Oscillator strength (*f*): quantum mechanical model

- For an electronic transition to occur an oscillating dipole must be induced by interaction of the molecules electric field with electromagnetic radiation.
- In fact both ε and k^0 can be related to the transition dipole moment (μ_{ge})
- If two equal and opposite electrical charges (e) are separated by a vectorial distance (**r**), a dipole moment (μ) of magnitude equal to e**r** is created.

$$\mu = e\,\mathbf{r}$$

(e = electron charge,
r = extent of charge displacement)

- The magnitude of charge separation, as the electron density is redistributed in an electronically excited state, is determined by the ***polarizability*** (α) of the electron cloud which is defined by the transition dipole moment (μ_{ge})

$$\alpha = \mu_{ge} / \boldsymbol{E}$$

(***E*** = electrical force)

$$\mu_{ge} = e\,\mathbf{r}$$

- The magnitude of the oscillator strength (f) for an electronic transition is proportional to the square of the transition dipole moment produced by the action of electromagnetic radiation on an electric dipole.

$$f \propto \mu_{ge}{}^2 = (e\,\mathbf{r})^2$$

$$f \propto \mu_{ge}{}^2$$

$$f \propto \varepsilon_{\max} \Delta\bar{\nu}_{fwhm}$$

$$f \propto k_e^0 \left(\bar{\nu}^2\right)^{-1}$$

$$f_{\mathrm{obs}} = f_{\max} \left(f_e \;\; f_v \;\; f_s \right)$$

f_{obs} = observed oscillator strength

$f_{\max}$ = ideal oscillator strength (~1)

f_e = orbital configuration factor

f_v = vibrational configuration factor

f_s = spin configuration factor

- There are two major contributions to the electronic factor f_e :
  - ***Poor overlap:*** weak mixing of electronic wavefunctions, e.g. <n|π*>, due to poor spatial overlap of orbitals involved in the electronic transition, e.g. HOMO→LUMO.
  - ***Symmetry forbidden:*** even if significant spatial overlap of orbitals exists, the resonant photon needs to induce a large transition dipole moment. If the symmetry of source and destination orbitals contributing to the electronic transition is similar there is a negligible transition dipole moment resulting in a weak oscillator strength and molar absorption coefficient.
- For example, if a π→π* transition (strong MO mixing) displays a weak electronic transition it is likely offset by a similar symmetry of HOMO and LUMO transitions.

$$f \propto \boldsymbol{\mu}_{\mathrm{ge}}{}^{2} \qquad f_{\mathrm{obs}} = f_{\mathrm{max}}\,(f_{\mathrm{e}}\ f_{\mathrm{v}}\ f_{\mathrm{s}})$$

$$f \propto \varepsilon_{\mathrm{max}} \Delta\bar{\nu}_{fwhm} \qquad \varepsilon_{\mathrm{max}} \propto \frac{f}{\Delta\bar{\nu}_{fwhm}}$$

$$f \propto k_{\mathrm{e}}^{0}\left(\bar{\nu}^{2}\right)^{-1} \qquad k_{\mathrm{e}}^{0} \propto f\ \bar{\nu}^{2}$$

- The rate of emission $k_e{}^0$ is dependent upon the ε_{max} and the square of the frequency of the electronic transition.

- For example, as we see in the following slide, 1,4-dimethylbenzene and pyrene possess similar values of ε_{max} (500 – 700 M^{-1} cm^{-1}) but they absorb and emit at different wavelengths.

- As a result their oscillator strengths *f* and emission decay rate constants differ significantly.

- Assuming comparable *fwhm* this trend is mostly dependent upon the wavelength of emission.

$$f \propto \boldsymbol{\mu}_{\mathrm{ge}}{}^{2} \qquad f_{\mathrm{obs}} = f_{\mathrm{max}}\,(f_{\mathrm{e}}\ \ f_{\mathrm{v}}\ \ f_{\mathrm{s}})$$

$$f \propto \varepsilon_{\mathrm{max}}\Delta\bar{\nu}_{fwhm} \qquad \varepsilon_{\mathrm{max}} \propto \frac{f}{\Delta\bar{\nu}_{fwhm}}$$

$$f \propto k_{\mathrm{e}}^{0}\left(\bar{\nu}^{2}\right)^{-1} \qquad k_{\mathrm{e}}^{0} \propto f\ \bar{\nu}^{2}$$

	k_e(s^{-1})	example	transition	ε_{max}	f	ν_{max}(cm^{-1})
Spin allowed	10^9	*p*-terphenyl	$S_1(\pi,\pi^*) \rightarrow S_0$	3×10^4	1	30,000
	10^8	perylene	$S_1(\pi,\pi^*) \rightarrow S_0$	4×10^4	10^{-1}	22,850
	10^7	1,4-dimethylbenzene	$S_1(\pi,\pi^*) \rightarrow S_0$	7×10^2	10^{-2}	36,000
	10^6	pyrene	$S_1(\pi,\pi^*) \rightarrow S_0$	5×10^2	10^{-3}	26,850
	10^5	acetone	$S_1(n,\pi^*) \rightarrow S_0$	10	10^{-4}	30,000
Spin forbidden	10^4	xanthone	$T_1(n,\pi^*) \rightarrow S_0$	1	10^{-5}	15,000
	10^3	acetone	$T_1(n,\pi^*) \rightarrow S_0$	10^{-1}	10^{-6}	27,000
	10^2	1-bromonapthalene	$T_1(\pi,\pi^*) \rightarrow S_0$	10^{-2}	10^{-7}	20,000
	10	1-chloronaphtalene	$T_1(\pi,\pi^*) \rightarrow S_0$	10^{-3}	10^{-8}	20,600
	10^{-1}	naphtalene	$T_1(\pi,\pi^*) \rightarrow S_0$	10^{-4}	10^{-9}	21,300

Representative examples of ε_{max} and f values for prototype electronic transitions.

Benchmarks for
fully allowed and
weakly allowed
spin allowed
transitions of organic
chromophores.

$$f \propto \mu_{ge}^{2}$$

$$f \propto \varepsilon_{\max} \Delta\bar{\nu}_{fwhm}$$

$$f \propto k_{\mathrm{e}}^{0} \left(\bar{\nu}^{2}\right)^{-1}$$

$$f_{\mathrm{obs}} = f_{\max}\,(f_{\mathrm{e}}\ f_{\mathrm{v}}\ f_{\mathrm{s}})$$

$$\varepsilon_{\max} \propto \frac{f}{\Delta\bar{\nu}_{fwhm}}$$

$$k_{\mathrm{e}}^{0} \propto f\ \bar{\nu}^{2}$$

	k_e(s^{-1})	example	transition	ε_{max}	*f*	ν_{max}(cm^{-1})
Spin allowed	10^9	*p*-terphenyl	$S_1(\pi,\pi^*) \rightarrow S_0$	3×10^4	1	30,000
	10^8	perylene	$S_1(\pi,\pi^*) \rightarrow S_0$	4×10^4	10^{-1}	22,850
	10^7	1,4-dimethylbenzene	$S_1(\pi,\pi^*) \rightarrow S_0$	7×10^2	10^{-2}	36,000
	10^6	pyrene	$S_1(\pi,\pi^*) \rightarrow S_0$	5×10^2	10^{-3}	26,850
	10^5	acetone	$S_1(n,\pi^*) \rightarrow S_0$	10	10^{-4}	30,000
Spin forbidden	10^4	xanthone	$T_1(n,\pi^*) \rightarrow S_0$	1	10^{-5}	15,000
	10^3	acetone	$T_1(n,\pi^*) \rightarrow S_0$	10^{-1}	10^{-6}	27,000
	10^2	1-bromonapthalene	$T_1(\pi,\pi^*) \rightarrow S_0$	10^{-2}	10^{-7}	20,000
	10	1-chloronaphtalene	$T_1(\pi,\pi^*) \rightarrow S_0$	10^{-3}	10^{-8}	20,600
	10^{-1}	naphtalene	$T_1(\pi,\pi^*) \rightarrow S_0$	10^{-4}	10^{-9}	21,300

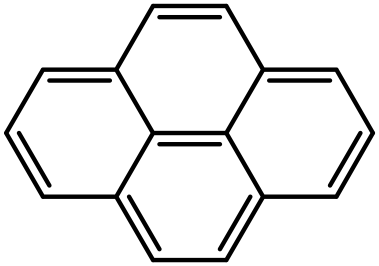
Representative examples of ε_{max} and *f* values for prototype electronic transitions.

$$f \propto \boldsymbol{\mu}_{\mathrm{ge}}{}^{2} \qquad f_{\mathrm{obs}} = f_{\max}\left(f_{\mathrm{e}}\ f_{\mathrm{v}}\ f_{\mathrm{s}}\right)$$

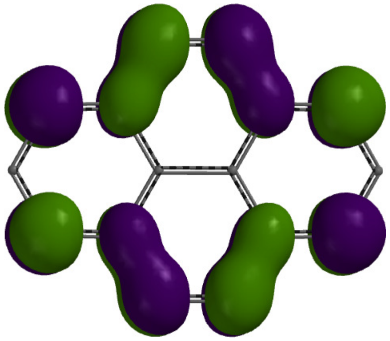
$$f \propto \varepsilon_{\max}\Delta\bar{\nu}_{fwhm} \qquad \varepsilon_{\max} \propto \frac{f}{\Delta\bar{\nu}_{fwhm}}$$

$$f \propto k_{\mathrm{e}}^{0}\left(\bar{\nu}^{2}\right)^{-1} \qquad k_{\mathrm{e}}^{0} \propto f\ \bar{\nu}^{2}$$

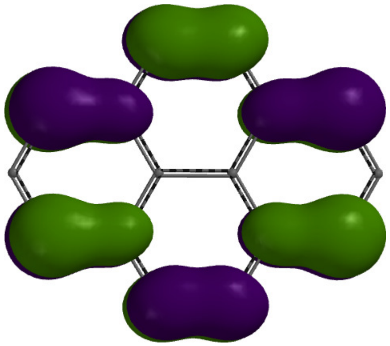
- If we ignore f_{v} (i.e. for rigid molecules with little distortion of excited state PECs) and f_{s} the k_{obs} is ultimately determined by f_{e}
- For rigid molecules k_{obs} is thus determined by the spatial overlap of contributing MOs and their symmetries.
- For molecules with distorted excited state PECs f_{v} becomes more important due to Franck-Condon factors.

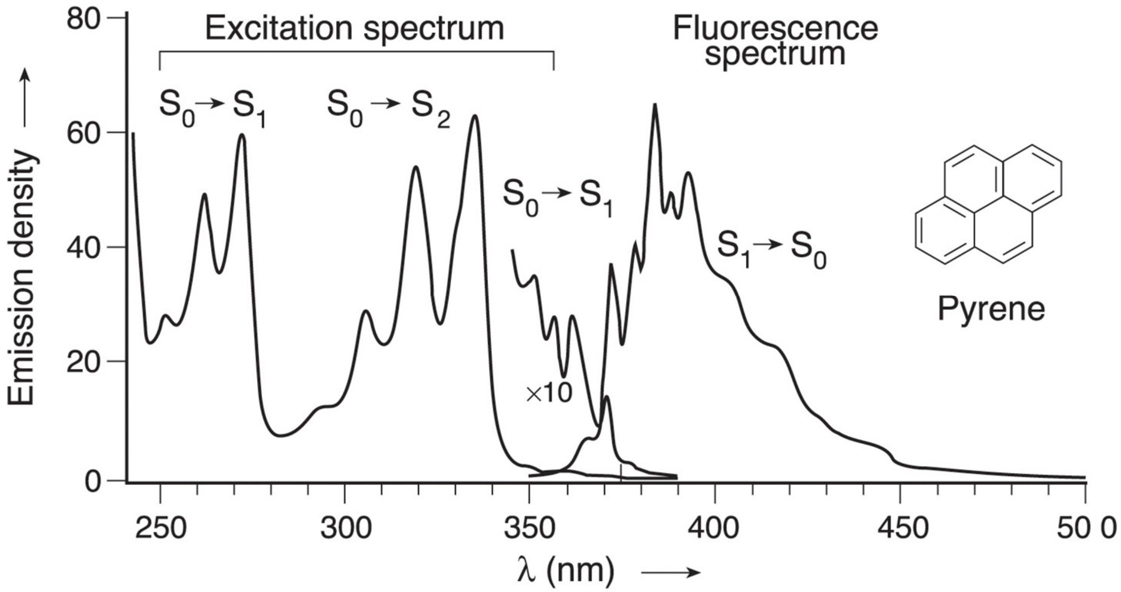


LUMO



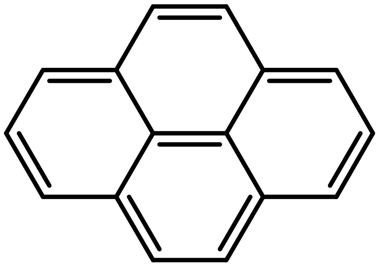
HOMO



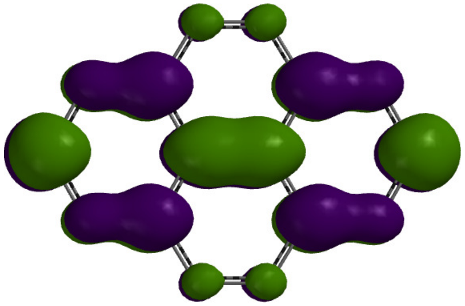


- As pyrene is a rigid planar organic system with little distortion of excited state PECs k_{obs} is ultimately determined by the spatial overlap of contributing MOs and their symmetries.

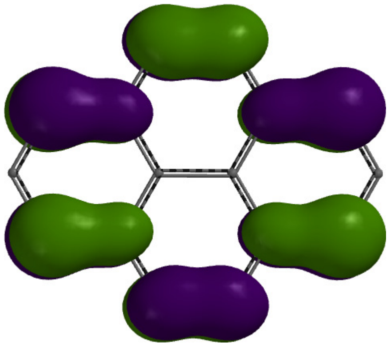
- Spatial overlap of the HOMO and LUMO appears to be sufficient such that the weak intensity of the $S_0 \rightarrow S_1$ transition must be due to a low transition dipole moment due to the analogous symmetries of the HOMO and LUMO wavefunctions.

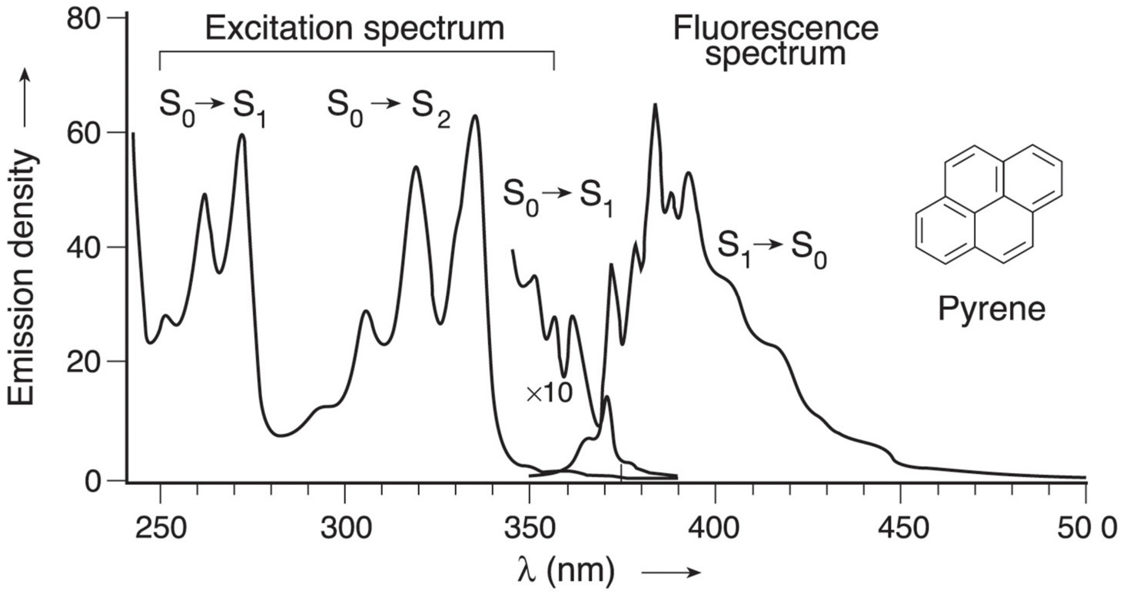


LUMO+1



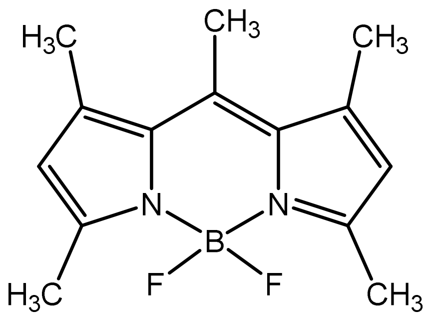
HOMO

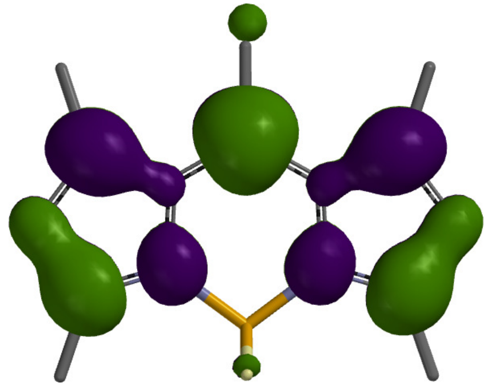




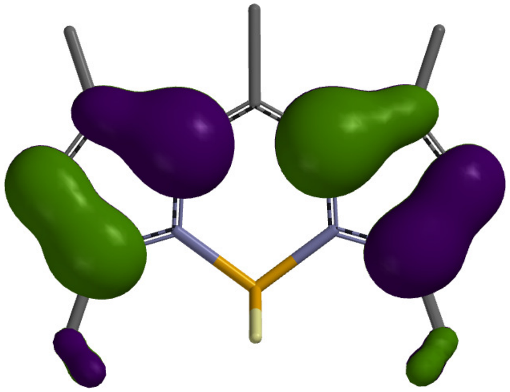
- The HOMO and LUMO+1 orbitals appears to have a greater spatial overlap of wavefunctions.

- Here a larger transition dipole moment is anticipated due to the distortion in electron density distribution across the molecular framework. Sufficient enough to realize an intense $S_0 \rightarrow S_2$ electronic transition.

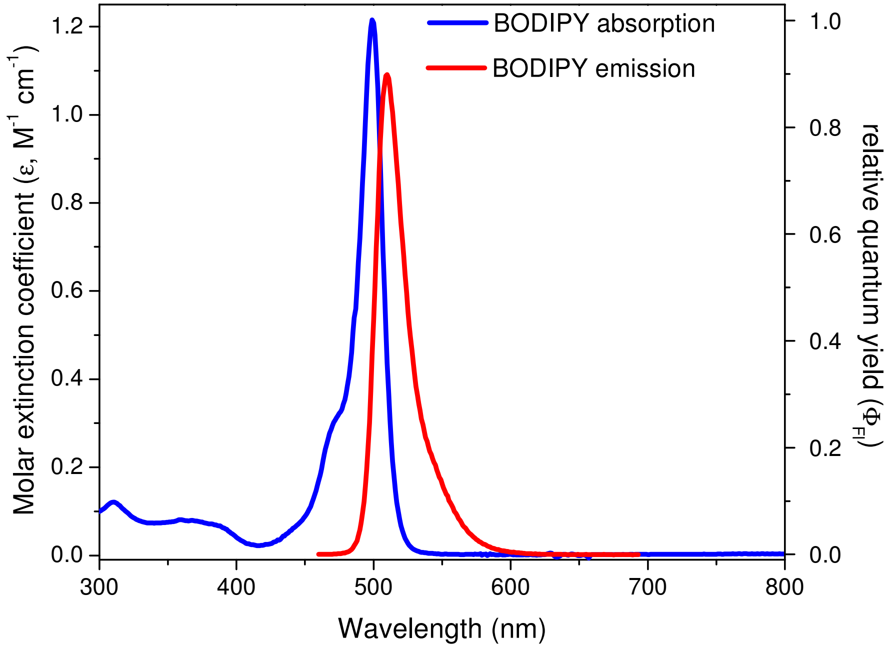




LUMO



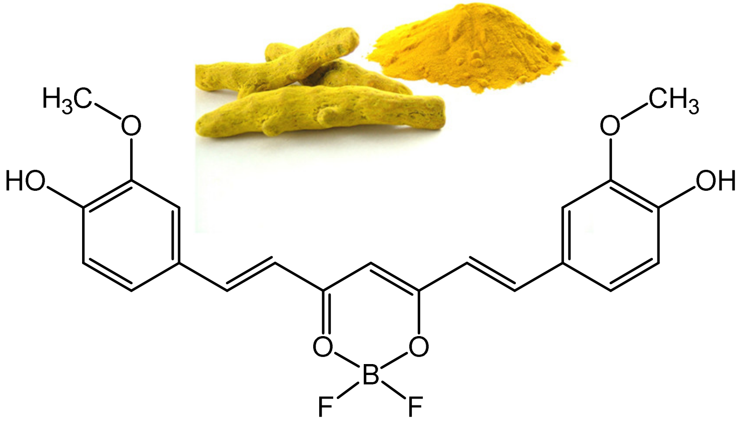
HOMO

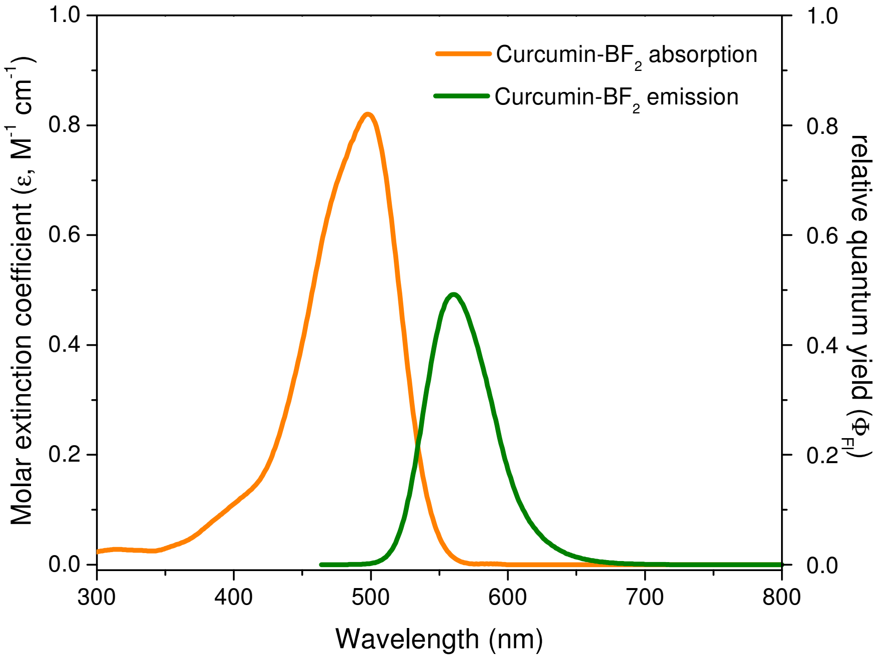


- BODIPY is another example of a rigid planar organic system with little distortion of excited state PECs (evident from its small Stoke's shift)

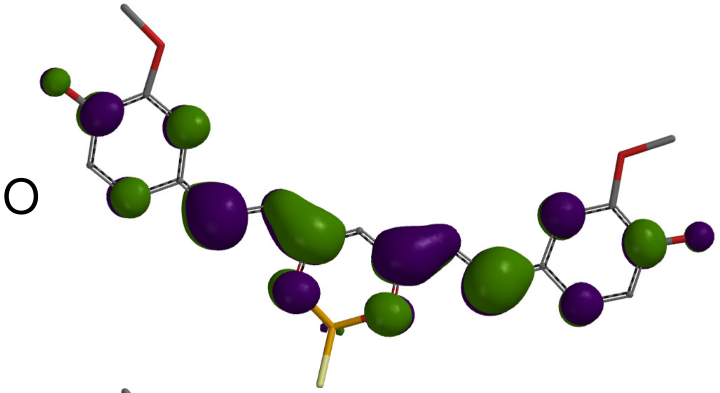
- Spatial overlap of the HOMO and LUMO appears to be sufficient to realize an intense $S_0 \rightarrow S_1$ electronic transition.

- Notice how the electron density is redistributed from HOMO to LUMO contributing to an oscillating transition dipole.

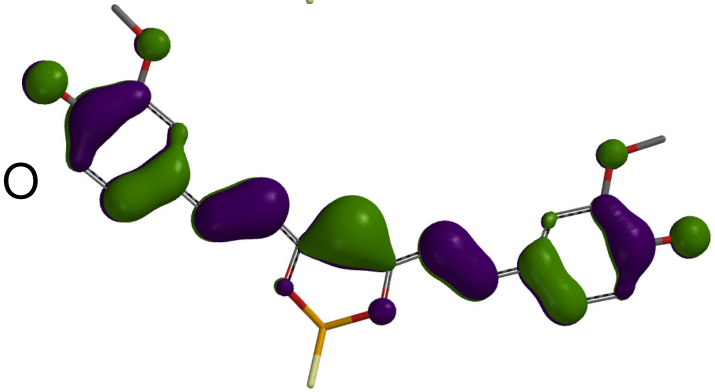




LUMO



HOMO



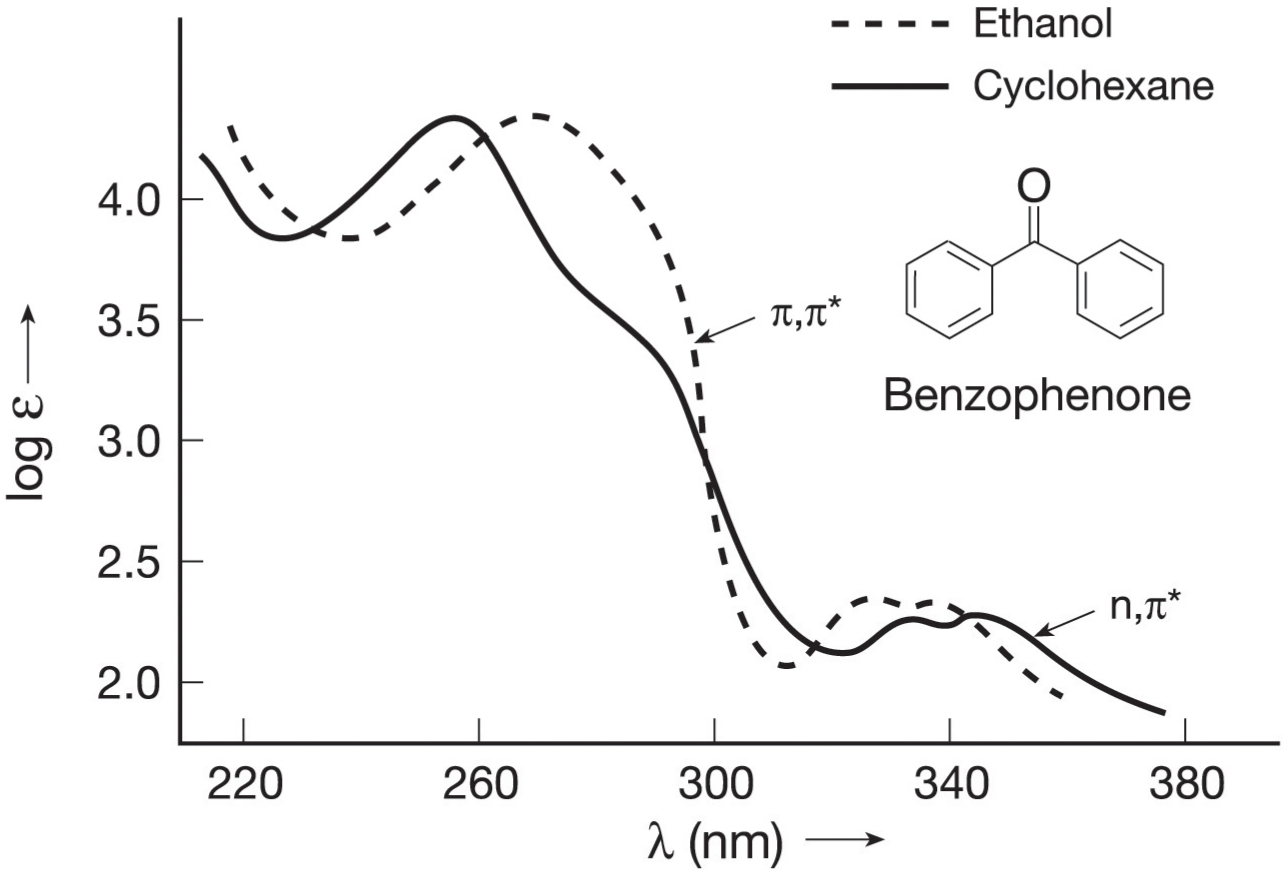
- Curcumin-BF$_2$ is an example of a semi-rigid planar organic system with significant distortion of excited state PECs (evident from its slarger Stoke's shift relative to BODIPY)

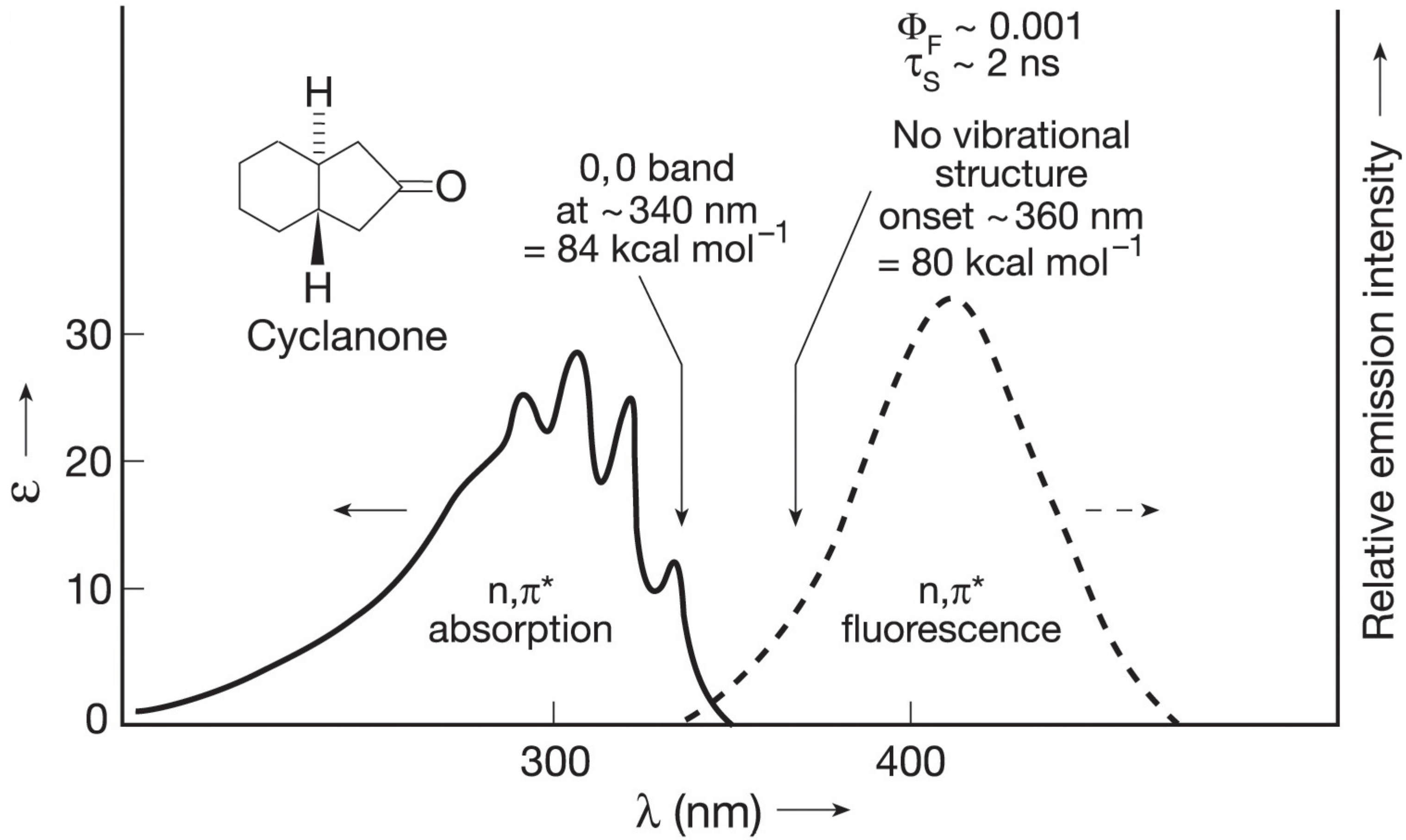
- Spatial overlap of the HOMO and LUMO appears to be sufficient to realize an intense $S_0 \rightarrow S_1$ electronic transition.

- Notice again how the electron density is redistributed from HOMO to LUMO contributing to an oscillating transition dipole.

- Empirically, a number of criteria have been developed that allow an orbital configuration change to be identified from characteristics of absorption and emission spectra:

property	n → π*		π → π*	
	$S_0 \rightarrow S_1$	$S_0 \rightarrow T_1$	$S_0 \rightarrow S_1$	$S_0 \rightarrow T_1$
ε_{max}	< 200	$> 10^{-2}$	> 1000	$< 10^{-3}$
k_e (s^{-1})	$10^5 - 10^6$	$10^3 - 10^2$	$10^7 - 10^8$	$1 - 10^{-1}$
solvatochromism	negative		positive	
Vibrational structure	localized		delocalized	
Heavy atom effect	none		yes	
ΔE_{ST}	< 10 kcal mol^{-1}		> 20 kcal mol^{-1}	
polarization of μ_{ge}	⊥	‖	‖	⊥
Φ_{em} (77 K)	< 0.01	~ 0.5	0.05 – 1.0	< 0.5
E_T	< 75	< 65	variable	


Ethanol
Cyclohexane
4.0
3.5
3.0
2.5
2.0
log ε ⟶
220
260
300
340
380
λ (nm) ⟶
π,π*
n,π*
O
Benzophenone


H
H
O
Cyclanone
0,0 band
at ~340 nm
= 84 kcal mol^{-1}
Φ_F ~ 0.001
τ_S ~ 2 ns
No vibrational
structure
onset ~360 nm
= 80 kcal mol^{-1}
n,π*
absorption
n,π*
fluorescence
ε →
30
20
10
0
300
400
λ (nm) →
Relative emission intensity →

Quantum yield for emission (Φ_e)

- Always recall the Jablosnksi diagram when “bookkeeping” of state electronic configurations and competing photochemical processes.
- In an electronic excited state there is competition between radiative decay and non-radiative decay processes.
- For simplicity, let’s assume for now that radiative decay is the only decay process.
- In this case k_{fl}^{0} represents the sole decay rate constant.
- By definition, the lifetime of an excited state is equal to the reciprocal of the rate of deactivation of the state.

$$\tau^0 = \frac{1}{k_{\mathrm{fl}}^{0}}$$

τ^0 = singlet radiative lifetime in absence of non-radiative processes (s)

k_{fl}^{0} = fluorescence rate constant (s^{-1})

Quantum yield for emission (Φ_e)

- The **absolute quantum yield (Φ_e)** is an important experimental parameter containing useful information relating the structure and dynamics of electronically excited states.

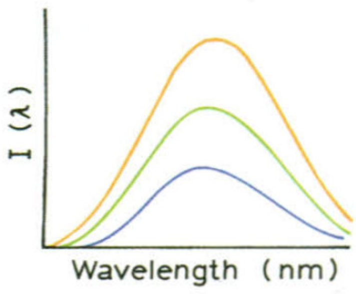
- Φ_e is directly proportional to the emission rate constant (k_e^o) and inversely proportional to the rate of any deactivating non-radiative processes ($\sum k_{nr}$)

$$\Phi_e \propto \frac{k_e^o}{k_e^o + \sum k_i}$$

- Invoking Kasha's rule, whether emission is observed from an excited state molecule is determined by the quantum yields of fluorescence and phosphorescence.

- Although emission can be observed for many chromophores in solution at room temperature it is very common to record emission spectra at 77 K in a frozen glass to minimize $\sum k_{nr}$ via prevention of diffusion controlled bimolecular quenching processes and vibrational relaxation.

- Even under these conditions it is rare to observe a Φ_e of unity.



$$\Phi_f = \text{no. of photons emitted / no. of photons absorbed}$$

- Fluorescence quantum yields (Φ_f) are calculated using *steady state* methods by ***actinometry***:

  Typically, in de-aerated, optically dilute solutions fluorescence spectra of both the actinometer (ref) and sample (s) are recorded following *identical monochromatic excitation* of uniform intensity

  $$\Phi_f = (A_{ref}/A_s)(I_s/I_{ref})(\eta_s/\eta_{ref})^2\Phi_{ref}$$

  where A is the absorbance at the excitation wavelength, I is the integrated emission area and η is the solvent refractive index.

- If an actinometer is used which allows use of the same solvent this equation reduces to

  $$\Phi_f = (A_{ref}/A_s)(I_s/I_{ref})\Phi_{ref}$$

Relating k_{fl} and Φ_{fl}

$$^{1}\tau_0 = \frac{1}{k_{\mathrm{fl}}} \qquad k_{\mathrm{fl}} = \frac{1}{^{1}\tau_0}$$

$$^{1}\tau = \frac{1}{k_{\mathrm{fl}} + k_{\mathrm{ic}} + k_{\mathrm{isc}}} = \frac{1}{k_{\mathrm{total}}}$$

$$k_{\mathrm{total}} = k_{\mathrm{fl}} + k_{\mathrm{ic}} + k_{\mathrm{isc}} = \frac{1}{^{1}\tau}$$

$$\Phi_{\mathrm{fl}} = \frac{^{1}\tau}{^{1}\tau_0} = \frac{k_{\mathrm{fl}}}{k_{\mathrm{total}}} = \frac{k_{\mathrm{fl}}}{k_{\mathrm{fl}} + k_{\mathrm{ic}} + k_{\mathrm{isc}}} = \frac{k_{\mathrm{fl}}}{k_{\mathrm{fl}} + k_{\mathrm{nr}}}$$

τ_0 = singlet radiative lifetime in absence of non-radiative processes (s)

$^{1}\tau$ = singlet radiative lifetime (s)

k_{fl} = fluorescence rate constant (s^{-1})

k_{ic} = internal conversion rate constant (s^{-1})

k_{isc} = intersystem crossing rate constant (s^{-1})

k_{nr} = non-radiative rate constant ($k_{\mathrm{ic}} + k_{\mathrm{isc}}$; s^{-1})

Φ_{fl} = fluorescence quantum yield

$$\boxed{\Phi_{\mathrm{fl}} = \frac{k_{\mathrm{fl}}}{k_{\mathrm{fl}} + k_{\mathrm{nr}}}}$$

- There are two limiting situations:
  - $k_{\mathrm{fl}} >> k_{\mathrm{nr}}$ in which case $\Phi_{\mathrm{fl}} \sim 1.0$
  - $k_{\mathrm{nr}} >> k_{\mathrm{fl}}$ in which case $\Phi_{\mathrm{fl}} \sim k_{\mathrm{fl}} / k_{\mathrm{nr}} \sim 0$

Radiative lifetimes

$$\boxed{\tau_0 \approx \frac{10^{-4}}{\varepsilon_{\max}}}$$

	ε_{max} (L mol^{-1} cm^{-1})	τ_0 (s)
$^1(\pi \rightarrow \pi^*)$	10^2 - 10^5	ns - µs
$^1(n \rightarrow \pi^*)$	10 - 10^2	µs - ms
$^3(\pi \rightarrow \pi^*)$	10^{-4} - 10	ms - s
$^3(n \rightarrow \pi^*)$	10 – 10^2	µs - ms

Structural influences on Φ_{fl}

1. Most rigid aromatic hydrocarbons and their derivatives possess measurable, but variable, fluorescence quantum yields ($1.0 > \Phi_{fl} < 0.01$) even at 77 K.

2. Low values of Φ_{fl} are commonly observed for systems with vibrational freedom, for example the S_1 state of stilbene undergoes efficient cis-trans isomerization and internal conversion via vibrational relaxation.

3. Substitution with heavy elements results in enhanced spin-orbit coupling and reduced Φ_{fl} in the order $\Phi_{fl}^{H} > \Phi_{fl}^{F} > \Phi_{fl}^{Cl} > \Phi_{fl}^{Br} > \Phi_{fl}^{I}$

4. Substitution of an aromatic C-H bond with a carbonyl functionality generally results in a decreased Φ_{fl} due to enhanced intersystem crossing to the T_1 state.

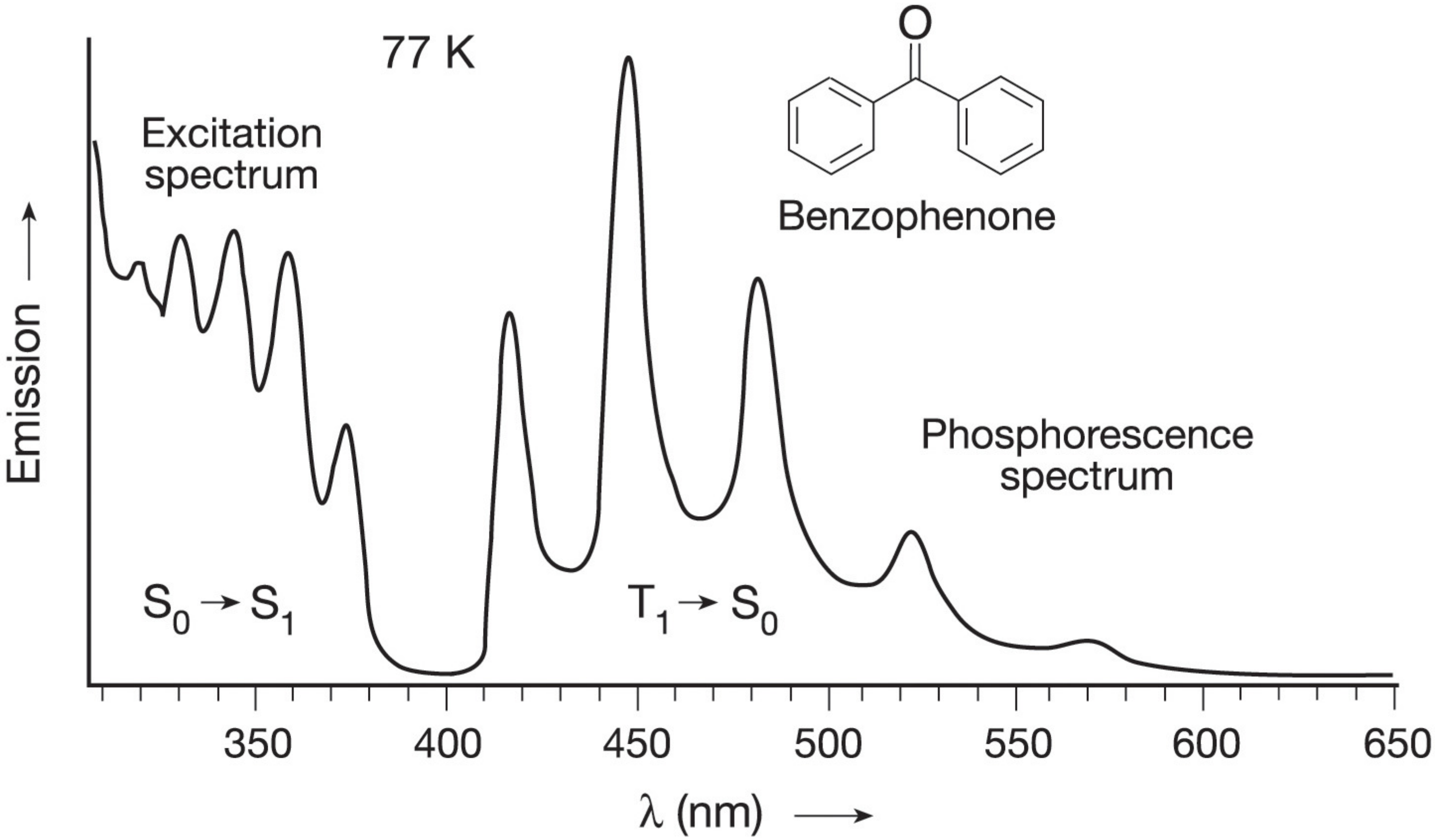
5. Molecular rigidity (due to environmental, steric or covalent constraints) prohibits vibrational motion and increases Φ_{fl}

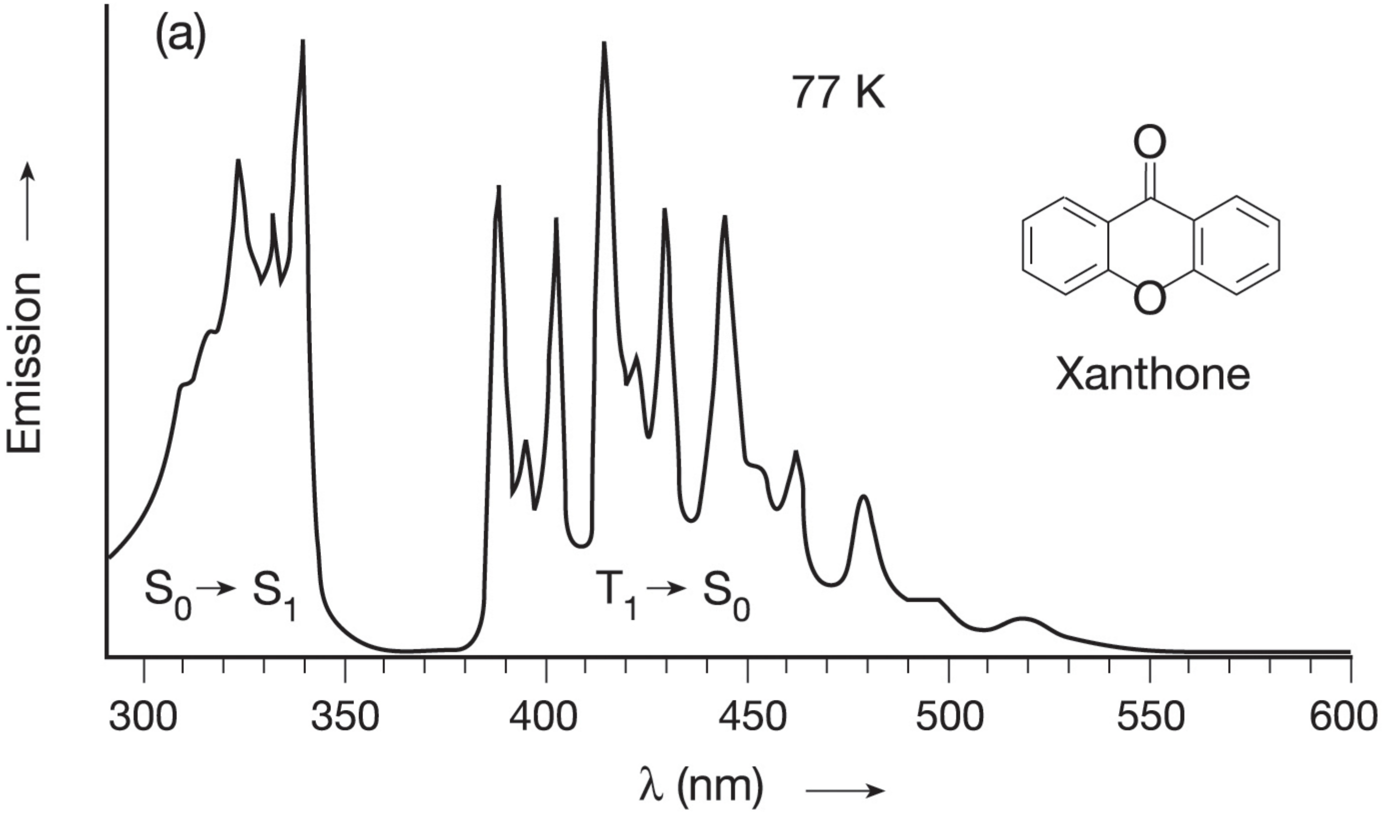
6. For rigid organic molecules, internal conversion does not compete effectively with fluorescence decay or intersystem crossing.

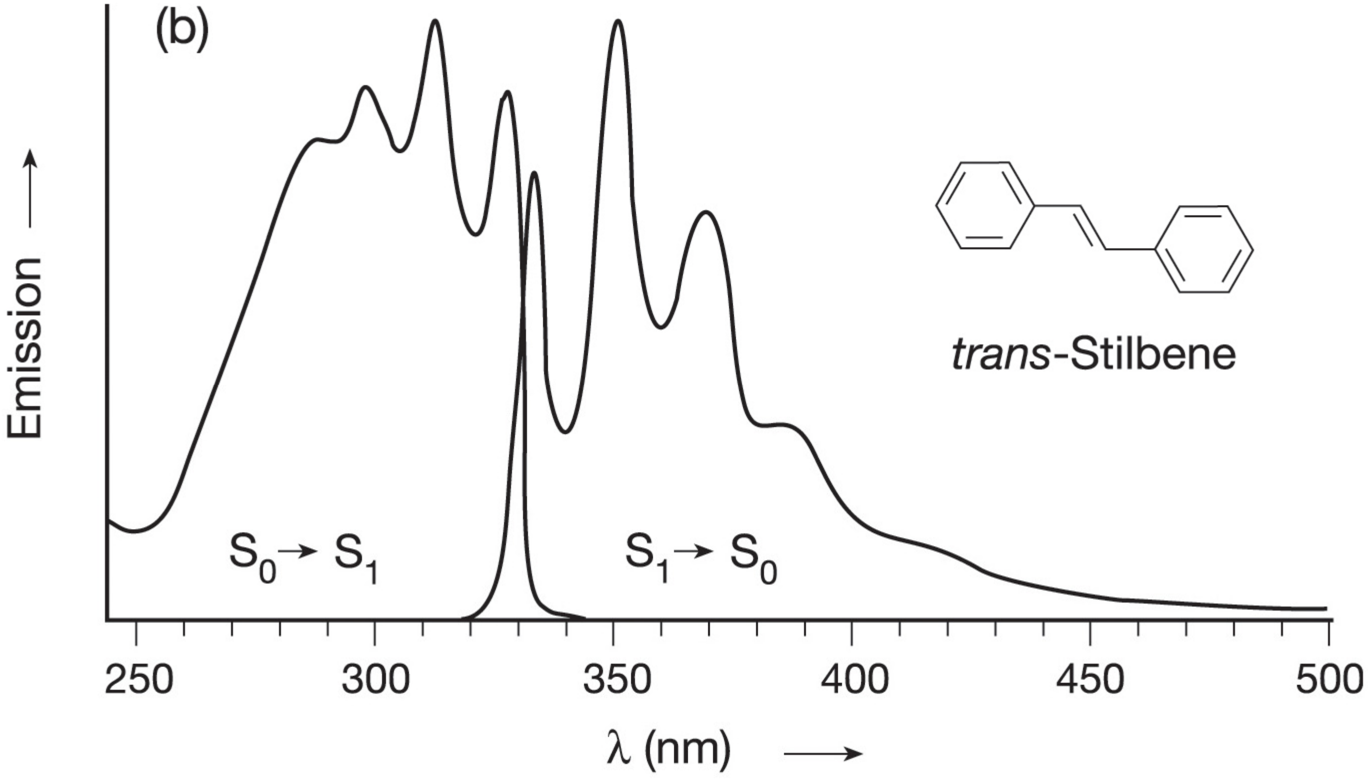
7. In some cases, e.g. benzene, naphthalene, pyrene, $S_0 \rightarrow S_1$ transitions have low ε_{max} due to weak μ_{ge} *(symmetry forbidden)* resulting in low relatively weak fluorescence.

8. In bromoperylene and pyrene-3-carboxaldehyde ΔE_{ST} is sufficiently large to inhibit *isc* hence there exception to the above trends.

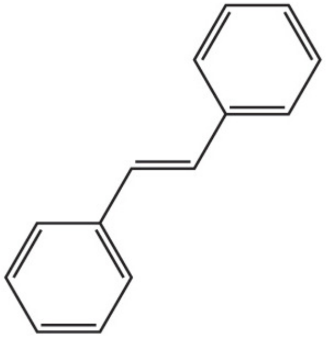
Compound	Transition	ε_{max} (M^{-1} cm^{-1})	$k_{fl}(s^{-1})$	$k_{nr}(s^{-1})$	Φ_{fl}
benzene	$S_1(\pi,\pi^*) \rightarrow S_0$	250	2×10^6	10^7	0.2
naphtalene	$S_1(\pi,\pi^*) \rightarrow S_0$	270	2×10^6	5×10^6	0.2
anthracene	$S_1(\pi,\pi^*) \rightarrow S_0$	8,500	5×10^7	5×10^7	0.4
9,10-diphenylanthracene	$S_1(\pi,\pi^*) \rightarrow S_0$	12,600	5×10^8	10^7	1.0
pyrene	$S_1(n,\pi^*) \rightarrow S_0$	510	10^6	10^5	0.7
triphenylene	$S_1(\pi,\pi^*) \rightarrow S_0$	355	2×10^6	10^7	0.1
perylene	$S_1(\pi,\pi^*) \rightarrow S_0$	39,500	10^8	10^7	1.0
stilbene	$S_1(\pi,\pi^*) \rightarrow S_0$	24,000	10^8	10^9	0.05
1-chloronaphtalene	$S_1(\pi,\pi^*) \rightarrow S_0$	300	10^6	5×10^8	0.05
1-bromonaphtalene	$S_1(\pi,\pi^*) \rightarrow S_0$	300	10^6	10^9	0.002
1-iodonaphtalene	$S_1(\pi,\pi^*) \rightarrow S_0$	300	10^6	10^{10}	0
benzophenone	$S_1(n,\pi^*) \rightarrow S_0$	200	10^6	10^{11}	0
acetone	$S_1(n,\pi^*) \rightarrow S_0$	20	10^5	10^9	0.001
perfluoroacetone	$S_1(n,\pi^*) \rightarrow S_0$	20	10^5	10^7	0.1
3-bromoperylene	$S_1(\pi,\pi^*) \rightarrow S_0$	40,000	10^8	10^6	1.0
pyrene-3-carboxaldehyde	$S_1(\pi,\pi^*) \rightarrow S_0$	70,000	10^8	10^8	0.25


77 K
Excitation spectrum
Benzophenone
Phosphorescence spectrum
$S_0 \rightarrow S_1$
$T_1 \rightarrow S_0$
Emission →
350
400
450
500
550
600
650
λ (nm) →
O

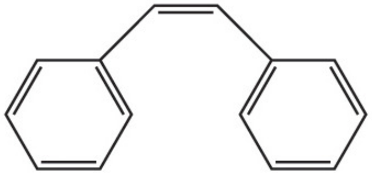

(a)
77 K
Xanthone
Emission
$S_0 \rightarrow S_1$
$T_1 \rightarrow S_0$
300
350
400
450
500
550
600
λ (nm)


(b)
Emission
$S_0 \rightarrow S_1$
$S_1 \rightarrow S_0$
trans-Stilbene
250
300
350
400
450
500
λ (nm)

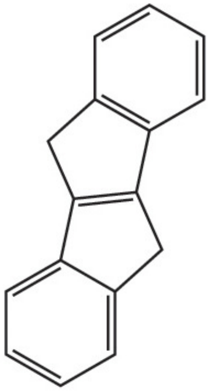
Molecular rigidity and Φ_{fl}



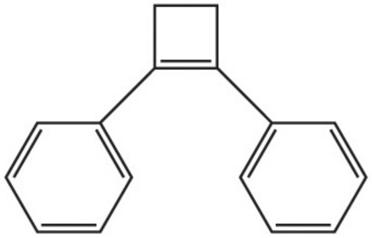
3
trans-Stilbene



4
cis-Stilbene



5

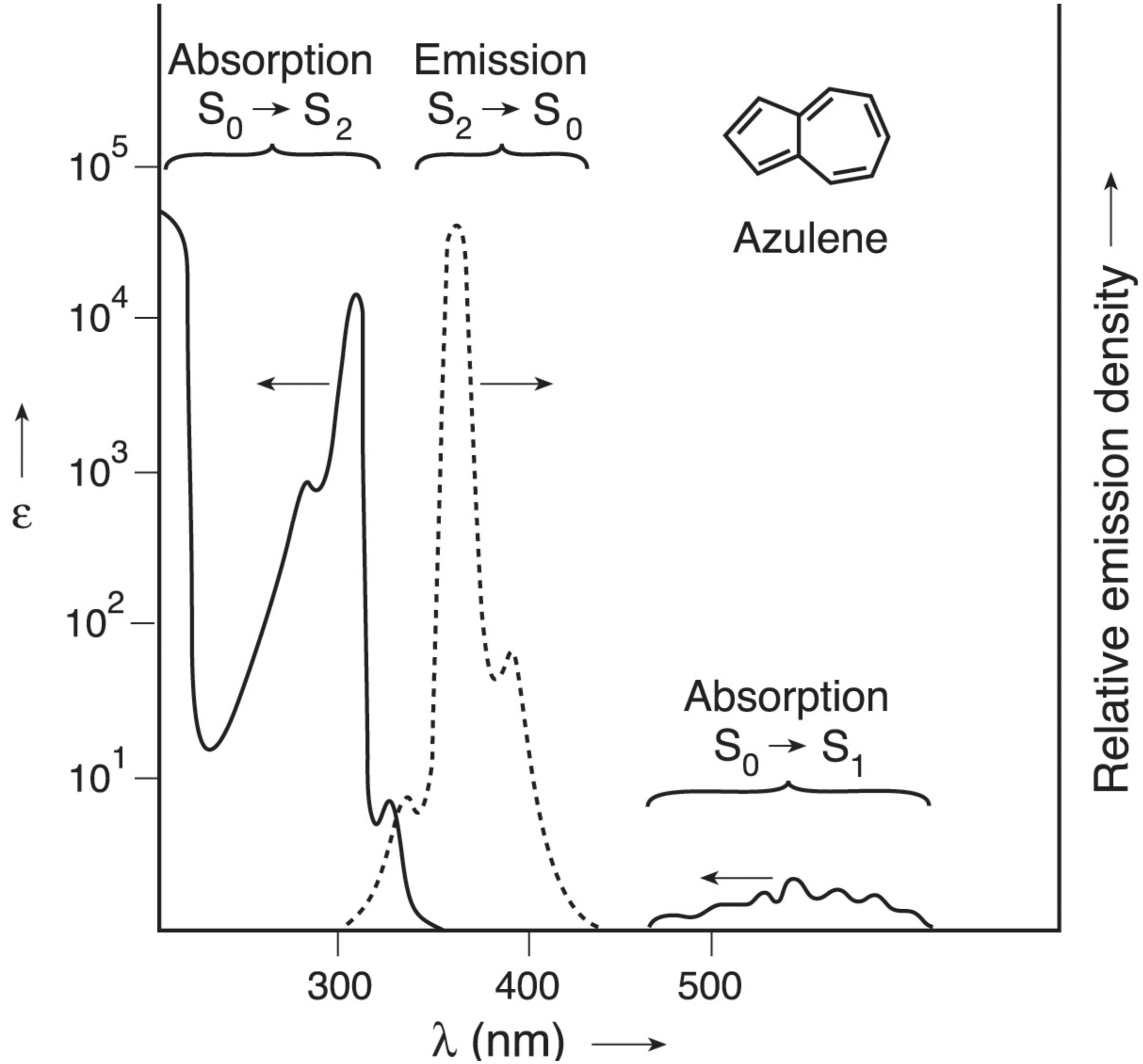


6

Compound	Φ_{fl} (298 K)	Φ_{fl} (77 K)
3	0.05	0.75
4	0	0.75
5	1.0	1.0
6	1.0	1.0

$S_2 \rightarrow S_0$ emission in azulene

- The large $S_2 \rightarrow S_1$ energy gap precludes internal conversion by minimizing the FC factor for radiationless transitions.
- The opposite is true for the $S_1 \rightarrow S_0$ transition whose energy gap is so small rapid internal conversion takes place



Spin-orbital coupling and Φ_{fl}

- Substitution with heavy elements results in enhanced spin-orbit coupling and reduced Φ_{fl} in the order $\Phi_{fl}^{H} > \Phi_{fl}^{F} > \Phi_{fl}^{Cl} > \Phi_{fl}^{Br} > \Phi_{fl}^{I}$
- There is a rapid increase in magnitude of the spin-orbit coupling parameter ζ_{SO} as atomic number increases.
- The spin-orbit coupling parameter ζ_{SO} is smaller than the energy of vibrational coupling χ_v for first and second row elements so is only considered for third row and beyond.
- For very heavy atoms, e.g .Pb and Xe, ζ_{SO} is greater than χ_v and approaches energies of electronic band gaps.

atom	Atomic number	ζ_{SO} (kcal mol^{-1})	atom	Atomic number	ζ_{SO} (kcal mol^{-1})
C	6	0.1	Cl	17	1.7
N	7	0.2	Br	35	7.0
O	8	0.4	I	53	14.0
F	9	0.7	Xe	54	28
Si	14	0.4	Cs	55	2.4
P	15	0.7	Pb	82	21
S	16	1.0	Hg	80	18

An MO model for spin-orbital coupling (El Sayed's rule)

- For spin-forbidden electronic transitions oscillator strengths fall in the range of $10^{-5} > f > 10^{-9}$ in contrast to spin-allowed transitions where $1 > f > 10^{-3}$
- *ISC* is generally of a low probability unless heavy atoms are preset to enhance ζ_{SO} or if ΔE_{ST} is small enough to allow mixing of states.
- It is generally found for spin-forbidden transitions that

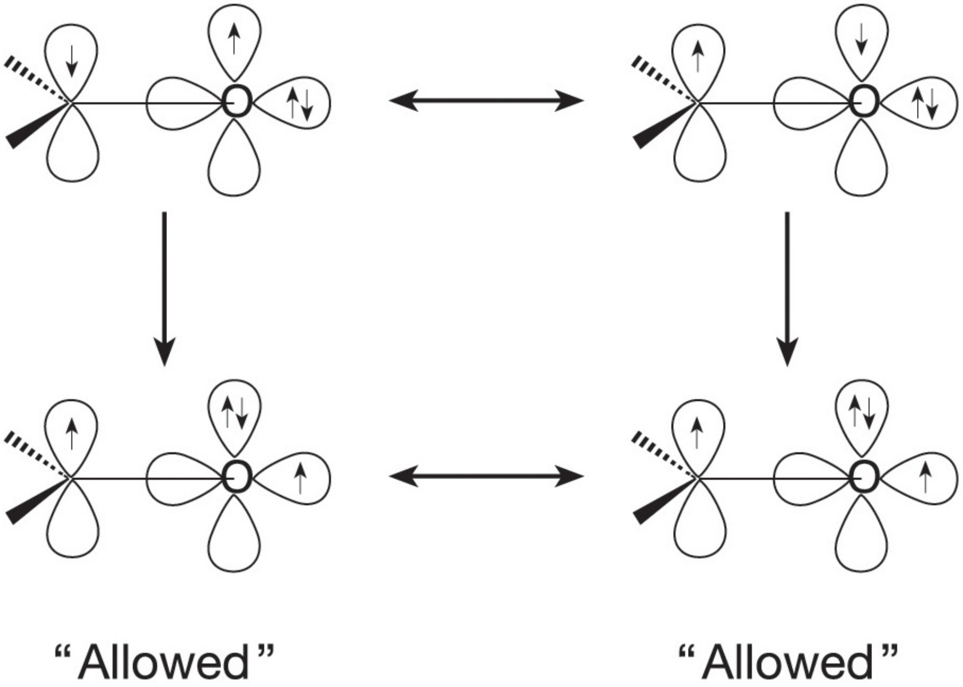
$$f\,[S_0 \leftrightarrow T(n,\pi*)] >> f\,[S_0 \leftrightarrow T(\pi,\pi*)]$$

which is opposite of the trend observed for spin-allowed transitions.

- Recall that f is composed of f_e, f_v and f_{SO}
- In general, for spin-allowed transitions $\varepsilon\,(\pi,\pi*) >> \varepsilon\,(n,\pi*)$

  such that $f_e f_v\,(\pi,\pi*) >> f_e f_v\,(n,\pi*)$
- Implying for spin-forbidden transitions $f_{SO}\,(n,\pi*) >> f_{SO}\,(\pi,\pi*)$
- To explain this phenomenon we will consider the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ electronic transitions for formaldehyde and ethylene, respectively.

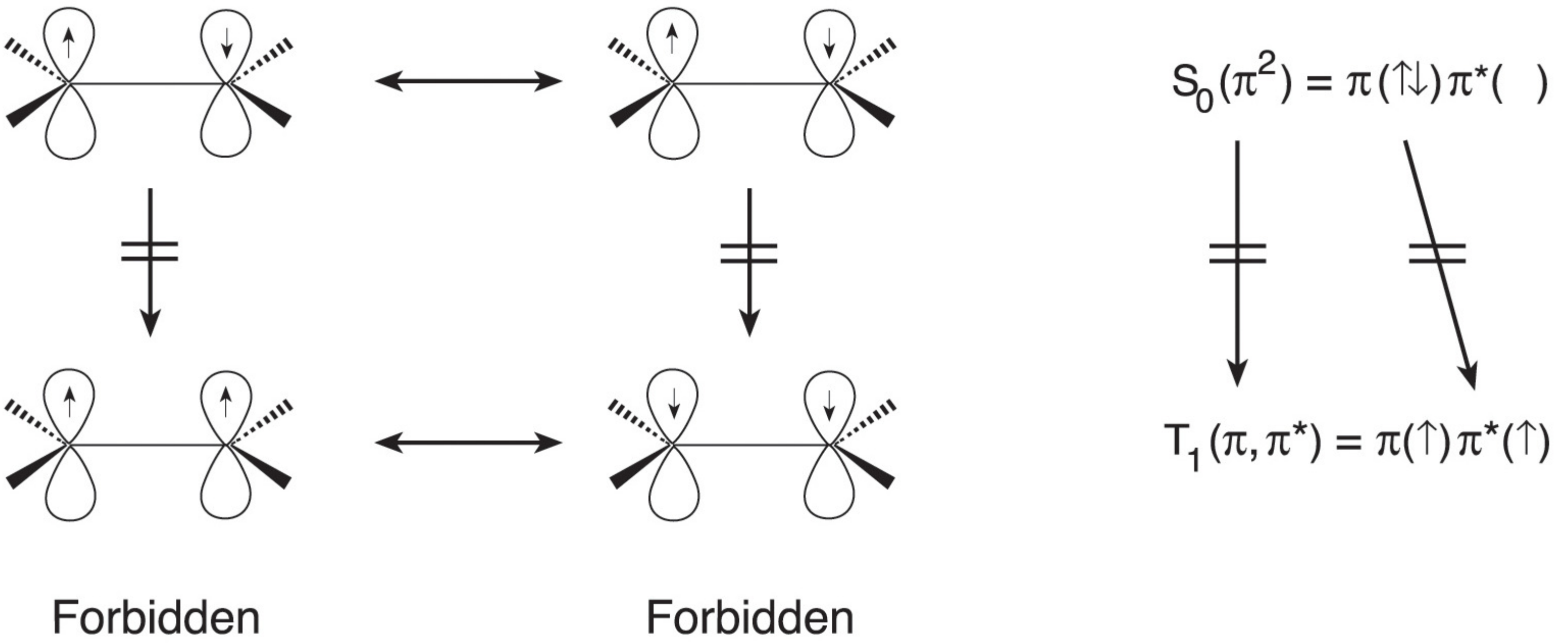
Overall $S_0(n^2) \longrightarrow T_1(n,\pi^*)$



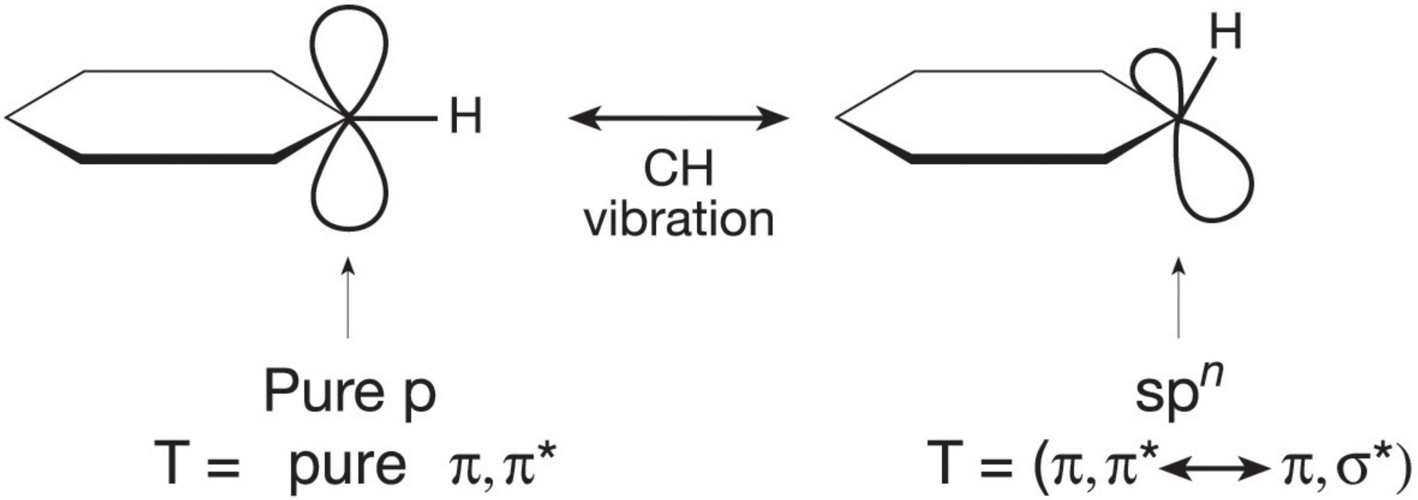
$$\begin{tikzcd}
S_0(n^2) = \pi(\uparrow\downarrow)n(\uparrow\downarrow)\pi^*(\;\;) \arrow[d, shift right=6, "\text{Spin flip}"] \arrow[d, shift left=6, "\text{Spin–orbit coupling favored}"] \\
T_1(n,\pi^*) = \pi(\uparrow\downarrow)n(\uparrow)\pi^*(\uparrow)
\end{tikzcd}$$

- The $n \rightarrow \pi^*$ transition of formaldehyde can be understood as an electron transition from a non-bonding O *p*-orbital to a perpendicular C π-orbital; or more simply a $p_x \rightarrow p_y$ transition which has an associated change in orbital angular momentum.
- The change in orbital angular momentum of the $p_x \rightarrow p_y$ transition couples with the spin angular momentum associated with the $\alpha\beta \rightarrow \alpha\alpha$ (or $\alpha\beta \rightarrow \beta\beta$) spin flip.

Overall $S_0(\pi^2) \longrightarrow T_1(\pi,\pi^*)$



- The only orthogonal orbitals relative to the $\pi \rightarrow \pi^*$ transition of ethylene are σ, σ^* in nature and are too far removed in energy to couple with the electrons in the S_1 ($\pi \rightarrow \pi^*$) excited state of ethylene.



- Out-of-plane C-H vibrations can increase the orbital overlap integral of σ and π orbitals allowing the typically high energy $\pi \rightarrow \sigma^*$ transition to mix with the lower energy $\pi \rightarrow \pi^*$ transition.
- This out of plane distortion increases spatial overlap and introduces spin-orbital coupling into the pure $\pi \rightarrow \pi^*$ transition increasing intersystem crossing.

Phosphorescence radiative lifetime & rate-constant

$$ {}^{3}\tau_{0} = \frac{1}{k_{\mathrm{ph}}} \qquad k_{\mathrm{ph}} = \frac{1}{{}^{3}\tau_{0}} $$

$$ {}^{3}\tau = \frac{1}{k_{\mathrm{fl}} + k_{\mathrm{ic}} + k_{\mathrm{isc}}} = \frac{1}{k_{\mathrm{total}}} $$

$$ {}^{3}\tau = \frac{1}{k_{\mathrm{ph}} + k_{\mathrm{isc}}^{\mathrm{TS}}} $$

$$ \Phi_{\mathrm{ph}} = \frac{\Phi_{\mathrm{isc}}\, k_{\mathrm{ph}}^{0}}{k_{\mathrm{ph}}^{0} + k_{\mathrm{isc}}} $$

τ_{0} = singlet radiative lifetime in absence of non-radiative processes (s)

${}^{1}\tau$ = singlet radiative lifetime (s)

k_{fl} = fluorescence rate constant (s^{-1})

k_{ic} = internal conversion rate constant (s^{-1})

k_{isc} = intersystem crossing rate constant (s^{-1})

k_{nr} = non-radiative rate constant ($k_{\mathrm{ic}} + k_{\mathrm{isc}}$; s^{-1})

Φ_{fl} = fluorescence quantum yield