Chapter 2

EXPERIMENTAL TECHNIQUES
2.1 Synthetic procedure

Chemical colloidal method for the nanoparticle synthesis has been widely adopted as it needs only a low energy input to build nanocrystals from the molecular level and does not require any special equipment. Of the various methods available as discussed in Section 1.4 of the previous chapter, the high temperature synthesis method has been widely applied for the synthesis of a variety of metal chalcogenide nanocrystals primarily because of the high crystallinity and narrow size distribution of the nanoparticles.\(^1\)\(^2\) The formation of the nanoparticles is achieved by rapid injection of one of the precursor (e.g. chalcogenide precursor) into a hot coordinating solvent that contains the other precursor reagent (e.g. metal precursor) along with the presence of surfactants that act as the capping agent of the nanoparticles preventing them from agglomeration. In our case, the metal salts (oxide or other organic salts like acetate or stearate) served as the metal precursor while the chalcogenide source was mostly in the elemental form (like elemental Sulfur or Selenium) dissolved either in a non coordinating solvent (like Octadecene) or coordinating solvent (like tributyl phosphine). The surfactants used included long chain amines (like octadecyl amine or hexadecyl amine) or long chain fatty acids (like decanoic acid, stearic acid). The metal precursors dissolved in a non coordinating solvent (mostly octadecene) was purged with argon at room temperature for sufficient time to ensure the absence of dissolved moisture and oxygen and the temperature was then increased to the desired level under nitrogenous atmosphere. At desired temperature, chalcogenide precursor was swiftly injected to the reaction mixture and the reaction annealed for various time periods to attain the desired size and shape of the resultant nanoparticles. After a certain time period, the reaction was stopped at a desired state by removing the heat and cooling to room temperature. The usual reaction set up is described in the Figure 1).
Another alternative procedure involves the decomposition of single source precursor in which both the metal and nonmetal component of the compound semiconductors are incorporated within a single molecule. In our case, the single source precursor used includes ethyl or hexadecyl xanthate salts of metal ions like zinc and lead. The single source precursor is usually injected into a hot boiling solvent cum surfactant, where the thermal decomposition of the precursor generates the desired nanoparticles. In a typical experimental set up, the surfactant was heated to a desired temperature using an oil bath under nitrogen atmosphere upon which the desired amount of the single source precursor was injected. The injection temperature, annealing temperature and the annealing time was varied to achieve nanoparticles with varying sizes and morphology. The shape and size tunability can also be obtained by varying the ratio of the surfactant and the
precursor. Utilizing this technique, metal chalcogenide nanoparticles (like PbS and ZnS) have been synthesized of various shape and dimensionality. The molecular mechanism of the decomposition reaction is supposedly related to the Chugaev reaction as described in the Figure 2.5,6

![Scheme depicting the Chugaev Reaction (top) and Chugaev like Mechanism for the decomposition of Cd-Xanthate (bottom)](image)

**Figure 2.** Scheme depicting the Chugaev Reaction (top) and Chugaev like Mechanism for the decomposition of Cd-Xanthate (bottom)

The solvent used by us includes coordinating solvents like long chain alkyl amines and phosphines. These solvent provides an organic (surfactant) template that co-crystallizes with the inorganic mineral cores, resulting in a uniform monolayer coating to the cores. Apart from this, the surfactants used also causes significant lowering of the decomposition temperature of the metal xanthate precursors. This substantial reduction in the decomposition temperature can be well understood on the basis of the molecular mechanism of the decomposition reaction. The solvent is found to coordinate with the metal center of the compound thus weakening the metal sulfur bond and activating the other part as a convenient
leaving group. Also the solvent which is itself a Lewis base due to the presence of lone pair of electrons can serve as a protonated intermediate and facilitate the proton transfer required in the reaction.

2.2 Structural Characterization Technique

The nanoparticles thus synthesized were subjected to various characterization techniques. While different microscopic techniques were used to ascertain the sample morphology, the crystal structure and sample ordering is determined using various diffraction techniques. Brief descriptions of these techniques are discussed in the following sections.

2.2.1 Microscopic technique

The sample morphology was determined using electron microscope of different varieties. An electron microscope is found to achieve better resolution and magnification compared to the ordinary non focal microscope as it uses beams of electrons to illuminate and obtain a magnified image of the sample. These electron beams are controlled and focused using electrostatic and electromagnetic lenses analogous to the glass lenses for an optical microscope. The different electron microscopes that were used for morphology determination of the synthesized nanoparticles along with a brief description of their working principal are listed below:

2.2.1.1 Scanning Electron Microscopy (SEM)

Scanning electron microscope (SEM) is generally used to ascertain the surface morphology of the samples. In a typical SEM, an electron beam is thermoionically emitted from an electron gun fitted with a tungsten filament.
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cathode with an energy range of ~0.2 KeV to 40 KeV which is focused on the sample surface within a size of 0.5 to 5 nm by means of various focusing lenses. Of the various phenomena possible due to the interaction of the incident electron beam and the electrons in the vicinity of the surface of the sample, the ones which are mention worthy includes the emission of the secondary electrons (SE) due to the inelastic scattering, back scattered electrons (BSE) due to the elastic scattering and electromagnetic radiation generated by the electronic transition from an excited atom. Among them, the imaging of the sample surface by detecting the SE is the mostly used technique for determination of the topography of the surface. The image is collected as a 2D intensity distribution which is found to have a one to one correspondence to the density of SE. The latter one is found to be nearly independent of the atomic number of an atom and depends only on the atomic density and the interaction area between the beam and the sample surface. The schematic diagram of the SEM instrument is described in Figure 3a.

For our case, the samples were prepared by drop casting a dilute solution of sample dispersed in a non polar volatile solvent usually chloroform over a glass cover slip which after drying was mounted on to a metal stub using a carbon tape and sputter coated with platinum to minimize charging. The images were then recorded by placing the sample under a JEOL JSM-6700F electron microscope operated at an accelerating voltage of 5 kV.
Transmission Electron Microscopy (TEM)

Transmission electron microscopy (TEM) is capable of imaging at a significant higher resolution as compared to SEM. The high resolution transmission electron microscopy (HRTEM) even allows the production of images below 0.5Å or 50 picometers and the fact that it has an ability to explore at that atomic level makes it a useful tool for imaging the nanoparticles. In TEM, the electron beam, accelerated by an anode typically in the range 40 to 400 KeV with respect to the cathode, is focused by electrostatic and electromagnetic lenses and transmitted through the specimen that is in part transparent to the electrons and in part scatters them out of the beam. A typical TEM is composed of several components which includes a vacuum system in which the electron travel, an electron emission source for generation of the electron stream, a series of electromagnetic lenses and electrostatic plates. The latter two allows guiding and manipulating the electron beam. Imaging devices are subsequently used to create...
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an image from the electrons that exit the system. The schematic diagram of a typical TEM instrument is described in Figure 3b.

In our case, the sample was prepared by drop casting from a solution of the sample dispersed in a non polar solvent usually chloroform over a lacy carbon coated copper grid followed by drying. The grid was then observed using a JEOL JEM 2012 electron microscope operated at an accelerating voltage of 200kV.

2.2.1.3 Atomic Force microscopy (AFM)

Apart from the electron microscopes, scanning probe microscopy is also a quite popular technique for imaging, morphology determination and current voltage measurements (contact mode C-AFM). Atomic force microscopy (AFM) is a type of scanning probe microscopy with quite high resolution in the order of fractions of a nanometer. Typically, AFM consists of a cantilever with a sharp tip whose radius is in the order of nanometers. In proximity of a sample surface, forces between the tip and the sample lead to a deflection of the cantilever according to the Hooke's law and this deflection is measured using a laser spot reflected from the top surface of the cantilever into an array of photodiodes. The AFM can be operated in various modes, depending on the application and the primary imaging modes include static (also called contact) modes and dynamic (non contact or tapping) modes. In static mode, the cantilever is dragged across the surface of the sample and the contours of the surface are directly measured using the deflection of the cantilever. In the dynamic mode, the cantilever is externally oscillated at or close to its fundamental resonance frequency or in a harmonic. The oscillation amplitude, phase and resonance frequency are modified by tip sample interaction forces. These changes in oscillation with respect to the external reference oscillation provide information about the sample's characteristics. The major advantage of AFM over other microscopic technique is the fact that AFM provides a three dimensional surface profile instead of a two dimensional
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projection of the sample. Thus AFM provides important information regarding the height profile of the sample. The working principle of a typical AFM is described in Figure 4.

Figure 4. Schematic diagram of AFM depicting the main components of the instrument

In our case, the AFM images were recorded using ultrahigh vacuum (~ $10^{-11}$ mbar) with variable temperature SPM instrument (VT-STM-AFM, Omicron Nanotechnology, Germany). The measurements were done in contact mode atomic force microscope (AFM) using the force set-point of 0.1 nN. The sample was prepared by drop casting from chloroform suspension on top of a silicon substrate prior to the AFM measurements.

2.2.2 X-Ray diffraction technique (XRD)

X-ray diffraction is a standard characterization technique which reveals information about the crystal structure, chemical composition and physical properties of the sample and is based on the analysis of the scattered intensity of an
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X-ray beam hitting the sample as a function of the incident angle, an example of elastic scattering. Depending on the range, XRD technique can be broadly classified into two categories: small angle X-ray scattering (SAXS) and wide angle X-ray scattering (WAXS).

2.2.2.1 Small angle X-Ray scattering technique (SAXS):

Small angle X-ray scattering (SAXS) is recorded at very low angle of incident typically in the range 0.1-10°. This angular range is capable of extracting structural information and the repeat distances in partially ordered systems. In a typical SAXS instrument, beam of X-rays is brought to a sample from which some of the X-rays scatter from the sample. The scattered X-rays generate a scattering pattern which is then detected using a 2-dimensional flat x-ray detector situated behind the sample perpendicular to the direction of the primary beam that initially hit the sample. Thus the major problem that must be overcome in SAXS instrumentation is the separation of the weak scattered intensity from the strong main beam. Another experimental challenge in SAXS is the poor signal-to-noise ratio due to low scattering cross section which can be improved up on using an exceedingly bright source such as synchrotron source. A synchrotron light source is a combination of different electron accelerator types, including a storage ring in which the desired electromagnetic radiation is generated. This radiation is then used in experimental stations located on different beamlines.

SAXS patterns are typically represented as scattered intensity as a function of the magnitude of the scattering vector \( q = \frac{4\pi \sin \theta}{\lambda} \) where \( \theta \) is the angle between the incident X-ray beam and the detector measuring the scattered intensity and \( \lambda \) is the wavelength of the X-ray. Since according to Bragg's law, \( 2d \sin \theta = n\lambda \), where \( d \) is the distance between the two diffracting planes, the scattering vector can be converted to the corresponding distance, \( d \) according to the equation \( d = \frac{2\pi}{q} \). The SAXS spectrum thus obtained can be used for the determination of the
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microscale or nanoscale structural properties with the evaluation of parameters like averaged particle sizes, shapes, distribution and surface to volume ratio. The method is accurate, non-destructive and usually requires a minimum of sample preparation.

In our case, in situ SAXS measurements were recorded using an image plate detector, Mar 180 (MarResearch, Hamburg, Germany), at the Austrian SAXS beamline at the Italian synchrotron center, ELETTRA, Trieste, operated at 2 GeV. The beamline was set to a camera length of 1.65 m and X-ray energy of 16 keV. Silver behenate \([\text{CH}_3(\text{CH}_2)_{20}\text{COOAg}]\), with a d-spacing of 58.38Å was used as a standard to calibrate the angular scale of the 2-D detector. SAXS of blank solvent was used as background. The reaction solution was circulated in a 2 mm quartz capillary using a flow through technique to avoid deposition of the particles on the walls of the capillary. The reaction mixture was kept at a constant temperature using an oil bath and a KHR sample stage (Anton Paar, Graz, Austria).

2.2.2.2 Wide angle X-Ray scattering technique (WAXS):

Compared to SAXS, in wide angle X-ray scattering (WAXS) the diffraction maxima occurs at larger angles and is used to determine not only the crystalline phase of the sample but also the particle size, anisotropic strain and the extent of ordering etc. Typically, the incident X-ray is a monochromatic beam of electromagnetic wave (normally Cu Kα) which falls at an angle \(\theta\) with the sample surface and the diffracted beam is collected at an angle \(2\theta\) with respect to the incident beam. A distinct peak in the collected intensity pattern is observed only when the constructive interference occurs between the scattered beams from the periodically arranged atoms of a crystal. The condition for the constructive interference can be derived by equating the path difference \((2d \sin \theta)\) between two consecutive scattered wave fronts with the integer \((n)\) multiple of the wave length \((\lambda)\) according to the equation \(2d \sin \theta = n\lambda\) commonly known as the Bragg Law.
The schematic diagrams for the interference of the diffracted x-rays are described in Figure 5 which also includes the schematic representation of the Bragg-Brentano focusing geometry using a flat sample.

For nanomaterials, the broadening of the XRD peaks is observed compared to the bulk counterpart and the extent of broadening can be used to have an estimate of the particle size according to the Scherrer equation $\tau = \frac{K\lambda}{\beta \cos \theta}$, where $K$ is the shape factor, $\lambda$ is the X-ray wavelength, $\beta$ is the line broadening at half maximum intensity (FWHM) in radians, and $\theta$ is the Bragg angle, $\tau$ is the mean size of the ordered crystalline domains, which is usually smaller or equal to the grain size. The dimensionless shape factor has a typical value of about 0.9 but varies with the actual shape of the crystallite.

In our case the sample is usually taken either in the powder form or prepared as a thin film by drop casting from a suspension in nonpolar volatile solvent like chloroform. The XRD was done by using a Bruker AXS:D8 advanced X-ray diffractometer. Cu K$\lambda$ ($\lambda = 1.54069\text{Å}$) is used as the monochromatic x-ray source after filtering $k\beta$, generated from a x-ray generator equipped with a Cu anode.
2.3 Elemental Characterization Technique

Both the qualitative and quantitative estimation of the constituent elements of an as synthesized nanoparticle can be done using different spectroscopic techniques of which the most widely used are Energy Dispersive Spectroscopy (EDS) and Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES). The working principle for both the techniques along with the specifications of the respective instruments used by us is described in the following sections.

2.3.1 Energy dispersive spectroscopy (EDS)

Energy dispersive spectroscopy is a widely used chemical characterization technique and is generally associated with an imaging tool (like TEM and SEM) in order to have one to one correspondence between the composition and the morphology. The high energy electron beam associated with the imaging sample is used to excite the electrons from the core of the elements creating a hole in the lower levels. The subsequent de-excitation which occurs via the electron transition from the valence/upper band to the core hole is a radiative process producing characteristic x-ray emissions. The emitted x-ray wavelength is the characteristic of the element which can be analyzed and the intensity can be used to quantify the element. The different transitions that are associated with the de-excitation of the electrons are described in Figure 6a. In our case, the detailed EDS mapping was performed using a JEOL2010 TEM.
2.3.2 Inductively coupled plasma-optical emission spectroscopy (ICP-OES)

Inductively coupled plasma optical emission spectroscopy is a technique for quantitative identification of the element. Here, the elements are excited using inductively coupled plasma, a very high temperature zone produced by means of Argon gas, and they emit electromagnetic radiation at wavelengths characteristic of a particular element. The intensity of this emission compared to the standard solutions gives an estimation of the concentration of the element within the sample. The ICP portion consists of an ICP torch which is essentially quartz tube surrounded by the output coil of the radio frequency generator. The stable high temperature plasma is generated by the ignition of the Argon gas through the RF generator. A peristaltic pump delivers an aqueous or organic sample into a nebulizer where it is changed into aerogel and introduced directly inside the plasma flame. The sample immediately breaks down into its constituent atoms which then lose electrons and recombine repeatedly in the plasma giving off radiation at the characteristic wavelengths of the elements involved. The schematic diagram of the basic instrumentation of a typical ICP-OES instrument is described in Figure 6b. The calibration to quantify each element involves three steps namely
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analyzing blank, standard and sample. The calibration curve can be drawn taking the corresponding intensities of the blank and the standard solutions taking the blank intensity as the origin. The concentrations of the elements are calculated by interpolation along the calibration lines.

In our case, we have analyzed the concentration and the constituent elements by ICP-OES (Optima 2100DV, Perkin-Elmer). The purified dried samples were taken in each case and treated with concentrated nitric acid overnight followed by filtration to obtain a clear solution. The samples were then diluted with water to match standard of ICP concentration required for the instrument.

2.4 Optical characterization technique

Upon excitation of the nanomaterials with an incident photon, different transitions takes place in the electronic, vibrational and the rotational states of these nanoclusters which is reflected in different spectroscopic techniques which can be quite effectively used for characterizing the as synthesized nanoparticles. Some of the widely used spectroscopic technique along with their brief description is being discussed in the following sections.

2.4.1 Absorption Spectroscopy

Absorption spectroscopy refers to the spectroscopic technique that measures the absorption of radiation as a function of frequency or wavelength due to its interaction with a sample. Ultraviolet-visible spectroscopy refers to the absorption spectroscopy in the ultraviolet visible spectral region. On going to nanometer regime, the continuous conduction and the valence band of the bulk semiconductor is discreetized and the absorption measures the electronic transitions from the ground state to the excited state upon irradiation with photon.
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The position of the peak in the absorption spectrum gives an estimation of the band gap of the material and also can be related to the size of the nanoparticles for some systems. A basic spectrophotometer consists of a light source (a deuterium arc lamp for the UV region and Tungsten filament for the visible region), a sample holder, and a diffraction grating in a monochromator to separate the different wavelengths of light, and a detector usually a photomultiplier tube. For our measurements, absorption spectra were recorded using a Shimadzu UV-1601 spectrometer of the sample solution dispersed in a non polar solvent like chloroform.

![Figure 7. Schematic representation of the different absorption and emission processes that occurs in a semiconductor nanomaterial up on excitation with an external source of energy hv](image)

2.4.2 Fluorescence Spectroscopy

Fluorescence spectroscopy involves excitation of the electrons in the sample and causing them to emit light typically in the visible region. Typically, an
emission spectrum can be obtained by measuring the different wavelengths of the fluorescent light emitted by the sample fixing the excitation light at a constant wavelength. In a typical experimental set up, the light from an excitation source passes through a monochromator, a proportion of the incident light is absorbed and the sample fluoresces. Some of this fluorescent light passes through a monochromator and reaches a detector which is usually placed at 90° C to the incident light to minimize the risk of transmitted or reflected incident light reaching the detector.

The nanoparticles due to the quantization effect are supposed to have discreet energy levels in both the conduction and the valence band. After excitation, the recombination may directly take place between the electron in the lowest energy level of the conduction band and the hole in highest energy level of the valence band resulting in the excitonic emission. Excitonic emissions are characterized with narrow full width half maximum (FWHM) and lower wavelength emissions. Alternatively, if the surface of the nanomaterial is not well passivated, there are a lot of dangling bonds which results in low lying trap states in the system. The electron now has an alternative pathway of recombination through these resultant trap states and is commonly referred to as trap emission. Trap emissions are on the contrary characterized with broad peaks at longer wavelength regions. The different electronic transitions that occur in a nanoparticle upon excitation with a photon that results in the absorption and the emission spectra are described in Figure 7. We have recorded the emission spectra using Fluoromax-4 from Jobin Yvon.

Alternatively, one can measure the excitation spectrum where one fixes the emission wavelength and the excitation light is scanned through many different wavelengths. Thus the excitation spectrum represents the relative emission of the particle at each excitation wavelength. Theoretically, the excitation spectrum of the particle would be typically super imposable on its absorption spectrum. However, such correspondence requires the pure transition states and the absence
of other complicating factors such as nonlinear response resulting from a high optical density of the sample or the presence of other fluorescence materials in the sample.

Time resolved fluorescence spectroscopy is an extension of fluorescence spectroscopy where the fluorescence of a sample is monitored as a function of time after being excited with pulsed laser. Time correlated single photon counting (TCSPC) is used to analyze the relaxation of molecules from an excited state to a lower energy state. The generated intensity vs. time graph usually follows an exponential decay behavior associated with different rate constants which can be associated with the different relaxation processes occurring for different molecules at different environments. The fluorescence lifetime refers to the average time the molecule stays in its excited state before emitting a photon. Various radiative and non-radiative processes can depopulate the excited state and in such a case the average life time is defined as the amplitude corrected average of all the decay rates that can be defined for the system. In our case, the fluorescence lifetime measurements were carried out using time-correlated single-photon counting (TCSPC) from Horiba Jobin Yvon with nano-LED-340 (pulse duration of 1 ns) excitation source.

2.4.3 Resonance Energy Transfer:

Another important phenomenon that occurs in the excited state is energy transfer (RET) which is a mechanism describing the transfer of energy between two fluorophore entities. This process occurs whenever the emission spectrum of one of the fluorophore called the donor, overlaps with the absorption spectrum of another molecule called the acceptor. The donor chromophore, initially in its electronic excited state can transfer energy to an acceptor molecule through non radiative dipole-dipole coupling. A schematic diagram corresponding to the energy transfer process is described in Figure 8.
The rate of this energy transfer depends on many physical parameters that include the distance between the donor and the acceptor, the spectral overlap of the donor emission spectrum and the acceptor absorption spectrum and the relative orientation of the donor emission dipole moment and the acceptor absorption dipole moment. The extent of energy transfer is determined by the distance between the donor and acceptor and the extent of spectral overlap. The rate of energy transfer $\kappa_T(r)$ is given by,

$$\kappa_T(r) = \frac{1}{\tau_D} \left( \frac{R_0}{r} \right)^6$$

Where $r$ is the distance between the donor (D) and the acceptor (A), $\tau_D$ is the lifetime of the donor in the absence of energy transfer and $R_0$ is defined as the Förster distance of this pair of donor and acceptor, i.e. the distance at which the
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The energy transfer efficiency is 50%. The RET efficiency relates to the quantum yield and the fluorescence lifetime of the donor as follows:

\[ E = 1 - \frac{\tau_D}{\tau'_D} \]  \hspace{1cm} (ii)

Where \( \tau'_D \) and \( \tau_D \) are the donor fluorescence lifetimes in the presence and absence of the acceptor respectively or as,

\[ E = 1 - \frac{F'_D}{F_D} \]  \hspace{1cm} (iii)

Where \( F'_D \) and \( F_D \) are the donor fluorescence intensities with and without an acceptor respectively.

The efficiency of the energy transfer is inversely proportional to the sixth power of the distance between the donor and the acceptor as a result of which RET is extremely sensitive to small distances and can be effectively used to determine the distances between the two fluorophores popularly known as “spectroscopic ruler”.

2.4.4 Fourier transformation infrared spectroscopy (FTIR)

Fourier transform infrared spectroscopy has been extensively developed over the past decade and refers broadly to the technique used to obtain an infrared spectrum which is the part of the electromagnetic spectrum between the visible and microwave regions though of greatest practical use is the limited portion between 4000 and 400 cm\(^{-1}\). These infra red radiations of frequencies are absorbed by the organic molecules and are utilized for molecular vibrations coupled with a number of rotational energy changes. The frequency or wavelength of absorption depends on the relative masses of the atoms, the force constants of the bonds and the geometry of the atoms. There are two basically types of molecular vibrations: stretching and bending. Stretching vibration is a rhythmical movement along the bond axis while the bending vibrations may consist of a change in bond angle. Only those vibrations that result in a change in the dipole
moment of the molecule are observed in the IR. The characteristic group absorptions for different bonds are available in the literature and thus comparing the obtained spectra with the literature values one obtains the possible structure of the compound. Many of the group absorption may vary over a wide range because the bands arise from complex interacting vibrations within the molecule. Shifts in absorption positions and changes in the band contours accompanying changes in the molecular environment also suggest important structural details. The high frequency portion of the spectrum 400-1300 cm$^{-1}$ is called the functional group region. The characteristic stretching frequency for important functional groups such as OH, NH, C=O occur in this region and the absence of absorption peak in the assigned ranges indicate the absence of such groups in the molecule. The lack of strong absorption bands in the 900-650 cm$^{-1}$ region generally indicates a non aromatic structure. The intermediate portion of the spectrum, 1300-900 cm$^{-1}$, is usually referred to as the “fingerprint” region. The absorption pattern in this region is frequently complex, with the bands originating because of interacting vibrational modes.

In FTIR spectrometer, radiation containing all IR wavelengths (e.g. 5000-400 cm$^{-1}$) is split into two beams. One beam is of fixed length, the other of variable length (movable mirror). The varying distances between two pathlengths result in a sequence of constructive and destructive interferences and hence variations in intensities: an interferogram. Fourier transformation converts this interferogram from the time domain into one spectral point on the more familiar form of the frequency domain. Fourier transformation at successive points throughout the variation of the movable mirror gives rise to the complete IR spectrum. The typical experimental set up of an FTIR instrument is schematically described in Figure 9a.
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In our case, sample was prepared as pellets by mixing a very small amount of the sample (~1 mg) with KBr (~100 mg). A blank KBr pellet is used as the reference. The absorption spectrum of the sample pellet was recorded using Nicolet 6700 FTIR spectrometer by Thermo Scientific.

![Diagram of FT-IR and Raman spectroscopy]

**Figure 9.** (a) Schematic representation of the instrumentation of FT-IR and (b) scheme depicting the working principle of Raman spectroscopy.

2.4.5 Raman spectroscopy

Raman spectroscopy is a spectroscopic technique employed to ascertain the vibrational, rotational and other low frequency modes in a system. Raman scattering is an example of inelastic scattering because of the energy transfer between the photons and the molecules during their interaction. When a molecule is excited with light, the photons interact with the electron cloud and excite it from the ground state to a virtual energy state. When the molecule relaxes, it emits a photon and it returns to a different rotational or vibrational state. The difference in energy between the original state and this new state leads to a shift in the emitted photon’s frequency. If the final vibrational state of the molecule is more energetic than the initial state, then the emitted photon will be shifted to the lower energy and this shift in the frequency is designated as the Stokes shift. If the final vibrational energy is less energetic than the initial state, then the emitted photon is...
shifted to higher frequency and this is designated as Anti Stokes shift. The scheme showing all these associated transitions is described in Figure 9b.

In bulk semiconductors, the free exciton is most strongly coupled to the long wavelength optical phonons via the Fröhlich interaction. In this effect, the displacement of the partially ionic nuclei is accompanied by a radial electric field extending over many unit cells, the potential of which is proportional to the amplitude of the phonon. This electric field Coulombically couples to the exciton. As long as the effective mass of the electron and hole are different the coupling to the electron and to the hole is not equal in magnitude, though opposite in sign, and therefore there is a net coupling moment. The strength of this exciton phonon coupling is strongly peaked for those phonons whose wavelength matches the spatial extent of the exciton. This coupling is manifested in the resonance Raman spectrum in the bulk semiconductors by a series of overtones of the LO phonon of the appropriate wave vector. Since the dispersion of the LO phonons is weak, the peaks which are observed occur at very nearly integer multiples of the \( k=0 \) optical phonon frequency. The highly delocalized excitonic states of the bulk semiconductor couple mainly with comparable wavelengths to the size of the exciton. Very short wavelength vibrations couple more weakly to the delocalized electronic states. In smaller clusters like nanoparticles, this situation is altered and the coupling to short wavelength vibrations will dominate. As the electron and hole are confined into a smaller volume, the Fröhlich coupling strength should be diminished, because the electric field caused by the vibration should be less effective in polarizing the exciton. Systematic trends in the electron vibration coupling strength with the variation of cluster size and shape are of particular interest as this coupling strength can determine the shape and width of the electronic absorption spectrum of the cluster. In our case, confocal Raman measurements were carried out in Jobin Yvon T64000 spectrophotometer with different laser lines as excitation source.
2.5 References


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