NMR – Experimental Aspects

$$h\nu = g_N\beta_N B_z$$ For ^{1}H   60 MHz $\Leftrightarrow$ 14.1 kG permanent magnet possible

100 MHz $\Leftrightarrow$ 23.5 kG electromagnet OK

300 MHz $\Leftrightarrow$ 70.5 kG superconducting magnet essential

❖ Resonance can be achieved by: sweeping magnetic field
sweeping r.f. frequency   but always recorded in Hz
pulsing r.f.

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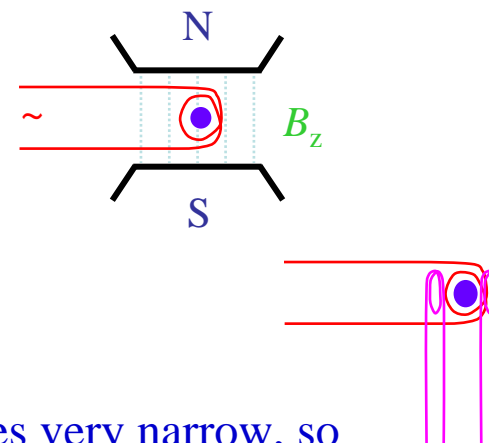
❖ The field sweep is usually very small ($\lesssim$ 1 in 10^4) and the lines very narrow, so both r.f. and magnetic field must be very stable. The field must also be very homogeneous (up to 1 in 10^9), so special sample tubes, sample spinning and field shimming coils are used.
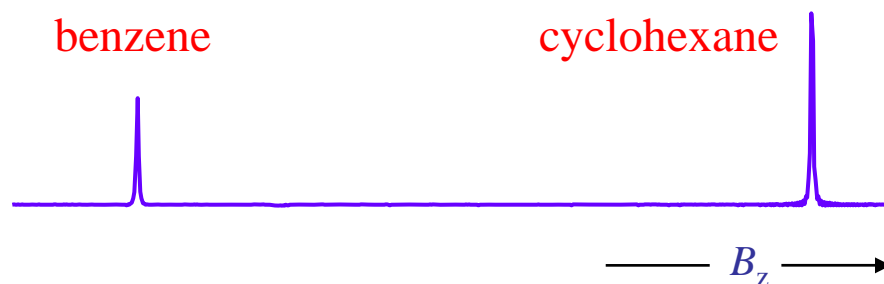
NMR in Liquids

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

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

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

e.g. equimolar mixture of   benzene   cyclohexane

B_z →

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*.

-CHO   -CH$_3$

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

so for non-equivalent nuclei j and k $\qquad \nu_j - \nu_k = \gamma B_z(\sigma_k - \sigma_j) = \nu_0(\sigma_k - \sigma_j)$

The chemical shift is usually quoted as a ratio $\qquad \delta_{jk} = \dfrac{\nu_j - \nu_k}{\nu_0} = \sigma_k - \sigma_j \quad$ 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.
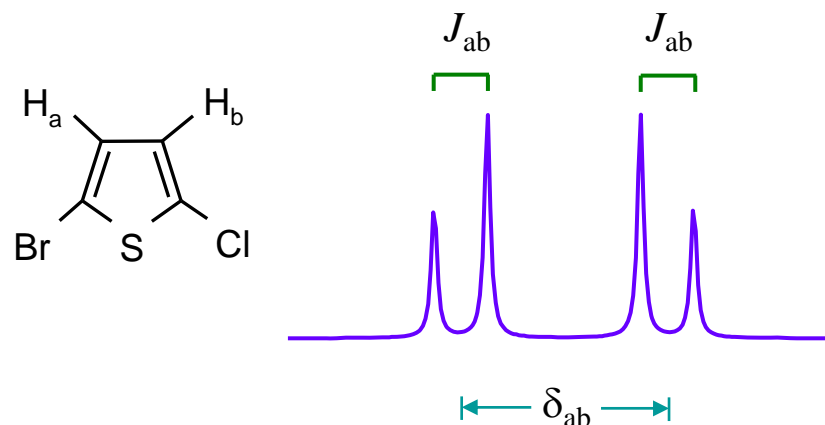
Nuclear Spin-Spin Coupling

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.
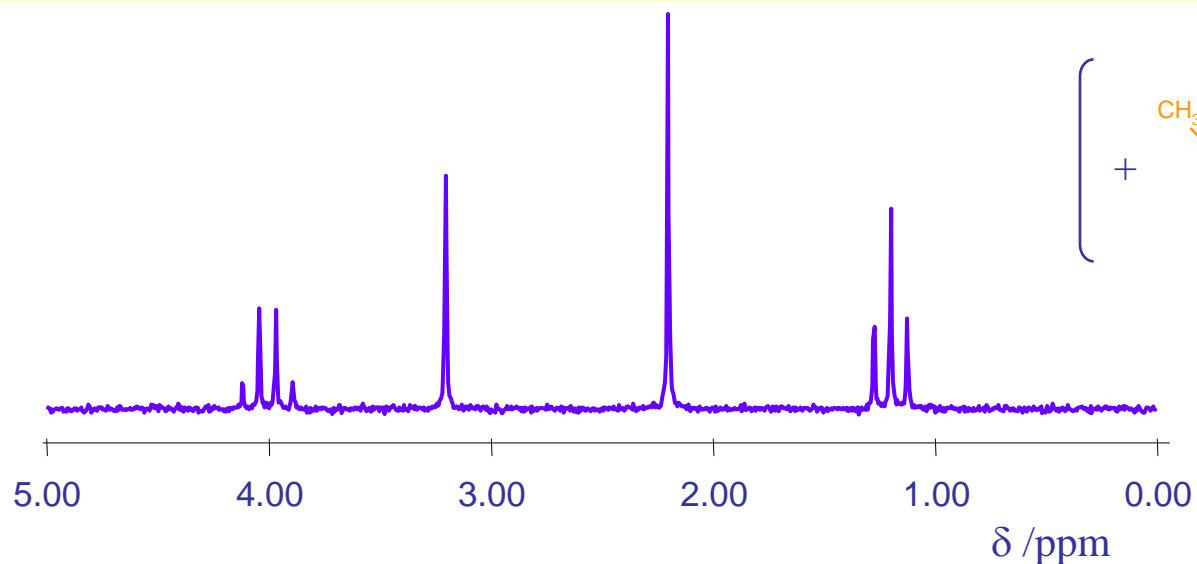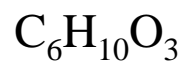
CH_3CH_2-O-CH_2CH_3
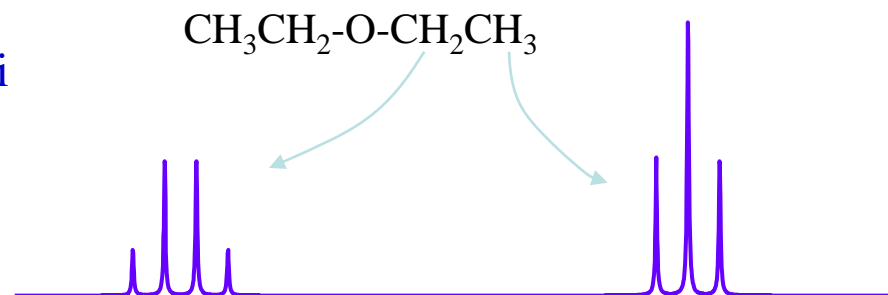
Nuclei with equal chemical shift couple together but do not give splitting at that resonance. e.g. CH_3I has a single line.

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

H_a H_b

Br   S   Cl

J_{ab} J_{ab}

δ_{ab}

NMR Spectral Analysis – Example

$C_6H_{10}O_3$

Intensities	2	2	3	3
Splitting	CH$_2$	CH$_2$	CH$_3$	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

$CH_3COCH_2COOCH_2CH_3$
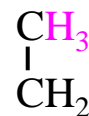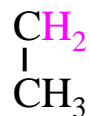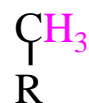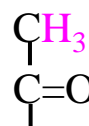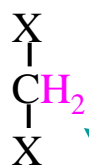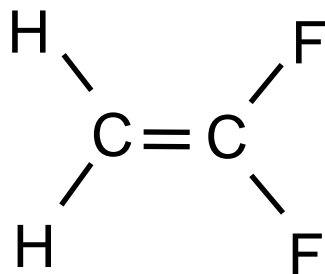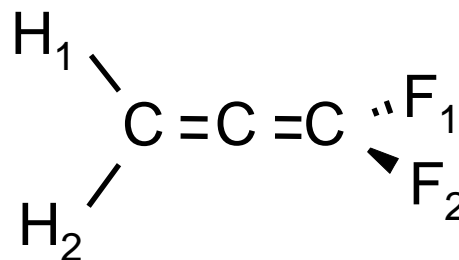
Equivalent Spins ?
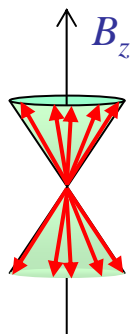
chemically equivalent

but *not* magnetic

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

magnetic *and* chemical

equivalence

The Vector Model of Magnetic Resonance

It is important to distinguish between…
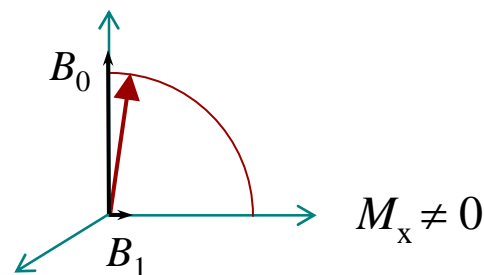
B_z

M_z

M_x, $M_y = 0$

precession of individual spins

motion of the total magnetization

An oscillating magnetic field transverse to the applied field B_0 can be represented by a static vector B_1 in the rotating reference frame.

B_0

B_1

$M_x \neq 0$

Alignment of the magnetization along the combined magnetic field results in a small component of M in the xy plane, where it can induce a signal in the pick-up coil.

Pulsed NMR (and ESR)

Apply a short rf pulse to tip M into the xy plane

– a 90° pulse
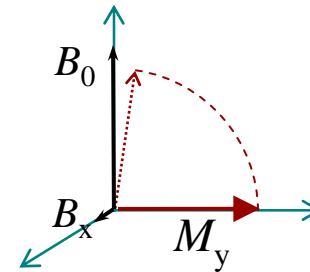
This gives a strong signal as M precesses.

A short pulse of duration Δt centred at frequency ω_0 contains all frequencies in the range $(\omega_0 - 1/\Delta t)$ to $(\omega_0 + 1/\Delta t)$ so that nuclei of all chemical shifts are excited.

The resulting free induction decay signal is processed by Fourier Transform to give a frequency spectrum.

time

frequency