

Understanding the sensitivity of the photophysical properties of organometallic complexes

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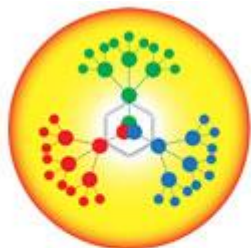
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The University of Queensland*

arxiv.org/abs/arXiv:1005.3897

J. Chem. Phys. in press

arxiv.org/abs/arXiv:1007.0289

J. Mat. Chem. in press



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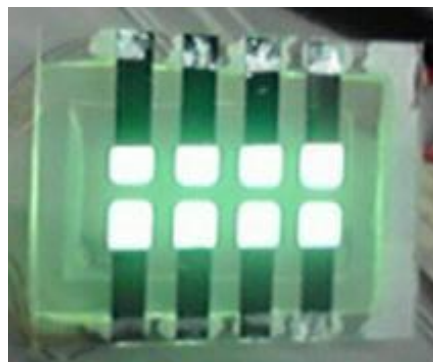
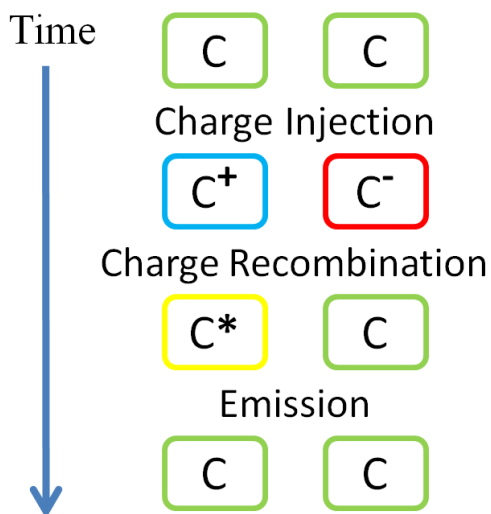


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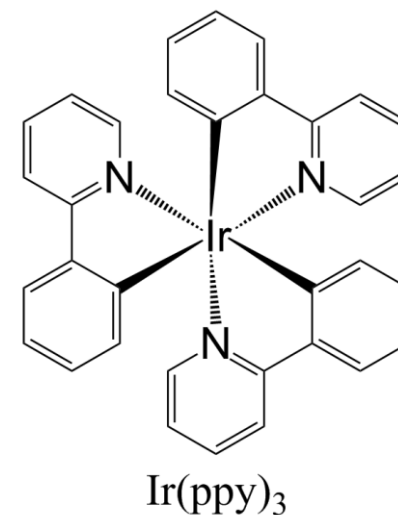
Phosphorescent OLEDs

Phosphorescence is desirable as it means we have radiative decay from triplet states. This means we have a higher potential efficiency.

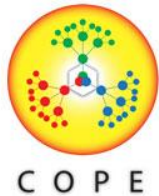
Transition metal complexes have a large spin-orbit coupling, allowing for phosphorescence.



Phosphorescent Ir(ppy)₃ OLEDs from Mikami *et al*, Kanazawa Institute of Technology



We would like to understand the decay path in phosphorescent OLED materials.

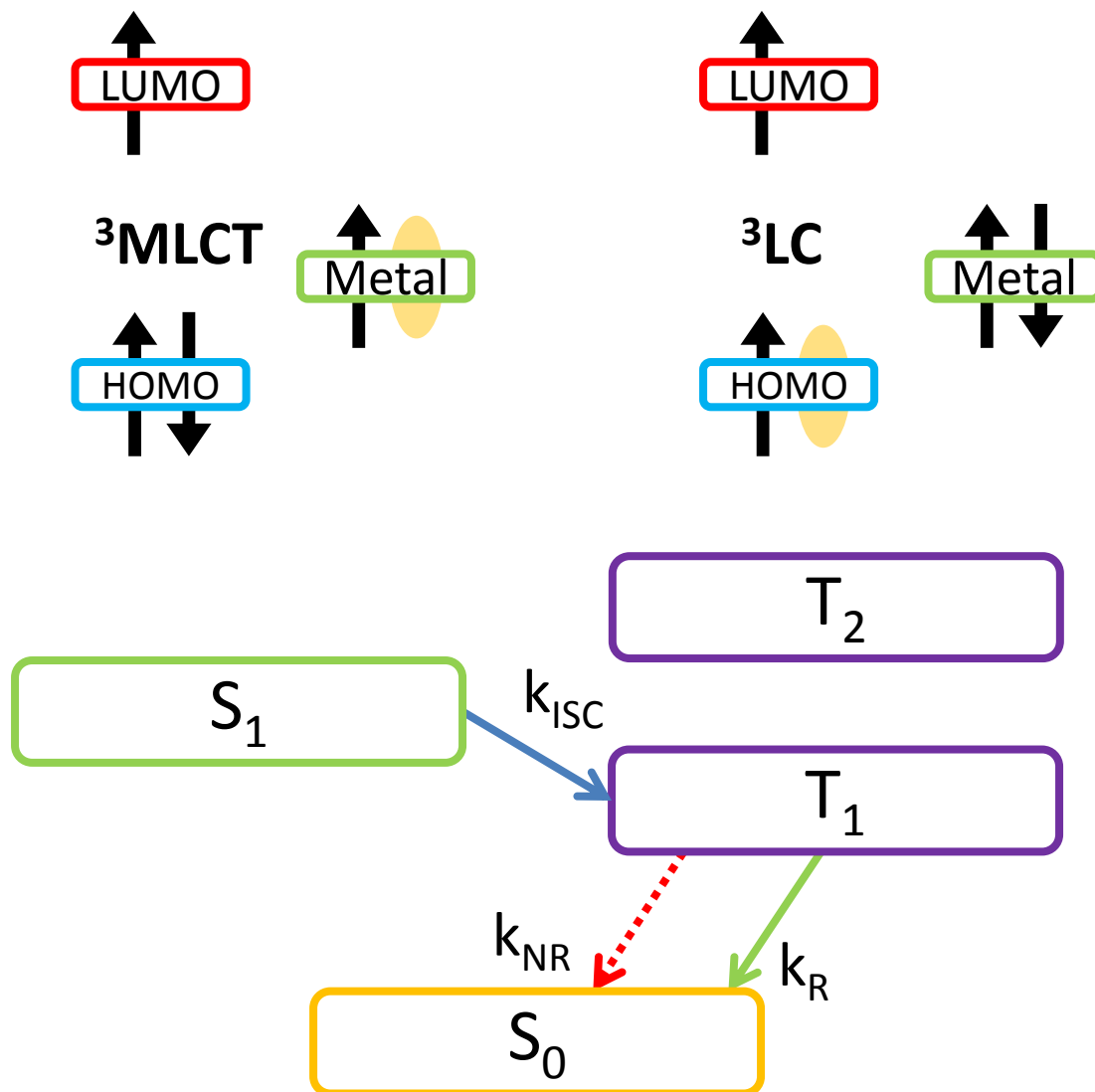


Some Key Questions about Organometallic Complexes

- What is the **character** of the emitting **triplet** state?
- What **fraction** of injected charges result in **triplet excitations**?
- Why are their emission properties so **sensitive to chemical substitutions**?

Key Questions

What is the **character** of the **emitting triplet state**?



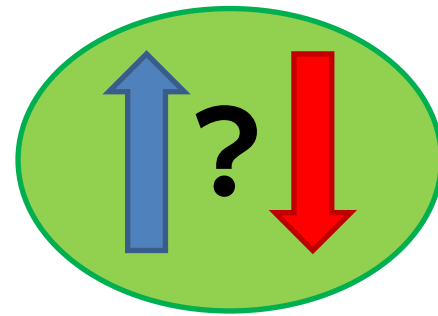
The character of the lowest excited states determines the **transfer rates** (k_{R} , k_{NR} , k_{ISC}).

Key Questions

What fraction of injected charges result in **triplet excitations**?

Spin statistics:

There are four possible ways of combining a pair of spins:



$\frac{3}{4}$ triplet

$\frac{1}{4}$ singlet

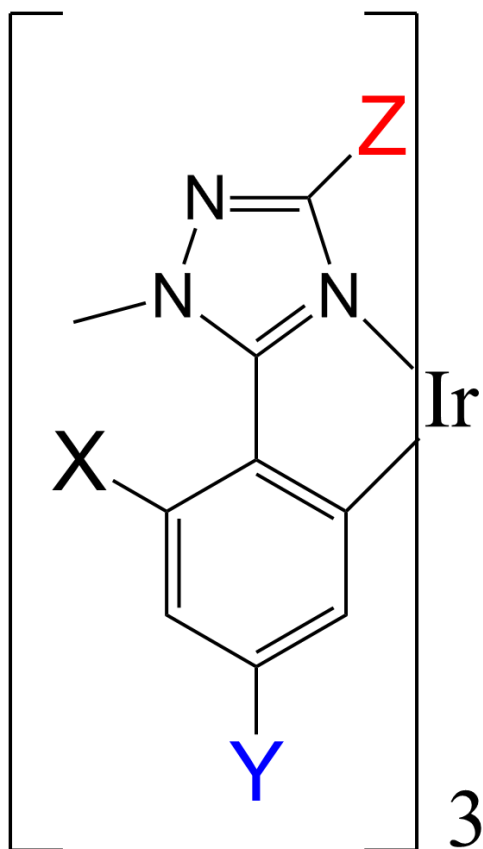
This result is *only* valid for a **non-interacting** model – one without electron-electron interactions.

Key Questions

Why are their emission properties **so sensitive to small chemical changes?**

Both k_R and k_{NR} are sensitive to **small** chemical changes.

E.g. data from S.-C. Lo *et al.*,
Chem. Mater. **18**, 5119 (2006).



X	Y	Z	PLQY (%)	k_R ($\times 10^5 \text{ s}^{-1}$)	k_{NR} ($\times 10^5 \text{ s}^{-1}$)
H	H	n-Pr	66	6.1	3.1
H	F	n-Pr	27	2.2	5.8
F	F	n-Pr	3.0	2.0	65

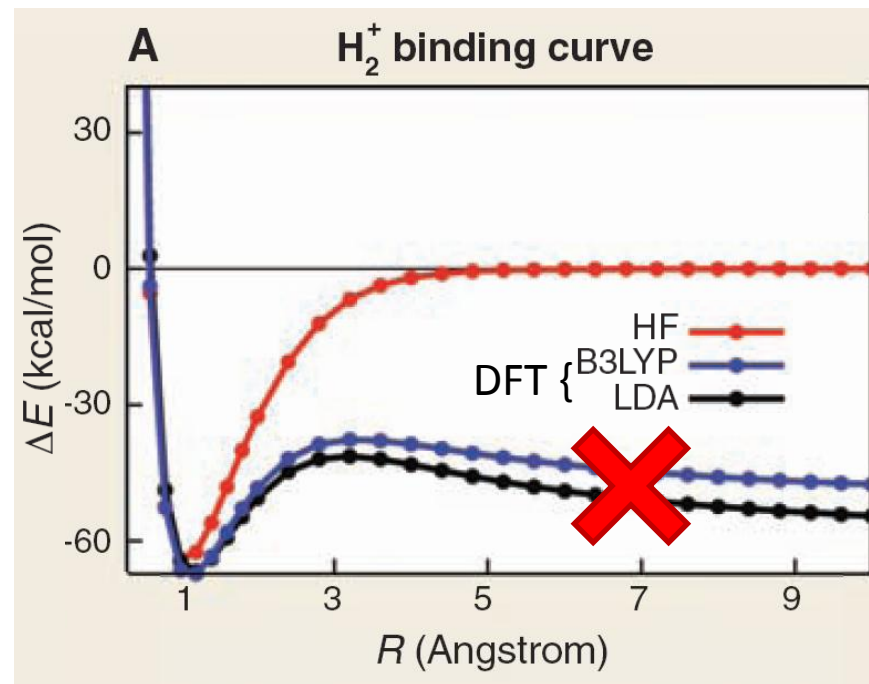
Density functional theory

DFT is one of the most widespread approaches to modelling organometallic complexes.

DFT is known to be bad for charge transfer processes and over estimates the delocalisation of charge.

Hence DFT is **not good** for estimating the **character** of the excited states.

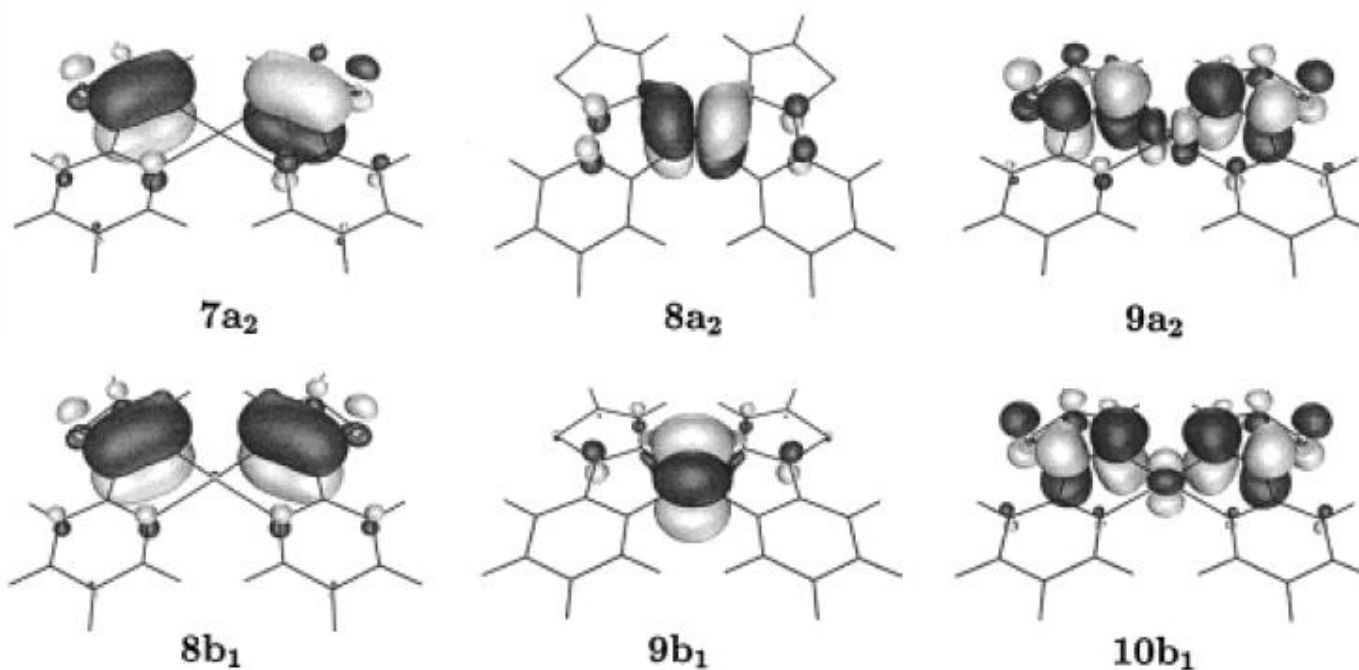
An **effective low energy model** can be simpler to interpret, and allows one to **investigate trends**.



Cohen, Mori-Sanchez, Yang
Science **321**, 792 (2008)

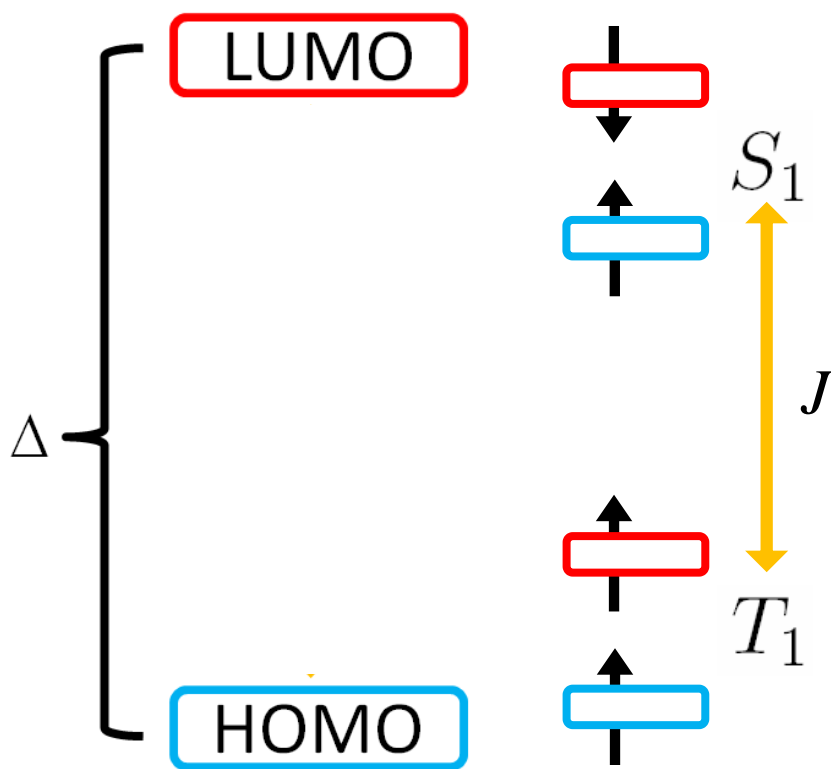
Frontier orbitals

Pierloot *et al* showed that just a few 'active' orbitals are enough to qualitatively reproduce the experimental spectra of Pd(thpy)₂ and related complexes.



J. Phys. Chem. A **104**, 4374 (2000)

Example Model : Ligand



$$T_1 = \Delta - \frac{J}{2} \quad S_1 = \Delta + \frac{J}{2}$$

Ligand	S_1 (eV)	T_1 (eV)	J (eV)	Δ (eV)
thpy	4.08	2.54	1.54	3.31
ppy	4.99	2.87	2.12	3.93
bzq	3.57	2.69	0.88	3.13
biphenyl	4.33	2.84	1.49	3.59
carbazole	3.60	3.05	0.55	3.33
fluorene	4.11	2.94	1.17	3.53

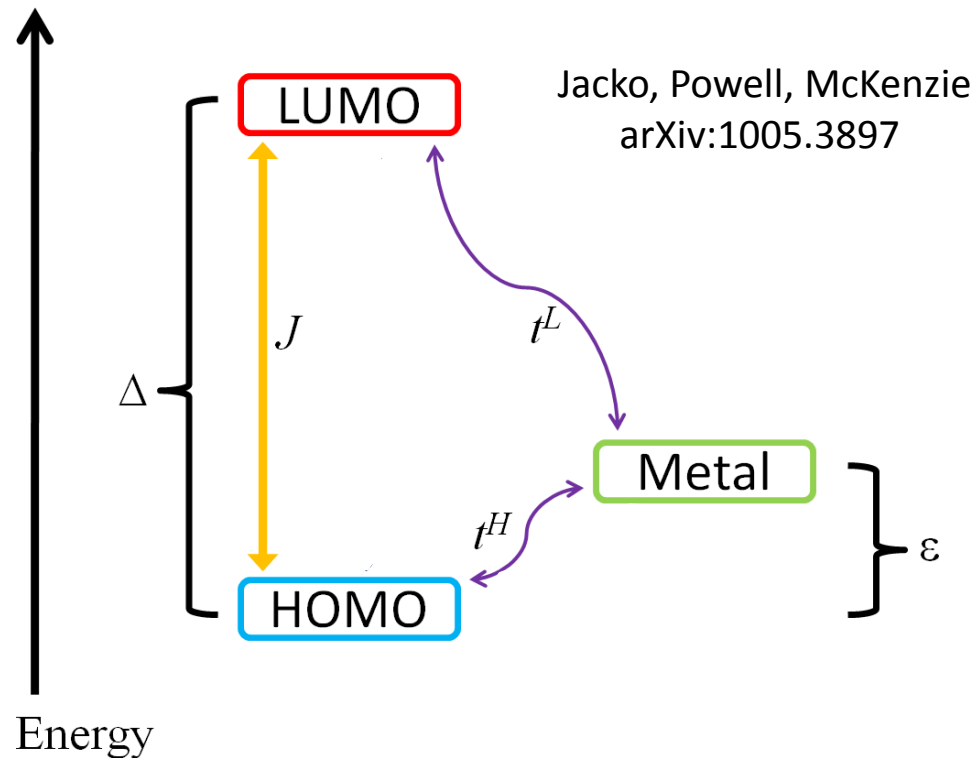
Typically: $\Delta \approx 3.5$ eV
 J varies a lot

For more details on the estimation procedures for these and other parameters, see
 Jacko, Powell, McKenzie, arXiv:1005.3897

Effective Model

We construct a model in the **frontier orbitals** of the ligand and metal fragments.

We can estimate parameters from measurements on isolated fragments.



- | | |
|-----------------------|-------------------------------|
| J | – Spin Exchange |
| t^H, t^L | – Orbital Overlap (β) |
| ε, Δ | – Orbital Energy (α) |

We can solve this model **exactly**:

- Loses some chemical detail
- Captures more physics

One Unknown Parameter

Only **one parameter** remains:

$$\epsilon^* \equiv \epsilon + \underbrace{U_M - U_H + V_{LM} - V_{HL}}_{\text{Coulomb Terms}}$$

Renormalised HOMO-metal gap

Bare HOMO-metal gap

This depends **explicitly on the particular complex**, not just a fragment.

Small variation in the Coloumb terms can have a large effect on ϵ^* (typically < 0.5 eV).

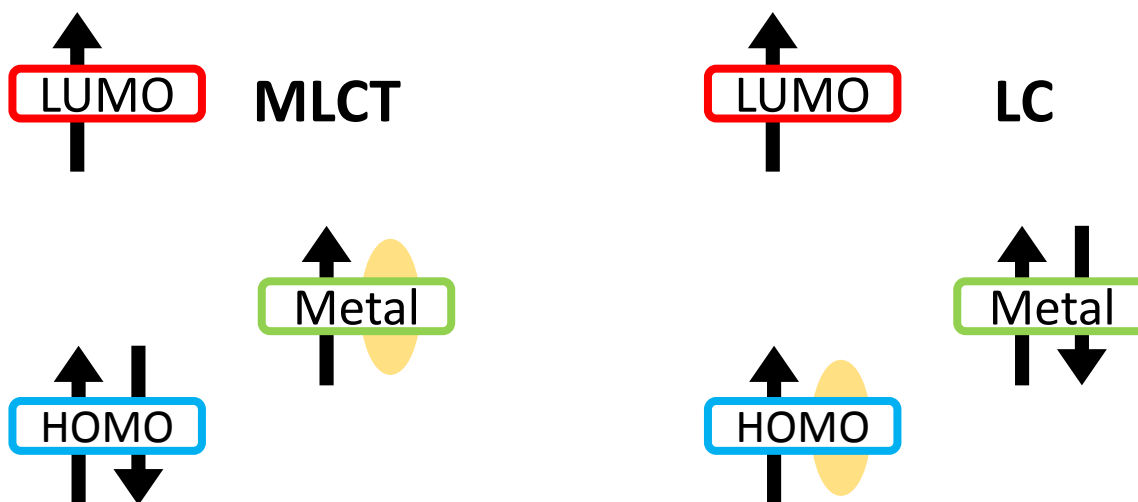
($\epsilon^* = \epsilon$ in a non-interacting model)

Key Parameter

ϵ^* and J determine the properties of the lowest excited states.

$$\epsilon^* \equiv \epsilon + U_M - U_H + V_{LM} - V_{HL}$$

$\epsilon^* - J/4$: Energy gap between LC and MLCT triplets.



MLCT character

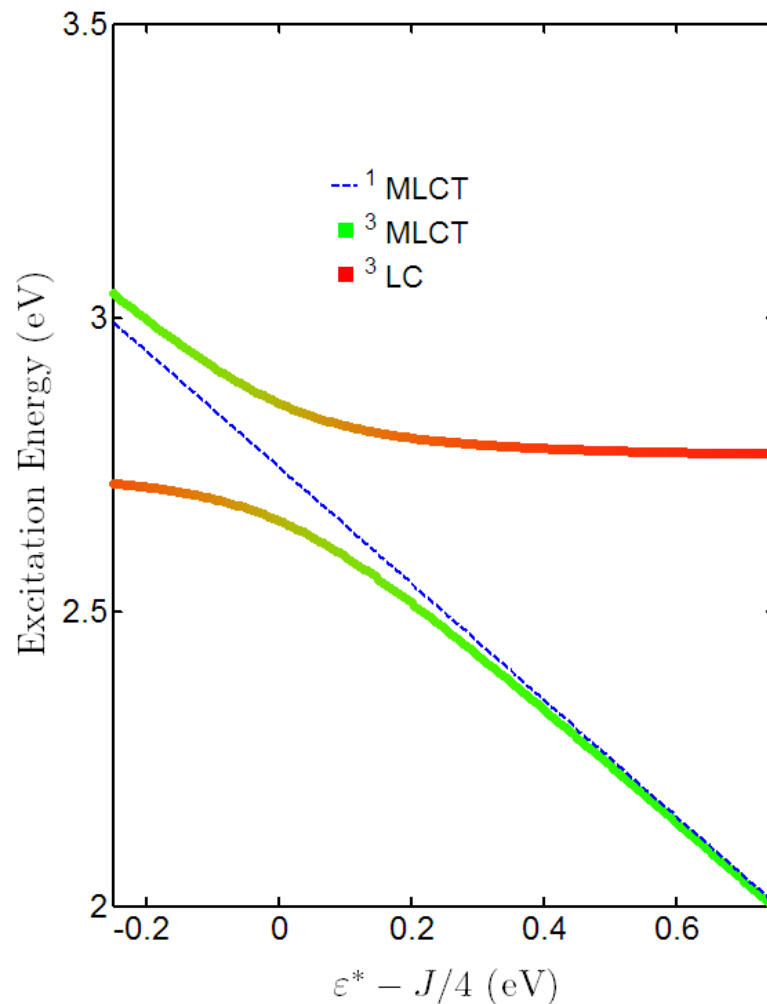
Two regimes:

T_1 state either predominantly **MLCT** or **LC**.

Li [1], Pierloot [2] and others suggest **LC** with a perturbative **MLCT** component.

Small ϵ^* regime of our model.

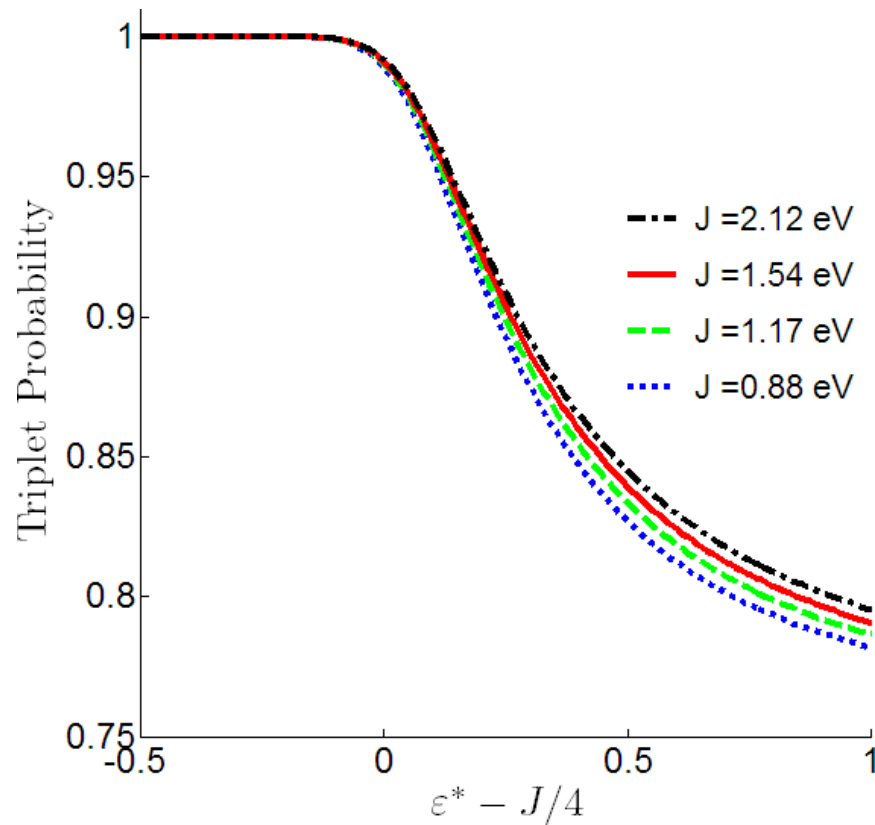
In the small ϵ^* regime, **small changes in ϵ^* strongly affect the T_1 - S_1 gap.**



[1] Li *et al*, *Inorg. Chem.* **44**, 1713-1727 (2005)

[2] Pierloot *et al*, *J. Phys. Chem. A* **104**, 4374-4382 (2000)

Charge Injection



Jacko, Powell, McKenzie
arXiv:1005.3897

Triplet probability after charge injection is often assumed to be **75%** based on a **non-interacting picture**.

We find that this is **not true in general**. Fast inter-system crossing (compared to the decay rates) allows for a thermal distribution of excited states.

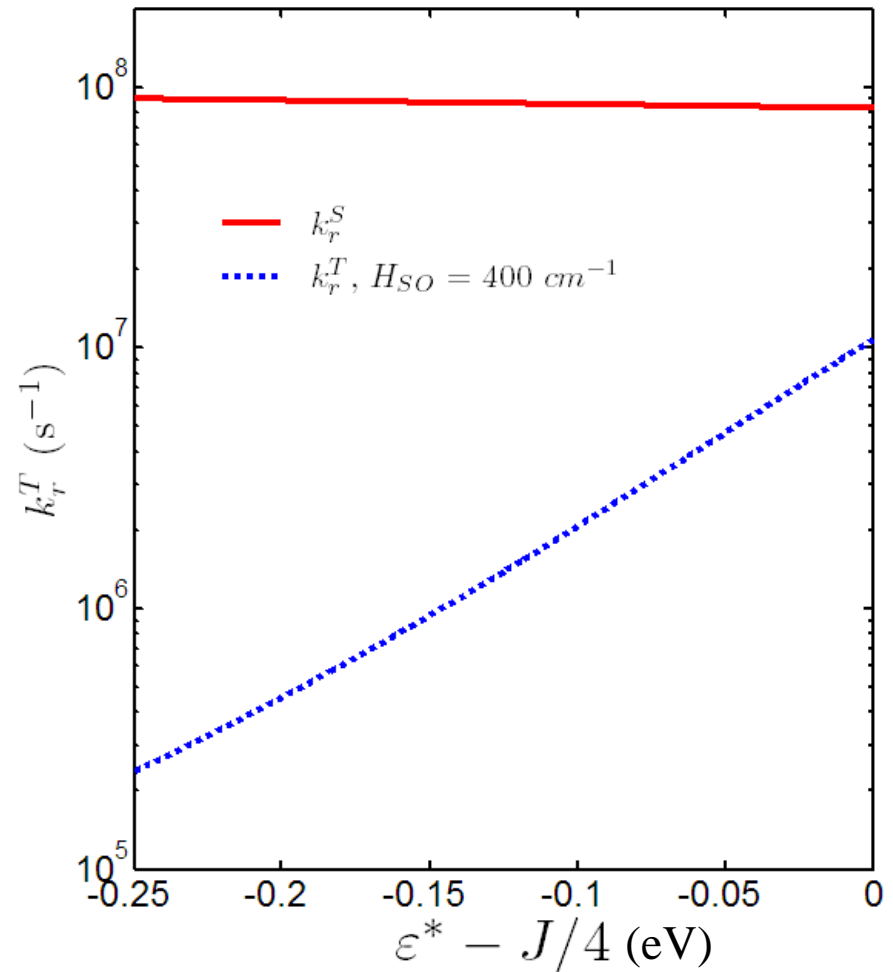
Small changes in $\epsilon^* - J/4$ can cause large changes in the triplet probability.

Triplet Radiative Rate

We can calculate the triplet radiative decay rate versus $\epsilon^* - J/4$ by including spin-orbit coupling H_{SO} .

Radiative decay rate varies nearly exponentially with $\epsilon^* - J/4$ (really a large power law).

Small changes in ϵ^* cause large changes in the radiative decay rate.





Summary

There are two key parameters –
 ϵ^* , the **renormalised HOMO-metal gap**,
and the **exchange J** .

They strongly influence

- The singlet-triplet gap
- The triplet probability
- The triplet radiative decay rate
- The triplet non-radiative decay rate (k_{NR}) since it is an activated process.

Small variations in ϵ^* and J can explain the sensitivity to chemical substitutions of organometallic complexes.

Jacko, Powell, McKenzie [arXiv:1005.3897](https://arxiv.org/abs/1005.3897), *J. Chem. Phys.* in press.

Jacko, McKenzie, Powell [arXiv:1007.0289](https://arxiv.org/abs/1007.0289), *J. Mat. Chem.* in press.