Carrier multiplication in quantum dots for more efficient solar cells

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Outline

Introduction

- Semiconductor nanocrystal quantum dots (QDs)
- Efficiency of solar cells, energy losses
- Carrier multiplication (CM)

Review of experimental results

- PbSe & PbS QDs
- Controversy
- Latest results

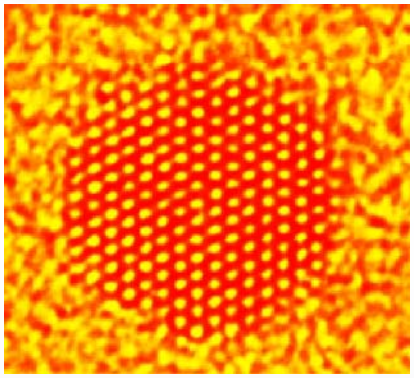
Our theoretical works

- Theory of impact ionization & CM
- Efficiency of CM in PbS nanocrystals
- Possible strategy to improve CM
- Case of α-Sn QDs

On-going works

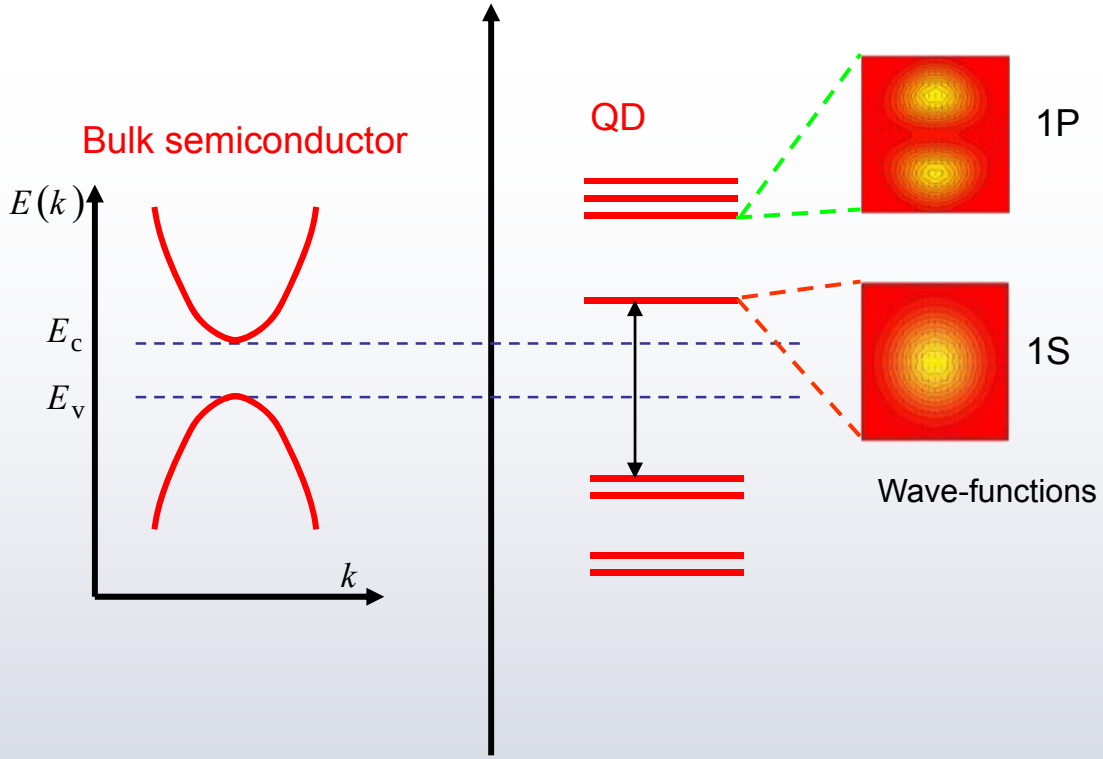
- Relaxation of carriers by emission of phonons

Semiconductor nanocrystals



CdSe Nanocrystal

Quantum dot (QD) for electrons and holes

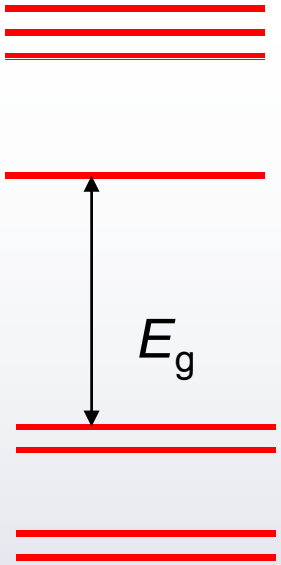


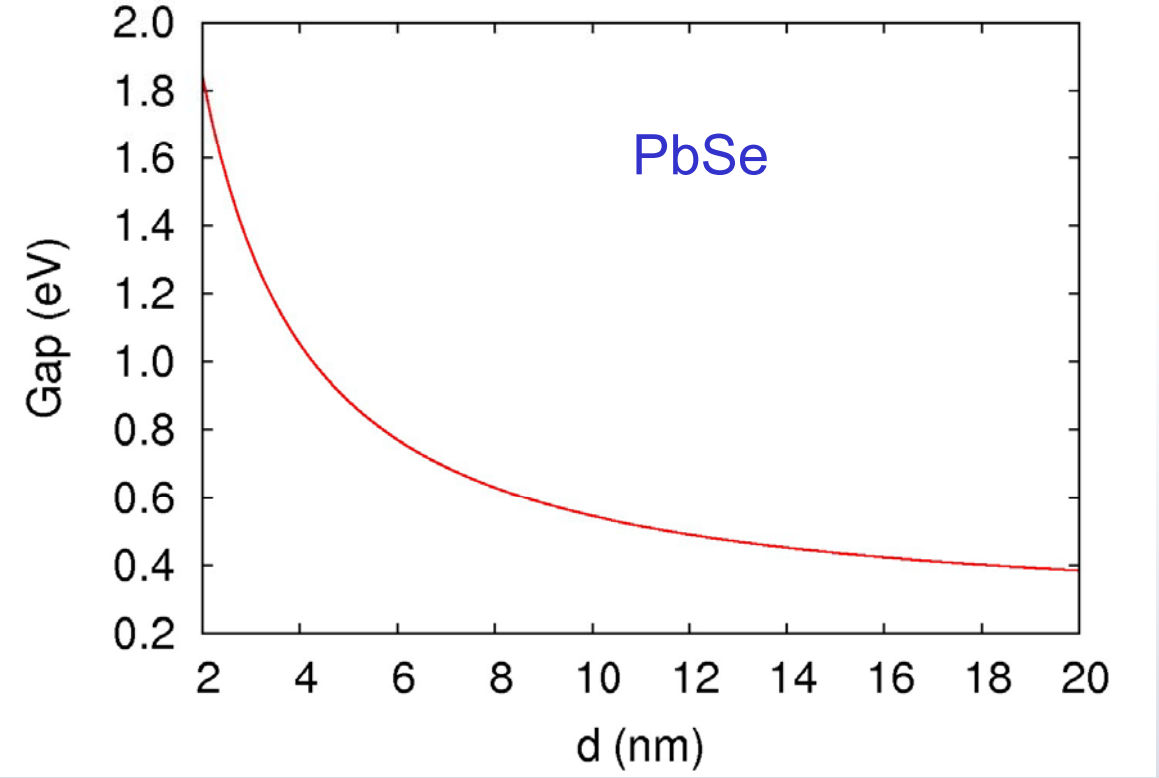
Increasing diameter

Size-dependent optical properties
Attractive materials for new generation of PV

Quantum confinement in PbSe

QD





Bulk bandgap: 0.28 eV at 300K

PV efficiency

Schockley-Queisser limit
Max theoretical efficiency of a single c-Si solar cell ~30%.

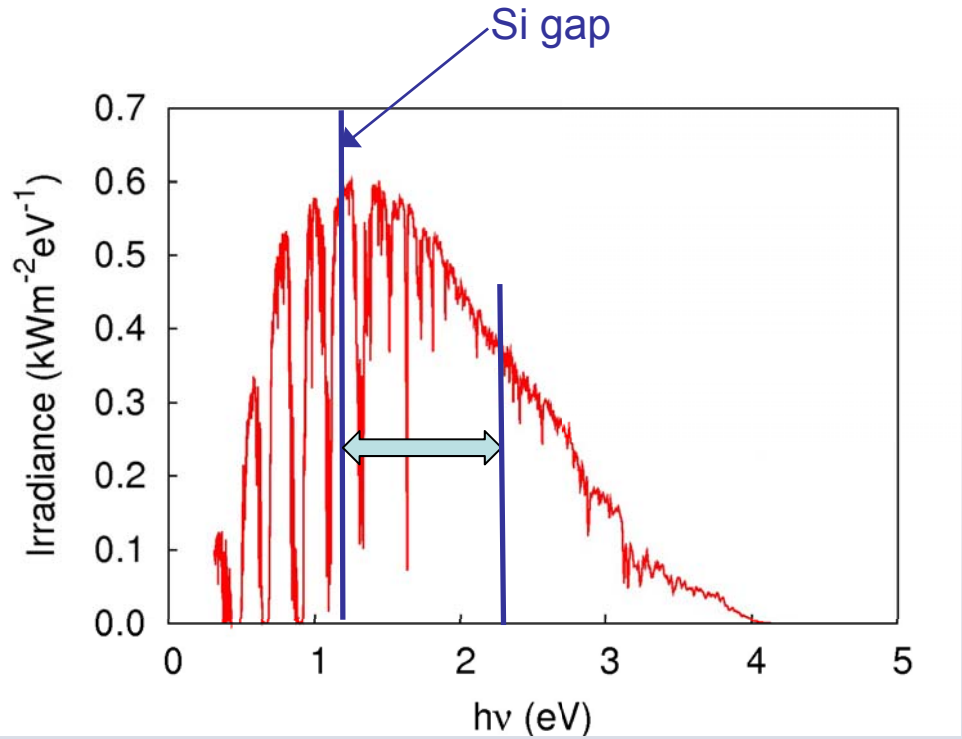
Actual c-Si solar cell efficiency : ~ 20 %

New strategies to improve PV efficiency

⇒ Carrier multiplication : fundamental physical process that could potentially improve PV efficiency

PV efficiency

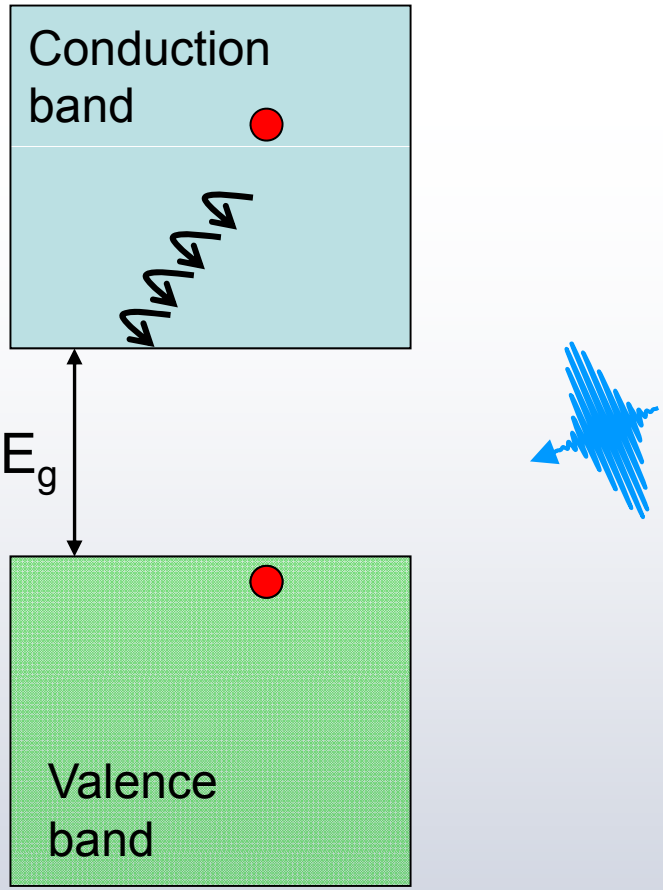
Main sources of energy loss in c-Si PV cells ?



Excess energy → heat

Multi-phonon relaxation

Carrier cooling by sequential phonon emission



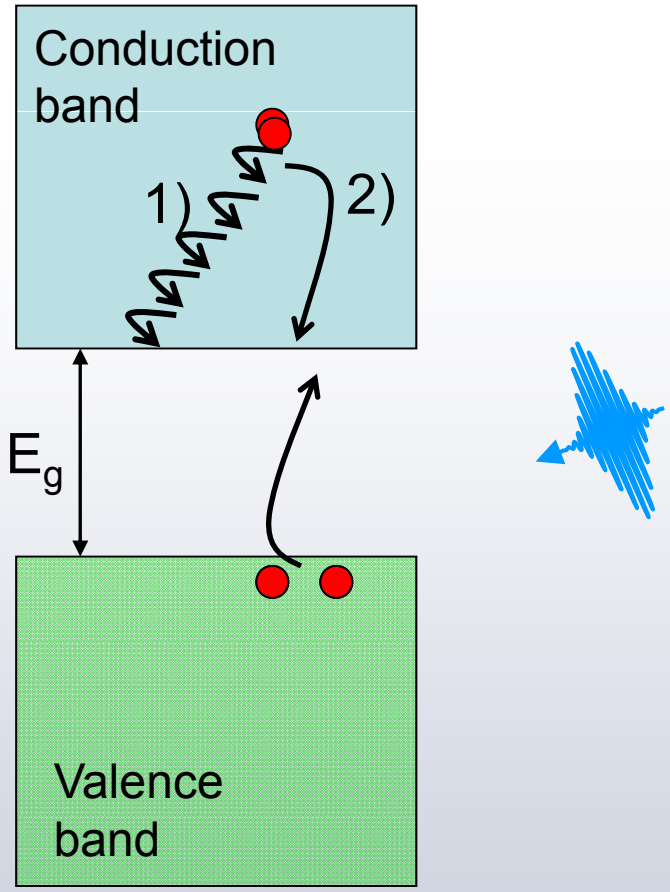
Relaxation pathways:

1) Multi-phonon → heat

Relaxation pathways:

Impact ionization → carrier multiplication

CM: generation of 2 or more e-h pairs after absorption of single photon

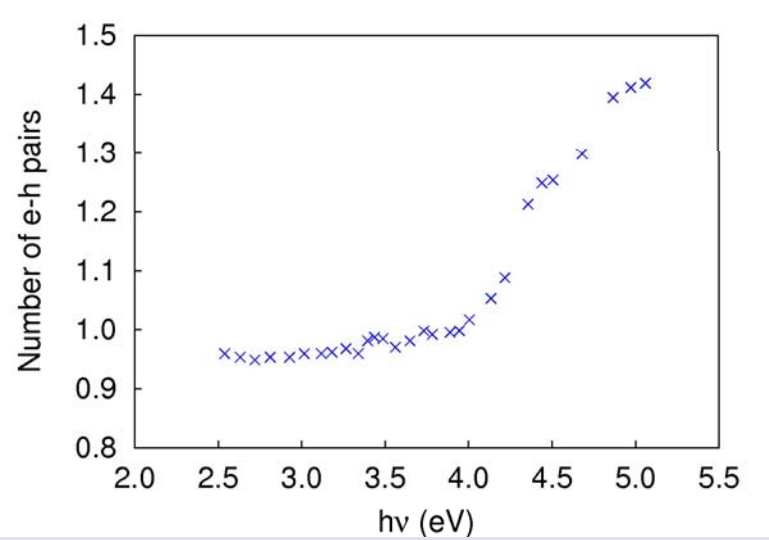


Relaxation pathways:

1) Multi-phonon → heat
2) CM → multiple e^-h^+ per photon

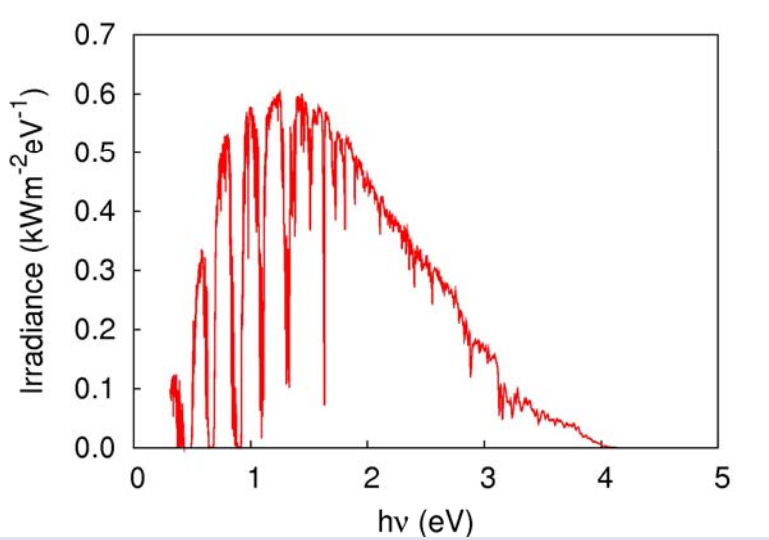
CM in bulk Si

Bulk Si: CM efficient only above the threshold at ~3.8 eV [~3.5 × E_g(Si)]



Number of photo-generated e-h pairs in bulk Si

Wolf et al, J. Appl. Phys. 1998

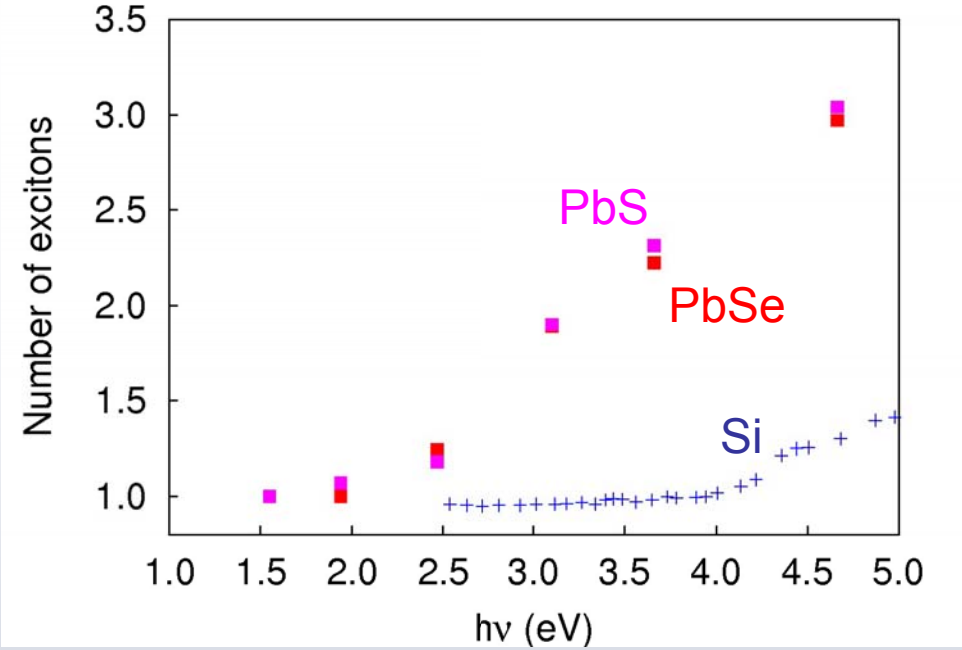


Solar spectrum

CM in bulk PbSe & PbS

Bulk PbSe & PbS: CM efficient above ~2.3 eV (much lower threshold)

but PbSe gap = 0.28 eV, PbS gap = 0.43 eV !



+ : Wolf et al, J. Appl. Phys. 1998

■ , ■ : J. J. H. Pijpers, R. Ulbricht, K.J. Tielrooij, A. Osherov, Y. Golan, C. Delerue, G. Allan & M. Bonn, Nature Physics 5, 811 (2009)

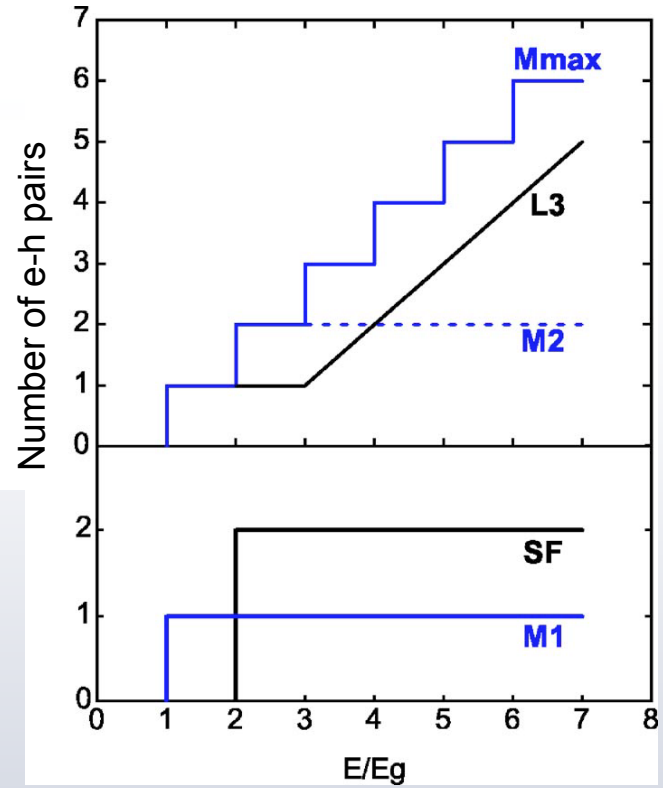
CM: best situation for PV?

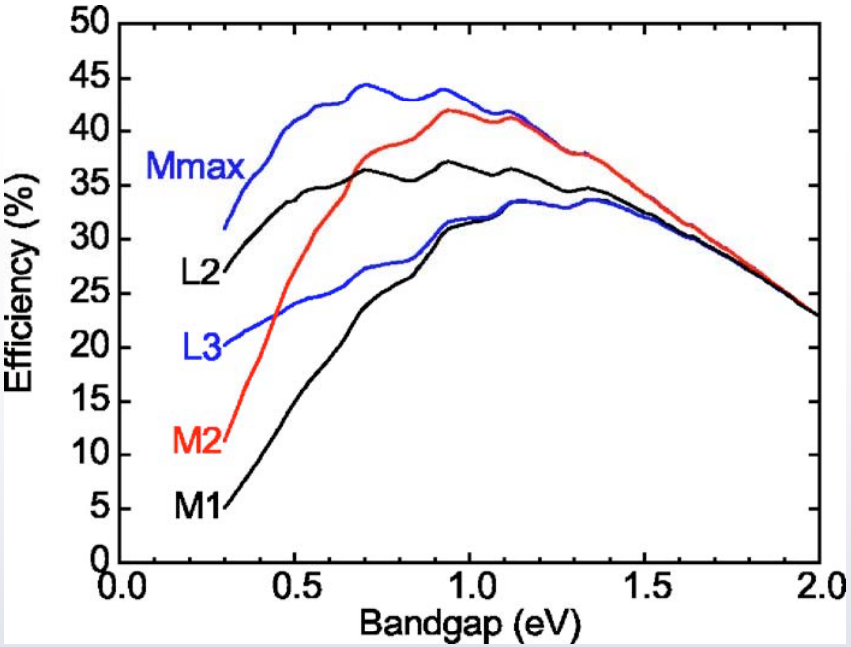
CM:
For PV, the goal (dream ?) is to find materials with:

1) The lowest threshold for CM
2) A sufficiently large gap E_g (determines the V_{oc} of the solar cell)

Constraint (energy conservation): threshold > 2 E_g

Potential impact of CM on PV efficiency ?





Maximum power conversion efficiency for single gap devices with various absorber types

Hanna & Nozik, J. Appl. Phys. 100, 074510 (2006)

Impact ionization & CM in QDs

02 : A. Nozik: CM could be enhanced in QDs

Nozik, Physica E 14, 115–120 (2002)

1) strong e-e interactions favor impact ionization
2) confinement breaks *k* conservation rules
3) less efficient multi-phonon relaxation

04 : group of V. Klimov reported efficient CM in PbSe QDs

Schaller & Klimov, Phys. Rev. Lett. 92, 186601 (2004).

Since then: many contradictory reports

CM in QDs: controversy

• InAs QDs:

CM observed:
- Klimov, Nano Lett. 7, p3469, 2007
- Pijpers/Bonn, JPC, 111, p4146, 2007

No CM:
- Pijpers/Bonn, JPC, 112, p4783, 2008
- Ben Lulu, Nano Lett. 8, p1207, 2008

• CdSe QDs:

CM observed:
- Klimov, APL 87, p253102, 2005

No CM:
- Bawendi, PRB, 76, 081304, 2007

• PbS QDs:

CM observed:
- Nozik, Nano Lett, 5, p865, 2006
- Nootz, Sargent… Phys. Rev. B 83, 155302 (2011)

No CM:
- Bawendi, PRB, 78, 125325, 2008

• PbSe QDs:

Efficient CM:
- Klimov: PRL(2004), Nano Lett. (2006), Nature Phys. (2005), APL (2005)
- Nozik: Nano Lett. (2006), JACS (2006)

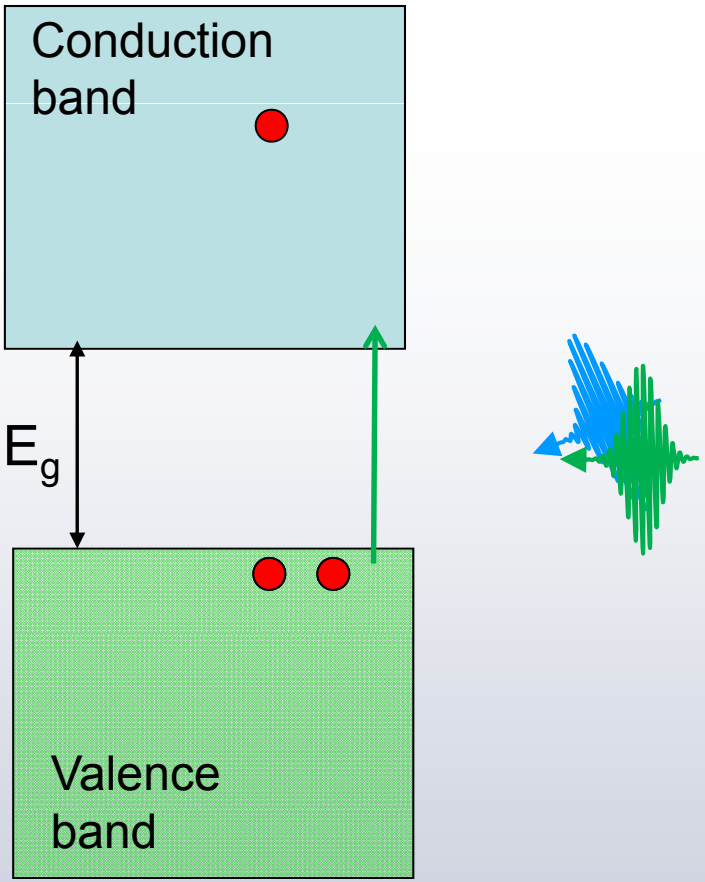
Intermediate:
- Trinh et al, Nano Lett., 8, 1713 (2008)
- Klimov, Acounts Chem. Res. (2008)
- Trinh et al, Nano Lett 11, 1623 (2011)

Weak CM:
- Bawendi, PRB, 78, 125325 (2008)

No CM:
- Bawendi, ACS Nano (2012)
- Miaja-Avila et al, Nano Lett (2012)

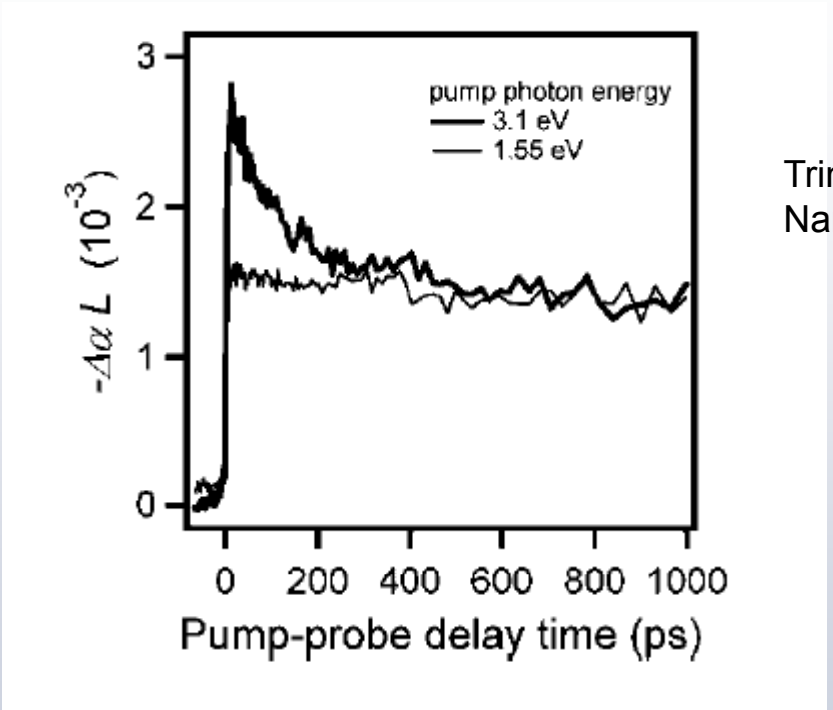
Transient absorption experiments

Pump-probe experiments



Pump-pulse-induced absorption change : $\Delta\alpha$

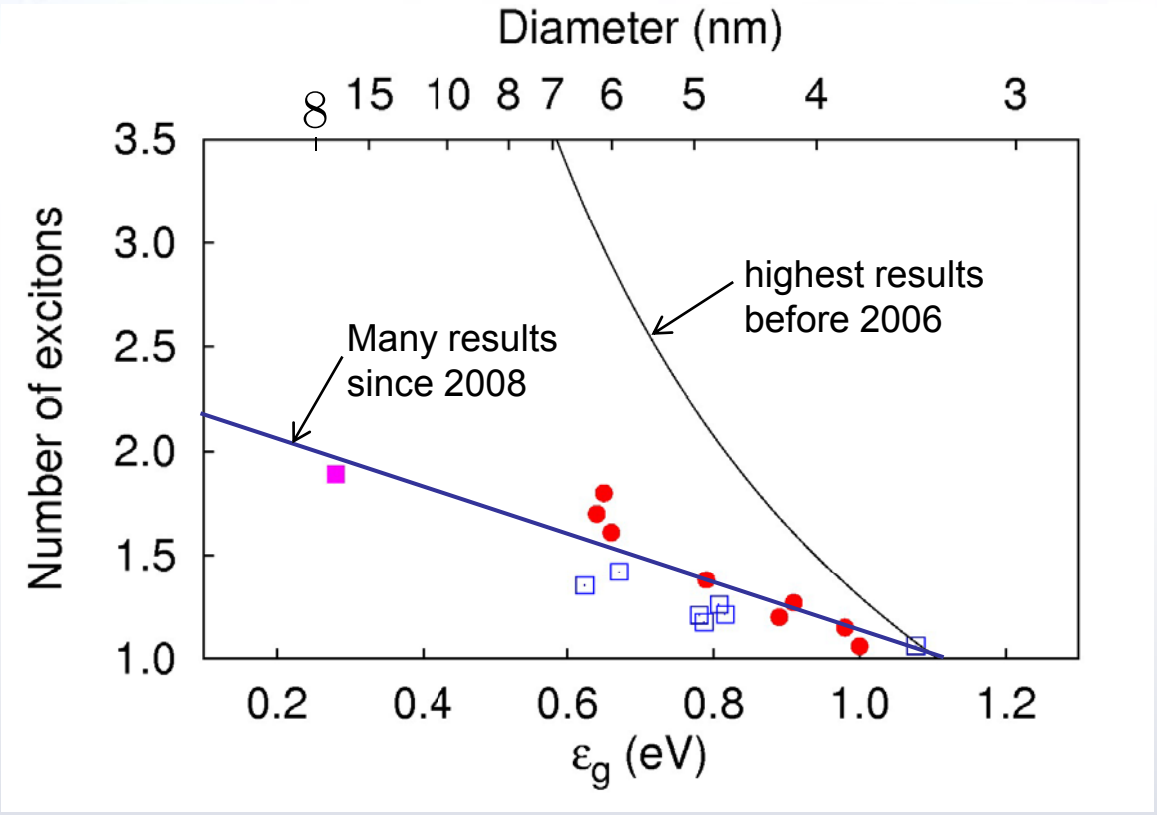
Lifetime of bi-excitons << mono-excitons



Trinh et al,
Nano Lett 08

Convergence of the latest results ?

$h\nu$ = 3.1 eV
PbSe QDs
Variable size → ε_g

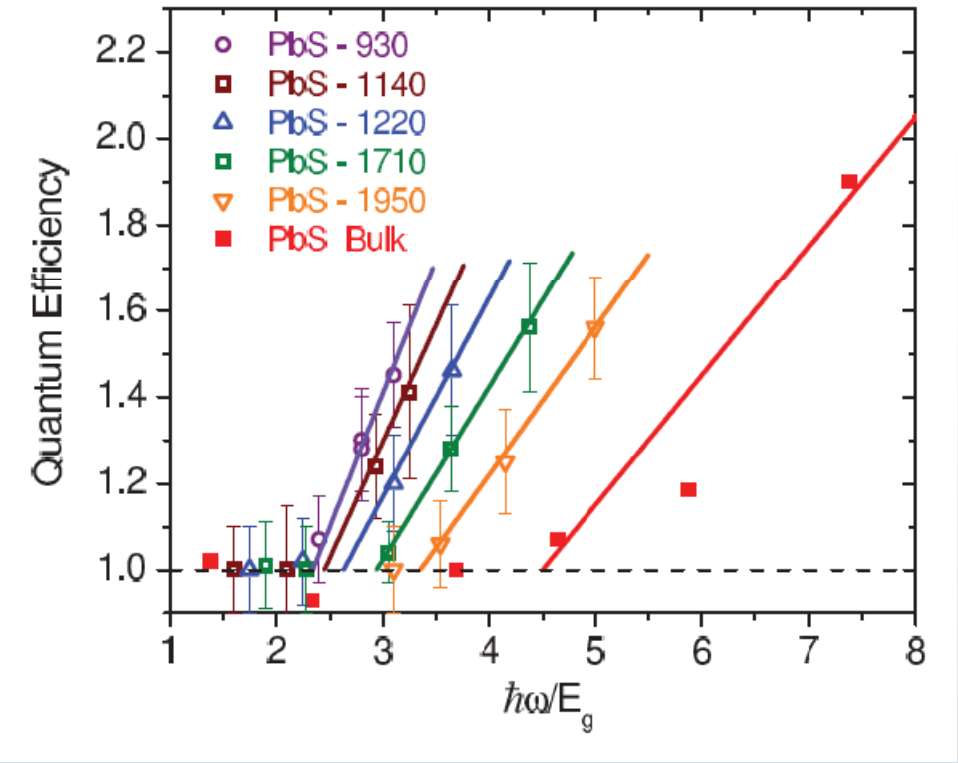


■ : J. J. H. Pijpers, R. Ulbricht, K.J. Tielrooij, A. Osherov, Y. Golan, C. Delerue, G. Allan & M. Bonn, Nature Physics (2009)
□ : John A. McGuire, Jin Joo, Jeffrey M. Pietryga, Richard D. Schaller, and Victor I. Klimov, Acc. Chem. Res. (2008)

● : M. Aerts, C.S.S. Sandeep, Y. Gao, T.J. Savenije, J.M. Schins, A.J. Houtepen, S. Kinge, and L.D.A. Siebbeles, Nano Lett (2011)
_____ : R.D. Schaller, V.M. Agranovitch, V.I. Klimov, Nature Physics (2005)

CM in PbS QDs

Recent systematic studies
CM in PbS QDs



G. Nootz et al
Phys. Rev. B 83, 155302 (2011)

Interpretation of these results ?
Impact on the power conversion efficiency ?

Theoretical description of CM

Possible approaches:

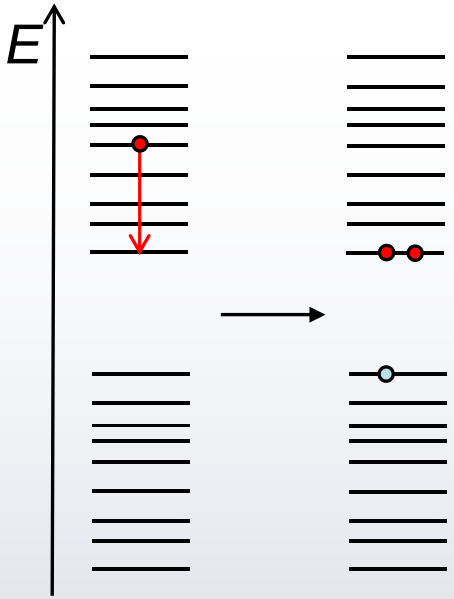
- Models (many free parameters)
- *Ab initio* Time-Domain Studies (e.g. group of O. Prezhdo, Rochester). Time-consuming, small clusters (10 atoms).

Our approach: Two steps:

1) Step 1: Calculation of the impact ionization rates
2) Step 2 : Simulation of the relaxation of the carriers $\Rightarrow$ CM

Step 1: calculation of impact ionization rates

Calculation of the impact ionization rate W versus energy E
(lifetime $\tau = 1/W$)

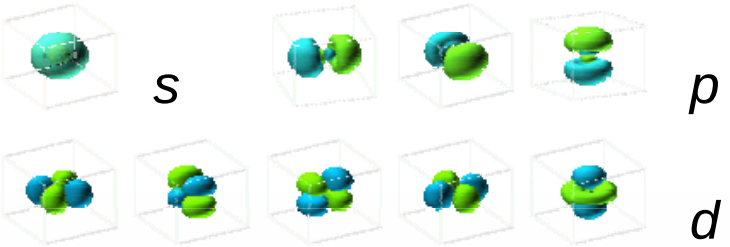


$E = 0$: top of the bulk valence band

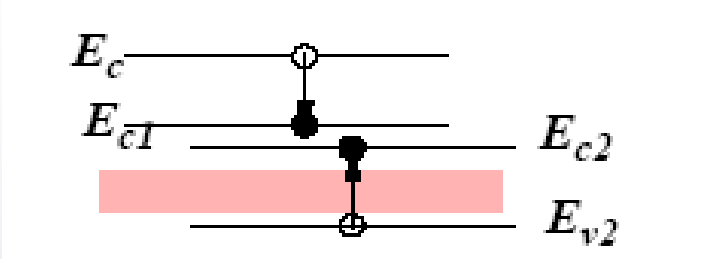
Methodology / calculations:
Electronic structure in tight-binding
Dielectric matrix in RPA
Matrix elements of the Coulomb interaction
W : Fermi golden rule

Step 1: calculation of impact ionization rates

Transition rate?



Electronic states calculated in tight binding
Calculation of the dielectric screening (RPA)
Calculation of the screened Coulomb interaction
Fermi golden rule → transition rate

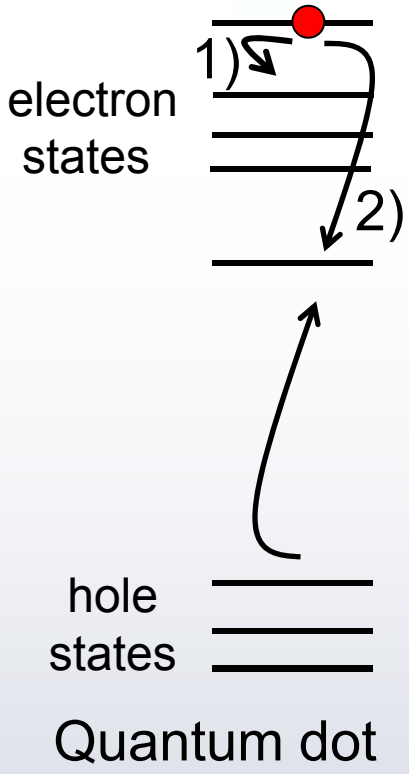


$$W = \frac{2\pi}{\hbar} \sum_{i,f} p(i) \left| \langle f | V | i \rangle \right|^2 \delta(E_f - E_i)$$

$|i\rangle, |f\rangle$: Slater determinants built on tight binding wave-functions

$$V(r,r') = \int \varepsilon^{-1}(r,r'') \frac{e^2}{|r-r'|} d^3r''$$

Step 2: simulation of the relaxation of the carriers



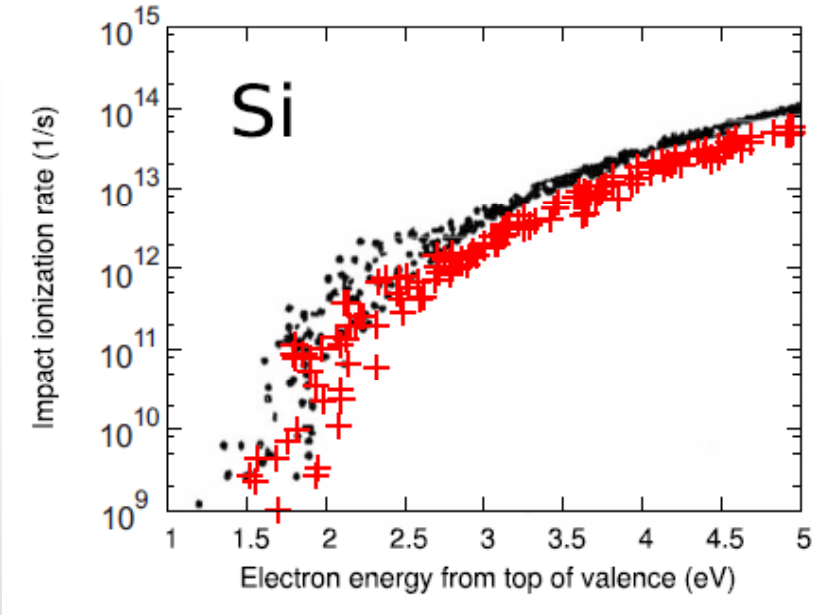
Calculation of CM efficiency

Competition between:
1) multi-phonon relaxation
2) impact ionization

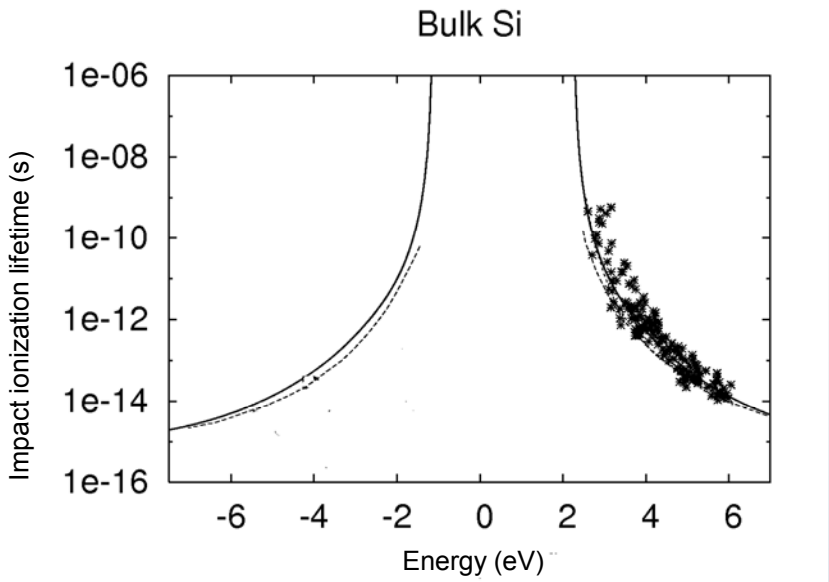
Methodology:
1) Calculation of oscillator strengths and $\alpha(h\nu)$
2) Multi-phonon relaxation: assume an energy-independent relaxation time τ_{ph}
3) Impact ionization: using calculated lifetimes
4) Numerical simulation of the relaxation

Impact ionization in bulk Si

Calculated impact ionization rates/lifetimes in bulk Si:



+ : Kotani et al, PRB 81, 125201 (2010)
• = Sano et al, JAP 75, 5102 (94)

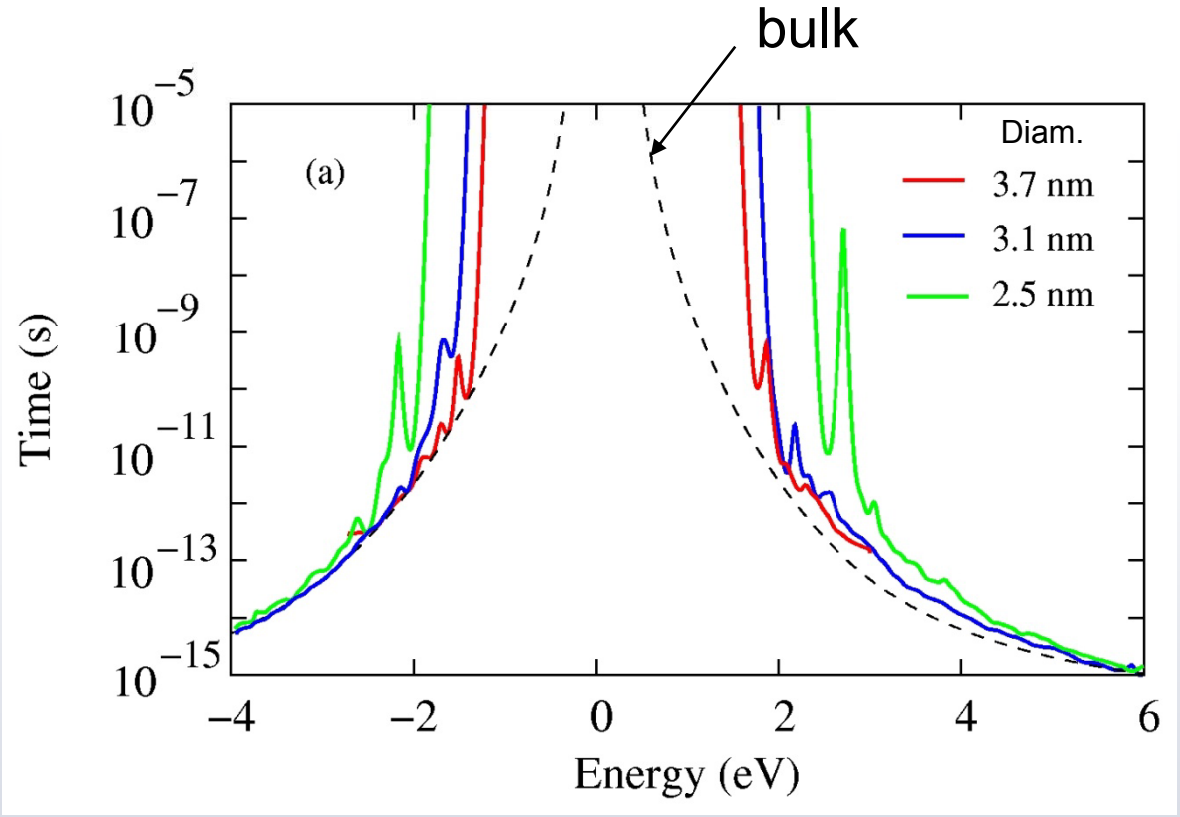


Continuous line : our calculations.
Dashed line: Sano et al, JAP (1994).
* = Kunikiyo et al, 1993

$E>0$: E_c
$E<0$: E_v

Impact ionization lifetime in PbSe QDs

$\tau = 1/W$



$E>0 : E_c$
$E<0 : E_v$

(0 = top of bulk valence band)

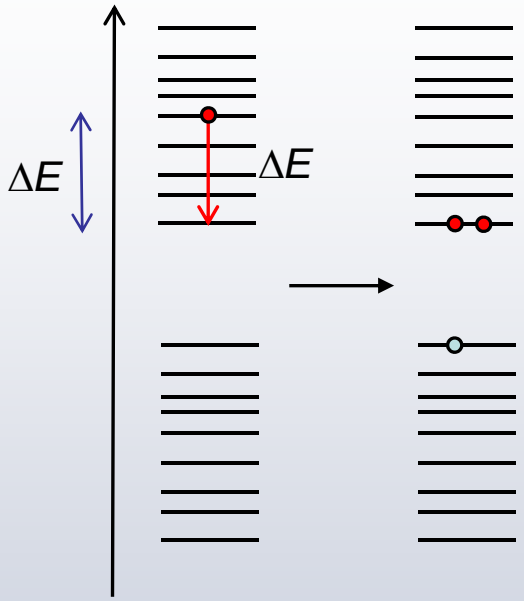
G. Allan & C. Delerue, PRB 73, 205423 (2006)

Very similar behavior in PbS, InAs, Si

Origin of the energy dependence

The variations of the impact ionization rate are mainly due to the variations of the density of final states

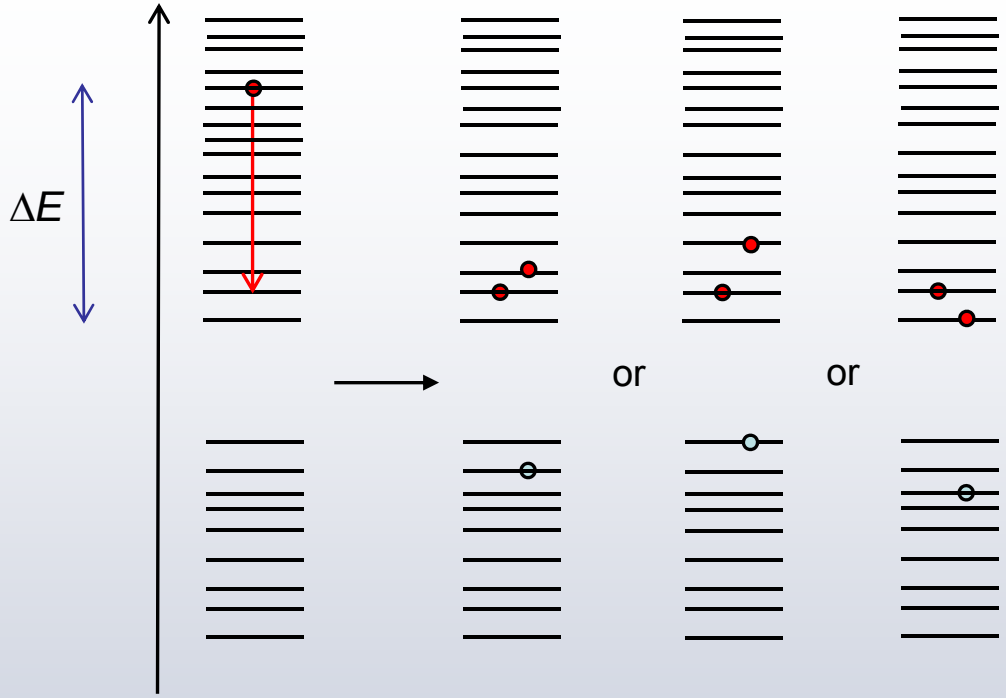
If $\Delta E = E_g$, only one final state



Origin of the energy dependence

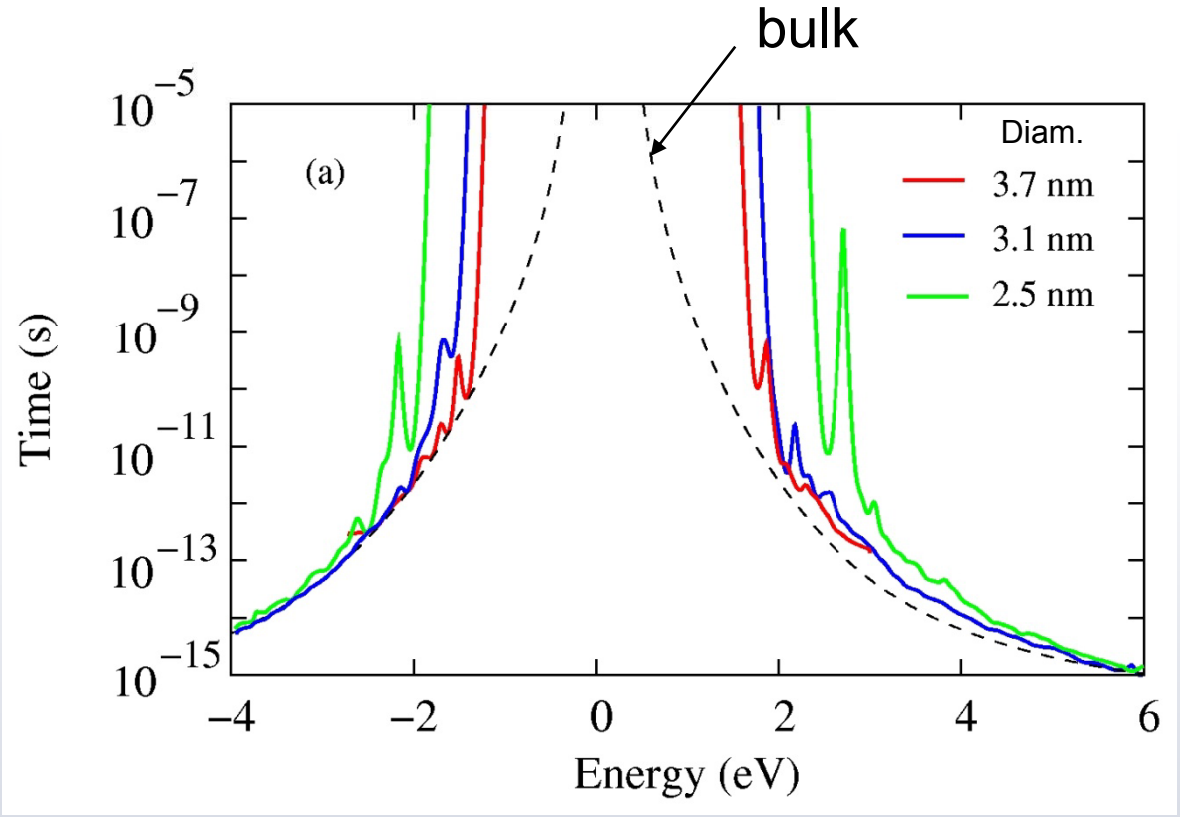
The variations of the impact ionization rate are mainly due to the variations of the density of final states

If $\Delta E >> E_g$, many final states



Impact ionization lifetime in PbSe QDs

$\tau = 1/W$



$E>0 : E_c$
$E<0 : E_v$

(0 = top of bulk valence band)

G. Allan & C. Delerue, PRB 73, 205423 (2006)

Very similar behavior in PbS, InAs, Si

Impact ionization: QD / bulk

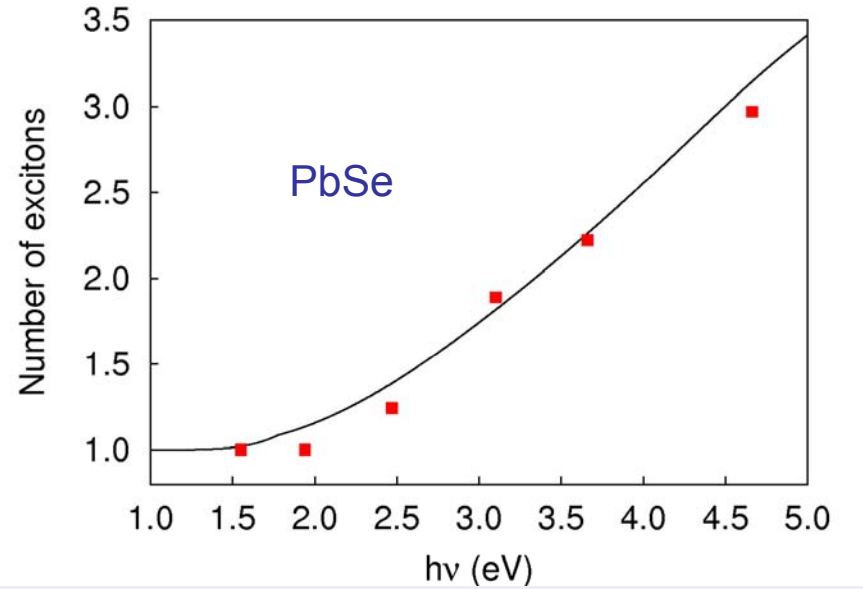
Impact ionization is less efficient in QDs than in bulk
(same efficiency at high excess energy)

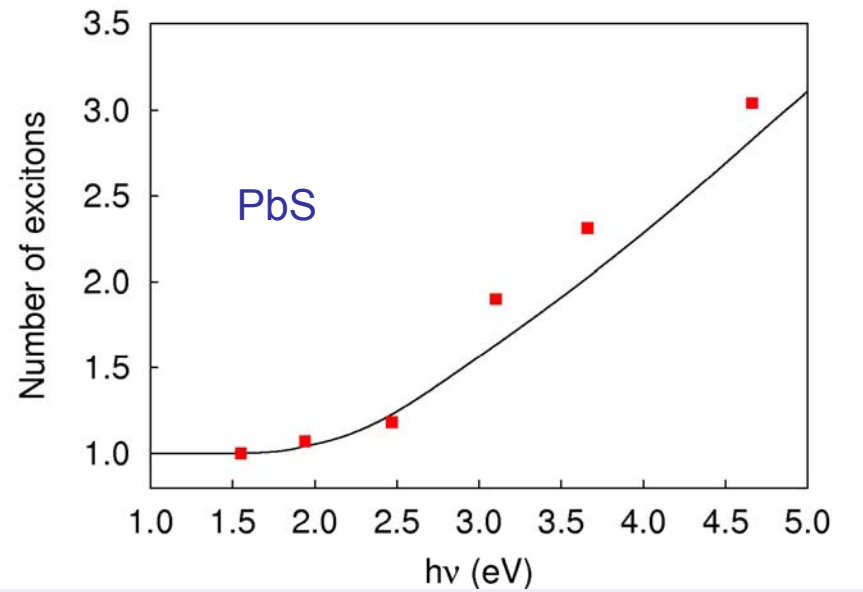
Reasons :

1) The momentum conservation rule plays no role at high excess energy.
In bulk, k conservation can be ignored.
E.O. Kane, Phys. Rev., 159 (1967)

2) The density of final states is smaller in QDs than in bulk

Calculations: case of bulk PbSe & PbS



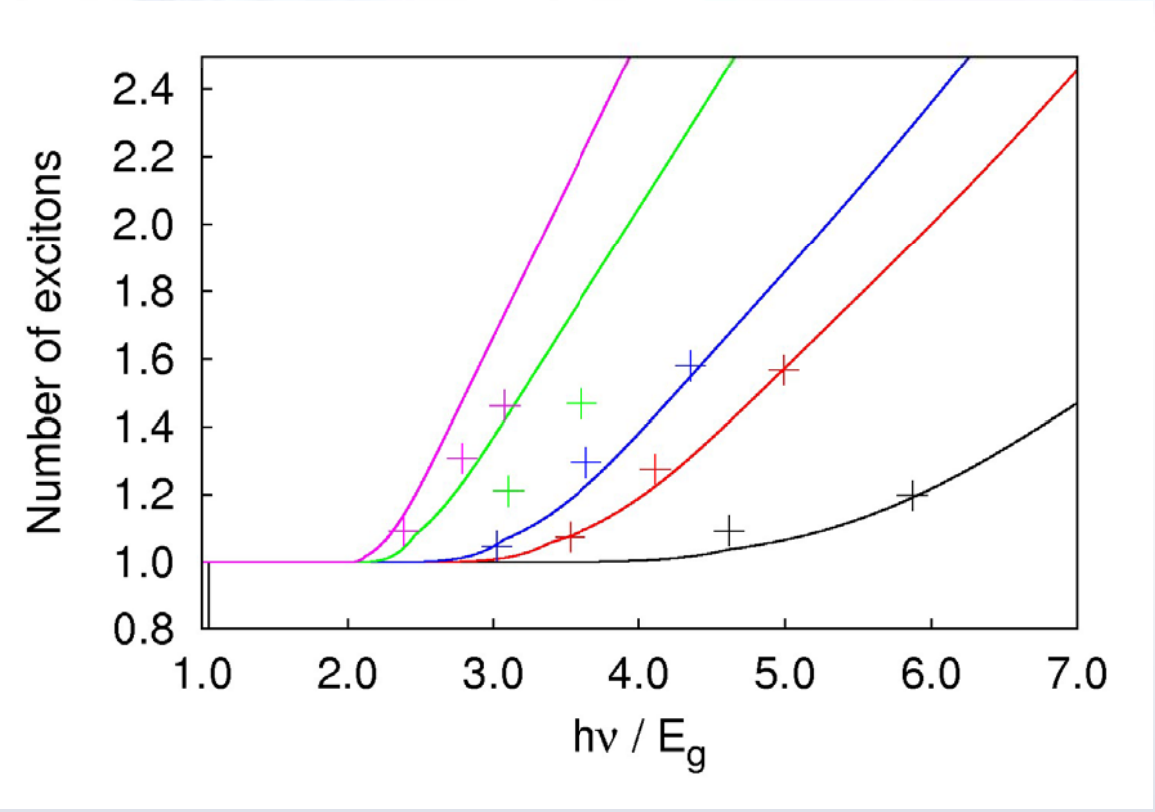


■ : experiments

_____ : theory (τ_{ph} = 0.5 ps)

J. J. H. Pijpers, R. Ulbricht, K.J. Tielrooij, A. Osherov, Y. Golan, C. Delerue, G. Allan & M. Bonn, Nature Physics (2009)

Calculations: case of PbS QDs

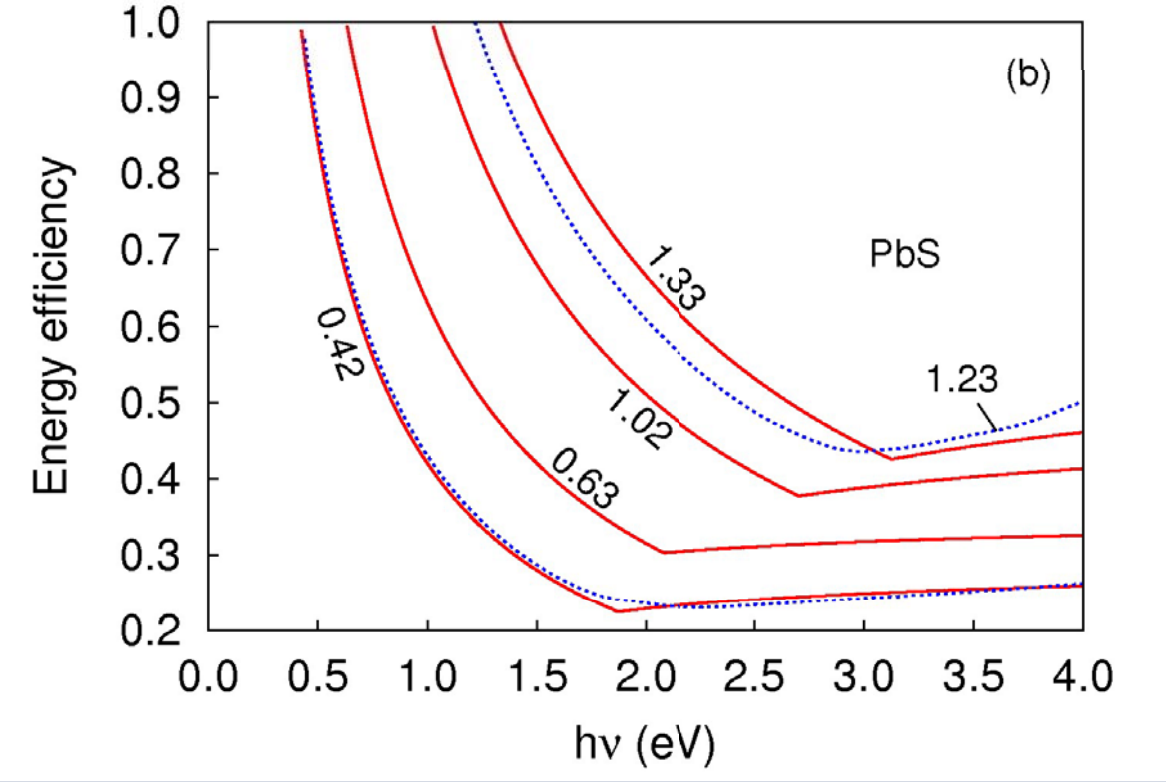


Experiments: G. Nootz et al, Phys. Rev. B 83, 155302 (2011)
+ : E_g = 0.42 eV (bulk) + : E_g = 0.63 eV
+ : E_g = 0.72 eV + : E_g = 1.02 eV
+ : E_g = 1.33 eV

Lines : theory (τ_{ph} = 0.5 ps)

PbS: energy efficiency of CM

$$\text{CM Energy efficiency} = \frac{\text{number of excitons} * \text{energy gap}}{\text{photon energy } h\nu}$$



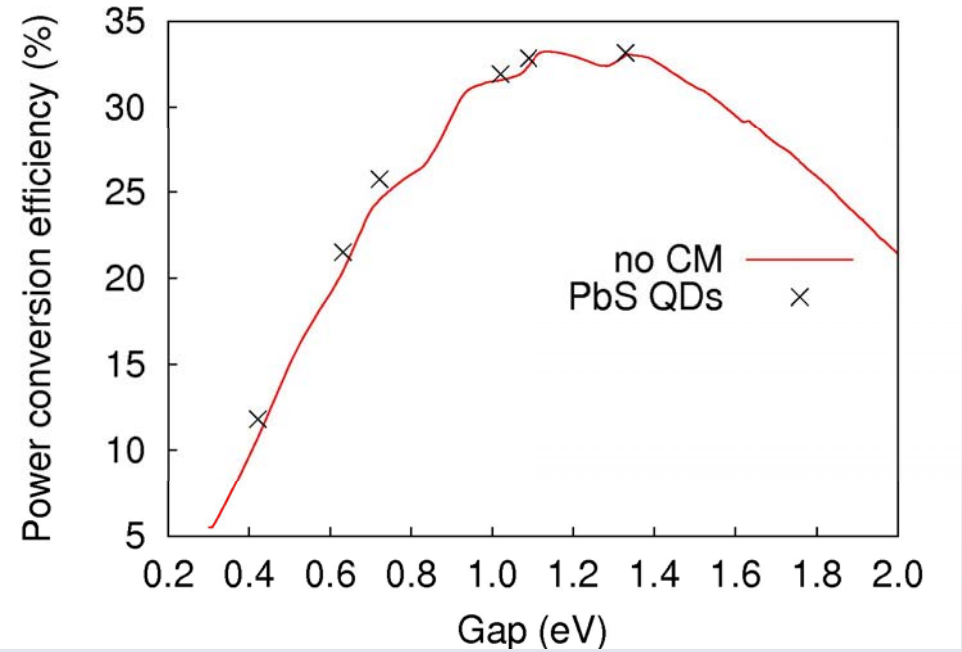
Energy efficiency versus hν for PbS QDs

_____: Experiments: G. Nootz et al, Phys. Rev. B 83, 155302 (2011)

.....: theory (τ_{ph} = 1 ps)

Max PV efficiency of PbS QD cell

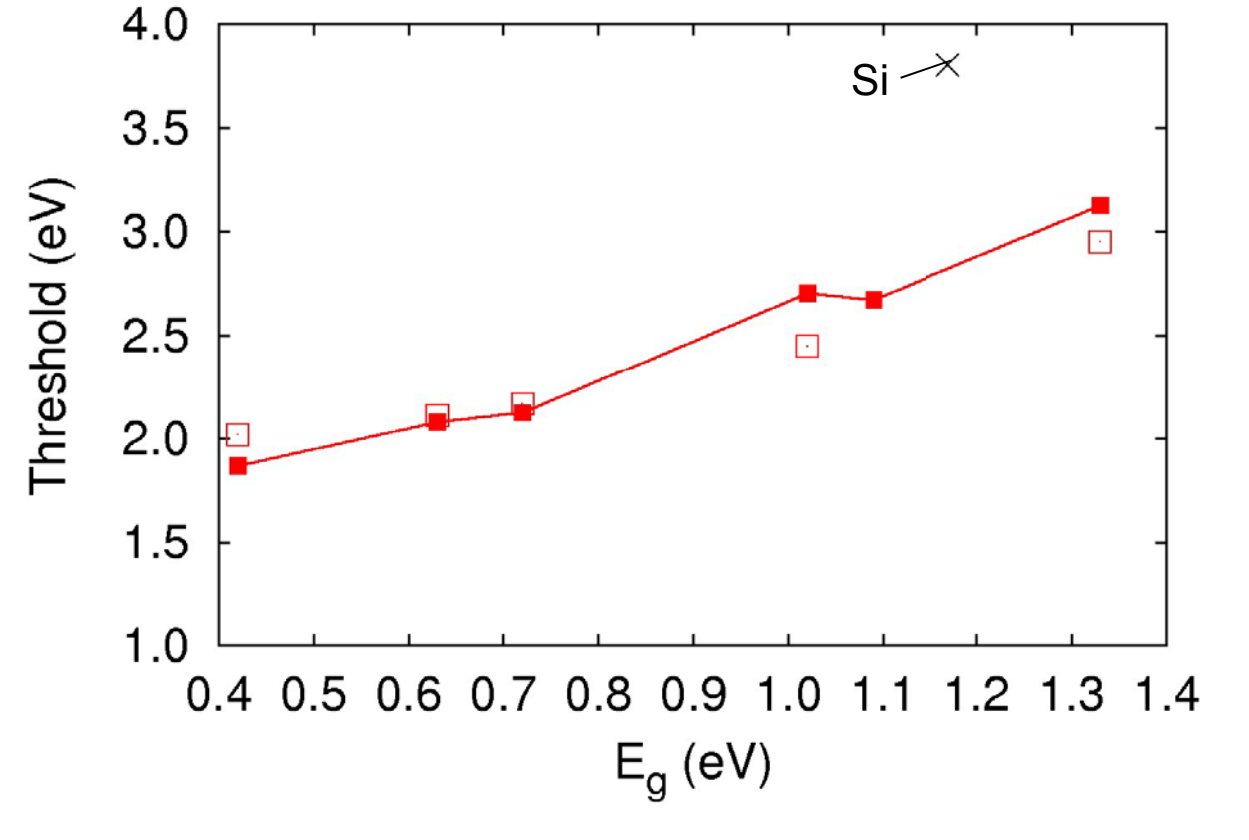
Maximum power conversion efficiency for single gap devices



Efficiency calculated from the experimental CM yields
Similar results using calculated CM yields

⇒Small impact of CM in PbS QD PV devices
(could be higher using concentrated light)

CM threshold in PbS QDs

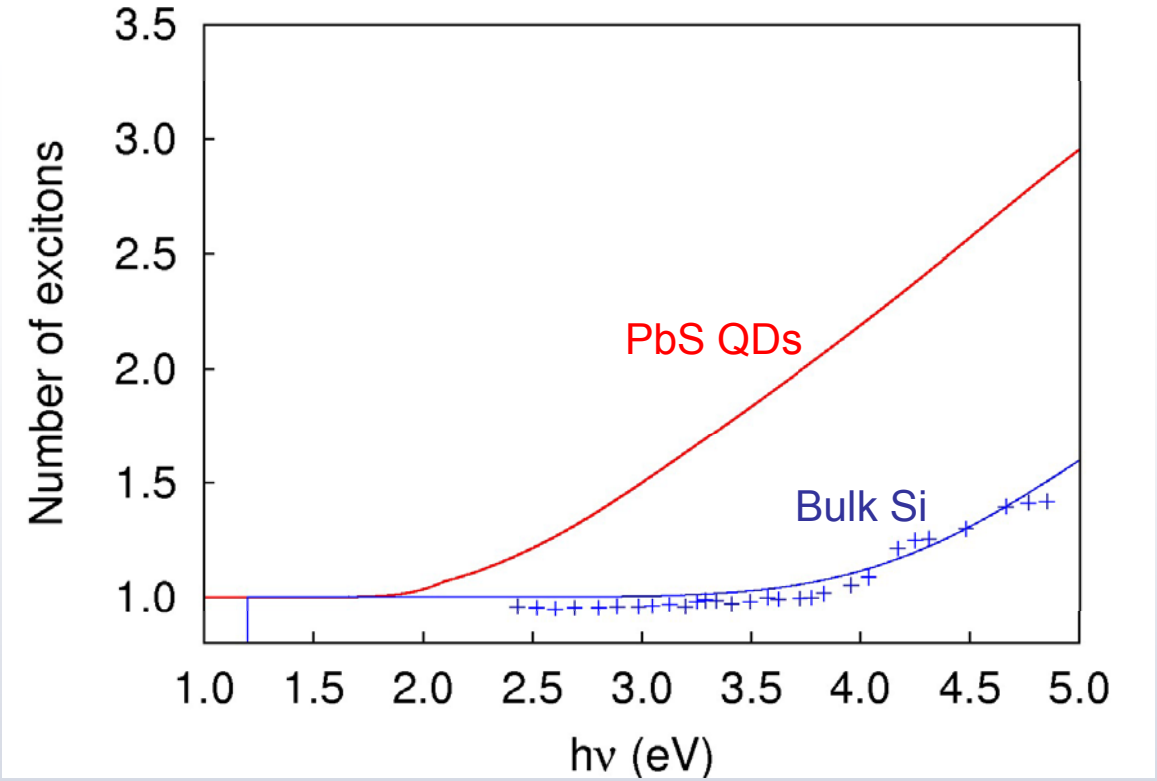


■ : experiments (Nootz et al, PRB 11)
□ : theory (τ_{ph} = 0.5 ps)

CM threshold remains too high in energy
even if it is considerably smaller than in Si

CM yield: Si bulk / PbS QDs

Comparison : PbS QDs / bulk Si (gap = 1.2 eV)

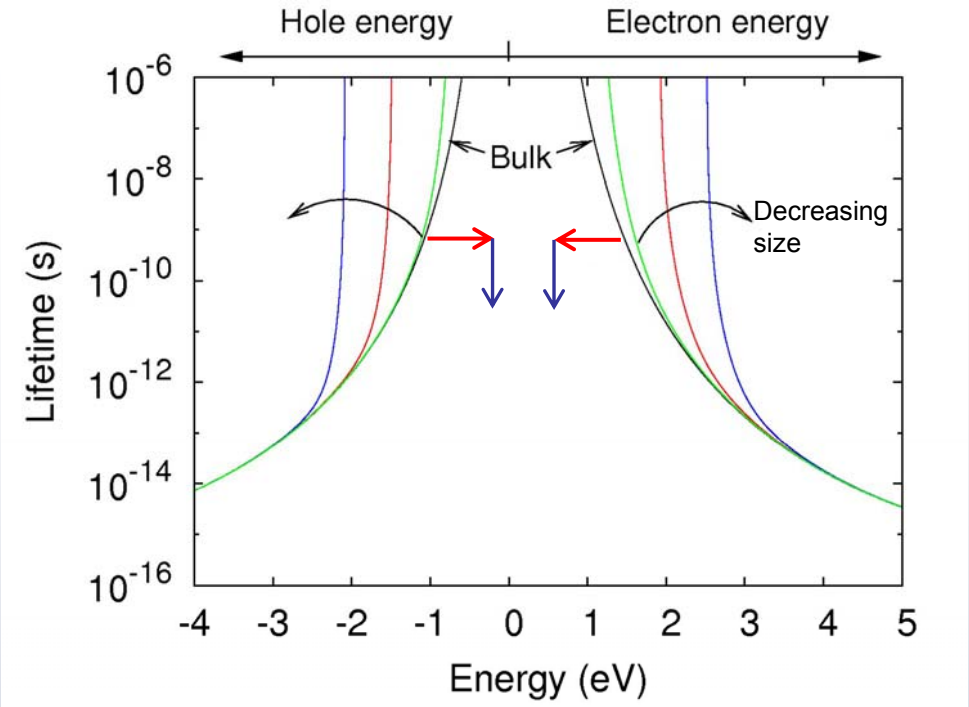


Lines : our calculations.
τ_{ph} = 0.5 ps

+ : Wolf, M.; Brendel, R.; Werner, J. H.; Queisser, H. J. J. Appl. Phys. 1998

Strategy to get more efficient CM

General behavior of the impact ionization lifetime



Possible strategy:

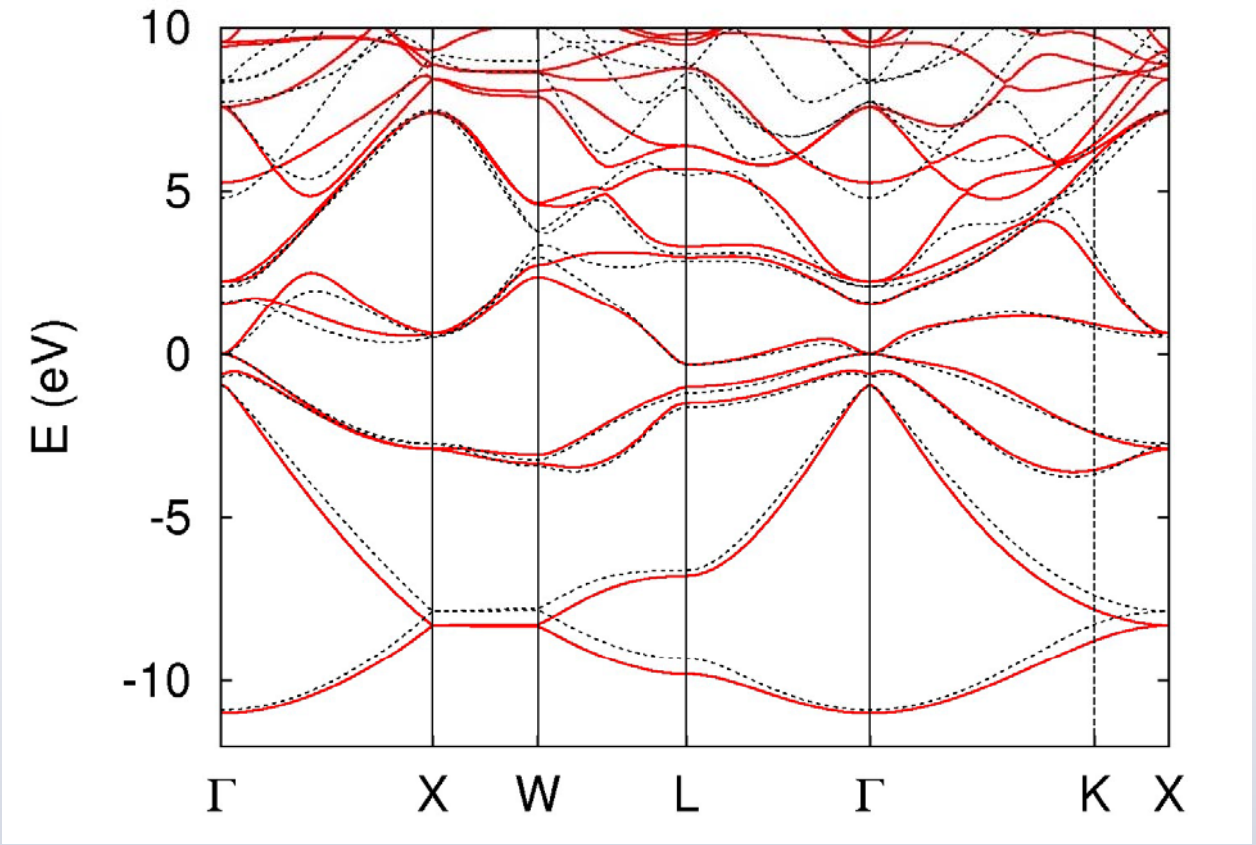
1) Horizontal shift : to small |E|
⇒ small bandgap materials

2) Vertical shift : to high density of final states
⇒ materials with degenerate bands

3) To adjust the gap using quantum confinement

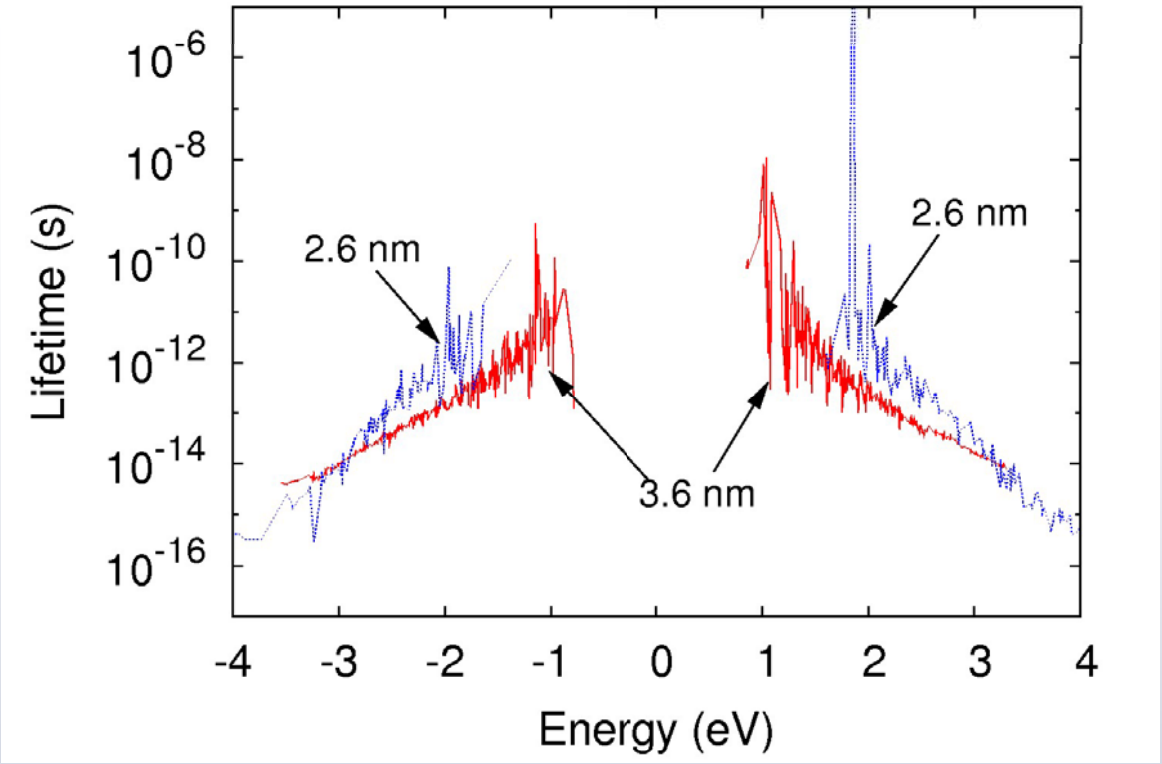
Test of the strategy: α-Sn

Calculated band structure of α-Sn

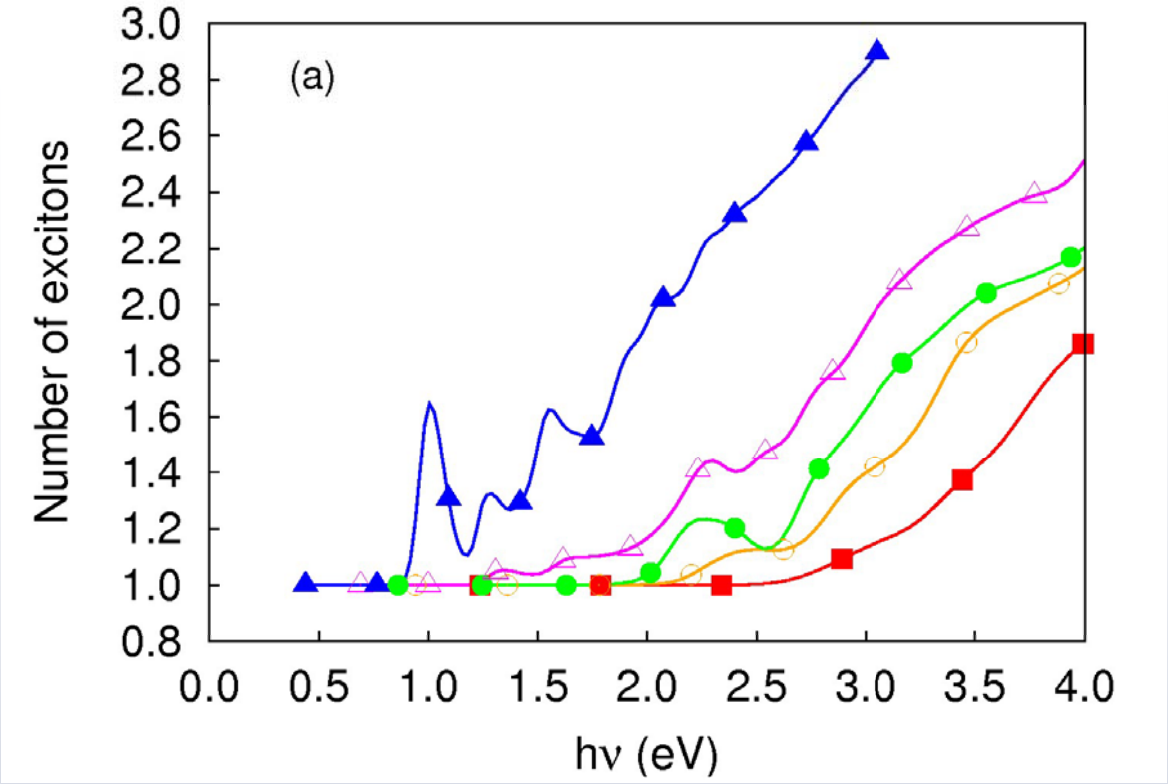


_ _: DFT
___: tight-binding

α-Sn: impact ionization lifetime



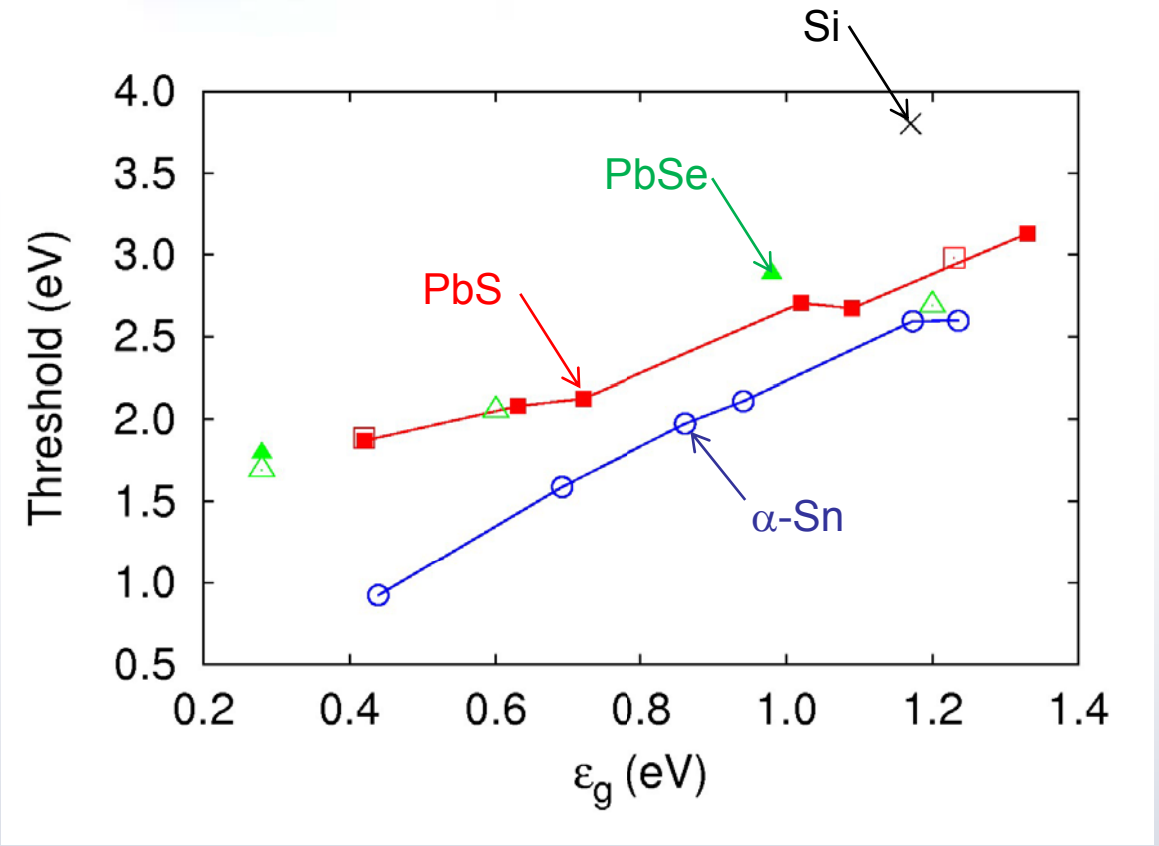
α-Sn: CM yield



—: E_g = 0.44 eV
—: E_g = 0.69 eV
—: E_g = 0.86 eV
—: E_g = 0.94 eV
—: E_g = 1.24 eV

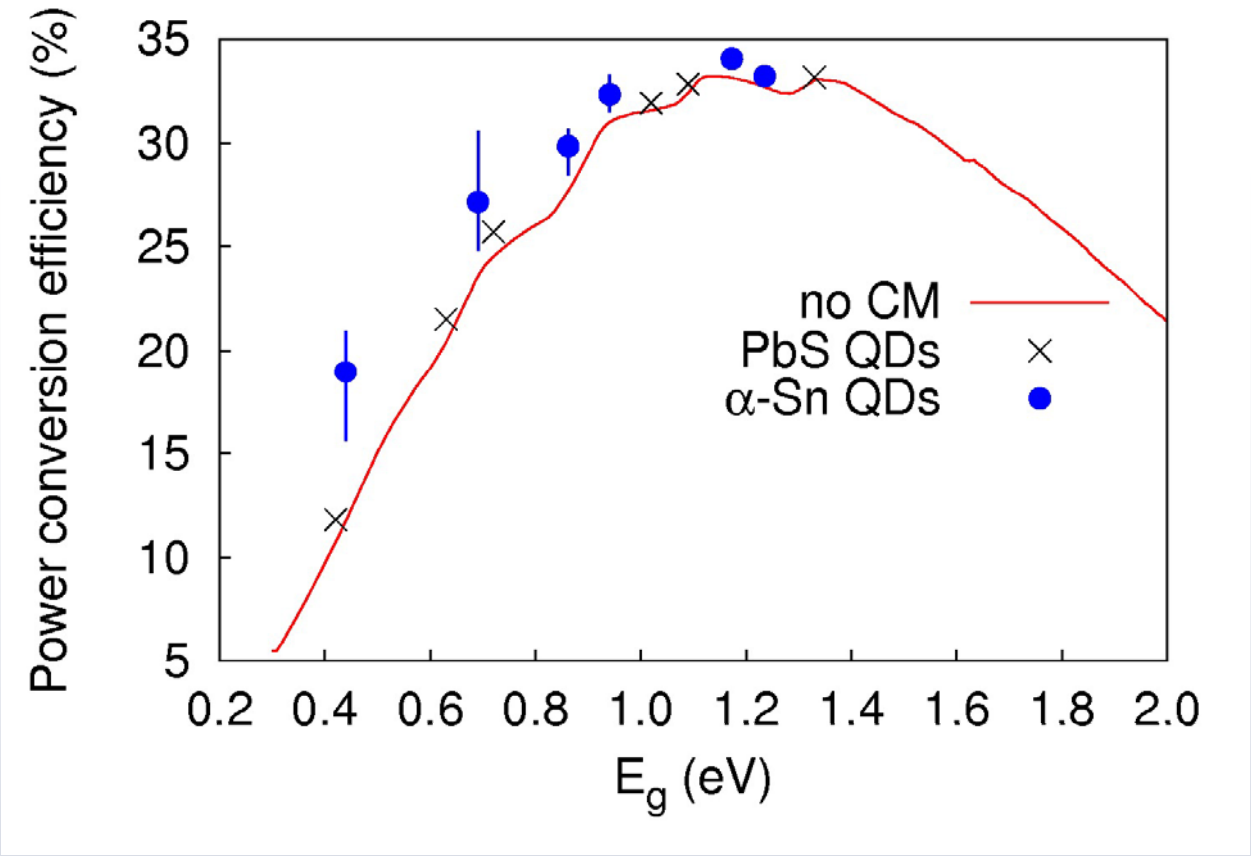
τ_{ph} = 1 ps

Test of the strategy: α-Sn



G. Allan and C. Delerue, ACS Nano 5, 7318 (2011).

Test of the strategy: α-Sn



G. Allan and C. Delerue, ACS Nano 5, 7318 (2011).

On-going work

Weak point of all these works:

The phonon-assisted relaxation lifetime τ_{ph} is a parameter

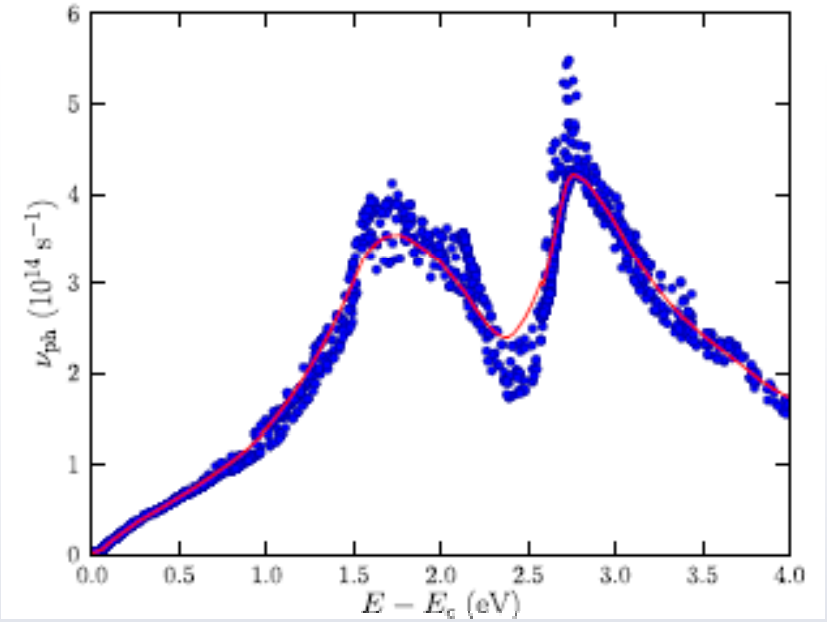
$\Rightarrow$ Calculation of scattering rates for the relaxation by emission of phonons

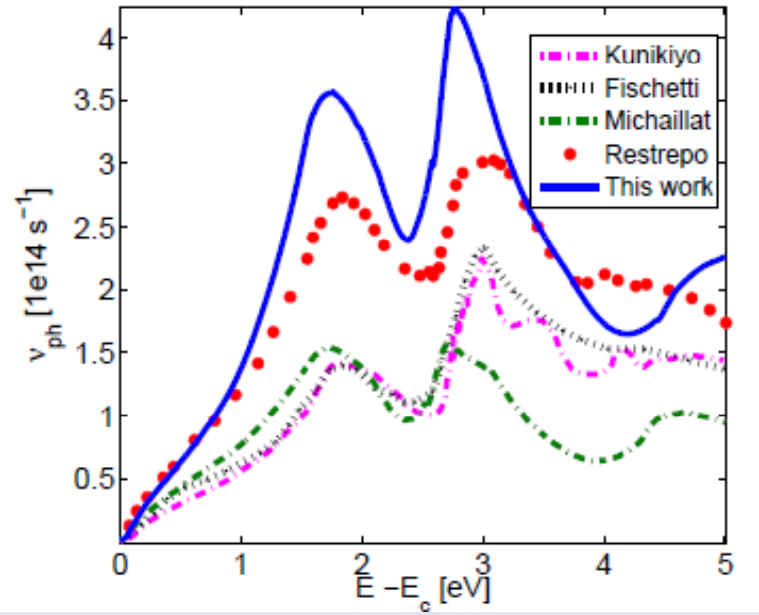
Our approach:

1) Electronic structure in TB
2) Phonons using a valence-force field model
3) Calculation of the e-ph coupling Hamiltonian (position-dependent TB)
4) Calculation of the couplings and scattering rates

Collaboration: Y.M. Niquet, INAC/CEA

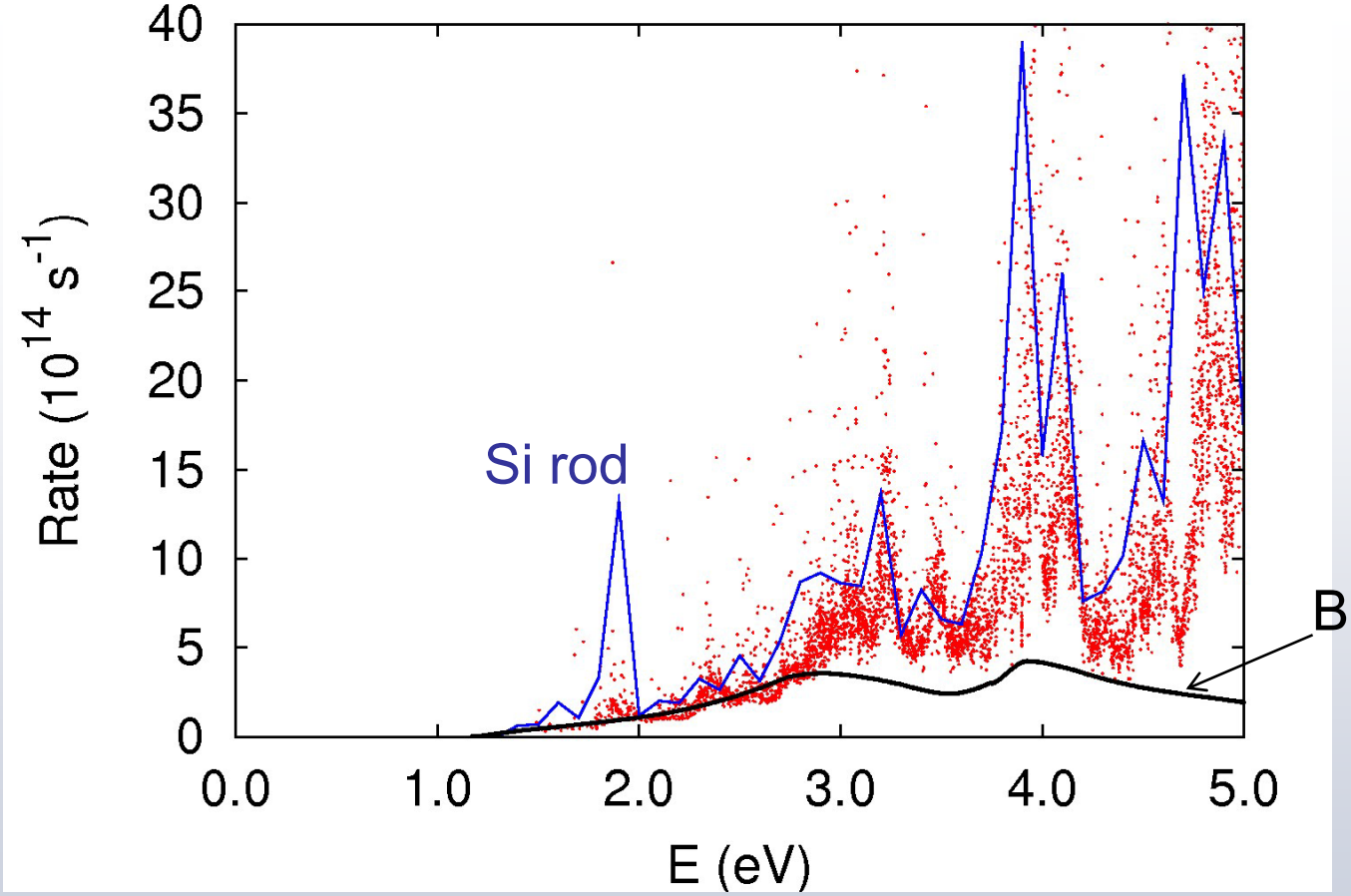
Scattering rates: bulk Si





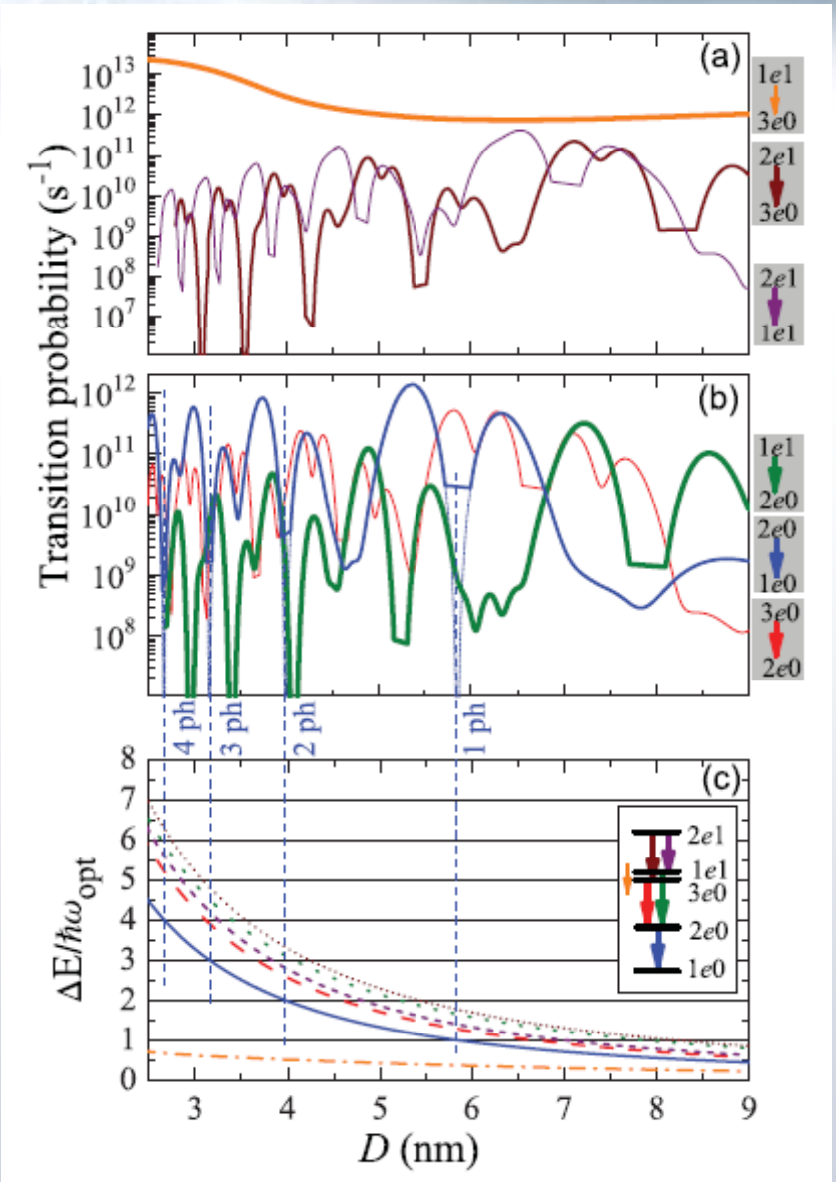
Scattering rates: Si nanorods

Cylindrical rod: 77 nm x 2 nm



Scattering rates: Si QDs

Spherical Si QD



Moskalenko et al, PRB 85, 085432 (2012)

Future work

Next steps:

1) Calculation of the impact ionization rates
2) Full simulation of the CM process

Conclusion

CM in QDs:

- Controversies remain
- Origin of the discrepancies not really known
- Latest experimental results (with CM >0) explained by impact ionization
- Small influence of CM in PbS & PbSe QDs solar cells
- But still room for improvement $\Rightarrow$ CM engineering
- We have proposed a possible strategy
- On-going calculations for phonon-assisted processes

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G. Allan and C. Delerue, ACS Nano 5, 7318 (2011).