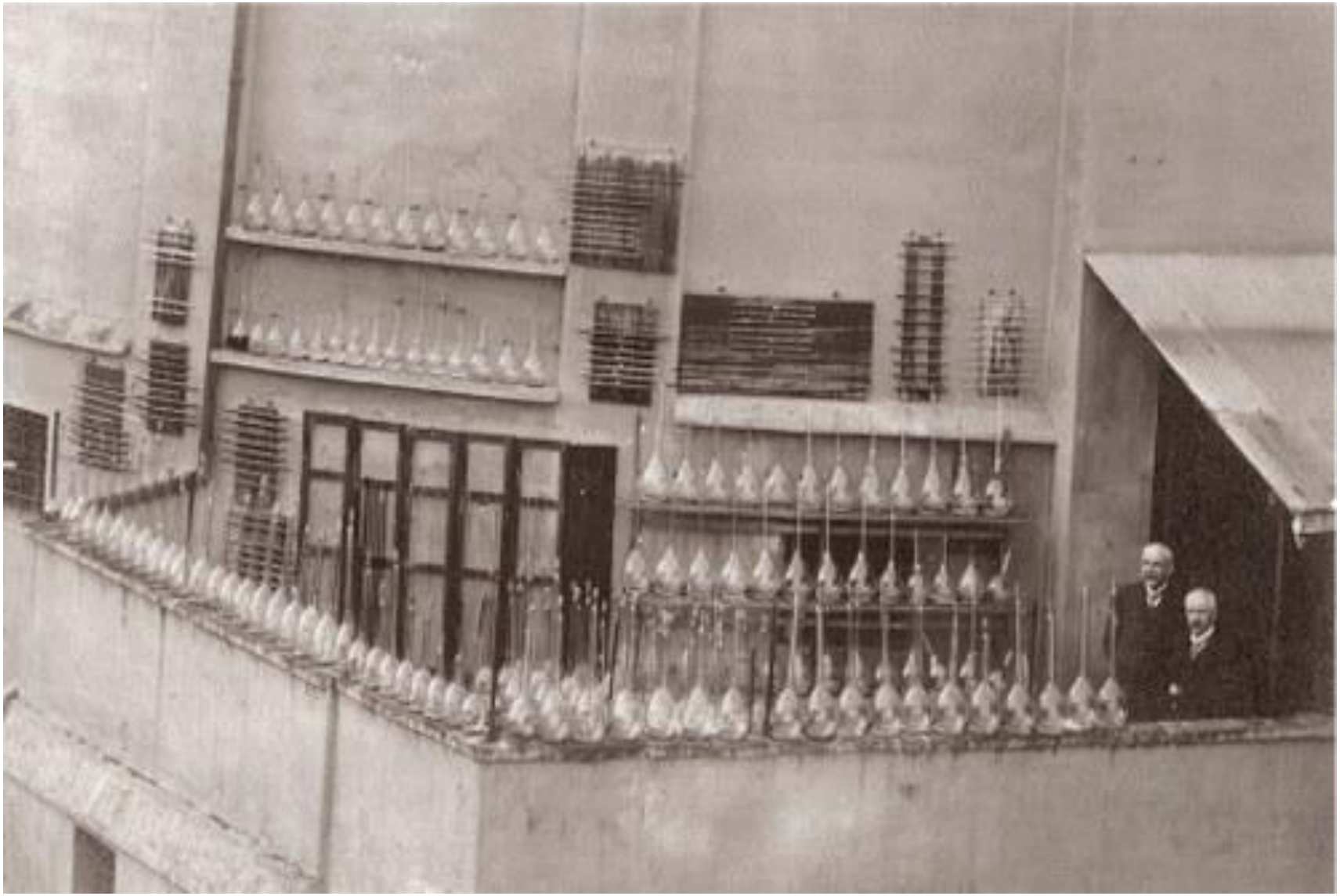
Photochemistry

Giacomo Luigi Ciamician

Trieste 1857 – Bologna 1922

Chissà che in avvenire non sia possibile mandare in effetto delle reazioni fotochimiche, come sarebbe la seguente: gli ultimi prodotti della combustione, i rifiuti che le fabbriche mandano nell'aria, sono l'anidride carbonica e il vapore acqueo. **Dato un opportuno catalizzatore** si dovrebbe potere, con la partecipazione dell'energia solare, trasformarli in metano ed ossigeno i quali, bruciando, ridarebbero, naturalmente, in forma di calore tutta l'energia acquistata dal sole. Quando un tale sogno fosse realizzato le industrie sarebbero ricondotte ad un ciclo perfetto, a macchine che produrrebbero lavoro colla forza della luce del giorno, che non costa nulla e non paga tasse!
(Giacomo Luigi Ciamician)

Impariamo a imitare la natura e a fare come le piante, piuttosto che fare concorrenza alle piante con l'industria chimica fondata sul "catrame".



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MSS. intended for publication and books, etc., intended for review should be sent to the Editor of SCIENCE, Garrison-on-Hudson, N. Y.

THE PHOTOCHEMISTRY OF THE FUTURE[1]

MODERN civilization is the daughter of coal, for this offers to mankind the solar energy in its most concentrated form; that is, in a form in which it has been accumulated in a long series of centuries. Modern man uses it with increasing eagerness and thoughtless prodigality for the conquest of the world and, like the mythical gold of the Rhine, coal is to-day the greatest source of energy and wealth.

The earth still holds enormous quantities of it, but coal is not inexhaustible. The problem of the future begins to interest us, and a proof of this may be seen in the fact that the subject was treated last year almost at the same time by Sir William Ramsay before the British Association for the Advancement of Science at Portsmouth and by Professor Carl Engler before the Versammlung deutscher Naturforscher und Aerzte at Karlsruhe. According to the calculations of Professor Engler Europe possesses to-day about 700 billion tons of coal and America about as much; to this must be added the coal of the unknown parts of Asia. The supply is enormous but, with increasing consumption, the mining of coal becomes more expensive on account of the greater depth to which it is necessary to go. It must therefore be remembered that in some regions the deposits of coal may become practically useless long before their exhaustion.

Is *fossil* solar energy the only one that may be used in modern life and civilization? That is the question.

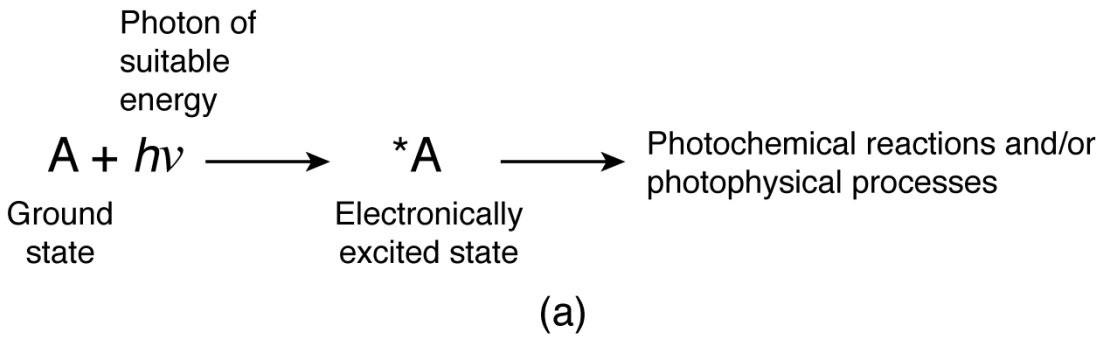
[1] General lecture before the International Congress of Applied Chemistry, New York, September 11, 1912.

THE PHOTOCHEMISTRY OF THE FUTURE (1912)
GIACOMO CIAMICIAN (1857-1922)
(Translation supplied by the author)

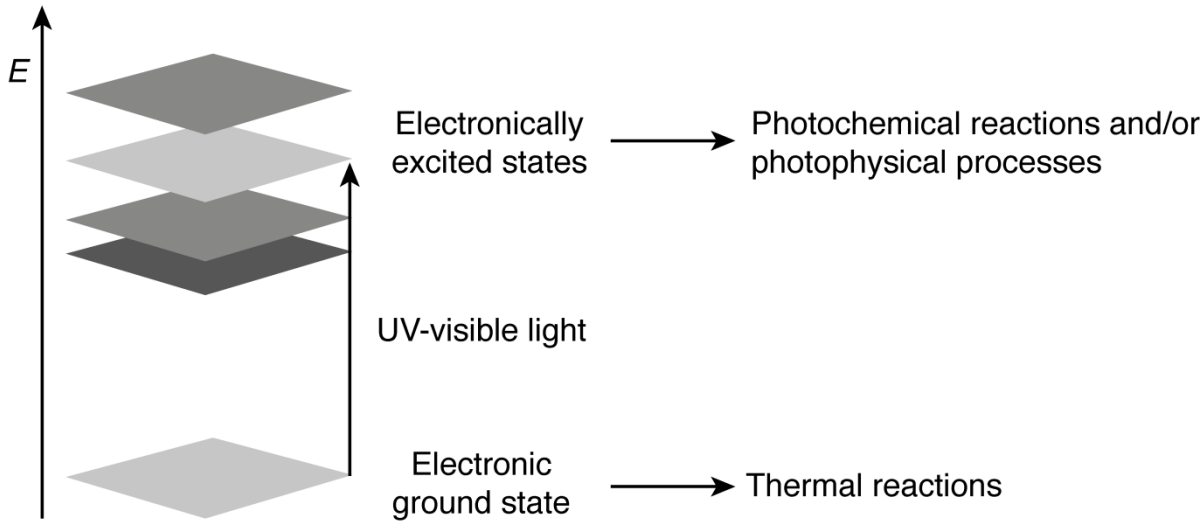
Modern civilization is the daughter of coal for this offers to mankind the solar energy in its most concentrated form: that is in a form in which it has been accumulated in a long series of centuries.

And if in a distant future the supply of coal becomes completely exhausted, civilization will not be checked by that, for life and civilization will continue as long as the sun shines! If our black and nervous civilization, based on coal, shall be followed by a quieter civilization based on the utilization of solar energy, that will not be harmful to progress and to human happiness.
The photochemistry of the future should not however be postponed to such distant times; I believe that industry will do well in using from this every day all the energies that nature puts at its disposal. So far, human civilization has made use almost exclusively of fossil solar energy. Would it not be advantageous to make better use of radiant energy?

Photochemistry and photophysics

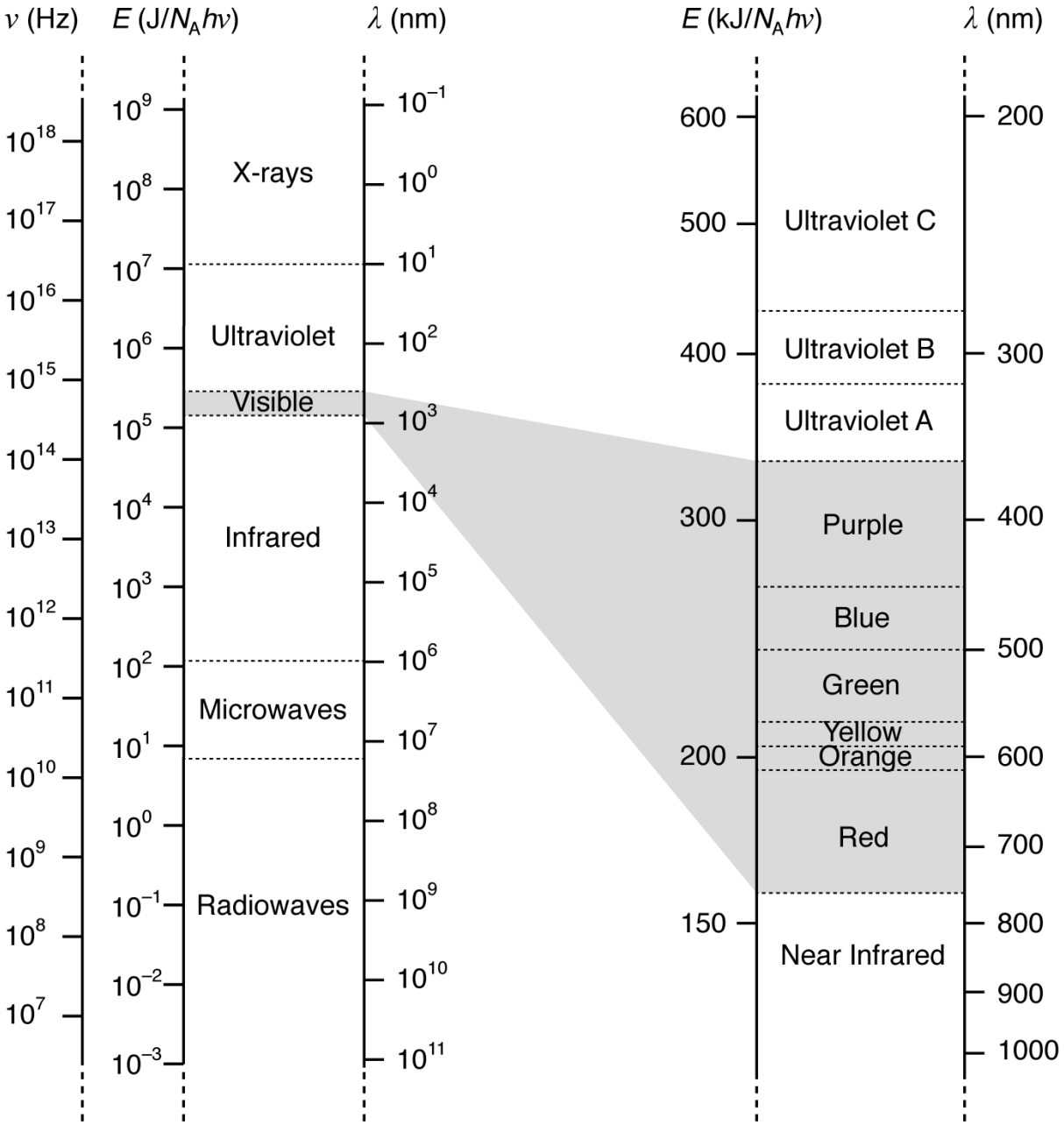


(a)



(b)

Electromagnetic spectrum



Which is the involved energy

The simplest and most common paradigm:

One molecule absorbs one photon.

The energy of one PHOTON at 200 nm = $9.95 \cdot 10^{-19}$ J

The energy of one PHOTON at 1000 nm = $1.99 \cdot 10^{-19}$ J

One mole of photons = one EINSTEIN

The energy of one EINSTEIN at 200 nm = 599 kJ (143 kcal)

The energy of one EINSTEIN at 1000 nm = 119.8 kJ (28.6 kcal)

Green photons of 550 nm carry energy equivalent of to a thermal temperature of approximately 26.000 K.

Quantitative aspects

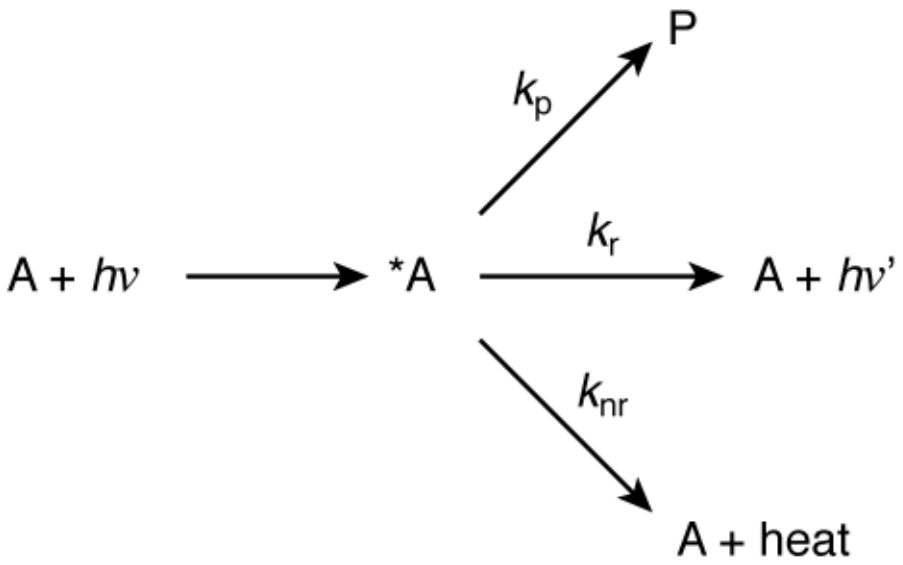
The Grotthus-Draper law:

Only the light absorbed is effective in producing photochemical change.

The Lambert – Beer law $\mathrm{A} = \log\left(I_0 / I\right) = \varepsilon b c$

Quantitative aspects

Primary processes



Photoreaction
(chemical reaction)

Luminescence
(radiative deactivation)

Degradation to heat
(non radiative deactivation)

Lifetime of the excited state:

$$\tau(^*\mathrm{A}) = \frac{1}{k_p + k_r + k_{nr}} = \frac{1}{\sum_j k_j}$$

Efficiency of each process:

$$\eta_i(^*\mathrm{A}) = \frac{k_i}{\sum_j k_j} = k_i \tau(^*\mathrm{A})$$

Quantitative aspects

Quantum Yield of a primary process:

$$\Phi_i = \frac{\text{Number of molecules undergoing that process}}{\text{Number of photons absorbed by the reactant}}$$

Under conditions for a stationary state:

$$\frac{\mathrm{d}[^*\mathrm{A}]}{\mathrm{d}t} = I_\mathrm{m} - k_\mathrm{p}[^*\mathrm{A}] - k_\mathrm{r}[^*\mathrm{A}] - k_\mathrm{nr}[^*\mathrm{A}] = 0$$

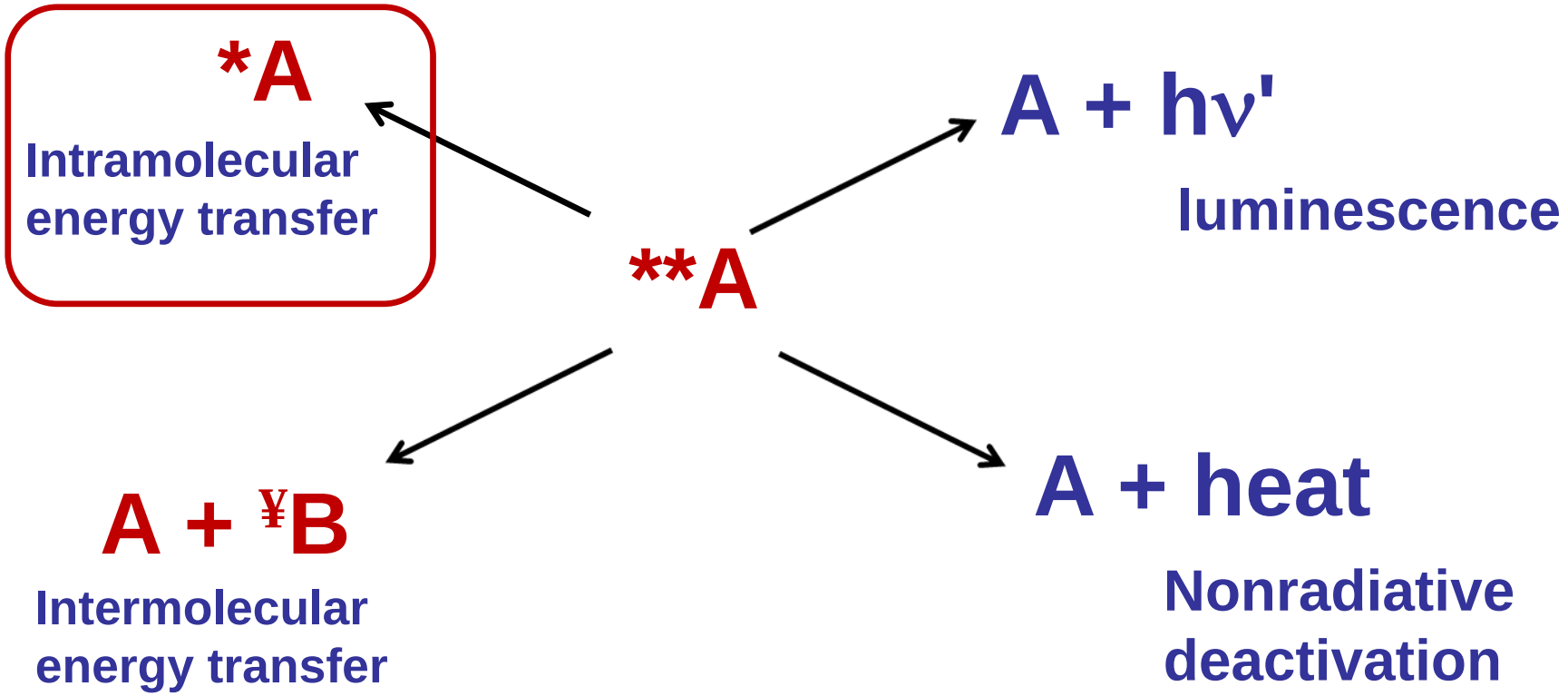
Quantum Yield of process p:

$$\Phi_\mathrm{p} = \frac{k_\mathrm{p}[^*\mathrm{A}]}{I_\mathrm{m}} = \frac{k_\mathrm{p}}{k_\mathrm{p} + k_\mathrm{r} + k_\mathrm{nr}}$$

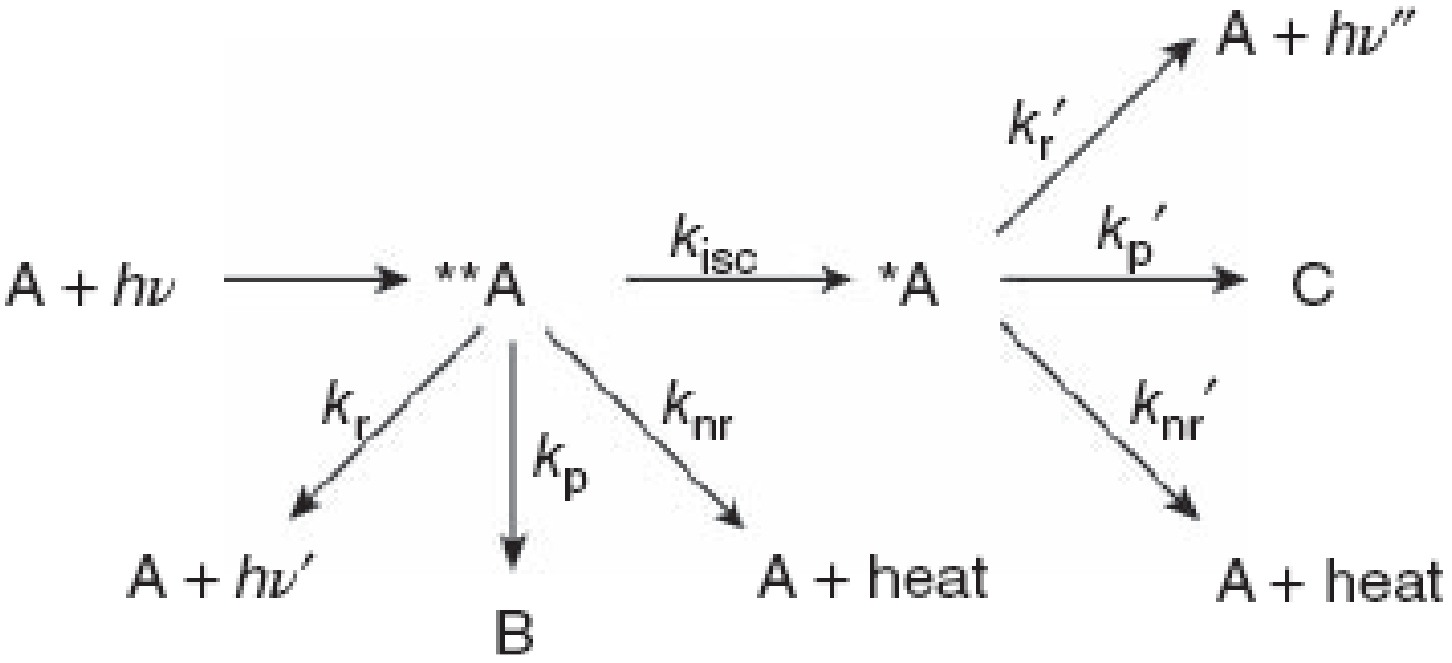
Quantum Yield of process i:

$$\Phi_i = \frac{k_i}{\sum_j k_j} \longrightarrow \Phi_i = k_i \tau(^*\mathrm{A}) = \eta_i(^*\mathrm{A})$$

Photophysical Processes

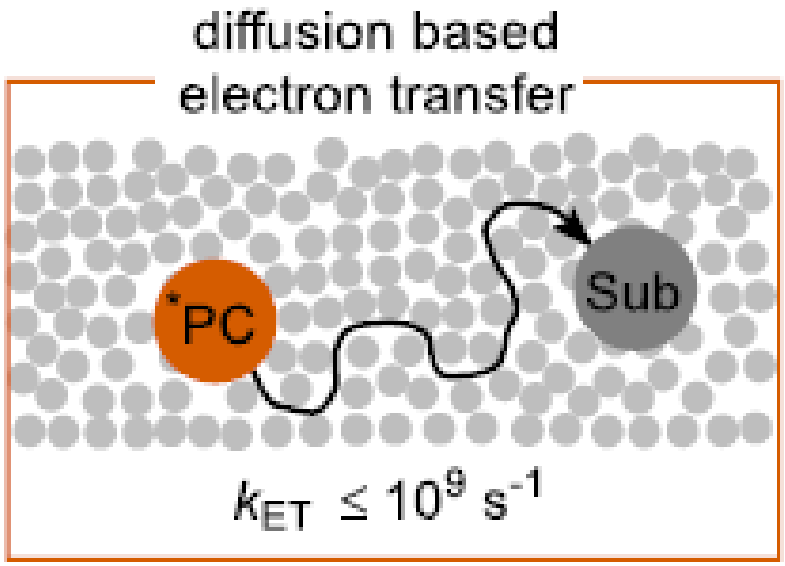


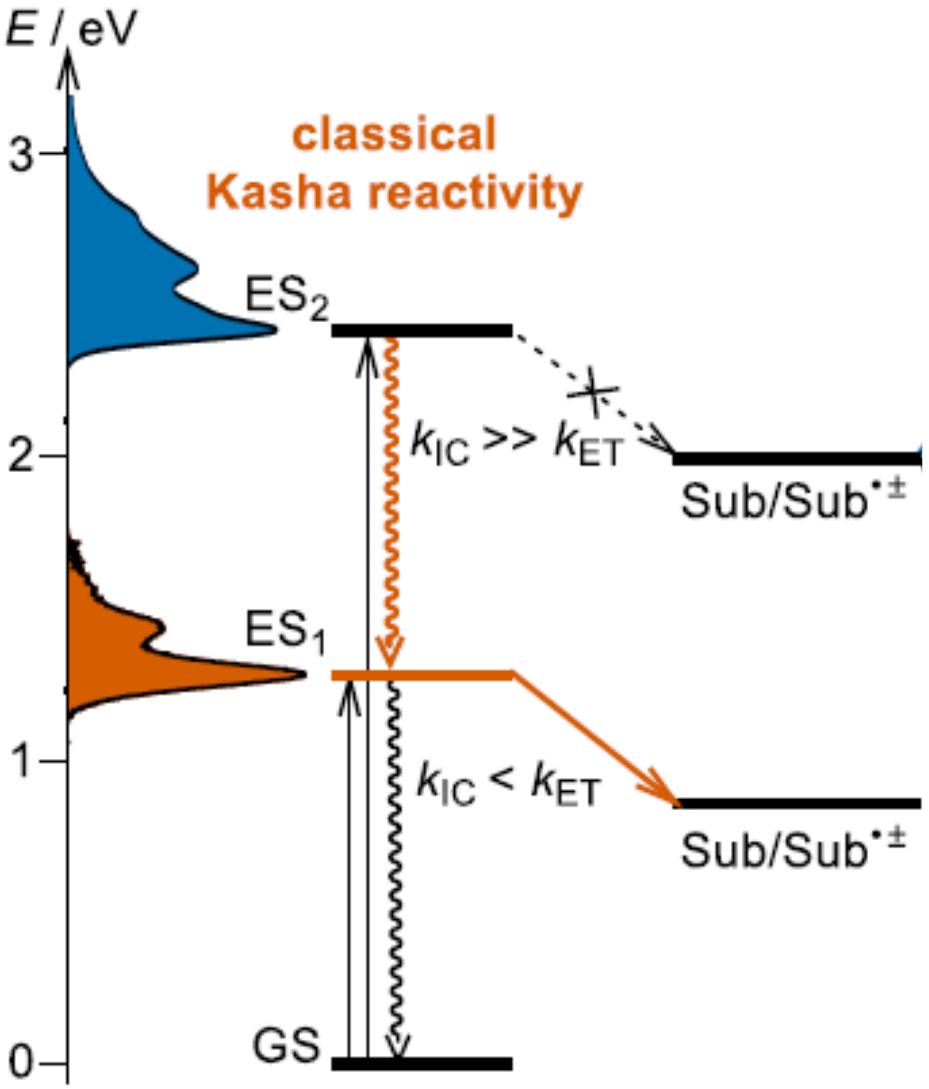
Schematic representation of photophysical and photochemical processes



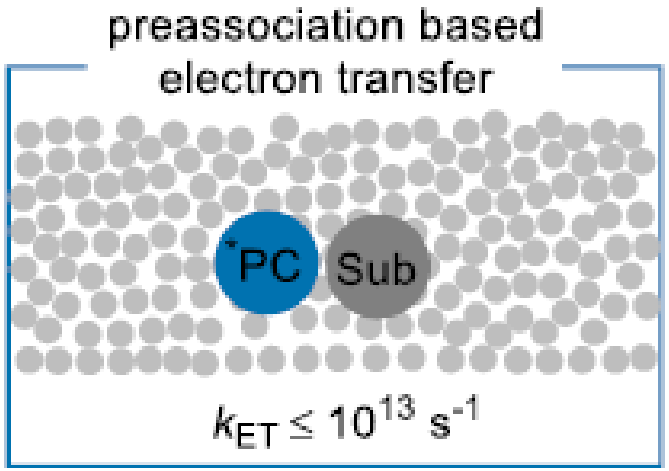
The Kasha's Rule

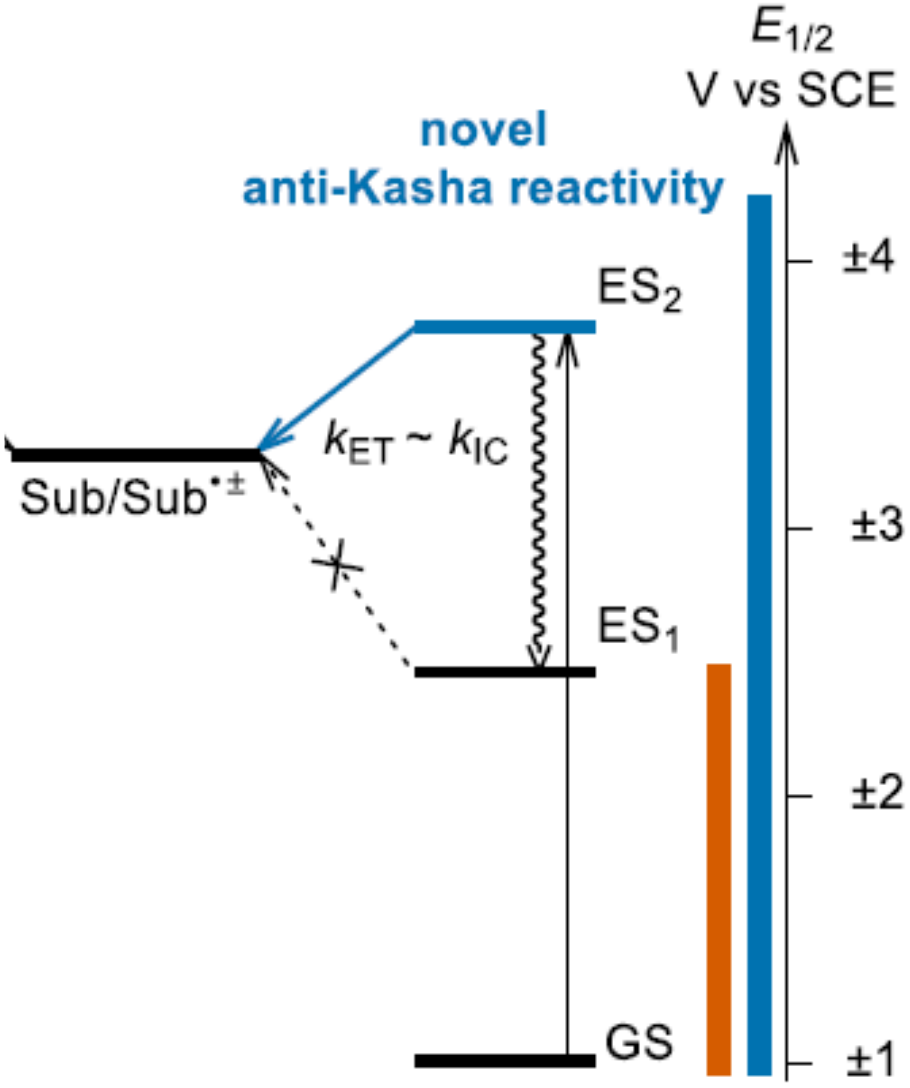
The light emission (and/or the photochemical reactions) usually occurs exclusively from the lowest electronically excited state of a given spin multiplicity.





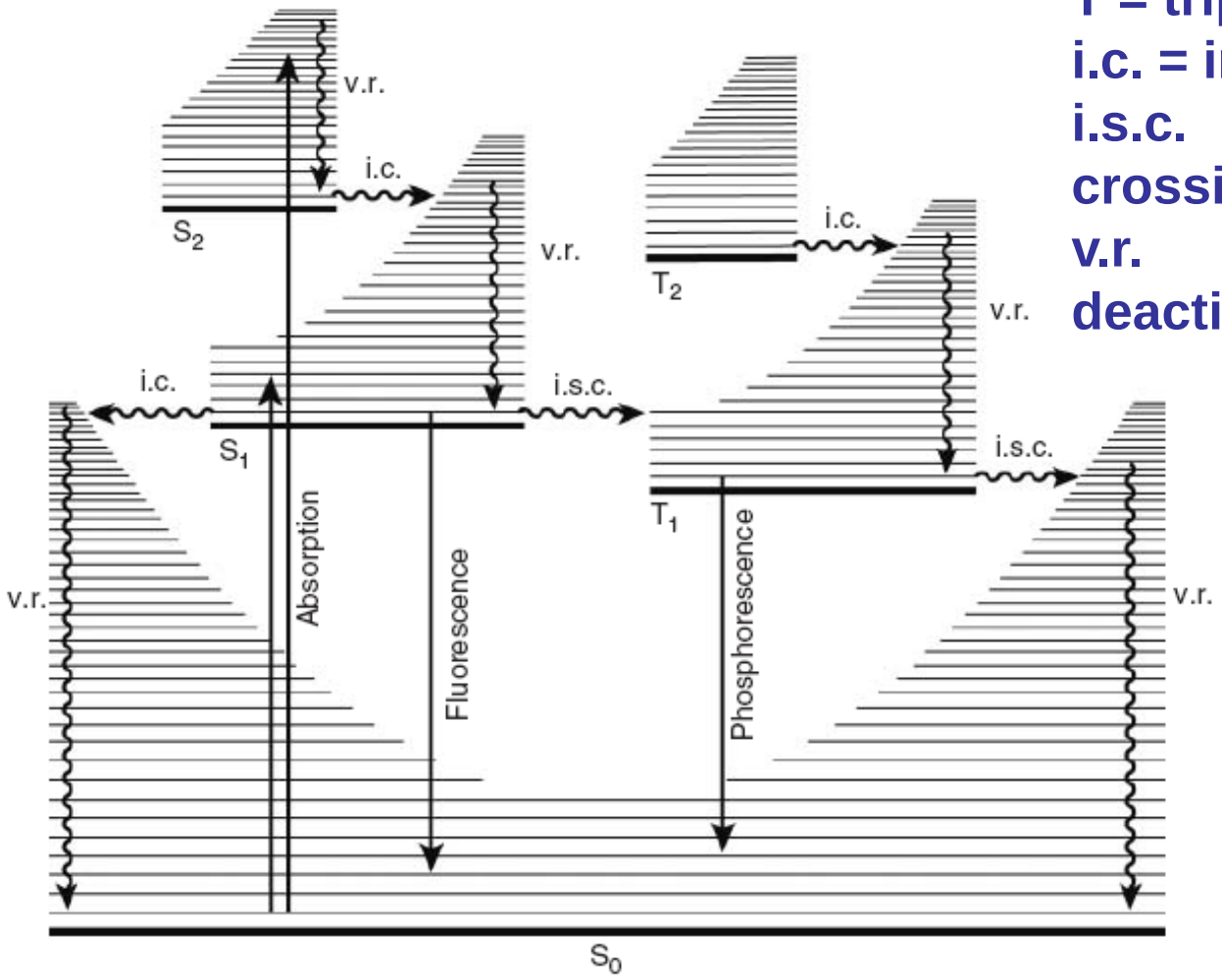
The anti-Kasha's Rule





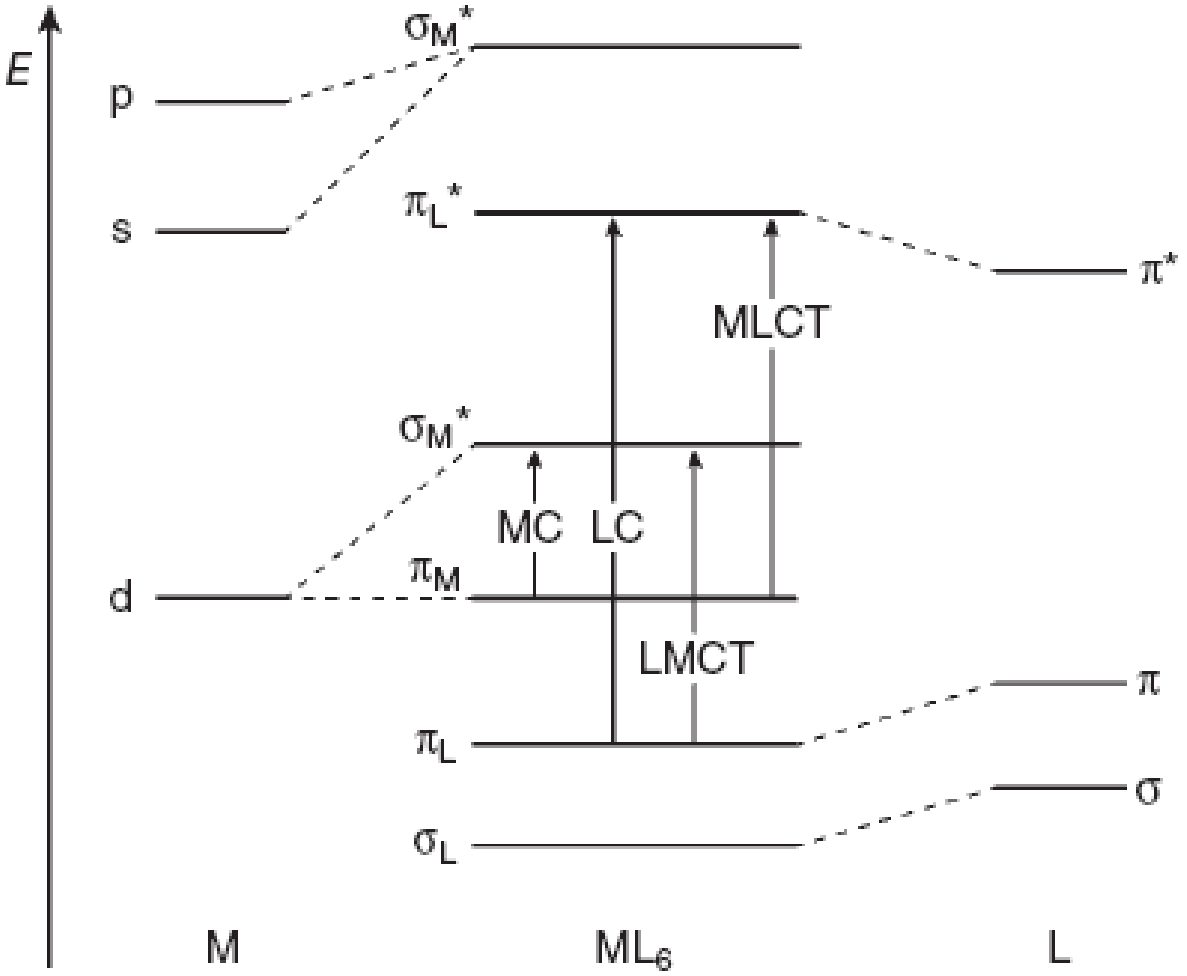
Pfund, B.; Wenger O. S., J. Am. Chem. Soc.. 2025, 147, 26477.

Jablonski diagram

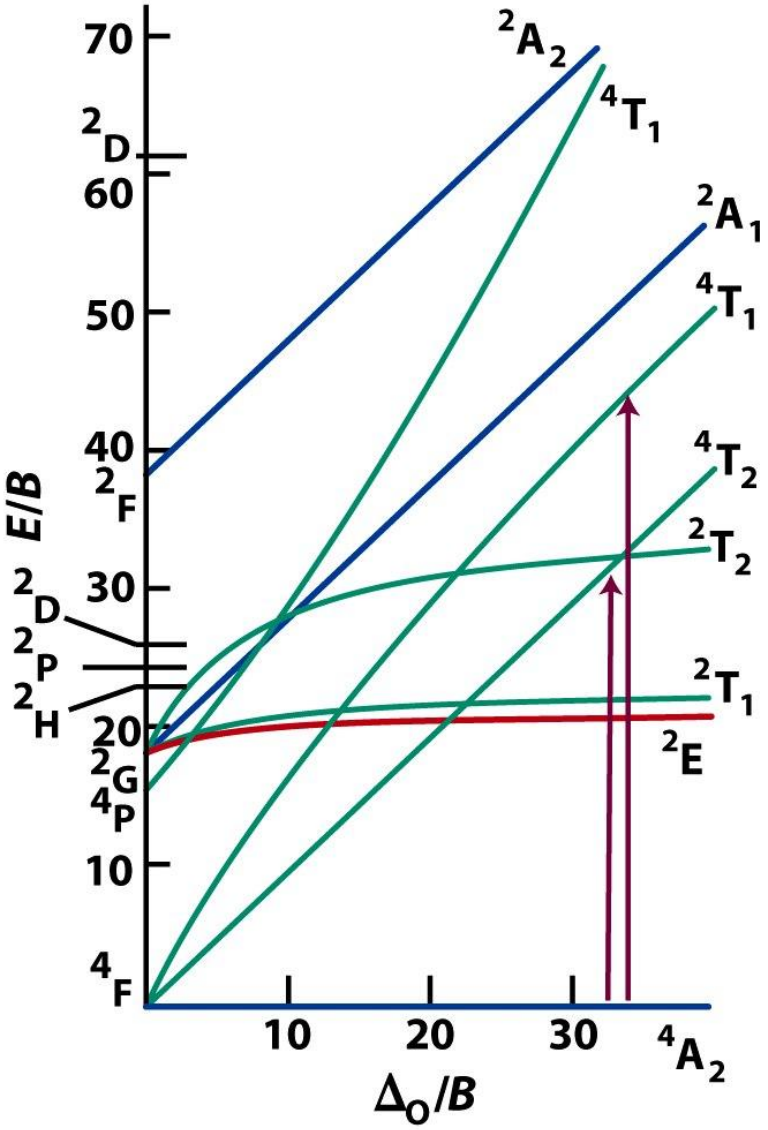


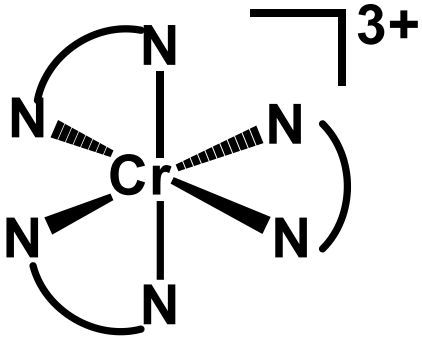
S = singlet state
T = triplet state
i.c. = internal conversion
i.s.c. = intersystem crossing
v.r. = vibrational deactivation

Possible electronic transitions for an octahedral complex ML_6



Tanabe-Sugano diagram for $[Cr(en)_3]^{3+}$





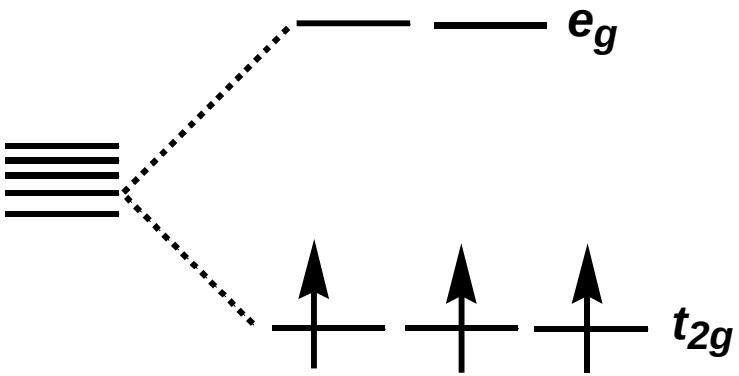
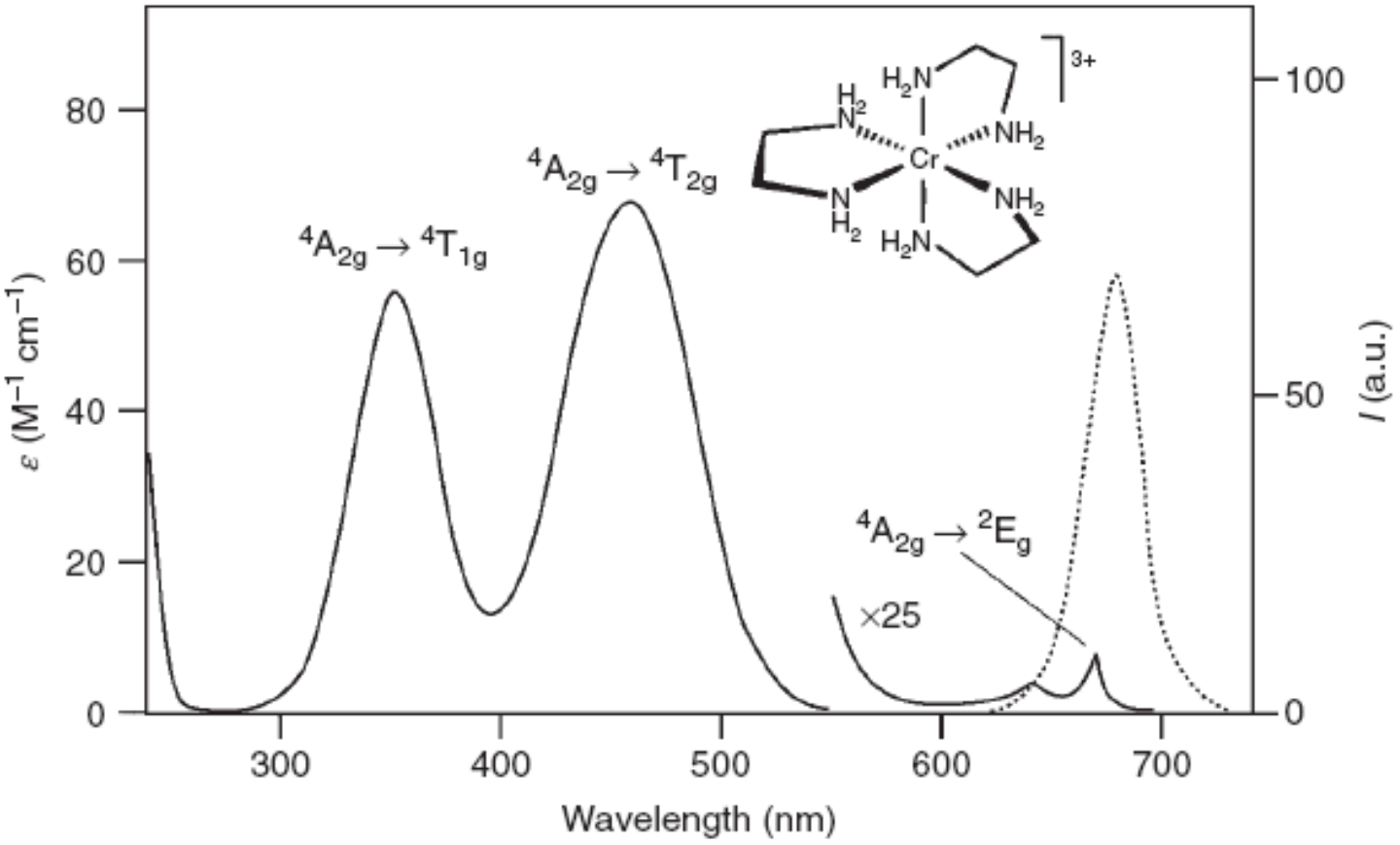


Figure 19-27
Shriver & Atkins Inorganic Chemistry, Fourth Edition

Absorption and emission spectra of $[Cr(en)_3]^{3+}$



Jablonski diagram of $[Cr(en)_3]^{3+}$

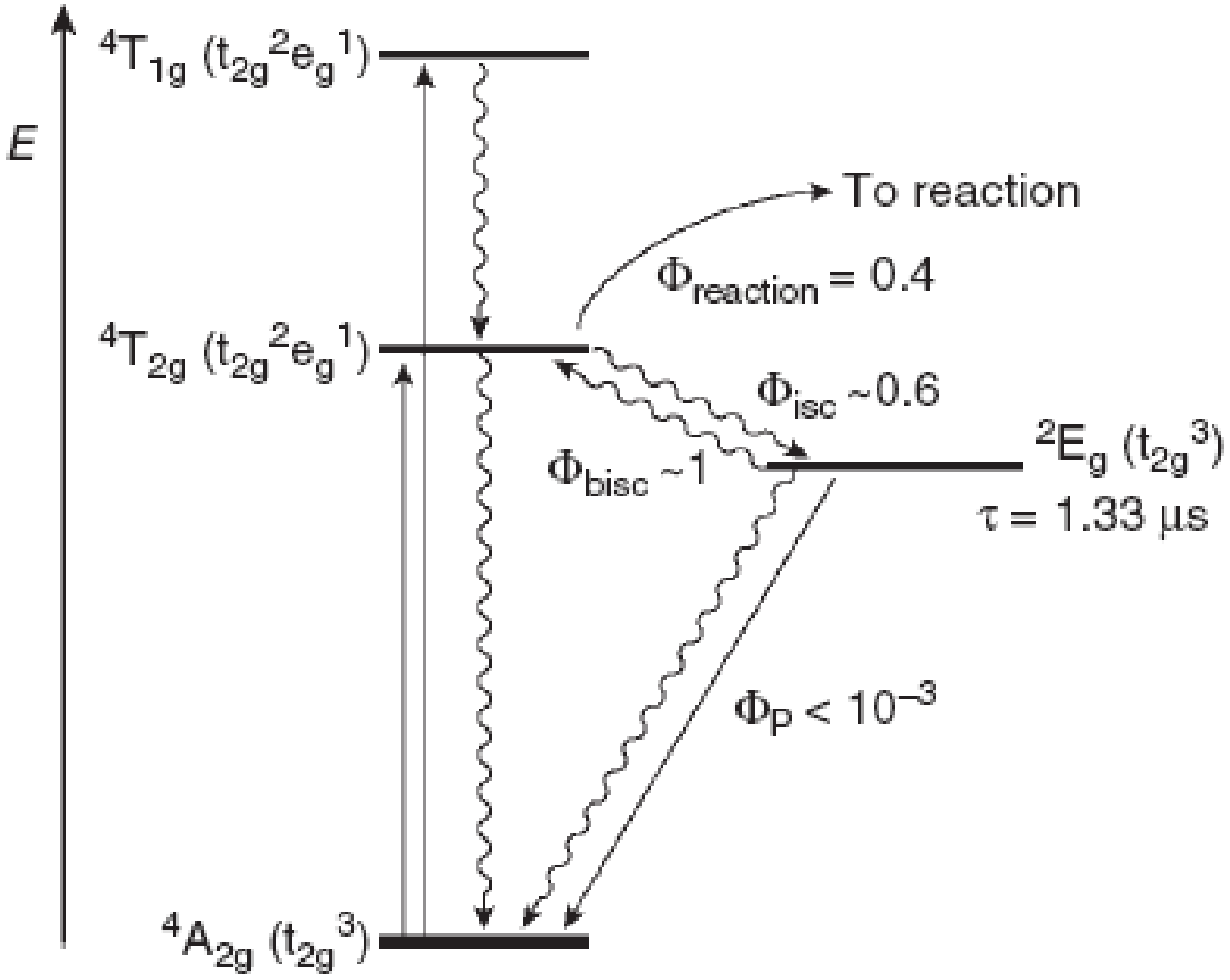
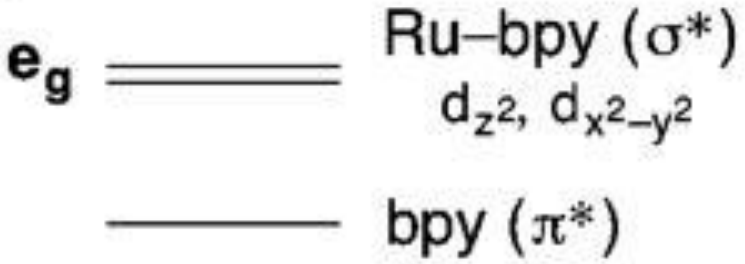
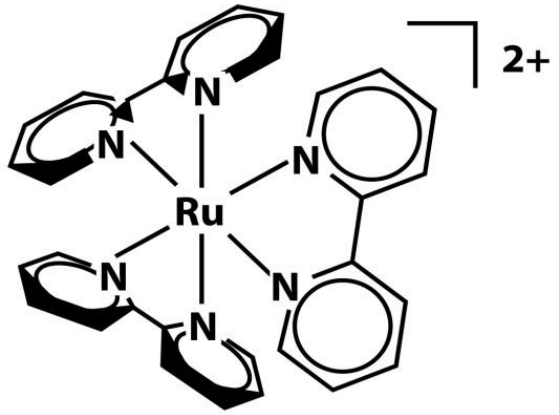
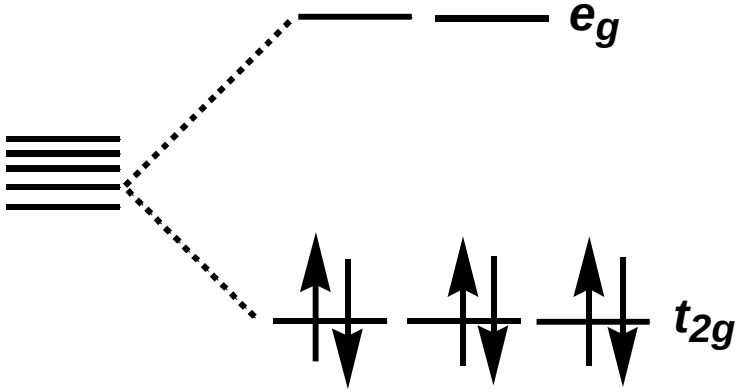
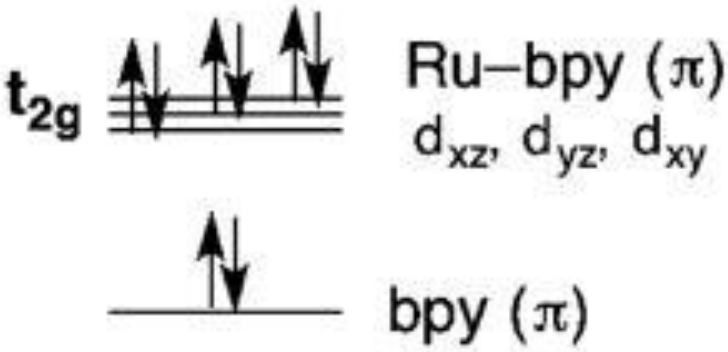


Diagram of frontier orbitals of $[Ru(bpy)_3]^{2+}$

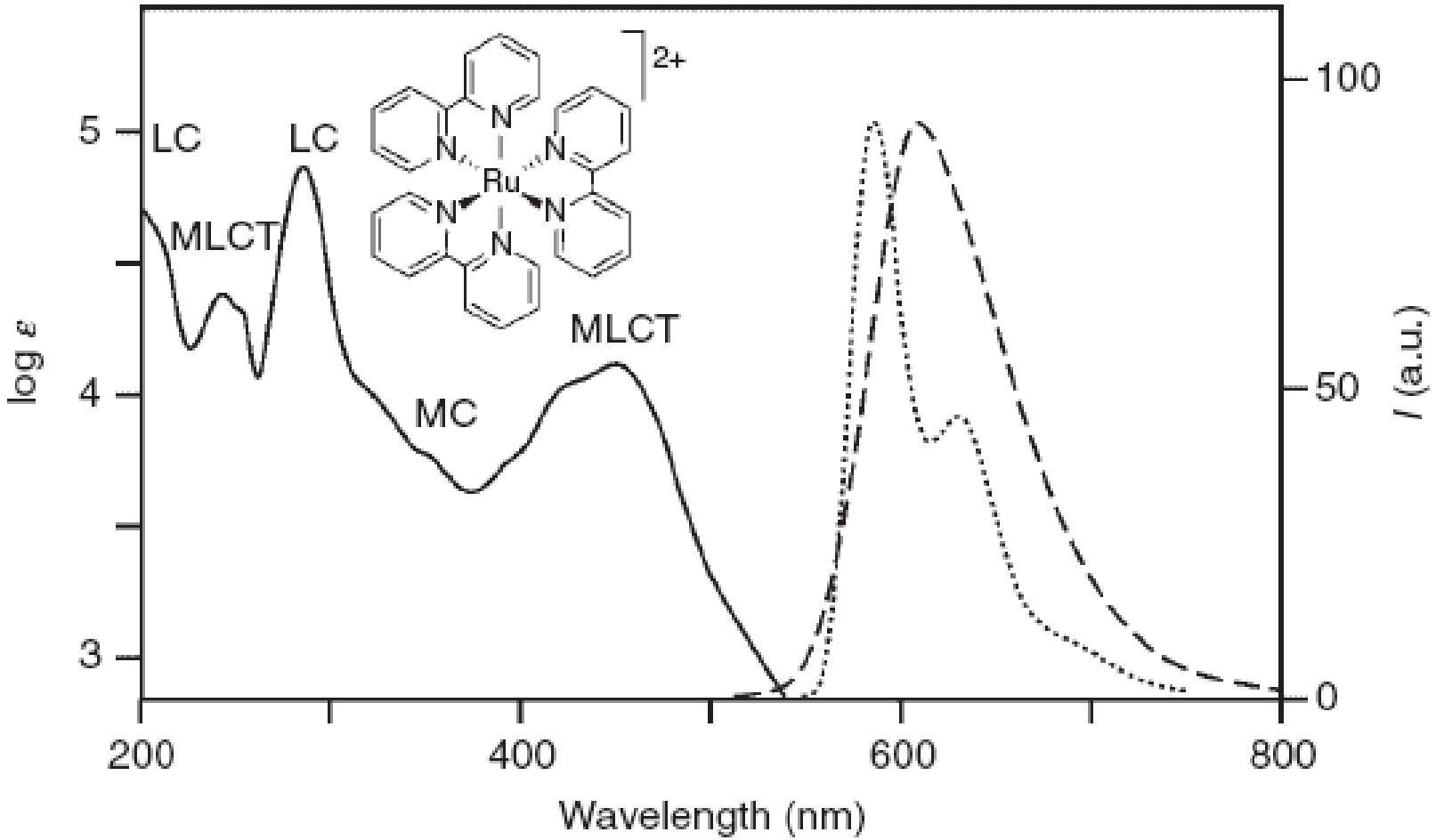




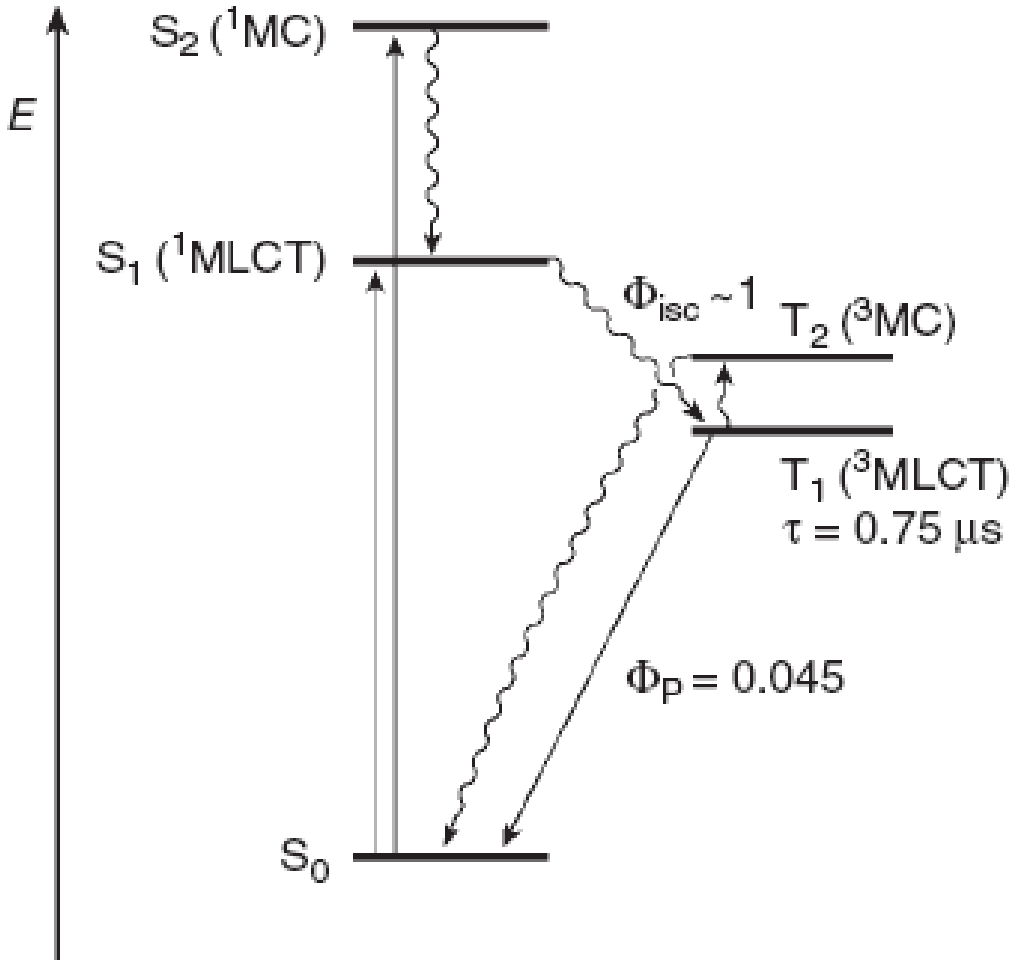




Absorption and emission spectra of $[Ru(bpy)_3]^{2+}$



Jablonski diagram of $[Ru(bpy)_3]^{2+}$



The excited state as a new molecule

Properties which vary from ground-state molecules to excited-state molecules:

- ✓ **Lifetime;**
- ✓ **Energy;**
- ✓ **Geometry;**
- ✓ **Dipole moments;**
- ✓ **Electron transfer;**
- ✓ **Proton transfer;**
- ✓ **Aggregation.**

Lifetime

Lifetime of excited states which decay following processes with first-order rate constant

$$\tau(^*\mathrm{A}) = \frac{1}{k_\mathrm{p} + k_\mathrm{r} + k_\mathrm{nr}} = \frac{1}{\sum_j k_j}$$

10^{-12} s – tens of s

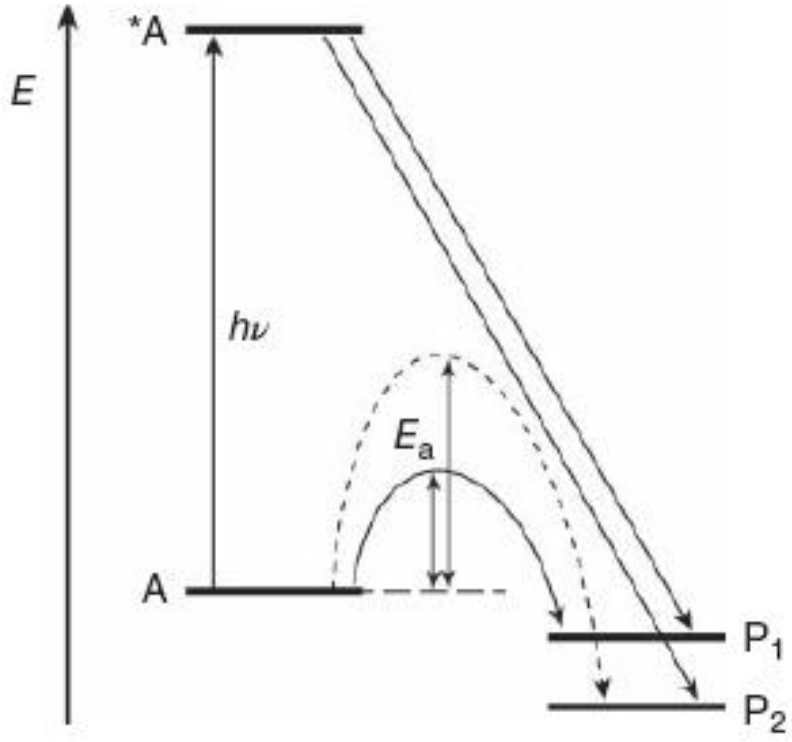
Energy

The energy of an excited state is taken as the energy difference between the lowest vibrational levels of the excited state and the corresponding ground state.

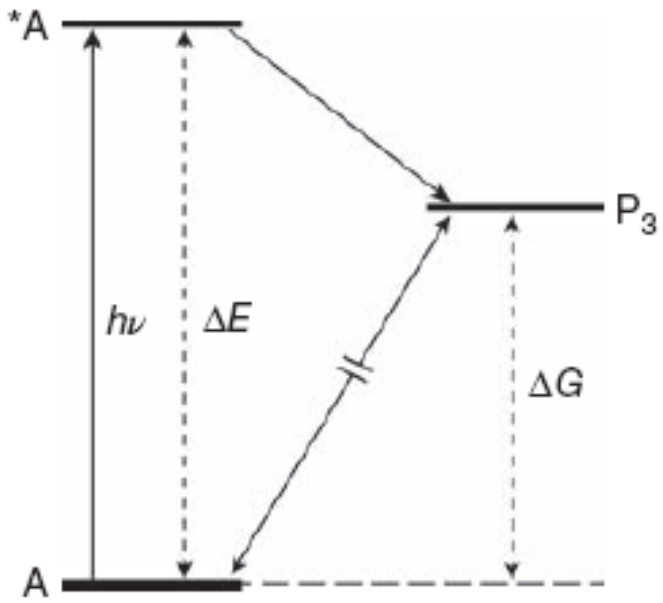
150 – 1250 kJ mol^{-1} > E_{gs}

Energy and reaction paths

Kinetic aspects



Thermodynamic aspects

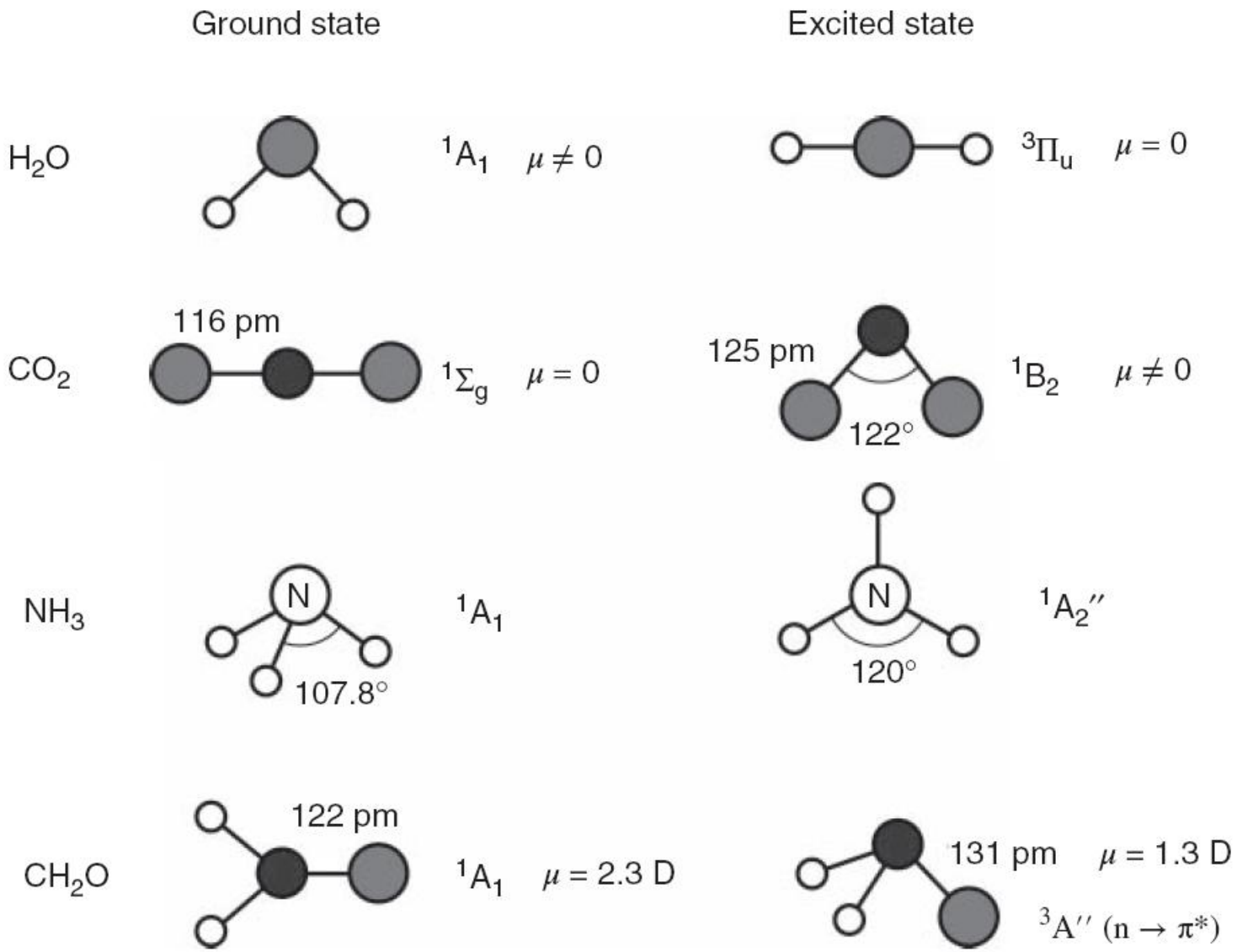


In photochemical reactions selectivity is assured by the peculiar electronic structure of the excited state.

Geometry

Since the electronic configuration of the excited state is significantly different from that of the ground state, it is then reasonable to expect that the geometry of the excited state is different from that of the ground state.

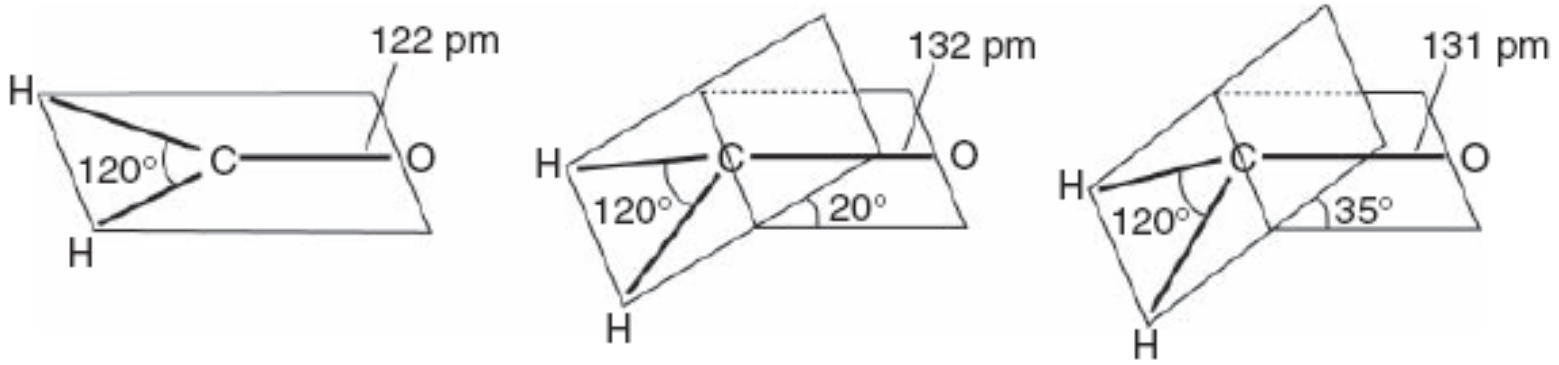
Geometry


Ground state
Excited state
H_2O
$^1A_1$ $\mu \neq 0$
$^3\Pi_u$ $\mu = 0$
CO_2
116 pm
$^1\Sigma_g$ $\mu = 0$
125 pm
122°
$^1B_2$ $\mu \neq 0$
NH_3
N
107.8°
$^1A_1$
N
120°
$^1A_2''$
CH_2O
122 pm
$^1A_1$ $\mu = 2.3$ D
131 pm
$\mu = 1.3$ D
$^3A''$ (n → π*)

Dipole moments

Dipole moments of molecules in electronic excited states might be different from those of the molecules in the ground state, as a consequence of both changes in geometry and redistribution of electrons.

Formaldehyde



$^1A_1$

(a) Planar, μ = 2.3 D

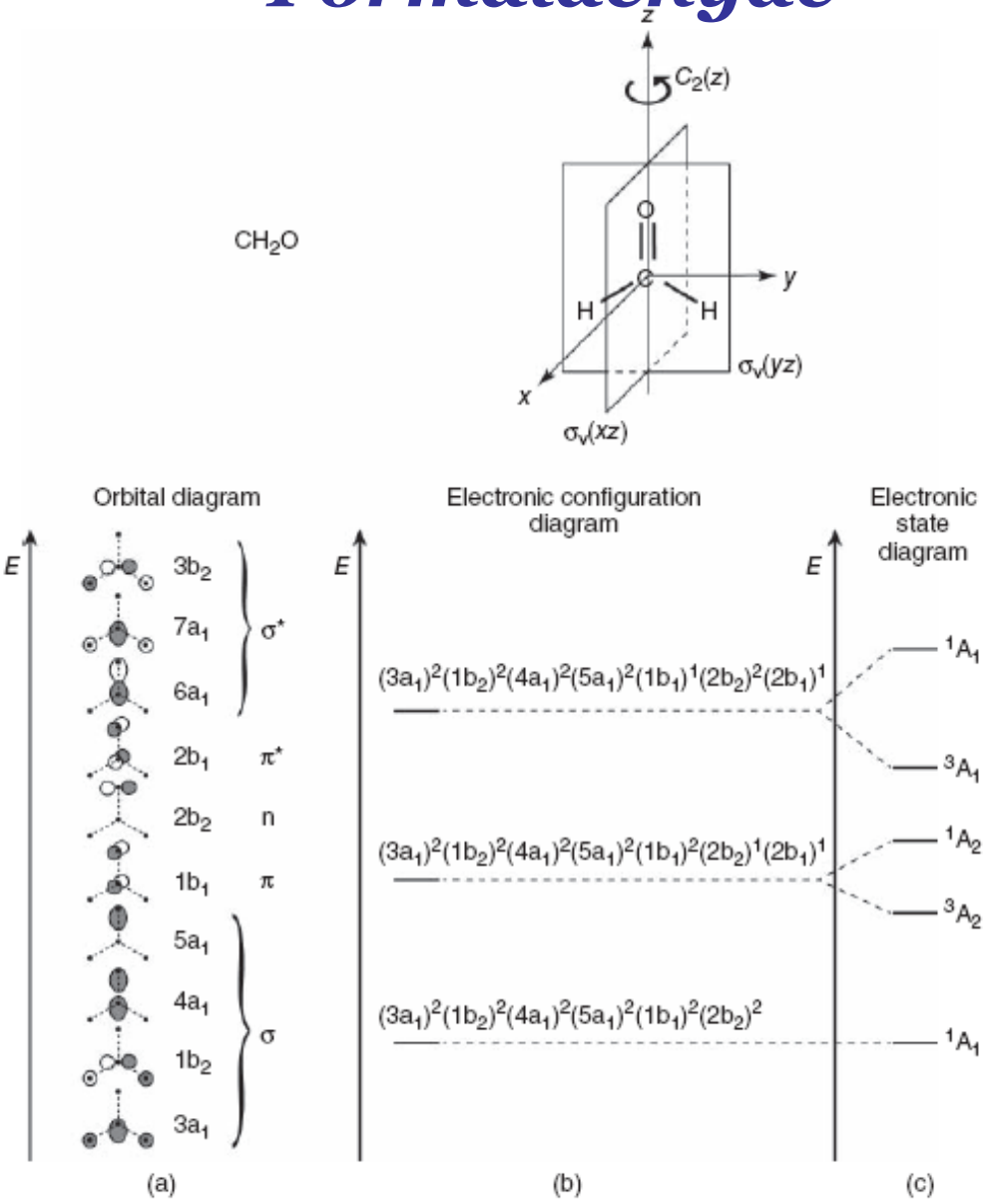
$^1A_2$ (n,π^*)

(b) Bent, μ = 1.6 D

$^3A_2$ (n,π^*)

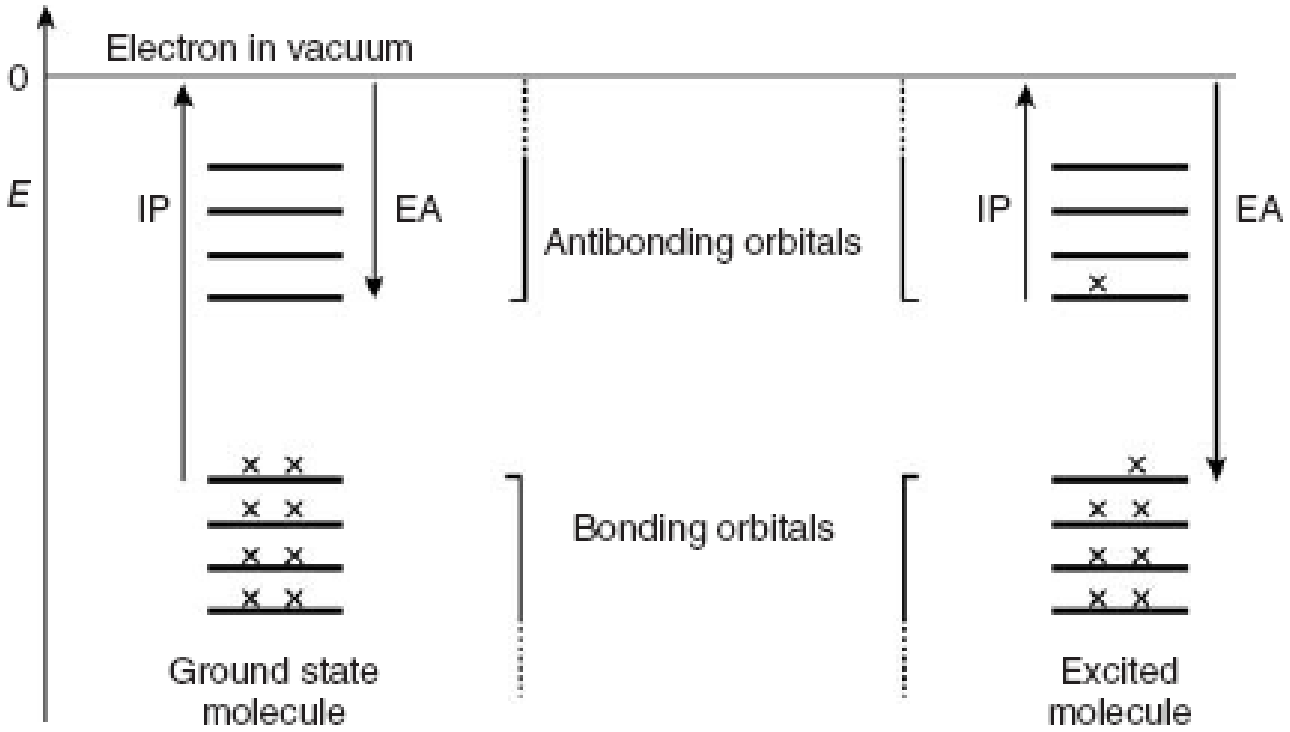
(c) Bent, μ = 1.3 D

Formaldehyde

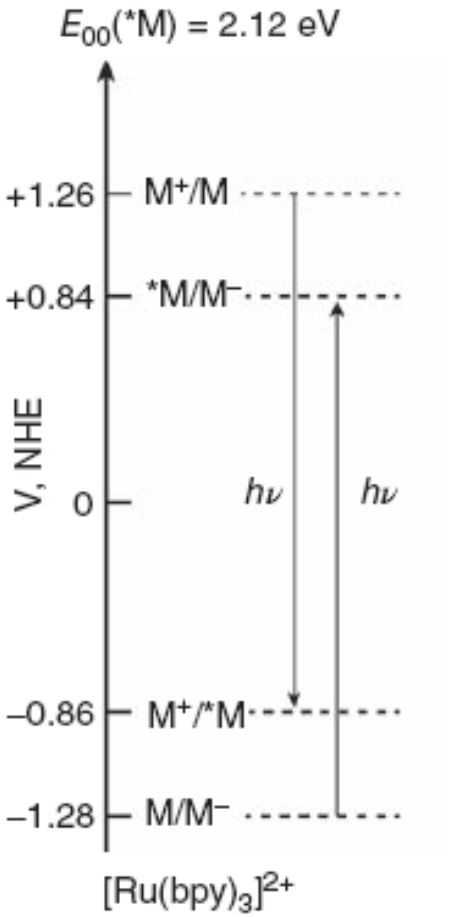


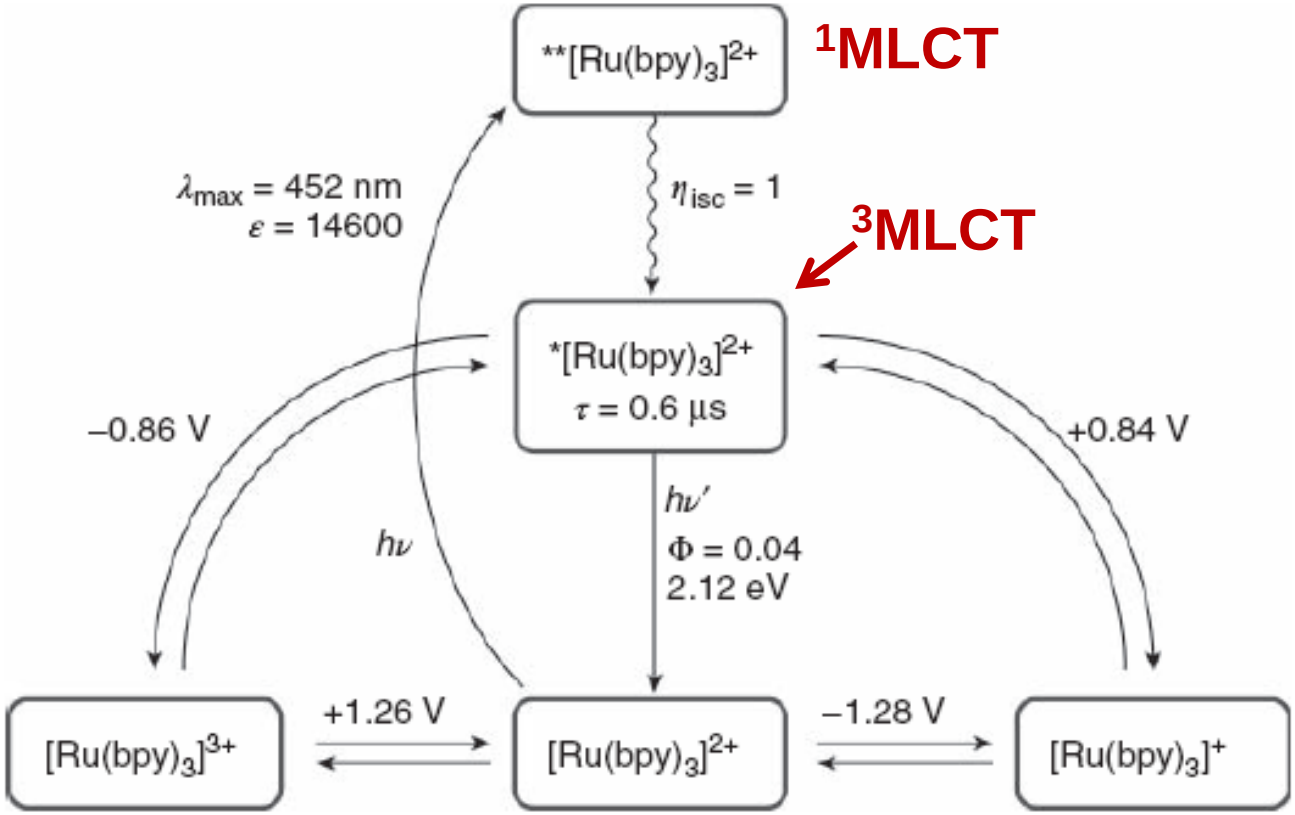
Electron transfer

Molecules in electronically excited states are both better electron donors and better electron acceptors than when they are in their ground state.



Electrochemistry of the excited state $^3\{[Ru^{III}(bpy)_2(bpy^-)]^{2+}\}^*$





Better electron donor for 2.12 V (1.26 V + 0.86 V)

Better electron acceptor for 2.12 V (0.84 V + 1.28 V)

Possible processes of the excited state $^3\{[Ru^{III}(bpy)_2(bpy^-)]^{2+}\}^*$

$$* [Ru(bpy)_3]^{2+} + Q \rightarrow [Ru(bpy)_3]^{2++} + * Q \quad \textit{energy transfer}$$

Better electron acceptor for 2.12 V (0.84 V + 1.28 V)

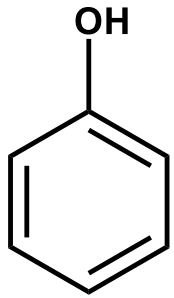
$$* [Ru(bpy)_3]^{2+} + Q \rightarrow [Ru(bpy)_3]^{+} + Q^{+} \quad \textit{reductive quenching}$$

Better electron donor for 2.12 V (1.26 V + 0.86 V)

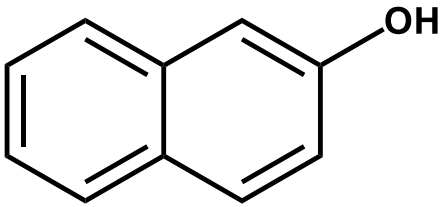
$$* [Ru(bpy)_3]^{2+} + Q \rightarrow [Ru(bpy)_3]^{3+} + Q^{-} \quad \textit{oxidative quenching}$$

Proton transfer

Charge redistribution caused by light excitation is also expected to influence the acid-base behaviour of a molecule.

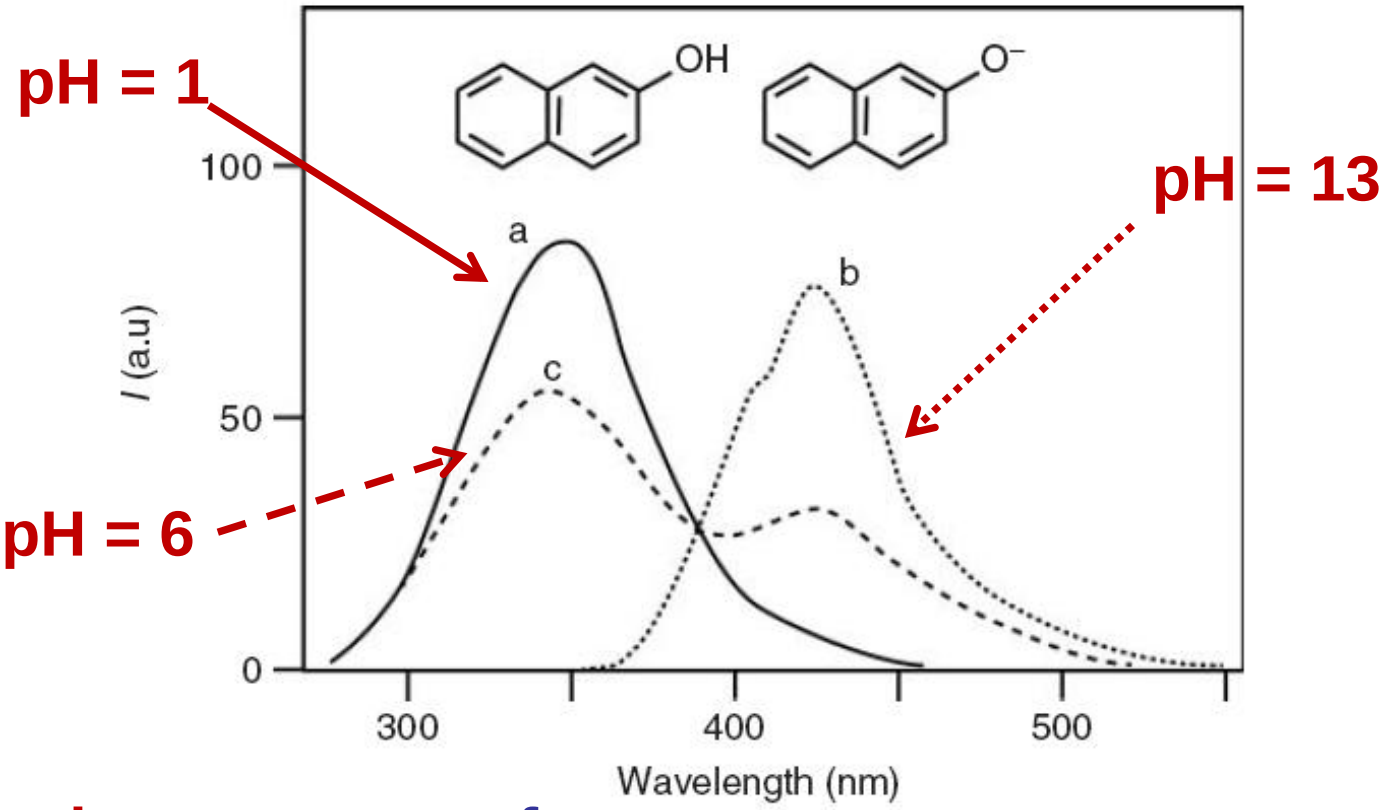


$pK_a\,(S_0) = 10$ $pK_a\,(S_1) = 4$

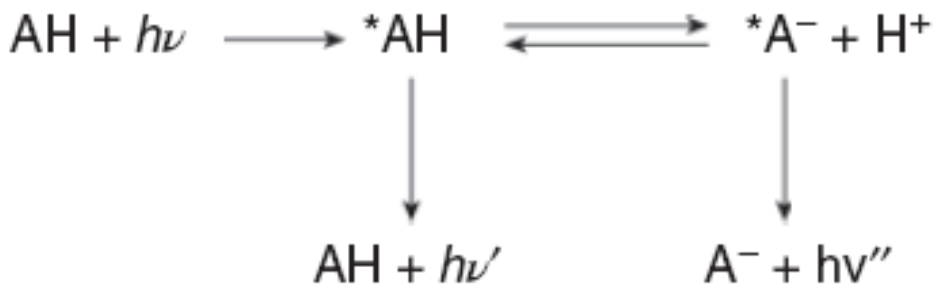


$pK_a\,(S_0) = 9.5$ $pK_a\,(S_1) = 3.1$

Proton transfer



Adiabatic proton transfer



Excimers and exciplexes

Excimer:

$$^{*}\mathrm{A} + \mathrm{A} \rightarrow {}^{*}[\mathrm{A} - \mathrm{A}]\ excimer$$

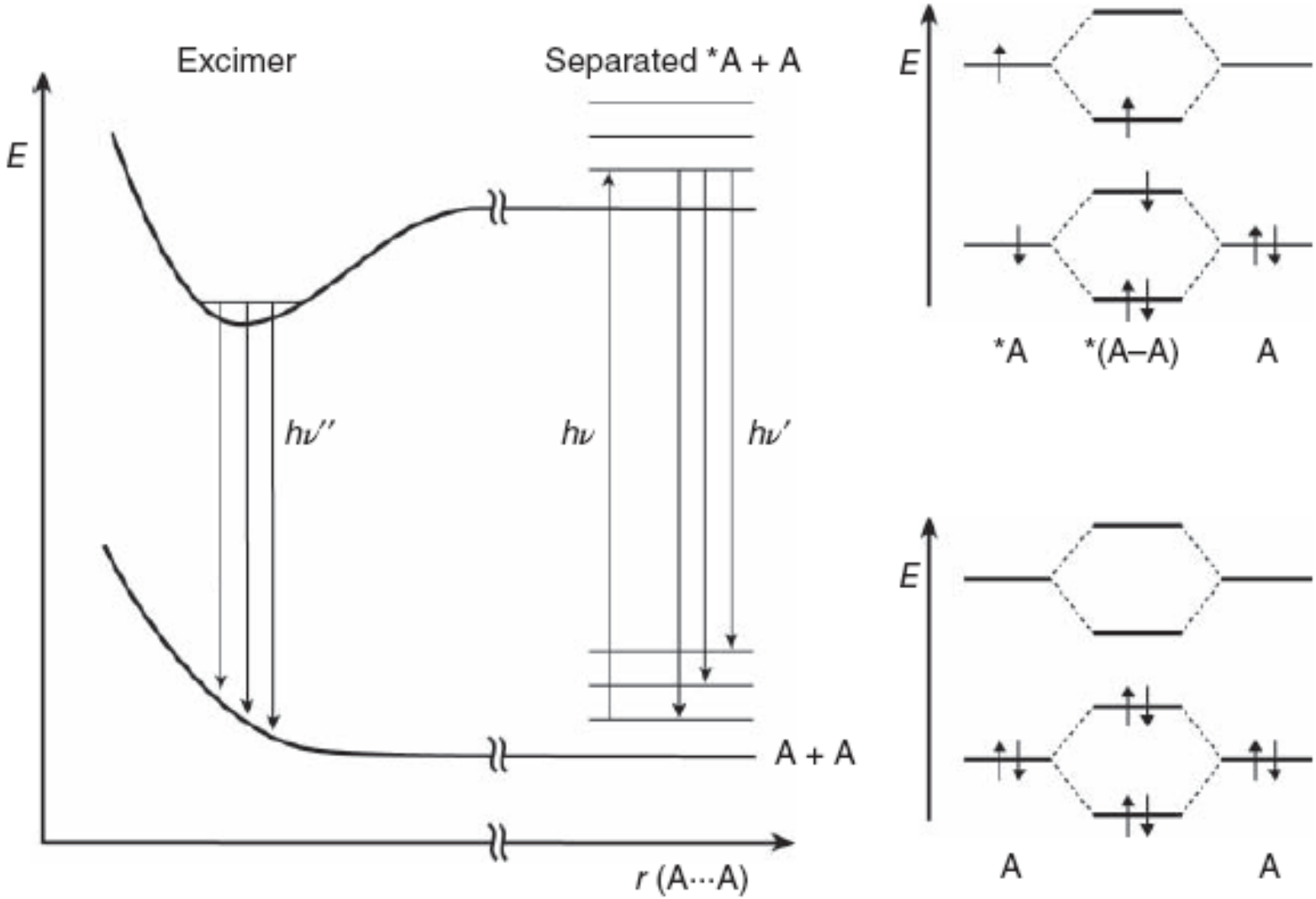
$$\mathrm{A} + \mathrm{A} \leftarrow [\mathrm{A} - \mathrm{A}]$$

Exciplex:

$$^{*}\mathrm{A} + \mathrm{B} \rightarrow {}^{*}[\mathrm{A} - \mathrm{B}]\ exciplex$$

$$\mathrm{A} + \mathrm{B} \leftarrow [\mathrm{A} - \mathrm{B}]$$

Excimers and exciplexes



Emission spectrum of pyrene