Introduction to excitons and their role in photovoltaic processes

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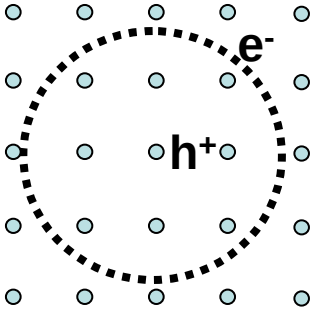
MICHIGAN STATE UNIVERSITY

Complex Materials and their Energy Applications
March 27th 2008 MSU

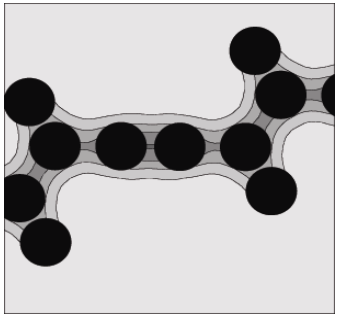
Outline

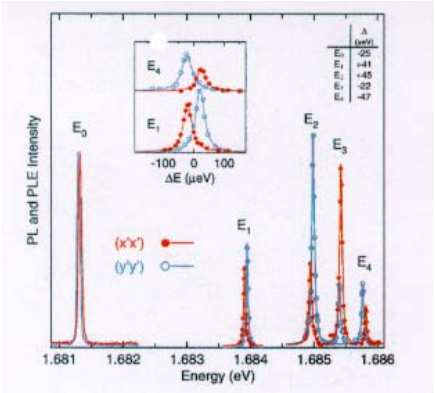
Solar Cells



Wannier and Frenkel excitons

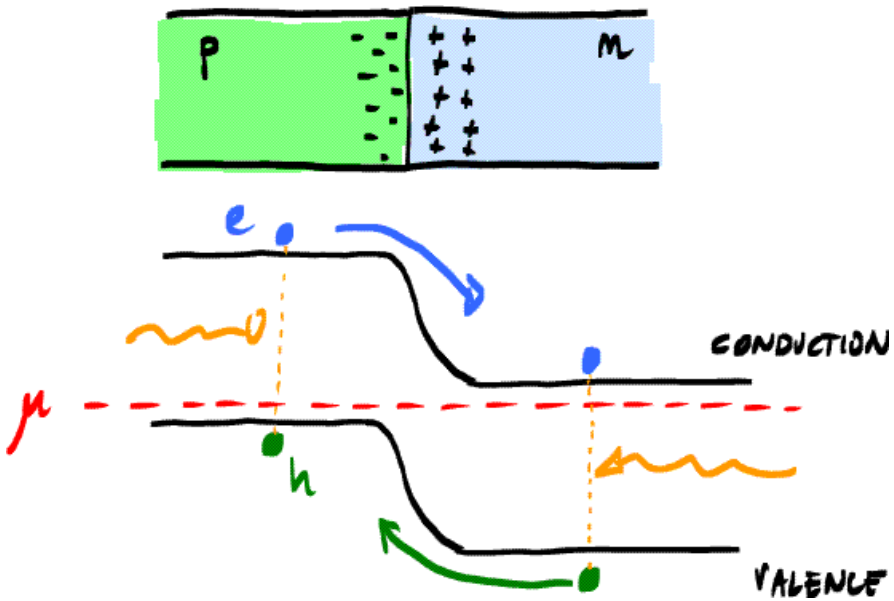
Exciton-phonon effects





Excitons in Quantum Dots

First Generation Solar Cells



Large p-n junction diode

Silicon wafers quite expensive

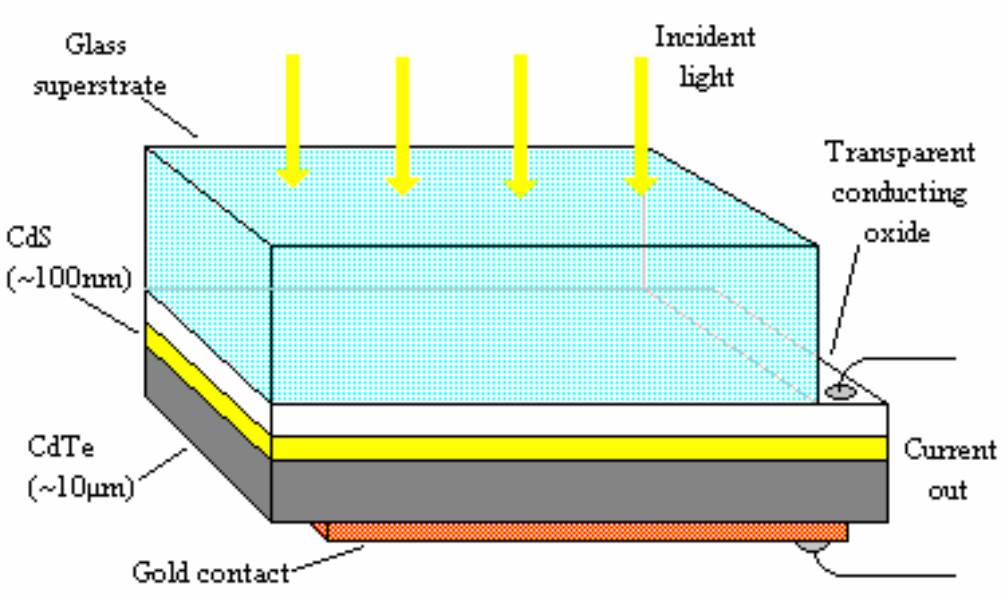
About 25% efficiency

90% Market

Second Generation Solar Cells

Thin films technologies to lower cost: use polycrystalline, amorphous, cheap inorganic crystals

p-n junction with thin films



CdS is n doped

2.5 eV gap window layer

CdTe is p-doped

1.5 eV gap active layer

p<<n: depletion region larger on p side

About 10-20% efficiency

Thin films also used in multi-junction with III-V

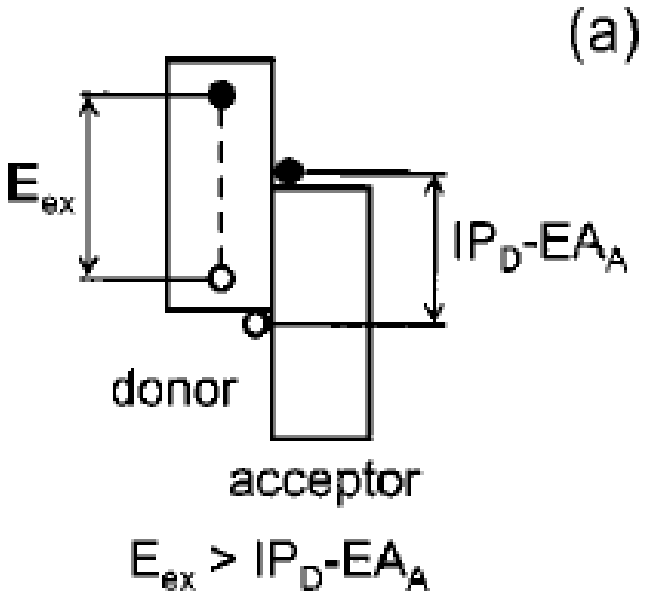
High efficiency (40%) but costly

10% Market

Third Generation Solar Cells

No p-n junction

Nanotechnology (dots rods wires nanoparticles), Polymers, Dyes

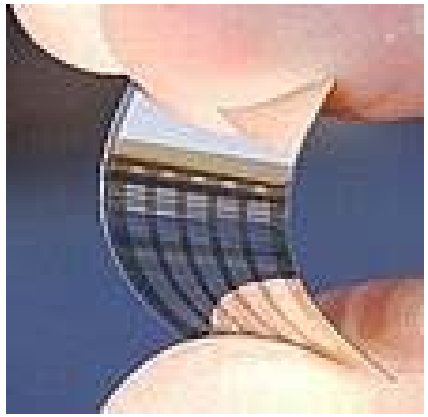


Based on Donor-Acceptor Interface

Strong excitonic effects

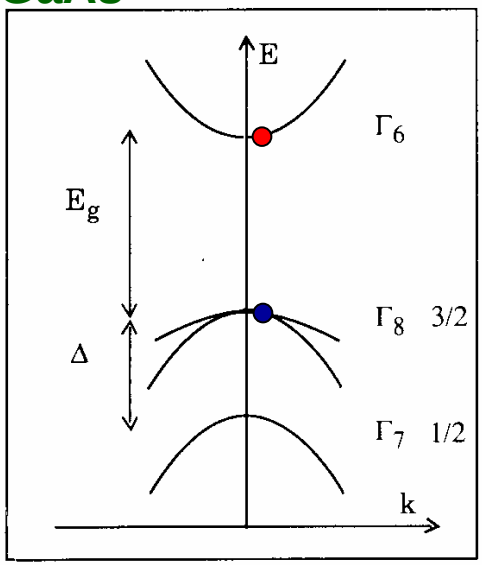
e-h separation has to occur before radiative recombination

Less than 10% efficiency



0% Market

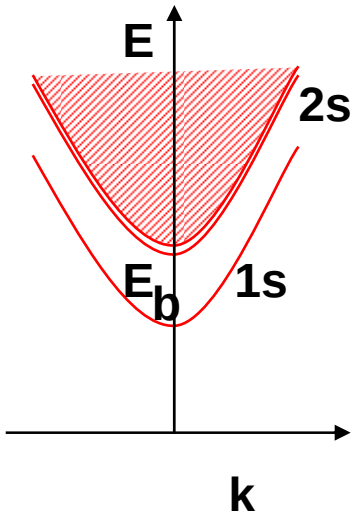
GaAs



Excitons are elementary optical excitations in semiconductors

The photo-excited electron and hole bind and propagate through the crystal (G. H. Wannier PR 37)

Hydrogen-like spectrum



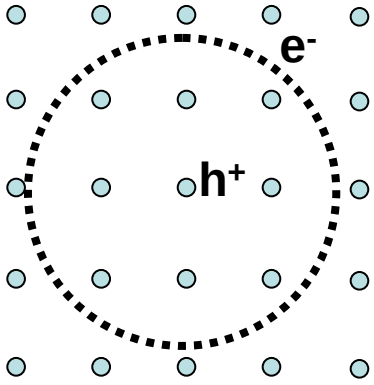
$$a_B = \frac{\hbar^2 \varepsilon}{\mu^* e^2} \approx 80 \ \text{Å}$$

$$E_b = \frac{\mu^* e^4}{2\varepsilon^2 \hbar^2} \approx 5 \ \text{meV}$$

$$\mu^* \approx 0.05 \, m_0$$

$$\varepsilon \approx 13$$

Wannier-Mott excitons (large Bohr radius)



Wannier Exciton

Electron is bound only very weakly, with an average radius larger than the lattice spacing

Exciton dynamics can be described within the *effective mass* picture. Center of mass and relative motion are separated.

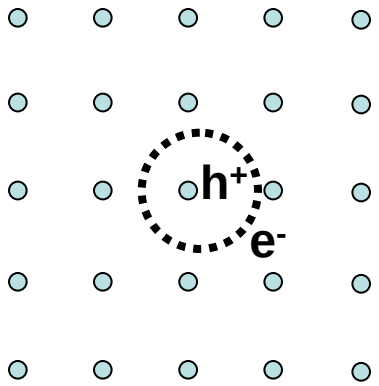
Important for: fundamental physics studies (e.g. BEC), Optoelectronics devices (@ low T)

Frenkel-Peierls
(small Bohr radius)

Mostly in organic materials (molecular crystals, polymers and many others organic structures). Alkali Halides (e.g. KI, NaCl). Noble Gas Crystals (e.g solid Kr).

Electron is bound strongly, essentially confined to within a single lattice constant

Exciton propagates through *energy transfer* processes



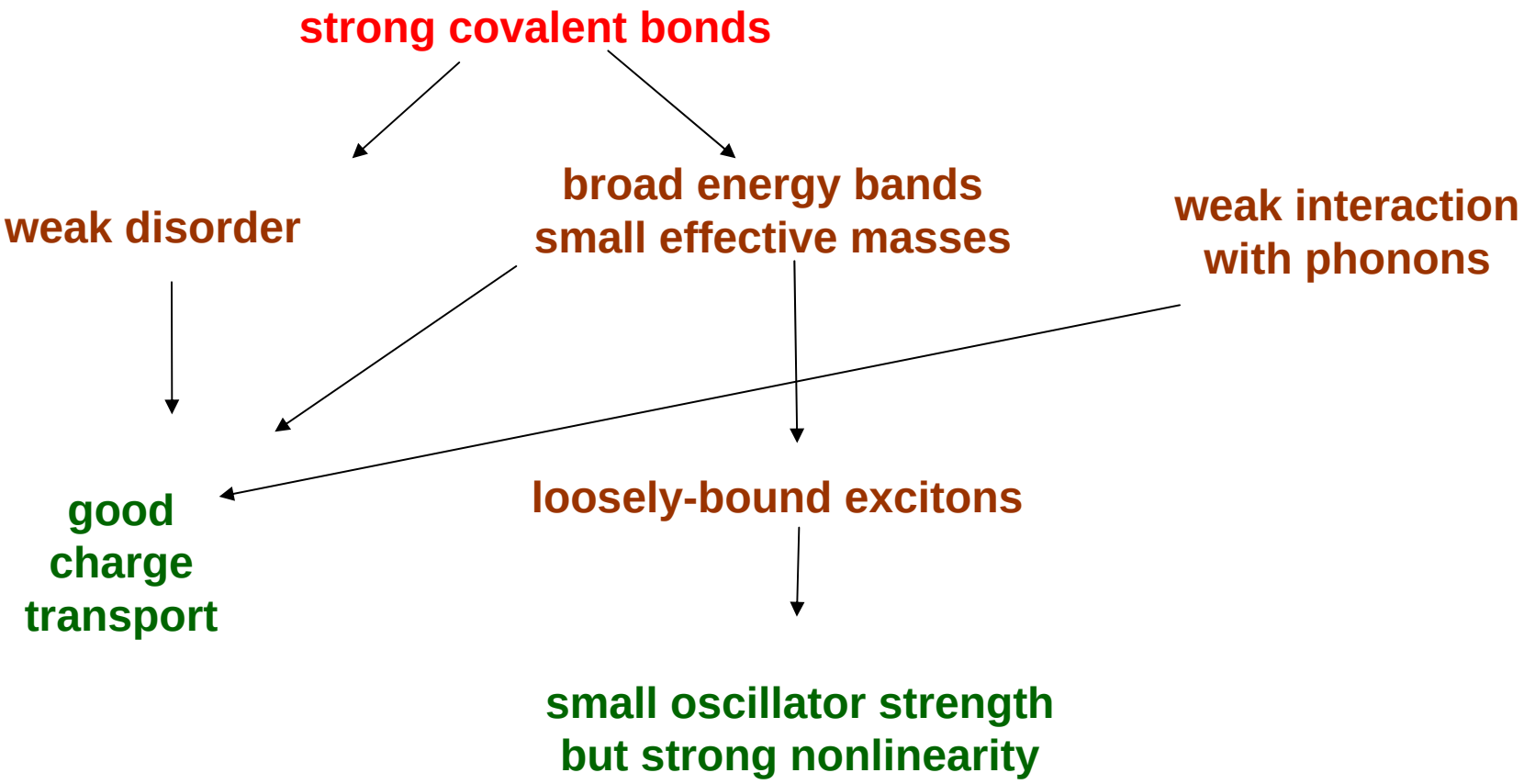
Frenkel Exciton

Important for: organic LEDs, organic solar cells

Charge Transfer excitons

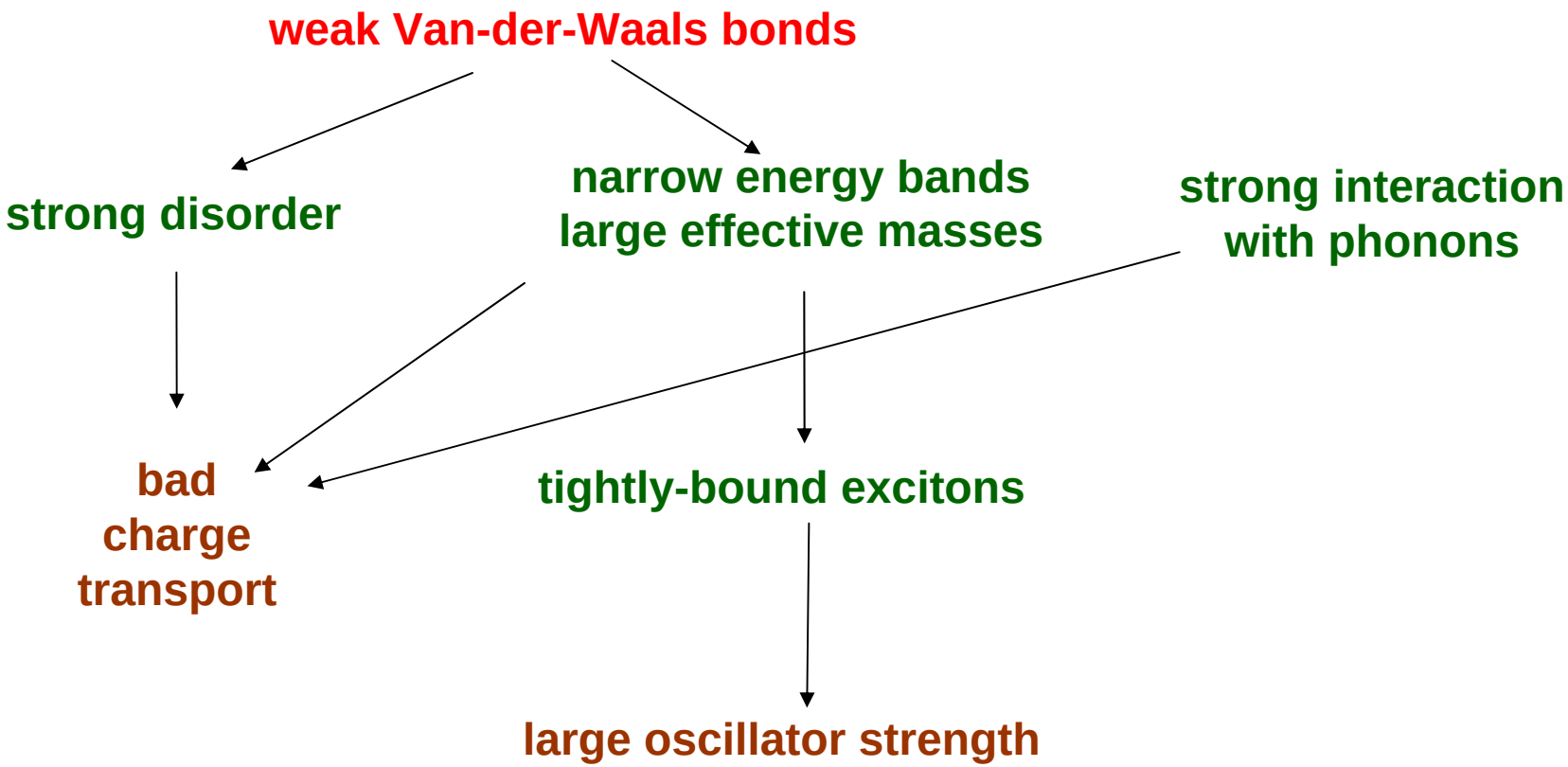
GaAs, ZnS, ZnO, ZnTe, ZnSe, Cu_2O, CuCl, CdTe, SiF_4, and many others;

Wannier-Mott excitons are typical for these materials.

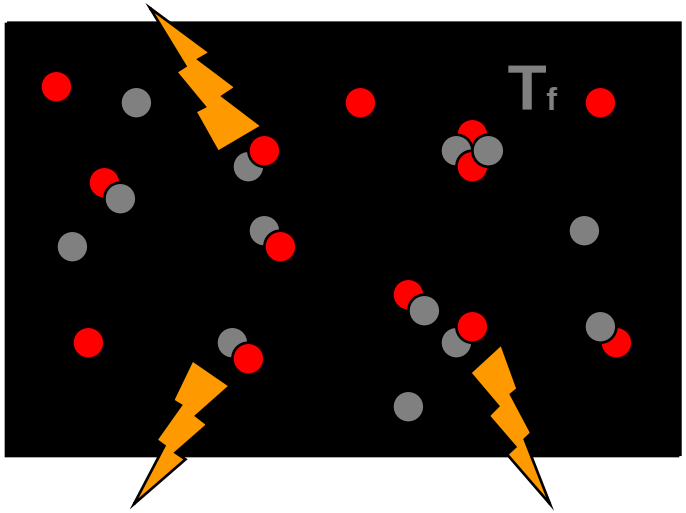


Anthracene, Tetracene, Pentacene, Phenanthrene, Porphyrin, Phenazine, PTCDA, and many many others

The Frenkel excitons are typical for these materials.



Exciton Phonon Dynamics



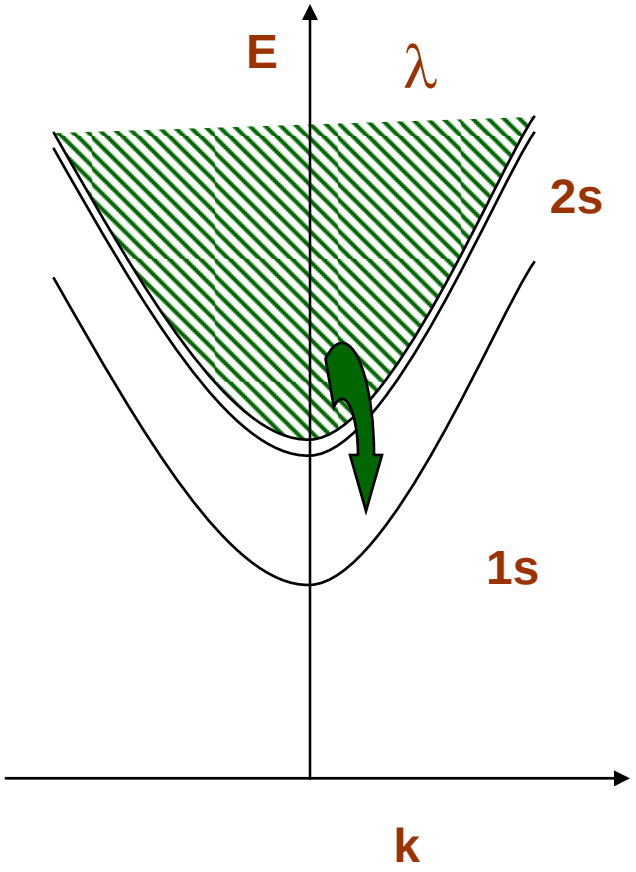
Cooling by phonon emission → **Formation of bound states**

$$1\ Sun = \frac{1\ W}{m^2}, \alpha \sim 10^4\ cm^{-1}, \gamma_{rad} \sim 10^{-8}\ s \rightarrow n_{ex} \sim 10^{10}\ cm^{-3}$$

Auger processes (Coulomb scattering) weak

Boltzmann equation

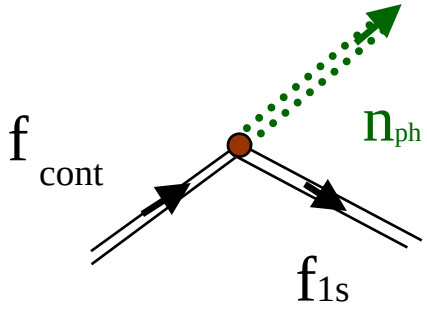
Bimolecular Formation and Dissociation of Excitons



Boltzmann Eq. in the pair basis

$$\frac{df_{ex}^{1s}(q')}{dt} = \sum_{\lambda,q} W(\lambda, q \to 1s, q')(1 + n^{ph}(q - q'))\, f_{ex}^{\lambda}(q)$$

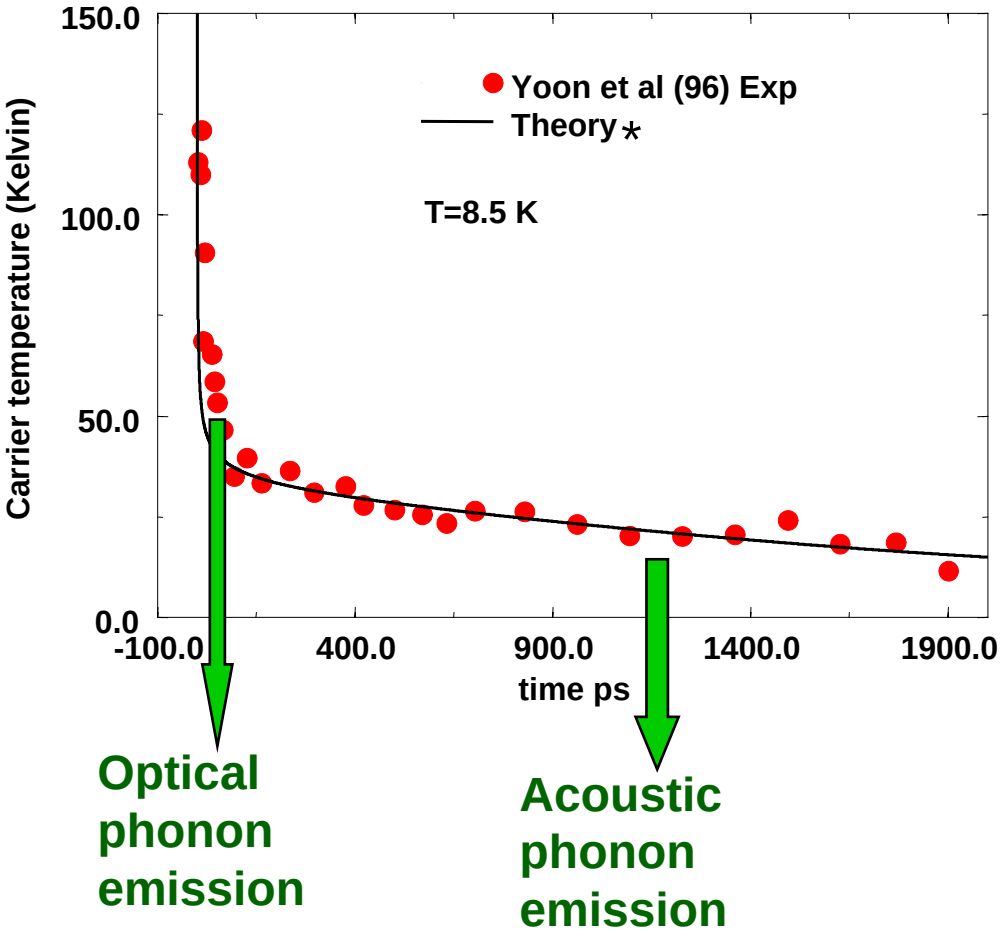
$$\left|\phi^{\lambda}(k)\right|^2 \approx 1$$



$$\frac{df_{ex}^{1s}(q')}{dt} = \sum_{k_e, k_h} F(k_e, k_h \to 1s, q')\, f_e(k_e)\, f_h(k_h)$$

Fast thermalization

Quantum Well Excitons



Deformation potential

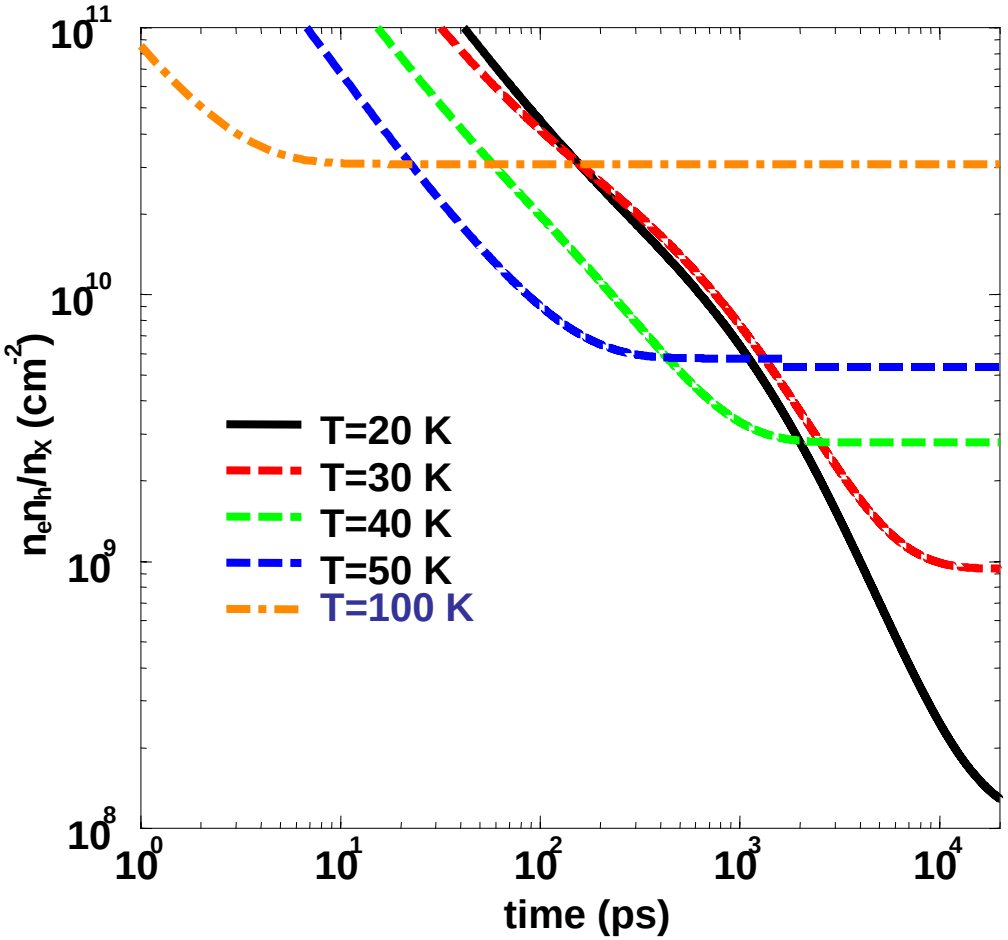
Frolich interaction

Optical phonon emission

Acoustic phonon emission

Very Accurate Predictions

* C. Piermarocchi PhD thesis (98) EPFL (www.epfl.ch)



$$\dot{n}_{ex} = Cn_e n_h - Dn_{ex}$$

$$\dot{n}_e = -Cn_e n_h + Dn_{ex}$$

Exciton Dissociation Rate (calculated)

At 100 K quasi-thermal equilibrium in 1 ps

$$[e] + [h] \Leftrightarrow [ex]$$

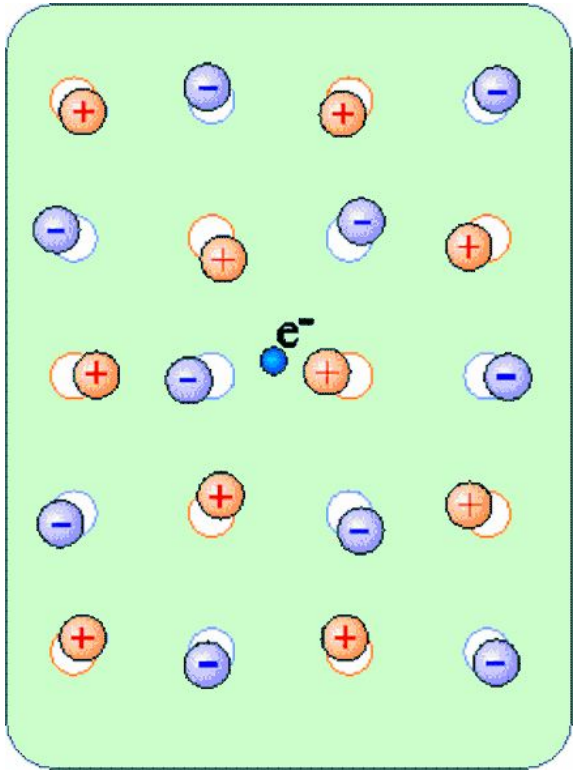
$$\frac{n_{ex}}{n_e} \sim \frac{n_e}{n^*(T)} \ll 1$$

$$n^*(T) = \frac{n_e n_h}{n_{ex}} = \frac{2\mu K_B T}{2\pi\hbar^2} e^{-E_b/K_B T}$$

In inorganic based solar cells most excitons are not bound

Exciton-phonon in organic systems

Dominated by polaronic effects



Photon Absorption

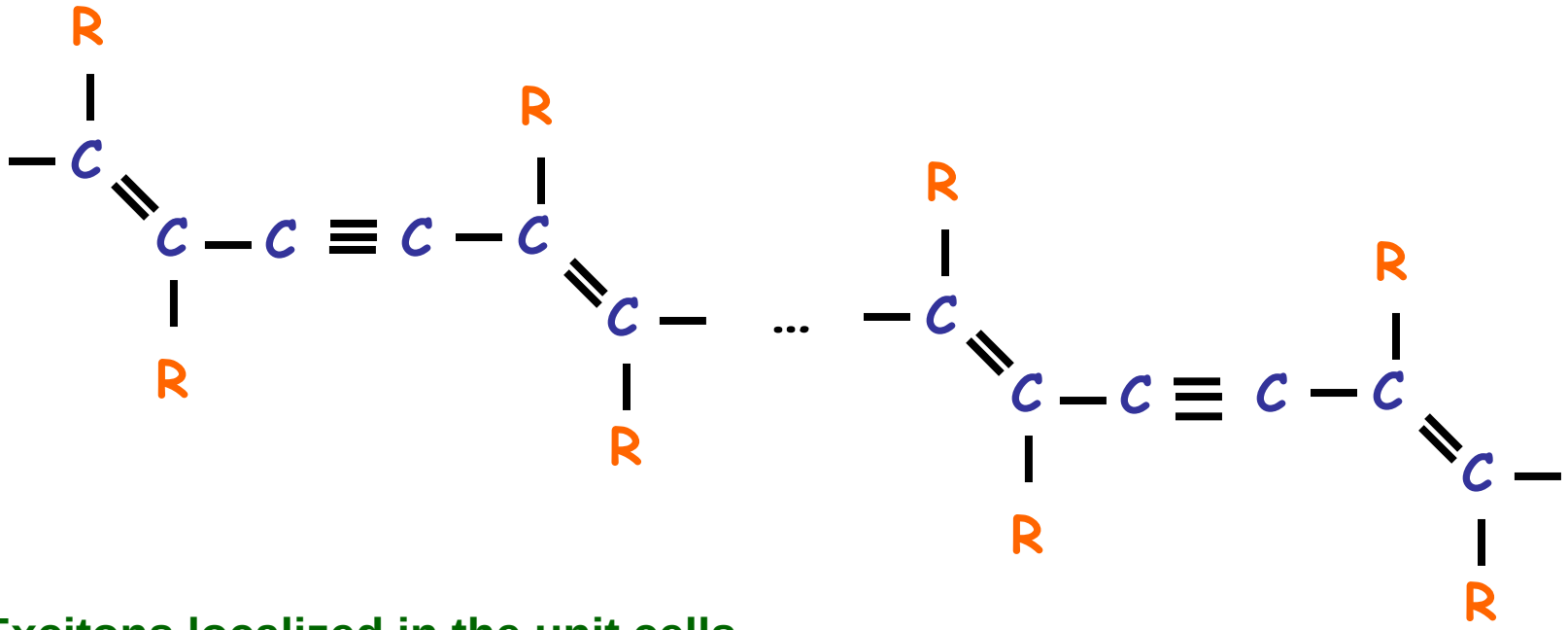
Frenkel-Exciton self-trapping (polaron exciton)

Exciton dissociation at Donor-Acceptor Interface

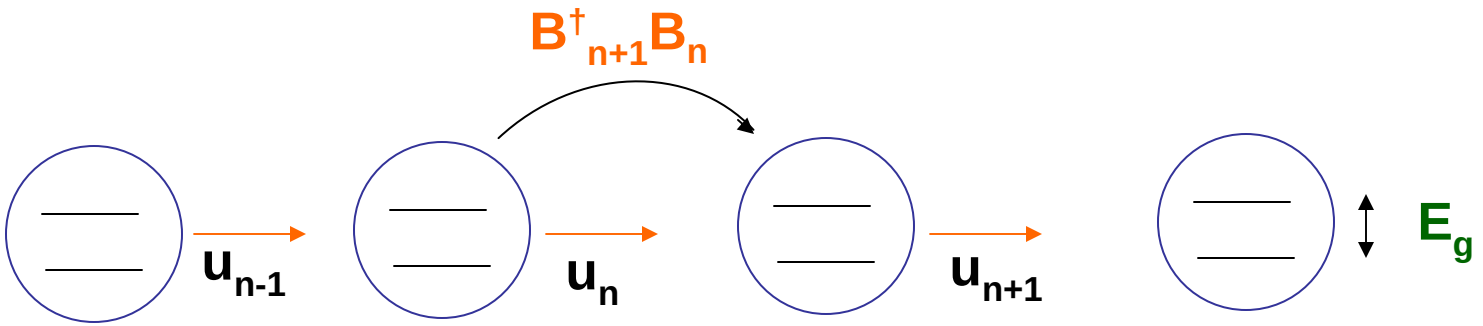
e-polaron

h-polaron

POLYDIACETYLENE



Excitons localized in the unit cells



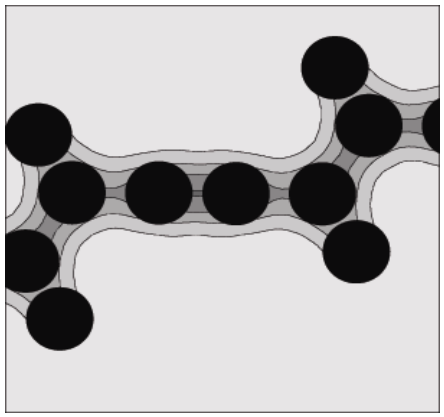
Su-Schrieffer-Heeger for excitons

Exciton propagation is described by a nonlinear Schrodinger equation

$$H_0 = \sum \frac{p_n^2}{2M} + \sum \frac{1}{2} C \left(u_{n+1} - u_n\right)^2 - \sum t_{n+1,n} \left(B_{n+1}^{\dagger} B_n + B_n^{\dagger} B_{n+1}\right)$$

$$t_{n+1,n} = t_0 - \alpha\left(u_{n+1} - u_n\right)$$

DFT calculations*



Exciton self-trapping

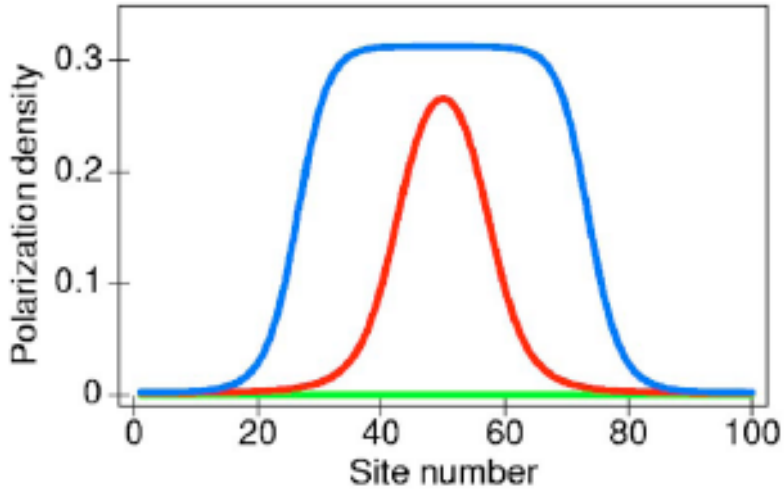


FIG. 1. (Color online) Polarization density $|\psi_n|^2$ for $\delta/t_0=0.05$, $\Omega/t_0=10^{-4}$ (green line at the bottom), $\Omega/t_0=1.99\times10^{-3}$ (red line in the middle), and $\Omega/t_0=2.06\times10^{-3}$ (blue line at the top).

*** M.V. Katkov PhD Thesis (06) MSU**

Lattice deformation

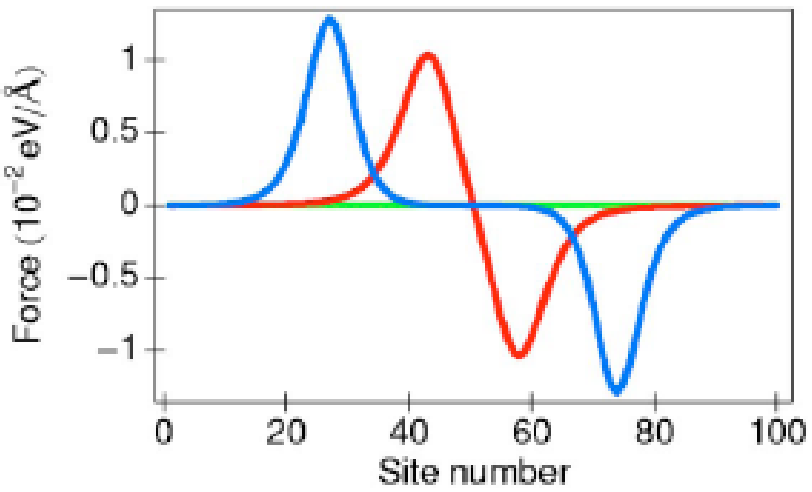


FIG. 2. (Color online) Force as a function of the site number for $\delta/t_0=0.05$, $\Omega/t_0=10^{-4}$ (green line across the middle), $\Omega/t_0=1.99\times10^{-3}$ (red line), and $\Omega/t_0=2.06\times10^{-3}$ (blue line on the left).

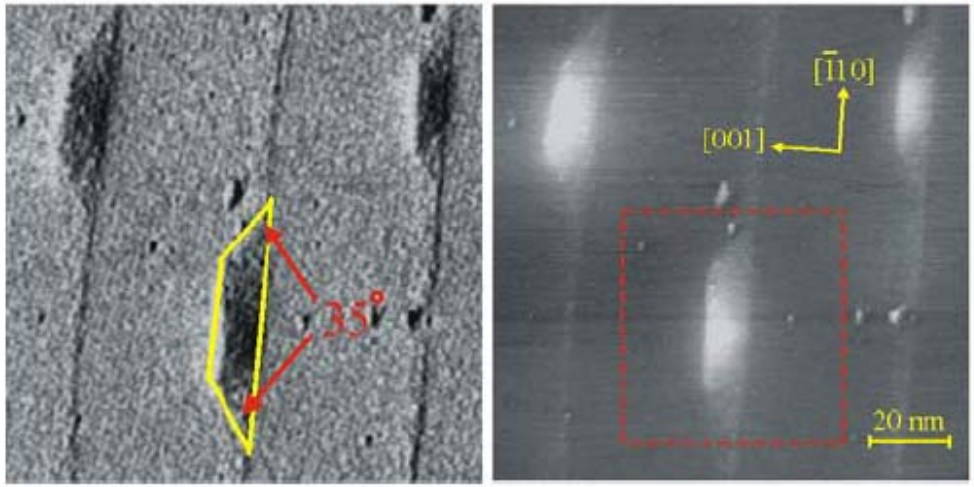
M. V. Katkov. Y. V. Pershin, C.P. PRB 74 224306 (2006)

Without excitons

With excitons

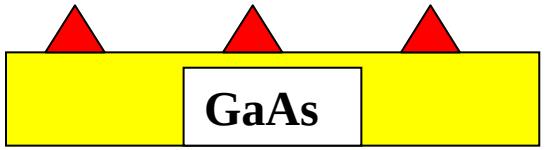
Implications of these effects on solar cells dynamics are not fully known

Excitons in Quantum Dots



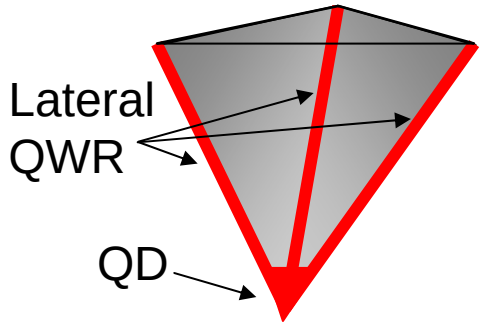
Self assembled

InAs lattice mismatch



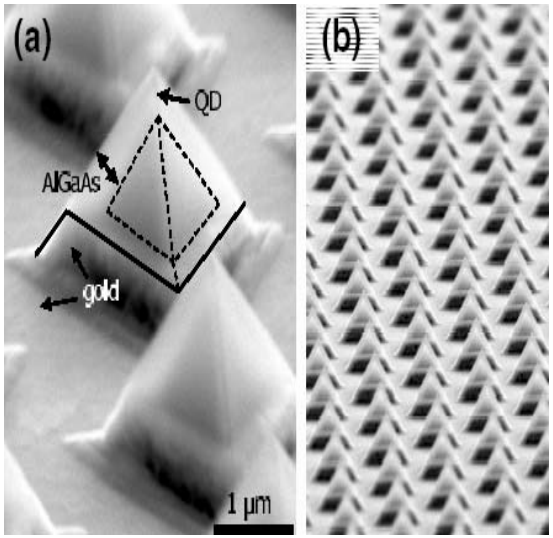
K. Shih UT Austin

Pyramidal dots



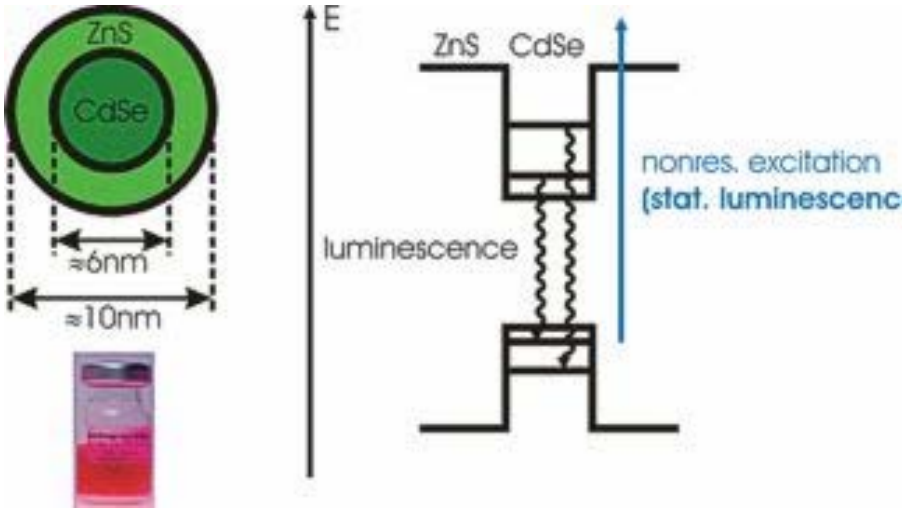
Self-limited growth (6 nm)

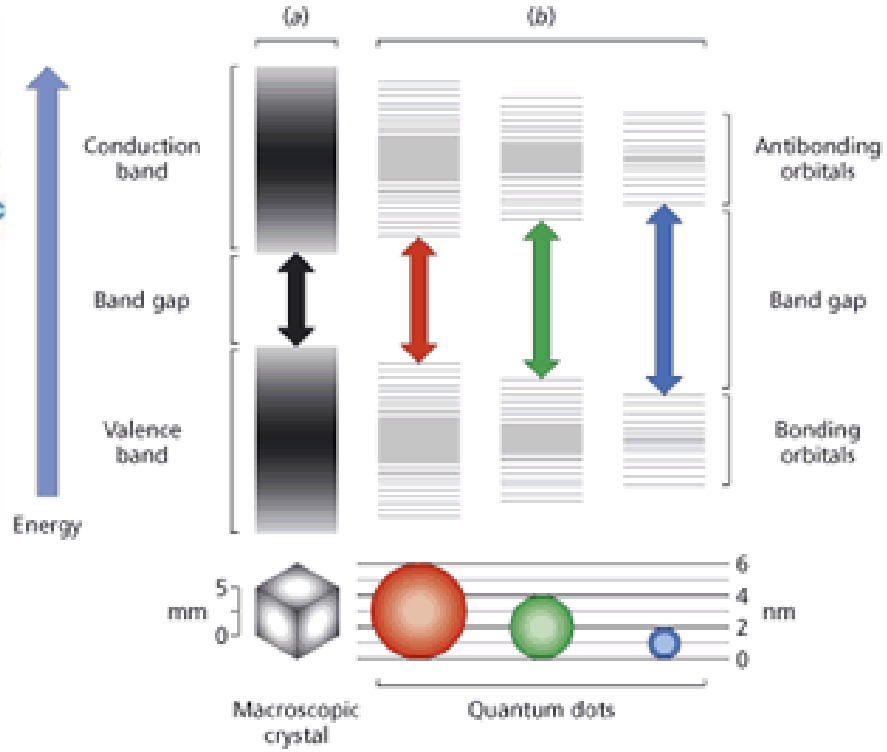
Hartmann *et al.*
J. Phys. Cond. Matt. 11, 5901 (1999)



Colloidal quantum dots

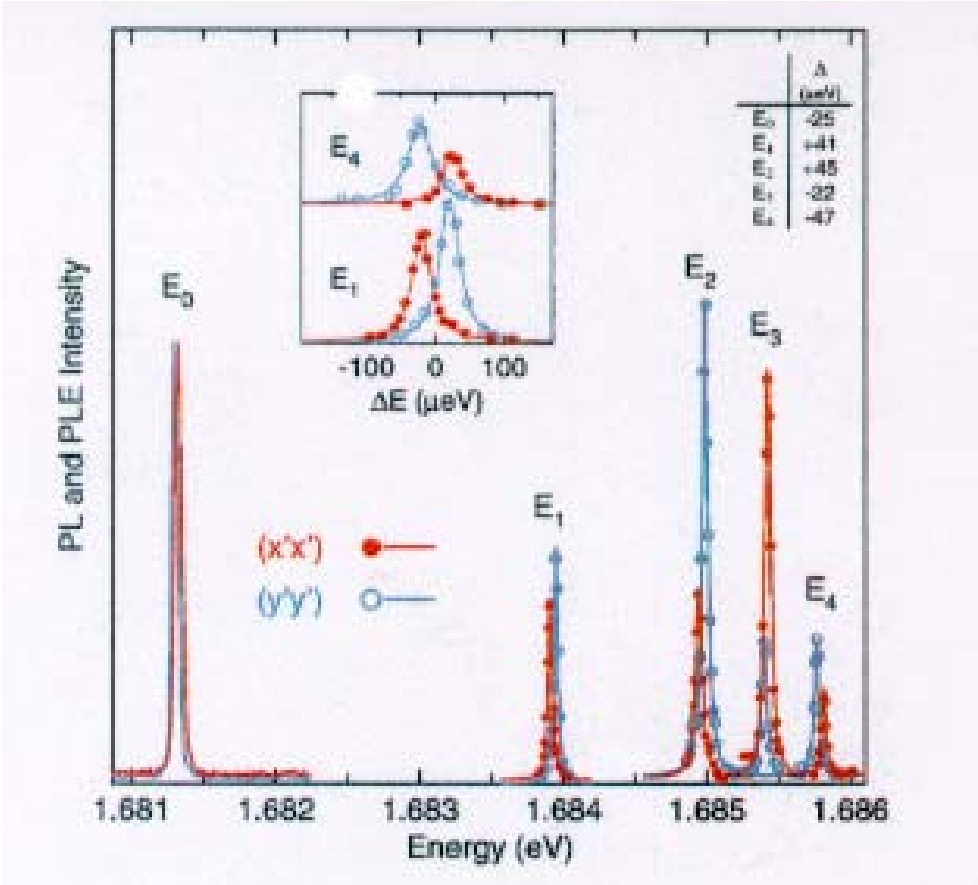
Chemical synthesis **External shell** **Large tunability**



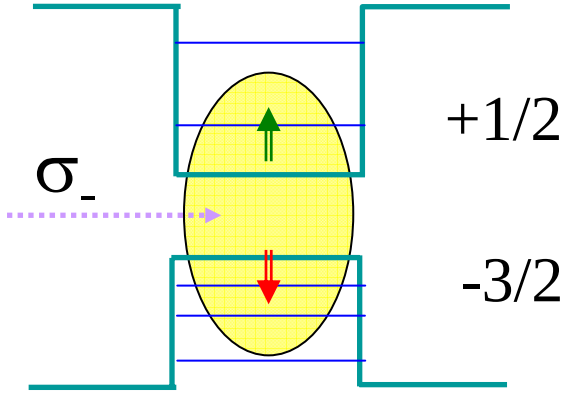


Excitons in a single QD

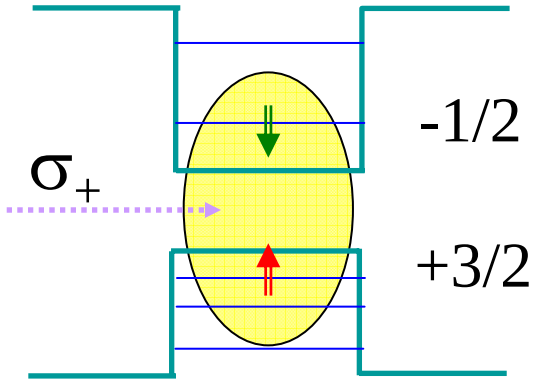
Interface fluctuation QD



D. Gammon, PRL 76,3005 (1996)



$X_{-}=e^{+}_{\uparrow}h^{+}_{\downarrow}|G>$



$X_{+}=e^{+}_{\downarrow}h^{+}_{\uparrow}|G>$

Multiexciton States

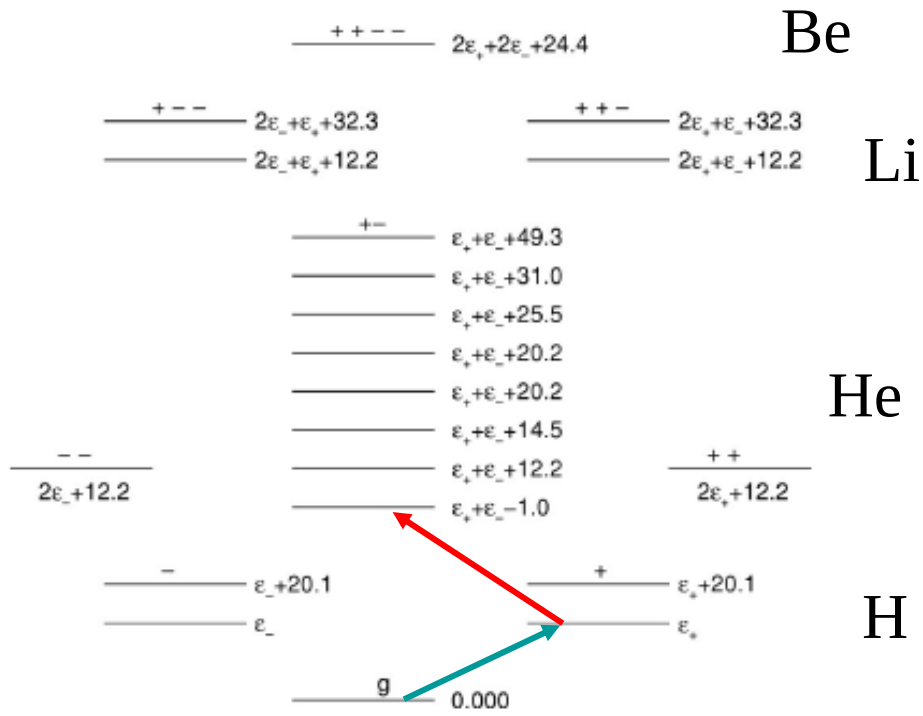
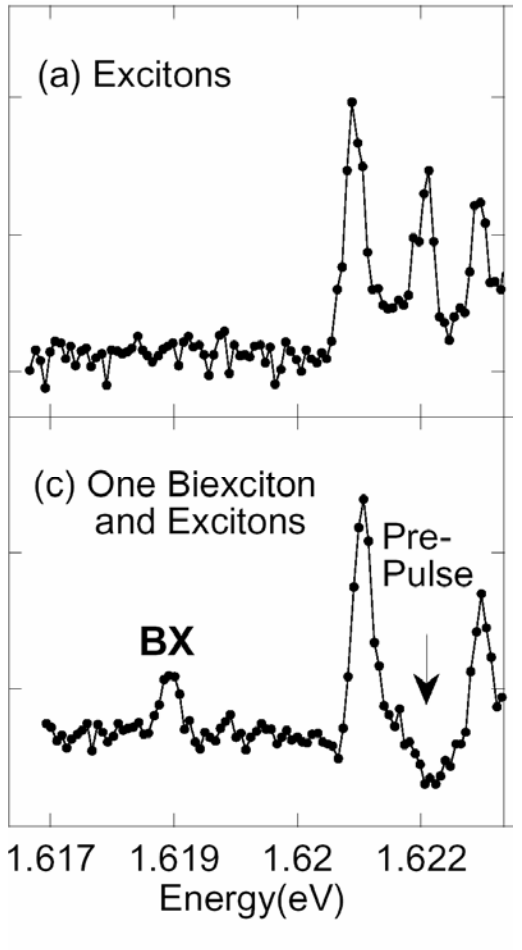


FIG. 1. Energy levels of the multiexciton states in a quantum dot in meV. $\epsilon_+ = \epsilon_- = 1764$ meV.



A QD is an "atom" where the number of protons and electrons can be controlled

C.P. et al PRB 65 075307

X. Li Science 301 809 (2003)

Multiexciton generation in Quantum Dots

VOLUME 92, NUMBER 18 PHYSICAL REVIEW LETTERS week ending 7 MAY 2004

High Efficiency Carrier Multiplication in PbSe Nanocrystals: Implications for Solar Energy Conversion

R. D. Schaller and V. I. Klimov

Chemistry Division, C-PCS, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA

(Received 25 November 2003; published 5 May 2004)

We demonstrate for the first time that impact ionization (II) (the inverse of Auger recombination) occurs with very high efficiency in semiconductor nanocrystals (NCs). Interband optical excitation of PbSe NCs at low pump intensities, for which less than one exciton is initially generated per NC on average, results in the formation of two or more excitons (carrier multiplication) when pump photon energies are more than 3 times the NC band gap energy. The generation of multiexcitons from a single photon absorption event is observed to take place on an ultrafast (picosecond) time scale and occurs with up to 100% efficiency depending upon the excess energy of the absorbed photon. Efficient II in NCs can be used to considerably increase the power conversion efficiency of NC-based solar cells.

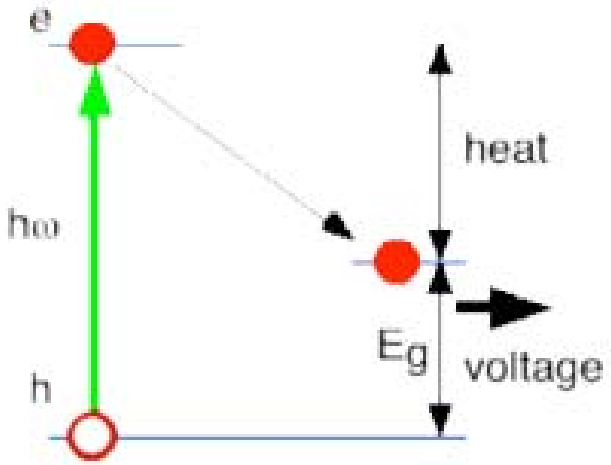
Enhanced Coulomb effects

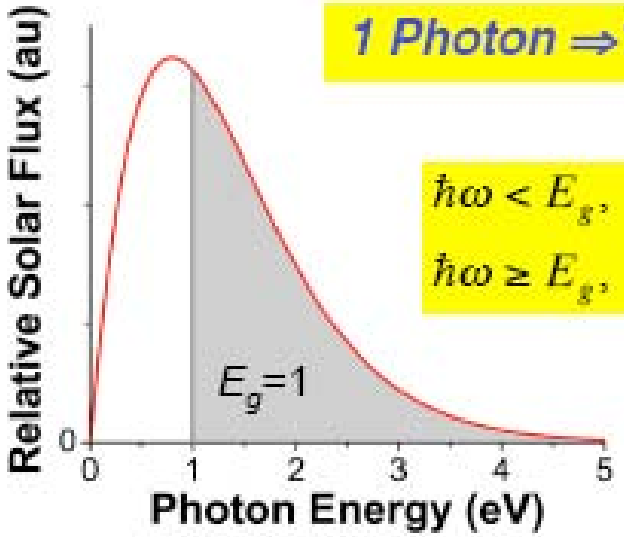
Break momentum conservation

Tunable Eg

Traditional Solar Cell: *Ultimate Efficiency*

- **Traditional solar cell:**





1 Photon ⇒1 e-h pair

$\hbar\omega < E_g, \quad QE = 0$

$\hbar\omega \geq E_g, \quad QE = 1$

"Ultimate" efficiency :

$$\eta = \frac{1}{\Phi_0} x_g \int_{x_g}^{\infty} \frac{x^2}{e^x - 1} dx, \; x_g = \frac{E_g}{kT_S}$$

Total solar flux :

$$\Phi_0 = \int_{x_g}^{\infty} \frac{x^3}{e^x - 1} dx$$

- **"Ultimate" QE for silicon:**

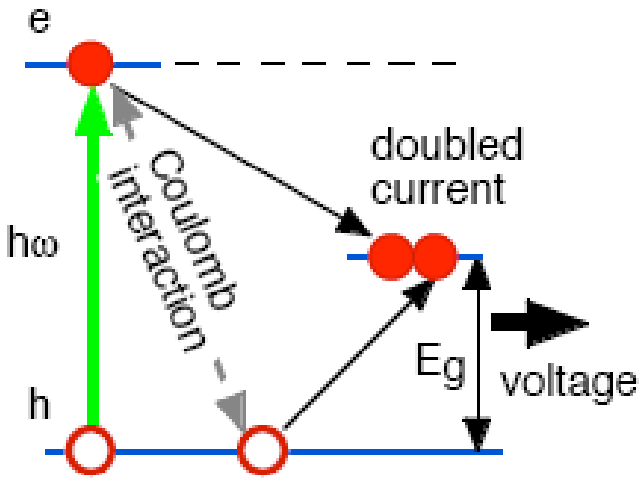
$E_g = 1.1$ eV, $T_s = 6000$ K

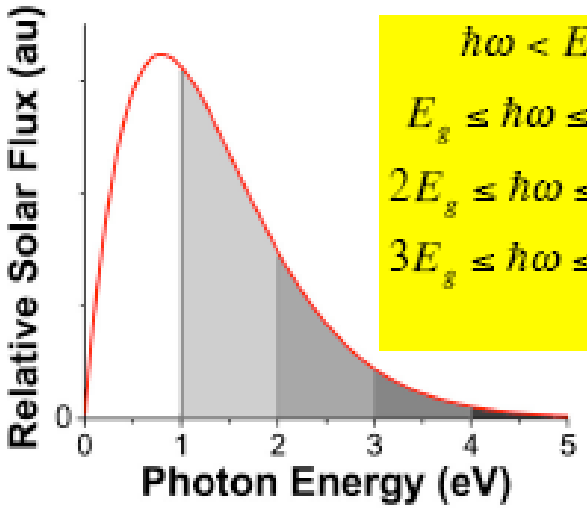
$\eta = 44\%$

W. Shockley and H. J. Queisser, *J. Appl. Phys.* 32, 510 (1961)

Impact-ionization-based solar cell:

1 Photon ⇒2 e-h pairs or more





$$\hbar\omega < E_g, \quad QE = 0$$
$$E_g \le \hbar\omega \le 2E_g, \quad QE = 1$$
$$2E_g \le \hbar\omega \le 3E_g, \quad QE = 2$$
$$3E_g \le \hbar\omega \le 4E_g, \quad QE = 3$$
$$\ldots$$

New "ultimate" efficiency:

"Ultimate" efficiency with Impact Ionization:

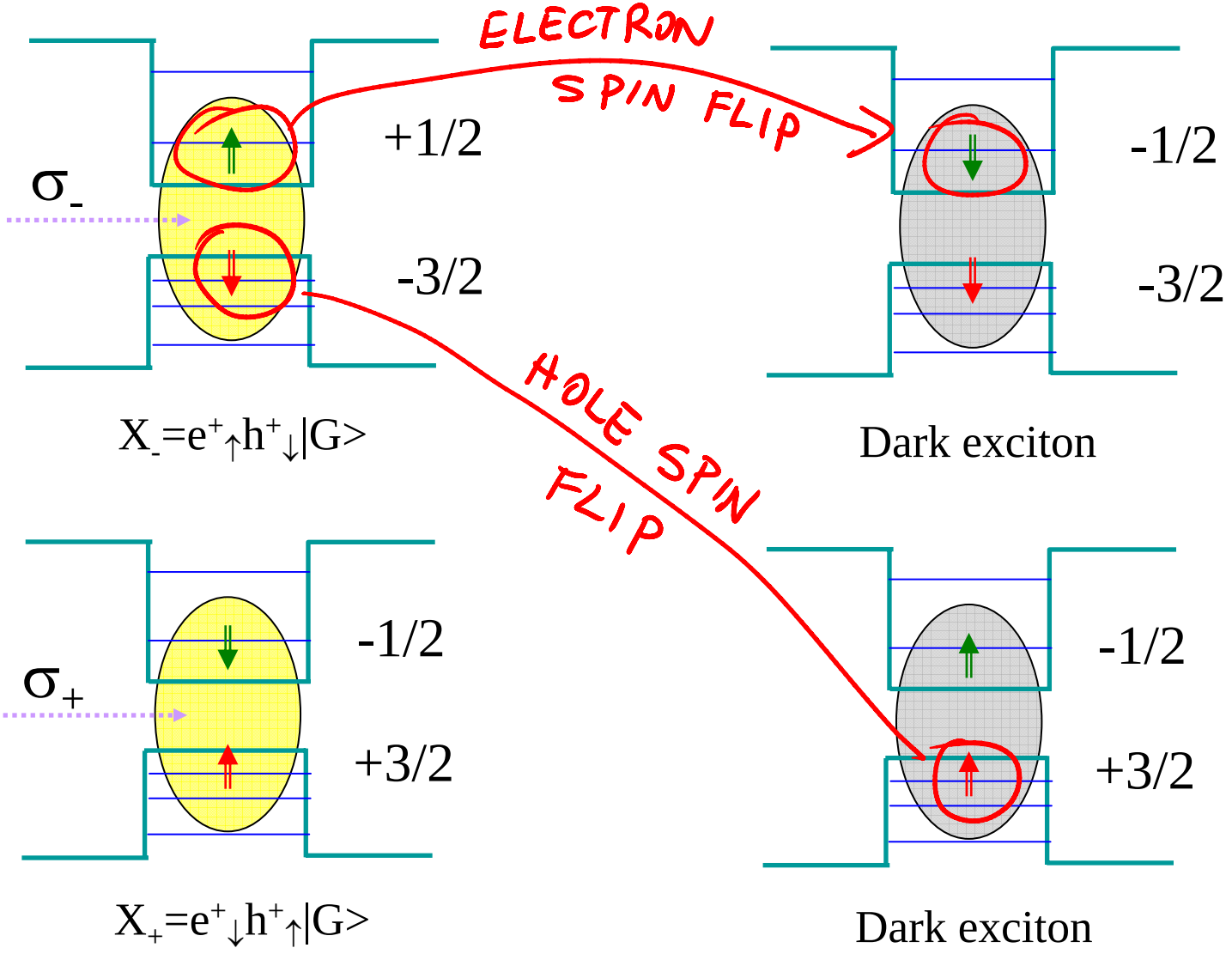
$$\eta = \frac{1}{\Phi_0} x_g \sum_{1}^{\infty} QE(i) \int_{ix_g}^{(i+1)} \frac{x^2}{e^x - 1} dx,$$

$$QE(i \ge 2) = 2$$
$$E_g = 0.88 \text{ eV}, T_s = 6000 \text{ K}$$
$$\eta = 60\%$$
(36% increase compared to $QE = 1$)

S. Kolodinski, J. H. Werner, H. J. Queisser, *Solar En. Mat. & Sol. Cells*, 33, 275 (1994)

Use dark excitons

Infinite lifetime !



APPLIED PHYSICS LETTERS 90, 133509 (2007)

Enhanced photovoltaic response of organic solar cell by singlet-to-triplet exciton conversion

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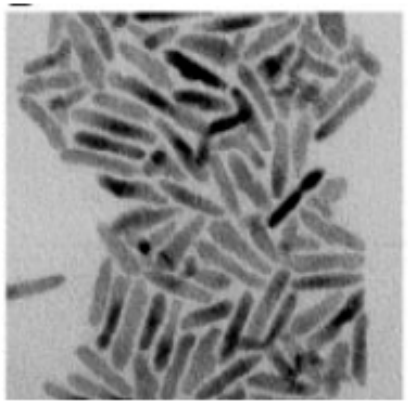
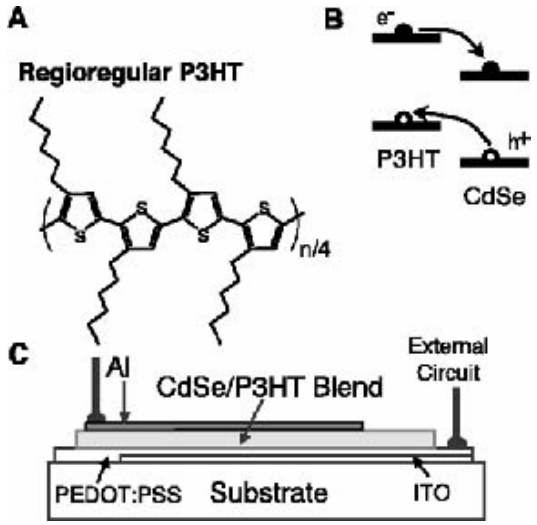
Ir complex was doped to conjugated polymers, and the photoinduced absorption of triplet excitons in host materials was examined. A greatly enhanced intersystem crossing rate was observed, despite the decrease in triplet exciton lifetime. The authors find that the steady-state triplet exciton population in host polymer would increase by an order of magnitude. Conjugated polymer/colloidal CdSe nanocrystal hybrid solar cells were fabricated and the effect of Ir-complex doping on photovoltaic response was studied. It was found that due to the enhanced singlet-to-triplet conversion, greatly enhanced photovoltaic response of these hybrid organic solar cells was observed. The results suggest that triplet solar cells may be achieved by doping conventional photovoltaic materials with transition-metal complexes. © *2007 American Institute of Physics.*
[DOI: 10.1063/1.2716209]



CdSe quantum rods



Dope organic with Ir complex to make excitons dark by spin flipping

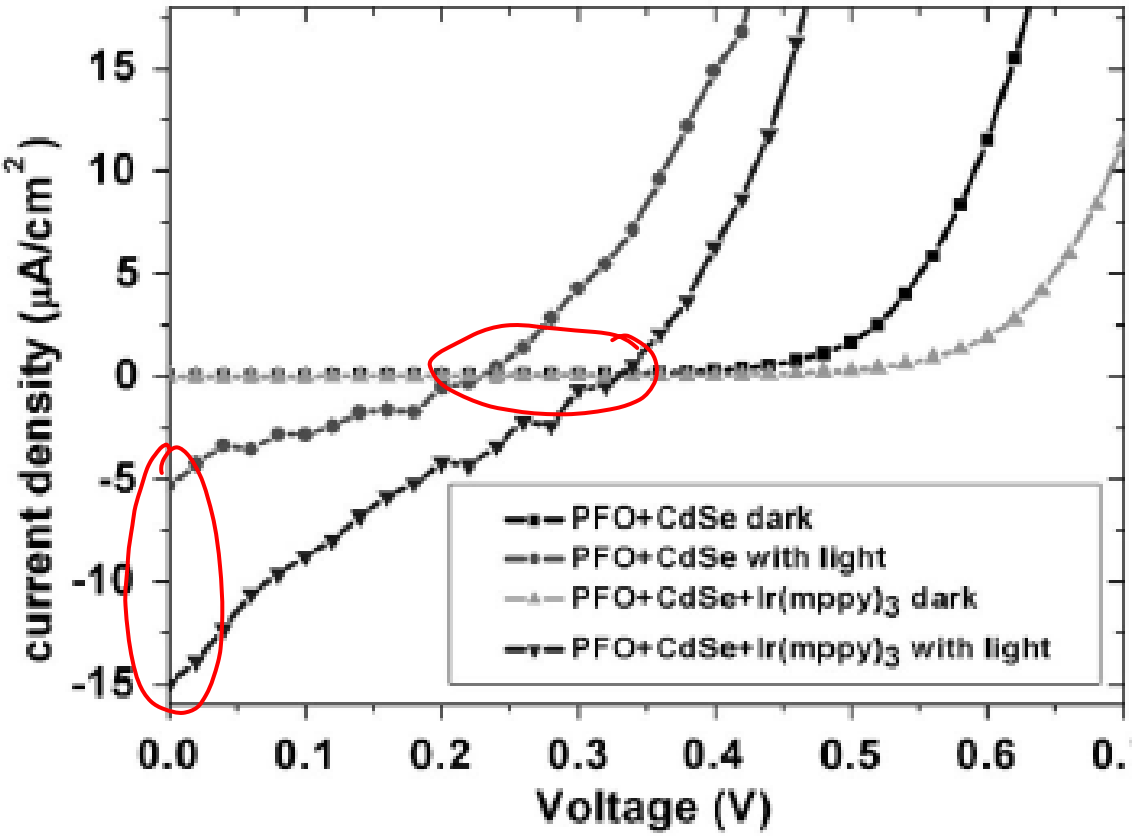


FIG. 2. Dark and photovoltaic responses of hybrid solar cells made from PFO/CdSe with and without $Ir(mppy)_3$, showing 200% increase in short-circuit current and 50% increase in open-circuit voltage upon doping of $Ir(mppy)_3$.

Conclusions

Investigations on fundamental physical properties of excitons is very important for solar cell applications

Dynamics of formation and dissociation

Polaronic effects in transport

Coulomb effects in confined excitons (Impact Ionization in QD)

Spin degrees of freedom

Experiment

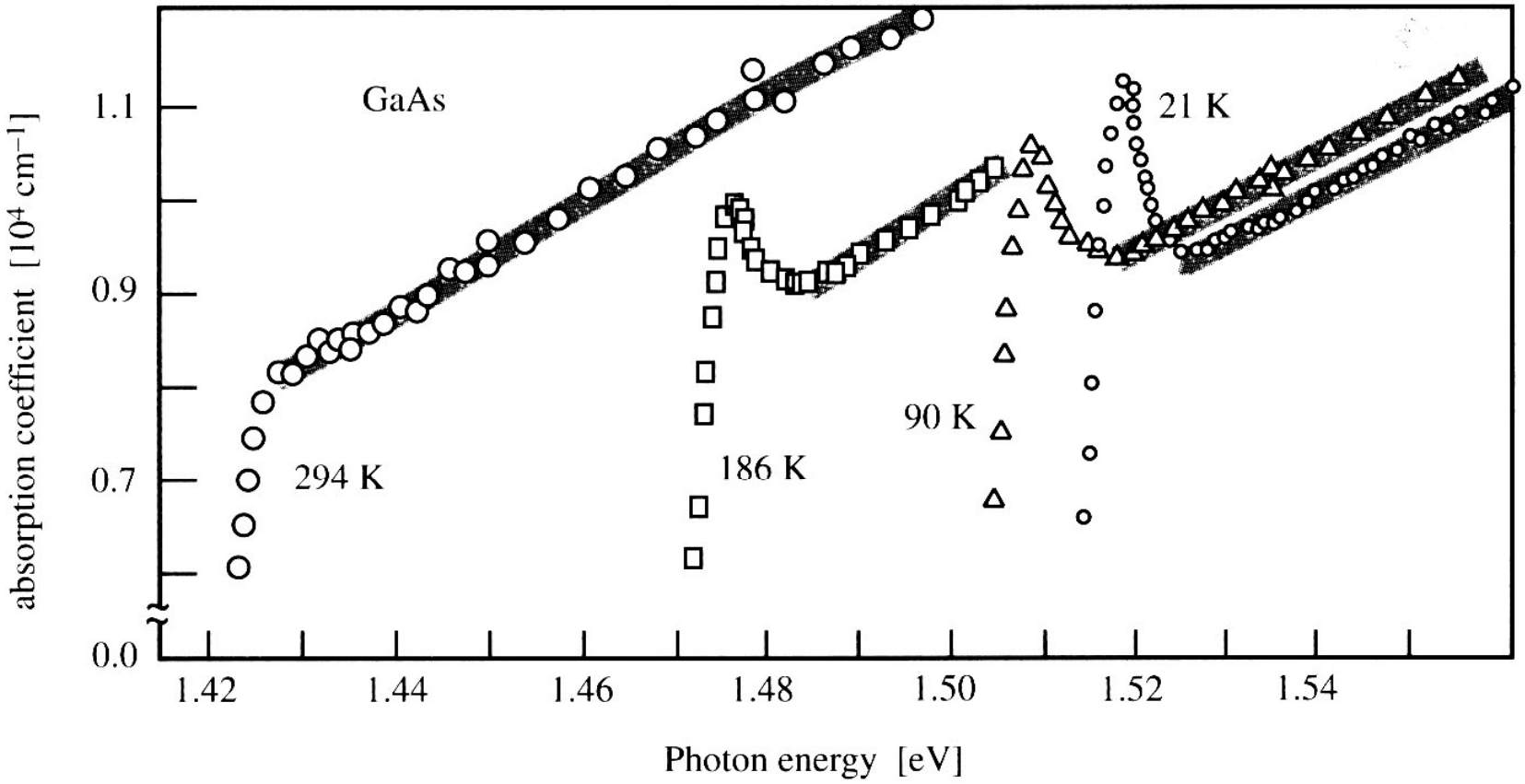


Fig. 6.25. Excitonic absorption spectra of GaAs near its bandgap for several sample temperatures. The *gray lines* drawn through the 21, 90 and 294 K data points represent fits with (6.90) [6.48]

In inorganic solar cell devices bound excitons can be neglected

Dynamics by phonon scattering can be simulated without phenomenological parameters