

Molecular Spectroscopy - Chapter B

Interaction of electromagnetic Radiation with (atomic and) molecular

Microwave For infrared

$$10^8 - \omega'' \text{ Hz} \quad \omega'' - 10^{13}$$

$$< 3\text{ cm}^{-1}$$

$$\omega'' - \omega^+ 4$$

$$10^{13} - 10^{16}$$

$$\text{UV-Vis}$$

$$10^{14} - 10^{16}$$

$$3 - 300\text{ cm}^{-1}$$

$$300 - 15000\text{ cm}^{-1}$$

$$15000\text{ cm}^{-1}$$

Rotations
of polyatomic
molecules,

Rotations
of small
molecules

Bond
Vibrations

Electronic
Transitions

Rigid Rota

Harmonic
Oscillate

Molecular
Oscill.

1. Deviations from idealized model.

- Rigid Rota \rightarrow Centrifugal Distortion

- Harmonic Oscillate \rightarrow Anharmonic Vibrations

2. Coupling Between Transitions

- Rot-Vib coupling

- Vibronic coupling

Selection Rules + Fermi's Golden Rule

$$\begin{cases}
 (\Delta S = 0, \Delta L = \pm 1) \\
 (\Delta J = \pm 1, \mu \neq 0) \\
 (\Delta J = \pm 1, \langle \mu \rangle \neq 0)
 \end{cases} \quad \overbrace{\Delta E = h\nu}$$

Time-Dependent S.E.

$$\hat{H}\Psi = i\hbar \frac{\partial \Psi}{\partial t}$$

$$\overline{\Psi}_n(n,+) = \Psi_n(n) e^{-\frac{iE_n t}{\hbar}}, \text{ where } \hat{H}\Psi_n(n) = E_n \Psi_n(n)$$

2-state system:

$$\overline{\Psi}_2 = \Psi_2 e^{-\frac{iE_2 t}{\hbar}}$$

$$\overline{\Psi}_1 = \Psi_1 e^{-\frac{iE_1 t}{\hbar}}$$

$$\hat{H} = \hat{H}^{(0)} + \hat{H}^{(c)}$$

time independent
hamiltonian

time
dependent
perturbation

Perturbation: Electromagnetic wave

$$\hat{H}^{(c)} = -\vec{\mu} \cdot \vec{E} = -\mu \underbrace{E_0 \cos(\omega t)}_{E\text{-field oscillates with freq. } \omega}$$

molecule dipole moment electric field

$$\overline{\Psi}(n,+) = \Psi_1(+) \overline{\Psi}_1(n,+) + \Psi_2(+) \overline{\Psi}_2(n,+)$$

$\Psi_1(+) \cdot \Psi_1^*(+)$ \Rightarrow probability of state 1

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$$\hat{H} \bar{\Psi}(r,+) = i\hbar \frac{\partial \bar{\Psi}(r,+)}{\partial t}$$

$$\begin{aligned} & \underbrace{\hat{H}^{(0)} \cdot \underline{\phi}_1(+)}_{=} \cdot \bar{\Psi}_1 + \hat{H}^{(0)} \underline{\phi}_2(+) \cdot \bar{\Psi}_2 + \hat{H}^{(1)} \cdot \underline{\phi}_1(+) \cdot \bar{\Psi}_1 + \hat{H}^{(1)} \underline{\phi}_2(+) \cdot \bar{\Psi}_2 = \\ &= i\hbar \underline{\phi}_1(+)^* \frac{\partial \bar{\Psi}_1}{\partial t} + i\hbar \underline{\phi}_2(+)^* \frac{\partial \bar{\Psi}_2}{\partial t} + i\hbar \bar{\Psi}_1^* \frac{\partial \underline{\phi}_1(+)}{\partial t} + i\hbar \bar{\Psi}_2^* \frac{\partial \underline{\phi}_2(+)}{\partial t} \\ & \hat{H}^{(0)} \cdot \underline{\phi}_1(+)^* \bar{\Psi}_1 = \underline{\phi}_1(+)^* \hat{H}^{(0)} \cdot \bar{\Psi}_1 \cdot e^{-\frac{iE_1 t}{\hbar}} = \underline{\phi}_1(+)^* \underbrace{e^{-\frac{iE_1 t}{\hbar}}}_{\bar{\Psi}_1^*} \bar{\Psi}_1 \cdot \bar{e}_1 \\ & i\hbar \underline{\phi}_1(+)^* \frac{\partial \bar{\Psi}_1}{\partial t} = i\hbar \underline{\phi}_1(+)^* \bar{\Psi}_1 \cdot \bar{e}_1 \cdot \left(-\frac{i}{\hbar}\right) \cdot e^{-\frac{iE_1 t}{\hbar}} = \frac{\underline{\phi}_1(+)^* \bar{\Psi}_1 \cdot \bar{e}_1}{\underline{\phi}_1(+)} \cdot \bar{\Psi}_1^* \\ & \underline{\phi}_1(+)^* \hat{H}^{(1)} \bar{\Psi}_1 + \underline{\phi}_2(+)^* \hat{H}^{(1)} \bar{\Psi}_2 = i\hbar \bar{\Psi}_1^* \frac{\partial \bar{\Psi}_1}{\partial t} + i\hbar \bar{\Psi}_2^* \frac{\partial \bar{\Psi}_2}{\partial t} \end{aligned}$$

$$\begin{aligned} & \underline{\phi}_1(+)^* \int \bar{\Psi}_2^* \hat{H}^{(1)} \bar{\Psi}_1 d\tau_1 + \underline{\phi}_2(+)^* \int \bar{\Psi}_2^* \hat{H}^{(1)} \bar{\Psi}_2 d\tau_1 = i\hbar \frac{\partial \underline{\phi}_1(+)^*}{\partial t} \int \bar{\Psi}_2^* \bar{\Psi}_1 d\tau_1 + \\ & + i\hbar \frac{\partial \underline{\phi}_2(+)^*}{\partial t} \int \bar{\Psi}_2^* \bar{\Psi}_2 d\tau_1 \end{aligned}$$

$$\begin{aligned} & i\hbar \frac{\partial \underline{\phi}_2(+)^*}{\partial t} = \underline{\phi}_1(+)^* \cdot e^{+\frac{iE_2 t}{\hbar}} \int \bar{\Psi}_2^* \hat{H}^{(1)} \bar{\Psi}_1 d\tau_1 + \\ & + \underline{\phi}_2(+)^* \cdot e^{+\frac{iE_2 t}{\hbar}} \int \bar{\Psi}_2^* \hat{H}^{(1)} \bar{\Psi}_2 d\tau_1 \\ & = \underline{\phi}_1(+)^* e^{-\frac{i(E_1 - E_2)t}{\hbar}} \int \bar{\Psi}_2^* \hat{H}^{(1)} \bar{\Psi}_1 d\tau_1 + \underline{\phi}_2(+)^* \int \bar{\Psi}_2^* \hat{H}^{(1)} \bar{\Psi}_2 d\tau_1 \end{aligned}$$

Initial conditions:

$$\alpha_1(0) = 1 \quad \alpha_2(0) = 0$$

$$i\hbar \frac{d\alpha_2(t)}{dt} = e^{-\frac{i(E_1 - E_2)}{\hbar}} + \int \psi_2^* H^{(1)} \psi_1 dt$$

$$H^{(1)} = -\mu_2 E_{0z} \cdot \cos 2\omega t + \text{(z-component only)}$$

$$= -\frac{\mu_2}{2} E_{0z} (e^{i2\omega t} + e^{-i2\omega t})$$

hence: $\frac{d\alpha_2}{dt} \propto (\mu_2)_{12} E_{0z} \left\{ e^{+\frac{i(E_2 - E_1 - h\omega)}{\hbar} t} + e^{+\frac{i(E_2 - E_1 + h\omega)}{\hbar} t} \right\}$

$\int \psi_2^* \mu_2 \psi_1 dt / \text{transition dipole moment.}$

integrating: if $0 \rightarrow \frac{d\alpha_2}{dt} = 0$

$$\alpha_2(t) = (\mu_2)_{12} E_{0z} \cdot \left(\underbrace{\frac{1 - e^{\frac{i(E_2 - E_1 + h\omega)}{\hbar} t}}{E_2 - E_1 + h\omega}}_{\Delta E = -h\omega} + \underbrace{\frac{1 - e^{\frac{i(E_2 - E_1 - h\omega)}{\hbar} t}}{E_2 - E_1 - h\omega}}_{\Delta E = h\omega} \right)$$

population of excited state (if)

$$*\psi_2^*(t)\psi_2(t) \propto *$$

$$*\sin^2 \left(\frac{(E_2 - E_1 - h\omega)t}{2\hbar} \right)$$

$$\frac{(E_2 - E_1 - h\omega)^2}{(E_2 - E_1 - h\omega)^2}$$

$\alpha_2(t)$ significantly different from 0.
Resonance frequencies.

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Selection Rules:

Rigid Rotor: $\Delta J = \pm 1 \quad \mu \neq 0$

$$(\mu_z)_{J,M \rightarrow J'M'} = \int_0^{\pi} \int_0^{2\pi} Y_J^{-M*} \underbrace{\mu_z}_{\downarrow} Y_J^{-M} \sin \Theta d\Theta d\varphi$$

$$\mu_z = \mu \cos \Theta$$

$$Y_J^M = N_{JM} \cdot P_J^{IM} \underbrace{(\cos \Theta)}_x e^{i M \varphi}$$

$$(\mu_z)_{J,M \rightarrow J'M'} = \mu \cancel{N_{JM}} N_{JM} N_{J'M'} \int_0^{\pi} e^{i(M-M')\varphi} \underbrace{d\varphi}_{-\pi} \int_{-1}^1 dx \times P_J^{(M)}(x) P_{J'}^{(M')}(-x)$$

$$(2J+1)_x P_J^M = (J-M+1) P_{J+1}^{(M)}(x) \stackrel{M=M'}{\text{if}} \text{(otherwise 0)} + (J+M) P_{J-1}^{(M)}(x)$$

$$(\mu_z)_{J,M \rightarrow J'M'} = \int_{-1}^1 N_{JM} N_{J'M'} \int_{-1}^1 P_{J'}^{(M')}(x) \left(\alpha P_{J+1}^{(M)}(x) + \beta P_{J-1}^{(M)}(x) \right) dx$$

$$\begin{cases} \Delta J = \pm 1 \\ \Delta M = 0 \\ \mu \neq 0 \end{cases}$$

Hermite Oscillator $\omega_0 = \pm 1$

$$Q_\sigma = N_0 H_0(\xi^{\frac{1}{2}} p) e^{-\frac{\xi p^2}{2}} \quad \xi = \left(\frac{k\mu}{\hbar^2}\right)^{\frac{1}{2}}$$

$$\mu_z(p) = \mu_0 + \left(\frac{\partial \mu}{\partial p}\right)_0 p + \dots \quad / \text{molecule vibrates} \rightarrow \text{cliques.}$$

$$(\mu_z)_{\sigma \rightarrow \sigma'} = N_0 N_{\sigma'} \underbrace{H_0'(\xi^{\frac{1}{2}} p) \cdot H_0(\xi^{\frac{1}{2}} p)}_{+ \infty} e^{-\xi p^2} \mu_0 dp \\ + N_0 N_{\sigma'} \int_{-\infty}^{+\infty} H_0'(\xi^{\frac{1}{2}} p) \left(\frac{\partial \mu}{\partial p} \right)_0 H_0(\xi^{\frac{1}{2}} p) dp e^{-\xi p^2} dp$$

$$\xi = \omega^{\frac{1}{2}} p$$

$$\xi^{\frac{1}{2}} H_0(\xi) = \omega H_{0-1}(\xi) + \frac{1}{2} H_{0+1}(\xi)$$

$$(\mu_z)_{\sigma \rightarrow \sigma'} = \frac{N_0 N_{\sigma'}}{\omega} \left(\frac{\partial \mu}{\partial p} \right)_0 \int_{-\infty}^{+\infty} H_0(\xi) \left[\omega H_{0-1}(\xi) + \frac{1}{2} H_{0+1}(\xi) \right] e^{-\xi^2} d\xi$$

$$\left(\frac{\partial \mu}{\partial p} \right)_0 \neq 0$$

does not vanish only for
 $\sigma = \pm 1$

Rotational + Vibrational Spectroscopy

$$E(\sigma) = (\sigma + \frac{1}{2})\bar{\sigma}$$

where $\bar{\sigma} = \frac{1}{2\pi c} \left(\frac{k}{\mu} \right)^{\frac{1}{2}}$

Vibrational Energy

$$F(J) = \tilde{B}J(J+1)$$

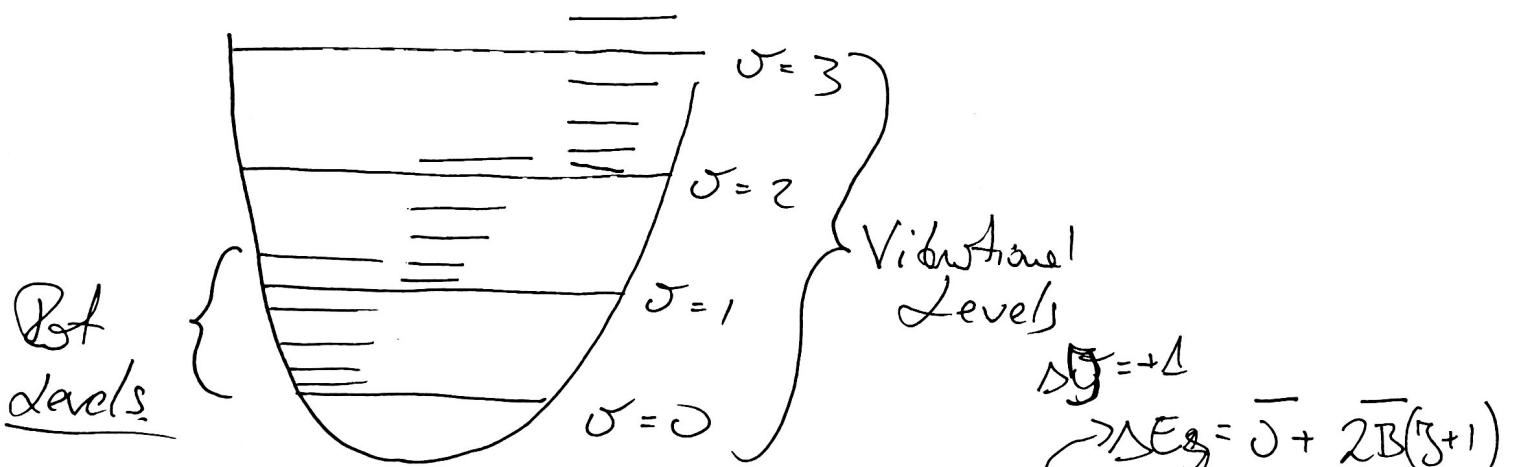
where $\tilde{B} = \frac{h}{8\pi^2 c I}$

Rotational Energy.

Rot-Vib E of a molecule:

$$\bar{E}_{\sigma, J} = E(\sigma) + F(J)$$

$$\begin{array}{l} \sigma = 0, 1, 2, \dots \\ J = 0, 1, 2, \dots \end{array}$$



Selection Rules:

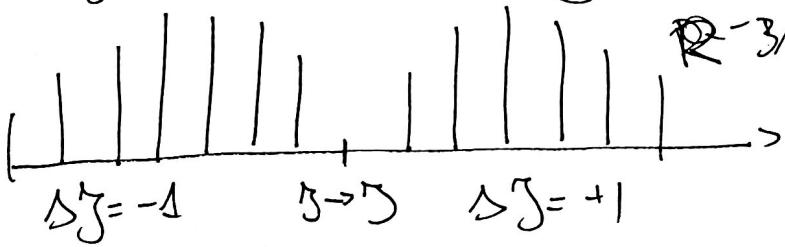
P-Band
 $\Delta J = \pm 1$

$$\Delta J = \pm 1$$

$$\Delta J = -1$$

R-Band

$$\Delta E = \bar{\sigma} - 2\tilde{B}J$$



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The equilibrium distance is $\sigma=0$ and $\sigma=1$
 can be different \rightarrow de Lise
 are treated differently.

$$\tilde{B} \rightarrow \tilde{B}_g = \tilde{B}_c - \tilde{\alpha}(\sigma + \frac{1}{2})$$

The equilibrium \leftrightarrow Rot-Vib coupling.

$$\Delta E_{(\sigma g+1)} = \bar{\sigma} + 2\bar{B}_1 + (\bar{3}(\bar{B}_1 - \bar{B}_0)) \gamma + (\bar{B}_1 - \bar{B}_0) \gamma^2$$

$$\Delta \hat{E}_{(\sigma g-1)} = \bar{\sigma} - (\bar{B}_1 + \bar{B}_0) \gamma + (\bar{B}_1 - \bar{B}_0) \gamma^2$$

$\bar{B}_1 < \bar{B}_0$ (bond length increases with σ)

spring in P decreases with γ

species in T increases with γ .

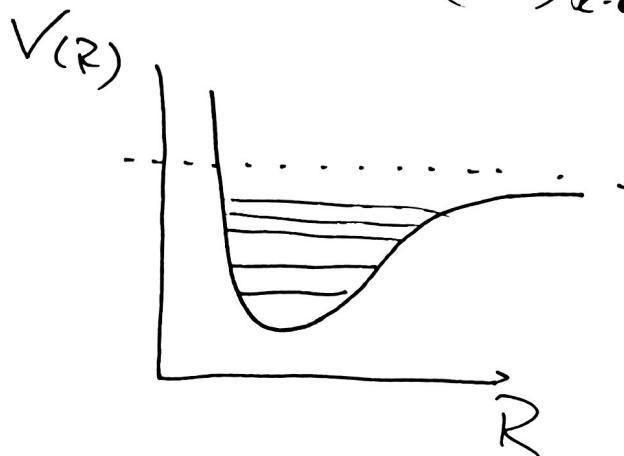
- Centrifugal Distortion (bond length increases with γ)

$$F(\gamma) = \tilde{B}\gamma(\gamma+1) - \tilde{D}\gamma^2(\gamma+1)^2$$

C.D. effect \rightarrow lowers the E-level.
 (empirical parameter).

Anharmonic Vibrations.

$$V(R) - V(R_e) = \frac{1}{2} \left(\frac{\partial^2 V}{\partial R^2} \right)_{R=R_e} (R-R_e)^2 + \frac{1}{6} \left(\frac{\partial^3 V}{\partial R^3} \right)_{R=R_e} (R-R_e)^3 + \dots$$



Fitting with harmonic potential.

Anharmonic correction:

$$\zeta(v) = \bar{\omega}_e (\sigma + \frac{1}{2}) - \overline{\chi_e} \bar{\omega}_e (\sigma + \frac{1}{2})^2$$

anharmonic constant $\ll 1$

The spectra results in overtones when

$$\Delta \sigma = \pm 2, \pm 3, \dots \text{ and } \Delta E < 2 \cdot \bar{\omega}_e, 3 \cdot \bar{\omega}_e, \dots$$

$$\bar{\omega}_{\Delta E} = \bar{\omega}_e \sigma - \overline{\chi_e} \bar{\omega}_e \sigma (\sigma + 1)$$

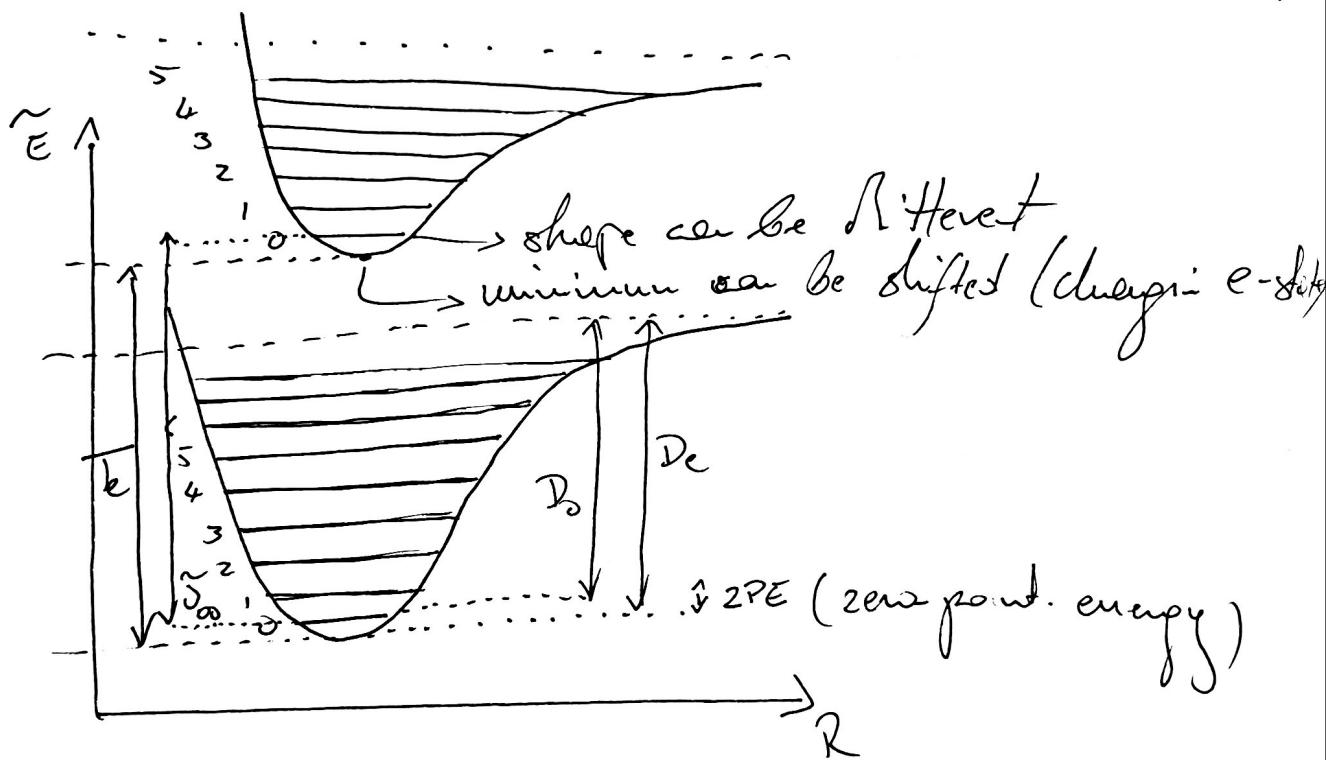
- ↑ ... Presence of overtones indicates strongly anharmonic potentials.
 - $\sigma=3$
 - $\sigma=2$ (avilable of selection Rules)
 - $\sigma=1$
 - $\sigma=0$
- H.O. Au.O.

Vibronic Excitation (Vibration + Electronic)

$$\begin{aligned}\tilde{E} &= \tilde{\omega}_{el} + \underbrace{\zeta(v)}_{\text{vibrational energy}} + F(\zeta) \\ &= \tilde{\omega}_{el} + \tilde{\omega}_e(J+\frac{1}{2}) + \tilde{\chi}_e \tilde{\omega}_e (J+\frac{1}{2})^2 + \underbrace{\tilde{\beta}_e(J+1) - D_e \tilde{\beta}_e(J+1)^2}_{\text{electronic energy}}\end{aligned}$$

Fig 13.7

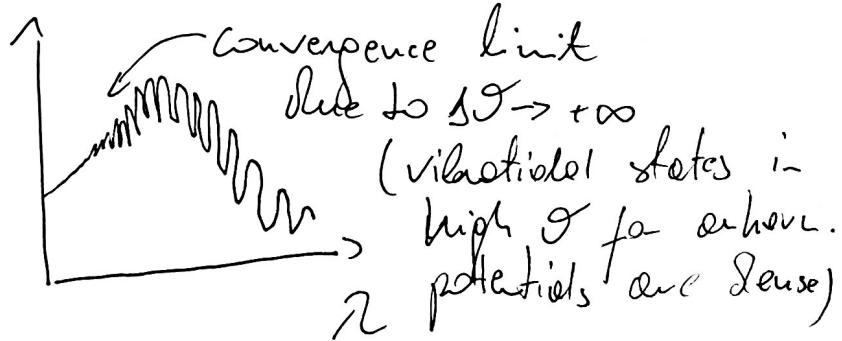
Too small energies
to be on the same scale.



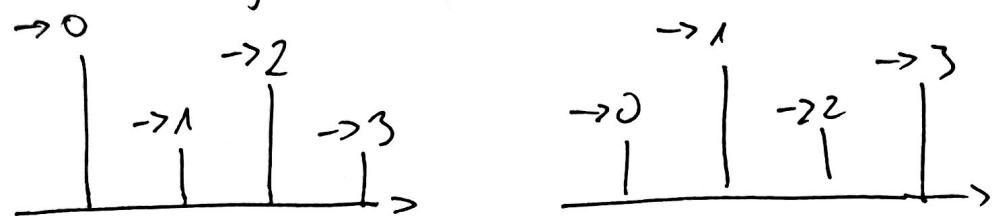
$$\tilde{\omega}_{obs} = \tilde{\omega}_{00} + \tilde{\omega}'_e J' - \tilde{\chi}'_e \tilde{\omega}'_e J'(J'+1) \quad J' \rightarrow \text{vibrational level of upper state}$$

where $\tilde{\omega}_{00} = \tilde{\omega}_e + \Delta ZPE$

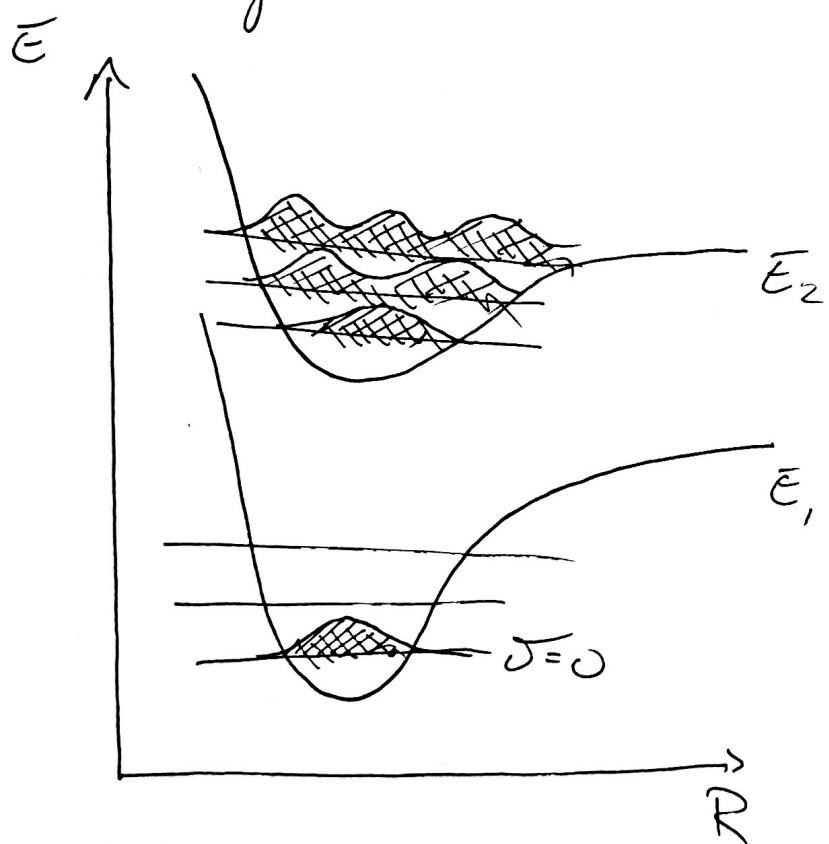
Fig 13.8, 13.9



Intensity of Vibrations, Franck-Condon Principle



Depends on the overlaps of the vibrational wavefunction in the state
(Fig 13.10 - 13.12 in the textbook)



Polyatomic Molecules:

Potential spectra



3 axis of inertia (asymmetric top)

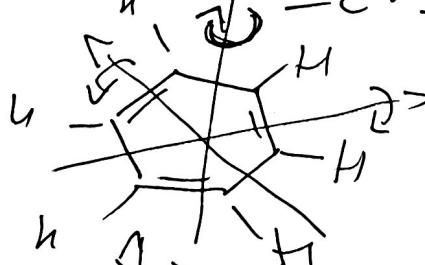
$$\overline{I_A} < \overline{I_B} < \overline{I_C} \rightarrow \tilde{A} > \tilde{B} > \tilde{C}$$

$I = \mu \cdot R^2 \rightarrow \sum m_i r_i^2$ defines species.

- if $\overline{I_A} = \overline{I_B} = \overline{I_C} \rightarrow$ spherical top
 $\mu \neq 0 \rightarrow$ not IR.

- if $\overline{I_A} = \overline{I_B} \neq \overline{I_C}$ symmetric top.

~~oblate~~ $I_c > I_a$ ~~oblate~~



larger species along \tilde{C}

$I_c < I_a$ Prolate

smaller species along \tilde{C} .

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Vibrational Spectroscopy of polyacrylic acid

$$\left(\frac{\partial^2 V}{\partial R^2} \right)_{R=R_c} \rightarrow \frac{1}{2} \sum_{i=1}^{N_{\text{vib}}} \sum_{j=1}^{N_{\text{vib}}} \left(\frac{\partial^2 V}{\partial Q_i \partial Q_j} \right) \rho_i \rho_j \rightarrow \sum_{i=1}^{N_{\text{vib}}} \tilde{\rho}_i Q_i^2$$

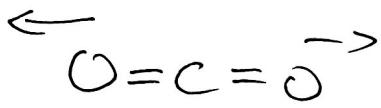
$$\Phi_{\text{vib}}(Q_1, Q_2, \dots) = \Phi_1(Q_1) \cdot \Phi_2(Q_2) \dots$$

coupled
matrix

$$E_{\text{vib}} = \sum_i \tilde{\rho}_i (Q_i + \frac{1}{2})$$

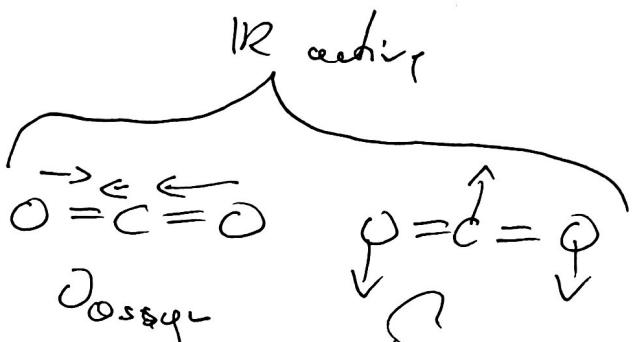
Kernel modes.

ω_i :



σ_{sym}

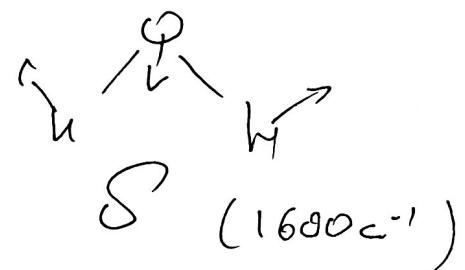
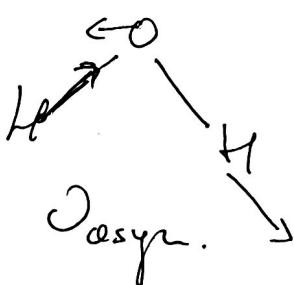
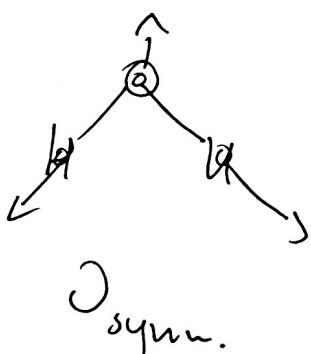
not IR active



σ_{asym}

δ
(doubly degenerate)

H_2O



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