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.

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.
Solution

One of the greatest advantages of $^{13}\text{C}$-NMR compared to $^1\text{H}$-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, $^{13}\text{C}$ 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.

![Proton and Carbon Spectra of 1-Heptanol](image)

In the $^{13}\text{C}$ 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 system, which leads to downshifted chemical shifts. Figure 9 shows typical $^{13}$C chemical shift regions of the major chemical class.
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.
Fig 10. Decoupling in the $^{13}$C NMR

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