

NMR mini course

Amy Kelly

Outline

- Basics of NMR
- ^1H NMR
- ^{13}C NMR
- COESY & NOESY

Basics

- Nuclei are immersed in a static magnetic field and exposed to a second oscillating magnetic field
- Some nuclei experience this phenomenon, and others do not, dependent on whether or not they have spin
- Superconducting magnet produces the B_0 field necessary
- Immediately within the bore of the magnet are the shim coils for homogenizing the B_0 field
- Within the shim coils is the probe
- Probe contains the RF coils for producing the B_1 magnetic field necessary to rotate the spins by 90° or 180°
- RF coil also detects the signal from the spins within the sample
- Sample is positioned within the RF coil of the probe

- Nuclear magnetic resonance (NMR) spectroscopy involves using energy in the form of electromagnetic radiation (radio waves) to orient nuclei into the less energetically favorable beta state
- When the energy is removed, the energized nuclei relax back to the alpha state
- The fluctuation of the magnetic field associated with this relaxation process is called resonance and this resonance can be detected and converted into peaks
- Nuclei that are not in identical structural situations do not experience the external magnetic field to the same extent

^1H Chemical Shifts

- Nuclei are shielded or deshielded due to small local fields generated by circulating sigma, pi and lone pair electrons
- Shielded = lower frequency
- Hydrogens near an electronegative atom require a higher frequency to flip, thus they appear at a higher ppm in the spectrum
- Exact frequency depends on solvent
- If paramagnetic species are included, range become much wider

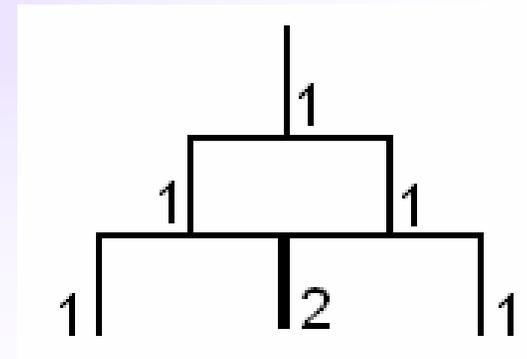
Image removed due to copyright considerations.

$$\delta = \frac{\text{difference in precession frequency between the nuclei and the reference nuclei}}{\text{operating frequency of the magnet}}$$

Multiplicity

N+1 rule

Image removed due to copyright considerations.



-OH usually exchanges rapidly and is a broad singlet

Coupling Constants

Image removed due to copyright considerations.

^{13}C NMR

- ^{13}C has only about 1.1% natural abundance (of carbon atoms)
- ^{13}C is about 400 times less sensitive than ^1H nucleus to the NMR phenomena
- Chemical shifts measured with respect to tetramethylsilane, $(\text{CH}_3)_4\text{Si}$ (*i.e.* TMS)
- Chemical shift range is normally 0 to 220 ppm
- Similar factors affect the chemical shifts in ^{13}C as seen for ^1H NMR
- Long relaxation times (excited state to ground state) mean no integrations (carbon signals don't relax equally)
- Due to low abundance, do not usually see ^{13}C - ^{13}C coupling
- Carbons couple with the hydrogen atoms that are directly attached to them
- "Normal" ^{13}C spectra are "broadband, proton decoupled" so the peaks show as single lines
- Number of peaks indicates the number of types of C
- From NOE enhancements we can usually say the peak intensity range $\text{CH}_3 > \text{CH}_2 > \text{CH} > \text{C}$

Chemical Shift (δ) Type of Carbon

10-40 ppm Alkane C's	115-150 ppm Aromatic
40-70 ppm Adjacent to an electronegative atom	160-185 Carbonyl carbon of acid derivatives
65-90 ppm sp carbon of an alkyne	190-220 ppm carbonyl carbon of ketones and aldehydes
110-140 ppm sp ² carbon of an alkene or sp of a nitrile	Multiple functional groups (Chemical shift effects are approximately additive)

Image removed due to copyright considerations.

2D Techniques: COSY

- COrrrelation SpectroscopY
- Determine the connectivity of a molecule by determining which protons are spin-spin coupled
- The proton spectrum is plotted on each of the two axes
- The diagonal within the box is the spectrum as seen from "above"
- Off-diagonal peaks denote splitting between protons on adjacent carbons

Image removed due to copyright considerations.

2D Techniques: NOESY

- **Nuclear Overhauser Effect Spectroscopy** is useful for determining which signals arise from protons that are close to each other in space even if they are not bonded

Image removed due to copyright considerations.