Electronic Structure of the Polymer Phase of CsC$_{60}$: Refocused INADEQUATE Experiments

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Carbon-13 MAS refocused INADEQUATE experiments have been carried out on the polymer phase of CsC$_{60}$ and provide a complete and unambiguous assignment of the high-resolution carbon-13 MAS spectrum. This allows experimental Knight shifts for each carbon site on the fullerene molecule to be compared with calculated hyperfine coupling constants. The comparison supports a model for the electronic structure which predicts high electron density away from the linkages between fullerene molecules with electron transport dominated by interchain hopping.

Introduction

The alkali metal intercalated fullerides[1,2] AC$_{60}$ where A represents Rb or Cs form a variety of phases with interesting electronic and magnetic properties. Above approximately 350 K, these compounds adopt a cubic NaCl structure[3] with the metal cations located in octahedrally coordinated sites between the C$_{60}$ anions. This phase shows paramagnetism,[4] suggesting a large degree of localization of the electrons on the fullerene molecules. In the room temperature orthorhombic phase, formed by a reversible solid-state transformation from the cubic structure, the separation between fullerene molecules along one crystallographic axis is approximately 9% smaller than along the others.[5] Powder X-ray diffraction studies[6] confirmed that this unusually short distance is indicative of the formation of linkages between fullerene molecules formed by a [2+2] cycloaddition[7] resulting in polymeric chains along the *a* axis. This model is largely supported by Raman,[8] neutron diffraction,[9] and inelastic scattering[10] data, although several structural details such as the deformation of the fullerene molecules[11] and the rotational orientation of the polymer chains[12] remain uncertain. Magnetic spin susceptibility and frequency-dependent conductivity measurements[5,13] suggested that the polymeric phase is a quasi-one-dimensional metallic conductor with a phase transition to a magnetically ordered insulator occurring at temperatures below approximately 50 K.

Solid-state NMR spectroscopy has made several important contributions to the study of RbC$_{60}$ and CsC$_{60}$. The variation with temperature of the carbon-13, rubidium-87, and cesium-133 resonance frequencies and spin−lattice relaxation times[4] provided evidence for a phase transition at 350 K associated with a qualitative change in electronic properties. Carbon-13 magic angle spinning (MAS) measurements at rates up to 18 kHz[14,15] provided sufficient spectral resolution to separate resonances from inequivalent sites on the fullerene molecule with resonance frequencies determined by the sum of Knight shift and chemical shift contributions. Spectral intensities gave an indication of the number of carbon atoms associated with

each resolved resonance, and measurements of the shift anisotropy suggested that the carbon atoms comprising the inter-fullerene linkage are sp^3 hybridized. The hyperfine interaction for each resonance was extracted from the temperature variation of the Knight shift. These NMR data confirmed theoretical band structure calculations[16] which predict that the fullerene molecules are connected by insulating contacts and that electron transport is dominated by interchain hopping, suggesting a full three-dimensional character to the electronic structure. However, to fully test models for the electronic structure, the resonances must be assigned to the different carbon sites in the fullerene molecule, so that the variation of the hyperfine interaction with position can be established.

In a recent paper,[17] we used a two-dimensional carbon-13 MAS NMR correlation spectrum, as well as double resonance carbon-13 cesium-133 MAS NMR measurements, to make a partial assignment of the carbon-13 MAS spectrum of the polymer phase of CsC$_{60}$. NMR correlation spectra show characteristic peaks at frequency coordinates determined by the shifts of pairs of coupled nuclei, and in the variant of the experiment[18] used in our previous work such peaks identify interactions via through-space dipolar couplings. A problem with this study was that an unambiguous assignment of the resonances was not possible. Hence, a comparison of experimental Knight shifts with hyperfine couplings calculated[14] from models[16,19] of the electronic structure was required to distinguish between two possibilities and so complete the assignment.

In this paper, we present an unambiguous assignment of the carbon-13 NMR spectrum of the polymer phase of CsC$_{60}$ which is based solely on experimental data and is independent of any model for the electronic structure. This is achieved using a complementary two-dimensional carbon-13 MAS NMR correlation experiment which identifies nuclei coupled via a through-bond scalar interaction. The data obtained are of sufficient quality that the majority of the bonded pairs of carbon atoms in the fullerene molecule can be unambiguously identified. The resulting assignment largely confirms that published in ref 17, with some minor differences, and the experimental Knight shifts are in good agreement with calculated values of the hyperfine coupling.[14]

The carbon-13 MAS spectrum of CsC$_{60}$ recorded at ambient temperature and a MAS rate of 17 kHz (Figure 1) shows Knight-shifted resonances which extend well beyond the normal carbon-

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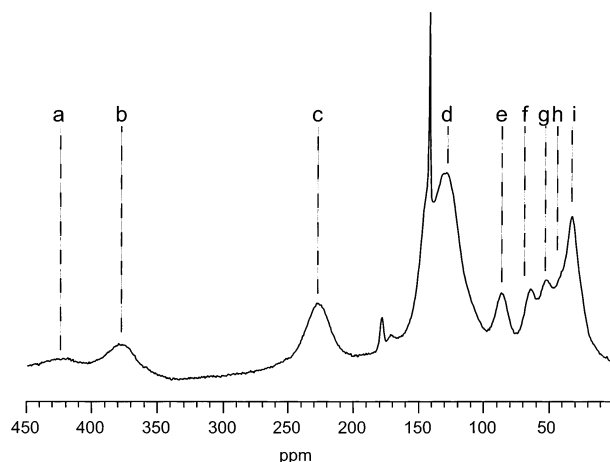† Current Address: Varian Inc., 3120 Hansen Way, Palo Alto, California, USA.

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Figure 1. Carbon-13 MAS spectrum of polymer CsC$_{60}$, recorded using parameters described in the text, showing the designations of the peaks used in this work. Note the Knight-shifted resonances which extend well beyond the normal carbon-13 chemical shift range.

13 chemical shift range. The linkage site which is sp^{3}hybridized is expected to have a chemical shift of 30−45 ppm[14] and can be assigned to peak (i). Other sites on the fullerene molecule are expected to be shifted from the C$_{60}$ position of 143 ppm by the Knight shift. Peaks a−c have substantial positive Knight shifts and hyperfine couplings. The small differences between this spectrum and that in ref 17 arise from variations in Knight shifts because of sample heating effects arising from the spinning. As described in ref 17, the spectrum fits to 11 Lorentzian lines, with the resonances at 143 and 179 ppm corresponding to residual unpolymerized C$_{60}$ and high-temperature cubic CsC$_{60}$, respectively. The complexity of the MAS spectrum and the broad lines arising from shift distributions caused by effects such as incomplete polymerization mean that recording a two-dimensional scalar correlation spectrum of CsC$_{60}$ is an experimentally challenging task.

Experimental Section

To obtain sufficient sensitivity in the two-dimensional scalar correlation experiment, isotopically enriched samples of polymer CsC$_{60}$ were prepared by de Swiet et al.[17] The sample used here, designated sample 1 in ref 17, was prepared from 50% carbon-13 enriched C$_{60}$ as confirmed by mass spectrometry. Carbon-13 MAS spectra of polymer CsC$_{60}$ were recorded at a Larmor frequency of 75.47 MHz on approximately 10 mg of material packed into a 3.2 mm MAS rotor spinning at 17 kHz. The MAS rate was chosen to ensure that spinning sidebands were negligible. The full spectral width was 50 kHz, the free induction decay was acquired for 20.48, ms and a relaxation delay of 5 s was inserted between scans. Spin−echo experiments with echo times up to 15 ms were carried out in order to measure the homogeneous contribution to the carbon-13 line widths.

Two approaches to the development of scalar correlation experiments for solids have been described recently. The first of these[20] relies on refocusing the inhomogeneous line width to improve the effective resolution so that scalar couplings can be resolved and standard solution-state pulse sequences, such as INADEQUATE,[21] can be used. The second[22,23] involves magnetization transfer under an isotropic mixing Hamiltonian induced by a MAS-synchronized rf pulse sequence which removes resonance offsets without inadvertently recoupling dipolar interactions. Sample heating concerns and the need to distinguish any multiple-bond transfer dictated the choice of the first approach here.
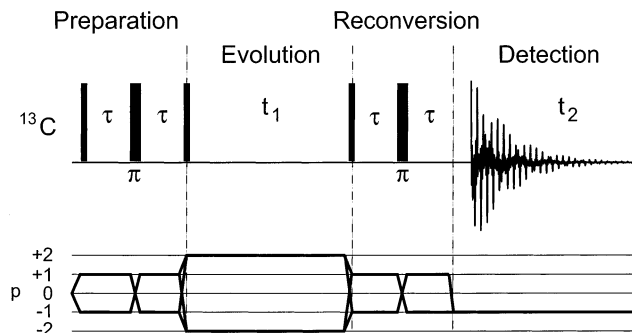

Figure 2. Refocused INADEQUATE pulse sequence as used in this work with associated coherence transfer pathway. The narrow vertical bars represent pulses with a flip angle of $\pi/2$, whereas the wide ones indicate a flip angle of π.

Two-dimensional carbon-13 refocused INADEQUATE experiments were recorded using the pulse sequence[20] shown in Figure 2. Carbon-13 magnetization generated by the first $\pi/2$ pulse evolves solely under the isotropic scalar coupling Hamiltonian for the preparation delay 2τ. This is because carbon-13 dipolar couplings and shift anisotropies are averaged by the fast magic angle spinning, and the π pulse in the middle of the preparation delay refocuses evolution due to the isotropic shift. In scalar-coupled spin systems, the second $\pi/2$ pulse creates multiple-quantum coherences associated with normally forbidden transitions, and the phase of the second $\pi/2$ pulse is cycled to restrict these to double-quantum contributions. The generation of double-quantum coherence can be optimized under ideal conditions by choosing $\tau = 1/(4J_{CC})$ where J_{CC} is the carbon-13 scalar coupling constant. This coherence evolves during t_1 at the sum frequency of the coupled spins i and j

$$\omega_{DQ}^{ij} = \omega_{SQ}^{i} + \omega_{SQ}^{j} \qquad (1)$$

where ω_{SQ} is the normal shift frequency. In the refocused variant of the experiment, double-quantum coherence is converted back to observable magnetization by the third $\pi/2$ pulse followed by a reconversion delay identical in duration to the preparation period. Magnetization is detected as normal in t_2, and a two-dimensional Fourier transformation of the resulting signal $S(t_1,t_2)$ gives a two-dimensional spectrum $S(\omega_1,\omega_2)$. Scalar-coupled pairs of nuclei can be identified by the appearance of two peaks in the spectrum at coordinates $(\omega_{DQ}^{ij},\omega_{SQ}^{i})$ and $(\omega_{DQ}^{ij},\omega_{SQ}^{j})$.

Carbon-13 refocused INADEQUATE spectra of polymer CsC$_{60}$ were recorded with preparation delays (2τ) of between 2.14 and 6.14 ms. There were 150 values of the evolution time t_1, and the dwell time in this dimension was 5 μs. Pure absorption two-dimensional lines were achieved using TPPI. All other experimental parameters were as given for the one-dimensional spectrum above.

It has been shown[20] that the refocused INADEQUATE experiment is particularly effective in disordered systems. In these cases, a substantial contribution to the apparent line width because of distributions of shift frequencies can be refocused by a π pulse. The efficiency[20] of the experiment is largely determined by the ratio of the time constants associated with the refocused line width and the apparent line width T_2'/T_2^*. The value of T_2' was measured for polymer CsC$_{60}$ in a spin−echo experiment and found to be of the order of 5 ms giving values of the ratio T_2'/T_2^* of between 10 and 25 depending on the site. In these circumstances, the refocused variant of the INADEQUATE experiment is expected to be as much as 10
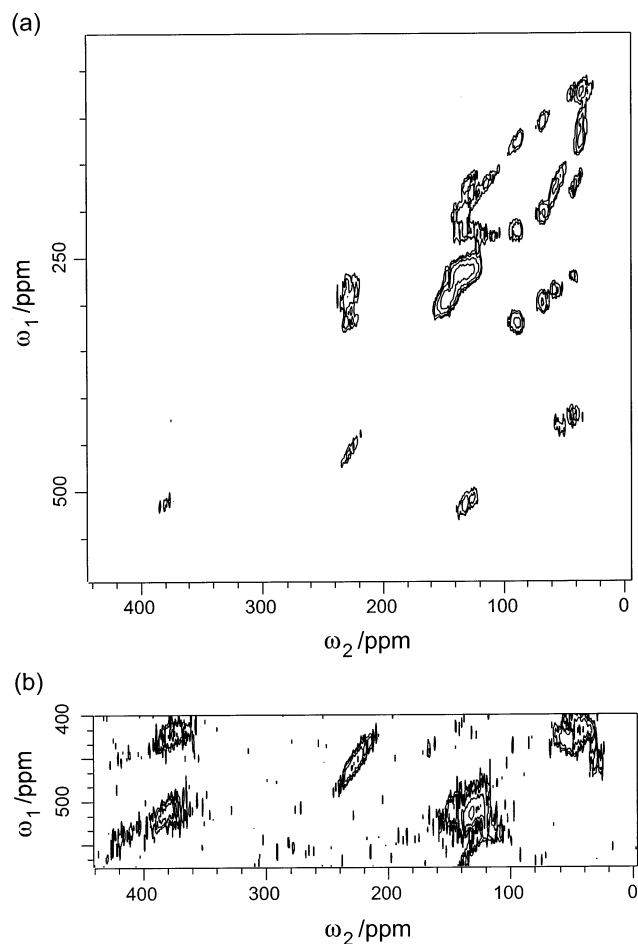
(a)

(b)

Figure 3. Part of a refocused INADEQUATE spectrum of polymer CsC_{60} recorded using parameters described in the text and a preparation delay (2τ) of 2.94 ms. In part a, five positive contour levels are plotted between 17.5 and 100% of the maximum intensity. This allows individual peaks in the crowded upper right-hand quadrant of the two-dimensional spectrum to be discriminated from one another. In part b, a region of the spectrum has been extracted and plotted with five positive contour levels between 6 and 50% of maximum intensity. Scalar-coupled pairs of nuclei can be identified by the appearance of two peaks in the spectrum which share a common ω_1 frequency.

times more sensitive than the straightforward INADEQUATE which is routinely used in solution.

Results and Discussion

Figure 3 shows a refocused INADEQUATE spectrum of polymer CsC_{60} recorded with a preparation delay (2τ) of 2.94 ms. In part a, a region is plotted with five positive contour levels between 17.5 and 100% of the maximum intensity. This plot allows individual peaks in the crowded upper right-hand quadrant of the two-dimensional spectrum to be discriminated from one another, but the levels are too high to allow a number of broader and/or less intense peaks in the lower half of the spectrum to be observed. To overcome this cosmetic problem, the region of the spectrum with ω_1 between 400 and 550 ppm has been extracted and plotted in part b with five positive contour levels between 6 and 50% of maximum intensity. It should be noted that the coordinates of all the peaks visible in Figure 3 parts a and b obey eq 1, except for one at (450 ppm, 29 ppm) for which the ω_2 coordinate is outside the range observed in the MAS spectrum. Peaks visible in Figure 3 were reproduced in all of the refocused INADEQUATE spectra recorded. Each of the sum frequencies observed in the ω_1
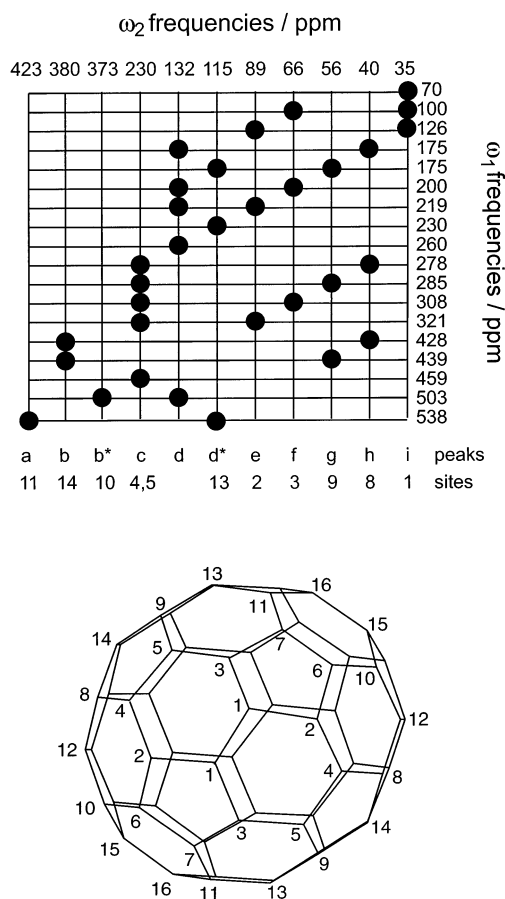

Figure 4. Summary of the peak positions in the refocused INADEQUATE spectrum, and the resulting assignment of peaks (a−i) in the MAS spectrum to sites (1−16) in the fullerene molecule. Note that peak positions obey eq 1 and that peak d results from the overlap of resonances due to sites (6), (7), (12), (15), and (16). In addition, the structure of a single fullerene unit from polymer CsC_{60} is shown oriented such that the crystallographic *a* axis and the polymer chain run approximately perpendicular to the paper. The inequivalent carbon-13 sites (1−16) are labeled.

dimension of the spectrum in Figure 3 can be assigned to a pair of carbon sites which are directly bonded in the molecule. All of the peaks in the MAS spectrum can be assigned to sites in this way, using two further pieces of experimental evidence, namely, that the sp^3 linkage site (1) corresponds to peak (i) which has been verified previously[14,15] and that the pairs of sites (2)/(3) and (8)/(9) can be distinguished by the REDOR experiments described in ref 17.

The peak positions in the refocused INADEQUATE spectrum are summarized in Figure 4 which also gives the resulting assignment of the MAS spectrum. Only one of the sum frequencies expected on the basis of the assignment is missing from the spectrum; this is discussed in more detail below. It should be noted that the difference between the observed ω_1 frequency and the sum of the corresponding single-quantum frequencies is never more than 10 ppm and is less than 3 ppm in the vast majority of cases. In slices of the two-dimensional spectrum, it is possible to resolve a shoulder at 114 ppm on the high-field side of peak d which has been designated d*[17] and can be assigned to site (13) on the basis of its connection to site (9). Resonance b appears to be split into two separate peaks with the high-field peak at 375 ppm assigned to site (14) on the basis of its connections to sites (8) and (9). This last point can be verified by a careful inspection of the peak positions in the low-field region of Figure 3b. The assignments given in

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Figure 4 are consistent with the peak positions observed in all of the refocused INADEQUATE spectra recorded.

Several comments about the form of the spectrum are worthy of note, not least the fact that a number of peaks occur at coordinates $(2\omega_{SQ}^i, \omega_{SQ}^i)$, notably at ω_1 frequencies of 70, 228, 265, and 456 ppm. In the following discussion, these are referred to as "equivalence" peaks. Equivalence peaks would not normally be expected in a solution-state INADEQUATE spectrum, because magnetically equivalent nuclei have a vanishing scalar coupling even when chemically bonded. However, in materials such as polymer CsC$_{60}$, the apparent line width arises in part from a superposition of resonances from nuclei made inequivalent by, for example, chain end effects, defects in packing, or incomplete polymerization. Chemically bonded pairs of such inequivalent but unresolved nuclei will show a scalar coupling. It should be noted that the appearance of the equivalence peak at 70 ppm is further evidence that peak (i) does indeed correspond to site (1), because only a limited number of sites can result in this type of peak. This equivalence peak is the only one in the high-field part of the spectrum. The missing peak expected from the assignment is also an equivalence peak, namely, that for site (14), at a ω_1 coordinate of 750 ppm. This part of the two-dimensional spectrum is not shown in Figure 3, as there is no evidence for a peak above the noise in this region. However, the large apparent line width for peak b in the MAS spectrum means this peak is expected to be weak.

With the large degree of isotopic enrichment in this sample of CsC$_{60}$, so-called "remote" peaks connecting two nonbonded nuclei i and k which share a common coupling partner j might also be expected. Such peaks are commonly observed in solution-state INADEQUATE spectra of abundant spins such as protons at frequencies given by $(\omega_{DQ}^{ik}, \omega_{SQ}^j)$. However, they have not been observed to our knowledge for carbon-13 in solids, even with 100% isotopic enrichment. It should be noted that these peaks require a longer preparation time to reach their maximum intensity than their direct counterparts and that they appear with negative intensity in the refocused variant of the INADEQUATE experiment. A small number of remote peaks are just visible above the noise at longer preparation times, and their positions provide further verification of the assignment of Figure 4. Two examples taken from a refocused INADEQUATE spectrum with a preparation delay (2τ) of 5.9 ms are shown in Figure 5 in which cross-sections parallel to ω_1 at (a) 130 ppm and (b) 348 ppm are shown. The high-field peak in Figure 5b is consistent with the assignment of peak (d*) at 114 ppm to site (13), because it arises from the remote connection between sites (5) and (13) via site (9).

In ref 17, two possible assignments were found to be consistent with the NMR data. The difference between these hinges around sites (4) and (5) which are assigned to either peak (c) or peak (d) in the two possibilities. A choice between these could only be made on the basis of calculated hyperfine coupling constants which suggested the former was the correct assignment. However, this ambiguity is removed by the refocused INADEQUATE spectrum because of the observed sum frequencies which involve peak d*. In both possibilities, this peak corresponds to site (13) which is bonded to sites (11) and (9). In the second possibility, designated choice B in ref 17, peak (g) is assigned to site (11), whereas site (9) contributes to the intense peak (d). This assignment is not consistent with the refocused INADEQUATE spectrum, because it requires the appearance of peaks with a sum frequency of 247 ppm at (247 ppm, 133 ppm) and (247 ppm, 114 ppm) which are not observed. On the other hand, the possibility designated choice
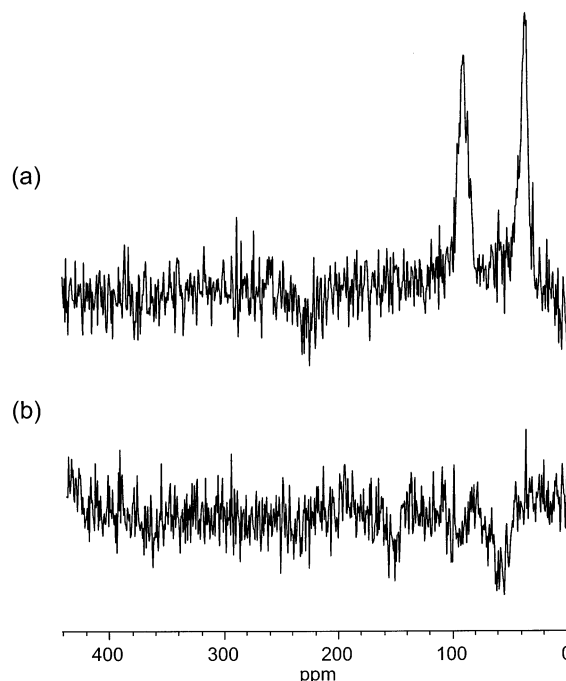

Figure 5. Cross-sections parallel to ω_2 taken from a refocused INADEQUATE spectrum of polymer CsC$_{60}$ recorded using parameters described in the text and a preparation delay (2τ) of 5.9 ms at ω_1 frequencies of (a) 130 and (b) 348 ppm. These show examples of remote peaks which connect two nonbonded nuclei which share a common coupling partner. Note that these peaks are of low intensity and opposite phase to the direct peaks as expected. In part a, the negative peak at 228 ppm arises from the remote connection between sites (2) and (8) via site (5), whereas in part b, the negative peak at 55 ppm arises from the remote connection between sites (5) and (13) via site (9). In part a, there is some interference at high field from the direct peaks connecting sites (1) and (2) which have maximum intensity at $\omega_1 = 123$ ppm, while in part b.

A in ref 17 is consistent with the refocused INADEQUATE spectrum. This choice requires peaks with a sum frequency of greater than 500 ppm linking peak (d*) with one of the low-field peaks (a) or (b). Such peaks are apparent in the refocused INADEQUATE spectrum, particularly at the lower contour levels plotted in Figure 3b. Because the whole assignment depends on the peaks which involve site (13), cross-sections through the spectrum of Figure 3 parallel to ω_2 at ω_1 frequencies of 168, 228, and 534 ppm are shown in Figure 6 parts a–c, respectively. The quality of the refocused INADEQUATE spectrum is sufficient to assign peak (a) to site (11) on the basis of the low-field peak at (538 ppm, 420 ppm) in Figure 6c. It should be noted that although the signal-to-noise is low this peak is visible in all of the refocused INADEQUATE spectra recorded.

With the assignment completed, experimental Knight shift values can be extracted for each site on the fullerene molecule by estimating the chemical shift for all sites except (1) to be that of the carbon-13 resonance in C$_{60}$, namely, 143 ppm. These values are shown in Table 1. Electron density values calculated from

$$\rho(j) = \frac{K(j)}{\sum_j |K(j)|} \quad (2)$$

are given for each site in Table 2. It should be noted that sites 4, 5, 10, 11, and 14 were predicted to have the largest Knight

TABLE 1: Assignment, Positions and Experimental Knight Shifts for Resonances in the Carbon-13 MAS Spectrum of CsC_{60}[a]

peak	a	b	b*	c	d	d*	e	f	g	h	i
position/ppm	420	378	375	227	133	114	88	68	56	41	35
K/ppm	277	235	232	84	−10	−29	−55	−75	−87	−102	0
assignment	11	10	14	4,5	a	13	2	3	9	8	1

[a] Peak d is assigned to sites 6, 7, 12, 15, and 16.

TABLE 2: Experimental Knight Shifts and Electron Densities for Sites in CsC_{60}

site	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
K/ppm	0	−55	−75	84	84	−10	−10	−102	−87	235	277	−10	−29	232	−10	−10
$\rho \times 100$	0	−1.1	−1.4	1.6	1.6	−0.2	−0.2	−2.0	−1.7	4.5	5.3	−0.2	−0.6	4.5	−0.2	−0.2
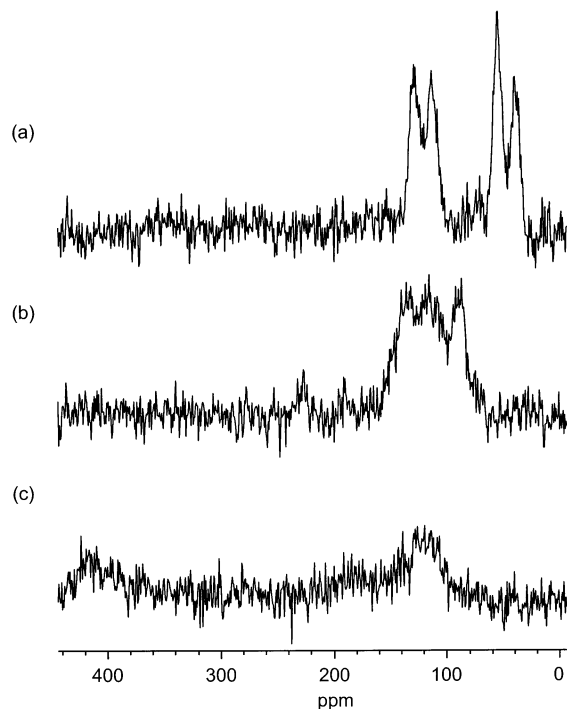
Figure 6. Cross-sections parallel to ω_2 taken from the refocused INADEQUATE spectrum of polymer CsC_{60} shown in Figure 3 at ω_1 frequencies of (a) 168, (b) 228, and (c) 534 ppm. Of these, parts a and c arise from the connections between site (13) which is assigned to the resonance at 114 ppm in the MAS spectrum and sites (9) and (11) at 56 and 420 ppm respectively, whereas part b shows an equivalence peak for site (13) at 114 ppm. Note the interference from peaks with similar ω_1 frequencies in parts a and b.

shifts by de Swiet et al.[17] Density functional calculations on a C_{60} trimer predict hyperfine couplings of 2.6, 2.6, 6.6, 6.6, and 6.8 MHz for these sites, respectively. It should be noted that these calculations were carried out in the vacuum and do not include effects of packing in the solid which clearly break the symmetry between sites 10 and 11.

Conclusions

The carbon-13 INADEQUATE spectra presented here show, for the first time in a solid, "remote" cross-peaks between nonbonded pairs of nuclei which share a common coupling partner. These cross-peaks are expected from a comparison with solution-state INADEQUATE at high levels of isotropic enrichment. In addition, new "equivalence" cross-peaks, unique to solid-state INADEQUATE, have also been observed, and their origin has been explained.

An unambiguous assignment for the carbon-13 spectrum of CsC_{60} has been obtained using a refocused INADEQUATE

experiment. In contrast to previous work, the assignment does not rely on knowledge of the electronic structure of this material. Experimental Knight shifts and spin densities extracted from the spectrum are in agreement with density functional calculations performed by de Swiet et al.[17] These in turn are based on models[16,19] in which the conduction electrons reside on sites around the equator of the fullerene molecule with insulating cycloaddition linkages between molecules. Hence, the current data support a fully three-dimensional electronic structure for this material as opposed to a quasi-one-dimensional one.[5]

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