AN INSIGHT ON BASIC PRINCIPLES OF $^{13}$C-NMR

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ABSTRACT
In all carbon atoms about 1.1% of all carbon atoms are the C-13 isotope; the rest (apart from tiny amounts of the radioactive C-14) is C-12. Obtaining C-13 spectra is more complex than for proton NMR. This is primarily because of the low isotopic abundance of $^{13}$C in nature. C-13 NMR relies on the magnetic properties of the C-13 nuclei. Carbon-13 nuclei fall into a class known as "spin ½" nuclei for reasons which don't really need to concern us at the introductory level[19]. The effect of this is that a C-13 nucleus can behave as a little magnet. C-12 nuclei don't have this property.

Key words: Proton decoupled technique, FT-NMR, TMS- tetramethylsilane.

INTRODUCTION
WHAT IS C-13 NMR?
$^{12}$C nucleus is not magnetically active, but the $^{13}$C nucleus has a spin quantum no. of ½ so $^{13}$C exhibit NMR Phenomena where as C$^{12}$ does not. Natural Abundance of $^{13}$C is only 1.08% & C$^{12}$ – 98.9%.

The background of C-13 NMR spectroscopy
Nuclear magnetic resonance is concerned with the magnetic properties of certain nuclei. On this mainly to focus on the magnetic behavior of carbon-13 nuclei.

Carbon-13 nuclei as little magnets
About 1% of all carbon atoms are the C-13 isotope; the rest (apart from tiny amounts of the radioactive C-14) is C-12. C-13 NMR relies on the magnetic properties of the C-13 nuclei. Carbon-13 nuclei fall into a class known as "spin ½" nuclei for reasons which don't really need to concern us at the introductory level[19]. The effect of this is that a C-13 nucleus can behave as a little magnet. C-12 nuclei don't have this property. If you have a compass needle, it normally lines up with the Earth's magnetic field with the north-seeking end pointing north. Provided it isn't sealed in some sort of container, you could twist the needle around with your fingers so that it pointed south - lining it up opposed to the Earth's magnetic field. It is very unstable opposed to the Earth's field, and as soon as you let it go again, it will flip back to its more stable state.

The energy needed to make this flip depends on the strength of the external magnetic field used, but is usually in the range of energies found in radio waves - at frequencies of about 25 - 100 MHz. (BBC Radio 4 is found between 92 - 95 MHz!).

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Natural Abundance of $^{13}$C is only 1.08% & $^{12}$C (98.9 and Spin No. of $^{13}$C is $\frac{1}{2}$). $^{13}$C sensitivity is only 1.1% that of $^1$H. The overall sensitivity of $^{13}$C absorption is about 1/5700. Because of this low sensitivity of $^{13}$C, gives rise to extremely weak signals and in CW-NMR require very large sample and large time \[8,17,29\].

Gyromagnetic ratio of $^{13}$C = gyromagnetic ratio of $^1$H so

\[ \frac{13}{15.1 \text{ MHz}} \quad \text{at} \quad 14092 \text{C} \]

\[ \frac{12}{60 \text{ Hz}} \quad \text{at} \quad 14092 \text{H} \]

$^{13}$C chemical shift Range from 0 to about 250ppm. As In H-NMR, $^{13}$C TMS is also used as reference standards. If $^{13}$C 1 & 0 tops come to lie next to each other this situation has very low probability (1 in 10,000). Most $^{13}$C nuclei surrounded by only $^{12}$Nuclei C have no spin, Don’t give rise to spin-spin splitting, consequently $^{13}$C-NMR spectra appreciably simplified.

It is useful to compare and contrast H-NMR and C-NMR as there are certain differences and similarities:

- $^{13}$C has only about 1.1% natural abundance (of carbon atoms)
- $^{12}$C does not exhibit NMR behaviour (nuclear spin, $I = 0$)
- As a result, C is about 400 times less sensitive than H nucleus to the NMR phenomena
- Due to low abundance, we do not usually see $^{13}$C-$^{13}$C coupling
- Chemical shift range is normally 0 to 220 ppm

Normal $^{13}$C spectra are "broadband, proton decoupled" so the peaks show as single lines
- Number of peaks indicates the number of types of C \[4,32\].

**Proton Decoupled Techniques:**

(a) Broad Band hydrogen (or proton) Decoupling

(b) Off – resonance Decoupling

(c) DEPT – NMR

(a) **Broad – Band Hydrogen Decoupling:**

C-H coupling is removed by a technique called broad band decoupling.

In this method, as the carbon spectrum is being obtained, the sample is simultaneously irradiated with band of radio frequency radiation that excited all of Hydrogen. This causes each of Hydrogen to flip rapidly between its two spin states.

In a magnetic field of 58750 G, C-13 resonates at 62.8 MHZ while Hydrogen at 250 MHZ. In this frequencies causes all the Hydrogen to undergoes rapid $\alpha, \beta$ spin flips, very fast to average their local magnetic field contribution. The overall results is the absence of coupling \[7,26\].

(b) **Off – Resonance Decoupling:**

In off – Resonance Decoupling simplifies the spectrum by allowing some of splitting information to be retained. Using off-Resonance Decoupling techniques the $^{13}$C nuclei are split only by the protons directly bonded to them and not by any other protons

Ex. Only one bond coupling $^{13}$C-H two bond coupling $^{15}$C – $^1$H are not observed.

(c) **DEPT-NMR (Distortionless enhancement by polarization transfer):**

DEPT-NMR also allows the determination of number of hydrogen attached to each carbons.

In this technique three spectra are obtained, one is a normal broad band decoupled spectrum.

The second spectrum (DEP-90 spectrum) is obtained under special condition in which only carbons bonded to single hydrogen (CH$^1$) appear.

The third spectrum DEPT 135$^0$ spectrum is obtained under conditions in which CH & CH$^3$ appear as normal signal, but CH$^1$ appear as negative absorption, and no peak for quaternary carbons \[9,16,21,29\].

**FT-NMR (Fourier Transform – NMR):**

In FT-NMR, a powerful but short burst of energy is utilized which called a pulse, that excites all of the magnetic Nuclei in the molecule simultaneously. When the pulse is discontinued, the excited Nuclei begin to lose their excitation energy and return to their original spin state, or relax.

The pulsed FT method has suffered advantages over the CW method. It is more sensitive, and it
can measure weaker signals. 5-10 minutes are required to scan and record a CW spectrum; A pulsed experiment is much faster, and a measurement of an FID can be performed in a few seconds\textsuperscript{[3,7,11]}.

Block diagram of a Fourier transform NMR spectrometer

Time domain spectra instead of frequency domain

(a) FID signal for Carbon-13 in cyclohexane. (b) Fourier transform of cyclohexane

**Summary:**
For a given radio frequency (say, 25 MHz) each carbon-13 atom will need a slightly different magnetic field applied to it to bring it into the resonance condition depending on what exactly it is attached to - in other words the magnetic field needed is a useful guide to the carbon atom's environment in the molecule.

**Features of a C-13 NMR spectrum:**

*The C-13 NMR spectrum for ethanol*

This is a simple example of a C-13 NMR spectrum.

There are two peaks because there are two different environments for the carbons. The carbon in the CH\textsubscript{3} group is attached to 3 hydrogens and a carbon. The carbon in the CH\textsubscript{2} group is attached to 2 hydrogens, a carbon and oxygen.
The two lines are in different places in the NMR spectrum because they need different external magnetic fields to bring them in to resonance at a particular radio frequency.

*The C-13 NMR spectrum for a more complicated compound*

This is the C-13 NMR spectrum for 1-methylethyl propanoate (also known as isopropyl propanoate or isopropyl propionate)\textsuperscript{[5,13]}.

This time there are 5 lines in the spectrum. That means that there must be 5 different environments for the carbon atoms in the compound. Is that reasonable from the structure?

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Well - if you count the carbon atoms, there are 6 of them. So why only 5 lines? In this case, two of the carbons are in exactly the same environment. They are attached to exactly the same things.
Look at the two CH₃ groups on the right-hand side of the molecule. That's not exactly the same environment as the carbons in the right-hand CH₃ groups. They are attached to a carbon which is attached to a single oxygen - and so on down the molecule. We'll look at this spectrum again in detail on the next page - and look at some more similar examples as well. This all gets easier the more examples you look at.[17,21]

The need for a standard for comparison – TMS

Before we can explain what the horizontal scale means, we need to explain the fact that it has a zero point - at the right-hand end of the scale. The zero is where you would find a peak due to the carbon-13 atoms in tetramethylsilane - usually called TMS. Everything else is compared with this.[29]

You will find that some NMR spectra show the peak due to TMS (at zero), and others leave it out. Essentially, if you have to analyse a spectrum which has a peak at zero, you can ignore it because that's the TMS peak.

TMS is chosen as the standard for several reasons. The most important are:

- It has 4 carbon atoms all of which are in exactly the same environment. They are joined to exactly the same things in exactly the same way. That produces a single peak, but it's also a strong peak (because there are lots of carbon atoms all doing the same thing).
- The electrons in the C-Si bonds are closer to the carbons in this compound than in almost any other one. That means that these carbon nuclei are the most shielded from the external magnetic field, and so you would have to increase the magnetic field by the greatest amount to bring the carbons back into resonance.

The net effect of this is that TMS produces a peak on the spectrum at the extreme right-hand side. Almost everything else produces peaks to the left of it.[24]

CONCLUSION

- Provided it isn't sealed in some sort of container, you could twist the needle around with your fingers so that it pointed south - lining it up opposed to the Earth's magnetic field.
- About 1% of all carbon atoms are the C-13 isotope; the rest (apart from tiny amounts of the radioactive C-14) is C-12. C-13 NMR relies on the magnetic properties of the C-13 nuclei.
- It is very unstable opposed to the Earth's field, and as soon as you let it go again, it will flip back to its more stable state.

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