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ARTICLES

Anomalous Relaxation and Molecular Dynamics of Buckminsterfullerene in Carbon Disulfide

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We have employed the Hubbard relation to acquire semiquantitative information on the ^{13}C spin−lattice relaxation rate of buckminsterfullerene in CS_2. We found the spin rotation mechanism to be operative and its contribution to be significant at all temperatures studied here. With the exception of values at 303 K, we found very different chemical shift and spin rotation contributions in this solvent than in 1,2-dichlorobenzene-*d*$_4$. In fact, the respective contributions were reversed at 313 K. This observation indicates that solvent effects play a critical role in determining how effective these mechanisms will be in a given solvent. Three hydrodynamic-based models were applied in an attempt at theoretically describing the rotational motion of the title molecule in CS_2. The Stokes−Einstein−Debye (SED) model proved superior in duplicating our experimental findings. The agreement between the SED predictions and our experimental reorientational times suggests that C_{60} reorients in the "stick" limit where solute−solvent velocities are predicted to be similar. We, however, believe that the velocity coherence is not due to their separate matched velocities but rather originates from the presence of intermolecular interactions.

Introduction

The discovery of C_{60} has generated a considerable amount of interest in the study of the physiochemical properties of this very fascinating molecule.[1−5] In the past few years our efforts have been directed toward developing a comprehensive understanding of the factors affecting the ^{13}C spin−lattice relaxation process of this molecule under a variety of conditions. Early spin−lattice relaxation studies assumed that the chemical shift anisotropy mechanism (CSA) was the only efficient pathway by which carbon nuclei in C_{60} could undergo this type of relaxation.[6,7] Later studies showed, however, that spin rotation interactions (SR) were also efficient at promoting spin−lattice relaxation.[8,9] Our very recent investigation of the ^{13}C spin−lattice relaxation rate of the title molecule in 1,2 dichlorobenzene-*d*$_4$ (1,2-DCB-*d*$_4$) provided further evidence of the importance of the SR interaction in the overall relaxation process.[10] In line with these later observations, our present measurements in CS_2 show the spin rotation contribution to be indeed significant, even at low temperatures. We found this to be amazing, since SR interactions are generally not effective at such low temperatures. Moreover, when we compared our CSA and SR values in CS_2 with quantities obtained in 1,2-DCB-*d*$_4$, we found these contributions to be considerably different at almost all temperatures, suggesting that solvent effects play a very important role in determining the magnitude of these two contributions. Also surprising was our finding that C_{60} reorients much more slowly in CS_2 than in 1,2-DCB-*d*$_4$. One would have expected C_{60} to reorient more quickly in CS_2 than in the more viscous 1,2-DCB-*d*$_4$. Besides viscosity, we believe that solute−solvent interactions also affect the observed CSA and SR

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TABLE 1: Experimental Spin−Lattice Relaxation Rates, Chemical Shift Anisotropy, Spin Rotation, and % Contributions at Various Temperatures of C_{60} in CS_2[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
278	9.35(0.49)	8.34	1.01	89.2	10.8
293	7.10(0.28)	5.59	1.51	78.8	21.2
303	6.11(0.38)	4.01	2.01	65.6	34.4
313	11.2(0.98)	3.74	7.46	33.4	66.6

[a] Values in parentheses represent one standard deviation.

contributions as well as the rotational motion of C_{60} in these two solvents.

In this communication we present our analysis of C_{60}'s spin−lattice relaxation rate and its reorientational dynamics in CS_2 at a field strength of 4.7 T. Also, to further expand our understanding of the factors affecting the relaxation process and the dynamics of this molecule in various environments, we have compared our CS_2 results to observations made in 1,2-dichlorobenzene-*d*$_4$. We have attempted to explain our findings in terms solute−solvent interactions.

Experimental Section

Raw soot, containing roughly 10% C_{60}, was purchased from the Texas Fullerenes Corporation.[11] The separation of C_{60} from the raw soot and its purification were accomplished by the same procedure as described previously.[7]

The C_{60}/CS_2 sample, with a mole fraction of 9.0×10^{-4}, was contained in a 8 mm tube that was degassed via a series of three pump−thaw cycles. The sample tube was sealed under vacuum and placed in a 10 mm tube in a coaxial configuration. The outer annulus of the 10 mm tube contained deuterated water, which served as a lock solvent.

All measurements were performed on an instrument operating at 50.3 MHz (i.e., 4.7 T) and at temperatures of 278, 293, 303, and 313 K. Lower or higher temperature measurements were not possible owing to precipitation and boiling point restrictions. Sample temperatures were controlled by the previously calibrated spectrometer (accuracy is estimated to be ±0.1 K).

Since we are limited to a single instrument in our department, we employed the Hubbard relation to separate the CSA from the SR contribution at the three lower temperatures where this relation is known to hold.[8] Although ideally one would prefer to perform this separation via field dependent measurements, we have shown that the Hubbard relation provides an excellent alternative to this separation.[10]

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 $5 \times T_1$ was used between repetitions.

To guard against any pulse imperfections, all carbon magnetization data were fitted according to a three-parameter equation given by[12] Average experimental relaxation rates are

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

given in column two of Table 1. Values in parentheses represent one standard deviation.

Theory

It is now well established that the only two pathways for spin−lattice relaxation in buckminsterfullerene is via the spin rotation and chemical shift anisotropy mechanisms.[8,9] Their contribution to the overall relaxation rate, R_1, is given by eq 2:[13]

$$R_1 = 1/T_1 = R_1^{CSA} + R_1^{SR} \qquad (2)$$

Expansion of eq 2 with the respective theoretical expressions for R_1^{CSA} and R_1^{SR} yields eq 3:[13]

$$R_1 = 1/T_1 = \frac{2}{15}(\gamma H_o S)^2 \tau_c + \left(\frac{8\pi^2 IkT}{h^2}\right) C^2 \tau_J \qquad (3)$$

In eq 3, H_o 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),[8] and τ_J is the angular momentum correlation time. All remaining parameters have their usual meaning.

As briefly cited above, the CSA and SR contributions can typically be separated by measuring the relaxation rate at various field strengths. Alternatively, this separation can be accomplished by employing the Hubbard relation (i.e., $\tau_J = I/(6kT\tau_c)$).[14] This alternative approach, however, requires that the system be undergoing small step diffusion (i.e., $\tau_J \ll \tau_c$). Although this approach is subject to more uncertainty, we recently demonstrated that this procedure provides reliable data when applied under the right conditions.[10,15] Briefly, inclusion of the Hubbard relation into eq 3, followed by rearrangement, yields a quadratic expression with respect to τ_c.

$$\frac{2}{15}(\gamma H_o S)^2 \tau_c^{\,2} - R_1 \tau_c + \left(\frac{1.1547\pi IC}{h}\right) = 0 \qquad (4)$$

Experimental relaxation rates, R_1, were fitted according to eq 4 to render two possible values for τ_c. However, only the positive root of τ_c leads to the theoretically acceptable temperature behavior of R_1^{SR}. τ_c values obtained at the three lower temperatures were used to calculate CSA contributions at these temperatures. These CSA values were then fitted vs the temperature to interpolate this contribution at 313 K. CSA values were subsequently used in eq 2 to obtain spin rotation quantities at each temperature. R_1^{CSA} and R_1^{SR} values obtained via this procedure are listed in columns three and four of Table 1.

Results and Discussion

Table 1 clearly shows the spin rotation mechanism to be an important pathway for spin−lattice relaxation at each temperature. In column two one observes the overall relaxation rate steadily decreases with rising temperature with a dramatic reversal occurring at 313 K. At 313 K, the relaxation rate experiences a significant enhancement, which can only be due to the increased efficiency of the SR mechanism. At the lower temperatures one observes the CSA mechanism to be the preferred mode for relaxation. The temperature behavior of these two interactions is better illustrated in Figure 1. According to this fit, SR will become the dominating pathway for ^{13}C relaxation in C_{60} at 308 K. The dominance of the SR mechanism at such a moderate temperature is due primarily to the inefficiency of the CSA interaction to promote relaxation at this field strength. Interestingly, we found our interpolated SR contribution at 283 K (12%) to be much lower than the solid-state finding of 56%.[9] This suggests that solvent effects play an important role in determining the magnitude of these mechanisms in C_{60}.

With this in mind, we compared our present CSA and SR data to values obtained in 1,2-dichlorobenzene-*d*$_4$. CSA and SR data in 1,2-DCB-*d*$_4$ is found in Table 2. With the exception

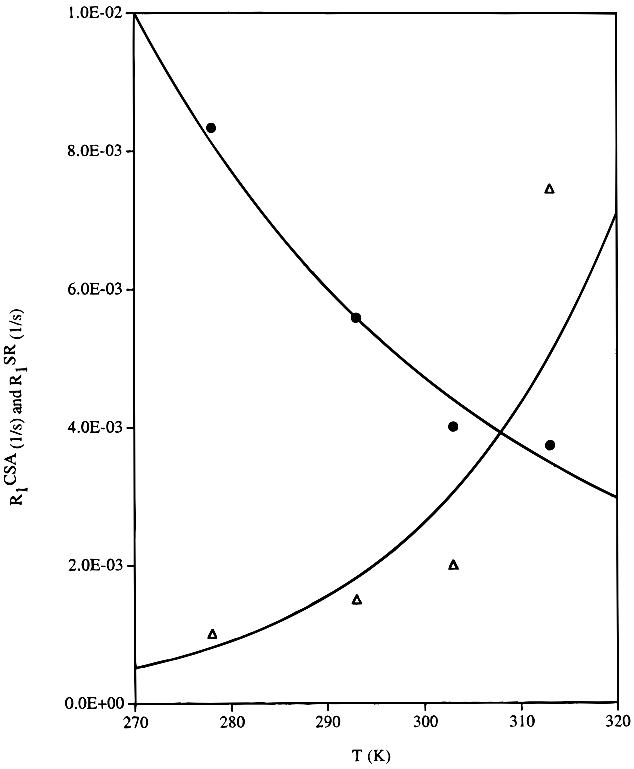

Figure 1. Temperature behavior of the chemical shift anisotropy (●) and spin rotation contributions (△) in CS_2.

TABLE 2: Experimental Spin−Lattice Relaxation Rates, Chemical Shift Anisotropy, Spin Rotation, and % Contributions at Various Temperatures of C_{60} in 1,2-Dichlorobenzene-d_4

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
278	6.81	5.19	1.62	76.2	23.8
293[a]	6.37	4.48	1.89	70.3	29.7
303	6.20	4.19	2.01	67.6	32.4
313	5.82	3.63	2.19	62.4	37.6

[a] Values at this temperature were interpolated from the graphs given in ref 10.

of values at 303 K, one finds very different CSA and SR contributions in these two solvents. In fact, the respective contributions are reversed at 313 K. Unlike our findings in CS_2, we found that in 1,2-dichlorobenzene-d_4, the SR mechanism becomes the dominant pathway for relaxation at a much higher temperature of 346 K. These findings once again suggest that solvent-related factors (e.g., solute−solvent interactions) can cause a noticeable affect on the spin−lattice relaxation process at a given temperature and field strength. In terms of solute−solvent interactions, the larger SR contributions in 1,2-dichlorobenzene-d_4 at the two lower temperatures suggest that C_{60} is experiencing greater rotational freedom in this solvent than in CS_2. This is conceivable if solute−solvent interactions are stronger in CS_2 than in 1,2-dichlorobenzene-d_4. In fact, we believe this to be the case, since recent studies have found the strength of these interactions to follow the order $CS_2 >$ 1,2-dichlorobenzene-d_4.[16,17] At higher temperatures these dispersive-type interactions are overcome by thermal motion, and expected spin rotation behavior is then observed.

The rotational dynamics of C_{60} in this solvent were probed through the rotational correlation times, τ_c. These reorientational times, which are listed in column 3 of Table 3, were obtained via the CSA contribution. One sees from these values that C_{60} is undergoing rapid molecular reorientation in CS_2. A linear fit of ln τ_c vs 1000/T yielded an activation energy of 17.5 kJ/mol. In surveying our τ_c values, we noticed that C_{60} reorients somewhat more slowly in this liquid than in its solid phase (e.g., 9.2 ps at 283 K).[9] This once again suggests that solvation is affecting the rotational motion of C_{60} in this solvent. Perhaps more interesting is the comparison of τ_c values in this solvent to those obtained in 1,2-DCB-d_4. τ_c values in 1,2-DCB-d_4 are found in the last column of Table 3. Hydrodynamic-based arguments would lead one to expect the rotational motion of C_{60} to be much more rapid in CS_2 than in the more viscous 1,2-DCB-d_4. However, at the lower temperatures, one sees that C_{60} reorients much more quickly in 1,2-DCB-d_4. The reorientational motion is seen to be about the same at the two higher temperatures even though the viscosity difference of these solvents is still very large. The anomalous behavior of τ_c can best be explained by considering solute−solvent interactions. Reed and co-workers found that solvent effects on the electronic spectrum of C_{60} were greater in CS_2 than in 1,2-dichlorobenzene (band shift of 364 cm^{-1} vs 168 cm^{-1}, respectively), indicating that intermolecular forces are much stronger in CS_2 than in 1,2-dichlorobenzene.[16,17] This observation correlates exceptionally well with our activation energy difference in these two solvents: 17.5 kJ/mol in CS_2 and 7.7 kJ/mol in 1,2-DCB-d_4. When solute−solvent interactions are taken into account, one would then expect C_{60} to experience greater rotational freedom in 1,2-DCB-d_4 than in CS_2. Consequently, shorter rotational times are seen in 1,2-DCB-d_4 than in CS_2.

TABLE 3: Comparison of the Reorientational Times of C_{60} in CS_2 and in 1,2-Dichlorobenzene-d_4

	CS_2		1,2-DCB-d_4	
T (K)	η (cP)	τ_c (ps)	η (cP)	τ_c (ps)
278	0.423	19.8	1.47	12.3
293[a]	0.363	13.3	1.28	10.4
303	0.348	9.50	1.18	9.93
313	0.318	8.86	1.09	8.60

[a] Values at this temperature were interpolated from the graphs given in ref 10.

The theoretical interpretation of the reorientational motion of C_{60} in CS_2 was accomplished by comparing our experimental reorientational times to those predicted by several hydrodynamic-based models. For brevity, we present only essential details regarding the theories employed in this analysis. A much broader treatment can be found in several previous communications.[10,18,19] Theoretically, reorientational correlation times are usually expressed as a sum of a hydrodynamic and an inertial contribution:

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

where r is the radius of the solute molecule (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 molecule (e.g., it is equal to 1 for a sphere), C is an experimentally determined correlation coefficient, 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 frequently ignored. As one can see, a successful theoretical analysis of experimental τ_c values very frequently depends on the interpretation of C. We applied three commonly employed theories in an attempt at analyzing our experimental correlation times. These comparisons are discussed in the following paragraphs.

The first model attempted, and which has been successfully applied in a number of systems, was first proposed by Gierer and Wirtz.[20] According to this theory, C depends only on the

TABLE 4: Comparison of Experimental Correlation Times with Model Predictions at Various Temperatures in CS_2

T (K)	η (cP)	τ_c (ps)	τ_c(GW) (ps)	τ_c(HKW) (ps)	τ_c(SED) (ps)
278	0.423	19.8	5.41	7.24	20.0
293	0.363	13.3	4.40	5.89	16.3
303	0.348	9.50	4.07	5.44	15.1
313	0.318	8.86	3.59	4.81	13.3

solvent-to-solute molecular diameter ratio. For the C_{60} (diameter $= 7.024$ Å) $-$ CS_2 (diameter $= 2.70$ Å) pair, C has a value of 0.373. The Gierer−Wirtz predictions, τ_c(GW), are found in the fourth column of Table 4. On sees that the agreement between τ_c and τ_c(GW) is far from satisfactory. All predicted values are at least a factor of 3 smaller than what is observed experimentally. This lack of agreement indicates that the G−W model overestimates the degree of rotational freedom being experienced by C_{60} in this solvent.

An alternative approach proposed by Hynes, Kapral, and Weinberg (HKW) introduces the concept of a microscopic boundary layer and a slip coefficient (β).[21] In this model f is still unity, but C is defined as $(\beta r/(3\eta + \beta r))^{-1}$. According to this theory, a molecule will experience increasing rotational freedom (i.e., the “slip” limit) as $\beta \rightarrow 0$. The reversed condition (i.e., the “stick” limit) is approached as $\beta \rightarrow \infty$. We used Kivelson’s definition for β to calculate τ_c (HKW) at the various temperatures.[22,23] These quantities are shown in column five of Table 4. Using this model, one observes only slight improvement in the predicted rotational times. In all cases the model underestimates the degree of friction being experienced by C_{60} in CS_2 and thereupon predicts rotational times that are shorter than what is experimentally observed.

Lastly, we applied the Stokes−Einstein−Debye (SED) model to characterize C_{60}’s rotational motion.[24] These predictions, τ_c (SED), are listed in the last column of Table 4. Using this model, one observes improved agreement with our experimental times. One also notices that the agreement becomes noticeably worse with rising temperature. The improved predictions generated by this model were somewhat surprising, since this theory very frequently overestimates experimental results. Nevertheless, the closeness of this fit suggests that C_{60} reorients near the “stick limit” (i.e., C is closer to unity than to zero) where carbon disulfide’s viscosity plays the greater role in determining C_{60}’s rotational behavior.

The fact that these models were unable to generate predictions that were better in line with our experimental correlation times was not completely unexpected, since none of these theories account for the presence of intermolecular interactions. In our opinion, the success of the SED model is somewhat fortuitous, since the velocity coherence predicted by this model is not due to C_{60}’s and CS_2’s separate matched velocities but rather results from the presence of intermolecular interactions.

Conclusions

We have employed the Hubbard relation to acquire semiquantitative information on the ^{13}C spin−lattice relaxation rate of buckminsterfullerene in CS_2. We found the SR mechanism to be operative and its contribution to be significant at all temperatures studied here. With the exception of values at 303 K, we found very different CSA and SR contributions in 1,2-dichlorobenzene-d_4 than in CS_2. In fact, the respective contributions were reversed at 313 K. This observation indicates that solvent effects play an important role in determining how effective these mechanisms will be in a given solvent.

Reorientational correlation times were obtained via the CSA contribution and show that C_{60} is undergoing rapid rotational motion in CS_2. The motion in CS_2 is, however, slower than in 1,2-DCB-d_4. The activation energy for this mode of motion was found to be 17.5 kJ/mol compared to 7.7 kJ/mol in 1,2-DCB-d_4. Of the hydrodynamic-based models employed to characterize the rotational motion of the title molecule, the Stokes−Einstein−Debye (SED) model proved to be slightly better in duplicating our experimental findings. The closer agreement between the SED predictions and our experimental reorientational times suggests that C_{60} reorients in the “stick” limit where solute−solvent velocities are predicted to be similar. We, however, believe that the velocity coherence between C_{60} and CS_2 is not due to their separate matched velocities but rather originates from the presence of intermolecular interactions.

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