Determination of dipole moment, linear polarizability, and energy gap of ZnO nanoclusters using semiempirical method

Experiment No:

Date:

1 Aim:

1. To determine the dipole moment, linear polarizability and energy gap of five ZnO nanoclusters of different point groups and different energies, using semiempirical PM7 method.

2. To analyse the variation of dipole moment, linear polarizability and energy gap with respect to molecular energy.

2 Requirements:

Avogadro software to draw molecules and to create the input geometries, MOPAC2016 package for geometry optimization and polarizability calculation, Gabedit package for HOMO, LUMO calculation.

3 Theory:

3.1 Semiempirical Formalism

Molecular properties vary with respect to the molecular energy and often same molecules of different point groups possess different molecular energy. In this experiment five different ZnO nanoclusters of different point groups are considered for the analysis. Since it would take much time to simulate the properties of moleculae on *ab initio* and DFT level theories semiempirical formalism is used for the analysis. In

semiempirical algorithms, experimental and accurate theoretical data are substituted to the current molecule and the optimization process is normalized to get good qulaity results in a short span of time. The molecules are pre-optimized using universal force field theory (UFF) in order to get a resonable structure.

3.2 PM6 Algorithm

In this experiment Parametrization Model Number 7 (PM7) is used for the calculations. It is a successor of PM3 model and based on *Neglect of Differential Diatomic Overlap* integral approximation and uses two Gaussian functions for the core repulsion function. This method supports all the elements in the periodic table and included hydrogen bond correction in its core function. So, highly correlated materials like transition metals can be studied with good accuracy.

3.3 Transition Dipole Moment (μ)

Transition dipole moment is a type of electric dipole moment denotes a transition from intial state to final state ($m \rightarrow n$). In mathematical terms it is a complex vector quantity and its direction gives the polarization of the transition, which determines how the system will interact with an electromagnetic wave of a given polarization and its square of the magnitude gives the strength of the interaction due to the distribution of charge within the system.

3.4 Linear Polarizability (α)

Polarizability is one of basic properties of materials and it gives the ability of a material to form instaneous dipoles. It is used as an estimation for the dynamical response of a bound system to external fields and can be used to interpret the electronic structure of molecular systems.

3.5 Energy Gap (eV)

In molecular chemistry, energy gap corresponds to the energy difference between highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital

(LUMO). Since a molecule may possesses different energy levels, HOMO and LUMO are often termed as frontier orbitals and their energy difference gets major concern. Energy gap can be used to predict the optical and electrical properties of materials and further can be used to predict the stregth and stability of a particular transition metal complex.

4 Procedure:

1. Draw the molecules as given in **Figure 1** using avogadro package.
2. Pre-optimize them with UFF algorithm using the same package.
3. Create the MOPAC input file and edit it with necessary parameters.
4. Submit the job to MOPAC package and edit the generated .arc output file for polarizability calculations.
5. Use .aux file in Gabedit and calculate the HOMO, LUMO and E_g values.
6. Note down the values and plot the variation of dipole moment, linear polarizability and energy gap with respect to molecular energy (*See sample graph. Three similar graphs to be plotted.*)

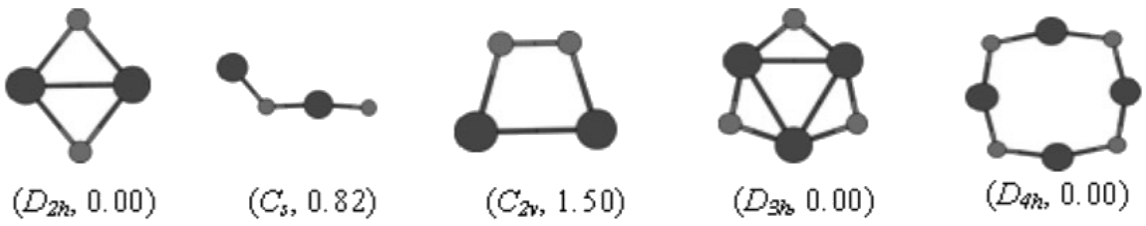


FIGURE 1

ZnO nanoclusters of different point groups and energy

5 Input Comments:

1. **Molecular Charge:** `CHARGES`
2. **Geometry Optimization:** `LET CHARGE=N PM7 AUX GNORM=10` (substitute N with the above value)

3. **Polarizability Calculation:** `LET CHARGE=-N PM7 POLAR`

6 Observations:

Tabulation:

Point group	Energy $((eV))$	μ $((Debye))$	α $(a.u.)$	E_g (eV)
D_{2h}				
C_s				
C_{2v}				
D_{4h}				

Sample Graph:

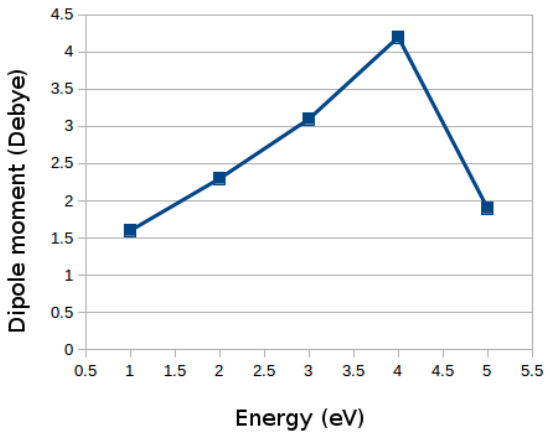


FIGURE 2

Variation of dipole moment with respect to molecular energy

7 Results:

The dipole moment, linear polarizability and energy gap of ZnO nanoclusters of different point groups and different energies are calculated and their variation with respect to energy is plotted.

Determination of Planck's constant by Photoelectric Effect

Experiment No:

Date:

1 Aim

To determine the Planck's constant and work function of a metal by demonstrating photo electric effect.

2 Apparatus

The present experimental set-up comprises of a tungsten light source with five different colour filters, a Caesium-type vacuum phototube, a built-in power supply and a current multiplier. The base of the phototube is built into a dark room and infront of it a receptor (pipe) is installed to mount filters.

3 Procedure

- Plug in and switch on the apparatus using the red button at the bottom right corner of the set up.
- Before the lamp is switched on, put the toggle switch in current mode and check that the dark current is zero.
- Turn on the lamp source. Set the light intensity near to maximum. Note that the intensity should be such that the value of current should not exceed the display range. In case it happens, reduce the intensity.
- Insert one of the five specified filters into the drawtube of the receptor.

- Now, set the voltage direction switch to '-ve' polarity. Adjust the voltage knob at minimum and current multiplier at X 0.001. Vary the voltage and record the current till the value of current becomes 0. Use the display mode switch to record the values of voltage each time.
- Repeat the above two steps for all the filters provided.
- Fill up the observation tables and draw necessary plots. Determine the values of Planck's constant and work function of the metal used in the phototube.

4 Formulas and constants

1. Standard Planck's constant = 6.626 x 10^{-34}Js

2. Frequency of light ν =c/λ, where c is the velocity of light in vacuum (3 x 10^{8}m/s)and λ is the wavelength of light.

3. Charge of the electron (e) =1.602 x 10^{-19}C

4. Linear regression formula: y = mx + c

5. Slope=b/a= Δv / ΔV_0

6. The linear fit of the experimental data in graph resembles V_0= (h/e)ν - Φ.

(a) So, h/e = Slope, and h = Slope xe and

(b) The intercept of the graph equals to work function (Φ) of the metal

7. 'h' Error % = (6.626-h(calc))/6.626) x 100 %

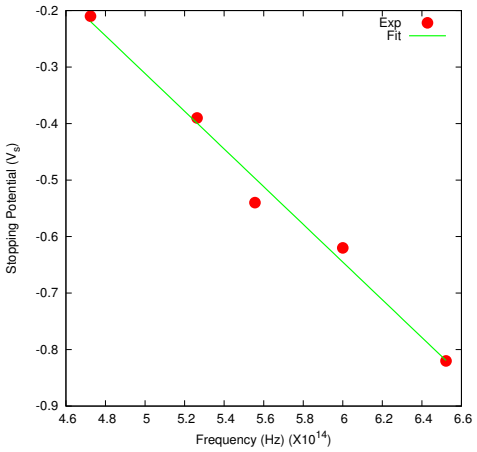
Table 1: Specification of filters

Colour	**Blue**	**Green**	**Yellow**	**Orange**	**Red**
Wavelength (nm)	460	500	540	570	635
Frequency (Hz)					

Table 2: Stopping Potential

Colour	**Blue**	**Green**	**Yellow**	**Orange**	**Red**
Frequency (Hz)					
Stopping potential (V_0)					

Graph Results



1. Calculated Planck's constant value h=

2. 'h' Error % =

3. Calculated working function of the metal=

Determination of the wavelength of laser and refractive index of the given materials – using He-Ne laser

Experiment No:

Date:

1 Aim

- To determine the wavelength of the Helium-Neon laser using diffraction pattern.
- To determine the refractive index of given material using Helium-Neon laser

2 Apparatus

He-Ne laser, Screen, a meter scale, millimeter graph paper, a plate of transparent material, graduated turn table, a photo detector with inducting instrument

Formula

The wavelength of the laser is, $\lambda = \frac{d}{2Z}\left[\frac{Y_m - Y}{M}\right]$

Where

d=diffraction grating width

Z_o=distance between the grating element and the diffraction pattern are obtained on the screen ($\times 10^{-2}$)

M=order of the fringes

λ=wavelength of He-Ne laser to be determined

Y_o- distance between the first diffraction pattern and central diffraction pattern

Y_m-distance between the central pattern and n^{th} order pattern

3 Procedure

(i) **Determination of the wavelength of the laser :**

This experiment was first demonstrated by shadow using a ruler. Initially the scale must be engraved. The Vernier calliper is placed on the horizontal table and the laser is in alignment such that the unexpected beam is incident at the grating angle as shown in the figure 1. The diffraction pattern is observed at a distance of 3 to 4 meter from the scale. The beam can be aligned so that the diffraction pattern is at its best as shown in figure 1.

The pattern arises due to diffraction at the engraving on the scale and governed by the grating equation

d sin(-sinθ m) = mλ

Where m is the diffraction order and d is the grating constant. For m=0, the beam is specularly reflected. The grating equation is expressed in terms of angle α and β in the form

d (cosα-cosβ)=mλ

Where, π/2-i and β_m=π/2-0

The distance between the region of distance of the rule and the screen is Zo. The diffraction spots are taken to lie along Y-axis and the position of M^{th} spot is represented by Y_m.

For zeroth order $\alpha = \beta_o$. Therefore

cosβ_m= [1-(Y_m/Z_o)^2]$^{1/2}$ = 1-1/2 Y_m^2/Z_o^2

Similarly,

cos α = cos β_o = 1-1/2, Y_o^2/Z_o^2

Therefore

cos α-cos β_m= $\left(\frac{Y_m^2 - Y_o^2}{2Z^2}\right)$

The wavelength of light is given by

λ=d/2Z^2. $\frac{Y_m^2 - Y_o^2}{M}$

Here the distance are measured from the horizontal plane by making purpose the position of the direct beam on the screen and the distance of various diffraction spots are measured from this position and later reduced to the position midway between the direct beam and secularly reflected beam positions. This distance can be measured on millimetre graph paper pasted on the screen. The distance Zo can be measured with a scale.

Table 1: Wavelength of laser

S.No	Order of fringes (m)	Y_m ($\times 10^{-2}$m)	Y^2_m ($\times 10^{-4}$ m)	Y^2_m- Y^2_o ($\times 10^{-4}$ m)	$\frac{Y_m^2 - Y_o^2}{M}$ ($\times 10^{-4}$ m)

(i) **To determine the refractive index of the given material using Helium – Neon laser :**

The plate of transparent material is mounted on the turn-table such that the plane of incidence is horizontal as in figure 2. In front a spectrometer with the eye-piece replaced by a photo-detector will be appropriate. The output of laser should be bare its vector is confined to horizontal plane. As goniometer is rotated the intensity of reflected beam keeps on decreasing first reached almost zero value and then increases again. The angle at which the irradiance reaches almost zero is the Brewster angle.

The refractive index of the plate will be obtained from

μ=tan θ_β

Where

θ_β– Brewster's angle (degree)

Table 2: Refractive index of the material.

S.No	Transparent material	Main scale meter ($\times 10^{-2}$)	Vernier scale (division)	μ=tan θ_β

Results

- The wavelength of the He-Ne laser is found out by diffraction method

  λ=---------- nm

  Z_o =----------m

- The refractive index of the different transparent materials is determined by measuring the Brewster's angle

  The refractive index of

I) Glass = ----------

II) Mica = ----------

Determination of dispersion relation for mono-atomic and diatomic lattices

Experiment No:

Date:

1 Aim

- To study the dispersion relation for mono atomic and diatomic lattices.
- To determine the cut-off frequency for the corresponding lattices.

2 Apparatus

Lattice dynamics kit and CRO operating in XY mode

3 Description of the kit

1. Switch positions: Low (LO) in the frequency range 0.8 – 8.9 kHz and High (HI) in the frequency range 8.7 – 91 kHz (There might be slight variation depending on the individual kits)
2. Toggle Switches for mono-atomic and di-atomic modes
3. An amplitude controller and two variable resistor (R1 and R2)

4 Procedure

1. Connect the horizontal (H) and vertical (V) lines of the kit to the X and Y of the CRO (should be in XY mode)
2. Adjust the amplitude, R1 and R2 knobs to the maximum value (maximum turn on the clock-wise direction) and toggle the switch LO

3. Choose 'Mono-atomic' lattice switch, adjust TTP to minimum and then switch on the kit and CRO
4. Lissajous figures of line/circle/ellipsoid can be achieved
5. Vary R2 slightly to approach nearly circle pattern in CRO
6. Vary the TTP values and determine the frequencies corresponding to phase diifer-ences
7. After the maximum LO frequency, adjust TTp to minimum and continue the ex-periment by toggle HI switch
8. Repeat the same for di-atomic lattices

Table 1: Mono-atomic and Di-atomic Lattices

S. No	CRO Pattern	N(θ)	($\theta = \frac{N(\theta)}{10}$)	Obs Frequency (kHz)	Calc. Frequency (kHz)

5 Calculations

In the given kit, L = 1mH, C = 0.047 μF, C_1 = 0.147 μF

Mono-atomic Lattices: The dispersion relation for mono-atomic lattice can be given as,

$$\omega^2 = \frac{2}{\mathrm{LC}}(1 - \cos\theta)$$

6 Di-atomic Lattices

The dispersion relation for diatomic lattice can be written as,

$$\omega^2 = \frac{1}{L}[\frac{1}{C} + \frac{1}{C_1}] \pm \frac{1}{L}[(\frac{1}{C} + \frac{1}{C_1})^2 - \frac{4\sin^2\theta}{CC_1}]^{\frac{1}{2}}$$

Substitute and the L and C, C_1, values in the corresponding equations and calculate the values for mono-atomic and di-atomic lattices.

$$\frac{1}{L}[\frac{1}{C}+\frac{1}{C_1}] \pm \frac{1}{L}[(\frac{1}{C}+\frac{1}{C_1})^2 - \frac{4\sin^2\theta}{CC_1}]$$

7 Result

The dispersion curves for the mono-atomic and di-atomic lattices are drawn.

Determination of Hall Coefficient

Experiment No:

Date:

1 Aim

To measure the Hall voltage of the given semiconductor sample and to estimate the Hall coefficient, carrier charge density and carrier mobility.

2 Apparatus Required

- Hall probe (Ge Crystal)
- Hall effect Set-up
- Electromagnet
- Constant current power supply
- Digital Gauss meter

3 Theory

The Hall effect is basic to solid-state physics and an important diagnostic tool for the characterization of materials - particularly semiconductors. It provides a direct determination of both the sign of the charge carriers, e.g. electron or holes, and their density in a given sample. The objectives of this experiment are to demonstrate the effects of a magnetic field (B) on a current carrying conductor (semiconductor/metal). If a current carrying conductor is placed in a magnetic field oriented perpendicular to the direction of the current, a voltage is developed across the conductor in a direction perpendicular to both the magnetic field and the direction of the current. This effect is known as the Hall effect.

4 Procedure

- Connect the red coloured contacts of the Hall probe to the terminals marked 'Voltage' and green coloured contacts to terminals marked 'Current'.
- Switch 'ON' the Hall effect set-up and check that the adjustment current is in zero.
- Switch over the display to voltage side. There may be some voltage reading even outside the magnetic field. This is due to imperfect alignment of the four contacts of the Hall probe and is generally known as the 'Zero field Potential'. In case its value is comparable to the Hall Voltage it should be adjusted to a minimum possible (for Hall Probe (Ge) only). In all cases, this error should be subtracted from the Hall Voltage reading.
- Now place the probe in the magnetic field and switch on the electromagnet power supply and adjust the current to the desired value. Rotate the Hall probe till it become perpendicular to magnetic field. Hall voltage will be maximum in this adjustment.
- Measure Hall voltage for both the directions of the current and magnetic field (i.e. four observations for a particular value of current and magnetic field).
- Measure the Hall voltage as a function of current keeping the magnetic field constant. Plot a graph.
- Measure the Hall voltage as a function of magnetic field keeping a suitable value of current as constant. Plot a graph.

5 Formula Used

With the help of this experiment we can calculate the following terms of the given semiconductor. The value of Hall coefficient can be calculated using the relation

$$R = \frac{V_H.d}{I.H} \tag{1}$$

where, V_H is the Hall voltage (volt), d is the sample thickness (metre), I is the current (ampere) and H is the magnetic field (Gauss).

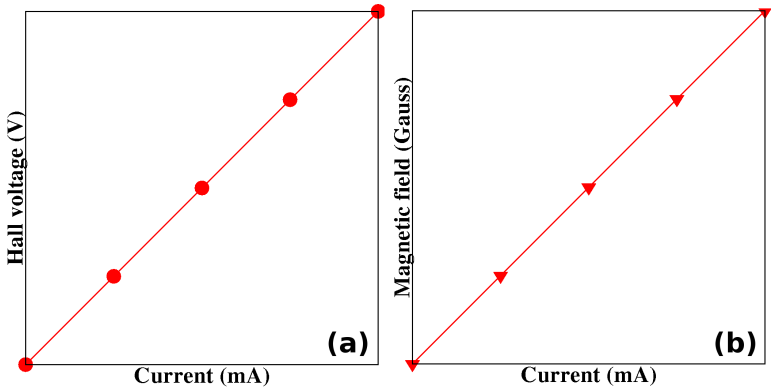


FIGURE 1

Graph: (a) Current in Hall voltage and (b) Current in the magnetic field

Calculate charge carrier density from the relation

$$R = \frac{1}{n.q}; n = \frac{1}{R.q} \tag{2}$$

where q is the electron charge (q = 1.6 $\times$ 10^{-19} Coulomb)

Calculate carrier mobility, using the formula

$$\mu_n(\text{or } \mu_p) = R\sigma$$

Where, μ_n is the mobility of charge carrier (electrons), μ_p is the mobility of charge carrier (holes) and σ is the conductivity of Ge semiconductor sample and it is about 0.1 coulomb volt^{-1} sec^{-1} cm^{-1} at room temperature.

6 Observations – Table 1

Current Vs. Hall Voltage

d=1.5 mm, Constant magnetic field at 0.5 A of coil current is Hz =----------

-Gauss

Current (mA)	**Hall Voltage (mV)**	**Mean H ($\times 10^{-3}$ volts)**
	Current	**Magnetic field**
	H1	**H2**
0.5		
1.0		
1.5		
2.0		

Observations – Table 2

1.0			
1.5			
2.0			

7 Result

Hall parameters for as given semiconductor sample is measured and its

- Hall coefficient (R) is
- Carrier density (n) is
- Carrier mobility (μ) is

Measurement of Thickness of Polymeric Thin Films using Air Wedge Technique

Experiment No:

Date:

1 Aim

- To deposit thin films of polyvinyl alcohol (PVA) by dip coating method.
- To estimate the thickness of the deposited thin films using air wedge technique.

2 Apparatus Required

For thin film deposition

- Glass beakers
- polyvinyl alcohol (PVA)
- double distilled water
- microscopic glass slides

For thickness measurement

- Travelling microscope
- Optically plane glass plates
- Sodium vapour lamp
- Sample mounter
- Scale

3 Theory

The monochromatic light incident normally on the air wedge will be divided into two parts by the wave amplitude-division method. One part is reflected at the upper glass surface OP and the other part passes to the lower glass surface OP' where it undergoes a further reflection upon striking that surface. Since this reflection is from an optically denser (higher refractive index) medium (glass) to a lower optical density medium (air), the reflected light waves will be phase shifted by 180° (this is equivalent to an additional optical path difference of $\lambda/2$ between the two upper and lower reflected beams). Due to the overlapping (interference) of the two reflected light beams, bright and dark straight fringes are observed in the traveling microscopes' field of view.

The fringe at point A is formed by interfering light ray, reflected off the upper glass surface OP, with the one reflected from the lower glass plate which suffered a 180° – phase shift in addition to traversing double the distance AA' when it propagates back and forth. If the total phase shift equals odd multiples of the half the light wavelength, then a dark interference fringe will be formed. On the other hand, the interference fringe will be bright whenever the total phase shift equals even multiples of the light wavelengths used. The next interference fringe formed at point B is due to the increase of air-wedge width by an amount of half the light wavelength (the distance BC in the figure 1).

If α is the wedge angle in degrees, then from the triangle ABC, it is apparently that

$$\frac{BC}{AC} = \frac{BC}{A'C'} = \frac{\lambda/2}{\beta} = \frac{\lambda}{2\beta} \tag{1}$$

where β represents the distance between two successive (dark or bright) fringes. In the triangle OPP'

$$tan(\alpha) = \frac{PP'}{OP'} = \frac{t}{l} \tag{2}$$

where t = PP' represents the width of the thin films and OP = l is the separation between the inner edge of the thin films and line of contact of the two glass plates.

$$\frac{t}{\lambda} = \frac{l}{2\beta} \tag{3}$$

$$t = \frac{\lambda l}{2\beta} \tag{4}$$

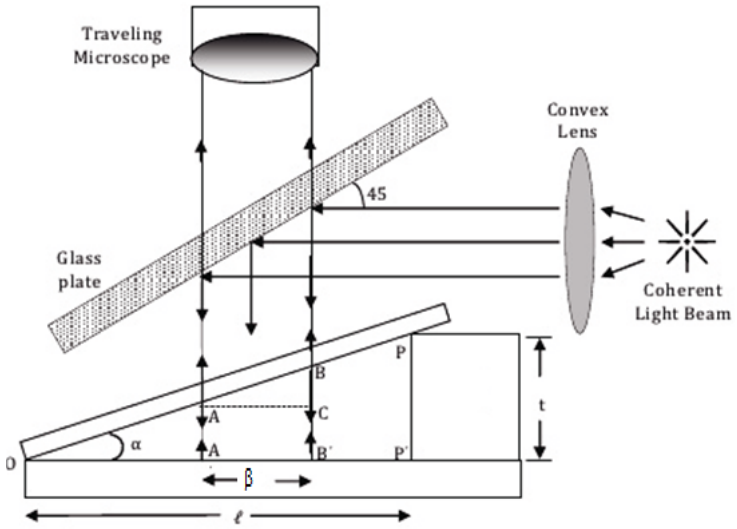


FIGURE 1

The air wedge formed between two glass plates, illumination of the wedge by monochromatic light and collection of reflected rays by the objective of the telescope

4 Procedure

Step 1: A convex lens is used to get a parallel light beam emerging from the monochromatic light source (typically the monochromatic sodium light $\lambda_{\text{average}} = 589.3$ nm). This parallel light beam is to be making 45° angle of incidence with a horizontally oriented 45° angle, half-silvered glass plate. The light rays reflected off this plate will perpendicularly incident on the lower thick glass plate of the air-wedge.

Step 2: The traveling microscope is then focused until getting the lower thick glass plate of the air-wedge at the focal plane of the traveling microscope's eyepiece. Doing so, a distinct interference pattern should become viewable.

Step 3: The distance between a suitable numbers of dark (or bright) fringes is measured using the traveling microscope Vernier and the width of the dark of bright fringe is deduced by dividing the measured distance on the number of fringes. The measurement is then recorded in a suitable table.

Step 4: Step 3 is repeated for a number of times and the average of such measurements is evaluated.

Step 5: Using a micrometer Vernier, the distance l is measured.

Step 6: Finally, the thickness of the thin films t is estimated by applying the formula 1.

Least Count for Travelling Microscope

Least Count (LC) = Value of 1 Main Scale Division (MSD)/ Number of divisions in the Vernier

20 MSD = 1 cm

Value of 1 MSD = 1/20 cm = 0.05 cm

Number of divisions in the vernier = 50

LC = 0.05/50= 0.001 cm

Formula Used

Thickness of the dip coated polymeric thin films

$$t = \frac{\lambda l}{2\beta} \tag{5}$$

t = thickness of the coated thin films

λ = wavelength of the sodium vapour light

l = is the separation between the inner edge of the thin films and line of contact of the two glass plates

β = fringe width

To determine the fringe width (β)

LC = 0.001 cm *TR = MSR + (VSC $\times$ LC)

Order of fringes	**Microscope Reading MSR (10^{-2} m)**	**Fringe width (β) (10^{-2} m) VSC (div)**

Mean = ---------- 10^{-2} m

5 Results

- The PVA thin films were deposited by dip coating method
- The thickness of the films is calculated as --------- μm

Synthesis of CdO Nanoparticles by Microwave Assisted Wet Chemical Method

Experiment No:

Date:

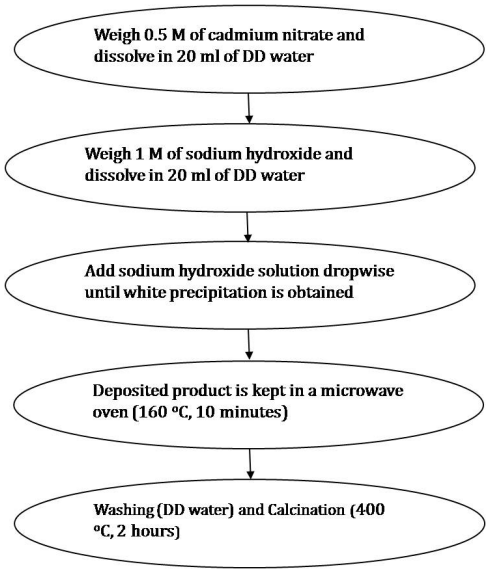
Aim

To synthesize CdO nanoparticles by microwave assisted wet chemical method and study its molecular structure by FTIR analysis.

1 Required materials

Cadmium nitrate ($Cd(NO_3)_2.4H_2O$), sodium hydroxide (NaOH), Beakers, Stirrer, Acetone, Double distilled water (DD), Microwave oven.

Flowchart for synthesis of cadmium oxide



2 Procedure

- Beakers are cleaned with double distilled water and rinsed with acetone to dry the water molecules.
- 0.5 M of Cadmium nitrate [Cd $(NO_3)_2.4H_2O$] and 1 M of sodium hydroxide (NaOH) is taken as a precursor.
- Cd $(NO_3)_2.4H_2O$ is dissolved in 20 ml of double distilled water. The solution is kept for stirring using magnetic stirrer for 10 minutes at room temperature.
- NaOH is separately dissolved in 20 ml of DD and stirred for 10 minutes at room temperature.
- The prepared NaOH solution is slowly added to the cadmium solution on constant stirring. Cadmium hydroxide forms themselves as white precipitation and gets deposited at the bottom of the beaker.
- The deposited product is washed with DD to remove the impurities and kept in a microwave oven for irradiation at 160 °C for about 10 minutes.
- The product is grinded well and calcinated at 400 °C, 2 hours in a furnace.
- FTIR spectrum of synthesized product is analysed and various vibrational peaks are assigned to confirm the molecular structure.

Table 1: Vibrational Mode Assignments with FTIR

Vibrational Peaks	Assignments

3 Result

Cadmium oxide nanoparticles were prepared by microwave assisted wet chemical method and their molecular structure was analysed by FTIR analysis.