Electron spin coherence in metallofullerenes: Y, Sc, and La@C_{82}

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Endohedral fullerenes encapsulating a spin-active atom or ion within a carbon cage offer a route to self-assembled arrays such as spin chains. In the case of metallofullerenes the charge transfer between the atom and the fullerene cage has been thought to limit the electron spin phase coherence time (T_2) to the order of a few microseconds. We study electron spin relaxation in several species of metallofullerene as a function of temperature and solvent environment, yielding a maximum T_2 in deuterated o-terphenyl greater than 200 μs for Y, Sc, and La@C_{82}. The mechanisms governing relaxation (T_1, T_2) arise from metal-cage vibrational modes, spin-orbit coupling and the nuclear spin environment. The T_2 times are over 2 orders of magnitude longer than previously reported and consequently make metallofullerenes of interest in areas such as spin labeling, spintronics, and quantum computing.

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The possibility of encapsulating an atom inside a fullerene cage was discovered by Heath *et al.*[1] in 1985 and has led to widespread research into these novel materials. Encapsulation of a nitrogen atom within a C_{60} cage (N@C_{60}) has been the subject of particular interest due to the remarkably long electron spin coherence times (T_2) reported from 80 to 250 μs.[2,3] Metallofullerenes, containing metal ions encased in a similar way, benefit from faster purification and higher production yields than N@C_{60}. However, they have not shown particularly long coherence times (<1.5 μs), attributed to much greater spin density on the fullerene cage.[4,5]

The prospect of exploiting the self-assembly of spin-active fullerene molecules into larger structures[6] has stimulated interest in spintronics[7] and quantum information processing (QIP).[8,9] In particular, metallofullerenes can self-assemble within carbon nanotubes in a "peapod" structure, creating a one-dimensional (1D) spin chain.[6,10–12] For the potential of such structures to be fully realized, longer electron spin coherence times are required of the constituent metallofullerenes.

Several electron paramagnetic resonance (EPR) studies have been conducted on the metallofullerenes Sc-, Y-, and La@C_{82} focusing on geometric and electronic properties of the molecules.[4,5,13–18] These, along with x-ray diffraction measurements, have shown the metal atom to be off center in the cage,[19–21] with charge transfer to the cage dependent on the metal ion species.[22] These previous EPR studies have primarily used continuous wave (CW) spectroscopy and few T_2 times have been accurately extracted. Using pulsed EPR, Knorr *et al.* report a T_2 of 600 ns for Sc@C_{82} (in trichlorobenzene solvent at 2.5 K) but a measured T_2 of 4.1 μs in a Y@C_{82} sample was attributed to a "background" signal.[4] Okabe *et al.* report a temperature and m_I dependence of T_1 and T_2 for La@C_{82} (in CS_2) arising from motional effects of anisotropic interactions and coherence times <1.5 μs, in the range 183–283 K.[5]

In this Brief Report, we report pulsed EPR studies of spin relaxation times over a range of temperatures in toluene, deuterated toluene and deuterated o-terphenyl. These are convenient solvents due to their low number of nuclear spins and ability to form a glass at low temperatures, preventing alternative decoherence pathways and clustering (relaxation via dipole-dipole interaction), respectively. We discuss mechanisms governing decoherence (T_2) and relaxation (T_1) for different solvents and metallofullerenes species. We find that under optimized conditions, spin coherence times can exceed previously reported values by over two orders of magnitude, rising to over 200 μs.

Experiments were conducted at X-band (9–10 GHz) using a Bruker Elexsys pulsed EPR spectrometer. T_1 and T_2 were measured by standard inversion recovery ($\pi-\tau-\pi/2-T-\pi-T-echo$) and Hahn echo techniques ($\pi/2-\tau-\pi-\tau-echo$) [23] with a $\pi/2$ pulse length of 40 ns. Dilute solutions of Y-, Sc-, and La@C_{82} (10^{-6}–10^{-7} M) were prepared in toluene, deuterated toluene and deuterated o-terphenyl, and degassed using several freeze-pump-thaw cycles. Samples were flash frozen using liquid N_2 to produce a glass. ^{45}Sc and ^{139}La are both nuclear spin $I=7/2$, while ^{89}Y has $I=1/2$ (each of these isotopes has 100% natural abundance). In liquid solution, the isotropic hyperfine structure is clearly visible for all samples but in frozen solutions an anisotropic powder pattern results for Y- and La@C_{82} from which individual m_I lines cannot be resolved, as previously shown.[4] In Sc@C_{82} the strong hyperfine coupling can be more clearly resolved[17] and relaxation measurements were conducted on the $m_I=1/2$ line, and on the $g_\perp$ peak for Y- and La@C_{82}. The broad background as seen by Knorr *et al.*[4] was not observed.

The g factors for each metallofullerene were obtained by fitting CW data using Easyspin[24] giving, (g_x, g_y, g_z) $=(2.0022, 2.0023, 1.9974)$, (1.9969, 2.0036, 1.9999) and (2.0060, 2.0044, 1.9980) for Y-, Sc-, and La@C_{82}, respectively. These are in good agreement with previous studies.[4,17] The hyperfine tensor for Sc@C_{82} is found to be $A=[15.4, 7.8, 7.3]$ MHz in agreement with Morley *et al.*[17] but in contrast to Knorr *et al.*[4] where hyperfine coupling was not resolved.

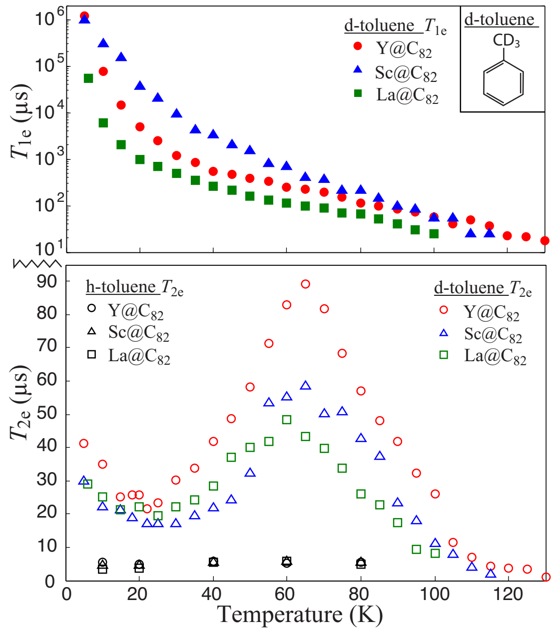

FIG. 1. (Color online) T_1 (top, closed shape) and T_2 (bottom, open shape) as a function of temperature for $Y@C_{82}$ (circle), $Sc@C_{82}$ (triangle), and $La@C_{82}$ (square) in deuterated toluene. T_2 in h-toluene in black shape. T_1 and T_2 shown on different y scales for clarity. Insert: Structural representation of d-toluene.

Figure 1 shows T_1 and T_2 measured as a function of temperature in h- and d-toluene. T_1 increases monotonically with decreasing temperature through mechanisms discussed below. T_2 in h-toluene is fairly independent of temperature and limited to <6 μs due to spectral diffusion, a mechanism whereby nuclear spin flips produce a fluctuating local magnetic field that drives electron spin decoherence.[25,26] This is identified by a characteristic stretched exponential decay:

$$I(t) = I(t_0)e^{-(t/T_2)^x}, \quad (1)$$

with $x>1$. This decoherence mechanism is suppressed for metallofullerenes in d-toluene, due to the much weaker nuclear magnetic moment of deuterium. In this deuterated solvent the measured T_2 is longer and a monoexponential decay $(x=1)$ is observed for $T>40$ K. T_2 passes through a maximum around 60–70 K of approximately 50, 60, and 90 μs for $La@C_{82}$, $Sc@C_{82}$, and $Y@C_{82}$, respectively. This is over an order of magnitude longer than previously reported. The longer coherence times of $Y@C_{82}$ can be attributed to the weaker hyperfine coupling and smaller nuclear spin of Y compared to Sc and La.

The decrease in T_2 below 60–70 K reflects the emergence of an alternative relaxation mechanism independent of the metal ion species, leading to a similar T_2 value for all three metallofullerenes at around 20 K. A prime candidate is the slow rotation of the toluene solvent methyl group which drives deuterium nuclear spin flips and electron spin decoherence via spectral diffusion.[27] The deuterium spin flip rate is maximized at $\omega_a^{-1}=\tau_c$, where ω_a is the deuterium Larmor frequency (2 MHz in the 0.35 T field used here) and τ_c the correlation time.[27] We assume an Arrhenius temperature dependence for τ_c with an energy barrier equivalent to 150–160 K and $\tau_{\infty,c}^{-1}=10^{12}$ s^{-1}.[28] Thus, the maximum spin flip rate, corresponding to a minimum in T_2, will occur at about 14 K (where $\tau_c^{-1}=1.4\times10^7$ s^{-1}) slightly lower than the value of $\sim$20 K predicted by our measurements.

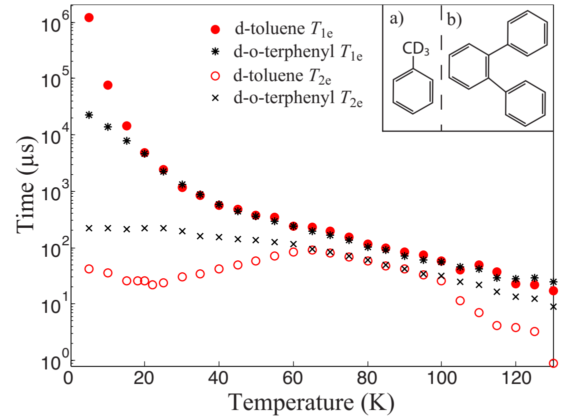

FIG. 2. (Color online) $Y@C_{82}$ relaxation and coherence times as a function of temperature in deuterated toluene (circle, T_1 closed, T_2 open) and deuterated o-terphenyl (symbol black, T_1 star, T_2 cross). Insert: Structural representation of a) d-toluene and b) o-terphenyl.

To overcome this decoherence mechanism and extend T_2 further we chose deuterated o-terphenyl, which contains no methyl groups, as a suitable glass-forming solvent for fullerenes. The T_1 and T_2 times for $Y@C_{82}$ in this solvent and d-toluene are compared in Fig. 2 (we observed similar results for La and $Sc@C_{82}$). T_1 is largely the same for both solvents, with a deviation at temperatures below 15 K. As predicted, the drop in T_2 observed in d-toluene as the temperature is reduced below 65 K is not observed in deuterated o-terphenyl, due to the absence of methyl groups in this solvent. In the range $T<65$ K, T_2 rises slowly with decreasing temperature, and fits well to a stretched exponential in which the stretching factor increases from $x=1$ at 65 K to a limit of $x\approx1.7$ at low temperatures. We attribute this new limit to the emergence of spectral diffusion from the deuterium nuclear spins in the frozen solvent environment.

In the range from 65 to 100 K, T_2 fits to a monoexponential decay and reveals the same coherence times as d-toluene, which appear to be determined by T_1 relaxation, discussed below. Above 100 K, the T_2 values of the two solvents again deviate, which can be associated with the different glass transition temperatures (T_g), where $T_g=117$ K for toluene and 243 K for o-terphenyl.

In these optimized conditions, we have measured a maximum T_2 of 225 ± 7, 245 ± 9, and 204 ± 2 μs for $Y@C_{82}$, $Sc@C_{82}$, and $La@C_{82}$, respectively at 5–10 K, with $x=1.6-1.7$. A typical electron spin echo decay trace is shown in Fig. 3, and fits well to a simple stretched exponential, or a decay of the form:

$$I(t) = I(t_0)e^{-(t/T_{2,\mathrm{int}})-(t/T_{SD})^2} \quad (2)$$

from which an intrinsic $T_{2,\mathrm{int}}$ can be extracted, as the T_{SD} term accounts for spectral diffusion.[26] This gives $T_{2,\mathrm{int}}=610\pm80$ μs, offering an estimate of the decoherence

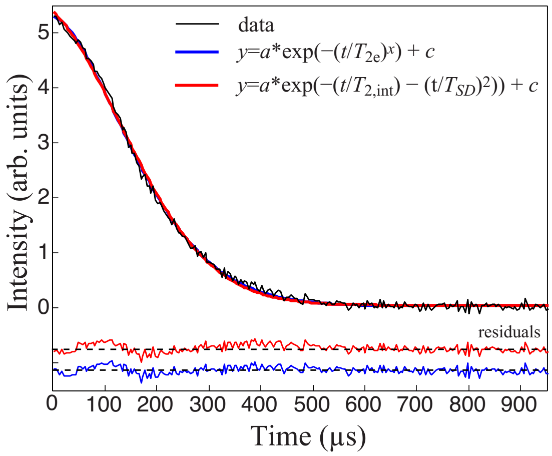

FIG. 3. (Color online) Hahn echo decay for La@C_{82} at 10K, data (black) showing spectral diffusion and fit with a stretched exponential decay [blue (dark gray)] and a curve to extract the intrinsic T_2 in the limit of no environmental nuclear spins [red (gray)]. Curves are similar and thus overlap, the residual to the fits is shown at the bottom of the figure.

time in the absence of spectral diffusion, i.e., if all environmental nuclear spins were removed ($T_{SD}=249\pm 7\ \mu s$).

In contrast to T_2, measurements of T_1 are relatively independent of the solvent environment (see Fig. 2), indicating that over the range 20 to 130 K the glass matrix does not have a dominant effect on relaxation. Figure 1 (top) further shows there is a systematic shift in both the magnitude and temperature dependence of T_1 which follows the increasing mass of the ions. In the N@C_{60} fullerene, electron spin relaxation has been found to show an Arrhenius-type temperature dependence corresponding to a two-phonon relaxation process via the vibrational motion of the cage.[2] This has the form:

$$T_1 \propto e^{(\Delta/k_B T)} - 1, \quad (3)$$

where Δ is the energy of the molecular vibrational mode. The temperature dependence of T_1 in Y-, Sc-, and La@C_{82} can be described by two such processes over the range of 15 to 100 K, as shown in Fig. 4. The extracted vibrational mode

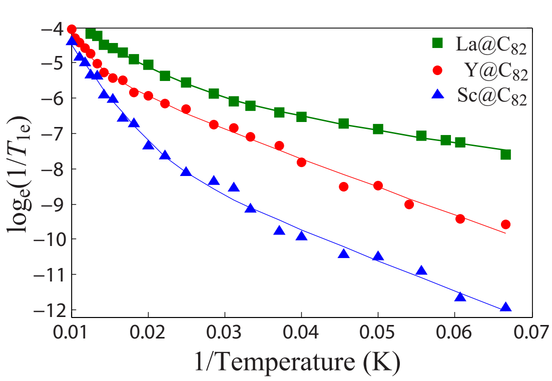

FIG. 4. (Color online) T_1 fit to two Arrhenius dependent mechanisms for La@C_{82} (square), Y@C_{82} (circle), and Sc@C_{82} (triangle) in d-toluene. The resonant frequencies extracted from the slope of the lines are shown in Table I

TABLE I. Extracted molecular vibrational modes from fitting T_1 temperature dependence in the range 15–100 K, following Eq. (3).

Mode	Wave number (cm^{-1}) Y@C_{82}	Sc@C_{82}	La@C_{82}
ν_1	54 ± 4	59 ± 8	19 ± 5
ν_2	403 ± 214	229 ± 43	125 ± 33

energies for each of the two processes are shown in Table I. Below 20 K, an additional relaxation mechanism is present arising from the glassy solvent environment, particularly effective in the case of the deuterated o-terphenyl solvent.

The resonant frequencies can be compared to far infrared (FIR) and Raman studies of metallofullerenes that have shown frequencies $<200-300\ cm^{-1}$ to be characteristic of metal-cage vibrations.[29–31] If metal-cage motion is considered in terms of a simple linear oscillator model, the vibrational frequency (ν) would be proportional to $\mu^{-1/2}$ (where μ is the reduced mass). Thus, one would expect the wave number to follow La<Y<Sc as observed for the extracted low frequency mode (ν_1) in Table I. The experimental data will deviate from this model due to, for instance, charge transfer, which is known to be quite different for the metallofullerenes studied.[22,30] However, the general trend holds and therefore is a good indicator that ν_1 may be due to metal-cage vibrations.

Lebedkin *et al.* identify a mode for Y@C_{82} at 54 cm^{-1} which they attribute to a "lateral" metal-cage vibration,[29] in good agreement with the Y@C_{82} extracted vibrational mode ν_1. Similar experimental data on La@C_{82} is less conclusive, with a broader mode centered at ~45–50 cm^{-1} for La@C_{82} (Ref. 29), though theoretical studies have predicted 'lateral' La-cage modes at 27 and 30 cm^{-1} (Ref. 32), slightly higher than our extracted value. This lateral metal-cage mode in La@C_{82} has also been identified using x-ray powder diffraction maximum entropy method (MEM) analysis,[19] where a large charge density distribution was attributed to "giant motion." La would therefore be expected to give a significantly lower metal-cage frequency than from the tight distribution observed for Sc and Y in the C_{82} cage,[20,21] consistent with our results. It therefore appears that the lower frequency excited state (ν_1) may be due to metal-cage vibrational modes and that this is the dominant cause of T_1 relaxation in the system over the temperature range 15–60 K.

Above this temperature, the data can be fit by a higher resonant frequency (ν_2) (Fig. 4), though this value is harder to interpret as it may derive from a combination of many higher energy cage vibrational modes. However, ν_2 in La@C_{82} could correspond to the "longitudinal" metal-cage vibrational mode observed at 163 cm^{-1}.[29] In addition to the different slopes in the temperature dependence of T_1, the magnitude of T_1 follows La>Y>Sc in accordance with the varying extent of charge transfer between the metal and cage.[22] This charge transfer would increase the spin orbit coupling to these molecular vibrational modes, giving the observed order of T_1^{-1} La>Y>Sc.

In conclusion, we have found long coherence times (T_2) over 200 μs for all Group III (Sc, Y, La) metallofullerenes limited by spectral diffusion. We have shown T_1 to depend on metal ion mass and charge state, with evidence that it is driven by metal-cage vibrations. The long coherence times observed, combined with the ability to manipulate spins within tens of nanoseconds put metallofullerenes in a regime where quantum error correction is feasible.[33] Our identification of the relevant decoherence mechanisms will help inform the choice of structure for larger fullerene arrays. In addition to potential applications in quantum information and spintronics, these long coherence times could make metallofullerenes a candidate EPR spin label.

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