M. Sc. Physics

Materials Science

Laboratory Manual

(Based on given experimental data analysis)

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DEPARTMENT OF PURE & APPLIED PHYSICS

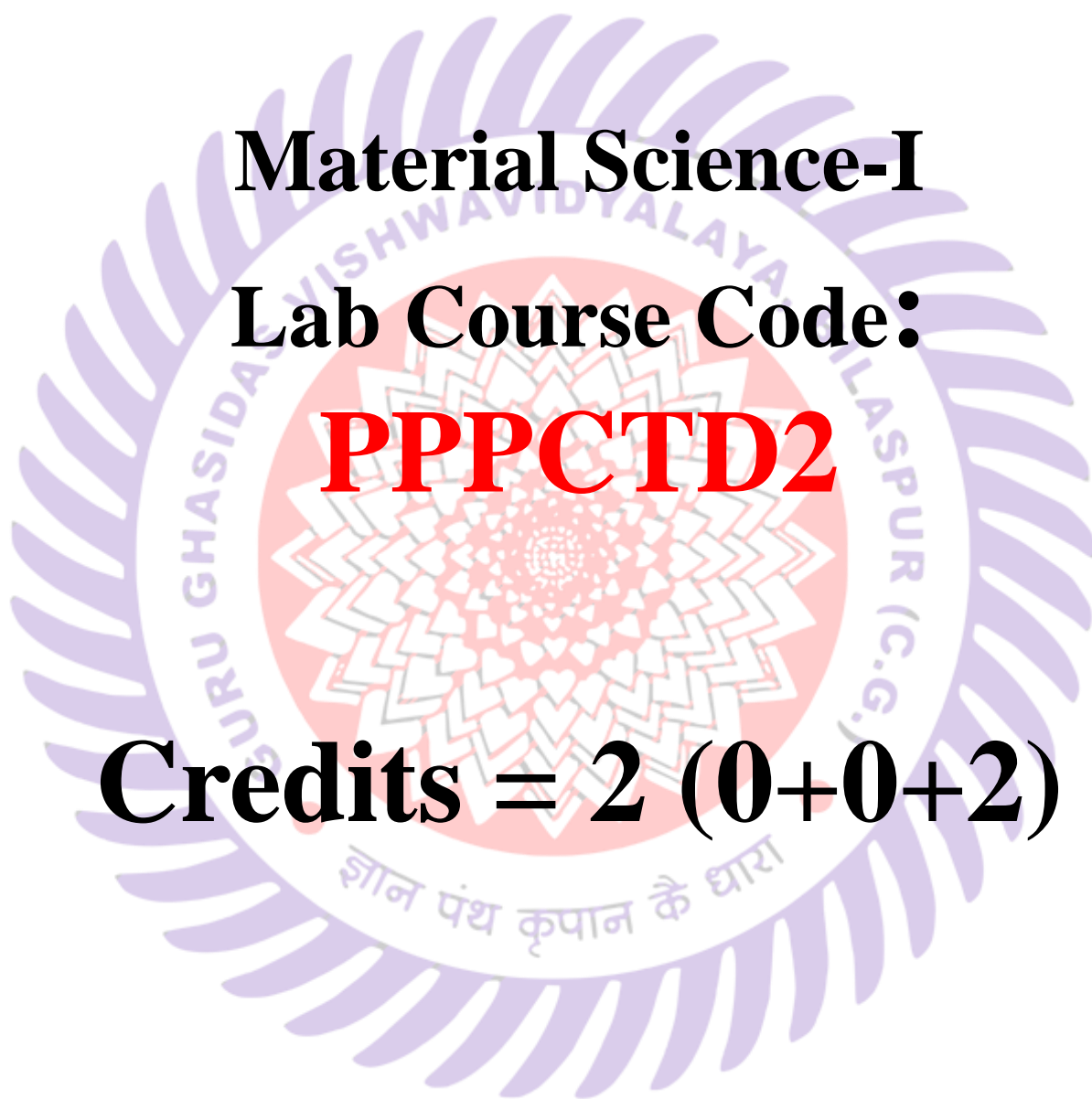# M. Sc. Physics 3rd Semester

Material Science-I

Lab Course Code:

PPPCTD2

Credits = 2 (0+0+2)

List of experiments:

1. Indexing powder X-ray diffraction (XRD) pattern of a given cubic crystal.
2. Estimation of particle size from given XRD data of powder sample using Scherer formula.
3. To calculate strain produced in a material using Williamson-Hall plot from given XRD data.
4. To study the heat flow associated with physical and chemical transitions in a material as a function of temperature.
5. To analyse Raman spectra and calculate the force constant of a given sample.
6. Determination of band gap using Tauc's plots for given UV-Visible spectra.
7. To analyse and calculate force constant from FTIR spectra.
8. To find the thickness of the thin films for a given set of samples from UV-Visible spectra.

EXPERIMENT NO. 1

Aim: Indexing powder X-ray diffraction (XRD) pattern of a given cubic crystal.

Requirements: PowderXRD data of sample.

Theory: XRD is one of several experimental tools used to identify the structures of crystalline solids. XRD pattern determines:

(1) The size and shape of the unit cells determine the relative positions of the diffraction peaks;

(2) Atomic positions within the unit cell determine the relative intensities of the diffraction peaks.

For cubic system, expected lines of diffraction pattern can be generated from the following relations:

(1.) The relation between Miller indices of a particular peak and the interplanar spacing d can be written as:

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

(2.) Bragg's law:

$$\lambda = 2d \sin\theta$$

For indexing the powder diffraction patterns above two equations are used i.e.,

$$\frac{\lambda}{4a^2} = \frac{sin^2\theta}{h^2 + k^2 + l^2} = \frac{sin^2\theta}{s}$$

In the above equation:

(1.) $\frac{\lambda}{4a^2}$ is always constant for a given crystal.

(2.) $S = h^2 + k^2 + l^2$ will always be an integer regardless of the sign of each of the h,k,l values.

Each of the four common cubic lattice types has characteristic sequence of X-ray diffraction lines described by their successive 'S' values:

1. **Simple cubic: 1, 2, 3, 4, 5, 6, 8, 9, 10, 11, 12, 13,..........**
2. **Body centred cubic: 2, 4, 6, 8, 10 ,12 ,14, 16,..........**
3. **Face cantered cubic: 3, 4, 8, 11, 12, 16,..........**
4. **Diamond cubic: 3, 8, 11, 16,.........**

Procedure:

(1) Identify the peaks.

(2) Find 2θ from XRD pattern for each peak. Determine $sin^2\theta$ using Cu K□$_1$ = 1.54024 Å

(3) Calculate the ratio $sin^2\theta$ / $sin^2\theta_{min}$ and multiply by the appropriate integers.

(4) Select the result from (3) that yields $h^2 + k^2 + l^2$ as an integer.

(5) Compare results with the sequences of $h^2 + k^2 + l^2$ values to identify the Bravais lattice.

(6) Calculate lattice parameters.
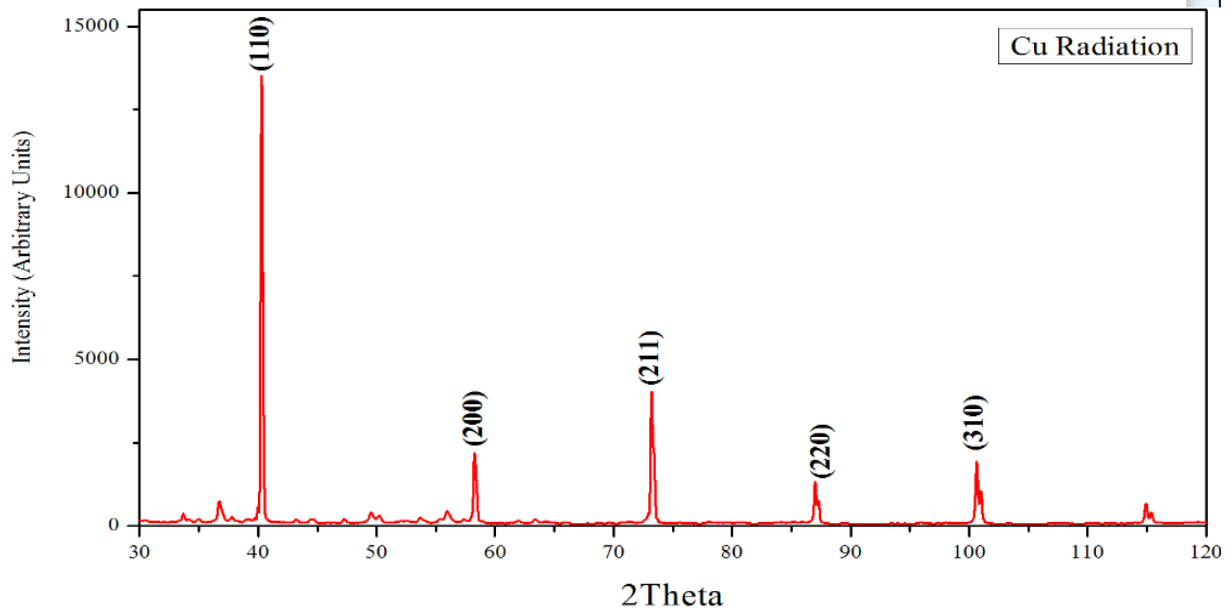
Observations:

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

Line	2θ	$\sin^2\theta$	$\dfrac{\sin^2\theta}{\sin^2\theta_{min}}$	$s = (h^2 + k^2 + l^2)$	$\dfrac{\lambda}{4a^2}$	a (Aº)	d_{hkl}	hkl
1								
2								
3								
4								
5								

(2) Discuss obtained results and compare with the actual value of lattice parameters.

Analysis:

Conclusions:

EXPERIMENT NO. - 2

Aim: Estimation of particle size from given XRD data of powder sample using Scherer formula.

Requirements: XRD data of powder sample.

Theory: X-ray diffraction is a convenient method for determining the mean size of nano-crystallites in nano-crystalline bulk materials with phase certain. The determination refers to the main peaks of the pattern diffractogram through the approach of Debye Scherer'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 cosθ from the value of 2θ value.
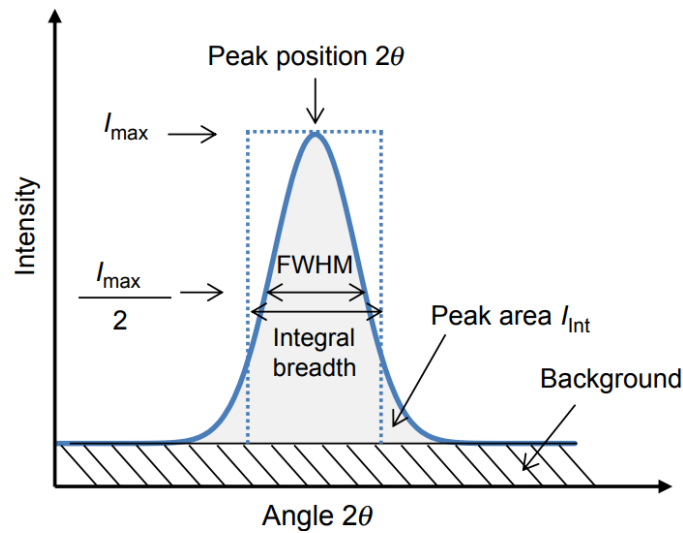
The steps to determine the value of cos from the value of 2θ are as follows:

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)to obtain the crystal size.

In short, by performing a curve selection of the diffraction peaks of each plane crystal at position 2θ, we can see a 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 (degree)	θ (degree)	Cosθ

Analysis:

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

Conclusions:

<p style="text-align:center">**EXPERIMENT NO. 3**</p>

Aim: To calculate strain produced in a material using Williamson-Hall plot from given XRD data.

Requirements: XRD data of powder sample.

Theory: Williamson-Hall (W-H) analysis is a simplified integral breadth method where both size-induced and strain-induced broadening are de-convoluted by considering the peak width as a function of 2θ. W-H analysis is employed for estimating crystallite size and lattice strain. The significance of the broadening of peaks evidences grain refinement along with the large strain associated with the powder. The instrumental broadening (β_{hkl}) is corrected corresponding to each diffraction peak XRD pattern using the equation:

$$\beta_{hkl}^2 = (\beta_{hkl})^2_{Measured} - (\beta_{hkl})^2_{Instrument} \quad \dots (1)$$

The average nano-crystalline size was calculated using Debye-Scherer's formula:

$$D = \frac{K\lambda}{\beta \cos\theta} \quad \dots \quad (2)$$

where D = crystalline size, K = shape factor (0.9), and λ = wavelength of Cu kα radiation.

The strain induced in powders due to crystal imperfection and distortion:

$$\in = \frac{\beta_{hkl}}{tan\theta} \quad \dots\dots (3)$$

From Equations 2 and 3, it was confirmed that the peak width from crystallite size varies as $\frac{1}{cos\theta}$ strain varies as tanθ. Assuming that the particle size and strain contributions to line broadening are independent to each other and both have a Cauchy-like profile, the observed line breadth is simply the sum of Equations 2 and 3.

$$\beta_{hkl} = \frac{K\lambda}{D\,cos\theta} + 4\epsilon\,tan\theta \dots\dots\dots(4)$$

By rearranging the above equation, we get:

$$\beta_{hkl} = \frac{K\lambda}{D\,cos\theta} + 4\epsilon\,tan\theta \dots\dots\dots\dots (5)$$

The above equations are W-H equations. A plot is drawn with 4sinθ along the x-axis and $\beta_{hkl}\,cos\theta$ along the y-axis for as prepared samples. From the linear fit to the data, the crystalline size was estimated from the y-intercept, and the strain ε, from the slope of the fit.

Uniform deformation stress and uniform deformation energy density were taken into account; the anisotropic nature of Young's modulus of the crystal is more realistic. The generalized Hook's law referred to the strain, keeping only the linear proportionality between the stress and strain, i.e., σ = E. Here, the stress is proportional to the strain, with the constant of proportionality being the modulus of elasticity or Young's modulus, denoted by E. In this approach, the Williamson-Hall equation is modified by substituting the value of ε in Equation 5.

$$\beta_{hkl}cos\theta = \frac{K\lambda}{D} + \frac{4\,sin\theta\sigma}{E_{hkl}}$$
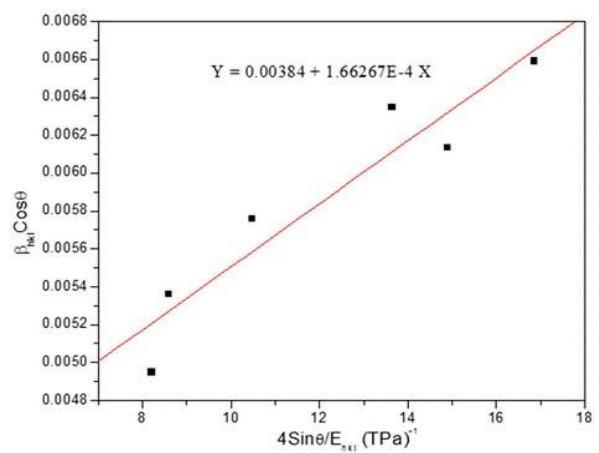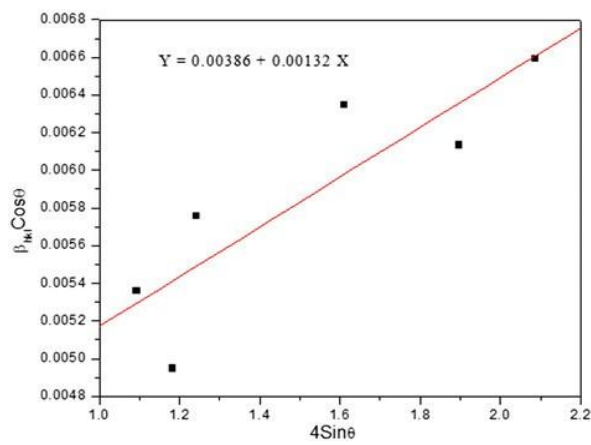
E_{hkl} is Young's modulus in the direction perpendicular to the set of the crystal lattice plane (hkl). The uniform stress can be calculated from the slope line plotted between 4sinθ/Ehkl and βhkl cosθ, and the crystallite size D, from the intercept as shown in the figure below.

Observations:

Conclusions:

Analysis:

Experiment No 4

Aim: To study the heat flow associated with physical and chemical transitions in materials as a function of temperature.

Requirements: DSC instrument, materials

Theory and procedure:

Endothermic and Exothermic Peaks: Examine the DSC curve for endothermic (heat absorption) and exothermic (heat release) peaks. Peaks indicate phase transitions or chemical reactions.

1. Thermal Stability:

Onset Temperature of Decomposition: Identify the onset temperature at which the material starts to decompose. A lower onset temperature may indicate lower thermal stability.

Peak Temperature of Decomposition: Determine the peak temperature of the decomposition reaction. A higher peak temperature often suggests higher thermal stability.

2. Purity:

Baseline Assessment: Examine the baseline of the DSC curve. Impurities or contaminants may introduce additional peaks or affect the baseline.

Peak Purity: Evaluate the purity of the material based on the sharpness and symmetry of the observed peaks. A pure substance typically exhibits well-defined peaks.

3. Phase Transitions:

Melting/Freezing Points: Identify melting and freezing points, which can provide insights into the material's crystalline structure. Consistency in melting points across runs indicates purity.

Glass Transition Temperature (Tg): Determine the Tg for amorphous materials. Tg is critical for understanding the material's transition from a glassy to a rubbery state.

Crystallization Peaks: Look for crystallization peaks after the melting point.

The absence of crystallization peaks may suggest the material is amorphous. **4.**

Enthalpy Changes:

Enthalpy of Fusion: Measure the enthalpy change during melting (endothermic peak).

Higher enthalpy may indicate higher purity or crystallinity.

Assess the enthalpy change for any exothermic peaks corresponding to reactions.

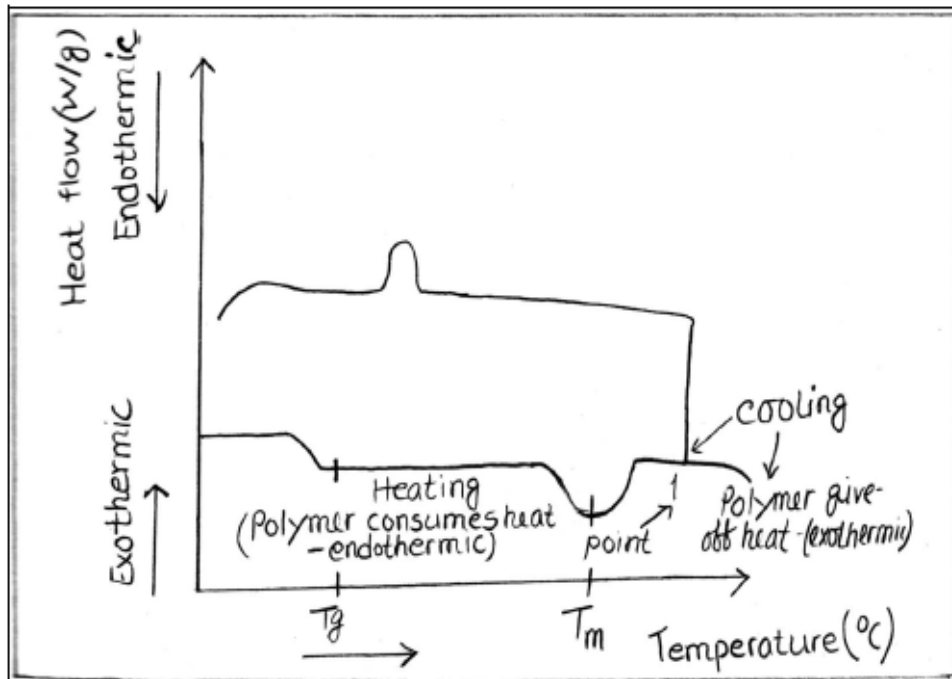Evaluate the significance of the reaction in terms of purity and stability.

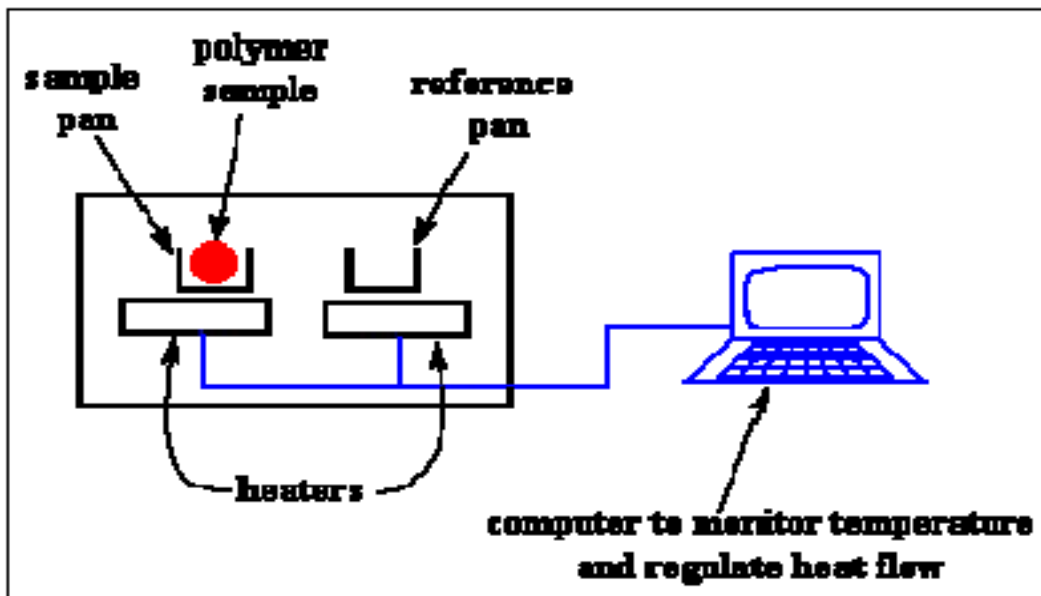**Figure-2:** *The working principle of DSC*

Figure-1: *DSC apparatus*

DSC Data: Prepare your sample and reference materials. The sample and reference should have similar masses.

1. Load the sample and reference into the DSC instrument.

2. Initiate the experiment according to the specified temperature program. 3.

Record the heat flow data as a function of temperature.

The sharpness or flatness of peaks in a DSC curve provides insights into the nature and characteristics of the thermal transitions occurring in a material. Sharp peaks are often associated with well-defined processes, while flat peaks may indicate broader or more complex transitions.
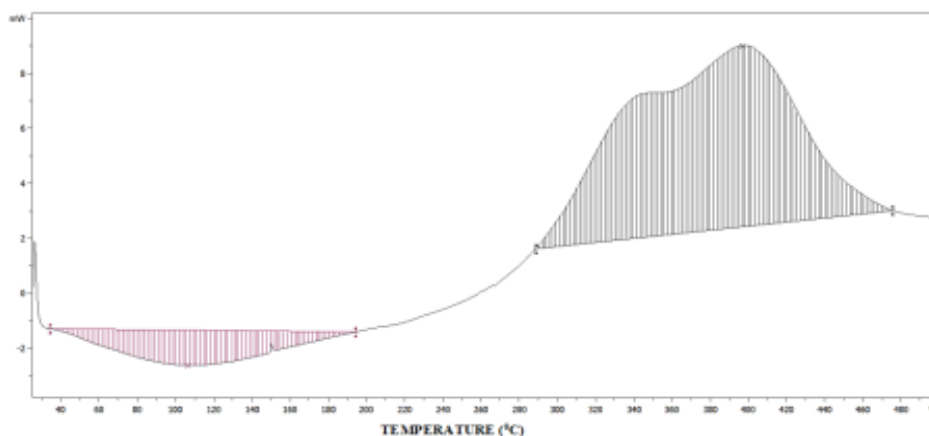
Observations:

Table: 1 Phase transitions or chemical reactions data.

S.N.	Peak No.	Onset Temperature	Peak Temperature	Enthalpy Change

Table:2 Material properties data

| S.N.	Peak No.	Thermal stability	Purity	Phase transition(Y/N)	Enthalpy

Analysis:

Conclusion:

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.
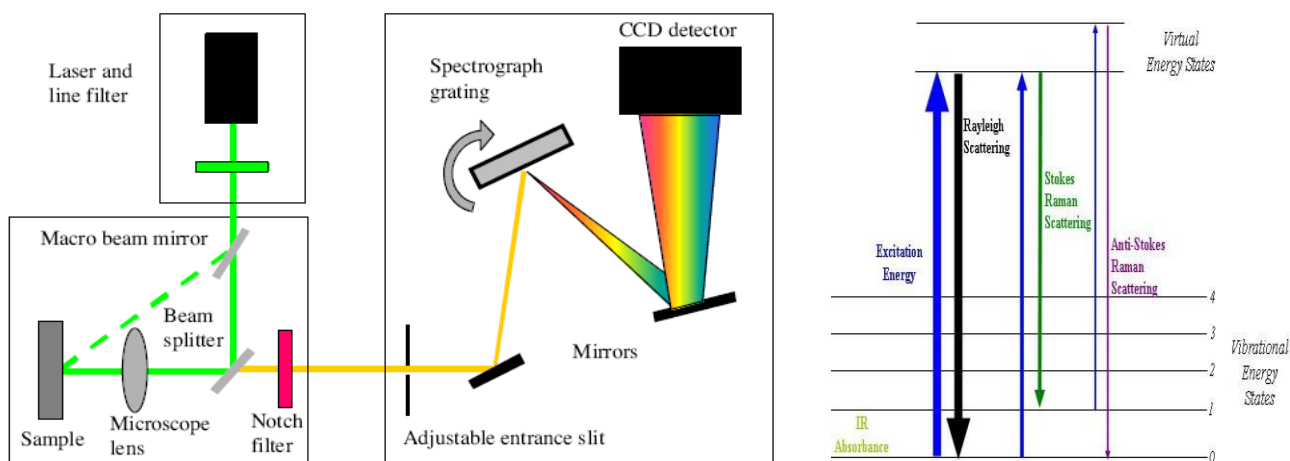
bond: Diatomic molecule may be considered as s simple vibrating harmonic oscillator. In such oscillator, the restoring force is proportional to the displacement of the atom from its original position (Hook's law).

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.

$\omega = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$ 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 abond 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.
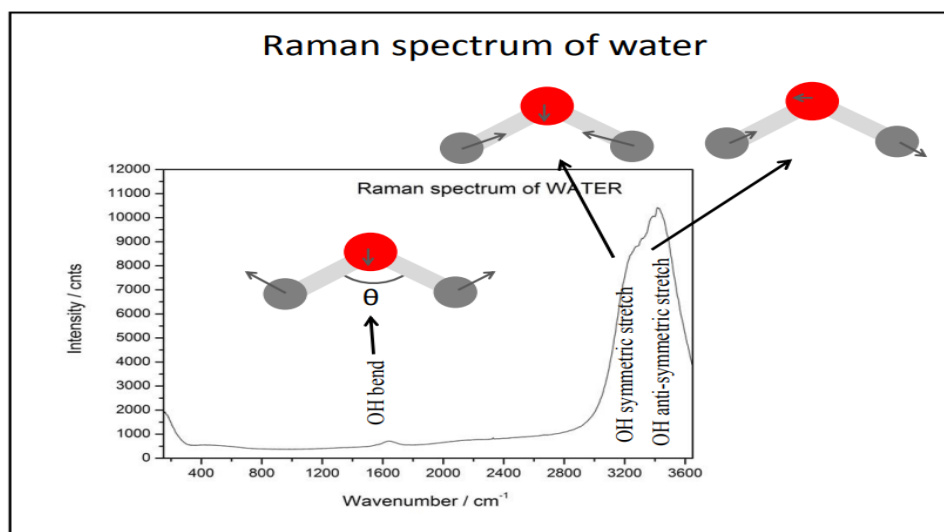

Figure:- Raman spectra of water molecule indicating various vibrational modes and stretching.

Observations:

Tabulate the data from the calculated values.

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

Conclusions:

Analysis:

Experiment No. 6

Aim: Determination of band gap using Tauc's plots for given UV-Visible spectra.

Requirements: UV- Visible spectrum 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).

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

Where **α** is the absorption coefficient

h is the planks constant

A is the proportionality constant

E_g is the band gap energy and

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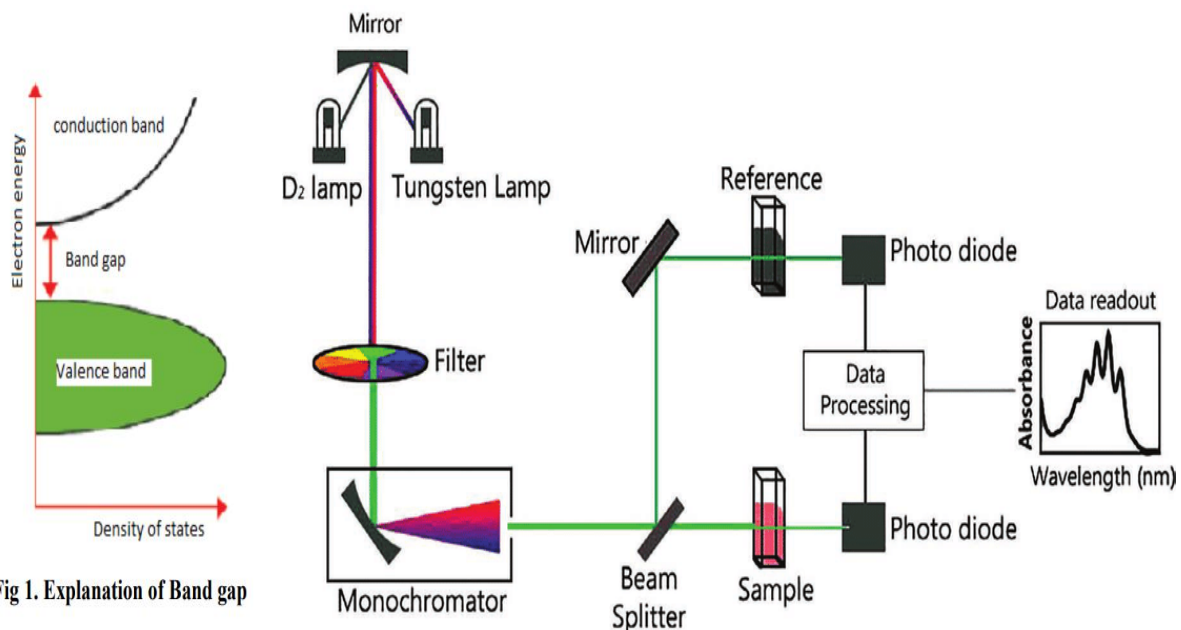
$\gamma = 1/3$ for indirect forbidden transition

Fig 1. Explanation of Band gap

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

1. Plotting the value of $(\alpha h\upsilon)^{\gamma}$ with hυ

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 hυ (energy)

1. α can be estimated by using formula α=2.303×Absorbance (for liquid sample) and α=Absorbance/film thickness (for thin film sample)

2. Energy (hυ) can be calculated by using formula E= hυ=hc/λ=1240/ λ

Observations:

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

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

**Analysis:**

Conclusions:

Aim: To analyse and calculate force constant from FTIR spectra.

Requirements: FTIR instrument, FTIR spectra.

Theory and procedure: IR spectroscopy is a very powerful method for the identification of functional groups. The most important regions of the IR spectrum are >1650 cm^{-1}, whereas the fingerprint region (600 - 1500 cm^{-1}) of the spectrum cannot easily be used for identification of unknown compounds. Many references exist which tabulate the IR frequencies for various functional groups and organic compounds (a short table appears at the end of this section). However, the most valuable resource available to you for the interpretation of IR spectra is understanding the five basic principles of IR spectroscopy. Transitions between vibrational energy levels follow the same equation as for a classical harmonic oscillator:

Equation for the Classical Harmonic Oscillator:

$$\nu = \frac{1}{2PC}\sqrt{\frac{k}{\mu}}, \quad \mu = \text{reduced mass} = \frac{m_1 m_2}{m_1 + m_2}$$
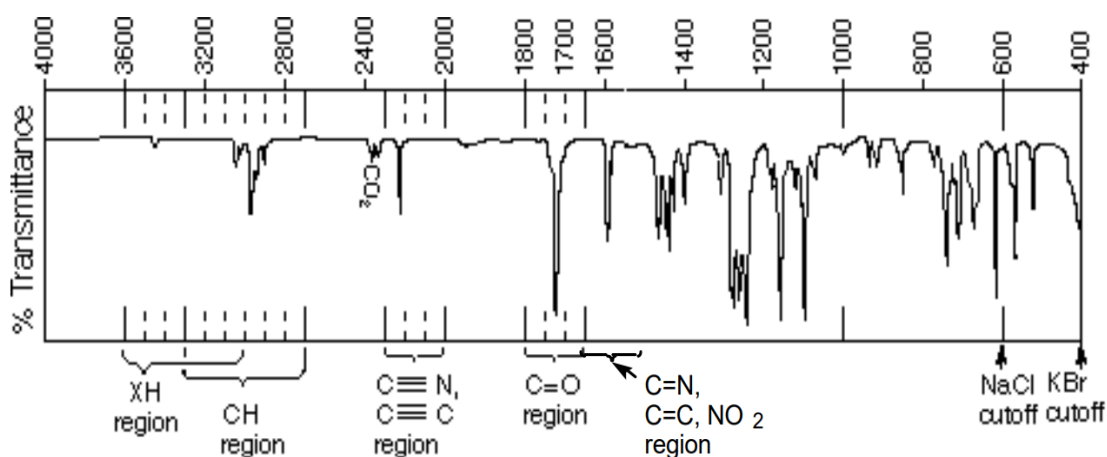
1) **k is the force constant:** k is proportional to bond strength or bond order. C=O vibrates at a higher frequency than C-O. Furthermore, the change in the force constant of different carbonyl groups can be understood based on the contribution of resonance structures. The base value for the stretching frequency of a carbonyl (e.g., acetone) is $\nu_{co} \sim 1715$ cm^{-1}. Acid chlorides have bond order slightly greater than 2 because an acylium ion resonance structure may be drawn ($\nu_{co} \sim 1800$ cm-1). Alternatively, Phenyl ketones, vinyl ketones and amides have a CO bond order slightly less than 2 and display a lower energy ν_{co}.

Acid Chloride
ν_{CO}= 1800 cm-1

Methyl Vinyl Ketone
ν_{CO}= 1675 cm-1

Amide
ν_{CO}= 1650 cm-1
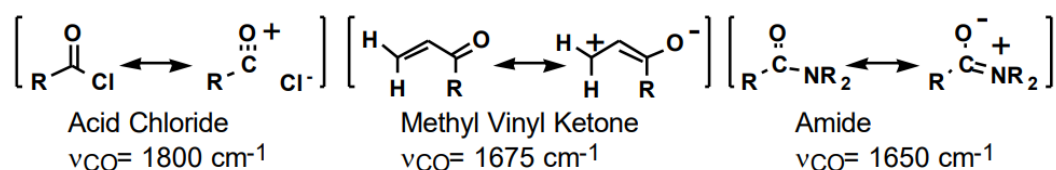
2) **μ is the reduced mass**: Heavier atoms slower vibration, lower energy. Compare C-O vs. H-O or H-O vs H-S.

3) **Overtone Peaks:** Notice in the above spectrum that a small peak is found at 3450 cm^{-1}, even though the compound does not contain any O-H or C-H bonds. This peak is the overtone of the C=O vibration (at 1735 cm^{-1}). It corresponds to the transition from the ground vibrational state (n=0) to the second vibrationally excited state -5- (n=2) rather than the first. Carbonyl overtones are always small and are easily found at slightly less than twice the normal C=O frequency.

4) **Dipole moment:** The strength of an IR peak is roughly dependent on the change in dipole moment during vibration. C=O bonds are very polar because of the greater electronegativity of oxygen and so give very intense bands. Also note that if a molecule is so symmetrical that the stretching of a bond does not produce any change in dipole moment, then no IR peak will be found in the spectrum. Compare the spectra of 1-butyne and 3-hexyne. 1-butyne shows an alkyne C-H stretch at 3280 cm-1 and an alkyne C=_ C stretch at 2080 cm^{-1}. -hexyne shows no C=_ C stretching peak.
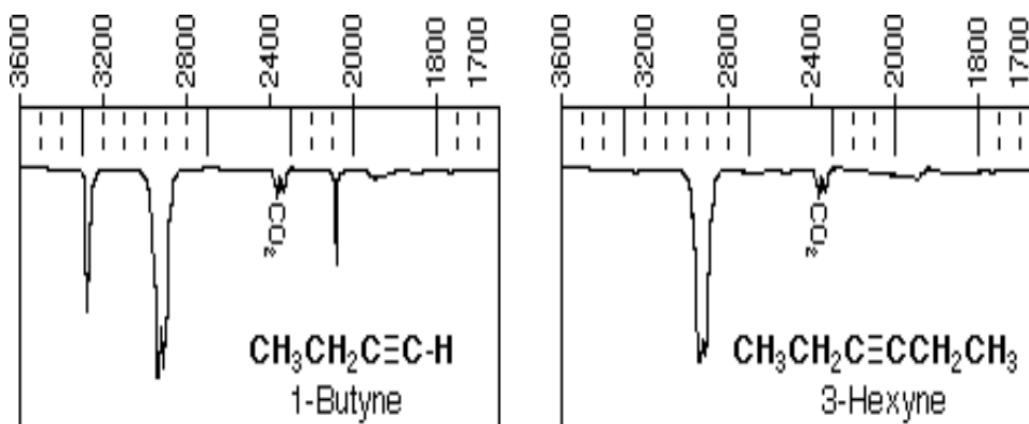
5)**Vibrational Modes.** The vibrations of two neighboring bonds can be coupled into symmetric and antisymmetric vibrational modes. One example is the vibration of CH2 groups within an alkane (or the NH2 group of a primary amine). The symmetric stretch requires slightly more energy (2925 cm^{-1}) for a transition while an antisymmetric stretch requires slightly less energy (2850 cm^{-1}). For acetic anhydride, notice that although the two C=O groups are identical by symmetry, two peaks are found in the C=O region of the IR spectrum.

Acetic Anhydride
Symmetric Stretch ($v = 1810$ cm^{-1})
Antisymmetric Stretch ($v = 1750$ cm^{-1})
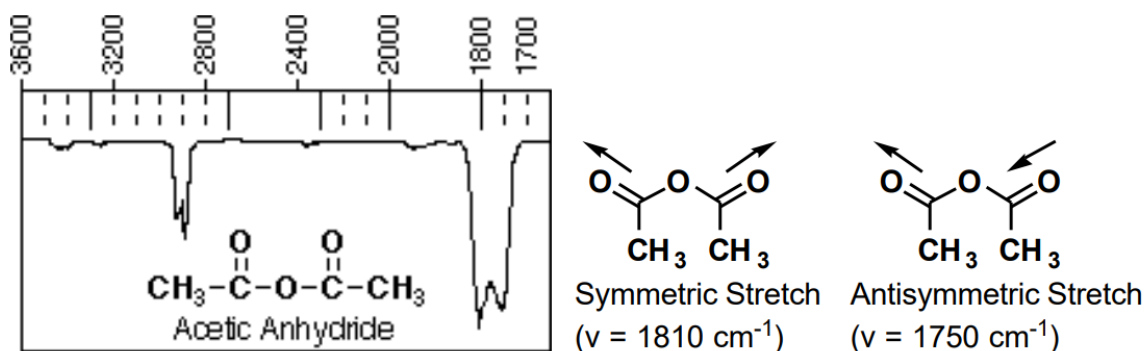
If a functional group's normal vibrational frequency happens to coincide in frequency with a weak overtone peak of a neighboring bond, then the peak will be observed as a Fermi doublet. In the case of aliphatic aldehydes, the aldehydic C-H stretching frequency at 2720 cm-1 couples with the overtone of the C-H bending transition at 1380 cm-1. Fermi coupling also explains the observation of two peaks near 2300 cm-1 in the spectrum of CO2.

CHARACTERISTIC IR FREQUENCIES

XH Region (3600 cm^{-1} to 2400 cm^{-1})

cm^{-1}		comments		
3600	v(free OH)	Sharp peak	Alcohol or Phenol free OH	
3600-2800	v(H-bonded OH)	Very Broad peak:	Alcohol: Phenol: Carboxylic Acid:	3400 to 3200 cm-1 3600 to 3000 cm-1 3600 to 2400 cm-1
3500-3300	v(NH)	Amines show broad peaks, Amides show sharp peaks Primary Amines display two peaks (v_s and v_{as})		

CH Region (3300 cm^{-1} to 2700 cm^{-1})

cm^{-1}		comments
3300	Alkyne v(CH)	strong, sharp
3150-3000	Alkene or Phenyl v(CH)	medium intensity
3050	Cyclopropane or Epoxide v(CH)	weak
2960,2870	Alkane v(CH)	v_s(CH), v_{as}(CH) observed for CH_2 or CH_3 groups
2750	Aldehyde v(CH)	sharp, medium intensity

-C≡N, -C≡C-, >C=C=C< Region (2300 cm^{-1} to 2000 cm^{-1})		
cm^{-1}		**comments**
2250	ν(-C≡N)	sharp, weak to med intens, almost always observed
2150	ν(RC≡CH)	sharp, weak to med intens, check for ν(C-H) at 3300
2260-2190	ν(R-C≡C-R')	sharp, weak to med intens, obsd only for R,R' different
1950	ν(>C=C=C<)	sharp, strong allene

>C=O Region (1800 cm^{-1} to 1650 cm^{-1})		
cm^{-1}		**comments**
1800	Acid Chloride	CO Bond Order >2
1820,1760	Anhydride	two peaks are observed (ν_s ν_{as})
1735	Ester	RCO$_2$R'
1755	Carbonate	ROCO$_2$R'
1735	Urethane	ROCONR'$_2$
1720	Aldehyde/Ketone	aldehyde has ν(CH) at 2750 cm^{-1}
1650	Amide	CO Bond Order <2
1630	Urea	R$_2$NCONR'$_2$

| C=N, C=C, NO$_2$ Region (1660 cm^{-1} to 1500 cm^{-1})		
cm^{-1}		**comments**
1690-1640	ν(C=N)	weak to med intensity, sharp
1660-1640	ν(C=C)	weak to med intensity, sharp
1590	ν(NO$_2$)	strong, sharp

Conclusions:

Analysis:

Experiment No. 8

Aim: To find the thickness of the thin films for a given set of samples from UV-Visible spectra.

Requirements: UV-Visible instrument and its spectra.

Theory: UV-Visible spectrometer measures the intensity of light passing through the sample (I) and compares it to the calibrated intensity (I_0). The ratio I/I_0 is called the transmittance for a particular wavelength. The absorbance A is defined as,

$A = -\text{Log}(I/I_0)$
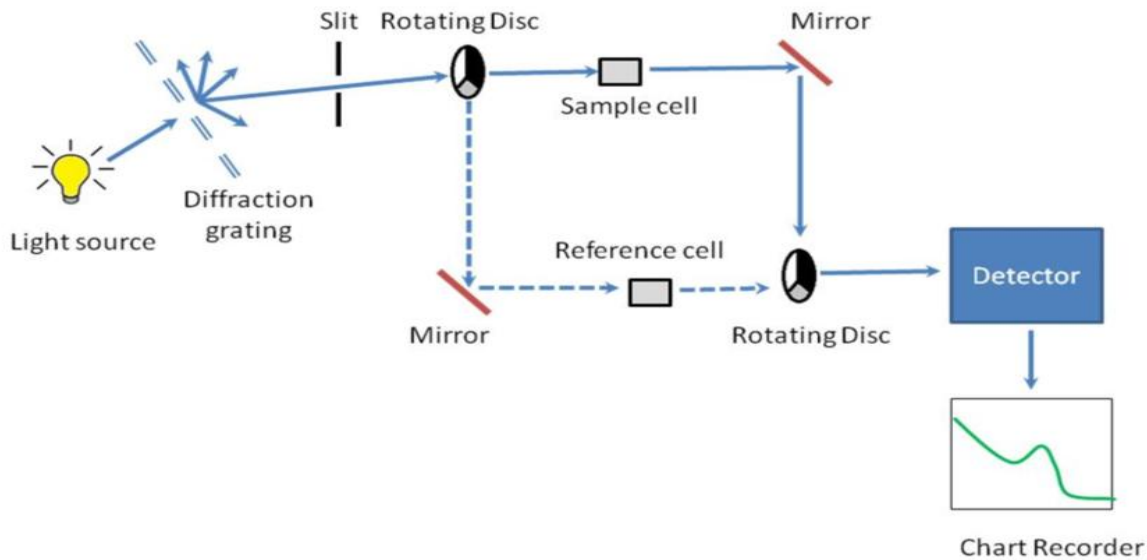
Thickness calculations:

Absorbance, $A = -\text{Log}(I/I_0)$

$$I = I_0 e^{-t/\delta}$$

Where, I_0 = intensity of the glass plate,

I = intensity of the coated glass sample,

t = thickness of the sample,

δ = skin depth of the material.

$$\delta = \sqrt{\frac{\rho\lambda}{\pi c \mu}}$$

Where,

ρ = resistivity

λ = wavelength

c = velocity of light.

μ = absolute magnetic permeability.

Calculate thickness for 3 wavelengths for a given sample/slide and take the average of them.

Procedure:

1. First turn on the switch provided back side of the device and leave it for 15 minutes for warm up.
2. Take air as reference.
3. Scan plain glass plate sample and take the reading as I_0.
4. Scan the coated sample and take the reading as I for your further calculation.

Observations:

Conclusions:

Analysis: