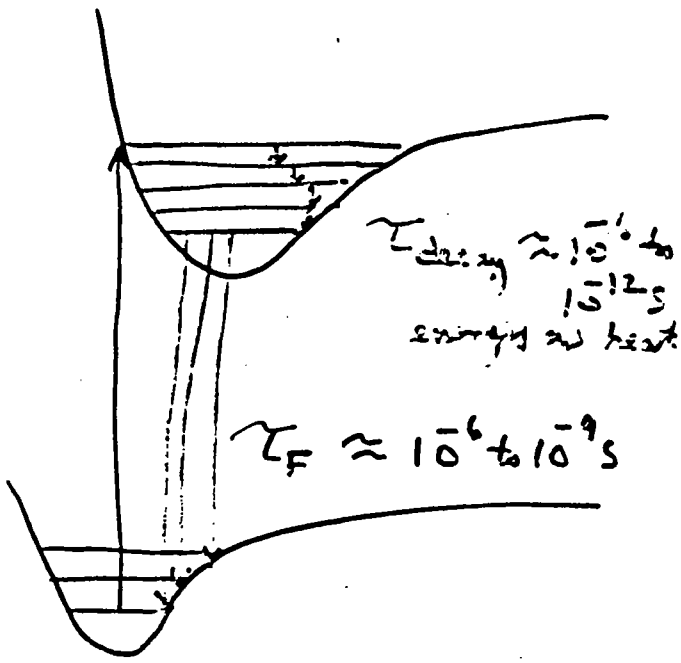
Fate of Excited States

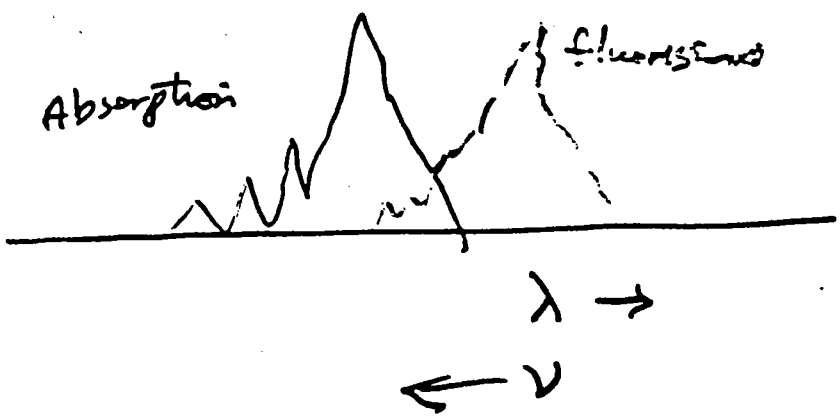
Lecture #29

Fluorescence



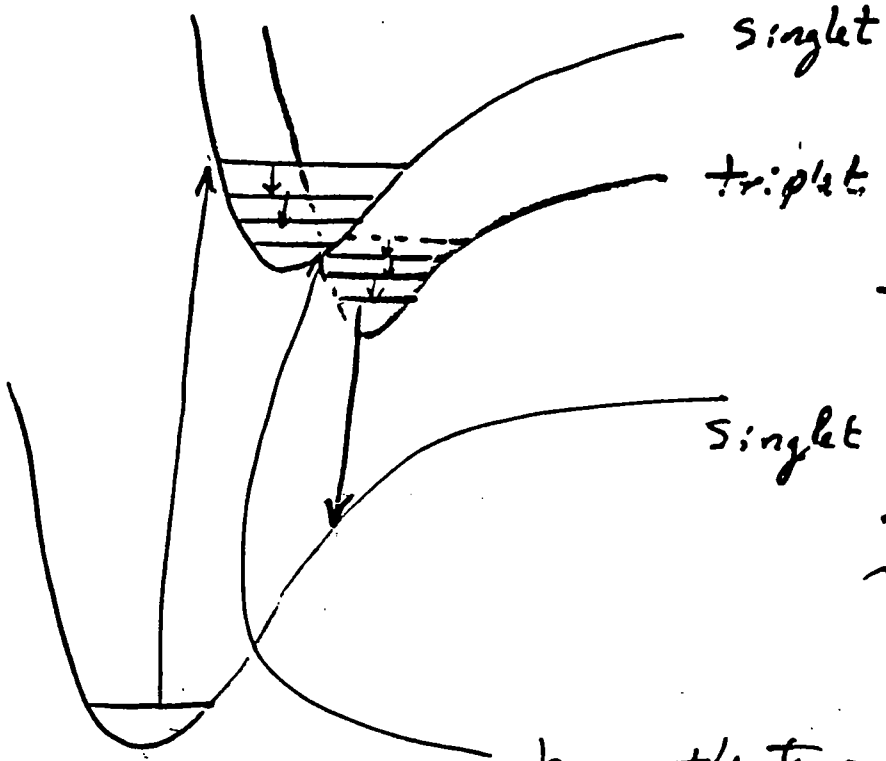
absorption - spectra reflects the upper levels - due to collisions, these (upper levels) become depopulated by non-radiative processes

as get down levels in energy, the spacing- become greater - spacings can't be long enough to give up the photons (i.e. fluoresce)



fluorescence reflects ~ ground state well!
fluorescent dyes - absorb UV, blue
fluoresce in green → orange after some energy

Phosphorescence – depends on triplet excited state (two electrons of parallel spin)



$\tau_p \geq 10^{-4}$ sec

here the two states share a common geometry – get intersystem crossing due to spin-orbit coupling

$\tau_{ix} \simeq 10^{-12} - 10^{-4}$ sec

return to ground state – spin forbidden ∴ Trapped

But: Spin-orbit coupling breaks the selection rule – get a weak emission over long times.

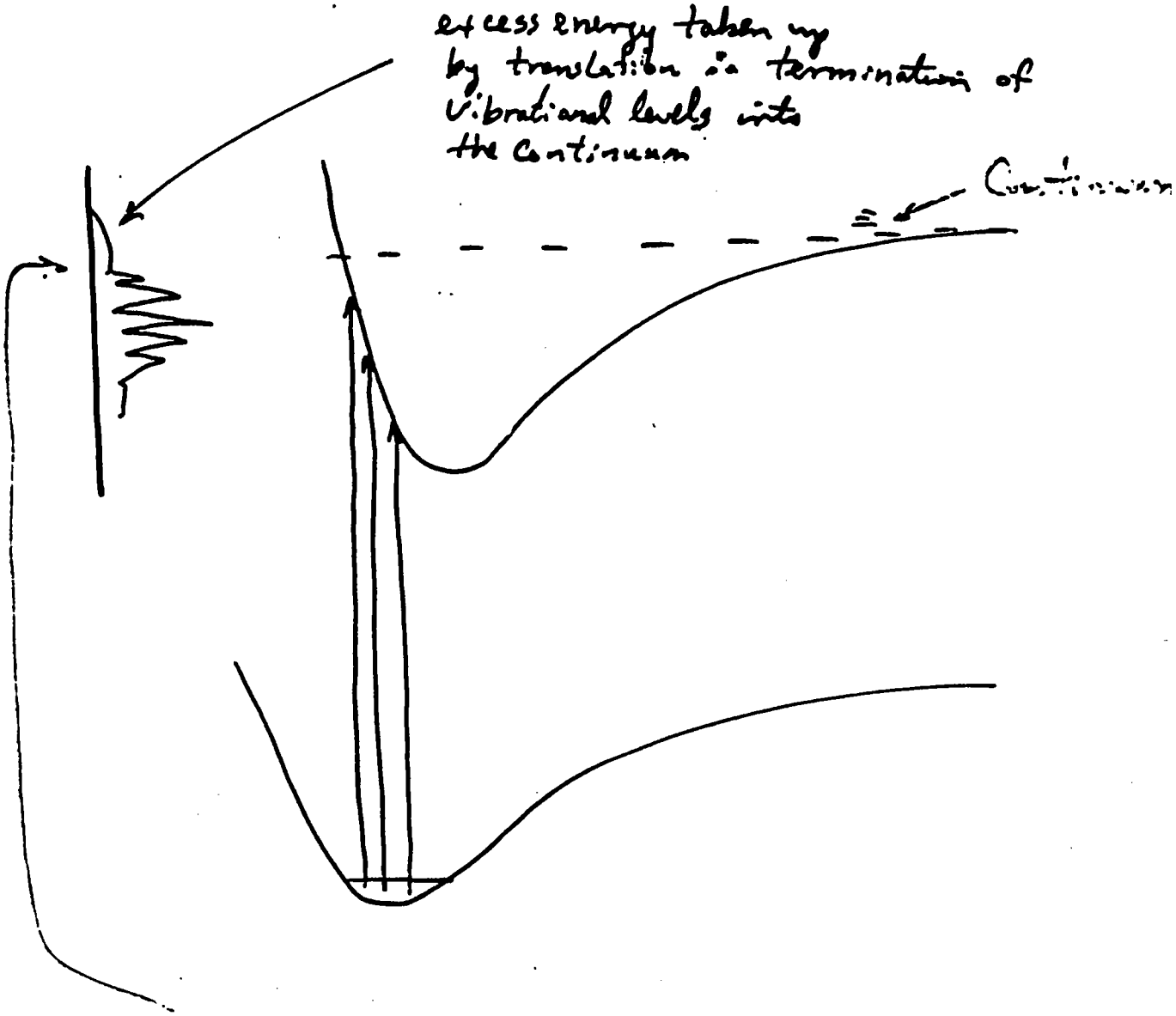
Phosphorescence (cont.)

Heavy atoms — spin-orbit coupling is large and electrons can become unpaired

Solid Samples — longer effect

since energy transfer is less efficient and intersystem crossing has time to occur

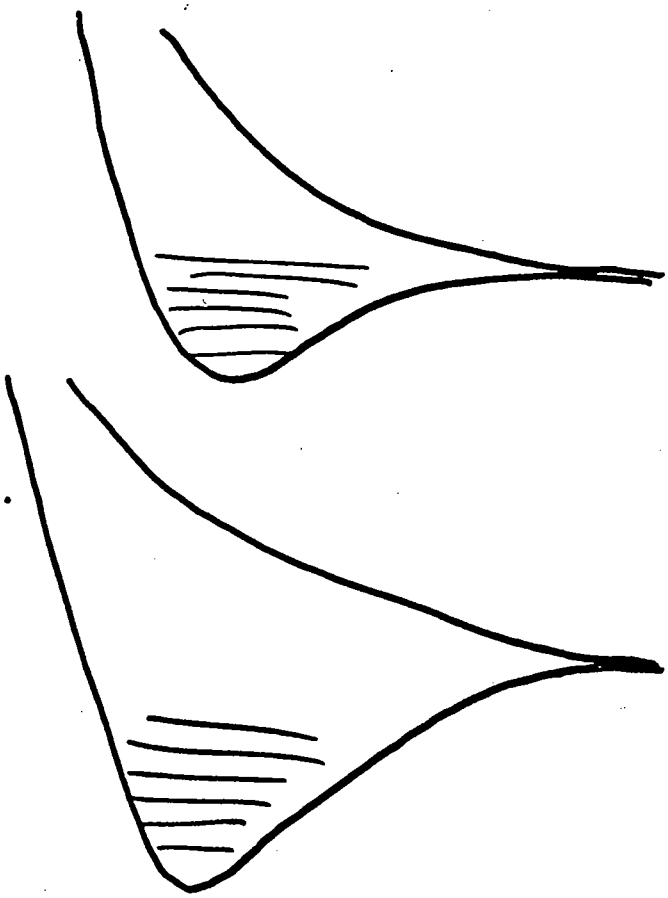
Photodissociation



∴ Can determine the bond dissociation energy of the upper state

Other Excitations Leading to Dissociation Phenomena

Antibonding, repulsive, as well as bonding states



Can dissociate to ground or excited state atoms

Photodissociation

Consider the following experimental determinations:

$$B_2 \xrightarrow{h\nu} B + B^*$$

$$17,300\ cm^{-1}$$

$$B \xrightarrow{h\nu} B^*$$

$$43,500\ cm^{-1}$$

$$B_2(v=0) \xrightarrow{h\nu} B_2^*(v=0)$$

$$50,200\ cm^{-1}$$

1) determine D_0 for B_2.

2) What is D_0 for B_2^*?