

Introduction to excitons and their role in photovoltaic processes

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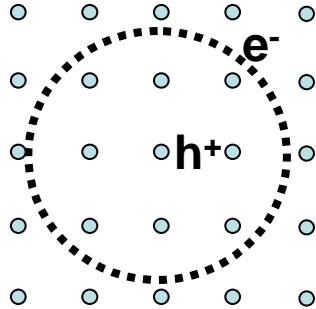


**MICHIGAN STATE
UNIVERSITY**

**Complex Materials and their Energy Applications
March 27th 2008 MSU**

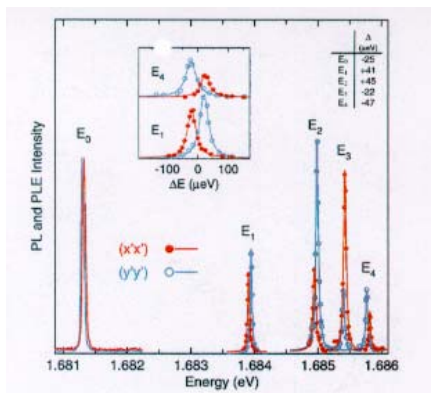
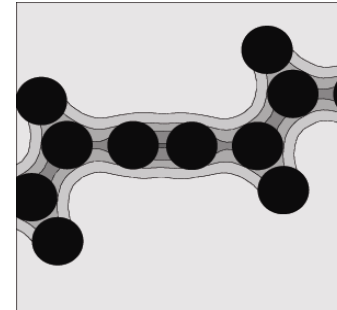
Outline

Solar Cells



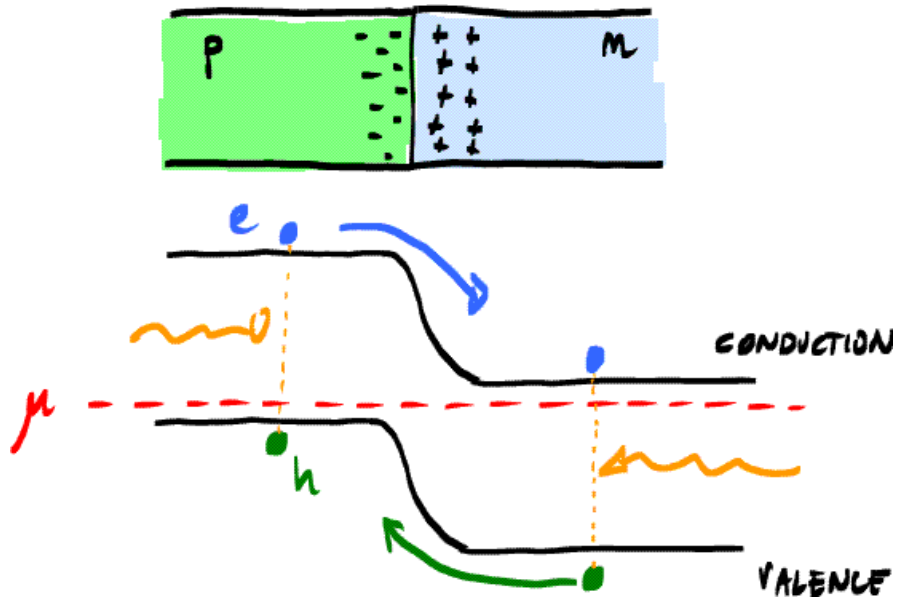
Wannier and Frenkel excitons

Exciton-phonon effects



Excitons in Quantum Dots

First Generation Solar Cells



Silicon wafers quite expensive

About 25% efficiency

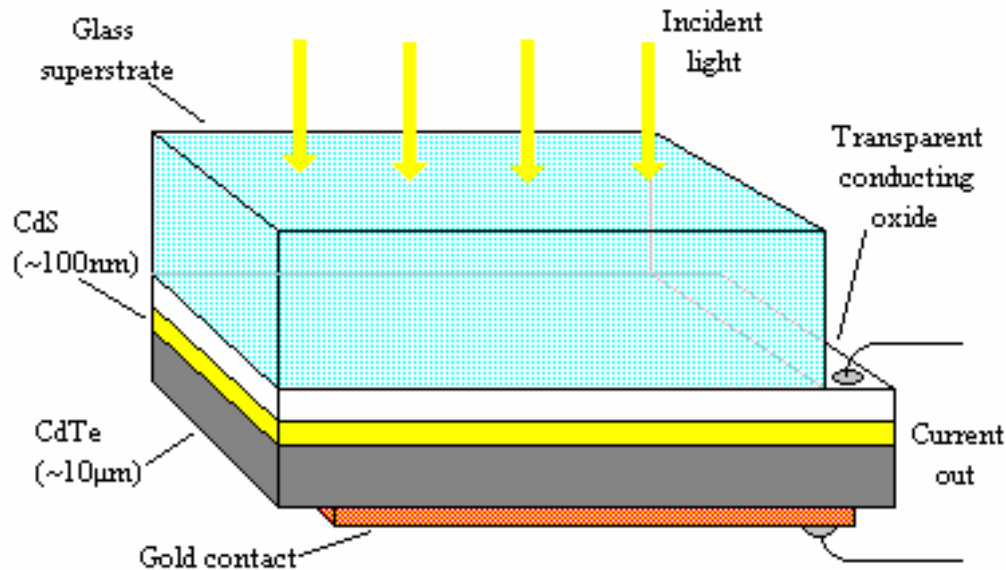
Large p-n junction diode



90% Market

Second Generation Solar Cells

p-n junction with thin films



About 10-20% efficiency

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

High efficiency (40%) but costly

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

CdS is n doped
2.5 eV gap window layer

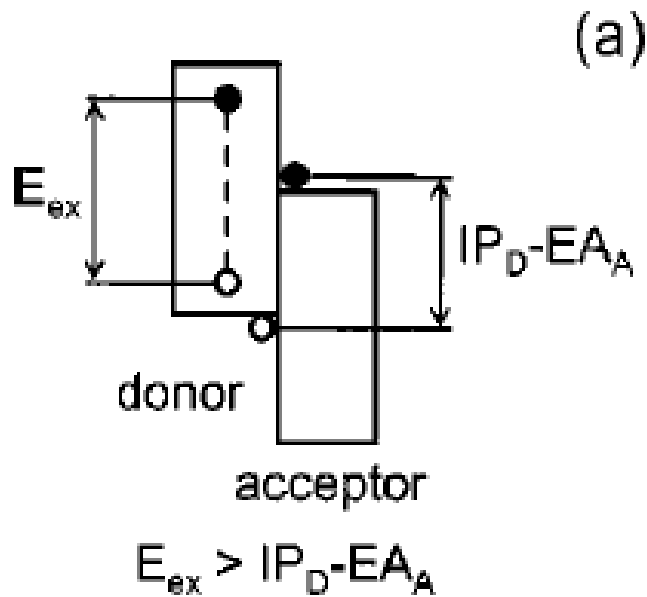
CdTe is p-doped
1.5 eV gap active layer

$p \ll n$: depletion region
larger on p side

10% Market

Third Generation Solar Cells

No p-n junction



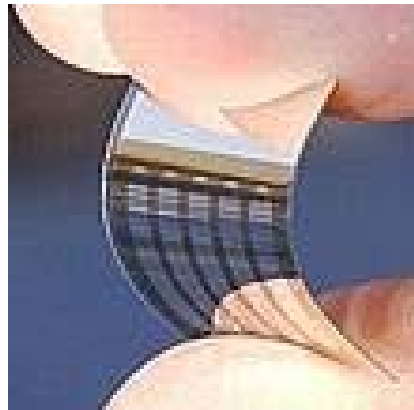
Less than 10% efficiency

Nanotechnology (dots rods wires nanoparticles), Polymers, Dyes

Based on Donor-Acceptor Interface

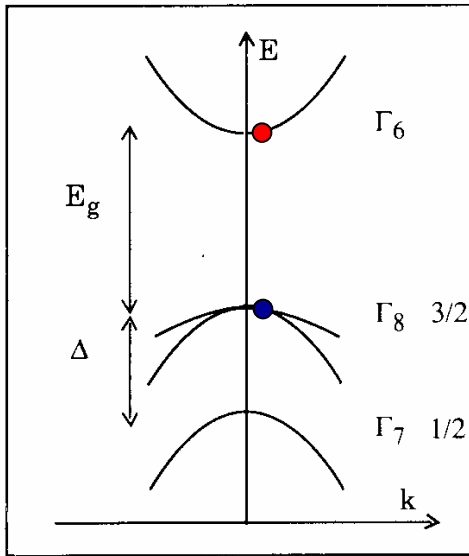
Strong excitonic effects

e-h separation has to occur before radiative recombination



0% Market

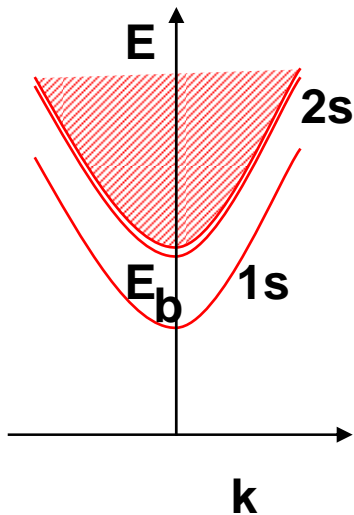
GaAs



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



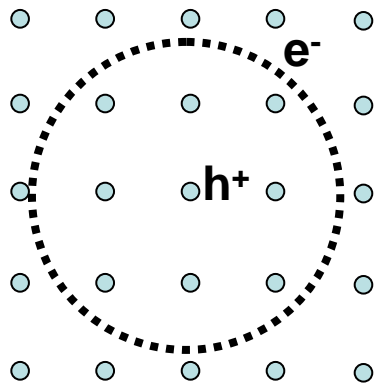
$$a_B = \frac{\hbar^2 \epsilon}{\mu^* e^2} \approx 80 \text{ \AA}$$

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

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

$$\epsilon \approx 13$$

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)

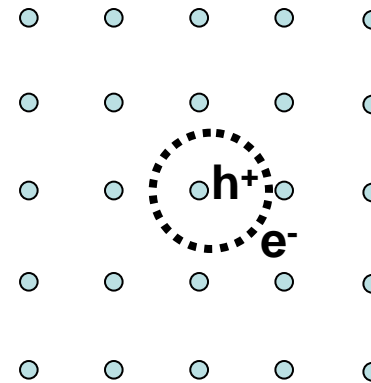
Mostly in organic materials (molecular crystals, polymers and many others organic structures). Alkali Halides (e.g. KI, NaCl). Noble Gas Crystals (e.g. solid Kr).

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

Exciton propagates through
energy transfer processes

Important for: organic LEDs,
organic solar cells

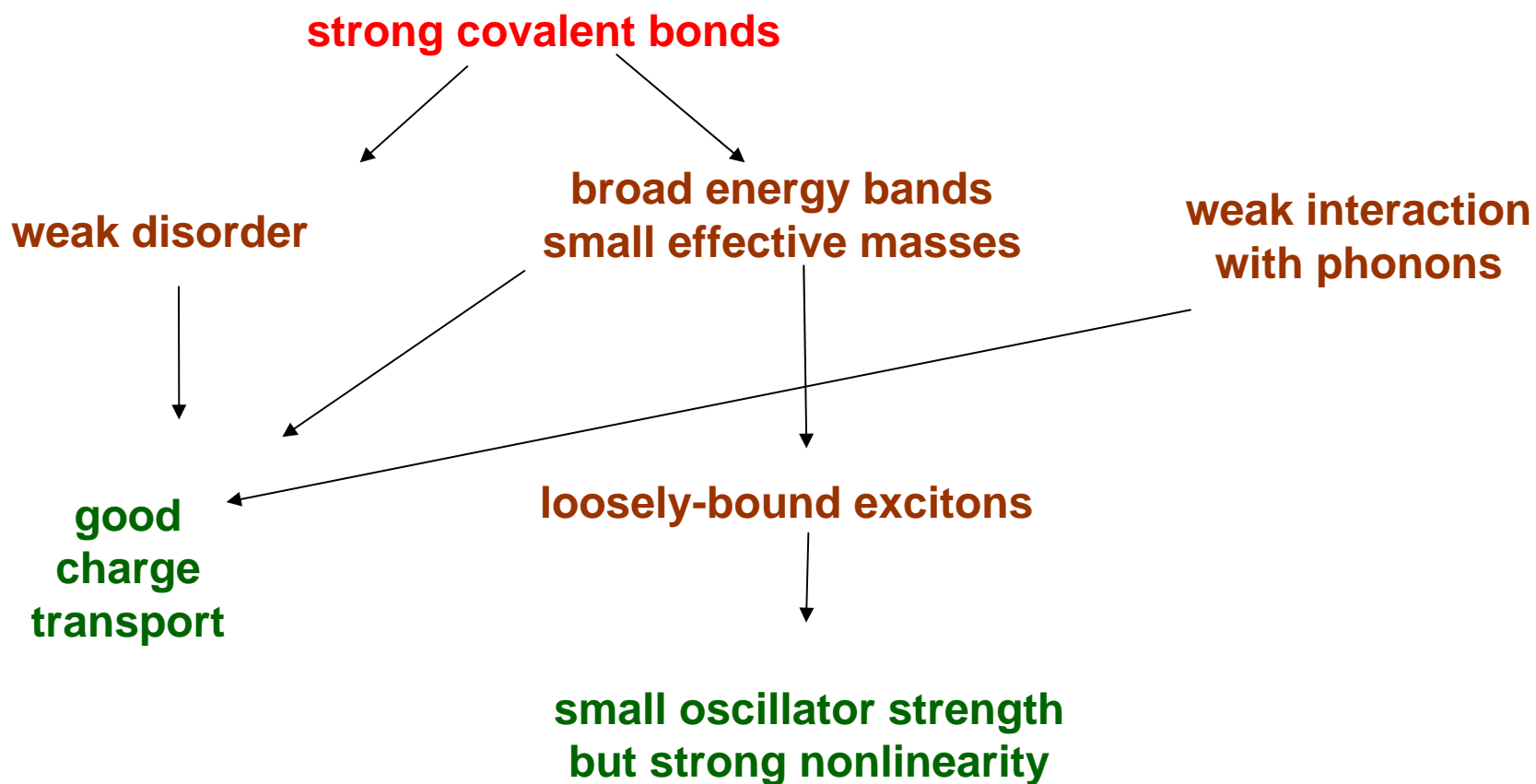
Charge Transfer excitons



Frenkel Exciton

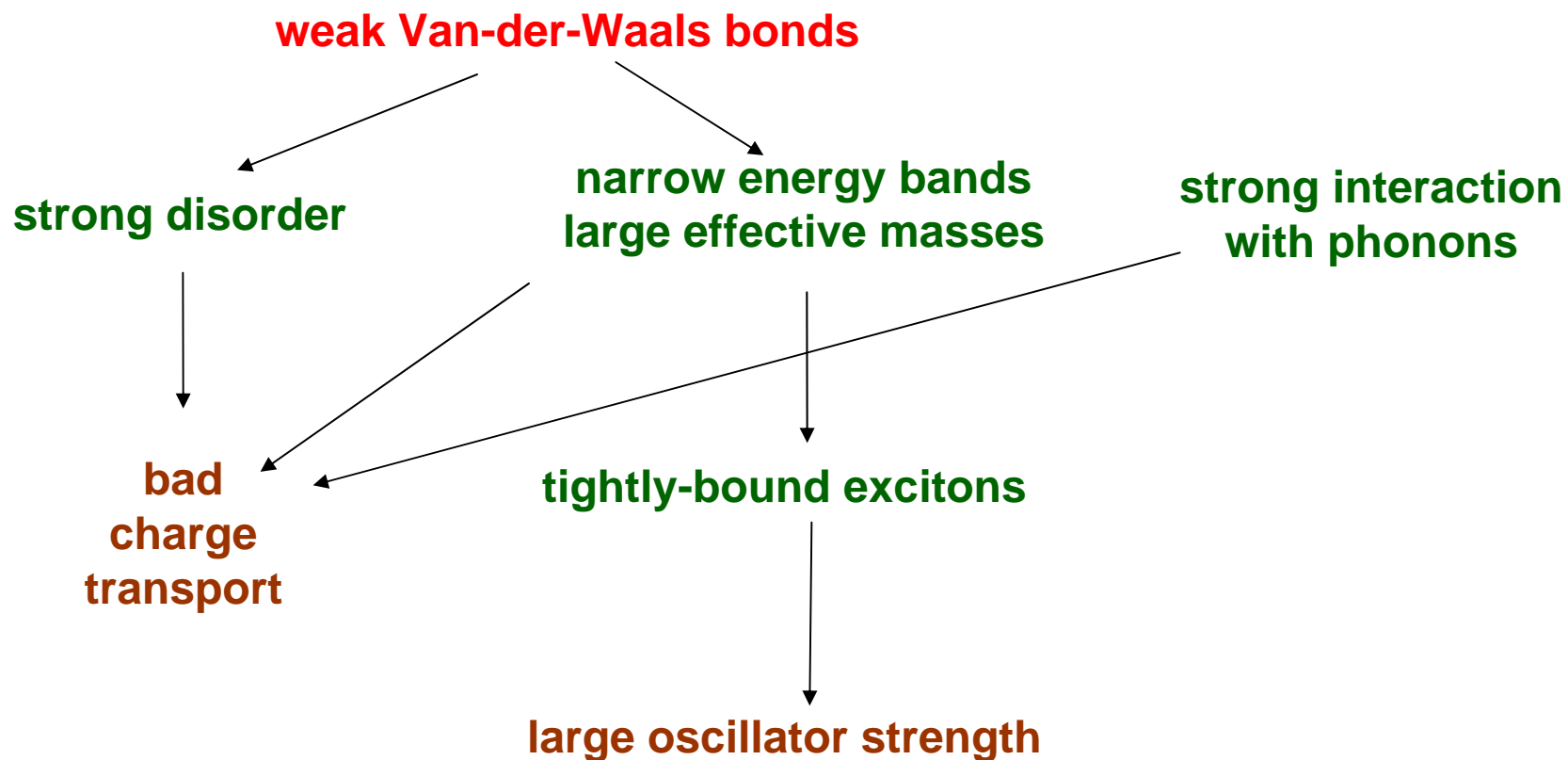
GaAs, ZnS, ZnO, ZnTe, ZnSe, Cu₂O, CuCl, CdTe, SiF₄, and many others;

Wannier-Mott excitons are typical for these materials.

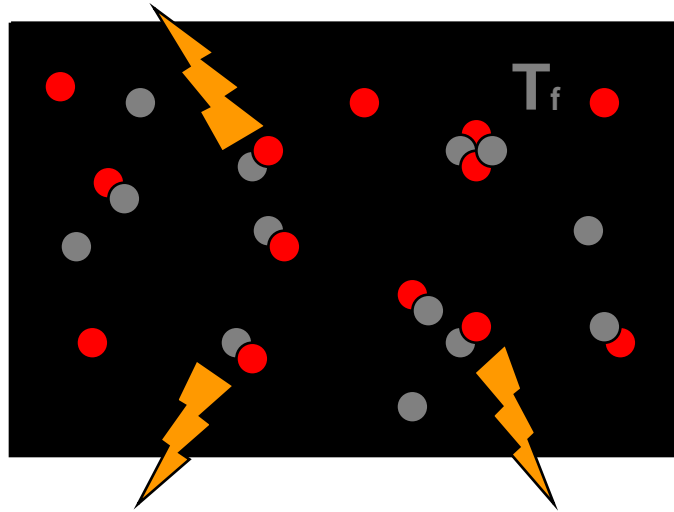


**Anthracene, Tetracene, Pentacene, Phenanthrene, Porphyrin, Phenazine, PTCDA,
and many many others**

The Frenkel excitons are typical for these materials.



Exciton Phonon Dynamics



Cooling by phonon emission



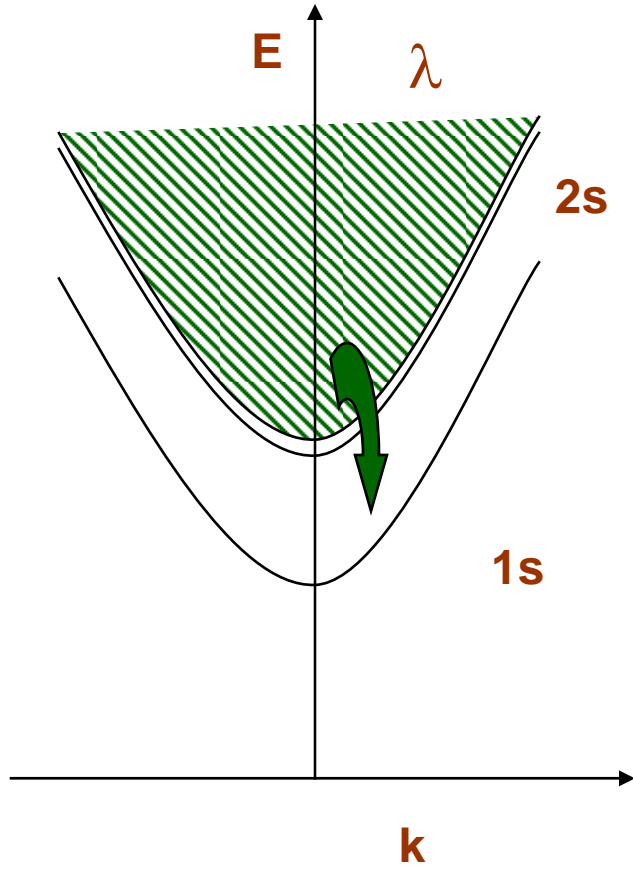
Formation of bound states

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

Auger processes (Coulomb scattering) weak

Boltzmann equation

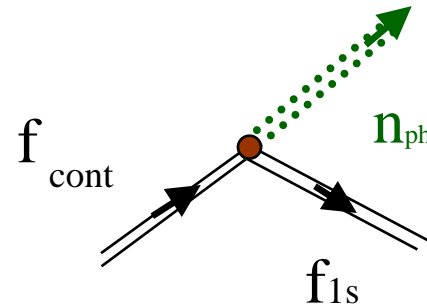
Bimolecular Formation and Dissociation of Excitons



Boltzmann Eq. in the pair basis

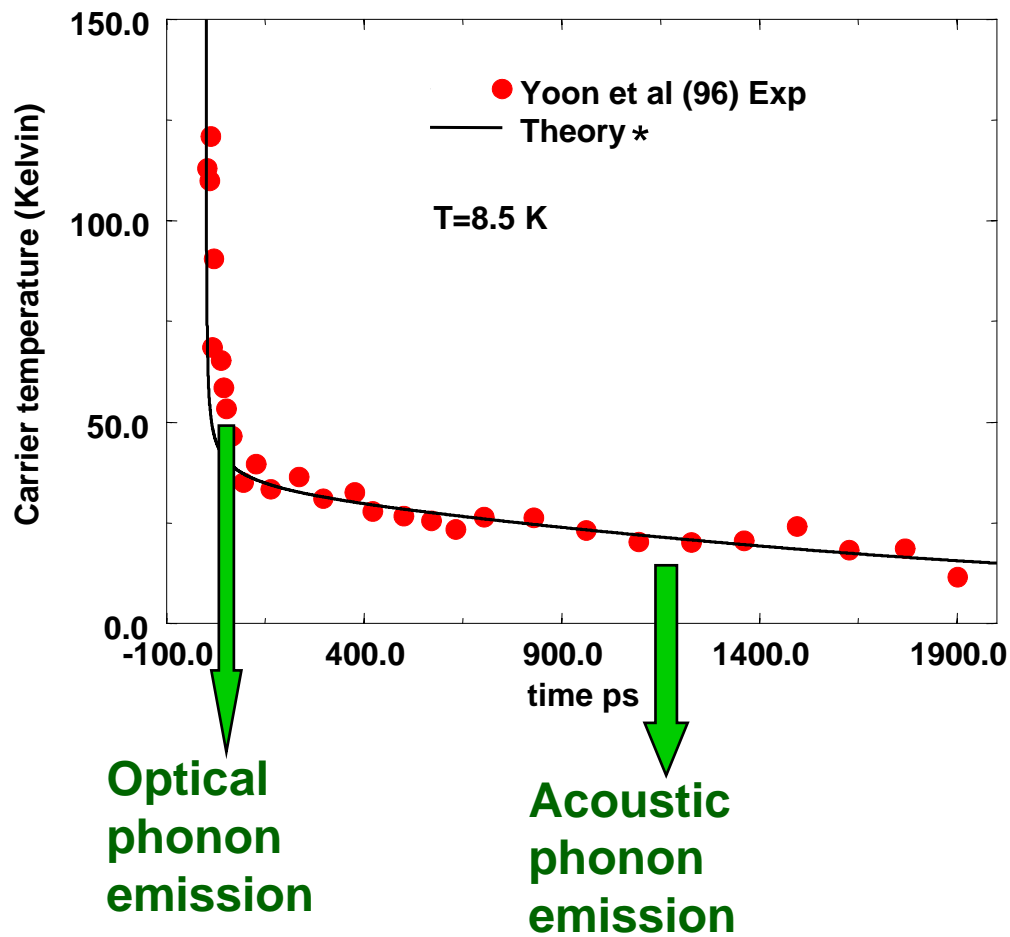
$$\frac{df_{ex}^{1s}(q')}{dt} = \sum_{\lambda, q} W(\lambda, q \rightarrow 1s, q') (1 + n^{ph}(q - q')) f_{ex}^{\lambda}(q)$$

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



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

Fast thermalization



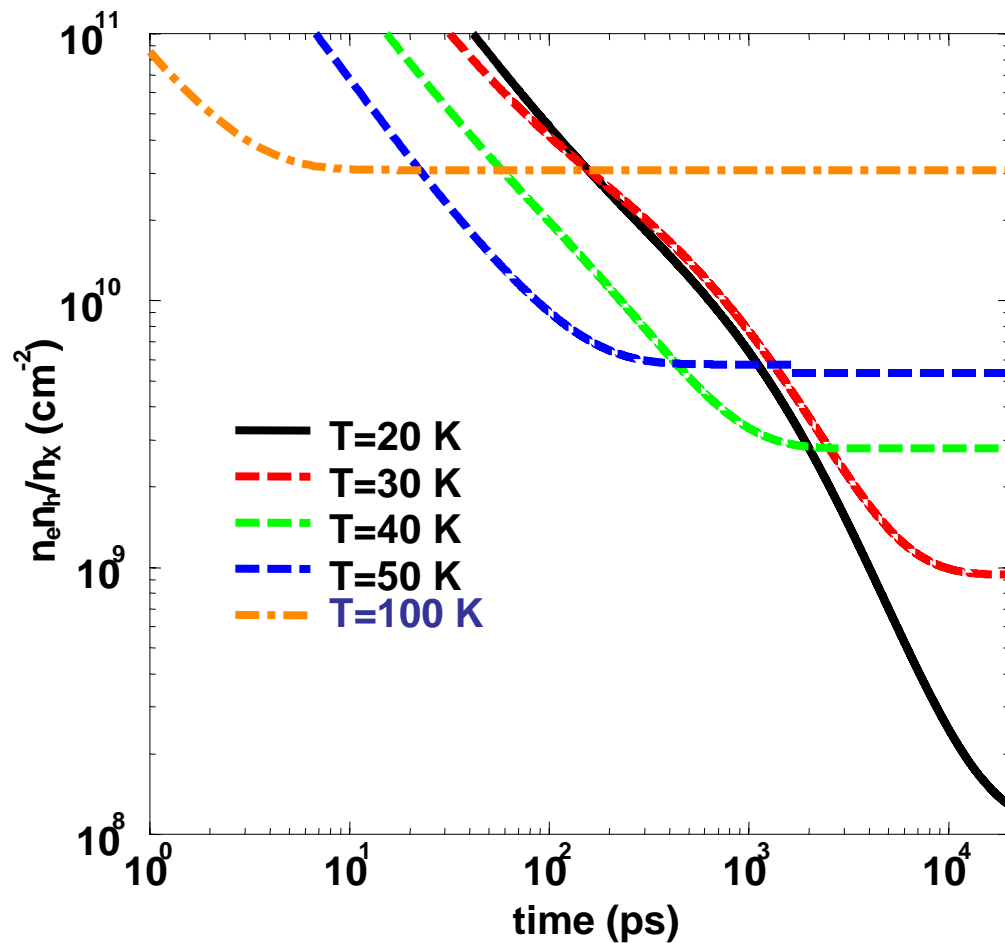
Quantum Well Excitons

Deformation potential

Frolich interaction

Very Accurate Predictions

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

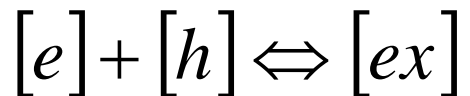


$$\dot{n}_{ex} = C n_e n_h - D n_{ex}$$

$$\dot{n}_e = -C n_e n_h + D n_{ex}$$

Exciton Dissociation Rate
(calculated)

At 100 K quasi-thermal
equilibrium in 1 ps



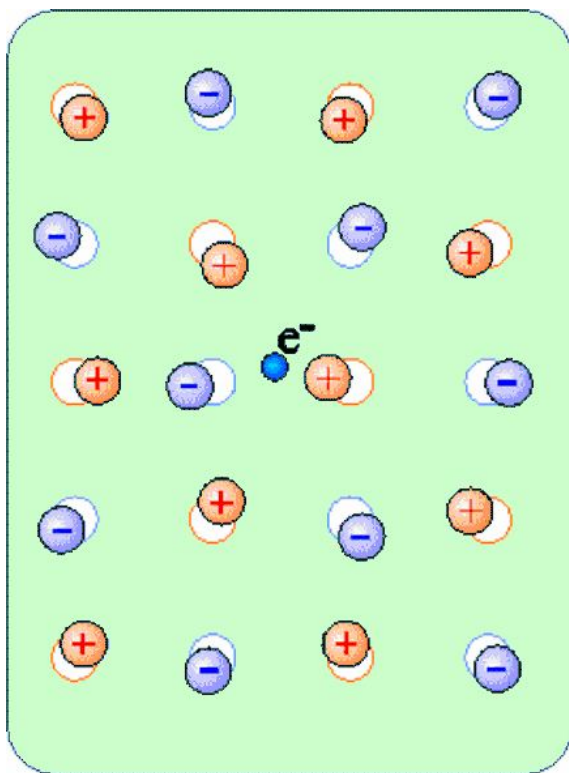
$$\frac{n_{ex}}{n_e} \sim \frac{n_e}{n^*(T)} \ll 1$$

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

In inorganic based solar cells
most excitons are not bound

Exciton-phonon in organic systems

Dominated by polaronic effects

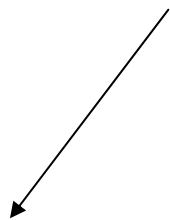


Photon
Absorption

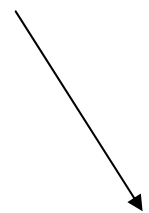


Frenkel-Exciton self-trapping
(polaron exciton)

Exciton dissociation at
Donor-Acceptor Interface

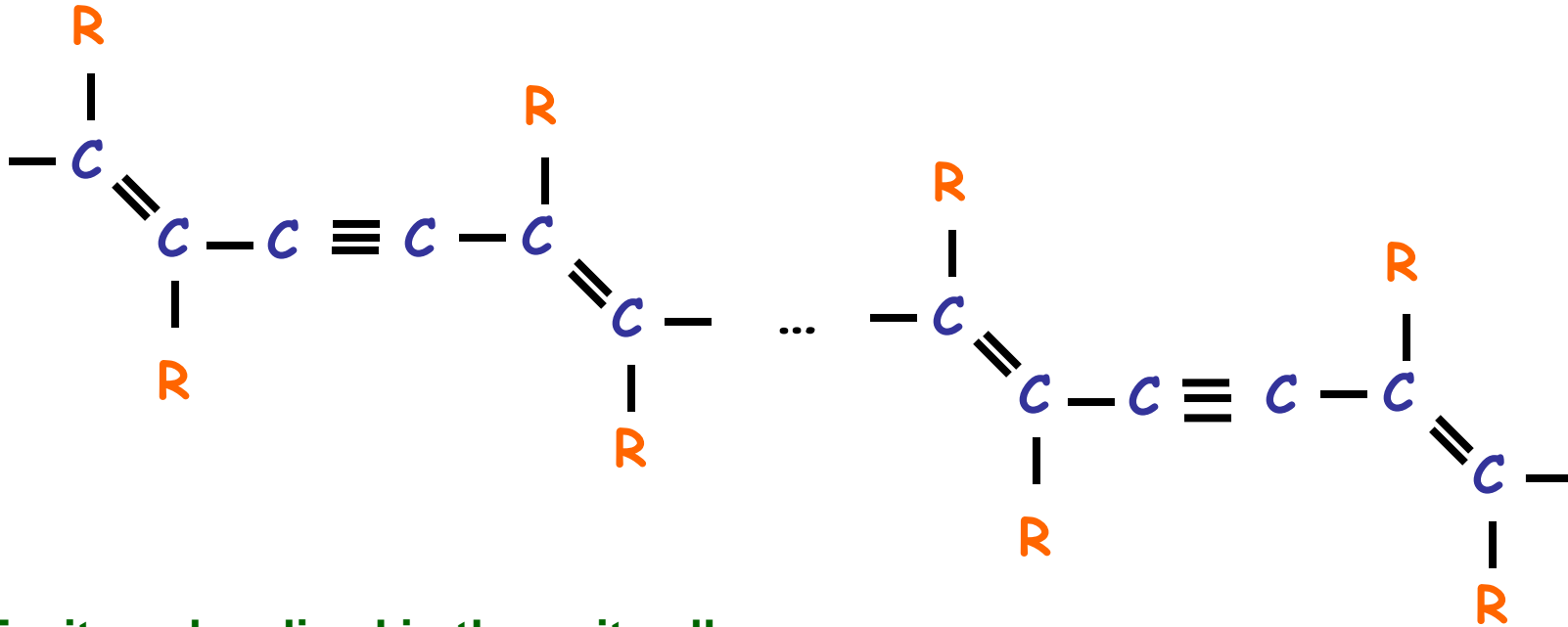


e-polaron

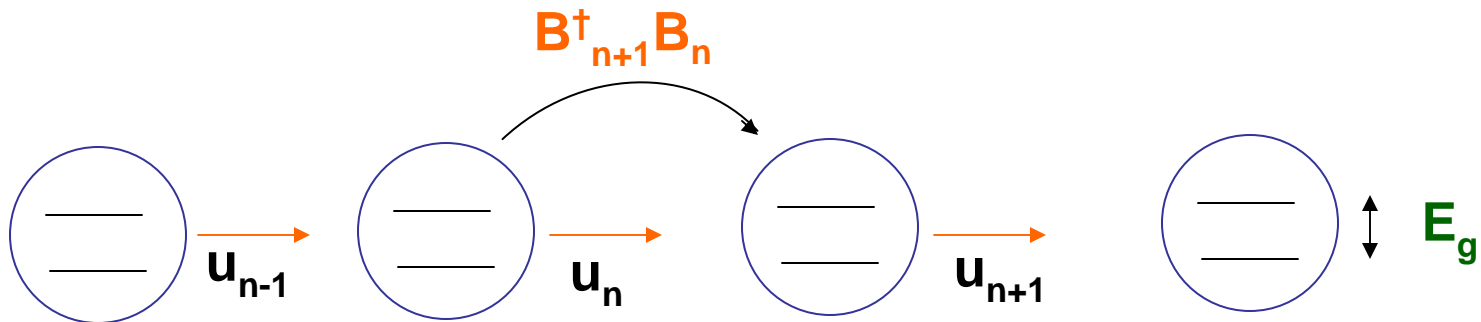


h-polaron

POLYDIACETYLENE



Excitons localized in the unit cells

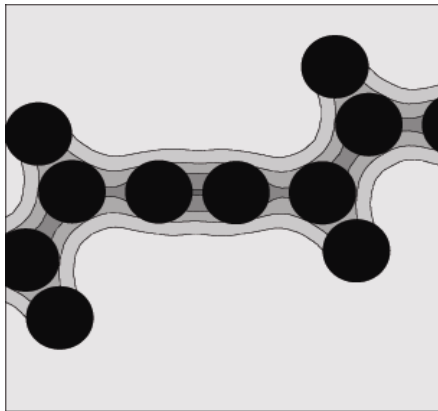


Su-Schrieffer-Heeger for excitons

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

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

DFT calculations*



Exciton propagation is described by a nonlinear Schrodinger equation

Exciton self-trapping

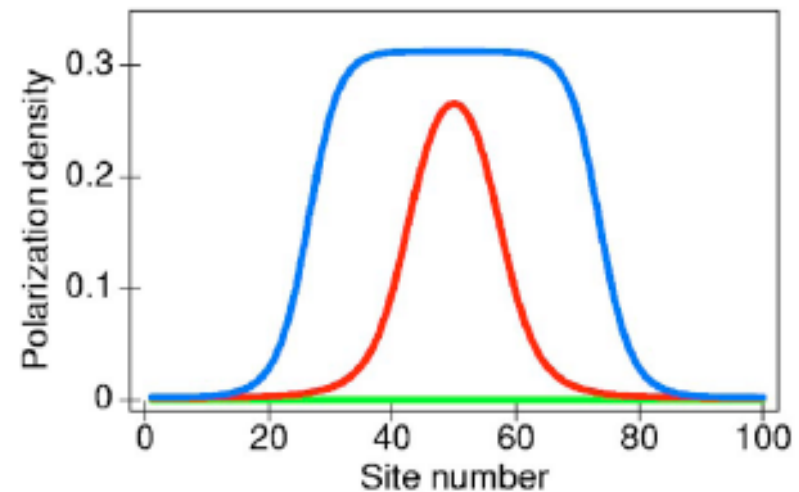


FIG. 1. (Color online) Polarization density $|\psi_n|^2$ for $\delta/t_0=0.05$, $\Omega/t_0=10^{-4}$ (green line at the bottom), $\Omega/t_0=1.99 \times 10^{-3}$ (red line in the middle), and $\Omega/t_0=2.06 \times 10^{-3}$ (blue line at the top).

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

Lattice deformation

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

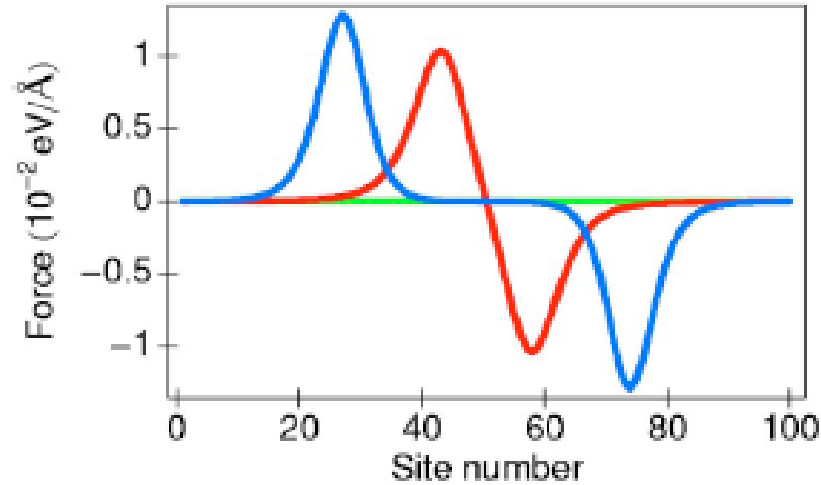


FIG. 2. (Color online) Force as a function of the site number for $\delta/t_0=0.05$, $\Omega/t_0=10^{-4}$ (green line across the middle), $\Omega/t_0=1.99 \times 10^{-3}$ (red line), and $\Omega/t_0=2.06 \times 10^{-3}$ (blue line on the left).



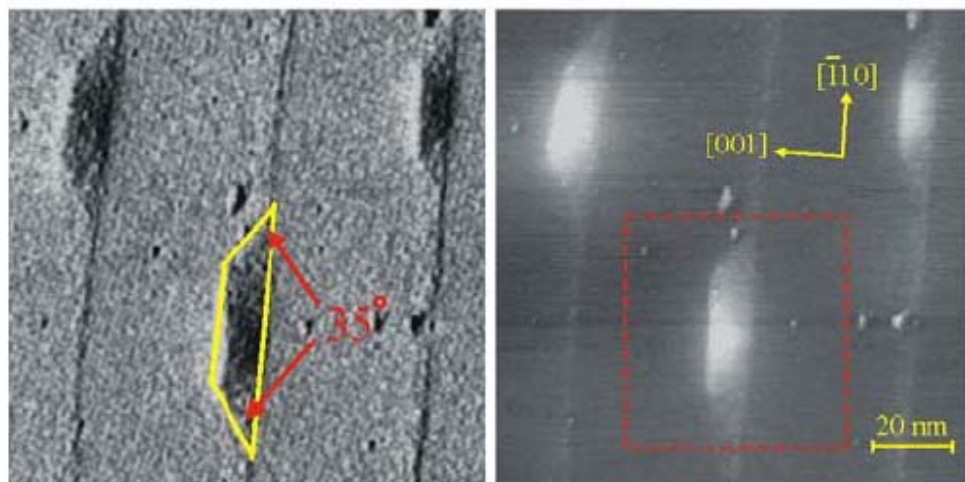
Without excitons



With excitons

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

Excitons in Quantum Dots



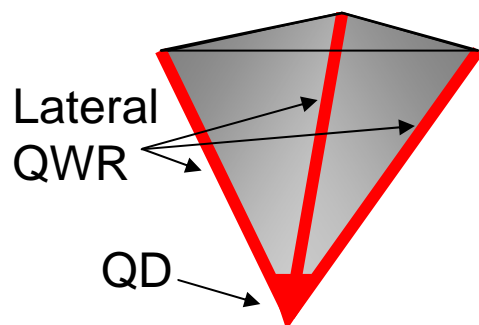
Self assembled

InAs lattice mismatch



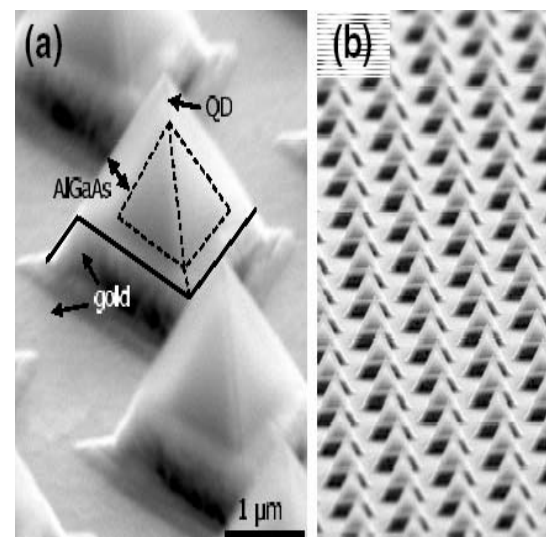
K. Shih UT Austin

Pyramidal dots



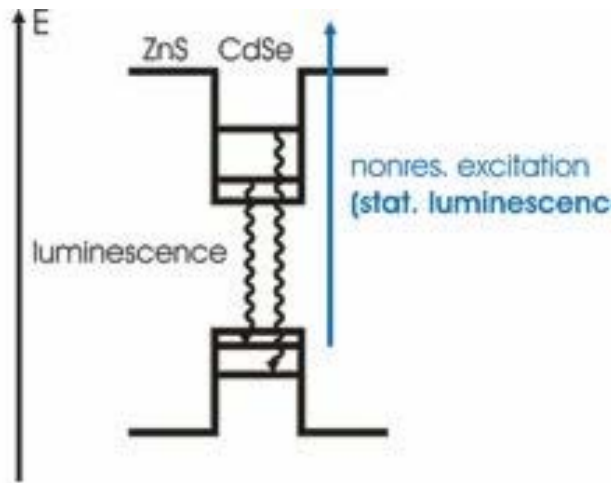
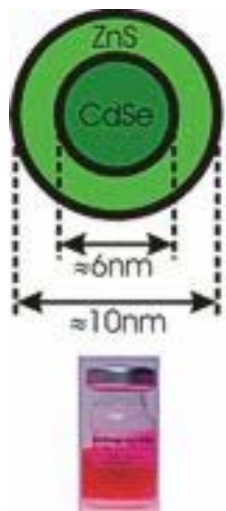
Self-limited growth
(6 nm)

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



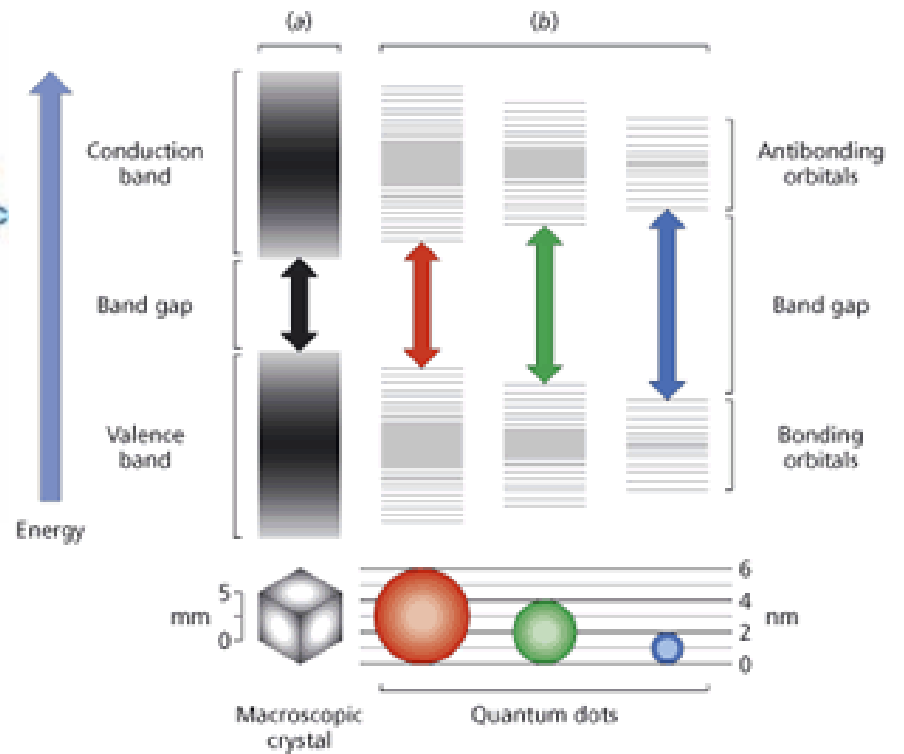
Colloidal quantum dots

Chemical synthesis



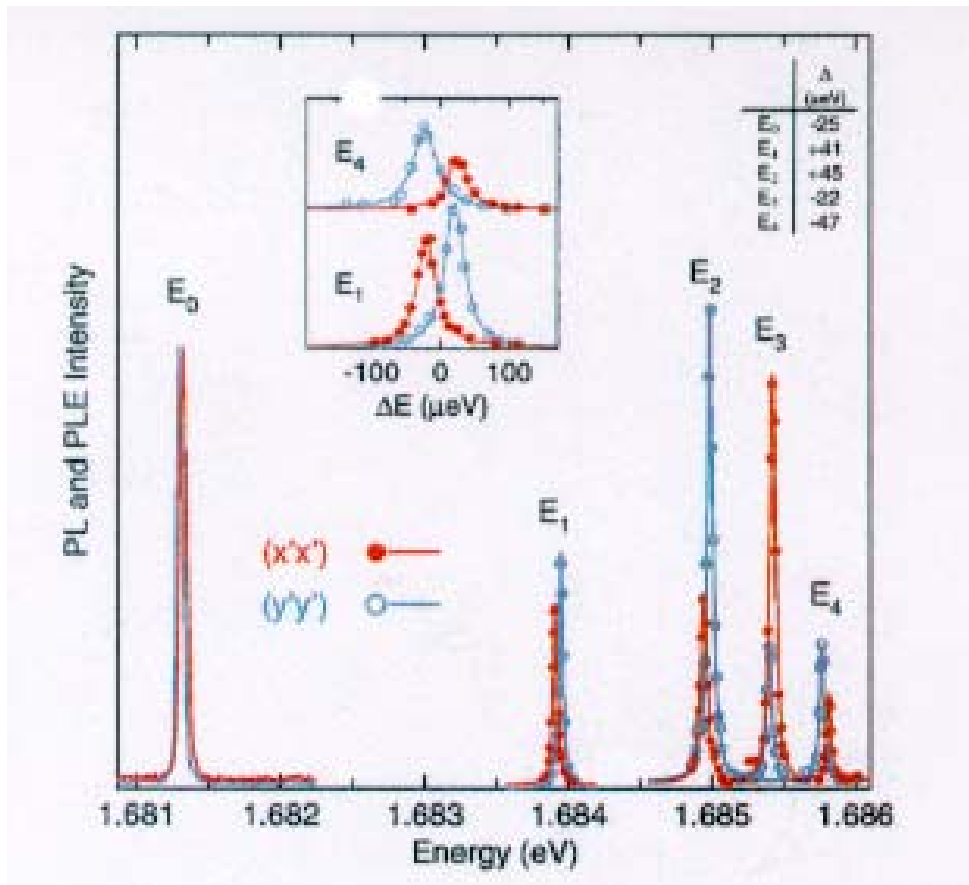
External shell

Large tunability

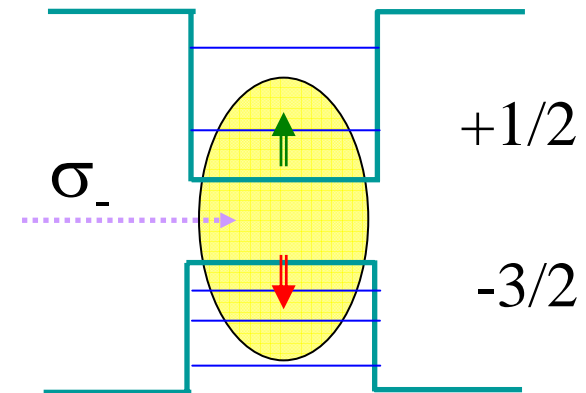


Excitons in a single QD

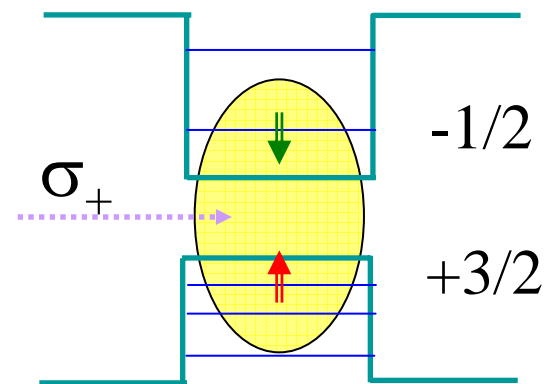
Interface fluctuation QD



D. Gammon, PRL 76,3005 (1996)



$$X_- = e^+ \uparrow h^- \downarrow |G\rangle$$



$$X_+ = e^+ \downarrow h^- \uparrow |G\rangle$$

Multiexciton States

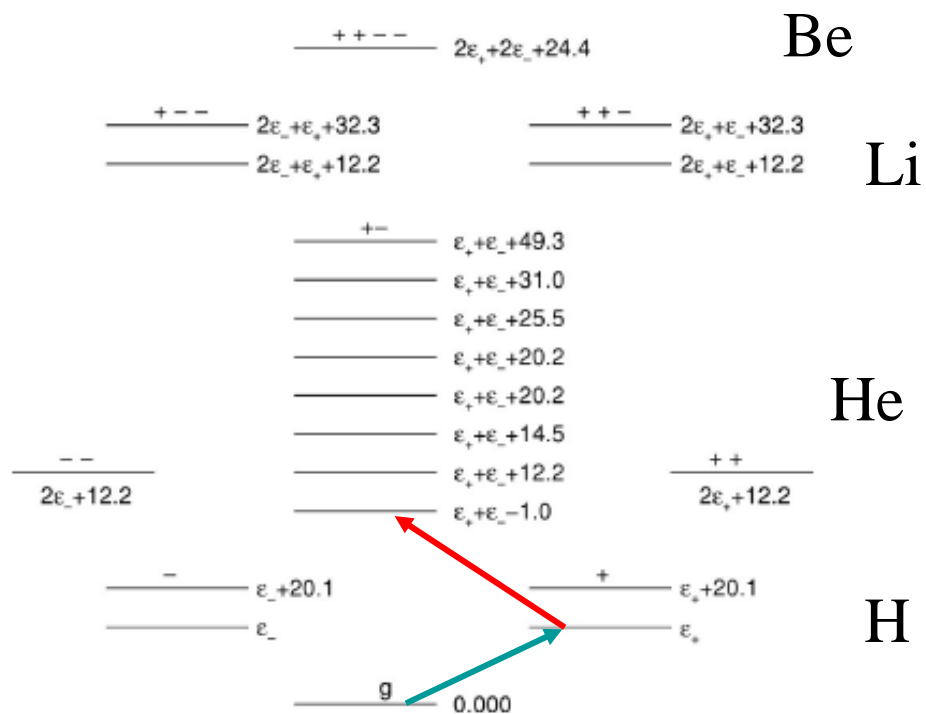
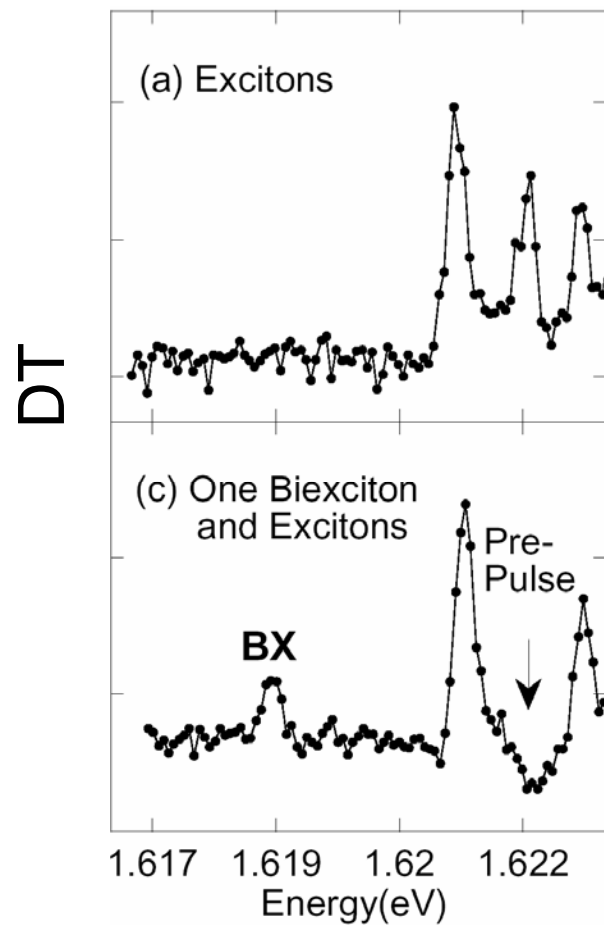


FIG. 1. Energy levels of the multiexciton states in a quantum dot in meV. $\epsilon_+ = \epsilon_- = 1764$ meV.

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

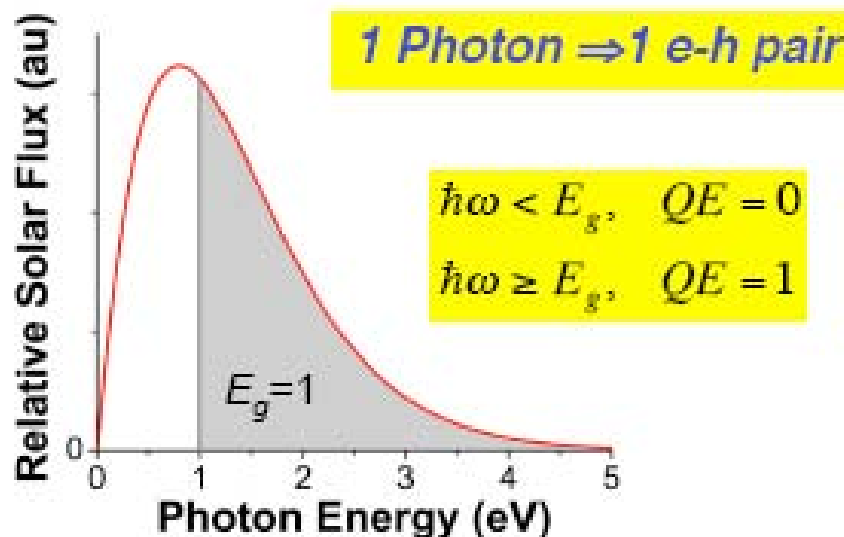
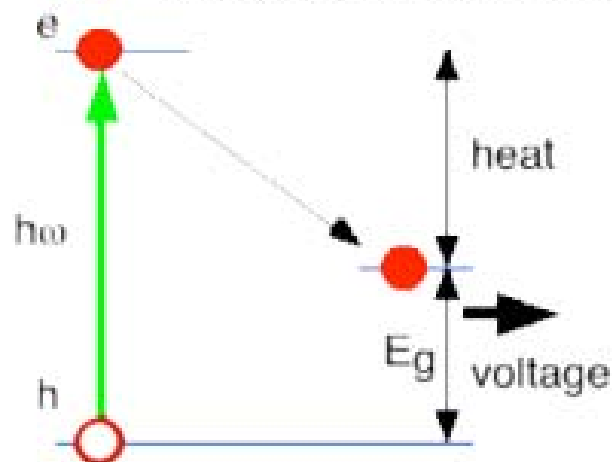
Break momentum conservation

Tunable E_g



Traditional Solar Cell: *Ultimate Efficiency*

Traditional solar cell:



"Ultimate" efficiency:

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

Total solar flux:

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

"Ultimate" QE for silicon:

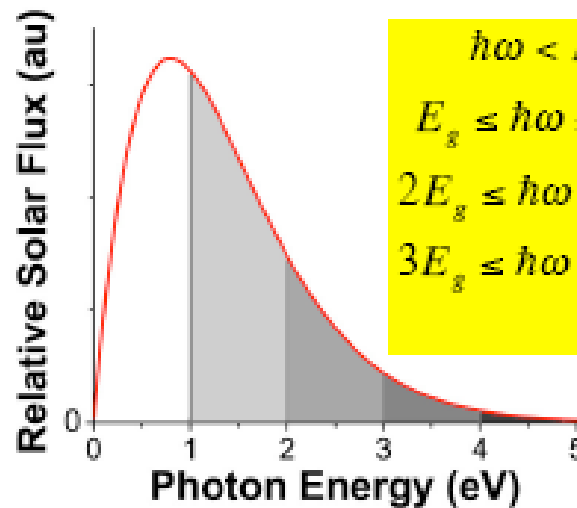
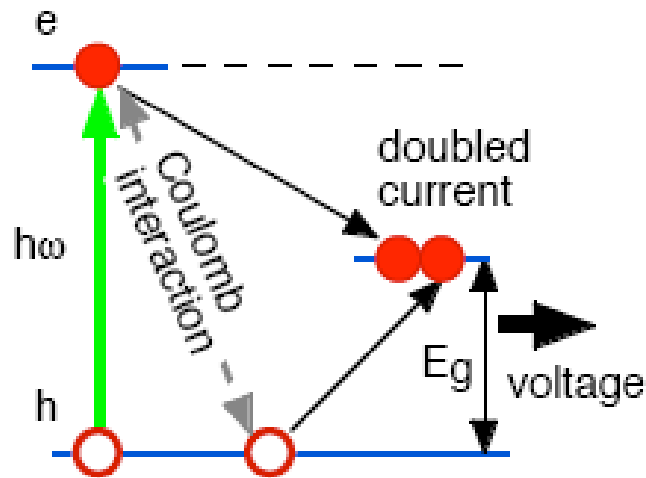
$$E_g = 1.1 \text{ eV}, \quad T_s = 6000 \text{ K}$$

$$\eta = 44\%$$

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

■ Impact-ionization-based solar cell:

1 Photon \Rightarrow 2 e-h pairs or more



$h\omega < E_g, \quad QE = 0$
 $E_g \leq h\omega \leq 2E_g, \quad QE = 1$
 $2E_g \leq h\omega \leq 3E_g, \quad QE = 2$
 $3E_g \leq h\omega \leq 4E_g, \quad QE = 3$
 ...

■ New “ultimate” efficiency:

"Ultimate" efficiency with Impact Ionization:

$$\eta = \frac{1}{\Phi_0} x_g \sum_1^{\infty} QE(i) \int_{ix_g}^{(i+1)x_g} \frac{x^2}{e^x - 1} dx,$$

$$QE(i \geq 2) = 2$$

$$E_g = 0.88 \text{ eV}, T_s = 6000 \text{ K}$$

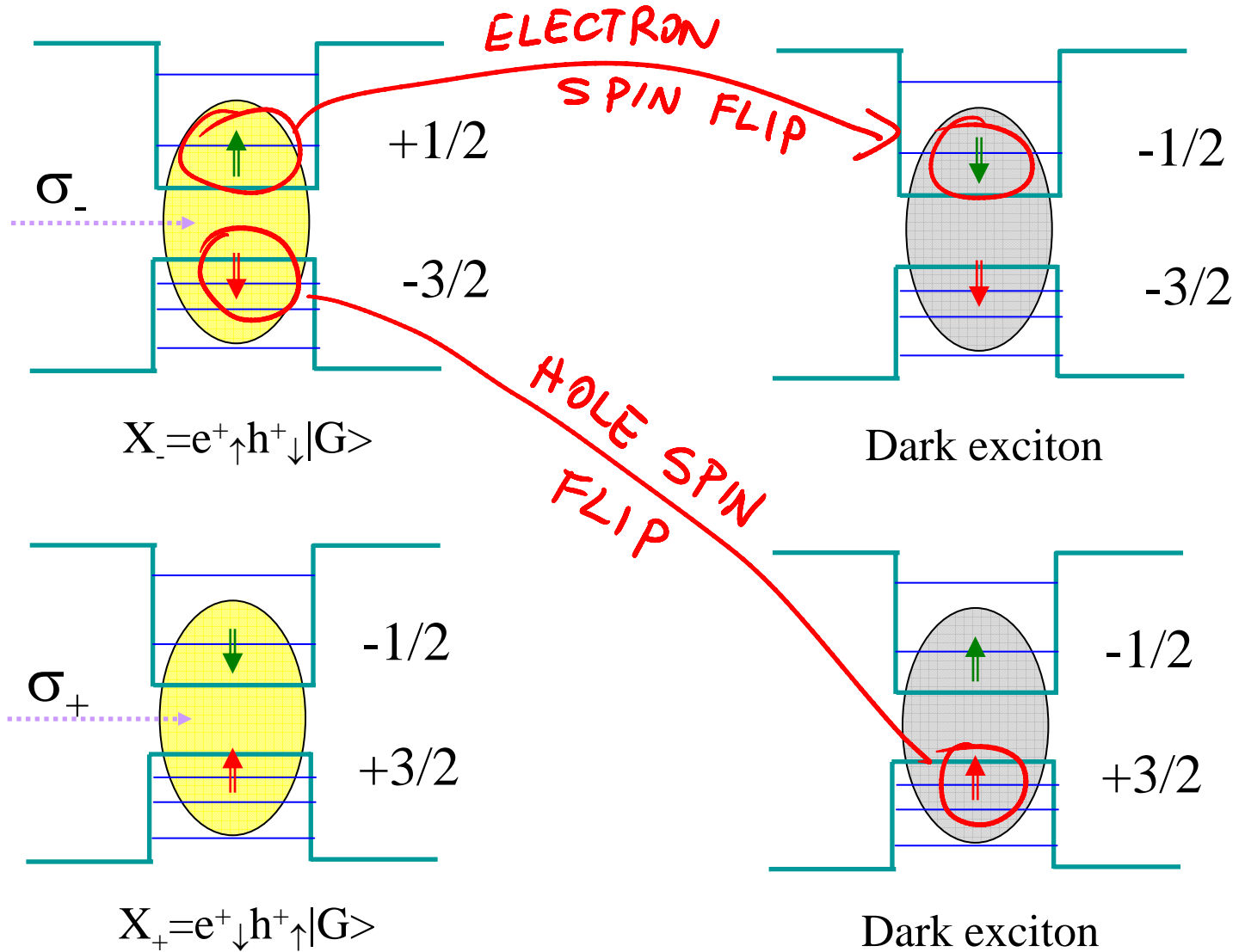
$$\eta = 60\%$$

(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 !



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

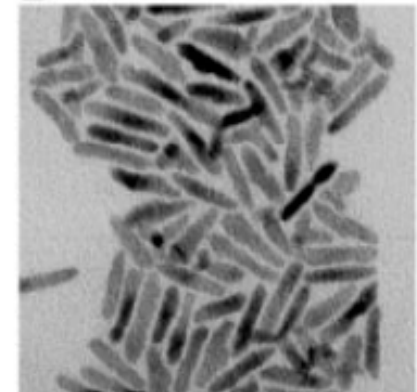
Chia-Ming Yang, Chi-Hui Wu, Hua-Hsin Liao, Kuei-Yuan Lai,
Hong-Ping Cheng, and Sheng-Fu Horng^{a)}
*Department of Electric Engineering, National Tsing Hua University, Hsinchu, 300 Taiwan,
Republic of China*

Hsin-Fei Meng
Institute of Physics, National Chiao Tung University, Hsinchu, 300 Taiwan, Republic of China

Jow-Tsong Shy
Department of Physics, National Tsing Hua University, Hsinchu, 300 Taiwan, Republic of China

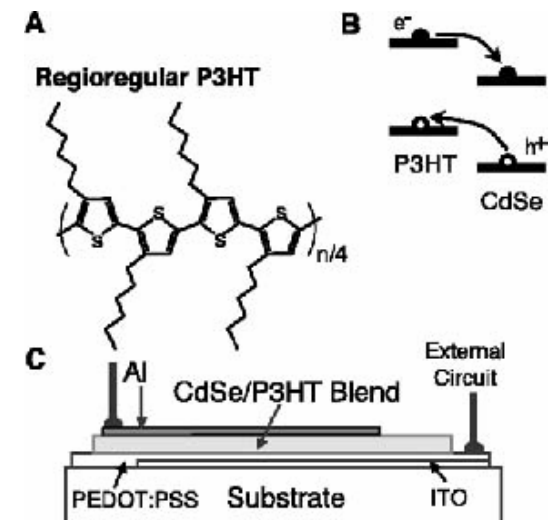
(Received 15 November 2006; accepted 18 February 2007; published online 29 March 2007)

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



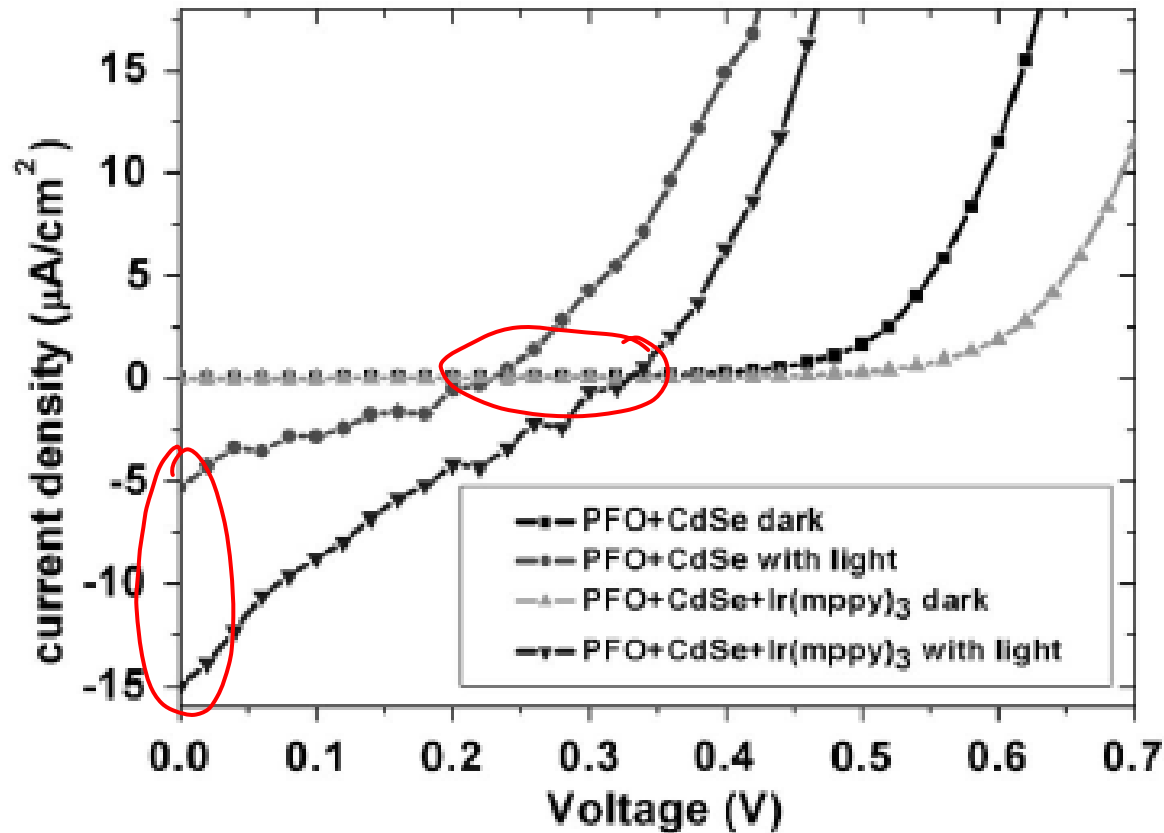


FIG. 2. Dark and photovoltaic responses of hybrid solar cells made from PFO/CdSe with and without Ir(mppy)₃, showing 200% increase in short-circuit current and 50% increase in open-circuit voltage upon doping of Ir(mppy)₃.

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

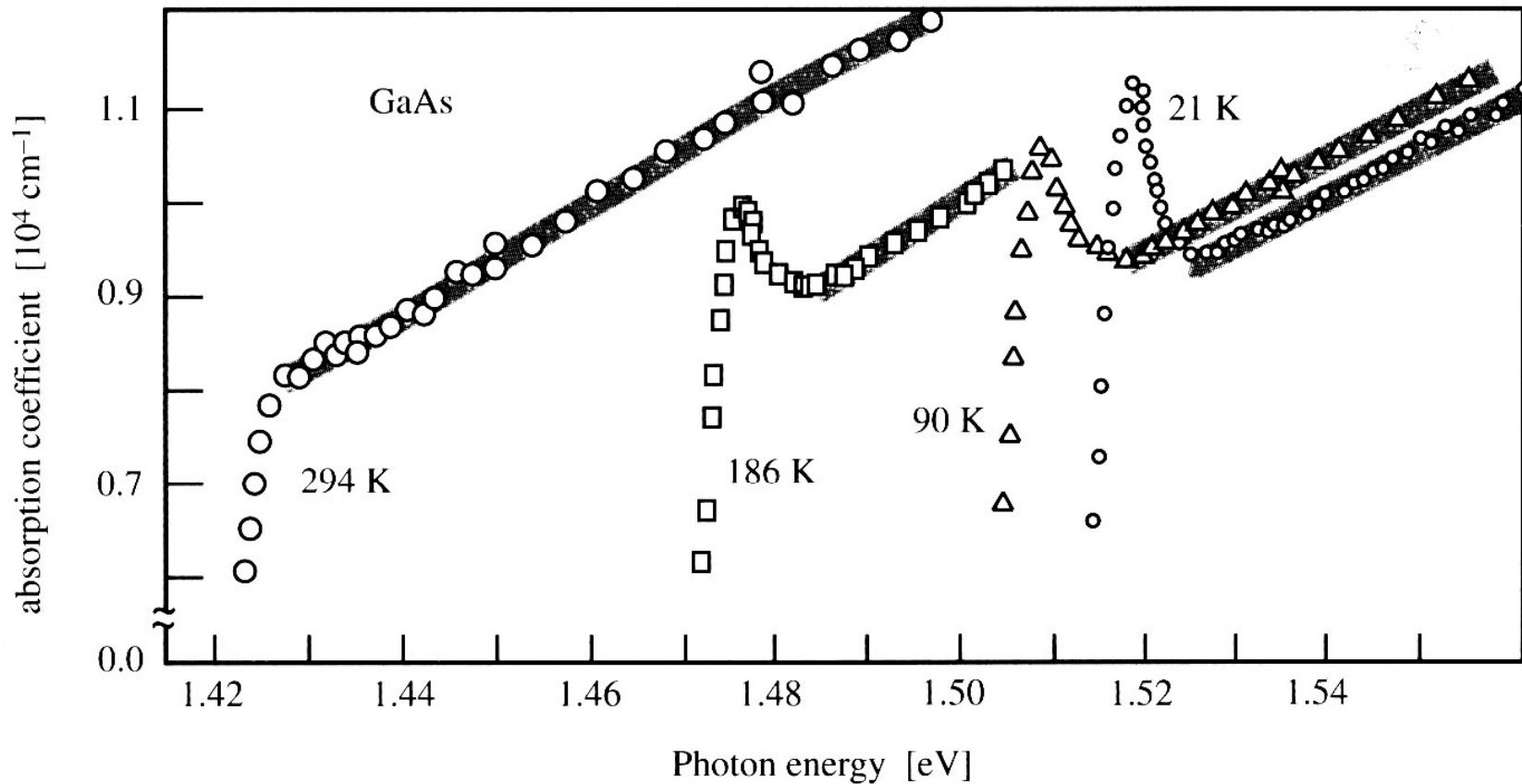


Fig. 6.25. Excitonic absorption spectra of GaAs near its bandgap for several sample temperatures. The *gray lines* drawn through the 21, 90 and 294 K data points represent fits with (6.90) [6.48]

In inorganic solar cell devices bound excitons can be neglected

Dynamics by phonon scattering can be simulated without phenomenological parameters