

# Photogeneration, Transport and Recombination of Charge Carriers in Organic Donor-Acceptor Solar Cells

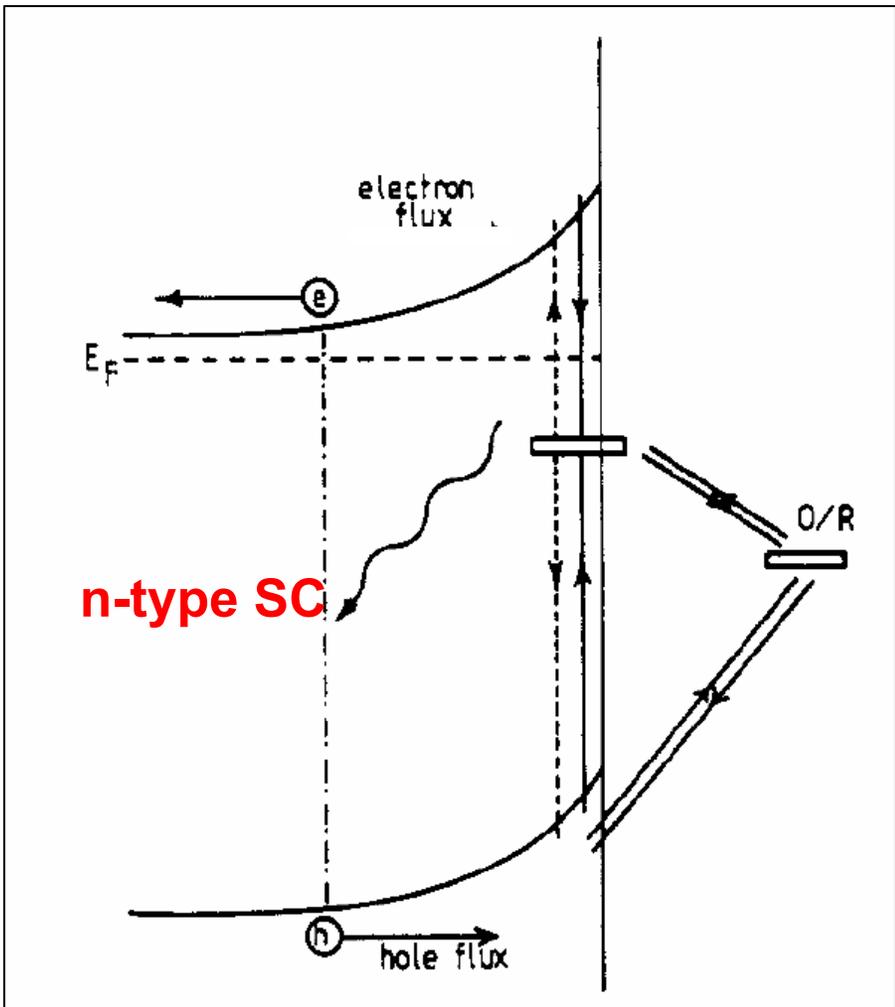
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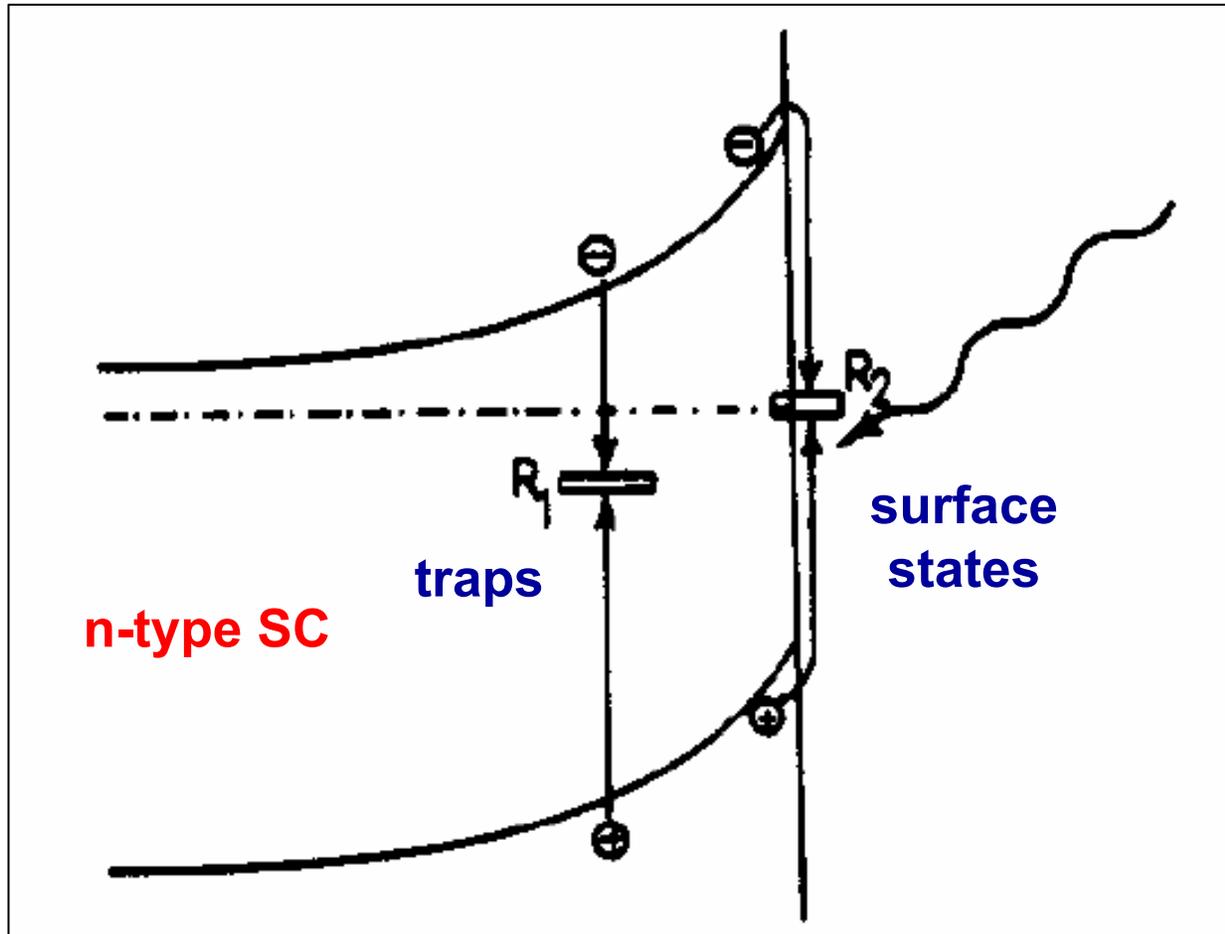


**Molecular Aspects of Solid State and Interfacial Electrochemistry (MolE) 2012, Dubna, Russia**

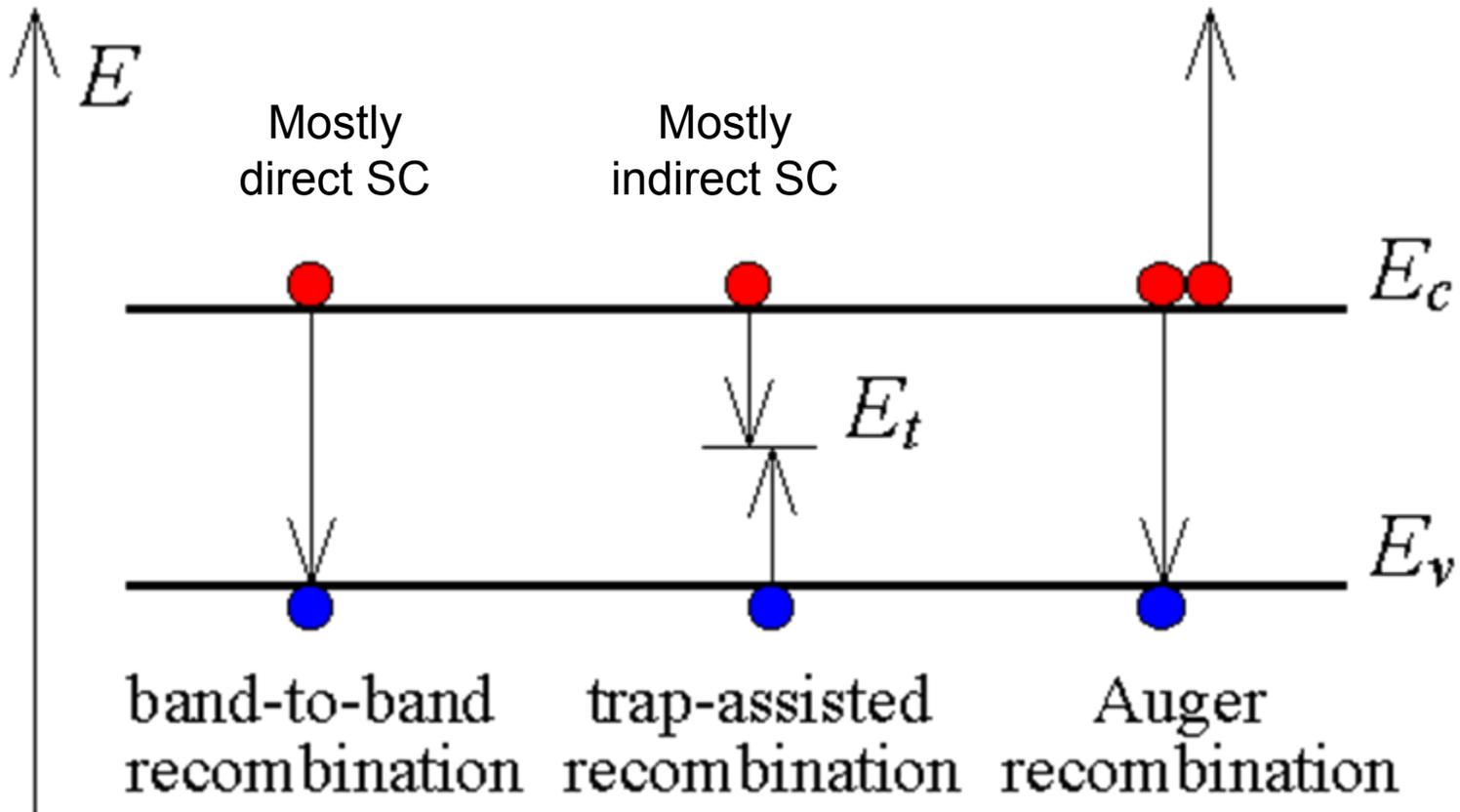
# Generation and Separation of Electron-Hole Pairs in Semiconductors



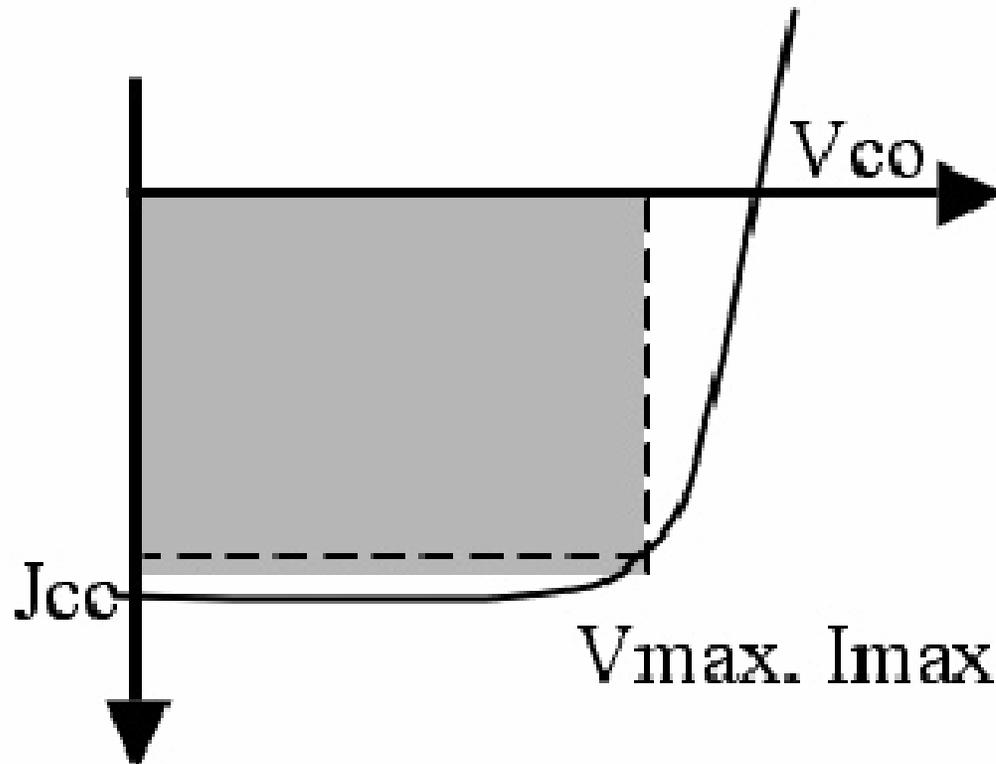
# Bulk and Surface Recombination



# Types of Bulk Recombination



# A Characteristic Current-Voltage Curve for a Photovoltaic Cells



# Transport, Generation and Recombination in the Bulk

concentration of excess minority carriers

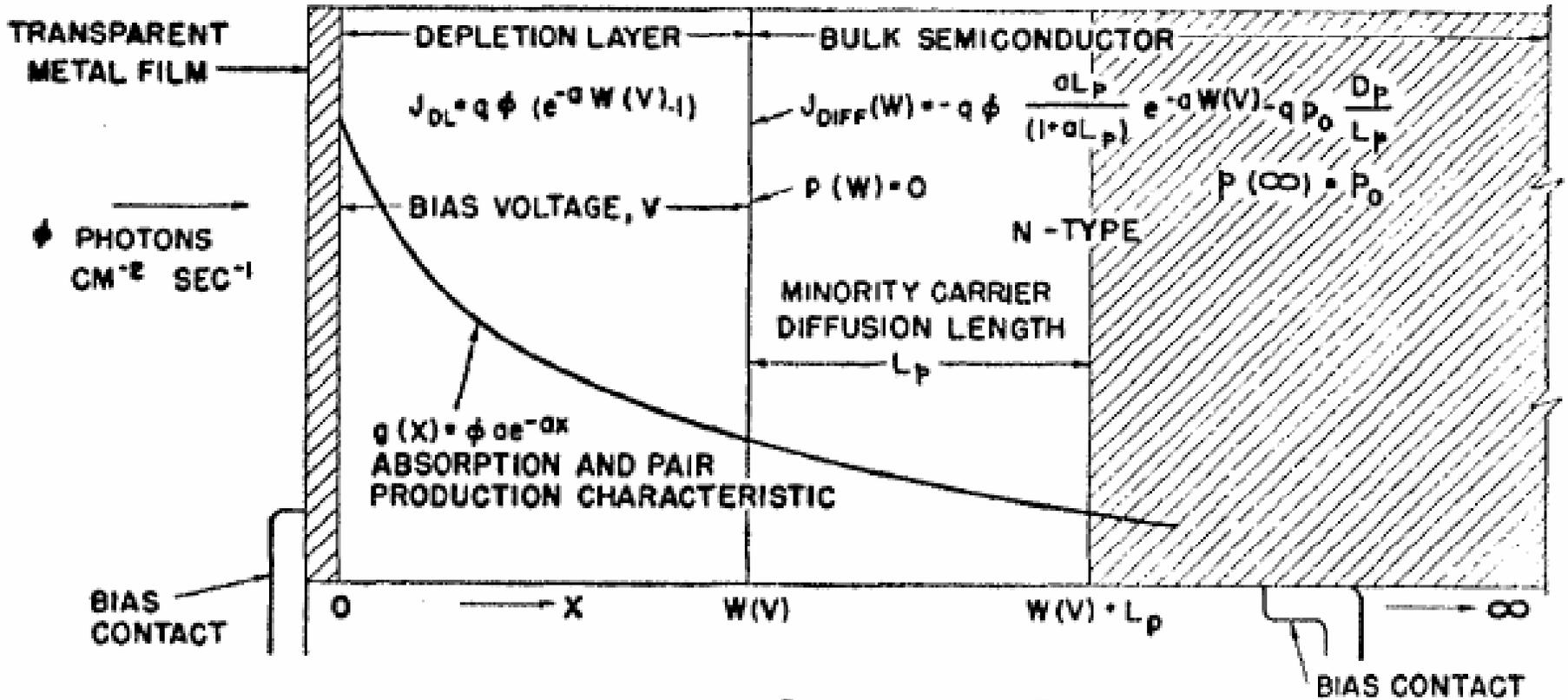
generation

$$\frac{\partial n}{\partial t} = D \frac{\partial^2 n}{\partial x^2} - \frac{n}{\tau} + \alpha I_0 e^{-\alpha x}$$

minority carrier diffusion

minority carrier lifetime defined by bulk recombination

# Gaertner's Model (1959)



$$J_{TOT} = J_{DL} + J_{DIFF} = -q\phi \left[ 1 - e^{-\alpha W} / (1 + \alpha L_p) \right] - qP_0 \frac{D_p}{L_p}$$

All light absorbed in the depletion layer gives rise to photocurrent!

The last term is usually omitted since in an n-type semiconductor  $p_0$  can be neglected

# Gaertner's Model

All light absorbed in the depletion layer gives rise to photocurrent! No recombination!

$$J_{DL} = q \int_0^W g(x) dx = q\Phi(e^{-\alpha W} - 1)$$

$$g(x) = \alpha \cdot \Phi e^{-\alpha \cdot x}$$

# Gaertner's Model

Furthermore, if  $\alpha^{-1} \ll W$  (weakly absorbed light), then

$$\begin{aligned} j_{photo} &= -q\Phi \left(1 - \frac{1}{1 + \alpha L_p} (1 - \alpha W)\right) = \\ &= -q\alpha\Phi \frac{L_p + W}{1 + \alpha L_p} \end{aligned}$$

If further  $L_p \ll W$  (high recombination in the quasi-neutral region or low mobility), then

$$j_{photo} = -q\alpha\Phi W$$

**The photocurrent is proportional to the width of the space-charge layer!**

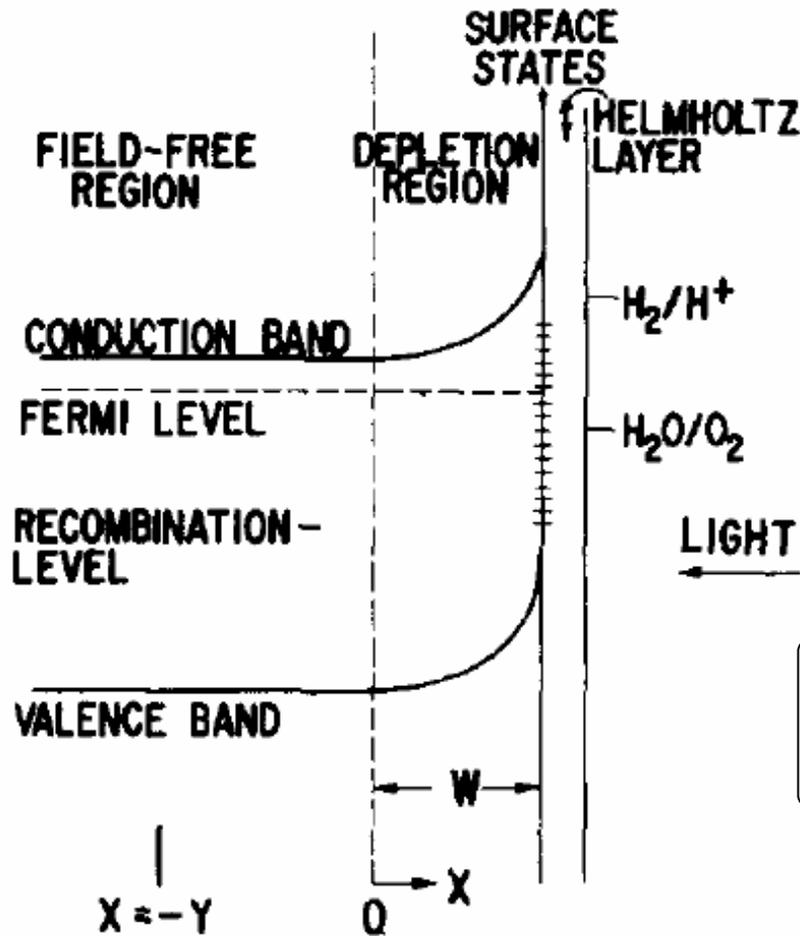
# Gaertner's Model

$$j_{photo} = - q \cdot a \cdot \Phi \cdot W$$

$$W = \sqrt{\frac{2\epsilon\epsilon_0}{e_0 N_D} |\phi - \phi_{fb}|}$$

- The photocurrent is proportional to the square root of the bias applied across the space-charge region and will also increase with a decrease in the donor density (wider SCR).
- Gaertner's model does not account for recombination in the SCR and at the interface! The only factor is the minority carrier diffusion length  $L_p$ .

# Wilson's Model (1977)



Using the boundary conditions

$$p \text{ finite at } x \rightarrow -\infty,$$

$$p \text{ continuous at } x = -y,$$

and

$$-D \frac{dp}{dx} = Sp, \quad \text{at } x = 0,$$

$S$  is the kinetic parameter related to the rates of surface reactions, recombination and charge transfer

$$S = S_r + S_t$$

# Wilson's Model

$$j_{photo} = -q\Phi \frac{S_t}{S_t + S_r} \left( 1 - \exp(-\alpha W) + \exp(-\alpha W) \frac{L_p}{L_p + D/S} \frac{\alpha L_p}{\alpha L_p + 1} \right)$$

**cf.** (Gaertner's model):

$$j_{photo} = -q\Phi \left( 1 - \exp(-\alpha W) \frac{1}{\alpha L_p + 1} \right)$$

# Wilson's Model

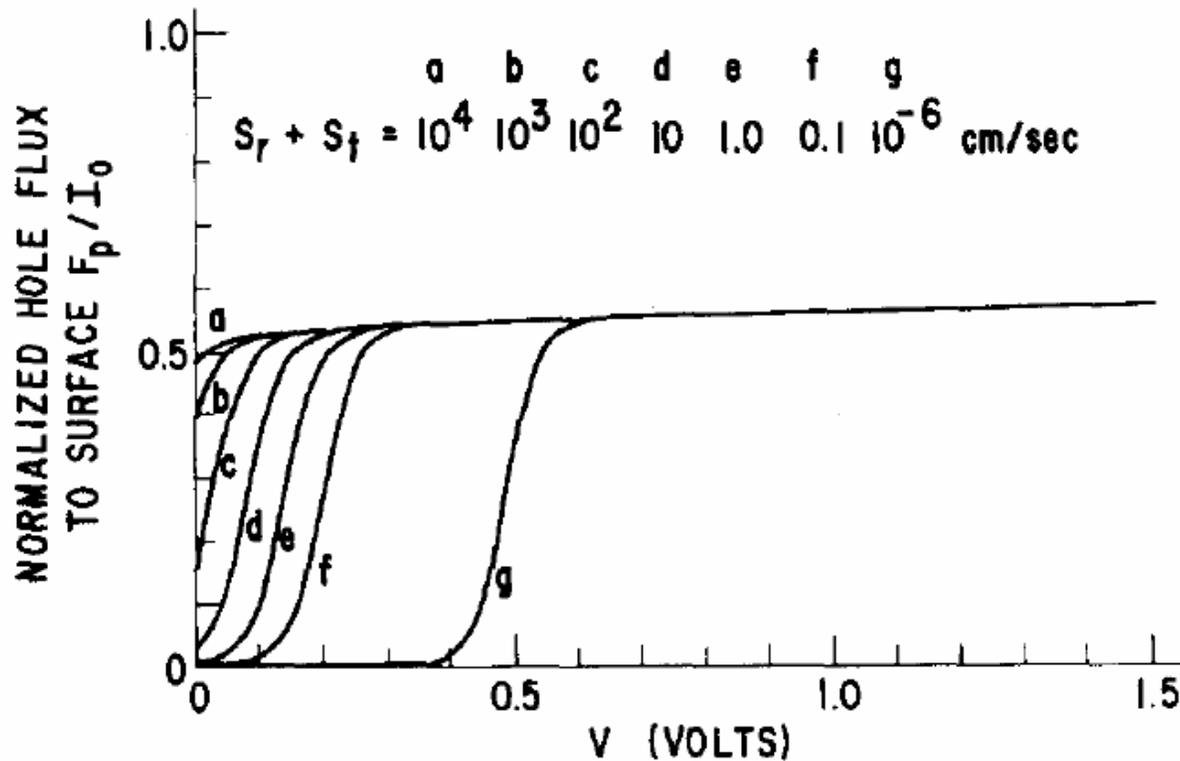
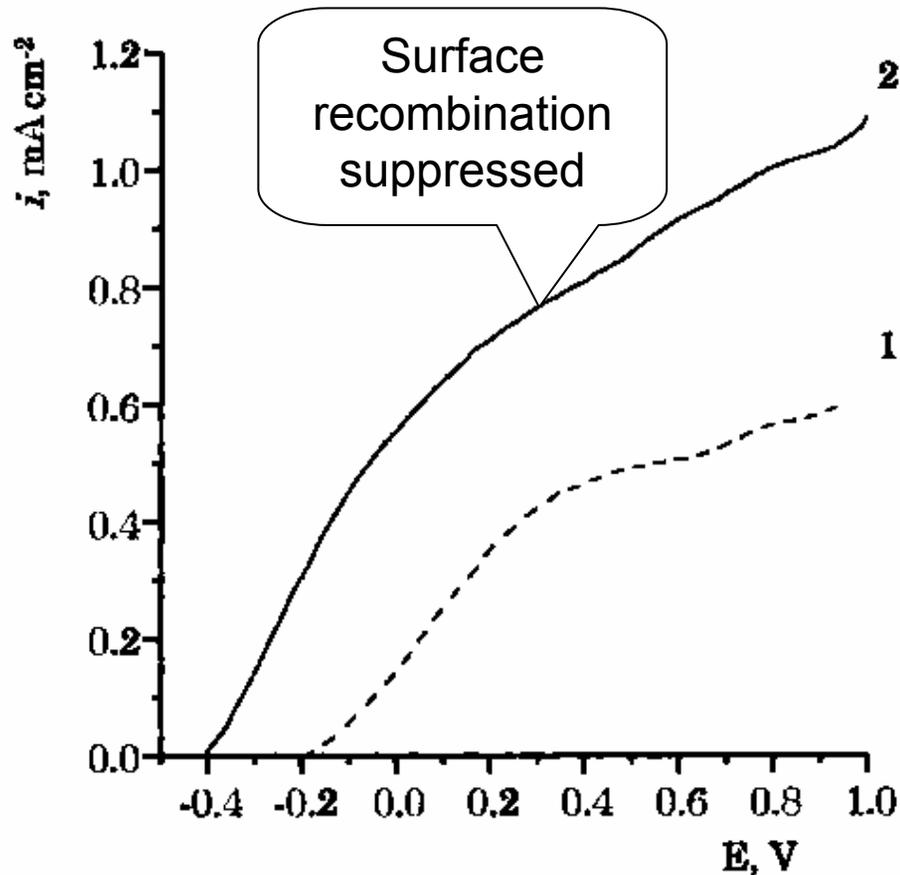


FIG. 2. Calculated hole flux to the surface with the surface re-action parameters indicated. Diffusion length  $L = 10^{-4}$  cm; absorption coefficient  $\alpha = 10^4$  cm $^{-1}$ ; doping density  $N = 10^{18}$  cm $^{-3}$ .

# Experimental effect of surface recombination



Semenikhin et al Langmuir 15, 1999, 3731

# Intensity Modulated Illumination

$$\frac{\partial n}{\partial t} = D \frac{\partial^2 n}{\partial x^2} - \frac{n}{\tau} + \alpha I_0 e^{-\alpha x}$$

$$I_0 = I_{dc} + I_{ac} \cdot \exp(i\omega t) \cdot \exp(i\varphi)$$

$$I_{dc}; I_{ac}; \omega = \text{var}$$

# Intensity Modulated Photocurrent/ Photovoltage Spectroscopy (IMPS/IMVS)

– sinusoidal modulation of the laser light intensity

- MHz  $\rightarrow$  mHz
- 10 ns  $\rightarrow$  100 s

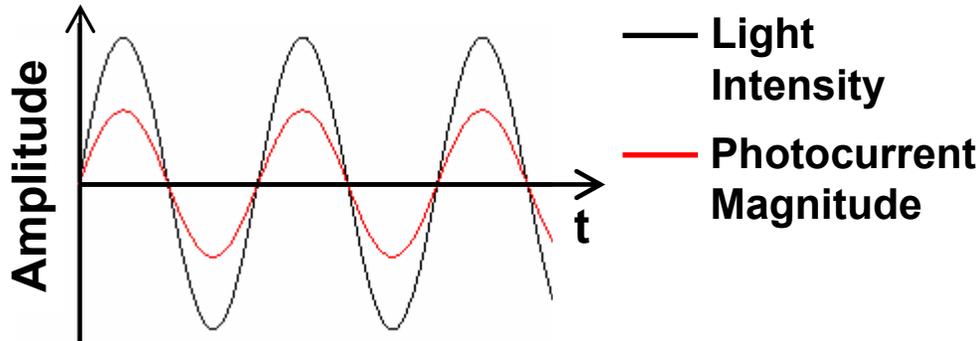


– the modulation depth can be varied  $\rightarrow$  allows studies of non-linear behaviour

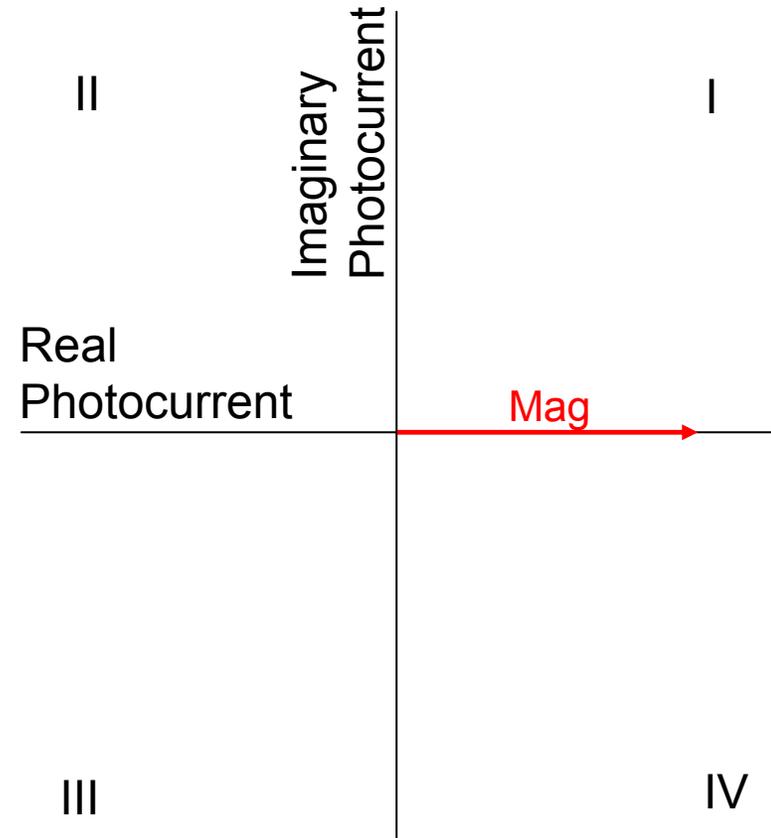
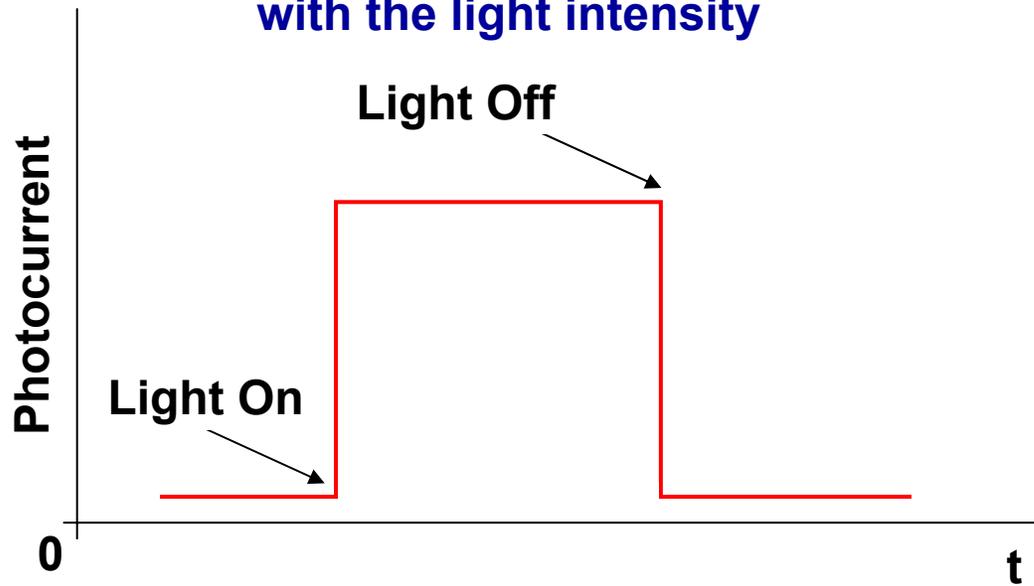
– *ac* photocurrent and *ac* photovoltage measured using a Frequency Response Analyzer (FRA)

– the frequency dependencies are presented on the complex plane (Nyquist plots) and as Bode plots of the photocurrent magnitude and phase vs. frequency.

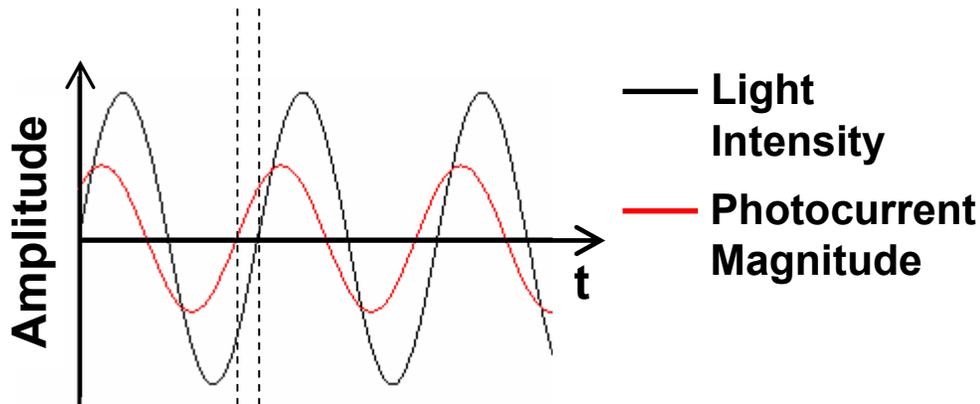
# IMPS Background



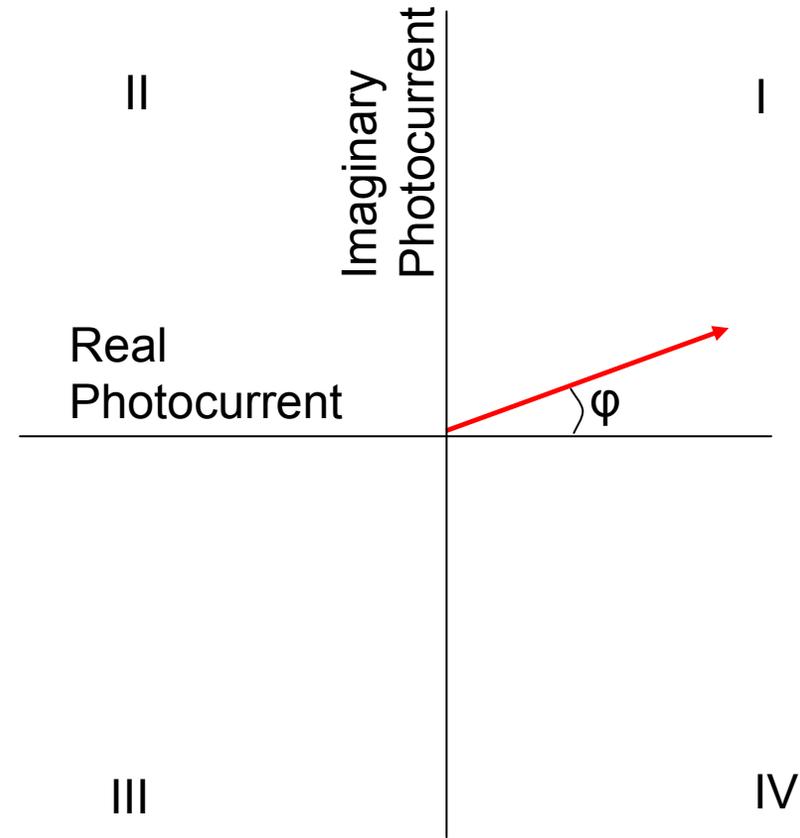
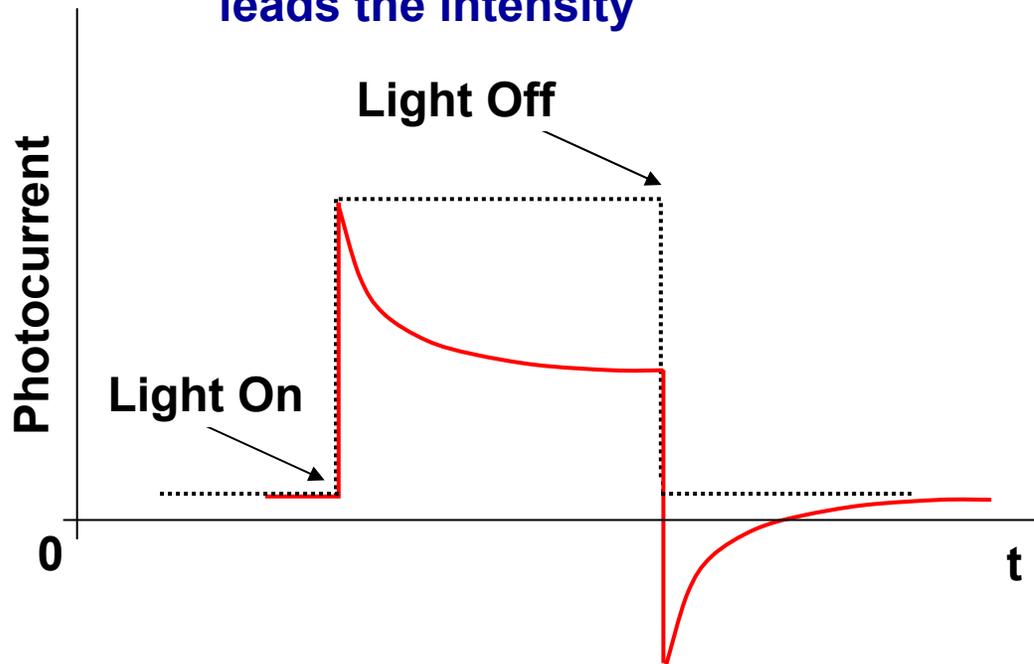
$\phi = 0$ , photocurrent is in phase with the light intensity



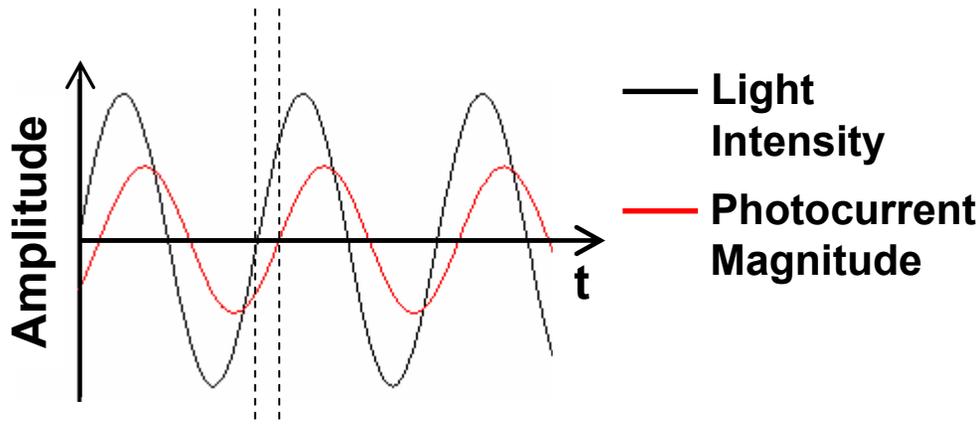
# IMPS Background



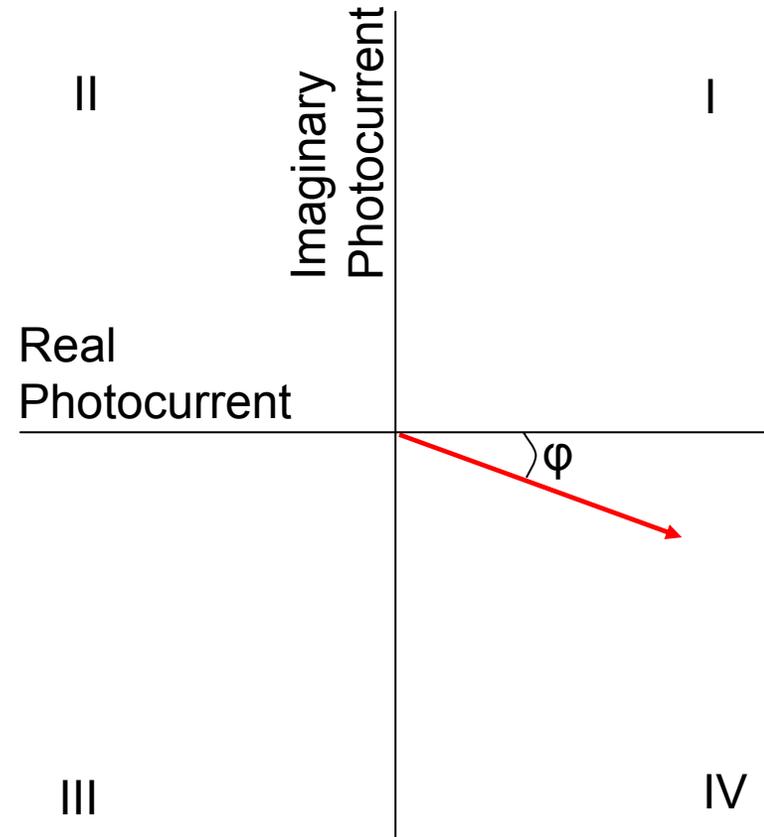
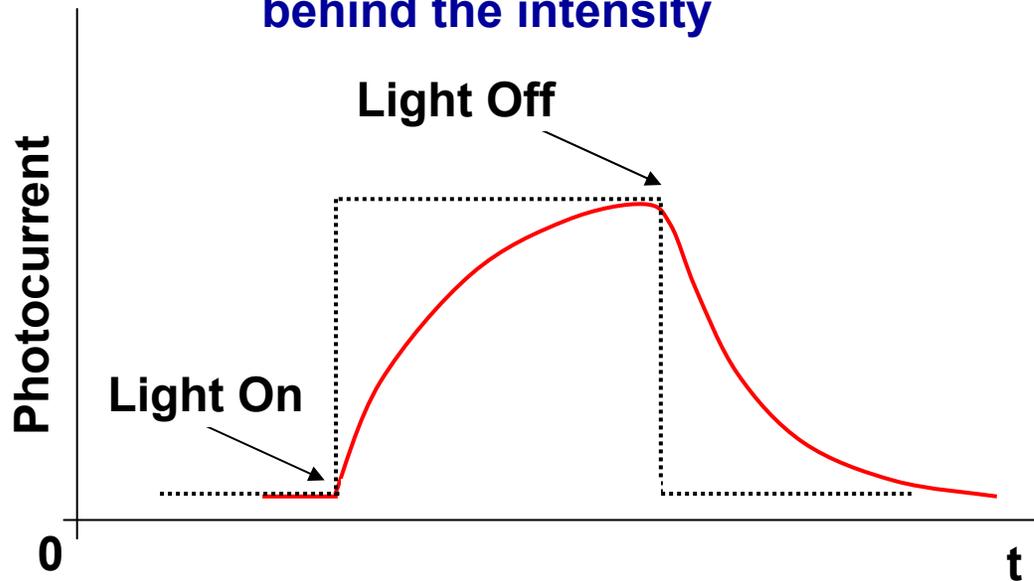
Positive  $\phi$ , photocurrent leads the intensity



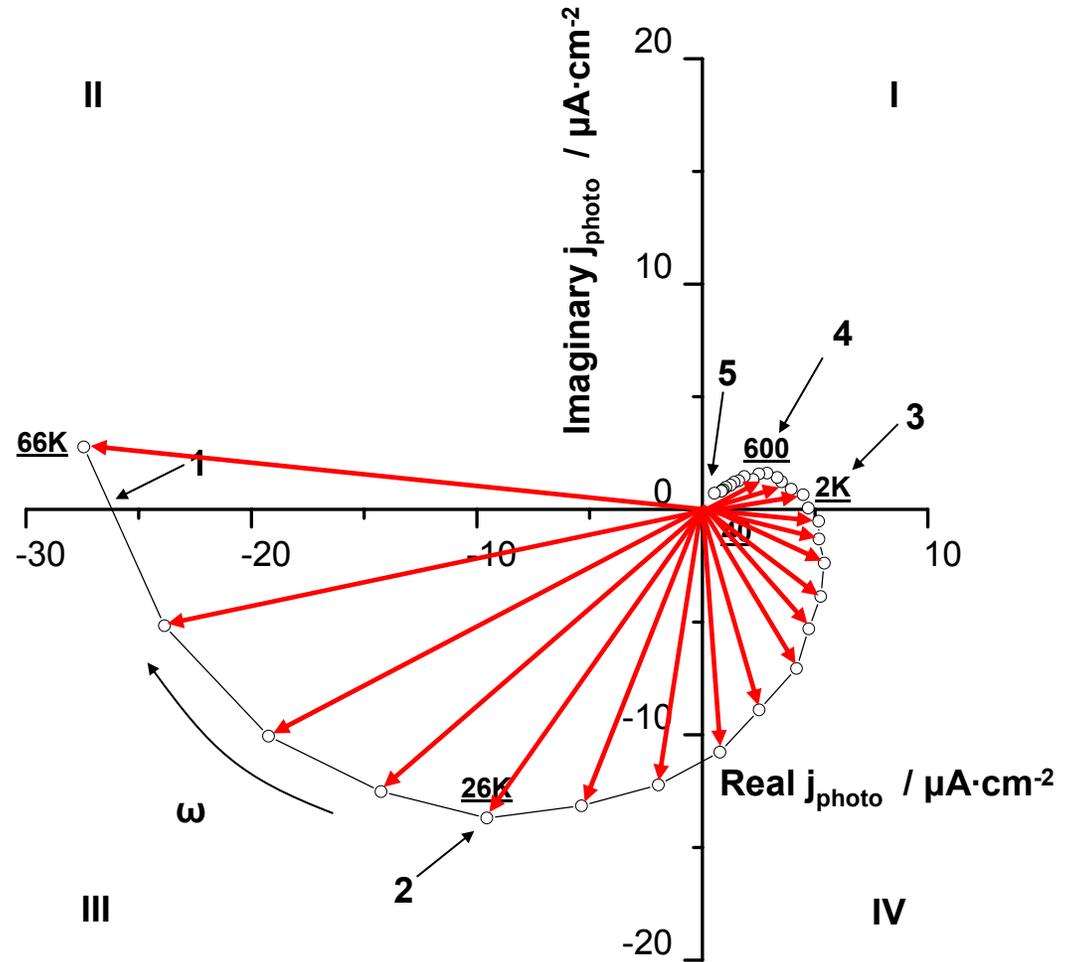
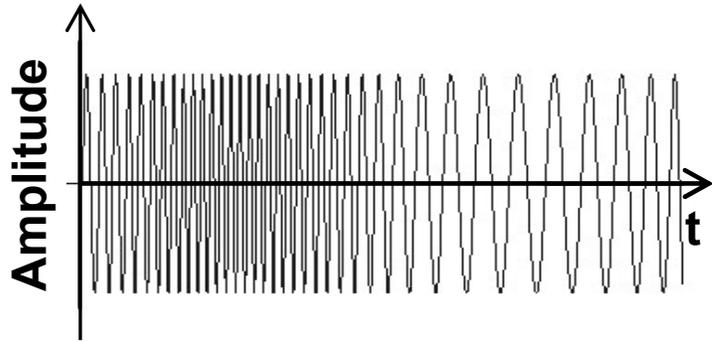
# IMPS Background



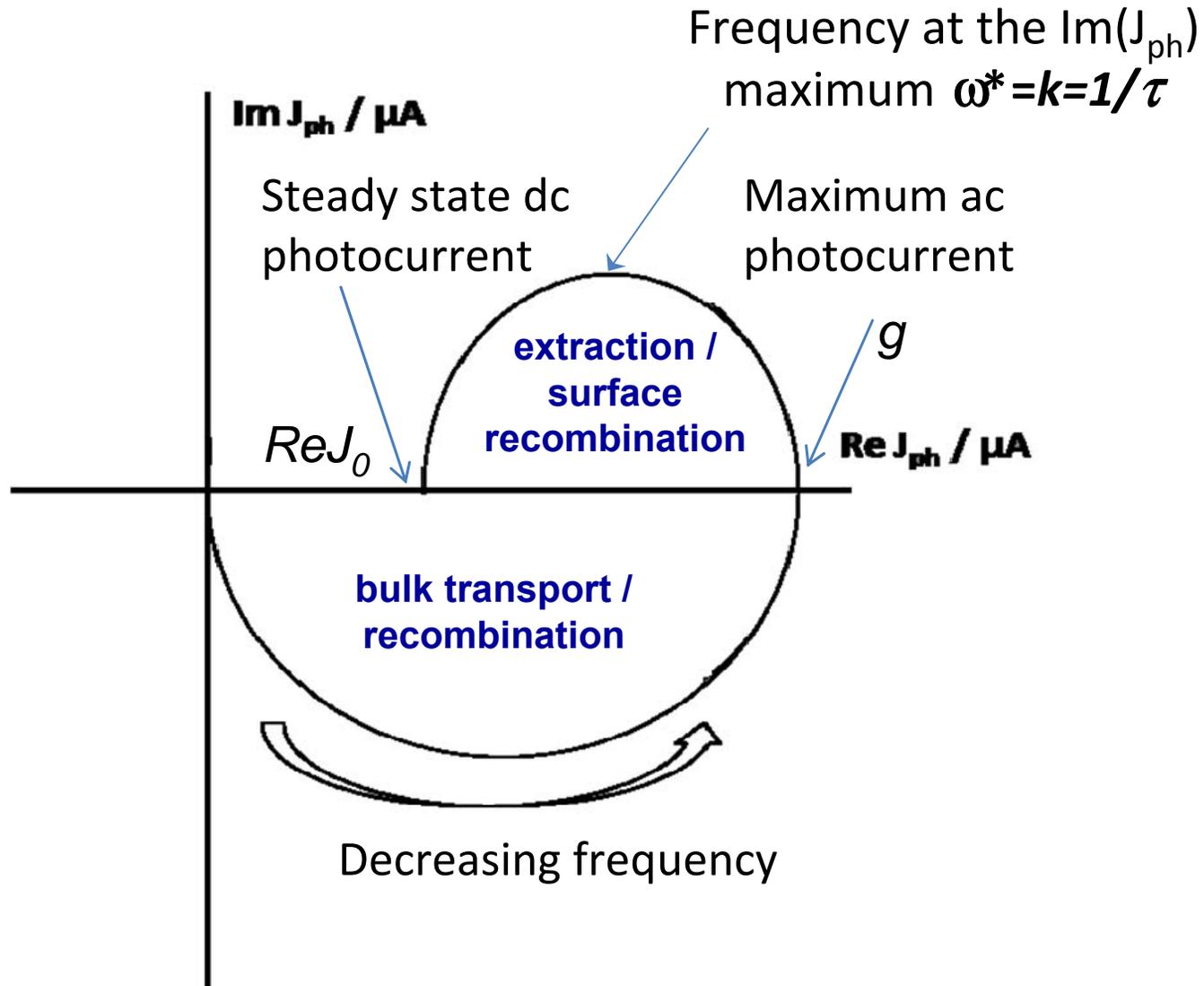
**Negative  $\phi$ , photocurrent lags behind the intensity**



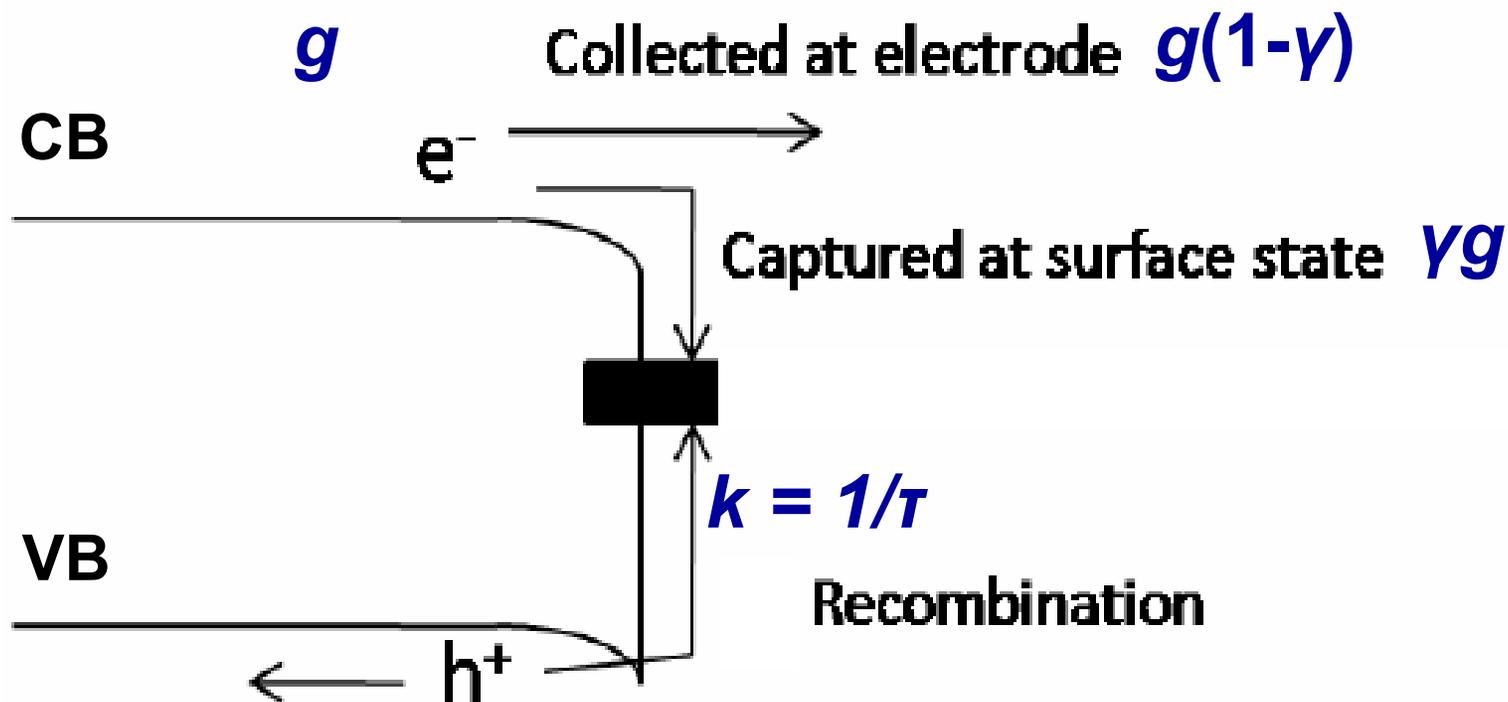
# IMPS Background



# An example of an IMPS plot



# Photoinduced interfacial processes



# Intensity Modulated Illumination: Surface Processes

$$\frac{dp}{dt} = \gamma g - kp$$

$$I = I \cdot \exp(i\alpha t);$$

$$p = p \cdot \exp(i\omega t); g = g \cdot \exp(i\omega t)$$

$$i\alpha p = \gamma g - kp$$

$$p = \frac{\gamma g}{k + i\alpha}; j_{photo} = g \cdot (1 - k \cdot p)$$

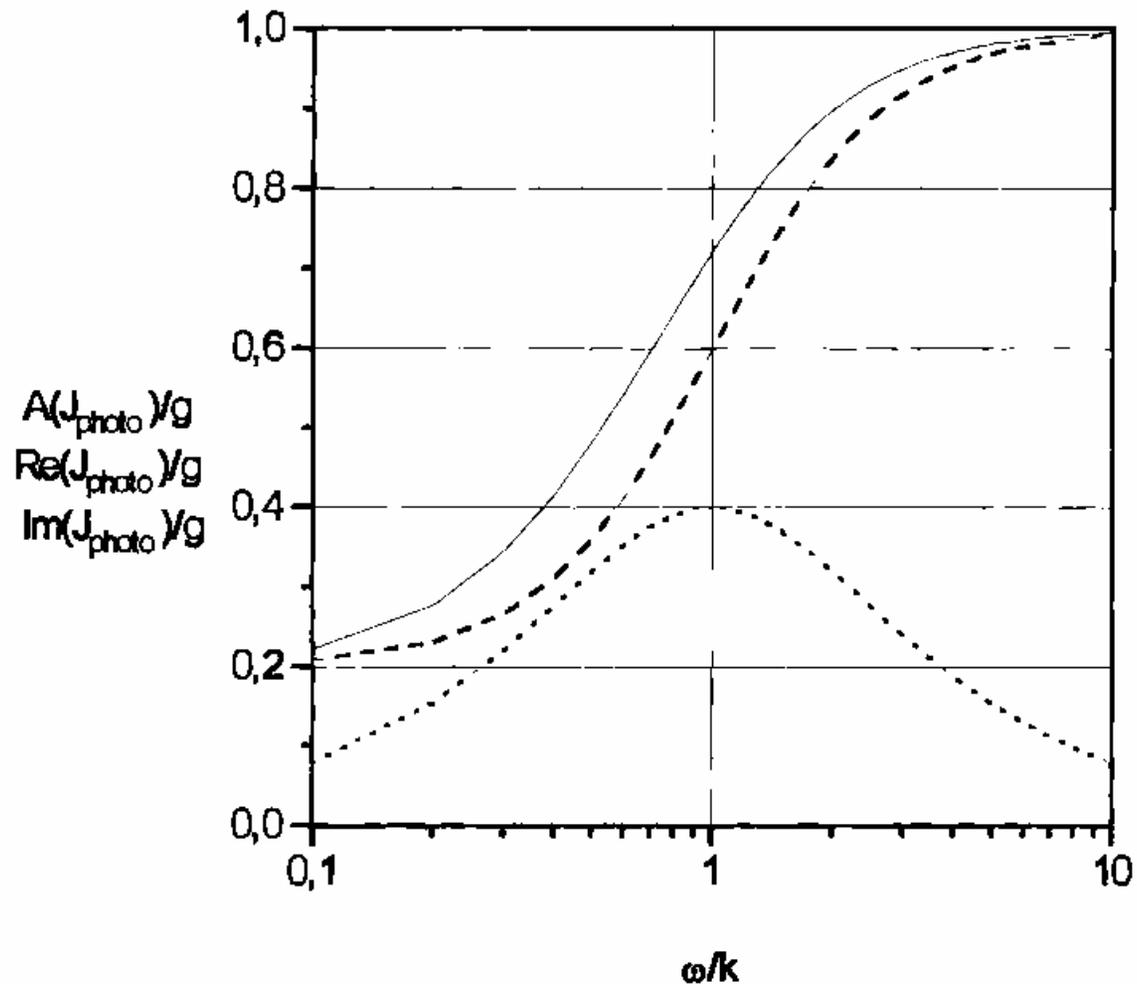
# Intensity Modulated Illumination: Surface Processes

$$j_{photo} = g \cdot (1 - k \cdot p) = g \left( 1 - \frac{\gamma \cdot k}{k + i\alpha} \right)$$

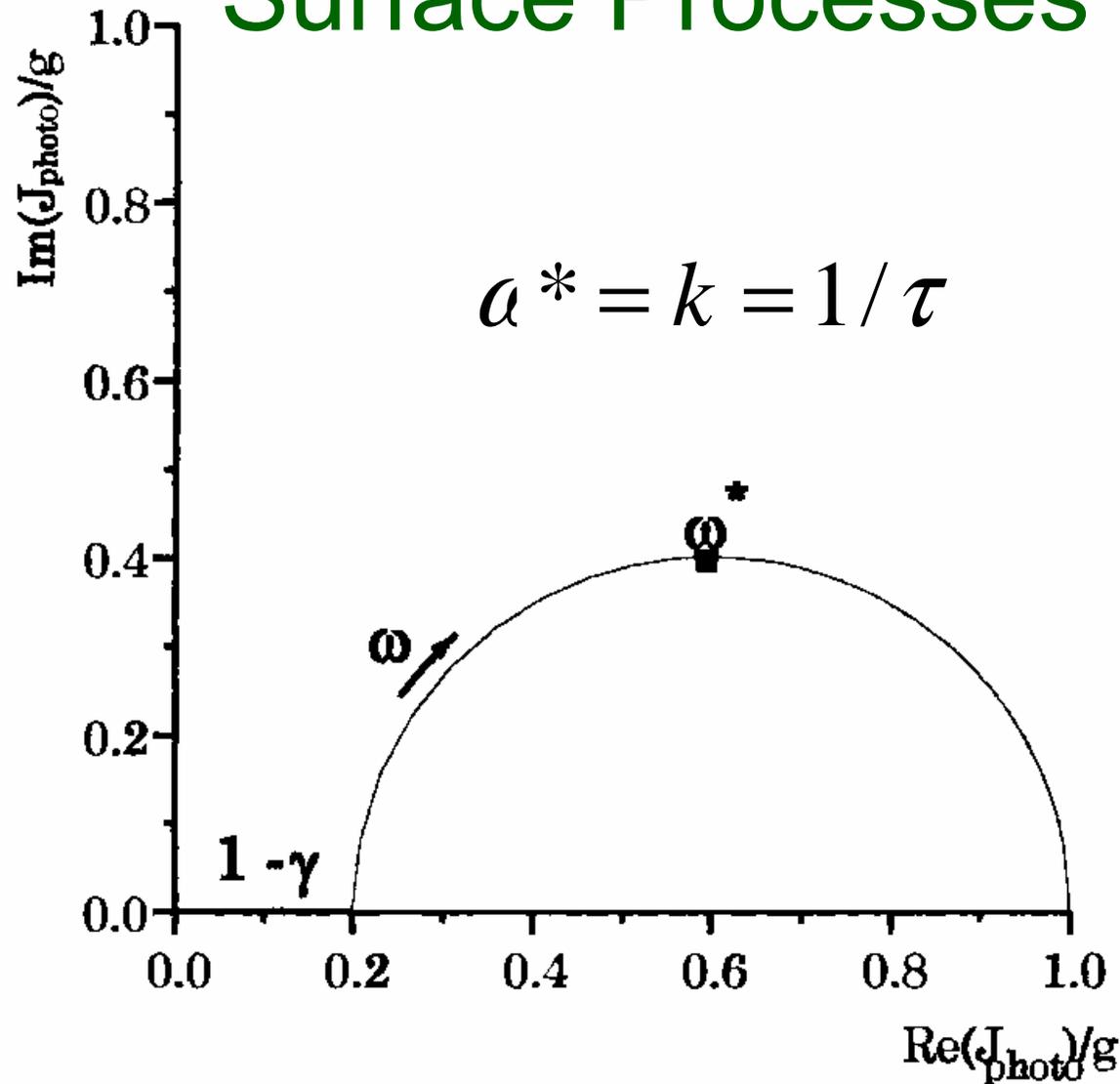
$$\text{Re}(j_{photo}) = g \left\{ 1 - \gamma / \left( 1 + \frac{\omega^2}{k^2} \right) \right\}$$

$$\text{Im}(j_{photo}) = g\gamma\omega / \left\{ k \left( 1 + \frac{\omega^2}{k^2} \right) \right\}$$

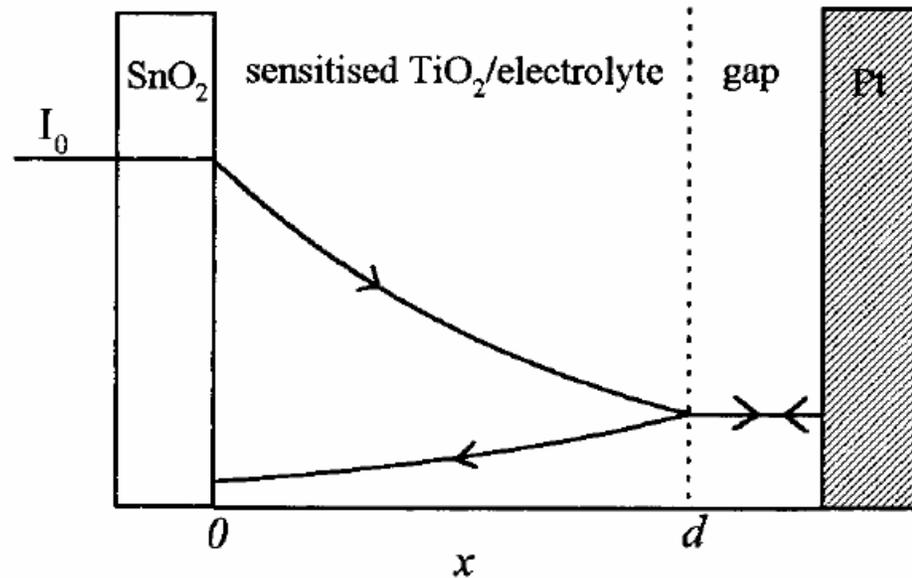
# Intensity Modulated Illumination: Surface Processes



# Intensity Modulated Illumination: Surface Processes



# Intensity Modulated Illumination: Bulk Processes



$$\Phi(\omega) = \frac{\alpha}{\alpha + \gamma} \cdot \frac{e^{\gamma d} - e^{-\gamma d} + 2\alpha \frac{e^{-\alpha d} - e^{-\gamma d}}{\gamma - \alpha}}{e^{\gamma d} + e^{-\gamma d} + \frac{D\gamma}{k_{\text{ext}}}(e^{\gamma d} - e^{-\gamma d})} \quad \gamma = \sqrt{\left(\frac{1}{D\tau} + \frac{i\omega}{D}\right)}$$

$$\frac{\partial n(x, t)}{\partial t} = D_n \frac{\partial^2 n(x, t)}{\partial x^2} - \frac{n(x, t) - n_0}{\tau_n} + \alpha I_0 e^{-\alpha x}$$

$$\left. \frac{\partial n}{\partial x} \right|_{x=d} = 0 \quad k_{\text{ext}} n(0, t) = D_n \left( \left. \frac{\partial n}{\partial x} \right|_{x=0} \right)$$

$$n(x) = A e^{\gamma x} + B e^{-\gamma x} + C e^{-\alpha x} \quad \gamma = \left( \frac{1}{D_n \tau_n} \right)^{1/2}$$

$$C = \frac{\alpha I_0 / D_n}{\gamma^2 - \alpha^2}$$

$$A = C \frac{\alpha e^{-\alpha d} (k_{\text{ext}} + \gamma D_n) - \gamma e^{-\gamma d} (k_{\text{ext}} + \alpha D_n)}{\gamma (k_{\text{ext}} (e^{\gamma d} + e^{-\gamma d}) + D_n \gamma (e^{\gamma d} - e^{-\gamma d}))}$$

$$B = -C \frac{\alpha e^{-\alpha d} (k_{\text{ext}} - \gamma D_n) + \gamma e^{\gamma d} (k_{\text{ext}} + \alpha D_n)}{\gamma (k_{\text{ext}} (e^{\gamma d} + e^{-\gamma d}) + D_n \gamma (e^{\gamma d} - e^{-\gamma d}))}$$

## steady state

$$\gamma = \left( \frac{1}{D_n \tau_n} \right)^{1/2}$$

$$n(x) = A e^{\gamma x} + B e^{-\gamma x} + C e^{-\alpha x}$$

## periodic illumination

$$\gamma = \sqrt{\frac{1}{D_n \tau_n} + i \frac{\omega}{D_n}}$$

## IMPS response

$$\frac{j_{\text{photo}}}{q \delta I_0} = \Phi(\omega) = \frac{\alpha}{\alpha + \gamma} \cdot \frac{e^{\gamma d} - e^{-\gamma d} + 2\alpha \frac{e^{-\alpha d} - e^{-\gamma d}}{\gamma - \alpha}}{e^{\gamma d} + e^{-\gamma d}}$$

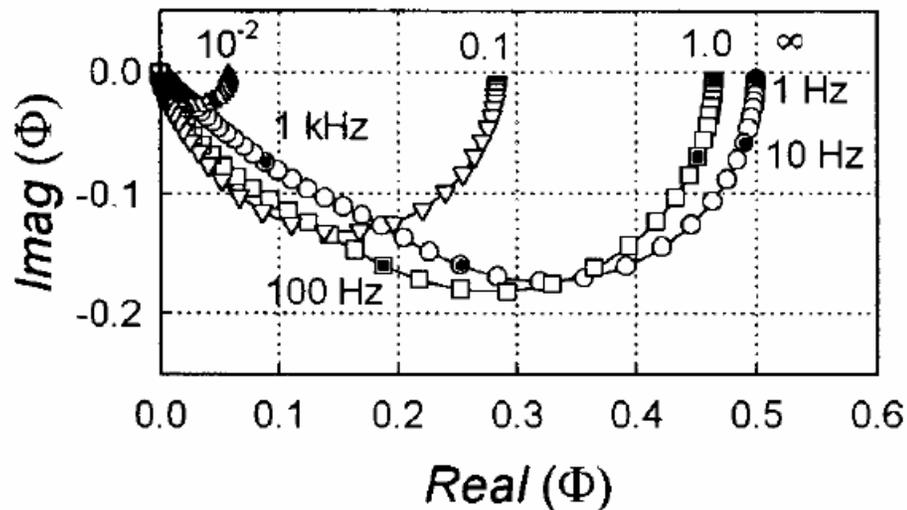
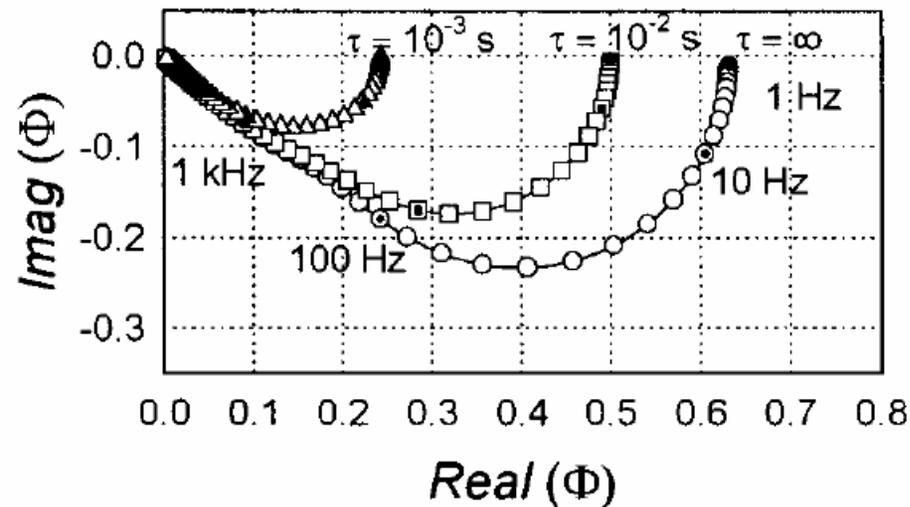
# IMPS of bulk diffusion/recombination in dye-sensitized solar cells

Diffusion-limited case:  $k_{\text{ext}} \gg \gamma D$  (fast extraction):

$$\Phi(\omega) = \frac{\alpha}{\alpha + \gamma} \cdot \frac{e^{\gamma d} - e^{-\gamma d} + 2\alpha \frac{e^{-\alpha d} - e^{-\gamma d}}{\gamma - \alpha}}{e^{\gamma d} + e^{-\gamma d}}$$

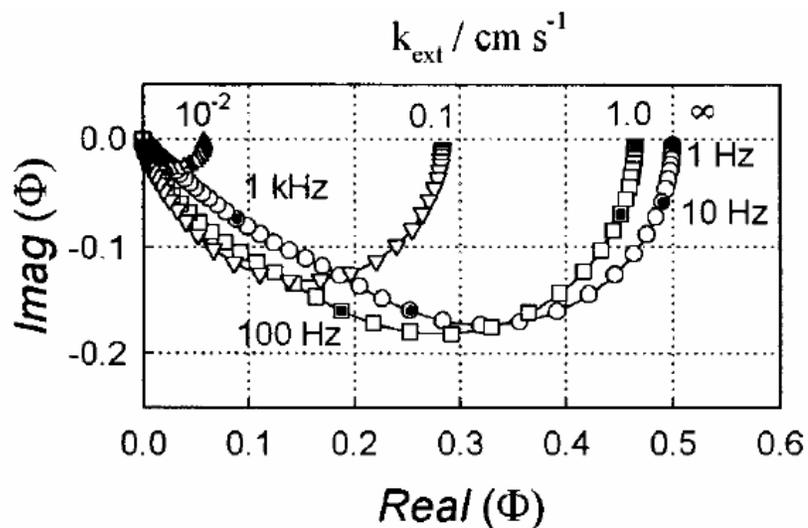
$$\gamma = \sqrt{\left(\frac{1}{D\tau} + \frac{i\omega}{D}\right)}$$

$k_{\text{ext}} / \text{cm s}^{-1}$

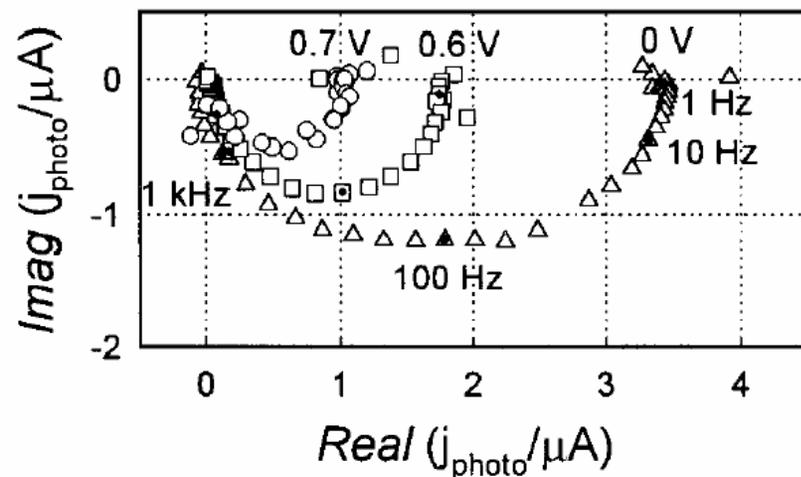


# IMPS of bulk diffusion/recombination in dye-sensitized solar cells

theory

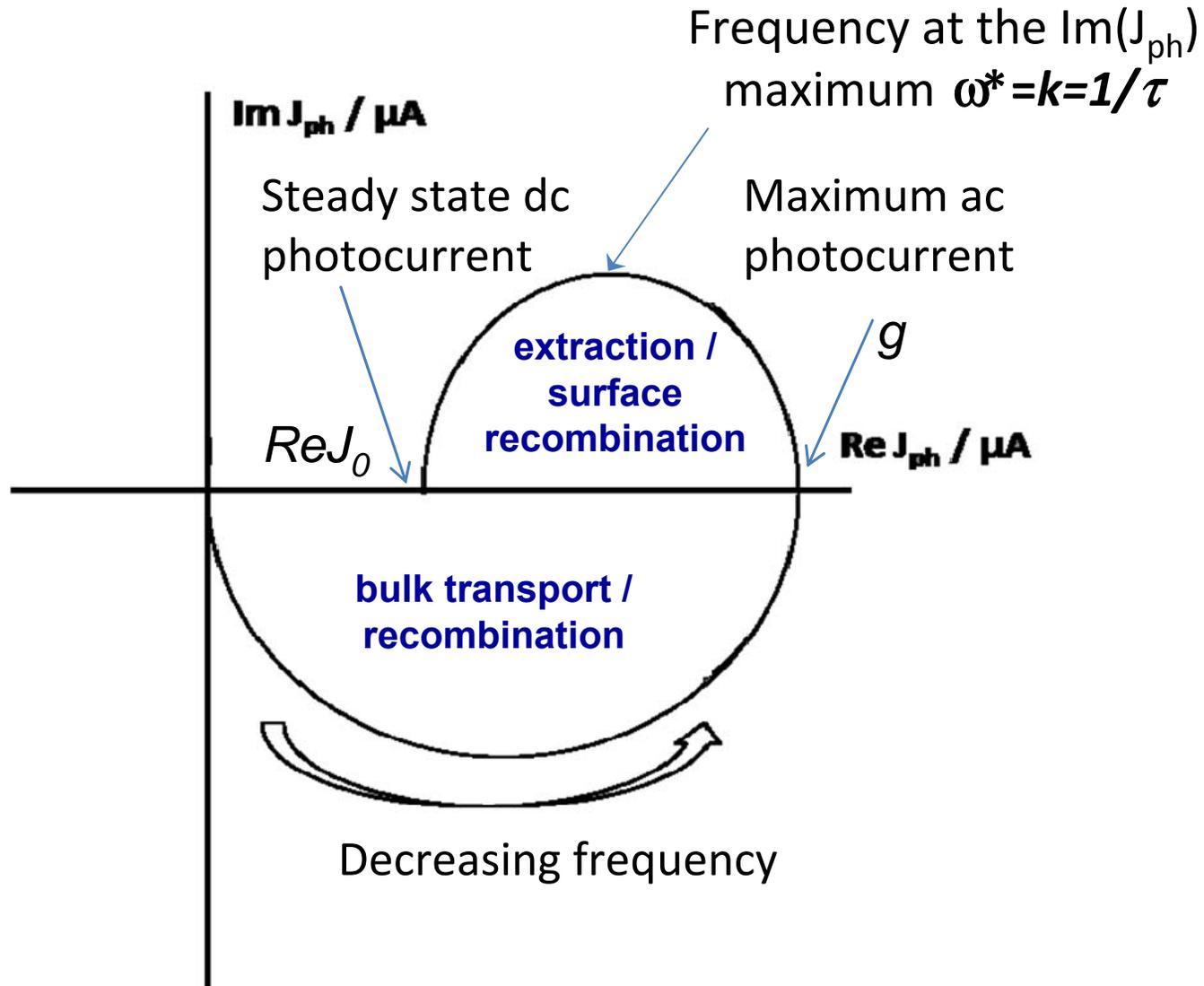


experiment



The electrode potential changes the interfacial rate constant of carrier extraction

# An example of an IMPS plot



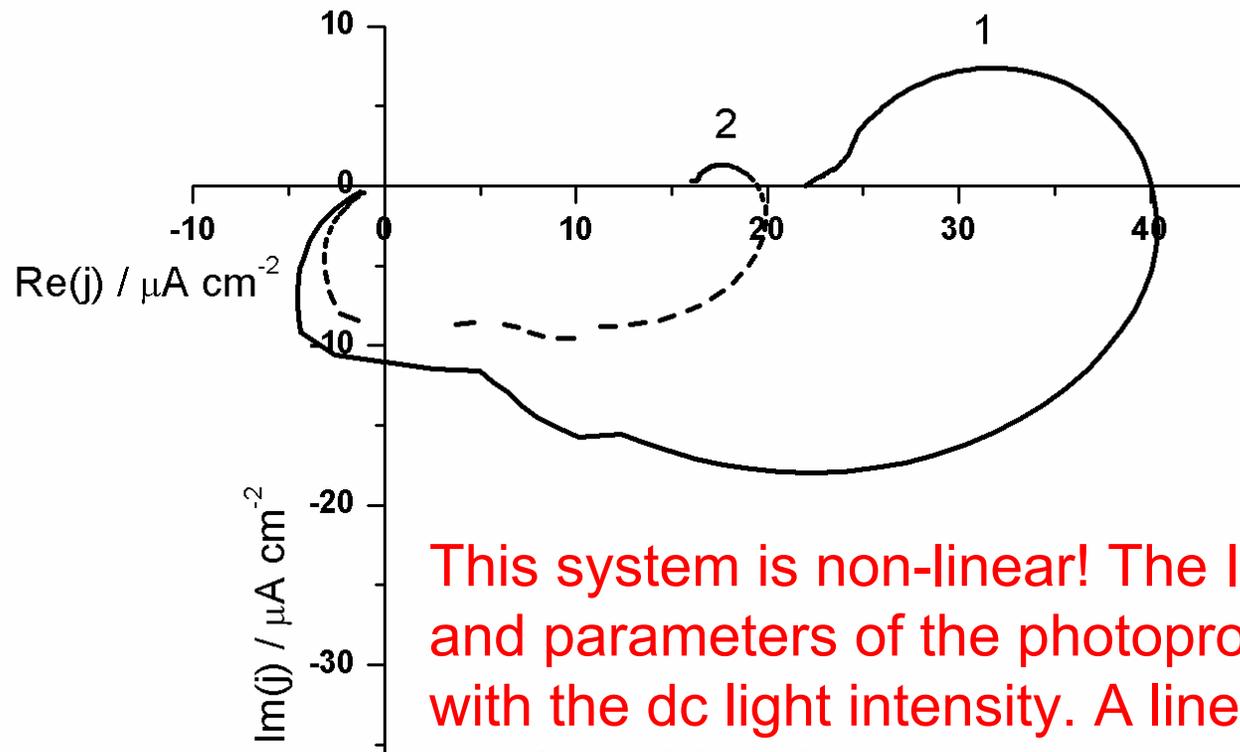
# IMPS studies of non-linear systems

$$I(\omega) = I_{dc} + I_{ac} \sin(\omega t)$$

$$I_{dc} = \text{var}, I_{ac} = \text{const}$$

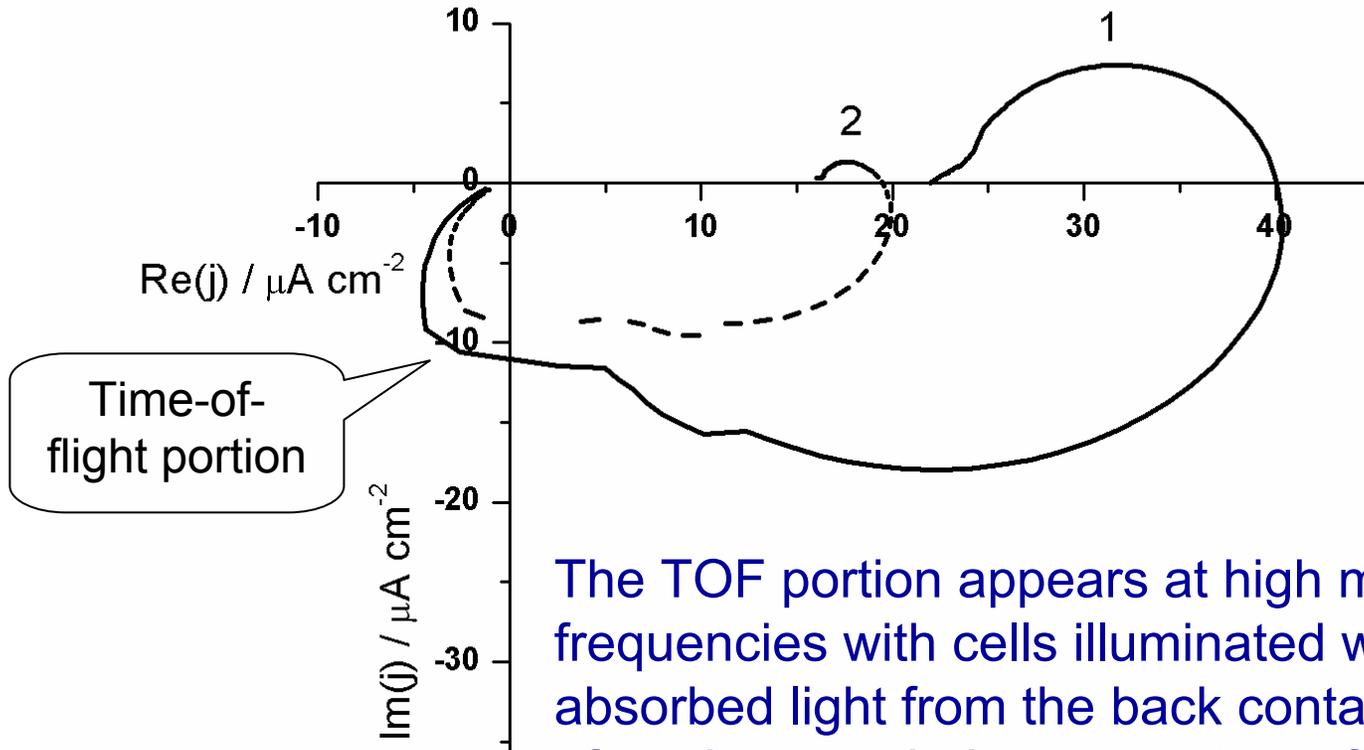
$$j_{\text{photo}}(\omega) = j_{\text{photo } dc} + j_{\text{photo } ac} \sin(\omega t + \varphi)$$

$$j_{\text{photo},ac} = f(\omega, I_{dc})$$



This system is non-linear! The IMPS traces and parameters of the photoprocess change with the dc light intensity. A linear system would exhibit the same trace for all intensities.

# The Time-of-Flight Portion



The TOF portion appears at high modulation frequencies with cells illuminated with strongly absorbed light from the back contact. The packets of carriers reach the top contact after a TOF delay, which is translated in the frequency domain into a spiral loop at high frequencies.

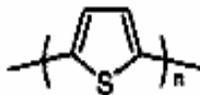
# Organic Donor-Acceptor Solar Cells

# Molecular Structures of Some Conjugated Polymers

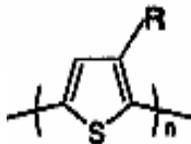
Polyacetylene (PA)



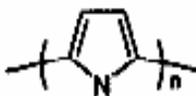
Polythiophene (PT)



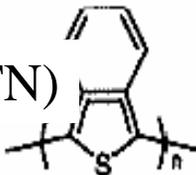
Poly(3-alkyl)thiophene



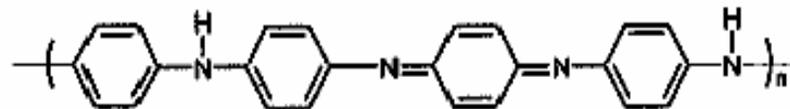
Polypyrrole (Ppy)



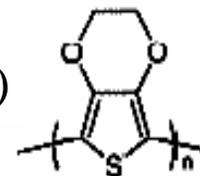
Polyisothianaphthene (PITN)



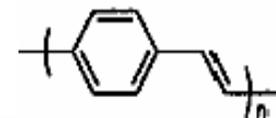
Polyaniline (PANI)



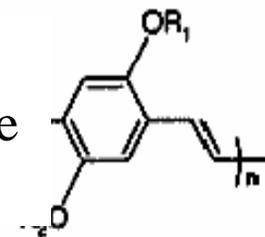
Polyethylenedioxy  
thiophene (PEDOT)



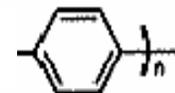
Polyparaphenylene  
vinylene (PPV)



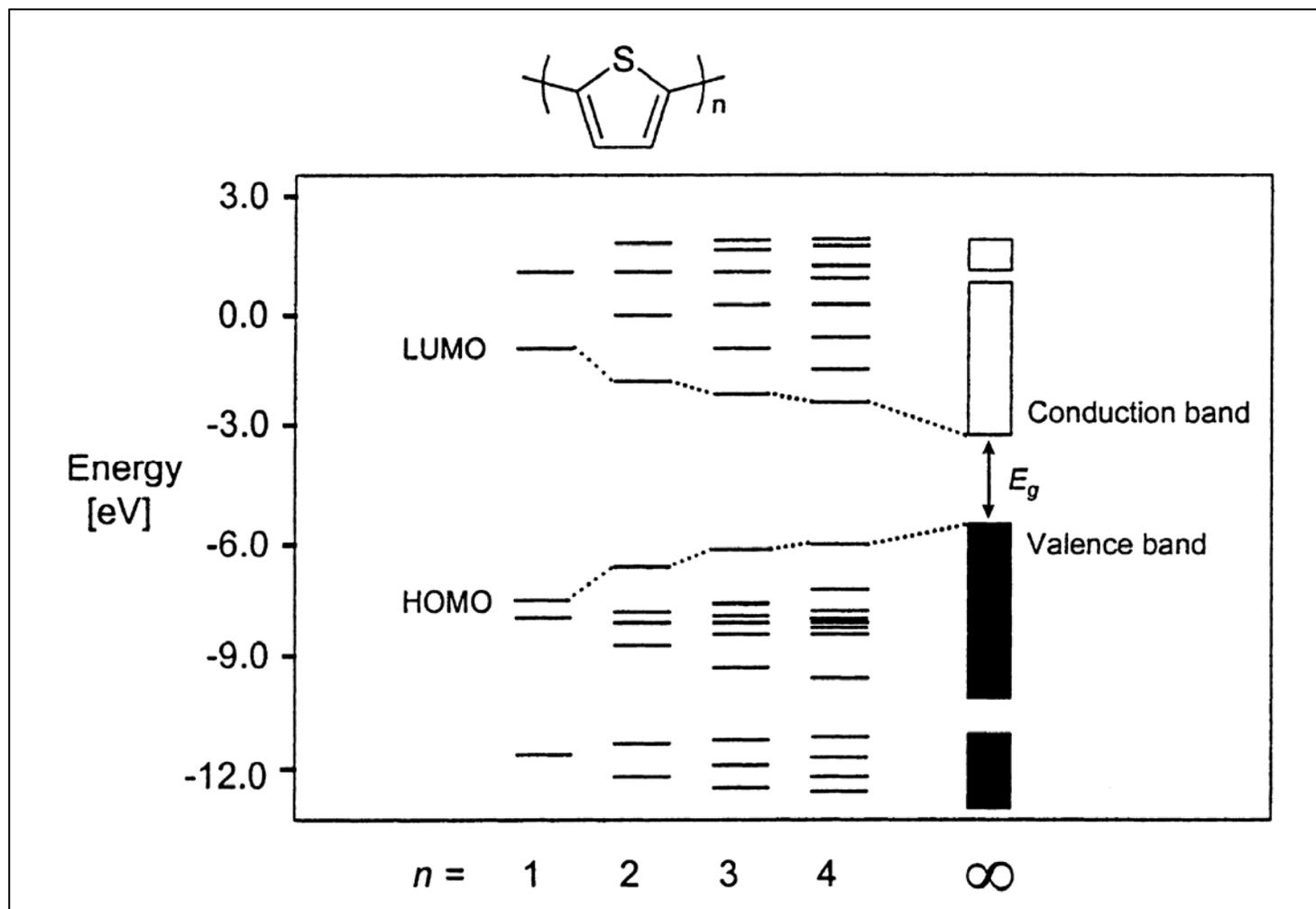
Poly(2,5dialkoxy)  
paraphenylene vinylene  
(e.g. MEH-PPV)



Polyparaphenylene (PPP)



# Calculated (frontier) energy levels of oligothiophenes and polythiophene



# Photovoltaics and Photoconductivity in Organic Molecular Solids

- Organic molecular solids are semiconductors with **wide band gaps** and **narrow bands**.
- This is due to the fact that the **overlapping  $\pi$ -orbitals** belong to **different molecules** and **overlapping** is necessarily rather **weak**.
- **Narrow bands** mean relatively **low conductivity**. In other terms, the **effective masses** of carriers in molecular solids are **high**.
- The main uses of semiconductors are in electronics and in various photovoltaic/photoconductive/luminescent devices.
- Narrow bands and low mobilities do not favour the use of these materials in electronics. However, wide bandgaps and low dark conductivities are perfect for various photo-related technologies.

# Photovoltaics and Photoconductivity in Organic Molecular Solids (cont-d)

- Photoconduction in organic molecular solids (anthracene) was discovered as early as in 1906, at the same time as that of Si.
- A prototype of an organic photovoltaic cell was made by the father of electrochemical kinetics Max Vollmer in 1913.
- All these photo-related phenomena are based on generation of mobile charge carriers upon absorption of light by an organic material.
- The light should possess a certain threshold energy. This energy is related but not always equal to the band gap.
- Photoconductivity is carrier movement in external electric field.
- The difference between photoconductivity and photovoltaic effect is that in the latter case photoexcited carriers can also create an internal electric field.

# Photoexcitation in organic materials.

## Excitons vs. free electrons and holes.

- What are the elementary photoexcitations responsible for photoconductivity and other related properties?
- We have heard many times that in inorganic semiconductors such as Si, the photogenerated charge carriers are free electrons and holes. But what does the term “free” means?
- In fact, elementary photoexcitations in organic materials and also in many cases in inorganic semiconductors are so-called excitons rather than free electrons and holes.
- An exciton is an electron and a hole bound together by Coulombic attraction that lowers their energy. This energy difference between free and bound e-h pairs is called the exciton binding energy.
- The difference between excitons and elementary excited states is that excitons are moving excited states 😊 Their lifetime is long enough to move inside the material.

# Photoexcitation in organic materials. Excitons vs. free electrons and holes.

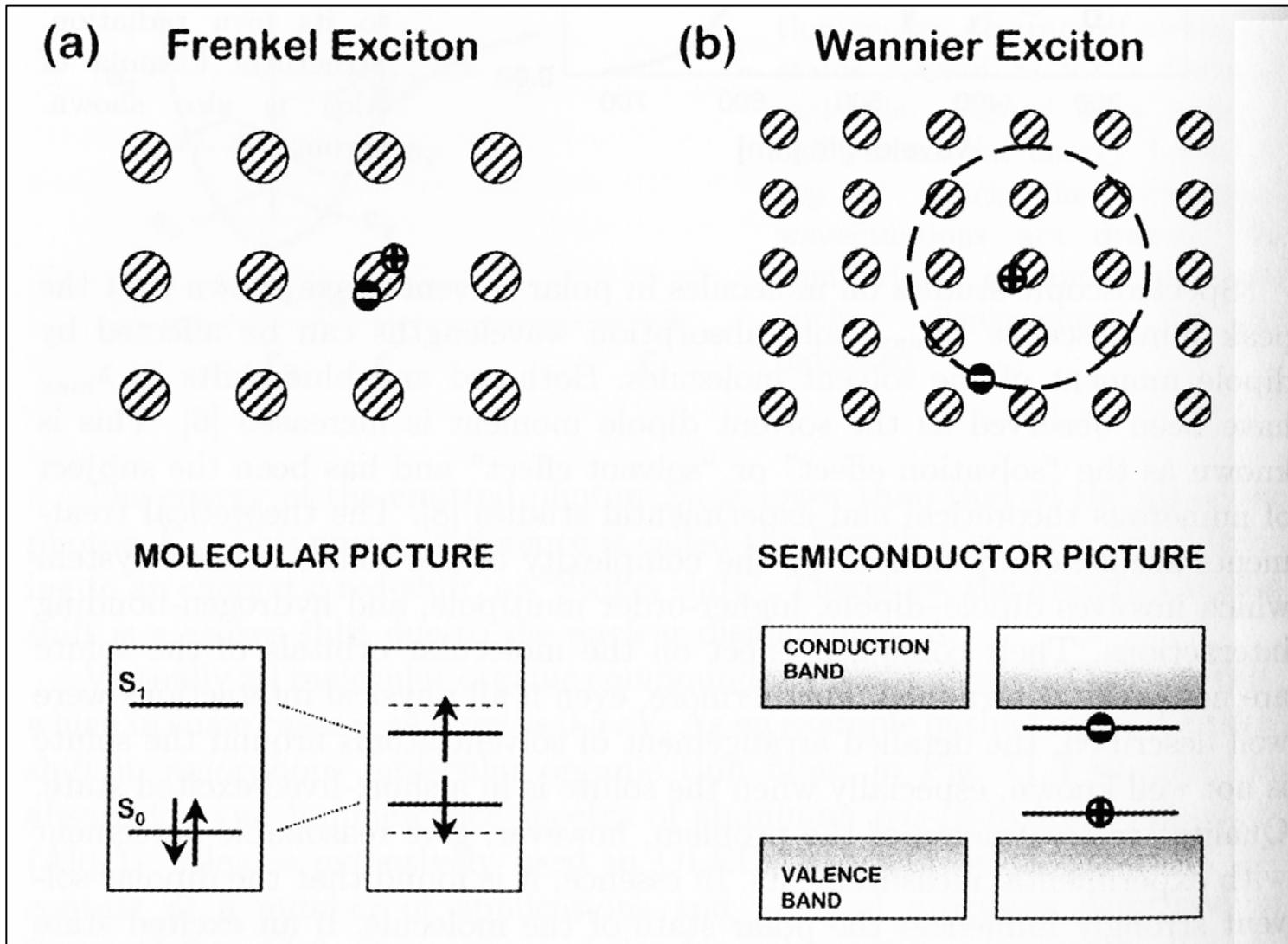
- Well, how about free electrons and holes? Was that model absolutely wrong? Since an electron is always negative and a hole is always positive, there will always be some Coulombic interaction between them and they should always be bound in excitons, right?
- Well, yes, to a point, but in many practical cases this binding energy is as small as a few meV and insignificant as compared to the thermal motion energy  $k_B T$ .
- If a material has many charge carriers and many charges, these charges efficiently screen the Coulombic interaction and the exciton binding energies are small. This is the case with inorganic semiconductors.
- If a material has a few charges, the screening is not efficient and excitons have large binding energies. This is the case with molecular crystals.



# Excitons in Molecular Crystals

- As can be inferred from the above, there are various degrees of delocalization between photoexcited electrons and holes. As dependent on the delocalization, several types of excitons can be defined.
- The first case, photoexcited electron and hole on the same molecule, is called a Frenkel exciton. It is the most localized excitation with the radius similar to the size of a molecule and smaller than the intermolecular distance. It is neutral and moves by diffusion. Usually, its lifetime is very short, although it can be longer in luminescent materials.
- The second case corresponds to the most delocalized Wannier-Mott exciton. Due to very efficient screening (many charge carriers or efficient orbital overlapping resulting in high polarizability), the exciton radius is very large, many times the size of the lattice constant. This exciton can be readily dissociated, e.g., by electric field.

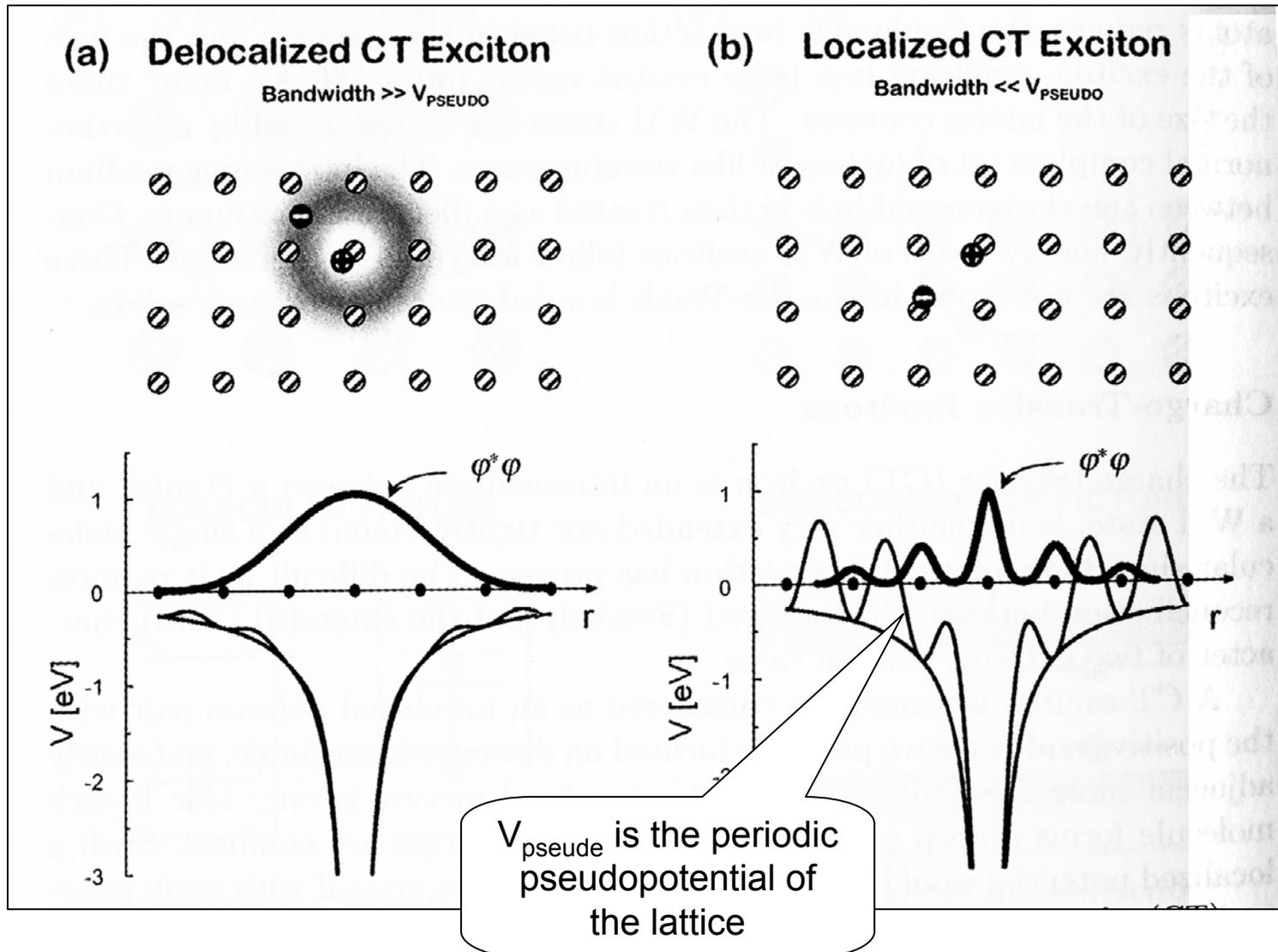
# Excitons in Molecular Crystals



# Excitons in Molecular Crystals

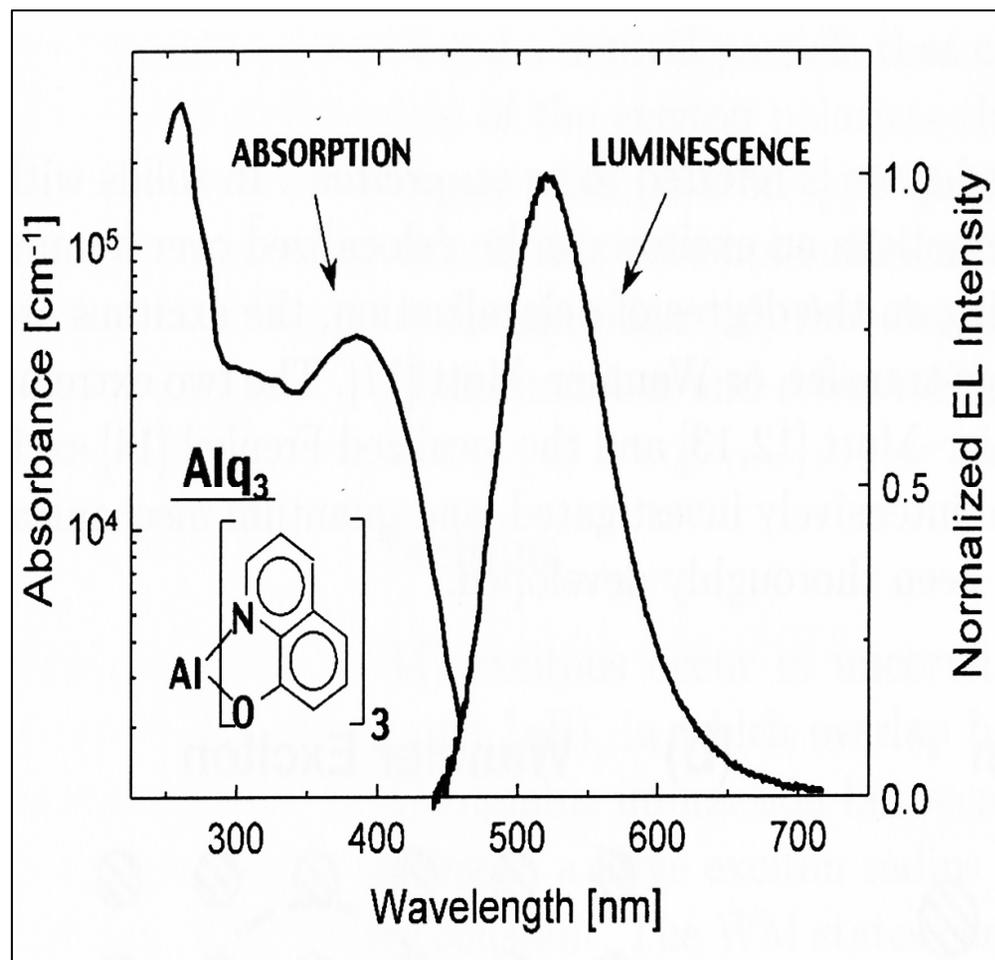
- At intermediate delocalizations, we have charge-transfer (CT) excitons. They are neither very extended nor tightly bound to a single molecular site.
- However, additional localization can occur if the charge-lattice interaction (sometimes given by periodic lattice pseudo-potential  $V_{\text{pseudo}}$ ) is strong.
- In covalently bound solids, the correlation between excited electronic states is strong because of efficient overlap of neighbouring molecular orbitals (relatively wide bands). This weakens the interaction of charges with the lattice. The charge density is delocalized but the delocalization is less than in the case of Wannier-Mott excitons.
- In weakly bonded molecular crystals, the overlap is small (narrow bands). The variations in the electron energy due to  $V_{\text{pseudo}}$  are larger than the band width. Extended bands may cease to exist. Carriers are localized on individual molecules.

# Excitons in Molecular Crystals



# Another View of Excitons

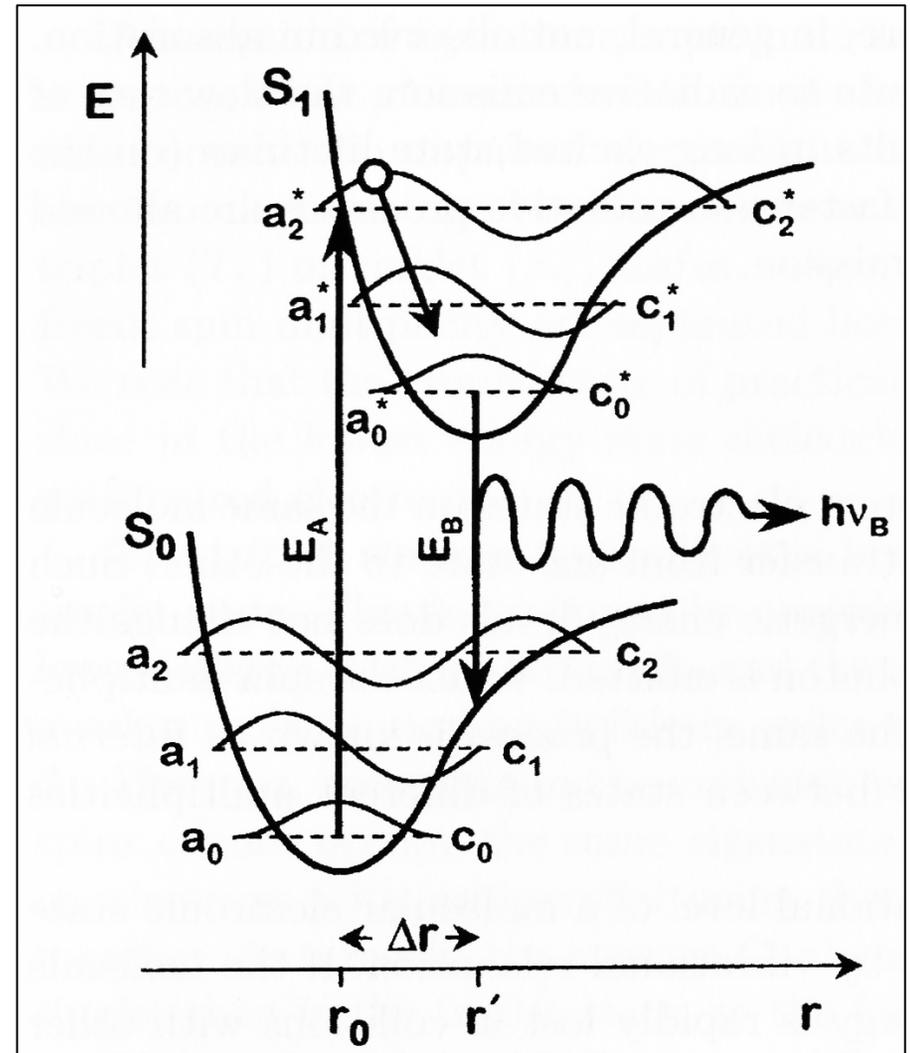
- Excitons can be also understood if we consider the well-known fact that usually emission and adsorption bands of a material are different (otherwise the material would not be transparent to the light it emits and no emitted light would reach us 😊)
- This is called the Franck-Condon shift.



Alq<sub>3</sub>=Aluminum hydroxyquinoline

# Another View of Excitons

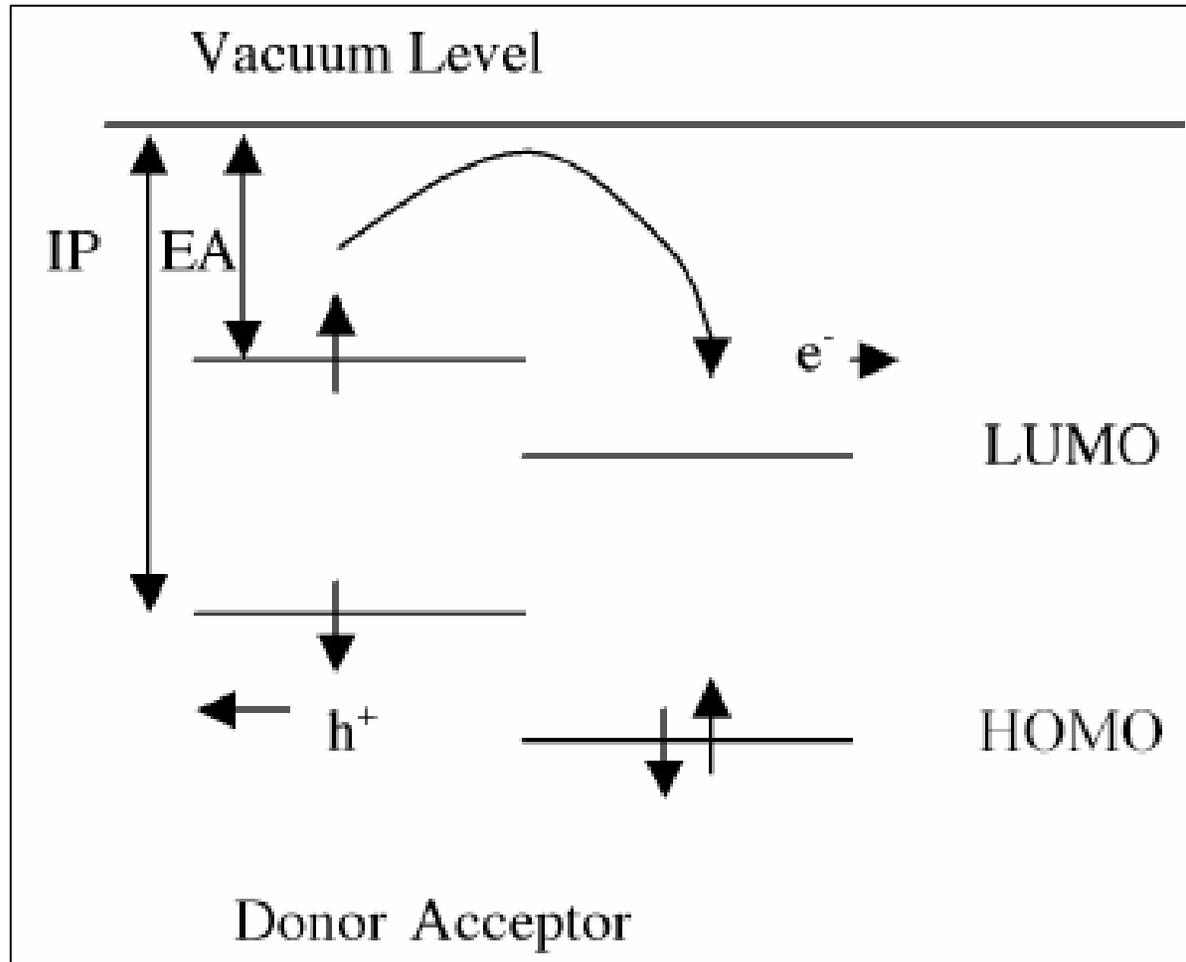
- The Franck-Condon shift is due to rearrangement of the lattice because the excited-state geometry differs from that of the ground state.
- This is the result of charge-lattice interaction, the same that brought about excitons.
- In chemical terms, exciton formation is a change in molecular geometry.
- The greater the required change in geometry, the more localized is the exciton and the higher is its binding energy.



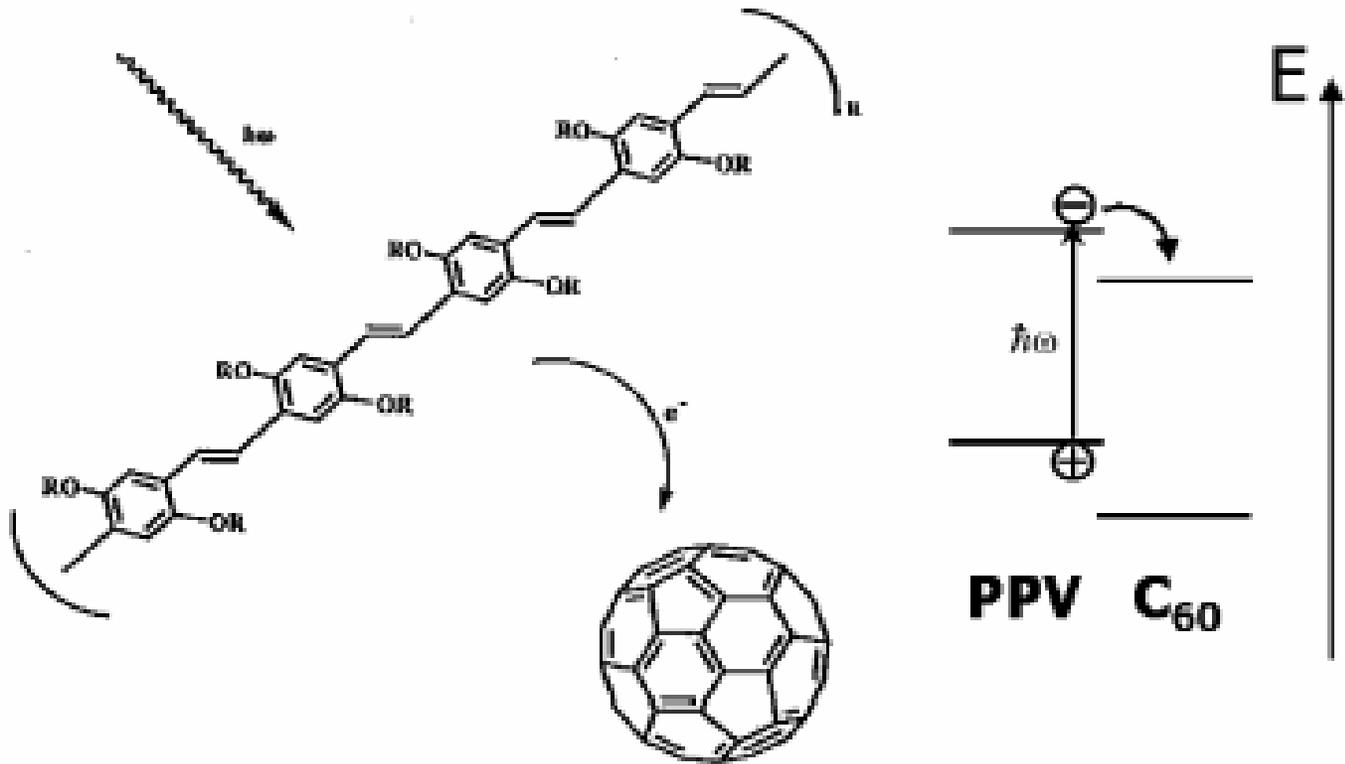
# Excitons and Photogeneration

- Well, as we have seen, in some materials photoexcitation results in formation of various types of excitons.
- However, excitons are neutral and cannot carry charge so that no energy can be collected.
- To ensure photogeneration of energy, excitons must be separated to produce electron-hole pairs.
- This process require overcoming of the exciton binding energy (usually, by external electric field).
- A competing process is recombination (relaxation of photoexcited electrons back to the ground state). The excess energy is either dissipated into lattice vibrations (non-radiative recombination) or emitted as light (radiative recombination).
- Tightly bound excitons are hard to separate =>poor photogeneration.
- If exciton lifetime is very short (high recombination rate) they cannot be separated and again we have poor photogeneration.

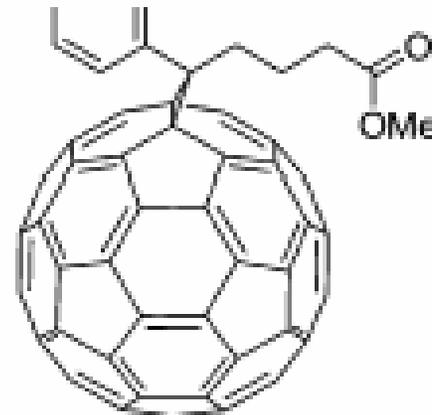
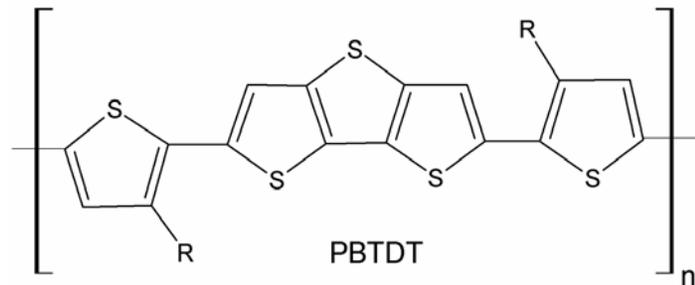
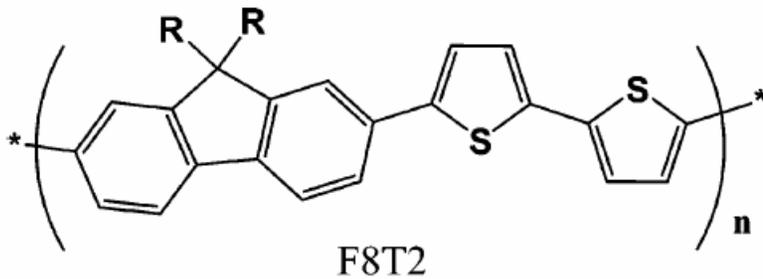
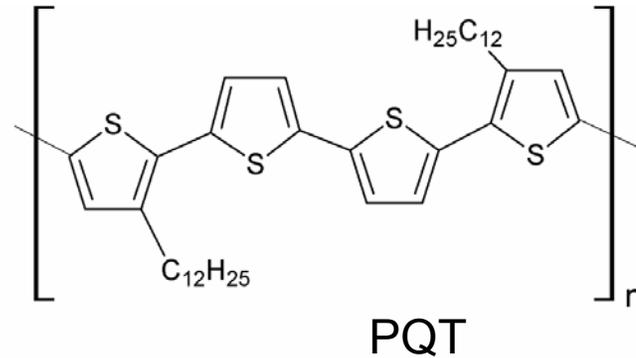
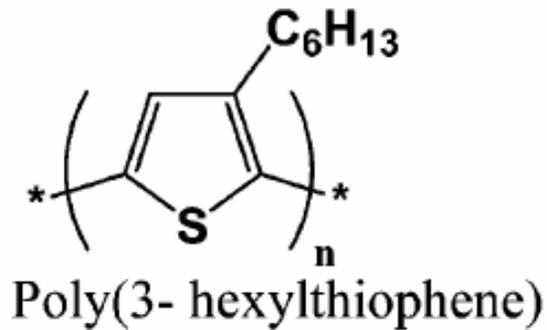
# Organic Donor-Acceptor Photovoltaic Cells



# Organic Donor-Acceptor Photovoltaic Cells



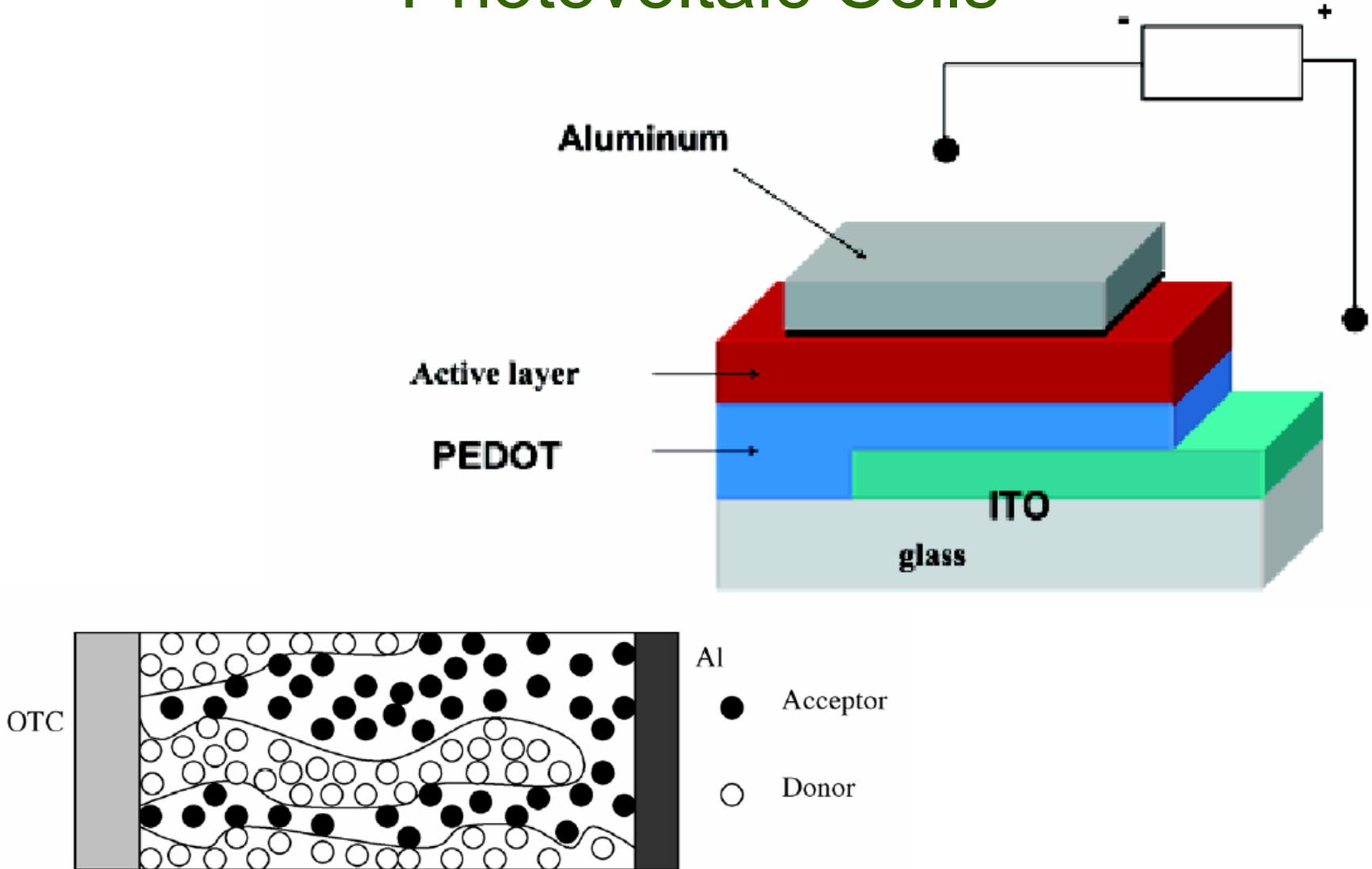
# Organic Photovoltaic Cells



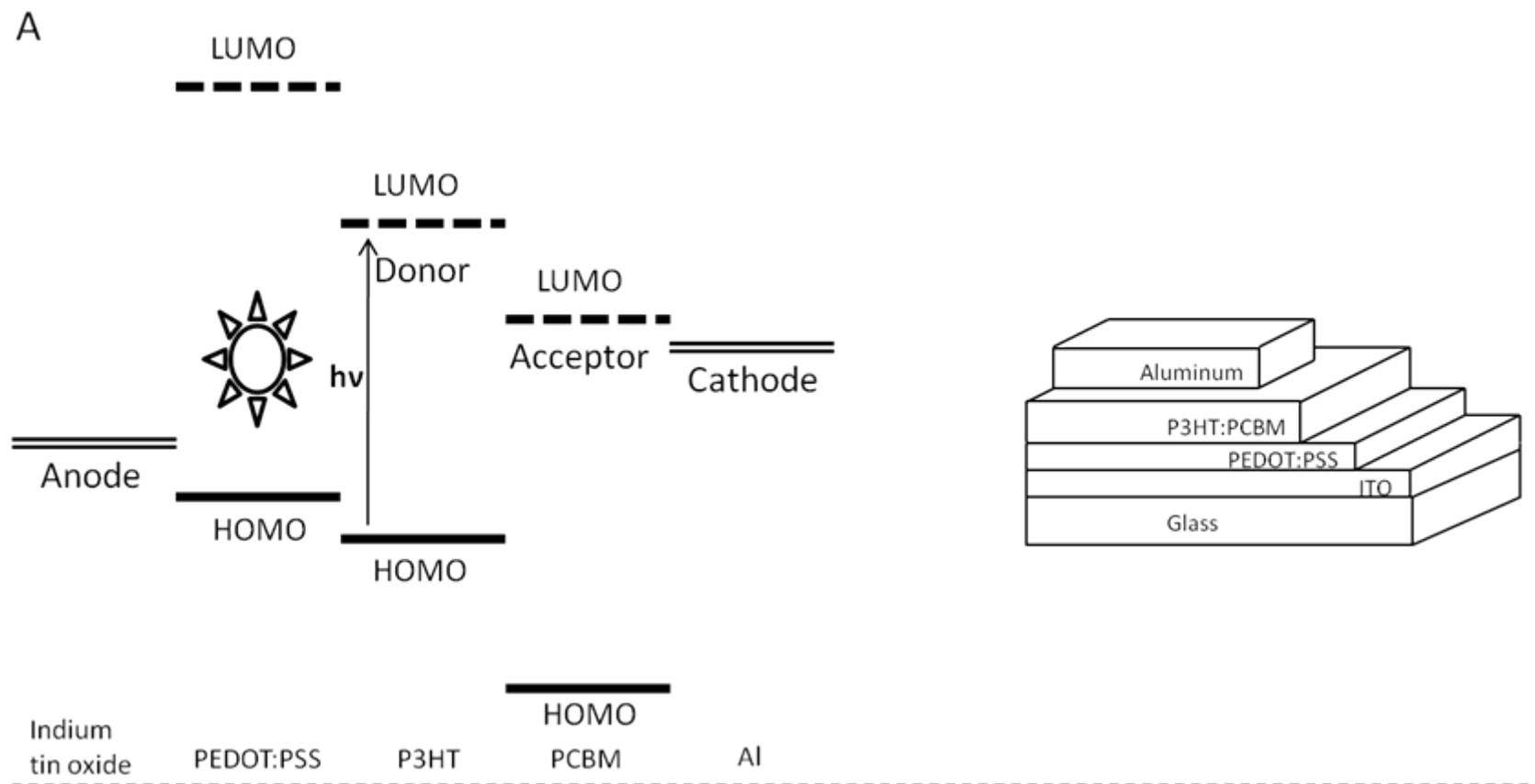
PCBM

PCBM = phenyl-C<sub>61</sub>-butyric acid methyl ester

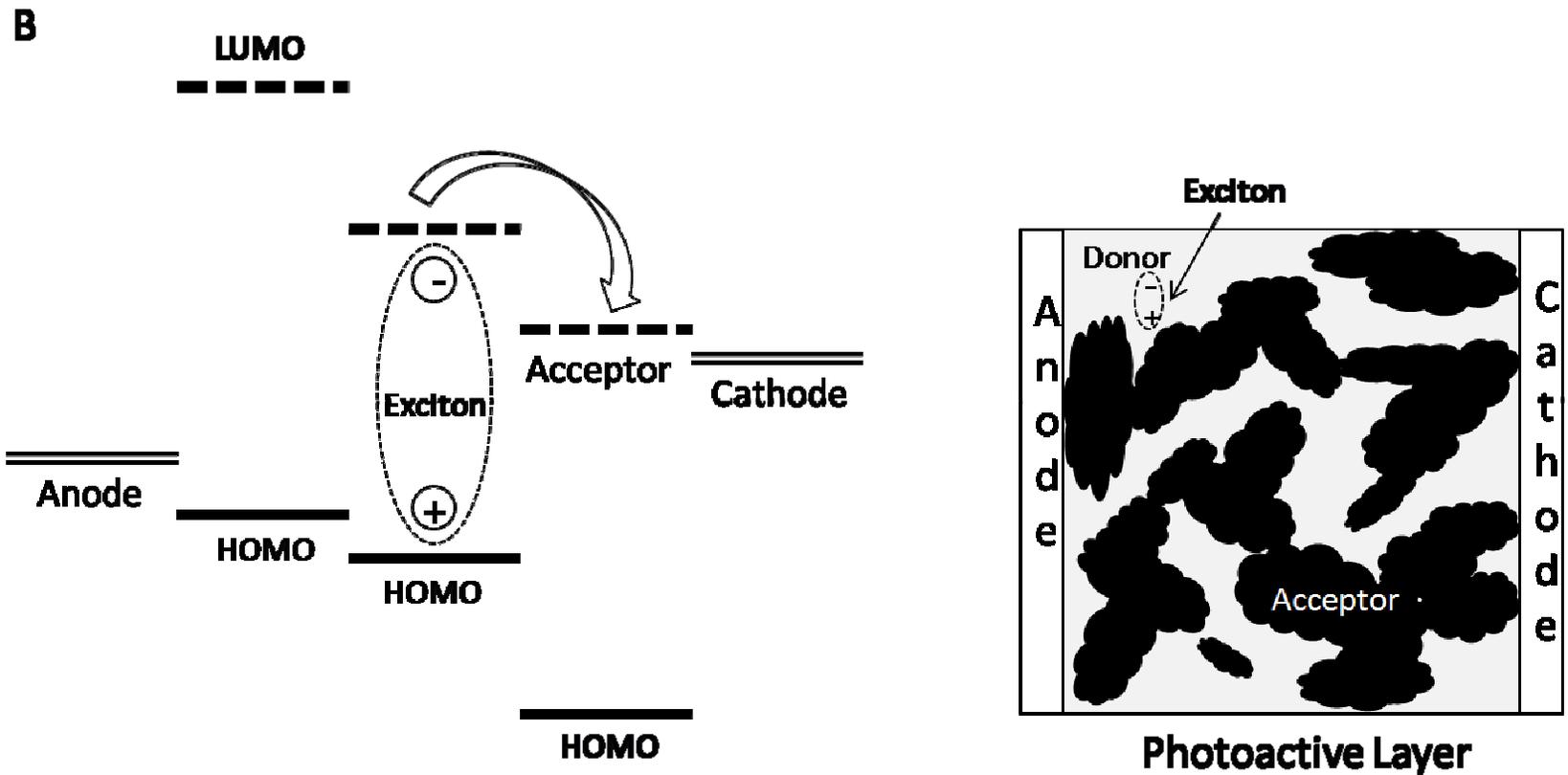
# Bulk Heterojunction Organic Photovoltaic Cells



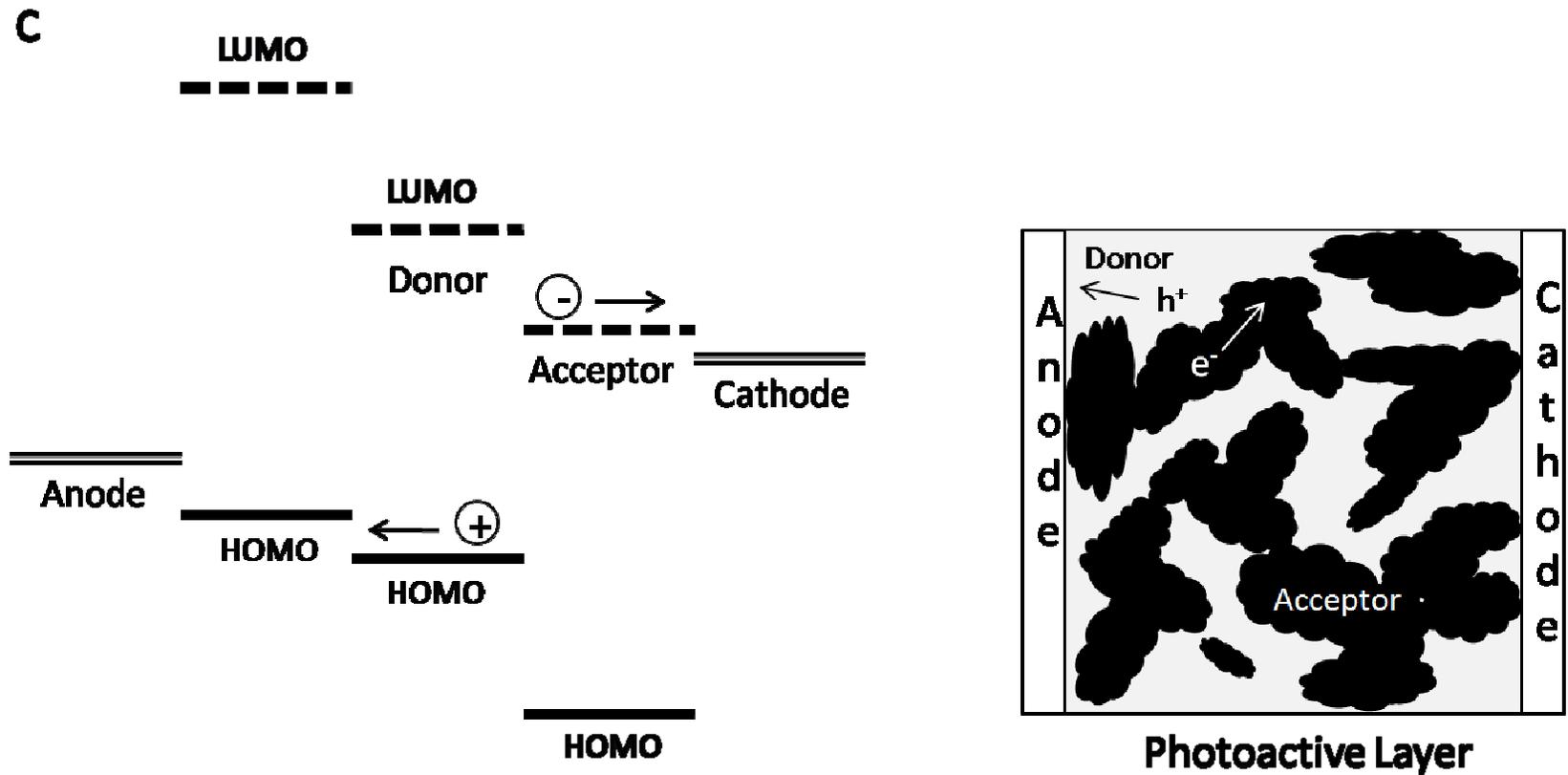
# Photovoltaic Device Structure



# Donor-Acceptor Effect and Exciton Dissociation



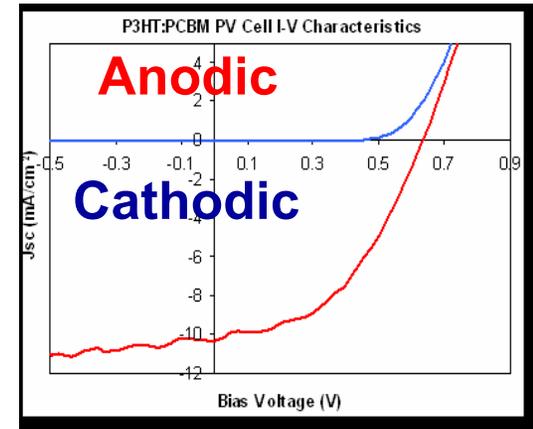
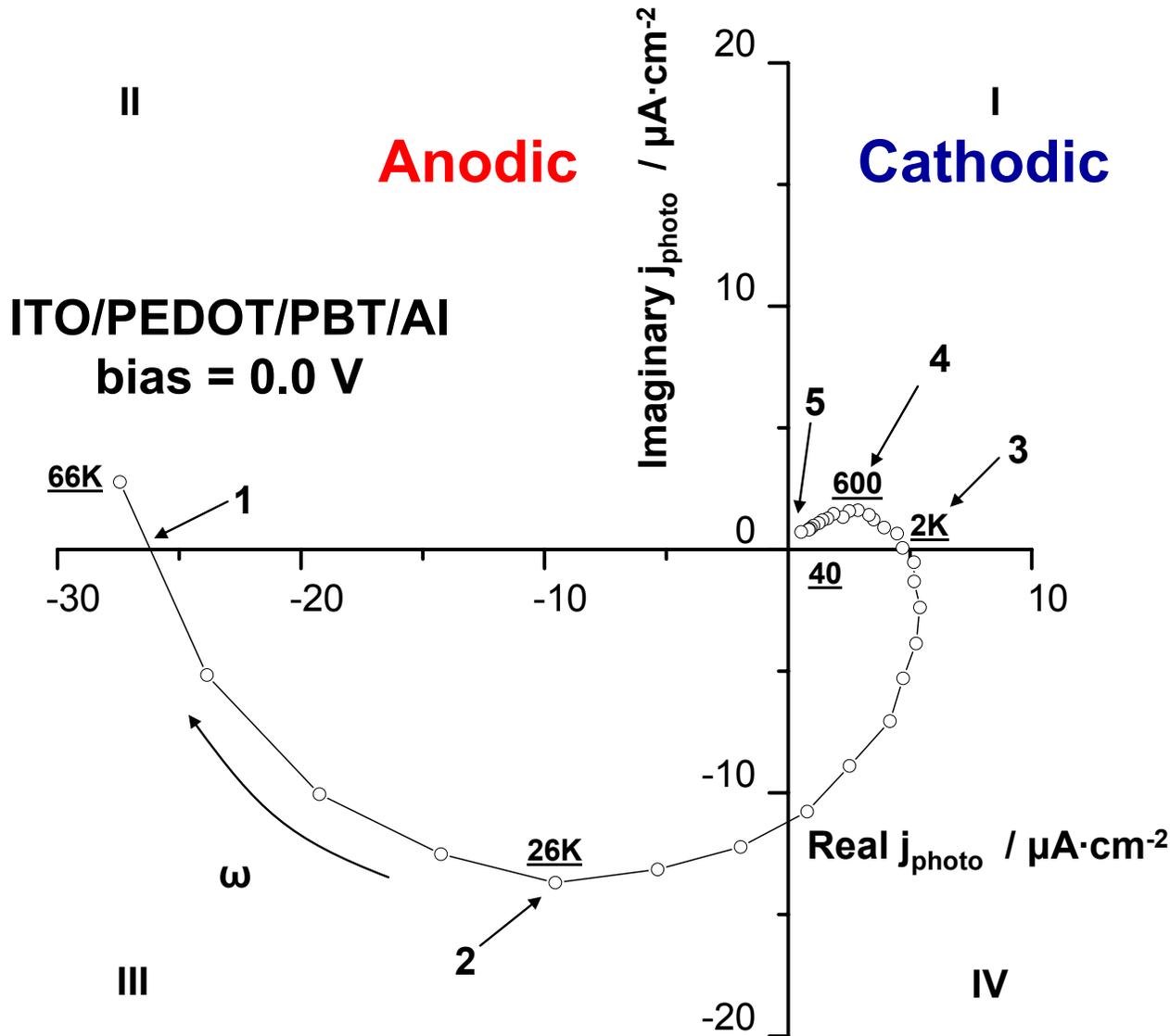
# Charge Transport through Percolation Pathways



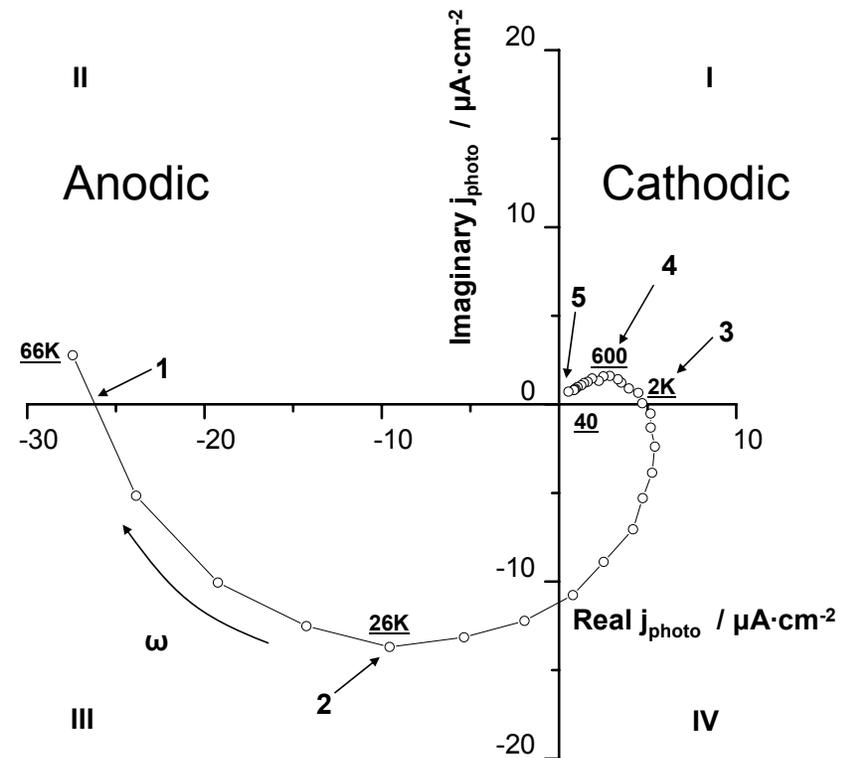
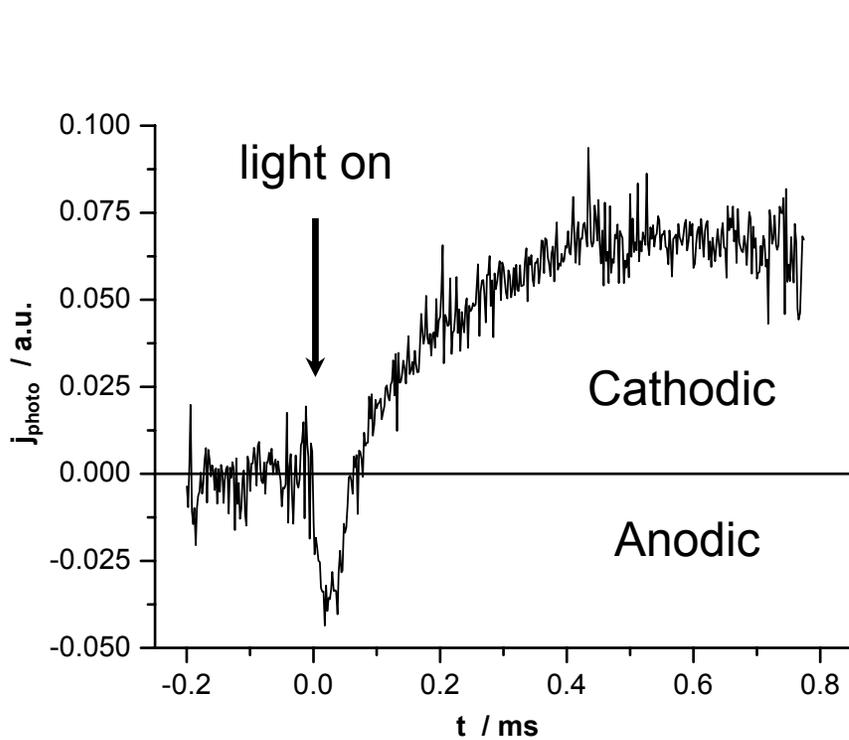
# Carrier Transport, Extraction and Recombination

- The efficiency of a solar cell is largely determined not only by the primary exciton dissociation but also by the transport in the photoactive material and the processes at the interfaces, as well as recombination losses both in the bulk and at the interfaces.
- The carriers must be extracted efficiently; otherwise, the efficiency of even a very good material will be low.
- The efficiency of the transport and extraction of carriers depends on many factors. They can be studied by using IMPS and IMVS.

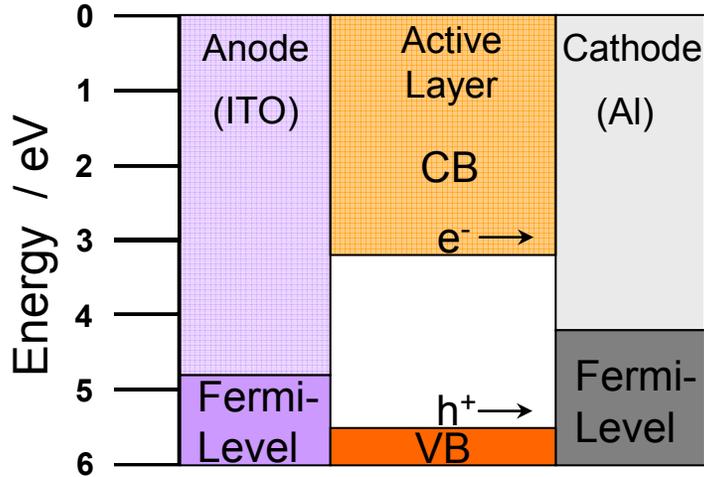
# IMPS plots without acceptor moiety



# High Frequency Anodic Photocurrent

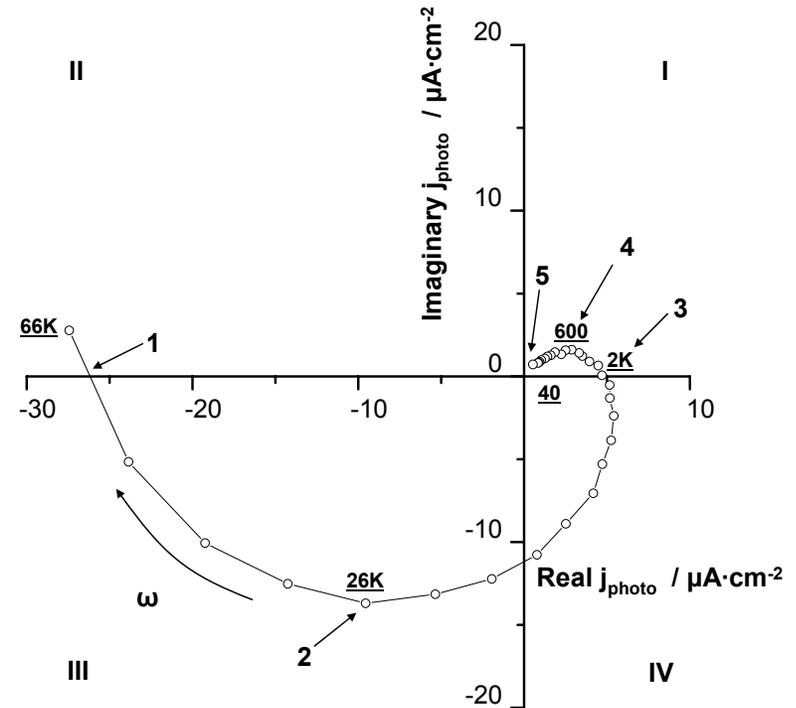


# IMPS plots without acceptor moiety



Not only excitons are poorly dissociated, but also:

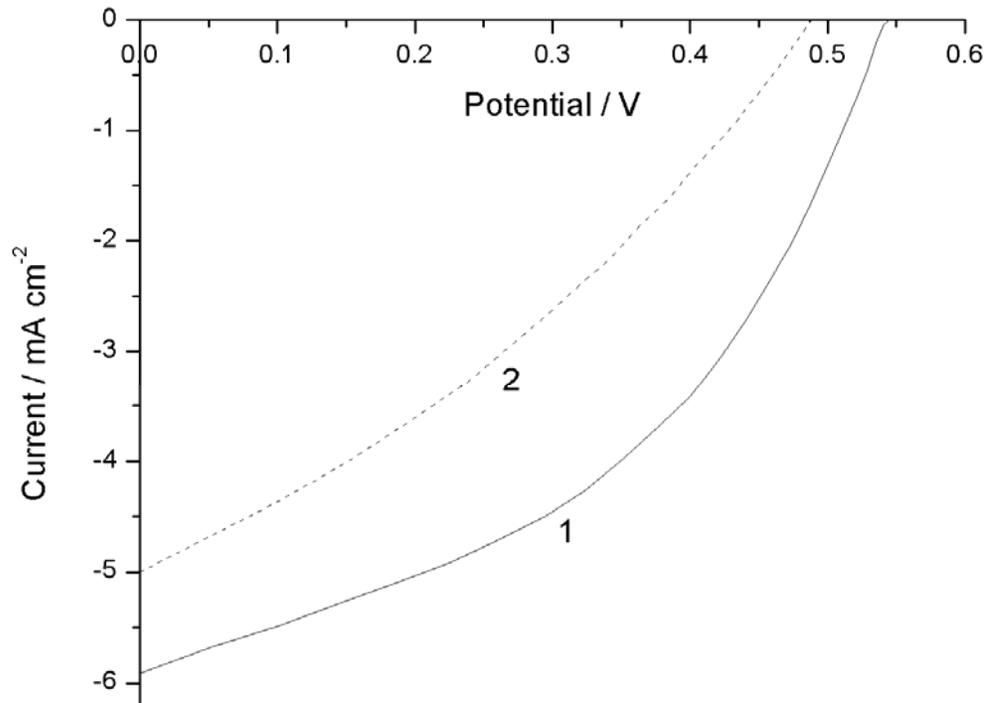
- Holes move in wrong direction (to the Al cathode).
  - Trapped at electrode.
- Electrons flow to cathode at lower  $\omega$ .
  - Recombine with holes.



# IMPS studies of “standard” ITO/PEDOT/P3HT:PCBM/AI Donor-Acceptor Solar Cells

**See also:** J. C. Byers, S. Ballantyne, K. Rodionov, A. Mann, and O. A. Semenikhin. Mechanism of Recombination Losses in Bulk Heterojunction P3HT:PCBM Solar Cells Studied Using Intensity Modulated Photocurrent Spectroscopy. *ACS Advanced Materials and Interfaces*, 2011, vol. 3, pp.392-401

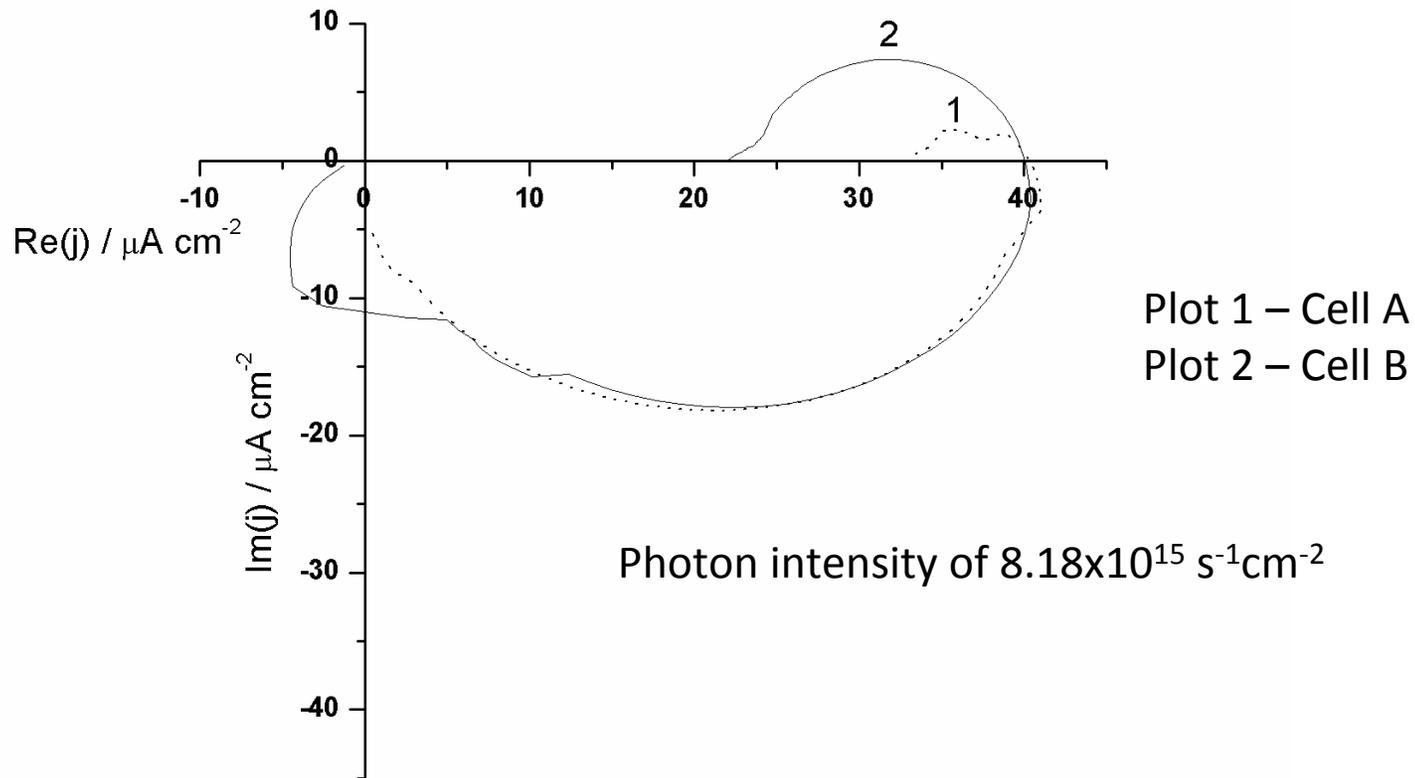
# DC Photocurrent Measurements



Curve 1 – Cell A  
Curve 2 – Cell B

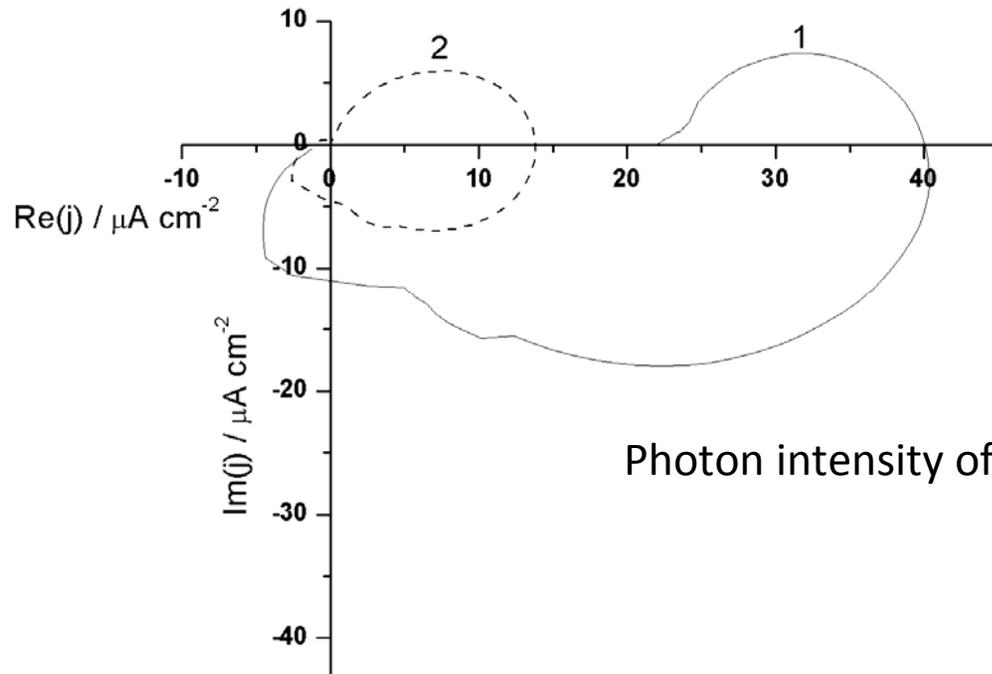
Sample	$V_{oc} / V$	$I_{sc} / \text{mA cm}^{-2}$	FF	Efficiency %
Cell A	0.55	-5.91	0.43	1.40
Cell B	0.51	-5.00	0.32	0.816

# IMPS spectra - Efficient and Less Efficient Cells



Less efficient Cell B shows larger surface recombination

# IMPS spectra – Effect of ageing

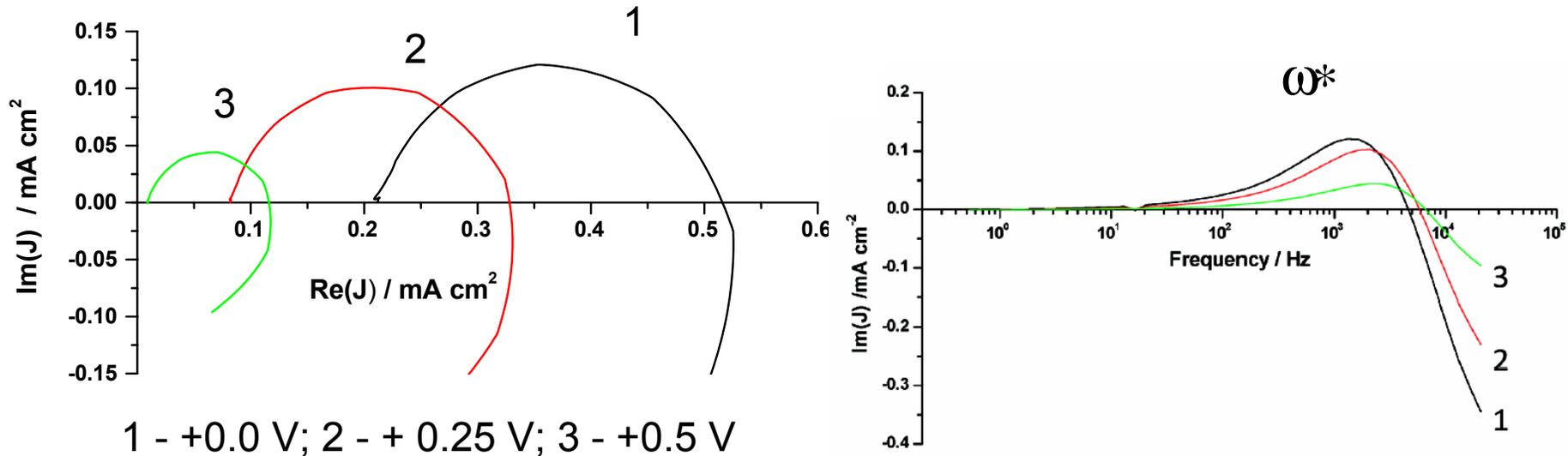


Plot 1 – Cell B after fabrication  
Plot 2 – Cell B two months later

Photon intensity of  $8.18 \times 10^{15} \text{ s}^{-1} \text{ cm}^{-2}$

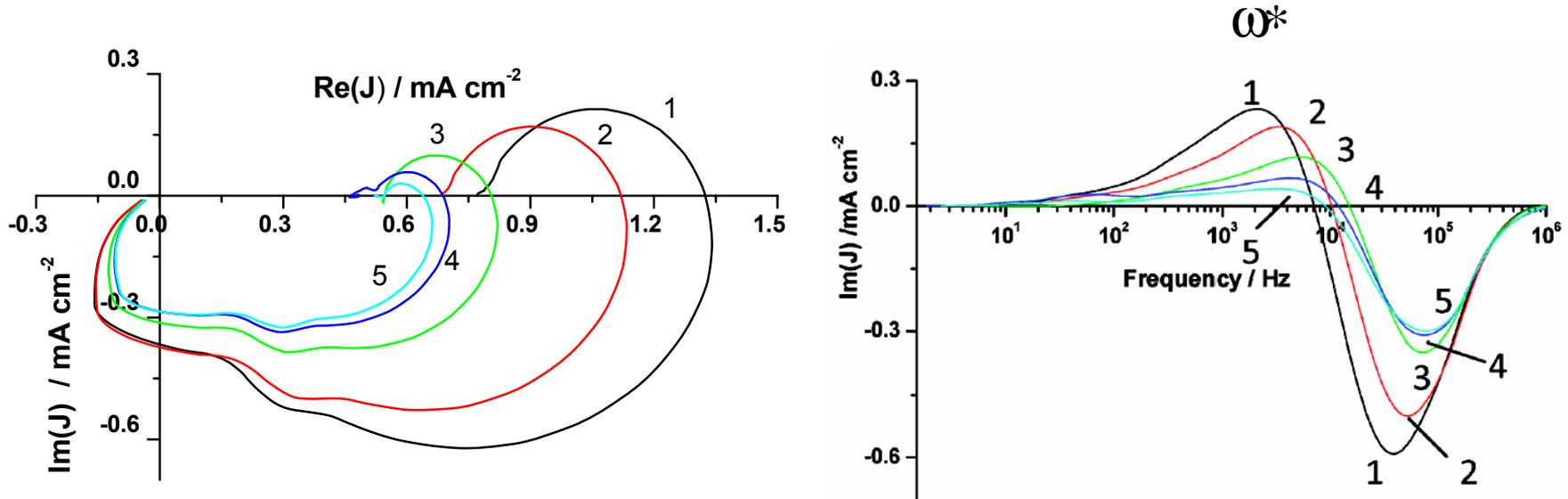
The *dc* photocurrent is zero after ageing; however, there is still an *ac* photocurrent. IMPS shows that surface recombination is a major reason of the deterioration of the aged cells performance!

# The Effect of *dc* Bias



- IMPS spectra taken at bias values ranging from 0.0 V (short-circuit) to +0.5 (near open-circuit) show that the generation current decreases and the surface recombination rate increases near the open-circuit conditions.
- This is one of the reasons for reduced fill factor and lower efficiency.

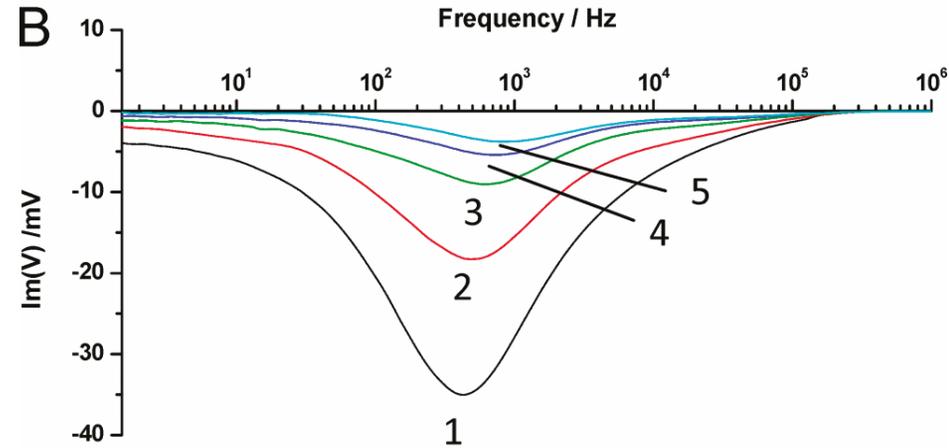
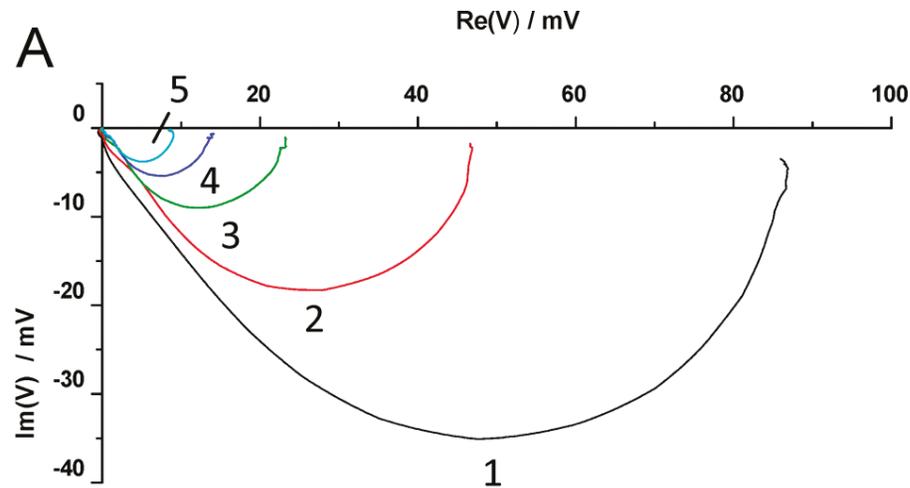
# The Effect of *dc* Light Intensity



The *dc* intensity increases 1→5

- The *ac* photocurrent decreases with the *dc* light intensity. The system is non-linear!
- The frequency at the maximum of the imaginary component  $\omega^*$ , which corresponds to the surface recombination rate, increases with the *dc* light intensity.
- This means that electrons recombine in part with photogenerated holes trapped at the interface.

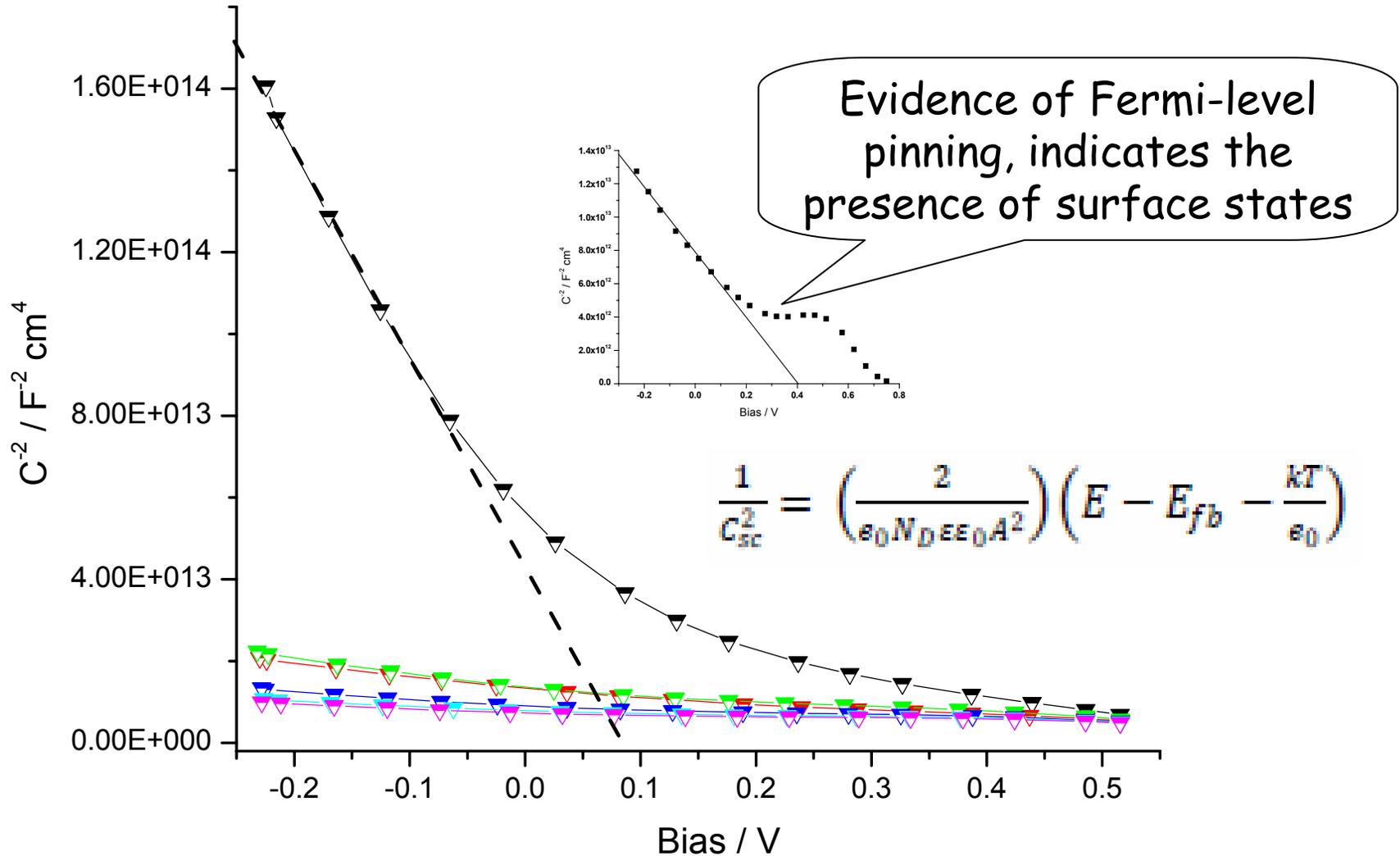
# IMVS: charge transport and accumulation at open circuit



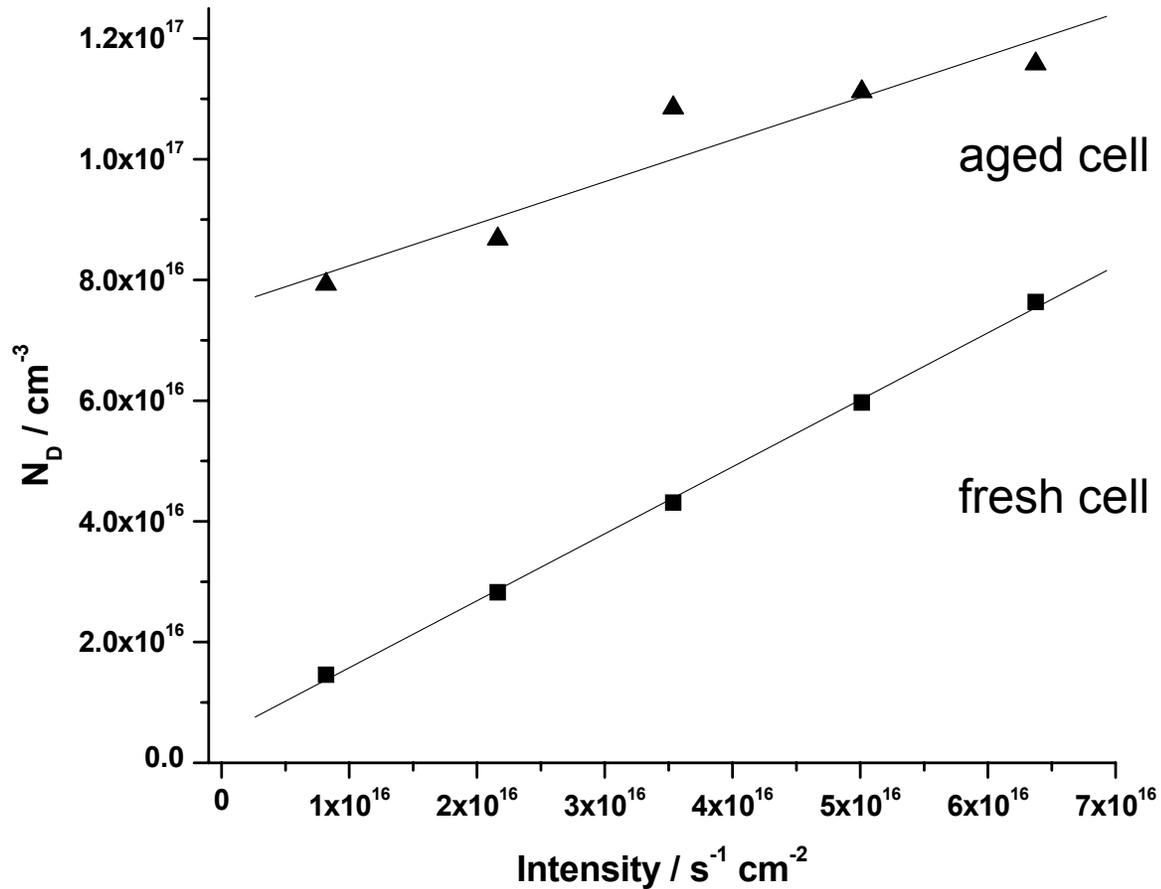
The **dc** intensity increases 1→5

- The IMVS also shows that the system is non-linear.
- The frequency at the maximum of the imaginary component  $\omega^*$  increases with the *dc* light intensity. This again suggests that the lifetime of the carriers decreases with an increase in the light intensity due to surface and the bulk recombination. The mathematical model of the bulk photoprocesses is needed to separate these from the surface recombination.

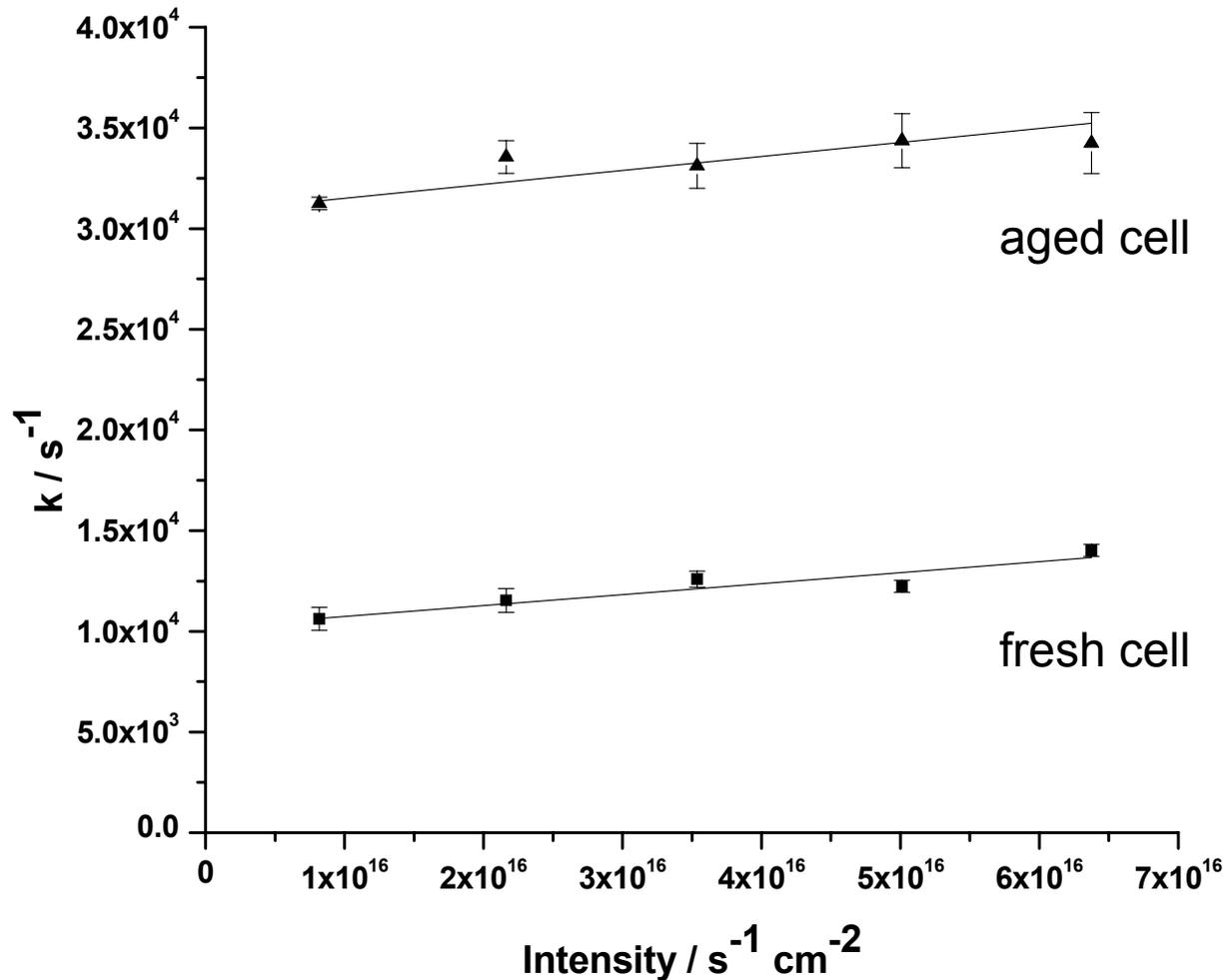
# Mott-Schottky plots indicate photoinduced hole trapping



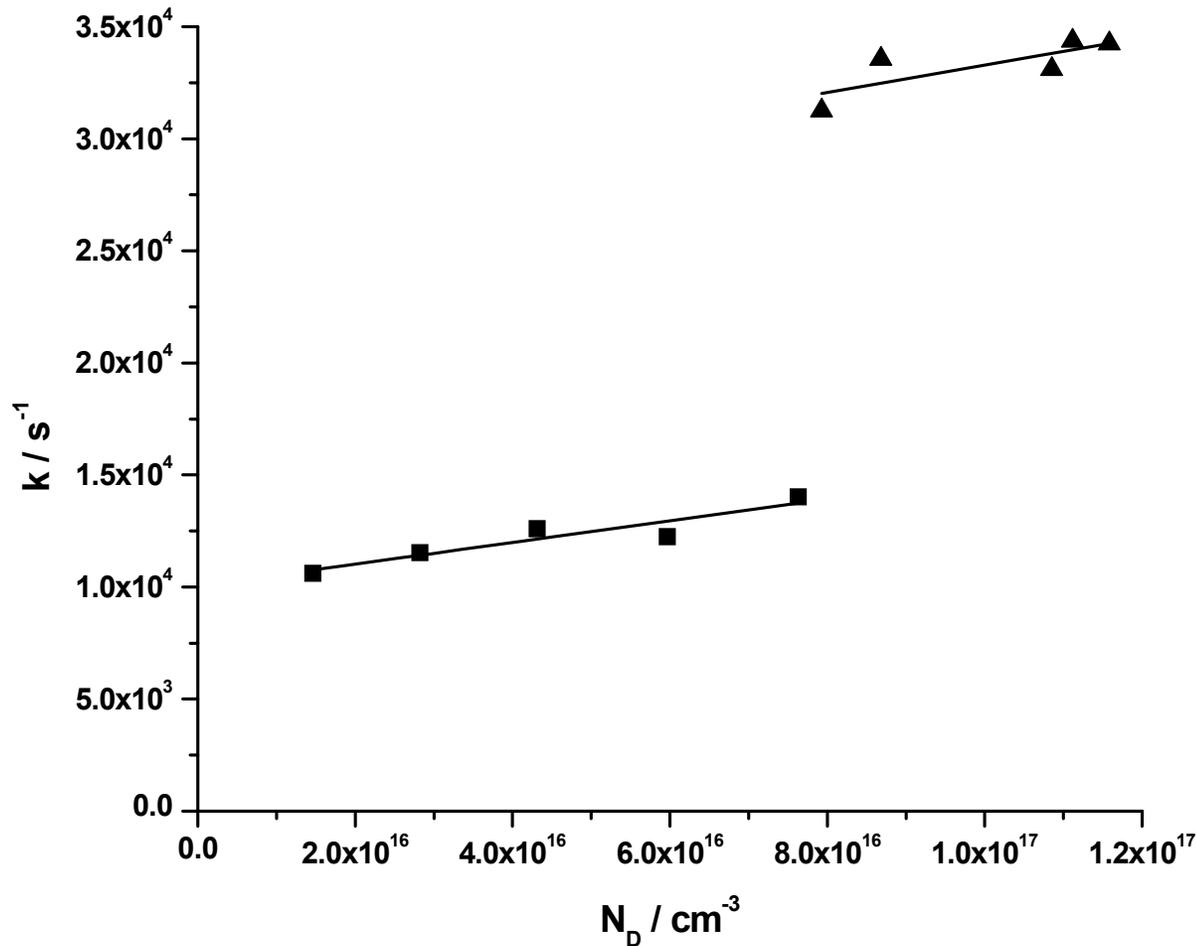
# The trap densities from Mott-Schottky plots at various $dc$ light intensities...



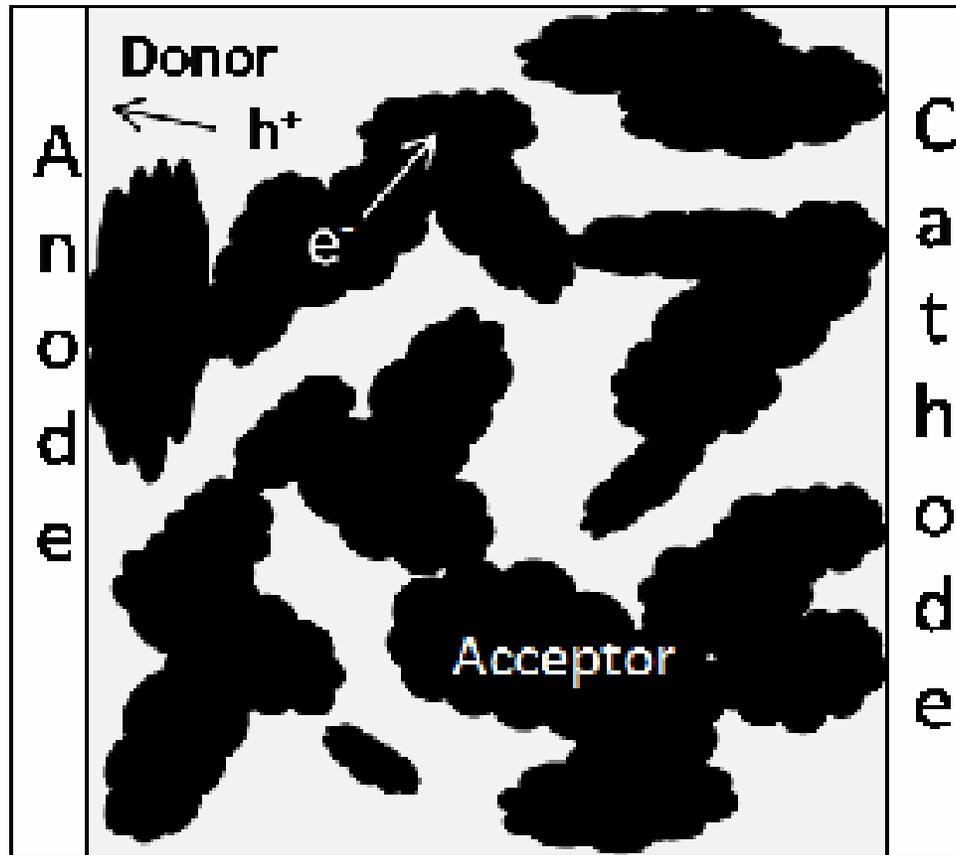
...and the values of the recombination rate constant from IMPS plots...



The recombination of electrons in the acceptor layer is in part related to photogenerated holes trapped in the photovoltaic layer!

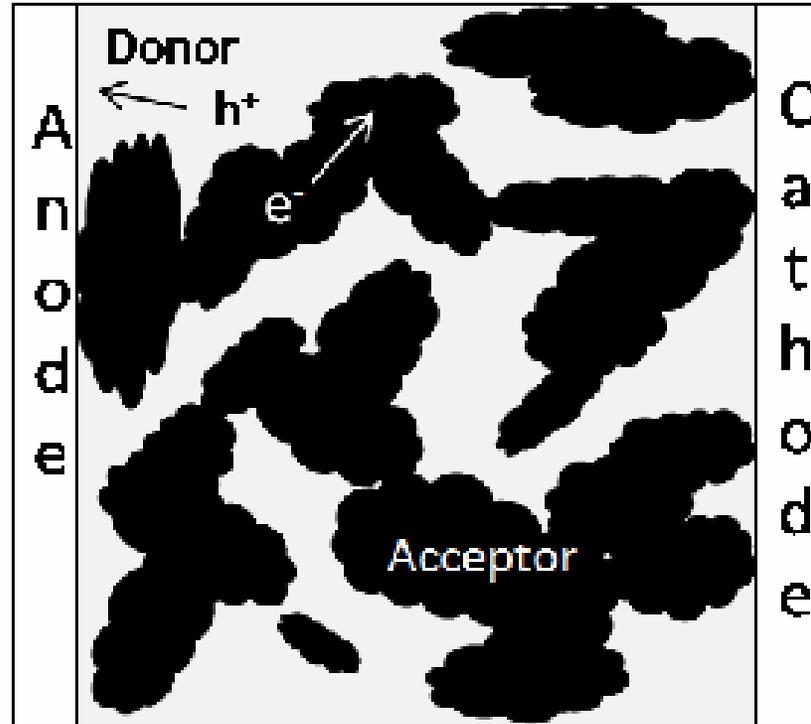


The hole transport problem - again! Even in bulk heterojunction solar cells, some photogenerated holes are not removed fast enough and recombine with photogenerated electrons.



Photoactive Layer

# The 2<sup>nd</sup> problem: electrons captured at surface states



Photoactive Layer

- The interfacial states responsible for the recombination must be located at the interface between the donor P3HT and the acceptor PCBM phases.
- Finding a way to get rid of these states would greatly increase the cell performance and stability towards ageing.

# Conclusions

- The use of IMPS/IMVS allows one to clearly separate the bulk and interfacial recombination processes in solar cells. Additionally, carrier transport may be characterised too (mobilities, trapping...).
- 2. The light intensity dependence can be studied with great precision by applying quazi-linear conditions (dc+ac light intensity).
- 3. The analysis is performed under normal working conditions of a solar cell, just using modulated illumination. This makes it easier to relate the results of the IMPS experiments to regular steady-state photocurrent / efficiency measurements, unlike many other transient techniques.

## Students

- Josh Byers

## Collaborations

- Thomas Heiser, Institut d'Électronique du Solide et des Systèmes (InESS), University of Strabsourg

## Industrial Partner



## Financial Support



**NSERC  
CRSNG**

Discovery  
Engage



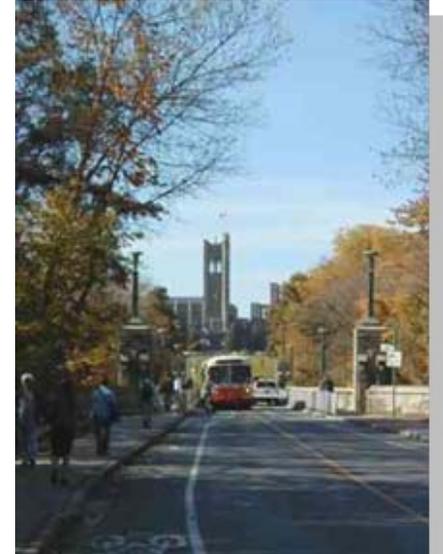
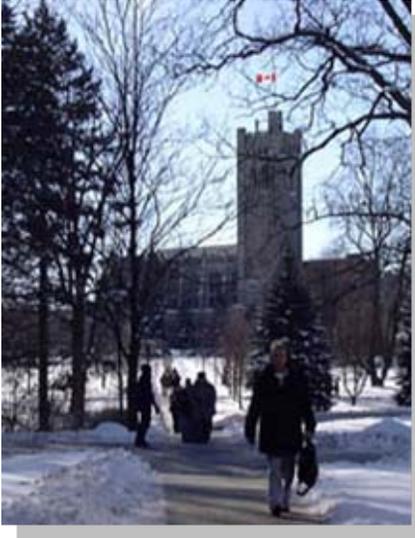
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# London, Ontario, Canada



# The University of Western Ontario



# Our Department

