Photothermal Imaging and Absorption Spectroscopy of Individual Nano-objects:

Metallic Nanoparticles, Semiconductor Nanocrystals, Carbon Nanotubes

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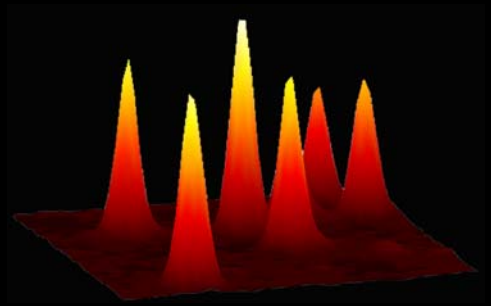

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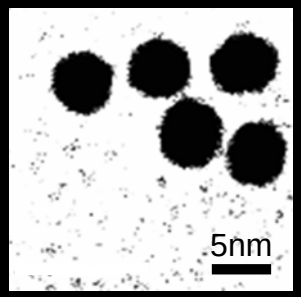
Scientific Context

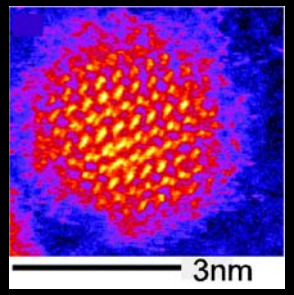
- *Nano-objects*

  → Dimensions between atomic scale and bulk

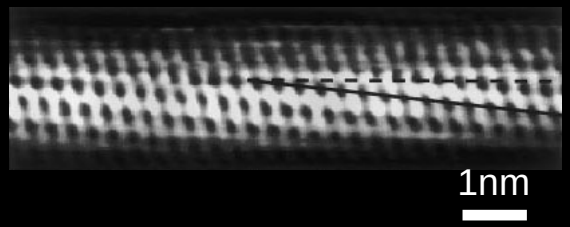
  Metallic nanoparticles, Semiconductor Nanocrystals, Carbon nanotubes, etc…



Gold NPs



CdSe NCs



Carbon Nanotubes

- *Size dependent physical properties*

  → Fundamental studies

  → Technological applications (material sciences, electronics, photonics, biotechnology, etc…)

TEM image of a single CdSe Nanocrystal : Mc Bride *et al.* Nano. Lett. **4**, 1279 (2004)

STM image of a single carbon nanotube : Wildöer *et al.* Nature **391**, 59 (1998)

Optical detection of individual nano-objects (1)

- *Far Field Optical Detection Techniques*
  - → Non-invasive measurement
  - → Large variety of spectroscopic tools
- *Individual Nano-Objects*
  - → No ensemble averaging
  - → Statistical distributions
  - → Single quantum systems
  - → *Nanoprobes* of their local environment
  - → …

Optical detection of individual nano-objects (2)

- *Luminescence microscopy:*

→ *Luminescent nano-objects only!*

→ Bleaching (eg. Fluorescent Dyes)

→ Blinking (eg. Semiconductor Nanocrystals)

- *Rayleigh scattering intensity:*

→ Particle Size

→ Scattering Background

How to detect as small as possible, non-luminescent nano-objects ?

- Scattering decreases faster with size than absorption
- eg. : spherical nanoparticles : $\sigma_{abs} \sim D^3$, *whereas* $\sigma_{scatt} \sim D^6$

→ ***Absorption based detection of individual nano-objects…***

Imaging Individual Nano-Objects *via* Absorption

- *Good candidates for absorption-based detection*

→ 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*)

→ Very low luminescence yield

→ Absorbed energy converted into heat

Detection of this photothermal effect…

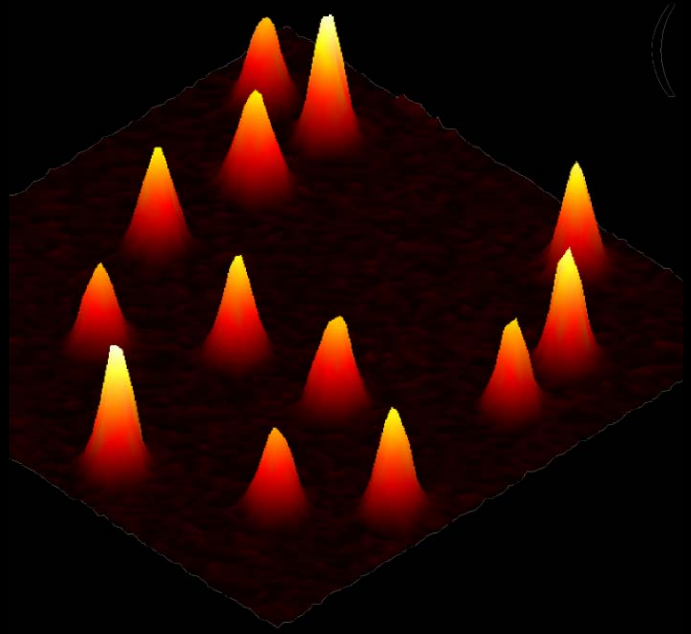
D. Boyer *et al*., *Science* **297**, *1160* (2002)

Outline

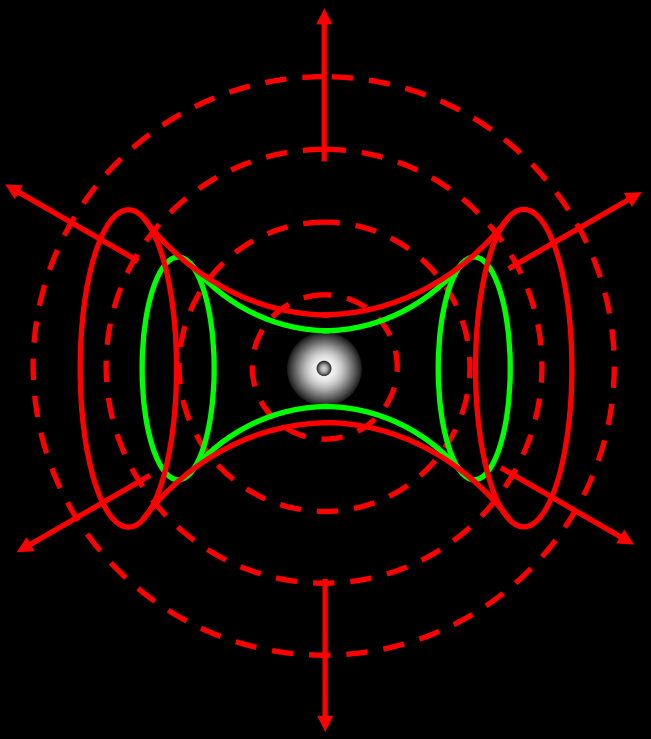
- Photothermal heterodyne imaging
  - → Principle and performances
  - → Characterization of the photothermal signal
- Applications to absorption spectroscopy
  - → Surface Plasmon Resonance of individual gold nanoparticles
  - → Individual semiconductor nanocrystals
  - → Individual carbon nanotubes

Coll. P. Poulin (CRPP, Bordeaux) et R. B. Weisman (Rice University, USA)

Photothermal Heterodyne Imaging of Individual Nano-objects



Photothermal Heterodyne Imaging (PHI)



Modulated Heating Beam (at Ω)

Nanoparticle: Heat point source

Refractive index profile

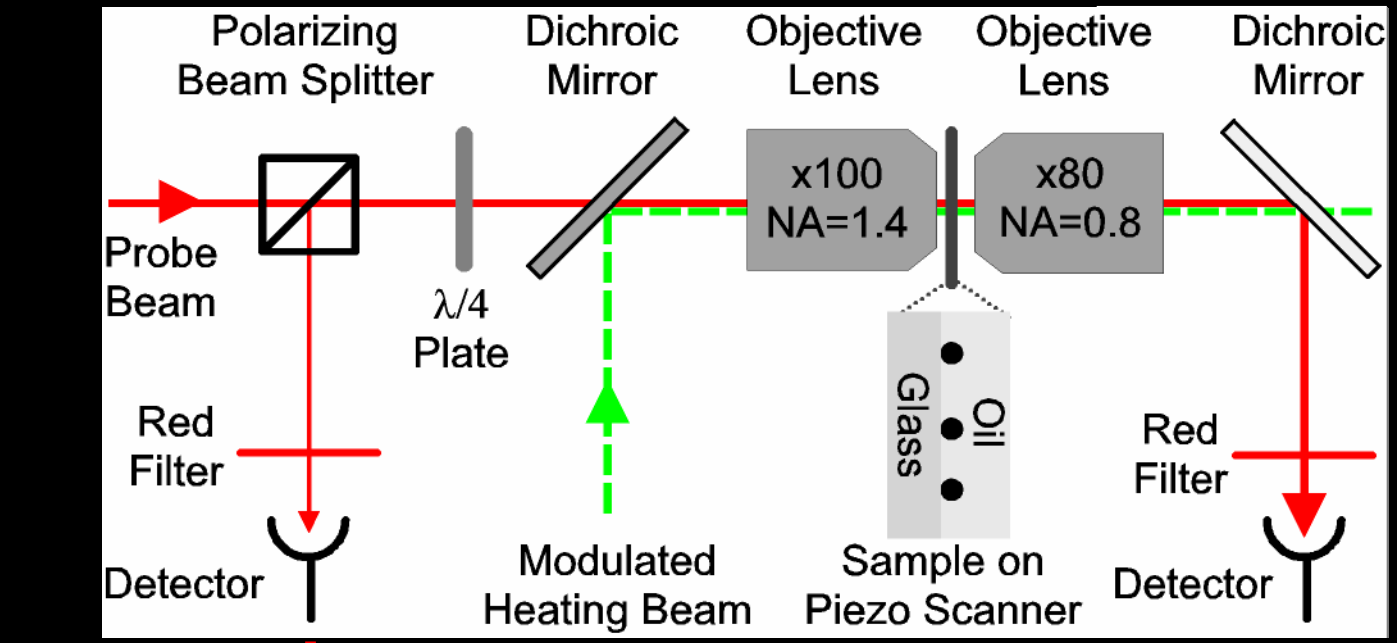
characteristic size r_{th}

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



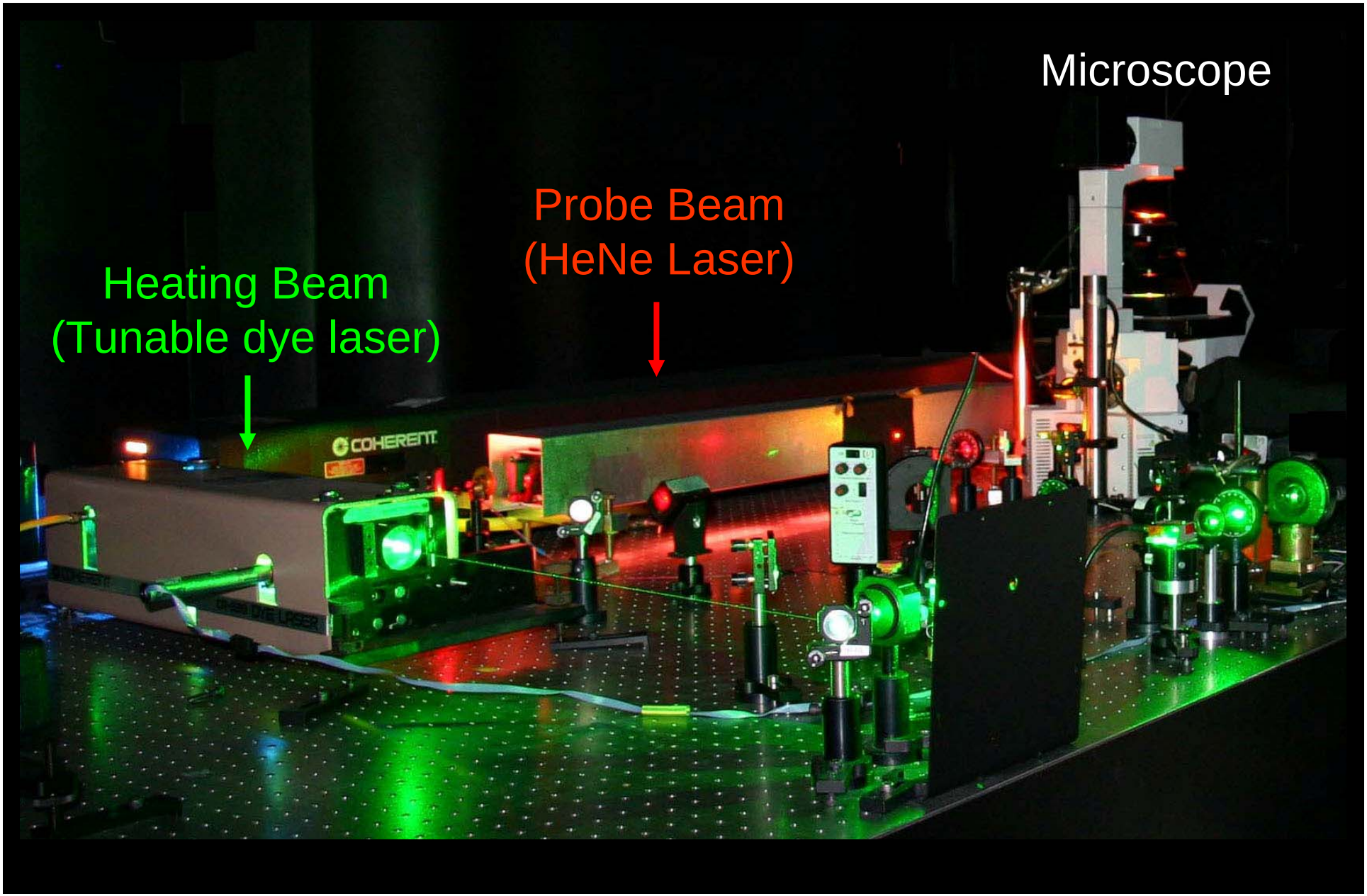
Beatnote at Ω extracted by lock-in detection

Backward signal

Beatnote at Ω extracted by lock-in detection

Forward signal

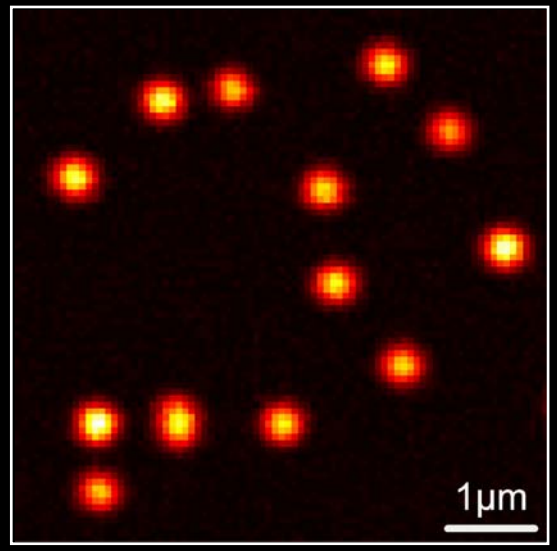
Experimental Setup

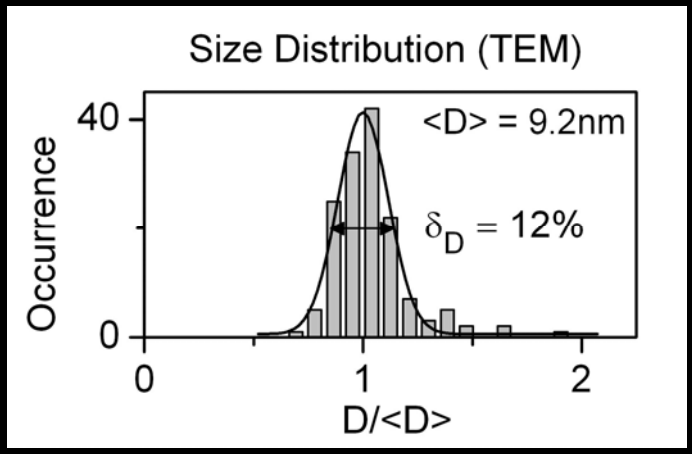


Imaging of 10 nm Individual Gold Nanoparticles

Backward

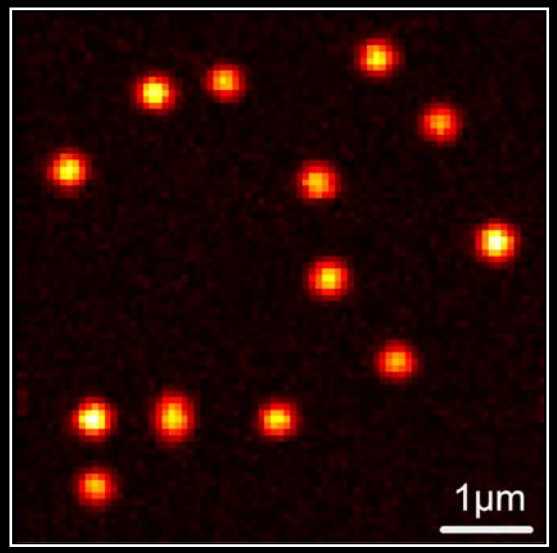
I_{heat} = 500 kW/cm²
Δt = 10 ms/pixel

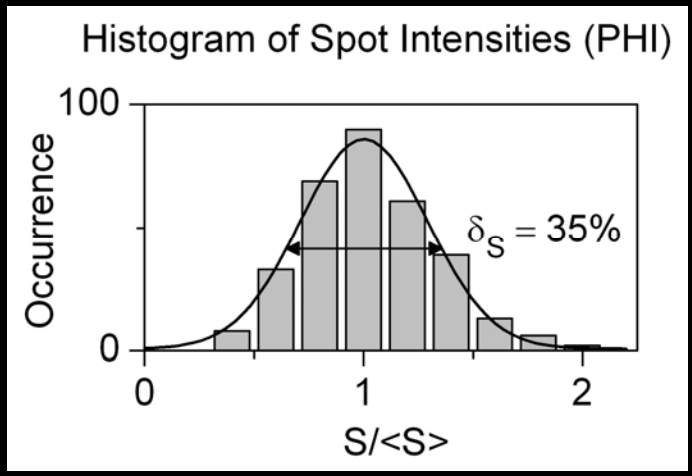




Forward

I_{heat} = 500 kW/cm²
Δt = 10 ms/pixel

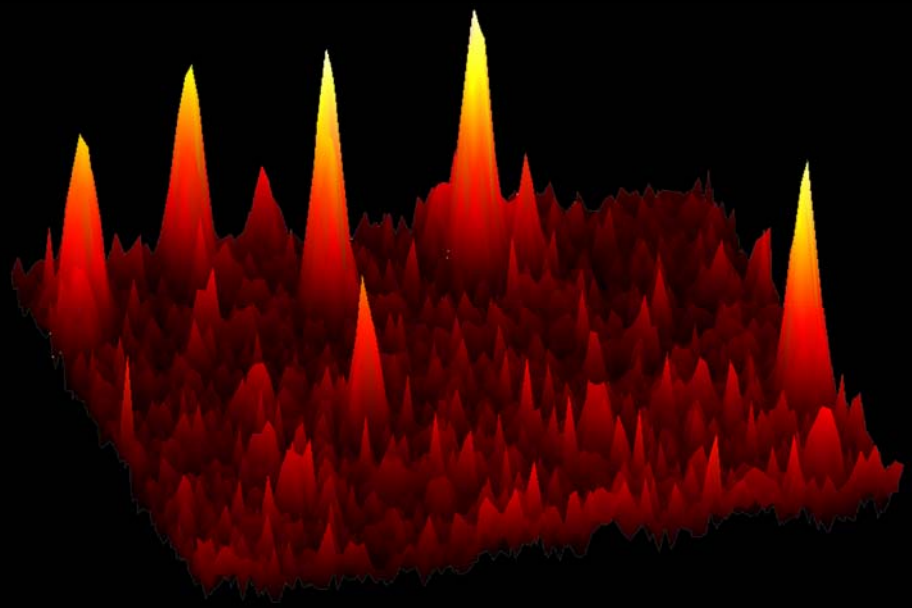




→ ***Individual*** Nanoparticles

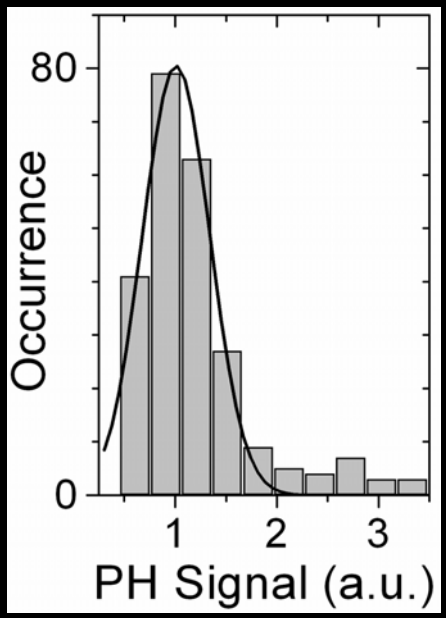
Optical Detection of Individual 1.4 *nm* Gold Nanoparticles

- Sample of 1.4*nm* gold nanoparticles (~70 atoms) embedded into a PVA matrix
- Nanoparticle absorption cross section $\sigma_{abs} \sim 10^{-15}\ cm^2$



Photothermal Heterodyne Image

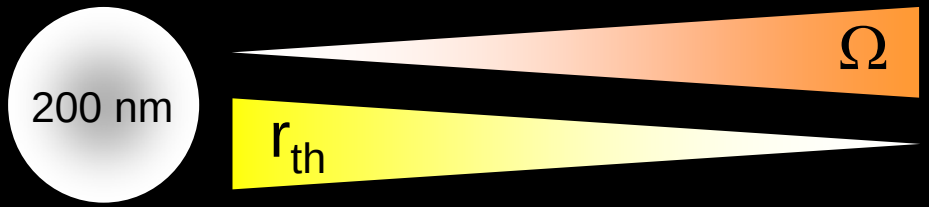
5 x 5 μm^2 (80 *nm* / pixel, 10 *ms* / pixel)



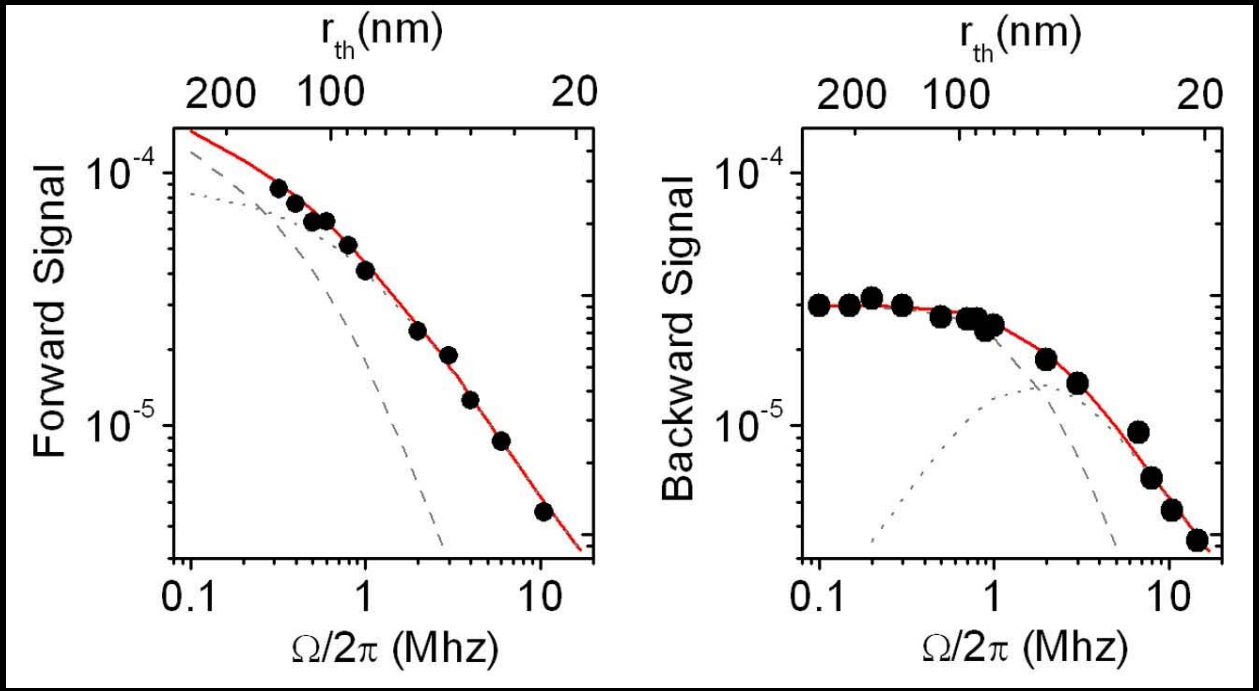
Unimodal Histogram of spot intensities

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

Signal vs Modulation Frequency



$$r_{th} = \sqrt{\frac{2D}{\Omega}}$$



$D = 2.10^{-8}\ m^2 s^{-1}$

Total Signal

In phase

In quadrature

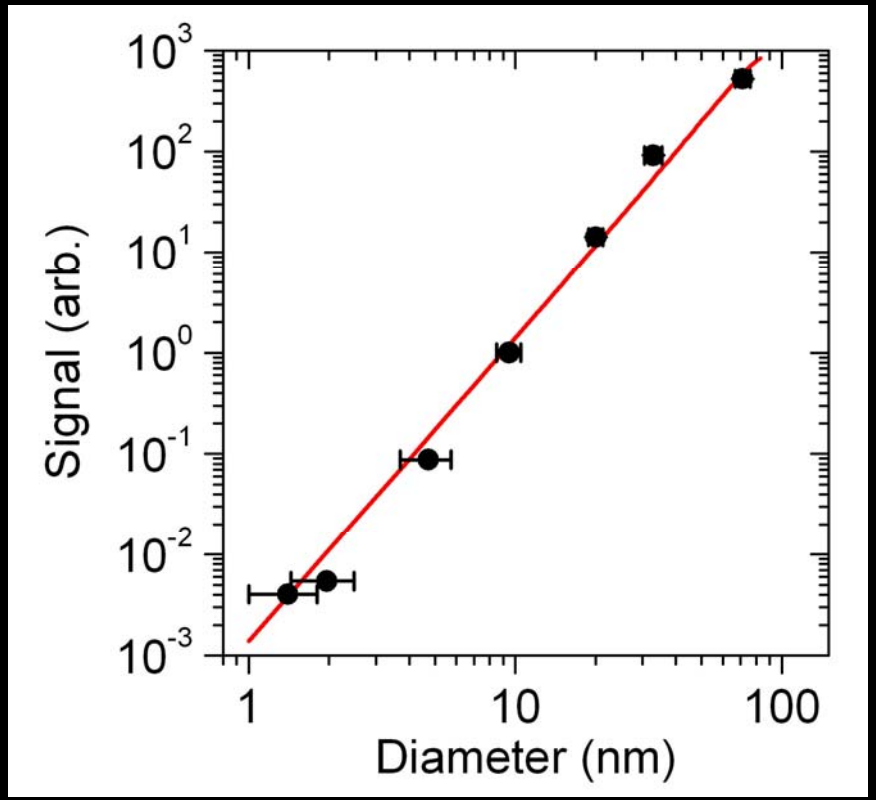
- "Low pass" behavior : cut-off for $r_{th} = \lambda/(2\pi n) \Rightarrow \Omega_c \sim 1$MHz
- For $r_{th} > r_{thc}$: Forward scattering dominates

S. Berciaud *et al., Phys. Rev. B* **73**, 045424 (2006)

Size Dependence of the Absorption Cross Section of Gold Nanoparticles

- Samples containing nanoparticles of two different (successive) sizes
- Bimodal distributions for the histogram of signal amplitude

- *Here : 2 nm & 5 nm $\Rightarrow$ x 15 in signal*



- Third-order law of σ_{abs} vs Diameter

$\rightarrow$ In agreement with Mie theory

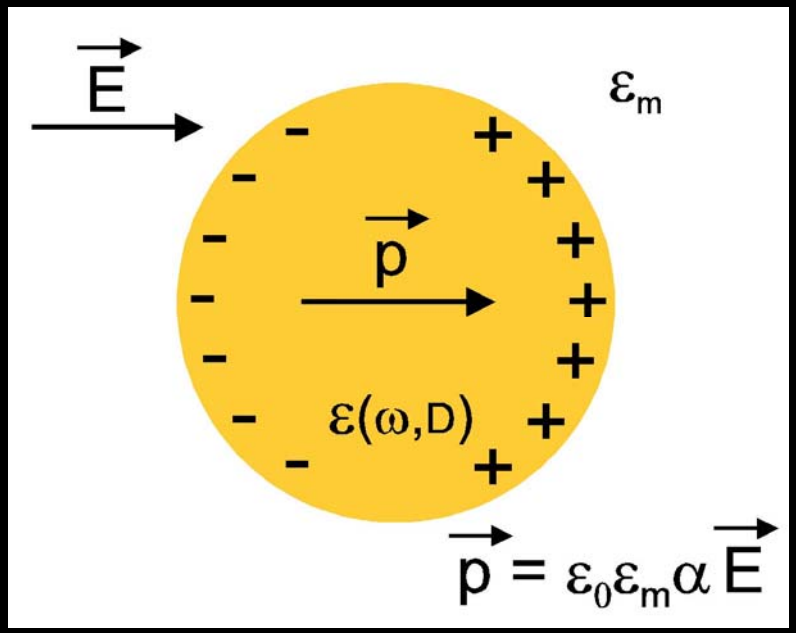
Surface Plasmon Resonance Spectroscopy of Individual Gold Nanoparticles

Lycurgus Cup (IVth century AD)
(British Museum)

SPR in the Dipolar Approximation

- Dipolar approximation :

→ Valid for D << $\lambda_{excitation}$



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

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

- Restoring Force
- *Resonant Oscillation* for $\varepsilon_1 + 2\,\varepsilon_m = 0$
- Achievable in metals, where $\varepsilon_1 < 0$ in the optical domain

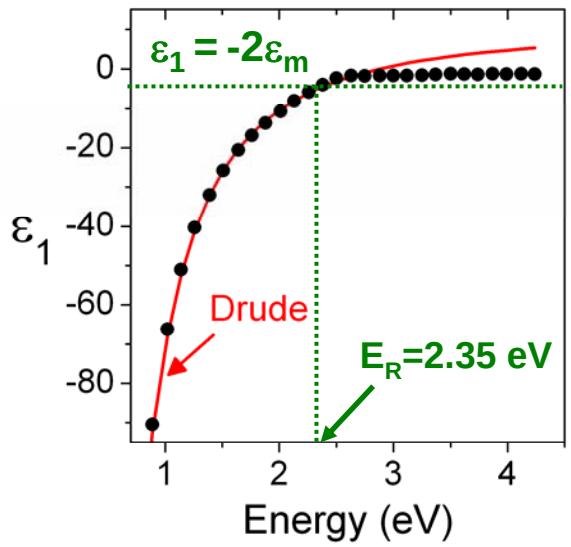
SPR in Gold Nanoparticles

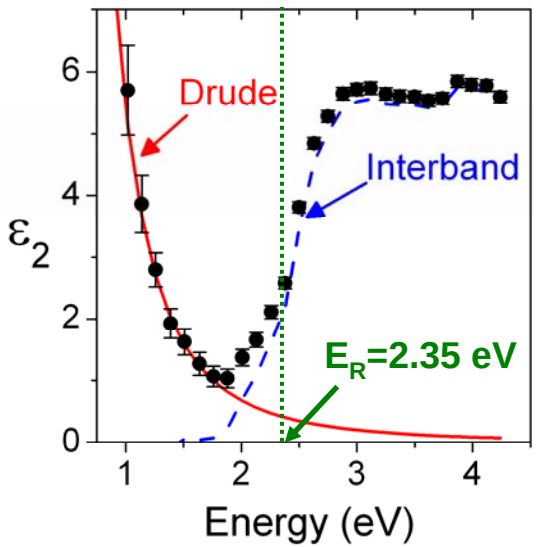
$$\varepsilon(\omega) = \varepsilon_{DC} - \frac{\Omega_p^2}{\omega(\omega + i\gamma_0)} + \varepsilon_{IB}(\omega)$$

Modified Drude Term Interband Term

$\gamma_0 = \tau^{-1}$: electron collision rate

$L_e = v_f \tau$: electron mean free path





$\varepsilon_1 \leftrightarrow$ SPR position $\varepsilon_2 \leftrightarrow$ SPR linewidth

Interband transitions
$\Rightarrow$ additional damping
SPR linewidth > γ_0

Johnson & Christy, Phys. Rev. B **6**, 4370 (1972)

Size Effects

Extrinsic

• For D > 20 nm

→ Red shift of the RPS ("dynamic depolarization")

→ Broadening (radiation damping and contribution from higher order modes)

Intrinsic

• Electron mean free path in bulk gold : $L_e \sim 14\ nm$

→ For D < L_e : Size dependent term in the dielectric constant of a gold NP

$$\gamma(D) = \gamma_0 + \frac{2Av_F}{D} \Rightarrow \varepsilon(\omega, D) \approx \varepsilon_{bulk}(\omega) + i\frac{\Omega_p^2}{\omega^3}\frac{2Av_f}{D}$$

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

• Individual particles ➡ Measure of the homogeneous width of the SPR

Examples of Measured SPR Spectra

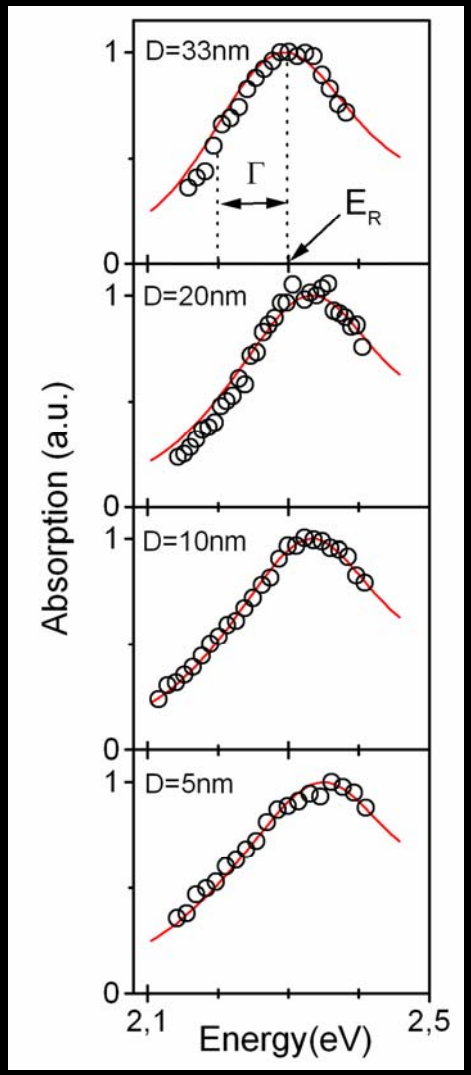
Diameter

33 *nm*

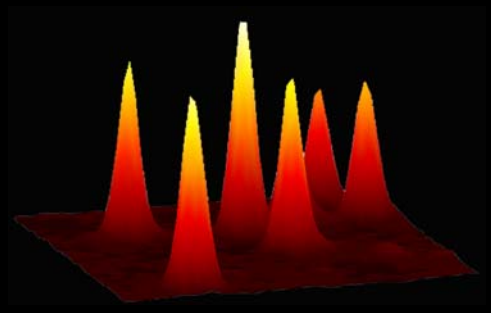
20 *nm*

10 *nm*

5 *nm*



- Red shift
  with *increasing* size (*D* > 20 *nm*)
- Broadening
  with *decreasing* size (*D* < 10 *nm*)
- E_R : Resonant Peak Energy
- Γ : SPR half width



Single 5nm gold nanoparticles

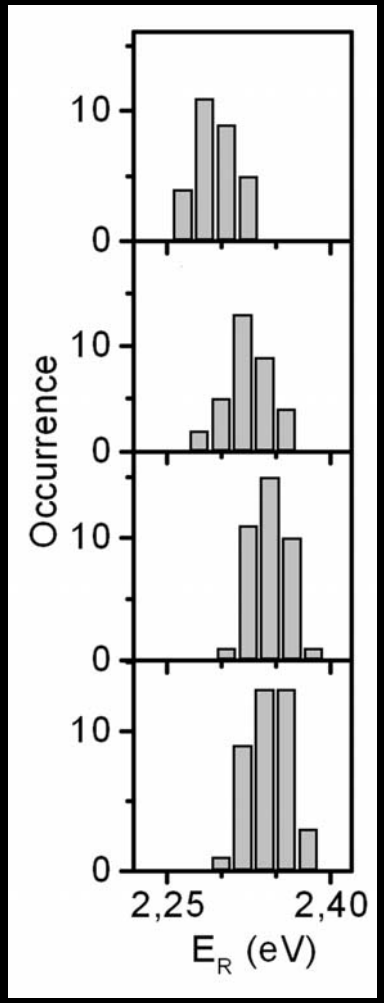
Size Dependence of E_R

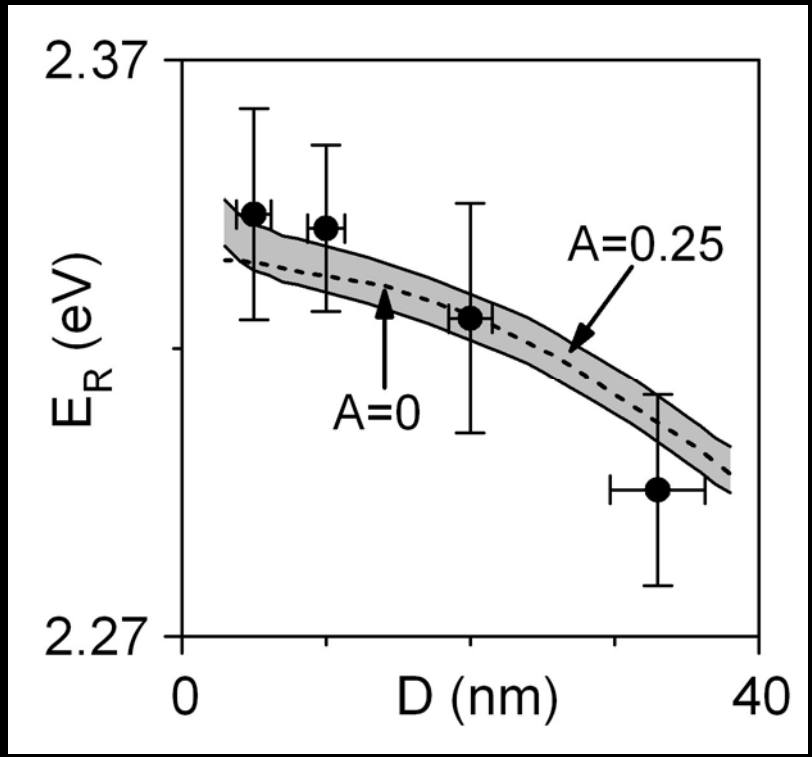
33 *nm*

20 *nm*

10 *nm*

5 *nm*





- Good agreement with Mie theory
- No change of E_R due to intrinsic size effects

Dispersion in E_R due to the slight ellipticity of our NPs

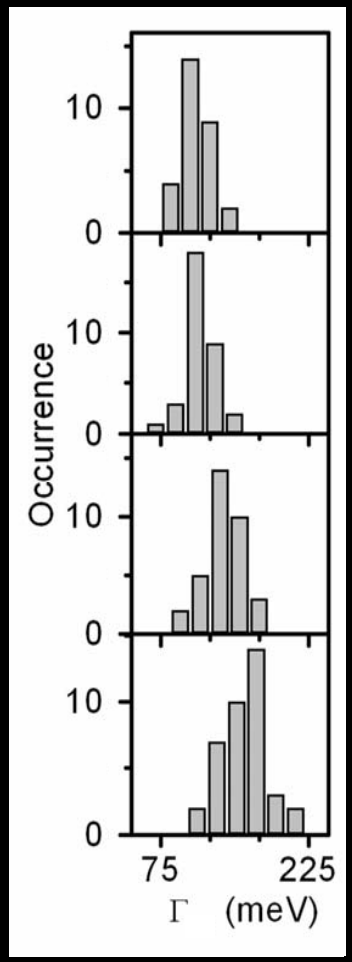
Size Dependence of Γ
Observation of Intrinsic Size Effects

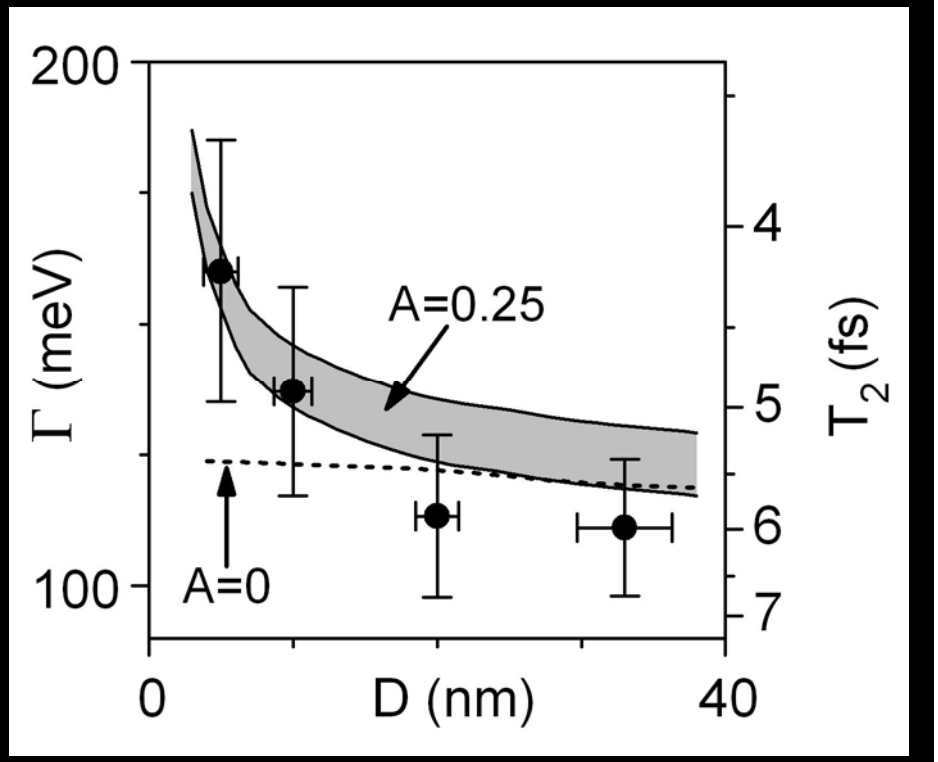
33 *nm*

20 *nm*

10 *nm*

5 *nm*





• Larger Dispersion in Γ for small sizes

→ Heterogeneities in interface decay channels

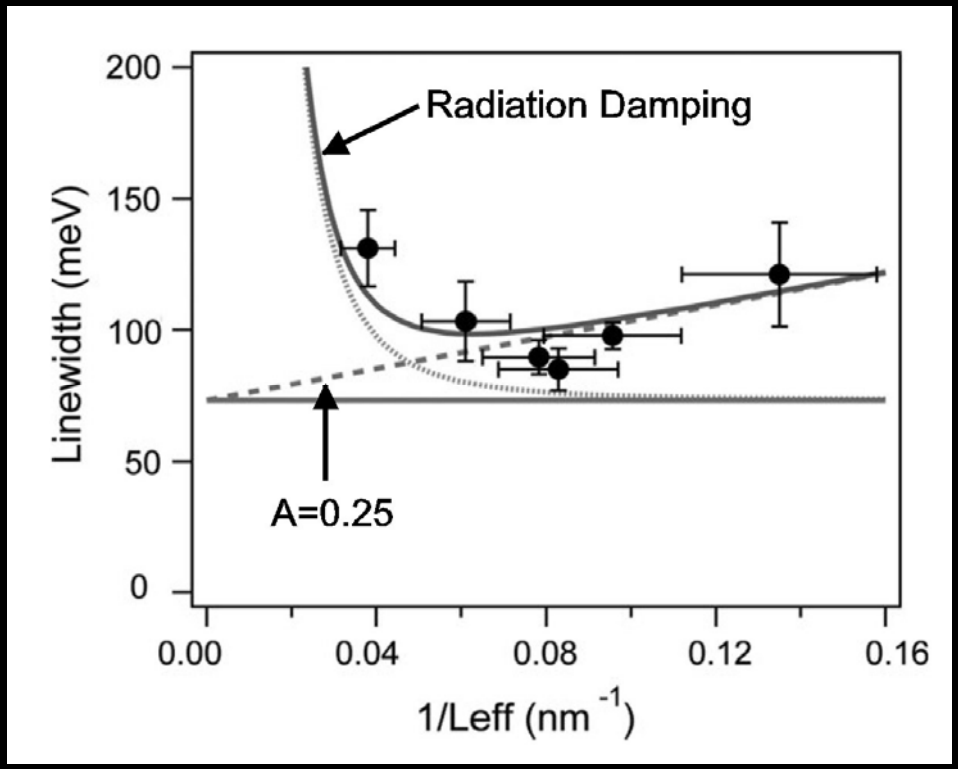
→ Small NPs more sensitive

• Good agreement with Mie theory for A=0.25

• Broadening due to additional surface damping

S. Berciaud *et al.*, *Nano Lett.* **5**, 515 (2005)

Recent related results

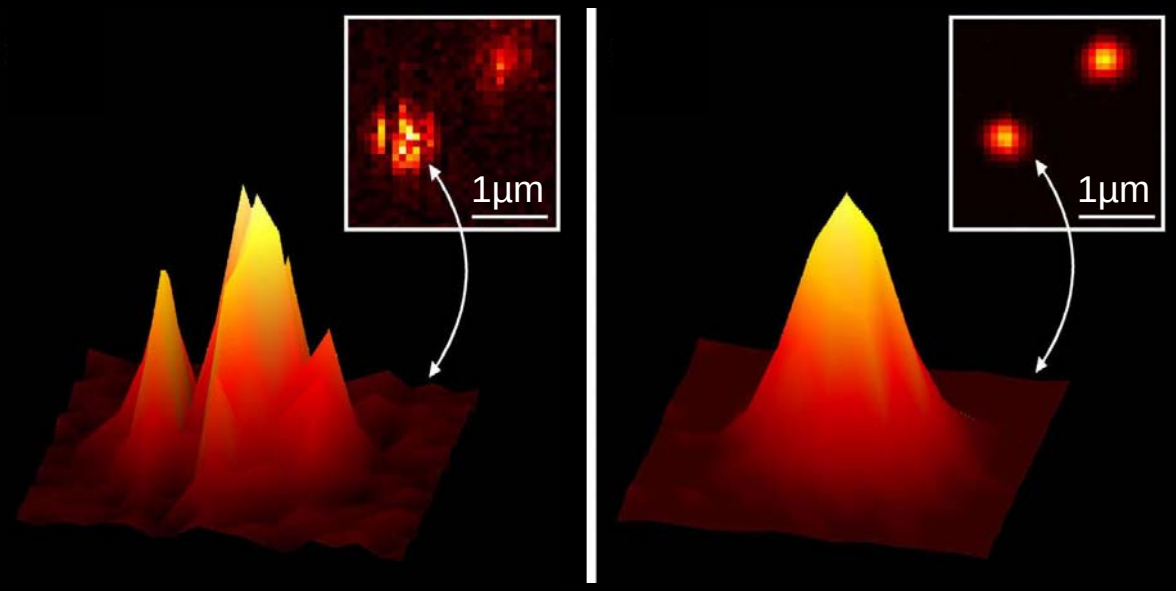


- Recent experiments on Gold nanorods (13nm< D_{eq} <40nm)

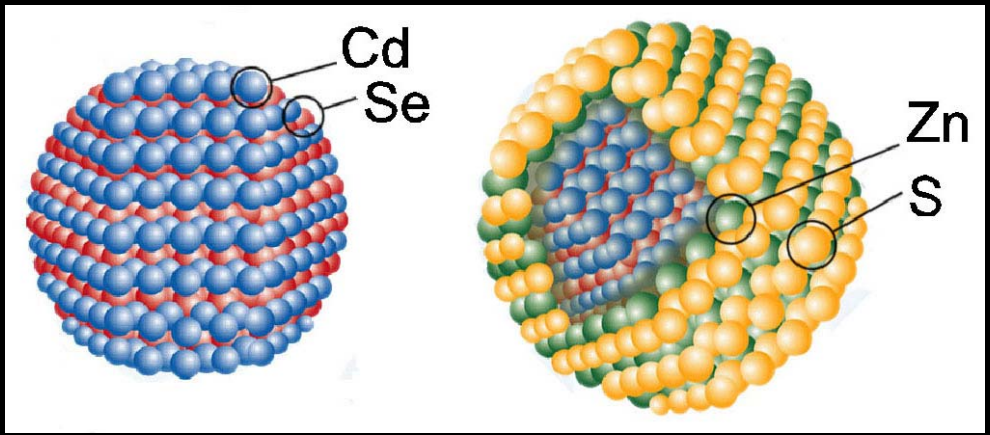
  $\rightarrow$ Same size parameter : A=0.25

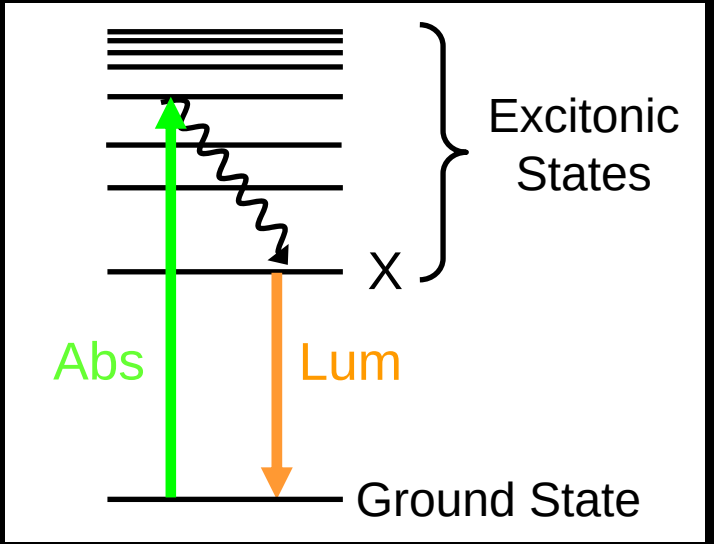
Novo *et al. Phys. Chem. Chem. Phys.* **8**, 3540 (2006)

Imaging & Absorption Spectroscopy of Individual Semiconductor Nanocrysals



CdSe/ZnS Semiconductor Nanocrystals





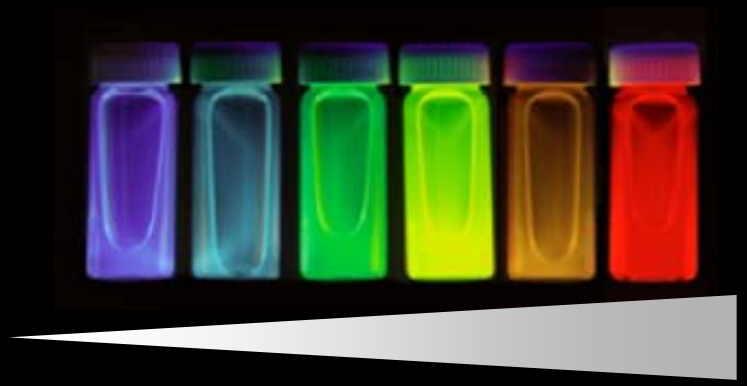
- Colloidal Nanocrystals
- Strong carrier confinement

→ Atom-like level structure

- Size dependent optical properties

→ Tunable Absorption & Emission

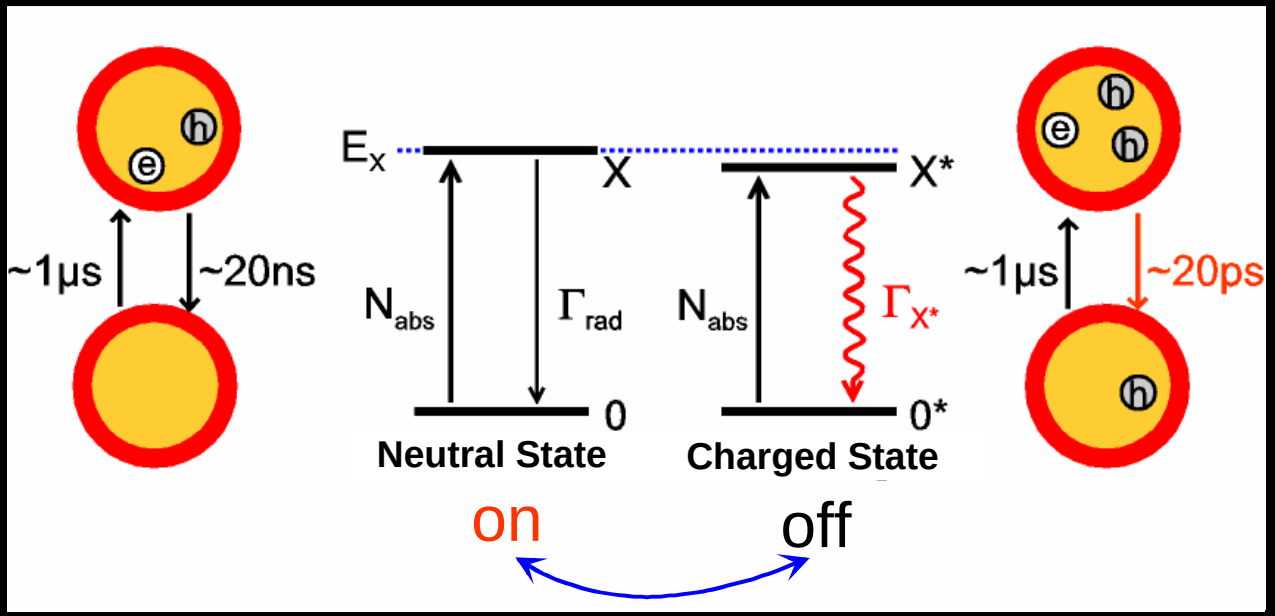
Excitation @ ~400nm



Photophysics in the *low* excitation regime

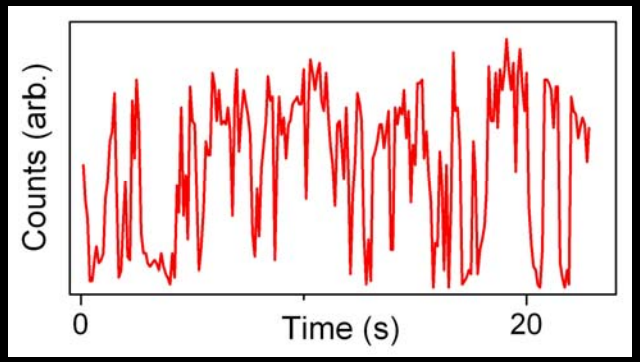
Low excitation: $N_{abs} \sim 1\ \mu s^{-1} << \Gamma_{rad} = (1/20)\ ns^{-1}$
→ Monoexcitonic regime

Exciton



Trion
Non-radiative recombination

Luminescent Nanocrystals
" Blinking "



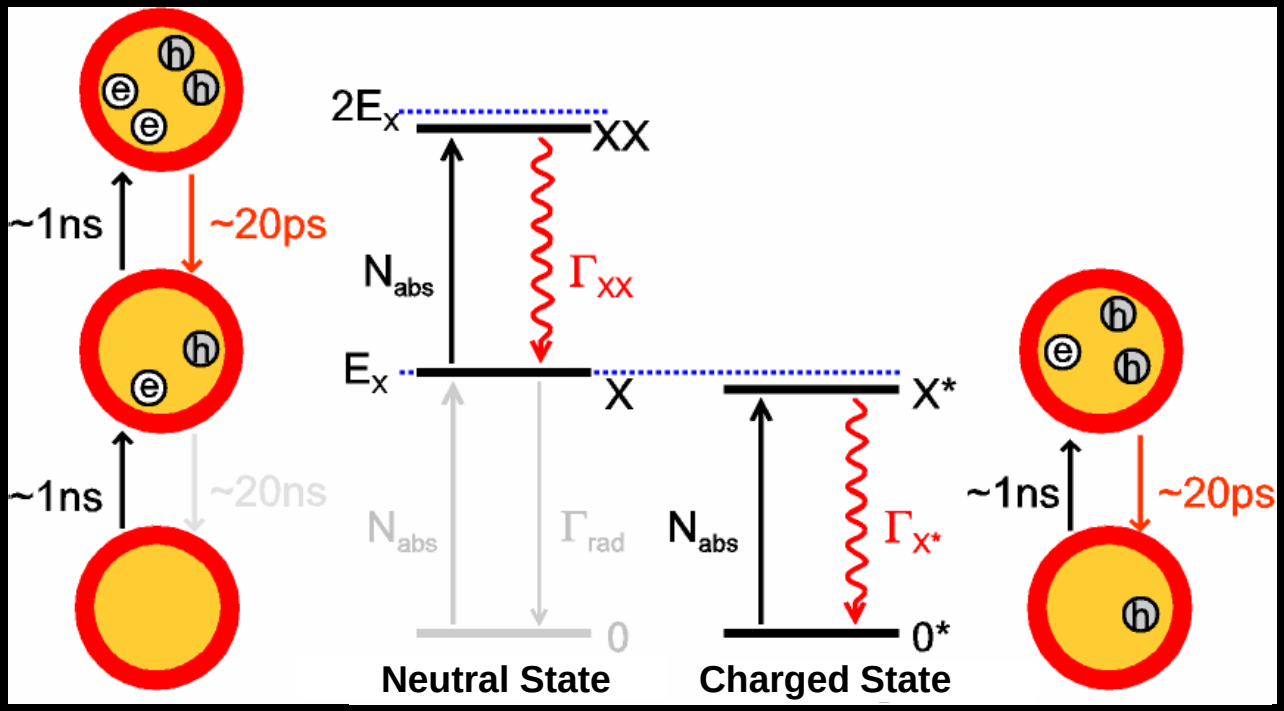
Photophysics in the *high* excitation regime

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

→ Formation of *biexcitons*

Biexciton

Exciton



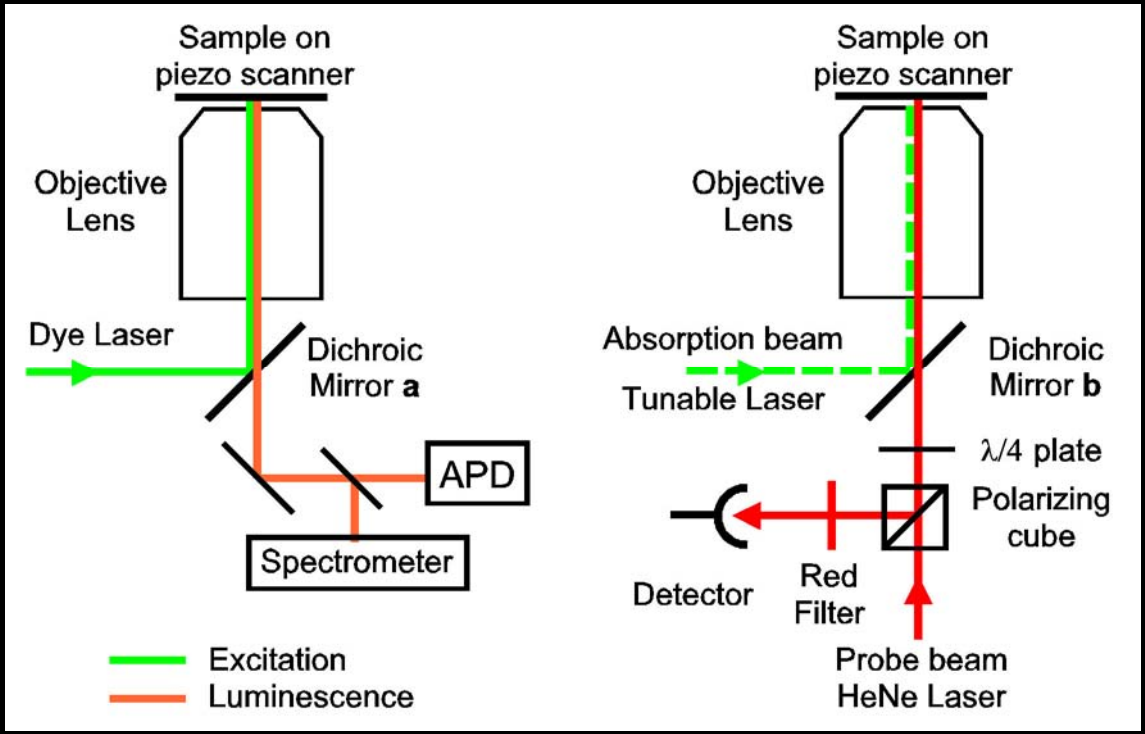
Trion

Γ_{rad} << Γ_{XX}, Γ_{X^*} → Very weak luminescence:

High absorption & rapid non-radiative relaxation via Auger processes

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

Experimental Setup



Confocal luminescence microscopy

& Photothermal heterodyne detection

*Absorption **and** emission spectroscopy of a same nanocrystal*

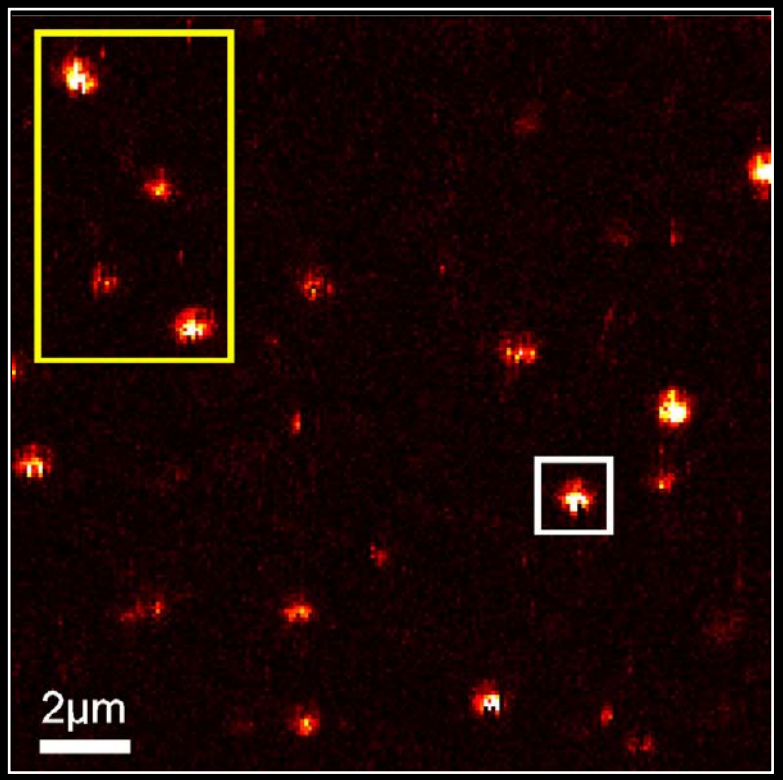
Photothermal Imaging of CdSe/ZnS Semiconductor Nanocrystals

Luminescence

N_{abs}~1photon / µs

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

Low excitation regime

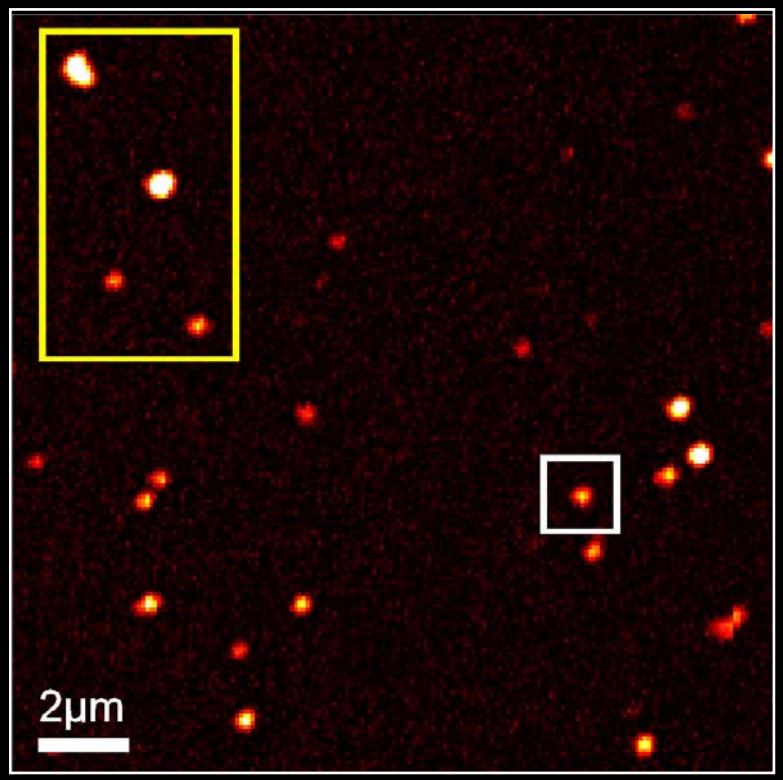


Photothermal

N_{abs}~1 photon / ns

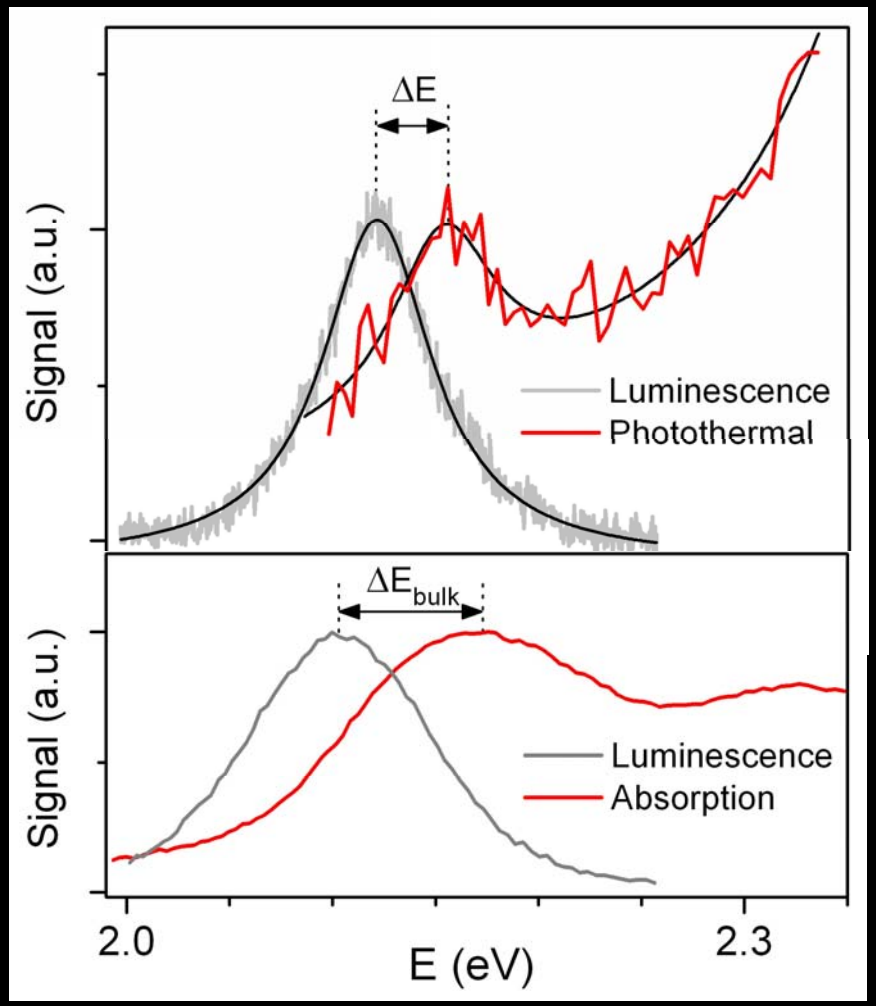
σ_{abs}~10^{-15} cm^2, τ_{relax}~20 ps !

High excitation regime



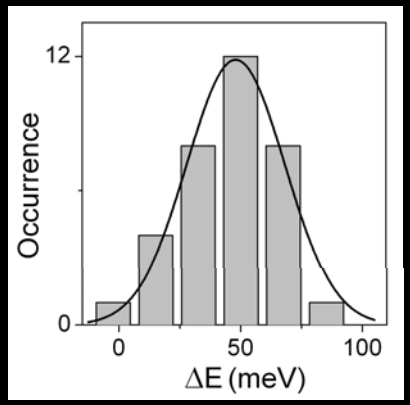
Spectroscopy

Luminescence: *Low excitation regime*: $N_{abs} << \Gamma_{rad}$



- *Single Nanocrystal*

→ Absorption in the ***high excitation*** regime



<ΔE>=50 meV

- *Ensemble Measurement*

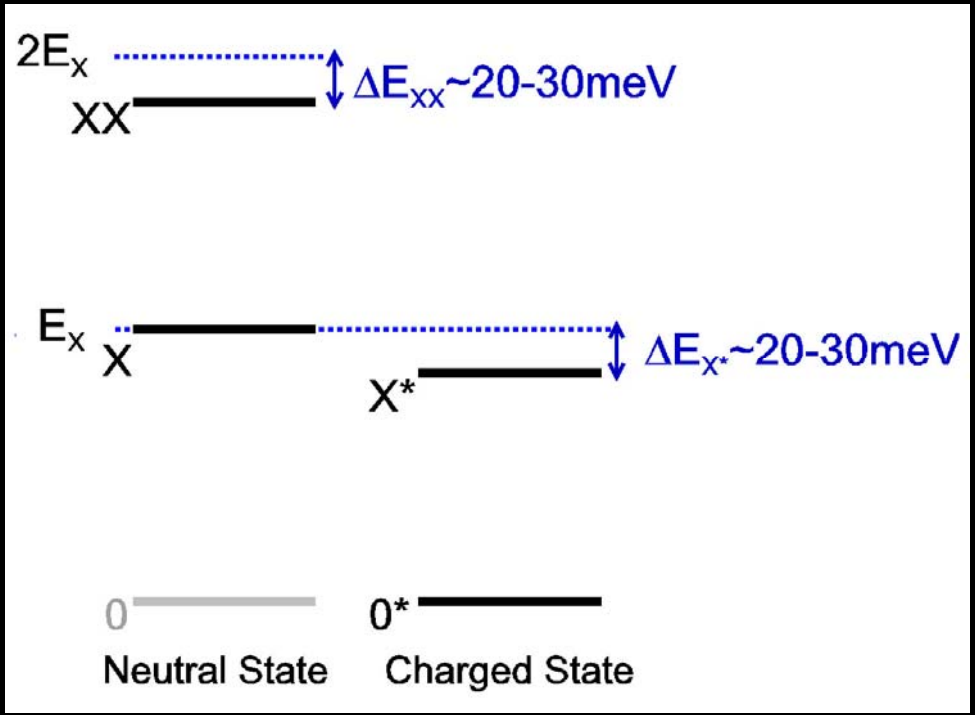
→ Absorption in the ***low excitation*** regime

ΔE_{bulk}=70 meV

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

Interpretation

Biexciton and Trion binding energies



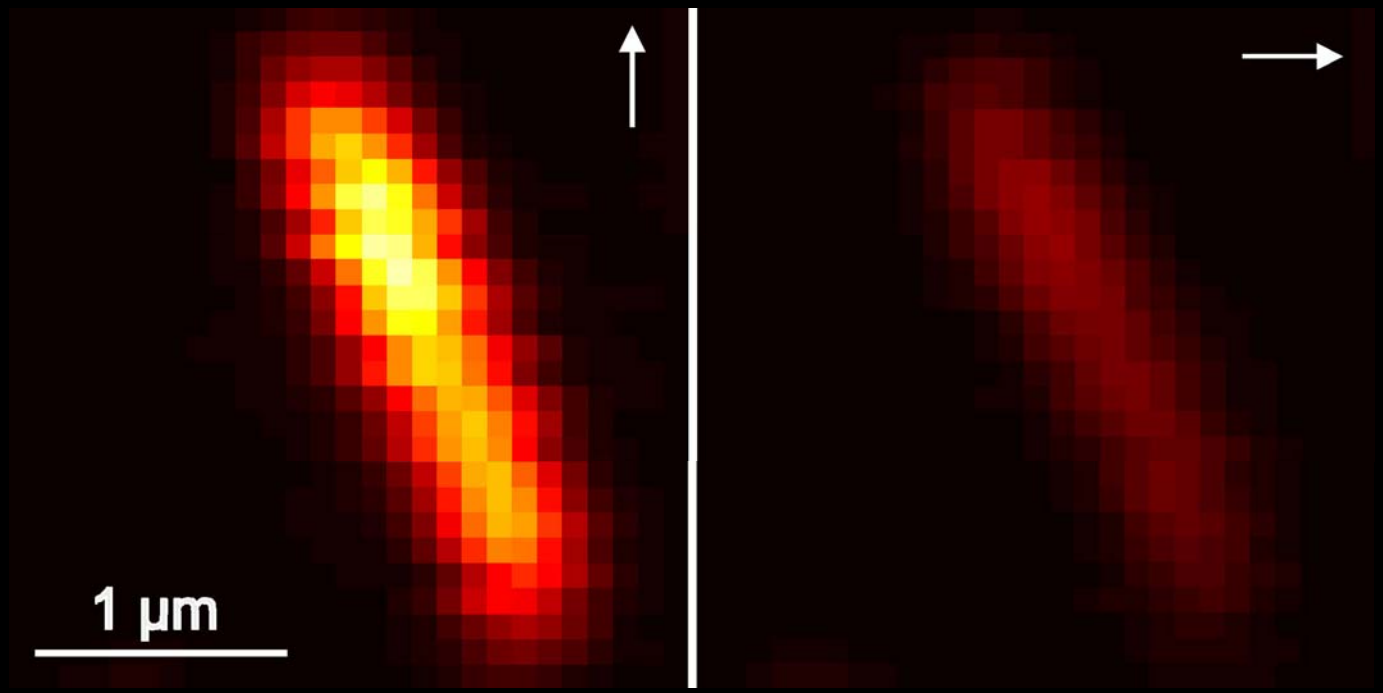
ΔE_{bulk} - $<\Delta E>$= 20 meV

Close to ΔE_{XX} and ΔE_{X^*}

Photothermal absorption peak due to XX $\leftrightarrow$ X et X* $\leftrightarrow$ 0* transitions

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

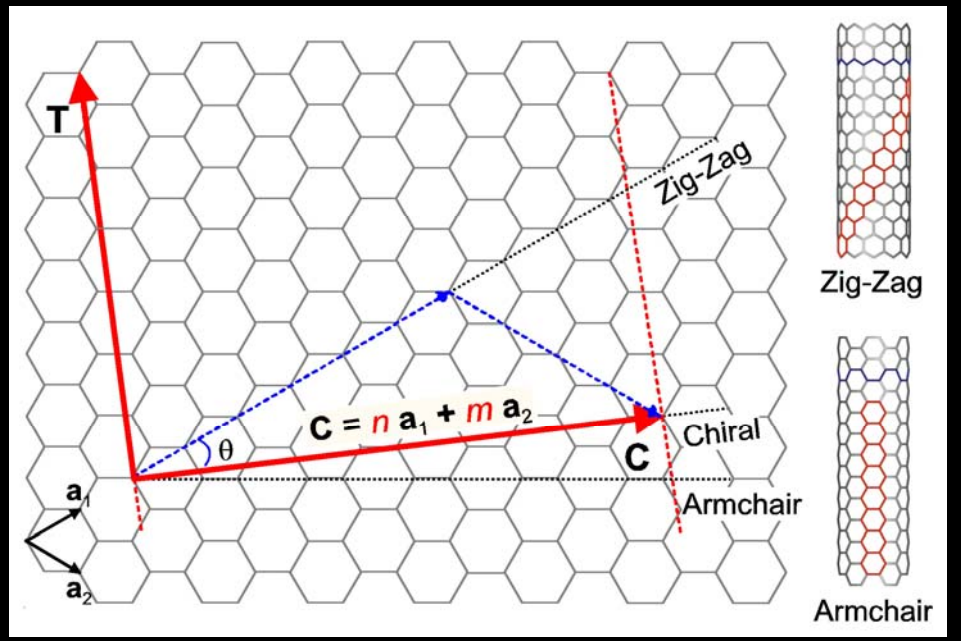
- Diameter ~1nm, length up to ~1cm

→ 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

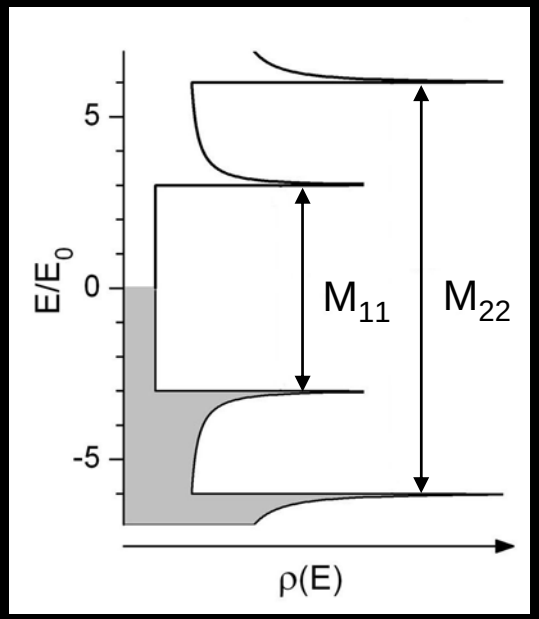


Example : (6,4) semiconducting tube

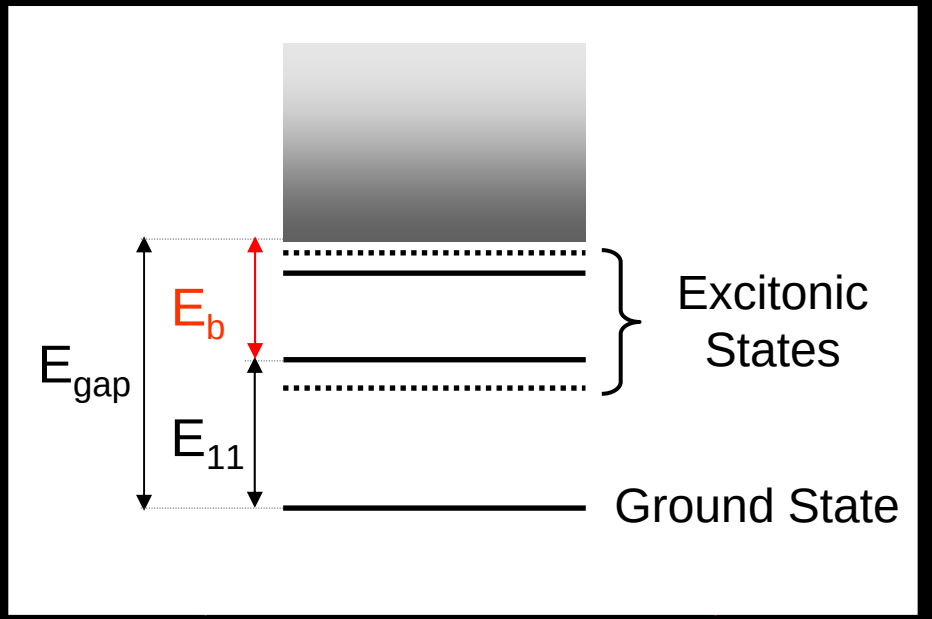
Optical Properties

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

- *Metallic* SWNTs



- *Semiconducting* SWNTs:



What about optical transitions?

- One electron picture

→ *Band to band* transitions

- ~~Strong *e-h* interactions~~

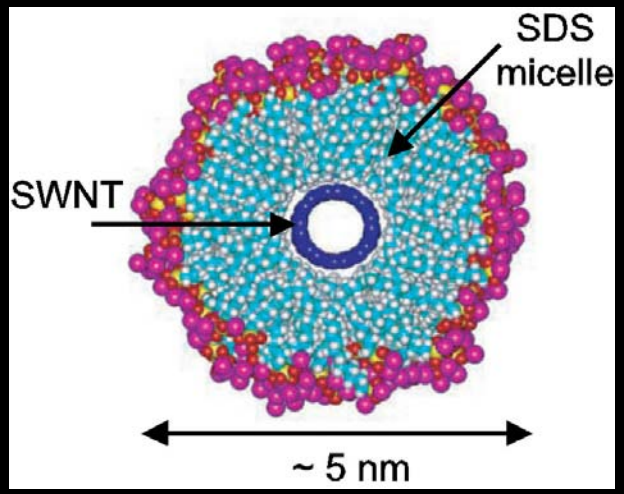
→ Excitonic effects

→ Transition energies < Band Gap

Optical Studies

- Nanotubes tend to aggregate into bundles

→ Isolation of single SWNTs in surfactant micelles

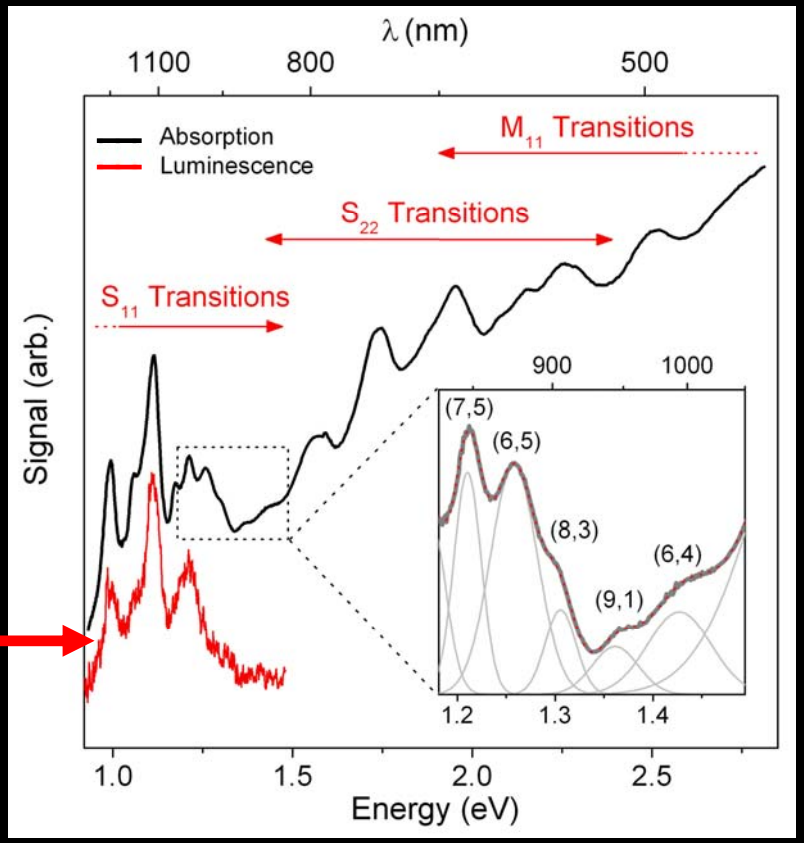


- Ensemble spectra not affected by tube-tube interactions
- Observation of luminescence from Semiconducting tubes

O'Connell *et al,* Science **297**, 593 (2002)

Ensemble Spectra

- *Absorption Spectra dominated by sharp resonances (M_{ii} , S_{ii})*



Luminescence from S_{11} transitions

(n,m) assignment from Bachillo *et al,* Science **298**, 2363 (2002)

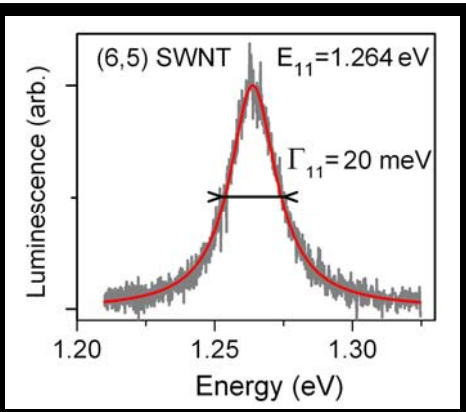
- Chirality dependent optical properties
- Broad distribution of transition energies

→ Single nanotube detection methods…

Optical Characterization of Individual SWNTs

- Luminescence Spectroscopy

→ Limited to individual Semiconducting SWNTs

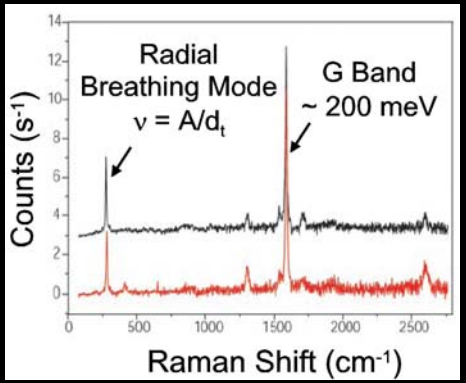


- Raman Scattering Spectroscopy

→ Semiconducting & Metallic SWNTs

→ Very weak signal

→ Indirect method (fitting procedure)

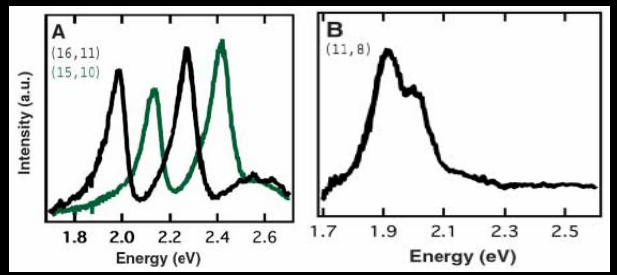


Hartschuh *et al.* Science **301**, 1354 (2003)

- Rayleigh Scattering Spectroscopy

→ Semiconducting (A) & Metallic (B) SWNTs

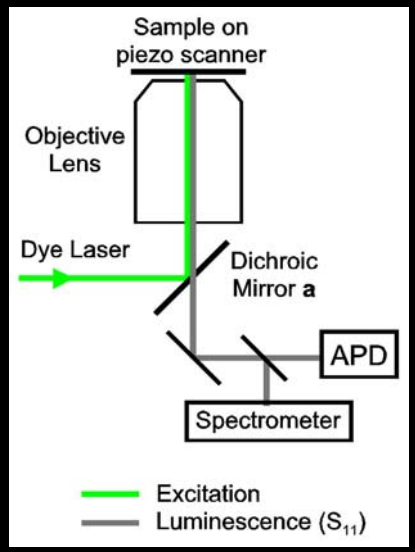
→ Limited to long, large diameter, *suspended* tubes

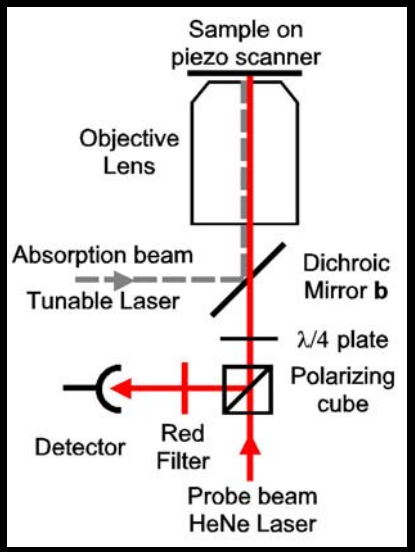


Sfeir *et al.* Science **312**, 554, (2006)

What about Photothermal Detection ?

- High Absorption (~10^{-18} cm^2 *per* carbon atom)
- Fast non-radiative relaxation :
  - *Metallic* nanotubes :
    - → Sub-picosecond non-radiative relaxation
  - *Semiconducting* nanotubes :
    - → First excitonic state lifetime from 1 to 100 ps
    - → Low luminescence yield (~10^{-3})



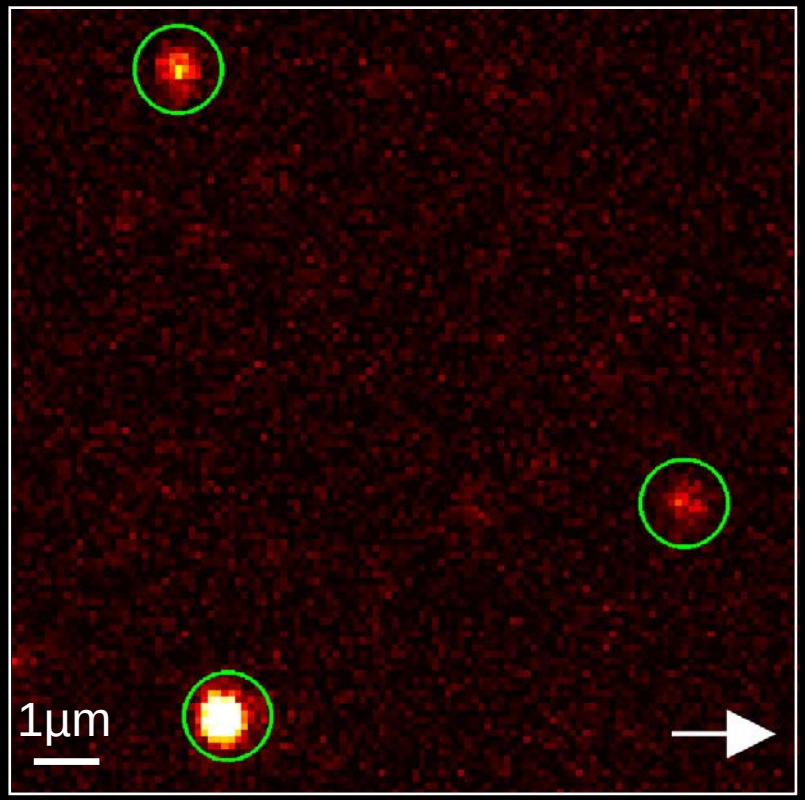


Luminescence : (S_{11} transitions) Photothermal : (S_{11}, M_{11} transitions)

Photothermal Imaging of Individual SWNTs

Luminescence

I_{exc} = 20 kW/cm^2

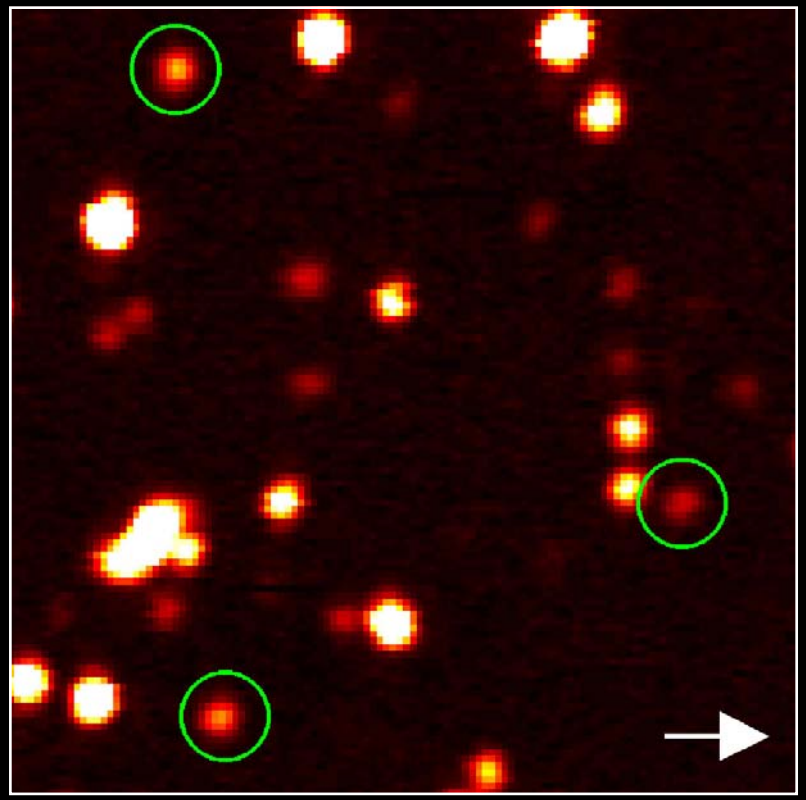


Semiconducting SWNTs

With 850nm< λ_{11} <1050nm

Photothermal

I_{heat} = 500 kW/cm^2

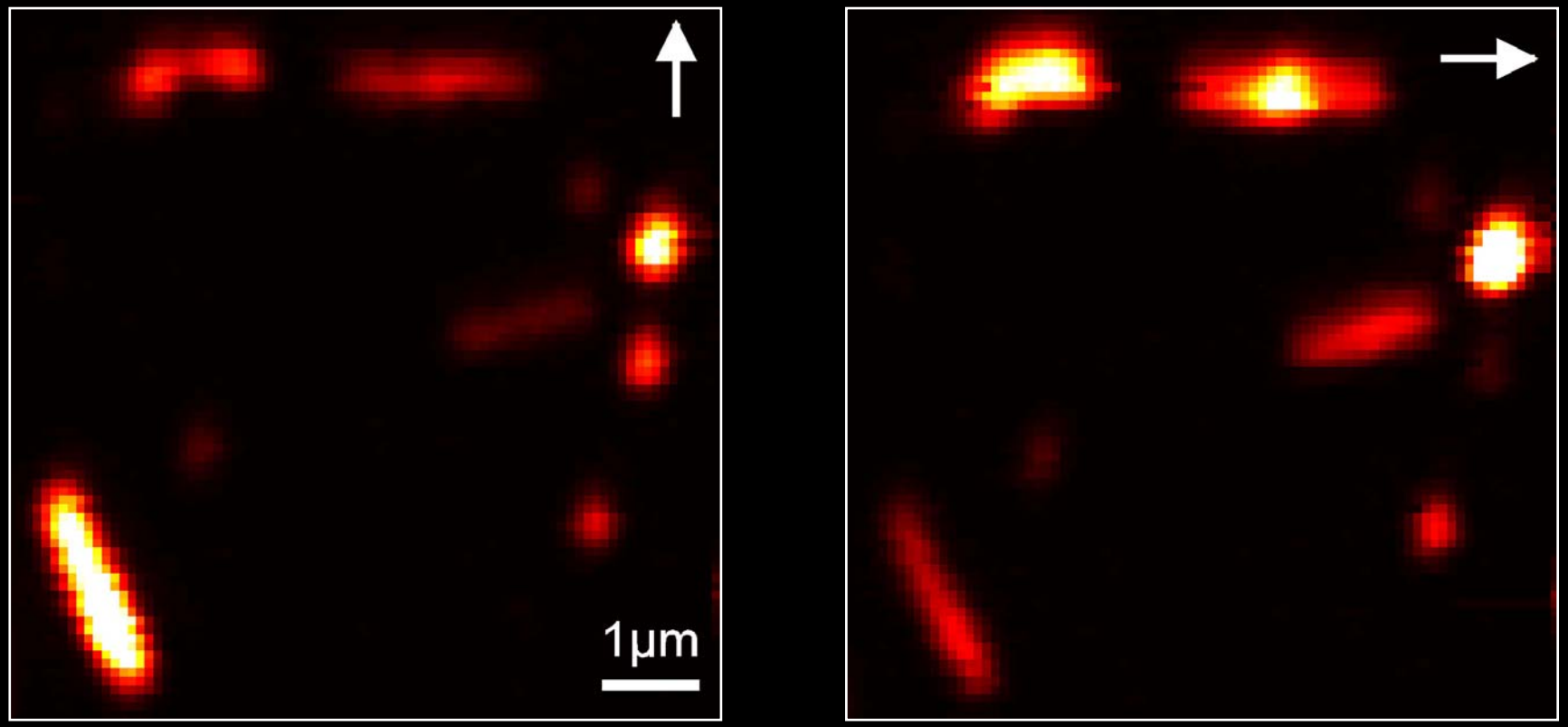


All Semiconducting

AND Metallic SWNTs

Polarization dependence

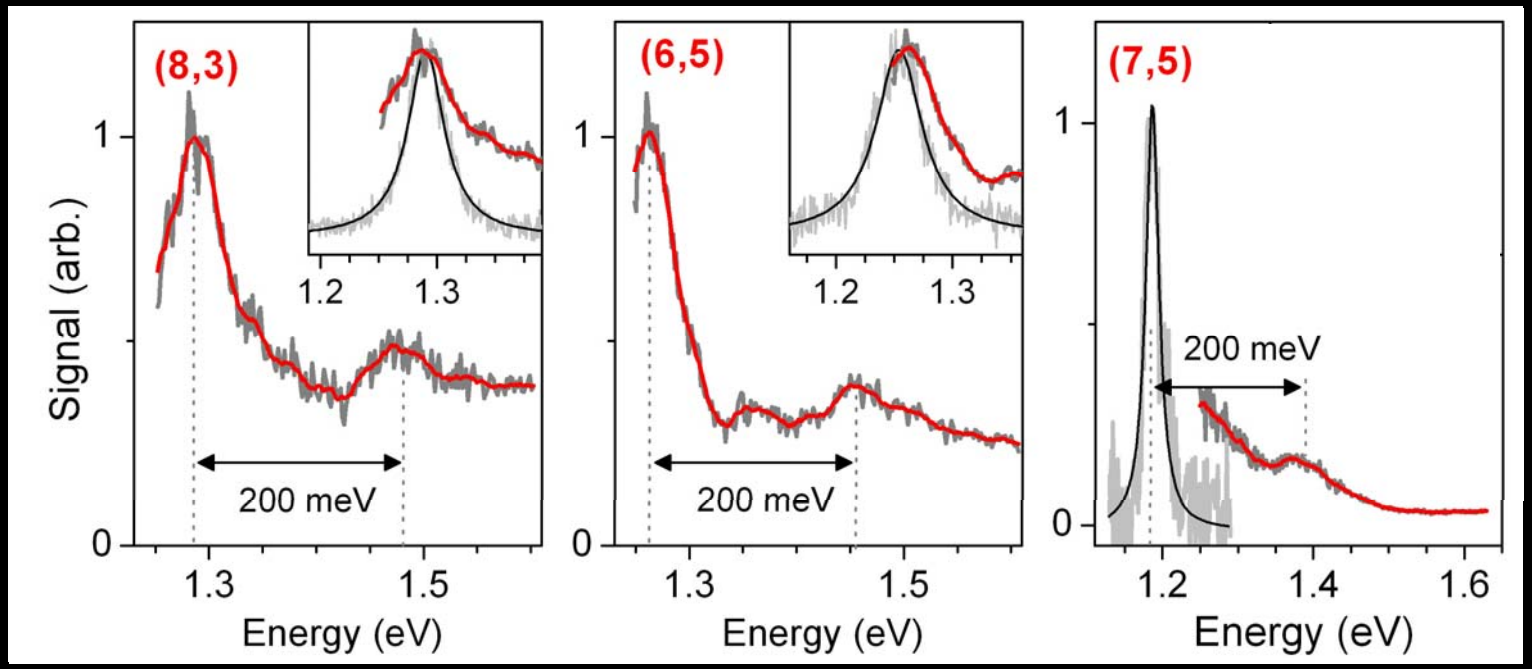
- Photothermal images with two orthogonal polarizations



- Strong polarization dependence :

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

Absorption Spectroscopy : S_{11} Transitions



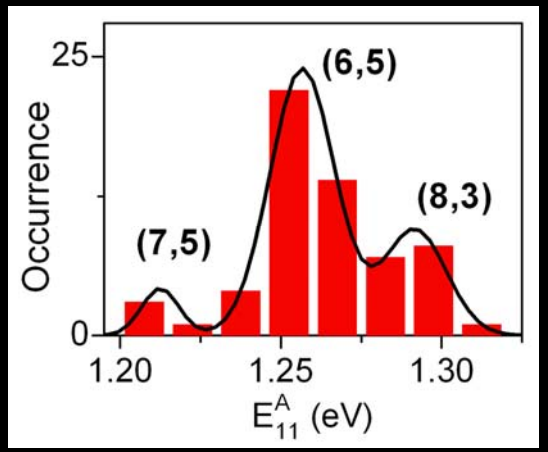
- Absorption Peaks:

→ S_{11} transitions in Semiconducting SWNTs

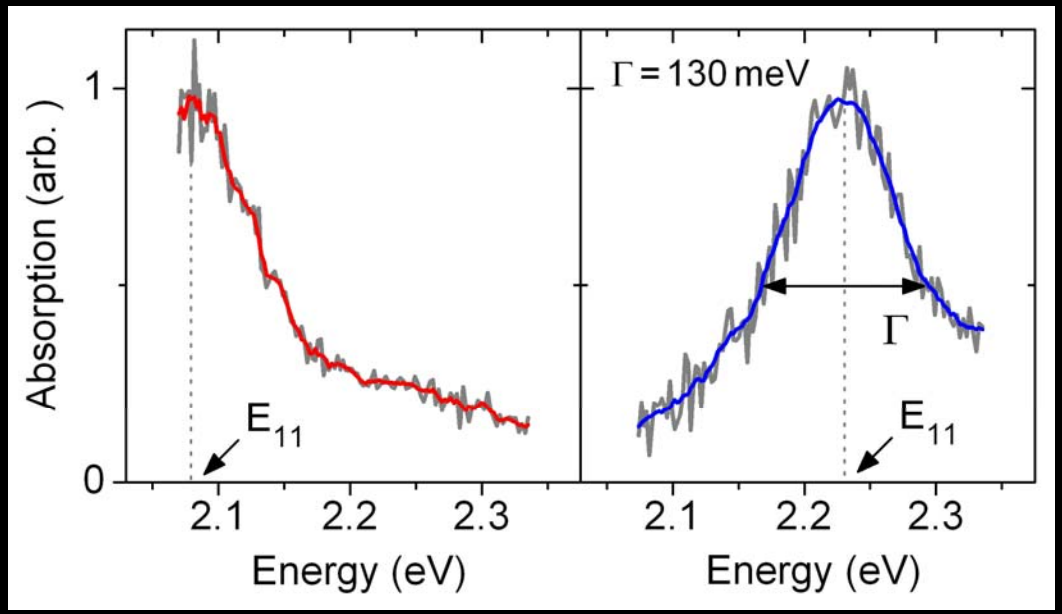
→ Very small Stokes Shifts (~10 meV)

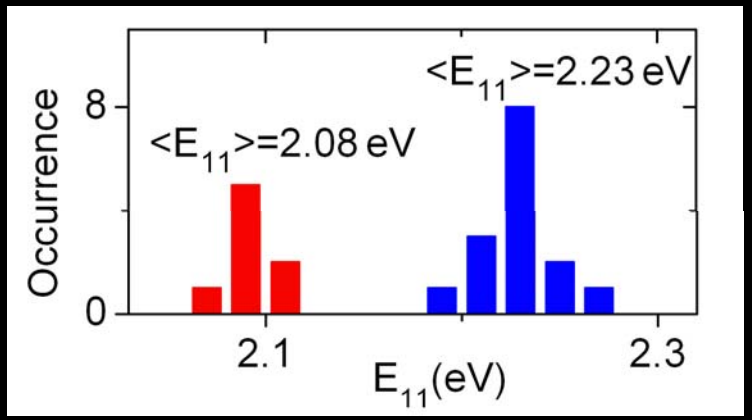
- Side bands at ~200 meV (Raman G band)
- (n,m) independent Shift

→ Exciton-Phonon bound states



Absorption Spectroscopy : M_{11} Transitions





Two sub-populations

2n+m=27

2n+m=24

- No Exciton-Phonon Sidebands

→ M_{11} transitions in Metallic Nanotubes

(n,m) Assignments from Jorio *et al. Phys. Rev. Lett.* **93**, 147406 (2004)

General Conclusion

- *Highly sensitive optical detection method*
  - Simple experimental setup
  - Detection of 1.4nm gold nanoparticles, CdSe nanocrystals, carbon nanotubes…
  - Signal in agreement with an electrodynamical model
- *Absorption spectroscopy at the single particle level*
  - Intrinsic size effects in the SPR of gold nanoparticles
  - Photothermal absorption spectroscopy of CdSe nanocrystals
  - Characterization of semiconducting ***and*** metallic carbon nanotubes

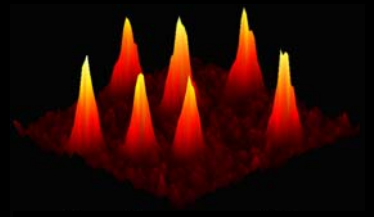
Further Applications

- Single gold nanoparticle tracking in live cells

(David Lasne : PhD Thesis)

- Spectroscopy of other metallic nanoparticles

Silver nanoparticles, gold nanorods, core shell nanoparticles, nanoparticle pairs… (Coll. M. Brust & D. Fernig, Liverpool)



5 nm Silver NPs

- Photothermal detection
& Absorption spectroscopy at low temperature

Merci !

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