

(49)

However, the moment of inertia may be larger, the B values correspondingly smaller, and the P or R line spacing will be less.

Ex: for HCN, a linear molecule $H-C\equiv N$.

The band concerned is the symmetric stretching frequency at about 3310 cm^{-1} , and the spacing B observed to be about $2.8-3.0 \text{ cm}^{-1}$ near the band centre. In CO_2 the spacing is about 4.0 cm^{-1} .

For still larger molecules $\rightarrow B$ values may be so small that separate lines can no longer be resolved in the P and R branches.

Perpendicular vibrations: The selection rules are found to be

$$\Delta v = \pm 1, \quad \Delta J = 0, \pm 1 \quad \text{for simple harmonic motion.}$$

-- (26)

\Rightarrow A vibrational change can take place with no simultaneous rotational transition.

If the oscillation is taken as simple harmonic the energy levels are given by

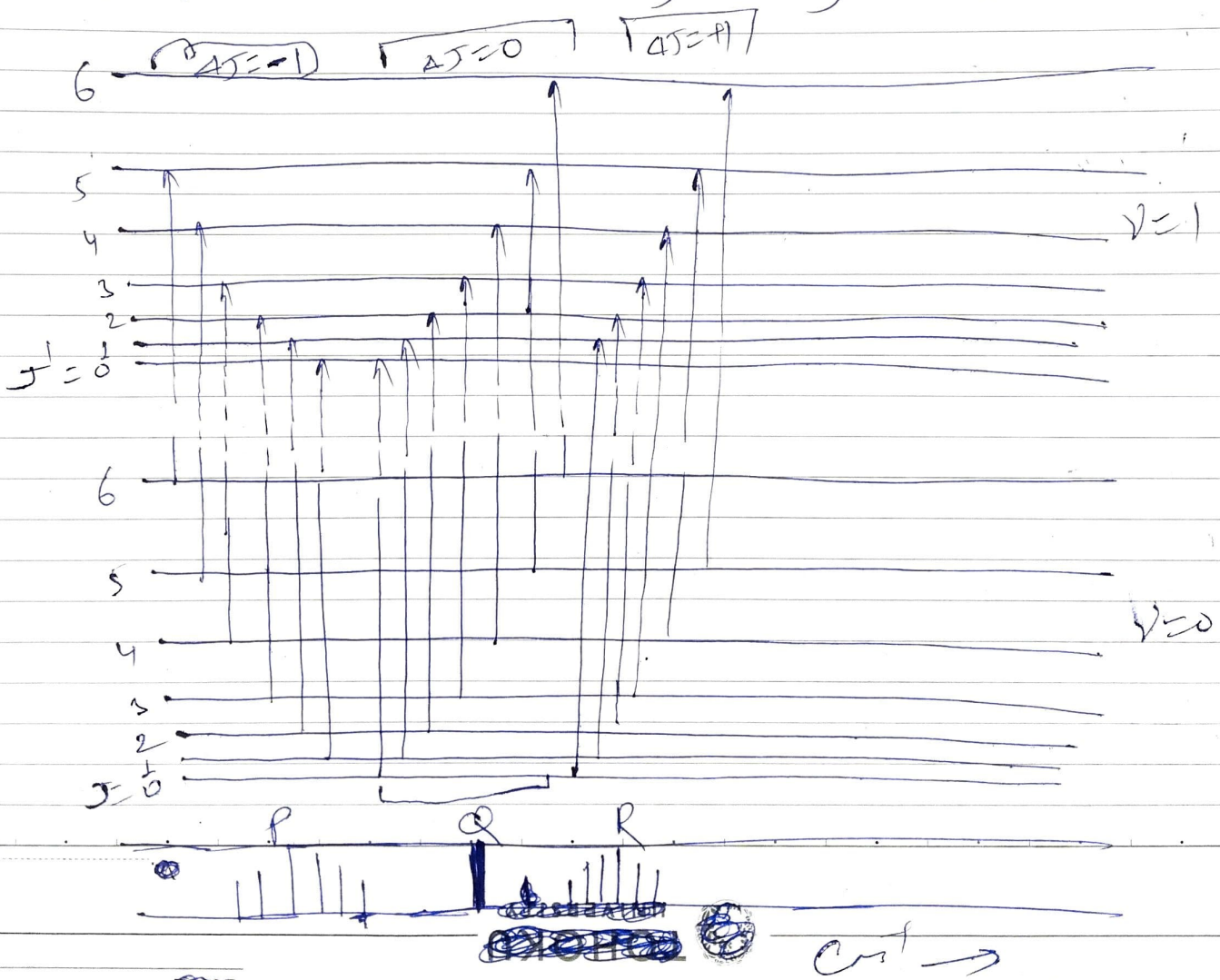
$$E_{\text{total}} = E_{J,v} = B J(J+1) + (v + \frac{1}{2}) \bar{\nu}_e + \chi_e (v + \frac{1}{2})^2 \bar{\nu}_e$$

and the P and R branch lines are given as before.

Transitions with $\Delta J = 0$ correspond to a Q branch whose lines may be derived from the eq^s.

$$\begin{aligned} \Delta E &= E_{J, \nu+1} - E_{J, \nu} \\ &= 1 \frac{1}{2} \bar{\omega}_e - 2 \frac{1}{4} x_e \bar{\omega}_e + B J(J+1) - \left[\frac{1}{2} \bar{\omega}_e - \frac{1}{4} x_e \bar{\omega}_e + B J(J+1) \right] \\ &= \bar{\omega}_0 \text{ cm}^{-1} \quad \text{for all } J \quad (27) \end{aligned}$$

Thus Q branch consists of lines superimposed upon each other at the band centre $\bar{\omega}_0$, the resultant line is usually very intense.

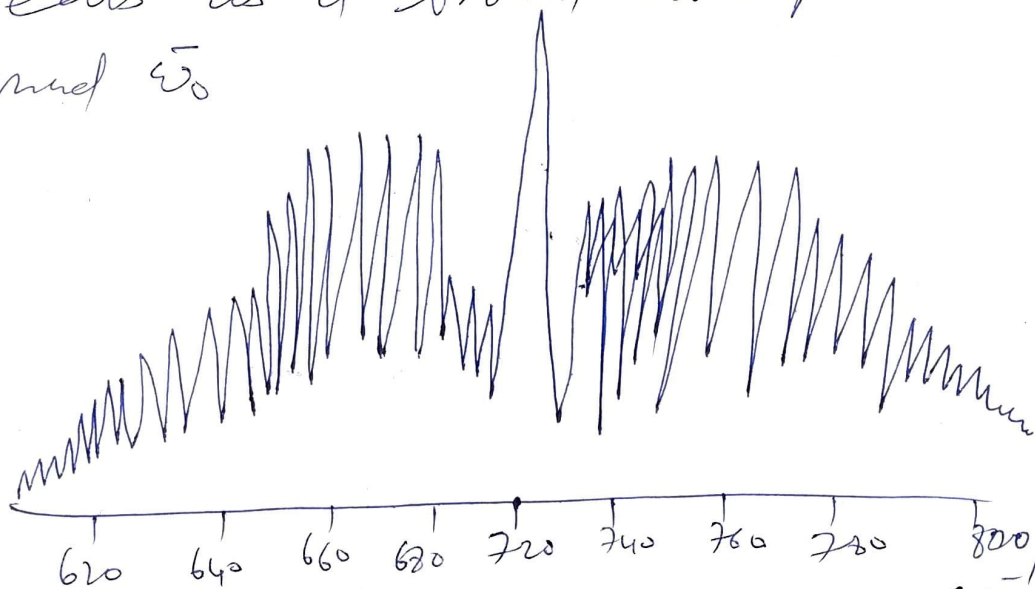


The rotational energy levels for two vibrational states showing the effect on the spectrum for which $\Delta J = 0$

If the B values differ slightly in the upper and lower vibrational states (5)

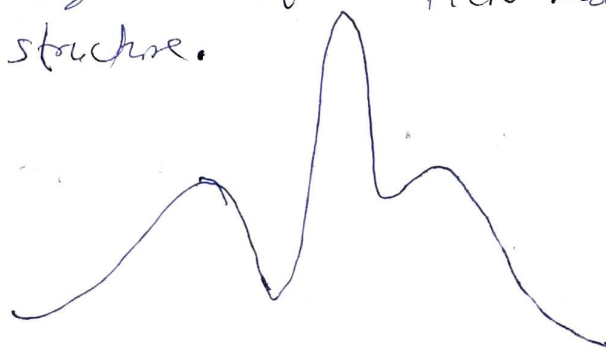
$$\begin{aligned} \Delta E &= E_{J, v+1} - E_{J, v} \\ &= 1 \frac{1}{2} \bar{\omega}_e - 2 \frac{1}{4} x_e \bar{\omega}_e + B' J(J+1) - \left\{ \frac{1}{2} \bar{\omega}_e - \frac{1}{4} x_e \bar{\omega}_e \right. \\ &\quad \left. + B'' J(J+1) \right\} \\ &= \bar{\omega}_0 + J(J+1)(B' - B'') \quad \text{--- (28)} \end{aligned}$$

Further, if $B' < B''$ we see that the Q branch line would become split into a series of lines on the low-frequency side of $\bar{\omega}_0$. Normally, $B' - B''$ is so small that the lines cannot be resolved and the Q branch appears as a broad absorption centred around $\bar{\omega}_0$.



Spectrum of the bending mode of the HCN molecule showing the PQR structure.

The contour of a PQR band under low resolution.



Polyatomic molecules with zero dipole moment do not give rise to pure rotational spectra in the microwave region (for example, CO_2 , $HCCCH$, CS_2).

Such molecules do, however, show vibrational spectra in the infra-red region, and if these spectra exhibit resolved fine structure, the moment of inertia of the molecule can be obtained.

I-R Spectrometer: Techniques and Instrumentation

Components of the spectrometer → for infra-red work

1. Source → Some form of filament which is maintained at red- or white-heat by an electric current.

Nerst filament → spindle of rare-earth oxides about 1 inch long and 0.1 inch in diameter

glowbar filament → a rod of carbon arc discharge.

2. Optical path and monochromator → The beam is guided and focussed by mirrors silvered on their surfaces. Normally a focus is produced at the point where sample is to be placed.

Ordinary mirrors and lenses are not suitable. Any window which ~~is essential~~ ~~is essential~~ are essential

must be made of mineral salts transparent to infra-red radiation ($NaCl$ and KBr), highly polished to reduce scattering to minimum.

Monochromator → in some instruments made of (53) a rock salt or potassium bromide prism. Modern instruments use a rotatable grating instead of a prism → better resolving power

3. Detector: Two main types are in common use:
* One sensing the heating effect of the radiation
* Other depending on photoconductivity.

In both the greater the effect (temp. or conductivity rise) at a given frequency, the greater the transmittance (and the less the absorbance) of the sample at that frequency.

4. Sample: The sample is held between plates of polished mineral salt rather than glass.

Pure liquids are studied in thicknesses of about 0.01 mm, while solutions are usually 0.1 - 10 mm thick, depending on the dilution.

Crystalline samples at pressures of up to 1 ~~atm~~ atmospheres or greater are usually contained in glass cells either 5 or 10 cm long, closed at their ends with rock salt windows.

Solid samples → more difficult to examine → particles reflect and scatter the incident radiation and transmittance is always low.

If the solid can not be dissolved in a suitable solvent → best examined by grinding it very finely in paraffin oil and forming a suspension.