Topic 11Measurement and Data Processing

Lesson 1

11.1 Uncertainties and Errors in Measurements and Results

Qualitative vs. Quantitative

- Qualitative data includes all non-numerical information obtained from observations not from measurement. (Chemical and Physical Properties)
  - Solubility
  - Melting Point

- Quantitative data are obtained from measurements, and are always associated with random errors/uncertainties, determined by the apparatus, and by human limitations such as reaction times
  - Amount
  - Concentration

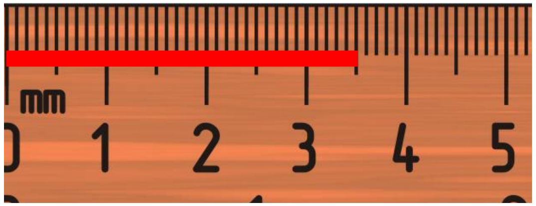
Qualitative vs. Quantitative

What Is An Uncertainty?

- No measuring instrument (be it a plastic ruler or the world's most accurate thermometer) is perfectly accurate

- When you make any measurement, there always is some uncertainty as to the exact value.

- For example:
  The ruler says this red line is 3.5 cm long
  Due to imperfections in the design and manufacturing of the ruler, I can't be sure that it is exactly 3.500 cm, just something close to that, p erhaps 3.492. or 3.521



Uncertainty in Measurements

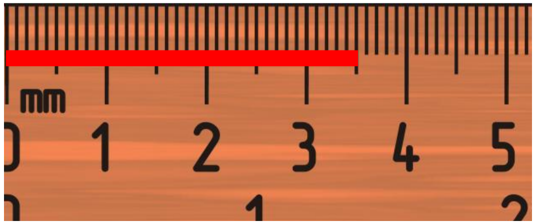
- Data involving exact numbers-the values are known exactly and there is no uncertainty
  - A dozen donuts
  - 8 students

- Data involving inexact numbers-there is a degree of uncertainty
  - Height of a student
  - Temperature of a student

Measuring Uncertainties

- Most equipment manufacturers know the level of uncertainty in their instruments, and will tell you.

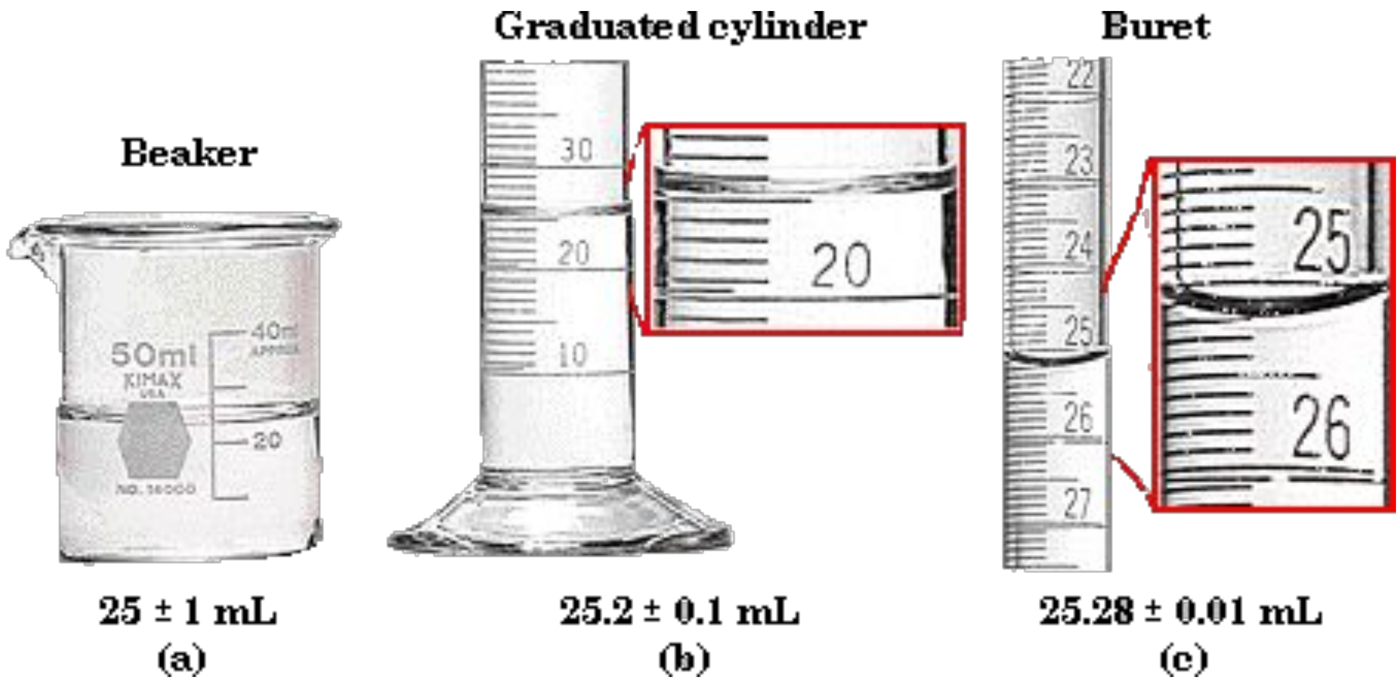
- For example:
  - The instruction manual that came with my ruler tells me it is accurate to +/- 0.05 cm.
  - This means my 3.5 cm line is actually anywhere between 3.45 and 3.55 cm long
  - **Importantly:** we have no way of knowing where in this range the actual length is, unless we use a more accurate ruler



How Big Are The Uncertainties?

- Most good apparatus will have the uncertainty written on it, so make a note of it.
- Where this is not the case, use half the smallest division:
  - For example: if a balance can measure to two decimal places, the uncertainty would by +/- 0.005 g
- When manually measuring time, you should round to the nearest whole second, and decide the uncertainty based on the nature of your measurement.

Analogue Instruments



	Beaker	Graduated Cylinder	Volumetric Flask
10 mL	$4.44	$13.77	$29.53
250 mL	$3.86	$33.21	$60.55

Balances

Top Pan Balance: measure

in a school lab setting

Analytical Balance: measure mass
to a high degree of precision.
Shutters allow the reduction
of air flow and dust collection

Balance Precision

Balance reads to 1 place = $118.95

Balance reads to 0.1 place = $159.95

Balance reads to 0.01 place = $277.90

Balance reads to 0.001 place = $407.40

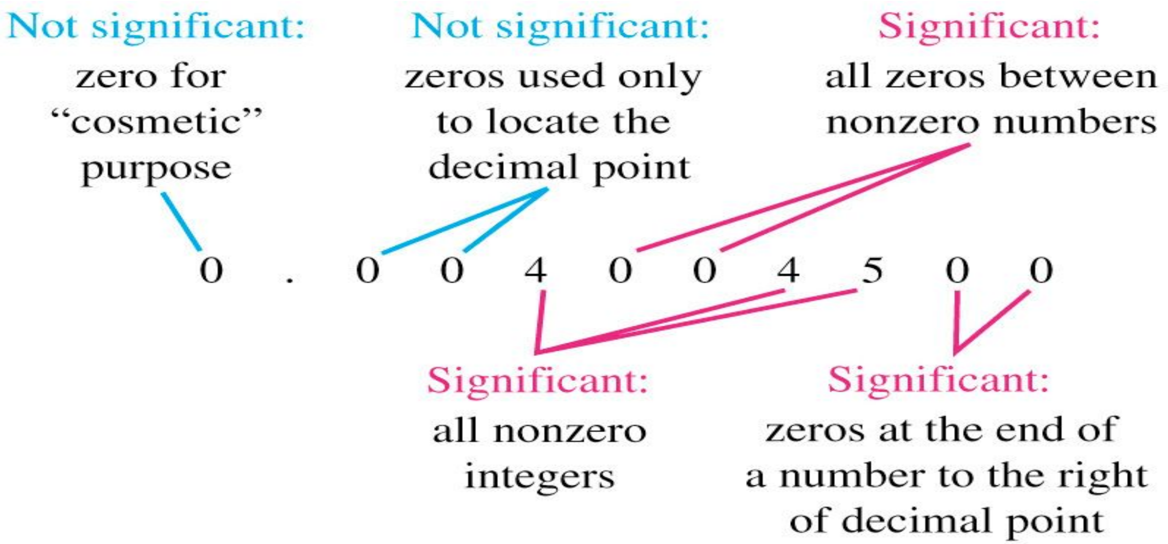
Precision vs Accuracy

- Closeness of agreement between independent test results obtained by applying the experimental procedure under stipulated conditions
- The smaller the random part of the experimental errors, the more precise the procedure

- Closeness of the agreement between the result of a measurement and the true value of the measurand-the particular quantity to be measured

Significant Figures

- The number of digits reflecting the precision of a given measurement
- The greater the certainty the greater the certainty about the numerical value of the measured or calculated quantity

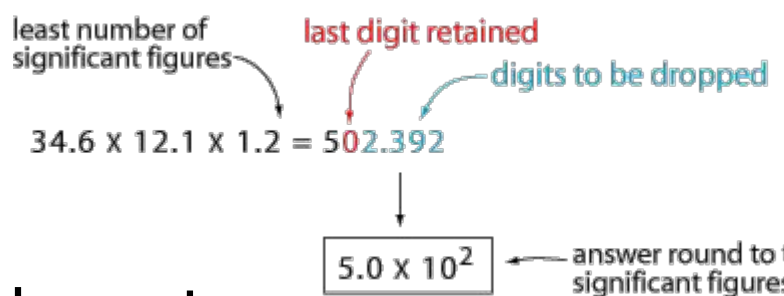


Scientific Notation

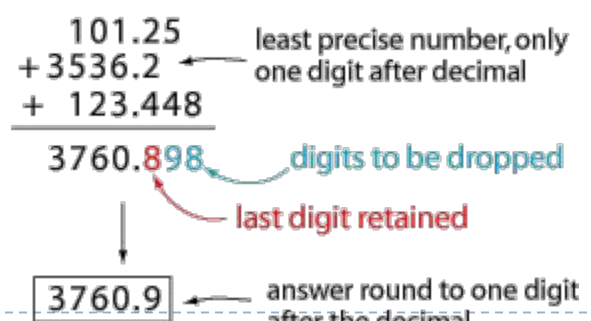
Measurement	Scientific Notation	# of Sig Figs
135.680g	1.35680×10^2g	6
0.00620dm^3	6.20×10^{-3}dm^3	3
300kg	3×10^2kg	1

Scientific Notation

- Multiplying or Dividing
  - The result should be expressed based on the measurement with the smallest number of significant figures



- Adding or Subtracting
  - The result should be expressed based on the measurement with the smallest number of decimal places



Experimental Errors

Systematic Errors

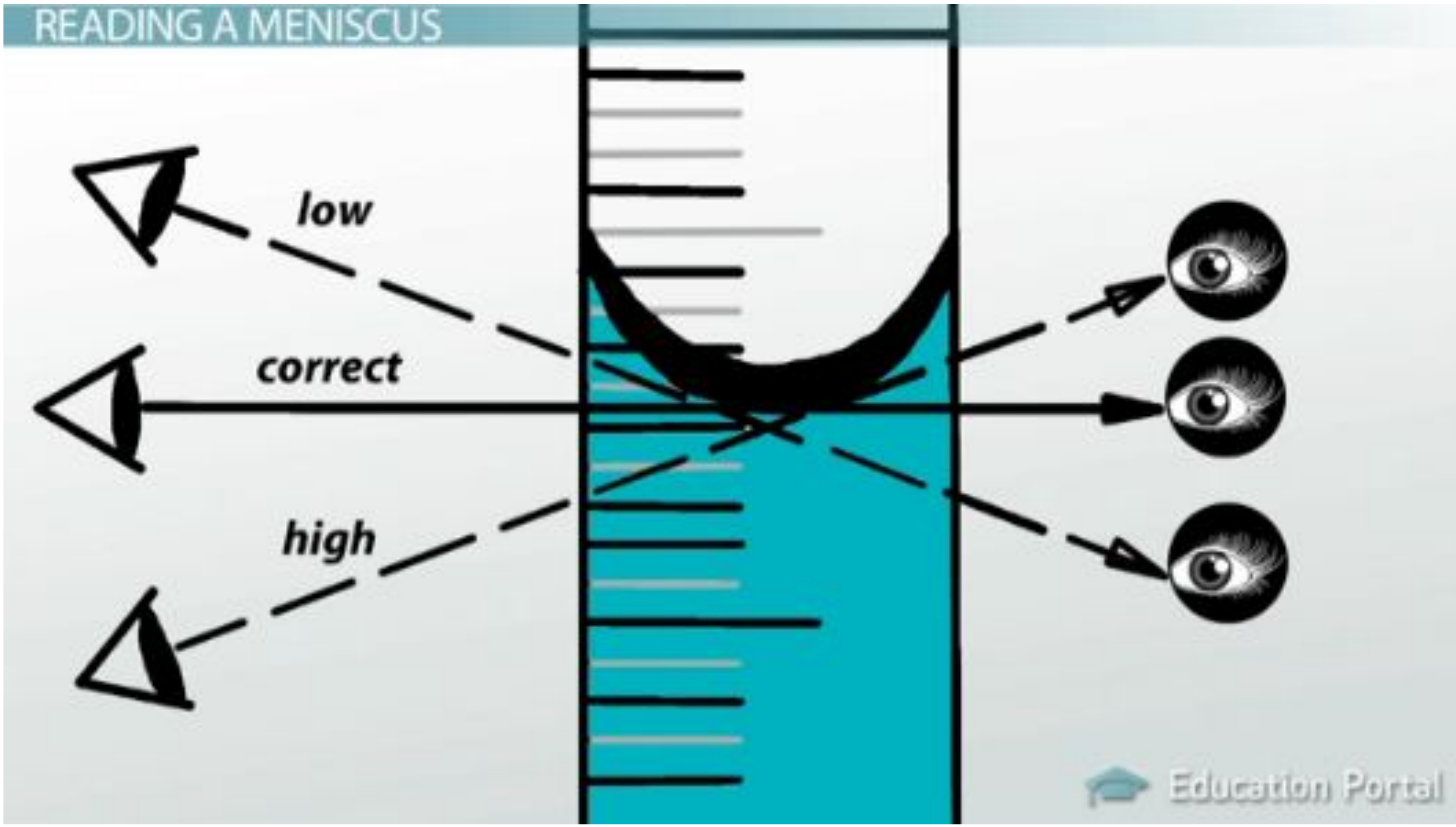
- Associated with flaw in the actual experimental design or with the instrumentation used
- Imply that the measured quantity will always be greater or less than the true value
- Types of systematic errors:
  - Instrumentation errors
  - Experimental methodology
  - Personal errors

Experimental Errors

Systematic Errors

- Faulty gas syringes that have associated leakage
  - Instrumentation Error
- Poorly insulated calorimeter in a thermochemistry experiment
  - Experimental Methodology Error
- The exact color of a solution at its end point
  - Personal Error
- Systematic error can be reduced by adopting greater care to the experimental design
- Such errors are consistent and can be detected and ultimately corrected
- Systematic errors will affect accuracy of results

Systematic Error



Experimental Errors

Random Errors

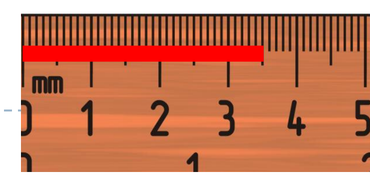
- Occur because of uncontrolled variables in an experiment and therefore cannot be eliminated
- Can be reduced by repeating measurements
- Affect the precision of the results
- Examples
  - Estimating quantity which lies between marked graduations of a particular instrument (burette, graduated cylinder)
  - Not being able to read an instrument due to fluctuations in readings (temperature, airflow)
  - Reaction time

Absolute and Relative Uncertainty

- Absolute uncertainty is the actual size of the uncertainty in the units used to measure it.
- This is what the previous slide referred to
- In our ruler example, the absolute uncertainty is

  +/- 0.05 cm
- To minimise absolute uncertainty, you should use the most accurate equipment possible.

- This is the size of the uncertainty relative to the value measured, and is usually expressed as a percentage
- Relative uncertainty can be calculated by dividing the absolute uncertainty by the measured value and multiplying by 100
- In our ruler example, the relative uncertainty is
  - 0.05 / 3.5 x 100 = 1.4%
- To minimise relative uncertainty, you should aim to make bigger measurements



How do uncertainties affect my calculations?

- If the numbers you are putting into a calculation are uncertain, the result of the calculation will be too

- You need to be able to calculate the degree of uncertainty

- **The Golden Rules**:

  - When adding/subtracting: ***add the <u>absolute</u> uncertainty***

  - When multiplying/dividing: ***add the <u>relative</u> uncertainty***

Absolute and Relative Uncertainty

- Absolute uncertainty: margin of uncertainty associated with the result from a given measurement, ΔA
- Relative uncertainty: ratio comparing the size of the absolute uncertainty, ΔA, to the size of the measured experimental result

$$\text{relative uncertainty} = \frac{\Delta A}{A}$$

- Experimental results should be reported as:

$$\text{experimental result} = (A \pm \Delta A)\ \text{unit}$$

Example: A Titration

- A calibrated burette has an absolute uncertainty of ±0.02 cm^3. During a titration, the volume of a 0.15mol dm^{-3} solution of hydrochloric acid at the end point was recorded as 12.25cm^3. Calculate the associated relative uncertainty

- Absolute uncertainty = ±0.02 cm^3
- Measured experimental result (A) = (12.25 ±0.02) cm^3
- Relative uncertainty = $\frac{\Delta A}{A} = \frac{0.02cm^3}{12.25cm^3} = 2 \times 10^{-3}$
- Relative uncertainty ~~percentage = 0.2%~~

Example 2: A rate of reaction

- In an experiment on the rate of a reaction, a student timed how long it would take to produce 100 cm^3 of gas, at a variety of different temperatures. At 30^{O}C, it took 26.67 seconds. The gas syringe used was accurate to +/- 0.25 cm^3. What is the average rate of reaction, and what is the relative uncertainty in this value?

- Rate = volume / time = 100 / 27 = 3.70 cm^3s^{-1}
  - Time is rounded to the nearest whole second as human reaction times do not allow for 2 decimal places of accuracy
- Absolute uncertainty of volume: +/- 0.25 cm^3
- Absolute uncertainty of time: +/- 0.5s
  - This is an approximation, taking into account reaction time and the difficulty of pressing stop exactly at 100 cm^3.
  - You should make similar approximations whenever you are manually recording time, and should write a short sentence to justify them

Example 2 continued

- Relative uncertainty of volume
  - % Uncertainty = (absolute uncertainty / measured value) x 100 = 0.25/100 x 100 = 0.25%

- Relative uncertainty of time
  - % Uncertainty = (0.5 / 27) x 100 = 1.85%

- Relative uncertainty of rate
  - % Uncertainty (rate) = % uncertainty (volume) + % uncertainty (time) = 0.25 + 1.85 = 2.10%
  - The relative uncertainties were added as the rate calculation required a division calculation

Propagation of Uncertainty

- After identifying the uncertainties associated with experimentally measured quantities, the next step is to figure out how these different uncertainties combine to give the resultant uncertainty
- Rule 1:
  - When adding or subtracting measurements, the absolute uncertainty associated with the net measured parameter is the square root of the sum of the squares of the absolute uncertainty
- Rule 2:
  - When multiplying or dividing measurements, the relative uncertainty associated with the net measured parameter is the square root of the sum of the squares of their relative uncertainties

Percent Error

$$\% \text{ Error} = \left| \frac{\text{measured - accepted}}{\text{accepted}} \right| \text{x100}$$

- The literature value for the standard enthalpy change of the decomposition reaction of calcium carbonate was found to be +178.1kJ. The experimental value was found to be +172.0kJ

$$\% \text{ error} = \left| \frac{178.1-172.0}{178.1} \right| \text{x } 100\%$$

$$= 3.4\%$$

Lesson 2

11.2 Graphical Techniques

Graphical Techniques

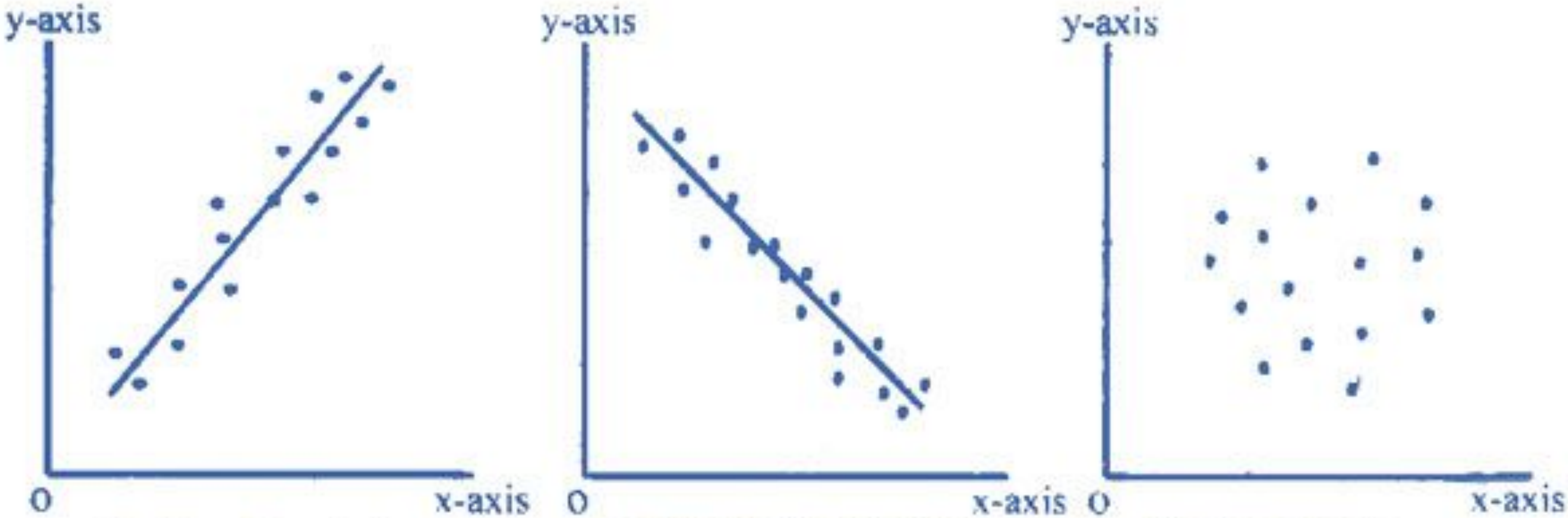
- Graphical techniques are effective means of communicating the effect of an independent variable on a dependent variable, and can lead to the determination of physical quantities
- Sketched graphs have labelled but unscaled axes, and are used to show qualitative trends, such as variables that are proportional or inversely proportional. Units generally would not be shown on a sketch, only the variables
- Drawn graphs have labelled and scaled axes, and are based on quantitative measurements. Drawn graphs always diplay the appropriate units for variables

Key Terms

- Dependence: any statistical relationship between two sets of data or between two random variables
- Independent Variable: the “cause” is plotted on the x-axis
- Dependent Variable: the “effect” is plotted on the y-axis
- Correlation: statistical measure and technique that indicates the degree and relationship between two sets of variables

Key Terms

- Positive Correlation: where the two variables increase or decrease in parallel to one another
- Negative Correlation: one variable increases while the second decreases or vice versa
- Correlation Coefficient: measure of the strength of the relationship between two variables, r
  - r= +1 : perfect positive linear relationship
  - r= 0: no linear relationship exists
  - r= -1: perfect negative linear relationship
- Scatter Plots: show the scatter of various points on a graph



Positive Correlation

Negative Correlation

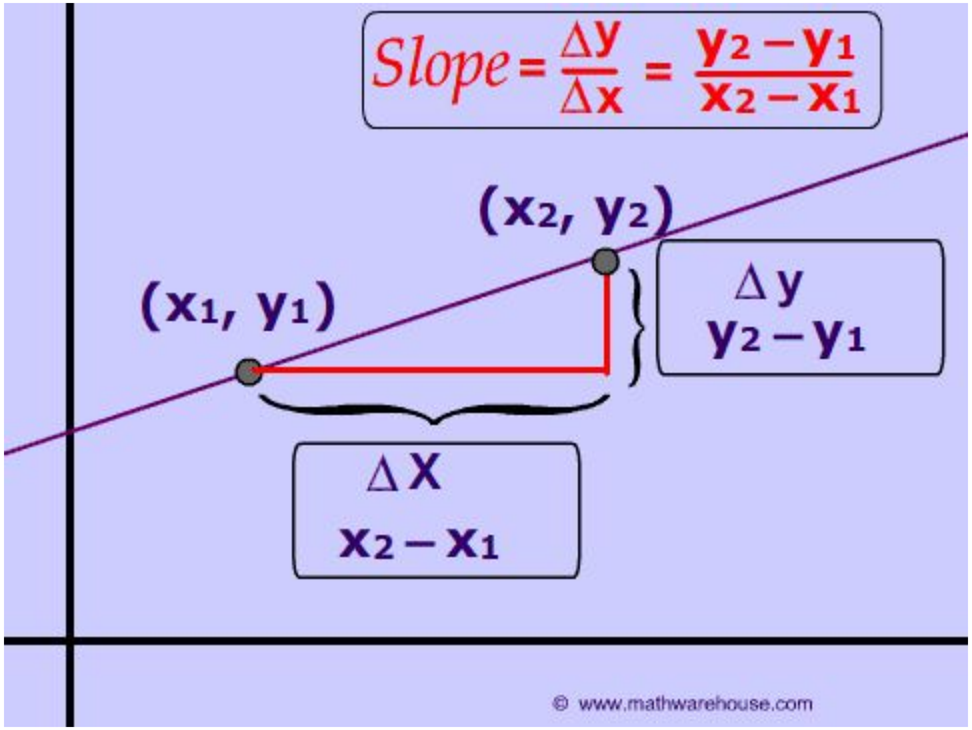
No Correlation

Slope or Gradient of Line, m

- The tangent of the angle that the line makes with the positive direction of the x-axis.

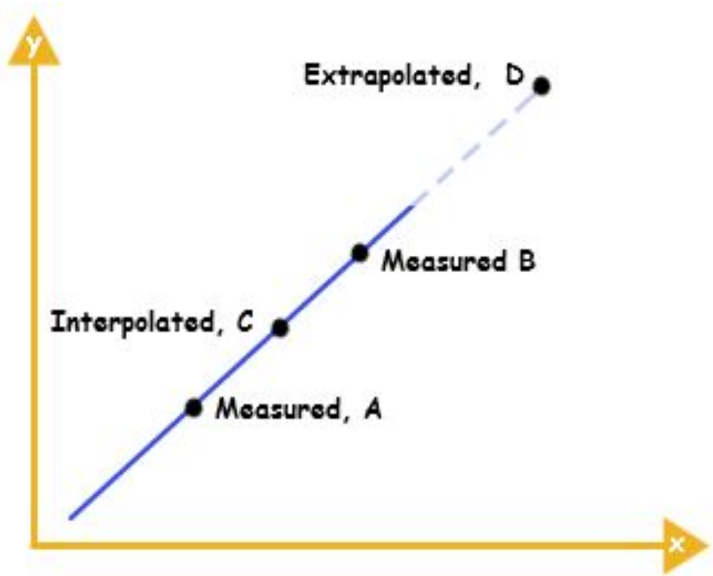
- Incline: + slope

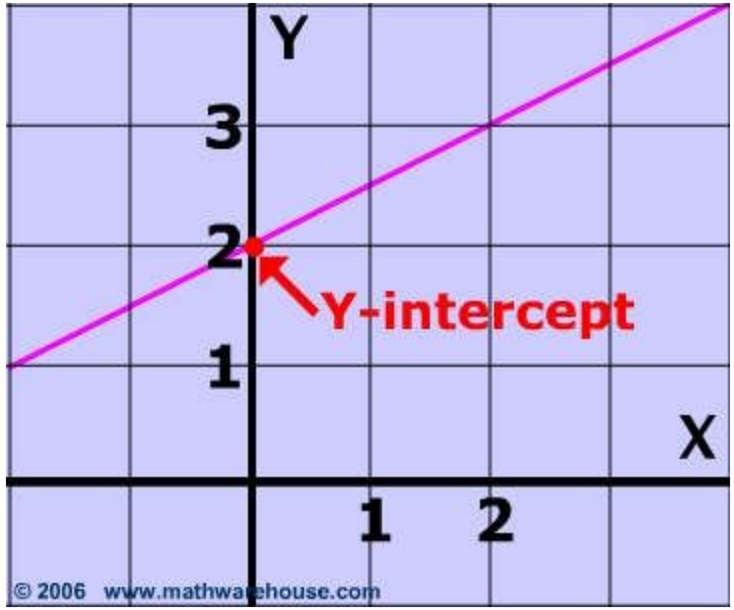
- Decline: - slope



The Intercept, c

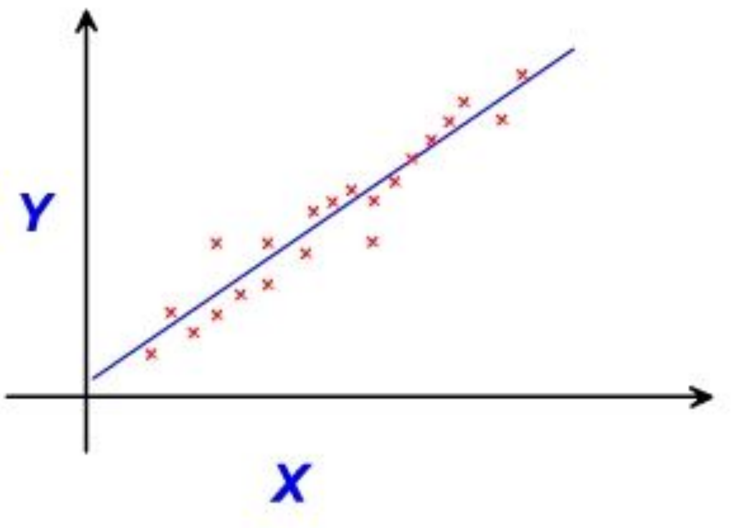
- The point where the line cuts the y-axis at x=0
- The intercept can be found by:
  - Extrapolation: extending the line
  - Equation of the line as long as the slope is known y=mx + c





Best-Fit Line

- Data obtained from an experiment does not always contain data points that lie exactly along the line
- Best fit line does not always necessarily contain all the experimental data points



Lesson 3

11.3 Spectroscopic Identification of Organic Compounds

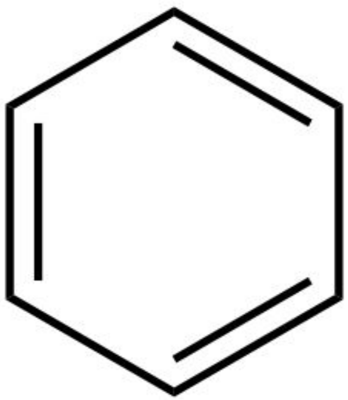
Degree of Unsaturation

- The degree of unsaturation or index of hydrogen deficiency (IHD) can be used to determine from a molecular formula the number of rings or multiple bonds in a molecule

  - Double bond-1 degree of unsaturation
  - Triple bond-2 degrees of unsaturation
  - RIng: 1 degree of unsaturation
  - Aromatic ring-4 degrees of unsaturation

Degree of Unsaturation

Benzene



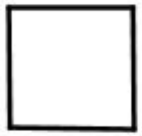
-One ring

- Three double bonds

IHD: 4

Cyclopentadiene

Cyclobutane



-One ring

IHD: 1

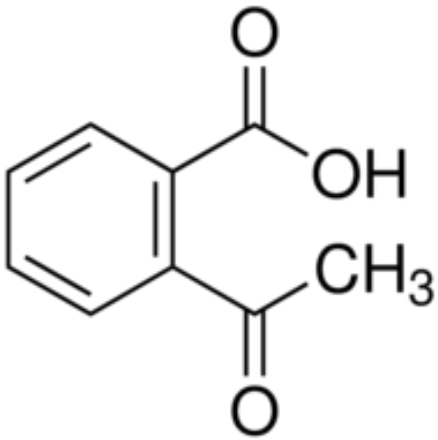
-One ring

-Two double bonds

IHD: 3

Degree of Unsaturation

2-acetylbenzoic acid (aspirin)

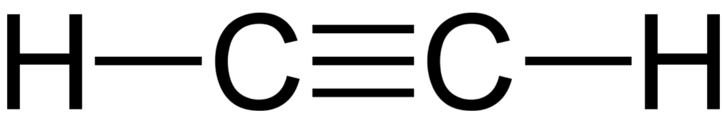


-One ring

-Five double bonds

IHD: 6

Ethyne



-One triple bond

IHD: 2

Degree of Unsaturation

$C_cH_hN_nO_oX_x$ X is a halogen (F, Cl, Br, or I)

IHD= 0.5(2c+2-h-x+n)

- Given $C_4H_8O_2$ deduce the IHD

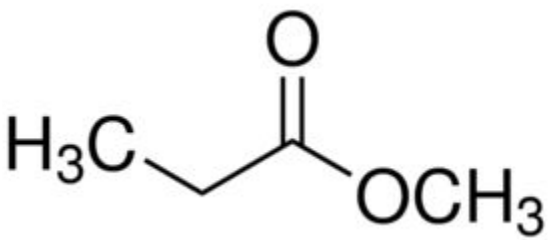
c=4 h=8 n=0 o=2 x=0

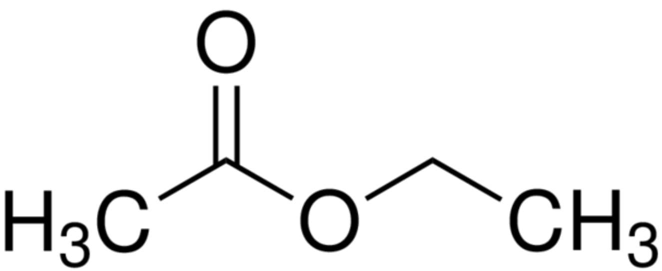
IHD=0.5(8+2-8-0-0) = 1

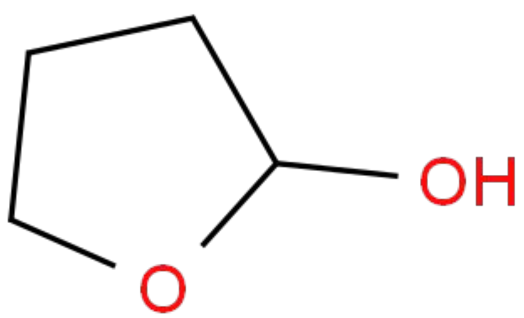
The molecule must contain either one double bond or one ring. There are several isomers of $C_4H_8O_2$

Degree of Unsaturation

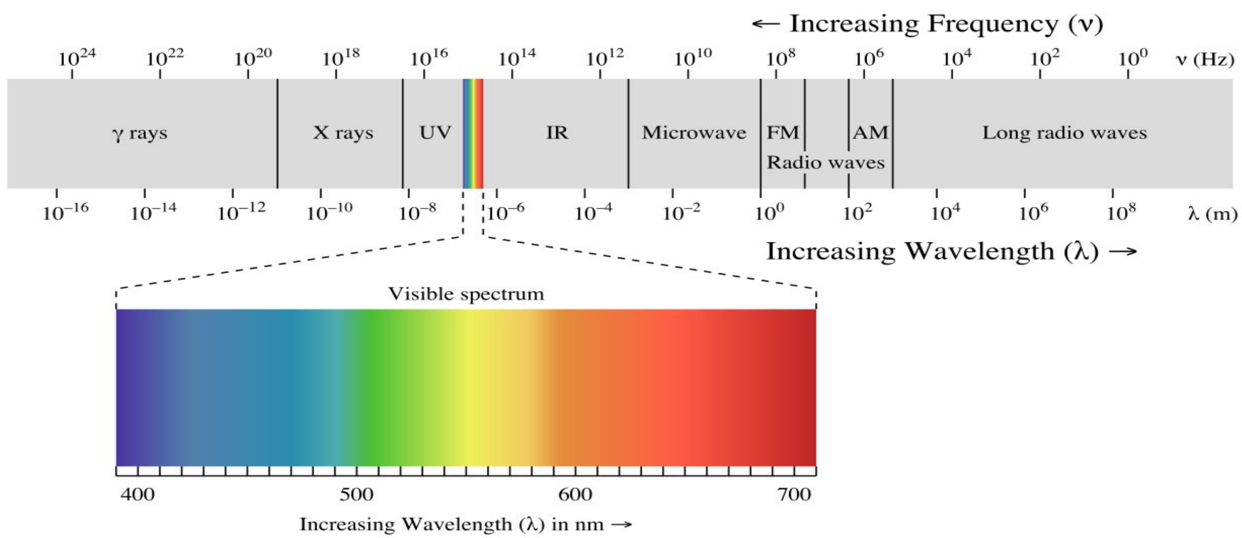
Possible isomers of $C_4H_8O_2$ with IHD of 1







Electromagnetic Spectrum



Energy, E is directly related to the frequency, ν, and inversely related to wavelength, λ

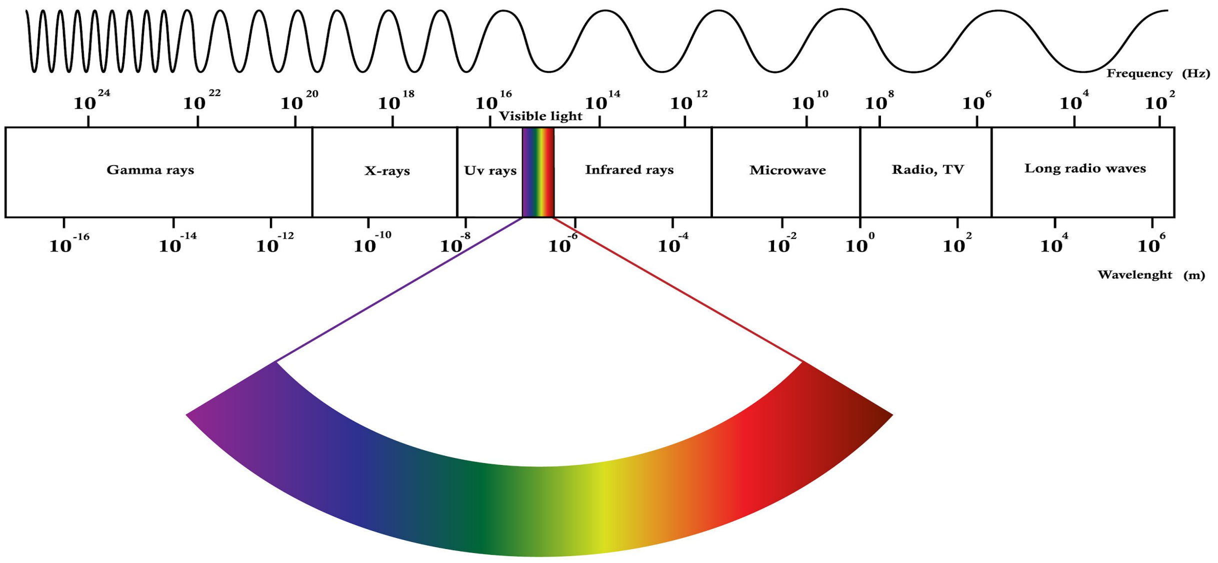
$$E = h\nu = \frac{hc}{\lambda}$$

c (speed of light): $3.00 \times 10^{8}\ ms^{-1}$

h (Plank's constant): 6.626×10^{-34} J s

Electromagnetic Spectrum

- The various regions are the basis of different types of spectroscopy (the study of the way matter interacts with radiation) and various techniques are used to identify the structures of substances



Regions of the EMS

- X-rays: high energy, cause electrons to be removed from the inner energy levels of atoms. Diffraction patterns can lead to information such as bond distances and bond angles in a structure
  - Basis for x-ray crystallography
- Visible light and Ultraviolet (UV) light: give rise to electronic transitions and hence this type of spectroscopy gives information about the electronic energy levels in an atom or molecule.
  - Basis for UV-vis spectroscopy
- Infrared Radiation: causes certain bonds in a molecule to vibrate (stretch and bend) and provides information on the functional groups present.
  - Basis of IR spectroscopy

Regions of the EMS

- Microwaves: cause molecular rotations and can give information on bond lengths
- Radio Waves: cause nuclear transitions in a strong magnetic field because radio waves can be absorbed by certain nuclei, which causes their spin states to change.
  - Nuclear Magnetic Resonance (NMR) is based on this and information on different chemical environments of atoms can be deduced, which leads to information on the connectivity of the atoms present in a molecule

Types of Spectroscopy

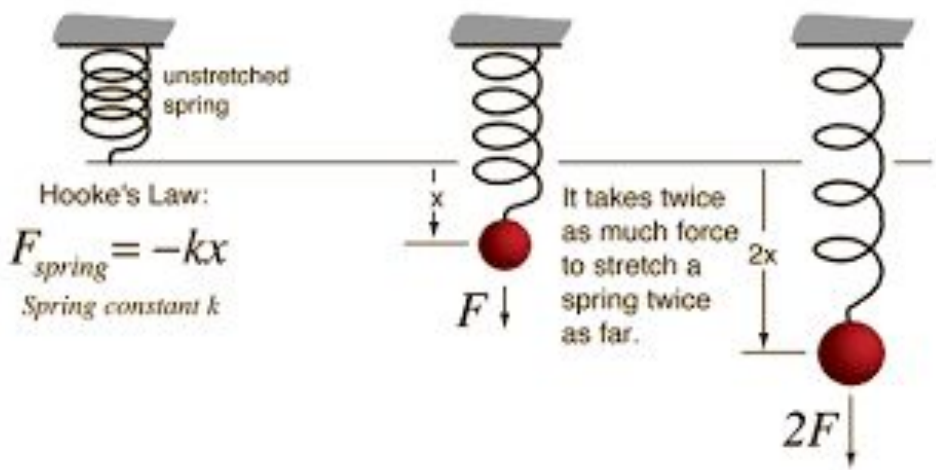
- Three different types of spectroscopy that form the cornerstone of the spectroscopic identification of organic molecules
  - Infrared (IR) spectroscopy: determines the bonds in organic molecules
  - Proton nuclear magnetic resonance (^{1}H NMR) spectroscopy: shows the chemical environments of isotopes (mostly used with hydrogen)
  - Mass spectrometry (MS): determines the relative atomic and molecular masses. Fragmentation patterns are useful with organic

Infrared Spectroscopy

- IR radiation does not have sufficient energy to result in electronic transitions but can cause molecular vibrations which result from the vibration of certain groups of molecules about their bonds
- Helps identify various functional groups in a molecule
- Vibrational transitions correspond to definite energy levels

Infrared Spectroscopy

- Spring model: covalent bonds are thought of as springs that have vibrations
- Spring can be stretched (symmetrically and asymmetrically), bent, or twisted
- The force required to cause the vibration is based on Hooke's law



Infrared Spectroscopy

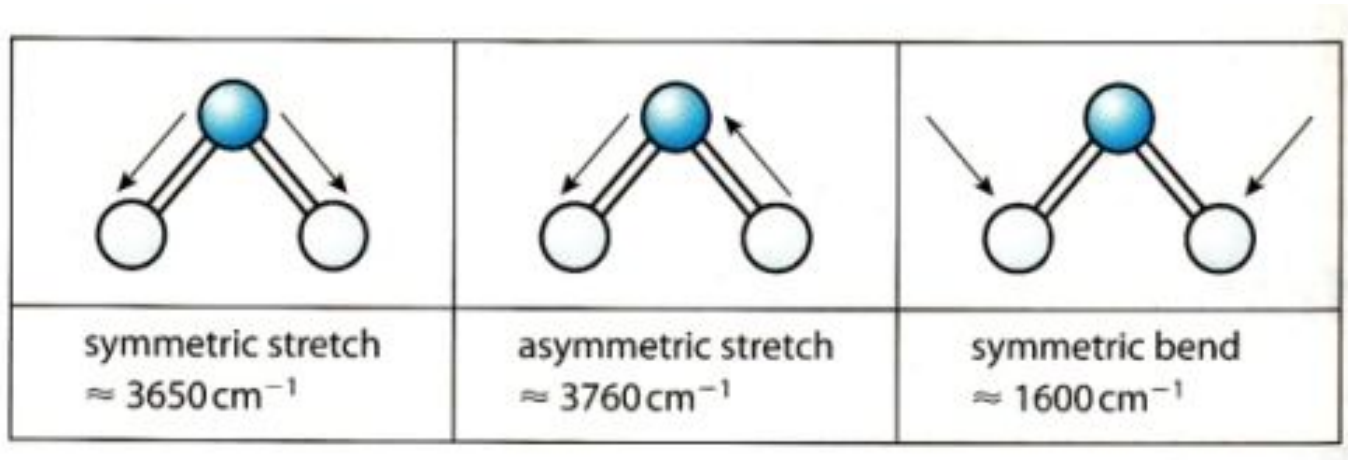
- Lighter atoms will vibrate at higher frequencies and heavier atoms will vibrate at lower frequencies

Molecule	Bond Enthalpy/ kJ mol^{-1}	Wavenumber/cm-^{1}
H-Cl	431	2886
H-Br	366	2559
H-I	298	2230

- The same applies for multiple bonds
- Imagine two atoms connected by a spring, the stronger the bond connecting the two atoms the tighter the string will be and therefore more energy is required to stretch it
- For diatomic molecules only one form of vibration is possible, stretching

Infrared Spectroscopy

- Polyatomic species may have several modes of vibration
  - Symmetric stretch
  - Asymmetric stretch
  - Symmetric bend

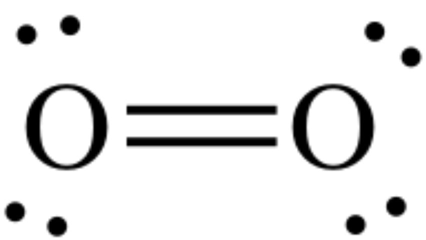


Infrared Spectroscopy

- For a covalent bond to absorb IR radiation there must be a change in the molecular dipole moment associated with the vibration mode

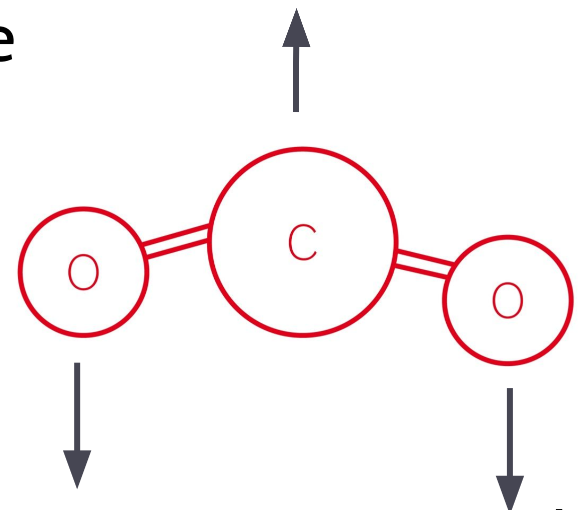
non-polar

IR inactive



non-polar

IR inactive



asymmetric stretch

symmetric bend

Infrared Spectroscopy

- The absorbance, A, is related to the transmittance by

$$A = -\log_{10} T$$

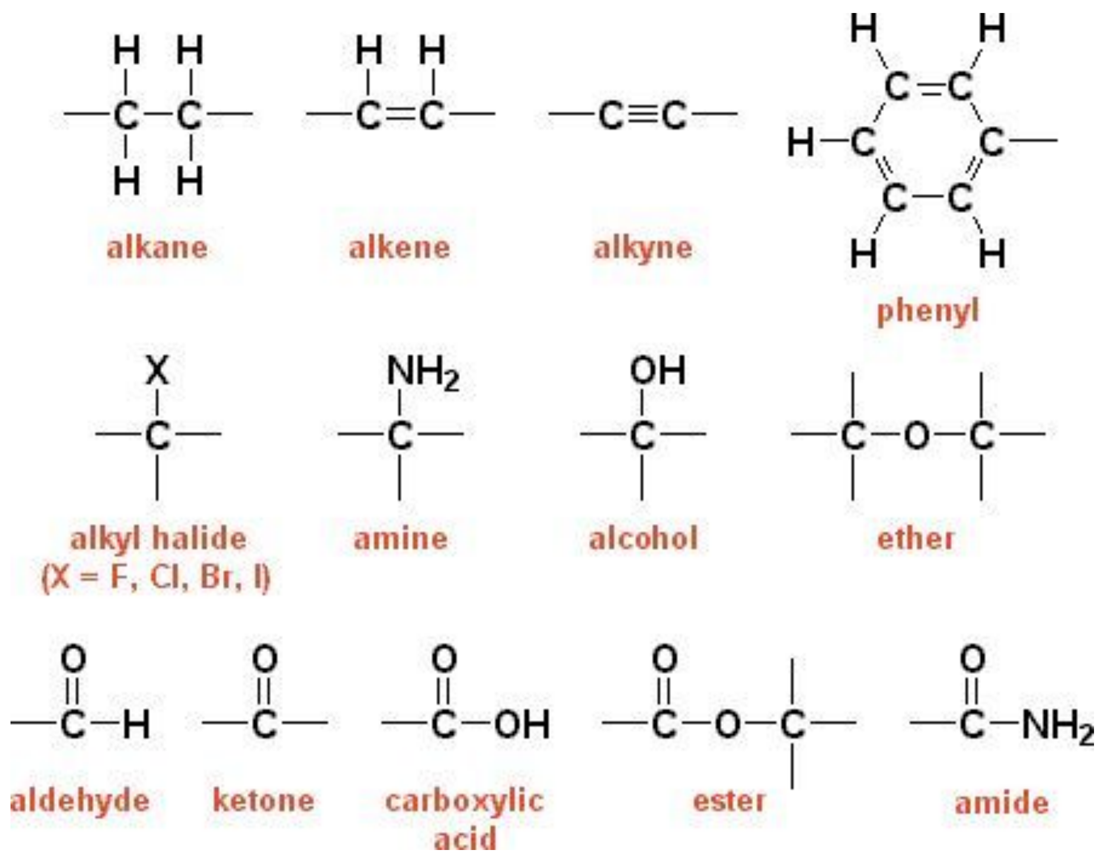
- IR spectrum is a plot of the percentage transmittance, %T versus the wavenumber in cm^{-1}, where %T ranges from 0% to 100%.
- Functional groups can be identified
  - YOU WILL NEED TO BE VERY FAMILIAR WITH THE NAME AND STRUCTURE OF **FUNCTIONAL GROUPS**

Infrared Spectroscopy

- A bond will only interact with IR radiation if it is a polar covalent bond
- Non-polar bonds DO NOT absorb IR radiation
- Intensity depends on dipole moment of bonds:
  - Strong polar bonds produce strong bands
  - Bonds with medium polarity produce medium bonds
  - Weak bonds produce weak bands

Infrared Spectroscopy

Functional Groups



Infrared Spectroscopy

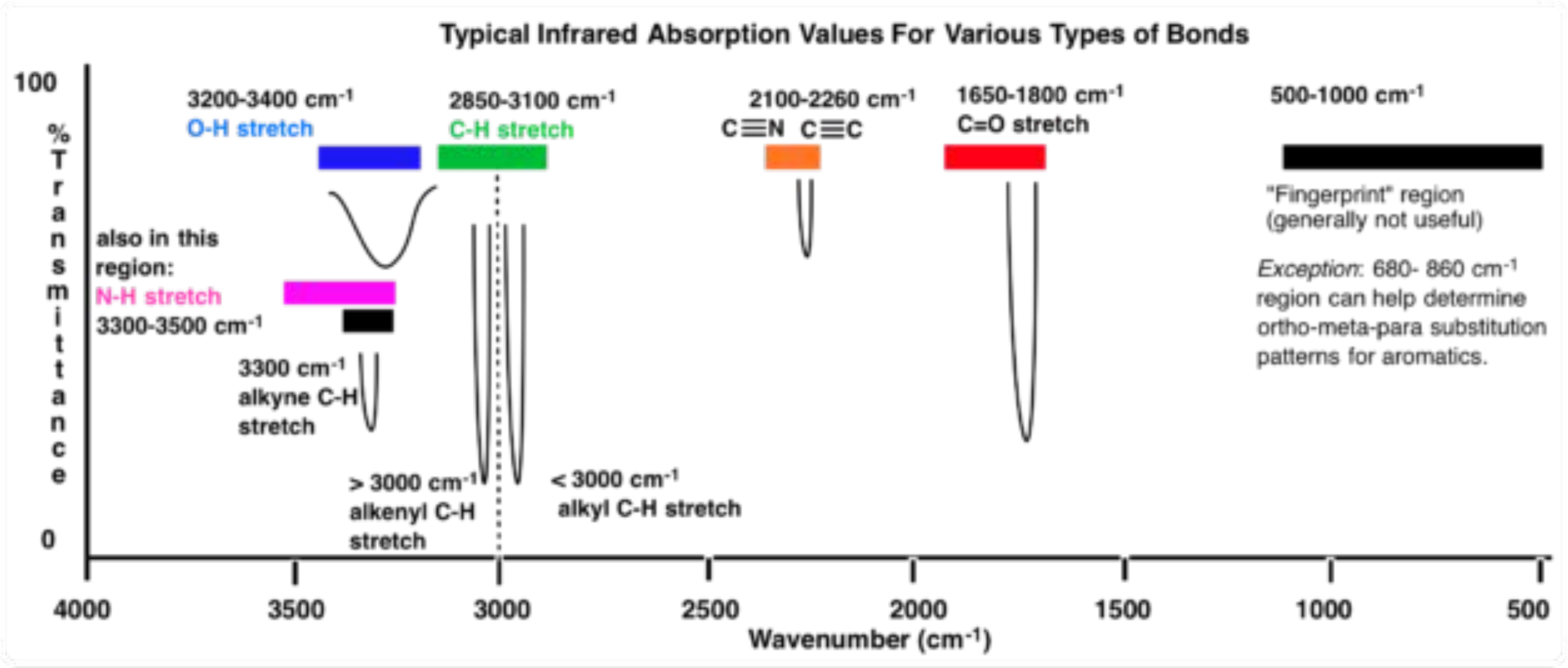
- Typical proton shift

26. Infrared data

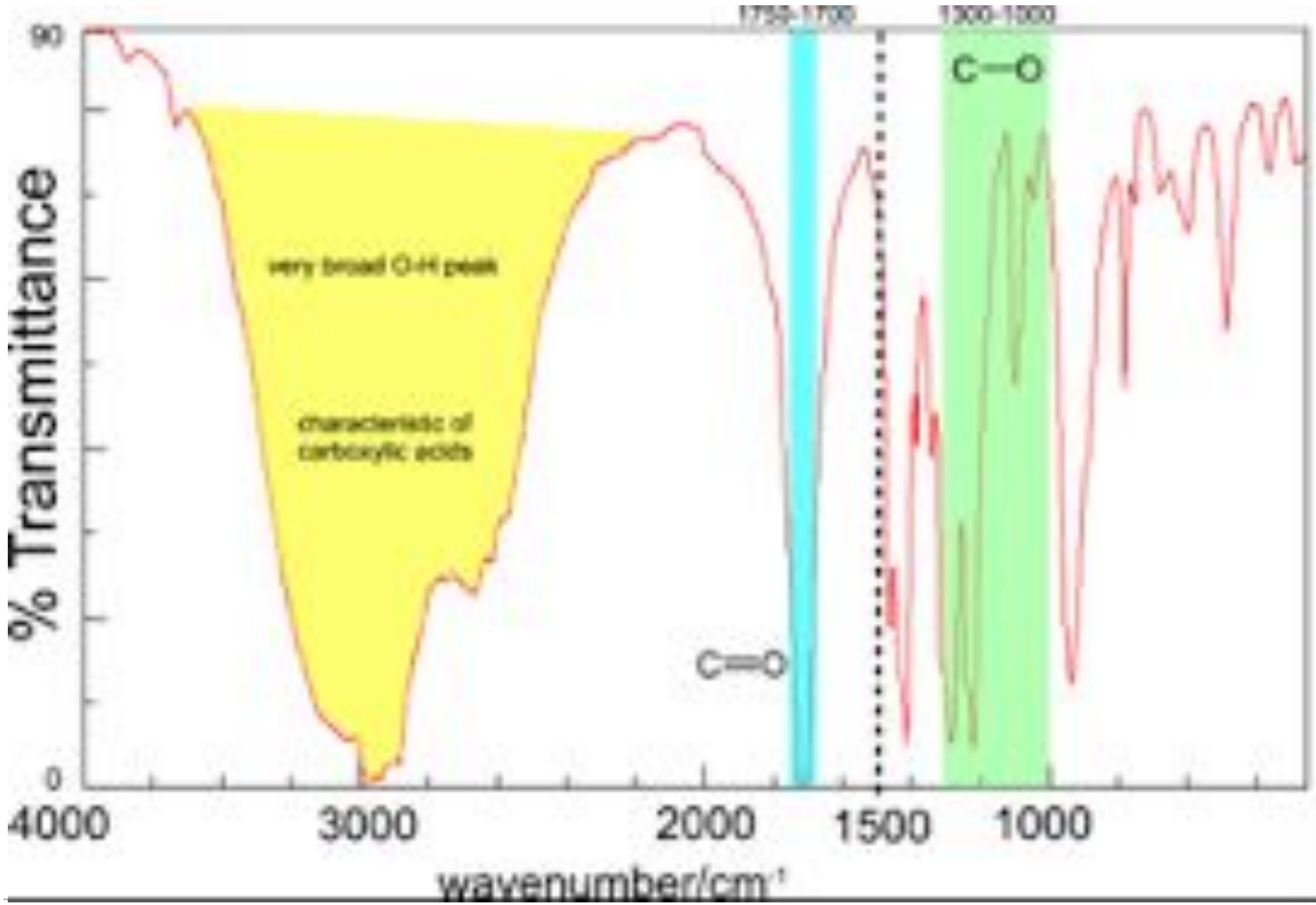
Characteristic ranges for infrared absorption due to stretching vibrations in organic molecules.

Bond	Organic molecules	Wavenumber (cm^{-1})	Intensity
C–I	iodoalkanes	490–620	strong
C–Br	bromoalkanes	500–600	strong
C–Cl	chloroalkanes	600–800	strong
C–F	fluoroalkanes	1000–1400	strong
C–O	alcohols, esters, ethers	1050–1410	strong
C=C	alkenes	1620–1680	medium-weak; multiple bands
C=O	aldehydes, ketones, carboxylic acids and esters	1700–1750	strong
C≡C	alkynes	2100–2260	variable
O–H	hydrogen bonding in carboxylic acids	2500–3000	strong, very broad
C–H	alkanes, alkenes, arenes	2850–3090	strong
O–H	hydrogen bonding in alcohols and phenols	3200–3600	strong, broad
N–H	primary amines	3300–3500	medium, two bands

Infrared Spectroscopy



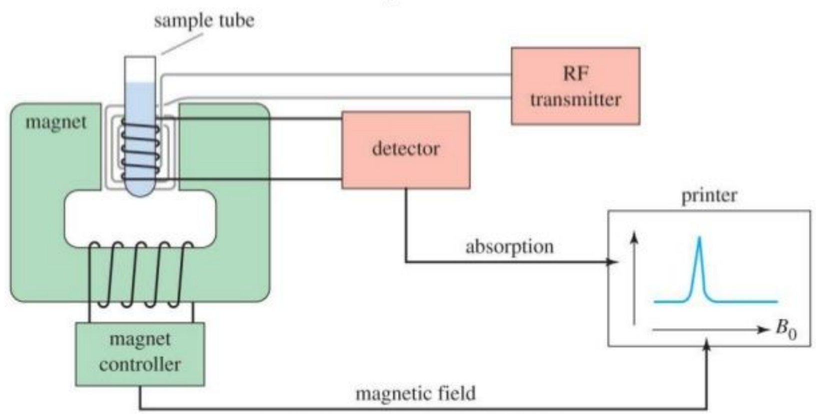
Infrared Spectroscopy



^{1}H NMR Spectroscopy

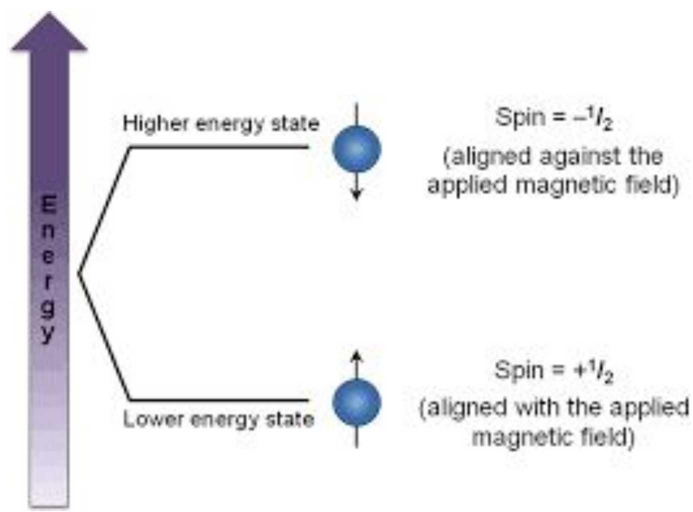
- Gives information on the different chemical environments of hydrogen atoms in a molecule
- Considered the most important structural technique available to organic chemists

The NMR Spectrometer



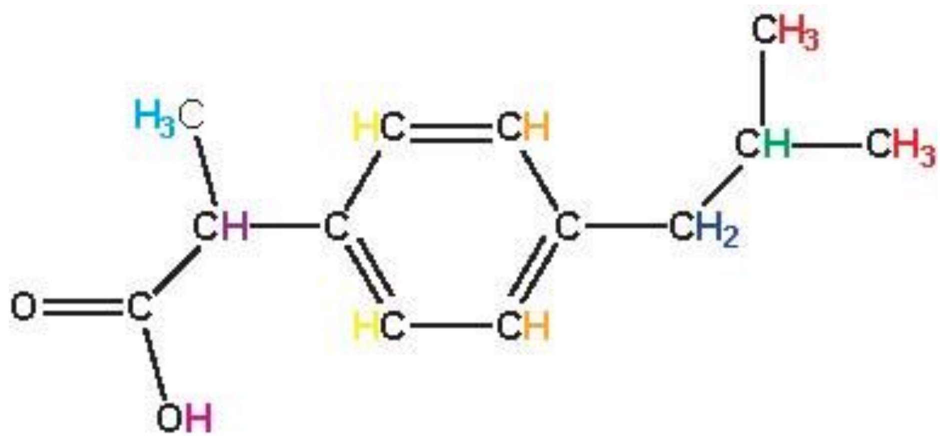
^{1}H NMR Spectroscopy

- Nuceli of hydrogen atoms can exist in two possible spin states and behave as tiny magnets
- When nuclei are placed in magnetic fields the spin states may align with the magnetic field or against it creating two nuclear energy levels



^{1}H NMR Spectroscopy

- The position of the NMR signal relative to a standard (tetramethylsilane, TMS) is the chemical shift, □, expressed in parts per million (ppm) of the proton
- □ for TMS is 0 ppm
- ^{1}H NMR spectrum shows the number of different chemical environments in which the hydrogen atoms are found



^{1}H NMR Spectroscopy

Typical proton shift

27. ^{1}H NMR data

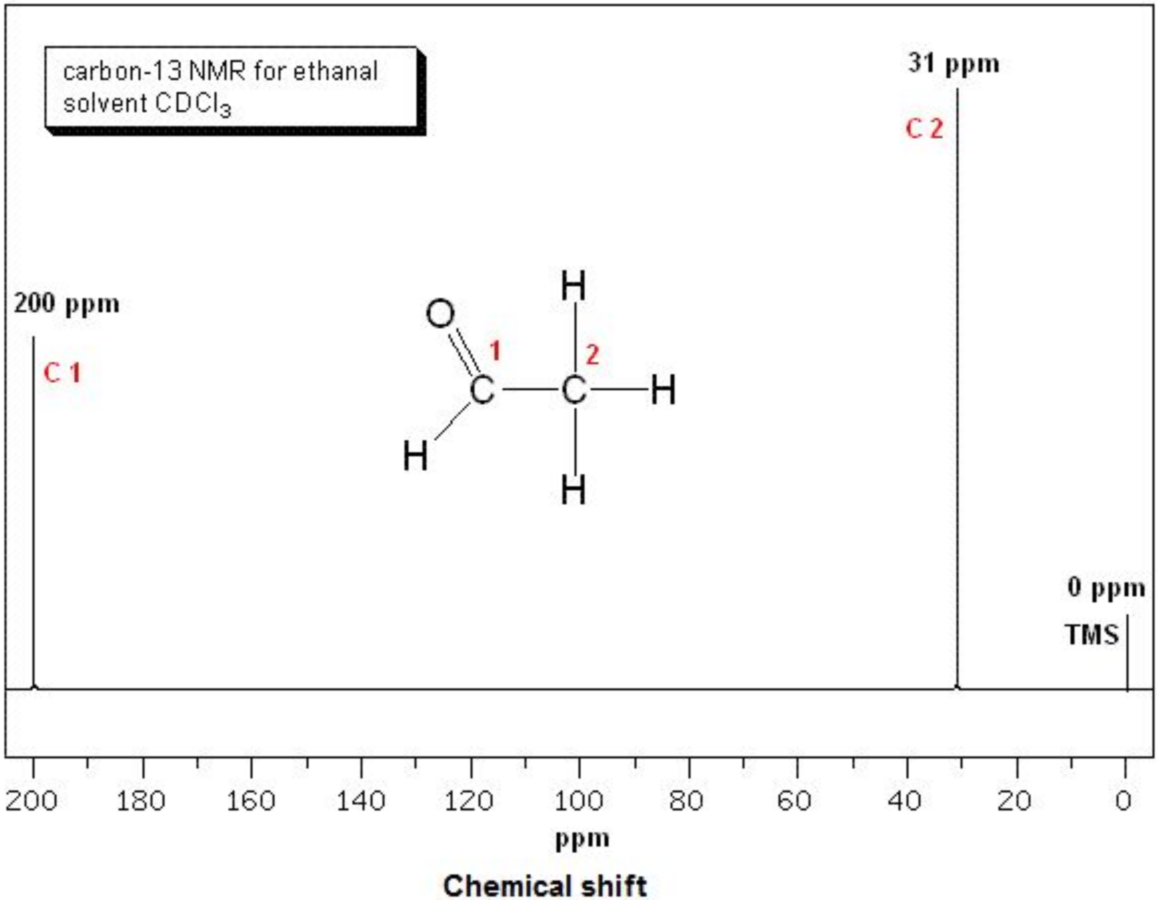
Typical proton chemical shift values (δ) relative to tetramethylsilane (TMS) = 0.

R represents an alkyl group, and Hal represents F, Cl, Br, or I.

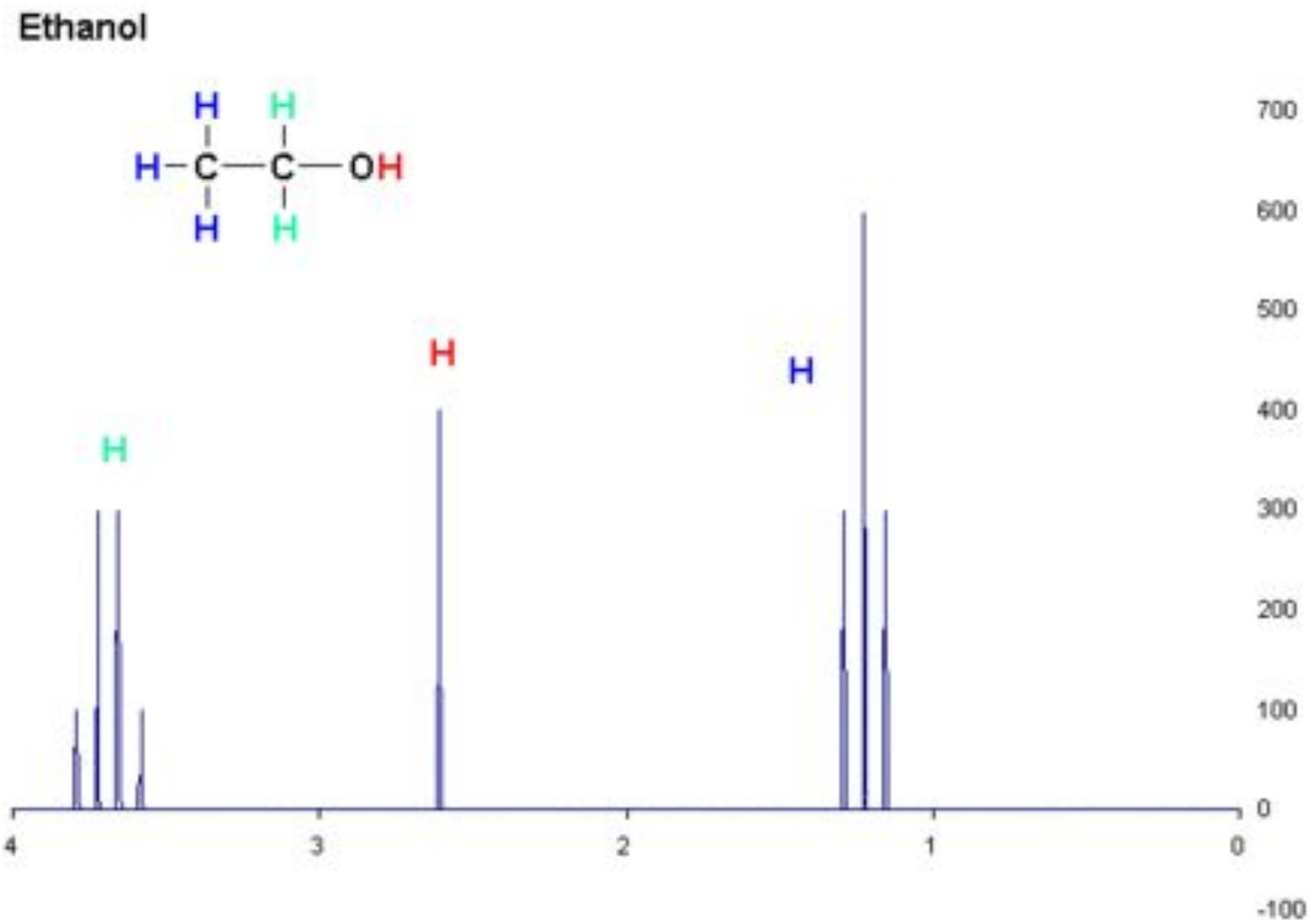
These values may vary in different solvents and conditions.

Type of proton	Chemical shift (ppm)
$—CH_3$	0.9–1.0
$—CH_2$-R	1.3–1.4
—R_2CH	1.5
RO–C(=O)–CH_2—	2.0–2.5
R–C(=O)–CH_2—	2.2–2.7
—C_6H_4—CH_3	2.5–3.5
—C≡C—H	1.8–3.1
—CH_2-Hal	3.5–4.4
R–O–CH_2—	3.3–3.7
R–C(=O)–O–CH_2—	3.7–4.8
R–C(=O)–O—H	9.0–13.0
R—O—H	1.0–6.0
—HC=CH_2	4.5–6.0

^{1}H NMR Spectroscopy

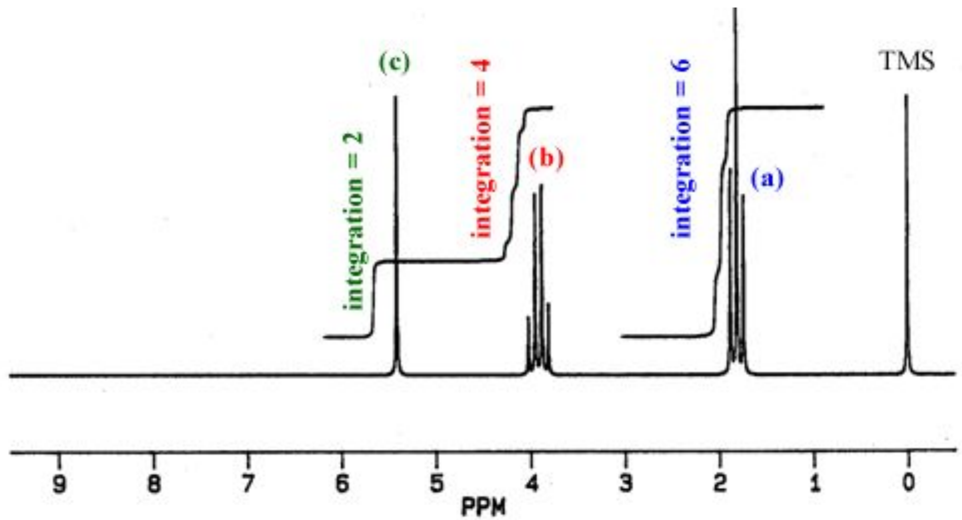


^{1}H NMR Spectroscopy



^{1}H NMR Spectroscopy

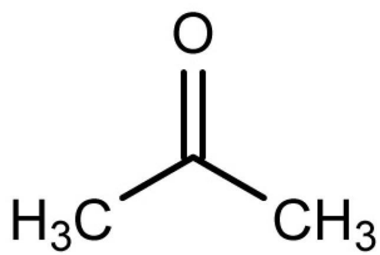
- Integration trace: shows the relative number of hydrogen atoms present



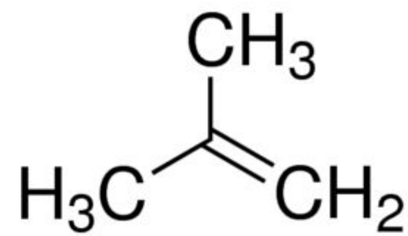
- Magnetic Resonance Imaging (MRI): gives a 3D view of organs in the human body

^{1}H NMR Spectroscopy

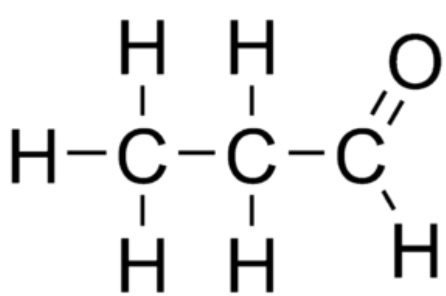
Number of peaks



1 chemical environment
1 peak



2 chemical environments
2 peaks

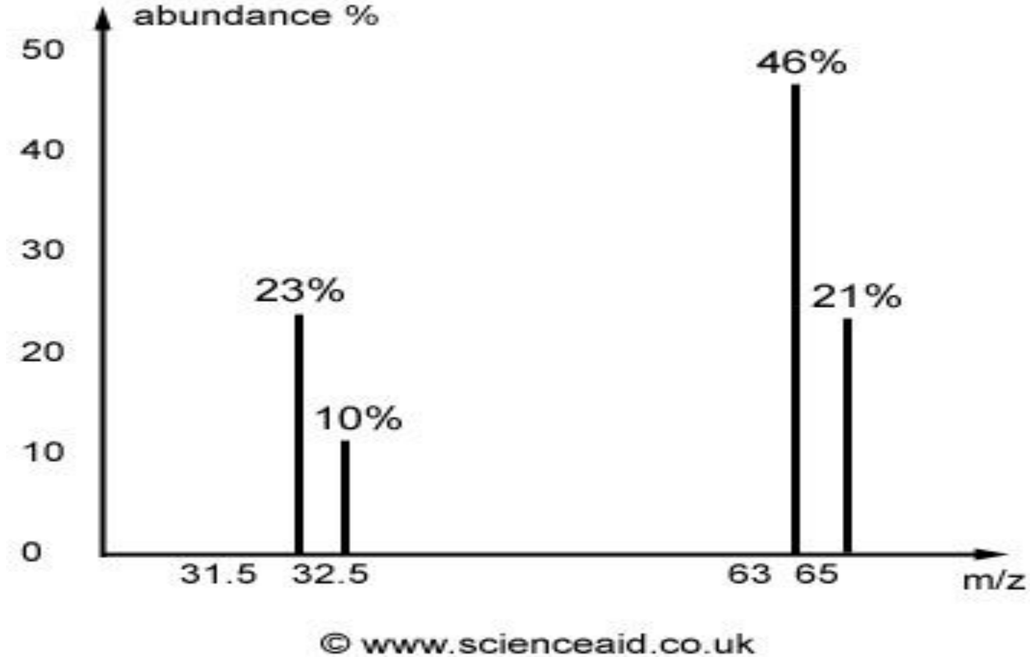


3 chemical environments
3 peaks

Mass Spectrometry (MS)

- When a gaseous molecule is ionized its molecular ion, M^+ is formed
- The molecular ion peak in a mass spectrum corresponds to the molecular mass of the compound
- Due to the highly energetic ionization process involved in a mass spectrometer, the molecule can break up into fragments, some being ions
- The fragmentation pattern provides further information on certain functional groups present in a molecule

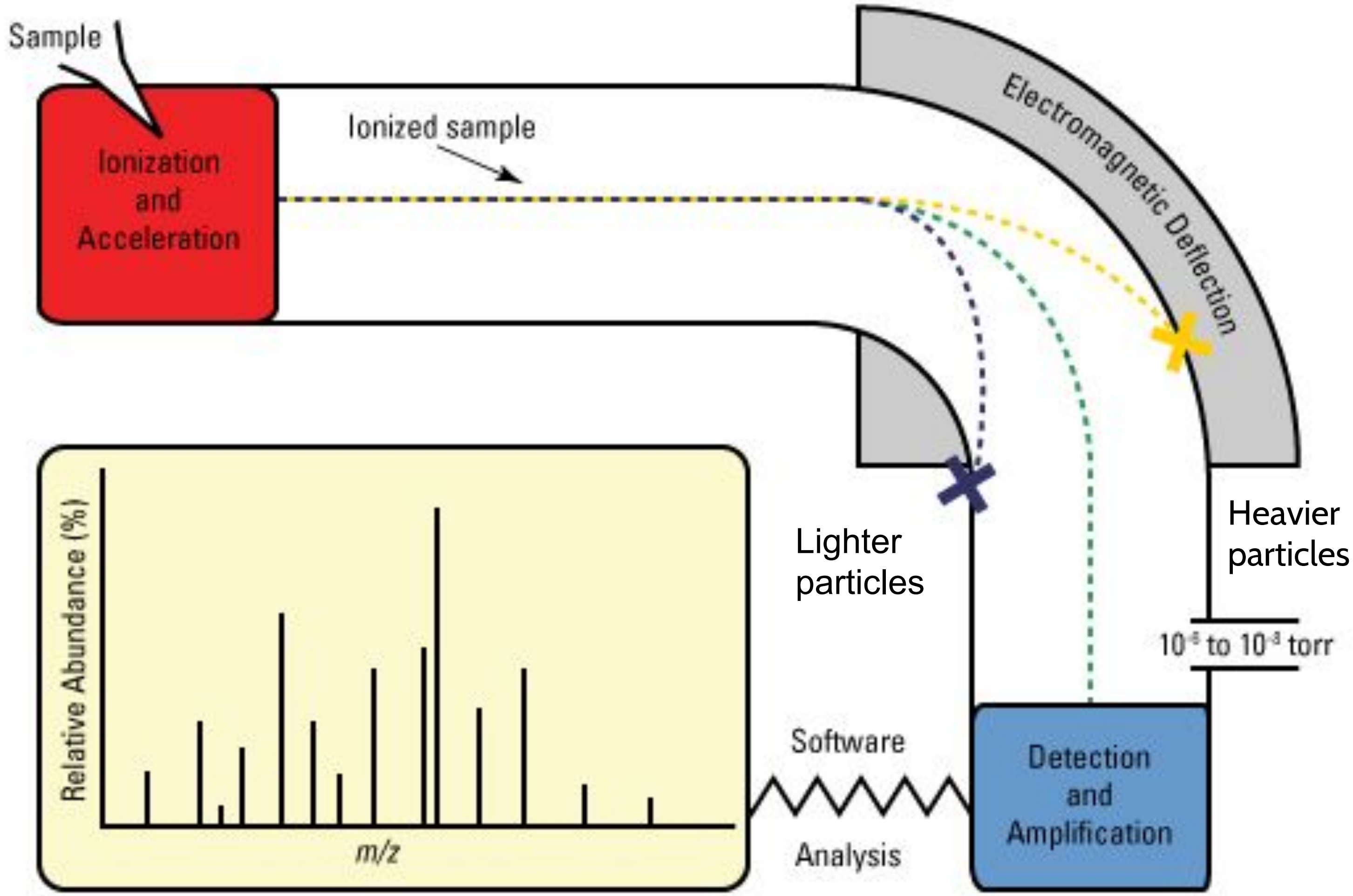
Mass Spectrometry (MS)



$A_r = (31.5)(23) + (32.5)(10) + (63)(46) + (65)(21) / 100$

$A_r = 53.2$

Mass Spectrometry (MS)



Mass Spectrometry (MS)

- When the vaporized organic sample passes into the ionization chamber, it is bombarded by a stream of electrons

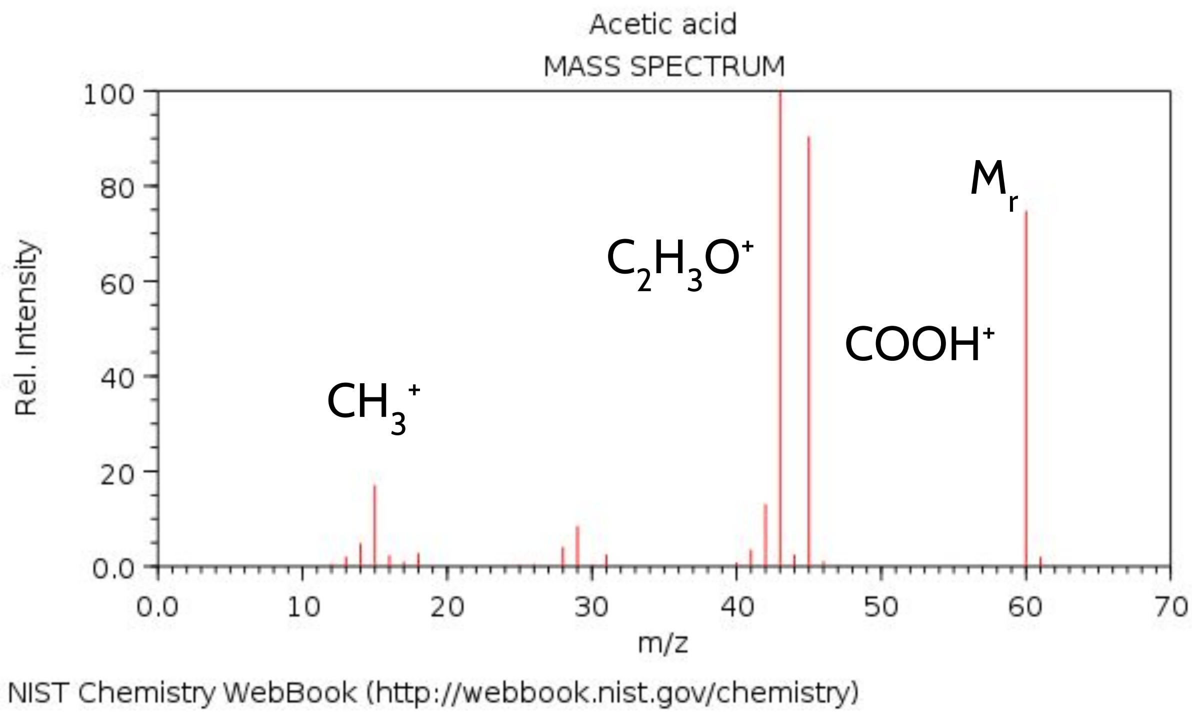
$$M(g) + e^- \rightarrow M^+(g) + 2e^-$$

- The M^+ ion is known as the molecular ion
- Fragments are produced to produce information about structure

Mass Spectrometry (MS)

- Examples:
- (Table 15 from Data Booklet)
  - $(M_r-15)^+$ results from the loss of $-CH_3$
  - $(M_r-17)^+$ results from the loss of $-OH$
  - $(M_r-29)^+$ results from the loss of $-CHO$ or $-CH_2CH_3$
  - $(M_r-31)^+$ results from the loss of $-OCH_3$
  - $(M_r-45)^+$ results from the loss of $-COOH$

Mass Spectrometry (MS)



Peak at m/z 45

(60-45)=15 mass loss

$-CH_3$

Peak at m/z 43

(60-43)=17 mass loss

-OH

Peak at m/z 15

(60-15)=45 mass loss

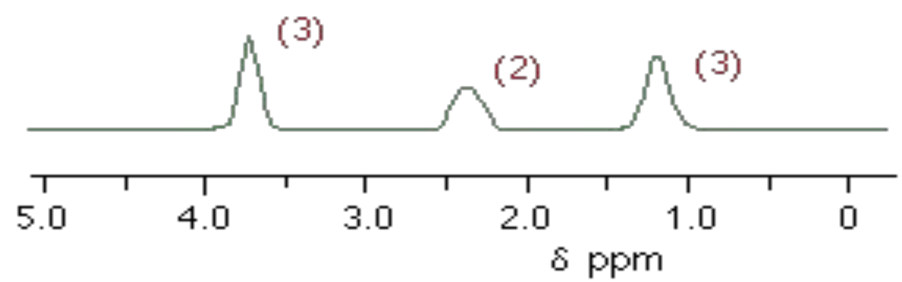
-COOH

Lesson 4

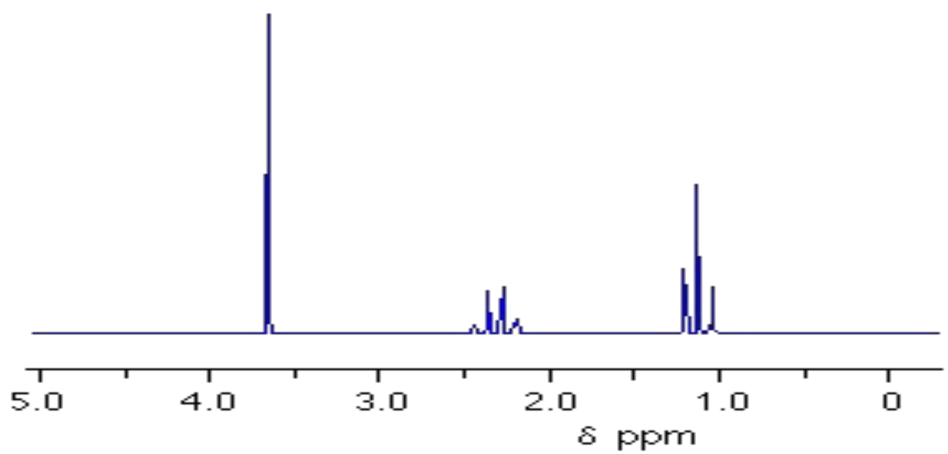
21.1 Spectroscopic Identification of Organic Compounds

High Resolution ^1H NMR

low resolution nmr spectrum for methyl propanoate, $CH_3CH_2COOCH_3$

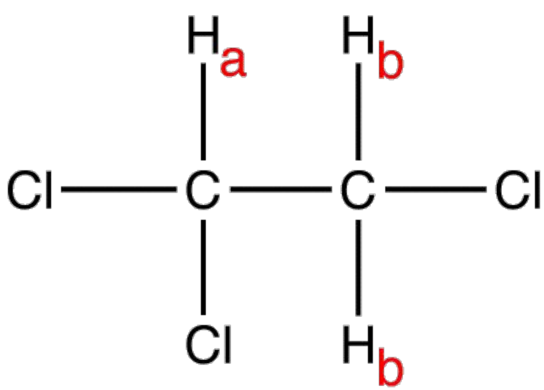


high resolution nmr spectrum for methyl propanoate, $CH_3CH_2COOCH_3$

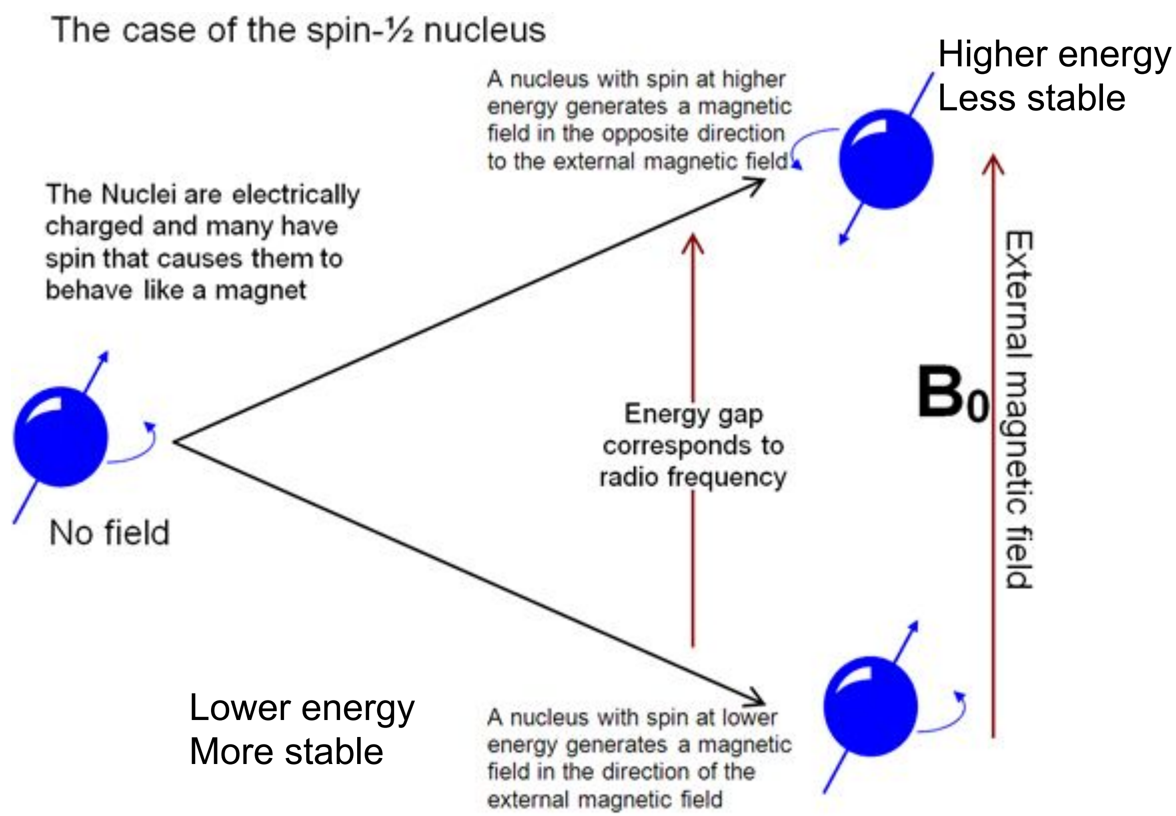


High Resolution ^{1}H NMR

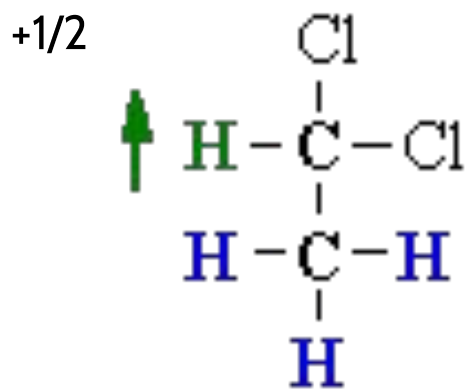
- Shows further splitting of some absorptions
- Splitting patterns result from spin-spin coupling



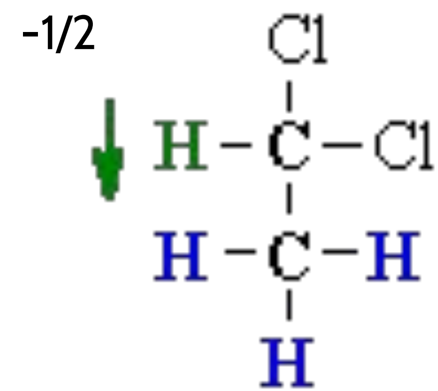
1



spectrometer field



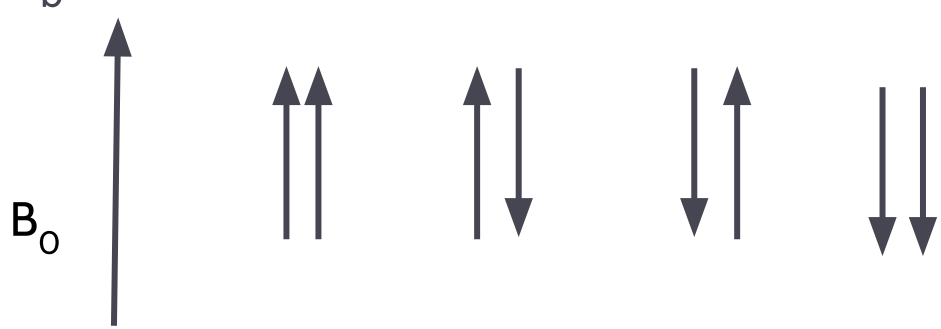
Fields are aligned which effectively deshields the neighbouring protons, and resonance occurs at higher frequency



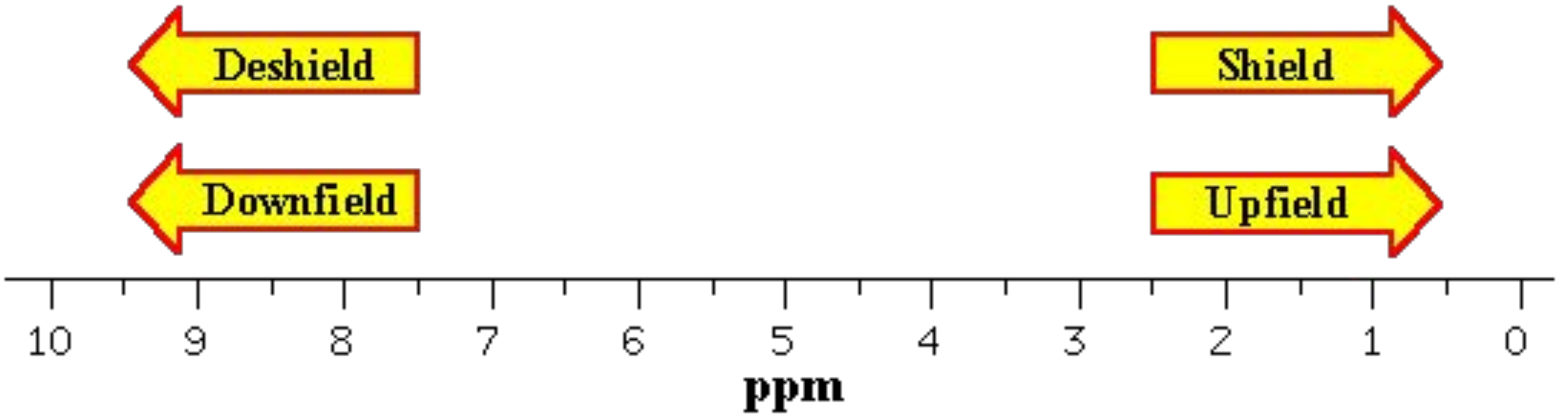
Fields are opposed which effectively shields the neighbouring protons, and resonance occurs lower frequency

High Resolution [1]H NMR

- Four combination possible:
  - H_{a1} and H_{a2} magnetic moment aligned with B_o (deshields H_b, so signal is shifted downfield to higher □)
  - H_{a1} magnetic moment aligned with B_o and H_{a2} magnetic moment aligned against B_o
  - H_{a1} magnetic moment aligned against B_o and H_{a2} magnetic moment aligned with B_o
  - H_{a1} and H_{a2} magnetic moments aligned against B_o (shields H_b, so signal is shifted upfield to a lower □)



High Resolution ^{1}H NMR



Increased magnetic field strength →

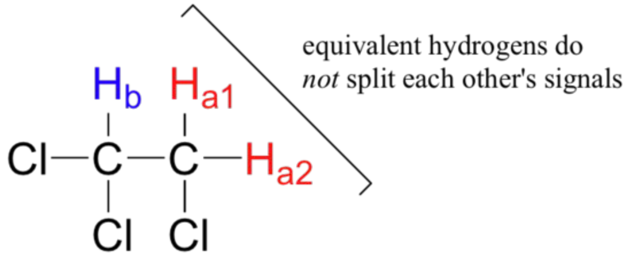
High Resolution ^{1}H NMR

n	(n+1) multiplicity	relative intensities	multiplet name
0	1	1	singlet
1	2	1:1	doublet
2	3	1:2:1	triplet
3	4	1:3:3:1	quartet
4	5	1:4:6:4:1	quintet
5	6	1:5:10:10:5:1	sextet
6	7	1:6:15:20:15:6:1	septet
7	8	1:7:21:35:35:21:7:1	octet
8	9	1:8:28:56:70:56:28:8:1	nonet

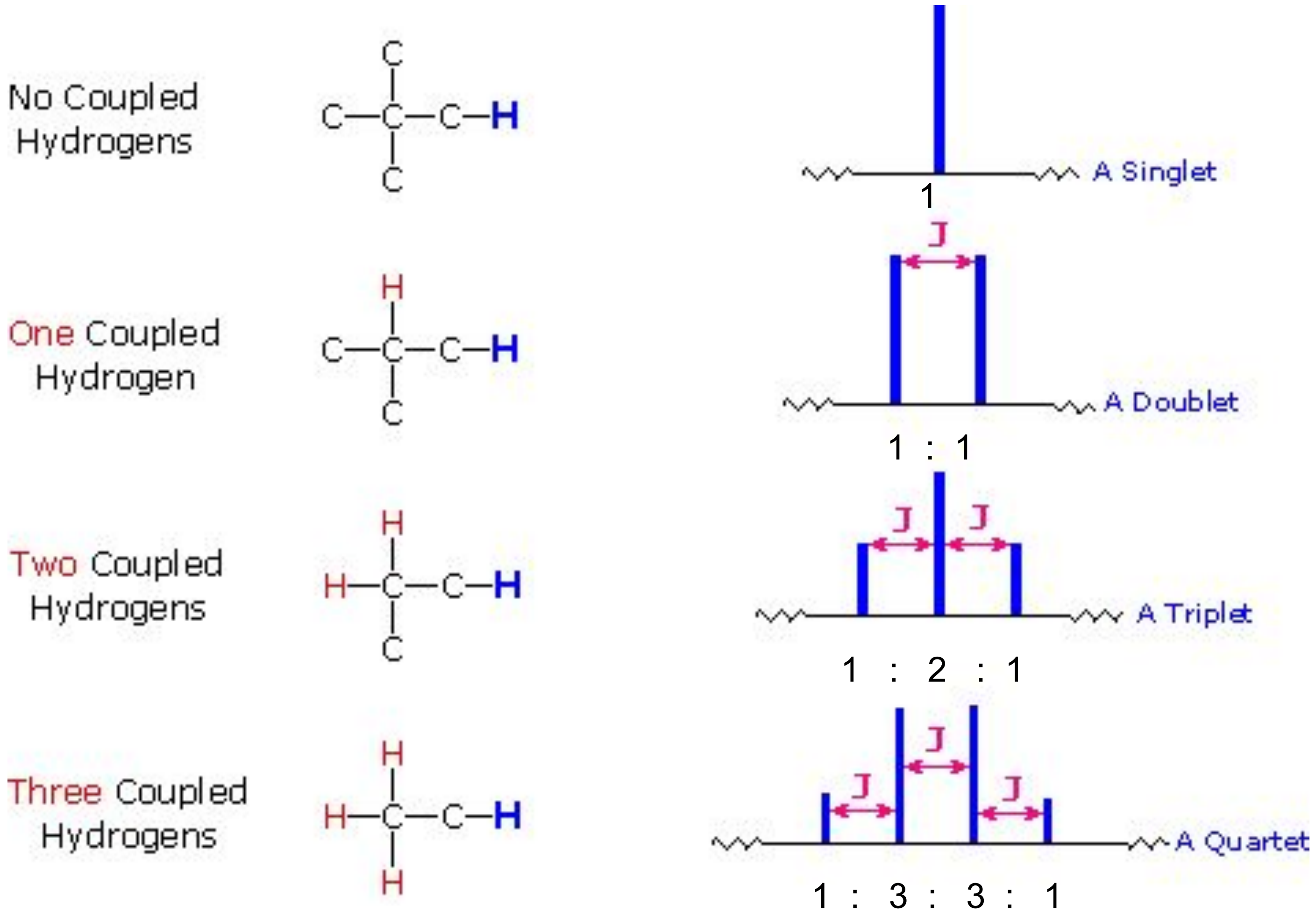
- Pascal's triangle can be used to deduce the splitting patterns
- This gives the ratio of intensities

High Resolution ^{1}H NMR

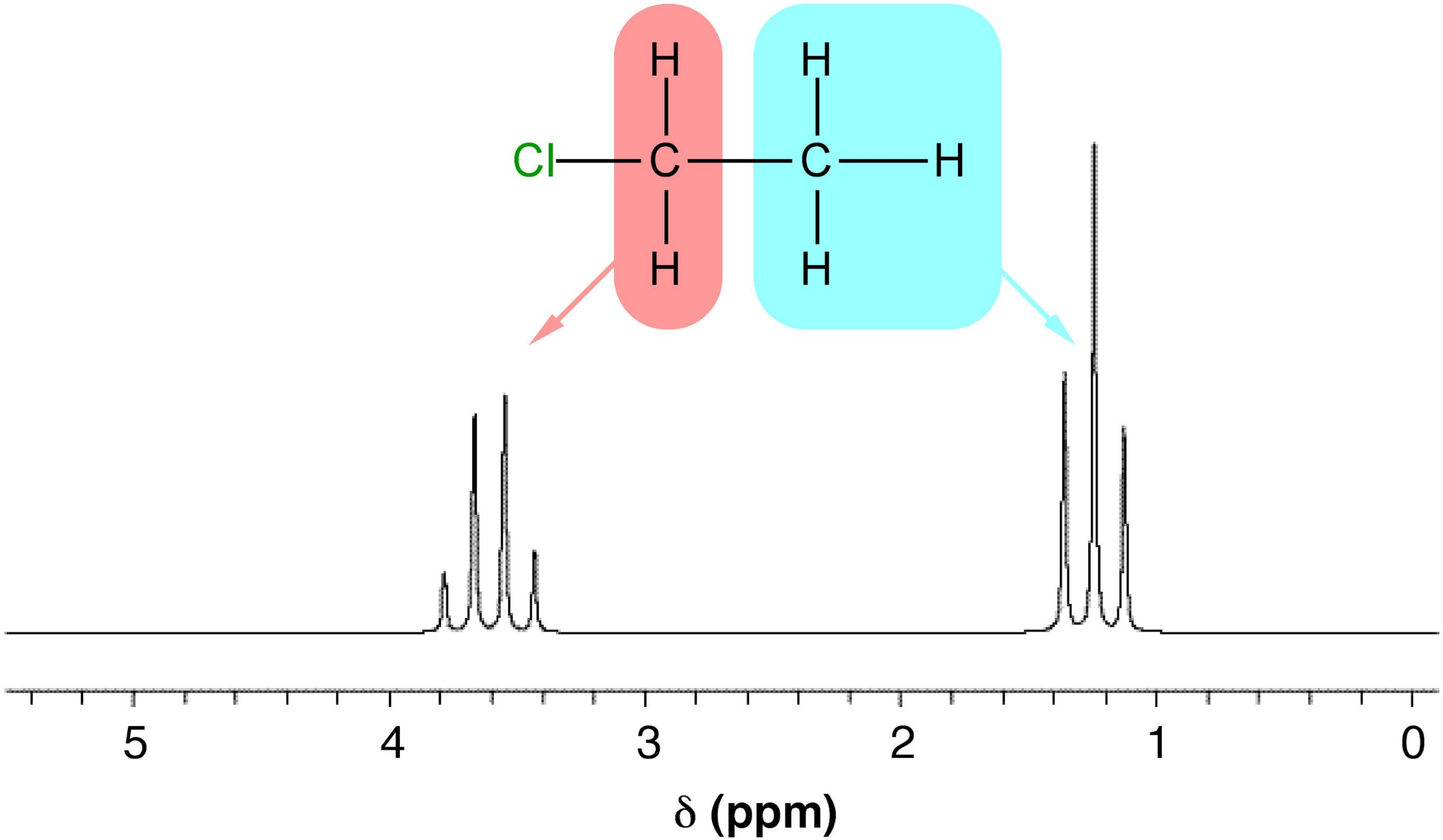
- Spin-Spin coupling depends on the way hydrogens are related to each other in the bonding arrangements within the molecule
- Two Rules
  1. If a proton H_a, has n protons as its nearest neighbors, that is n x H_b, then the peak of Ha will split into (n+1) peaks
  2. The ratio of the intensities of the lines of the split peak can be deduced from Pascal's triangle



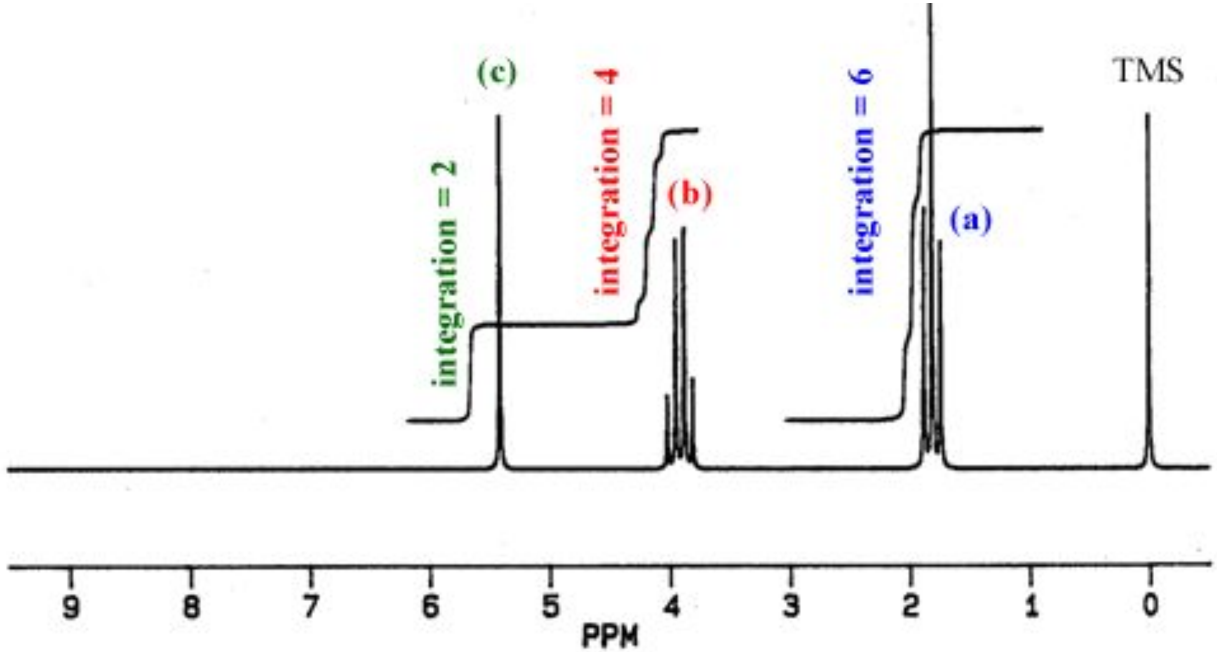
High Resolution ^{1}H NMR



High Resolution ^{1}H NMR



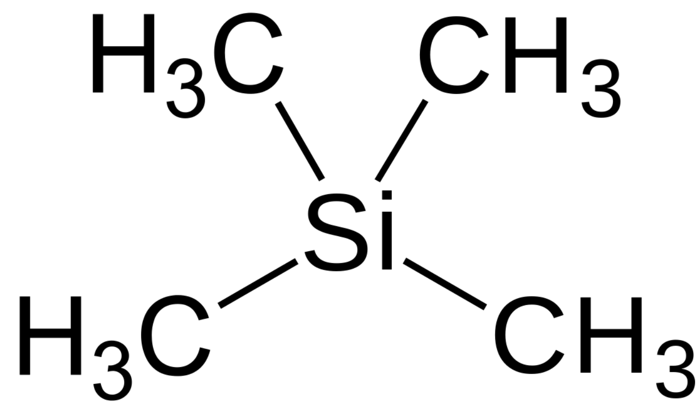
High Resolution ^{1}H NMR



Heights can be used to obtain the ratio of the number of protons in each environment

High Resolution ^{1}H NMR

- TMS is used because the 12 protons are in the same chemical environment causing a single peak which will be strong
- □ = 0 ppm, protons in organic compounds will typically absorb more downfield in relation to TMS
- TMS is inert so it is fairly unreactive and will not interfere with the sample being analyzed
- It can be easily removed from the sample because it is volatile with low boiling point

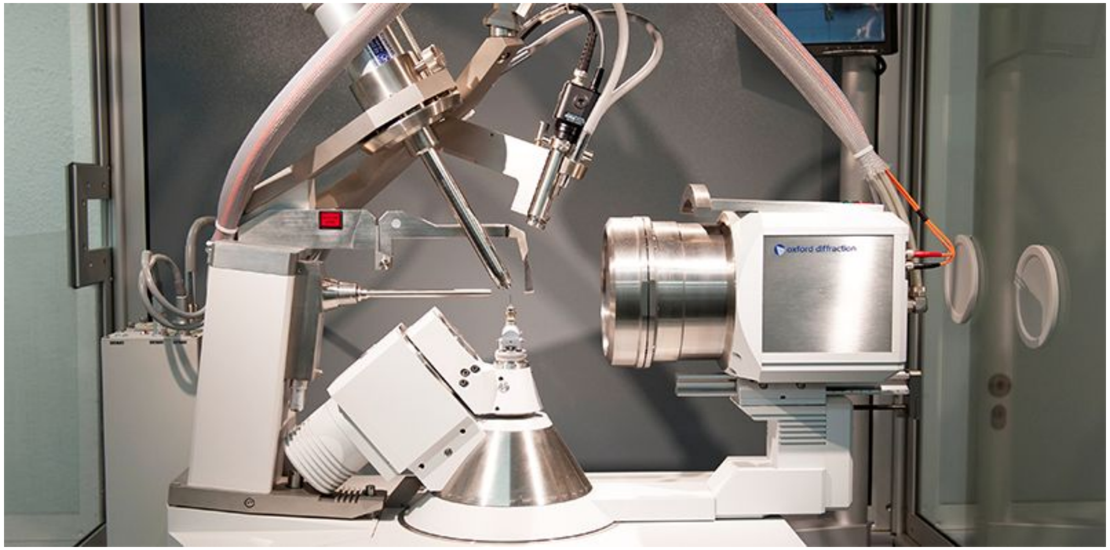


High Resolution ^1H NMR

- Protons in water molecules within human cells can be detected by magnetic resonance imaging (MRI), giving 3D view of organs in the human body
- MRI instruments can detect chemical changes in the brain
- This has allowed scientists to pinpoint specific regions of the brain itself where brain activity is taking place and gain an understanding of chemical principles of the thought process

X-Ray Crystallography

- The structural technique of single crystal X-ray crystallography can be used to identify the bond lengths and bond angles of crystalline structures, both organic and inorganic



X-Ray Crystallography

- The X-rays strike the crystals and are diffracted into many specific directions depending on the location of electrons within the sample
- The 3D model of the electron density can be created and the mean position of the atoms are calculated