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**BASIC PRINCIPLE OF <sup>13</sup>C-NMR**  
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**Abstract:**

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 1/2" nuclei for reasons which don't really need to concern us at the introductory level this page is aimed at (UK A level and its equivalents). 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.

**Introduction:**

**WHAT IS C-13 NMR?**

C<sup>12</sup> nucleus is not magnetically active, but the C<sup>13</sup> nucleus has a spin no. of 1/2 so C<sup>13</sup> exhibit NMR Phenomena  
C<sup>12</sup> Spin No. zero

Natural Abundance of C<sup>13</sup> is only 1.08% & C<sup>12</sup> – 98.9%

**The background to 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**

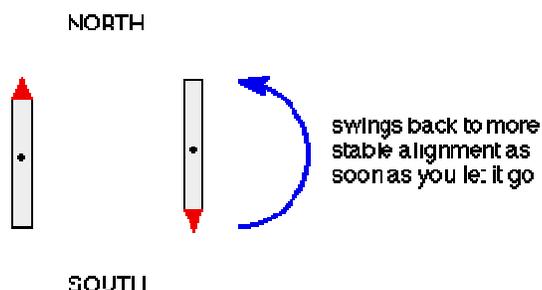
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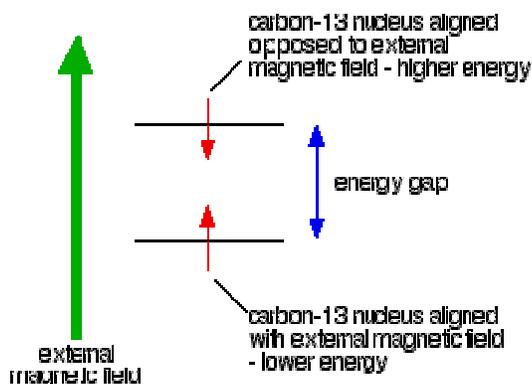
If you have a compass needle, it normally lines up with the Earth's magnetic field with the north-seeking end pointing north. Provided it isn't sealed in some sort of container, you could twist the needle around with your fingers so that it pointed south - lining it up opposed to the Earth's magnetic field.[pavia, yadav]

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.



Because a C-13 nucleus behaves like a little magnet, it means that it can also be aligned with an external magnetic field or opposed to it.

Again, the alignment where it is opposed to the field is less stable (at a higher energy). It is possible to make it flip from the more stable alignment to the less stable one by supplying exactly the right amount of energy.



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

*Nikunj Vora\* et al. /International Journal Of Pharmacy&Technology*

between 92 - 95 MHz!) If you have also looked at proton-NMR, the frequency is about a quarter of that used to flip a hydrogen nucleus for a given magnetic field strength.

It's possible to detect this interaction between the radio waves of just the right frequency and the carbon-13 nucleus as it flips from one orientation to the other as a peak on a graph. This flipping of the carbon-13 nucleus from one magnetic alignment to the other by the radio waves is known as the **resonance condition**.

Natural Abundance of  $C^{13}$  is only 1.1% &  $C^{12}$  (98.9 and Spin No. of  $C^{13}$  is  $\frac{1}{2}$  . $C^{13}$  sensitivity is only 1.6% that of  $^1H$ . The overall sensitivity of  $C^{13}$  absorption is about 1/5700. Because of this low sensitivity of  $C^{13}$  ,gives rise to extremely weak signals and in CW-NMR require very large sample and large time.[Y.R.Sharma ,Silverstein, P.S.Kalsi]

Gyromagnetic ratio of  $C^{13}$   $\frac{1}{4}$  gyromagnetic ratio of  $^1H$  so

$C^{13}$	15.1 MHZ	at	14092 gauss
$H^1$	60 HZ	at	14092 gauss

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

A Relative complexity of absorption caused by extensive  $C^{13}$ -H spin-spin splitting. The directly bound hydrogen are most strongly coupled (125-200HZ).While splitting is often useful in study of simple molecules, in several situations, it makes the spectrum more difficult to interpret for this reason, and to increase the signal strength CMR spectra are normally recorded under condition in which the protons are decoupled from carbon.

For eg. :- Ethyl Phenylacetate show 8 peak

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  $^{13}\text{C}$ - $^{13}\text{C}$  coupling
  - Chemical shift range is normally 0 to 220 ppm
  - Chemical shifts measured with respect to tetramethylsilane,  $(\text{CH}_3)_4\text{Si}$  (*i.e.* TMS)
  - Similar factors affect the chemical shifts in  $^{13}\text{C}$  as seen for H NMR
  - Long relaxation times (excited state to ground state) mean no integrations
  - "Normal"  $^{13}\text{C}$  spectra are "broadband, proton decoupled" so the peaks show as single lines
  - Number of peaks indicates the number of types of C[Chatwal Gurdeep]
1. The general implications of these points are that  $^{13}\text{C}$  take longer to acquire, though they tend to look simpler. Overlap of peaks is much less common than for H-NMR which makes it easier to determine how many types of C are present.

[Dr. S.Bruce King , Jim Clark 1,Jim Clark 2 link ]

### 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.

#### (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  $\text{C}^{13}$  nuclei are split only by the protons directly bonded to them and not by any other protons

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

		H	H
- C -	- C -	- C -	- C - H
	H	H	H
No Protons	One Proton	Two Protons	Three Protons
Singal	Doublet	Triplet	Quartet

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### Off-Resonance Decoupling

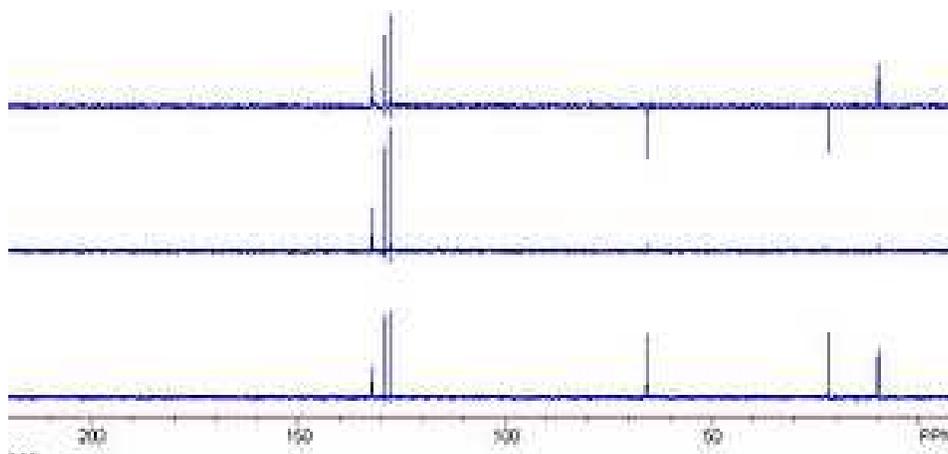
**(c) DEPT-NMR ( Distortionless enhancement by polarization transfer ) :-**

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 a single hydrogen ( $\text{CH}^1$ ) appear.

The third spectrum (DEPT  $135^\circ$  spectrum is obtained under conditions in which  $\text{CH}$  &  $\text{CH}^3$  appear as normal signal, but  $\text{CH}^1$  appear as negative absorption, and no peak for quaternary carbons.[Mc cash ,Eliel Ernest,Edehard.Kenneth Connors]



DEPT spectra of propyl benzoate

**FT-NMR (Fourier Transform – NMR)**

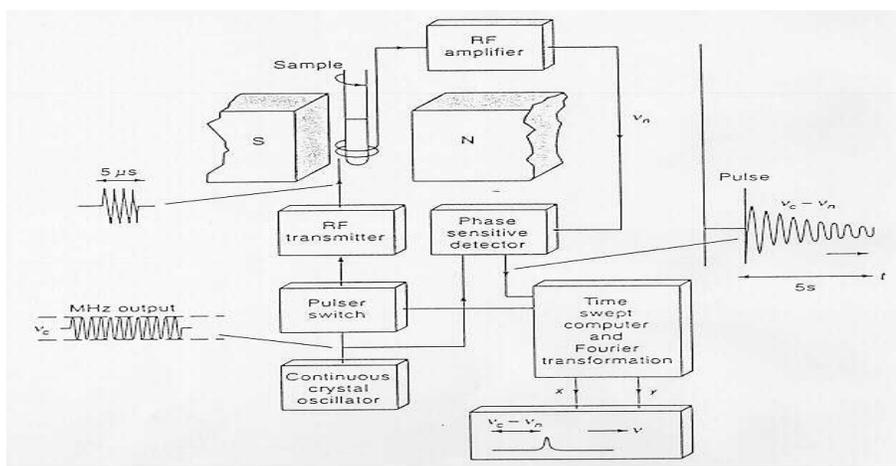
IN CW Type NMR, operates by exciting the nuclei of the isotope under observation one type at a time. In the case of  $^1\text{H}$  Nuclei, each distinct type of proton (Phenyl, vinyl, methyl & so on) is excited individually, and its resonance peak is observed recorded independently of all the other. As we scan, we look at first one type of Hydrogen and then another, scanning until all of the types have come into resonance.

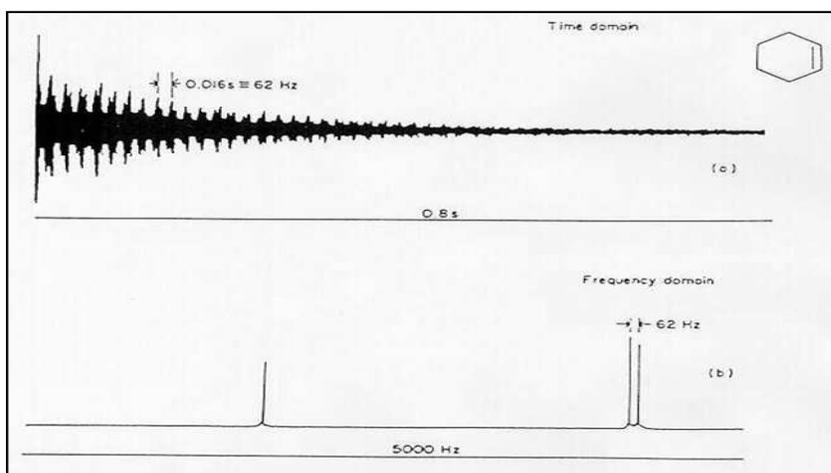
In FT-NMR, a powerful but short burst of energy is utilized which called a pulse, that excites all of the magnetic Nuclei in the molecule simultaneously. When the pulse is discontinued, the excited Nuclei begin to lose their excitation energy and return to their original spin state, or relax. As each excited Nuclei relaxes, it emits electromagnetic radiation. Since the molecule contains many different Nuclei, many different frequencies of electromagnetic radiations are emitted simultaneously. This emission is called a free-induction decay (FID) signals.

The intensity of FID decays with time as all of the Nuclei eventually lose their excitation. The FID is a superimposed combination of all the frequencies emitted and can be quite complex. We usually extract the individual frequencies due to different Nuclei by using a computer and a mathematical method called a fourier transform analysis.

The pulsed FT method has several advantages over the CW method. It is more sensitive, and it can measure weaker signals. 5-10 minutes are required to scan and record.

CW spectrum; A pulsed experiment is much faster, and a measurement of an FID can be performed in a few seconds. [ Kenneth Connors, Ahutosh Kar].





Time domain spectra instead of frequency domain

(a) FID signal for Carbon-13 in cyclohexane.

(b) Fourier transform of cyclohexane

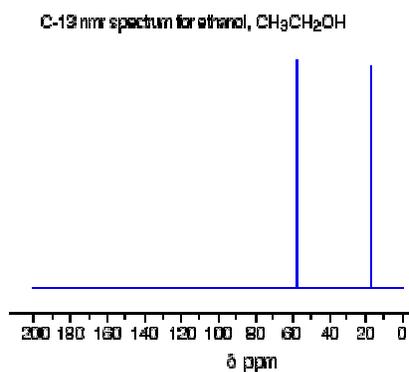
## Summary

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.



**Note:** The nmr spectra on this page have been produced from graphs taken from the Spectral Data Base System for Organic Compounds (SDBS) at the National Institute of Materials and Chemical Research in Japan. It is possible that small errors may have been introduced during the process of converting them for use on this site, but these won't affect the argument in any way.

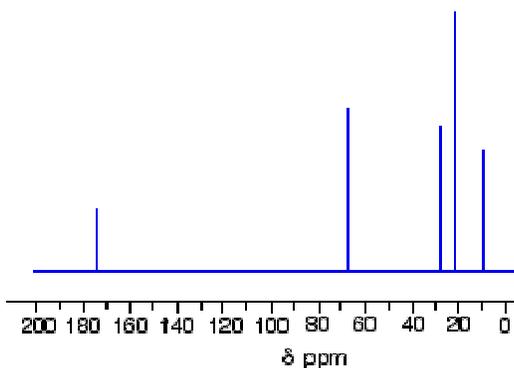
There are two peaks because there are two different environments for the carbons.

The carbon in the CH<sub>3</sub> group is attached to 3 hydrogens and a carbon. The carbon in the CH<sub>2</sub> group is attached to 2 hydrogens, a carbon and an oxygen.

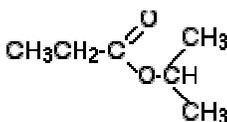
The two lines are in different places in the NMR spectrum because they need different external magnetic fields to bring them in to resonance at a particular radio frequency.

*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).



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 CH<sub>3</sub> groups on the right-hand side of the molecule.

You might reasonably ask why the carbon in the CH<sub>3</sub> on the left isn't also in the same environment. Just like the ones on the right, the carbon is attached to 3 hydrogens and another carbon. But the similarity isn't exact - you have to chase the similarity along the rest of the molecule as well to be sure.

The carbon in the left-hand CH<sub>3</sub> group is attached to a carbon atom which in turn is attached to a carbon with two oxygens on it - and so on down the molecule.

That's not exactly the same environment as the carbons in the right-hand CH<sub>3</sub> 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. [Ducket ,Kenneth Connors]

For now, all you need to realise is that each line in a C-13 NMR spectrum recognises a carbon atom in one particular environment in the compound. If two (or more) carbon atoms in a compound have exactly the same environment, they will be represented by a single line.

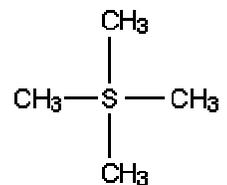
**Note:** If you are fairly wide-awake, you might wonder why all this works, since only about 1% of carbon atoms are C-13. These are the only ones picked up by this form of NMR. If you had a single molecule of ethanol, then the chances are only about 1 in 50 of there being one C-13 atom in it, and only about 1 in 10,000 of both being C-13.

But you have got to remember that you will be working with a sample containing huge numbers of molecules.

The instrument can pick up the magnetic effect of the C-13 nuclei in the carbon of the CH<sub>3</sub> group and the carbon of the CH<sub>2</sub> group even if they are in separate molecules. There's no need for them to be in the same one. [Y.R.Sharma,Skoog,Pavia].

## 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.



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. [P.Parimao]

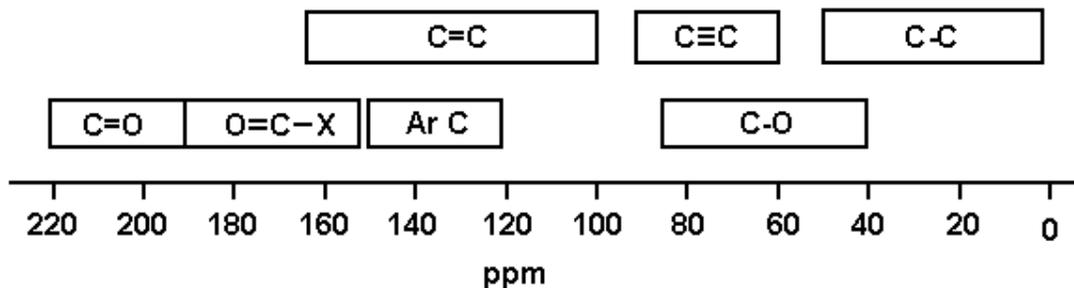
## The chemical shift

The horizontal scale is shown as (ppm). is called the chemical shift and is measured in parts per million-ppm.

A peak at a chemical shift of, say, 60 means that the carbon atoms which caused that peak need a magnetic field 60 millionths less than the field needed by TMS to produce resonance.

A peak at a chemical shift of 60 is said to be downfield of TMS. The further to the left a peak is, the more downfield it is.

Here is the simple correlation table of <sup>13</sup>C chemical shifts:



C=O indicates aldehydes and ketones.

O=C-X indicates carboxylic acids and derivatives such as esters and amides

**Note:** If you are familiar with proton-NMR, you will notice that the chemical shifts for C-13 NMR are much bigger than for proton-NMR. In C-13 NMR, they range up to about 200 ppm. In proton-NMR they only go up to about 12 ppm. You don't need to worry about the reasons for this at this level. [Pavia, Edehard]

### Solvents for NMR spectroscopy

NMR spectra are usually measured using solutions of the substance being investigated. A commonly used solvent is CDCl<sub>3</sub>. This is a trichloromethane (chloroform) molecule in which the hydrogen has been replaced by its isotope, deuterium.

CDCl<sub>3</sub> is also commonly used as the solvent in proton-NMR because it doesn't have any ordinary hydrogen nuclei (protons) which would give a line in a proton-NMR spectrum. It does, of course, have a carbon atom-so why doesn't it give a potentially confusing line in a C-13 NMR spectrum?

In fact it does give a line, but the line has an easily recognisable chemical shift and so can be removed from the final spectrum. All of the spectra from the SDBS have this line removed to avoid any confusion.

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