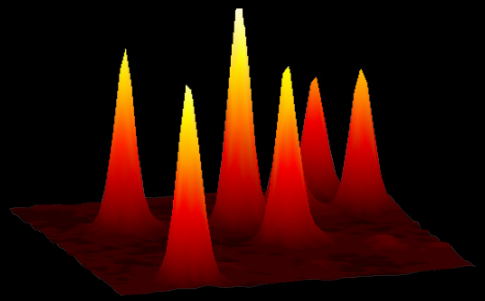
UNIVERSITÉ DE BORDEAUX

CENTRE NATIONAL DE LA RECHERCHE SCIENTIFIQUE

Optical detection and Spectoscopy of individual nano-objects



NanoPhotonics group
Centre de Physique Moléculaire Optique et Hertzienne
CNRS & Bordeaux University, France

http://www.cpmoh.cnrs.fr/nanophotonics

Scientific Context (1)

Single Nano-objects detection

Why?

No ensemble averaging (distributions)

- Time evolution, no synchronization needed
- Sub-wavelength localization possible
- Extreme sensitivity to local environment
- Isolate a single quantum system

How?

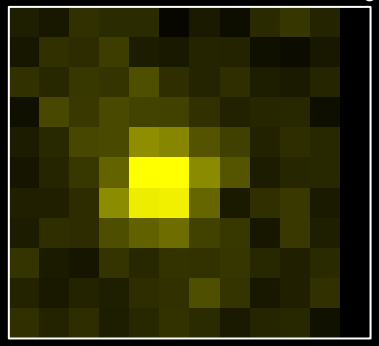
- *Far Field Optical Detection Techniques*
  - → Simple & Non-invasive measurements
  - → Large variety of spectroscopic tools

- Make sure that :
  - only one nanoobject interacts with the laser in the excitation volume (→ very low concentrations and volumes at diffraction limit)
  - the signal from the nanoobject dominate all sources of background

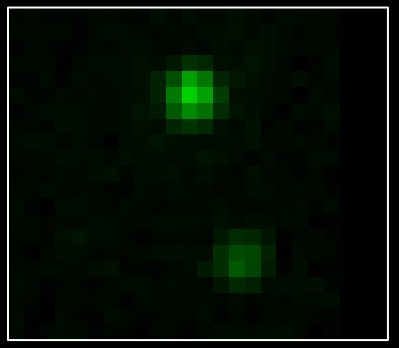
Scientific Context (2)

- *Luminescence based methods:*

→ *Luminescent nano-objets only !*



Fluorescent Dyes : Photobleaching



Semiconductor Nanocrystals: Blinking

- *Rayleigh scattering based methods:*

→ Particle Size

→ Scattering Background

How to detect small, *non-luminescent* individual nano-objects ?

- *Absorption based detection methods*

→ eg. for small spherical nanoparticles : $\sigma_{abs} \sim D^3$, *whereas* $\sigma_{scatt} \sim D^6$

Imaging Individual Nano-Objects *via* Absorption

- *Good candidates for absorption-based methods*

→ Large absorption cross sections

→ Small time intervals between consecutive absorption events

- *Metal Nanoparticles fulfill both requirements*

→High absorption near the Surface Plasmon Resonance

5*nm* gold NP: $\sigma_{abs} \sim 6.10^{-14}\ cm^2 \sim 10^2\ \sigma_{abs\text{-}molecule}$

→ Short electron-electron and electron-phonon relaxation times (~1 *ps*)

- Direct absorption measurement would not work in a scattering environment. Need a "dark field" method

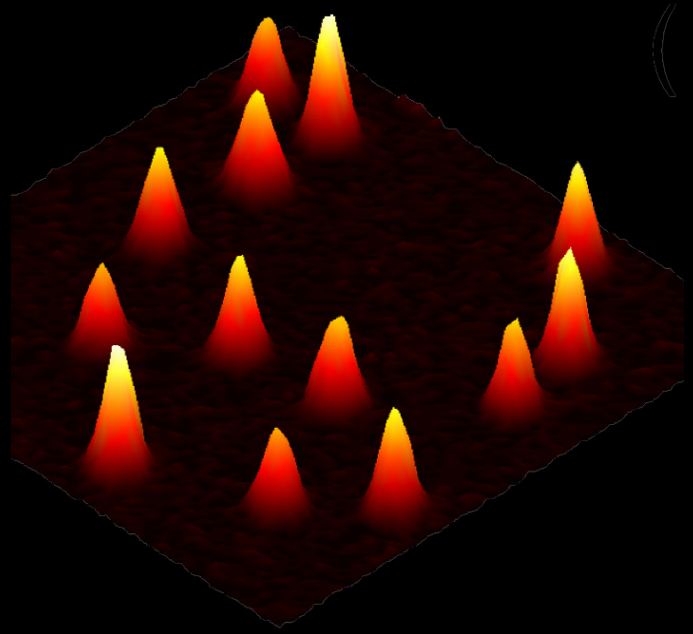
→ Particles have a very low luminescence yield

→ Absorbed energy converted into heat

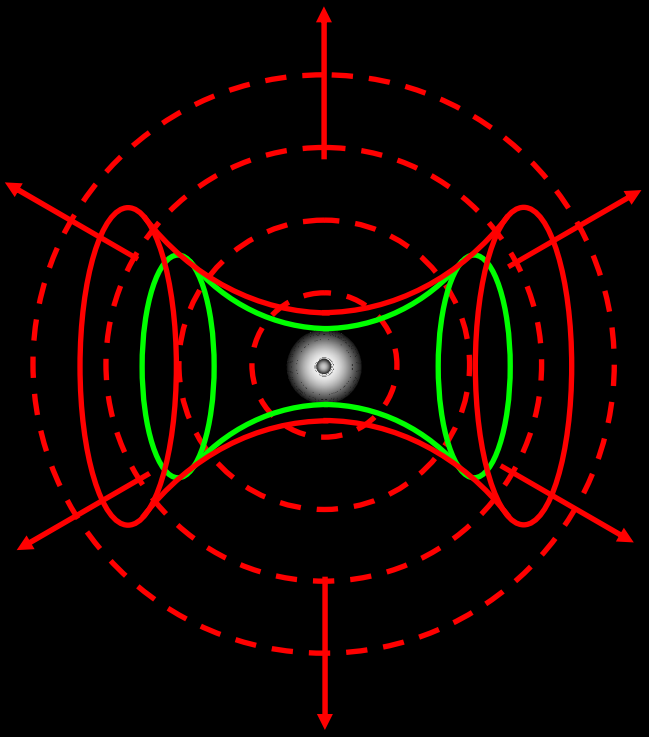
Detection using the photothermal effect…

D. Boyer *et al.*, *Science* **297**, *1160* (2002)
L. Cognet et al. PNAS (2003)

Photothermal Heterodyne Imaging of Individual Nano-objects



Photothermal Heterodyne Imaging (PHI)



Modulated Heating Beam (at Ω)

Nanoparticle: Heat point source

Refractive index profile

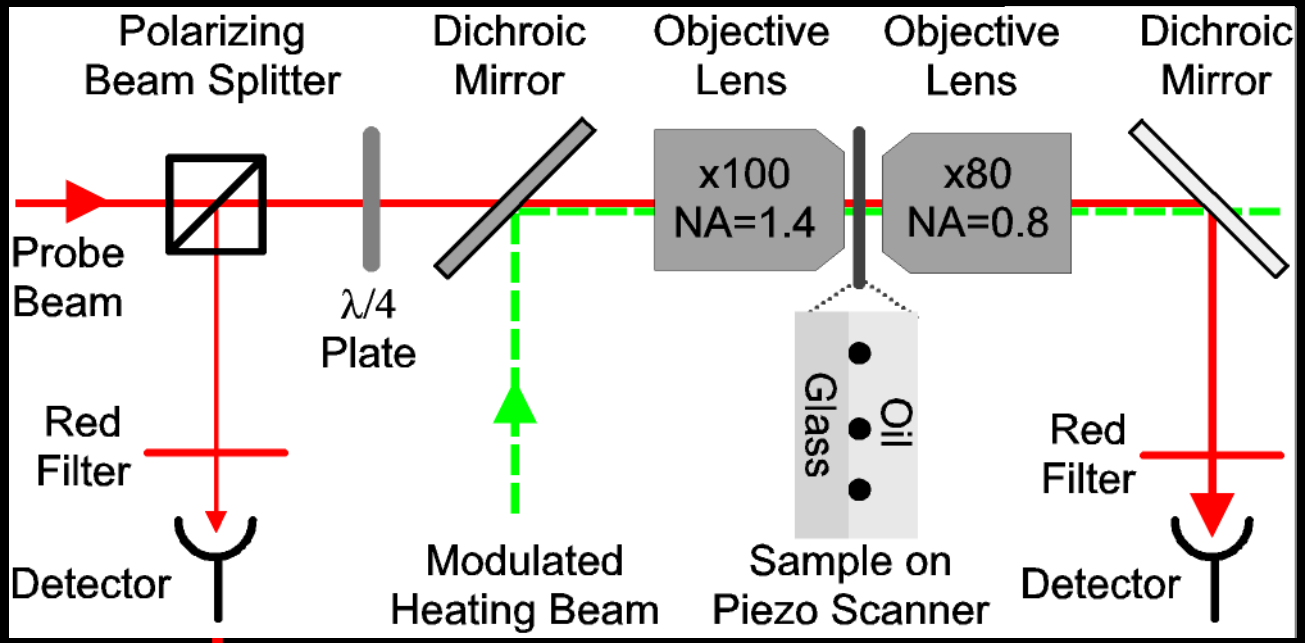
characteristic size r_{th}

Non-resonant Probe beam

Scattered field (with sidebands at $\pm\ \Omega$)

Detection of the Beatnote at Ω between the scattered field and the reflected (or transmitted) probe field

Experimental Setup

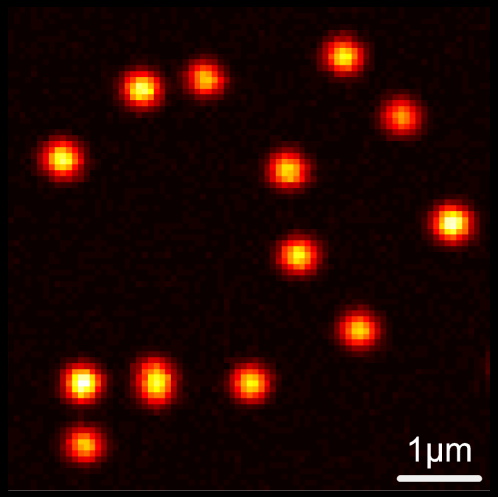


Beatnote at Ω between backward scattered field and the reflected probe beam extracted by lock-in detection

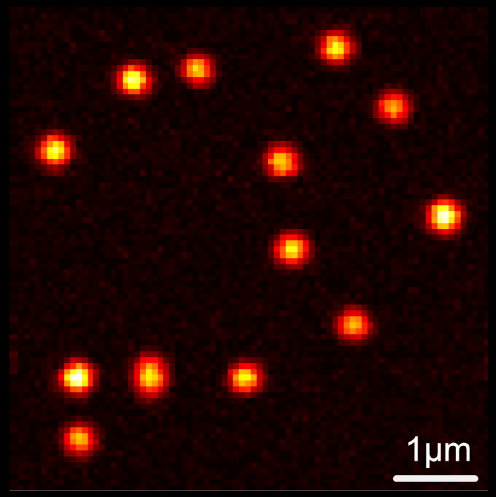
Beatnote at Ω between forward scattered field and the transmitted probe beam extracted by lock-in detection

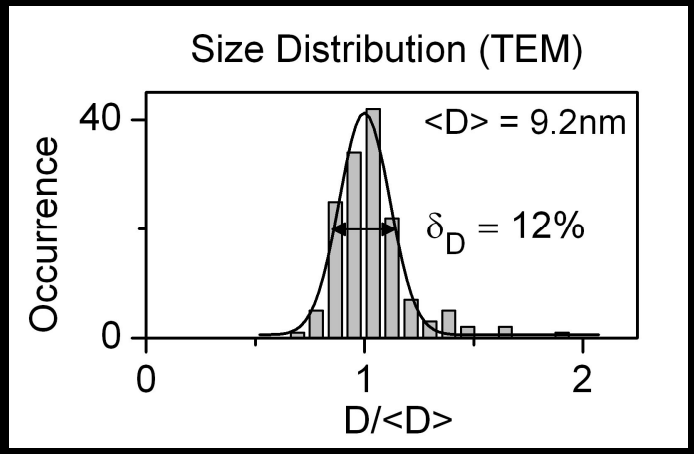
Imaging of 10 *nm* Individual Gold Nanoparticles

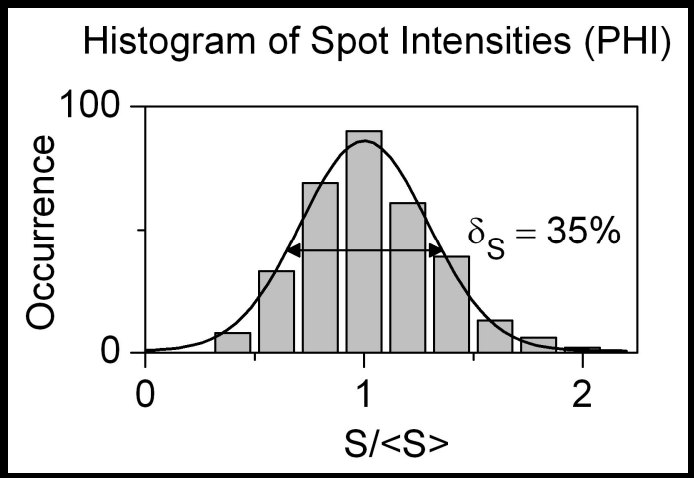
Backward



Forward



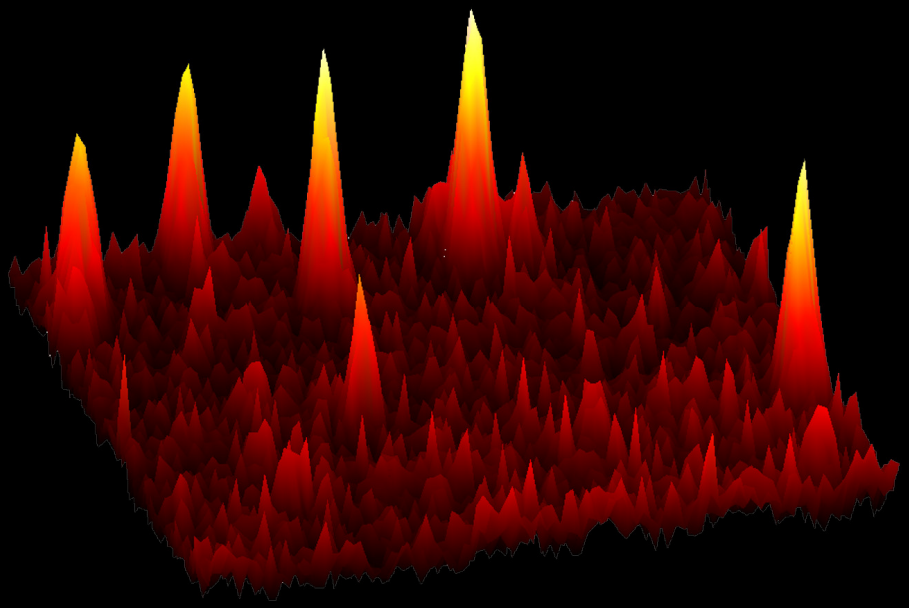




→ ***Individual*** Nanoparticles

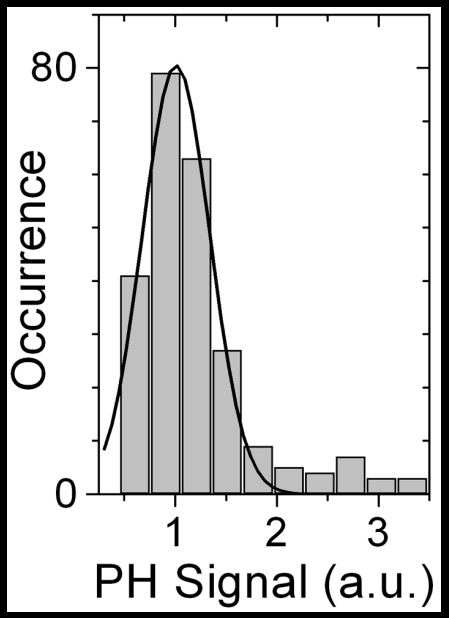
Optical Detection of Individual 1.4 *nm* Gold Nanoparticles

- Sample of 1.4*nm* gold nanoparticles (~67 atoms) embedded into a PVA matrix
- Nanoparticle absorption cross section $\sigma_{abs} \sim 10^{-15}\ cm^2$



Photothermal Heterodyne Image

5 x 5 μm^2 (80 *nm* / pixel, 10 *ms* / pixel)

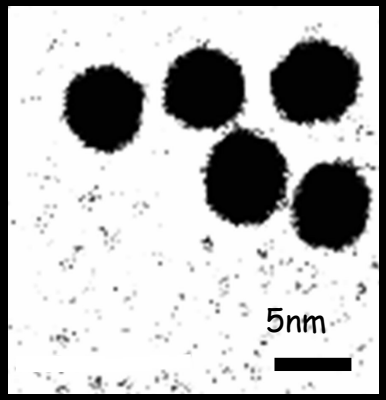


Unimodal Histogram of spot intensities

S. Berciaud *et al., Phys. Rev. Lett.* **93**, 257402, (2004)

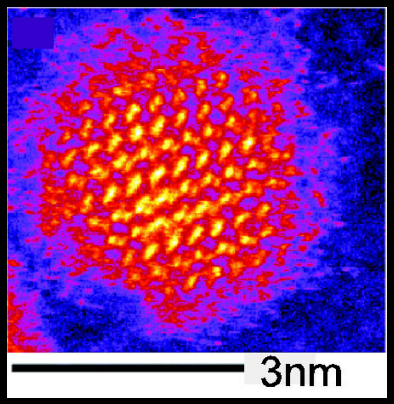
Absorption sopectroscopy of Individual nanoobjects

Au NPs



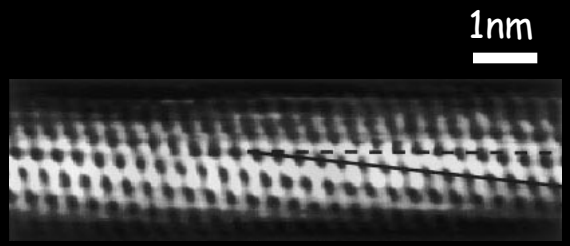
Berciaud et al.
Nano Lett. 3 (2005)

CdSe NCs



Berciaud et al.
Nano Lett. 5 (2005)

Carbon Nanotubes

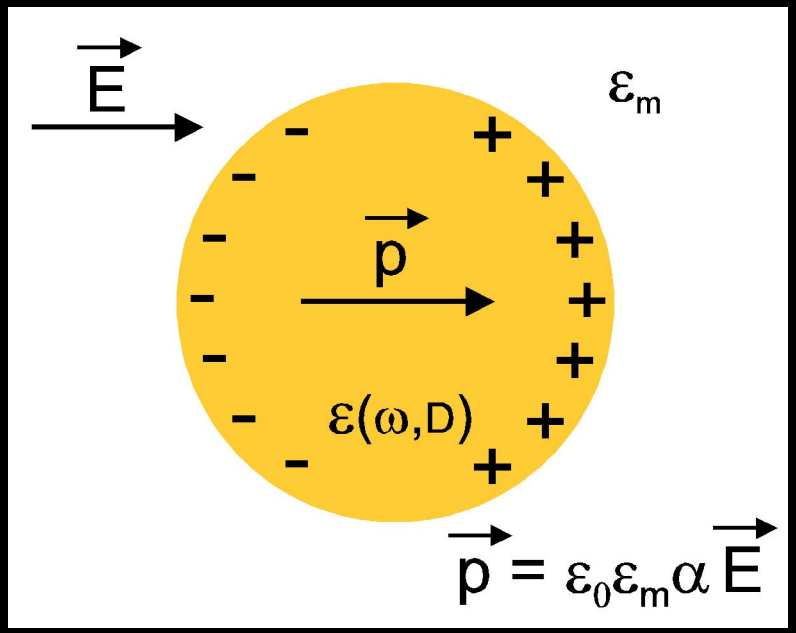


Berciaud et al.
Nano Lett. (2007)

TEM image of gold Nanoparticles : Berciaud et al. Nano Lett. (2005)
TEM image of a single CdSe Nanocrystal : Mc Bride *et al.* Nano. Lett. (2004)
STM image of a single carbon nanotube : Wildöer *et al.* Nature (1998)

Surface Plasmon Resonance Spectroscopy of Individual Gold Nanoparticles

a << $\lambda_{excitation}$: Quasistatic (or dipolar) Approximation :



$$\alpha = \frac{\pi}{2} D^3 \frac{\varepsilon - \varepsilon_m}{\varepsilon + 2\varepsilon_m} \quad \text{and} \quad \sigma_{abs} = k\,\mathrm{Im}(\alpha)$$

$$\sigma_{abs} = 4\pi D^3 \varepsilon_m^{3/2} \frac{\omega}{c} \frac{3\varepsilon_2}{(\varepsilon_1 + 2\varepsilon_m)^2 + \varepsilon_2^2}$$

$$\varepsilon = \varepsilon_1 + i\varepsilon_2$$

- *Resonant Oscillation* for minimal $\varepsilon_1 + 2\varepsilon_m$
- Achievable in metals where Re(ε)<0 in the optical domain

SPR in Gold Nanoparticles

$$\varepsilon(\omega) = \varepsilon_{DC} - \frac{\Omega_p^2}{\omega(\omega + i\gamma_0)} + \varepsilon_{IB}(\omega)$$

Modified Drude Term Interband Term

Ω_p : plasma frequency, γ_0 : optical dephasing rate

Intrinsic size effects

- Electron mean free path in bulk gold : L_e ~ 14 *nm*

→ For D < L_e : Size dependent dielectric constant

$$\gamma(\mathrm{D}) = \gamma_0 + \frac{2\mathrm{g}\,\mathrm{v_F}}{\mathrm{D}} \Rightarrow \varepsilon(\omega, \mathrm{D}) \approx \varepsilon_{bulk}(\omega) + \mathrm{i}\frac{\Omega_\mathrm{p}^2}{\omega^3}\frac{2\mathrm{g}\,\mathrm{v_f}}{\mathrm{D}}$$

- Observable effects : Broadening of the SPR with decreasing NP size

Size Dependence of SPR width Γ
Observation of Intrinsic Size Effects

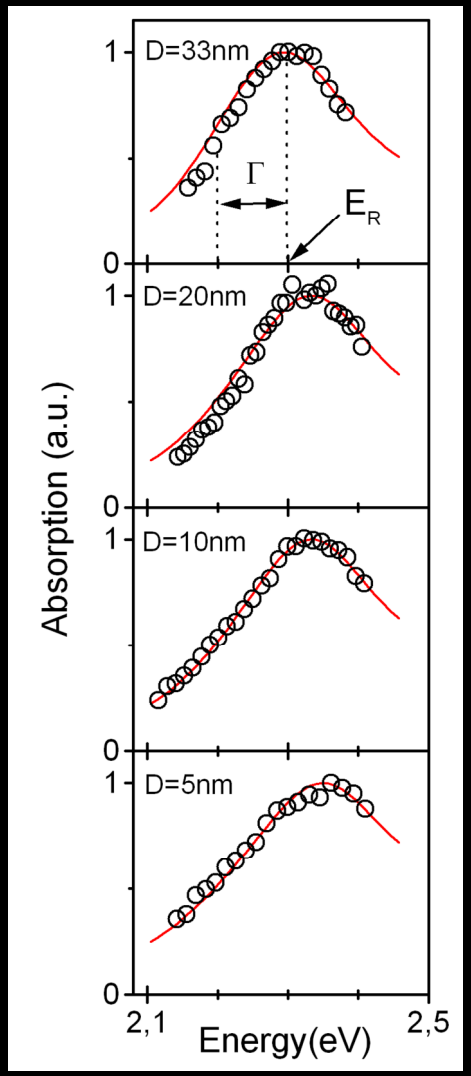
Diameter:

33 *nm*

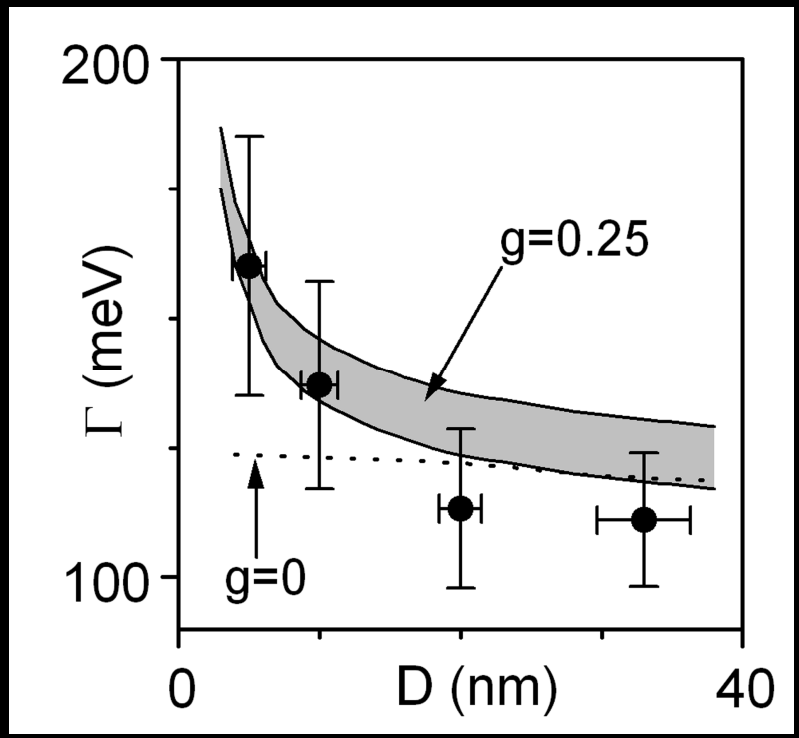
20 *nm*

10 *nm*

5 *nm*

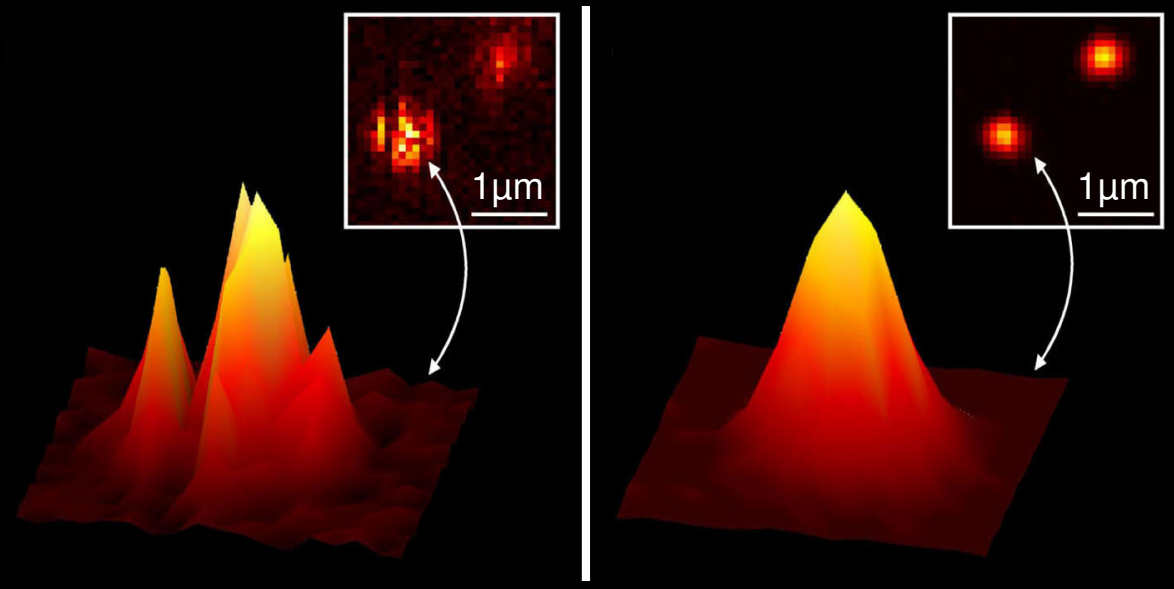


- Red shift with increasing size ($D > 20$ *nm*)
- Broadening with decrasing size ($D < 10$ *nm*)



S. Berciaud *et al.*, *Nano Letters* **3**, 515 (2005)

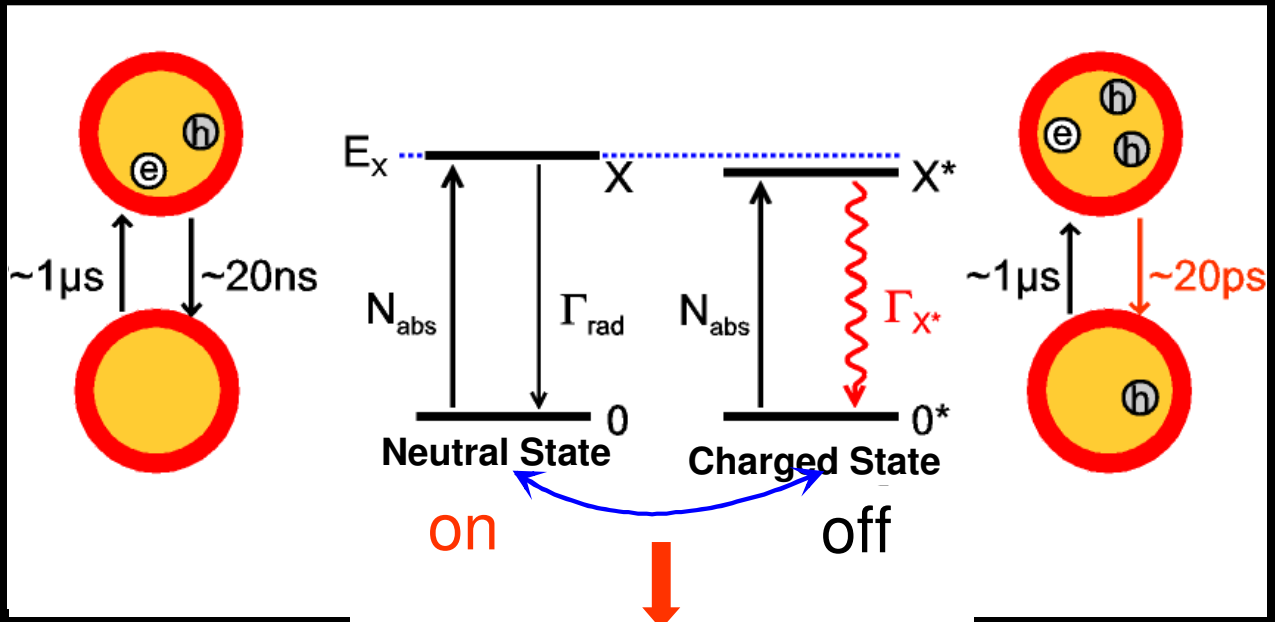
Imaging & Absorption Spectroscopy of Individual Semiconductor Nanocrysals



Photophysics of Nanocrystals (1)

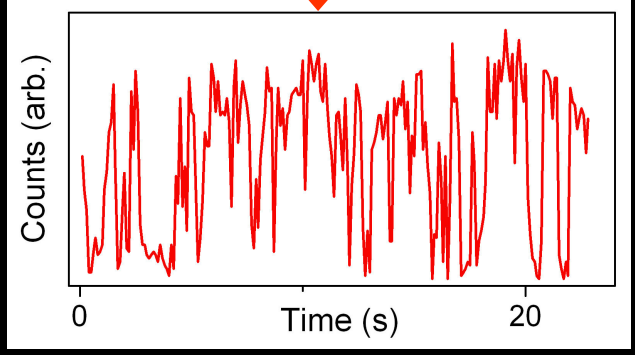
Low excitation: $N_{abs} \sim 1\ \mu s^{-1} << \Gamma_{rad} = (1/20)\ ns^{-1}$
→ Monoexcitonic regime

Monoexciton



Trion
Non-radiative Recombination

Luminescent Nanocrystals
" Blinking "

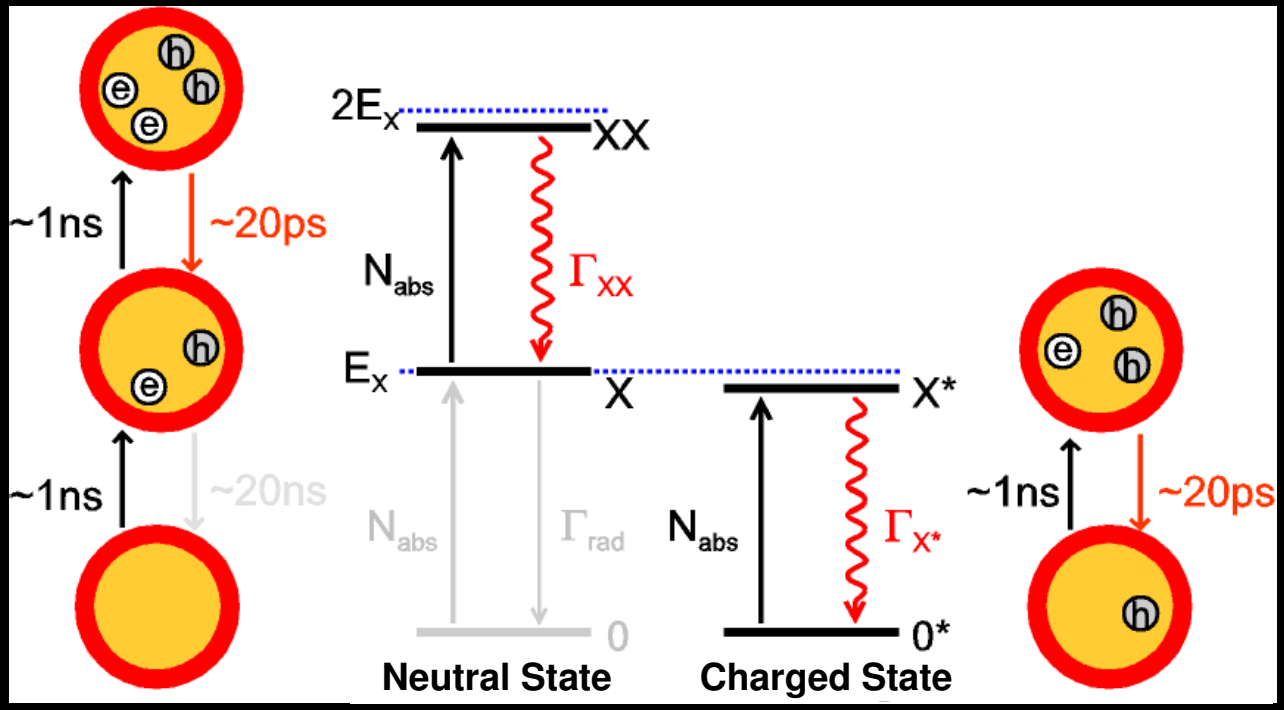


Photophysics of Nanocrystals (2)

High excitation: N_{abs} ~ 1 ns^{-1} >> Γ_{rad} = (1/20) ns^{-1}
→ Formation of *biexcitons*

Biexciton

Monoexciton



Trion

$\Gamma_{rad} << \Gamma_{XX}, \Gamma_{X^*}$ → Very weak luminescence:

High absorption & rapid non-radiative relaxation via Auger processes

→ Photothermal Signal due to XX ↔ X & X* ↔ 0* ?

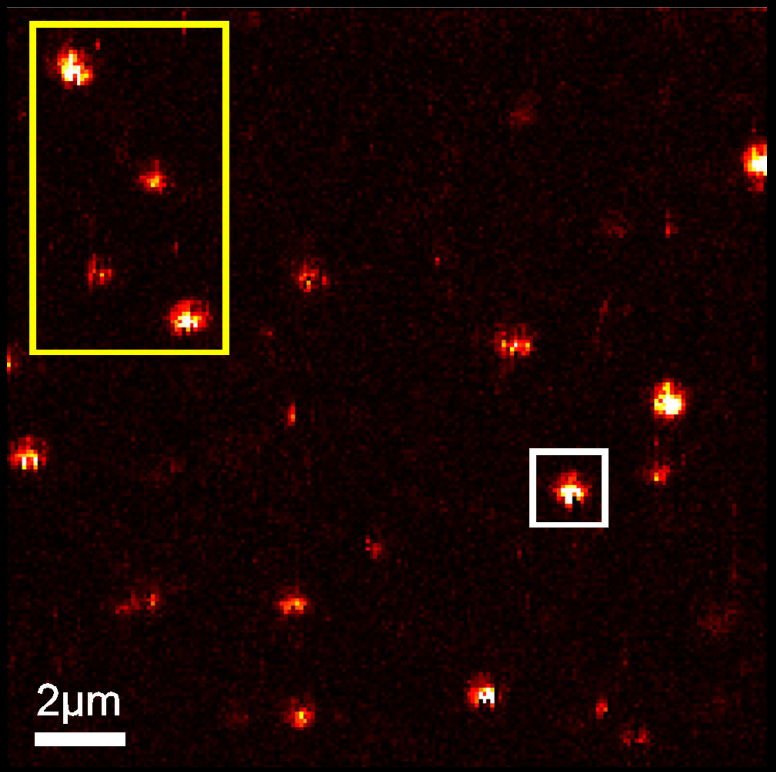
Photothermal Imaging of CdSe/ZnS Semiconductor Nanocrystals

Luminescence

N_{abs}~1photon / µs

σ_{abs}~10^{-15} cm^2, τ_{relax}~20 ns

Monoexcitonic Regime

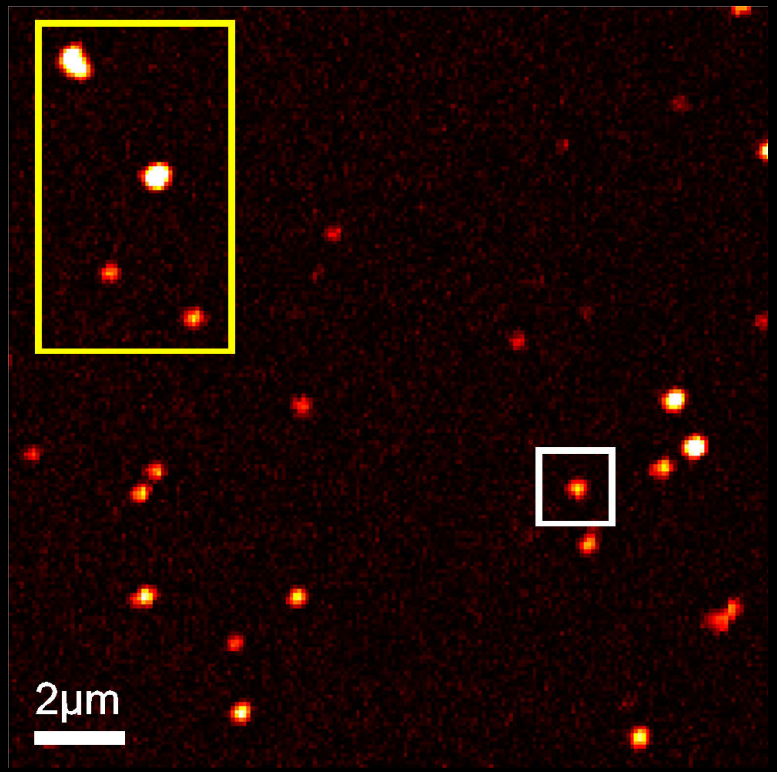


Photothermal

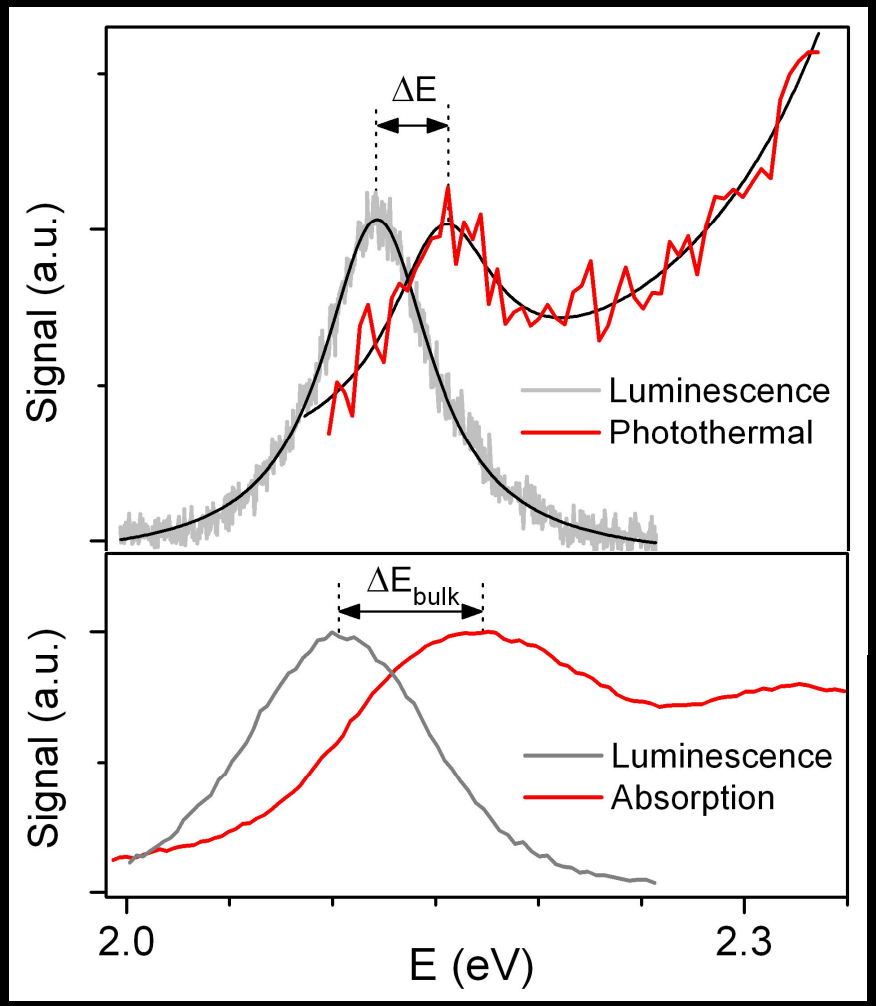
N_{abs}~1 photon / ns

σ_{abs}~10^{-15} cm^2, τ_{relax}~20 ps !

Biexcitonic Regime



Single CdSe Spectroscopy



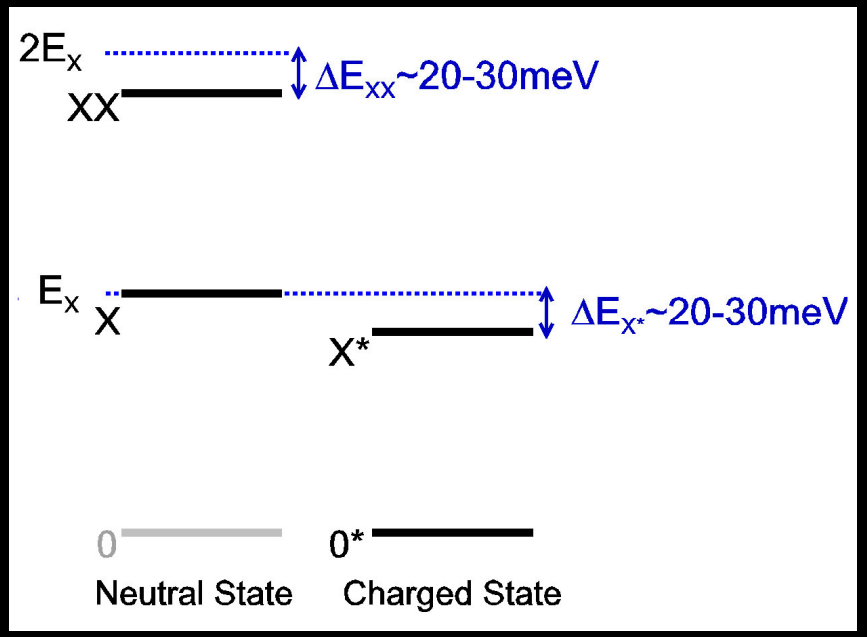
- *Same Nanocrystal*

Luminescence: *Monoexcitonic regime*

$N_{abs} << \Gamma_{rad}$

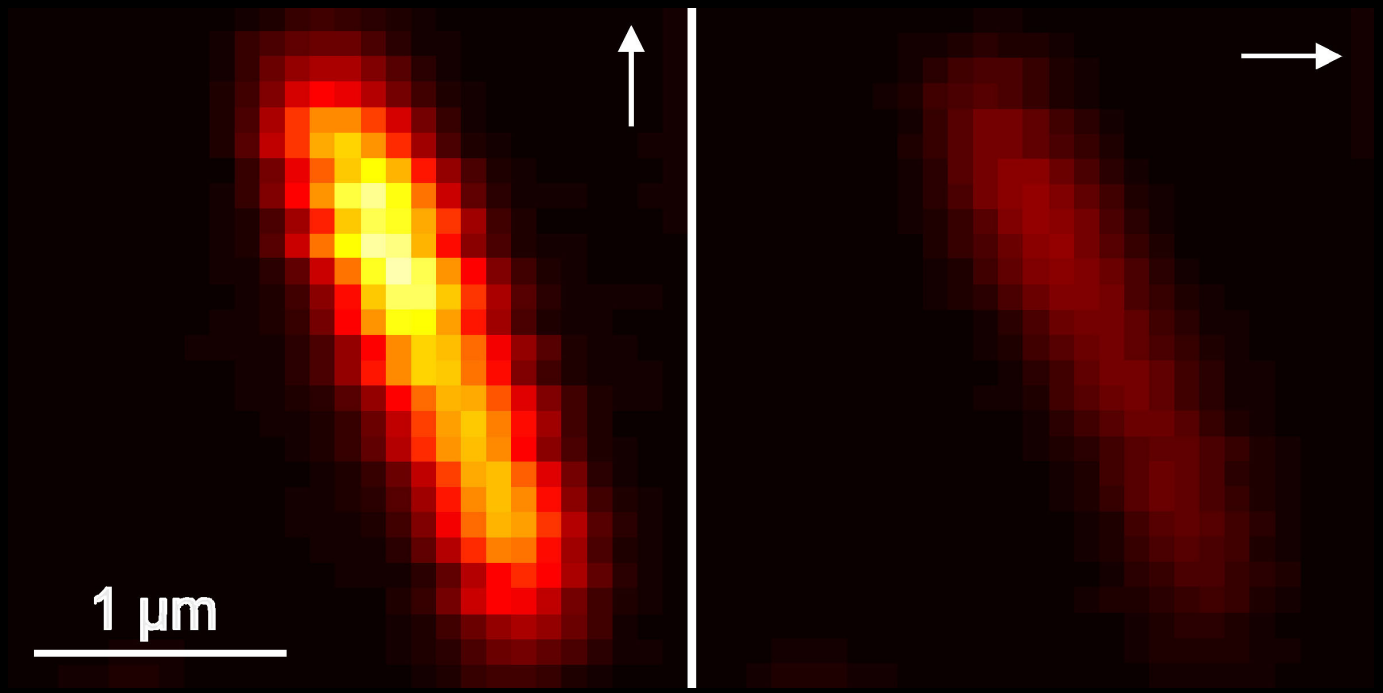
Absorption : the ***biexcitonic*** regime

$N_{abs} >> \Gamma_{rad}$



S. Berciaud *et al.*, *Nano Letters* **5**, 2160 (2005)

Imaging and Spectroscopy of Individual Single Walled Carbon Nanotubes



Single Walled Carbon Nanotubes (SWNTs)

SWNT = Rolled-up *single* graphene sheet

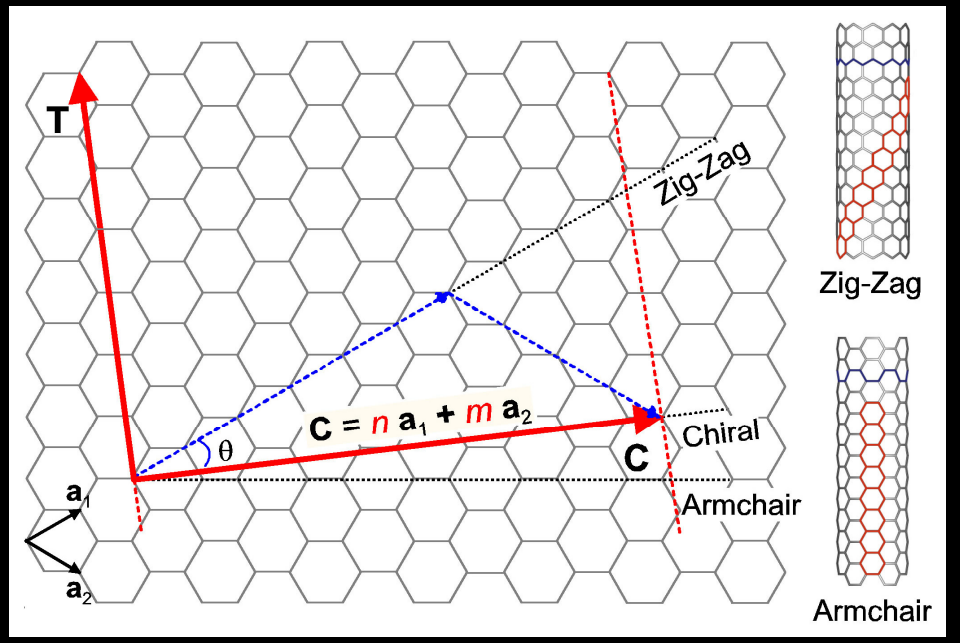
- Diameter ~1nm, length up to ~1cm

→ Quasi 1D systems

- Outstanding mechanical, thermal, electrical,… properties

- SWNT diameter, chiral angle and electronic structure given by two (n,m) integers:

- Metallic if mod(n-m,3)=0
- Semiconducting if mod(n-m,3)=1, 2

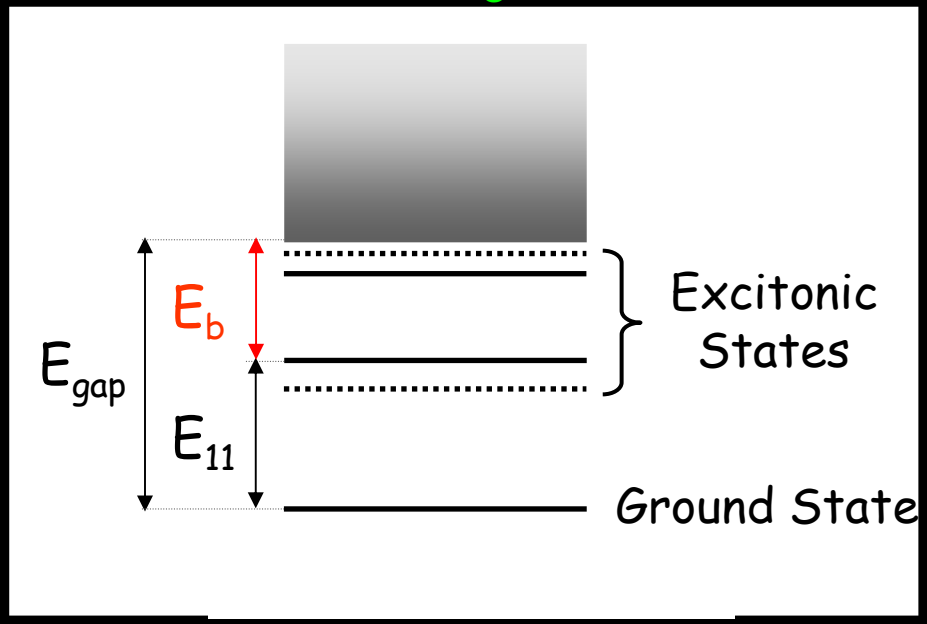


Example : (6,4) semiconducting tube

Background on the SWNTs optical properties

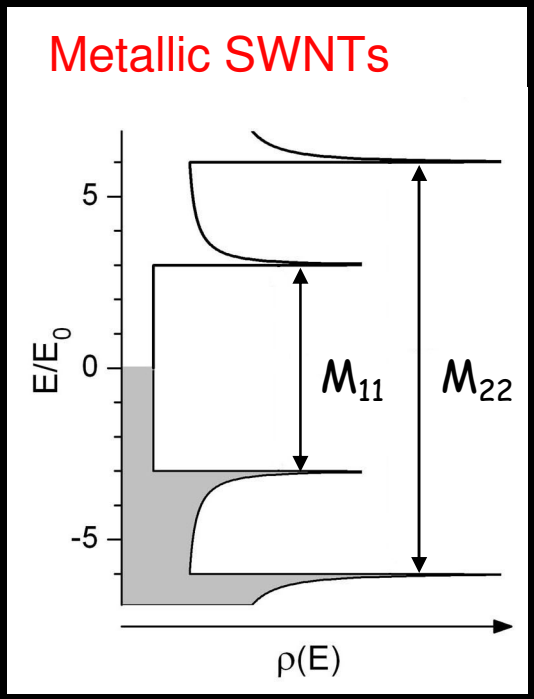
1D Density of states dominated by sharp van Hove singularities ($\propto (E-E_i)^{-1/2}$)

Semiconducting SWNTs



Wang et al, *Science* (2005), Maultzsch et al *Phys.Rev. B* (2005)

Metallic SWNTs



- Strong *e-h* interactions

→ Excitonic effects

→ Transition energies < Band Gap

Luminescence:

Decay, sensitivity to local environment, absorption cross-section, quantum yield….

What about optical transitions?

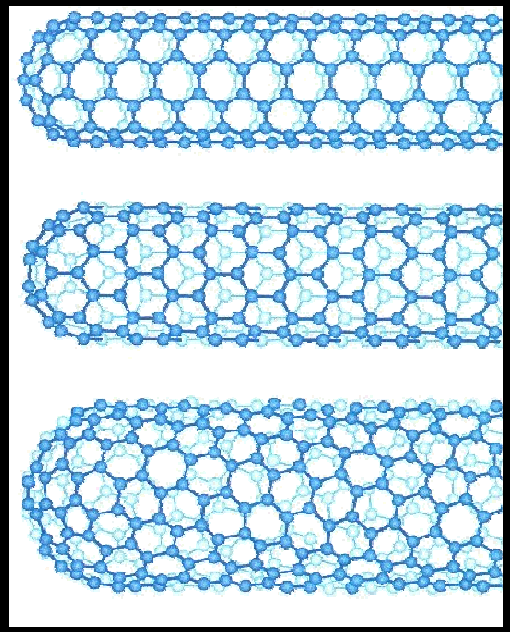
Absorption features arise from inter-band transitions of largely non-interacting quasiparticles or from an excitonic transition of strongly correlated electron-hole pairs?

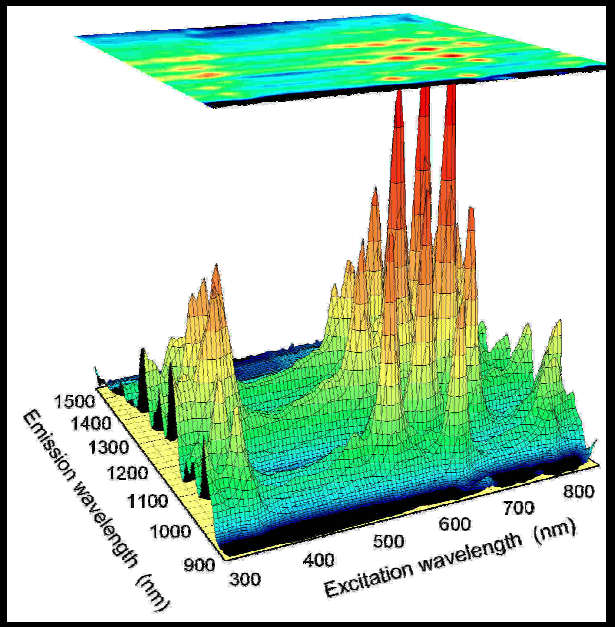
Ensemble spectra

Suspensions of individualized SWNTs display a great *heterogeneity* in terms of:

- Structure and Electronic properties
- Quality/defects …

and thus *optical properties*





Luminescence Map

From Weisman Lab, Rice

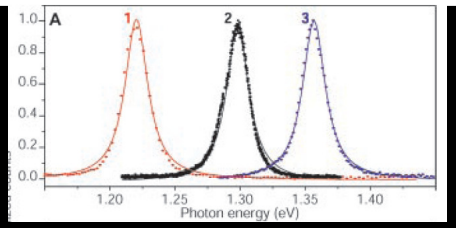
This makes *ensemble* studies not *fully* adequate for a precise understanding of the SWNTs spectroscopic properties.

☞ *Studies on Individual SWNTs*

Optical detection of individual SWNTs

• Luminescence Spectroscopy

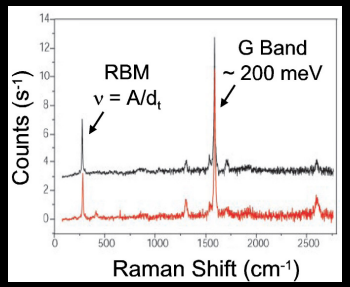
→ Limited to semiconducting SWNTs
→ Highly sensitive to environmental effects



Hartschuh et al. *Science* (2003)
Lefebvre et al., *Phys. Rev. B* (2004)
Htoon et al., *Phys. Rev. Lett.* (2004)

• Raman Spectroscopy

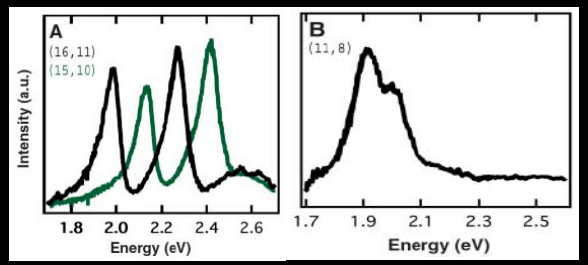
→ Semiconducting & Metallic
→ Weak signals
→ Indirect method (fiting procedure)



Hartschuh et al. *Science* (2003)
Meyer et al, *Phys. Rev. Lett.* (2005).

• Rayleigh Spectroscopy

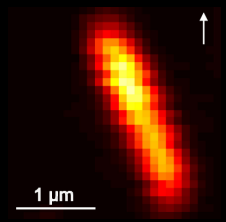
→ Semiconducting & Metallic
→Limited to long, large diameter, suspended tubes to avoid background



Sfeir et al. *Science* (2006)

• Photothermal (absorption) Spectroscopy

→ Semiconducting & Metallic
→ Insensitive to scattering environment



Berciaud et al. *Nanoletters* (2007)

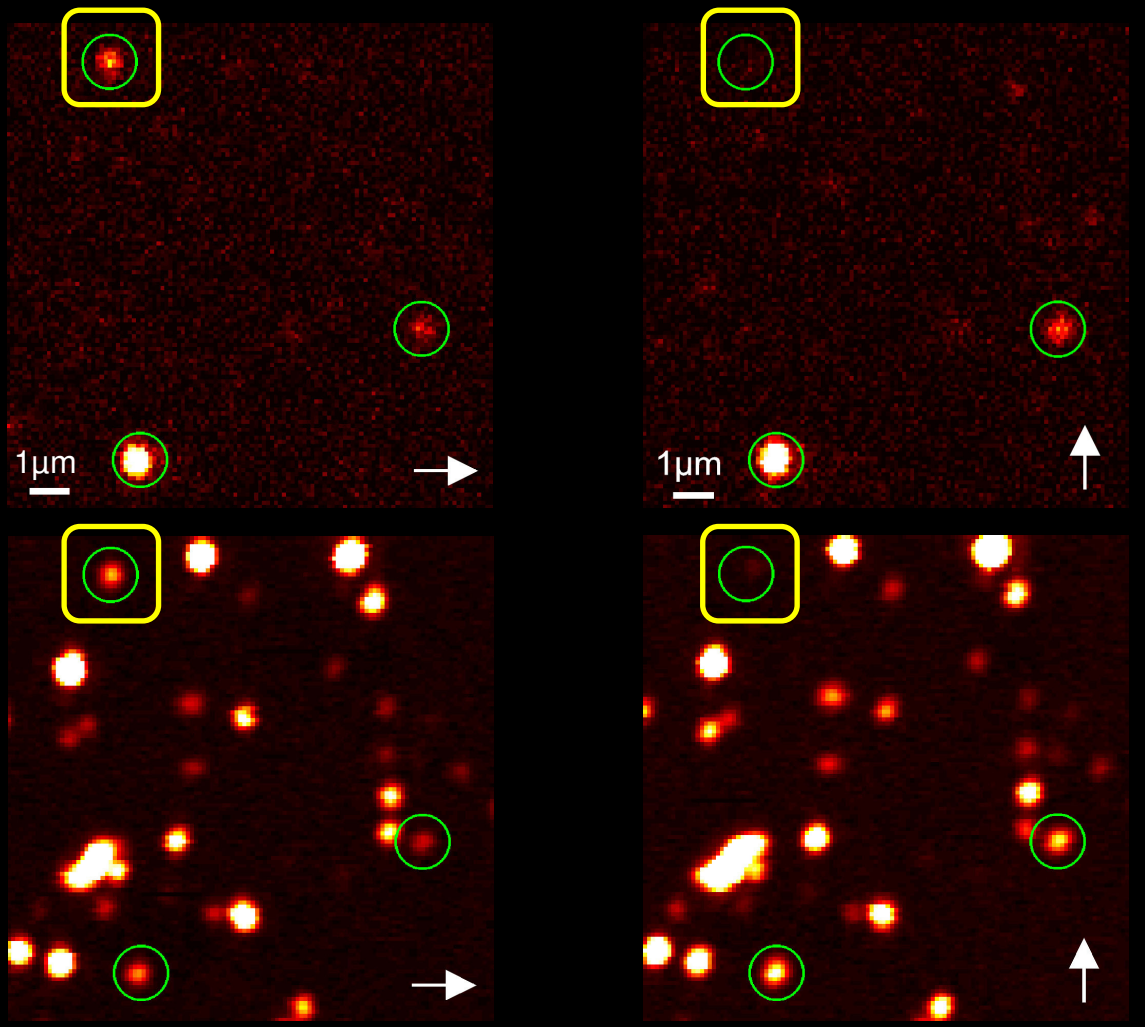
Photothermal Imaging of Individual SWNTs

Luminescence

Semiconducting SWNTs
With 850nm< λ_{11} <1050nm

Photothermal

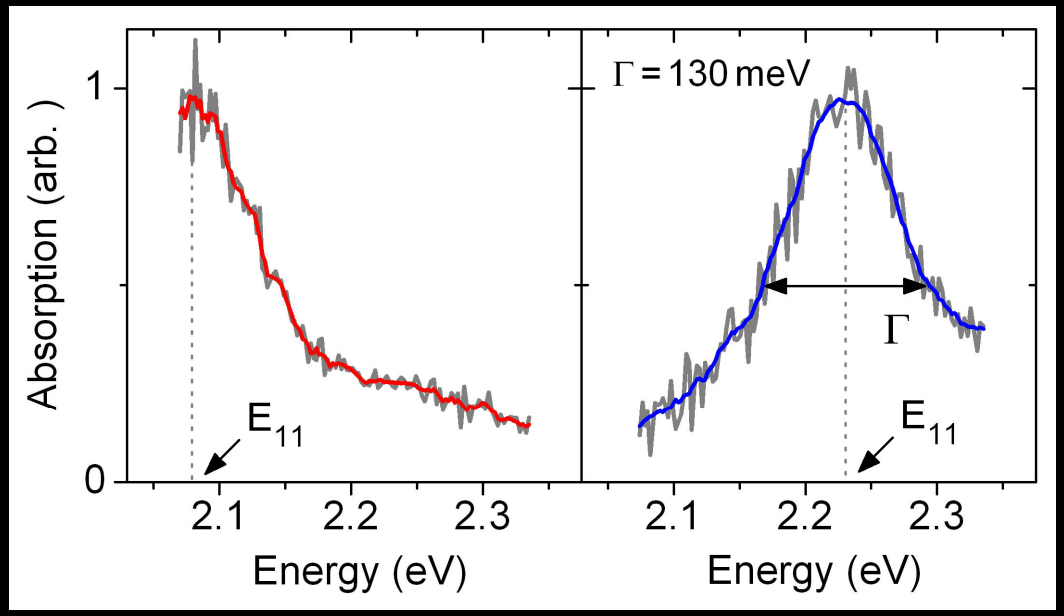
All Semiconducting
AND Metallic SWNTs



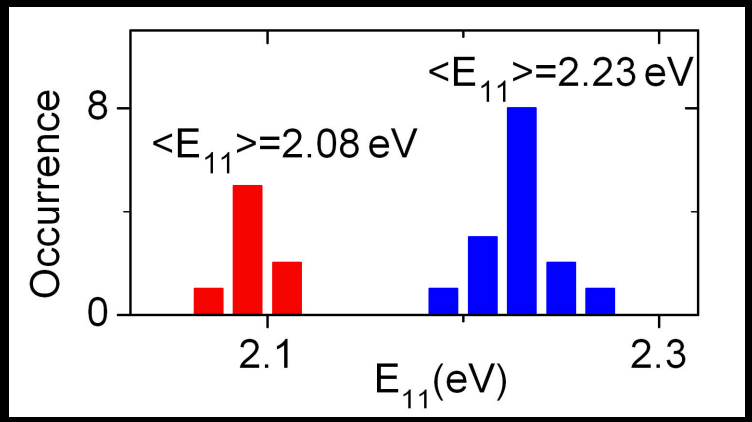
- Strong polarization dependence:

→ Maximum signal for $\mathbf{E}_{laser}$ // SWNT axis

Excitonic effects in metallic nanotubes



2 sub-populations



M_{11} transitions of metallic tubes

Berciaud, et al *Nano Lett.* **7** (2007) 1203

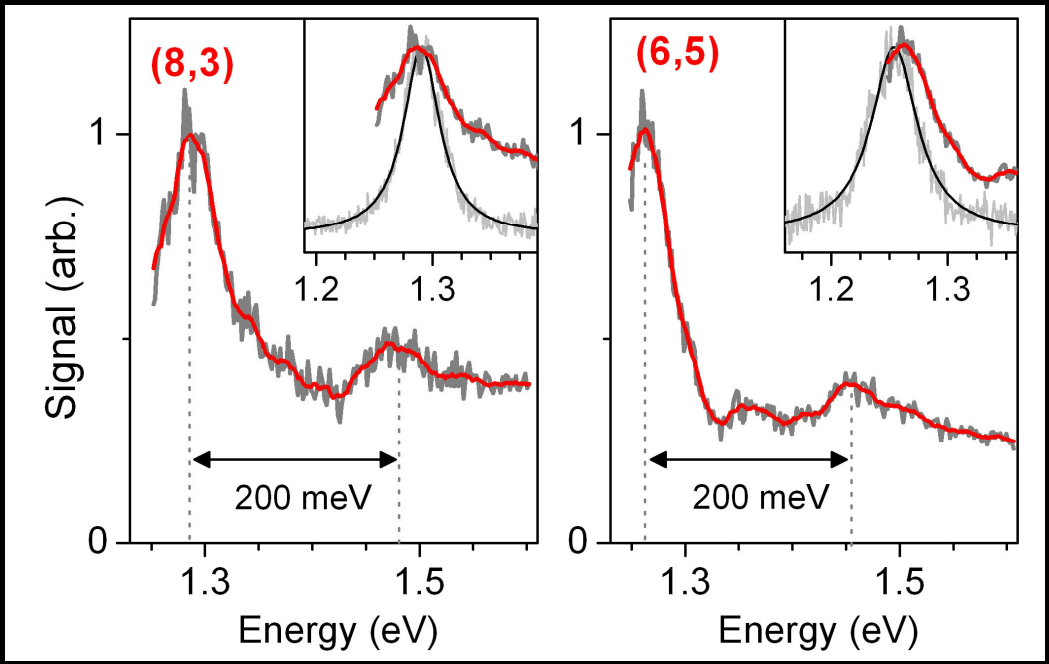
2n+m=27

2n+m=24

Symmetric absorption bands: a signature of excitonic effects in metallic tubes!

- *Theoretical predictions by Steven G. Louie et al.* *Nano Lett 7 (2007) 1626*
- *Demonstration by the Berkeley/Columbia groups on higher transition M_{22} of larger metallic nanotubes,* Wang et al *Phys. Rev. Lett.* **99**, 227401 (2007)

Semiconducting Nanotubes



- Absorption peaks :

→ S_{11} transitions of semiconductor tubes

→ very small Stokes shifts (~10 meV)

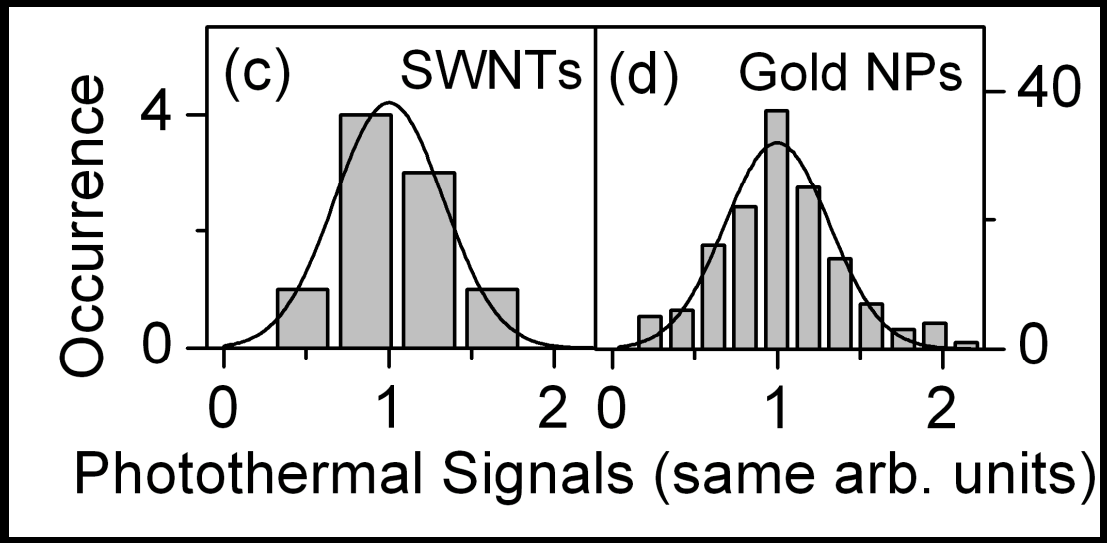
- Side Band at ~200 meV (*G* band)
- independent of chirality (n,m)

→ Exciton-Phonon bound state

Berciaud, et al *Nano Lett.* **7** (2007) 1203

Absorption cross-section

Calibration of absorption signals to well known gold nanoparticles (10nm)



σ_{22} ~ 90 nm^2/µm for (6,5) nanotubes

$(1 \pm 0.3) \times 10^{-17}$cm^2 per Carbon atom

Berciaud et al. Phys. Rev. Lett 2008

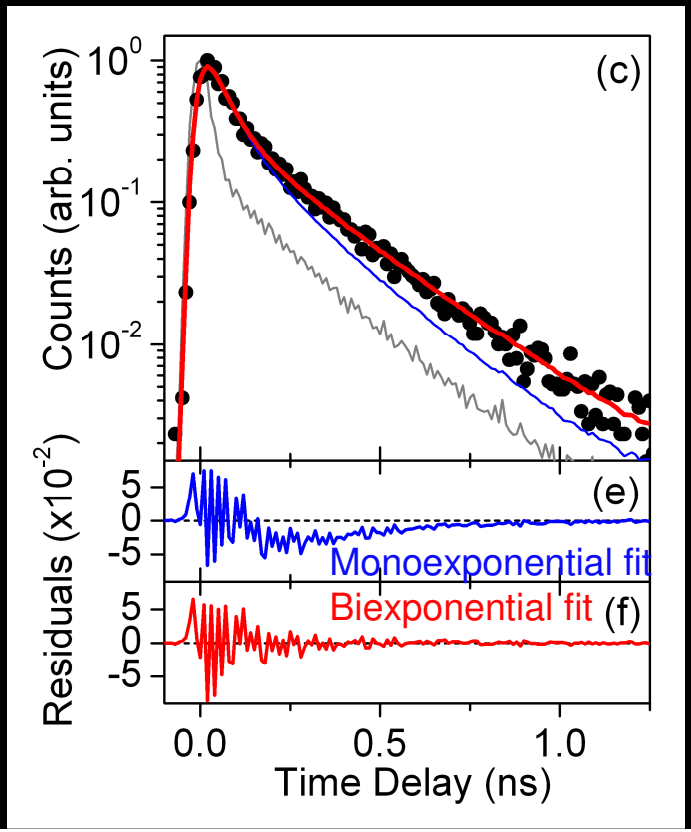
Up to one order of magnitude larger than previous bulk determinations (Islam et al, PRL, 2004)

Time resolved luminescence of *individual* SWNTs

The presence of *defects/surface interactions* affect the luminescence decay of:

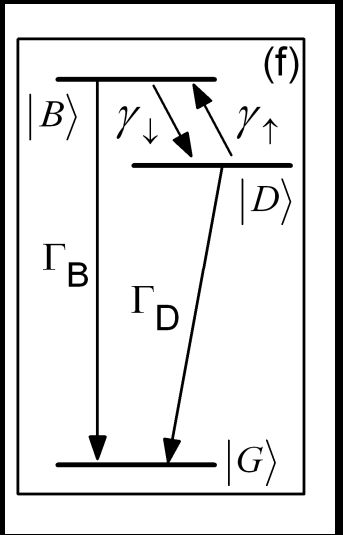
- nanotube suspensions (multi-exponential decays) *Hirori et al, PRL (2006), Berger et al, NanoLett. (2007)*
- isolated short nanotubes near a surface (short decays) *Hagen et al, PRL (2005), Gokus et al, APL (2008)*

Luminescence decays of high quality *individual* SWNTs (SDBS wrapped (6,5) tubes immobilized in agarose gels)



2 intrinsic decay times: 30-70 ps and 150-400 ps

- Excitonic level fine structure
- « Weak » coupling between bright and dark excitonic states



Berciaud et al. Phys. Rev. Lett 2008

Absorption cross-section of individual (6,5) SWNTs

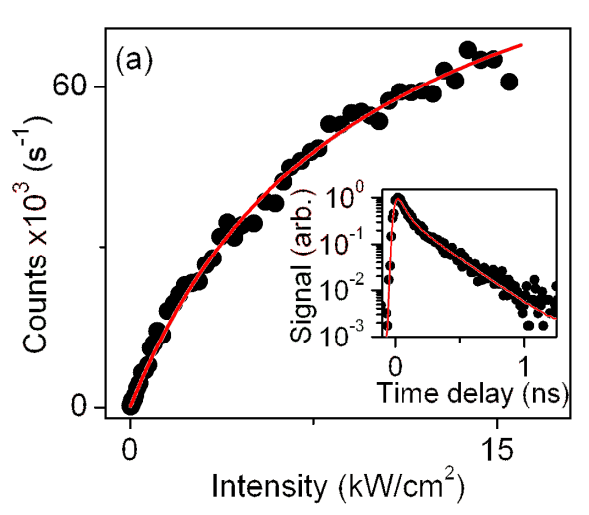
- Detected count rate in the *monoexcitonic regime* (1/Γx effective lifetime)

$$N = N_0 \frac{N_{abs}/\Gamma_X}{1 + N_{abs}/\Gamma_X}$$

- Rate of photons absorbed by a nanotube length of Λ

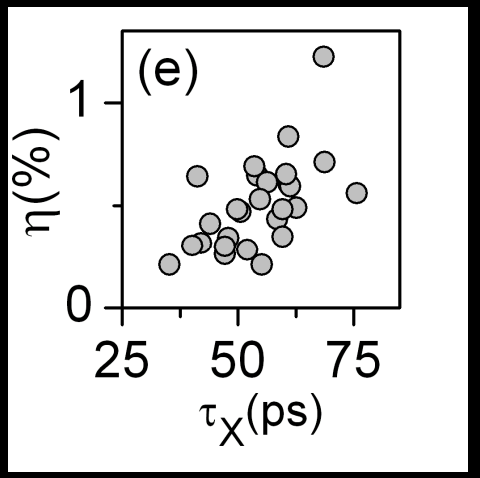
$$N_{abs} = \sigma_{22} \Lambda \frac{I}{\hbar\omega}$$

Measurement of the luminescence decay times + detected count rate as a function of cw excitation intensity in the monoexcitonic regime on each single SWNT



σ_{22} ~ 85 ± 30 nm²/µm
or
Comparable to the photothermal value!

Implications for the luminescence quantum yield:



Consistent with Lefebvre et al, Tsyboulski et al, etc…
after corrections for the absorption cross-section

Berciaud et al., PRL 2008

General Conclusion

- *Highly sensitive optical detection method*
  - Simple experimental setup
  - Detection of 1.4nm gold nanoparticles, CdSe nanocrystals, Carbon Nanotubes…
- *Quantitative spectroscopy at the single particle level*
  - Measure of the homogeneous linewidth
  - Intrinsic size effects in the SPR of gold nanoparticles
  - Photothermal absorption spectroscopy of CdSe Nanocrystals

    (biexciton and trion binding energies)
  - Characterization of semiconducting ***and*** metallic Carbon Nanotubes

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€ :

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