Orientational Dynamics of the Sc_3 Trimer in C_{82}: An EPR Study

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Electron paramagnetic resonance experiments on endohedral Sc_3 in C_{82} show 22 hyperfine coupling split transitions with unusually large linewidths. Both the nuclear hyperfine coupling and the linewidths are found to be strongly temperature dependent. The data show that the three Sc ions are equivalent, and strongly suggest that they form a trimer which rapidly reorients within the C_{82} cage. A simple model is proposed which is in good agreement with the data.

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Shortly after the discovery of the fullerenes, it was proposed that these cagelike all-carbon molecules can encapsulate atoms or even small molecules [1]. Subsequent experimental results [2,3] have strongly indicated the existence of such endohedral fullerenes (EF's), the most direct evidence being perhaps a recent high resolution electron microscopy study of Sc_2 in C_{84} ($Sc_2@C_{84}$) crystals, showing scattering from the Sc ions *inside* the C_{84} cage [4]. Although many atoms have been encapsulated, research has mainly concentrated on the La, Y, and Sc EF's [2]. Interest in this new class of molecules has partly been inspired by the idea that the properties of EF's could be deliberately altered by using various encapsulated species, for example, rare earth ions with interesting magnetic and optical properties or perhaps dipolar molecules. Evidence that some EF's (such as $La@C_{82}$) have cages in a 3^- valence state led to suggestions that solid EF's might superconduct at relatively high temperatures, as do various alkali-doped C_{60} crystals [5]. However, magnetization experiments on $Sc_3@C_{82}$, the material used in the present study, did not show a superconducting transition for temperatures above 4.2 K. The highly anharmonic potential for the metal atoms in metallofullerenes leads to the expectation that these species will exhibit novel dynamical properties. Calculations on $Na@C_{60}$ [6] and $Li@C_{60}$ [7], for example, predicted new types of vibrations in these EF's, with the encapsulated atoms "rattling and rolling" inside the fullerene cage. In the present Letter we focus on the dynamical properties of the metallofullerene $Sc_3@C_{82}$. A systematic study was made of the electron paramagnetic resonance (EPR) spectrum of this species for temperatures varying from 77 to 333 K. The observed spectra exhibit anomalously large linewidths, and both the linewidths and the nuclear hyperfine coupling have anomalous temperature dependences. We propose that these unusual properties arise from the reorientational dynamics of the Sc_3 trimer inside the C_{82} cage.

$Sc_3@C_{82}$ samples were obtained from soot produced by arc burning cored graphite rods packed with a mixture of powdered graphite and scandium oxide and purified using high performance liquid chromatography separation with on-line EPR detection [8]. Mass spectroscopy showed a sample purity of 80%, with empty C_{2n} cages as the major impurities, and EPR spectra showed no active metallofullerenes other than $Sc_3@C_{82}$. For the EPR experiments, dilute solutions of $Sc_3@C_{82}$ in decaline or toluene were thoroughly degassed and sealed in quartz tubes. EPR spectra were recorded using a Varian E209 EPR spectrometer operating at 9.125 GHz, with the sample mounted in a continuous nitrogen flow cryostat. Temperature stabilization was better than 1 K.

Figure 1(a) shows an EPR spectrum of a dilute solution of $Sc_3@C_{82}$ in supercooled decaline at $T = 193$ K. The figure shows an isotropic spectrum with Lorentzian line shapes, which closely matches the spectrum expected for an unpaired spin $S = 1/2$ with hyperfine coupling to three *equivalent* ^{45}Sc nuclei ($I = 7/2$, 100% abundance) [9]. The g factor for $Sc_3@C_{82}$ is found to be 1.9985. Each line can be indexed by the magnetic quantum number for the total nuclear spin state, $m_i = -21/2, -19/2, \ldots, 21/2$, giving a total of 22 lines. The transitions are equally spaced in magnetic field, have equal linewidths (Γ), and have intensities in good agreement with the spin adding statistics for three Sc nuclei (dashed envelope function). No ^{13}C hyperfine splitting is observed in the spectrum. A striking feature of this spectrum is the rather large width of the lines, ~0.8 G, more than 1 order of magnitude greater than the linewidths found for $Sc_3@C_{82}$, for instance [10]. Such large linewidths could be due to incomplete motional averaging of local field variations due to strong magnetic anisotropy of the entire molecule. For rotation correlation times τ_b comparable to the microwave period, this effect leads to a broadening proportional to τ_b [11]. However, experiments on $Sc_3@C_{82}$ in toluene, which at room temperature has a viscosity approximately 3 times smaller than decaline and a correspondingly smaller orientational correlation time, show a change in Γ of only about 10%.

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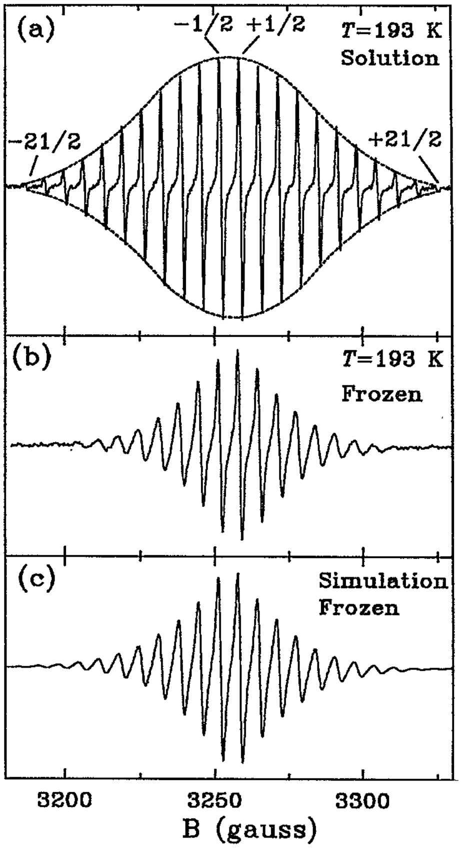

FIG. 1. EPR spectrum of $Sc_3@C_{82}$ in (a) fluid and (b) frozen decaline at $T = 193$ K. Some of the nuclear magnetic quantum numbers of the states involved in the transitions are indicated in (a). The dashed line is the envelope of a simulation of the fluid spectrum. (c) Simulation of the frozen spectrum as discussed in the text.

Hence Brownian motion in combination with molecular magnetic anisotropy can explain only a minor part of the observed linewidth. We are thus led to consider a second possible origin of the large linewidth: reorientational motion of the scandium ions within the cage.

Support for the idea that there is rapid internal scandium motion is provided by examining the EPR spectrum of $Sc_3@C_{82}$ in frozen decaline. In this case one expects that the C_{82} cage motion is at least partially frozen out. An example of a spectrum of $Sc_3@C_{82}$ in frozen decaline is shown in Fig. 1(b) for $T = 193$ K. Instead of a spectrum completely broadened due to magnetic anisotropy, one still observes a large number of equidistant lines that are best described by Lorentzians, confirming that rapid reorientational motion is still present. This remains the case at least down to $T = 100$ K. Only at liquid nitrogen temperature was a completely broadened spectrum obtained, consisting of a single resonance line with a width comparable to the total width of the isotropic spectrum. This suggests that the barrier to Sc motion within the cage is small.

The spectrum in Fig. 1(b) differs from the spectrum in Fig. 1(a) in several respects. The linewidths are no longer equal, and they now show a strong dependence on the nuclear magnetic quantum number m_i of the states involved in the transitions. A similar m_i dependence is observed in liquid spectra at lower temperatures. Figure 2 shows the m_i dependence of the linewidth for several temperatures, for both the liquid and frozen states. Γ exhibits a roughly linear dependence on the *absolute value* of m_i both in the frozen state, as well as in the liquid state at lower temperatures. Since the hyperfine spacings are still equal, this dependence apparently does not arise from inequivalence of the Sc atoms. As will be discussed below, the m_i dependence of the linewidth can be related to modulation of the hyperfine coupling by reorientational motion of the scandiums with the C_{82} cage.

Both the linewidth and the hyperfine coupling show a strong temperature dependence. Figure 3, for example, shows the temperature dependence of the linewidth of the $m_i = 1/2$ line (see Fig. 1) of $Sc_3@C_{82}$ in fluid (filled circles) and frozen decaline (open circles). In the liquid state, the linewidth increases both toward higher and lower temperatures with a minimum at ~200 K. In general the linewidth in the frozen state is larger due to the absence of reorientational magnetic averaging by the Brownian motion of the molecules. The increase in linewidth toward lower temperature can be understood in terms of an increasing orientational correlation time for the molecules, leading eventually to the anisotropic spectrum observed at 77 K. On the high temperature side, the increasing linewidth results from spin-rotational interactions [12].

The temperature dependence of the ^{45}Sc hyperfine coupling a_{hfc} is shown in Fig. 4 (filled circles). The coupling strength varies linearly with temperature from 6.22 G at $T = 333$ K to 680 G at $T = 103$ K and essentially is the

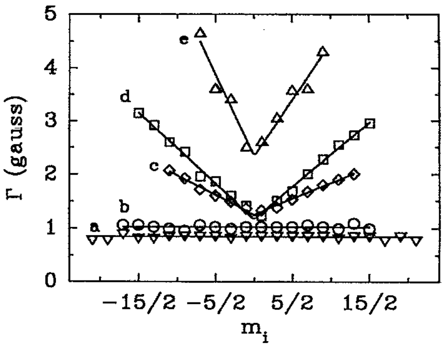

FIG. 2. Dependence of the linewidth for $Sc_3@C_{82}$ in liquid [(a) 293 K, (b) 183 K, (c) 153 K] and frozen [(d) 183 K, (e) 113 K] decaline on the Sc_3 nuclear magnetic quantum number. The solid lines are fits to the data of the dynamic model discussed in the text.

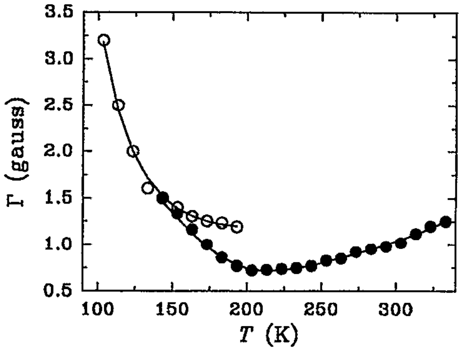

FIG. 3. Temperature dependence of the linewidth of the $m_I = +1/2$ (see Fig. 1) EPR transitions for $Sc_3@C_{82}$ in frozen (filled circles) and fluid (open circles) decaline. The solid lines are fits of the dynamical model discussed in the text to the data.

same in both the liquid and frozen states. As detailed below, this rather strong temperature dependence can be attributed to fluctuations in the hyperfine coupling due to the reorientational motion of the Sc ions [13].

To explain the observations discussed above , we propose the following simple model. The observed spectra show that the Sc ions are equivalent. They must either form an equilateral triangle inside the cage or move sufficiently rapidly to give equivalence on the time scale of the EPR experiment, even down to temperatures of ~100 K. The hyperfine coupling constant observed for the Sc-trimer in C_{82} is similar to that found in matrix isolation EPR experiments on Sc trimers (8.5 G [14]), as is its g value. It therefore seems reasonable to assume that the Sc ions form a trimer inside the fullerene cage.

Calculations on metallofullerenes have shown that there are typically several local potential minima for the metal atom, with a local maximum in the center of the cage [15]. For the $Sc_3@C_{82}$ case, a likely possibility is that the Sc atoms form an equilateral triangle centered in the cage. Theoretical calculations on the Sc_2 dimer found a Sc-Sc distance of 2.7 Å [16]. Using this value for the Sc-Sc distance in the Sc_3 trimer, and estimating the C_{82} cage diameter to be ~8.3 Å, one finds a minimum Sc-C distance of ~2.8 Å. Since this is a fairly large distance compared to the Sc-C distance in scandium carbide, for instance (2.3 Å [17]), the interaction with the cage may be rather weak, with a relatively low energy barrier for reorientational motions of the Sc_3 trimer around its threefold axis and possibly even for tumbling about an orthogonal axis. The orientational correlation time for such tunneling motion can be expressed as $\tau_t = \tau_0 \exp(E_t/kT)$, where E_t is the height of the reorientational potential barrier and τ_0 depends on the details of the potential [18].

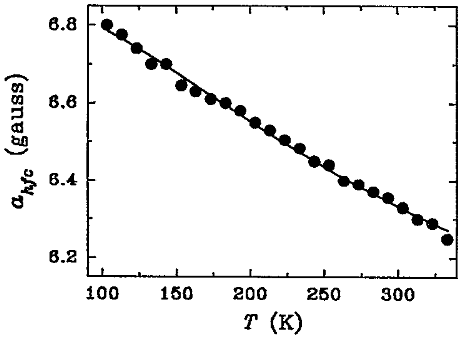

FIG. 4. Temperature dependence of the nuclear hyperfine coupling observed for $Sc_3@C_{82}$ in liquid and frozen decaline. The solid line is a fit to the data of the dynamical model discussed in the text.

In order to understand the broadening of the EPR transitions observed in $Sc_3@C_{82}$, we consider several mechanisms that are likely to be dominant: anisotropy broadening, spin-rotational interactions, and modulations of the hyperfine coupling. To first order the temperature dependence of the overall linewidth can be expressed as [13]

$$\Gamma(T) = C^{\mathrm{ani}}\tau + \frac{C^{\mathrm{rot}}}{\tau}, \qquad (1)$$

where τ is an orientational correlation time, C^{ani} describes the magnetic anisotropy and the modulation of the hyperfine coupling, and C^{rot} is the spin-rotational interaction. The temperature dependent quantity in this equation is the correlation time. For the motion of the Sc trimer with respect to the C_{82} cage, the appropriate correlation time is τ_t. For Brownian motion, one has $\tau_b = 4\pi R^3 \eta / 3k_b T$, where R is the hydrodynamic radius of $Sc_3@C_{82}$ [13]. Since in frozen decaline one expects only reorientational motions of the Sc ions to be important, one can use Eq. (1) with $\tau = \tau_t$ to describe the temperature dependence of the linewidth. In solution we must generalize Eq. (1) to include Brownian motion of the entire molecule. If one assumes that the dominant magnetic anisotropy is that of the Sc trimer, which is justified by the absence of g-factor broadening over most of the temperature range, then the temperature dependence can be expressed as

$$\Gamma(T) = C^{\mathrm{ani}} \left\{ \frac{1}{\tau_t} + \frac{1}{\tau_b} \right\}^{-1} + \frac{C^{\mathrm{rot}}_{\mathrm{Sc}}}{\tau_t} + \frac{C^{\mathrm{rot}}_{82}}{\tau}, \qquad (2)$$

where there are now two types of spin-rotational interactions, one with the Sc trimer and one with the fullerene cage, and where the correlation time associated with the anisotropy broadening is a composite of τ_t and τ_b.

We have simultaneously fitted Eqs. (1) and (2) to the linewidth data for $Sc_3@C_{82}$ in frozen and fluid decaline, respectively. In the fits we used the viscosity data of Ref. [19], extrapolating to the low temperature region where no data are available. The result shown in Fig. 3 (solid lines) is clearly in good agreement with the data. From the fit we find a reorientational barrier height of 28 meV (330 K), a reasonable value for the model discussed above. The fit shows that the contribution of the

Brownian motion to the broadening is small relative to the contribution due to the tunneling of the Sc ions, consistent with the weak viscosity dependence of the linewidths. From the fit we estimate the orientational correlation time for the Sc trimer to be $\tau_t \sim 5 \times 10^{-9}$ s at $T = 200$ K.

The observed temperature dependence of the hyperfine interaction (Fig. 4) can also be accounted for in terms of the tunneling motion of the Sc trimer. The reorientational motion will modulate the hyperfine coupling constant. On average, the Sc trimer will be in a given potential minimum with a hyperfine coupling a_0 for a time τ_t and for a short time Δ in a transition state characterized by a hyperfine coupling a_1. This leads to a time averaged hyperfine coupling given by

$$a_{\mathrm{hfc}}(T) = \frac{\tau_t a_0 + \Delta a_1}{\tau_t + \Delta} \approx a_0 + \frac{\Delta}{\tau_t}(a_1 - a_0) . \qquad (3)$$

Indeed, with the barrier height of 330 K obtained from the fit to the linewidth data, this leads to an approximately linear temperature dependence of the hyperfine constant within the measured range. Fitting Eq. (3) to the data gives a satisfactory result (see Fig. 4, solid line) with $a_0 = 6.85$ G.

When the reorientation rate slows down, the hyperfine coupling modulation will affect not only the observed splitting, but also the linewidths of the transitions. This broadening mechanism will become increasingly important for lines with increasing m_i. This is evident if one allows for higher order hyperfine effects in the position of the lines and their linewidth. Phenomenologically the contribution to the linewidth due to hyperfine fluctuations δa can be written as [13,20]

$$\begin{aligned}\delta\Gamma &= \left| \frac{\partial H_r}{\partial a_{\mathrm{hfc}}} \right| \delta a \\ &= \mathrm{sgn}(m_i) \left(m_i + \frac{a_{\mathrm{hfc}}}{H_r} [I(I+1) - m_i^2] \right) \delta a , \qquad (4)\end{aligned}$$

where H_r is the magnetic field at resonance and I is the nuclear magnetic moment. Simulations of the low temperature spectra with $\delta a \sim 0.2$ G at 193 K, for example, show good agreement with the data, as can be seen from the simulated spectrum in Fig. 1(c), and the fits of the m_i dependence of the linewidth shown in Fig. 2. The simulations also allow for a determination of the sign of the nuclear hyperfine interaction, which is found to be positive.

In summary, from the data presented in this Letter we conclude that the Sc ions reorient rapidly inside the encapsulating C_{82} cage. The temperature dependence of both the nuclear hyperfine coupling as well as the linewidths predicted by the tunneling model presented here are found to be in good agreement with the data. We find a reorientational energy barrier for the Sc ions of 28 meV and an estimated correlation time of $\sim 5 \times 10^{-9}$ s at $T = 200$ K.

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