

- Highest resolutions are obtained for gaseous samples and low temp. the collisions between the molecules are infrequent.
- ~~For~~ Gaseous samples in microwave are very significant as molecules can freely rotate in gaseous sample.
- Long pathlengths are achieved by using multiple passage of beams between two parallel mirrors at the end of sample cavity.
- For IR spectroscopy, the sample is typically a liquid held between windows of sodium chloride (transparent down to 700 cm^{-1}) or KBr ~~pellets~~ (400 cm^{-1})
- The sample is prepared by pressing into solid disk with KBr (finely powdered) or grinded with Nujol mull or Hydrocarbon oil.

* Fourier Transform technique in spectroscopy is a newly introduced technique into IR and NMR spectroscopy. An interferogram is produced which is superposition of waves each of which is representation of spectrum in terms of wave number and frequency.

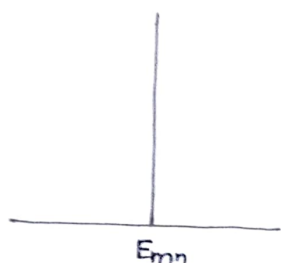
- A Fourier transform of interferogram is then used to produce a well resolved absorption spectrum of the species with a good signal-to-noise (S/N) ratio (SNR).

Selection Rules:-

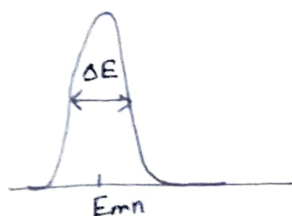
They specify the change in the quantum number accompanying a particular transition. They form the backbone of spectroscopy. For pure rotational transition the selection rule is $\Delta J = \pm 1$. For pure vibrational spectra $\Delta v = \pm 1$ where v is vibrational quantum number.

- Selection rules are not always ~~obeyed~~ obeyed strictly. This is because most of the approximations that are applied in the derivation of selection rules are not valid strictly.
- The spectral transitions which obey a given rule of selection is called allowed transitions. Those transitions that violate a given selection rules are called forbidden transitions.
- Allowed transitions are much more intense than forbidden transitions which are very weak.

Natural linewidth:-



(a) Sharp spectral line



(b) Spectral line with width.

→ It is also referred as life-time broadening.

→ It is determined by the application of Heisenberg uncertainty principle i.e.

$$\Delta E \Delta t \geq \frac{h}{4\pi}$$

ΔE → Uncertainty in energy
 Δt → " " " time

h → Planck's constant

For a photon

$$E = h\nu$$

$$\text{or } \Delta E = h \Delta \nu$$

Hence natural linewidth is given by

$$\Delta \nu \geq (4\pi \Delta t)^{-1}$$

Width and Intensity of spectral line:-

Two factors contribute to the broadening of spectral line. They are:-

- ① collisional broadening
- ② Doppler broadening

- Collisional broadening is mainly responsible for the width of spectral line in UV and visible regions. These mainly occur in electrons in outer shell of molecules.
- When molecules in gaseous or liquid phase collide with one another, they deform the cloud of charge (of outer electrons) and perturb the energy levels. Therefore, the spectral transitions are perturbed and hence broadening in the spectral lines are observed.
- Doppler broadening:- Doppler broadening arises when the molecule under investigation has a velocity relative to the observer or the observing instrument. This is mainly used for explaining the spectral line broadening in case of ~~spectral~~ gaseous sample. The molecules in gaseous state are mostly undergoing random motion according to kinetic energy of gas.

→ If the molecule is moving towards the measuring instrument with velocity u , then the frequency ν' of the radiation seen by the molecule is given by:-

$$\nu' = \nu(1 + u/c) \quad \text{--- (1)}$$

→ ν → radiation frequency
 c → velocity of light
 u → velocity of molecule

→ If the molecule is moving away from the instrument, the frequency ν' of the radiation observed by the instrument.

$$\nu' = \nu(1 - u/c) \quad \text{--- (2)}$$

Rearranging eqn (1) we get

$$(\nu - \nu') / \nu = \Delta\nu / \nu = -u/c \quad \text{--- (3)}$$

And rearranging eqn (2) we get

$$(\nu - \nu') / \nu = \Delta\nu / \nu = u/c \quad \text{--- (4)}$$

Here $\Delta\nu$ is Doppler Broadening.

→ Depending upon the direction of molecule relative to that of instrument, the observed frequency may be higher or ~~right~~ lower than the actual radiation frequency.

From K.E. theory of gases, Doppler broadening can be given by

$$\Delta\nu / \nu = (2/c)(2kT \ln 2 / m)^{1/2} \quad \text{--- (5)}$$

Since $\Delta\nu / \nu \propto T^{1/2}$, it can be reduced by using cold gaseous sample.