

# Mechanism of long-lived luminescence

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2018-02-02

# Singlet vs triplet

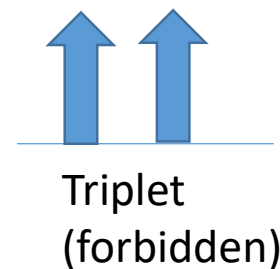
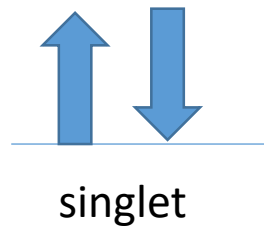
- *For two electrons system, total spin momentum*

$s = 1$ , when eigenstate is  $|+ +\rangle$ ,  $| - -\rangle$ , or  $\frac{1}{\sqrt{2}}(|+ -\rangle + |- +\rangle)$

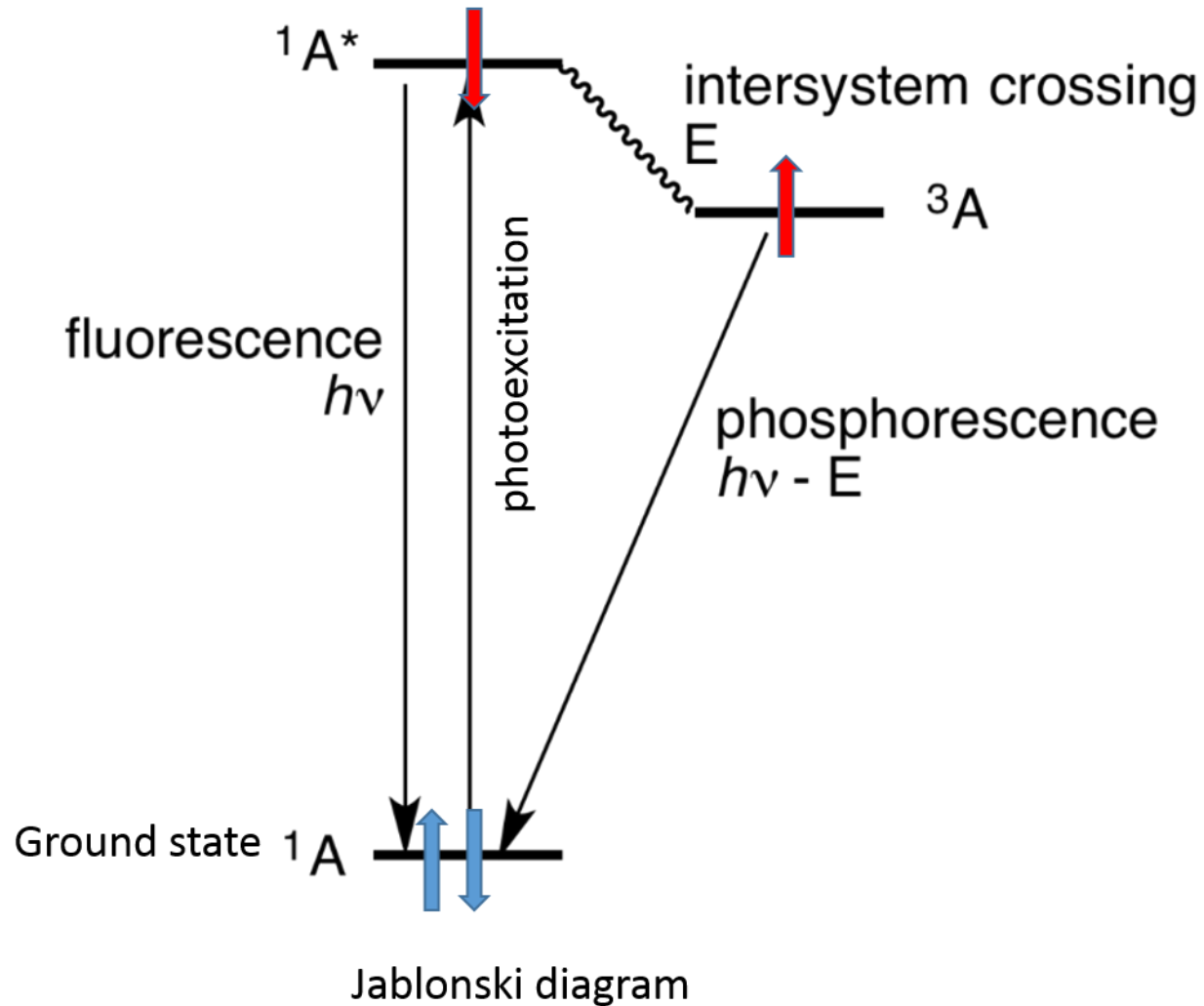
$s = 0$ , when eigenstate is  $\frac{1}{\sqrt{2}}(|+ -\rangle - |- +\rangle)$

In terminology,  $S=1$  is called triplet state for two spin directions are parallel.

While  $S=0$  is called singlet state for two spin directions are antiparallel.



# Fluorescence vs phosphorescence



Fluorescence lifetime  $\sim$ ns, depends on wavelength of absorbed photons. Phosphorescence lifetime is much longer due to spin forbidden. So to get longer luminescence, we need electrons excited to triplet state through intersystem crossing.

# How to increase intersystem crossing?

- Intersystem crossing from the singlet to the triplet is made possible by spin-orbit coupling, which leads to a mixing of the singlet ( $S_n$ ) and triplet ( $T_n$ ) wave functions. So to increase spin-orbit coupling can increase exciton population in triplet states.

$$H_{so} = \alpha^2 \sum_{\mu}^N \sum_i^n \frac{Z_{\mu}}{r_{i\mu}^3} \vec{L}_i \cdot \vec{S}_i,$$

$$\text{initial state } |\psi^1\rangle = |\varphi^1\rangle \frac{1}{\sqrt{2}} (|+ -\rangle - |- +\rangle)$$

$$\text{final state } |\psi^3\rangle = |\varphi^3\rangle \begin{pmatrix} |+ +\rangle \\ |- -\rangle \\ \frac{1}{\sqrt{2}} (|+ -\rangle + |- +\rangle) \end{pmatrix}$$

# Transition rate

- Fermi golden rule  $w = \frac{2\pi}{\hbar} |\langle B, n_r(k) + 1 | H_I | A, n_r(k) \rangle|^2 \delta(E_A - E_B - \hbar\omega_k)$

- Frank-Condon vibrational model

$$w = \frac{2\pi}{\hbar} |\langle \psi^3 | H_{so} | \psi^1 \rangle|^2 \frac{1}{\sqrt{4\pi\lambda RT}} \exp\left(-\frac{(\Delta E + \lambda)^2}{4\lambda RT}\right), \lambda \text{ is Marcus reorganization energy}$$

So to get larger transition rate, we need larger spin-orbit coupling and smaller energy splitting.

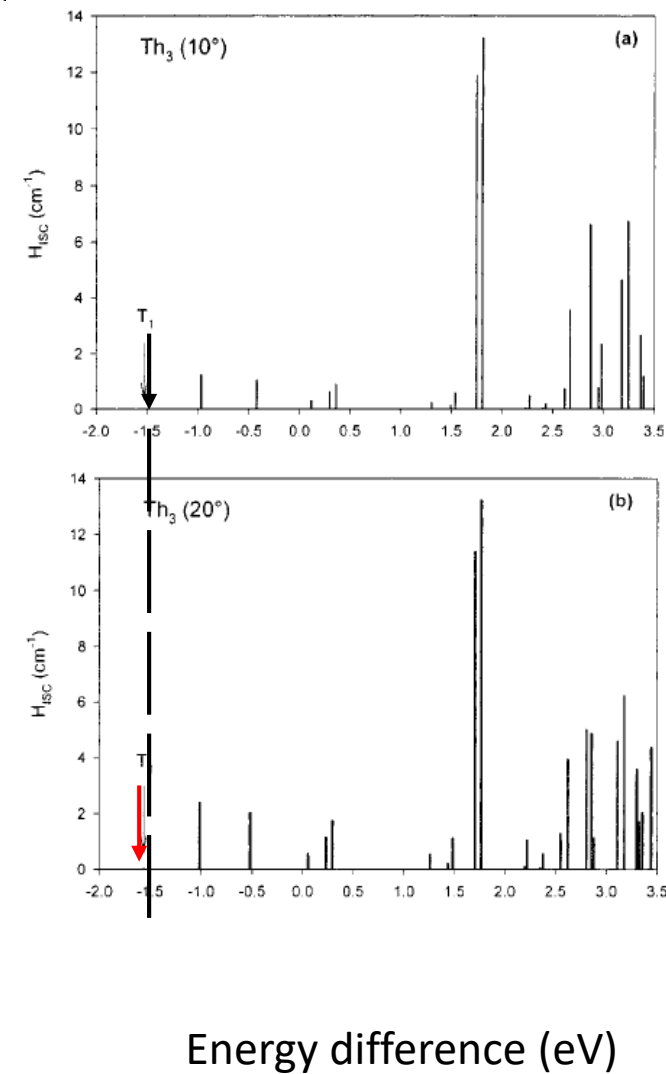
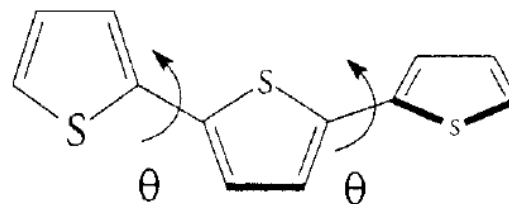
$$\langle \psi^3 | H_{so} | \psi^1 \rangle = \alpha^2 \sum_{\mu}^N \sum_i^n \frac{Z_{\mu}}{r_{\mu i}^3} \langle \varphi^3 | \vec{L}_i | \varphi^1 \rangle \left\langle \begin{array}{c} |++\rangle \\ |--\rangle \\ \frac{1}{\sqrt{2}}(|+-\rangle + |-+\rangle) \end{array} \middle| \vec{S}_i \right| \frac{1}{\sqrt{2}} (|+ -\rangle - |- +\rangle) \right\rangle$$

# How to get larger transition rate?

Only specific initial and final orbitals with certain symmetries can have permitted orbital matrix. Molecules with larger distortions will have larger probability with nonzero orbital transition matrix.

**TABLE 1: Symmetry Selection Rules for Intersystem Crossing**

symmetry group	initial state symmetry	final state symmetry	polarization
$D_{2h}$	$B_{3u}$	$B_{3u}$	forbidden
	$B_{2u}$	$B_{2u}$	forbidden
	$B_{2u}$	$B_{1u}$	out-of-plane
$C_{2h}$	$B_u$	$B_u$	out-of-plane
	$A_g$	$A_g$	out-of-plane
	$A_g$	$B_u$	forbidden
$C_{2v}$	$B_1$	$B_1$	forbidden
	$A_1$	$A_1$	forbidden
	$A_1$	$B_1$	out-of-plane
$C_2$	$B$	$B$	in-plane (short axis)
	$A$	$A$	in-plane (short axis)
	$A$	$B$	in-plane (long axis)



# Ways to increase intersystem crossing

- Smaller energy splitting between excited singlets and triplets.  $\Delta E$  is small.
- More transition channels.
- Larger spin-orbit coupling,  $\langle \varphi^3 | \vec{L}_i | \varphi^1 \rangle$  proper orbital symmetries.
- Heavier atoms, Z is big.