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Instrumentation of IR spectra

Theory:- Infrared spectroscopy involves the interaction of IR radiation with matter. It coveros a range of techniques, mostly based on absorption spectroscopy. The techniques can be used to identify and study the chemical substances. The sample may solid, liquid, gas. The method or techniques of IR spectroscopy is conducted with an instrument called spectrophotometer to produce an IR spectrum. The IR portion of the electromagnetic spectrum is visually devided into three regions; Near-, mid, far-IR spectrum.

*** Core theory of IR is discussed in vibrational spectroscopy

· **Practical IR spectroscopy:** The IR spectrum of a sample is recorded by passing a beam of IR light through the sample. When the frequency of a bond is the same as the vibrational frequency of a bonds or collection of bonds, absorption occurs. Examination of the transmitted light reveals how much energy was absorbed at each frequency or wavelength. This measurement can be achived by scanning the wavelength range using a monochromator. Alternatively, the entir wavelength is measure Fourier transformed instrument and then a transmittence or absorbance spectrum is generated.

· **Sample preparation:-**

(i) Gaseous samples requir a sample cell with a long pathlength to compensate for the diluteness, A sample glass tube with length of 5 to 10 cm equipped with infrared transparent windows.

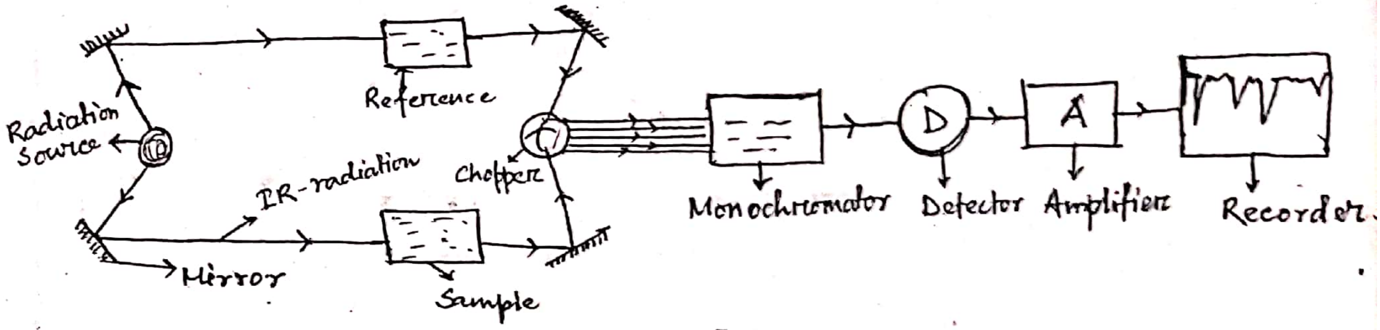
(ii) Liquid sample can be sandwiched between two plates of a salt (commonly NaCl, CaF_2, KBr). The plates are transparent to the IR light.

(iii) Solid samples can be prepared in a variety of ways. One common method is to crush the sample with an oily mulling agent (usually mineral oil Nujol). A thin film of the mull is applied onto salt plates and measured.

(iv) For polymeric solid sample 'cast film' technique is used. The sample is first dissolved in a suitable non-hygroscopic solvent. A drop of this solution is diposited on surface of KBr or NaCl cell. The solution is then evaporated to dryness and the film formed on the is ~~and~~ analysed directly

~~Photodetectors~~

Instrumentation



Instrumental set up for IR-spectrum.

Radiation Source

→ Nernst Glower: i) Oxides of Zr, Y, Er
ii) A hollow rod, diameter - 2mm, length 30 mm
iii) Non conducting at room temp, heating required at (1000 - 1800°c)
iv) Produce wide IR range and intense spectra.

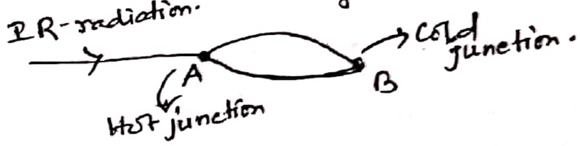
→ Globar :- i) Rod of sintered Silicon Carbide
ii) Diameter is 4 mm & length 50 mm.
iii) Heating required to produce IR-~~spectrum~~ radiation at 1300 - 1700°c.
iv) less intense - IR radiation produce.

* In referace generally KBr is used as, becaus it can transmitte all IR radiation.

Monochromator: → ① Prism (Basically NaCl prism is used)
② Gratings

Detector:- ① Bolometer : a) It consist a ~~f~~ thin metal conductor.
b) With increasing temp. resistance of of metal conductor increases hence current flow changes which record by recorder.

② Thermocouple: Due to temp. difference potential difference will produce. Hence current flow changes.



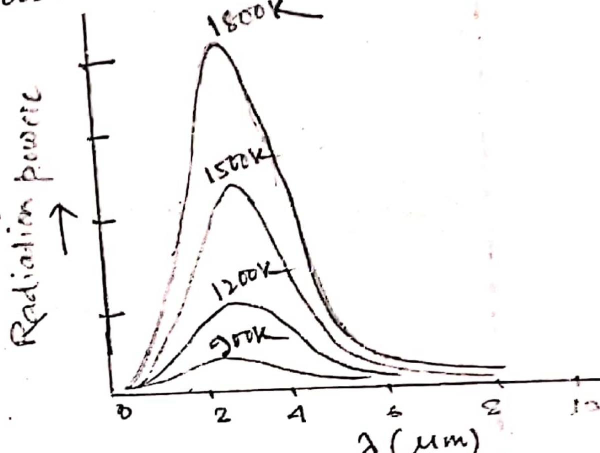
(iii) Thermositor: fused mixture of metal oxides are used. Due to IR-radiation temp. of metal oxid are ~~changes~~, increases as a result resistance will decrease.

(iv) Golay detector

(v) ~~&~~ photoconductivity detector.

Radiation Sources:- The essential element for absorption spectroscopy is a radiation sources which show an as high as possible intensity in the wavelength area under the investigation. Thermal radiator are mainly used which provide a very broad band, so called continuum radiation. In contrast the use of laser for measuring absorption spectra presumes the use of monochromatic radiation that have an extreamely narrow band.

In IR spectroscopy, Plank radiator are used as radiation sources for sample excitation. The intensity of radiation emitted by a black radiator ~~to~~ is subjected to the plank radiation principle. According to this principle, the emmited spectral radiation power reaches a maximum depending on temp. On the short wavelength side the radiation power reaches maximum and the curve falls steeply and towards high wavelength region the curve drops off flatter. Depending on the spectral region of interest, weather it be the far, middle or near IR, different sources are used.



• The most frequenlly used radiation source in the mid-IR spectral region is the Globar. It consist by SiC (sillicon carbide) in the forms of rod or helixes. As the result of its electrical conductivity in a cold state, the Globar can be directly ignited. At a burning temp. of about 1500K, its power uptake is quite substantial, so that in most cases the sources casing in the spectrometer is equiped with water cooling. ~~A~~ The use of Glober has an advantage that, its emissivity is relatively high to about 100 cm⁻¹, thereby allowing it also to be used as a sources in the far-IR region.

Advantages of use of Nernst Rod radiator over Globar:

In comparison, the Nernst Rod is used as a radiation sources. Because-

(i) It has higher working temp. than Globar.

(ii) The rod is relatively sinsitive, mechanically speaking and particularly upon improper mounting is prone to deformation possibly imparing the optical stability of spectrometer.

(iii) It made of ZrO_2 with additives Y_2O_3 (Yttrium oxide) which as a -ve temp. coefficient of electrical ~~conductivity~~ resistance.

(iv) It is a non conductor at ~~room~~ room temp hence an initial auxiliary heating is required for ignition.

(v) The nomal operation temp. lies at about 1900K so that its emission maximus appears at between 1 and 2 μm.

Characteristics of spectrometer used for Near-IR:—

(i) The spectrometer contain a sources which is made by metallic helices mainly - Cr-Ni alloys (Tungsten).

(ii) For the near-IR region tungsten-halogen lamps are used exclusively which allow a higher operating temp, ~~this~~ thus a higher radiation is produced.

- For the far-IR region, particularly for the measurement below 100 cm^{-1}, a mercury high pressure lamp is suited.

<u>Infrared Detectors</u>:— Before the principles of spectral resolution, the common radiation detector for IR-spectroscopy should be introduced. Their job is to convert the optical signal into further applicable electrical signal. There are several detectors.—

i) Thermal detectors
ii) Pyroelectric detectors
iii) Pneumatic detectors.
iv) Photoelectric detectors.

Besides the detection, lifespan, other criteria for evaluating detectors is the applicable wavelength range as well as the sensitivity, represented by the change of measurements signal as a function of the change of the radiation power. Moreover, important is the signal to noise ratio (SNR) and the time constant of the response velocity.

- A characteristic parameter, the specific detectivity D^*, has been shown useful for comparing different detectors with one another —

$$D^* = F_D^{1/2} / NEP$$

Unit of D^* = $cm \cdot Hz^{1/2} W^{-1}$

F_D = Detector area in cm^2

NEP = Noise equivalent power in $W Hz^{-1/2}$

<u>NEP</u>:— It is the incident radiation power on the detector that leads to a signal-to-noise ratio of one at the available electric band width. This power can be defined and measured by the following equation—

$$NEP = \frac{\Phi}{(\Delta f^{1/2}, S/N)}$$

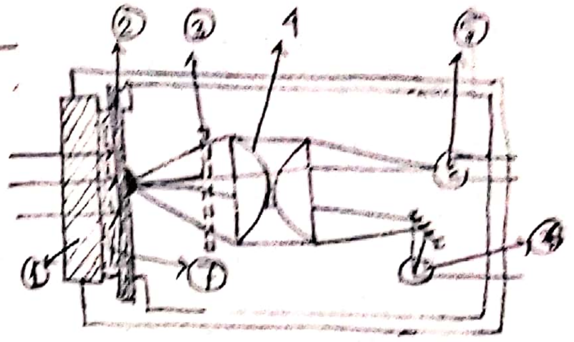
Φ = Radiation power in W
Δf = electric bandwidth in Hz
S/N = Signal to noise ratio

Thermal Detectors :-

Basic principle of Golay detector :-

Golay detector belongs to a subgroup of thermal detectors. The principle of Golay ~~dect~~ detector can be describe as follows. —

~~Radiation entires through an IR-permeable window into a gas filled cell and is absorbed there on a blackened film. The absorption heat causes an increase of a gas pressure to which the back wall of the cell~~



Golay detector.

① IR-permeable window
② Blackened membrane with a reflective coating on the backside
③ Gratting ④ Lens
⑤ Light source ⑥ Photocell.

It consists of a gas filled enclosere(?) with an infrared absorbing material and a flexible diaphram or membrane. When IR radiation absorbed, it heats the gas, causing it to expand. The gas pressure will be increased ~~wh~~ which deforms the membrane. Light reflected off the membrane is detected by photo~~ic~~diode and motion of the mamebrane produces a change in the signal on the photodiode.

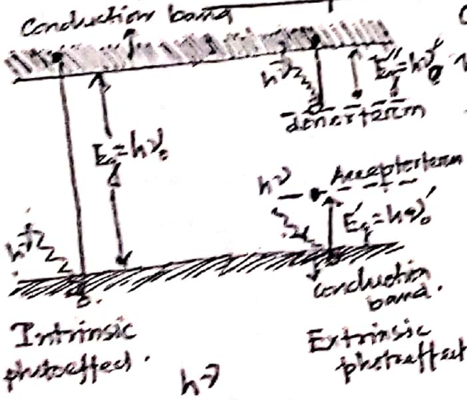
Advantage: ⓘ The Golay cell has high sensitivity and a flat response over a very broad range of frequency. ⓘⓘ The response time is modest, of order 10 ms. ⓘⓘⓘ It must be protected from the foreign light by an automatic lid.

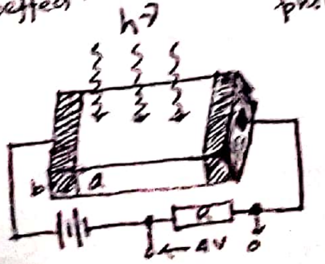
Photodetectors:

Electromagnetic radiation can interact in many ways with the material. Because of their higher sensitivity, photoelectric detectors are mostly used in IR spectrophotometer.

Principle:- Incident radiation alters the electrical conductivity in the irradiated semiconductor material. The photosignal is measured either as a change ~~of~~ in voltage via the resistance R or as change in current.

The elementary process of photoconduction is always the production of an 'electron-hole pair', whereby either both charge carries are free to move in the electric field (Intrinsic process) or one of the two charge carries is spatially bound (extrinsic process).





Spectrometer:-

For observing the spectrum, one needs an instruments for measuring the electromagnetic radiation transmittance. The transmittance is defined as the ratio of transmitted radiation to incident radiation power.

Previously spectroscopes are used for recording spectra in the visible region. Latter on spectrographs were developed with with a spectrum could be photographically captured. With the help of speially photo sensitized photo plates spectoroscopy could takes place in short wave near-infrared (NIR) region. Generally now-a-days, the used spectrometer contain several detector for measuring the characteristics of the spectrum.

Depending on the spectral apparatus, there are two types of spectrometer—

i) Non dispersive spectrometer

ii) Dispercsive spectrometer.

In non-dispersive spectrometer no variable wavelength selection is possible. It is often used to detect gas. No dispersive elements like prism, diffraction grating are used in this spectrometer. It measure the concentration of CO_2, CO.

Principle of Non-dispersive IR:-

An infra-red beam passes through the sampling chamber and each gas component in the sample chamber absorbs some particular IR frequency. In parallel a reference gas, typically N_2 is used in another chamber by measuring the amount of absorbed IR at the necessary frequency, the concentration of the gas component can be measured. It is called non-dispercive because the wavelength which passes through the sampling chamber is not pre-filtered.

Disadvantage of non-dispersive IR:- Due to absence of obtical filter in front of detector the sample can not absorbe monochromatic ~~radical~~ radiation. As a result we do not obtain exact data which we expect.

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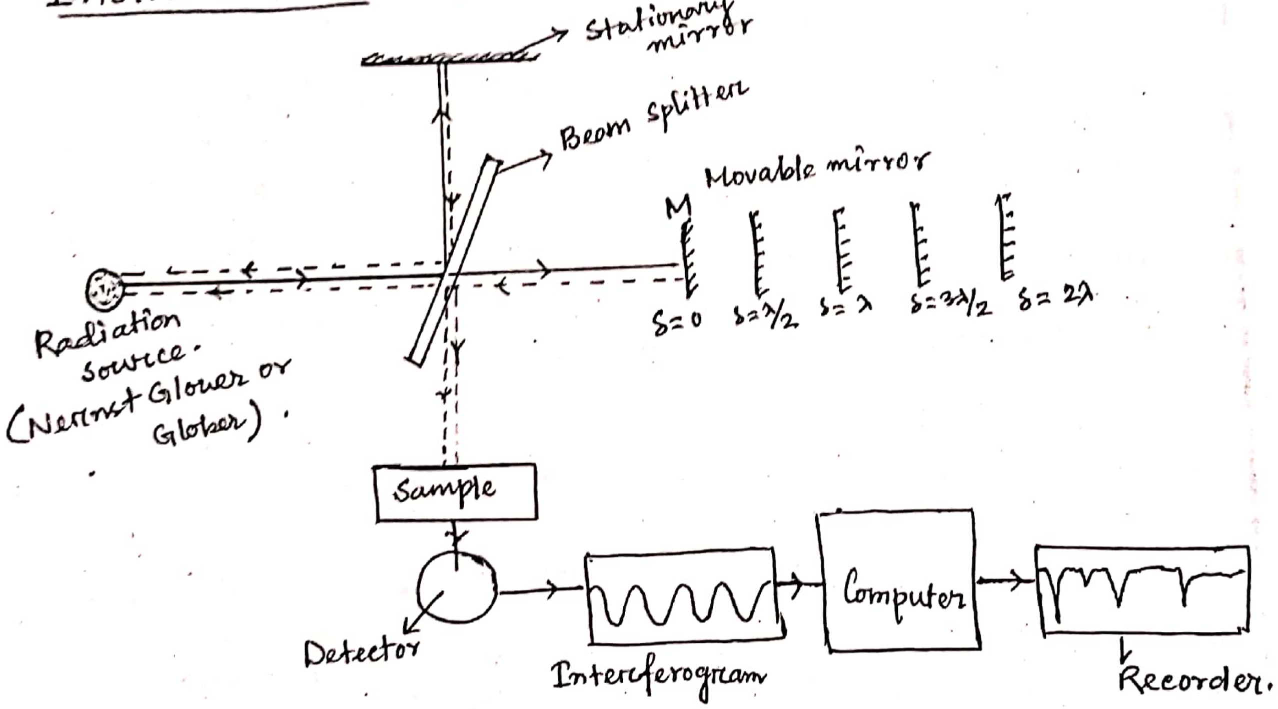
Fourier - transform IR spectroscopy

FTIR - is a technique used to obtain an IR spectrum of absorption or emission of a solid, liquid or gas. An FTIR spectrometer simultanously collect high spectral resolution data over a wide spectral range. This confers a significant advantage over a dispersive spectrometer, which measures intensity over a narrow range of wavelengths at a time.

Principle: FTIR is based on the principle of interferrometry and interferrogram will be obtained, which is a complex signal occurs in wavelike pattern.
Interferogram signal is plotted wave intensity Vs time. From this plot a mathametical operation is carries out called Fourier transformation. The spectra is called FTIR.

Instrumentation:- FTIR is also known as interferometer.



Block diagram of FTIR

In a Michelson interferometer adapted for FTIR, light from the polychromatic IR source, approximately a Nernst Glower or Glober is collimated and directed to a semi-permeable beam-splitter. Ideally 50% of the light is refracted towards the fixed mirror and 50% is transmitted towards the movable mirror. Light is reflected from the two mirrors back to the beam-splitter and some fraction of original light passes into the sample compartment.

The difference in optical path length between the two arms to the ~~interferogram~~ interferometer is known as retardation or optical path difference.

An interferogram is obtained by varying the retardation and recording the signal from the detector for various value of retardation.

Measuring and processing the Interferogram:

The interferogram has to be measured from zero path difference to a maximum lengths that depends on the resolution required. The interferogram is converted to a spectrum by fourier transformation. This requires is to be stored in digital form as a series of values at equal intervals of the path difference between the two ~~bands~~ beams. To measure the path difference a laser beam is sent through the interferometer, generating sinusoidal signal. Where the separation between successive ~~difference~~ maxima is equal to the wavelength of the laser. Typically 633 nm He-Ne laser is used.

The result of FT is a spectrum of the signal at a series of discreate wavelengths. The spectral resolution i.e. the separation between wavelengths that can be distinguished, is determined by the maximum OPD. The wavelength used in calculating the FT are such that an exact number of wavelengths fit into the length of the interferogram from zero to maximus OPD.

Advantages of FT spectrometers over dispersive instrument

Multiplex Advantage:- This advantage is also known as spectroscopic Fellgett. All wavelengths are measured simultaniously in the interferometer, ~~white~~ while these are measured in the monochromator successively.