

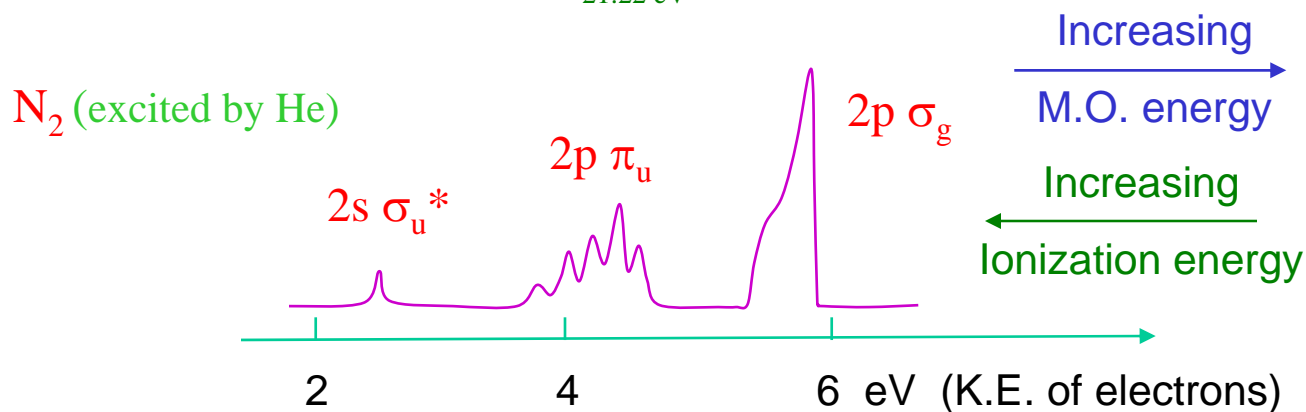
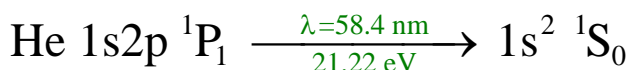
Photoelectron Spectroscopy

Ionization energies of atoms and molecules can be measured by means of the photoelectric effect.

$$h\nu_{\text{exc}} = \frac{1}{2}m_e v_e^2 + I_i$$

The source must be intense, monochromatic and energetic.

In conventional (UV) P.E.S. a common source of excitation is.



Koopman's Theorem assumes that the molecular geometry remains unchanged on ionization, whence orbital energy = I_i

The existence of fine structure in the P.E. spectrum shows that the ion is vibrationally excited: $h\nu_{\text{exc}} = \frac{1}{2}m_e v_e^2 + I_i + \Delta E_{\text{vib}}^+$ consistent with changes in bond lengths/angles in the ion.

ESCA (Electron Spectroscopy for Chemical Analysis) is the X-ray equivalent of P.E.S. and is used to ionize electrons from low-lying atomic orbitals.

Cr (5400 eV) or Al (1490 eV) excitation is commonly used.

Vibronic Transitions

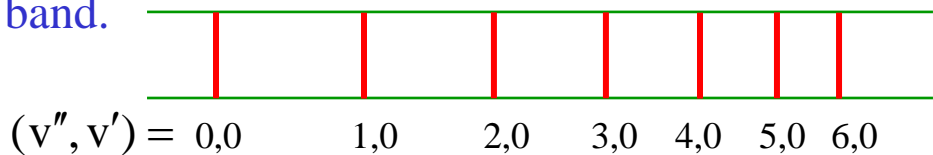
vibrational-electronic

$$h\nu = \Delta E = \Delta E_{\text{elec}} + \Delta E_{\text{vib}}$$

$\Delta v = 0, \pm 1, \pm 2, \dots$ but only the ground vibrational state is significantly populated at room temperature. Therefore, for absorption:

$$\Delta E = \Delta E_{\text{elec}} + \hbar\omega'_e \left[(v' + \frac{1}{2}) - x'_e (v' + \frac{1}{2})^2 \right] - \hbar\omega''_e \left[\frac{1}{2} - \frac{1}{4} x''_e \right]$$

There is a well-defined progression of vibrational lines in the electronic band.



The Franck-Condon Principle

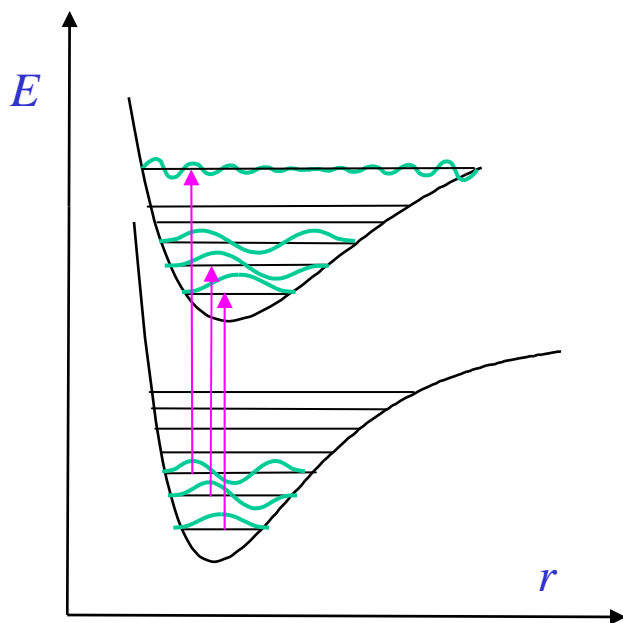
The intensity of a transition depends on the transition moment.

$$\begin{aligned} \langle \Psi' | \hat{d} | \Psi'' \rangle &= \langle \psi'_e \psi'_v | \hat{d}_e | \psi''_e \psi''_v \rangle + \langle \psi'_e \psi'_v | \hat{d}_k | \psi''_e \psi''_v \rangle \\ &= \langle \psi'_v | \psi''_v \rangle \langle \psi'_e | \hat{d}_e | \psi''_e \rangle + \langle \psi'_e | \psi''_e \rangle \langle \psi'_v | \hat{d}_k | \psi''_v \rangle \\ &\approx \langle \psi'_v | \psi''_v \rangle \langle d_e \rangle_{mn} \quad 0 \end{aligned}$$

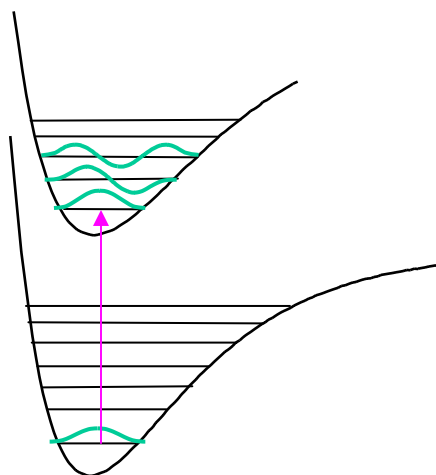
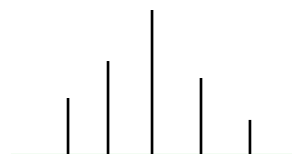
i.e. the transition moment depends on the overlap of vibrational wave functions.

The approximation necessary to derive this principle is tantamount to assuming that the electronic transition takes place in a static nuclear framework. **The Born-Oppenheimer Principle.**

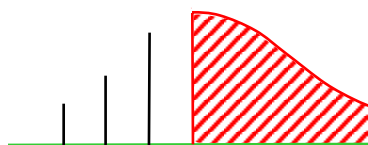
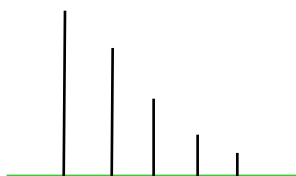
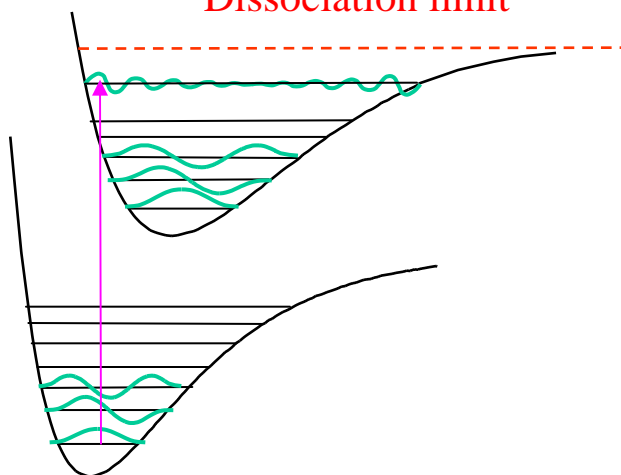
Franck-Condon Principle



Spectrum

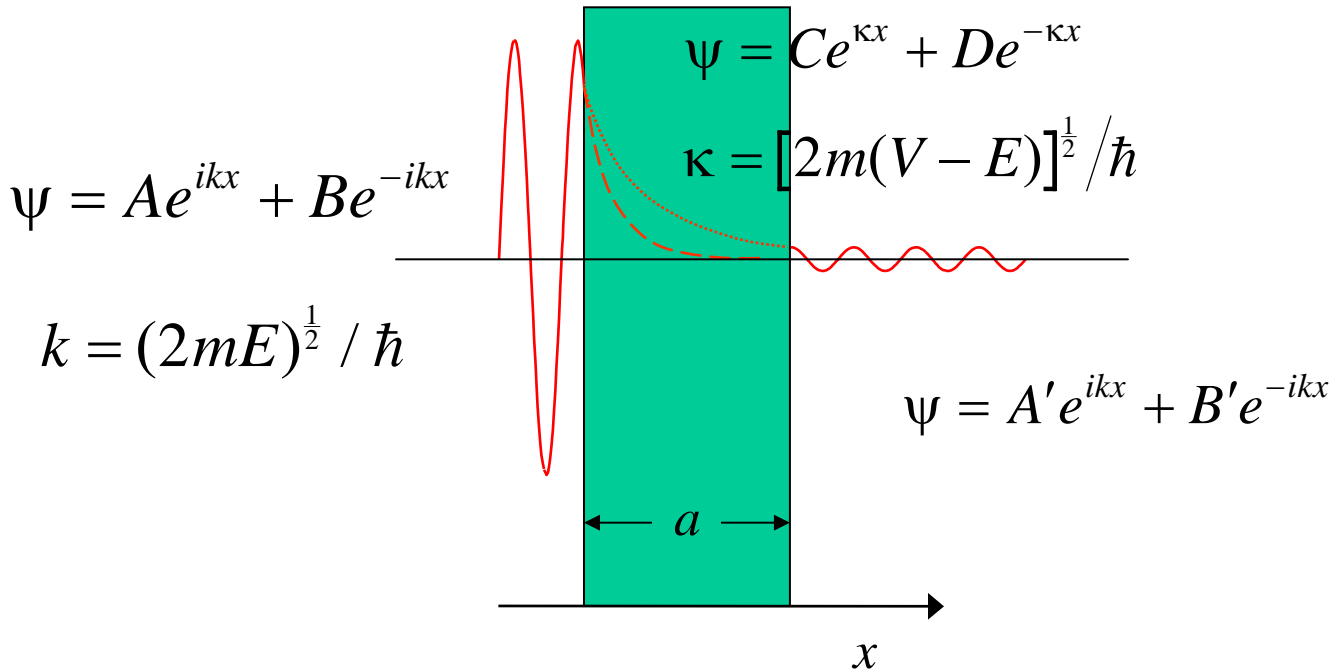


Dissociation limit



Tunnelling

Consider a particle of energy E striking a potential barrier of height V .



Application of boundary conditions gives the transmission probability:

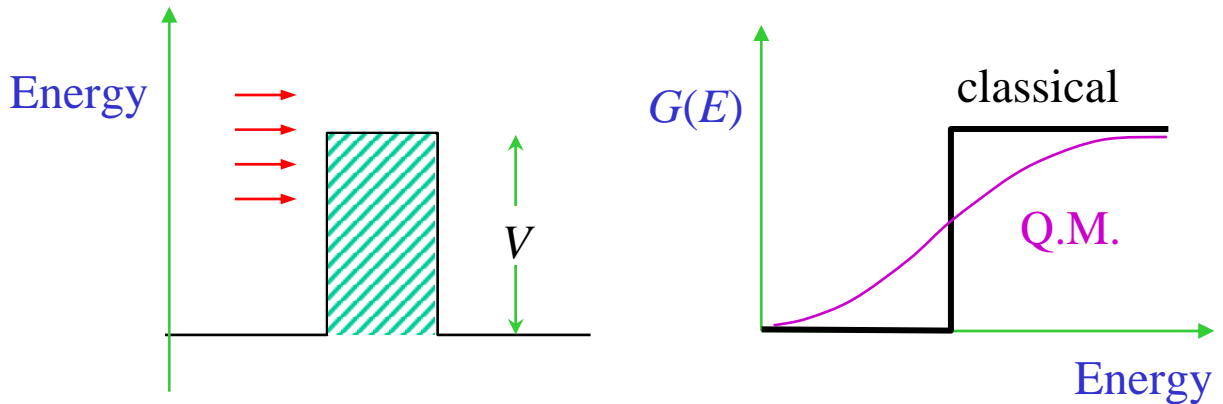
$$T = \frac{A'^2}{A^2} = \left\{ 1 + \frac{(e^{\kappa a} - e^{-\kappa a})^2}{16 \frac{E}{V} (1 - \frac{E}{V})} \right\}^{-1}$$

Tunnelling depends on the mass of the particle, its energy (compared to the barrier), and the width of the barrier.

Tunnelling in Chemical Reactions

Sometimes reactions occur even if the reactants have $E < E_{\text{act}}$.

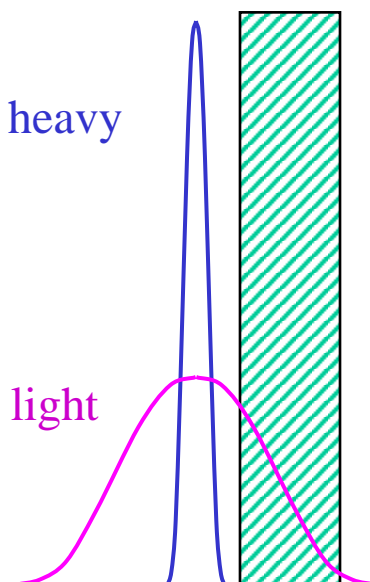
This is **tunnelling**, a consequence of the wave nature of matter.



The transmission coefficient G depends on $E - V$, the barrier width, and the particle mass.

Tunnelling is only important for light particles (H, Mu, e^-).

This is because they have a large spread in their wave packets.



Tunnelling occurs if the wave packet width \gtrsim barrier width.