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ARTICLES

Analysis of the Reorientational Motion of C_{60} in Toluene-d_8: Effects of Solute−Solvent Interactions on Rotational Times in Various Solvents

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Studies probing the molecular dynamics of C_{60} in various environments, and conditions, have been generating a great deal of attention since these investigations have the potential of providing baseline information that might be useful in predicting similar behavior in other members of the fullerene family. We have used ^{13}C spin−lattice relaxation measurements to analyze the rotational motion of C_{60} in toluene-d_8 and have compared these results with data obtained in carbon disulfide and 1,2-dichlorobenzene-d_4. We found that the reorientational times, τ_c, of C_{60} in these solvents did not conform to conventional viscosity arguments but were better correlated to the strength of solute−solvent interactions. Consequently, our attempt at theoretically duplicating our correlation times via hydrodynamic-based models proved unsuccessful. Nevertheless, our observations suggest that the success of any future theoretical models will be critically dependent on whether solvent effects are included in the analysis of this type of motion.

Introduction

In our continuing effort to investigate the rotational dynamics of C_{60} in various environments, we have employed ^{13}C spin−lattice relaxation measurements to obtain reorientational information on this very interesting molecule in deuterated toluene. Due to its ideal geometry, C_{60}'s rotational behavior lends itself nicely to analysis by a number of existing hydrodynamic models.[1−3] Surprisingly, as of yet, not one model has proven superior in explaining all experimental observations. We believe the fundamental reason for their inability to duplicate experimental results is their failure to account for the presence of solute−solvent interactions. Although weak, these interactions appear to play an important role in the reorientational behavior of C_{60}. Nevertheless, buckminsterfullerene's geometrical dimensions still make it an excellent candidate for developing an all-encompassing model for characterizing rotational motion.

^{13}C spin−lattice relaxation in C_{60} is known to proceed via only two pathways: chemical shift anisotropy (CSA) and spin rotation (SR). We employed the Hubbard relation to separate CSA contributions from those arising from SR interactions. Although not ideal, this approach has in the past provided acceptable experimental data.[4,5] Once separated, the CSA contributions were used to obtain reorientational correlation times, τ_c. These times were then used to probe the rotational behavior of C_{60} in this solvent at various temperatures. To gain a much broader understanding of the factors influencing molecular rotation in this molecule, we compared these values with reorientational times obtained in CS_2 and in 1,2-dichlorobenzene-d_4 (1,2-DCB-d_4) and found surprisingly that C_{60}'s rotational dynamics in the present solvent more closely parallel its behavior in CS_2 than in 1,2-DCB-d_4. We also attempted to theoretically model the rotational behavior of C_{60} in this solvent but found that none of the theories employed were able to successfully duplicate our experimental data. However, by comparing the correlation times in the various solvents in terms of intermolecular interactions, we were able to establish a qualitative trend that appears to explain our findings. We believe these fundamental observations will be useful in predicting and/or explaining the reorientational behavior of other members of the fullerene family.

Experimental Section

Raw soot, containing roughly 10% C_{60}, was purchased from Texas Fullerene Co. C_{60} was separated and purified by the same procedures as described elsewhere.[6]

The C_{60}/toluene-d_8 solution, with a mole fraction of 3.6×10^{-4}, was contained in a 10 mm tube which was degassed via three pump−thaw cycles. All measurements were performed on an instrument operating at 50.3 MHz (i.e., 4.7 T) and at temperatures of 273, 288, 303, 318, and 333 K. Lower temperature measurements were not possible due to precipitation restrictions. Sample temperatures were controlled by the previously calibrated spectrometer (accuracy is estimated to be ±0.1 K). All relaxation times were obtained using the standard inversion−recovery pulse sequence (e.g., $D_1-\pi-\tau-\pi/2$). Seven τ values ranging from 0.1 to 1.5 times the measured T_1 were employed in acquiring the magnetization data. A delay time (D_1) of $5T_1$ was used between repetitions. To guard against pulse imperfections, all carbon magnetization data were fitted according to a three-parameter equation given by

$$M(\tau) = M_0[1 - (1 - \cos\theta)\exp(-\tau/T_1)] \qquad (1)$$

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TABLE 1: Spin Rotation, Chemical Shift Anisotropy Contributions, and Angular Momentum Correlation Times Obtained from the Positive Root of τ_c Using Experimental R_1 Values at the Three Lower Temperatures[a]

T (K)	$R \times 10^3$ (1/s)	τ_c (ps)	τ_J (ps)	τ_c/τ_J	$R_1^{SR} \times 10^3$ (1/s)	$R_1^{CSA} \times 10^3$ (1/s)
273	8.88 (0.60)	18.5	0.240	77.1	1.08	7.80
288	7.99 (0.72)	16.0	0.262	61.1	1.25	6.74
303	6.20 (0.33)	9.93	0.401	24.8	2.01	4.19

[a] At these temperatures the Hubbard relation is known to apply.[10] Values in parentheses represent one standard deviation.

TABLE 2: Experimental Spin−Lattice Relaxation Rates, Chemical Shift Anisotropy, Spin Rotation, and Reorientational Times of C_{60} in Toluene-d_8 at All 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)	τ_c (ps)
273	8.88 (0.60)	7.80	1.08	18.5
288	7.99 (0.72)	6.74	1.25	16.0
303	6.20 (0.33)	4.19	2.01	9.93
318	6.57 (0.71)	2.74	3.83	6.49
333	11.1 (1.20)	0.94	10.2	2.22

[a] Values in parentheses represent one standard deviation.

where M_0 is the magnetization at infinite τ and the $(1 - \cos \theta)$ term corrects for any variations in the initial pulse. Average experimental relaxation rates are given in column two of Tables1 and 2. Values in parentheses represent one standard deviation.

Separation of Relaxation Mechanisms

There are only two efficient pathways for spin−lattice relaxation in buckminsterfullerene. These are via the spin rotation and chemical shift anisotropy mechanisms. Although intermolecular dipole−dipole ^{2}H interactions are theoretically possible, these effects have been experimentally determined to be negligibly small.[7] Hence, the overall relaxation rate, R_1, can be expressed as[8]

$$R_1 = \frac{1}{T_1} = \frac{2}{15}(\gamma H_0 S)^2 \tau_c + \frac{8\pi^2 IkT}{h^2} C^2 \tau_J \tag{2}$$

In eq 2, H_0 is the field strength (4.7 T), S is the shielding anisotropy (1.78×10^{-4}),[9] 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),[10] and τ_J is the angular momentum correlation time. All remaining parameters have their usual meaning.

The two contributions were separated by employing the Hubbard relation (i.e., $\tau_J = I/(6kT\tau_c)$).[11] Briefly, inclusion of the Hubbard relation into eq 2, followed by rearrangement, yields a quadratic expression with respect to τ_c.

$$\frac{2}{15}(\gamma H_0 S)^2 {\tau_c}^2 - R_1 \tau_c + \left(\frac{1.1547\pi IC}{h}\right)^2 = 0 \tag{3}$$

Experimental relaxation rates (R_1), at the three lower temperatures where the Hubbard relation is known to apply,[10] were fitted according to eq 3 to render two possible values for τ_c. Only the positive root of τ_c leads to the theoretically acceptable temperature behavior of R_1^{CSA} and R_1^{SR}. The results at these temperatures are shown in Table 1. R_1^{CSA} values obtained at these reduced temperatures were then fitted against the temperature to yield chemical shift contributions at the two higher temperatures. CSA values were subsequently used in eq 2 to obtain spin rotation quantities at each temperature. All R_1^{CSA} and R_1^{SR} values obtained via this procedure are listed in columns 3 and 4 of Table 2.

TABLE 3: Experimental Correlation Times, Rotational Diffusion Rates,[a] **and Model Prediction at Various Temperatures in Toluene-d_8**

T (K)	η (cP)	τ_c (ps)	$D \times 10^{-10}$ (1/s)	τ_c(SED) (ps)	τ_c(GW) (ps)	τ_c(HKW) (ps)
273	0.761	18.5	0.90	36.6	7.56	2.92
288	0.624	16.0	1.04	28.5	5.89	2.83
303	0.526	9.93	1.68	22.8	4.71	2.74
318	0.445	6.49	2.57	18.4	3.80	2.48
333	0.384	2.22	7.51	15.1	3.13	2.28

[a] Rotational diffusion rates were obtained according to the relation $D = 1/6\tau_c$.

Reorientational correlation times, τ_c, were obtained directly through the chemical shift contribution and are listed in columns 3 and 5 of Tables 1 and 2, respectively.

Molecular Dynamics

A prerequisite for using the Hubbard relation in relating angular momentum correlation times, τ_J, to τ_c is that the solute be experiencing small-step diffusion during its rotational motion. Under this regime, τ_J is expected to be much smaller than the reorientational time (i.e., $\tau_J \ll \tau_c$). A quick comparison of columns 3 and 4 in Table 1 clearly illustrates the rotational behavior of C_{60} to be in this regime; τ_J ranges from 0.2 ps at 273 K to 0.4 ps at 303 K. In fact, we have found from previous studies that C_{60} obeys this condition more strictly in toluene-d_8 than in 1,2-dichlorobenzene-d_4. One also sees from column 5 of Table 2 that C_{60} reorients somewhat slow at low temperatures but increases dramatically as temperature rises, with free rotation being approached at 333 K.

Theoretically, reorientational correlation times are frequently expressed as a sum of a hydrodynamic and an inertial contribution:

$$\tau_c = \left(\frac{4\pi r^3 \eta}{3kT}\right) f\phi + \tau_0 \tag{4}$$

where r is the solute radius (3.512 Å for C_{60}), η is the bulk viscosity, T is the temperature, f is a friction coefficient (i.e., a shape parameter for the solute which is equal to one for a sphere), ϕ is an experimentally determined correlation coefficient, and τ_0 is the inertial contribution to the rotational motion. Since in liquids inertial effects are found to be negligibly small, τ_0 is frequently ignored. The success of eq 4 in generating acceptable rotational times is critically dependent on the treatment of ϕ. We used three of the most widely employed theories for computing ϕ in attempting to further analyze our experimental correlation times. These comparisons are discussed in the following paragraphs.

All experimental correlation times and model predictions are found in Table 3. Experimental correlation times indicate a gradual increase in the rotational diffusion of C_{60} as solvent viscosity decreases (i.e., the rotational diffusion constant, D, is observed to go from 0.90×10^{10} to 7.5×10^{10} 1/s). However, a sudden jump is seen to take place at 333 K. A value of 2.22

ps for τ_c at 333 K implies that C_{60} is experiencing little or no retarding force during its rotational motion. The significance of this value becomes more apparent if we revisit eq 4:

$$\tau_c = \left(\frac{4\pi r^3 \eta}{3kT}\right) f\phi + \tau_0$$

Little or no retarding force suggests that

$$\left(\frac{4\pi r^3 \eta}{3kT}\right) f\phi \approx 0$$

and hence

$$\tau_c \approx \tau_0$$

At temperatures beyond 333 K, our data indicate that inertial effects will be the only factors determining the rotational velocity of C_{60} in this solvent.

We theoretically analyzed the rotational dynamics of C_{60} in this solvent by applying three commonly used theories for liquid-phase molecular rotation: Stokes−Einstein−Debye (SED), Gier−Wartz (GW), and the Hynes, Kapral, and Weinberg (HKW) models.[1−3] These model predictions, along with the experimental reorientational times, are found in Table 3.

According to the Stokes, Einstein, and Debye model, experimental correlation time should reflect the following relation:

$$\tau_c = \left(\frac{4\pi r^3 \eta}{3kT}\right) f\phi \qquad (5)$$

The factors f and ϕ are set to unity under this approach, and τ_0 is ignored. As one can see from the fifth column of Table 3, the SED model seriously overestimates the effect of the retarding force on the motion of C_{60}. Hence, all the times predicted by this model are significantly longer than what is experimentally observed. We can therefore conclude that viscosity arguments do not fully explain the rotational behavior of C_{60} in this solvent.

In the Gier−Wartz approach, the f parameter is still set to unity, but the ϕ factor is defined as

$$\phi = \left(6\left(\frac{ds}{d}\right) + \left(1 + \frac{ds}{d}\right)^{-3}\right)^{-1} \qquad (6)$$

where ds and d are the solvent and solute molecular diameters, respectively.[2] In this approach τ_0 is also ignored. A scan of the Gier−Wartz predictions shows these values to be as bad as those found via the SED approach. However, unlike the SED model, this theory critically underestimates the influence of the retarding force. Hence, all predictions are at least an order of magnitude smaller than experimental values.

The Hynes, Kapral, and Weinberg (HKW) model introduces the concept of a microscopic boundary layer and a slip coefficient (β).[3] The slip coefficient provides information regarding the velocity coherence between the solvent continuum and the solute molecule. Decreasing velocity coherence will be observed as β approaches zero. Under this boundary condition a molecule is expected to experience increased rotational freedom. This condition has historically been referred as the "slip" limit. The reversed condition, where $\beta \rightarrow \infty$, is known as the "stick" limit, and a higher degree of velocity coherence is predicted under this regime. In this model f is still unity, but ϕ is defined as $(\beta r/(3\eta + \beta r))^{-1}$. Using Kivelson's approach for calculating β, we computed values for ϕ at the various temperatures.[12] These values were then used, along with eq 5, to obtain a prediction for the correlation time, τ_c(HKW). The HKW predictions are listed in the last column of Table 3. As one can see, these predictions are not any better than those obtained via the first two models. As a matter of fact, this model, without question, generates the poorest correlation. Our values for β range from 4.9×10^{-4} − to 5.1×10^{-4} kg/(m s) within this temperature range, indicating that the HKW model predicts that there should be very little velocity coherence between C_{60} and solvent molecules.

TABLE 4: Comparison of Reorientational Times in Toluene-d_8, CS_2, and 1,2-Dichlorobenzene-d_4[a]

	CS_2		toluene-d_8		1,2-DCB-d_4	
T (K)	η (cP)	τ_c (ps)	η (cP)	τ_c (ps)	η (cP)	τ_c (ps)
278	0.423	19.8	0.713	20.0[b]	1.47	12.3
293	0.363	13.3	0.589	11.4[b]	1.28	10.4[b]
303	0.348	9.50	0.524	9.93	1.18	9.93
313	0.318	8.86	0.470	5.86[b]	1.09	8.60

[a] Listed according to increasing viscosity and at four common temperatures. [b] These values were interpolated via the relation $\ln \tau_c = \ln \tau_0 + E_a/RT$ from their respective experimental correlation times.

In retrospect, it should not be completely surprising to find that these models did not generate predictions that were more consistent with experimental observations since none of these theories account for the presence of intermolecular forces and/or the formation of solute aggregates. Some experimental observations have suggested the possible formation of C_{60} aggregates in certain solvents, in particular benzene solutions.[13−15] While C_{60} aggregation is possible in toluene, aggregation in this solvent is believed to occur at temperatures ranging from 210 to 170 K, temperatures much lower than used in this study.[14] These weakly bound clusters lose their cohesiveness when temperatures rise beyond 210 K. One can therefore safely neglect any effects arising from solute aggregation. Consequently, we believe that the rotational motion of C_{60} in a given solvent is primarily determined by two factors: the solvent's viscosity and the strength of any C_{60}−solvent interactions. In terms of viscosity, buckminsterfullerene's rotational freedom will be inversely related to a solvent's viscosity. Therefore, one expects higher rotational rates (i.e., short τ_c) in low-viscosity solvents and slower rates (i.e., long τ_c) in higher-viscosity solvents. If viscosity was the dominating factor in determining the magnitude of the rotational times, one would expect correlation times to follow the order $\tau_c(CS_2) < \tau_c(\text{toluene-}d_8) < \tau_c(\text{1,2-DCB-}d_4)$. Our reorientational times listed in Table 4 basically indicate the reverse trend, especially at the lower temperatures. On the average, the longest correlation times are seen in CS_2, which has the lowest viscosities.

In terms of solute−solvent interactions, rotational rates can be roughly correlated to the strength of the interactions—short τ_c in weakly interacting solvents and long τ_c should be observed in strongly interacting solvents. Reed and co-workers recently found that C_{60}−solvent interactions are indeed present and that they are primarily of two types: π-stacking and of the London dispersive variety.[16,17] They also determined the strength of these interactions followed the order CS_2 > toluene > 1,2-dichlorobenzene-d_4. If we now consider the presence of solute−solvent interactions in the analysis of our data, our observations begin to make more physical sense. The faster rotational rates in 1,2-dichlorobenzene-d_4 at the two lower temperatures imply that C_{60} is experiencing greater rotational freedom in this solvent than in CS_2 and toluene-d_8. This is conceivable if solute−solvent interactions are stronger in CS_2 and toluene-d_8 than in 1,2-dichlorobenzene-d_4. As temperature rises, these weak interactions are overcome by thermal motion, and viscosity effects begin to play a greater role in the observed rotational behavior. Our data therefore suggest that the development, and success, of future theoretical models will be critically dependent on whether solute−solvent interactions are accounted for when analyzing this type of motion.

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