

## Diatomic Molecules

Electronic (gross, low res) spectra of diatomics has  
parallel in atoms  $\rightarrow$  just reduce  
sym spherical  $\rightarrow$  cylindrical (Cov, Doh)

effect  $\rightarrow$  angular momentum about  
z axis  $\leftrightarrow$  molec bond axis  
conserved, total not defined in elect only  
 $\rightarrow$  term symbols based on  
S, "ML"  $\rightarrow$   $\Lambda$

But - lots of fine structure  $\rightarrow$  now  
can have nuclear motion - quantized  
that not just translata - rot + vib

This nuclear motion can be addressed directly  
in infrared and  $\mu$ -wave regions of spectrum

Get series of very sharp spectra / can interpret  
in terms of bond strength & length of molecule

Do not need understanding of electronic structure  
 $\Rightarrow$  decoupling possible

Born - Oppenheimer

Strove Ch 3.1

Levine Ch 13.1

Molecule  $N$  nuclei  
 $n$  electrons

$$\mathcal{H} \Psi_{en}(r_i, R_\alpha) = E_{en} \Psi_{en}(r_i, R_\alpha)$$

total  $\mathcal{H} \Psi$ 

$$\mathcal{H} = \underbrace{-\sum_{\alpha=1}^N \frac{\hbar^2}{2M_\alpha} \nabla_\alpha^2}_{\text{nuc KE } -T_N} - \underbrace{\sum \frac{\hbar^2}{2m_e} \nabla_i^2}_{\text{elect KE } -T_e} - \underbrace{\sum_{i \neq j} \frac{Z_i e^2}{r_{ij}}}_{V_{ni}} + \underbrace{\sum_{ij} \frac{e^2}{r_{ij}}}_{V_{ee}} + \underbrace{\sum_{\alpha \beta} \frac{Z_\alpha Z_\beta}{R_{\alpha\beta}}}_{V_{nn}}$$

Not separable, even not  $e + \text{nuclei}$ Approx define electron Hamiltonian

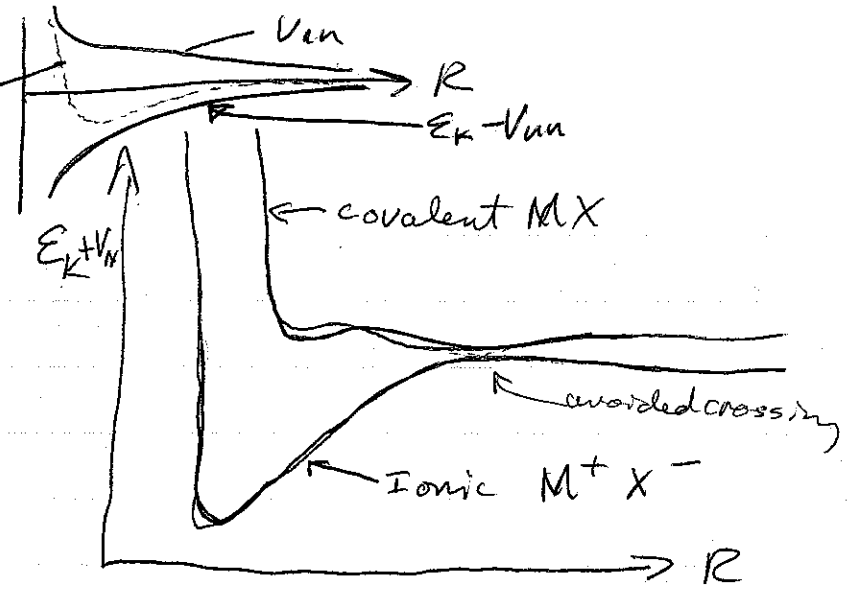
$$\mathcal{H}_{el} \phi_k(r, R) = E_k(R) \phi_k(r, R) \quad \text{where (Strove notation)}$$

$$\mathcal{H}_{el} = \mathcal{H} - T_N$$

Note  $\phi_k(r, R)$  depend parametricallyon  $R$  - nuclei pos'n[i.e. potential will change  
but no motional coord in  $R$ ]Result  $E_k(R)$  will be a potential curve  
for nuclear motion —describe how elect energy change  
as molec geom changesNote  $(E_k - V_N)$  sol'n to elect  $\mathcal{H}$ ,  $V_N$  indep  $r$   
just add on

generic diatomic

$E_k(R)$



For example  
 Fig 3.4  
 Struene

This tells us that ionic form has shorter equilibrium bond length (lowest energy on its curve) and lower overall energy than ~~the~~ neutral form (covalent)

But how do we handle the nuclear coordinates?  
 Simplest approach is to use  $E_k(R)$  as a potential energy

$$\mathcal{H}_N \chi^k(R) = (T_N + E_k(R)) \chi^k(R) = E_{k0} \chi^k(R)$$

Then (if)  $\mathcal{H} \sim \mathcal{H}_{el} + \mathcal{H}_N$   
 simple result:

$$\Psi(r, R) \sim \phi_k(r, R) \chi^k(R)$$

Born Oppenheimer says this approx useful accounts what is left out?

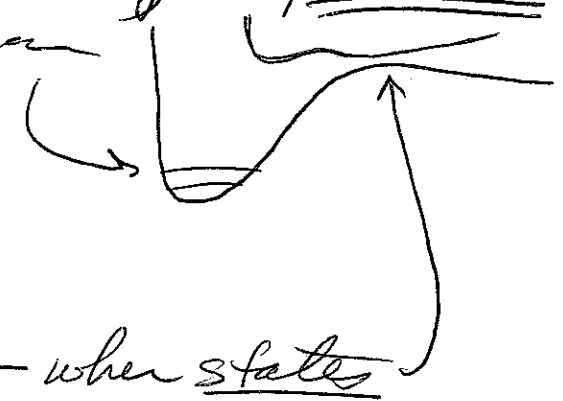
$$\mathcal{H} \Psi(r, R) = [\mathcal{H}_{el} + T_N] \phi_k \chi^k = (\mathcal{H}_{el} \phi_k) \chi^k + T_N (\phi_k \chi^k)$$

$\uparrow$  only acts on  $\phi$  - set  $r$  only       $\uparrow$  only acts on  $R$  but both  $\phi, \chi$  dep on  $R$

$$T_N \phi \chi^k = \underbrace{\left( \frac{-\hbar^2}{2m_e} \right) \left[ (\nabla^2 \phi) \chi + (\nabla \phi)(\nabla \chi) + \phi (\nabla^2 \chi) \right]}_{\text{Cross terms, B-O assumes neglect}} + \underbrace{\phi (\nabla^2 \chi)}_{\substack{\uparrow \\ \text{separated nuclear} \\ \text{K.E. term}}}$$

idea if  $\phi(r, R)$  varies slowly with  $R$   
 i.e. nature of the state almost const  
 [elect. dist. orbitals, etc.]  
 then  $\nabla \phi \sim 0 \rightarrow$  measure rate of change w/  $R$

Normally safe — particularly in pot. min  
 ex — 3.4 Sturm again  
 at bottom of well  
 have well defined  
 ionic states



Problem (Sturm p 79-82) — when states  
cross — if sym same, big mix  
 and  $\nabla \phi \neq 0$  "Breakdown BO"  $\rightarrow$  JT effect

Now if  $\boxed{\nabla^2 \phi = \nabla \phi = 0}$   $\rightarrow$  solving problem  
 for  $\phi$  is same as assuming  
 nuclei are fixed at  $R$   
 or  $\mathcal{H} \phi(r) = \epsilon(R) \phi(r, R) \rightarrow$  just like  
 standard

Now if assume  $\square$

$$(\mathcal{H}_e + T_N) \phi \chi = (\mathcal{H}_e \phi) \chi^k + \phi_k T_N \chi^k = \epsilon^k \phi_k \chi^k$$

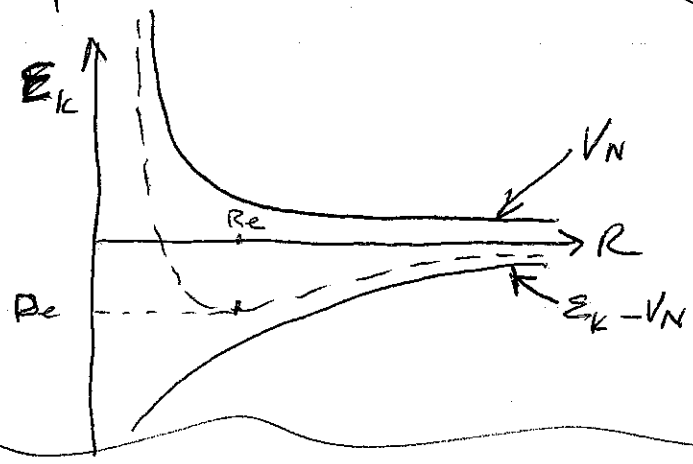
divide by  $\phi \chi$

$$(\mathcal{H}_e \phi / \phi) + T_N \chi / \chi = \epsilon^k$$

This separates to  $\chi\phi/\phi = \epsilon = -T_N\chi/\chi + \epsilon$   
 so  $\phi_k = \epsilon_k \phi_k$  as before

$T_N \chi_k + \epsilon_k \chi_k = \epsilon_k^k \chi_k$  — nuclear Hamiltonian for motion of nuclei

Diatomic picture



$V_N$  — positive repulsion — blow up  
 $E_k - V_N$  negative — attr. elect to both nuclei inc. close nuclei (united atom)  
 → attractive potential  
 → equilibrium,  $\frac{\partial E}{\partial R} = 0$

Refocus on above equation → interest is energy of molecule (internal) — quantize independent of where it is (assid sum trans K.E. which is continuous — classical)

Separate out coord of center of Mass — No term above mix i.e.  $E(R)$  internal

$\chi_{ij}^k(R) = \chi_{ij}^k(R') \cdot T(XYZ)$   
 $R' = R - (X, Y, Z)$  shift origin to cofM  
 $X = \sum m_\alpha x_\alpha / \sum m_\alpha$  etc  
 $\sum m_\alpha x'_\alpha = 0$

at cofM  
General Treatment WDC ch. 11

Only an issue for assum diatomic  
 $T_N \chi T = \left( \frac{-\hbar^2}{2M_A} \nabla_A^2 + \frac{-\hbar^2}{2M_B} \nabla_B^2 \right) \chi T$   
 $= \frac{-\hbar^2}{2} \left( \frac{1}{M_A + M_B} \nabla_C^2 + \frac{1}{\mu} \nabla_{R'}^2 \right) \chi T$

hence  $\mu = \frac{M_A M_B}{M_A + M_B}$  - reduced mass

→ Prove this for Hooke + k  $X' = X_A - X_B$

$M_{rot} = M_A + M_B = M_{tot}$

in 4-D:  $\left( \frac{1}{M_A} \frac{\partial^2}{\partial X_A^2} + \frac{1}{M_B} \frac{\partial^2}{\partial X_B^2} \right) \rightarrow \left( \frac{1}{M_A + M_B} \frac{\partial^2}{\partial X_C^2} + \frac{1}{\mu} \frac{\partial^2}{\partial X'^2} \right)$

Now have separation - divide by  $\chi(T)$

$$\frac{1}{T} \left( \frac{-\hbar^2}{2(M_A + M_B)} \right) \nabla_C^2 T + \frac{1}{\chi} \left( \frac{-\hbar^2}{2\mu} \right) \nabla_{R'}^2 \chi = E - E_k(R)$$

$$\frac{-\hbar^2}{2M_{tot}} \nabla_C^2 T = E_{trans} T \rightarrow \text{free moving}$$

$$T = e^{i\vec{k} \cdot \vec{R}_C} \rightarrow \text{plane wave soln}$$

$$E_{trans} = \left( \frac{-\hbar^2}{2M_{tot}} (-k^2) \right) = \frac{\hbar^2 k^2}{2M_{tot}} \quad k = \sqrt{2E_{trans} M} / \hbar$$

Note # coord reduce →  $3N(R) \rightarrow (3N-3)R'$

Internal solution:  $\frac{-\hbar^2}{2\mu} \nabla_{R'}^2 \chi + E_k(R') \chi = (E + E_{trans}) \chi$

1-31-92

in general - this vib + rot, sep out Euler angles (rot) →  $3N-6$  vib

Diatomic: Now note that  $E(R')$  only depends on sep'n of nuclei - not orientation

Change to Spherical Coordinates

$$x', y', z' \rightarrow R, \theta, \phi$$

2 coord describe orientation  $\theta, \phi$  (rot)

1 coord describe vibration  $(3N-5=1)$

Again a central force problem same as for H-atom soln

F-31-92

Ch 3 - Sturm diatomic vib/rat

We have used B-O approx to separate nuclear & elect coord

Nuclear Hamiltonian

$$T_N \chi_v^k(R) + E_k(R) \chi_v^k(R) = (E_v^k + E_{trans}) \chi_v^k(R)$$

$\uparrow$  kinetic energy nucl       $\uparrow$  pot  $E$  nuclei is soln to elect Hamiltonian + nucl repuls

$3N - R$  values

if shift origin  $R' = R - (x^c, y^c, z^c)$

$3N - R'$  values

However if  $(x^c, y^c, z^c)$  center of mass

3 equations:  $\sum m_i x_i^c = 0$

These are restrictions on  $R' \rightarrow$  Now  $3N - 3$  independent coordinates

$$\chi_v^k(R) = \chi_v^k(R') T(x^c, y^c, z^c)$$

This separates,  $T \rightarrow$  plane wave /  $E_{trans}$  not quantized

Now solve:  $\frac{-\hbar^2}{2\mu_N} \nabla_{R'}^2 \chi(R') + E_k(R') \chi(R') = E_v^k \chi(R')$

but  $E(R')$  only depends on bond distance (scalar)  
 $x^c, y^c, z^c \rightarrow R, \theta, \phi$  2 coord  $\theta, \phi \rightarrow$  orientable + KE  
central force 1 coord  $R \rightarrow$  has pot energy

$\mu_N = \frac{M_A M_B}{M_A + M_B}$

$3N - 5 = 1$

In  $R, \theta, \phi$  just some transformation as for the H-atom problem

$$\left\{ \frac{-\hbar^2}{2\mu} \left[ \frac{1}{R^2} \frac{\partial}{\partial R} (R^2 \frac{\partial}{\partial R}) + \frac{1}{R^2 \sin \theta} \frac{\partial}{\partial \theta} (\sin \theta \frac{\partial}{\partial \theta}) + \frac{1}{R^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] + E(R) \right\} \chi = E \chi$$

Now if  $\chi(R, \theta, \phi) = \chi_r(R) Y_{JM}(\theta, \phi)$

Then this equation separates =

mult  $R^2$

divide by  $\chi(R) Y_{JM}(\theta, \phi)$

let:

$$-J(J+1) \frac{\hbar^2}{2\mu R^2} = \underbrace{\frac{1}{Y_{JM}} \left[ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} (\sin \theta \frac{\partial}{\partial \theta}) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right]}_{\hat{J}^2 / \hbar^2} \frac{1}{\chi_r} \left[ \frac{1}{R^2} \frac{\partial}{\partial R} (R^2 \frac{\partial}{\partial R}) \chi_r \right] - \frac{E(R)}{\hbar^2}$$

Now from any mom :

$$\hat{J}^2 Y_{JM} = J(J+1) \hbar^2$$

$$\hat{J}_z Y_{JM} = J_z \hbar = i \hbar \frac{\partial}{\partial \phi} Y_{JM}$$

Strove 3.2

→ Rigid rotator

assume  $R = \text{const} = R_0$

(no loss general)

then  $E_k(R) = U(R) = \text{const} \rightarrow$  let be zero

$$\frac{-\hbar^2}{2\mu R_0^2} \left[ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} (\sin \theta \frac{\partial}{\partial \theta}) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] \chi_{\text{rot}} = E_{\text{rot}} \chi_{\text{rot}}$$

this is total angular momentum op  $-\hat{J}^2 / \hbar^2$

$$\frac{-\hbar^2}{2\mu R_0^2} \left( \frac{-\hat{J}^2}{\hbar^2} \right) \chi_{\text{rot}} = \frac{\hat{J}^2}{2I} \chi_{\text{rot}} = E_{\text{rot}} \chi_{\text{rot}}$$

$I = \mu R_0^2$   
 moment inertia

however show  $I = \mu R_0^2 + m R_0^2$



eigen functions of  $\hat{J}^2$  are  $Y_{JM}(\theta, \phi) = Y_{rot}$

$$\hat{J}^2 Y_{JM} = J(J+1) \hbar^2 Y_{JM}$$

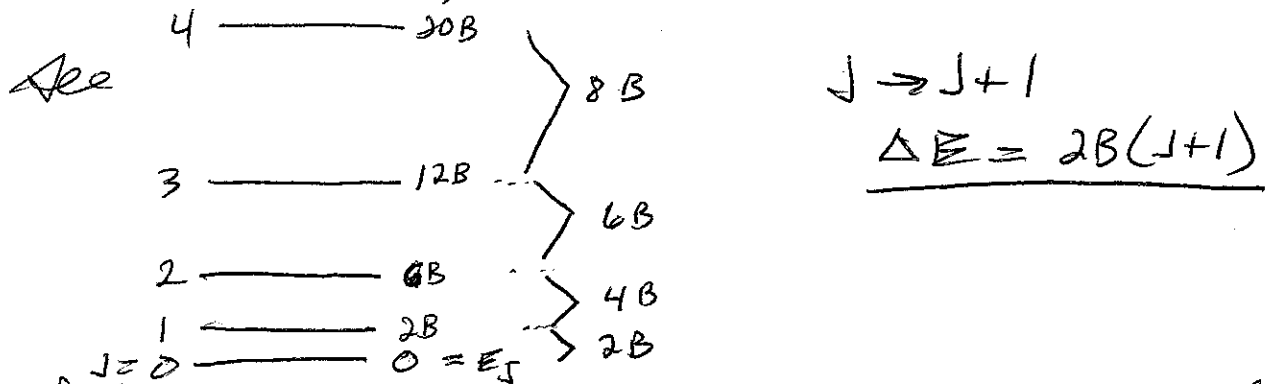
$$\hat{J}_z Y_{JM} = M \hbar Y_{JM}$$

Therefore  $E_{rot} = \frac{J(J+1) \hbar^2}{2I}$

commonly express  $= B J(J+1)$

$$B = \frac{\hbar^2}{2I}$$

Now since  $J = 0, 1, 2, 3, \dots$   
no energy dependence on  $M$



Pure rotation

molecule has a permanent (equiv)

Selector rules: if electric dipole moment

$$\mu \sim (x, y, z) \sim R_0 \sin \theta \cos \phi, R_0 \sin \theta \sin \phi, R_0 \cos \theta$$

leads to:  $\Delta J = \pm 1$        $\Delta M = 0, \pm 1$

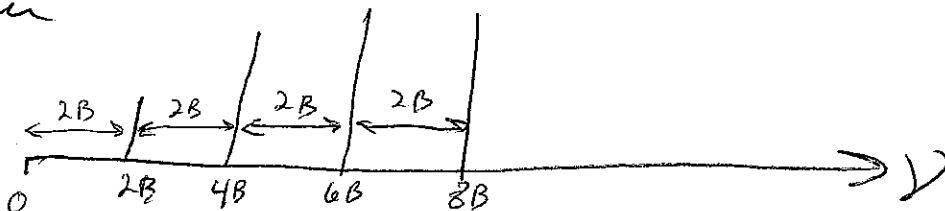
Regular Spacing between transitions

$$\Delta E_{J \rightarrow J+1} = 2B(J+1)$$

$$\Delta E_{J+1 \rightarrow J+2} = 2B(J+2)$$

shift  $\neq 2B$

Spectrum



Measure spacing  $\rightarrow$  get equil bond dist III-9

$$R_0 = (\hbar^2 / 2hc\mu B)$$

Where do you measure?

depends on B  $\rightarrow$  inverse on I

Lighter / smaller molecules ( $\mu B^2 \sim$  small)

have large B  $\rightarrow$  far-ir

ex: B -  $\text{H}_2$  - 60.8  $\text{cm}^{-1}$   $\rightarrow$  nope mount

$\uparrow$   $^{35}\text{HCl}$  - 10.6 (heavier)  
 $\uparrow$   $^{16}\text{OH}$  - 18.9 (longer)  
 $\uparrow$  HF - 20.9

Heavier - need to go to  $\mu$ -wave region ( $\mu B^2 \sim$  big, B small)

ex: CO - 1.93  $\text{cm}^{-1}$

ICI - 0.114  $\text{cm}^{-1}$  (heavy)

NO - 1.67 (longer bond)

$\mu$ -wave covers large range from few  $\rightarrow$  many GHz

$$1 \text{ cm}^{-1} \sim 30 \text{ GHz}$$

$$1 \text{ cm}^{-1} = 3 \times 10^{10} \text{ cm/sec} \sim 30 \times 10^9 \text{ sec}^{-1}$$

Intensity also contains information  $\rightarrow$

intensity of  $\Delta E_J$   $J \rightarrow J+1$

proportional to number

molecules in  $E_J$

Boltzmann factor n-molecules

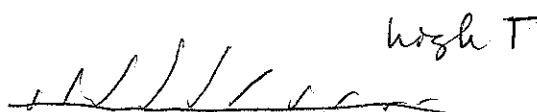
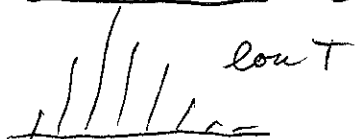
$$n_J / n = d_J \exp(-E_J / kT)$$

$$d_J = \text{degeneracy} = (2J+1)$$

$$= (2J+1) \exp(-hcBJ(J+1) / kT)$$

hc - convert to eV

So intensity builds  $(2J+1)$  + decays  $\exp$



see Strune  
 84  
 Table 3.1

$\mu$  wave [aside]

Strune  
 Fig 3.6

Now lets return to total nuclear Hamiltonian

$$\left\{ \frac{-\hbar^2}{2\mu_N} \left[ \frac{1}{R^2} \frac{\partial}{\partial R} \left( R^2 \frac{\partial}{\partial R} \right) - \frac{J^2}{\hbar^2 R^2} \right] \right\} \chi_k = E \chi_k$$

Now hope to separate use:  $\chi_k = \frac{1}{R} S(R) Y_{JM}(\theta, \phi)$

$$\text{recall } J^2 Y_{JM} = J(J+1) \hbar^2 Y_{JM}$$

left term operate only on  $\frac{1}{R} S(R)$ ,  $J$  only on  $Y_{JM}$   
so can divide out  $Y_{JM}$

$$\frac{-\hbar^2}{2\mu_N} \left[ \frac{1}{R} \frac{\partial^2 S}{\partial R^2} Y_{JM} \right] - \frac{J(J+1)}{R^2} \left( \frac{S}{R} \right) (Y_{JM}) = E \frac{S}{R} Y_{JM}$$

$$T = \frac{\partial}{\partial R} \left( \frac{S(R)}{R} \right) = \frac{1}{R^2} S(R) + \frac{1}{R} S'(R)$$

$$\frac{\partial}{\partial R} (R^2 T) = -S'(R) + S'(R) + R S''$$

divide  $Y_{JM}$  mult  $R$ ,  $-2\mu/\hbar^2$

$$\frac{\partial^2 S(R)}{dR^2} + \frac{2\mu_N}{\hbar^2} \left[ E - \underbrace{E_k}_{\text{struc}} - \frac{J(J+1)\hbar^2}{2\mu R^2} \right] = 0$$

$$U_{\text{vib}} = U_{kk}(R) - \frac{J(J+1)\hbar^2}{2\mu R^2}$$

↑  
electronic  
energy

↑  
centrifugal  
potential } coupling  
rot-vib

Normally assume

$$2\mu R^2 \sim 2I$$

(rigid  
rotor)

then 2nd term is just rot energy

$$\underline{B J(J+1)}$$

rewrite  $\left( \frac{-\hbar^2}{2\mu} \frac{d^2}{dR^2} + U_{kk}(R) \right) S = (E - E_{\text{rot}}) S = E_{\text{vib}} S$

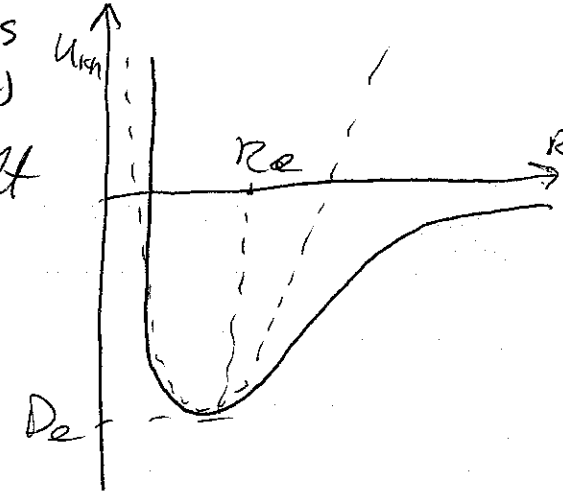
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for diatomic - solved rot. prob / assume Rigid

III-11

Vibrational H:  $\frac{-\hbar^2}{2\mu} \frac{d^2 S}{dR^2} + U_{\text{vib}}(R) = (E - E_{\text{rot}}) S = E_{\text{vib}} S(R)$

Treating potential is difficult  
very non linear / non analyt



So try to evaluate where most important  $\rightarrow R_e$   
expand around potential min.

$$U_{\text{vib}}(R) = U_{\text{vib}}(R_e) + \left(\frac{\partial U_{\text{vib}}}{\partial R}\right)_{R=R_e} (R-R_e) + \frac{1}{2} \left(\frac{\partial^2 U_{\text{vib}}}{\partial R^2}\right)_{R=R_e} (R-R_e)^2 + \dots$$

$\uparrow$  constant no effect on motion  $\rightarrow$  put in  $E_{\text{vib}}$

$\uparrow$  zero at  $R_e$  (min)

harmonic term - parabolic potential

Simplification

$$\frac{-\hbar^2}{2\mu} \frac{d^2 S(R)}{dR^2} + \frac{1}{2} \left(\frac{d^2 U}{dR^2}\right)_{R_e} (R-R_e)^2 S(R) = E_{\text{vib}} S(R)$$

$\uparrow$  k - force constant

This is 1-D harmonic oscillator

sols:

$$S(R) = N v e^{-x^2/2} H_v(x) \equiv |v\rangle$$

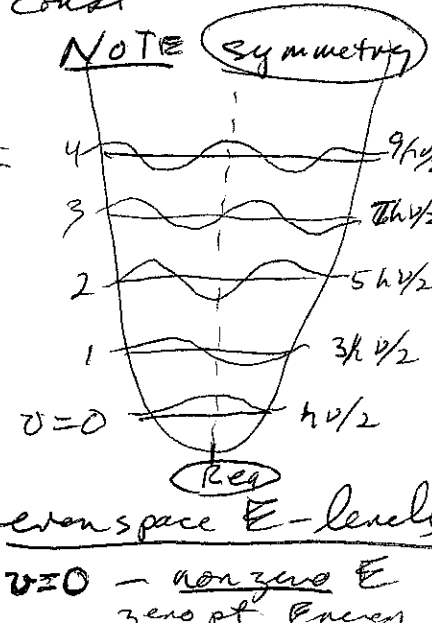
$$E_{\text{vib}} = \hbar \omega (v + 1/2) = (v + 1/2) h \nu$$

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

$$x = (R - R_e) \sqrt{\mu \omega / \hbar} \quad \omega = \sqrt{k/\mu} = 2\pi \nu$$

Hermite polynomials

$$\begin{cases} H_0(x) = 1 & H_2(x) = 4x^2 - 2 \\ H_1(x) = 2x & H_3(x) = 8x^3 - 12x \end{cases}$$



Spectroscopy: see facts even/odd alternate  
 operators  $\mu$ -odd  $\langle \psi_a | \mu | \psi_b \rangle$   
 must be even to be non-zero  
 $\psi_a + \psi_b$  must be odd/even or even/odd

let  $q = (R - R_e)$

$$\mu = \mu_0 + \left(\frac{\partial \mu}{\partial q}\right)_0 q + \frac{1}{2} \left(\frac{\partial^2 \mu}{\partial q^2}\right)_0 q^2 + \dots$$

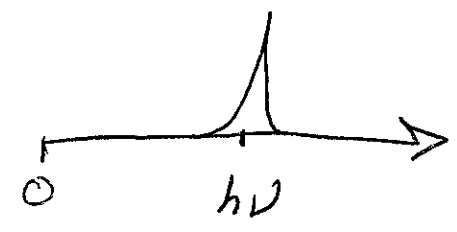
↑  
 has no effect on  $q \rightarrow$  so a const  
 $\langle \chi_a | \mu_0 | \chi_b \rangle = \mu_0 \langle \chi_a | \chi_b \rangle = \delta_{ab}$   
 $\Rightarrow$  no transition const

2nd term:  $\langle \chi_a | \left(\frac{\partial \mu}{\partial q}\right) q | \chi_b \rangle = \left(\frac{\partial \mu}{\partial q}\right) \langle \chi_a | q | \chi_b \rangle$   
 from properties of Hermite polynomials

$\Delta v = \pm 1$  only plus  $\frac{\partial \mu}{\partial q} \neq 0$  { hetero nuclear diatomic

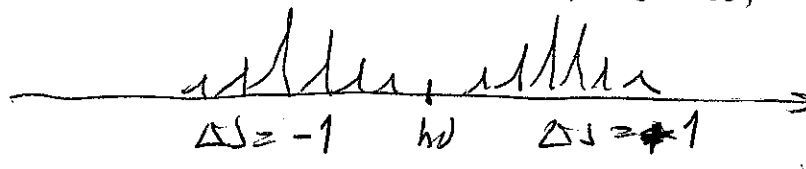
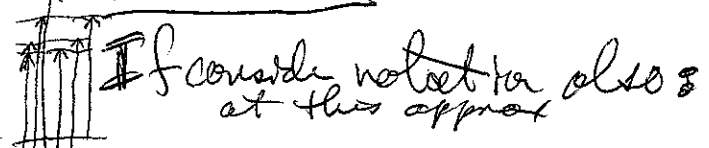
[easy to see  $\rightarrow$   $H_v(q) q \approx (H_{v+1}(q) + H_{v-1}(q))$ ]

Result - E levels equally spaced  
harm - single obs line



Handout  $0 \rightarrow 1, 1 \rightarrow 2, 2 \rightarrow 3$  etc,

P-branch R-branch



Note no peak at  $h\nu \rightarrow$  ~~50%~~ forbidden / equal space 2B (rot)

Where are these transitions  $\rightarrow v = \frac{1}{2\pi} \sqrt{k/\mu}$   
 inc. mass  $\rightarrow$  dec  $v$   
 inc. force constant  $\rightarrow$  inc bond strength  $\rightarrow$  inc  $v$

ex:

|                                |   |         |                 |  |
|--------------------------------|---|---------|-----------------|--|
| ${}^2\text{H}_2$               | - | 4401.21 | } mass          | $\left\langle \begin{array}{l} \text{I}_2 - 214 \\ \text{ICl} - 384 \end{array} \right.$ |
| ${}^1\text{H}^{35}\text{Cl}$   | - | 2890 ?  |                 |  |
| ${}^{16}\text{O}_2$            | - | 1580    | } bond strength |  |
| ${}^{12}\text{C}^{16}\text{O}$ | - | 2169    |                 |  |

these are  $\omega_2$  values  
electronic anharmonicity

Now what about other transitions?

$$\mu = \mu_0 + \frac{2e}{29} q + \frac{1}{2} \frac{2^2 e^2}{29^2} q^2 + \dots$$

3rd term can lead to  $\Delta v = \pm 2$   
 & 4th " " "  $\Delta v = \pm 3$

These will be progressively weaker  
 Typical decrease 7 orders mag  $2 \rightarrow 3 \rightarrow 4$   
 and maybe 2 orders  $1 \rightarrow 2$

For the most part we will ignore these,  
 but should remember that still exist  
 and lead to means of investigating  
 energy levels higher than  $v=1$

Reality — spacings not constant for  
 $v=2 \neq v=1$   
 — spacing rotational lines change  $B_{v=0} \neq B_{v=1}$



normally in  $^1\Sigma_g^+$  state  $\rightarrow$  closed shell homonuclear  
 then

$$P_{ab} \psi = (-1)^J \psi_{el}(vJM) \cdot (P_{ab} f_{ns})$$

For homonuclear diatomics

If nuclei are fermions ( $I = \frac{n+1}{2}$ ) half int  
 then all (total)  $\psi$  must be antisym

If nuclei are bosons ( $I = 2n$ ) integers  
 then all (total)  $\psi$  must be sym

This leads to an alternation in intensity  
 for the rotational transitions  
 (i.e.  $2J+1$  is insufficient to  
 account for degeneracy  $\rightarrow$  include  
 effects of  $I$ )

observe  $\rightarrow$  lect spect  
 or Raman effect  
 $\Delta J = \pm 2$

**ex**  $(H_2)$ :  $^1\Sigma_g^+$   $\rightarrow$   $J = 1, 3, 5, \dots$  odd  
 $\rightarrow$  require sym  $f_{ns} \rightarrow d_N = (\frac{1}{2}+1)(1+1) = 3$

$J = 0, 2, 4, \dots$  even  
 $\rightarrow$  require anti  $f_{ns} \rightarrow d_N = \frac{1}{2}(1+1) = 1$

$\therefore$  relative pop

(no IR!)

but for  $(^{12}C_2) \rightarrow ^1\Sigma_g^+$   
 $I = 0$

boson  $\rightarrow$  req sym w/f

$J = 0, 2, 4, \dots$   $d_N = (0+1)(0+1) = 1$

$J = 1, 3, 5, \dots$   $\rightarrow$  asym  $f_{ns}$   
 $d_N = 0(0+1) = 0$

missing levels

rel. pop.



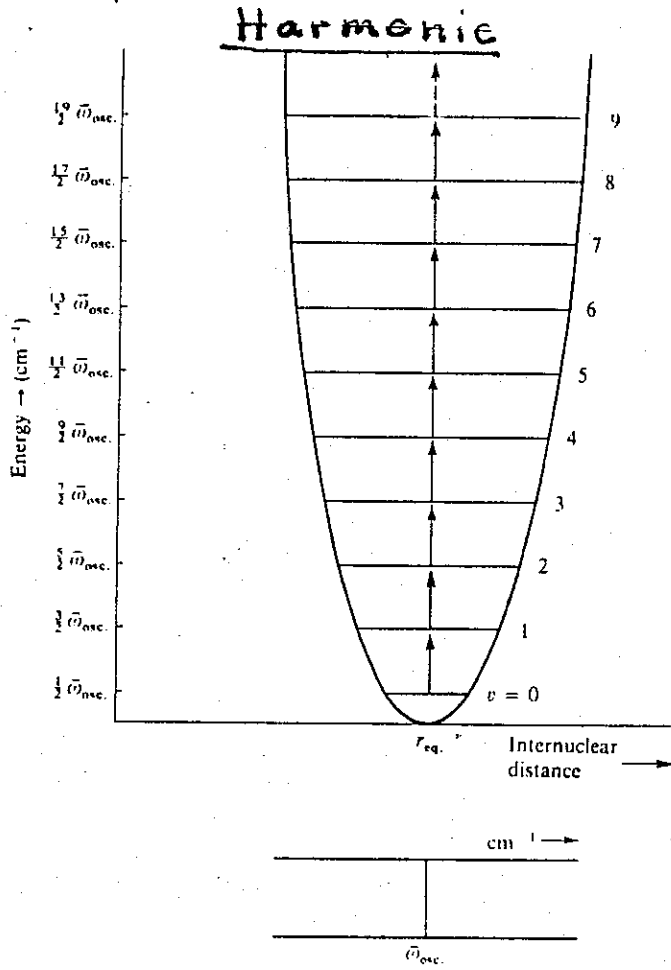


Fig. 3.2: The allowed vibrational energy levels and transitions between them for a diatomic molecule undergoing simple harmonic motion.

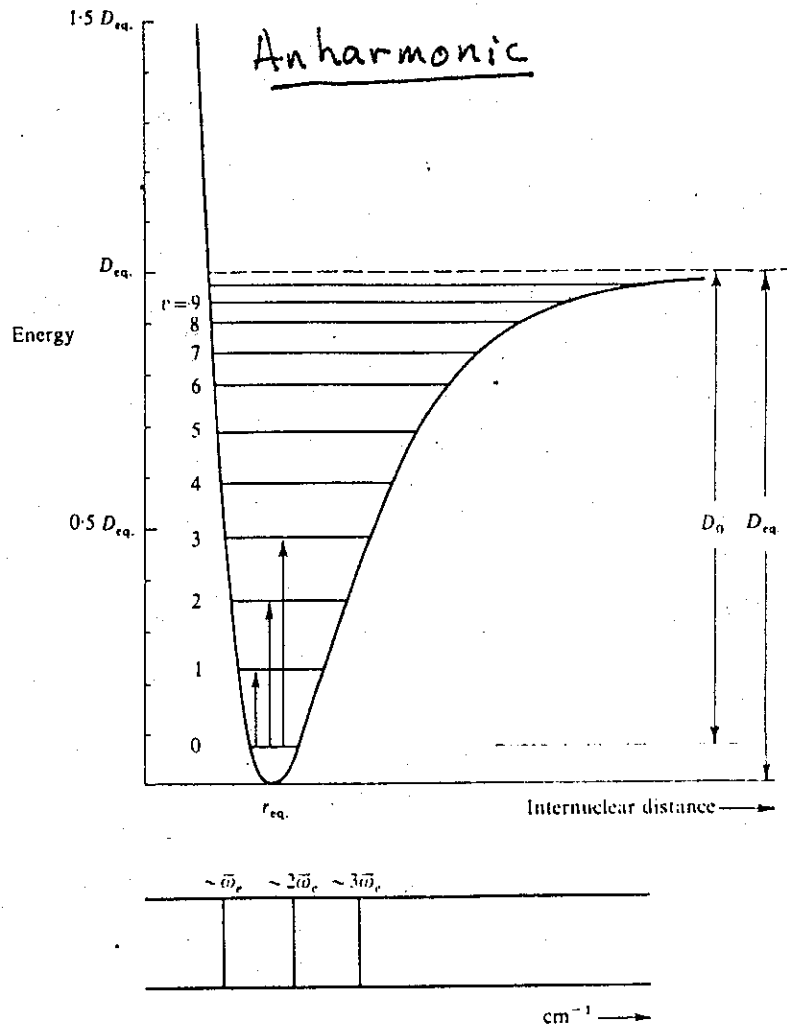


Fig. 3.4: The allowed vibrational energy levels and some transitions between them for a diatomic molecule undergoing anharmonic oscillations.

Chem 347 = Rotational-Vibrational Spectra  
 C.N. Banwell "Fundamentals of Molecular Spectroscopy"  
 McGraw-Hill, 1972, 2nd ed.

Allowed Transitions  
 P + R branches

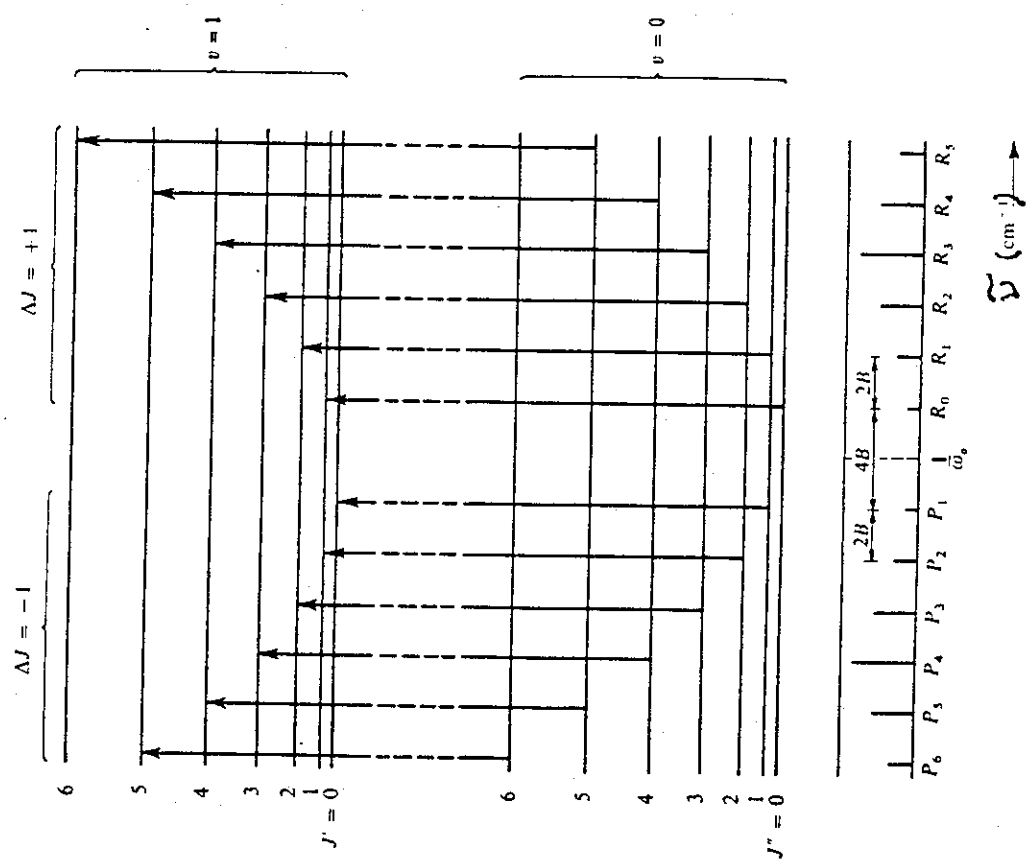


Fig. 3.6 Some transitions between the rotational vibrational energy levels of a diatomic molecule together with the spectrum arising from them.

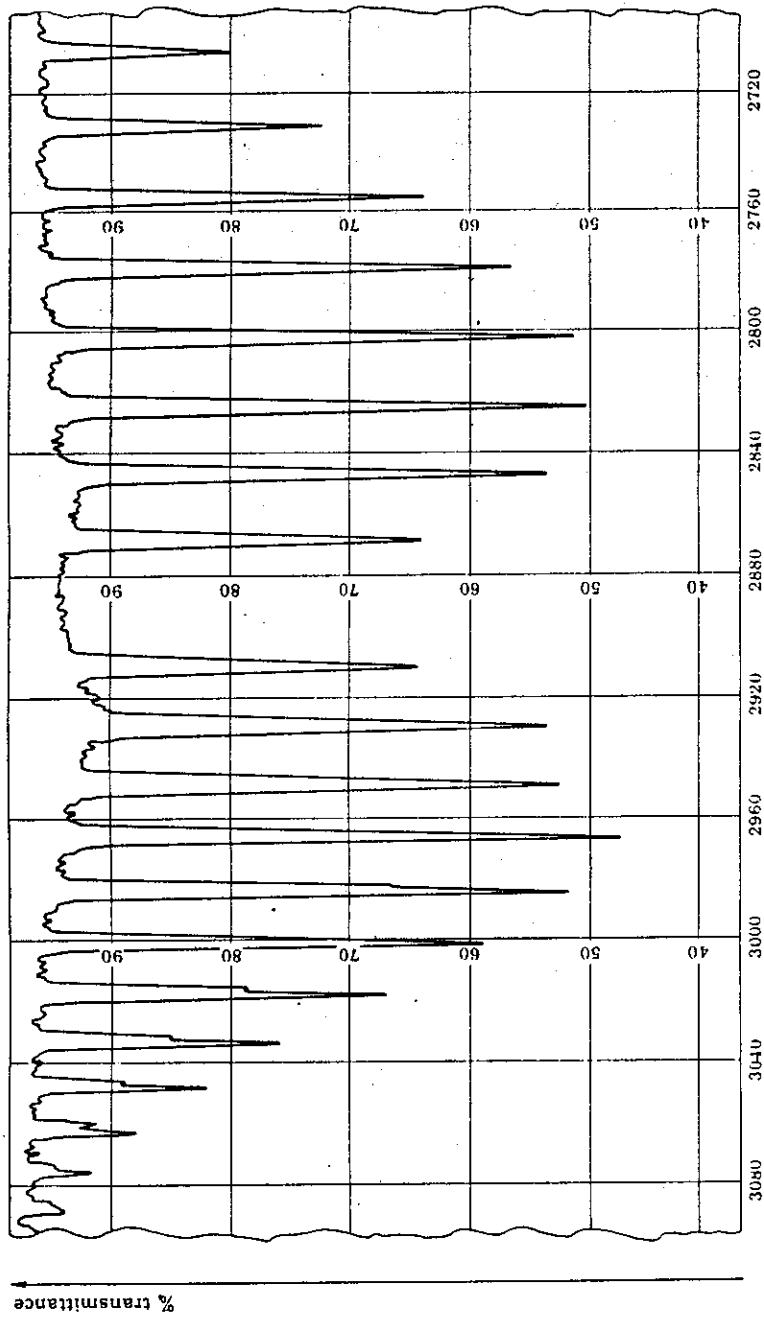


Fig. V-22 High-resolution HCl spectrum (on a Beckman IR-7).

$\bar{\nu}$  (cm<sup>-1</sup>)

PQR  
contour

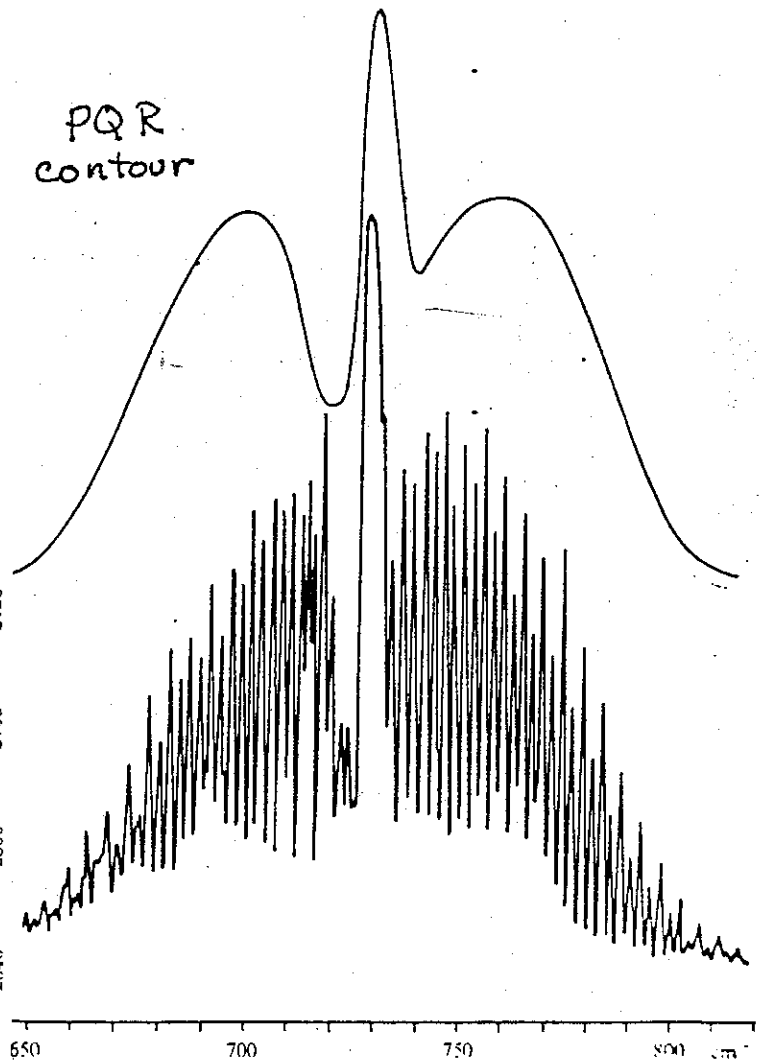


Fig. 3.16: The spectrum of a bending mode of acetylene, HC≡CH, showing the strong, weak, strong, weak, . . . intensity alternation in the rotational fine structure due to the nuclear spin of the hydrogen atoms.

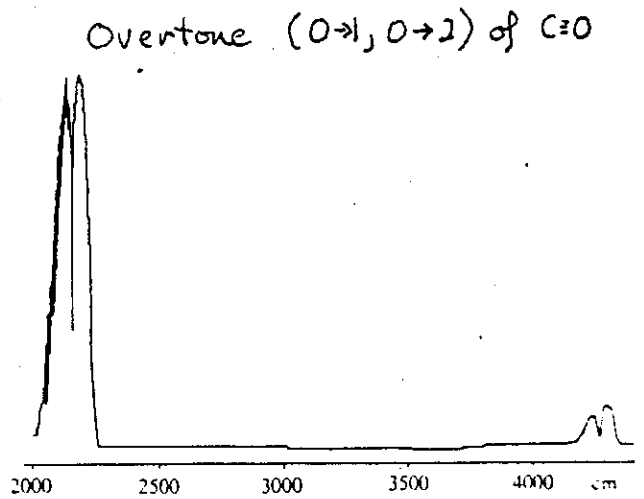
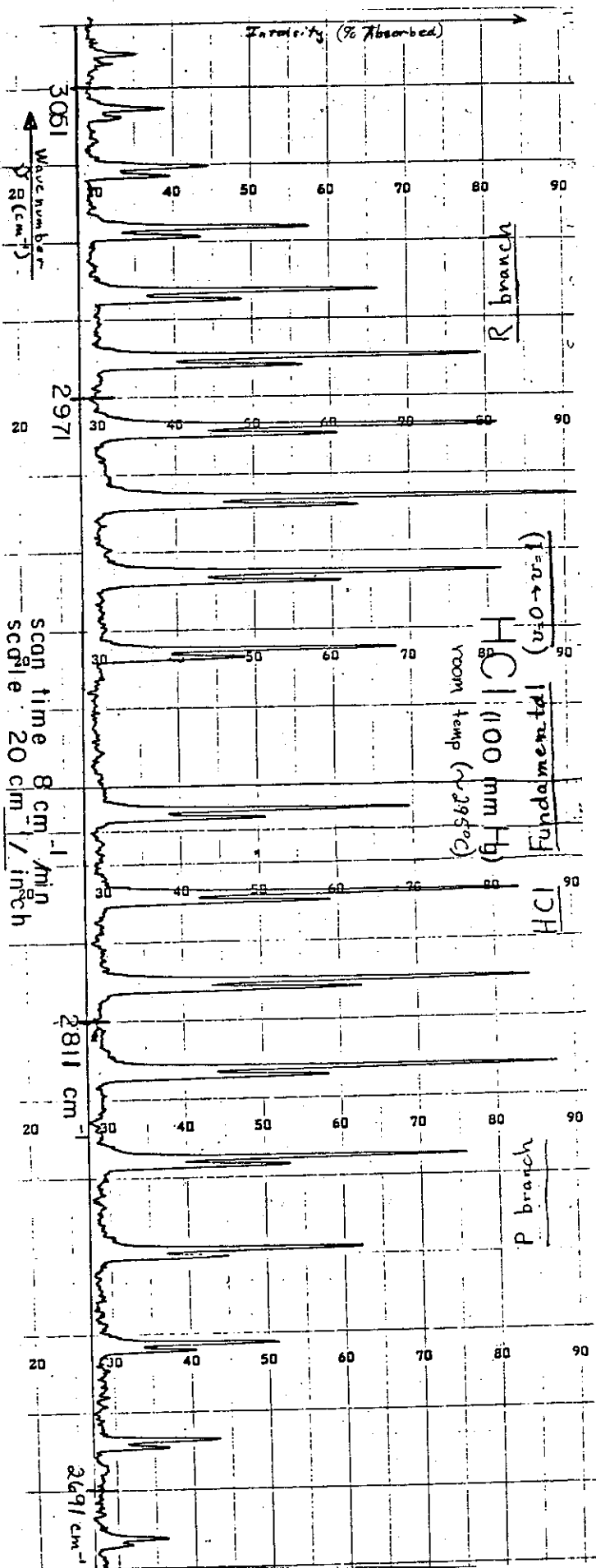
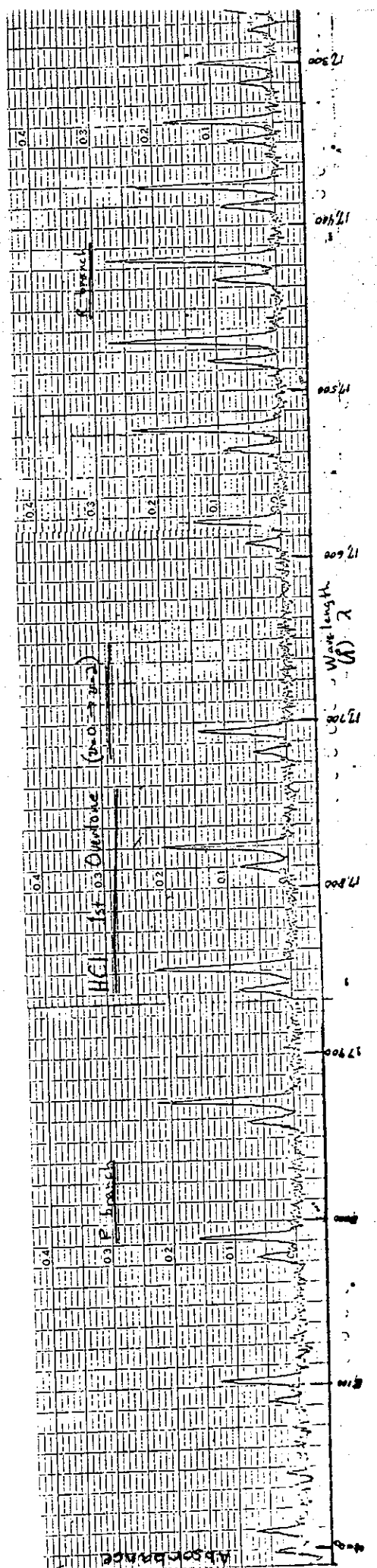


Fig. 3.7(a): The fundamental absorption (centred at about 2143 cm<sup>-1</sup>) and the first overtone (centred at about 4260 cm<sup>-1</sup>) of carbon monoxide; the fine structure of the P branch in the fundamental is partially resolved (at a pressure 650 mm Hg in a 10 cm cell.)

Banwell, Fundamentals of Mol Spectroscopy



HCl rotation-vibration Spectra



example of increased resolution (ability to sep  $\lambda$  &  $\lambda'$ )

Discuss HCl spectra:  $0 \rightarrow 1$  &  $0 \rightarrow 2$  spectra

a) note: doubling of peaks due to  $Cl^{35}$  &  $Cl^{37}$   
 $HCl^{35}$  - higher energy & bigger  
 (Cl mw  $\sim 35.5 \Rightarrow 75\% 35, 25\% 37$ )  
 i.e.  $\nu_0$  different  $\sim \sqrt{K/m}$  - same k  
 if had DCl where peak?  $\sim 2100 cm^{-1}$

b) note: splitting of peaks (blend) bigger in P branch than in R branch - due to diff in B  $gnd$  &  $ex$   $\rightarrow$  most obvious in  $0 \rightarrow 2$  spectrum

c) note: splitting of  $35-37$  changes slightly due to diff of  $B^{35}$  &  $B^{37}$

d) note:  $\nu_0(0 \rightarrow 2) \neq 2 \nu_0(0 \rightarrow 1)$

|                   |                               |                               |
|-------------------|-------------------------------|-------------------------------|
| $0 \rightarrow 1$ | $\nu_0^{35} = 2885.9 cm^{-1}$ | $\nu_0^{37} = 2883.6 cm^{-1}$ |
| $0 \rightarrow 2$ | $\nu_0^{35} \sim 5668$        | $\nu_0^{37} \sim 5664$        |
| $\Delta(2-2.1)$   | $-104 cm^{-1}$                | $-103 cm^{-1}$                |

e) could use formula from class to detm  $B_0$  &  $B_1$  on  $B_0$  &  $B_2$  from diff in peaks - to describe would need series of  $B_i$ 's

more useful:  
 evaluate

$$E = h\nu_0(v + \frac{1}{2}) + B_e J(J+1) - \alpha_e(v + \frac{1}{2})J(J+1)$$

$$\nu_e = \nu_0 + (2B_e - 3\alpha_e) + (2B_e - 4\alpha_e)J - \alpha_e J^2$$

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

$$(\Delta J = -1) \quad v_p = \hat{v}_0 + (2B_e - 2\alpha_e)J - \alpha_e J^2 \quad J = 1, 2, 3, \dots$$

now can analyse spectra by introducing  

$$m = \begin{cases} J+1 & \text{R branch} \\ -J & \text{P branch} \end{cases}$$

$$v = \hat{v}_0 + (2B_e - 2\alpha_e)m - \alpha_e m^2$$

so if measure all frequencies & make a table can also measure differences between them ( $\Delta v$ 's)

consider  $\Delta v(m) = v(m+1) - v(m)$

$$\Delta v = (2B_e - 2\alpha_e) - 2\alpha_e m - \alpha_e = \underline{-2\alpha_e m + (2B_e - 3\alpha_e)}$$

this last is a linear equation in  $m$   
hence, plot  $\Delta v(m)$  vs  $m$

slope :  $-2\alpha_e$

intercept :  $2B_e - 3\alpha_e$

for  $0 \rightarrow 1$  spectra:

(was determined by a physical chemistry lab student)

|            | $\text{HCl}^{35}$        | $\text{HCl}^{37}$        |
|------------|--------------------------|--------------------------|
| $B_e$      | $10.492 \text{ cm}^{-1}$ | $10.456 \text{ cm}^{-1}$ |
| $\alpha_e$ | $0.2877 \text{ cm}^{-1}$ | $0.2875 \text{ cm}^{-1}$ |
| $r_e$      | $1.280 \text{ \AA}$      | $1.279 \text{ \AA}$      |

→  
geometry!