}}$ (ps)	Carbon 4 $\tau_C^{\text{eff}}$ (ps)	$D_X \times 10^{-10}$ (1/s)	$D_Z \times 10^{-10}$ (1/s)
283	26.1	15.9	15.9	17.9	0.6	1.9
293	13.5	13.8	13.7	14.2	1.2	1.2
303	10.3	11.3	10.5	11.7	1.5	1.5
313	8.9	7.6	8.0	8.5	1.9	2.3
323	7.8	6.5	6.2	6.2	2.1	3.6

## 5. Conclusions

Reorientational times for all carbons, in solution and in the solid phase, decrease with rising temperature indicating faster rotational motion with escalating temperature. The effective correlation times,  $\tau_C^{\text{eff}}$ , of  $C_{70}$  in the solid-state are 2 to 3 times longer than in solution. A comparison of the rotational dynamics of solids  $C_{60}$  and  $C_{70}$  indicates that  $C_{70}$  reorients slower which can be attributed to differences in the orientational ordering of their lattice structures. A noticeable decrease in all the carbons' correlation times is observed between 293 K to 303 K; suggesting a definite transition from isotropic to anisotropic reorientational behavior at this temperature change. Solution correlation times are seen to be significantly shorter than in the solid phase indicating faster reorientational motion in the liquid environment. Although  $C_{70}$  in solution experiences van der Waals type interactions, these interactions do not appear strong enough to slow the solution-state motion below what is observed in the solid state. All observed differences in the diffusion constants,  $D_X$  and  $D_Z$ , in solution are smaller than in the solid state suggesting a lower energy of activation between these two modes of reorientation in the liquid phase. A small-step diffusion "like" condition appears to be thermally generated in the solid phase at 323 K.

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