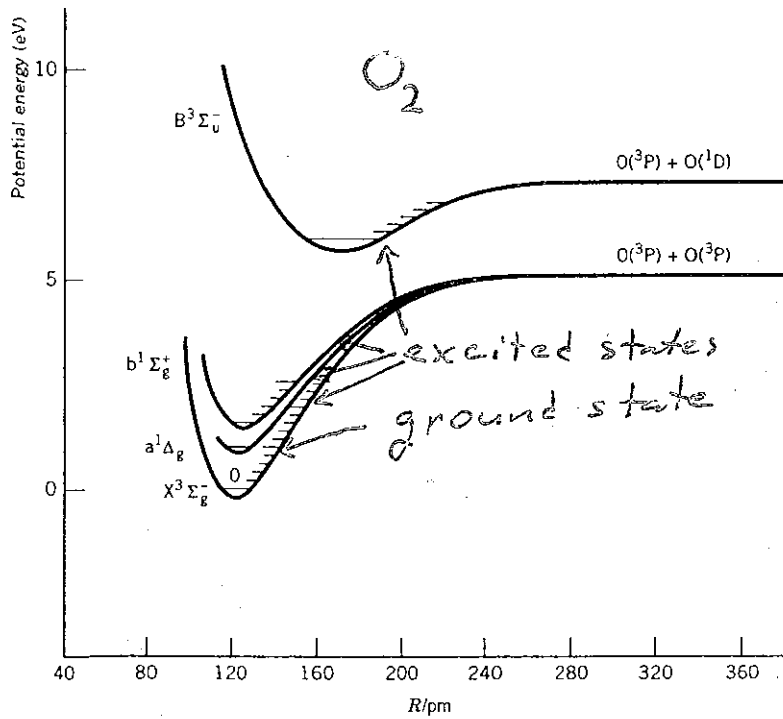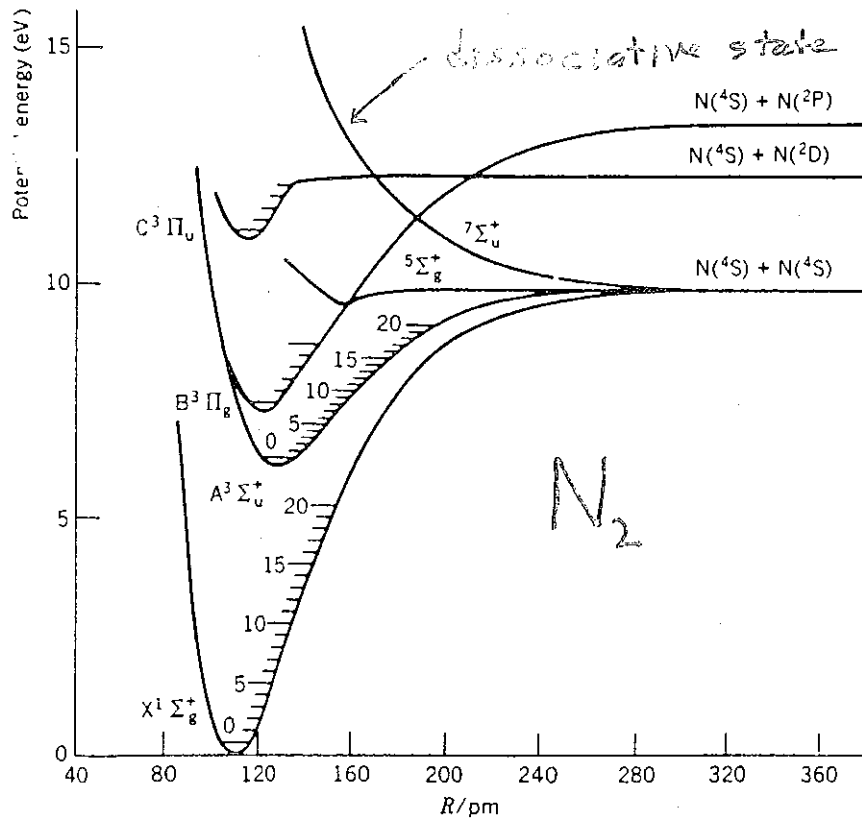# Potential Energy Surfaces

When an excited electronic state is formed,
the electron cloud is redistributed, creating
a new set of forces in the molecule. In
the excited electronic state, the molecule is
not static, but is dynamic just as in the
ground state, responding to the new forces.
Consequently, each excited state has its
own PES, just as the ground state.

Let's look at a few examples. To note E_S
we do:

- Each el. state has vibr. + rot. levels.
  Only vibr. levels are shown.
- Excited el. states tend to have longer R_e
  b/c they generally have more antibonding
  character.
- Vibr. and Rot. constants are different in
  the excited el. states b/c the internal
  forces (e.g. bond strength) and geometry
  (hence moment of inertia) are different.
  [Often use ' for exc. el. state: $\tilde{\nu}, \tilde{\nu}'; \tilde{B}, \tilde{B}'$
- Some excited el. states are dissociative;
  the PES has no well.

Potential energy (eV)

O_2

$B^3\Sigma_u^-$

$O(^3P) + O(^1D)$

$O(^3P) + O(^3P)$

$b^1\Sigma_g^+$

$a^1\Delta_g$

0

$X^3\Sigma_g^-$

excited states

ground state

R/pm

40   80   120   160   200   240   280   320   360

10

5

0

Potential energy (eV)

dissociative state

$N(^4S) + N(^2P)$

$N(^4S) + N(^2D)$

$C^3\Pi_u$

$^7\Sigma_u^+$

$^5\Sigma_g^+$

$N(^4S) + N(^4S)$

$B^3\Pi_g$

$A^3\Sigma_u^+$

$X^1\Sigma_g^+$

N_2

R/pm

Electronic Transitions: Franck-Condon Principle

Spec. transitions may take place btw el.
states. Some transitions are allowed, others
forbidden. For example, one sel. rule is
$\Delta S = 0$. This sel. rule is sometimes broken,
though, b/c spin-orbit coupling provides
a mech. for spin transitions.

El. transitions require a lot of energy and
tend to occur at visible and UV frequencies.
They do not occur in isolation, but are
accompanied by vibr. + rot. transitions.
The rot. levels are so closely spaced that
rot. transitions are often not resolved. The
vibr. structure in spectra is important, though,
so we will give it attention.

We now introduce an important paradigm
for understanding the vibr. structure in
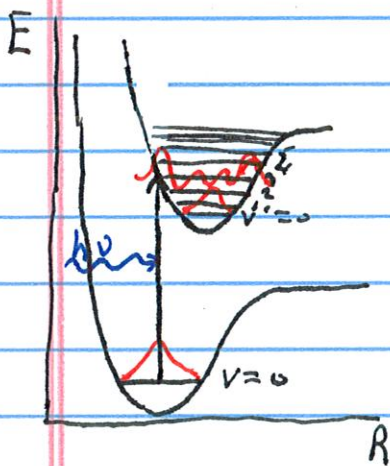el. spectra.

Franck-Condon principle

Classical formulation:

B/c they are so massive, nuclei do not move during an el. transition.

QM formulation:

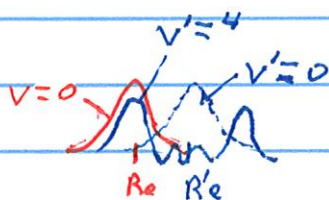The nuclei retain their initial dynamical state during an el. transition.

Let's understand this in stages, beginning with a simple rule.

Draw vertical line from mid-point of $v=0$ level in lower el. state to where it crosses upper PES. Most probable transition is to nearest v' level in upper el. state.

"Vertical transition"

Reason for rule: Consider vibr. wavefn.

$v'=4 \leftarrow v=0$ good over $\Rightarrow$ intense tr.

$v'=0 \leftarrow$ "   poor " $\Rightarrow$ weak "

Mathematical underpinning

$$P_{V_f V_i} \propto |\vec{\mu}_{fi}|^2 \qquad \vec{\mu}_{fi} = \int \Psi_f^* \hat{\vec{\mu}} \, \Psi_i \, d\tau$$

not concerned with
— will integrate out or descr. rot. transit.

$$\Psi \approx \Psi_{el} \, \Psi_{vib} \, \Psi_{rot} \, \Psi_{tr}$$

$$\hat{\vec{\mu}} = \sum_{\substack{all \\ part.}} q_i \vec{r}_i = -e \sum_{elec.} \vec{r}_i + e \sum_{nuc.} Z_j \vec{R}_j$$

$$\vec{\mu}_{fi} = \int \Psi_{\mathcal{E},f}^* \Psi_{v,f}^* \left(-e \sum_i \vec{r}_i + e \sum_j Z_j \vec{R}_j \right) \Psi_{\mathcal{E},i} \Psi_{v,i} \, d\tau$$

$$\underbrace{= -e \sum_i \int \Psi_{\mathcal{E},f}^* \vec{r}_i \Psi_{\mathcal{E},i} \, d\tau_e}_{\vec{\mu}_{\mathcal{E},fi}} \underbrace{\int \Psi_{v,f}^* \Psi_{v,i} \, d\tau_n}_{S(v_f, v_i)}$$

$S(v_f, v_i)$
Franck–Condon factor

not orthog.

$$+ e \sum_j Z_j \underbrace{\int \Psi_{\mathcal{E}_f}^* \Psi_{\mathcal{E}_i} \, d\tau_e}_{0} \int \Psi_{v_f}^* \vec{R}_j \Psi_{v_i} \, d\tau_n$$

$$P_{V_f V_i} = |\vec{\mu}_{e,fi}|^2 |S_{v_f, v_i}|^2$$

- $P \propto |S_{v_f, v_i}|^2$
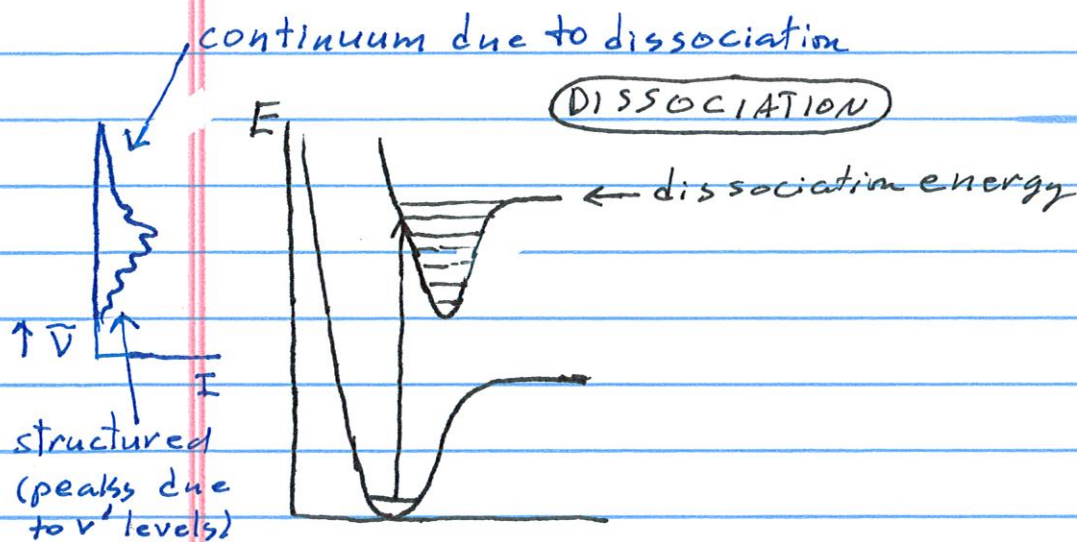- Many trans. possible, but most intense for largest $|S|^2$

Absorption spectrum
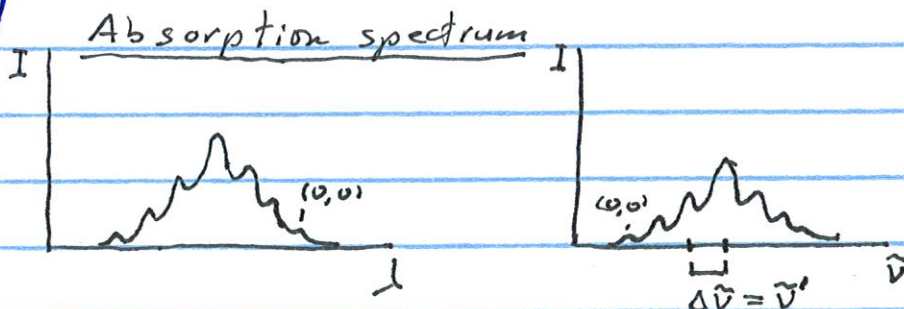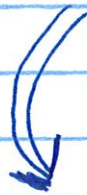
- (v', v)
- 0-0 trans. barely discernable
- $\Longrightarrow k'$!!

$$\Delta \tilde{\nu} = \tilde{\nu}' = \frac{1}{2\pi c} \sqrt{\frac{k'}{m_{eff}}}$$

Dissociation + Pre-dissociation

continuum due to dissociation

(DISSOCIATION)

E

← dissociation energy

$\uparrow \tilde{v}$

I

structured
(peaks due
to v' levels)

---

contin: dissoc.

(PRE-DISSOCIATION)

B_1

D

B_0

$\uparrow \tilde{v}$

I

contin: pre-dissoc.

- B_0, B_1 = bound states

  D = dissociative state

- At energies where D & B_1 cross,
  transition $D \rightarrow B_1$ is likely

  $\Rightarrow$ short lifetimes for v' states

  $\Rightarrow$ large uncertainty in E

  $\Rightarrow$ loss of spectrum structure
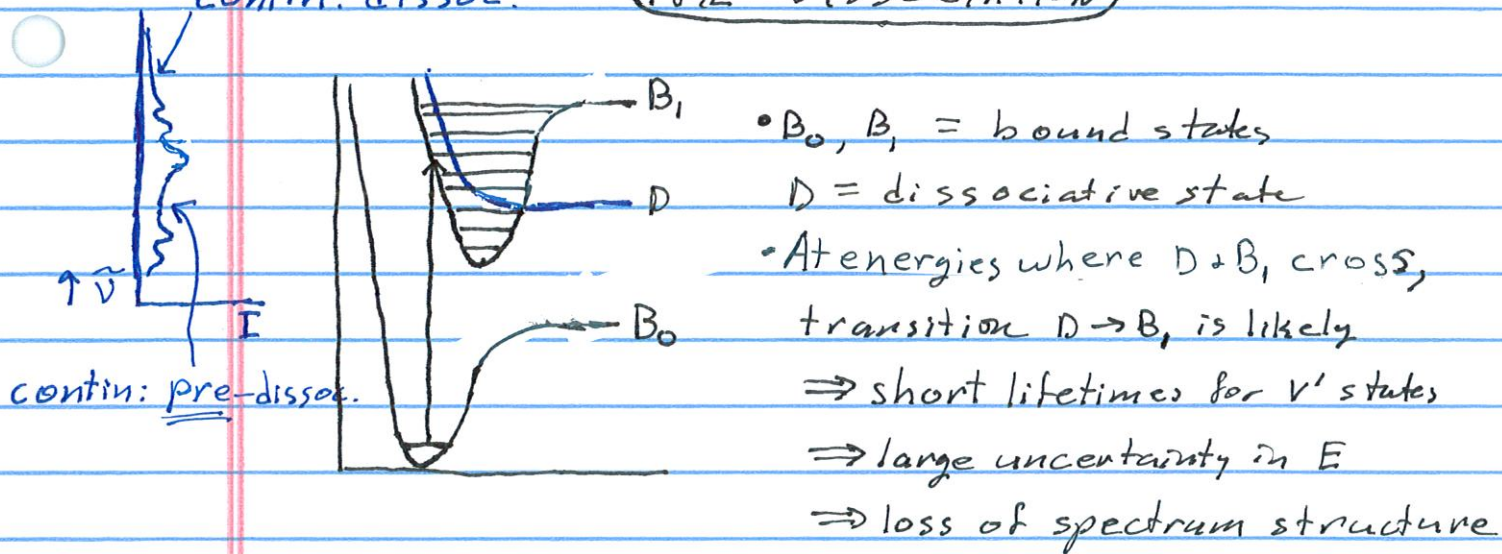
Fluorescence

Both singlet (S) or both triplet (T)...

Absorp. $h\nu_a$ $h\nu_e$ Emiss.

S_1 } radiationless decay
S_0 } radiative decay

• collisions w/ matrix
• faster than radiative decay for small ΔE
• ΔE too large for radiationless decay
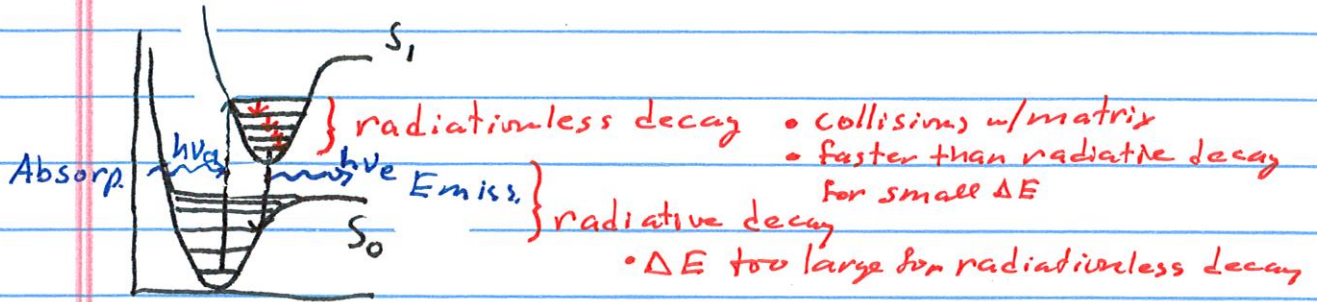
• Emission is called fluorescence
• Both el. states must have same multiplicity
• Fluoresc. is perceptible almost immediately after irradiation
• Franck-Condon principle applies
• Spacing of lines in emiss. spectrum = $\tilde{\nu}$ (vib. freq. of lower el. state)
• Fluor. radiation is @ lower freq (larger λ) than incident rad.

I

Absorp.   (0,0)   Fluor.

$\Delta\lambda \Rightarrow \tilde{\nu}'$ $\Delta\lambda \Rightarrow \tilde{\nu}$ λ
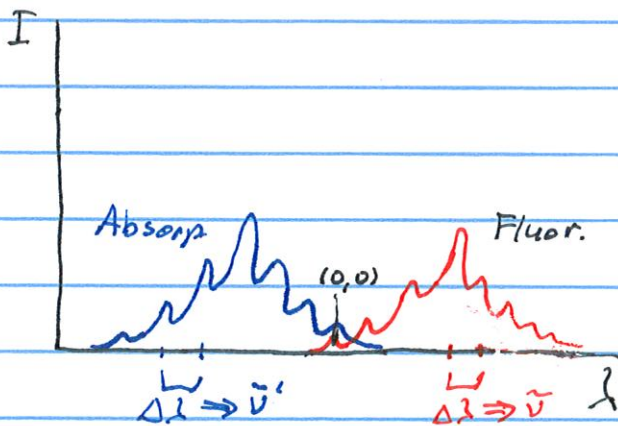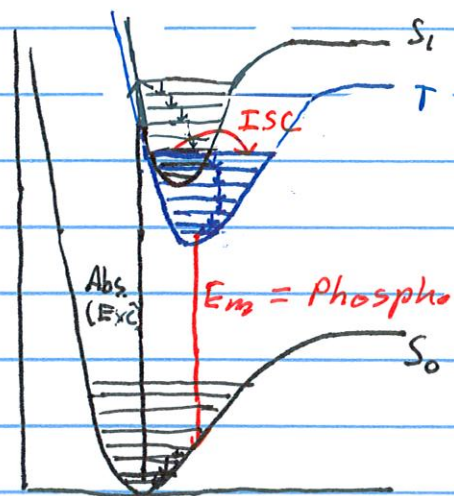
lower state pref. stabil.

Solvent effect: Increase freq. of absorp., decrease " emission.

upper state pref. stabil.

Phosphorescence

- Abs. (Excitation) is btw states of same multiplicity (e.g. singlets), here $S_1 \leftarrow S_0$
- Radiationless decay until state with different mult. (e.g. triplet) has crossing, here T with S_1
- Intersystem Crossing (ISC) occurs, $S_1 \rightarrow T$
- Radiationless decay to $V_p \geq 0$
- Phosphorescence: radiative decay $T \rightarrow S_0$
  $\Rightarrow$ Slow process b/c spin transition forbidden

Simplified representation
↓
Jablonski Diagram

Many other situations possible, e.g.→
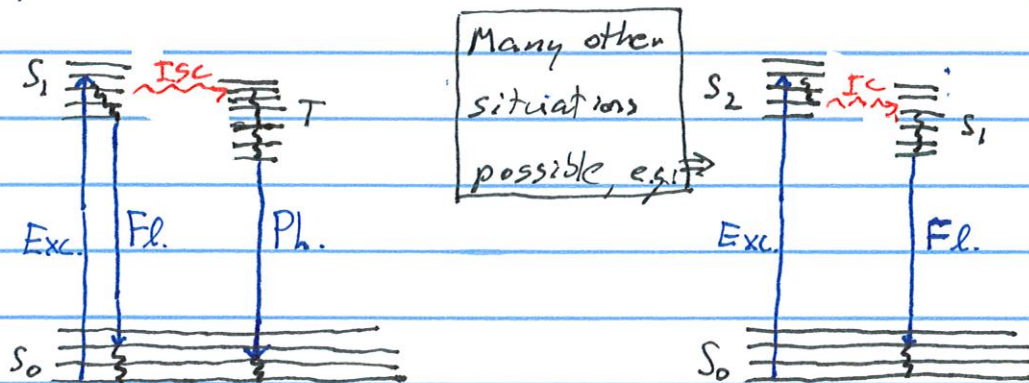
ISC = Intersystem Crossing (radiationless, btw states of different multiplicity)

IC = Internal Conversion (radiationless, btw states of same multiplicity)