Ultrafast nonlinear plasmonics in metallic and hybrid nanoparticles

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Optical response of a metal nanoparticle

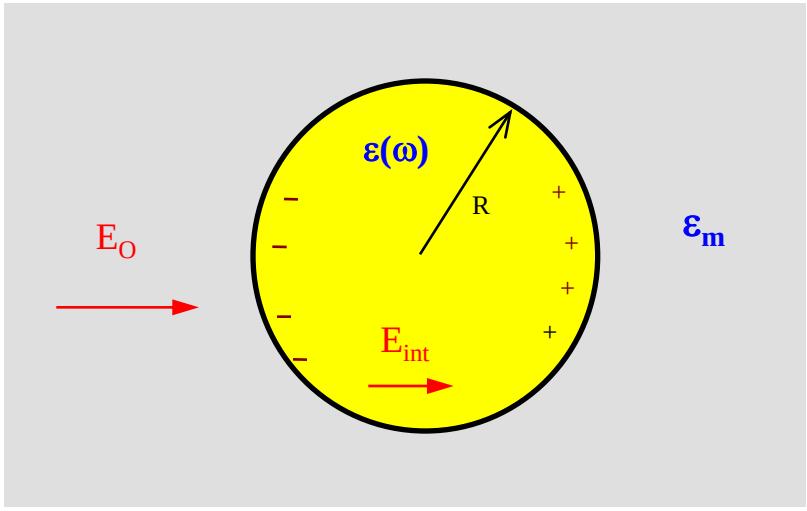
- **Metal nanosphere ($\varepsilon = \varepsilon_1 + i\varepsilon_2$) in a matrix ($\varepsilon_m$):**

  Mie theory for sphere $R << \lambda$ (dipolar):

$$\sigma_{abs} = \frac{18\pi V \varepsilon_m^{3/2}}{\lambda} \frac{\varepsilon_2(\lambda)}{[\varepsilon_1(\lambda) + 2\varepsilon_m]^2 + \varepsilon_2^2(\lambda)}$$

resonance for $\varepsilon_1(\lambda) + 2\varepsilon_m \approx 0$

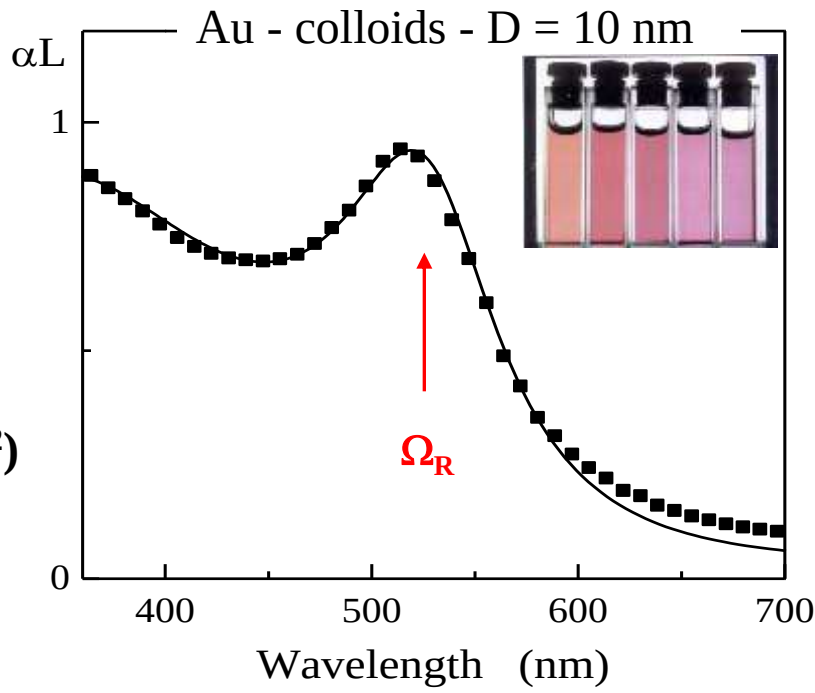
→ Surface Plasmon Resonance, SPR



→ **Resonance depends on:**

- **size**
- **environment**
- ***shape + light polarization (ellipsoids, rods, ...)***

⇒ ***signature of particle geometry and environment***



- **Small sphere: Absorption ($\propto$ V) >> Scattering ($\propto V^2$)**

  ($\sigma_{abs}/\sigma_{scatt} \approx 100$ for a 20 nm gold nanosphere)

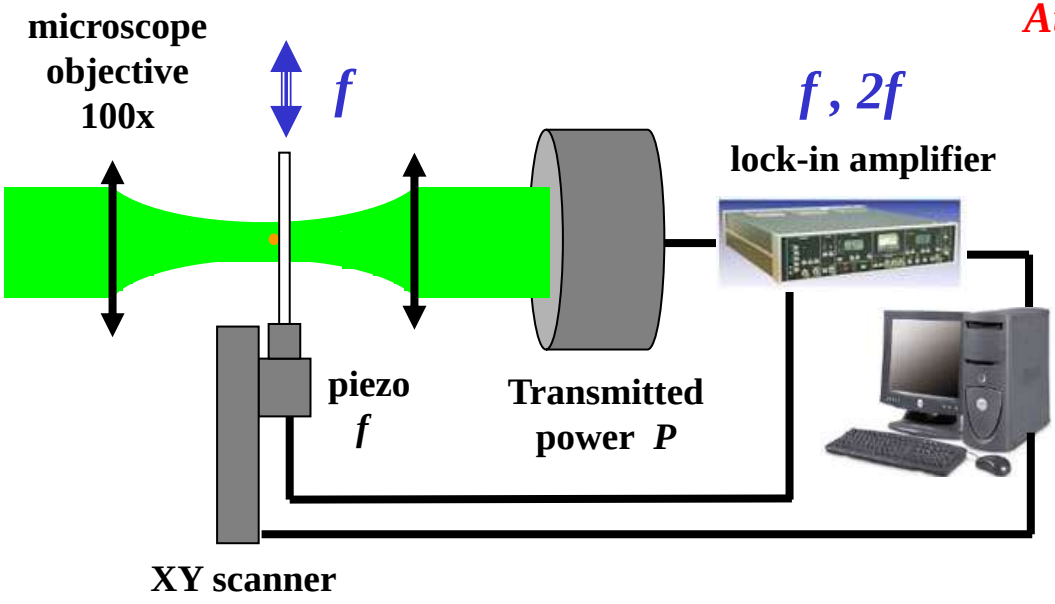
Ensemble measurement: 10^4 to 10^6 particles

⇒ Size and shape fluctuations

I. Single nanoparticles: "spatial modulation technique"

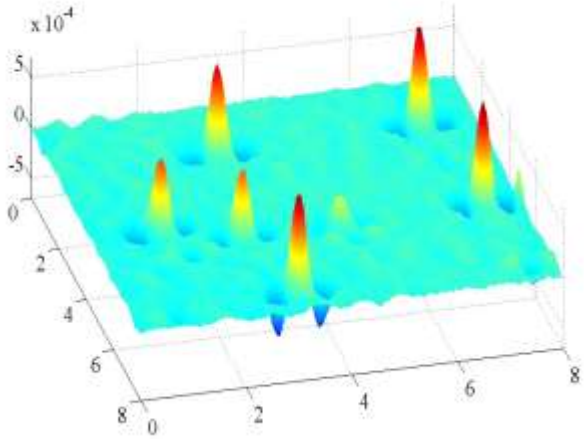
- *Detection of small particles: far field microscopy*
  - **Focused beam: 300 - 500 nm**
  - **Gold nano-sphere D = 10 nm: extinction of 10^{-4} of the incident light (absorption)**

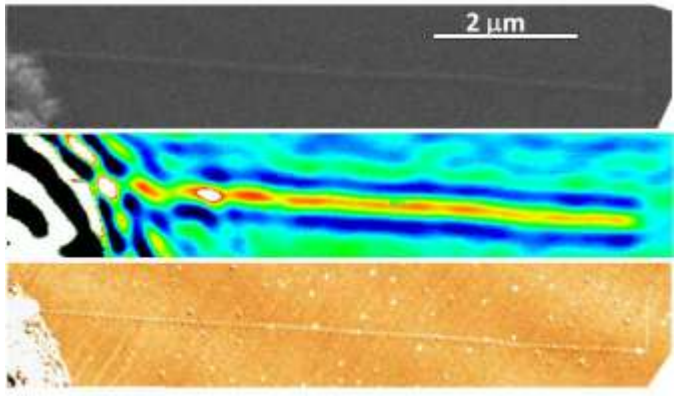
- **Spatial Modulation Technique (SMS):** *Arbouet et al., Phys. Rev. Lett. 2004*
  Modulation of the nanoparticle position ⇔ Modulation of the transmitted light



Muskens et al., APL 2006 ; PRB 2008
Christofilos et al., JPCL 2012

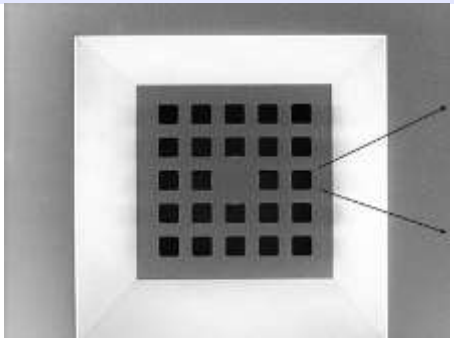
ΔTx/Tx
Au 10nm





ΔRx/Rx
1.6 nm
SWCNT

One – by – one correlation with electron microscopy (TEM):

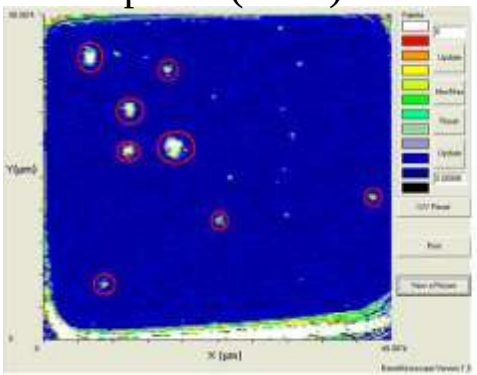


Optical SMS image & TEM micrograph of the same 50 x 50 µm² square (SiO_2 grids)

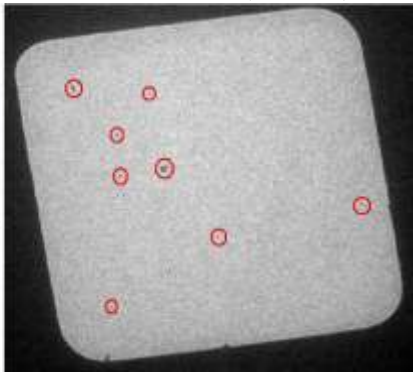
→ one-by-one correlation

P. Billaud et al., J. Phys. Chem. C 2008

Optical (SMS)

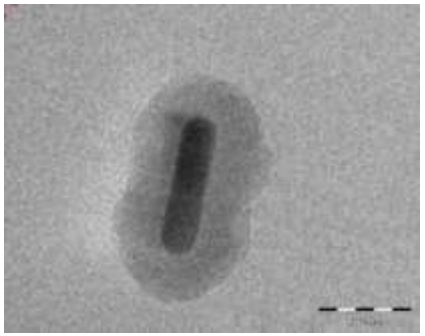


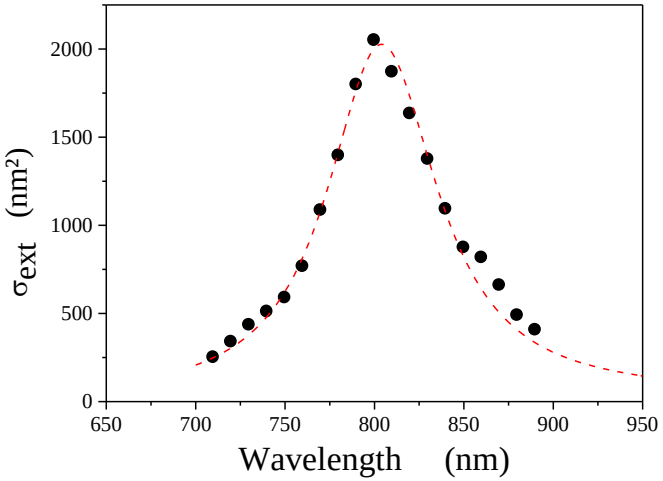
Electronic (TEM)

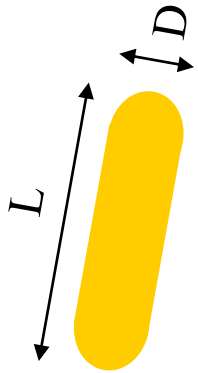


L. Liz-Marzan, Univ. Vigo, Spain

Au nanorods @ SiO_2



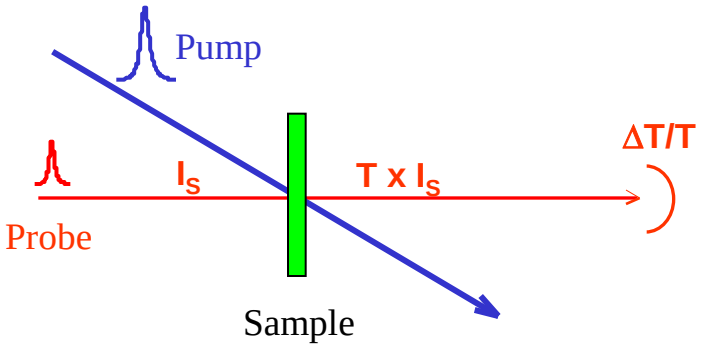




Au nanorod	TEM	Optics
Length	L = 33 nm	33.5 nm
Diameter	D = 9 nm	8.7 nm
Aspect ratio	η = 3.7	3.8

Quantitative measurement : $\sigma_{ext}(\lambda)$

Femtosecond spectroscopy of a single nanoparticle



Femtosecond pump – probe:

Pump : selective electron excitation,
modification of metal dielectric constants ε_1 and ε_2

Probe : time-dependent changes of optical properties (absorption)

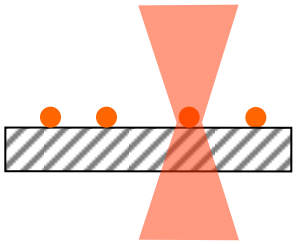
$$\left.\frac{\Delta T}{T}\right|_{1 nanoparticle} = -\frac{\Delta\sigma_{ext}}{S_{probe}}$$

Linear absorption: probe beam

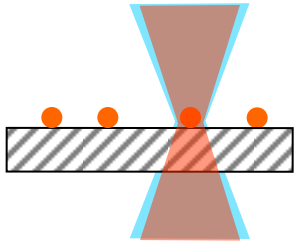
detection and optical characterisation

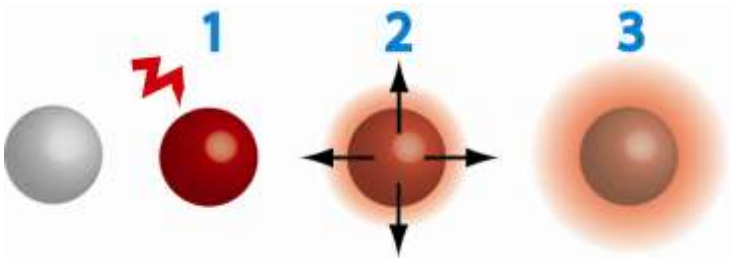
Nonlinear femtosecond response

pump (2ω) & probe (ω)



First measurements:
single silver nanosphere 20 - 30 nm
O.Muskens et al., Nano Letters 2006

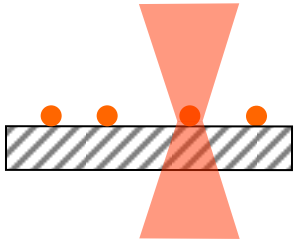




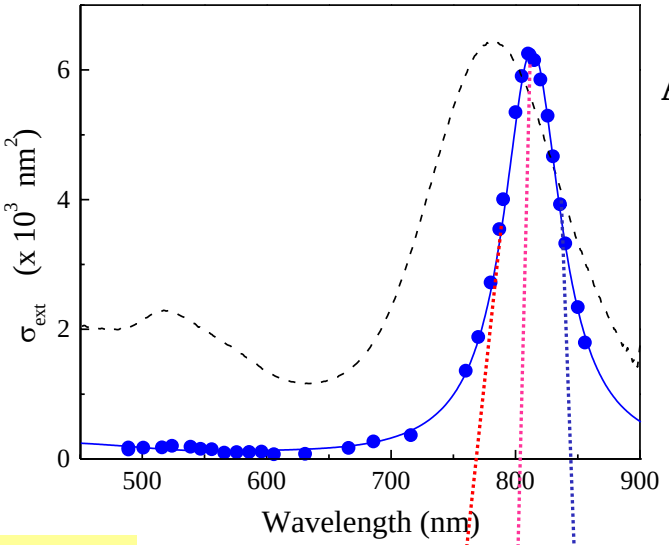
1. **Internal thermalization /ultrafast plasmonics**
   electron-electron and electron-phonon *(fs / ps)*
2. **Lattice vibrations** *(1 - 10 ps)*
   fundamental breathing mode
3. **Cooling** *(10 - 100 ps)*
   energy transfer to the environment

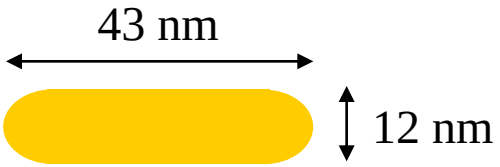
Ultrafast plasmonics: single gold nanorod

i) detection and optical characterisation



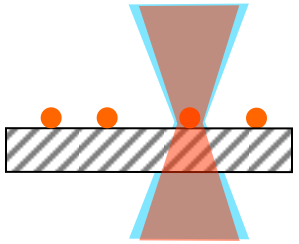
linear absorption





Absorption modeling: finite element calculation

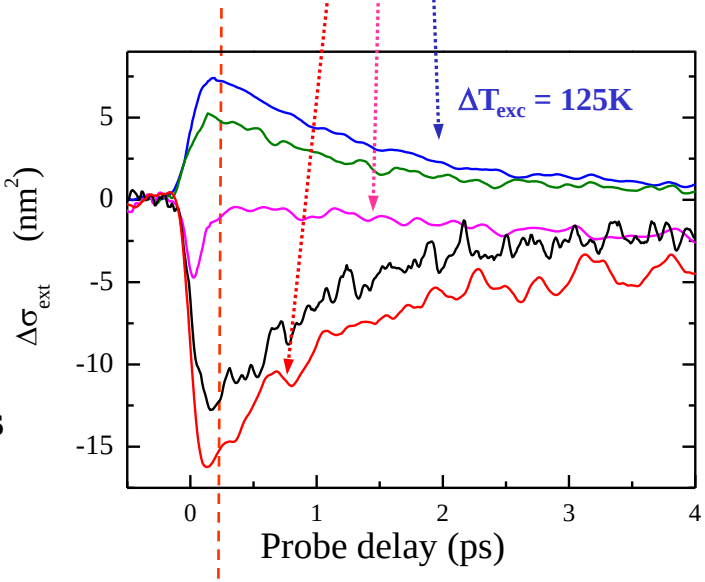
ii) Nonlinear femtosecond response

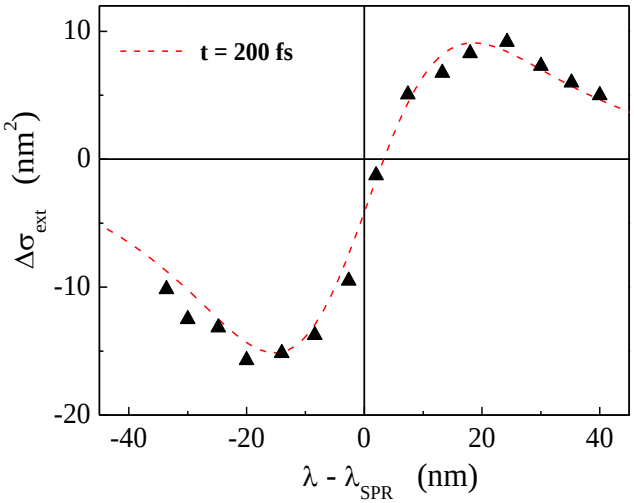


pump & probe

Single nanorod nonlinearity:
(no orientation or shape averaging)
→ Quantitative study
H. Baida et al. PRL 2011

Theoretical model:
- electron distribution kinetics
- band structure model
⇒ change of ε ⇒ $\Delta\sigma_{ext}$

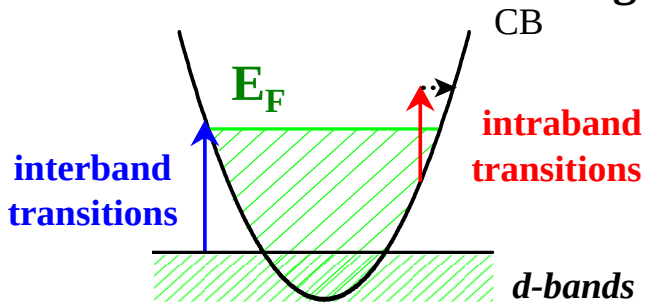




Ultrafast plasmonics: modeling

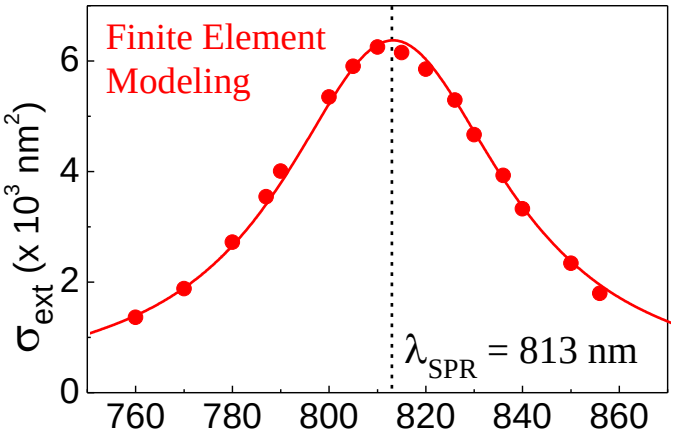
Metal dielectric function changes:

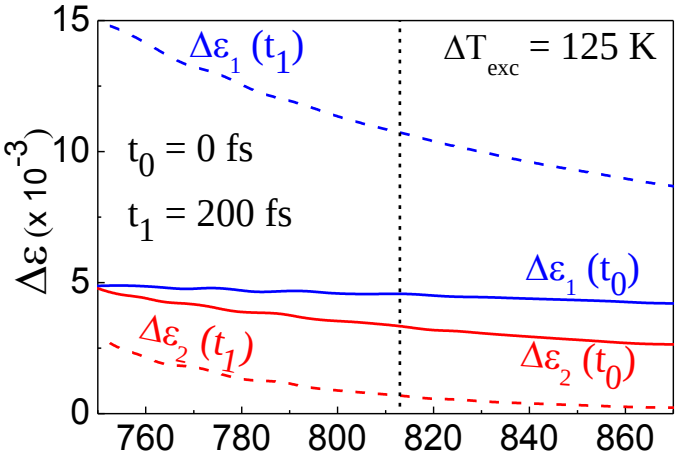
$$\Delta\varepsilon_{1,2} = \Delta\varepsilon_{1,2}^{ib} + \Delta\varepsilon_{1,2}^{Drude} \Rightarrow \Delta\sigma(\lambda,t) = \Delta\sigma^{ib}(\lambda,t) + \Delta\sigma^{Drude}(\lambda,t)$$



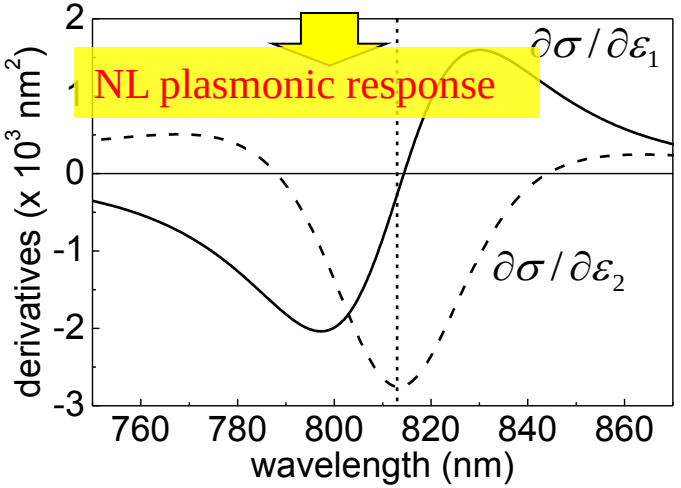
Short time: interband contribution dominant (hot electrons)
[long time scale: lattice heating, Drude term modifications]

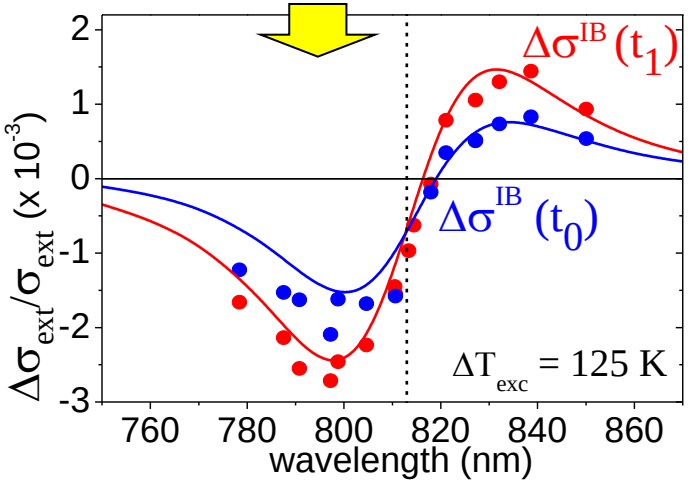
$$\Delta\sigma^{ib}(\lambda,t) = \left.\frac{\partial\sigma}{\partial\varepsilon_1}\right|_\lambda \Delta\varepsilon_1^{ib}(\lambda,t) + \left.\frac{\partial\sigma}{\partial\varepsilon_2}\right|_\lambda \Delta\varepsilon_2^{ib}(\lambda,t)$$





excitation
+
Boltzmann equation
+
band structure model

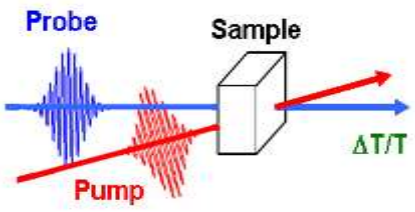


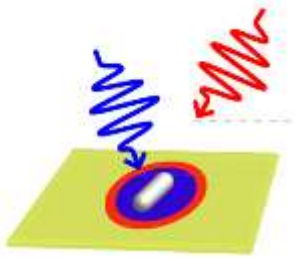


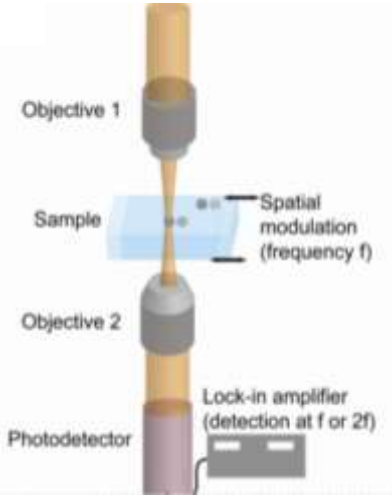
- no fitting parameters
- Au nonlinearity enhanced by plasmonic effects

Conclusion (I)

- **Single metal nanoparticle optical absorption measurement**
  - → **spatial modulation technique: direct absorption measurement**
  - → **far-field technique ⇒ dilute sample (< 1 particle per μm²)**
  - → **spectroscopy: optical identification of a single nanoobject**
  - → **surface plasmon resonance characteristics: size and shape effect**







- **Femtosecond time-resolved spectroscopy**
  - → **nonlinear optics with a single nanoobject**
  - → **physical origin of the optical nonlinear response**
  - → **quantitative measurement of the nonlinear response**
  - → **Quantitative calculation of the nonlinear susceptibility for ensembles / plasmonic devices**

Ensemble experiments metal nanoparticles — C. Voisin et al., *Phys. Rev. B 2004*

Single metal nanoparticle experiments — O. Muskens et al., *Phys. Rev. B 2008*

II. Hybrid metal - semiconductor nanoparticles

10nm

- **Hybrid nanoparticles: two materials**

metal + semiconductor or metal or dielectric or organic /inorganic

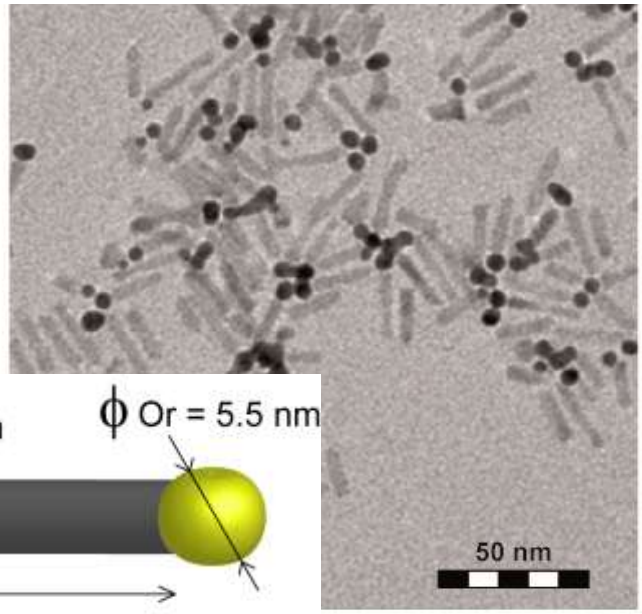
→ ***New properties: optical, ...***

→ ***Modeling***

→ ***Growth / interface***

Direct growth of gold (Au) on the semiconductor (CdS, CdSe) nanorod

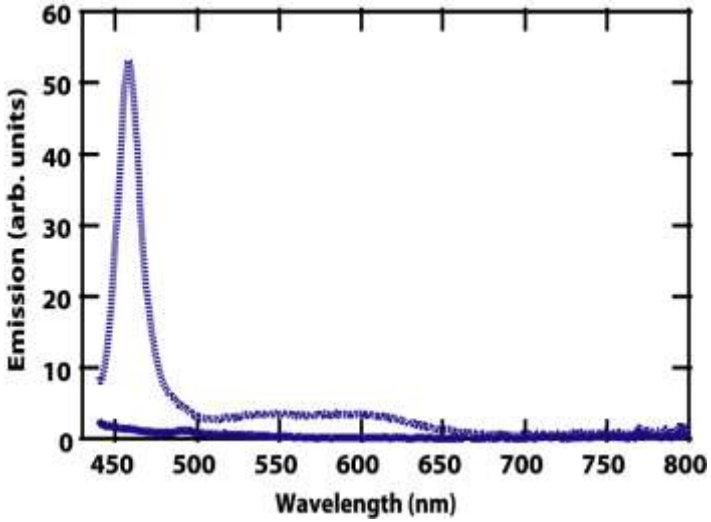
T. Mokari, E. Rothenberg, I. Popov, R. Costi, U. Banin, Science 304, 1787-1790 (2004)



CdS-Au nano-matchsticks

(~ 70% Au-CdS, 30% residual bare CdS)

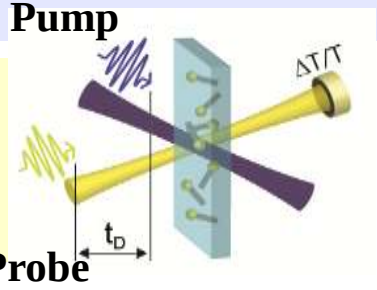
Au growth on CdS and CdSe nanorods:
Photoluminescence quenching



Semiconductor - metal energy & charge transfers ?

Time-resolved pump-probe spectroscopy: Au-CdS nano-matchsticks

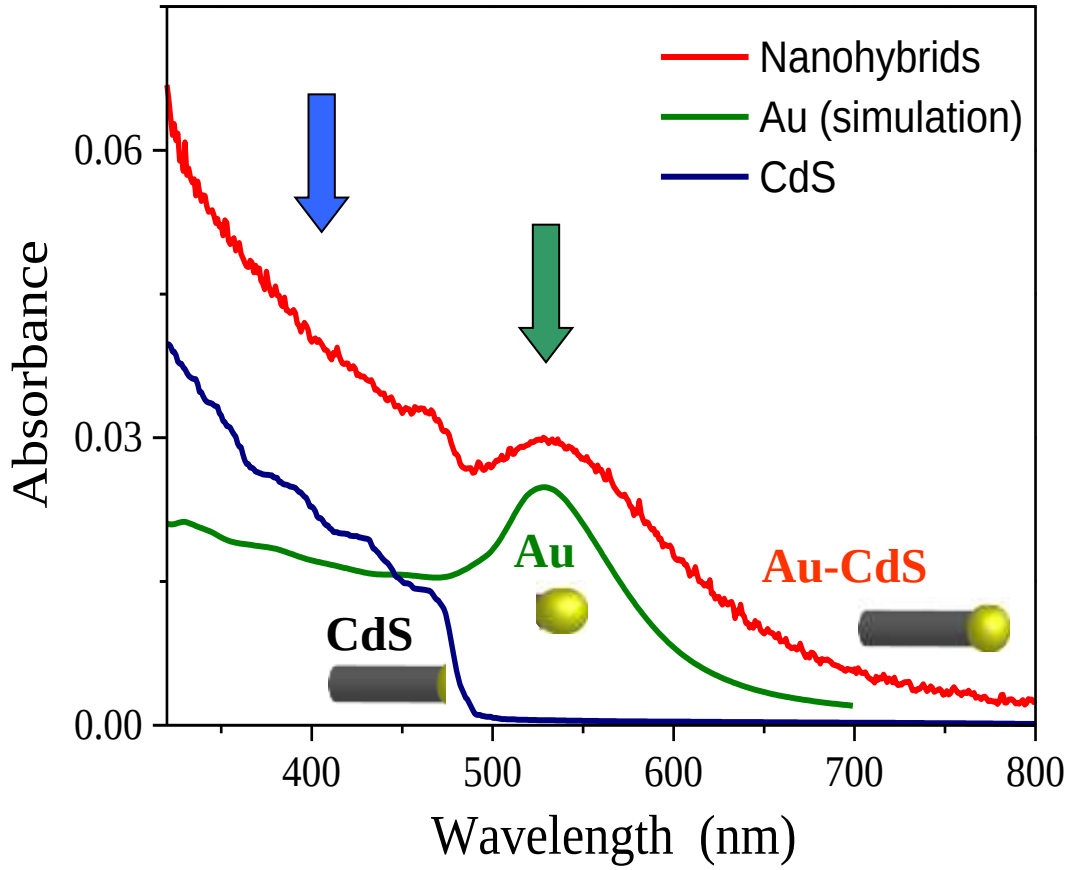
Ultrafast nonlinearity: - semiconductor (band filling)
- metal (electron heating, lattice heating)
- semiconductor-metal coupling



- **CdS gap ≈ 480 nm**
- **Plasmon resonance ≈ 540 nm**

- **Pump wavelength**
  - **≤ 480 nm → excitation Au and CdS**
  - **≥ 500 nm → excitation Au only**

- **Probe wavelength**
  - **≤ 480 nm → CdS (and Au)**
  - **≥ 500 nm → Au only**

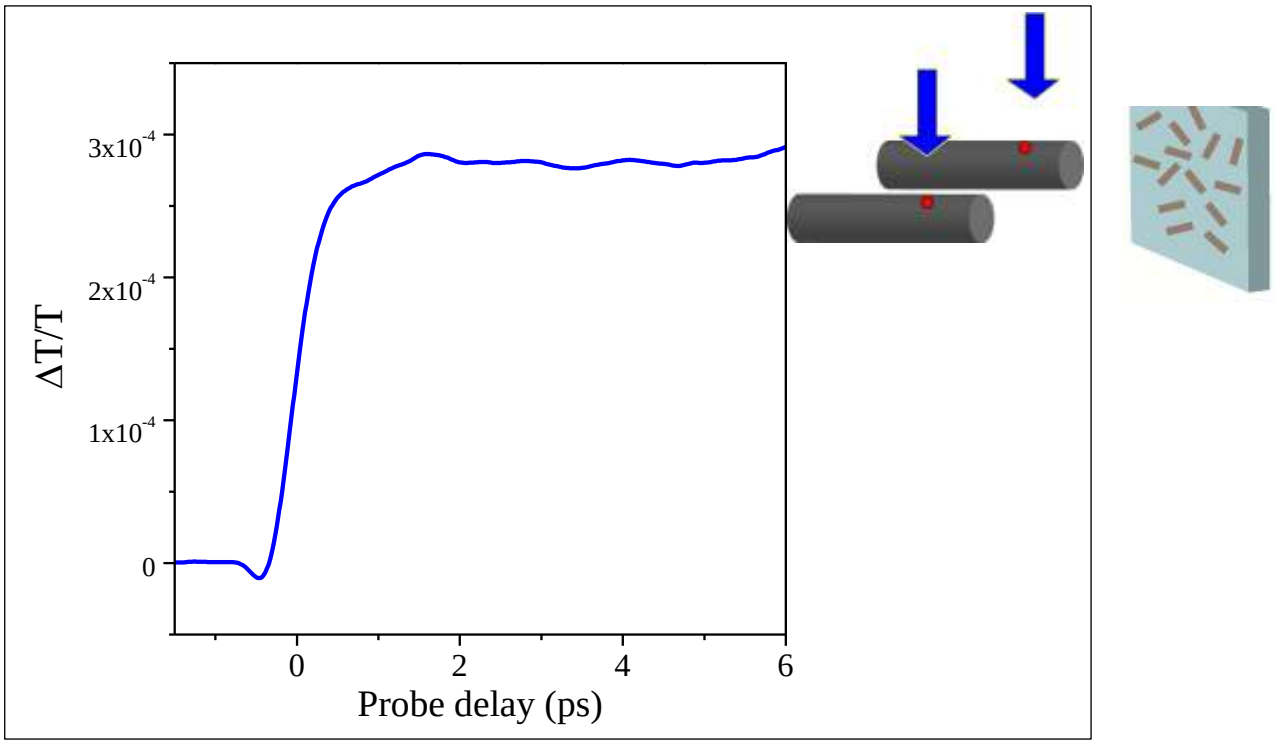


+ comparison CdS-Au with bare CdS or Au: separation of the different mechanisms

Semiconductor ultrafast response: CdS

Probe wavelength: 480 nm (CdS response dominant)
Pump wavelength: 400 nm (e-h pairs in CdS)

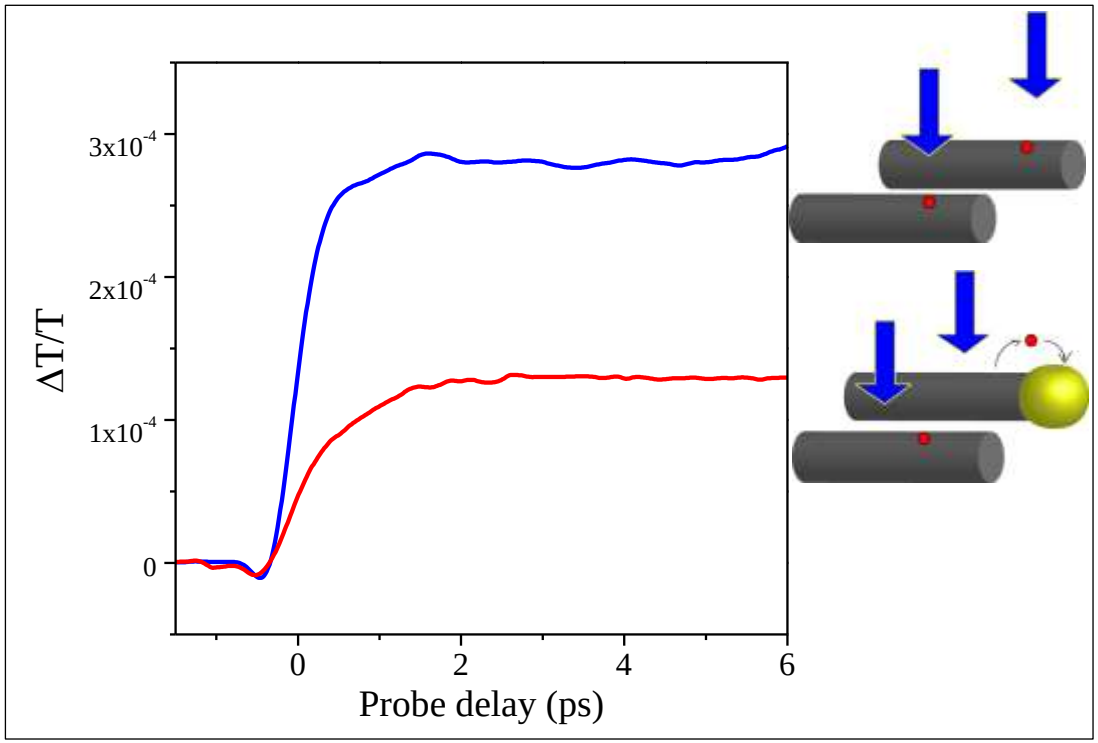
- **Bare CdS**: $\Delta T/T > 0$ $\Rightarrow$ **absorption bleaching / plateau:**
  conduction band filling $\Rightarrow$ **photoexcited electron density (1 e/rod)**



Semiconductor ultrafast response: CdS-Au

Probe wavelength: 480 nm (CdS response dominant)
Pump wavelength: 400 nm (e-h pairs in CdS + heating of Au electrons)

- **Bare CdS: Absorption saturation: band filling ⇒ electron density**
- **Au-CdS (normalized for same excitation): reduced amplitude (electron density)**



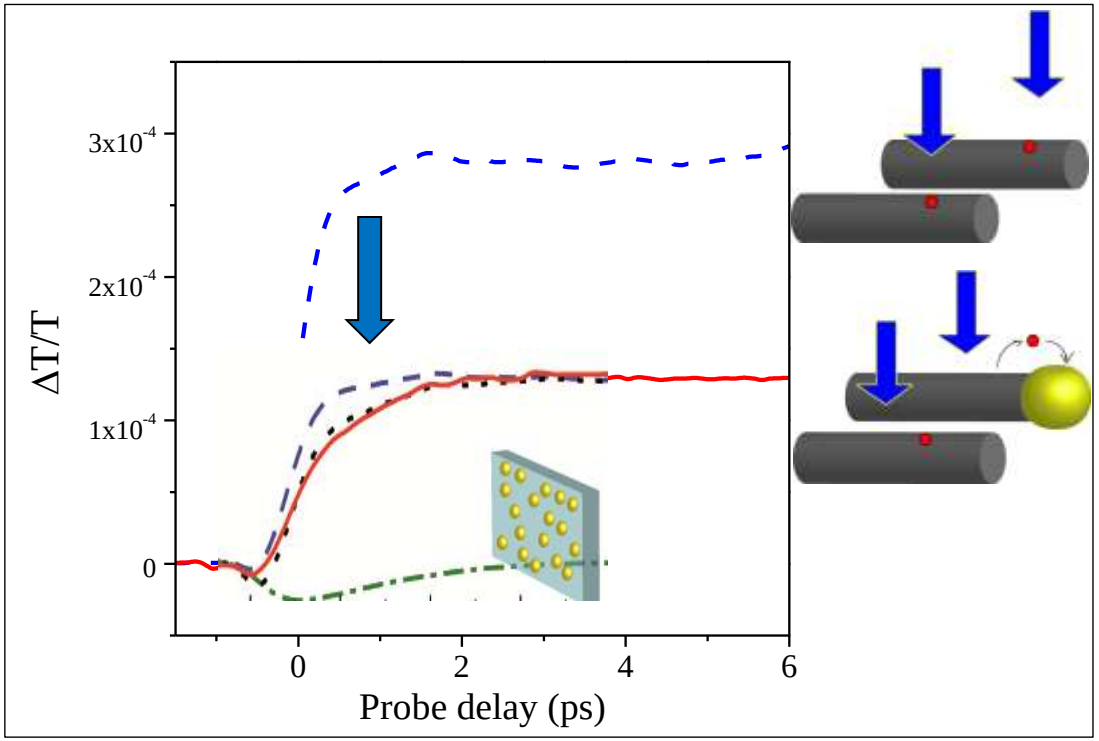
bare CdS

decorated Au-CdS
+ residual bare CdS

Semiconductor ultrafast response: CdS-Au

Probe wavelength: 480 nm (CdS response dominant)
Pump wavelength: 400 nm (e-h pairs in CdS + heating of Au electrons)

- **Bare CdS: Absorption saturation: band filling ⇒ electron density**
- **Au-CdS (same pump power and rod density): reduced amplitude (electron density)**



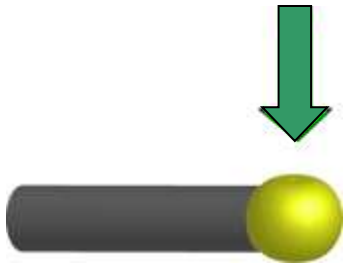
bare CdS

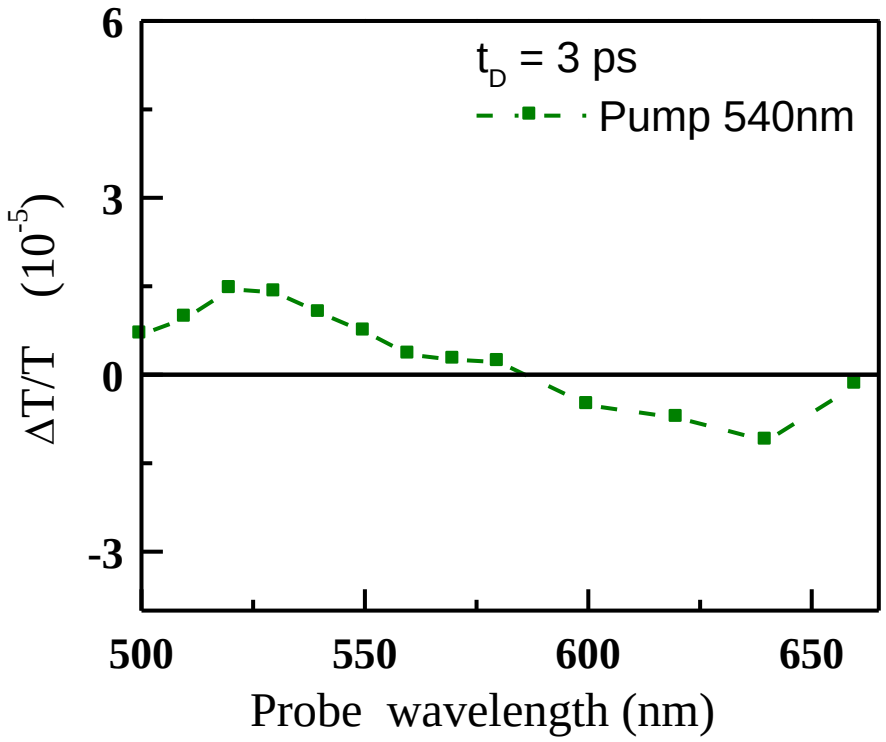
decorated Au-CdS
+ residual bare CdS

- **Au weak induced absorption (electron heating)**
- **80% of the hybrids have lost their charge: transfer time < 20 fs**

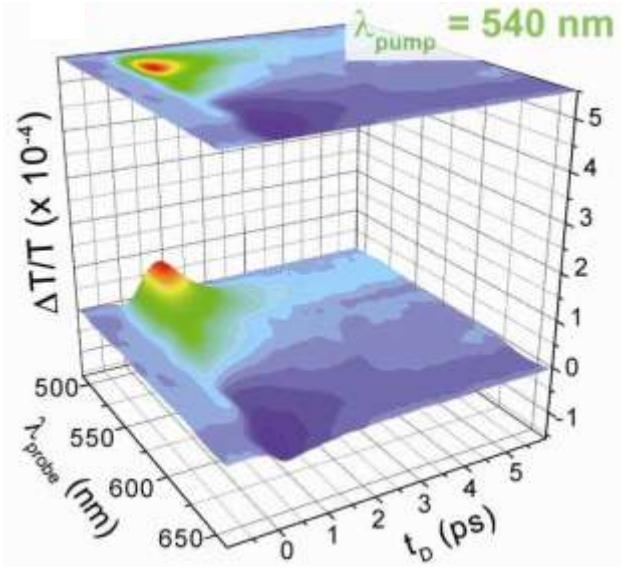
Metal ultrafast response: Au

Probe wavelength > 500 nm (Au Surface Plasmon Resonance response)
Pump wavelength: 540 nm (only Au excitation)





Ultrafast plasmonics in Au nanospheres:
Au nonlinear response due to heating
(C. Voisin et al, Phys. Rev. B 2004)

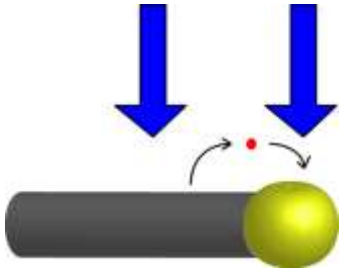


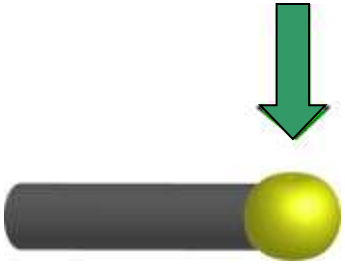
Metal ultrafast response: Au-CdS

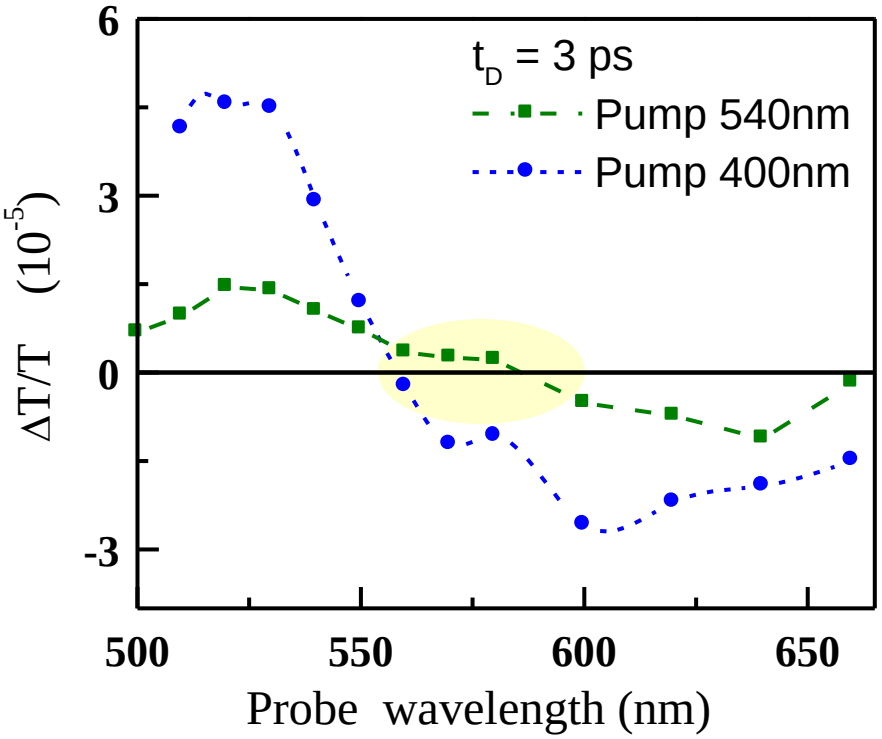
Probe wavelength > 500 nm (Au Surface Plasmon Resonance response)

Pump wavelength: 540 nm (only Au excitation)

400 nm: electron transfer possible (Au and CdS excitation)







540 nm:

Au nonlinear response due to gold heating

(C. Voisin et al, Phys. Rev. B 2004)

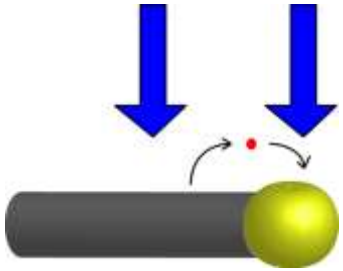
400 nm:

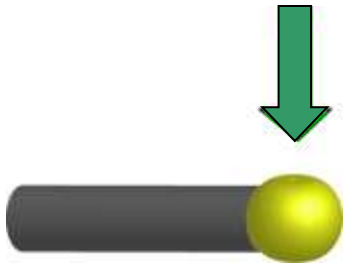
Spectral shift: **charge transfer**

ΔT/T amplitude: **direct Au heating + energy transfer**

Metal ultrafast response: charge transfer

Probe wavelength > 500 nm (Au Surface Plasmon Resonance response)
Pump wavelength: 540 nm (only Au excitation)
400 nm: electron transfer possible (Au and CdS excitation)





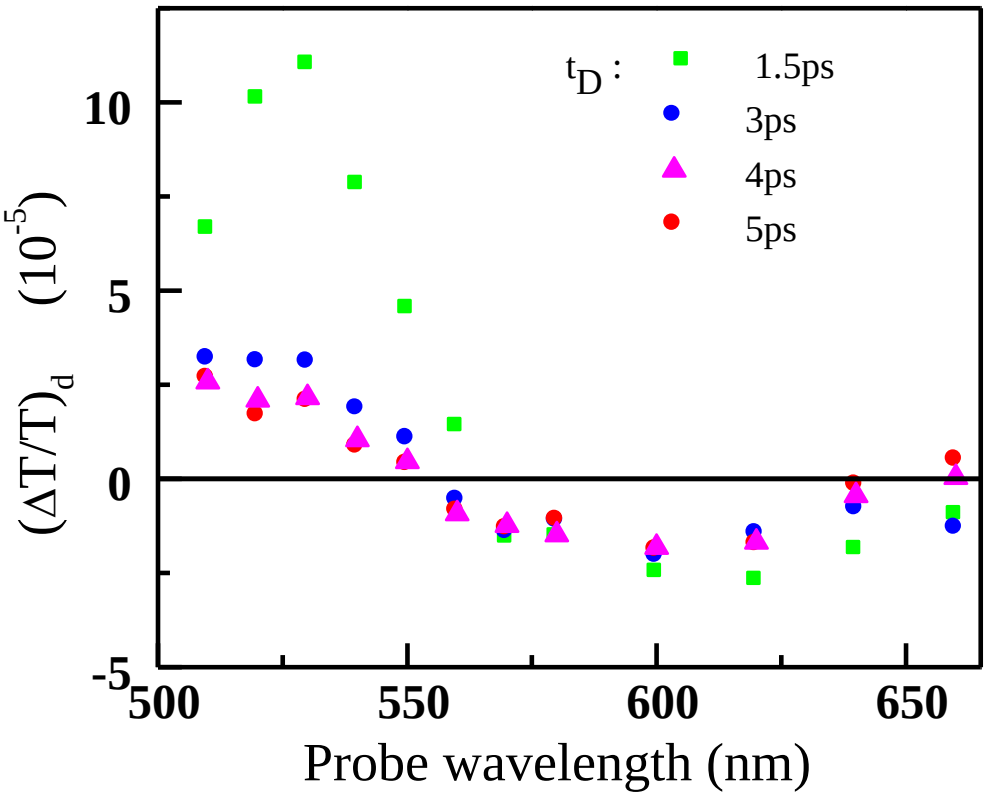
Effect of CdS excitation only:

differential spectra

$(\Delta T/T)_d = \Delta T/T(400nm) - \Delta T/T(540nm)$

for the same pump power absorbed by gold

Long delay ($t_D \geq 3$ ps):
thermalized Au electron-lattice
→ stationary signal



Gold ultrafast response: modeling

- **Transient transmission change ΔT/T ⇔ change of the metal dielectric function Δε :**

$$\frac{\Delta T}{T}(\lambda,t) = t_1(\lambda)\,\Delta\varepsilon_1(\lambda,t) + t_2(\lambda)\,\Delta\varepsilon_2(\lambda,t) \quad = \quad -\Delta\alpha\, L$$

With $t_{1,2}(\lambda) = \frac{\partial \ln T}{\partial \varepsilon_{1,2}}(\lambda) = -\frac{\partial \alpha(\lambda)}{\partial \varepsilon_{1,2}} L$ **(α : absorption coefficient)**

- **Metal dielectric function change:** $\Delta\varepsilon_{1,2} = \Delta\varepsilon_{1,2}^{\text{interband}} + \Delta\varepsilon_{1,2}^{\text{Drude}}$

- **Interband contribution:**
  - ***hot electrons***
  - ***dominant on short time scale***

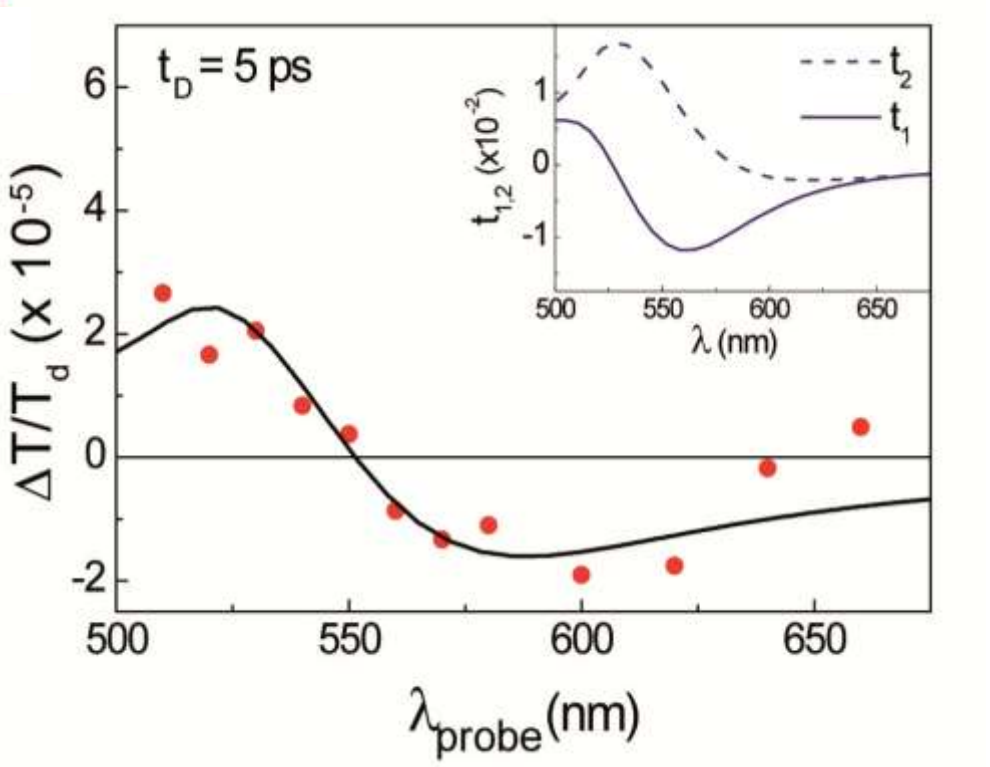
$$\varepsilon^{Drude} = 1 - \frac{\omega_p^2}{\omega(\omega + i\gamma)}$$

$$\omega_p^2 = \frac{n e^2}{\varepsilon_0 m}$$

- **Intraband contribution :**
  - ***modification of the electron density n***
    and of the electron scattering rate γ (∝ lattice heating)
  - ***dominant for thermalized electron-lattice ($t_D \geq 3$ ps)***

Gold ultrafast response: modeling

Charge and energy transfer to the gold part: fitting with $\Delta\varepsilon^{Drude}$



Electron density:

$$\frac{\Delta n}{n} = -5 \cdot 10^{-5}$$

Electron scattering rate:

$$\frac{\Delta \gamma}{\gamma} = 1.1 \cdot 10^{-3}$$

One e-h pair per CdS rod ⇒ electron and energy transfer to gold

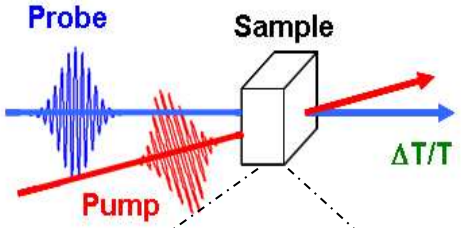
- energy: ⇒ $\Delta T_L \sim 0.6K$ ⇒ $\Delta\gamma / \gamma \approx 1 \cdot 10^{-3}$

- charge: + one electron and spill out effect (coulomb repulsion) : $\frac{\Delta n}{n} = \frac{\Delta N}{N} - \frac{\Delta V}{V} = \frac{1}{N} - 3\frac{\Delta r_e}{r_e}$

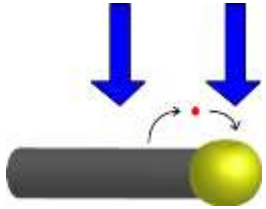
⇒ $\Delta n < 0$ and $\Delta n/n \approx -5.10^{-5}$ (from cluster physics experiments and calculations)

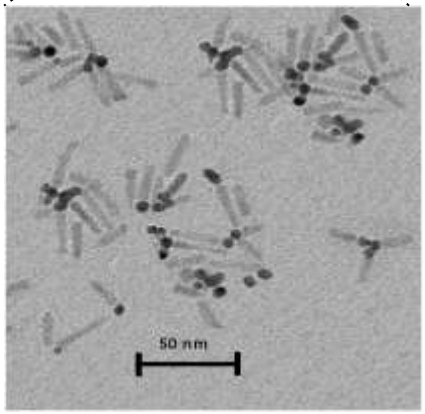
Conclusion (II)

Collaboration Jerusalem, Modena, Mainz, Lyon



- **Linear optical absorption of Nano-hybrids Au–CdS**
  Dielectric modeling (non resonant exciton - plasmon)
- **Time resolved non linear spectroscopy:**
  → combined nonlinear responses of semiconductor and metal
  + coupling: charge separation
  → Ultrafast charge transfer ≤ 10 fs





- **Extension to other hybrid systems and single nanoparticle investigations**

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