

Rotation and vibration of diatomic molecules

Recall;

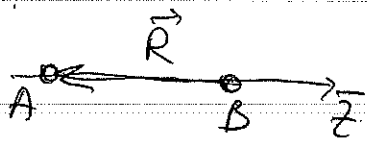
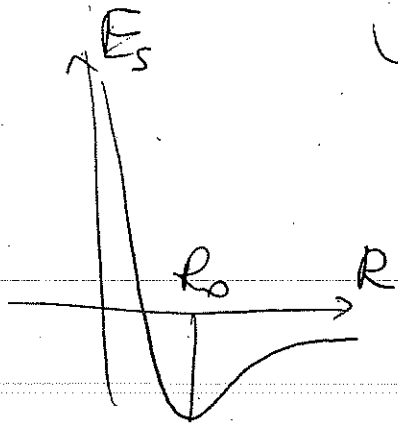
↑
Lecture #21

$$\left[-\frac{\hbar^2}{2\mu} \frac{1}{R^2} \frac{\partial}{\partial R} \left(R^2 \frac{\partial}{\partial R} \right) + \frac{\langle \phi_s | \vec{N}^2 | \phi_s \rangle}{2\mu R^2} + E_s(R) - E \right] F_s(\vec{R}) = 0$$

↑ effective potential

↑ equation describing motion of nuclei

$$\vec{N} = \vec{R} \times \vec{P}$$



$$\frac{F(R)}{R} \mathcal{H}(R, \varphi)$$

$$\langle \phi_s | \vec{N}^2 | \phi_s \rangle = \langle \phi_s | \vec{K}^2 + \vec{L}^2 - 2\vec{K} \cdot \vec{L} | \phi_s \rangle \quad (\Sigma\text{-states})$$

$K_z = L_z$ for $\Lambda = 0$

$$\Rightarrow \hbar^2 K(K+1) - \hbar^2 \Lambda^2 + \langle \phi_s | L_x^2 + L_y^2 | \phi_s \rangle$$

$$\vec{K}^2 \psi_s = \hbar^2 K(K+1) \psi_s$$

↑ rotational quantum number

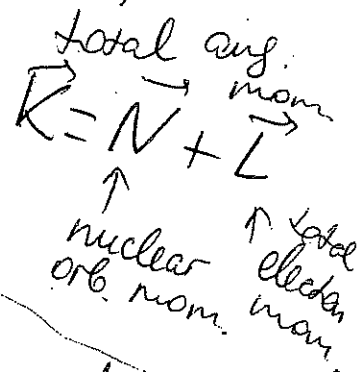
$$F_s(\vec{R}) \phi_s(\vec{R}; \vec{r}_1, \dots, \vec{r}_N)$$

$$K_z \psi_s = \hbar M_K \psi_s$$

We also know that

$$L_z \psi_s = \pm \hbar \Lambda \psi_s \quad \text{and}$$

$$K_z = L_z \leftarrow \text{since } N_z = 0 \Rightarrow |K| \geq K_z = L_z \Rightarrow K = \Lambda, \Lambda+1, \dots$$



For $\Lambda=0 \Rightarrow \vec{K} = \vec{N} \Rightarrow \langle \psi_s | \vec{N}^2 | \psi_s \rangle = \textcircled{2}$
 (Σ states) $= \hbar^2 K(K+1)$

Then, $\left[-\frac{\hbar^2}{2\mu} \left(\frac{d^2}{dR^2} - \frac{K(K+1)}{R^2} \right) + E_s(R) - E \right] F(R) = 0$

angular part $\Rightarrow Y_{KM_K}(\theta, \phi)$ \uparrow radial part of $F(\vec{R})$
 can be solved numerically for a given $E_s(R)$ with boundary conditions

Since nuclear motion in a stable molecule confined to region around R_0

$F(0) = 0$

$E_s(R) = E_s(R_0) + (R-R_0) \left. \frac{dE_s}{dR} \right|_{R_0} + \frac{1}{2} (R-R_0)^2 \left. \frac{d^2E_s}{dR^2} \right|_{R_0} + \dots$

Also, set $R \approx R_0$ in the $K(K+1)$ term

$\left[-\frac{\hbar^2}{2\mu} \frac{d^2}{dR^2} + \frac{\hbar^2 K(K+1)}{2\mu R_0^2} + E_s(R_0) + \frac{1}{2} k_s (R-R_0)^2 - E \right] F(R) = 0$

$E_r = \frac{\hbar^2}{2I_0} K(K+1) = BK(K+1)$

\uparrow moment of inertia

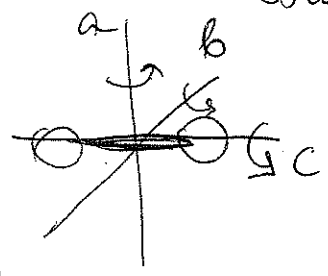
\uparrow rotational constant

\uparrow harmonic oscillator $K = A, A + \dots$

$E = E_s(R_0) + E_r + E_v$

$E_v = \hbar \omega \left(v + \frac{1}{2} \right)$
 $\sqrt{\frac{k_s}{\mu}}$ $v = 0, 1, 2, \dots$

Note: If $\Lambda \neq 0 \Rightarrow E_r = \frac{\hbar^2}{2I_0} K(K+1) +$
 (excited states)

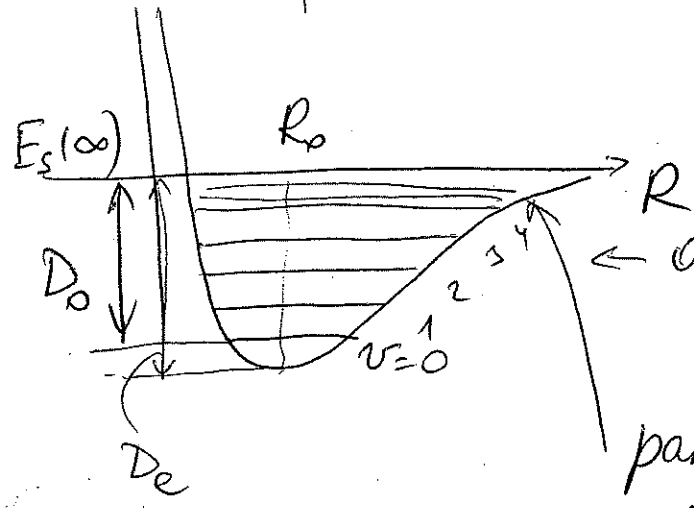


diatomic: $I_a = I_b$

$$+ \left(\frac{1}{2I_c} - \frac{1}{2I_0} \right) \Lambda^2 \hbar^2$$

↑ depends on the electronic state

↑ can be included in the electronic energy



← only a finite number of vibrational levels fits in, before the molecule dissociates

parabolic approx. not valid =>

$$D_0 = D_e - \frac{\hbar \omega_0}{2}$$

$$E_v = \hbar \omega_0 \left[v + \frac{1}{2} - \beta \left(v + \frac{1}{2} \right)^2 \right]$$

↑ true dissociation energy

$$\beta \omega_0 = \frac{\hbar \omega_0^2}{4D_e} \leftarrow \text{anharmonicity constant}$$

Molecular spectroscopy

Introduce $\vec{D} = e \left(\sum_i z_i \vec{R}_i - \sum_j \vec{r}_j \right)$ ← electric dipole operator

↑ positions of nuclei ↑ positions of electrons

$$\vec{D}_{aa} = \langle \Psi_a | \vec{D} | \Psi_a \rangle$$

0 for homonuclear diatomic molecules and for symmetric molecules e.g. C6H6

↑ permanent electric dipole moment of the molecule in state $|\Psi_a\rangle$

$D_{aa} \neq 0$ for heteronuclear molecules

(4)

Since rotational and vibrational motions preserve symmetry of the molecule \Rightarrow probability of rot. or vibrat. transitions without changing electronic state ($\sim |\vec{D}_{aa}|^2$) = 0 for symmetric molecules

But \Rightarrow can be observed for heteronuclear ones (e.g. HCl)

$$h\nu_{K+1, K} = E_r(K+1) - E_r(K) = 2B(K+1) \quad (K \geq \Lambda)$$

purely rotational

$$\Delta K = \pm 1, \Delta M_K = 0, \pm 1$$

for $\Delta = 0$

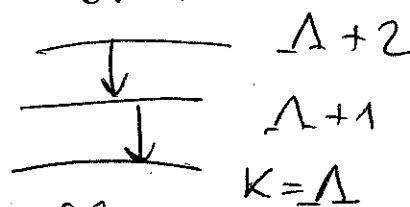
0, ± 1 for $\Delta \neq 0$ and change in vibrational state

electronic

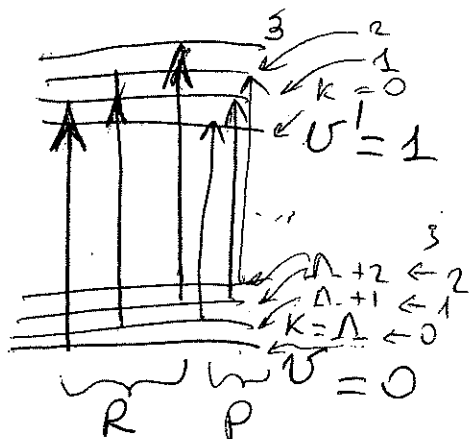
vibrational

rotational (fine) structure

rotational structure



$\Delta v = \pm 1$ \leftarrow selection rules for vibrational transitions
vibrational-rotational band $\Rightarrow v, K \rightarrow v', K'$



$$h\nu^R = E(v+1, K+1) - E(v, K) = 2B(K+1) + h\nu_0, \quad K=0, 1, 2, \dots$$

R-branch

$$h\nu^P = E(v+1, K-1) - E(v, K) = -2BK + h\nu_0 \leftarrow \text{P-branch}$$

$$h\nu^Q = E(v+1, K) - E(v, K) = h\nu_0 \quad (5)$$

2. branch (for $\Lambda \neq 0$ states)

Other transitions: $\sim |\vec{D}_{ba}|^2 \Rightarrow$

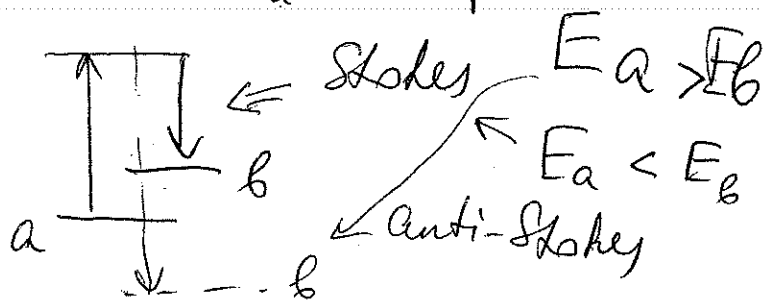
$$\Delta K = 0, \pm 2$$

$\omega' = \omega + \frac{E_a - E_b}{h} \Rightarrow \omega = \omega' - \text{Rayleigh scattering}$
 $\omega \neq \omega' \Rightarrow \text{Raman scattering}$

Recall:

$$\frac{d\sigma}{d\Omega} = r_0^2 \omega \omega'^3 \frac{m^2}{h^2 e^4} \left| \sum_n \frac{(\vec{E}' \cdot \vec{D}_{bn})(\vec{E} \cdot \vec{D}_{na})}{\omega_{na} - \omega} + \frac{(\vec{E}' \cdot \vec{D}_{bn})(\vec{E} \cdot \vec{D}_{na})}{\omega_{na} + \omega'} \right|^2$$

↑
sum over rotational and vibrational levels \Rightarrow closely spaced



Note: $D_{bn}, D_{na} \neq 0$

induced transition moments due to

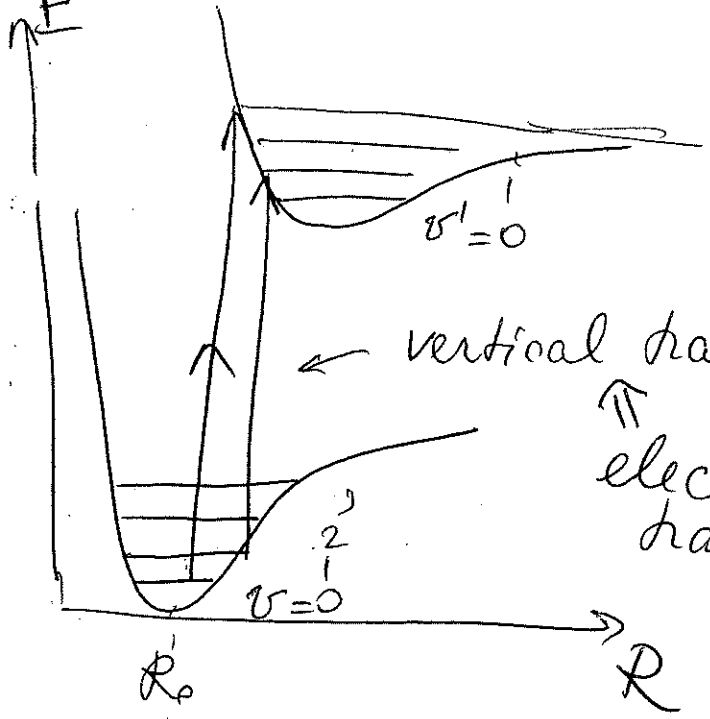
coupling with EM field
 observe \Leftarrow Raman from symmetric molecules

Electronic transitions $\Rightarrow \nu = \frac{E_{s'} + E_{v'} + E_{r'} - E_s - E_v - E_r}{h}$

For given $s, s' \Rightarrow$ (neglect rotations)

$$h\nu = h\nu_{s's} + h\nu_0'(v' + \frac{1}{2}) - h\nu_0'(v' + \frac{1}{2})^2 - h\nu_0(v + \frac{1}{2}) + h\nu_0(v + \frac{1}{2})^2$$

Déslandres formula same v (or v') \rightarrow progression



If Λ or $\Lambda' \neq 0 \Rightarrow$ 6
 $\Delta K = \pm 1, 0$; $\Delta \Lambda = 0, \pm 1$

If $\Lambda = \Lambda' = 0$ (Σ -state)

$\Delta K = \pm 1$, $\Sigma^\pm \rightarrow \Sigma^\pm$

$g \rightarrow u$ (homonuclear)

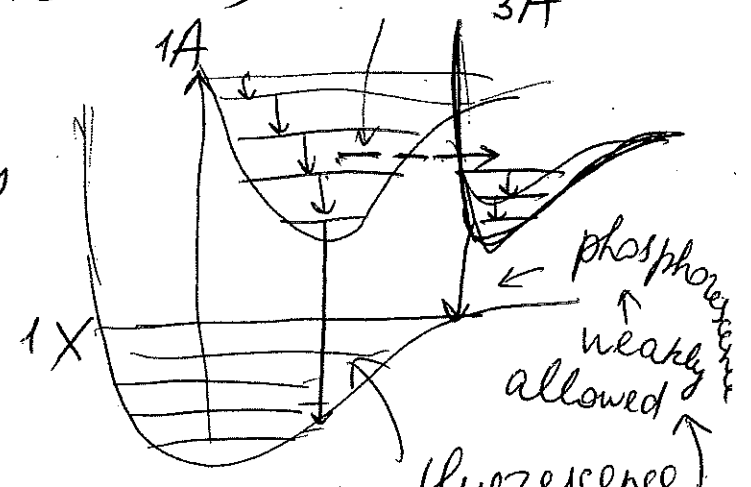
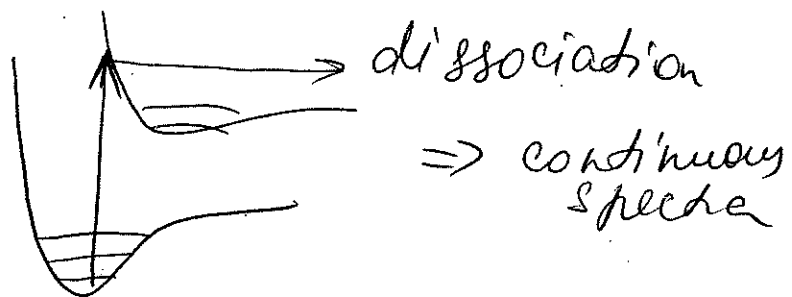
occurs instantaneously at a const value of R
 compared to vibrations

intensity distribution \Rightarrow Franck-Condon principle

$$f_{v'v} \approx \int_0^\infty \Psi_{v'}^* \Psi_v dR$$

$$D_{el}(R) \approx D_{el}(R_0)$$

overlap between vibrational wave functions in different electronic states



$$\langle \Psi_b | \vec{D} | \Psi_a \rangle = \int \Psi_b^* \vec{D} \Psi_a dR$$

$$-e \int \Psi_s^* (\sum_j \vec{r}_j) \Psi_s d\vec{r}_1 \dots d\vec{r}_N \sim ps - ns'$$

spin-orbit interaction
 ns - seconds