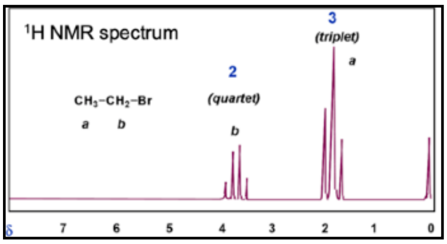


# **NMR Spectroscopy Part 1** (W1)

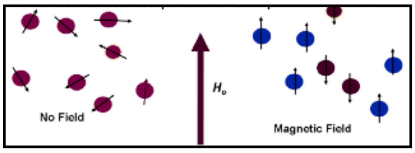
## **Introduction to NMR Spectroscopy (L1)**

### What is NMR Spectroscopy?

- A spectroscopic technique that gives us information about the number and types of atoms in a molecule
  - Hydrogen using $^1$H-NMR spectroscopy
  - Carbons using $^{13}$C-NMR spectroscopy
  - Phosphorus using $^{31}$P-NMR spectroscopy
- Horizontal axis: chemical shift (ppm)
- Vertical axis: relative number of hydrogens in the atom (specific to HNMR)

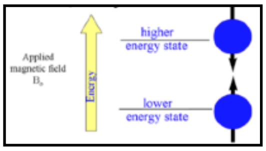
### Nuclear Spins

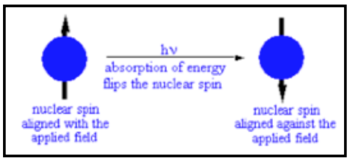
- Nuclear spins in a magnetic field
- A **spinning** charge creates an associated **magnetic field**
- If a nucleus of $^1$H is placed in a **strong external magnetic field** ($B_o$ Tesla, 1T=104 Gauss), its **magnetic moment** will **line up** with the field
- The moment can be **parallel** or **anti-parallel** to the field



### Nuclear Spin

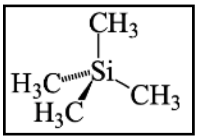
- For $^1$H, $^{31}$P and $^{13}$C, only two orientations are allowed
  - **Lower** energy state: **parallel** to applied magnetic field ($B_o$)
  - **Higher** energy state: **anti-parallel** to applied magnetic field ($B_o$)
- Absorption of **radio-frequency** radiation of the appropriate energy **flips** the **nuclear spin**
  - A proton with nuclear spin aligned with the applied field can absorb energy in radio frequency that will flip the orientation





### Nuclear spins in a magnetic field

- Shielding of nuclei from an applied magnetic field by electrons
- Small induced magnetic field shielding the nucleus -> neighbouring electrons
- Changes in the **distribution of electrons** around a nucleus **affects:**
  - The **local magnetic field** that the **nucleus experiences**
  - The **frequency** at which the **nucleus resonates**
  - The **chemistry** of the molecule at that atom
  - Variation in frequency is known as the **chemical shift** (δ, delta)
    - The **smaller distribution** of **electrons** around nucleus -> **larger chemical shift**
    - Occurs when electronegative atoms are near the nucleus, results in **deshielding**



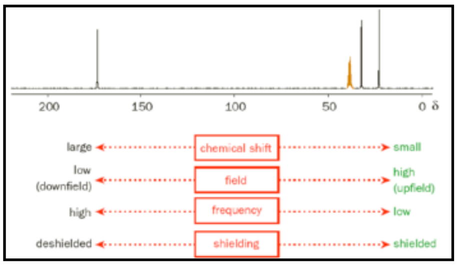
### Reference Sample - TMS

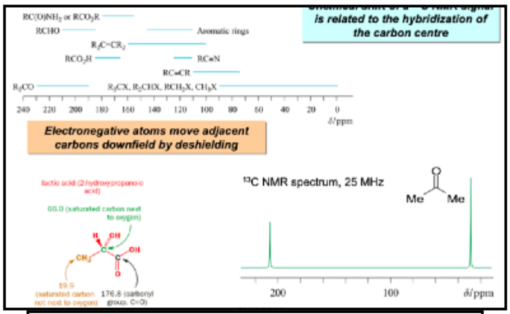
- The sample is dissolved in a solvent, most commonly **$CDCl_3$** or **$D_2O$**, and **tetramethylsilane**, **TMS**, is added (shown on right)
  - D = deuterium
- Chemical shift (δ) = $\nu_{sample}$ (Hz) - $\nu_{TMS}$ (Hz) / **operating frequency** (MHz)
- Example
  - A sample which gives a signal at **54 Hz** when recorded on a **60 MHz** spectrometer will be said to resonate at (54 Hz / 60 MHz) = **δ 0.9 or 0.9ppm**

$$\textbf{Chemical Shift } (\delta) = \frac{\nu_{sample}\text{ (Hz)} - \nu_{TMS}\text{ (Hz)}}{\text{operating frequency (MHz)}}$$

### Ways of describing chemical shift

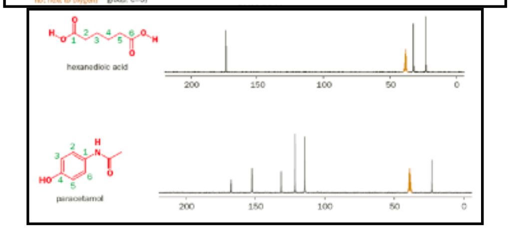
- **Chemical shift**: small on right, large on left
- **Field**: high (upfield) on right and low (downfield) on left
- **Frequency**: low on right and high on left
- **Shielding**: shielded on right and deshielded on left





## CNMR and chemical shift

- Chemical shift of a $^{13}$CNMR signal is related to the hybridisation of the carbon centre
- Electronegative atoms move adjacent carbons downfield by deshielding

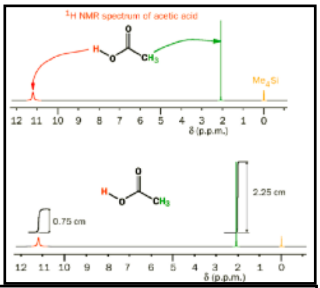


## Assigning peaks

- The brown solvent peaks are from DMSO (Dimethylsulfoxide)
- First identify the solvent peaks

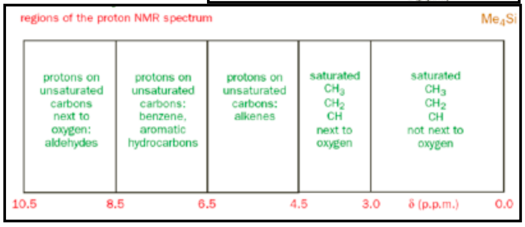
## The differences between carbon and proton NMR

- $^1$H is the major isotope of hydrogen (99.985%), $^{13}$C is a minor isotope (1.1%)
- $^1$HNMR is **quantitative**, area under the peaks tells us the **number of hydrogen nuclei**. Same is **not true** for **$^{13}$CNMR** spectroscopy
- Protons interact **magnetically** (‘**couple**’) to reveal **connectivity structure**. $^{13}$C is **too rare** for this to be seen
- $^1$HNMR shifts gives a **more reliable** indication of local environment
- They are both recorded in the same manner; radio waves used to study the energy level differences of nuclei



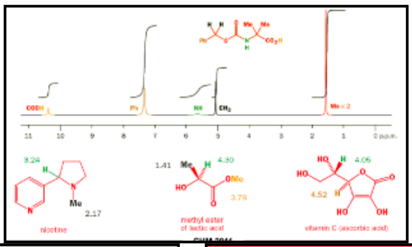
## HNMR Integration

- Integration tells us the number of hydrogen atoms in a peak
- Relative peak area is used

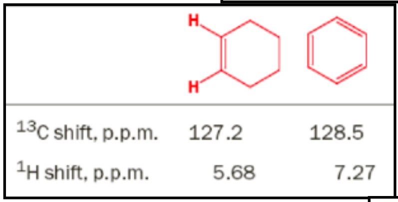


## 1HNMR spectra: chemical environments

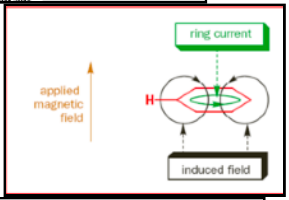
- **0-3**: saturated, CH3, CH2, CH, not next to oxygen
- **3-4.5**: saturated, CH3, CH2, CH, next to oxygen
- **4.5-6.5**: protons on unsaturated carbons: alkenes
- **6.5-8.5**: protons on unsaturated carbons: benzene, aromatic hydrocarbons
- **8.5-10.5**: protons on unsaturated carbons next to oxygen: aldehydes



## Examples of chemical environments:

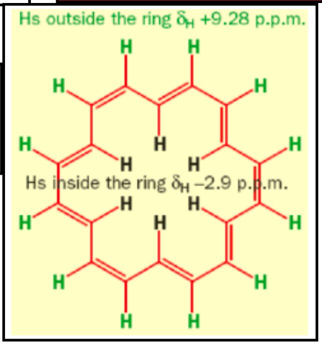


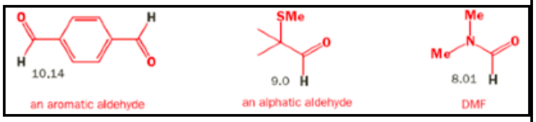
| | | |
|---|---|---|
| $^{13}$C shift, p.p.m. | 127.2 | 128.5 |
| $^1$H shift, p.p.m. | 5.68 | 7.27 |



## The alkene and benzene region

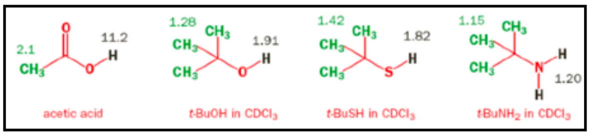
- Benzene has six delocalised pi electrons
- Benzene ring current causes large shifts for aromatic protons
- Hs inside ring show strong shielding by the ring current





## The aldehyde region

- An aromatic aldehyde: 10.14
- An aliphatic aldehyde: 9.0
- DMF: 8.01
- Carbonyl group is one of the most electron withdrawing group
- In DMF, H is less deshielded as amide delocalisation feeds electrons into carbonyl group -> more upfield chemical shift

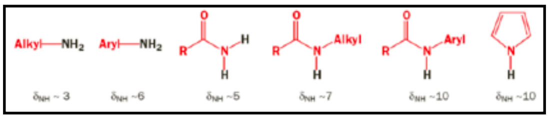


## Protons on heteroatoms

- Acetic acid
- t-Bu**O**H in CDCl3: 1.91
- t-Bu**S**H in CDCl3: 1.82
- t-Bu**N**H2 in CDCl3: 1.20
- Protons directly attached to O, N, or S have variable chemical shifts
  - Less electronegative, less deshielding, smaller chemical shift (δ)

## Chemical shifts of NH protons

- OH and NH2 protons can give broad signals due to exchange processes
- Presence of aryl group increases deshielding of H -> δ increases

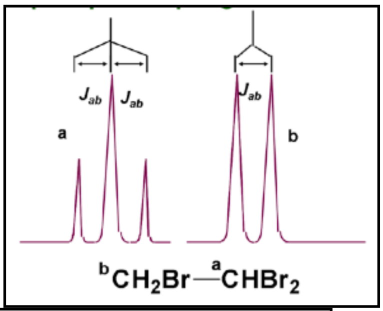


## Coupling in the proton NMR spectrum

- **Nearby** hydrogen nuclei interact and give **multiple peaks**
- The interaction is known as **coupling**

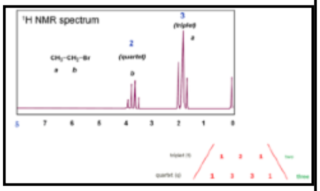
## Nuclear spin-spin coupling

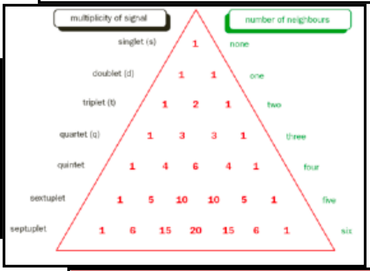
- Chemically equivalent protons show no splitting
  - CClH2: all protons equivalent = no splitting
- A proton with ***n*** equivalent neighbours will be split into ***n+1*** lines with **coupling constant *J:*** Hz equivalent between each split peaks
- Two groups of protons coupled with each other will have the same coupling constant J



## Splitting

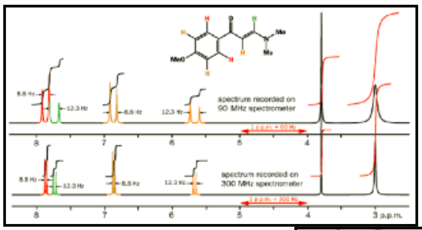
- Multiplicity of signal vs number of neighbours
- The numbers inside the triangle gives the relative intensities of the multiplet signals
- This is all $^3J$ coupling (3 bonds away)

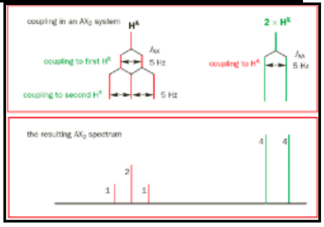




## Coupling constant (J)

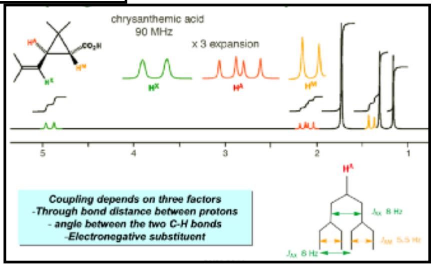
- Coupling constant (J) is the separation between the peaks in hertz (Hz)
- To determine the coupling constant, determine the difference between the lines (ppm) and divide by the operating frequency (MHz)
- When you change machines the chemical shifts (ppm) and coupling constants (Hz) stay the same





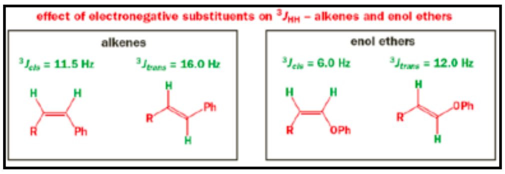
## Coupling between different protons

- Coupling depends on three factors
  - Through bond distance between protons
  - Angle between the two C-H bonds
  - Electronegative substituent
- Possible to have 2 unequivalent environments $^3J$ distances from H: Different splitting pattern

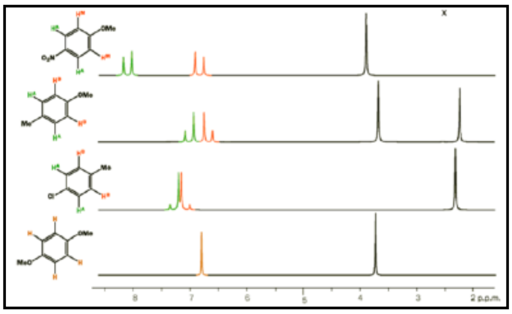


## Coupling between different protons

- Open chain single bond (free rotation): J~ 7Hz
- Benzene ring longer bond (0.5 pi bond) (60 deg angle): J 8-10 Hz
- Cis alkene double bond (60 deg angle): J 10-12 Hz
- Trans alkene double bond (180 deg angle): J 14-18 Hz
- **Cis/trans position and bond angle effects J coupling**

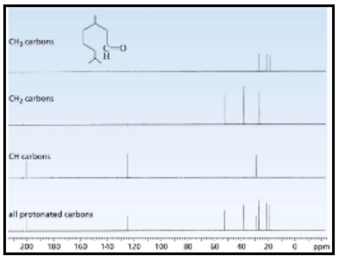


### Examples of coupling between similar protons



### DEPT Method

- The DEPT methods use a complex series of pulses in both the $^1$H and $^{13}$C ranges, with the result that CH3, CH2 and CH signals exhibit different phases
    - Signals for **CH3** and **CH** carbons are recorded as **positive** signals
    - Signals for **CH2** carbons are recorded as **negative** signals
    - **Quaternary** carbons give **no signal** in the DEPT method



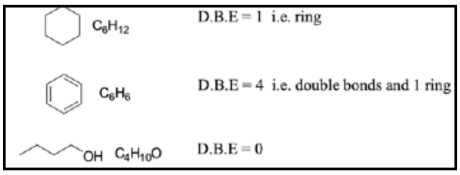
### DEPT Experiment:

### Summary

- Recognise and interpret a NMR spectrum
    - Identify the difference between $^1$H, $^{13}$C (DEPT) NMR spectra
- Interpet NMR spectra of molecules with one environment and molecules with more than one environment
    - Understand how NMR can be used to ‘count’ the number of environments
- Interpret a $^1$H NMR spectrum, understand and apply the key features of spectroscopy, chemical shift and the number of protons
    - Shielding - influence on chemical shift, integration - number of equivalent hydrogens

### The Chemical Detective

- Deducing the number of Double Bond Equivalents
- DBE = double bond equivalents
- C6H12: DBE = 1 i.e. ring
- C6H6: DBE = 4 i.e. 3 double bonds 1 ring
- C4H10O: DBE = 0
- DBE is also known as the index of hydrogen deficiency



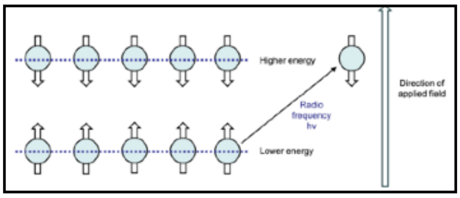
## Multi-Nuclear NMR Spectroscopy (L2)

### Nuclear Magnetic Resonance (NMR) Recap

- Spectroscopic technique probing nuclei in a magnetic field
- Nuclei can be probed if they have a non-zero nuclear spin quantum number, I (uppercase i)
- Nuclei are affected by their chemical environment (change in chemical shift) and by nearby nuclei (splitting due to spin-spin coupling by local field)
- Information about the position of the signal and splitting enables us to work out the position of the atom in the molecule

### NMR 101

- A spinning charge (e.g. nucleus) creates an associated magnetic field. In the absence of an applied external field, these are **randomly** oriented
- In the presence of a magnetic field the magnetic moments become **aligned** or **anti-aligned** (in the case of a simple I=1/2 nucleus, e.g. $^1$H, $^{13}$C, $^{31}$P, $^{19}$F) in **equal amounts**
    - Half aligned half anti-aligned
- Energy in the radio frequency range is used to “flip the nuclear spin” (for I = 1/2 nuclei). This should be thought of as changing to a higher energy level
    - Lower energy = alligned. Higher energy anti-alligned. Aligned becomes anti-aligned when radio frequency absorbed

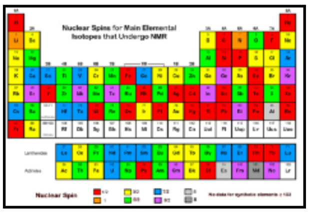


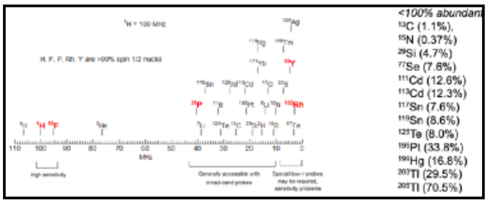
- Upon relaxation of the excited nuclei, we detect the emitted radio frequency signal and this is what makes the recorded NMR spectrum
- Although we think of “spins” aligned with or against a magnetic field for I = 1/2 nuclei, you should think about this as two allowed energy levels
- These allowed levels are in integer steps between -I and +I
- For I = 1/2 this means values of +1/2 and -1/2 (hence we think of with (+) and against (-) the field

- For I = 3/2 there are four allowed values (-3/2, -1/2, +1/2, +3/2) which are equally populated in an applied field. We will look at this next week

## Multinuclear NMR - study of other NMR active elements (P, Hg, F, N)

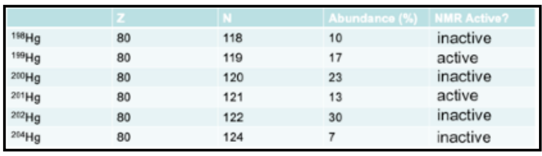
- Every element has a ground state nuclear spin quantum number (I) with a value of x/2 (where x is an integer)
- If an isotope has I = 0, it s NMR **inactive**
- $^{13}C$, $^{1}H$, $^{31}P$ are all I=1/2
- Limitations:
  - Relaxation times are important for many nuclei (Expert users needed)
  - Very large chemical shift ranges for many nuclei make observation difficult. Can indicate oxidation state
  - Problems with low natural abundance e.g. $^{17}O$, $^{15}N$
  - Are the compounds stable in solution?
  - Choosing reference compounds can be difficult e.g. secondary references and/or external references
- Isotopes with I = 1/2 are the most commonly studied by NMR due to the simpler analysis, especially if the active nucleus is 100% abundant (i.e. $^{1}H$)
- Less abundant nuclei need long collection times or isotopic enrichment





## Multinuclear NMR

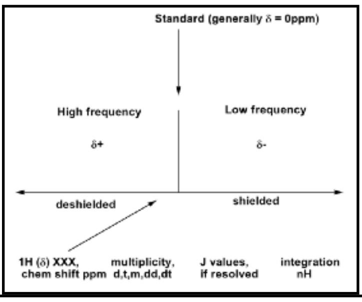
- The nuclear spin quantum number can be predicted (to some extent) from the relative numbers of nucleons
  - Protons = **even** and neutrons = **even**: **I=0 (NMR inactive)**
  - Protons = **odd** and neutrons = **odd**: **I=integer**
  - Other combination: **I=1/2 integer** (1/2,3/2,5/2,7/2)
- Example: $^{12}C$ has 6 protons and 6 neutrons, therefore not NMR active because I=0
- Lots of NMR active isotopes for a given element can make NMR challenging



| | Z | N | Abundance (%) | NMR Active? |
|---|---|---|---|---|
| $^{198}Hg$ | 80 | 118 | 10 | inactive |
| $^{199}Hg$ | 80 | 119 | 17 | active |
| $^{200}Hg$ | 80 | 120 | 23 | inactive |
| $^{201}Hg$ | 80 | 121 | 13 | active |
| $^{202}Hg$ | 80 | 122 | 30 | inactive |
| $^{204}Hg$ | 80 | 124 | 7 | inactive |

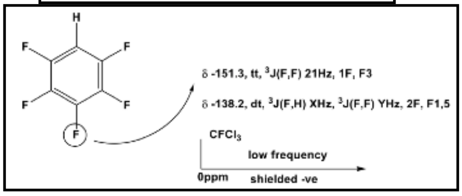
## NMR and Structural Information

- Structural information can be provided by analysing features of the NMR spectrum
  - **Chemical shift** values - where is the signal?
  - **Multiplicity** - is the signal split?
  - **Coupling constants** - what is magnitude of any splitting?
  - **Integration** (+/-10%) - what is the ratio of areas under signals?



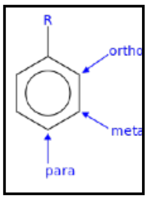
## Reporting 1HNMR Spectra

- Position, multiplicity, coupling, integration, assignment
- e.g. CH3CH2OH: **1.20 ppm, t, $^{3}$J(H,H) 7Hz, 3H, Me**
- Reporting multinuclear NMR follows the same pattern
- Each nucleus has a separate reference compound
- E.g. 199Hg uses external HgMe2. 31P uses external 85% H3PO4.
  - External means that it is not in the tube with the sample



## Integration

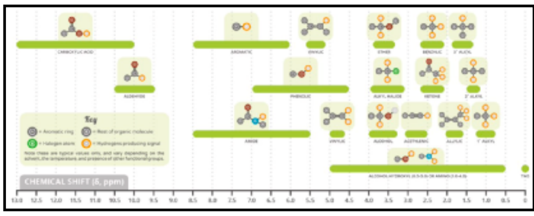
- For a pure compound, integration of the signals gives the relative amounts of different types of the same nucleus
- Example: C6F5H has a 19F NMR spectrum with a 2:1:2 integration for the 3 F resonances, assigned to 2x ortho-F, 1x para-F, 2 x meta-F
- Non-integer integrations can indicate impurities
- Integration only gives relative amounts of the different types of nucleus. 1:2 could be 2:4 or 3:6
- Absolute numbers can be determined by addition of a known amount of a standard



## Chemical shifts

- Position of NMR signal gives an indication of the chemical environment. Easy for nuclei such as 1H for which there are established tables

- The same is true for other relatively common nuclei (19F, 31P) but others are much less well documented, especially metals
- For multinuclear NMR it is normal to compare your experimental data with data for model compounds (closely related compound(s) of known purity). Similar compounds should show similar chemical shift values
- Very large chemical shifts ranges exist for some nuclei (e.g., $^{119}$Hg, $^{195}$Pt) so you need to know where to look! And for **metals**, **oxidation** state can result in **different ranges**



Chemical shifts

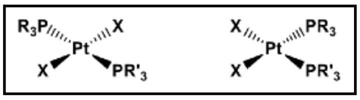
- Reported relative to a standard as ppm, so independent of instrument field strength

Coupling and Multiplicity

- The NMR signal for a given atom is affected by the **magnetic environment** provided by **neighbouring atoms**
- This **effect** gets **weaker** with **distance**, typically seen for atoms 2,3, or 4 bonds away
- Referred to as $^{x}$**J coupling**, where x=number of bonds away
- To be more specific, $^{x}J_{AB}$ where A and B define the atoms involved

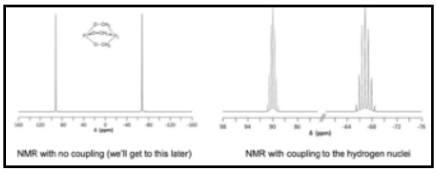
Coupling and Multiplicity - Example

- Given suitable standard compounds, the magnitude of J can be used to establish coordination number stereochemistry, even the donor atoms trans to a particular ligand
- **Trans** has a **larger coupling** than **cis**
- e.g. HPt(PR3)3 the P coupling to H in the $^{1}$HNMR spectrum is greater for the trans phosphine
- However, electronic affects can influence the coupling to Pt due to **trans effects** (the observation that certain ligands **increase the rate of ligand substitution** when positioned **trans** to the **departing ligand**) , so can lessen this coupling
- Makes cis and trans non-equivalent



Coupling and Multiplicity - Example

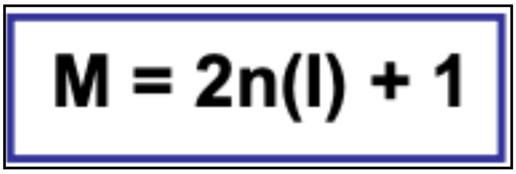
- $^{31}$P NMR of the compound shown. Which signal is which P?



NMR with no coupling (we'll get to this later)
NMR with coupling to the hydrogen nuclei

Coupling and Multiplicity

- For organic molecules and $^{1}$HNMR, $^{3}$J coupling is most common, e.g. 2-butanol
- Inorganic and organometallic multinuclear NMR can be more complex
- Closer atoms give stronger coupling
- You would have been taught that the multiplicity of the resonance for 1H is given by:
  - M = n + 1
  - where: M is the multiplicity of the resonance, n is the number of coupled atoms
- The general form of this equation is:
  - **M = 2n(I) + 1**
  - Where: **I** is the nuclear spin quantum number, **n** is the number of coupled atoms

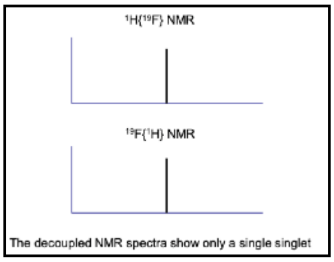


$$M = 2n(I) + 1$$

Decoupling

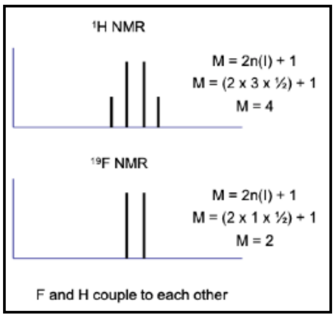
- It is possible, with appropriate programming of the spectrometer, to obtain a spectrum in which heteronuclei show **no coupling** in the spectrum
- This is called a **decoupled spectrum** and can be useful to simplify spectra to aid understanding
- We use the nomenclature **X{Y}** decoupled to mean the spectrum of X which shows no coupling from Y
- E.g. **$^{13}$C{$^{1}$H}** is the standard carbon spectra that we collect in which we see no effects from coupling to hydrogen

Multiplicity - Decoupled
- Coupling to other nuclei is useful for discerning additional structural information
- Consider trifluoromethane ($CF_3H$)
    - $^1H$: I = 1/2 (100% abundance)
    - $^{19}F$: I = 1/2 (100% abundance)
    - $^{13}C$: I = 1/2 (1.1% abundance) <— very low %, in practise we ignore it



The decoupled NMR spectra show only a single singlet

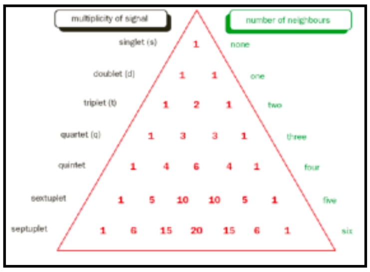
Multiplicity - Coupled
- Coupling to other nuclei is useful for discerning additional structural information
- Consider trifluoromethane ($CF_3H$)
    - $^1H$: I = 1/2 (100% abundance)
    - $^{19}F$: I = 1/2 (100% abundance)
    - $^{13}C$: I = 1/2 (1.1% abundance) <— very low %, in practise we ignore it



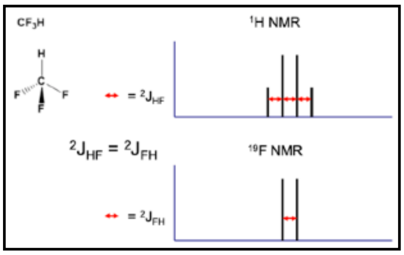
F and H couple to each other

Multiplicity - why is splitting observed?
- The combination of possible spin states for the neighbouring atoms results in different microenvironment of the nucleus being probed
- For CF3H, 19FNMR will show double (M=2n(I)+1 = 2*1*1/2 + 1 = 2)
    - There is one hydrogen atom adjacent to the equivalent fluorine atoms, with an equal probability of having spin values of +1/2 and -1/2. This gives the **two combinations/ environments** that give the two signals in the splitting
- For CF3H, 1HNMR will show quartet (M = 2*3*1/2+1 = 4)
    - There are 3 fluorine atoms adjacent to the hydrogen atoms, each with an equal probability of having spin values of +1/2 or -1/2. This gives **four combinations** of possibilities with statistical, non-equal probabilities of occurring

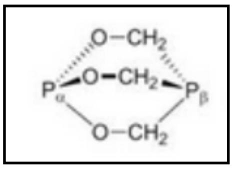
Multiplicity - Intensities
- Relative intensities in multiplets are given by Pascal's triangle (binomial coefficients) for nuclei with I=1/2. It is more complicated for higher values of I
- In Pascal's triangle each row is made up from the sums of the numbers on the previous row

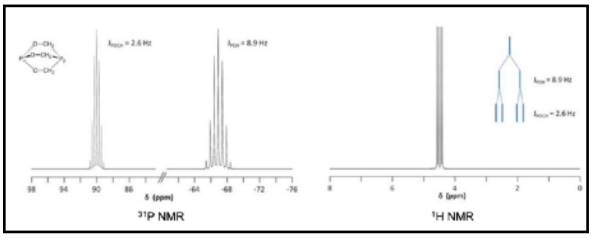


Multiplicity - Coupling Constants
- Coupling constants are measured (in Hz) between any two parts of a peak that comprises multiple signals
- Coupling constants can be measured between any two adjacent parts of the split signal
- Written $^xJ_{AB}$ where X=number of bonds and A and B are the atoms
- The effect of the atoms on each other is equal, hence we can determine which signals result from neighbouring atoms
- $^2J_{HF} = {}^2J_{FH}$

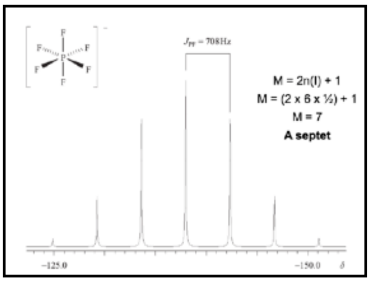


Coupling and Multiplicity - Example
- Coupling between nuclei is the same regardless of which you are measuring
- Right: Doublet of doublets ($^3J$ splitting then $^4J$ splitting)
- Left: 1 septet ($^4J$ downfield) 1 septet ($^3J$ upfield)





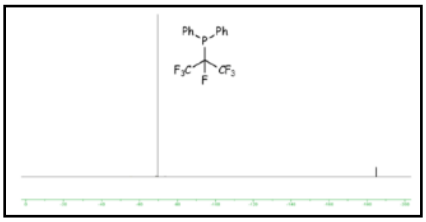
Multiplicity - An example
- The PF6- anion
    - $^{19}F$: I = 1/2 (100%)
    - $^{31}P$: I = 1/2 (100%)
- **$^{31}$P NMR spectrum** will consist of a (7-line) **septet** with intensities
    - 1:6:15:20:15:6:1 (shown on right). M = 2x6x1/2 + 1 = 7



- $^{19}$**F spectrum** will be a **doublet** (coupling to a single P atom)

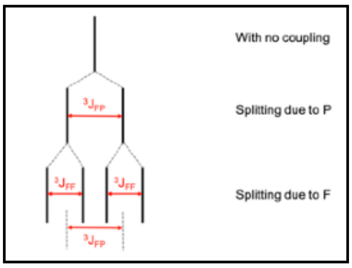
### Multiplicity - A question

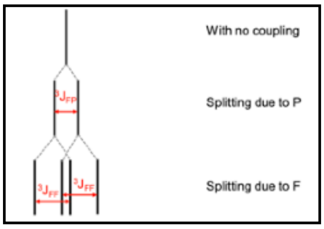
- $^{19}$FNMR is shown for the molecule below, with two signals for the two chemical environments. Which is which and what splitting would you expect?



### Multiplicity - Sequential Splitting

- If a nucleus is coupled to two or more different nuclei then the splitting is sequential
- Coupling constants may not be as obvious if signals overlap. Need to check the other nucleus or atoms to find proper values
- For lone F (left):
  - First no coupling
  - Then splitting due to P ($^2J_{FP}$)
  - Then splitting due to F ($^3J_{FF}$)
- For F3C (right):
  - First no coupling
  - Then splitting due to P ($^3J_{FP}$)
  - Then splitting due to F ($^3J_{FF}$)

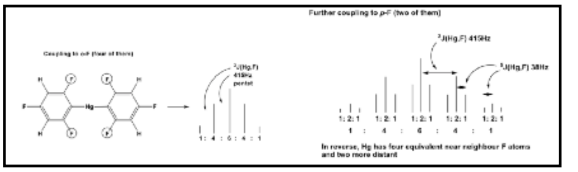




# NMR Spectroscopy Part 2 (W2)

## Multiplicity (L1)

### Multiplicity - Coupling to Distant Atoms

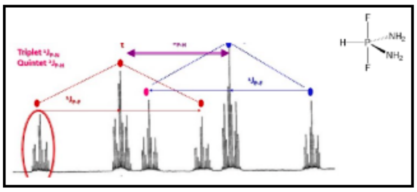


- If overlapping can be disentangled, and the resolution of the spectrum is good, the number of more distant atoms can be established
- e.g. $^{199}$Hg{$^{1}$H} NMR of bis(2,4,6-trifluorophenyl)mercury
- Pentet of triplets
- Initially coupling to ortho-F (four of them so pent), then further coupling to para-F (two of them so triplet via $^{5}$J coupling)
- Basically, Hg has four equivalent near neighbour F atoms and two more distant

### Multiplicity - More Complicated Coupling #1

- Consider PF2N(NH2)2 enrichiched with $^{15}$N, all nuclei are 100% I=1/2. What would the $^{31}$P NMR look like?
- A mess! But one we can rationalise

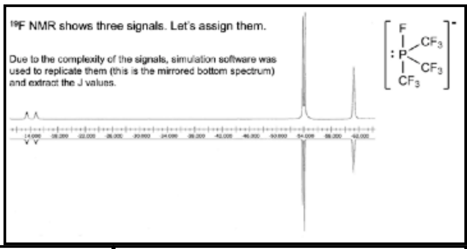
1. $^{1}J_{PH}$ = doublet from 1H
2. $^{1}J_{PF}$ = triplet from 2 F's
3. $^{1}J_{PN}$ = triplet as two N's
4. $^{2}J_{PH}$ = quintet from 4 H's



### Multiplicity - More Complicated Coupling #1

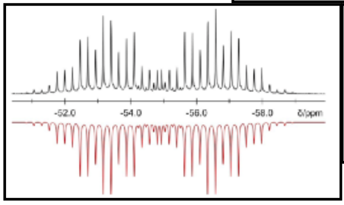
- Strongest splitting is $^{1}J_{PH}$ with the hydride ($^{1}$H) to give a doublet (largest J constant)
- 2 fluorine atoms ($^{19}$F) cause triplet splitting ($^{1}J_{PF}$)
- Coupling to 2 $^{15}$N nuclei give further triplets ($^{1}J_{PN}$)
- Finally, 4 equivalent $^{1}$H nuclei forms quintets ($^{2}J_{PH}$)
- **OVERALL**: **A doublet of triplets of triplets of quintets (90 lines!)**

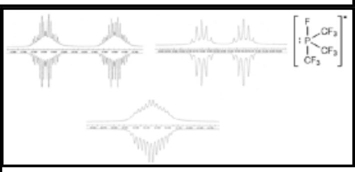
### Multiplicity - More Complicated Coupling #2


$^{19}$F NMR shows three signals. Let's assign them.

Due to the complexity of the signals, simulation software was used to replicate them (this is the mirrored bottom spectrum) and extract the J values.

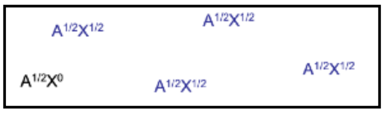
- Here is an example from a recent publication, where $^{31}$P and $^{19}$F NMR were essential to working out the reactivity and structure
- The compound below is phosphoranide (tetracoordinated P with formal negative charge)
- $^{19}$F NMR shows three signals. Lets assign them
- Due to the complexity of the signals, simulation software was used to replicate them (this is the mirrored bottom spectrum) and extract the J values





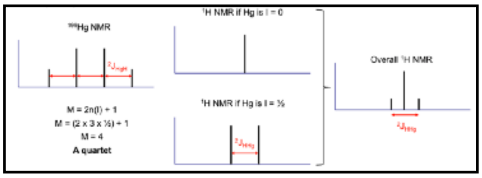
### Nuclei < 100% Abundant

- The situation can be more complicated in systems where there are multiple natural isotopes, i.e. where one active isotope does not have 100% abundance
- Consider a hypothetical molecule **AX** where A = 100%, spin=1/2; **X** = <100% spin 1/2
- **X** spectrum not affected (split by 100%, I=1/2 nuclei), but the **A** spectrum is more complex as there will only sometimes be splitting with X
- Example:
  - If X was 80% I=1/2, 20% I=0 then the distribution of molecules would look like this… 20% of the time it will be X with spin=0 -> no NMR activity
  - A is 100% I=1/2
  - And we would expect the A NMR to be a superposition of the two types of molecules



### Nuclei < 100% Abundant - Example

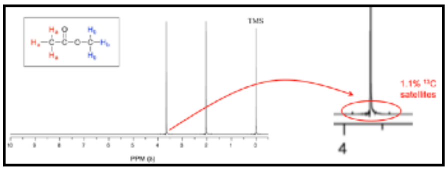
- The example is methyl mercury chloride, MeHgCl
- $^{199}$Hg (16.8%) I=1/2 (other isotopes have spin 0 or ignore)
- $^{1}$H (100%) I=1/2
- $^{199}$Hg NMR will be unchanged: a quartet
- For $^{1}$HNMR if Hg is I=0 then singlet, if Hg is I=1/2 then doublet



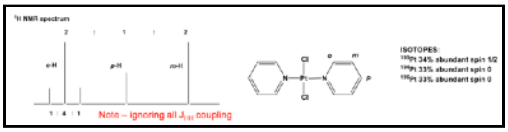
with $^2J_{HHg}$ coupling
- Overall $^1$HNMR will be triplet: combination of both singlet and doublet

<u>Nuclei < 100% Abundant - Example</u>
- Thing to note about the $^1$H NMR of MeHgC
  - The **ratio** of **integrals** of the peaks reflects the **abundance** of isotopes (not a 1:3:1 triplet)
  - The splitting between the “satellite peaks” is the $^2$J coupling (they are a doublet)
  - Confirmation that this is $^2$J coupling comes from comparison with $^{199}$Hg spectrum

<u>Nuclei < 100% Abundant - $^{13}$C</u>
- You can see splitting to non-100% abundant nuclei in $^1$H NMR of organics, but this is typically ignored
- Due to 1.1% $^{13}$C satellites

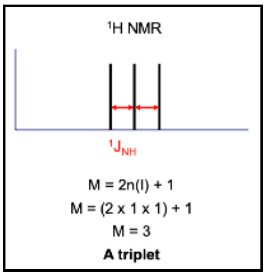


<u>Nuclei < 100% Abundant</u>
- Sometimes the presence of satellites simply helps to confirm connectivity
- Ratio of spin active Pt isotopes (I=1/2) to non active (I=0) is 1:2, but observed as 1:4 in the spectrum because the resonance is a 1:1 doublet superimposed over a singlet (i.e. 16:67:16)
- Observations of Pt satellites on the ortho-H signal establishes that the pyridine is bound to Pt
  - $^3$J(Pt,H) ~34 Hz

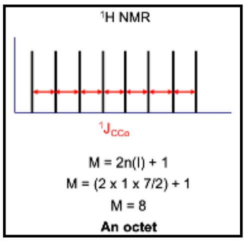


<u>Quadrupolar Nuclei (I>1/2)</u>
- Nuclei with I > 1/2 are called **quadrupolar** nuclei
- NMR of these nuclei can be a bit trickier, especially ratios of peaks within multiplets
- Common quadrupolar nuclei:
- D ($^2$H) I = 1; $^6$Li I=1; $^{14}$N I=1; $^{11}$B I=3/2; $^{59}$Co I=7/2
- Although trickier in concept, the standard rule for calculating coupling and multiplets still holds true, although Pascal’s triangle no longer works
- **M = 2n(I) + 1**

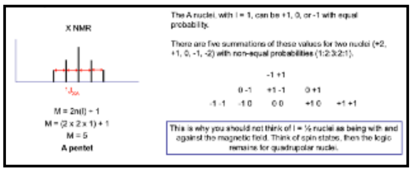
<u>Quadrupolar Nuclei (I>1/2) - Example 1</u>
- The $^1$HNMR of ammonia, containing 100% $^{14}$N (I=1) is a peak with multiplicity of 3, a triplet
- The relative intensities of the peaks within the signal do **not** follow Pascal’s triangle for quadrupolar nuclei
- $^1$H is coupled to $^{14}$N with the splitting due to the spin states that the nitrogen nucleus can adopt
- These states are in intervals of 1 between +I and -I
- So, for I=1, 14N can be **+1, 0, -1** with **equal probability**
- Hence, **three equivalent peaks** in the signal



<u>Quadrupolar Nuclei (I>1/2) - Example 2</u>
- The $^{13}$C NMR of [Co(CO)4] containing 100% $^{59}$Co (I=7/2) is a peak with a multiplicity of 8, an octet
- Remember, spin states are in intervals of 1 between +I and -I
- For **I= 7/2**, $^{59}$Co can be: **+7/2, +5/2, +3/2, +1/2, -1/2, -3/2, -5/2 or -7/2** with equal probability
- Hence, **8 equivalent peaks in the signal**



<u>Quadrupolar Nuclei (I>1/2) - Example 3</u>
- An imaginary compound A-X-A, where A has I=1 and X has I=1/2. What is the X NMR spectrum
- The A nuclei, with I=1, can be **+1, 0, -1** with **equal** probabilities
- There are **five summations** of these values for **two nuclei** (+2, +1, 0,



The A nuclei, with I = 1, can be +1, 0, or -1 with equal probability.

There are five summations of these values for two nuclei (+2, +1, 0, -1, -2) with non-equal probabilities (1:2:3:2:1).

This is why you should not think of I = ½ nuclei as being with and against the magnetic field. Think of spin states, then the logic remains for quadrupolar nuclei.