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Fine structure in the solution state ^{13}C-NMR spectrum of C_{60} and its endofullerene derivatives[†]

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Electronic supporting information[†]

Contents

1 Spectral fitting procedure

The ^{13}C solution NMR spectrum of C_{60} at 295 K is seen in fig. 1, where Wilmad precision NMR tubes rated for 900MHz were used to reduce the line width. On this figure the isotope shifted peaks are seen upfield from the main C_{60} by -12.6 ppb (HP) and -20.0 pbb (HH). The ratio of these peaks is generally HP:HH = 2:1 which very well corresponds to the abundance of these bonds in the C_{60}.

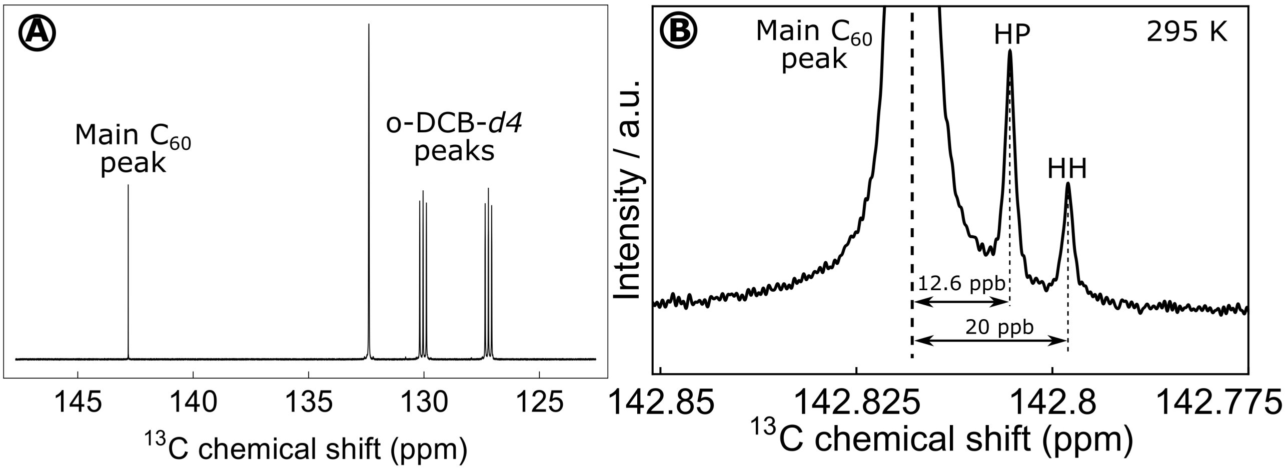

Figure 1: A: Experimental ^{13}C NMR spectrum of ∼25 mM C_{60} (natural abundance) dissolved in o-DCB-d_4 solvent acquired at 16.45 T (^{13}C nuclear Larmor frequency = 176 MHz) and 295 K with 856 transients. The main C_{60} peak is around 142.8 ppm and on the right are the o-DCB-d_4 peaks. B: is just A zoomed in around the C_{60} peak. Upfield from the main C_{60} peak the ^{13}C-^{13}C isotope shifted peaks denoted HP (-12.6 ppb, Hexagon-Pentagon ^{13}C-^{13}C bond) and HH (-20.0 ppb, Hexagon-Hexagon ^{13}C-^{13}C bond). Fitting in fig 2 and peak integrals in table 1, see text for more details.

In table 1 the peak areas of HP (a_1) and HH (a_2) from fig. 1 are given with respect to the main C_{60} peak (a_0). Three methods were used to calculate the peak area. Firstly the spectra were fitted in TopSpin where HP and HH were fitted with a single Lorentzian and the main C_{60} peak was fitted with 45% Lorentzian + 55% Gaussian. This fitting is shown in fig. 2 where in blue is the experimental spectrum, in red is the fitted spectrum and in black is the difference of the two. The difference spectrum shows just noise for HP and HH but it shows a significant remainder for the main C_{60} peak, this remainder was taken into account when calculating the ratios in table 1. The other two methods were done using Mathematica software. Lorentzian means the HP and HH peaks were fitted with a single Lorentzian and the main C_{60} was fitted with a two Lorentzian functions, each functions having three free parameters. Interpolation means the peaks were interpolated with a spline function and then integrated to give the area, the raised baseline under the HP/HH peaks was corrected by a double Lorentzian fit for the main C_{60} peak (from the previous fitting).

Table 1: Ratios relative to the main C_{60} peak (a_0/a_0=100%) for HP (a_1/a_0) and HH (a_2/a_0) (from fig. 1). Integration methods are defined in text

Method	HP (a_1/a_0)	HH (a_2/a_0)	HP/HH (a_1/a_2)
TopSpin	1.969%	0.981%	2.007
Lorentzian	1.5215%	0.754%	2.016
Interpolation	1.416%	0.688%	2.056
Average	1.63 ± 0.15 %	0.81 ± 0.08 %	2.02 ± 0.01

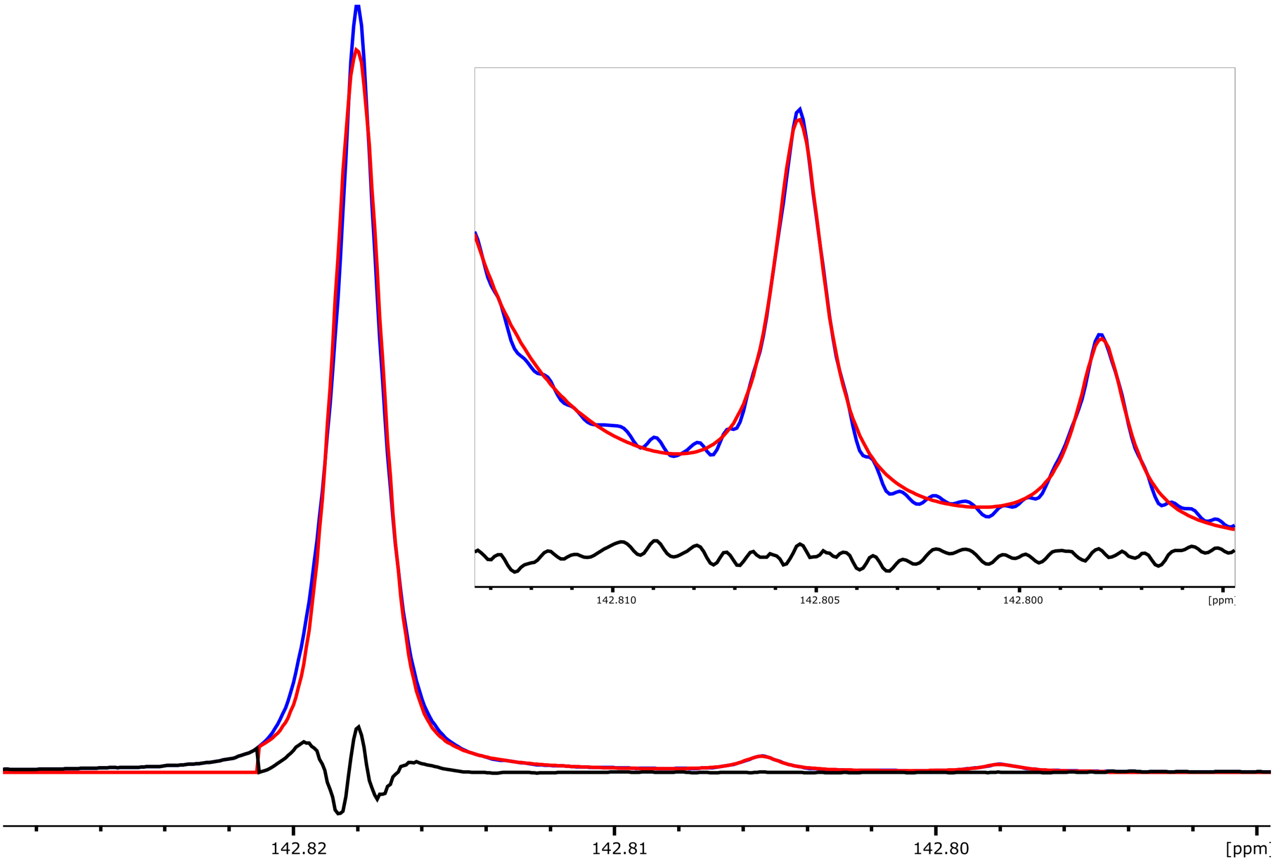

Figure 2: Blue: Experimental ^{13}C NMR spectrum from fig 1. Red is the fitted spectrum using TopSpin, a single Lorentzian function was used for HP and HH, and main C_{60} peak was fitted with 45% Lorentzian and 55% Gaussian. Black is the diferece between Blue and Red. Peak integrals are found in table 1 on the TopSpin row.

2 Spin-lattice relaxation times

2.1 C_{60} natural abundance, ^{13}C T_1

The ^{13}C T_1 of natural abundance C_{60} was measured using saturation recovery. The relaxation curve is seen in fig. 3 which gives the ^{13}C T_1 = 16.6±0.3 s.

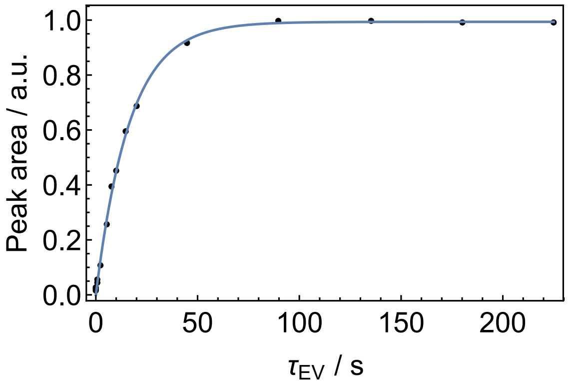

Figure 3: Saturation Recovery relaxation curve for C_{60} natural abundance 4.5 mM at 16.45 T ($\Omega^{13}C = 176\,\text{MHz}$) and 295 K with 80 transients and degassed by bubbling N_2 for 10 mins. ^{13}C T_1 = 16.6±0.3 s, fitted with $I_0 * (1 - exp(\frac{-t}{T_1}))$, where $I_0 = 0.994 \pm 0.005$

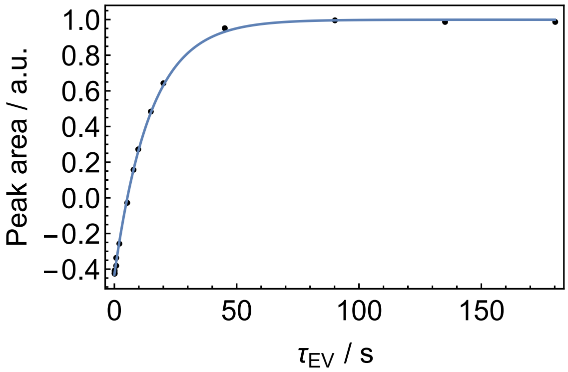

Figure 4: Inversion Recovery relaxation curve for C_{60} 20-30% ^{13}C 20 mM at 16.45 T ($\Omega^{13}C =$ 176 MHz) and 295 K with 32 transients and degassed by bubbling N_2 for 10 mins. ^{13}C T_1 = 14.8±0.2 s, fitted with $I_0 * (1 - A * exp(\frac{-t}{T_1}))$, where $I_0 = 0.999 \pm 0.005$ and A=1.431 ± 0.004.

2.2 C_{60} 20-30% ^{13}C, ^{13}C T_1

The ^{13}C T_1 20-30% ^{13}C C_{60} was measured using inversion recovery in order to compare with the natural abundance C_{60}. The relaxation curve is seen in fig. 4 which gives the ^{13}C T_1 = 14.8±0.2 s.

The ^{13}C T_1 for 20-30% ^{13}C C_{60} is only slightly shorter than the natural abundance C_{60}, which is expected due more ^{13}C's giving rise to dipolar relaxation. This excludes the possibility of the significant broadening seen in the 20-30% ^{13}C C_{60} spectrum (fig. 5 green) to arise solely due to very fast relaxation. Thus we conclude that the broad feature in the ^{13}C NMR spectrum of 20-30% ^{13}C C_{60} arises due to isotope shift distributions and possibly J couplings.

3 Chemical shift referencing of ^{13}C enriched C_{60}

The ^{13}C solution NMR spectrum of 20-30% ^{13}C enriched C_{60} is seen in green in fig. 5 A and B. To accurately measure the chemical shift of the enriched C_{60} with respect to natural abundance C_{60}, both were added to a solution (and TMS ∼ 10 μL) and then the NMR spectrum of the mixture was measured. The NMR spectrum of the mixture can be seen in blue in fig. 5 A.

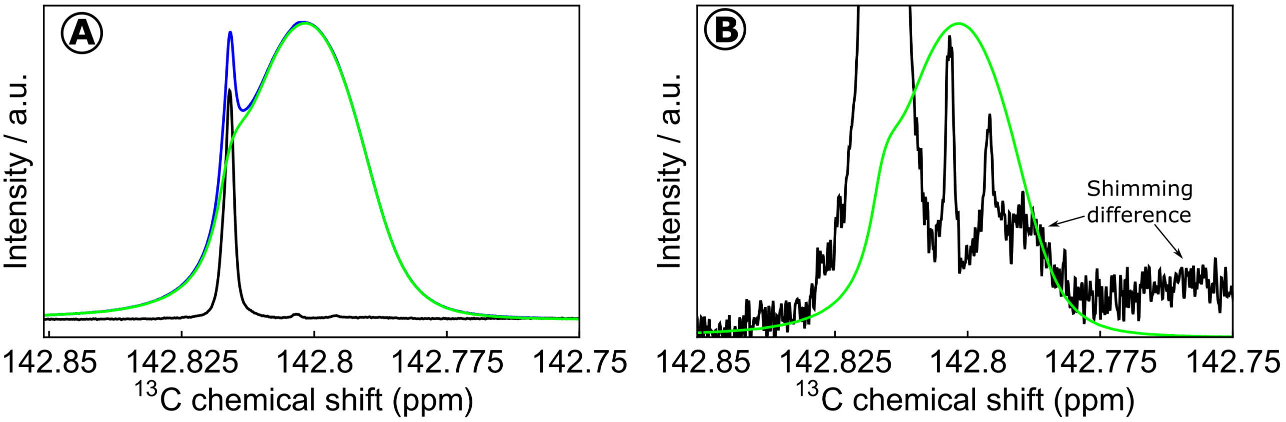

Figure 5: Experimental ^{13}C NMR spectrum of ~25 mM C_{60} dissolved in o-DCB-d_4 solvent acquired at 16.45 T (^{13}C nuclear Larmor frequency = 176 MHz) and 295 K. Green- C_{60} 20-30% ^{13}C enriched (16 scans, scaled to match Blue), Blue- C_{60} natural abundance + C_{60} 20-30% ^{13}C enriched (1:0.6 mass ratio, 512 scans), Black- is Blue minus Green. B: is the same as A just without Blue and with Black scaled up to see the isotope shifted peaks match the mean chemical shift of the 20-30% ^{13}C enriched C_{60} peak. In B some broader features appear due to shimming differences in the two samples.

A clear change can be seen between green and blue. The shoulder seen in the enriched sample (green) increases when adding natural abundance C_{60}. This proves that the shoulder in the 20-30% ^{13}C enriched C_{60} arises from isolated ^{13}C's in the cage. This can be seen more clearly when the difference between the mixture (blue) and purely enriched C_{60} (green) is plotted, see black spectrum in fig. 5 A and B. In A (black line) the peak for the main C_{60} matches very well with the shoulder of the enriched C_{60} (green line). In B the black line was scaled to magnify the HP and HH peaks such that the overlap with the broad peak of the enriched C_{60} (green line). In B the black line has some minor broader features arising due to shimming differences between the enriched C_{60} and the mixture.

4 Monte Carlo simulations

In fig. 6 some selected simulated ^{13}C NMR spectra of C_{60} are shown, with increasing ^{13}C probability.

5 C_{60} isotopomer probabilities

The probability for a number of $m \times {}^{13}$C to be substituted into a C_{60} cage needs to be computed. For this a statistical equation implementing the total number of carbon sites "n_C" = 60, the number of ^{13}C's substituted in the cage "m" and the ^{13}C (natural) abundance "x= 0.01108" is needed, eq. 1.[1] The binomial coefficient $\binom{n_c}{m} = \frac{n_c!}{(n_c-m)!m!}$ is needed to take into account equivalent configurations, since all ^{12}C's and ^{13}C's are indistinguishable amongst themselves. This probability will be written as $\mathrm{P^{x}_{m,\,n_c}}$ and it its shown in equation 1.[1]

$$\mathrm{P^{x}_{m,\,n_c}} = \binom{\mathrm{n_c}}{\mathrm{m}}\mathrm{x^{m}(1-x)^{n_c-m}} \tag{1}$$

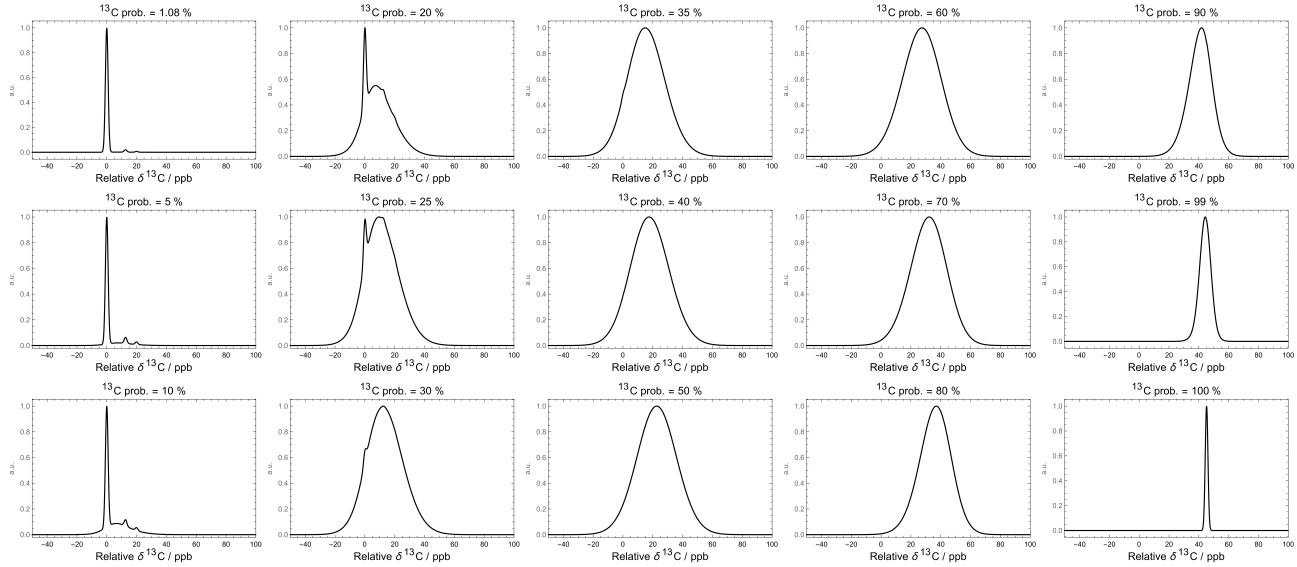

Figure 6: Monte Carlo simulations of the ^{13}C NMR spectra of C_{60} with different ^{13}C abundances. Considering spins to be coupled if they are within 3 bonds or less away from each other. Simulations done by averaging the spectra of 10000 random C_{60} configurations. Spectra were normalised for clarity.

The probabilities for $m\times{}^{13}$C's to be substituted in the natural abundance C_{60} are shown in table 2, up to m=5.

Table 2: Probability for $m\times{}^{13}$C's to be substituted anywhere in the C_{60} cage, $\mathrm{P}^{\mathrm{x}}_{\mathrm{m,\,n_c}}$ where x= 0.01108 (natural abundance), $n_C = 60$ and $m = 0, 1, 2, 3, 4, 5$. The ^{13}C NMR signal is just $m \times P^{x}_{m,n_c}$ and in brackets is shown the relative contribution to the total ^{13}C NMR signal.

m	0	1	2	3	4	5
$\mathrm{P}^{0.01108}_{\mathrm{m,\,60}}$	0.512471	0.344508	0.113868	0.0246652	0.00393803	0.000494169
^{13}C NMR signal	0 (0%)	0.344508 (51.8%)	0.227735 (34.3%)	0.0739957 (11.1 %)	0.0157521 (2.4 %)	0.00247085 (0.4%)

The probability for a number (m) of ^{13}C's to substituted in the C_{60} cage can be calculated using eq. 1 if the ^{13}C abundance (x) is know (where n_C=60). Thus eq. 1 is plotted in fig. 7 for different ^{13}C abundances (x): black- natural abundance (1.108% ^{13}C), orange- 20% ^{13}C, green- 25% ^{13}C and blue- 30% ^{13}C. These plots essentially represent the pattern an ideal mass spectrum would look like for C_{60} with a given ^{13}C abundance (x).

5.1 C_{60} isotope shift natural abundance statistical analysis, up to three ^{13}C substitutions

From the HP and HH peak integral ratio of 2:1 it seems that they arise from the HP and HH bonds. But the relative ratios with respect to the main C_{60} peak are needed to fully elucidate the origin of these peaks. For this the statistical substitutions of ^{13}C's in the C_{60} cage are required. In the section below this was done statistically by considering up to maximum three ^{13}C's being substituted in the cage at one time.

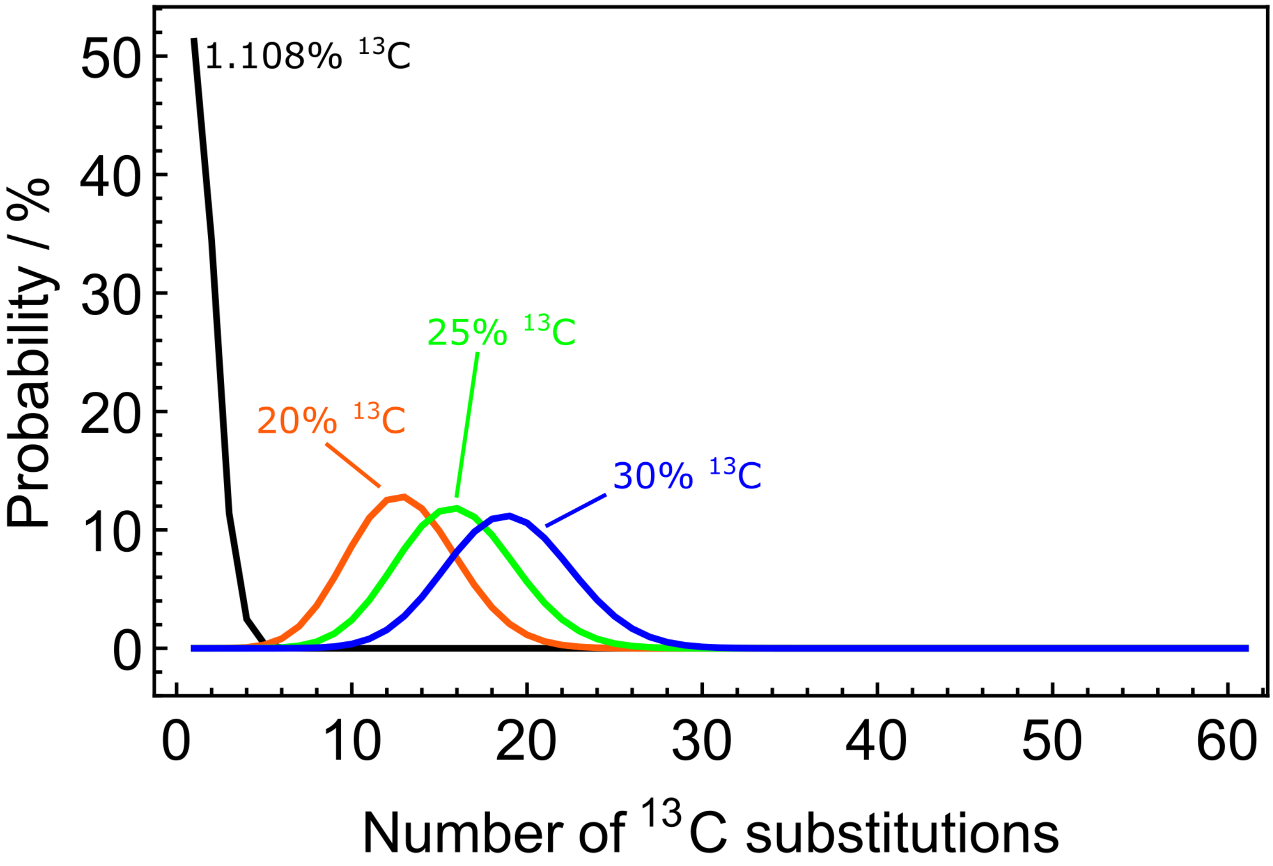

Figure 7: Probability for a number (m) of ^{13}C's to substituted in the C_{60} cage given the ^{13}C abundance (x). Essentially eq. 1 plotted against m for different values of x. Black- natural abundance (x = 1.108% ^{13}C), Orange- 20% ^{13}C, Green- 25% ^{13}C, Blue- 30% ^{13}C. The centres of the distributions are found at: $13\times^{13}$C for 20% ^{13}C, $16\times^{13}$C for 25% ^{13}C and $19\times^{13}$C for 30% ^{13}C.

It must be noted that an approximation has been made, such that if two ^{13}C's are more than 3 bonds apart, they are treated as fully decoupled (as in the main manuscript). Thus if two ^{13}C's are more than 3 bond apart we assume each one contributes to the main C_{60} peak and not the HP or HH peaks. This applies to three ^{13}C's such that if all three are connected by more than 3 bonds, each one contributes to the main C_{60} peak. When all three are connected together (by maximum 3 bonds) we ignore this contribution because the chemical shift of the cluster would end up somewhere else on the spectrum, not within the three peaks (main C_{60}, HP or HH), also the contribution is so small that it does not make much of difference for natural abundance C_{60}. Importantly for the HP and HH peaks in the spectrum when three ^{13}C's are present, for a configuration to contribute to the isotope shifted peaks firstly two ^{13}C's need to be adjacent (along a HP or HH bond) and the third one must be more than 3 bonds away from any of the two adjacent ^{13}C's.

However when only two ^{13}C's are substituted in the cage, if they are not adjacent we assume that both contribute to the main C_{60} peak. Because even if they were 2-3 bonds away and considered as coupled spins, they would still be magnetically equivalent and with a negligible 2-3 bonds away isotope shift they contribute to the main C_{60} peak and not the isotope shifted peaks.

From table 2 it can be seen that the main contribution to the ^{13}C NMR signal comes from substitutions up to m=3 and it represents 97.2% of the total signal arising from natural abundance C_{60}. In the analytic prediction of the NMR peak intensities below only substitutions up to m=3 will be considered, accounting for most of the signal.

C_{60} configurations for each m, up to m=3

Mathematica has a feature called Chemical Data in which it has chemical information about the C_{60}, physico-chemical properties like bond lengths, structure etc. Most importantly it provides atom connectivities as a list of rules, showing which carbon atom is directly bonded to another, for example if atom 1 is directly bonded to atom 2 is shown as "$1 \rightarrow 2$". It seems that the bond types corresponding to the connectivities Mathematica provided were wrong, this has been corrected for in these calculations and Wolfram has been informed about the error.

To find out which C_{60} configuration, with its ^{13}C's substituted, contributes to the main C_{60} or HP or HH NMR peak a Mathematica code has been implemented to count all of the configurations. In order to achieve this, all inequivalent C_{60} configurations corresponding to m ^{13}C's randomly substituted were generated. The number of configurations for a given m equals the binomial coefficient $\binom{n_c}{m} = \frac{n_c!}{(n_c-m)!m!}$ above. Now each configuration is a list of "m" numbers, each number is between 1-60 and it represents the location of the ^{13}C's, since the ^{12}C's are the rest and are not important for this analysis. Then the Mathematica code essentially goes through all of these configurations checking the ^{13}C's connectivities by comparing with the list of rules provided for the C_{60} connectivities. Each time the configurations are red a pattern check is done by Mathematica, when the pattern check is true that particular configuration is counted and added to the total number of satisfactory configurations. Then the ratio between satisfactory configurations and total configurations represents how much of the percentage given in the columns of table 2 contributes to the main C_{60} or HP or HH peak in the ^{13}C NMR spectrum. This has been done for all configurations up to $m = 3$ below.

5.1.1 m=0

The probability for all carbons to be ^{12}C is $\mathrm{P}_{0,\,60}^{0.01108} = 0.512471$ but it does not contribute to the ^{13}C NMR spectrum. Its contribution to the ^{13}C NMR spectrum is denoted as $\{0\}$ and:
$\{0\} = 0$.

5.1.2 m=1

The probability for one carbon to be ^{13}C and the rest ^{12}C is $\mathrm{P}_{1,\,60}^{0.01108} = 0.344508$ and all of it contributes to the main C_{60} peak in the ^{13}C NMR spectrum. Its contribution to the ^{13}C NMR spectrum is denoted as $\{1\}$ and:
$\{1\} = 0.344508$.

5.1.3 m=2

The probability for two carbons to be ^{13}C and the rest ^{12}C is $\mathrm{P}_{2,\,60}^{0.01108} = 0.113868$ and it contributes to all peaks in the ^{13}C NMR spectrum. There are 1770 ($= \binom{60}{2}$) total configurations with m=3, but the configurations need to be classified as follows:

m=2, all ^{13}C's remote

When both ^{13}C's are not directly connected in a configuration that will make a contribution to the main C_{60} peak. There are 1680 configurations (out of 1770 $= \binom{60}{2}$) with this property and to get the contribution to the main C_{60} peak an additional factor of 2 is need (the number of ^{13}C's). Its contribution to the ^{13}C NMR spectrum is denoted as $\{2, \mathrm{remote}\}$.

$$\{2, \mathrm{remote}\} = 2 * \frac{1680}{1770} * \mathrm{P}_{2,\,60}^{0.01108} = 0.216155$$

m=2, HP

When both ^{13}C's are directly connected along a HP bond in a configuration that will make a contribution to the HP peak. There are 60 configurations (out of 1770 $= \binom{60}{2}$) with this property and to get the contribution to the HP peak an additional factor of 2 is need (the number of ^{13}C's). Its contribution to the ^{13}C NMR spectrum is denoted as $\{2, \mathrm{HP}\}$.

$$\{2, \mathrm{HP}\} = 2 * \frac{60}{1770} * \mathrm{P}_{2,\,60}^{0.01108} = 0.00771984$$

m=2, HH

When both ^{13}C's are directly connected along a HH bond in a configuration that will make a contribution to the HH peak. There are 30 configurations (out of 1770 $= \binom{60}{2}$) with this property and to get the contribution to the HH peak an additional factor of 2 is need (the number of ^{13}C's). Its contribution to the ^{13}C NMR spectrum is denoted as $\{2, \mathrm{HH}\}$.

$$\{2, \mathrm{HH}\} = 2 * \frac{30}{1770} * \mathrm{P}_{2,\,60}^{0.01108} = 0.00385992$$

When adding all the cases together 1680 + 60 + 30 = 1770 the total number of m=2 configurations (i.e. $\binom{60}{2}$).

5.1.4 m=3

The probability for three carbons to be ^{13}C and the rest ^{12}C is $\mathrm{P}_{3,\,60}^{0.01108} = 0.0246652$ and it contributes to all peaks in the ^{13}C NMR spectrum. There are 34220 ($= \binom{60}{3}$) total configurations with m=3, but the configurations need to be classified as follows:

m=3, all ^{13}C's in a cluster

When all three ^{13}C's are connected by 3 bonds or less in a configuration we consider it will not make a contribution to the NMR signal. The spectrum of the cluster will be broadened and will in most cases overlap with all peaks (main C_{60}, HP and HH) thus contributing to all equally. There are 5080 configurations (out of $34220 = \binom{60}{3}$) with this property and to get the contribution to NMR signal an additional factor of 0 is need (because of the approximation made). Its contribution to the ^{13}C NMR spectrum is denoted as $\{3, \mathrm{cluster}\}$.

$$\{3, \mathrm{cluster}\} = 0 * \frac{5085}{34220} * \mathrm{P}_{3,\,60}^{0.01108} = 0 * 0.00366159 = 0$$

m=3, all ^{13}C's remote

When all three ^{13}C's are more than 3 bonds apart from each other in a configuration that will make a contribution to the main C_{60} peak. There are 11260 configurations (out of $34220 = \binom{60}{3}$) with this property and to get the contribution to the main C_{60} peak an additional factor of 3 is need (the number of ^{13}C's). Its contribution to the ^{13}C NMR spectrum is denoted as $\{3, \mathrm{all\ remote}\}$.

$$\{3, \mathrm{all\ remote}\} = 3 * \frac{11260}{34220} * \mathrm{P}_{3,\,60}^{0.01108} = 0.0243481$$

m=3, two ^{13}C's in a cluster and one remote

When two ^{13}C's are in a cluster (1-3 bonds away) and the third far away (more than 3 bonds away from both) in a configuration that will make a contribution to the main C_{60} peak (from the remote ^{13}C) and some contribution to the HP or HH peak (when the two ^{13}C's are adjacent in the cluster) or the main C60 peak (when the two ^{13}C's are not adjacent in the cluster). There are 17880 configurations (from the Mathematica code), out of $34220 = \binom{60}{3}$ with this property. When adding all the three cases above (for m=3) we get: 5080 + 11260 + 17880 = 34220 (i.e. $\binom{60}{3}$)). The 17880 cases in this section need to be further divided into 3 classes:

- "HP + remote" when two ^{13}C's are adjacent along HP bond and the third ^{13}C is remote.
- "HH + remote" when two ^{13}C's are adjacent along HH bond and the third ^{13}C is remote.
- "cluster (not adj.) + remote" when two ^{13}C's are 2-3 bonds away in a cluster and the third ^{13}C is remote from either of them.

m=3, HP + remote

When two ^{13}C's are adjacent along a HP bond and the third is remote in a configuration that will make a contribution to the main C_{60} peak (from the remote ^{13}C) and a double contribution to the HP peak (from the two adjacent ^{13}'s). There are 2280 configurations (from the Mathematica code), out of $34220 = \binom{60}{3}$, with this property and their contribution to the ^{13}C NMR spectrum is denoted as {3, HP + remote}.

$$\{3, \mathrm{HP}\ +\ \mathrm{remote}\} \rightarrow \text{main } \mathrm{C}_{60} \text{ peak} = 1 * \frac{2280}{34220} * \mathrm{P}_{3,\,60}^{0.01108} = 0.00164339$$

$$\rightarrow \text{HP peak} = 2 * \frac{2280}{34220} * \mathrm{P}_{3,\,60}^{0.01108} = 0.00328678$$

m=3, HH + remote

When two ^{13}C's are adjacent along a HH bond and the third is remote in a configuration that will make a contribution to the main C_{60} peak (from the remote ^{13}C) and a double contribution to the HH peak (from the two adjacent ^{13}C's). There are 1140 configurations (from the Mathematica code), out of 34220 = $\binom{60}{3}$, with this property and their contribution to the ^{13}C NMR spectrum is denoted as {3, HH + remote}.

$$\{3, \mathrm{HH}\ +\ \mathrm{remote}\} \rightarrow \text{main } \mathrm{C}_{60} \text{ peak} = 1 * \frac{1140}{34220} * \mathrm{P}^{0.01108}_{3,\,60} = 0.000821694$$
$$\rightarrow \mathrm{HH} \text{ peak} = 2 * \frac{1140}{34220} * \mathrm{P}^{0.01108}_{3,\,60} = 0.00164339$$

m=3, cluster (not adj.) + remote

Two ^{13}C's are 2-3 bonds away from each other in a cluster and the third one is remote in a configuration. The remote ^{13}C will make a contribution to the main C_{60} peak. The two ^{13}C's 2-3 bonds away will also contribute to the main C_{60} peak. Because the third ^{13}C is far enough to make the other two nearly equivalent and they are not adjacent so the isotope shift is assumed to be be negligible in this case. There are 14460 (17880 - (2280 + 1140)) configurations, out of 34220 = $\binom{60}{3}$, with this property. Their contribution to the ^{13}C NMR spectrum is denoted as {3, cluster (not adj.) + remote} and a factor of 3 is needed because all 3 spins contribute to the main C_{60} peak.

$$\{3, \text{cluster (not adj.)}\ +\ \text{remote}\} \rightarrow \text{main } \mathrm{C}_{60} \text{ peak} = 3 * \frac{14460}{34220} * \mathrm{P}^{0.01108}_{3,\,60} = 0.0312676$$

5.2 Predicted ^{13}C NMR spectrum of natural abundance C_{60} considering up to m=3 ^{13}C substitutions

All the cases presented above are shown as a histogram in fig. 8 where all the contributions to the NMR peaks (main C_{60}, HP and HH) from the configurations above are summarised.

From these the predicted ratios of the peaks was obtained and shown in table 3 together with the experimentally measured ratios

Table 3: Predicted (from fig. 8) and experimental ^{13}C NMR peak ratios for natural abundance C_{60}. Here main C_{60} peak + HP + HH = 100%.

Peak	Predicted ratios (up to m = 3)	Experimental ratios
Main C_{60}	97.401 %	$97.62 \pm 0.21\%$
HP	1.733%	$1.59 \pm 0.14\%$
HH	0.866%	$0.79 \pm 0.07\%$

From the table it can be seen that the predicted ratios are close to the experimental ones but not exactly the same. The reason for this could be that only substitutions up to m=3 were considered, these account for 97.2% of the total NMR signal and the mismatch could be due to the leftover 2.8%. This 2.8% would have intensity distributed among all three peaks and in between them due to the clustering effect on the isotope shift discussed in the main manuscript. Thus final intensities when all ^{13}C substitutions in natural abundance C_{60} are considered would be close to the ones shown in table 3. Other possible reasons for the discrepancies would be the assumptions and approximations made when building up the arguments above.

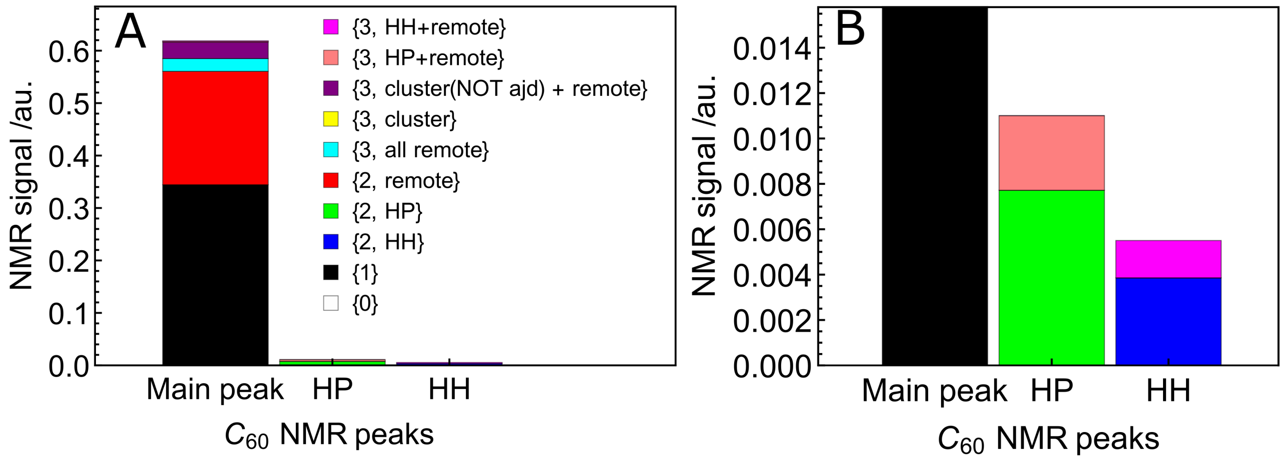

Figure 8: Statistically predicted ^{13}C NMR intensities of natural abundance C_{60} considering up to m=3 ^{13}C substitutions, A- full size and B- zoomed to see HP and HP. All contributions discussed previously are presented in the legend and the histogram shows how they build up the ^{13}C NMR peaks.{0} and {3, cluster} are assumed to have zero contribution.

6 Mass spectrum of C_{60} 20-30% ^{13}C enriched sample

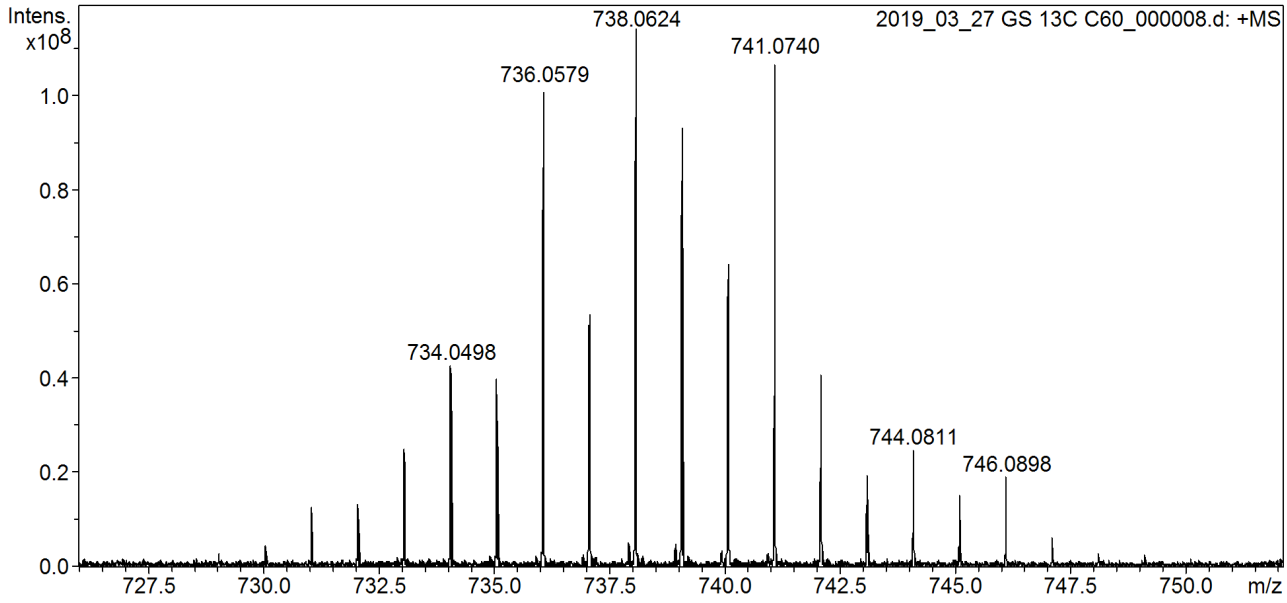

Figure 9: Experimental FT-Mass Spectrometry spectrum of C_{60} 20-30% ^{13}C enriched. It serves to show the rather non-binomial distribution of ^{13}C's substituted in the cage for this sample. The peak of this distributions is at $18\times{}^{13}$C's in the cage, which matches well with the theoretical statistical distribution of 30% (where the distribution is predicted to be peaked at $19\times{}^{13}$C).

The mass spectrum of C_{60} 20-30% ^{13}C enriched sample was acquired and it is seen in fig. 9. Sample was measured using a solariX (Bruker Daltonics, Bremen, Germany) FT-ICR mass spectrometer equipped with a 4.7T superconducting magnet. Sample was infused via a syringe driver at a flow rate of 5 $\mu L/minute$. Mass spectra were recorded using positive ion atmospheric pressure photoionisation (APPI). Mass spectrum of C_{60} 20-30% ^{13}C in fig. 9 shows a nearly binomial distribution centred at 738 m/z, which corresponds to 18×^{13}C present in the cage.

In fig. 7 the centre of the distributions are at: 13×^{13}C for 20% ^{13}C, 16 ×^{13}C for 25% ^{13}C and 19 ×^{13}C for 30% ^{13}C. From this predicted distribution of ^{13}C's substituted in the C_{60} and fig. 9 it can be concluded that the enriched C_{60} had a percentage of ^{13}C very close to 30%. This was also seen in the Monte Carlo simulations of the 30% ^{13}C C_{60} which matched best with the experimental ^{13}C NMR spectrum of 20-30% ^{13}C C_{60}. Although the mass distribution is roughly consistent with uniform ∼30% ^{13}C enrichment, strong deviations from the expected binomial distribution (Fig. 7) are observed . We do not understand the reasons for these variations, but they may reflect some mechanistic details of the enrichment procedure, which are not known to us.

References

[1] M. S. Dresselhaus, G. Dresselhaus and P. C. Eklund, *Science of Fullerenes and Carbon Nanotubes*, Academic Press, New York, 1996.