The Interactions of NMR

- Zeeman interaction (basic NMR phenomenon)
- Shifts (interactions that change NMR frequency)
  - Chemical shift
  - others (e.g. Knight shift, paramagnetic shifts)
- Couplings (interactions that split NMR signals)
  - *J* coupling
  - Dipolar coupling
  - Quadrupole coupling

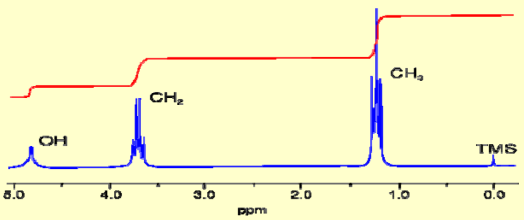
NMR Signals

- Lower frequency is to the left in the spectrum;
  - these absorptions are said to be downfield
- Higher frequency is to the right in the spectrum:
  - these absorptions are said to be upfield
- The small signal at δ 0 corresponds to an internal standard called tetramethylsilane (TMS) used to calibrate the chemical shift scale
- The number of signals in the spectrum corresponds to the number of unique sets of protons

protons in electron-poor environments	protons in electron-dense environments
deshielded protons	shielded protons
downfield	upfield
high frequency	low frequency
large δ values	small δ values

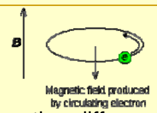
← δ
← frequency

Chemical Shift



HO-CH_2-CH_3

Chemical Shift



- **Chemical shift** is defined as the difference in the resonance position of a signal with respect to a reference signal.
- The **Resonance Frequency** is defined as the frequency difference between the reference signal and a proton signal.
- The δ scale for chemical shifts is independent of the magnetic field strength of the instrument (whereas the resonance frequency depends on field strength)

$$\delta = \frac{(\text{observed shift from TMS in hertz}) \times 10^6}{(\text{operating frequency of the instrument in hertz})}$$

Chemical Shift

- Thus, the chemical shift in δ units for protons on benzene is the same whether a 60 MHz or 300 MHz instrument is used

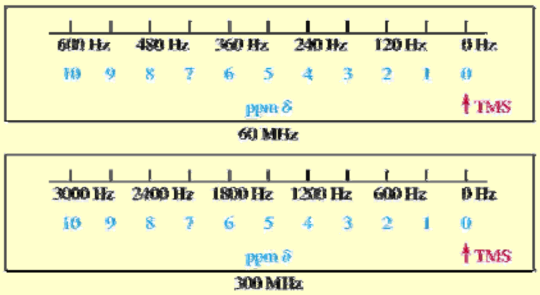
$$\delta = \frac{2181 \text{ Hz} \times 10^6}{300 \times 10^6 \text{ Hz}} = 7.27$$

$$\delta = \frac{436 \text{ Hz} \times 10^6}{60 \times 10^6 \text{ Hz}} = 7.27$$

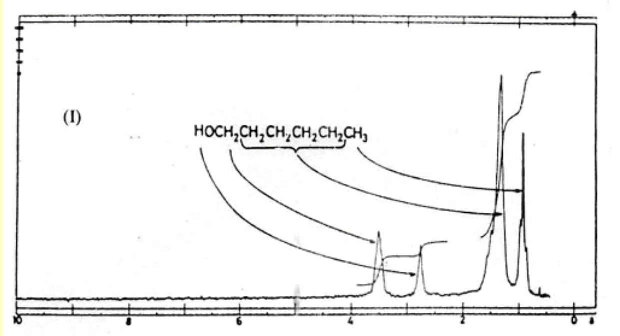
Chemical Shift

Delta Scale

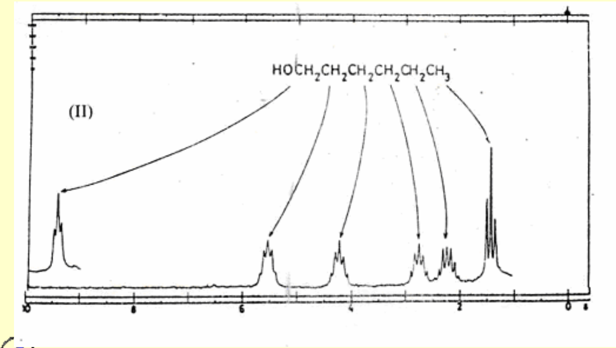
$$\text{chemical shift, ppm } \delta = \frac{\text{shift downfield from TMS (in Hz)}}{\text{spectrometer frequency (in MHz)}}$$



High Resolution



High Resolution



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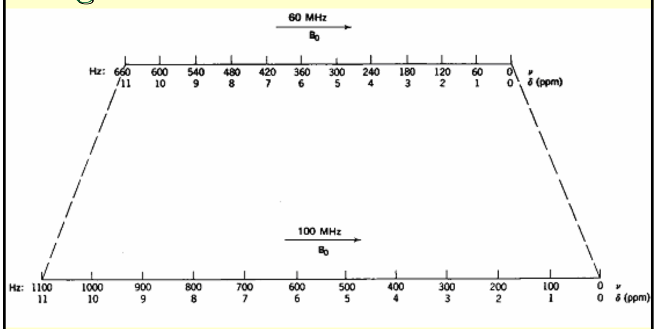

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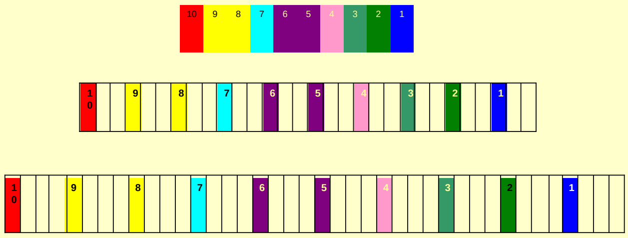
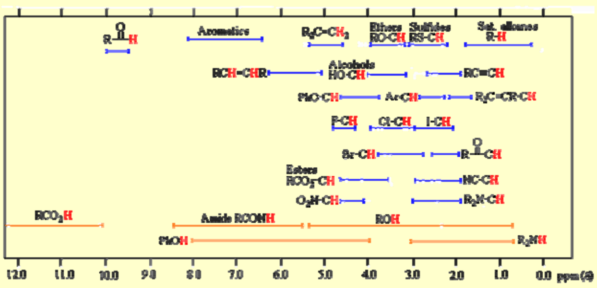


Chemical Shift Trends

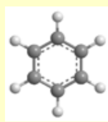


Diamagnetic Anisotropy

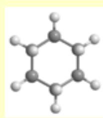
Ring Current Effect

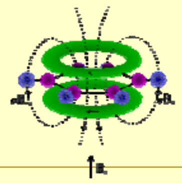
1) external field induces a flow (current) of electrons in π system – ring current effect
2) ring current induces a local magnetic field with shielding (decreased chemical shift) and deshielding (increased chemical shifts)

Benzene:
^1H : 7.16 ppm
^{13}C: 128.39 ppm



Cyclohexane:
^1H : 1.38 ppm
^{13}C: 26.43 ppm

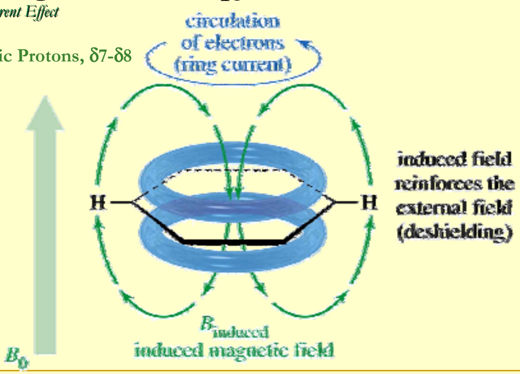




Diamagnetic Anisotropy

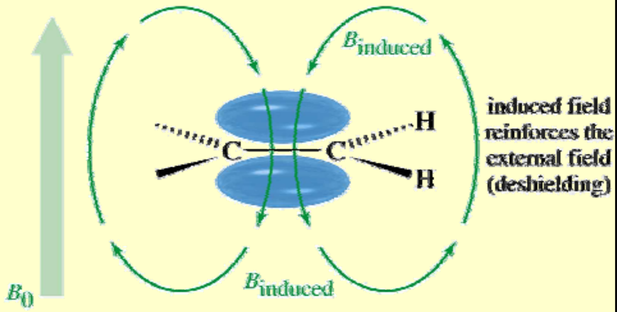
Ring Current Effect

Aromatic Protons, δ7-δ8



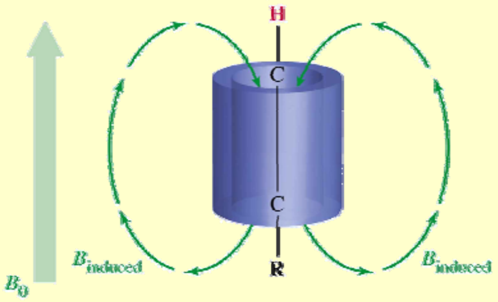
Diamagnetic Anisotropy

Vinyl Protons, δ5-δ6



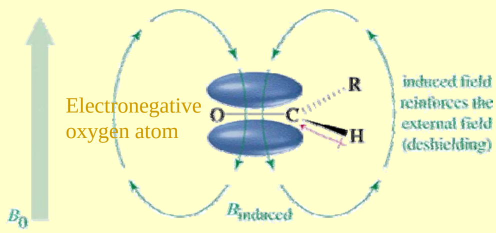
Diamagnetic Anisotropy

Acetylenic Protons, δ2.5



Diamagnetic Anisotropy

Aldehyde Proton, δ9-δ10



Diamagnetic Anisotropy

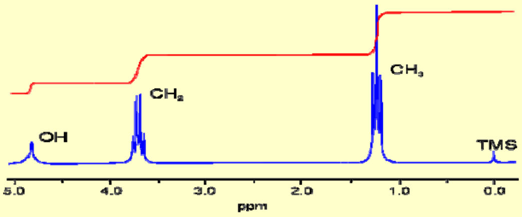
NMR Signals

- The ***number*** of signals shows how many different kinds of protons are present.
- The ***location*** of the signals shows how shielded or deshielded the proton is.
- The ***intensity*** of the signal shows the number of protons of that type.
- Signal ***splitting*** shows the number of protons on adjacent atoms.

Integration Line

- The area under each signal is proportional to the number of protons that give rise to that signal
- The height of each integration step is proportional to the area under a specific signal
- The integration tells us the relative number of protons that give rise to each signal, not absolute number

Integration Line

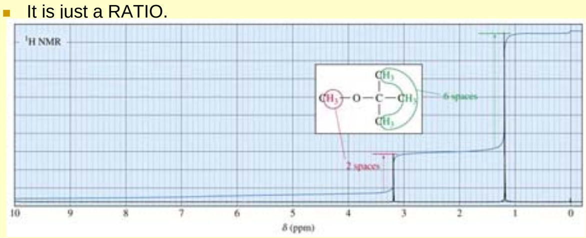


$HO\text{-}CH_2\text{-}CH_3$

Integration Line

Intensity of Signals

- The area under each peak is proportional to the number of protons. (The Integral Trace)
- It is just a RATIO.



NMR Signals

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Nuclear Spin Interactions

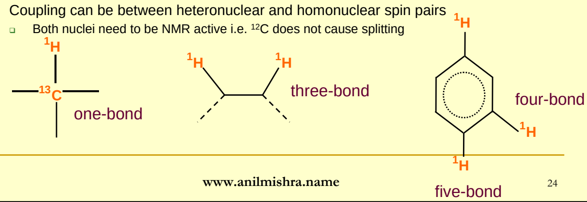
Scalar J Coupling

- The energy levels of a nucleus will be affected by the spin state of nuclei nearby. The two nuclei that show this are said to be ***coupled*** to each other.
- This manifests in particular in cases were we have through bond connectivity
- The magnitude of the separation is called ***coupling constant*** (**J**) and has units of Hz.

Nuclear Spin Interactions

Scalar J Coupling

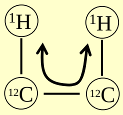
- Through-bond interaction that results in the splitting of a single peak into multiple peaks of various intensities
  - The spacing in hertz (Hz) between the peaks is a constant Independent of magnetic field strength
- Multiple coupling interactions may exist
  - Increase complexity of splitting pattern
- Coupling can range from one-bond to four-bond
  - One, two and three bond coupling are most common
  - Longer range coupling usually occur through aromatic systems
- Coupling can be between heteronuclear and homonuclear spin pairs
  - Both nuclei need to be NMR active i.e. ^{12}C does not cause splitting



Nuclear Spin Interactions

Scalar J Coupling

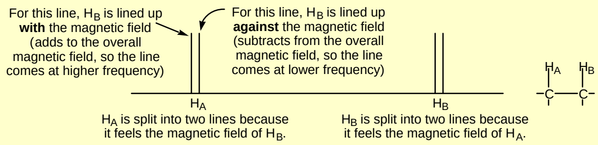
- Electrons have a magnetic moment and are spin 1/2 particles.
- J coupling is facilitated by the electrons in the bonds separating the two nuclei.
  - This through-bond interaction results in splitting of the nuclei into 2I+1states.
- Thus, for a spin 1/2 nucleus the NMR lines are split into 2(1/2) + 1 = 2 states
  - Multiplet = 2nI + 1
    - n - number of identical adjacent nuclei
    - I - spin quantum number



Nuclear Spin Interactions

Scalar J Coupling

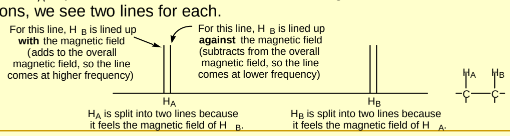
- Splitting of signal is due to 1H - 1H coupling (also called spin-spin coupling or J-coupling). Here's how it works:
- Imagine we have a molecule which contains a proton (let's call it H_A) attached to a carbon, and that this carbon is attached to another carbon which also contains a proton (let's call it H_B).



Nuclear Spin Interactions

Scalar J Coupling

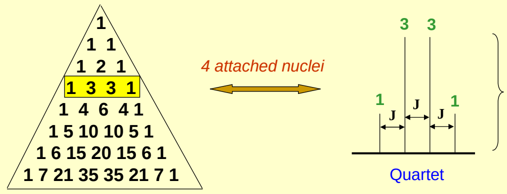
- It turns out that H_A feels the presence of H_B.
  - Recall that these protons are tiny little magnets, that can be oriented either with or against the magnetic field of the NMR machine.
- When the field created by H_B reinforces the magnetic field of the NMR machine (B_0) H_A feels a slightly stronger field, but when the field created by H_B opposes B_0, H_A feels a slightly weaker field.
  - So, we see two signals for HA depending on the alignment of H_B.
- The same is true for H_B, it can feel either a slightly stronger or weaker field due to H_A's presence. So, rather than see a single line for each of these protons, we see two lines for each.



Nuclear Spin Interactions

Scalar J Coupling

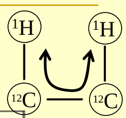
- *Splitting pattern follows Pascal's triangle*
  - Number of peaks and relative peak intensity determined by the number of attached nuclei
  - Peak separation determined by coupling constant (J)

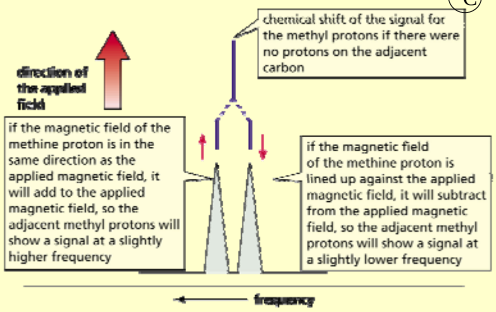


Pascal's triangle

Nuclear Spin Interactions

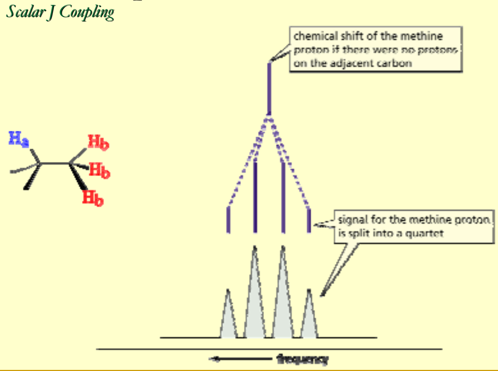
Scalar J Coupling





Nuclear Spin Interactions

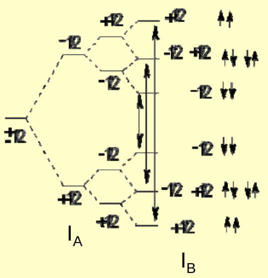
Scalar J Coupling



Nuclear Spin Interactions

Scalar J Coupling

Signal Splitting

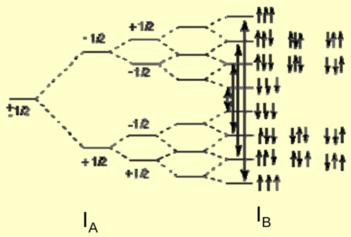


Allowed Transitions $\Delta I_A = \pm 1$ Δ $I_B = 0$

Nuclear Spin Interactions

Scalar J Coupling

Signal Splitting

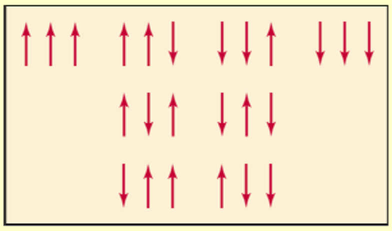


Allowed Transitions $\Delta I_A = \pm 1$ Δ $I_B = 0$

Nuclear Spin Interactions

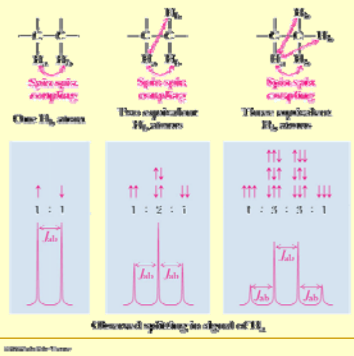
Scalar J Coupling

- The ways in which the magnetic fields of three protons can be aligned



Nuclear Spin Interactions

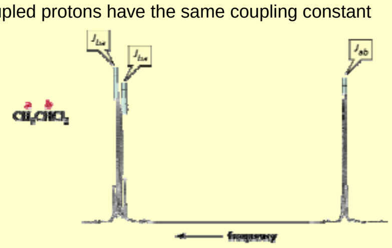
Scalar J Coupling



Nuclear Spin Interactions

Coupling Constant

- The coupling constant (*J*) is the distance between two adjacent peaks of a split NMR signal in hertz
- Coupled protons have the same coupling constant



Nuclear Spin Interactions

Scalar J Coupling

Coupling Rules:

- Equivalent nuclei do not interact
- Coupling constants decreases with separation
  - typically # 3 bonds
- Multiplicity given by number of attached equivalent protons (n+1)
- Multiple spin systems → multiplicity → $(n_a+1)(n_b+1)$
- Relative peak heights/area follows Pascal's triangle
- Coupling constant are independent of applied field strength