The trends here are exactly the same as in carbon spectra. Wherever the carbon goes, it takes the proton with it. By analogy with carbon spectra,

- hydrogens on sp$^3$ carbons usually show up in the upfield half of the spectrum, about 0 to 5 ppm.
- hydrogens on sp$^2$ carbons usually show up in the downfield half of the spectrum, about 5 to 10 ppm.
- within these two halves of the spectrum, electronegative atoms attached to the same carbon as a proton will draw that proton downfield.

![Figure NMR11. $^1$H NMR spectrum of hexane.](image)

Source: Simulated spectrum.

![Figure NMR12. $^1$H NMR spectrum of 1-hexene.](image)

Source: Simulated spectrum.

![Figure NMR13. $^1$H NMR spectrum of butanal.](image)
As before, there are also hydrogens on linear carbons, although they are much less common than tetrahedral or trigonal carbons.

- hydrogens on sp carbons show up between 2 and 6 ppm.

Remember, these are general rules that you should know. There will occasionally be exceptions; the proton in a carboxylic acid may be seen at 12 ppm, and the proton in chloroform shows up at 7 ppm although it is attached to a tetrahedral carbon. (World-record shifts occur for hydrogens attached to transition metals: "late" metals like ruthenium or rhodium can move hydrogen peaks all the way up to -20 ppm, but "early" metals like tantalum can move them down as far as 25 ppm.)

**Problem NMR.5.**

Looking at the $^1$H NMR spectra of the following compounds, indicate which peak belongs to which proton.

1. dibutyl ether
2. methyl phenyl ether
3. benzaldehyde
4. acetophenone

Notice that a major difference from $^{13}$C NMR is that a carbon spectrum is spread out over 200 ppm, while a typical proton spectrum is compressed into about 10 ppm. There is a consequence of that difference, and it can be frustrating. It is usually easy to distinguish two different $^{13}$C peaks, whereas two peaks in the $^1$H spectrum could easily be so close together that they overlap. For example, the aliphatic hydrocarbons hexane and nonane display only two distinct peaks in the $^1$H spectrum, one for the methyl hydrogens and one for the methylene hydrogens, because the latter are all too similar to tell apart given the limited amount of resolution in the spectrum.

- coincidental overlap of peaks in the $^1$H spectrum is common.

There is another complication in the chemical shifts seen in $^1$H spectroscopy, and that is the behaviour of protons attached directly to heteroatoms such as oxygen and nitrogen. Oxygen is very electronegative, and hydrogen is not, so it stands to reason that an OH proton would absorb at very low field, say 10 ppm. That's completely wrong. OH protons in aliphatic alcohols show up between 2 and 6 ppm, phenolic OH protons between 5 and 9 ppm, and carboxylic acid OH protons between 11 and 12 ppm. Water shows up around 1.6 ppm when dissolved in chloroform, but if the water is present in high concentrations it can show up further downfield. Thus:

- a proton attached to oxygen shows up between 1 and 12 ppm.
- hydroxy proton shifts can vary depending on factors such as hydrogen bonding with the solvent and other molecules.
- except for carboxylic acid protons, which occur beyond the normal range of other peaks, a peak showing up at a particular shift is not strong evidence for the presence of an OH proton.
Although oxygen is very electronegative, it also has two lone pairs of electrons; those lone pairs on oxygen are often crucial in understanding chemistry. The oxygen atom does pull electron density away from the hydrogen through the sigma bond between them, but the lone pairs also bathe the nearby hydrogen in the shielding effects of their electron density. Depending on how these two factors balance out, OH and NH protons don't absorb nearly as far downfield as expected.

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