MSc. Physics 1ˢᵗ Sem.

# Open Elective: Nanomaterials and Its Applications Lab

Course Code: OPNPPL1

Credits = 2 (0+2+0)

List of Experiments

1. To determine the crystallite size of given sample and observe the influence of do-pants through given XRD data.

2. To analyse the particle size Scanning Electron Microscopy and Transmission Electron Microscopy images of given samples.

3. To determine the crystallinity of the given sample through selective area electron diffraction.

4. To determine the electronic band-gap of given sample through Tauc plots derived from UV-Vis diffused reflectance spectroscopy.

5. To analyse Raman spectra and calculate the force constant of a given sample.

6. To analyse the elemental species, present in the given sample through X-ray photoelectron spectroscopy
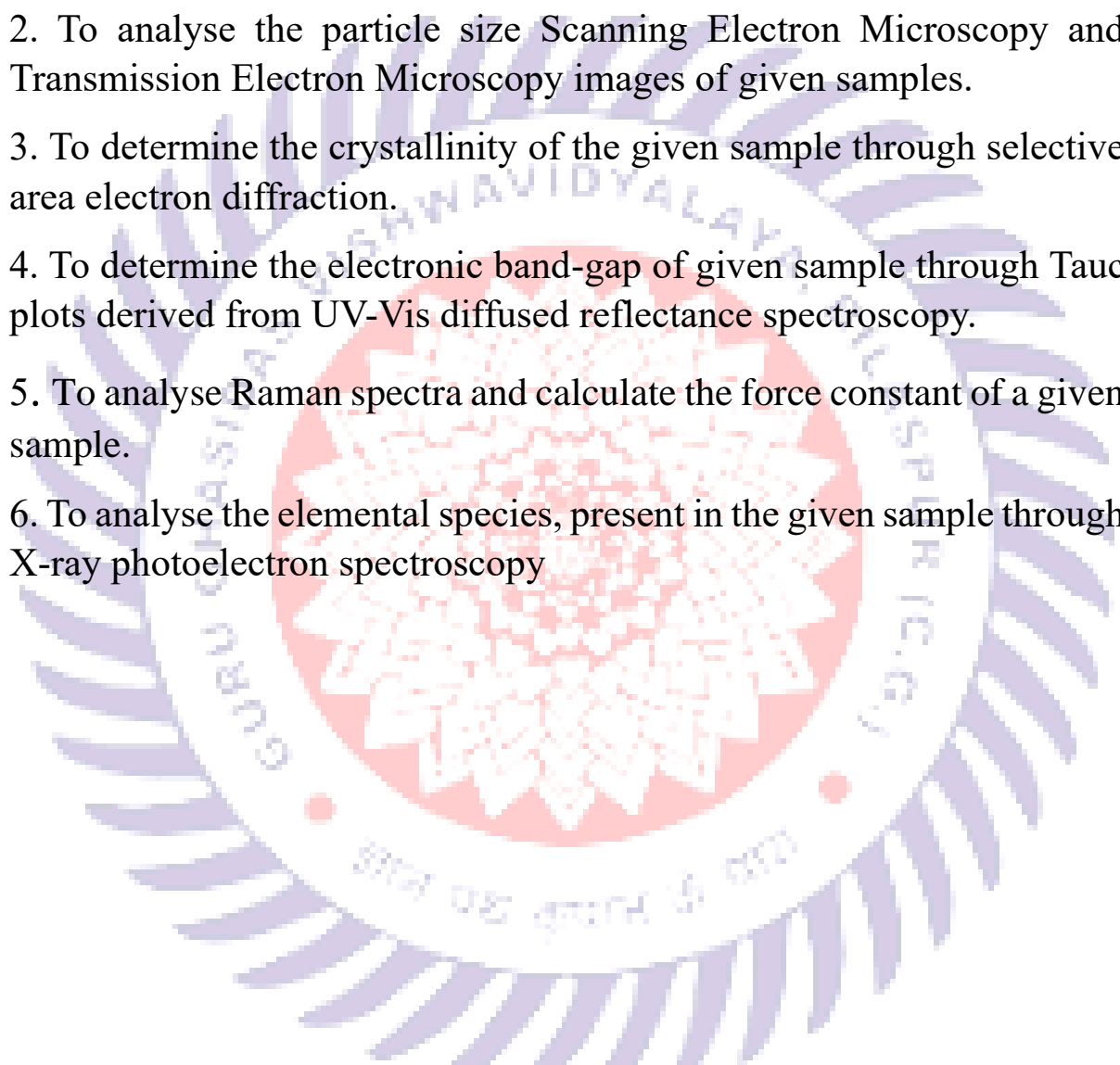
Experiment No 1

Aim: To determine the crystallite size of given sample and observe the influence of do-pants through given XRD data.

Requirements: XRD data of powder sample.

Theory: X-ray diffraction is a convenient method for determining the mean size of nano crystallites in nanocrystalline bulk materials with phase certain. The determination refers to the main peaks of the pattern diffractogram through the approach of Debye Scherrer's equation formulated in Equation. The Scherrer equation, in X-ray diffraction and crystallography, is a formula that relates the size of sub-micrometre crystallites in a solid to the broadening of a peak in a diffraction pattern. It is often referred to, incorrectly, as a formula for particle size measurement or analysis. It is named after Paul Scherrer. It is used in the determination of the size of crystals in the form of powder.

The Scherrer equation can be written as:

$$D = \frac{K\lambda}{\beta\cos\theta} \qquad (1)$$

where:

D is the mean size of the ordered (crystalline) domains, which may be smaller or equal to the grain size, which may be smaller or equal to the particle size.

K is a dimensionless shape factor, with a value close to unity. The shape factor has a typical value of about 0.9 but varies with the actual shape of the crystallite.

λ is the X-ray wavelength.

β is the line broadening at half the maximum intensity (FWHM) as shown in the figure below, after subtracting the instrumental line broadening, in radians.

θ is denoted as Bragg's law.

Procedure:

1. Identify the K value.
2. Identify the λ value.
3. Identify FWHM (β).

To determine the value of FWHM (β) can be done using the following ways:

Step 1: Identify the sharpest peak or crystalline area in the diffraction pattern generated by XRD.

Step 2: Determine the value of 2θ at the peak with the maximum intensity of the XRD diffraction pattern.

Step 3: Determine the value of half of the maximum peak intensity.

Step 4: Determine the minimum 2θ value and the maximum 2θ value at half the maximum intensity of the peak.

Step 5: Determine the FWHM (β) value using Equation $\beta = \frac{1}{2}(2\theta_{max} - 2\theta_{min})$

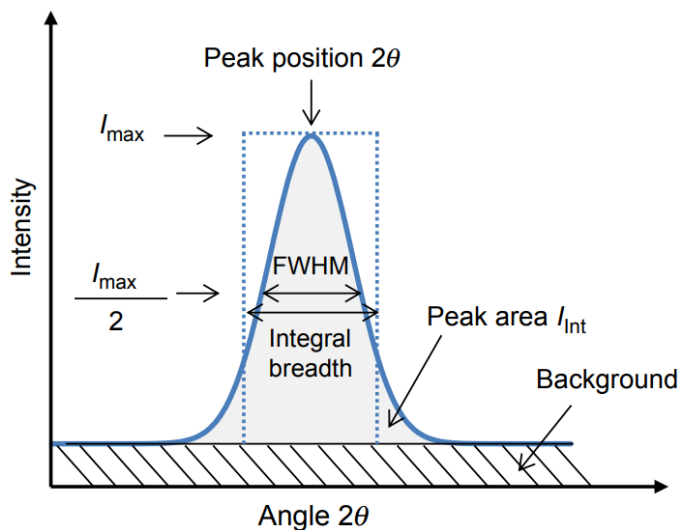4. Determine the value of $\cos\theta$ from the value of 2θ value.

The steps to determine the value of cos from the value of 2θ are as follows:

Step 1: Divide the value of 2θ theta by the number 2 thus θ is known.

Step 2: Change θ value to $cos\theta$.

5. After all the values from step 1 to step 4 are known, the last step is to put these values in Equation (1) so that the crystal size is obtained.

In short, by performing a curve selection of the diffraction peaks of each plane crystal at position 2θ, we can see half-peak curve widening value diffraction (FWHM), then with a value of is put into the equation Scherrer to determine the size crystal.

Observations:

1. Tabulate the calculated data for every 2θ in the table below:

2θ	θ	cosθ

2θ (º)	cos θ	K (rad/$A^{°2}$)	λ (nm)	FWHM β (º)	FWHM β (rad)	Crystallite Size (nm)

Analysis: Check the Shift in different peaks to analyse effect of dopant.

Conclusions:

Experiment No 2

Aim: - To analyse the particle size Scanning Electron Microscopy and Transmission Electron Microscopy images of given samples.

Requirements: SEM/TEM MICROGRAPHS

Theory: Grain size (or particle size) is the diameter of individual grains of sediment, or the lithified particles in clastic rocks. The term may also be applied to other granular materials. This is different from the crystallite size, which refers to the size of a single crystal inside a particle or grain. A single grain can be composed of several crystals. Granular material can range from very small colloidal particles, through clay, silt, sand, gravel, and cobbles, to boulders.

Procedure

Once an image has been captured by SEM/TEM, the grain boundaries can be measured using an image processing software, such as ImageJ. ImageJ is free software that utilizes either a desktop or a browser. It uses pixel values to determine a host of different properties of the image. These pixel values will convert into a measurement using the scale on your SEM/TEM picture. For this experiment, the contrast threshold can be set to accentuate the grain boundaries. ImageJ has a built-in function that will calculate the average grain size. By clicking 'Analyze' then 'Analyze Particles…', you can produce an image of where the software observes a grain boundary. ImageJ is not perfect, so adjust the contrast accordingly to give a more complete picture of the sample surface. If this method fails, there is also the option to manually select each grain boundary using the 'freehand selection' tool.

Conclusions:

Grain/Paericle size:
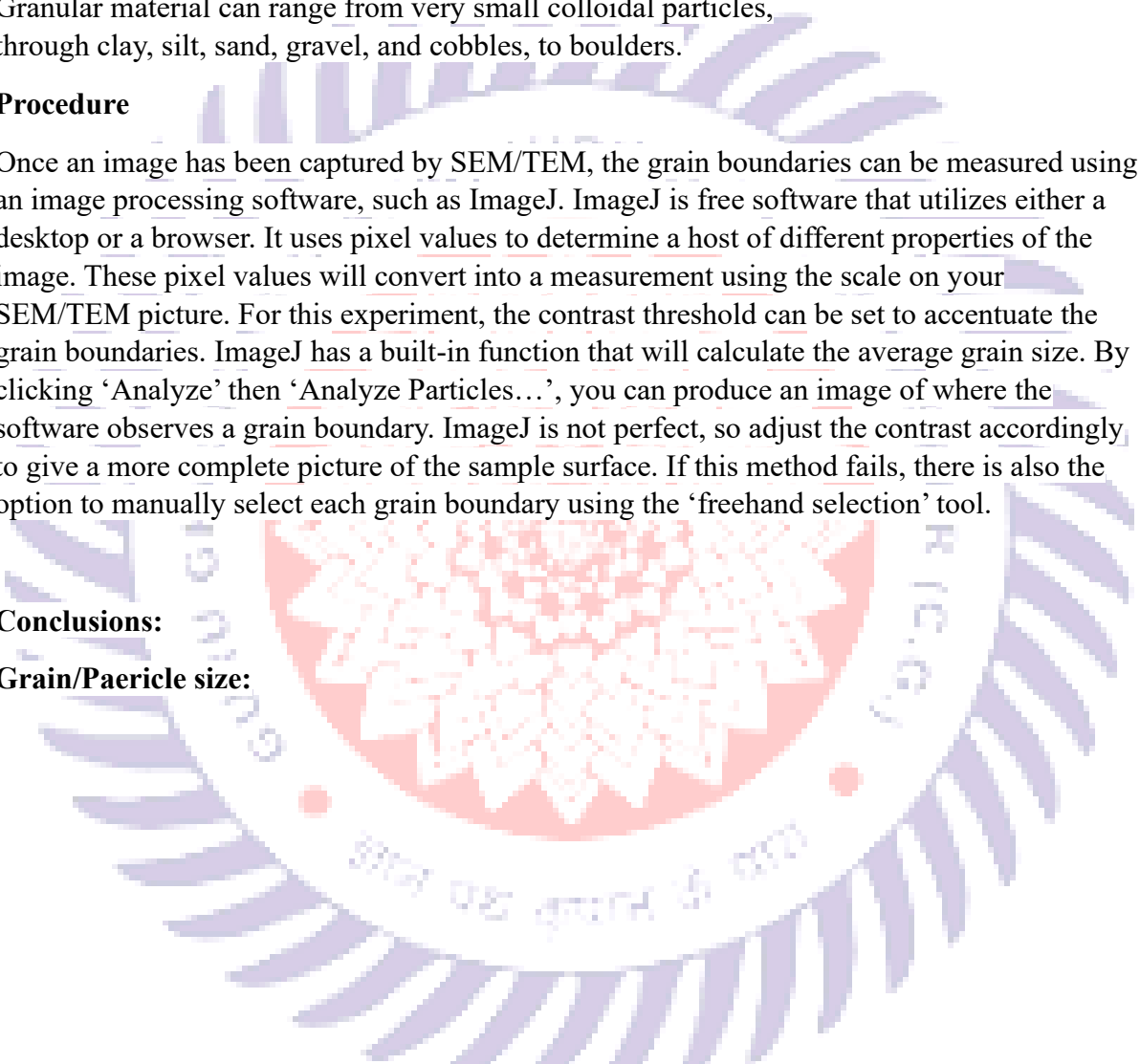
**Experiment No 3**

Aim: To determine the crystallinity of the given sample through selective area electron diffraction.

Requirements: SAED pattern.

Theory:Selected area (electron) diffraction (abbreviated as SAD or SAED) is a crystallographic experimental technique typically performed using a transmission electron microscope (TEM). It is a specific case of electron diffraction used primarily in material science and solid state physics as one of the most common experimental techniques. Especially with appropriate analytical software, SAD patterns (SADP) can be used to determine crystal orientation, measure lattice constants or examine its defects.

If the SAD is taken from one a or a few single crystals, the diffractogram depicts a regular pattern of bright spots. Since the diffraction pattern can be seen as a two-dimensional projection of reciprocal crystal lattice, the pattern can be used to measure lattice constants, specifically the distances and angles between crystallographic planes. The lattice parameters are typically distinctive for various materials and their phases which allows to identify the examined material or at least differentiate between possible candidates.

If the illuminated area selected by the aperture covers many differently oriented crystallites, their diffraction patterns superimpose forming an image of concentric rings. The ring diffractogram is typical for polycrystalline samples, powders or nanoparticles. Diameter of each ring corresponds to interplanar distance of a plane system present in the sample. Instead of information about individual grains or the sample orientation. Ring diffractograms can be also used to discriminate between nanocrystalline and amorphous phases.
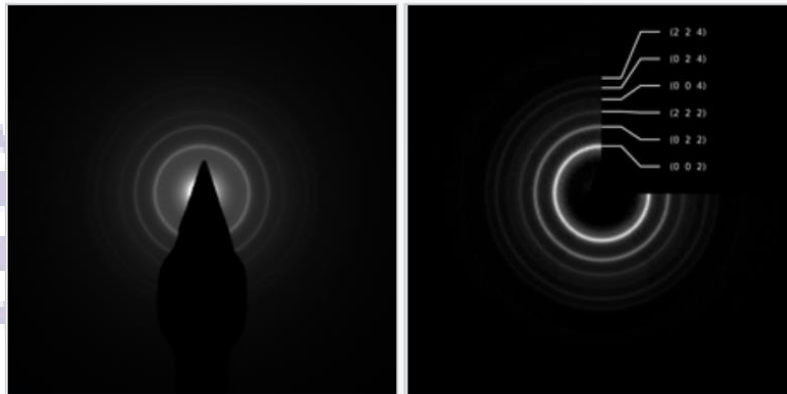
Ring diffraction image of MgO as recorded (left) and processed with CrysTBox ringGUI (right).

Steps

After getting an SAED pattern

1.Calculate radius of rings by image-J software.

2.Calculate radius of the ring.

3.Convert to angstrom.

4.Match the interplanar spacings with the miller indices from the corresponding JCPDS/ICDD card and index them.

SN	1/D(nm^{-1})	1/r(nm^{-1})	r(nm)	d(Å)	(hkl)
1					
2					
3					

Where

D-Diameter of ring

r-radius of ring

d-interplaner spacing

hkl-Miller indices

Conclusion

Result

Experiment No 4

Aim: . To determine the electronic band-gap of given sample through Tauc plots derived from UV-Vis diffused reflectance spectroscopy.

Requirements: UV- Vis data of a sample.

Theory: Ultraviolet- visible (UV-Vis) spectroscopy is an analytical technique that measures the amount of discrete wavelengths of UV or visible light that are absorbed by or transmitted through a sample in comparison to a reference (or blank) sample. The band gap energy of a semiconductor describes the energy needed to excite an electron from the valence band to the conduction band. In 1966 Tauc proposed a method of estimating the band gap energy of semiconductors using optical absorption spectra. The Tauc method is based on the assumption that the energy-dependent absorption coefficient (α) can be expressed by the following equation (1).

$$(\alpha h\upsilon)^{\gamma} = A(h\upsilon - E_g) \quad ..(1)$$

Where α is the absorption coefficient

h is the planks constant

A is the proportionality constant

E_g is the band gap energy and

γ denotes the nature of the electronic transitions

$\gamma=2$ for direct allowed transitions

$\gamma=1/2$ for indirect allowed transitions

$\gamma=2/3$ for direct forbidden transition

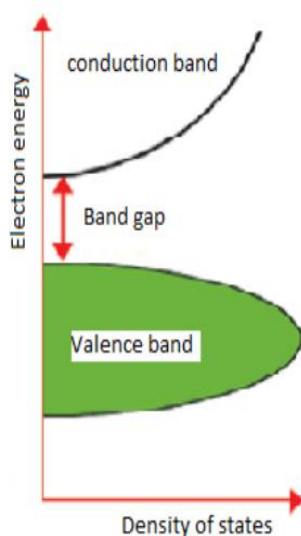$\gamma=1/3$ for indirect forbidden transition

Fig 1. Explanation of Band gap   **Fig: 2 UV-VIS Photo spectrometer**

Procedure: The determination of band gap energy by using Tauc's plot

1. Plotting the value of $(\alpha h\upsilon)^{\gamma}$ with $h\upsilon$
2. Taking the extrapolation in the linear area across the energy axis in the corresponding graph
3. The intersection with energy-axis is the estimation of the corresponding energy gap

Calculations of α (absorption coefficient) and $h\upsilon$ (energy)

1. α can be estimated by using formula $\alpha = 2.303 \times$ Absorbance (for liquid sample) and $\alpha =$ Absorbance/film thickness (for thin film sample)
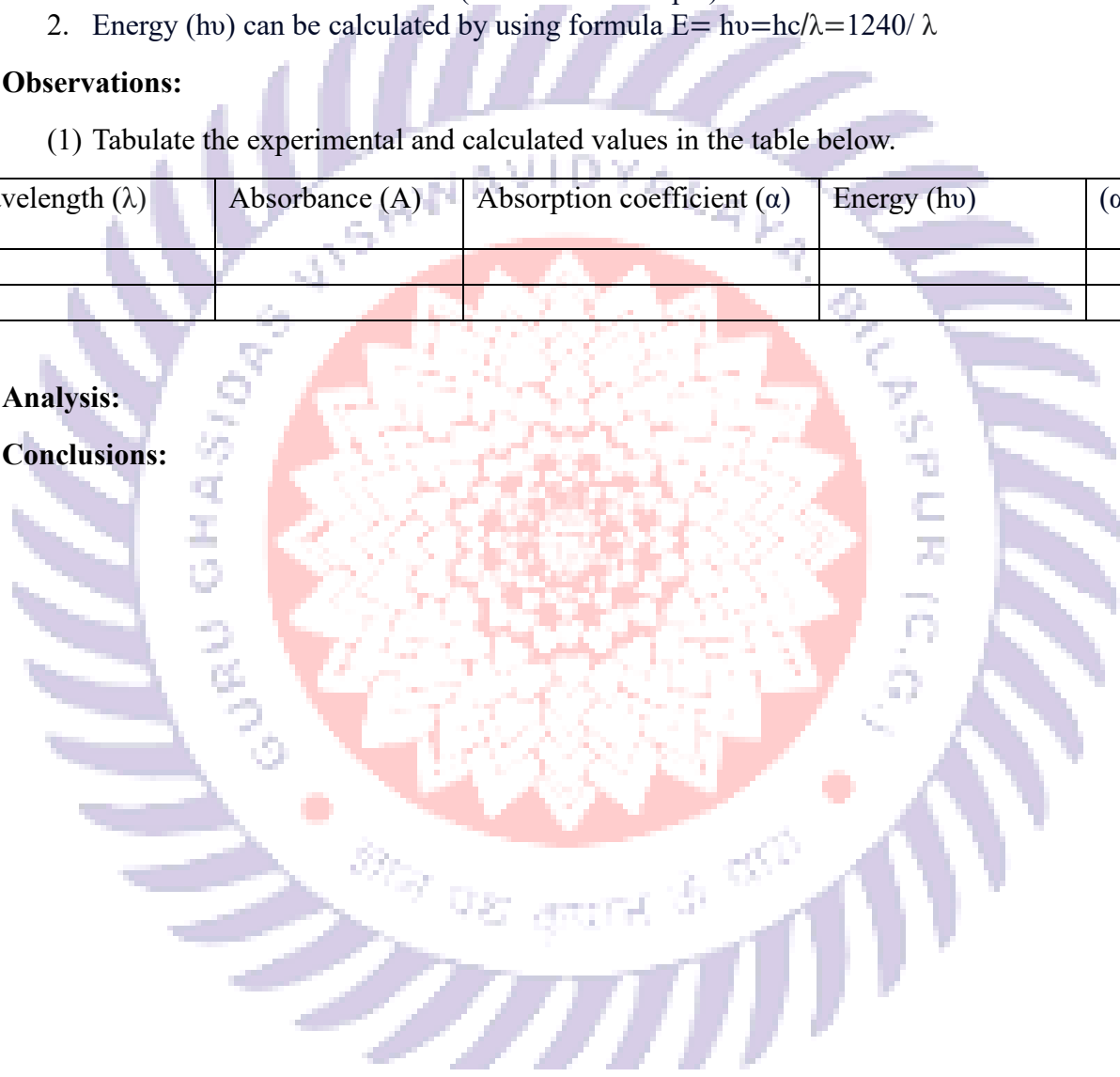2. Energy ($h\upsilon$) can be calculated by using formula $E = h\upsilon = hc/\lambda = 1240/\lambda$

Observations:

(1) Tabulate the experimental and calculated values in the table below.

Wavelength (λ)	Absorbance (A)	Absorption coefficient (α)	Energy ($h\upsilon$)	$(\alpha h\upsilon)^{\gamma}$

Analysis:

Conclusions:

Experiment No 5

Aim: To analyse Raman spectra and calculate the force constant of a given sample.

Requirements: Raman spectroscopy instrument, Raman spectra.

Theory: Monochromatic light incident on a transparent substance is transmitted with almost no attenuation. A small fraction of the light is scattered by the substance in all directions (though preferentially in the forward direction). The weakly scattered radiation contains photons at the incident frequency ν_0 (elastic or Rayleigh scattering), but also contains other frequencies such as $\nu_0 - \nu_i$, where ν_i is the frequency of a molecular transition (typically rotational or vibrational) of the material. This inelastic light scattering is known as Raman scattering. In a typical Raman experiment, a polarized monochromatic light source (usually a laser) is focused into a sample, and the scattered light at 90° to the laser beam is collected and dispersed by a high-resolution monochromator. The incident laser wavelength (chosen such that the sample does not absorb, in ordinary Raman Spectroscopy) is fixed, and the scattered light is dispersed and detected to obtain the frequency spectrum of the scattered light. The scattered light is very weak.
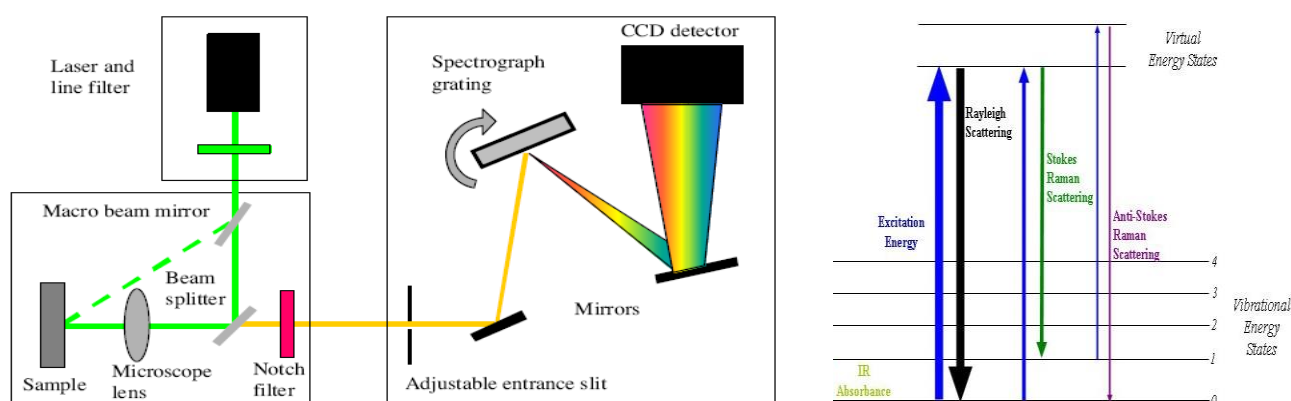

Figure. Layout of Raman spectrometer and Energy level diagram.

Relationship between vibrational (or Oscillational) frequency and force constant of a covalent bond: Diatomic molecule may be considered as s simple vibrating harmonic oscillator. In such oscillator, the restoring force is proportional to the displacement of the atom from its original position (Hook's law).

According to Hook's law,

$F\alpha\ X$ OR F = kX OR k = $\frac{F}{X}$ where, k = force constant = $\frac{Restoring\ force}{Displacement}$

The restoring force per unit displacement is called as force constant. It is related to the vibrational frequency by the equation.

$$\omega = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \quad \text{OR, } \omega_{osc}^2 = \frac{1}{4\pi^2}*\frac{k}{\mu}$$

Where, μ = reduced mass $= \frac{m_1 m_2}{m_1 + m_2}$

m_1= mass of one atom $m_1 = mass\ of\ another\ atom$

$$\omega_{osc} = C\bar{\omega}_{osc}$$

$$K = 4\pi^2 \mu C^2 \bar{\omega}_{osc}^2$$

$\bar{\omega}_{osc}$ = vibrational frequency in term of wave number (in cm^{-1})

C = velocity of light.

Thus, if $\bar{\omega}_{osc}$ is known, the force constant of a bond can be calculated.

The unit of k is dyne/cm. in CGS system while S.I. unt is newton/meter (Nm^{-1}).

Procedure:

1.) Identify and characterize the internal coordinates used in each structure, implied atoms, number of occurrences in the primitive cell

2.) characteristic value (interatomic distance for stretching coordinates, angle for bending coordinates)

3.) calculate value of the force constant from the data obtained from the internal coordinates and modes of vibration of the atoms.

Observations:

Tabulate the data from the calacuted values.

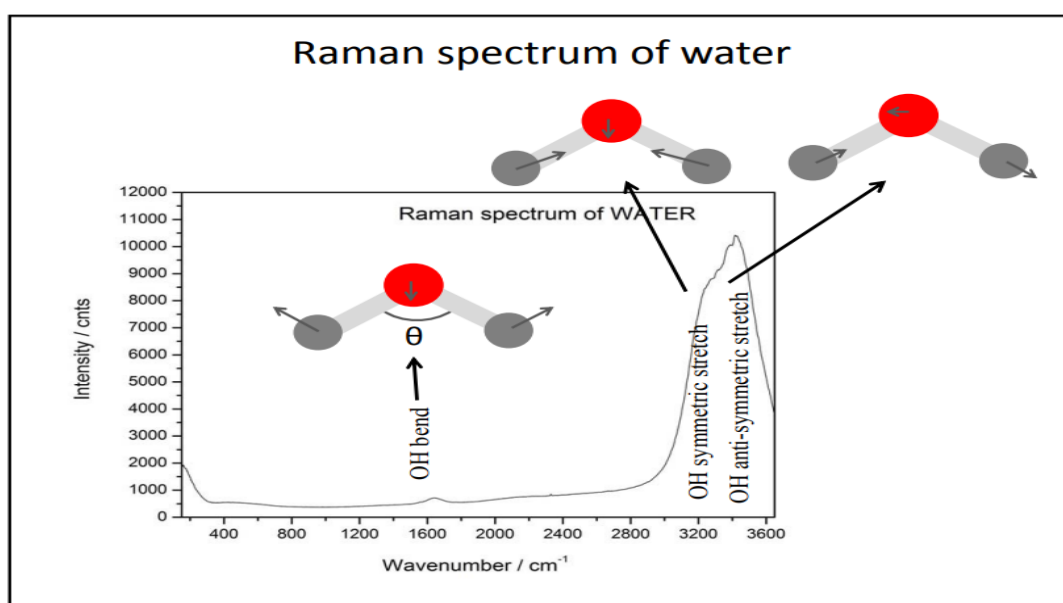| Name	Atoms vibrational modes	Occurences	Interatomic distances (A°)	Force Constant (Ncm^{-1})

Figure. Raman spectra of water molecule indicating various vibrational modes and stretching.

Conclusions:

Analysis:

Experiment 6

Aim: To analyse the elemental species, present in the given sample through Xray photoelectron spectroscopy

Requirements: XPS Data, Origin software.

Theory: -
X-ray Photoelectron Spectroscopy (XPS), also known as Electron Spectroscopy for Chemical Analysis (ESCA), is used to determine quantitative atomic composition and chemistry. A sample is irradiated with monochromatic x-rays, resulting in the emission of photoelectrons whose energies are characteristic of the elements within the sampling volume. An XPS spectra is created by plotting the number of electrons verses their binding energy.
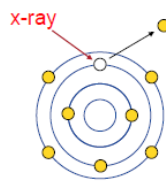
Based on Einstein's photoelectric effect. Many materials emit electrons when light shines upon them.
Core electrons with kinetic energy E_k are ejected by incident X-rays.
$E_K = h\nu - Eb - \varphi_{sp}$ E_K = kinetic energy E_b= binding energy h = Planck's constant ν = frequency of X-rays φ_{sp} = spectrometer work function

An x-ray beam usually comprised of k-alpha x-rays is focused on the sample. The absorption of incident x-rays results in the ejection of electrons. The energy of the ejected electrons is measured by the detector.

Each atom has a unique XPS spectra. XPS can determine elemental composition, stoichiometry, electrical/chemical states and examine surface contamination. XPS is an elemental analysis technique that is unique in providing chemical state information of the detected elements, such as distinguishing between sulphate and sulphide forms of the element sulphur.
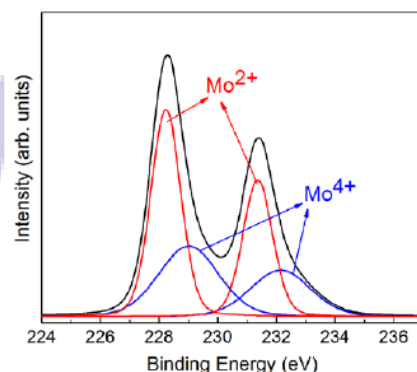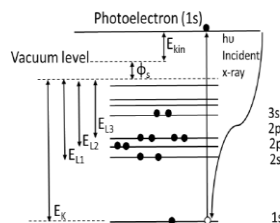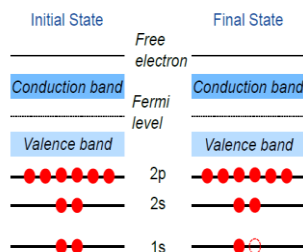

Fig 1: Example Energy levels of any element.

Fig 2: Fitted Example XPS data of Different oxidation states of Mo

STEPS TO ANALYSE DATA

1.Take the XPS DATA and fit it to the origin software.

2.Indentify the Binding Energies from fitted data(Generally they are the peaks)

3.Match the binding energies from Literature or database.

4.Matches binding energy of sample gives the information about the Oxidation states of elements peresnt in the sample.

5.The oxidation state of sample gives the stoichiometric or non-stoichiometry nature of the sample.

Result: - Write about the matching of Binding energies and oxidation states

Conclusion: -