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Field-Dependent Relaxation and Molecular Reorientation of C_{60} in Chlorobenzene

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To advance our understanding of the ^{13}C spin−lattice relaxation process and rotational dynamics of C_{60} in various environments, we have acquired relaxation data on this molecule in chlorobenzene-d_5 as a function of field strength and at various temperatures. Field-dependent measurements allowed us to separate the contributions arising from the two possible modes for relaxation in this molecule: chemical shift anisotropy (CSA) and spin−rotation (SR). The CSA and SR values were used to extract the reorientational time, τ_c, and the angular momentum time, τ_J, which allowed us to investigate the rotational dynamics of C_{60} in this solvent. We found that the longitudinal relaxation rate is dominated by the chemical shift anisotropy mechanism and that spin−rotation becomes rapidly more important with rising temperature. This is seen especially at 4.7 T, where SR dominates at the moderate temperature of 333 K. We also compared our field-dependent findings with values derived via the Hubbard relation, and we have found the Hubbard approach to overestimate the CSA contribution, causing underestimation of the SR effect. Finally, in an attempt at characterizing our experimental correlation times, we applied the Stokes−Einstein−Debye (SED), Gierer−Wirtz (GW), and Hynes−Kapral−Weinberg (HKW) models to our system and found their predictions to be inconsistent with our experimental findings. Far better agreement was obtained with the GW and HKW theories when these models were expanded to account for the inertial contribution to the overall rotational time. Our investigation also revealed that C_{60} reorients in the intermediate regime rather than at either the “slip” or the “stick” extremes.

Introduction

NMR relaxation measurements have long proven to be one of the most useful techniques for probing rotational dynamics. For the past few years, we have been using these types of measurements to systematically investigate the ^{13}C spin−lattice relaxation process and rotational dynamics of buckminsterfullerene (C_{60}) in various organic liquids.[1−4] The lengthy relaxation times (>120 s at 4.7 T) seen in these liquids have been a unique characteristic of C_{60}. This is due to the inefficient nature of the two modes of relaxation available to this molecule. In the absence of paramagnetics, and at moderate field strengths and temperatures, these two pathways are chemical shift anisotropy (CSA) and spin−rotation (SR) interactions.[5,6] Previous studies in this laboratory have revealed the rotational motion of C_{60} and its relaxation process to be abnormally sensitive to solvent properties.[1−3] To further our understanding of the relaxation process in C_{60} and its rotational behavior in various environments, we have acquired the relaxation data of this very interesting molecule in chlorobenzene-d_5 as a function of field strength and at various temperatures. Unlike our previous method of utilizing the Hubbard relation to separate the various contributions,[1−4] we have performed field-dependent measurements to accomplish this task. Once separated, CSA and SR values were used to extract rotational and angular correlation times, which allowed us to investigate the rotational dynamics of C_{60} in this solvent.

Additionally, to more thoroughly analyze the rotational motion of C_{60}, we employed several theories to generate predictions of the correlation times, and we have compared these values to our experimental rotational times.[7−10] We believe that this study provides fundamental information which will be useful in explaining the longitudinal relaxation times and rotational behavior of other members of the fullerene family.

Experimental Section

Buckminsterfullerene was obtained commercially from the Aldrich Chemical Co. HPLC analysis of this sample showed its purity to be at the 99.8% level, with trace amounts of C_{70}. Chlorobenzene-d_5 was also purchased from Aldrich and was used as received. The C_{60}/chlorobenzene-d_5 solution, with a mole fraction of 3.87×10^{-2}, was contained in a 5 and a 10 mm tube for measurement at 9.4 and at 4.7 T, respectively. The samples were degassed by four freeze−pump−thaw cycles and sealed under vacuum.

Measurements at 9.4 T were performed on a Bruker spectrometer, while measurements at 4.7 T were obtained on a Varian instrument. All spin−lattice relaxation times were obtained using the standard $180° - \tau - 90°$ pulse sequence. Seven τ values, ranging from 0.1 to 1.5 of the estimated T_1, were used. A delay of $5T_1$ between acquisitions was employed. A minimum of three measurements at each temperature was performed. To guard against any pulse imperfections, all magnetization data were fitted according to the following three-parameter equation:

$$M(\tau) = M_o[1 - (1 - \cos\theta)\exp(-\tau/T_1)] \qquad (1)$$

where $M(\tau)$ is the magnetization at various τ values, M_o is the magnetization at infinite τ, and θ is the pulse angle.

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TABLE 1: Experimental Relaxation Rates (R_1), Chemical Shift Anisotropy (R_1^{CSA}), and Spin−Rotation Contributions (R_1^{SR}) at 9.4 T and Various Temperatures[a]

T (K)	$R_1 \times 10^2$ (1/s)	$R_1^{CSA} \times 10^2$ (1/s)	$R_1^{SR} \times 10^3$ (1/s)	%CSA	%SR
273	2.44 (0.01)	2.42	0.16	99	1
288	2.00 (0.04)	1.84	1.59	92	8
303	1.72 (0.03)	1.52	1.99	88	12
318	1.47 (0.02)	1.25	2.25	85	15
333	1.23 (0.02)	0.82	4.11	67	33

[a] Values in parentheses represent one standard deviation.

TABLE 2: Experimental Relaxation Rates (R_1), Chemical Shift Anisotropy (R_1^{CSA}), and Spin−Rotation Contributions (R_1^{SR}) at 4.7 T and Various Temperatures[a]

T (K)	$R_1 \times 10^3$ (1/s)	$R_1^{CSA} \times 10^3$ (1/s)	$R_1^{SR} \times 10^3$ (1/s)	%CSA	%SR
273	6.22 (0.39)	6.06	0.16	97	3
288	6.19 (0.28)	4.60	1.59	74	26
303	5.79 (0.36)	3.80	1.99	66	34
318	5.36 (0.23)	3.11	2.25	58	42
333	6.16 (0.25)	2.05	4.11	33	67

[a] Values in parentheses represent one standard deviation.

Temperatures were maintained by the previously calibrated instruments using the chemical shift of ethylene glycol as the reference. Temperature accuracy is estimated at ±0.5 K. Measurements below 273 K were not performed due to solubility restriction. The relaxation rates ($1/T_1$) are listed in column 2 of Tables 1 and 2 for 9.4 and 4.7 T, respectively. The values in parentheses represent one standard deviation.

Relaxation Mechanisms

It is now well-established that the only two pathways for spin−lattice relaxation in C_{60} is via the spin−rotation and chemical shift anisotropy mechanisms. Their contribution to the overall relaxation rate, R_1, is given by[11]

$$R_1 = R_1^{CSA} + R_1^{SR} \tag{2}$$

Expansion of eq 2 with the respective theoretical expressions for R_1^{CSA} and R_1^{SR} yields

$$R_1 = \frac{2}{15}(\gamma\, H_o S)^2\, \tau_c + \left(\frac{8\pi^2 IkT}{h^2}\right) C^2 \tau_J \tag{3}$$

In eq 3, H_o is the field strength, S is the shielding anisotropy (1.78×10^{-4}),[6] τ_c is the reorientational correlation time, I is the moment of inertia (1.00×10^{-43} kg m^2), C is the spin−rotation coupling constant (258 rad/s),[5] and τ_J is the angular momentum correlation time.

The separation of R_1 into its two components can be accomplished either directly or indirectly depending on the instrumentation available to the investigator. Although we employed the direct method in this investigation, we also present data obtained via the indirect approach to illustrate the inherent error associated with this method. In the direct method, the various contributions are isolated by measuring the relaxation rate as a function of field strength, since R_1^{CSA} shows a direct field dependence while R_1^{SR} has no such dependence on field strength. As can be seen from eq 3, a fit of R_1 versus H_o can provide the desired separation. At the intercept, the CSA contribution to R_1 vanishes, and R_1 equals R_1^{SR}. The R_1^{CSA} contribution can then be determined from the difference between R_1 and R_1^{SR}. R_1^{CSA} and R_1^{SR} values obtained via this approach are listed in columns 3 and 4 of Tables 1 and 2, respectively.

Tables 1 and 2 illustrate some interesting results. At a field strength of 9.4 T, ^{13}C relaxation is dominated by the CSA mechanism at all temperatures. In fact, at 273 K, relaxation occurs almost exclusively via this pathway. The spin−rotation contribution is seen to increase gradually with rising temperature, with its highest value found at 333 K. At this temperature, this mechanism accounts for $^1/_3$ of the relaxation process. Although not as effective as CSA, the magnitude of SR at 333 K is exceptional, since this high of a contribution is usually not found in most molecules. From Table 2, one sees the CSA and SR contributions to be somewhat different at a field strength of 4.7 T. The CSA pathway still dominates at the lower temperatures, but its dominance disappears more rapidly with rising temperature. It is interesting to see that the SR mechanism is not only more effective at this field strength, but its effectiveness is approximately a factor of 3 higher at this field strength than that at 9.4 T. At 333 K, the spin−rotation mechanism is observed to be the dominant pathway for relaxation.

The indirect method is a technique commonly employed when multiple instruments are not available to the investigator. This approach, however, requires the system to exhibit small-step diffusional dynamics (i.e., $\tau_J \ll \tau_c$).[12] Provided that the system obeys this condition, the Hubbard relation can be employed, along with eq 3, to separate the two contributions.[12]

The Hubbard relationship is given as[12]

$$\tau_J = \frac{I}{6kT\tau_c} \tag{4}$$

Substitution of the Hubbard definition for τ_J into eq 3, followed by rearrangement, results in a quadratic expression with respect to τ_c:

$$\frac{2}{15}(\gamma H_o S)^2 \tau_c^2 - R_1 \tau_c + \left(\frac{1.1547\pi IC}{h}\right)^2 = 0 \tag{5}$$

For each R_1, this approach provides two possible values of τ_c. We have found, however, that the positive root of τ_c leads to the theoretically acceptable temperature behavior for R_1^{SR}. Once values for τ_c have been obtained at the three lower temperatures where $\tau_J \ll \tau_C$, eqs 4, 3, and 2 are used to extract the R_1^{SR} and R_1^{CSA} values at these temperatures. These contributions are then fitted opposite the temperature to interpolate the values at other temperatures. The values obtained via this approach are found in Table 3, along with the values obtained via the direct method.

Inspection of the data in Tables 3 shows that the indirect method introduces a small but measurable error in the calculated quantities. In most cases, the indirect approach overestimates the CSA contribution, causing the SR values to be underrepresented. The variation of the two methods range from 1% to 13%, with the mean error being approximately 7%. Although the average error is within acceptable limits for these types of experiments, the direct method must be used if possible when

TABLE 3: Comparison of the Various Contributions Obtained via the Direct and Indirect Methods[a]

	direct method		indirect method	
T (K)	$R_1^{\mathrm{CSA}} \times 10^2$ (1/s)	$R_1^{\mathrm{CSA}} \times 10^3$ (1/s)	$R_1^{\mathrm{CSA}} \times 10^2$ (1/s)	$R_1^{\mathrm{SR}} \times 10^3$ (1/s)
273	2.42	0.16	2.40	0.35
288	1.84	1.59	1.96	0.40
303	1.52	1.99	1.67	0.54
318	1.25	2.25	1.29	1.80
333	0.82	4.11	0.93	3.00

[a] Comparison is made to values obtained via the direct method at a field strength of 9.4 T. Identical trends are observed when the comparison is made at 4.7 T.

TABLE 4: Experimental Rotational Times (τ_c), Angular Momentum Correlation Times (τ_J), Rotational Diffusion Constants (D), and χ Test Values for C_{60} in Chlorobenzene-d$_5$ at Various Temperatures[a]

T (K)	η (cP)	τ_c (ps)	τ_J (ps)	$D \times 10^{-10}$ (1/s)	χ test
273	1.07	14.3	0.03	1.17	4.6
288	0.90	10.9	0.27	1.53	3.6
303	0.72	8.99	0.32	1.85	3.1
318	0.61	7.40	0.34	2.25	2.6
333	0.52	4.85	0.60	3.44	1.7

[a] Rotational diffusion constants were obtained via the relation $D = 1/6\tau_c$.

acquiring relaxation data, since these types of measurements frequently serve as conduits to dynamical information on molecular systems.

Molecular Dynamics

The rotational, τ_c, and angular momentum, τ_J, correlation times are two parameters frequently employed to describe rotational dynamics. In the classical diffusion picture, τ_c represents the time period required for an average molecule to reorient itself through one radian, while τ_J is viewed as approximately the time period between molecular collisions. We have utilized our experimental CSA and SR contributions to obtain τ_c and τ_J times at the various temperatures in this solvent. These values are listed in Table 4 according to increasing temperature. In column three of Table 4, the rotational motion of C_{60} is observed to be moderately slow at 273 K but steadily rises at a rate of 0.16 ps/K with temperature. An Arrhenius fit of τ_c versus temperature reveals an activation energy (E_a) of 13.8 kJ/mol. Surprisingly, the magnitude of E_a suggests that C_{60} is experiencing less rotational hindrance in this solvent than in carbon disulfide and toluene, where activation energies were found to be 17.5 and 25.2 kJ/mol, respectively.[3,13]

The angular momentum correlation times, τ_J, are seen to be substantially smaller than τ_c, indicating that C_{60} might be experiencing small-step diffusion (i.e., $\tau_J \ll \tau_c$). This possibility can readily be investigated via the simple χ test.[14] According to this test, a value of $\chi > 5$ indicates small-step diffusion, while a value of $\chi < 3$ suggests rotation in the inertial region. A value of χ between these two limits characterizes motion in the intermediate region. χ values are given in the last column of Table 4, and these values imply C_{60}'s rotational motion to be in the intermediate region between 273 and 318 K and in the inertial region at the highest temperature. Hence, the χ values reveal that the inertial condition will be entered slightly above room temperature and that small-step diffusion will certainly be realized at temperatures below 273 K.

Theoretical Analysis of Rotational Motion

We used the Stokes–Einstein–Debye (SED), Gierer–Wirtz (GW), and Hynes–Kapral–Weinberg (HKW) models to obtain theoretical predictions for τ_c in this solvent.[7–9] Theoretically, the rotational motion of a solute in a viscous environment is given by[10]

$$\tau_c = \left(\frac{4\pi r^3 \eta}{3kT}\right)\phi C + \tau_o \tag{6}$$

where r is the radius of C_{60} (3.512 Å), η is the bulk viscosity, T is the temperature, ϕ is a shape parameter (1 for a sphere), and τ_o is the inertial contribution to the overall reorientational time. Since inertial effects are usually found to be negligibly small in liquids, τ_o is normally ignored. C is a "slip" coefficient, which can be calculated via several theories and measures the hindrance to rotation experienced by a molecule in dense liquid. A value of 1 refers to a condition commonly known as "stick", while a value of 0 is known as the "slip" limit.

Rotational motion in the SED theory is viewed as being affected primarily by solvent viscosity. The shape parameter ϕ and the slip coefficient C are both set to 1, corresponding to the stick condition. The inertial contribution, τ_o, is completely disregarded under this approach, and eq 6 reduces to

$$\tau_c\,(\mathrm{SED}) = \frac{4\pi r^3 \eta}{3kT} \tag{7}$$

While the slip coefficient C is set to unity in the SED model, its value in the Gierer–Wirtz approach is dependent on the solvent-to-C_{60} molecular diameter ratio. According to this model, C is given by

$$C = [6(d_s/d) + (1 + d_s/d)^{-3}]^{-1} \tag{8}$$

where d_s and d are the solvent and solute molecular diameters, respectively.[15] The shape parameter and the inertial contribution are treated in the same manner as in the SED model.

The Hynes–Kapral–Weinberg (HKW) model treats rotational correlation times in a slightly different way. The HKW model introduces the concept of a microscopic boundary layer which surrounds the rotating molecule and proposes that collisional effects within this layer determine the rotational behavior of the molecule. A slip coefficient, β, is used to measure the velocity coherence (i.e., coupling) between the boundary layer and the outer hydrodynamic region. As β approaches zero, the "slip" limit is approached, signifying little or no velocity coherence. Molecules in this limit are believed to be experiencing free rotation. The other extreme, the stick limit, is approached as β nears infinity. A values of β between these two extremes is referred as the "intermediate" region. Under the HKW model, C is defined as

$$C = \beta/(3\eta + \beta) \tag{9}$$

In eq 9, η is the bulk viscosity and β is the slip coefficient. We employed Kivelson's method to calculate β and eq 9 and eq 6 to calculate τ_c(HKW) at various temperatures.[16,17] The experimental correlation times and model predictions are listed in Table 5 according to decreasing solvent viscosity. As indicated earlier, the SED model assumes reorientational motion to be in the stick limit (i.e., $C = 1$), where solvent viscosity is the only factor affecting rotational motion. As can be seen in column 4, this model provides predictions that are extremely poor. Each τ_c (SED) value is far longer than experimental times, indicating

TABLE 5: Experimental Rotational Times (τ_c) and TheoreticalPredictions at Various Temperatures

T (K)	η (cP)	τ_c (ps)	τ_c (SED) (ps)	τ_c (GW) (ps)	τ_c (HKW) (ps)	τ_o(ps)	τ_c (HKW)[a] (ps)	τ_c (GW)[a] (ps)
273	1.07	14.3	51.6	8.72	7.02	2.99	10.0	11.7
288	0.90	10.9	41.1	6.94	6.54	2.91	9.45	9.85
303	0.72	8.99	31.2	5.27	6.04	2.84	8.88	8.11
318	0.61	7.40	25.0	4.23	5.59	2.77	8.36	7.00
333	0.52	4.85	20.5	3.46	5.18	2.71	7.89	6.17

[a] These values correspond to τ_c (HKW) and τ_c (HKW) after the inertial contribution, τ_o, has been taken into consideration.

this model's inability to reliably estimate the effects of viscosity on the rotational motion of C_{60} in this solvent. This lack of correlation implies that buckminsterfullerene's rotational motion is not solely dependent on chlorobenzene's viscosity and that other factors also play a significant role.

The Gierer–Wirtz approach, whose values are found in column 5 of the same table, is seen to provide τ_c values that are more in line with experimental values. However, even these predictions are far from acceptable. τ_c (GW) values are lower by an average of 38%, suggesting that this model also underestimates the importance of microviscosity effects on the rotational motion of C_{60} in this solvent.

Slightly better correlation is observed via the HKW theory. However, even these predictions are not quantitative. Nevertheless, the fact that HKW provides closer values suggests that collisions within the microscopic layer are more important than bulk hydrodynamic effects. It is interesting to note that the predictions become increasingly better as temperature rises. The C values calculated via this theory ranged from 0.14 at 273 K to 0.25 at 333 K, indicating that the rotational motion of C_{60} in this solvent is in the intermediate regime. Support for this observation was obtained by plotting experimental τ_c values versus τ_c (SED), and C (i.e., the slope) was found to equal 0.281.

We believe that the failure of these models to adequately reproduce our experimental correlations times stems from their disregard for the free rotor contribution (i.e., τ_o in eq 6 is set to zero in each of the three models) to the overall rotational time. Several theories have been proposed for calculating this contribution, with the most popular[18–21] being

$$\tau_o = 0.6[I/(kT)]^{1/2} \tag{10}$$

Using eq 10, we have calculated τ_o at the various temperatures and incorporated this contribution into the Gierer–Wirtz and Hynes–Kapral–Weinberg models, the two which give closer agreements. As can be seen from the last two columns of Table 5, significant improvement is realized once these two models are expanded to include the inertial contribution. In fact, the GW predictions are well within experimental certainty. The improved agreement therefore suggests that events at the microscopic level, rather than bulk properties, are better descriptors of the factors affecting molecular rotation and that inertial contributions are significant enough to warrant inclusion in the various theoretical approaches describing reorientational motion.

In summary, we have found that the ^{13}C spin–lattice relaxation rate in C_{60} to be dominated by the chemical shift anisotropy mechanism and that spin–rotation becomes increasingly more important with rising temperature, especially at 4.7 T, where SR is seen to dominate at the moderate temperature of 333 K. Reorientational correlation times are seen to systematically decrease from 14.3 to 4.85 ps, with rising temperature indicating increased rotational motion. A plot of τ_c versus $1/T$ provided a rotational activation energy of 13.8 kJ/mol, which is lower than in CS_2 and toluene, indicating less hindered rotation in the chlorobenzene. We also found poor agreement between our experimental rotational times and those predicted by the SED, HKW, and GW models. Improved predictions were produced by the GW and HKW models once these theories were expanded to include the inertial contribution. The closer agreement obtained upon the inclusion of τ_o suggests that inertial effects cannot be simply ignored but need to be considered when fully analyzing reorientational motion. Finally, a plot of our experimental τ_c values against τ_c (SED) revealed a slip coefficient of 0.281, indicating the rotational motion of C_{60} to be in the intermediate region rather than at either the slip or stick extremes.

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