The $^{12}\text{C}$ isotope of carbon - which accounts for up about 99% of the carbons in organic molecules - does not have a nuclear magnetic moment, and thus is NMR-inactive. Fortunately for organic chemists, however, the $^{13}\text{C}$ isotope, which accounts for most of the remaining 1% of carbon atoms in nature, has a magnetic moment just like protons. Most of what we have learned about $^1\text{H}$-NMR spectroscopy also applies to $^{13}\text{C}$-NMR, although there are several important differences.

### The basics of $^{13}\text{C}$-NMR spectroscopy

The magnetic moment of a $^{13}\text{C}$ nucleus is much weaker than that of a proton, meaning that NMR signals from $^{13}\text{C}$ nuclei are inherently much weaker than proton signals. This, combined with the low natural abundance of $^{13}\text{C}$, means that it is much more difficult to observe carbon signals: more sample is required, and often the data from hundreds of scans must be averaged in order to bring the signal-to-noise ratio down to acceptable levels. Unlike $^1\text{H}$-NMR signals, the area under a $^{13}\text{C}$-NMR signal cannot be used to determine the number of carbons to which it corresponds. This is because the signals for some types of carbons are inherently weaker than for other types – peaks corresponding to carbonyl carbons, for example, are much smaller than those for methyl or methylene ($\text{CH}_2$) peaks. Peak integration is generally not useful in $^{13}\text{C}$-NMR spectroscopy, except when investigating molecules that have been enriched with $^{13}\text{C}$ isotope (see section 5.6B).

The resonance frequencies of $^{13}\text{C}$ nuclei are lower than those of protons in the same applied field - in a 7.05 Tesla instrument, protons resonate at about 300 MHz, while carbons resonate at about 75 MHz. This is fortunate, as it allows us to look at $^{13}\text{C}$ signals using a completely separate 'window' of radio frequencies. Just like in $^1\text{H}$-NMR, the standard used in $^{13}\text{C}$-NMR experiments to define the 0 ppm point is tetramethylsilane (TMS), although of course in $^{13}\text{C}$-NMR it is the signal from the four equivalent carbons in TMS that serves as the standard. Chemical shifts for $^{13}\text{C}$ nuclei in organic molecules are spread out over a much wider range than for protons – up to 200 ppm for $^{13}\text{C}$ compared to 12 ppm for protons (see Table 3 for a list of typical $^{13}\text{C}$-NMR chemical shifts). This is also fortunate, because it means that the signal from each carbon in a compound can almost always be seen as a distinct peak, without the overlapping that often plagues $^1\text{H}$-NMR spectra. The chemical shift of a $^{13}\text{C}$ nucleus is influenced by essentially the same factors that influence a proton's chemical shift: bonds to electronegative atoms and diamagnetic anisotropy effects tend to shift signals downfield (higher resonance frequency). In addition, $sp^2$ hybridization results in a large downfield shift. The $^{13}\text{C}$-NMR signals for carbonyl carbons are generally the furthest downfield (170-220 ppm), due to both $sp^2$ hybridization and to the double bond to oxygen.

### Example 13.5.1

Exercise 5.11: How many sets of non-equivalent carbons are there in each of the molecules shown in exercise 5.1?

Exercise 5.12: How many sets of non-equivalent carbons are there in:

- a. toluene
- b. 2-pentanone
c. para-xylene
d. triclosan

*(all structures are shown earlier in this chapter)*

**Solution**

Because of the low natural abundance of $^{13}$C nuclei, it is very unlikely to find two $^{13}$C atoms near each other in the same molecule, and thus we do not see spin-spin coupling between neighboring carbons in a $^{13}$C-NMR spectrum. There is, however, heteronuclear coupling between $^{13}$C carbons and the hydrogens to which they are bound. Carbon-proton coupling constants are very large, on the order of 100 – 250 Hz. For clarity, chemists generally use a technique called broadband decoupling, which essentially 'turns off' C-H coupling, resulting in a spectrum in which all carbon signals are singlets. Below is the proton-decoupled $^{13}$C-NMR spectrum of ethyl acetate, showing the expected four signals, one for each of the carbons.

![Proton-decoupled $^{13}$C-NMR spectrum of ethyl acetate](image)

While broadband decoupling results in a much simpler spectrum, useful information about the presence of neighboring protons is lost. However, another modern NMR technique called DEPT (Distortionless Enhancement by Polarization Transfer) allows us to determine how many hydrogens are bound to each carbon. For example, a DEPT experiment tells us that the signal at 171 ppm in the ethyl acetate spectrum is a quaternary carbon (no hydrogens bound, in this case a carbonyl carbon), that the 61 ppm signal is from a methylene (CH$_2$) carbon, and that the 21 ppm and 14 ppm signals are both methyl (CH$_3$) carbons. The details of the DEPT experiment are beyond the scope of this text, but DEPT information will often be provided along with $^{13}$C spectral data in examples and problems.

Below are two more examples of $^{13}$C NMR spectra of simple organic molecules, along with DEPT information.
Example 13.5.2

Give peak assignments for the $^{13}$C-NMR spectrum of methyl methacrylate, shown above.
One of the greatest advantages of $^{13}$C-NMR compared to $^1$H-NMR is the breadth of the spectrum - recall that carbons resonate from 0-220 ppm relative to the TMS standard, as opposed to only 0-12 ppm for protons. Because of this, $^{13}$C signals rarely overlap, and we can almost always distinguish separate peaks for each carbon, even in a relatively large compound containing carbons in very similar environments. In the proton spectrum of 1-heptanol, for example, only the signals for the alcohol proton ($H_a$) and the two protons on the adjacent carbon ($H_b$) are easily analyzed. The other proton signals overlap, making analysis difficult.

In the $^{13}$C spectrum of the same molecule, however, we can easily distinguish each carbon signal, and we know from this data that our sample has seven non-equivalent carbons. (Notice also that, as we would expect, the chemical shifts of the carbons get progressively smaller as they get farther away from the deshielding oxygen.)
This property of $^{13}$C-NMR makes it very helpful in the elucidation of larger, more complex structures.

Example 13.5.3

$^{13}$C-NMR (and DEPT) data for some common biomolecules are shown below (data is from the Aldrich Library of $^1$H and $^{13}$C NMR). Match the NMR data to the correct structure, and make complete peak assignments.

- spectrum a: 168.10 ppm (C), 159.91 ppm (C), 144.05 ppm (CH), 95.79 ppm (CH)
- spectrum b: 207.85 ppm (C), 172.69 ppm (C), 29.29 ppm (CH$_3$)
- spectrum c: 178.54 ppm (C), 53.25 ppm (CH), 18.95 ppm (CH$_3$)
- spectrum d: 183.81 ppm (C), 182.63 ppm (C), 73.06 ppm (CH), 45.35 ppm (CH$_2$)
The Carbon NMR is used for determining functional groups using characteristic shift values. $^{13}$C chemical shift is affected by electronegative effect and steric effect. If an H atoms in an alkane is replaced by substituent X, electronegative atoms (O, N, halogen), $\beta$-carbon and $\gamma$-carbon shift to downfield (left; increase in ppm) while $\alpha$-carbon shifts to upfield. The steric effect is observed in acyclic and cyclic systems, which leads to downshifted chemical shifts. Figure 9 shows typical $^{13}$C chemical shift regions of the major chemical classes.
Figure 9: $^{13}$C Chemical shift range for organic compound

Spin-Spin splitting

Comparing the $^1$H NMR, there is a big difference thing in the $^{13}$C NMR. The $^{13}$C-$^{13}$C spin-spin splitting rarely exit between adjacent carbons because $^{13}$C is naturally lower abundant (1.1%)

- **$^{13}$C-$^1$H Spin coupling**: $^{13}$C-$^1$H Spin coupling provides useful information about the number of protons attached a carbon atom. In case of one bond coupling ($^{1}$J$_{CH}$), -CH, -CH$_2$, and CH$_3$ have respectively doublet, triplet, quartets for the $^{13}$C resonances in the spectrum. However, $^{13}$C-$^1$H Spin coupling has an disadvantage for $^{13}$C spectrum interpretation. $^{13}$C-$^1$H Spin coupling is hard to analyze and reveal structure due to a forest of overlapping peaks that result from 100% abundance of $^1$H.

- **Decoupling**: Decoupling is the process of removing $^{13}$C-$^1$H coupling interaction to simplify a spectrum and identify which pair of nuclei is involved in the J coupling. The decoupling $^{13}$C spectra shows only one peak(singlet) for each unique carbon in the molecule(Fig 10.). Decoupling is performed by irradiating at the frequency of one proton with continuous low-power RF.
The interpretation of $^{13}\text{C}$ NMR spectra does not form a part of Chemistry 350; hence, you may omit Section 13.7. Interested students may wish to read this section for enrichment purposes.

### Features of a C-13 NMR spectrum

**Edit section**

Butane shows two different peaks in the $^{13}\text{C}$ NMR spectrum, below. Note that: the chemical shifts of these peaks are not very different from methane. The carbons in butane are in a similar environment to the one in methane.

- there are two distinct carbons in butane: the methyl, or CH$_3$, carbon, and the methylene, or CH$_2$, carbon.
- the methyl carbon absorbs slightly upfield, or at lower shift, around 10 ppm.
- the methylene carbon absorbs at slightly downfield, or at higher shift, around 20 ppm.
- other factors being equal, methylene carbons show up at slightly higher shift than methyl carbons.

![Simulated $^{13}\text{C}$ NMR spectrum of butane](image)

*Figure NMR2. Simulated $^{13}\text{C}$ NMR spectrum of butane (showing only the upfield portion of the spectrum).*
In the $^{13}\text{C}$ NMR spectrum of pentane (below), you can see three different peaks, even though pentane just contains methyl carbons and methylene carbons like butane. As far as the NMR spectrometer is concerned, pentane contains three different kinds of carbon, in three different environments. That result comes from symmetry.

![Image of NMR spectrum of pentane](http://riodb01.ibase.aist.go.jp/sdbs/)

Symmetry is an important factor in spectroscopy. Nature says:

- atoms that are symmetry-inequivalent can absorb at different shifts.
- atoms that are symmetry-equivalent must absorb at the same shift.

To learn about symmetry, take a model of pentane and do the following:

- make sure the model is twisted into the most symmetric shape possible: a nice "W".
- choose one of the methyl carbons to focus on.
- rotate the model 180 degrees so that you are looking at the same "W" but from the other side.
- note that the methyl you were focusing on has simply switched places with the other methyl group. These two carbons are symmetry-equivalent via two-fold rotation.

Animation NMR1. A three-dimensional model of pentane. Grab the model with the mouse and rotate it so that you are convinced that the second and fourth carbons are symmetry-equivalent, but the third carbon is not.

By the same process, you can see that the second and fourth carbons along the chain are also symmetry-equivalent. However, the middle carbon is not; it never switches places with the other carbons if you rotate the model. There are three different sets of inequivalent carbons; these three groups are not the same as each other according to symmetry.

Example 13.7.1

Determine how many inequivalent carbons there are in each of the following compounds. How many peaks do you expect in each $^{13}\text{C}$ NMR spectrum?
Practically speaking, there is only so much room in the spectrum from one end to the other. At some point, peaks can get so crowded together that you can't distinguish one from another. You might expect to see ten different peaks in eicosane, a twenty-carbon alkane chain, but when you look at the spectrum you can only see seven different peaks. That may be frustrating, because the experiment does not seem to agree with your expectation. However, you will be using a number of methods together to minimize the problem of misleading data.

The C-13 NMR spectrum for ethanol

Edit section

This is a simple example of a C-13 NMR spectrum. Don't worry about the scale for now - we'll look at that in a minute.

C-13 nmr spectrum for ethanol, CH₃CH₂OH

Note

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.

There are two peaks because there are two different environments for the carbons. The carbon in the CH₃ group is attached to 3 hydrogens and a carbon. The carbon in the CH₂ 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?

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 is not 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 is not 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.

For now, all you need to realize is that each line in a C-13 NMR spectrum recognizes 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

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$_3$ group and the carbon of the CH$_2$ group even if they are in separate molecules. There's no need for them to be in the same one.

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