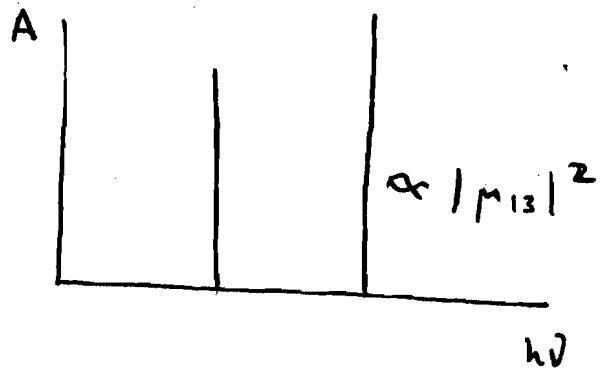
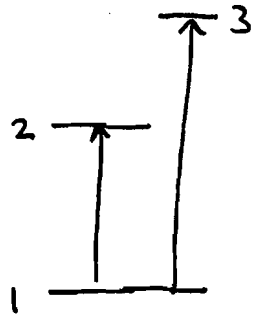


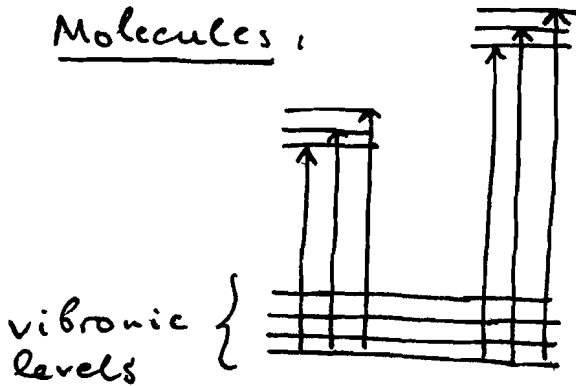
# Electronic transitions in molecules

## Atomic vs molecular spectroscopy

Atoms:

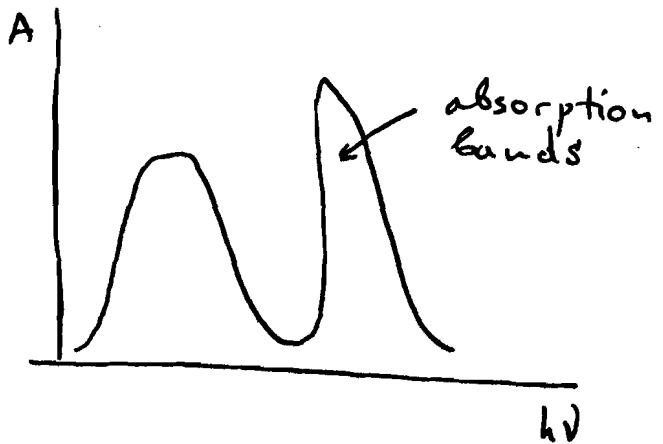
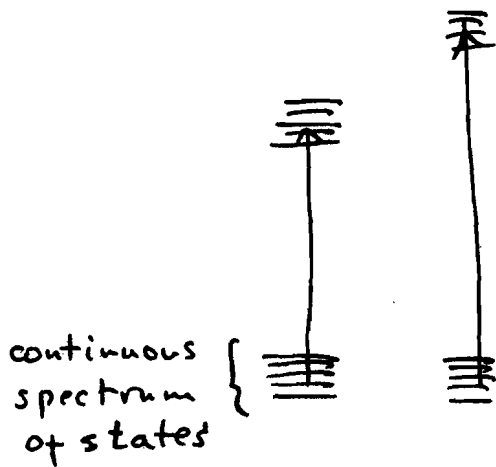


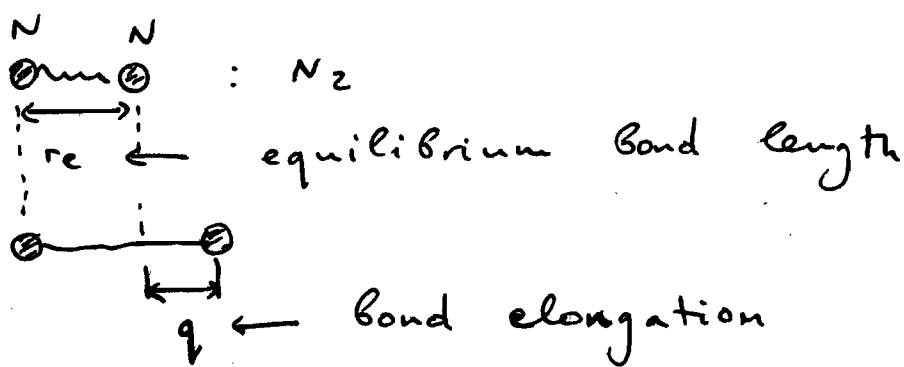
Molecules:



Franck-Condon progression

## Molecules in condensed phase:

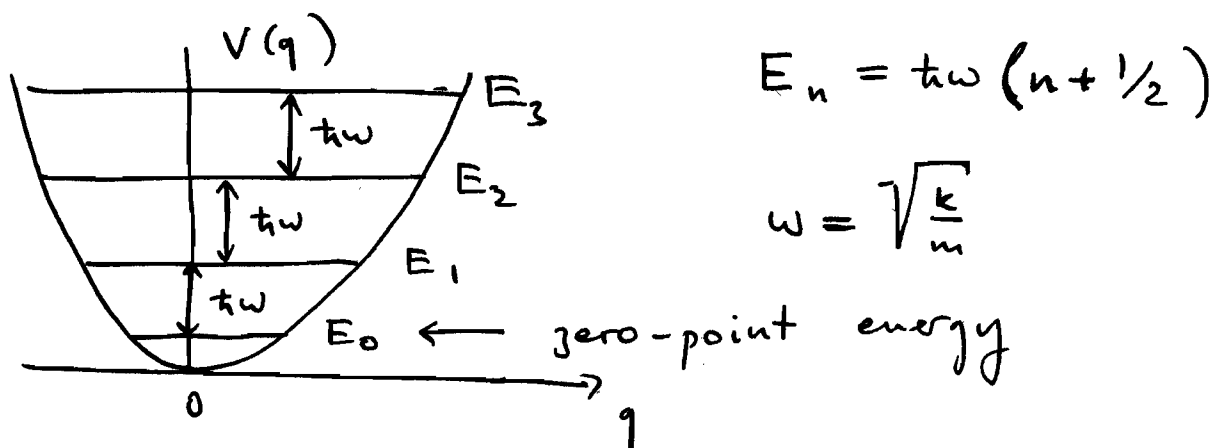




Harmonic potential :  $V(q) = \frac{1}{2} \underset{\substack{\uparrow \\ \text{force constant}}}{k} q^2$

Hamiltonian:  $H(q, \dot{q}) = \frac{m\dot{q}^2}{2} + \frac{1}{2} k q^2$

Quantum harmonic oscillator:



Selection rules for dipolar transitions

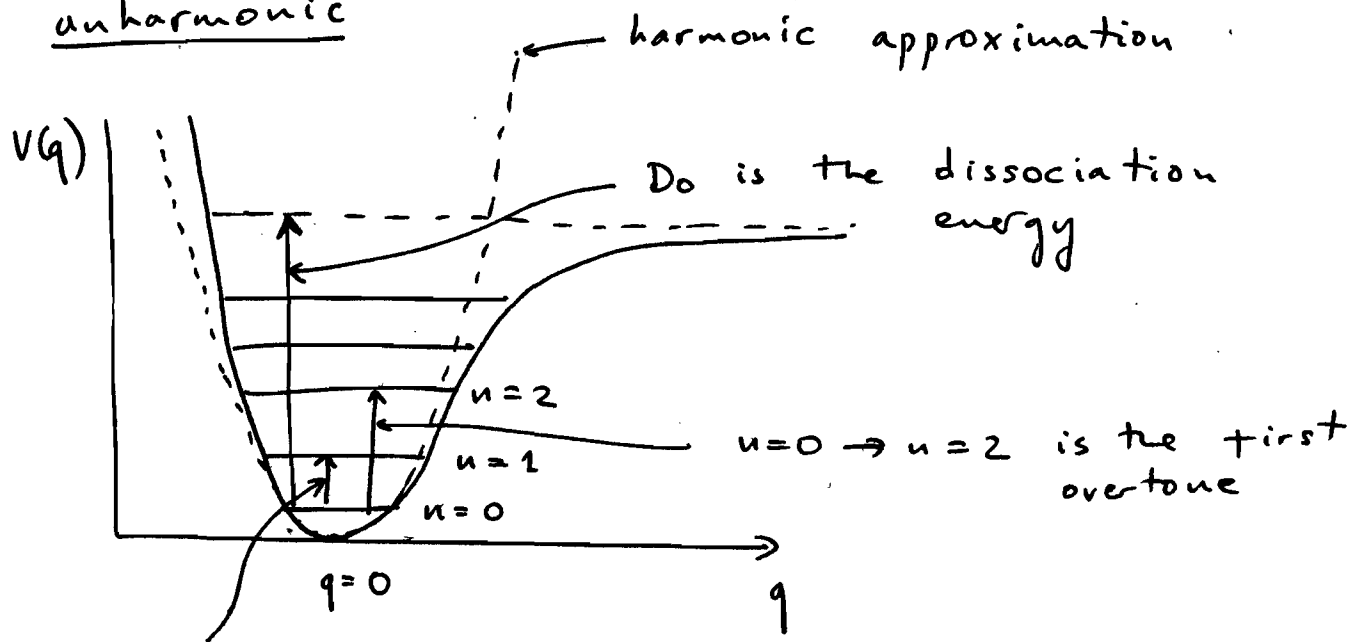
$$\langle n_1 | \vec{\mu} | n_2 \rangle \neq 0$$

if  $\Delta n = n_2 - n_1 = \pm 1$ . Vibrational excitation  
and cooling can happen only by one step  
up or down.

# The anharmonic oscillator

S-3

Stretching the molecular bond eventually leads to dissociation, the potential must be anharmonic



$n=0 \rightarrow n=1$  is the fundamental transition

x vibrational spacing decreases with increasing  $n$  for the anharmonic potential

x Common approximation: Morse potential

$$V(q) = D_e (1 - e^{-\rho q})^2$$

$$q < 0 \quad V(q) \approx D_e e^{2\rho|q|} \leftarrow \text{exponential repulsion}$$

$$q > 0, \quad q \gg 1 \quad V(q) \approx D_e (1 - 2e^{-\rho|q|})$$

# x Energy levels of the Morse potential

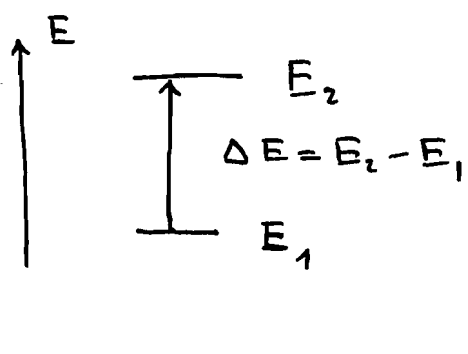
$$E_n = \hbar\omega \left(n + \frac{1}{2}\right) - \hbar\omega x_e \left(n + \frac{1}{2}\right)^2$$

$\underbrace{\hbar\omega x_e}_{\text{anharmonicity parameter}}$

$$E_{n+1} - E_n = \hbar\omega - 2\hbar\omega x_e (n+1)$$

spacing between energy levels linearly decreasing with increasing  $n$

## The population of the vibrational states



$$\frac{N_2}{N_1} = e^{-\frac{\Delta E}{kT}}$$

Boltzmann distribution

For harmonic oscillator:

$$\frac{N_n}{N_0} = \frac{e^{-(n+1/2) \frac{\hbar\omega}{kT}}}{e^{-\frac{1}{2} \frac{\hbar\omega}{kT}}} = e^{-n \frac{\hbar\omega}{kT}}$$

$$kT \approx 200 \text{ cm}^{-1} \approx \frac{1}{40} \text{ eV at } T \approx 300 \text{ K}$$

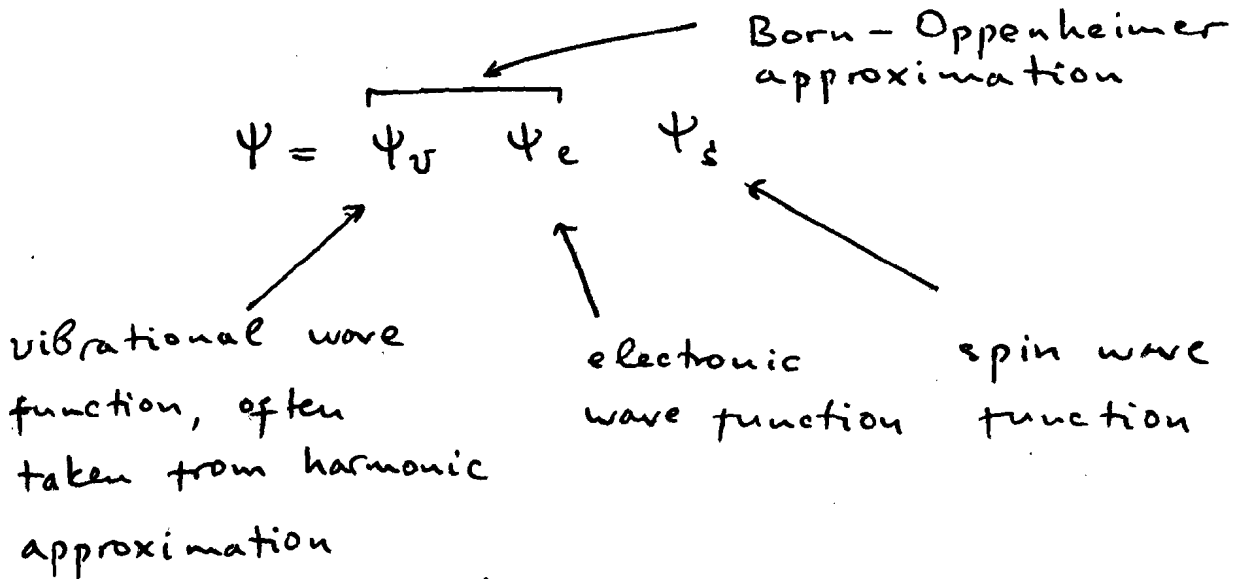
	$\bar{\omega} (\text{cm}^{-1})$	$N_1/N_0$
$\text{H}_2$	4159	$2.2 \times 10^{-3}$
$\text{I}_2$	213	0.36

# Electronic transitions

Q: How to decide which transition will have a non-zero intensity?

A: One needs to formulate molecular selection rules.

Molecular wave function:



"a" x "s"

$\Psi_e \times \Psi_s$

"s" x "a"

← antisymmetric  
(Pauli exclusion principle)



Transition dipole:

S-7

$$\begin{aligned}\vec{M} &= \langle \psi_{e^*} \psi_{s^*} \psi_{v^*} | (\vec{\mu}_e + \vec{\mu}_n) | \psi_e \psi_s \psi_v \rangle \\ &= \langle \dots | \vec{\mu}_e | \dots \rangle + \langle \dots | \vec{\mu}_n | \dots \rangle \\ &= \langle \psi_{e^*} | \vec{\mu}_e | \psi_e \rangle \langle \psi_{v^*} | \psi_v \rangle \langle \psi_{s^*} | \psi_s \rangle \\ &\quad + \langle \psi_{e^*} | \psi_e \rangle \langle \psi_{v^*} | \vec{\mu}_n | \psi_v \rangle \langle \psi_{s^*} | \psi_s \rangle\end{aligned}$$

One can always orthogonalize the electronic wave functions to make  $\langle \psi_{e^*} | \psi_e \rangle = 0$

$$\vec{M} = \underbrace{\langle \psi_{e^*} | \mu_e | \psi_e \rangle}_{\text{orbital selection rules}} \underbrace{\langle \psi_{v^*} | \psi_v \rangle}_{\text{Franck-Condon factor}} \underbrace{\langle \psi_{s^*} | \psi_s \rangle}_{\text{spin selection rule}}$$

Approximations:

- x Born - Oppenheimer approximation
- x Neglect of spin-orbit coupling (terms  $\propto \vec{S} \cdot \vec{L}$  in the Hamiltonian)

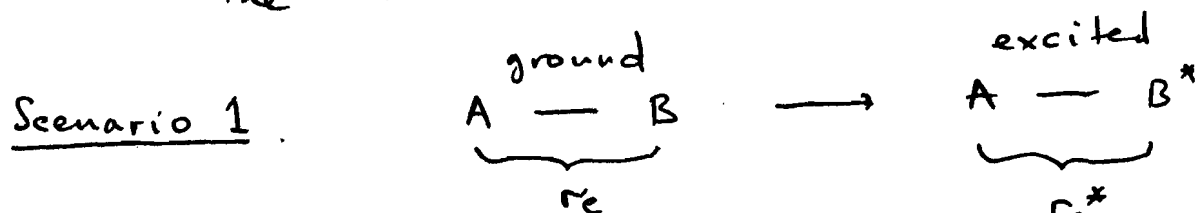
Selection rules are not rigorous

# Selection Rules :

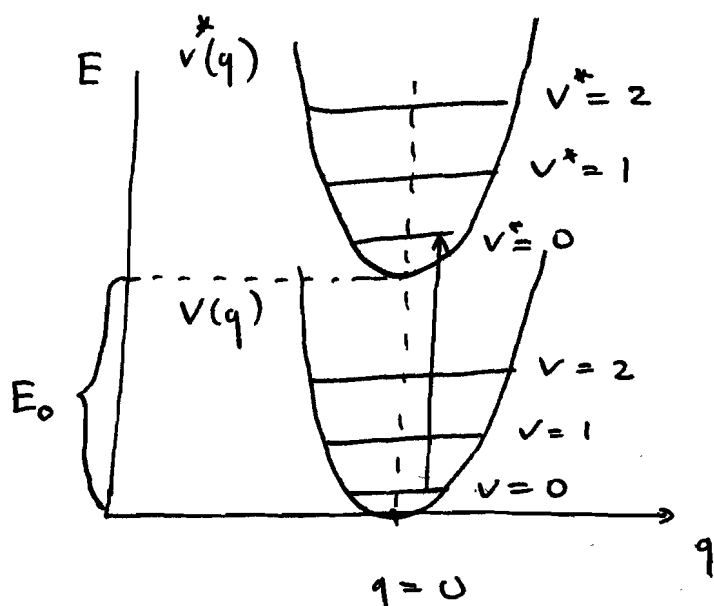
x A transition is spin-allowed if the spin multiplicities of the two states are identical,  $\Delta S = 0$

This is the strongest selection rule, spin-forbidden transitions result in lowest intensities in the electronic spectra

x Q: Are there any selection rules for the Franck-Condon factor?



assume that  $r_e = r_e^*$ , the bond length is not affected by excitation



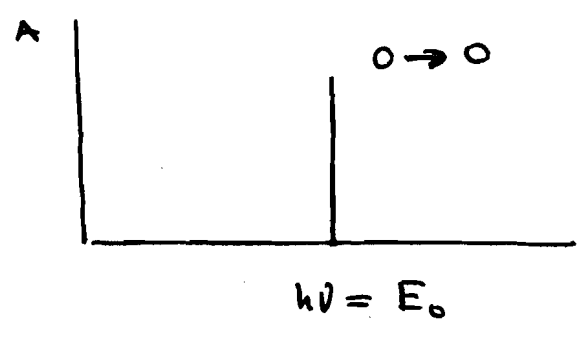
$$-E_0 + V^*(q) = V(q) = \frac{kq^2}{2}$$

Since the potential energies for harmonic vibrations are shifted by a constant, the wave functions of vibrations are identical,

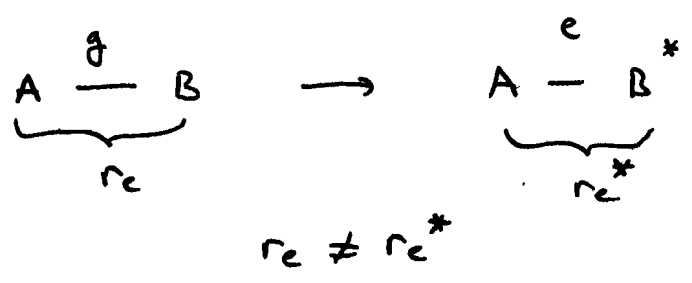
$$\langle \Psi_{v^*} | \Psi_v \rangle = \delta_{v^*,v}$$



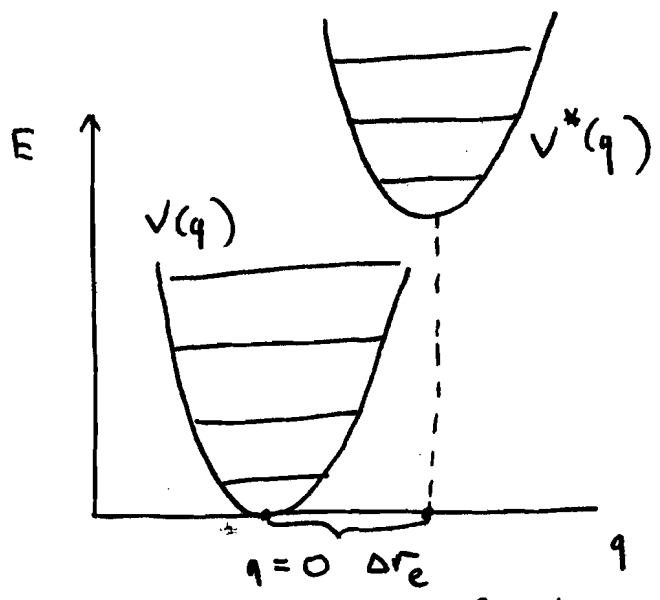
If  $h\nu \gg kT$ , only ground vibrational state is occupied and one will observe only  $0 \rightarrow 0$  transition



Scenario 2.



The common situation is  $r_e^* - r_e \approx 0.1 - 0.3 \text{ \AA}$



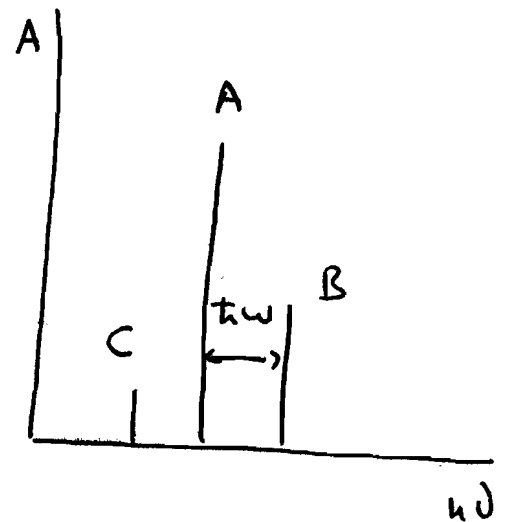
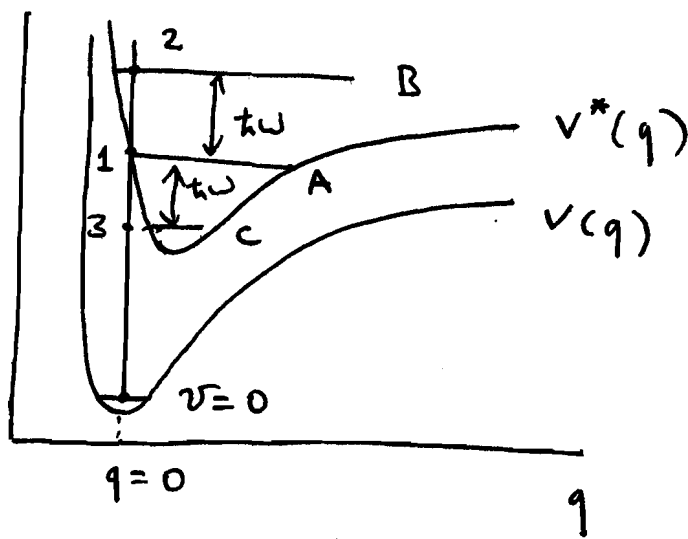
Since harmonic oscillators are displaced  
 $\langle \Psi_{v^*} | \Psi_v \rangle \neq 0$  for any  $v^*, v$

# Franck-Condon principle

Q: Can we say anything about the Franck-Condon factor  $\langle \psi_{v^*} | \psi_v \rangle$ ?

A: Franck-Condon principle:

An electron transition is so fast ( $\sim 10^{-15}$  s) compared to the nuclear motion ( $\sim 10^{-13}$  s) that the nuclei do not change their positions and momenta during the transition

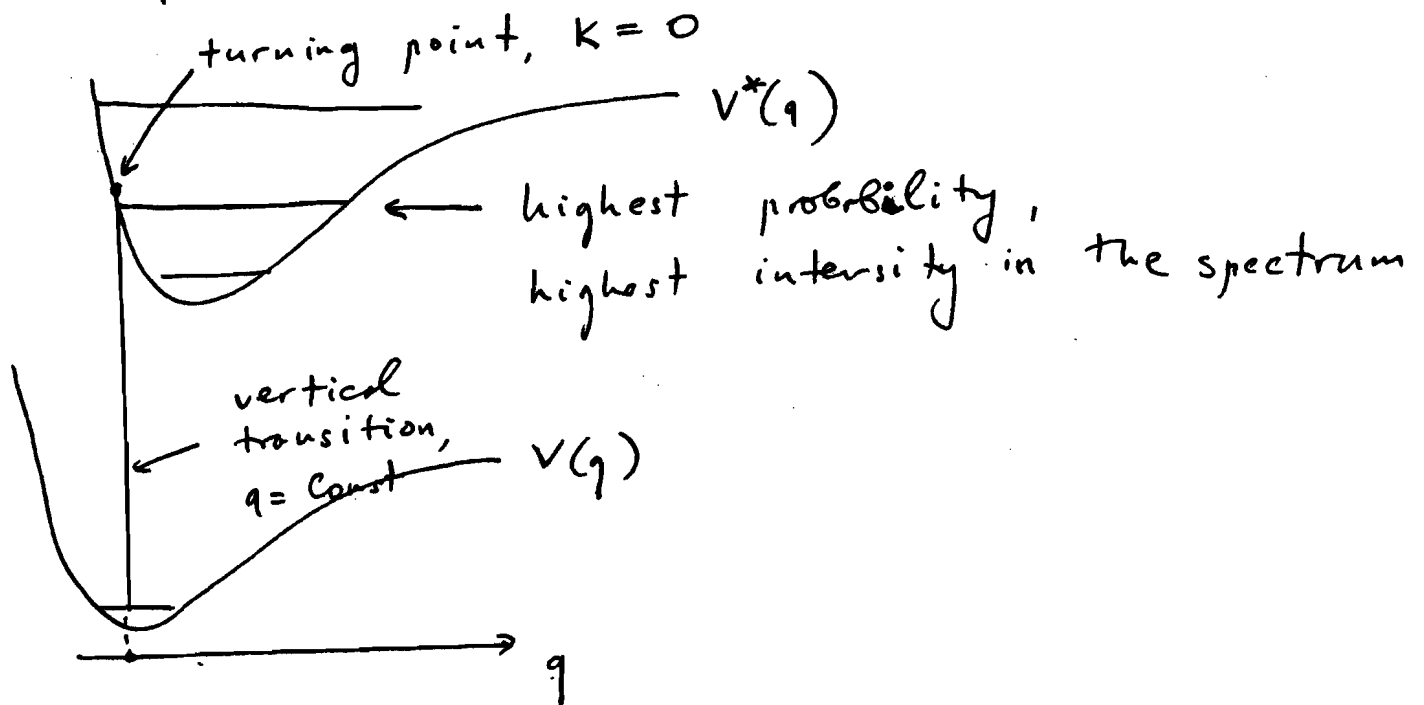


- x The momentum is small at  $q \approx 0$
- x The momentum is still small at 1
- x Transition to B involves change in momentum (2), transition to C is forbidden by classical mechanics

## Frank-Condon principle (consequence) :

Vertical transition to a state closest to the turning point has the highest

probability



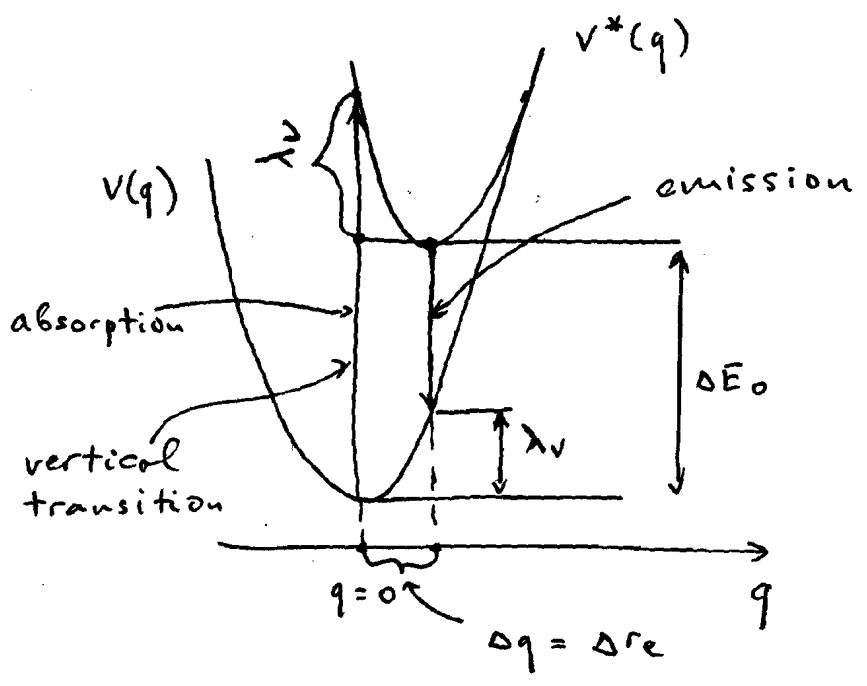
## Frank-Condon factor for harmonic vibrations

$$|\langle \Psi_{v^*} | \Psi_0 \rangle|^2 = \frac{s^{v^*}}{(v^*)!} e^{-s} \leftarrow \text{Huang \& Rhys, 1950}$$

$$s = \frac{\lambda_v}{\hbar \omega_v} \leftarrow \text{Huang-Rhys factor}$$

$\lambda_v \leftarrow$  vibrational reorganization energy

$$\lambda_v = \frac{1}{2} k (\Delta q)^2 = \frac{1}{2} k (\Delta r_e)^2 \leftarrow \text{harmonic potential energy to extend the bond length by } \Delta r_e$$



In Franck-Condon approximation :

$$\begin{aligned} \text{absorption energy : } \hbar \omega_{abs} &= \Delta E_0 + \lambda_v \\ \text{emission energy : } \hbar \omega_{em} &= \Delta E_0 - \lambda_v \end{aligned}$$

$$\hbar(\omega_{abs} - \omega_{em}) = \hbar \underline{\underline{\Delta \omega_{st}}} = 2\lambda_v$$

Stokes shift

$\hbar \Delta \omega_{st} = 2\lambda_v \leftarrow$  energy dissipated to heat in absorption/emission cycle