Week 1-6

Optical Properties 3

Classification of excitons

Charge transfer states
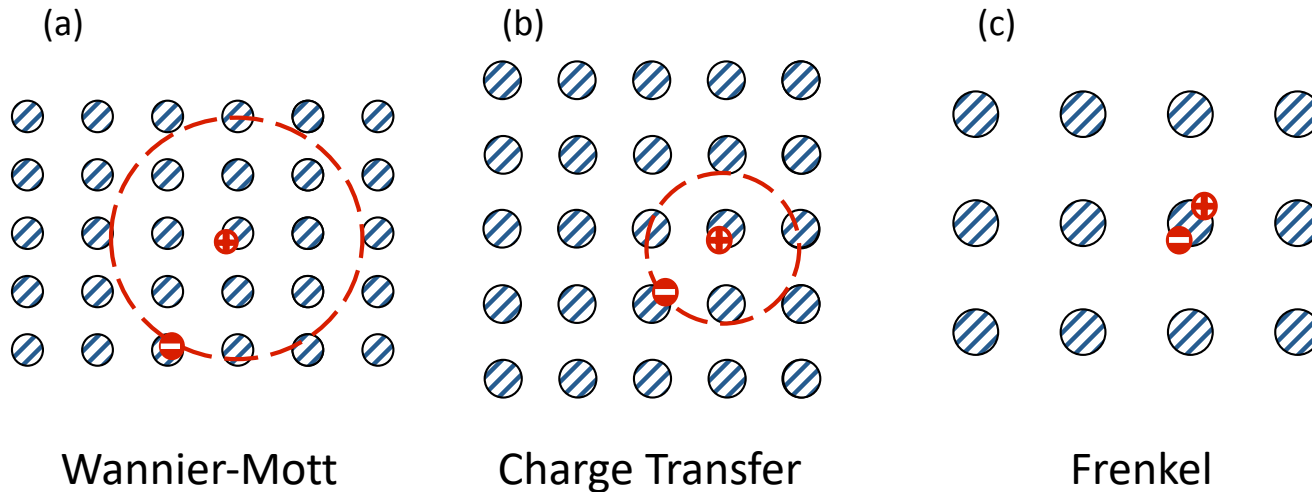
Spin

Energy transfer

Chapter 3.6.6 – 3.8.2

Three Types of Exciton

(a)

(b)

(c)

Wannier-Mott   Charge Transfer   Frenkel

Bohr Model:

$$E_B = -\frac{q^2}{8\pi \, a_0 \left(\varepsilon_r \varepsilon_0\right)} \frac{1}{n^2}$$

$$a_0 = \frac{4\pi \left(\varepsilon_0 \varepsilon_r\right) \hbar^2}{m_r^* q^2}$$

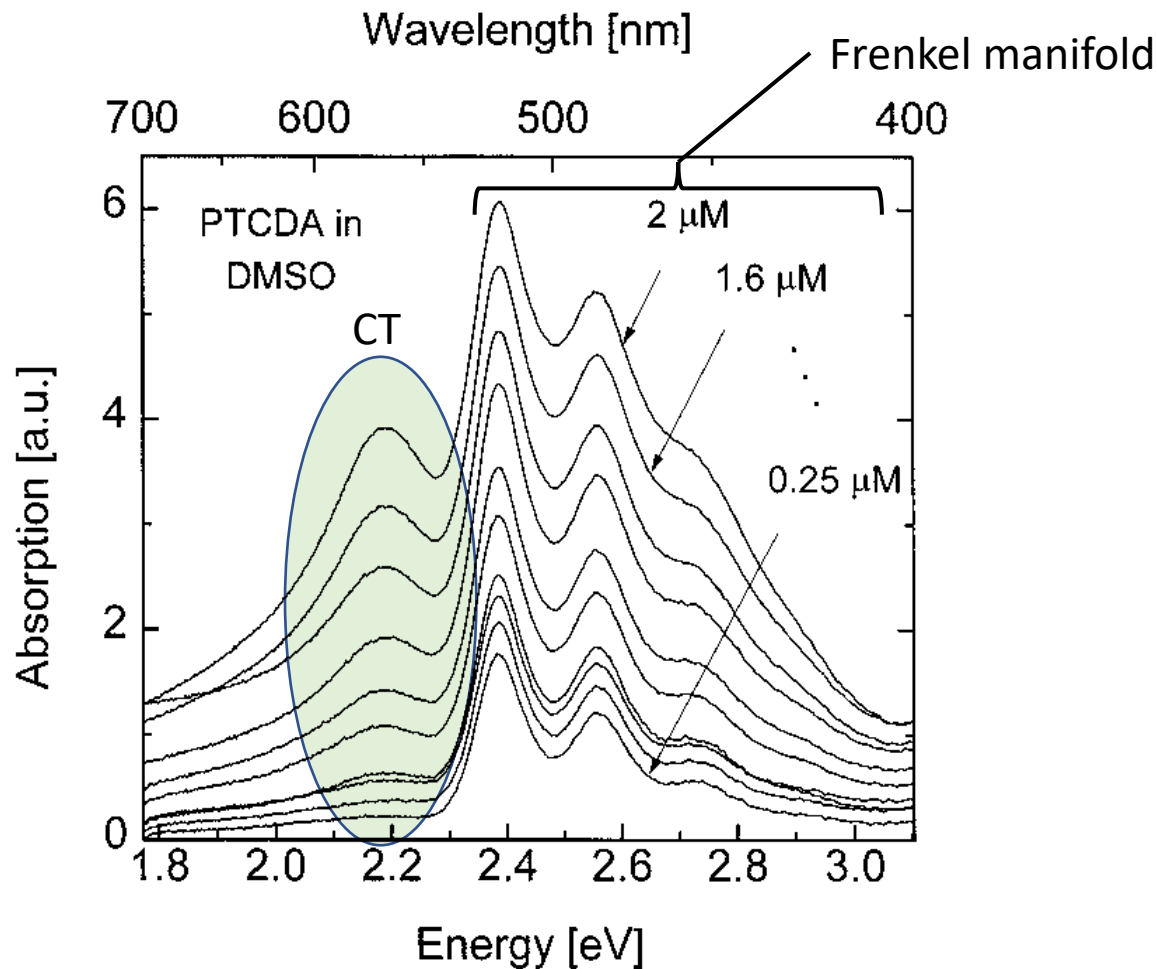| Medium	ε_r	m_r^* / m_e	a_0 (Å)	E_B (eV)
Vacuum (H atom)	1	1	0.5	13.6
Anthracene[a]	2.4-4.1	1	1.2-2.1	0.8-2.4
PTCDA[b]	2.0-4.4	0.14-1	2.2-7.1	0.5-0.7
ZnS[c]	5.2	0.4	5.2	0.2
Si[c]	11.9	0.14	43	0.014
GaAs[c]	13.1	0.07	94	0.006

Charge Transfer States:
Intermediates between molecule and solid

- CT states similar to excimers and exciplexes: e-h pair shared between 1 or more neighboring molecules
- For excitons to be mobile, during their hop between molecules they must have CT properties

Tight packing in PTCDA leads to strong CT oscillator strength

Considerable oscillator strength from the CT (lowest energy) state

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Bulovic, V., et al. 1996. *Chem. Phys.,* 210, 1.

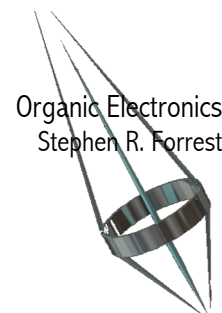Hoffmann, M., et al. 2000. *Chem. Phys.,* 258, 73.
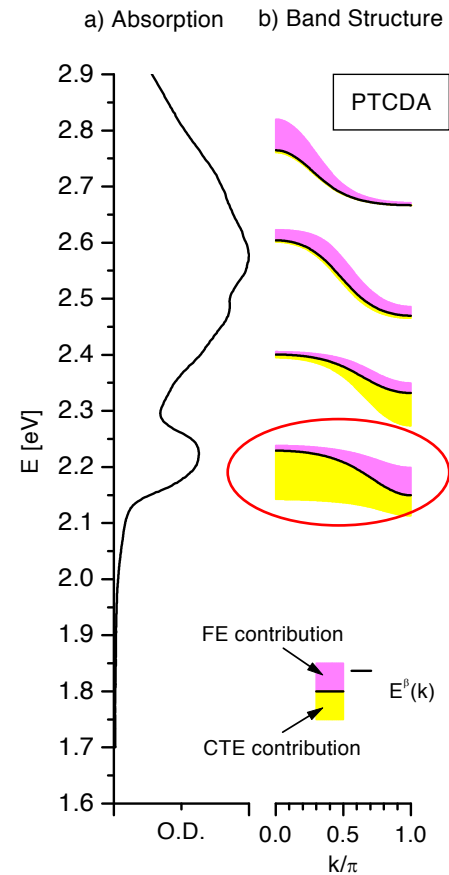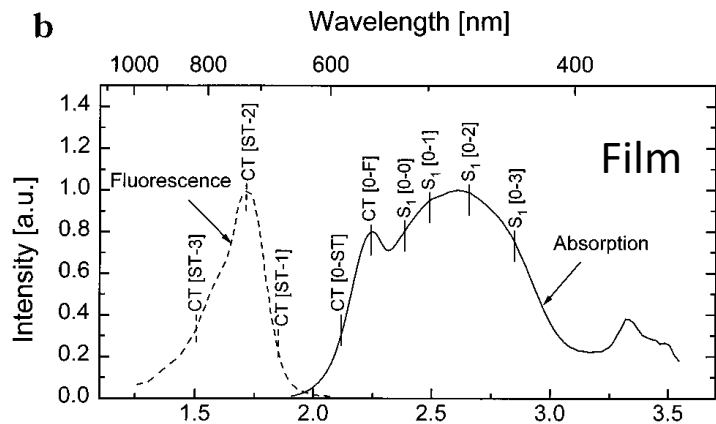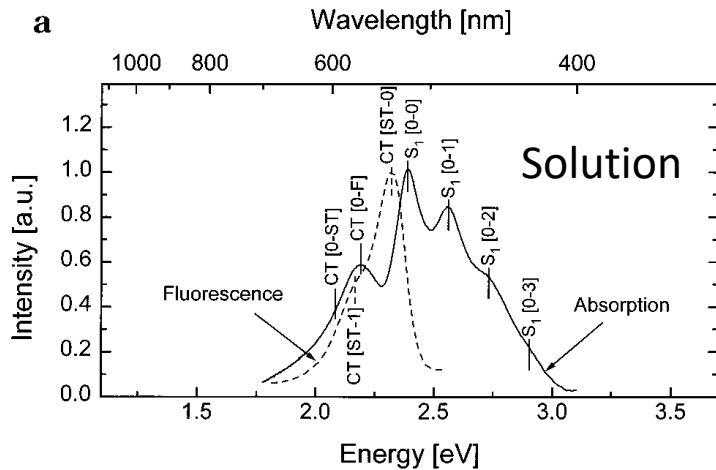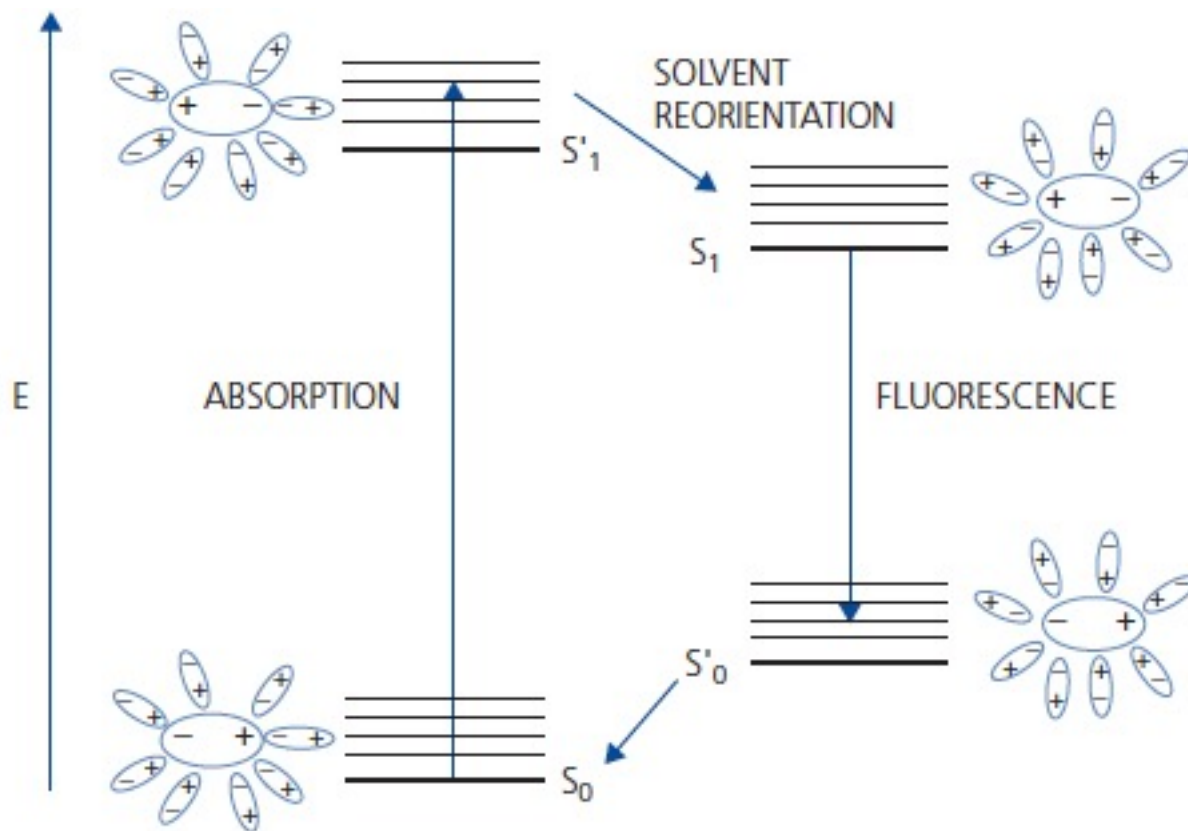
How can we be sure it's a CT state?

CT state intensity drops much faster than Frenkel intensity with dilution due to their collective nature

Bulovic, V., et al. 1996. *Chem. Phys.,* 210**,** 1.

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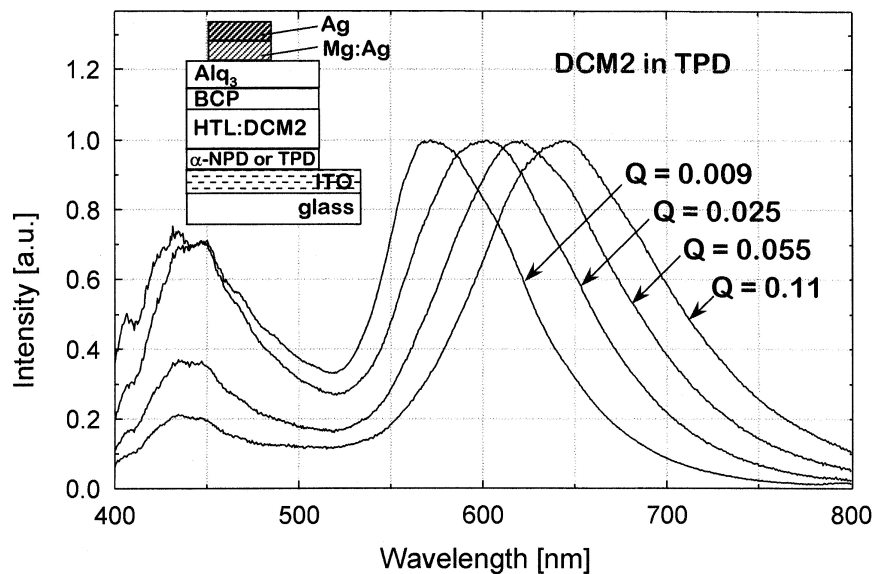Stephen R. Forrest

Solvatochromism and Polarization

- The environment responds to changes in the dipole of the central molecule.
- The energy difference due to this response is the polarization energy
- *Positive solvatochromism* = red spectral shift = *bathochromic shift*.
- *Negative solvatochromism* = blue spectral shift = *hypsochromic shift*.

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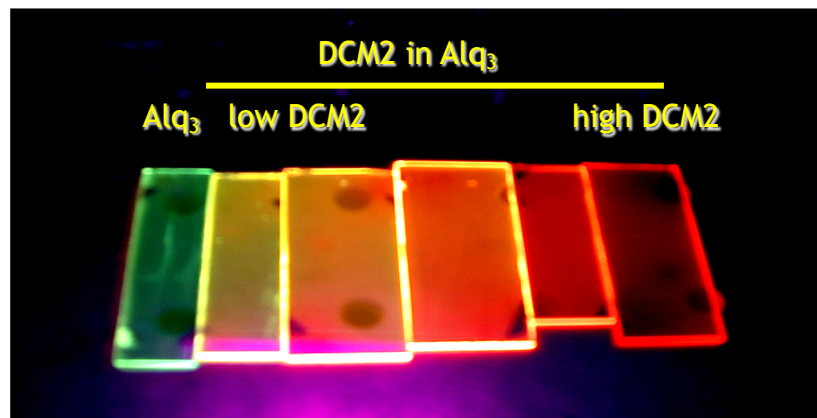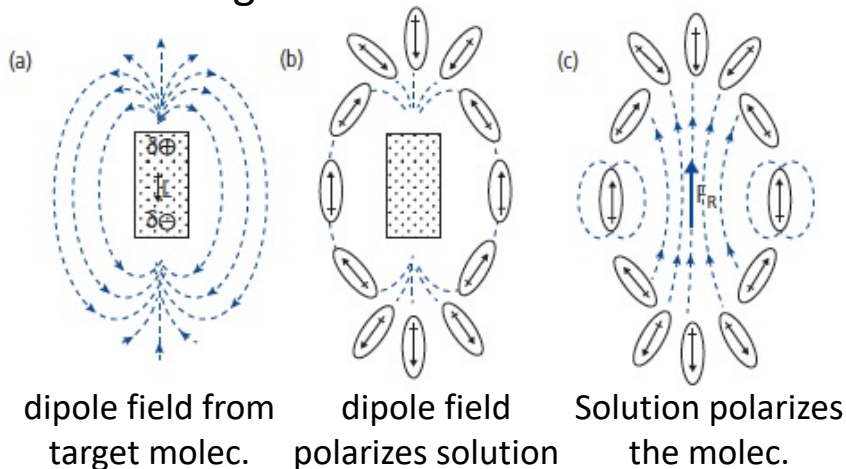# Place a dipolar (fluorescent) molecule in increasingly polar solvents

In solution
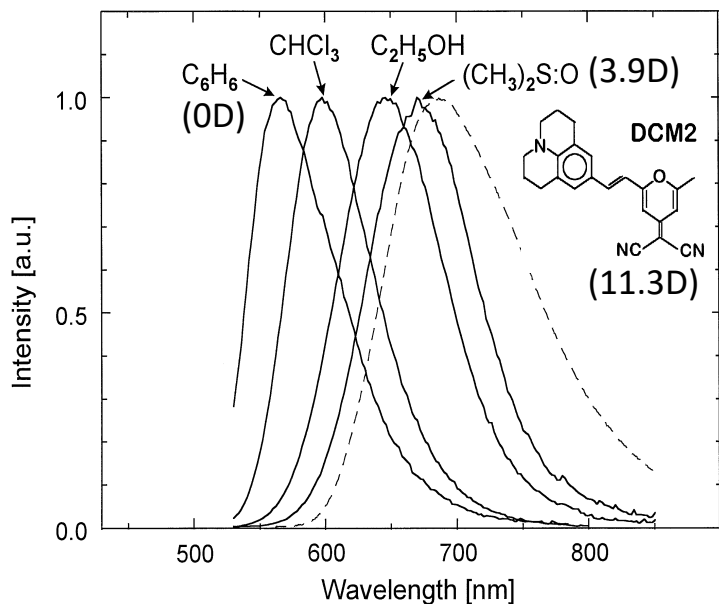
In solid: Solid-state solvation effect

Bulovic, V.,et al.. *Chem. Phys. Lett.,* 287, 455.

The origin of solvatochromism

dipole field from target molec.

dipole field polarizes solution

Solution polarizes the molec.

DCM2 in Alq$_3$

Alq$_3$ low DCM2   high DCM2

Putting polarization in context

Electronic polarization (10^{-16}s)

vdW binding

Vibronic polarization (10^{-15}–10^{-14}s)

Intramolecular phonons

Lattice polarization (10^{-13}–10^{-12}s)

Polarons & solvation effects

ernal
ersion

ission
(E_{an})

.minescence

Vibrational levels

Franck–Condon Shift

aka Stokes Shift

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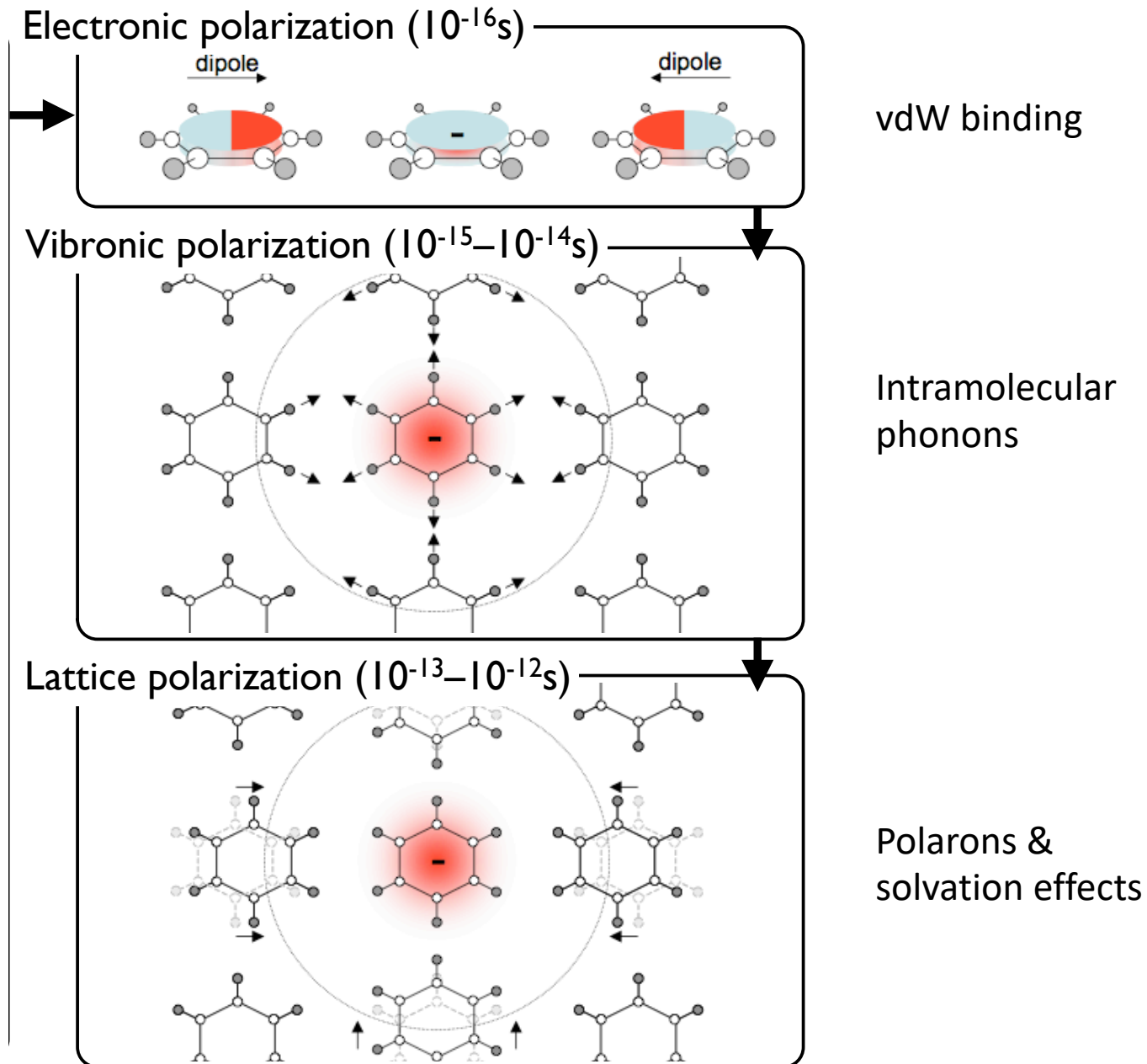
Exciton Spin

- Organic solids are not strongly coupled
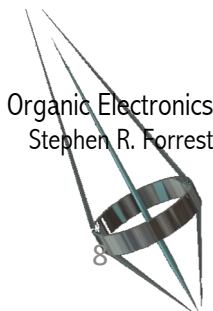   - Individual molecular properties retained in the solid
    - Lack of degeneracy in the bands

    ⇒Spin of individual molecules largely preserved in the solid
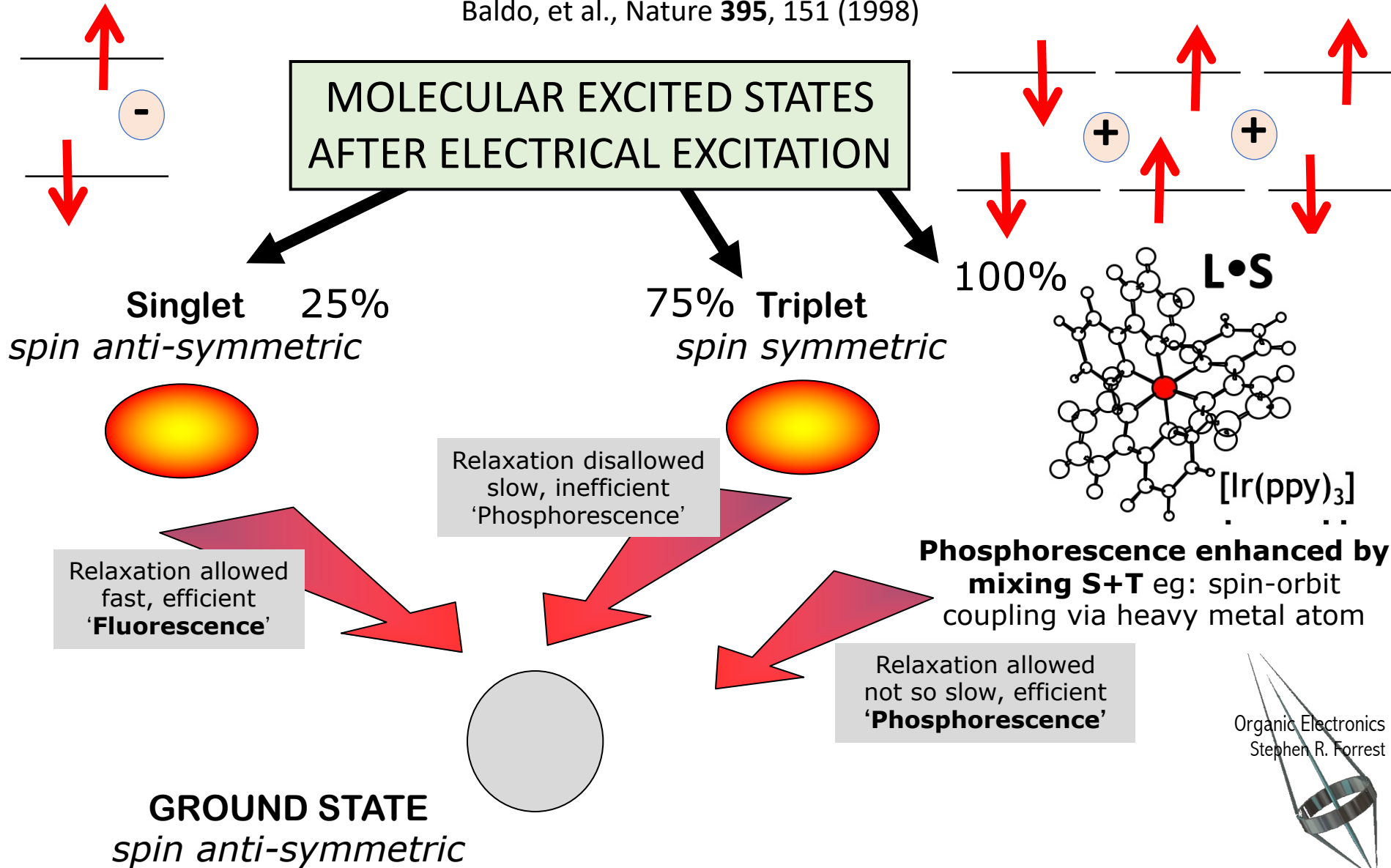
    This situation is substantially different than for <u>strongly correlated</u> inorganic semiconductors and metals.

- Spin multiplicity (and its violation) determines optical properties
    - S=0, singlets; S=1,triplets

100% Internal Efficiency via Spin-Orbit Coupling
Heavy metal induced electrophosphorescence ~100% QE

Baldo, et al., Nature **395**, 151 (1998)

MOLECULAR EXCITED STATES
AFTER ELECTRICAL EXCITATION

Singlet 25%
spin anti-symmetric

75% **Triplet**
spin symmetric

100%

L•S

[Ir(ppy)$_3$]

Phosphorescence enhanced by mixing S+T eg: spin-orbit coupling via heavy metal atom

Relaxation disallowed slow, inefficient 'Phosphorescence'

Relaxation allowed fast, efficient '**Fluorescence**'

Relaxation allowed not so slow, efficient '**Phosphorescence**'

GROUND STATE
spin anti-symmetric

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Spin-Orbit Coupling

- Primary mechanism that results in violation of spin conservation
- Results in phosphorescence
- A result of quantum mechanical interactions of electron spin and relativistic orbital angular momentum

Magnetic field due to a charge of velocity **v** in field **F**: $\mathbf{B} = -\dfrac{\mathbf{v} \times \mathbf{F}}{c^2}$

and $\mathbf{F}(\mathbf{r}) = -\hat{\mathbf{r}}\dfrac{dV}{dr}$ $\mathbf{B} = \dfrac{\mathbf{v} \times \hat{\mathbf{r}}}{c^2}\dfrac{dV}{dr}$

Orbital angular momentum is given by: $\mathbf{l} = \mathbf{r} \times m_e \mathbf{v}$

Giving: $\mathbf{B} = -\dfrac{1}{m_e r c^2}\dfrac{dV}{dr}\mathbf{l}$

As in the case for an electric dipole, the energy due to a magnetic dipole moment, **m** is

$$E_{\text{int}} = -\mathbf{m} \cdot \mathbf{B}$$

Spin-Orbit Coupling, cont'd

The magnetic moment due to electron spin is: $\mathbf{m}_s = -g_S\mu_B\dfrac{\mathbf{s}}{\hbar} = -g_S\dfrac{q}{2m_e}\mathbf{s}$

g-factor≈2   Bohr magneton

This gives spin-orbit coupling *in the electron reference frame* of

$$H_{SO} = -g_S\frac{q}{2m_e^2 c^2}\frac{1}{r}\frac{dV}{dr}\mathbf{l}\bullet\mathbf{s}$$

Relativisitic effects: precession of the spin in its orbit *in the laboratory frame* gives:

$$\mathbf{B} \rightarrow -\frac{\mathbf{v}\times\mathbf{F}}{2c^2}$$ (Thomas precession)

From which we finally arrive at:

$$H_{SO} = -\frac{q}{2m_e^2 c^2}\frac{1}{r}\frac{dV}{dr}\mathbf{l}\bullet\mathbf{s} = \xi(r)\mathbf{l}\bullet\mathbf{s}$$

Spin-Orbit Coupling, cont'd

$$H_{SO} = -\frac{q}{2m_e^2 c^2} \frac{1}{r} \frac{dV}{dr} \mathbf{l} \cdot \mathbf{s} = \xi(r)\mathbf{l} \cdot \mathbf{s}$$

For a hydrogenic atom:
gives:

$$V(r) = -Zq / 4\pi\varepsilon_0 r$$

$$\xi(r) = -\frac{Zq^2}{8\pi\varepsilon_0 m_e^2 c^2} \frac{1}{r^3}$$

Using the hydrogenic wavefunctions gives: $\left|nlm_l\right\rangle = R_{nl}(r)Y_{lm_l}(\theta,\phi)$

Rydberg (13.6 eV)

$(R_{nl} \sim (Z / a_0)^{3/2})$

$$E_{SO} = \frac{2\pi\alpha^2 R_\infty Z^4 c}{n^3 l\left(l+\frac{1}{2}\right)(l+1)\hbar} \left\langle \mathbf{l} \cdot \mathbf{s} \right\rangle$$

Fine structure constant

$$R_\infty = \frac{m_e e^4}{8\varepsilon_0^2 h^3 c}$$

$$\alpha = \frac{1}{4\pi\varepsilon_0} \frac{e^2}{\hbar c}$$

Spin-Orbit Coupling, cont'd

Lastly, we need to evaluate $\langle \mathbf{l} \cdot \mathbf{s} \rangle$

Total angular momentum: $\mathbf{j} = \mathbf{l} + \mathbf{s}$ $j^2 \rightarrow |\mathbf{l} + \mathbf{s}|^2 = l^2 + s^2 + 2\mathbf{l} \cdot \mathbf{s}$

But: $l^2 |nlm\rangle = \hbar^2 l(l+1)|nlm\rangle$

So, solving for **l•s** we finally obtain for the SO energy:

$$E_{SO} = \frac{\alpha^2 R_\infty Z^4 hc \left[j(j+1) - l(l+1) - s(s+1) \right]}{2n^3 l \left(l + \frac{1}{2} \right)(l+1)}$$

Thus, as *l* increases, so does E_{SO}.

For example, an s-state has $l=0 \Rightarrow$ $j=s$, and $E_{SO}=0$.

 [Careful! <u>s</u> is the spin quantum number, not the orbitally symmetric s-state]

We've done the math, but we haven't explained the physics. How does $H_{SO} = \xi(r)\mathbf{l} \cdot \mathbf{s}$ help to violate the spin conservation law?

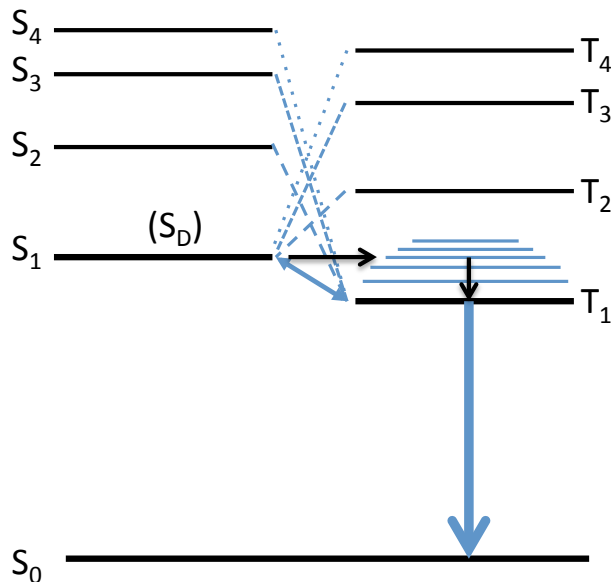The coupling of **l** and **s** allows for intersystem crossing (ISC) by *mixing* S and T states

The Process of Intersystem Crossing

Formally, from 1st order perturbation theory, the singlet and triplet states are coupled by H$_{SO}$:

$$|S_0'\rangle = |S_0\rangle + \sum_i^N \sum_{k=-1}^1 |T_i^k\rangle \frac{\langle T_i^k | H_{SO} | S_0 \rangle}{E(S_0) - E(T_i)} \qquad |T_1'^{m_S}\rangle \approx |T_1^{m_S}\rangle + |S_D\rangle \frac{\langle S_D | H_{SO} | T_1^{m_S} \rangle}{E(T_1) - E(S_D)}$$

Dominant S-state mixed with T$_1$, giving T$_1$ S-like character.

- The same interaction that gives rise to ISC also allows for phosphorescence.
- From **Fermi's Golden Rule:**

$$k_{Ph} = \frac{4\alpha\omega^3}{3c^2} \sum_{k=-1}^1 \left| \langle S_0 | \mathbf{r} | T_1'^k \rangle \right|^2 \quad \text{with} \quad \rho(E_{fi}) = \frac{1}{3} \frac{\alpha h \omega^3}{(\pi q c)^2}$$

Then $\quad k_{Ph} = \frac{4\alpha\omega^3}{3c^2} \sum_{k=-1}^1 \left| \frac{\langle S_D | H_{SO} | T_1'^k \rangle}{E(T_1) - E(S_D)} \right|^2 \left| \langle S_0 | \mathbf{r} | S_D \rangle \right|^2$ due to **singlet** dipole transition

Stronger interactions leading to S-T mixing are indicated by bolder lines

k$_{Ph}$ increases with **l•s** and Z^4!
It also increases as $E(T_1) \to E(S_D)$ (singlet-triplet resonance).

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Electrophosphorescence

Use metal-organic complexes with heavy transition metals
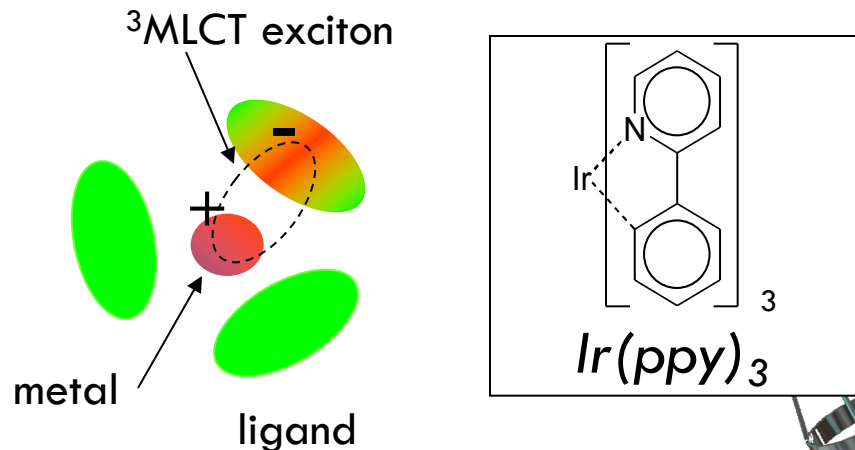(take advantage of Z^4 dependence):

Pt, Ir, etc...

Ligand molecular orbital
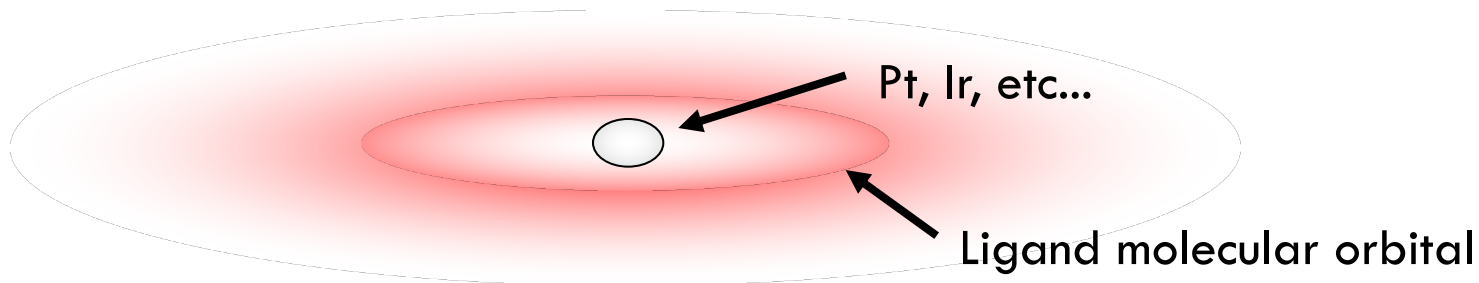
Two Types of Phosphors

Type I phosphor
Exciton localized on organic

ligand (^{3}LC)

exciton

metal

ligand

PtOEP
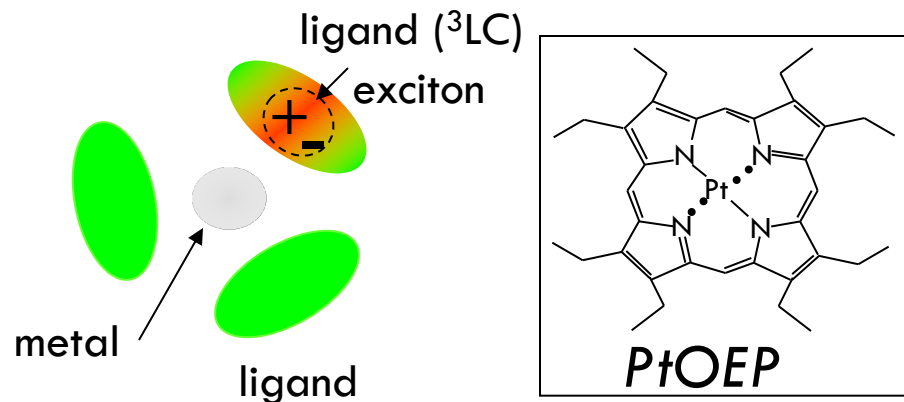
less mixing ~ 100 μs triplet lifetime

Type II phosphor
Metal-ligand charge transfer exciton

^{3}MLCT exciton

metal

ligand

Ir(ppy)$_3$

tronics
Forrest

most mixing ~ 1 μs triplet lifetime
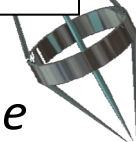
Zero Field Splitting:
Why some phosphors emit faster than others

- ZFS is the splitting of the 3 mS levels of T_1
- The emission rate depends on the thermodynamic balance between the 3 substates.
- Transitions between substates can delay emission according to:

$$\bar{k}_{Ph} = \frac{k_1 + k_2 \exp(-\Delta E_{12}/k_B T) + k_3 \exp(-\Delta E_{13}/k_B T)}{1 + \exp(-\Delta E_{12}/k_B T) + \exp(-\Delta E_{13}/k_B T)}$$

Example:
Pyrazolate-bridged cyclometallated Pt(II) complex

k_{ph} vs. 1/T and fit using ZFS = E_{13} = 113 cm^{-1}; $E_1$2 = 33 cm^{-1}
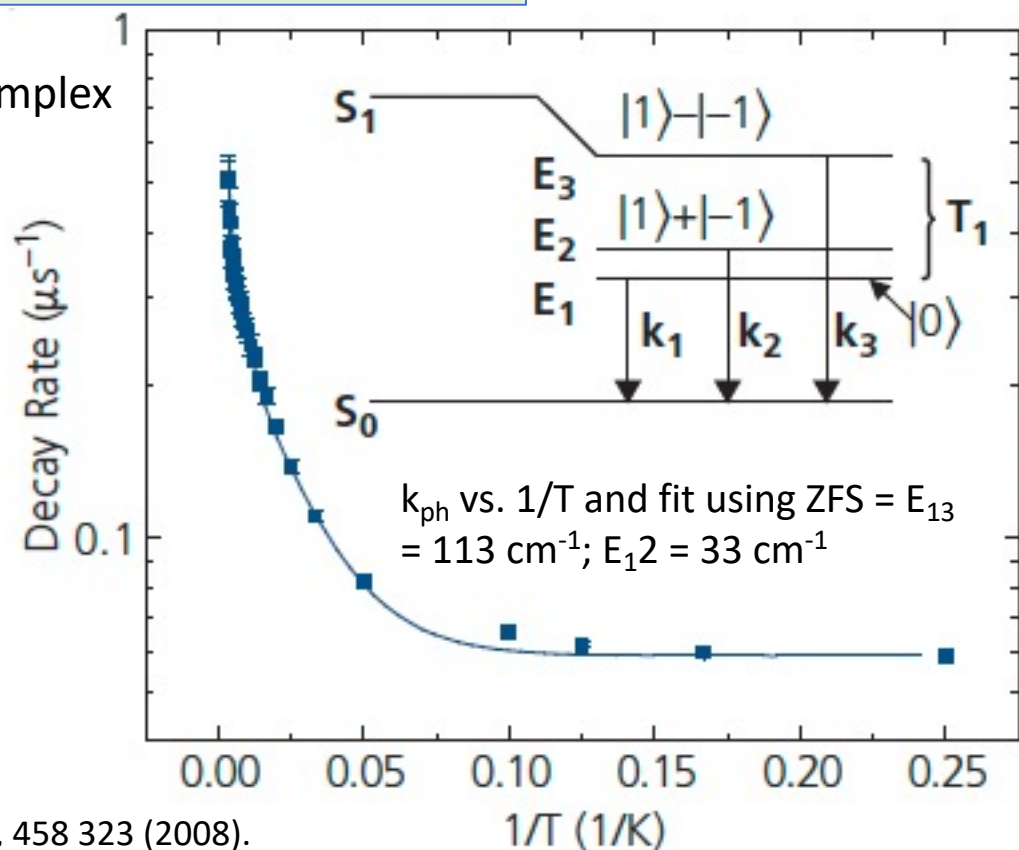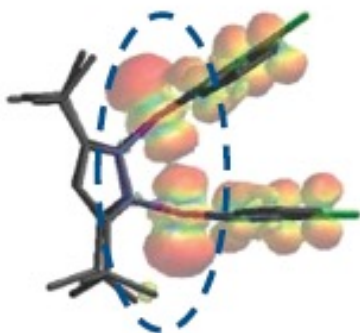
- The Pt · · · Pt (red) interaction varied by controlling the angle between ligands
- This controls the ZFS

Qi et al., Chem. Phys. Lett., 458 323 (2008).
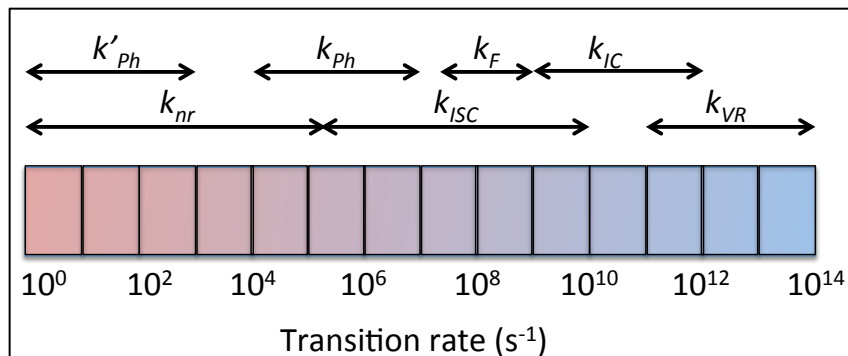
Limits to Phosphorescence Lifetime

- Larger ZFS $\Rightarrow$ Faster response due to reduced accessibility of E_3 at room temp.
- The magnitude of ZFS limited by ligand-field interaction strength
  - Ir(ppy)$_3$ (the first Ir complex used in PHOLEDs) is about as good as it gets!
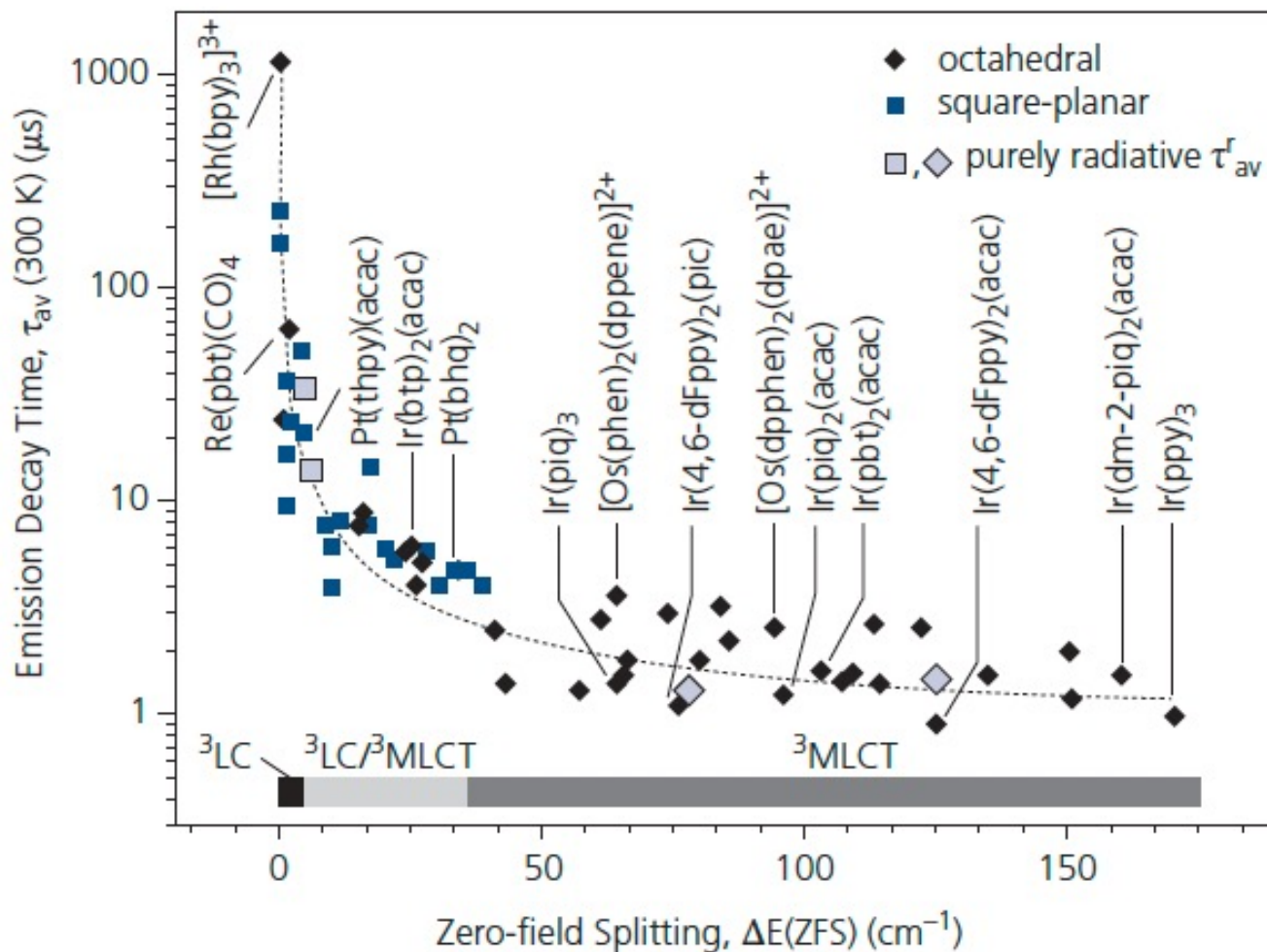
Yersin et al. Coord. Chem. Rev. 255, 2622 (2011).

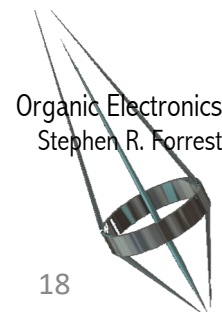# Characteristic Transition Rates

k_{ph}' = phosphorescent transition rate in the absence of S-O coupling
k_{ph} = phosphorescent transition rate in the presence of S-O coupling

Quantum yields: (Ratio of photons emitted to photons absorbed into 4π solid angle)

Fluorescence:
$$\Phi_F = \frac{k_F}{k_F + k_{nrS} + k_{ISC}}$$

Phosphorescence:
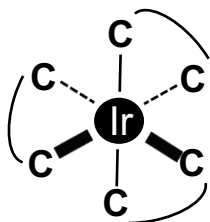$$\Phi_P = \frac{\Phi_{ISC} k_{Ph}}{k_{Ph} + k_{nrT}} \; ; \qquad \Phi_{ISC} = \frac{k_{ISC}}{k_{ISC} + k_F + k_{nrS}}$$
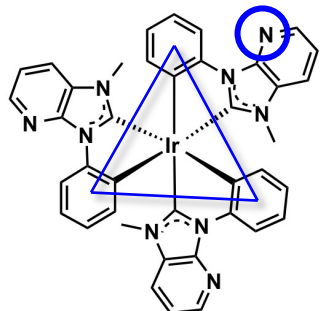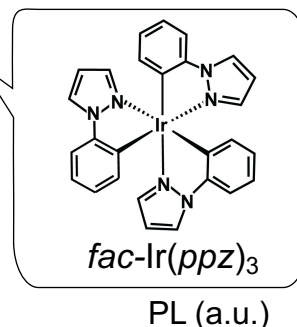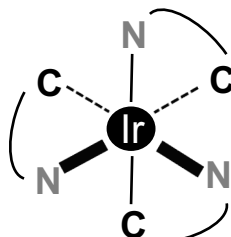
Differences between Type I and Type II Phosphors

N-Heterocyclic carbene (NHC) ligand for blue

| NHC Ir (III) complex = Ir(C^C:)$_3$ | Conventional design = Ir(C^N)$_3$ |

fac-Ir(*ppz*)$_3$

vs.
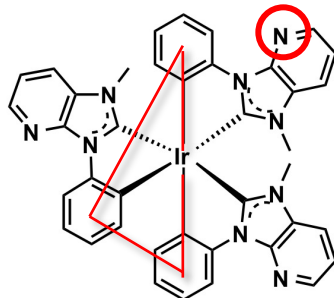
fac-Ir(*pmP*)$_3$ *mer*-Ir(*pmP*)$_3$
Type I   Type II

J. Lee, et al. Nat. Mater., 14, 92 (2016)

PL (a.u.)

- △ *fac*-Ir(*pmB*)$_3$
- ☐ *fac*-Ir(*pmP*)$_3$
- ○ *mer*-Ir(*pmP*)$_3$

Wavelength (nm)
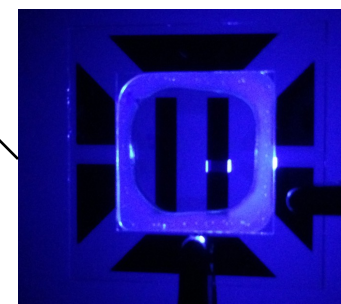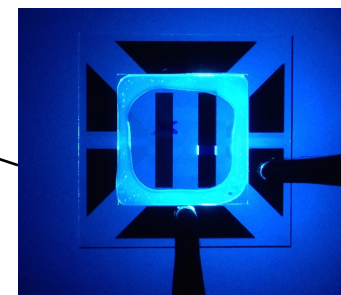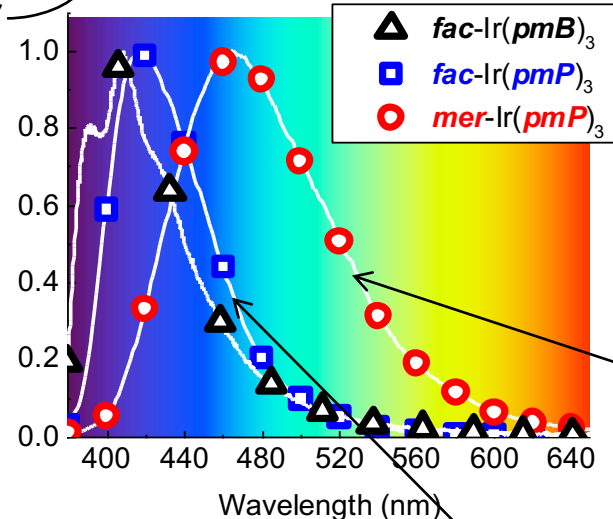
Property	*fac*-Ir(*pmp*)$_3$	*mer*-Ir(*pmp*)$_3$
Emission energy	3.0 eV	2.7 eV
Solvatochromism (in DCM)	-0.19 eV	-0.33 eV
Rigidochromic shift (300 → 77K)	+0.19 eV	+0.34 eV
FWHM change (300 → 77K)	58 → 30 nm	93 → 55 nm
Excited state dipole	Small (localized)	Large (extended)

Delayed Fluorescence

- Triplet can be endothermally promoted (over time) into the singlet manifold.

  o Recall $E(T) < E(S)$

  o For delayed fluorescence: $E(S)-E(T) \leq k_B T$ (near resonance required)

  o Process slows and becomes less efficient as temperature decreases

  o Sometimes called reverse intersystem crossing (RISC)

     ➢ But it is still just ISC

  o Also known as thermally assisted delayed fluorescence (TADF)

- Occurs following fluorescent emission (~5-10 ns), and is on time scale of phosphorescence (~10-100 μs)

- The process is **cyclic** and can take many attempts.

- Can have quantum yields ~100% for S and T in near resonance when exchange energy (ΔE_{ST}) is small.
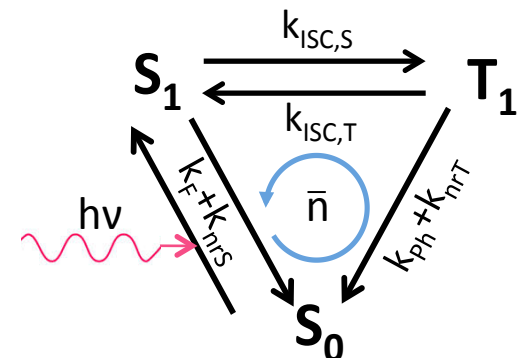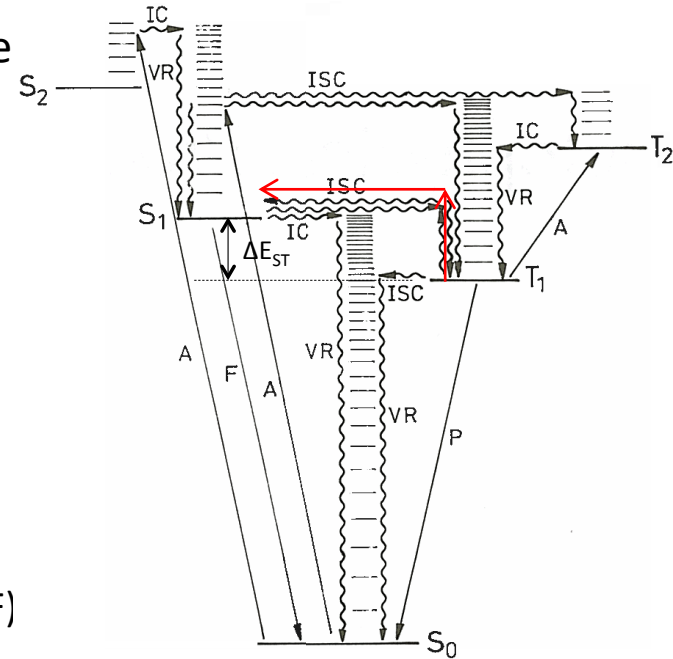
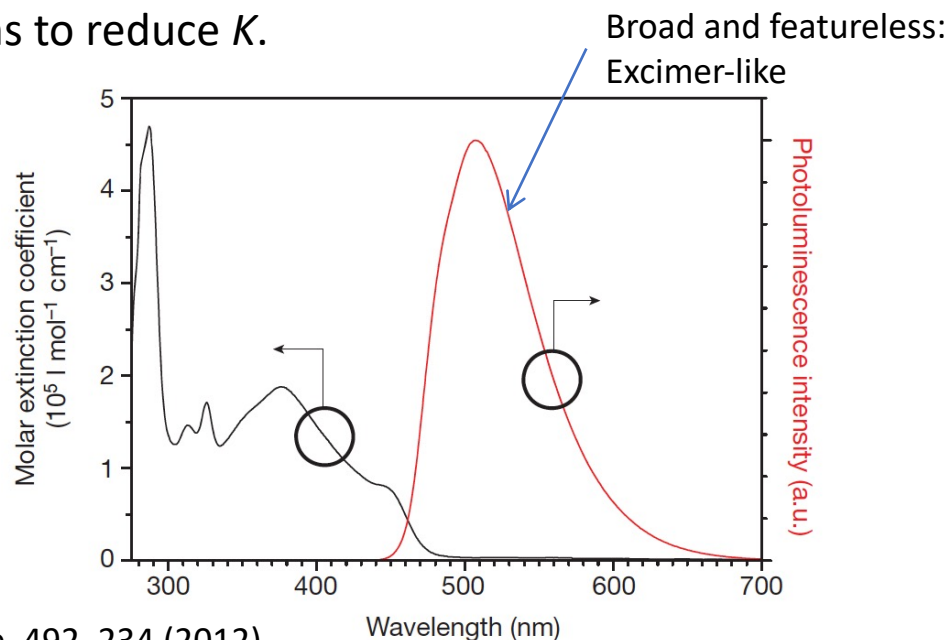# Designing Molecules With Small ΔE$_{ST}$

(Thermally assisted delayed fluorescence)

Recall from molecular orbital theory:

$$J_j = \left\langle \phi_j^0 \left| \frac{q^2}{4\pi\varepsilon_0 \left| \mathbf{r}_i - \mathbf{r}_j \right|} \right| \phi_j^0 \right\rangle \text{ and } K_j = \left\langle \phi_j^0 \left| \frac{q^2}{4\pi\varepsilon_0 \left| \mathbf{r}_i - \mathbf{r}_j \right|} \right| \phi_i^0 \right\rangle$$

Exchange operator ~ ΔE$_{ST}$

Thus, if $\left| \phi_j^0 \right\rangle = \left| S_1 \right\rangle$ and $\left| \phi_i^0 \right\rangle = \left| S_0 \right\rangle$

Then we need to reduce the overlap of these functions to reduce *K*.

4CzIPN

(a)

(b)

(c)

Broad and featureless: Excimer-like

Uoyama et al., Nature, 492, 234 (2012).
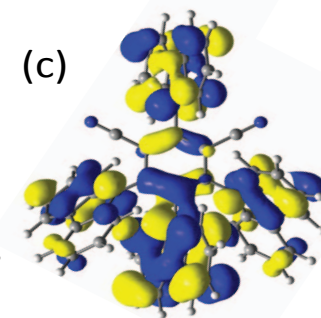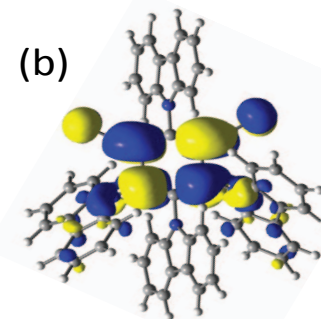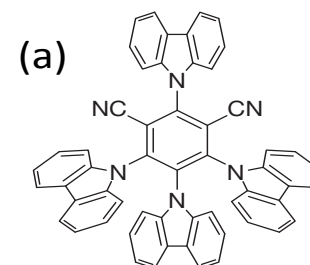
Energy Transfer

- We have seen that the exciton has a band structure – E($\mathbf{k}$) = dispersion
    - ⇒ Excitons have a momentum: $\hbar\mathbf{k}$
- If excitons are mobile in the solid, they must move from molecule to molecule
    - ✧ The microscopic "hopping" between neighboring molecules = energy transfer

Contact zone
(Exchange: Dexter)

Near field zone
(FRET: Förster)

Intermediate zone

Far field zone
(Radiative: 1/r)

≤1

≤10

>100

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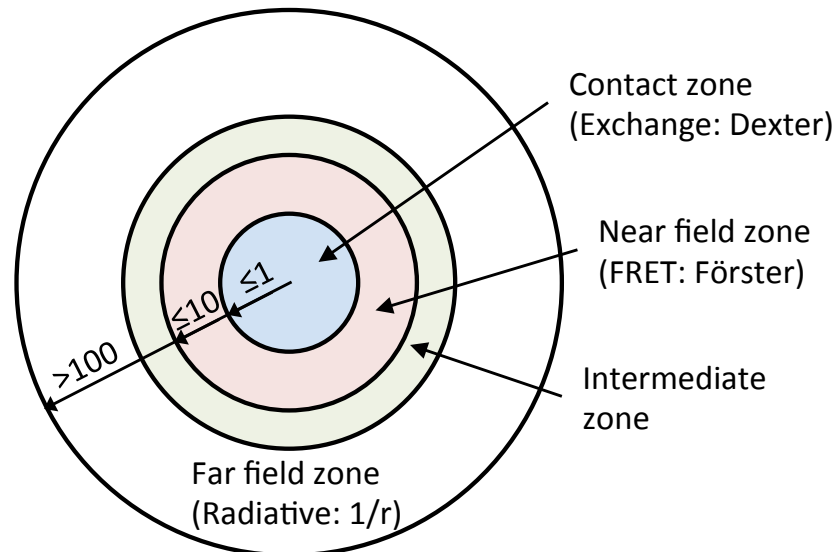
Different transfer ranges accessed by different processes

Förster Resonant Energy Transfer (FRET)

- Förster, T. 1948. Zwischenmolekulare Energiewanderung Und Fluoreszenz. *Ann. Physik,* 55**,** 2.
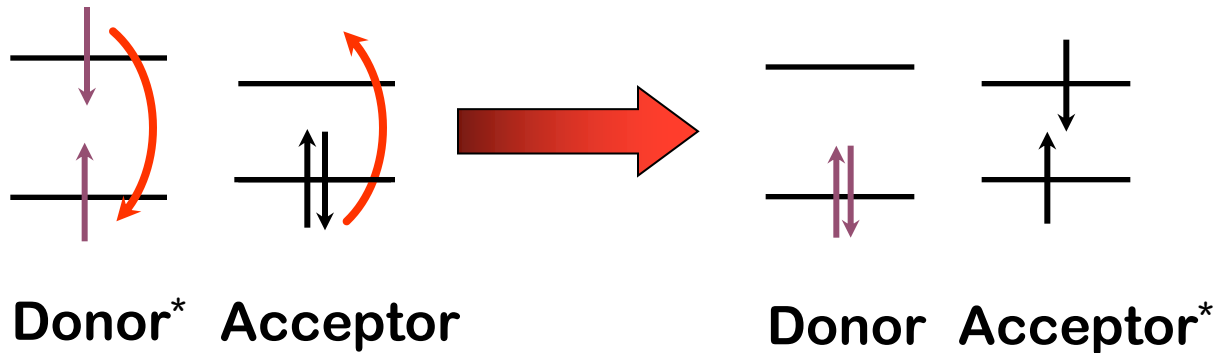- Förster, T. 1959. 10th Spiers Memorial Lecture: Transfer Mechanisms of Electronic Excitations. *Disc. Faraday Soc.,* 27**,** 7.

- resonant dipole-dipole coupling
- donor and acceptor transitions
    must be allowed

up to ~ 100Å

Acceptor (dye)

Donor

Donor * **Acceptor**   **Donor Acceptor** *
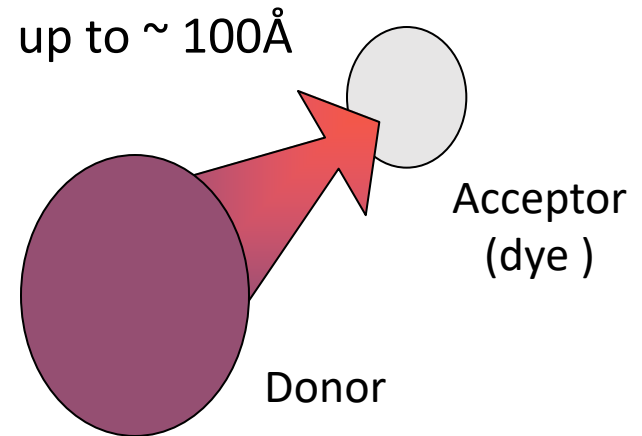
Efficient method for singlet transfer to fluorescent dye
Triplet-singlet transfer possible if donor is strongly phosphorescent

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Förster Transfer Routes

Förster also known as <u>F</u>luorescent <u>R</u>esonant <u>E</u>nergy <u>T</u>ransfer
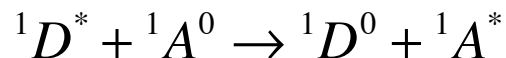In both cases, this is **FRET**

Spin conserving singlet transfer:

$$^1D^* + {}^1A^0 \rightarrow {}^1D^0 + {}^1A^*$$

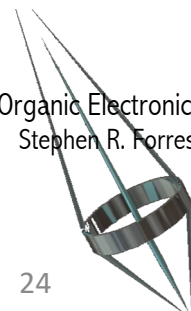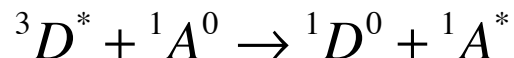Efficient transfer should be exothermic: $E_D^* \geq E_A^0$

These processes also allowed: $^1D^* + {}^3A^m \rightarrow {}^1D^0 + {}^3A^n$

(still spin conserving in transition from $i \rightarrow f$ but initial triplet must be populated for this to occur)
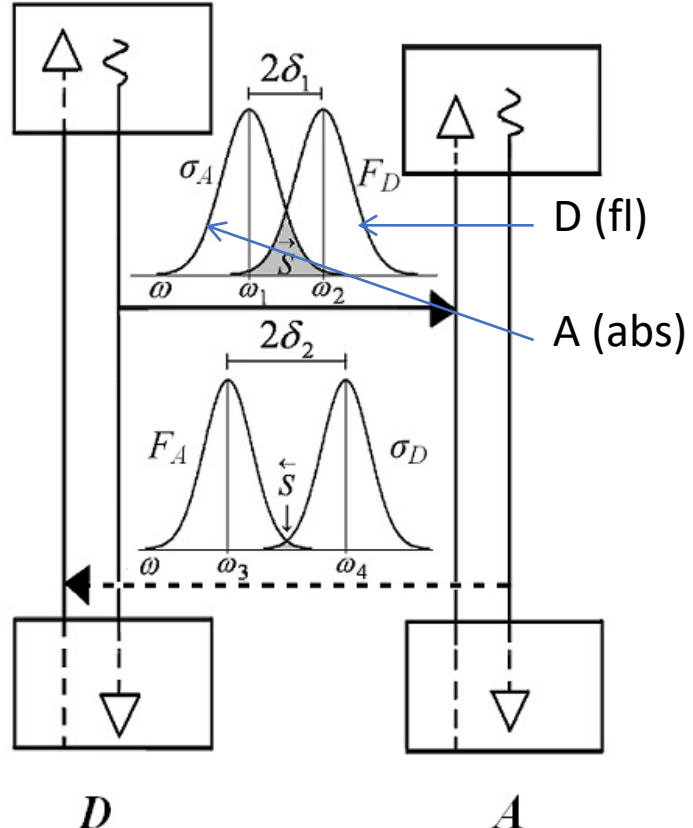
And for highly emissive triplets (where S-O coupling is strong) then spin not conserved:

$$^3D^* + {}^1A^0 \rightarrow {}^1D^0 + {}^1A^*$$

Transfer occurs via electric dipole interactions

$$H_{\text{int}} = \frac{q^2}{4\pi\varepsilon_0\varepsilon_r R^3}\left\{\mathbf{r}_D \cdot \mathbf{r}_A - \frac{3(\mathbf{r}_D \cdot \mathbf{R})(\mathbf{r}_A \cdot \mathbf{R})}{R^2}\right\} + O\left(\frac{1}{R^4}\right) + \ldots$$

Relative orientation of *excited state* donor and *ground state* acceptor dipoles determines coupling strength (i.e. its efficiency):
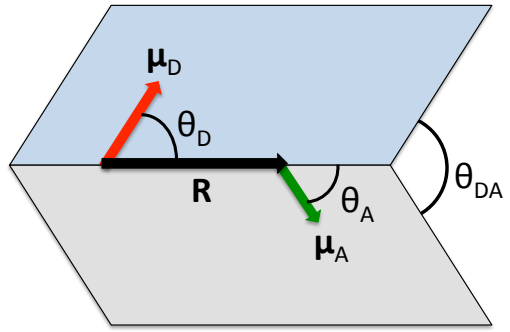
Calculating the transfer rate: FGR to the rescue!

$$k_{ET}(E) = \frac{2\pi}{\hbar}\left|\left\langle \Phi_f \left| H_{\text{int}} \right| \Phi_i \right\rangle\right|^2 \rho(E) = \frac{2\pi}{\hbar}\left|M_{fi}\right|^2 \rho(E)$$

D (fl)

A (abs)

Overlap of the initial and final state energies simply equals the overlap of the donor fluorescence and acceptor absorption spectra!

It all comes down to calculating M_{fi}

Born-Oppenheimer allows for separation of variables:

$$\left| M_{fi} \right|^2 = \left| \left\langle \Phi_f \left| H_{int} \right| \Phi_i \right\rangle \right|^2 = \left| \left\langle \phi_e^{D^0} \phi_e^{A^*} \left| H_{int} \right| \phi_e^{D^*} \phi_e^{A^0} \right\rangle \right|^2 \times$$

$$\left| \left\langle \phi_N^{D^0} \left(E_{D^*} - E \right) \left| \phi_N^{D^*} \left(E_{D^*} \right) \right\rangle \right|^2 \left| \left\langle \phi_N^{A^*} \left(E_{A^0} + E \right) \left| \phi_N^{A^0} \left(E_{A^0} \right) \right\rangle \right|^2$$

$$== \left| M_{e;fi} \right|^2 FC_D \left(E_{D^*}; E_{D^*} - E \right) \times FC_A \left(E_{A^0}; E_{A^0} + E \right)$$

E = energy transferred from D* to A^0

The strength of the transfer thus depends on the <u>overlap of the vibronics</u> in the initial and final states (nothing new there) but also on the Coulomb interaction between electronic states (M_{fi})
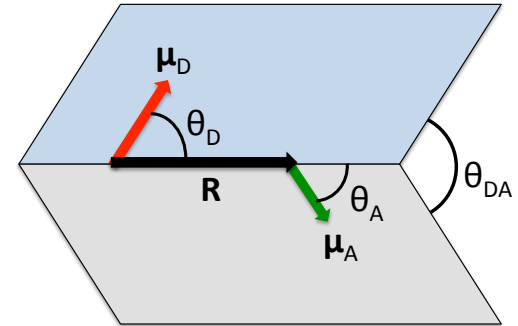
Calculating FRET

$$q^2\left\{\mathbf{r}_D \bullet \mathbf{r}_A - \frac{3(\mathbf{r}_D \bullet \mathbf{R})(\mathbf{r}_A \bullet \mathbf{R})}{R^2}\right\} = q^2 r_D r_A \left\{\cos\theta_{DA} - 3\cos\theta_D \cos\theta_A\right\} = \kappa_F \mu_D \mu_A$$

This gives us the **orientation factor**:

$$\kappa_F^2 = \left(\cos\theta_{DA} - 3\cos\theta_D \cos\theta_A\right)^2$$

That is, FRET can only occur if the initial and final dipoles are non-orthogonal

and
$$\left|M_{fi}\right|^2 = \frac{\kappa_F^2 \mu_D^2 \mu_A^2}{\left(4\pi\varepsilon_0\right)^2 n_r^4 R_{DA}^6} FC\left(E_{D^*}; E_{D^*} - \hbar\omega\right) \times FC\left(E_{A^0}; E_{A^0} + \hbar\omega\right)$$

Distance between dipoles ~ vdW energy!

$$k_{ET} = \frac{9c^4}{128\pi^5}\frac{\kappa^2 \Phi_D}{N_A n_r^4 \tau_D R_{DA}^6}\frac{M_{wA}}{\rho_{MA}}\int\frac{f_D(\nu)\alpha_A(\nu)}{\nu^4}d\nu$$

Absorption coeff't of acceptor

Fluorescence quantum yield of donor

Normalized fluorescence spectrum of donor

Donor natural lifetime

Molar mass/mass density of acceptor

Calculating FRET, cont'd.

$$k_{ET} = \frac{\kappa^2 \mu_D^2 \mu_A^2}{(2\pi)^3 (4\pi\varepsilon_0)^2 n^4 \hbar^2 R_{DA}^6} \times$$

$$\int g_D^*(E_{D^*}) g_A^0(E_{A^0}) FC_D(E_{D^*}; E_{D^*} - \hbar\omega) \times FC_A(E_{A^0}; E_{A^0} + \hbar\omega) d\omega$$

Boltzmann factors for the donor and acceptor states

And, using Einstein coefficients to find the density of states we finally arrive at the well-known Förster equation:

$$k_{ET} = \frac{9c^4}{128\pi^5} \frac{\kappa^2 \Phi_D}{N_A n_r^4 \tau_D R_{DA}^6} \frac{M_{wA}}{\rho_{MA}} \int \frac{f_D(v)\alpha_A(v)}{v^4} dv$$

Absorption coeff't of acceptor

Fluorescence quantum yield of donor

Molar mass/mass density of acceptor

Normalized fluorescence spectrum of donor

What FRET Implies

Simply put:

$$k_{ET} = \frac{1}{\tau_D}\left(\frac{R_0}{R_{DA}}\right)^6$$

Where

$$R_0^6 = \frac{9c^4}{128\pi^5}\frac{\kappa^2\Phi_D}{N_A n_r^4}\frac{M_{wA}}{\rho_{MA}}\int\frac{f_D(v)\alpha_A(v)}{v^4}dv = KJ_v$$

R_0 is the **Förster radius**, or transfer distance.

That is, when $R_0 = R_{DA}$, then $k_{ET} = 1/\tau_D$, the natural radiative lifetime. Thus, the transfer efficiency is:

$$\eta_{ET} = \frac{\tau_D + \tau_{NR}}{\tau_{ET} + \tau_D + \tau_{NR}} \rightarrow \frac{1}{2}$$

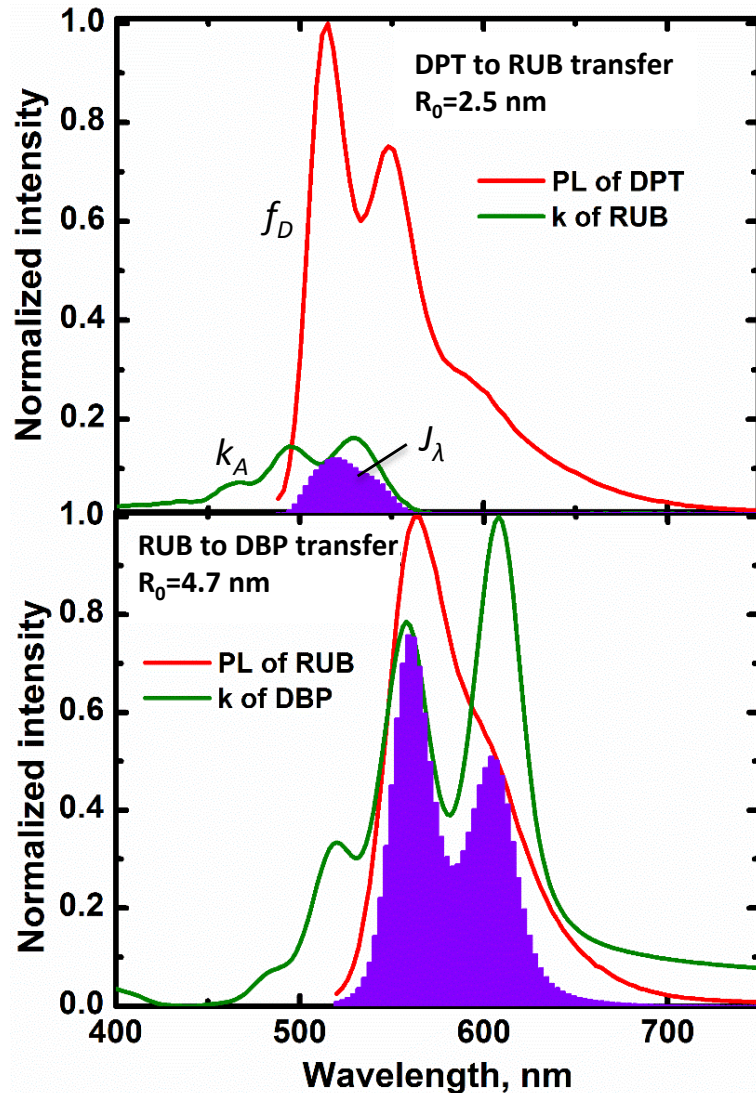(i.e. half of the energy is lost to transfer)

- Keep in mind that **FRET is orientation dependent** : this makes it a probe of molecular orientation by using polarized input light, and determining the polarization of the light emitted from the acceptors
- **FRET transfer time ~ radiative emission time**: k_{ET}~1-10 ns.
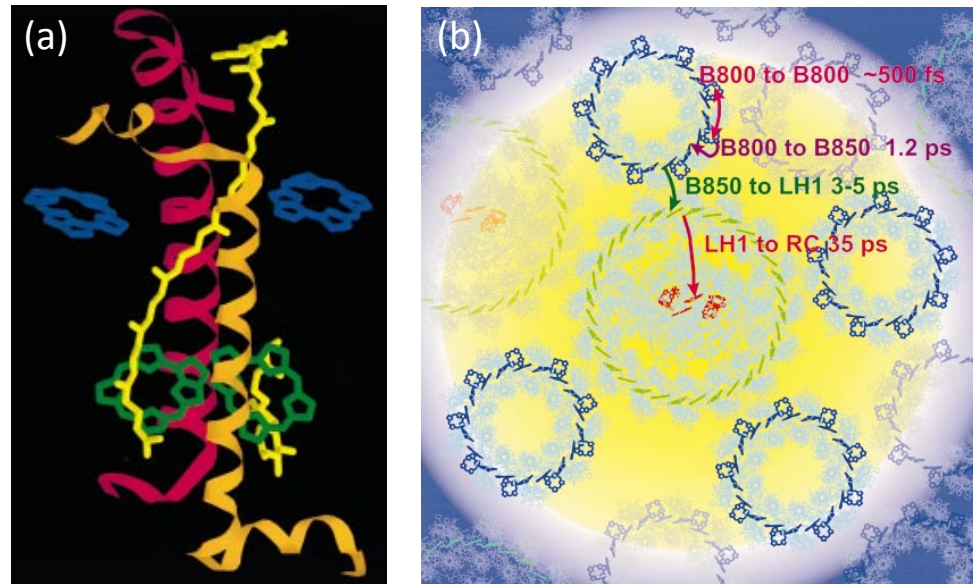- Primary route to diffusion

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Two examples

FRET is important in OLEDs, OPVs, biology,....

Typical molecules used in OPVs and OLEDs

Photosynthetic light harvesting complex LH2

Sundström et al., J. Phys. Chem. B, 103, 2327 (1999).

Griffith & Forrest, Nano Lett., 14, 2353 (2014).
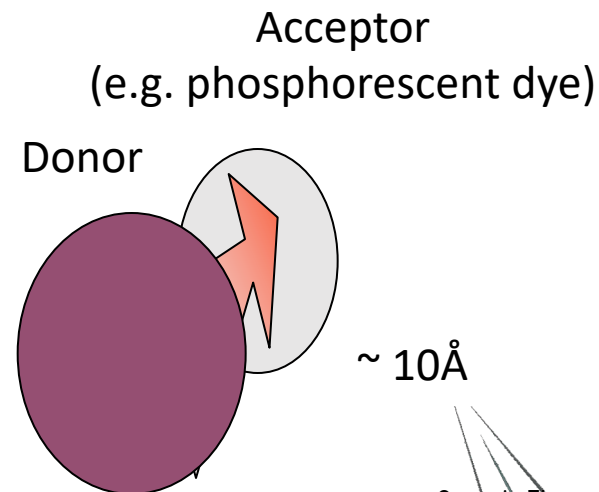
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Exchange Energy Transfer

- Coherent transfer of excitons from donor to acceptor by simultaneous charge exchange <u>in the contact zone</u>

- Also known as **Dexter transfer**
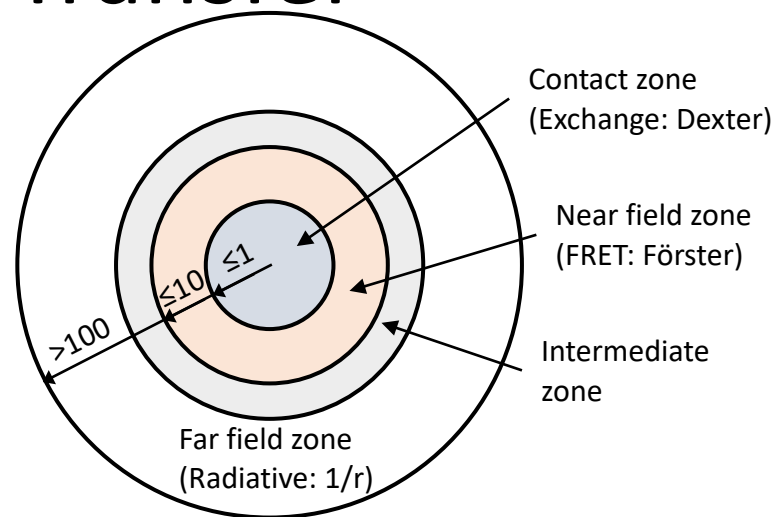
spin is conserved: e.g. singlet-singlet or triplet-triplet

Contact zone
(Exchange: Dexter)

Near field zone
(FRET: Förster)

Intermediate zone

Far field zone
(Radiative: 1/r)

>100   ≤10   ≤1

Donor* Acceptor → Donor Acceptor*

Donor

Acceptor
(e.g. phosphorescent dye)

~ 10Å
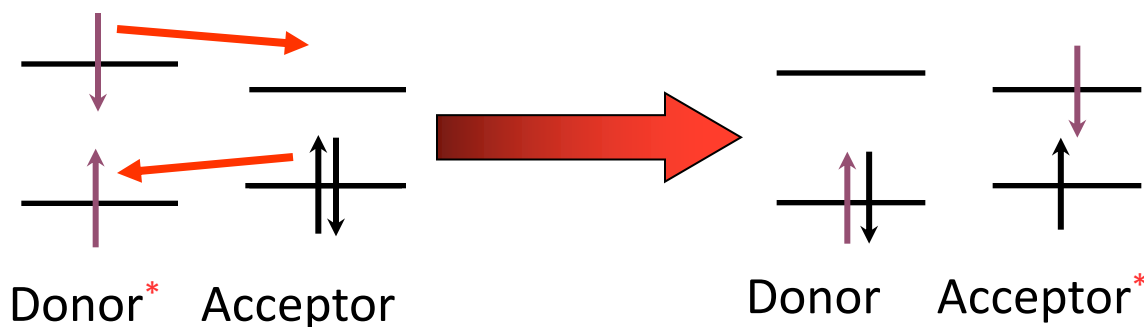
Dexter, L. 1953. A Theory of Sensitized Luminescence in Solids. *J. Chem. Phys. ,* 21**,** 836.

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Spin conserving exchange interactions

$$^1D^* + {}^1A \rightarrow {}^1D + {}^1A^* \qquad \text{(a)}$$

$$^3D^* + {}^1A \rightarrow {}^1D + {}^3A^* \qquad \text{(b)}$$

(a)   (b)

Donor   Acceptor   Donor   Acceptor

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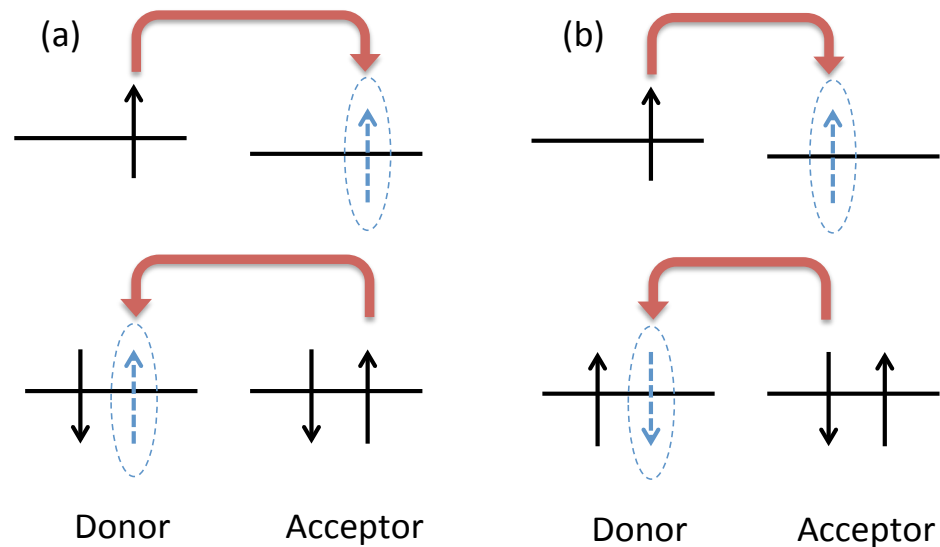
Dexter Also Requires Resonance between D* and A⁰

FGR:
$$k_{ET} = \frac{2\pi}{\hbar} \Gamma^2 \int f_D(\omega) \sigma_A(\omega) d\omega$$

Overlap, Γ, is due to sum of the transition matrix elements over all initial and final states

$$\Gamma = \sum_{if} M_{fi} = \sum_{i,f} \left\langle \psi_f(\mathbf{r}_f, Q_f) \middle| q^2 / 4\pi\varepsilon_0 \varepsilon_r R_{DA} \middle| \psi_i(\mathbf{r}_i, Q_i) \right\rangle$$

For hyrdogenic initial and final states, we get approximately

$$\Gamma^2 \propto \frac{q^2}{\left(4\pi\varepsilon_0\right)^2 n_r R_{DA}^2} \exp(-2R_{DA}/L)$$

vdW radius

Very rapidly decreasing "tunneling" between nearest neighbors

Finally resulting in the Dexter transfer equation:

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$$k_{ET} \approx K \frac{q^2}{8\pi\varepsilon_0^2 \hbar n_r R_{DA}^2} \left\{ \int f_D(\omega)\sigma_A(\omega)d\omega \right\} \exp(-2R_{DA}/L) = \frac{K'J_\omega}{R_{DA}^2} \exp(-2R_{DA}/L)$$

Important facts about Dexter Exchange

- **Spin of the donor and acceptor can change during exchange**
  - Spin of the excited and ground states cannot change
  - Effective in transfer of non-radiative triplet states (FRET is not since triplets are *generally* non-radiative)
- **Transfer is in the contact zone, only between nearest neighbors**
  - Range determined by vdW radius of the molecules
- **To first order (s-like states), there is no dependence on orientation**
  - κ in FRET not found in exchange equation
  - Not due to dipole-dipole coupling; only Coulomb forces
- **Rate of exchange is on the order of a tunneling time**
  - $k_{ET} \sim 10^{10} - 10^{11} s^{-1}$

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