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C₆₀ solid state rotational dynamics and production and EPR spectroscopy of fullerenes containing metal atoms

Robert D Johnson†, Costantino S Yannoni†, Mattanjah S de Vries†, Harry C Dorn‡, Jesse R Salem† and Donald S Bethune†

† IBM Research Division, Almaden Research Center, 650 Harry Road, San Jose, CA 95120-6099, USA

‡ Department of Chemistry, Virginia Polytechnic Institute, Blacksburg, VA 24061, USA

Abstract. The narrow single-line NMR spectrum of solid C₆₀ at ambient temperature demonstrates that the molecules rapidly reorient within the crystal lattice. The rate of this motion can be quantitatively probed using solid-state NMR by measuring the relaxation rate, $1/T_1$. The dominant contribution to this rate at ambient temperature arises from the combination of rotation and chemical shift anisotropy (CSA). The contribution, $1/T_1^{\text{CSA}}$, is isolated by measuring the magnetic field dependence of T_1 , allowing the molecular reorientational correlation time, τ , to be determined from T_1^{CSA} and the CSA tensor components. At 283 K $\tau = 9.1$ ps, only three times longer than the calculated τ for free rotation, and shorter than the value measured for C₆₀ in solution (15.5 ps). This τ corresponds to a rotational diffusion constant $D = 1.8 \times 10^{10} \text{ s}^{-1}$. Below 260 K a second phase with a much longer reorientation time is observed, consistent with recent reports of an orientational phase transition in solid C₆₀. In both phases τ shows Arrhenius behaviour, with apparent activation energies of 1.4 and 4.2 kcal mol⁻¹ for the high-temperature (rotator) and low-temperature (ratchet) phases, respectively. Recently we succeeded in producing quantities of fullerene cages containing metal atoms sufficient to allow the first characterization of such a species by electron spin resonance spectroscopy. The EPR spectrum of La@C₈₂ shows an octet of lines centered in the region characteristic of fullerene anion radicals, with a small hyperfine splitting which indicates that the spin is predominantly associated with the carbon shell, leaving the lanthanum atom in its preferred +3 oxidation state.

1. Rotational dynamics of C₆₀ in the solid state

The spectrum of solid C₆₀ changes very dramatically as a function of temperature [1, 2]. At ambient temperature a single relatively narrow peak is found at 143 ppm, implying that the molecules reorient rapidly and isotropically in the solid. For stationary randomly oriented molecules, variation in the magnetic shielding of a nucleus with molecular orientation (chemical shift anisotropy or CSA) leads to a broad characteristic powder pattern [3, 4]. Such a powder pattern does develop as a C₆₀ sample is cooled, and by 77 K the narrow peak is gone. A fit of the powder pattern [1] yields an asymmetric chemical shift tensor with principal values 220, 186 and 25 ppm, similar to values found for aromatic carbons [3, 4].

The evolution of the spectrum from a narrow peak reflecting rapid rotation to a spectrum reflecting static molecules, with both spectra superimposed for a range of temperatures, reflects the coexistence of a mobile

phase with a phase in which molecular rotation is inhibited [1, 5, 6]. NMR can be used to quantitatively characterize the dynamics of both of these phases. In particular, the relaxation rate of NMR magnetization depends on the intensity of magnetic field fluctuations which are governed by the motional dynamics. At sufficiently high magnetic fields ¹³C NMR relaxation for C₆₀ is dominated by the CSA mechanism, which arises when the combination of molecular rotation and CSA modulates the effective magnetic field, causing relaxation. The CSA contribution to the relaxation rate is uniquely proportional to the square of the external magnetic field; thus by measuring the relaxation rate at various magnetic fields the CSA contribution can be precisely obtained [7].

Measurements of the T_1 relaxation rate were carried out using the inversion-recovery experiment at four magnetic field strengths. At 283 K monocomponent relaxation behaviour was observed. The relaxation rate shows a strong field dependence, linear with the square

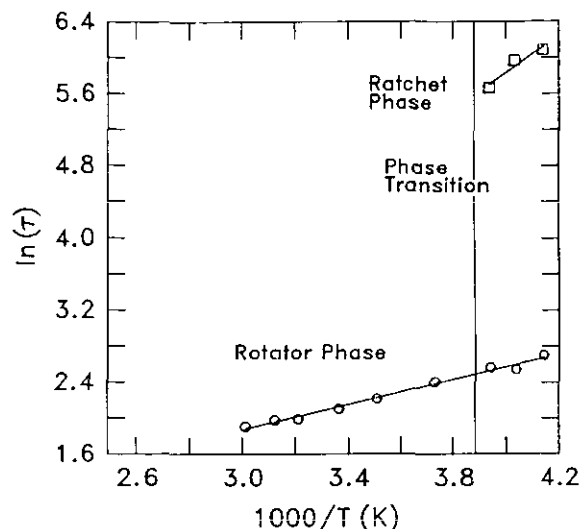


Figure 1. Arrhenius plot of $\ln(\tau)$ versus $1000/T$ for the ratchet and rotator phases, with slopes giving activation energies of 4.2 and 1.4 kcal mol⁻¹, respectively. τ is in ps.

of the field, with a slope of 0.191 ± 0.003 mHz T⁻². From this data and the measured components of the chemical shift tensor, the rotational correlation time τ can be calculated [8, 9]. We obtain a rotational correlation time $\tau = 9.2 (\pm 2)$ ps at 283 K, corresponding to a rotational diffusion constant $D \equiv 1/6\tau = 1.8 \times 10^{10}$ s⁻¹. This is an extremely short rotational correlation time, comparable to those found for small molecules in solution. The corresponding correlation time calculated for C₆₀ in the gas phase is 3.1 ps, only three times shorter than the value we measure in the solid. Similar experiments carried out on C₆₀ in solution (1, 1, 2, 2-tetrachloroethane) at 283 K yield $\tau = 15.5$ ps, significantly slower than the solid phase result.

Recently Heiney *et al* [5] found from x-ray studies and calorimetry that solid C₆₀ exhibits a phase transition near 249 K, from a simple cubic structure at low temperatures to a FCC structure. This transition was examined using NMR by Tycko *et al* [6], who found a sharp break in the T_1 relaxation rate at the transition. These papers suggest that the phase above the transition temperature is characterized by free rotation or rotational diffusion (the 'rotator' phase), and the phase below the transition is characterized by jump rotational diffusion between symmetry equivalent orientations (the 'ratchet' phase). Inversion-recovery experiments below the transition show the appearance of the ratchet phase, which is characterized by much more efficient relaxation, and hence much slower reorientation (relative to the rotator phase). Figure 1 shows the dependence of $\ln(\tau)$ on $1/T$ for both phases. For the high-temperature rotator phase (lower set of points), measurements were made in the temperature range 241–331 K, both above and below the phase transition (indicated on the plot by the vertical line). Over this temperature range τ varies from 14.9 to 6.8 ps. The faster ratchet phase CSA relaxation rates correspond to much longer correlation

times: τ varies from 0.44 to 0.29 ns as the temperature increases from 241 to 254 K. The slopes of the fit lines yield apparent activation energies of 1.4 kcal mol⁻¹ for the rotator phase and 4.2 kcal mol⁻¹ for the ratchet phase for our sample. The orientational ordering for the ratchet phase results in a potential energy surface with deep minima. In contrast, in the rotator phase random orientation of nearest neighbour molecules leads to a much smoother potential energy surface and correspondingly faster reorientation. Evidence indicating the physical origin of the deep minima in the oriented phase was recently obtained by David *et al* [10] who used neutron diffraction to show that in the ordered phase electron-rich double bonds are positioned adjacent to the electron-poor centers of pentagonal rings on neighbouring molecules, giving favourable Coulomb interactions.

2. Fullerenes containing metals: EPR of La@C₈₂

The provocative conjecture that it may be possible to trap atoms and molecules inside fullerene cages [11], initially supported by mass spectroscopic studies [12], has subsequently been corroborated by photofragmentation, reactivity and dissociation experiments [13, 14]. These results provide compelling evidence that metal atoms can indeed be trapped inside carbon cages. A nomenclature for these moieties has been suggested: M@C_n for a metal atom M contained in C_n fullerene [15].

The first study of the detailed structure of these remarkable species was made on a bulk sample of La@C₈₂ using electron paramagnetic resonance (EPR) spectroscopy [16]. For these experiments, bulk samples were prepared by arc burning of a composite rod of graphite and La₂O₃. The mass spectrum of the toluene extract of the soot from this burning showed only C₆₀, C₇₀ and La@C₈₂. The X-band EPR spectrum of the solid extract is shown in figure 2(a). The spectrum is centered at $g = 2.001$, close to the value found for fullerene radical anions [17–20]. The spectrum has an overall width of 10 gauss, with a hint of rich structure. The EPR spectrum of a degassed solution of the extract in 1, 1, 2, 2-tetrachloroethane, shown in figure 2(b), consists of eight extremely narrow (0.125 gauss) equally spaced (1.25 gauss interval) lines of equal intensity centered at $g = 2.0010$, with several weak satellite lines on either side of each large peak. The main eight-line spectrum is unambiguously diagnostic for isotropic hyperfine coupling of an electron spin to a nuclear magnetic moment with spin $\frac{7}{2}$ [21], the value for the ¹³⁹La nucleus. This proves that the unpaired electron spin has density in the s orbitals of the lanthanum atom. The coupling constant (91.25 gauss) is very small. In contrast, the hyperfine coupling constant measured for a La⁺² defect created in a CaF₄ lattice is about 50 gauss [22]. Furthermore, a calculation of the hyperfine coupling for La⁺² made using unrestricted Hartree-Fock wavefunctions yields the much larger value of 186 gauss.

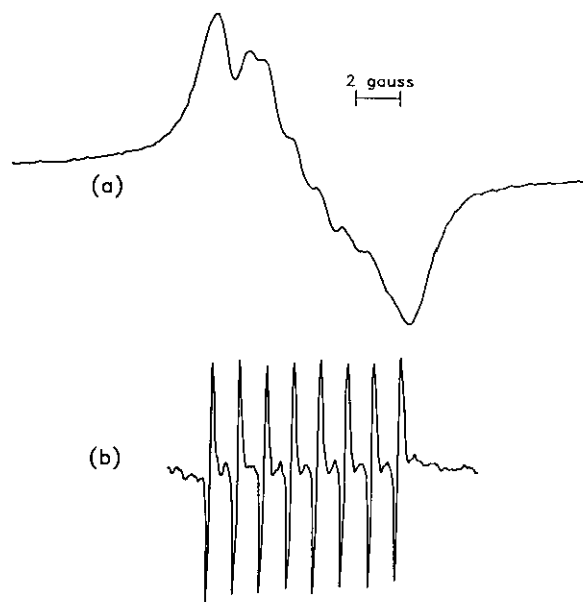


Figure 2. EPR spectrum (9.5112 GHz) at ambient temperature of (a) solid degassed toluene extract (dried) resulting from arc burning of a composite graphite/La₂O₃ rod and (b) a degassed solution of the extract in 1, 1, 2, 2-tetrachloroethane.

Thus both experiment and theory argue strongly against a +2 oxidation state for the lanthanum atom, and indicate that it is in its preferred +3 oxidation state. We note that electronic structure calculations on La@C₆₀ predict a change of +2.85 for the lanthanum atom [23]. The peaks between the ¹³⁹La hyperfine lines are due to hyperfine coupling to ¹³C nuclei in the La@C₈₂ that contain a single ¹³C atom. The observation of coupled electron, ¹³⁹La and ¹³C spins provides direct evidence for association of a lanthanum atom with the C₈₂ framework.

The EPR spectra suggest that La⁺³ is trapped inside a fullerene anion radical. A picture of La@C₈₂ consistent with the spectra is that the lanthanum 6s electrons pair in the C₈₂ LUMO while the third (5d) electron occupies the next-higher-energy orbital. Polarization of the atomic orbitals on the La⁺³ results in spin density in the s orbitals of this formally diamagnetic lanthanum ion with concomitant isotropic hyperfine coupling. We conclude that La⁺³@C₈₂⁻³ is a ground state doublet, rather than a closed shell species [15], and furthermore that the paramagnetism originates from an unpaired electron spin in the π system of the fullerene framework. The small ¹³⁹La hyperfine coupling suggests that the lanthanum ion is relatively unperturbed. Thus fullerene incarceration provides an alternative to traditional cryogenic matrix techniques [24] as a means for isolating reactive species. Recently we have also observed species containing multiple atoms by EPR, for example Sc₃@C₈₂. The availability of bulk samples of metallofullerenes opens the door to exploration of the properties and uses of this entirely new class of materials.

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