

# Fullerene Structure and Dynamics: A Magnetic Resonance Potpourri

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## Introduction

The stability of geodesic structures was realized and exploited by the architect R. Buckminster Fuller. It was not suspected that such structures are realized on a molecular scale until 1985, when Kroto et al. observed a striking prominence of 60-atom carbon clusters in certain molecular beam experiments.<sup>1</sup> They suggested that C<sub>60</sub> possessed the truncated icosahedral geometry of a soccer ball. The C<sub>70</sub> mass peak was also prominent, and a series of larger C<sub>2n</sub> clusters was observed to extend out to the limit of the spectrometer. These observations gave rise to the elegant picture of a family of closed-shell carbon molecules, the fullerenes, consisting of 12 pentagonal and two or more six-membered rings.<sup>2,3</sup> The discovery of new methods to produce and purify macroscopic quantities of fullerenes<sup>4-8</sup> has allowed spectacular confirmation of this picture.

Magnetic resonance spectroscopy has been a particularly powerful tool for probing the structure and dynamical behavior of these fascinating molecules. Solution NMR has been used to establish molecular symmetries, to examine the nature of the bonding, and to determine bonding topology; it has also given useful information about the formation mechanism of fullerenes. Solid-state NMR measurements have revealed directly that C<sub>60</sub> molecules rotate in the solid, have characterized this motion quantitatively, and have provided the first bond-length measurements for this molecule. Electron paramagnetic resonance (EPR) spectra of a fullerene containing a metal atom have given the first detailed information about the electronic structure of a member of this new class of materials. This Account provides a review of this body of work.

## Solution NMR

**1D NMR of C<sub>60</sub> and 2D NMR of C<sub>70</sub>.** Some of the first data supporting the soccer-ball structure for C<sub>60</sub> was obtained using <sup>13</sup>C NMR. A key aspect of this structure—the exact equivalence of all 60 atoms im-

plied by the *I<sub>h</sub>* symmetry—can be directly tested using NMR spectroscopy. This equivalence implies that the solution NMR spectrum of buckminsterfullerene should consist of a single sharp line. This NMR result was pursued by two groups using different approaches. Kroto and co-workers were able to obtain milligram amounts of separated C<sub>60</sub> and C<sub>70</sub> by soot extraction, enabling them to measure NMR spectra for both molecules.<sup>7</sup> In an independent effort, we found that purified material consisting almost entirely of C<sub>60</sub> and C<sub>70</sub> could be sublimed directly from carbon dust produced by resistively heating graphite in a helium atmosphere.<sup>4,9,10</sup> Sublimed C<sub>60</sub> with a trace of C<sub>70</sub> obtained in this fashion was dissolved in CCl<sub>4</sub> with the relaxation agent Cr(ac)<sub>3</sub> added to minimize saturation. Figure 1 shows the downfield portion of the <sup>13</sup>C NMR spectrum of this solution, a sharp single resonance at 142.5 ppm.<sup>11</sup> This remarkable single-line spectrum, obtained without <sup>1</sup>H decoupling, shows that all the carbons in C<sub>60</sub> are chemically equivalent. Typically <sup>13</sup>C NMR spectra of organic molecules are acquired with <sup>1</sup>H decoupling, which removes both short- and long-range <sup>13</sup>C-<sup>1</sup>H coupling. The unusual homoatomic nature of the fullerenes makes such decoupling unnecessary. The resonance position of C<sub>60</sub> is in excellent accord with quaternary carbons in azulene (140.2 ppm), fluorene (141.6 and 143.2 ppm), and 3,5,8-trimethylaceheptylene (146.8 ppm),<sup>12</sup> which are similar to the carbon in buckminsterfullerene. The single-line spectrum is very strong evidence for the icosahedral symmetry of C<sub>60</sub>.<sup>7,11</sup>

Kroto and co-workers<sup>7</sup> were able to show that the NMR spectrum of C<sub>70</sub> consists of five lines in the ratio 10:20:10:20:10, with chemical shifts 150.07, 147.52, 146.82, 144.77, and 130.28 ppm. This spectrum confirmed the *D<sub>5h</sub>* structure for C<sub>70</sub> (shown in Figure 2) proposed in 1985 by Heath et al.<sup>13</sup> The structure has

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Costantino S. Yannoni attended Harvard College and received his doctorate from Columbia University. He is a research staff member at the IBM Almaden Research Center in San Jose, where he has been developing magnetic resonance techniques for probing molecular structure and dynamics. Fullerenes and fullerene-based materials are of current interest; abiding interests include reactive intermediates and molecules adsorbed on surfaces.

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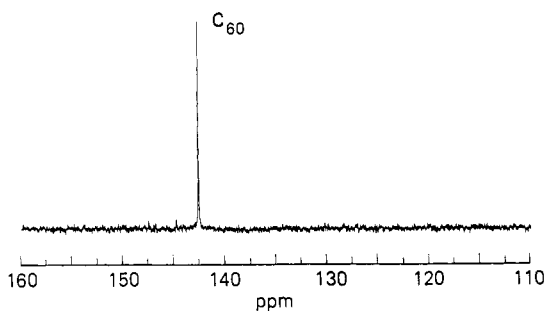
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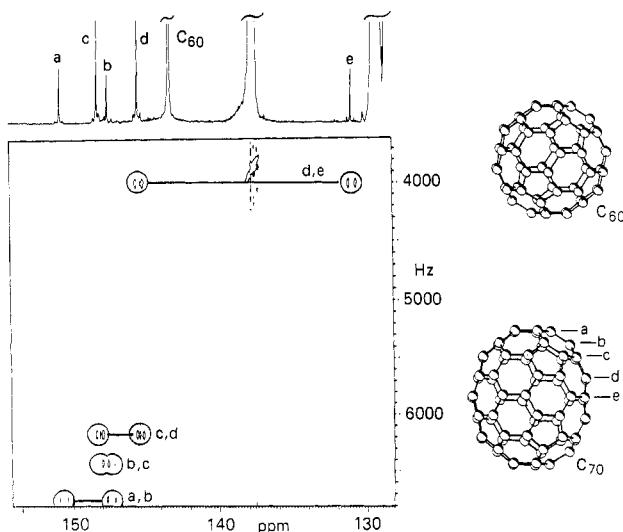
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**Figure 1.** Aromatic region of the 125.7-MHz  $^{13}\text{C}$  NMR spectrum of  $\sim 60\ \mu\text{g}$  of  $\text{C}_{60}/\text{C}_{70}$  in  $\text{CCl}_4$ , without  $^1\text{H}$  decoupling. The resonance at 142.5 ppm is assigned to  $\text{C}_{60}$ .



**Figure 2.** Upper trace: aromatic region of the 125.7-MHz  $^{13}\text{C}$  NMR spectrum of  $\sim 60\ \mu\text{g}$  of a  $^{13}\text{C}$ -enriched mixture of  $\text{C}_{70}$  and  $\text{C}_{60}$ . Lower spectrum: the 2D NMR "INADEQUATE" spectrum of  $\text{C}_{70}$ . Doublets (circled) are obtained at a common double-quantum frequency for the two resonances of a bonded carbon pair. The connectivity obtained is linear and is highlighted by lines. The spectrum was obtained in the presence of  $\text{Cr}(\text{ac})_3$ , using the pulse sequence of Mareci and Freeman.<sup>16</sup>

five chemically distinct kinds of carbon atoms, labeled a–e. To determine the bonding topology of  $\text{C}_{70}$ , we applied the 2D "INADEQUATE" NMR experiment,<sup>14–16</sup> which correlates the  $^{13}\text{C}$  NMR line of a carbon to that of its bonded neighbor by excitation of a shared double-quantum coherence via scalar coupling. This yields the carbon connectivity within the molecule. The first 2D NMR spectrum of a fullerene<sup>17</sup> is shown in Figure 2. It was obtained using a  $\text{C}_{70}$  sample enriched to  $\sim 10\%$   $^{13}\text{C}$  to increase the probability of adjacent  $^{13}\text{C}$  atoms, thus reducing the required data acquisition time to a reasonable length despite low solubility. The enriched clusters were prepared by using cored carbon rods packed with amorphous  $^{13}\text{C}$  powder (Cambridge Isotopes) in an arc fullerene generator.<sup>5,18,19</sup>

The 1D spectrum of 10%  $^{13}\text{C}$ -enriched  $\text{C}_{70}$  is displayed at the top of the figure. In this spectrum, weak satellites due to coupling of bonded  $^{13}\text{C}$  nuclei flank each of the  $\text{C}_{70}$  peaks. It is important to note that, despite the fact that 90% of the  $^{13}\text{C}$  originates from the 99%-labeled carbon packed into the core of the graphite rod, the sideband to central peak intensity ratio is as predicted for assembly of the clusters from a completely mixed atomic gas.<sup>20,21</sup> If dimers or higher aggregates originating from the  $^{13}\text{C}$  core had been incorporated intact into the clusters with significant probability, this ratio would have been much greater. This result was subsequently confirmed by a  $^{13}\text{C}$  NMR experiment on isotopically enriched osmylated  $\text{C}_{60}$ .<sup>22</sup>

In the 2D spectrum, two bonded carbons share a double-quantum frequency in the vertical dimension, and peaks due to the excitation of the double-quantum coherence occur at their respective chemical shifts in the horizontal dimension, allowing a correlation to be made. Each peak will be split into a doublet by the relevant  $^1J_{\text{CC}}$  coupling constant. The 2D spectrum shows a single string of connected resonances (a–b–c–d–e) with respective intensities 10:10:20:20:10. This bonding topology is that expected for the  $D_{5h}$  structure. The crucial connectivity obtained between the intensity-10 lines at 150.8 ppm and 147.8 ppm forces the assignment of the line at 150.8 ppm to the polar end cap carbon a. Thus the asymmetry in the string of resonance intensities allows an unequivocal experimental assignment of the carbons in  $\text{C}_{70}$ , confirming the assignment proposed previously.<sup>7</sup> We note that the end-cap carbon a has a similar structural environment to those in  $\text{C}_{60}$ , but resonates 7 ppm further downfield; the origin of this large shift is not understood.<sup>23</sup>

One-bond carbon–carbon coupling constants ( $^1J_{\text{CC}}$ ) are measured directly in this 2D experiment. These quantities are relevant to reactivity and bonding in fullerenes and correlate with the s character of the bond, its length, and its  $\pi$  bond order.<sup>24–28</sup> For  $\text{C}_{70}$ , the 2D spectrum gives the  $^1J_{\text{CC}}$  values  $^1J_{\text{a,b}} = 68\ \text{Hz}$ ,  $^1J_{\text{b,c}} = 55\ \text{Hz}$ ,  $^1J_{\text{c,d}} = 55\ \text{Hz}$ , and  $^1J_{\text{d,e}} = 62\ \text{Hz}$ , indicating that the bonds have substantial s character and  $\pi$  bond order. The  $^1J_{\text{CC}}$  values for bonds fusing the six-membered rings (a–b and d–e) are quite large relative to those of similar bonds in model aromatic systems, indicating

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substantial olefinic character (in contrast,  $^1J_{9,10}$  for naphthalene is 57 Hz<sup>29</sup>). The large values are also evidence against proposed structures for fullerenes involving three-membered rings,<sup>30</sup> which are expected to have markedly smaller coupling constants.<sup>31,32</sup> Note that such couplings are *not* observable for multiply labeled C<sub>60</sub> due to the equivalence or near degeneracy of all <sup>13</sup>C carbons.<sup>33</sup> A 2D NMR experiment on an osmium derivative of C<sub>60</sub>, where the adduct breaks the carbon equivalence, has furnished an interesting correlation between the  $^1J_{CC}$  and bond lengths in that molecule.<sup>34</sup>

The 2D NMR spectrum of C<sub>70</sub> yields bonding topology, coupling constants, and an experimental assignment of the <sup>13</sup>C NMR spectrum consistent with the "rugby ball" D<sub>5h</sub> structure for this molecule. For larger fullerenes the number of possible isomers increases rapidly, and 2D NMR will likely prove very useful in confirming that a set of resonances is associated with a single species and in identifying the bonding topology and structure of that species. For C<sub>76</sub>, the next most prevalent species beyond C<sub>70</sub>, a recent 1D <sup>13</sup>C study provided an elegant solution by revealing a spectrum with 19 lines of equal intensity, confirming a remarkable chiral structure with D<sub>2</sub> symmetry for the favored isomer of this molecule.<sup>35</sup>

### Solid-State NMR

**C<sub>60</sub> Rotational Dynamics in the Solid.** The experiments described so far used solution NMR as a tool to study the symmetry and bonding in individual fullerenes. Solid-state <sup>13</sup>C NMR spectroscopy has also proven to be a powerful tool, both for studying the detailed geometry of C<sub>60</sub> and for probing the collective properties of fullerenes. It was found quite early that the spectrum of solid C<sub>60</sub> changes very dramatically as a function of temperature,<sup>36,37</sup> as shown in Figure 3. At ambient temperature a single relatively narrow peak is found at 143 ppm. This implies 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 (known as chemical shift anisotropy or CSA) leads to a broad characteristic powder pattern.<sup>38,39</sup> Figure 3 shows that such a powder pattern does develop as the sample is cooled. At 123 K a broad skirt has developed at the base of the main resonance at 143 ppm. At 100 K, the spectrum is predominantly a CSA powder pattern with minor intensity in the narrow peak at 143 ppm. At 77 K the narrow line is essentially gone.

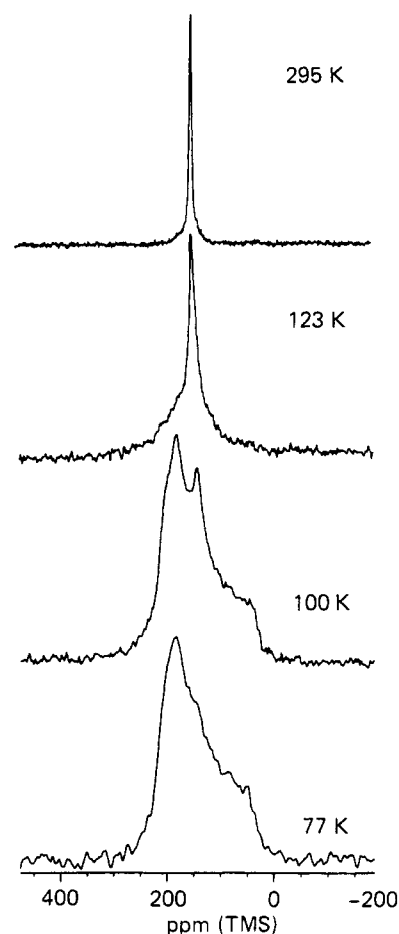


Figure 3. Variable-temperature 15-MHz <sup>13</sup>C NMR spectra of a solid sample of C<sub>60</sub>.

A fit of the powder pattern yields an asymmetric chemical shift tensor,<sup>38,39</sup> with principal values 220, 186, and 25 ppm.<sup>36</sup> These values are similar to those typical of aromatic carbons.<sup>38,39</sup> Analysis of the spinning sidebands in a <sup>13</sup>C magic-angle spinning NMR experiment showed that the motion of C<sub>70</sub> in the solid at room temperature is highly anisotropic with rapid motion about the long axis of the molecule.<sup>37</sup>

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.<sup>36,40,41</sup> NMR can be used to quantitatively characterize the dynamics in 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, <sup>13</sup>C NMR relaxation for C<sub>60</sub> is dominated by the CSA mechanism, which arises when the combination of molecular rotation and chemical shift anisotropy modulates the effective magnetic field, causing relaxation. Generally the relaxation rate has contributions due to several mechanisms which are difficult to separate. The CSA contribution, however, has the unique feature that it is

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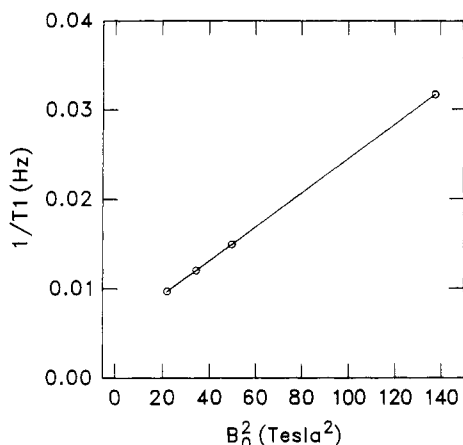
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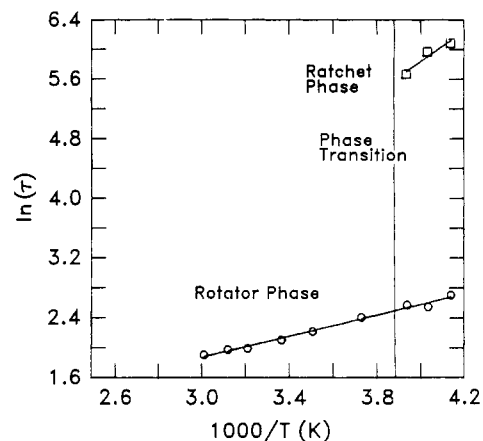


**Figure 4.** Plot of  $^{13}\text{C}$  relaxation rate  $1/T_1$  versus the square of the magnetic field for a sample of solid  $\text{C}_{60}$  at 283 K.

proportional to the square of the external magnetic field. Thus measuring the relaxation rate at various magnetic fields allows the CSA contribution to be obtained with precision.

Measurements of the relaxation rate,  $1/T_1$ , were carried out using the inversion-recovery experiment at four magnetic field strengths.<sup>42</sup> At 283 K, monocomponent relaxation behavior was observed, with the relaxation rate showing a strong field dependence. Figure 4 shows a plot of  $1/T_1$  versus the square of the field. A linear dependence is observed, with a slope of  $0.191 \pm 0.003 \text{ mHz/T}^2$ . From this slope the CSA contribution to  $1/T_1$  can be found. In the case where the rotational correlation time,  $\tau$ , is short compared to the Larmor period of the nucleus (as it is here),  $\tau$  is proportional to the CSA contribution to  $1/T_1$ . The proportionality constant can be obtained if the symmetric and antisymmetric components of the chemical shift tensor are known.<sup>43,44</sup> The symmetric part was determined from experiment (see above), but the antisymmetric component is extremely difficult to measure. However, the antisymmetric contribution to the rate is estimated to be small ( $\sim 6\%$ ).<sup>45</sup> Thus we obtain a rotational correlation time  $\tau = 9.2 (\pm 2) \text{ ps}$  at 283 K, corresponding to a rotational diffusion constant  $D \equiv 1/6\tau = 1.8 \times 10^{10} \text{ s}^{-1}$ . This is an extremely short rotational correlation time, comparable to those found for small molecules in solution. The corresponding correlation time calculated for  $\text{C}_{60}$  in the gas phase is 3.1 ps, only 3 times shorter than the value we measure in the solid. Similar experiments carried out on  $\text{C}_{60}$  in solution (1,1,2,2-tetrachloroethane) at 283 K yield the value  $\tau = 15.5 \text{ ps}$ , which is significantly longer than the solid-phase result.<sup>42</sup>

Recently Heiney et al.<sup>40</sup> found from X-ray studies and calorimetry that solid  $\text{C}_{60}$  exhibits a phase transition near 249 K, from a simple cubic structure at low temperatures to a fcc structure. This transition was examined by Tycko et al.<sup>41</sup> using NMR, who found a sharp break in the  $T_1$  relaxation rate at the transition. These



**Figure 5.** Arrhenius plot for the ratchet and rotator phases of solid  $\text{C}_{60}$ , with fit lines giving apparent activation energies of 4.2 and 1.4 kcal/(mol deg), respectively;  $\tau$  units are picoseconds.

papers suggest that the high-temperature phase is characterized by free rotation or rotational diffusion (the "rotator" phase), and the low-temperature phase is characterized by jump rotational diffusion between symmetry-equivalent orientations (the "ratchet" phase). Inversion-recovery experiments below the transition temperature show the appearance of the ratchet phase, which is characterized by a much higher relaxation rate, implying much slower reorientation (relative to the rotator phase). Figure 5 shows the temperature dependence of the reorientational correlation times  $\tau$  for both phases. The rotator phase has an apparent activation energy of 1.4 kcal/mol, while the value for the ratchet phase for this sample is 4.5 kcal/mol. The orientational ordering for the ratchet phase apparently results in a potential energy surface with deep minima. It was recently suggested by David et al.,<sup>46</sup> on the basis of a neutron diffraction study of  $\text{C}_{60}$  at low temperature, that these deep minima result from an orientational ordering in which electron-rich interpentagon bonds face the electron-poor pentagon centers of adjacent  $\text{C}_{60}$  units, giving favorable intermolecular interactions. In contrast, in the rotator phase, random orientation of nearest-neighbor molecules leads to a much smoother potential energy surface and correspondingly faster reorientation rates.

**Measurement of Bond Lengths in  $\text{C}_{60}$ .** Facile reorientation of the nearly spherical  $\text{C}_{60}$  molecules in the solid results in both static<sup>5</sup> and dynamic<sup>40</sup> disorder, which pose obstacles to the use of X-ray diffraction measurements to determine the detailed geometry of the molecule. For the truncated icosahedral structure there are two types of bonds: pentagon edges (60) and links between pentagons (30), which may be expected to have different lengths. Solid-state NMR methods have been developed which are eminently well-suited for measuring bond lengths in systems which exhibit static orientational disorder.<sup>47,48</sup> Furthermore, the solid-state NMR results discussed above show that the effects of dynamic disorder can be eliminated by doing experiments at low temperatures. The bond lengths in  $\text{C}_{60}$  were obtained from a measurement of  $^{13}\text{C}$ - $^{13}\text{C}$

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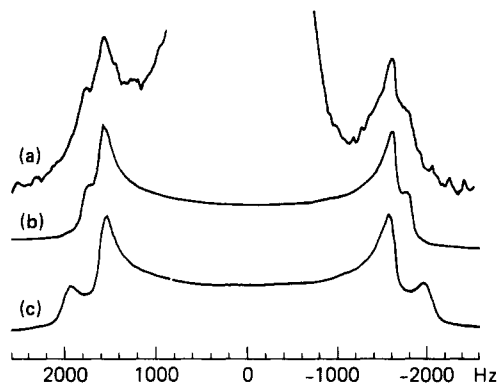
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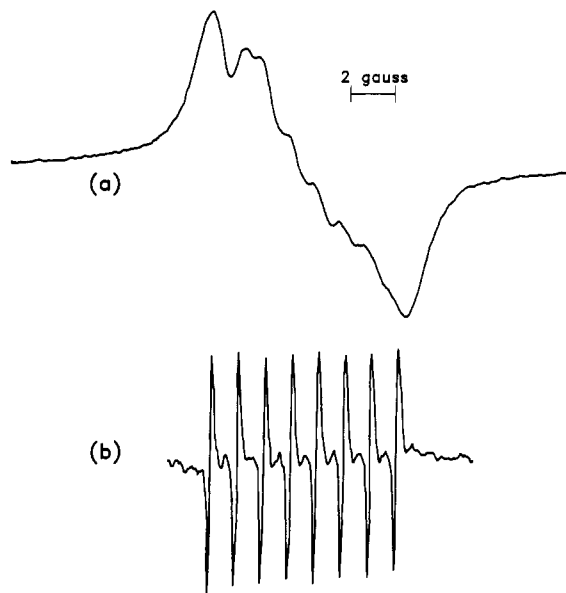
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**Figure 6.** (a) Fourier transform of the  $^{13}\text{C}$  signal obtained in a Carr–Purcell Meiboom–Gill sequence on  $^{13}\text{C}$ -enriched  $\text{C}_{60}$  at 77 K. The intense center line has been cropped for clarity (see text). (b) Simulation of two Pake doublets with carbon–carbon bond lengths of 1.45 and 1.40 Å. (c) As in b, but with bond lengths of 1.451 and 1.345 Å.

magnetic dipolar coupling, which depends on the inverse cube of the C–C distance.<sup>49</sup> The sample was isotopically enriched to  $\sim 6\%$  in order for this coupling to be observed.<sup>50</sup> We used the Carr–Purcell Meiboom–Gill sequence<sup>51,52</sup> to selectively remove the broadening effects of  $^{13}\text{C}$  chemical shift anisotropy, while retaining the dipolar coupling. This coupling is spectrally manifest in powder samples as a pattern with features that appear as a relatively sharp (“Pake”) doublet.<sup>49</sup> The doublet splitting is proportional to the inverse cube of the internuclear distance and provides an accurate measure of the C–C bond length.<sup>53</sup> The Fourier transform of the signal obtained using this sequence on the  $^{13}\text{C}$ -enriched sample of  $\text{C}_{60}$  (77 K, 1.4-T field) is shown in Figure 6.<sup>50</sup>

The spectrum consists of a very strong center line (cropped for clarity) flanked by a weak pair of doublets. The intensity in the center line is mainly due to  $^{13}\text{C}$  spins with no  $^{13}\text{C}$  nearest neighbors. The inner and outer pairs of lines are the Pake doublets due to coupling between directly bonded  $^{13}\text{C}$  atoms, confirming the presence of the two different C–C bonds in  $\text{C}_{60}$ . The bond lengths were obtained by spectral simulation<sup>53</sup> giving the values  $1.45 \pm 0.015$  and  $1.40 \pm 0.015$  Å. The simulation used for the best fit had twice as many long (pentagonal) bonds, in agreement with what is expected for the icosahedral structure. Using these bond lengths, we calculate a diameter for  $\text{C}_{60}$  of  $7.10 \pm 0.07$  Å. More recently, gas-phase electron diffraction,<sup>54</sup> solid-state neutron diffraction,<sup>46,55</sup> and low-temperature X-ray diffraction of a twinned crystal of  $\text{C}_{60}$ <sup>56</sup> have all yielded bond lengths which confirm the solid-state NMR results. A simulation made using the bond lengths predicted for a truncated dodecahedral structure for  $\text{C}_{60}$ <sup>30</sup> (1.451 and 1.345 Å) shows poor agreement with experiment (Figure 6c), providing strong support for the



**Figure 7.** EPR spectra at ambient temperature of  $(\text{La}@\text{C}_{82})$  mixed with  $\text{C}_{60}$  and  $\text{C}_{70}$  (a) in the solid state and (b) in solution.

truncated icosahedral form.

**A  $^{13}\text{C}$  Solid-State NMR Study of  $\text{K}_x\text{C}_{60}$ .** The discovery that alkali-metal-doped fullerenes form conducting and surprisingly high-temperature superconducting phases further heightened interest in the fullerene area.<sup>57,58</sup> Tycko and co-workers carried out a series of elegant  $^{13}\text{C}$  NMR experiments on the  $\text{K}_x\text{C}_{60}$  fullerenes which provided detailed information about the morphology and electronic structure of these materials.<sup>59</sup> Spectra were obtained for a range of fullerenes  $\text{K}_x\text{C}_{60}$  with  $x = 1.5, 2.0, 3.1,$  and  $6.0$ . At room temperature a single  $^{13}\text{C}$  line is observed at 186 ppm for  $\text{K}_{3.1}\text{C}_{60}$ , 43 ppm downfield from  $\text{C}_{60}$ . Materials with intermediate values of  $x$  (1.5, 2.0) yielded lines only for  $\text{C}_{60}$  and  $\text{K}_3\text{C}_{60}$ , showing that material with  $0 < x < 3$  is a two-phase system at equilibrium with  $x = 0$  and  $x = 3$ . The width of the  $^{13}\text{C}$  resonance for the  $\text{K}_3$  material is small (15 ppm), showing that the  $\text{C}_{60}^{3-}$  ions rotate rapidly at room temperature, averaging out the chemical shift anisotropy as in  $\text{C}_{60}$ .<sup>36,37</sup> In contrast, the resonance for the insulating  $\text{K}_6\text{C}_{60}$  phase shows the broad asymmetric line shape expected for a nonrotating  $\text{C}_{60}$ . Variable-temperature  $^{13}\text{C}$  relaxation time measurements on  $\text{K}_3\text{C}_{60}$  showed Korringa-like behavior with  $T_1T = 140$  K s. This result indicates that the electrons donated by the potassium ions to the molecular orbitals on the  $\text{C}_{60}$  units form the conduction band. The shift of the  $^{13}\text{C}$  resonance in  $\text{K}_3\text{C}_{60}$  is primarily a Knight shift<sup>60</sup> attributable to hyperfine coupling between the  $^{13}\text{C}$  nuclei and the conduction electrons. These results established the central role played by  $\text{C}_{60}^{3-}$  in the conductivity of  $\text{K}_3\text{C}_{60}$  and demonstrated that NMR can serve as an important probe of the superconducting

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state of the alkali-metal fullerenes.

### Fullerenes Containing Metals: EPR of (La@C<sub>82</sub>)

The provocative conjecture that it might be possible to trap atoms and molecules inside fullerene cages,<sup>1</sup> initially supported by mass spectroscopic studies,<sup>13</sup> has subsequently been corroborated by photofragmentation, reactivity, and dissociation experiments.<sup>19,61,62</sup> 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<sub>n</sub>) for a metal atom M contained in a C<sub>n</sub> fullerene.<sup>62</sup>

The first study of the detailed structure of these remarkable species was made on a sample of (La@C<sub>82</sub>) using electron paramagnetic resonance (EPR) spectroscopy.<sup>63</sup> For these experiments, bulk samples (~0.1 mg of (La@C<sub>82</sub>)) were prepared by arc-burning of a composite rod of graphite and La<sub>2</sub>O<sub>3</sub>. The mass spectrum of the toluene extract of the soot from this burning showed only C<sub>60</sub>, C<sub>70</sub>, and (La@C<sub>82</sub>). The X-band EPR spectrum of the toluene extract containing (La@C<sub>82</sub>) is shown in Figure 7 and is centered at  $g = 2.001$ , close to the value found for fullerene radical anions.<sup>64-67</sup> The spectrum has an overall width of 10 G, with a hint of rich structure. The EPR spectrum of a degassed solution of the extract in 1,1,2,2-tetrachloroethane is shown in Figure 7b and consists of eight extremely narrow (0.125-G) equally spaced (1.25-G 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  $7/2$ ,<sup>68</sup> the value for the <sup>139</sup>La nucleus. This proves that the unpaired electron spin has density in the s orbitals of the lanthanum atom. The coupling constant (1.25 G) is very small. In contrast, the hyperfine coupling constant measured for an La<sup>2+</sup> defect created in a CaF<sub>2</sub> lattice is ~50 G.<sup>69</sup> Furthermore, a calculation of the hyperfine coupling for La<sup>2+</sup> made using unrestricted Hartree-Fock wave functions yields the much larger value of 186 G. 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@C<sub>60</sub>) predict a charge of 2.85+ for the lanthanum atom.<sup>70</sup> The peaks between the <sup>139</sup>La hyperfine lines are due to hyperfine coupling to <sup>13</sup>C nuclei in the

(La@C<sub>82</sub>) that contain a single <sup>13</sup>C atom. The observation of coupled electron, <sup>139</sup>La, and <sup>13</sup>C spins provides direct evidence for association of a lanthanum atom with the C<sub>82</sub> framework.

The EPR spectra suggest that La<sup>3+</sup> is trapped inside a fullerene anion radical. A picture of (La@C<sub>82</sub>) consistent with the spectra is that the lanthanum 6s electrons pair in the C<sub>82</sub> LUMO while the third (5d) electron occupies the next higher energy orbital. Polarization of the atomic orbitals on the La<sup>3+</sup> results in spin density in the s orbitals of this formally diamagnetic lanthanum ion with concomitant isotropic hyperfine coupling. We conclude that (La<sup>3+</sup>@C<sub>82</sub><sup>3-</sup>) is a ground-state doublet, rather than a closed-shell species,<sup>62</sup> and furthermore that the paramagnetism originates in an unpaired electron spin in the  $\pi$  system of the fullerene framework. The small <sup>139</sup>La hyperfine coupling suggests that the lanthanum ion is relatively unperturbed. Thus fullerene incarceration provides an alternative to traditional cryogenic matrix techniques<sup>71</sup> as a means for isolating reactive species.

### Concluding Remarks

Solution <sup>13</sup>C NMR studies of C<sub>60</sub> and C<sub>70</sub> have permitted determination of their symmetries and of the bonding topology of C<sub>70</sub>. Solution NMR is at the heart of current efforts to elucidate the general formation mechanism of fullerenes and to account for patterns of cluster abundance and observed isomer distributions. Recently NMR spectra of two isolated C<sub>78</sub> isomers of low symmetry (*D*<sub>2v</sub>, *D*<sub>3</sub>) were presented by Diederich et al.,<sup>72</sup> while isolation of higher fullerenes (C<sub>76</sub>, C<sub>78</sub>, C<sub>82</sub>, C<sub>84</sub>, C<sub>90</sub>, C<sub>96</sub>) and evidence for multiple isomerism in the species above C<sub>76</sub> were reported by Kikuchi et al.<sup>73</sup> The predominance of multiple low-symmetry isomers indicated by NMR spectroscopy for higher fullerenes has recently led to the proposal of a very interesting model for fullerene assembly based on sequential addition of even-numbered monocyclic rings to a 10-carbon radical precursor.<sup>74</sup> Further NMR work, both 1D and 2D, will be required to confirm this proposal. Solid-state NMR experiments have provided quantitative information about the motional dynamics of C<sub>60</sub> and have yielded accurate bond lengths for this species. As bulk amounts of purified higher fullerenes and metallofullerenes become available, it will be interesting to see if they also show facile reorientation in the solid, and to explore their transport properties using NMR. EPR spectra of (La@C<sub>82</sub>), produced in sufficient quantity to allow its characterization by magnetic resonance techniques, have given us the first information about the electronic structure of a metallofullerene. Recent work by Alvarez et al.<sup>75</sup> demonstrates by mass spectrometry that a large number of species with one, two, or three lanthanum atoms associated with a fullerene are present in soot produced in a manner similar to that described here, and that La<sub>2</sub>C<sub>80</sub> is also soluble in toluene. Although

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separation and purification of metallofullerenes have not yet been achieved, the availability of bulk samples of metallofullerenes opens the door to exploration of the properties and uses of this entirely new class of materials. EPR spectroscopy will undoubtedly play an important role in these future investigations.

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