



# **NMR Spectroscopy**

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The nuclei of many isotopes have a characteristic spin (I).

Integral spins (e.g. I = 1, 2, 3 ....), Fractional spins (e.g. I = 1/2, 3/2, 5/2 ....), No spin, I = 0 (e.g.  ${}^{12}C$ ,  ${}^{16}O$ ,  ${}^{32}S$ , ....).

Isotopes of particular interest and use to organic chemists are <sup>1</sup>H, <sup>13</sup>C, <sup>19</sup>F and <sup>31</sup>P, all of which have I = 1/2.

## **Spin Properties of Nuclei**

Nuclear spin is related to the nucleon composition:



Odd mass nuclei (i.e. those having an odd number of nucleons) have fractional spins.

*Examples:*  $I = 1/2 ( {}^{1}H, {}^{13}C, {}^{19}F )$ 



 $I = 3/2 ( ^{11}B )$ I = 5/2 ( <sup>17</sup>O )

Even mass nuclei composed of odd numbers of protons and neutrons have integral spins.

*Examples:*  $I = 1 ({}^{2}H, {}^{14}N)$ 

Even mass nuclei composed of even numbers of protons and neutrons have zero spin ( I = 0 ).

Examples: <sup>12</sup>C and <sup>16</sup>O



Spin 1/2 nuclei have a spherical charge distribution, and their NMR behavior is the easiest to understand.

All nuclei with non-zero spins have magnetic moments ( $\mu$ ).



| Isotope                | Natural %<br>Abundance | Spin (I) | Magnetic<br>Moment<br>(µ) | Magnetogyric<br>Ratio (γ) * |  |
|------------------------|------------------------|----------|---------------------------|-----------------------------|--|
| чн                     | 99.9844                | 1/2      | 2.7927                    | 26.753                      |  |
| <sup>2</sup> H         | 0.0156                 | 1        | 0.8574                    | 4,107                       |  |
| <sup>11</sup> B        | 81.17                  | 3/2      | 2.6880                    |                             |  |
| <sup>13</sup> C        | 1.108                  | 1/2      | 0.7022                    | 6,728                       |  |
| <sup>17</sup> O        | 0.037                  | 5/2      | -1.8930                   | -3,628                      |  |
| <sup>19</sup> F        | 100.0                  | 1/2      | 2.6273 25,179             |                             |  |
| <sup>29</sup> Si       | 4.700                  | 1/2      | -0.5555                   | -5,319                      |  |
| <sup>31</sup> <b>P</b> | 100.0                  | 1/2      | 1.1305                    | 10,840                      |  |



\*  $\gamma$  has units of 10<sup>7</sup>rad T<sup>-1</sup> sec<sup>-1</sup>



## The following features lead to the NMR phenomenon:

1. A spinning charge generates a magnetic field.



The resulting spin-magnet has a magnetic moment  $(\mu)$  proportional to the spin.



 In the presence of an external magnetic field (B<sub>0</sub>), two spin states exist, +1/2 and -1/2.





The magnetic moment of the lower energy +1/2 state is aligned with the external field, but that of the higher energy -1/2 spin state is opposed to the external field.

Note that the arrow representing the external field points North.



**3.** The difference in energy between the two spin states is dependent on the external magnetic field strength, and is always very small.





The two spin states have the same energy when the external field is zero, but diverge as the field increases.







## **Energy Levels in a Magnetic Field**

The potential energy E of a nucleus is given by

$$E = -\frac{\gamma mh}{2\pi}B_0$$

where m is magnetic quantum states given by

$$m = I, I-1, I-2, ..., -I$$

and  $B_o$  is an external magnetic field.

The energy for the lower energy state (m = +1/2) is

$$E_{+1/2} = -\frac{\gamma h}{4\pi} B_0$$





Thus the difference in energy  $\Delta E$  between the two is

$$\Delta E = \frac{\gamma h}{4\pi} B_0 - \left(-\frac{\gamma h}{4\pi} B_0\right) = \frac{\gamma h}{2\pi} B_0$$

Recall that  $\Delta E = hv_o$ 

Thus the frequency required to bring about the transition is

$$v_0 = \frac{\gamma B_0}{2\pi}$$

Example

At what frequency would the hydrogen nucleus absorb in 4.69 T?

$$v_0 = \frac{\left(2.68 \times 10^8 T^{-1} s^{-1}\right) \left(4.69 T\right)}{2\pi}$$
  
= 2.00 x 10<sup>8</sup> s<sup>-1</sup> = 200 MHz





4. For spin 1/2 nuclei the energy difference between the two spin states at a given magnetic field strength will be proportional to their magnetic moments.

Magnetic Moments for the four common nuclei:

| <sup>1</sup> Η μ = 2.7927  | $^{31}P \mu = 1.1305$   |
|----------------------------|-------------------------|
| <sup>19</sup> F μ = 2.6273 | ${}^{13}C \mu = 0.7022$ |

Approximate frequencies that correspond to the spin state energy separations for each of these nuclei in an external magnetic field of 2.34 T.



![](_page_10_Picture_0.jpeg)

#### A Model for NMR Spectroscopy

Just as a spinning mass will precess in a gravitational field (a gyroscope), the magnetic moment  $\mu$  associated with a spinning spherical charge will precess in an external magnetic field.

![](_page_10_Figure_3.jpeg)

![](_page_10_Figure_4.jpeg)

![](_page_10_Picture_5.jpeg)

A Spinning Gyroscope in a Gravity Field

A Spinning Charge in a Magnetic Field

![](_page_11_Picture_0.jpeg)

The frequency of precession is proportional to the strength of the magnetic field, as noted by the equation:

 $\omega_{o} = \gamma B_{o}$ 

The frequency  $\omega_o$  is called the **Larmor frequency** and has units of radians per second.

The proportionality constant  $\gamma$  is known as the **gyromagnetic ratio** and is proportional to the magnetic moment.

If RF energy having a frequency matching the Larmor frequency is introduced at a right angle to the external field (e.g. along the x-axis), the precessing nucleus will absorb energy and the magnetic moment will flip to its I = -1/2 state.

![](_page_11_Picture_6.jpeg)

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This excitation is shown in the following diagram. Note that frequencies in radians per second may be converted to Hz (cps) by dividing by  $2\pi$ .

![](_page_12_Figure_2.jpeg)

![](_page_12_Picture_3.jpeg)

The energy difference between nuclear spin states is small compared with the average kinetic energy of room temperature samples, and the +1/2 and \_1/2 states are nearly equally populated.

## **Distribution of Particles Between Magnetic Spin States**

The Boltzmann equation can be written in the form

$$\frac{N_j}{N_o} = \exp\left(\frac{-\Delta E}{kT}\right)$$

where:  $N_j$  is the number of protons in the higher E state, N<sub>o</sub> is the number of protons in the lower E state, k is Boltzmann constant = 1.38 x 10<sup>-23</sup> J K<sup>-1</sup>

Substituting the expression for  $\Delta E$  gives

$$\frac{N_j}{N_o} = \exp\!\left(\frac{-\gamma h B_o}{2\pi kT}\right)$$

#### Example:

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Calculate the relative number of protons in the higher and lower magnetic states when a sample is placed in a 4.69-T field.

![](_page_14_Picture_0.jpeg)

$$\frac{N_j}{N_o} = \exp\left(-\frac{2.68 \times 10^8 \times 6.63 \times 10^{-34} \times 4.69}{(2\pi)1.38 \times 10^{-23} \times 293}\right)$$
$$\frac{N_j}{N_o} = \exp\left(-3.28 \times 10^{-5}\right) = 0.999967$$

Thus for exactly  $10^6$  protons in higher energy states there will be  $N_o = 10^6/0.999967 = 1,000,033$  in the lower energy state. This figure corresponds to a 33 ppm excess.

Expanding the right side of the equation (Maclaurin series) gives

$$\frac{N_j}{N_o} = 1 - \frac{\nu h B_0}{2\pi kT}$$

![](_page_14_Picture_5.jpeg)

This shows that the number of excess low energy nuclei is linearly related to the magnetic field strength  $B_0$ .

- sensitivity can be increased by increasing B<sub>o</sub>.

![](_page_15_Picture_0.jpeg)

In a field of 2.34 T the excess population of the lower energy state is only six nuclei per million.

But considering the number of atoms in a practical sample (remember Avogadro's number), the numerical excess in the lower energy state is sufficient for selective and sensitive spectroscopic measurements.

![](_page_15_Figure_3.jpeg)

![](_page_15_Picture_4.jpeg)

![](_page_16_Picture_0.jpeg)

#### Excitation by RF Energy and Subsequent Relaxation

![](_page_16_Figure_2.jpeg)

The net magnetization shifts away from the z-axis and toward the y-axis.

![](_page_16_Picture_4.jpeg)

After irradiation the nuclear spins return to equilibrium in a process called **relaxation**.

A fundamental requirement for absorption spectroscopy is a population imbalance between a lower energy ground state and a higher energy excited state.

 $\begin{array}{l} \textbf{Probability of Absorption} = \textbf{A} \times \textbf{p}(\textbf{v}_{o}) \times (\textbf{\eta}_{+} - \textbf{\eta}_{-}) \\ \left\{ \begin{array}{c} \text{radiation} \\ \text{flux} \end{array} \right\} \left\{ \begin{array}{c} \text{population} \\ \text{imbalance} \end{array} \right\} \end{array}$ 

If the mole fractions of the spin states are equal ( $\eta + = \eta$ -) then the population difference is zero and no absorption will occur.

#### **Relaxation Mechanisms**

**Spin-Lattice Relaxation** (or Longitudinal Relaxation)

![](_page_17_Picture_5.jpeg)

In a liquid phase (solution or neat) that there is close contact of sample molecules with a rapidly shifting crowd of other molecules (Brownian motion).

![](_page_18_Picture_0.jpeg)

The thermal motion of atoms and molecules generates local fluctuating electromagnetic fields, having components that match the Larmor frequency of the nucleus being studied.

These local fields stimulate emission/absorption events that establish spin equilibrium, the excess spin energy being detected as it is released.

#### **Pulsed Fourier Transform Spectroscopy**

![](_page_18_Picture_4.jpeg)

Like each tubular chime in percussion instrument, each structurally distinct set of hydrogens in a molecule has a characteristic resonance frequency.

![](_page_19_Picture_0.jpeg)

To discover the frequency of a chime we can strike it with a mallet and measure the sound emitted. This procedure can be repeated for each chime in the group so that all the characteristic frequencies are identified.

An alternative means of acquiring the same information is to strike all the chimes simultaneously, and to subject the complex collection of frequencies produced to mathematical analysis.

MMMMMMMMM

![](_page_19_Picture_4.jpeg)

![](_page_20_Figure_0.jpeg)

The overlapping resonance signals generated as the excited protons relax are collected by a computer and subjected to a Fourier transform mathematical analysis.

![](_page_20_Figure_2.jpeg)

the relaxation mechanism is a first order process, thus RF signal emitted by the sample decays exponentially. This is called a **free induction decay** (FID) signal.

![](_page_21_Picture_0.jpeg)

#### **Proton NMR Spectroscopy**

## Typical Continuous Wave (CW) Spectrometer

![](_page_21_Figure_3.jpeg)

![](_page_21_Picture_4.jpeg)

![](_page_22_Picture_0.jpeg)

#### Varian 300 MHz NMR instrument

![](_page_22_Picture_2.jpeg)

source of radiofrequency radiation

liquid heliumcooled magnet

![](_page_22_Picture_5.jpeg)

![](_page_23_Picture_0.jpeg)

#### **Procedure**

- 1. A solution of the sample in a uniform 5 mm glass tube is oriented between the poles of a powerful magnet.
- 2. It is spun to average any magnetic field variations, as well as tube imperfections.
- 3. Radio frequency radiation of appropriate energy is broadcast into the sample from an antenna coil (colored red).
- 4. A receiver coil surrounds the sample tube, and emission of absorbed RF energy is monitored by dedicated electronic devices and a computer.

![](_page_23_Picture_6.jpeg)

. An NMR spectrum is acquired by varying or sweeping the magnetic field over a small range while observing the RF signal from the sample.

![](_page_24_Picture_0.jpeg)

As an example, consider a sample of water in a 2.3487 T external magnetic field, irradiated by 100 MHz radiation.

If the magnetic field is smoothly increased to 2.3488 T, the hydrogen nuclei of the water molecules will at some point absorb RF energy and a resonance signal will appear.

![](_page_24_Figure_3.jpeg)

![](_page_24_Picture_4.jpeg)

Since protons all have the same magnetic moment, we might expect all hydrogen atoms to give resonance signals at the same field / frequency values.

![](_page_25_Picture_0.jpeg)

#### Fortunately for chemistry applications, this is not true.

![](_page_25_Figure_2.jpeg)

#### Why should the proton nuclei in different compounds behave differently in the NMR experiment ?

![](_page_25_Picture_4.jpeg)

Since electrons are charged particles, they move in response to the external magnetic field ( $B_0$ ) so as to generate a secondary field that opposes the much stronger applied field.

![](_page_26_Picture_0.jpeg)

![](_page_26_Picture_1.jpeg)

The secondary field **shields** the nucleus from the applied field, so B<sub>o</sub> must be increased in order to achieve resonance (absorption of RF energy.

![](_page_26_Figure_3.jpeg)

![](_page_27_Picture_0.jpeg)

The location of different NMR resonance signals is dependent on both the external magnetic field strength and the RF frequency.

![](_page_27_Figure_2.jpeg)

<sup>1</sup>H NMR Resonance Signals for some Different Compounds

![](_page_27_Picture_4.jpeg)

![](_page_28_Picture_0.jpeg)

An alternative method for characterizing and specifying the location of NMR signals is needed.

### Method

The location of an NMR signal in a spectrum is reported relative to a reference signal from a standard compound added to the sample.

## A reference standard should be

- 1. Chemically unreactive
- 2. Easily removed from the sample after the measurement
- 3. Should give a single sharp NMR signal that does not interfere with the resonances normally observed for organic compounds.

![](_page_28_Picture_8.jpeg)

**Tetramethylsilane**,  $(CH_3)_4Si$ , usually referred to as **TMS**, meets all these characteristics.

![](_page_29_Picture_0.jpeg)

Since the separation of NMR signals is magnetic field dependent, one additional step must be taken in order to provide an unambiguous location unit.

![](_page_29_Figure_2.jpeg)

![](_page_29_Picture_3.jpeg)

The Separation of Resonance Signals (in Hz) Increases with Increasing Field Strength

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To correct these frequency differences for their field dependence, these differences are divided by the spectrometer frequency (100 or 500 MHz in the example)

![](_page_30_Figure_2.jpeg)

![](_page_30_Picture_3.jpeg)

Note that  $v_{ref}$  is the resonant frequency of the reference signal and  $v_{samp}$  is the frequency of the sample signal.

![](_page_31_Picture_0.jpeg)

This operation gives a locator number called the Chemical Shift, having units of parts-per-million (ppm), and designated by the symbol  $\delta_{\bullet}$ 

![](_page_31_Figure_2.jpeg)

![](_page_32_Picture_0.jpeg)

CCl<sub>4</sub> – no interfering H, but poor solvent for many polar compounds and is also toxic.

Deuterium labeled compounds:

deuterium oxide  $(D_2O)$ , chloroform-d  $(DCCl_3)$ , benzene-d<sub>6</sub>  $(C_6D_6)$ , acetone-d<sub>6</sub>  $(CD_3COCD_3)$  and DMSO-d<sub>6</sub>  $(CD_3SOCD_3)$  are now widely used as NMR solvents.

Deuterium is invisible in a spectrometer tuned to protons.

One factor contributing to chemical shift differences in proton resonance is the **inductive effect**.

![](_page_32_Picture_6.jpeg)

The shielding effect in protons with high electron density is large, and a higher external field (Bo) will be needed for the RF energy to excite the nuclear spin.

![](_page_33_Picture_0.jpeg)

#### Example

Since Si is less EN than C, the electron density about the methyl hydrogens in Si(CH<sub>3</sub>)<sub>4</sub> is expected to be greater than the electron density about the methyl hydrogens in C(CH<sub>3</sub>)<sub>4</sub>.

The protons in TMS (with high e density) are said be **shielded**, and lie at higher magnetic field (**upfield**).

Elements that are more electronegative than carbon should exert an opposite effect (reduce the electron density).

![](_page_33_Picture_5.jpeg)

Methyl groups bonded to such elements display lower field (downfield) signals (they are deshielded).

![](_page_34_Picture_0.jpeg)

| Proton Chemical Shifts of Methyl Derivatives |                                    |                                   |                                   |                    |  |  |  |
|--|------------------------------------|-----------------------------------|-----------------------------------|--------------------|--|--|--|
| Compound                                     | (CH <sub>3</sub> ) <sub>4</sub> C  | (CH <sub>3</sub> ) <sub>3</sub> N | (CH <sub>3</sub> ) <sub>2</sub> 0 | CH <sub>3</sub> F  |  |  |  |
| δ  | 0.9                                | 2.1                               | 3.2                               | 4.1                |  |  |  |
| Compound                                     | (CH <sub>3</sub> ) <sub>4</sub> Si | (CH <sub>3</sub> ) <sub>3</sub> P | (CH <sub>3</sub> ) <sub>2</sub> S | CH <sub>3</sub> Cl |  |  |  |
| δ  | 0.0                                | 0.9                               | 2.1                               | 3.0                |  |  |  |

#### Proton Chemical Shifts (ppm)

| Cpd. / Sub.       | X=CI | X=Br | X=I | X=OR | X=SR |
|-------------------|------|------|-----|------|------|
| CH <sub>3</sub> X | 3.0  | 2.7  | 2.1 | 3.1  | 2.1  |
| $CH_2X_2$         | 5.3  | 5.0  | 3.9 | 4.4  | 3.7  |
| CHX <sub>3</sub>  | 7.3  | 6.8  | 4.9 | 5.0  |      |

![](_page_34_Picture_4.jpeg)

Note that chemical shift increases as EN increases.

![](_page_35_Picture_0.jpeg)

The general distribution of proton chemical shifts associated with different functional groups is summarized in the following chart.

## **Proton Chemical Shift Ranges\***

![](_page_35_Figure_3.jpeg)


#### **Signal Strength**

The magnitude of NMR signals is proportional to the molar concentration of the sample.

#### Example

For equal molar amounts of benzene and cyclohexane, the signal from cyclohexane will be twice as intense as that from benzene because cyclohexane has twice as many hydrogens per molecule.

Similarly, for samples incorporating two or more different sets of hydrogen atoms, the ratio of hydrogen atoms in each distinct set can be determined.



# Methods

1) Through horizontal integrator trace (light green) which rises as it crosses each signal by a distance proportional to the signal strength.



2) Through an arbitrary number, selected by the instrument's computer to reflect the signal strength.





FI SFVIFR



















#### **The Influence of Magnetic Field Strength**





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### Influence of Hydrogen Bonding

The OH proton signal is seen at 2.37  $\delta$  in 2-methyl-3-butyne-2-ol, and at 3.87  $\delta$  in 4-hydroxy-4-methyl-2-pentanone.

A six-membered ring intramolecular hydrogen bond in the latter compound is in part responsible for its low field shift.





MDI

#### Hydroxyl Proton Exchange

One can take advantage of rapid OH exchange with the deuterium of heavy water to assign hydroxyl proton signal.

$$R-O-H + D_2O \implies R-O-D + D-O-H$$

This removes the hydroxyl proton from the sample and its resonance signal in the NMR spectrum disappears.



# **ELSEVIE** Hydrogen bonding shifts the resonance signal of a proton to lower field ( higher frequency )

The chemical shift of the hydroxyl hydrogen of an alcohol varies with concentration.





Intermolecular hydrogen bonding increases as concentration increases.



Because of their favored H-bonded dimeric association, the hydroxyl proton of carboxylic acids displays a resonance signal significantly down-field of other functions.





Intramolecular hydrogen bonds, especially those defining a sixmembered ring, generally display a very low-field proton resonance.





This also provides an instructive example of the sensitivity of the NMR experiment to dynamic change.



Hydrogen bonding also influences coupling with adjacent C- H groups.

The 60 MHz proton NMR spectrum of pure (neat) methanol exhibits two signals, as expected.





This interesting change in the NMR spectrum is due to increased stability of hydrogen bonded species at lower temperature



#### <sup>1</sup>H Chemical Shifts of Methanol in Selected Solvents

| Solvent                                     | CDCl <sub>3</sub> | CD <sub>3</sub> COCD <sub>3</sub> | CD <sub>3</sub> SOCD <sub>3</sub> | CD <sub>3</sub> C≡N |  |
|---|-------------------|-----------------------------------|-----------------------------------|---------------------|--|
| CH <sub>3</sub> OH<br>CH <sub>3</sub><br>OH | 3.40<br>1.10      | 3.31<br>3.12                      | 3.16<br>4.01                      | 3.28<br>2.16        |  |







## **п-Electron Functions**

Anomalous observations from chemical shift chart:

- 1. The low field resonance of hydrogens bonded to double bond or aromatic ring carbons.
- 2. the very low field signal from aldehyde hydrogens.
- 3. The hydrogen atom of a terminal alkyne, in contrast, appears at a relatively higher field.

All these anomalous cases seem to involve hydrogens bonded to pi-electron systems.

The field induced pi-electron movement produces strong secondary fields that perturb nearby nuclei.



#### Example:

The pi-electrons associated with a benzene ring

The electron cloud above and below the plane of the ring circulates in reaction to the external field so as to generate an opposing field at the center of the ring and a supporting field at the edge of the ring.





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This kind of spatial variation is called **anisotropy**, and it is common to nonspherical distributions of electrons 52



Regions in which the induced field supports or adds to the external field are said to be **deshielded.** 

Regions in which the induced field opposes the external field are termed **shielded**.

The anisotropy of some important unsaturated functions



δ = 7-8 ppm



δ = 5-7 ppm





δ = 2-3 ppm



δ = 9-10 ppm



Note that the anisotropy about the triple bond nicely accounts for the relatively high field chemical shift of ethynyl hydrogens.

#### **Examples of Anisotropy Influences on Chemical Shift**





The four hydrogen atoms over the face of the ring display resonance signals that are more than two ppm higher field than the two methylene groups bonded to the edge of the ring (a deshielding region).





All the propyl hydrogens are shielded, with the innermost methylene being the most affected.

The negative chemical shifts noted here indicate that the resonances occurs at a higher field than the TMS reference signal.

Anti-aromatic 4n π-electron systems are anisotropic in the opposite sense as their aromatic counterparts.



the Hs of the propyl group are all shifted downfield (deshielded).



16  $\pi$  e (anti-aromatic)

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 $C_{48}H_{24}$  fused benzene ring cycle, named "kekulene" and sometimes called "superbenzene", serves to probe the relative importance of benzenoid versus annulenoid aromaticity.







Н



#### coupled annulene contributor

Α

- If this is more important, the 6 H at the center would be shielded and the 18H at the periphery deshielded; and C-C bonds are of equal lengths.

#### benzene contributor

B

- If this is more important, all the benzene Hs will be deshielded; and bonds at periphery are fixed single and double. 56





The experimental evidence demonstrates clearly that the hexa-benzene ring structure on the right most accurately represents kekulene.



The extremely low field resonance of the inside hydrogens is assigned from similar downfield shifts in model compounds.



#### **Solvent Effects**

|   | CDCI <sub>3</sub> | C <sub>6</sub> D <sub>6</sub> | CD <sub>3</sub> COCD <sub>3</sub> | CD <sub>3</sub> SOCD | CD <sub>3</sub> C≡N | D <sub>2</sub> O |
|---|-------------------|-------------------------------|-----------------------------------|----------------------|---------------------|------------------|
| (CH <sub>3</sub> ) <sub>3</sub> C–O–CH <sub>3</sub><br>C–CH <sub>3</sub><br>O–CH <sub>3</sub>     | 1.19<br>3.22      | 1.07<br>3.04                  | 1.13<br>3.13                      | 1.11<br>3.03         | 1.14<br>3.13        | 1.21<br>3.22     |
| (CH <sub>3</sub> ) <sub>3</sub> C–O–H<br>C–CH <sub>3</sub><br>O–H                                 | 1.26<br>1.65      | 1.05<br>1.55                  | 1.18<br>3.10                      | 1.11<br>4.19         | 1.16<br>2.18        |                  |
| C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub><br>CH <sub>3</sub><br>C <sub>6</sub> H <sub>5</sub> | 2.36<br>7.15-7.20 | 2.11<br>7.00-7.10             | 2.32<br>7.10-7.20                 | 2.30<br>7.10-7.15    | 2.33<br>7.15-7.30   |                  |
| (CH <sub>3</sub> ) <sub>2</sub> C=O   | 2.17              | 1.55                          | 2.09                              | 2.09                 | 2.08                | 2.22             |





For most of the above resonance signals and solvents the changes are minor, being on the order of  $\pm 0.1$  ppm.

Spectra taken in benzene-d6 generally show upfield shifts of most C–H signals (5x in acetone).

- carbonyl groups form weak  $\pi$ - $\pi$  collision complexes with benzene rings, that persist long enough to exert a significant shielding influence on nearby groups.

In the spectrum of tert-butanol in DMSO, the hydroxyl proton is shifted 2.5 ppm down-field (vis-a-vis chloroform).

This is due to strong hydrogen bonding of the alcohol O–H to the sulfoxide oxygen, which not only deshields the hydroxyl proton, but secures it from very repid exchange reactions that prevent the display of spin-spin splitting.





Consider the dichloroethane isomers.



### 1,2-dichloroethane



displays a single resonance signal from the four structurally equivalent hydrogens



#### 1,1-dichloroethane

the two signals from the different hydrogens are split into close groupings of two or more resonances.



The signal splitting in proton spectra is usually small, ranging from fractions of a Hz to as much as 18 Hz, and is designated as J (referred to as the coupling constant).

In the 1,1-dichloroethane example all the coupling constants are 6.0 Hz.





of the proton chemical shift, and the central lines are always stronger than the outer lines.



The line separation is always constant within a given multiplet.

The magnitude of J, usually given in units of Hz, is magnetic field independent.



The splitting patterns shown above display the ideal or "First-Order" arrangement of lines; observed when  $\Delta\delta$  (in Hz) is large compared to J.

If the coupled nuclei have similar chemical shifts, the splitting patterns are distorted (second order behavior).

In fact, signal splitting disappears if the chemical shifts are the same.





ELSEVIENT he spectrum of 1,3-dichloropropane demonstrates that equivalent sets of hydrogens may combine their influence on a second, symmetrically located set.



Note also that the B set triplet lines closest to A are increased, and the A quintet lines nearest B are likewise stronger.





# Causes of signal splitting, and useful information obtained from it.

If an atom under examination is influenced by a nearby nuclear spin (or set of spins), the observed nucleus responds to such influences.

This **spin-coupling** is transmitted through the connecting bonds, and it functions in **both directions**.

Thus, when the perturbing nucleus becomes the observed nucleus, it also exhibits signal splitting with the same J.



For spin-coupling to be observed, the sets of interacting nuclei must be bonded in relatively close proximity (e.g. vicinal and geminal locations), or be oriented in certain optimal and rigid configurations. **ELSE** Some spectroscopists place a number before the symbol J to designate the number of bonds linking the coupled nuclei (colored orange below).





Geminal Hydrogens

Vicinal Hydrogens

a vicinal coupling constant is <sup>3</sup>J and a geminal constant is <sup>2</sup>J.

General rules summarizing important requirements and characteristics for spin 1/2 nuclei :



1. Nuclei having the same chemical shift (called **isochronous**) do not exhibit spin-splitting.



2. Nuclei separated by three or fewer bonds (e.g. vicinal and geminal nuclei) will usually be spin-coupled and will show mutual spin-splitting of the resonance signals (same J's), provided they have different chemical shifts.

Longer-range coupling may be observed in molecules having rigid configurations of atoms.

3. The magnitude of the observed spin-splitting depends on many factors and is given by the coupling constant **J** (units of Hz).

J is the same for both partners in a spin-splitting interaction and is independent of the external magnetic field strength.



 The splitting pattern of a given nucleus (or set of equivalent nuclei) can be predicted by the n+1 rule.



n is the number of neighboring spin-coupled nuclei with the same (or very similar) Js.

#### Example

If there are 2 neighboring, spin-coupled, nuclei the observed signal is a triplet ( 2+1=3 ).





The intensity ratio of the lines is given by the numbers in Pascal's triangle.



Pascal's Triangle



Thus, a doublet has 1:1 or equal intensities, a triplet has an intensity ratio of 1:2:1, a quartet 1:3:3:1, etc.

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If a given nucleus is spin-coupled to two or more sets of neighboring nuclei by different J values, the splitting due to one J set is added to that expected from the other J sets.







#### **Magnitude of Some Typical Coupling Constants**







#### **Coupling constants are independent of the external** magnetic field but dependent on orientation.

In simple, freely rotating alkane units such as  $CH_3CH_2X$  or  $YCH_2CH_2X$ the coupling constant reflects an average of all significant conformers, and usually lies in a range of 6 to 8 Hz.

In rigid structures, the influence of the dihedral orientation of the coupled hydrogens may be studied.









trans-4-tert-butyl-1-chlorocyclohexane


The inductive effect of chlorine shifts the resonance frequency of the red colored hydrogen to a lower field ( $\delta$  ca. 4.0),

In the trans isomer the red hydrogen is in an axial orientation; whereas for the cis isomer it is equatorial.

The values for the dihedral angles and the corresponding coupling constants are related by the **Karplus** equation.





### An Example of Extensive Spin-Splitting

### The 100 MHz 1H nmr spectrum of a $C_3H_5CIO$ compound





This spectrum is obviously complex and not easily interpreted, except for concluding that no olefinic C-H protons are present.



Here it is clear that each of the five hydrogen atoms in the molecule is structurally unique, and is producing a separate signal.

Also, it is clear there is considerable spin coupling of all the hydrogens



To see the coupling patterns more clearly it is necessary to expand and enhance the spectrum in these regions.





Hydrogens A, B & C are clearly different, and are spin-coupled to each other.

Hydrogens B & C are geminally related, whereas A is oriented to B & C in a vicinal manner.



Since  $J_{AB}$  and  $J_{BC}$  are similar, the HB signal is a broad triplet.

ELSEVIE AI though hydrogens D & E might seem identical at first glance, they are diastereotropic, and should therefore have different chemical shifts.

The DE geminal coupling constant is 11.7 Hz, so each of these hydrogens appears as a doublet of doublets.

The splitting of the HA signal is complex and not immediately obvious. The diagram on below shows the consequences of the four operating coupling constants.

H<sub>A</sub>  
$$J_{AB} = J_{AD} = 4.0 \text{ Hz}$$
  
 $J_{AE} = 6.6 \text{ Hz}$   
 $J_{AC} = 2.4 \text{ Hz}$   
3.20 ppm





#### **Spin Decoupling**









## **Some Examples**











# Thank you for your time and attention!