The Abdus Salam International Centre for Theoretical Physics

United Nations Educational, Scientific and Cultural Organization

IAEA International Atomic Energy Agency

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Winter College on Optics and Energy

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Photophysics for photovoltaics

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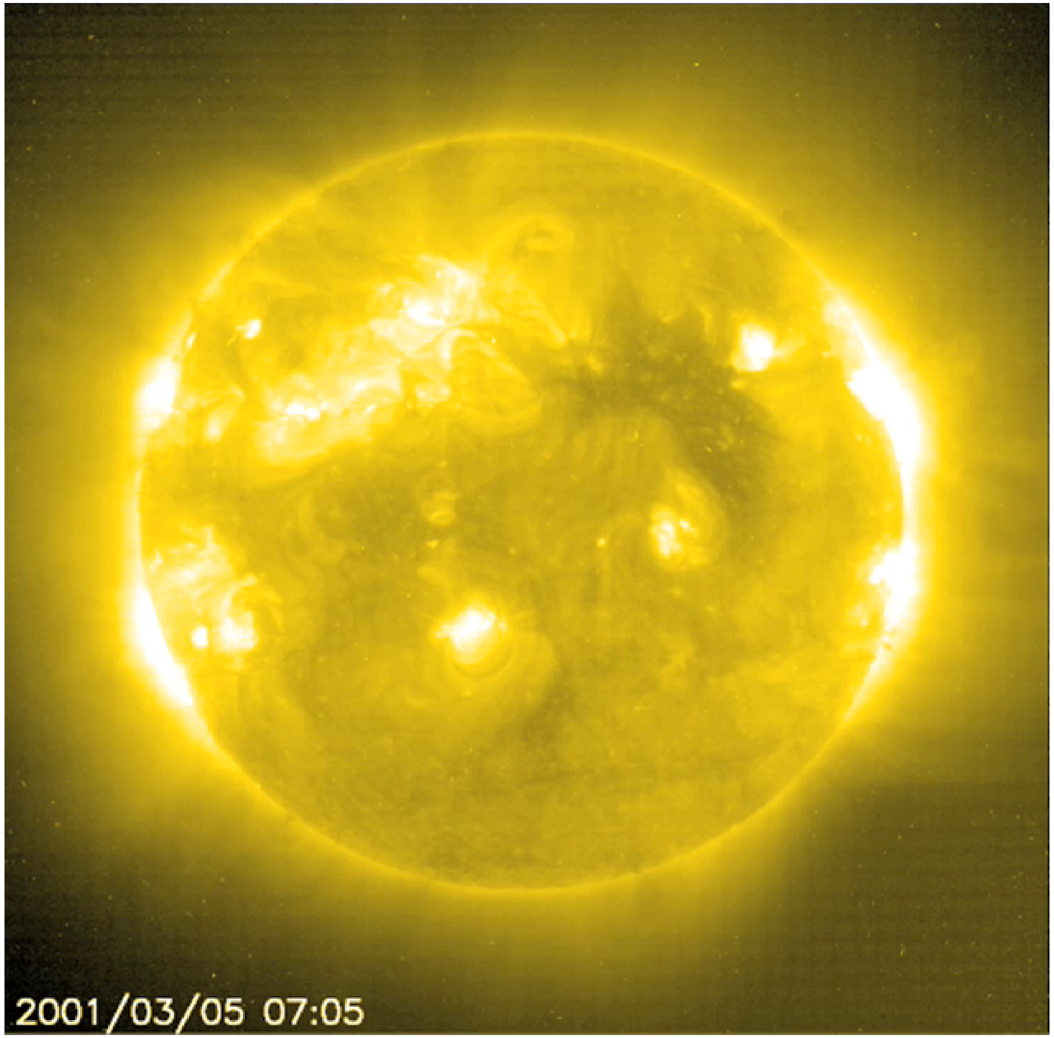
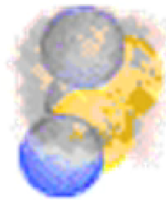
Safe, Cheap(?) Nuclear Energy





movie

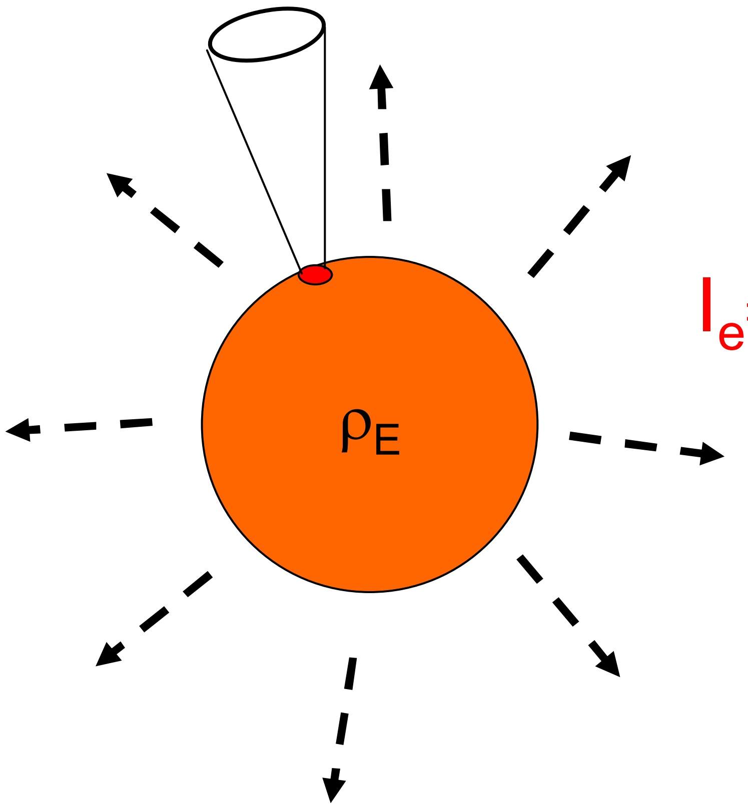
Core (15 million K), Photosphere (visible surface, 5800 K)

Is it enough?

Figure 5. The production of 20 TW of power, the world's mid-century projected demand, would require covering 0.16% of Earth's land (red squares) with 10%-efficient solar panels (courtesy of Prof. Nathan Lewis, Caltech, Pasadena).

The sun as a black body

$J_{e\Omega}=\sigma T^4/\pi$ (W/Sr m²)

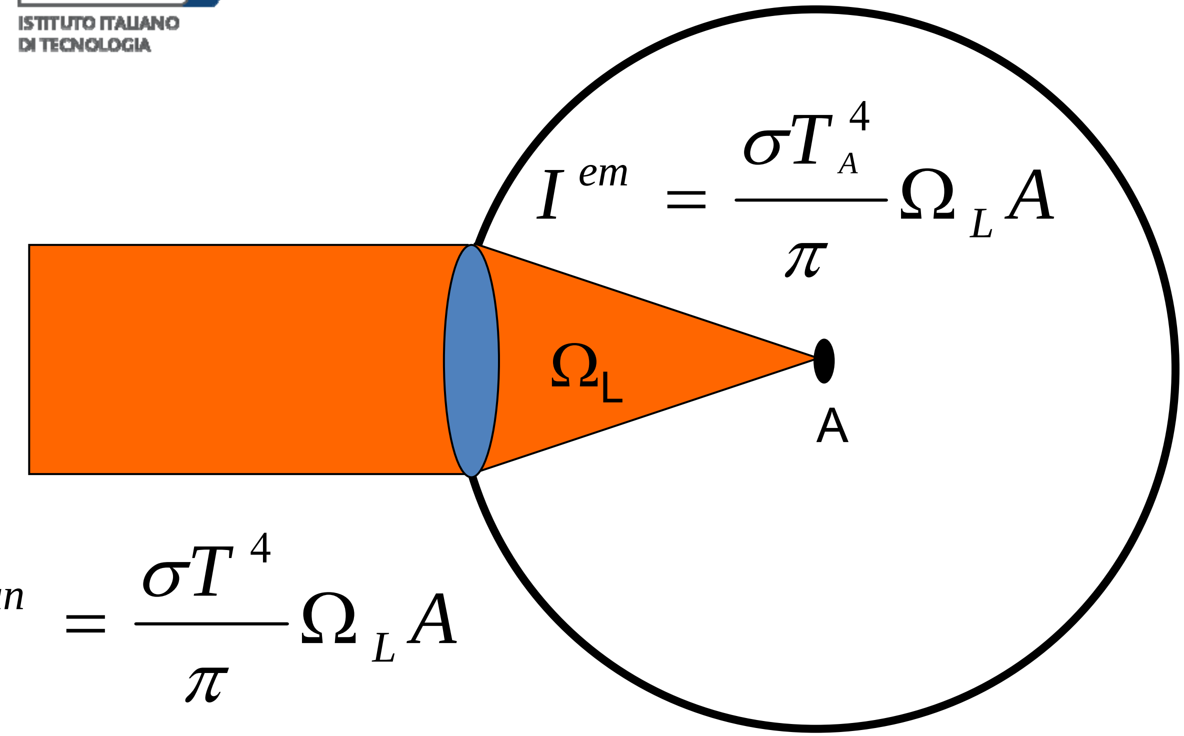


$I_e=\sigma T^4 A$ (W)

total power emitted

$J_{e\Omega}=(\rho_E/4\pi)$ x c (W/Sr m²)

Thermodynamic limit



$$I^{em} = \frac{\sigma T_A^4}{\pi}\Omega_L A$$

$$T_0 = 300\ K$$

$$T_S = 5800\ K$$

$$T_A = 2478K$$

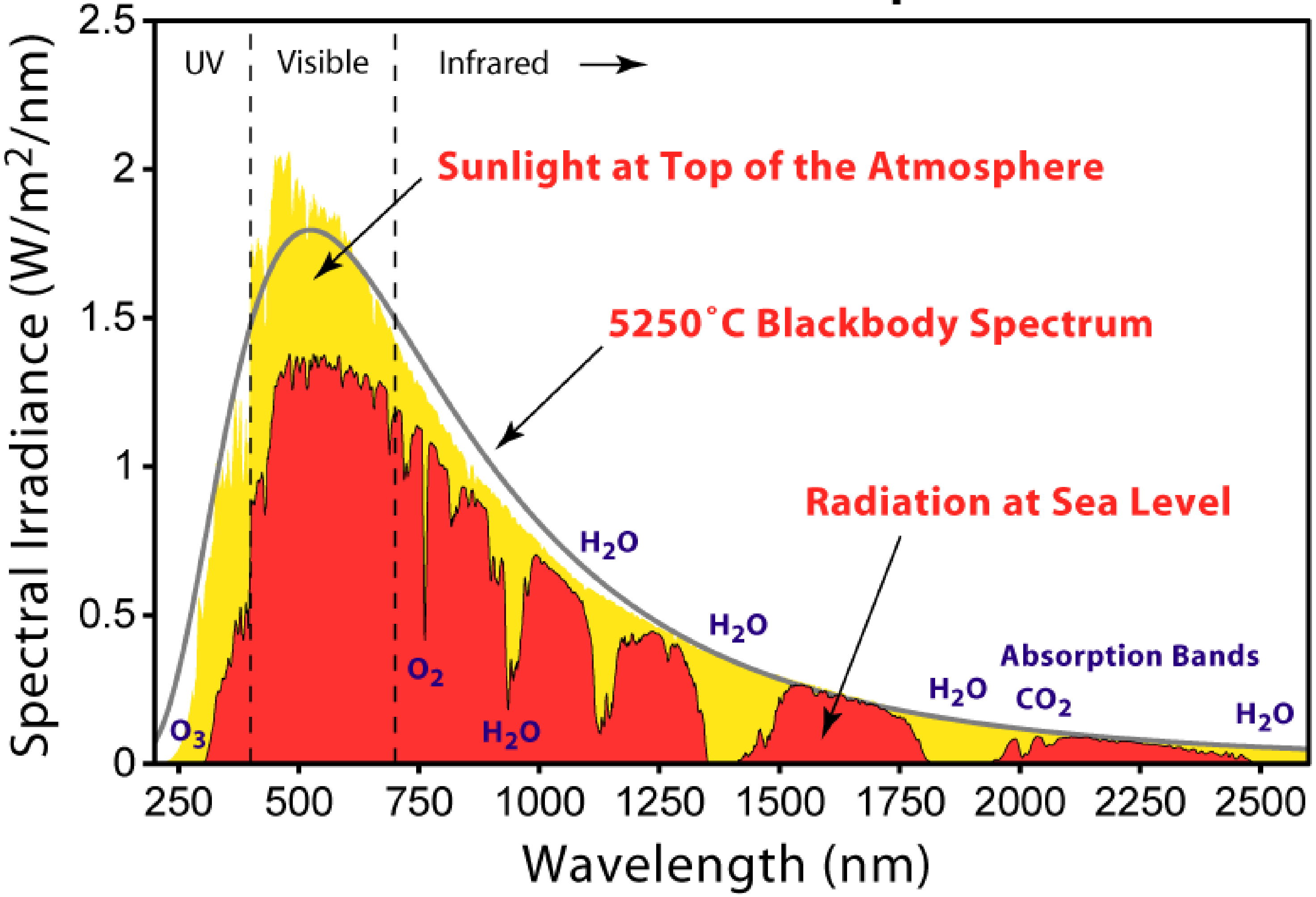
$$I^{sun} = \frac{\sigma T^4}{\pi}\Omega_L A$$

$$\eta_{abs} = \frac{I^{sun} - I^{em}}{I^{sun}} = 1 - \frac{T_A^4}{T_S^4}$$

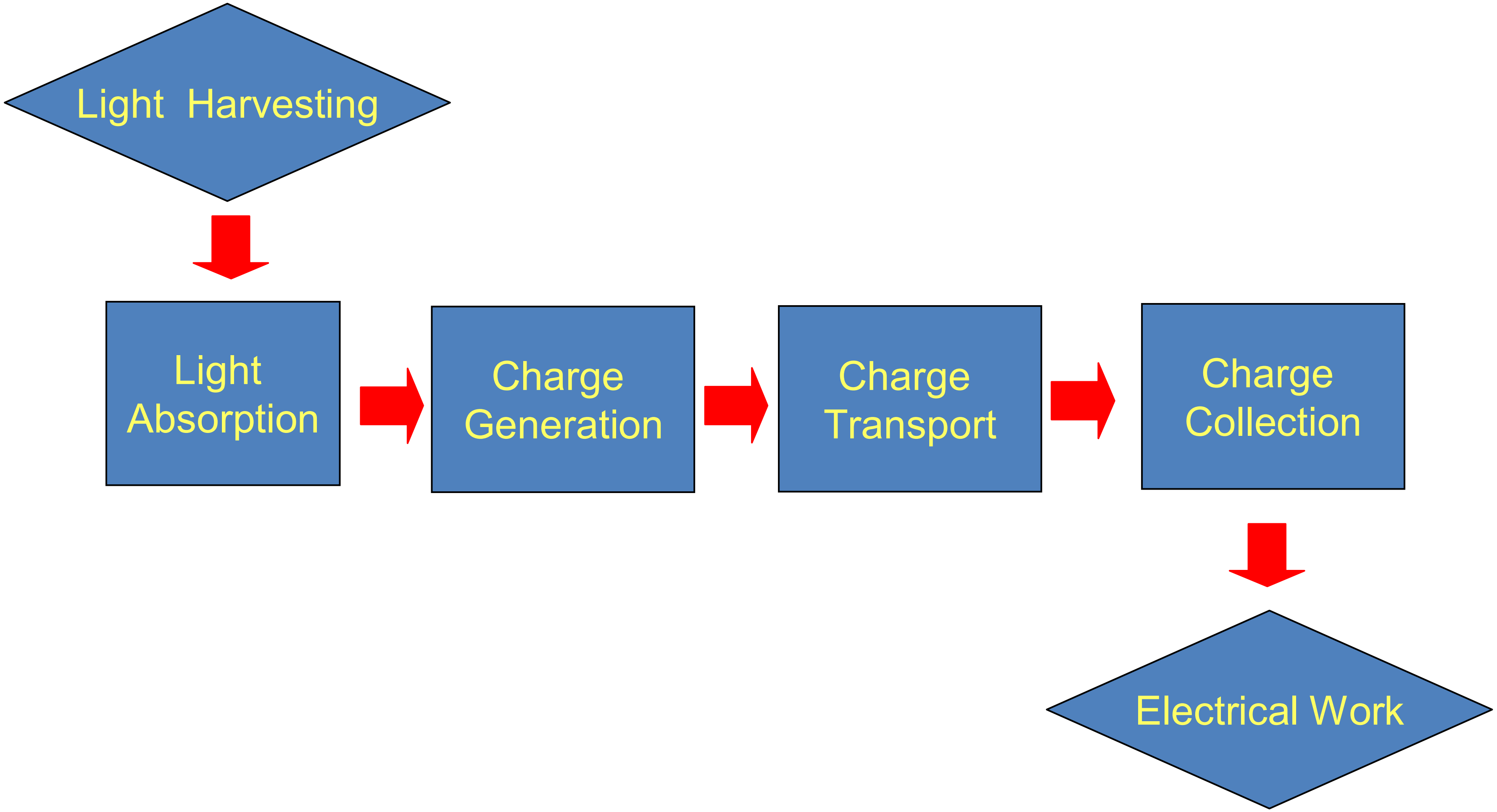
$$\eta_C = 1 - \frac{T_0}{T_A}$$

$$\eta_{TL} = \eta_{abs}\eta_C = \left(1 - \frac{T_A^4}{T_S^4}\right)\left(1 - \frac{T_0}{T_A}\right) = 85\,\%$$

Solar Radiation Spectrum



The PV lay-out



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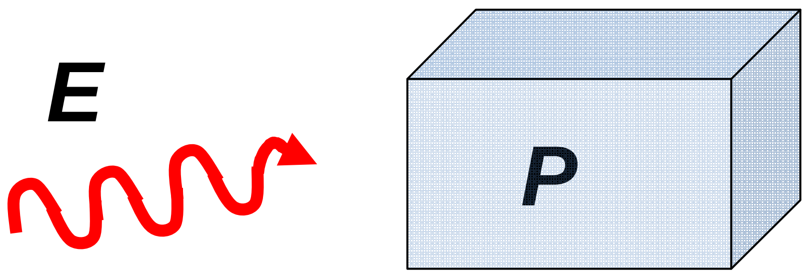
Absorption

The electro magnetic field interacting with a material can deposit energy at the characteristic frequency which defines the absorption spectrum.



$$\left\langle \frac{power}{volume} \right\rangle = \left\langle E_y(t)\frac{dP_y(t)}{dt} \right\rangle = \frac{1}{2}\mathrm{Re}\left[E(i\omega P)^*\right]$$

$$\langle \text{time - average} \rangle$$

$$\tilde{A}_y(t) = \mathrm{Re}\left[A_y(t)e^{i\omega t}\right]$$

P=P(E)

$$P = P^{(1)} + P^{(2)} + P^{(3)} +$$

$$P^{(1)}(\omega) = \varepsilon_0 \chi^{(1)}(\omega) E(\omega)$$

$$\chi^{(1)}(\omega) = \mathrm{Re}\,\chi^{(1)}(\omega) - i\,\mathrm{Im}\,\chi^{(1)}(\omega)$$

$$\left\langle \frac{power}{volume} \right\rangle = \frac{1}{2} \omega \varepsilon_0 \,\mathrm{Im}\,\chi^{(1)} \left|E\right|^2$$

The Lambert-Beer approximation

$$I_t = I_0 e^{-\alpha(\omega) z}$$

$$T = I_t / I_o$$

$$A = -\log_{10} T$$

$$\frac{dI}{dz} = -\left\langle \frac{power\ dissipated}{unit\ volume} \right\rangle = -\frac{1}{2}\omega\varepsilon_0 \operatorname{Im}\chi^{(1)}|E|^2$$

$$I = \frac{c\varepsilon}{2n}|E|^2$$

$$\frac{\varepsilon}{\varepsilon_0} = n^2$$

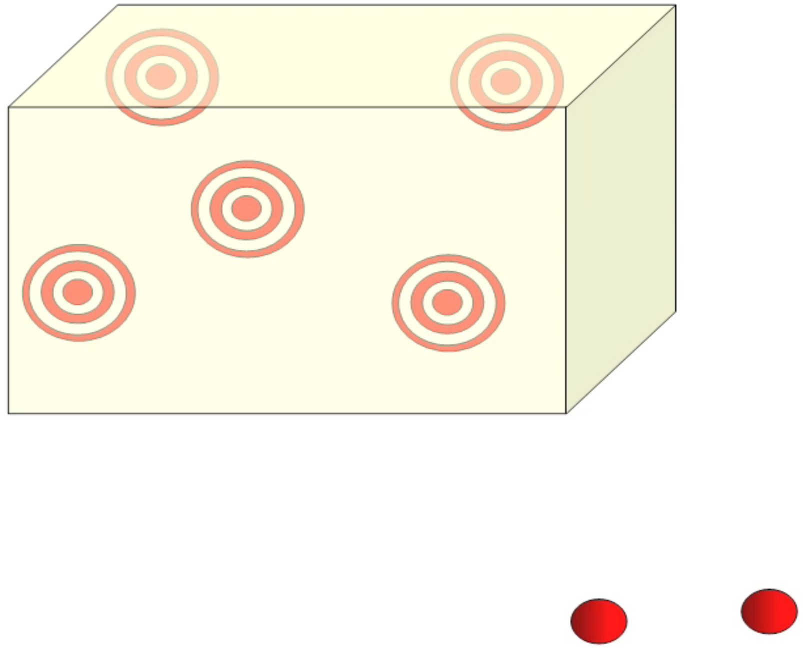
$$\alpha = \frac{\omega}{cn}\operatorname{Im}\chi^{(1)} = \sigma(\omega)\Delta N$$

POPULATION

Cross-section

The concept of cross-section

$[\sigma]=cm^2$



F = number of photons per unit area and unit time

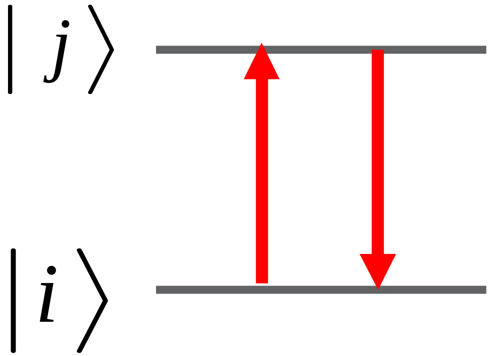
N = number of target per unit volume

σN = effective total area per unit volume [L^{-1}]

σNF = number of transition per unit time, i.e. transition rate

movie

Absorption and population

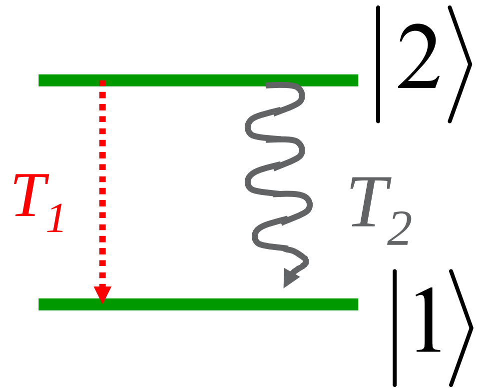


$$\alpha_{ij}(\omega) = \sigma_{ij}(\omega)(N_i - N_j)$$

$$\alpha = \sum_{i,j} \sigma_{ij}(\omega)(N_i - N_j)$$

Cross-section for the two level model

$$\sigma(\omega) = \frac{\omega}{2c}\frac{\mu^2}{\varepsilon_0 \hbar n} g(\omega)$$



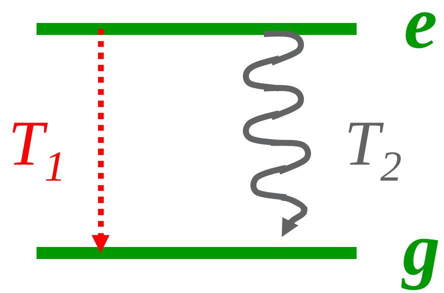
$$g(\omega) = \frac{\Delta\omega}{(\omega-\omega_0)^2 + \left(\frac{\Delta\omega}{2}\right)^2}$$

$$\Delta\omega = \frac{2}{T_2}$$

$$\mu_{12} = \langle 2|\tilde{\mu}|1\rangle = \mu_{21}^*$$

Optical Bloch Equation

$$\Delta n = N_e - N_g$$

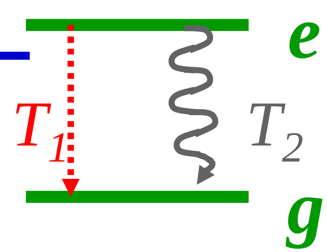


$$P = N\mu_{ge}$$

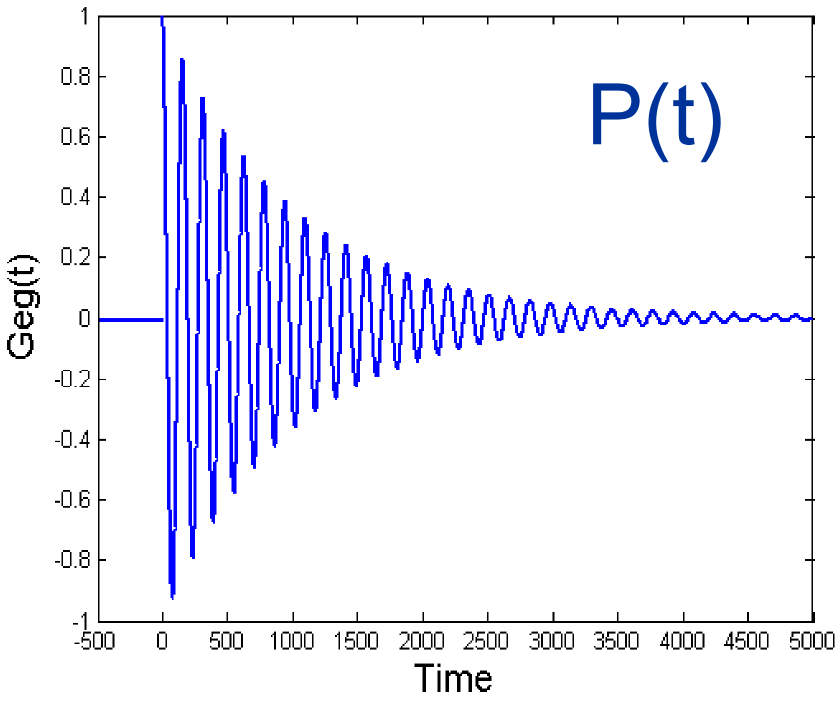
$$\frac{\partial \Delta n}{\partial t} + \frac{\Delta n - \Delta n_0}{T_1} = -\frac{2}{\hbar\omega}\overline{E}\cdot\frac{\partial \overline{P}}{\partial t}$$

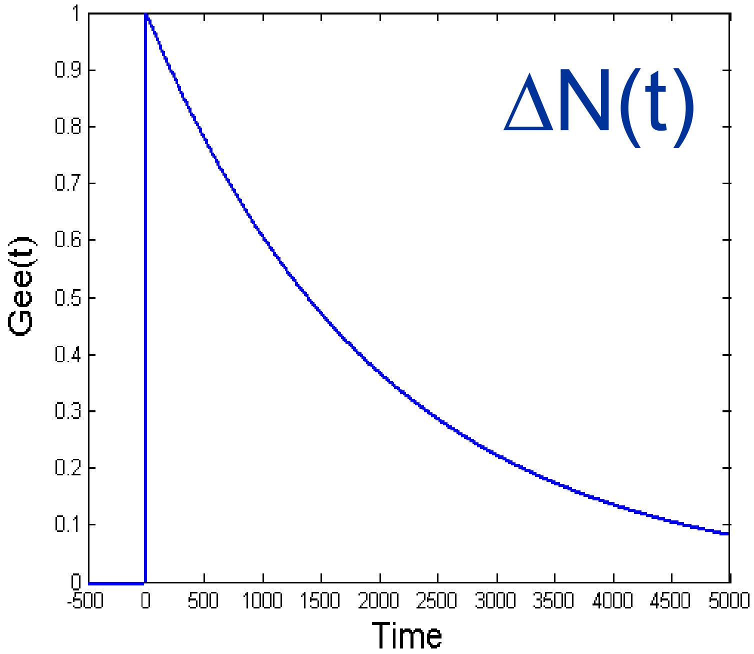
$$\frac{\partial^2 \overline{P}}{\partial t^2} + \frac{2}{T_2}\frac{\partial \overline{P}}{\partial t} + \omega^2 \overline{P} = \frac{2\omega|\mu|^2}{3\hbar}\Delta n\overline{E}$$

Impulsive response function of the material



$$G_{eg} = \frac{i}{\hbar}\vartheta(t)\exp\left(-i\omega_{eg}t - t/T_2\right) \qquad G_{ee} = \frac{i}{\hbar}\vartheta(t)\exp\left(-t/T_1\right)$$





Adibatic Approximation and Frank-Condon Overlap

$m_e/M_N << 1$ or $\Delta E_e/\Delta E_N >> 1$ ➡ $\Psi = \psi(q,Q)\phi(Q)$

$$\tilde{\mu} = \langle \psi_e(q,Q)\phi_{en}(Q) | \mu_{eg}(q) | \psi_g(q,Q)\phi_{gl}(Q) \rangle$$

Electronic contribution

$$\langle \psi_e(q,Q) | \mu_{eg}(q) | \psi_g(q,Q) \rangle = \tilde{\mu}_{eg} + \mu'_{eg} Q + \ldots$$

Condon approximation:

$$\alpha \propto \left| \langle \psi_e(q,Q) | \mu_{eg}(q) | \psi_g(q,Q) \rangle \langle \phi_{en}(Q) \phi_{gl}(Q) \rangle \right|^2$$

$$\alpha \propto \left| \tilde{\mu}_{eg} \right|^2 FC(n,l)\, g\left(\omega - \omega_{en/gl}\right)$$

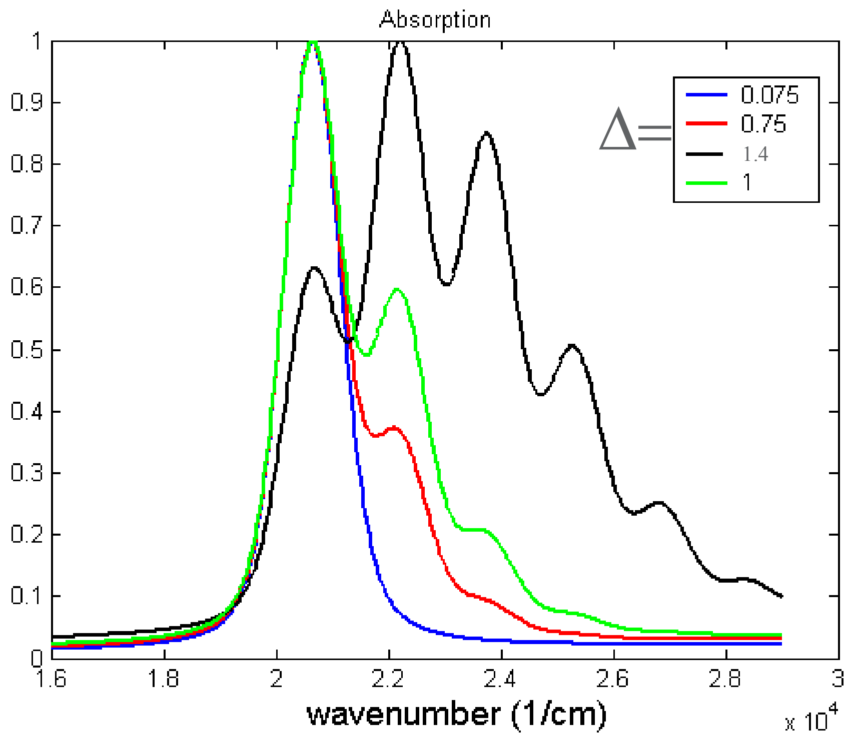
FC: Displaced Harmonic Oscillators (T=0)

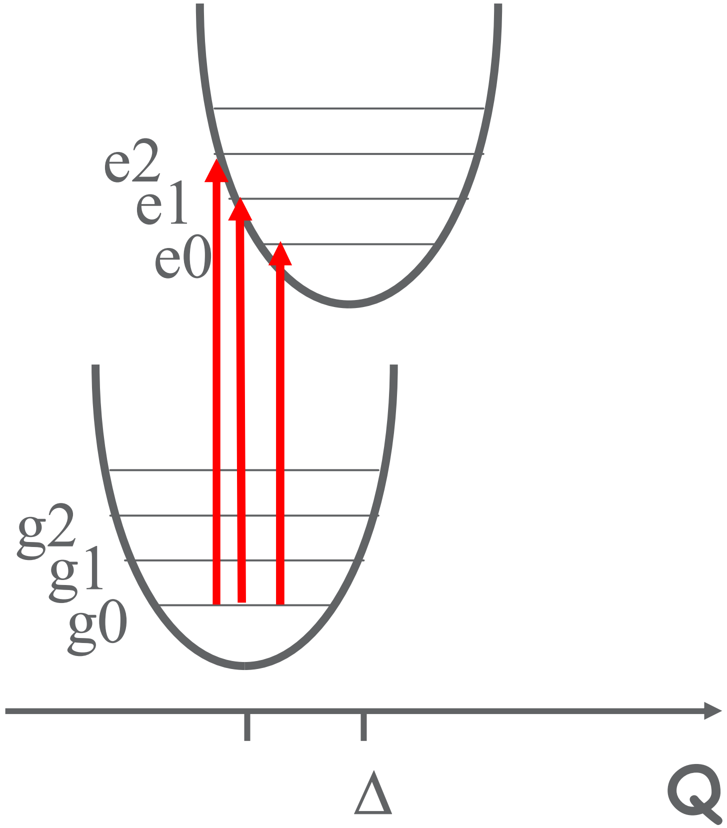
FC

$$I_{n0} \propto \left|\tilde{\mu}_{eg}\right|^2 \frac{e^{-S} S^n}{n!} g(\omega - \omega_{en/g0})$$

$$\left(\frac{I_{01}}{I_{00}} = S\right)$$

$$S = \frac{\Delta^2}{2} \qquad \Delta = \left(\frac{m\,\omega}{\hbar}\right)^{1/2} \delta Q$$





Molecular absorption cross-section

Adiabatic approximation $\Psi = \psi(q,Q)\phi(Q)$

Dipole allowed transition $\mu = \langle \psi_e | \hat{\mu} | \psi_g \rangle \neq 0$

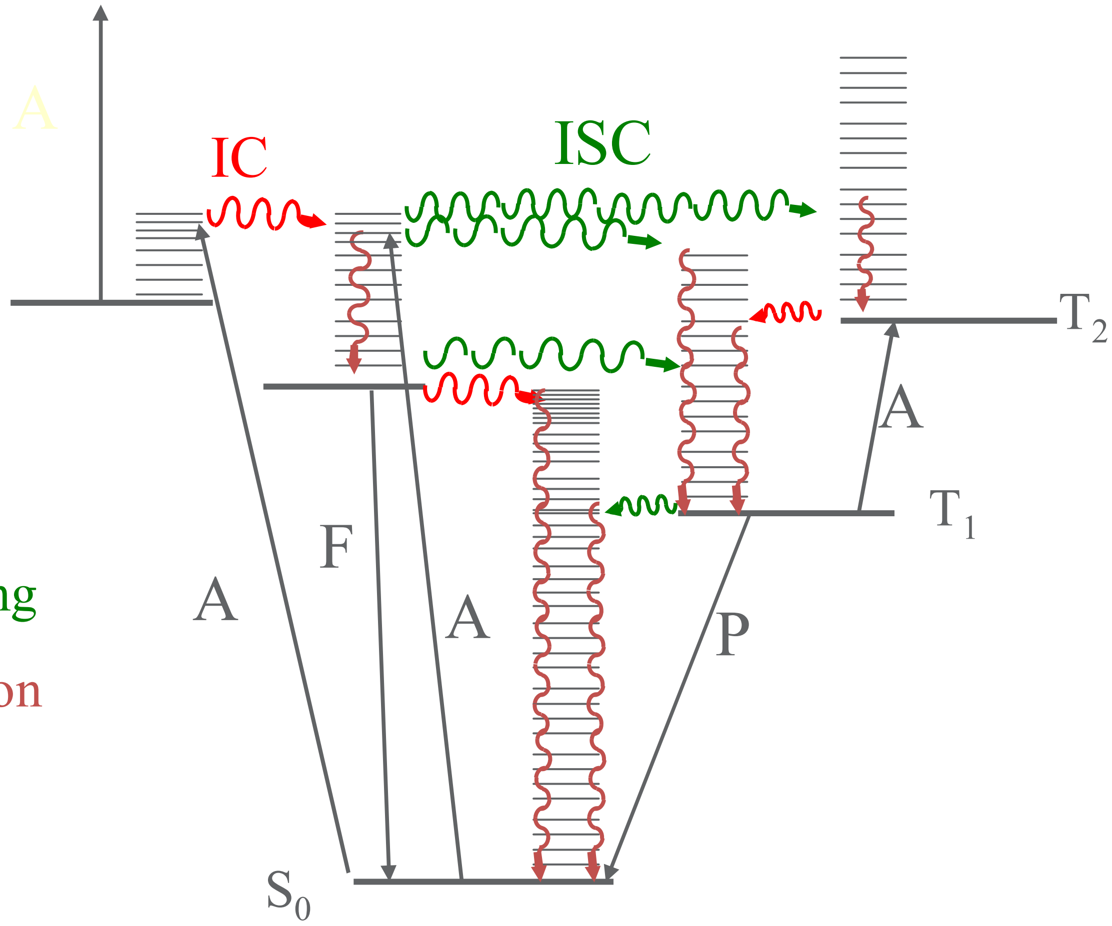
Condon approximation $\mu(Q) = \mu_0$

$$\sigma_A = \frac{\omega}{c}\frac{\mu_0^2}{2\varepsilon_0}\sum_i B_i \sum_f \frac{1}{\pi}\frac{\left|\langle \phi_f | \phi_i \rangle\right|^2 \Gamma}{(E_F - E_i - \hbar\omega)^2 + \Gamma^2}$$

$B_i \equiv \mathit{Boltzman\ factor}$

Jablonski diagram

unimolecular photophysical processes



IC≡ Internal Conversion

ISC ≡ Inter System Crossing

VR ≡ Vibrational Relaxation

A ≡ Absorption

F ≡ Fluorescence

P ≡ Phosphorescence

Dynamics comes in

For a given process "i" a monomolecular rate k_i is defined, $\mathbf{k_i = 1/\tau_i\ (s^{-1})}$

The total rate is $k_T = k_0 + \sum_i k_i$, efficiency $\eta_i = \frac{k_i}{k_T}$

$k_{VR} \approx 10^{12}\text{-}10^{13}\ s^{-1}$

$k_{IC} \approx 10^{12}\text{-}10^{14}\ s^{-1}\ (S_n \rightarrow S_1)$

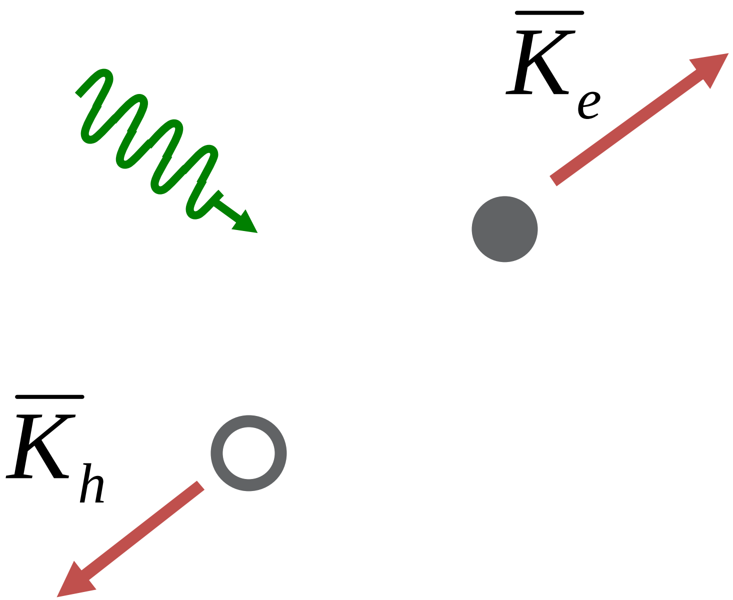
$k_{IC} \approx 10^{8}\text{-}10^{10}\ s^{-1}\ (S_1 \rightarrow S_0)$

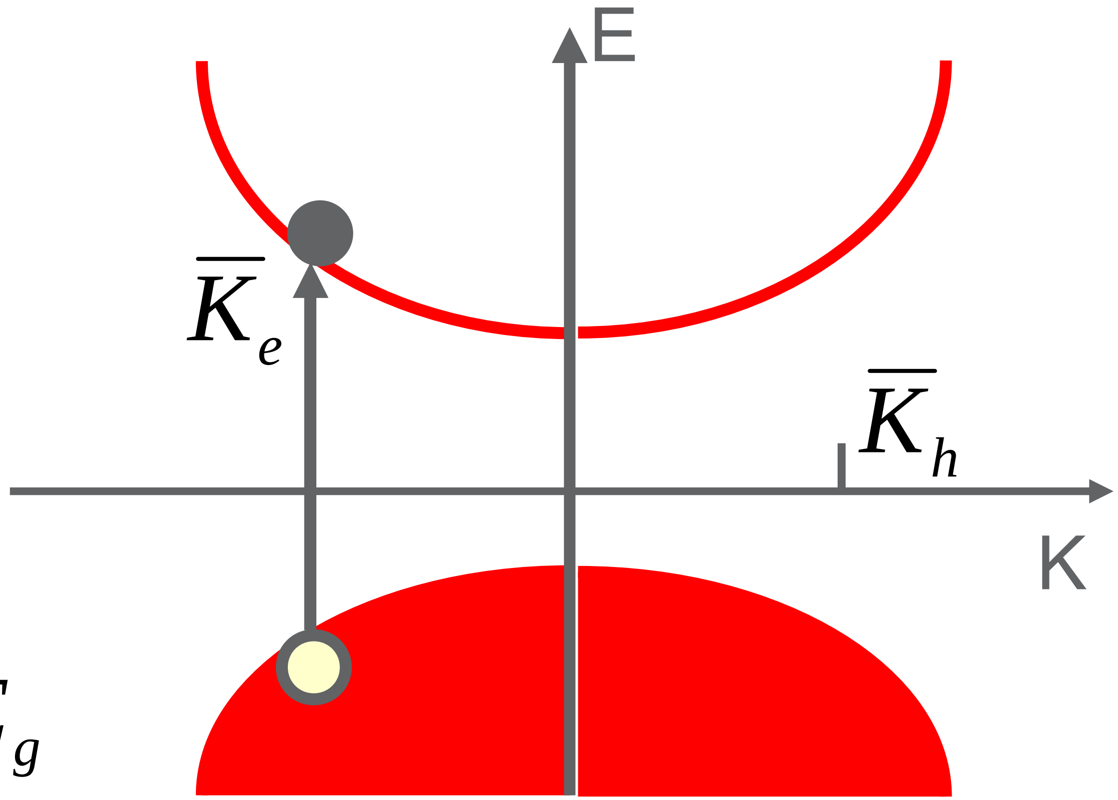
$k_{ST} \approx 10^{6}\text{-}10^{11}\ s^{-1}\ (S_1 \rightarrow T_1)$

$k_{TS} \approx 10^{4}\text{-}10^{1}\ s^{-1}\ (T_1 \rightarrow S_0)$

CHARGE PHOTO GENERATION (CPG)

Band-like semiconductor: CPG





$$\overline{K}_h + \overline{K}_e = 0$$

$$E_e + E_h = h\upsilon > E_g$$

Charge photo-generation

$$\eta = \frac{n.(e-h)}{n.\,photons}$$

CB-VB

Xtal, Inorganic

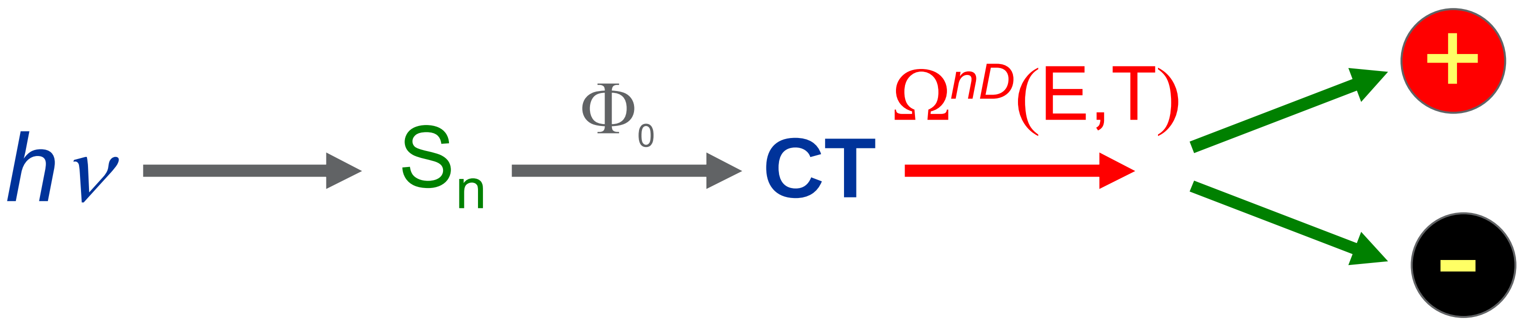
$$\eta \approx 1$$

$$h\nu \longrightarrow e^{+} - h^{-}$$

Localized state

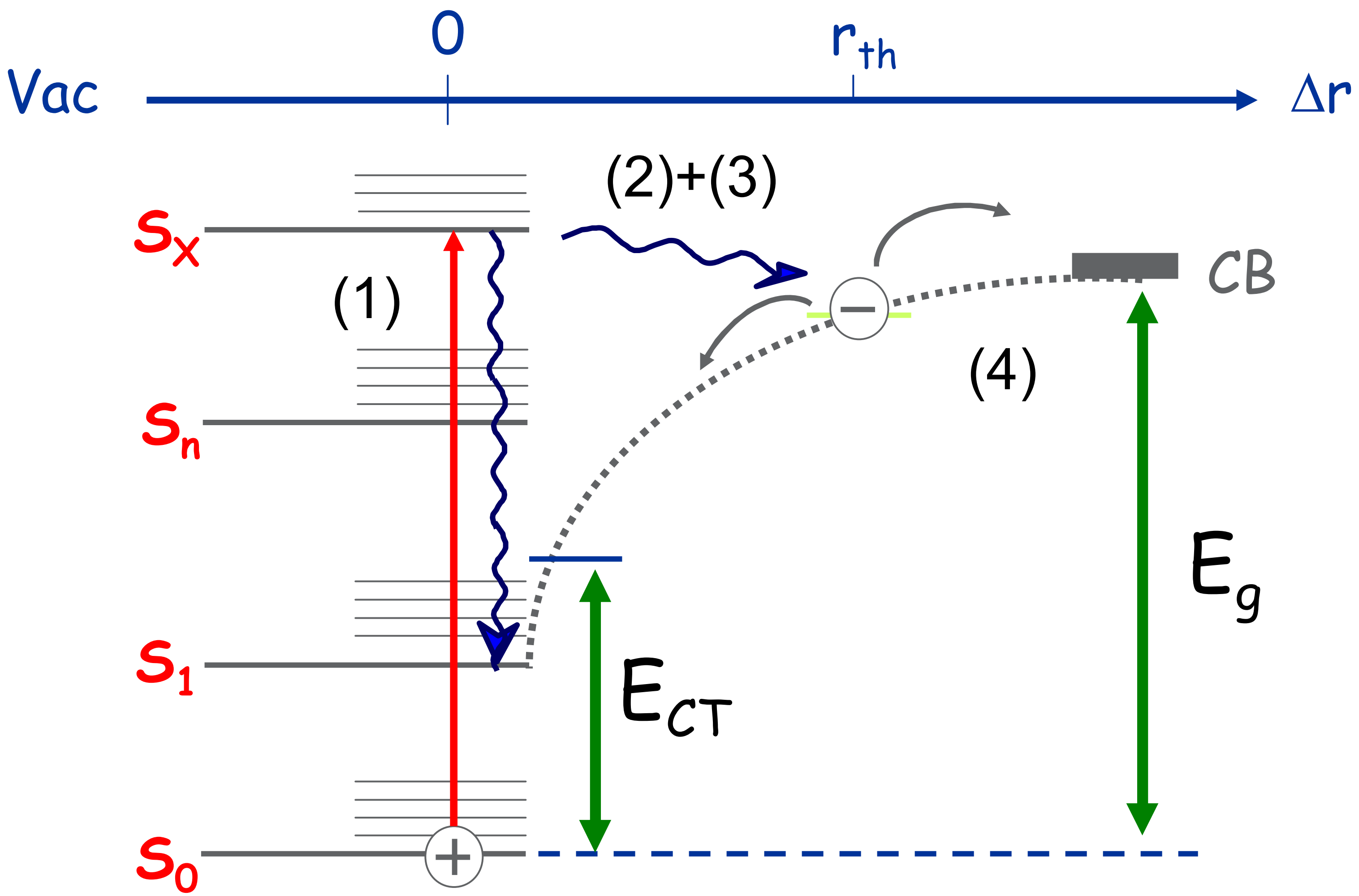
Amorphous, Organic

$$\eta = \Phi_0 \Omega << 1$$

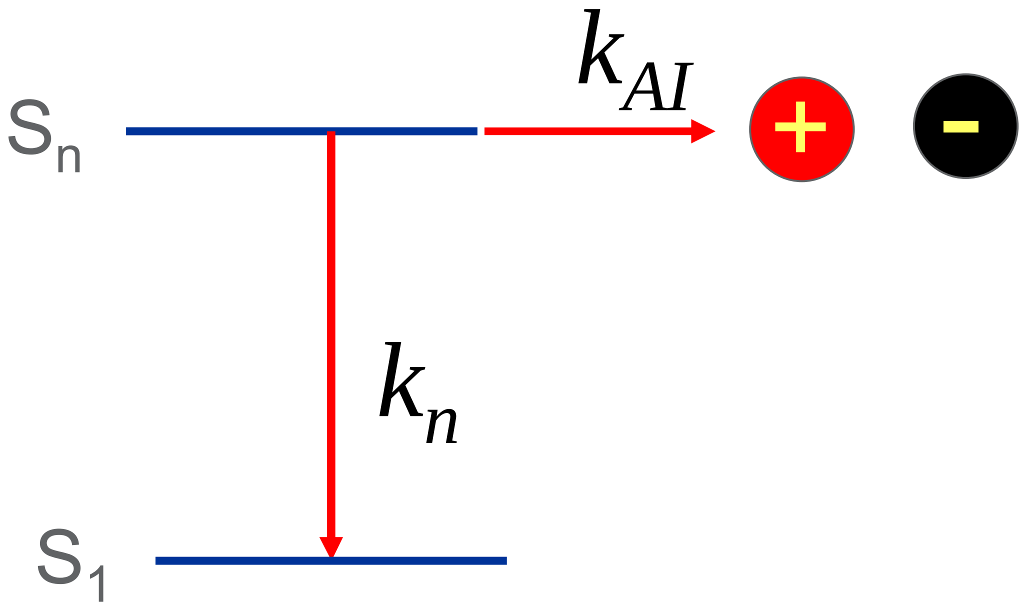


The multi-step process:

(1) Abs → (2) AI →(3) Thermalization → (4) Dissociation



Auto Ionization



Inorganic Amorphous Semicond $\Phi_0 = 1$

Organic Semicond $\Phi_0 << 1$

$$\Phi_0 = \frac{k_{AI}}{k_{AI} + k_n}$$

Critical Parameters

$$\Delta E = h\nu - E_{CT}$$ Excess energy

$$r_{th} = \sqrt{D\tau_{th}}$$ Thermalization distance

$$\tau_{th} \cong \frac{\Delta E}{h\nu_p^2} \quad \Rightarrow \quad r_{th} \cong \frac{D \cdot \Delta E}{h\nu_p^2}$$

Activation Energy:

$$E_A = \frac{e^2}{4\pi\varepsilon r_{th}}$$

Coulomb radius:

$$r_C = \frac{e^2}{4\pi\varepsilon KT}$$

ONSAGER model

Random Walk under mutual Coulomb attraction and External field

$$\frac{\partial n(\bar{r},t)}{\partial t} = \frac{kT}{e}\mu\nabla\cdot\left(e^{-U/KT}\nabla\left(ne^{U/KT}\right)\right)$$

$$U(r) = -\frac{e}{4\pi\varepsilon r} - eEr\cos\vartheta$$

n = density of diffusing particles

Boundary condition: r=0 is a sink (RECOMBINATION)

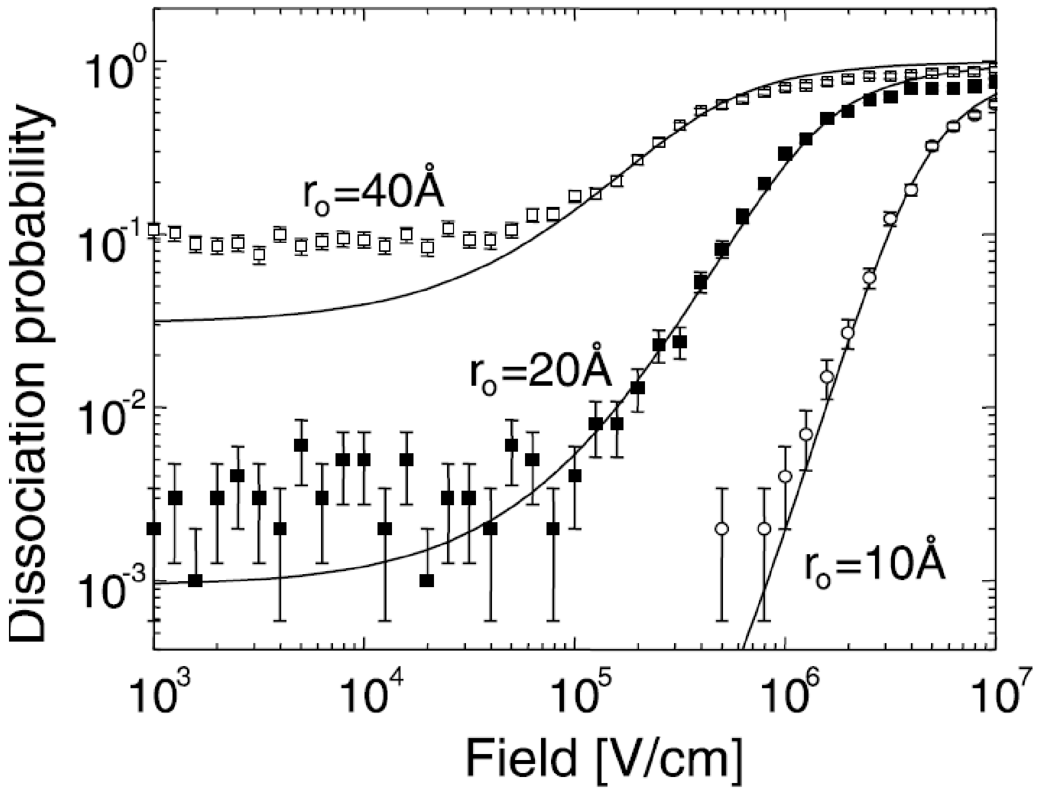
$n(r,0) = g(r_{th})$ *Initial condition*

3D ONSAGER solution $\eta = \Phi_0 \Omega$

$$\Omega^{3D} = e^{-r/r_{th}}\left[1 + \frac{e}{KT}\frac{r_c E}{2!} + \ldots\ldots\ldots\ldots\right.$$

Ω=escape probability

Chemical Physics Letters 398 (2004) 27–31



Weak Field:

$$\Omega^{3D} = A(T)e^{-r/r_{th}} \approx \Omega_0$$

Strong Field:

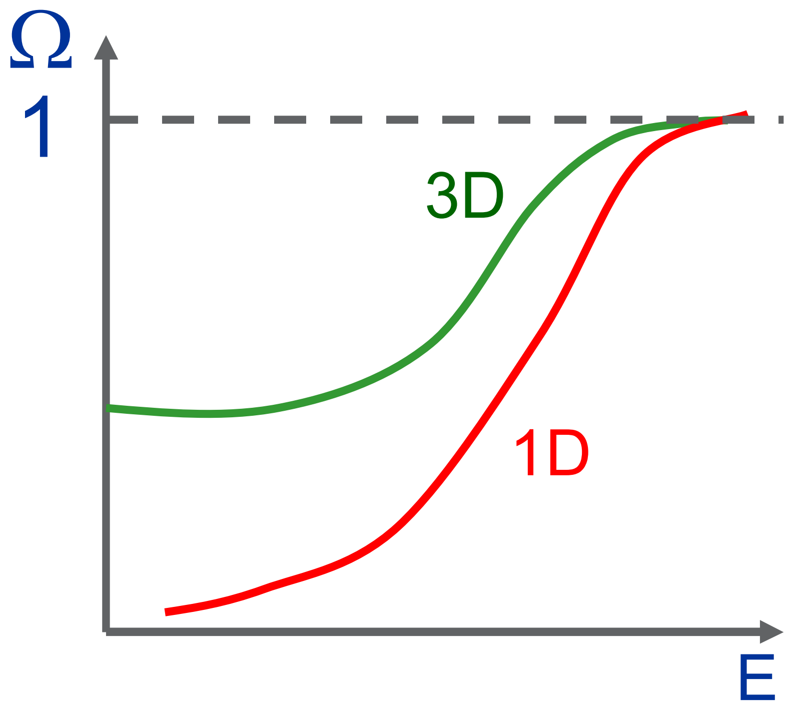
$$\Omega^{3D} \propto E \xrightarrow[E\to\infty]{} 1$$

Onsager behavior

$r_{th}=r_{th}(h\nu)$:

$r_{th} < r_C \quad \Omega^{3D} = \Omega^{3D}(F)$

$r_{th} > r_C \quad \Omega^{3D} \sim 1$



Dimensionality

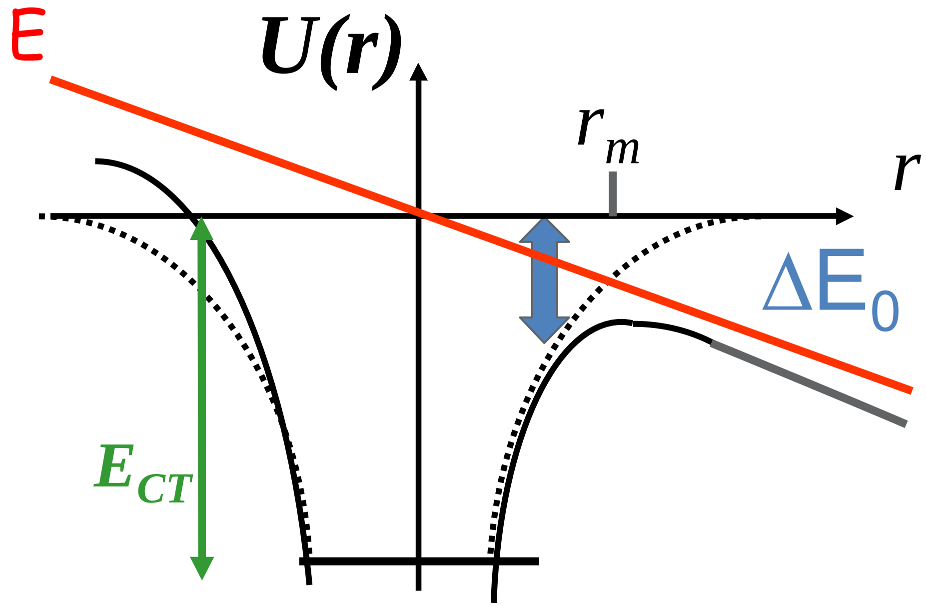
$$\Omega^{1D} = \frac{e r_{th}^2 E}{r_C KT} e^{-r/r_{th}} \propto E$$

Poole-Frenkel model

Thermal activation above Coulomb barrier

$$r_m = \sqrt{\frac{e}{\varepsilon E}}$$

$$\Delta E_0 = \sqrt{\frac{e^3 E}{\pi \varepsilon}}$$



$$E_b = E_{CT} - \Delta E_0 = E_{CT} - \beta F^{1/2}$$

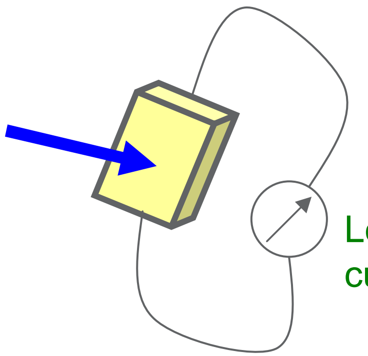
$$K_{PF} = \nu \exp\left(-\frac{E_{CT}}{KT}\right) \exp\left(\frac{\beta F^{1/2}}{KT}\right)$$

$$\Omega_{PF} = \frac{K_{PF}}{K_{PF} + K_{GPR}}$$

How to measure $\eta(E,T,h\nu)$

1) Photoconductivity

$$I_{PC} = A\Phi_0 \Omega E$$



$$A = ew\mu\tau I_\nu \left(1 - e^{-\alpha(\nu)D}\right)$$

Photon Fluence

Electrode width

mobility

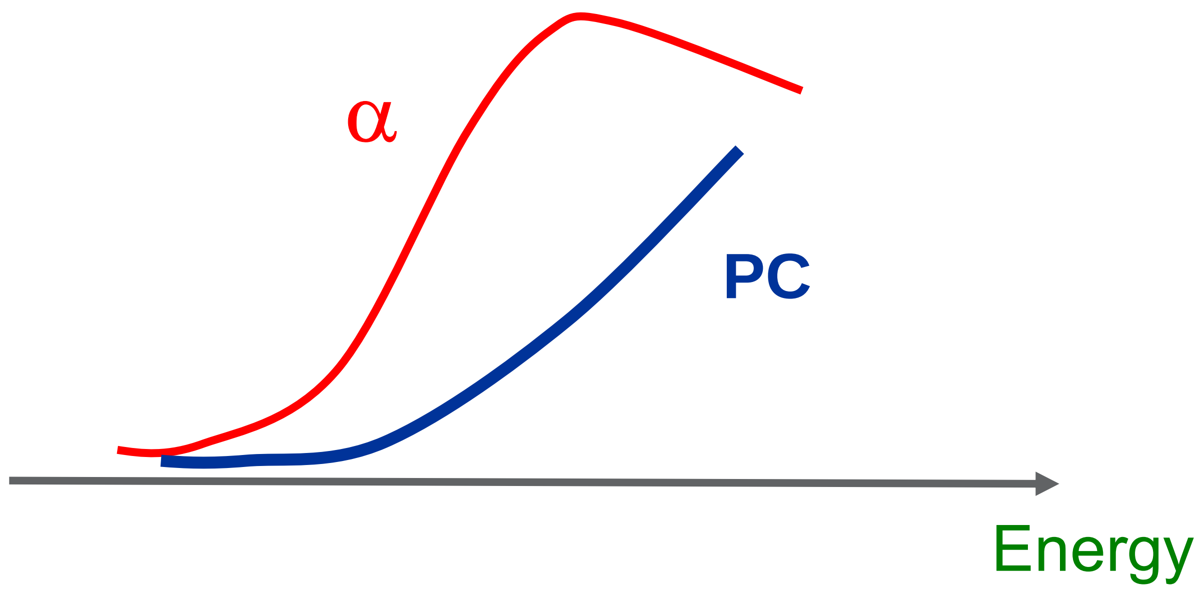
Carrier lifetime

2) Pump-probe

3) m-wave/THz

4) Field assisted PL quenching

Action spectra



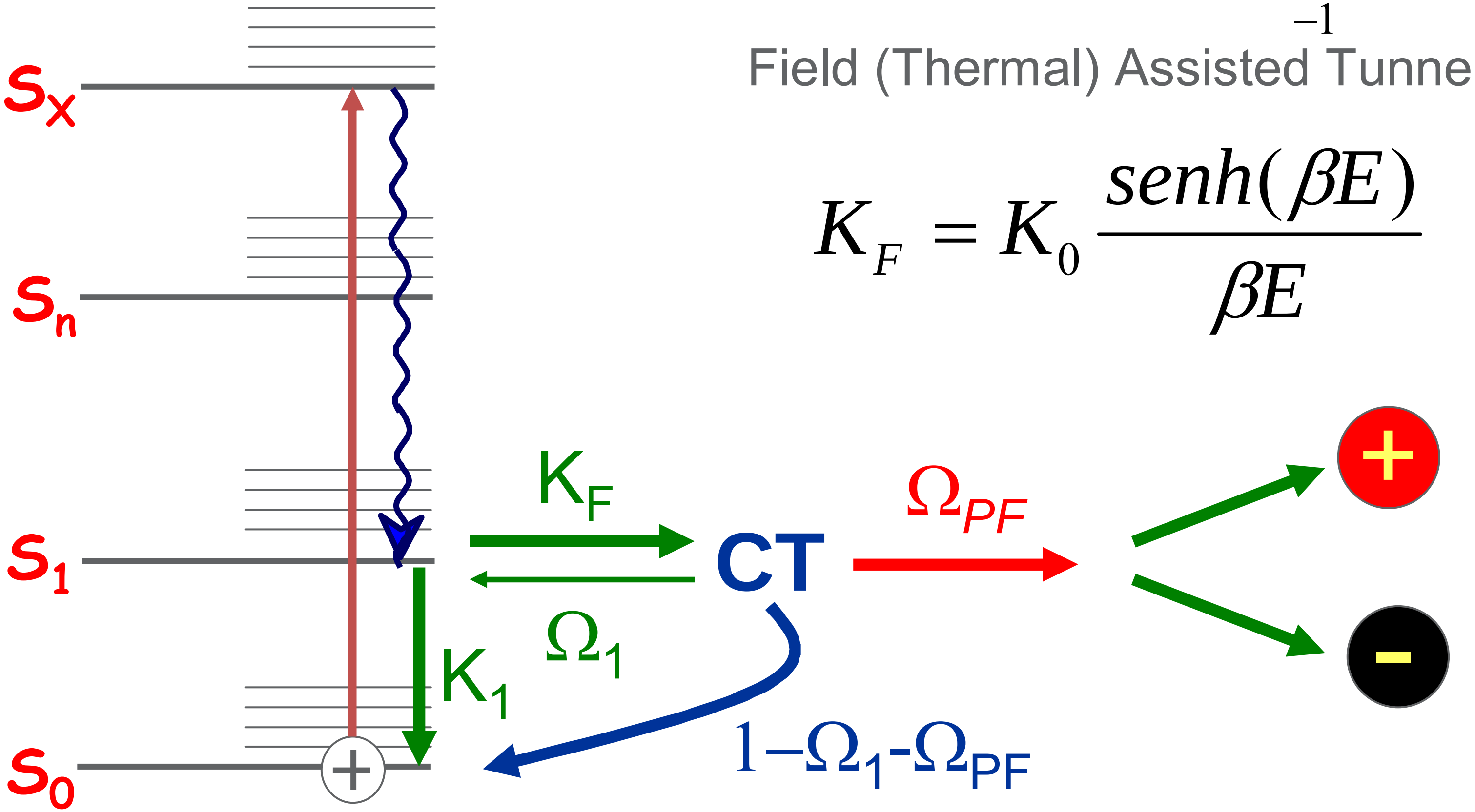
In organics the optical gap and the electrical gap are different

Organic Photoconductors: when α(ω)=PC(ω)

$$K_F = \tfrac{1}{2} K_O \int K_F^{\theta} d\Omega_{\theta} = \tfrac{1}{2} K_O \int_{-1}^{1} e^{\beta E \cos\theta} d(\cos\theta)$$

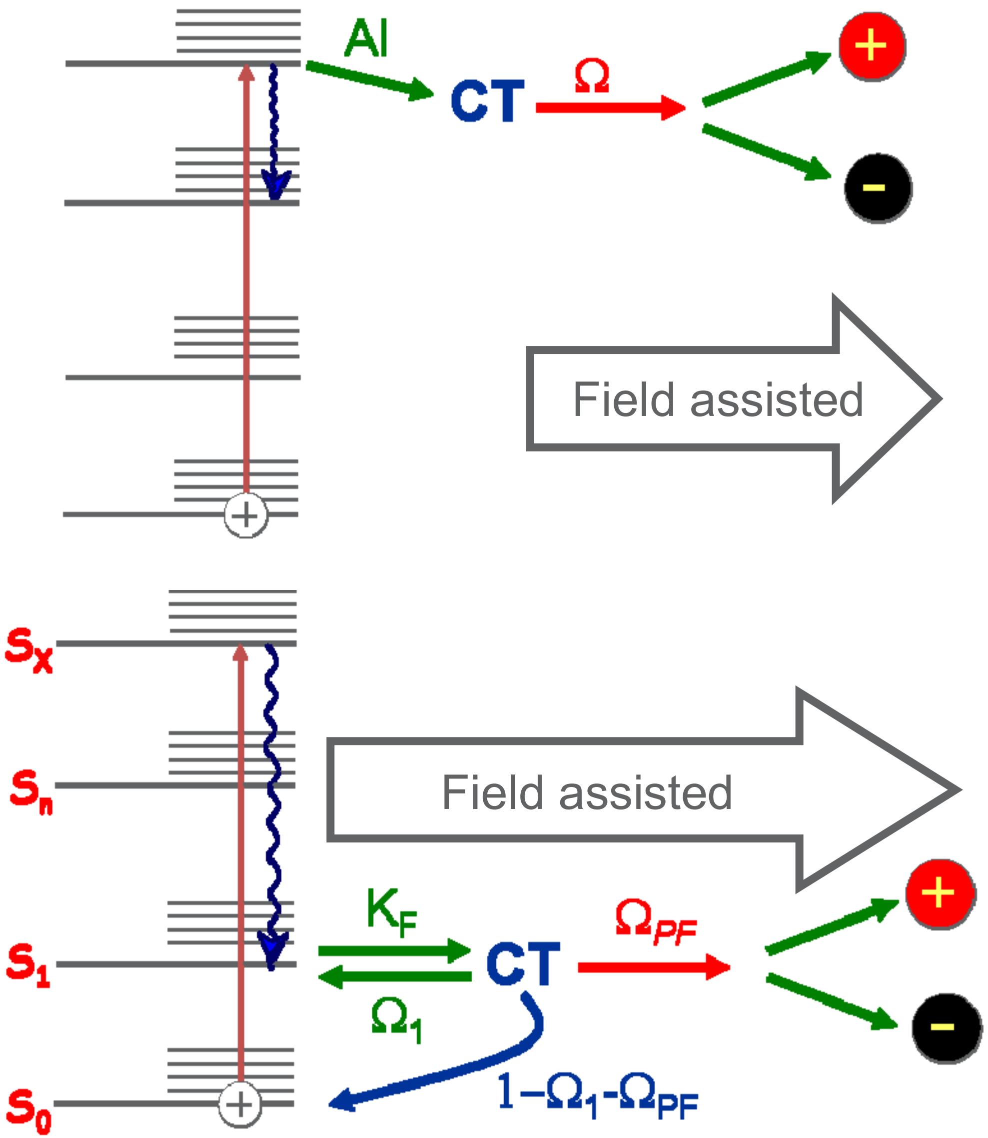
Field (Thermal) Assisted Tunneling

$$K_F = K_0 \frac{senh(\beta E)}{\beta E}$$

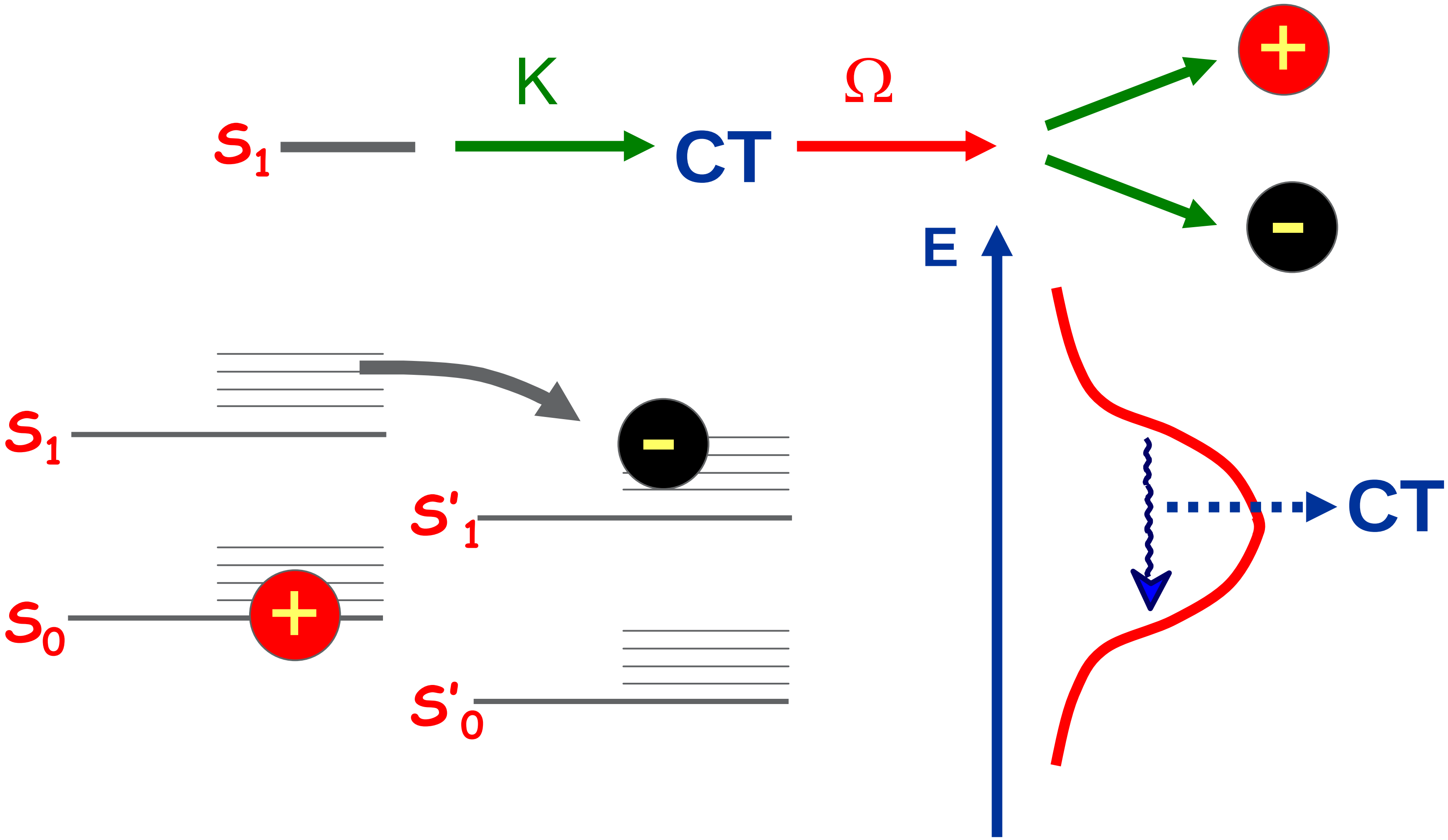


Z.D. Popovic Chem. Phys. 86, 311(1984)

Comparison

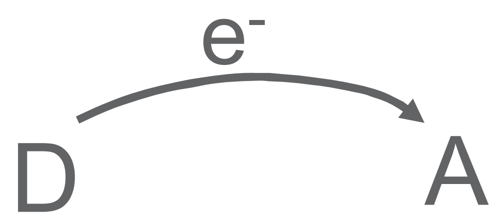

AI
CT
Ω
+
-
Field assisted
Sx
Sn
S1
S0
Field assisted
KF
CT
ΩPF
Ω1
1−Ω1-ΩPF
+
-

Zero Field?



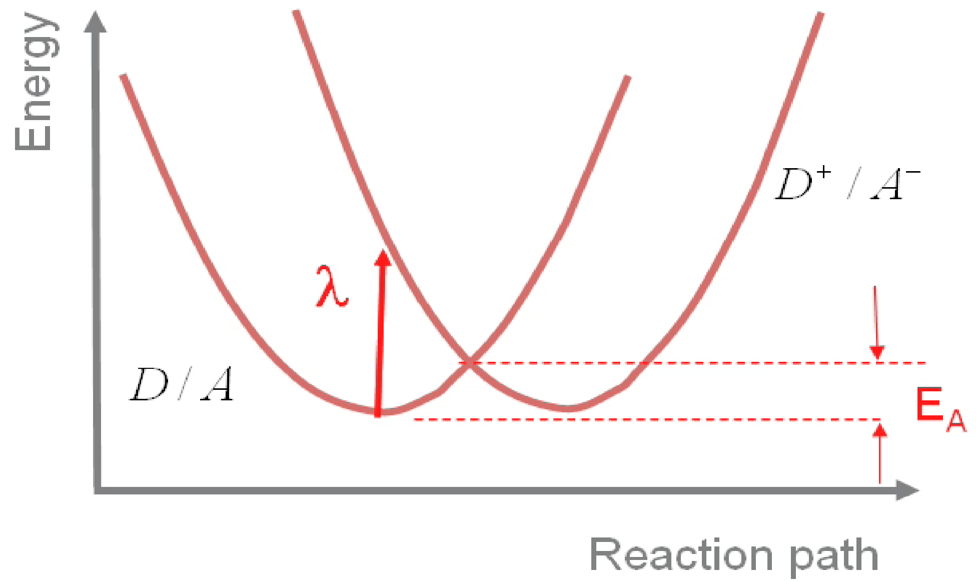
Disorder induced charge separation (H. Baessler)

The Marcus model

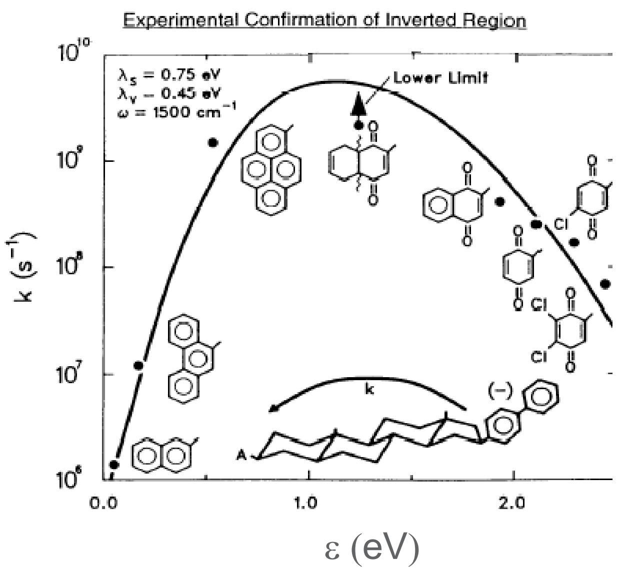


$$r = \nu \exp\left(- E_a / K_B T\right)$$

λ ≡ Reorganization Energy

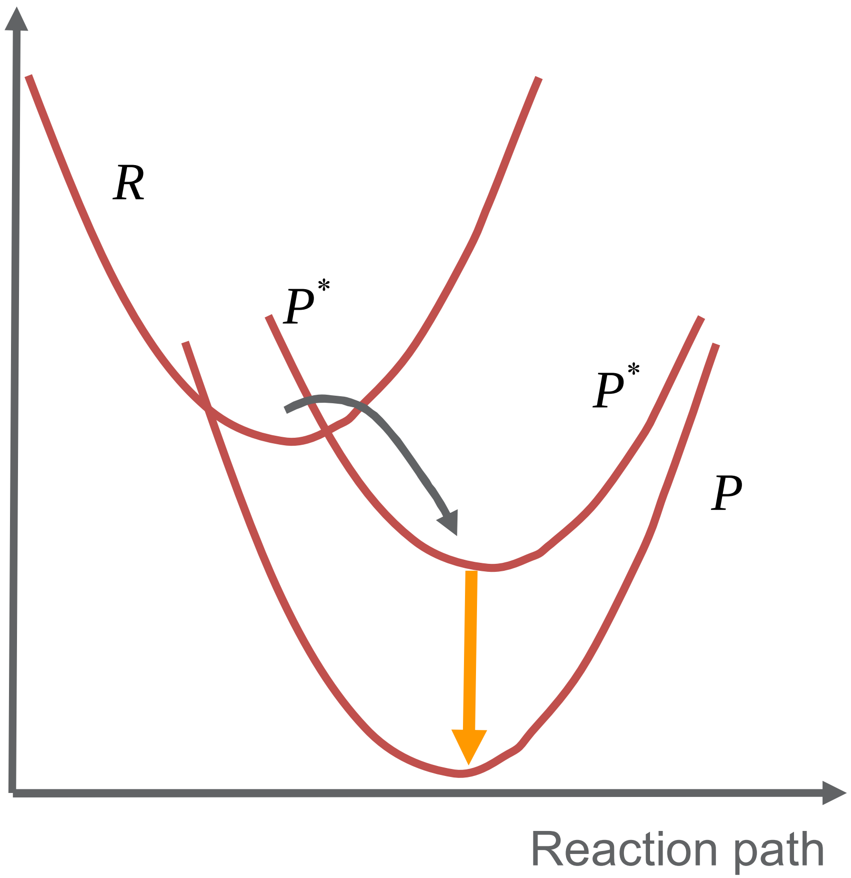


$$E_a = \frac{(\varepsilon - \lambda)^2}{4\lambda}$$



movie

A bright evidence for the inverted region

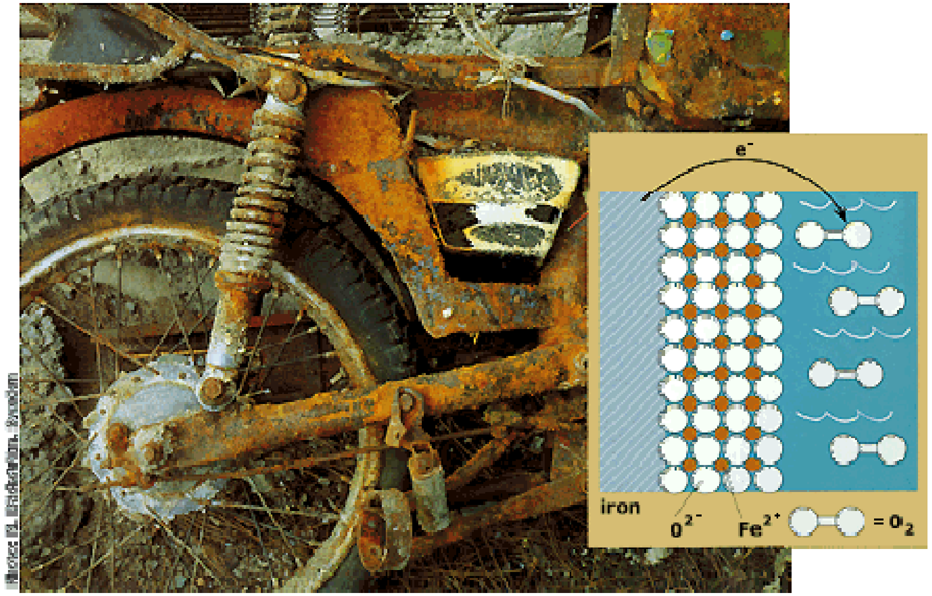


Safety light

The phenomenon is an example of chemiluminescence. Safety lights of this kind, which are non-flammable and waterproof are used by seamen and divers in emergency.

Examples of Charge Transfer reactions

☹



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To be

continued..........