

## Vibrations and Rotations of diatomic molecules

### Vibrational spectrum:

Neglecting  $e^-$  motion

$$K.E. : \frac{p_1^2}{2m_1} + \frac{p_2^2}{2m_2} \quad (\text{Nuclear momenta})$$

$$= \frac{p^2}{2\mu} + \frac{P^2}{2M}$$

where

$$\vec{p} = \frac{m_1 p_1 - m_2 p_2}{m_1 + m_2}$$

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

$$\vec{P} = \vec{p}_1 + \vec{p}_2$$

$$M = m_1 + m_2$$

Potential energy of vibration-rotational sys. will be function of relative co-ord.  $r = r_1 - r_2$ . Hence only relevant term for vib-rot. energy is  $\frac{p^2}{2\mu}$

Also at equilibrium distance  $r_e$  the potential energy  $V(r_e)$  is min.

The vibrations are in the potential of electronic part of the system.

Expanding this potential  $V$  about  $r_e$

$$V(r) = V(r_e) + \cancel{\frac{dV}{dr}} \bigg|_{r=r_e} (r-r_e) + \frac{1}{2} \left( \frac{d^2V}{dr^2} \right) \bigg|_{r=r_e} (r-r_e)^2 + \dots$$

0 due to minimum.

Hence

$$V(r) = -D_e + \frac{1}{2} k(r-r_e)^2$$

(Neglecting higher order terms)

$$\therefore H = \frac{p^2}{2\mu} + V(r)$$

$$\therefore \left( -\frac{\hbar^2}{2\mu} \nabla^2 + V(r) \right) \psi = E\psi$$

$$\therefore r^2 \left( \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} \right) \psi + \frac{2\mu r^2}{\hbar^2} [E - V(r)] \psi = L^2 \psi = J(J+1) \psi$$

With  $\psi = \frac{1}{r} P(r) Y_{J,M}(\theta, \phi)$

$$\frac{d^2 P}{dr^2} + \frac{2\mu}{\hbar^2} [E - V(r)] P(r) = \frac{J(J+1)}{r^2} P(r)$$

Now eliminating rotation i.e. taking  $J=0$

$$\frac{d^2 P}{dr^2} + \frac{2\mu}{\hbar^2} [E - V(r)] P(r) = 0$$

Now for  $V(r) = -D_e + \frac{1}{2} k(r-r_e)^2$

system behaves like harmonic oscillator

$$\therefore E_v = \hbar \omega_0 (v + 1/2) - D_e \quad v = 0, 1, 2, \dots$$

$$\text{with } \omega_0 = \sqrt{\frac{k}{\mu}}$$

$$\begin{aligned} \Delta E_v / \hbar &= \omega_e = \frac{\hbar \omega_0 (v+1+1/2)}{2\pi\hbar c} - \frac{\hbar \omega_0 (v+1/2)}{2\pi\hbar c} \\ &= \frac{\omega_0}{2\pi c} \quad (\text{in cm}^{-1}) \end{aligned}$$

e.g.

$$H_2: \omega_e (\text{cm}^{-1}) = 4403.2 \quad k = 5.736 \times 10^5 \text{ dyn/cm}$$

$$\text{Period of vib } T \sim 7.57 \times 10^{-15} \text{ sec.}$$

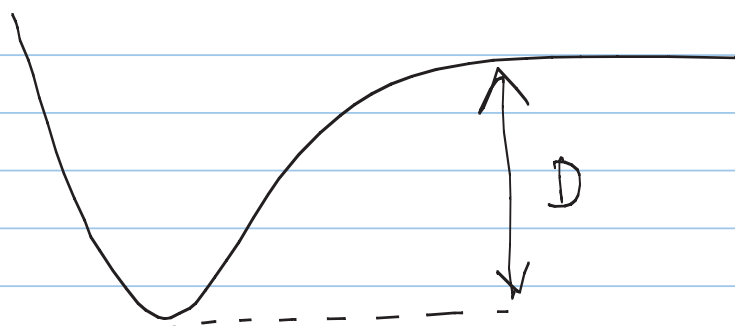
$$HCl: \omega_e = 2885.9, \quad k = 4.806 \times 10^5 \text{ dyn/cm} \quad T \sim 1.15 \times 10^{-14} \text{ sec.}$$

But Harmonic oscillator potential will not show any dissociation.

### Morse Potential

$$V = D \left[ 1 - e^{-\alpha(r-r_e)} \right]^2$$

$$= D (1 + e^{-2\alpha(r-r_e)} - 2e^{-\alpha(r-r_e)})$$



Energy (in  $\text{cm}^{-1}$ )

$$G(v) = \omega_e (v + 1/2) - \omega_e x_e (v + 1/2)^2$$

$$\omega_e = \alpha \sqrt{\frac{D\hbar}{\pi c \mu}} \quad x_e = \frac{\hbar \alpha^2}{4\pi c \mu}$$

$\omega_e x_e$ : anharmonicity constant.

As  $r \rightarrow \infty$ , energy levels get crowded and they are no more equispaced unlike harmonic oscillator.

Now for electric dipole transition between various vibrational states of a given electronic state: pure vibrational spectrum

\* For such transition, the molecule must carry permanent dipole moment. As homonuclear diatomic molecule does not

have permanent electric dipole moment  
no pure vibrational spectrum observed for  
homonuclear diatomic molecule

For heteronuclear diatomic molecule,

considering harmonic oscillator model  
selection rule

$$\Delta v = \pm 1 \quad (\text{prove!})$$

For anharmonic oscillator

$$\Delta v = \pm 1, \pm 2, \pm 3, \dots$$

but  $\Delta v = \pm 1$  is most intense.

$0 \rightarrow 1$  transition is called fundamental.

$0 \rightarrow 2, 0 \rightarrow 3$  : overtones

(Although for anharmonic oscillator  
 $0 \rightarrow 2, 0 \rightarrow 3$  transitions are not multiples of  
 $0 \rightarrow 1$  transition (freq.) but the  
nomenclature holds)

Some problems with Morse potential

1.  $V_M$  is finite at  $r \rightarrow 0$  which is not the case for real molecule. For real molecule  $V \rightarrow \infty$  as  $r \rightarrow 0$ .
2.  $V_M \rightarrow 0$  faster than  $r^{-6}$ . Real molecular potential  $V \sim r^{-6}$  at large  $r$  due to van der Waals interaction between neutral atoms at large separation!

## Lecture 19

### Rotational motion of diatomic molecule

Nuclear motion

$$\left[ \frac{-\hbar^2}{2m_\alpha} \nabla_\alpha^2 - \frac{\hbar^2}{2m_\beta} \nabla_\beta^2 + U(R) \right] \psi_N = E \psi_N$$

$$\psi_N = \psi_{N, \text{tr}} \cdot \psi_{N, \text{int}}$$

$$E = E_{\text{tr}} + E_{\text{int}}$$

$$\left[ \frac{-\hbar^2}{2\mu} \nabla^2 + U(R) \right] \psi_{\text{int}} = E_{\text{int}} \psi_{\text{int}}$$

Its a central force problem

$$\psi_{N, \text{int}} = P(R) Y_J^M(\theta_N, \phi_N)$$

$$J = 0, 1, 2, \dots$$

$$M = -J, -J+1, \dots, J$$

$$\therefore -\frac{\hbar^2}{2\mu} \left[ P''(R) + \frac{2}{R} P'(R) \right] + \frac{J(J+1)\hbar^2}{2\mu R^2} P(R)$$

$$+ U(R) P(R) = E_{\text{int}} P(R)$$

Putting  $P = \frac{F}{R}$

$$-\frac{\hbar^2}{2\mu} F''(R) + \left[ U(R) + \frac{J(J+1)\hbar^2}{2\mu R^2} \right] F(R) = E_{\text{int}} F(R) \quad \text{--- (A)}$$

- Solve electronic S.E. to get  $U(R)$  by adding  $z_\alpha z_\beta e^2/R$  to  $E_{\text{el}}$
- Obtain mathematical function to fit  $U(R)$
- Solve (A) by numerical method.

Putting  $J=0$  and expanding  $U(R)$  about equilibrium distance, gives vibrational spectrum.

with equilibrium force constant

$$k_e = \left. \frac{dU}{dR} \right|_{R=R_e}$$

Putting  $q = R - R_e$

$$\& S(q) = F(R)$$

$$\frac{-\hbar^2}{2\mu} S''(q) + \left[ U(R_e) + \frac{1}{2} k_e q^2 + \frac{J(J+1)\hbar^2}{2\mu(q+R_e)^2} \right] S(q) = E_{\text{INT}} S(q)$$

$$\text{Now, } \frac{1}{(q+R_e)^2} \approx \frac{1}{R_e^2} \left( 1 - \frac{2q}{R_e} + \frac{3q^2}{R_e^2} - \dots \right) \\ \sim \frac{1}{R_e^2} \quad \text{for small } q$$

This gives Harmonic oscillator behavior for small displacements from equilibrium positions. (We saw it in last lecture)

$$E_{\text{INT}} = U(R_e) + \hbar\omega_0 \left( v + \frac{1}{2} \right) + \frac{J(J+1)\hbar^2}{2\mu R_e^2}$$

This treatment is with assumption that the molecule behaves like rigid rotator.

For rigid rotator

$$\text{Moment of inertia} = I_e = \mu R_e^2$$

$$\therefore \frac{\hbar^2}{2I_e} = B \quad : \text{ rotational constant}$$

$$E_{\text{rot}} = B J(J+1)$$

$$B = \frac{\hbar^2}{2\mu R_e^2} \times \frac{1}{hc} \quad (\text{cm}^{-1}) = \frac{\hbar}{4\pi\mu R_e^2 c} \quad (\text{cm}^{-1})$$

A small remark.!

For Morse potential,

$$V_M(R) = D_e \left\{ \exp[-2\alpha(R-R_e)] - 2\exp[-\alpha(R-R_e)] \right\}$$

(compare with previous expression for  $V_M$  and get the appropriate factors)

$$\boxed{D_e \alpha^2 = \frac{k_e}{2}}$$

$$V_M(R) + \frac{\hbar^2}{2\mu} \frac{J(J+1)}{R^2} = V_0 + \frac{1}{2} \tilde{k} (R-R_1)^2 + C_1 (R-R_1)^3 + C_2 (R-R_1)^4$$

{ For  $J=0$  ,  $R_1 = R_e$  }

Taking  $C_1 = C_2 = 0$   $\tilde{k} \sim k_e$  and also

$$\frac{dV_{eff}}{dR} = 0$$

$$R_1 = R_e + \underbrace{\frac{\hbar^2}{2\mu} \frac{J(J+1)}{\alpha^2 R_e^3 D_e}}_{\text{centrifugal distortion of molecule due to rotation}}$$

centrifugal distortion of molecule due to rotation

In incorporating all these effects

$$E = -D_e + \hbar\omega_e \left[ (v+1/2) - \beta(v+1/2)^2 \right] + \frac{\hbar^2}{2\mu R_e^2} J(J+1) - a(v+1/2)J(J+1) - bJ^2(J+1)^2$$

with

$$a = \frac{3\hbar^2 \omega_e}{2\mu \alpha R_e^3 D_e} \left(1 - \frac{1}{\alpha R_e}\right)$$

$$b = \frac{\hbar^4}{2\mu^2 \alpha^2 R_e^6 D_e}$$

These expressions can also be obtained by equating the centrifugal force with restoring force of vibration.

These are the signatures of vibrations affecting rotational motion and rotations affecting vibrational motion.

Similarly for vibrating rotator

For a given vibrational level rotational constant

$$B_v (\text{cm}^{-1}) = \frac{\hbar}{4\pi c \mu} \left( \frac{1}{R_e^2} \right)$$

That gives

$$B_v = B - \alpha_e (v + 1/2) + \dots \quad \text{with } \alpha_e \ll B$$

$$F_v(J) = B_v J(J+1) - \underbrace{D_v J^2(J+1)^2}_{\text{correction due to non rigidity of rotator.}}$$

correction due to non rigidity of rotator.

Hence in principal for every vibrational state the rotational constant differs for given electronic state of a molecule.



Typically for each vibrational levels there are many rotational levels.

Typical vibrational energy spacing is few tens to hundreds of meV. Pure vibrational spectrum is observed in infrared regime (IR)

Typical rotational spacing is few hundreds of  $\mu\text{eV}$  to few meV. This pure rotational spectrum is observed in microwave regime.

$\omega_e, \omega_e x_e, \omega_e y_e, \dots$  are so chosen that they correspond to the potential

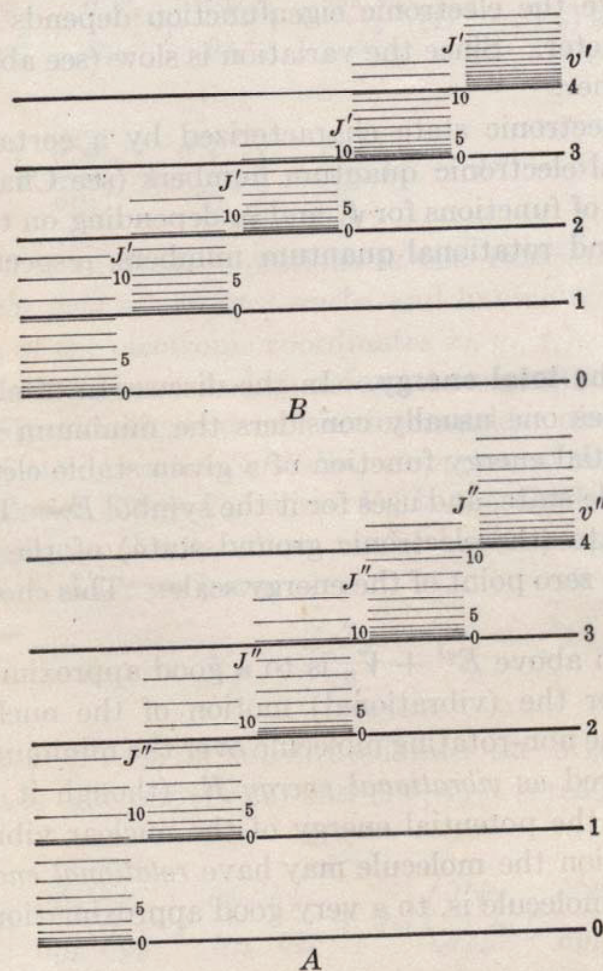


FIG. 69. Vibrational and Rotational Levels of Two Electronic States A and B of a Molecule (Schematic). Only the first few rotational and vibrational levels are drawn in each case.

including the main part of the inter-

## Rotational transitions

selection rule for rotational transition

$$\Delta J = \pm 1 \quad \text{for rigid rotator.}$$

The transition frequency

$$\nu(\text{cm}^{-1}) = B J'(J'+1) - B J''(J''+1)$$

$$\text{with } J' = J'' \pm 1.$$

The rotational lines are equispaced and the spacing is  $2B_0$  for pure rotational spectrum of a given vibrational state with rigid rotator model.

## Vibrational-rotational spectrum.

Upper state  $(v', J')$  lower state  $(v'', J'')$

$$\Delta J = \pm 1$$

$$\Delta J = J' - J'' = +1 \quad \text{R-branch}$$

$$\Delta J = J' - J'' = -1 \quad \text{P-branch}$$

$$\text{If } B_{v'} = B_{v''} = B$$

In Absorption spectrum.

$$F(J') + G(v') = B J'(J'+1) + G(v')$$

$\nu_0 = G(v') - G(v'')$  diff. in vibrational energies this is call band origin.

For R-branch

$$\nu_R = R(J'') = \nu_0 + F(J') - F(J'')$$

$$= \nu_0 + 2BJ'' + 2B \quad J'' = 0, 1, 2, \dots$$

For P-branch

$$\nu_P = P(J'') = \nu_0 - 2BJ'' \quad J'' = 1, 2, 3, \dots$$

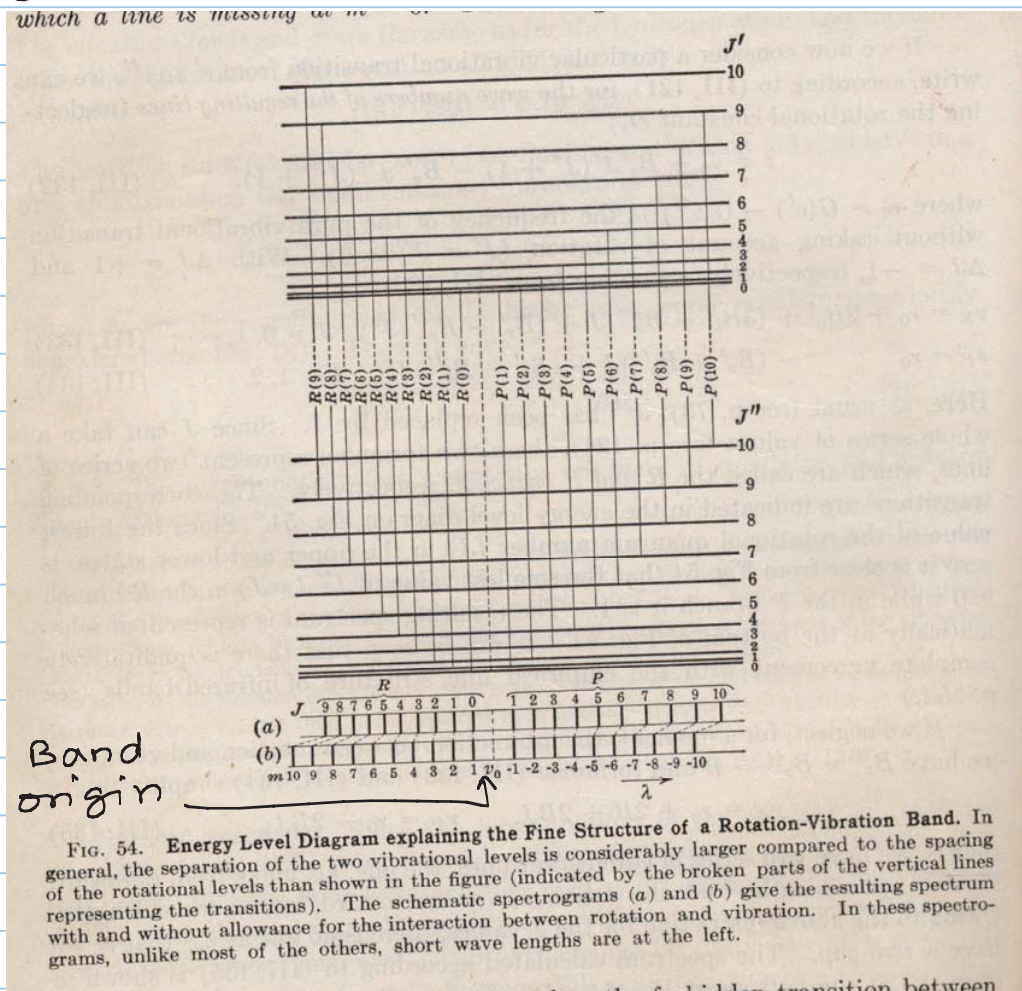
In general

$$\nu = \nu_0 + 2Bm$$

$$m = 1, 2, 3, \dots \quad \text{R-branch}$$

$$= -1, -2, -3, \dots \quad \text{P-branch.}$$

Following figure shows rotational transitions corresponding to R & P branches. Notice the absence of band origin.



If  $B_{v'} \neq B_{v''}$

$$\nu_R = \nu_0 + 2B_{v'} + (3B_{v'} - B_{v''}) J'' + (B_{v'} - B_{v''}) J''^2$$

$$J'' = 0, 1, 2, \dots$$

$$\nu_P = \nu_0 - (B_{v'} + B_{v''}) J'' + (B_{v'} - B_{v''}) J''^2$$

$$J'' = 1, 2, 3, \dots$$

In general

$$\nu = \nu_0 + (B_{v'} + B_{v''}) m + (B_{v'} - B_{v''}) m^2$$

$$m = 1, 2, \dots \quad \text{R-branch}$$

$$m = -1, -2, \dots \quad \text{P-branch}$$

$$\frac{d\nu}{dm} = 0 \Rightarrow m = -\frac{(B_{v'} + B_{v''})}{2(B_{v'} - B_{v''})}$$

If  $B_{v'} - B_{v''} < 0$  vertex is in R branch

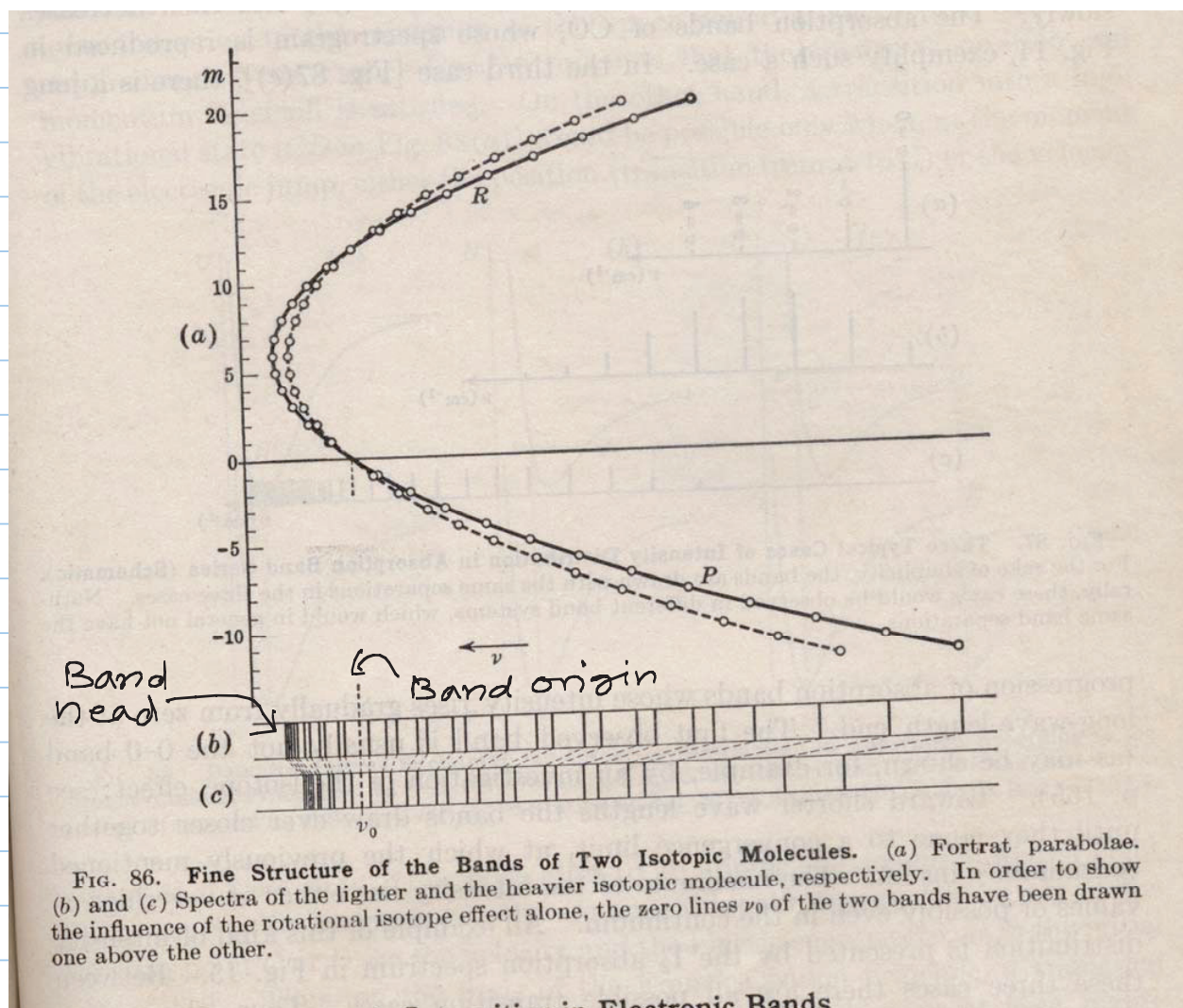
This usually is the case as for higher vib. or for higher electronic states the equilibrium or effective internuclear separation is larger than lower state.  $\Rightarrow$  moment of inertia is larger and hence rot. constant smaller  
 $\therefore B_{v'} < B_{v''}$  (usually)

The frequency of transition corresponding to the vertex is called band head. Beyond band head the rotational spectrum reverses as shown in figure below (2 figures below)

The  $\nu$  v/s  $m$  plot or parabola is called ~~Fortrat~~ Fortrat parabola.



## Fortrat Parabola



Here this figure shows the Fortrat parabola along with the corresponding rotational spectrum. Notice the absence of band origin and also the appearance of band head.

The slightly shrunk rotational spectrum is due to heavy isotope. We will see the isotope effect on vibrational and rotational spectrum later.

## Symmetric top

For symmetric top

$$I_A \neq I_B = I_C \quad (A, B \& C \text{ are 3 axes})$$

In the case of diatomic molecule,  $I_B = I_C$  are moment of inertiae about axes passing through center of mass of the molecule and  $\perp$  to the molecular axis.

A: along the molecular axis.

Although nuclear moment of inertia along A is zero electronic angular momentum and hence  $I_A$  is not zero.

$$\text{But } I_A \ll I_B \& I_C$$

$$H = \frac{P_A^2}{2I_A} + \frac{P_B^2}{2I_B} + \frac{P_C^2}{2I_C}$$
$$= P_A^2 \left[ \frac{1}{2I_A} - \frac{1}{2I_B} \right] + \frac{P^2}{2I_B}$$

$$\therefore E = \left( \frac{1}{2I_A} - \frac{1}{2I_B} \right) \hbar^2 \Lambda^2 + \frac{\hbar^2}{2I_B} J(J+1)$$

$$F_v(J) = B_v J(J+1) + (A - B_v) \Lambda^2 \quad \text{in cm}^{-1}$$

$$A = \frac{\hbar}{4\pi c I_A} \quad B_v = \frac{\hbar}{4\pi c I_B} \quad J = \Lambda, \Lambda+1, \dots$$

where  $\Lambda$  is projection of electronic orbital angular momentum about internuclear axis.

Ideally it should also include projection of spin angular momentum. Hence it should be projection of total angular momentum of  $e^-$  along the molecular axis. We will see this in Hund's coupling cases

selection rule for rotational transitions  
for symmetric top.

$$\Delta J = 0, \pm 1$$

$$= \pm 1$$

for  $\Lambda \neq 0$

for  $\Lambda = 0$

$$\Delta J = +1$$

R-branch

$$= -1$$

P-branch

$$= 0$$

Q-branch.

$$\nu_R = \nu_0 + (B_0'' - B_0') J^2 + 2B_0' + (3B_0' - B_0'') J$$

$$+ (B_0' - B_0'') J^2 \quad J = J'' = 0, 1, 2, \dots$$

$$\nu_P = \nu_0 + (B_0'' - B_0') J^2 - (B_0' + B_0'') J + (B_0' - B_0'') J^2$$

$$J = J'' = 1, 2, 3, \dots$$

$$\nu_Q = \nu_0 + (B_0'' - B_0') J^2 + (B_0' - B_0'') J + (B_0' - B_0'') J^2$$

$$J = J'' = 0, 1, 2, \dots$$

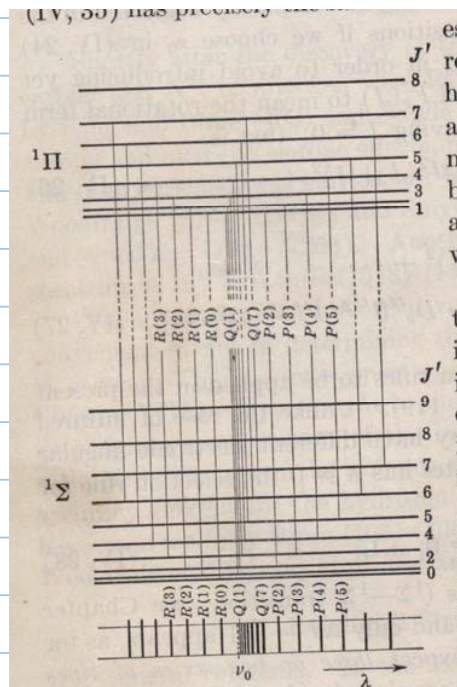
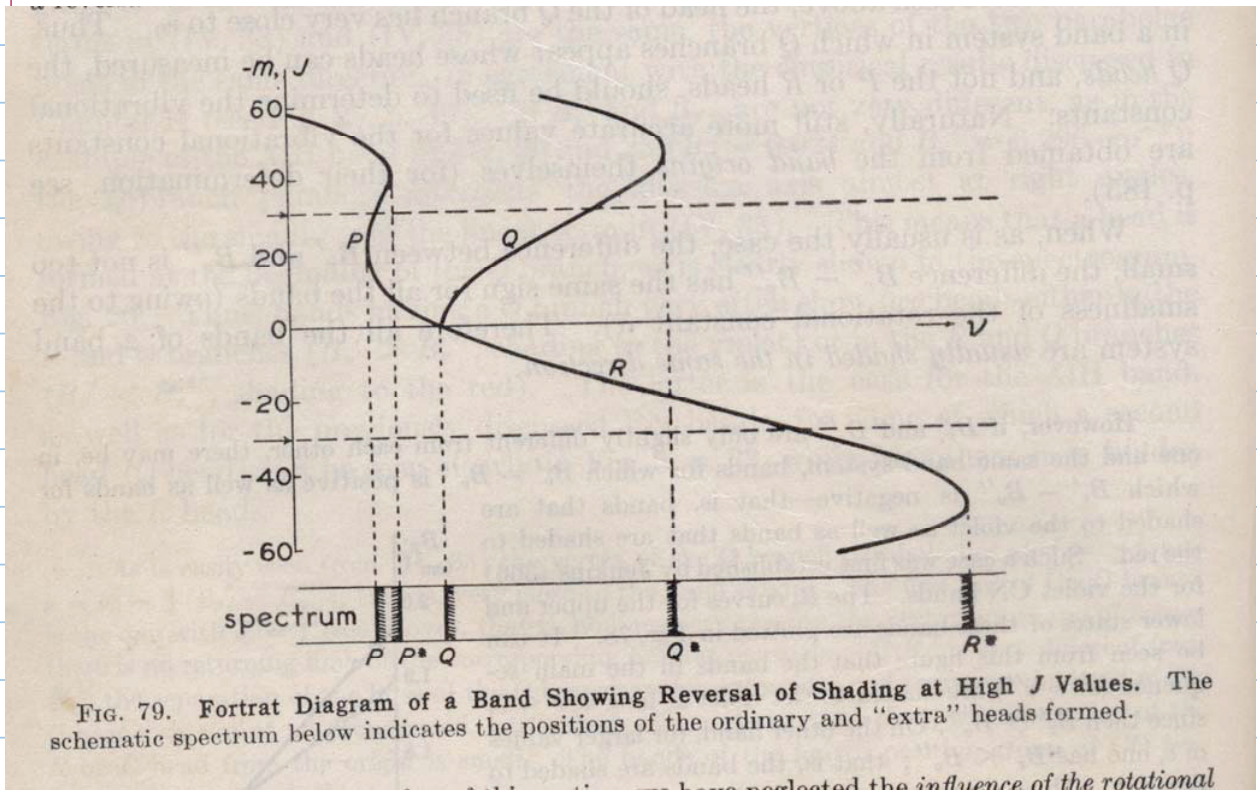


FIG. 77. Energy Level Diagram for a Band with P, Q, and R Branches. For the sake of clarity, in the spectrogram below, the lines of the P and R branches, which form a single series, are represented by longer lines than those of the Q branch. The separation of the lines in the Q branch has been made somewhat too large in order that the lines might be drawn separately. The convergence in the P and R branches is frequently much more rapid than shown.

Fortrat parabola that includes Q-branch as well. Multiple band heads are arising due to inclusion of higher powers of  $m$ .



Isotope effects on vibrations & rotations.

Vibrations

$$\frac{\nu_{osc}^i}{\nu_{osc}} = \sqrt{\frac{\mu}{\mu^i}} = \rho$$

$$\text{as } \nu_{osc} = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$

&  $k$  does not dep on nuclear mass

$$G(v) = \omega_e(v + 1/2)$$

$$G^i(v) = \rho \omega_e(v + 1/2)$$



$$G^i(u) = \rho \omega_e (u + 1/2) - \rho^2 \omega_e x_e (u + 1/2)^2 + \omega_e y_e \rho^3 (u + 1/2)^3 + \dots$$

### Rotations

$$B = \frac{\hbar}{4\pi c \mu R^2}$$

$$B^i = B \frac{\mu}{\mu^i} = \rho^2 B$$

$$F^i(J) = \rho^2 B J(J+1)$$

$$\alpha_e^i = \rho^3 \alpha_e$$

$$D_e^i = \rho^4 D_e$$

$$\Delta \nu_{\text{rot}} = \nu_{\text{rot}} - \nu_{\text{rot}}^i$$

$$= (1 - \rho^2) [B' J'(J'+1) - B'' J''(J''+1)]$$

$$\Delta \nu_{\text{rot}} \sim (1 - \rho^2) \nu_r$$

Hence for heavier isotopes the spectra shrink.

## Lecture 20

### Symmetry properties of rotational levels.

For rigid rotator the rotational wavefunction is

$$\psi_{\text{rot}} = N_{\text{rot}} P_J^{|M|}(\cos\theta) e^{iM\phi}$$

On inversion i.e.  $\theta \rightarrow \pi - \theta$  &  $\phi \rightarrow \phi + \pi$

even  $J$  levels correspond to symmetric

odd  $J$  levels correspond to antisymmetric rotational wavefunction

In the case of symmetric top

Total wavefunction

$$\psi = \psi_e \frac{1}{r} \psi_v \psi_{\text{rot.}}$$

Nomenclature: + :  $\psi$  Symm. on inversion

- :  $\psi$  antisymm. on inversion.

$\frac{1}{r} \psi_v$  is unchanged on reflection at the origin as it depends only on the internuclear separation.

For  $\Lambda = 0$

If  $\psi_e$  is symmetric then

even  $J$  + as  $\psi_{\text{rot.}}$  symmetric

odd  $J$  - as  $\psi_{\text{rot.}}$  antisymm.

If  $\psi_e$  is antisymmetric then

even  $J$  -

odd  $J$  +

For  $\Lambda \neq 0$

For each value of  $\Lambda$  there is a doublet one symmetric and other antisymmetric

For dipole transition additional selection rule due to symmetry of rotational level

$$+ \longrightarrow -$$

$$- \longrightarrow +$$

$$+ \not\longrightarrow +$$

$$- \not\longrightarrow -$$

For homonuclear diatomic molecule, there is additional symmetry w.r.t. exchange of nuclei. On exchange of nuclei

$+$  : symmetric in nuclei

$-$  : antisymmetric in nuclei

For  $\Lambda = 0$

$$+ \longrightarrow +$$

$$- \longrightarrow -$$

$$+ \not\longrightarrow -$$

$$- \not\longrightarrow +$$

} For all transitions including E1, M1, E2, Raman etc.