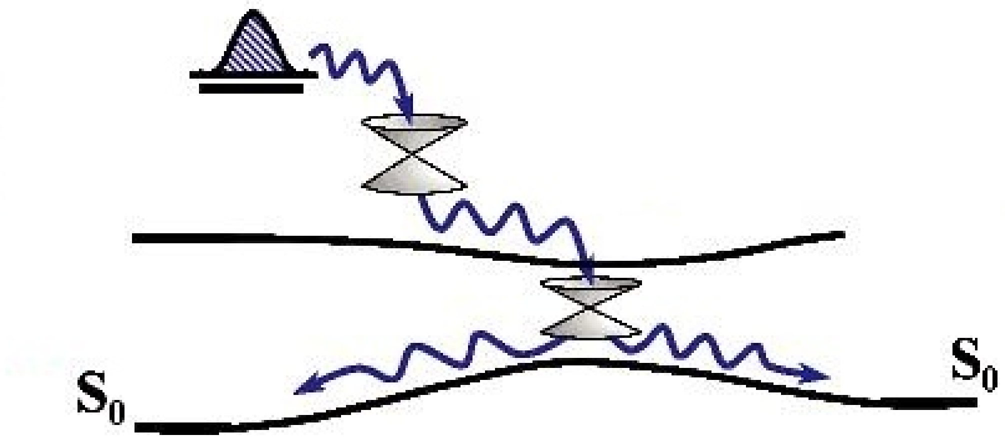
Theoretical Photochemistry WiSe 2017/18

Lecture 13



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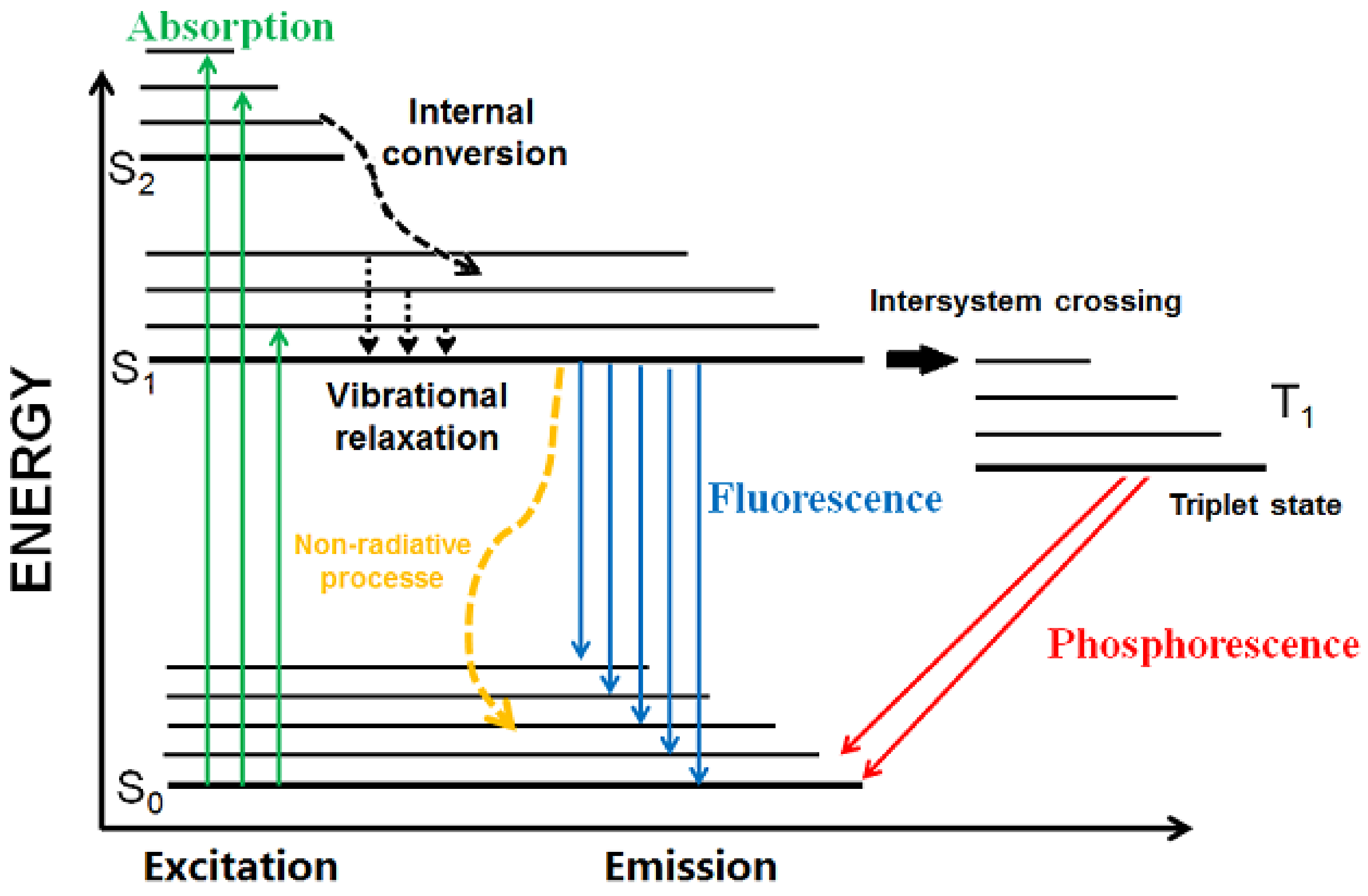
http://www.theochem.uni-frankfurt.de/teaching/ ⟶ Theoretical Photochemistry

Topics

1. Photophysical Processes
2. The Born-Oppenheimer approximation
3. Wavepackets
4. Beyond Born-Oppenheimer – non-adiabatic transitions
5. The Franck-Condon picture of electronic transitions
6. Interaction with light & what do we measure experimentally?
7. Conical intersections
8. Examples: Ethene, Protonated Schiff Bases (Retinal), Azobenzene
9. Some electronic structure aspects
10. Dynamics: trajectories or wavefunctions?
11. Wavefunction propagation techniques

12. **Trajectory surface hopping techniques**
13. **Non-linear optical spectroscopy: calculation of spectroscopic signals**
14. **Extended systems: Excitons, light-harvesting, etc.**
15. **Spin-orbit coupling**

Photochemical Pathways



Spin-Orbit Coupling

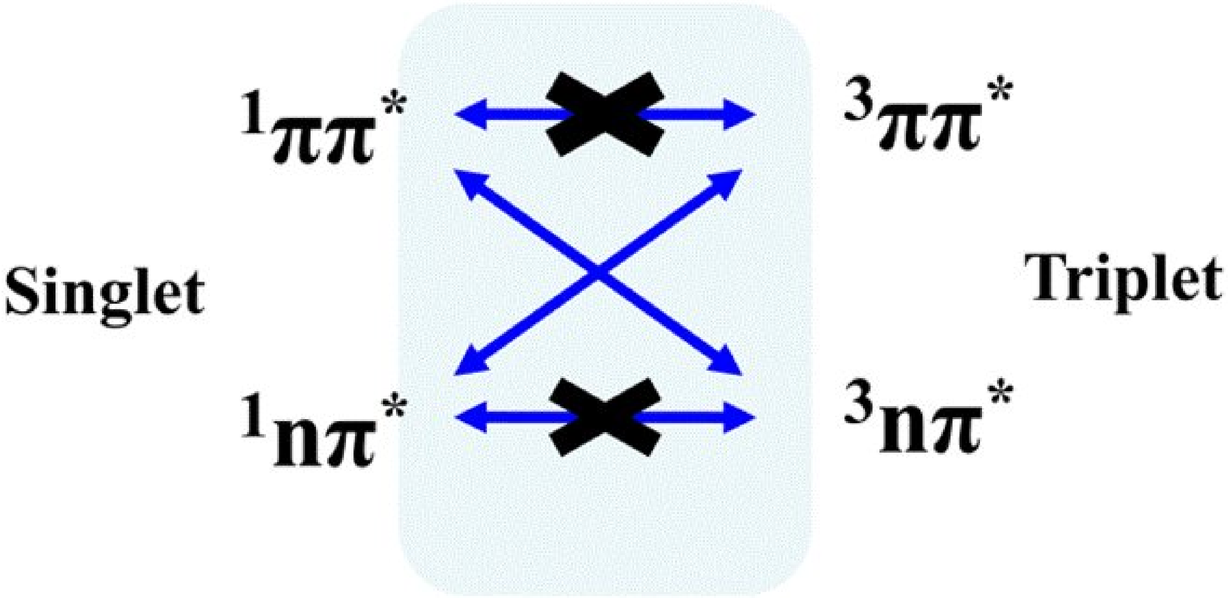
The spin-orbit interaction operator

$$\hat{H}_{\mathrm{SO}} = \sum_i \xi_i \, \hat{l}_i \cdot \hat{s}_i$$

- **can mix states of different multiplicity (e.g., singlet/triplet)**
- **"intersystem crossing"**

El Sayed's rule

Intersystem crossing is likely to be very slow unless it involves a change of orbital configuration



El Sayed’s rule, cont’d

Compound	Transition	A/F	$10^{-8} k_{isc} / s^{-1}$
Benzophenone	$S_1(n,\pi^*) \longrightarrow T_1(\pi,\pi^*)$	A	1000
9-acetoanthracene	$S_1(\pi,\pi^*) \longrightarrow T_1(n,\pi^*)$	A	100
Anthracene	$S_1(\pi,\pi^*) \longrightarrow T_1(\pi,\pi^*)$	F	1
Acetone	$S_1(n,\pi^*) \longrightarrow T_1(n,\pi^*)$	F	5
Biacetyl	$S_1(n,\pi^*) \longrightarrow T_1(n,\pi^*)$	F	0.7

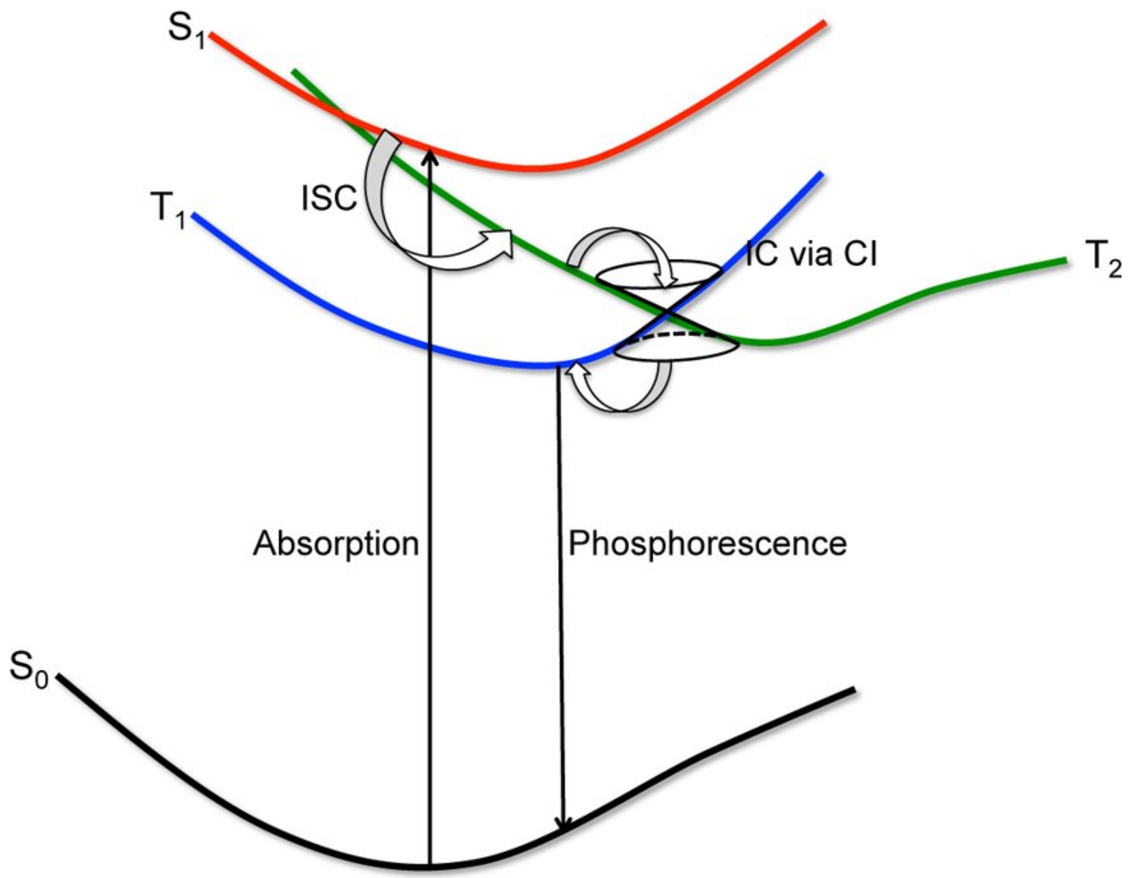
.

These examples show the gradation in k_{ISC} in going from "allowed" to "forbidden" (on El Sayed's rules) situations. Heavy atom substituents (and solvents) greatly enhance spin-orbit coupling and thence k_{ISC}.

Compound	$10^{-6} k(S_1 \longrightarrow T_1) / s^{-1}$	$k(T_1 \longrightarrow S_0) / s^{-1}$
Naphthalene	1.6	0.4
1-methylnaphthalene	0.5	0.34
1-chloronaphthalene	49	2.4
1-bromonaphthalene	1850	36
1-iodonaphthalene	>6000	310

All above k values measured at 77° K.

“Allowed” spin-forbidden transitions: benzaldehyde



Example: benzaldehyde

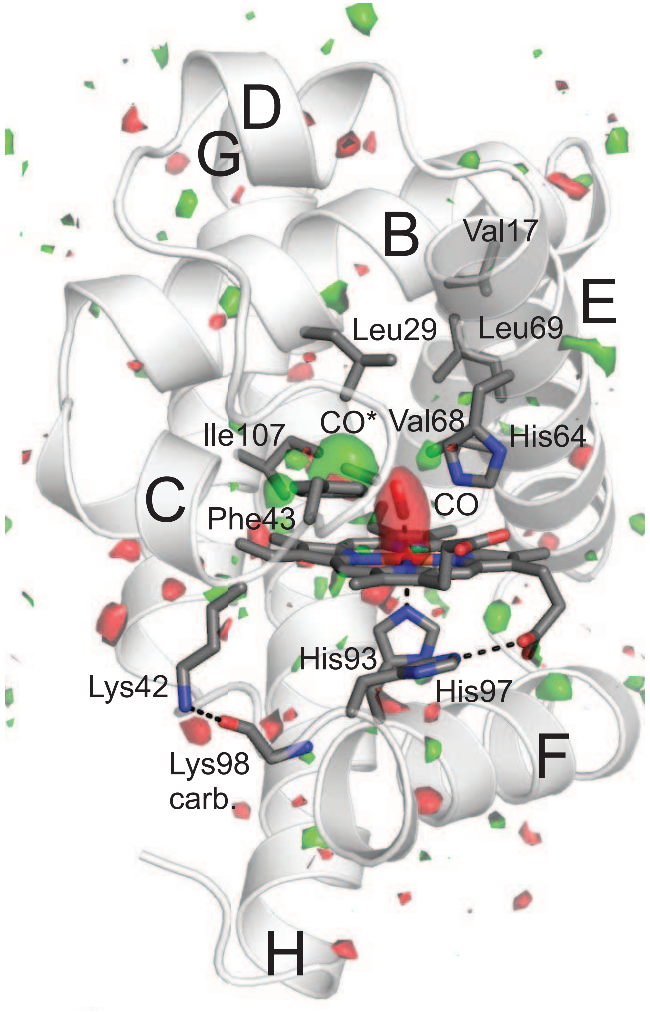
ISC = intersystem crossing

IC = internal conversion

CI = conical intersection

- **ISC time scale:** $\sim 10^{-9}$ **s (“untypically” fast!)**
- **phosphoresence lifetime** $\sim 2 \times 10^{-3}$ **s**

Transition metal complexes: Myoglobin



Science 350, 445 (2015)

Direct observation of ultrafast collective motions in CO myoglobin upon ligand dissociation

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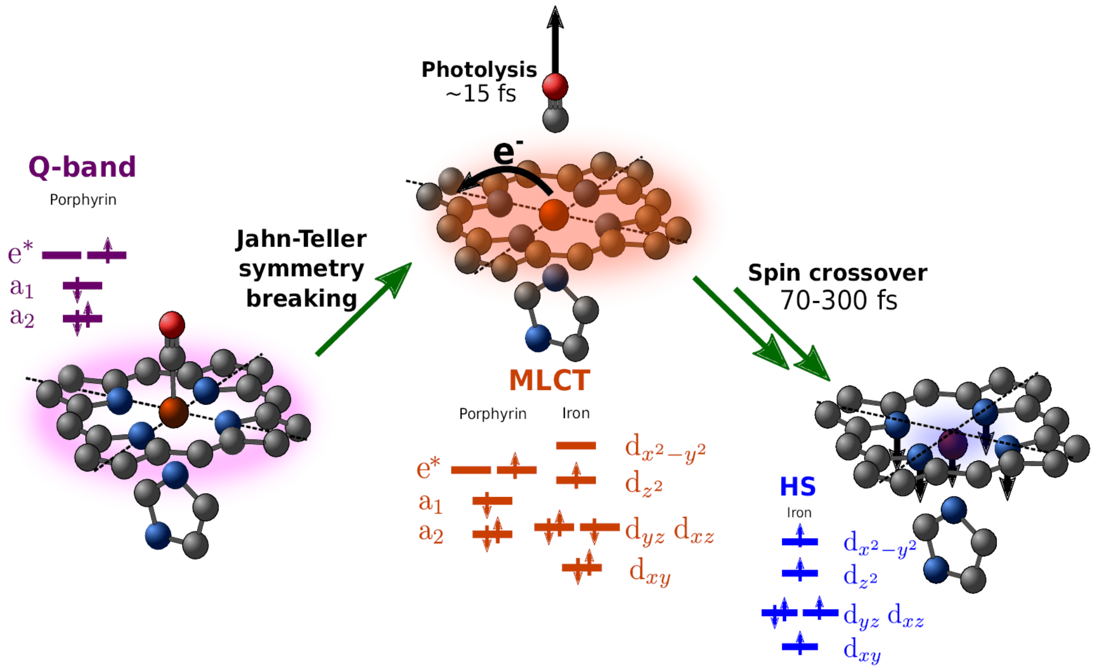
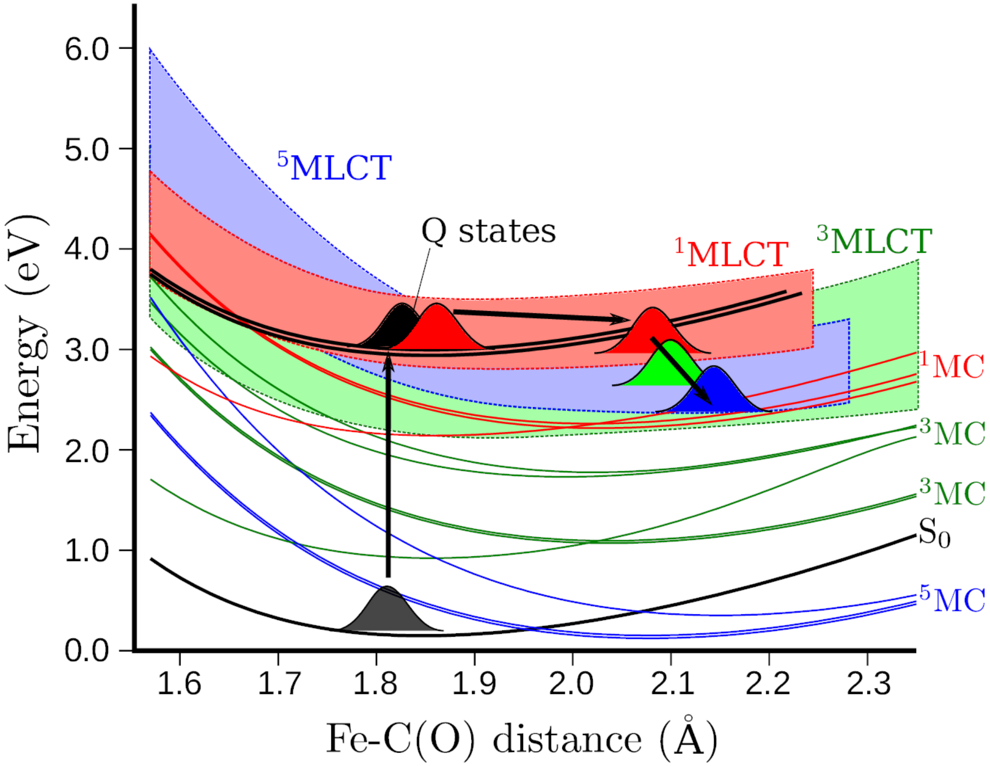
Transition metal complexes: Heme complex

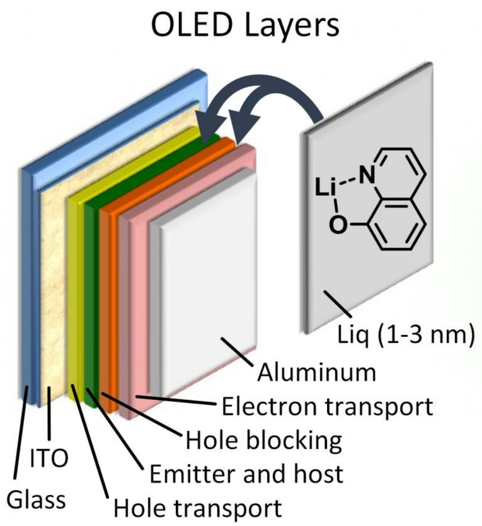


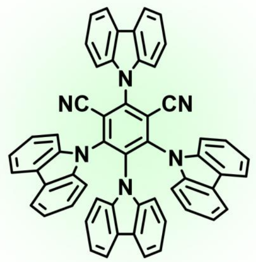


- **ultrafast dynamics (several hundred femtoseconds)**
- **combined effects of spin-orbit coupling and vibronic coupling**

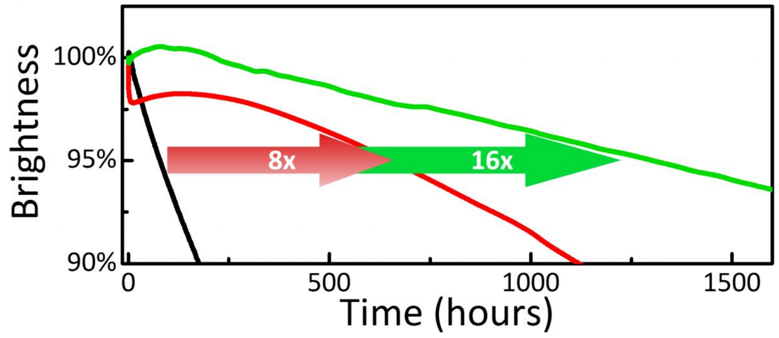
Falahati, Tamura, Burghardt, Huix-Rotllant, https://arxiv.org/abs/1709.03402

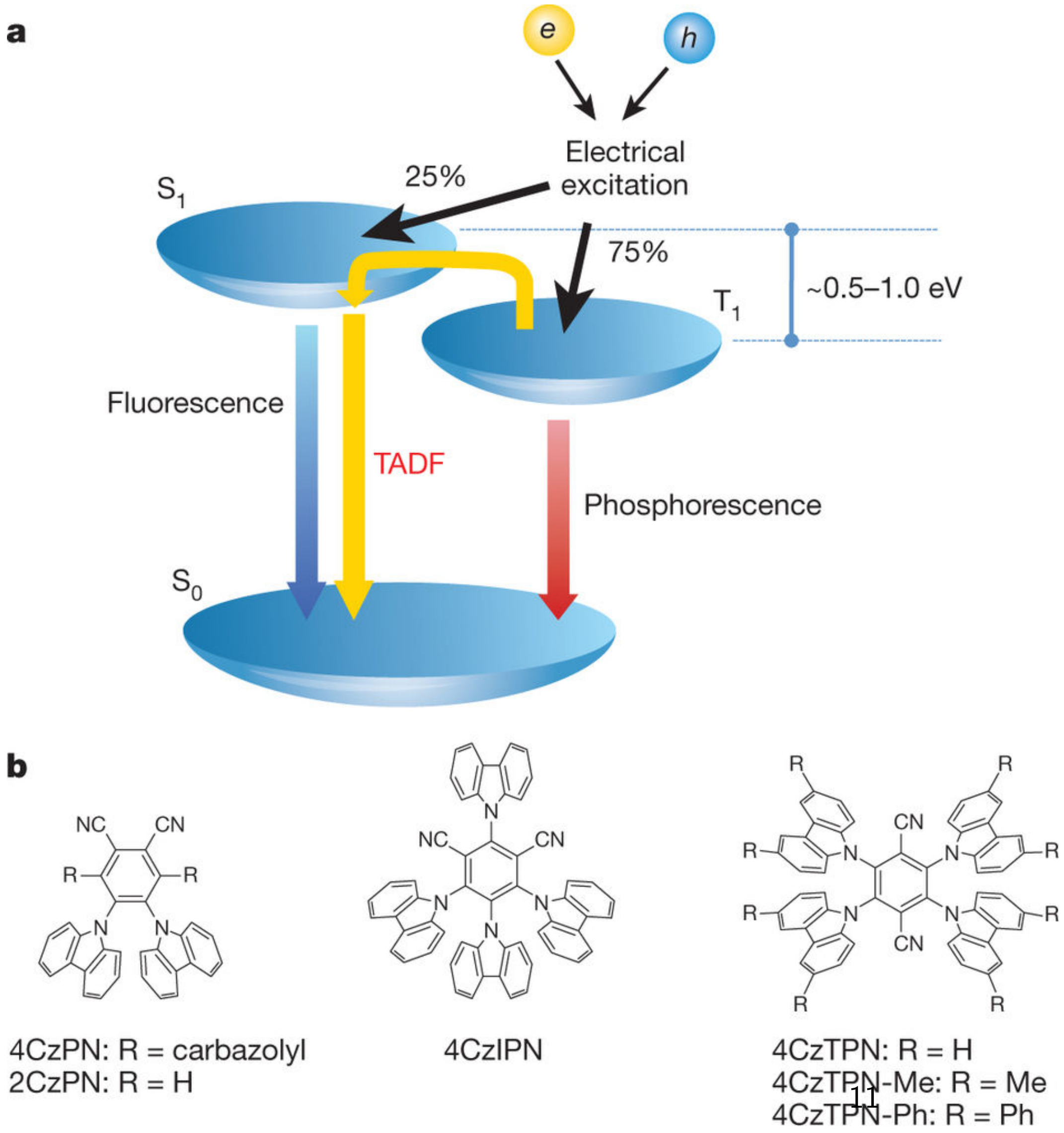
TADF: Thermally Activated Delayed Fluorescence





4CzIPN (TADF emitter)





Spin-orbit interaction – Theory

- **Interaction between the magnetic moments associated with the orbital angular momentum and the electron spin:**

$$\hat{\mu}_e = -\frac{e}{2m_e}\hat{l} \equiv \gamma_e \hat{l}$$

$$\hat{\mu}_s = -g_s \frac{e}{2m_e}\hat{s} \equiv \gamma_e \hat{s}$$

  - **γ_e = magnetogyric ratio**
  - **g_s = 2.0023 Landé factor (from a relativistic treatment)**

Spin-orbit interaction – Theory

Note that the orbital magnetic moment $\hat{\mu}_e$ generates a magnetic field that interacts with the spin magnetic moment (or vice versa)

We formulate the interaction as follows:

$$\hat{H}_{\mathrm{SO}} = -\hat{\mu}_s \cdot \hat{B}_l$$

where

$$\hat{B}_l = \frac{1}{2} \times \frac{Ze\mu_0}{4\pi r^3 m_e}\hat{l}$$

where the factor $1/2$ comes from a relativistic treatment ("Thomas factor") as compared with the classical Biot-Savart law, and $\mu_0 = (c^2\epsilon_0)$.

Spin-orbit interaction – Theory

We now get for the SO interaction:

$$\hat{H}_{\mathrm{SO}} = -\hat{\mu}_s \cdot \hat{B}_l = \frac{g_s e}{2m_e}\hat{s} \cdot \hat{B}_l \sim \frac{e}{m_e}\hat{s} \cdot \hat{B}_l$$

and when inserting the explicit expression for $\hat{B}_l$:

$$\hat{H}_{\mathrm{SO}} = \frac{Ze^2\mu_0}{8\pi m_e^2 r^3}\left(\hat{s} \cdot \hat{l}\right) \equiv \xi(r)\left(\hat{s} \cdot \hat{l}\right)$$

- **$\xi(r)$ is the spin-orbit coupling “constant”**

Spin-orbit interaction – Theory

For hydrogenic atoms, evaluate the spin-orbit coupling "constant" $\xi(r)$ as follows:

$$\begin{aligned}\langle\xi(r)\rangle = \frac{Ze^2\mu_0}{8\pi m_e^2}\langle\frac{1}{r^3}\rangle &= \frac{Ze^2\mu_0}{8\pi m_e^2}\left(\frac{Z^3}{n^3a_0^3l(l+\frac{1}{2})(l+1)}\right)\\ &= \frac{Z^4e^2\mu_0}{8\pi m_e^2n^3a_0^3l(l+\frac{1}{2})(l+1)}\end{aligned}$$

$$\hat{H}_{\mathrm{SO}} = \langle\xi(r)\rangle\Big(\hat{s}\cdot\hat{l}\Big) = \frac{Z^4e^2\mu_0}{8\pi m_e^2n^3a_0^3l(l+\frac{1}{2})(l+1)}\Big(\hat{s}\cdot\hat{l}\Big)$$

Spin-orbit interaction – Theory

Let's check this for a two-electron wavefunction (before taking the average $\langle \xi(r) \rangle$):

$$\hat{H}_{\mathrm{SO}} \propto \sum_I \frac{Z_I}{r_{1I}^3} \hat{l}(1) \cdot \hat{s}(1) + \sum_I \frac{Z_I}{r_{1I}^3} \hat{l}(2) \cdot \hat{s}(2)$$

Here,

$$\hat{l}(1) \cdot \hat{s}(1) = \hat{l}_x(1)\hat{s}_x(1) + \hat{l}_y(1)\hat{s}_y(1) + \hat{l}_z(1)\hat{s}_z(1)$$

- **due to the $1/r^3$ dependence, the spin-orbit interaction decays rapidly at a given atomic center**

Spin-orbit interaction – Theory

Now consider a typical matrix element, e.g., for an $^1(\pi\pi^*) -^3 (n\pi^*)$ transition:

$$\langle \pi(1)\pi^*(2)|\langle \alpha(1)\beta(2) - \beta(1)\alpha(2)|\hat{H}_{\mathrm{SO}}|\alpha(1)\beta(2) + \beta(1)\alpha(2)\rangle|n(1)\pi^*(2)\rangle$$

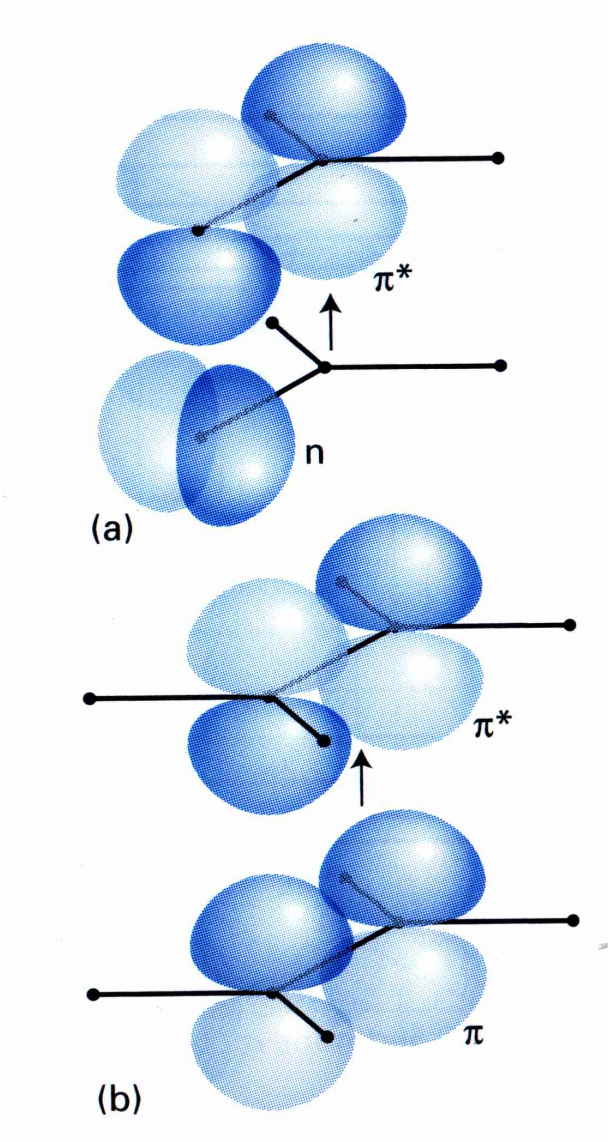
$$\sim \langle \pi(1)\pi^*(2)|\hat{l}(1)|n(1)\pi^*(2)\rangle\langle \alpha(1)\beta(2) - \beta(1)\alpha(2)|\hat{s}(1)|\alpha(1)\beta(2) + \beta(1)\alpha(2)\rangle$$

$$= \langle \pi(1)|\hat{l}(1)|n(1)\rangle\langle \alpha(1)\beta(2) - \beta(1)\alpha(2)|\hat{s}(1)|\alpha(1)\beta(2) + \beta(1)\alpha(2)\rangle$$

In this case , it turns out that $\langle \pi(1)|\hat{l}_z(1)|n(1)\rangle \neq 0$ since the $\hat{l}_z$ operator couples the orthogonal p orbitals contributing to the π vs. n orbitals.

At the same time, the corresponding spin matrix element is non-zero: $\langle \alpha(1)\beta(2) - \beta(1)\alpha(2)|\hat{s}_z(1)|\alpha(1)\beta(2) + \beta(1)\alpha(2)\rangle \neq 0$.

SO allowed/forbidden transitions



(a) carbonyl (C=O) group:
$\pi^* \leftarrow n$ **transition is SO allowed**

$$n \sim O2p_y$$
$$\psi_{\pi^*} = c'\chi(C2p_x) + c\chi(O2p_x)$$

$$\langle \pi^* | \hat{l} | n \rangle \sim c \langle Op_x | \hat{l} | Op_y \rangle \neq 0$$

(b) ethene:
$\pi^* \leftarrow \pi$ **transition is SO forbidden**

How to do the dynamics?

- **Fermi's Golden Rule:**

$$\Gamma_{a \to b} = \frac{2\pi}{\hbar} |\langle \psi_b^{(0)} | \hat{H}_{SO} | \psi_a^{(0)} \rangle|^2 \; \delta(E_b^0 - E_a^0)$$

- **mixed SO/vibronic version of Fermi's Golden Rule**
- **wavepacket dynamics (especially for short time scales)**