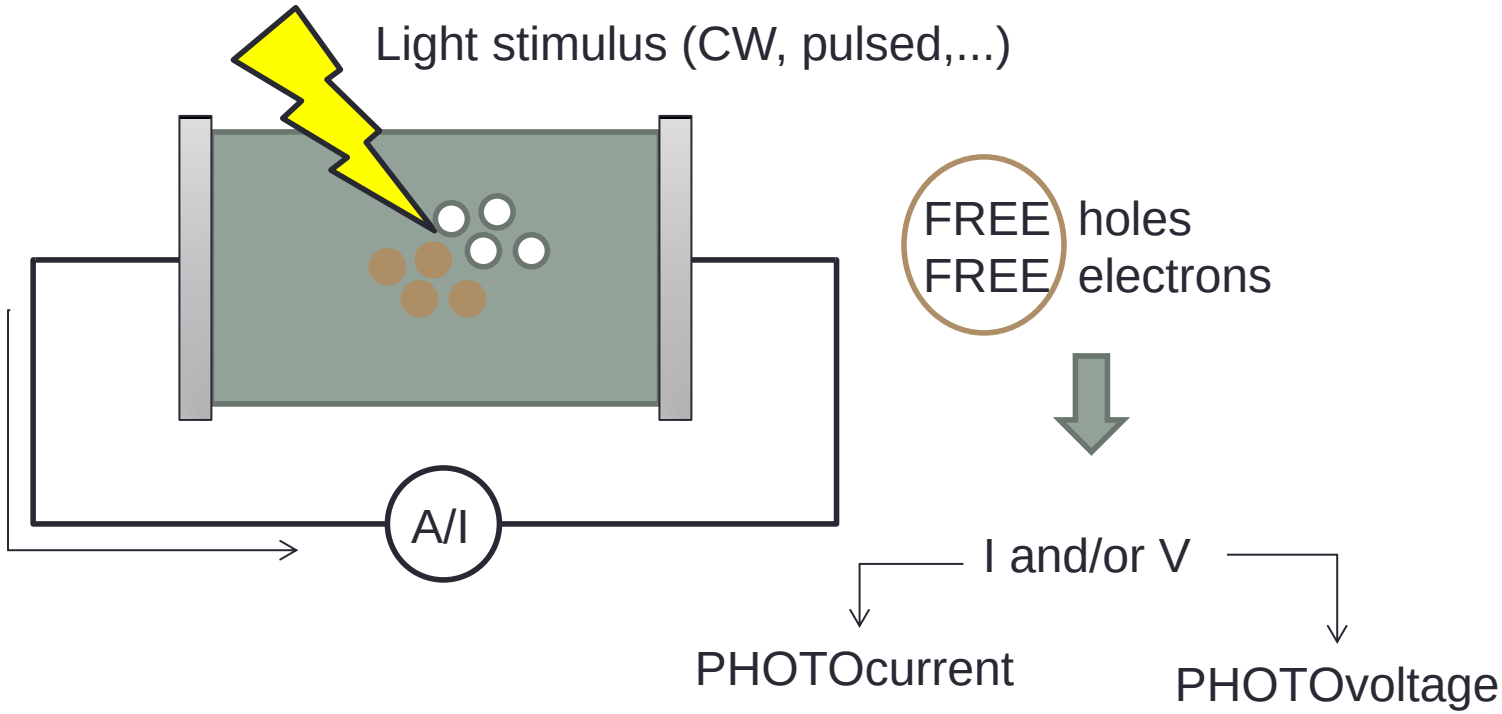
CHARGE CARRIERS PHOTOGENERATION

Maddalena Binda

Organic Electronics: principles, devices and applications

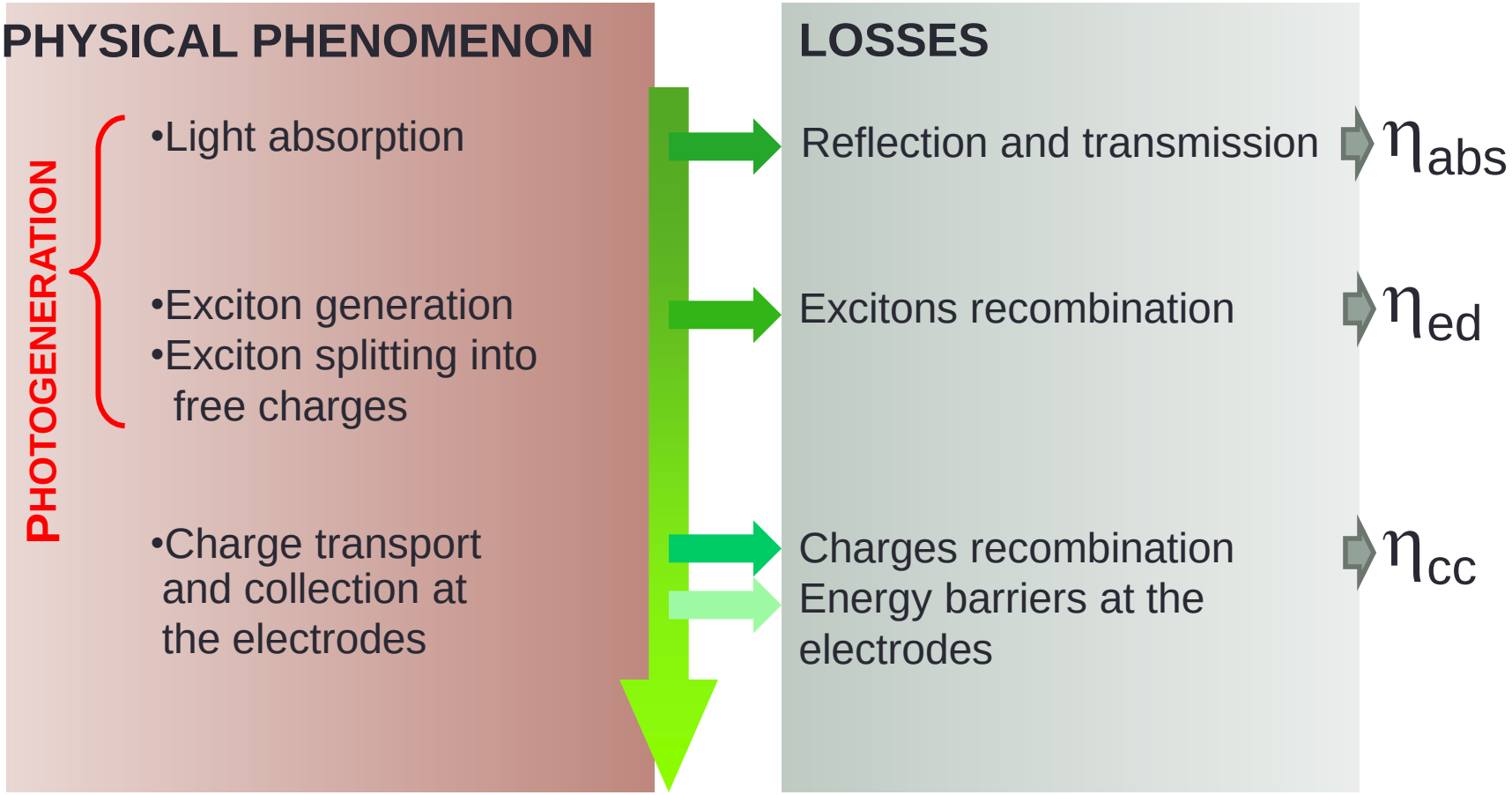
Milano, November 23-27th, 2015

Charge carriers photogeneration: what does it mean?



Other ways of generating carriers in organic semiconductors:
-Injection from the electrodes
-Doping
-Thermal excitation

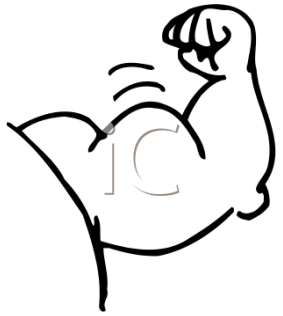
Photogeneration: a multistep process



Efficiency of photocurrent generation:

$$\eta = \eta_{abs} \cdot \eta_{ed} \cdot \eta_{cc}$$

Light absorption: a strength point of organics



- Reflection losses:

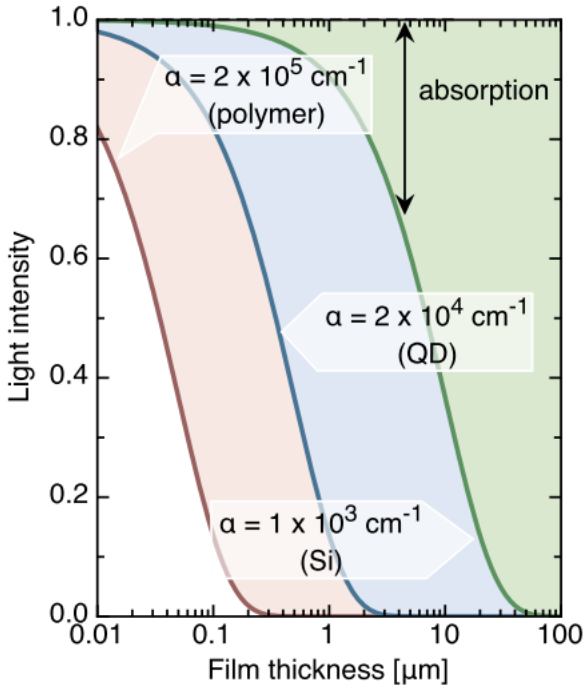
$$R^* = \left(\frac{n_1 - n_2}{n_1 + n_2}\right)^2$$

* normal incidence

We want low (n_1-n_2)...

- n_{air}=1
- n_{glass}=1.5
- n_{Si}=3.2
- n_o~1.7

- Transmission losses (or light absorption):



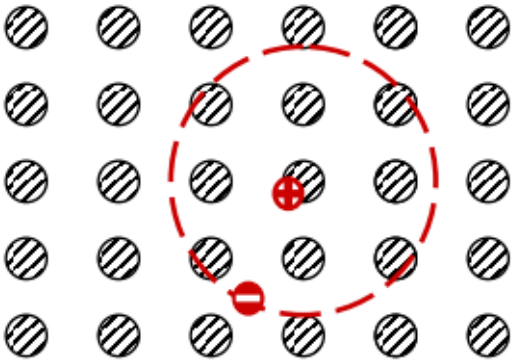
Beer-Lambert law:

$$I(x) = I_0 e^{-\alpha x}$$

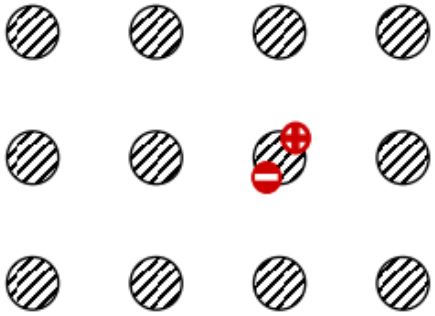
η_{abs} ✓

Exciton generation upon light absorption

Wannier exciton
(typical of inorganic semiconductors)



Frenkel exciton
(typical of organic materials)



COULOMB MUTUAL INTERACTION $U_{Ex} = \frac{q^2}{4\pi\epsilon_0\epsilon_i r_0}$

INORGANIC SEMICONDUCTORS:

High mobility (hundreds cm^2/Vs)
High ε (>10)

H. Pope and C. E. Swenberg, Electronic Processes in Organic Crystals and Polymers, 2nd ed. (Oxford, Univ. Press, 1999).

Exciton Radius ~100Å
Exciton Binding Energy (E_B)~10meV

kT(@300K)~25meV

Thermal dissociation of the exciton into free charges

ORGANIC SEMICONDUCTORS:

Low mobility (< 1 cm^2/Vs)
↓ ε (3÷4)

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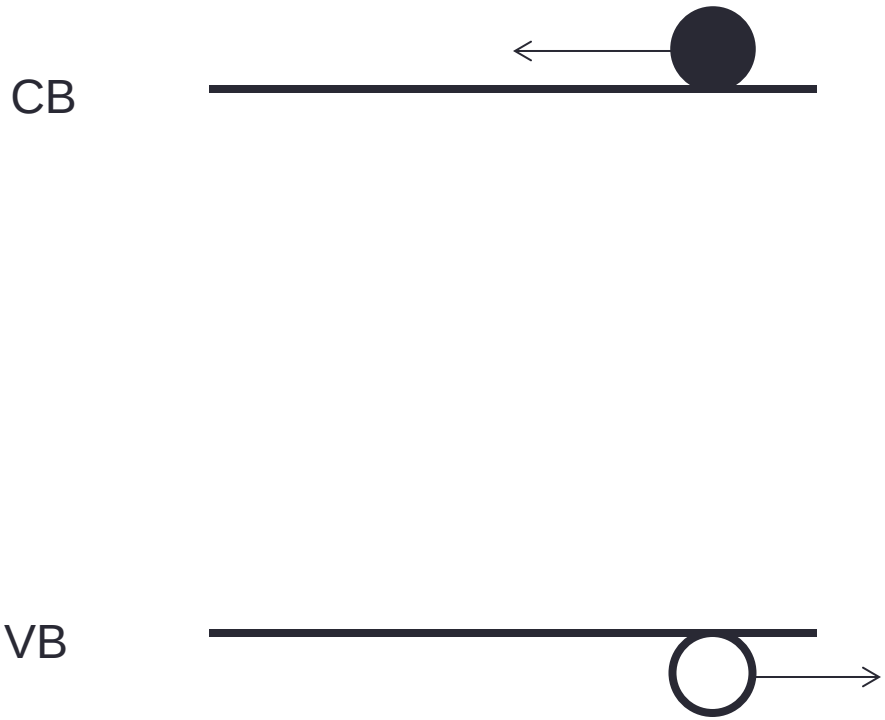

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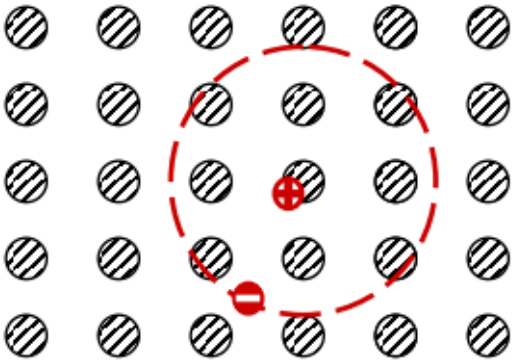

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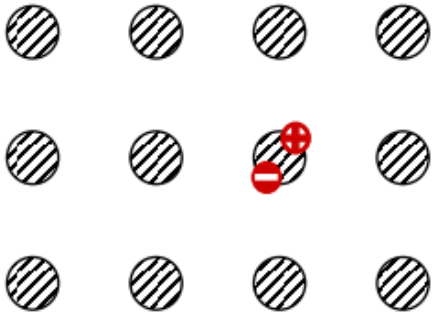

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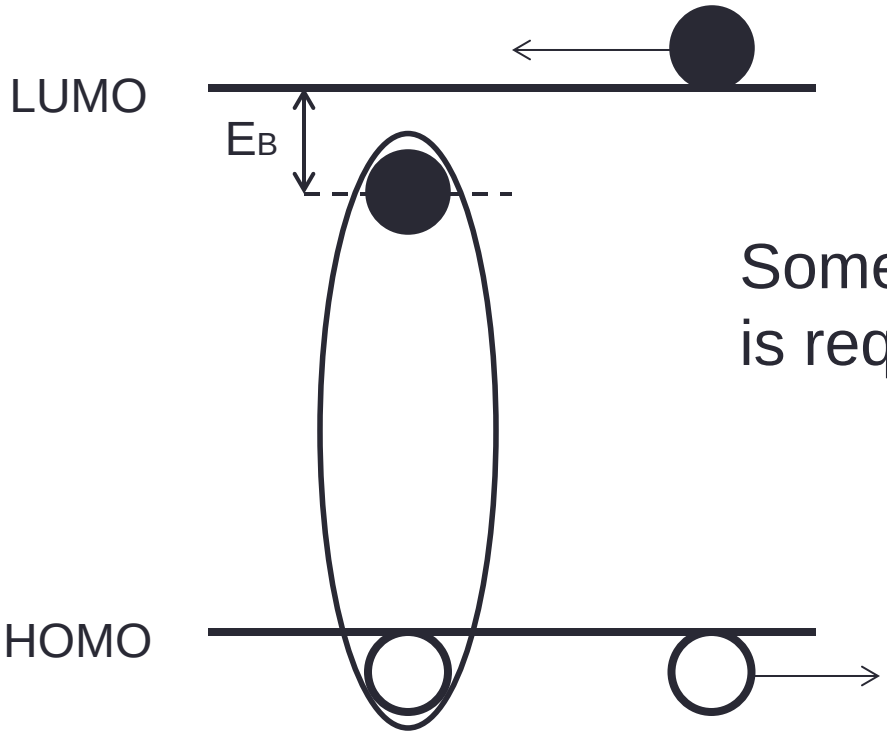
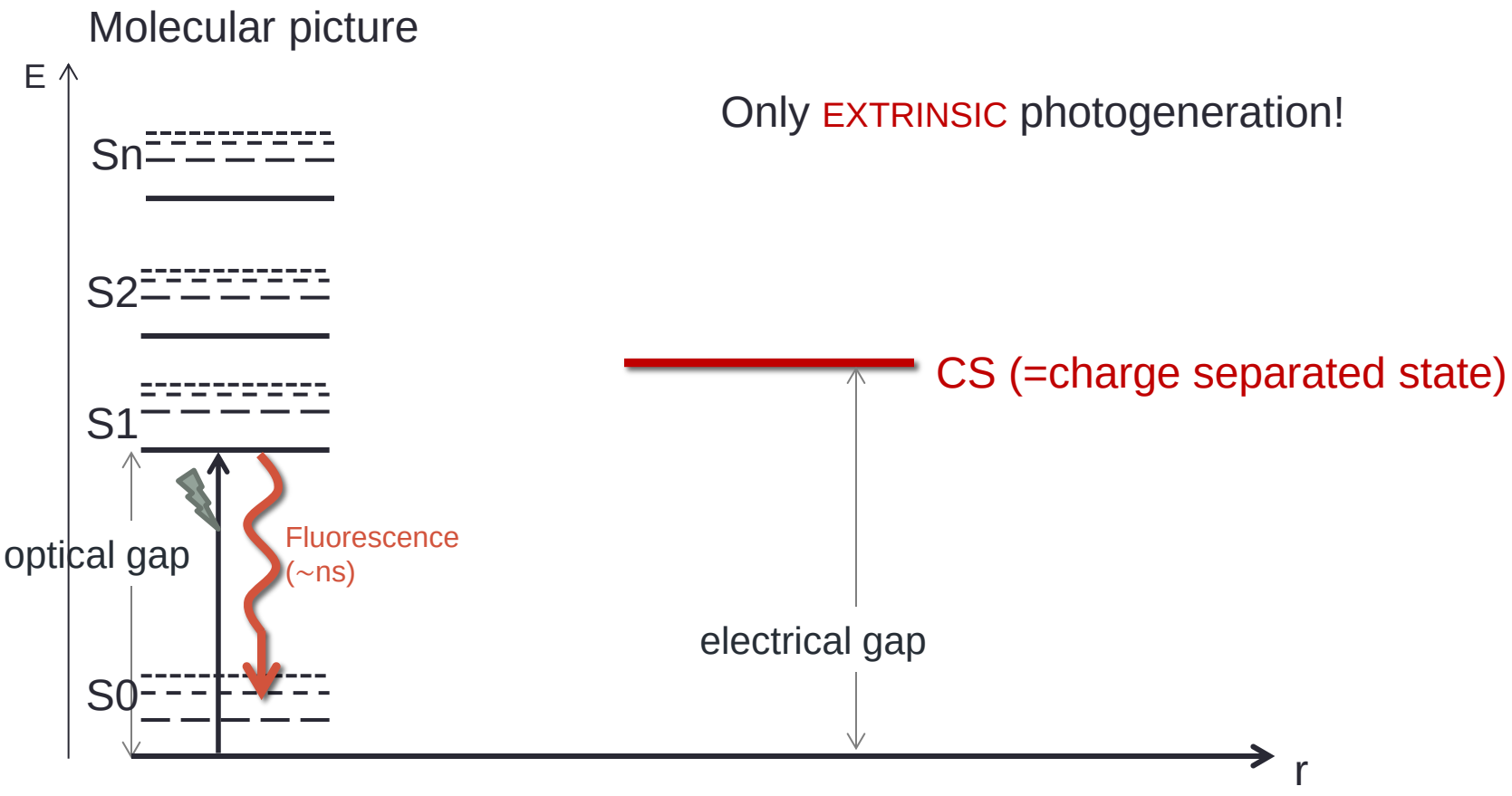


Some kind of extra-energy is required!

How to obtain free charges from a strongly bound exciton?



NOTE that: optical gap ≠ electrical gap

A. Kohler, H. Bassler – Electronic processes in organic semiconductors, Wiley-VCH 2015, Germany. ePFD ISBN: 978-3-527-68514-1

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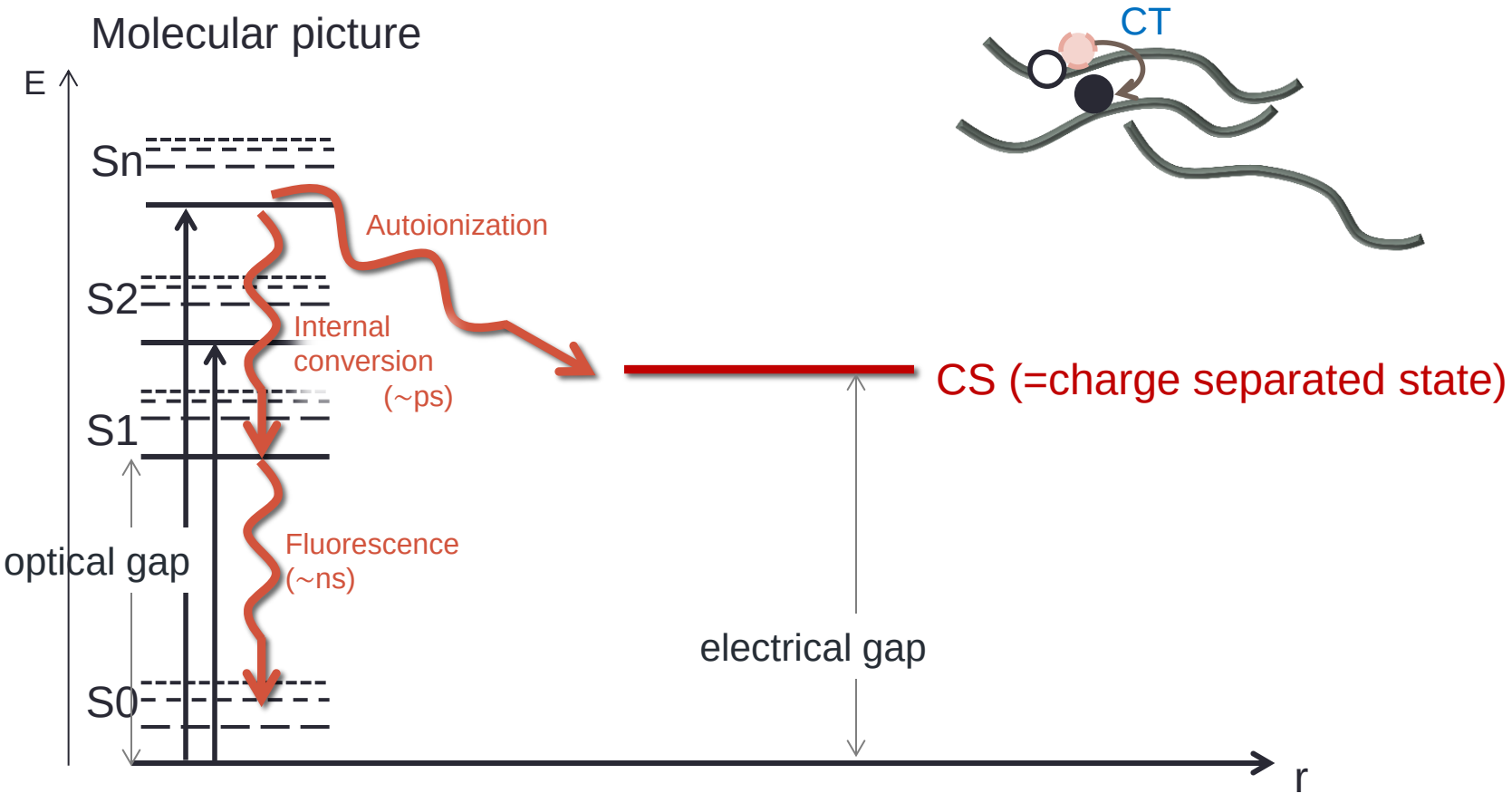

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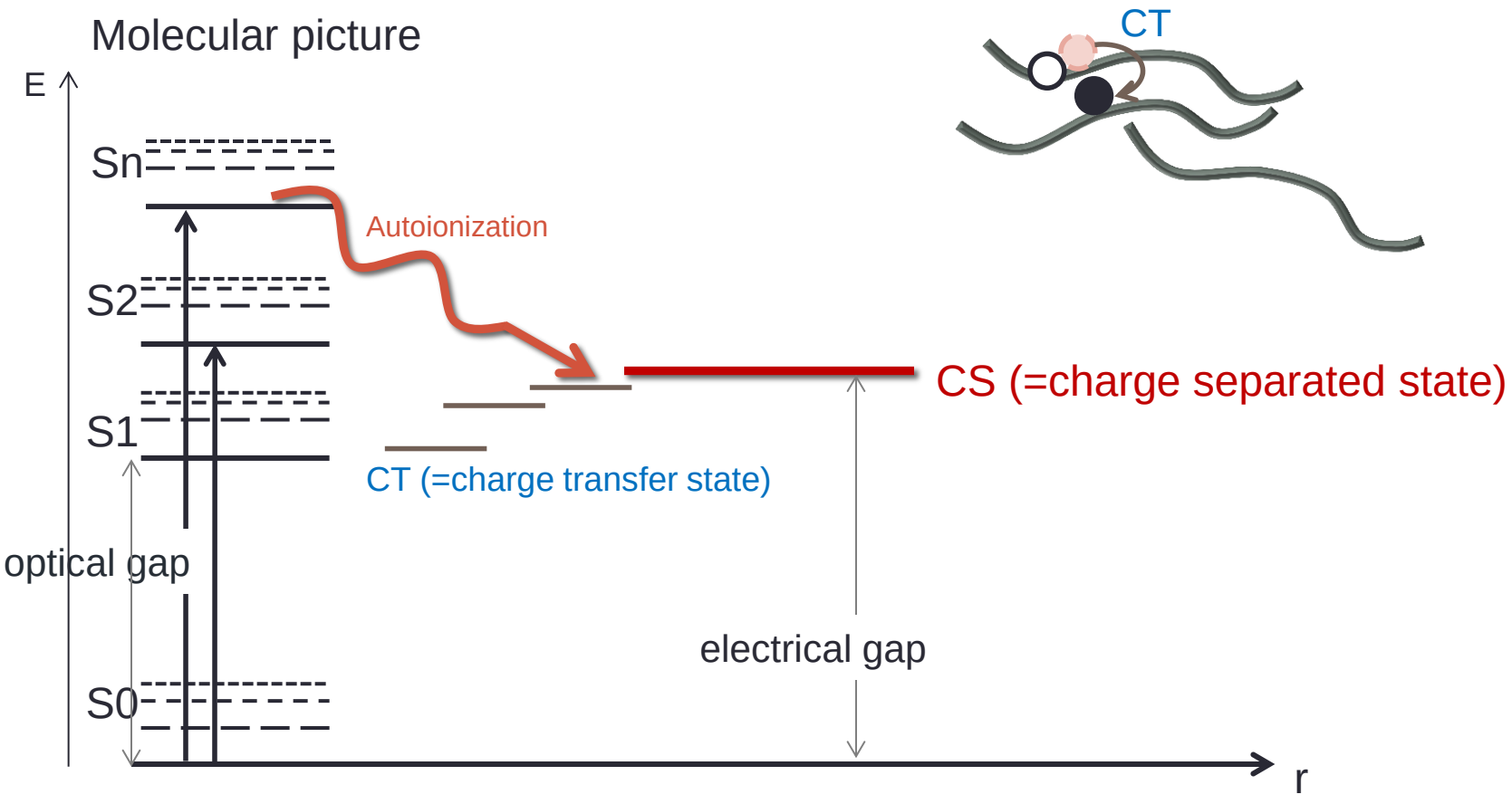

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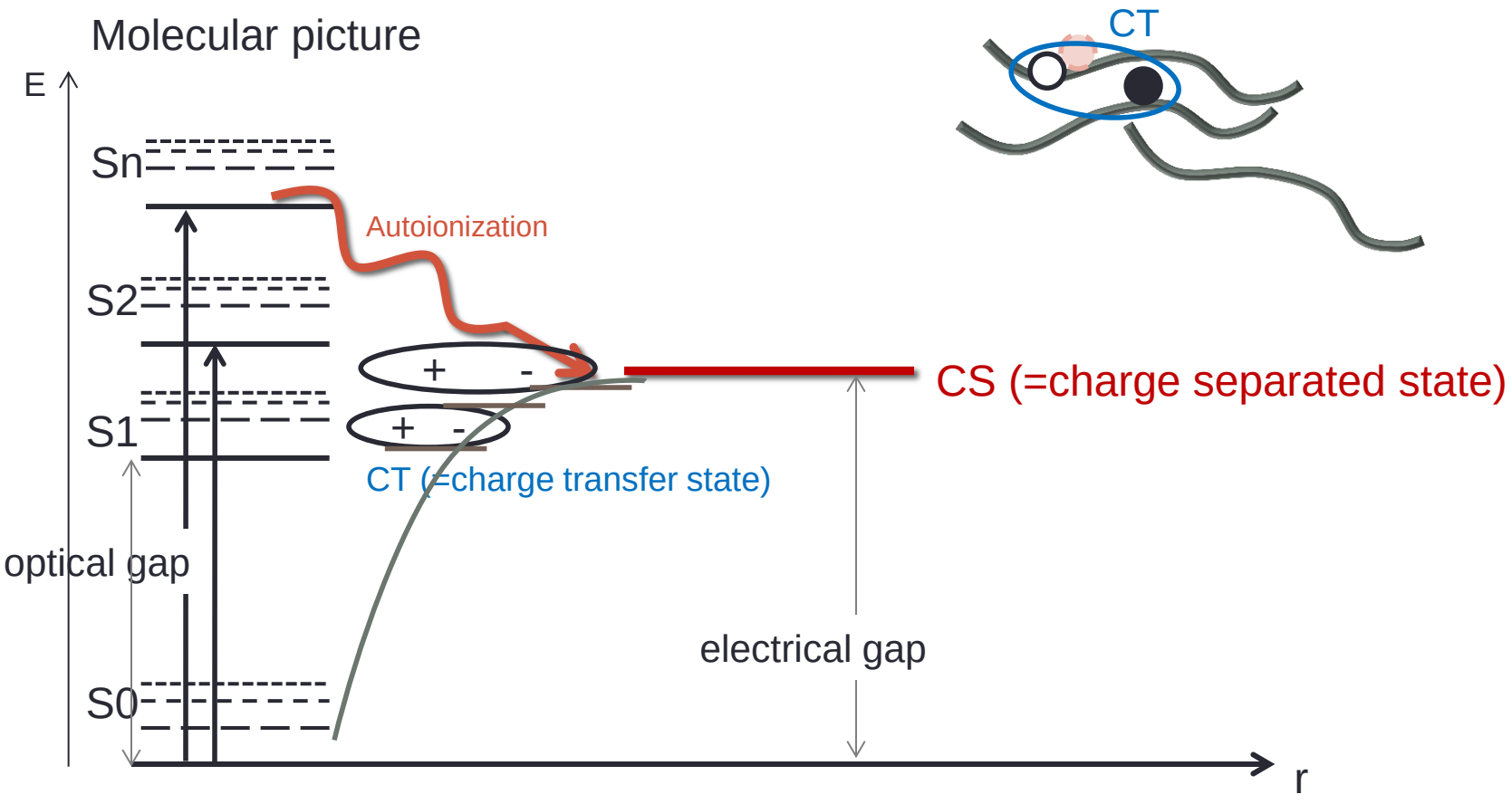

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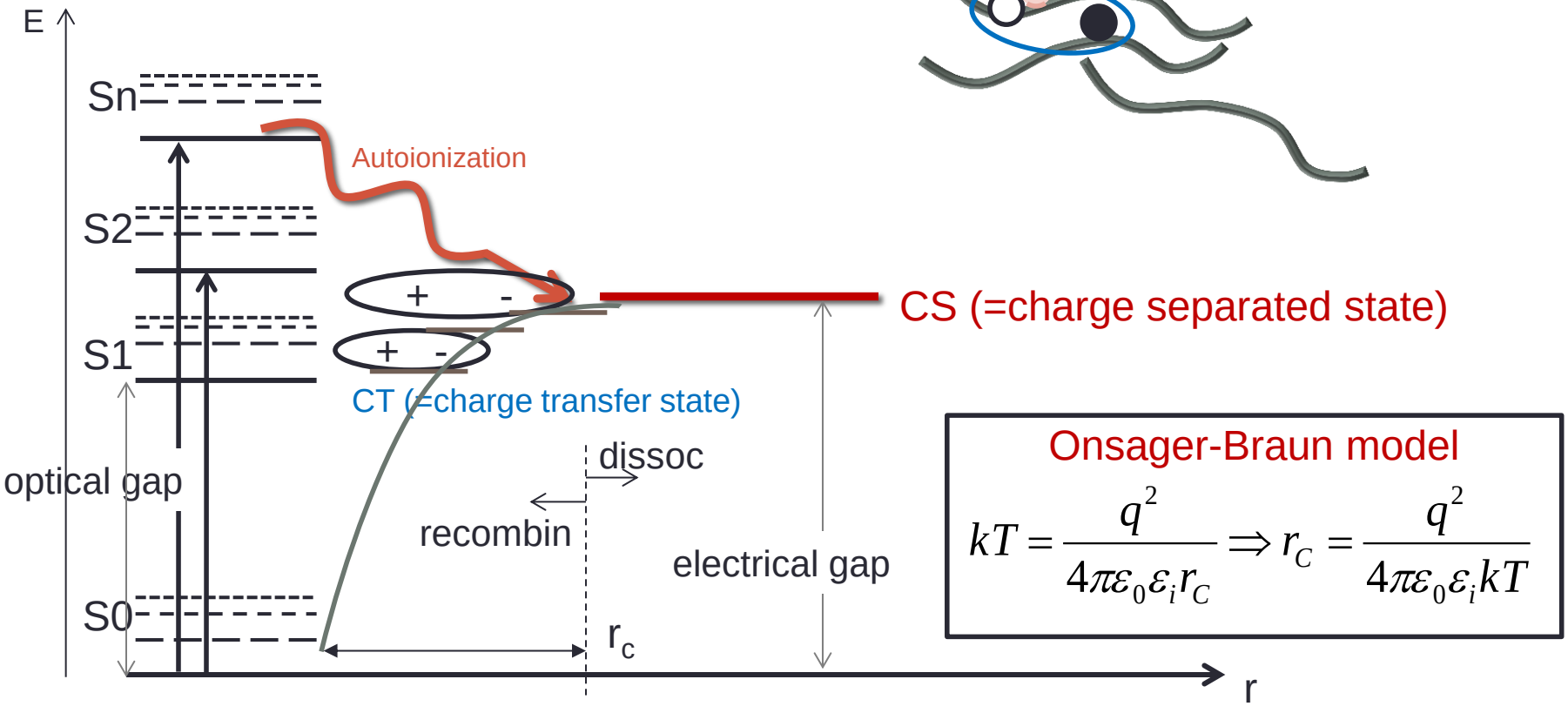
How to obtain free charges from a strongly bound exciton?

Molecular picture



Onsager-Braun model

$$kT = \frac{q^2}{4\pi\varepsilon_0\varepsilon_i r_C} \Rightarrow r_C = \frac{q^2}{4\pi\varepsilon_0\varepsilon_i kT}$$

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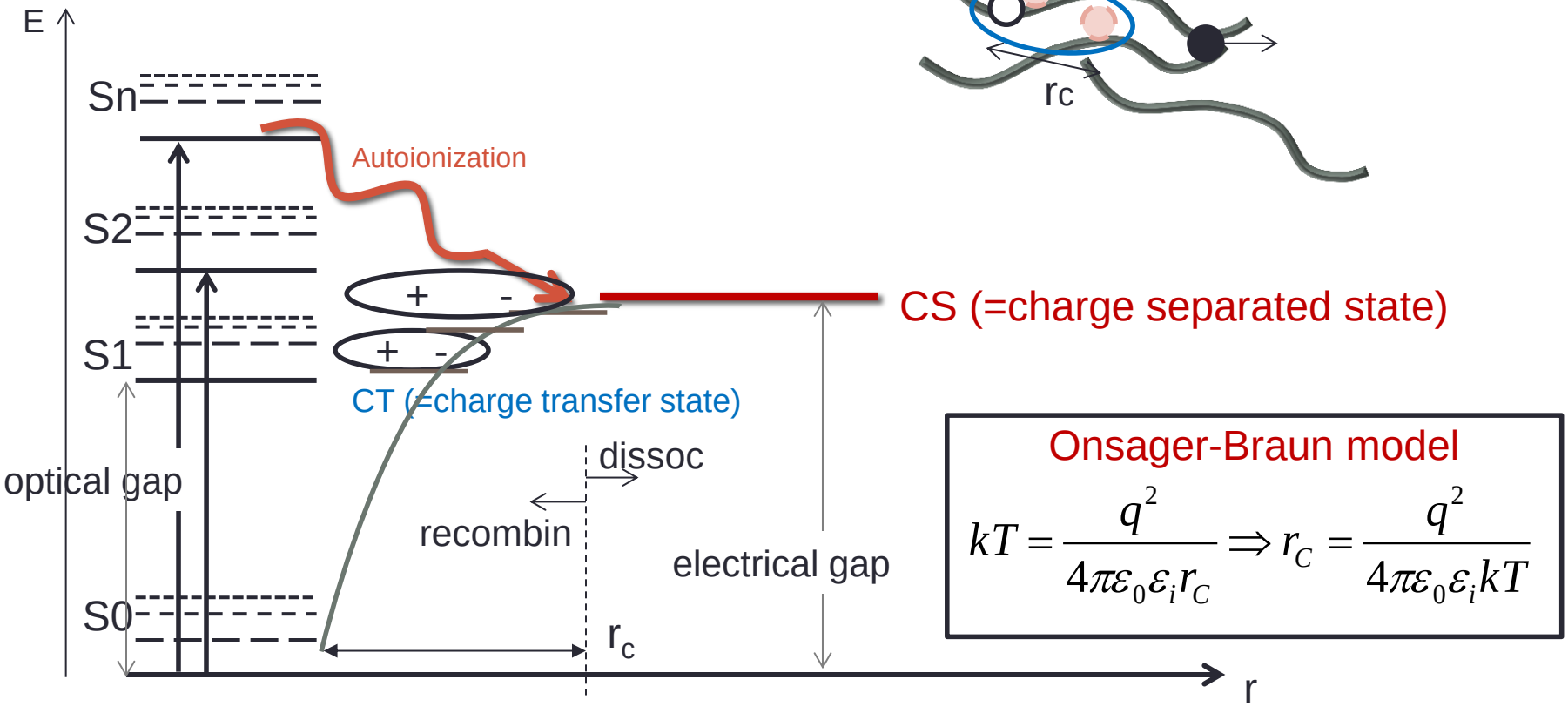

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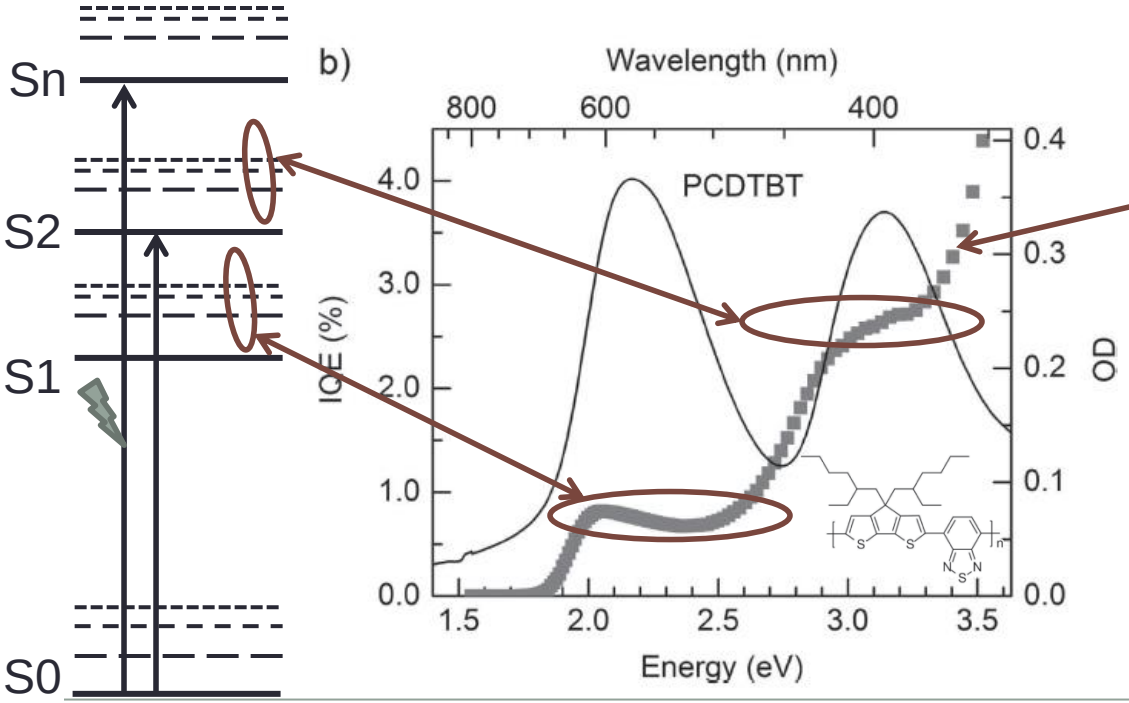
r_c>10 nm (ideal system)
r_c~few nm (energetic disorder)

NOTE that: optical gap ≠ electrical gap

On the excess energy…



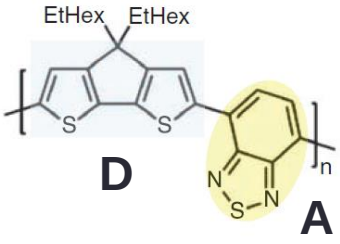
Charge generation efficiency (net of light absorption)

Increasing extention of excited state wavefunction for higher energy electronic states

Confirmed by quantum mechanical calculations!

DONOR/ACCEPTOR COPOLYMERS

(PCDTBT, PCPDTBT.…)



Primary excitation already has strong CT character

Adv. Funct. Mater. **2015**, *25*, 1287–1295

Nature Materials, 2013, 12, 29-33

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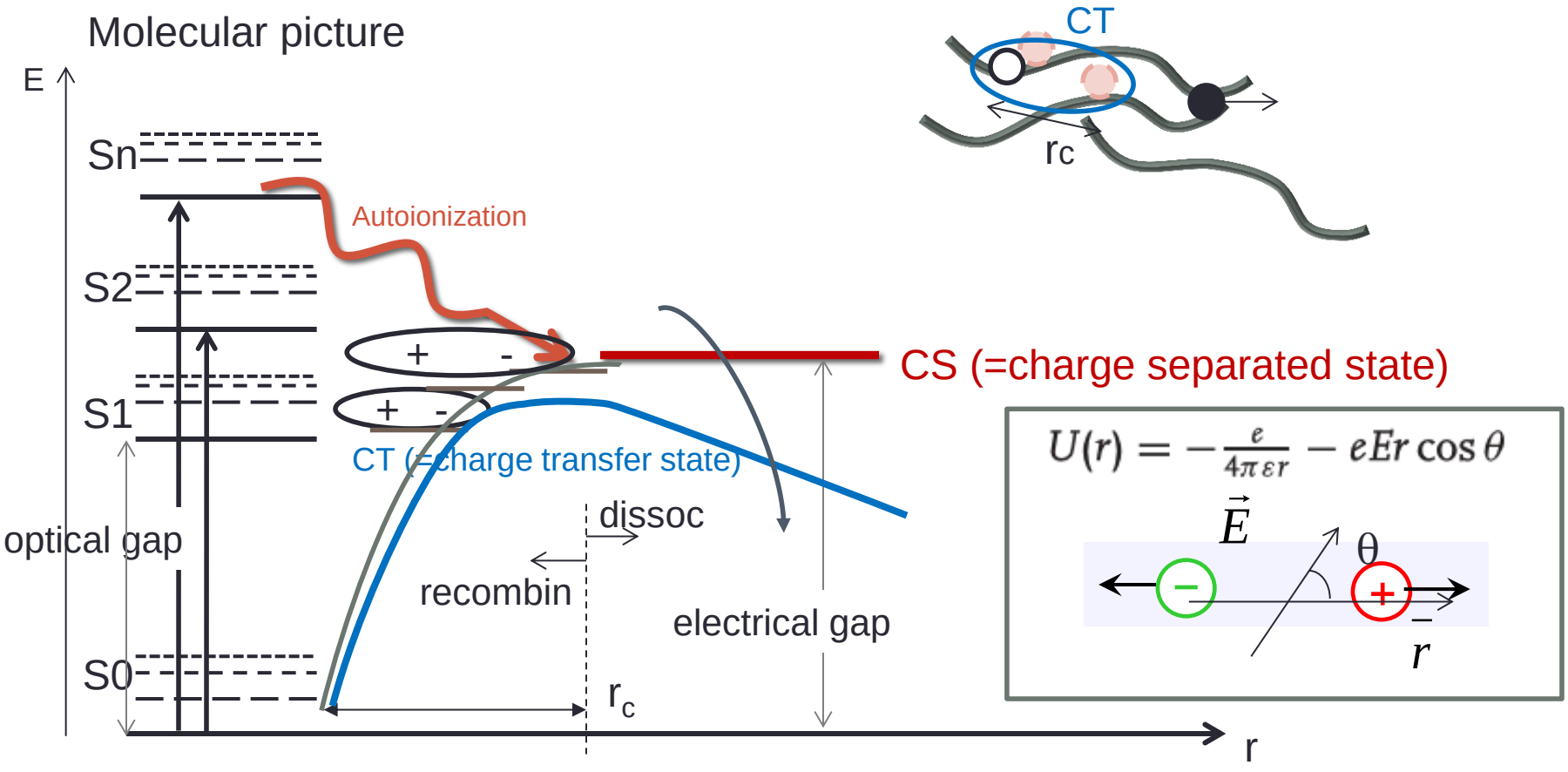

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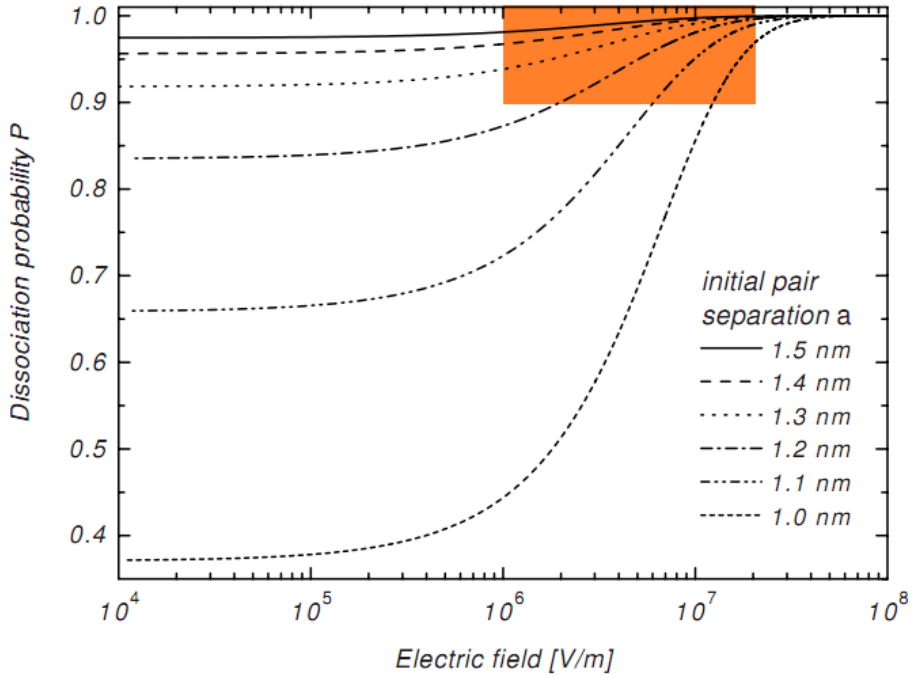


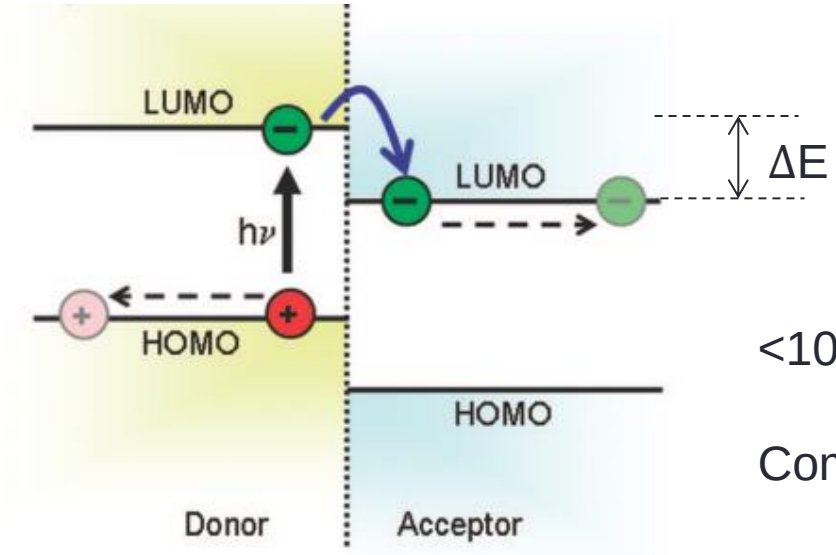
J. Appl. Phys. 106, 104507, 2009.

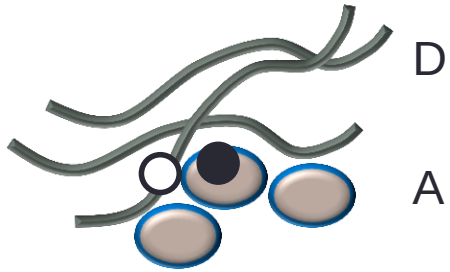
L. Onsager, J. Chem. Phys. 2 (1934) 599

C. L. Braun, J. Chem. Phys. 80, 4157, (1984).

Onsager-Braun model, refined by Wojcik and Tachiya (M. Wojcik and M. Tachiya, J. Chem. Phys. 130, 104107 (2009))

Photoinduced charge transfer: donor/acceptor interfaces



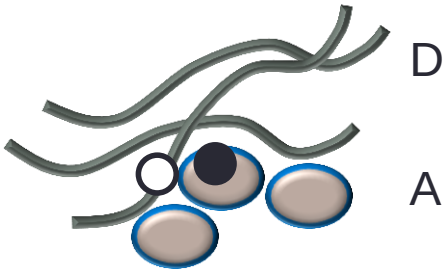


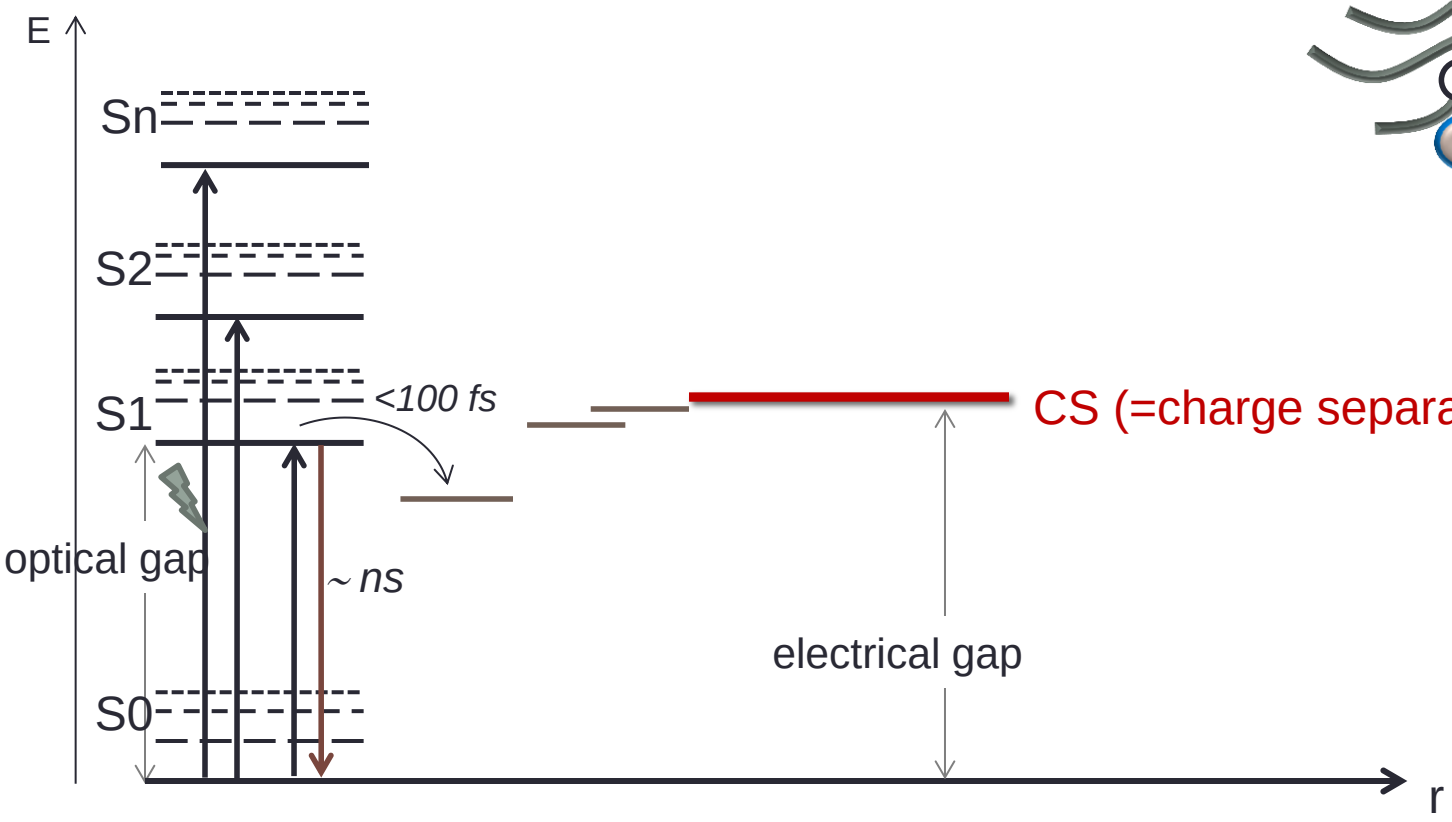
<100 fs time scale

Competitive with other relaxation phenomena

ΔE is a driving force to charge separation

Photoinduced charge transfer: donor/acceptor interface





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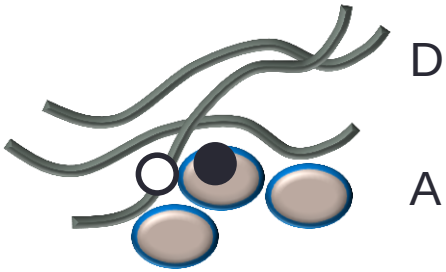

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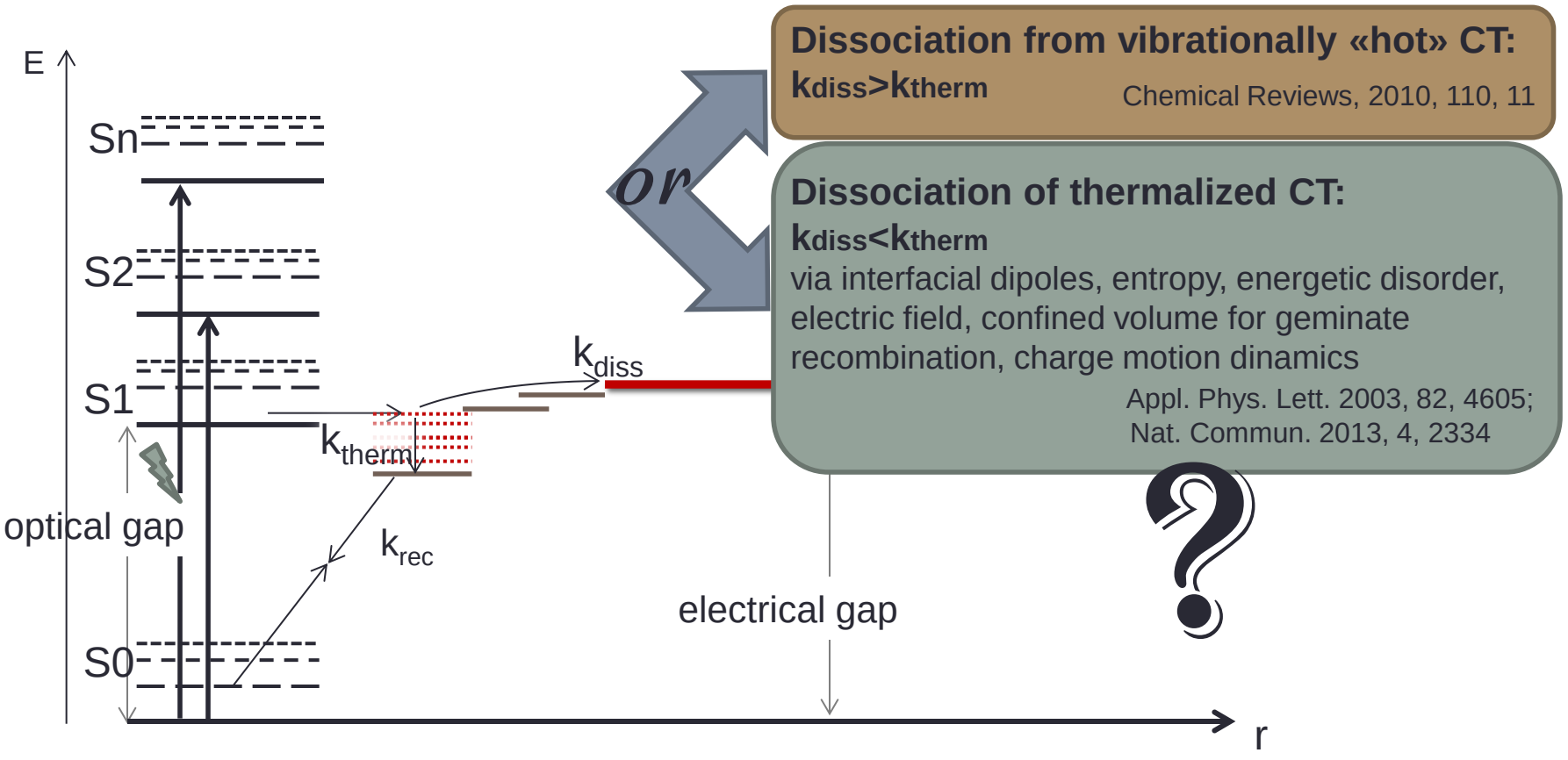

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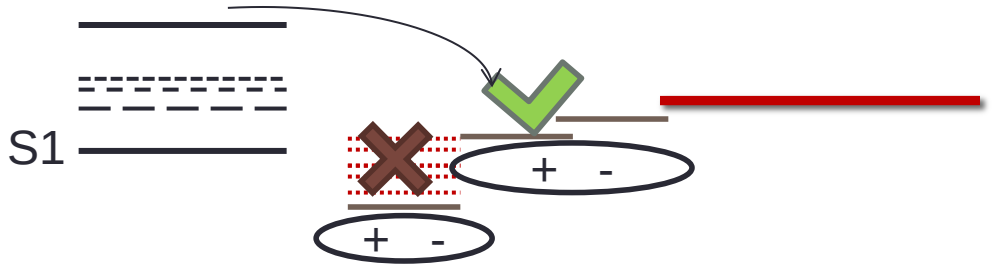


Only If excess energy ($LUMO_D/LUMO_A$ offset, high energy photon) gives access to a higher ELECTRONIC CT level, it can be exploited for dissociation.

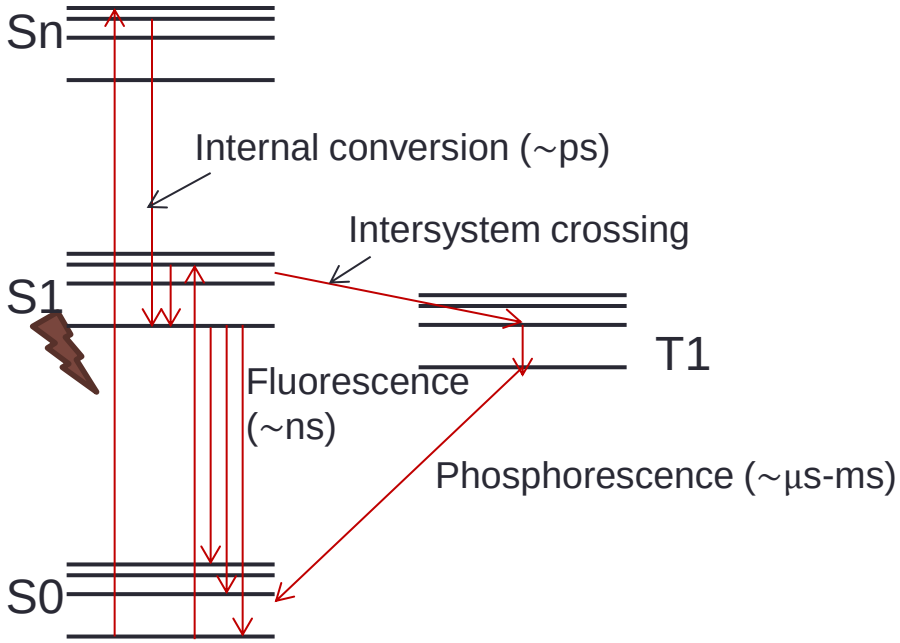
«Excess VIBRATIONAL energy has virtually no effect»

«It is the spatial extention of the wavefunction of the excited state that determines the yield of dissociation»

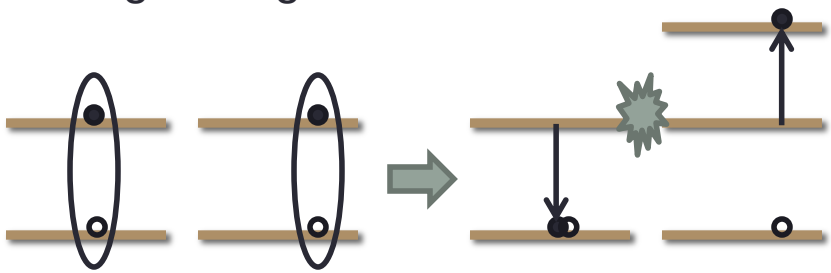
- Kohler - *Adv. Funct. Mater.* **2015**, *25*, 1287–1295

See also: Nature Materials, 2013, 12, 29-33

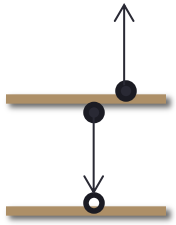
Exciton deactivation



- Radiative/non-radiative decay to the ground state (mediated by chemical defects, dopants, surface states)
- Singlet to triplet (ISC)
- Singlet/singlet annihilation



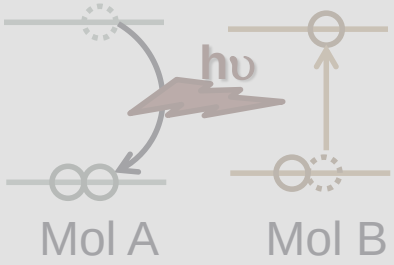
- Recombination with free charges (Auger recombination)



- Quenching at the metal/organic interface

Exciton diffusion

Radiative



C. Madigan, Phys. Rev. Lett. 96, 4, 046404, 2006.

Spectral overlap between A emission and B absorption required

Non-radiative

Förster

Electrostatic coupling

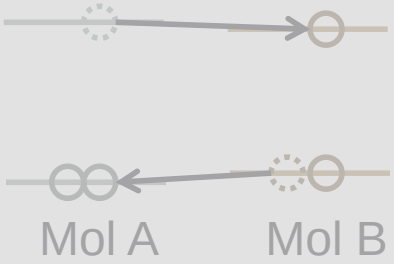
How?

Long range <10nm

SINGLET EXC.

Dexter

Simoultaneous double charge transition



If both hole transfer and electron transfer are favorable: spatial wavefunctions overlap of A and B sites

A nearest neighbor phenomenon <20Å

TRIPLET EXC.

Macromol. Rapid Commun. 2009, 30, 1203–1231

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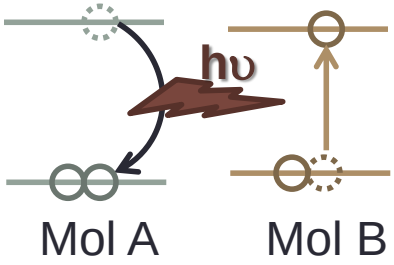

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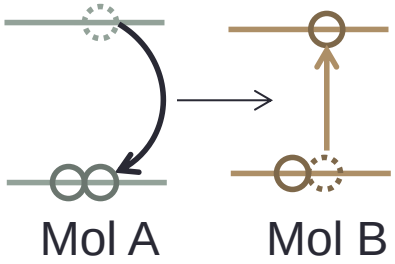

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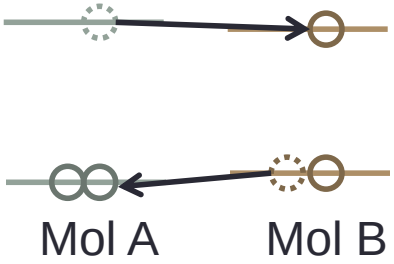

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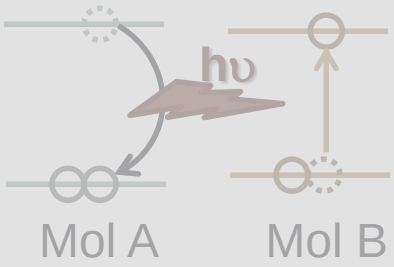

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Mol A Mol B

er and electron
able: spatial
erlap of A and B sites

nbor phenomenon
<20Å

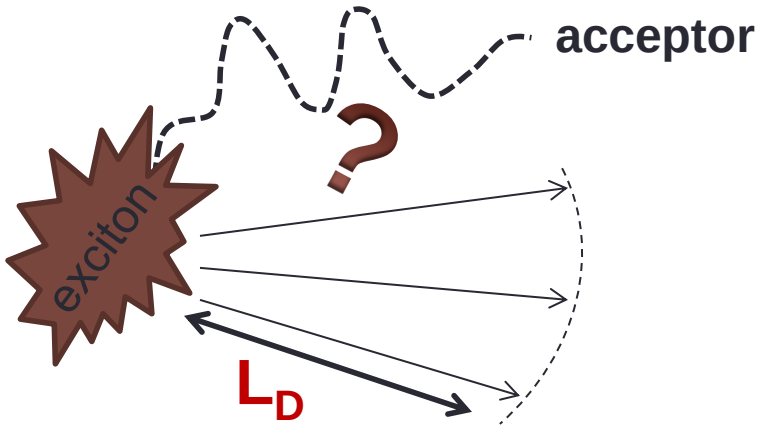
TRIPLET EXC.

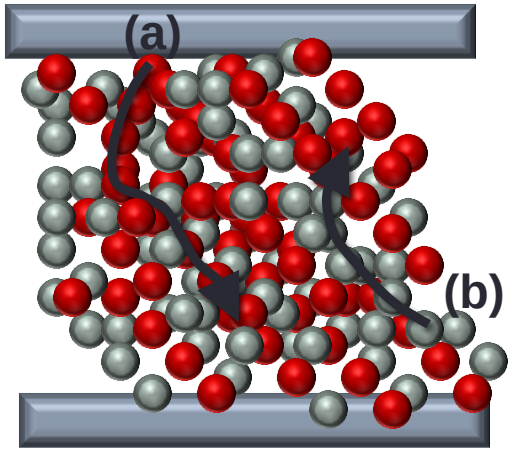
How far?

L_D<10 nm

Macromol. Rapid Commun. 2009, 30, 1203–1231

Donor/acceptor heterojunction: morphology



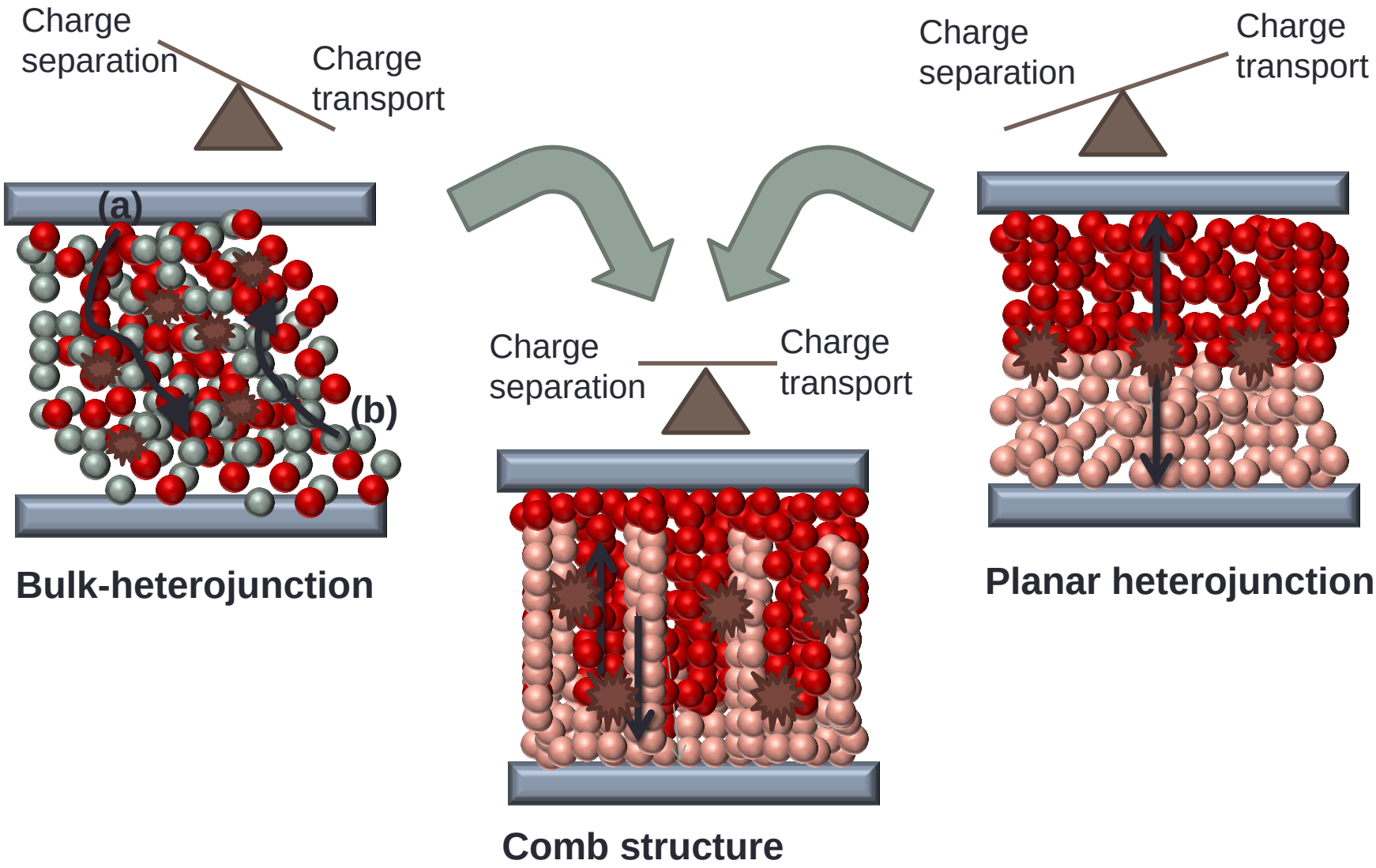


BULK-HETEROJUNCTION

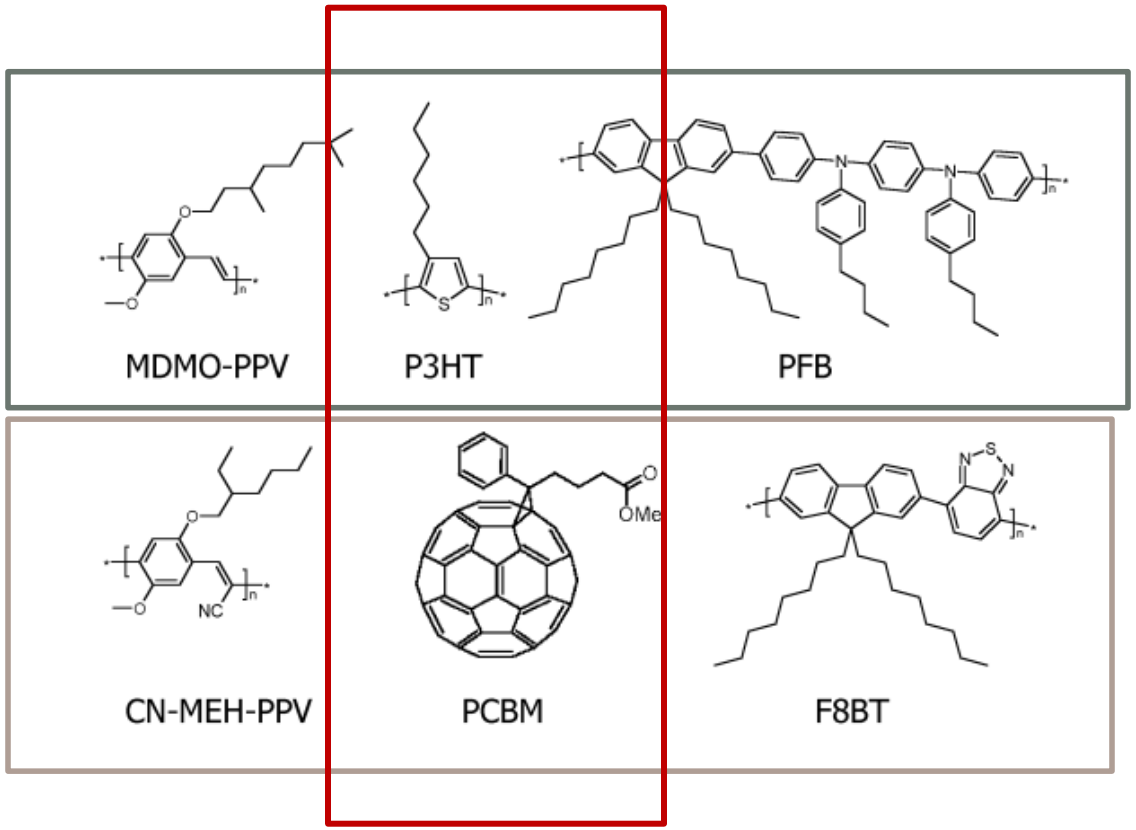
Randomly mixed donor/acceptor molecules

Maximized extension of donor/acceptor interface

Morphology of D/A heterojunction



Donor/acceptor materials: examples



p-type, DONORS

n-type, ACCEPTORS

H. Hoppe and N. Serdar Sariciftci, J. Mater. Res., Vol. 19, No. 7, Jul 2004

To the electrodes...

- **Charge Transport** D. Natali
- **Recombination:**

WITH OTHER CHARGE CARRIERS

Between FREE hole and electron:

- LANGEVIN
- Via CT states

1

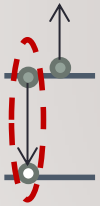
Between FREE hole(electron) and "trapped" electron(hole):

- Trap assisted
- Via tail

2

WITH EXCITONS

Auger recombination:
of an exciton with a
free hole or electron



but exciton lifetime ~10÷100fs

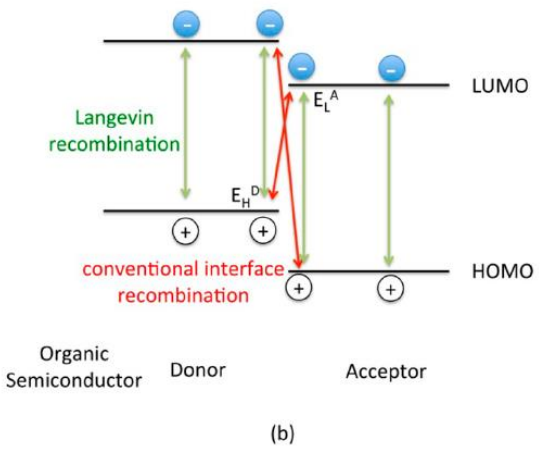
very unlikely to occur

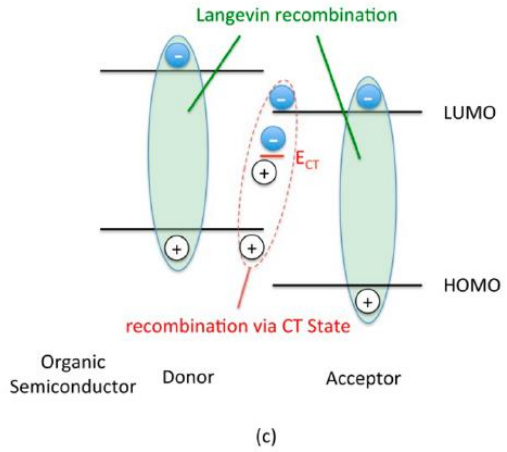
To the electrodes...

1

Between FREE hole and electron:

- LANGEVIN $R = \gamma(np - n_i^2)$ $\gamma = \frac{q(\mu_n + \mu_p)}{\varepsilon}$
- LANGEVIN in BHJ: $R_{BHJ} = \gamma \cdot \beta \cdot (n^A p^D - n_i^A \cdot p_i^D)$ $\begin{cases} \gamma = \frac{q(\mu_n^A + \mu_p^D)}{\bar{\varepsilon}} \\ \beta = 10^{-4} \div 10^{-1} \end{cases}$
- Via CT states: $R_{CT} = N_{CT} / \tau_{CT}$ $1/\tau'_{CT} = 1/\tau_{CT} + 1/\tau_{sep}$ $\Rightarrow$ $\begin{cases} R_{CT} = \alpha \cdot (n^A p^D - n_i^A \cdot p_i^D) \\ \alpha \propto \frac{\exp(\sigma_{CT}^2)}{\tau_{CT}} \end{cases}$





σ_{CT}=std dev of CT state energetic distribution

J. Phys. Chem. C, 2015 **DOI:** 10.1021/acs.jpcc.5b08936; Phys. Review B 2010, 81, 205307

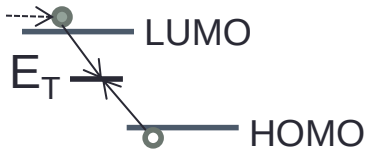
To the electrodes...

2 Between FREE hole(electron) and “trapped” electron(hole):

- Trap assisted (single trap)

$$R_{SHR} = \frac{C_n C_p N_t (np - n_i^2)}{C_n (n + n_1) + C_p (p + p_1)}$$

Shockley-Read-Hall (SRH)

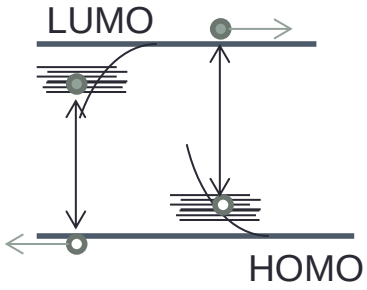


Cn,Cp=capture coeff
Nt=traps density

$$\begin{cases} n_1 \propto \exp((Et - Ec)/kT) \\ p_1 \propto \exp((Ev - Et)/kT) \end{cases}$$

$$p_1 \cdot n_1 = n_i^2$$

- Via «tail» (distribution of traps)



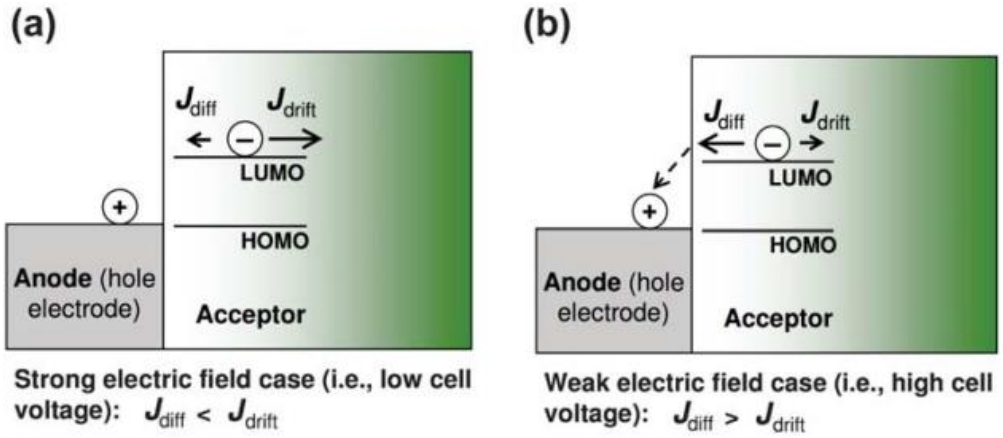
$$R = \int_{HOMO}^{LUMO} N(E) R_{SRH}(E) dE$$

R_{SRH}=recombination rate per energy state at a specific energy

Phys. Rev. Lett. 2011, 107, 256805

To the electrodes...

Reverse diffusive at the contacts: free carriers diffuse against the electric field and recombine at the metal contacts



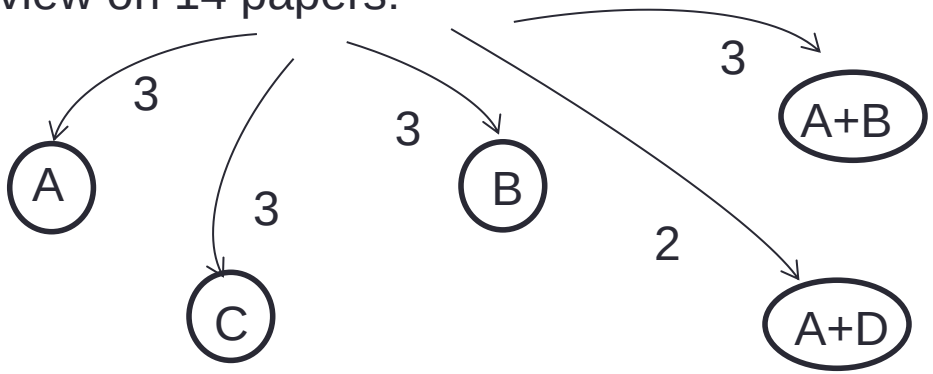
Energy Environ. Sci., 2011, 4, 4410–4422

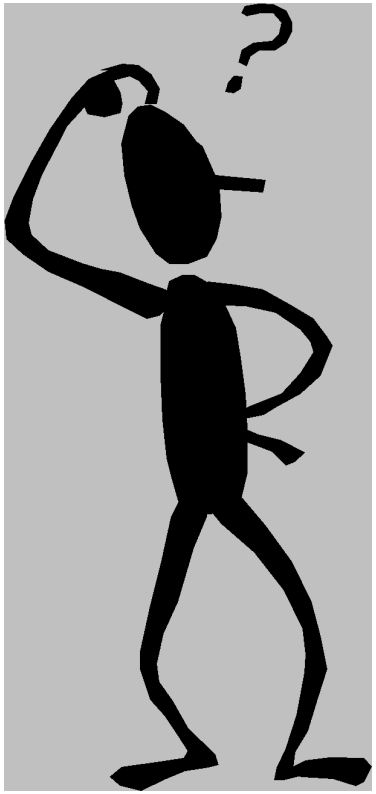
Investigating recombination losses

A. Geminate (CT recombination before splitting into free charges)
B. Langevin (o CT mediated)
C. Assisted by localized states (traps, tail states)
D. Reverse diffusive at the contacts

PHYSICAL REVIEW B 84, 075208 (2011)

Review on 14 papers:





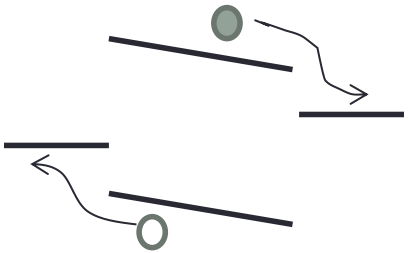
"Trap-dominated recombination should not be a surprise, because more carriers are trapped in localized states than are in the transport band under solar cell operating conditions" – R.A. Street

To the electrodes...

- **Collection at the electrodes**

Non-blocking contacts are required

GENERAL REQUIREMENT:



It's all about choosing suitable metals…

but...

- the choice of the metal contacts is driven by other requirements: leakage current, built-in electric field, availability and cost, stability,…
- life at metal/semiconductor interface is far more complicated...

D. Natali

Overall photogeneration efficiency?

External Quantum Efficiency:

$$EQE = \frac{\text{Number of collected charges/s}}{\text{Number of incoming photons/s}} = \frac{n_c/s}{n_v/s} = \eta_{abs} \cdot \eta_{ed} \cdot \eta_{cc}$$

Responsivity:

$$R = \frac{I}{P_{ott}} = \frac{\lambda q}{hc} \cdot EQE = \frac{\lambda[nm]}{1240} \cdot EQE$$