Nuclear Magnetic Resonance notes

Nuclear Magnetic Resonance (NMR) is a spectrometric technique which provides information about a particular type of atom contained within a sample. Not all atoms are 'visible' in NMR. The most commonly examined nuclei using NMR are $^1$H (proton) and $^{13}$C (carbon 13). A few of the other routinely examined nuclei include $^{19}$F (fluorine) and $^{17}$O (oxygen 17) and $^{31}$P (Phosphorous 31). In this class we will only use proton NMR and carbon NMR.

In a simplified manner an NMR works because nuclei have a charge and a spin. Spinning charges create a small magnetic dipole. When a sample is placed in a very strong magnetic field, the nuclei align themselves with the strong magnetic field. Then the nuclei are 'bumped' out of alignment by the application of a burst of electromagnetic energy usually in the radio frequency range. When this burst is removed, the nuclei realign themselves and give off a small amount of energy. The characteristics of the energy given off, reveals a great deal about the type, location and quantity of that nuclei. The energy given off is recorded as an NMR spectrum. The proper interpretation of an NMR spectrum can reveal the exact structure of a compound.

The strength of the NMR is determined by the electromagnetic frequency which generates the magnetic field. The higher the frequency the stronger the magnetic field. Within Xavier’s chemistry department there are five and soon to be six NMRs; two (soon to be three) 60 MHz (megahertz), 90 MHz NMR, 300 MHz and a 400 MHz

There are four basic pieces of information that can be obtained from standard proton NMR (pmr). These are 1) the number of non-equivalent protons 2) the chemical environment of each type of proton 3) the relative number of each proton present and 4) the number of adjacent protons. The correct interpretation of this information can reveal the chemical structure.

1. A picture of the Oxford Pular benchtop 60 MHz NMR located in the organic instrumentation lab is below.

2. Sample preparation, solvent and reference material.
NMR analyses are carried out by placing the sample into specially manufactured glass tubes having very precise diameters and uniform wall thickness. A single NMR sample tube can range in cost from $3.00 to more than $100.00 each. Most of these are not disposable and are very fragile. Handle NMR tubes and samples with care. NMR samples are made by placing a small amount of sample (1-2 drops, ~200mg) into an NMR appropriate solvent. The solvent must not be NMR active or else the signal from the solvent would overwhelm that from the sample. This means that if making a sample for proton NMR, the solvent cannot contain any $^1$H atoms. The most prevalent isotope of hydrogen with an added neutron is $^2$H (deuterium or D) which is not visible in the $^1$HNMR, hence all NMR solvents are deuterated. The solvent used in this experiment is deuterated chloroform, CDCl$_3$. A reference standard is normally added to all NMR samples. The common reference material tetramethylsilane (TMS, (CH$_3$)$_4$Si) has been added to all of the samples in this experiment. In a proton NMR the shift of the TMS is defined as 0.0 ppm.

1H NMR Interpretation
There are four main pieces of information that a $^1$HNMR may provide: the number of non-equivalent protons, the chemical environment of each proton, the number of neighboring protons and the relative ratio of each type of proton.

3. **Number of signals equals the number of non-equivalent protons.**

Every proton (that is, every $^1$H) in a sample can give a signal. If all of the protons in a sample are *equivalent* to one another, their signals will coincide, and chemists say that the spectrum contains one signal. For example, the pmr spectrum of a sample of CH$_4$ contains only one signal. When all the protons in the same molecule are *equivalent*, a sample of the compound will give only one signal in the pmr spectrum. Methanol (CH$_3$OH) gives two signals in its proton nmr spectrum. The three protons of the CH$_3$ group are equivalent to one another, but the proton of the OH group is not equivalent to the others.

Sample questions: How many signals are there in the proton nmr spectra of each of the following molecules?

- a) CH$_3$CH$_2$OH
- b) CH$_3$CH$_2$OCH$_2$CH$_3$
- c) ![Chemical Structure](image)

Answers:  
a) three  B) two  C) seven

4. **The Location of signals (chemical shift) indicates the chemical environment of the proton.**

The location of signals on a pmr spectrum along the x-axis is almost always expressed in units of parts per million (ppm) or $\sigma$, which is given along the bottom of the spectra shown above. The electron density around the proton, influence the location along the x-axis. There are three main factors that influence the
location of signals, also known as the chemical shift: (1) the presence of electronegative atoms near the proton giving a signal, (2) the presence of π bonds, and (3) the number of bonds between the proton and the electronegative atom or π bond.

A summary of the shifts of the different environments may be found on the 1H NMR guide sheet. This will be covered in lab.

5. The pattern of the signal indicates the number of hydrogen on the adjacent carbon.

The protons which produce a signal are influenced by the protons (or other magnetic nuclei) on the adjacent carbon. The adjacent or neighboring protons split the signal of the hydrogen of interest. The formula which describes the splitting pattern is the number of neighboring protons \( n \) plus 1 equals the pattern \( n+1 \) split. If no adjacent hydrogen are present, \( n=0, 0+1=1 \) no splitting is present and the signal appears as a singlet. If there is one adjacent hydrogen the split will be a \( 1 + 1 = 2 \) doublet. If there are two adjacent hydrogen the split will be a \( 2 + 1 = 3 \) triplet. If there are three adjacent hydrogen the split will be a \( 3 + 1 = 4 \) quartet. The patterns are shown at the top of the 1H NMR guide sheet.

A caveat in this interpretation is the fact that protons on OH, NH, and CHO groups do not act as neighbors and will not bring about a splitting pattern in the adjacent protons.

6. Relative size of the signal (the integration) is proportional to the number of that type of proton

The more of a particular proton type present in a molecule, the larger that signal will be compared to the other signals. If a molecule only has one type of proton such as with ethane, there will only be one signal present of relative size of 1 (100%). The nmr does not know the total number of protons present, so it cannot give an exact number of protons. It gives a relative size of one signal to the other signals. The size is calculated by integrating the area under each peak, so this value is often called the integration value. Diethylether \( \text{CH}_3\text{-CH}_2\text{-O-CH}_2\text{-CH}_3 \) has two types of protons. There are 4 methylene protons and 6 methyl protons. The relative size of the two peaks will be 1 to 1.5. The integration values of these two peaks will have this ratio. The absolute integration values may be 1 to 1.5, or 2 to 3, or 4 to 6, or 46 to 69, or 1.86 to 5.58 or any other pair of numbers with a 1 to 1.5 ratio.

7. The above 4 pieces of information are combined to fully interpret a spectra and devise a chemical structure for the material. You will practice this during the NMR laboratory class period. Note, the more NMR problems you work, the easier (and more fun) they become.
8. **13C NMR Interpretation**

A typical 13C NMR spectrum only provides information as to how many non-equivalent carbon atoms are present in a sample, and the environment in which these atoms exist. The integration of 13C NMR is not useful due to the low and non-uniform natural abundance of 13C isotope within molecules.

A guide sheet of how 13C chemical shift relates to the environment of the carbon will be provided in class.

Additional NMR problem solving skills will be reviewed in your lab class.

References

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John Wiley and Sons


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