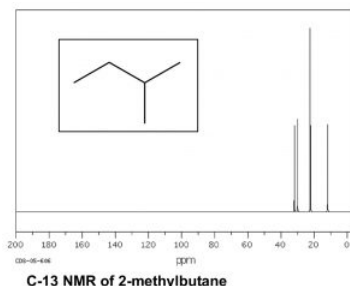
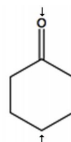


## 2.5: Carbon-13 NMR Spectroscopy

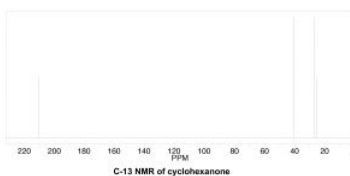
We begin by considering the use of  $C-13$  NMR spectroscopy because it can provide the simplest type of NMR spectrum.  $C-13$  is a minor isotope of carbon, usually  $\sim 1\%$  of carbon nuclei present in sample are  $C-13$  (the majority are  $C-12$  and a very small percentage (less than 1 in a million are  $C-14$ ). In a  $C-13$  spectrum, each chemically different carbon atom will give rise to a signal or peak in the spectrum. By chemically different, we mean that the carbons are in different environments; these environments impact the local magnetic field that a particular nucleus will experience. So, for example, while ethane  $CH_3CH_3$  (obviously) has two carbons, because of the symmetry of molecule, both carbon nuclei experience the same chemical (and local magnetic) environment; we would expect ethane to show a single  $C-13$  NMR peak.



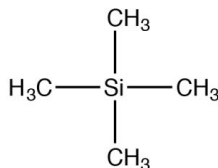
Now consider a more complex hydrocarbon such as 2-methylbutane ( $\beta$ ), which has a total of five carbons; of these the C1 and C2 methyl carbons are in identical chemical environments. The molecule as a whole has four distinct environments and therefore there are 4 peaks in its  $C-13$  NMR spectrum.



To determine the number of chemically distinct carbons that are present within a molecule, you need to look at the patterns of bonds within the molecule, that is, what each carbon bonded to. One quick way to check for identical chemical environments is to look for planes (or axes) of symmetry in the molecule (ignoring rotations around  $C-C$  single bonds). For example, cyclohexanone has a single symmetry axis (marked by arrows); the result is that molecule has only 4 chemically distinct carbons as shown in the spectrum below. Now we need to answer the question of why these signals appear at different places in the spectrum



### The chemical shift

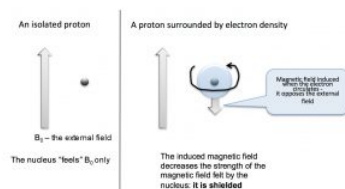


Since NMR instruments may have different field strengths, NMR spectra are often reported with reference to a standard material: tetramethyl silane (TMS). TMS has tetrahedral symmetry, so all of the carbons in the molecule have an identical chemical (local magnetic) environment. We can therefore confidently predict that the  $C-13$  NMR spectra for TMS has a single peak. The chemical shift (in ppm) = shift from TMS/total spectrometer frequency. By using this approach, the chemical shift is not dependent on the type of instrument used. For  $C-13$  NMR the chemical shifts usually range from about 220 to 0. The designation of 0 is where TMS would actually appear, although this signal is often removed from the spectrum for clarity (as in the two preceding

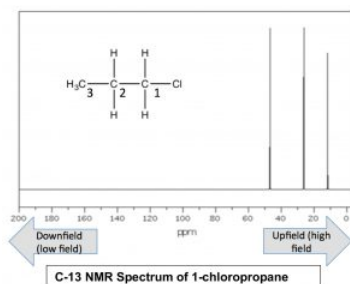
spectra). However, if you see spectra with a peak at 0 ppm it is almost certainly due to the TMS standard and should not be used in your determination of the structure.

## Shielding and Deshielding

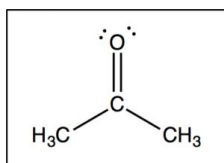
We can answer the question of why NMR signals appear at different places by first remembering that we are dealing not with isolated nuclei, but with molecules that consist of nuclear cores surrounded by electrons that can be described as occupying various molecular orbitals. The electron density around the nucleus has a marked effect on the local magnetic field—that is, the magnetic field that is “felt” by each nucleus. The electrons also “feel” the effect of the magnetic field and begin to circulate around the nuclei to induce a new magnetic field that opposes the original one. This overall impact of this is to reduce the effective nuclear field as shown in the figure below. It now takes a stronger external field to bring the nucleus to resonance at the same frequency (the flip the nuclear spin).



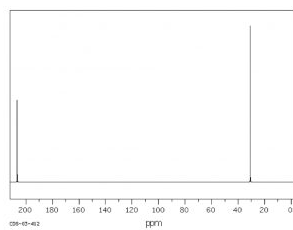
Nuclei that are surrounded by a larger amount of electron density are said to be shielded; they require a larger magnetic field to bring to spin flip than nuclei that are de-shielded (that is, surrounded by lower electron density). Absorption by shielded nuclei tend to be higher (“upfield”) in the spectrum and de-shielded nuclei appear downfield. Consider for example, the C–13 NMR spectrum of 1-chloropropane.



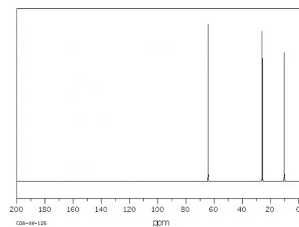
As we might expect, there are 3 peaks in the spectrum, but now we can figure out which is which, because we can predict the relative charge densities on each carbon. The carbon attached to the chlorine (C–1) is most de-shielded by the inductive effect, and therefore should appear at lowest field. Indeed the signal at around 47ppm belongs to the C–1. We can also see how the inductive effect dissipates with distance from the electron withdrawing group to the C–3 signal at around 11ppm. This is direct evidence for the inductive electron-withdrawing effect.



Now let us compare this spectrum to that of acetone. As we might predict, this spectrum has only two peaks in it because acetone only has two types of carbon, but what is even more interesting is that the C = O carbon appears at such low field, around 205ppm. This means that the C = O carbon must be very electron deficient—much more so than a carbon single-bonded to an oxygen (C – O) in an alcohol, which appears around 64ppm (as shown in the spectrum of 1-propanol) . This is direct evidence for a phenomenon that we will see time and again, which is that the C = O carbon is highly electron deficient and is very susceptible to nucleophilic attack. Note that the spectrum of acetone also shows this highly downfield shifted peak corresponding to the C = O carbon.



**C-13 NMR spectrum of acetone**



**C-13 Spectrum of 1-propanol**

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