Measurement of Infrared Spectrum

Inf. source of light is Nernst glower which consists of a rod (2cm length 0.2cm dia) of sintered mixture of the oxides of zirconium, yttrium & erbium.

→ Rod is electrically heated to 1500–2000°C To produce I.R. radiations in range 400–4000 cm^{-1}.

→ A rod of silicon carbide (globar) can also be electrically heated to produce infrared radiations.

→ Optical prisms/gratings can be used to obtain monochromatic light.

→ Light from the source is split into two beams.
One beam → passed thru sample → sample beam
Other beam → reference beam.

→ When beam → sample → become less intense due to absorption of certain frequencies.
Then there will be a diff. in intensities of two beams.

Absorbance $A = \log_{10} \frac{I_0}{I}$ $\because T = \frac{I}{I_0}$

$\therefore A = \log(1/T)$

I_0 = intensity of ref-beam.

I = intensity of beam after interaction with sample.

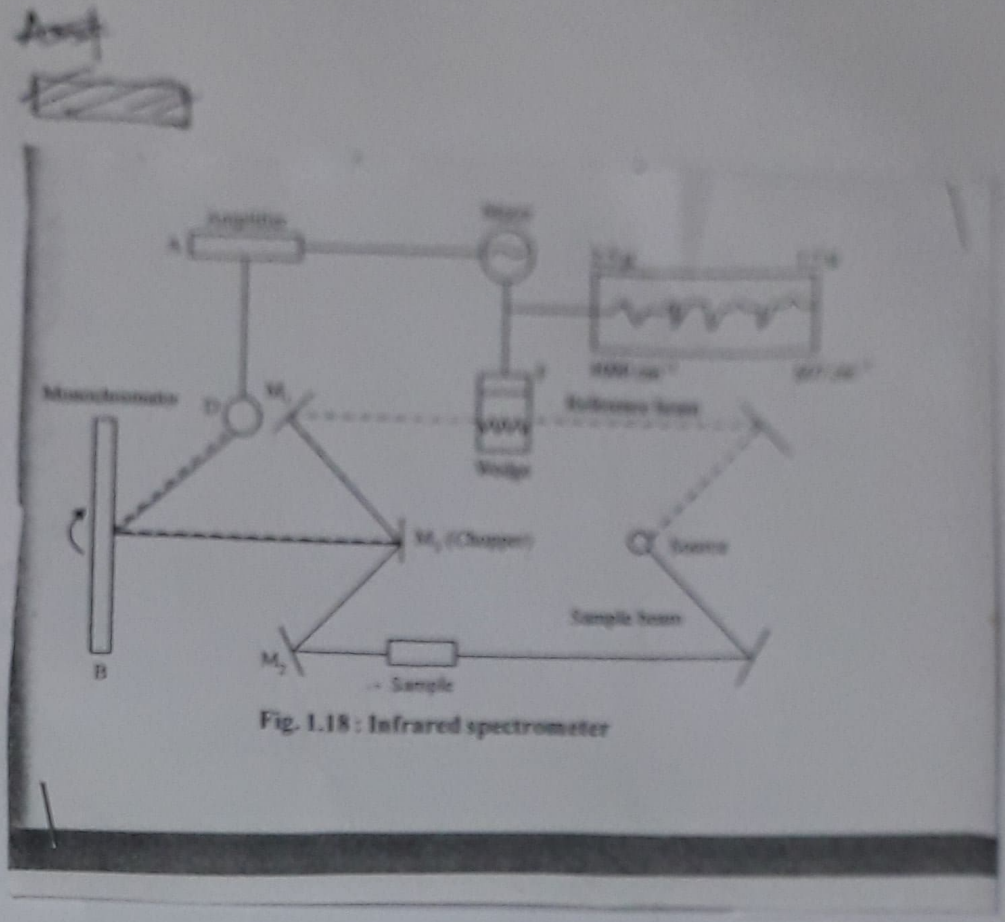


Fig. 1.18 : Infrared spectrometer

Intensities of two beams are converted into electrical energies and measured with the help of detector thermofile.

For this, the two beams are made to fall on a segmented mirror M_3 (Chopper) with help of M_1 & M_2.

→ Chopper which rotates at a definite speed reflects the sample and the ref. beam to a monochromatic grating (B),

→ As grating rotates slowly, it sends individual freq. to detector thermofile (D), which converts infrared into electrical energy. It is then amplified with the help of Amplifier (A). Amplifier is coupled to a small motor (E), which drives an optical wedge (F).

→ The movement of the wedge is in turn coupled to a pen recorder which draws absorption bands on calibrated chart.

Sample Handling

Compounds may be examined in vapour phase as well as in pure liquids, sol^n phase & solid state.

→ Solids may be studied as mix (KBr + sample) or as nujol mull.

→ KBr & resulting mix is pressed as discs of about 10 mm in dia. & 1–2 mm in thickness but for preparing nujol mull, abt 5 mg sample is finely mixed in a drop of nujol.

→ For liquid sample, sample can be prepared as thin film (0.1 mm – 0.3 mm) squeezed b/n two NaCl plates

→ For gas sample, it is introduced into a gas cell usually 10 cm long. Wall of the cell are made of NaCl.

Applications :-

① Determination of functional gp in a compound :-
eg If no band is observed in 1850-1540 cm^{-1} region, it confirms absence of C=O group.

② Structure Determination :-

③ Determination of purity of compound :-
→ If bands appear fairly sharp & clear, then comp. is pure.
But trace of impurity interfere with original absorption bands & some add^{n} bands also appear.

④ Hydrogen Bonding Studies :-
Molecules which contain active Hydrogen (OH, COOH) undergo self association (intermolecular H bonding).
→ Absorption in aggregate form occurs at lower freq. & bands formed are relatively broad.
→ But in non polar solvent (CCl_4), ~~agg~~ peaks become sharp & OH str. absorption shifts to higher freq.
→ Intramolecular bonded compounds (o-nitrophenol) do not show any shift in absorption on dilution while inter mol. H-bonded do.

(5) Dipole moments are measured with the help of IR spectroscopy.

(6) Diff b/w ald. & Ketone can be done with the help of IR.

(7) 1°, 2° & 3° amines can be differentiated.
cis & trans alkenes can be "

(8) Study of chemical Rx :-

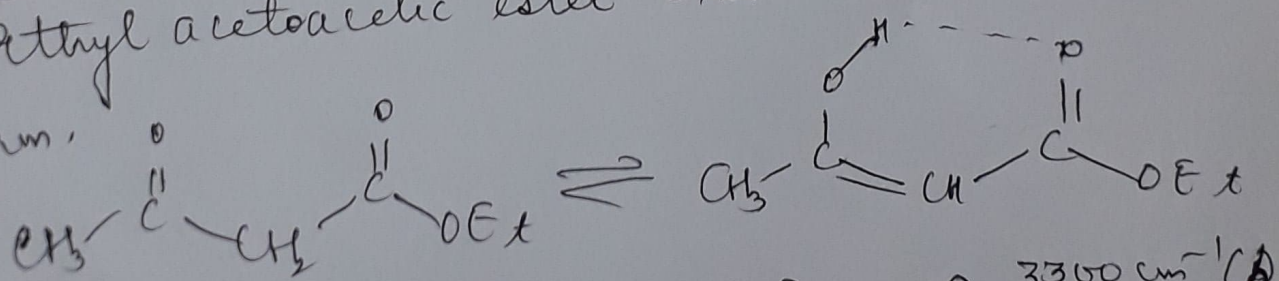
The progress of a rx. can easily be followed by examining IR spectrum of aliquots withdrawn from time to time.
As rx proceeds, some bands will disappear slowly & new bands will appear.
eg. oxidation of 2° alcohol to Ketone.

(3750 cm^{-1}) OH str.

(1725 cm^{-1}) (C=O str)

(9) Study of Tautomerism :-

→ Ethyl acetoacetic ester exists in keto enol form.



$\nu_{C=O(str)}$ 1733, 1710 cm^{-1}

ν_{O-H} ~ 3300 cm^{-1} (b)

$\nu_{C=O(str)}$ 1645 cm^{-1} (s)

Lowering of C=O str. in enolic form is due to intramolecular H bonding, which is stabilized by resonance. These bands clearly confirms keto-enol tautomerism in acetoacetic ester.