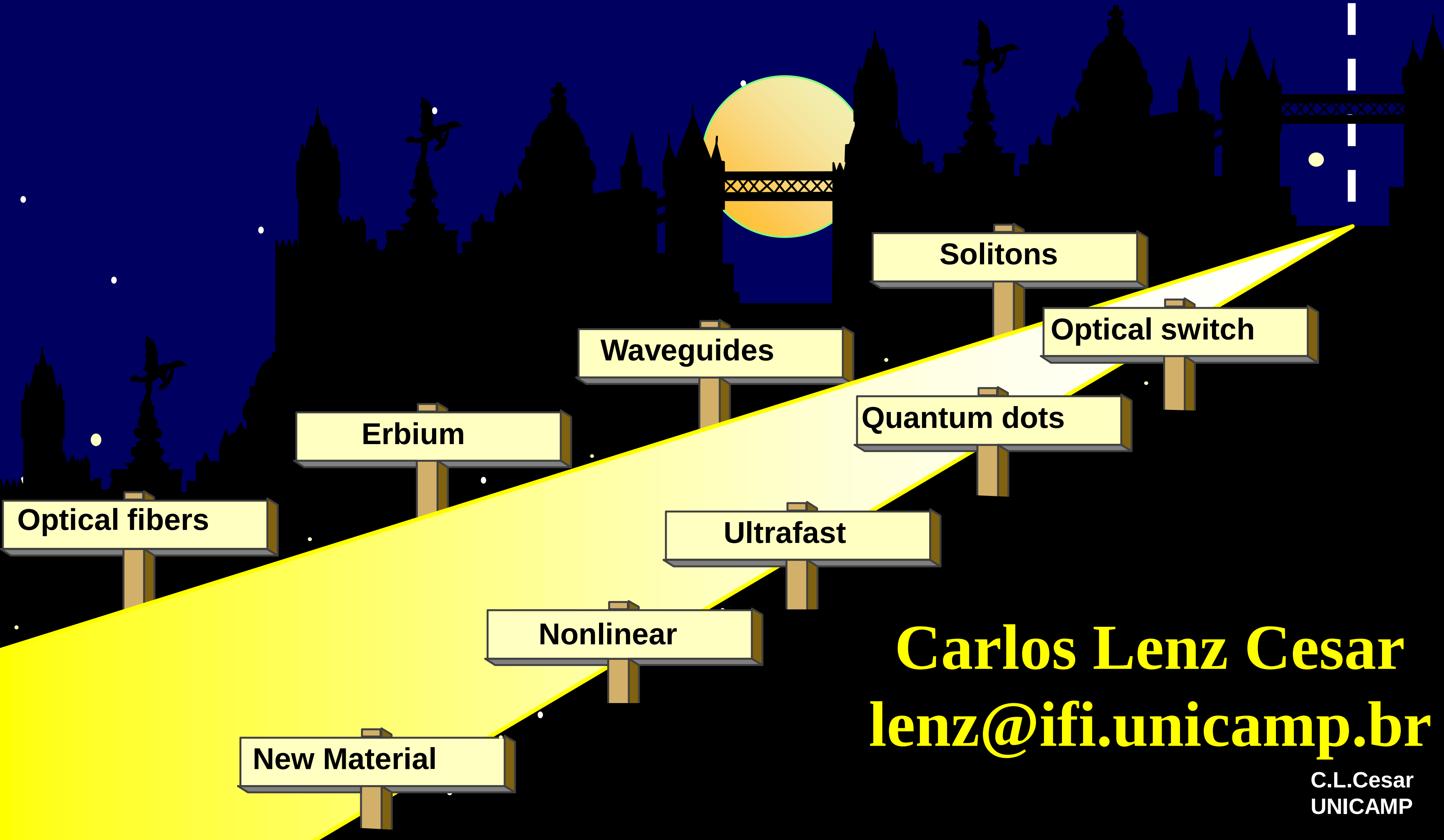
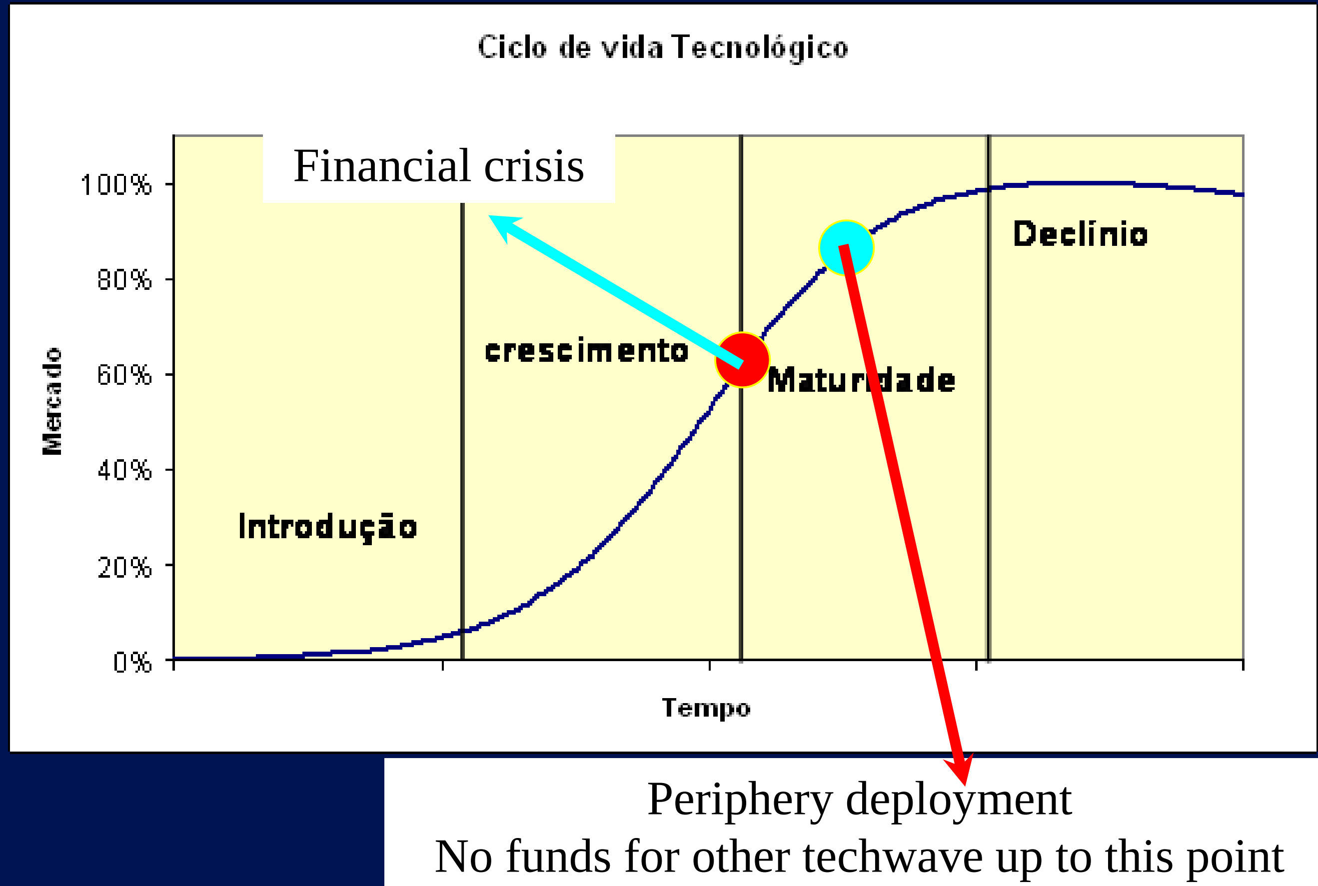
Quantum Dots

100 Gbit/s



Carlos Lenz Cesar
lenz@ifi.unicamp.br

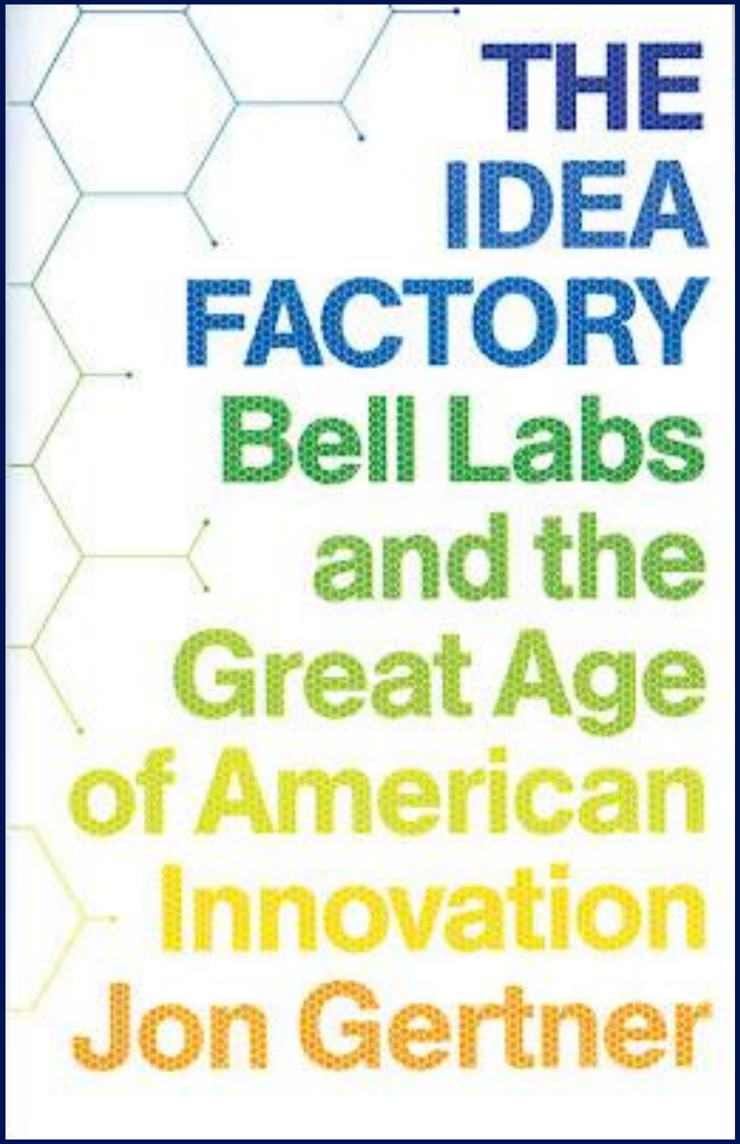
Carlota Perez: Technological Revolutions and Financial Capital



5 Revolutions - ~ 60 years total cycle

1. Industrial Rev. – England – 1771
2. Steam and rail-road – England – 1829
3. Steel and eletricity – England+USA+Germany – 1875
4. Oil, cars and mass production – USA – 1908
5. Information and comunications – USA – 1971

Bell Labs na Revolução da Informação



Amplification, amplification, amplification!

Beginning 20th century - Telephone calls < 30 km .
1913 - De Forest sell triode vacuum tube patent to AT&T
San Francisco 1915 World Fair 1st Transcontinental Call

Thomas Atson

Alexander Bell

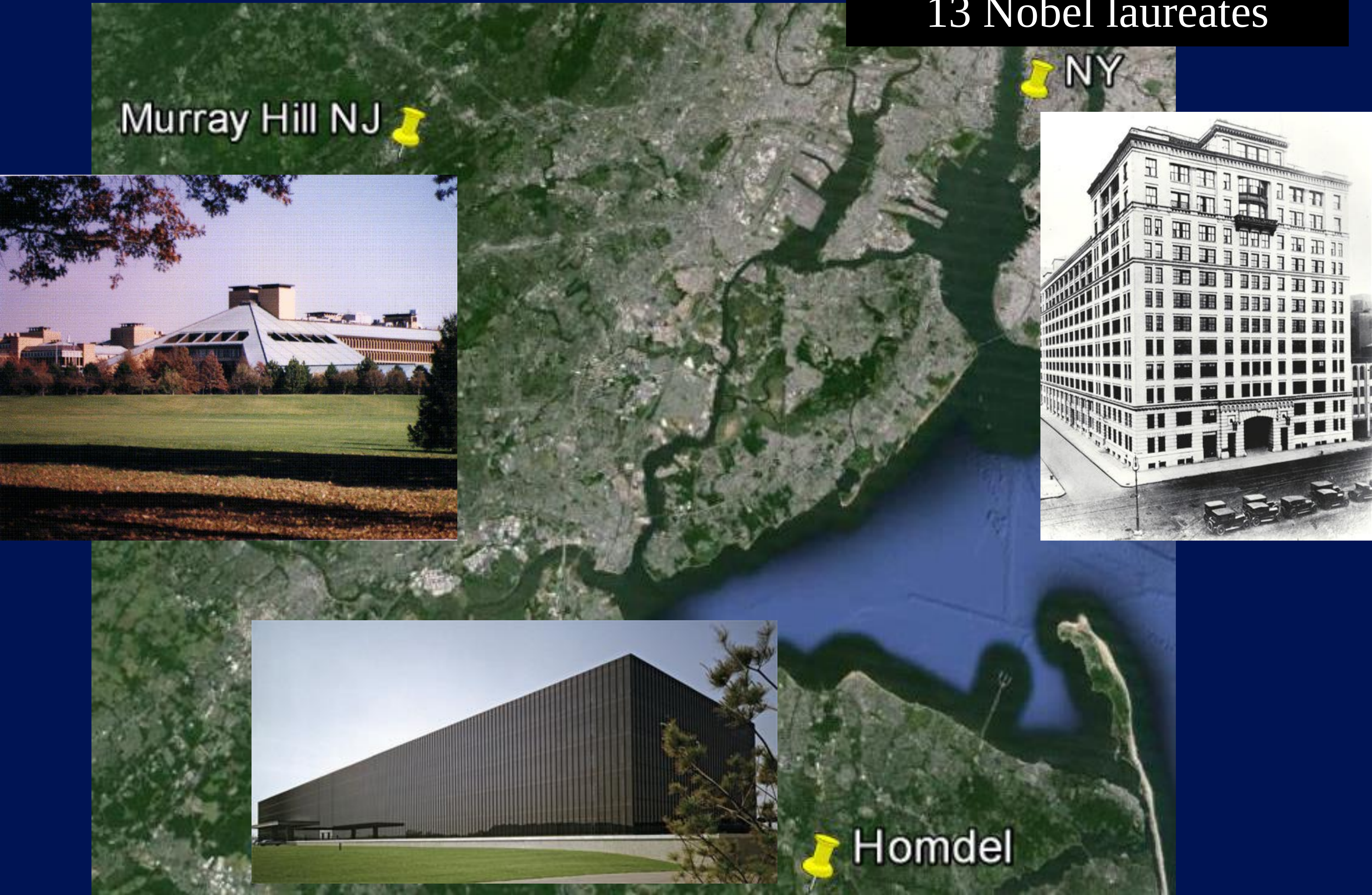
Theodor Vail

Repercussions: AT&T became a monopoly

1925: Bell Labs became a company

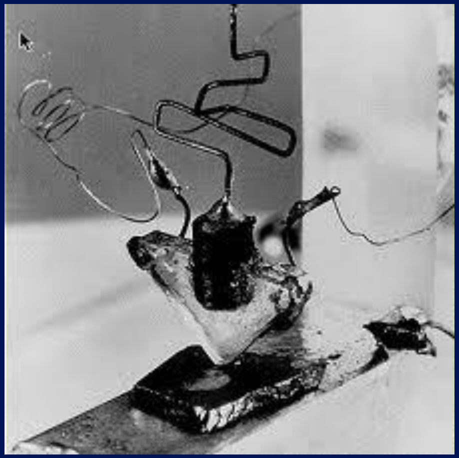
AT&T and Western Electric only costumers

Bell labs hired PhDs:
Millikan main provider
13 Nobel laureates



1947 marvelous year

Solid State: Transistor - Bardeen + Brattain + Shockley



Information Theory – Claude Shannon

Shockley - Stanford
Silicon Valley

Traitorous 8
Fairchild – 1957

Importance of Bell Labs – 1983 AT&T breakup

Vacuum tubes
Photovoltaics
Transistor
Satellites communicatios
Cell phone
Laser – semiconductors
Optical fibers
Ultrafast lasers
Non linear optics

Information theory
C
UNIX

13 Nobel laureates

Clinton Davisson – 1937
Bardeen + Brattain + Shockley – 1956
Phil Anderson – 1977
Penzias + Wilson - 1978
Steven Chu – 1997
Stormer + Laughlin + Tsuj - 1998
Boyle + Smith – 2009

The beggining: 1971 first INTEL chip

1946 – ENIAC

1951 – Texas Instruments

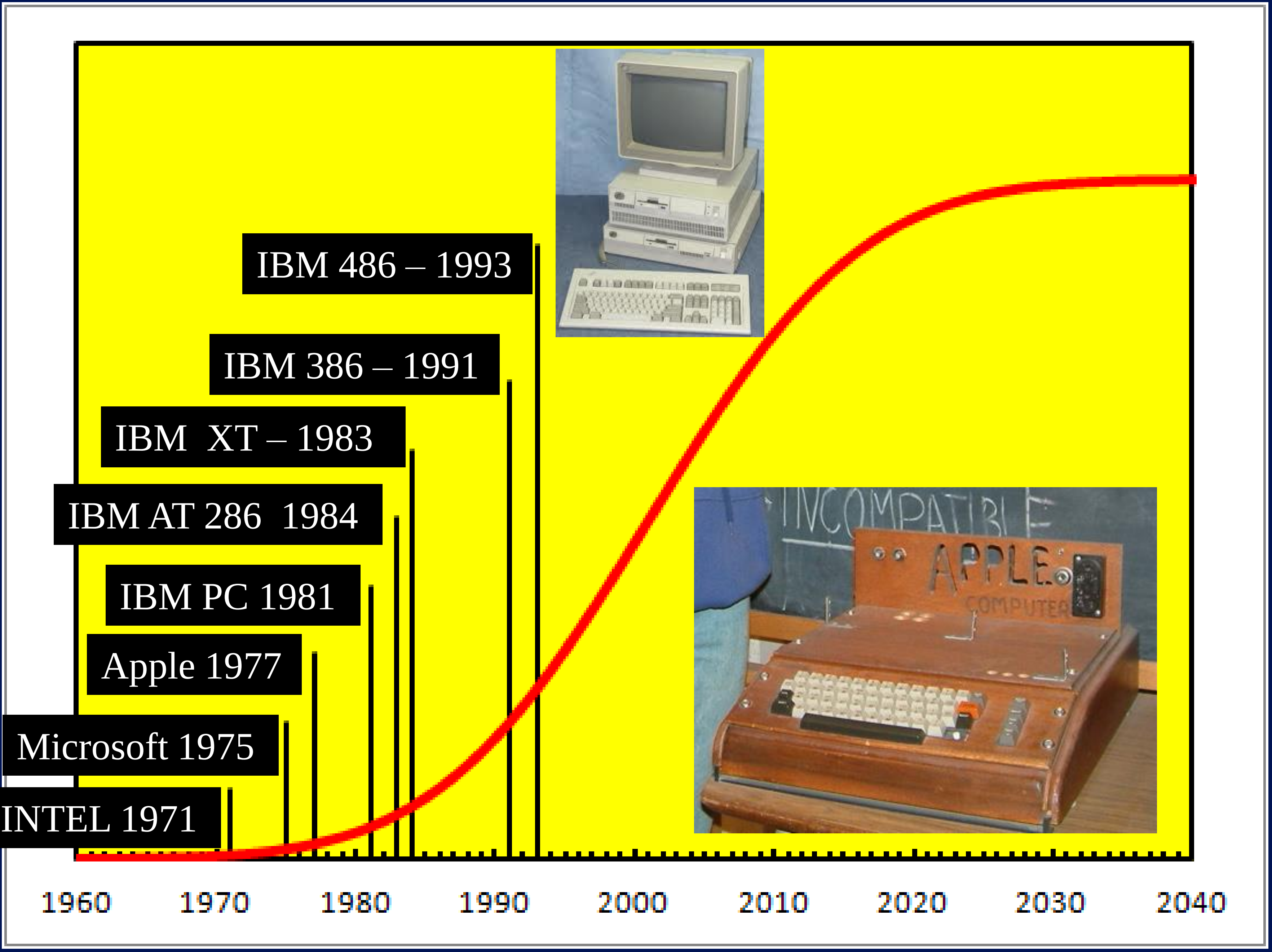
1958 – Noyce & Kilby (Nobel 2000) 1st integrated circuit

1968 - INTEL – 1968 Robert Noyce e Gordon Moore

Gordon Moore

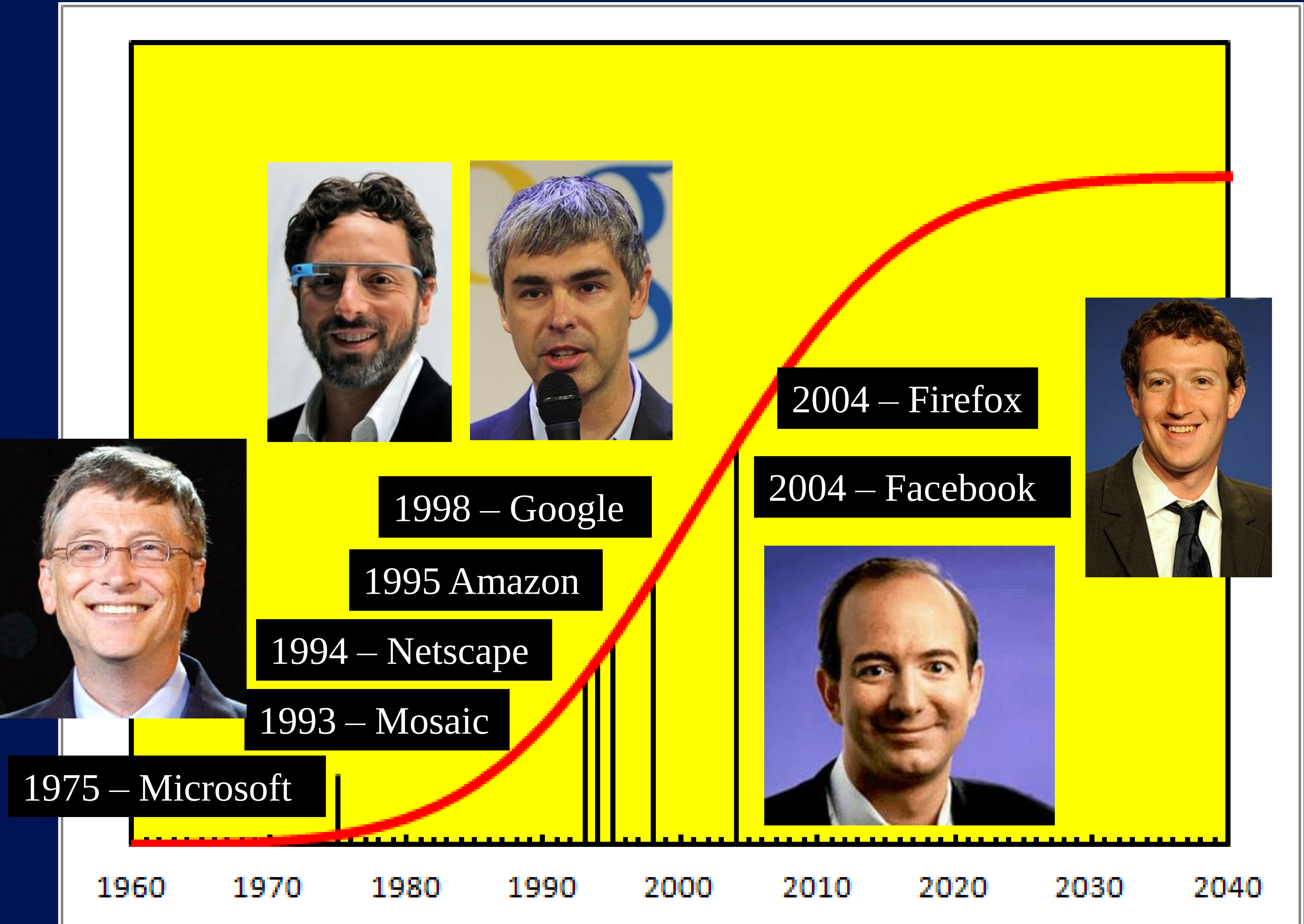
Robert Noyce

Hardware



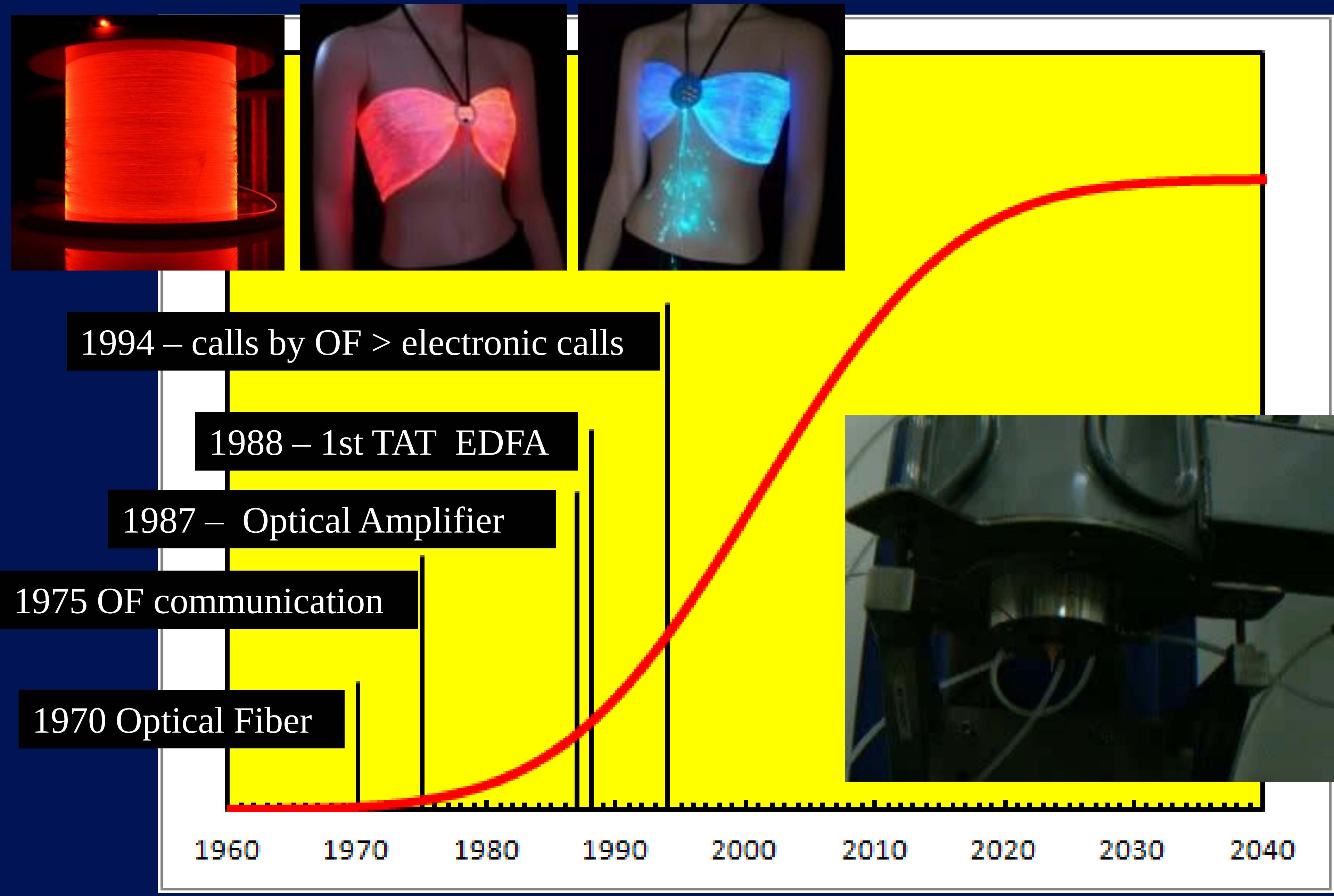
IBM 486 – 1993
IBM 386 – 1991
IBM XT – 1983
IBM AT 286 1984
IBM PC 1981
Apple 1977
Microsoft 1975
INTEL 1971
1960
1970
1980
1990
2000
2010
2020
2030
2040

Software

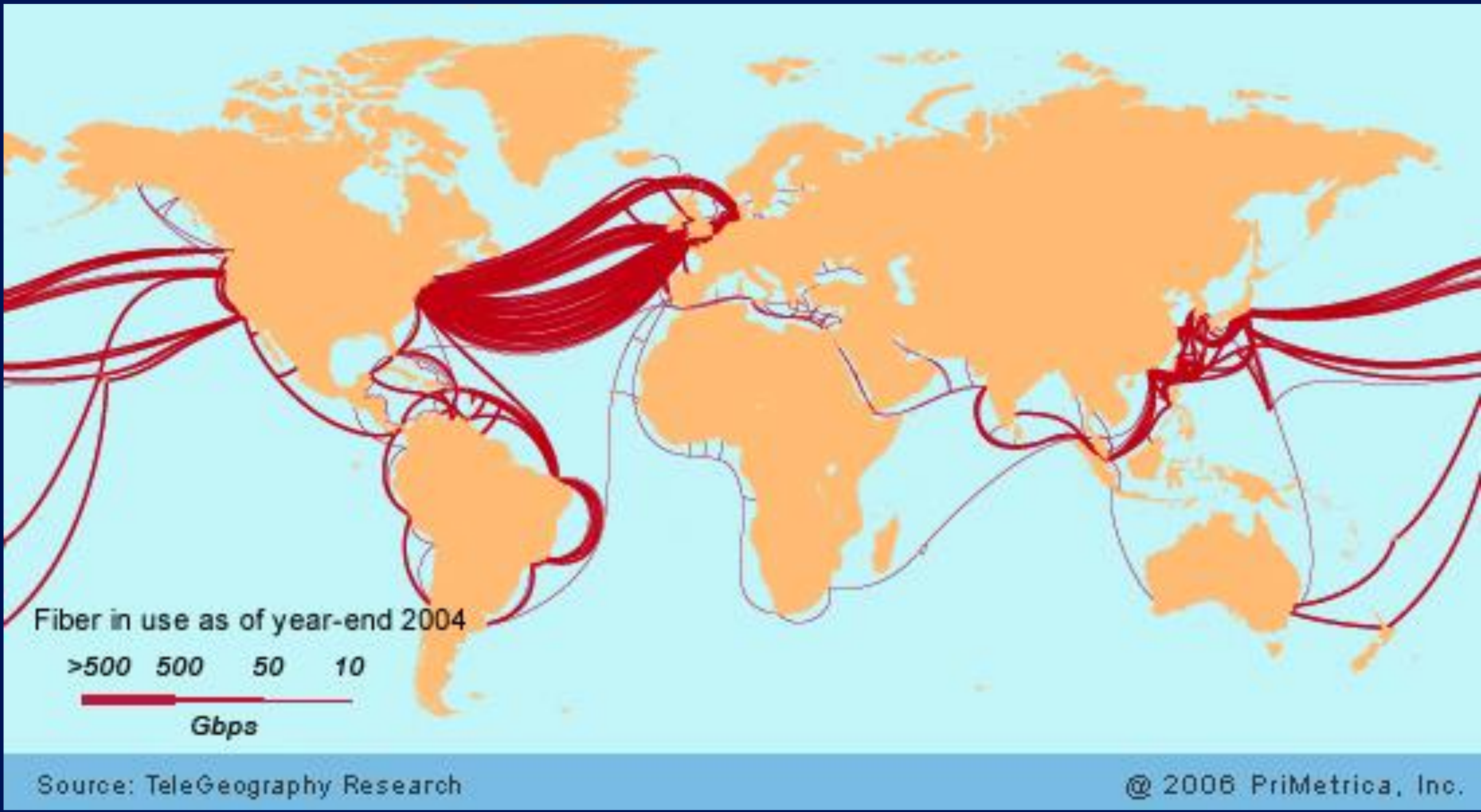


2004 – Firefox
2004 – Facebook
1998 – Google
1995 Amazon
1994 – Netscape
1993 – Mosaic
1975 – Microsoft
1960
1970
1980
1990
2000
2010
2020
2030
2040

Optical Network



Amplification, amplification, amplification!
Optical Erbium Doped Fiber Amplifier



Bell Labs and Brazil

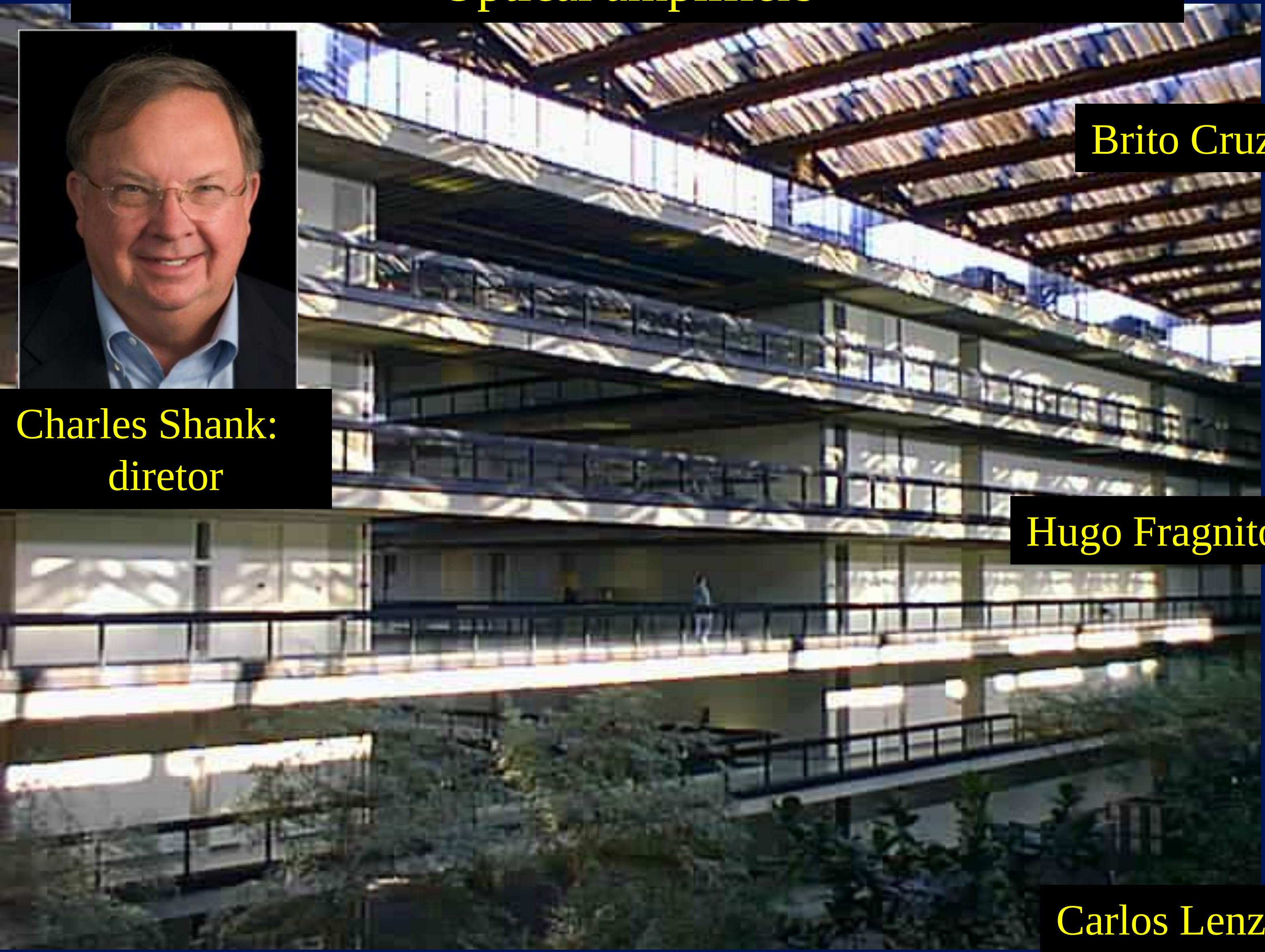
IFGW Founders

José Ellis Ripper Filho

Sérgio Porto

Rogério Cerqueira Leite

Photonics for communications: ultrafast lasers, Semicondutors, Non linear optics, Optical fibers, Optical amplifiers



Charles Shank: diretor

Brito Cruz: 1986-1987

Hugo Fragnito: 1987-1989

Carlos Lenz: 1988 – 1990

Quantum Dots in UNICAMP

Started with CdTe 1990

PbTe 1995

Colloidal 1999

Laser Ablation 2001

Teses sobre Quantum Dots disponíveis no site do IFGW
Orientação: Lenz

Doutorado

Carlos Roberto M. de Oliveira 1995
Gastón E. Tudury 2001
André A. de Thomaz 2013
Diogo B. Almeida 2014

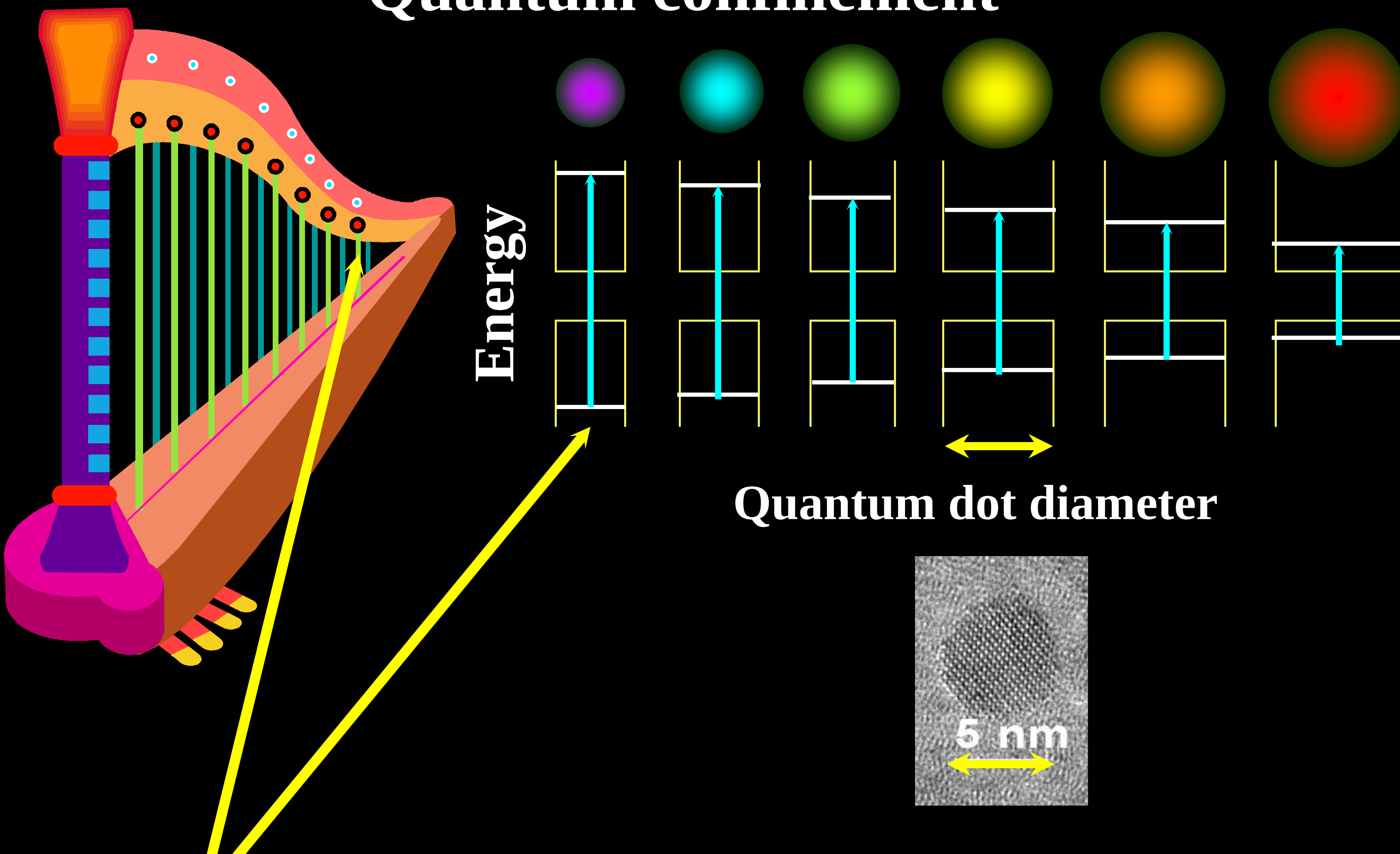
Mestrado

Cristiane O. Faria 2000
Antônio Á. R. Neves 2002
Wendel L. Moreira 2005
Gilberto Júnior Jacob 2005
Diogo B. Almeida 2008

Outras teses Dr. recomendadas:

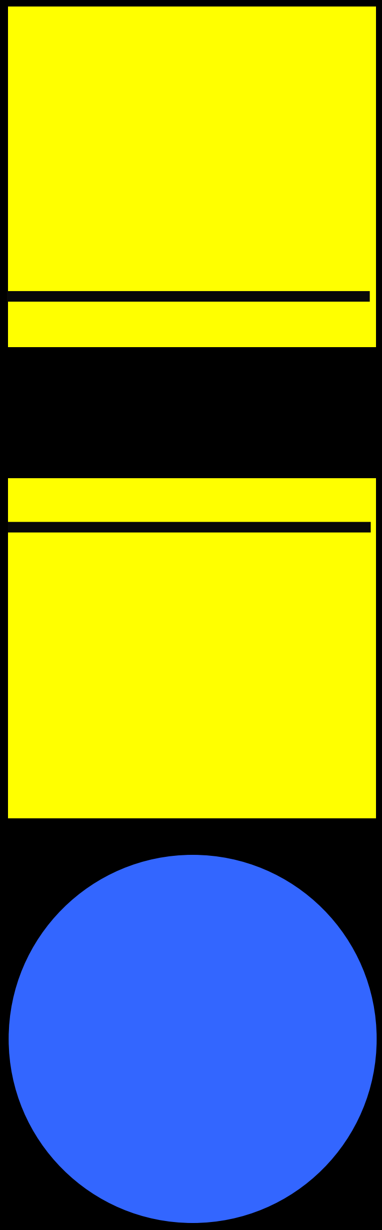
Eugenio Rodrigues Gonzales 2004
Lázaro A. Padilha Jr. 2006

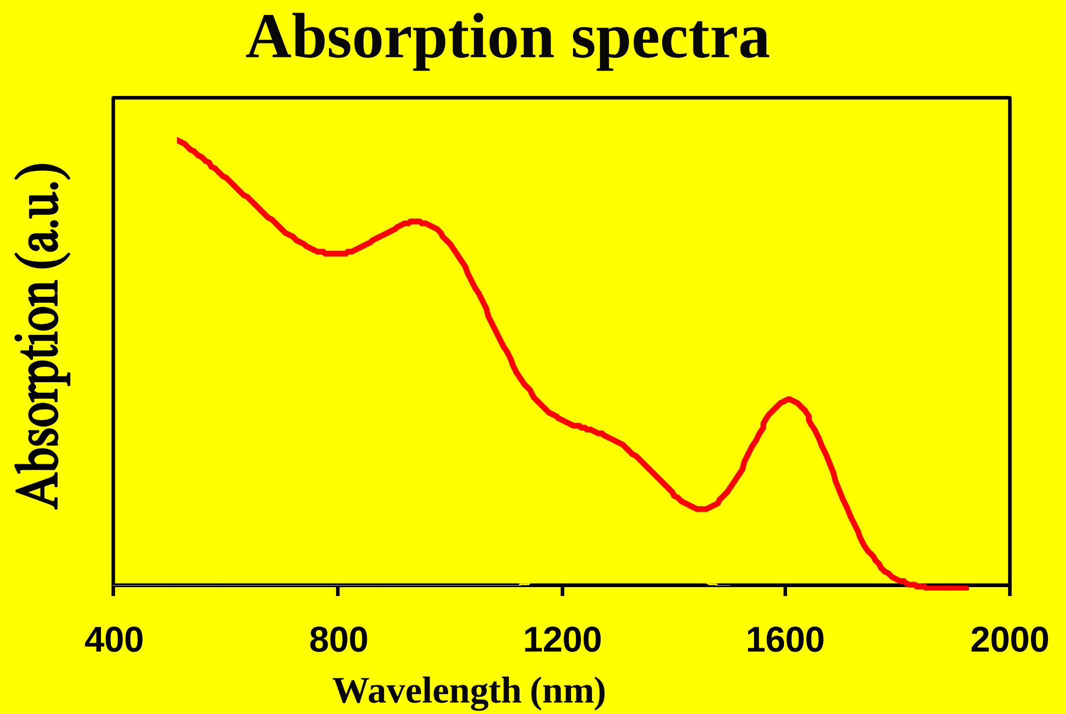
Quantum Dots: size controlled color!
Quantum confinement



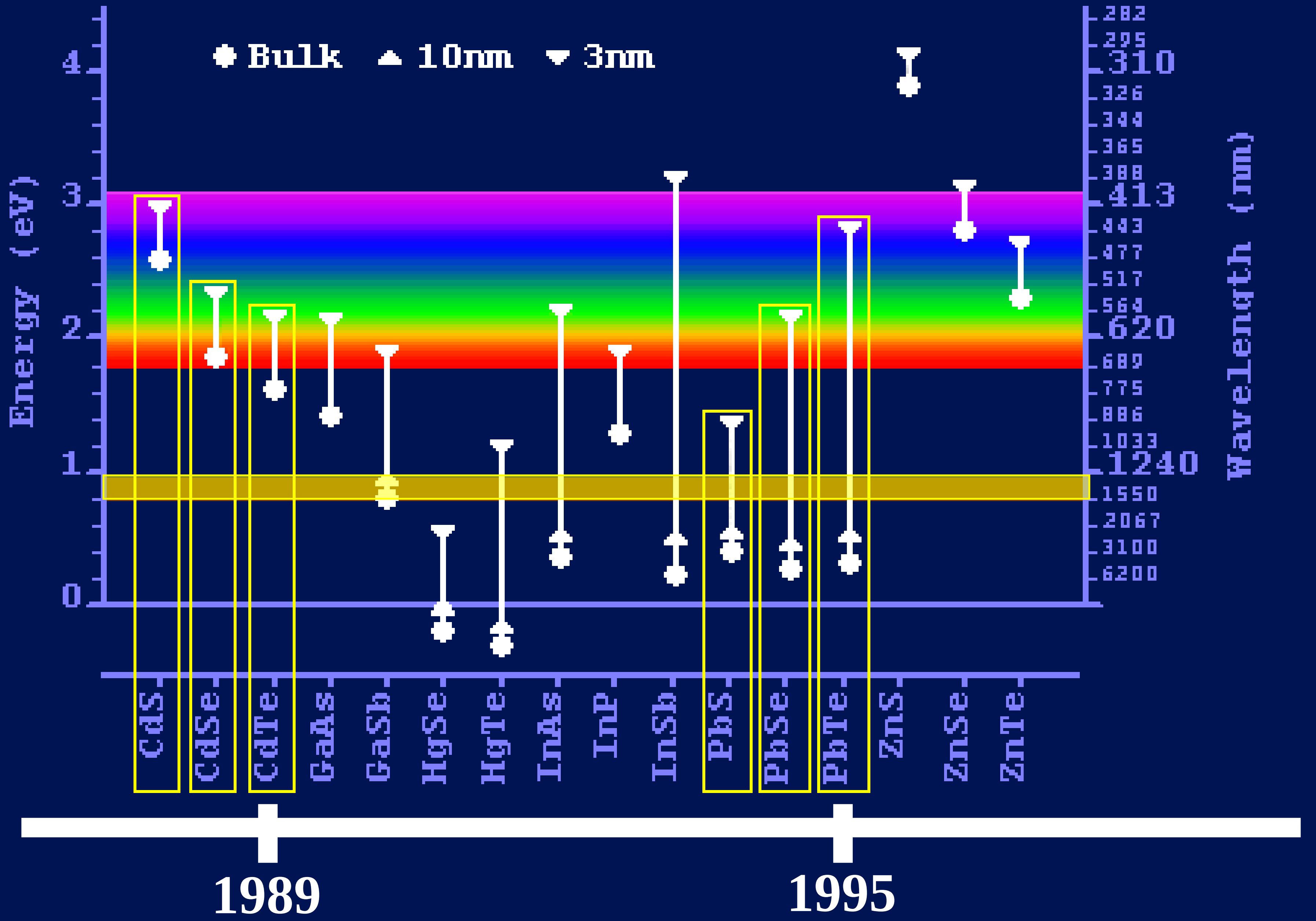
Smaller cord -> higher frequency -> higher E -> smaller λ

Quantum Dot: quantum confinement and size



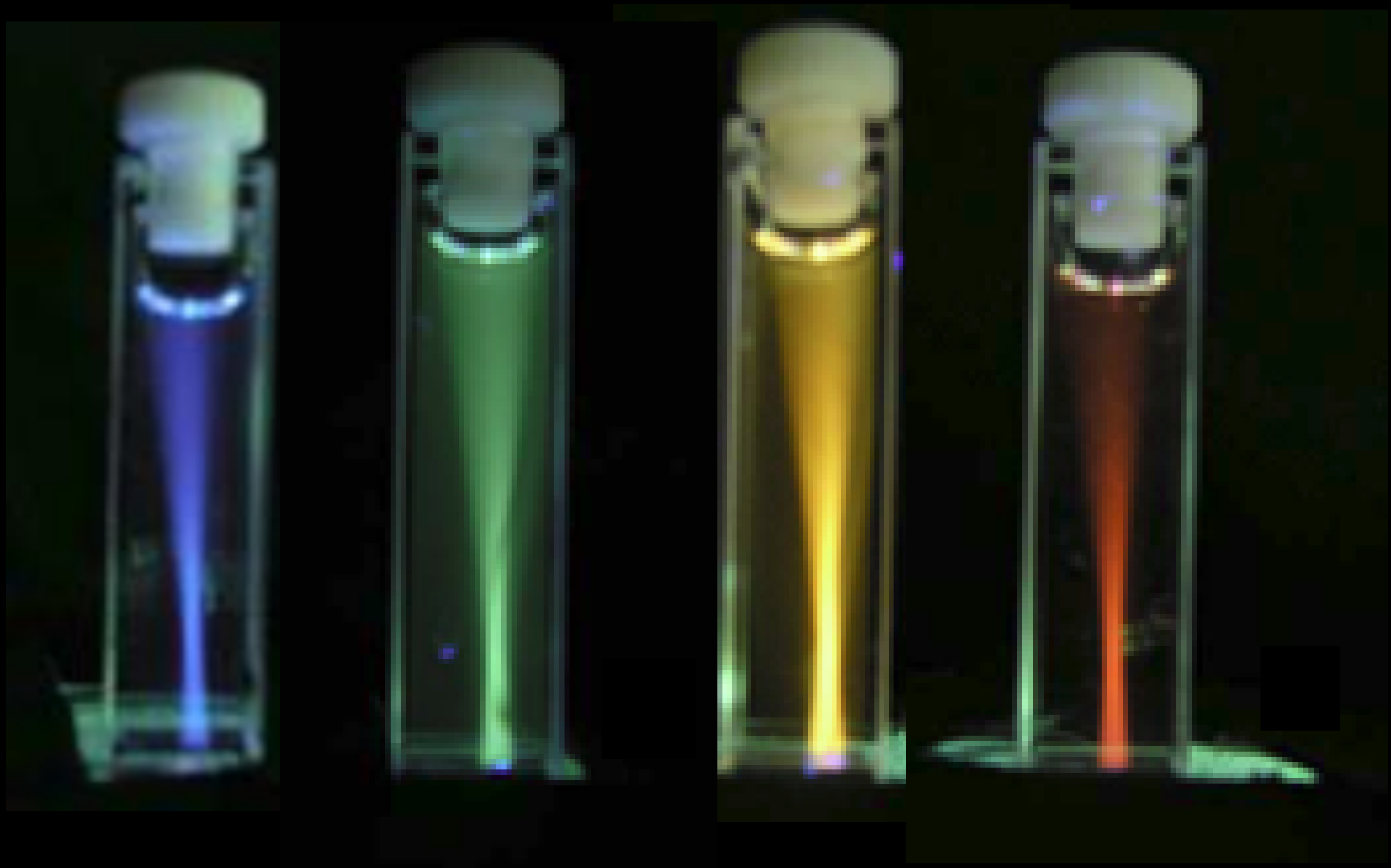


Right wavelength: optical properties tuning



End of controversy quantum confinement vs stechoimetric variation

CdTe Coloidal Quantum Dots Produced at UNICAMP



NATURE NANOTECHNOLOGY | VOL 5 | JUNE 2010 | www.nature.com/naturenanotechnology

editorial

The many aspects of quantum dots

From fundamental physics and chemistry to digital cameras, improved displays and more natural lighting, nanoscale semiconductor structures called quantum dots are having an impact on many areas of science and technology.

For some reason, semiconductor quantum dots do not feature prominently in the history of nanotechnology. Like molecular beam epitaxy[1], for instance, they have had a much lower profile than the carbon nanotube and various forms of scanning

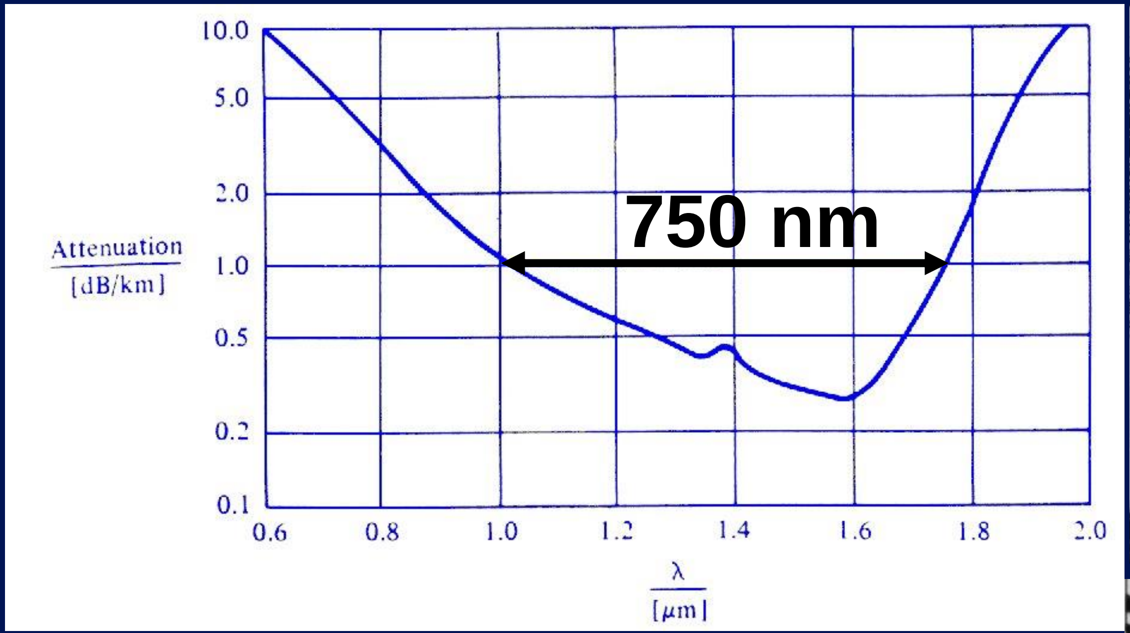
advantages over higher-profile carbon-based nanomaterials for some uses. This is reflected by the range of basic science that can be studied with quantum dots[3], and the breadth of potential applications for these materials — and disputes about patents.

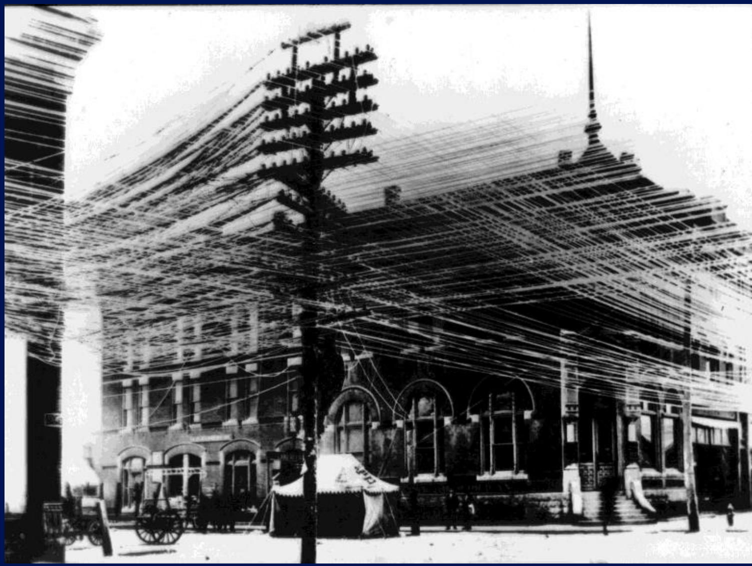
Applications and Technological Importance

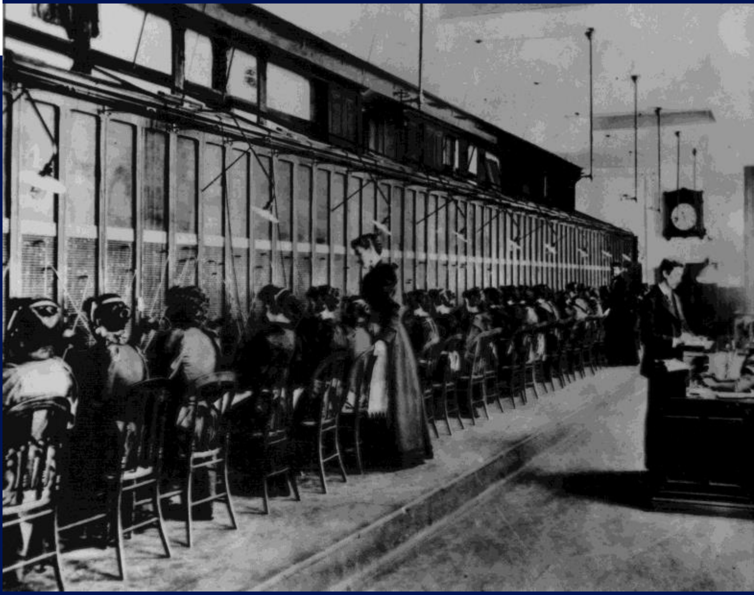
Switching:

Ultrafast Optical Devices

Optical Communication - On the edge







Typical optical fiber attenuation

Bandwidth for 1 dB/km losses

$\Delta\lambda = 750$ nm $\Rightarrow \Delta\nu\Delta\tau = 0.44$

Total Capacity of only one fiber

10^{14} = 100 Tbit/s

Optical Device Material Requirements

Devices always based on Δn or $\Delta\alpha$

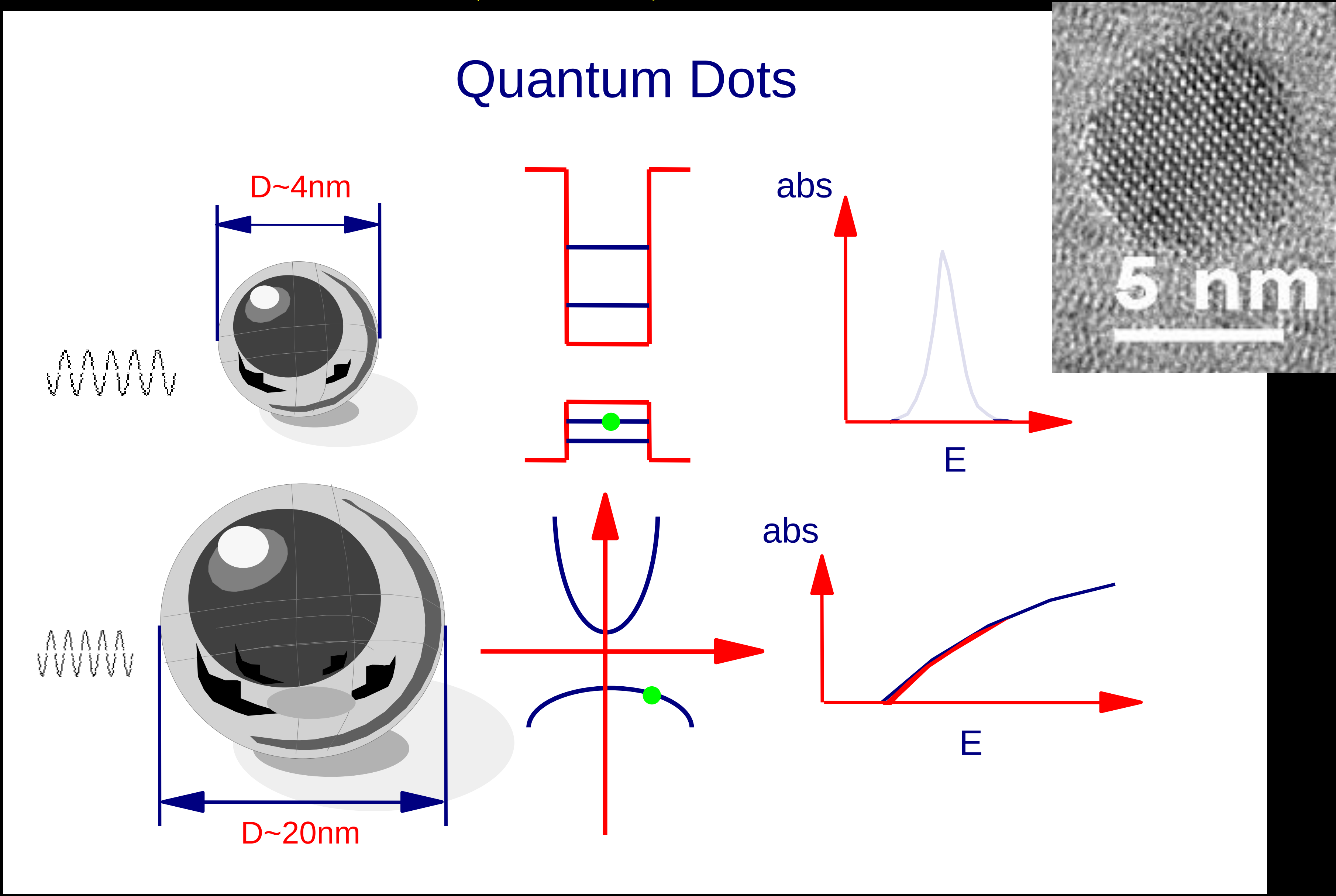
Dilemma

Δn or $\Delta\alpha$	vs	Response time
High Optical Nonlinearity		**Ultrafast Response time < 3 ps**
resonant: ↑		**resonant:** ↑
non resonant: ↓		**non resonante:** ↓

Wavelength: 1.5 or 1.3 μm

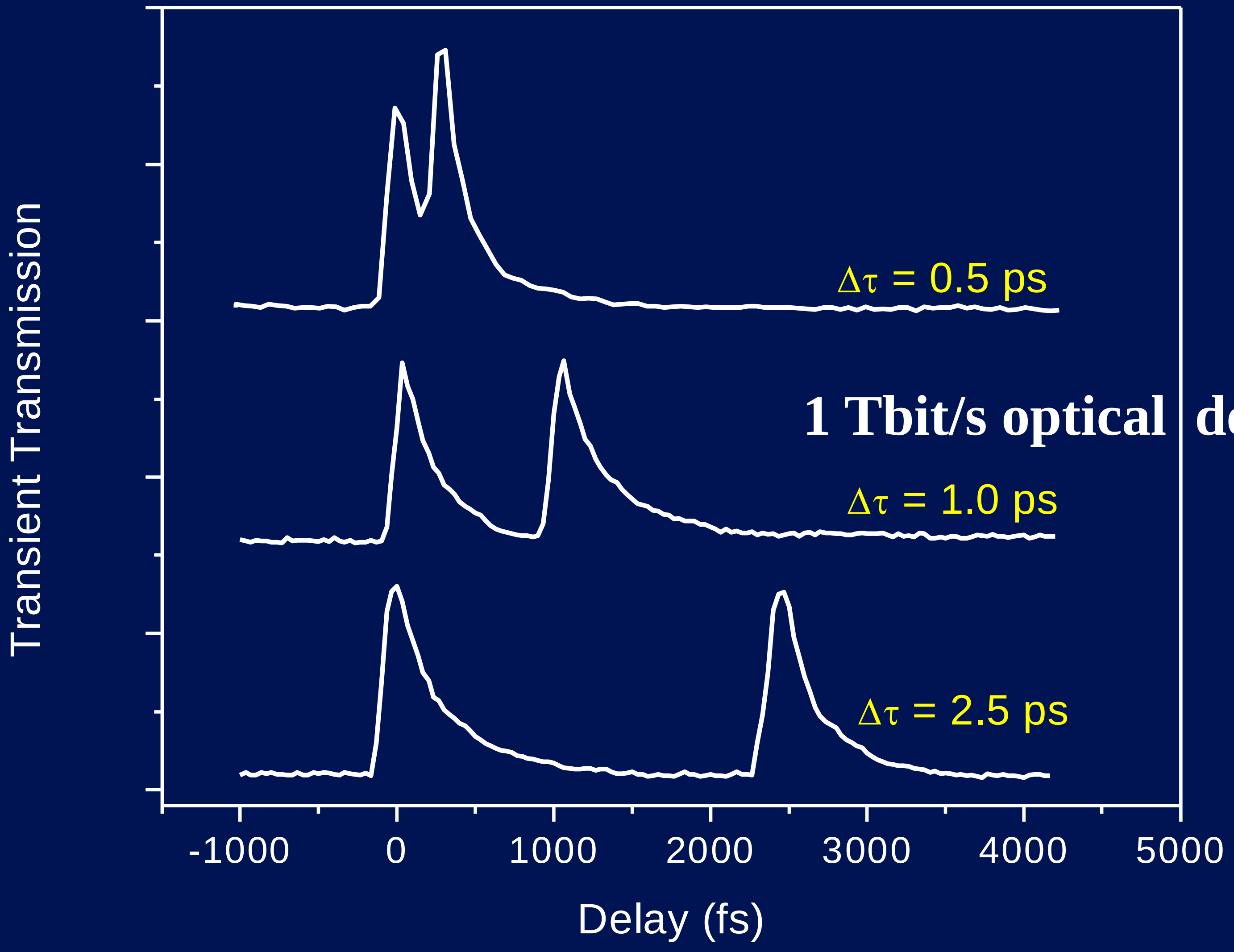
Compatible with Optical fibers

Quantum dots (QD's): dilemma solution



High nonlinearity & ultrafast response time:

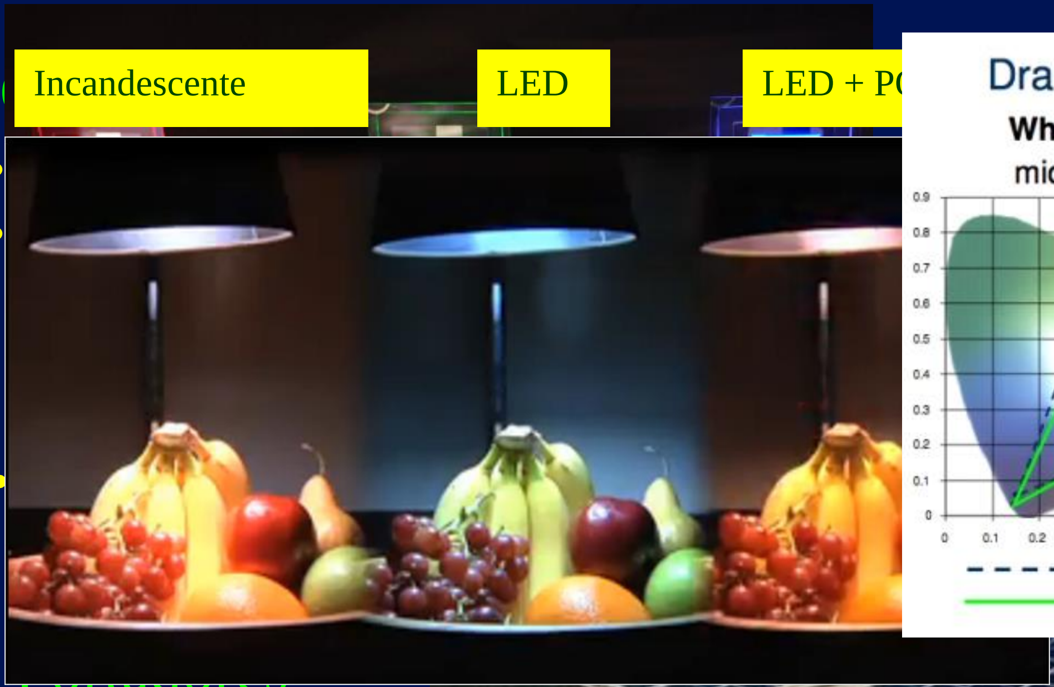
CdTe quantum dot

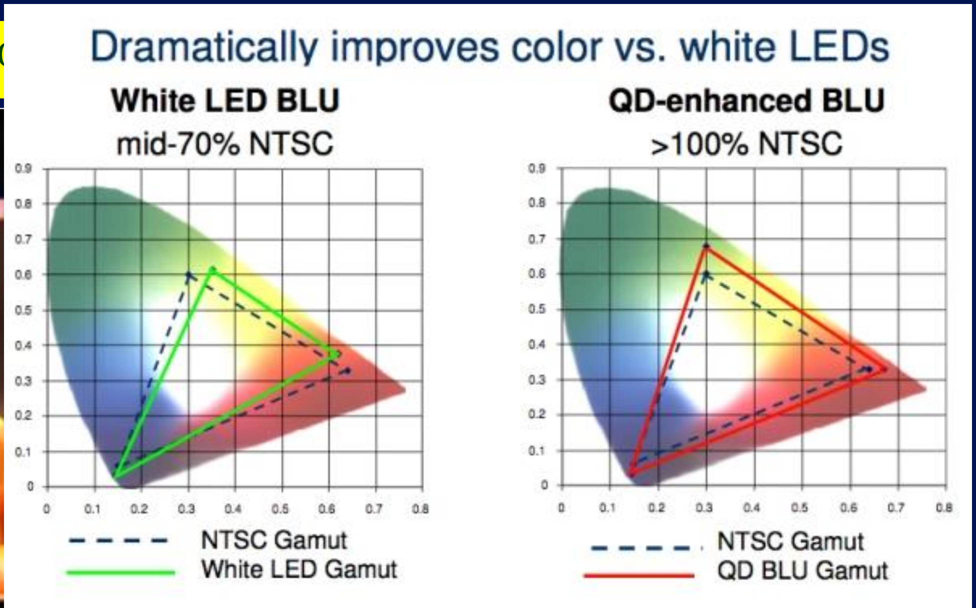


1 Tbit/s optical device?

Padilha et al, Appl. Phys. Lett. 86 (16), 161111 (2005)

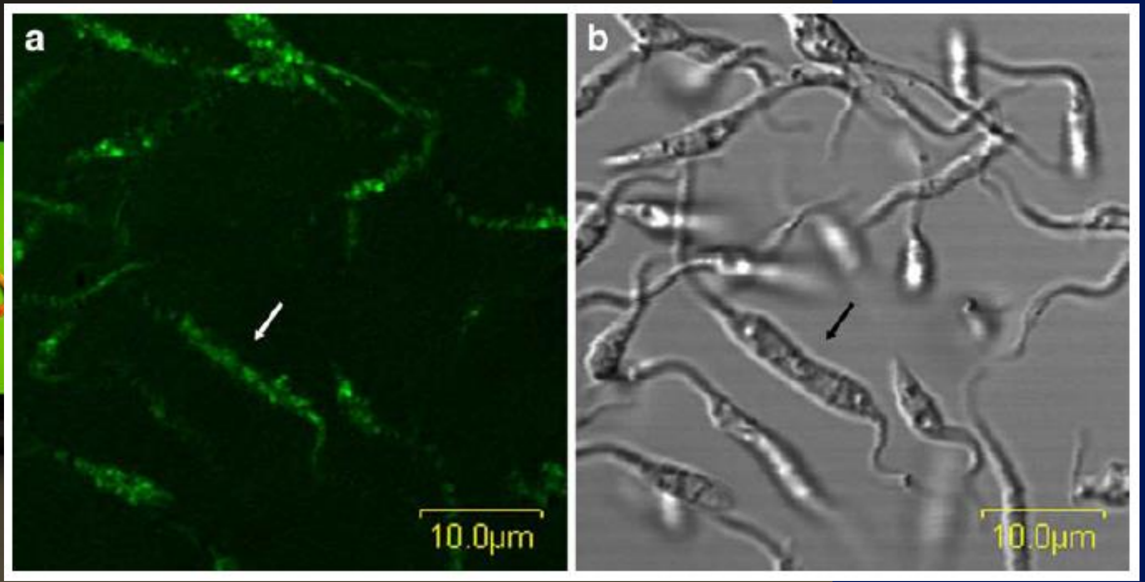
Aplicações dos PQs





Portadores

•LEDs
•Displays



Fótons

•Marcadores Fluore
•Iluminação

Aplicações PQs

Óptica não-linear:

- Chaveamento óptico
- Sistemas de 2 níveis (co

Processos que precisam de alta eficiência de fluorescência

Fótons → Portado

- Células fotovoltaicas (energia solar)

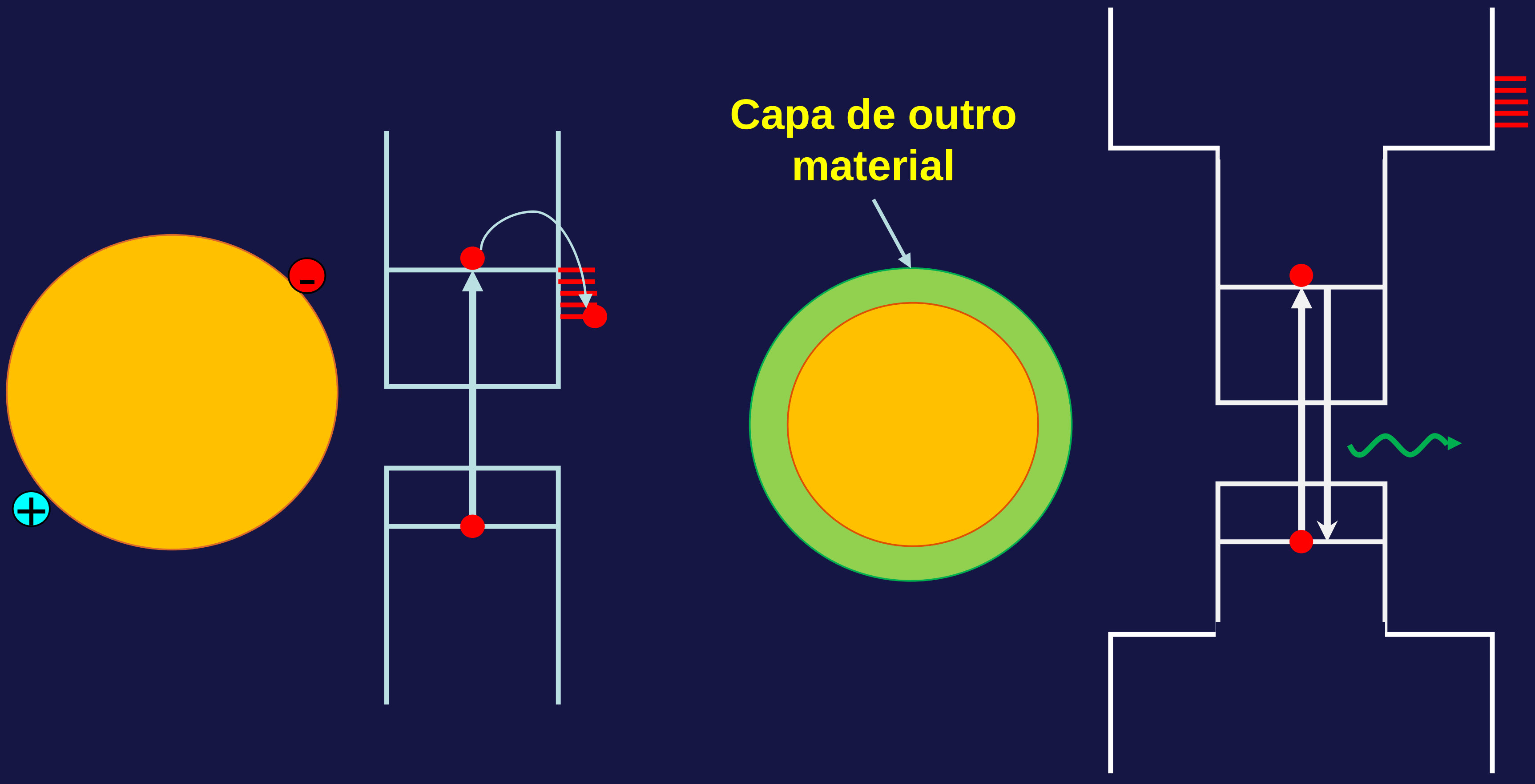
Portadores → Fótons

- LEDs
- Displays

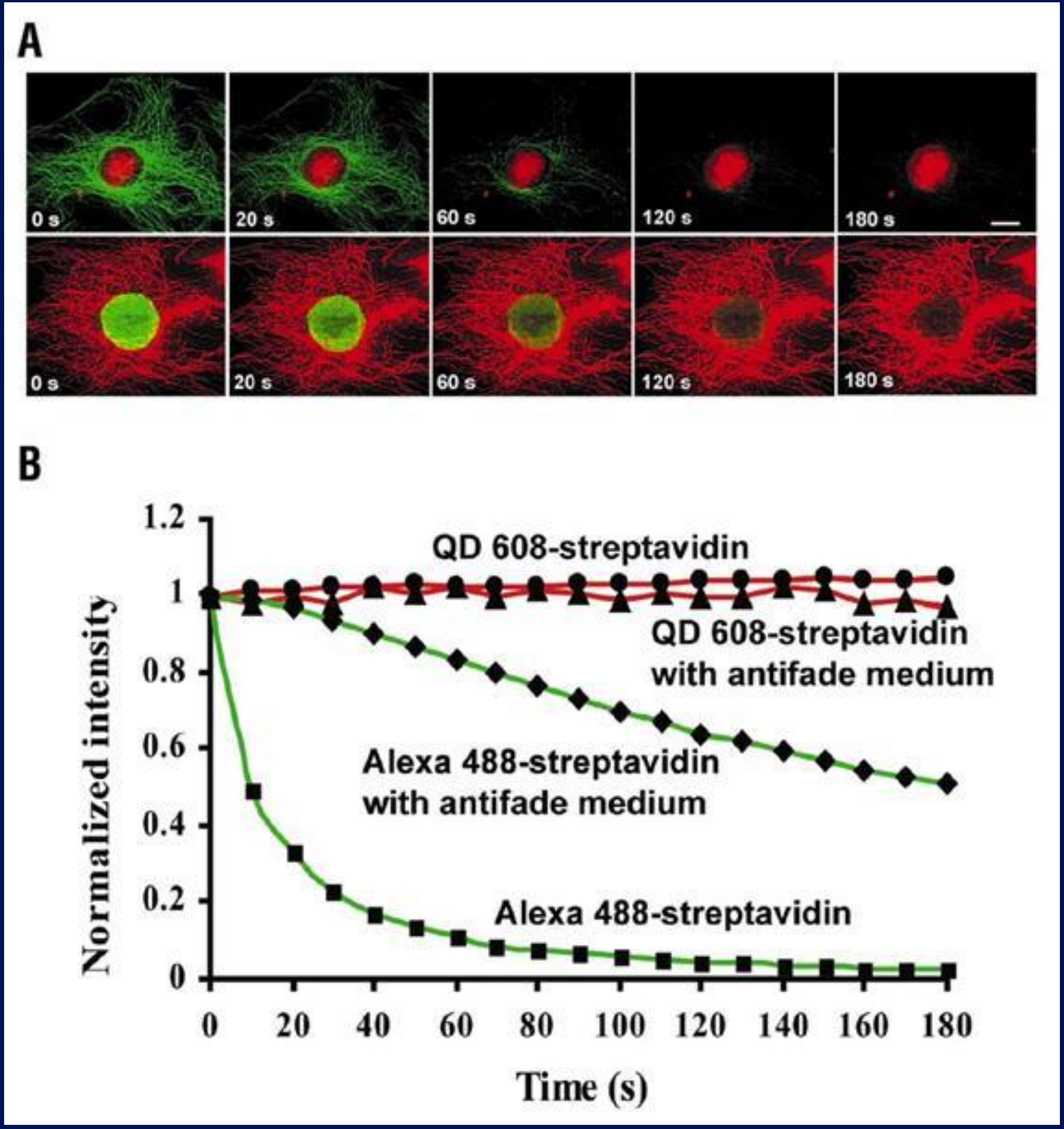
Fótons → Fótons

- Marcadores Fluorescentes (aplicações biológicas)
- Iluminação

Precisamos da passivação para aumentar a eficiência dos pontos quânticos

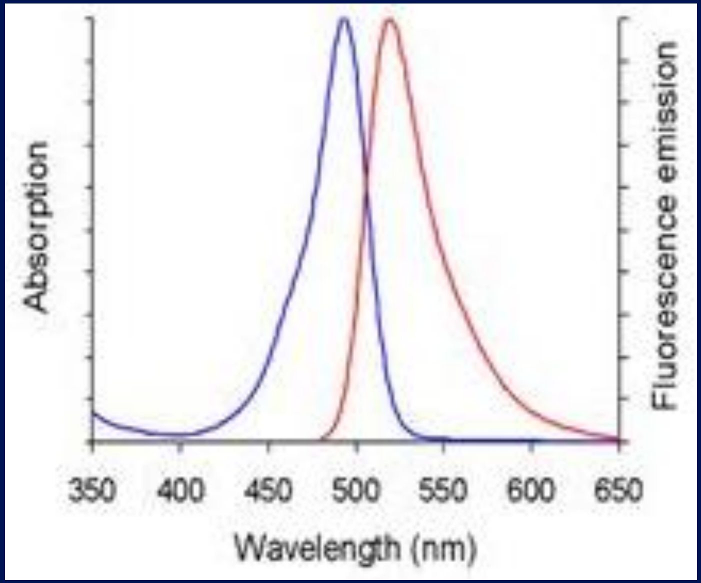


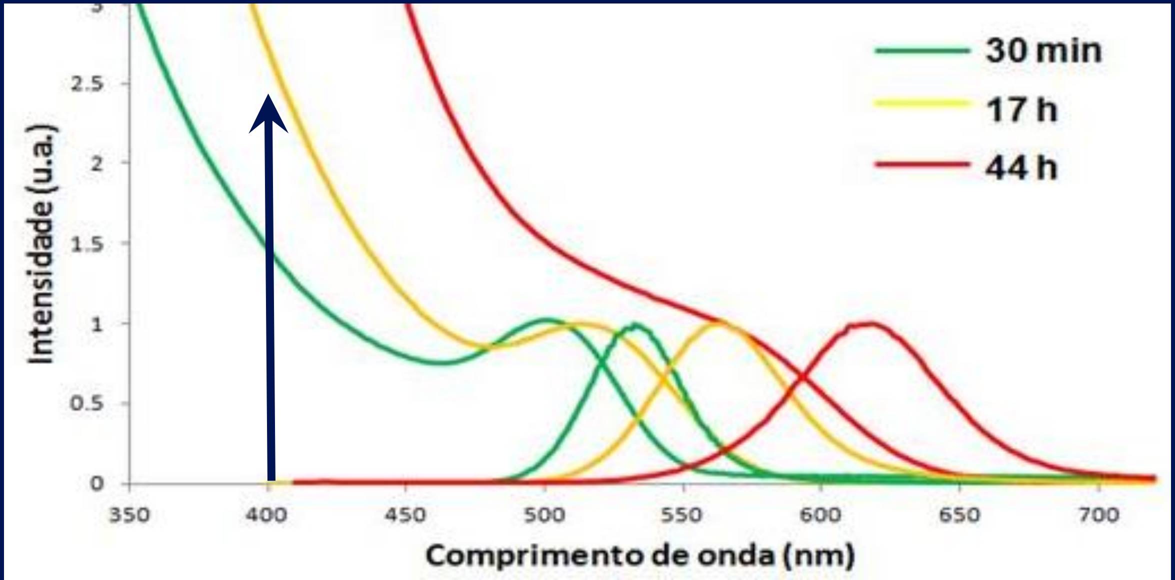
No photobleaching!

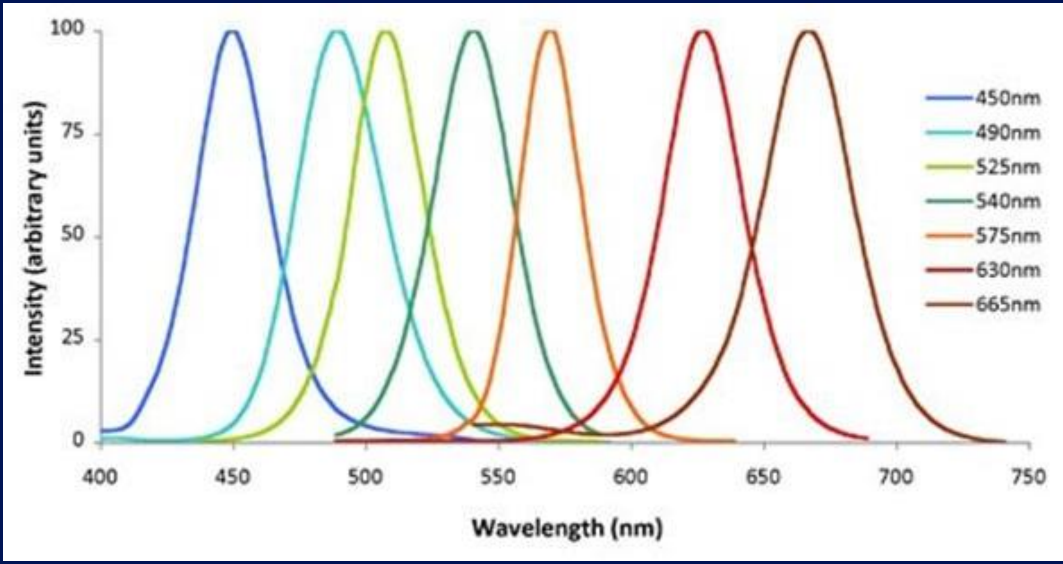


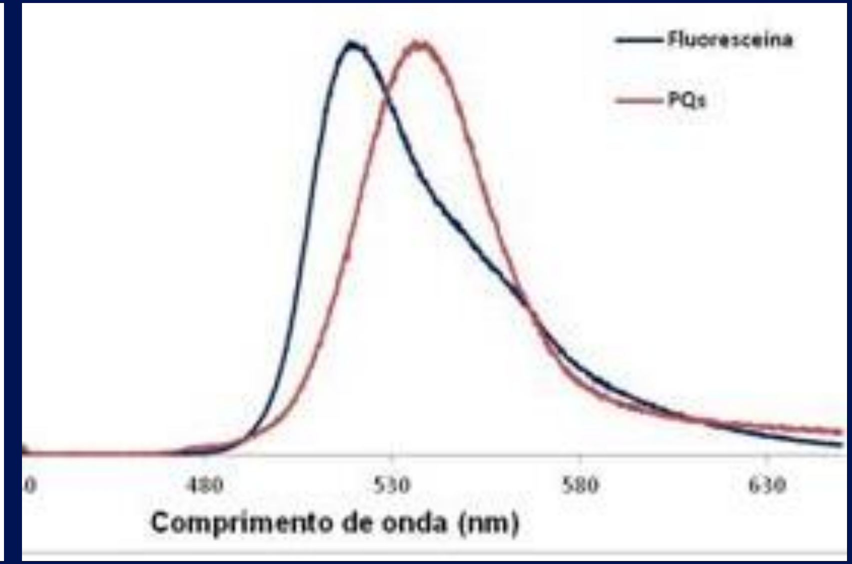
X. Wu et al, Nature Biotech. 21, 41 - 46 (2003).

One laser to excite all colors





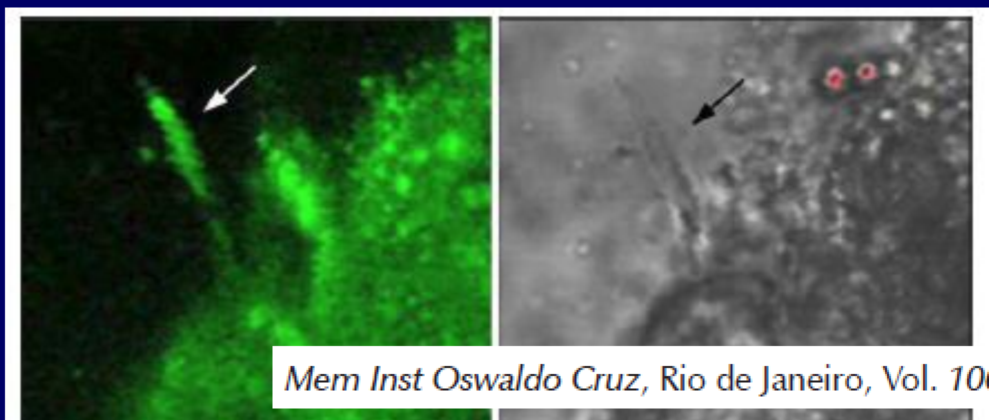


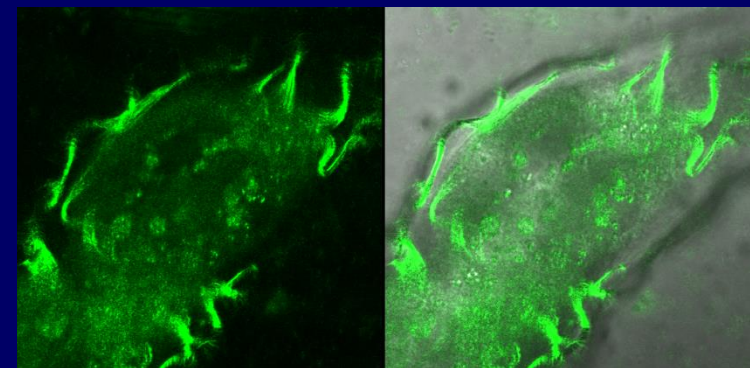


In vitro and in vivo documentation of quantum dots labeled *Trypanosoma cruzi–Rhodnius prolixus* interaction using confocal microscopy

Denise Feder · Suzete A. O. Gomes · André A. de Thomaz · Diogo B. Almeida · Wagner M. Faustino · Adriana Fontes · Cecília V. Stahl · Jacenir R. Santos-Mallet · Carlos L. Cesar

Parasitol Res (2009) 106:85–93





Mem Inst Oswaldo Cruz, Rio de Janeiro, Vol. *106*(2): 158-165, March 2011

Studying nanotoxic effects of CdTe quantum dots in *Trypanosoma cruzi*

Cecilia Stahl Vieira[1], Diogo Burigo Almeida[2], André Alexandre de Thomaz[2], Rubem Figueredo Sadok Menna-Barreto[3], Jacenir Reis dos Santos-Mallet[1], Carlos Lenz Cesar[2], Suzete Araujo Oliveira Gomes[1,4], Denise Feder[4]/+

Physics of the Quantum Dots

Particle in a box

Quantum Confinement: Simple Model

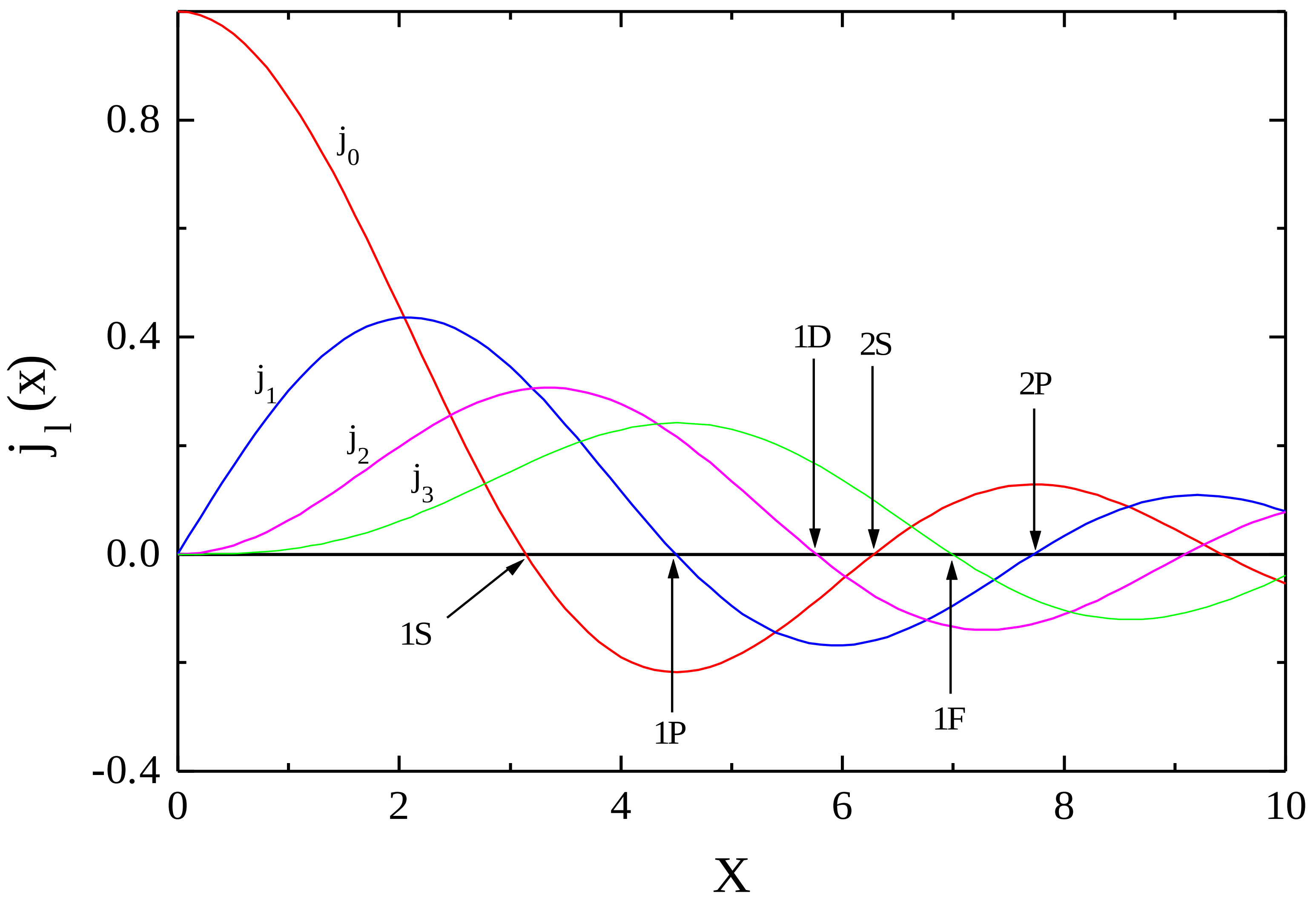
	Free electron function		Free electron energy
	↓		↓
Bulk:	$\Psi_{wave} = e^{ik\bullet R} \cdot u_{Bloch}$	→	$E = E_g + \hbar^2 k^2/(2m^*)$
Quantum dot:	$\Psi_{wave} = \xi(R) \cdot u_{Bloch}$	→	$E = E_g + E_{conf}$
	Envelope function		Confinement energy

Infinite spherical well

spherical Bessel function		Boundary condition		
↓		↓		
$\xi(R) = j_n(kR) \cdot Y_n^m(\theta, \phi)$	→	$j_n(ka) = 0$	→	$E_{conf} = \hbar^2 k_{root}^2/(2m^*)$

$$\left[-\frac{\hbar^2}{2m^*}\nabla^2 + U_{esf}\right] F_{n,l,m}(\vec{r}) = E_{n,l}\, F_{n,l,m}(\vec{r})$$

Spherical Bessel Functions Roots



Regras de seleção: 1-fóton $F \propto \left| \left\langle \Psi_{in} \middle| e_z \cdot \nabla \middle| \Psi_{fin} \right\rangle \right|^2$

Função de onda: $\left| \Psi_n \right\rangle = \left| \xi_n u_n \right\rangle$

Transição intersubbanda

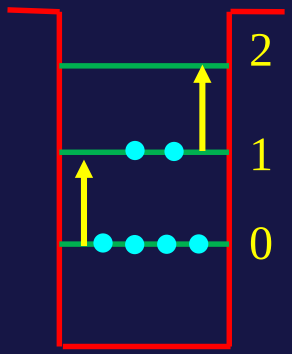
$$\left\langle \Psi_{in} \middle| e_z \cdot \nabla \middle| \Psi_{fin} \right\rangle = \left\langle u_n \middle| u_{n'} \right\rangle \left\langle \xi_n \middle| e_z \cdot \nabla \middle| \xi_{n'} \right\rangle +$$

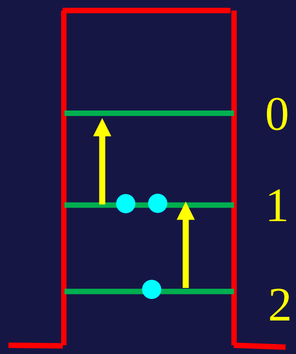
$$+ \left\langle \xi_n \middle| \xi_{n'} \right\rangle \left\langle u_n \middle| e_z \cdot \nabla \middle| u_{n'} \right\rangle$$

Transição interbanda

Transição Intersubbanda

$$\left\langle \Psi_{in} \middle| e_z \cdot \nabla \middle| \Psi_{fin} \right\rangle = \left\langle u_n \middle| u_{n'} \right\rangle \left\langle \xi_n \middle| e_z \cdot \nabla \middle| \xi_{n'} \right\rangle$$



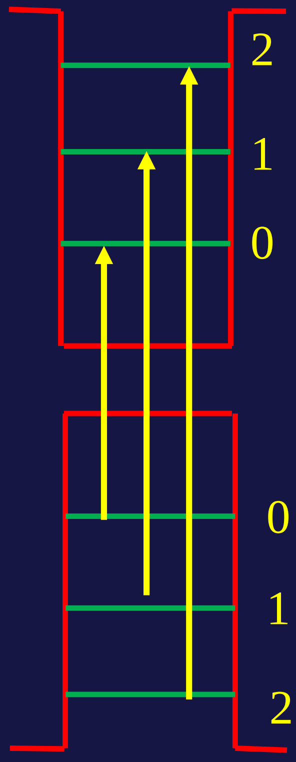


Transição só é possível se níveis excitados estiverem populados

Transição Interbanda

$$\left\langle \Psi_{in} \middle| e_z \cdot \nabla \middle| \Psi_{fin} \right\rangle = \left\langle \xi_n \middle| \xi_{n'} \right\rangle \left\langle u_n \middle| e_z \cdot \nabla \middle| u_{n'} \right\rangle$$

$$\Delta n = 0$$



Regras de seleção: 2-fótons

$$F \propto \left| \sum_b \frac{\langle \xi_{val} u_{val} | \vec{e} \cdot \nabla | \xi_b u_b \rangle \langle \xi_b u_b | \vec{e} \cdot \nabla | \xi_{cond} u_{cond} \rangle}{\Delta E_b} \right|^2$$

0

$$\left| \sum_b \langle \xi_{val} | \vec{e} \cdot \nabla | \xi_b \rangle \langle \xi_b | \vec{e} \cdot \nabla | \xi_{con} \rangle \langle u_{val} | u_b \rangle \langle u_b | u_{cond} \rangle \right| = 0$$

0

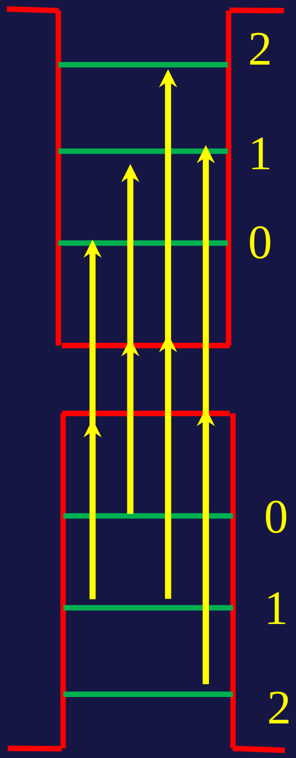
$$\left| \sum_b \langle \xi_{val} | \xi_b \rangle \langle \xi_b | \xi_{cond} \rangle \langle u_{val} | \vec{e} \cdot \nabla | u_b \rangle \langle u_b | \vec{e} \cdot \nabla | u_{cond} \rangle \right| = 0$$

$$F \propto \left| \sum_b \frac{\langle \xi_{val} | \vec{e} \cdot \nabla | \xi_b \rangle \langle \xi_b | \xi_{cond} \rangle \langle u_{val} | u_b \rangle \langle u_b | \vec{e} \cdot \nabla | u_{cond} \rangle}{\Delta E_b} + \sum_b \frac{\langle \xi_{val} | \xi_b \rangle \langle \xi_b | \vec{e} \cdot \nabla | \xi_{cond} \rangle \langle u_{val} | \vec{e} \cdot \nabla | u_b \rangle \langle u_b | u_{cond} \rangle}{\Delta E_b} \right|^2$$

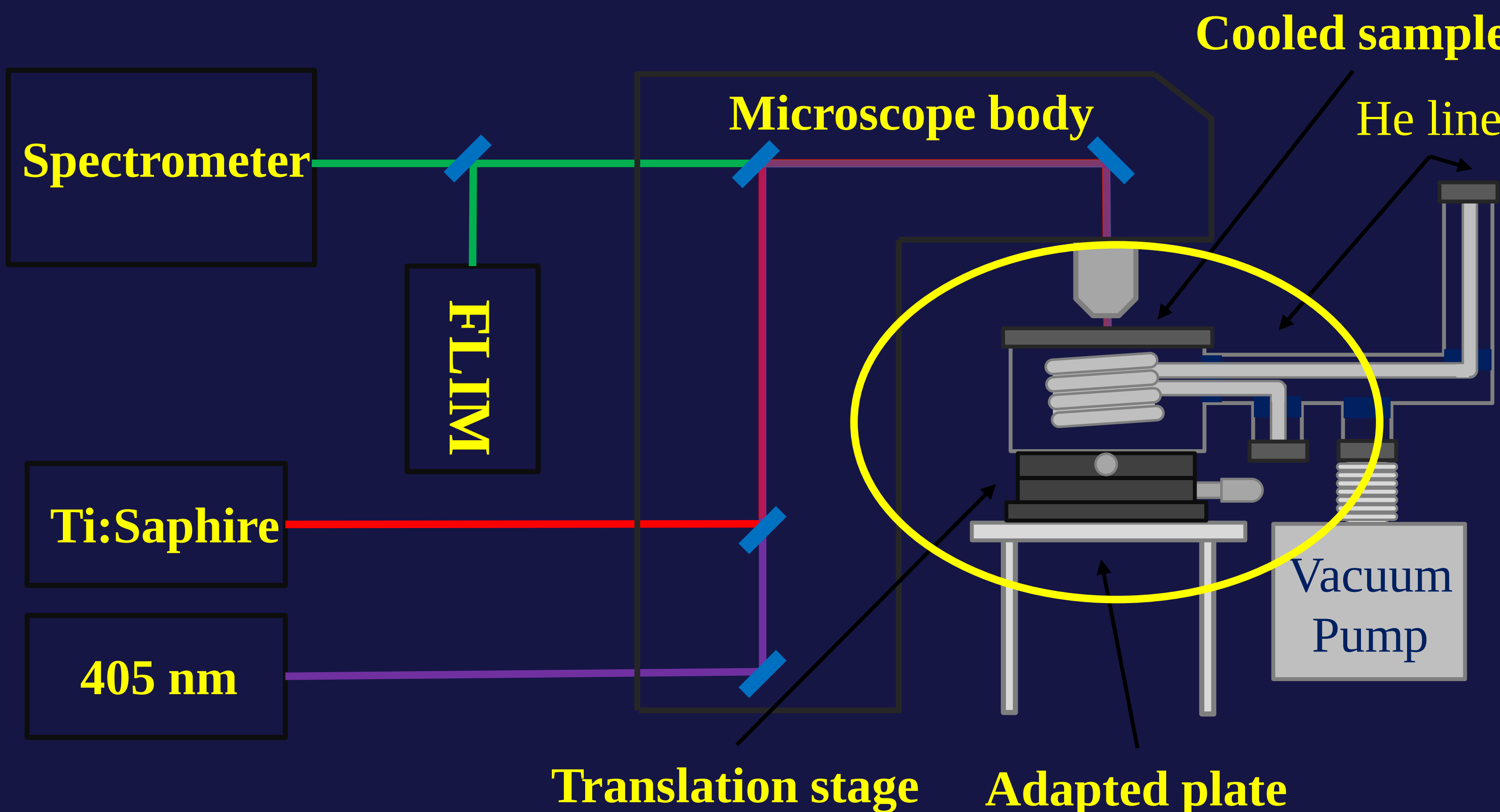
Absorção de 2-fótons

$$F \propto \left|\left\langle u_{val} \left| \vec{e}\cdot\nabla \right| u_{cond} \right\rangle\right|^2 \left| \sum_b \frac{\left\langle \xi_{val} \left| \vec{e}\cdot\nabla \right| \xi_b \right\rangle \left\langle \xi_b \middle| \xi_{cond} \right\rangle}{\Delta E_b} + \sum_b \frac{\left\langle \xi_{val} \middle| \xi_b \right\rangle \left\langle \xi_b \left| \vec{e}\cdot\nabla \right| \xi_{cond} \right\rangle}{\Delta E_b} \right|^2$$

$$\Delta n = \pm 1$$



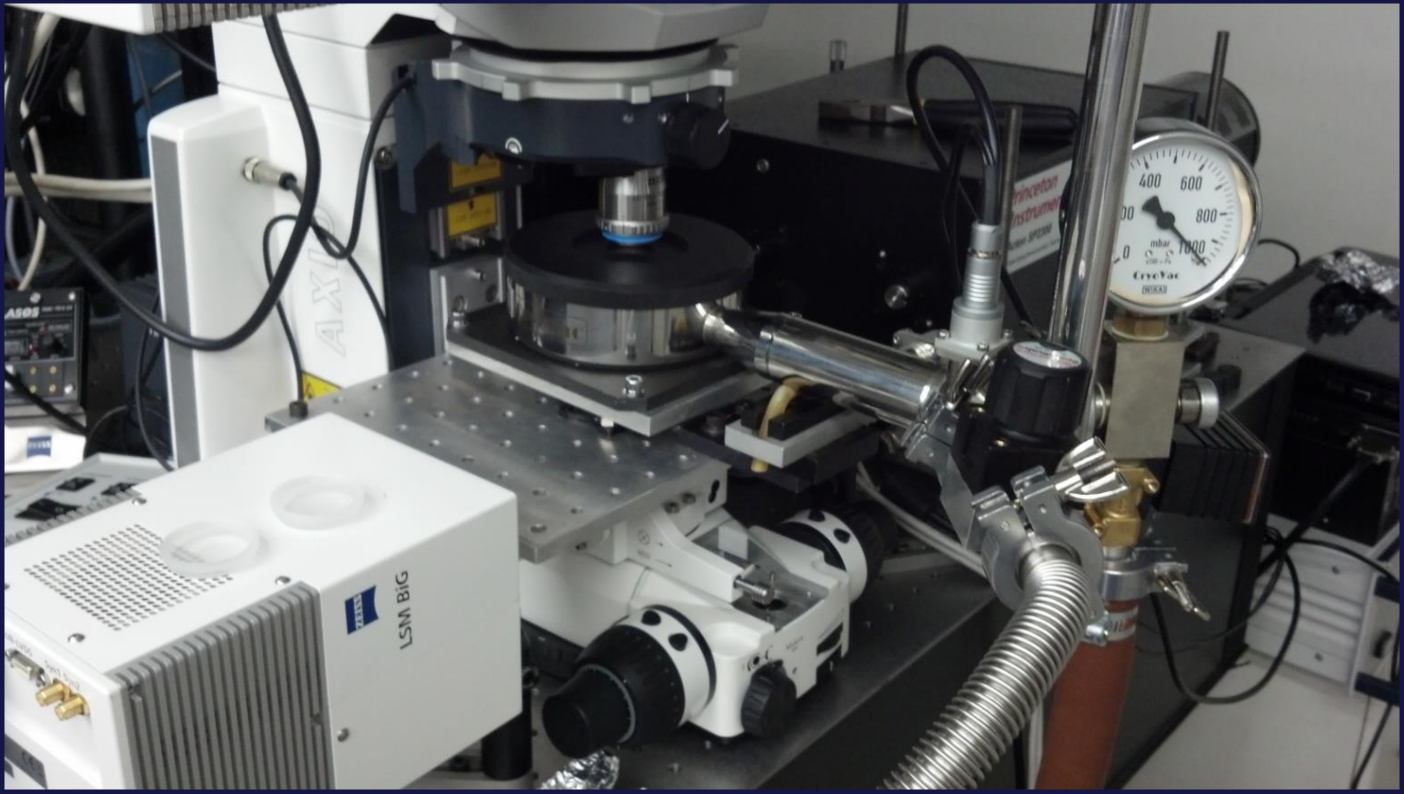
Fit a cryostat at the System and gain a Spectral platform with spatial resolution



Main Issues

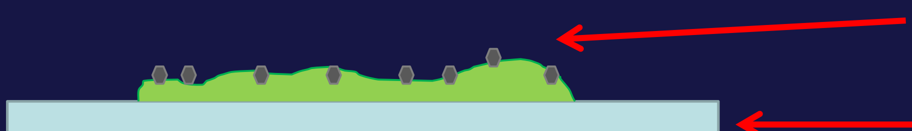
High NA but long working distance: we used NA=0.6 with WD = 3mm

Small cryostat to fit under a Zeiss LSM 780 upright



Small copper piece to bring the sample closer to optical window

Light collection must be done in backscatered geometry.
Sample deposited on a mirror to enhance light collection efficiency.

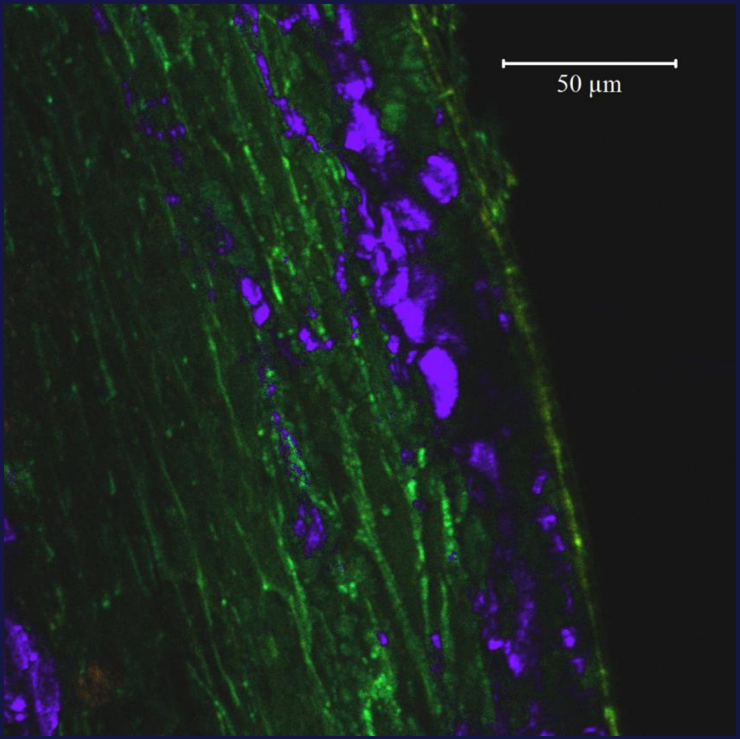


Colloidal QDs film with ureia small crystals

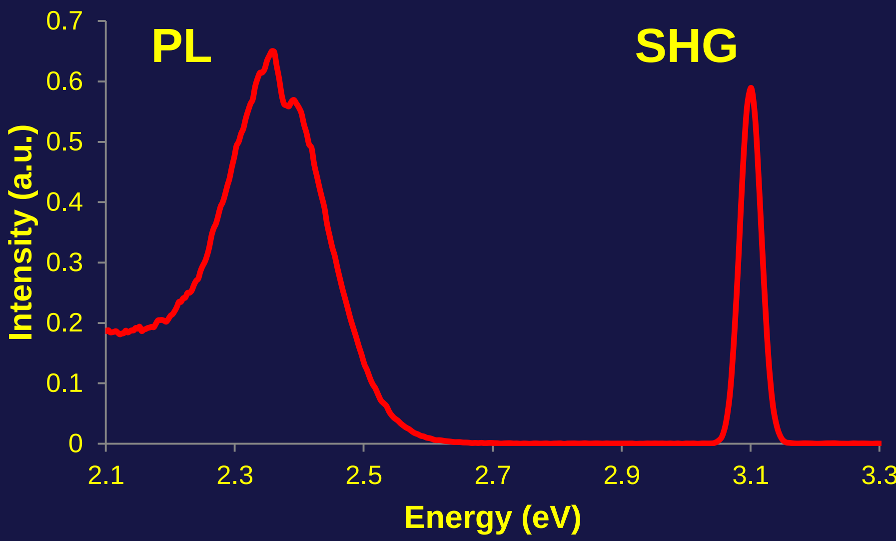
Mirrored microscope coverslip

Spatial/optical resolution

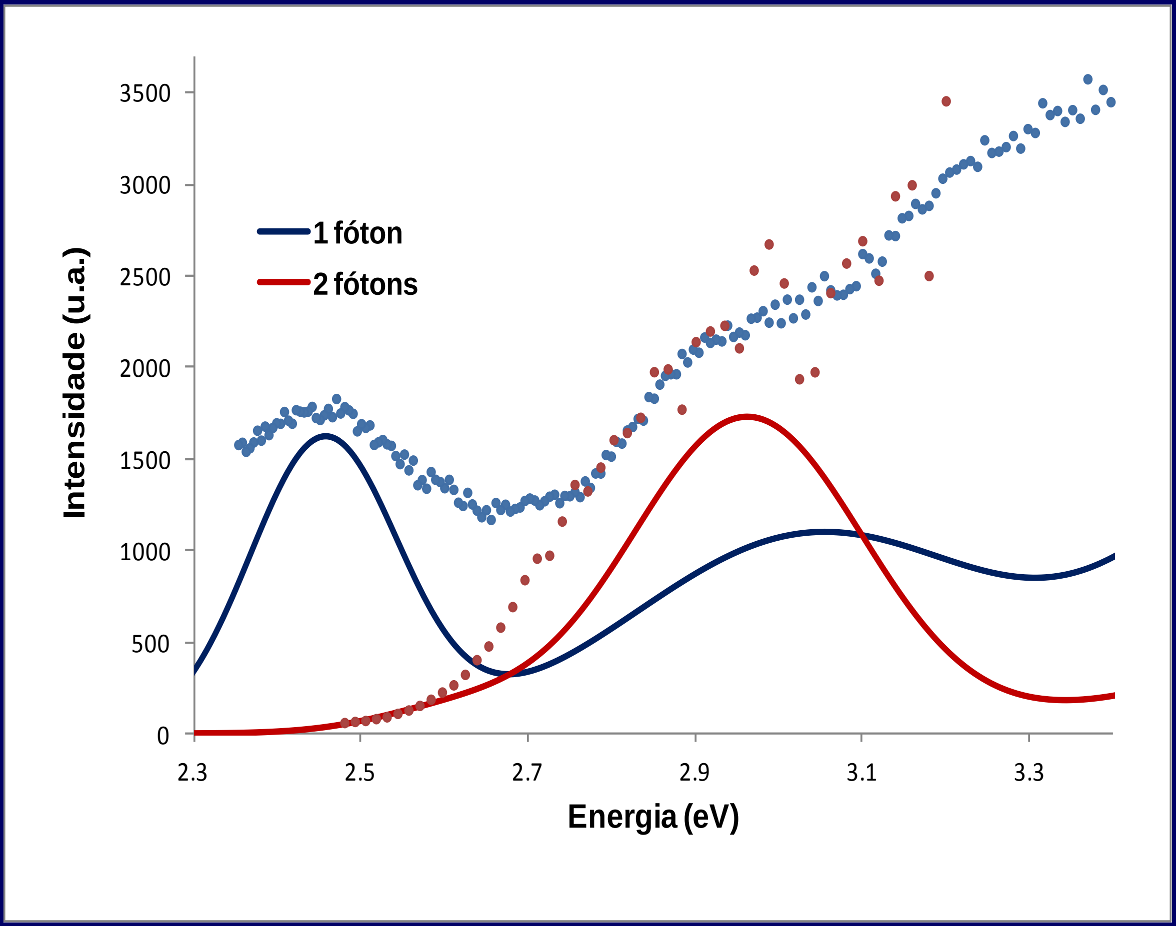
Pump: Ti:Saphire laser

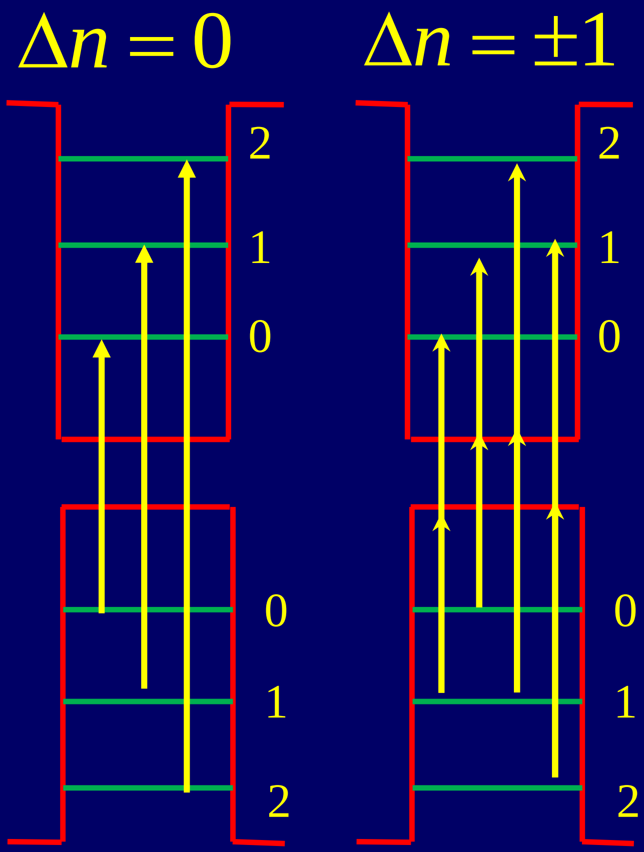


Green: QDs fluorescence
Purple: urea SHG

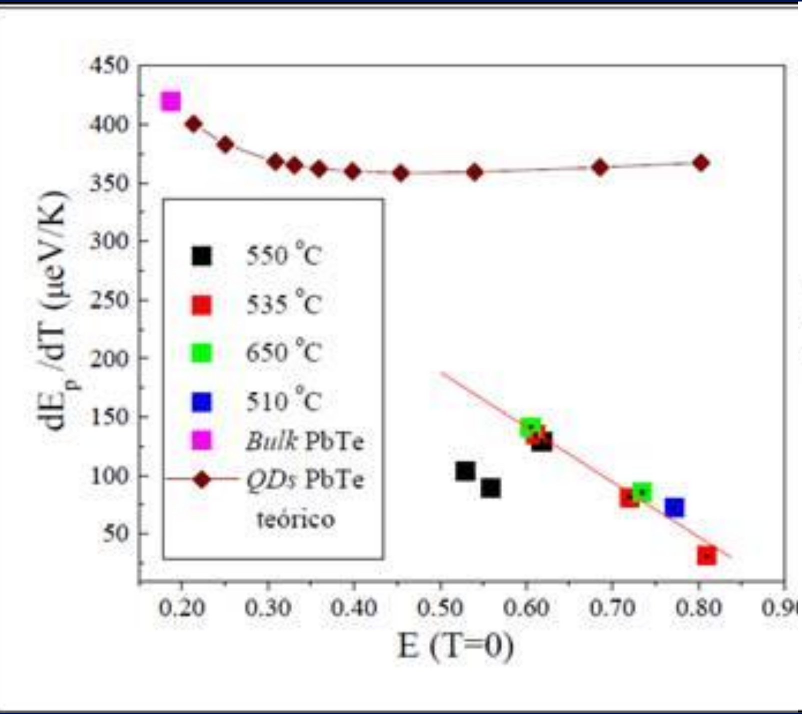


CdTe quantum dot 1 and 2 photons PLE at 40 K

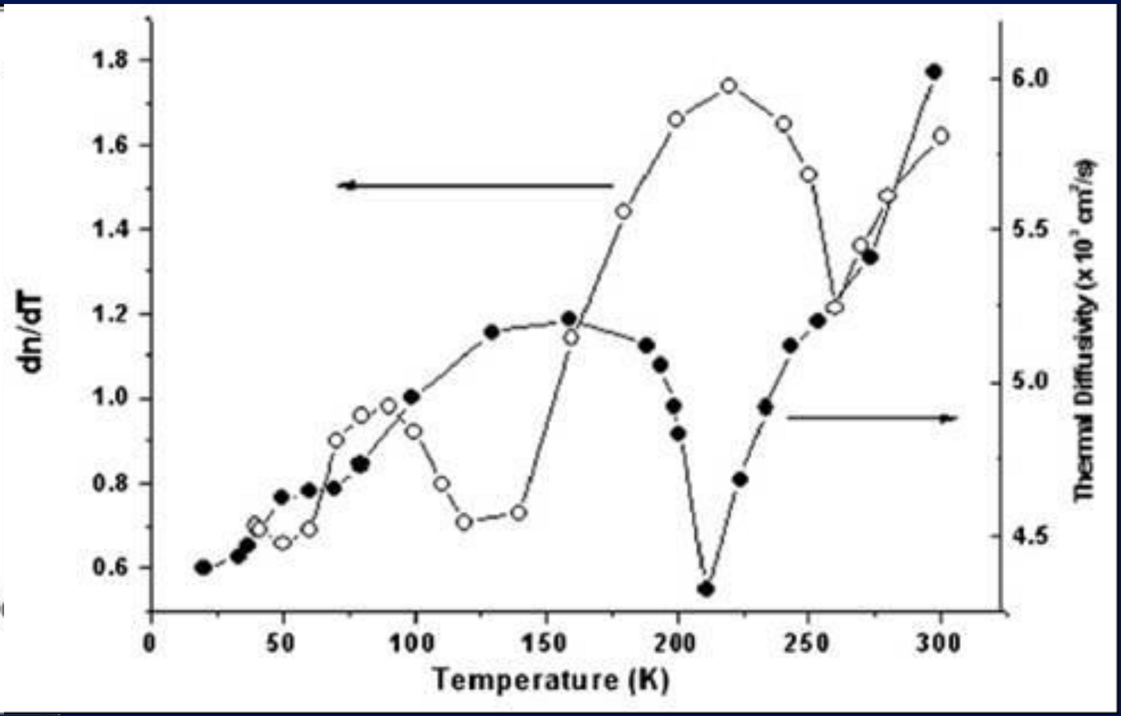




Stress Induced Phase Transition

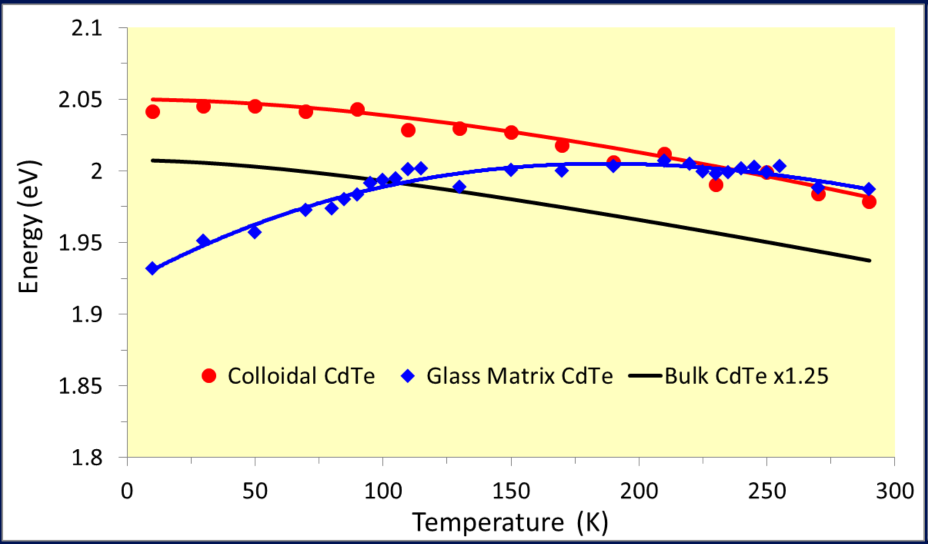


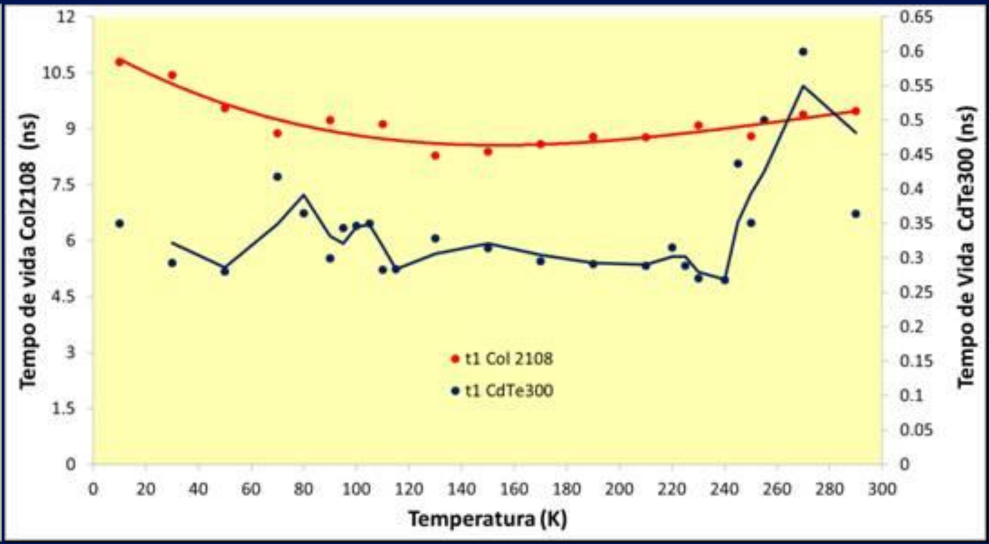
PbTe

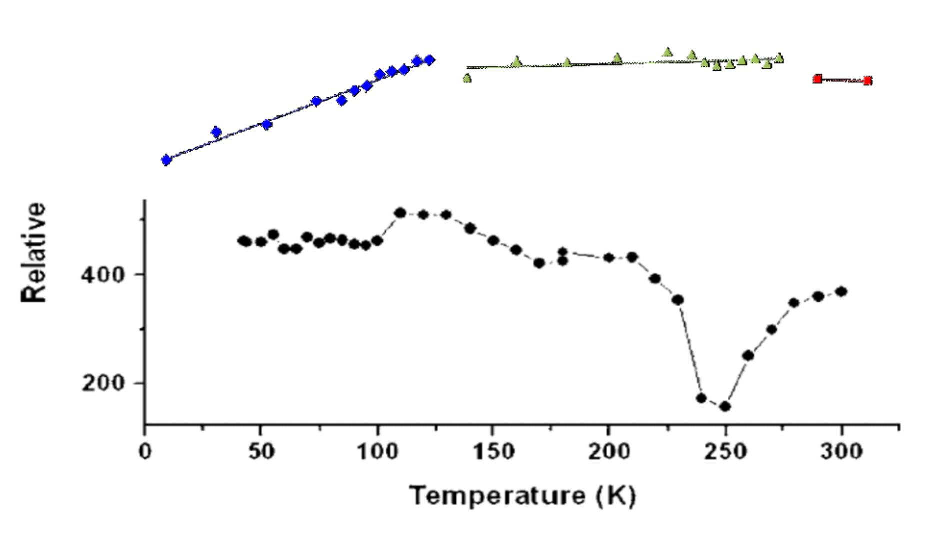


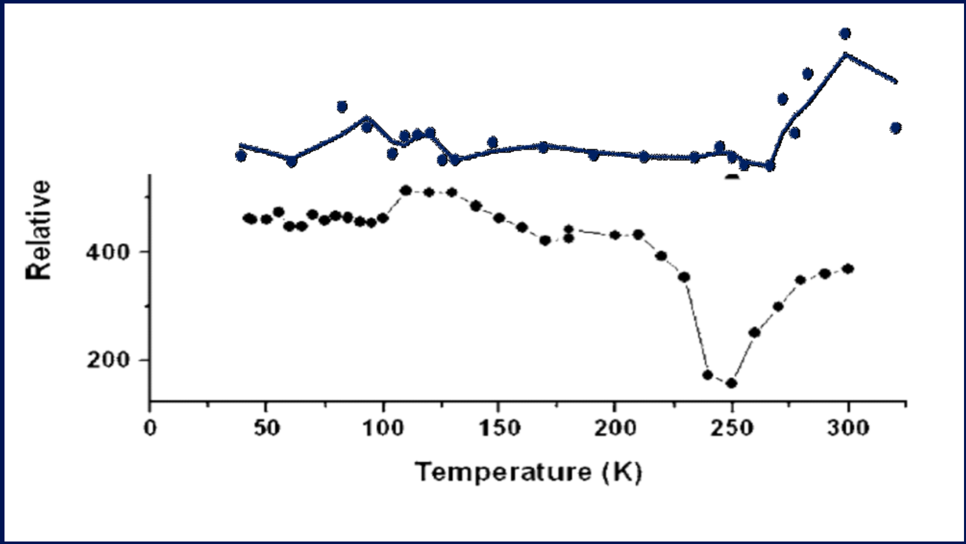
CdTe

Colloidal vs Doped Glass QDs



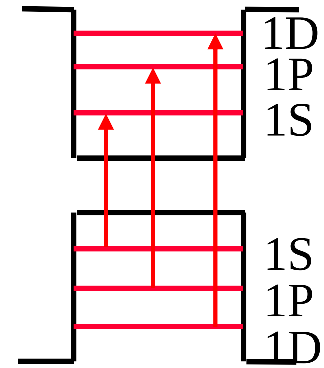






Confinement Models

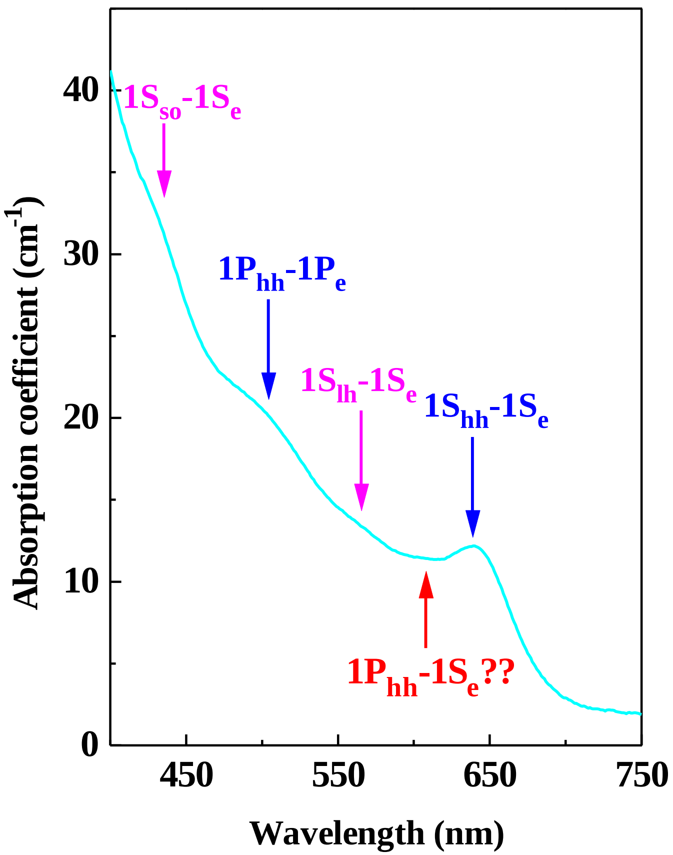
Optical Transition Selection Rules

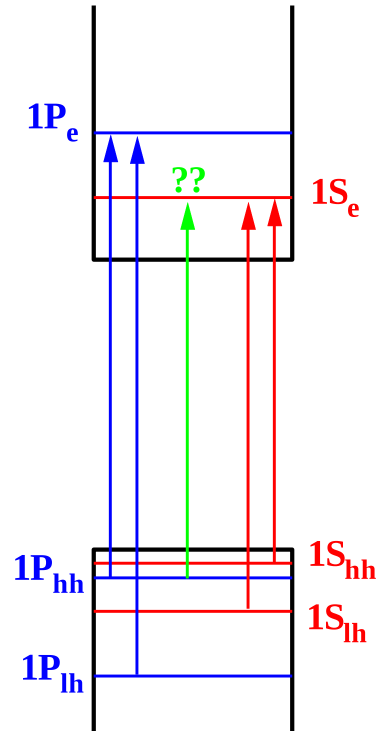


$$f=\frac{2}{m_0\hbar\omega}\left|\langle\psi_{fin}|\hat{\varepsilon}\cdot\vec{p}|\psi_{ini}\rangle\right|^2$$

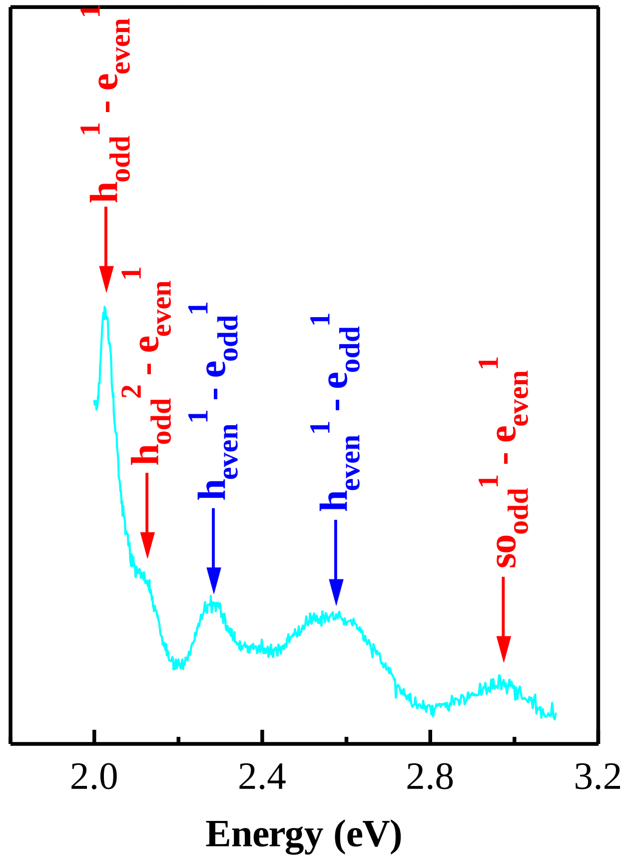
$$\langle F_{fin}|F_{ini}\rangle=\delta_{nn'}\,\delta_{ll'}\,\delta_{mm'}$$

Absorption spectrum





PLE Transitions assignement



Quantum Confinement: Full $\vec{k}\cdot\vec{P}$ Hamiltonian Model

two subspaces:

$\vec{r}$ = space inside a cell (Bloch); $\vec{R}$ = space between cells (envelope)

$$\frac{(\vec{P}_{\vec{r}} + \vec{P}_{\vec{R}})^2}{2m_0} \quad \text{dot potential} \quad \text{lattice potential} \quad \text{Spin-orbit interaction}$$

$$\downarrow \qquad \downarrow \qquad \downarrow \qquad \downarrow$$

$$H = \left(\frac{\vec{P}_{\vec{r}}^{\,2} + 2\vec{P}_{\vec{r}}\cdot\vec{P}_{\vec{R}} + \vec{P}_{\vec{R}}^{\,2}}{2m_0}\right) + V_{spheric} + V_{periodi} + \left(\frac{\vec{\nabla}V_{per} \times \vec{P}_{\vec{r}} \cdot \vec{S}}{m_0 c}\right)$$

comutes ↓ with: $\vec{L}_{\vec{r}} + \vec{L}_{\vec{R}}$

comutes ↓ with: $\vec{L}_{\vec{r}} + \vec{S}$

Conclusions:

$[\vec{F},H] = 0$ where $\vec{F} = \vec{L}_{\vec{R}} + \vec{L}_{\vec{r}} + \vec{S}$ → F = good quantum number

More*: $H(-\vec{r}) = H(\vec{r})$ → $\Psi(-\vec{r}) = \pm\Psi(\vec{r})$ → parity well defined

* Germanium model

Band Structure K·P

$$\left|J, L_R\right\rangle$$

Parity = $LR + Lr$	$L_R = 0$	$L_R = 1$	$L_R = 2$	$L_R = 3$
$J = \frac{1}{2}$ Conduction Band ($L_r = 0$)	$\frac{1}{2}$	$\frac{1}{2}$, $\frac{3}{2}$	$\frac{3}{2}$, $\frac{5}{2}$	$\frac{5}{2}$, $\frac{7}{2}$
$J = \frac{1}{2}$ Split off band ($L_r = 1$)	$\frac{1}{2}$	$\frac{1}{2}$, $\frac{3}{2}$	$\frac{3}{2}$, $\frac{5}{2}$	$\frac{5}{2}$, $\frac{7}{2}$
$J = \frac{3}{2}$ Valence Band ($L_r = 1$)	$\frac{3}{2}$	$\frac{1}{2}$, $\frac{3}{2}$, $\frac{5}{2}$	$\frac{1}{2}$, $\frac{3}{2}$, $\frac{5}{2}$, $\frac{7}{2}$	$\frac{3}{2}$, $\frac{5}{2}$, $\frac{7}{2}$, $\frac{9}{2}$

$$F^{+}_{1/2} = \left|\frac{1}{2},0\right\rangle_C + \left|\frac{3}{2},1\right\rangle_V + \left|\frac{1}{2},1\right\rangle_{SO}$$

$$F^{-}_{1/2} = \left|\frac{1}{2},1\right\rangle_C + \left|\frac{3}{2},2\right\rangle_V + \left|\frac{1}{2},0\right\rangle_{SO}$$

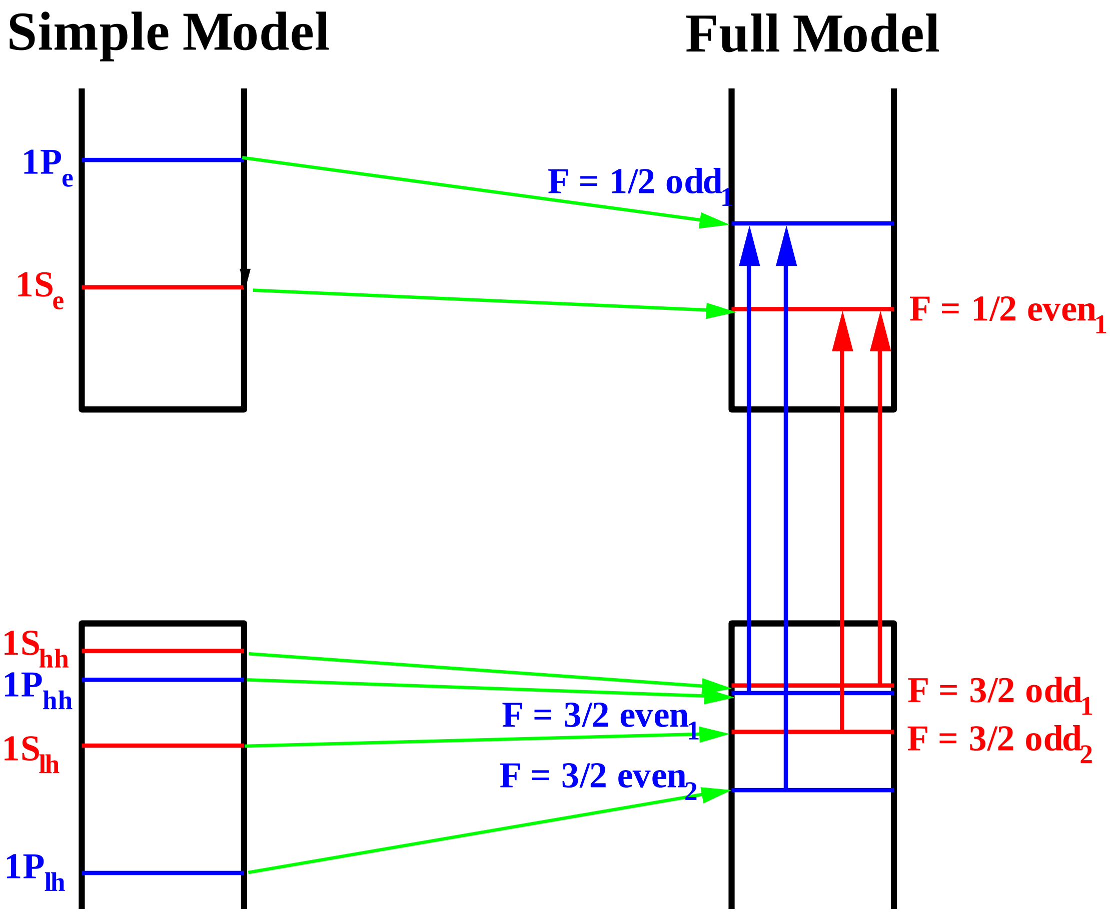
$$F^{+}_{3/2} = \left|\frac{1}{2},2\right\rangle_C + \left|\frac{3}{2},1\right\rangle_V + \left|\frac{3}{2},3\right\rangle_V + \left|\frac{1}{2},1\right\rangle_{SO}$$

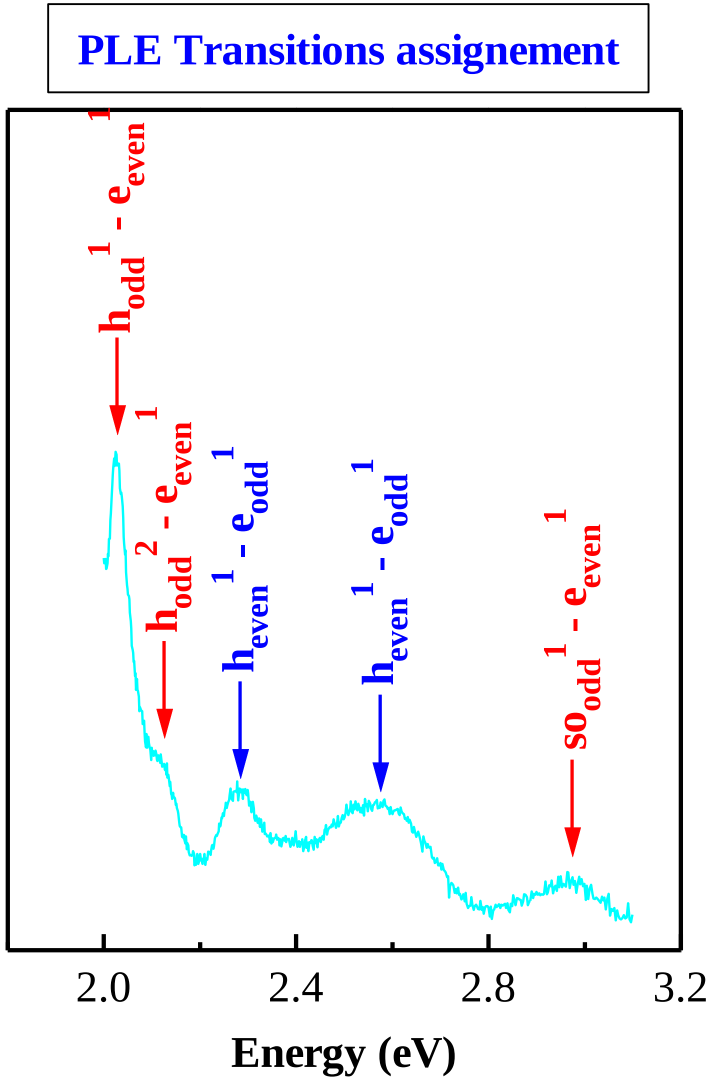
$$F^{-}_{3/2} = \left|\frac{1}{2},1\right\rangle_C + \left|\frac{3}{2},0\right\rangle_V + \left|\frac{3}{2},2\right\rangle_V + \left|\frac{1}{2},2\right\rangle_{SO}$$

Optical transitions in the full model

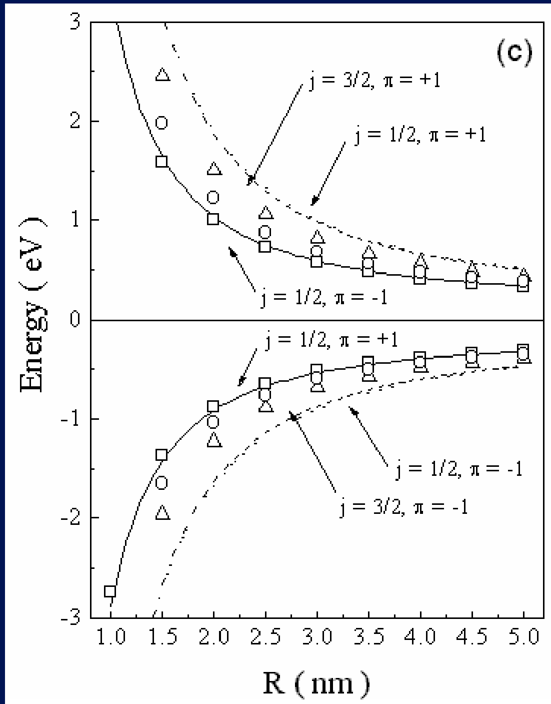
$\vec{E} \cdot \vec{p}$ = odd operator so:

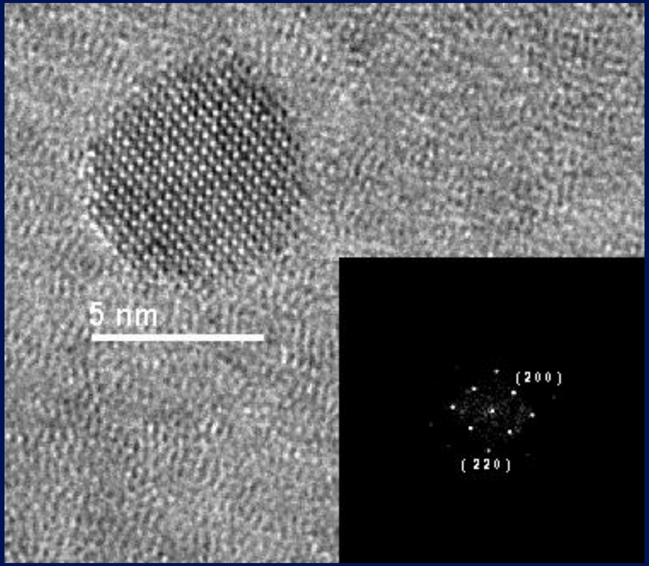
only even to odd or odd to even transitions are allowed

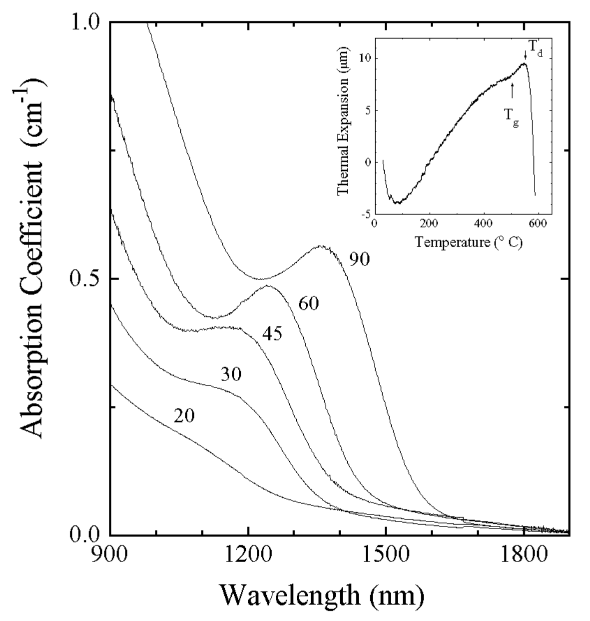


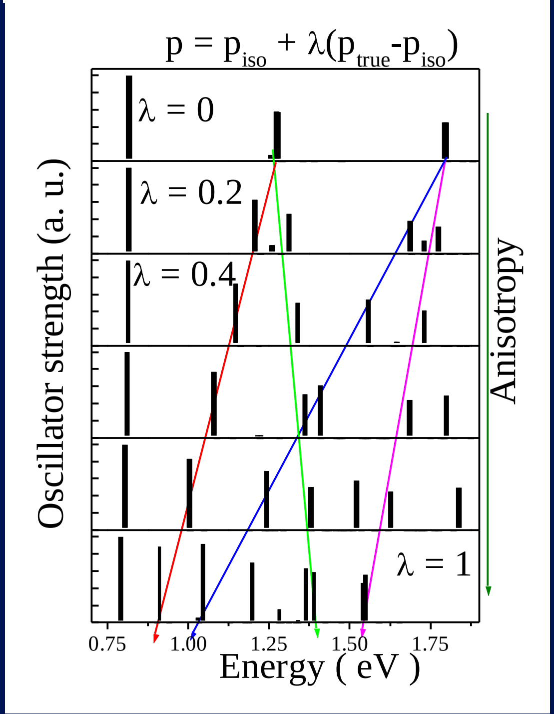


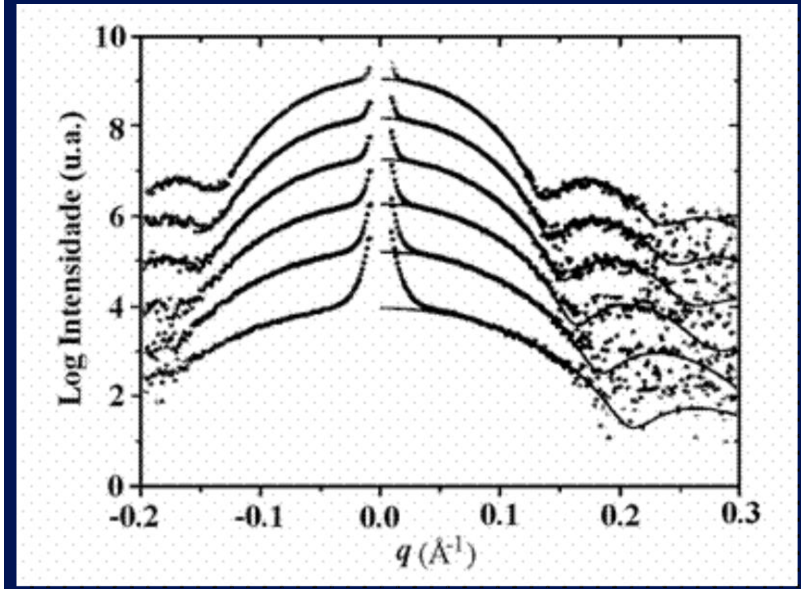
PbTe Quantum Dots Physics





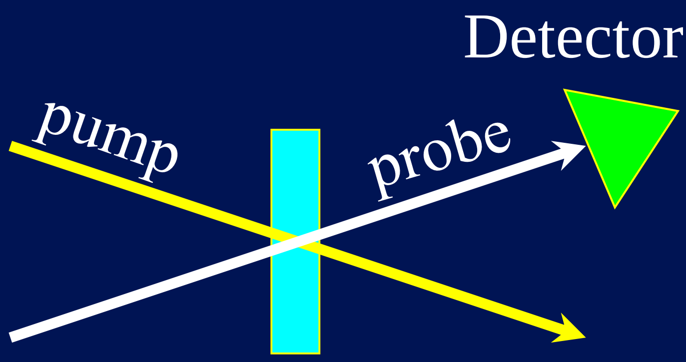


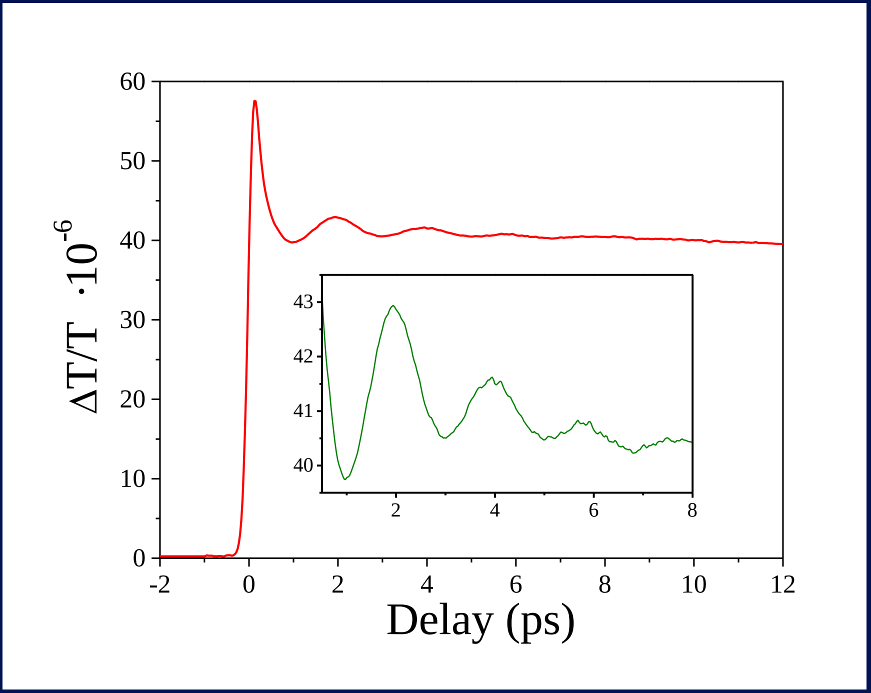


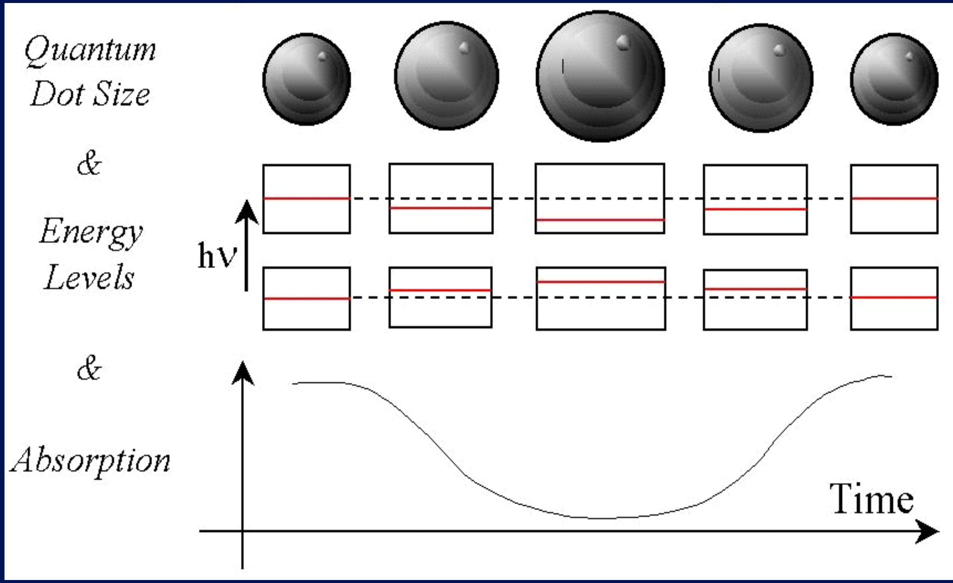


Pump&Probe: Coherent Phonons

E. R. Thoen et al; "Coherent Acoustic Phonons in PbTe Quantum Dots", Appl. Phys. Lett. 73, 2149 (1998)



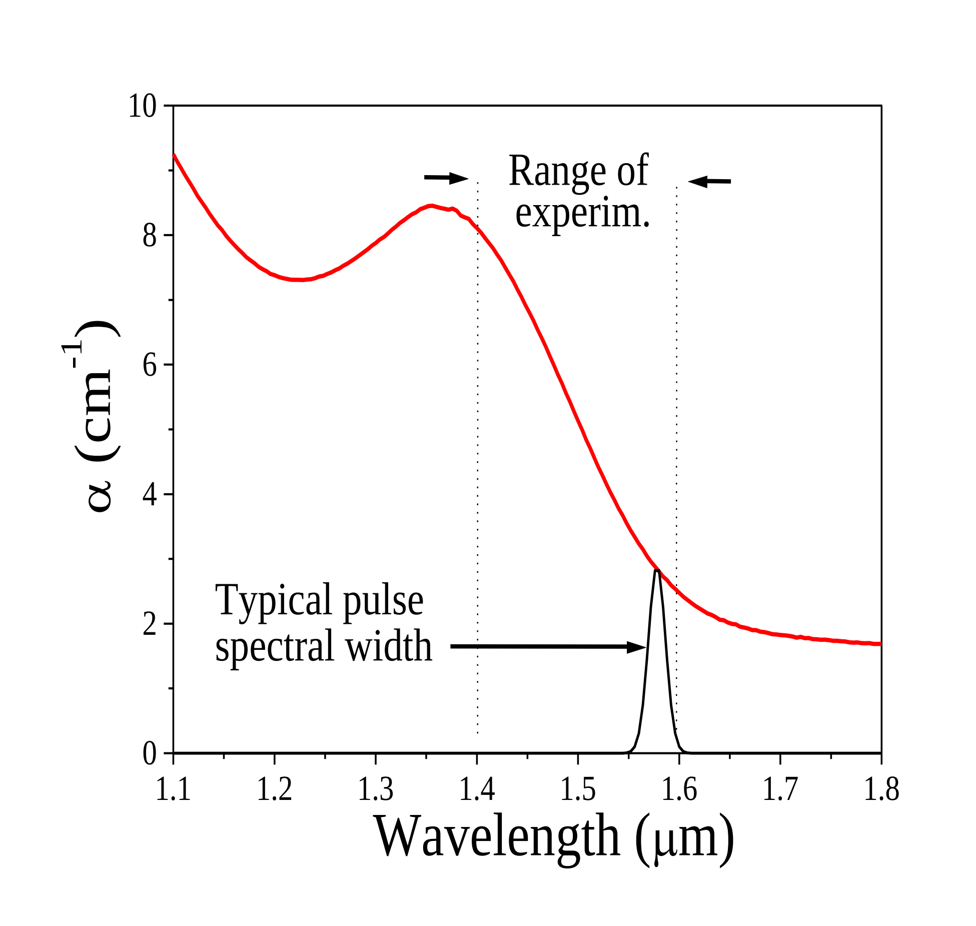


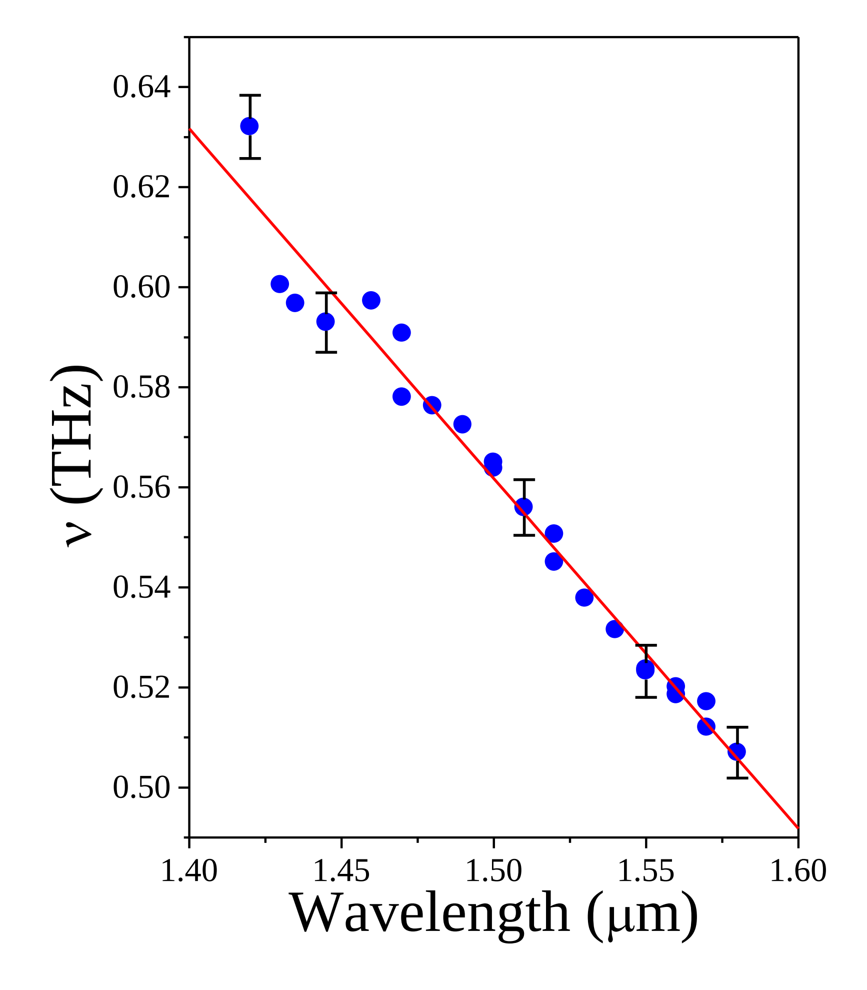


Breathing Modes

Coherent Phonons frequency

Simple Model: $\omega = \dfrac{2V_{sound}}{R}$

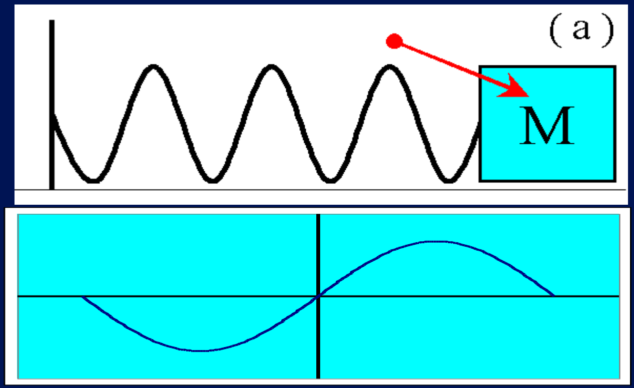


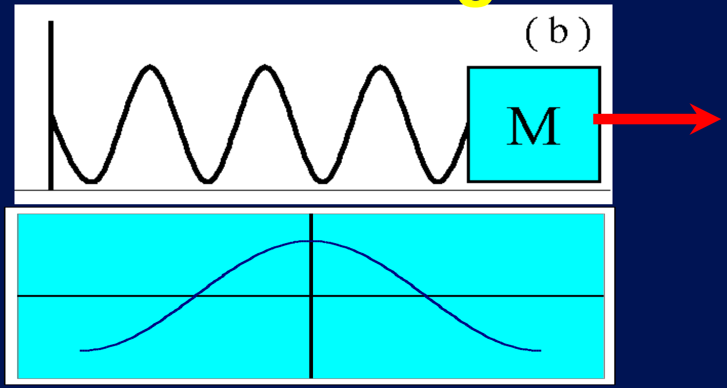


17 cm^{-1} to 20 cm^{-1}

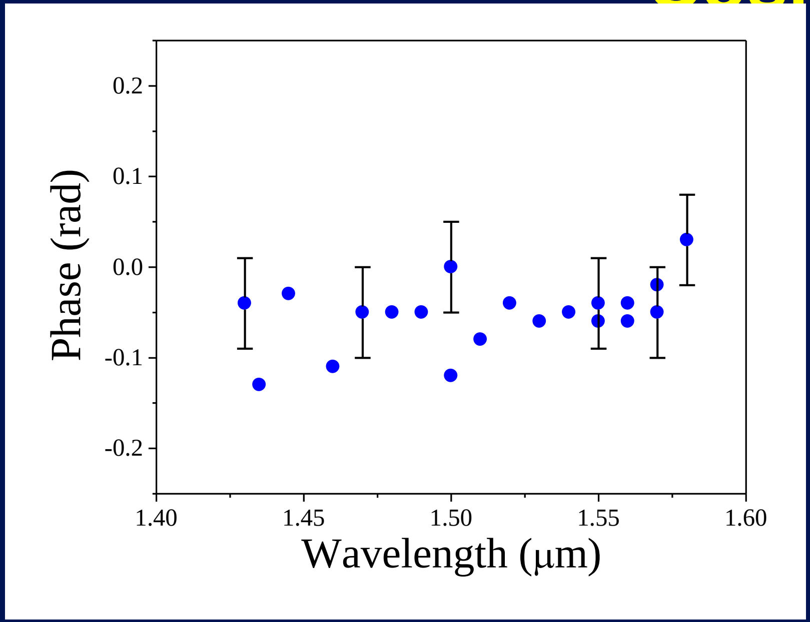
Excitation and phase

Impulse | **K - change**





Sine | **Cosine**

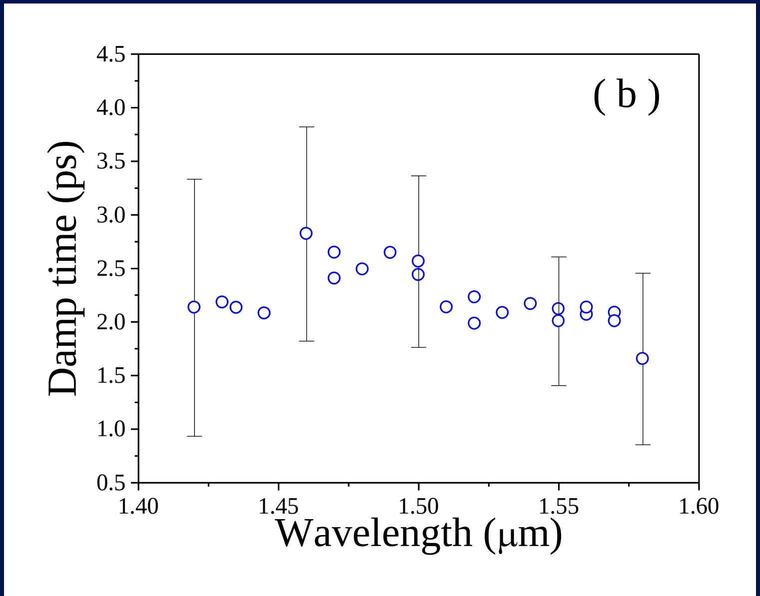


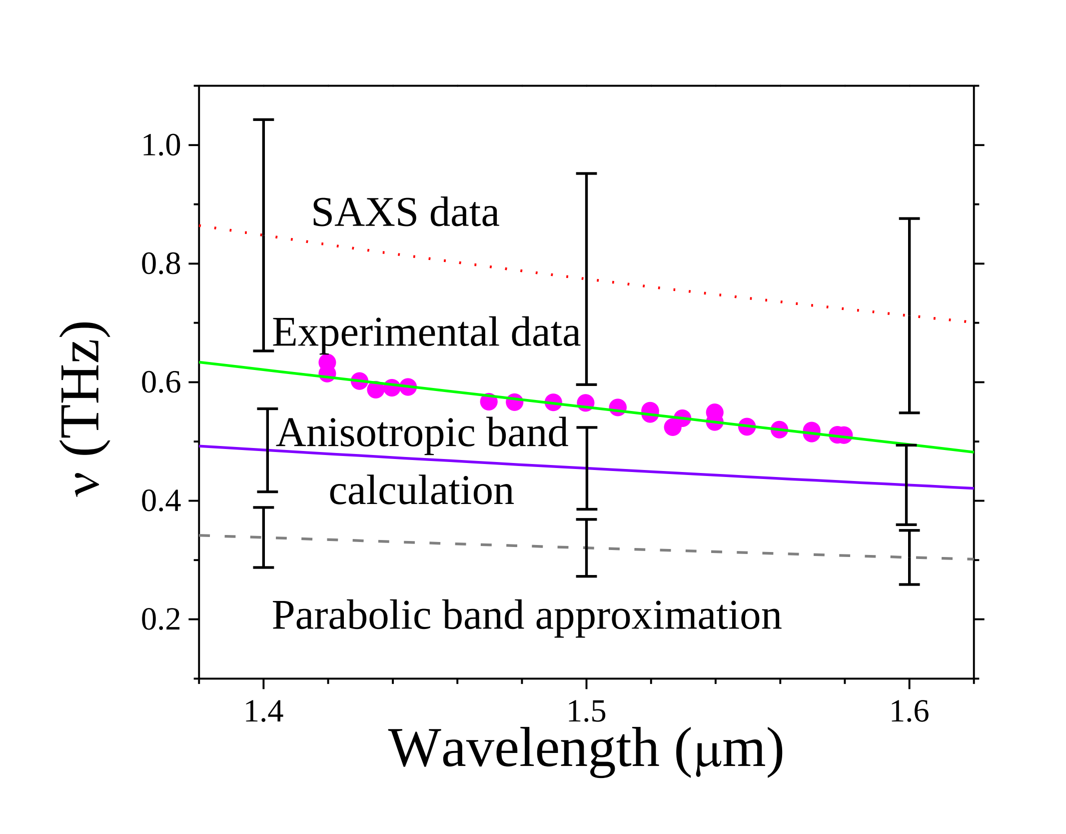
Phase ≈ 0° cosine Excitation

Damping Time

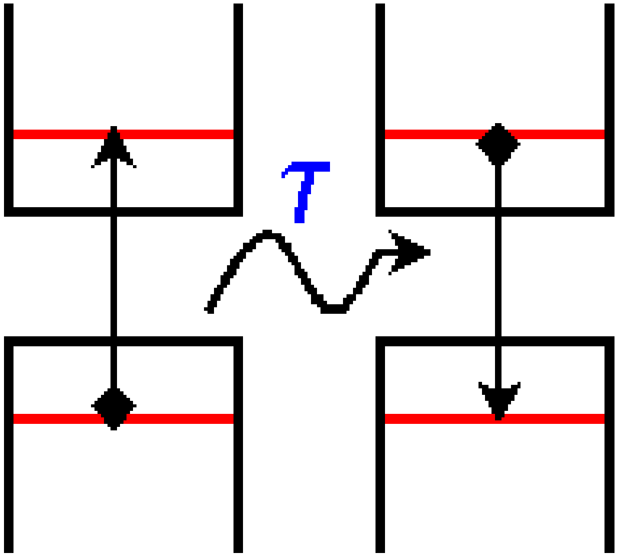
Sphere Acoustic Modes APL 73, 2149-2151 (1998)

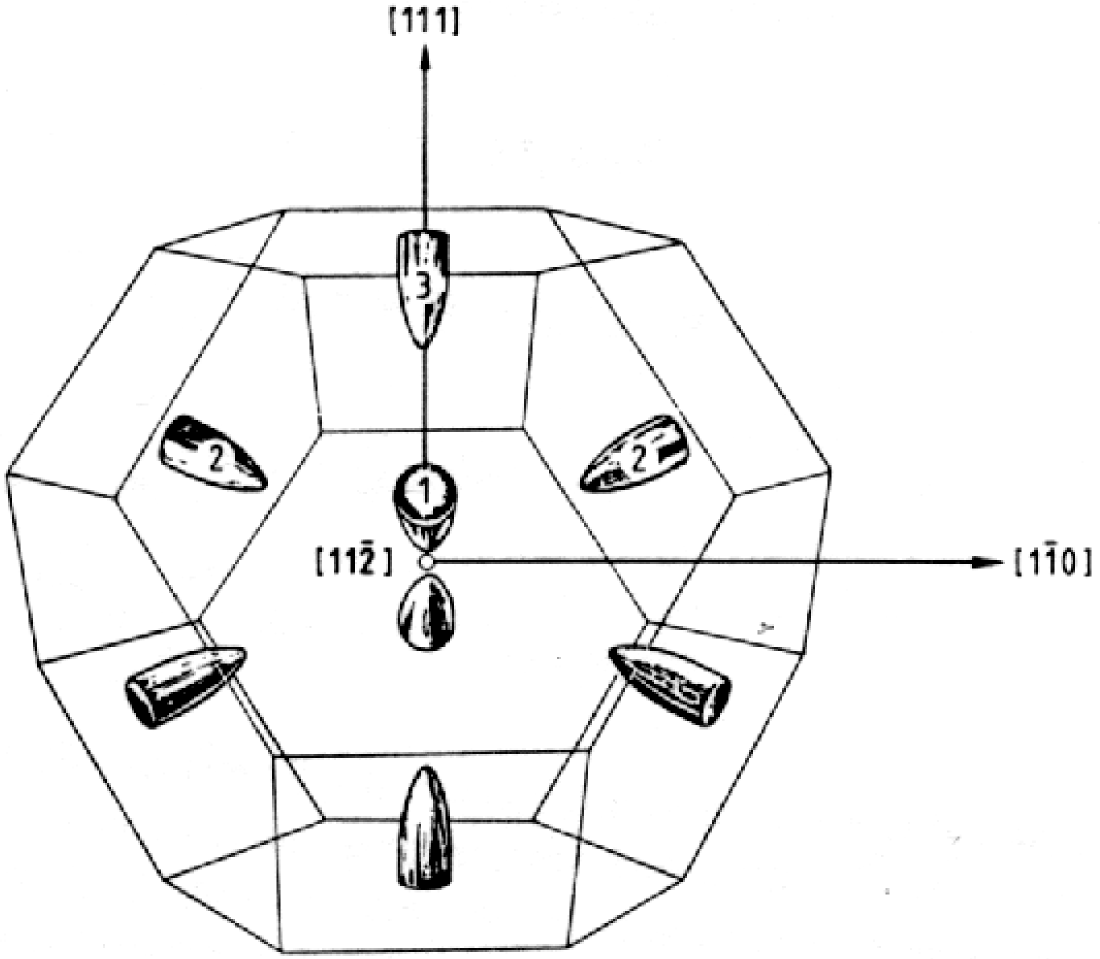
$$\rho\frac{\partial^2 \vec{\mathbf{u}}}{\partial t^2}+\mu\,\nabla\times\nabla\times\vec{\mathbf{u}}-(\lambda+2\mu)\,\nabla(\nabla\cdot\vec{\mathbf{u}})=0$$





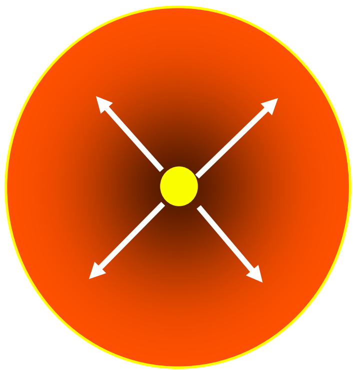
Coherent Phonons: pump & probe detection





Coherent Phonons: amplitude

$$PdV = P4\pi r^2 dr = dE_{conf}$$
$$\Rightarrow P = \frac{1}{4\pi r^2}\frac{dE_{conf}}{dr}$$

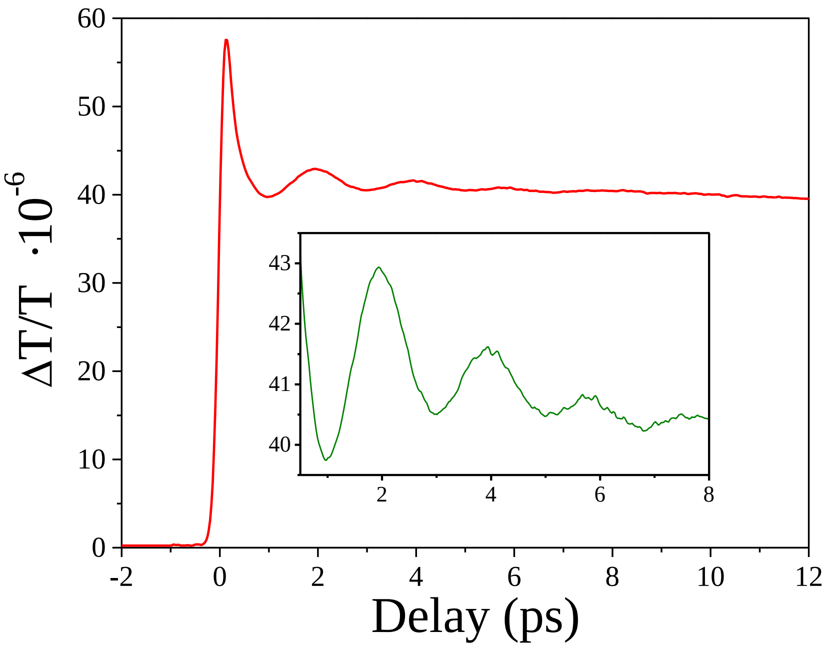


$$P = -K\frac{\Delta V}{V_0} = -K\frac{(r^3 - r_0^3)}{r_0^3} = -K\left[\left(\frac{r}{r_0}\right)^3 - 1\right] \Rightarrow$$
$$\Rightarrow \frac{\delta r}{r_0} = \frac{1}{3K}P$$

$$\frac{\delta A}{A} = 4.4\times 10^{-6}$$

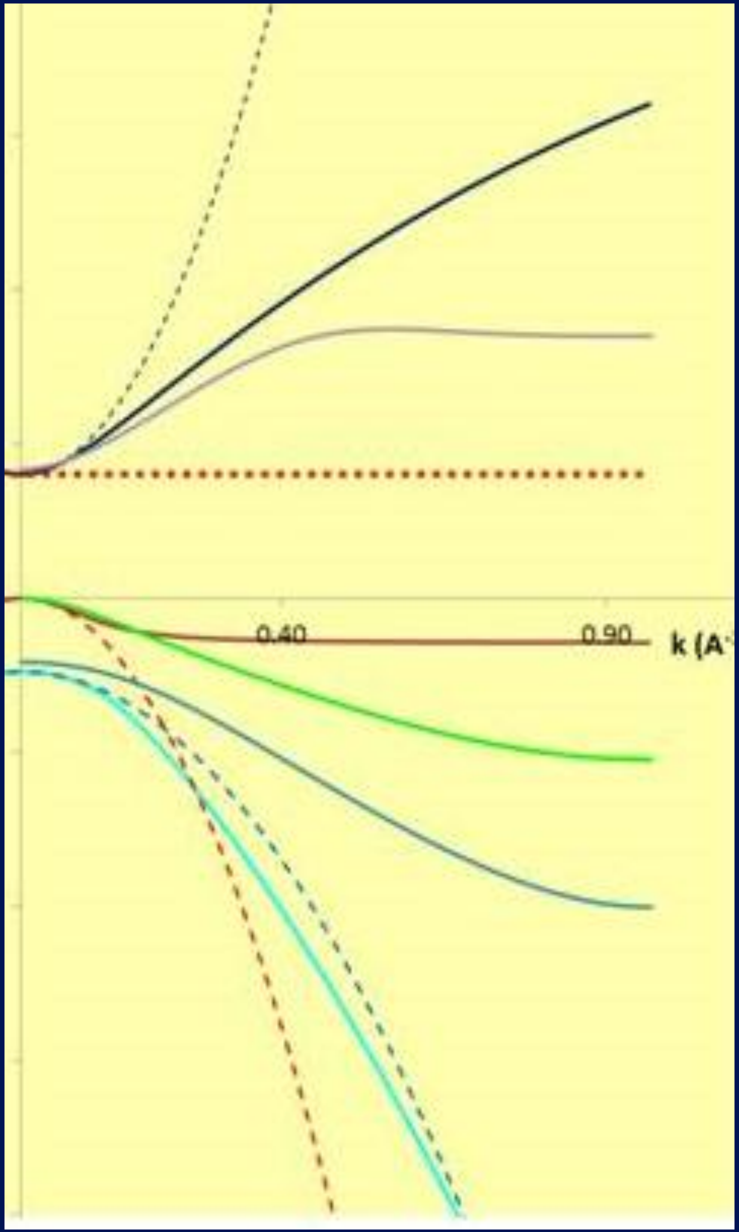
$$E_{conf}(r) = \frac{\alpha}{r^2}, \quad \frac{\delta E_{conf}}{E_0} = -2\frac{\delta r}{r_0}$$

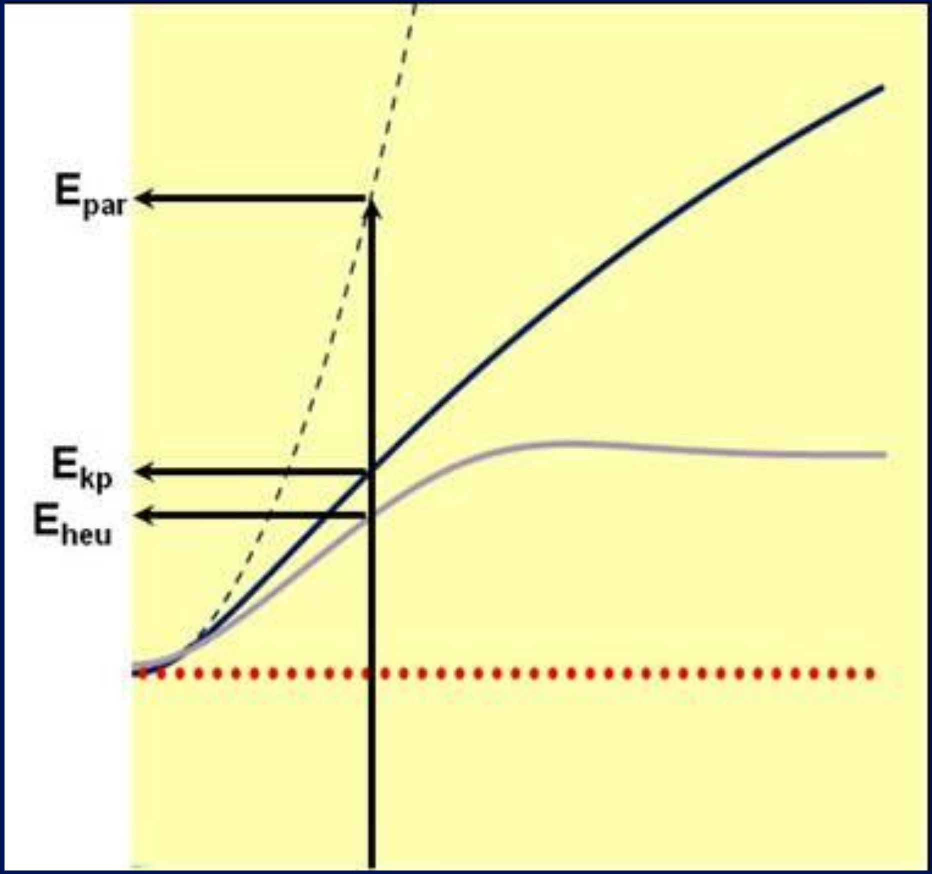
$$\frac{\delta T}{T} = \frac{\delta A}{A} \approx \frac{1}{2}\left(\frac{\delta E}{\sigma_{Tot}}\right)^2 = \frac{1}{2}\left(\frac{\delta E / E_0}{\sigma_{Tot} / E_0}\right)^2$$



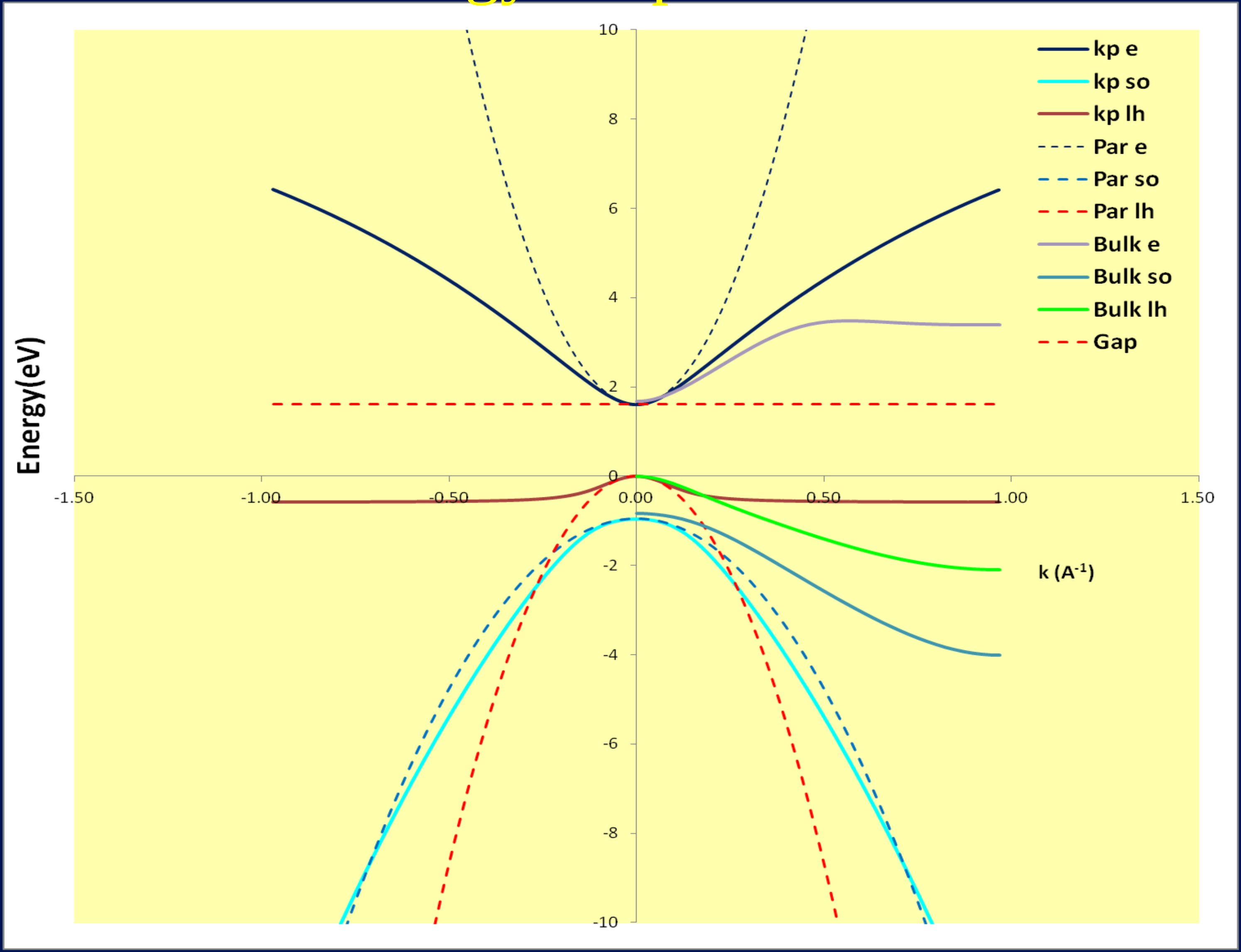
Critiscim to kp Models

Parabolic and kP Models are not good enough for very small quantum dots





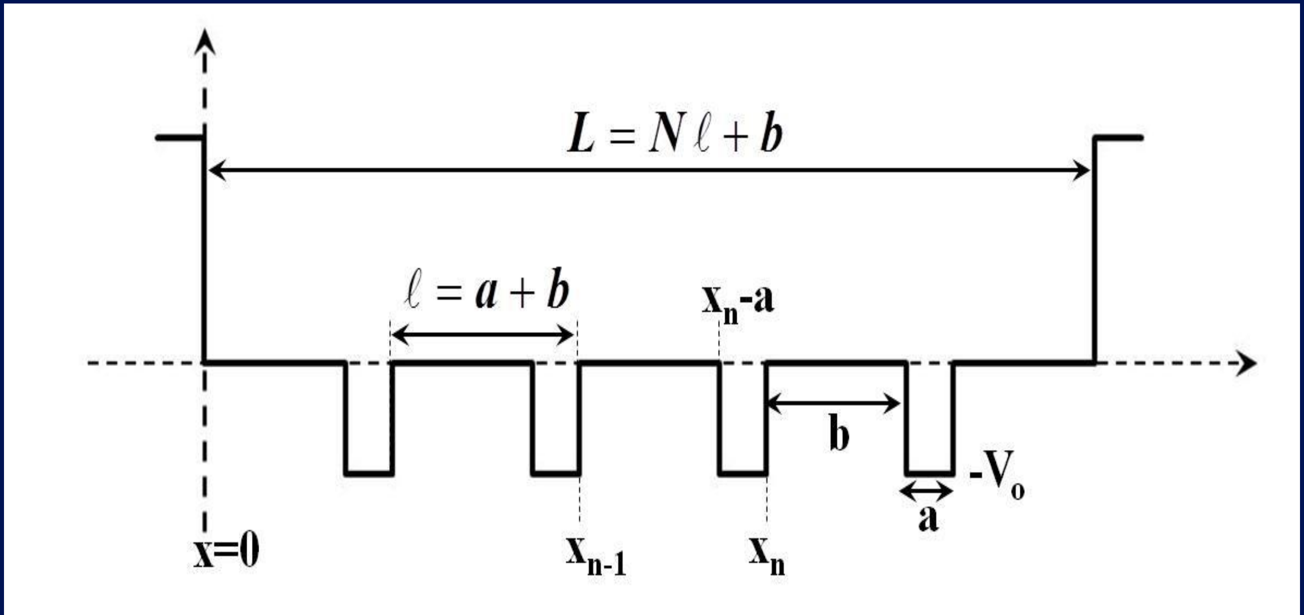
Energy Dispersion



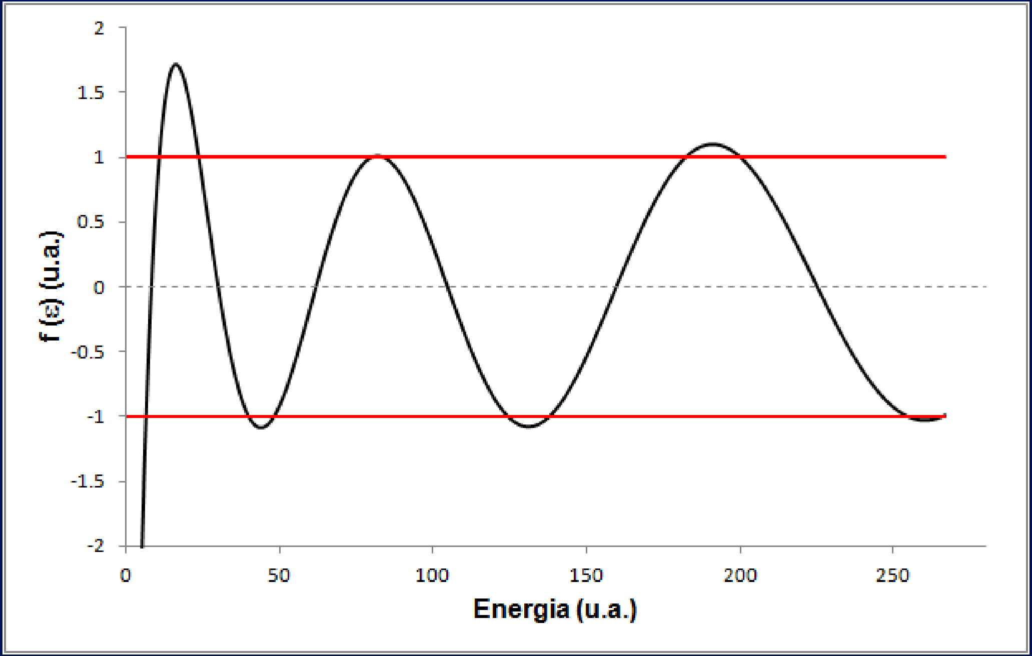
Bulk energy dispersion calculated by Prof. Guimarães USP/UNICAMP

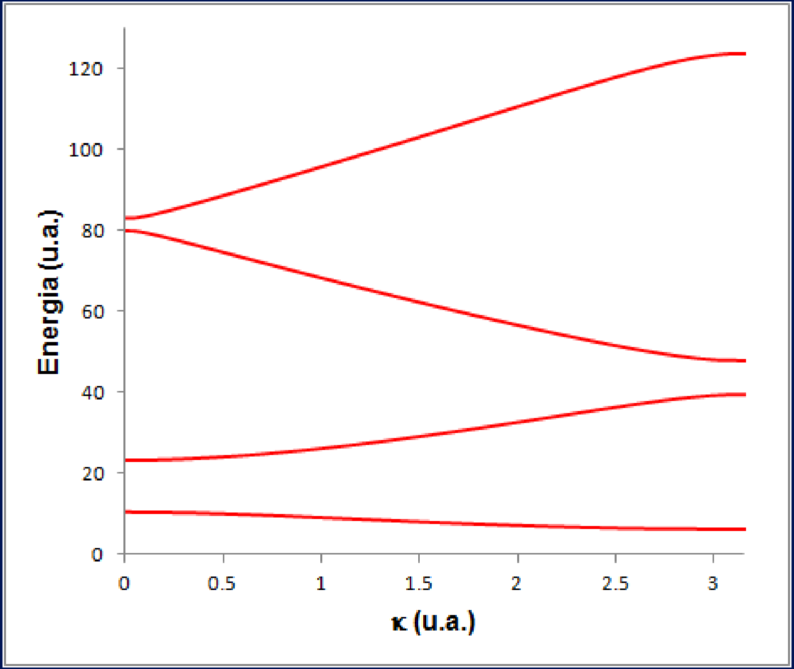
Modelo Unidimensional com solução analítica

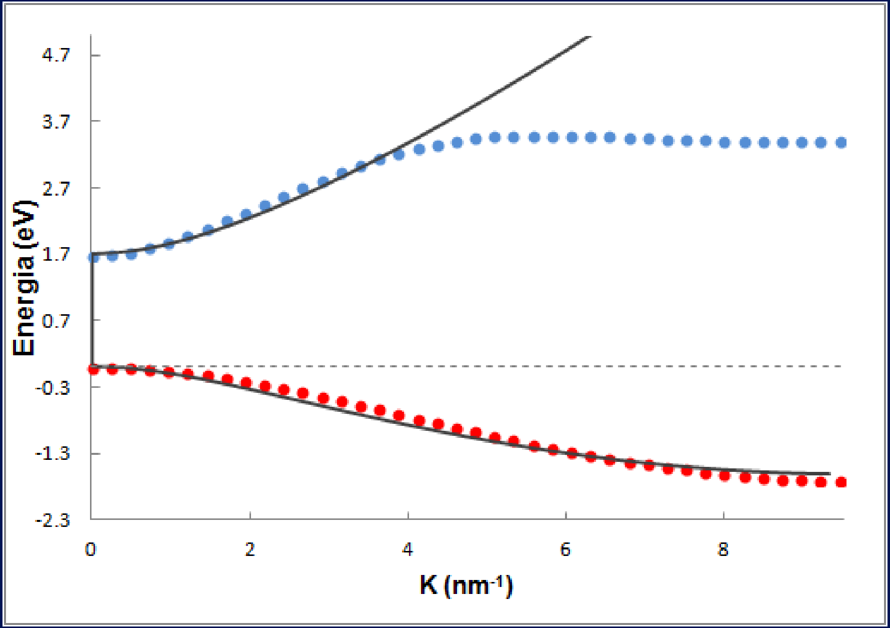
Cadeia de poços unidimensionais
Solução analítica



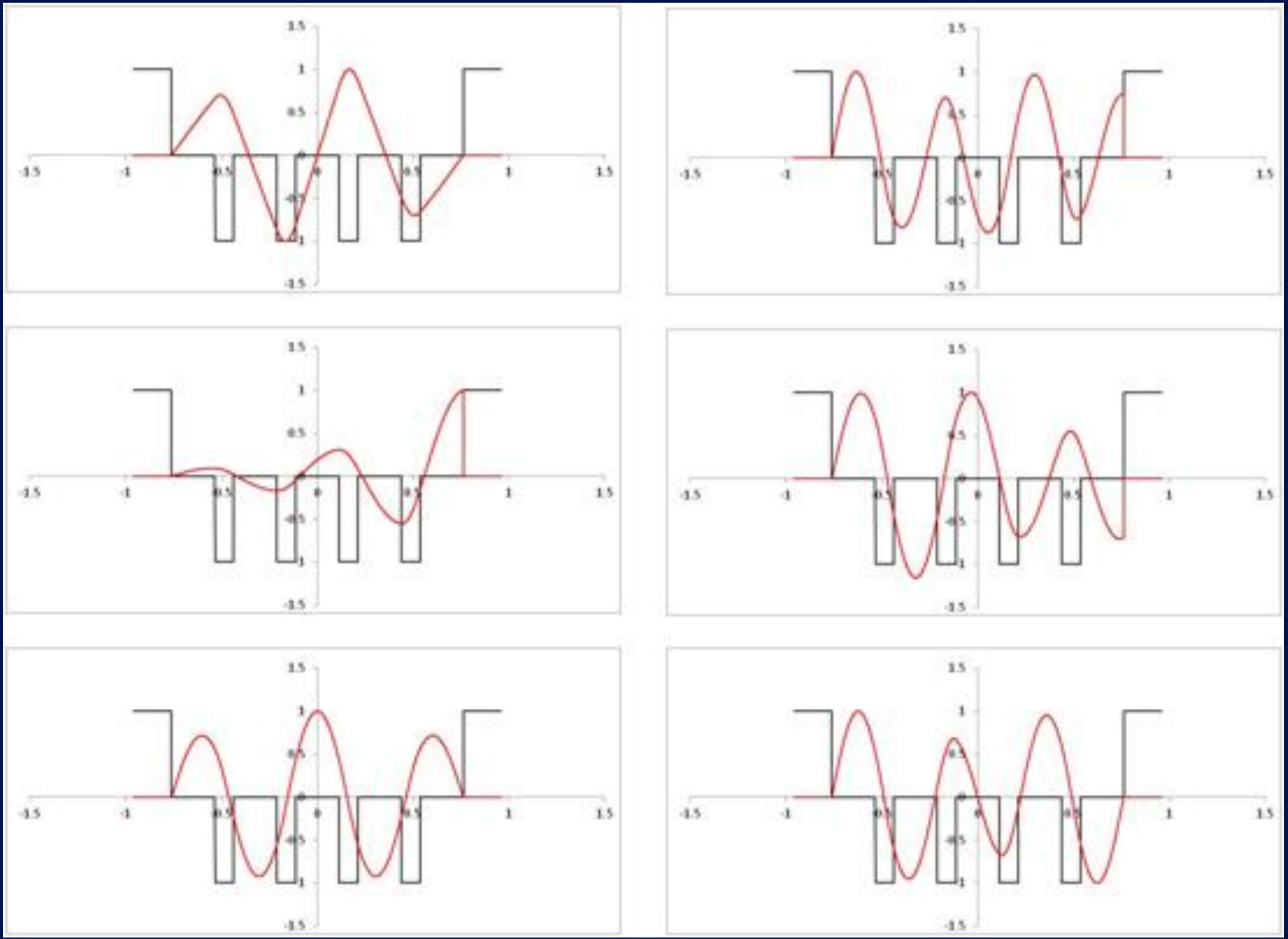
Estrutura de bandas



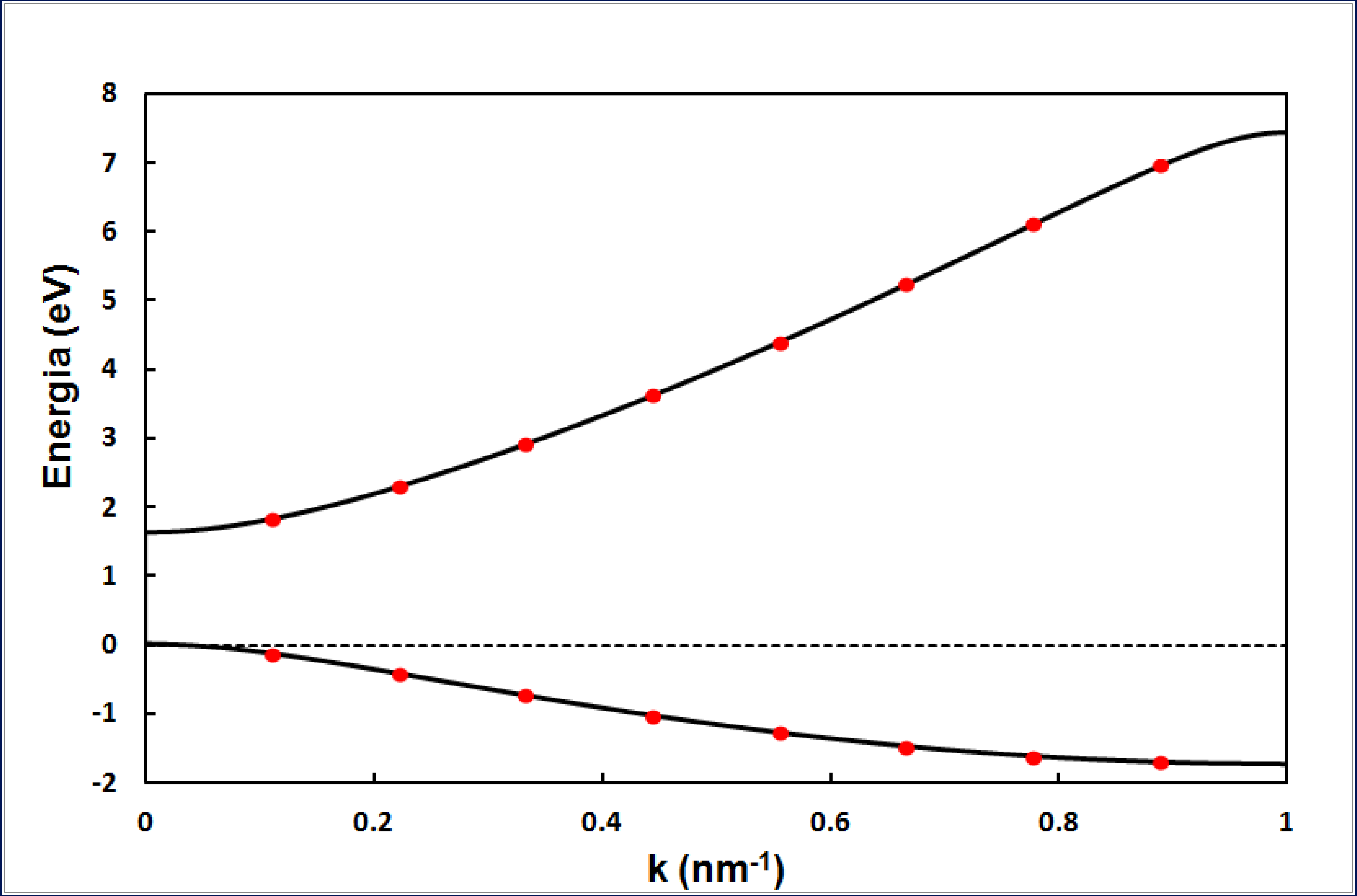




Estados confinados



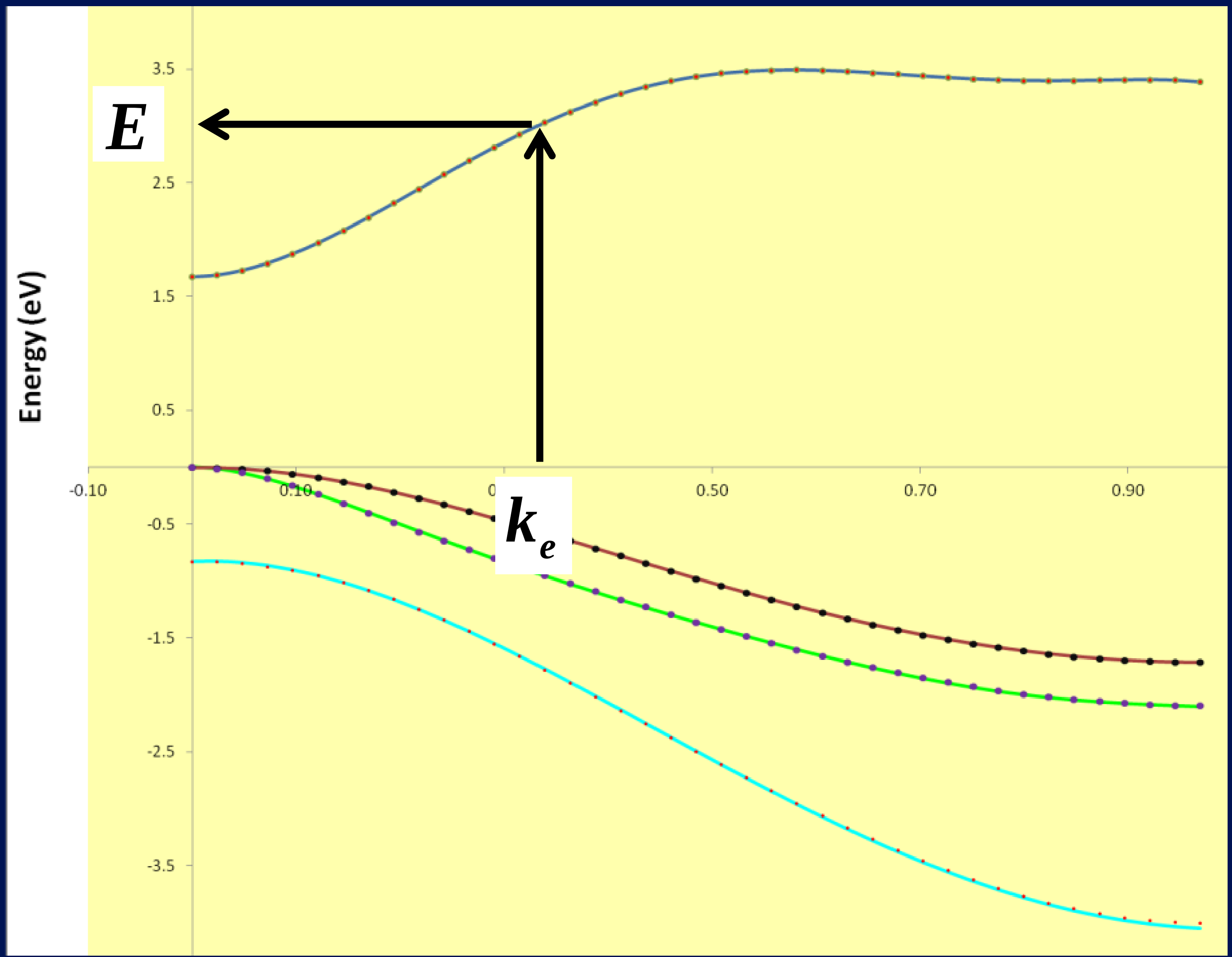
Energia de confinamento



Heuristic Model

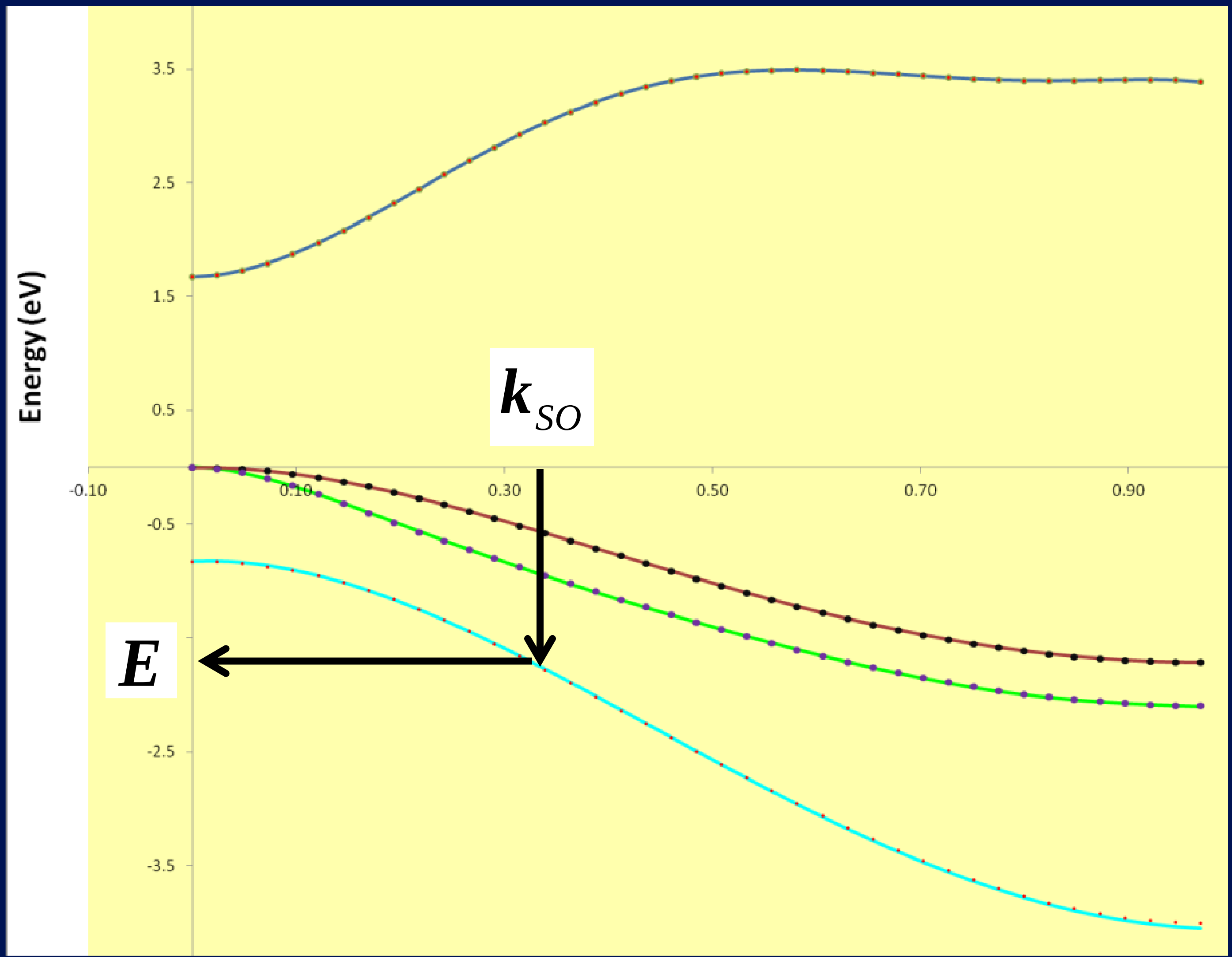
$$j_\ell(ka) = 0 \rightarrow k_{\ell n} = \frac{\chi_{\ell n}}{a}$$

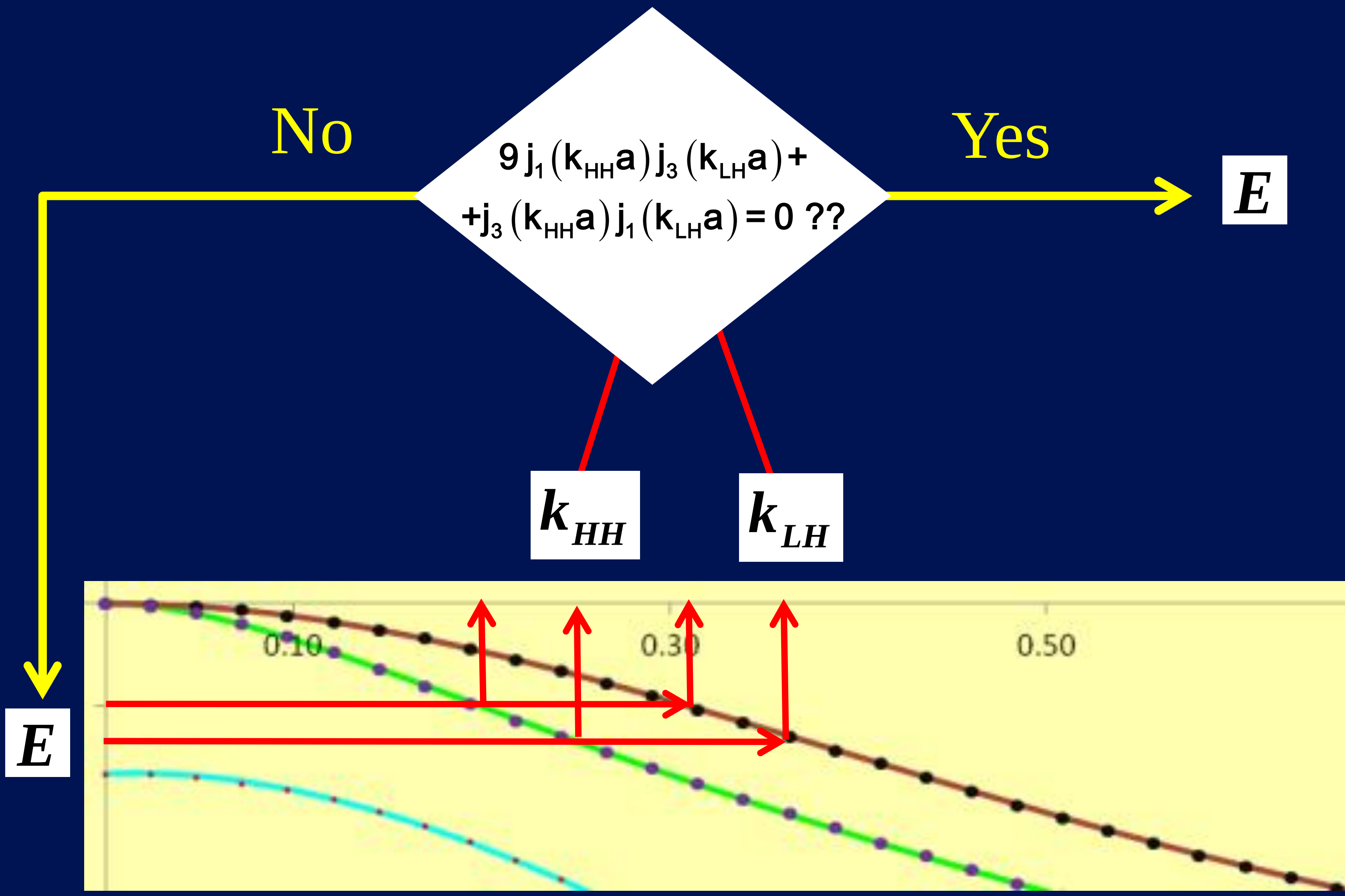
e



$$j_\ell(ka) = 0 \rightarrow k_{\ell n} = \frac{\chi_{\ell n}}{a}$$

e





No
$9\, j_1(k_{HH}a)\, j_3(k_{LH}a) +$
$+ j_3(k_{HH}a)\, j_1(k_{LH}a) = 0$??
Yes
E
k_{HH}
k_{LH}
0.10
0.30
0.50
E

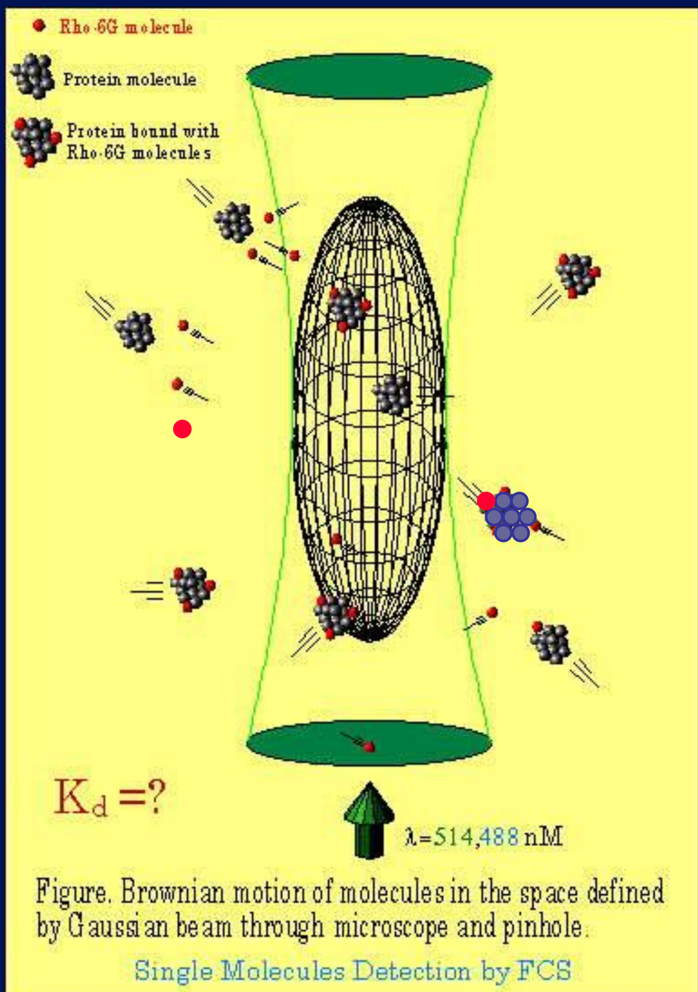
FCS

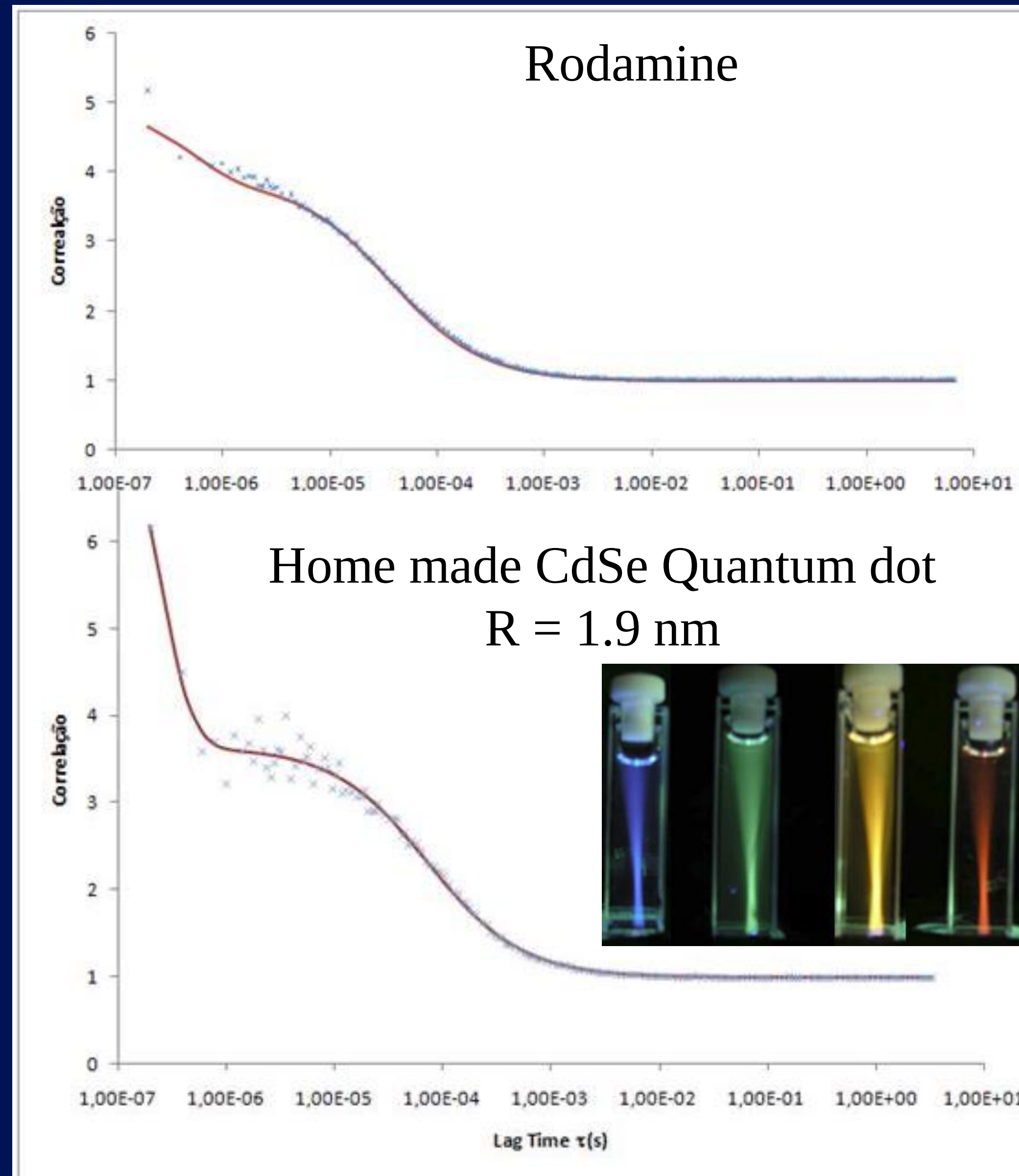
Fluorescence Correlation Spectroscopy

Fluorescence Correlation Spectroscopy FCS

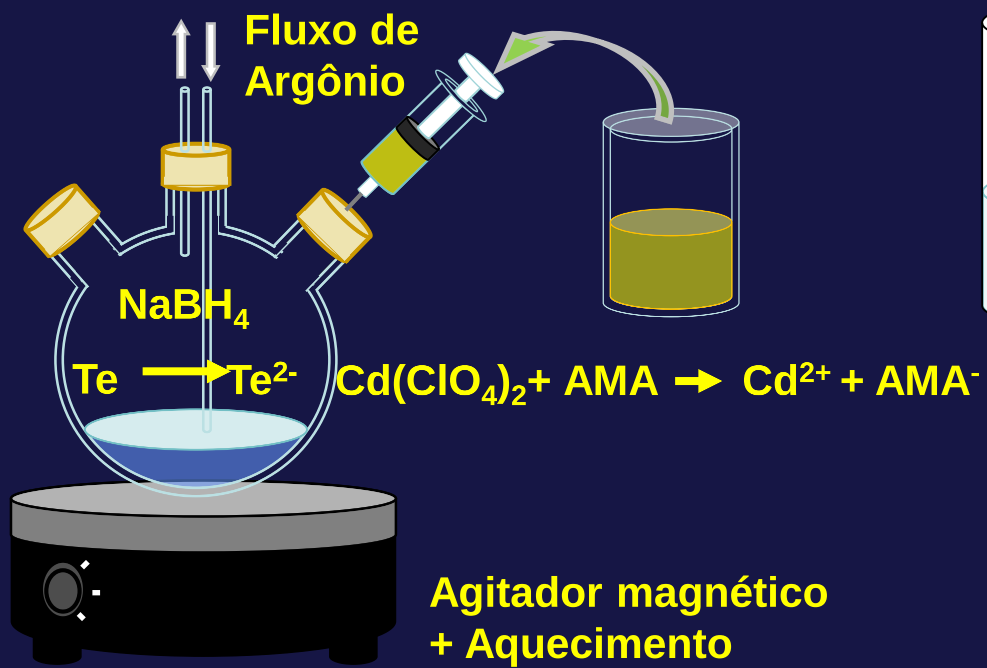
$(1\ \mu m)^3$ = 1 femtoliter mass spectrometry?

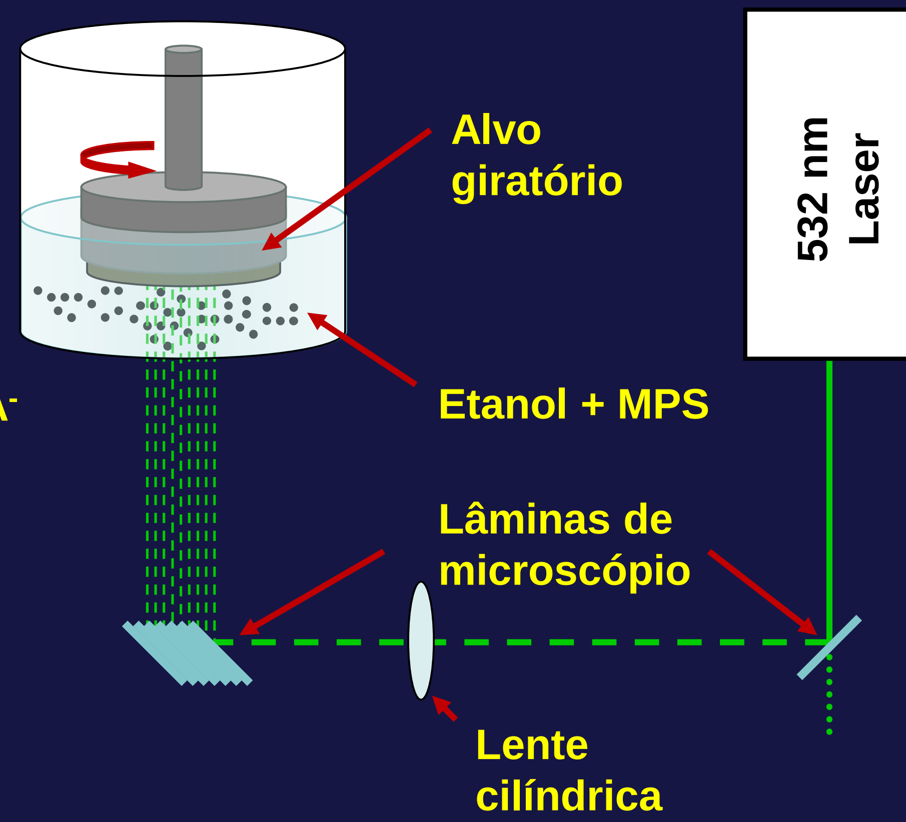
Hydrodynamic radius extracted from diffusion time



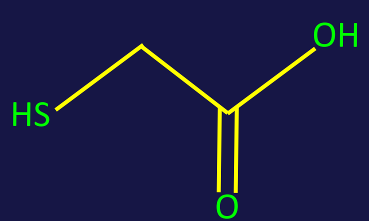


Quantum Dot Fabrication





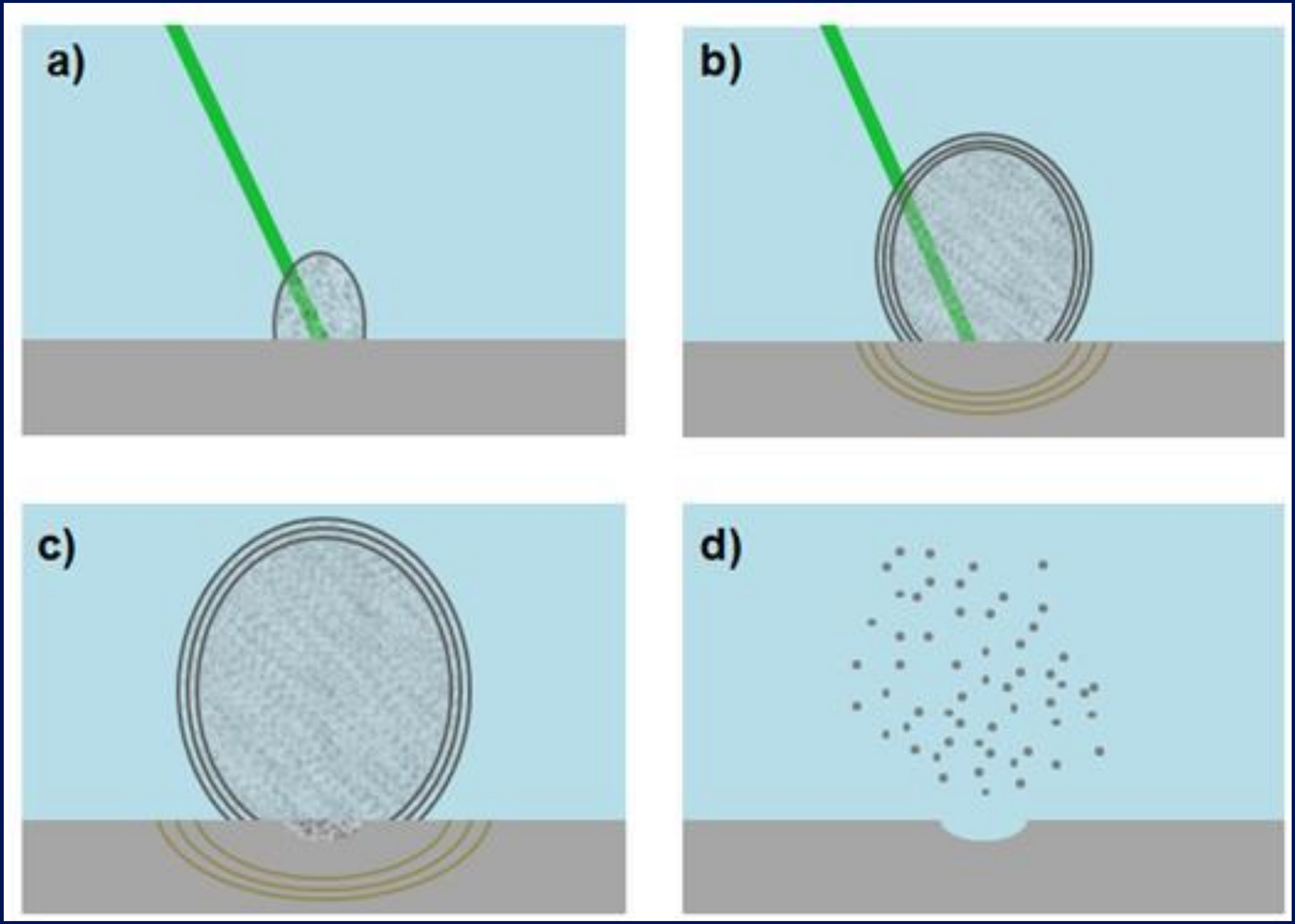
Ambas precisam de estabilização:



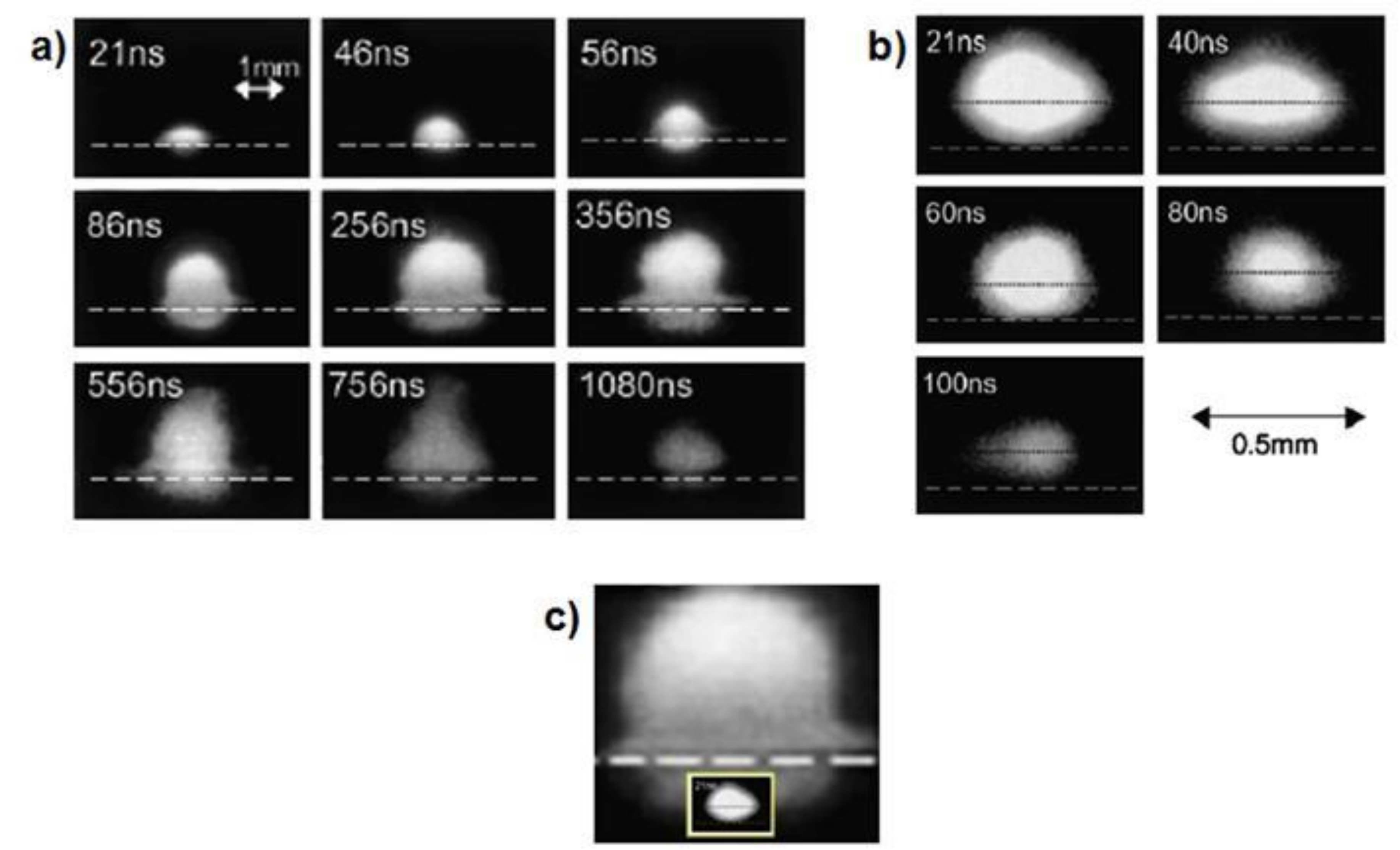
AMA (solúvel em água)

MPS (solúvel em etanol)

Laser Ablation in Liquids



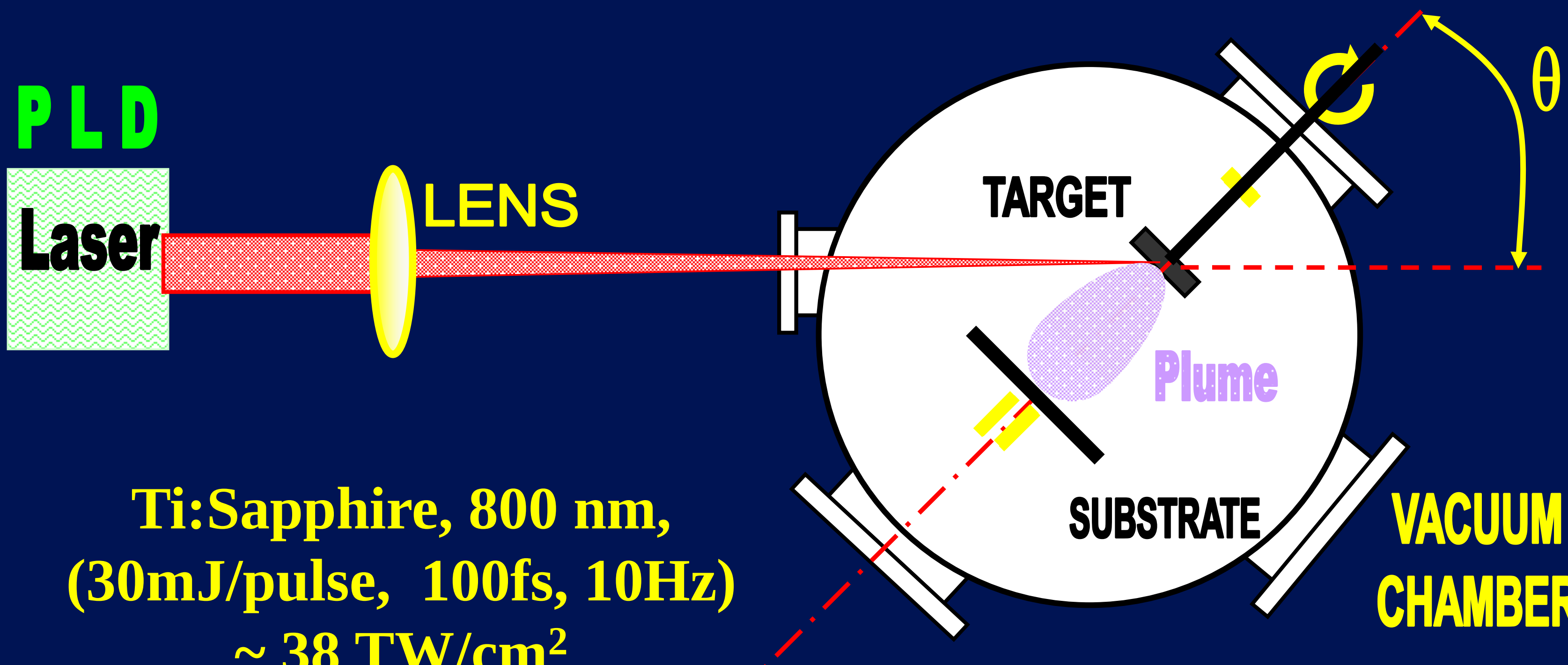
Vaccum versus liquid laser ablation



SAITO, K. et al. **Appl. Surf. Sci.** 197, 56-60, (2002)

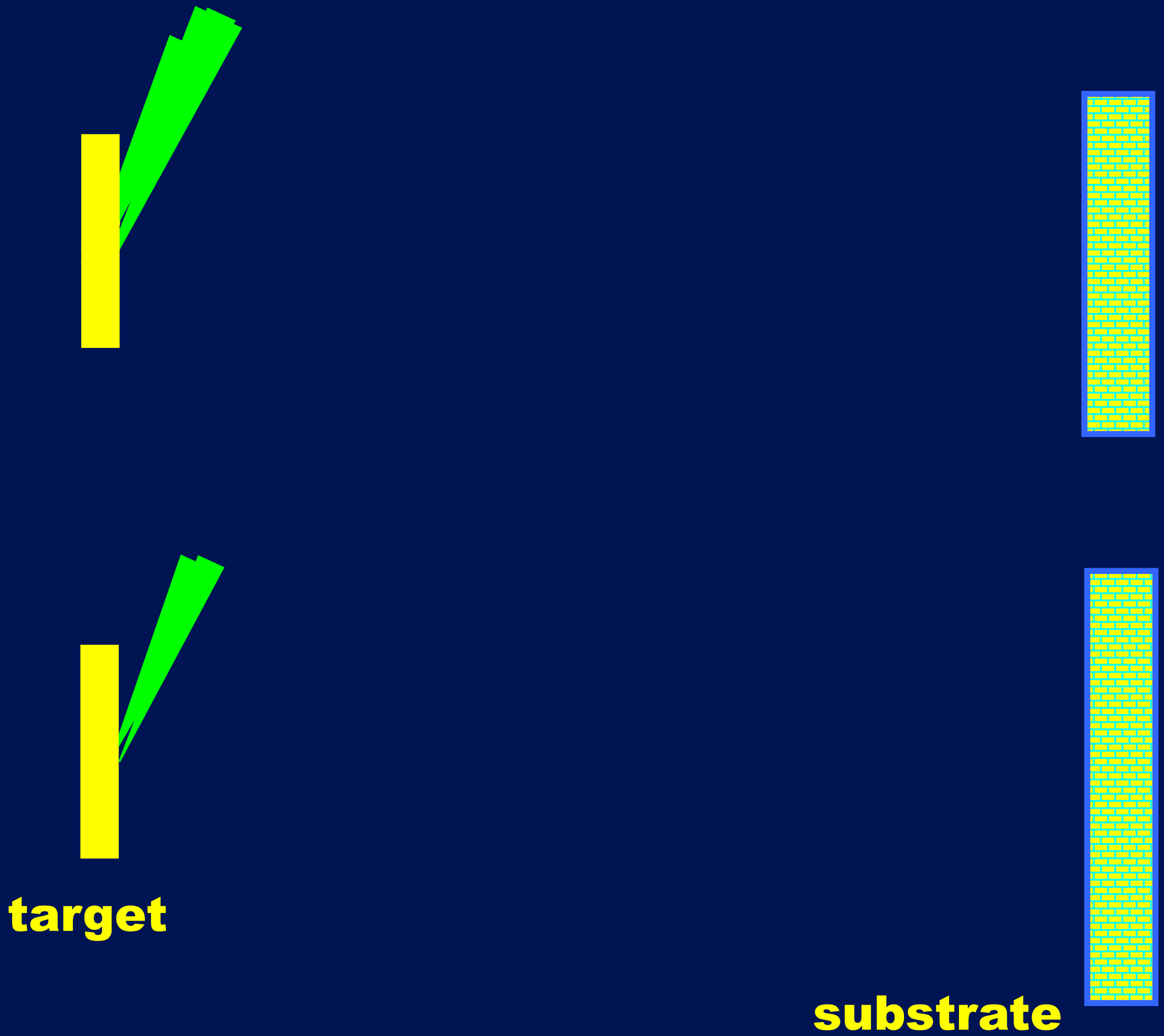
Laser Ablation in Vacuum

Experimental set up



Ti:Sapphire, 800 nm,
(30mJ/pulse, 100fs, 10Hz)
~ 38 TW/cm^2

SPIE Optics+Photonics



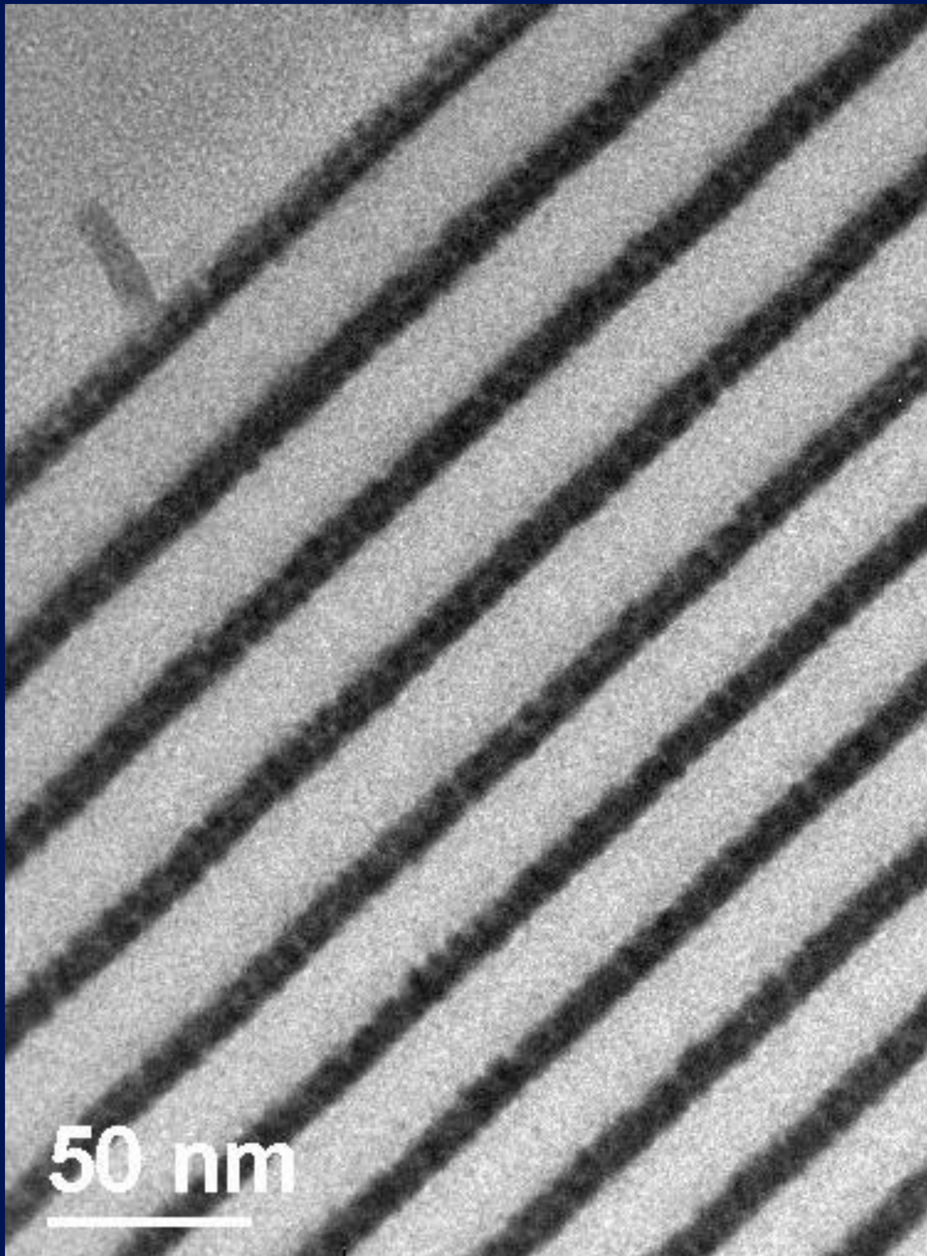
Lower bkg pressure
Higher nr. of pulses
QD growth on substrate

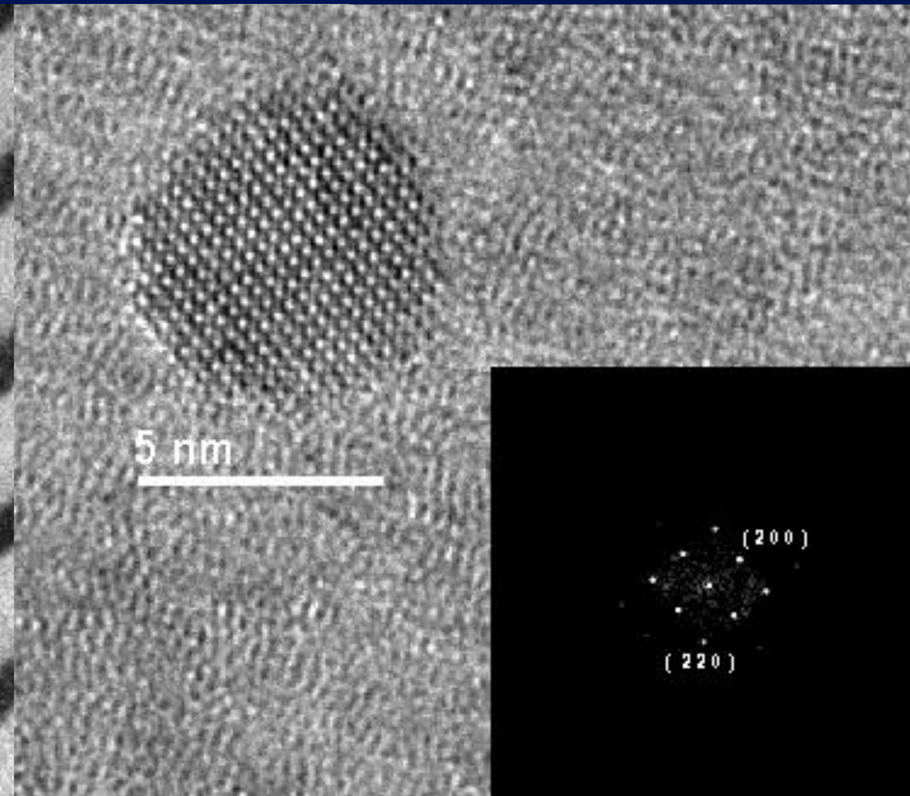
COALESCENCE

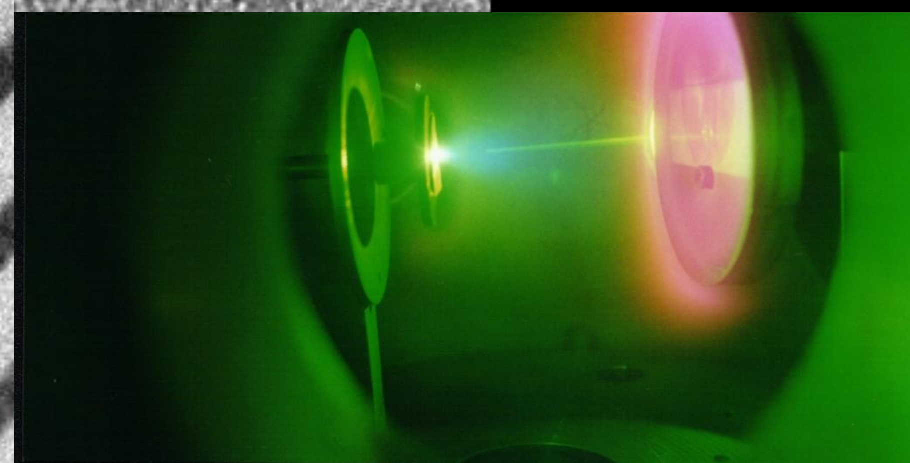
Higher bkg pressure
Lower nr. of pulses

QD Growth at vapor phase

HRTEM (LME-LNLS) PbTe QDs images







Quantum dot doped Glass

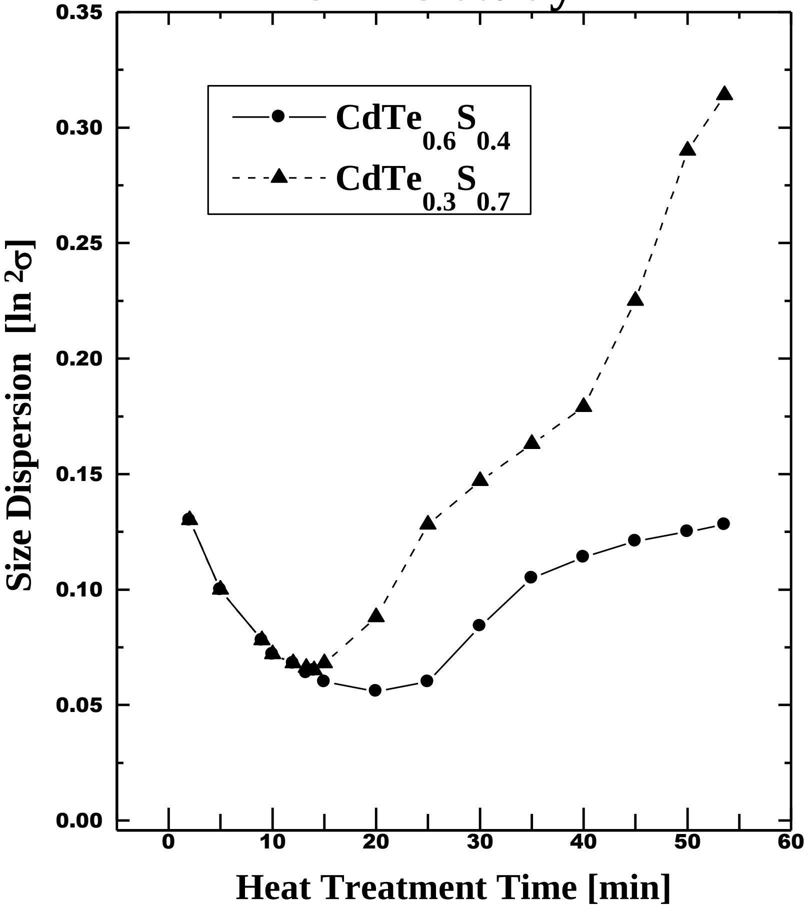
Growth Kinectics: How to Control Size and Dispersion

Glass and QD elements melted together 1200 ºC: transparent glass

→

Thermal annealing 460 - 560 ºC: QD's development - time →

Size dispersion vs time: SAXS study



Results

SAXS show nucleation&growth happening simultaneously

Double annealing method suggested:
first (460ºC): only nucleation
second (560ºC): only growth

- New method produced 6% size dispersion QD's

The End!!

Thanks for the attention