### What dictates the rate of radiative or nonradiative excited state decay?

Transitions are faster when there is minimum quantum mechanical reorganization of wavefunctions. This reorganization energy includes the energy required to change both electronic structure and nuclear geometry. i.e. the closer the resemblance of  $\Psi(S_0)$  and  $\Psi(S_1)$  the larger the rate constant  $k_{\rm fl}$  and shorter the radiative lifetime  ${}^{1}\tau$ 

• In *perturbation theory*, weak perturbations are applied to distort the zero-order wavefunction  $\Psi_0$  and give a more accurate estimate of the transition probability, *for example:* 

$$\begin{split} \Psi(\mathsf{S}_1) + P(\mathsf{S}_1 \to \mathsf{S}_0) & \to & \Psi(\mathsf{S}_1) \pm \lambda[\Psi(\mathsf{S}_0)] \to & \Psi(\mathsf{S}_0) \\ & & \lambda, resonance \\ mixing coefficient \\ \lambda &= \frac{strength \ of \ perturbation}{energy \ of \ separation} = \frac{\langle \Psi(\mathsf{S}_1) | P(\mathsf{S}_1 \to \mathsf{S}_0) | \Psi(\mathsf{S}_0) \rangle}{\Delta E(\mathsf{S}_1 \to \mathsf{S}_0)} \end{split}$$

 $\Psi_1 = \Psi_0 + \lambda [\Psi_0']$ 

Transition probability is dependent upon the resonance between states and the transition energy – commonly referred to as the ENERGY GAP LAW!

- Rates of "fully allowed" transitions are limited only by the zero-point electronic motion (~ 10<sup>15</sup> – 10<sup>16</sup> s<sup>-1</sup>)
- If nuclear (or spin) configurations of  $S_1$  (or  $T_1$ ) and  $S_0$  are not equal, mixing of  $\Psi(S_0)$ and  $\Psi(S_1)$  [or  $\Psi(T_1)$ ] is poor, and electron transition is rate-limited by the time needed for vibrational (and/or spin) reorganization

### > Why does molecular rigidity, increase emission lifetimes?

• Vibrational and spin reorganization may act as bottlenecks in electronic transitions.

$$k_{\text{obs}} = k_{\text{max}}^0 \mathbf{x} (f_{\text{e}} f_{\text{v}} f_{\text{s}})$$

 $k_{\rm obs}$  = observed rate constant

- $k_{\text{max}}^0$  = zero-point motion limited rate-constant (~ 10<sup>15</sup> 10<sup>16</sup> s<sup>-1</sup>)
- $f_{\rm e}$  = orbital configuration change factor (e.g.  $\Delta E$  and # nodal planes)
- $f_{\rm v}$  = vibrational configuration change factor
- $f_{\rm s}$  = spin configuration change factor
- Fermi's golden rule:  $k_{obs} \sim \rho \langle \Psi(S_1) | P(S_1 \rightarrow S_0) | \Psi(S_0) \rangle^2$

where  $\rho$  represents the **density of states** capable of mixing  $\Psi(S_0)$  and  $\Psi(S_1)$  and the matrix element corresponds to the transition dipole moment.

- For electronic transitions between states of the same spin, such as  $S_1 \rightarrow S_0$  the rate constant  $k_{obs}$  is limited by the time it takes for
  - the electronic wavefunction  $\Psi(S_1)$  to distort so that it can mix with  $\Psi(S_0)$
  - or for the vibrational wavefunction  $\chi(S_1)$  to distort so that it can mix with  $\chi(S_0)$
- The most important perturbation for "mixing" electronic wavefunctions is vibrational nuclear motion that is coupled to the electronic oscillation of the transition dipole (*vibronic coupling*)

$$k_{obs} = k_{max}^{0} \times \left[ \frac{\langle \Psi(S_1) | P_{vib} | \Psi(S_0) \rangle}{\Delta E_{S1-S0}} \right]^2 \times \langle \chi_{S1} | \chi_{S0} \rangle^2$$

- The matrix element here includes the vibrational operator  $P_{vib}$  that mixes  $\Psi(S_1)$  and  $\Psi(S_0)$ .
- Strong perturbation corresponds to a strong resonance between  $\Psi(S_1)$  and  $\Psi(S_0)$  such that the rate limiting factor is dependent upon the square of vibrational overlap, i.e. the *Frank-Condon factor*  $\langle \chi_1 | \chi_0 \rangle^2$
- The *Frank-Condon factor*  $\langle \chi_1 | \chi_0 \rangle^2$  is a measure of vibronic coupling between initial and final states in an electronic transition.

## **Transition probabilities**

$$k_{obs} = k_{max}^{0} \times \left[ \frac{\langle \Psi(S_0) | P_{vib} | \Psi(S_1) \rangle}{\Delta E_{1-0}} \right]^2 \times \langle \chi_0 | \chi_1 \rangle^2$$

What if the symmetry dictates that the matrix element  $P_{vib}$  = 0 ?

- In this case the electronic transition is *forbidden* (...zero-order approximation)
- All *allowed* transitions have a finite value of  $P_{vib} > 0$
- In the first order approximation perturbation of matrix elements  $P_{vib}$  and  $P_{SO}$  (vibronic and spin-orbit coupling) may overcame the zero-order forbidden transition character.
- If the transition probability is still small (< 1%) the process is "weakly allowed", i.e. the transition rate  $k_{obs}$  is too slow to compete with "strongly allowed" transitions



## Vibronic coupling contd...

- How do vibrational wave functions  $\chi$  influence the rate of radiative and nonradiative spin-allowed transitions?
- The Franck-Condon factor  $\langle \chi_0 | \chi_1 \rangle^2$  is a measure of the similarity of the vibrational wavefunctions for  $\Psi_0$  and  $\Psi_1$  and are critical in determining whether a transition is allowed or forbidden.

$$k_{obs} \sim \langle \chi_0 | \chi_1 \rangle^2$$

• The *Born-Oppenheimer approximation* allows a zero-order approximation of electronic structure & energy of an electronic state with a fixed nuclear *(nonvibrating)* and spin configuration

$$\Psi \cong \Psi_0 \chi S$$

To appreciate vibronic coupling and its influence on electronic transitions we must consider the effect of nuclear vibrational motion on the electronic structure & energy of a molecule and the perturbation it provides allowing resonance of difference electronic state wavefunctions:  $k_{obs} \sim \langle \Psi_1 | P_{vib} | \Psi_2 \rangle^2$   Molecular vibrations are constantly active opening the possibility of mixing electronic states should perturbation of the resonance mixing coefficient distort the initial electronic wavefunction to resemble that of the final state

 $\Psi(S_0) \pm \lambda[\Psi(S_1)]$ 

• The energy of a these weak vibronic perturbations  $E_{vib}$  are defined as

$$E_{vib} = \frac{\langle \Psi(S_0) | P_{vib} | \Psi(S_1) \rangle^2}{\Delta E_{0-1}}$$

• Applying Fermi's golden rule:

$$k_{obs} \sim \rho \langle \Psi(S_0) | P_{vib} | \Psi(S_1) \rangle^2$$

where  $\rho$  represents the **density of states** capable of mixing  $\Psi(S_0)$  and  $\Psi(S_1)$ 

$$\lambda \sim \frac{1}{\Delta E}$$

- $\blacktriangleright$  Large band-gap  $\rightarrow$  small resonance mixing coefficient = a low density of states
- > Small band-gap  $\rightarrow$  high resonance mixing coefficient = high density of states

$$E_{vib} = \frac{\langle \psi | P_{vib} | \psi \rangle^2}{\Delta E}$$

- Consider a low band-gap organic chromophore, with an absorption maximum at  $\lambda$  = 600 nm. This corresponds to  $\Delta E_{0-1}$  = 48 kcal mol<sup>-1</sup>
  - ▶ C−H stretch ~ 3000 cm<sup>-1</sup> ;  $E_{vib}$  = 8.58 kcal mol<sup>-1</sup>
  - $\blacktriangleright$  C=C stretch ~ 2180 cm<sup>-1</sup> ;  $E_{vib}$ = 6.23 kcal mol<sup>-1</sup>
  - > C=O stretch ~ 1700 cm<sup>-1</sup>;  $E_{vib}$  = 4.86 kcal mol<sup>-1</sup>
  - $\blacktriangleright$  C=C stretch ~ 1660 cm<sup>-1</sup> ;  $E_{vib}$ = 4.75 kcal mol<sup>-1</sup>
  - → C=N stretch ~ 1650 cm<sup>-1</sup>;  $E_{vib}$  = 4.72 kcal mol<sup>-1</sup>

Vibronic coupling between ground and excited states is very weak due to large  $\Delta E$ however excited state energy gaps are much smaller and vibronic coupling becomes very important. C–H stretches are very effective in mixing electronically excited states

- Radiative and nonradiative electronic transitions depend upon the ability of vibrations (distortion of the molecular geometry) to couple the initial electronic wavefunction to vibrations of the final electronic wavefunction, particularly for electronic excited states.
- a) "weak vibronic coupling"
   In-plane symmetric stretching for an sp<sup>2</sup> hybridized C atom has no effect of the spatial distribution of the p orbital. This vibrational stretch is decoupled from the electronic wavefunction.
- b) "strong vibronic coupling" Asymmetric stretching causes the atom to re-hybridize to sp<sup>3</sup> illustrating distortion of the electronic wavefunction for the molecule whose energy will change (lower) accordingly.



## Classical harmonic oscillator model of the Franck-Condon principle: radiative transitions

- Consider three different situations (a, b & c) for a heteronuclear diatomic molecule with  $m_1 >> m_2$  e.g. C–H



- The timescale for photoabsorption is on the order of ~  $10^{-15} 10^{-16}$  s such that the geometry produced at the instance of the electronic transition to the upper surface by a radiative transition, e.g. fro S<sub>0</sub> to S<sub>1</sub>, is governed by the relative positions of the PE surfaces controlling the vibrational motion.
- Assuming both PE curves have similar shapes (i.e. identical bond order) the most favored transitions are predicted to be

a)  $S_0(v_0) + hv \rightarrow S_1(v_0)$ 

- typical of extensively conjugated cyclic  $\pi$  systems, e.g. pyrene
- b)  $S_0(v_0) + hv \rightarrow S_1(v_n)$  n > 0
  - typical of  $n \rightarrow \pi *$  systems, e.g Ph<sub>2</sub>C=O
- c)  $S_0(v_0) + hv \rightarrow S_1(v_x)$  x > n
  - typical of poorly conjugated acyclic  $\pi$  systems, e.g. 2,3-butane
- It follows that the original nuclear geometry of the ground state is a turning point of the new vibrational motion in the excited state, and that vibrational energy is stored by the molecule in the excited state.

 In a semi-classical model where we impose quantization on the classical harmonic oscillator, radiative transitions from v = 0 are not initiated from a single geometry but from a range of geometries that are explored during the zero-point motion of the vibration.



# Quantum mechanical harmonic oscillator model of the Franck-Condon principle: <u>RADIATIVE TRANSITIONS</u>

- Expressed in quantum mechanical terms the Franck-Condon principle states that the most probably transitions between electronic states occur when the wave function of the initial vibrational state ( $\chi_i$ ) most closely resembles the wave function of the final vibrational state ( $\chi_f$ ).
- Mathematically we represent the vibrational wavefunction overlap integral as

 $<\chi_{0} | \chi_{1} >$ 

• Hence the term *Franck-Condon factor* 

$$k_{obs} = k_{max}^{0} \times \left[\frac{\left\langle \Psi_{i} \mid P_{vib} \mid \Psi_{f} \right\rangle}{\Delta E_{f-i}}\right]^{2} \times \left[\frac{\left\langle \Psi_{i} \mid P_{SO} \mid \Psi_{f} \right\rangle}{\Delta E_{f-i}}\right]^{2} \times \left\langle \chi_{i} \mid \chi_{f} \right\rangle^{2}$$

$$Vibrational$$

$$Spin-orbit$$

$$Franck-Condon$$

$$factor$$

• The Franck-Condon principle provides a useful visualization of both radiative and noradiative transitions

- The larger the FC factor  $<\chi_0 | \chi_1 >^2$  the greater constructive overlap of vibrational wavefunctions the smaller the nuclear reorganization the more probable the electronic transition.
- The FC factor provides a selection rule for electronic transitions and governs the relative intensities of radiative transitions (absorption and emission).
- For emissive processes the critical overlap is between the  $\chi$ corresponding to  $S_1(v_0)$  and the various vibrational levels  $(v_n)$ of  $S_0$



## The Franck-Condon principle: NONRADIATIVE TRANSITIONS

- For a radiationless transition, the initial and final electronic states must (apart from *isc*) be indistinguishable, i.e.
  - the same energy
  - the same nuclear geometry
- Typically a small amplitude vibration (e.g.  $v_0$ ) of a higher electronic state couples vibronically with a higher amplitude vibrational state  $v_n$  of a lower energy electronic state.
- Subsequent equilibration of the  $v_n$  state of the lower energy electronic state results in dissipation of heat to the molecules local environment (solvent).

 $S_1(v_0) \rightarrow [S_0(v_n)] \rightarrow S_0(v_0) + heat$ 

- Only at the crossing point of two wavefunctions does each state have the same energy and nuclear geometry...*almost like a crossroad of electronic states !*
- For a radiationless transition, e.g. from  $\rm S_1$  to  $\rm S_0$  , energy and momentum (PE) must be conserved

 Radiationless transitions are most probable when two PE curves for a vibration cross (or come very close to one another). In this scenario the energy, motion, and phase of the nuclei are conserved during the transition.



- If there is a spin change associated with the horizontal transition the transition is *strictly forbidden in a zero-order approximation*.
- Mixing of spin states requires a change in spin angular momentum.
- Total angular momentum must be conserved so any change in spin angular momentum is here associated with a change in orbital angular momentum...this defines *spin-orbit coupling*.
- A *first order approximation invokes spin-orbit coupling* which enables resonance between, e.g. singlet and triplet states, making *intersystem crossing* possible.

## Oscillator strength (f): classical model

- **f**, absorption oscillator strength, is a measure for the integrated intensity of electronic transitions. In classical terms; the ratio of light intensity absorbed by a chromophore relative to an electron which behaves as a perfect harmonic oscillator (f = 1).
- For *f* = 1, every photon of the appropriate frequency that interacts with the electron will be absorbed.
- The oscillator strength *f* may be related to the molar absorption coefficient ε assuming that the harmonic oscillating electronic excited state is unidimensional, i.e. an oscillating dipole.

$$f = 4.3 \times 10^{-9} \int \varepsilon \, d\bar{\nu}$$

• The integral component corresponds to the area under the absorption curve on a plot of molar absorptivity vs. wavenumber ( $\epsilon$  vs.  $\bar{\nu}$ ). <u>As  $\epsilon$  is characteristic for each</u> <u>frequency, line intensity is sufficient here without integration</u>.

## Oscillator strength (f): quantum mechanical model

- For an electronic transition to occur an oscillating dipole must be induced by interaction of the molecules electric field with electromagnetic radiation.
- In fact both  $\varepsilon$  and  $k^0$  can be related to the transition dipole moment ( $\mu_{ge}$ )
- If two equal and opposite electrical charges (e) are separated by a vectorial distance (r), a dipole moment ( $\mu$ ) of magnitude equal to er is created.

 $\mu = e \mathbf{r}$  (e = electron charge,  $\mathbf{r}$  = extent of charge displacement)

• The magnitude of charge separation, as the electron density is redistributed in an electronically excited state, is determined by the *polarizability* of the electron cloud ( $\alpha$ ) which is defined by the transition dipole moment ( $\mu_{ge}$ )

$$\alpha = \mu_{\rm ge} / E$$
 (*E* = electrical force)  
 $\mu_{\rm ge} = e r$ 

• The magnitude of the oscillator strength (*f*) for an electronic transition is proportional to the square of the transition dipole moment produced by the action of electromagnetic radiation on an electric dipole.

$$f \propto \mu_{\rm ge}^2$$
 = (e r)<sup>2</sup>

## Shapes of absorption and emission spectra

- The structure of absorption and emission spectra can be interpreted with respect to molecular structure.
- The agreement between calculated and experimental quantities for singlet-singlet electronic transitions are generally excellent when
  - ground and excited state structures are very similar.
  - Low symmetry precludes symmetry forbidden selection rules
- At low pressure, in the gas phase, atomic absorption and emission spectra are characteristic line spectra due to the absence of rotations, vibrations and collisions that "broaden" the ground-excited state transition energies.
- Molecular systems display broadening due to coupling of electronic and vibrational wavefunctions. In truth, what we typically refer to as electronic absorption or emission spectra are in reality a hybrid of electronic and vibrational spectra. Albeit we observe vibronic transitions that transverse electronic states.



- For some solvent phase molecules vibrational bands (aka vibrational fine structure) are still observed corresponding to a single electronic transition between discrete vibrational states.
- This occurs when coupling between the solvent electric field and the electronic transition is weak.
  - → The pyrene molecule displays  $\pi \rightarrow \pi^*$  vibrational fine structure in its absorption spectrum that inform on the nuclear geometry of the S<sub>1</sub> excited state.
  - → The pyrene molecule displays  $\pi^* \rightarrow \pi$  vibrational fine structure in its emission spectrum that inform on the nuclear geometry of the S<sub>0</sub> ground state.





The  $\pi$ -molecular orbitals of pyrene





# The Franck-Condon principle and molecular electronic absorption spectra

### 1. Small PEC displacement

- Consider ground  $\Psi_0$  and excited state \* $\Psi$  potential curves which only differ in magnitude of potential energy, i.e similar nuclear geometries in both states.
- In this case the FC principle dictates, since absorption must occur via a vertical transition, that the  $\Psi_0(v_0) \rightarrow^* \Psi(v_0)$  transition will be intense due to a large FC factor  $<\chi_0[\Psi_0(v_0)] |\chi_1[^*\Psi(v_0)] >^2$
- Vertical transitions that the  $\Psi_0(v_0) \rightarrow * \Psi(v_n)$  n > 0 have much smaller FC factors  $<\chi_0 | \chi_1 >^2$  and are considered Franck-Condon forbidden which results in weak intensity and low molar extinction coefficients.









#### 2. Significant PEC displacement

- Consider ground  $\Psi_0$  and excited state \* $\Psi$  potential curves where  $r_{eq}$  is larger in \* $\Psi$ .
- This is often the case due to population of antibonding orbitals in  ${}^*\Psi$  with corresponding bond weakening.
- In this case the FC principle dictates, since absorption must occur via a vertical transition, that the  $\Psi_0(v_0) \rightarrow *\Psi(v_0)$  transition will be weak due to a small FC factor  $<\chi_0[\Psi_0(v_0)] |\chi_1[*\Psi(v_0)] >^2$ .
- This transition is now considered Franck-Condon forbidden which results in weak intensity and low molar extinction coefficients.
- Vertical transitions  $\Psi_0(v_0) \rightarrow *\Psi(v_n)$ where n > 0 now have larger FC factors  $<\chi_0 | \chi_1 >^2$  and are considered Franck-Condon allowed which results in strong intensity and high molar extinction coefficients.







#### 3. Large PEC displacement

- Consider ground  $\Psi_0$  and excited state \* $\Psi$  potential curves where  $r_{eq}$  is so large bond dissociation occurs in \* $\Psi$ .
- In the case of a diatomic molecule X-Y for example there is no vibrational fine structure observed as the bond is broken and thus does not exist to give rise to bending, stretching etc.



# The Franck-Condon principle and molecular electronic emission spectra

- In solution, the rate of vibrational and electronic energy relaxation among excited states is very rapid compared to the rate of emission.
- Prior to emission, rapid internal conversion via multiple pertubations takes place from the  $S_n(v_n)$  state aided by molecular collisions in solution (with solvent). Polyatomic molecular systems display particularly rapid internal conversion due to perturbations induced by vibronic coupling across the nuclear framework.
- This is the basis of Kasha's rule which assumes that emission will only occur from the  $S_1(v_0)$  electronic state...exceptions do exist of course, e.g. azulene  $S_2 \rightarrow S_0$
- In analogy to absorption, the most probably emissions will occur via "vertically aligned" transitions with the largest FC factor.
- The equilibrium separation  $r_{eq}$  of the ground-state S<sub>0</sub> PEC is smaller than that of the S<sub>1</sub> excited state (or any excited state for that matter) as the latter electronic state includes an occupied antibonding orbital.
- As a consequence the most probable vertical transition produces a vibrationally excited, structurally distorted, form of the S<sub>0</sub> electronic state.



Experimental example: anthracene



- small PEC displacement
- Anthracene is one example of rigid fused aromatic ring hydrocarbons with a small displacement of its potential energy curves.
- In its excited state the molecule bends slight across its 9,10-positions.
- Strong  $S_0(v_0)-S_1(v_0)$  and  $S_0(v_0)-S_1(v_1)$  transitions are observed in both its absorption and emission spectra.
- Both absorption and emission  $S_0(v_0)-S_1(v_0)$  transitions overlap.
- Any energy difference between absorption  $S_0(v_0) \rightarrow S_1(v_n)$  and emission  $S_1(v_0) \rightarrow S_0(v_n)$  bands correspond to vibrational quanta.
- Vibrational fine structure for spin-allowed transitions differ slightly from those that are spin-forbidden .



## **Pi MO Energy Level Scheme for ethenes**







• As the number of nodes in the  $\pi$ -systems increases the MO is destabilized.

## Pi MO Energy Level Scheme for the Allyl Anion



• As the number of nodes on the allyl ligand increase the MOs of the free ligand increase in energy, i.e. become less stable.

## Pi MO Energy Level Scheme for *cis*-1,4-butadiene



• As the number of nodes in the  $\pi$ -systems increases the MO is destabilized.



 $B_{2g}$  (6 nodes) anti-bonding

 $E_{2u}$  (4 nodes) anti-bonding

 $E_{1g}$ (2 nodes)
bonding

 $A_{2u}$ (0 nodes)
bonding



### The $\pi\text{-molecular}$ orbitals of the cyclopentadienyl ring (D\_{\_{5h}})



The  $\pi\text{-molecular}$  orbitals of the pyrrole ring (C\_2\_v)

40



### The $\pi\text{-molecular}$ orbitals of the cyclopentadienyl ring (D\_{\_{5h}})



The  $\pi$ -molecular orbitals of the cyclopentadienyl ring (D $_{\rm 5h}$ )







The  $\pi$ -molecular orbitals of terthiophene

43





44