



MSc. Physics 4th Sem.

Material Science-II

Lab Course Code:

PPD1D1

Credits = 2 (0+0+2)

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Material Science-II

List of experiments

1. Estimation of particle size from given XRD data of powder sample using Scherer formula.
2. To determine the effect on nanosize by X-ray diffraction pattern.
3. To determine the grain size by image J software.
4. To analyse and calculate force constant from FTIR spectra.
5. To calculate vibrational frequency from Raman spectroscopy.
6. To study the heat flow associated with physical and chemical transitions in a material as a function of temperature.

EXPERIMENT NO. 1

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 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:

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

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.

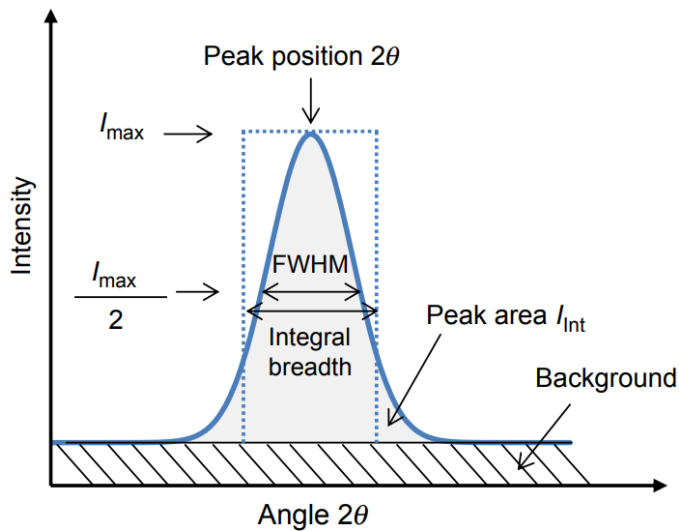
The steps to determine the value of \cos from the value of 2θ are as follows:

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) 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.



2θ (degree)	θ (degree)	$\cos\theta$

Observations:

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

2θ ($^\circ$)	$\cos \theta$	K (rad/A^2)	λ (nm)	FWHM β ($^\circ$)	FWHM β (rad)	Crystallite Size (nm)

Analysis:

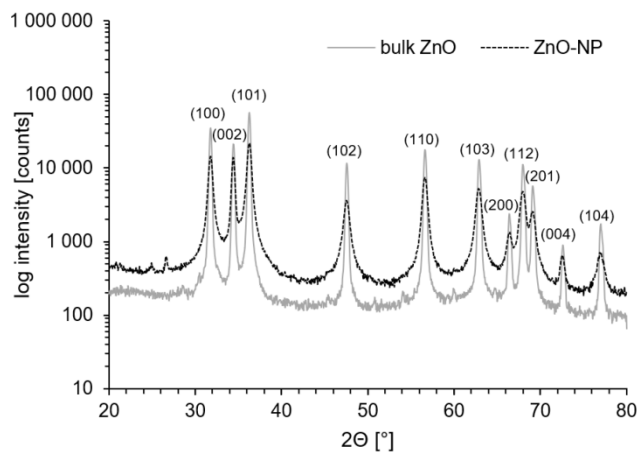
Conclusions:

Experiment No. 2

Aim: To determine the effect on nanosize by X-ray diffraction pattern.

Theory: X-Ray diffraction analysis (XRD) is a nondestructive technique that provides detailed information about the crystallographic structure, chemical composition, and physical properties of a material. It provides useful information on the crystal phase, lattice constant, and average particle size of nanoparticles. The sensitivity of XRD results with the size of nanocrystals can be advantages as well as limitations. Researchers reported that even the decrease in size from 50 to 25 nm causes dramatic peak broadening, which further increases significantly for the crystal with a size less than 10 nm. Such nanocrystal sizes have low peak intensity, which makes it challenging to identify them as they are often found overlapped with one another.

There are some important differences between the diffraction patterns of nano and bulk materials. Nano materials have small particle size and this causes the lines in their diffraction peak to broaden. The broadening of the peak is due to a small number of crystal planes. This broadening in turn causes a loss of intensity in the signal of their diffraction patterns. Bulk materials, on the contrary, have sharp, narrow and high-intensity peaks.



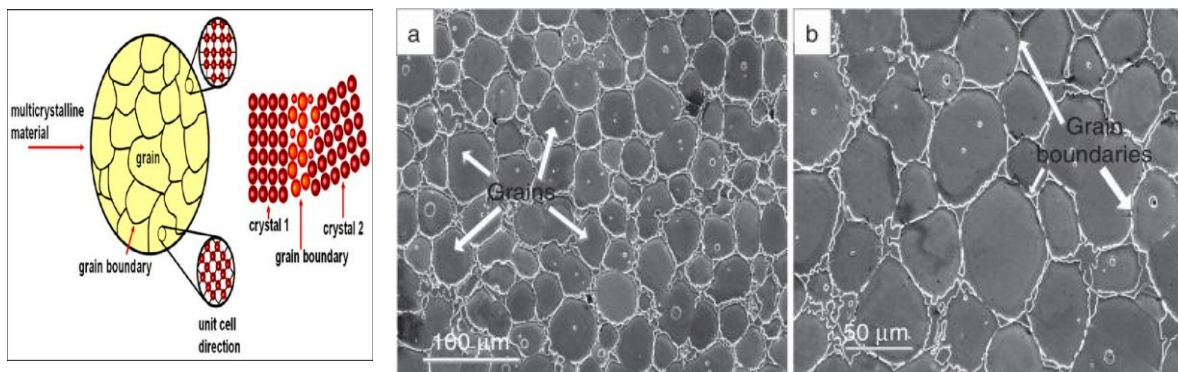
Conclusions:

Analysis:

Experiment No. 3

Aim: To determine the grain size by image J software.

Theory: Image J is a powerful image analysis program that was created at the National Institutes of Health. It is in the public domain, runs on a variety of operating systems and is updated frequently. You may download this program from the source (<http://rsb.info.nih.gov/ij/>) or copy the ImageJ folder from the C drive of your lab computer. The ImageJ website has instructions for use of the program and links to useful resources.



Installing ImageJ on your PC (Windows operating system): Copy the ImageJ folder and transfer it to the C drive of your personal computer. Open the ImageJ folder in the C drive and copy the shortcut (microscope with arrow) to your computer's desktop. Double click on this desktop shortcut to run ImageJ. See the ImageJ website for Macintosh instructions.

A grain is a single crystal, within which the atomic lattice and its orientation are continuous. Adjacent grains of the same phase with different orientations are separated by an immaterial surface called a grain boundary. The two crystallattices extend regularly right up to the boundary.

Method :

1. Set scale: Measure the scale bar with the line tool and then Analyze/Set Scale. Enter known distance and unit.
2. Select grain surfaces: Image/Adjust/Treshold, slide the bars until the grains are selected then apply
3. Separate individual grains: Process/Binary/Watershed
4. Analyze/Set Measurements, select Area and choose number of decimal places
5. Analyze/Analyze Particles, get the smallest grain size you want to consider by trial and error, Show/Outlines, then select display results and exclude on edges.

Experiment No. 4

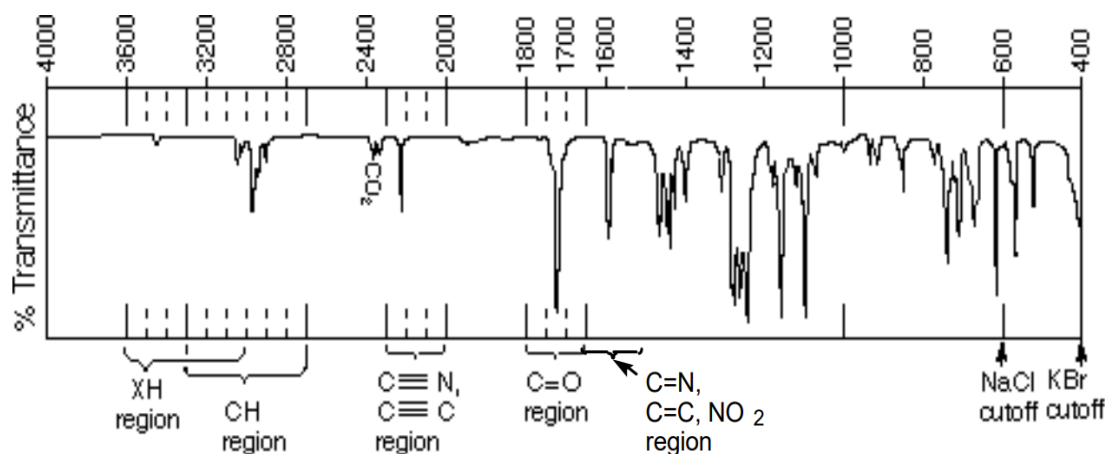
Aim: To analyse and calculate force constant from FTIR spectra.

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 $>1650\text{ cm}^{-1}$, whereas the fingerprint region ($600 - 1500\text{ cm}^{-1}$) 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:

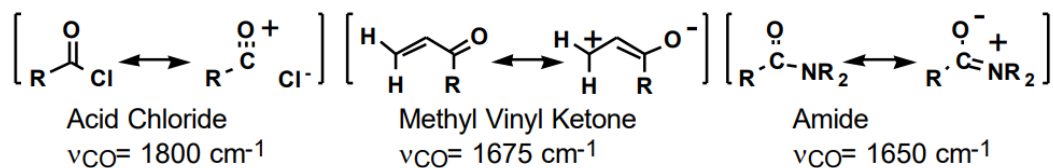
Equation for the Classical Harmonic Oscillator:

$$\nu = \frac{1}{2\pi C} \sqrt{\frac{k}{\mu}}, \quad \mu = \text{reduced mass} = \frac{m_1 m_2}{m_1 + m_2}$$

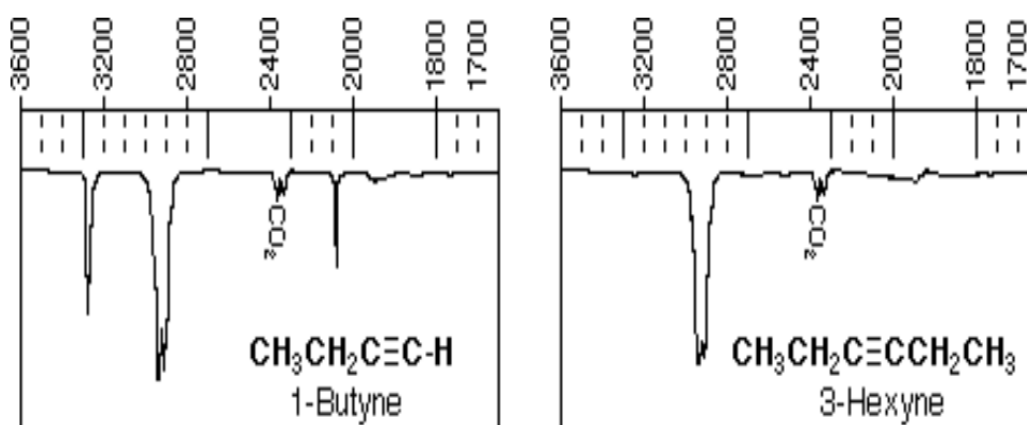


- 1) k is the force constant:** k is proportional to bond strength or bond order. C=O vibrates at a higher frequency than C-O. Furthermore, the change in the force constant of different carbonyl groups can be understood based on the contribution of resonance structures. The base value for the stretching frequency of a carbonyl (e.g., acetone) is $\nu_{CO} \sim 1715\text{ cm}^{-1}$. Acid chlorides have bond order slightly greater than 2 because an acylium ion resonance structure may be drawn ($\nu_{CO} \sim 1800\text{ cm}^{-1}$). Alternatively,

Phenyl ketones, vinyl ketones and amides have a CO bond order slightly less than 2 and display a lower energy ν_{CO} .

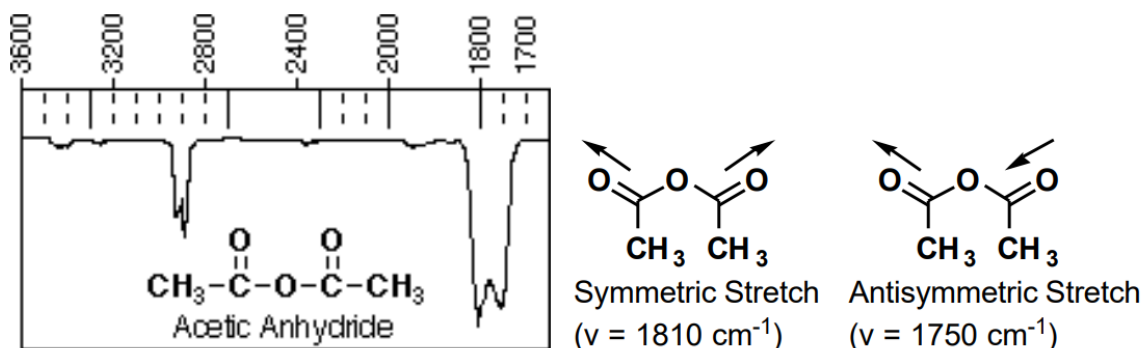


- 2) **μ is the reduced mass:** Heavier atoms slower vibration, lower energy. Compare C-O vs. H-O or H-O vs H-S.
- 3) **Overtone Peaks:** Notice in the above spectrum that a small peak is found at 3450 cm^{-1} , even though the compound does not contain any O-H or C-H bonds. This peak is the overtone 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.



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 CO_2 .

CHARACTERISTIC IR FREQUENCIES

XH Region (3600 cm^{-1} to 2400 cm^{-1})			
cm^{-1}		comments	
3600	$\nu(\text{free OH})$	Sharp peak	Alcohol or Phenol free OH
3600-2800	$\nu(\text{H-bonded OH})$	Very Broad peak:	Alcohol: 3400 to 3200 cm^{-1} Phenol: 3600 to 3000 cm^{-1} Carboxylic Acid: 3600 to 2400 cm^{-1}
3500-3300	$\nu(\text{NH})$	Amines show broad peaks, Amides show sharp peaks Primary Amines display two peaks (ν_s and ν_{as})	
CH Region (3300 cm^{-1} to 2700 cm^{-1})			
cm^{-1}		comments	
3300	Alkyne $\nu(\text{CH})$	strong, sharp	
3150-3000	Alkene or Phenyl $\nu(\text{CH})$	medium intensity	
3050	Cyclopropane or Epoxide $\nu(\text{CH})$	weak	
2960,2870	Alkane $\nu(\text{CH})$	$\nu_s(\text{CH})$, $\nu_{as}(\text{CH})$ observed for CH_2 or CH_3 groups	
2750	Aldehyde $\nu(\text{CH})$	sharp, medium intensity	

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

>C=O Region (1800 cm⁻¹ to 1650 cm⁻¹)		
cm⁻¹		comments
1800	Acid Chloride	$\left[\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{Cl} \end{array} \longleftrightarrow \begin{array}{c} \text{O}^+ \\ \parallel \\ \text{R}-\text{C} \\ \text{Cl}^- \end{array} \right] \text{ CO Bond Order } >2$
1820,1760	Anhydride	two peaks are observed ($\nu_s \nu_{as}$)
1735	Ester	$\text{RCO}_2\text{R}'$
1755	Carbonate	$\text{ROCO}_2\text{R}'$
1735	Urethane	ROCONR'_2
1720	Aldehyde/Ketone	aldehyde has $\nu(\text{CH})$ at 2750 cm ⁻¹
1650	Amide	$\left[\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{NR}_2 \end{array} \longleftrightarrow \begin{array}{c} \text{O}^- \\ \parallel \\ \text{R}-\text{C} \\ \text{NR}_2^+ \end{array} \right] \text{ CO Bond Order } <2$
1630	Urea	$\text{R}_2\text{NCONR}'_2$

C=N, C=C, NO₂ Region (1660 cm⁻¹ to 1500 cm⁻¹)		
cm⁻¹		comments
1690-1640	$\nu(\text{C}=\text{N})$	weak to med intensity, sharp
1660-1640	$\nu(\text{C}=\text{C})$	weak to med intensity, sharp
1590	$\nu(\text{NO}_2)$	strong, sharp

Conclusions:

Analysis:

EXPERIMENT NO. 5

Aim: To analyze Raman spectra and calculate the vibrational frequency from Raman spectra.

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.

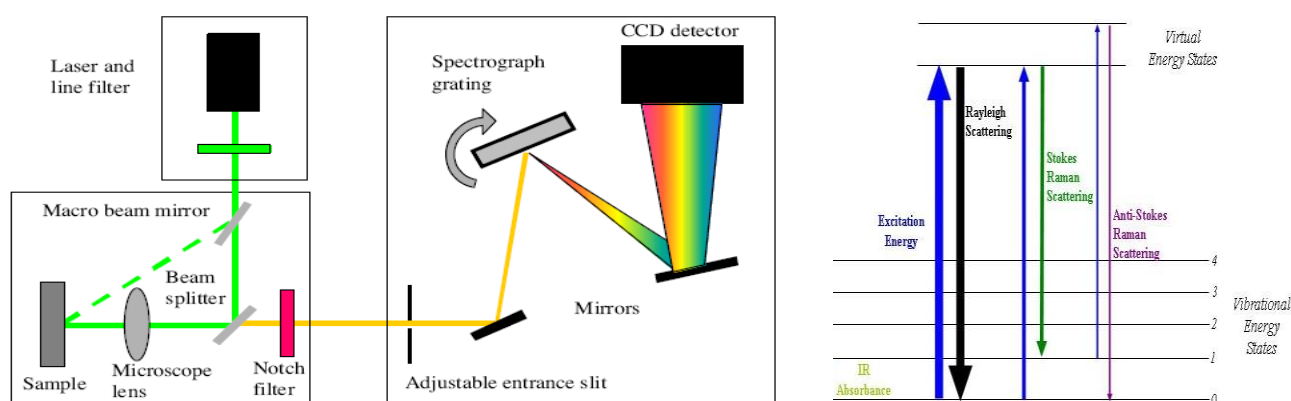


Figure. Layout of Raman spectrometer and Energy level diagram.

Relationship between vibrational (or Oscillational) frequency and force constant of a covalent bond: Diatomic molecule may be considered as a 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,

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

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, $\mu = \text{reduced mass} = \frac{m_1 m_2}{m_1 + m_2}$

$m_1 = \text{mass of one atom}$ $m_2 = \text{mass of another atom}$

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

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

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

C = velocity of light.

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

The unit of k is dyne/cm. in the CGS system while S.I. unit 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 vibrational frequency from the data obtained from the internal coordinates and modes of vibration of the atoms.

Observations:

Tabulate the data from the calculated values.

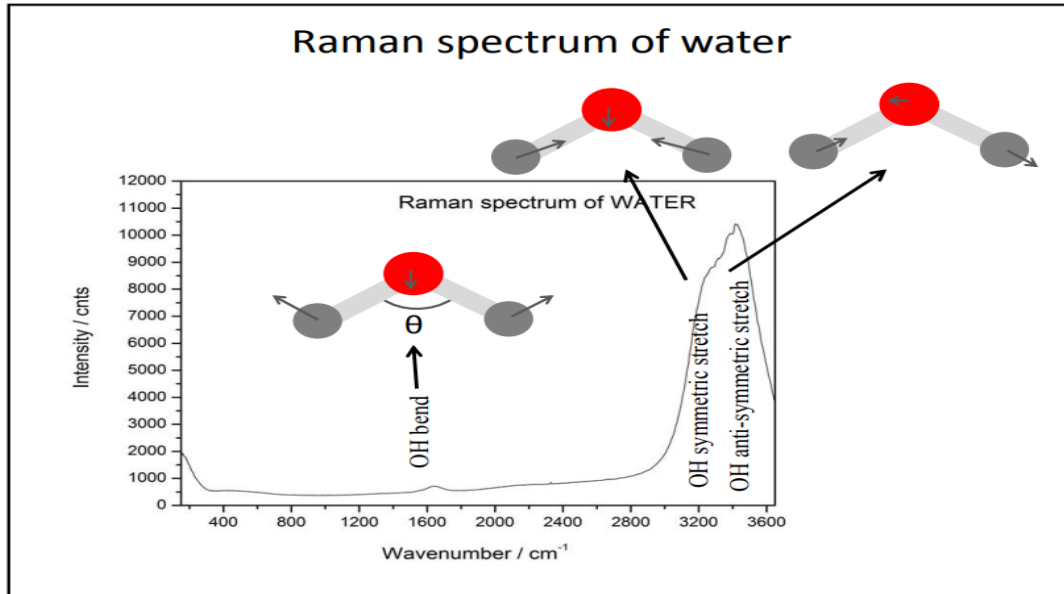


Figure. Raman spectra of water molecule indicating various vibrational modes and stretching.

Conclusions:

Analysis:

Experiment No 6

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 (T_g): Determine the T_g for amorphous materials. T_g 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.

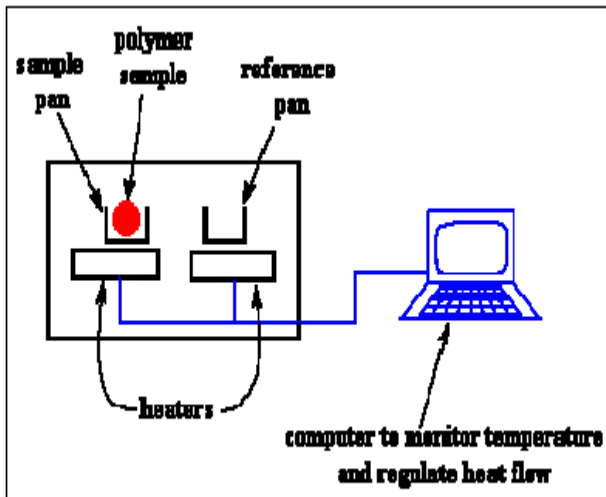


Figure-1: DSC apparatus

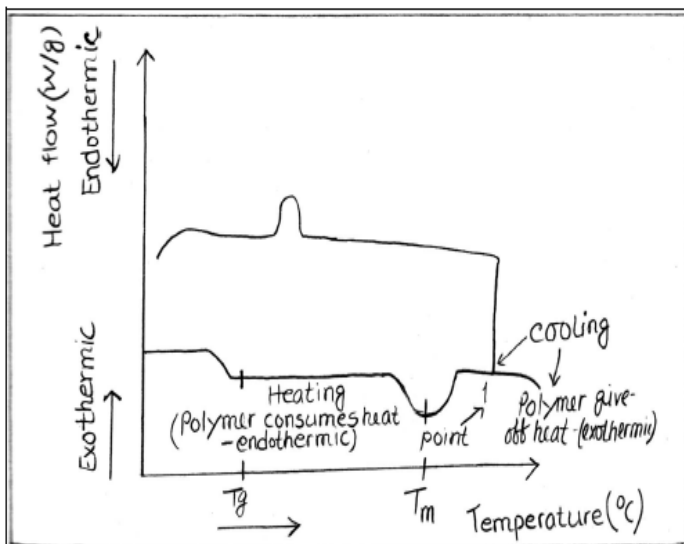
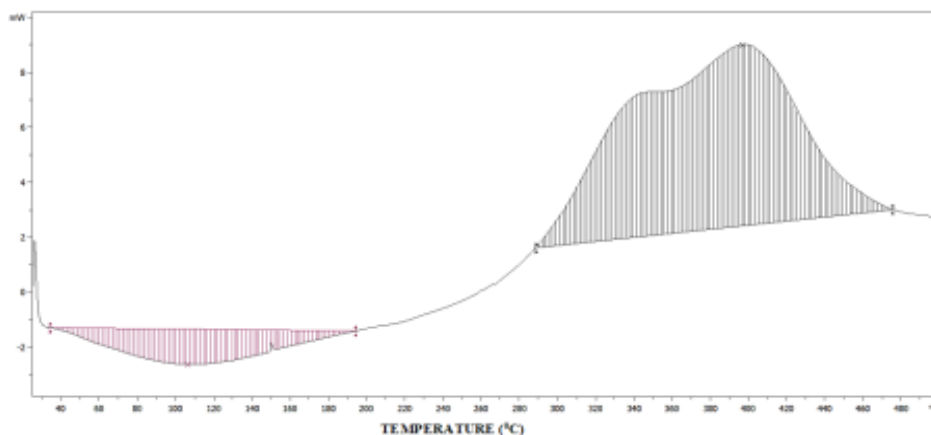


Figure-2: The working principle of DSC

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

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

Table:2 Material properties data

Analysis:

Conclusion: