Analyzing NMR Spectra

NMR stands for nuclear magnetic resonance. NMR spectroscopy is very helpful in determining the structure of a compound. IR spectroscopy, which we have used previously, provides information about the bonds which are present in a molecule, thus giving us an idea of what functional groups may be present, but it cannot be used to determine the actual structure of a compound. NMR spectroscopy can.

The mechanics of the spectrometer are very complicated, and we will not worry about them in this course. What is helpful for you to know is that NMR spectroscopy deals with energy states in the nuclei of atoms and their interaction with radio waves under an intense magnetic field. Only nuclei with an odd atomic mass can be detected. The most useful nucleus is ^{1}H, since there are usually quite a few hydrogen atoms in an organic molecule. By finding information about the magnetic environment of each of these H's, we can deduce a lot about the structure of the compound.

NMR spectra contain single peaks or clusters of peaks which represent sets of equivalent H's in a molecule. Each set of peaks has three kinds of information - chemical shift, integration, and splitting. You need to pay attention to all three kinds of data when interpreting an NMR spectrum.

The spectra you will receive are actual spectra taken under experimental conditions - they are a little different from spectra you will find in a textbook. They contain TMS and solvent peaks, and may also contain water, impurities, overlapping peaks, complex splitting, and so on.

The TMS peak is always at 0.0 ppm - it is caused by a small amount of TMS (tetramethylsilane, $Si(CH_3)_4$) added to the sample so that the scale can be set to 0. It is important to identify this peak so that you don't think it is part of the compound.

Solvent peaks come from the solvent. To prevent the H's in the solvent from showing up on an NMR spectrum, the ^{1}H's in NMR solvents are replaced with ^{2}H's (usually given the symbol D) - these are called deuterated solvents. However, these solvents always contain a small amount of ^{1}H's as impurities, which show up on the spectrum. You can locate solvent peaks by knowing what solvent the NMR was run in. The most common deuterated solvent is chloroform, written as $CDCl_3$. The $CHCl_3$ impurity shows up at 7.25 ppm. More polar samples are often run in deuterated dimethyl sulfoxide, written as DMSO-d_6, which shows up at 2.5 ppm. Solvent peaks are always singlets, since all H's in these two compounds are identical.

If the sample is contaminated with water, it will show up in different places depending on the solvent. Water shows up at 1.5 ppm in chloroform, and 3.35 ppm in DMSO, and is always a singlet.

Other impurities may appear as small peaks on the baseline. You can usually identify these by the fact that their integration is very small, making it unrealistic for them to be part of the compound.

When a compound contains an alcohol, amine, carboxylic acid, or amide, a second spectrum may be run with D_2O added to the sample. This allows the H's connected to O's or N's to be replaced by D's, which are invisible to NMR. In effect, the OH or NH peak disappears (or is significantly reduced), and a DHO (a water with one H and one D) takes its place. DHO appears at about 3.7 ppm, and is usually quite large. By comparing the D_2O spectrum to the original, it is easy to see which one was the OH or NH peak.

You will also find that in many spectra, more than one set of H's will overlap. This is common when there are sets of H's that have very similar chemical shifts, such as on a long carbon chain. Integration will often be obscured by the overlapping, so you'll have to use your best guess. Also please note that integrations don't always come out exact; the value of the integration changes a little from one end of the spectrum to the other, so don't worry if the ratios aren't exactly even.

Finally, complex splitting occurs when C=C's are present. Here, our approximation of splitting giving the number of neighbors breaks down because the H's doing the splitting are quite different. The result is that you will see a lot more peaks than you expected. Don't panic - you can usually use integration and chemical shift to assign the peaks without considering the splitting. You will also find that H's on benzene rings may or may not show the expected splitting - sometimes the splitting is so fine that peaks that you would expect to be multiplets appear as singlets. Don't worry about this if the assignment makes sense in all other ways. Imagine that you are a detective, putting together all of the clues that you can gather!

Below is a table of chemical shift values that you may refer to. Remember that these are guidelines, not hard and fast rules. Hydrogens which are shifted downfield by two different things (next to alcohol and next to a benzene ring) will be further down than either alone.

Chemical shift	Type of hydrogen
0.5-2.0 ppm	alkane H's far away from electron-withdrawing groups
1.0-5.0 ppm	H's on alcohols and amines (vary with concentration, broad)
2.0-2.5 ppm	H's next to C=O's
2.5-3.0 ppm	H's next to amines
2.0-3.0 ppm	H's next to aromatic rings
3.0-4.0 ppm	H's on carbons next to O or halogens
4.5-6.5 ppm	H's on C=C
6.5-8.5 ppm (~7 ppm)	H's on aromatic rings
7.5-9.5 ppm	H's on amides (sometimes broad)
9.0-11.0 ppm	H's on aldehydes
9.0-13.0 ppm	H's on carboxylic acids (often very broad)