Colloidal Quantum Dots for Guided Wave Photonics: from Optical Gain to Ultrafast Modulation

Public PhD Defense of ir. Pieter Geiregat

for the degree of

Doctor of Engineering in Engineering Physics

10/02/2015

What's in a title ?

Colloidal Quantum Dots
for
Guided Wave Photonics:
from
Optical Gain to Ultrafast Modulation

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Colloidal Quantum Dots

for

Guided Wave Photonics:

from

Optical Gain to Ultrafast Modulation

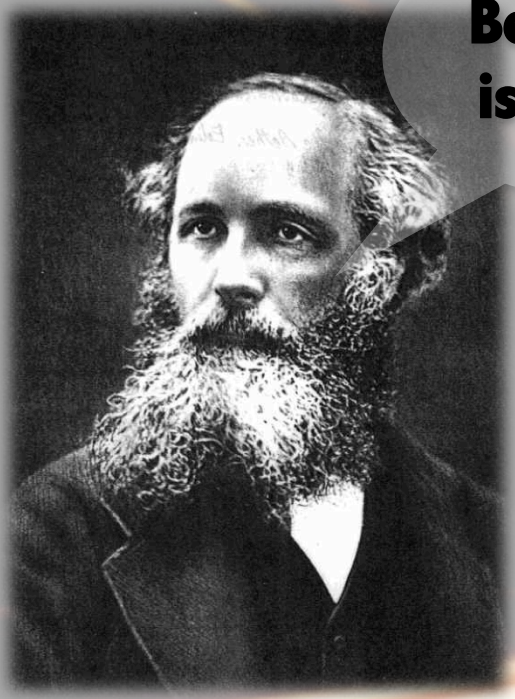
Photonics : why bother ?

“ Photonics “

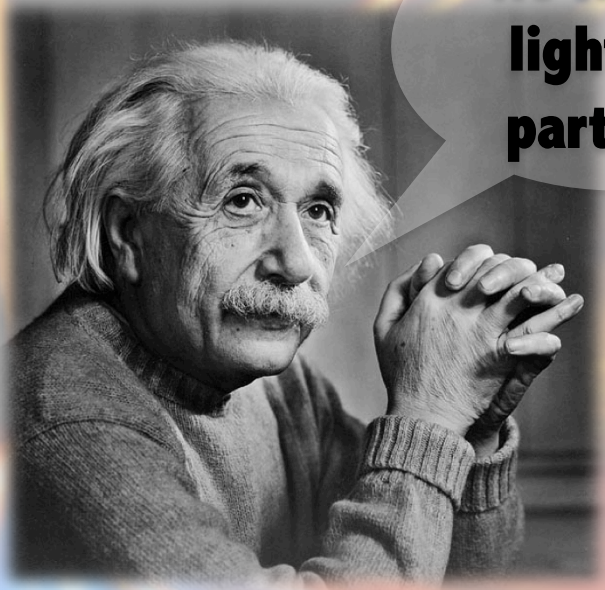
Field of Science and Engineering that occupies itself with the *generation, detection and manipulation of light (photons)* for applications in imaging, lighting, detection, energy conversion, …

But also **telecommunication** and (**bio-)sensing** !

Intermezzo: What is light ?



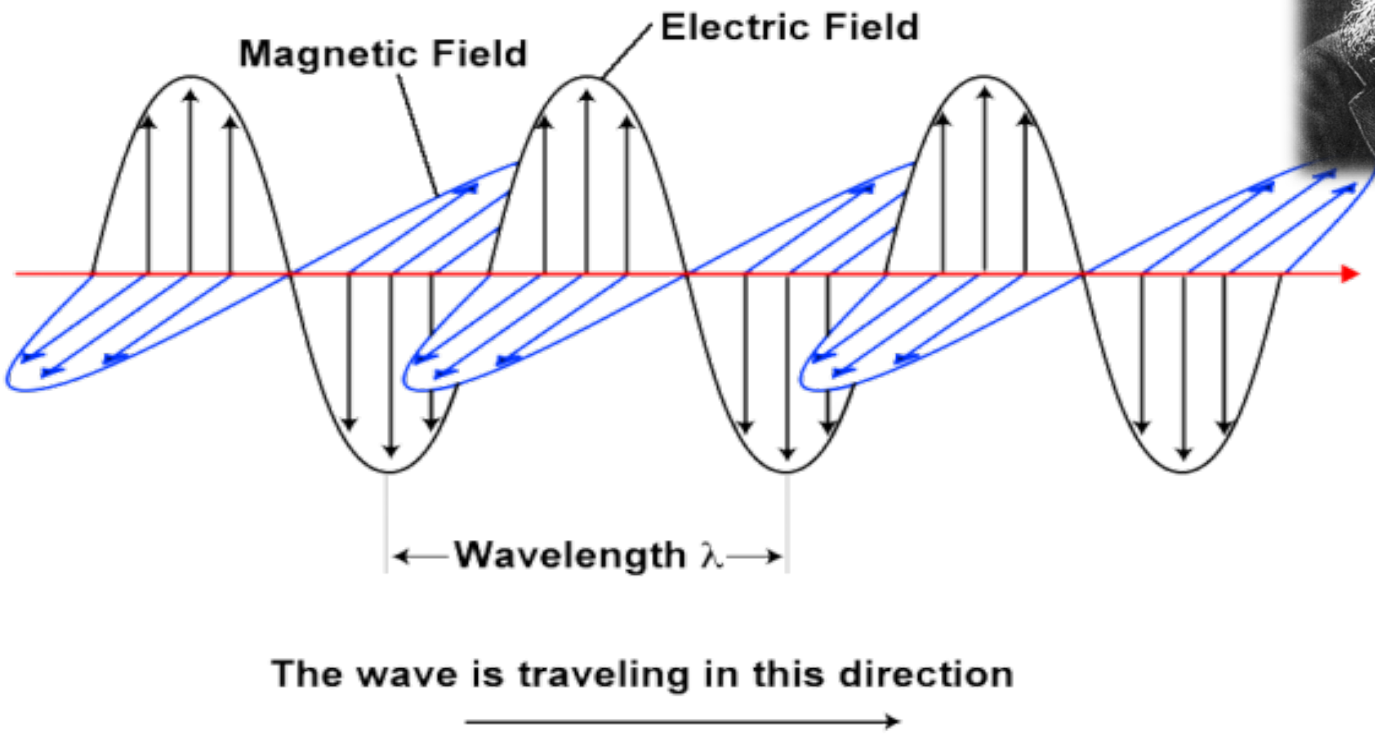
James Clerk Maxwell



Albert Einstein

Both are correct ! The '**wave-particle' duality**

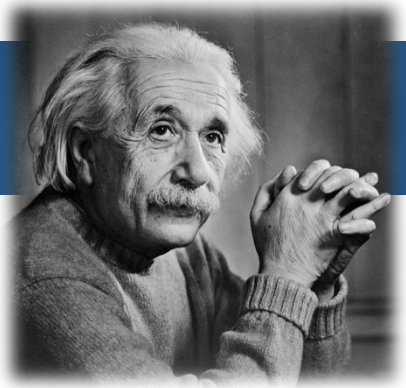
Intermezzo: What is light ?



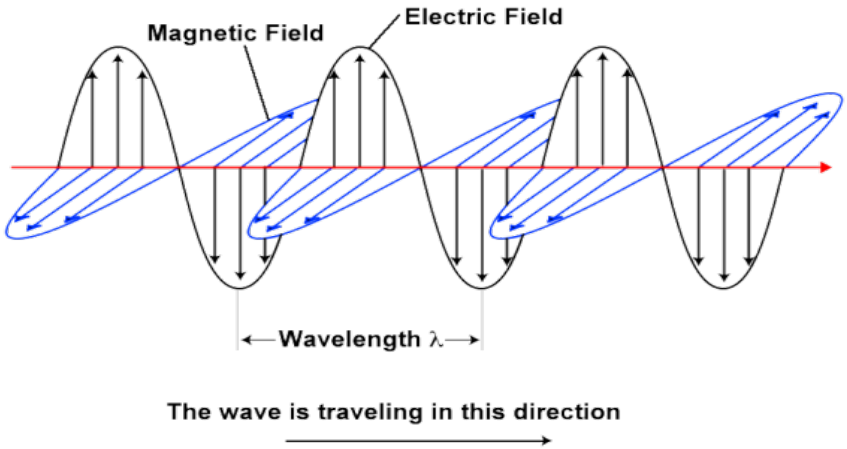
Light is an **electromagnetic** wave, **periodic** in **space** and **time**

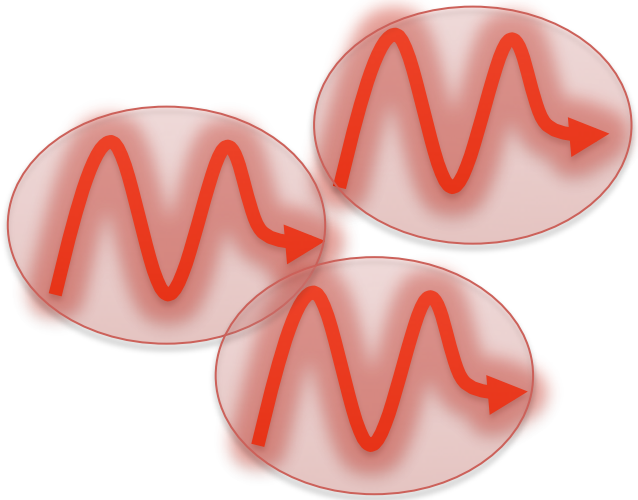
Characteristic:
Wavelength λ

Intermezzo: What is light ?



But it's also a particle ?!



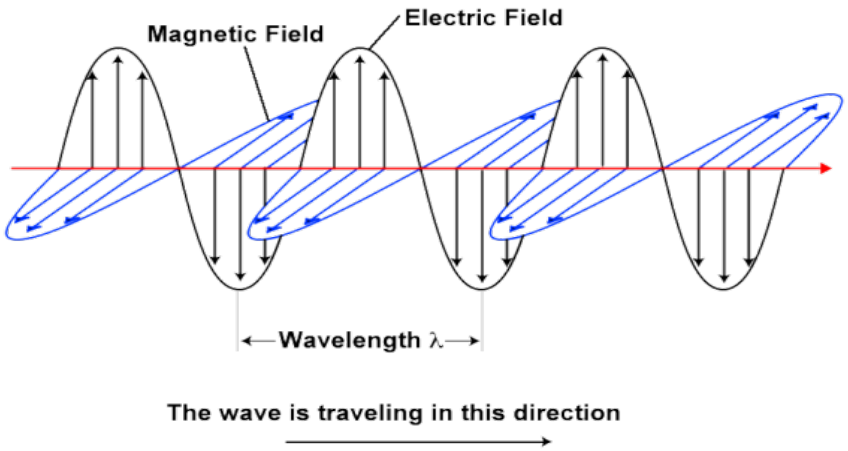


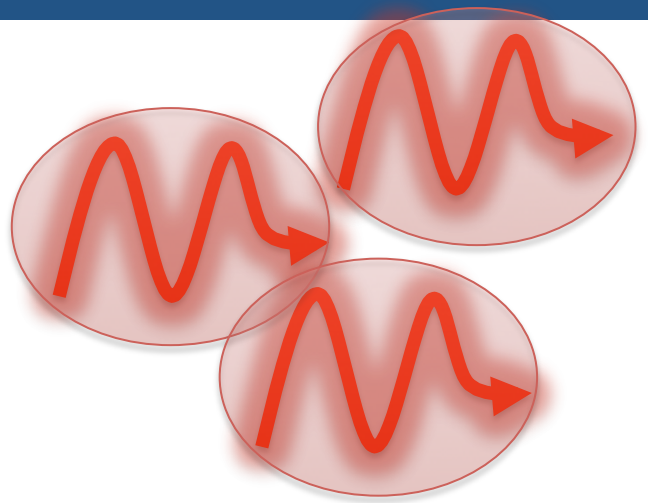
Light is stream of particles called 'photons' (hence: Photonics)

Characteristic:

Energy E

Wave - particle duality





De Broglie, L.

So, who's right ?

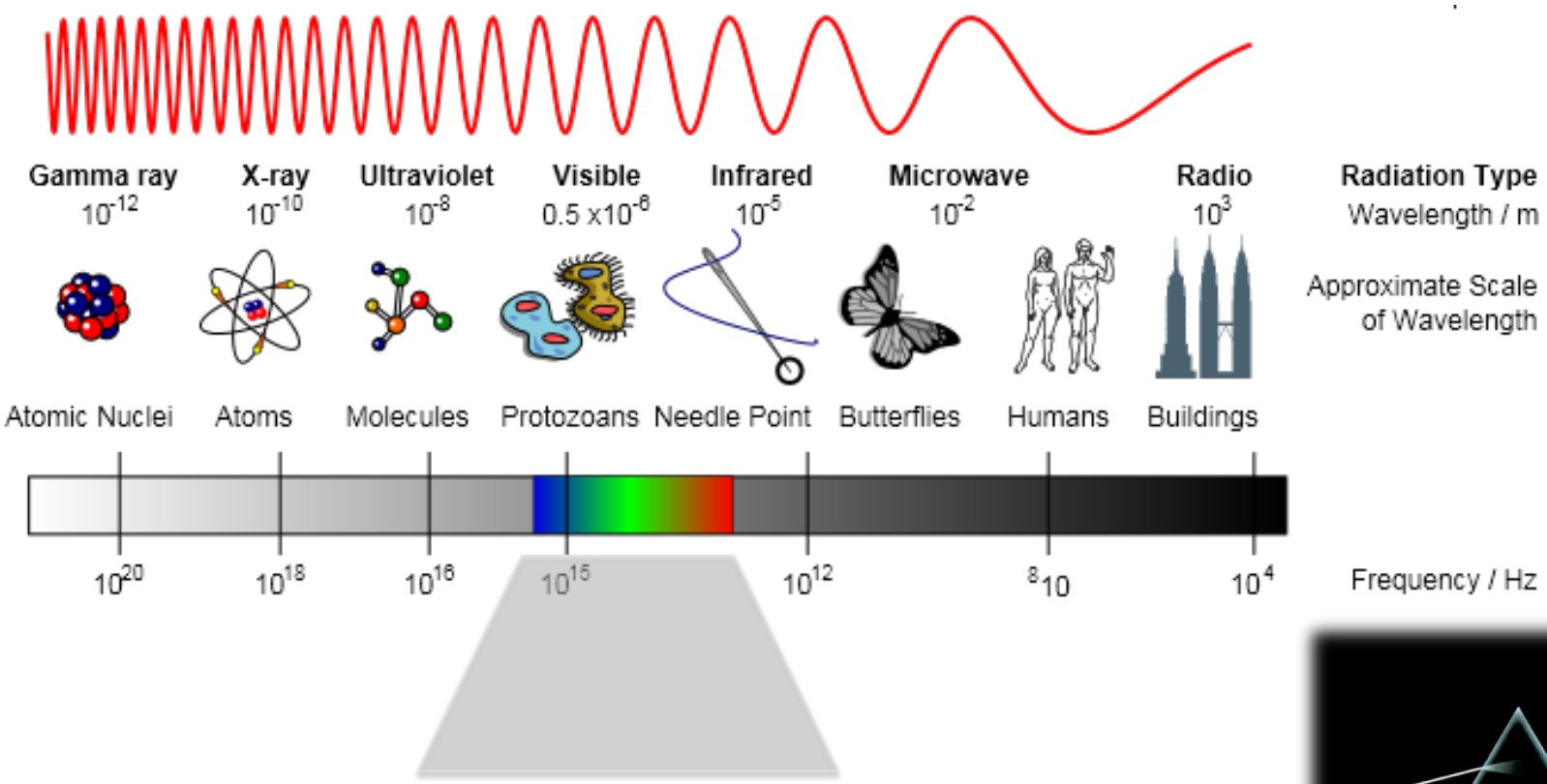
De Broglie: " Both !"

Energy x wavelength = Constant (= *hc*)

Important:

Energy (wavelength) cannot change in 'regular' media

Intermezzo: What is light ?



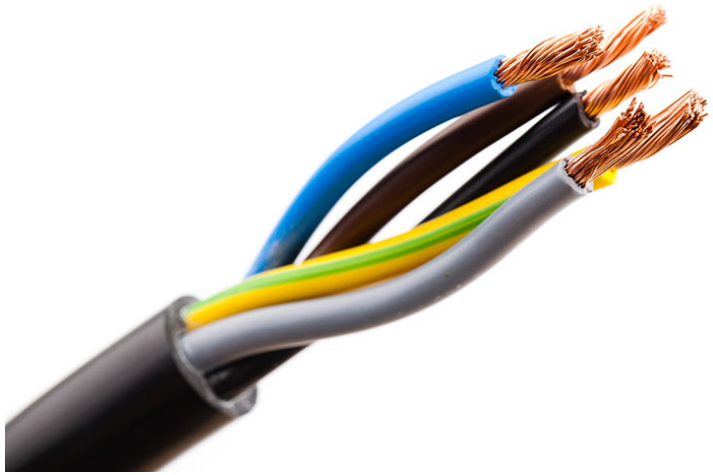
Visible light is only small part of the total spectrum !

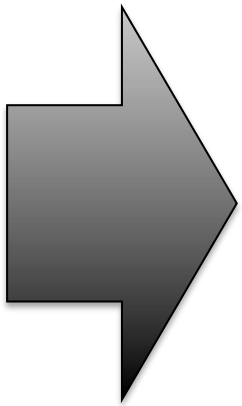
Photonics for data transfer and telecommunication

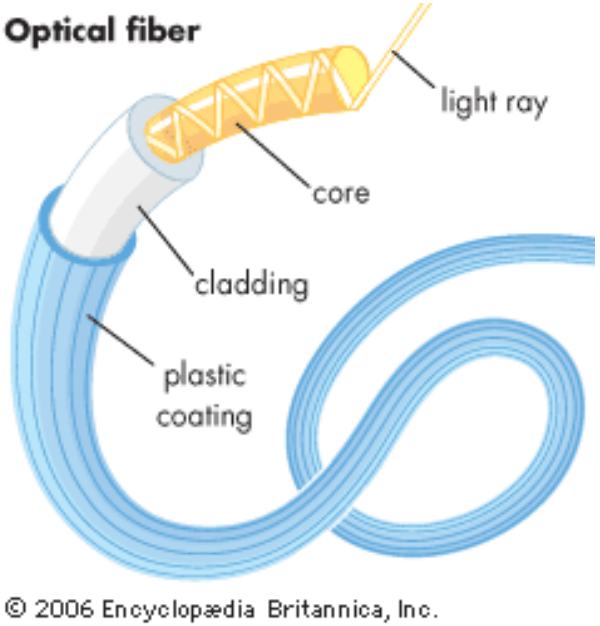
Copper is reaching its limits in terms of **bandwidth** and **energy consumption**

Use **light** instead of electricity to carry information

Around the globe & **within data centers / supercomputers**

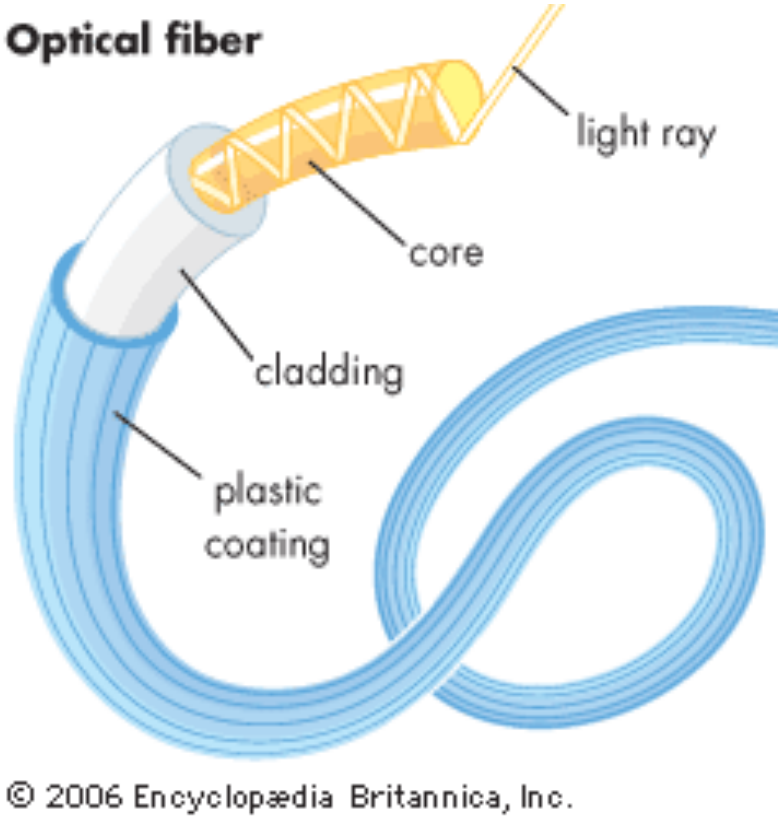




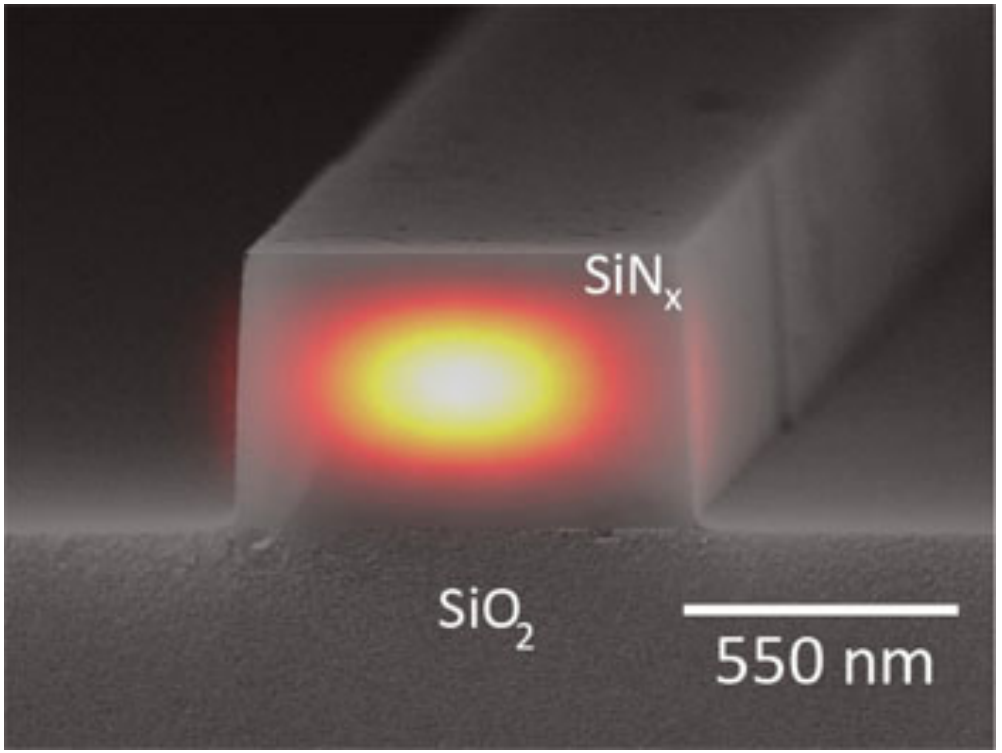


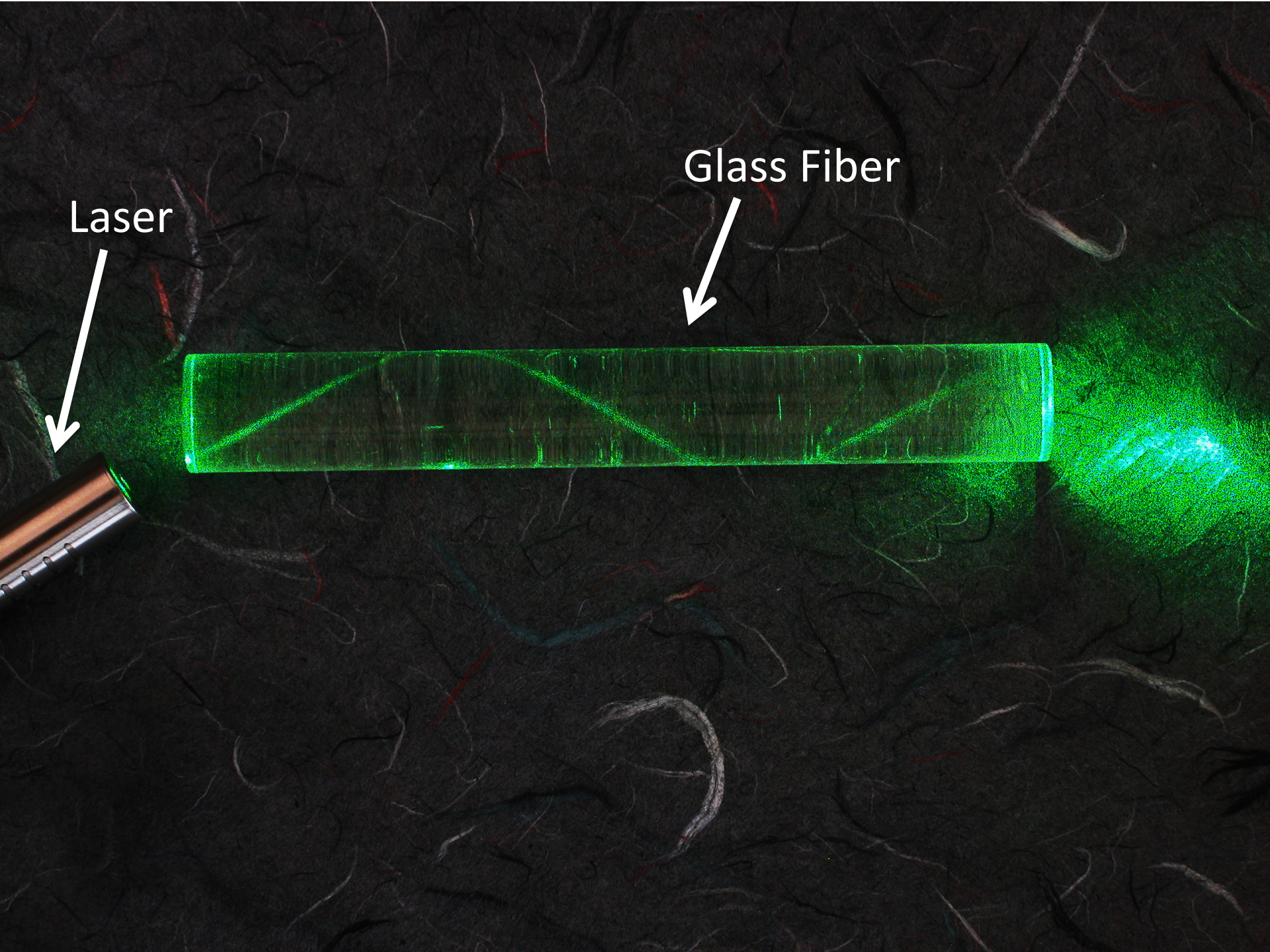
Guided Wave ?

Glass fibers



Waveguide

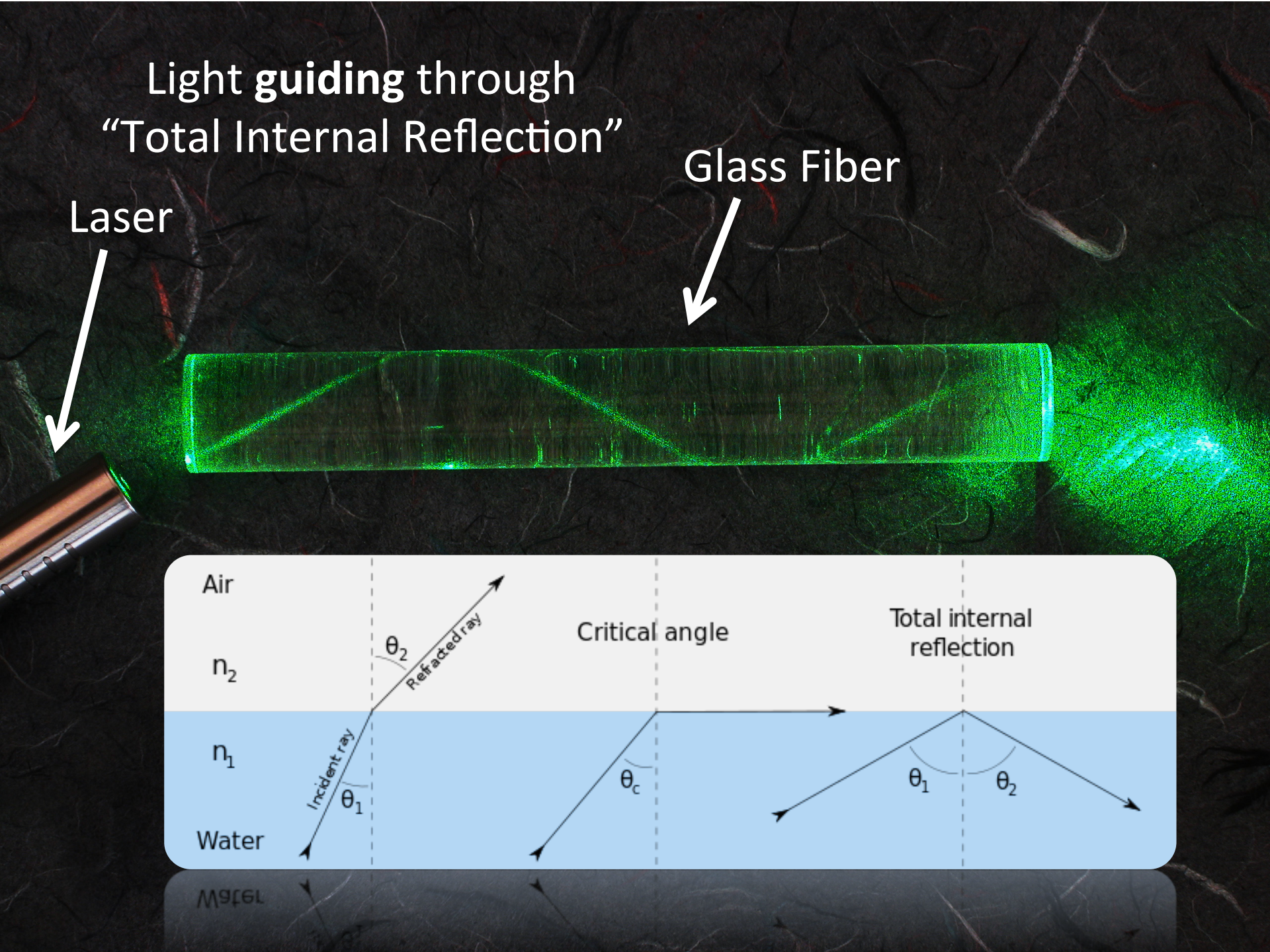



Glass Fiber
Laser

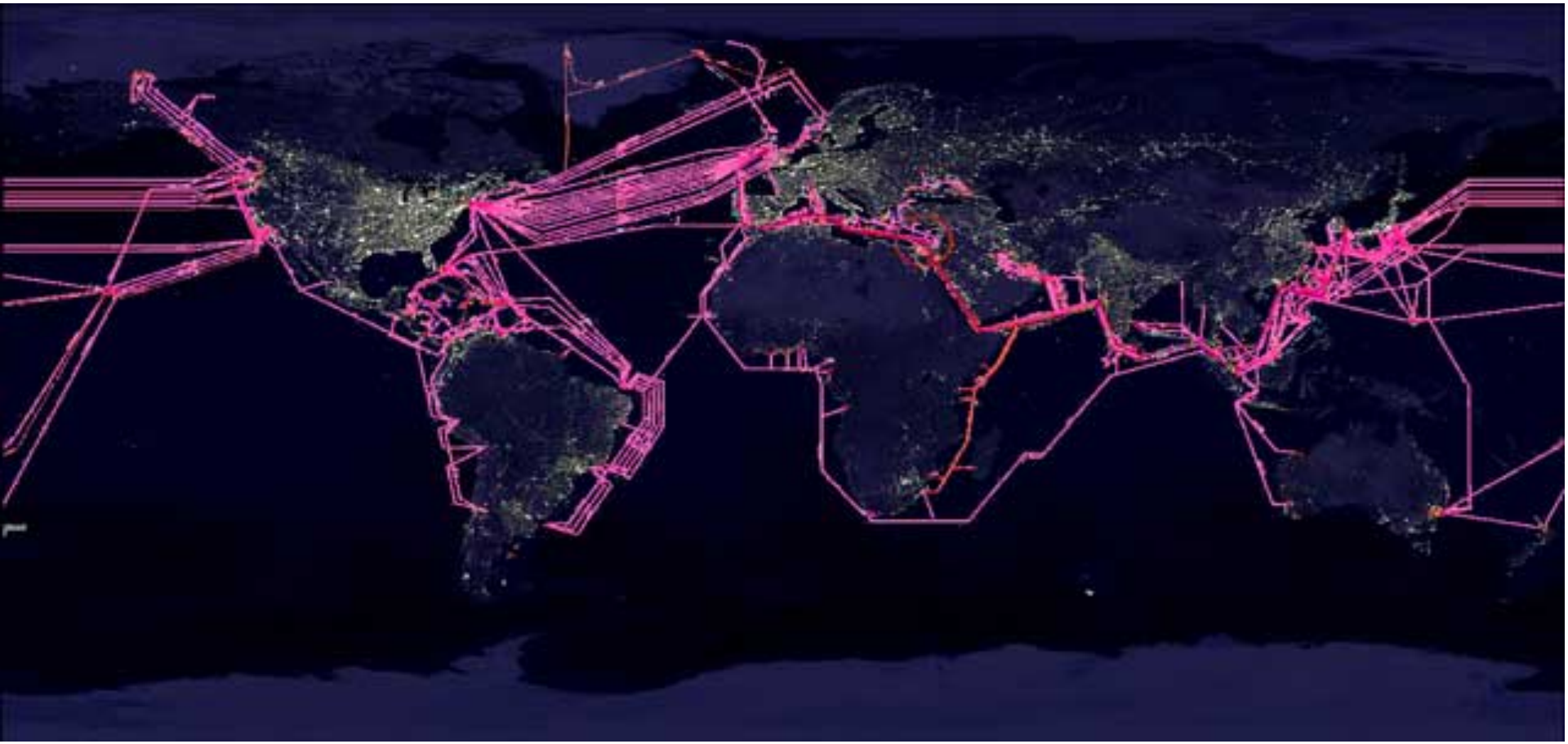
Light **guiding** through
"Total Internal Reflection"

Glass Fiber

Laser

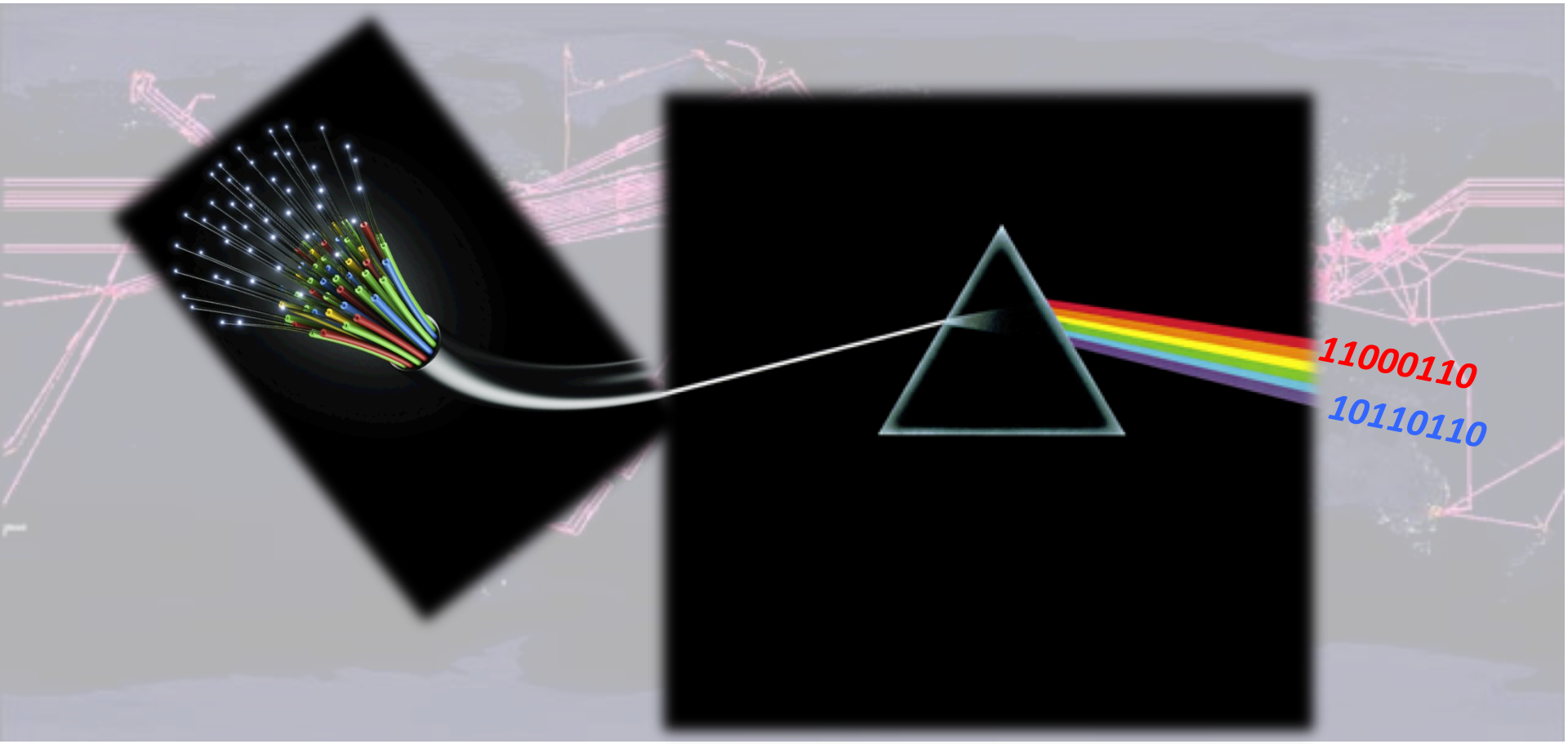


Photonics … for telecommunication



Fibers are the **backbone of the internet**
100s of Gigabit/s through a hair-thin glass fiber

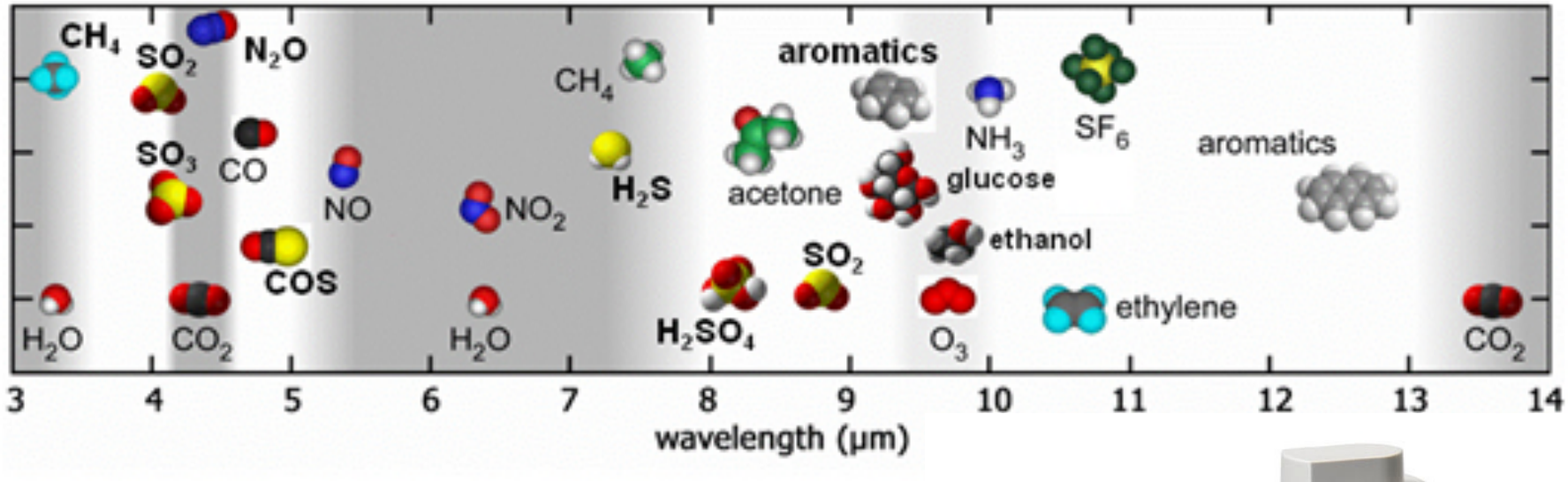
Photonics … for telecommunication



Bandwidth (≈different colours) much higher than in electronics

Photonics … for optical interconnects

Photonics … for sensing

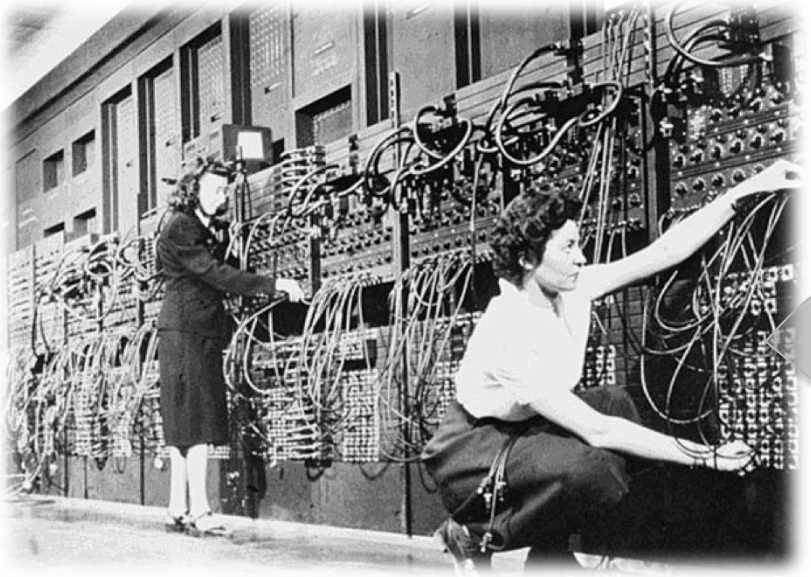


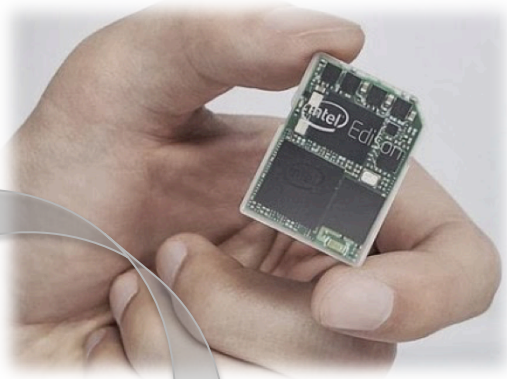
Every **molecule** (gas or liquid) has a specific **absorption** band

Use **light to trace molecules** for:

- Medical examination
- Analysis of the atmosphere / Safety
- Scientific analysis

Micro-electronics shows the way …

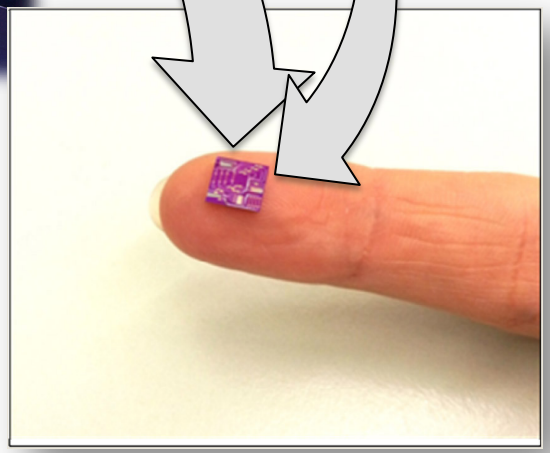




Integration leads to:

- Smaller device footprints and lower energy consumption
- Increased functionality

And Photonics follows !

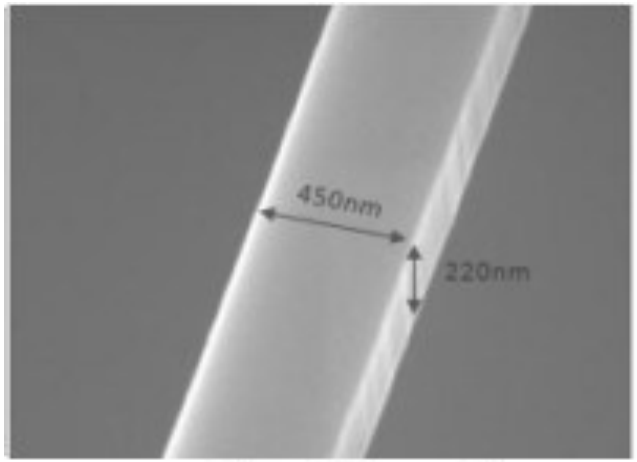


Replace **bulk optical components** (fiber switches, spectrometers, ..) by **integrated (photonic) circuits** !

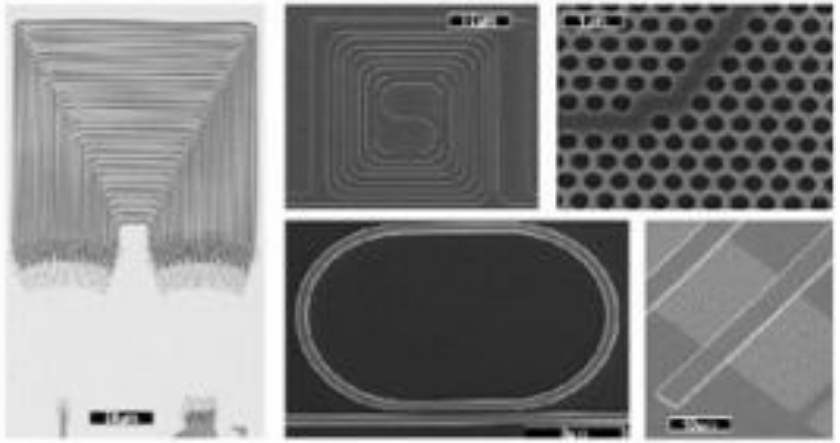
Photonic Circuits

Based on **silicon**, the CMOS standard of micro-electronics

- ✓ Large volume fabrication → low cost
- ✓ Increased functionality
- ✓ Dense integration with electronics

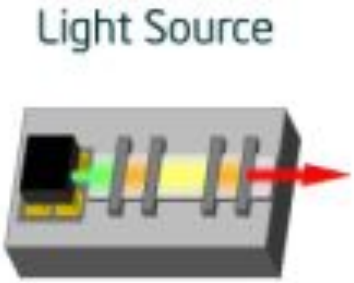


Silicon Waveguide

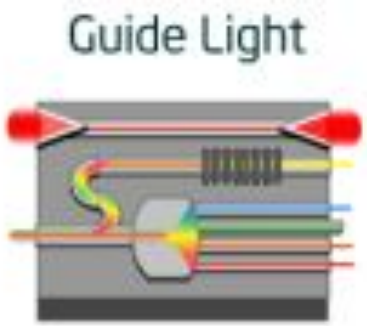


Optical functions in Silicon

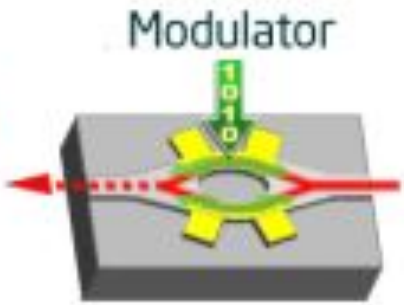
Photonic Circuit: Building Blocks



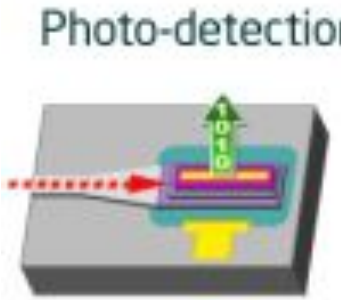
Generate light



Routing/Filtering/…



Electrical-Optical Conversion, Wavelength conversion

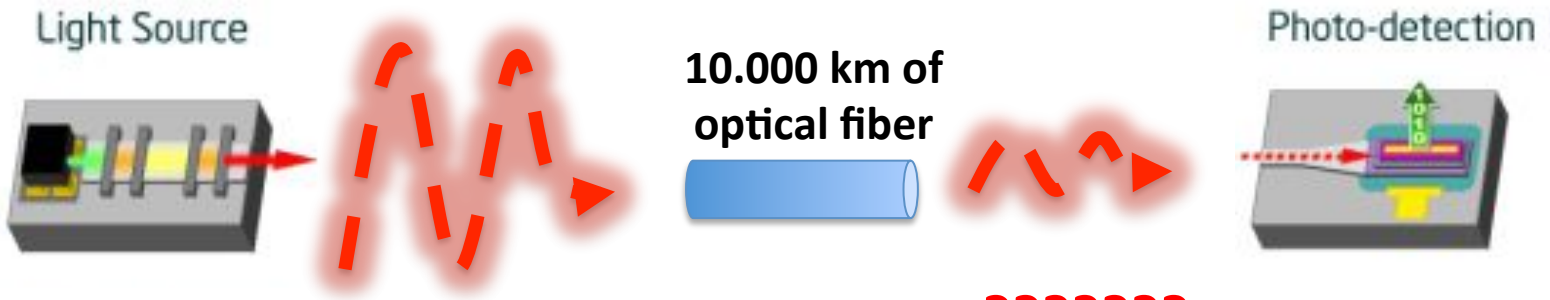


Translate optical information back to electrical domain (processor, …)

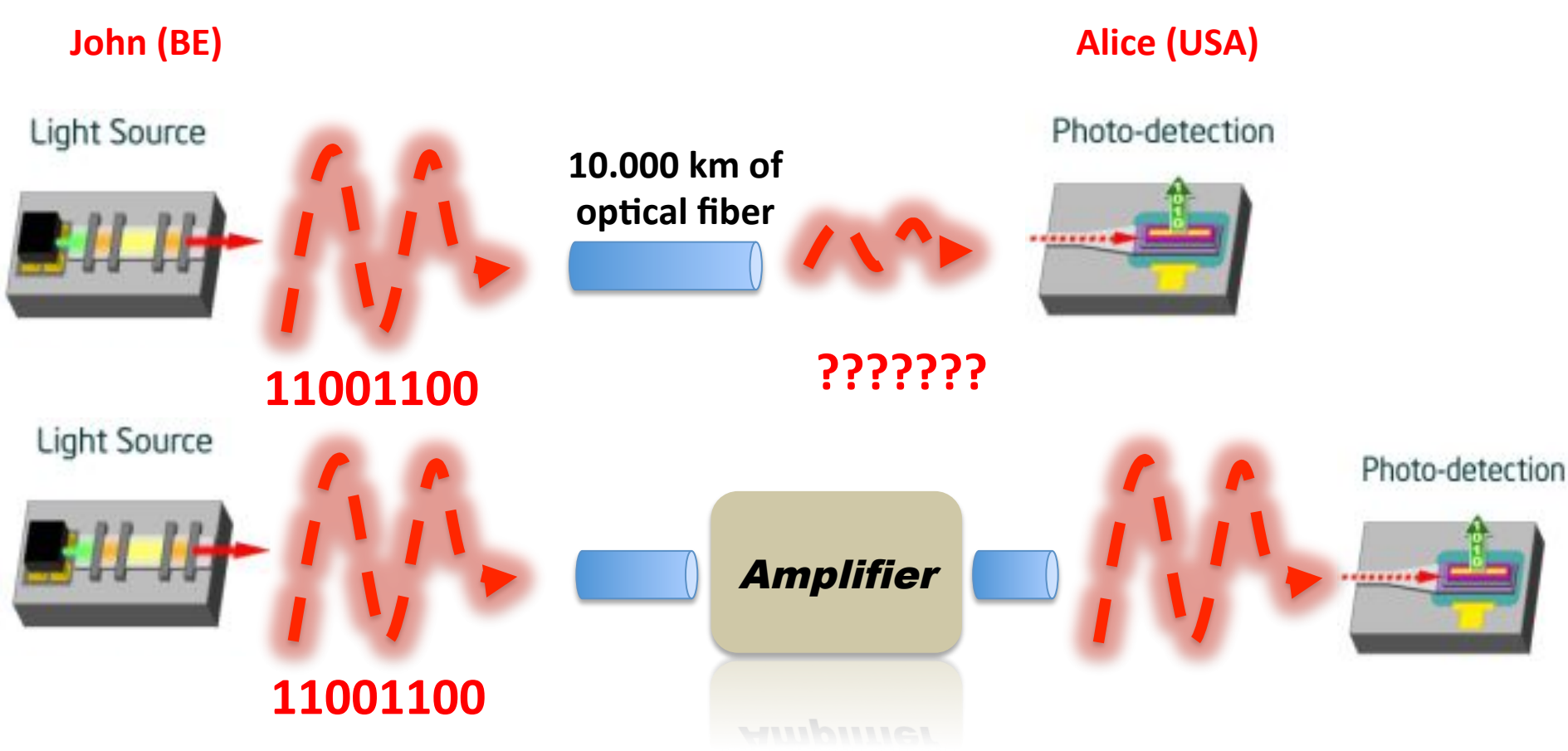
Amplification of light

John (BE)

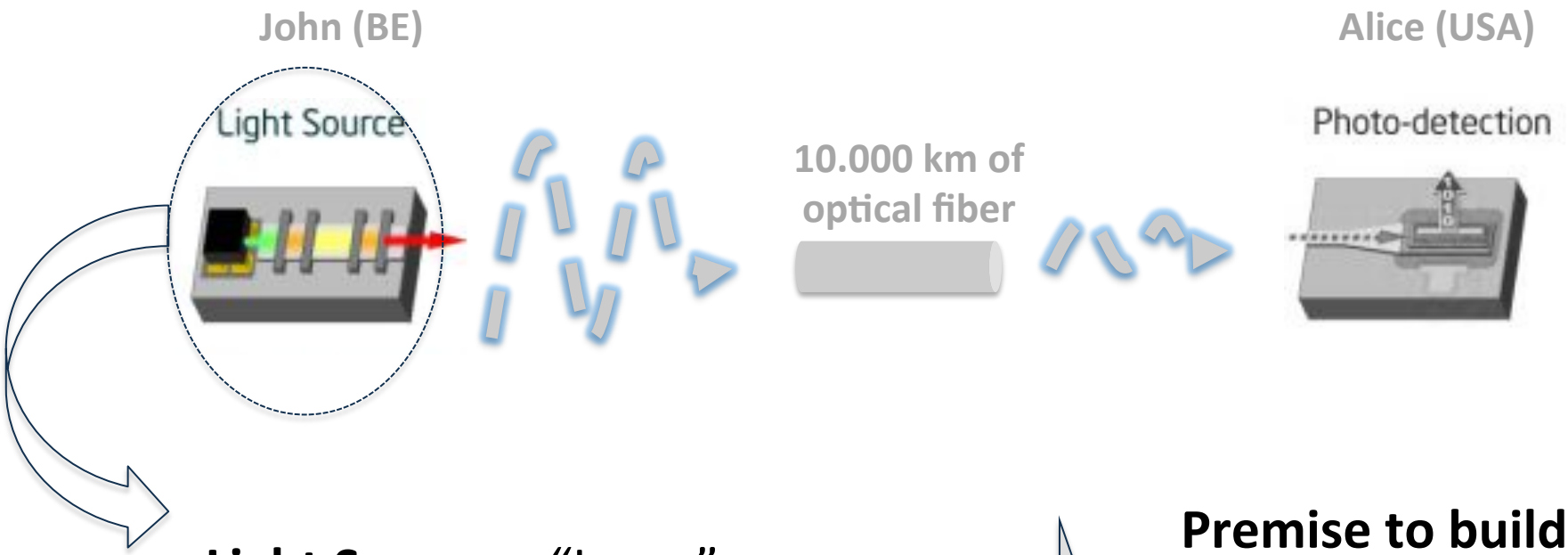
Alice (USA)



Amplification of light



Amplification of light



Light Source = "Laser"

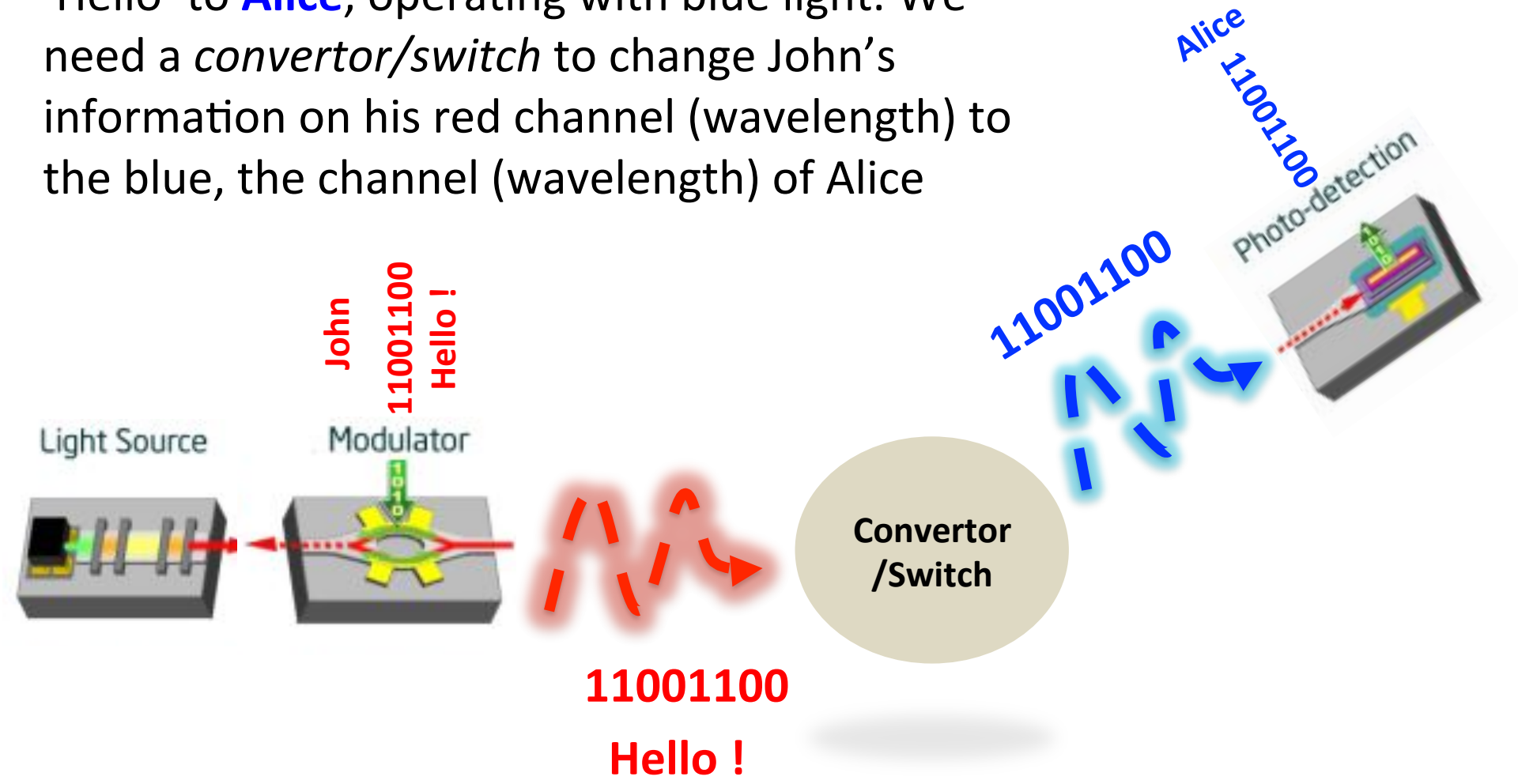
- ✓ Single Wavelength (*i.e.* 1 user)
- ✓ Coherence in time and space

Premise to build ?

A material with net optical gain (= Amplification)

Wavelength Conversion

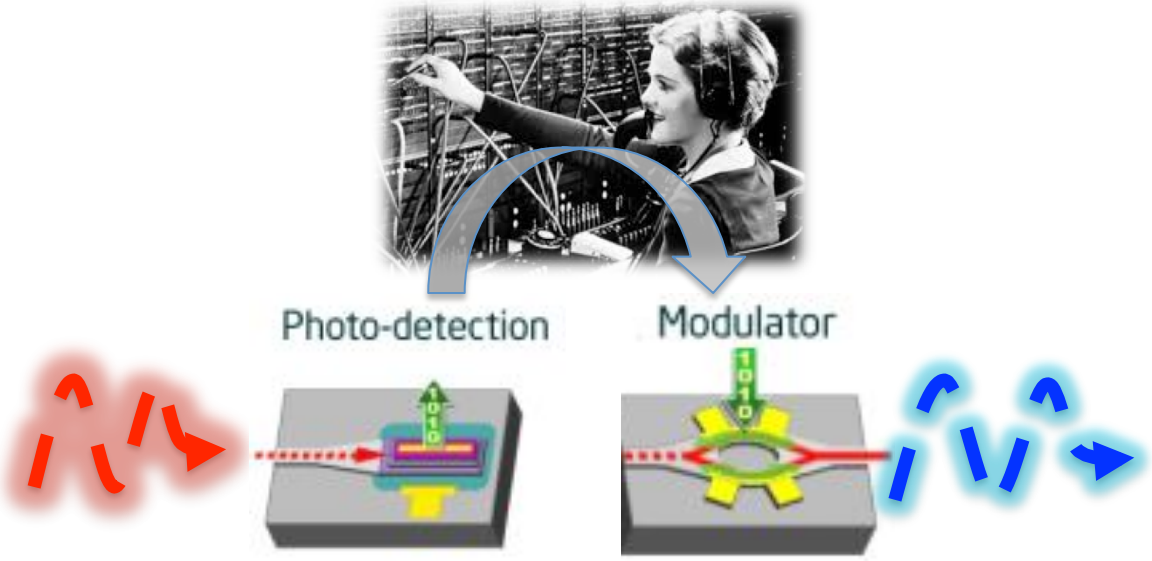
John, operating at red light, wants to say 'Hello' to **Alice**, operating with blue light. We need a *convertor/switch* to change John's information on his red channel (wavelength) to the blue, the channel (wavelength) of Alice



Wavelength Conversion

Convertor /Switch

Optical-Electrical-Optical

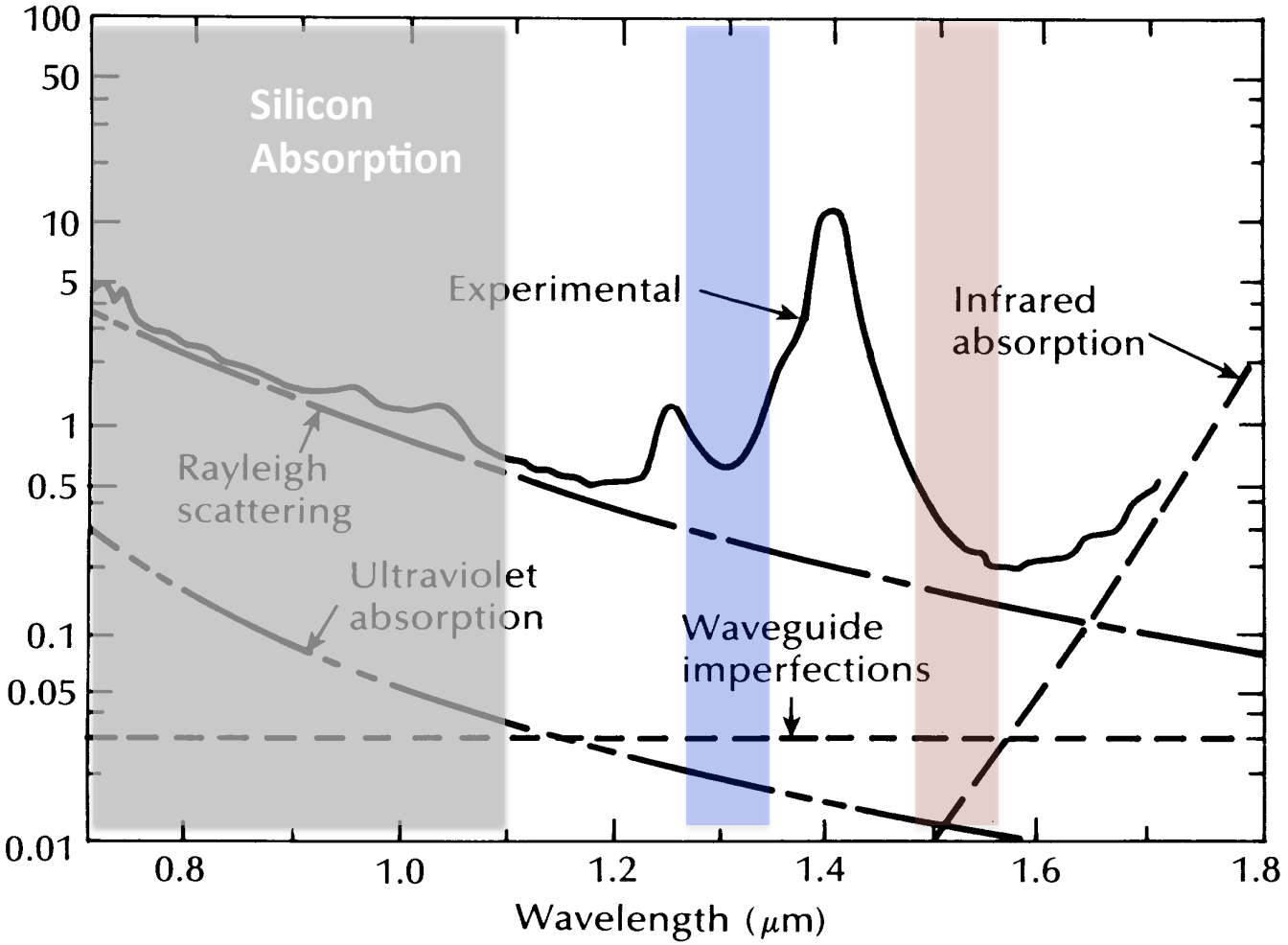


Energy consuming
and
not cost-effective !

All - Optical

Non-linear
materials ?
Silicon ?

So what light are we using ?

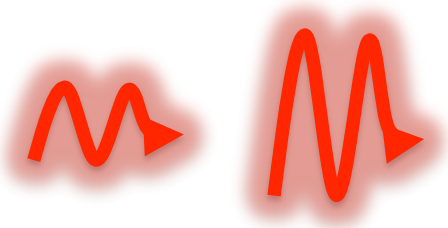


Visible

Near – Infrared

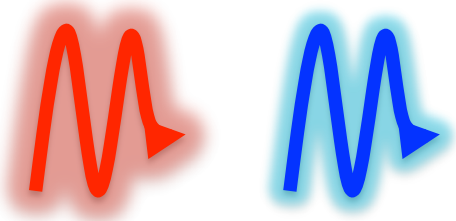
To recapture !

Amplification



- ✓ Intermediate amplification of light in long haul systems
- ✓ Building a laser for light sources in short and long range interconnects

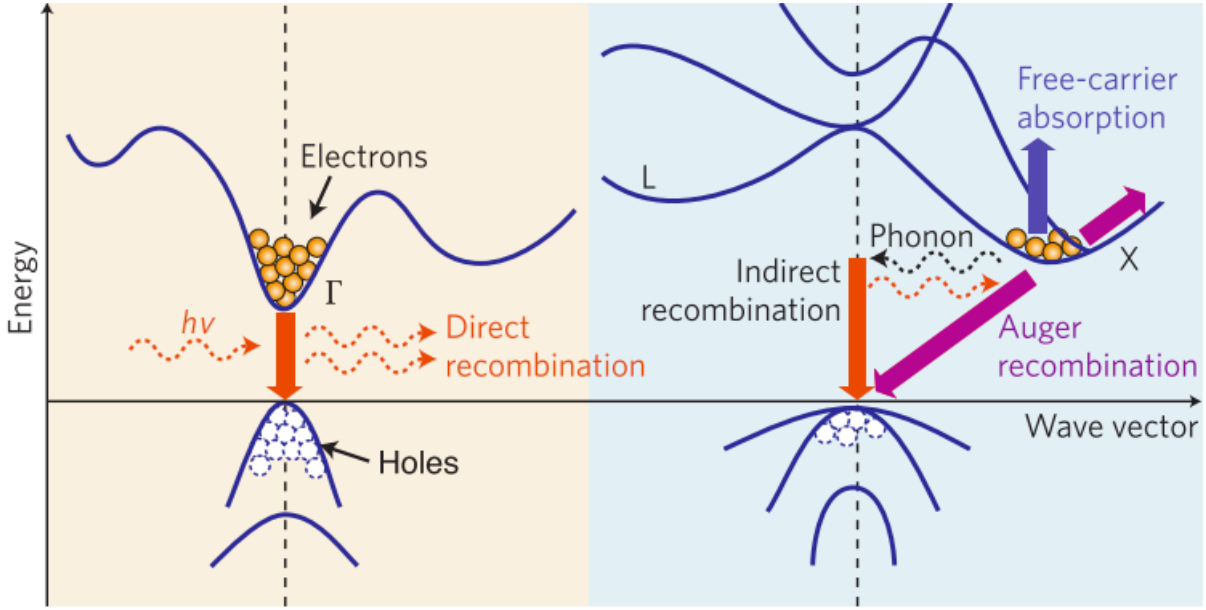
Wavelength Conversion

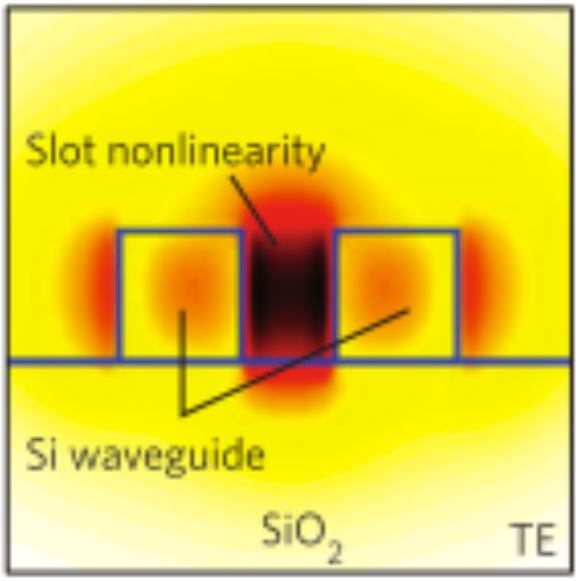


- ✓ Switch information between different channels/users

Can silicon help us here ?

Silicon can't do everything !





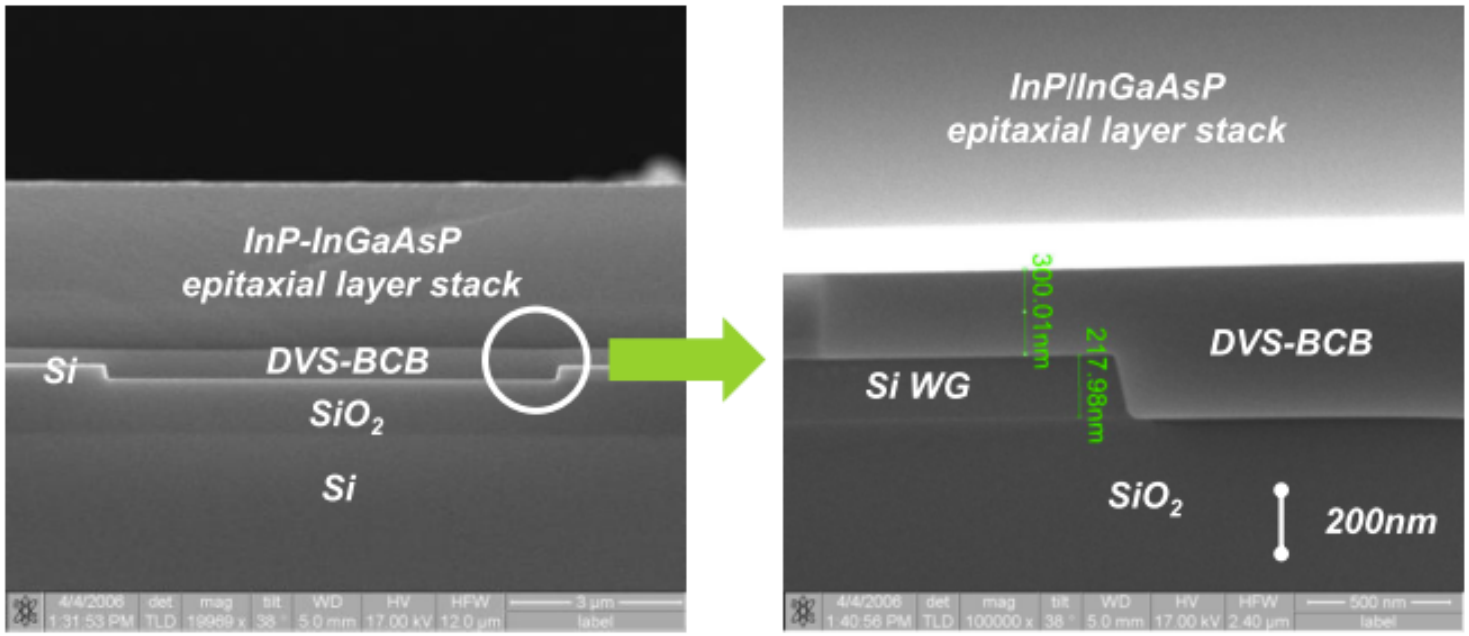
- Indirect band gap → **No efficient light emission**

- Centrosymmetric Crystal → **No efficient nonlinearities**

So ... how do solve this ?

We need to combine novel materials with silicon for light generation/amplification and conversion

Bonding of III-V Dies Direct Epitaxy Hybrid Schemes



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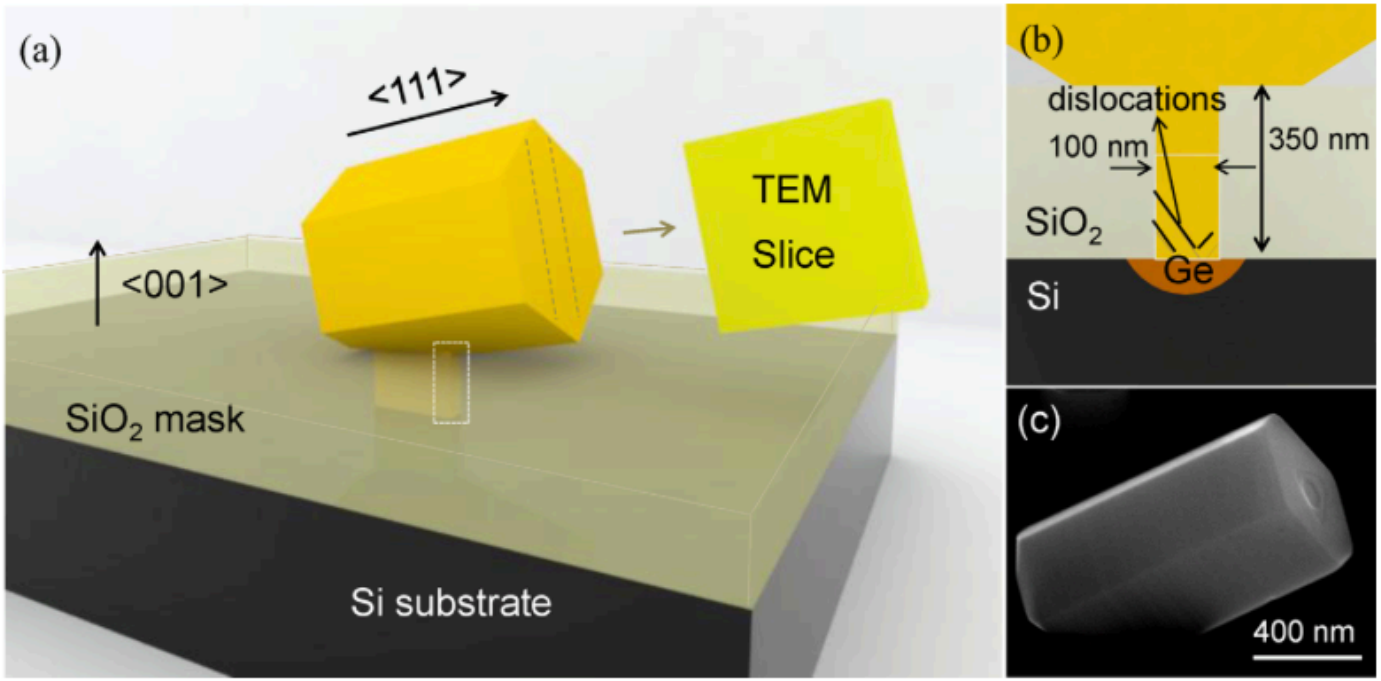
Bonding of III-V Dies **Direct Epitaxy** Hybrid Schemes

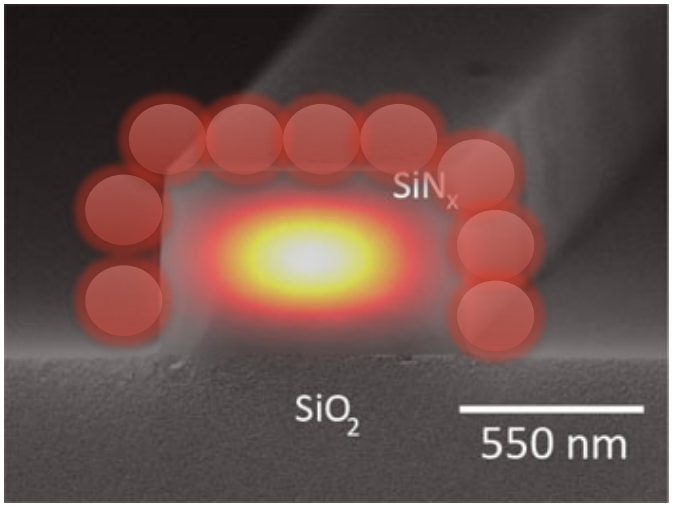


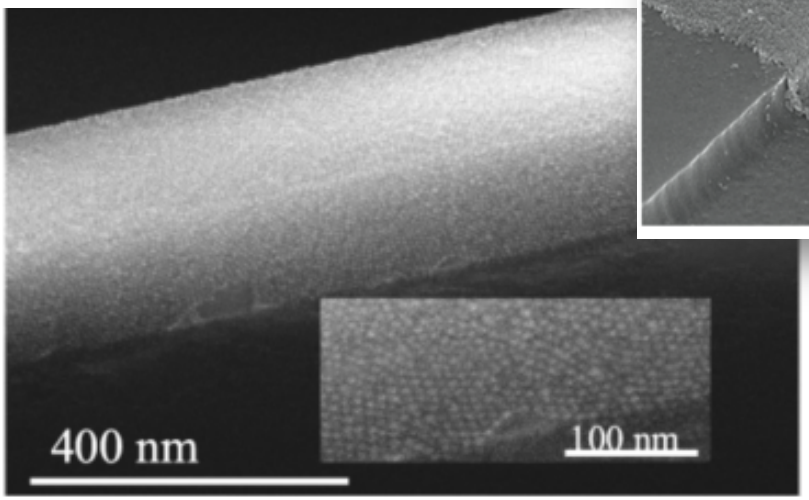
So .. how do solve this ?

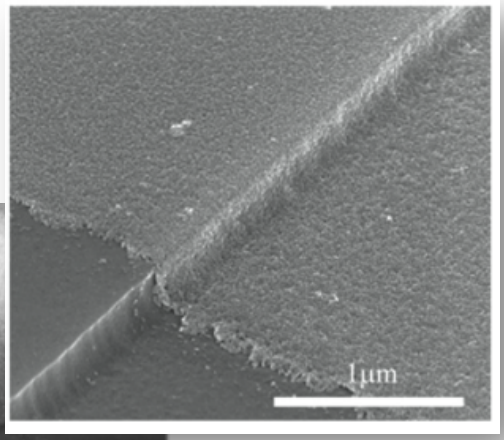
We need to combine novel materials with silicon for light generation/amplification and conversion

Bonding of III-V Dies Direct Epitaxy **Hybrid Schemes**

Combine novel light emitters (organics, graphene, … *quantum dots*!)







Rationale

Colloidal Quantum Dots

for

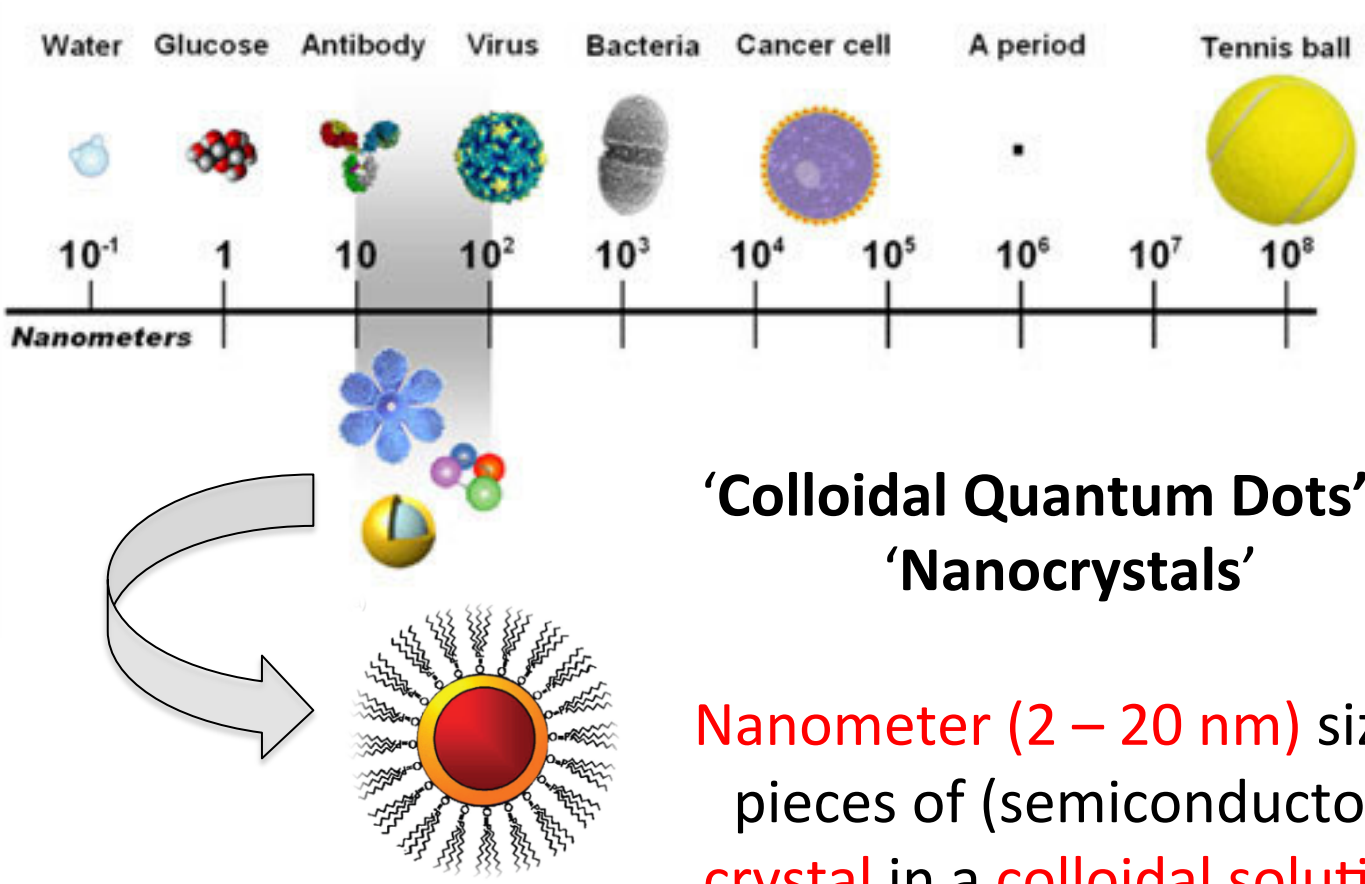
Guided Wave Photonics:

from

Optical Gain to Ultrafast Modulation

Quantum Dots – At the limits of nanotechnology

Nanotechnology = Manipulating matter on the "nanoscale"

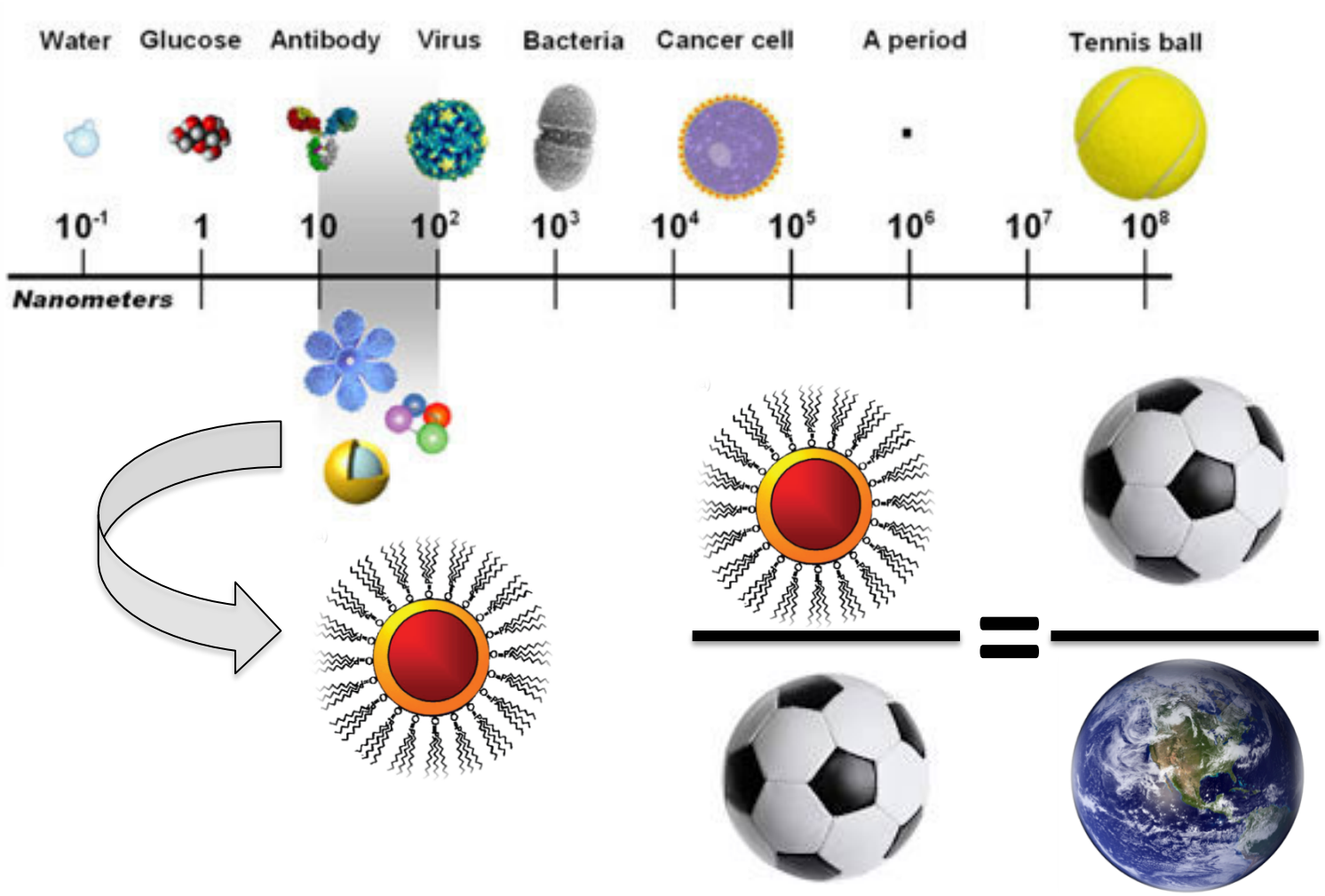


'Colloidal Quantum Dots' or **'Nanocrystals'**

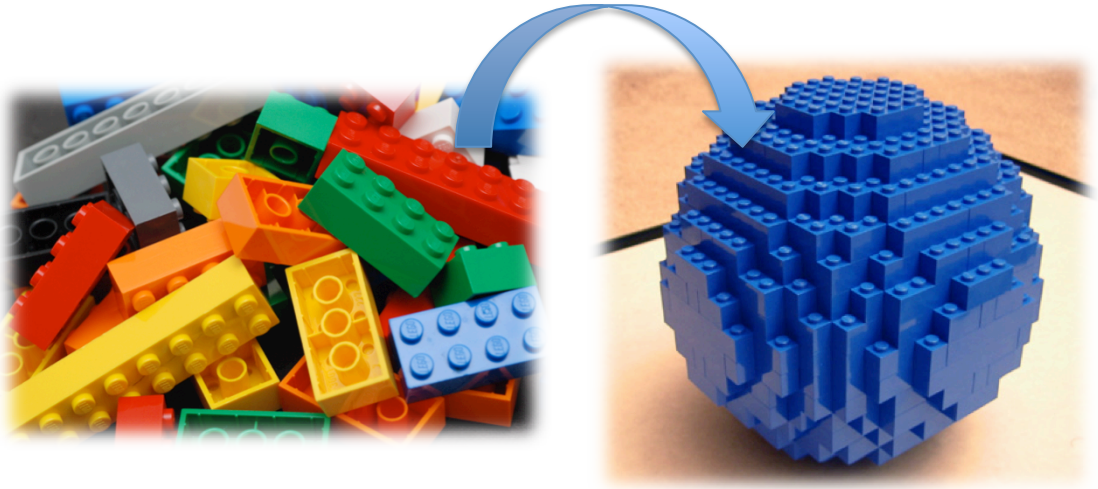
Nanometer (2 – 20 nm) sized pieces of (semiconductor) crystal in a colloidal solution phase

Quantum Dots – At the limits of nanotechnology

Nanotechnology = Manipulating matter on the “nanoscale”

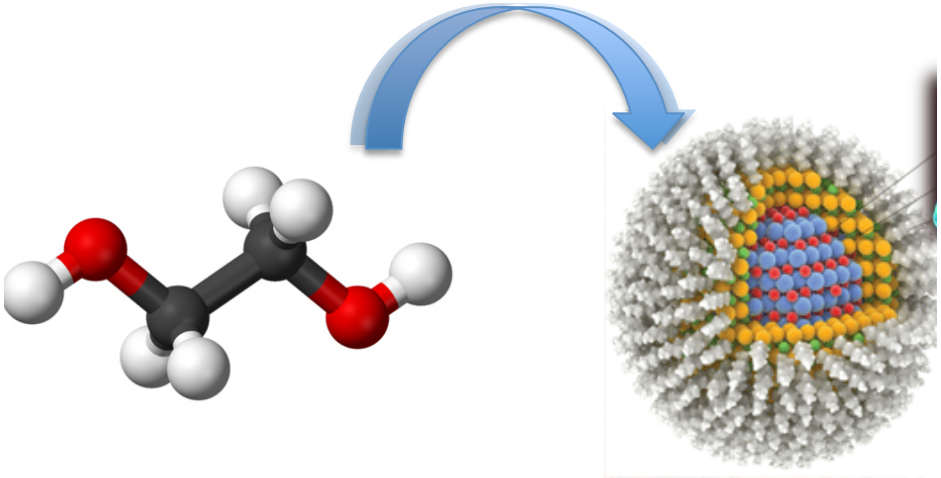


Colloidal Quantum Dots: From the Bottom Up



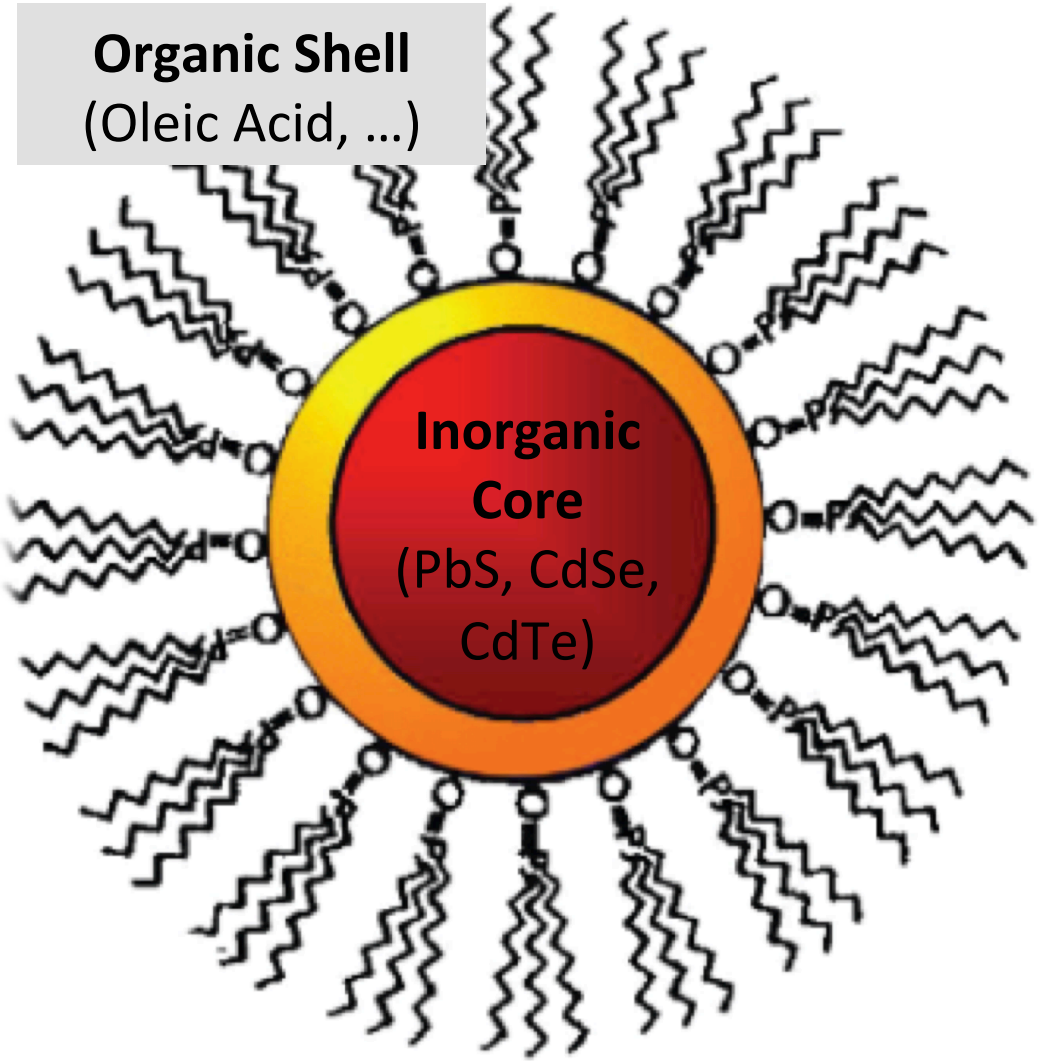
A **Lego sphere**
made of 1000
lego cubes

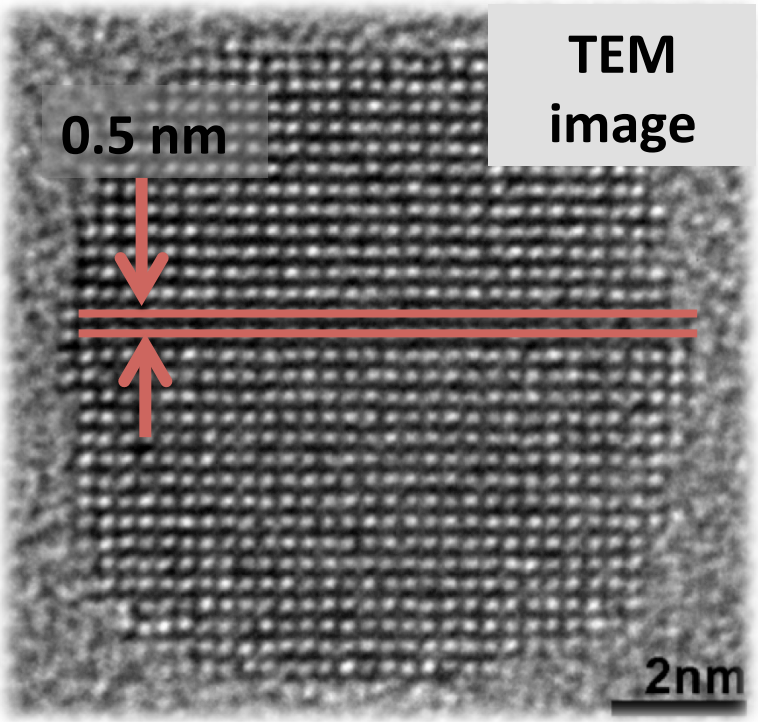
=



A **quantum dot**
made of 1000
atoms

Nanometer colloids built of individual atoms

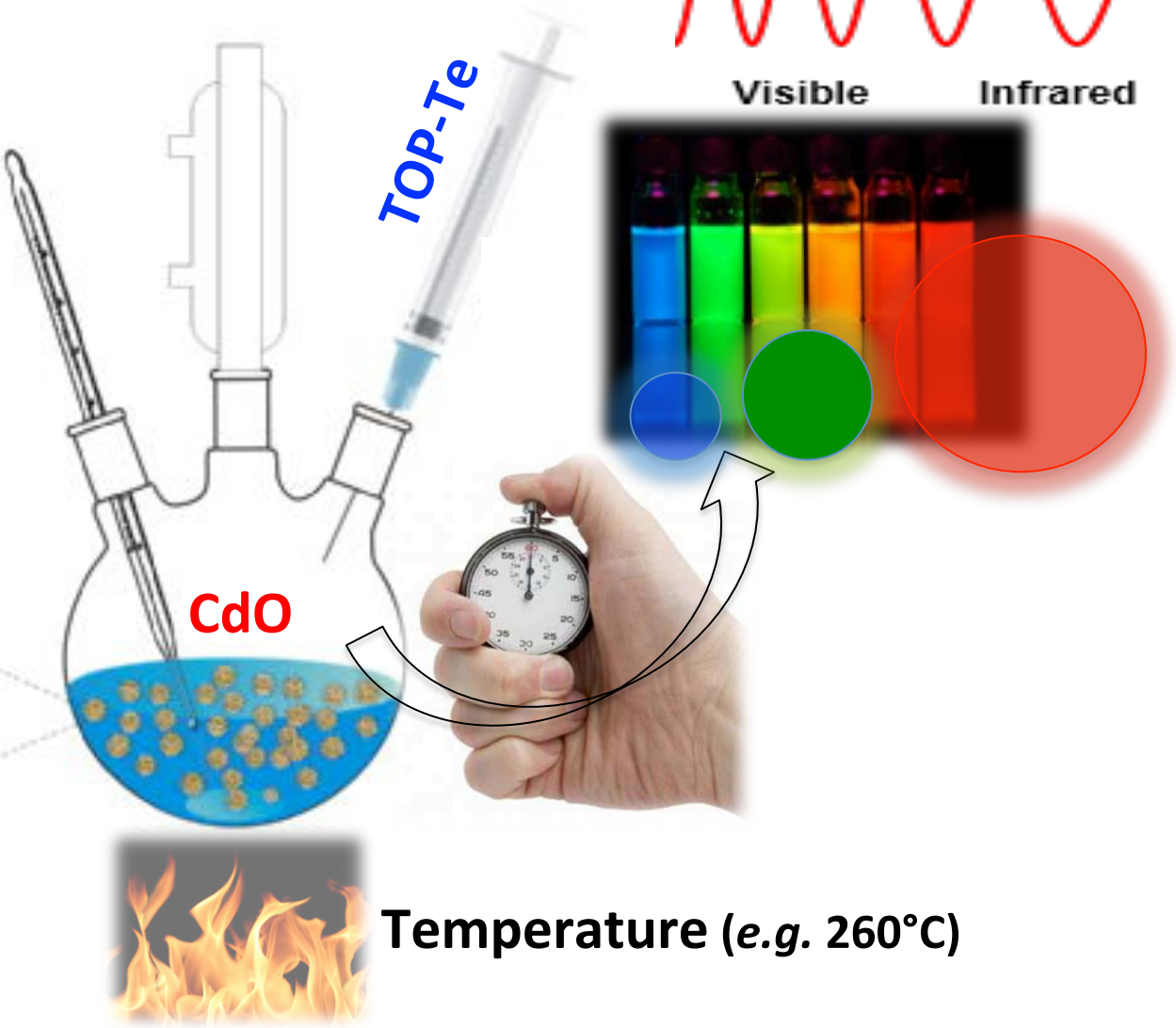




Nanometer sized pieces of **semiconductor crystal** in a **colloidal solution phase**

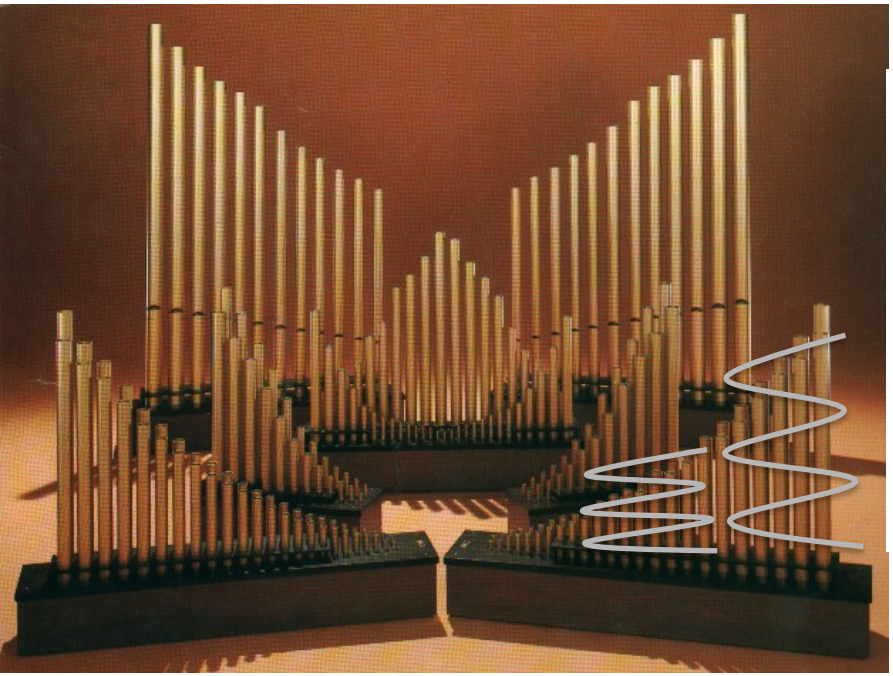
Hot Injection Synthesis

Example:
CdTe quantum dots
(Cadmium – Telluride)



Why ‘Quantum’ ?

Why would you make something smaller ?



Column length (m)	Resonant frequency (Hz)
0.2	440
0.5	172
1.0	86
1.5	57
2.0	43

High energy sound wave
=
Short pipe tube, guitar string, …

Link between **size of the tube** and **frequency** (energy) of the sound waves

1st Harmonic

$f = v / 2L$

Why ‘Quantum’ ?

The sound waves of the guitar, organ, … are **standing waves**

What happens if we squeeze an electron in a similar small volume ?

Remember! ***Particles can behave as waves***
Electrons have ‘a wavelength’

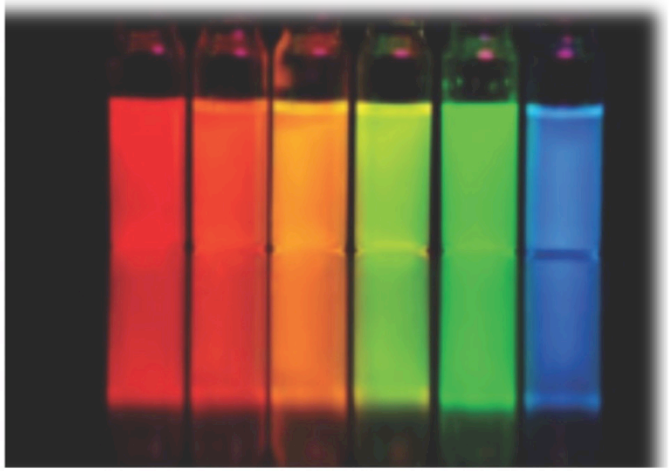
Wavelength has to fit the dimension of the resonator !

Instead of **meters** (instrument *sound* waves), now **nanometers** (electron *charge density* wave)

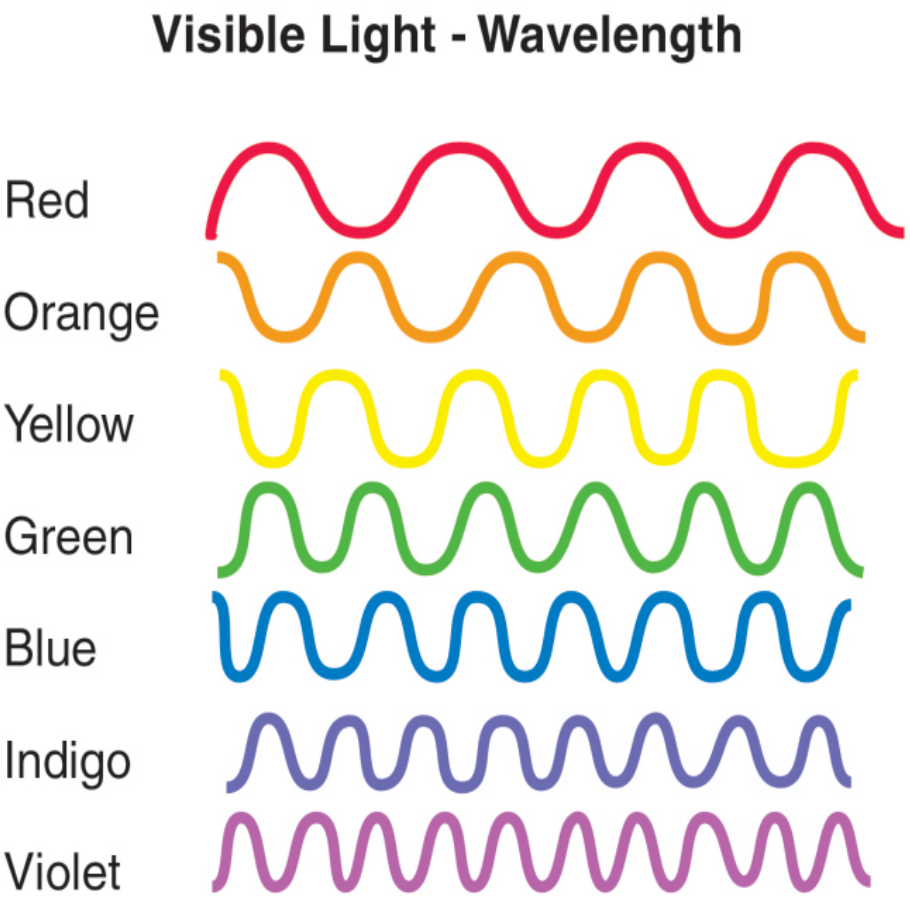
Why ‘Quantum’ ?

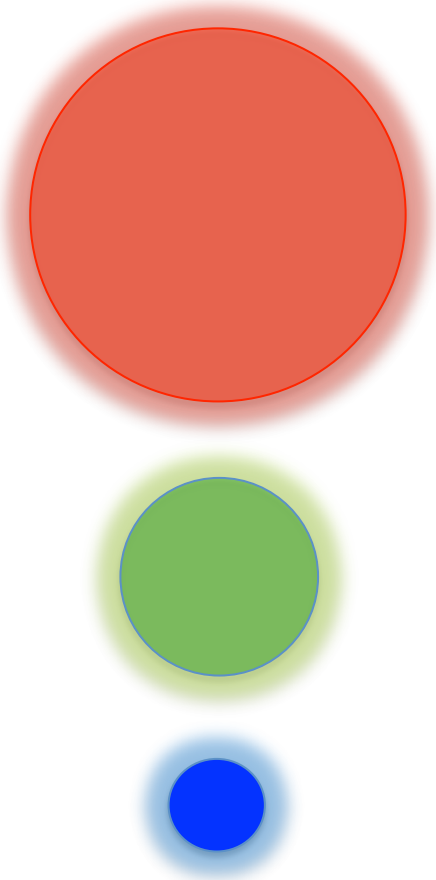
A small (large) box

Short (long) wavelength of the standing (sound, electron) wave



Size dependent optical properties





10.000 atoms

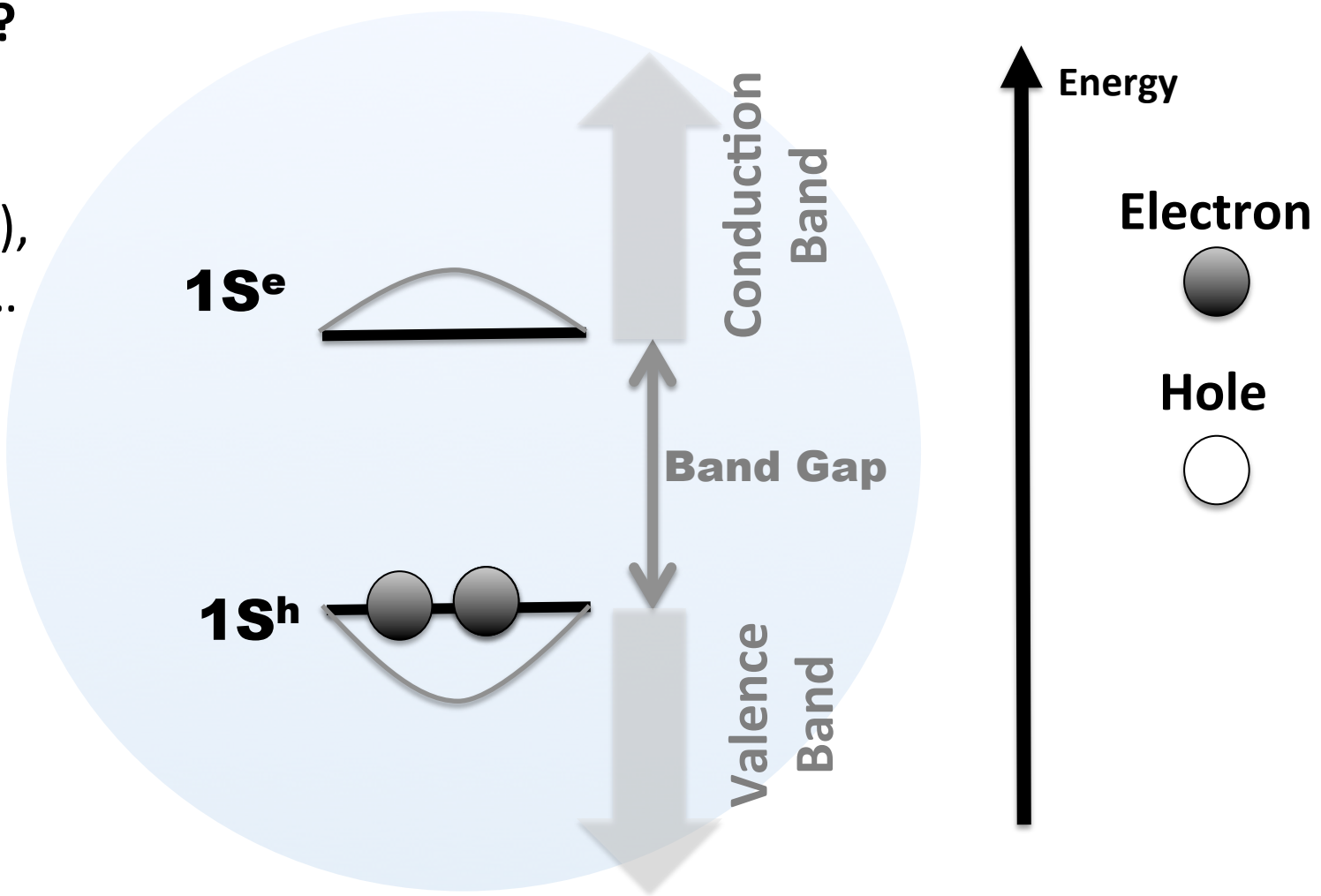
1.000 atoms

100 atoms

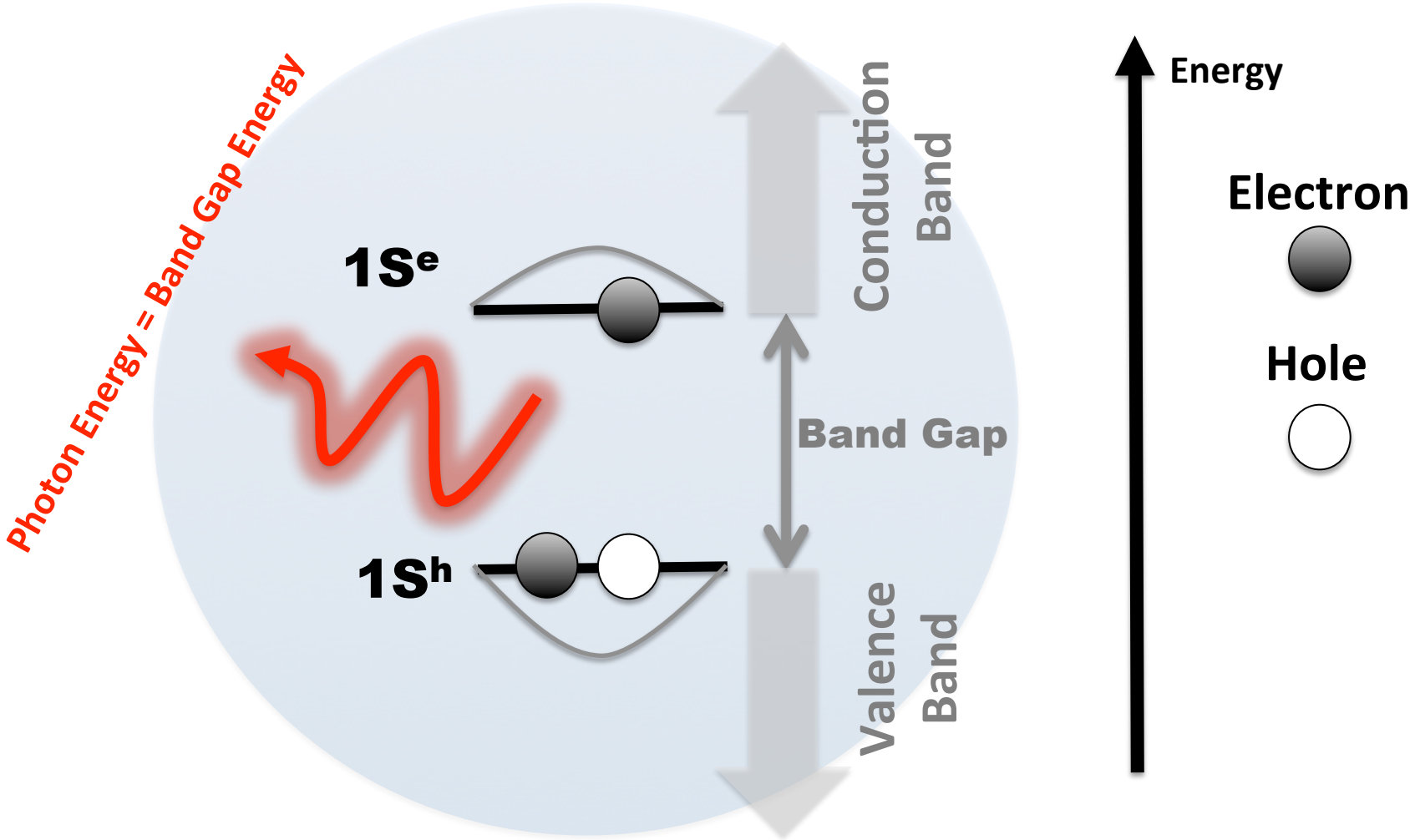
Semiconductor ?

Excitation ?

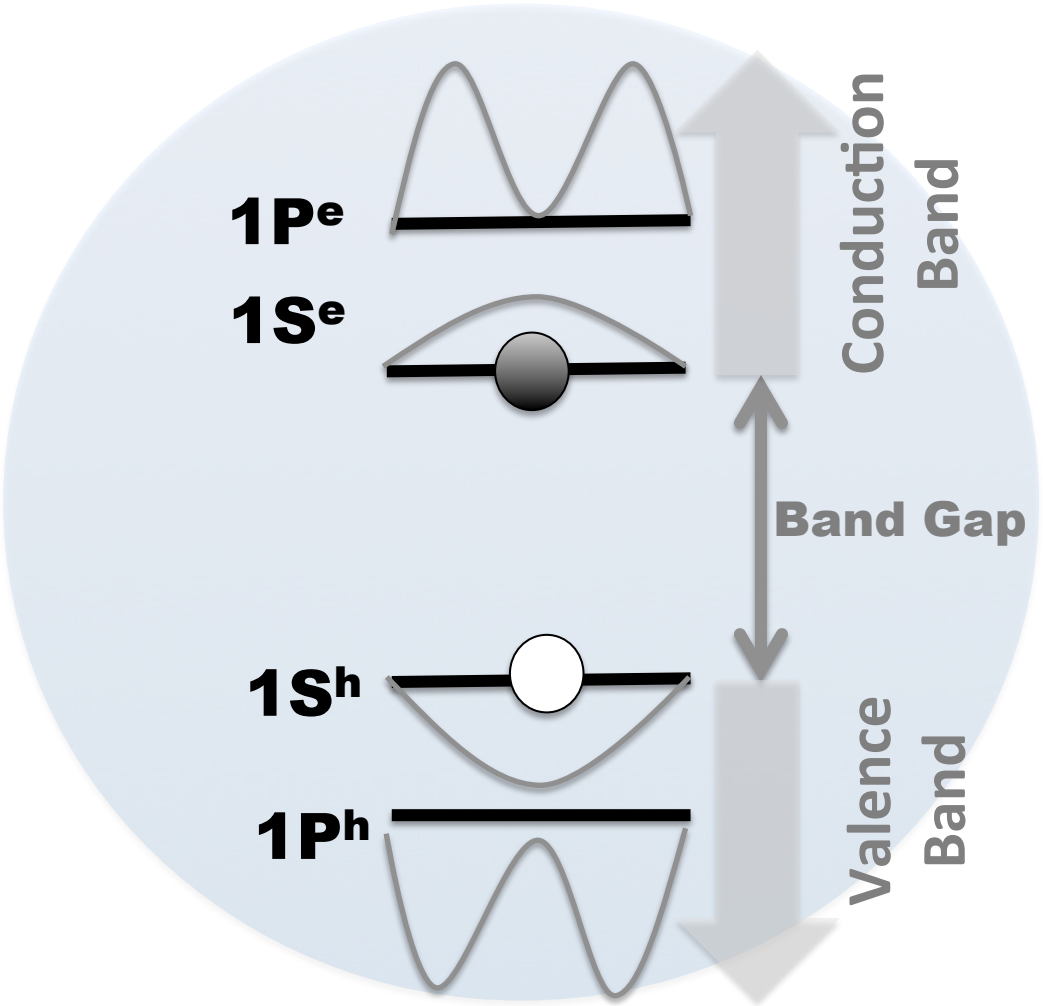
Light (absorption), electrical, …

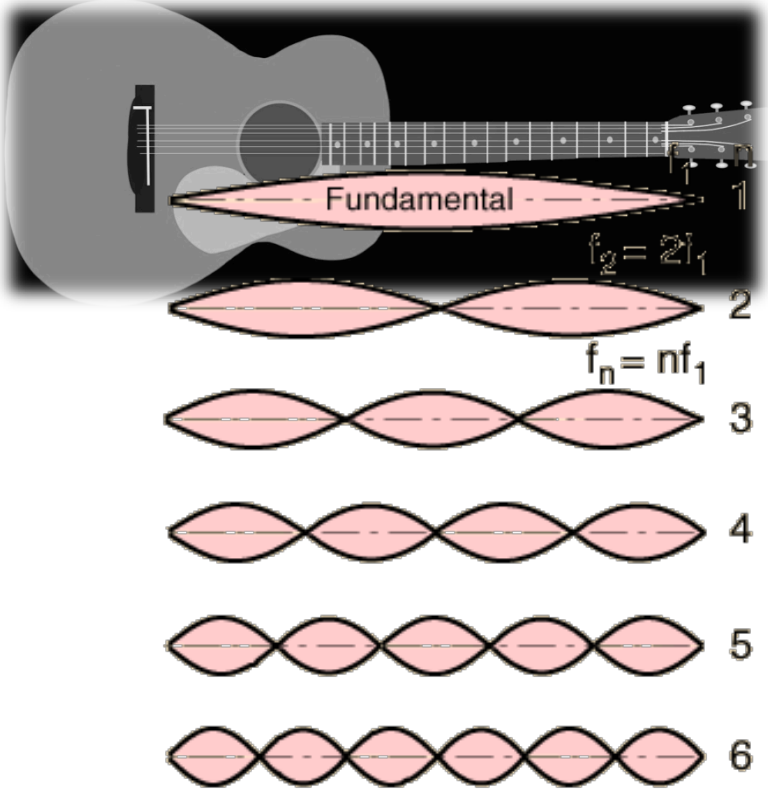


Semiconductor ?

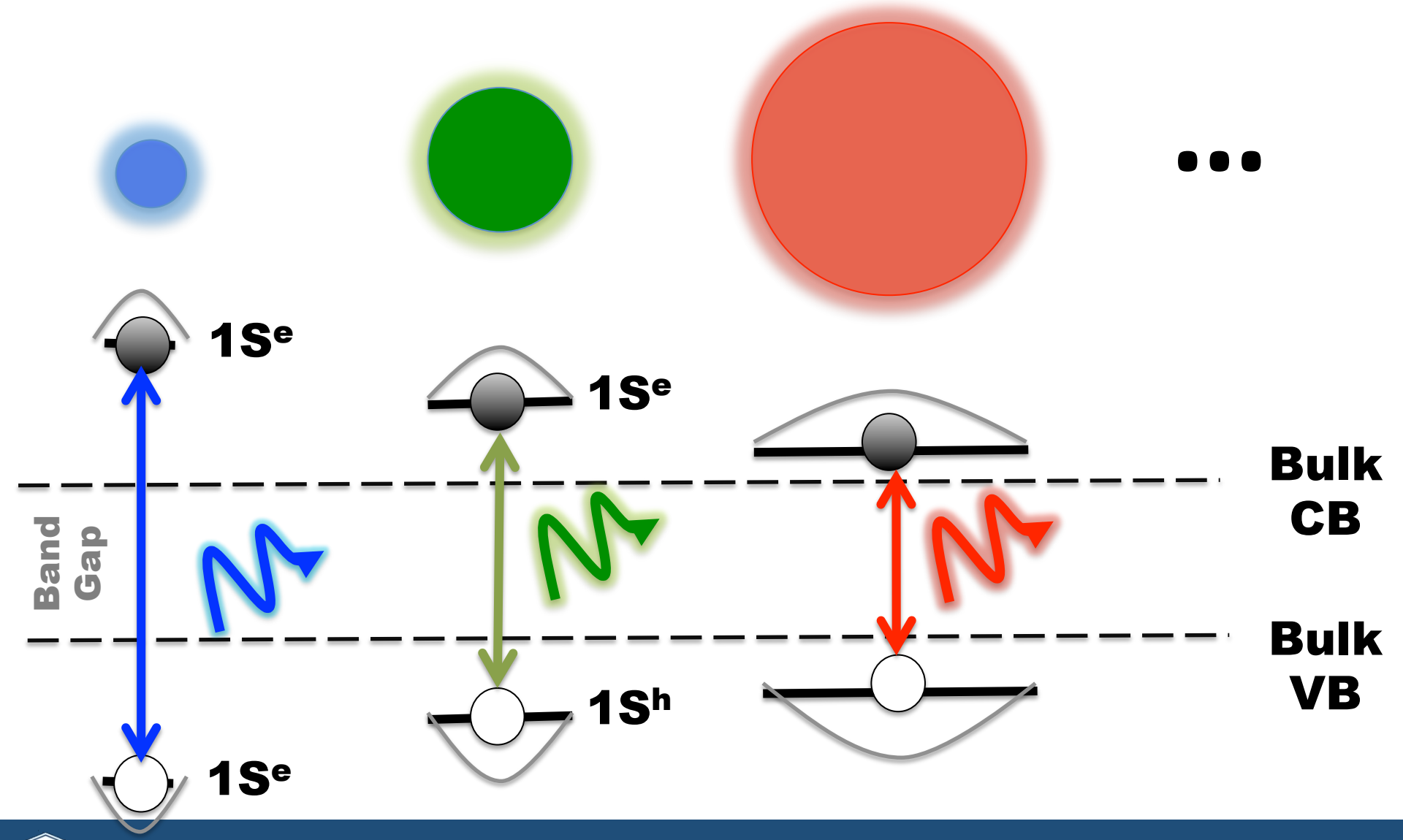


Energy levels or ‘modes’





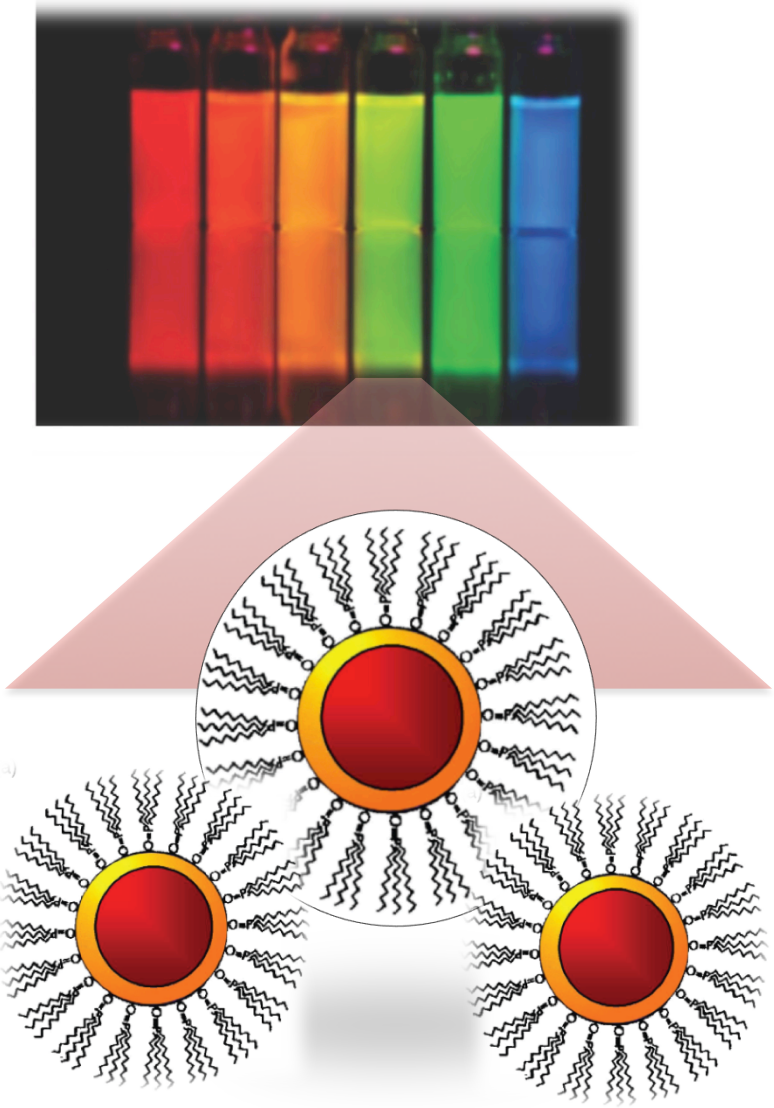
Size tunable band gap !



Colloidal Quantum Dots

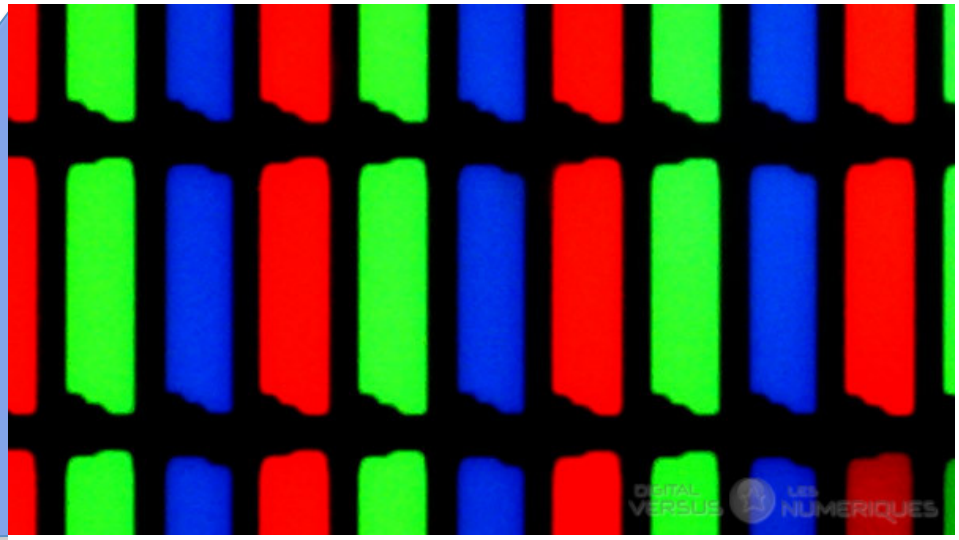
Nanometer sized pieces of **semiconductor crystal** in a **colloidal solution phase**

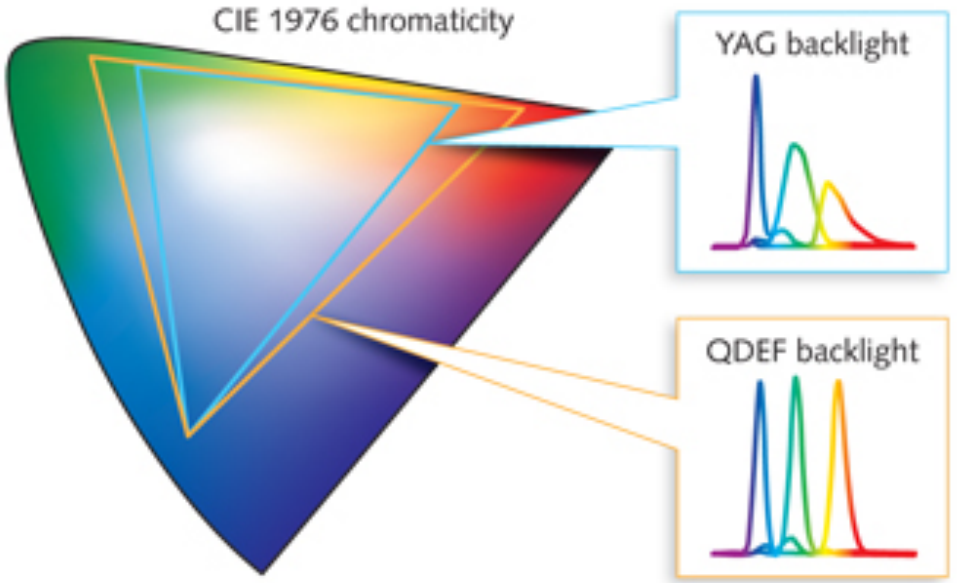
- ✓ Cheap, upscalable wet synthesis
- ✓ Easy deposition on *e.g.* silicon
- ✓ Size tunable optical properties



Quantum Dot Applications

Television Screens





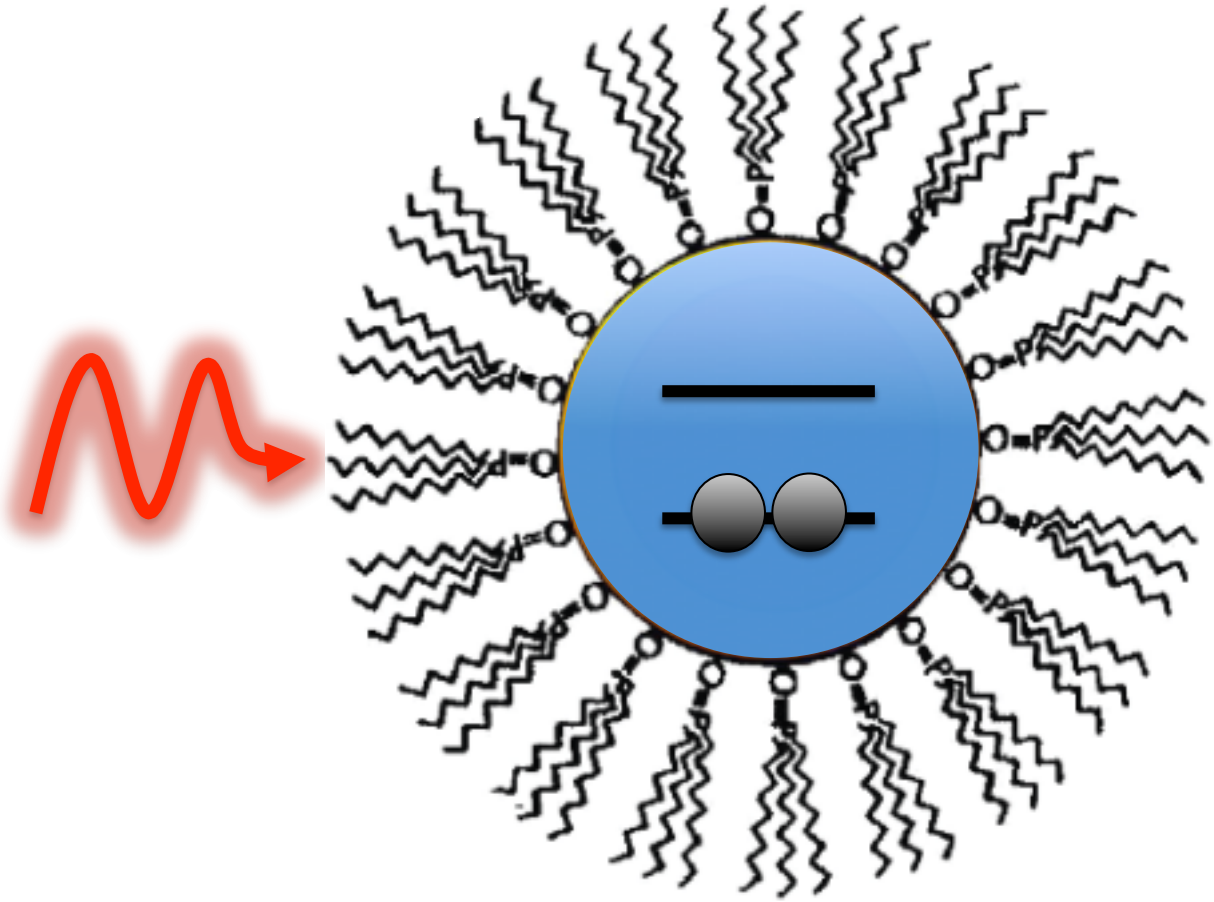
Quantum Dot Applications

Television Screens

At CES 2015: *Samsung S-UHD* with Qdots !

" … a TV with better color accuracy, a wider color gamut, brighter overall images and higher dynamic range (brighter brights and darker darks) "

Stimulated emission and Optical Gain



When a photon strikes a QD,
the type of interaction will depend on

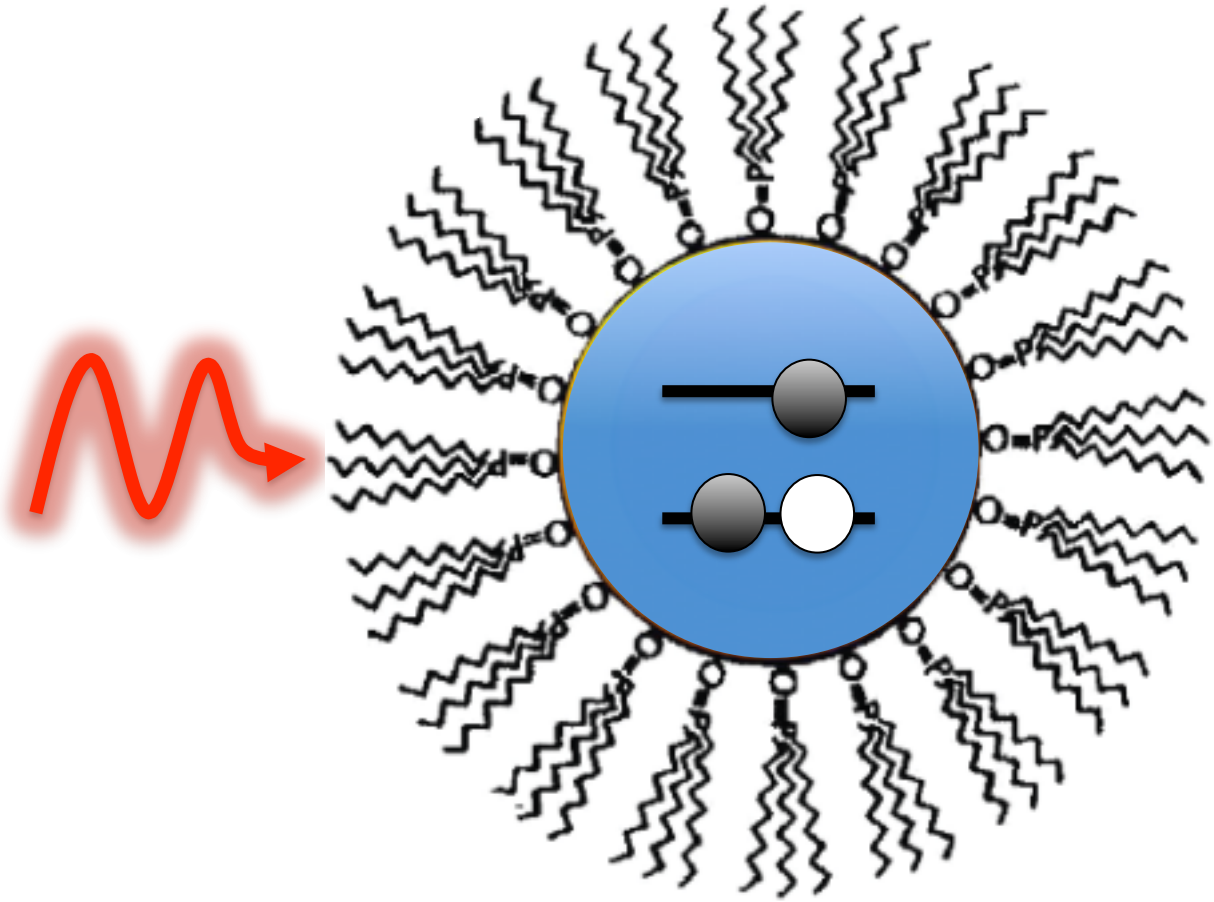
The state of the QD

No Charge

Single Charge

Double Charge

Stimulated emission and Optical Gain



When a photon strikes a QD,
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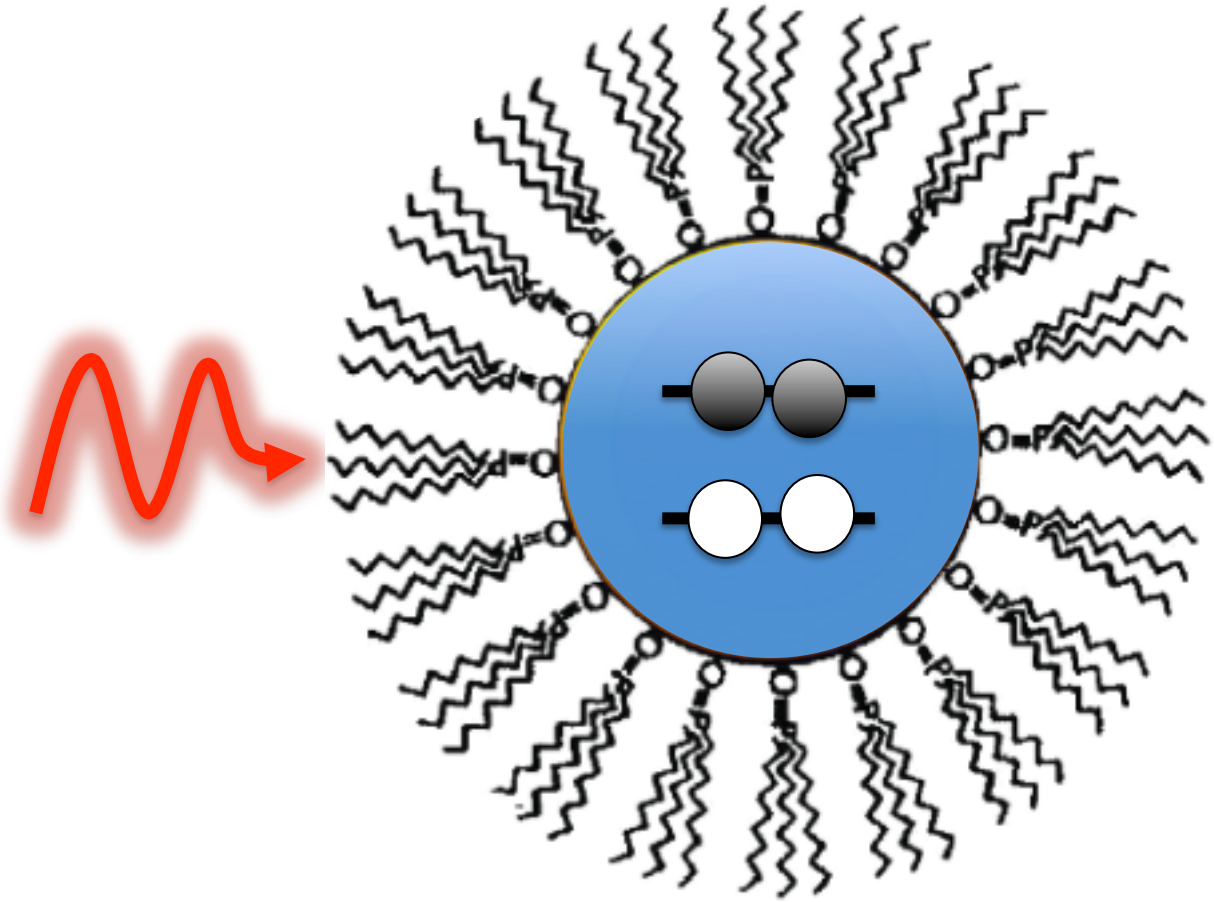
The state of the QD

No Charge

<u>Single Charge</u>

Double Charge

Stimulated emission and Optical Gain



When a photon strikes a QD,
the type of interaction will depend on

The state of the QD

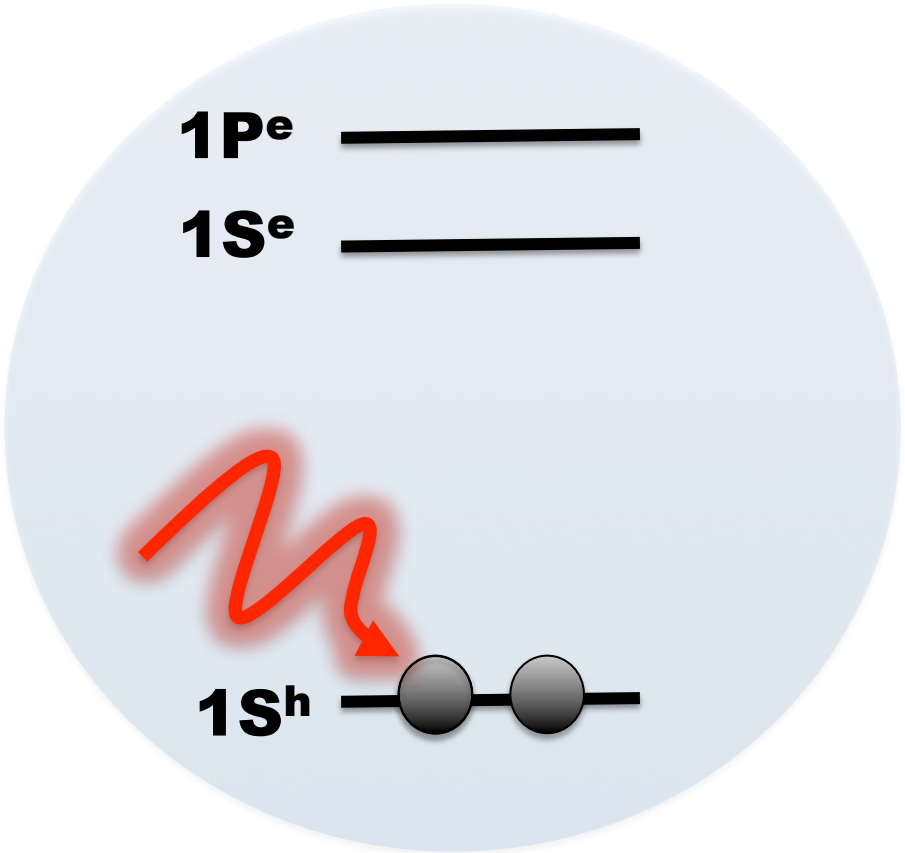
No Charge

Single Charge

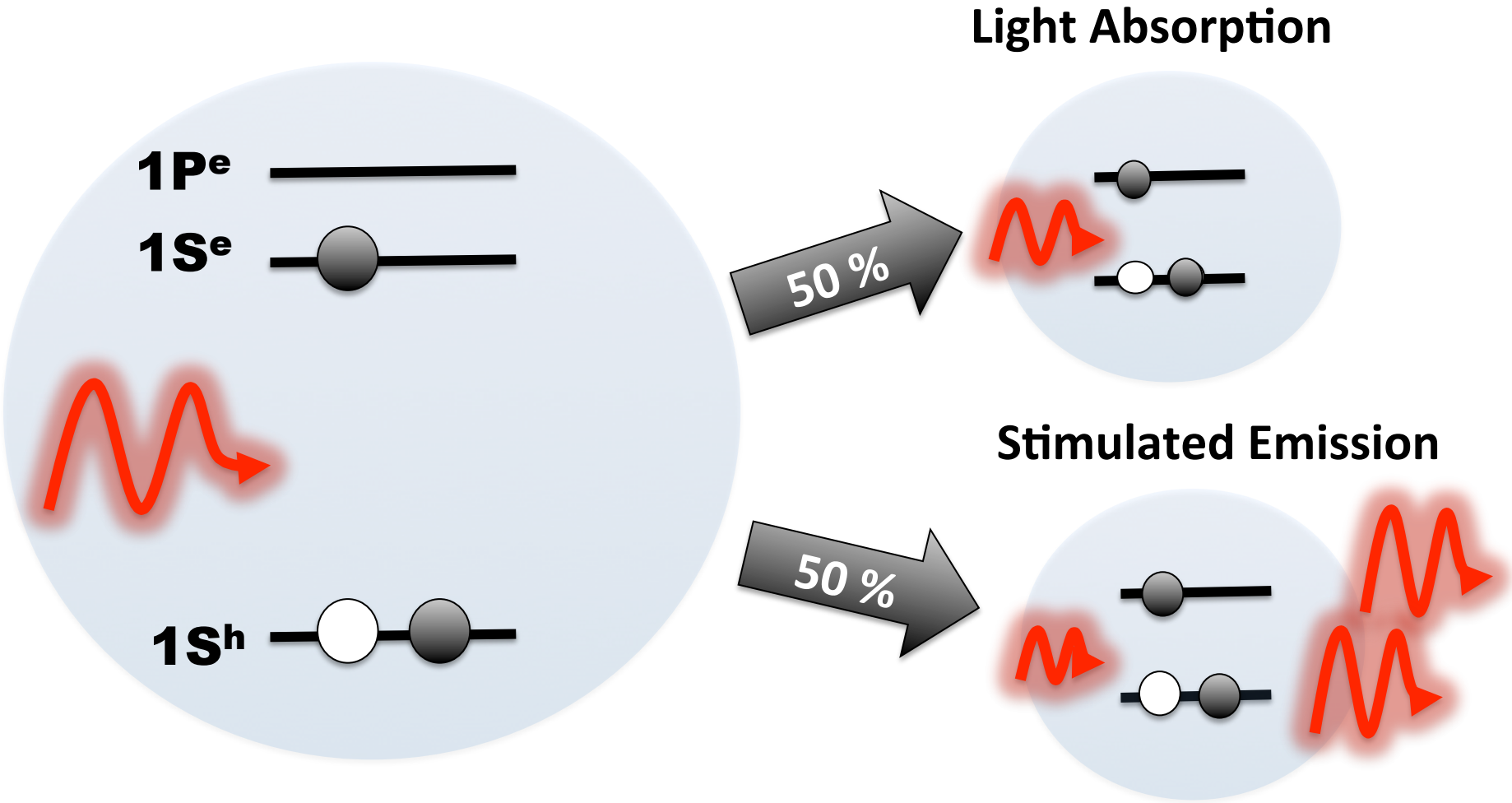
<u>Double Charge</u>

Empty Quantum Dot

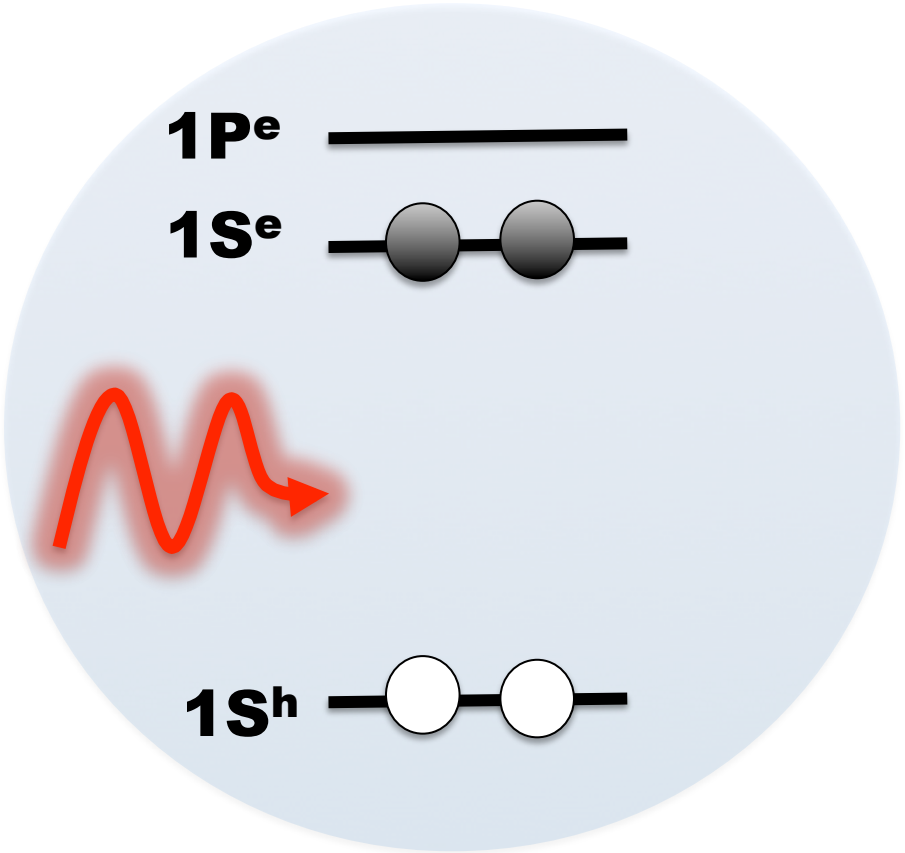
Light Absorption

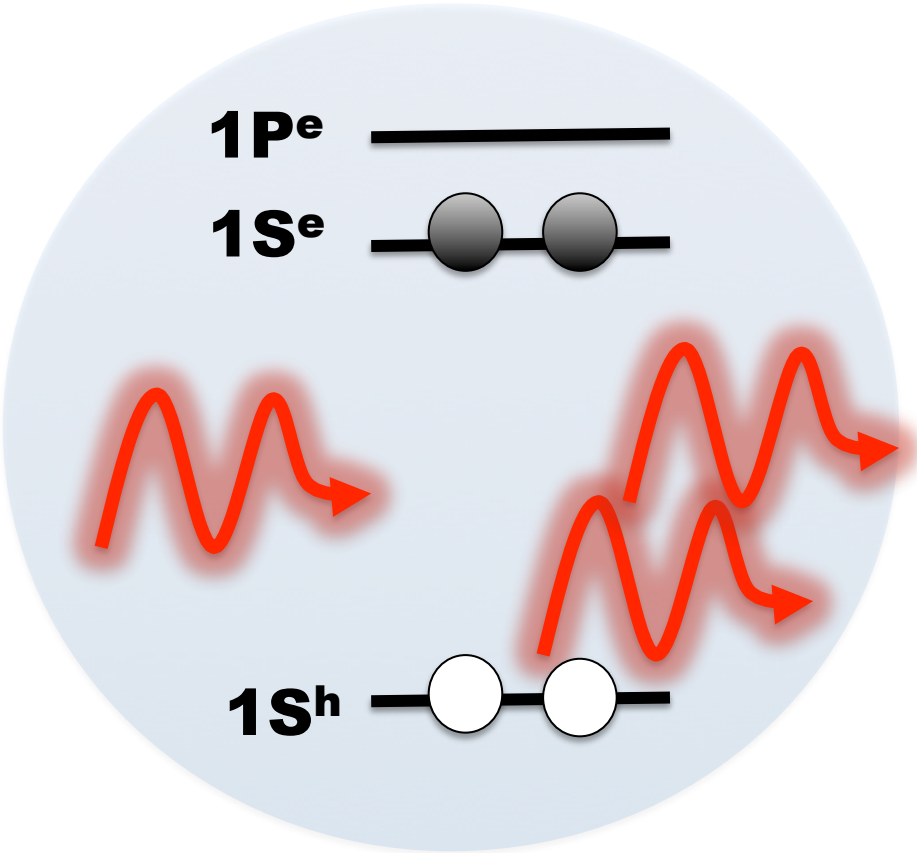


Single Excited Quantum Dot

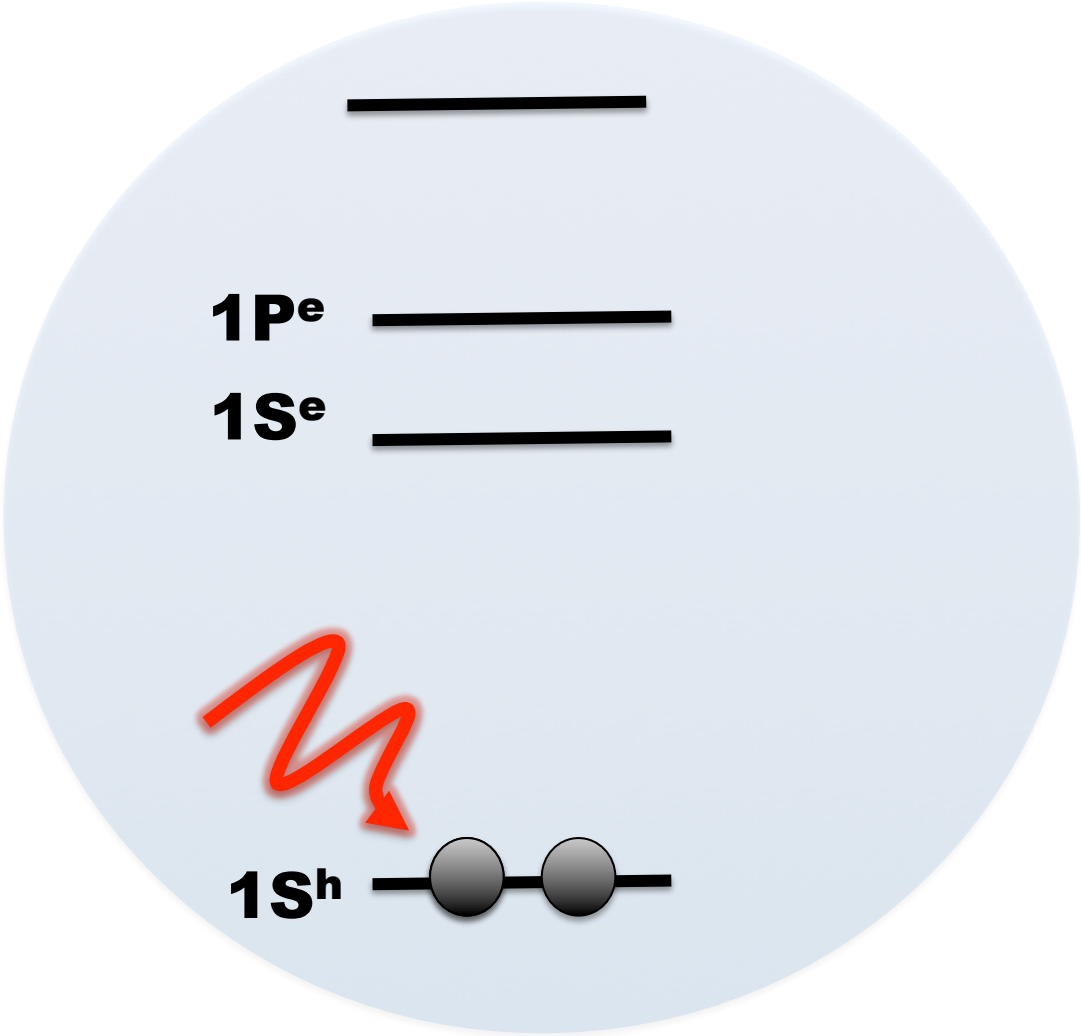


Double Excited Quantum Dot

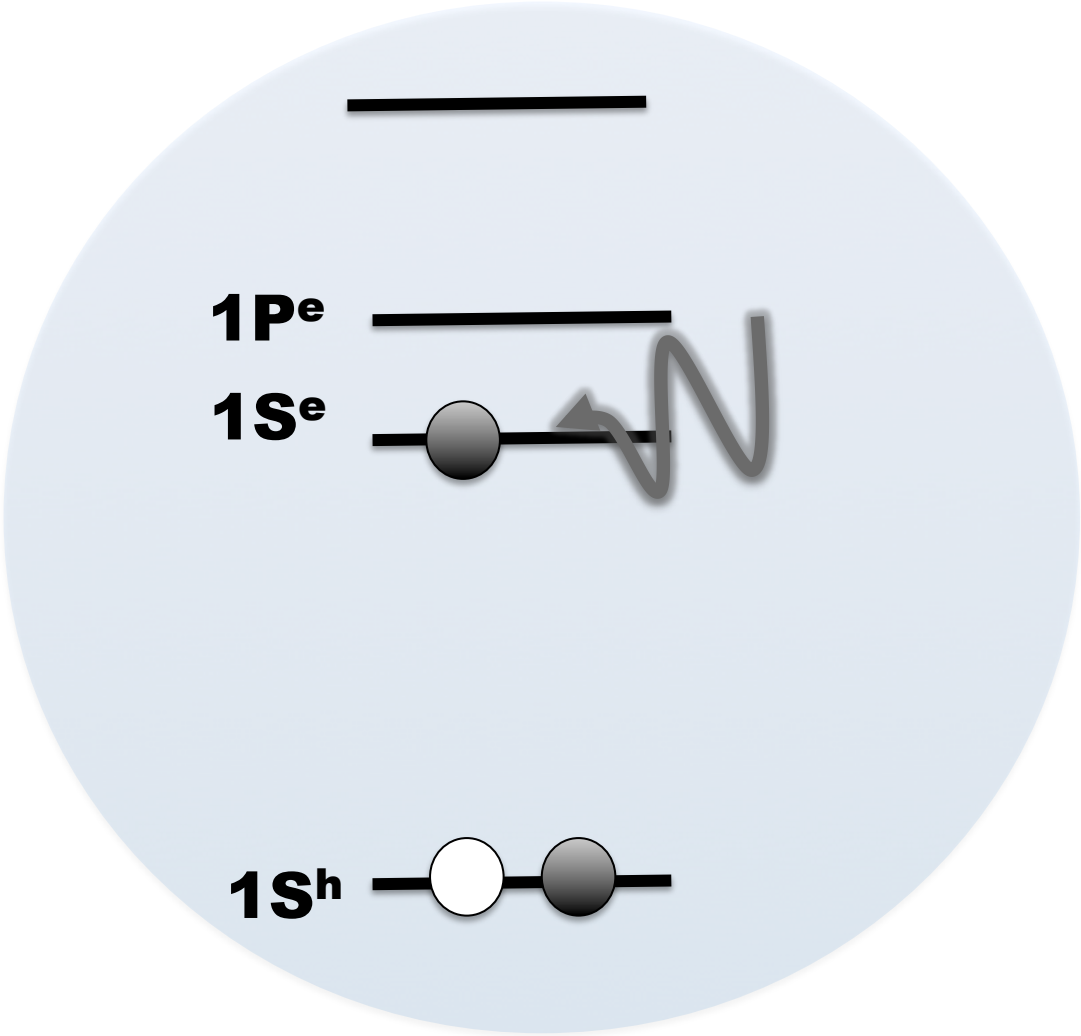




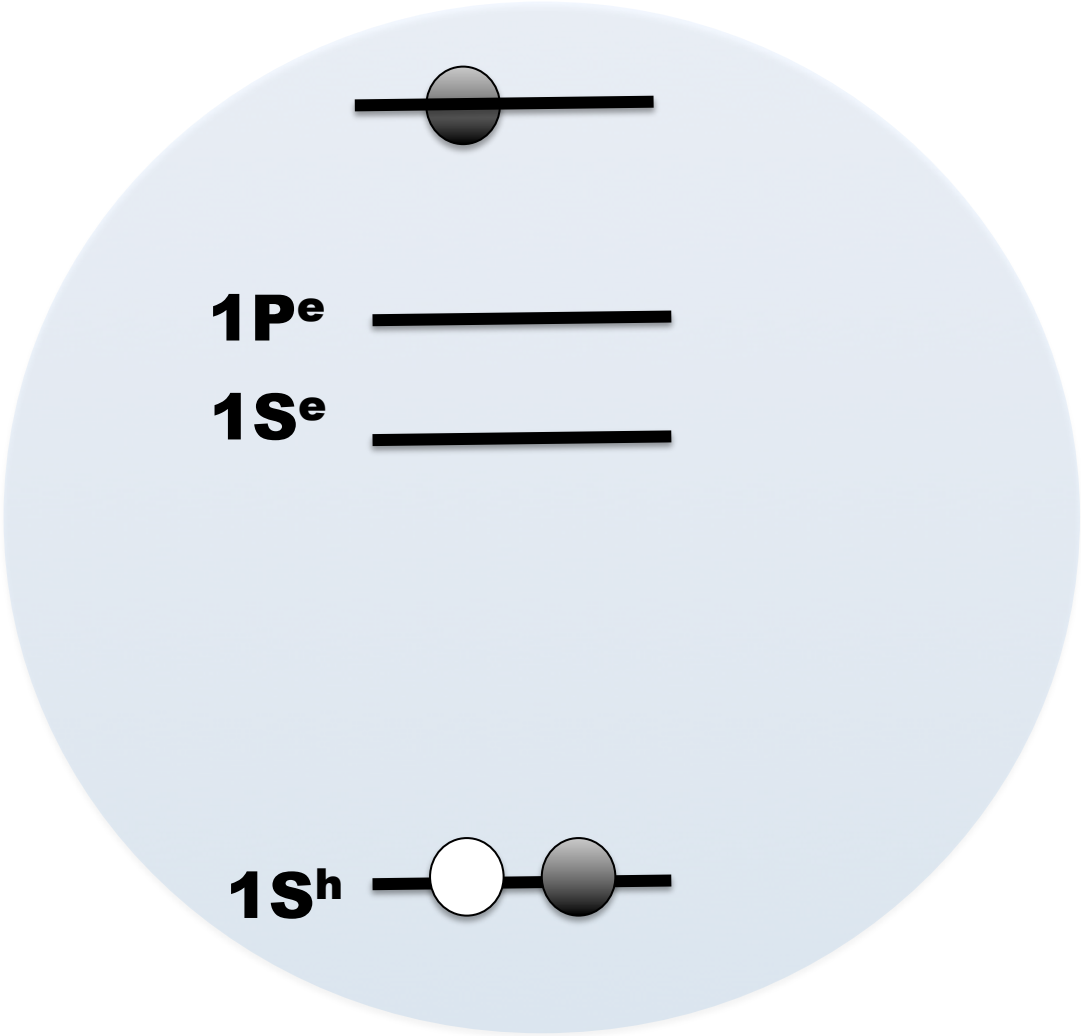
Intraband Absorption and Relaxation



Intraband Absorption and Relaxation



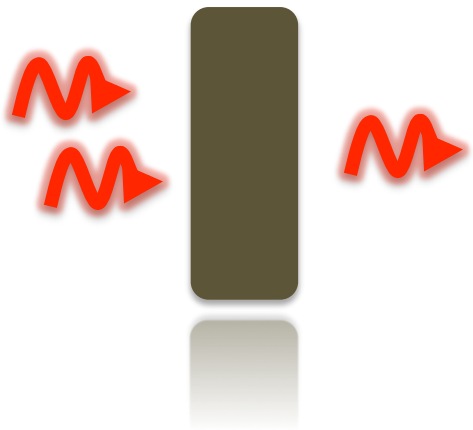
Intraband Absorption and Relaxation



How to describe these interactions ?

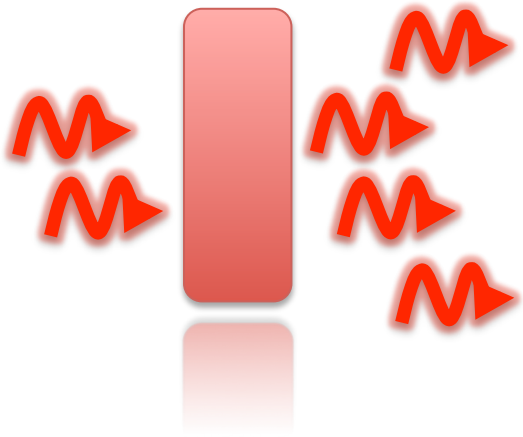
- ✓ **Sample Absorbance**, noted as ***A***
- ✓ **Change of Sample Absorbance (**upon photoexcitation), noted as ***ΔA***

A > 0



A = 0

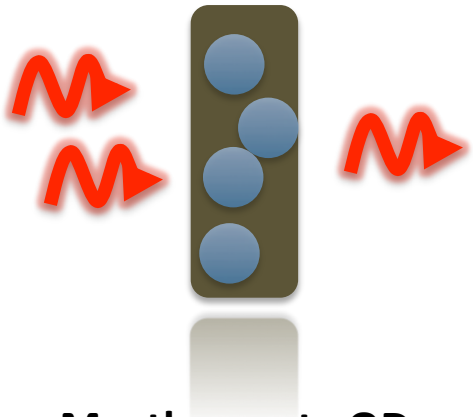
A < 0



How to describe these interactions ?

- ✓ **Sample Absorbance**, noted as ***A***
- ✓ **Change of Sample Absorbance (**upon photoexcitation), noted as ***ΔA***

A > 0



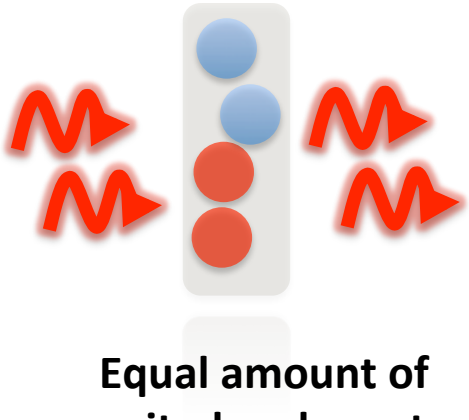
Mostly empty QDs

Absorption

V

Stimulated emission

A = 0



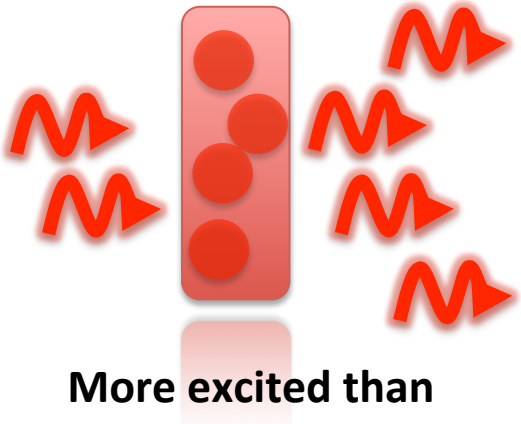
Equal amount of excited and empty

Absorption

II

Stimulated emission

A < 0



More excited than empty dots

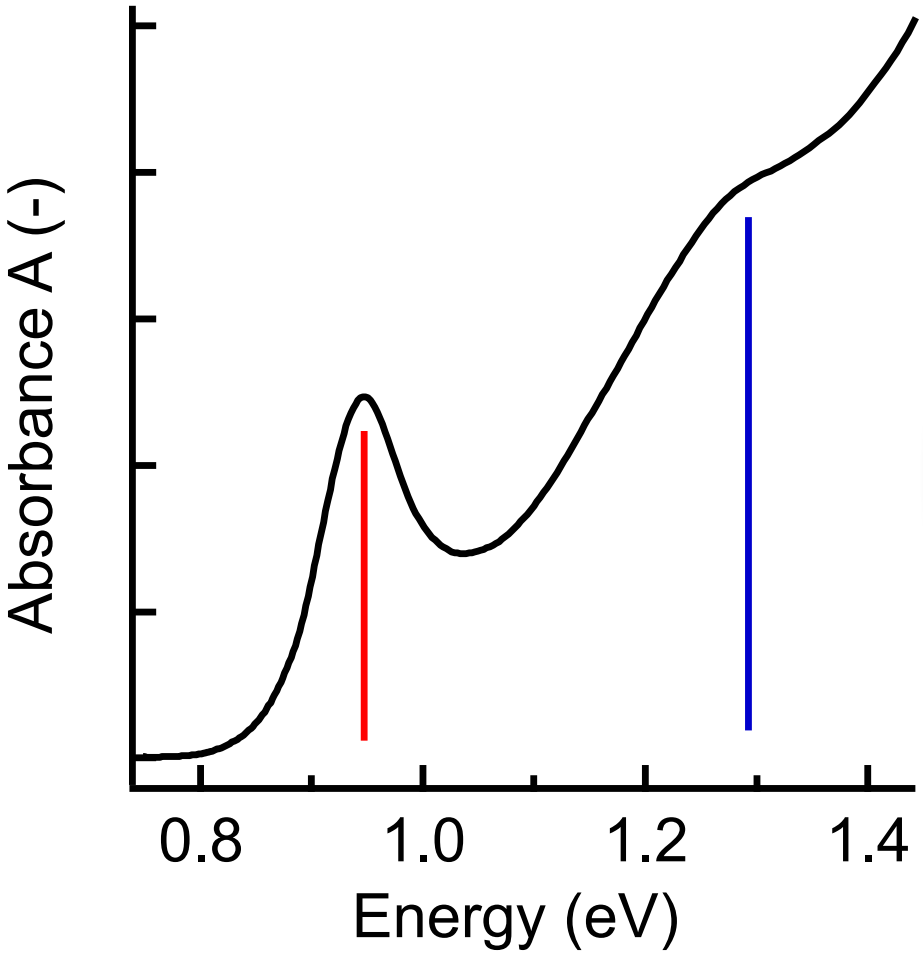
Absorption

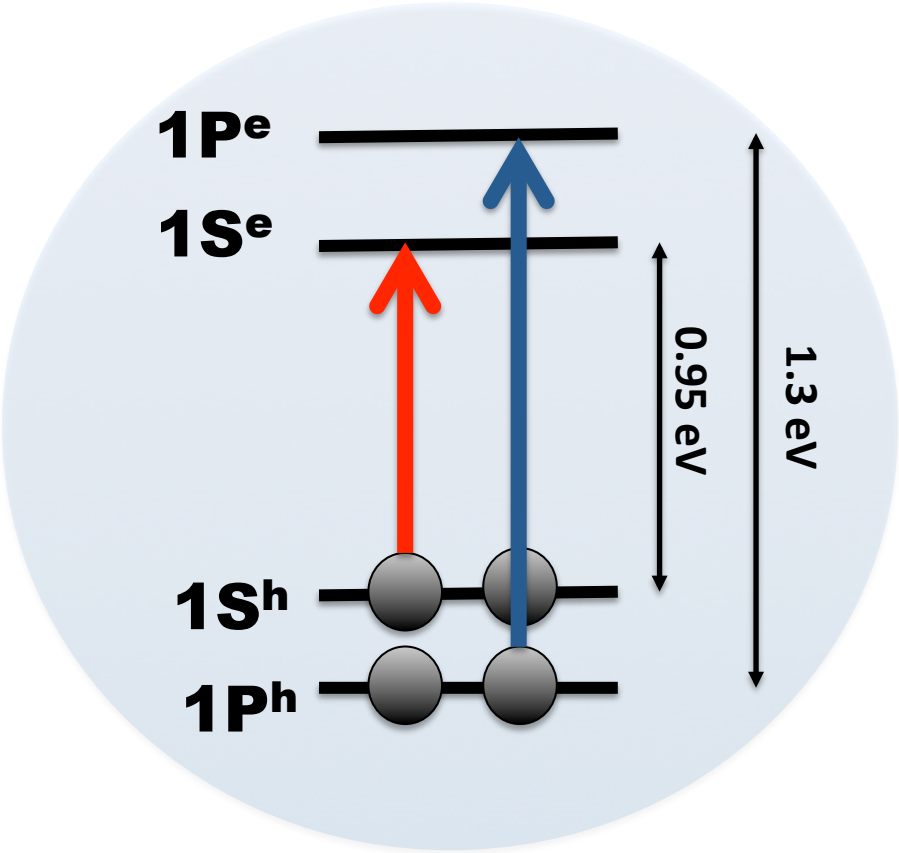
Λ

Stimulated emission

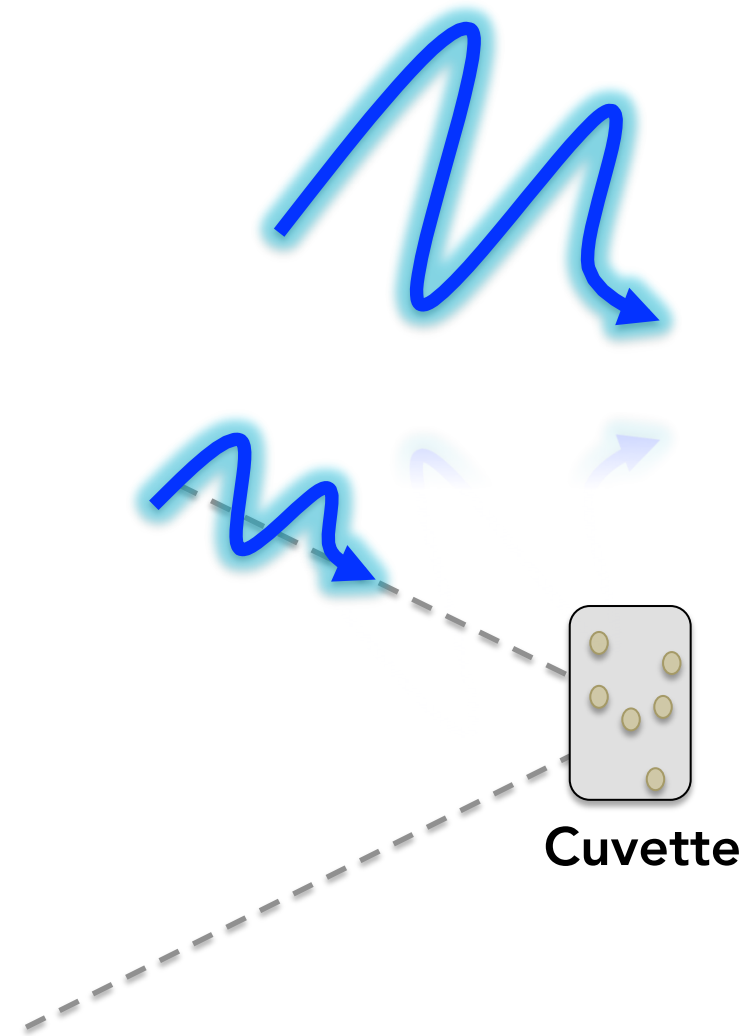
Sample absorbance of unexcited crystal A_0

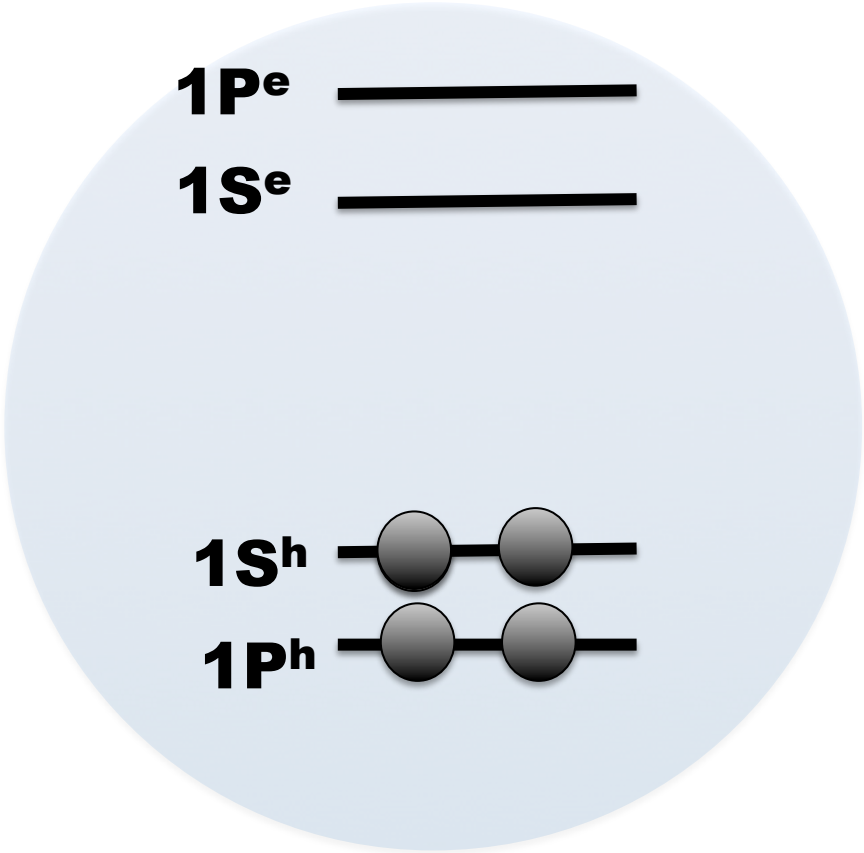
Depends on the energy of the incoming light (photons) !

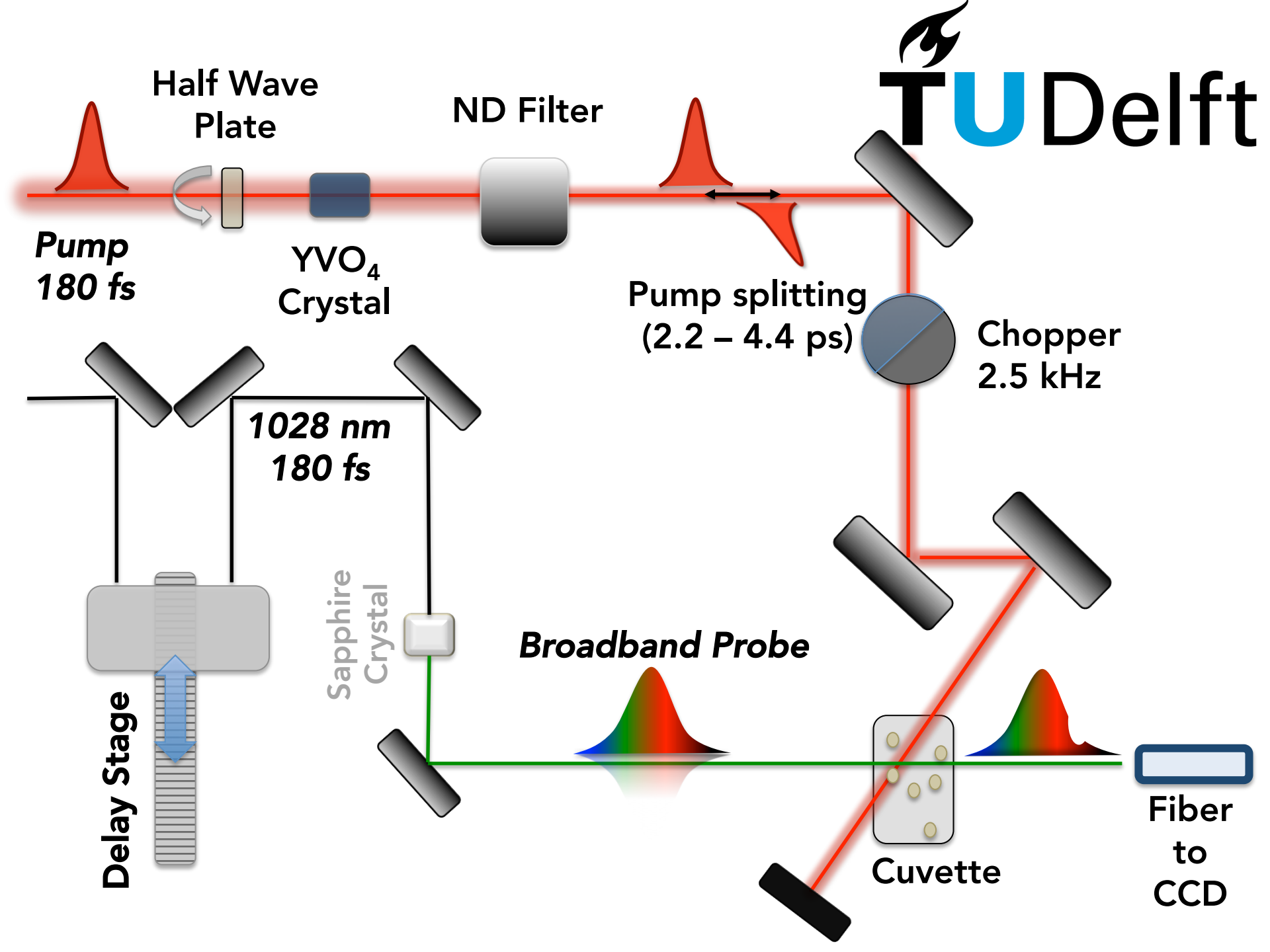


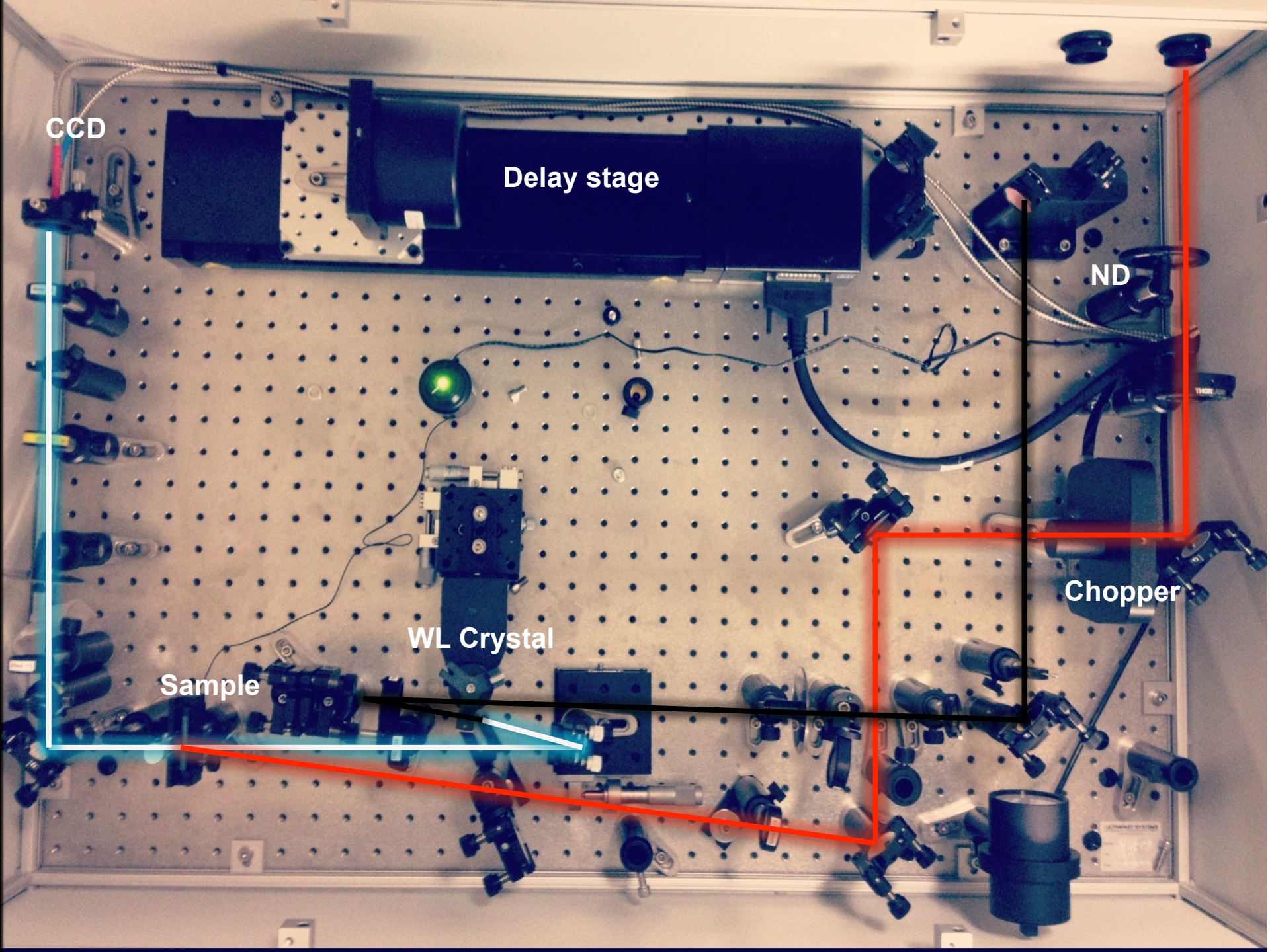


Pump – Probe Spectroscopy

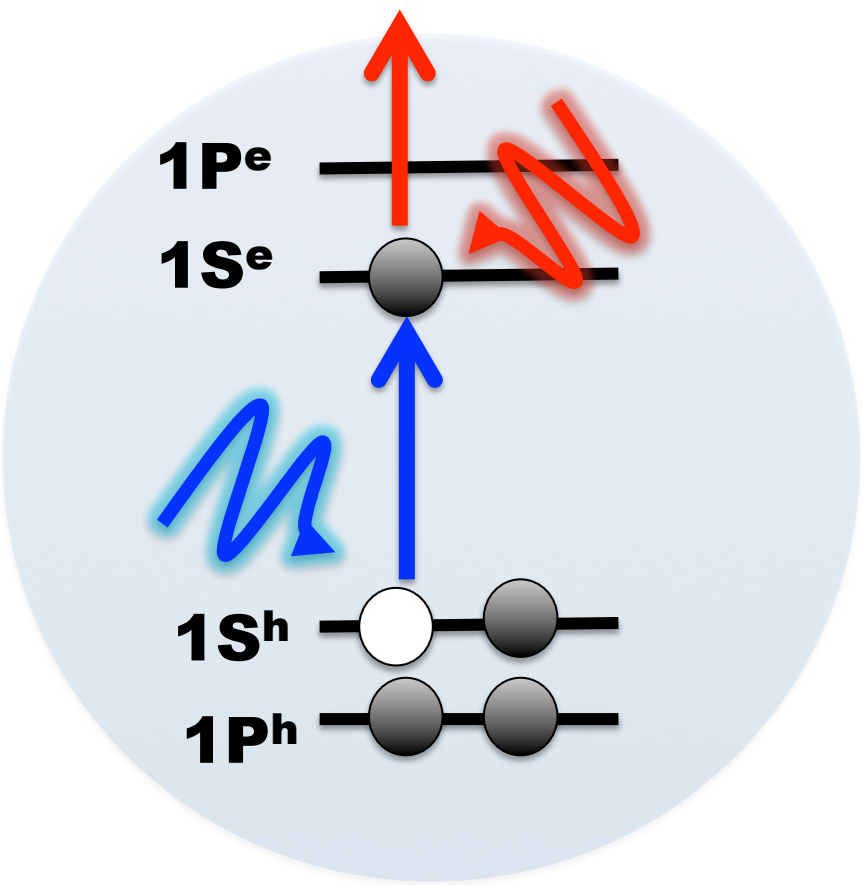





Half Wave Plate
ND Filter
Pump 180 fs
YVO4 Crystal
Pump splitting (2.2 – 4.4 ps)
Chopper 2.5 kHz
1028 nm 180 fs
Sapphire Crystal
Broadband Probe
Delay Stage
Cuvette
Fiber to CCD


CCD
Delay stage
ND
Chopper
WL Crystal
Sample

Sample absorbance upon photoexcitation



Effect of photo-excitation on incident probe ?

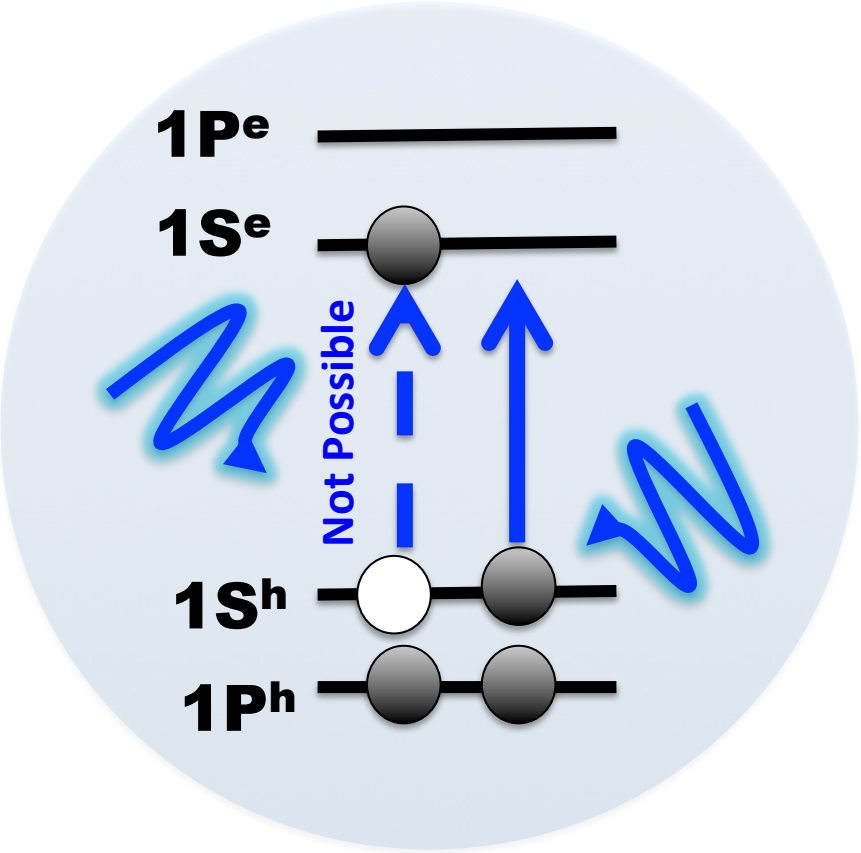
***Inter*-band bleaching** (reduction of absorbance) due to state filling with photogenerated carriers

ΔA < 0

***Intra*-band absorption** (increase of absorbance) between quantized states within same band

ΔA > 0

Sample absorbance upon photoexcitation



Effect of photo-excitation on incident probe ?

***Inter*-band bleaching**

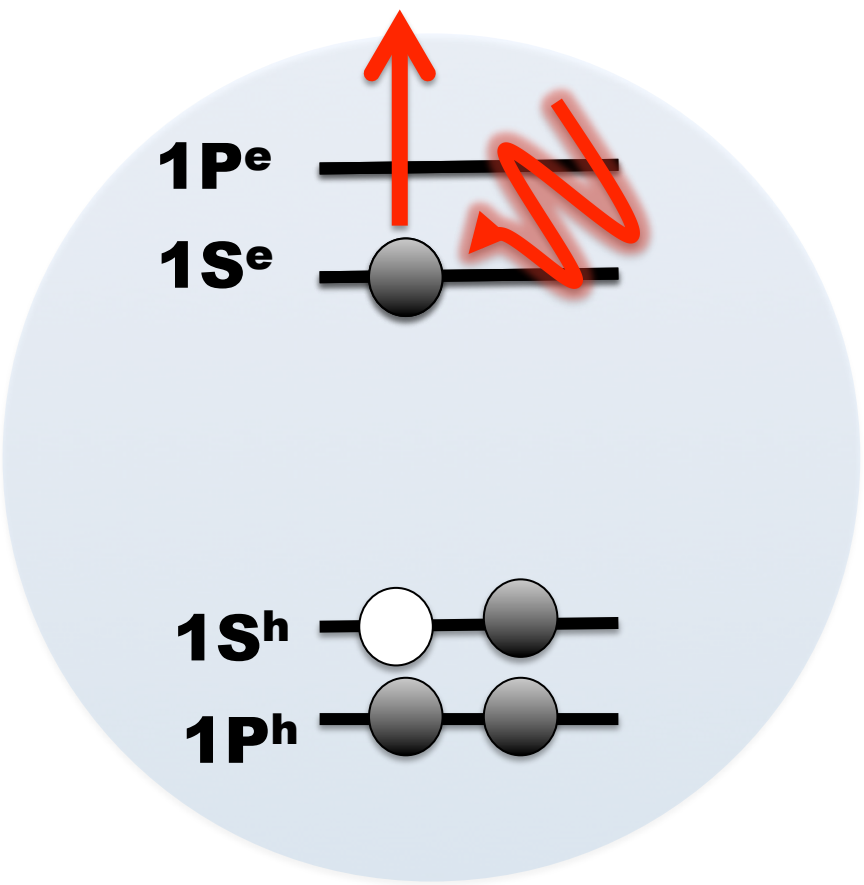
Reduction of absorbance due to state filling with photogenerated carriers

$\Delta A < 0$

With 1 excitation:

$\Delta A/A_0 = -1/2$

Sample absorbance upon photoexcitation



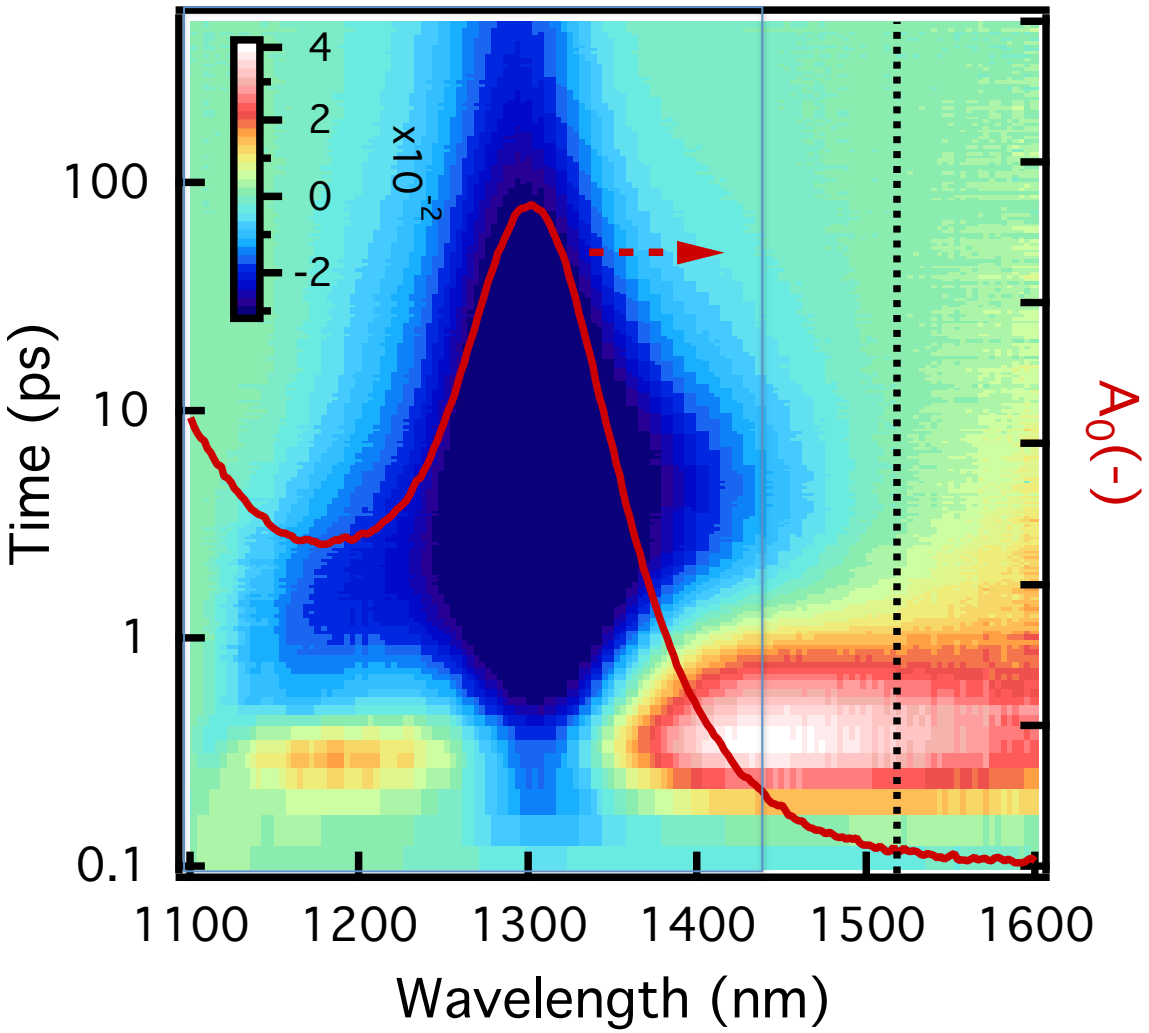
Effect of photo-excitation on incident probe ?

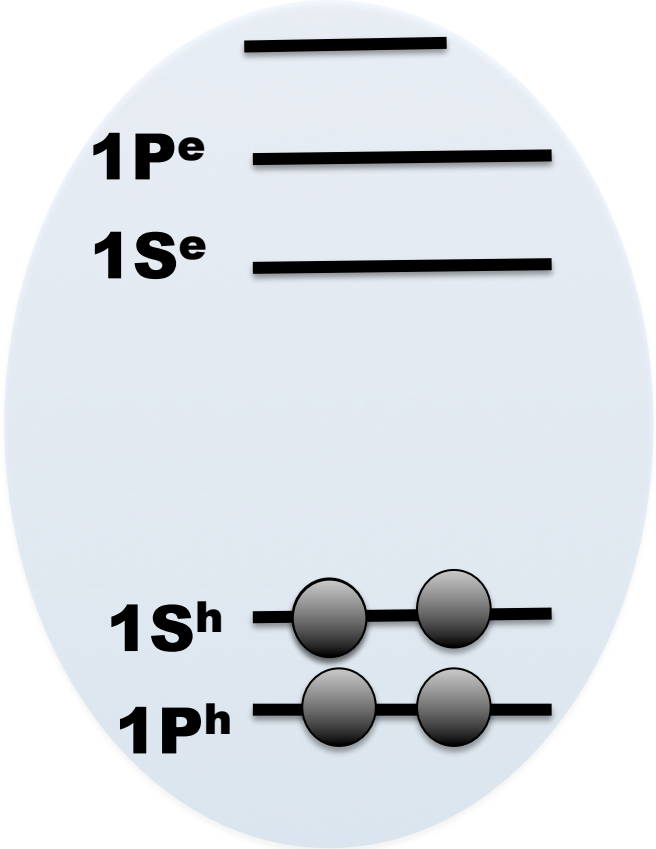
Intra-band absorption

Increase of absorbance due to state filling with photogenerated carriers

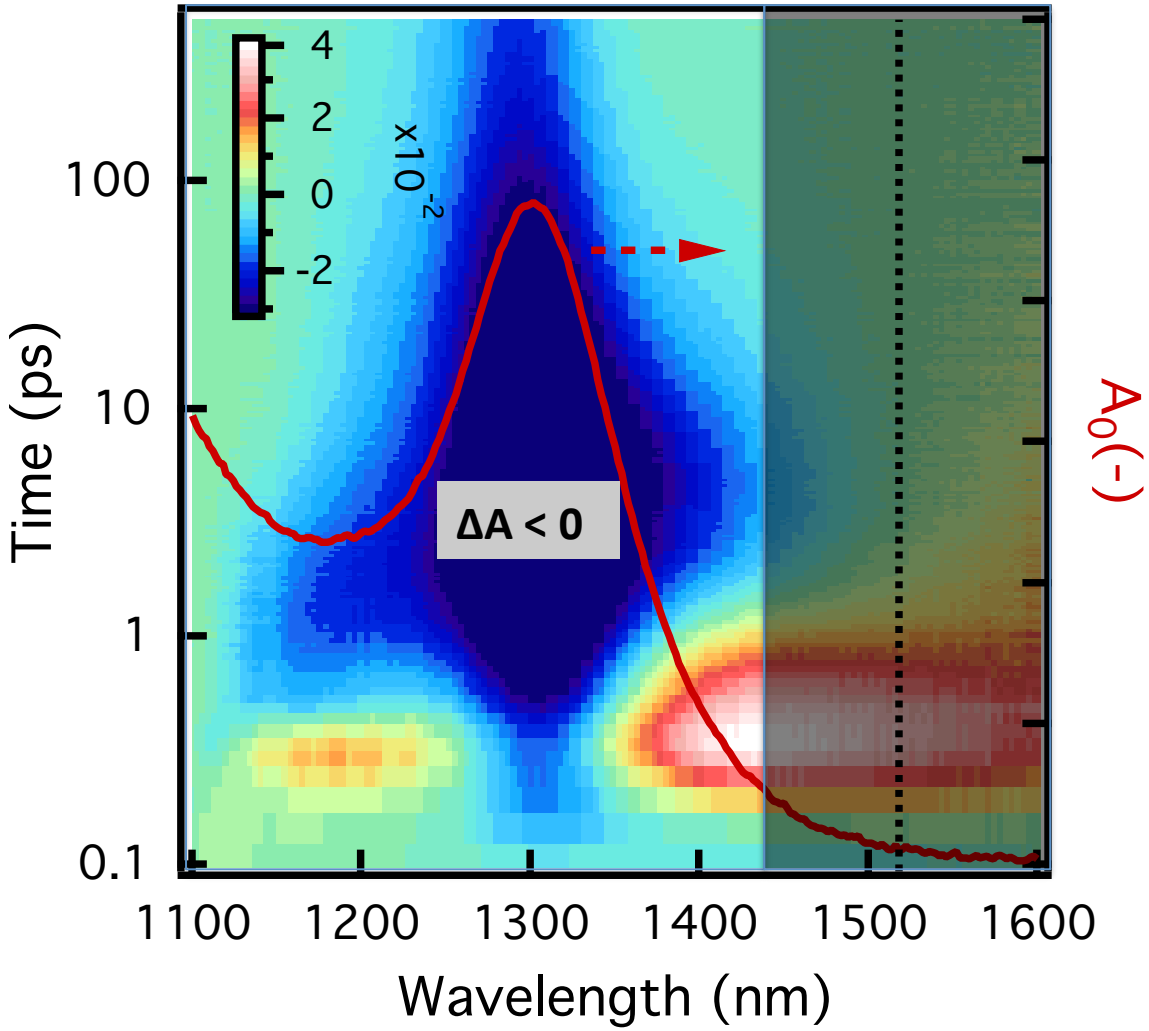
ΔA > 0

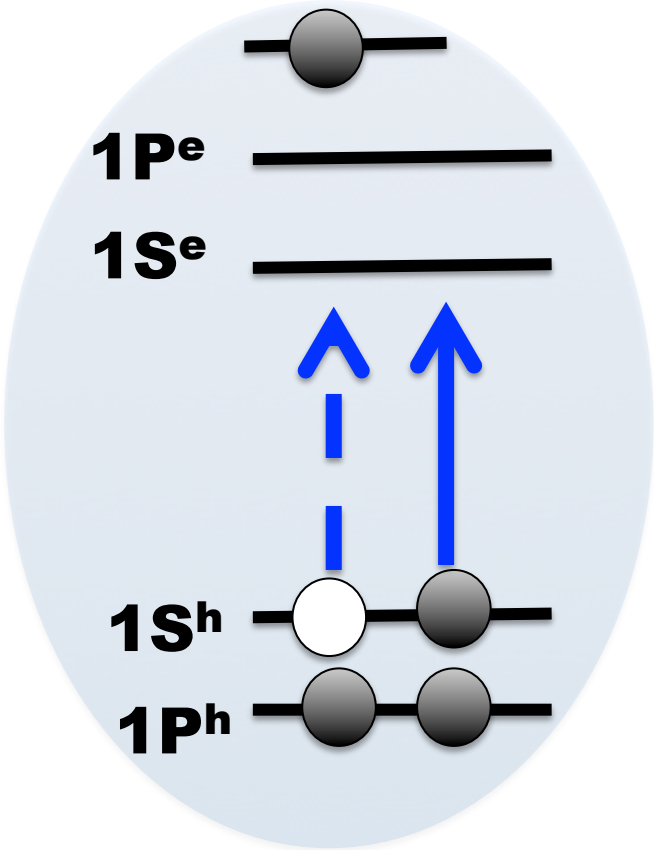
Time – Wavelength map of *ΔA*



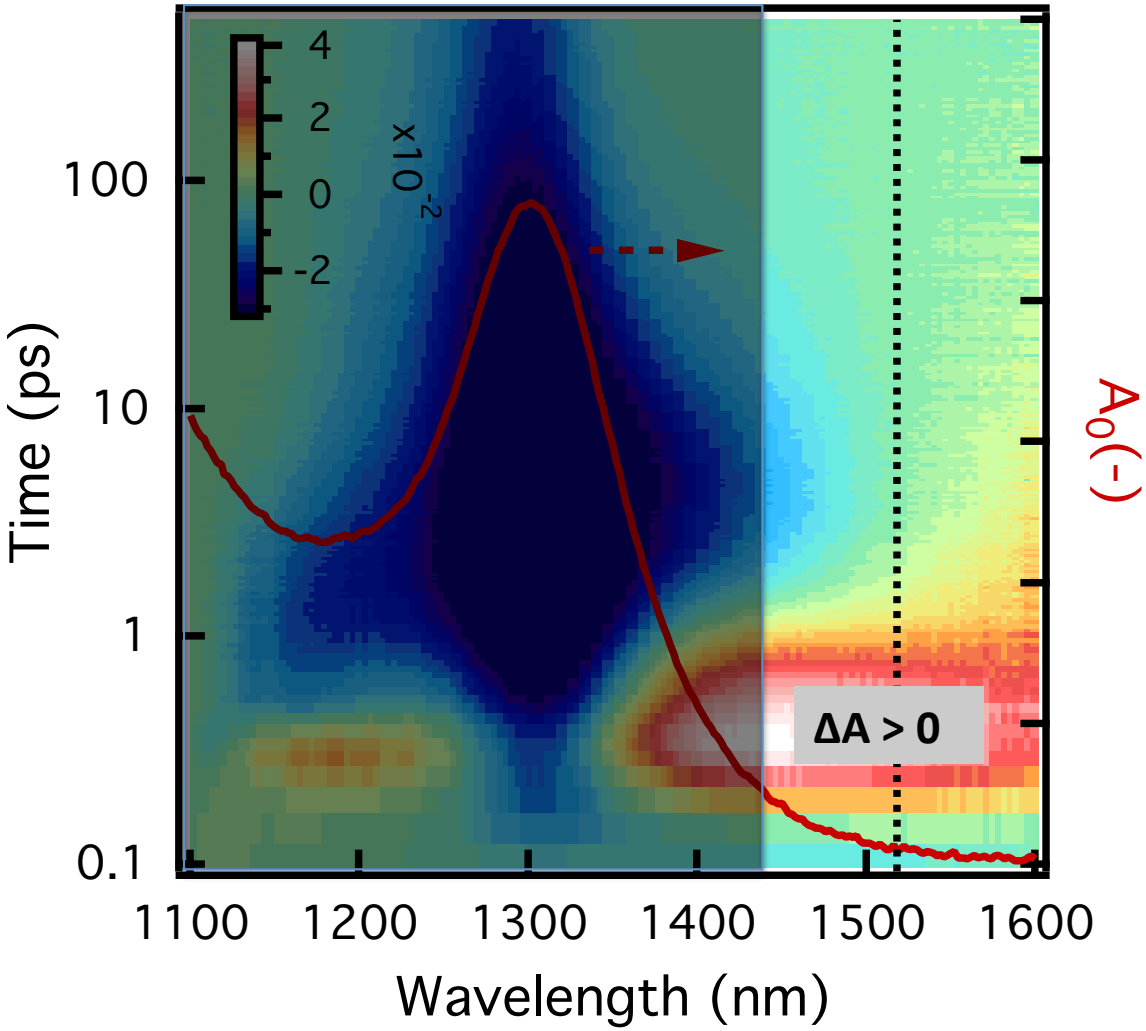


Time – Wavelength map of *ΔA*

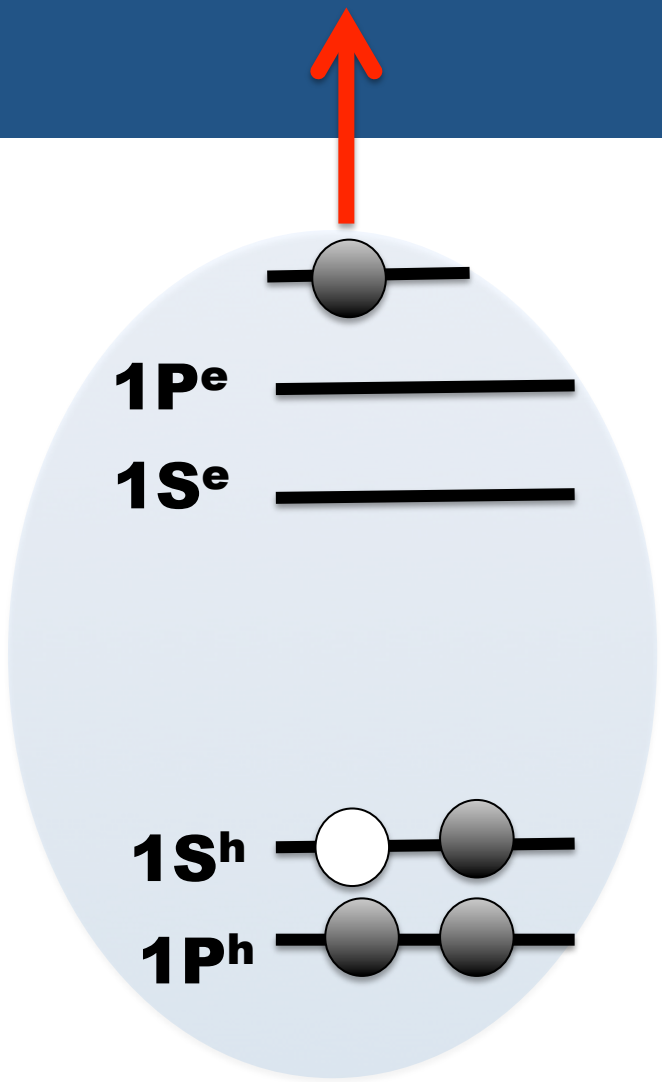




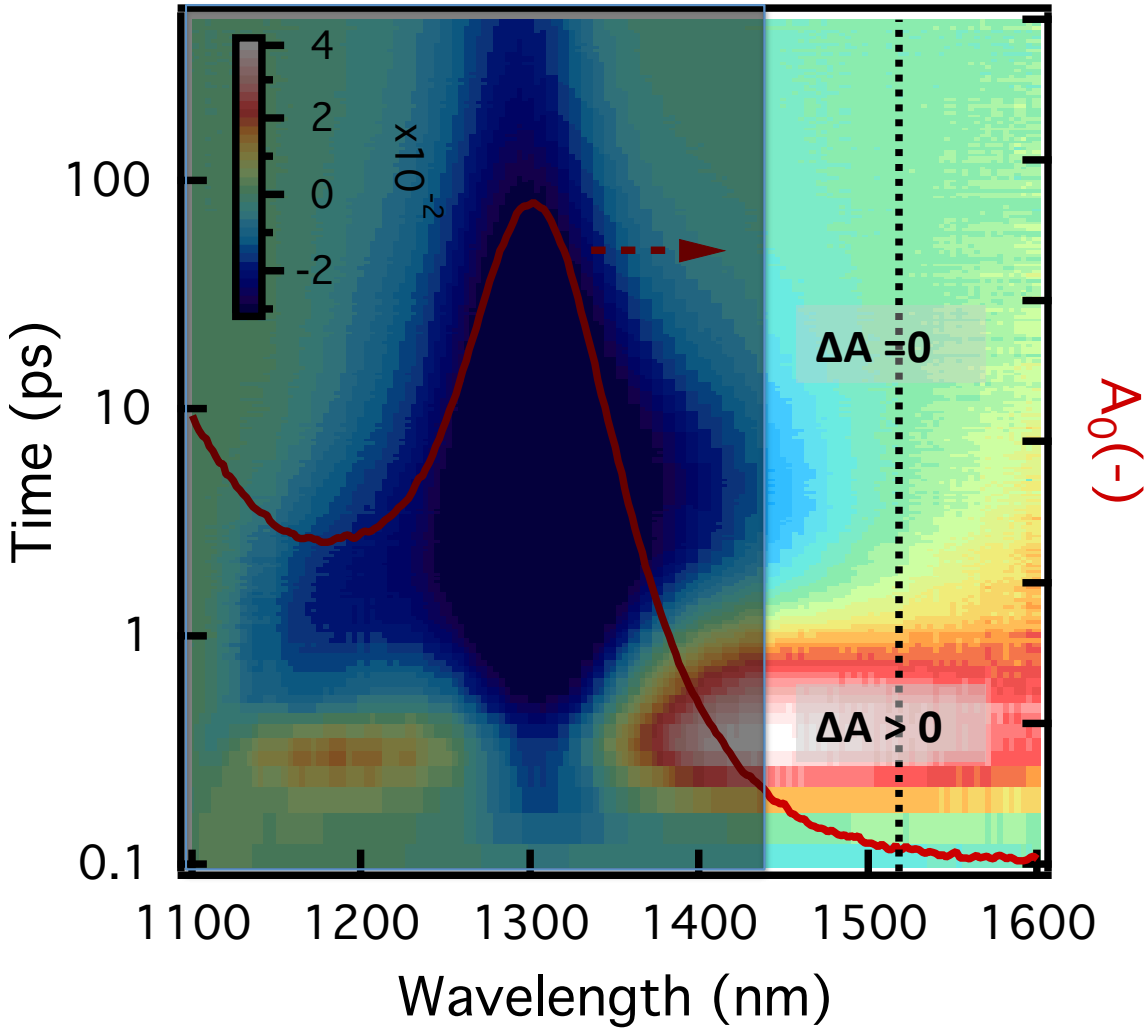
Time – Wavelength map of *ΔA*

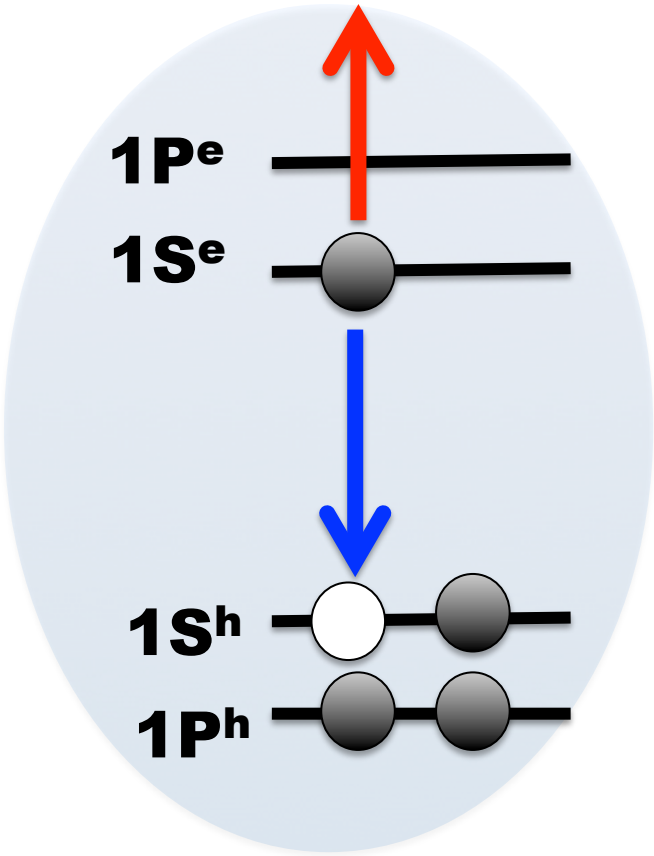


$A_0(-)$

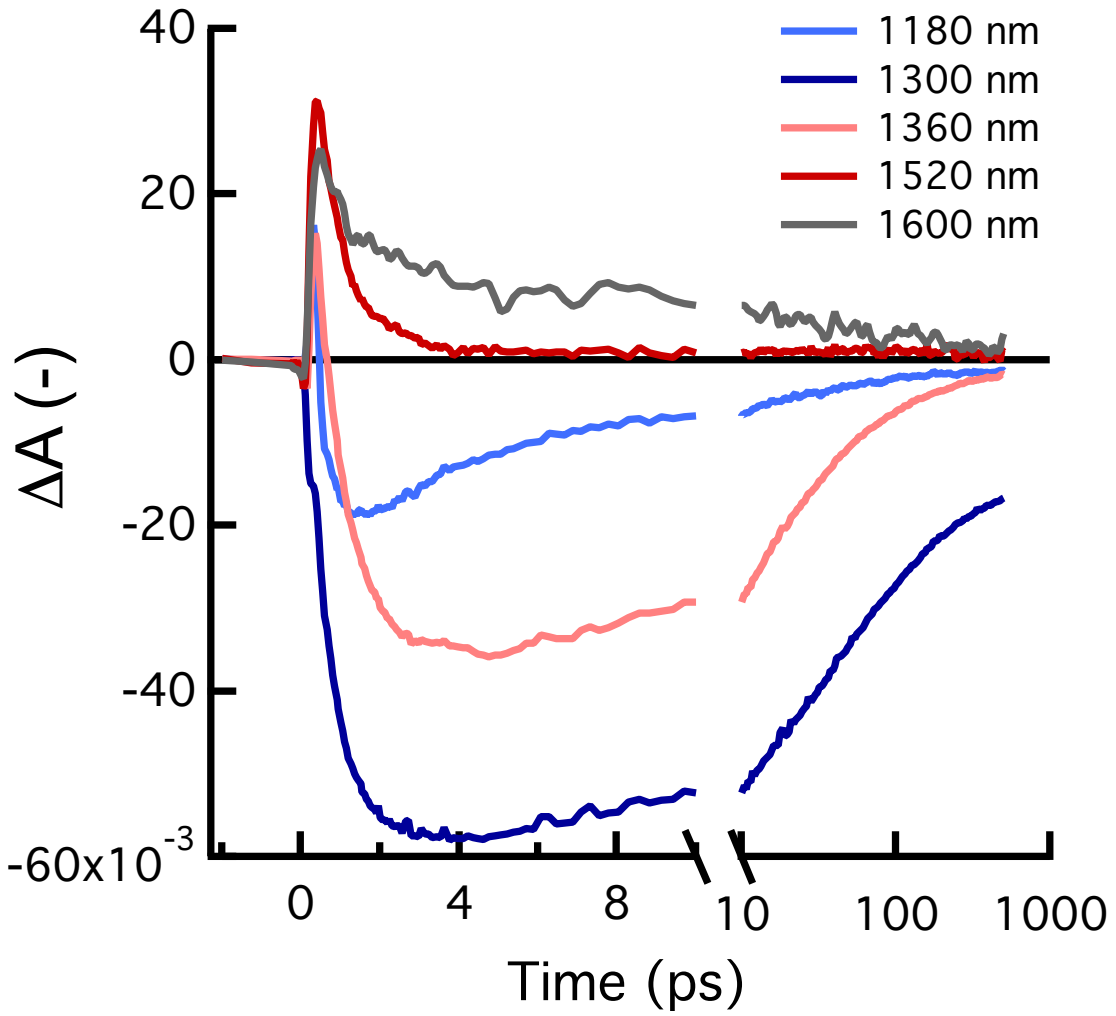


Time – Wavelength map of *ΔA*





All-Optical Wavelength Conversion



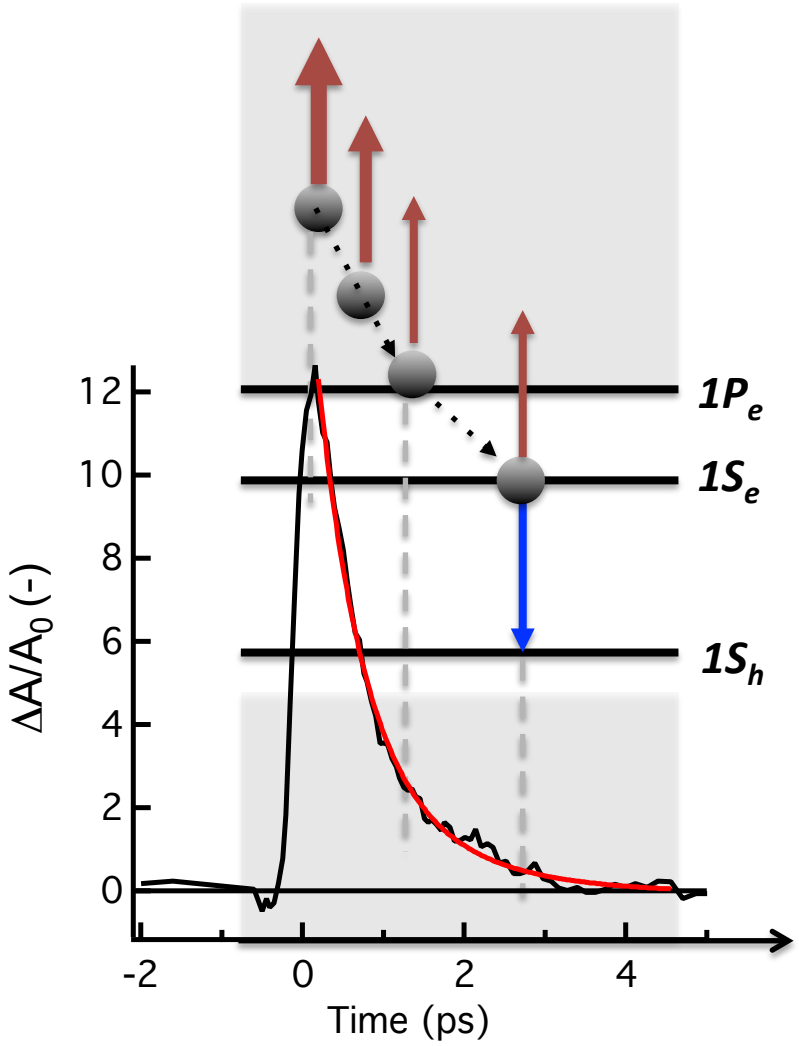
2 phenomena !

- Interband bleach:
  ΔA < 0
- Intraband absorption:
  ΔA > 0

At 1520 nm:

First, imbalance $\Delta A > 0$
After 1 ps, balance: $\Delta A = 0$

All – Optical Wavelength Conversion



Before cooling (0 - 2 ps):

✓ Hot Carrier Intraband Absorption

$\Delta A > 0$

After cooling (> 2 ps):

✓ Cold Carrier Intraband Absorption

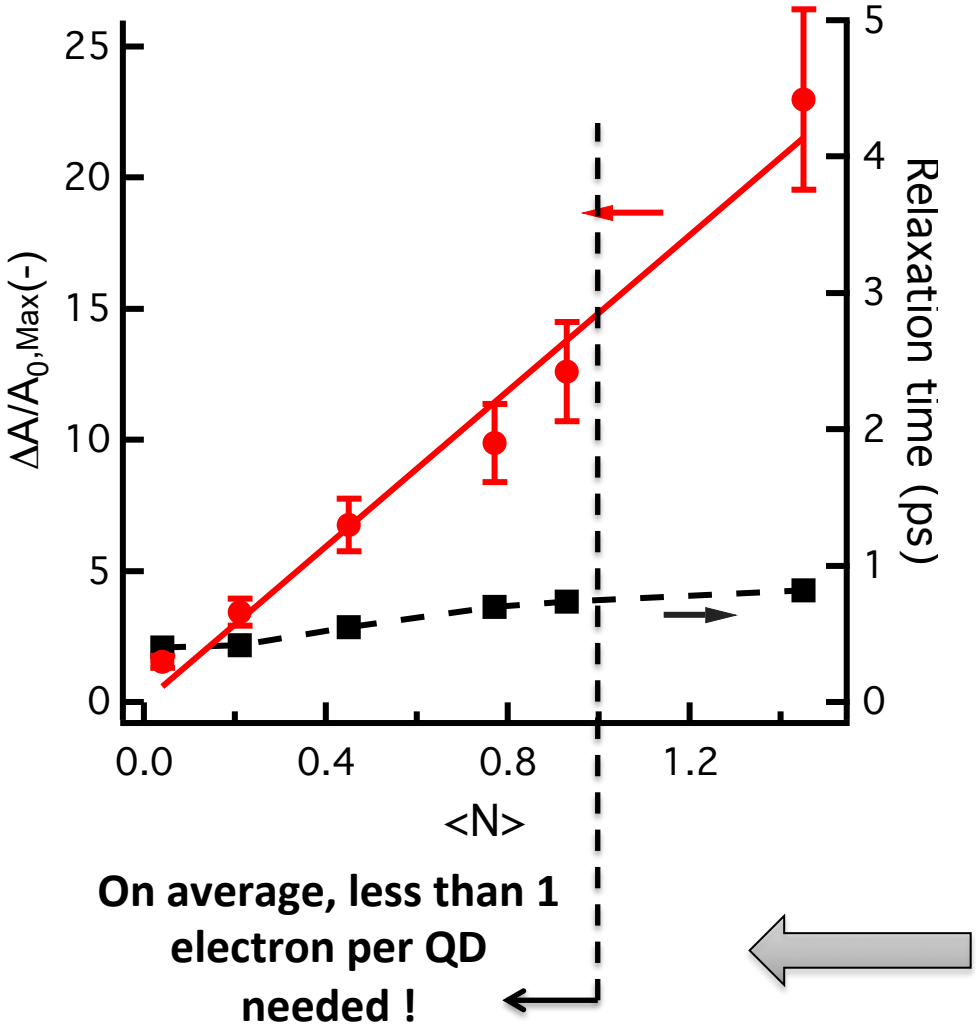
$\Delta A > 0$

✓ Cold Carrier Interband Bleach

$\Delta A < 0$

⇒ **Matching wavelength: $\Delta A = 0$**

All – Optical Wavelength Conversion



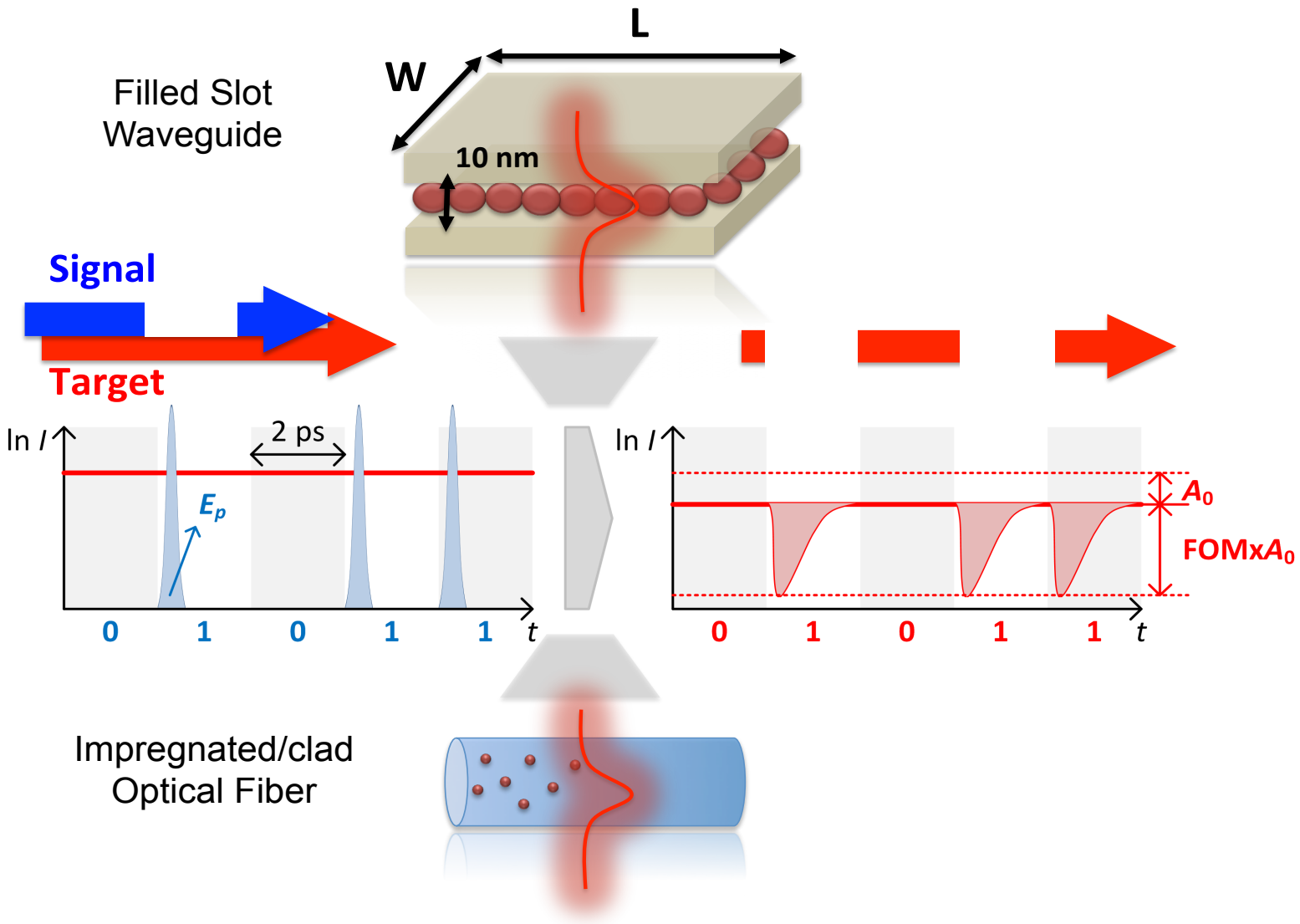
All-optical wavelength conversion ?

Convert pump (… - 1100 nm) to probe (1550 nm, **telecom** wavelength)

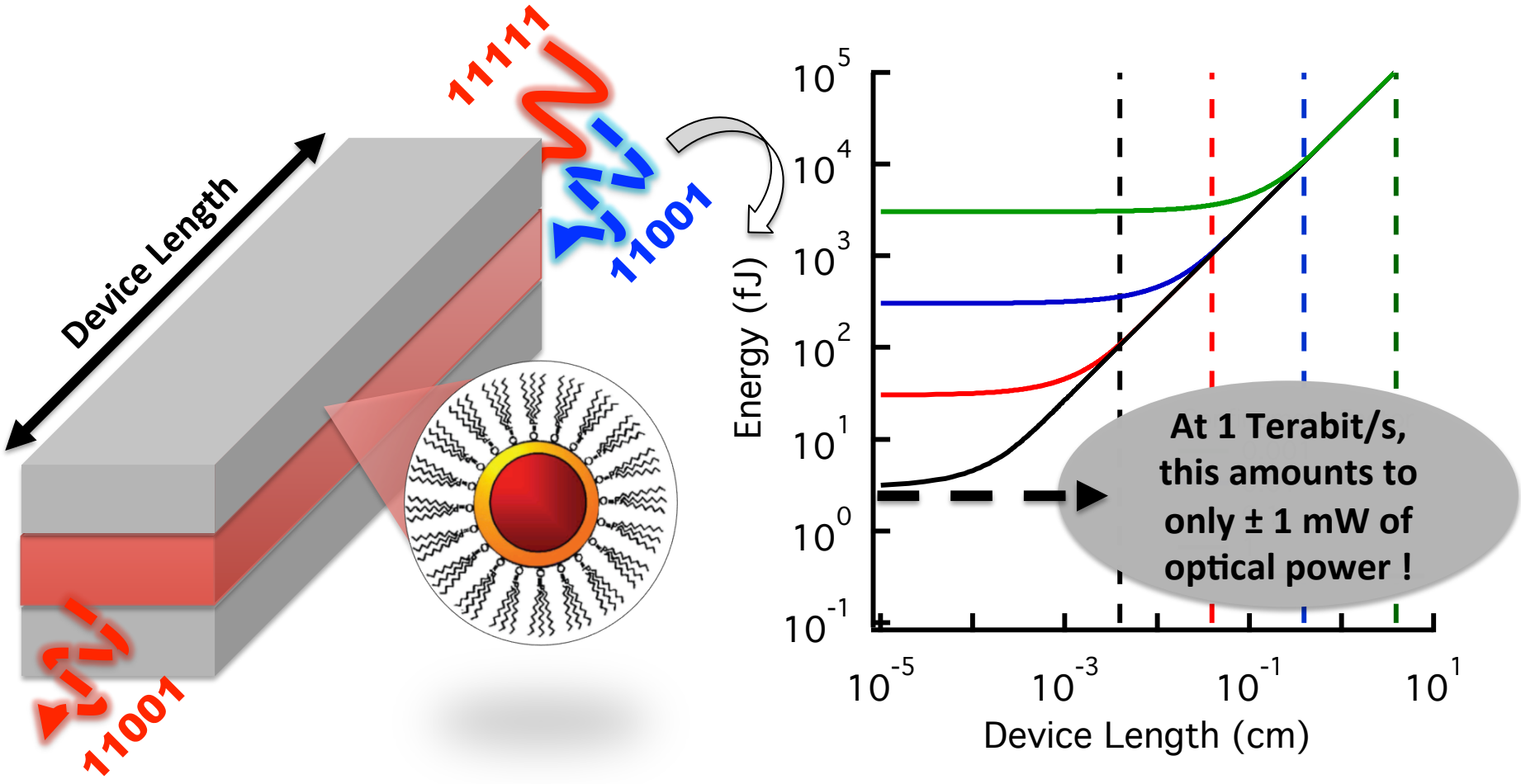
- ✓ **Picosecond dynamic (THz rate !)**
- ✓ **No residual absorption**
- ✓ **Linear** light-matter interaction

Moreover:
At low energy of the pump !

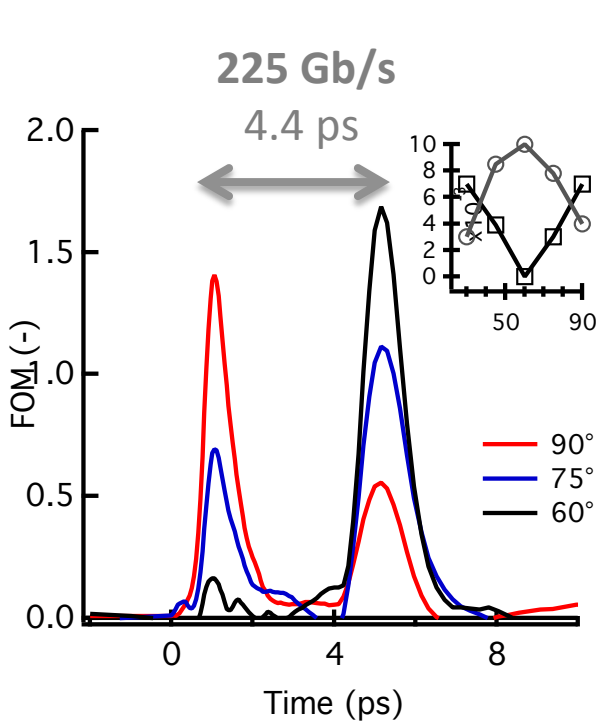
All – Optical Wavelength Conversion

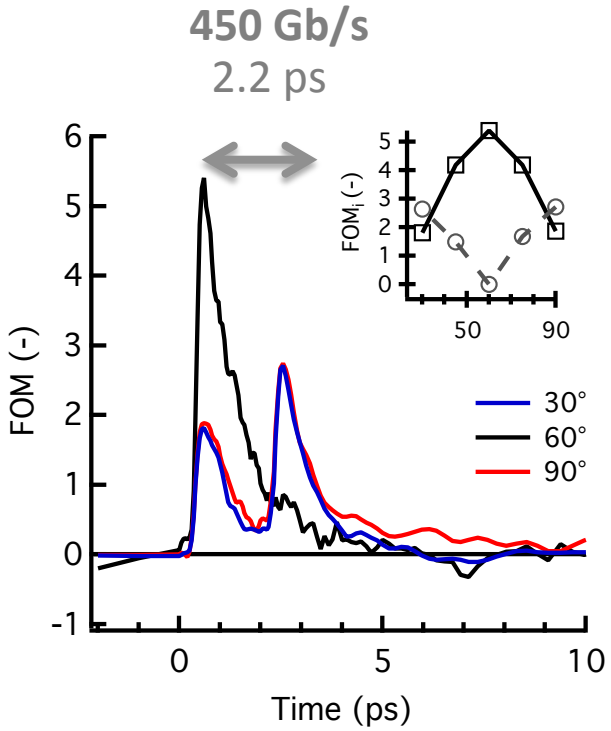


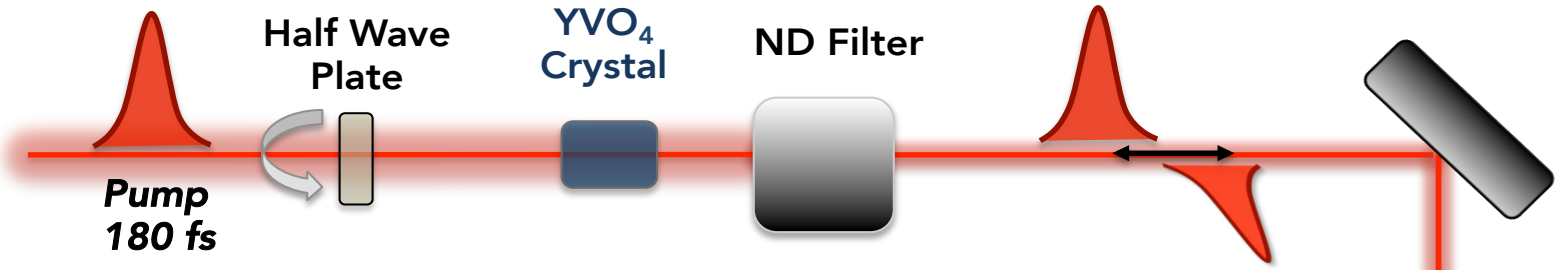
All – Optical Wavelength Conversion



All – Optical Wavelength Conversion

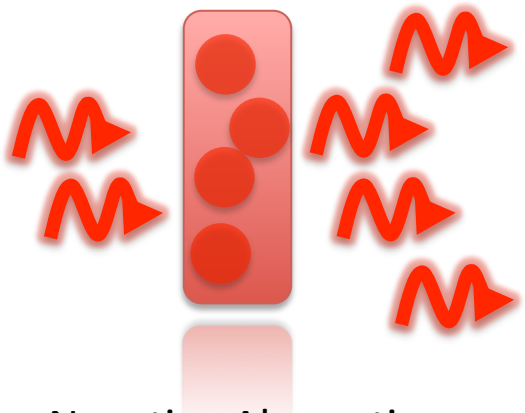






Optical Gain in Quantum Dots

A < 0

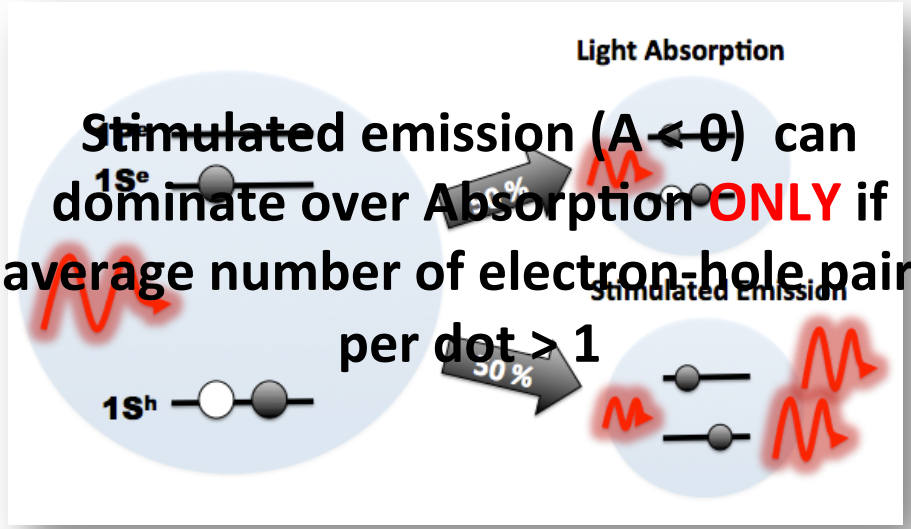


Negative Absorption
=
Amplification

$I/I_0 = 10^{-A}$

Absorption (A>0) or **Amplifcation (A<0) ?**

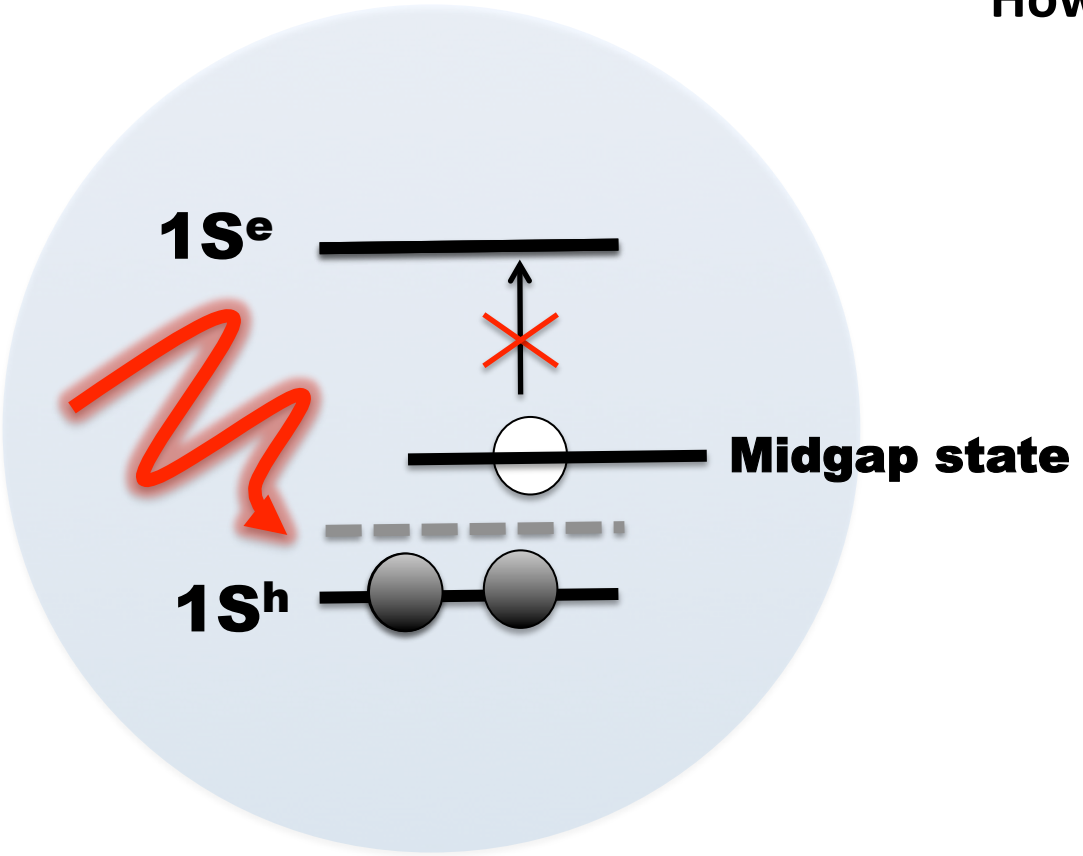
Balance between **absorption and stimulated emission !**



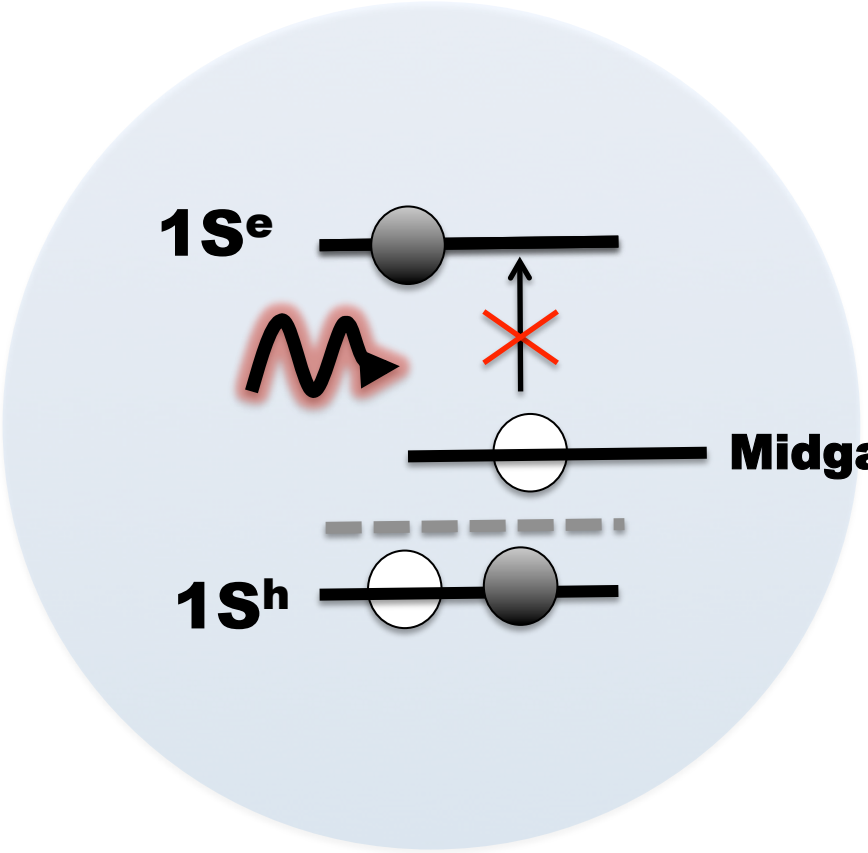
Stimulated emission (A < 0) can dominate over Absorption ONLY if average number of electron-hole pairs per dot > 1

Thresholdless Optical Gain using HgTe QDs

How to break the balance ?



Thresholdless Optical Gain using HgTe QDs



How to break the balance ?

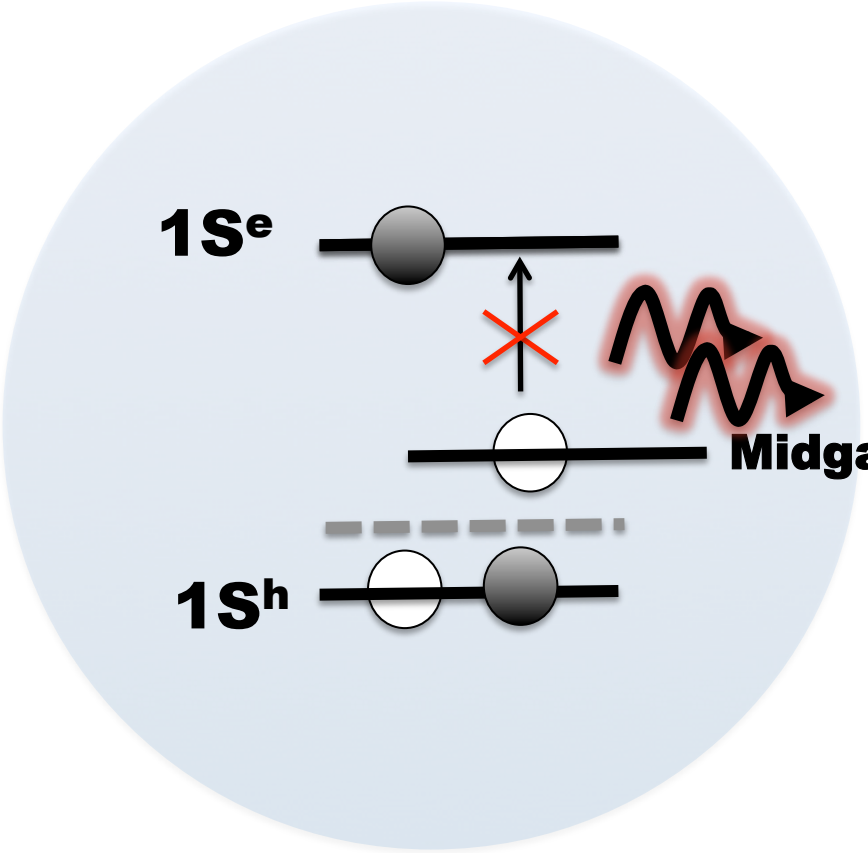
Create a **3-level system** !

$1S^e$ – Empty midgap State – $1S^h$

No absorption in unexcited crystal
Only Stimulated emission in excited !

Gain at no cost !

Thresholdless Optical Gain using HgTe QDs



How to break the balance ?

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$1S^e$ – Empty midgap State – $1S^h$

No absorption in unexcited crystal
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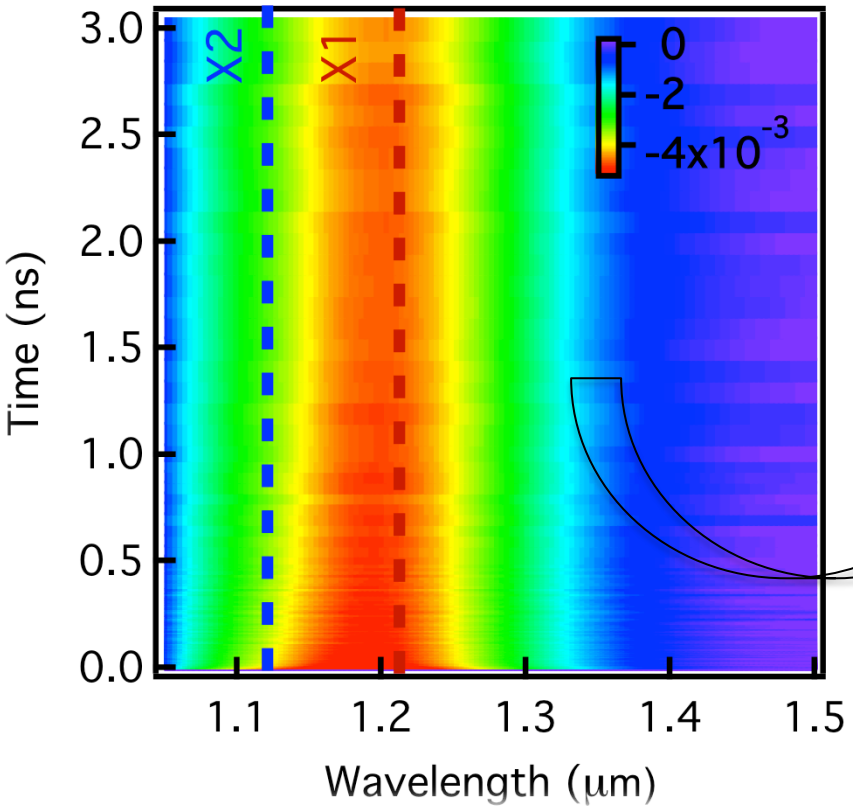
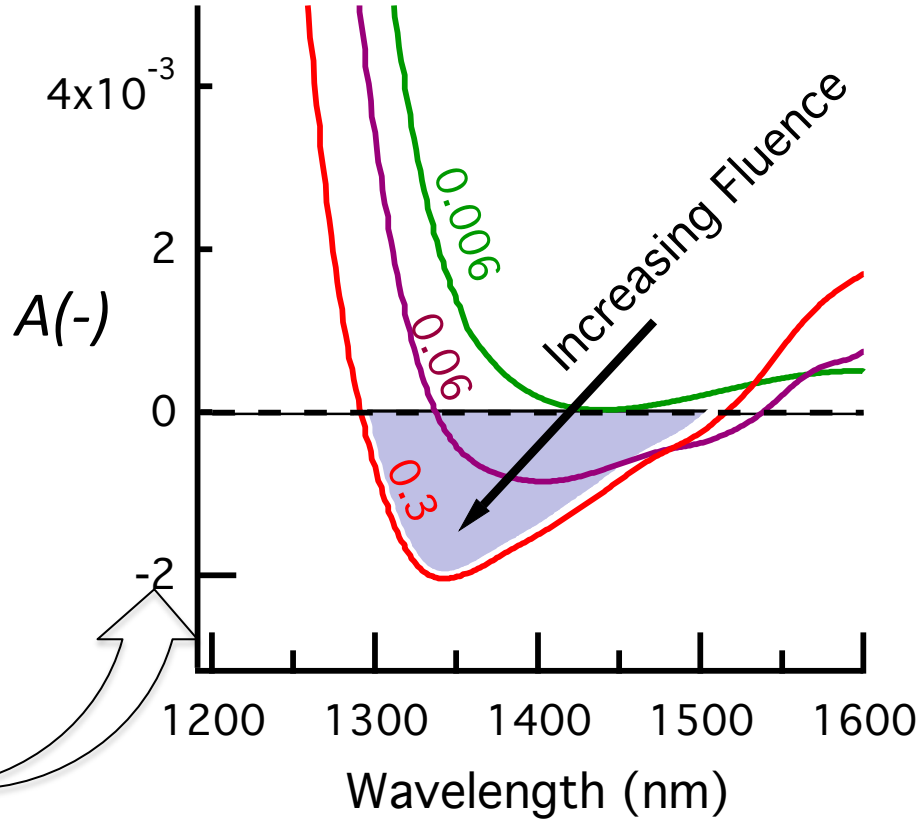
Thresholdless Optical Gain using HgTe QDs

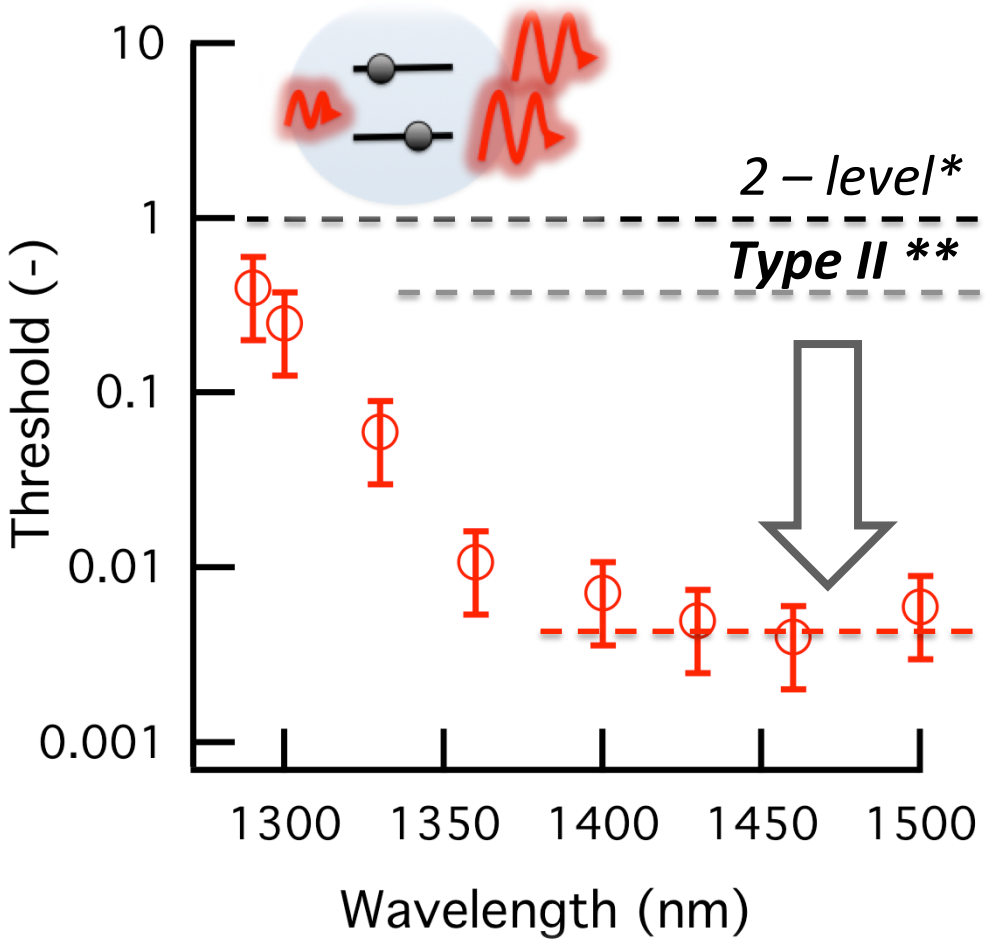
HgTe Quantum Dots
Pump = 700 nm

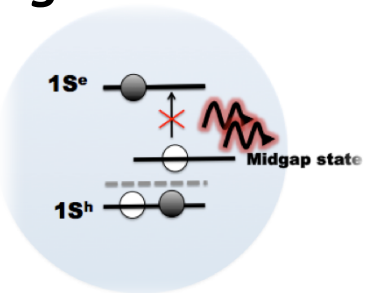




Net optical gain (A<0) for sub 1 exciton population (< 0.06)

Thresholdless Optical Gain using HgTe QDs

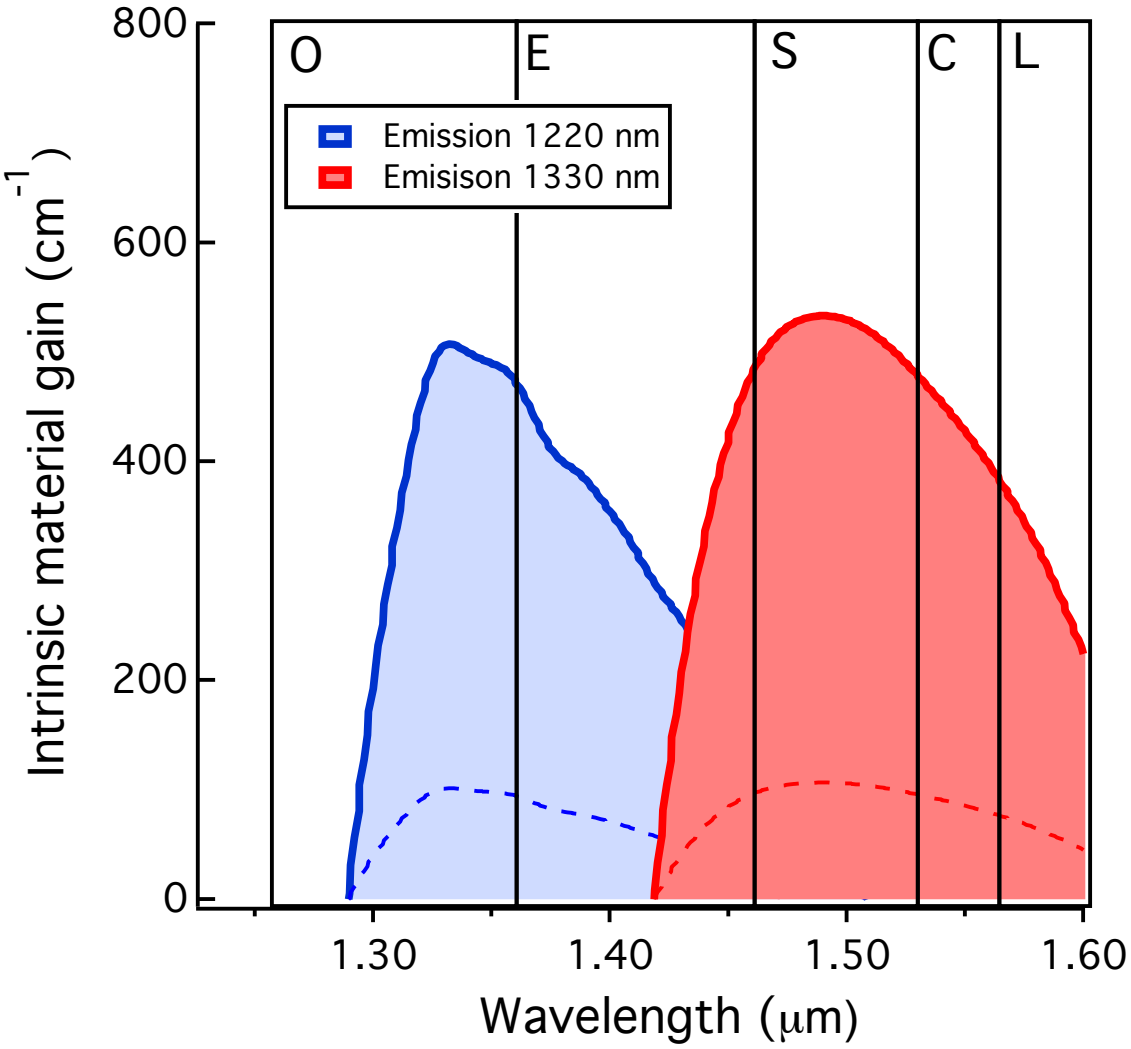




A < 0 for less than 1 electron-hole pair per QD on average !

✓ Outperforming regular QDs by 2 orders of magnitude **!**

Thresholdless Optical Gain using HgTe QDs



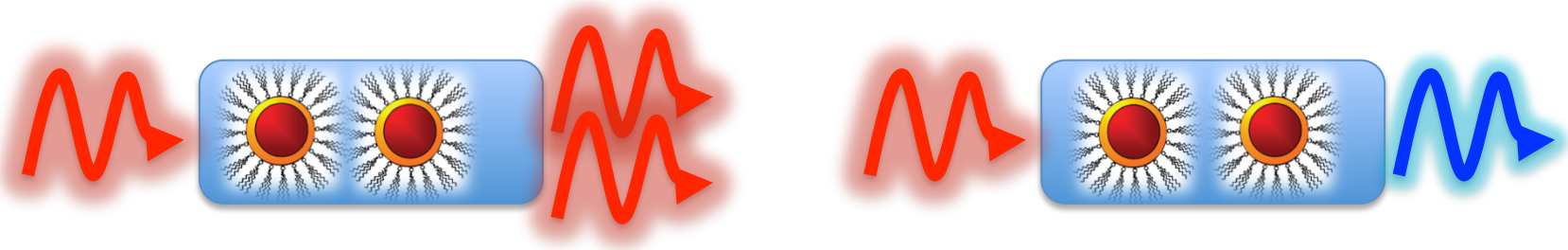
2 sizes of HgTe

Amplification over the entire telecommunication window !

- ✓ *Long gain lifetime*
- ✓ *Low thresholds*
- ✓ *Modal gains up to 100 cm^{-1} possible*

To conclude …

Compact, cheap and low power
optical amplifiers and **wavelength convertors**



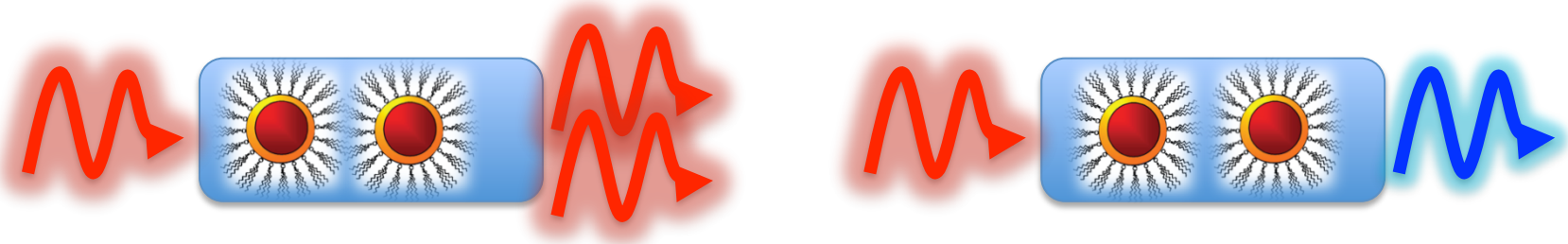
Through balancing of quantum dot properties

Absorption
versus
Stimulated emission

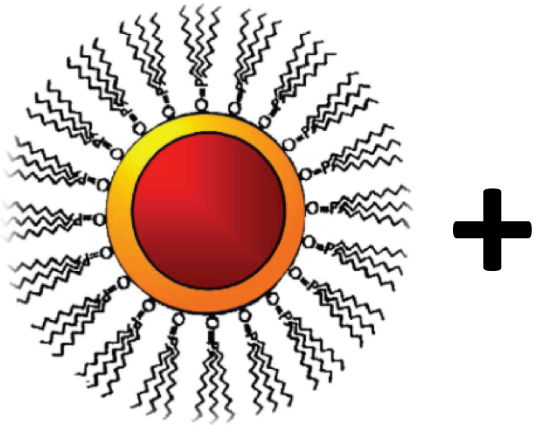
Inter-Band Absorption
versus
Intra-Band Absorption

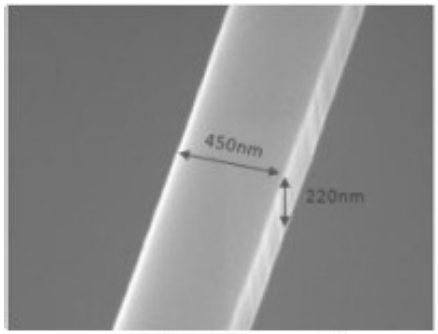
To conclude …

Compact, cheap and low power
optical amplifiers and **wavelength convertors**

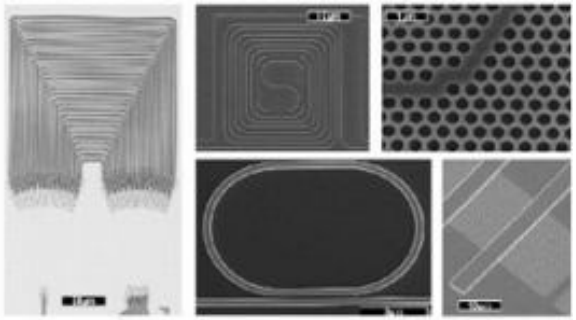


Using a combination of **colloidal quantum dots** and **guided wave photonics**

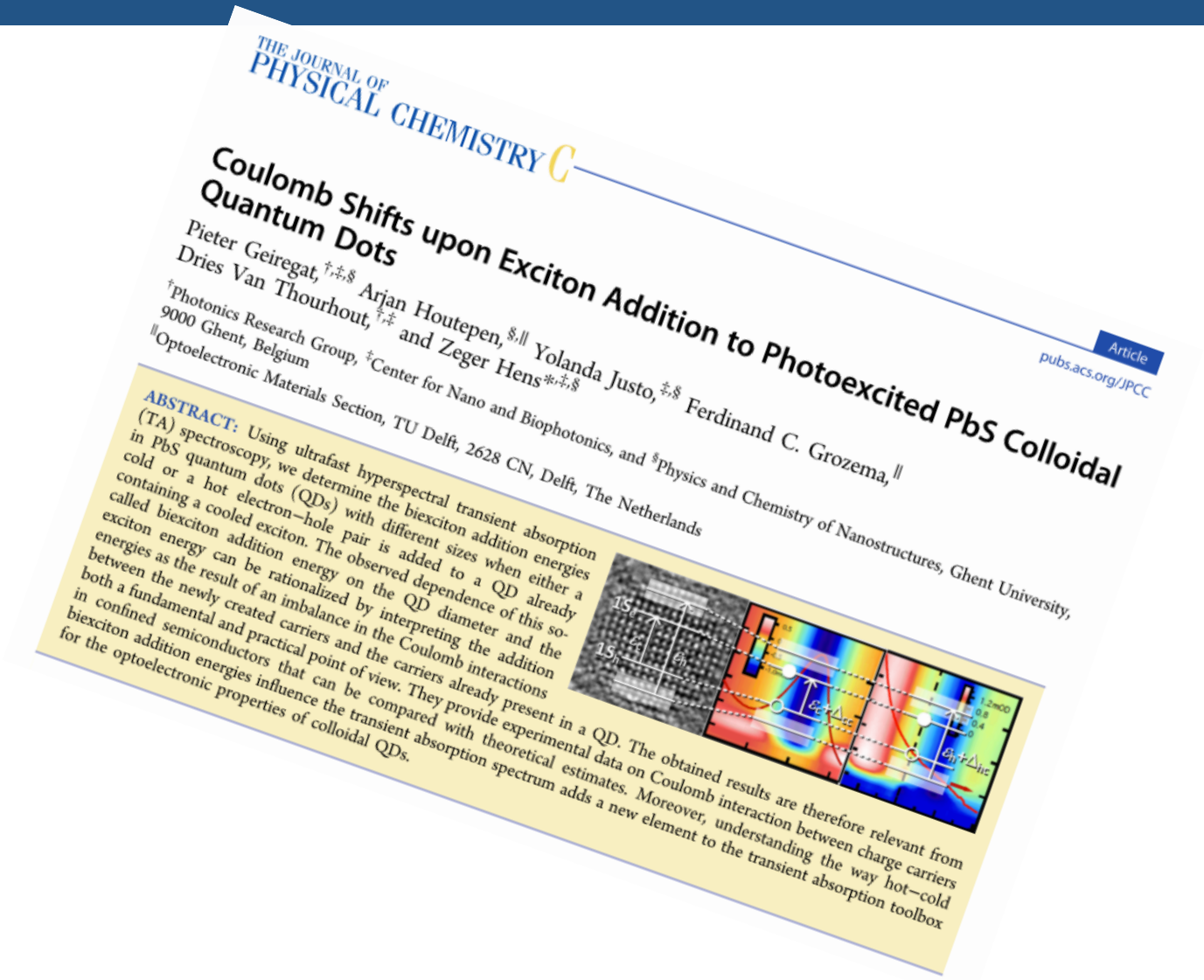




Silicon Waveguide


Optical functions in Silicon

More stories to read before bedtime !



THE JOURNAL OF PHYSICAL CHEMISTRY C

Article

pubs.acs.org/JPCC

Coulomb Shifts upon Exciton Addition to Photoexcited PbS Colloidal Quantum Dots

Pieter Geiregat,[†,‡,§] Arjan Houtepen,[§,∥] Yolanda Justo,[‡,§] Ferdinand C. Grozema,[∥] Dries Van Thourhout,[†,‡] and Zeger Hens*[,‡,§]

[†]Photonics Research Group, [‡]Center for Nano and Biophotonics, and [§]Physics and Chemistry of Nanostructures, Ghent University, 9000 Ghent, Belgium

[∥]Optoelectronic Materials Section, TU Delft, 2628 CN, Delft, The Netherlands

ABSTRACT: Using ultrafast hyperspectral transient absorption (TA) spectroscopy, we determine the biexciton addition energies in PbS quantum dots (QDs) with different sizes when either a cold or a hot electron–hole pair is added to a QD already containing a cooled exciton. The observed dependence of this so-called biexciton addition energy on the QD diameter and the exciton energy can be rationalized by interpreting the addition energies as the result of an imbalance in the Coulomb interactions between the newly created carriers and the carriers already present in a QD. The obtained results are therefore relevant from both a fundamental and practical point of view. They provide experimental data on Coulomb interaction between charge carriers in confined semiconductors that can be compared with theoretical estimates. Moreover, understanding the way hot–cold biexciton addition energies influence the transient absorption spectrum adds a new element to the transient absorption toolbox for the optoelectronic properties of colloidal QDs.

More stories to read before bedtime !

THE JOURNAL OF PHYSICAL

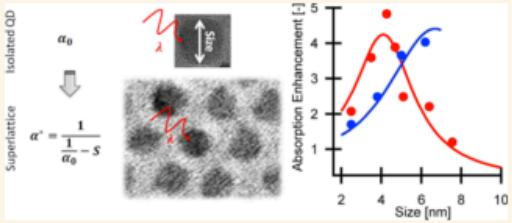
ARTICLE

Giant and Broad-Band Absorption Enhancement in Colloidal Quantum Dot Monolayers through Dipolar Coupling

Pieter Geiregat,[†,‡,§] Yolanda Justo,[†,§] Sofie Abe,[†,§] Stijn Flamee,[†,§] and Zeger Hens[†,§,*]

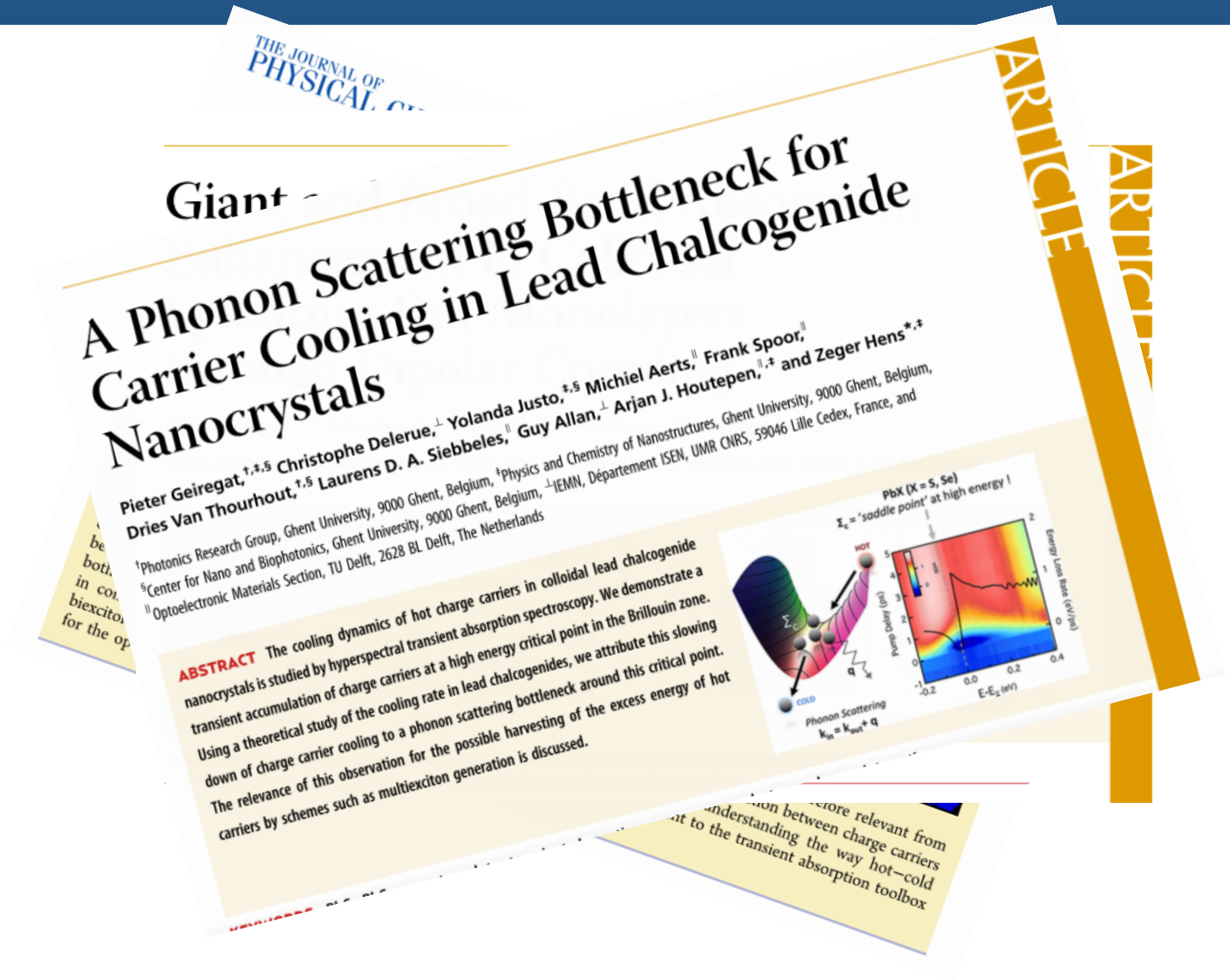
[†]Physics and Chemistry of Nanostructures, [‡]Photonics Research Group, and [§]Center for Nano and Biophotonics, Ghent University, B-9000 Ghent, Belgium

ABSTRACT The absorption cross section of colloidal quantum dots in close-packed monolayers shows a 4 (CdSe) to 5-fold (PbS) enhancement compared to quantum dots in a dilute dispersion. Quantitative agreement is demonstrated between the value and the size dependence of the enhancement and theoretical model predictions based on dipolar coupling between neighboring quantum dots. This collective optical behavior offers a new degree of freedom in the custom design of optical properties for electro-optical devices.



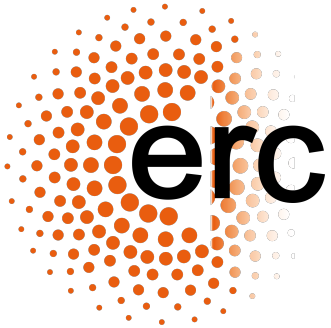
KEYWORDS: nanocrystals · superlattice · optical properties · light absorption · coupled dipole model

More stories to read before bedtime !



Acknowledgements

Physics and Chemistry of Nanostructures Group



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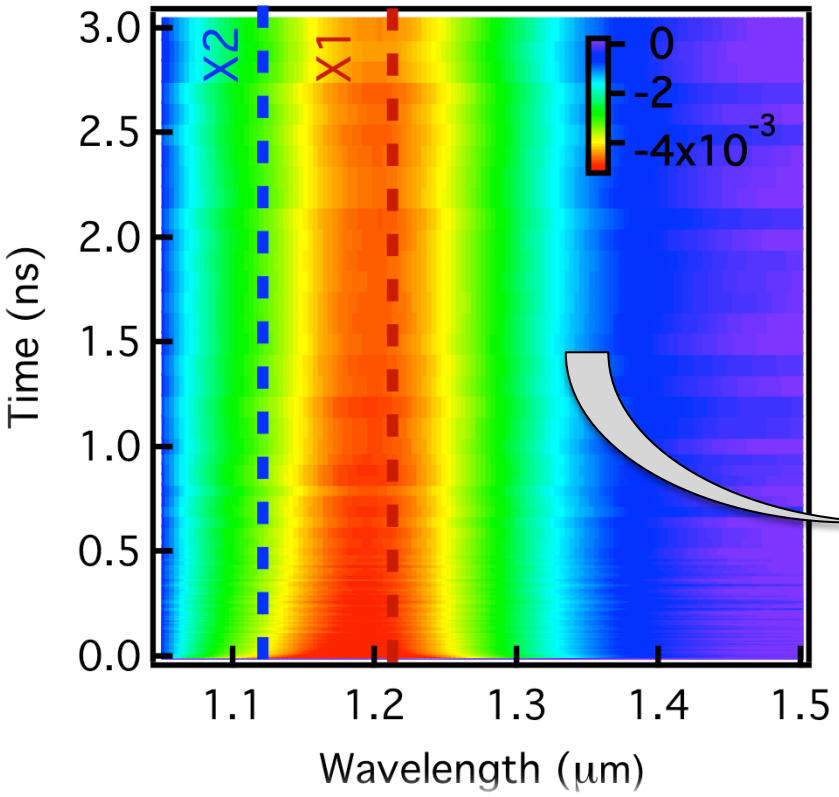
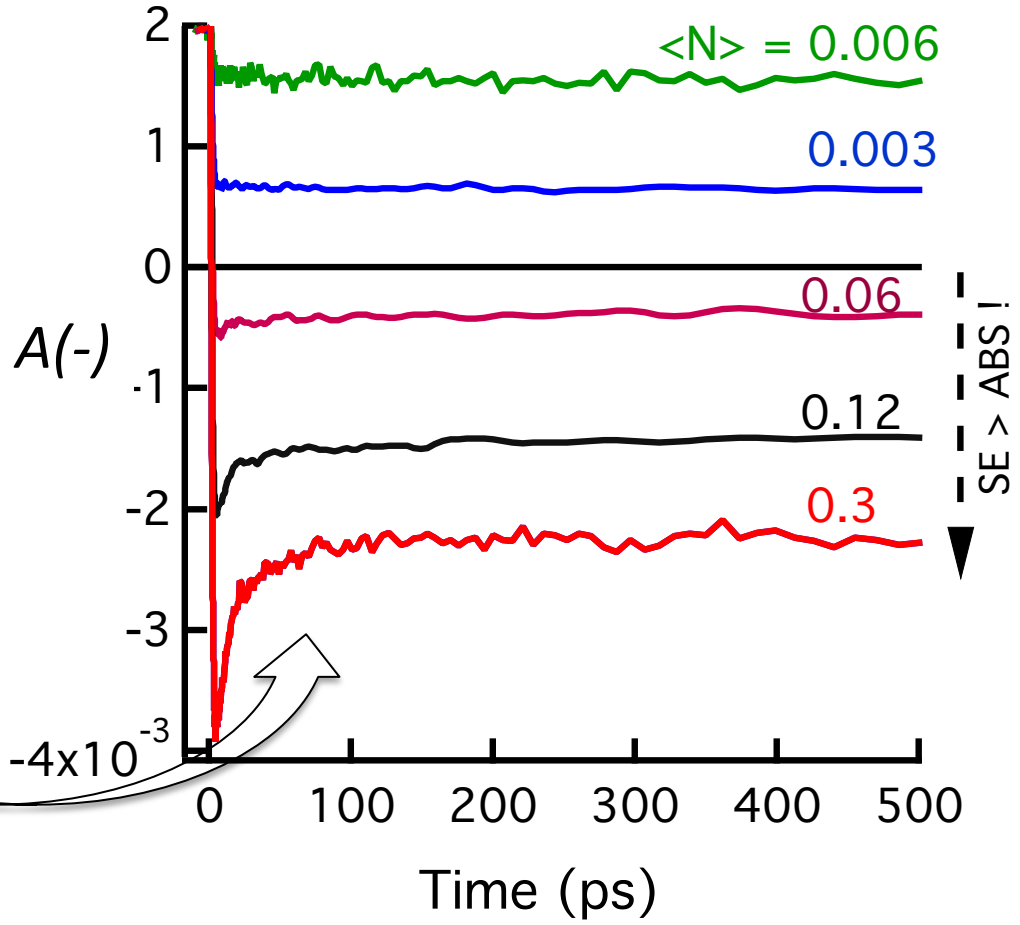
UMR CNRS 8520

Extra Slides

Thresholdless Optical gain using HgTe QDs

How long does this gain last ?



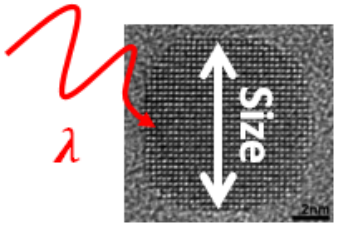


Gain lifetime on the order of the single X lifetime (30 ns)

Properties of Thin Films

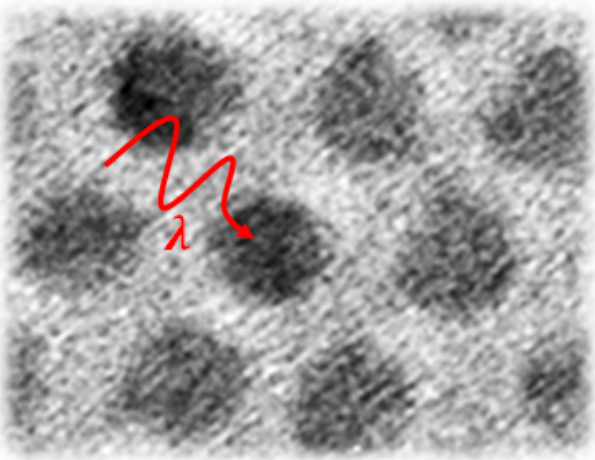
Isolated QD

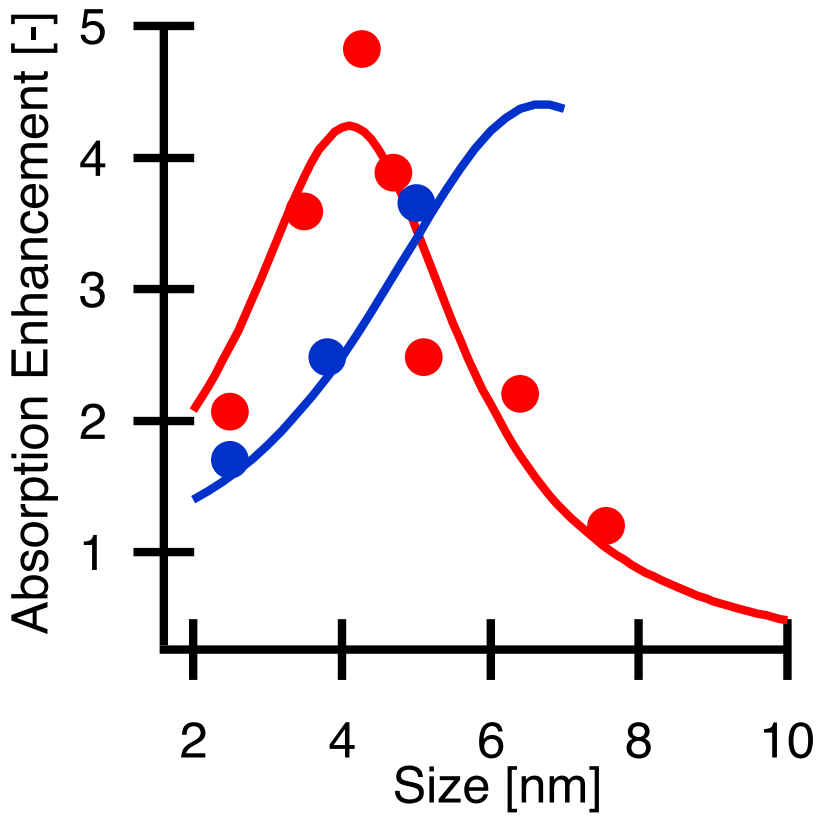
$$\alpha_0$$



Superlattice

$$\alpha^* = \frac{1}{\frac{1}{\alpha_0} - S}$$

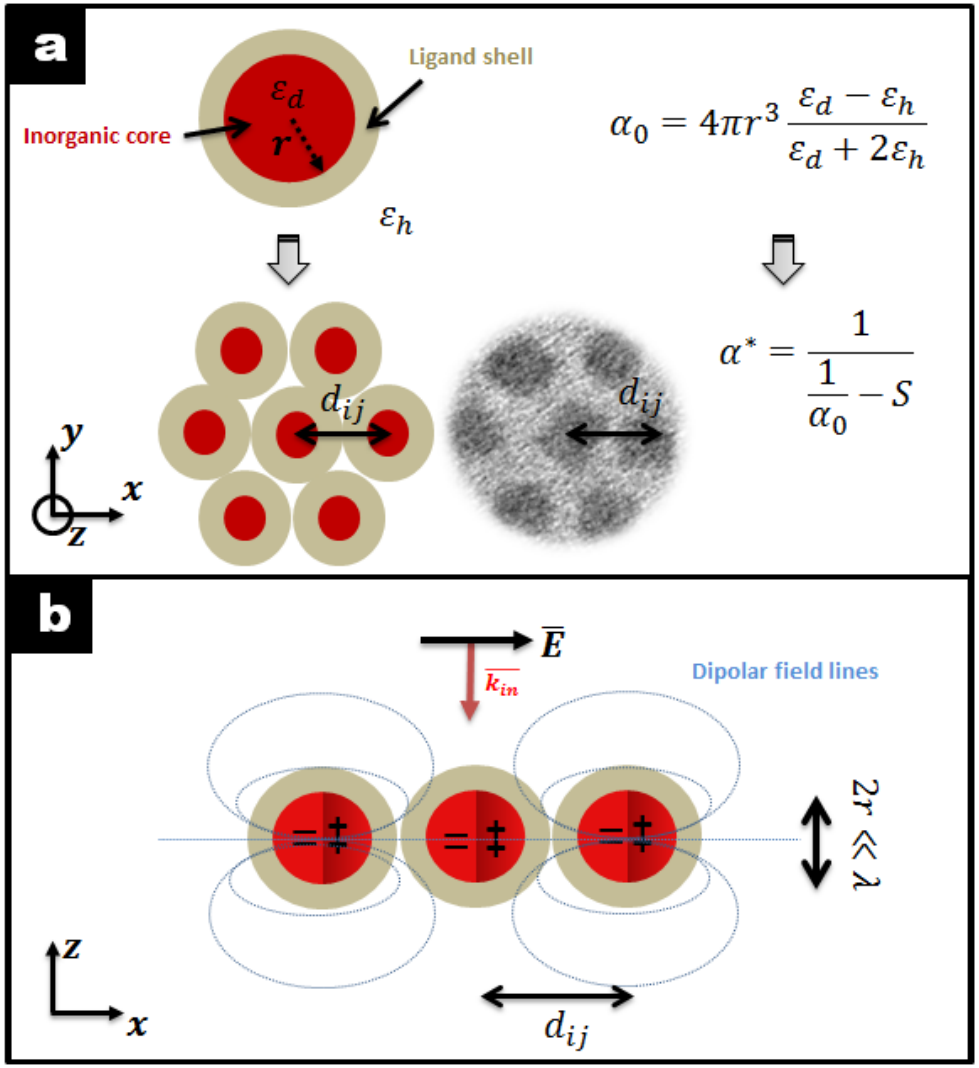




" Can we translate the properties measured in solution to thin film ? "

Geiregat et al., ACS Nano 6(7), 2012

Properties of Thin Films



Isolated particle

=

Isolated dipole

'Effective Medium'
(e.g. Maxwell-Garnett)

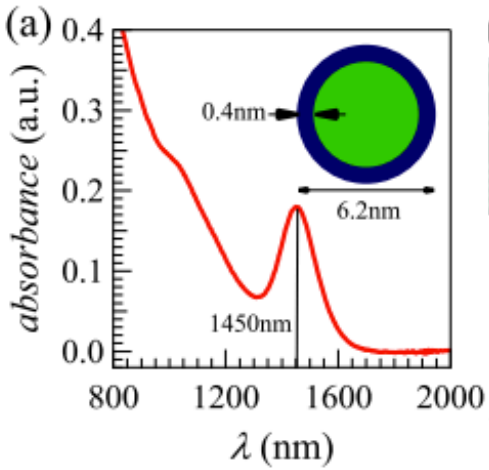
Particle in close packed film ?

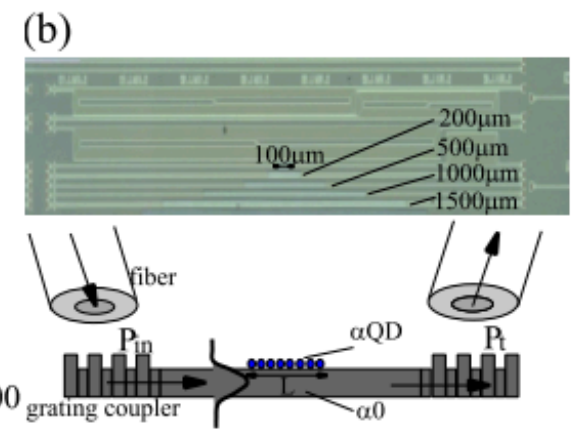
=

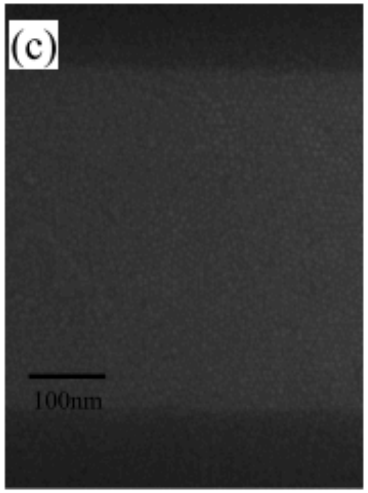
Subject to depolarization fields of neighbours (only ~ 5 nm away)

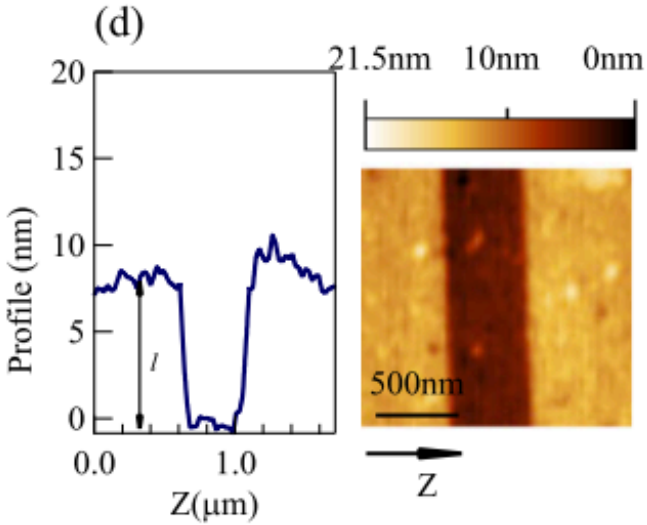
'Coupled Dipole Theory'

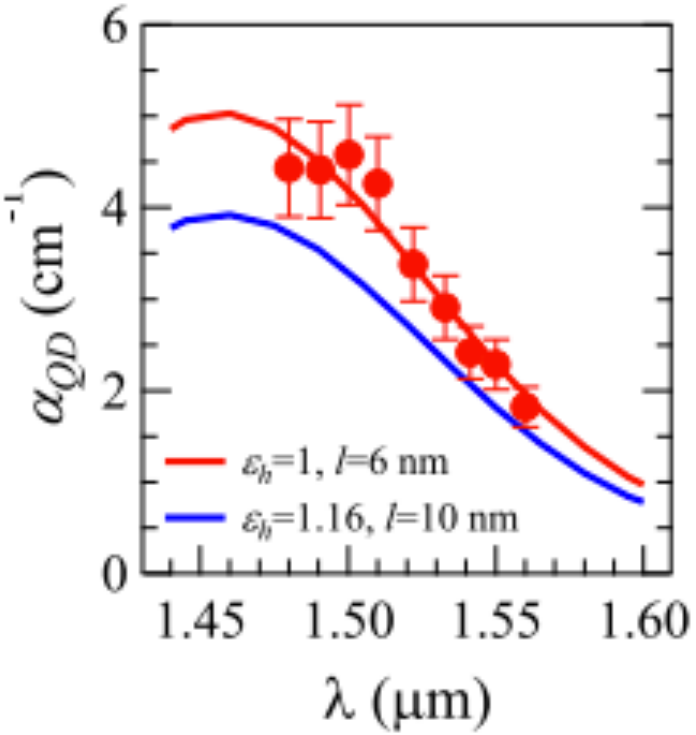
Interaction with Silicon Photonics





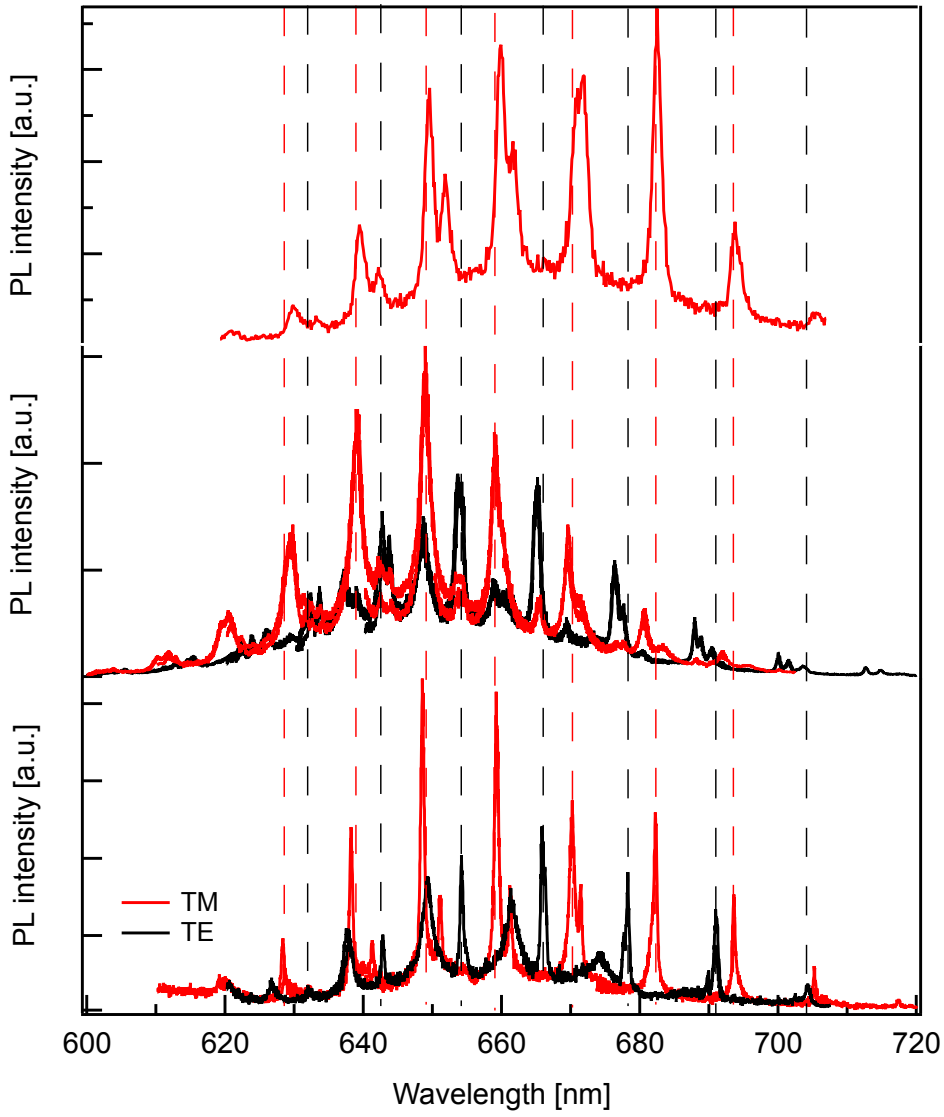


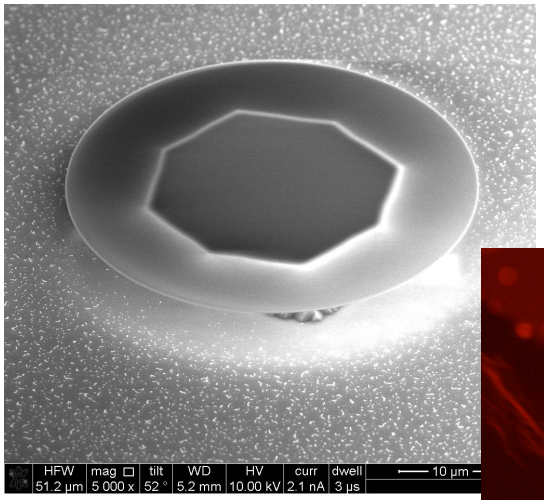


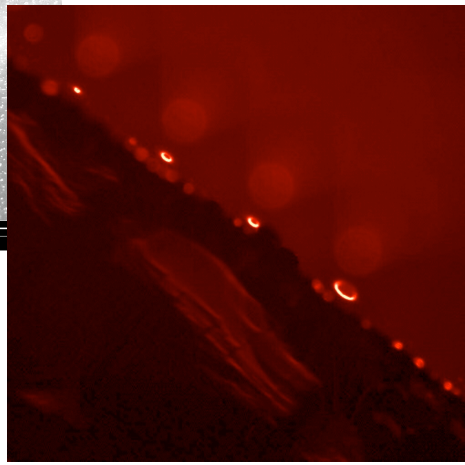


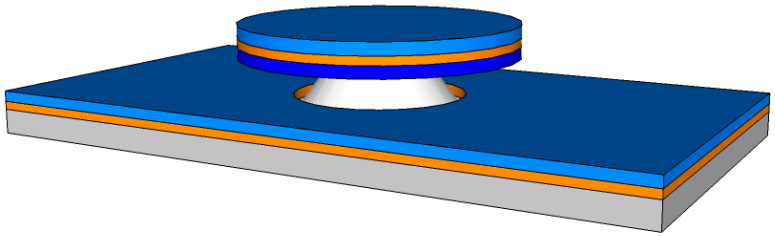
Omari et al. Opt. Expr. 21(20)
Omari et al. JSTQE. 20(4)

Interaction with Silicon Photonics



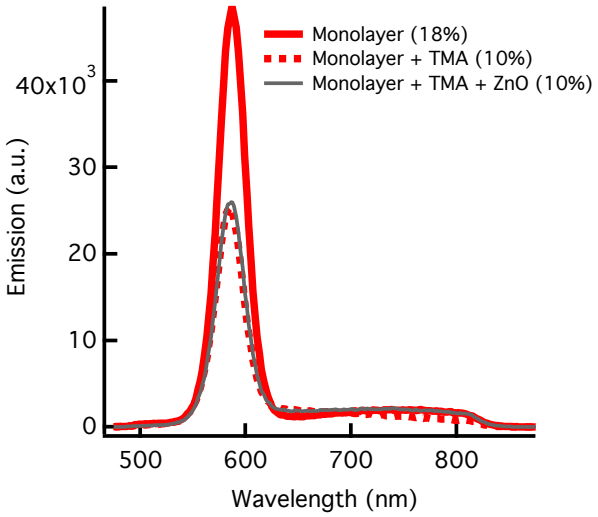


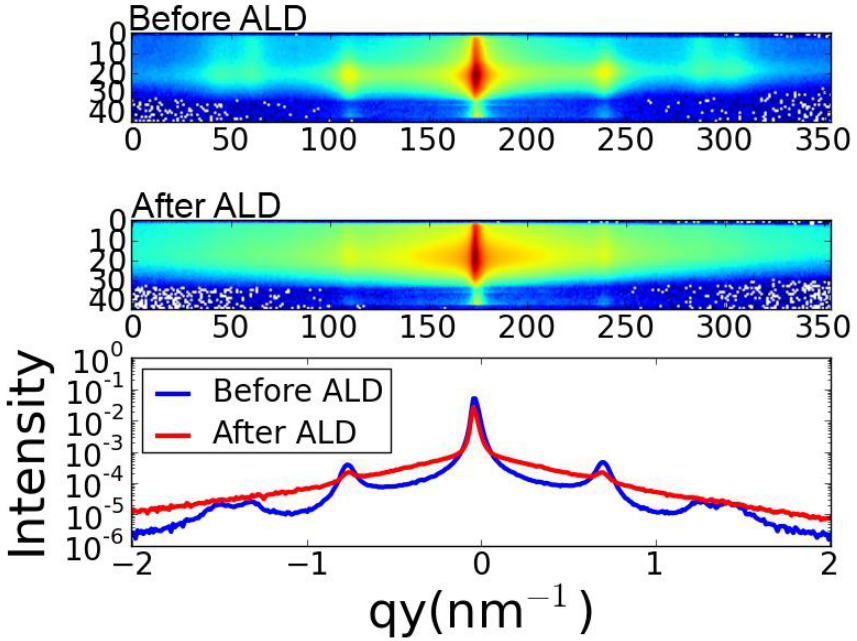


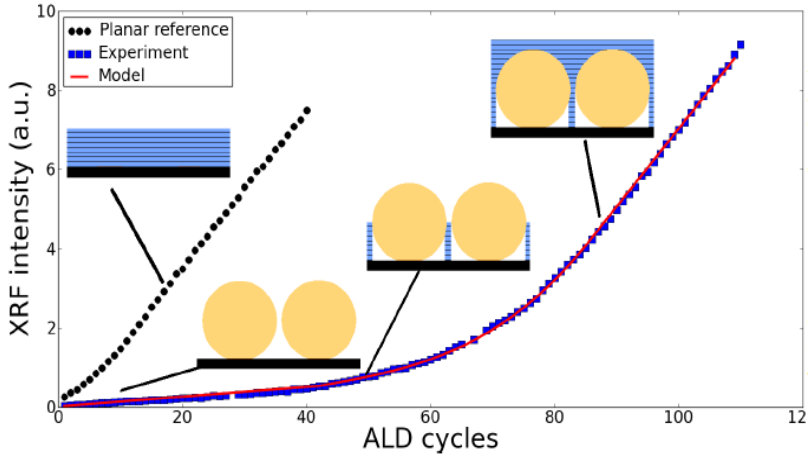


De Geyter et al. , APL 101(16)

Matrix Encapsulation

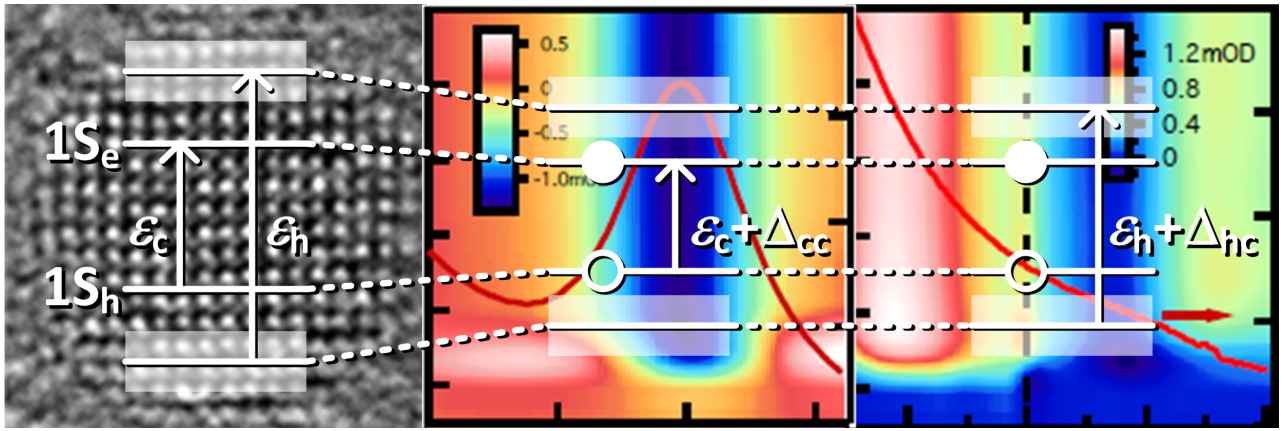


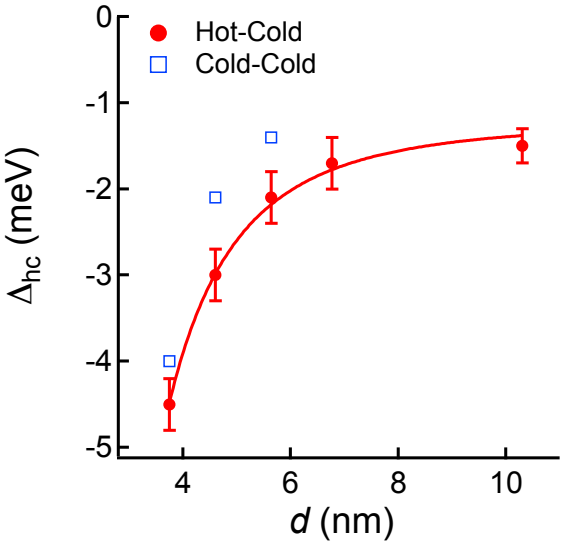




Combination of synchrotron enabled XRF and GISAXS with PL to study growth on monolayer

Spectral Shifts



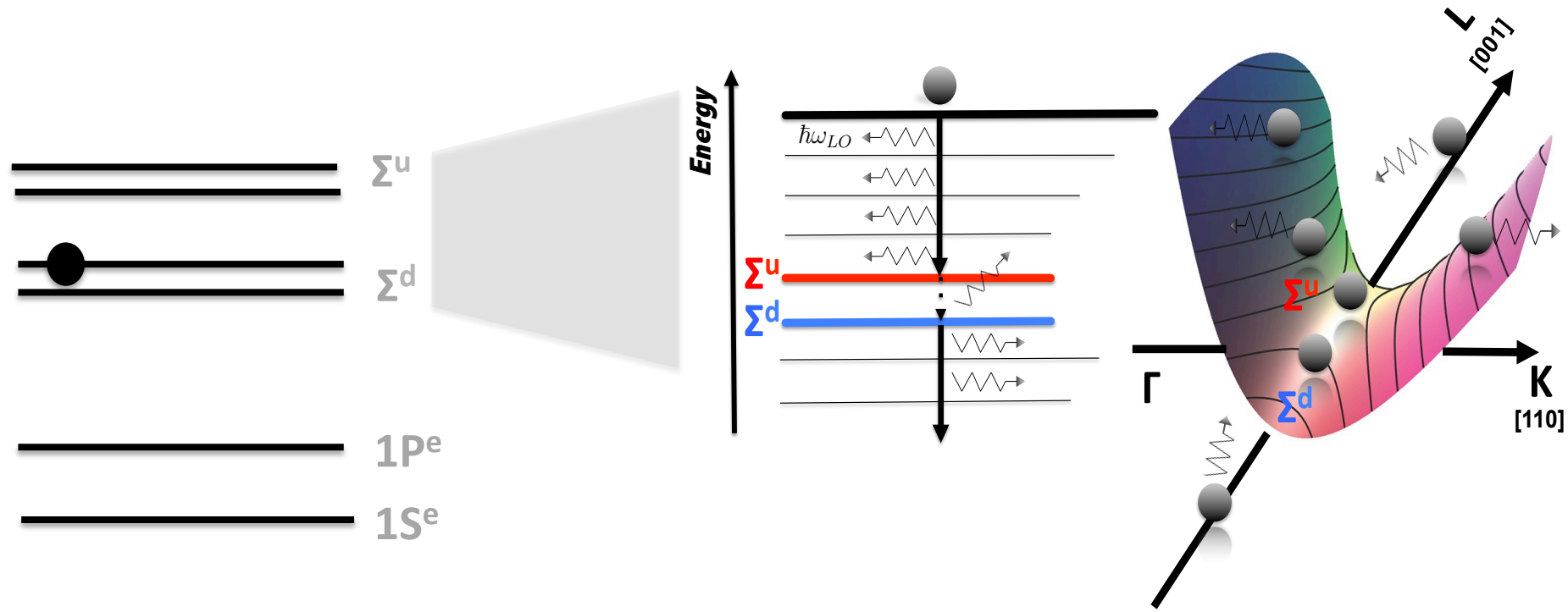


“ Interaction of hot and cold excitons gives rise to Coulomb shifts of the absorption spectrum ”

Interesting from both **experimental** (how to interpret TA spectra with spectral shifts) and **fundamental** point of view (hot/cold multi-X interactions)

Geiregat et al., J.Phys.Chem C. 118 (38), 2014

Dynamics of hot excitons in PbX QDs



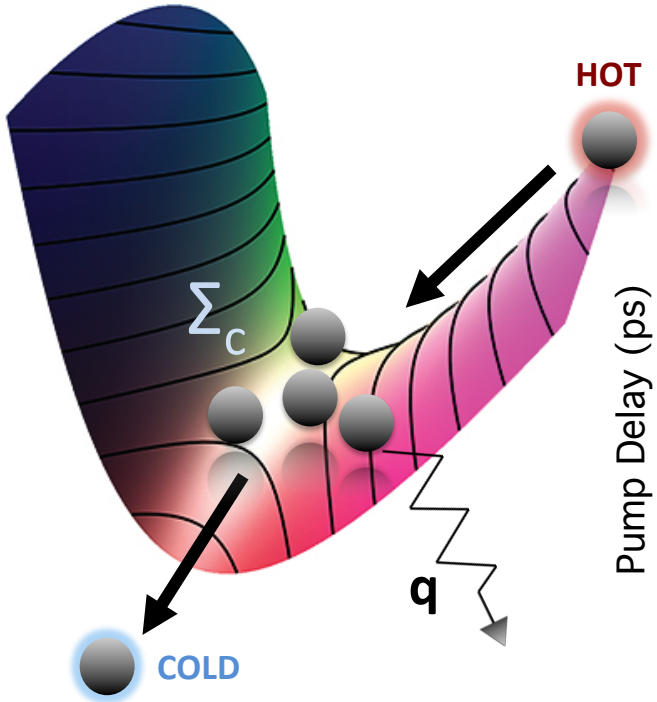
A Phonon Scattering Bottleneck for Hot Carrier Cooling in Lead Chalcogenide Nanocrystals

Geiregat et al., ACS Nano, 2015 (Just Accepted)

Dynamics of hot excitons in PbX QDs

PbX (X = S, Se)

Σ_c = '*saddle point*' at high energy !



Phonon Scattering

$k_{in} = k_{out} + q$