Basics of Experimental Techniques

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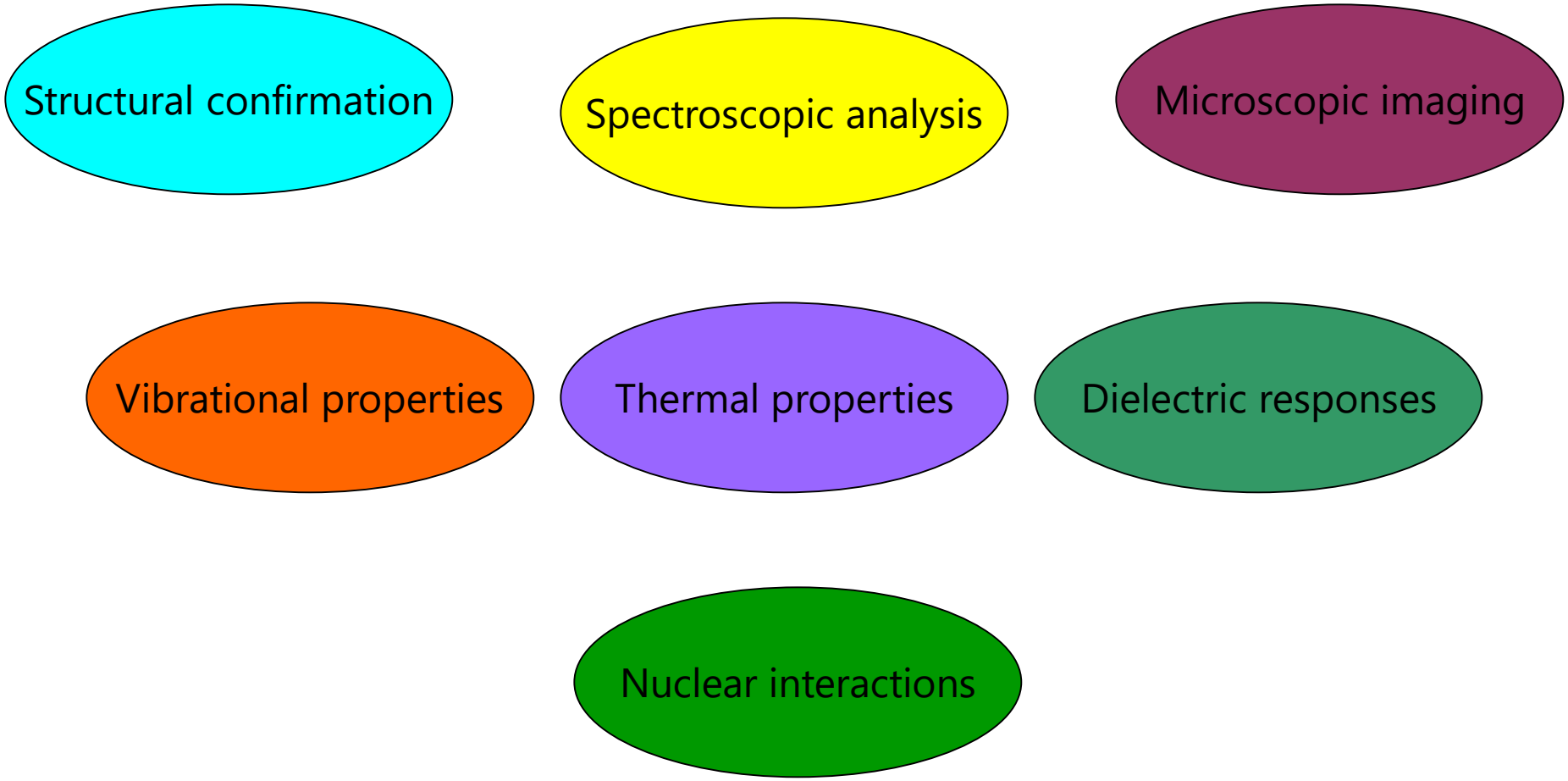
Characterization by various **Sophisticated Analytical Instruments**



Structural confirmation

X-Ray Diffraction (XRD)

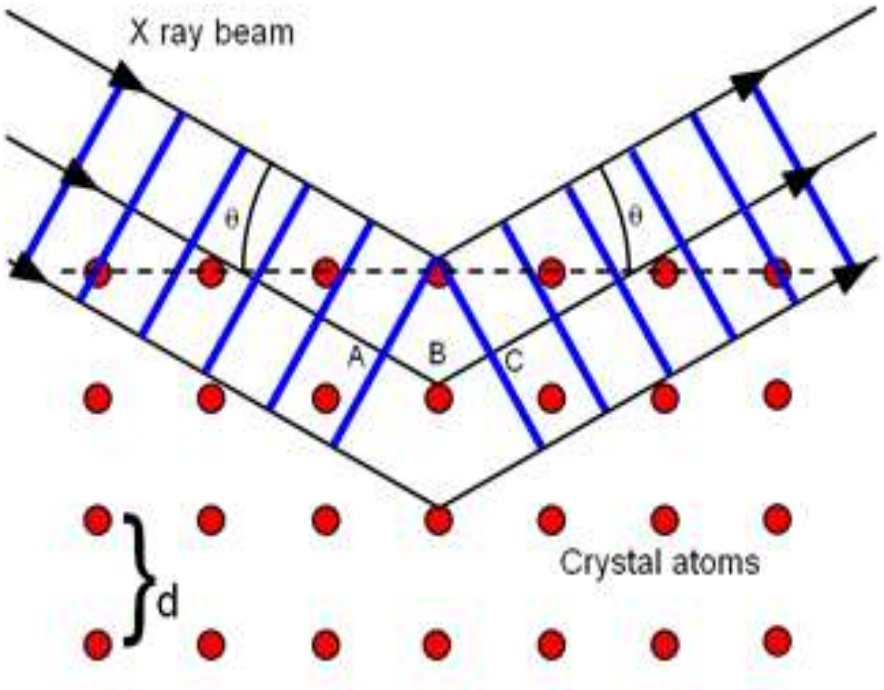
❖For electromagnetic radiation to be diffracted the spacing in the grating should be of the same order as the wavelength

❖ In crystals the typical interatomic spacing ~ 2-3 Å

❖ Hence, X-rays can be used for the study of crystal structures

❖X-ray diffraction is based on constructive interference of monochromatic X-rays and a crystalline sample.

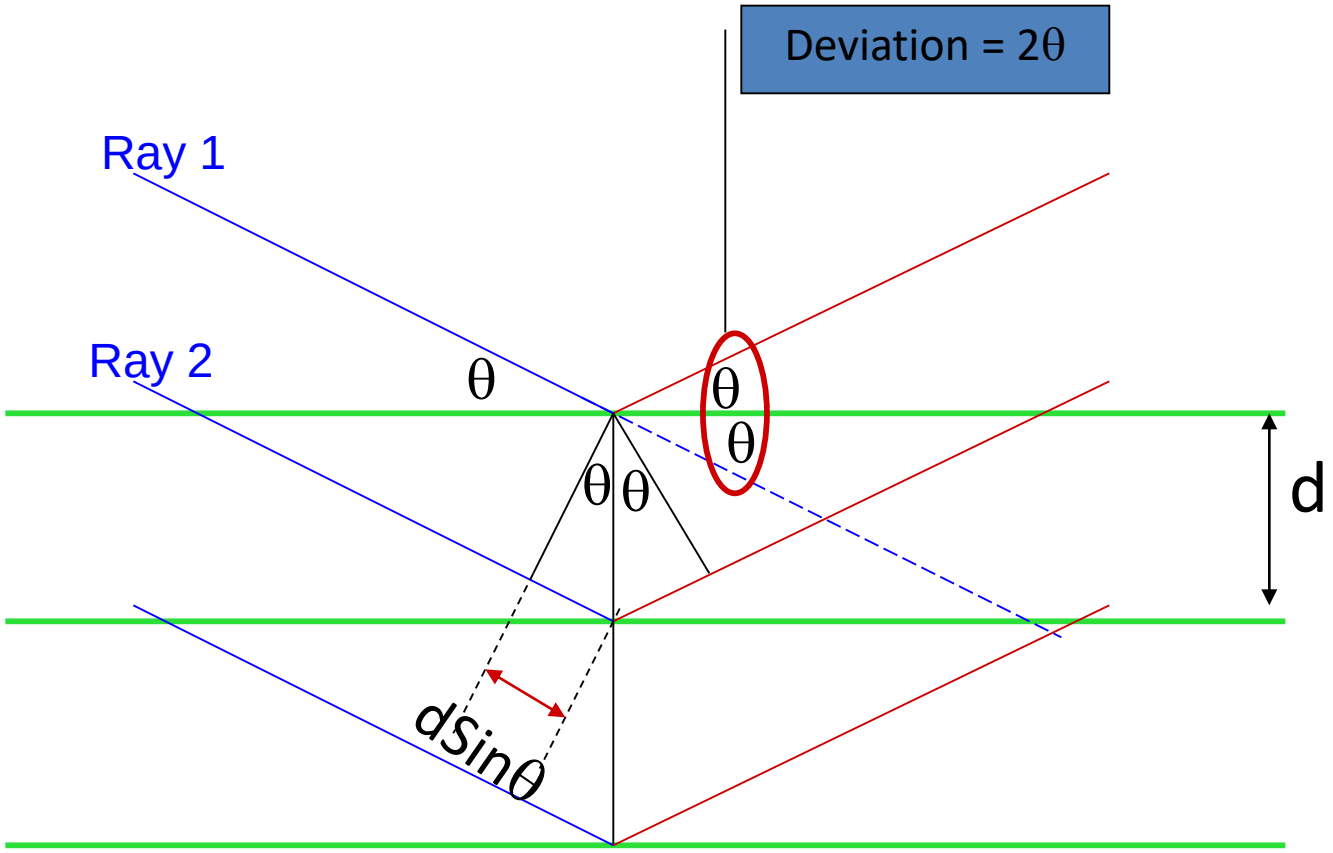
❖ The interaction of the incident rays with the sample produces constructive interferenc (and a diffracted ray) when conditions satisfy Bragg's Law



($n\lambda = 2d \sin\theta$)

❖By scanning the sample through a range of 2θ angles, all possible diffraction directions of the lattice should be attained due to the random orientation of the powdered material.

BRAGG's EQUATION



- The path difference between ray 1 and ray 2 = 2d Sinθ
- For constructive interference: nλ = 2d Sinθ

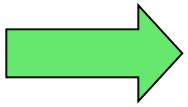
- $n\lambda = 2d \sin\theta$
- n is an integer and is the order of the reflection
- For Cu K_α radiation (λ = 1.54 Å) and d_{110}= 2.22 Å

n	Sinθ	θ	
1	0.34	20.7°	First order reflection from (110)
2	0.69	43.92°	Second order reflection from (110) Also written as (220)

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

$$d_{220} = \frac{a}{\sqrt{8}}$$

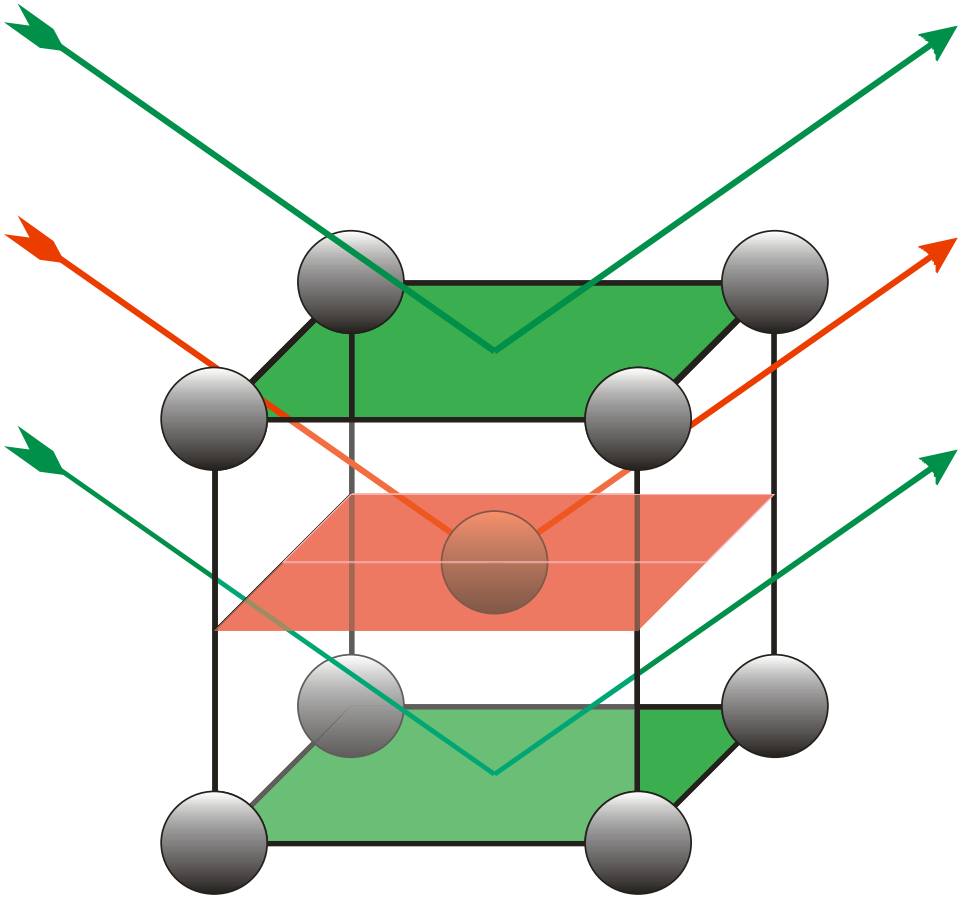
$$d_{110} = \frac{a}{\sqrt{2}}$$

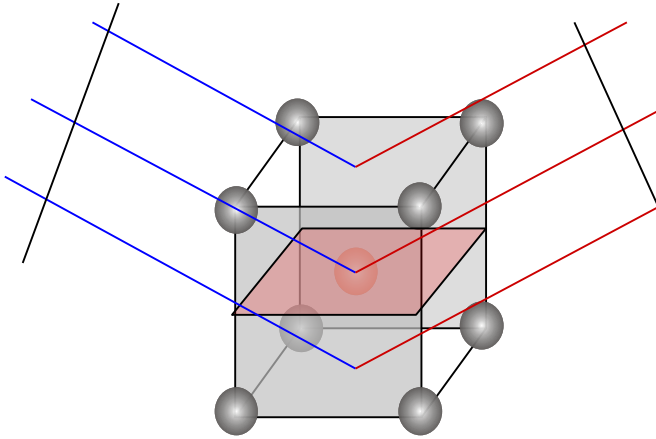


$$\frac{d_{220}}{d_{110}} = \frac{1}{2}$$

Scattering by the Unit cell (uc)

- *Coherent Scattering*
- *Unit Cell (UC) is representative of the crystal structure*
- *Scattered waves from various atoms in the UC interfere to create the diffraction pattern*



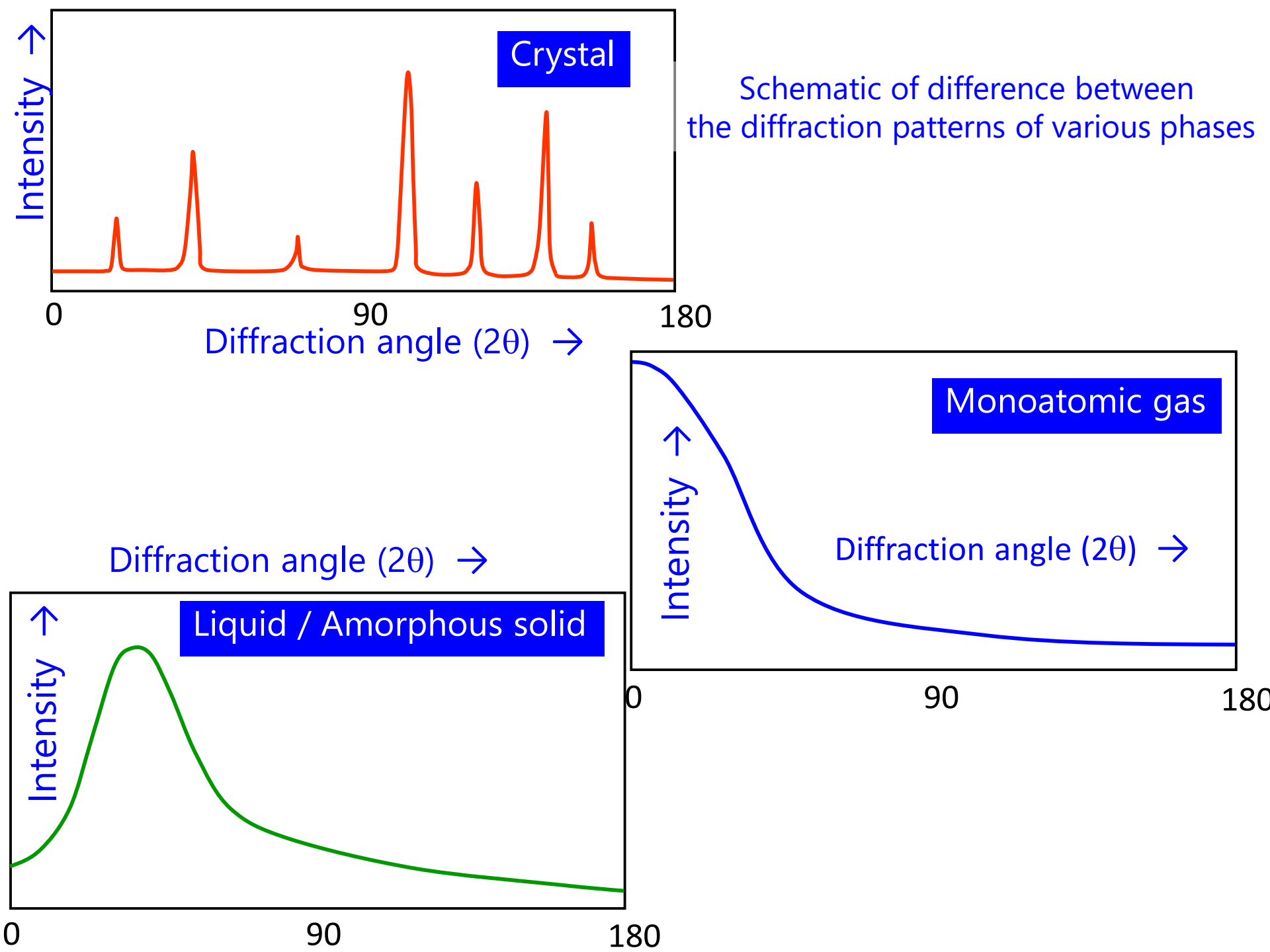


The wave scattered from the middle plane is out of phase with the ones scattered from top and bottom planes

Selection / Extinction Rules

Bravais Lattice	**Reflections which *may be* present**	**Reflections necessarily absent**
Simple	all	None
Body centred	(h + k + l) even	(h + k + l) odd
Face centred	h, k and l unmixed	h, k and l mixed
End centred	h and k unmixed *C centred*	h and k mixed *C centred*

Bravais Lattice	**Allowed Reflections**
SC	All
BCC	(h + k + l) even
FCC	h, k and l unmixed
DC	h, k and l are all odd *Or* all are even *& (h + k + l) divisible by 4*


Crystal
Intensity →
0
90
180
Diffraction angle (2θ) →
Schematic of difference between
the diffraction patterns of various phases
Monoatomic gas
Intensity →
Diffraction angle (2θ) →
0
90
180
Diffraction angle (2θ) →
Liquid / Amorphous solid
Intensity →
0
90
180

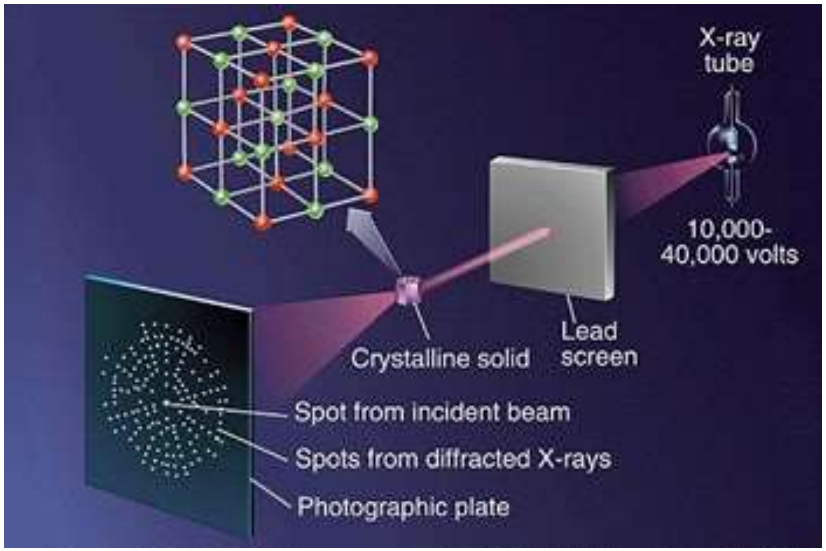
Crystallite size and Strain

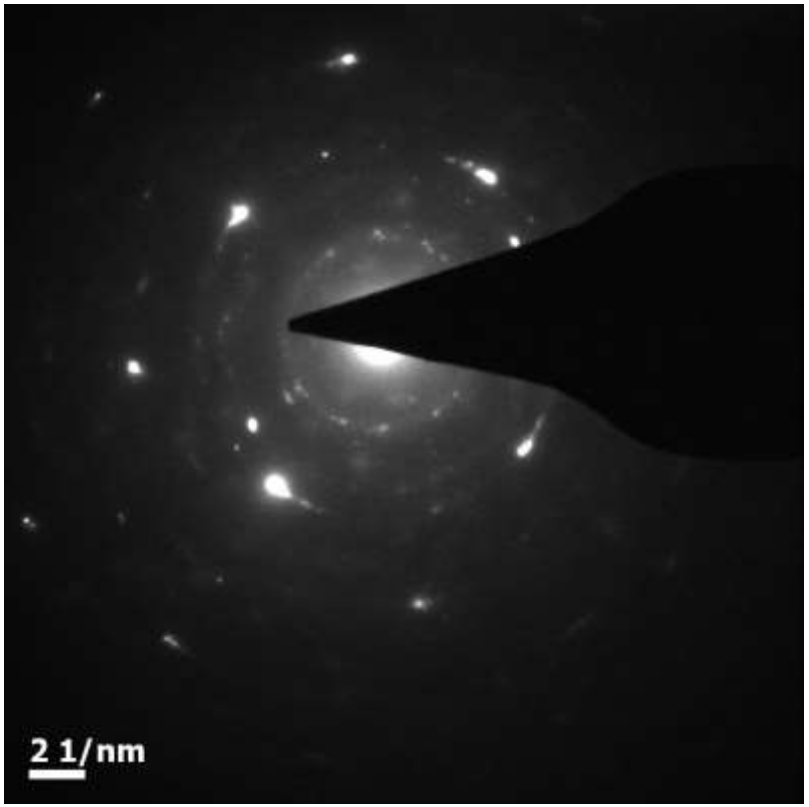
- Bragg's equation assumes:
  - Crystal is perfect and infinite
  - Incident beam is perfectly parallel and monochromatic
- Actual experimental conditions are different from these leading various kinds of deviations from Bragg's condition
  - Peaks are not 'δ' curves $\rightarrow$ Peaks are broadened
- There are also deviations from the assumptions involved in the generating powder patterns
  - Crystals may not be randomly oriented *(textured sample)* $\rightarrow$ Peak intensities are altered

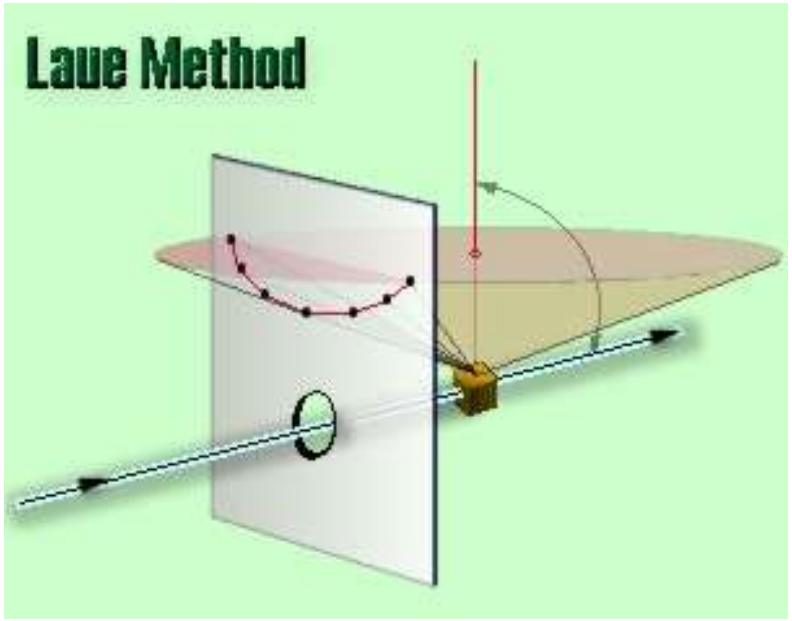
- In a powder sample if the crystallite size < 0.5 μm
  - there are insufficient number of planes to build up a sharp diffraction pattern

  $\Rightarrow$ *peaks are broadened*

Selected Area diffraction



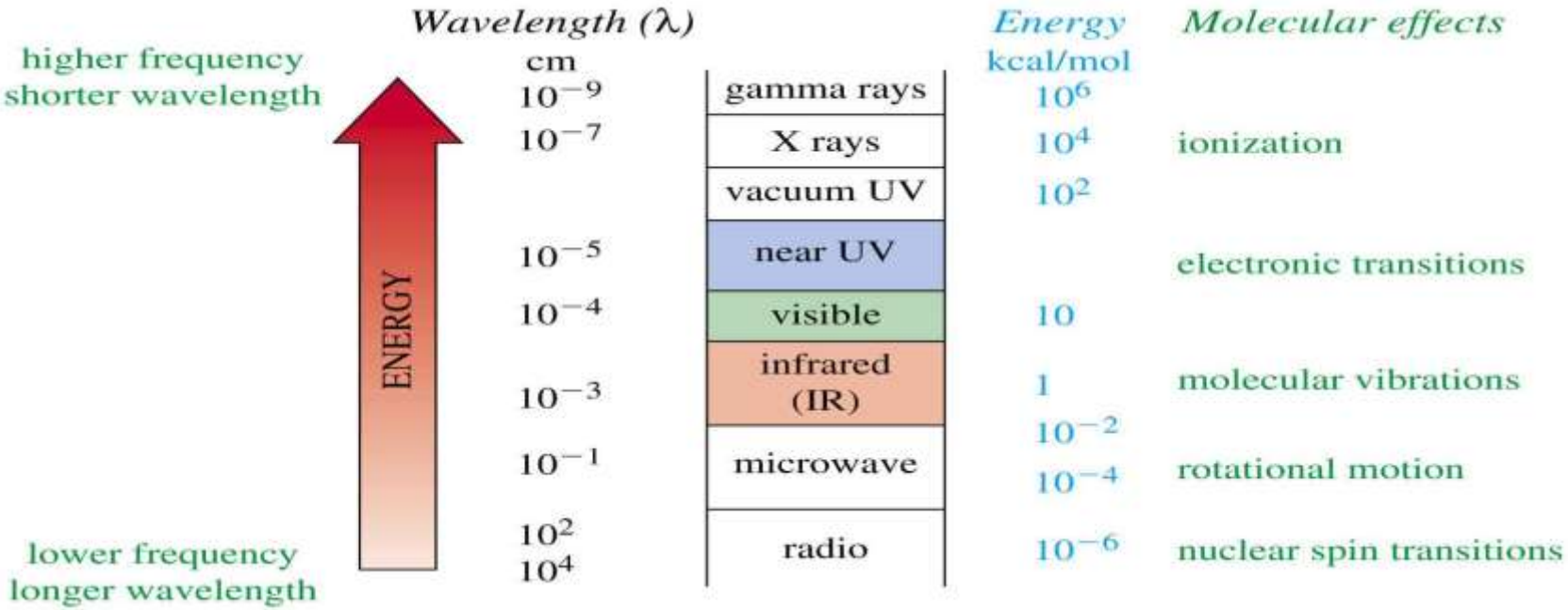




Spectroscopic Analysis

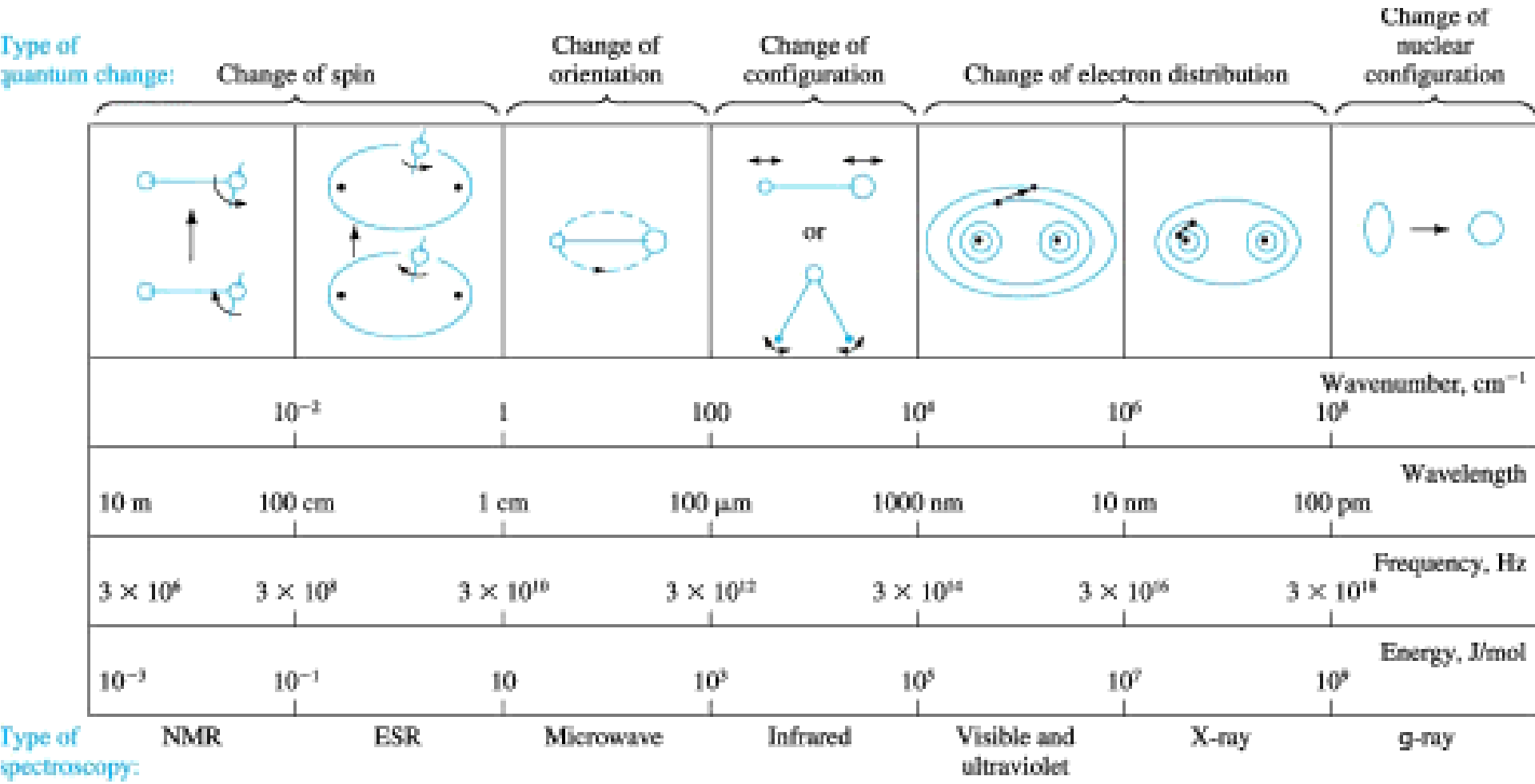
Spectroscopy

The study of molecular structure and dynamics through the absorption, emission and scattering of light.



$c = ln$, where c is the speed of light.

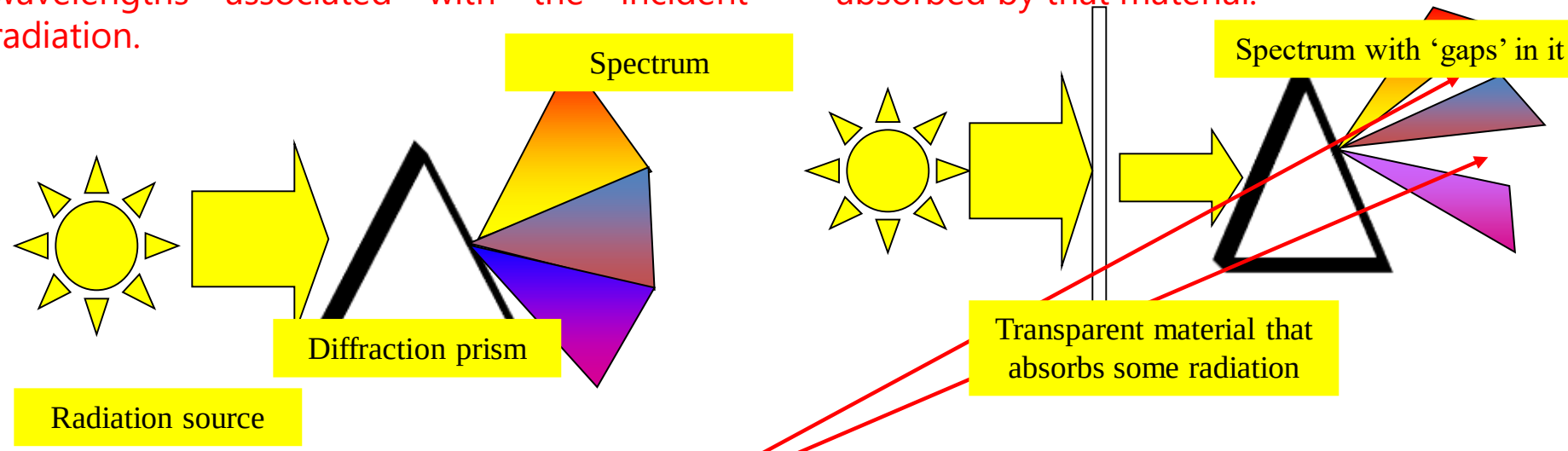
Energy per photon = hn, where h is Planck's constant



Ultraviolet (UV) Spectroscopy – Use and Analysis

When continuous wave radiation passes through a prism a diffraction pattern (spectrum) is produced made up of all the wavelengths associated with the incident radiation.

When continuous wave radiation passes through a transparent material (solid or liquid) some of the radiation might be absorbed by that material.

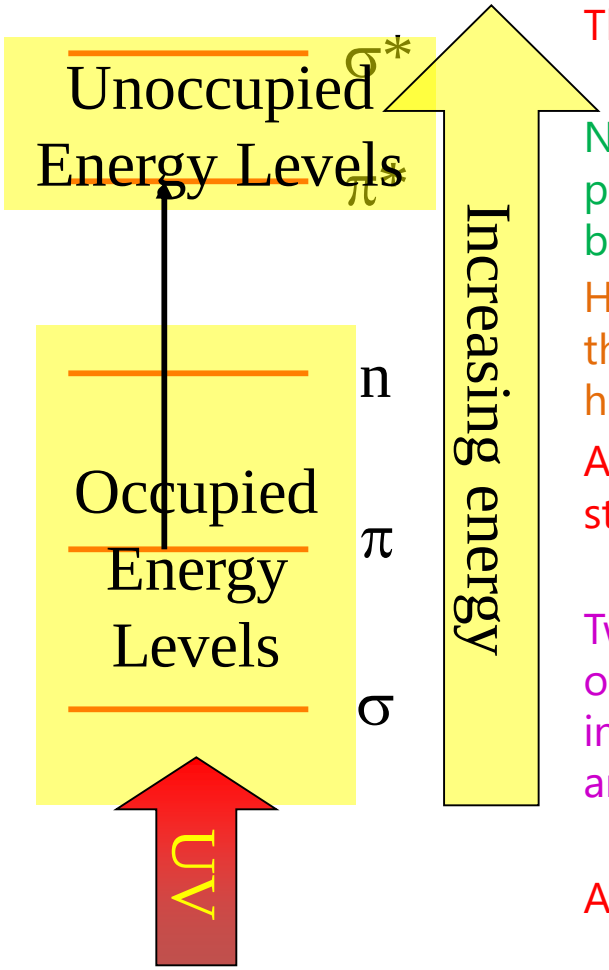


If, having passed through the material, the beam is diffracted by passing through a prism it will produce a light spectrum that has gaps in it (caused by the absorption of radiation by the transparent material through which is passed).

The effect of absorption of radiation on the transparent material is to change is from a low energy state (called the ground state) to a higher energy state (called the excited state).

The energy of the 'missing' parts of the spectrum corresponds exactly to the energy difference between the orbitals involved in the transition.

Ultraviolet (UV) Spectroscopy – Use and Analysis



The σ-bonding orbitals are low in energy (that is, stable).

Next (in terms of increasing energy) are the π-bonding orbitals present in all functional groups that contain double and triple bonds (*e.g.* carbonyl groups and alkenes).

Higher energy still are the non-bonding orbitals present on atoms that have lone pair(s) of electrons (oxygen, nitrogen, sulfur and halogen containing compounds).

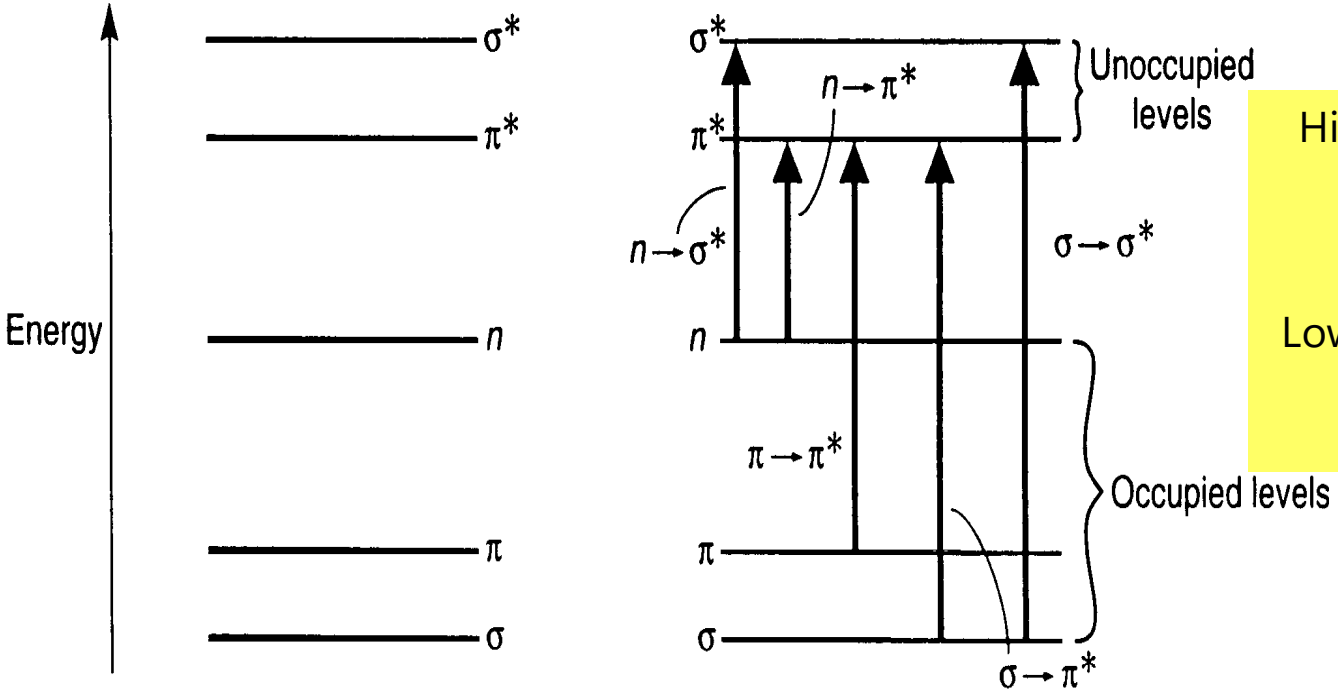
All of the above 3 kinds of orbitals may be occupied in the ground state.

Two other sort of orbitals, called antibonding orbitals, can only be occupied by an electron in an excited state (having absorbed UV for instance). These are the π* and σ* orbitals (the * denotes antibonding).

Antibonding orbitals are unoccupied in the ground state

A transition of an electron from occupied to an unoccupied energy level can be caused by UV radiation.

A schematic of the transition of an electron from π to π* is shown on the left.



Highest occupied molecular orbital
HOMO

Lowest unoccupied molecular orbital
LUMO

Electronic transitions involve the promotion of electrons from an occupied orbital to an unoccupied orbital.

Energy differences of 125 - 650 kJ/mol

Not all transitions are observed

There are restrictions called
Selection Rules

This results in
Forbidden Transitions

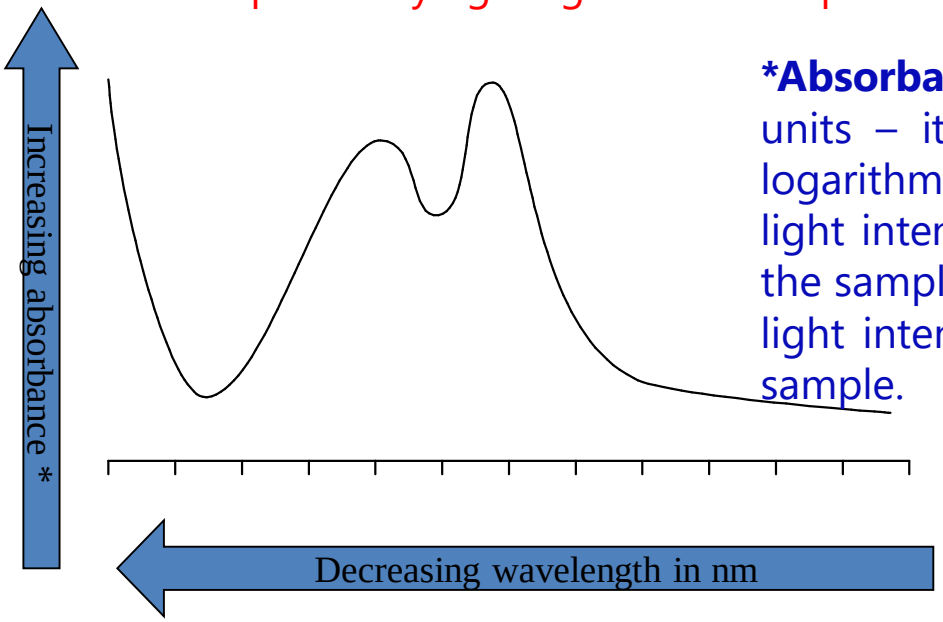
Spin selection rule: $\Delta S = 0$

allowed transitions: singlet → singlet or triplet → triplet
forbidden transitions: singlet → triplet or triplet → singlet

Changes in spin multiplicity are forbidden

Ultraviolet (UV) Spectroscopy – The Output

The output from a UV scanning spectrometer is not the most informative looking piece of data!! It looks like a series of broad humps of varying height. An example is shown below.



***Absorbance** has no units – it is actually the logarithm of the ratio of light intensity incident on the sample divided by the light intensity leaving the sample.

Beer Lambert Law

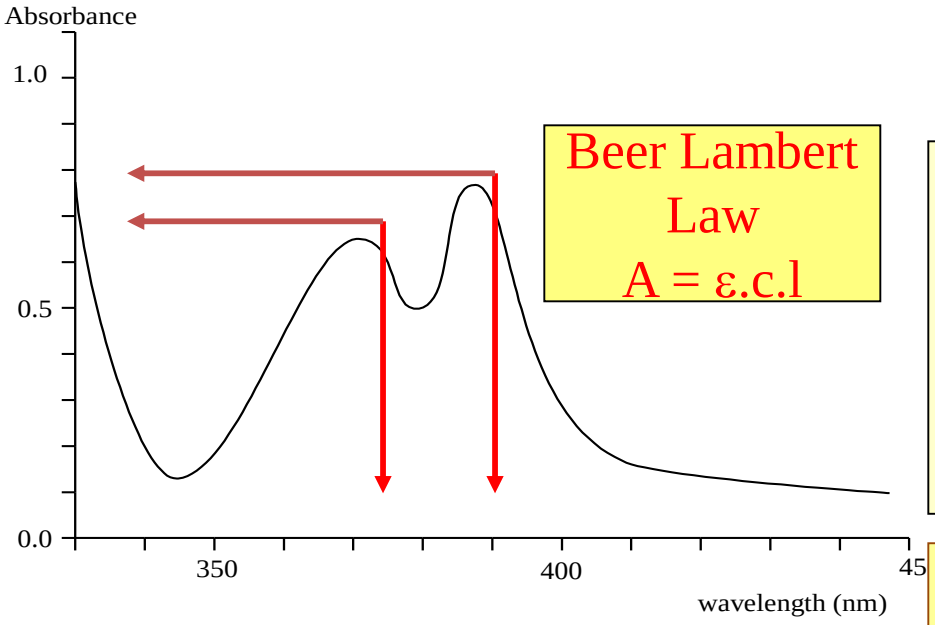
$$A = \log(I_O/I) = \varepsilon c l$$

A = **absorbance**;
I_O = Intensity of light on the sample cell
I = Intensity of light leaving the sample cell
c = **concentration** in moles
l = **pathlength** in cm
ε = **molar absorptivity** (**extinction coefficient**) in moles^{-1} L cm $^{-1}$.

There are two particular strengths of UV (i) it is very sensitive (ii) it is very useful in determining the quantity of a known compound in a solution of unknown concentration.

The concentration of a sample is related to the absorbance according to the Beer Lambert Law which is described above.

Ultraviolet (UV) Spectroscopy – Analysing the Output



Beer Lambert Law
$A = \varepsilon.c.l$

Handling samples of known concentration

If you know the structure of your **compound X** and you wish to acquire UV data you would do the following.

Prepare a known concentration solution of your sample.

Run a UV spectrum (typically from 500 down to 220 nm).

From the spectrum read off the wavelength values for each of the maxima of the spectra (see left)

Read off the absorbance values of each of the maxima (see left).

Then using the known concentration (in moles L^{-1}) and the known pathlength (1 cm) calculate the molar absorptivity (ε) for each of the maxima.

Finally quote the data as follows (for instance for the largest peak in the spectrum to the left and assuming a concentration of 0.0001 moles L^{-1}).

λmax = 487nm A= 0.75

ε = 0.75 /(0.001 x 1.0) = 7500 moles^{-1} L cm $^{-1}$

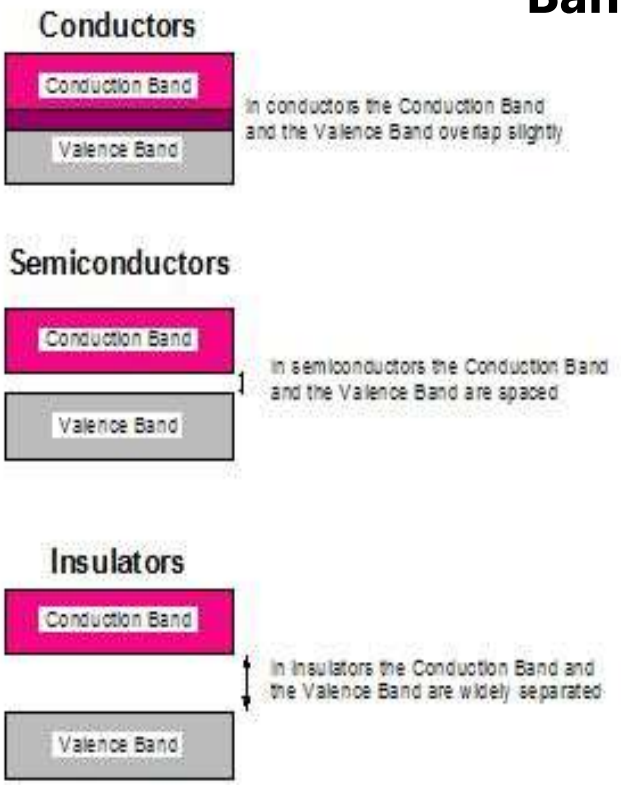
Determining concentration of samples with known molar absorptivity (ε).

Having used the calculation in the yellow box to work out the molar absorptivity of a compound you can now use UV to determine the concentration of compound X in other samples (provided that these sample only contain pure X).

Simply run the UV of the unknown and take the absorbance reading at the maxima for which you have a known value of **ε.** In the case above this is at the peak with the highest wavelength (see above).

Having found the absorbance value and knowing **ε** and **l** you can calculate **c.**

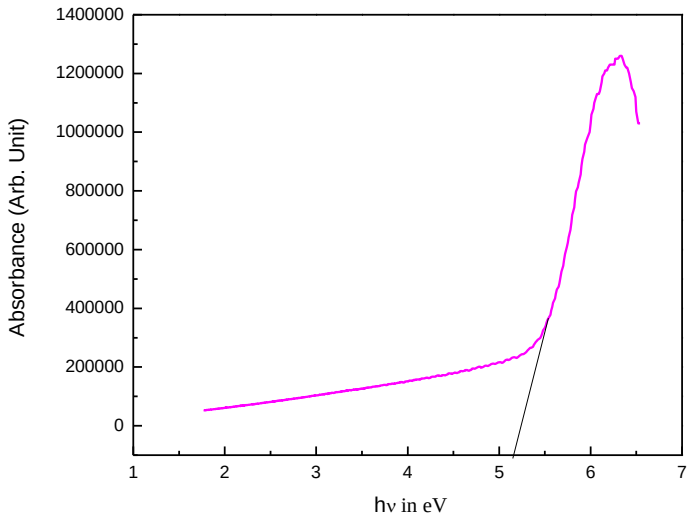
Band gap Calculation from UV-Vis.

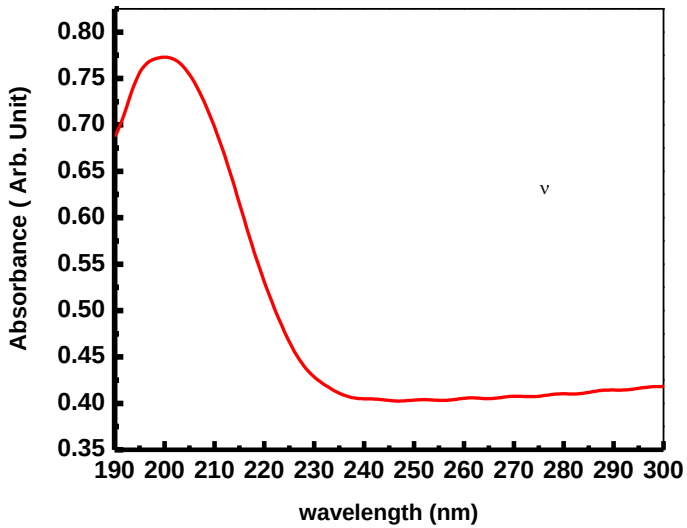


❖The band gap is calculated from the Tauc plot using the relations: $(\alpha h\nu)^2 = c\,(h\nu - E_g)$.

❖The band gaps of the materials are obtained by extrapolating the straight line fit on the energy or the frequency axis.

The calculated band gap is **5.25 eV**

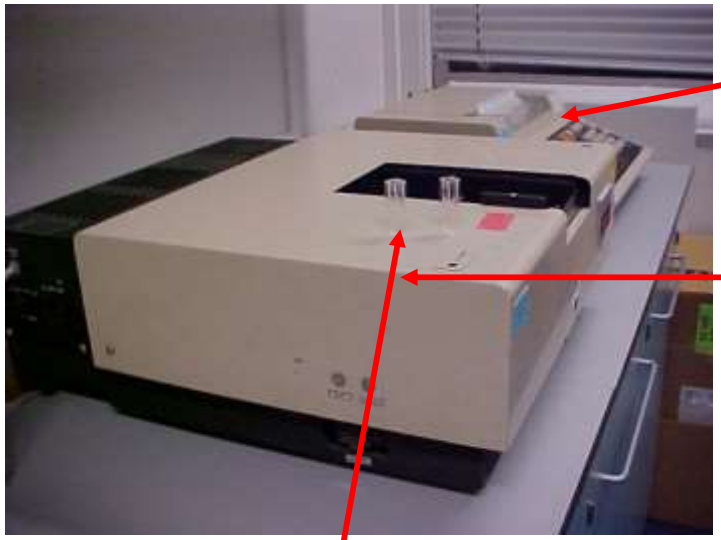




Ultraviolet (UV) Spectroscopy – The Instrumentation

Two lamps (one for visible light and one for UV light) and a series of mirrors and prisms as well as an appropriate detector. The spectrometer effectively varies the wavelength of the light directed through a sample from high wavelength (low energy) to low wavelength (high energy).

Any chemical dissolved in a sample cell through which the light is passing may undergo electronic transitions from the ground state to the excited state when the incident radiation energy is exactly the same as the energy difference between these two states. A recorder is then used to record, on a suitable scale, the absorption of energy that occurs at each of the wavelengths through which the spectrometer scans.



The recorder assembly

The spectrometer itself – this houses the lamps, mirrors, prisms and detector. The spectrometer splits the beam of radiation into two and passes one through a sample and one through a reference solution (that is always made up of the solvent in which you have dissolved the sample). The detector measures the difference between the sample and reference readings and communicates this to the recorder.

The samples are dissolved in a solvent which is transparent to UV light and put into sample cells called cuvettes. The cells themselves also have to be transparent to UV light and are accurately made in all dimensions. They are normally designed to allow the radiation to pass through the sample over a distance of 1cm.

Sources

- Tungten lamp (350-2500 nm)
- Deuterium (200-400 nm)
- Xenon Arc lamps (200-1000 nm)

Detectors

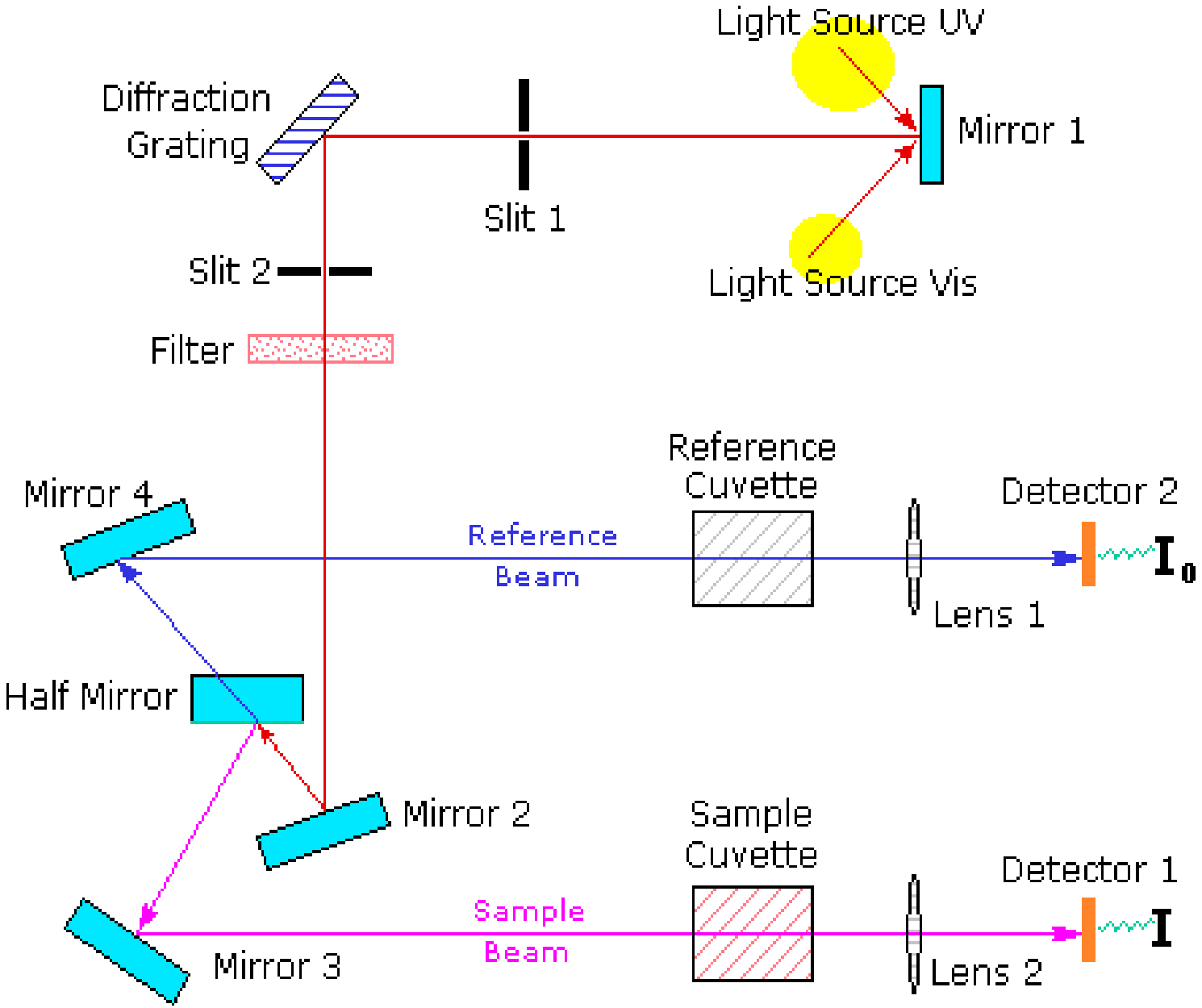
- High sensitivity
- High signal-to-noise ratio.
- Constant response over a considerable range of wavelengths
- Exhibit a fast response time and
- Zero output signal in the absence of illumination

Monochromator

- Braggs law, $nl = d(\sin i + \sin r)$
- Angular dispersion, $dr/d\lambda = n / d(\cos r)$
- Resolution, $R = \lambda / \Delta\lambda = nN$, resolutionis extended by concave mirrors to refocus the divergent beam at the exit slit

Sample Holders

- The cuvettes must be made of material that is transparent to radiation in the region
- Quartz or fused silica is required for UV region (blow 350 nm)
- Silicate glass can be employed in region between 350 and 2000 nm


Light Source UV
Diffraction Grating
Mirror 1
Slit 1
Slit 2
Light Source Vis
Filter
Reference Cuvette
Mirror 4
Detector 2
Reference Beam
I_0
Lens 1
Half Mirror
Mirror 2
Sample Cuvette
Detector 1
Sample Beam
I
Mirror 3
Lens 2

UV / visible Spectroscopy

ALWAYS

use in conjunction with

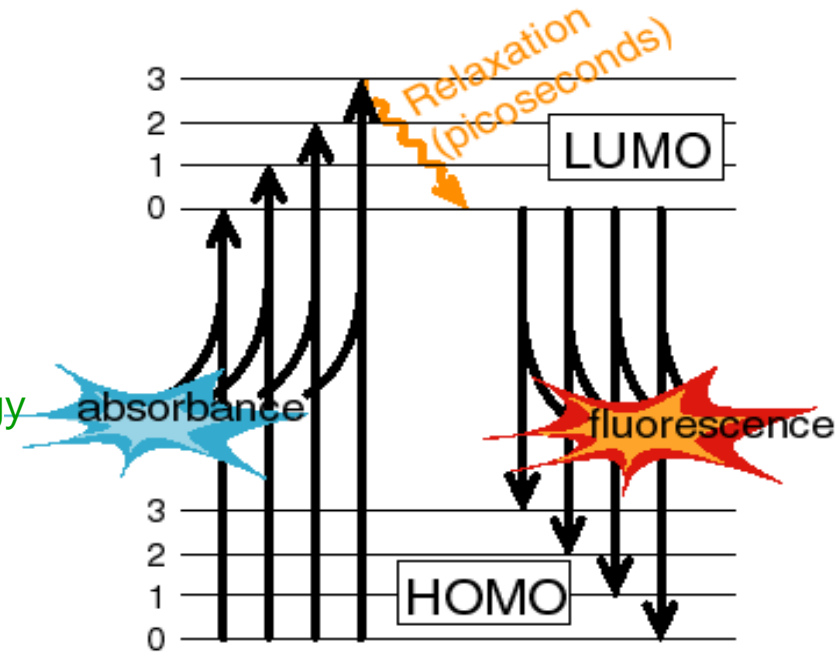
nmr and infrared spectra.

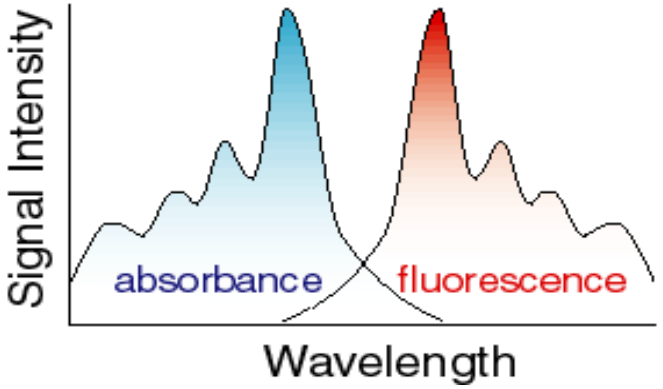
Photoluminescence Spectroscopy

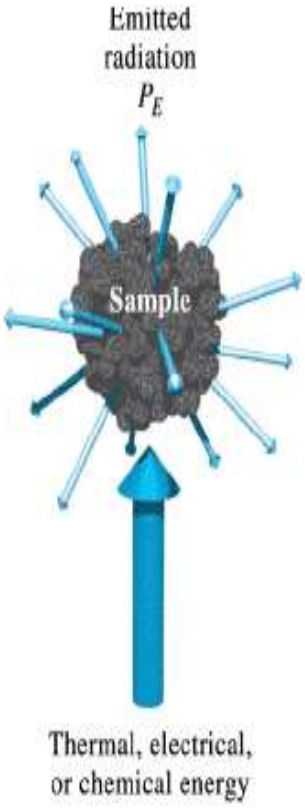
❖ Photoluminescence occurs when an external source of energy, in the form of electromagnetic radiation, is absorbed by a atom or molecule, resulting in the emission of photons.

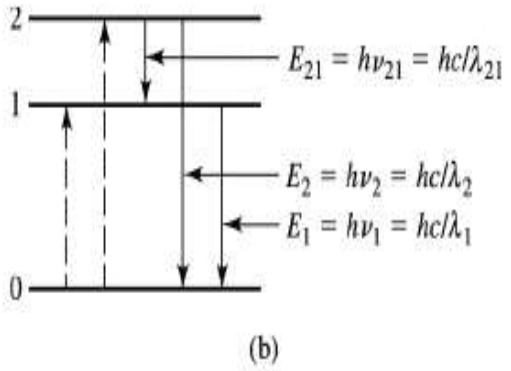
❖ Normally the absorbed light is at a higher energy level (frequency) than the emitted energy.

❖ In other words, this can be described as an excitation to a higher energy state and then a return to a lower energy state accompanied by the emission of a photon.









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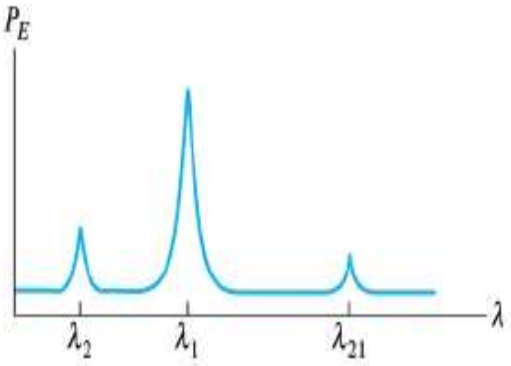
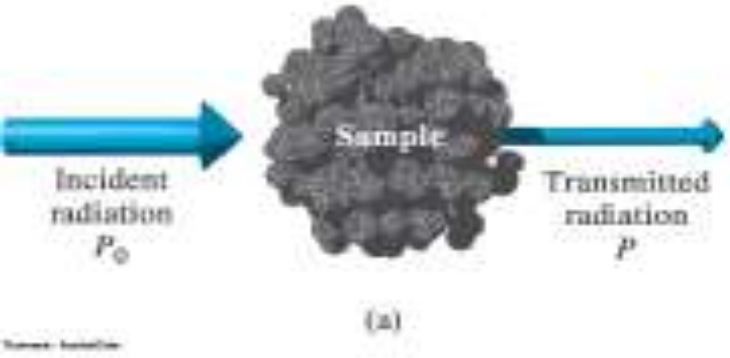
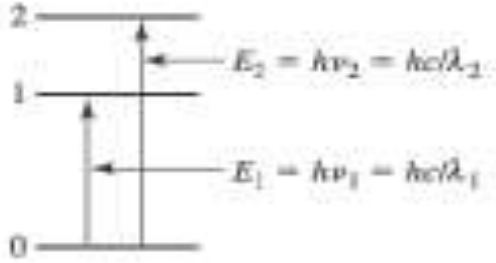


Emission spectroscopy usually refers to methods in which the stimulus is heat or electrical energy, whereas ***chemiluminescence spectroscopy*** refers to excitation of the analyte by a chemical reaction. Measurement of the radiant power emitted as the analyte returns to the ground state can give information about its identity and concentration. The results of such a measurement are often expressed graphically by a spectrum, which is a plot of the emitted radiation as a function of frequency or wavelength.



(a)



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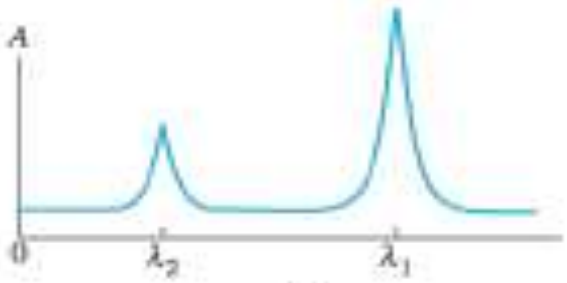
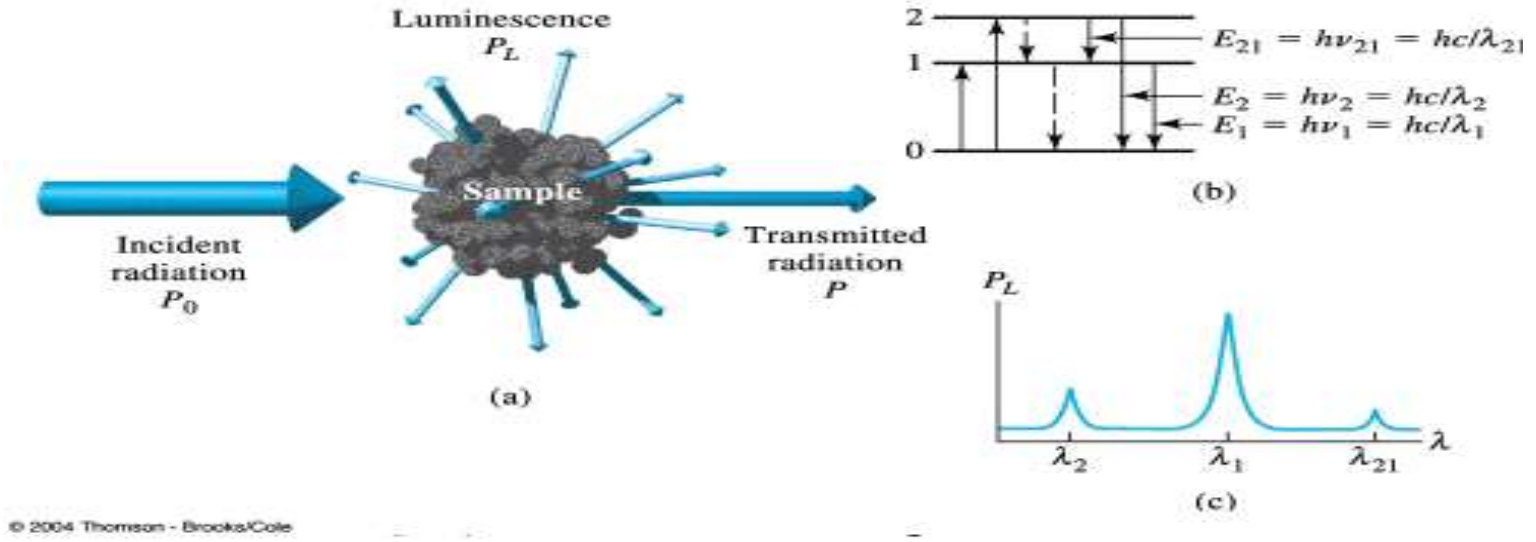


(c)



When the sample is stimulated by application of an external electromagnetic radiation source, several processes are possible. Some of the incident radiation can be absorbed and promote some of the analyte species to an excited state. In ***absorption spectroscopy***, the amount of light absorbed as a function of wavelength is measured, which can give qualitative and quantitative information about the sample. In ***photoluminescence spectroscopy*** the emission of photons is measured following absorption. The most important forms of photoluminescence for analytical purposes are ***fluorescence*** and ***phosphorescence spectroscopy***.

Fluorescence requires that the *spin state of the electron remains the same during the transition from the* lowest excited singlet state, S1, to the singlet ground state, S0

Phosphorescence requires that the *spin state of the electron changes during the transition from the* lowest excited triplet state, T1, to the singlet ground state, S0.

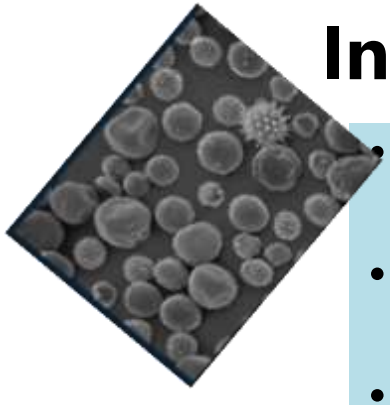
Phosphorescence decay is similar to fluorescence, except the electron undergoes a spin conversion into a "forbidden" triplet state (**T(1)) instead of** the lowest singlet excited state, a process known as **intersystem crossing.** Emission from the triplet state occurs with lower energy relative to fluorescence, hence emitted photons have longer wavelengths

Microscopic Imaging

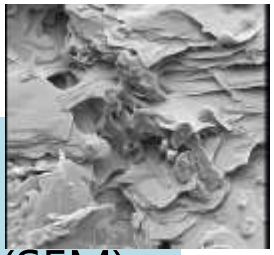
Investigating the small

It is necessary for scientists to make observations in their daily work. But what if their research occurs on a scale that is not visible to the naked eye?

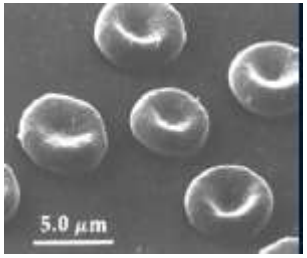
This presentation will introduce you to three instruments which aid scientists for this type of research.



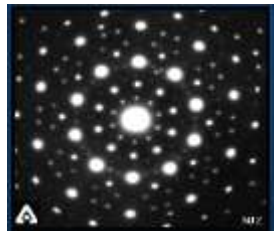
Introduction to Electron Microscopy



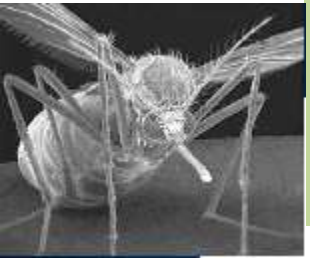
- Ultrastructural study = Electron microscopy
- Two types of EM: Transmission (TEM) and Scanning (SEM)
- Resolution of TEM : best at about 0.2 nm (nanometer = 10^-9 m),
  which is about 1000x better than ordinary light microscope
- TEM is far more useful for medical investigations than SEM

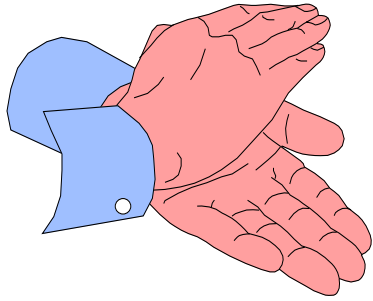


Merits of EM



- **high magnification at high resolution**
- technique largely standardized
- some ultrastructural features are highly specific for certain cell types or diseases





What are the limits of Resolution?

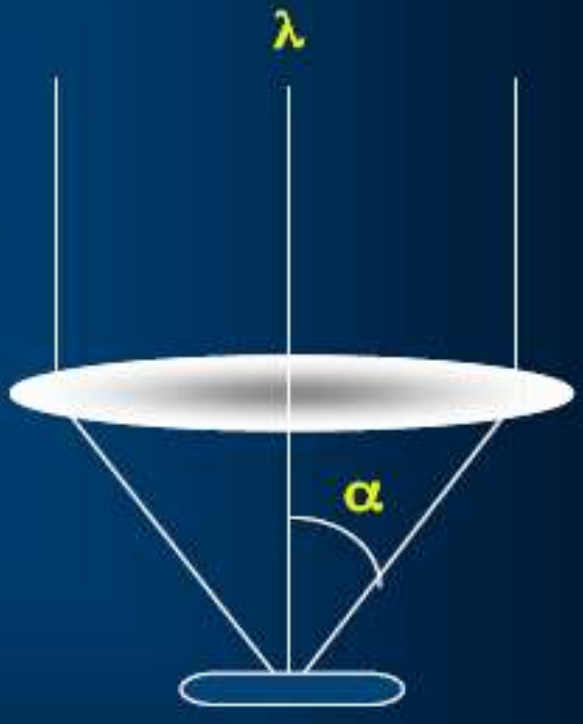
Abbe (Diffraction) Limit:

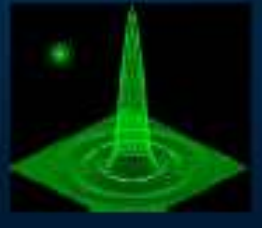
Defines the minimum resolvable distance between the image of two point objects using a perfect lens.

In any magnifying system a point object (i.e. zero dimension) cannot be imaged as a point but is imaged as a distribution of intensity having a finite width.

Resolution of an imaging system

$$\rho = \frac{0.6\lambda}{\eta \sin(\alpha)}$$





λ = wavelength of the imaging radiation
η = index of refraction of the lens
α= illumination semi-angle
NA = numerical aperture = η sin (α)

Some Fundamental Properties of Electrons

- Electron wavelength: based on de Broglie's ideas of wave-particle duality we know $\lambda = h/p$, where p is the electron momentum , h is Planck's constant, and λ is corresponding wavelength of the electron.
- In the TEM we impart momentum to the electron by accelerating it through a potential drop, V, giving it a kinetic energy eV This potential energy must equal the kinetic energy: $eV = m_o v^2/2$,

$$p = m_o v = (2 m_o v e V)^{1/2}$$

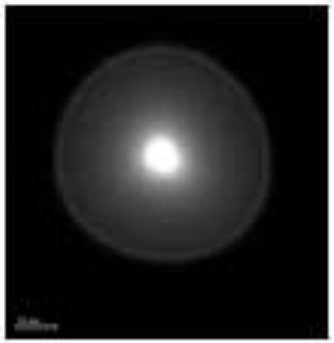
For nonrelativistic electron wavelength $\lambda = h/(2 m_o v\ eV)^{1/2}$

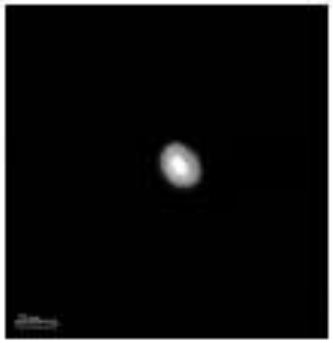
- However, for electron microscopy, relativistic effect cannot be ignored at 100-keV energies and above because the velocity of the electron become greater than half the speed of light. So the corrected (relativistic effect is considered) electron wavelength is:

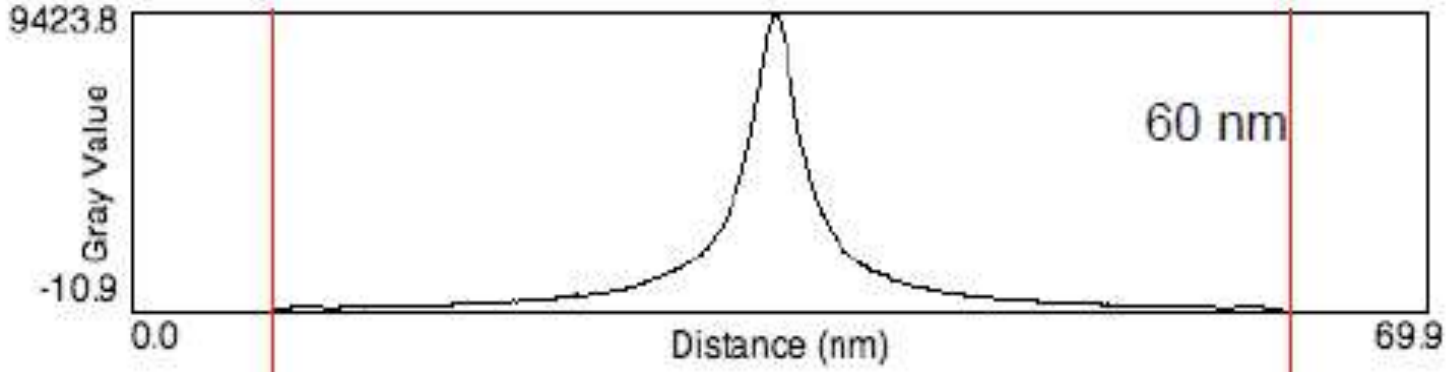
$$\lambda = h/[2 m_o eV(1 + eV/2 m_o c^2)]^{1/2}$$

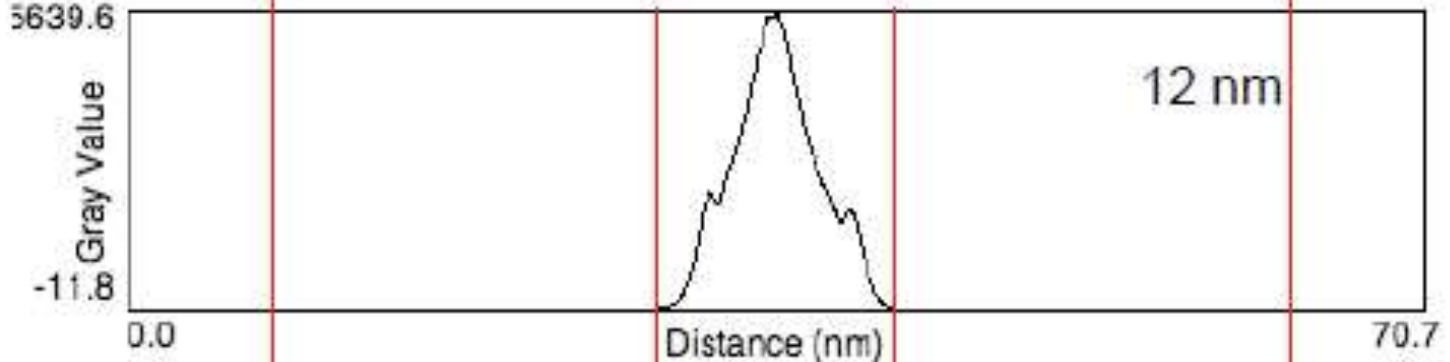
Light Microscope	Electron Microscope
$\lambda \sim 0.5\ \mu m$	$\lambda = \frac{h}{\sqrt{2 m_o e V_o}} = 0.068$ Å (30 kV)
$\eta = 1.5$ (glass)	$\eta = 1.0$ (Vacuum)
$\alpha \sim 70°$	$\alpha \leq 1°$
$\rho \sim 0.21\ \mu m = 2100$ Å	$\rho \sim 4.1$ Å

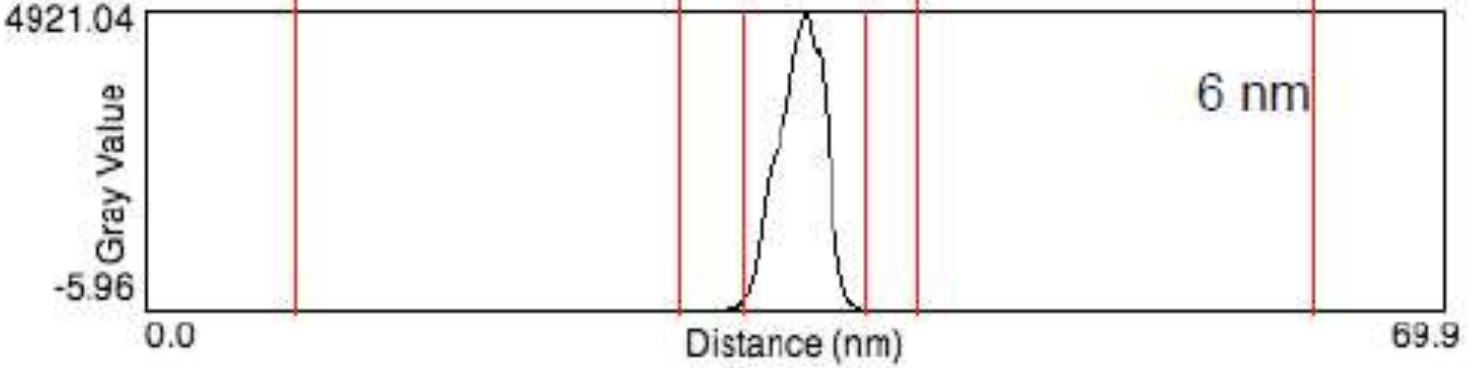
$$\rho = \frac{0.6\lambda}{\eta \sin(\alpha)}$$





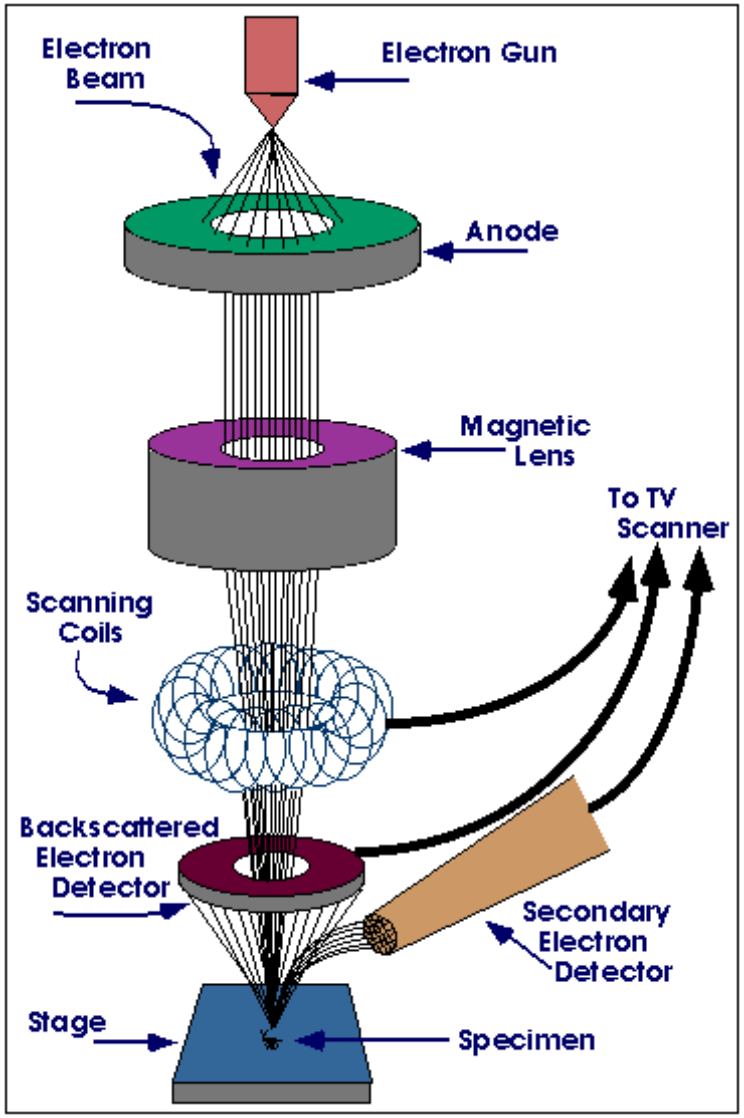

9423.8
Gray Value
-10.9
60 nm
0.0
Distance (nm)
69.9


5639.6
Gray Value
-11.8
12 nm
0.0
Distance (nm)
70.7

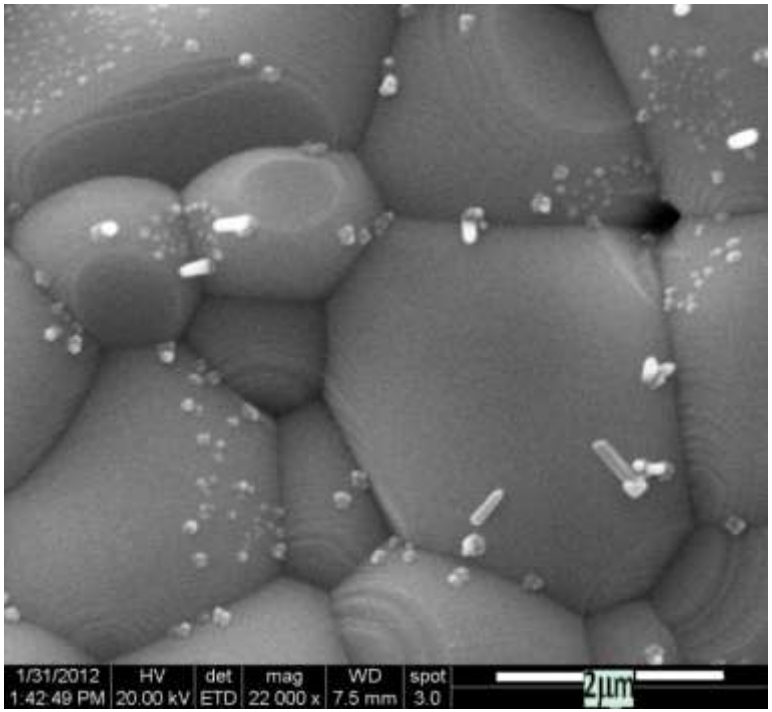

4921.04
Gray Value
-5.96
6 nm
0.0
Distance (nm)
69.9

Scanning Electron Microscope (SEM)

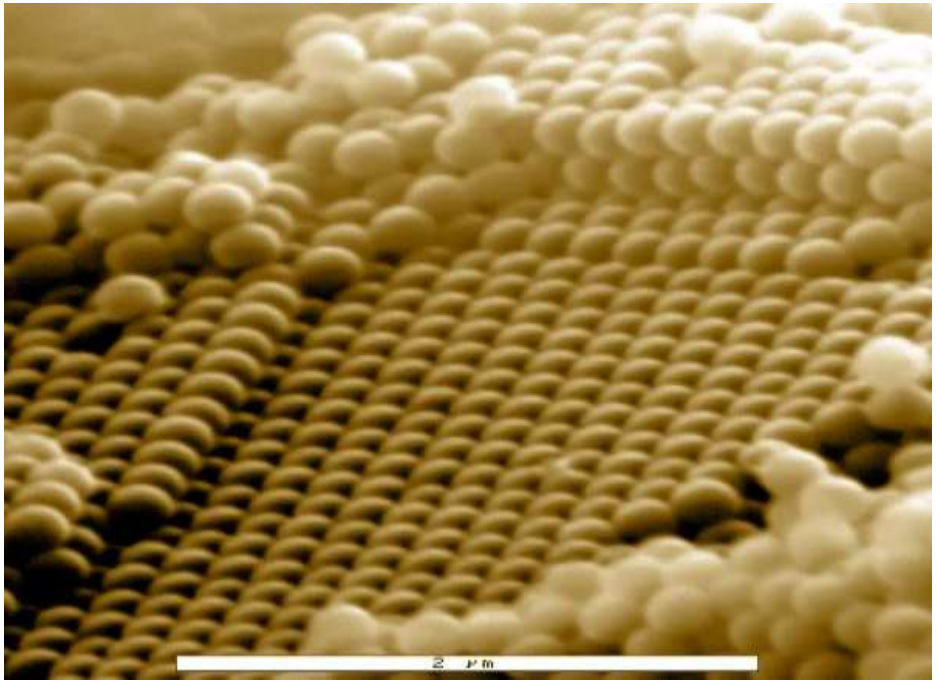
- The Scanning Electron Microscope (SEM) uses electrons to form an image.
- The cathode (tungsten filament) generates an electron beam due to thermionic emission.
- The anode, which is positive with respect to the tungsten filament, causes electrons to accelerate.
- Electrons accelerate in the space between the anode and the cathode and move down the evacuated column towards the sample.
- The electron beam is then collimated by the condenser and focused by the objective lens on the sample.
- The electron beam hits the sample, producing secondary electrons from the sample, collected by a detector



❖The image consists of thousands of spots of varying intensity on the cathode ray tube (CRT) that represent the topography of the sample. The pattern of deflection of the electron beam is the same as the pattern of deflection of the spot of light on the CRT.

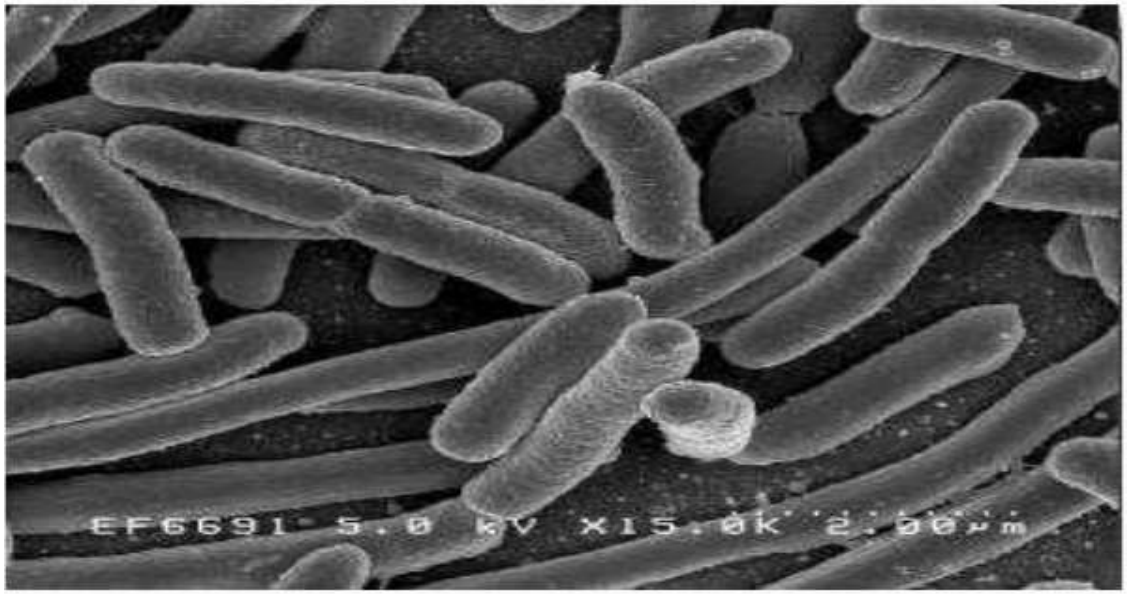


Grains of ceramic bulk crystal



Piece of crystallized polystrene latex

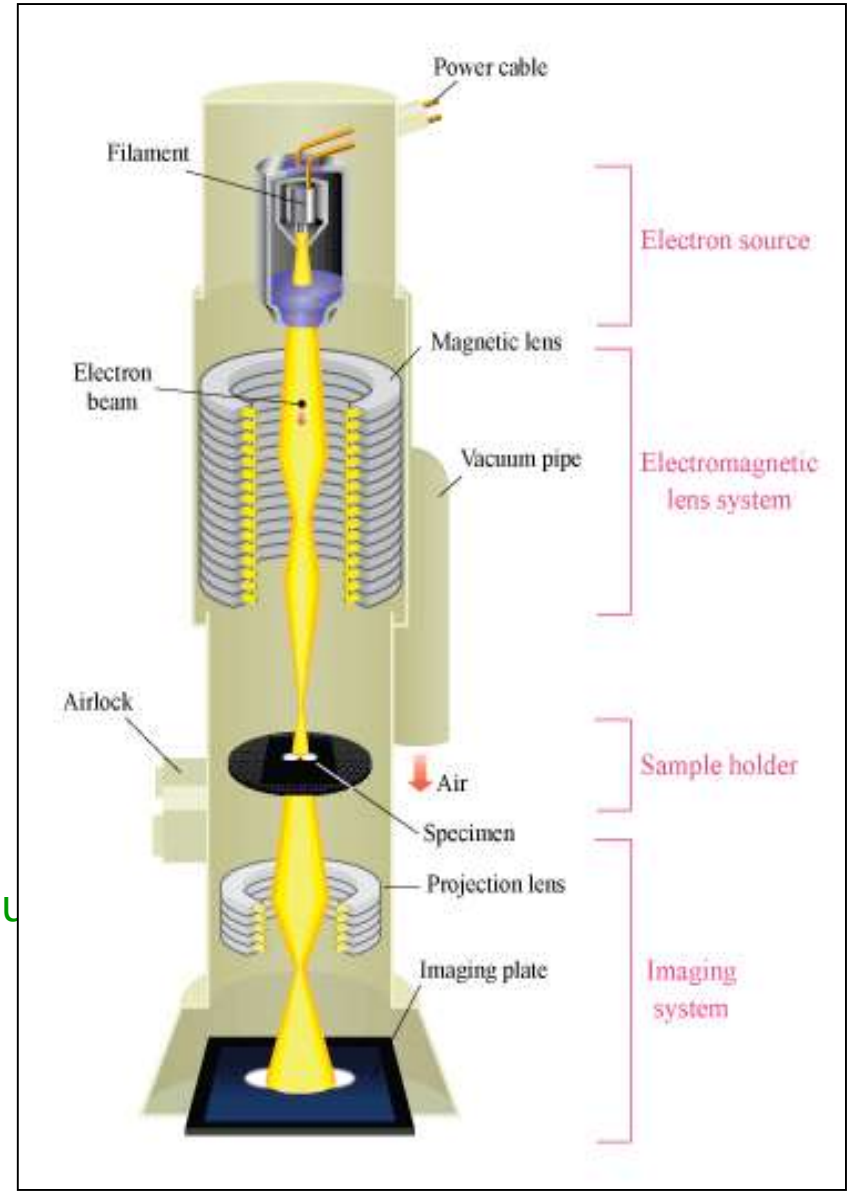
Typical SEM images

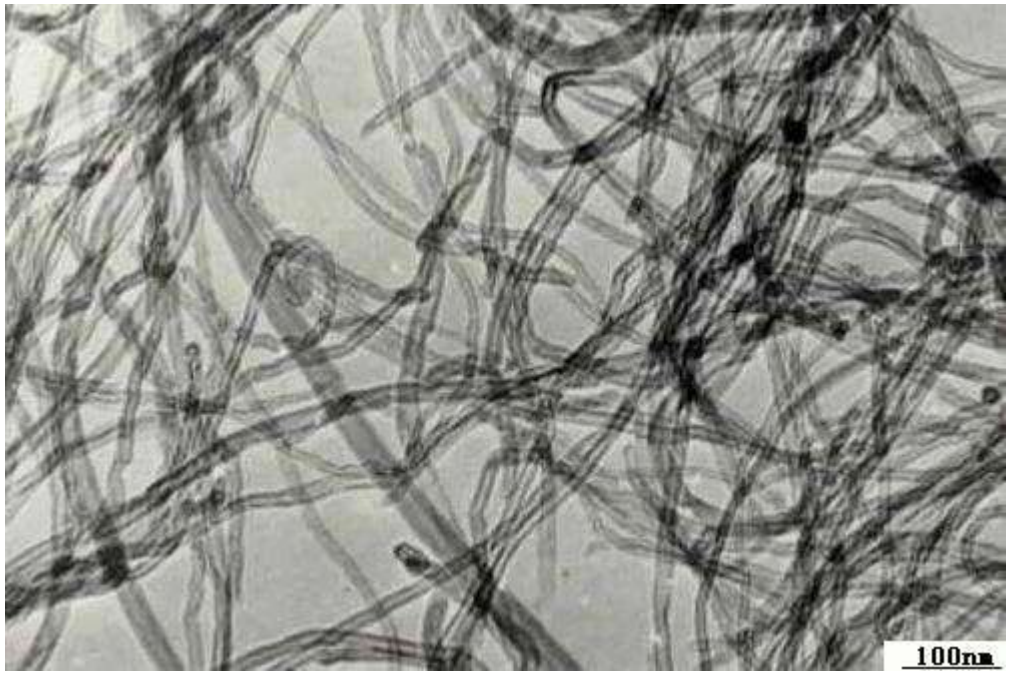


A scanning electron micrograph of the bacteria Escherichia coli (E.coli)

Transmission Electron Microscope (TEM)

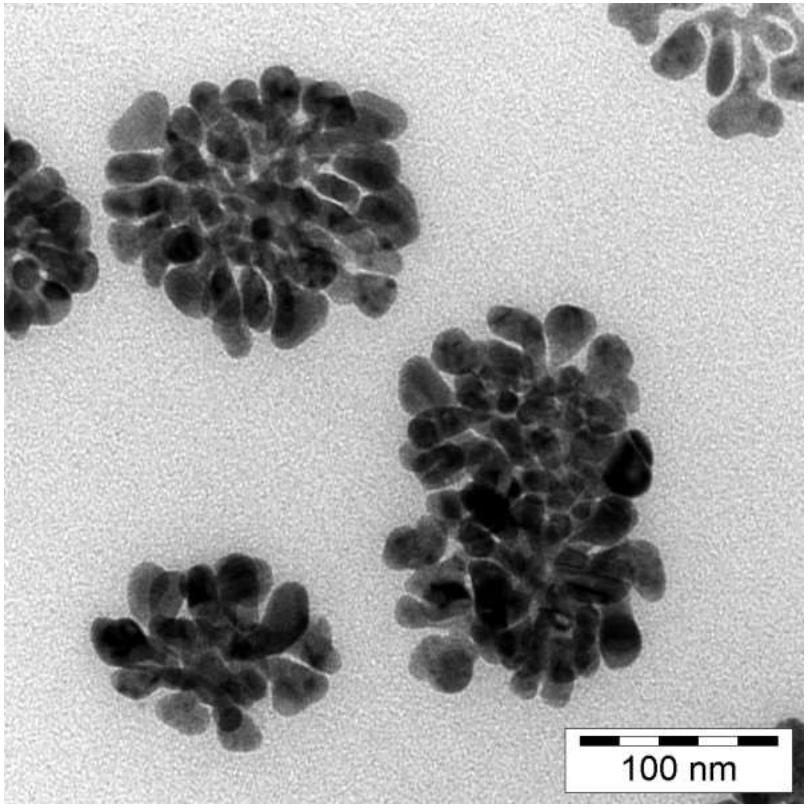
- Electron beam interacts and passes through a specimen.
- The electrons are emitted by a source and are focused and magnified by a system of magnetic lenses.
- The electron beam is confined by the two condenser lenses which also control the brightness of the beam, passes the condenser aperture and “hits” the sample surface
- The electrons that are elastically scattered consist the transmitted beams, which pass throu the objective lens
- The formed image is shown either on a fluorescent screen or in monitor or both and is printed on a photographic film.



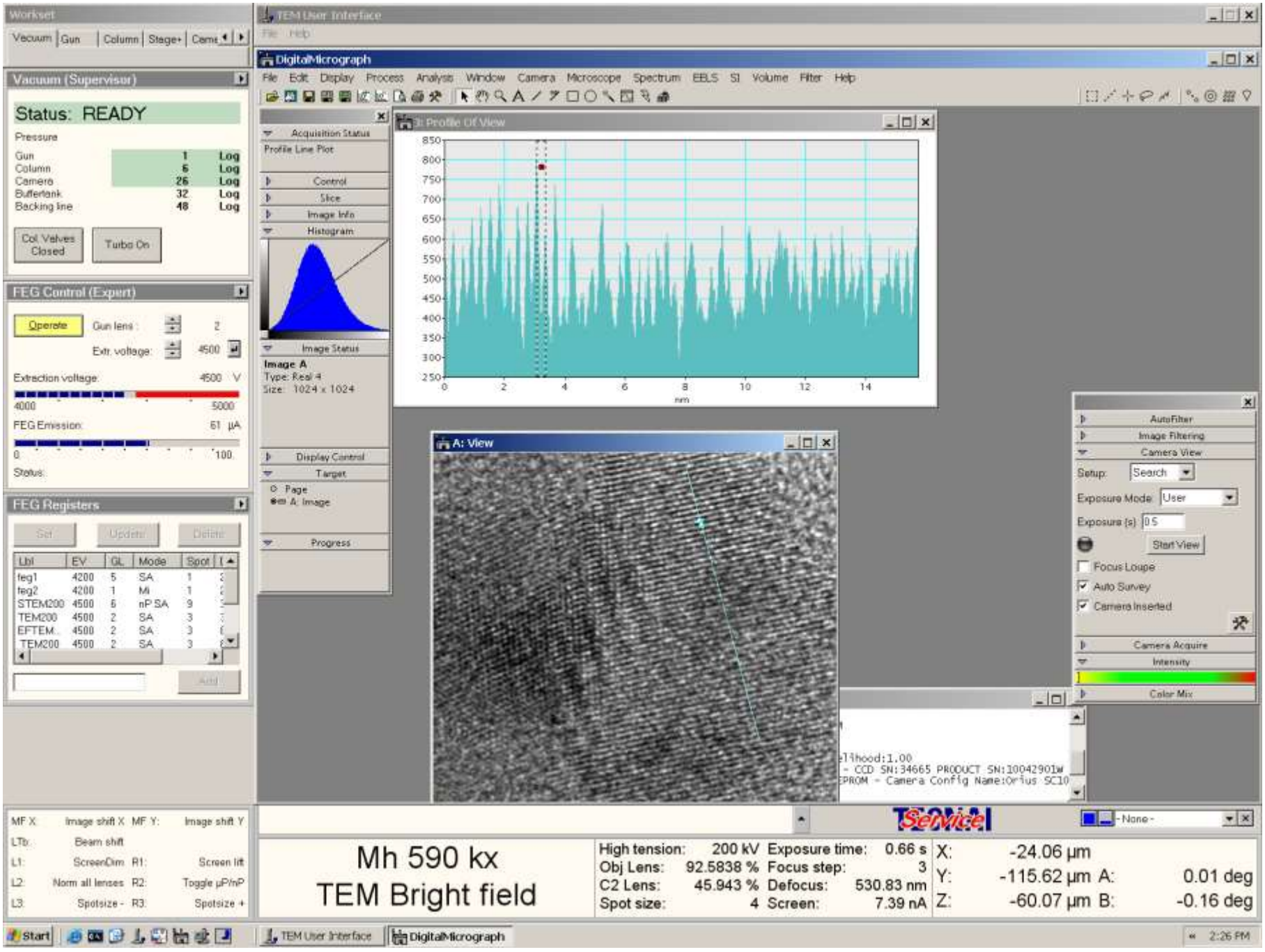


A TEM image of COOH nanotubes

Silver nanoparticles

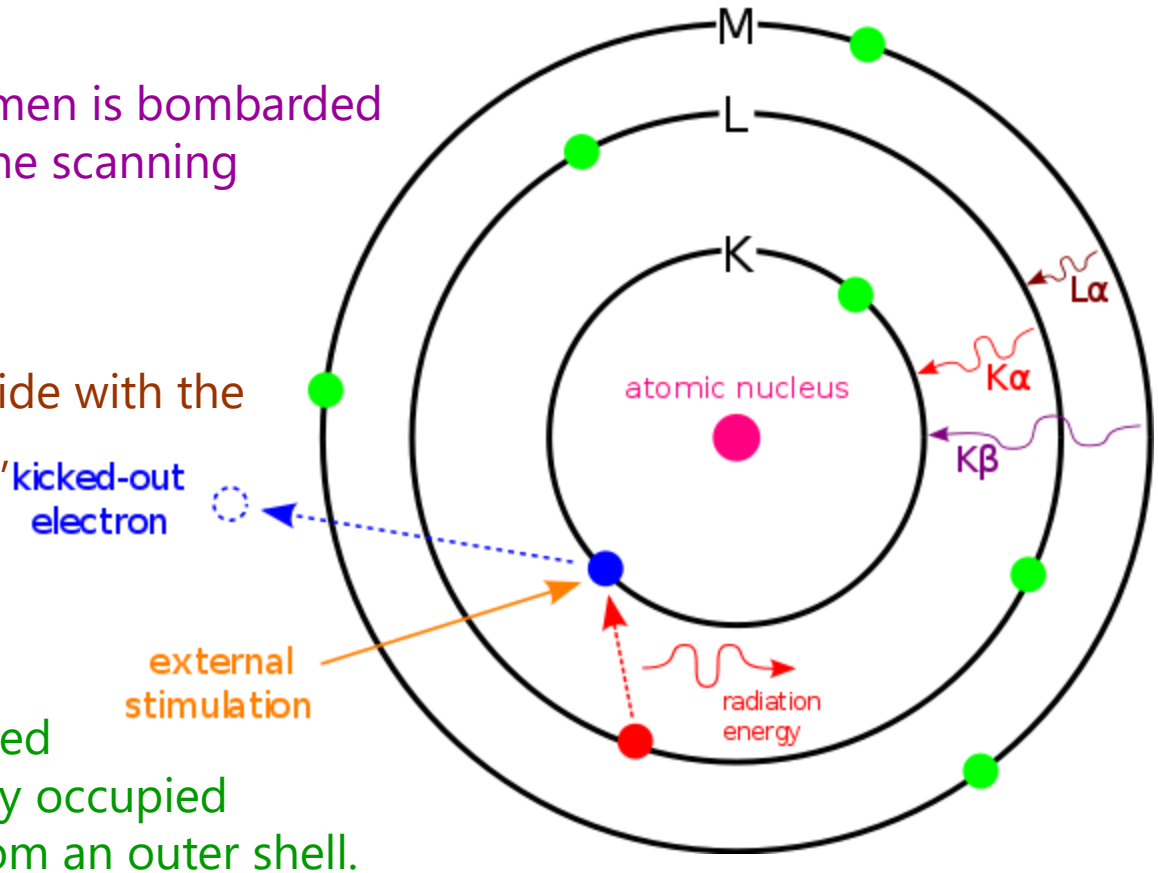


Typical TEM images

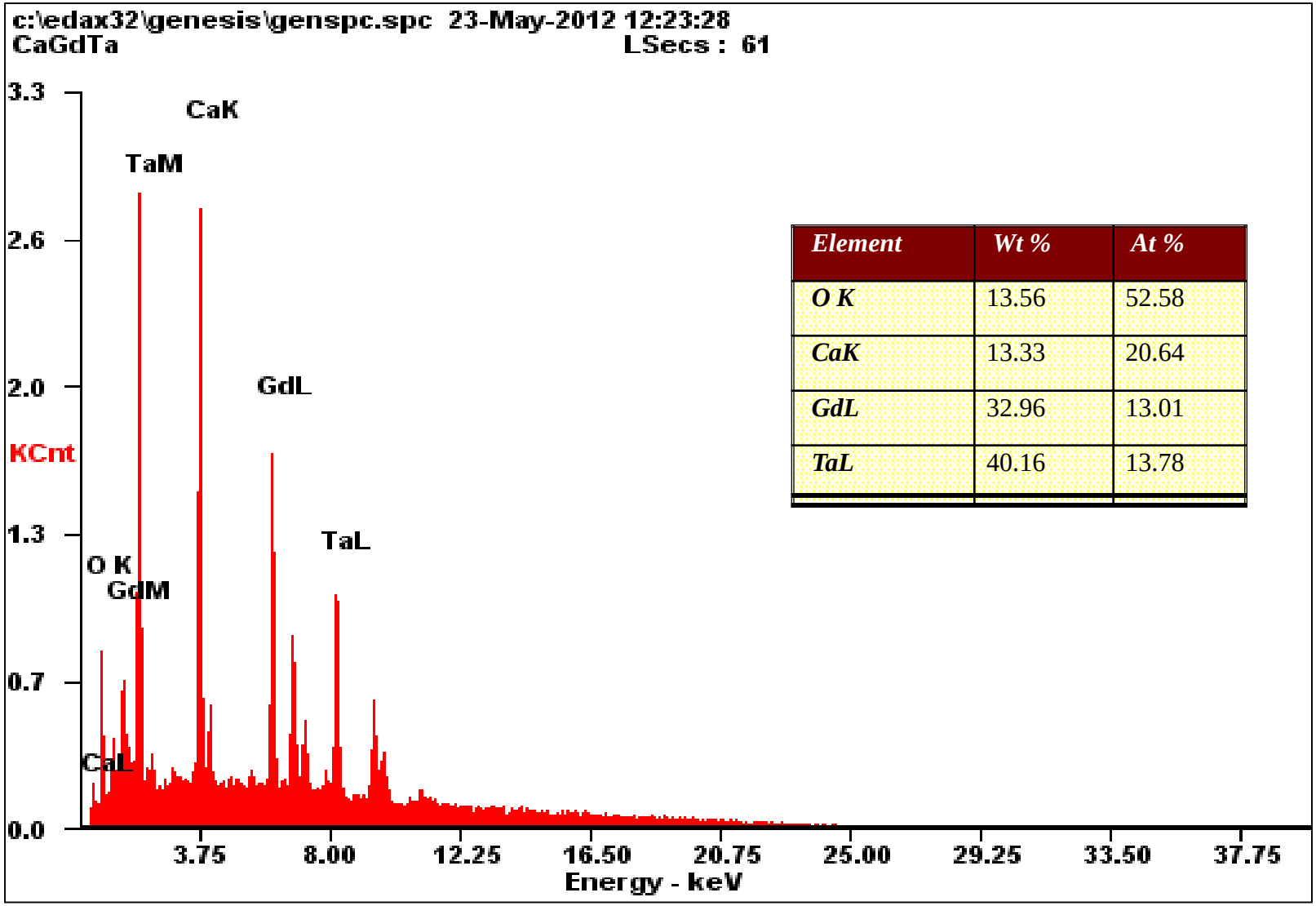

Workset
Vacuum
Gun
Column
Stage
Vacuum (Supervisor)
Status: READY
Pressure
Gun 1 Log
Column 6 Log
Camera 26 Log
Buffertank 32 Log
Backing line 48 Log
Col. Valves Closed
Turbo On
FEG Control (Expert)
Operate
Gun lens: 2
Extr. voltage: 4500
Extraction voltage: 4500 V
4000
5000
FEG Emission: 61 µA
0
100
Status:
FEG Registers
Set
Update
Delete
Lbl EV GL Mode Spot
feg1 4200 5 SA 1
feg2 4200 1 Mi 1
STEM200 4500 5 nP SA 9
TEM200 4500 2 SA 3
EFTEM 4500 2 SA 3
TEM200 4500 2 SA 3
Add
TEM User Interface
File Help
DigitalMicrograph
File Edit Display Process Analysis Window Camera Microscope Spectrum EELS SI Volume Filter Help
Acquisition Status
Profile Line Plot
Control
Slice
Image Info
Histogram
Image Status
Image A
Type: Real 4
Size: 1024 x 1024
Display Control
Target
Page
A: Image
Progress
Profile Of View
850
800
750
700
650
600
550
500
450
400
350
300
250
0 2 4 6 8 10 12 14
nm
A: View
AutoFilter
Image Filtering
Camera View
Setup: Search
Exposure Mode: User
Exposure (s): 0.5
Start View
Focus Loupe
Auto Survey
Camera Inserted
Camera Acquire
Intensity
Color Mix
ellhood:1.00
- CCD SN:34665 PRODUCT SN:10042901W
EPROM - Camera Config Name:Orius SC10
MF X: Image shift X MF Y: Image shift Y
LTb: Beam shift
L1: ScreenDim R1: Screen lift
L2: Norm all lenses R2: Toggle µP/nP
L3: Spotsize - R3: Spotsize +
Service
- None -
Mh 590 kx
TEM Bright field
High tension: 200 kV
Obj Lens: 92.5838 %
C2 Lens: 45.943 %
Spot size: 4
Exposure time: 0.66 s
Focus step: 3
Defocus: 530.83 nm
Screen: 7.39 nA
X: -24.06 µm
Y: -115.62 µm A: 0.01 deg
Z: -60.07 µm B: -0.16 deg
Start
TEM User Interface
DigitalMicrograph
2:26 PM

Energy Dispersive X-Ray (EDAX) Analysis

- During EDX analysis, the specimen is bombarded with an electron beam inside the scanning electron microscope.
- The bombarding electrons collide with the specimen atoms own electrons, knocking some of them off in the process.
- A position vacated by an ejected inner shell electron is eventually occupied by a higher-energy electron from an outer shell.



EDAX analysis of Ca_2GdTaO_6 double perovskites

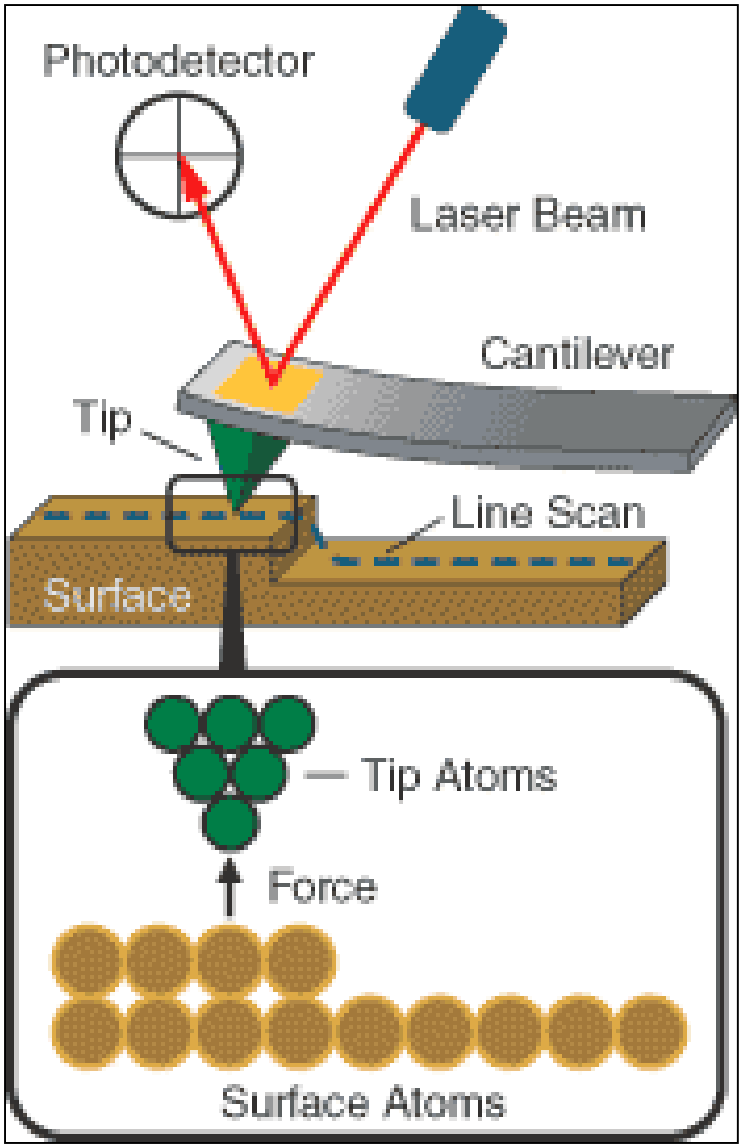


Element	*Wt %*	*At %*
O K	13.56	52.58
CaK	13.33	20.64
GdL	32.96	13.01
TaL	40.16	13.78

KV:24.98 TILT: 0.00 TAKE-OFF:35.01 AMPT:12.8
DETECTOR TYPE :SUTW-SAPPHIRE RESOLUTION :139.60

Atomic Force Microscope

- In simple terms, the atomic force microscope works by scanning a sharp probe over the surface of a sample in a raster pattern.
- A sharp tip touches a sample and forces between the atoms in the sample affect a lever on the tip. This creates a topographical map image for the user.
- By monitoring the movement of the probe, a 3-D image of the surface can be constructed.

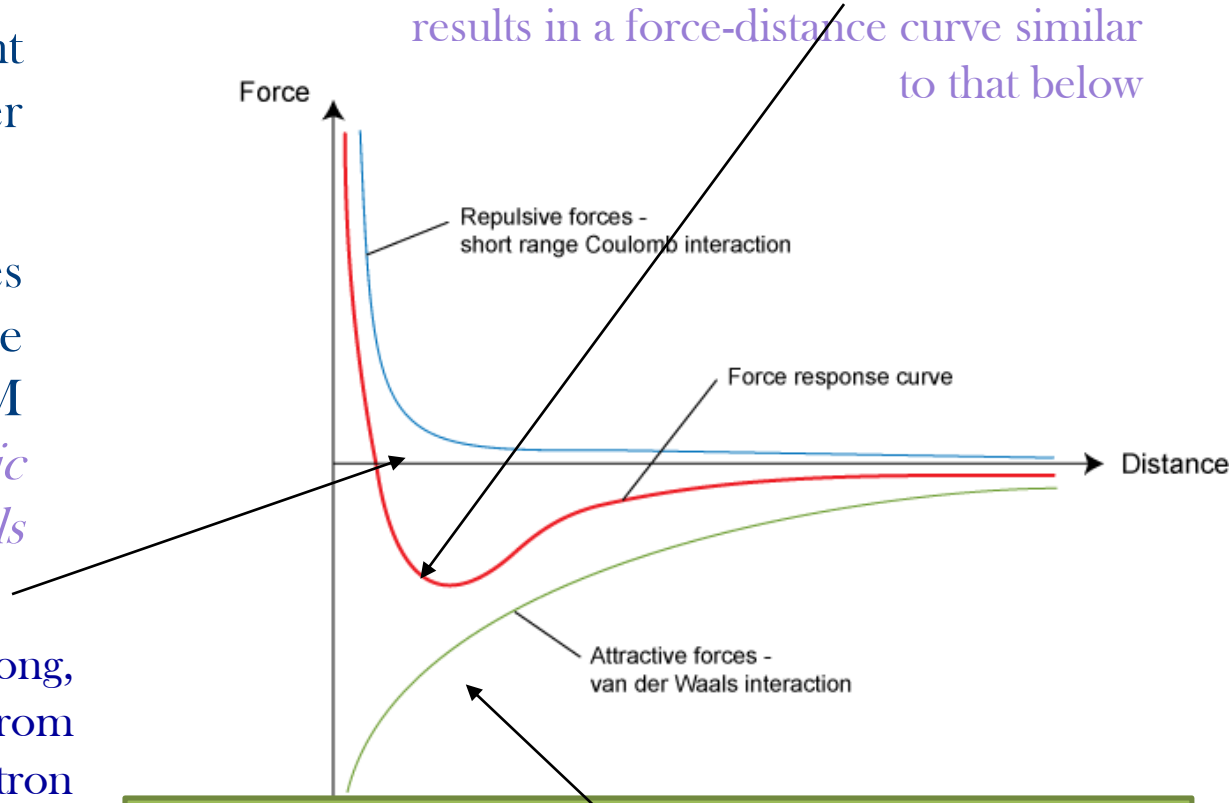


Atomic Force Microscopy -Tip – Surface Interaction

- When the tip is brought close to the sample, a number of forces may operate.
- Typically the forces contributing most to the movement of an AFM cantilever are the *coulombic* and *van der Waals* interactions.

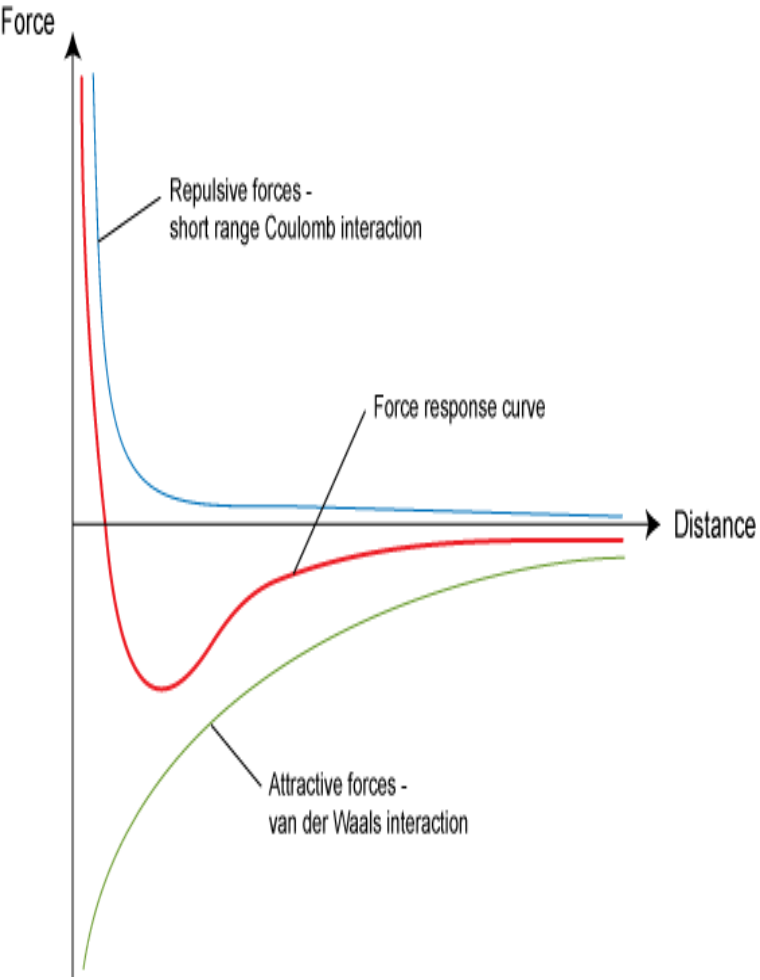
Coulombic Interaction: This strong, short range repulsive force arises from electrostatic repulsion by the electron clouds of the tip and sample. This repulsion increases as the separation decreases.

The combination of these interactions results in a force-distance curve similar to that below

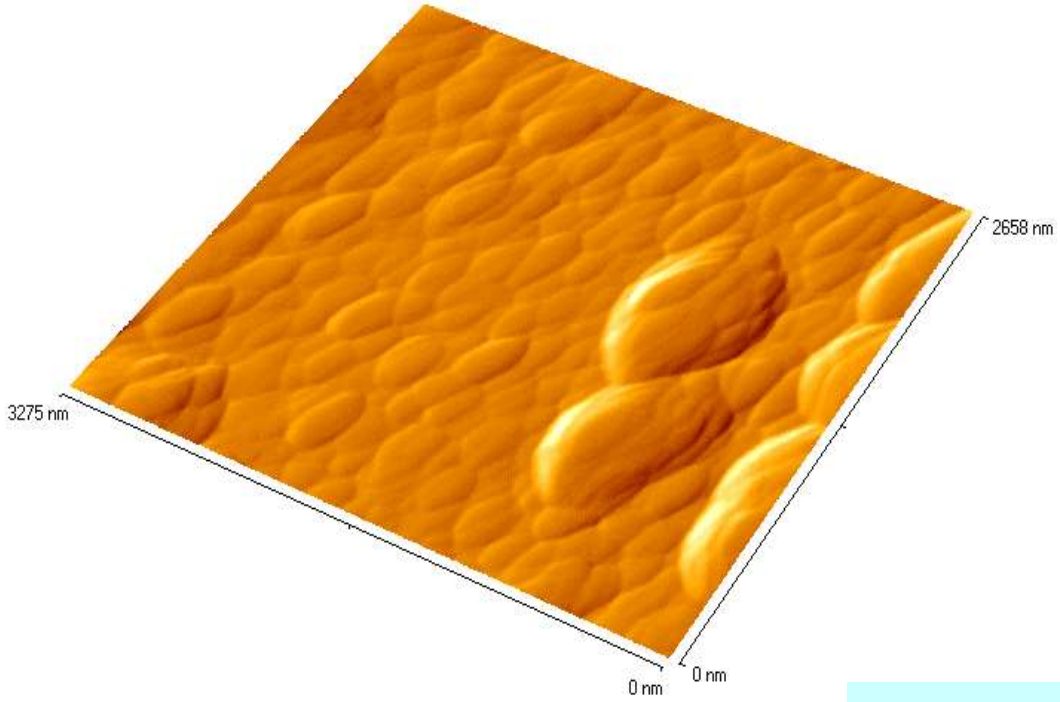


Van der Waals interactions: These are longer range attractive forces, which may be felt at separations of up to 10 nm or more. They arise due to temporary fluctuating dipoles.

Atomic Force Microscopy -Tip – Surface Interaction

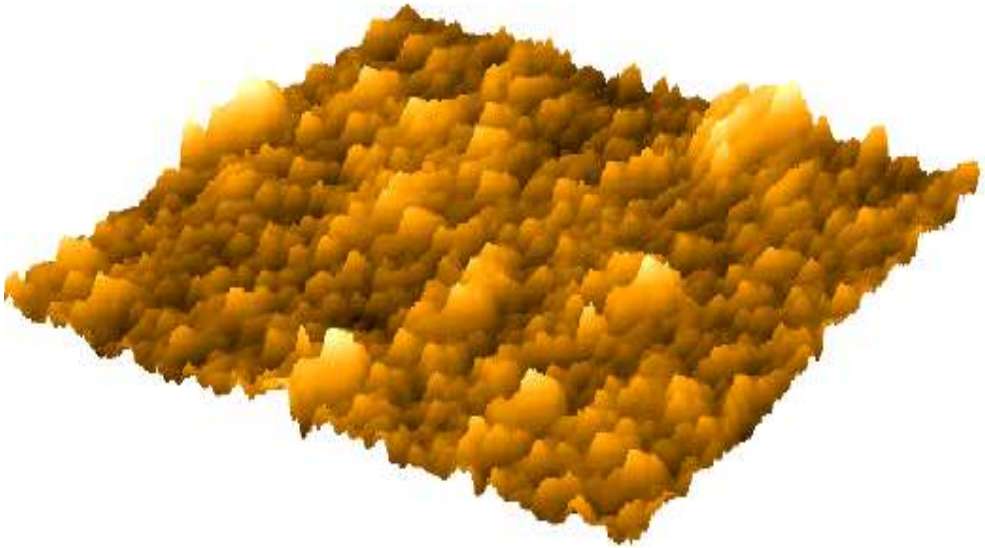


- As the tip is brought towards the sample, van der Waals forces cause attraction.
- As the tip gets closer to the sample this attraction increases.
- However at small separations the repulsive coulombic forces become dominant. The repulsive force causes the cantilever to bend as the tip is brought closer to the surface.
- There are other interactions besides coulombic and van der Waals forces which can have an effect.
  - When AFM is performed in ambient air, the sample and tip may be coated with a thin layer of fluid (mainly water).
  - When the tip comes close to the surface, *capillary forces* can arise between the tip and surface.



AFM contact image of BaTiO3 surface

Typical AFM images



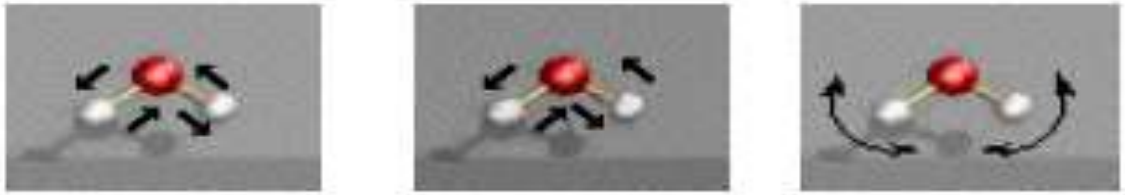
AFM contact image of ZnO:CuO/Si surface

Vibrational Properties

Vibrational Properties : (FTIR & Raman Spectroscopy)

Chemical bonds between atoms in a molecule or a crystal are not rigid ...

↳ Atoms move around their centre of gravity !
(small amplitude, up to a fraction of the atomic size)



Vibrations are characteristic for a material → *« Fingerprint »*
(structure, chemistry, physics, state)

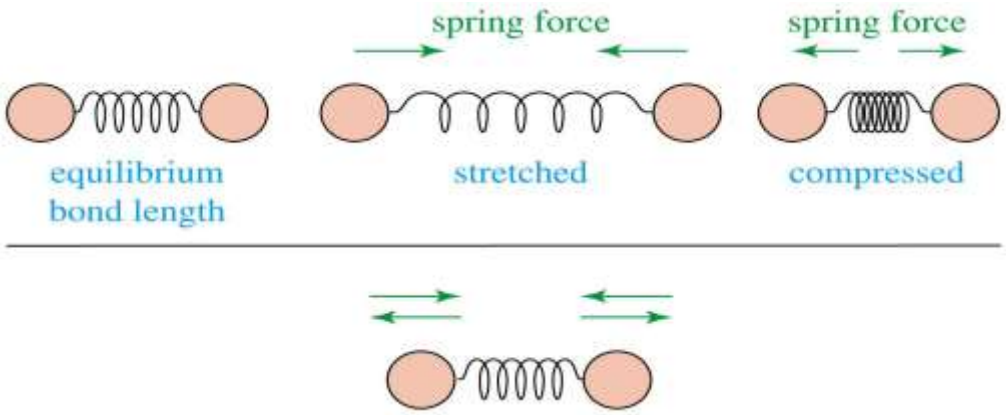
Methods

- **Infrared Spectroscopy**
- **Raman Spectroscopy**
- **Ab-initio calculation**
- **(Sometimes Inelastic neutron scattering)**

Infrared Spectroscopy carried out **in** the range of 350 and 4000 cm^{-1}

Raman spectrum of the sample was obtained at an excitation wavelength of 488 nm

Lattice Vibration : a racapitulation



What is a vibration in a molecule?

Any change in shape of the molecule- stretching of bonds, bending of bonds, or internal rotation around single bonds

The motion is governed by a restoring force directly proportional and opposite in sign to displacement of the body from equilibrium position

$\omega = \sqrt{\frac{k}{m}}$

$F = -kx$ *Hooke's law.* k *– is stiffness of the spring*

$md^2x/dt^2 + kx = 0$ *Differential equation of motion of* harmonic oscillator

Crystals: *N atoms in a periodic array vibrating in 3D space*

↓

3N degrees of freedom

↓

finite no. of normal modes

↓

Quantisation of crystal vibrational energy

PHONON: quanta of crystal vibrational energy

The lattice vibration energy

$$E = \int_0^{\infty} \left(\frac{1}{2}\hbar\omega + \frac{\hbar\omega}{e^{\hbar\omega/k_BT} - 1}\right) g(\omega) d\omega$$

Ensure the correct number of modes by imposing a cut-off frequency, above which there are no modes. Since there are 3N lattice vibration modes in a crystal having N atoms, the above equation reduces to

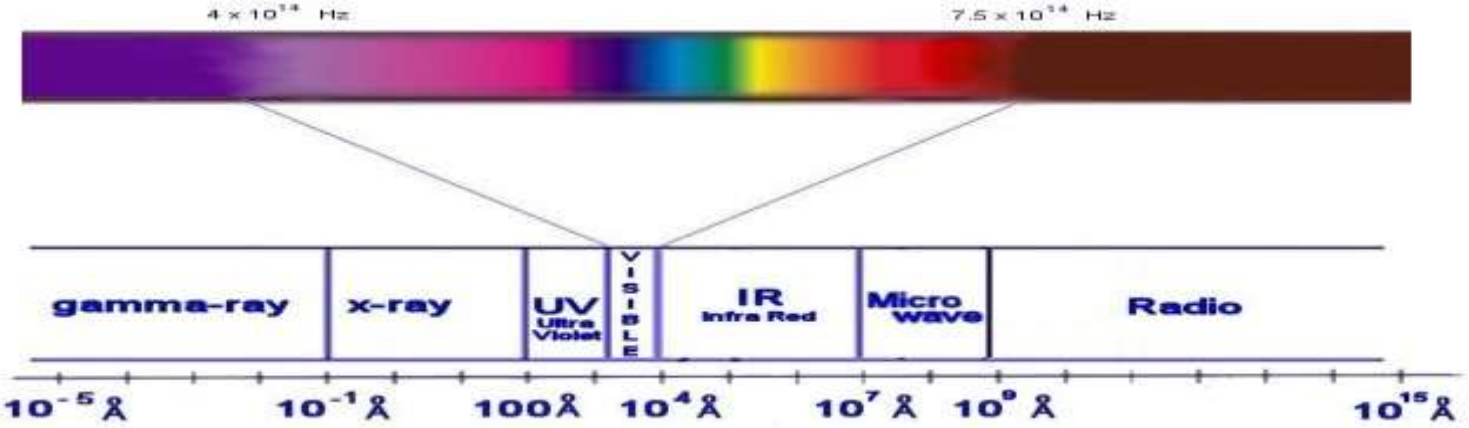
$$E = \frac{9N}{\omega_D^3} \int_0^{\omega_D} \left(\frac{1}{2}\hbar\omega + \frac{\hbar\omega}{e^{\hbar\omega/k_BT} - 1}\right) \omega^2 d\omega = \frac{9N}{\omega_D^3} \left[\int_0^{\omega_D} \frac{\hbar\omega^3}{2} d\omega + \int_0^{\omega_D} \frac{\hbar\omega^3}{e^{\hbar\omega/k_BT} - 1} d\omega \right]$$

$$E = \frac{9}{8} N\hbar\omega_D + \frac{9N}{\omega_D^3} \int_0^{\omega_D} \frac{\hbar\omega^3 d\omega}{e^{\hbar\omega/k_BT} - 1}$$

PHONON

Acoustic ⟷ Optical

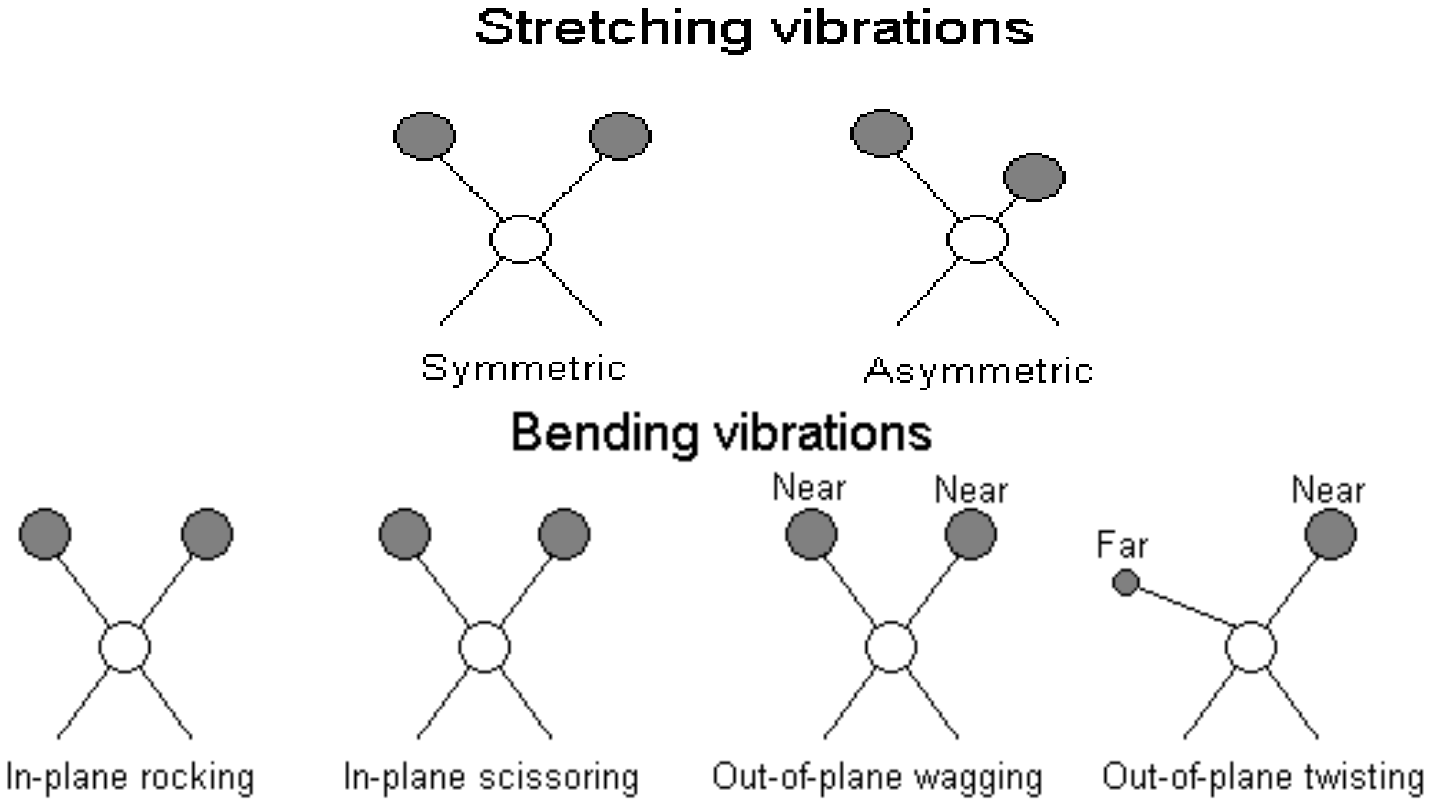
Interact with light



IR and Raman are the most common vibrational spectroscopies for assessing molecular motion Energy levels in Infrared Absorption

Infrared Spectroscopy

The bonds between atoms in the molecule stretch and bend, absorbing infrared energy and creating the infrared spectrum.



A molecule such as H_2O will absorb infrared light when the vibration (stretch or bend) results in a molecular dipole moment change

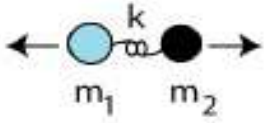
Raman Spectroscopy: Classical Treatment

- Number of peaks related to degrees of freedom

  DoF = 3N - 6 (bent) or 3N - 5 (linear) for N atoms

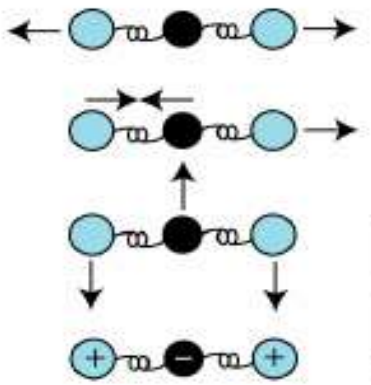
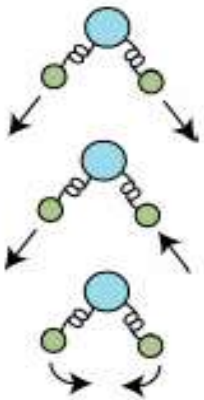
- Energy related to harmonic oscillator

$$\sigma \text{ or } \Delta\sigma = \frac{c}{2\pi}\sqrt{\frac{k(m_1+m_2)}{m_1 m_2}}$$



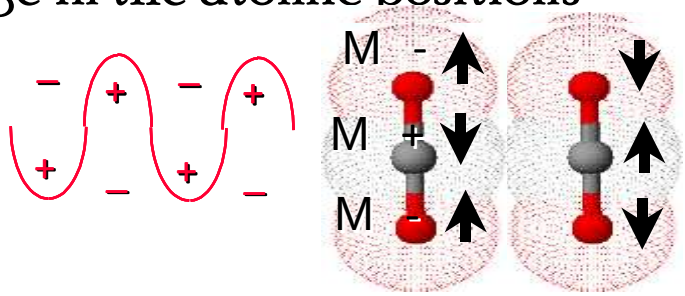
- Selection rules related to symmetry

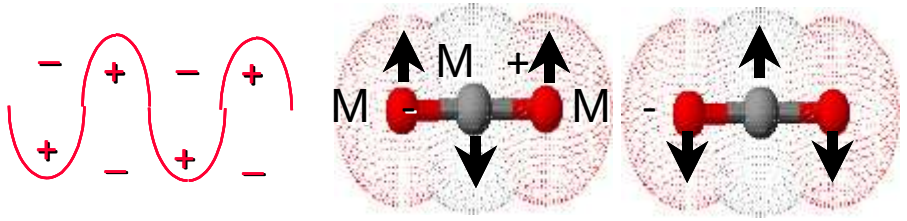
  Rule of thumb: symmetric=Raman active, asymmetric=IR active

CO_2	H_2O
 Raman: 1335 cm^{-1} IR: 2349 cm^{-1} IR: 667 cm^{-1}	 Raman + IR: 3657 cm^{-1} Raman + IR: 3756 cm^{-1} Raman + IR: 1594 cm^{-1}

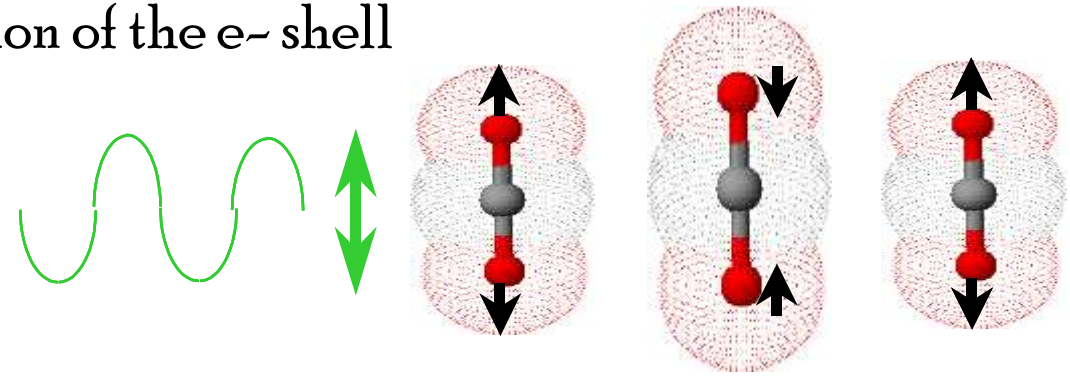
Why is Raman Different to IR?

IR : change in dipole moment i.e induced dipole moment due to change in the atomic positions





Raman : change in polarisibility i.e induced dipole moment due to the deformation of the e- shell



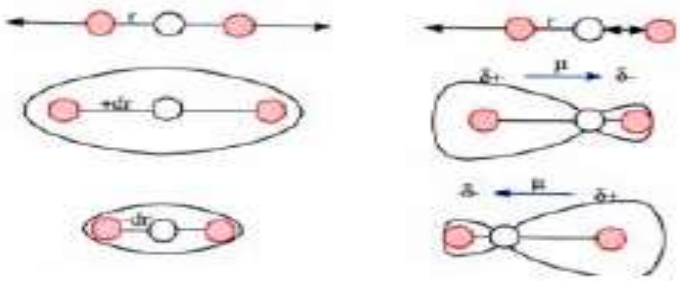
•Selection rules are therefore different

$$\vec{\mu}_{ind} = \alpha\vec{E}$$

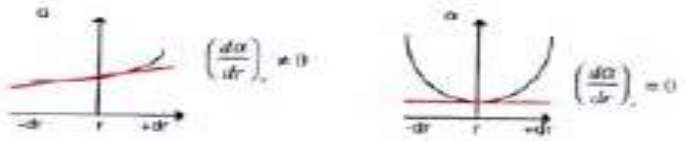
Induced dipole moment — Molecular polarizability

Illustration of the Raman activity & symmetry

Symmetric mode | Asymmetric mode



$$\left(\frac{\partial\alpha}{\partial x}\right)_{x_0} \neq 0$$



Raman active — Raman inactive

$$\left(\frac{\partial\mu}{\partial x}\right)_{x_0} \neq 0$$

IR inactive — IR active

Raman and IR spectroscopy are **complementary**!

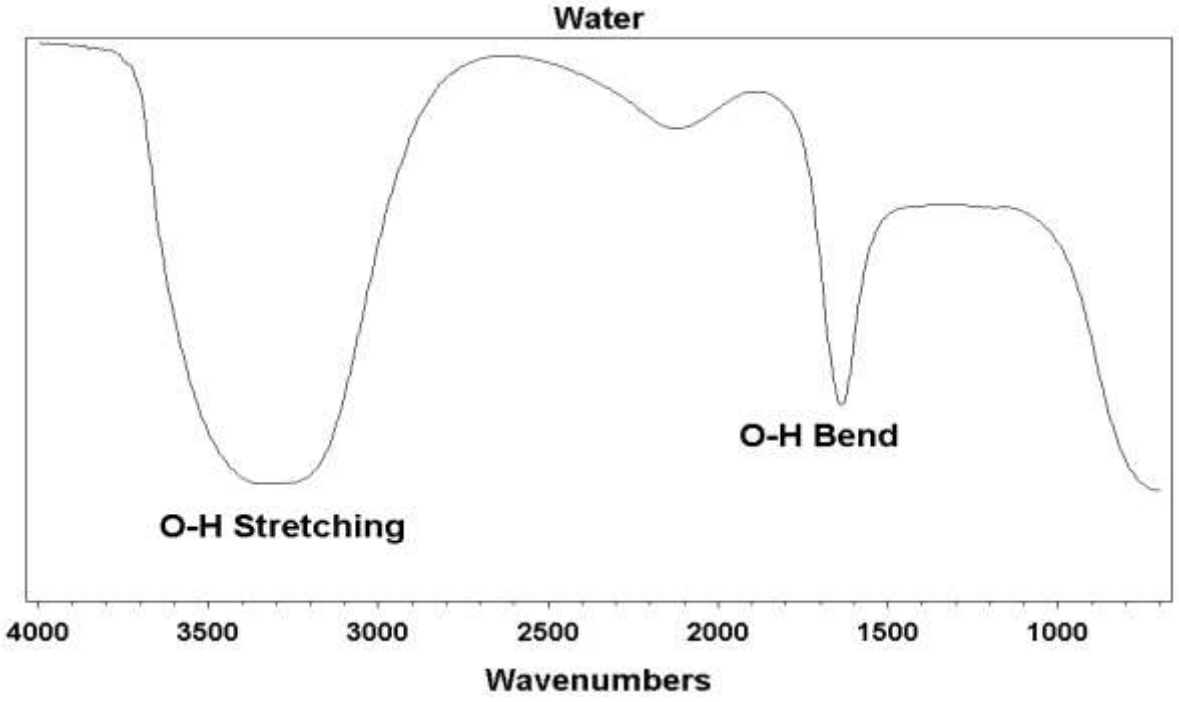
Exclusion rule

In a centro-symmetric molecule or crystal none of the Raman active modes is IR-active and vice versa.

The change in the molecular dipole moment when the atoms vibrate determines whether the vibration is or is not IR active.

Infrared Spectroscopy

A molecule can be characterized (identified) by its molecular vibrations, based on the absorption and intensity of specific infrared wavelengths.



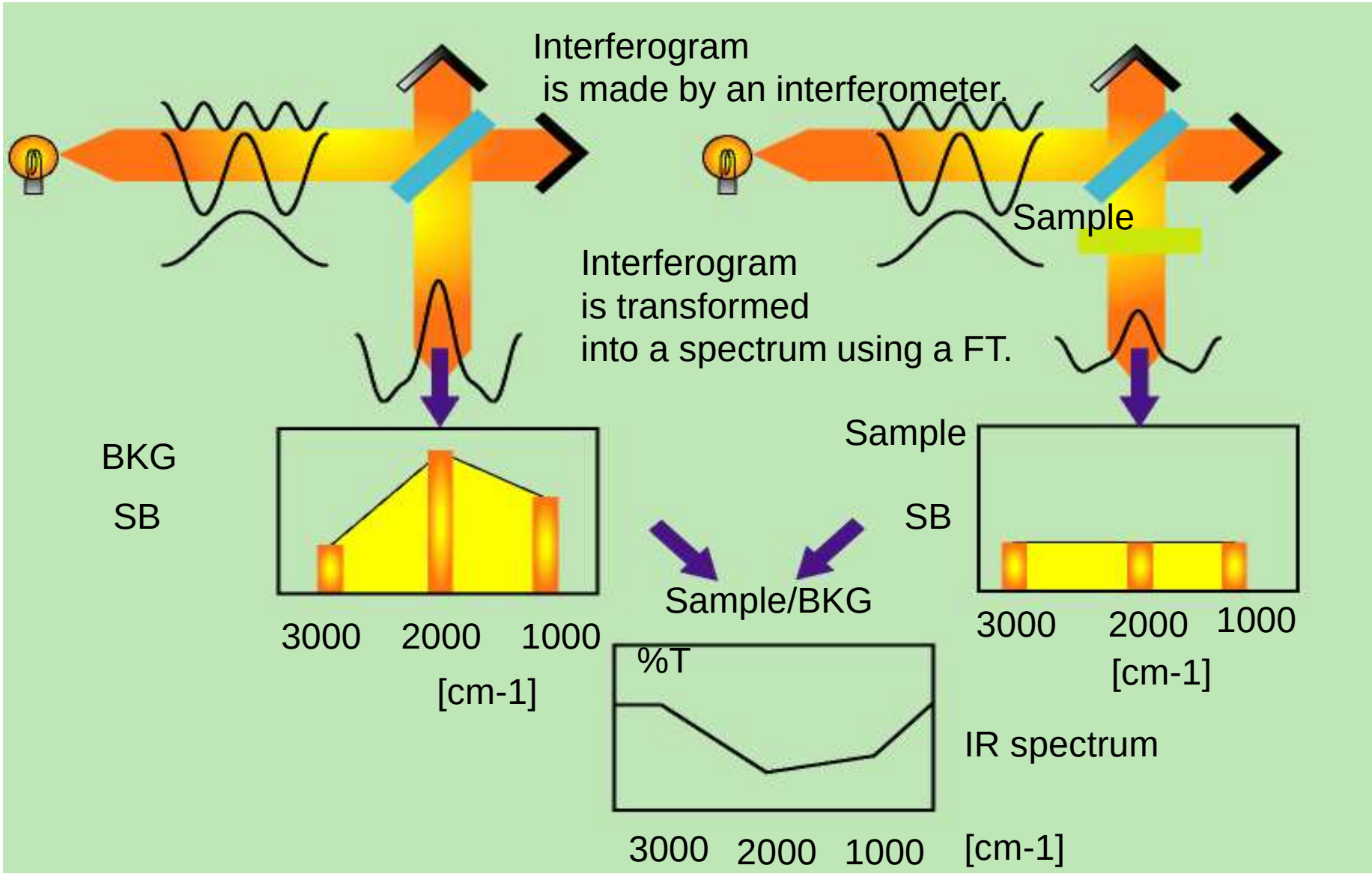
Capabilities of Infrared Analysis

- Identification and quantitation of organic solid, liquid or gas samples.
- Analysis of powders, solids, gels, emulsions, pastes, pure liquids and solutions, polymers, pure and mixed gases.
- Infrared used for research, methods development, quality control and quality assurance applications.
- Samples range in size from single fibers only 20 microns in length to atmospheric pollution studies involving large areas.

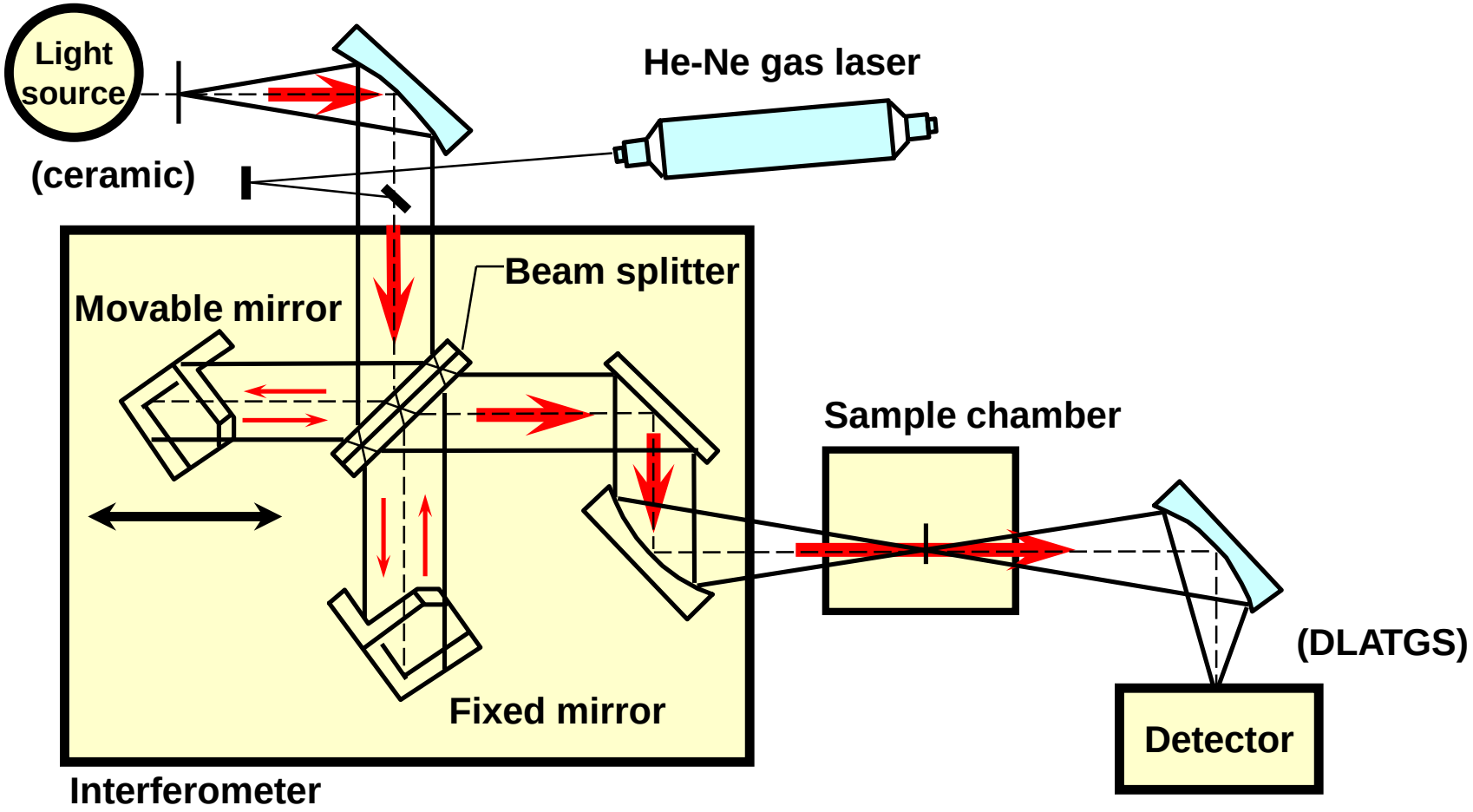
Applications of Infrared Analysis

- Pharmaceutical research
- Forensic investigations
- Polymer analysis
- Lubricant formulation and fuel additives
- Foods research
- Quality assurance and control
- Environmental and water quality analysis methods
- Biochemical and biomedical research
- Coatings and surfactants
- Etc.

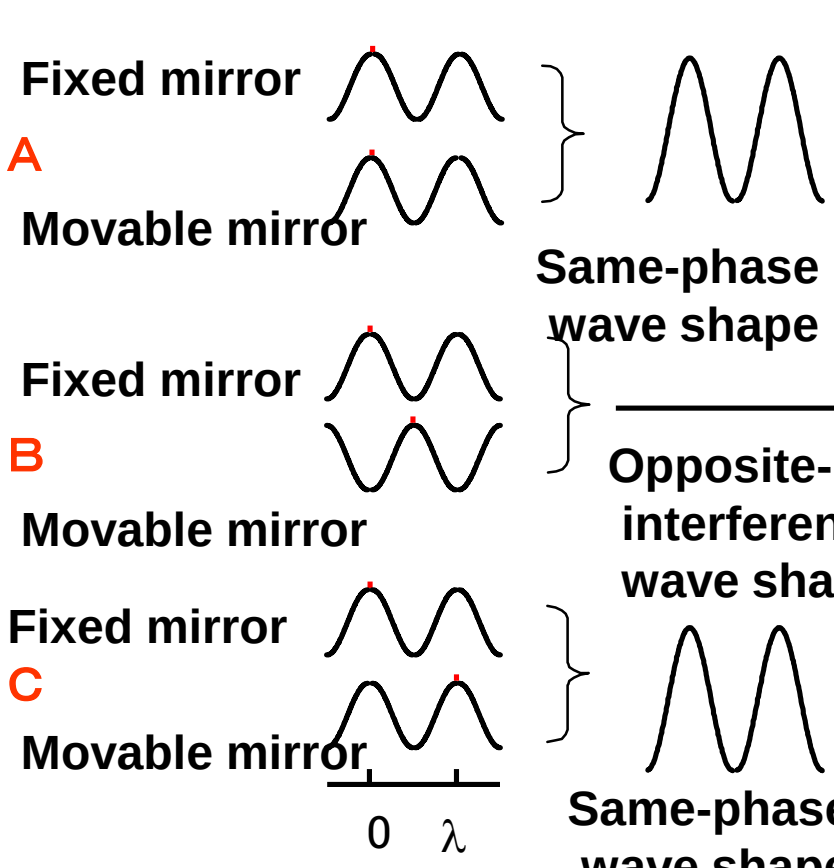
The Principles of FTIR Method

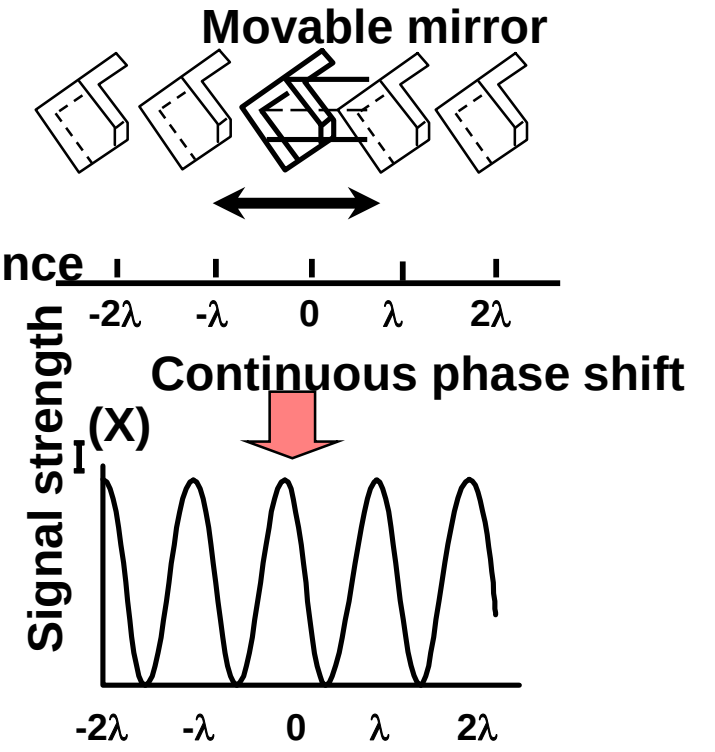


FT Optical System Diagram



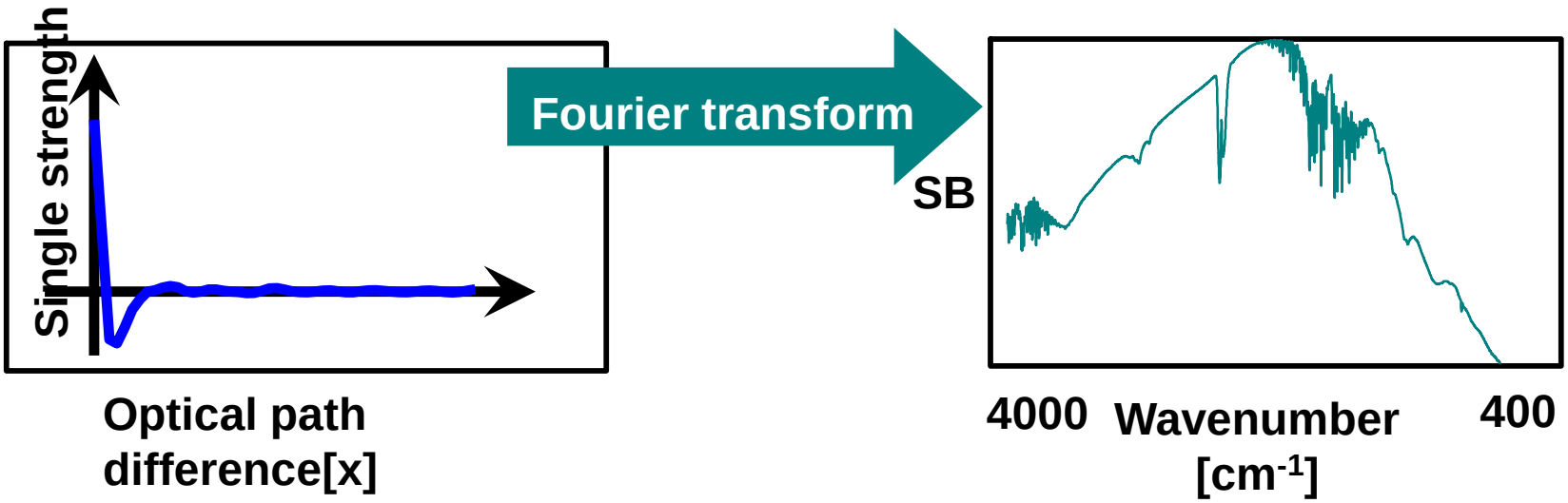
Interference of two beams of light



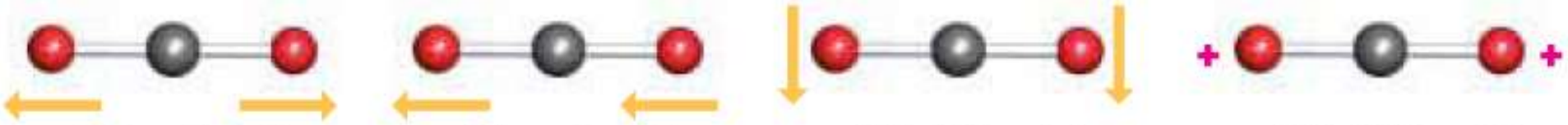


D Interference pattern of light manifested by the optical-path difference

Fourier Transform



Time axis by FFT → Wavenumber



(a) Symmetric stretch
IR inactive

(b) Asymmetric stretch
IR active (2349 cm^{-1})

(c) Bend (deformation)
IR active (667 cm^{-1})

(d) Bend (deformation)
IR active (667 cm^{-1})

Vibrational Degrees of Freedom (vibrational modes)

- $3N-6$ for non-linear molecules
- $3N-5$ for linear molecules
- $3N-3$ for crystals (no free rotation !)

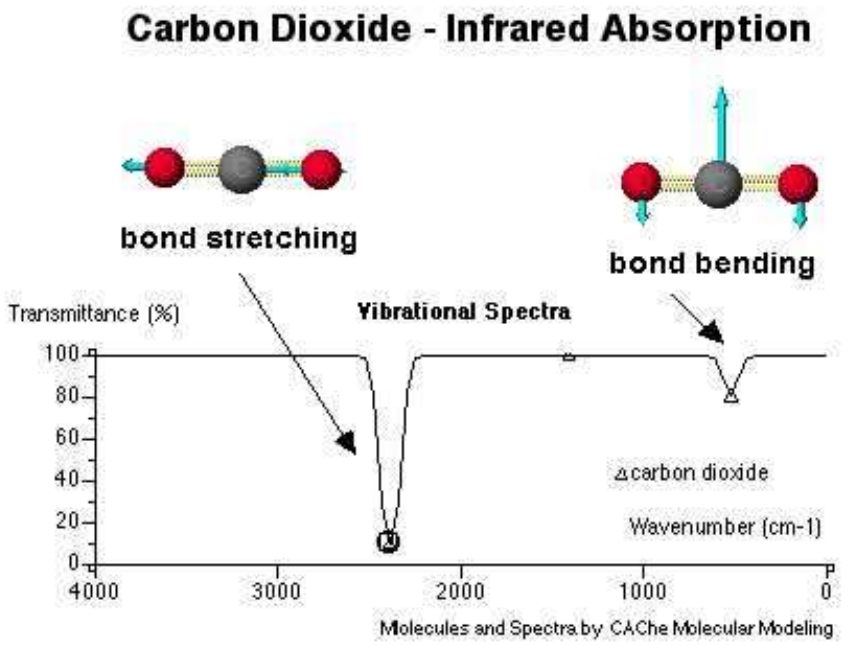
1st Example: **CO2**

IR : change in dipole moment i.e induced dipole moment due to change in the atomic positions

Raman : change in polarisibility i.e induced dipole moment due to the deformation of the e- shell

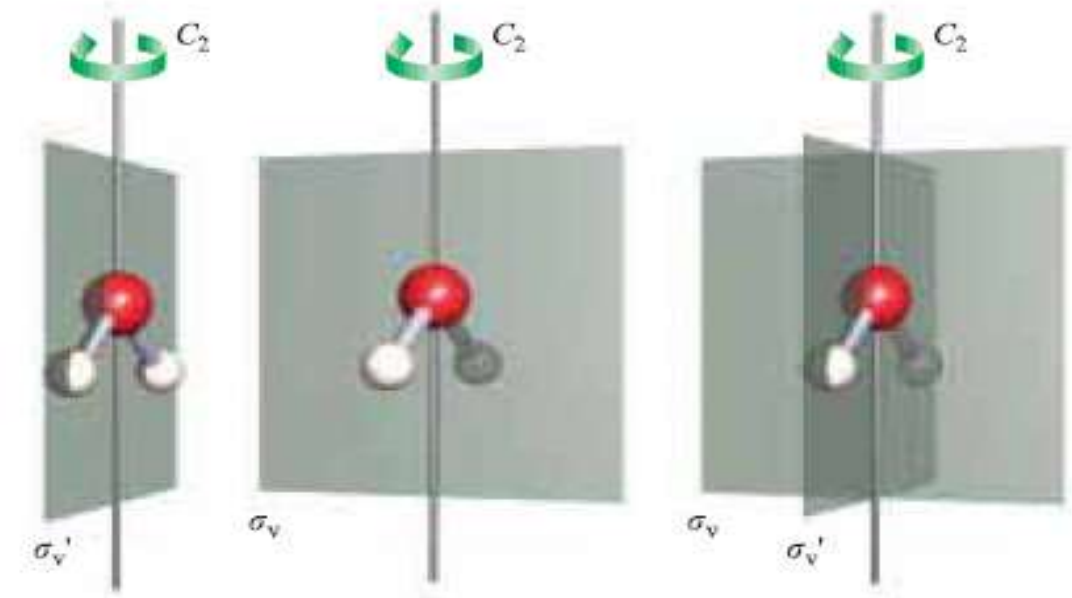
Working Examples

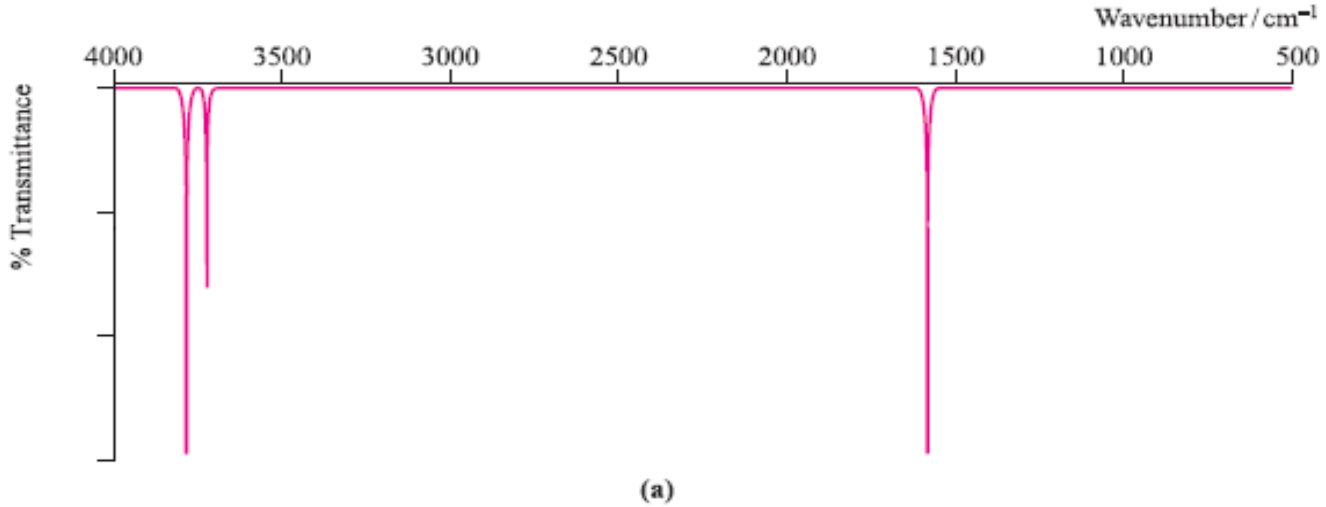
For centrosymmetric molecules, the rule of mutual exclusion states that vibrations that are IR active are Raman inactive, and vice versa.



H2O

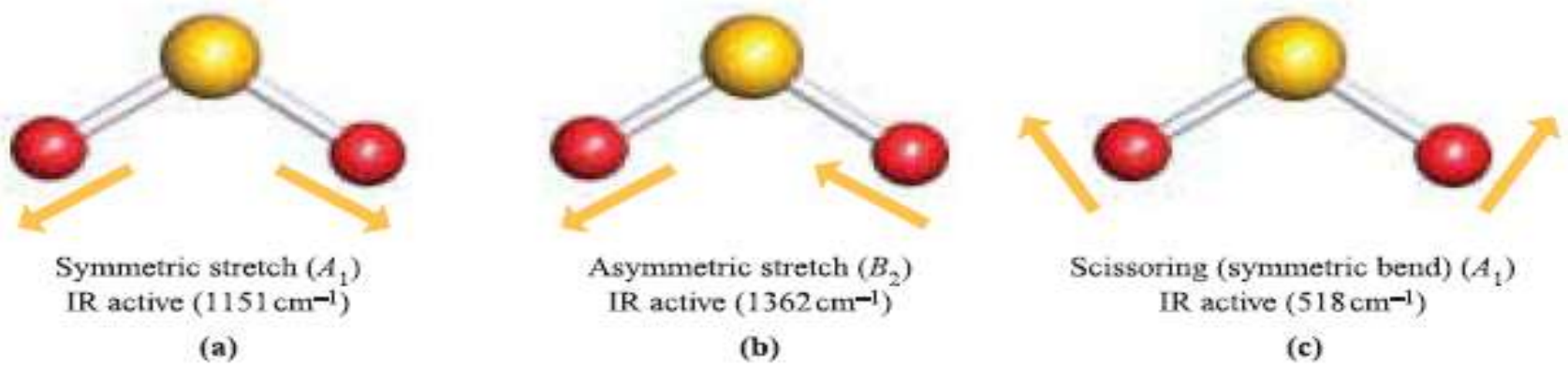
3N - 6 for non-linear molecules

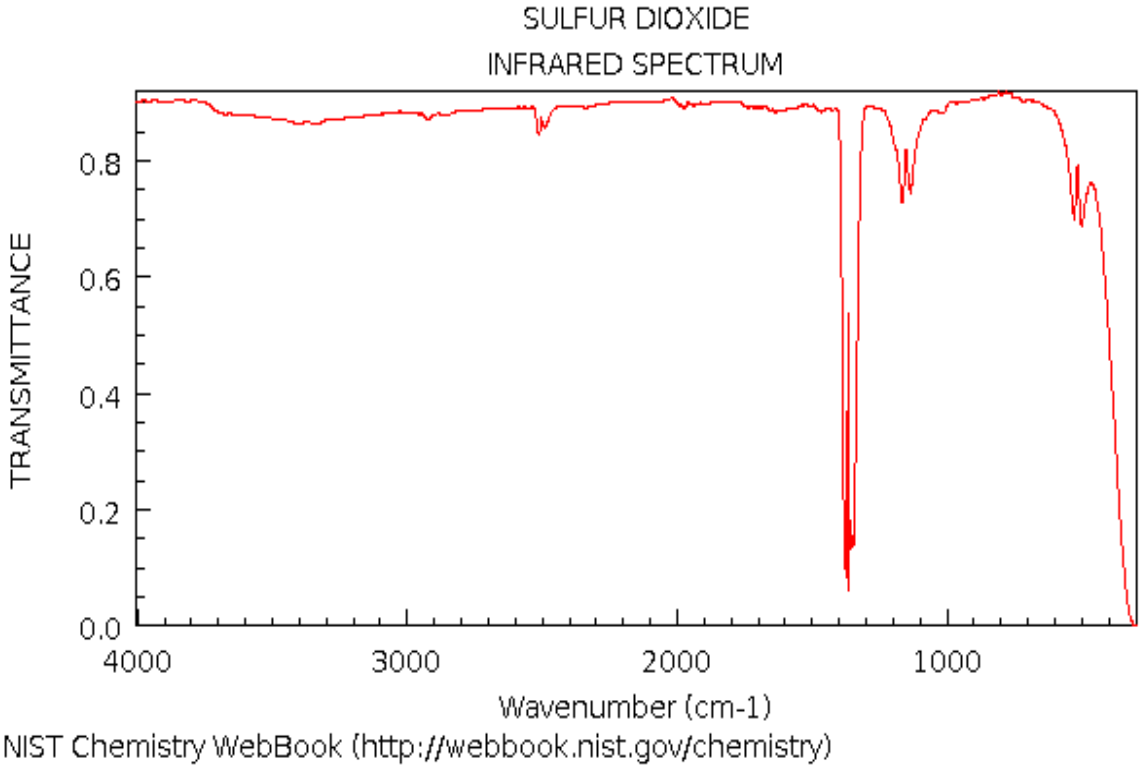




(a)

SO2





3N - 6 for non-linear molecules

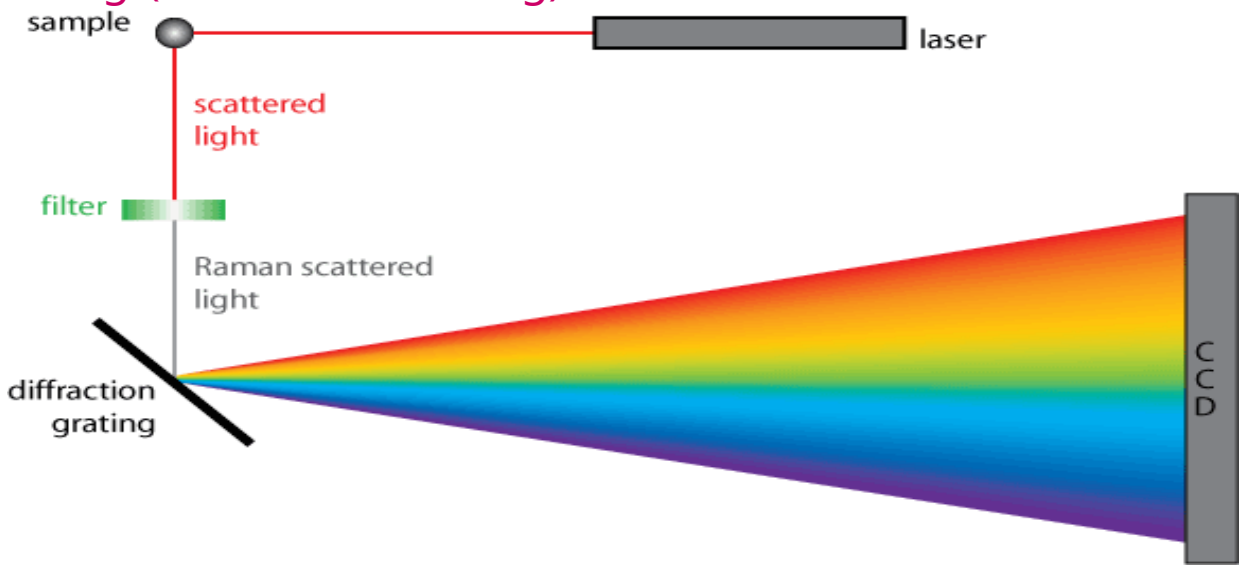
Raman spectroscopy

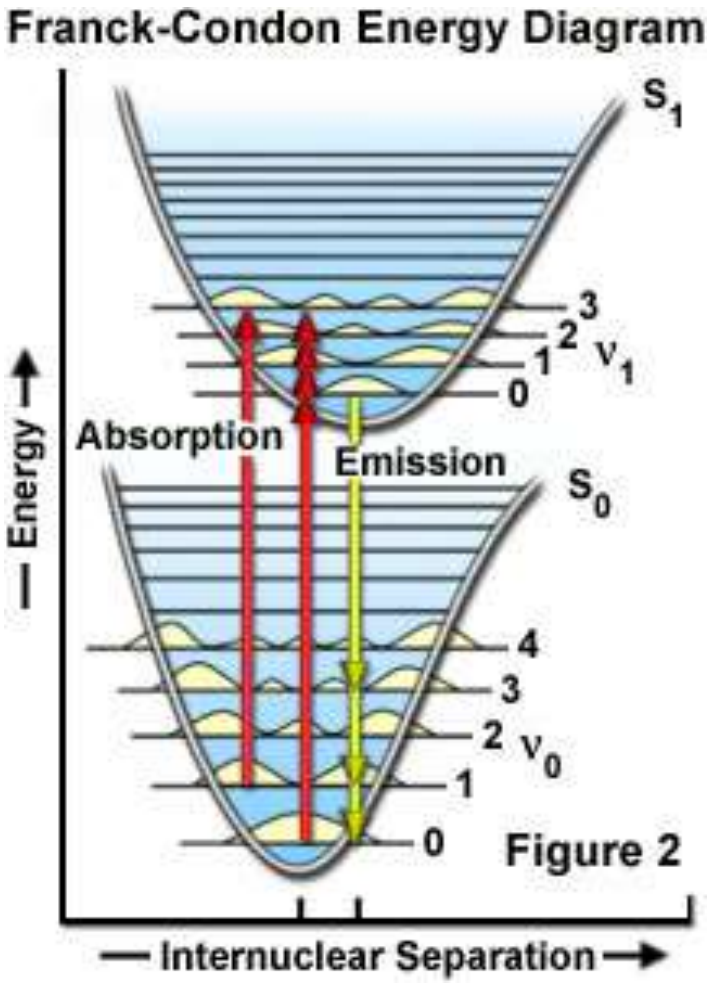
Uses a single frequency source of radiation (laser)

The photon interacts and distorts (polarizes) the electrons in the bond to form a short-lived "virtual state"

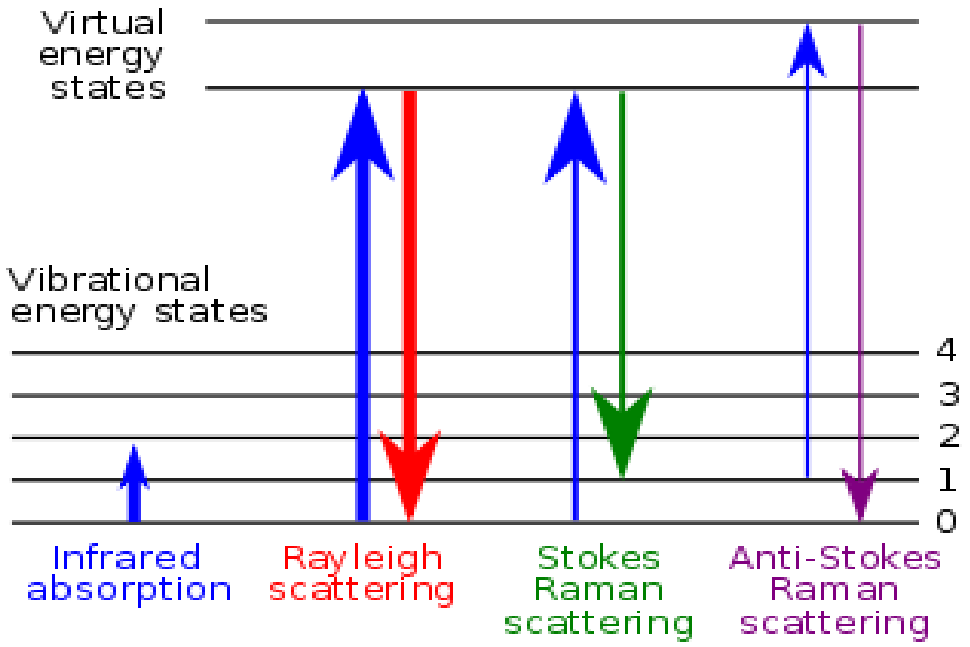
Return from this "virtual state" to ground state can either result in

1) no change to the frequency of the radiation .....Rayleigh scattering (elastic scattering)
2) increase or decrease in the frequency of the radiation .....
   Raman scattering (inelastic scattering)

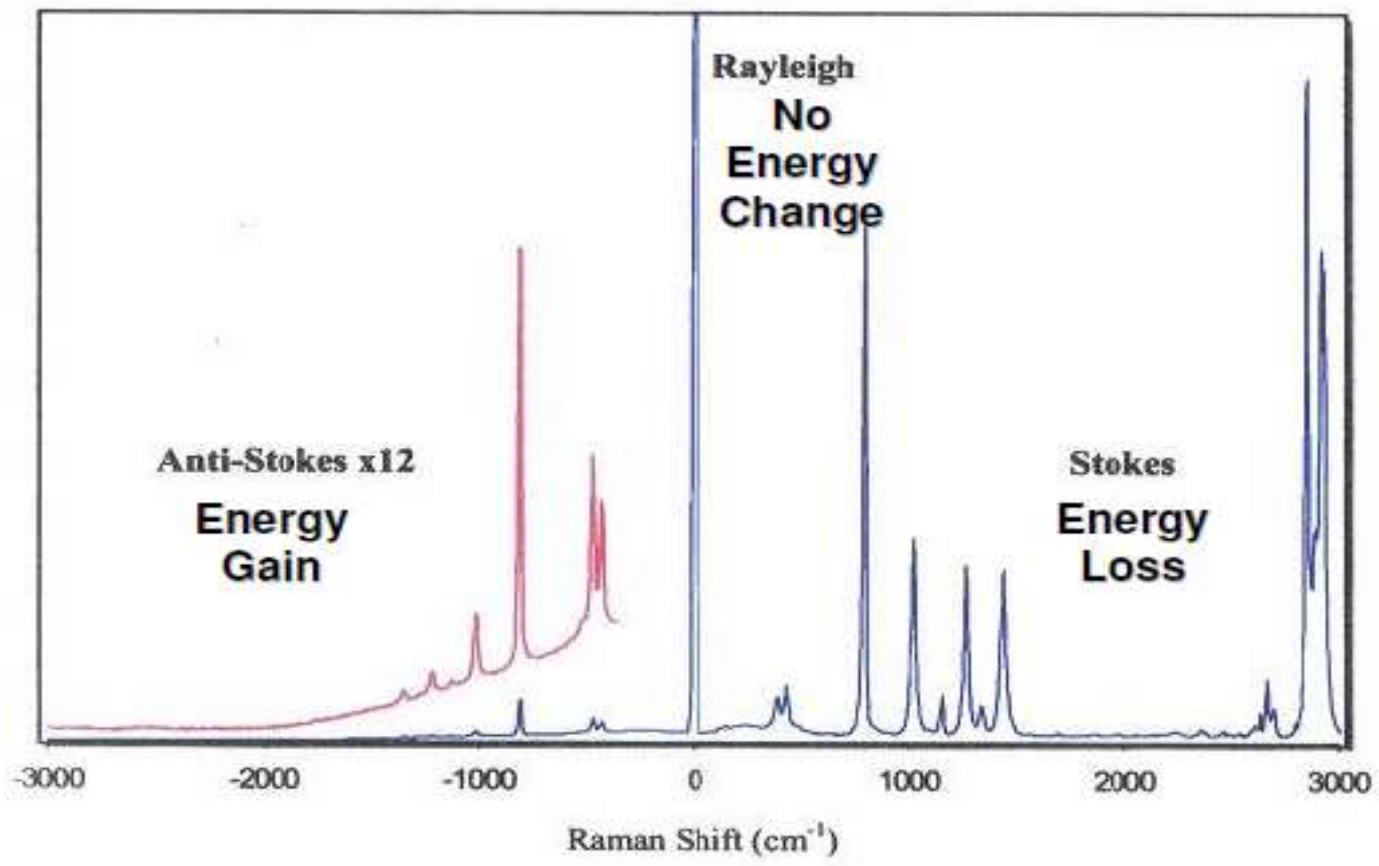




Infrared (IR) electromagnetic radiation causes vibrations in molecules (wavelengths of 2500-15,000 nm or 2.5 – 15 mm)

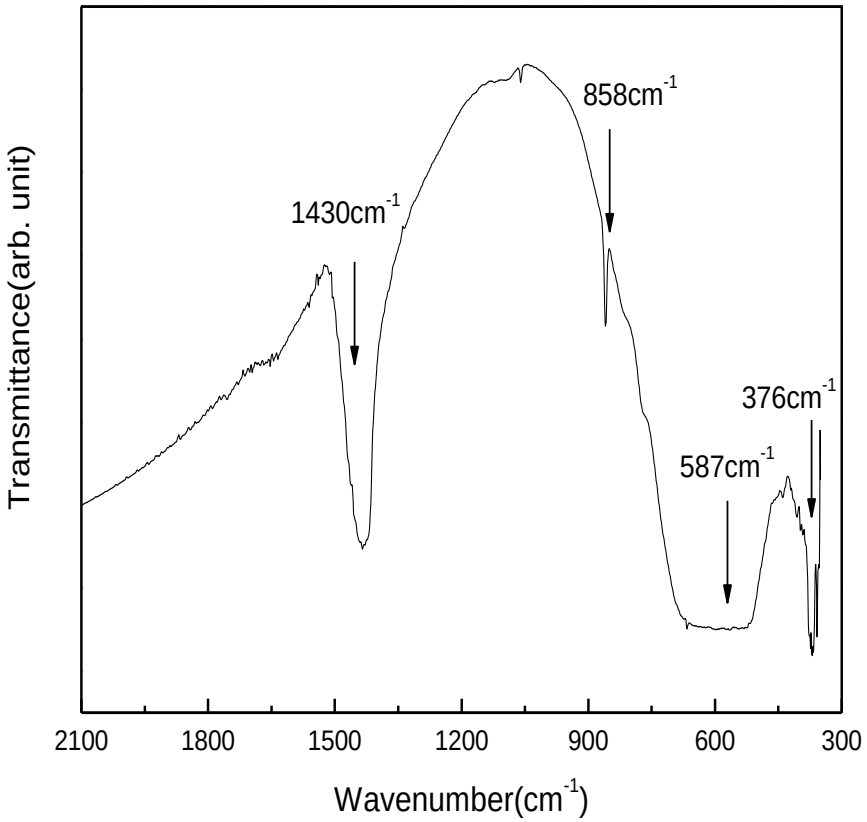


Stokes and Anti-Stokes Raman Cyclohexane Spectra



Advantages of Raman

- Selection rules allow for some vibrations (normally symmetric) to be seen only by Raman spectroscopy.
- Measurements of depolarization ratios yield information about molecular symmetry.
- Only a small sample area is needed (laser spot).
- Water is a weak Raman scatterer, allowing for the use of aqueous solutions. Can also sample through glass container walls.
- The region 4000 cm-1 to 50 cm-1 can be covered in a single scan without changing gratings, splitters, detectors, etc.



FTIR spectrum of Ba_2GdTaO_6

376 cm^{-1} ➡ asymmetric bending mode (F_{1u}) of the TaO_6 octahedra

587 cm^{-1} ➡ asymmetric stretching mode (F_{1u}) of the TaO_6 octahedra.

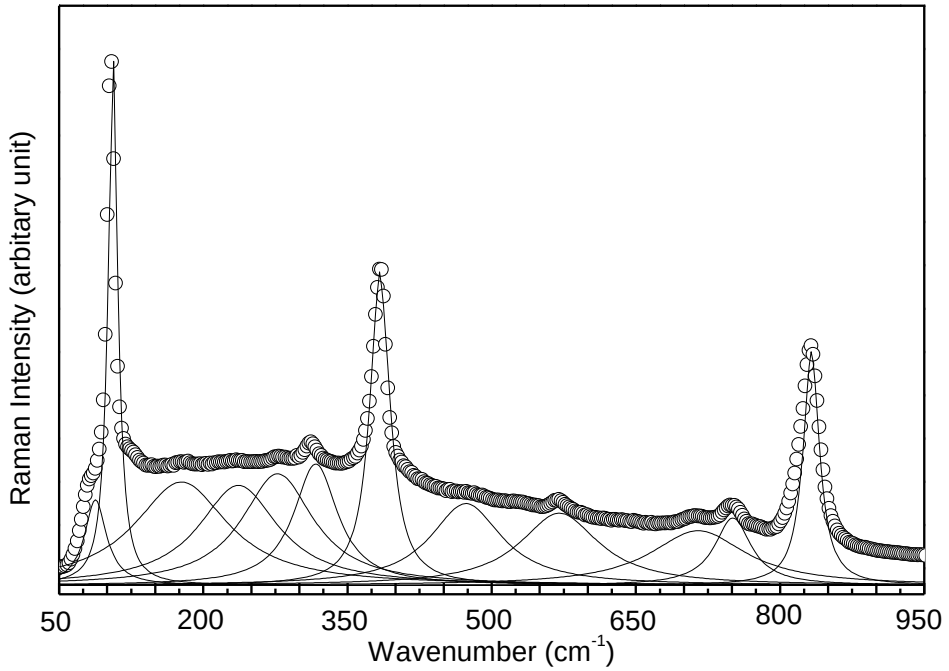
858 cm^{-1} ➡ symmetric stretching mode (A_{1g}) of the TaO_6 octahedra

The strong peak at around **1430 cm^{-1}** likely corresponds to overtones of the fundamental vibrations

For cubic system (Ba_2GdTaO_6) with *Fm3m* symmetry

$$\Gamma = A_{1g} + E_g + F_{1g} + 2F_{2g} + 5F_{1u} + F_{2u}$$

(from group theory)



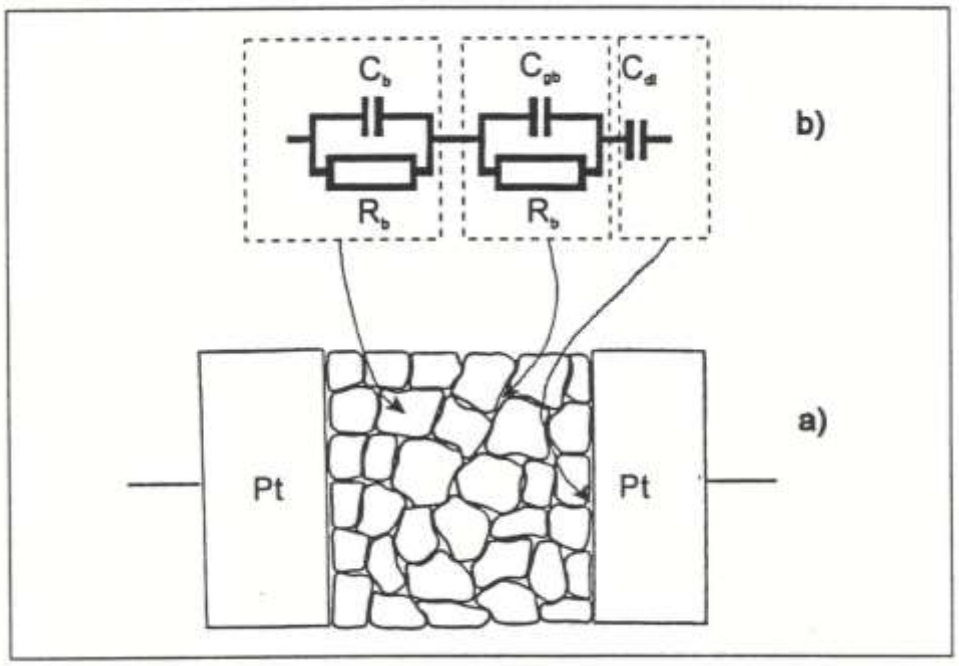
Observed Raman modes for the Ba_2GdTaO_6 ceramic

Frequency (cm^{-1})	FWHM (cm^{-1})	Symmetry	Vibrating atoms
832	17	A_{1g}	O
755	37	E_g	O
384	25	F_{2g}	A+O
106	12	F_{2g}	A+O

Impedance Spectroscopy

Impedance spectroscopy (basic aspects)

Purpose: Exploring the electrical behavior of a microcrystalline solid sample as function of an alternating current (ac) with a variable frequency.



three basically different regions for the exchange interactions between current and sample:

a) inside the grains („bulk“)

b) at grain boundaries

c) surface of the electrodes

the electrical behavior is simulated by a suitable combination of RC circuits: R = resistivity, C = capacity

Probing an electrochemical system with a small ac-perturbation, $V_0 \cdot e^{j\omega t}$, over a range of frequencies.

The **impedance** (resistance) is given by:

$$Z(\omega) = \frac{V(\omega)}{I(\omega)} = \frac{V_0 \; e^{j\omega t}}{I_0 \; e^{j(\omega t+\varphi)}} = \frac{V_0}{I_0}\left[\cos\varphi - j\sin\varphi\right]$$

$\omega = 2\pi f$

$j = \sqrt{-1}$

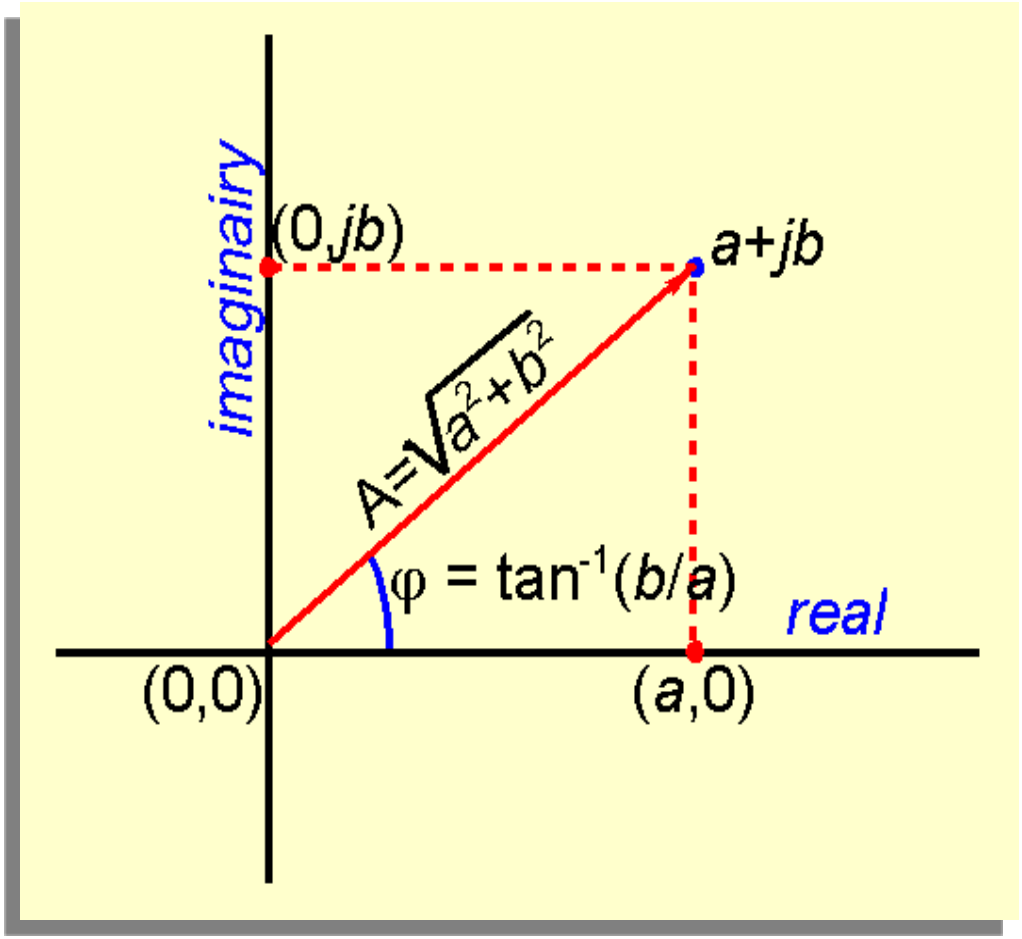
The magnitude and phase shift depend on frequency.

Also: **admittance** (conductance), inverse of impedance:

$$Y(\omega) = \frac{1}{Z(\omega)} = \frac{I_0 \, e^{j(\omega t+\varphi)}}{V_0 \, e^{j\omega t}} = \frac{I_0}{V_0}\left[\cos\varphi + j\sin\varphi\right]$$

"real +*j* imaginary"

Complex plane



Impedance ≡ 'resistance'
Admittance ≡ 'conductance':

hence:

$$Y(\omega) = \frac{1}{Z(\omega)} = \frac{Z_{re} - jZ_{im}}{Z_{re}^2 + Z_{im}^2}$$

$$Z(\omega) = \frac{1}{Y(\omega)} = \frac{Y_{re} - jY_{im}}{Y_{re}^2 + Y_{im}^2}$$

Representation of impedance value, $Z = a + jb$, in the complex plane

Simple elements

The most simple element
is the resistance:

$$Z_R = R \;;\quad Y_R = \frac{1}{R}$$

(e.g.: electronic- /ionic conductivity,
charge transfer resistance)

Other simple elements:

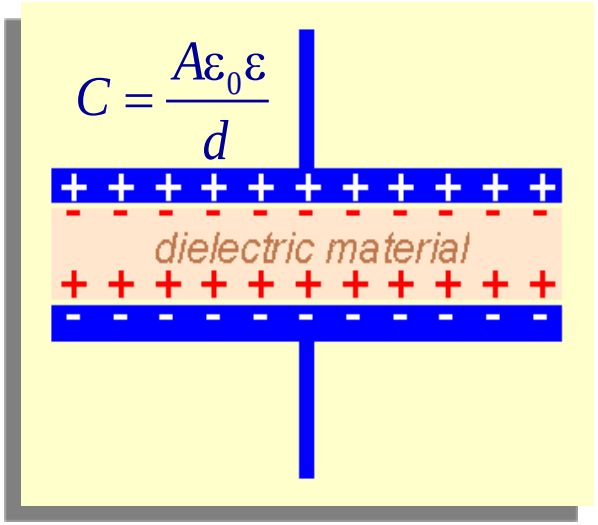
- Capacitance: dielectric capacitance, double layer C,
  adsorption C, 'chemical C' (redox)

- Inductance: instrument problems, leads,
  'negative differential
  capacitance' !

Capacitance

Take a look at the properties of a capacitor:
Charge stored (Coulombs):
Change of voltage results in current, *I*:

$$Q = C \cdot V$$



Alternating voltage (ac):

$$I = \frac{\mathrm{d}Q}{\mathrm{d}t} = C\frac{\mathrm{d}V}{\mathrm{d}t}$$

$$I(\omega t) = C\frac{\mathrm{d}V_0 \cdot e^{j\omega t}}{\mathrm{d}t} = j\omega C \cdot V_0 \cdot e^{j\omega t}$$

Impedance:

$$Z_C(\omega) = \frac{V(\omega)}{I(\omega)} = \frac{1}{j\omega C}$$

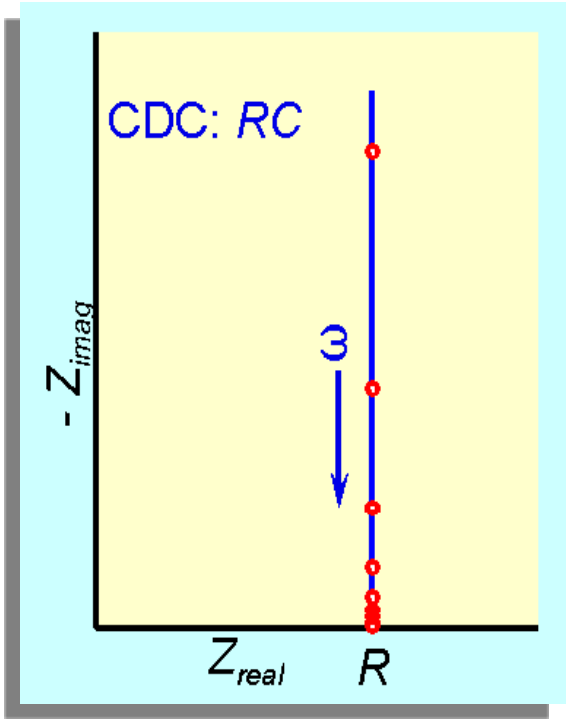
Admittance:

$$Y_C(\omega) = Z(\omega)^{-1} = j\omega C$$

Combination of elements

What is the impedance of an -R-C- circuit?

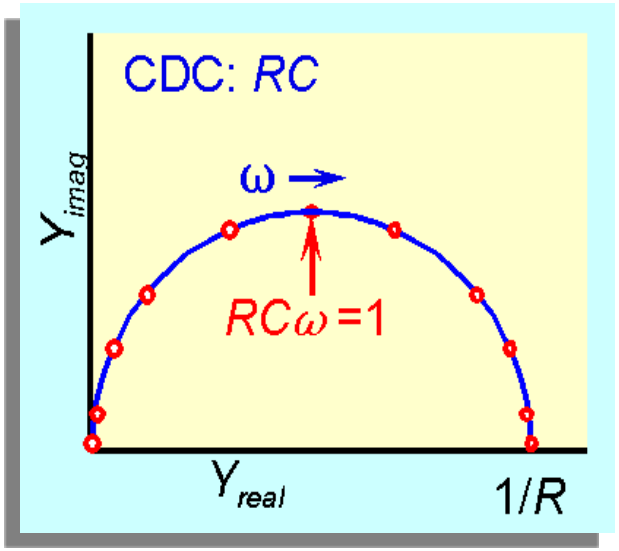
$$Z(\omega) = R + \frac{1}{j\omega C} = R - j/\omega C$$



Admittance

$$Y(\omega) = \frac{1}{R - j/\omega C} =$$

$$\frac{\omega^2 C^2 R}{1+\omega^2 C^2 R^2} + j\frac{\omega C}{1+\omega^2 C^2 R^2}$$



Semi-circle

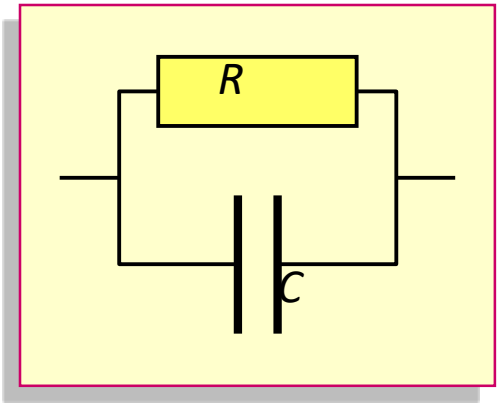
'time constant':

$\tau = RC$

A parallel R-C combination

The parallel combination of a resistance and a capacitance, start in the admittance representation:

$$Y(\omega) = \frac{1}{R} + j\omega C$$



Transform to impedance representation:

$$Z(\omega) = \frac{1}{Y(\omega)} = \frac{1}{1/R + j\omega C} \cdot \frac{1/R - j\omega C}{1/R - j\omega C} =$$

$$\frac{R - j\omega R^2 C}{1 + \omega^2 R^2 C^2} = R\frac{1 - j\omega\tau}{1 + \omega^2\tau^2}$$

A semicircle in the impedance plane!

Other representations

Capacitance: $C(\omega) = Y(\omega) / j\omega$ for an (RC) circuit:

$$C(\omega) = Y(\omega) / j\omega = \left[\frac{1}{R} + j\omega C \right] / j\omega = C - j\frac{1}{\omega R}$$

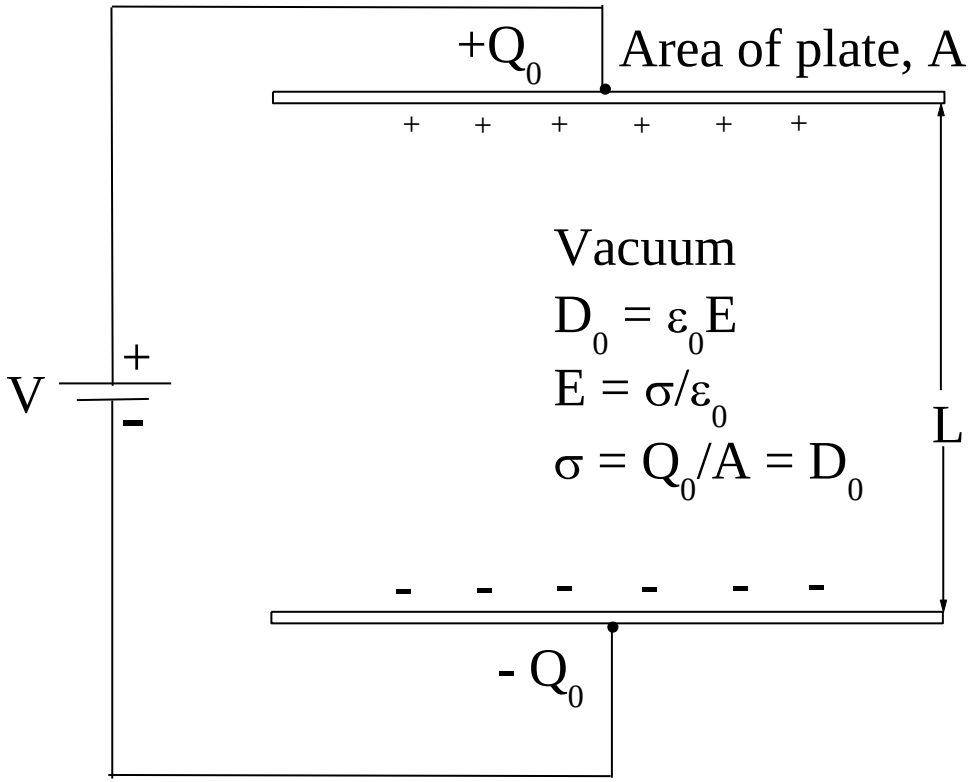
Dielectric: $\varepsilon(\omega) = Y(\omega) / j\omega C_0$ $C_0 = A\varepsilon_0/d$

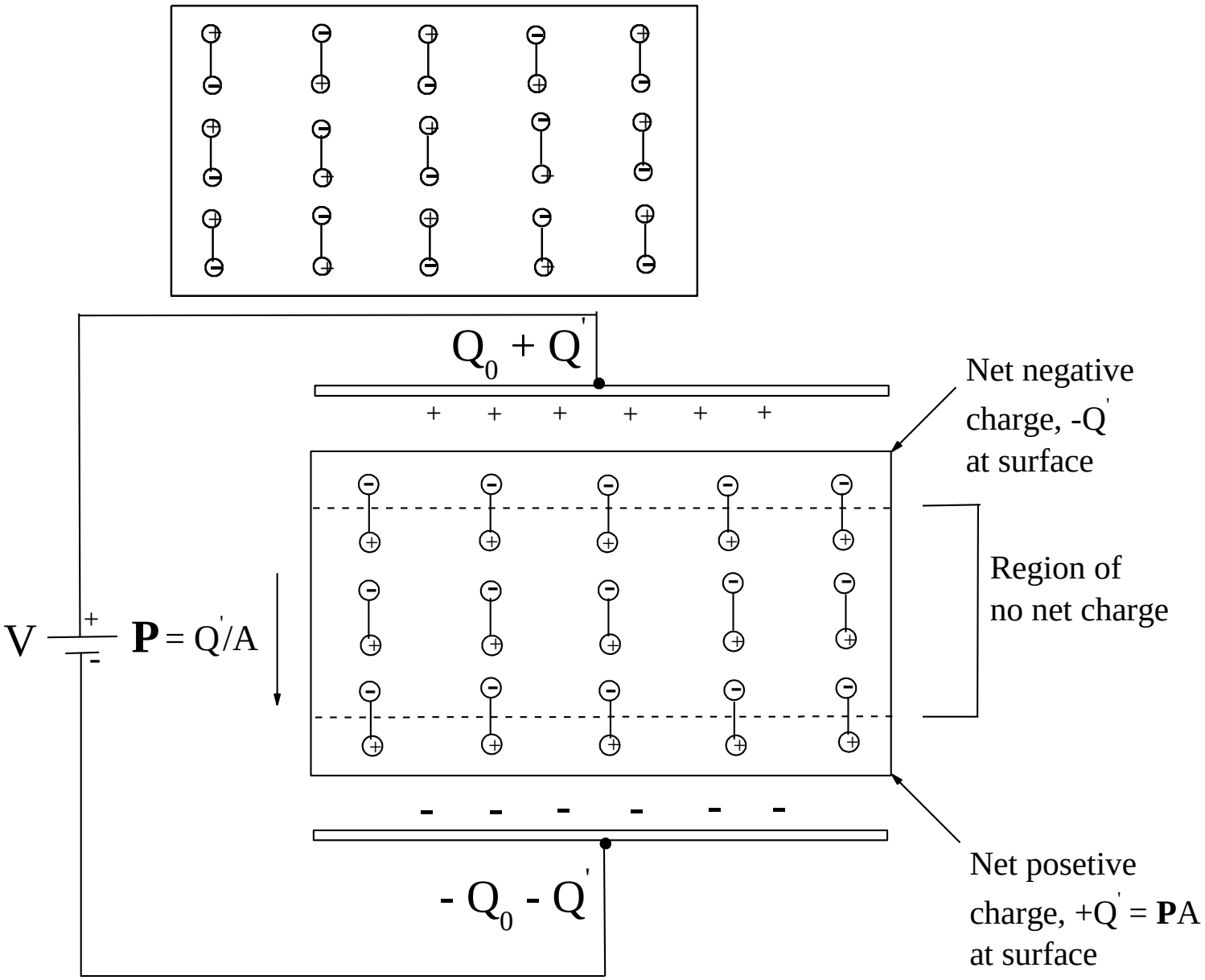
$$\varepsilon(\omega) = Y(\omega) \cdot \frac{d}{A\varepsilon_0} = \varepsilon' - j\frac{\sigma_{ion}}{\omega\varepsilon_0}$$

d: thickness
A: surf. area

Modulus: $M(\omega) = Z(\omega) \cdot j\omega$

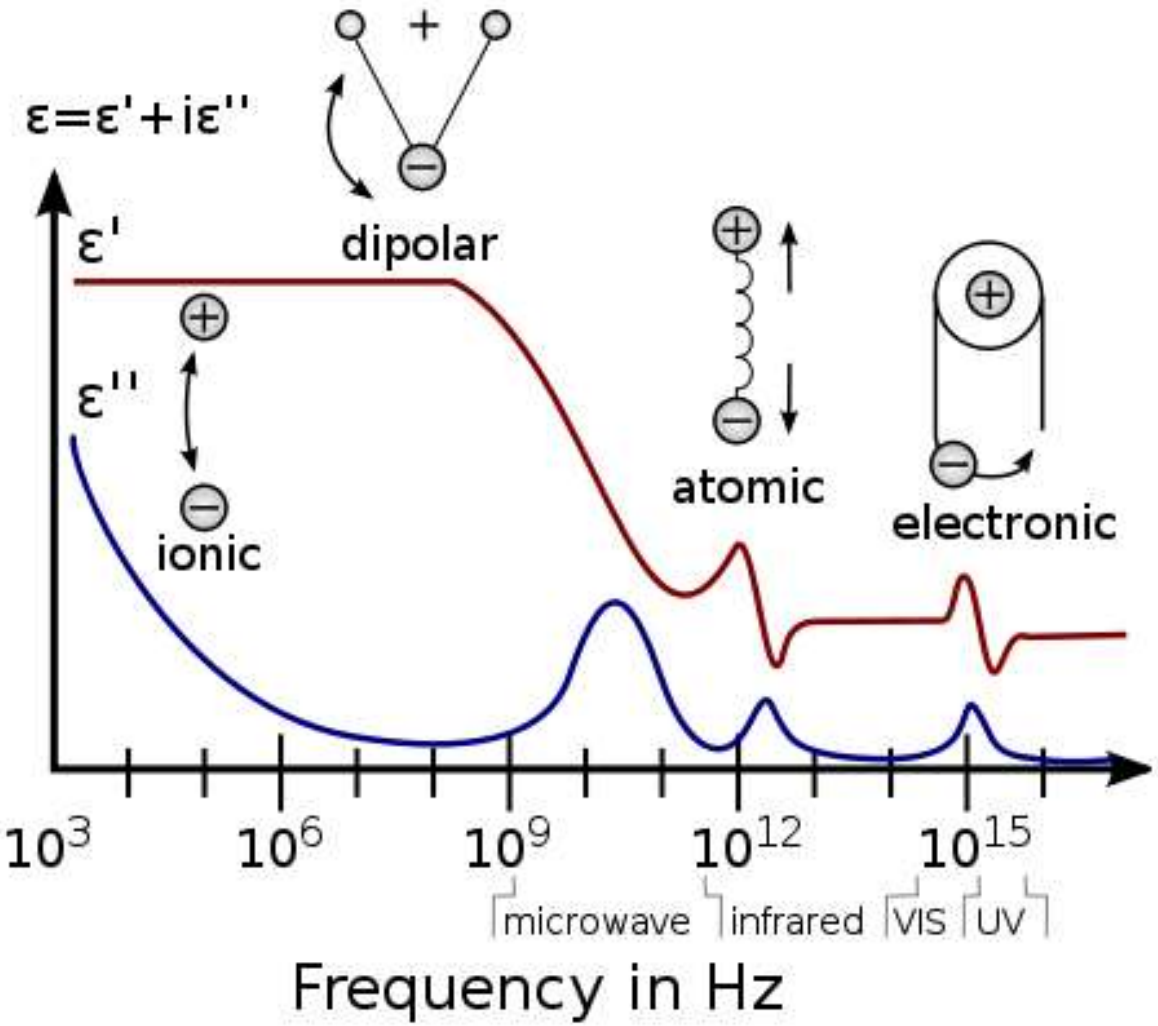
$$M(\omega) = Z(\omega) \cdot j\omega = \frac{\omega^2 CR^2 + j\omega R}{1 + \omega^2 C^2 R^2}$$


+Q0
Area of plate, A
+ + + + + +
Vacuum
D0 = ε0E
E = σ/ε0
σ = Q0/A = D0
L
V
+
-
- - - - - -
- Q0



$$\mathbf{D} = \varepsilon_0 \mathbf{E} + \mathbf{P}$$

Dielectric relaxation



➢The dielectric relaxation of insulating or semiconducting materials can be analyzed in terms of

(1) dipolar relaxation mechanism and
(2) conductivity relaxation mechanism.

➢ For dipolar relaxation which originates from dipole motion, the dielectric response can be described as a direct relationship between the dielectric constant and admittance.

➢Dipolar relaxation can be expressed by the Debye, Cole-Cole, Davidson-Cole and Havriliak-Negami equations:

$$\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{[1+(j\omega\tau)^{1-\alpha}]^\beta}$$

α =1, β = 1 gives Debye function; α =1, 0< β ≤1 gives the Cole-Cole function; β=1, 0< α ≤1 gives the Cole-Davidson function and α ≠ 1, β ≠ 1 gives Havriliak-Negami function. All these parameters are temperature dependent.

Dielectric studies by AC impedance spectroscopy (ACIS)

- AC properties of material is affected by interfaces (grain-boundaries, electrodes, pores etc.)
- ACIS is powerful tool to study the electrical properties.
- ACIS allows measurement of capacitance and loss tangent at various frequencies
- From measured capacitance and tan δ, four complex dielectric constant parameters may be computed:

$$\varepsilon^* = \varepsilon' - j\varepsilon'' \qquad M^* = M' + jM''$$
$$Z^* = Z' - jZ'' \qquad Y^* = Y' + jY''$$

$$\tan\delta = \frac{\varepsilon''}{\varepsilon'} = \frac{M''}{M'} = \frac{Z'}{Z''} = \frac{Y'}{Y''}$$

$[Z^* = (Y^*)^{-1}, M^* = (\varepsilon^*)^{-1} = j\omega C_o Z^*]$

$\varepsilon' = C/C_o$ ($C_o = A\varepsilon_o/t$; A= area, t = thickness), $\varepsilon'' = \varepsilon' \tan\delta$

Thank you