

# Molecular systems

## molecular energy scales

translation: not quantized

electronic: like atoms but modified by binding,  
~ few eV

vibrational modes: motion of nuclei

- slower, lower energy ~ few  $\cdot 0.1$  eV

rotational modes: entire molecule moves

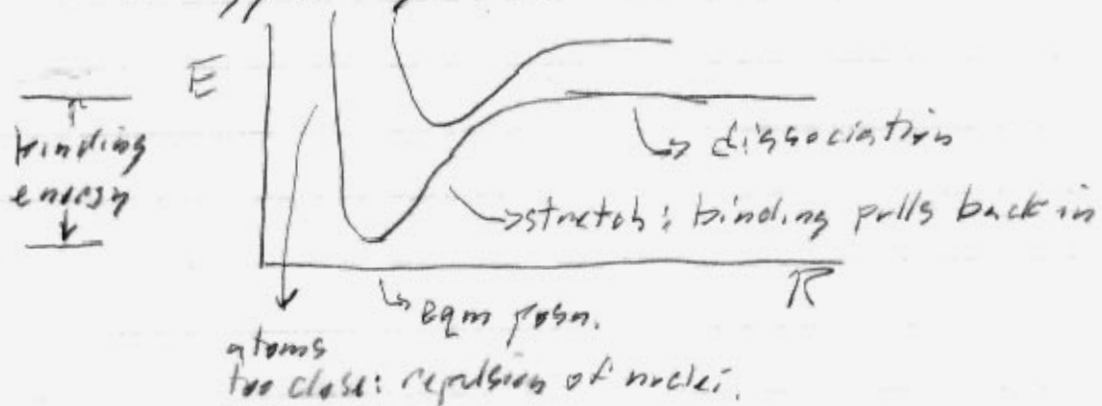
- 0.1 meV

## Born-Oppenheimer approximation:

- separate energy / time scales

vibrational:

for each internuclear separation, calc. electronic energy of system



upper curves: excited electronic states.

- dissociation  $\rightarrow$  one or more atoms excited.

- eqm. separation is different.

## vibrational modes:

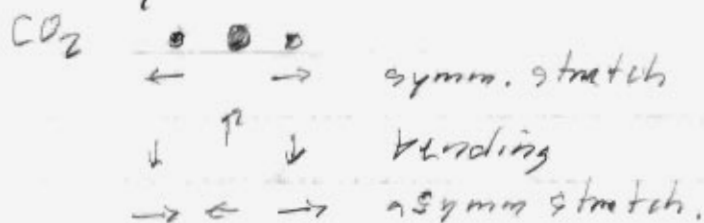
- expand  $E(R)$  around  $R_0$  in eqm.
- SHO for low-lying levels
- equal  $\Delta E_v$  spacing.  $E_v = h\nu_0(v + \frac{1}{2})$

As vibrational excitation ↑

- $\Delta E_v$  closer spacing → continuum at dissociation.

## poly atomic:

- many diff't normal modes



## rotational modes:

classical KE  $\frac{1}{2} I \dot{\theta}^2$   $I = \text{mom. of inertia} \sim Ma^2$   
 $= \frac{1}{2} \frac{L^2}{I}$   $L = \text{angular momentum}$

QM  $\hat{J}^2 \psi = \hbar^2 J(J+1) \psi$

$E_r = \frac{\hbar^2 J(J+1)}{2Ma^2}$  not equally spaced.

each QM state has a list of quantum numbers to describe:  
electronic, vib., rotation.

rotational  $\Delta E_r$  is small ∴ range of rotational states are thermally excited.

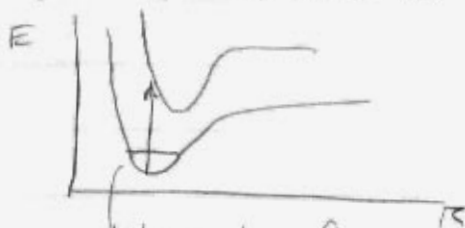
- for large molecules, some thermal excitation of vib. levels.

## Transitions in molecules

- low energy: rotational only  $\rightarrow$  far IR, microwave.  
 med energy: vibrational + rotational NIR, mid-IR.  
 high energy: electronic + vib + rot. VIS, UV  
 "vibronic"

Frank-Condon principle:

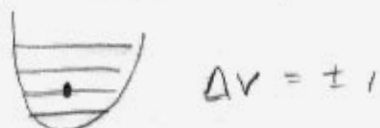
photon transitions are vertical on energy vs R plot.



transition from anywhere along line.

$\therefore$  excited electronic state is in higher vibrational state.

w/ in one electronic band  $\rightarrow$  no-vib transition



(small contribution from  $\Delta v = \pm 2, \pm 3$  b/c of anharmonic pot'l)

rotational transitions:

diatomic, linear triatomic  $\Delta J = \pm 1$

when  $\Delta J = +1 \rightarrow$  "P branch"

$\Delta J = -1 \rightarrow$  "R branch"

amplitudes of absorption lines are  $f(\text{temperature})$

$$\Delta E = E'' - E' = \frac{1}{2} \hbar \omega_0 (v'' + \frac{1}{2}) - \frac{1}{2} \hbar \omega_0 (v' + \frac{1}{2}) + \frac{1}{2} \frac{\hbar^2}{I} (J''(J''+1) - J'(J'+1))$$

$\Delta v = +1$  for absorption

$$\Delta J = \pm 1 \quad J'' = J' \pm 1 \quad (J'')^2 = J'^2 \pm 2J' + 1$$