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John J. L. Morton,^{1,2,*} Alexei M. Tyryshkin,³ Arzhang Ardavan,^{1,2} Kyriakos Porfyrakis,¹ S. A. Lyon,³ and
G. Andrew D. Briggs¹

¹*Department of Materials, Oxford University, Oxford OX1 3PH, United Kingdom*

²*Clarendon Laboratory, Department of Physics, Oxford University, Oxford OX1 3PU, United Kingdom*

³*Department of Electrical Engineering, Princeton University, Princeton, New Jersey 08544, USA*

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further agglomerate to form “flowerlike” structures with an open hole in the center. In toluene, clusters ranging from 3 to 55 fullerenes have been observed over a dilute range of concentrations (0.18–0.78 mg/ml).¹⁷ This clustering can have important consequences on electron spin relaxation rates, resulting in a distribution of the relaxation times depending on the location of N@C₆₀ within the cluster. An additional complication can arise in samples of higher N@C₆₀/C₆₀ purity—if the large C₆₀ cluster contains two N@C₆₀ molecules, their relaxation will be strongly affected by the dipole-dipole interaction between the two N@C₆₀ electron spins. For example, in a sample of 3% N@C₆₀/C₆₀ purity, we have observed a decrease in T_2 with increasing fullerene concentration above about 0.1 mg/ml.

To eliminate uncertainties associated with C₆₀ cluster formation, dilute solutions with concentrations of less than 0.06 mg/ml were used in this study. High-purity ($\approx 80\%$) endohedral N@C₆₀ was used to prepare samples in toluene, enabling the use of dilute solutions (2 $\mu\text{g}/\text{ml}$) of well-isolated fullerenes, which nevertheless provide a sufficient signal for pulsed EPR experiments. Solutions were degassed by freeze pumping in three cycles to remove paramagnetic O₂. We observe that while samples of N@C₆₀ in CS₂ are stable, the EPR signal from the sample in degassed toluene decayed when exposed to light. The precise nature of this decay is unknown and possibly occurs via the photoexcited triplet state of the C₆₀ cage, leading to the escape of the nitrogen from the cage. Other experimental parameters, including a brief description of the N@C₆₀ spin system are provided elsewhere.⁵ T_2 and T_1

it is concluded that the nature of the solvent-fullerene interaction can distort the icosahedral symmetry, leading to splittings of the H_g Raman transitions.²¹ Consistently, the results here could also be attributed to interactions between the cage and the solvent (e.g., a π -stacking arrangement in the case of the aromatic toluene molecule); the transitions involving the $H_g(1)$ mode may be suppressed, and electron spin relaxation of the endohedral nitrogen takes places more effectively via the higher-energy $A_g(1)$ squeezing mode.

The T_2 relaxation data in Fig. 2 reveal a nonmonotonic temperature dependence in contrast to that observed for N@C₆₀ in CS₂.⁵ In CS₂, a simple ratio of $T_2=2/3T_1$ was found over the broad temperature range, indicating that both T_1 and T_2 are determined by the same Orbach relaxation mechanism. In toluene, T_2 diverges noticeably from the T_1 dependence, indicating that an additional relaxation mechanism must be involved, which suppresses T_2 at low temperatures. In the following discussion, we argue that this additional relaxation mechanism is due to nuclear spins (protons) of the toluene solvent.

In liquid solutions, solvent molecules can diffuse around N@C₆₀. Therefore, the distance between the electron spin of N@C₆₀ and the nuclear spins of toluene molecules changes in time. This results in fluctuating hyperfine (contact and dipolar) fields seen by the electron spin, which can drive its relaxation. In the hard-sphere approximation, the spin-spin separation varies between a value called the *distance of closest approach* (d) and infinity. The translation diffusion time τ_D becomes the important correlation time,⁶

$$\tau_D = \frac{2d^2}{D(T)}, \quad (1)$$

where $D(T)=D_{C_{60}}(T)+D_{tol}(T)$ is the sum of the temperature-dependent diffusion coefficients of the fullerene and toluene molecules. According to common models for diffusion-induced spin relaxation,²²⁻²⁴ the resulting T_1 and T_2 are⁶

$$(T_1)^{-1} = 2\kappa \frac{c(T)}{d \cdot D(T)} 10J(\omega_e), \quad (2)$$

$$(T_2)^{-1} = \kappa \frac{c(T)}{d \cdot D(T)} [4J(0) + 10J(\omega_e) + 6J(\omega_n)]. \quad (3)$$

ω_e and ω_n

vent molecules can provide a significant mechanism for electron spin decoherence, e.g., via the process known as *spectral diffusion*

bach mechanism suggested for N@C₆₀ in CS₂ solution. Apparently, other (yet unidentified) relaxation mechanisms contribute significantly in both solid matrices at low temperatures, resulting in T_1 shorter than what would be expected from the Orbach mechanism alone. Relaxation experiments at different microwave frequencies will be required to shed light on these unidentified mechanisms.

On the other hand, T_2 , when measured on the $M_I=0$ line, shows a minimum at around 100 K, coinciding with the approximate glass transition temperature T_g of the solvent
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