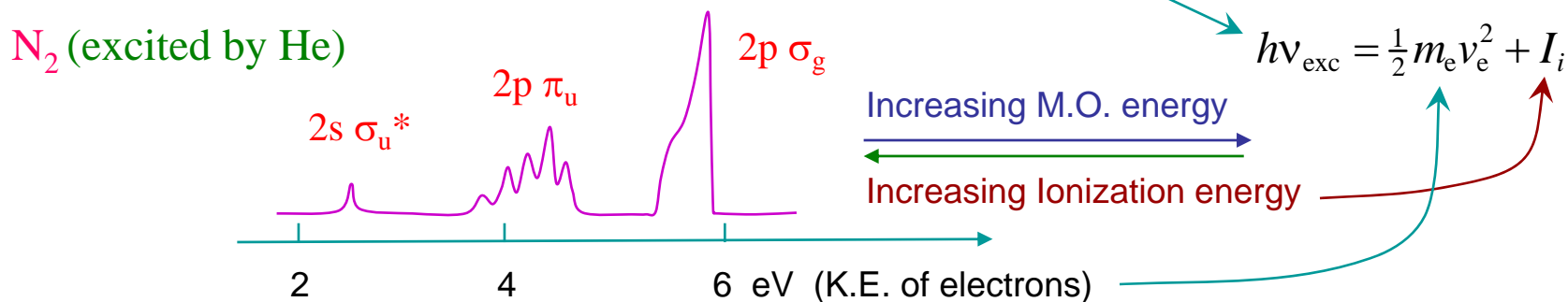


Photoelectron Spectroscopy

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

The source must be intense, monochromatic and energetic. In conventional (UV) P.E.S. a common source of excitation is $\text{He } 1s2p \ ^1P_1 \xrightarrow[\text{21.22 eV}]{\lambda=58.4 \text{ nm}} 1s^2 \ ^1S_0$



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

Fine structure in the P.E. spectrum shows that the ion is vibrationally excited,

$$h\nu_{\text{exc}} = \frac{1}{2} m_e v_e^2 + I_i + \Delta E_{\text{vib}}^+ \quad \text{consistent with changes in bond lengths/angles in the ion.}$$

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

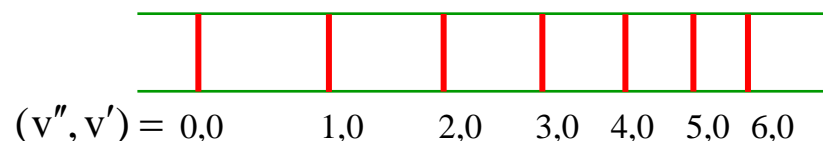
vibrational-electronic

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

$\Delta v = 0, \pm 1, \pm 2, \dots$ 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.

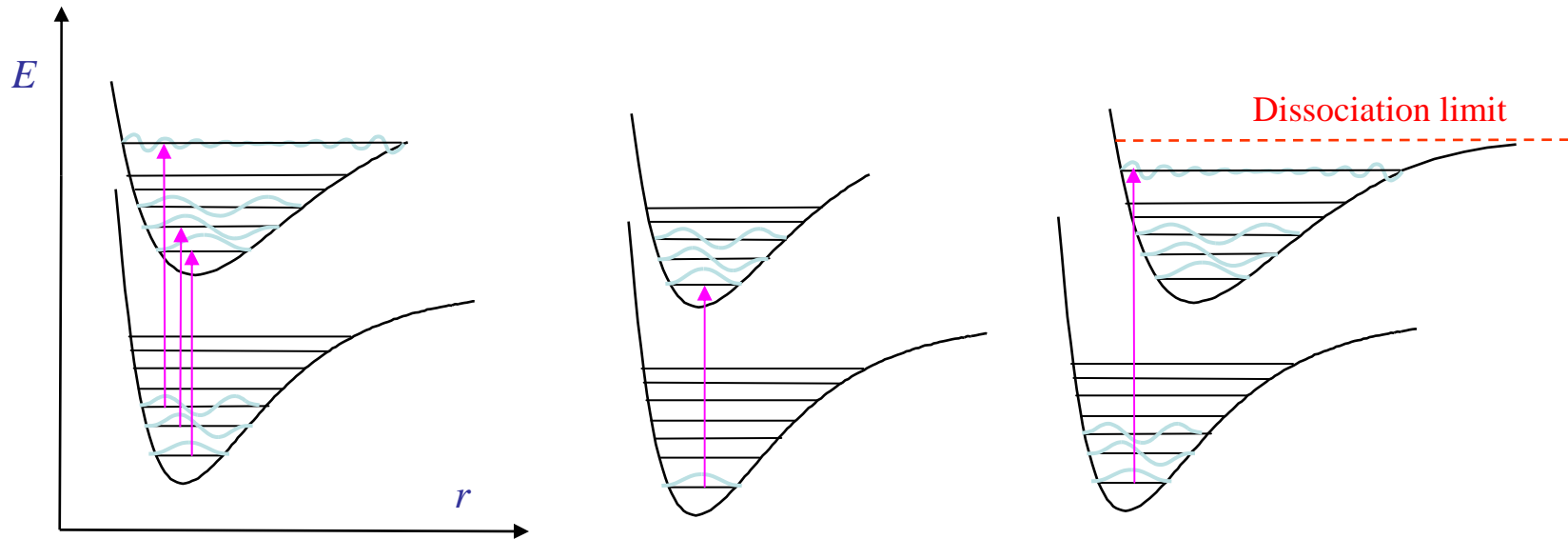
$$\begin{aligned} \langle \Psi' | \hat{d} | \Psi'' \rangle &= \langle \psi'_e \psi'_v | \hat{d}_e | \psi''_e \psi''_v \rangle + \langle \psi'_e \psi'_v | \hat{d}_k | \psi''_e \psi''_v \rangle \\ &= \langle \psi'_v | \psi''_v \rangle \langle \psi'_e | \hat{d}_e | \psi''_e \rangle + \langle \psi'_e | \psi''_e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

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

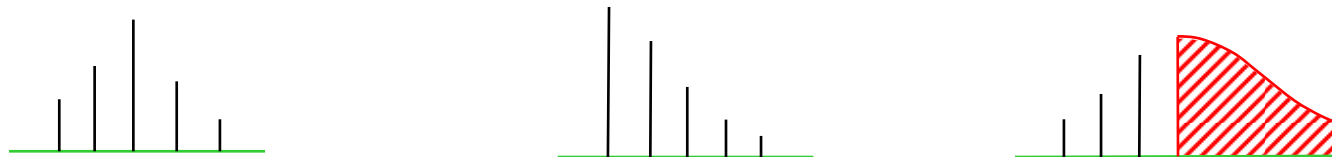
The approximation depends on the separability of electronic and vibrational wavefunctions, i.e. the **Born-Oppenheimer Principle**.

Franck-Condon Principle

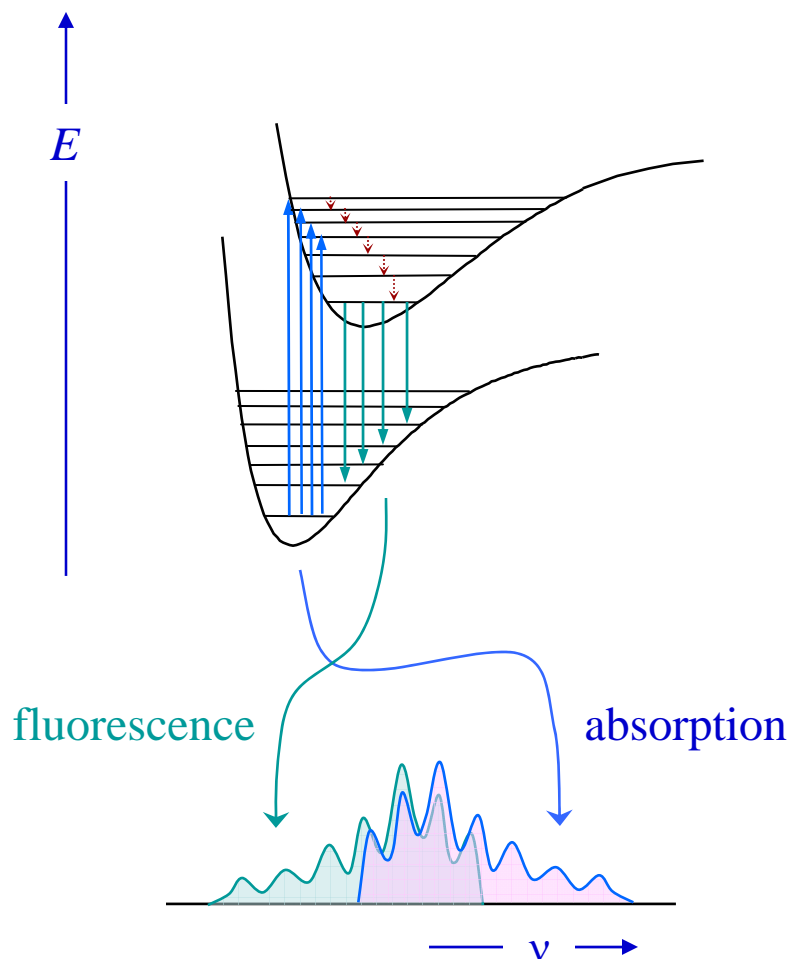
Electronic transitions occur faster than nuclei can respond. \Rightarrow Vertical transitions
Spectral intensities depend on the overlap integral for the upper and lower states.



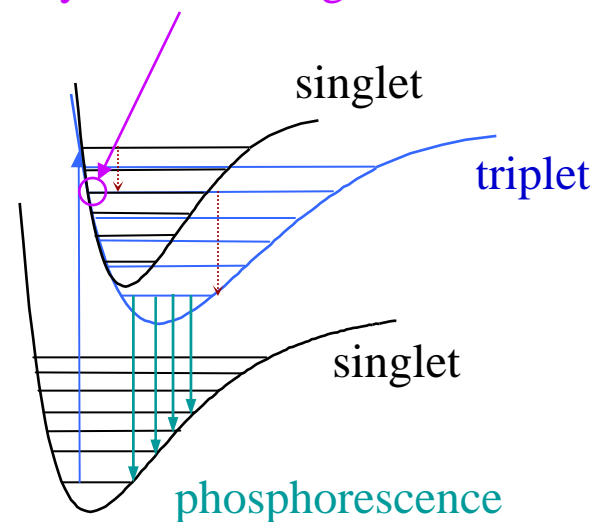
Spectra



Fluorescence and Phosphorescence



inter-system crossing: $S \rightarrow T$



Phosphorescence lifetimes are generally longer than fluorescence lifetimes because the triplet-singlet transition is “forbidden”. Such inter-system transitions are enhanced by the **heavy atom effect**.

Comparison of M.O. and V.B. Methods

- Both predict increased electron density between bound states.
- Both start with atomic orbitals but combine them in different ways:

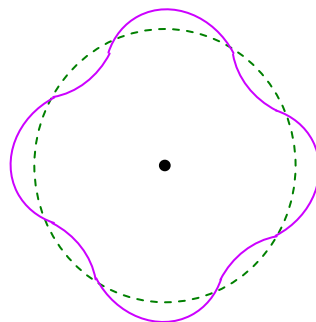
$$\Psi_{\text{MO}} \propto [a(1) \pm b(1)][a(2) \pm b(2)]$$

$$\Psi_{\text{VB}} \propto a(1)b(2) \pm b(1)a(2)$$
- Both require paired electron spins in the bond (**Pauli Principle**).
- M.O. theory predicts states; electrons are then added (**Aufbau**).
- M.O. electrons are naturally delocalized over a number of atoms, although a particular orbital may be localized.
- M.O. wavefunctions overemphasize ionic terms; C.I. is used to correct this.
- In M.O., hybridization is simply L.C.A.O. on a single centre.
- M.O. uses SCF to accommodate orbital distortion as electrons are added to states – easily handled by computer.
- V.B. starts with electron-pair bonds and builds up structures.
- V.B. uses resonant structures to achieve delocalization.
- V.B. wavefunctions naturally ignore ionic terms, but they can be added.
- V.B. needs hybridization to explain molecular shapes.
- V.B. calculations involve more complicated integrals, and a large number of resonant structures.

Why are Bohr orbits Quantized?

Treat the electron in orbit like the ‘particle on a ring’.

It must satisfy the cyclic boundary condition: $2\pi r = n\lambda$ $n = 1, 2, 3, \dots$



Combining this with the de Broglie relation $p = mv = h / \lambda$

gives the Bohr quantization condition: $L = mvr = \left(\frac{h}{\lambda}\right)\left(\frac{n\lambda}{2\pi}\right) = n\hbar$

The Virial Theorem

If the potential energy has a r^n dependence, then $\langle T \rangle = \frac{1}{2}n \langle V \rangle$

e.g. (1) the H atom

$$V \propto r^{-1}$$

$$\langle E \rangle = \langle T \rangle + \langle V \rangle$$

$$= -\frac{1}{2} \langle V \rangle + \langle V \rangle = \frac{1}{2} \langle V \rangle = -\langle T \rangle$$

e.g. (2) the harmonic oscillator $V \propto r^2$

$$\langle T \rangle = \langle V \rangle = \frac{1}{2} \langle E \rangle$$

A more general version of the **Quantum Mechanical Virial Theorem** is

$$\langle T \rangle = \frac{1}{2} \left\langle \sum_j q_j \frac{\partial V}{\partial q_j} \right\rangle$$

CHEM 260 Concepts

quantization of energy

quantization of angular momentum

boundary conditions

wave-particle duality

mass-energy conversion

momentum of mass-less particles (de Broglie)

Uncertainty Principle

tunneling

wavefunctions contain info on all properties

expectation value

orthogonality

degeneracy

resonant absorption/emission of radiation

selection rules

spin angular momentum

spin density

radial distribution function

Term symbol

anharmonicity

normal mode

potential energy surface

Born-Oppenheimer Principle

Valence Bond

LCAO

bond hybridization

Variation Principle

Overlap integral

Separation of variables

CHEM 260 Problems

Photoelectric effect

de Broglie

Particle in a box

Rigid Rotor / microwave spectroscopy

Atomic spectra of H-like atoms

Atomic term symbols

NMR

ESR

Vibrational spectroscopy

Vibration-rotation spectroscopy

Raman spectroscopy

Molecular electronic configurations

Hückel calculations on p systems

Energy-level Diagrams

Translation: particle in the box

Rotation: rigid rotor

Vibration: simple harmonic oscillator
anharmonic oscillator (Morse Curve)

Electronic: H atom
multi-electron atom
diatomic molecule
polyatomic (Hückel pi system)

Spin: NMR
ESR

Shapes of wavefunctions
atomic orbitals: radial functions
radial distribution functions
spherical harmonics
molecular orbitals