

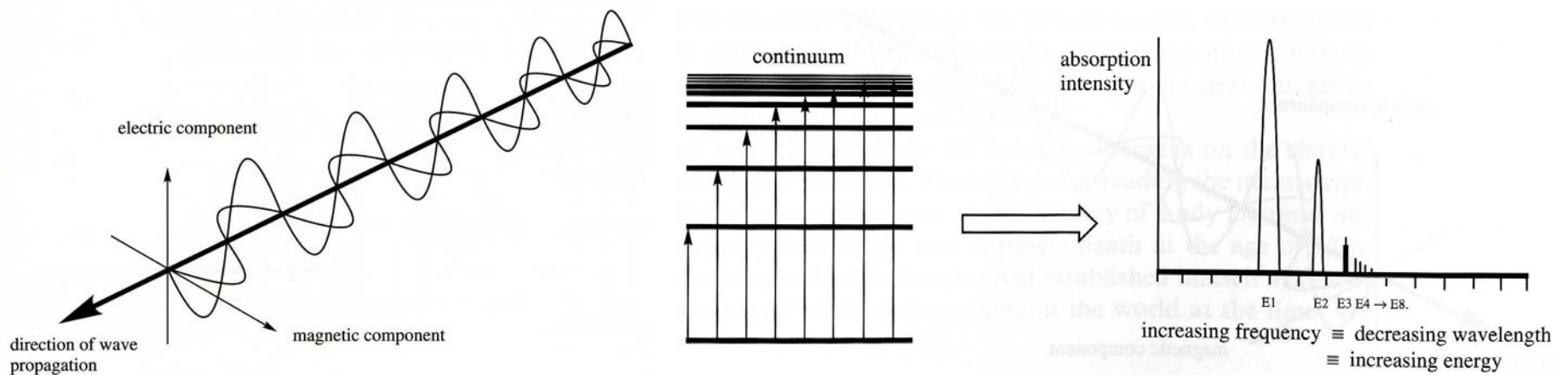
Spectroscopic Techniques

Outline

1. Vibrational Spectroscopy (IR and Raman)
2. UV-vis spectroscopy
3. Nuclear Magnetic Resonance (NMR)
4. Electron Spin Resonance (ESR)
5. X-ray spectroscopy
6. Electron spectroscopy
7. Mössbauer spectroscopy
8. Mass spectroscopy
9. Thermal analysis

Electromagnetic Radiation

Spectroscopic techniques all work on the principle of that, under certain conditions, *materials absorb or emit energy*



$$v\lambda = c$$

Quantized energy: photon

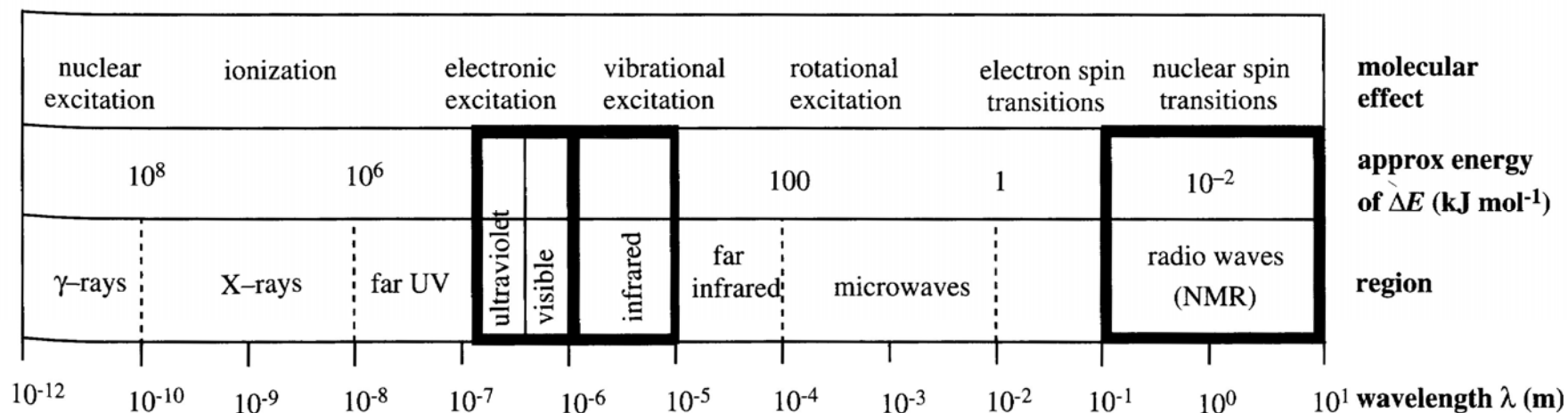
$$E = h\nu$$

$$\Delta E = h\nu = hc/\lambda$$

X-axis: Frequency or wavelength

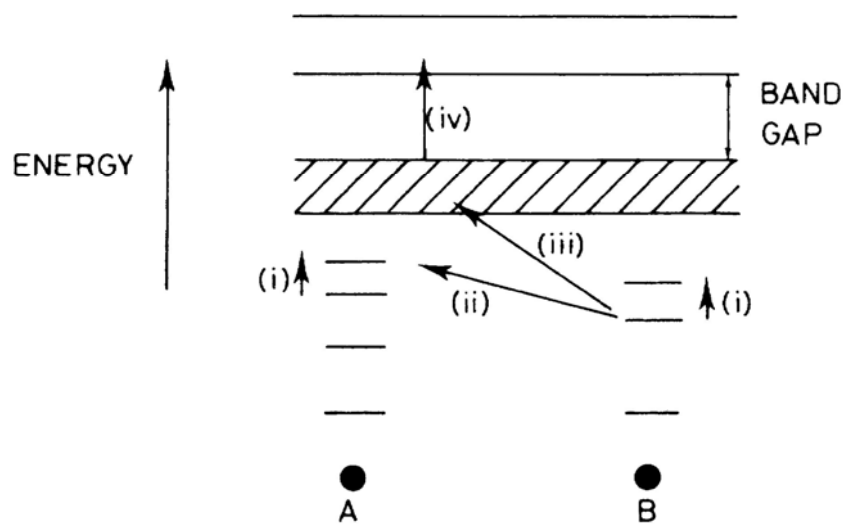
Electromagnetic Spectrum

Different spectroscopic techniques operate over different, limited frequency ranges within this broad spectrum, depending on the processes and magnitudes of the energy changes.



Visible and Ultraviolet Spectroscopy

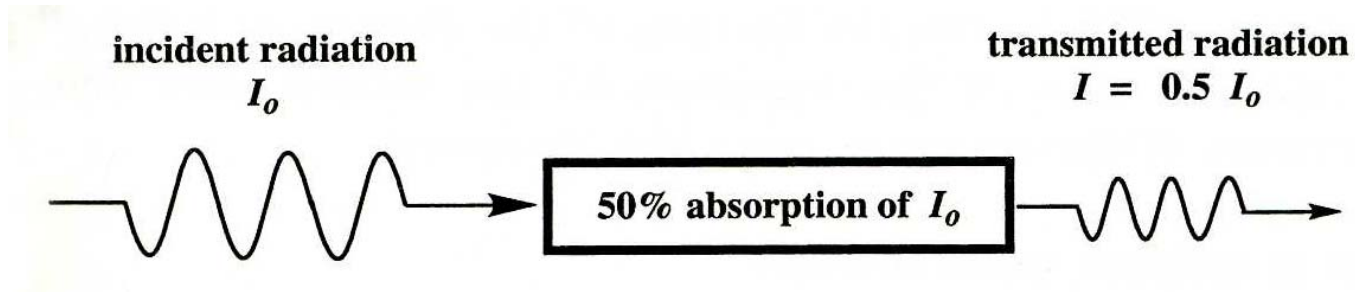
- Transitions in the *electronic energy levels* of the bonds of a molecule and results in excitation of electrons from *ground state* to *excited state*
- Energy changes: 10^4 to 10^5 cm^{-1} or 100 to 1000 kJ mol^{-1}



Four types of transitions:

- Within the same atom e.g. d-d or f-f transition
- To adjacent atom (charge transfer)
- To a delocalized energy band, conduction band (photoconductivity)
- Promotion of an electron from valence band to conduction band (bandgap in semiconductors)

Beer-Lambert Law



$$\log(I_0/I) = \epsilon cl$$
$$\epsilon = A/cl$$

ϵ : extinction coefficient

c : concentration

l : path length

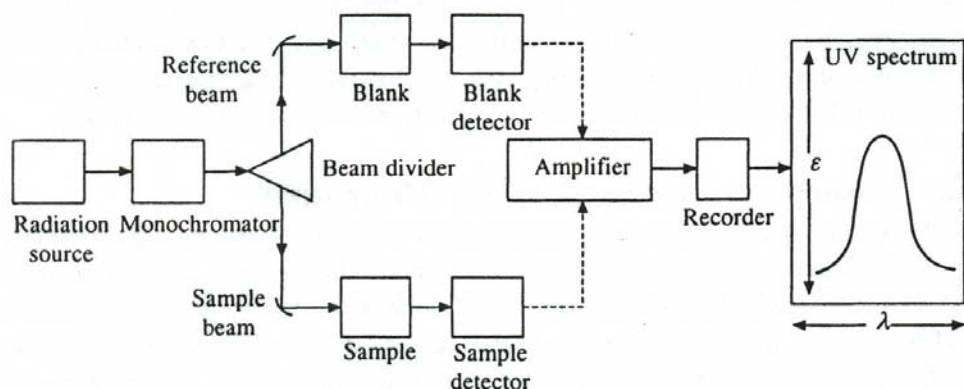
I_0 : incident radiation

I : transmitted radiation

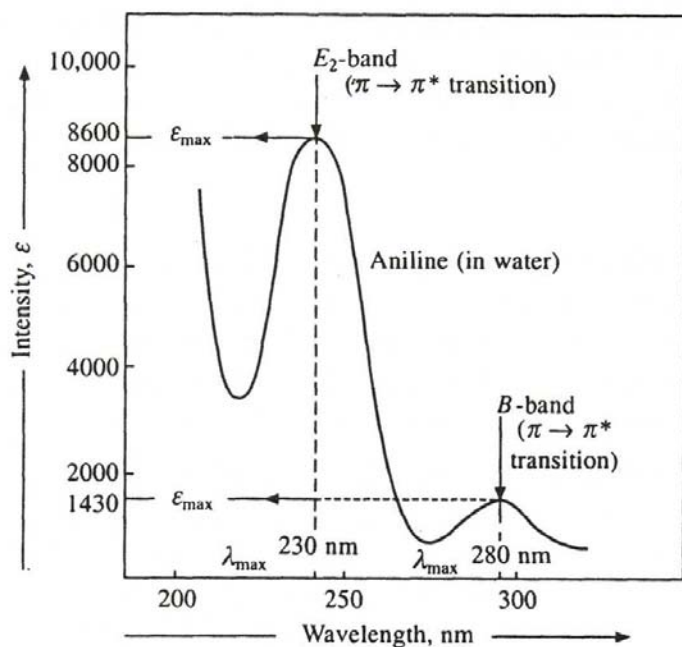
A : absorbance

ϵ value determine transition is *allowed* or *forbidden*

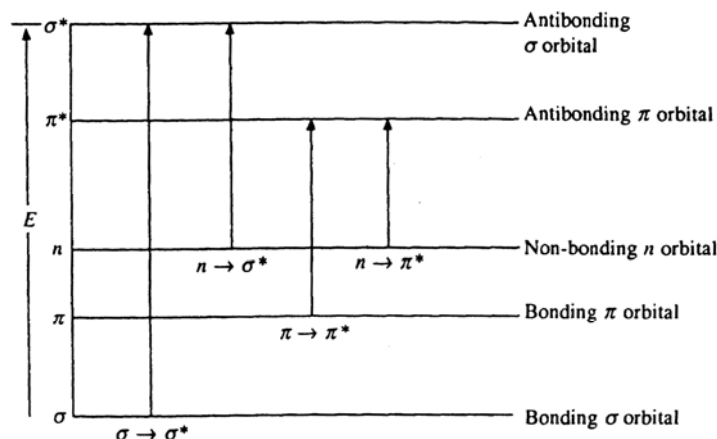
Recording and Interpreting UV-vis Spectra



- Determine the coordination environment of transition metal ions
- Detection of conjugation and elucidation of its nature



- (i) $\sigma \rightarrow \sigma^*$ (iii) $n \rightarrow \sigma^*$ (iii) $\pi \rightarrow \pi^*$ (iv) $n \rightarrow \pi^*$



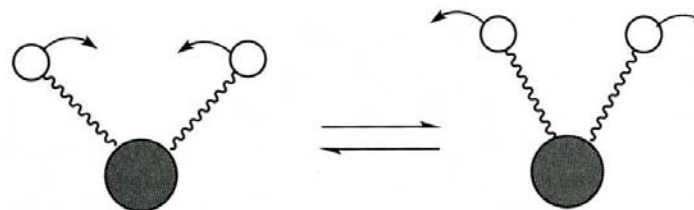
Vibrational Spectroscopy

Atoms in solids vibrate at frequencies of 10^{12} to 10^{14} Hz

Stretching



Bending



Hooke's Law:

$$\nu = (1/2\pi) \sqrt{k/\mu}$$

$$\mu = m_1 m_2 / (m_1 + m_2)$$

μ : reduced mass

ν : vibrational frequency

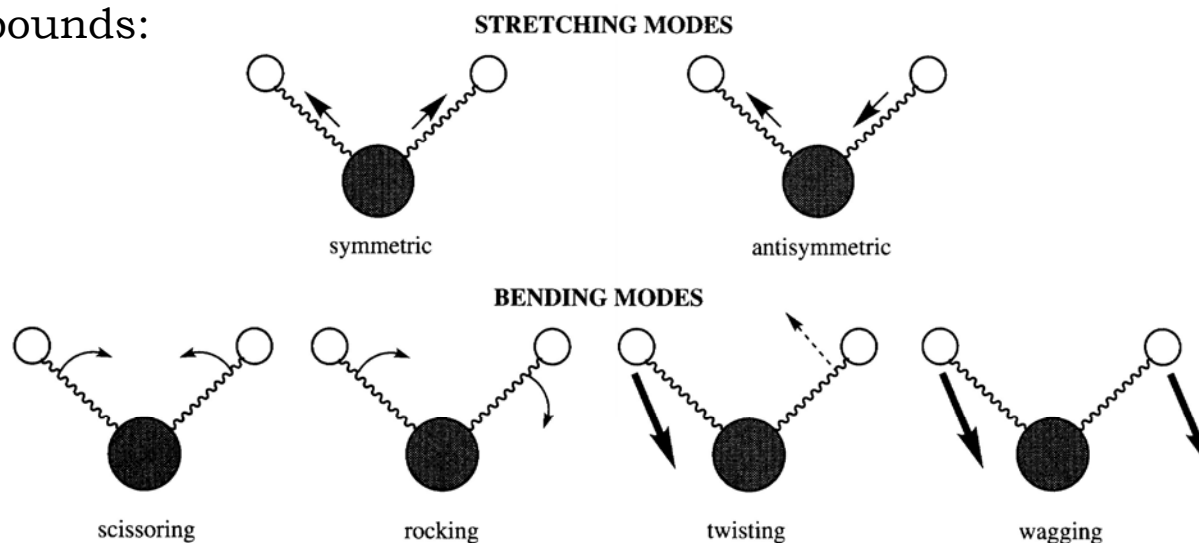
m : atomic mass

k : force constant

Identify the functional groups !

Fundamental Vibrational Modes

XY₂ compounds:



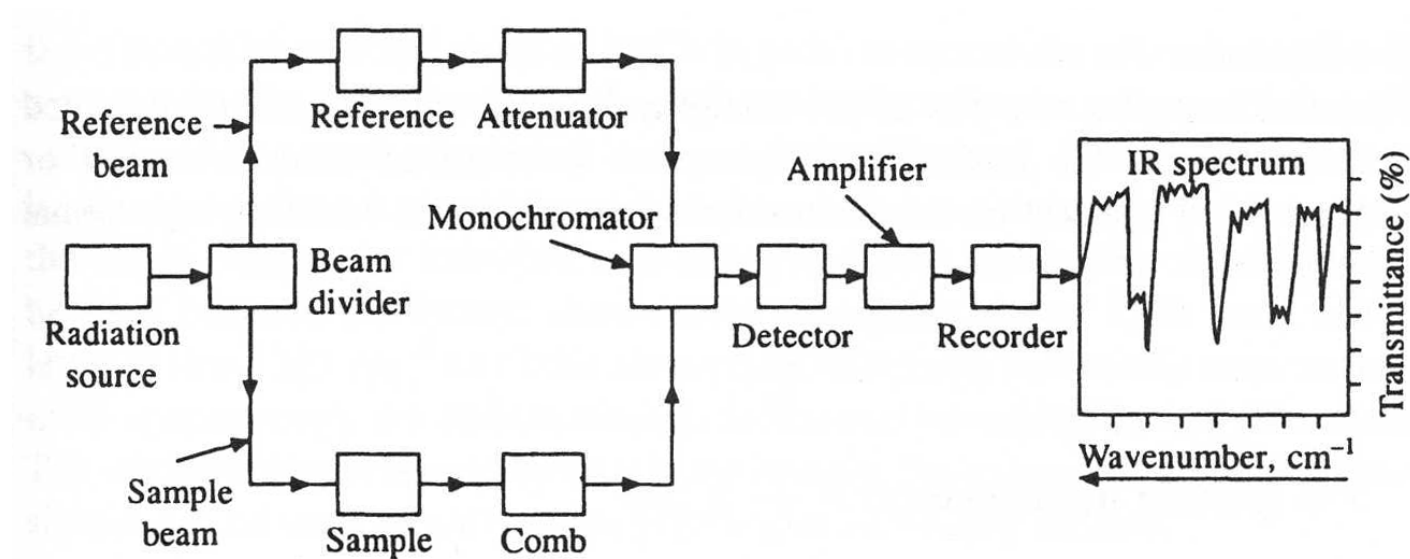
Linear molecule: $3N-5$ normal modes of vibration

Non-linear molecule: $3N-6$ normal modes of vibration

- Fundamental frequencies
- Overtone bands (multiples of fundamental vibrations)

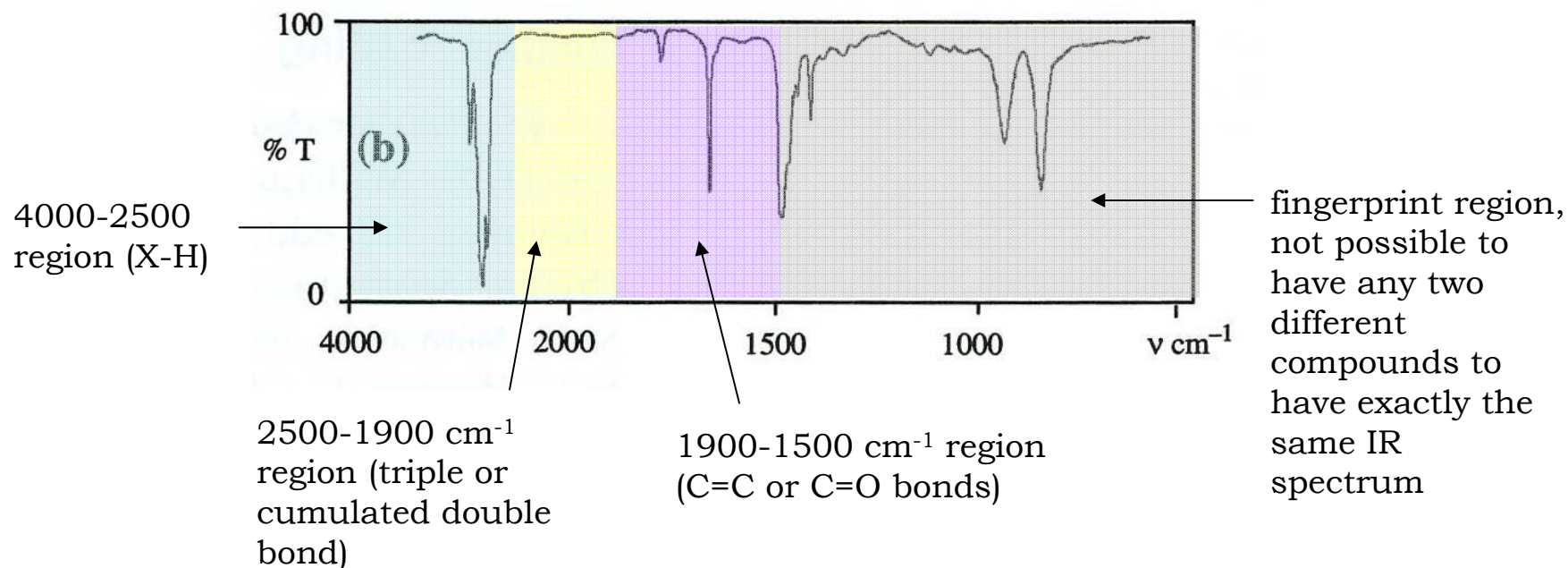
Infrared Spectroscopy

- Frequency of the incident radiation is varied and the quantity of radiation *absorbed or transmitted* by the sample is obtained
- $4000 - 400 \text{ cm}^{-1}$ ($2.5 - 25 \text{ }\mu\text{m}$)



- Solid:
- finely ground powder mixed with one or two drops of nujol
 - solid mixed with dry KBr powder to make a pressed disc

Infrared Spectra



- Identification
- Structural information
- Estimation of sample purity
- Calculation of force constant
- Monitor the progress of reaction
- Study of hydrogen bonding

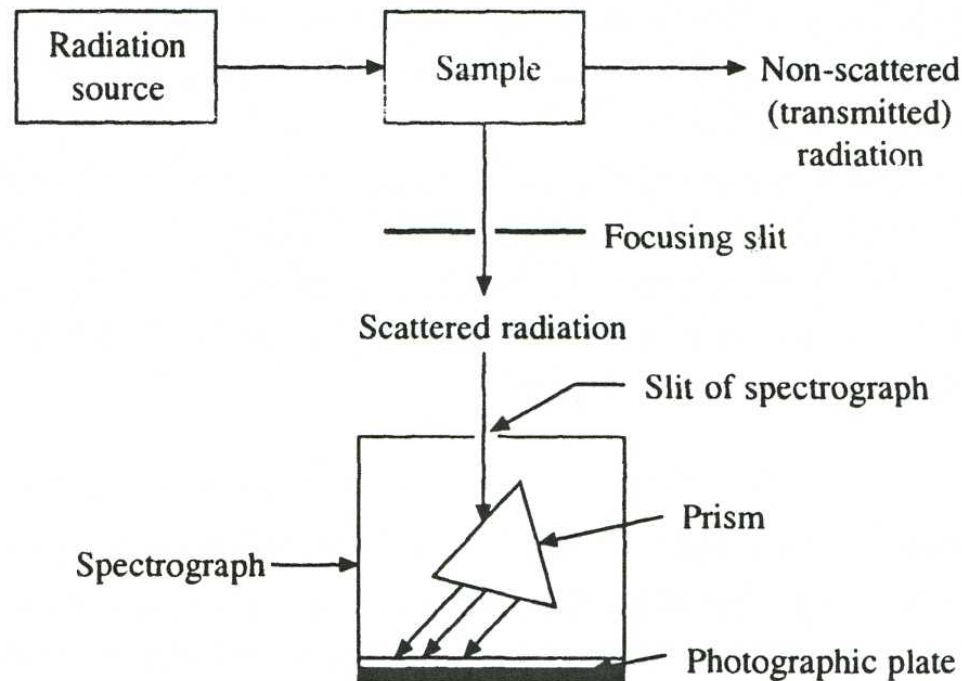
Selection rule for IR active transition:

Vibrations involve a *change of dipole moment!*

Raman Spectroscopy

Sir C.V. Raman:

“When a beam of strong radiation of a definite frequency is passed through a transparent substance, the radiation *scattered* at right angles has not only the original frequency (*Rayleigh Scattering*) but also some other frequencies, which are generally lower (*Stokes line*) and occasionally higher (*anti-Stokes line*) than that of the incident radiation”



Raman active: involve a *change of polarizability*

Origin of Raman Scattering

Quantum theory: $E_p + \frac{1}{2}mv_i^2 + hv_i = E_q + \frac{1}{2}mv_s^2 + hv_s$

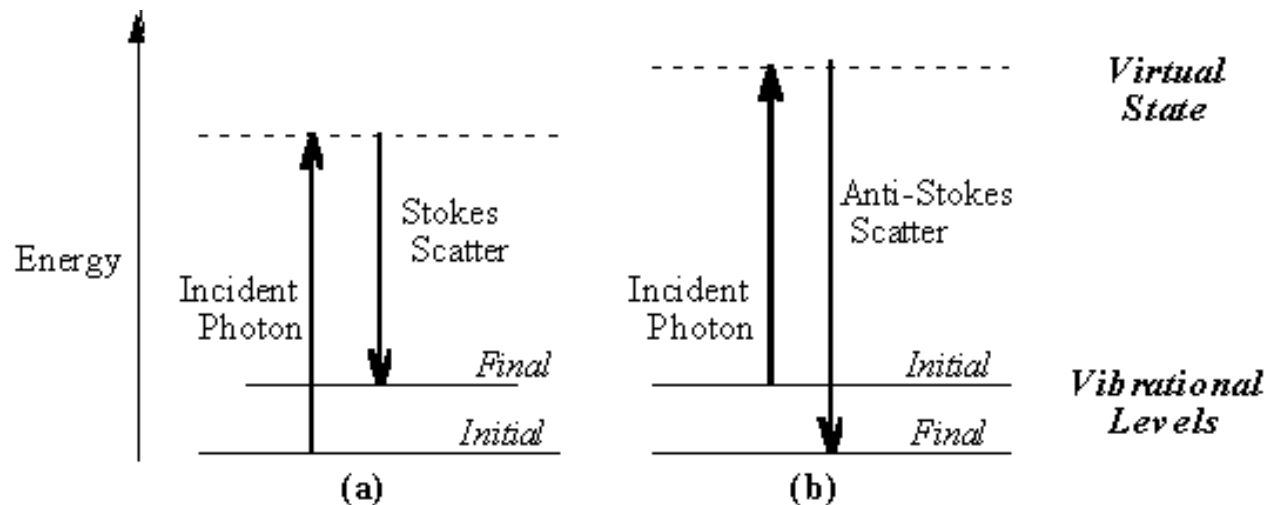
$$E_p + hv_i = E_q + hv_s$$

$$\nu_s = \nu_i + (E_p - E_q)/h$$

Rayleigh scattering: $E_p = E_q$; Stokes lines: $E_p < E_q$; anti-Stokes lines: $E_p > E_q$

Number of molecules in the particular state E_p :

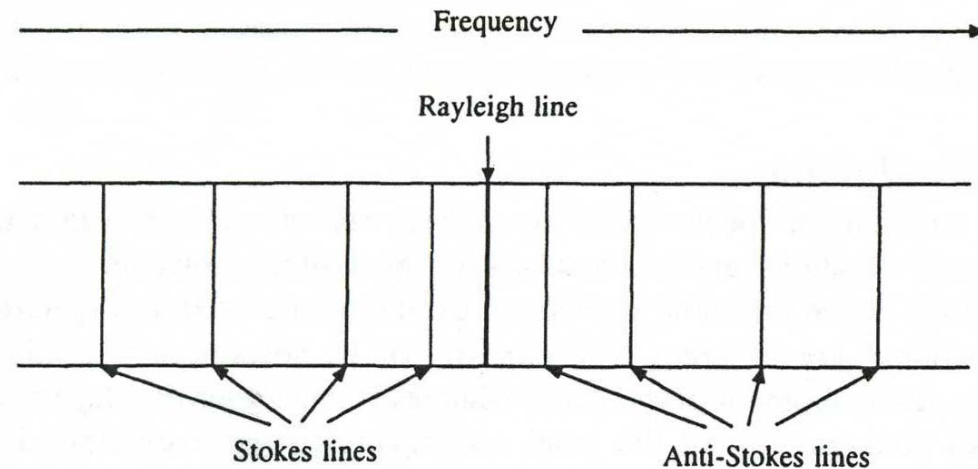
$$N_p = CNg_p e^{-E_p/kT}$$



Raman Scattering

Raman frequency *shift*:

$$\Delta\nu = \nu_i - \nu_s$$



The frequency difference is constant and characteristic of the substance exposed to radiation and is completely *independent of the incident radiation*

- Raman lines are symmetrically displaced about the parent line
- Intensity of Stokes lines > anti-Stokes lines
- Raman shifts represent the frequencies of absorption bands of substance
- Identical with absorption frequencies obtained from IR spectrum
- Complementary to IR spectroscopy (symmetrical bonds are Raman active)

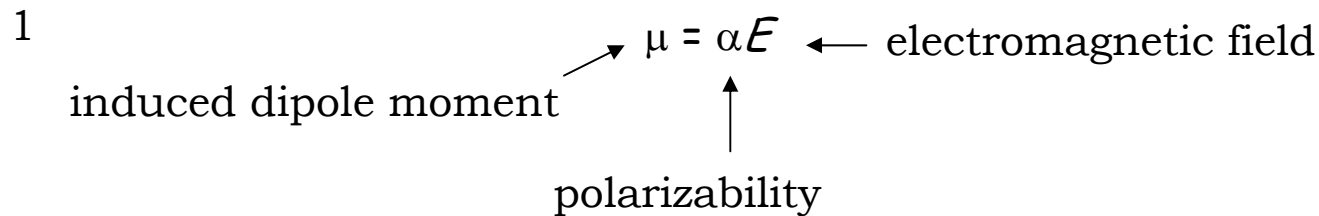
Raman *vs.* IR

Raman spectra	IR spectra
Originate from scattering of radiation	Originate from absorption of radiation
Change in molecular polarizability	Change in dipole moment
Weak in intensity	Strong in intensity
Water can be used as solvent	Water lead to strong absorption and attack the holder
Optical system: Glass, quartz	Optical system: NaCl, KBr
Record by using a beam of monochromatic radiation	Record by using a beam of radiation having a large number of frequencies
Homonuclear diatomic molecules are Raman active	Homonuclear diatomic molecules are IR inactive

Surface Enhanced Raman Spectroscopy (SERS)

SERS is a Raman spectroscopic technique that provides *greatly enhanced Raman signal* from Raman active analyte molecules that have been adsorbed onto certain *metal nanoparticles*

- Enhancement: $10^4 - 10^6$, up to 10^{14}
- *Electromagnetic* enhancement and *chemical* enhancement



- 2 The formation of a charge-transfer complex between the surface and analyte molecule \rightarrow resonance enhancement

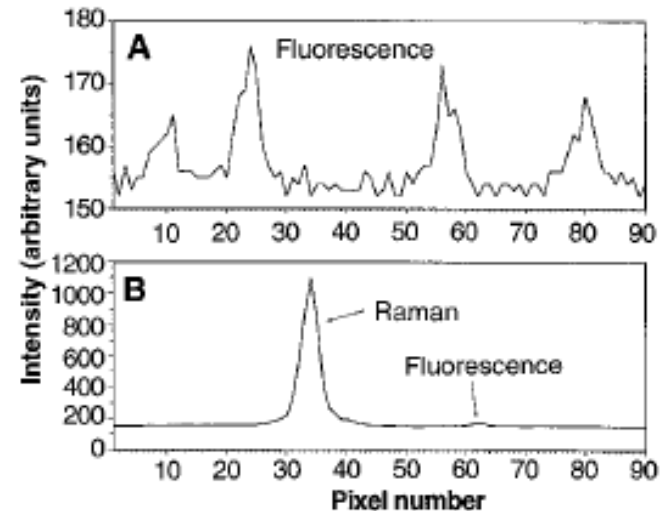
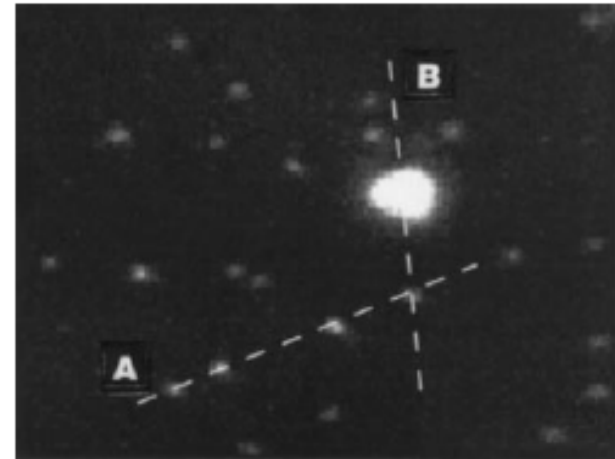
Single Molecule SERS

Probing Single Molecules and Single Nanoparticles by Surface-Enhanced Raman Scattering

Shuming Nie* and Steven R. Emory

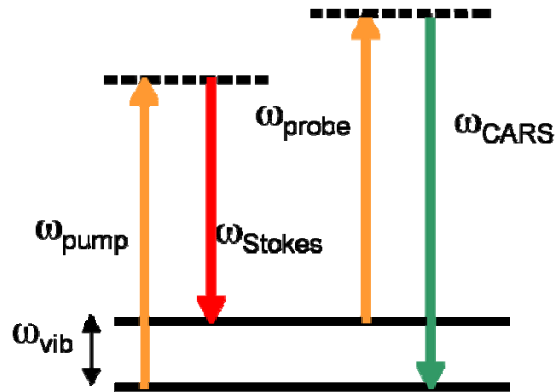
Optical detection and spectroscopy of single molecules and single nanoparticles have been achieved at room temperature with the use of surface-enhanced Raman scattering. Individual silver colloidal nanoparticles were screened from a large heterogeneous population for special size-dependent properties and were then used to amplify the spectroscopic signatures of adsorbed molecules. For single rhodamine 6G molecules adsorbed on the selected nanoparticles, the intrinsic Raman enhancement factors were on the order of 10^{14} to 10^{15} , much larger than the ensemble-averaged values derived from conventional measurements. This enormous enhancement leads to vibrational Raman signals that are more intense and more stable than single-molecule fluorescence.

- Silver colloidal nanoparticles
- Enhancement factor $\sim 10^{14}$ to 10^{15}
- More intense and stable than single-molecule fluorescence
- Molecular information
- No photobleaching



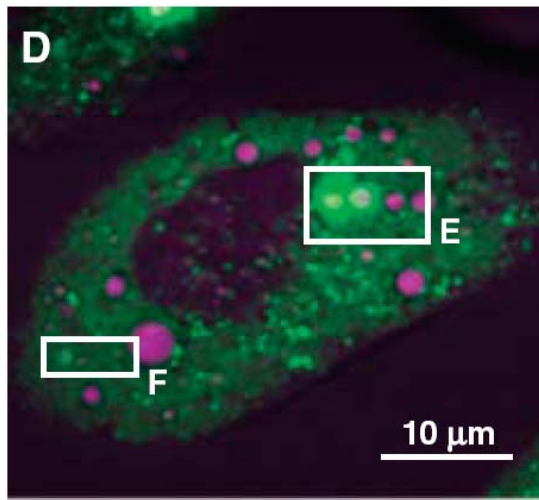
S. Nie and S. R. Emory, *Science* **275** 1102 (1997)

Coherent Anti-Stokes Raman Spectroscopy (CARS)



- Non-linear optical process (three wave mixing)
- Stronger signal ($\sim 10^5$) than spontaneous Raman response
- Blue shift

Biomedical imaging:



- Intrinsic vibrational contrast
- Strong signal
- Enable 3D imaging
- Higher frequency than fluorescence
- Little scattering and absorption of the near-infrared excitation beams (deep penetration and reduced photodamage)

Nuclear Magnetic Resonance Spectroscopy (NMR)

Absorption spectroscopy: radio-frequency region 3 MHz to 30000 MHz

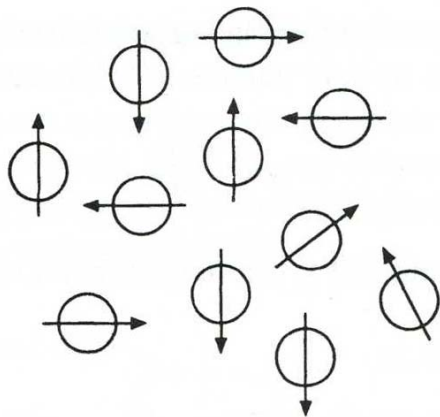
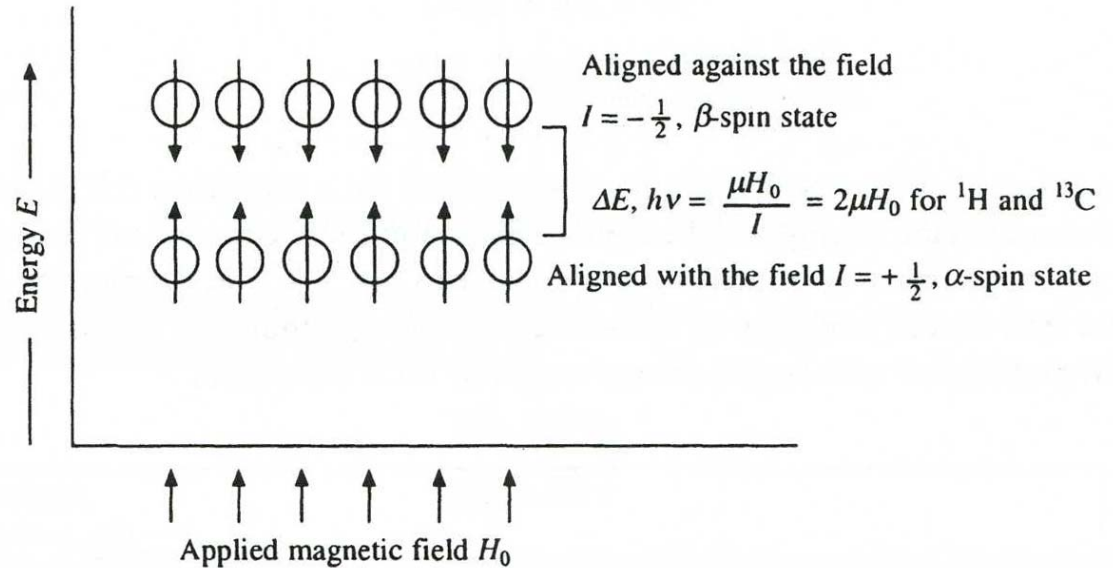
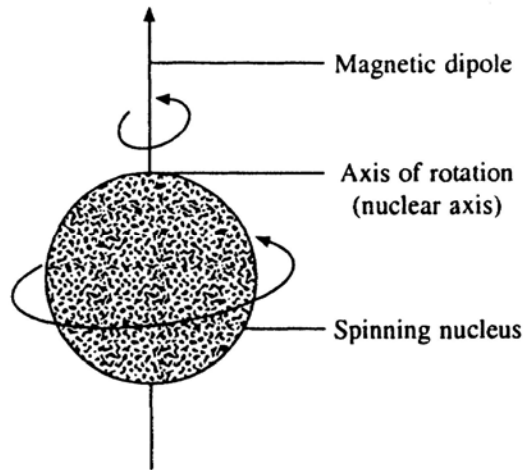
Transition between magnetic energy levels of the nuclei

Atomic nuclei possess *spin* (angular momentum, with *half integer spin* number)

Mass number	Atomic number	Spin number I	Examples ¹
Odd	Odd or even	$\frac{1}{2}$	^1H , ^{13}C , ^{15}N , ^{19}F , ^{31}P
		$\frac{3}{2}$	^{11}B , ^{35}Cl , ^{37}Cl , ^{79}Br , ^{81}Br
		$\frac{5}{2}$	^{127}I , ^{17}O
Even	Even	0	^{12}C , ^{16}O , ^{32}S , ^{34}S
		(no spin)	
Even	Odd	1	^{14}N , ^2H (or D)
		3	^{10}B

Theory of NMR

Spinning nuclei behave like a tiny bar magnet with a magnetic moment μ

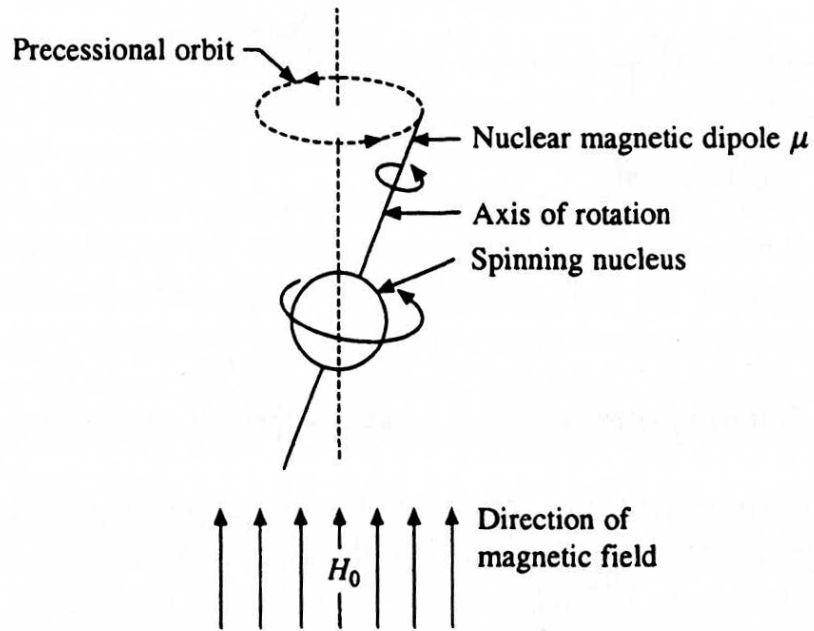


$$\nu = \gamma H_0 / 2\pi$$

$$\gamma = 2\pi\mu / hI$$

$$h\nu = \Delta E = \mu H_0 / I = 2\mu H_0$$

Theory of NMR



$$\omega_0 = \gamma H_0$$

$$\omega_0 = 2\pi\nu$$

$$2\pi\nu = \gamma H_0$$

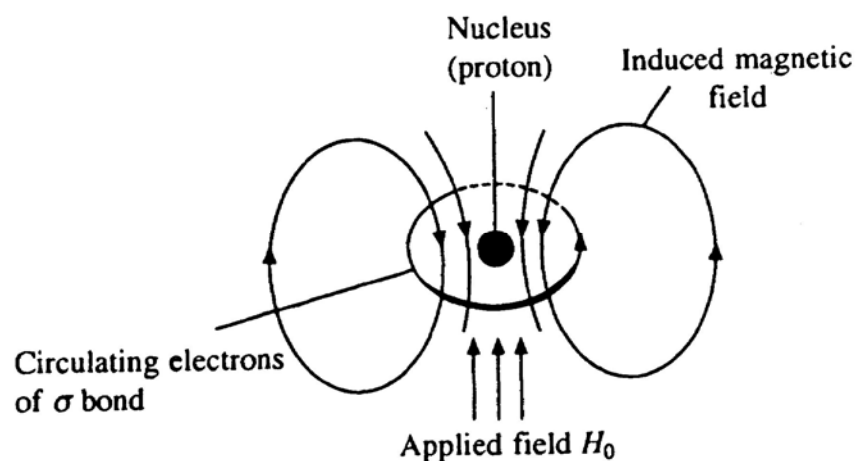
The precessional frequency of spinning nucleus is exactly equal to the frequency of EM radiation necessary to induce a transition from one nuclear spin state to another

$$\frac{N_\alpha}{N_\beta} = e^{\Delta E/RT}$$

N_α & N_β : population of α and β spin states

- Probability of observing absorption of energy is quite small
- Larger H_0 and lower T lead to higher sensitivity

Shielding → Chemical Shift



Chemical shift:

$$\delta \text{ (ppm)} = \frac{\text{chemical shift (Hz)}}{\text{oscillator frequency (Hz)}} \times 10^6$$

$$\delta = (\nu - \nu_{\text{ref}}) / \nu_{\text{ref}}$$

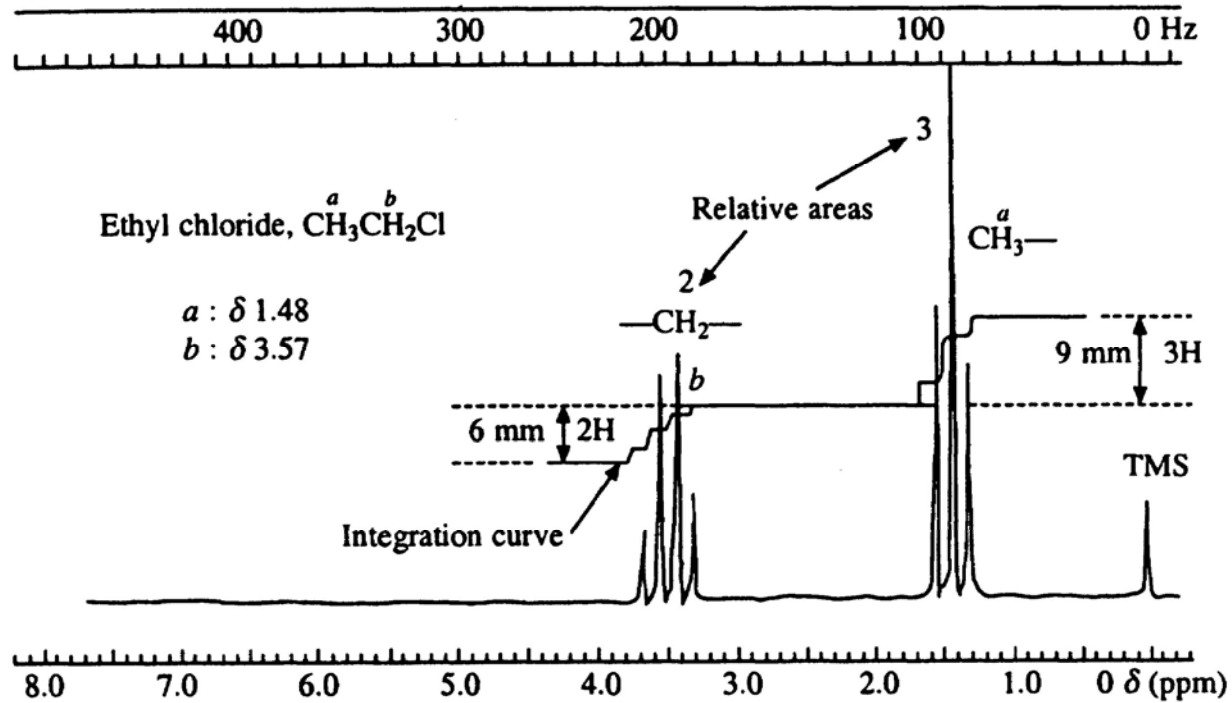
Reference compound: TMS

Circulating electron cloud:

- Shield or deshield applied field
- Resonance at different frequencies

Differences in the chemical environment modify the electron density and distribution about nuclei

NMR Spectra



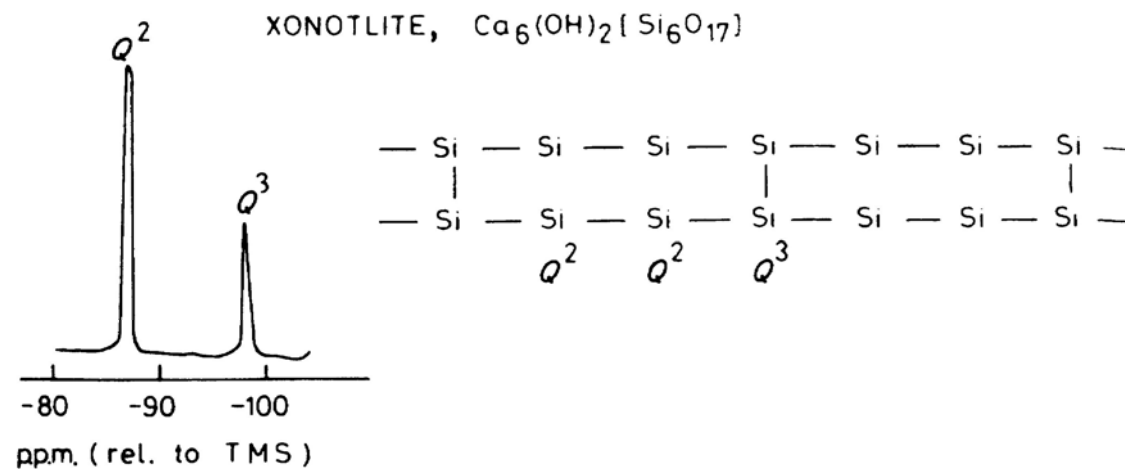
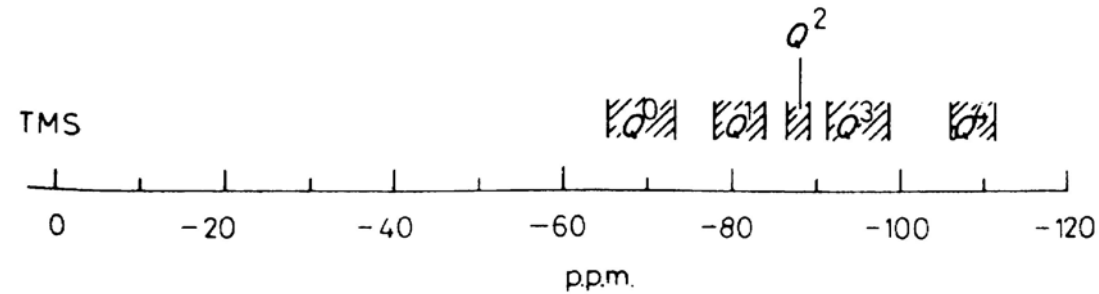
- Chemical shift: chemical environment
- Coupling: how nuclei interact with each other
- Intensity: number of nuclei

Solid State NMR

Magic angle spinning technique:

Sample is rotated at a high velocity at a critical angle of 54.74° to the applied magnetic field

^{29}Si NMR:



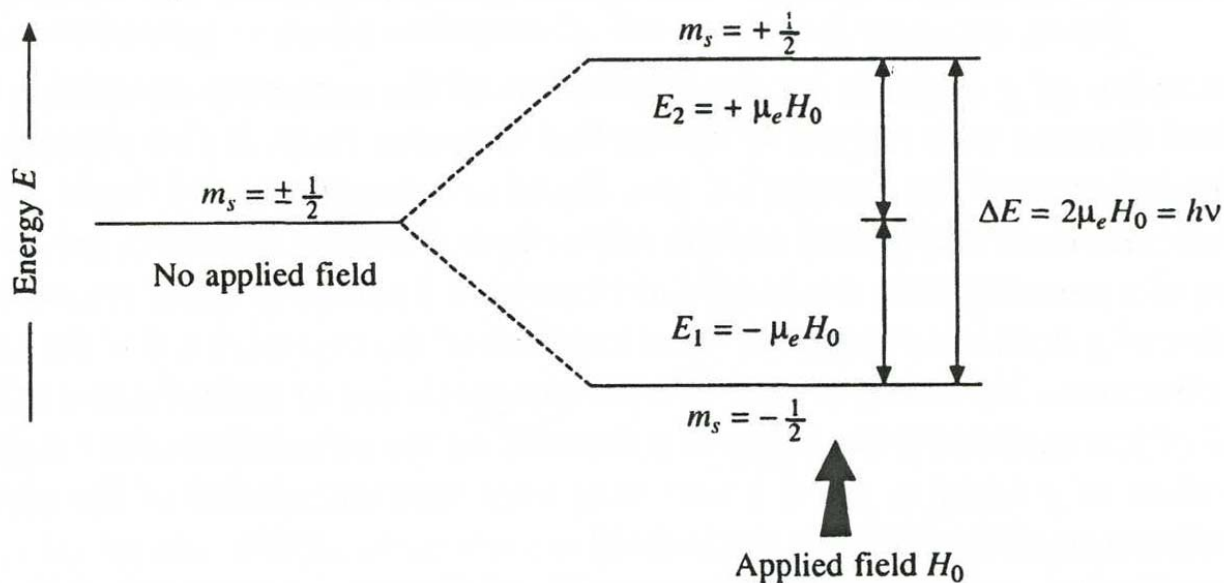
Electron Spin Resonance (ESR) Spectroscopy

It detects changes in *electron spin* configuration in substance containing one or more unpaired electrons

Absorption spectroscopy, operate at microwave frequency $10^4 - 10^6$ MHz ($\sim 1.0 \text{ J mol}^{-1}$)

Stable paramagnetic substances: simple molecules (e.g. NO, O₂) and ions of transition metals and their complexes e.g. Fe³⁺, [Fe(CN)₆]³⁻

Unstable paramagnetic substances: free radicals



Theory of ESR

Absorption of energy occurs at:

$$\Delta E = h\nu = g\beta_e H_0$$

H_0 : applied magnetic field

Bohr magneton:

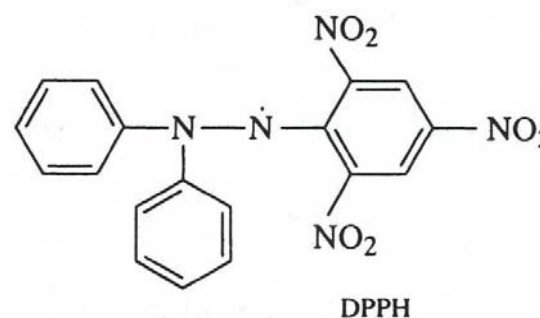
$$\beta_e = eh/4\pi mc = 9.273 \times 10^{-24} \text{ JT}^{-1}$$

g factor (g): depends on the particular ion, its oxidation state and coordination number

Determination of g values of free radicals:

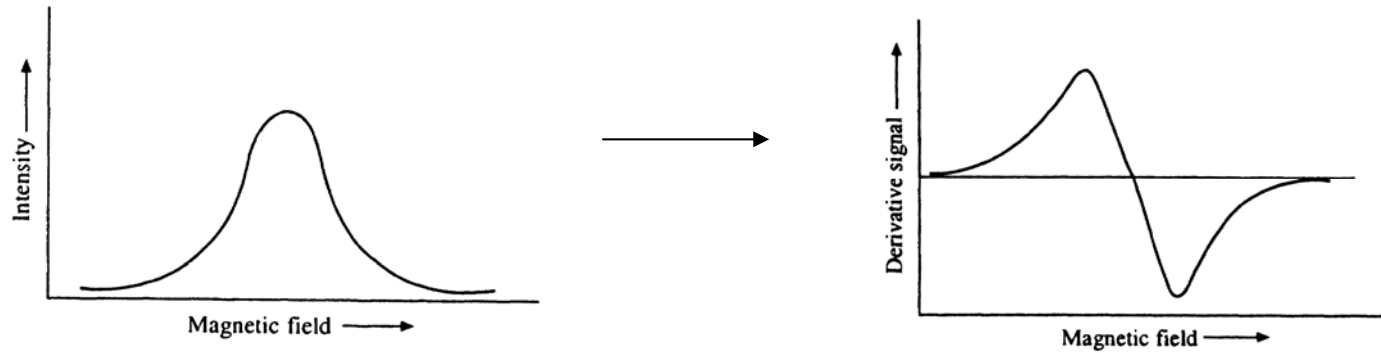
Reference substance: $g = 2.0036$

$$g = g_{\text{ref}} [1 - (\Delta H_0 / H)]$$



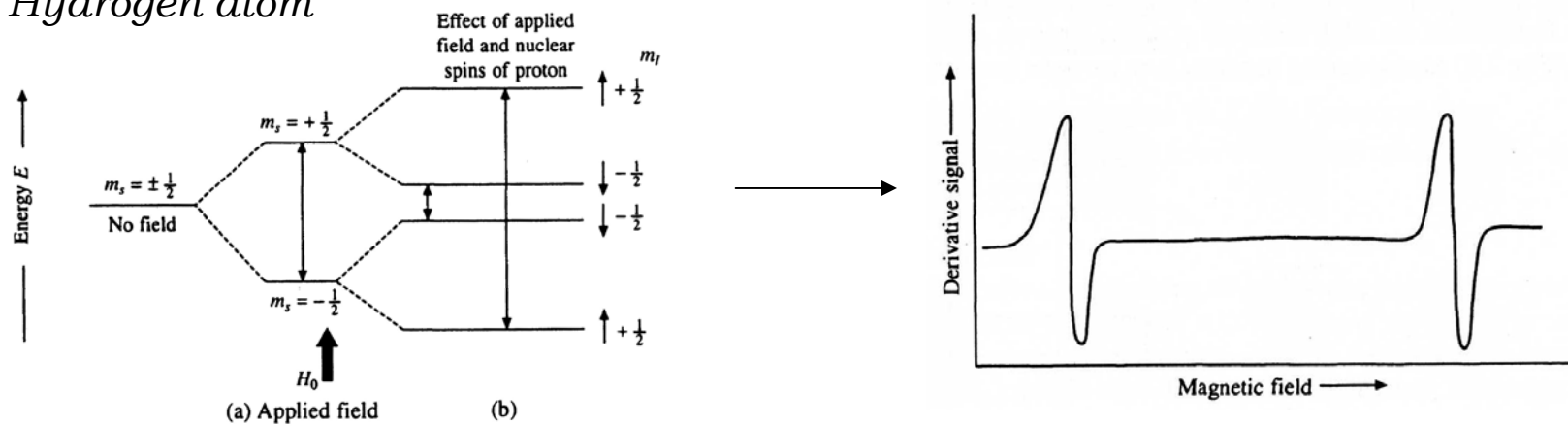
ESR Spectrum

First derivative of the absorption

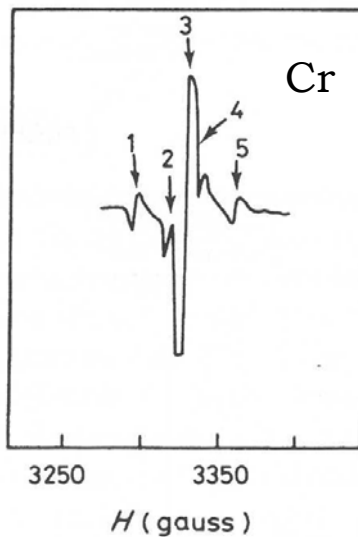
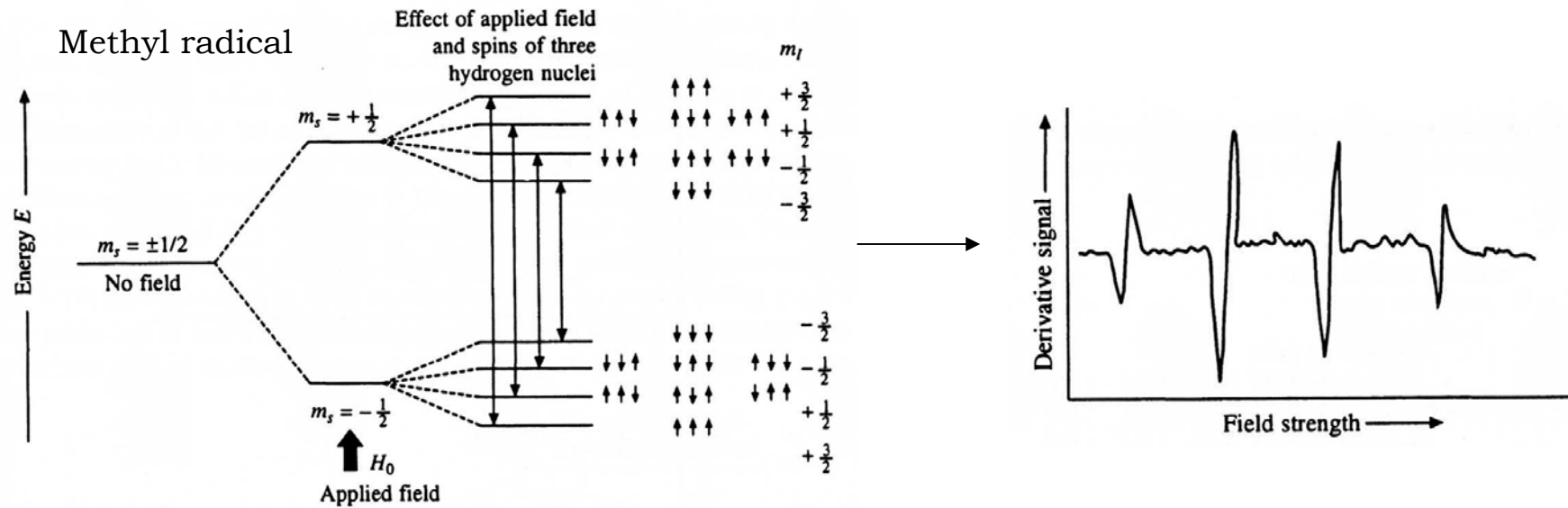


Hyperfine structure:

Hydrogen atom



ESR Spectrum



Associated with the unpaired electrons of the *isotope*, for example

Naturally occurring Cr is a mixture of ^{52}Cr (nucleus spin $I = 0$) and ^{53}Cr (nucleus spin $I = 3/2$)

NMR *vs.* ESR

NMR spectroscopy

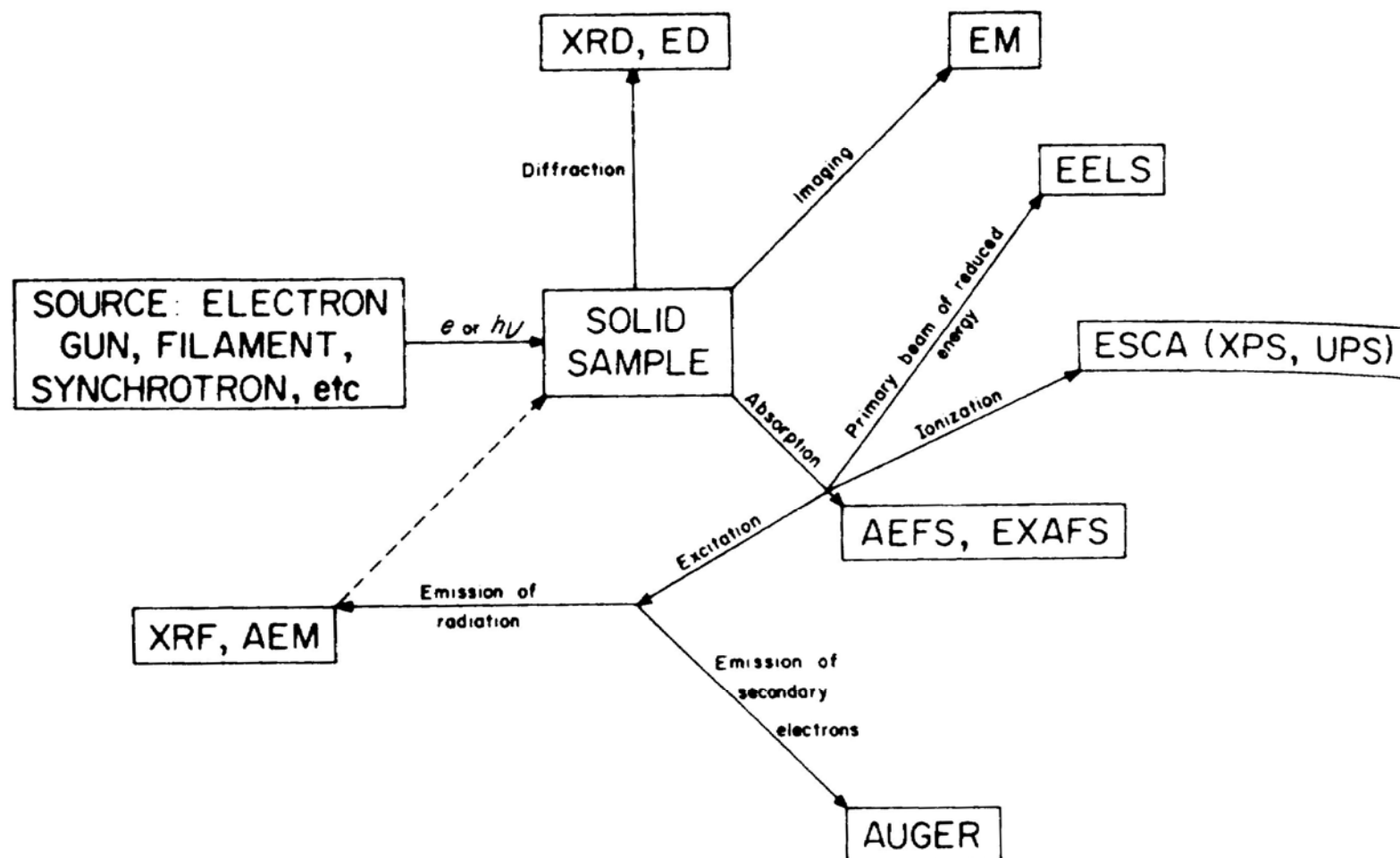
1. Different energy states are produced due to the alignment of the **nuclear** magnetic moments relative to the applied magnetic field and a transition between these energy states occurs on the application of an appropriate frequency in the radio frequency region.
2. NMR absorption positions are expressed in terms of **chemical shifts**.
3. Nuclear spin-spin coupling causes the splitting of NMR signals.

ESR Spectroscopy

1. Different energy states are produced due to the alignment of the **electronic** magnetic moments relative to the applied magnetic field and a transition between these energy states occurs on the application of an appropriate frequency in the microwave region.
2. ESR absorption positions are expressed in terms of **g values**.
3. Coupling of the electronic spin with nuclear spins (hyperfine coupling) causes the splitting of ESR signals.

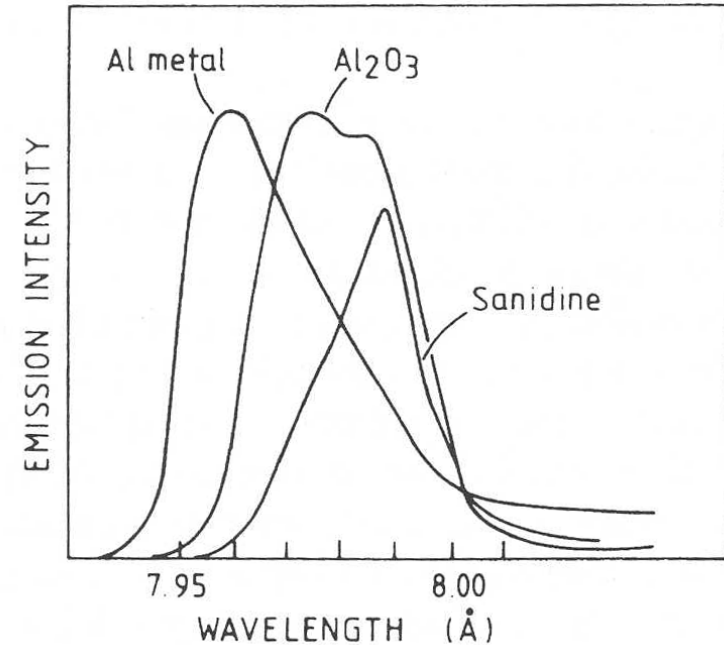
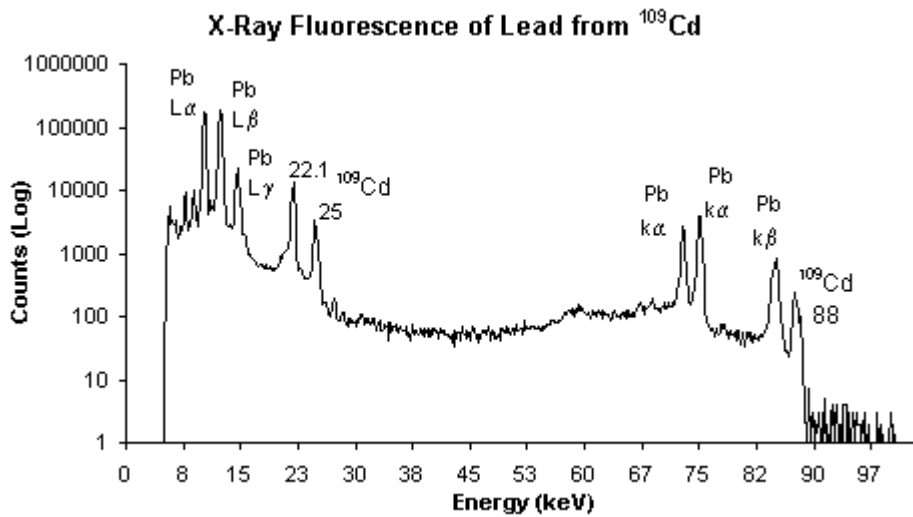
X-ray Spectroscopy

X-ray: Diffraction, Emission and Absorption



X-ray Emission

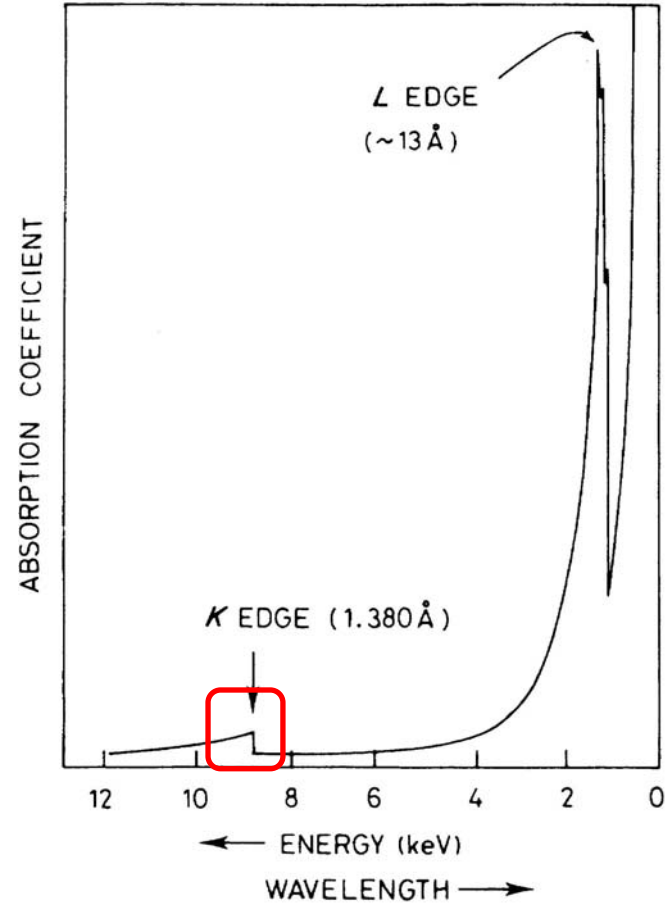
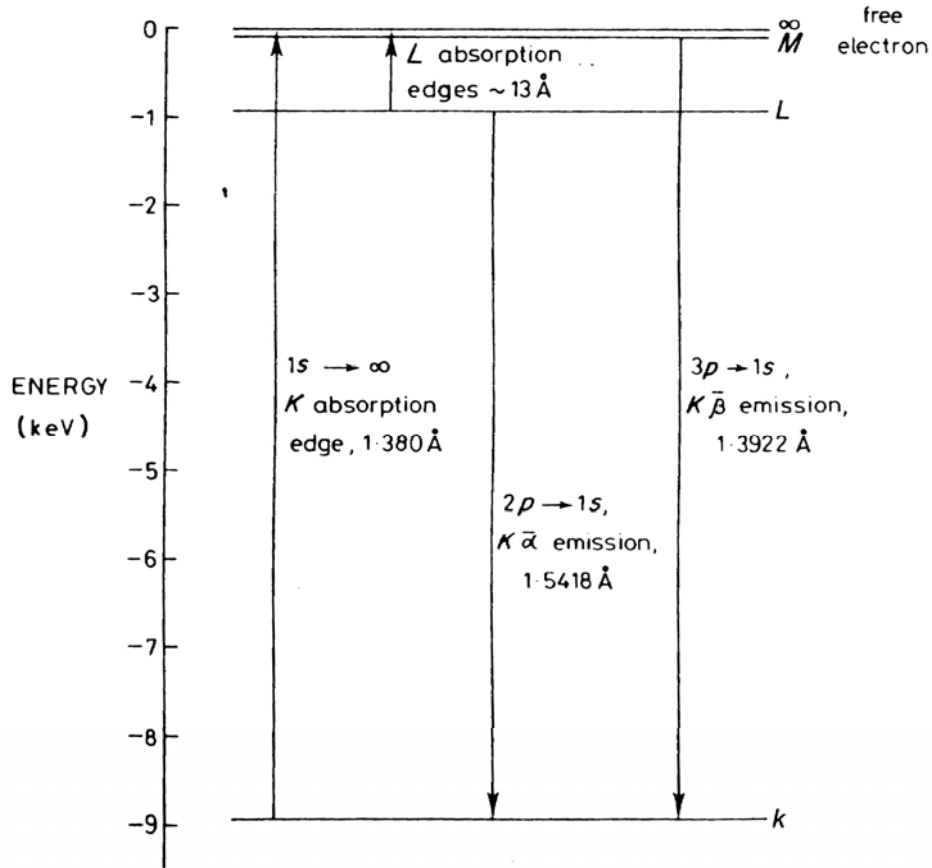
X-ray Fluorescence (XRF)



$$\lambda^{-1/2} = C(Z - \sigma)$$

Peak positions vary slightly with local environment of atoms such as coordination numbers and bond distances

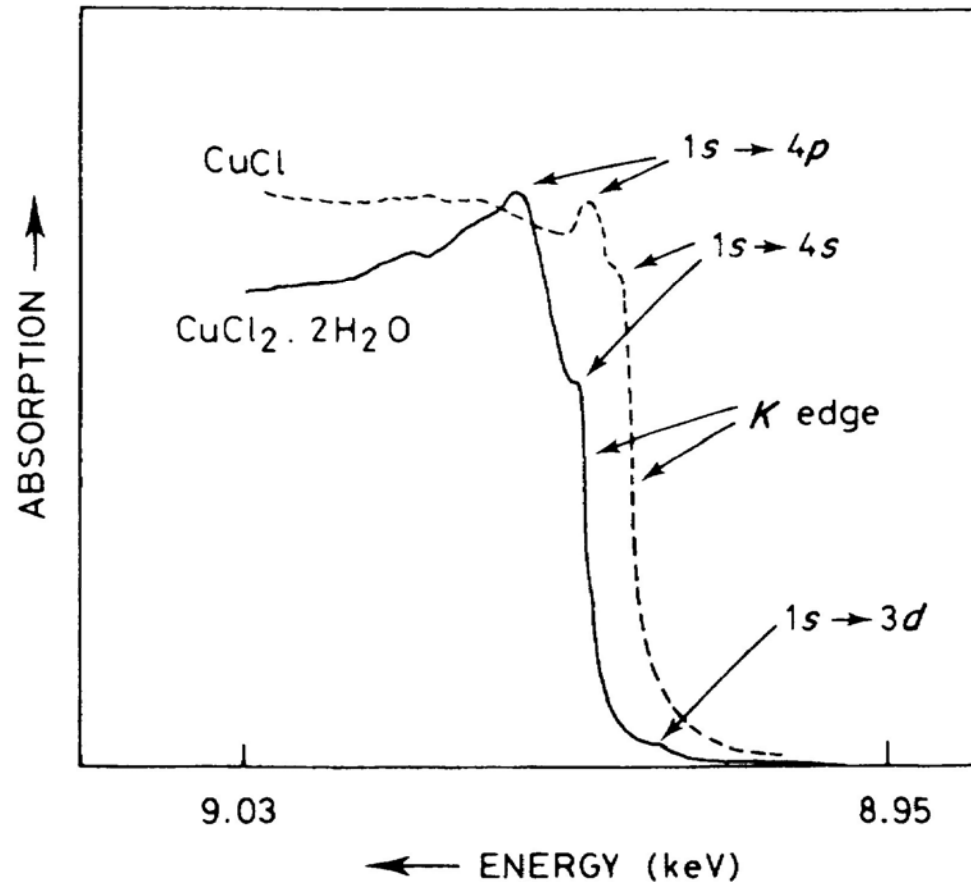
Absorption Techniques



Electron may leave the atom with a net kinetic energy:

$$E = h\nu - E_0$$

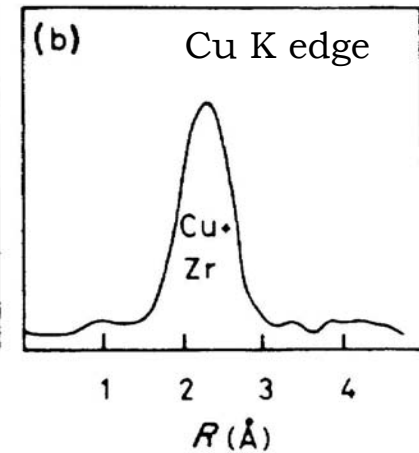
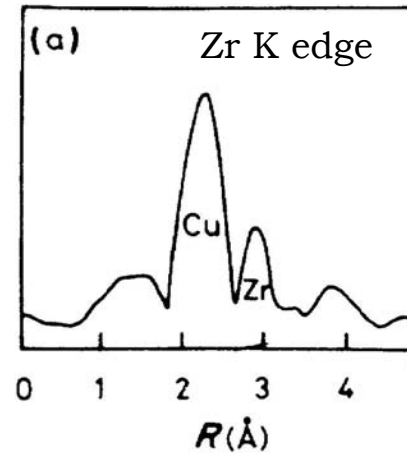
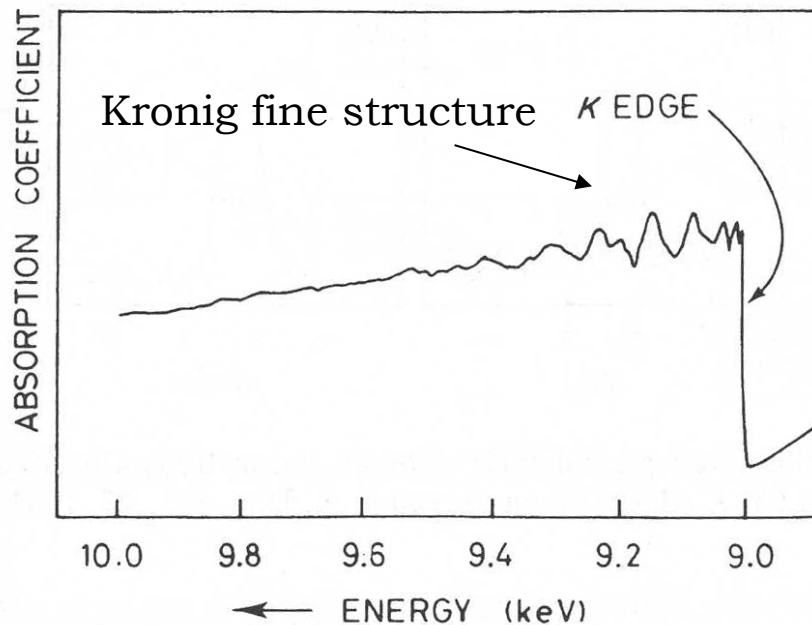
X-ray Absorption Near Edge Structure (XANES)



Fine structures on the an absorption edge

The peak positions depend on details of oxidation state, site symmetry, surrounding ligands and the nature of bonding

Extended X-ray Absorption Fine Structure (EXAFS)



In-situ electron diffraction event

Coordination number and bond distance

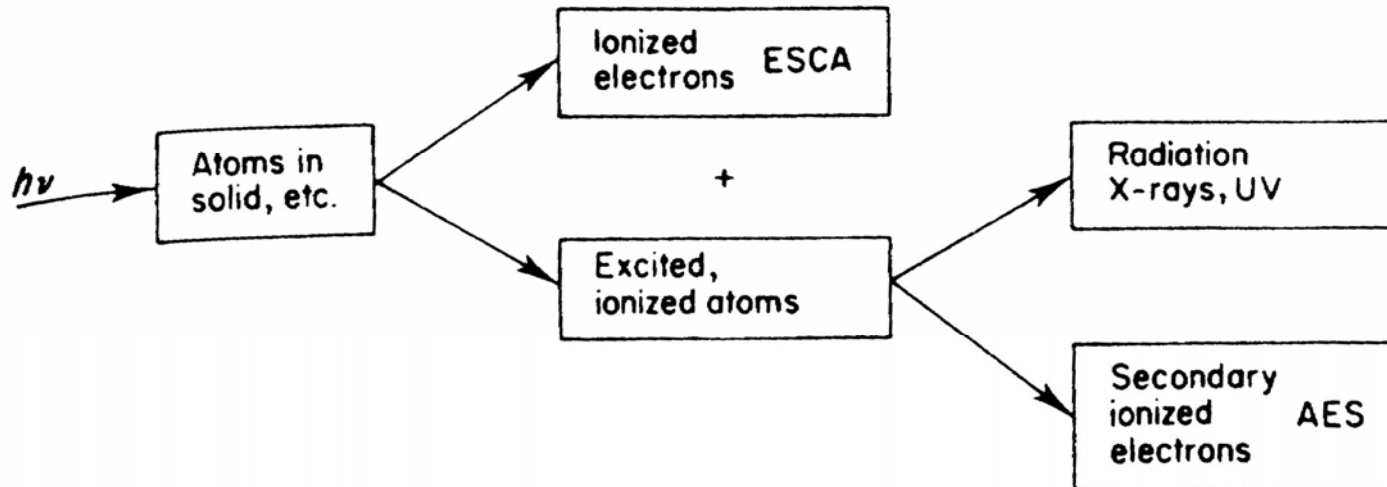
Equally suitable for non-crystalline and crystalline materials

Local environment of each element may be determined

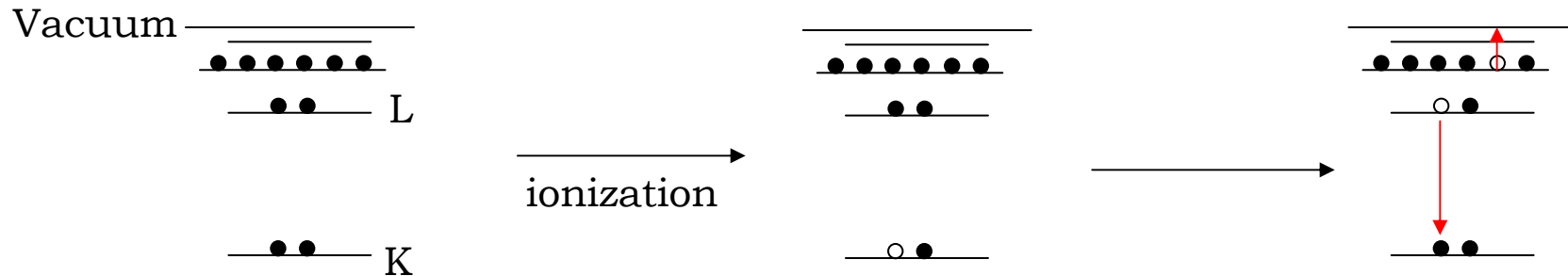
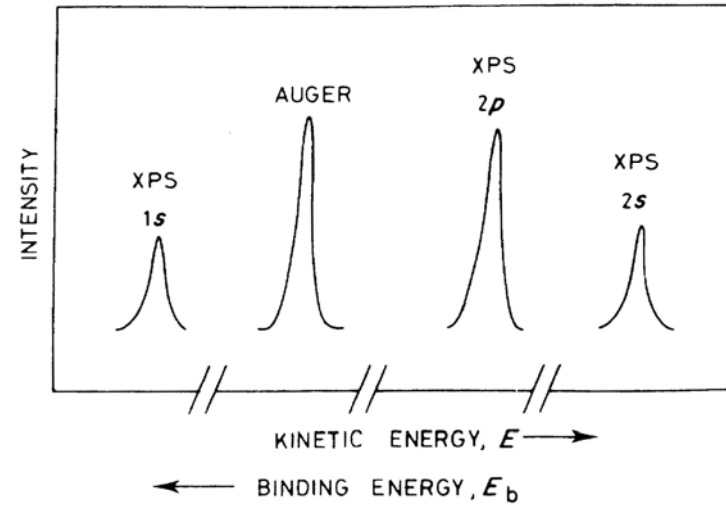
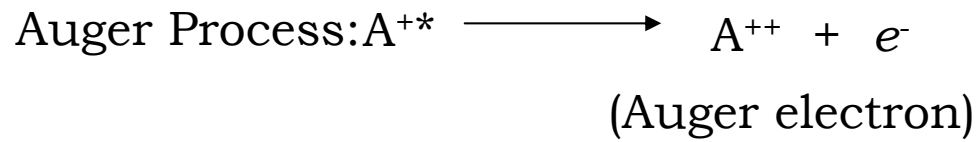
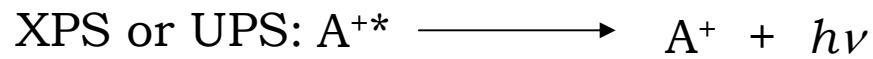
Electron Spectroscopics

Measure the *kinetic energy* of electrons that are emitted from matter as a consequence of bombarding it with ionizing radiation

$$\begin{array}{ccc} \text{Kinetic energy} & \longrightarrow E = h\nu - E_b \longleftarrow & \text{Ionization} \\ & \uparrow & \text{potential} \\ & \text{Incident radiation} & \text{(characteristic)} \\ & \text{(X-ray or UV)} & \end{array}$$



ESCA and Auger Process

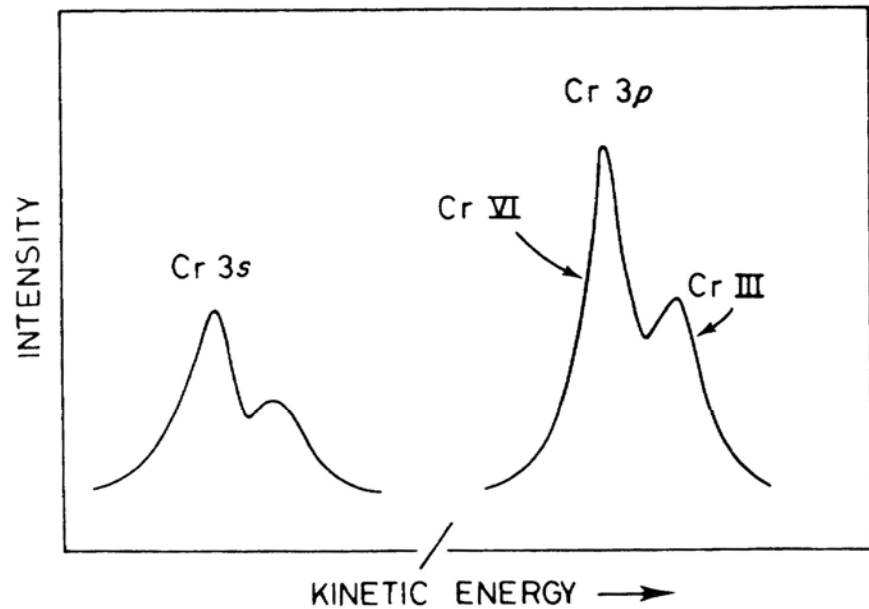
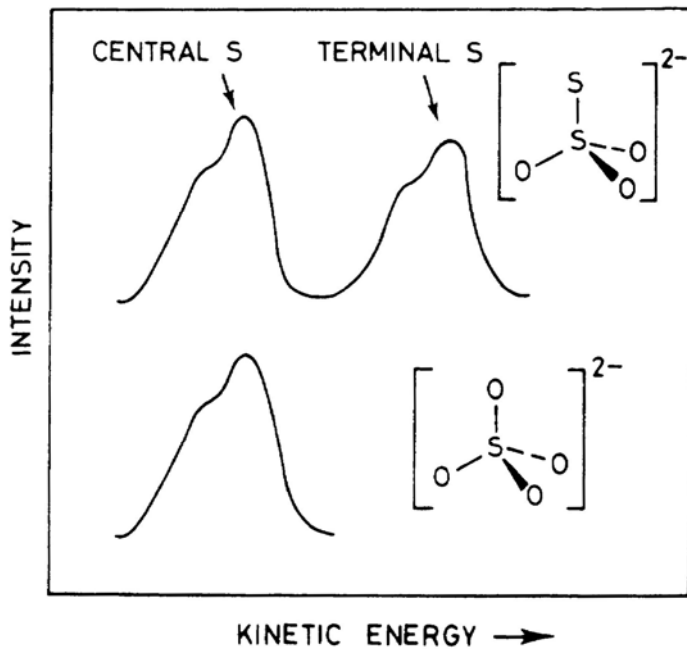


X-ray Photoelectron Spectroscopy (XPS)

Study surface properties (ionized electron energy $\ll 1$ keV)

2 to 5 nm from the surface

Electron binding energy E_b : charge and oxidation state

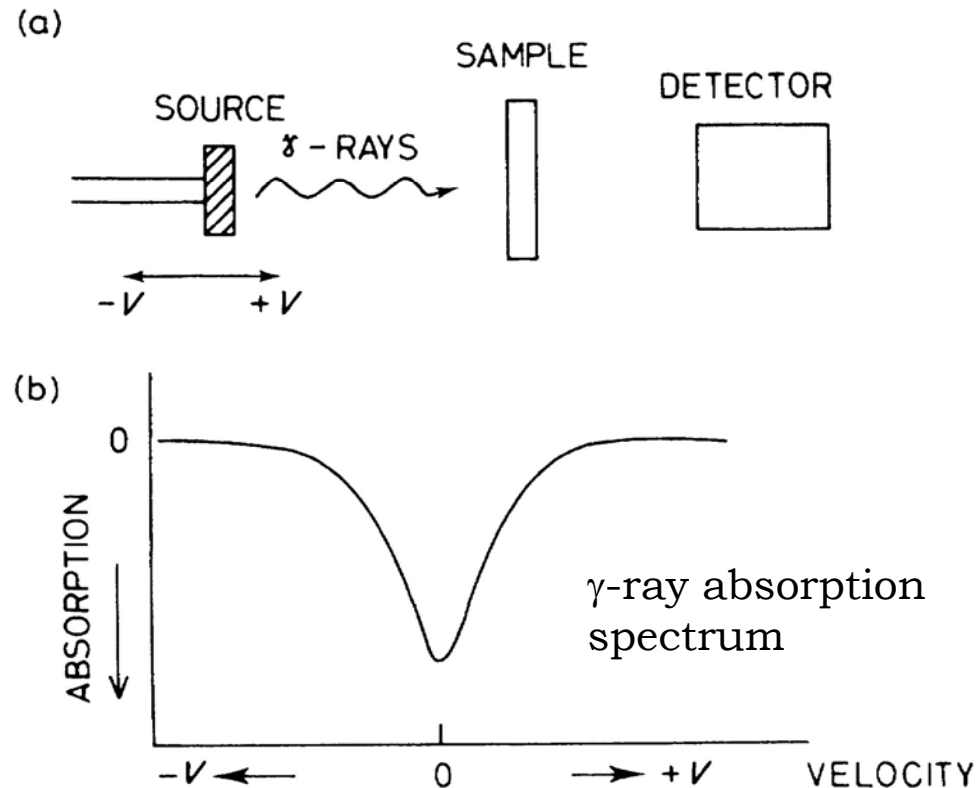


Mössbauer Spectroscopy

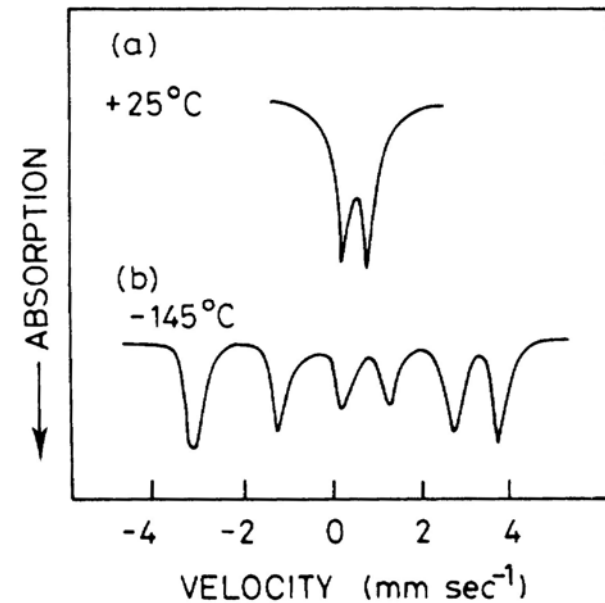
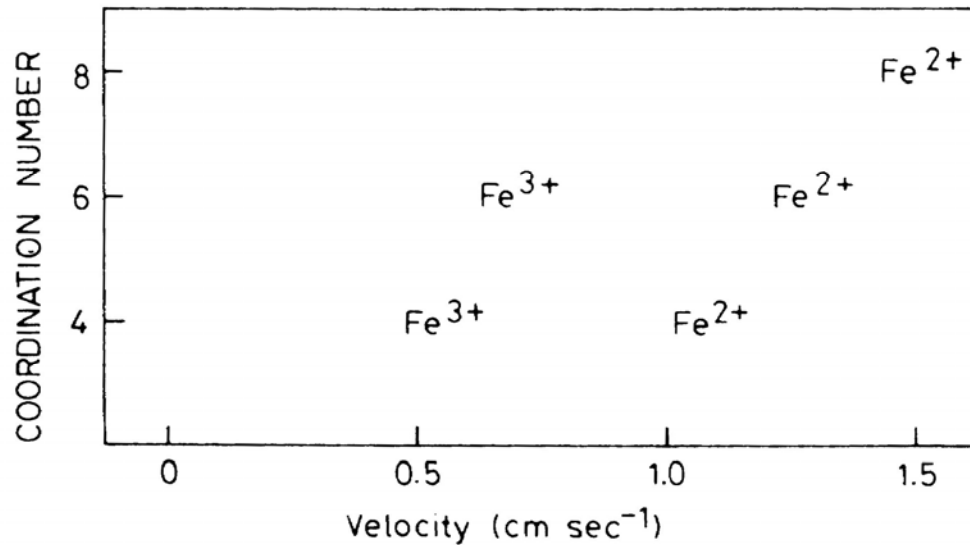
γ -ray spectroscopy, highly monochromatic beam

Change in population of energy levels *inside the nuclei*, $^{57}\text{Fe}_{29}^*$ or $^{119}\text{Sn}_{50}^*$

γ -ray energy is varied by making use of Doppler effect



Mössbauer Spectroscopy

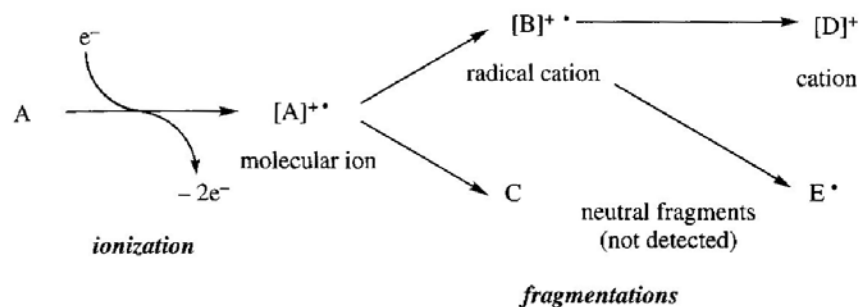
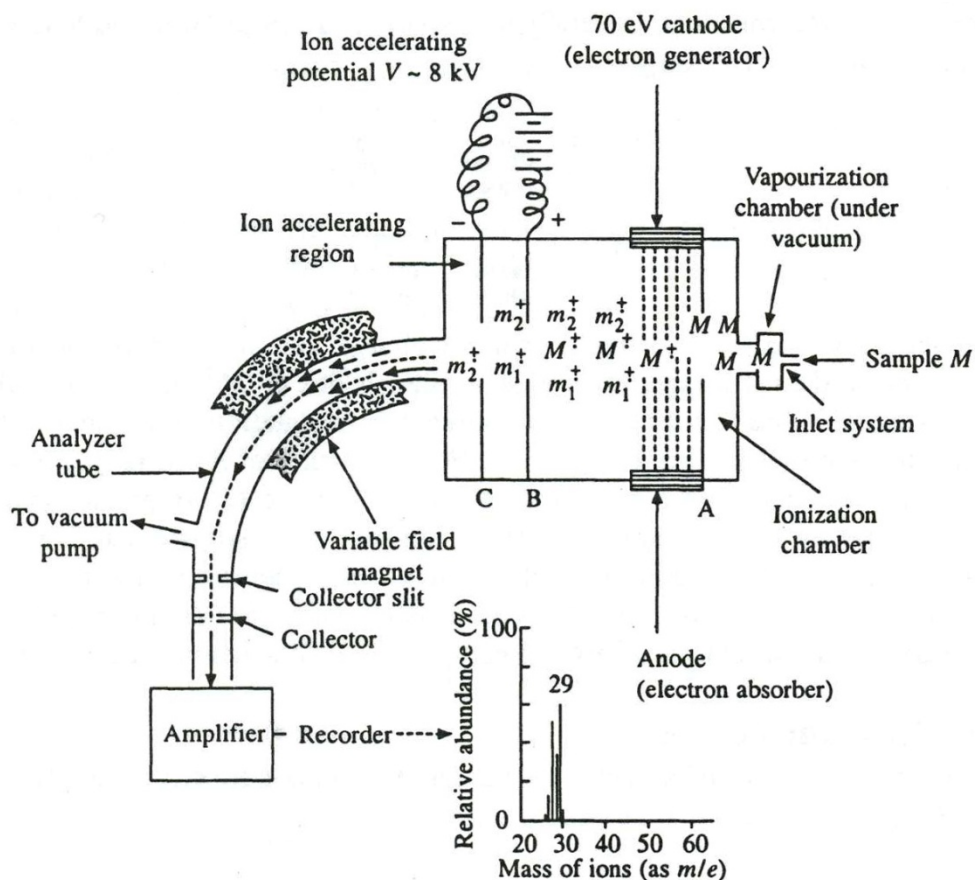


Emitter and sample are identical:
resonant absorption peak

Emitter and sample are not identical:
absorption peak shift

- Quadrupole splitting
- Magnetic hyperfine Zeeman splitting

Mass Spectrometry



$$\frac{1}{2} mv^2 = eV$$

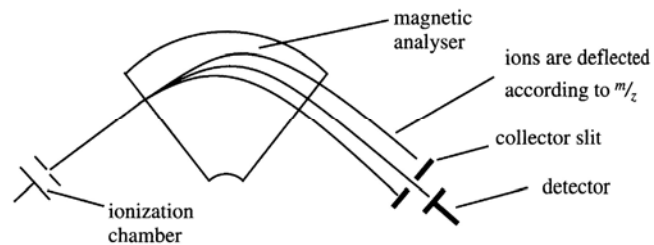
$$Hev = mv^2/r$$

$$m/e = H^2r^2/2V$$

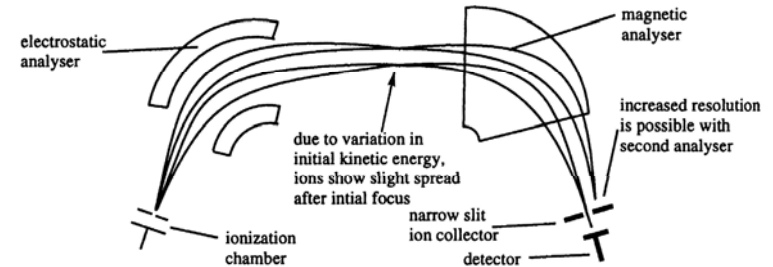
- Determine the *mass/charge ratio* (m/z) in the vapor phase
- Exact molecular masses
- Structure of the molecule

Instrumentation of Mass Spectrometer

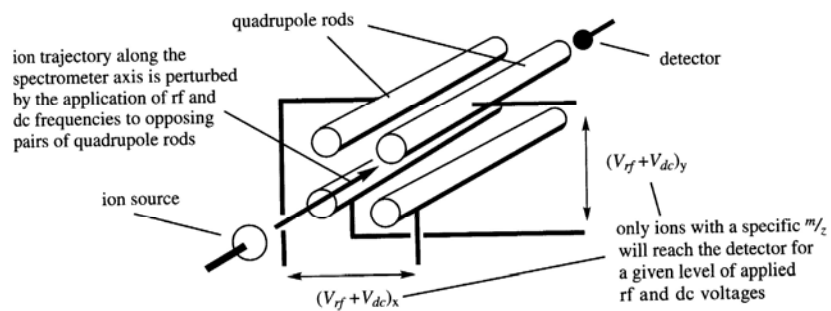
Single focusing MS



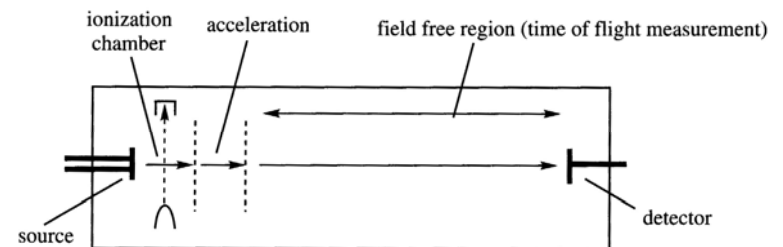
Double focusing MS



Quadrupole MS

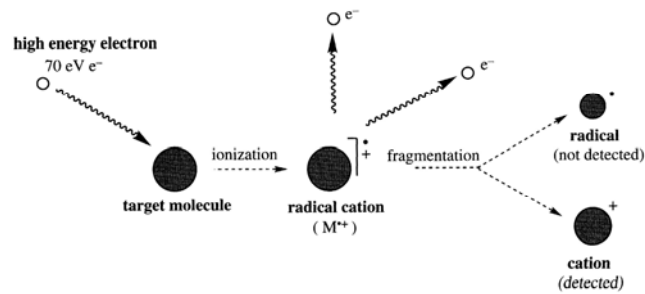


Time-of-Flight MS

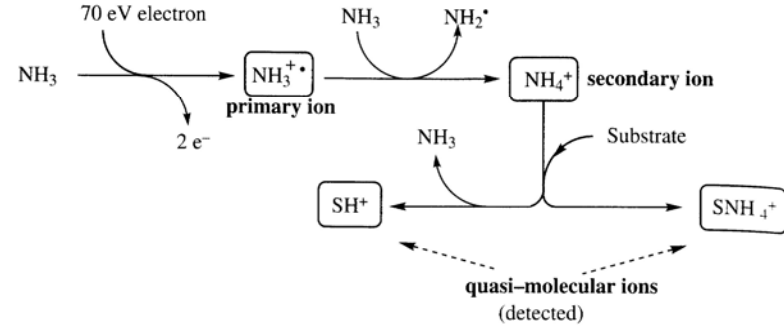


Ionization Methods

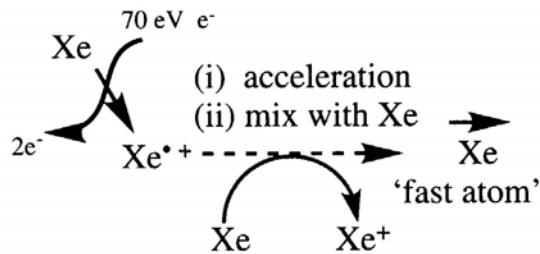
1. Electron impact method (electron)



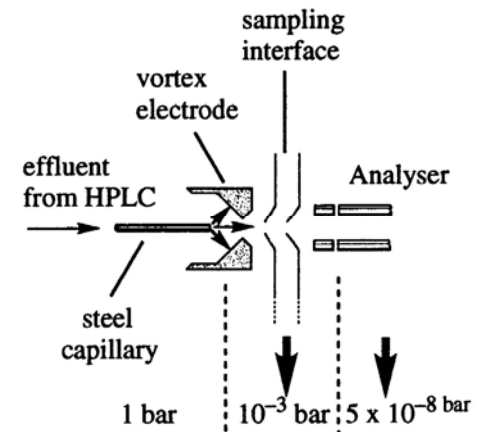
2. Chemical ionization method (ions)



3. Fast Atom Bombardment (atom)

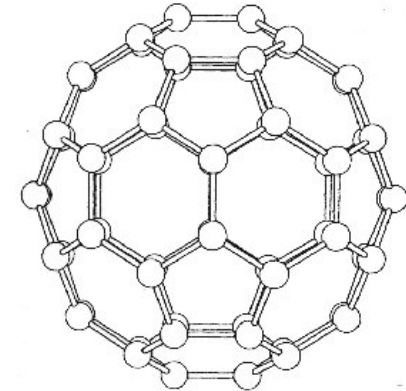
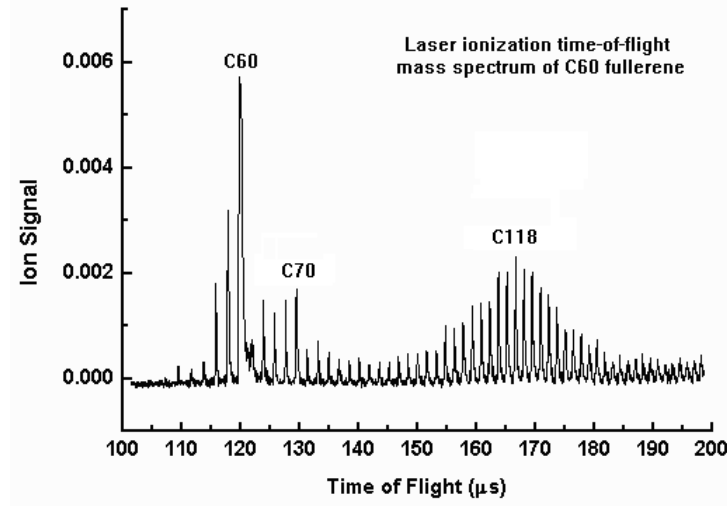


4. Electrospray (for macromolecules such as proteins)



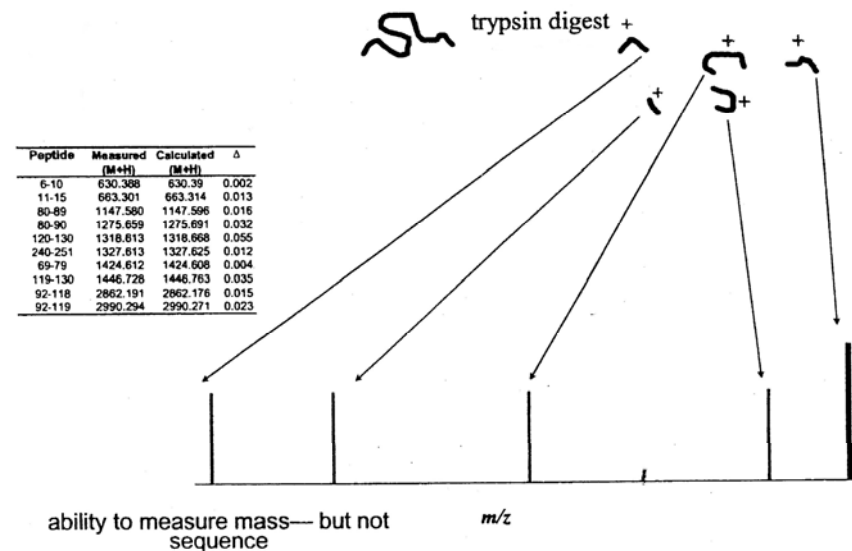
MS Spectrum

Molecular structure



Macromolecules (proteins, peptides)

Peptide mass fingerprint

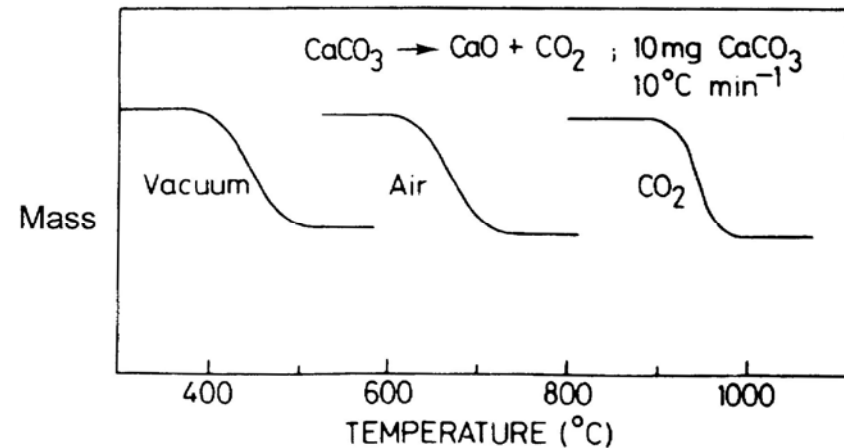
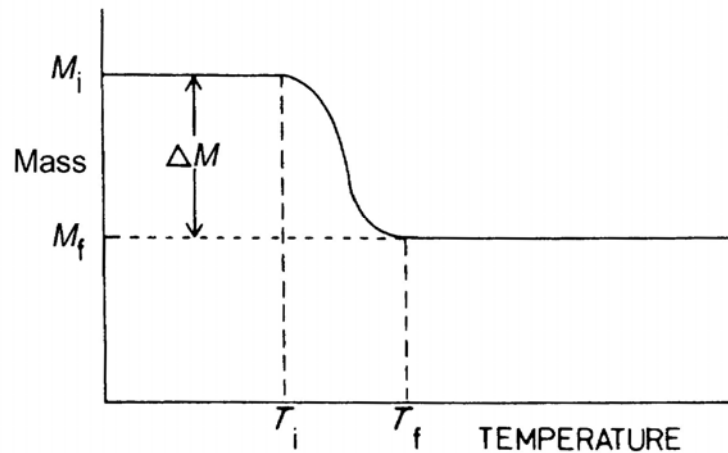


Thermal Analysis

- Measurement of certain physical and chemical properties as a function of temperature
- Enthalpy, heat capacity, mass and coefficient of thermal expansion

1. Thermogravimetry (TG)

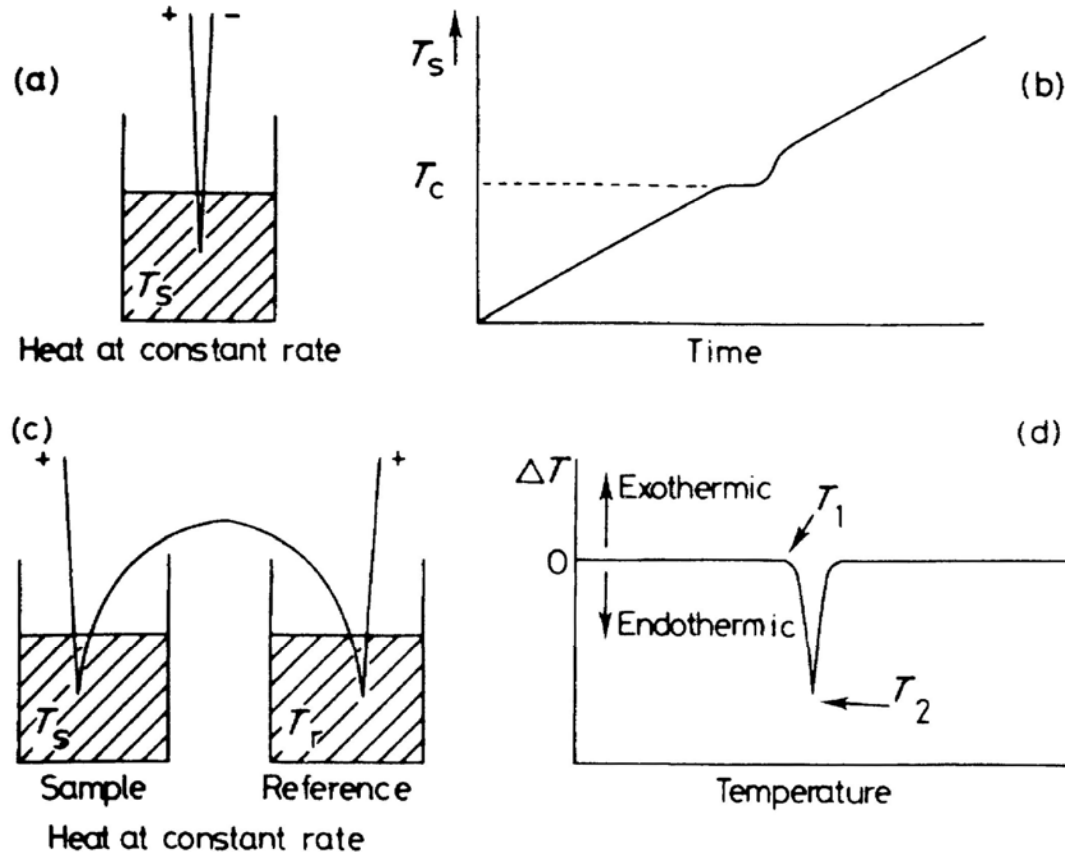
Measures the **changes in mass** of a substance as a function of **temperature or time**



Thermal Analysis

2. Differential Thermal Analysis (DTA) & Differential Scanning Calorimetry (DSC)

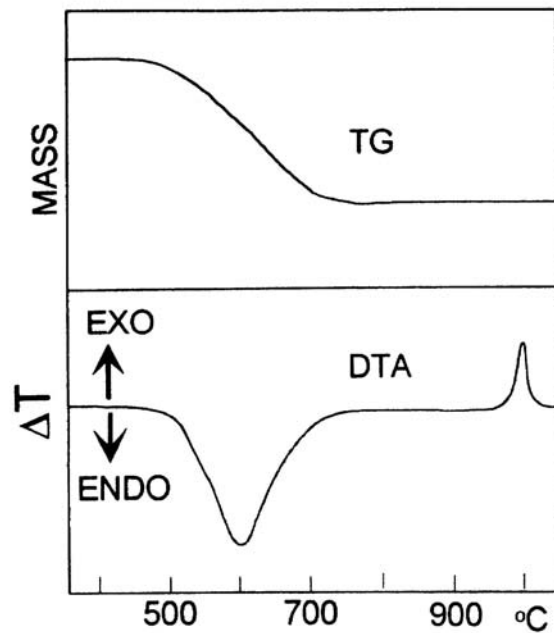
Temperature of a sample is *compared* with that of an inert reference materials during a programmed change of temperature



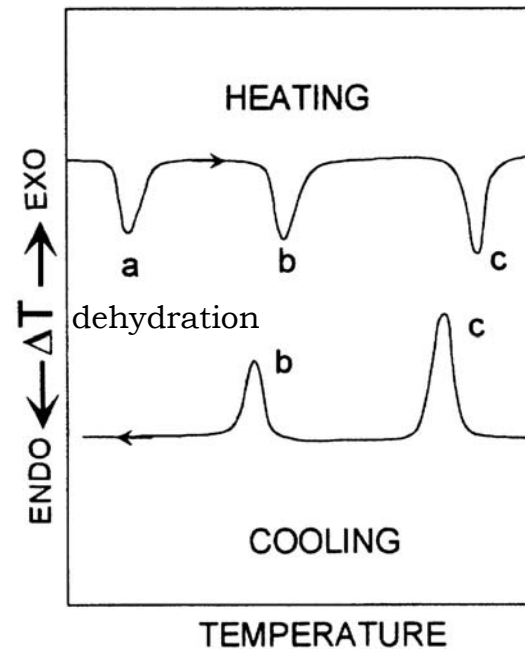
Applications of Thermal Analysis

- Combination of TG and DTA analysis

Decomposition of kaolin



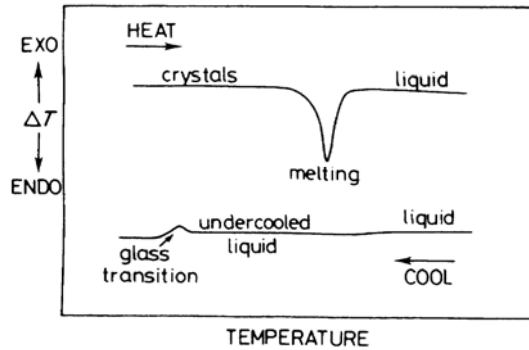
Exothermic reaction: phase transition from meta-stable to more stable structure



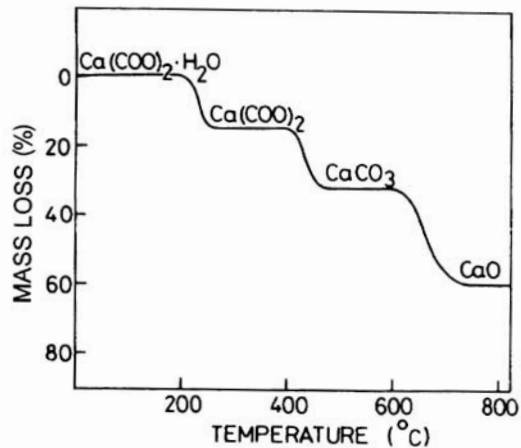
- Reversible vs. irreversible reaction
- Hysteresis

Applications of Thermal Analysis

1. Determination of glass transition temperature



2. Decomposition process



3. Determination of phase diagram

