La fotochimica

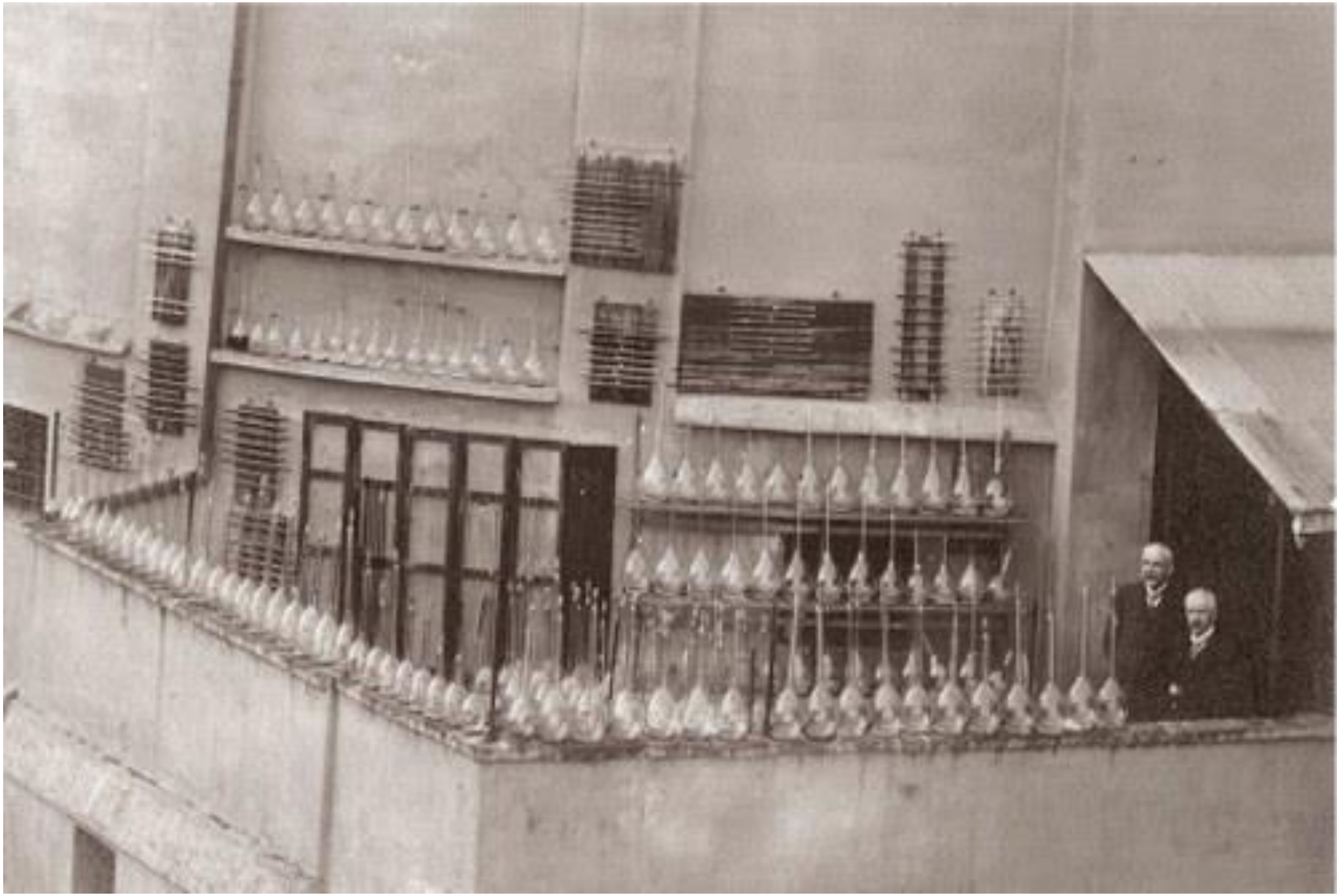
G. Ciamician

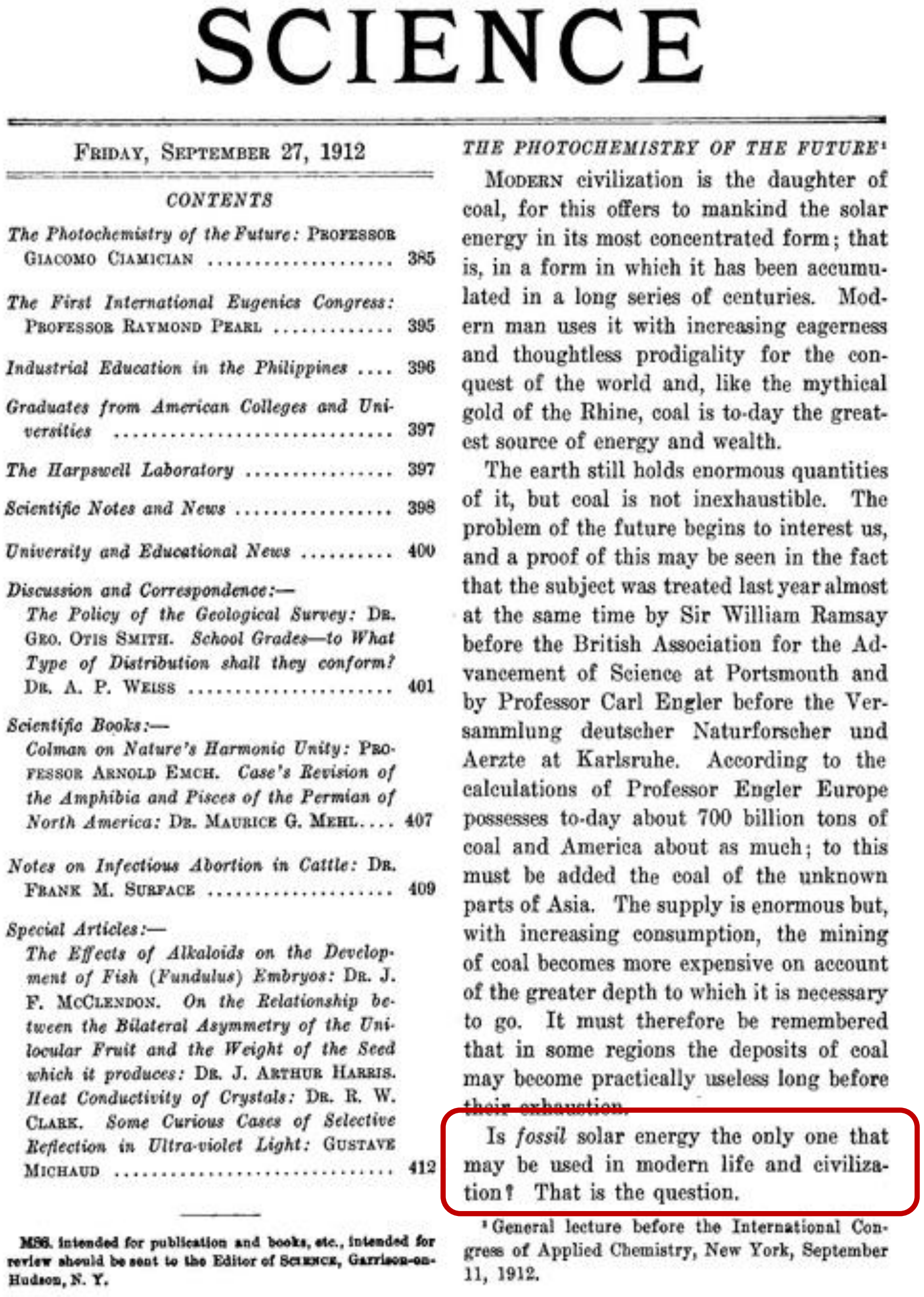
Giacomo Luigi Ciamician

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 che fare concorrenza alle piante con l'industria chimica fondata sul "catrame".





SCIENCE

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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.

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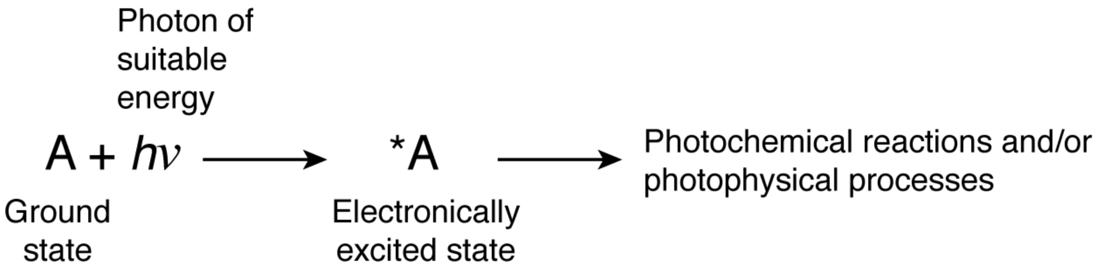
[1] General lecture before the International Congress of Applied Chemistry, New York, September 11, 1912.

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?

Fotochimica e fotofisica



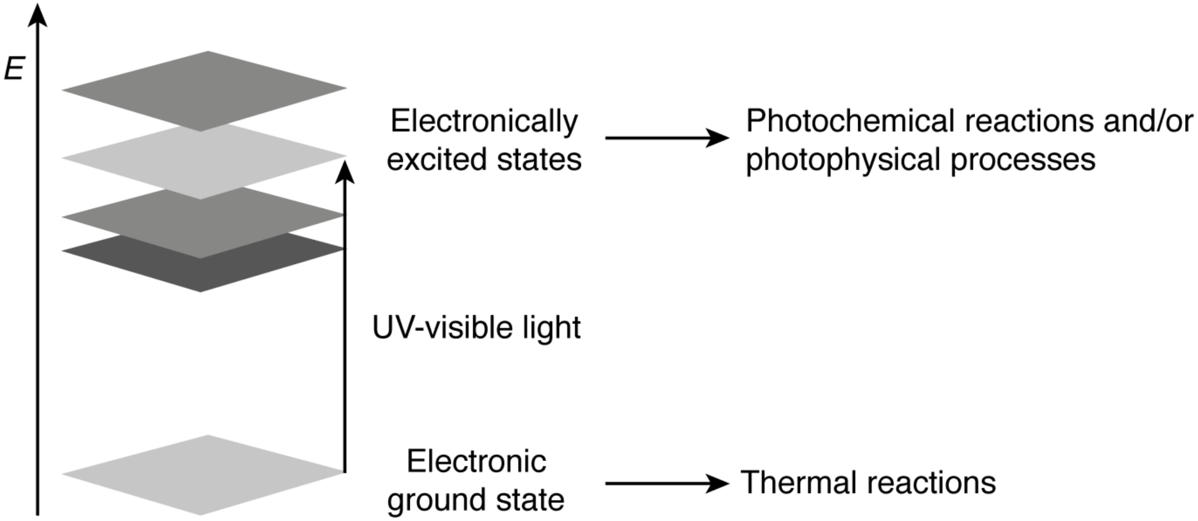
Photon of suitable energy

$$A + h\nu \longrightarrow {}^*A \longrightarrow$$ Photochemical reactions and/or photophysical processes

Ground state

Electronically excited state

(a)



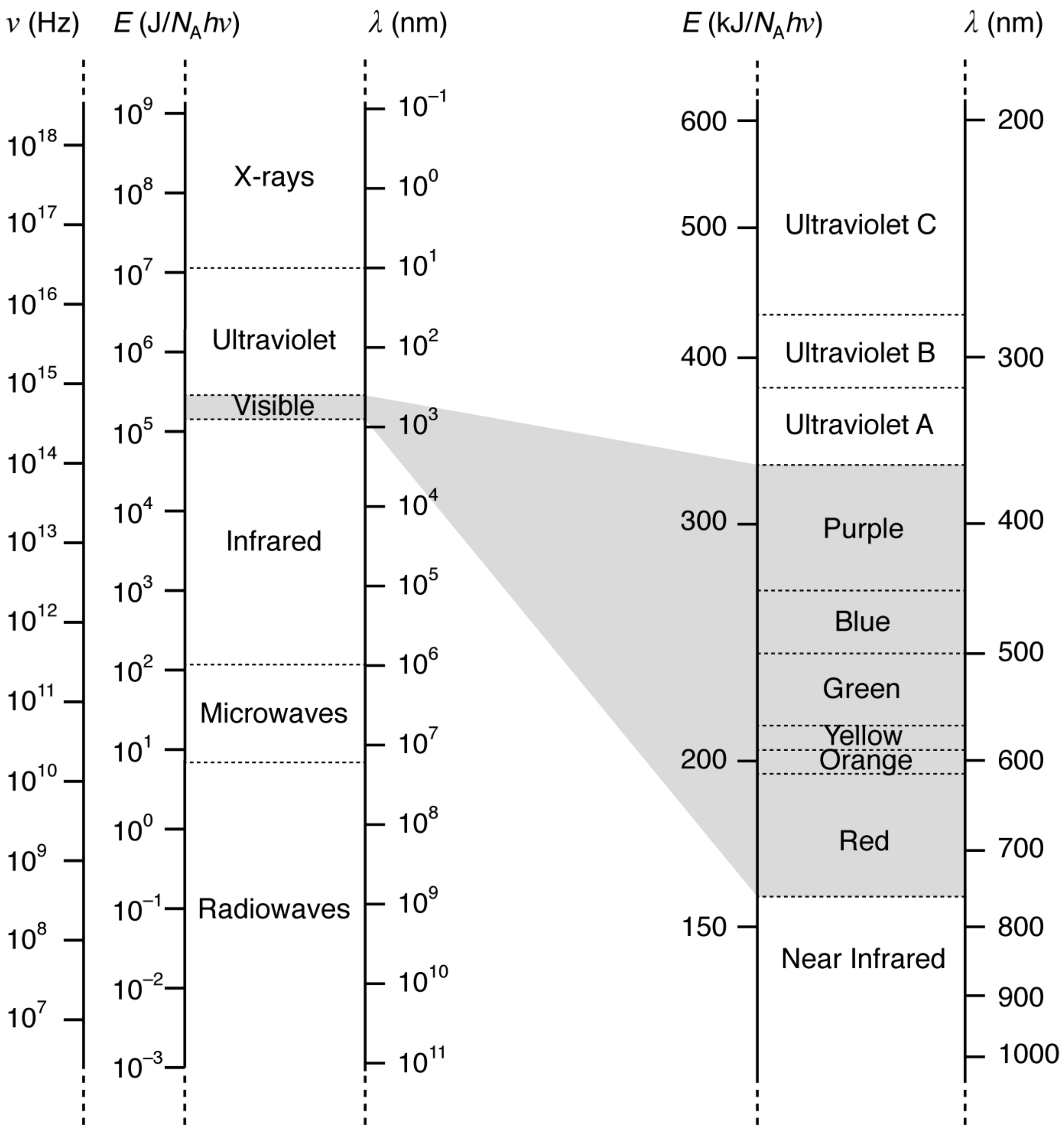
Electronically excited states → Photochemical reactions and/or photophysical processes

UV-visible light

Electronic ground state → Thermal reactions

(b)

Energie coinvolte



Energie coinvolte

Il paradigma più semplice e più comune:

Una molecola assorbe un fotone.

Energia di un FOTONE a 200 nm = $9.95 \cdot 10^{-19}$ J

Energia di un FOTONE a 1000 nm = $1.99 \cdot 10^{-19}$ J

Una mole di fotoni = un EINSTEIN

Energia di un EINSTEIN a 200 nm = 599 kJ (143 kcal)

Energia di un EINSTEIN a 1000 nm = 119.8 kJ (28.6 kcal)

Aspetti quantitativi

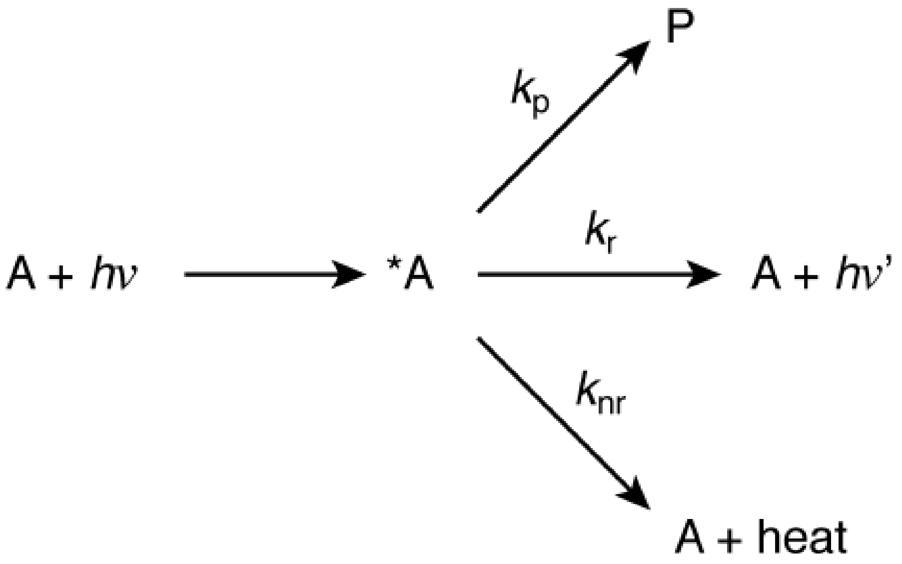
La legge di Grotthus-Draper:

Solo la luce assorbita è efficace nel produrre un cambiamento fotochimico.

La legge di Lambert - Beer: $A = \log(I_0/I) = \varepsilon bc$

Aspetti quantitativi

Processo primario



Photoreaction
(chemical reaction)

Luminescence
(radiative deactivation)

Degradation to heat
(non radiative deactivation)

Tempo di vita dello stato eccitato:

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

Efficienza di un processo:

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

Aspetti quantitativi

Resa quantica di un processo:

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

In condizioni di stato stazionario:

$$\frac{d[^*A]}{dt} = I_m - k_p[^*A] - k_r[^*A] - k_{nr}[^*A] = 0$$

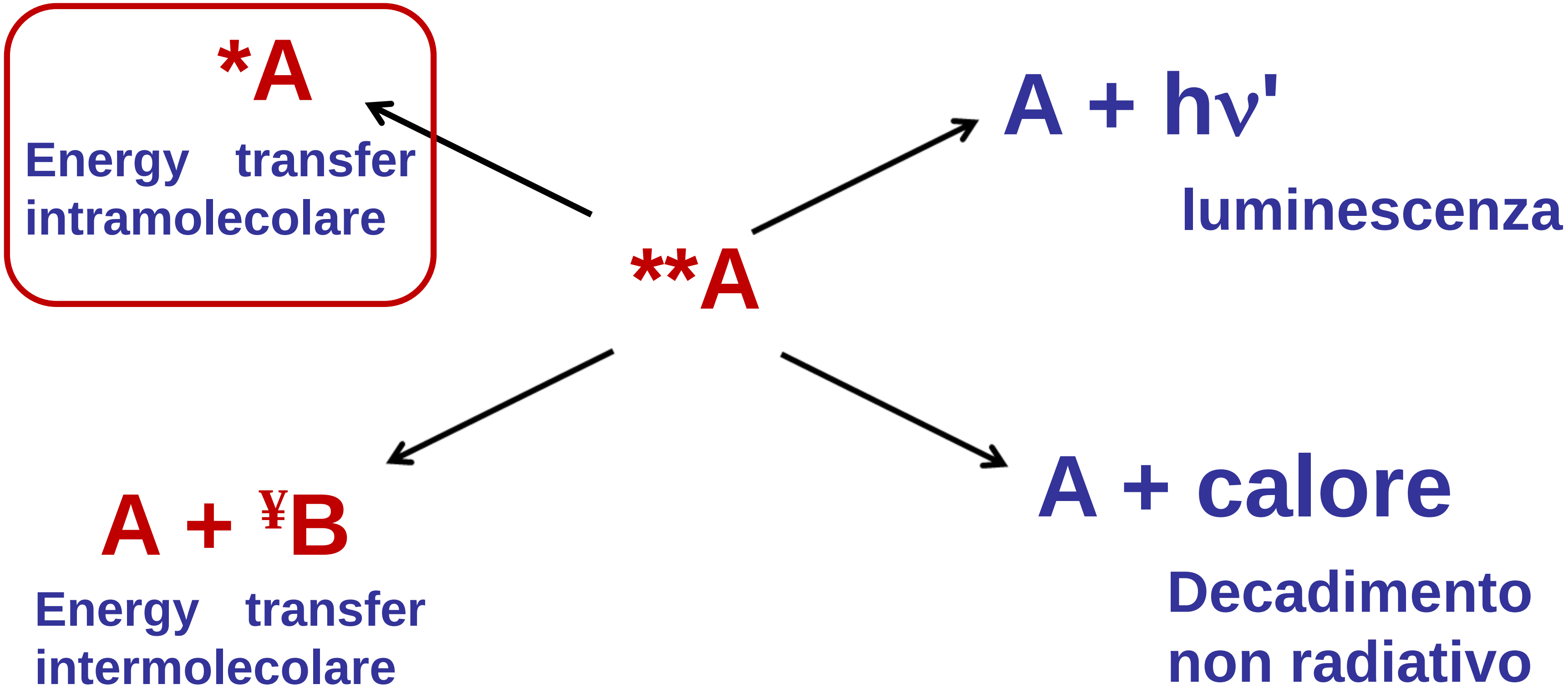
Resa quantica del processo p:

$$\Phi_p = \frac{k_p[^*A]}{I_m} = \frac{k_p}{k_p + k_r + k_{nr}}$$

Resa quantica del processo i:

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

Processi fotofisici



****A**

***A**

Energy transfer intramolecolare

A + $h\nu'$

luminescenza

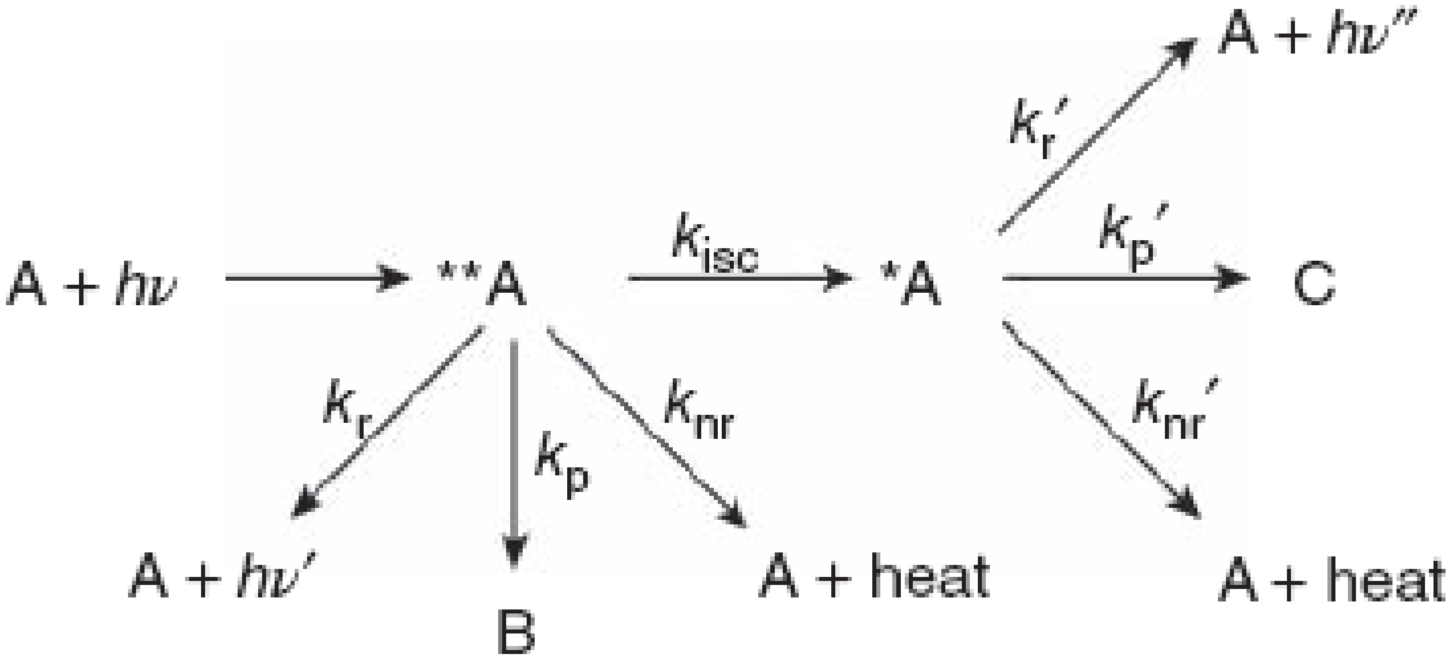
A + ¥B

Energy transfer intermolecolare

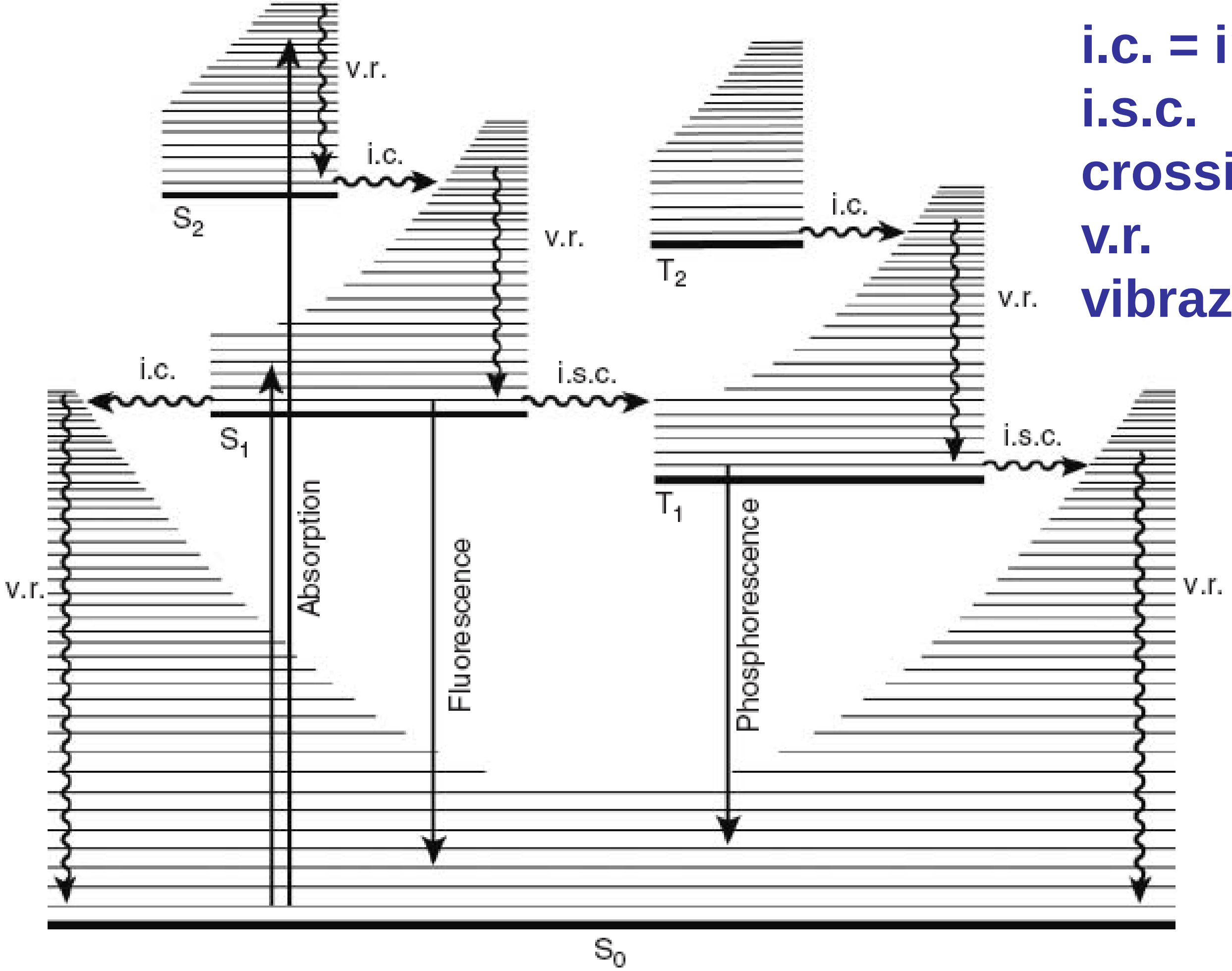
A + calore

Decadimento non radiativo

Rappresentazione schematica dell'insieme dei processi fotofisici e fotochimici

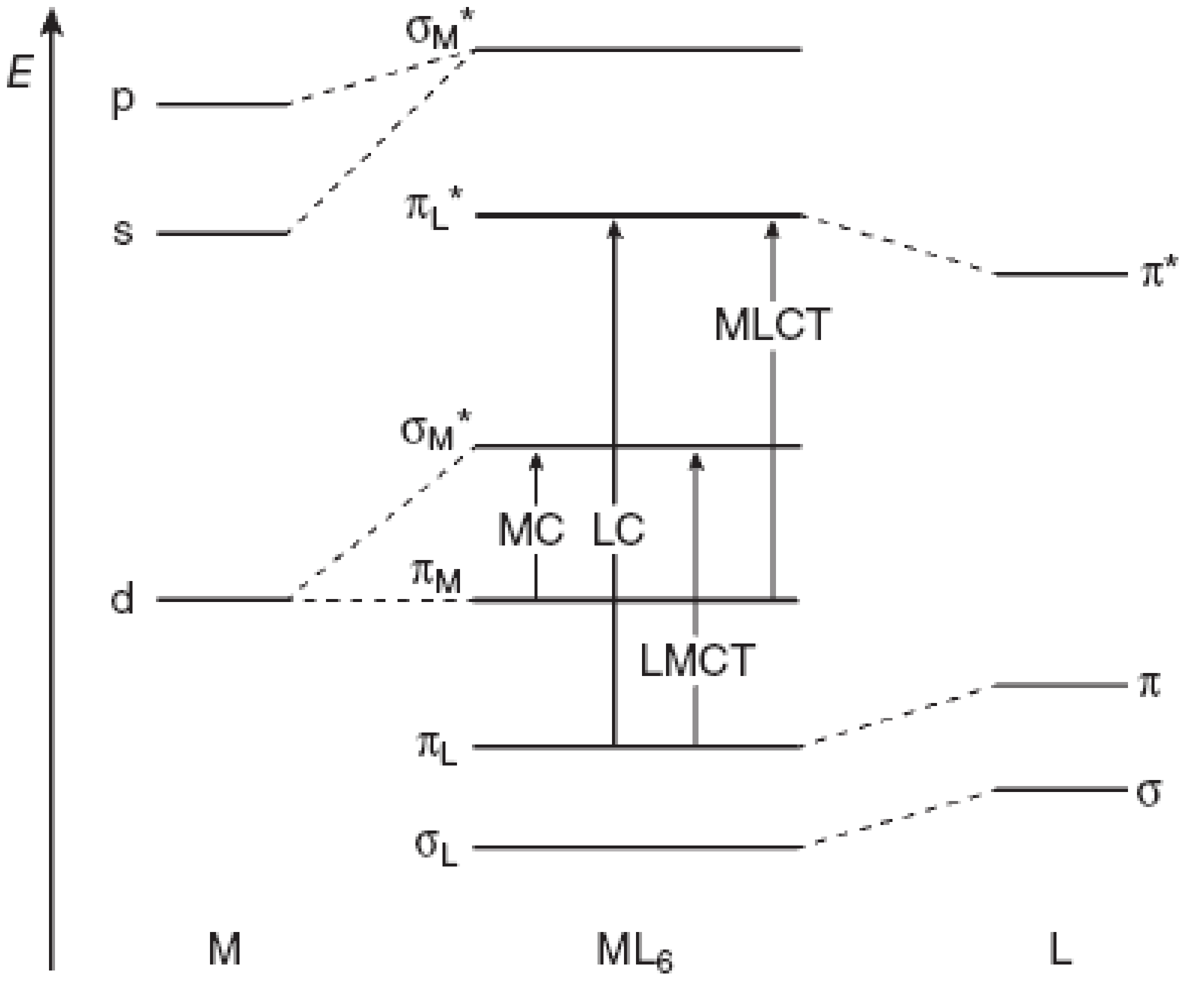


Il Diagramma di Jablonski



S = stato di singoletto
T = stato di tripletto
i.c. = internal conversion
i.s.c. = intersystem crossing
v.r. = rilassamento vibrazionale

Transizioni elettroniche possibili per complessi ottaedrici ML$_6$



Il Diagramma di Tanabe-Sugano di $[Cr(en)_3]^{3+}$

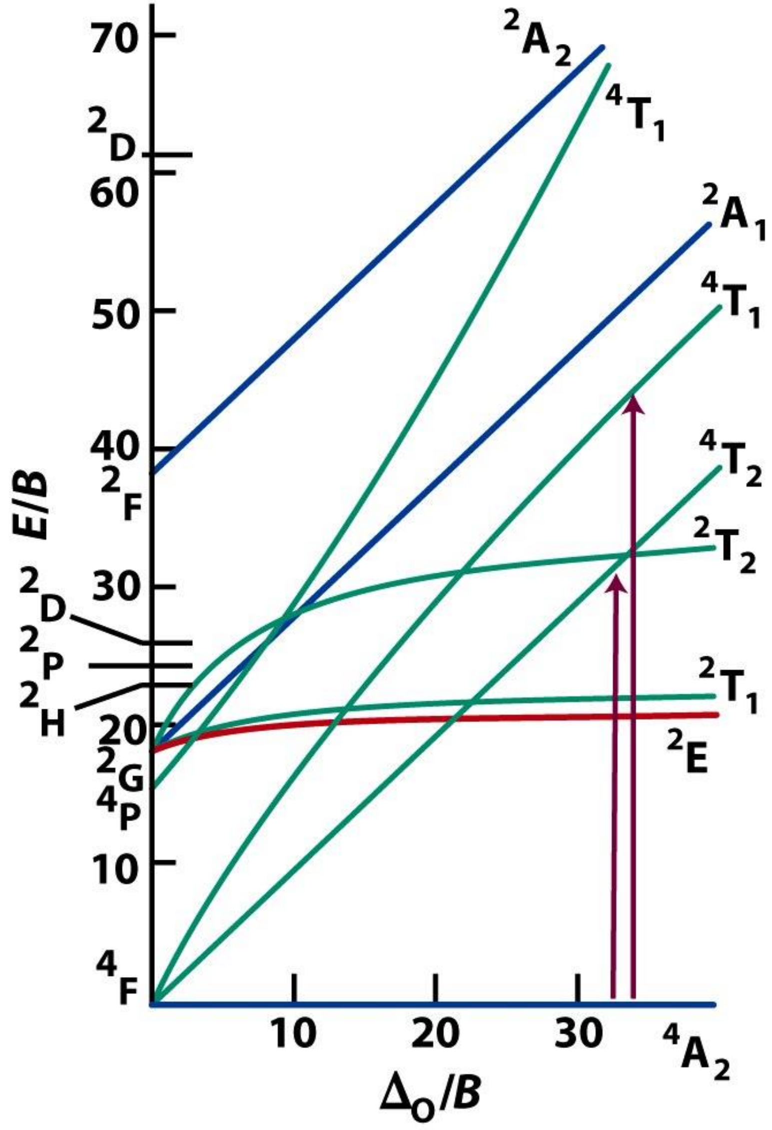
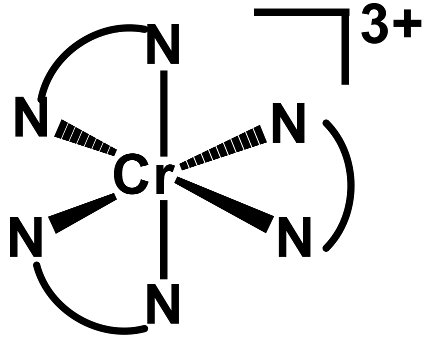
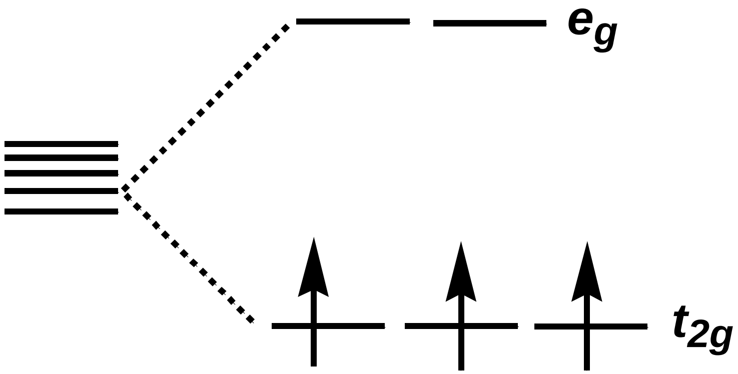


Figure 19-27
Shriver & Atkins Inorganic Chemistry, Fourth Edition





Spettro in assorbimento e in emissione di $[Cr(en)_3]^{3+}$

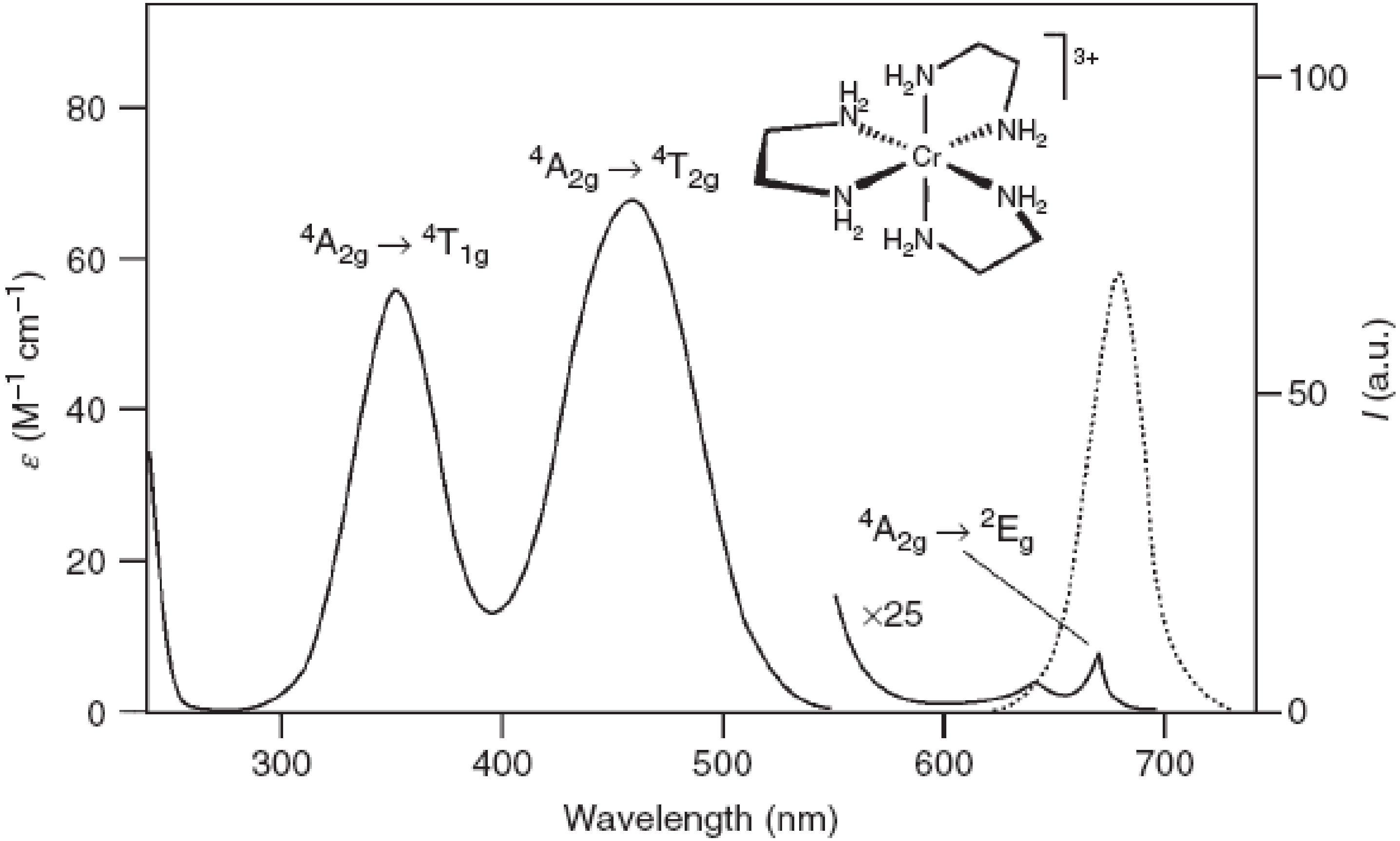


Diagramma di Jablonski di $[Cr(en)_3]^{3+}$

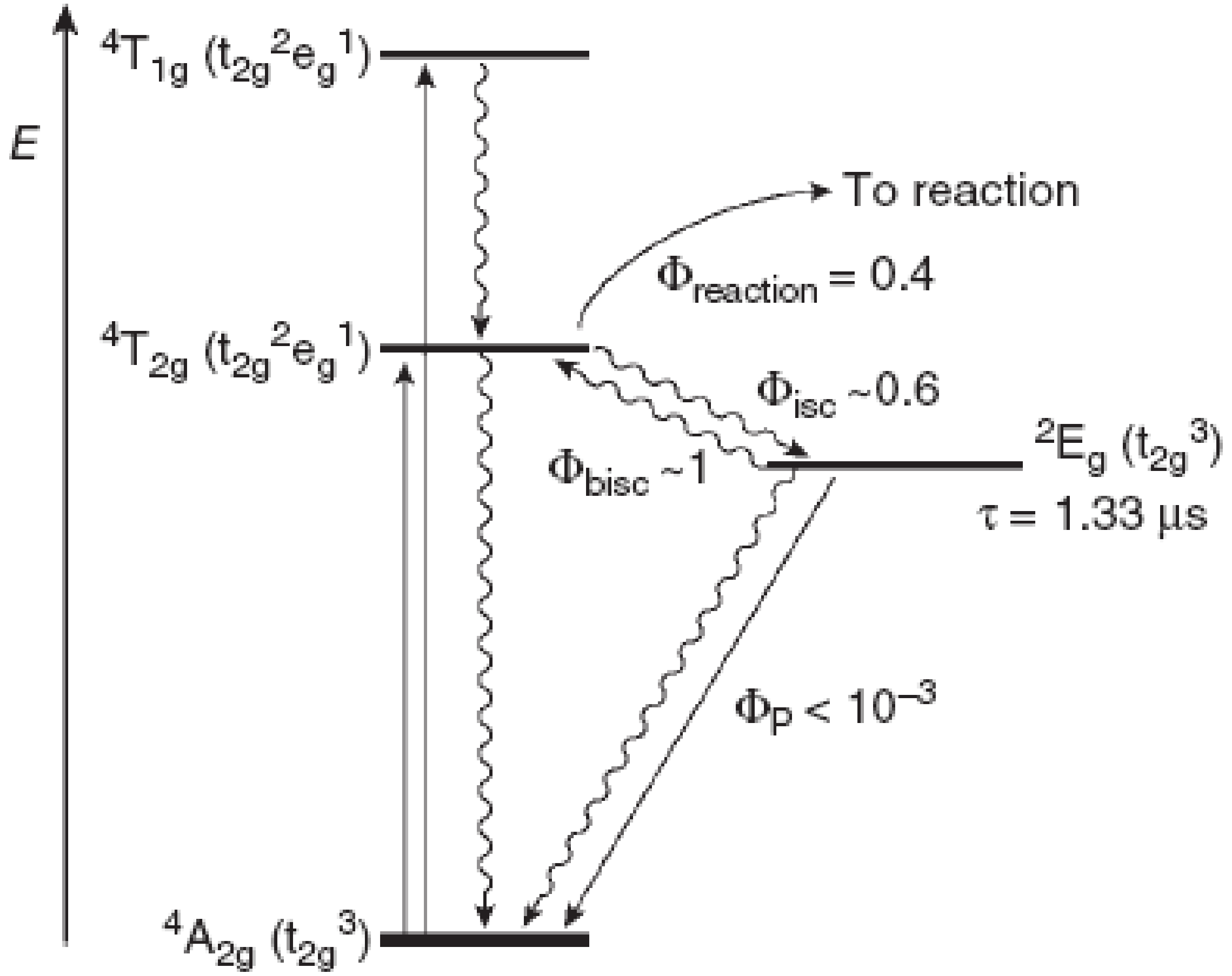
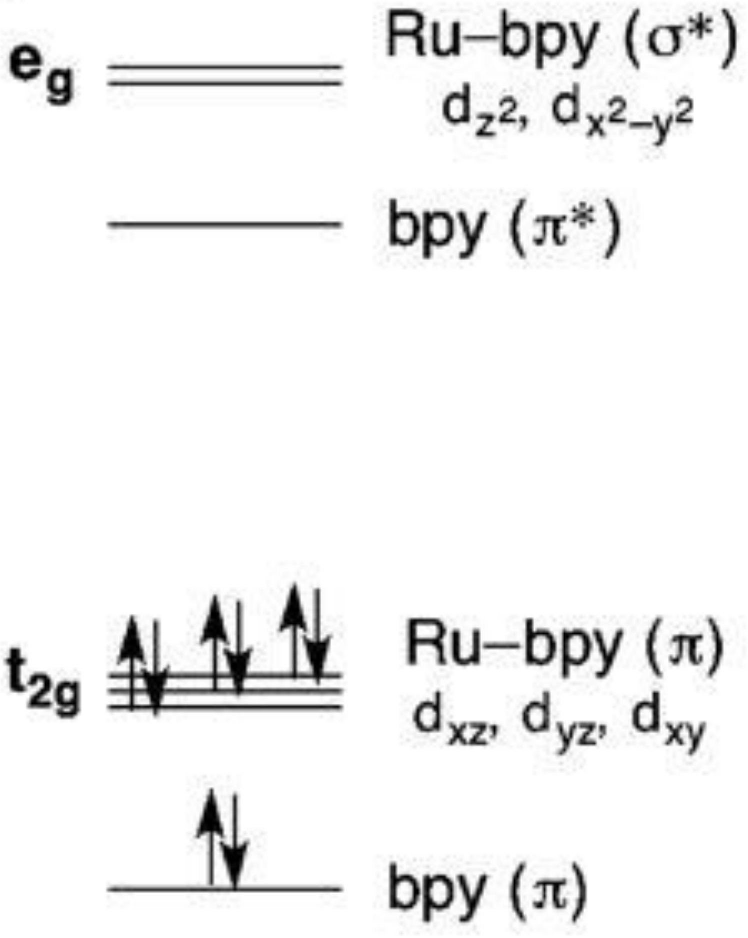
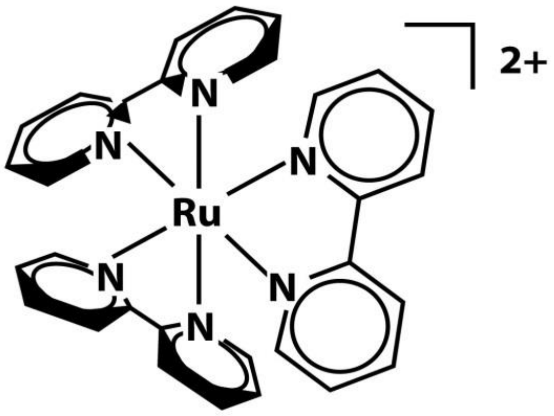
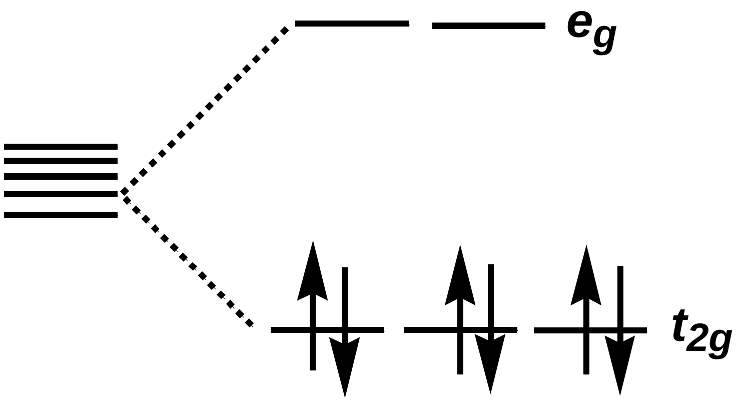


Diagramma degli orbitali di frontiera per $[Ru(bpy)_3]^{2+}$







Spettro di assorbimento e in emissione di $[Ru(bpy)_3]^{2+}$

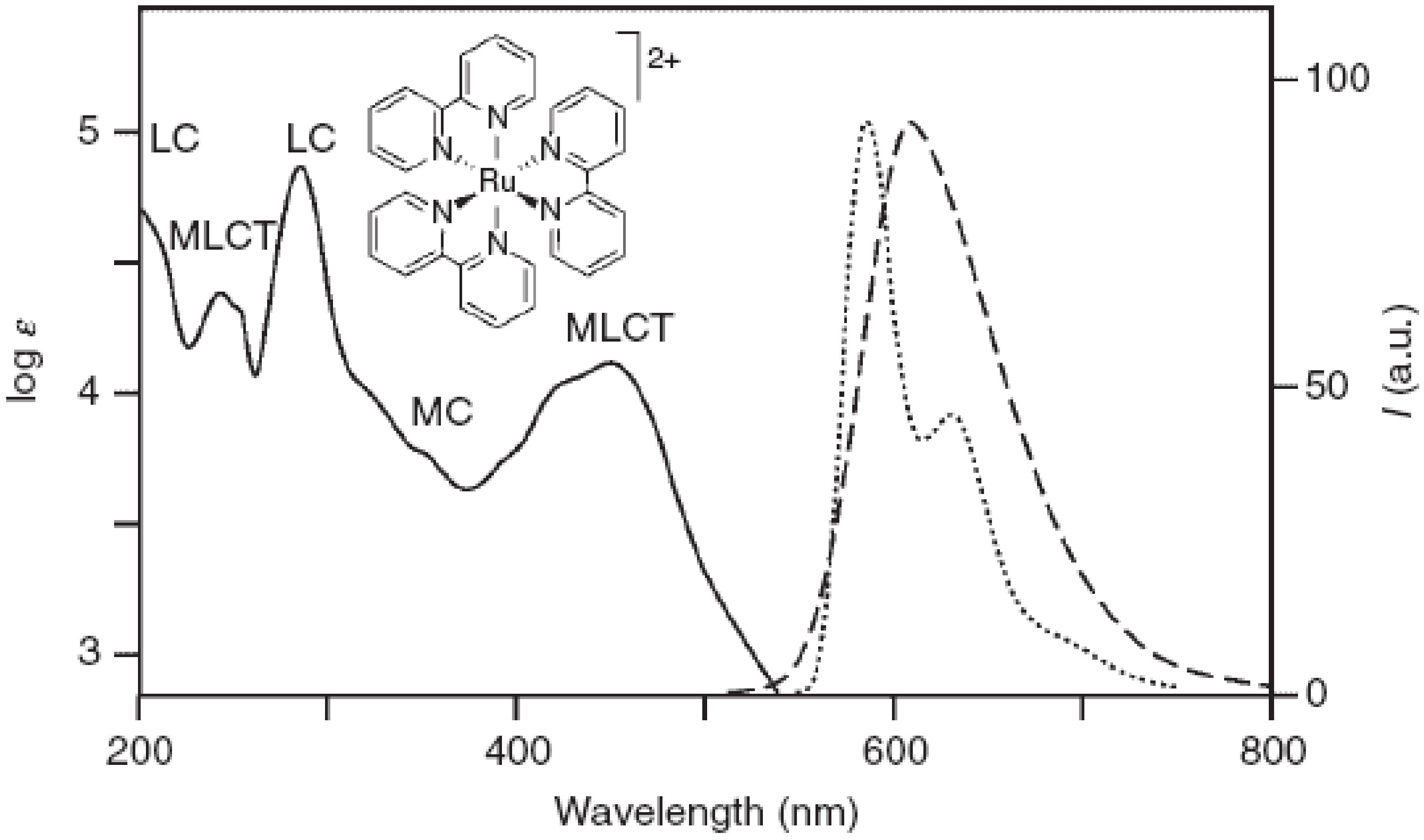
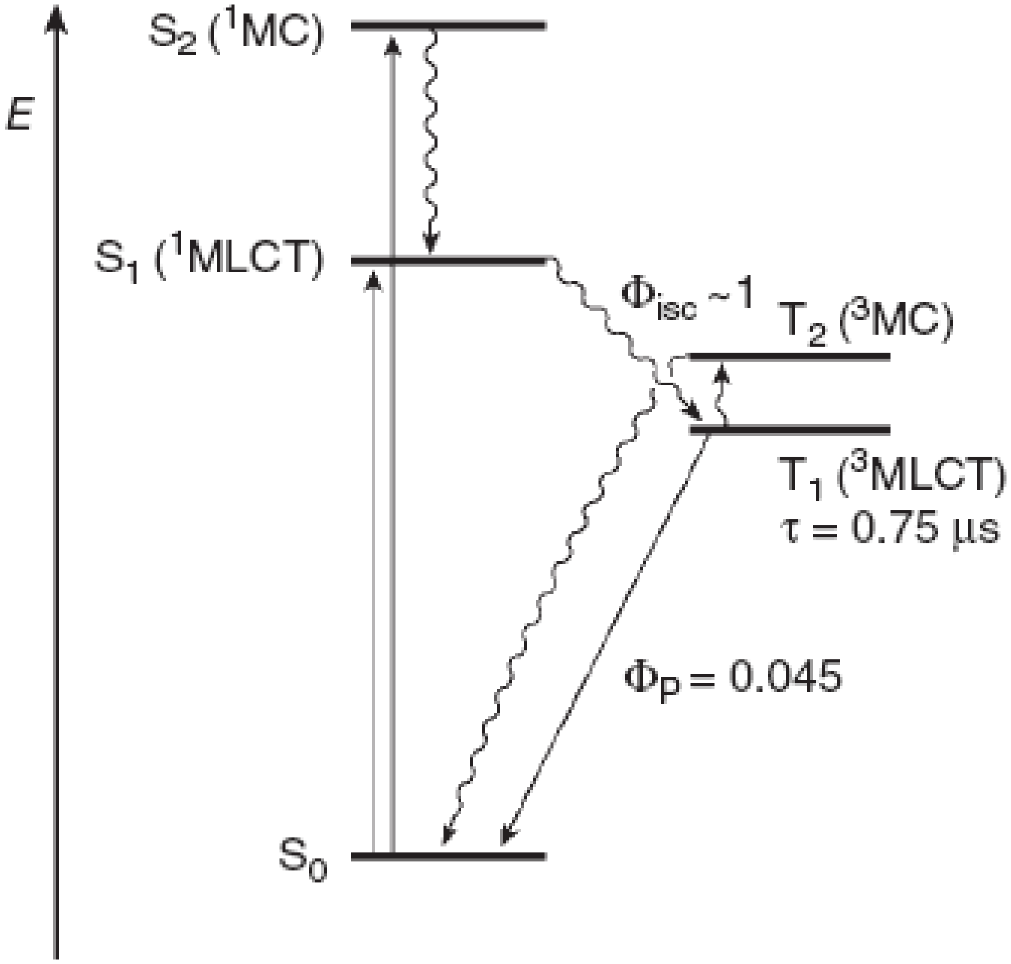


Diagramma di Jablonski di $[Ru(bpy)_3]^{2+}$



Lo stato eccitato come una nuova molecola

Proprietà differenti tra stato fondamentale e stato eccitato:

- ✓ **Tempo di vita;**
- ✓ **Energia;**
- ✓ **Geometria;**
- ✓ **Momento di dipolo;**
- ✓ **Trasferimento di elettroni;**
- ✓ **Trasferimento di protoni;**
- ✓ **Aggregazione.**

Tempo di vita

Tempo di vita dello stato eccitato per processi con cinetica del primo ordine

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

$\boxed{10^{-12}\ \text{s – decine di s}}$

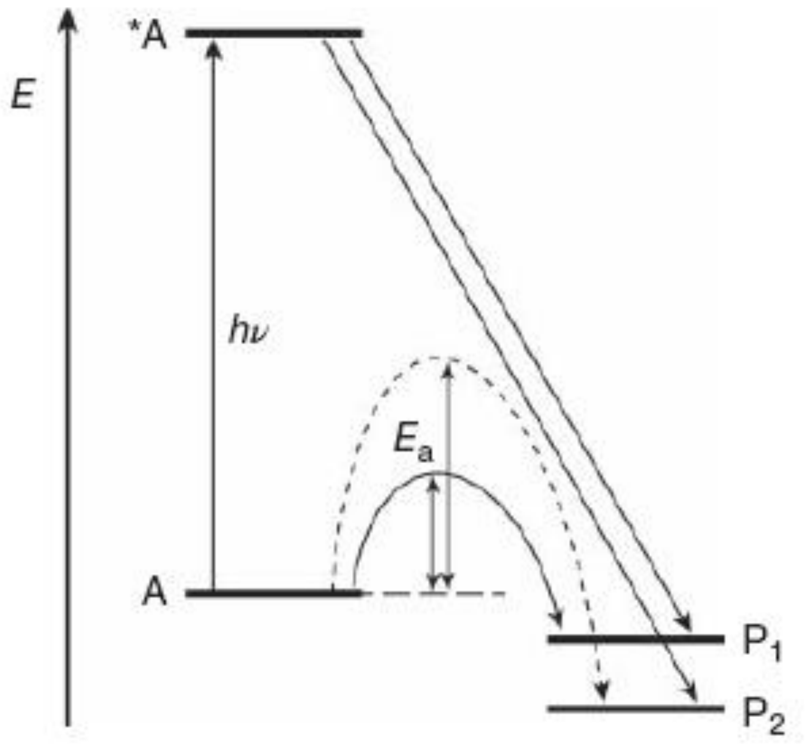
Energia

Energia dello stato eccitato si intende la differenza di energia tra il livello vibrazionale più basso dello stato eccitato e il corrispondente nello stato fondamentale.

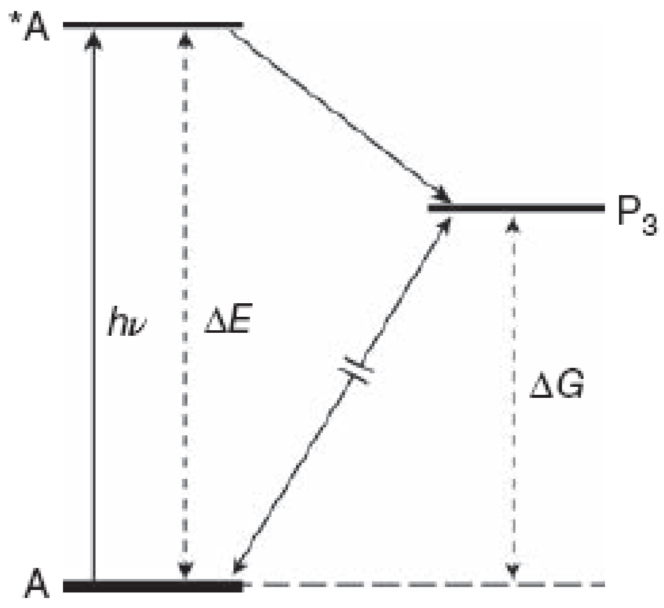
$\boxed{150 – 1250\ \text{kJ mol}^{-1} > E_{gs}}$

Energia e cammini di reazione

Aspetti cinetici



Aspetti termodinamici

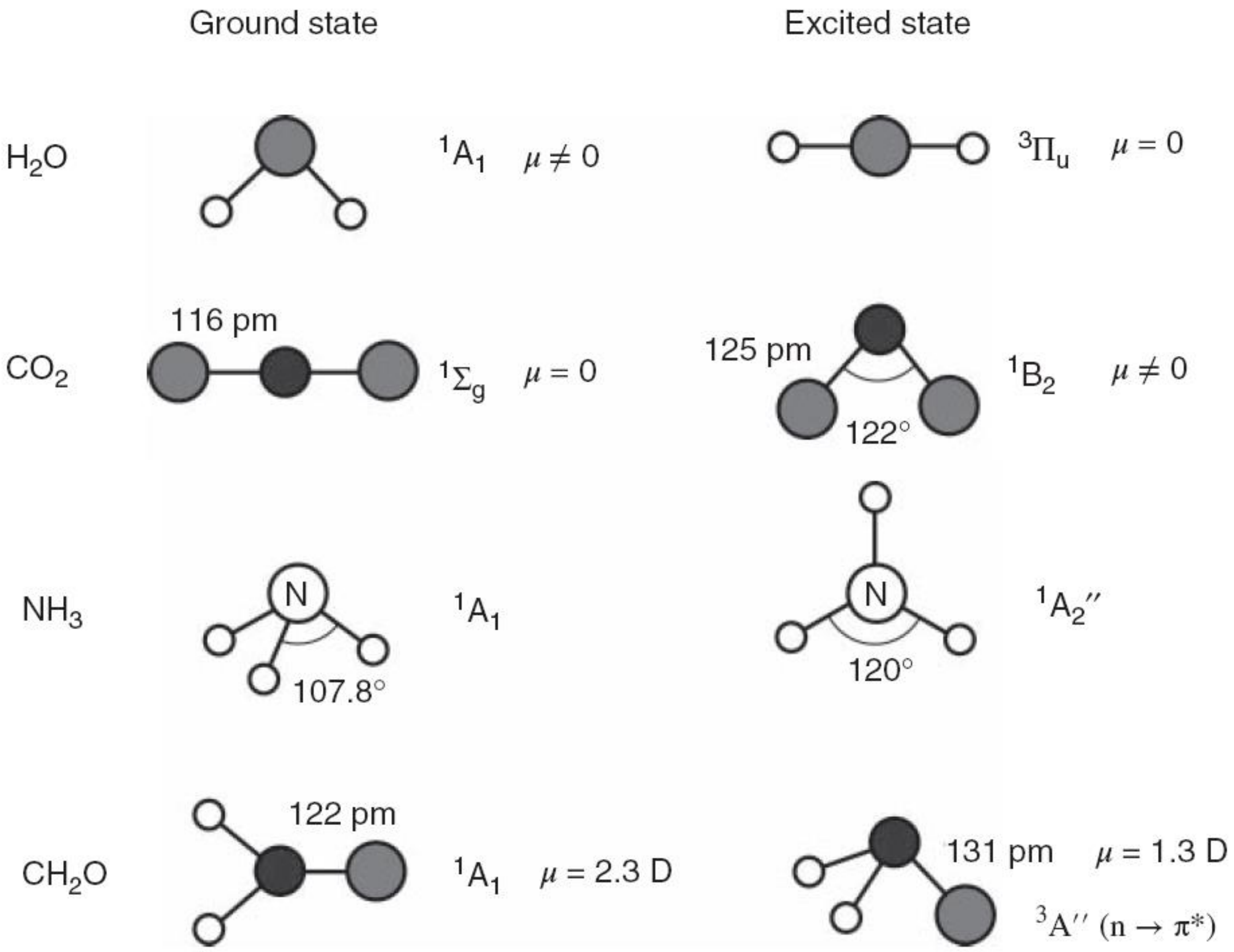


Nelle reazioni fotochimiche la selettività è assicurata dalle peculiari proprietà elettroniche dello stato eccitato.

Geometria

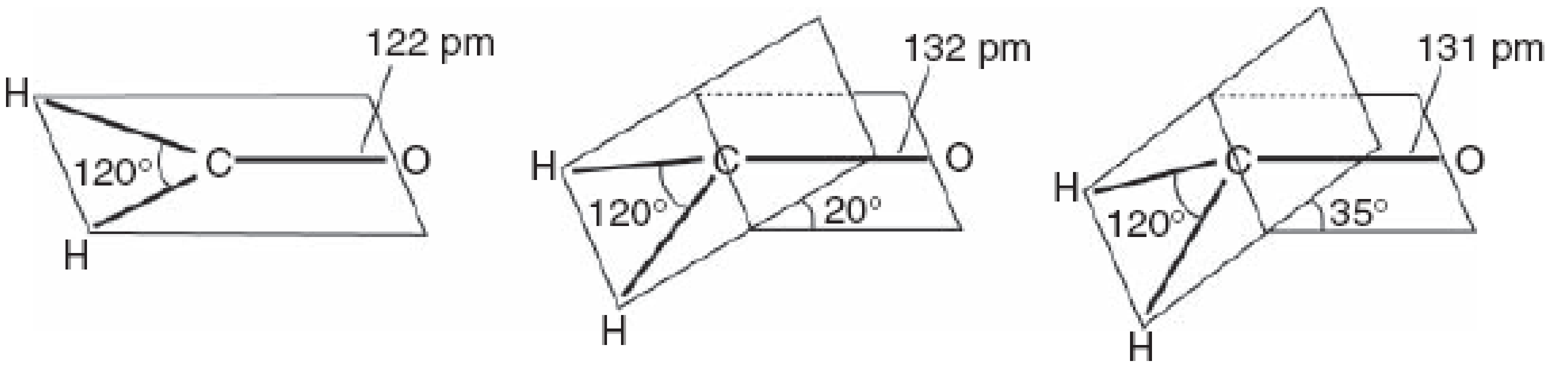
Se la configurazione elettronica dello stato eccitato è significativamente diversa da quella dello stato fondamentale, allora è ragionevole attendersi che la geometria dello stato eccitato sia diversa da quella dello stato fondamentale.

Geometria


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
$^3A''$ ($n \rightarrow \pi^*$)

Momento di dipolo

Il momento di dipolo nello stato elettronico eccitato può essere diverso che nello stato fondamentale, come conseguenza sia della variazione di geometria, che della semplice redistribuzione degli elettroni.

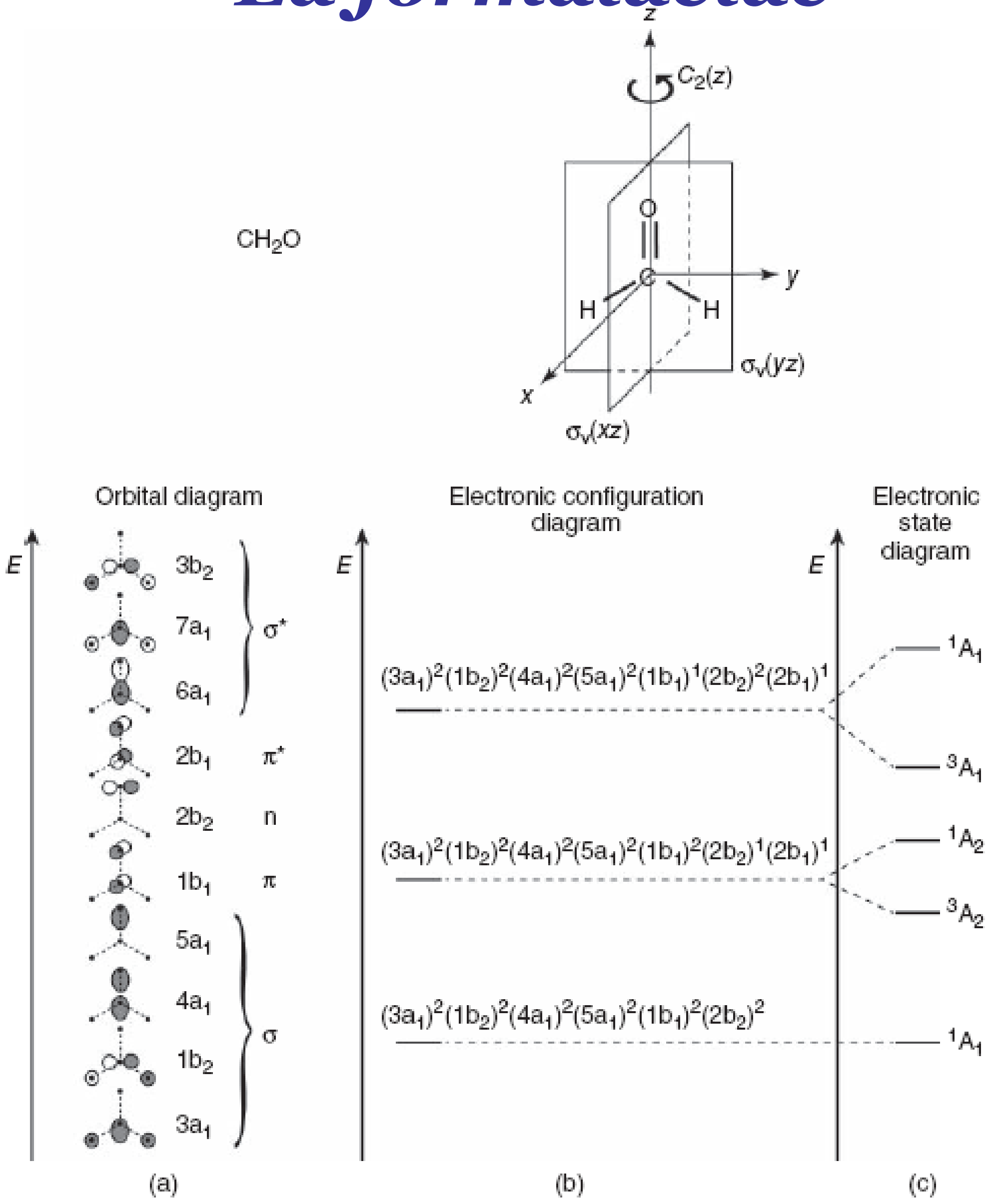


$^1A_1$ (a) Planar, $\mu = 2.3$ D

$^1A_2\ (n,\pi^*)$ (b) Bent, $\mu = 1.6$ D

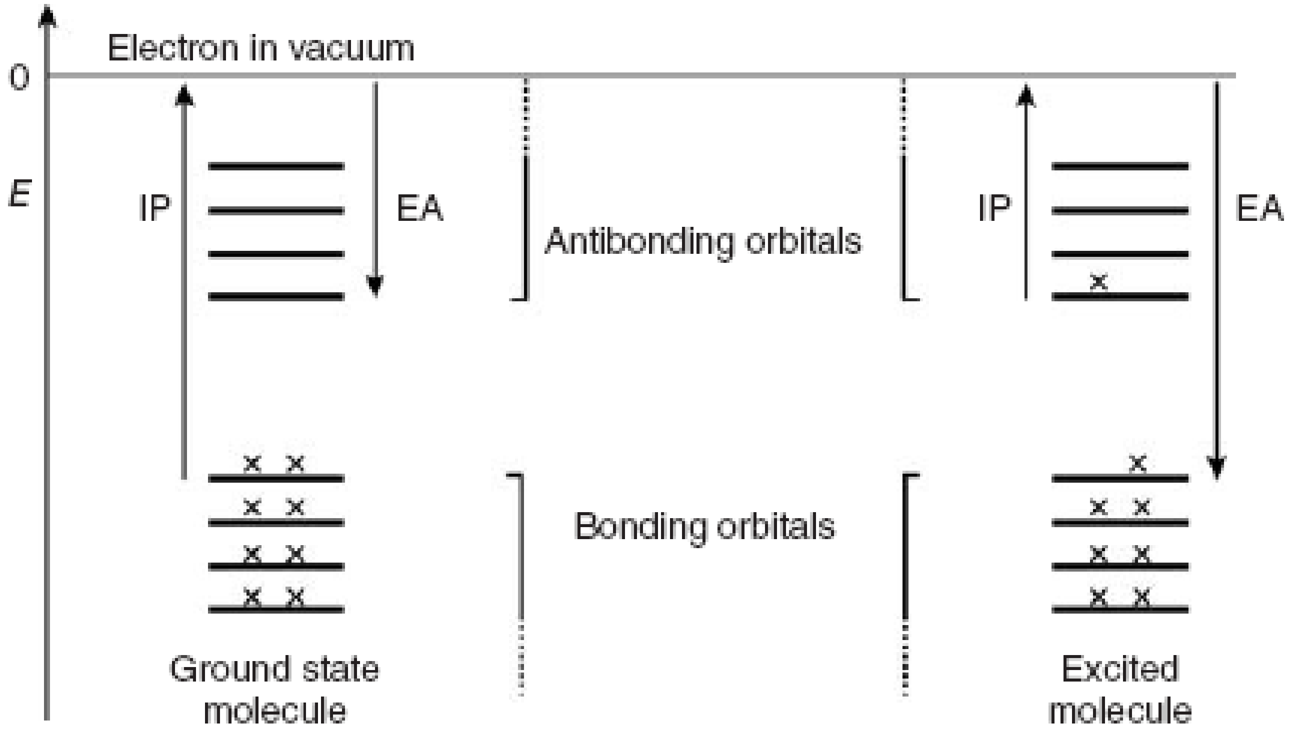
$^3A_2\ (n,\pi^*)$ (c) Bent, $\mu = 1.3$ D

La formaldeide



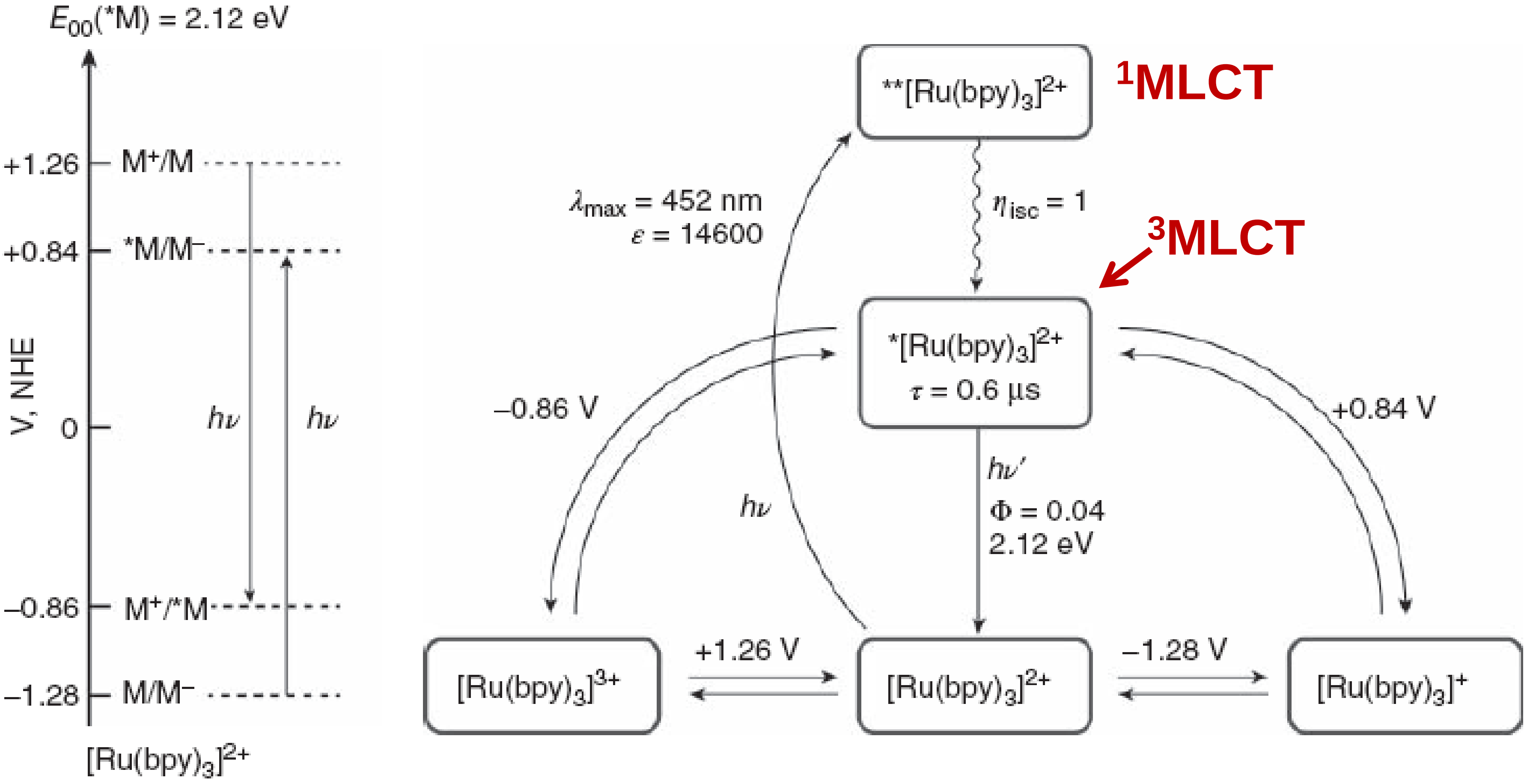
Trasferimento di elettroni

Le molecole nel loro stato elettronico eccitato sono sia dei migliori donatori che dei migliori accettori di elettroni che la stessa specie nello stato fondamentale.



Elettrochimica dello stato eccitato

$^{3}\{[\mathrm{RuIII(bpy)_2(bpy^{-})}]^{2+}\}^{*}$



^{1}MLCT

^{3}MLCT

agente riducente migliore per 2.12 V (1.26 V + 0.86 V)

agente ossidante migliore per 2.12 V (0.84 V + 1.28 V)

Processi possibili per lo stato eccitato $^{3}\{[\mathrm{RuIII}(\mathrm{bpy})_2(\mathrm{bpy}^{-})]^{2+}\}^{*}$

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

agente ossidante migliore per 2.12 V (0.84 V + 1.28 V)

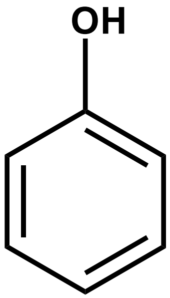
$$*\,[\mathrm{Ru(bpy)_3}]^{2+} + \mathrm{Q} \rightarrow [\mathrm{Ru(bpy)_3}]^{+} + \mathrm{Q}^{+}$$ *reductive quenching*

agente riducente migliore per 2.12 V (1.26 V + 0.86 V)

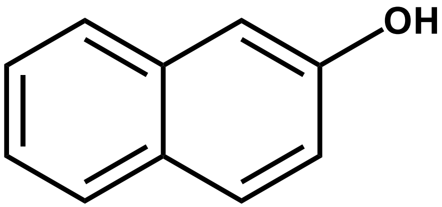
$$*\,[\mathrm{Ru(bpy)_3}]^{2+} + \mathrm{Q} \rightarrow [\mathrm{Ru(bpy)_3}]^{3+} + \mathrm{Q}^{-}$$ *oxidative quenching*

Trasferimento di protoni

La ridistribuzione di carica dovuta all’assorbimento di luce influenza il comportamento acido-base di una molecola.

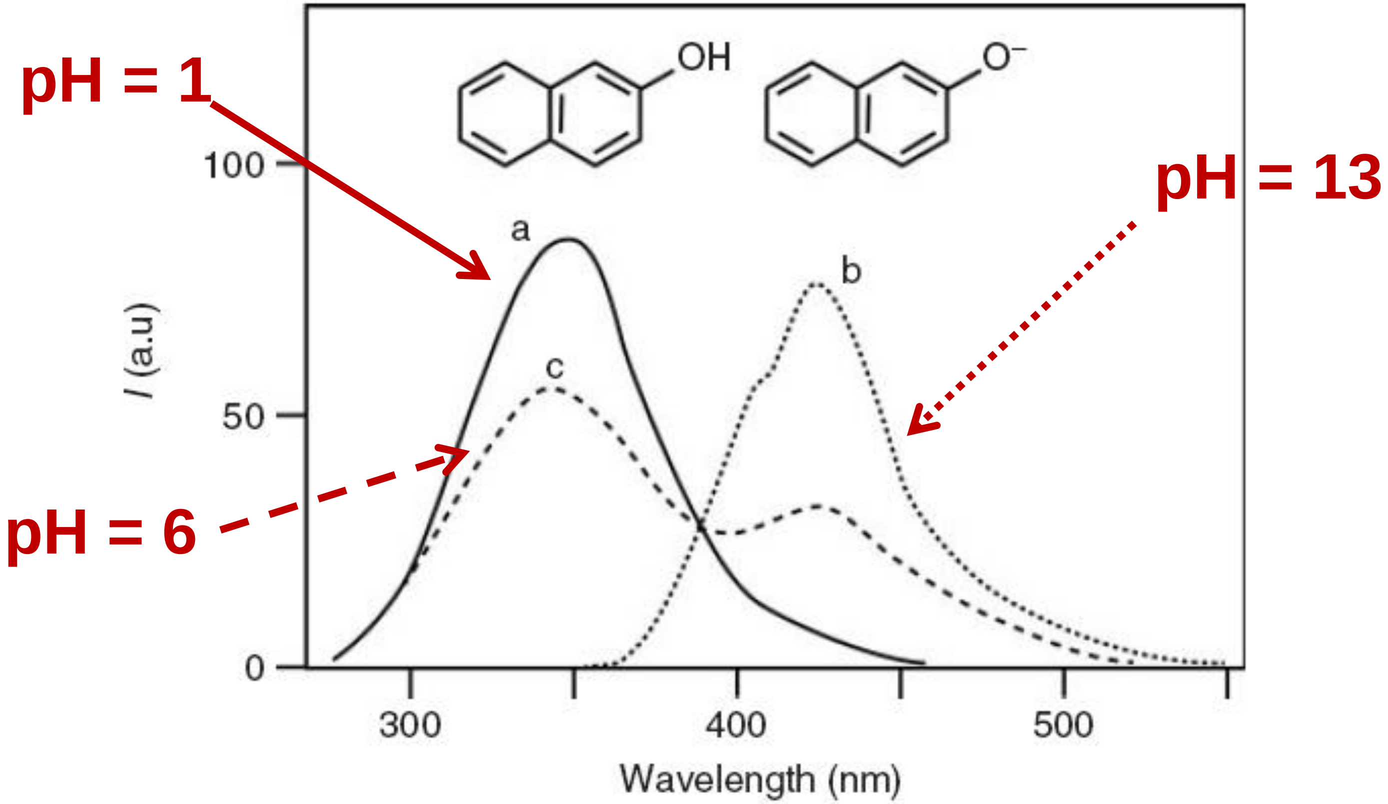


$pK_a\,(S_0) = 10$ **$pK_a\,(S_1) = 4$**



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

Trasferimento di protoni

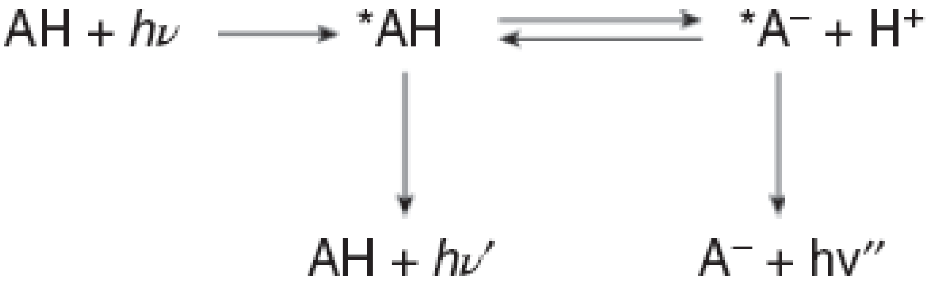


pH = 1

pH = 13

pH = 6

Reazione adiabatica



$$\begin{tikzcd}
AH + h\nu \arrow[r] & {}^{*}AH \arrow[r, shift left] \arrow[d] & {}^{*}A^{-} + H^{+} \arrow[l, shift left] \arrow[d] \\
 & AH + h\nu' & A^{-} + h\nu''
\end{tikzcd}$$

Eccimeri ed ecciplessi

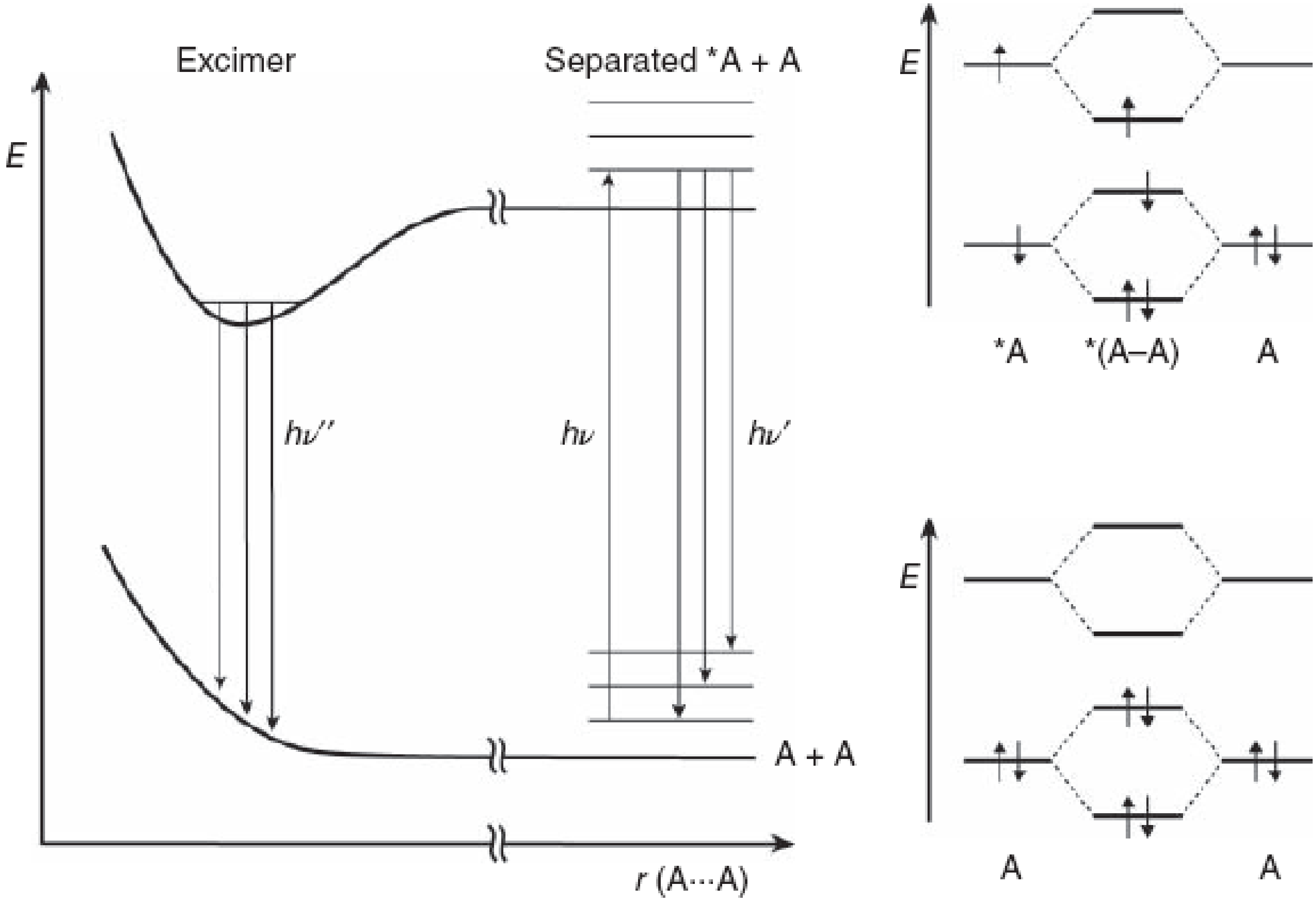
Eccimero: $^{*}\mathrm{A} + \mathrm{A} \rightarrow {}^{*}[\mathrm{A} - \mathrm{A}]$ *excimer*

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

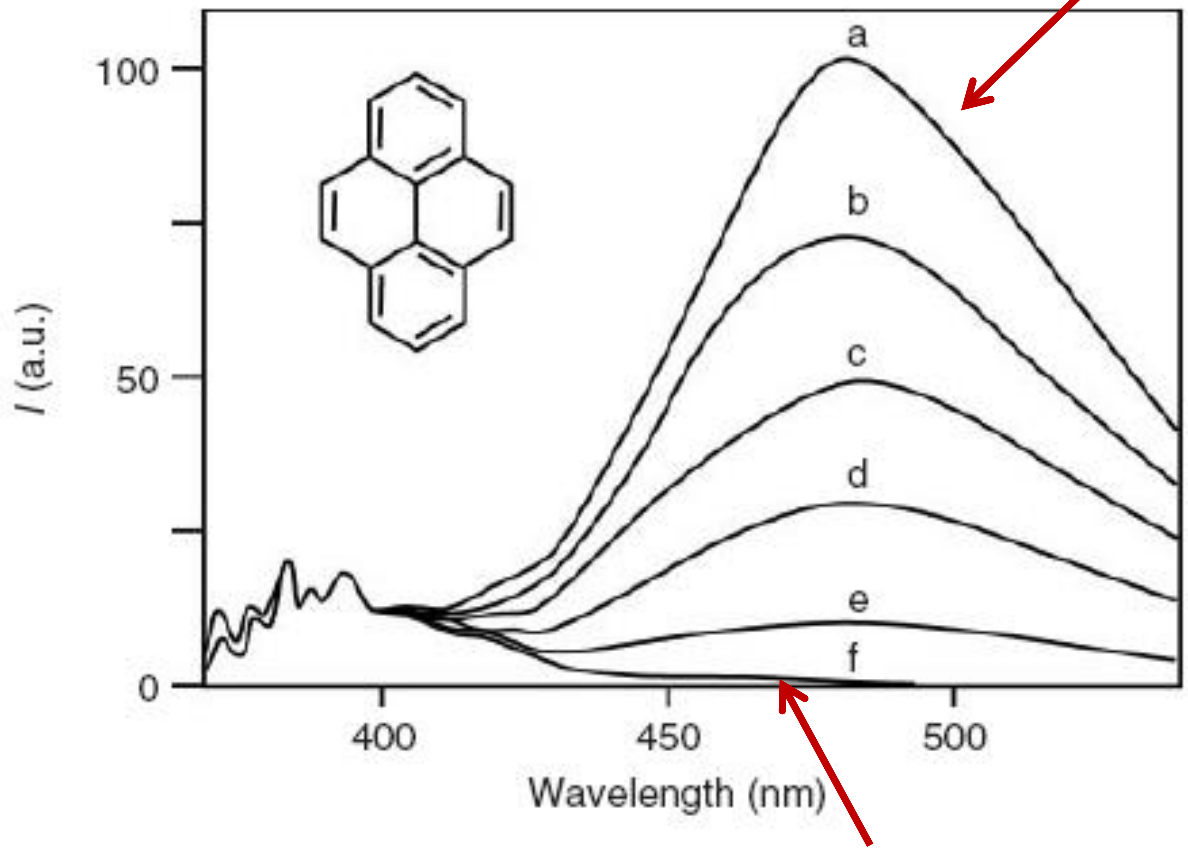
Ecciplesso: $^{*}\mathrm{A} + \mathrm{B} \rightarrow {}^{*}[\mathrm{A} - \mathrm{B}]$ *exciplex*

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

Eccimeri ed ecciplessi



Spettro di emissione del pirene



10^{-2} M

10^{-4} M