NMR – Experimental Aspects

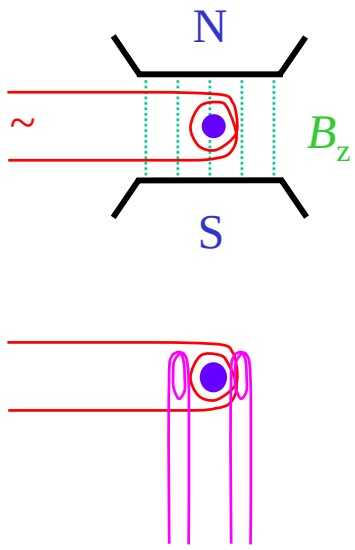
$$h\nu = g_N \beta_N B_z$$

For ^{1}H	60 MHz	↔	14.1 kG	permanent magnet OK
	100 MHz	↔	23.5 kG	electromagnet
	300 MHz	↔	70.5 kG	superconducting magnet

- Resonance can be achieved by
  - sweeping magnetic field
  - sweeping r.f. frequency
  - pulsing r.f.

  } but always recorded in Hz

- The r.f. oscillating magnetic field is oriented perpendicular to the static field (B_z). At resonance, energy is absorbed by the sample from the coil, unbalancing the r.f. bridge circuit. Alternatively, an r.f. signal is induced in a second coil perpendicular to the exciting coil.



- The field sweep is usually very small ($\lesssim$ 1 in 10^4) and the lines very narrow, so both r.f. and magnetic field must be very stable. The field must also be very homogeneous (up to 1 in 10^9), so special sample tubes, sample spinning and field shimming coils are used.

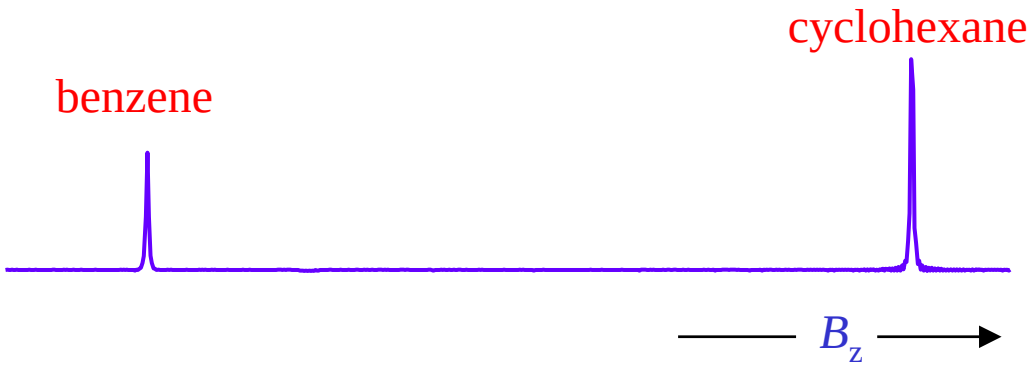
NMR in Liquids

Spin-½ nuclei in molecules tumbling in liquids usually have very narrow lines ~ 1 Hz MHz for ESR!

This is high resolution NMR, most commonly ^{1}H and ^{13}C.

The resonant frequency of each nucleus is determined by its electronic environment, described in terms of chemical shift.

e.g. equimolar mixture of



The spectrum is displayed as if for an increase in field, *but* differences in line positions are always quoted in frequency units.

Splitting of lines can arise from spin-spin coupling, characterized by the coupling constant *J*.

e.g. acetaldehyde

Chemical Shift

Resonances of chemically non-equivalent nuclei are separated by a chemical shift.

The local field at the nucleus differs from the applied field by an amount B_{ind}, which is directly proportional to B_z:

$$B_{local} = B_z - B_{ind} = B_z(1-\sigma) \qquad \sigma = \text{screening constant}$$

The applied field induces a circulation of electrons in the molecule resulting in an induced field which opposes B_z.

The resonant frequency varies with chemical shift:

$$\nu = \gamma B_{local} = \gamma B_z(1-\sigma)$$

so for non-equivalent nuclei j and k

$$\nu_j - \nu_k = \gamma B_z(\sigma_k - \sigma_j) = \nu_0(\sigma_k - \sigma_j)$$

The chemical shift is usually quoted as a ratio

$$\delta_{jk} = \frac{\nu_j - \nu_k}{\nu_0} = \sigma_k - \sigma_j \qquad \text{in units of ppm}$$

TMS (tetramethylsilane) is commonly used as a standard, so by definition

$$\delta_{TMS} = 0 \qquad \delta_j = \frac{\nu_j - \nu_{TMS}}{\nu_{TMS}}$$

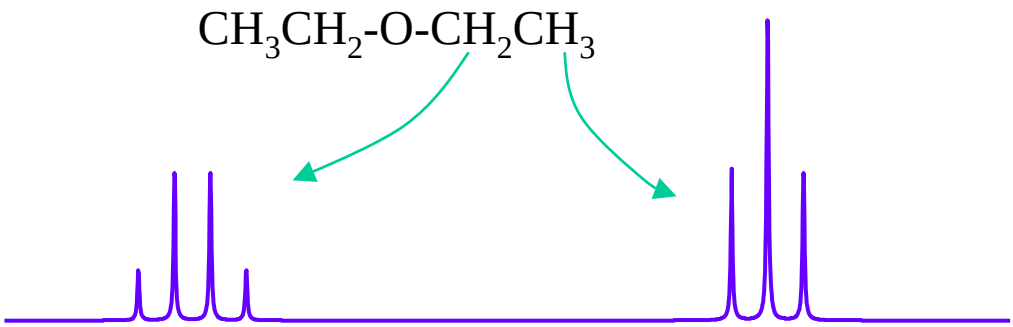
Most organic compounds have proton chemical shifts between 0 and 10 ppm.

Nuclear Spin-Spin Coupling

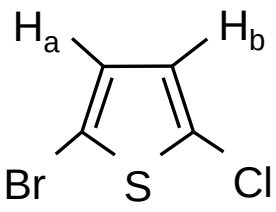
The resonance of a spin-½ nucleus which couples to another nucleus or group of nuclei of spin I is split into $2I+1$ lines.

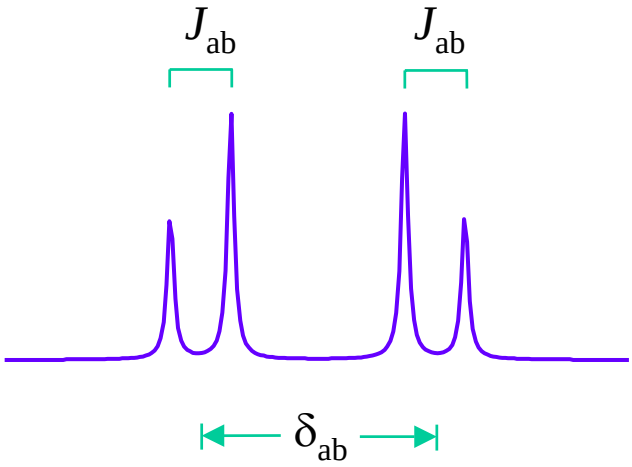
Equal coupling to n equivalent spin-½ nuclei results in $n+1$ lines with intensities corresponding to binomial coefficients.

Nuclei with equal chemical shift couple together but do not give splitting at that resonance. e.g. CH_3I has a single line.

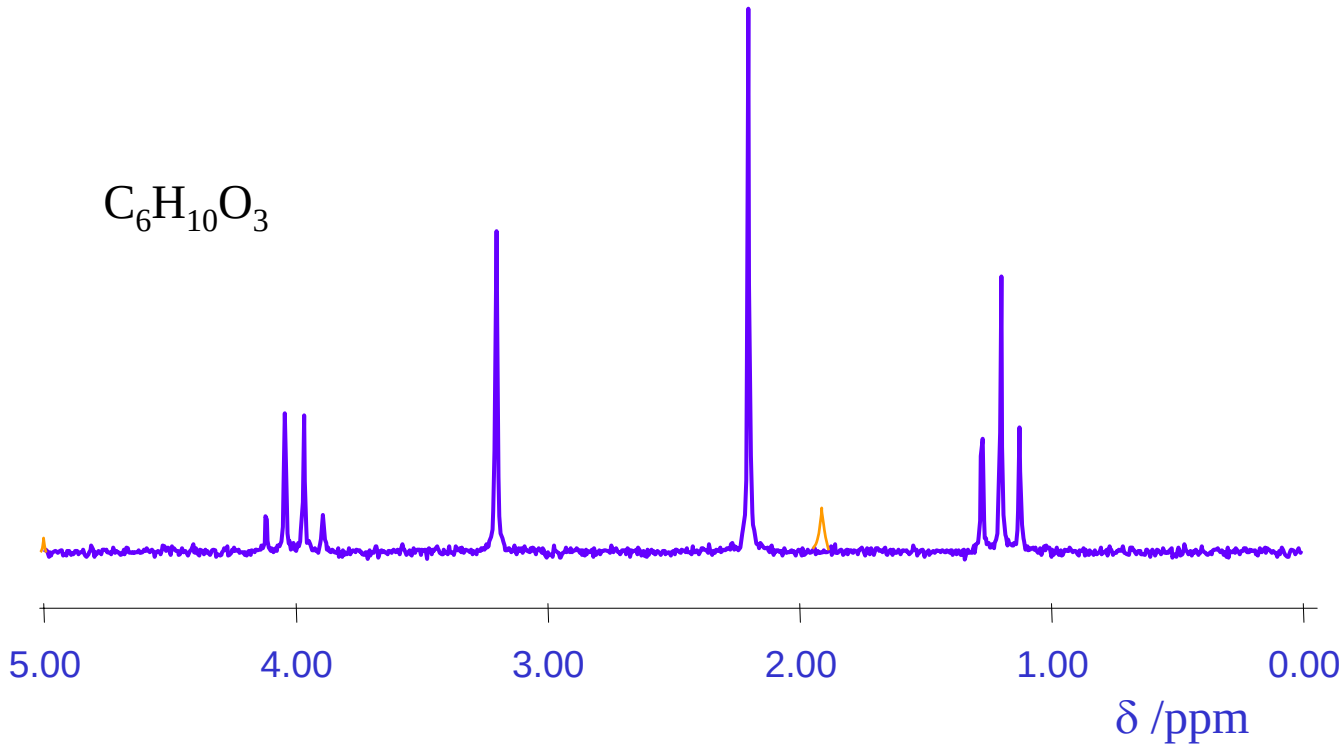


Intensity distortions occur when the first order condition $\delta_{ab} \gg J_{ab}$ is not satisfied



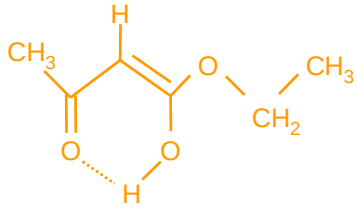


NMR Spectral Analysis – Example

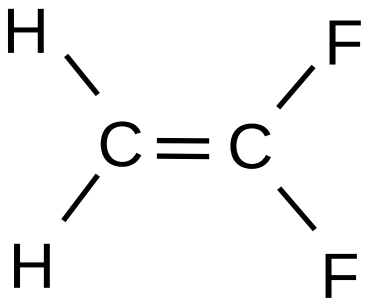


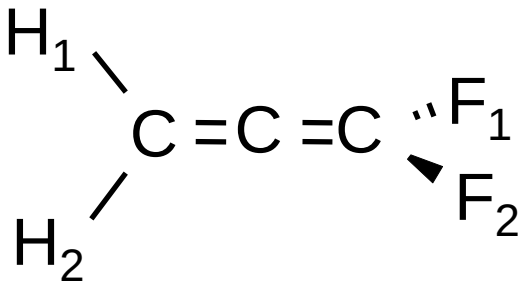
Intensities	2	2	3	3
Splitting	CH_2 – CH_3	CH_2	CH_3	CH_3 – CH_2
Shift	CH_3 – CH_2 – O – C=O – R	X – CH_2 – X	CH_3 – C=O	CH_3 – R

$CH_3COCH_2COOCH_2CH_3$

+ 

Equivalent Spins ?





chemically equivalent

but *not* magnetic

magnetic *and* chemical equivalence

$$J_{H_1F_1} = J_{H_2F_2} \neq J_{H_1F_2}, J_{H_2F_1}$$