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FULL PAPER

Proton, muon and ^{13}C hyperfine coupling constants of $C_{60}X$ and $C_{70}X$ (X=H, Mu)

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The reaction of H atoms with fullerene C_{70} has been investigated by identifying the radical products formed by addition of the atom muonium (Mu) to the fullerene in solution. Four of the five possible radical isomers of C_{70}Mu were detected by avoided level-crossing resonance (µLCR) spectroscopy, using a dilute solution of enriched $^{13}C_{70}$ in decalin. DFT calculations were used to predict muon and ^{13}C isotropic hyperfine constants as an aid to assigning the observed µLCR signals. Computational methods were benchmarked against previously published experimental data for $^{13}C_{60}$Mu in solution. Analysis of the µLCR spectrum resulted in the first experimental determination of ^{13}C hyperfine constants in either C_{70}Mu or $C_{70}H$. The large number of values confirms predictions that the four radical isomers have extended distributions of unpaired electron spin.

Introduction

Free radical reactions of fullerenes provide an important route to their functionalization.[1-3] In addition, the so-called "radical-sponge" characteristic of fullerenes has led to their use as antioxidants in biological systems and as stabilizing agents for polymers.[1] It is therefore important to understand the principles that lead to fullerene reactivity, including the unpaired electron spin distribution that affects subsequent radical additions. The application of electron paramagnetic resonance (EPR) to the study of fullerene radicals has been reviewed by Morton et al,[4-6] who carried out many key investigations of free radical additions to C_{60} and C_{70}.[7-12] Arguably, the most fundamental investigation of reactivity towards free radicals is to add hydrogen atoms.[10,11] However, H atoms as reagents are neither easy to produce nor simple to monitor. In fact, the muoniated radicals C_{60}Mu[13] and C_{70}Mu[14,15] were detected before $C_{60}H$[10,16] and $C_{70}H$.[11,17]

Muonium (Mu) is the single-electron atom with a positive muon as nucleus. Despite the small mass of the muon (0.11 u) the reduced masses of the atomic systems are very close, resulting in similar chemistry. Thus muonium is essentially a light isotope of hydrogen and can be used to study free radicals formed by addition of H to unsaturated molecules.[18-20] Muoniated free radicals (i.e. those for which a Mu replaces an H atom) have been studied by several magnetic resonance techniques: transverse-field muon spin rotation (TF-µSR), radio-frequency muon spin resonance (RF-µSR) and muon avoided level-crossing resonance (µLCR). The first two techniques are used to determine muon hyperfine constants (hfcs), while the last can be used to determine the hfcs of other spin-active nuclei in a muoniated radical.

The value of muon spectroscopic techniques is well illustrated by attempts to map the unpaired spin distribution in $C_{60}H$ via measurement of the ^{13}C hyperfine constants. The ESR spectrum of $C_{60}H$ provides only the magnitudes of hfcs from line splittings.[21] In contrast, µLCR is sensitive to both the magnitude and sign of hfcs. The simple relationship between hfc and resonance field allowed us to make an unambiguous determination of the hfcs in C_{60}Mu, in a µLCR study of a ^{13}C-enriched sample of C_{60} in solution.[22] Surprisingly, the largest hfc (which happens also to correspond to the most intense signal) revealed a ^{13}C hyperfine constant which was not reported in the ESR study. Since our value matches the ESR results for monoalkyl adducts of C_{60}, (C_{60}R, R = methyl,[21,24] t-butyl[8]), we can only surmise that the outermost pair of lines in the ^{13}C splitting pattern of $C_{60}H$ were somehow missed. On the other hand, a subsequent, independent ESR investigation also failed to find the missing lines,[25] and as far as we know the dilemma is unresolved.

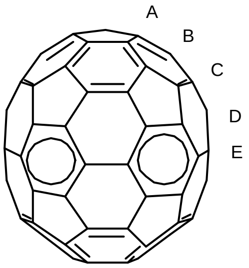

Fig. 1 C_{70} has five chemically inequivalent carbons, **A**-**E**, in relative abundance 10:10:20:20:10.

Whether by ESR or muon spin spectroscopy, investigation of the radical adducts of C_{70} is more complicated than for C_{60} because there are five chemically distinct carbons and thus five isomeric monoadducts. By convention, the carbon atoms are labelled **A** to **E** going from the pole of the oblate C_{70} molecule to its equator (see Fig. 1). At least four of the radicals have been detected by TF-μSR studies of solid samples.[14,15] Four $C_{70}H$ radicals have also been detected in solution by ESR.[11,17] The missing radical is probably the one corresponding to addition at site **E**. One report attributes a very weak signal in the μSR spectrum to the E adduct,[26] but this claim has been disputed on the grounds of molecular orbital calculations.[27]

The likelihood of radical attack at site **E** can also be challenged on chemical grounds. This carbon is at the intersection of three six-membered rings, and thus may be expected to behave as an "inner" carbon of a polycyclic aromatic hydrocarbon. Free radical addition at such a position involves considerable loss of resonance stabilization as well as increased distortion of the carbon framework from the ideal planar graphene configuration. In contrast, carbons **A**-**D** are each at the intersection of two six-membered rings and a five-membered ring (see Fig. 2). In this respect they resemble the carbons of C_{60}. Since five-membered rings permit curvature of fullerene surfaces, there is a smaller energy penalty for addition at this site.

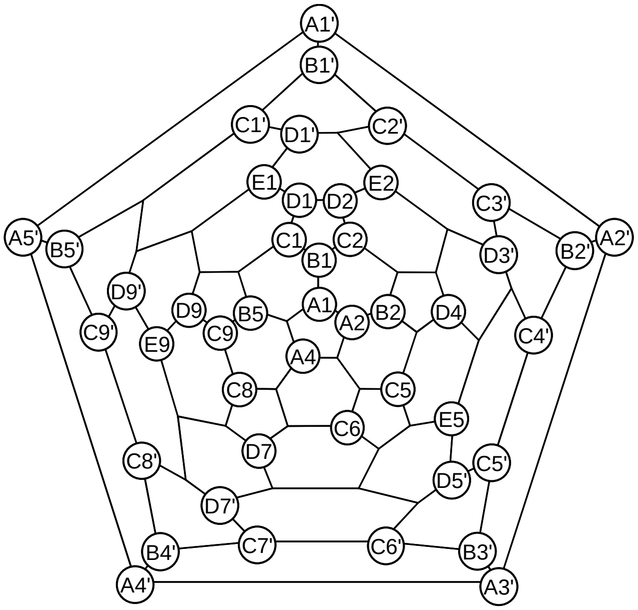

Fig. 2 Schlegel projection of C_{70} with selected labels to indicate the numbering system used in this paper. The carbons in each ring (denoted by a letter, as in Fig. 1) are numbered 1-5 or 1-10 in a clockwise direction.

In this work we present the μLCR spectrum obtained by adding Mu to $^{13}C_{70}$ in solution. It is a very rich spectrum formed from the overlap of spectra from at least three and probably four $C_{70}Mu$ isomers. We attempt an analysis of the spectrum by extracting ^{13}C hfcs and comparing them to the results of DFT calculations on $C_{60}Mu$ and $C_{70}Mu$.

Muon avoided level-crossing resonance

In muon avoided level-crossing resonance the longitudinal muon spin polarization is monitored as an external magnetic field is swept. The muon polarization is determined from the difference in number of decay positrons detected in the forward and reverse directions with respect to the applied field. Resonances occur at values of the magnetic field where a muon transition frequency is matched to that of some other nucleus (here ^{13}C) in the coupled spin system of the radical. The mixing of a pair of otherwise degenerate levels results in an avoided crossing and effective loss of muon spin polarization due to the mixing of muon and nuclear spin functions. The field at resonance is primarily determined by the difference between the hyperfine constants of the muon (A_μ) and that of the nucleus involved in the resonance. In the case of ^{13}C nuclei, the LCR field is given by

$$B_{\mathrm{LCR}} = \frac{1}{2}\left[\frac{A_\mu - A_{\mathrm{C}}}{\gamma_\mu - \gamma_{\mathrm{C}}} - \frac{A_\mu + A_{\mathrm{C}}}{\gamma_{\mathrm{e}}}\right] \qquad (1)$$

where γ_e, γ_μ and γ_C are the magnetogyric ratios of the electron, the muon and ^{13}C nucleus respectively.[18] The amplitude of each resonance (relative to the total muon polarization in the radical) is

$$\mathrm{Amplitude} = \frac{1}{4}\frac{\omega_{\mathrm{LCR}}^2}{\lambda_{\mathrm{eff}}^2 + \omega_{\mathrm{LCR}}^2} \qquad (2)$$

where λ_{eff} is the effective relaxation rate on resonance (including the muon decay constant), and

$$\omega_{\mathrm{LCR}} = z\frac{\pi A_\mu A_{\mathrm{C}}}{\gamma_{\mathrm{e}} B_{\mathrm{LCR}}} \qquad (3)$$

with $z = 1$ for a single nucleus, $z = \sqrt{2}$ for two-fold degeneracy (two magnetically equivalent nuclei).

The μLCR experiments were performed at the TRIUMF cyclotron facility in Vancouver, using standard equipment and techniques.[28] The sample consisted of a 3 mM solution of > 99% enriched $^{13}C_{70}$ in decalin, sealed oxygen-free in a stainless-steel cell equipped with a thin window; details of the preparation of similar samples are given elsewhere.[22] The use of a dilute solution was dictated by the small amount of $^{13}C_{70}$ available, but that is not a problem for μLCR, provided the muon polarization is transferred from Mu to the radical in a time short compared with the muon lifetime (2.2 μs). On the other hand, the weak signals resulting from the multiple radical products required extensive signal averaging, and the data-taking extended over several separate weeks of experiment. The spectrum shown in Fig. 3 is a composite of many overlapping field sweeps. All the results reported here were obtained at 298 K (± 0.5 K).

The resonances displayed in Fig. 3 have a differential-like shape as a result of the square wave field modulation used to suppress background fluctuations (caused, for example, by the effect of beam intensity on detector efficiency). The first step in the analysis of the spectrum was to fit each resonance with the difference of two Lorentzian line shapes separated by the peak-to-peak modulation amplitude (53 G). Thus, the resonance field is given by the point at which the signal goes through the baseline (similar to conventional ESR spectra). Each LCR signal is characterized by its own resonance field (B_{LCR}), amplitude and width (half-with at half-height: *HWHM*), as reported in Table 1. Only the 36 resonances which gave unambiguous, physically meaningful fit parameters are listed. The simulated spectrum is shown overlaying the experimental data in Fig. 3.

To extract the ^{13}C hfc values from the resonance fields using eqn. (1) it is necessary to know A_μ, the muon hfc of the radical to which each particular line belongs. We first attempted to use the muon hfcs obtained from our study of solid-state samples,[15] after adjustment for the 2% solvent effect noted in a previous study of $^{13}C_{60}$Mu.[29] However this approach does not resolve the ambiguity in assigning a particular A_μ value to each LCR resonance, although the lowest-field resonance can be confidently assigned to the radical with the lowest muon hfc.

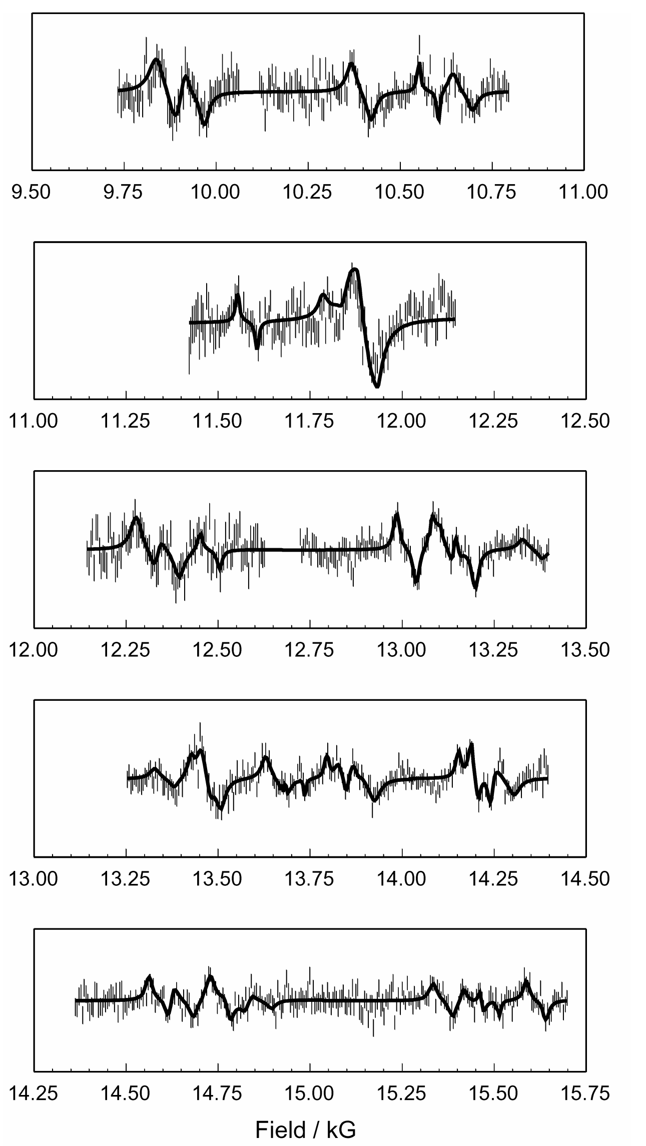

Fig. 3 Segments of the muon level-crossing spectrum obtained from a dilute solution of $^{13}C_{70}$. The thin vertical lines represent data points with 1-σ statistical error bars. The thick continuous line is a simulated spectrum comprised of fits to each of the resonance signals.

An alternative strategy, which we found useful, is to base the assignment on the pattern of intensities predicted by eqns. (2) and (3). This is best illustrated with data taken from our earlier study of $^{13}C_{60}$Mu.[22] Since the signal amplitudes depend on the product of A_μ and A_C, they tend to zero for very small values of A_C. This can be seen in Fig. 4, where signal amplitudes are plotted as a function of the resonance field predicted by eqn. (1). The points and curves correspond to a fixed value of A_μ and a series of A_C values, decreasing from positive, through zero, to negative from left to right. The two predicted curves represent different values of the degeneracy factor z. Clearly, given sufficient resonances associated with a given value of A_μ, it should be possible to extrapolate to the point where $A_C = 0$ to estimate the A_μ. For the $^{13}C_{60}$Mu spectrum the null point occurs at 13.20 kG, which corresponds to A_μ = 331.04 MHz, in good agreement with an independent measurement by radio-frequency muon spin resonance: $A_\mu = 330.89 \pm 0.15$ MHz.[29]

Table 1 Fitting parameters for the muon level-crossing spectrum of muoniated radicals obtained from a dilute solution of $^{13}C_{70}$.[a]

B_{LCR} /G	*HWHM* /G	Amplitude/10^{-3}
9866(1)	20(2)	0.78(6)
9938(1)	14(2)	0.79(7)
10395(2)	17(4)	0.59(7)
10578(1)	6(2)	0.62(15)
10670(4)	17(11)	0.38(8)
11579(2)	7(4)	0.54(18)
11825(2)	18(5)	0.36(4)
11891(1)	16(2)	1.28(4)
11934(1)	11(3)	0.42(4)
12304(3)	21(6)	0.7(9)
12368(4)	19(5)	0.56(9)
12478(3)	9(5)	0.35(11)
13014(1)	9(2)	0.74(8)
13109(4)	10(5)	0.56(23)
13127(5)	15(7)	0.45(11)
13173(1)	6(2)	0.75(9)
13355(7)	24(16)	0.2(6)
13453(6)	11(6)	0.38(12)
13477(3)	20(5)	0.65(7)
13657(2)	15(4)	0.45(6)
13710(2)	4(2)	0.34(14)
13822(2)	8(3)	0.42(9)
13850(4)	11(6)	0.27(8)
13898(4)	20(7)	0.46(6)
14180(1)	8(3)	0.5(8)
14214(1)	9(2)	0.71(9)
14277(3)	20(5)	0.35(6)
14590(2)	8(3)	0.45(1)
14655(3)	13(6)	0.33(7)
14755(2)	13(3)	0.47(7)
14791(8)	5(10)	0.16(13)
14879(6)	4(9)	0.3(11)
15361(3)	13(6)	0.38(7)
15444(4)	10(4)	0.29(9)
15488(3)	5(5)	0.31(13)
15614(2)	11(4)	0.42(8)

[a] Statistical uncertainties are shown in parentheses.

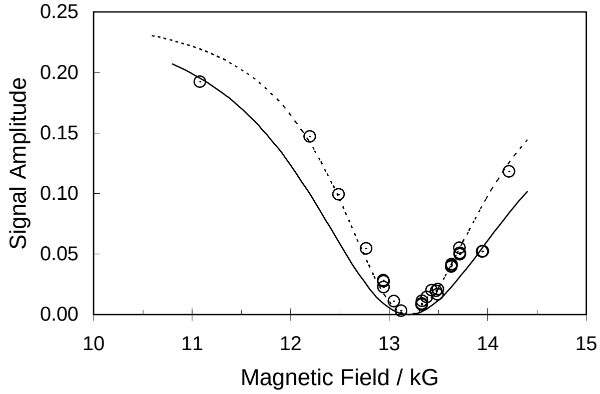

Fig. 4 Amplitudes of μLCR signals for Mu$^{13}C_{60}$ in decalin solution (data taken from ref. 22). The dotted and solid curves represent the theoretical predictions of eqns. (1) and (2), with $z = \sqrt{2}$ and $z = 1$, respectively.

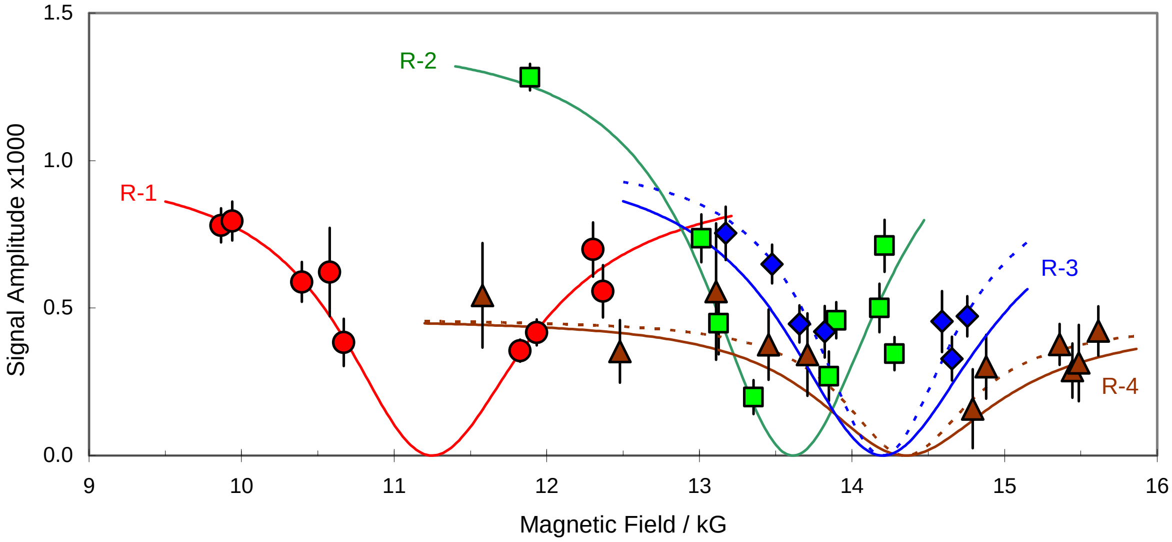

Fig. 5 Amplitudes of µLCR signals for Mu^{13}C$_{70}$ in decalin solution and their assignment to four C$_{70}$Mu isomers: R-1 (red circles), R-2 (green squares), R-3 (blue diamonds),and R-4 (brown triangles). The best fits to the amplitude envelopes are shown for singly degenerate signals (solid lines), and doubly degenerate signals (dashed lines).

Whatever approach is used, the extracted ^{13}C hfcs must have reasonable values, i.e. they should be in the range $-50 < A_C < 100$ MHz. (Further restrictions can be applied on the basis of computational predictions, as discussed later.) With this in mind, a global fit was attempted to all the data of Table 1, with the muon hfc and the abundance of each radical species as free parameters. It is significant that all our data could be accommodated with only four radical species (with an upper limit of ≈ 0.02 for the fractional abundance of a fifth radical). A graphical representation of the fit is given in Fig. 5. The curves show the envelopes of the predicted signal amplitudes. For radicals R-3 and R-4 the amplitudes mostly correspond to doubly degenerate resonances (denoted by dashed curves in the figure).

Table 2 Muon hyperfine coupling constants and relative abundances of C$_{70}$Mu radicals in C$_{70}$ powder and in decalin solution.

	C$_{70}$ powder sample [a]		^{13}C$_{70}$ in solution [b]	
Radical	A_μ /MHz	abundance	A_μ /MHz	abundance
R-1	274.82	0.41	282(1)	0.25(1)
R-2	339.00	0.30	342(1)	0.37(2)
R-3	354.00	0.11	356(1)	0.26(2)
R-4	359.80	0.15	360(5)	0.12(2)

[a] Ref. 15. [b] This work.

Table 2 compares the best fit values of A_μ and the associated radical abundances with the corresponding data determined from a TF-µSR study of a C$_{70}$ powder sample. At first glance there appears to be good agreement between the hfcs in the two phases, with the exception of R-1. On the other hand, if one applies the 2% solvent effect found for C$_{60}$H, then the R-1 values are close and the others less so. In any event, comparison of the abundances suggests that phase has a marked effect on the relative yields of the radical isomers. We speculate that the competitive reactivity of the C$_{70}$ sites in the solid could be affected by their proximity to voids in the crystal structure which would accommodate the attacking Mu atoms. An alternative possibility is that radical formation in the solid state occurs via an ionic mechanism (either Mu$^+$ addition to C$_{70}$ followed by charge neutralization, or Mu$^+$ addition to the C$_{70}$ anion).[30] In dilute solution the radicals should be formed only by direct addition of Mu, so in principle the solution data ought to better reflect the relative reactivities of carbons **A-E** in the isolated molecule, taking into account the different degeneracies (10:10:20:20:10). On the other hand, the empirical analysis presented in Fig. 5 yields relative abundances which depend heavily on the assignment of the 11891 G resonance to R-2. We turn to computational results for further insight.

Computational Investigation

Molecular geometries and hyperfine coupling constants of C$_{60}$H and the five C$_{70}$H isomers were calculated in Gaussian09[31] using the B3LYP hybrid functional and either the 6-31G(d) or the 6-311G(d,p) basis set. The analogous muoniated radicals were treated as isotopologues of their protiated counterparts. Within the Born-Oppenheimer Approximation the equilibrium molecular geometry is unaffected by isotopic substitution. However, this applies only to the (unattainable) minimum of the potential surface. Once zero-point vibrational effects are taken into account bond-lengths can change, due to averaging over anharmonic stretching vibrations, and hyperfine constants become isotope dependent (through averaging of both harmonic and anharmonic modes).[32] Vibrational averaging also gives rise to temperature dependence of hfcs. Both effects have been investigated for the case of C$_{60}$H.[33,34]

As a prelude to discussing our computational investigation of the C$_{70}$Mu isomers, we present results for C$_{60}$Mu. To facilitate comparison of muon and proton hyperfine constants we express the former as a *reduced* muon hfc: $A_\mu' = 0.31413A_\mu$, where the scale factor accounts for the trivial effect of the differing magnetic moments. Thus the benchmark experimental value for

C_{60}Mu in solution is $A_\mu' = 103.9$ MHz, while the proton hfc for C_{60}H is $A_p = 92.7$ MHz.[10] Our calculation with the 6-31G(d) basis set gave $A_p = 96.3$ MHz at the reference geometry. The discrepancy between observed and calculated hfc is due to a combination of basis set error and neglect of vibrational averaging. Tokunaga et al. reported a value of 94.2 MHz using an expanded basis set: 6-311G(d,f),[35] again without vibrational averaging.

In the case of C_{60}Mu the stretching and the two wagging motions of C-Mu are to a high degree isolated from the 174 normal modes of the carbon skeleton – we calculated harmonic frequencies of 8601, 3443 and 3307 cm^{-1} at the 6-31G(d) level, compared with 254–1613 cm^{-1} for the carbon framework. Since a full calculation is prohibitive in terms of available computing resources, we froze the carbon skeleton at the optimized (reference) geometry for the radical, and averaged the muon hfc over the three anharmonic C-Mu modes (using the Fermi keyword in Gaussian-09). This resulted in $A_\mu' = 109.4$ MHz. Note that this is a prediction of the hfc at 0 K. The temperature dependence is dominated by lower frequency modes, which are highly coupled and too numerous for us to handle. Empirical modelling of the temperature dependence for C_{60}H[34] suggests that the proton (and muon) hfc falls less than 1% over the range 0–300 K. Our conclusion is that the frozen skeleton procedure overestimates the muon hfc by a few percent. To reproduce the 300 K experimental value of A_μ' it is necessary to scale our frozen-skeleton vibrationally averaged value by 0.95.

Similar considerations apply to the computation of hfcs for C_{70}Mu, so the same scale factor is used to predict A_μ' from the vibrationally averaged 0 K values calculated at the 6-31G(d) level. The results are shown in Table 3, where they are compared with experimental data (obtained from C_{70} powder samples, adjusted for the solvent effect noted for C_{60}Mu). There is relatively good agreement between computed and experimental data, and the reduced muon hfcs are consistently 10% higher than the experimental proton hfcs. In view of this level of agreement we can confidently assert that isomer E has not been detected. We further assign radicals R-1, R-2, R-3 and R-4 to structures **D**, **C**, **A** and **B**. This agrees with the conclusion of Borghi et al.[27] except for the order of **A** and **B**.

Table 3 Comparison of computed and experimental values of proton and reduced[a] muon hyperfine constants (MHz) for C_{70}H and C_{70}Mu in solution.

	C_{70}H		C_{70}Mu [b]		
Radical	Calc.[b]	Expt.[c]	Calc.[d]	Expt.[e]	Isomer
R-1	81.6	78.4	89.4	88.0	**D**
R-2	99.5	96.9	109.1	108.6	**C**
R-3	103.1	101.4	112.7	113.4	**A**
R-4	104.5	103.2	114.9	115.2	**B**
	158.3		174.0		**E**

[a] $A_\mu' = 0.31413A_\mu$. [b] Ref. 35. [c] Ref. 11. [d] This work. [e] Ref. 15 scaled for solvent effect.

^{13}C Hyperfine Constants

In view of the prohibitively large resources needed to carry out a full vibrationally averaged calculation of ^{13}C hyperfine constants for C_{60}Mu, and C_{70}Mu, the best we could manage is to average over the C-Mu modes with the carbon skeleton frozen except for C1, the site of Mu attachment. As before, we benchmarked our results against the experimental results for C_{60}Mu. The computed hfcs at the 6-31G(d) level are too large (40% for positive hfcs, 15% for negative hfcs), but the pattern of values matches the experimental findings. Using the 6-311G(d,p) basis results in a much better match, as evident in Table 4, but we were unable to carry out the computationally intensive vibrational averaging procedure with this expanded basis set. Only the largest computed hfc values are included in the table. The values are doubly degenerate except for the few which correspond to carbons on the plane of symmetry of the radical. (See the Electronic Supplementary Information[†] for a complete list of calculated hfcs and nuclear coordinates.)

Similar calculations were carried out for the five isomers of C_{70}H and the results are listed in Supplementary Information.[†] These data apply also to C_{70}Mu since they refer to calculations at the optimized reference geometry, without any vibrational averaging. The omission of vibrational averaging means that anharmonicity and temperature dependence have been neglected. Nevertheless, they are useful as a guide in the derivation and interpretation of the experimental ^{13}C hfcs for C_{70}Mu.

Table 4 Comparison of computed[a] and experimental[b] values of ^{13}C hyperfine constants (MHz) for C_{60}Mu in solution.

Calc.	Exp.	Calc.	Exp.
50.1[c]	52.6[c]	-27.7	-25.4
23.8	24.8	-15.7[c]	-18.8[c]
18.6	17.6	-13.6	-13.0
10.9	10.7	-11.2	-10.9
6.8	6.2	-7.6	-7.5
5.2	3.6	-6.1	-6.0
4.2	1.8	-4.7	-4.7
3.6		-3.6	-3.7
2.9		-3.5[c]	-3.5
2.7		-3.4	-3.4

[a] UB3LYP//6-311G(d,p). [b] Ref. 22. [c] Single value; others are doubly degenerate.

To extract ^{13}C hfcs from the LCR resonance positions listed in Table 1 we reorganized eqn. (1) to express the ^{13}C hfc as a function of muon hfc and resonance field. After substituting for the various magnetogyric ratios the expression becomes

$$A_C = c_a A_\mu - c_b B_{LCR} \tag{4}$$

where $c_a = 0.99113$ and $c_b = 24.856$ MHz kG^{-1}. In principle, for each LCR resonance field B_{LCR}, this equation generates five alternative values of A_C corresponding to the five radical isomers with different values of A_μ. In practice a large number of possibilities can be dismissed on account of unrealistic answers. For example, none of the LCR resonances can be due to radical **E** because its high muon hfc (~550 MHz by computation) would result in A_C values in excess of 160 MHz. Similar (but less severe) constraints apply to radicals **A-D**. For their A_μ values we took the C_{70} powder data adjusted for a 2% solvent effect , as presented in Table 3. By comparing alternative A_C values with computed values we arrived at the values and assignments listed in Table 5.

Three resonances from the original list (Table 1) could not be assigned, and it is possible that this is due to imperfection in the spectrum simulation. The spectral ranges of the four isomers overlap, and there are several coincident resonances and ambiguous assignments. The accidental degeneracy at 11891 G calls into question the relative abundances reported in Table 2 because the empirical analysis reflected in fig. 5 assumed that this resonance was due to a single radical (R-2). In principle an iterative procedure might resolve these flaws in the assignment. However, we caution that the calculated values do not take into account anharmonicity or temperature dependence. It is perhaps significant that the resonances at 11579 G, 14590 G, 15361 G, and 15444 G show significant discrepancies between experimental and calculated hfcs. These correspond to the sites of Mu attachment and would therefore be influenced by C-Mu vibrations. With these exceptions the agreement between experimental and calculated hfcs gives us confidence in the assignments. It is important to realise, however, that the ^{13}C hfcs deduced from the LCR spectrum and listed in Table 5 are all subject to systematic error, since they depend on muon hfcs which have not been directly measured for $C_{70}Mu$ in solution.

Table 5 ^{13}C hyperfine constants (MHz) for $C_{70}Mu$ isomers in solution.

B_{LCR} /G	Isomer	Carbon #	Exp.^{a}	Calc.^{b}
9866	**D**	D1	32.4	33.5
9938	**D**	D1'	30.6	29.8
10395	**D**	E2	19.3	19.7
10578	**D**	C10'	14.7	14.9
10670	**D**	C10	12.4	13.4
11579	**D**	D2	-10.2	-13.5
11825	**D**	D2'	-16.3	-17.2
11891^c	**D**	C1'	-17.9	-18.3
11891^c	**C**	E1	46.9	44.1
11934	**D**	E1	-19.0	-20.2
12304	**B**	A1	57.7	55.2
12368	**A**	B1	51.8	50.5
12478	—^{d}	—	—	—
13014^c	**C**	A2	19.0	18.3
13014^c	**C**	B1	19.0	18.0
13109	**C**	D2	16.7	16.6
13127	**C**	D4'	16.2	16.0
13173	**C**	D4	15.1	14.8
13355	**C**	E3	10.6	11.8
13453	**C**	C5'	8.1	8.8
13477	**C**	B3	7.5	8.2
13477	**A**	C3, C10^e	22.7	21.5
13657	**A**	A2,A5^e	18.2	19.3
13710	—^{d}	—	—	—
13822	**B**	C1,C2^e	20.0	21.4
13850	—^{d}	—	—	—
13898	**B**	B2,B5^e	18.1	18.2
14180^c	**B**	C5,C8^e	11.1	10.8
14180^c	**C**	A1	-10.0	-9.3
14214	**C**	A3,C4'^{e}	-10.8	-10.3
14277	**C**	E4,D3'^{e}	-12.4	-12.2
14590	**C**	C2	-20.1	-17.3
14655^c	**C**	B2	-21.8	-23.1
14755^c	**C**	D3	-24.2	-25.5
14791	**A**	B2,B5^e	-10.0	-9.9
14879	**A**	D3,D10^e	-12.2	-12.1
15361	**A**	A1	-24.2	-15.6
15444	**B**	B1	-20.4	-16.2
15488	**A**	C1,C2^e	-27.3	-25.9
15614	**B**	A2,A5^e	-24.6	-25.6

[a] This work, from LCR spectrum. [b] UB3LYP//6-311G(d,p). [c] Accidental degeneracy or alternative assignments. [d] Unassigned. [e] Degeneracy due to radical symmetry.

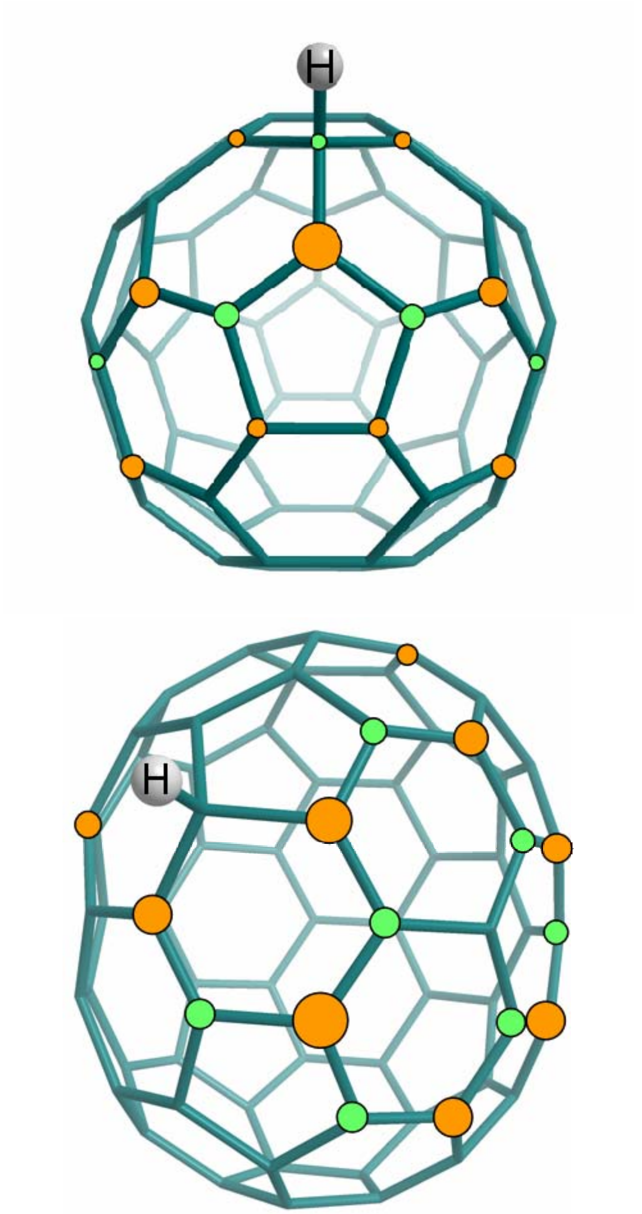

Fig. 6 Mulliken unpaired spin distributions in $C_{70}H$ isomers **A** (top) and **D** (bottom). Orange and green disks represent positive and negative spin density, respectively, with area proportional to magnitude. Only values greater than 0.05 are shown.

Conclusions

The free radicals $C_{60}Mu$ and $C_{70}Mu$ have been investigated both experimentally and with DFT calculations. The combination of density functional B3LYP and 6-31G(d) basis set was found to give reasonable values for the proton and muon hfcs of $C_{60}H$ and $C_{60}Mu$, but an expanded basis set, 6-311G(d,p), was necessary to predict adequate values of ^{13}C hfcs. The calculations were benchmarked against experimental data from our previous work, but also serve to confirm our conclusion[22] (shared by others)[5] that a pair of lines has been missed in the ESR spectrum of $C_{60}H$ in solution, perhaps as a result of chemically induced spin polarization.[21,25]

Our DFT predictions of muon and ^{13}C hfcs for the five isomeric C_{70}Mu radicals were used to guide the analysis of the μLCR spectrum. As anticipated by a preliminary empirical analysis, the recorded spectrum was found to be a composite of four overlapping spectra due to the four isomers labelled **A**-**D**. Not present is the radical **E**, formed by Mu addition to the polyaromatic equatorial "belt" of C_{70}. This conclusion is in accord with findings for C_{70}H,[11,27] as well as predictions of reactivity based on the effect of local curvature.[36,37] Also, our DFT calculations (see the Supplementary Information)† show that radical **E** is about 50 kJ mol^{-1} higher in energy than the other isomers, as reported by others.[35,38]

The large number of moderately sized ^{13}C hfcs determined for isomers **A**-**D** confirm earlier predictions of the extended unpaired spin distribution in these radicals.[11,27] This is evident from the examples shown in Fig. 6, where Mulliken spin densities are denoted by circles of different area (magnitude) and colour (sign). Radicals **A** and **B** have spin distributions in the coronene-like polar regions of the molecule, similar to C_{60}H, whereas the spin in **C**, **D** and **E** extends to the polyaromatic regions around the equator. The relative ease of bond conjugation in the less curved aromatic regions of the molecule results in asymmetric spin distributions for **C** and **D** (see Fig. 6). It is also a factor in the higher proton hfc calculated for **E**, where all three carbons adjacent to the site of attachment have significant π spin density. Hyperfine constants and Mulliken spin densities for all isomers are listed in the Supplementary Information.†

This work constitutes the first experimental determination of these hfcs. Notwithstanding the relatively good agreement between experimental and calculated hfcs, we caution that our data is subject to systematic error, since analysis of the μLCR spectrum relies on knowledge of the muon hfcs. Improved analysis could result from either (1) direct measurement of the muon hfcs of C_{70}Mu in solution; or (2) more accurate calculation of the muon hfcs, taking into account vibrational averaging over all modes.

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† Electronic Supplementary Information (ESI) available: Optimized geometries and ^{13}C hyperfine constants computed for C_{60}H and the five C_{70}H isomers. See DOI: 10.1039/b000000x/

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