Ultrafast Dynamics and Non-linear Light Emission from Metallic Nanoparticles

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CEMES - CNRS

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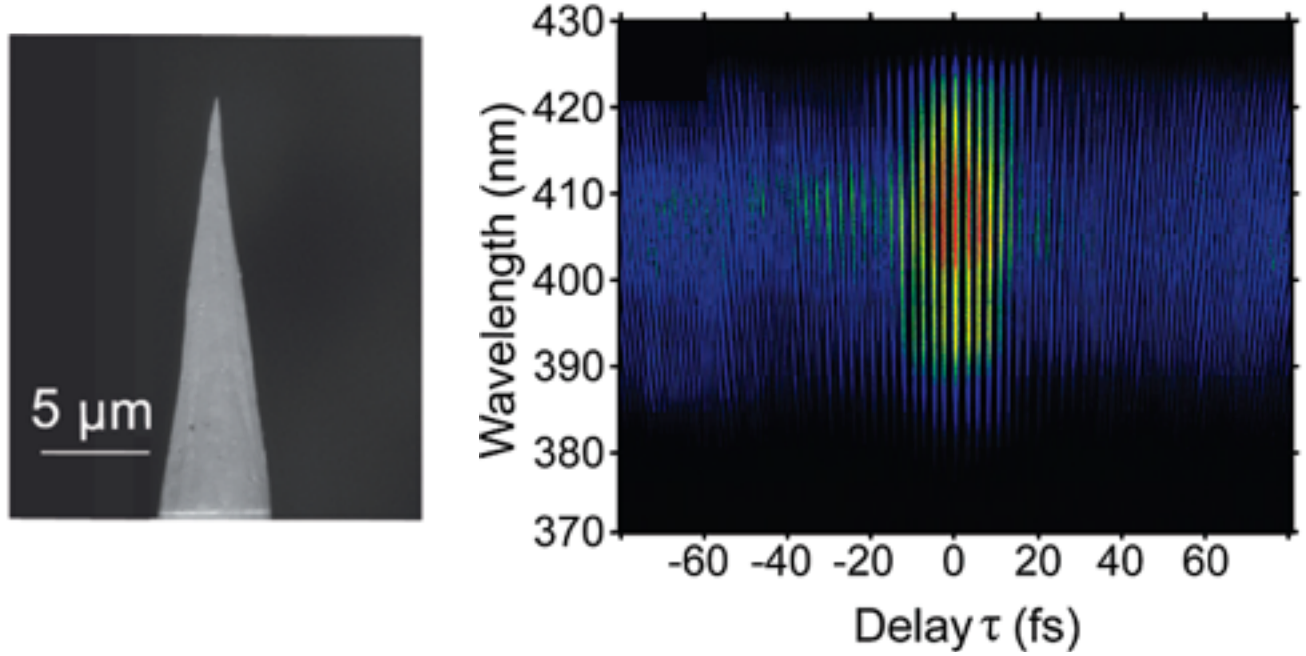
Plasmonics → Manipulation of light absorption at nanometer scale



Anderson et al
Nanoletters, 10, 2519 **2010**

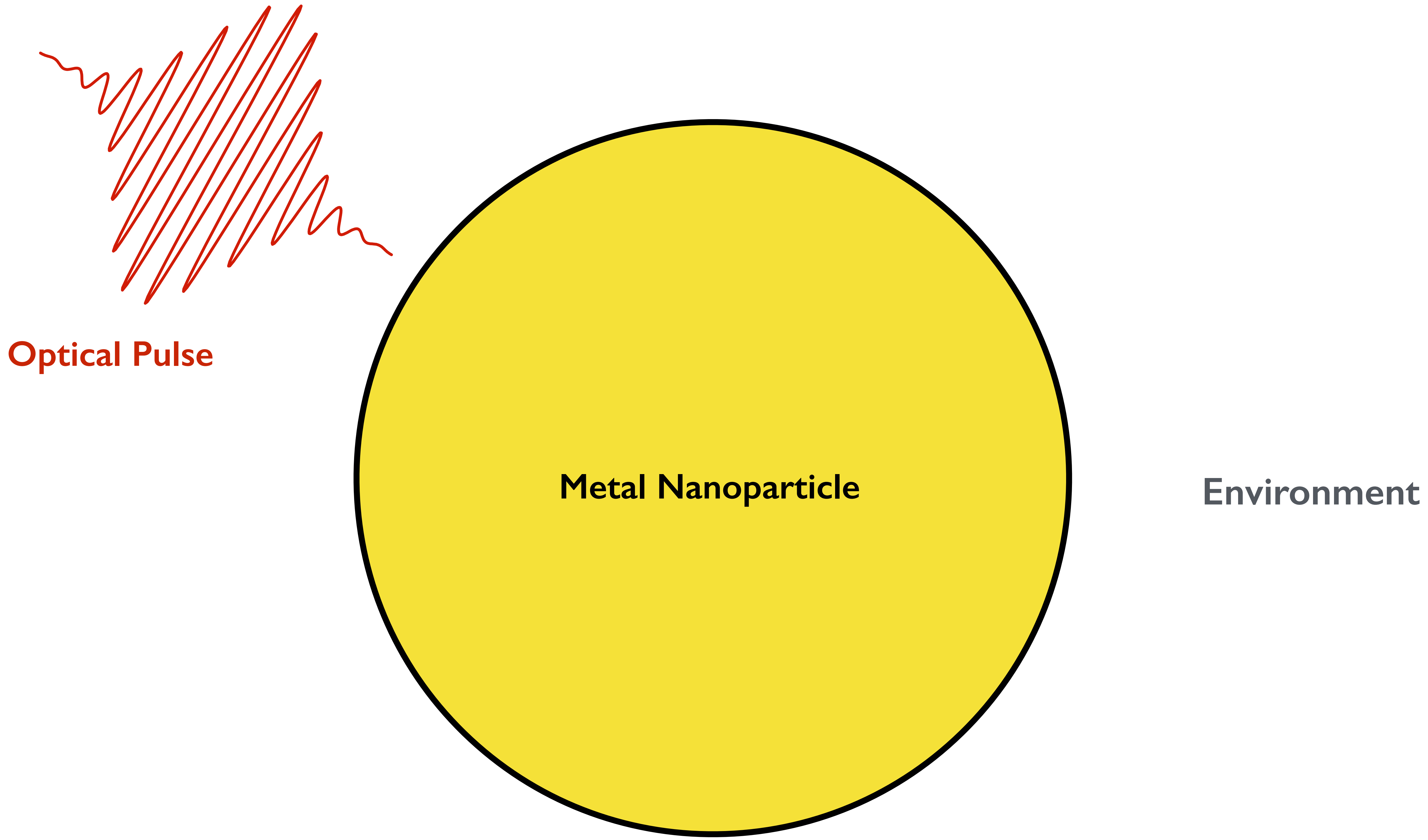
Light-Matter coherent coupling is **short-lived**

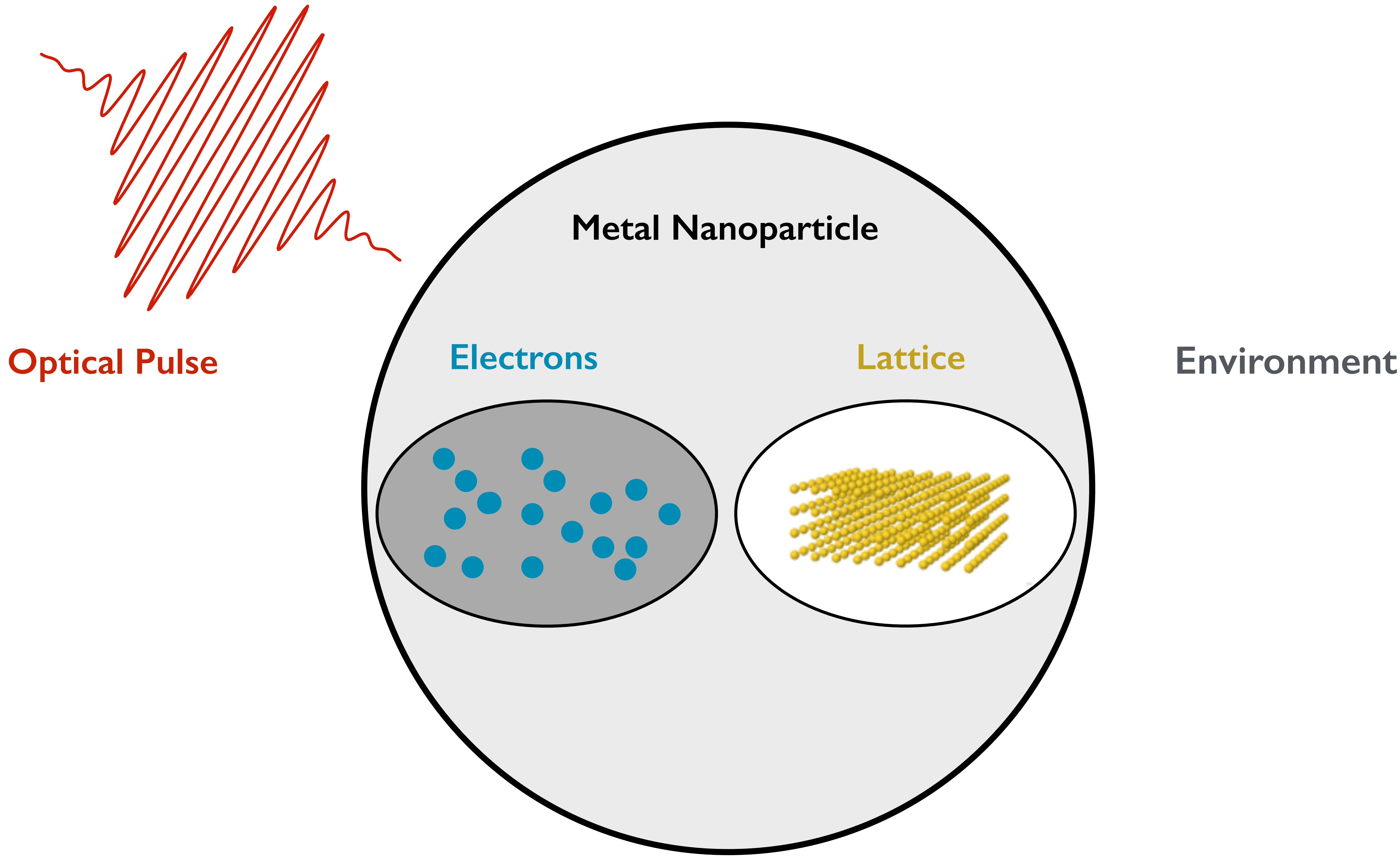
Central applications of plasmonics nanostructures involve **products of plasmon relaxation**

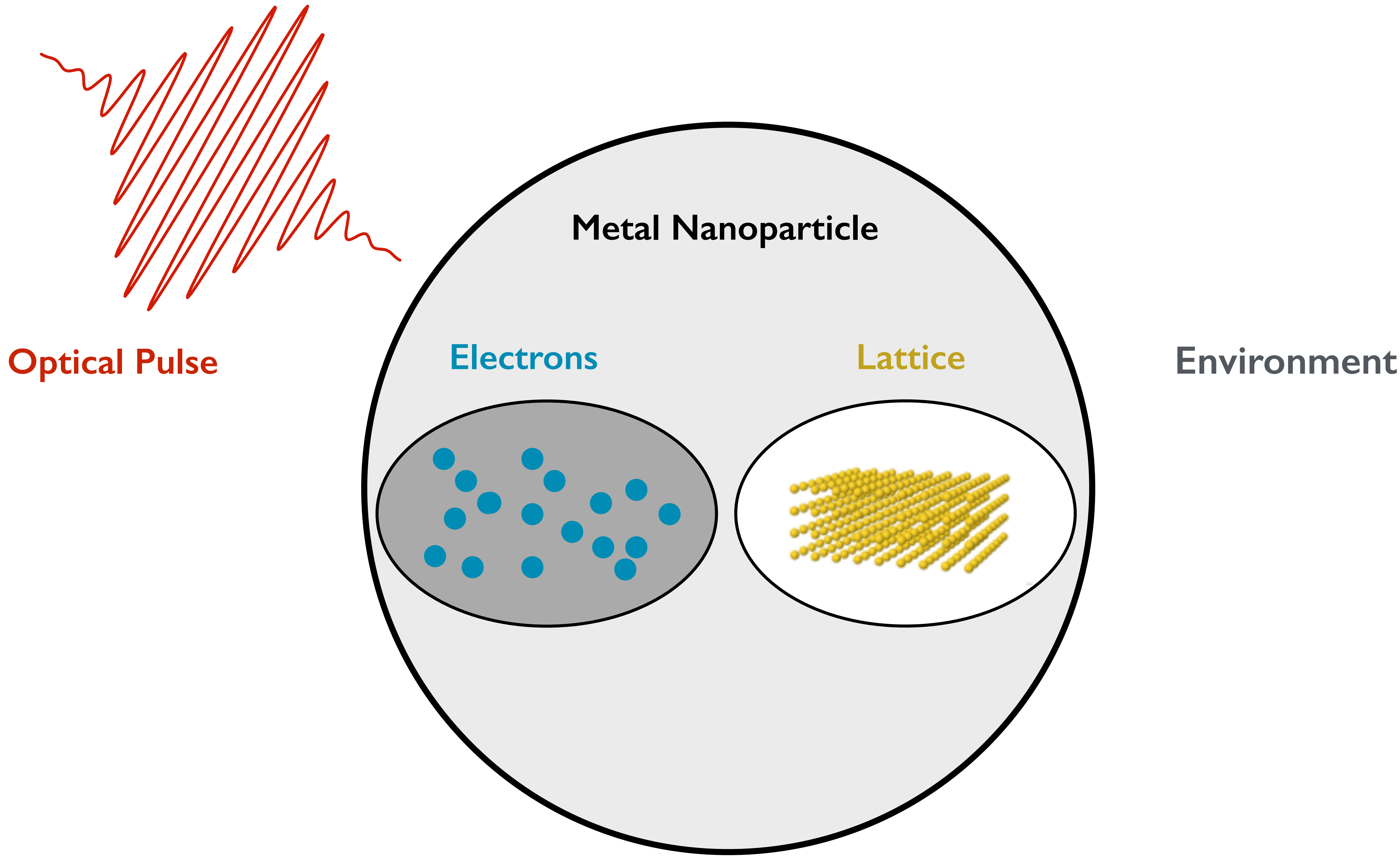
Hot electrons — Brongersma et al, *Nature Nanotech.*, 9, 25, **2015**
Heat — Huang & EL-Sayed, *J. Adv. Res.*, *1*, 13, **2010**

To **optimize** and even **control** → **Need to know relaxation processes and relevant timescales**

Introduction

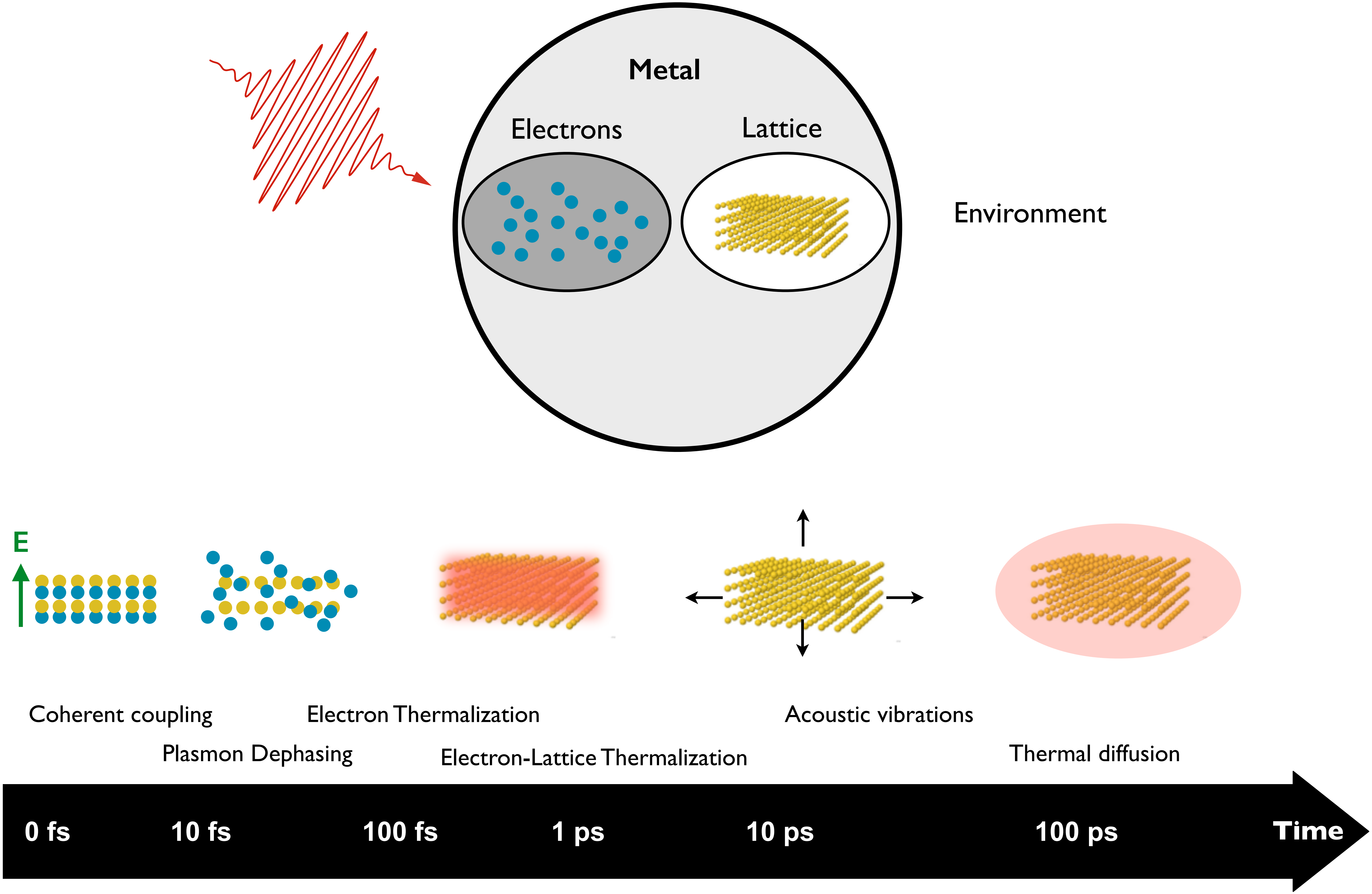



Metal Nanoparticle
Optical Pulse
Electrons
Lattice
Environment



Relaxation processes in metallic nanostructures ? **Timescales ?** **Size & Shape effects ?**

Ultrafast dynamics of metallic Nanostructures



Outline

Electronic and Optical Properties of Metallic Nanostructures

Light-Matter Coherent Coupling

Femtosecond Pump-Probe spectroscopy

Ultrafast electronic dynamics in metallic nanostructures

Two-Photon Photoluminescence

Acoustic Vibrations

Electronic and Optical Properties of Metallic Nanostructures

Optics of Metals - The Drude Model

The properties of **metals** are mainly governed by **free electrons**

Free electrons can be described by the **Drude Model**

$$m_e \frac{\partial^2 \mathbf{r}}{\partial t^2} + m_e \gamma \frac{\partial \mathbf{r}}{\partial t} = e\mathbf{E_0} e^{-i\omega t}$$

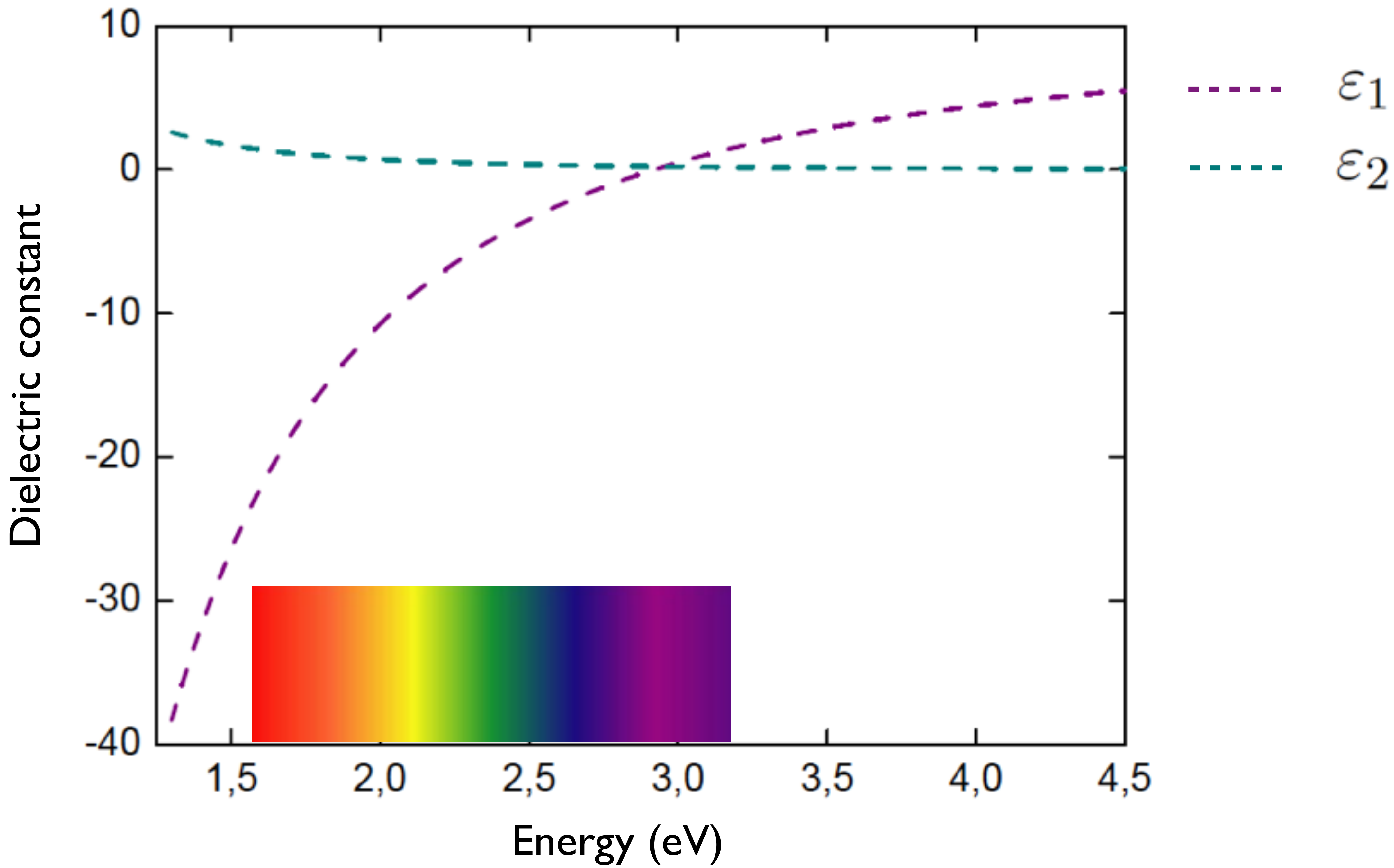
Electromagnetic response of a Material captured in its <u>**Dielectric constant**</u>

$$\varepsilon_{Drude} = \varepsilon_1 + i\ \varepsilon_2 = 1 - \frac{\omega_P^2}{\omega^2 + i\gamma\omega}$$

Gold : γ_{bulk} = 70 meV → Collision Time = 1/γ_{bulk} ~ **10 fs**

Silver : γ_{bulk} = 20 meV → Collision Time ~ **30 fs**

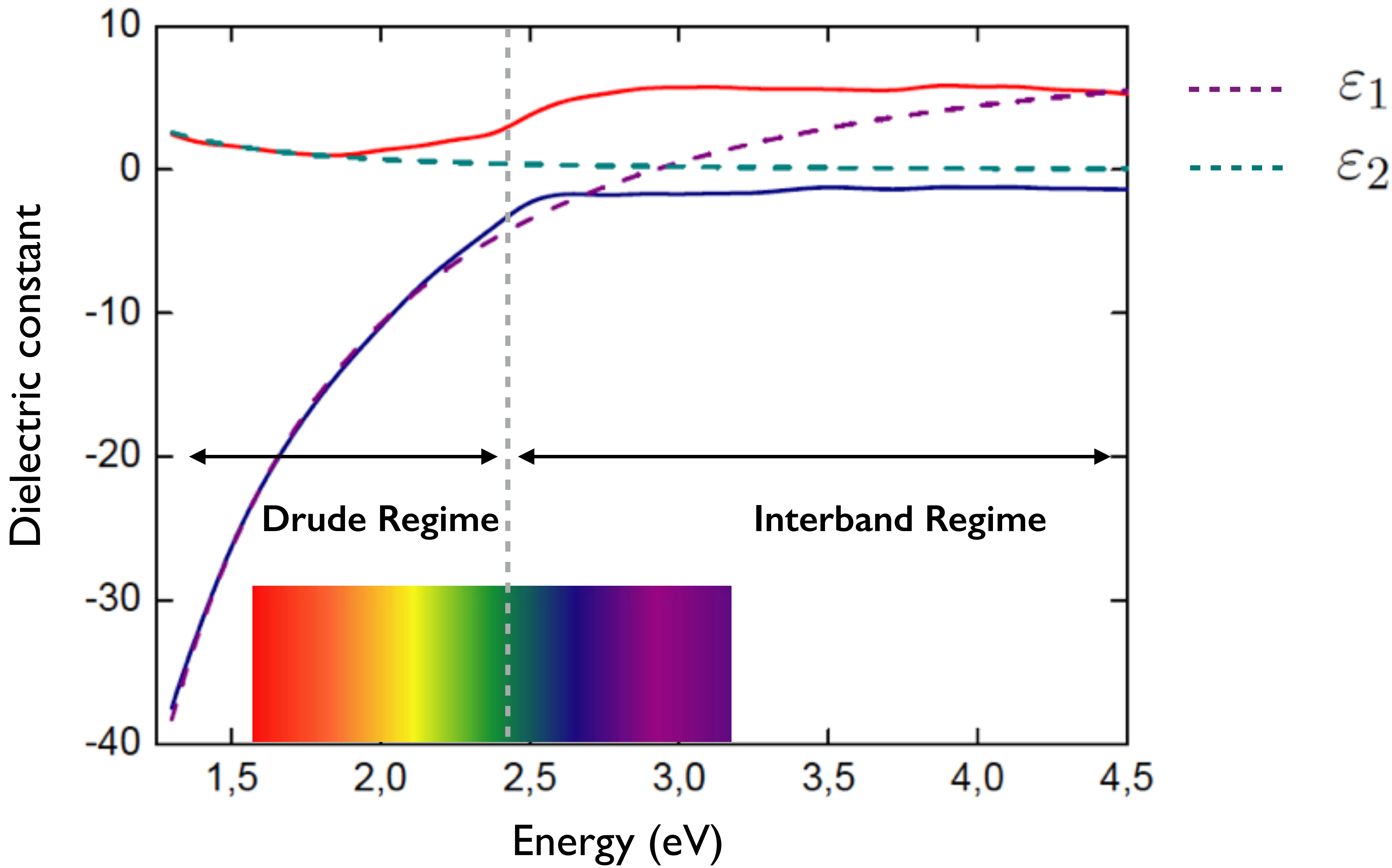
Drude model with values for Gold



Negative dielectric constant → Metals reflect light !

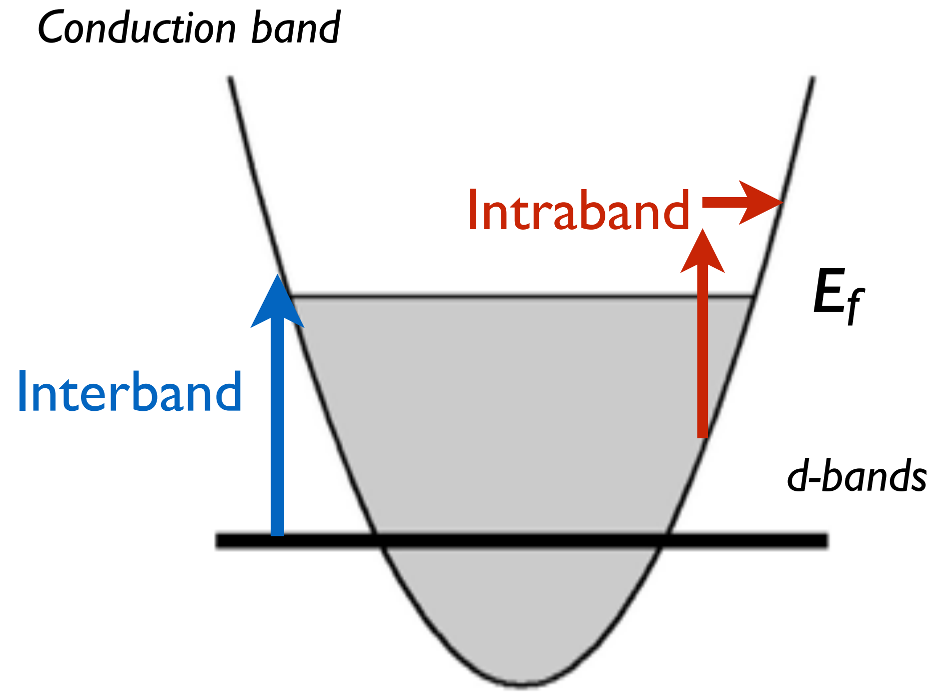
Noble metals : same conduction electrons but different colors ?

Drude model with values for Gold



Interband Transition threshold in Noble metals : **Cu** : 2.15 eV - **Au** : 2.4 eV - **Ag** : 4 eV

Different values → Different **colors** !



Noble metals (Ag, Au, ...)

Flat d-bands + quasi-free conduction electrons

Interband transition threshold : $\hbar\Omega_{ib} = 2.4\,\mathrm{eV}$ for Au

Dielectric constant:

$$\varepsilon_{bulk}(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega) = \varepsilon^{ib}(\omega) - \frac{\omega_P^2}{\omega(\omega + i\gamma_D)}$$

Interband — bound electrons

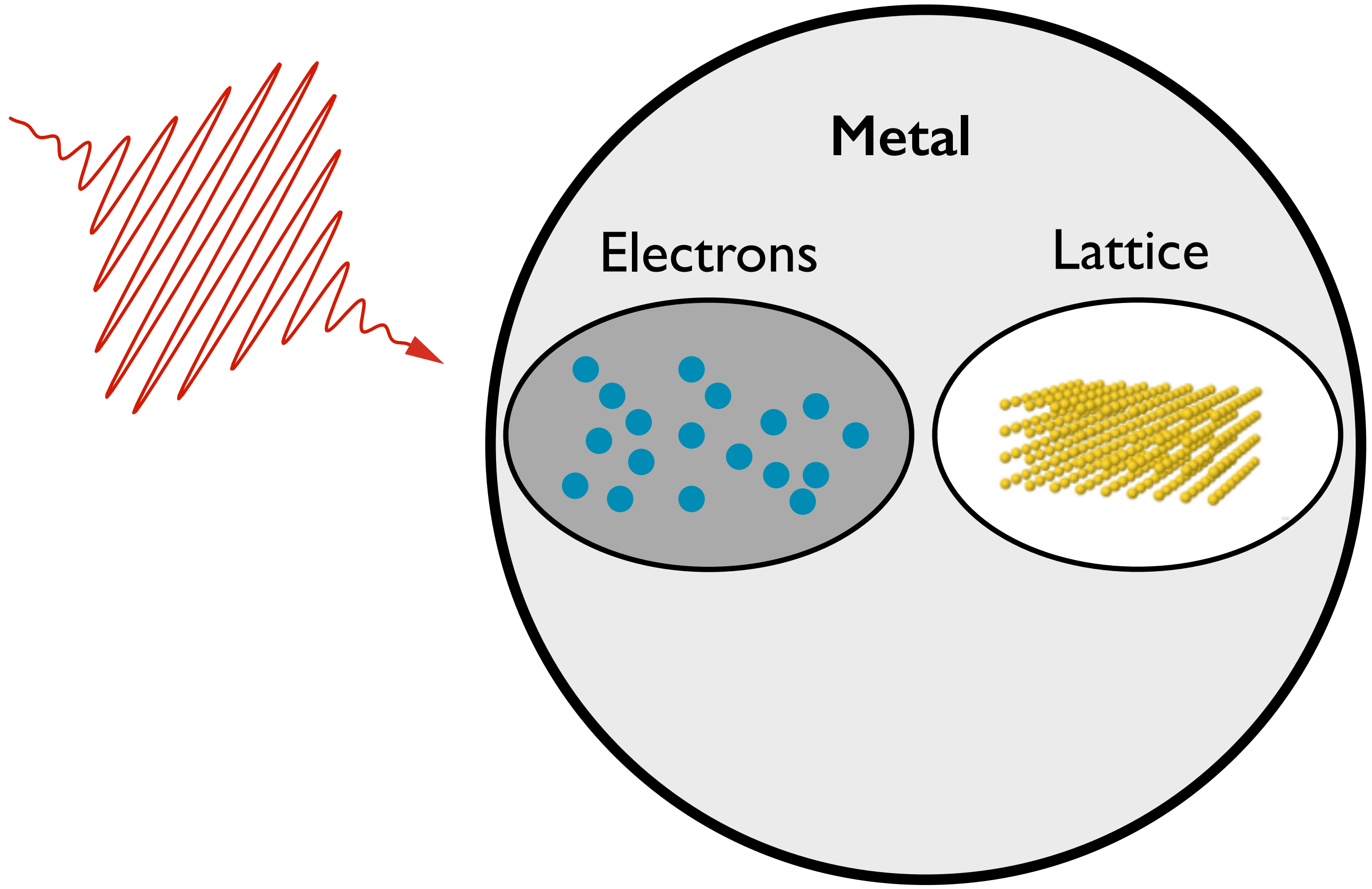
Intraband — Free electrons

Metal nanoparticles with sizes > 2 nm : $250 < N_{at} < 10^6$

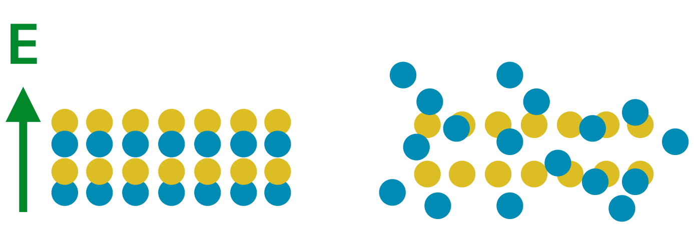
- ε^{ib} **unchanged**
- confinement : ↗ **scattering with surfaces** ⇒ increase in γ_D

Light-Matter Coherent Coupling

Ultrafast dynamics of metallic Nanostructures



Environment



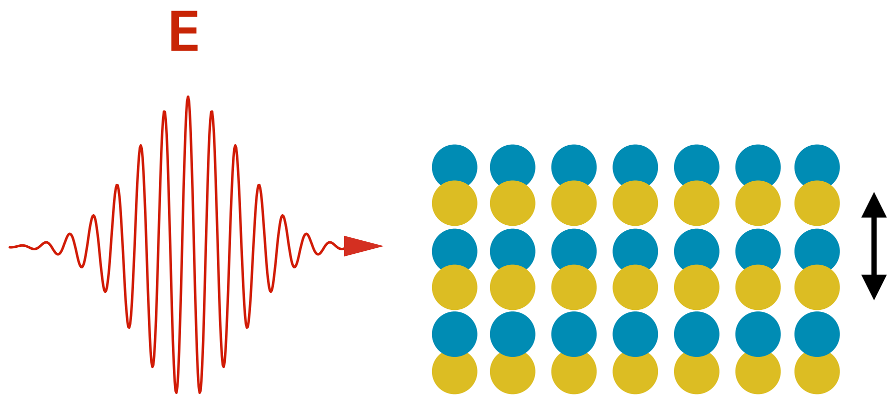
Coherent coupling

Plasmon Dephasing

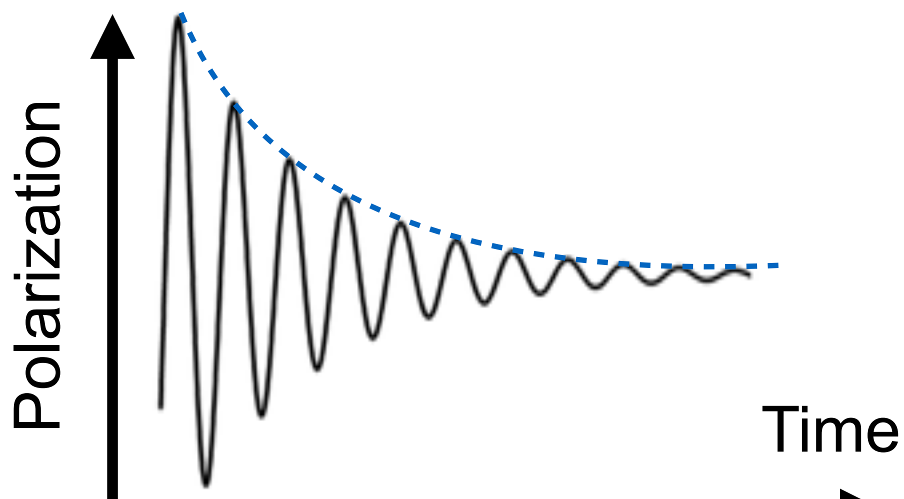
Surface Plasmon Quality factor and Dephasing time

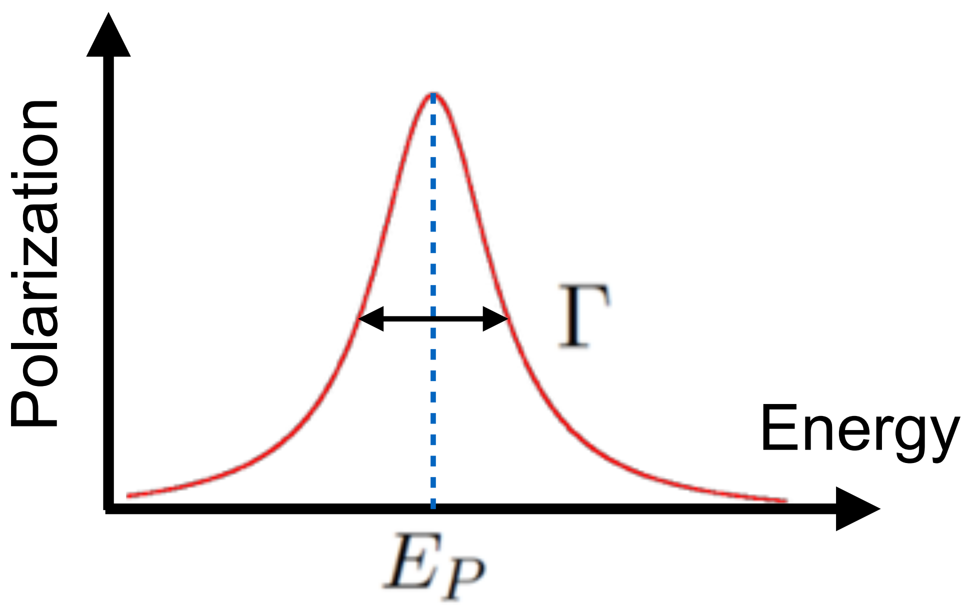
Interaction of incident EM wave and MNP is <u>initially coherent</u>

→ Phase relation between incident wave and electron gas density wave



Localized Surface Plasmon = <u>Damped harmonic oscillators</u>





Quality factor Q → Number of plasmon oscillations before damping

$$Q = \frac{E_P}{\Gamma}$$

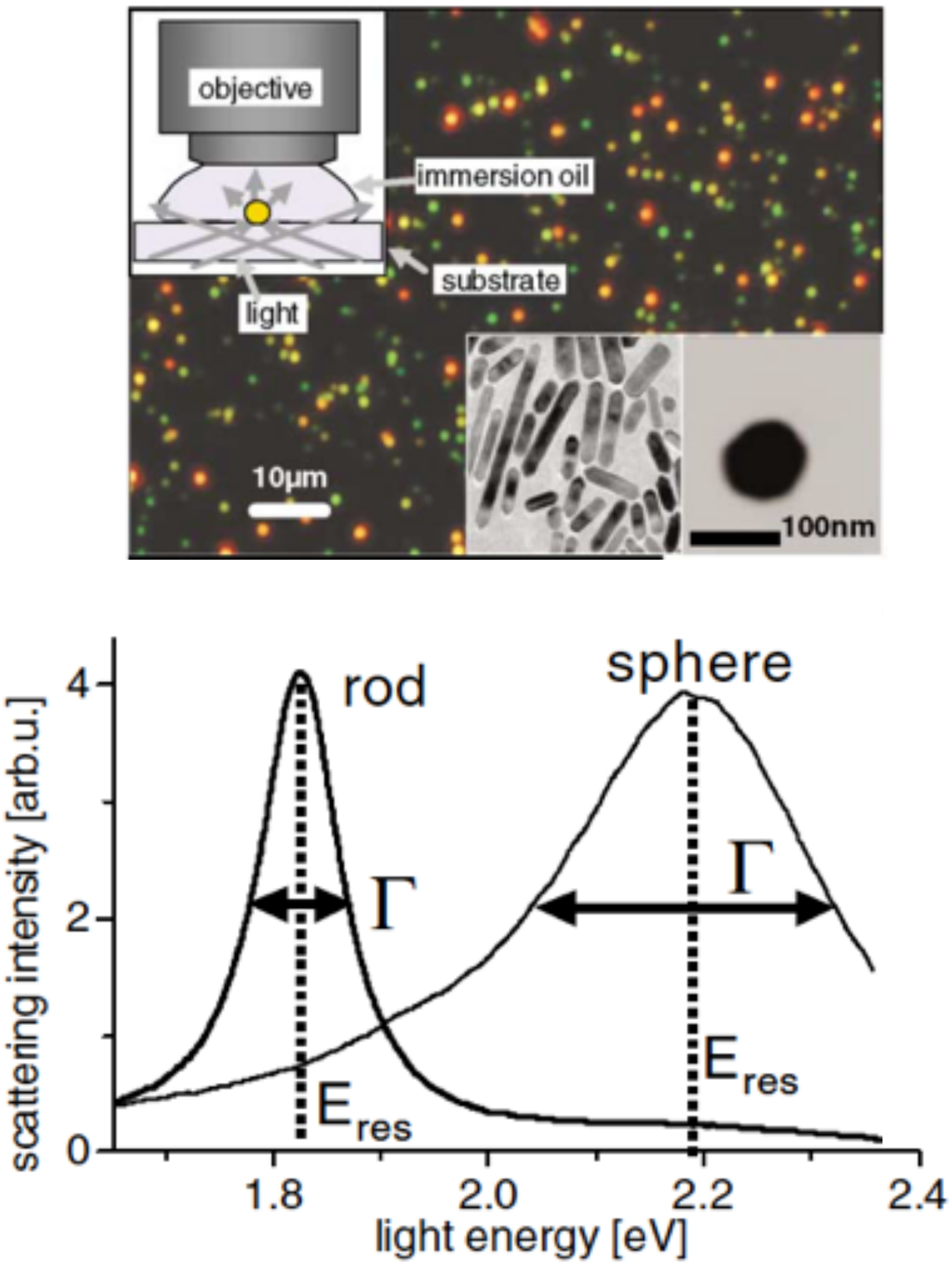
$$T_2 = \frac{2\hbar}{\Gamma}$$

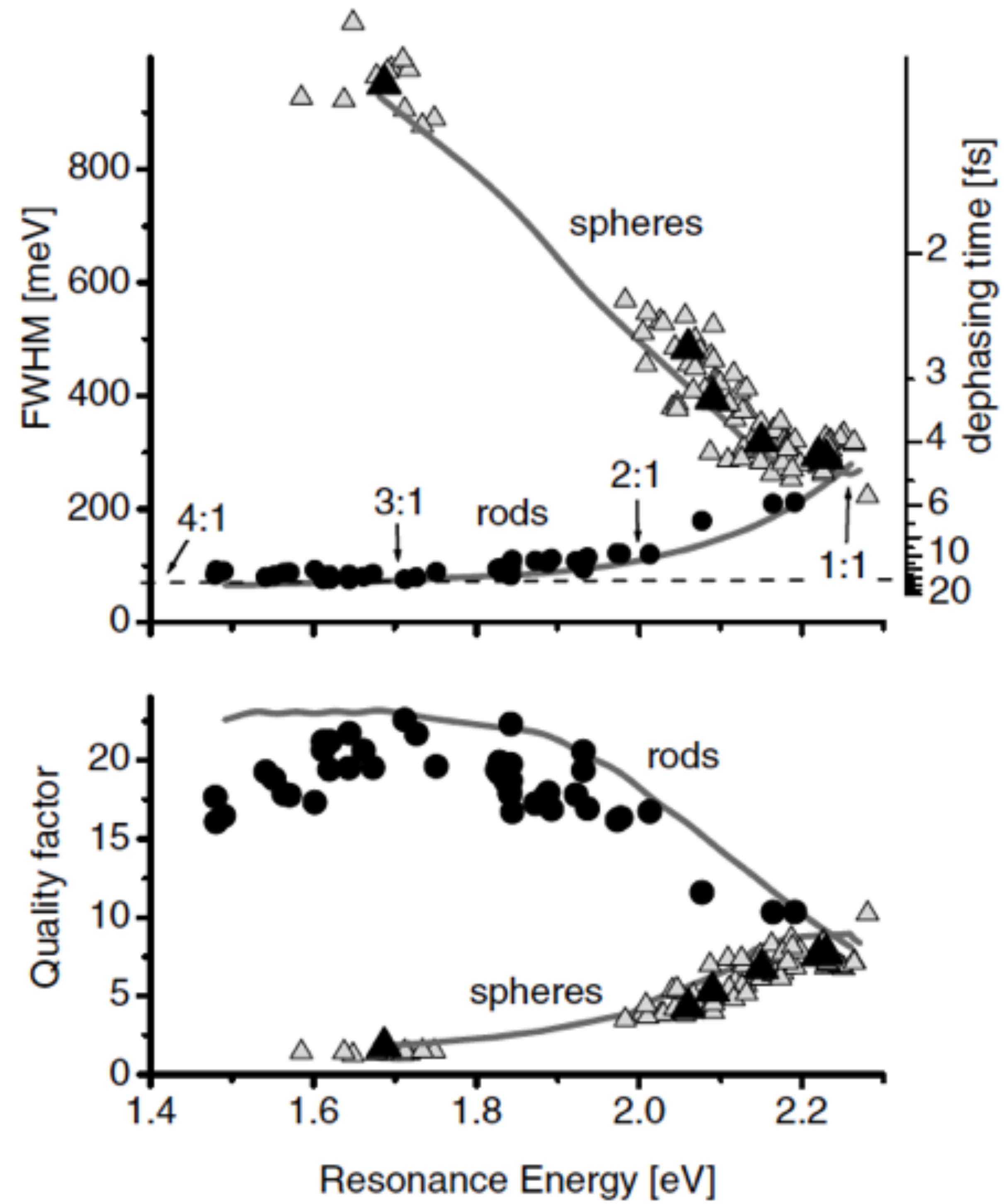
To get rid of <u>inhomogeneous</u> broadening → Spectroscopy of <u>individual</u> particles

Frequency-Resolved study of Surface Plasmon Dephasing time

Dark-Field Optical spectroscopy on <u>individual</u> nano-objects

Sönnichsen et al, *PRL*, 88, 077402, **2002**





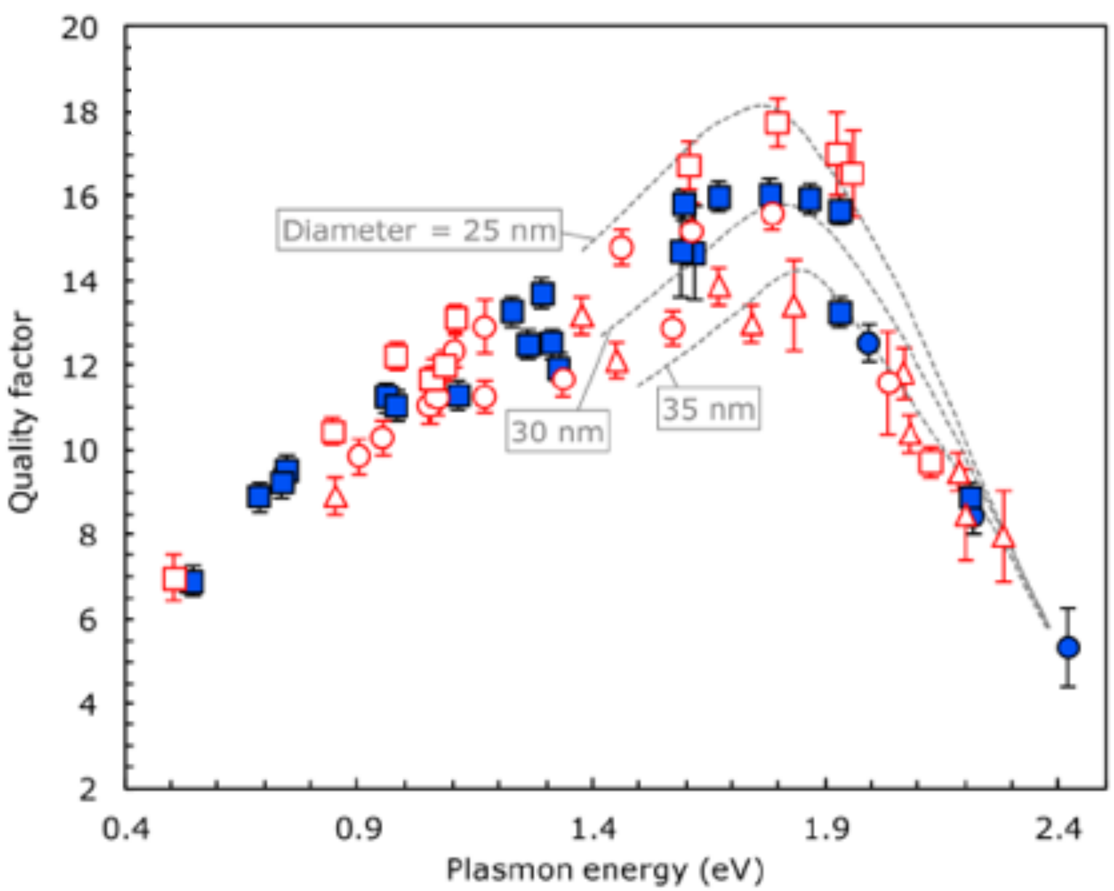
→ **Surface Plasmon dephasing Time ∝ 1-20 fs**

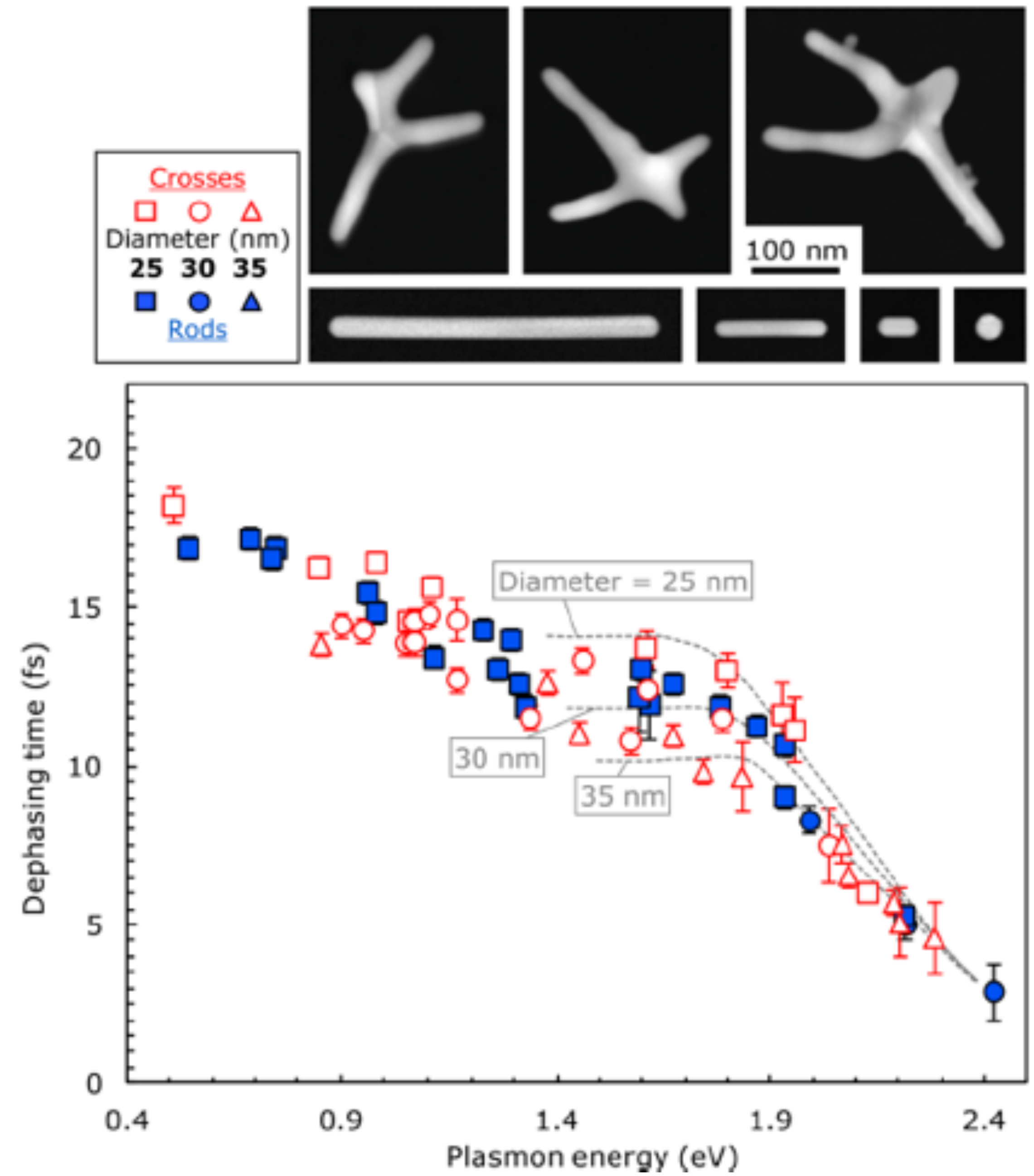
→ **Smaller dephasing rate <u>away from Interband Transitions</u> and for <u>small volumes</u>**

Measuring Plasmon line width in (S)TEMs → Highly <u>monochromatic</u> electron beam

Mono-λ FEI Titan Schottky, 70 meV FWHM

M. Bosman, IMRE, Singapore

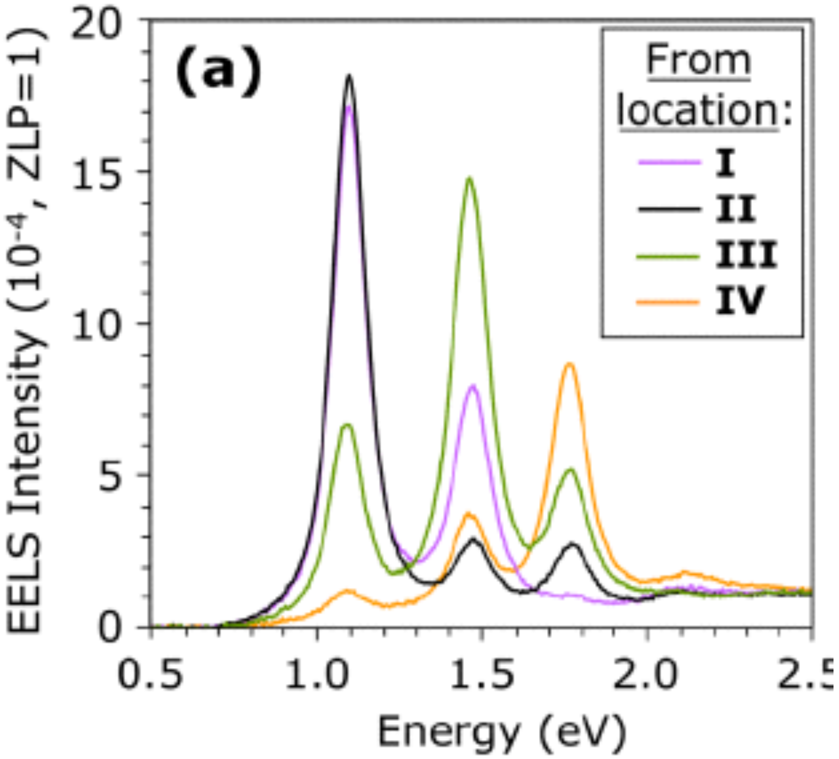




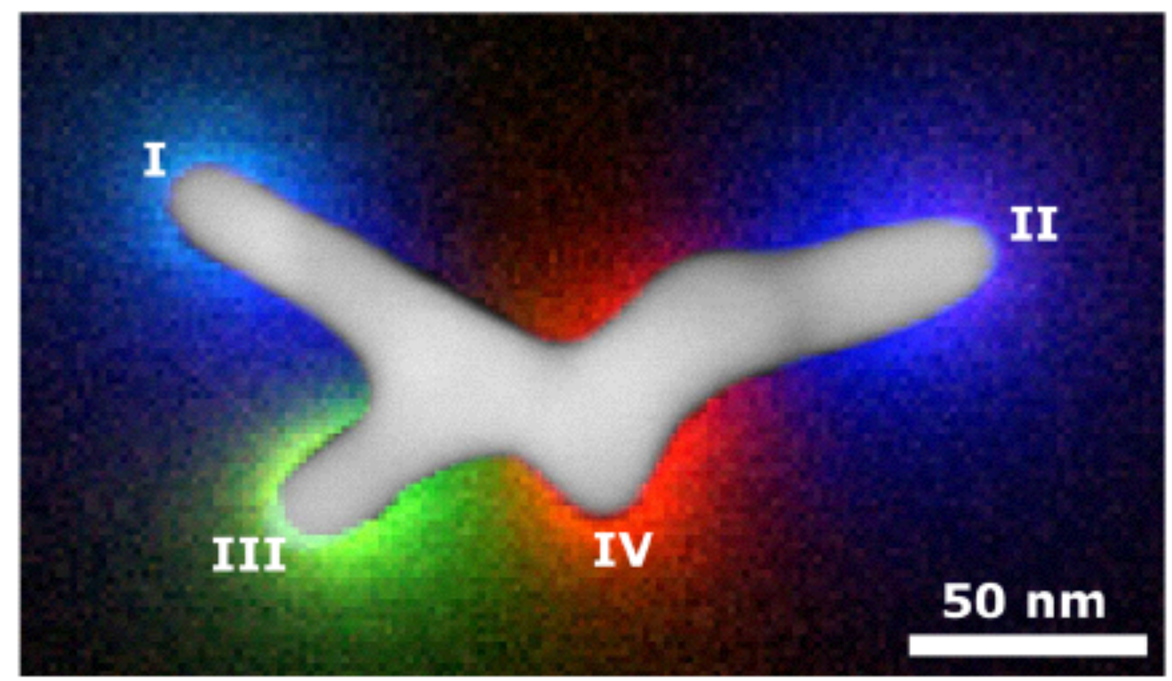
→ Surface Plasmon Damping depends on plasmon <u>Energy</u> not particle <u>Shape !</u>

Bosman et al, *Scientific Reports* 3, 1312, **2012**

High monochromaticity + Spatial Resolution



Q-factor		T_2 (fs)
12.4 ±0.36		14.8 ±0.40
14.8 ±0.33		13.4 ±0.32
15.0 ±0.20		11.2 ±0.22



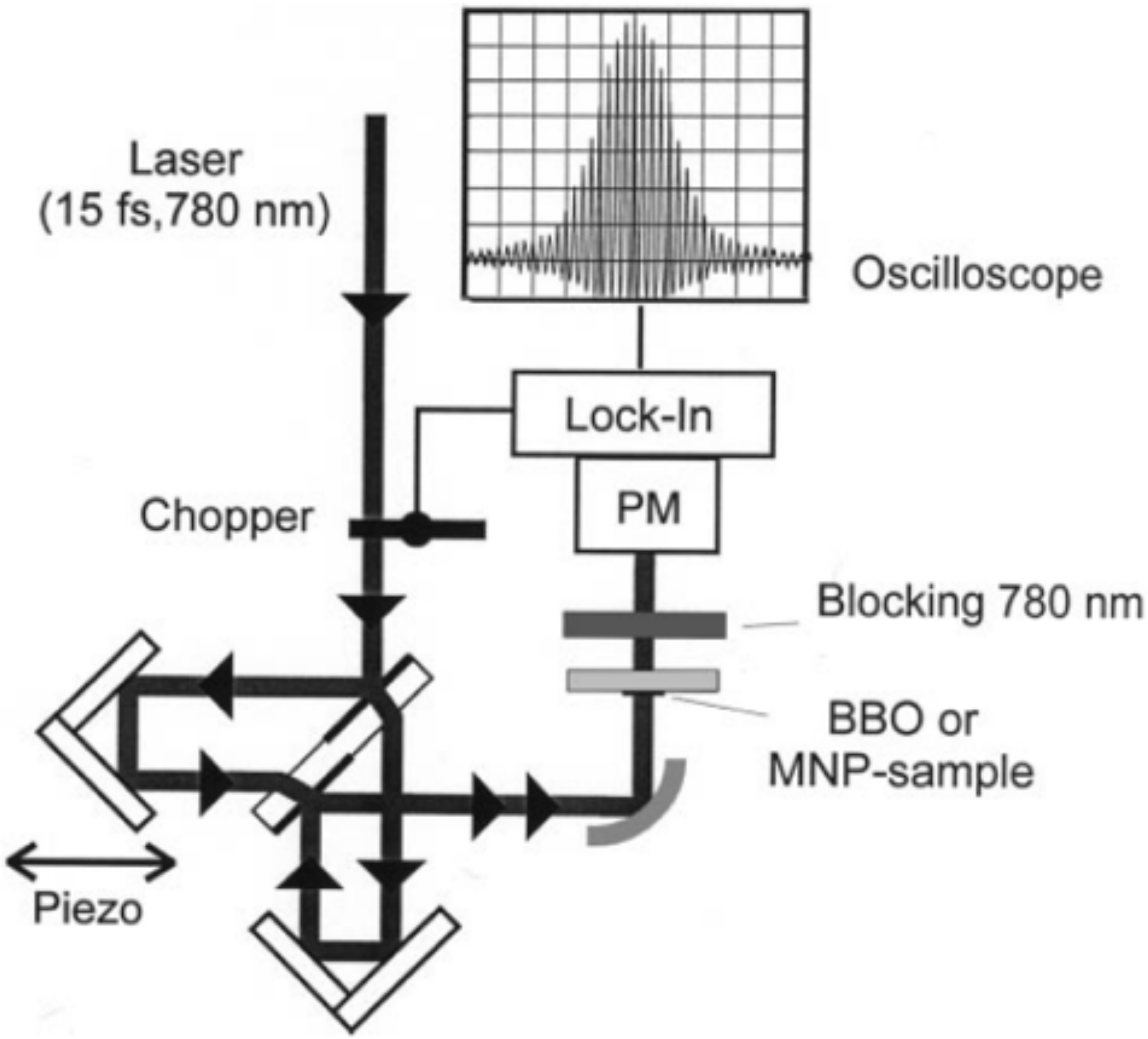
→ **Surface Plasmon Damping mapped within a nanostructure**

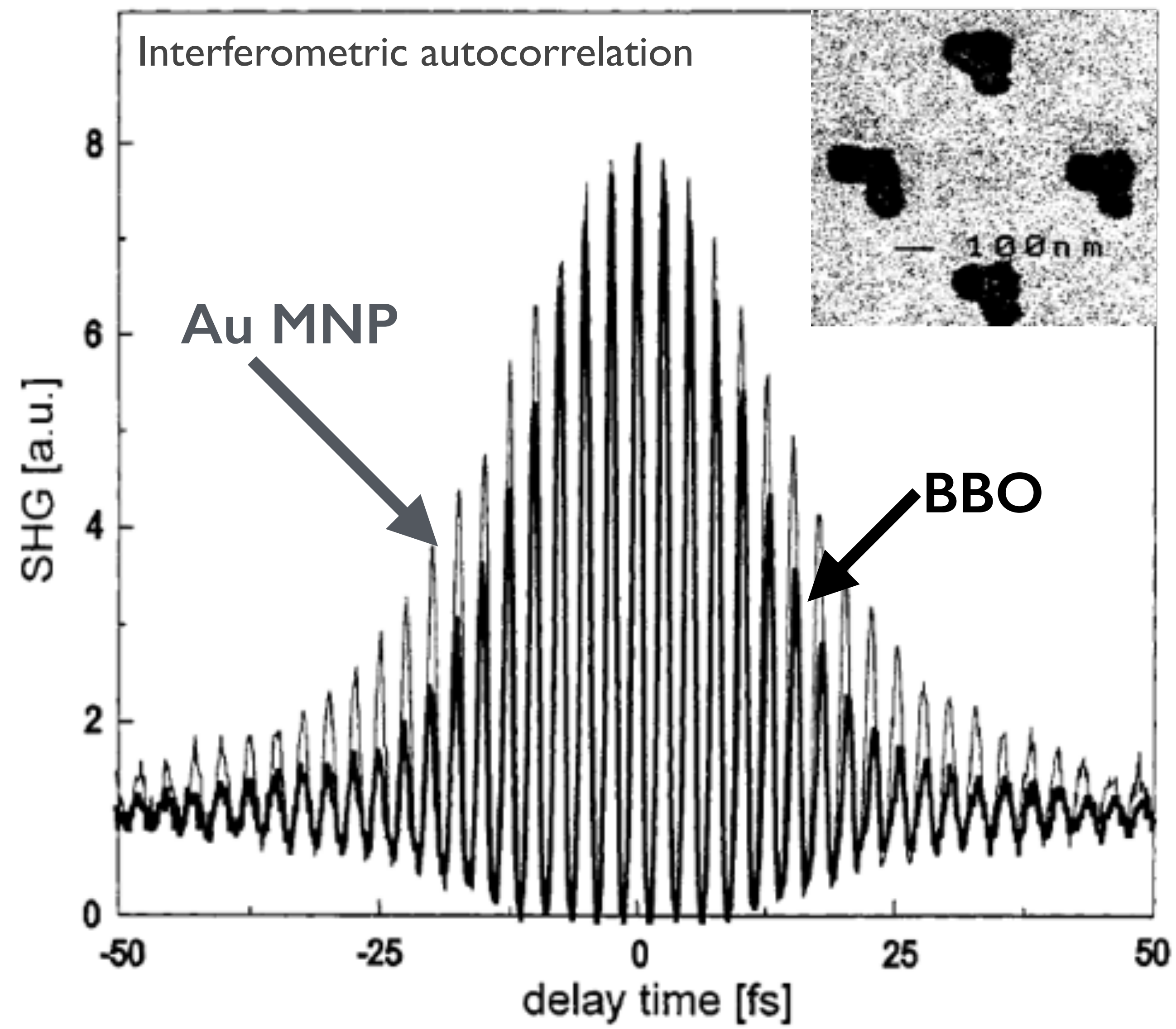
Bosman et al, *Scientific Reports* 3, 1312, **2012**

Time-Resolved Measurement of Surface Plasmon Damping using SHG

Time-Resolved studies of plasmon dephasing require ultrashort pulses (< 15 fs)

SHG Lambrecht et al, Appl. Phys. B 68, 419–423, **1999**
THG Lambrecht et al, Phys. Rev. Lett., 83, 4421, **1999**
FROG: Anderson et al, *Nanoletters*, 10, 2519 **2010**





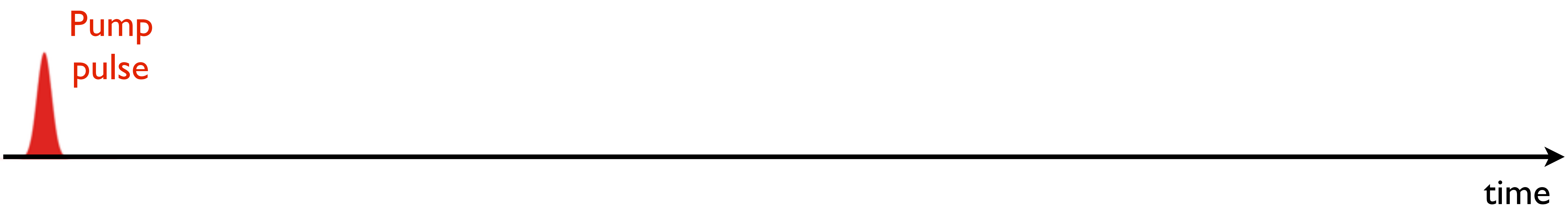
→ **Surface Plasmon dephasing Time: 6 fs (Au) 7 fs (Ag)**

Lambrecht et al, Appl. Phys. B 68, 419–423, **1999**

Femtosecond Pump-Probe Spectroscopy

Principle of pump-probe experiments

✓ **Reproducible process**



Principle of pump-probe experiments

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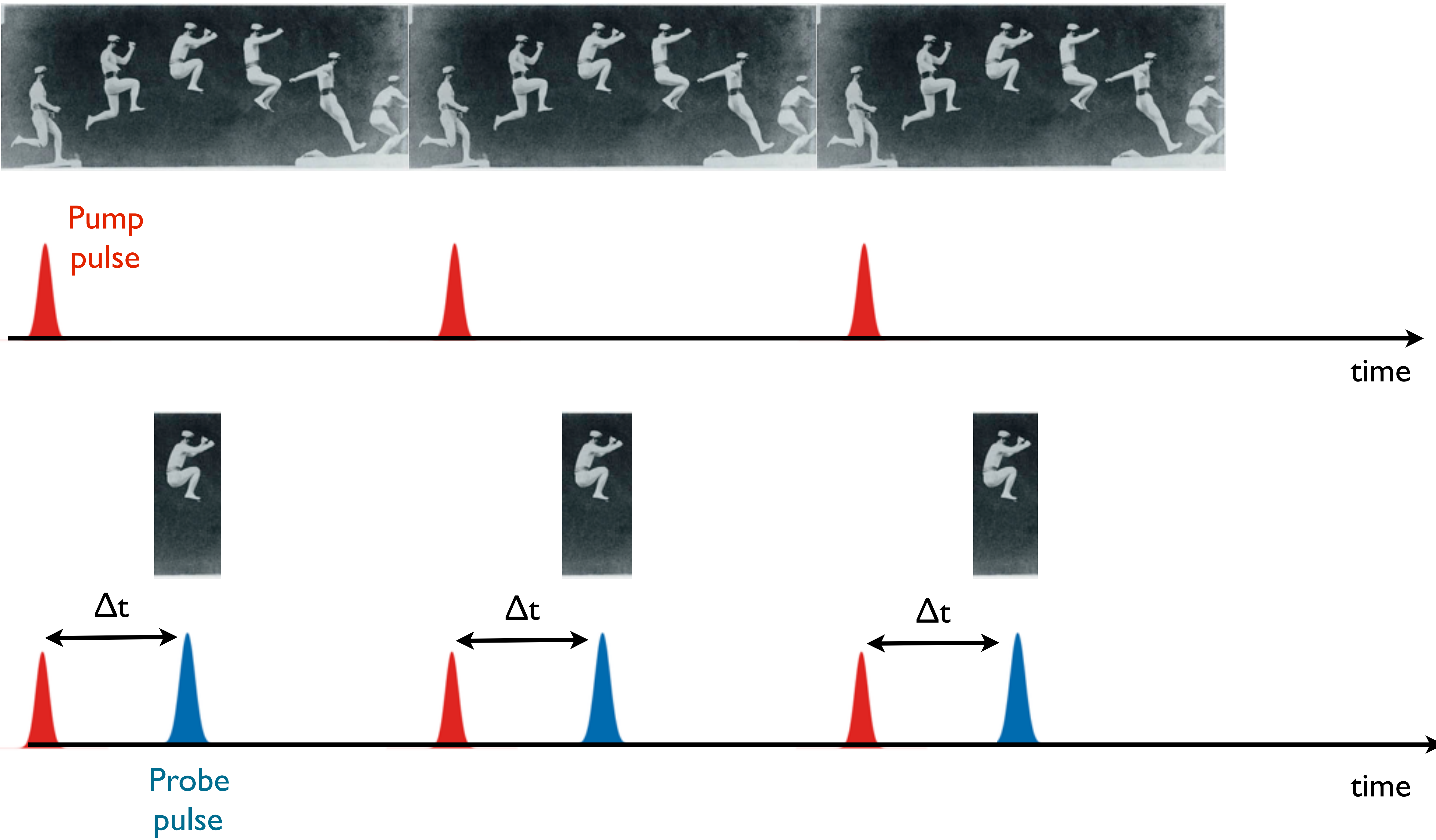

Principle of pump-probe experiments

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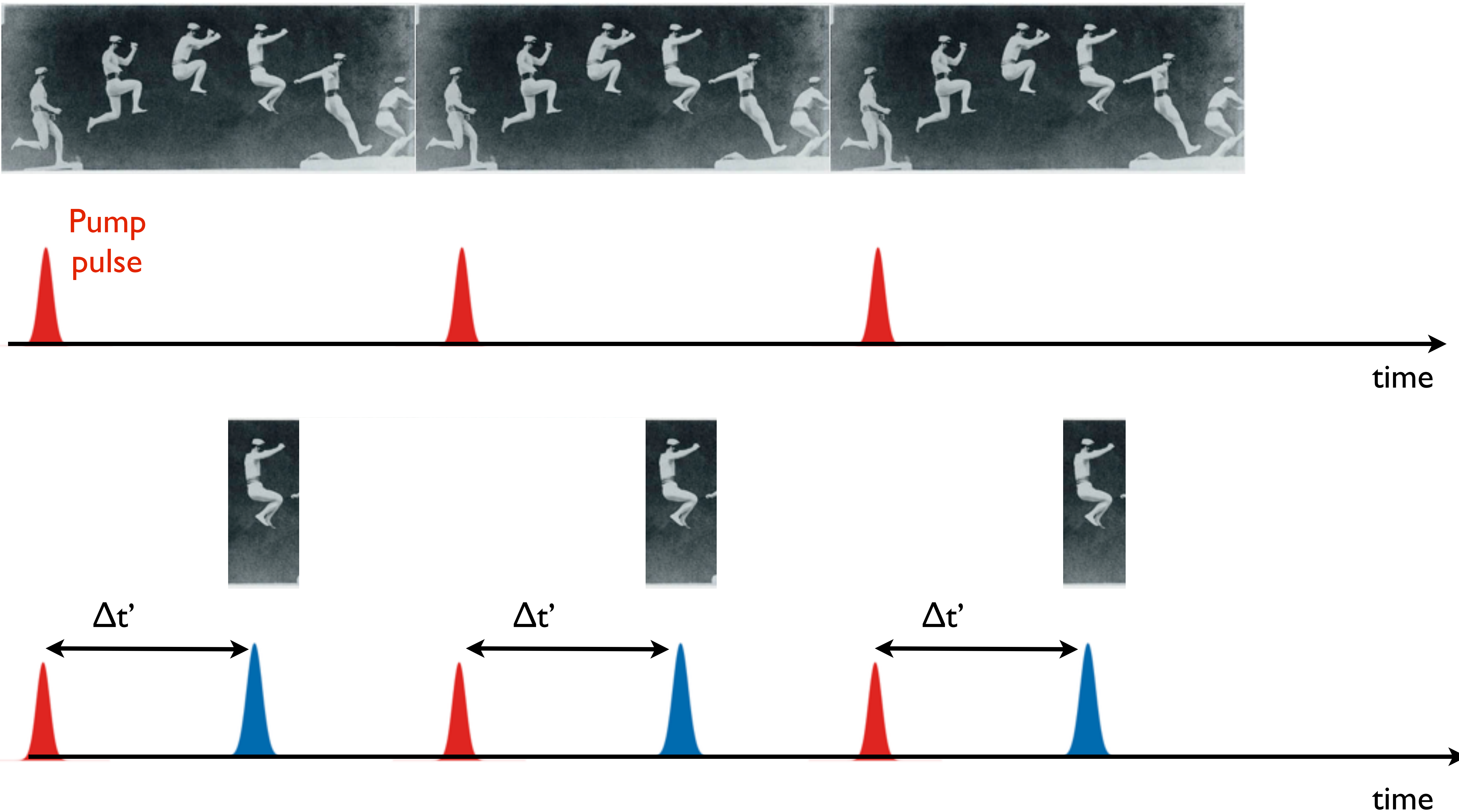
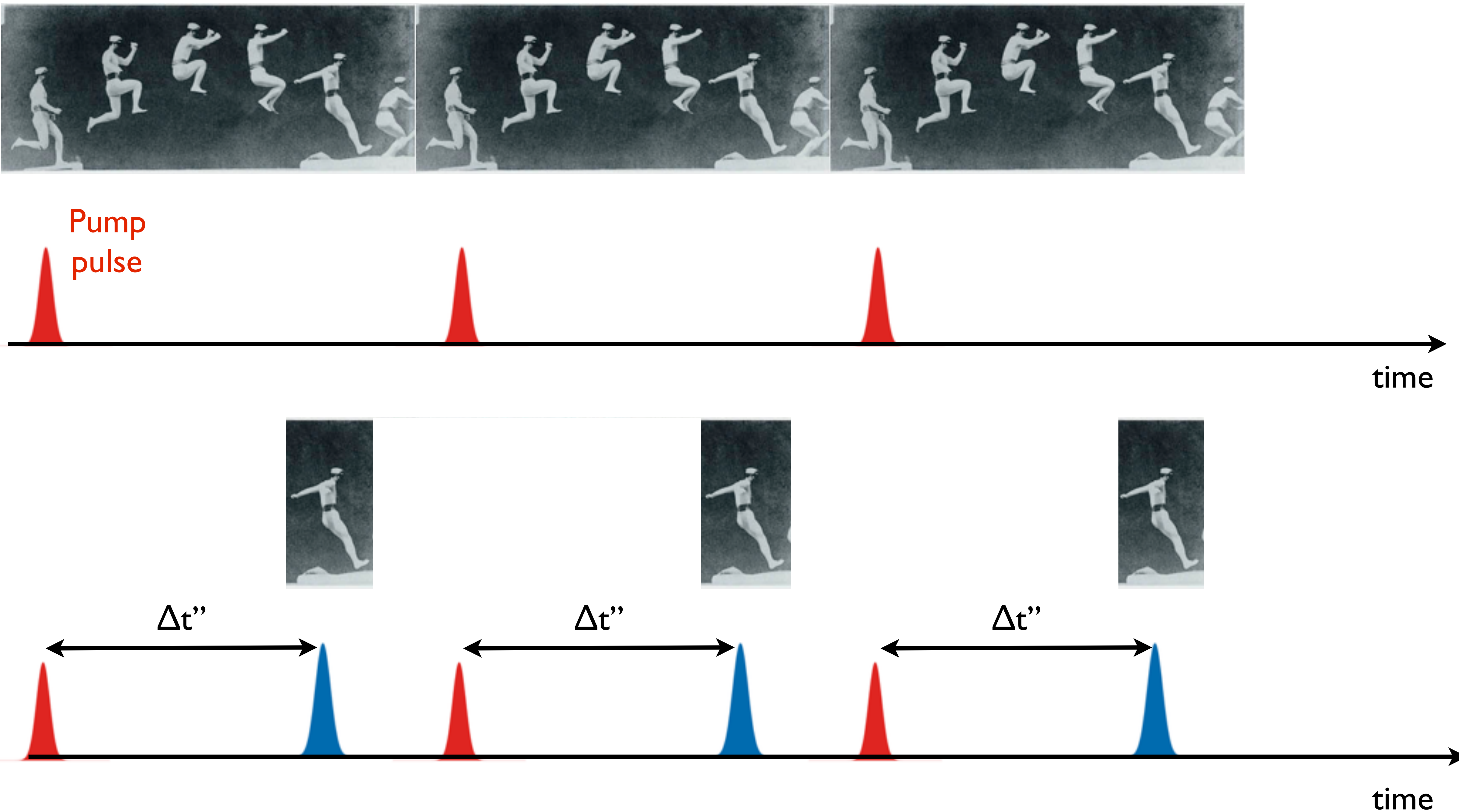
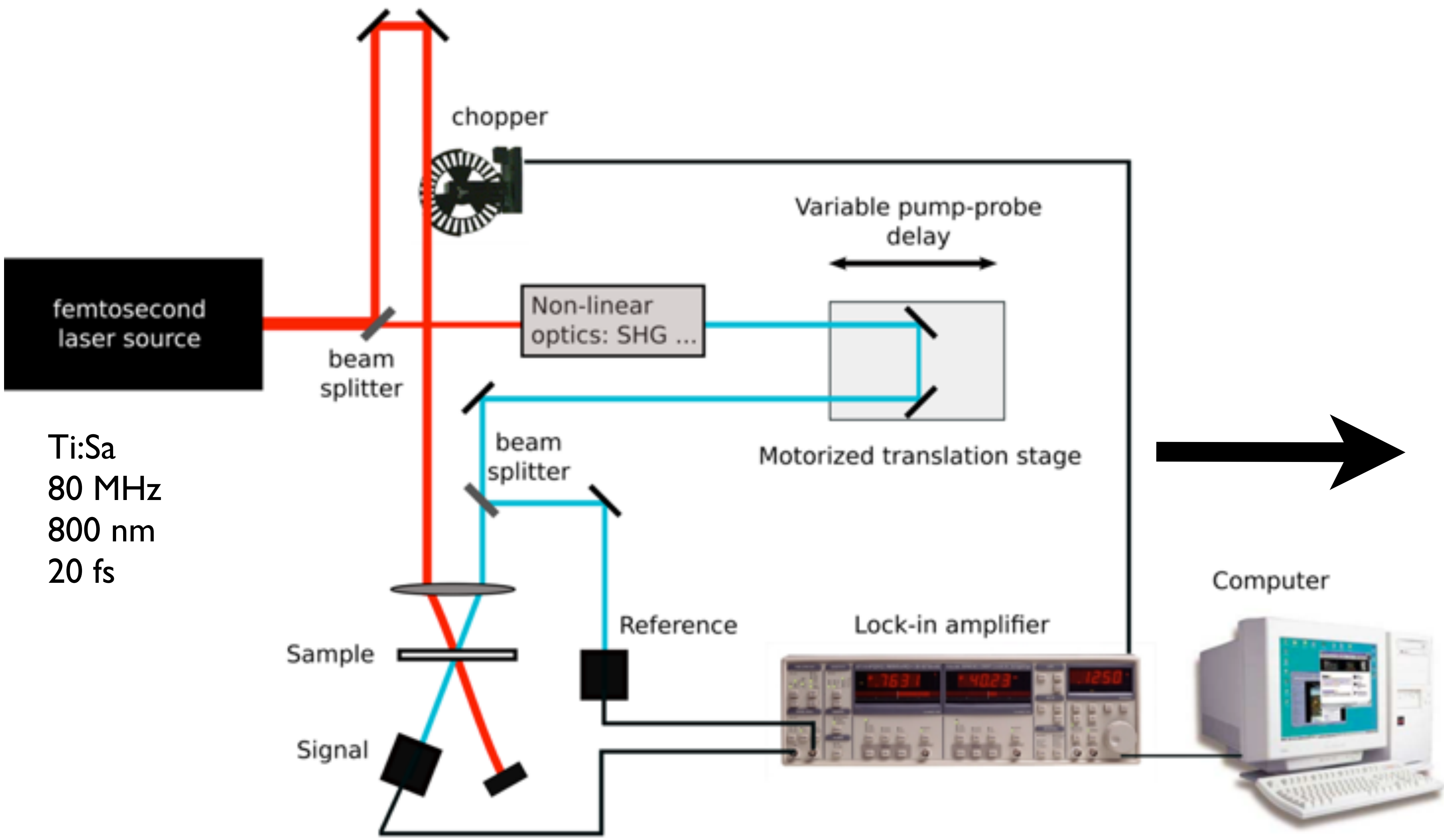


Principle of pump-probe experiments

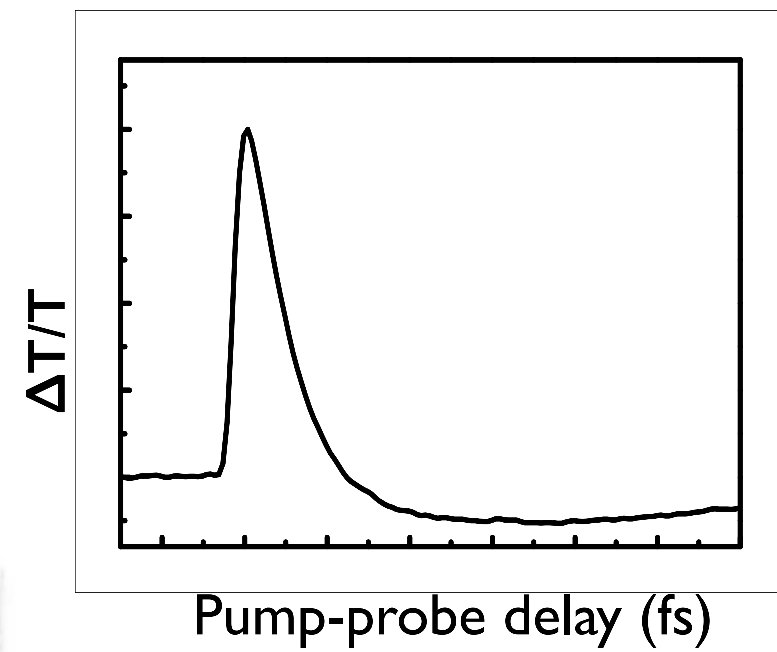
✓ **Reproducible process**



Femtosecond Pump-Probe Spectroscopy

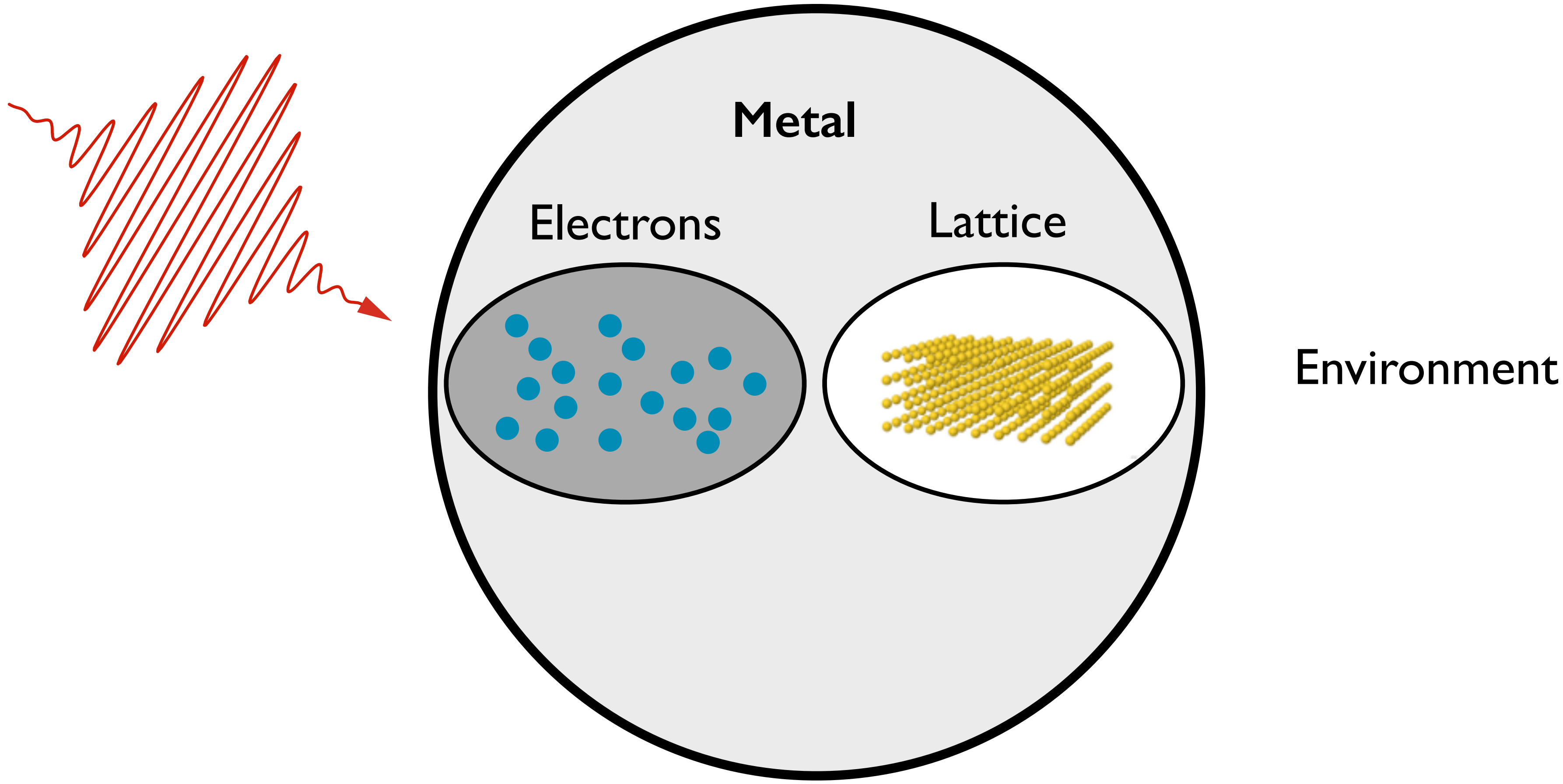


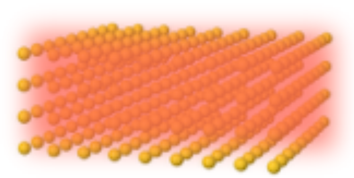
$\Delta T/T \sim 10^{-6} - 10^{-7}$



Ultrafast Electron Dynamics

Ultrafast dynamics of metallic Nanostructures





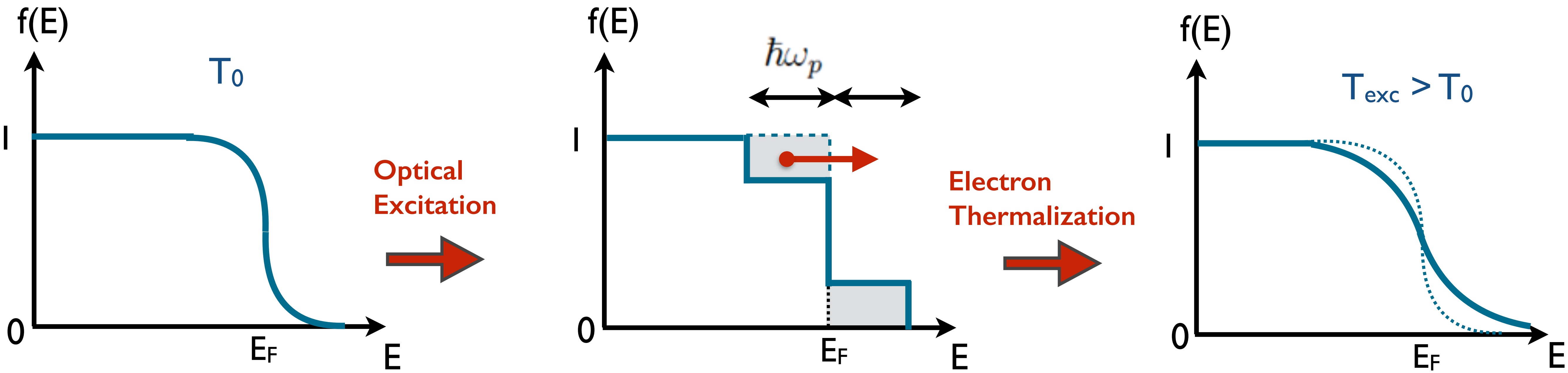
Electron Thermalization

Electron-Lattice Thermalization

0 fs | 10 fs | 100 fs | 1 ps | 10 ps | 100 ps | Time

The dephasing of the plasmon (~10 fs) yields an ensemble of electron-hole pairs

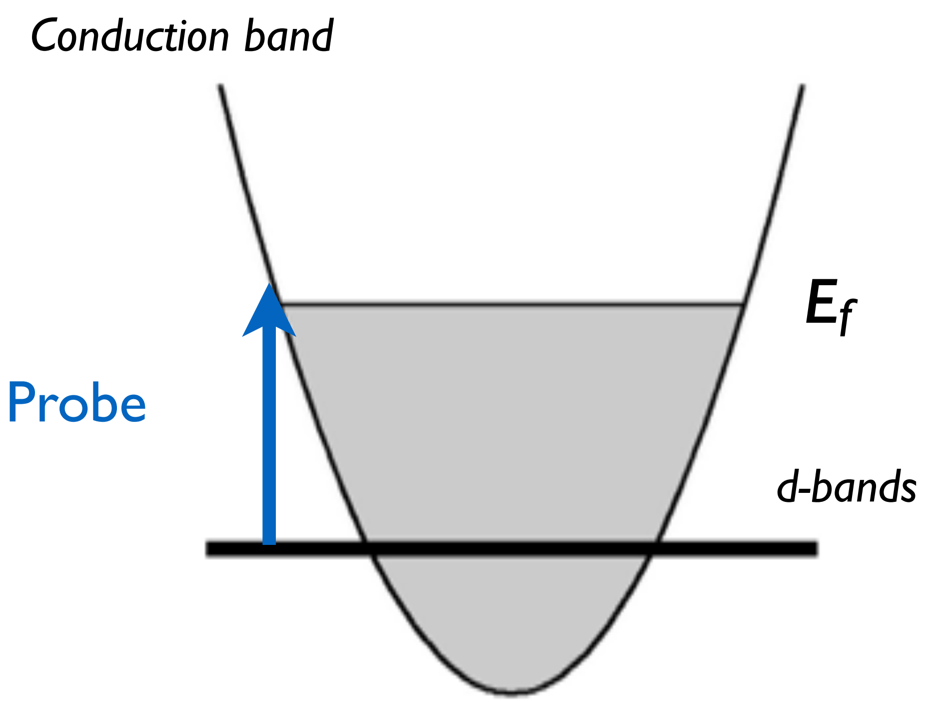
→ Athermal electronic distribution

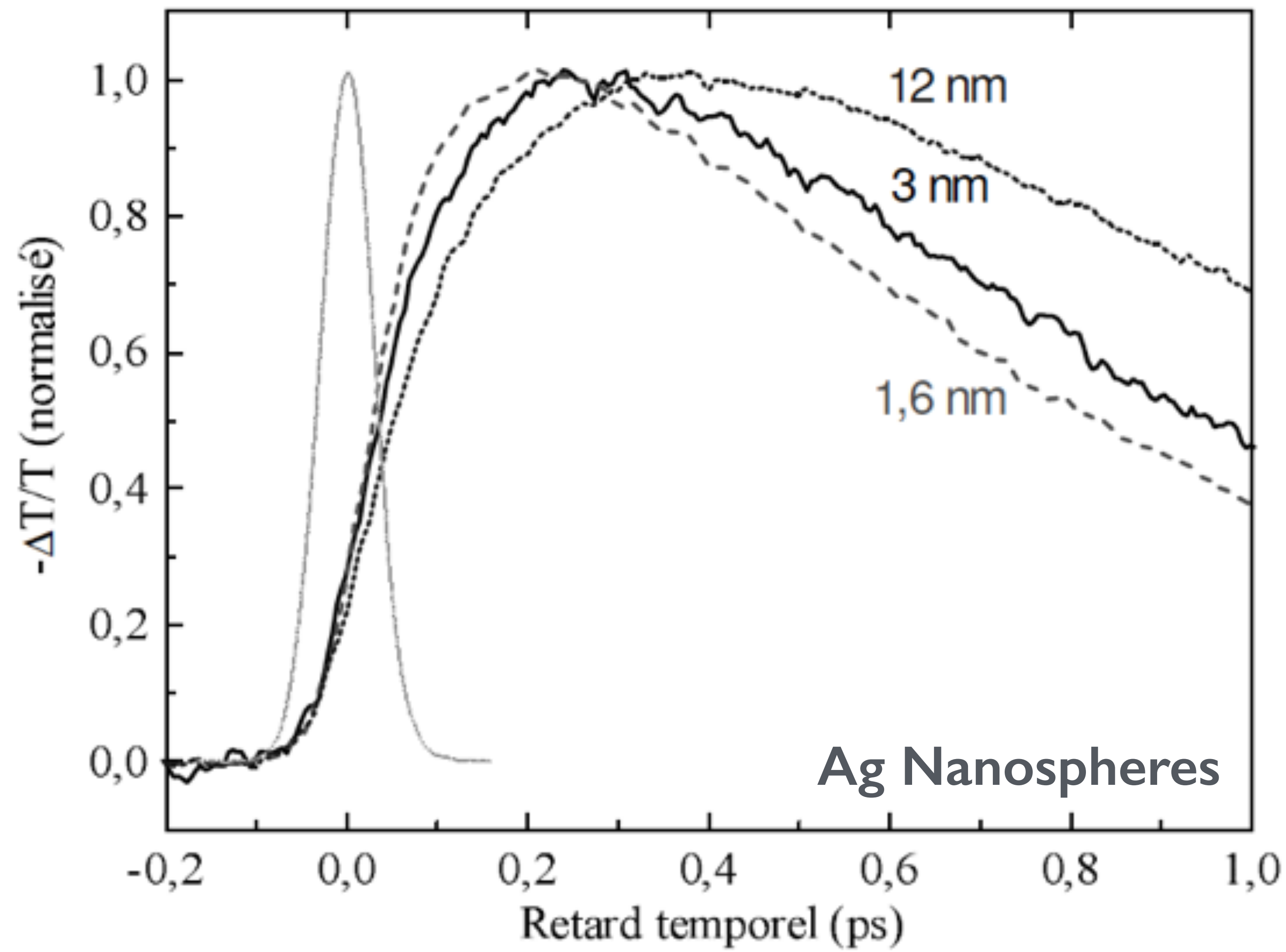


→ Internal thermalization of electron gas is mediated by electron-electron interactions

To selectively address electron internal thermalization

→ Probe <u>resonant</u> with <u>interband transitions</u>

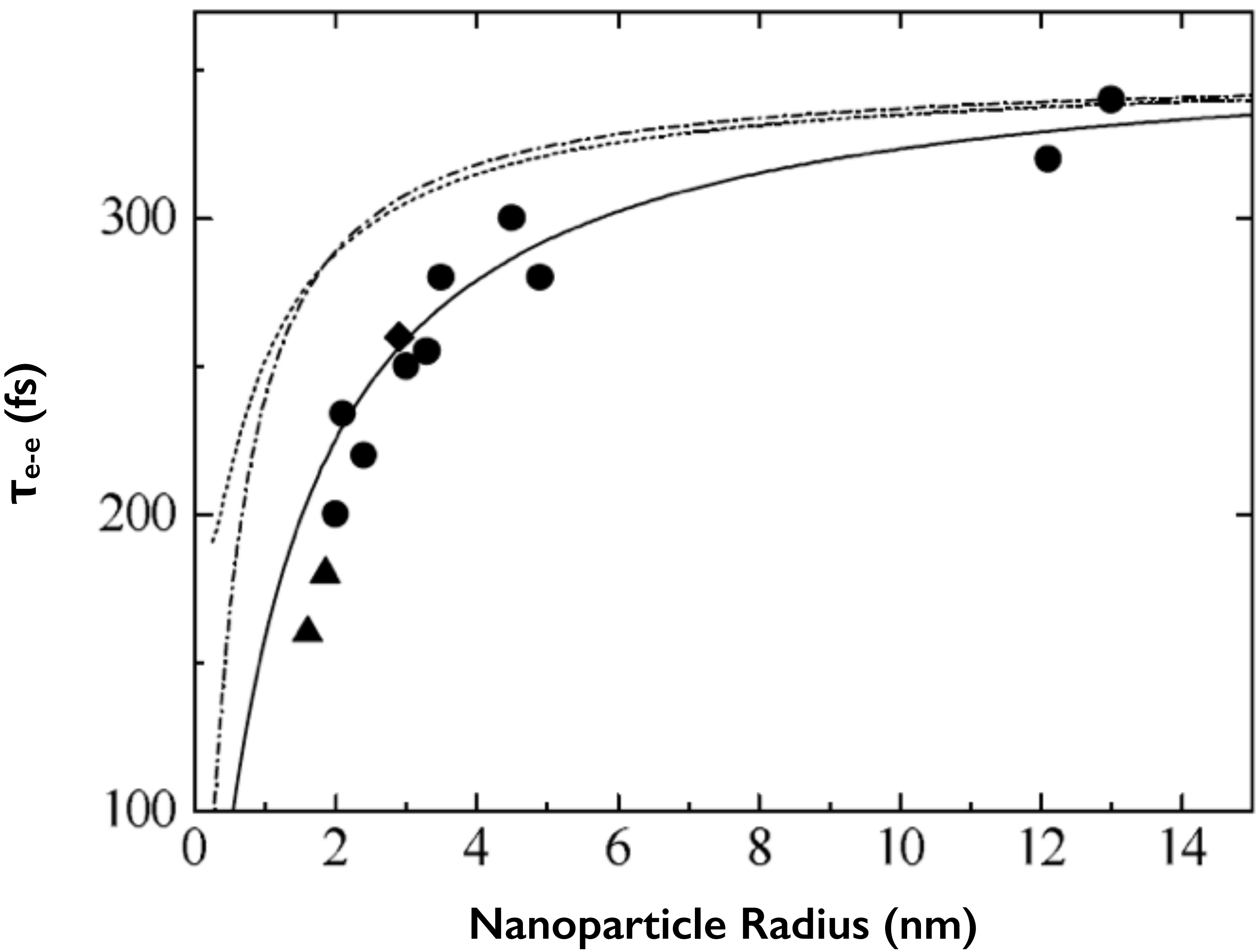




→ Acceleration of electronic thermalization in small nanoparticles

Christophe Voisin, PhD, **2001**

Voisin et al. Phys. Rev. Lett. 85, 2200, **2000**



Bulk Ag: 350 fs
Bulk Au: 500 fs

→ **Acceleration of electronic thermalization in small nanoparticles**

→ **Less efficient screening of Coulomb interaction close to surfaces**

Christophe Voisin, PhD, **2001**

Voisin et al. Phys. Rev. Lett. 85, 2200, **2000**

The Two-Temperature Model

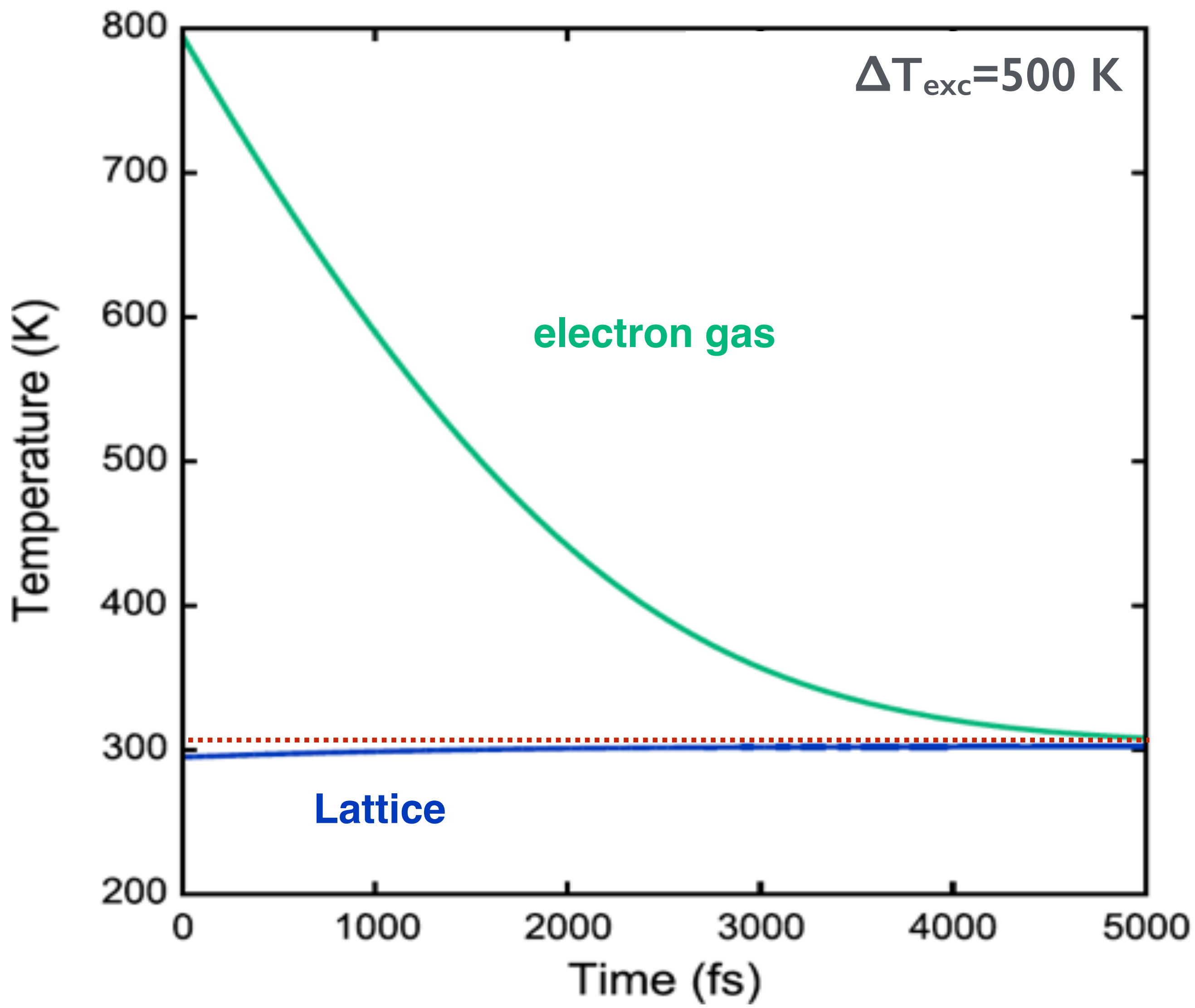
After a few hundreds fs, the electron gas is **thermalized** but **hotter** than lattice

The **Two-Temperature Model** assumes that electron gas and Lattice are **separately thermalized**

$$C_e \frac{dT_e}{dt} = \gamma T_e \frac{dT_e}{dt} = -G(T_e - T_L)$$

$$C_L \frac{dT_L}{dt} = G(T_e - T_L)$$

↑ electron-phonon coupling constant



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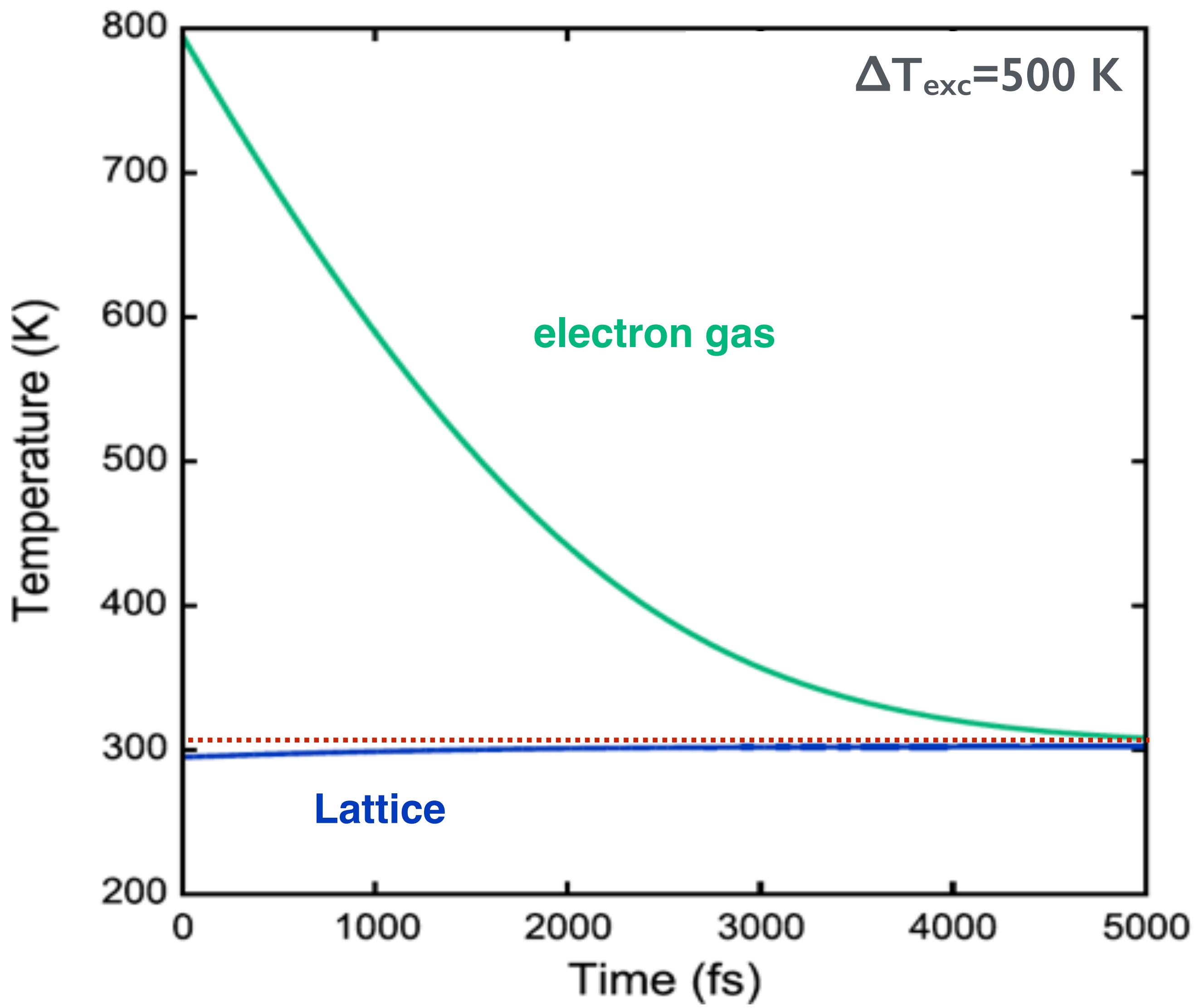


Weak perturbation: $\Delta T_{exc} = T_e(0) - T_L \ll T_L$

Monoexponential decrease of :

- *Electronic temperature* T_e
- *Excess electronic energy* Δu_e:

$$\Delta u_e(t) \approx C_e(T_o)(T_{exc} - T_L)\, e^{-t/\tau_{e-ph}}$$

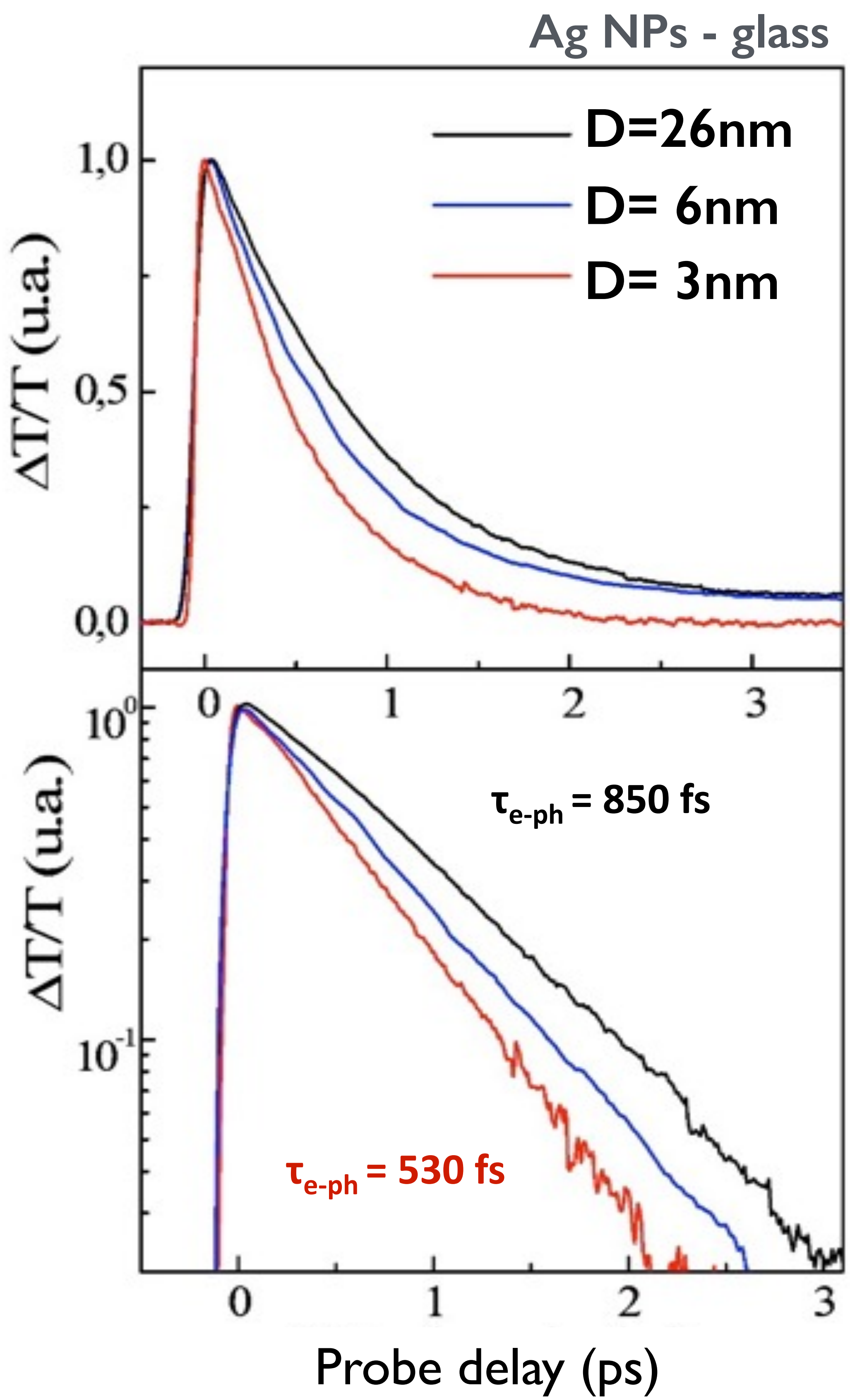
Electron-Lattice Thermalization characteristic Time:

$$\tau_{e-ph} \approx \frac{C_e(T_o)}{G}$$

Probe not resonant with interband transitions ($\omega_{pr} << \Omega_{ib}$)

$$\Delta T/T \propto \Delta u_e$$

→ **Energy stored in electron gas**



Systematic studies as a function of size

→**Decrease of τ_{e-ph} with nanoparticle size**

See also: Studies by Hartland, Aeschlimann, Bigot….

Arbouet et al. Phys. Rev. Lett. 90, 177401, **2003**

Electron-lattice characteristic coupling time: Size dependence

Systematic investigation: size, environment…

τ_{e-ph} **independent** from:

- environment
- Fabrication process

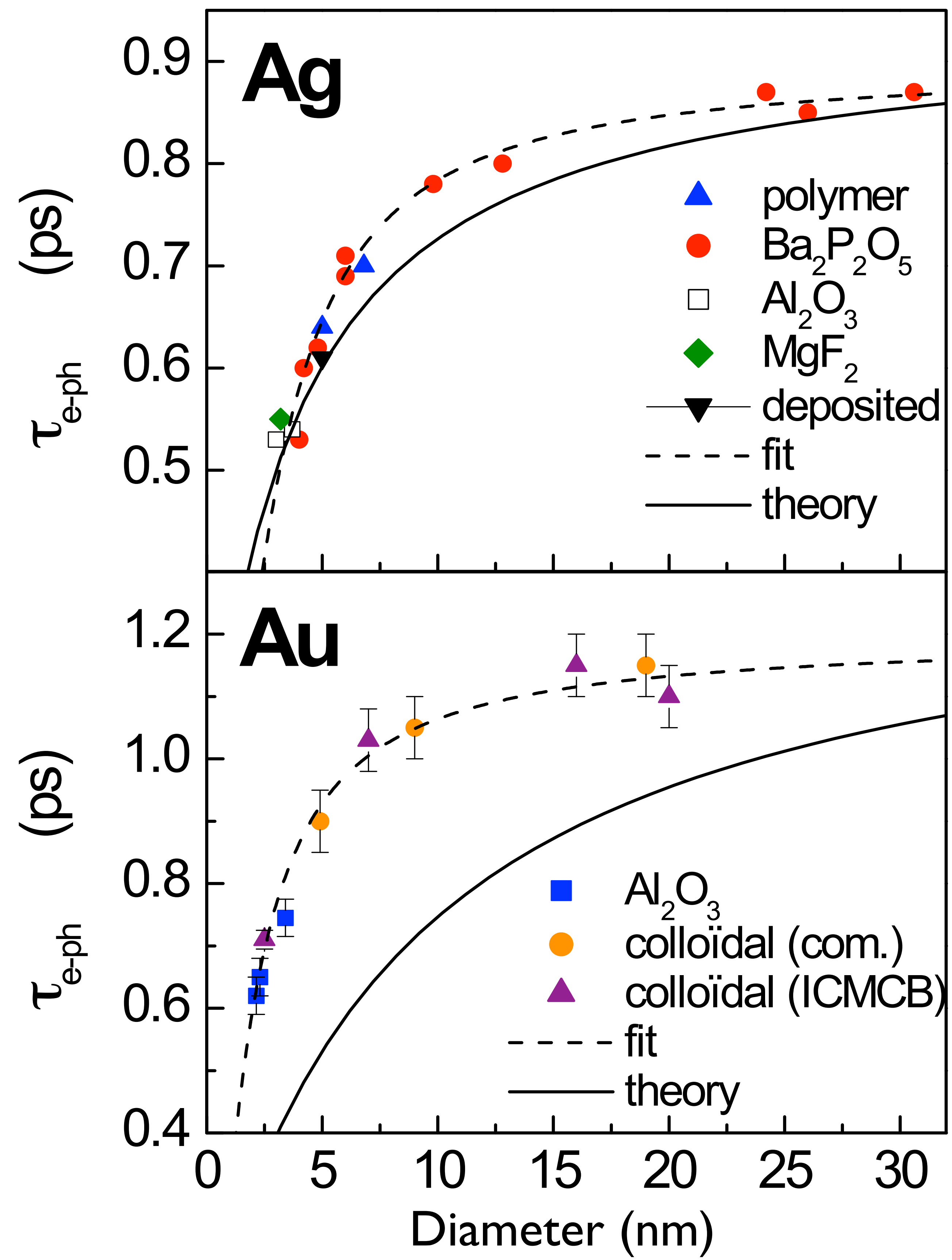
→ **intrinsic** effect

τ_{e-ph} **decreases** for D < 10 nm :

→ **Increase of electron-phonon coupling for smaller nanoparticles**

→ Reduced screening of Coulomb interaction in the vicinity of surfaces

Bulk Ag: 850 fs - Bulk Au: 1.15 ps



Arbouet et al. Phys. Rev. Lett. 90, 177401, **2003**

Transition from low perturbation regime to strong perturbation

Electron gas specific heat capacity depends on temperature

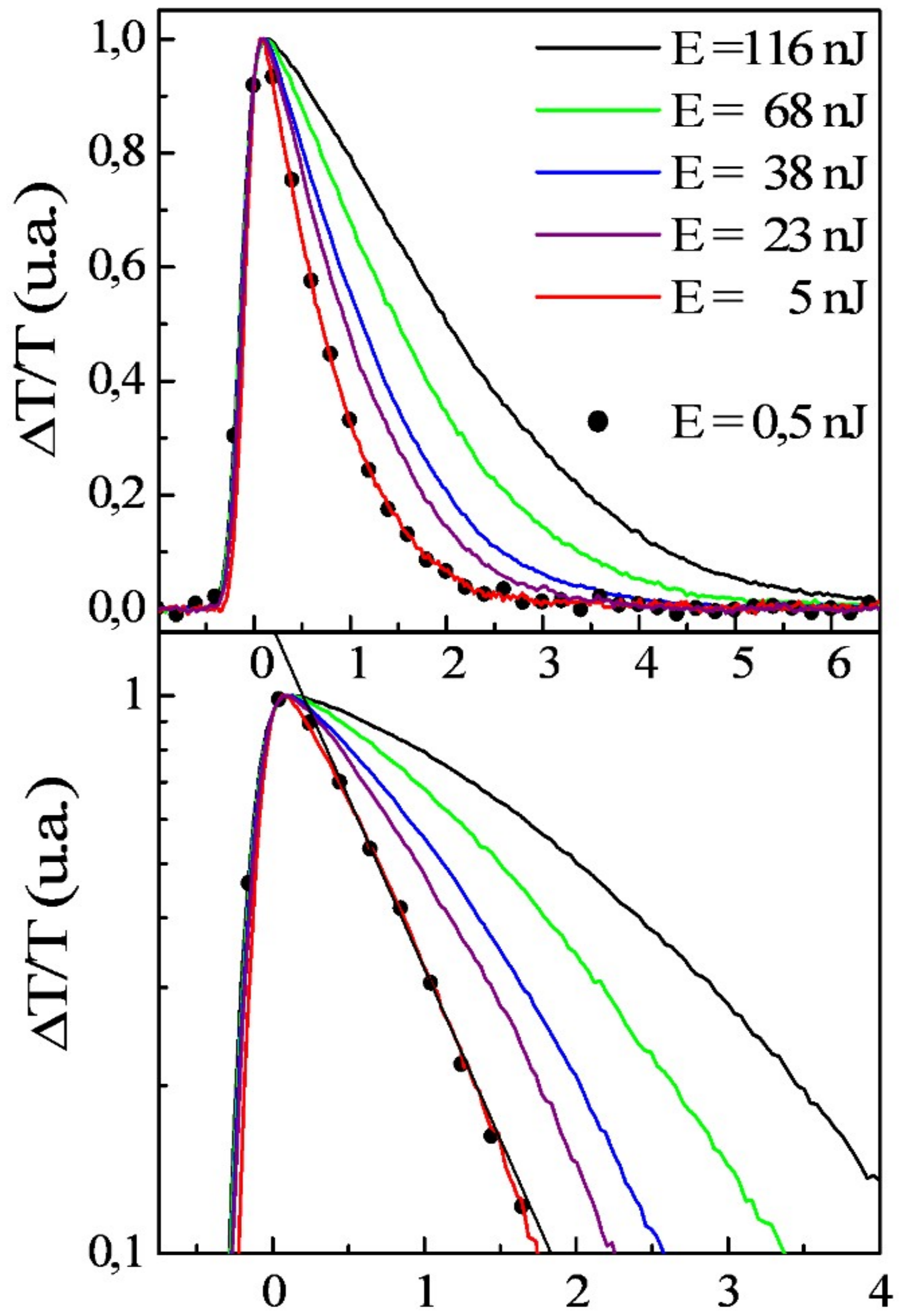
$$C_e = \gamma T_e$$

→ **No monoexponential decrease for higher pump fluences**

→ **<u>Increase</u> of measured Electron-Lattice thermalization Time**

→ **No more intrinsic effect**

→ **Caution when measuring electron-lattice thermalization time**



Del Fatti, N.; Arbouet, A. & Vallée, F.
Applied Physics B, 84, 175-18, **2006**

Nonequilibrium Electron Dynamics in Gold

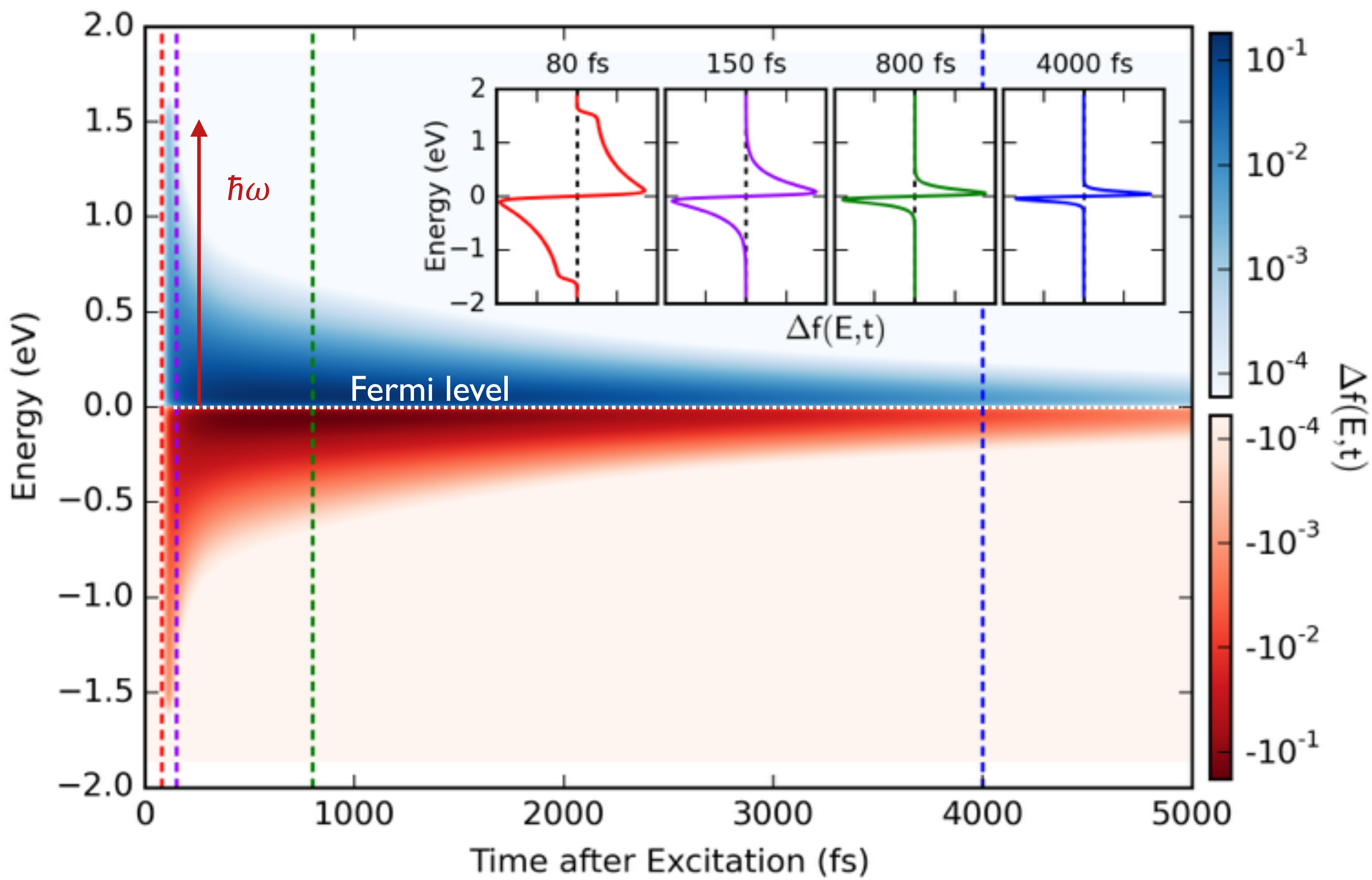
Both **electron-electron** and **electron-phonon** interactions can be taken into account using **<u>Boltzman's equation</u>**

$$\frac{df(E,t)}{dt} = \left.\frac{df(E,t)}{dt}\right|_{e-e} + \left.\frac{df(E,t)}{dt}\right|_{e-ph} + F(E,t)$$

Electron/electron Electron/phonon

Sun et al. Phys. Rev. B 50, 15337, **1994**

Del Fatti et al. Phys. Rev. B 61, 16956, **2000**



20 fs
hω=1.55 eV
ΔT=500 K

Zavelani-Rossi et al,
ACS Photonics, 2 (4), 521, **2015**

Alternatively, the non equilibrium dynamics can be described by a **<u>Three-Temperature Model</u>**

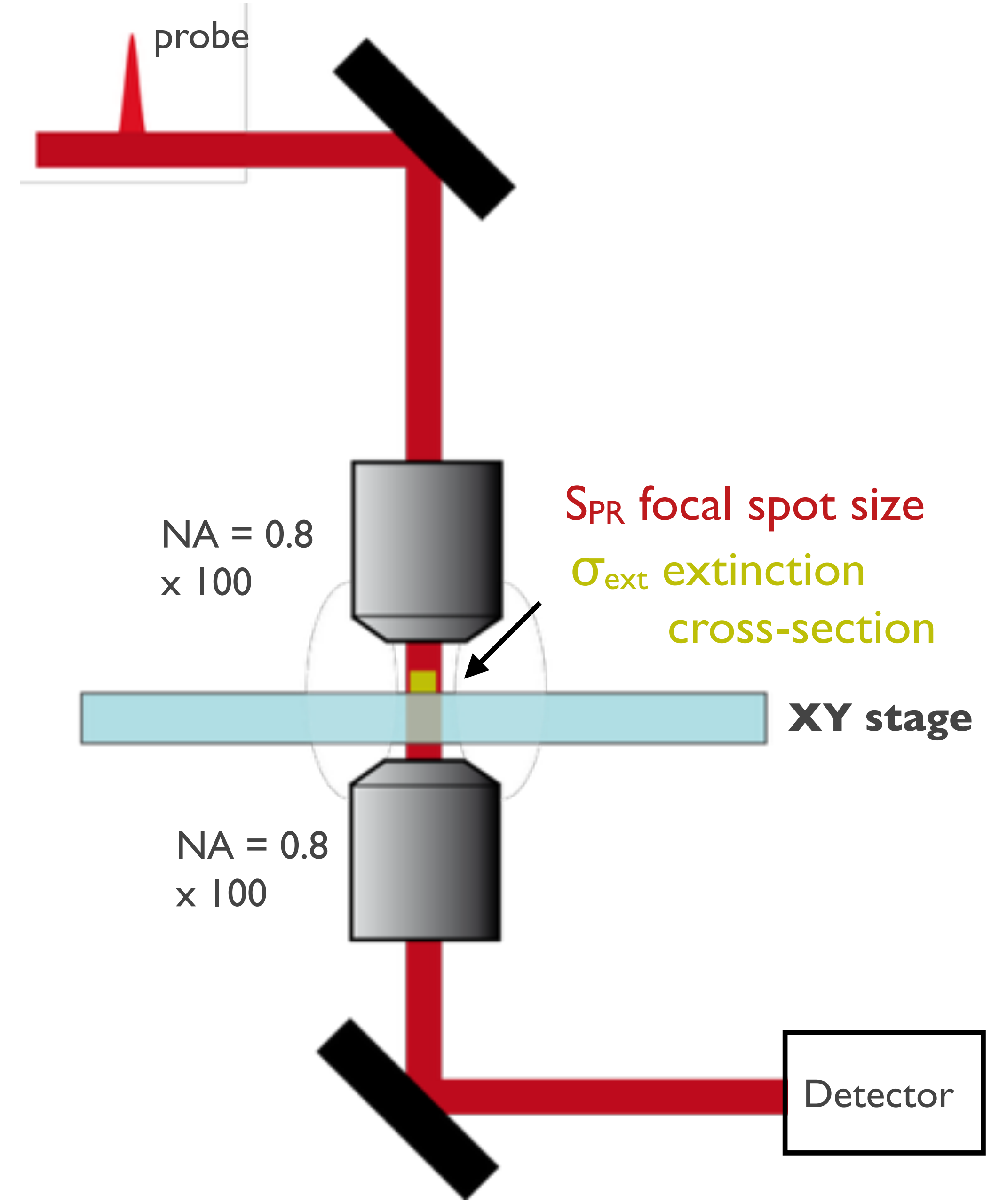
Time-Resolved Studies on individual Nano-Objects

To address a **single** metal nanoparticle : **<u>dilute</u>** samples

→ **1 nanoparticle in probe focal spot S_{PR}**

$$T \approx \left(1 - \frac{\sigma_{ext}}{S_{pr}}\right) \times T_0$$

← Transmission of probe beam without metal particle



To address a **single** metal nanoparticle : **dilute** samples

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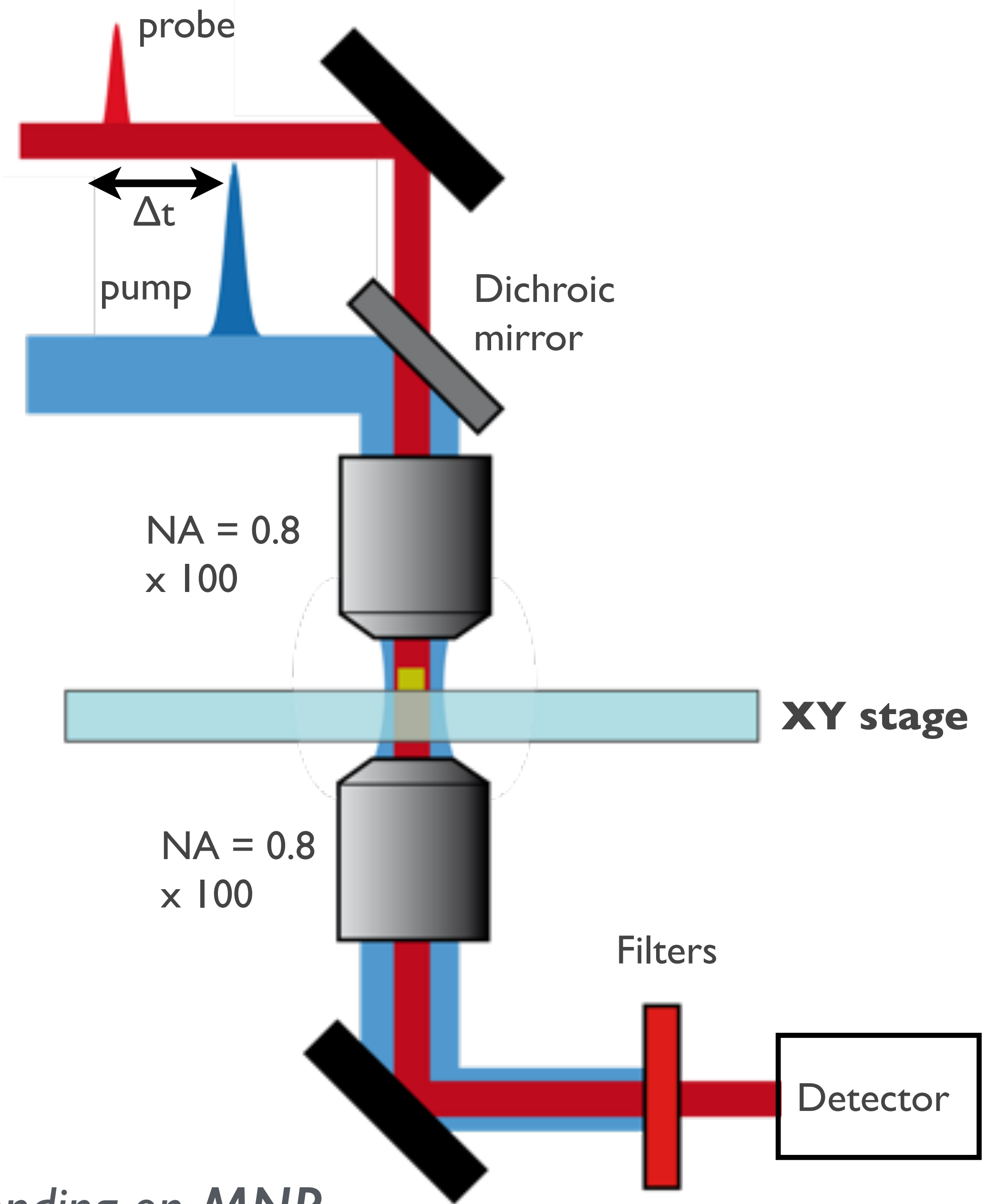


Pump-induced transmission change :

$$\frac{\Delta T}{T} \approx -\left(\frac{\Delta\sigma_{ext}}{\sigma_{ext}}\right)\left(\frac{\sigma_{ext}}{S_{pr}}\right)$$

*Relative modification of the extinction cross section induced by the **pump pulse***

*Typ. : **10^{-3} - 10^{-4}** for low perturbation*

*Geometrical factor depending on **MNP & focusing***

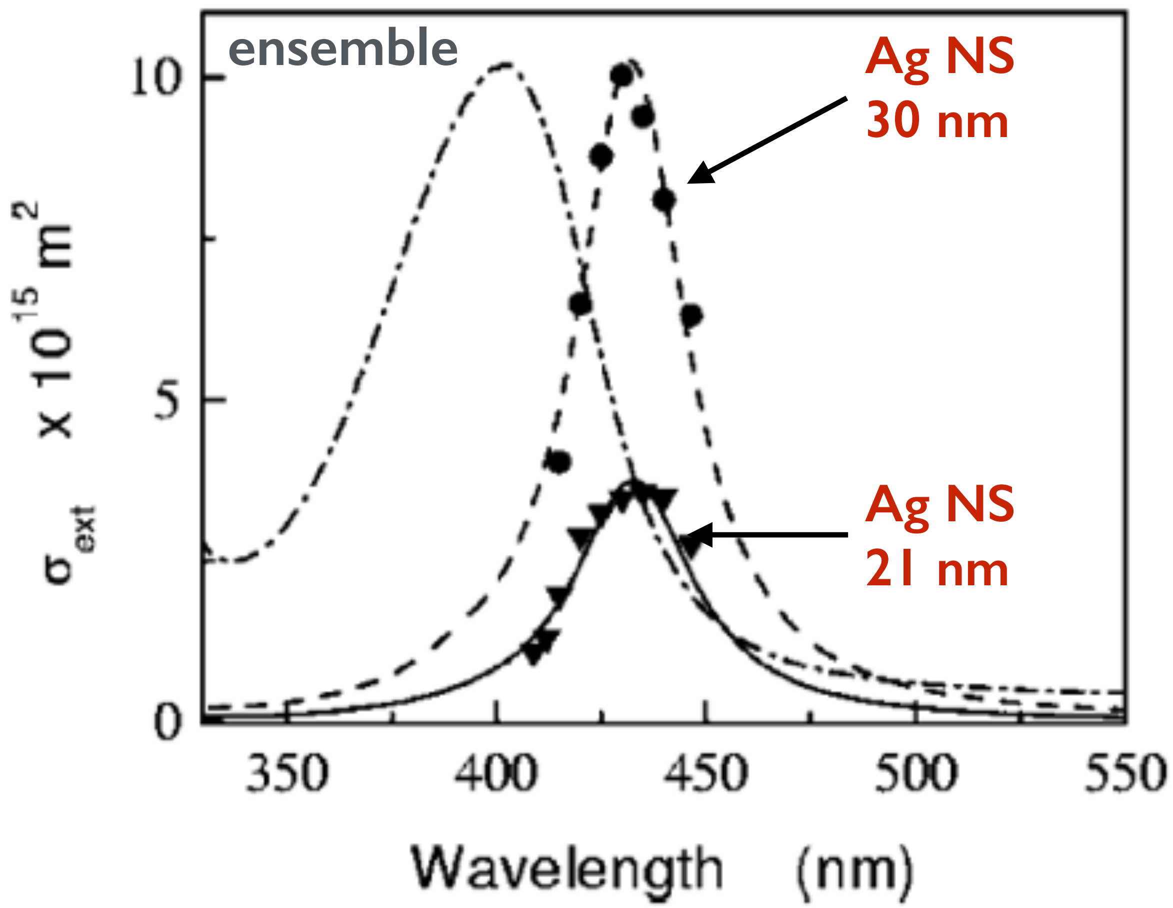
*Ex: NA = 0.8, Au NP 20 nm → **10^{-3}***

Pump-probe on a individual **nano-object** → **Dilute samples**

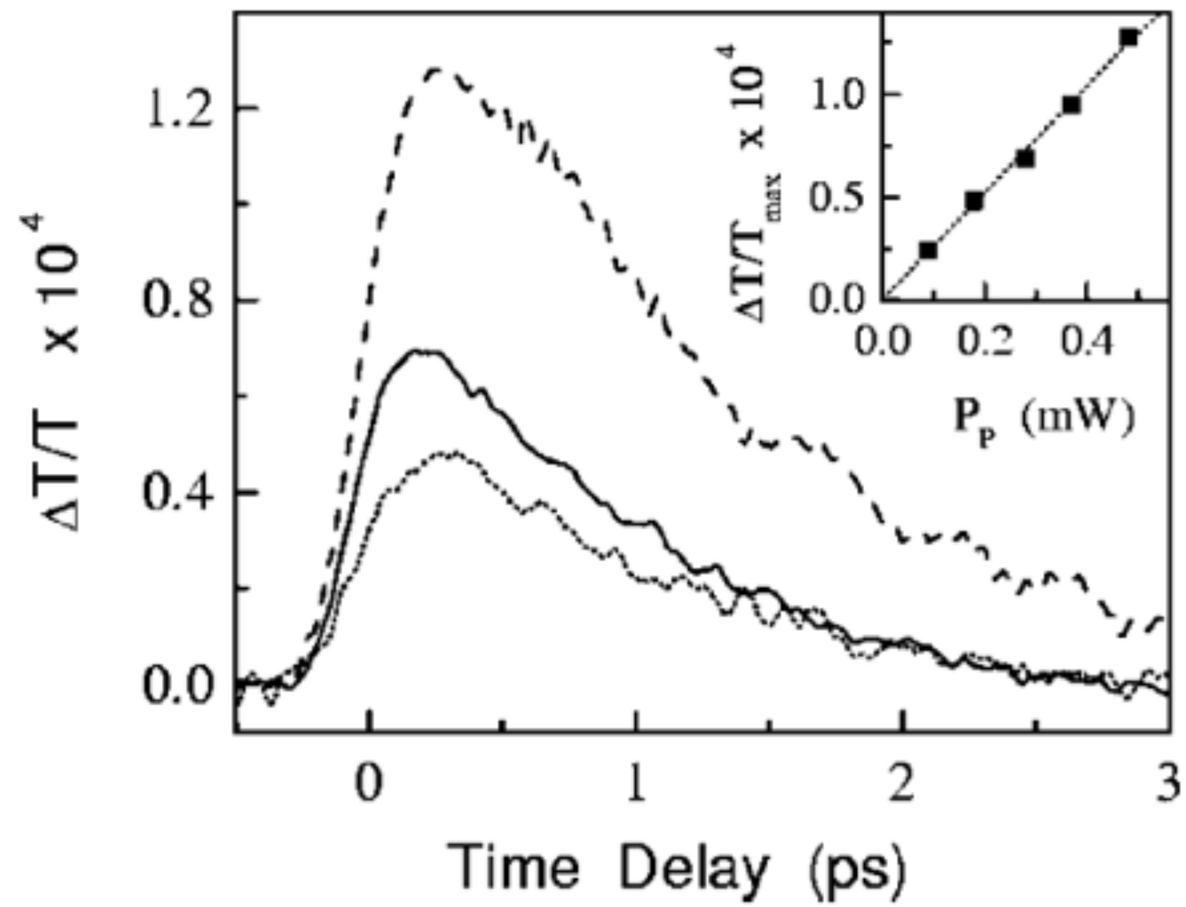
→ **Tight focusing + high S/N ratio (10^{-6} - 10^{-7})**

Studies on individual 20 nm Ag nanospheres

Spatial Modulation Spectroscopy



Transient absorption spectroscopy



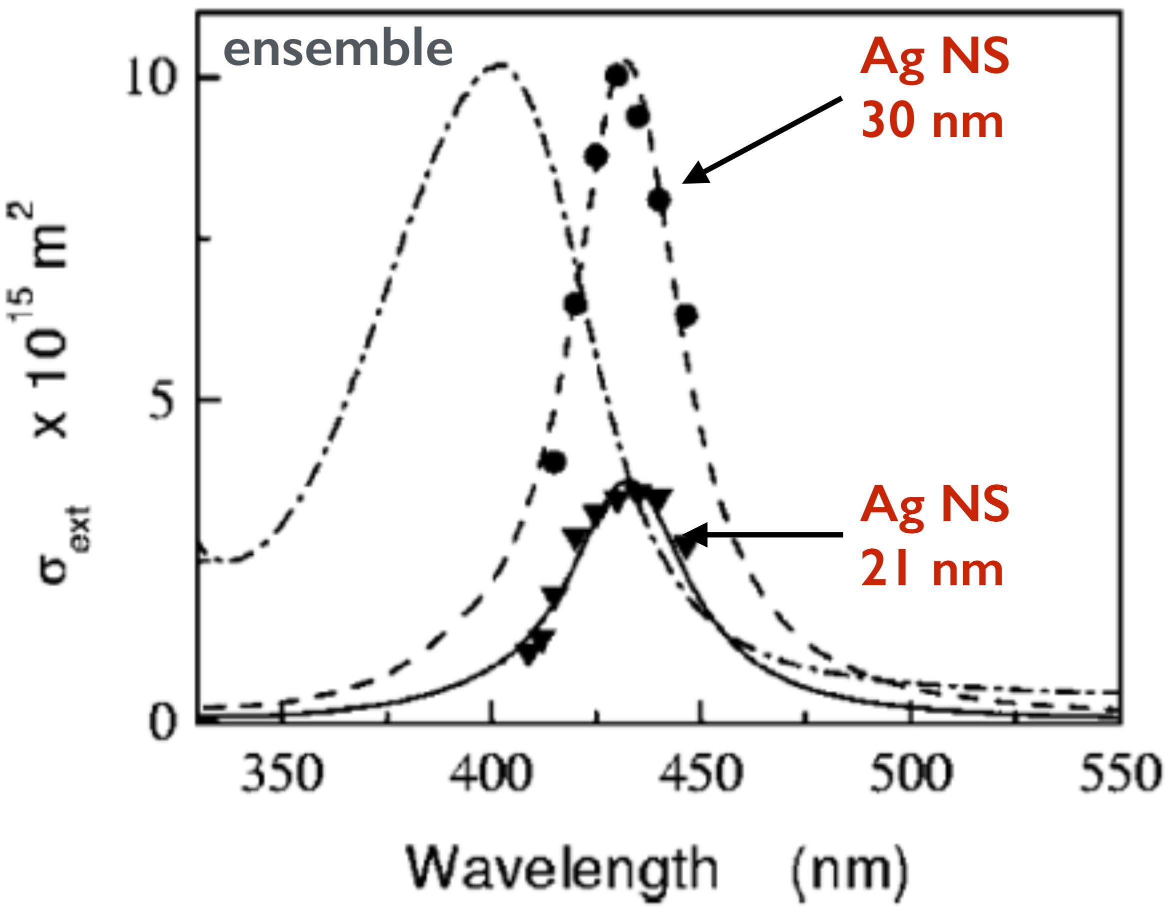
→ **Linear extinction spectrum + Ultrafast response**

Arbouet et al. Phys. Rev. Lett. 93, 127401, **2004**

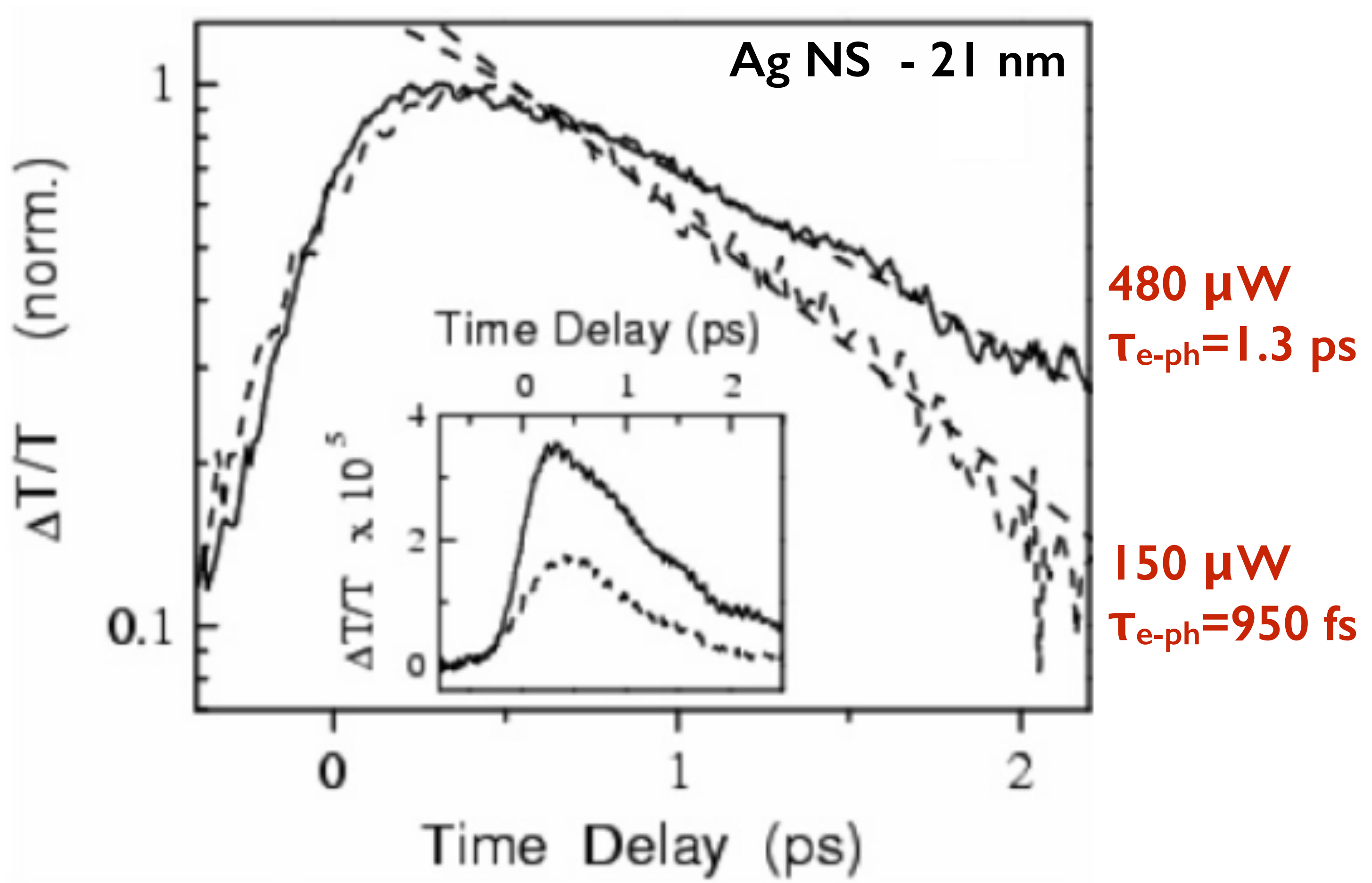
Muskens et al. Nanoletters, 6, 552, **2006**

Studies on <u>individual</u> 20 nm Ag nanospheres

Spatial Modulation Spectroscopy



Transient absorption spectroscopy



→ **<u>Increase</u> of electron-lattice thermalization time with excitation energy**

→ **Excellent agreement with Two-Temperature Model**

Muskens et al. Nanoletters, 6, 552, **2006**

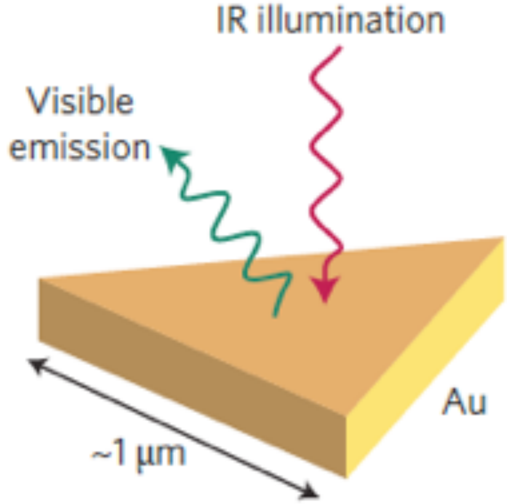
Two Photoluminescence in Gold Nanostructures

Two-Photon induced Photoluminescence from gold nanoparticles

2nd order incoherent non-linear emission mechanism

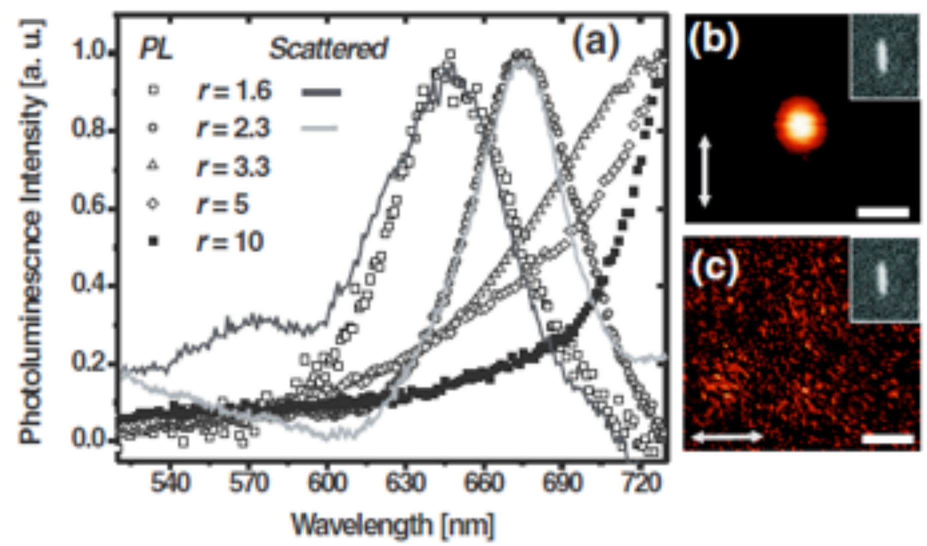
Beversluis et al, PRB, 68, 115433, **(2003)**

Biagioni et al, PRB, 80, 045411, **(2009)**

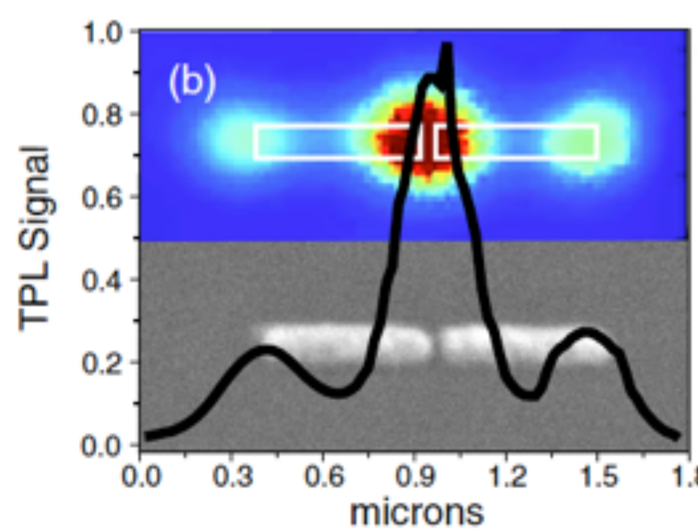


⇒ SP <u>spectral</u> characteristics

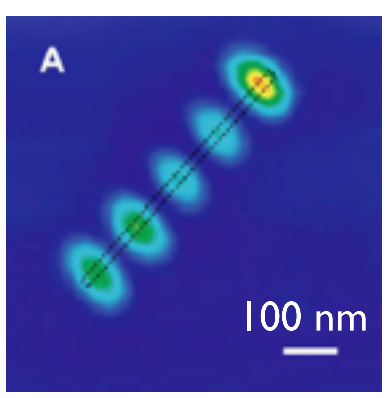
Bouhelier et al, PRL, 95, 267405, **(2005)**



⇒ SP <u>spatial</u> intensity distribution



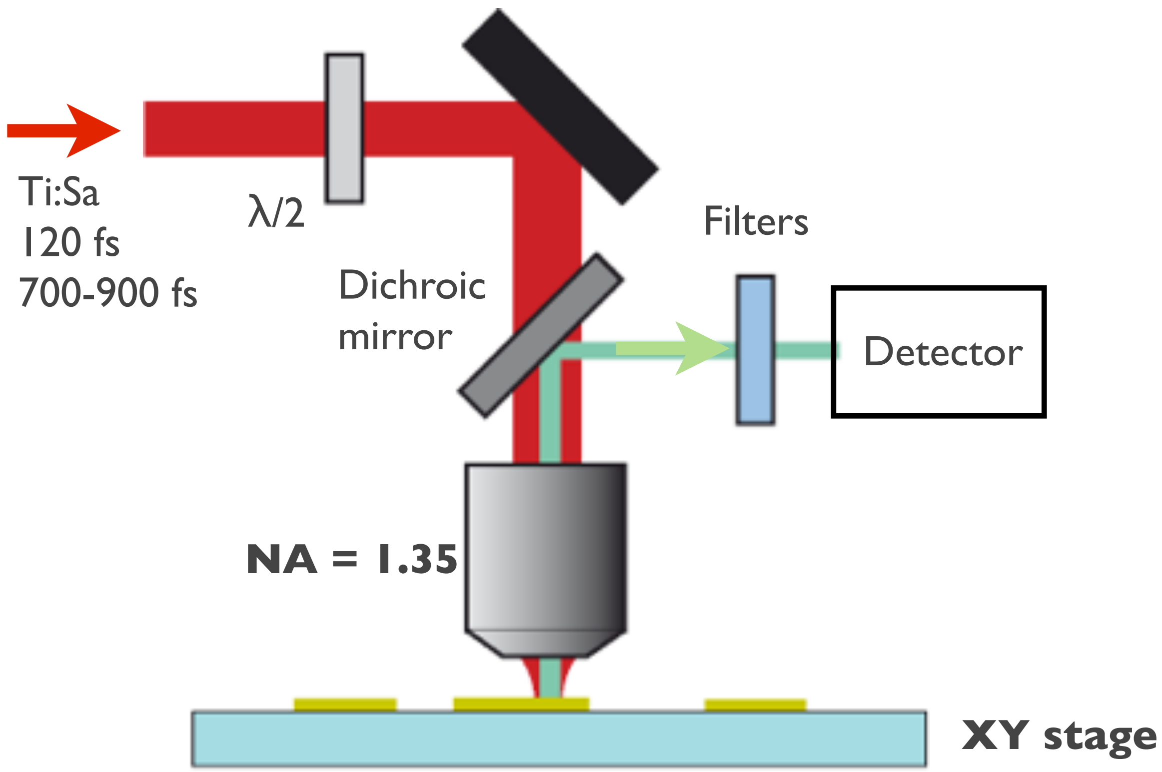
Ghenuche et al, PRL, 101, 116805, **(2008)**

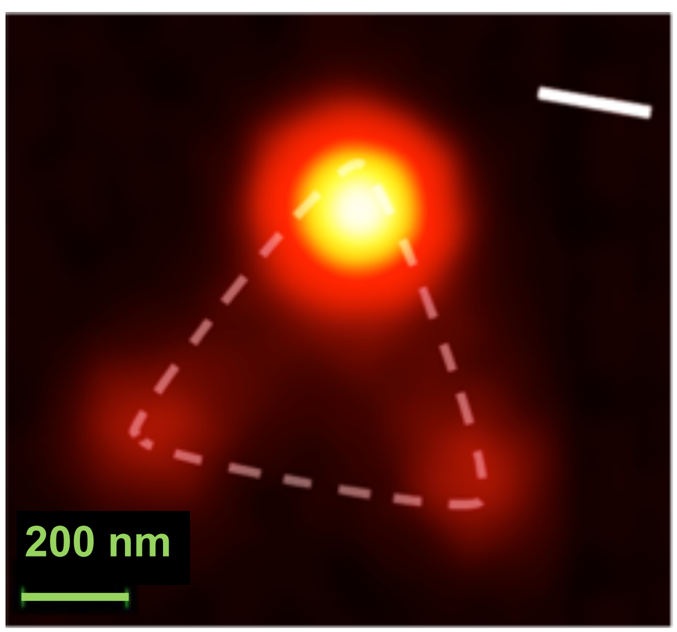


Okamoto et al, Prog. Surf. Sci., 84, 199, **(2009)**

Local E-field intensity mapping by Two-Photon Photoluminescence

Experiment





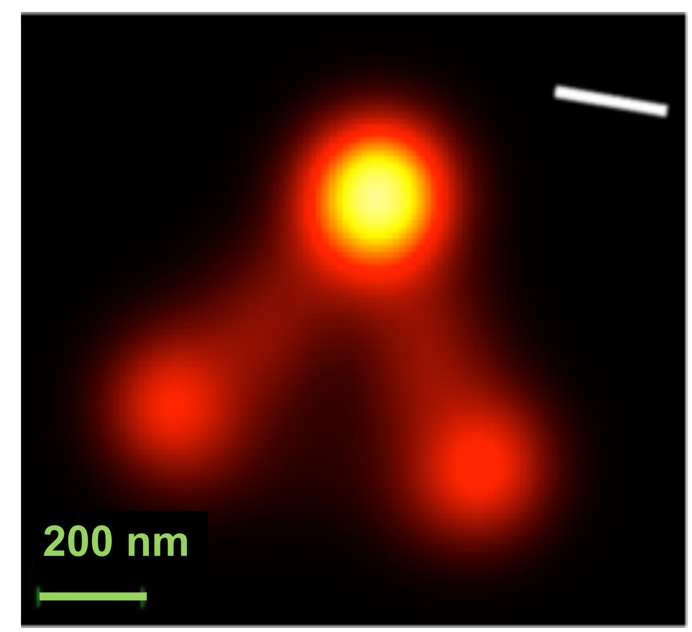
Viarbitskaya et al, Nature Materials 12, 426–432 **(2013)**

Theory

TPL = Incoherent 2nd order non-linear process

$$I_{\mathrm{TPL}}(\mathbf{r_0}, \omega_{exc}) = \int_V |\mathbf{E}(\mathbf{r}, \omega_{exc})|^4 dV$$

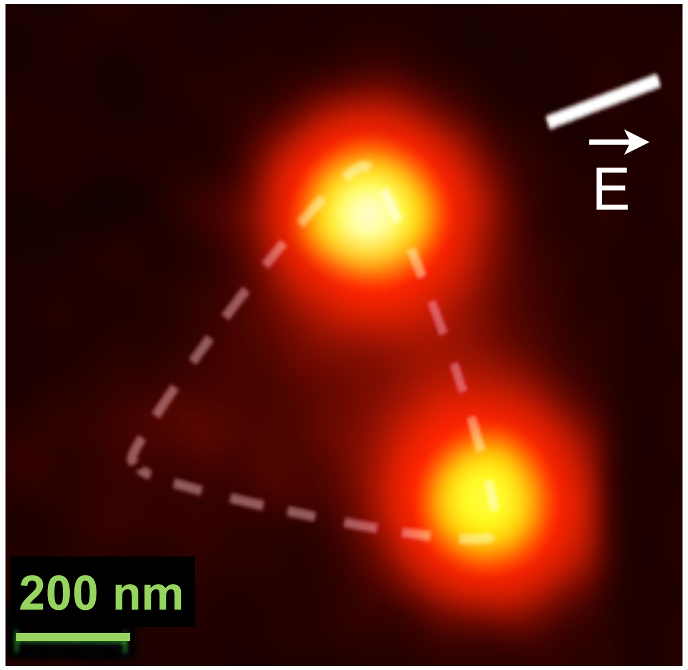
Green Dyadic Function formalism



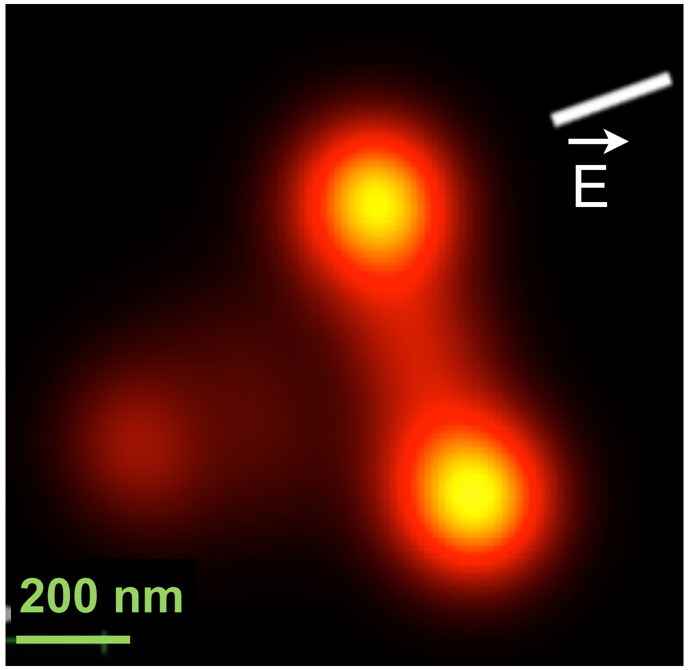
Teulle et al, JOSA B 29, 2431–2437 (**2012**)

Polarization-dependent intensity distribution

Experiment



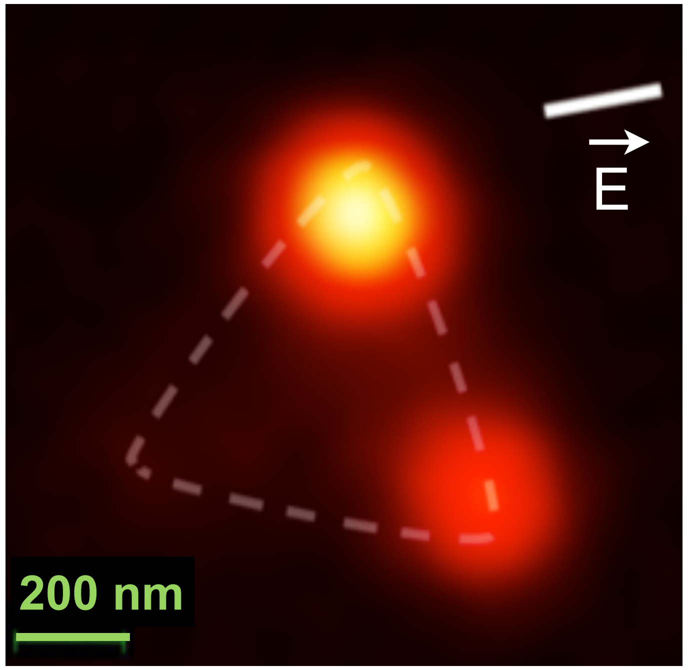
Theory



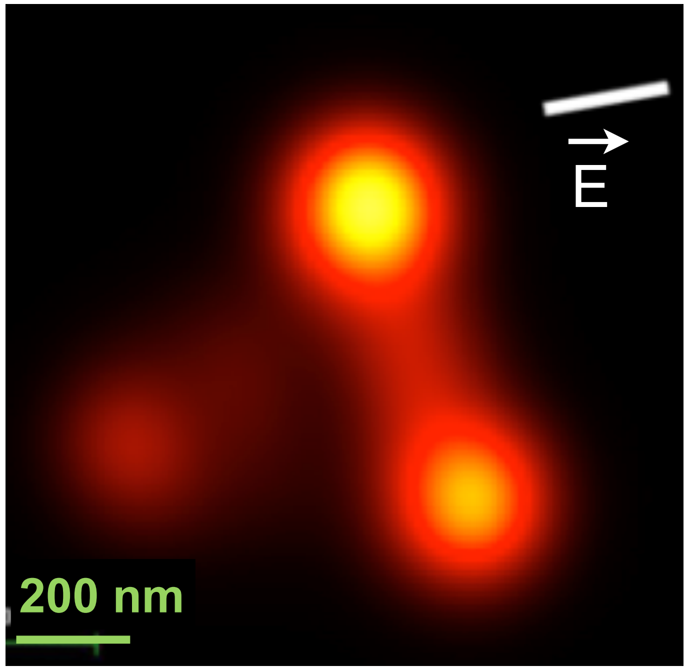
Viarbitskaya et al, Nature Materials 12, 426–432 **(2013)**

Polarization-dependent intensity distribution

Experiment



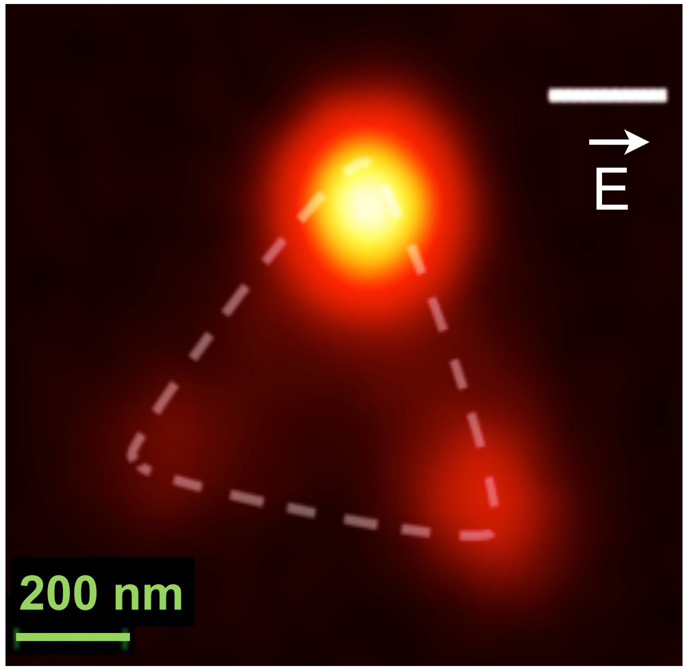
Theory



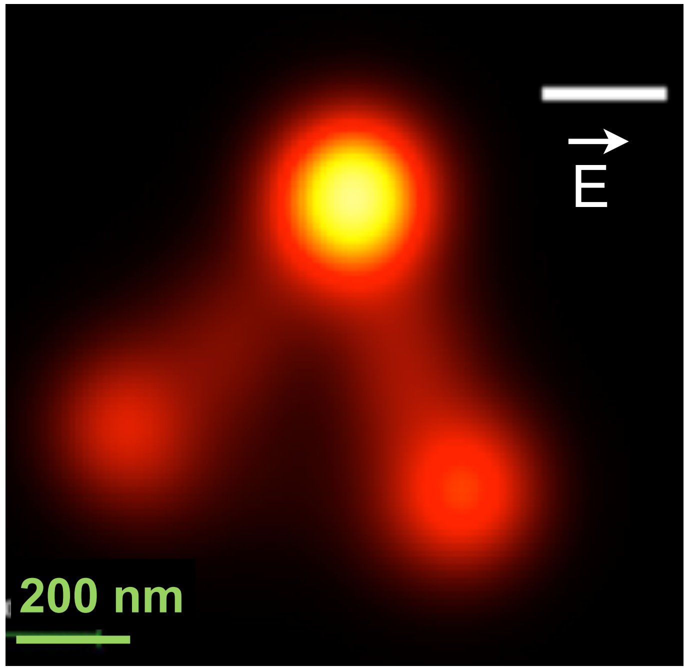
Viarbitskaya et al, Nature Materials 12, 426–432 **(2013)**

Polarization-dependent intensity distribution

Experiment



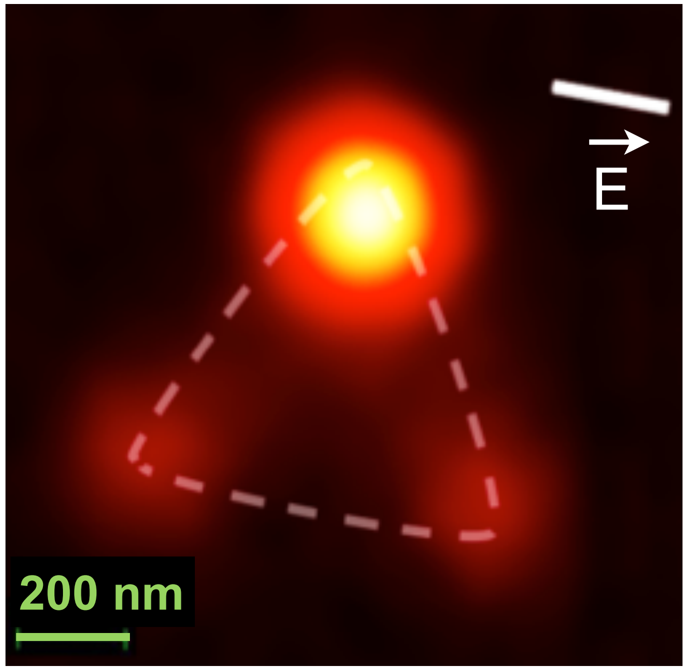
Theory



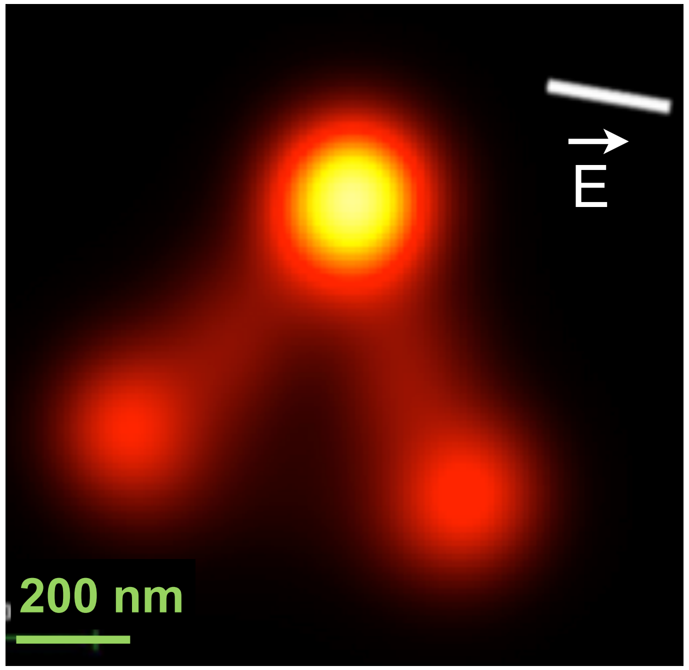
Viarbitskaya et al, Nature Materials 12, 426–432 **(2013)**

Polarization-dependent intensity distribution

Experiment



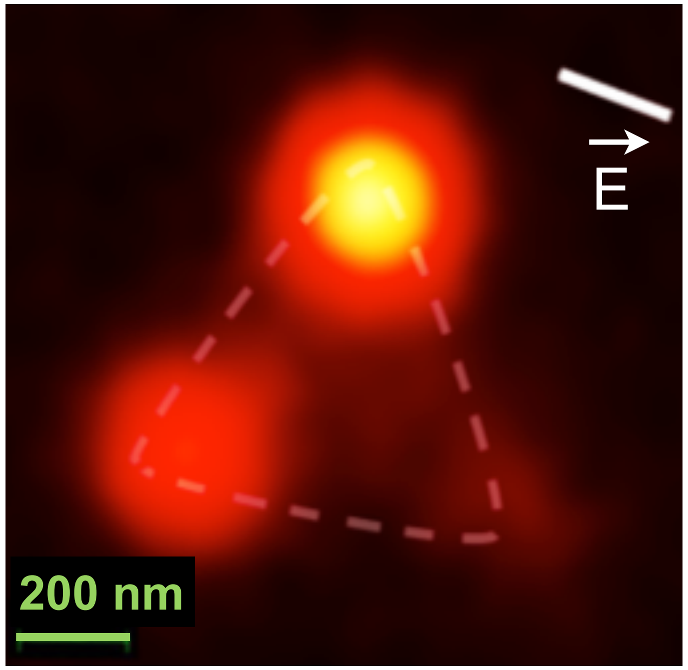
Theory



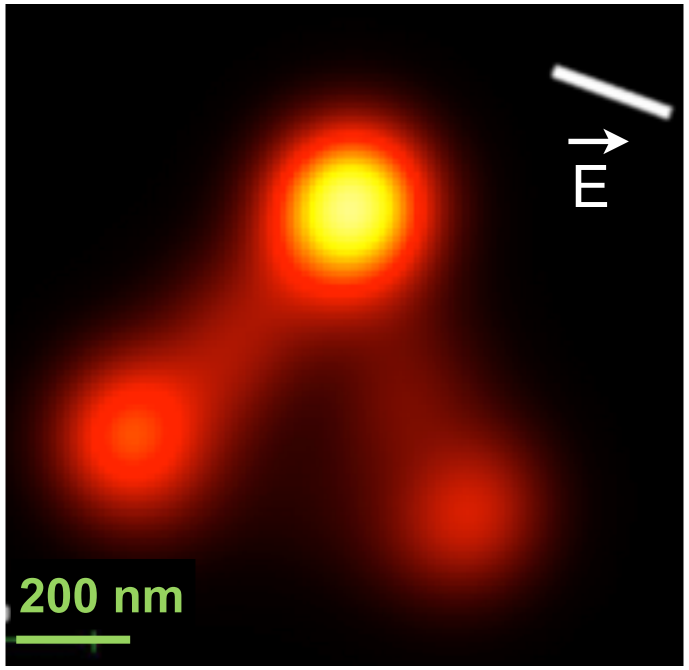
Viarbitskaya et al, Nature Materials 12, 426–432 **(2013)**

Polarization-dependent intensity distribution

Experiment



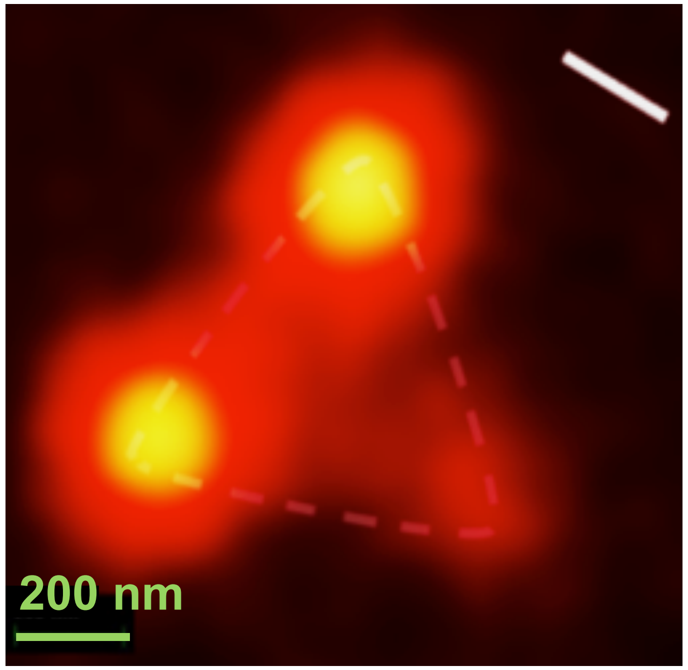
Theory



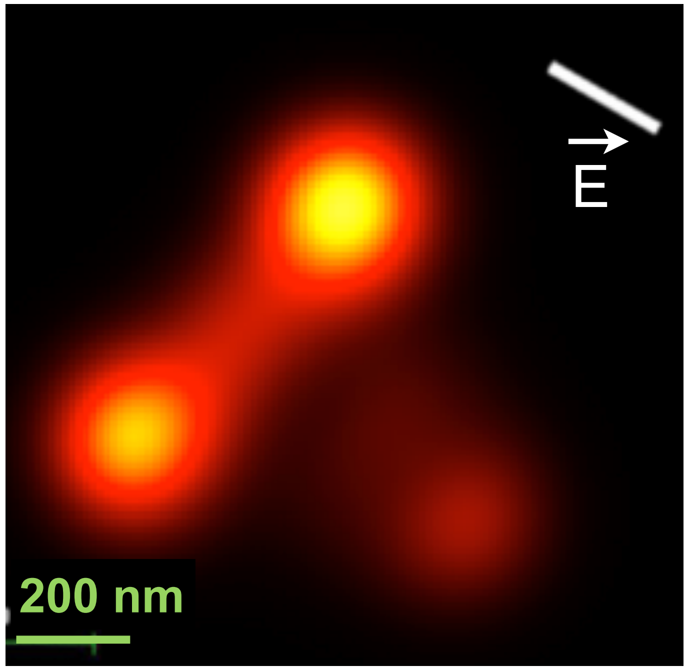
Viarbitskaya et al, Nature Materials 12, 426–432 **(2013)**

Polarization-dependent intensity distribution

Experiment



Theory

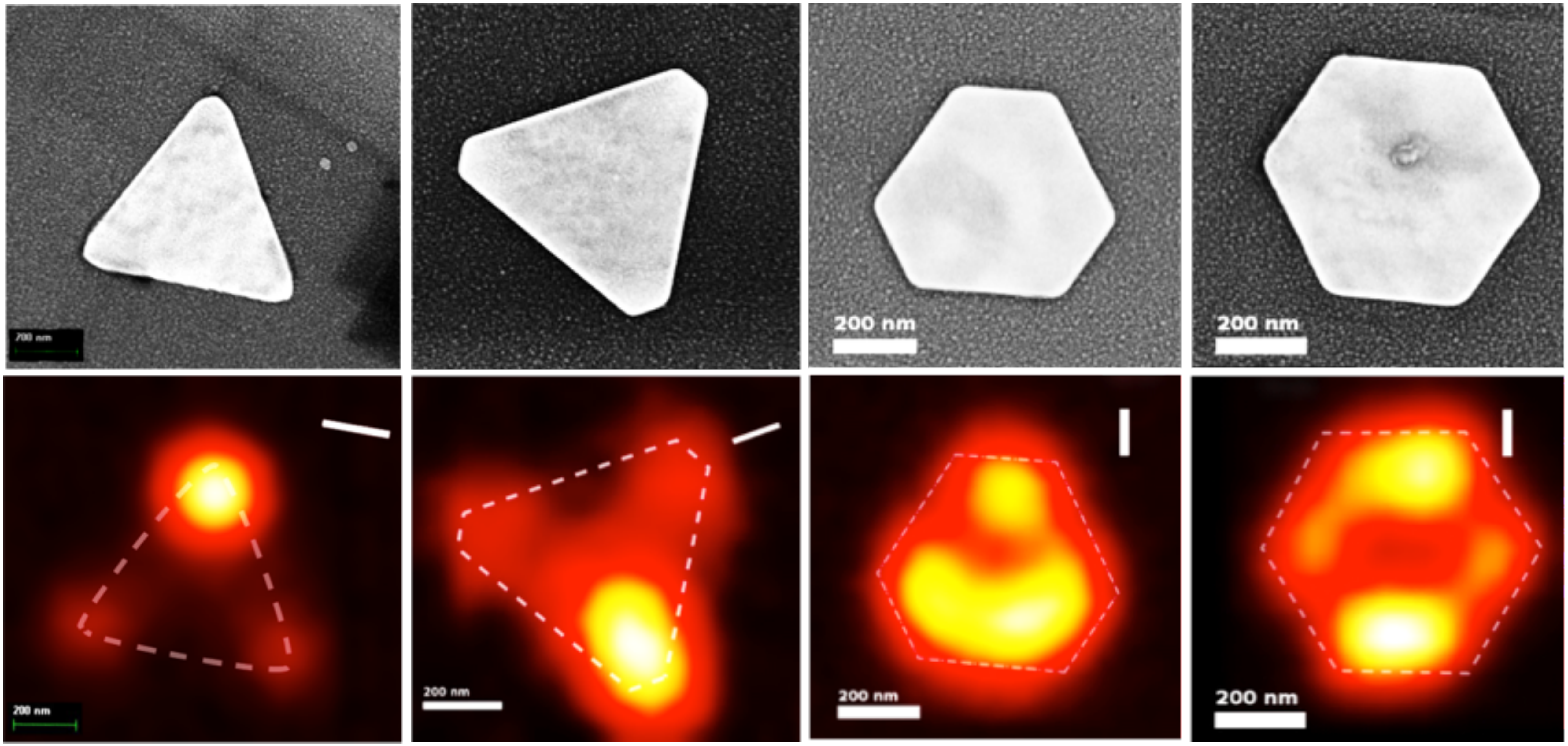


Local **E-field intensity distribution** depends on **polarization : optical adressing & control**

Excellent **agreement** with GDF simulations

Viarbitskaya et al, Nature Materials 12, 426–432 **(2013)**

Influence of the nanoparticle shape on the optical near-field intensity distribution



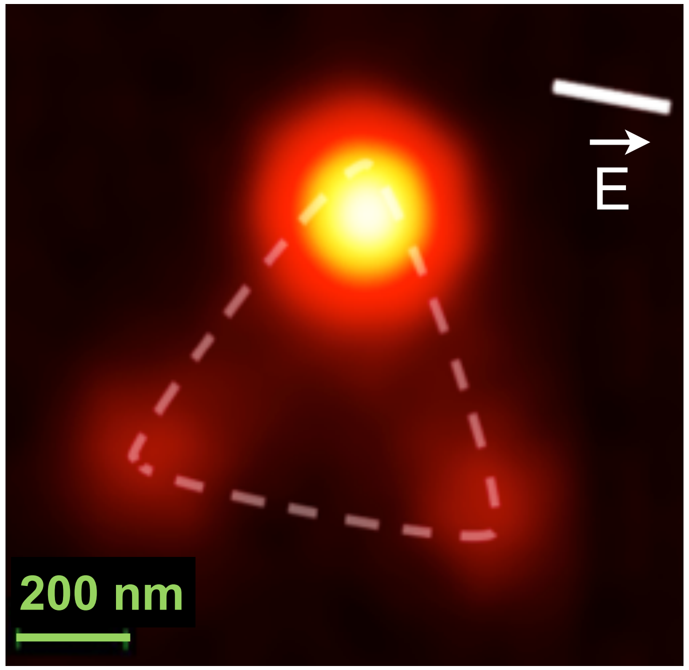
Fedou et al, PCCP, 15, 4205-4213, **2013**

Viarbitskaya et al, APL 103, 131112-4, **2013**

Spatial resolution : ~ 250 nm

TPL vs Electron Energy Loss Spectroscopy of Plasmonic Nanoprisms

TPL at 800 nm (1.55 eV)



TPL vs Electron Energy Loss Spectroscopy of Plasmonic Nanoprisms

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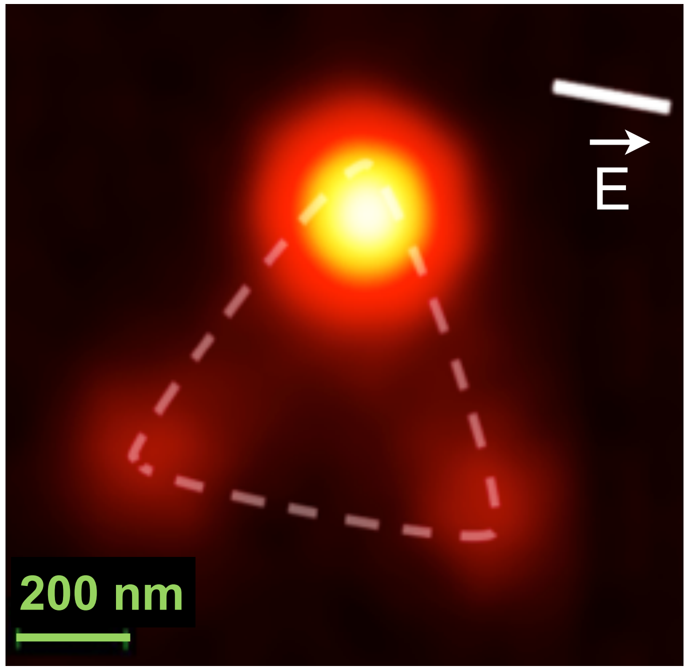
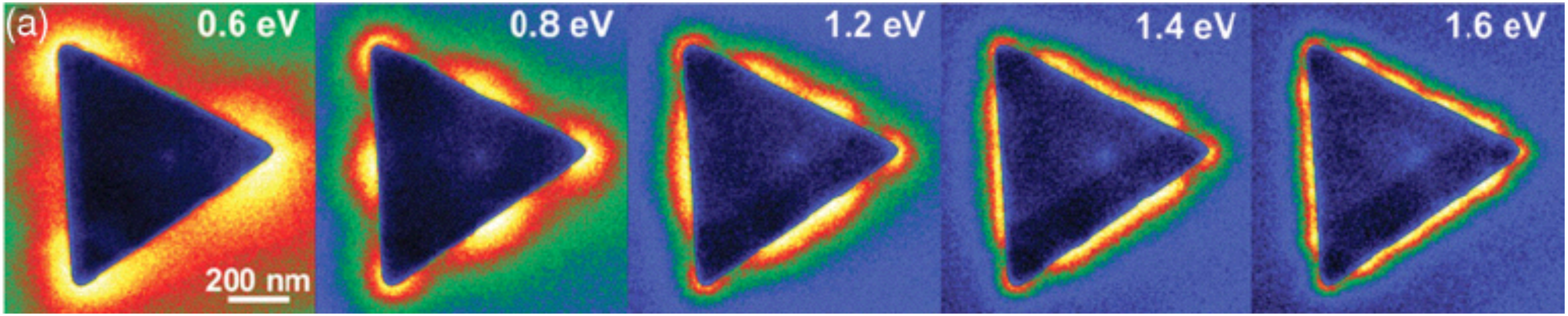
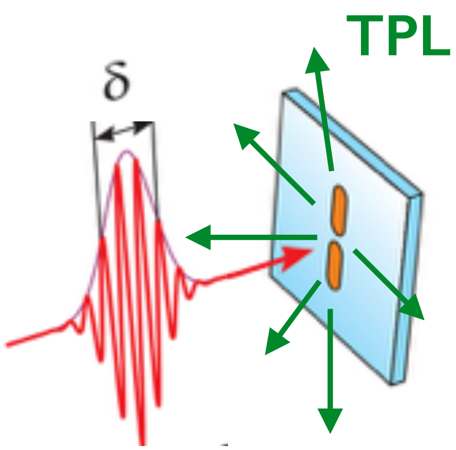


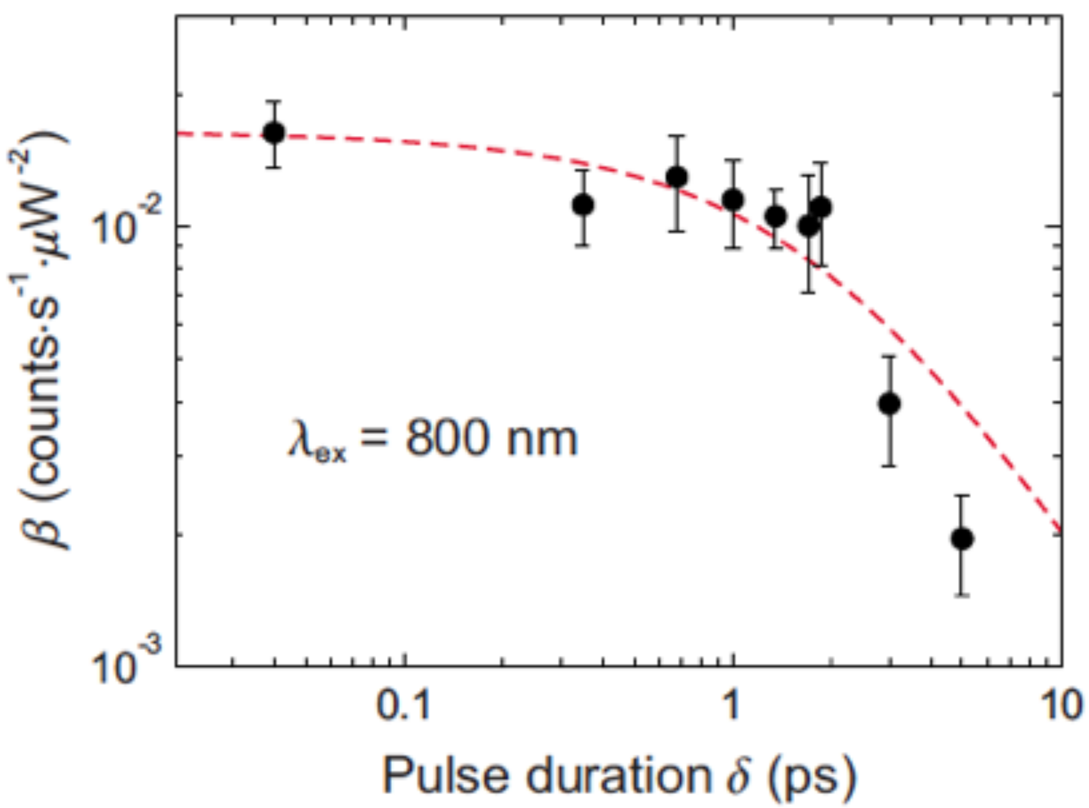
Energy Filtered TEM



Gu et al, PRB 83, 195433 **(2011)**

TPL as a function of pulse duration

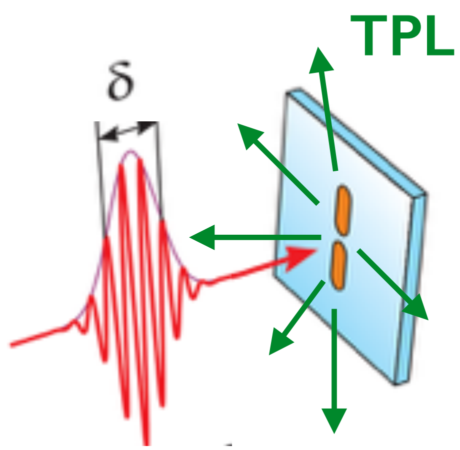




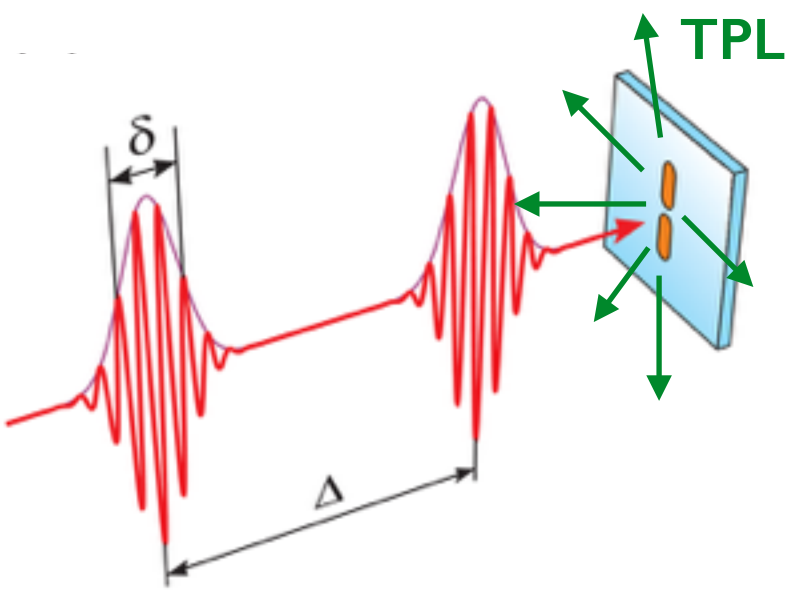
Biagioni et al, PRB, 80, 045411, **2009**

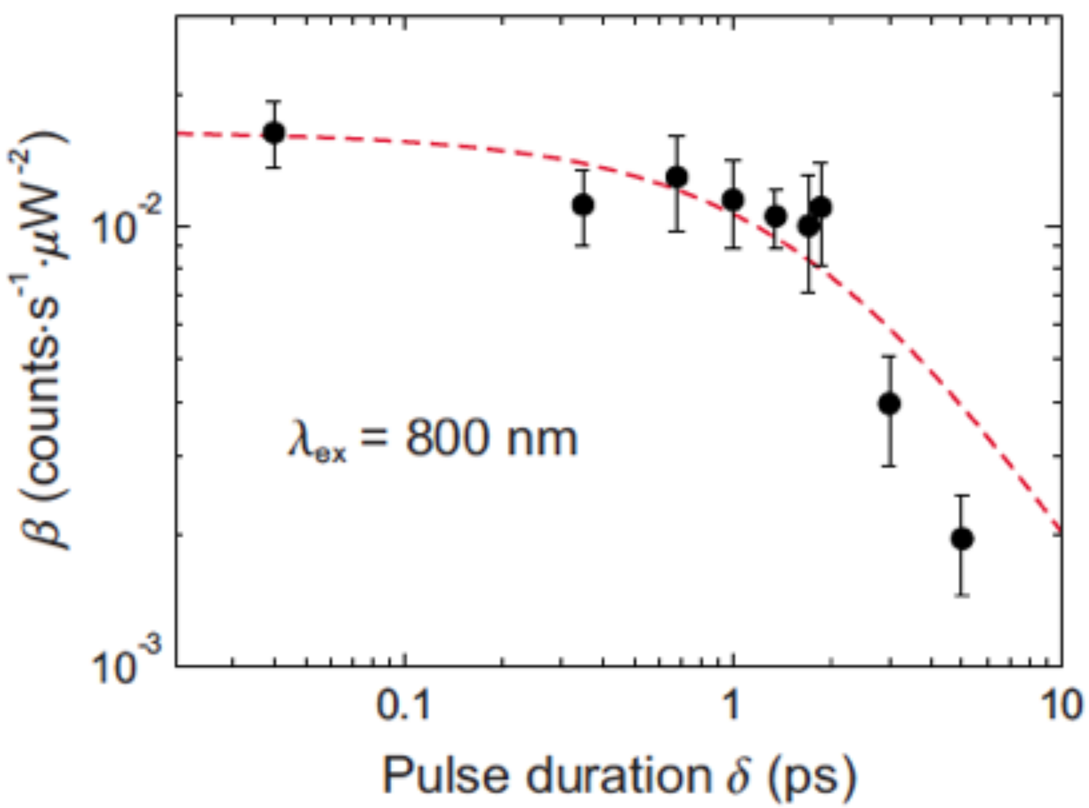
Dynamics of Two-Photon induced Photoluminescence from gold

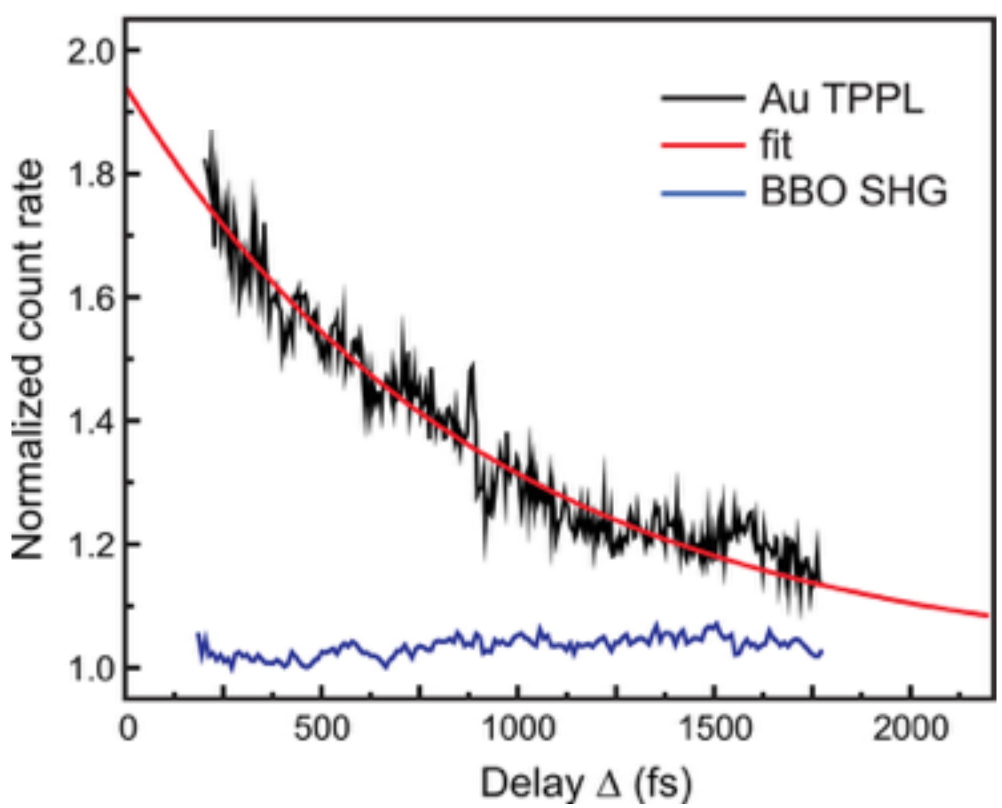
TPL as a function of pulse duration



Two-pulse correlation measurement







TPL ≠ SHG - Incoherent process !

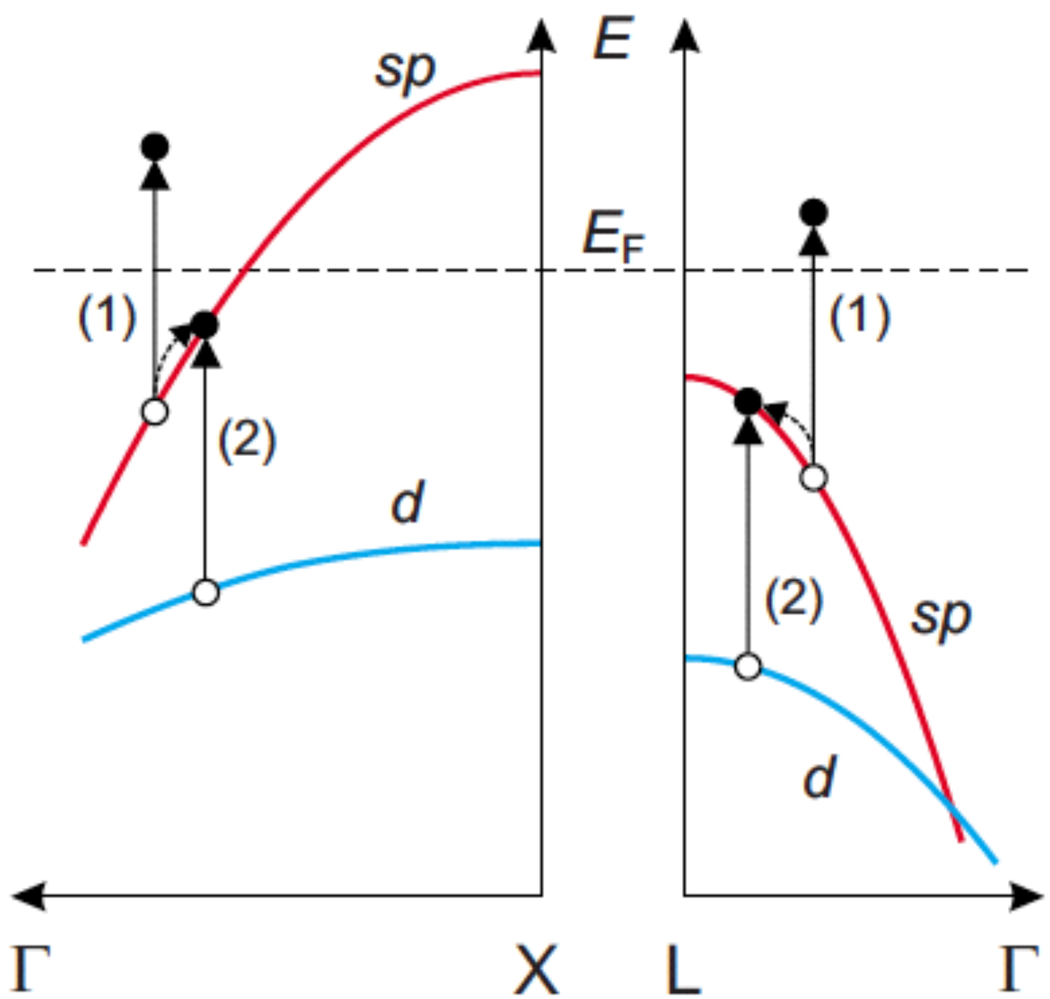
Biagioni et al, PRB, 80, 045411, **2009**

Biagioni et al, Nano Lett., 12, 2941, **2012**

Mechanism of Two-Photon induced Photoluminescence from gold

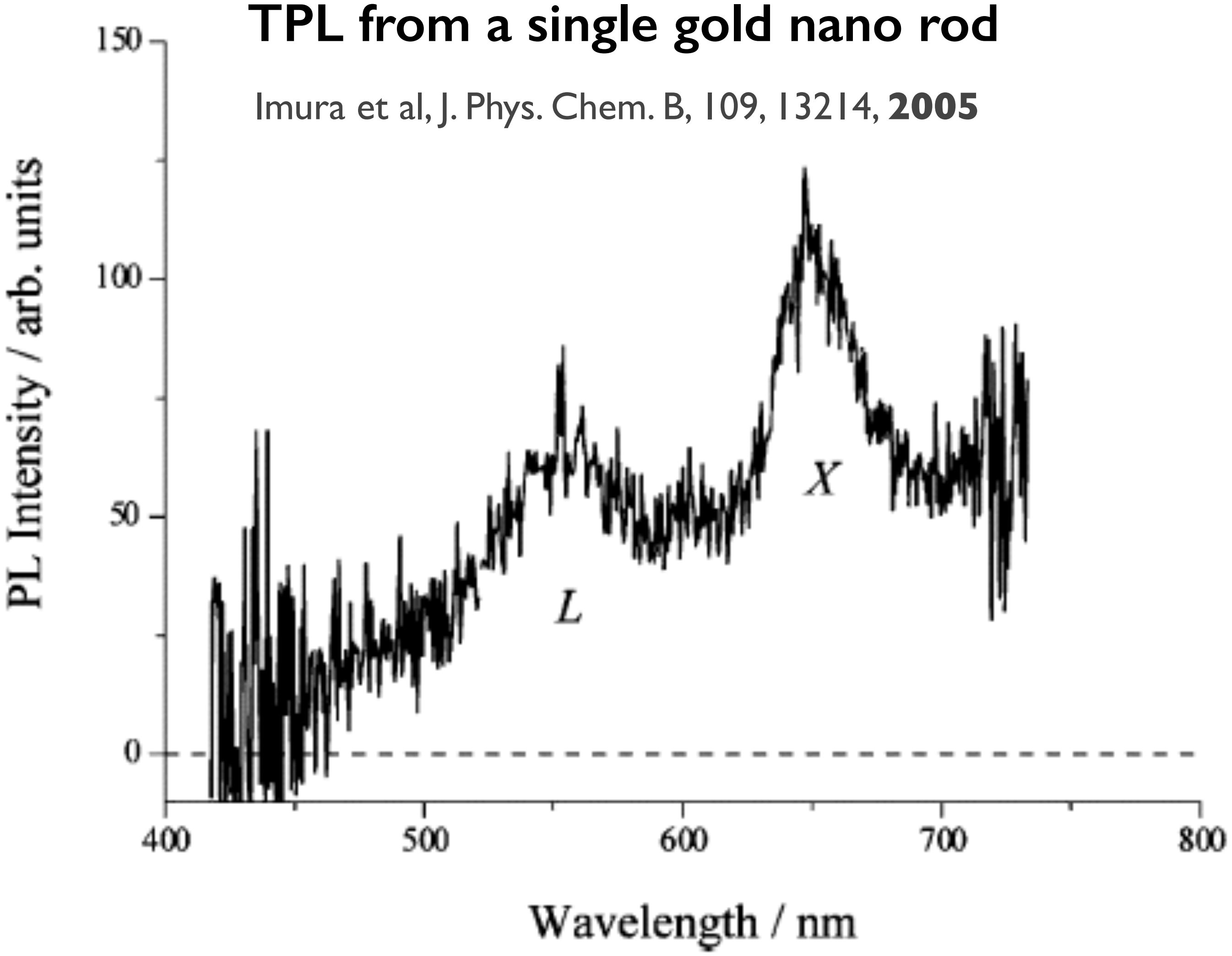
SHG: Two photon transition through a virtual state

TPL: Two sequential single-photon absorption steps mediated by a real electronic state



TPL from a single gold nano rod

Imura et al, J. Phys. Chem. B, 109, 13214, **2005**



Limiting step in TPL dynamics:

→ Relaxation of the transient distribution excited in the *sp* conduction band by the first photon

→ **Picosecond Timescale !**

Summary I

Plasmon dephasing

→ **Characteristic Timescale: 10-20 fs**

→ **Accessible via Frequency- or Time-Resolved techniques**

Electron gas thermalization

→ **Timescale: 350 fs (bulk Ag) and 500 fs (bulk Au)**

→ **Faster in smaller nano-objects (< 10 nm)**

→ **Bulk-like for sizes > 20 nm**

Electron-Lattice Thermalization

→ **Timescale: 850 fs (bulk Ag) and 1.15 ps (bulk Au)**

→ **Faster in smaller nano-objects (< 10 nm)**

→ **Bulk-like for sizes > 20 nm**

→ **The nanoparticle lattice is <u>heated in a few picoseconds</u>**

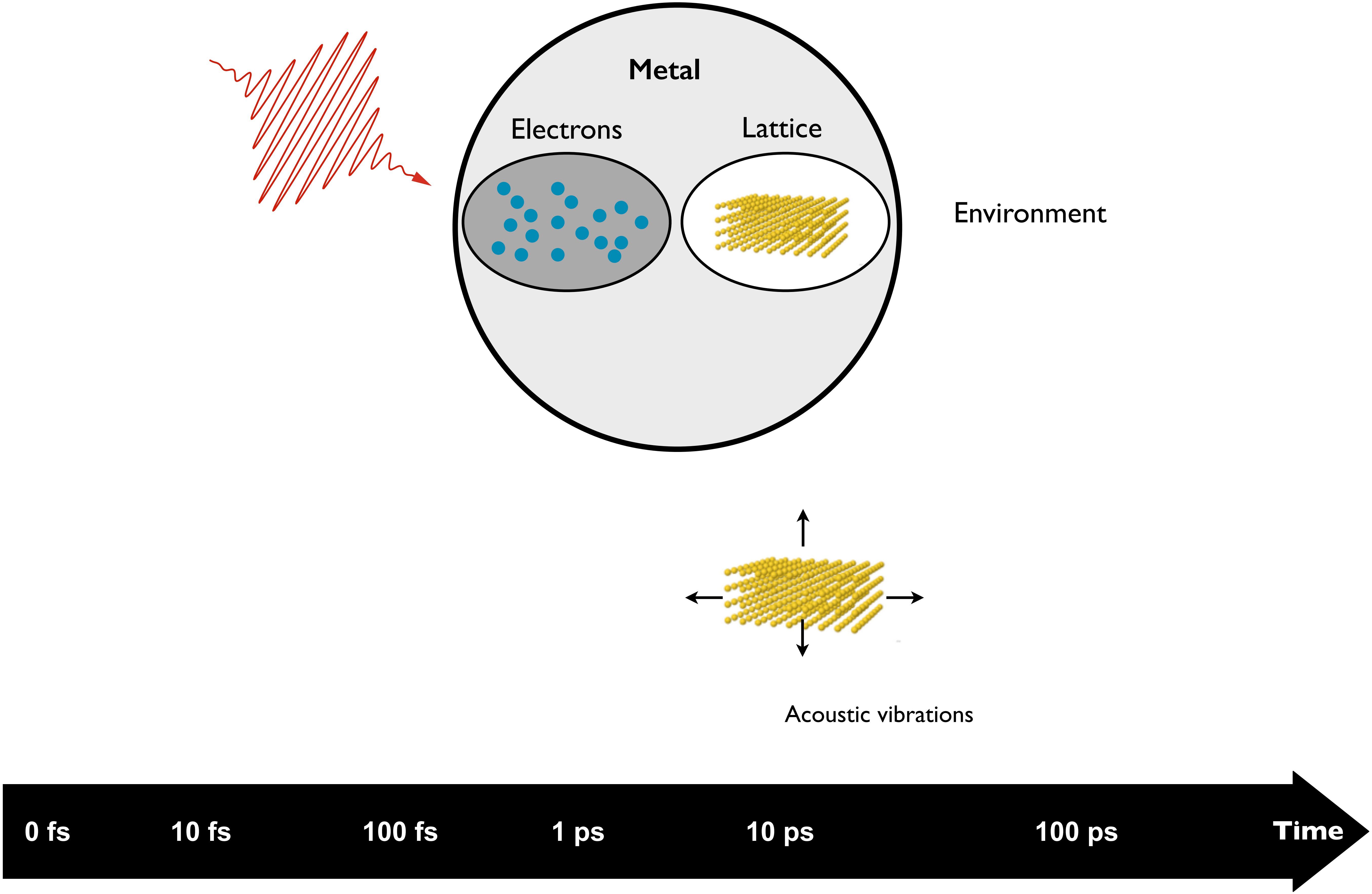
Two-Photon Photoluminescence

→ **TPL gives access to local electric field distribution**

→ **2nd order incoherent process influenced by electronic relaxation**

Acoustic Vibrations

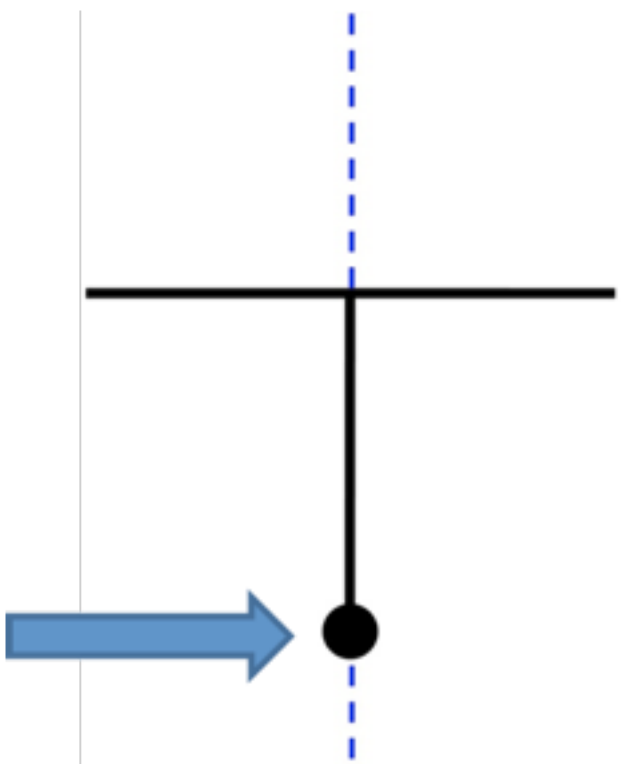
Ultrafast dynamics of metallic Nanostructures



Excitation of Acoustic Vibrations in Metallic Nanoparticles

Following absorption of pump pulse → **2 mechanisms** can launch acoustic vibrations

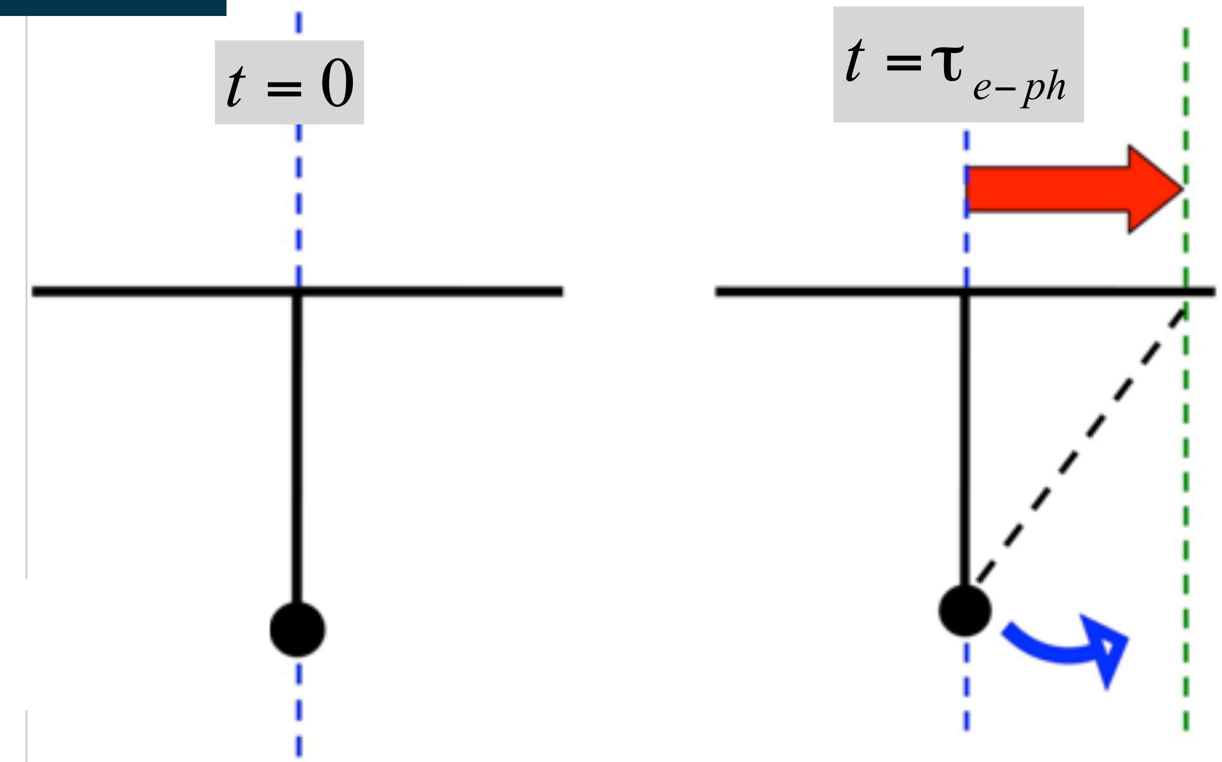
Direct



electron gas pressure increase

→ Force exerted on lattice

Indirect



Electron-Lattice thermalization : $\tau_{e-ph} \approx 1\ ps$

Vibration period ~ 10-100 ps

$\tau_{e\text{-}ph} << T_{vib} \Rightarrow$ MNP out of mechanical equilibrium

ISOTROPIC mechanisms → HIGH SYMMETRY acoustic vibrations modes

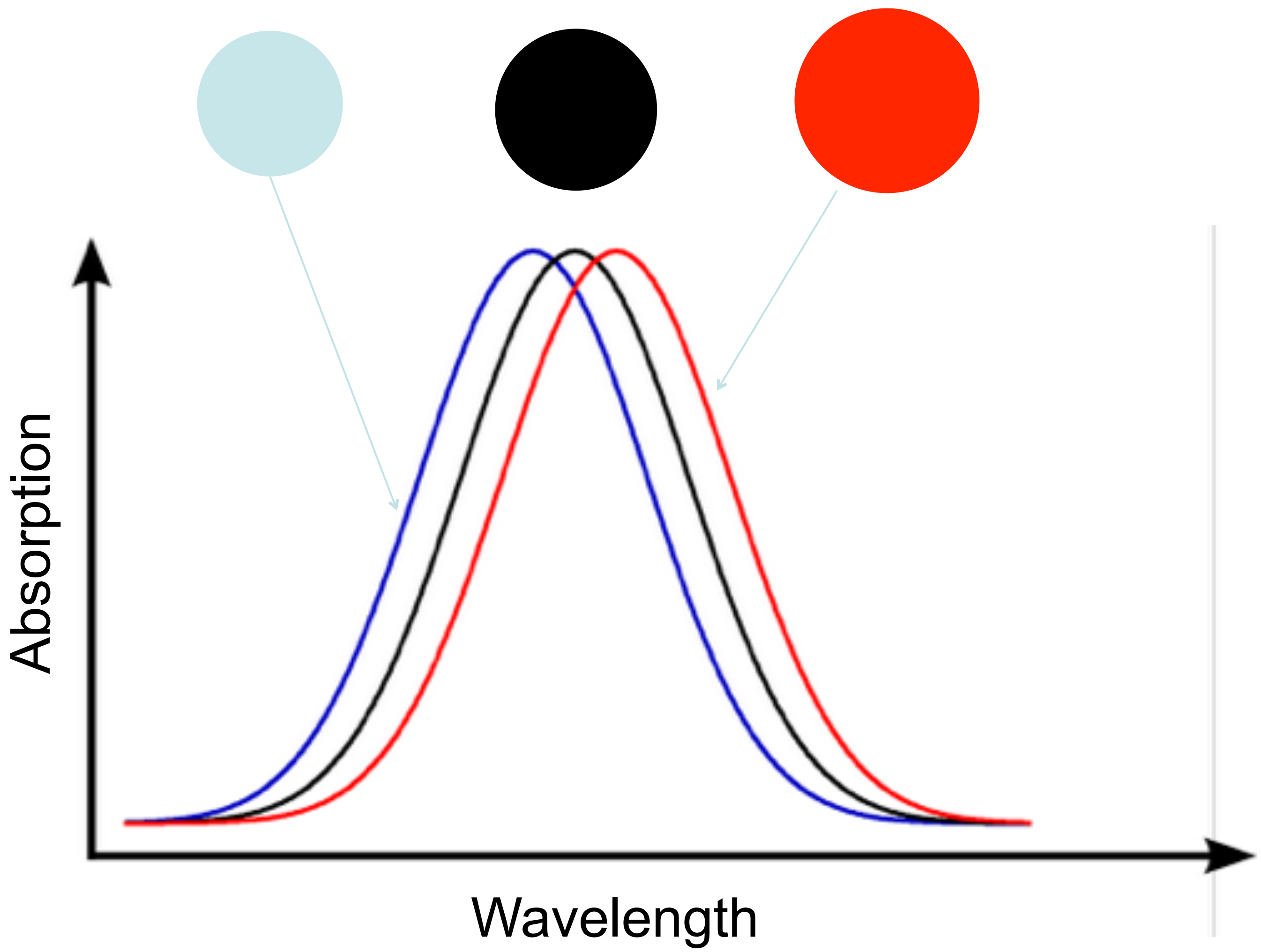
Excitation of an acoustic vibration mode → **atoms moving periodically**

→ Modulation of the **lattice constant** and **volume**

→ Modulation of the **electron density**, **dielectric constant** and **plasma frequency**

Surface Plasmon Resonance of a metallic nanosphere:

$$\Omega_{RPS} = \frac{\omega_p}{\sqrt{\varepsilon_1^{ib}(\Omega_R) + 2\varepsilon_m}}$$



Detection of the acoustic vibrations of plasmonic NPs

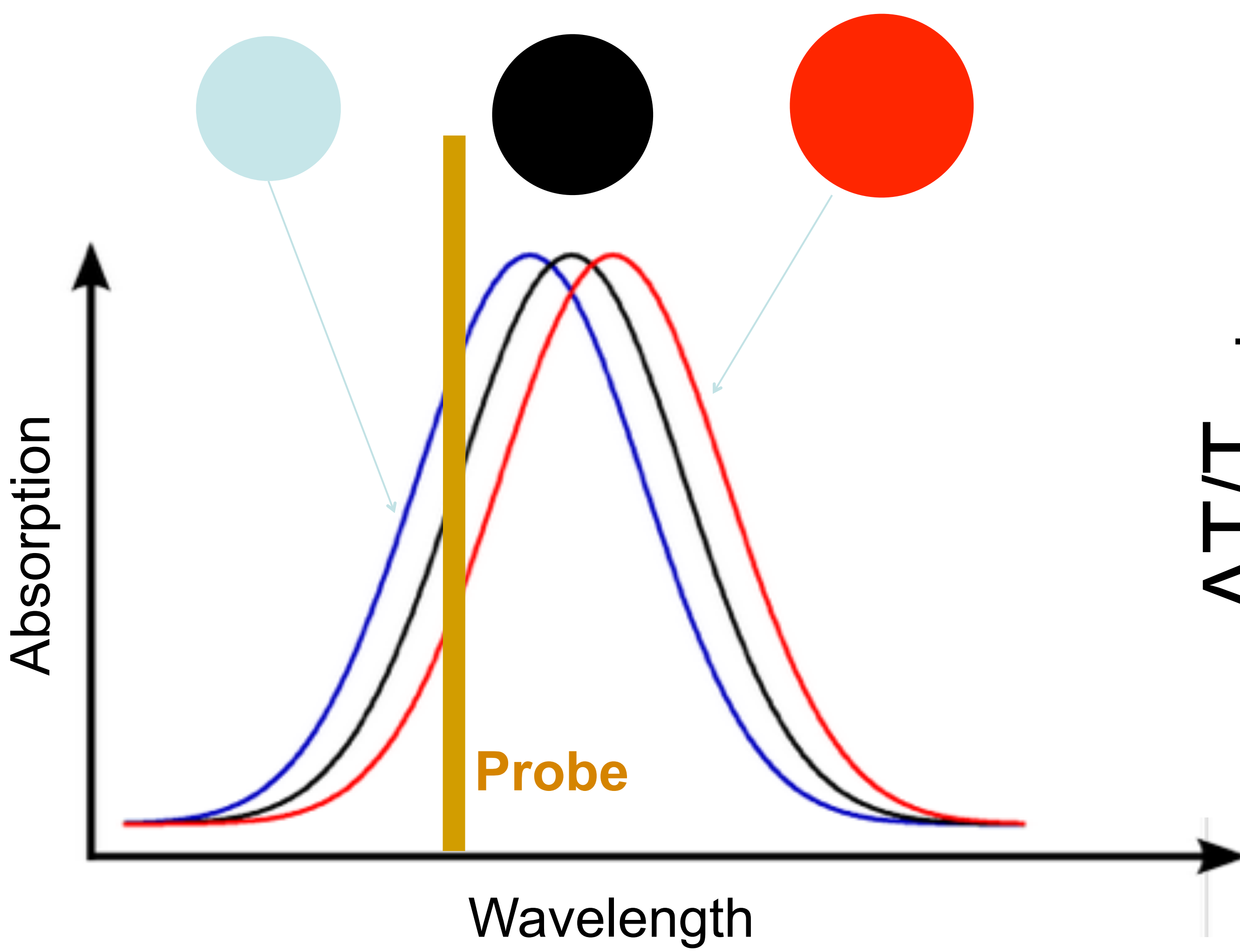
Excitation of an acoustic vibration mode → **atoms moving periodically**

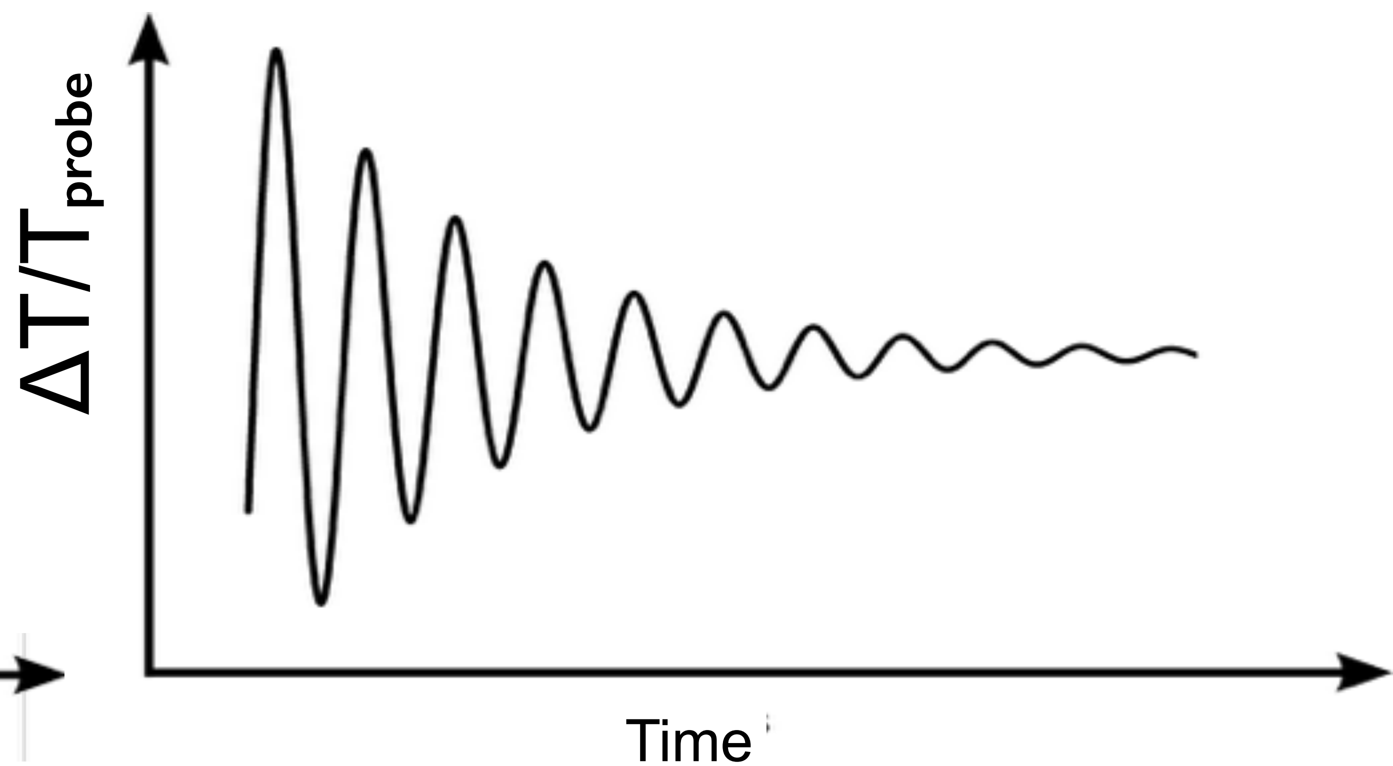
→ Modulation of the **lattice constant** and **volume**

→ Modulation of the **electron density, dielectric constant** and **plasma frequency**

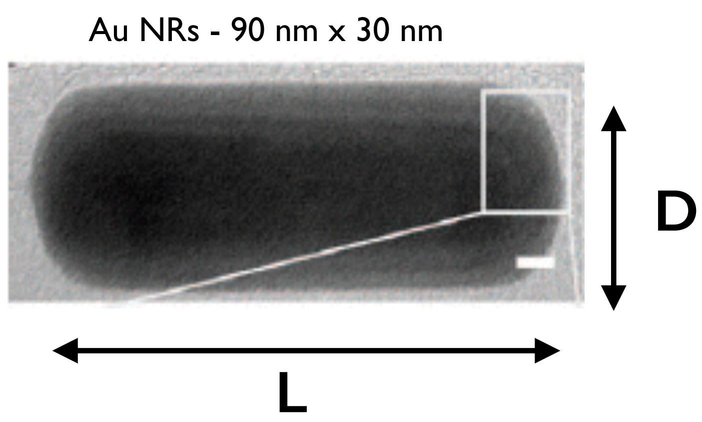
Surface Plasmon Resonance of a metallic nanosphere:

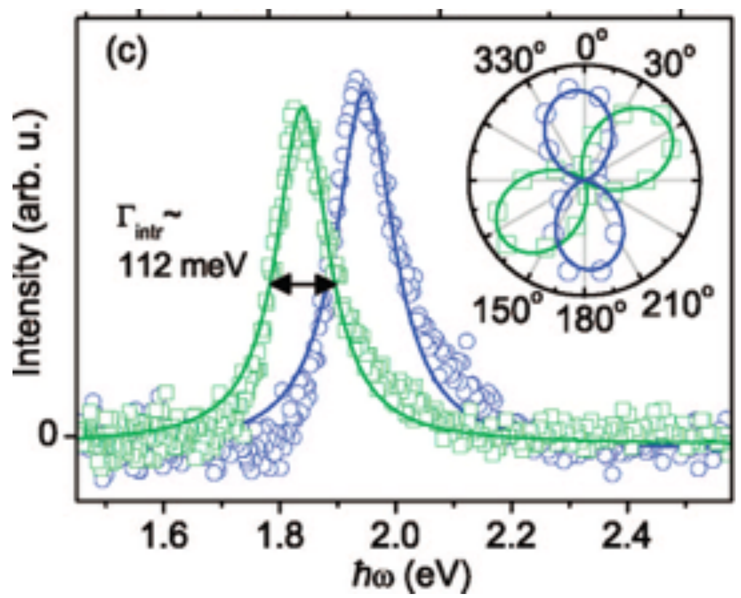
$$\Omega_{RPS} = \frac{\omega_p}{\sqrt{\varepsilon_1^{ib}(\Omega_R) + 2\varepsilon_m}}$$





First measurements of single gold nanorods with well-characterized dimensions and structure

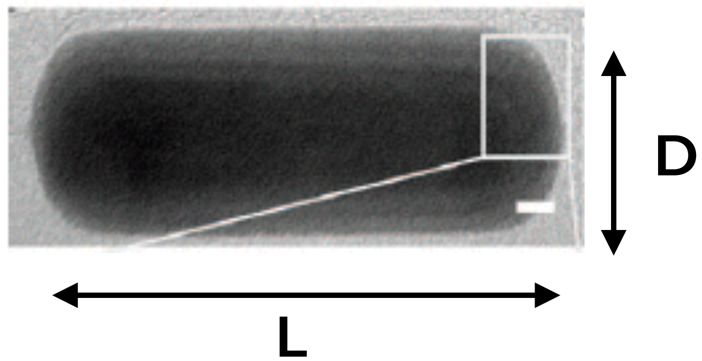


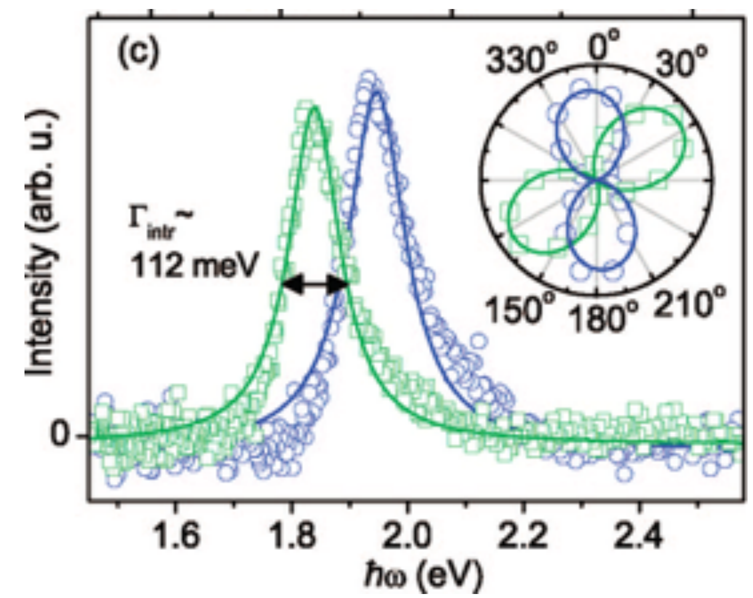


Acoustic Oscillations and Elastic Moduli of Single Gold Nanorods

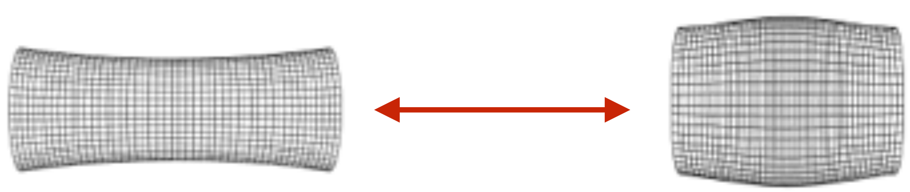
First measurements of single gold nanorods with well-characterized <u>dimensions</u> and <u>structure</u>

Au NRs - 90 nm x 30 nm

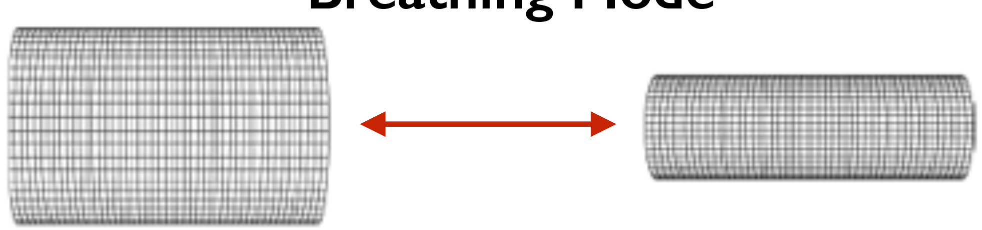


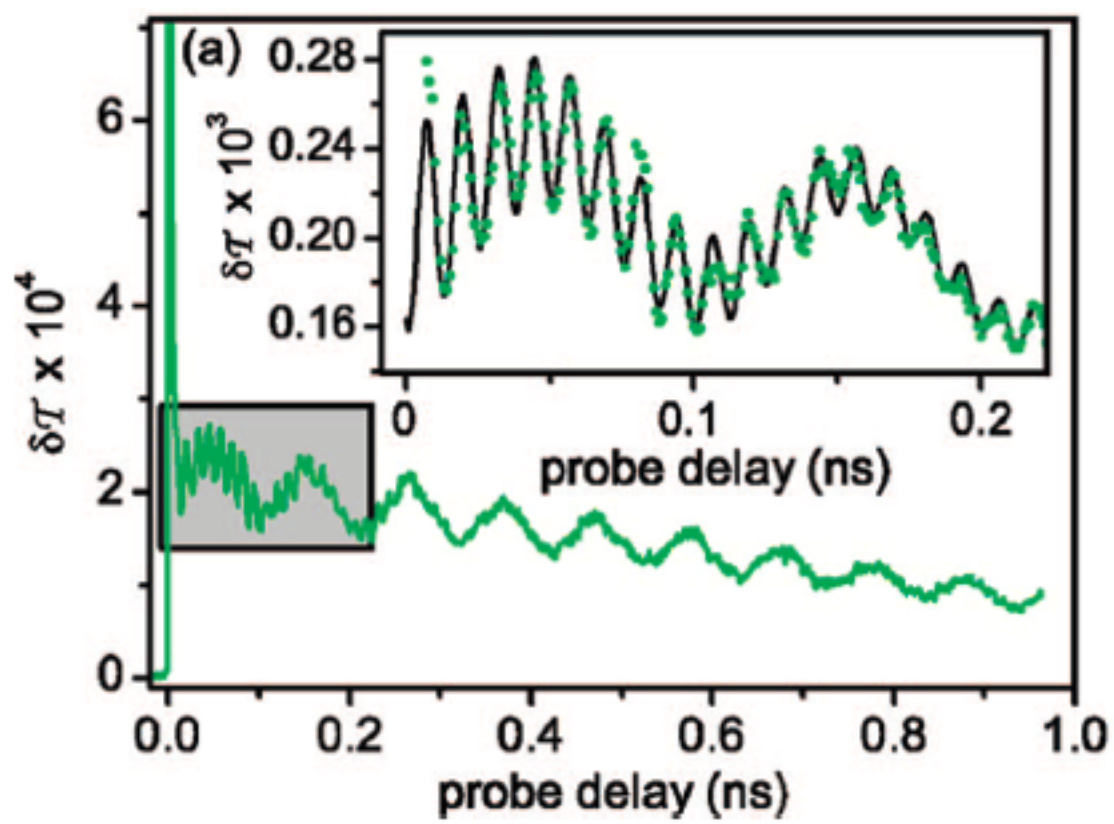


$T_{ext} \propto L$



$T_{br} \propto D$

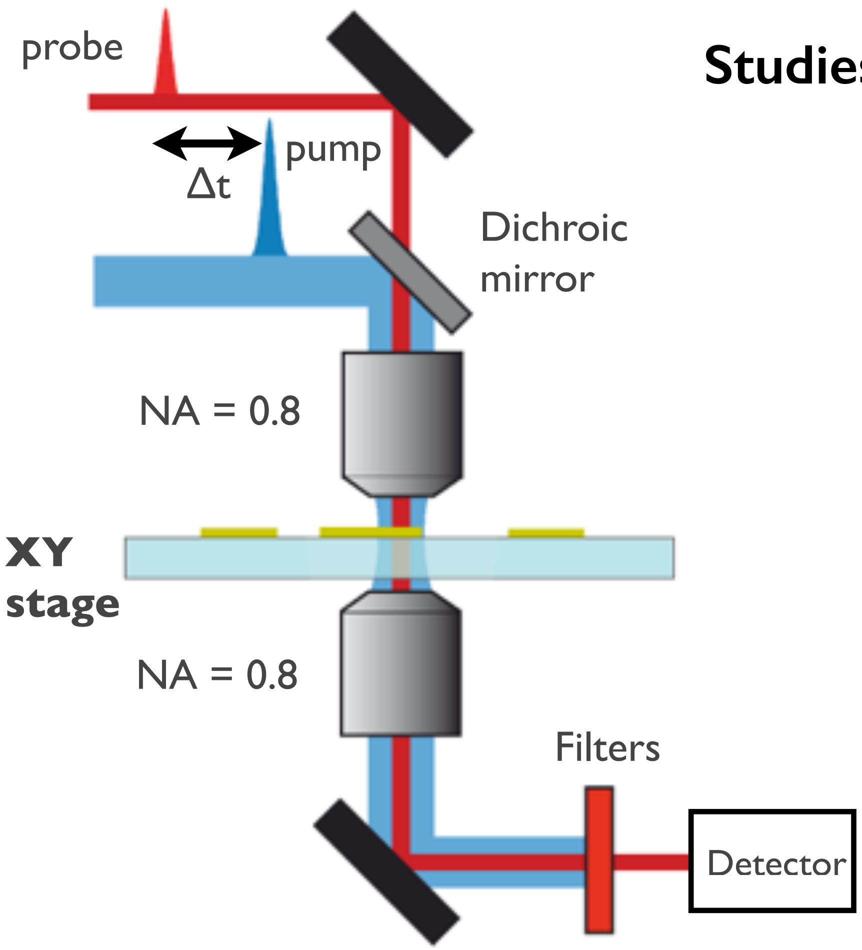




- → **<u>Breathing</u> and <u>Extensional</u> mode detected**
- → **Frequencies in agreement with <u>continuum mechanics</u>**
- → **Single particle <u>elastic moduli</u> agree well with <u>bulk values</u>**

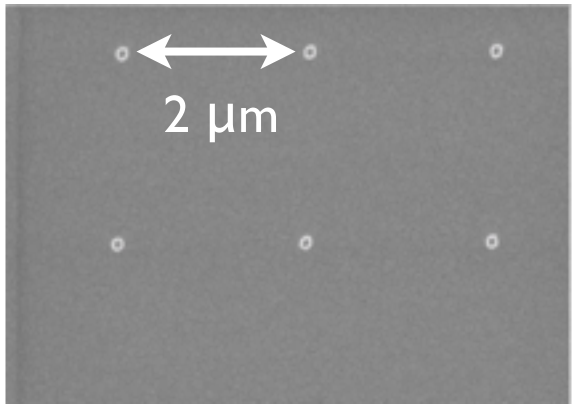
Hu et al, JACS, 125, 14925, **2003**
Van Dijk et al, Phys. Rev. Lett., 95, 267406, **2005**
Zijlstra et al, Nanoletters, 8, 3493, **2008**

Damping of the Acoustic Vibrations of Individual Gold Nanorings

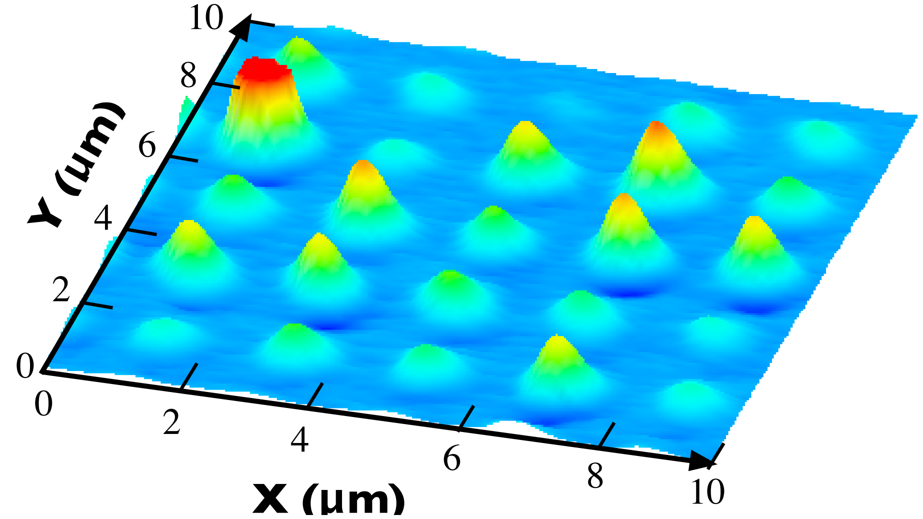


Studies on individual nano-objects → no more <u>inhomogeneous</u> damping

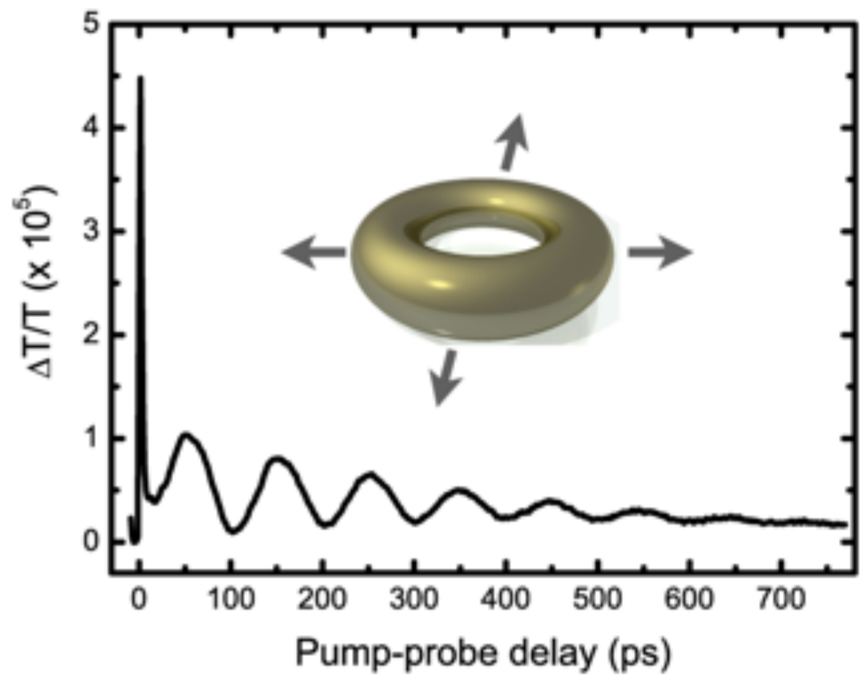
Au rings - D=100nm



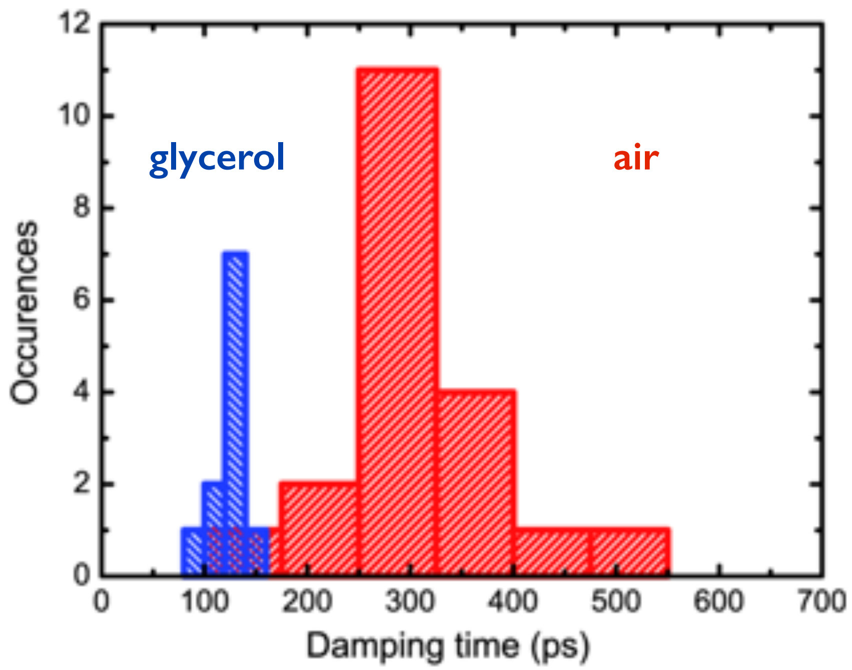
ΔT/T(x,y) map at zero pump-probe delay



ΔT/T(t) on an individual nanoparticle



Damping time on **single** particles



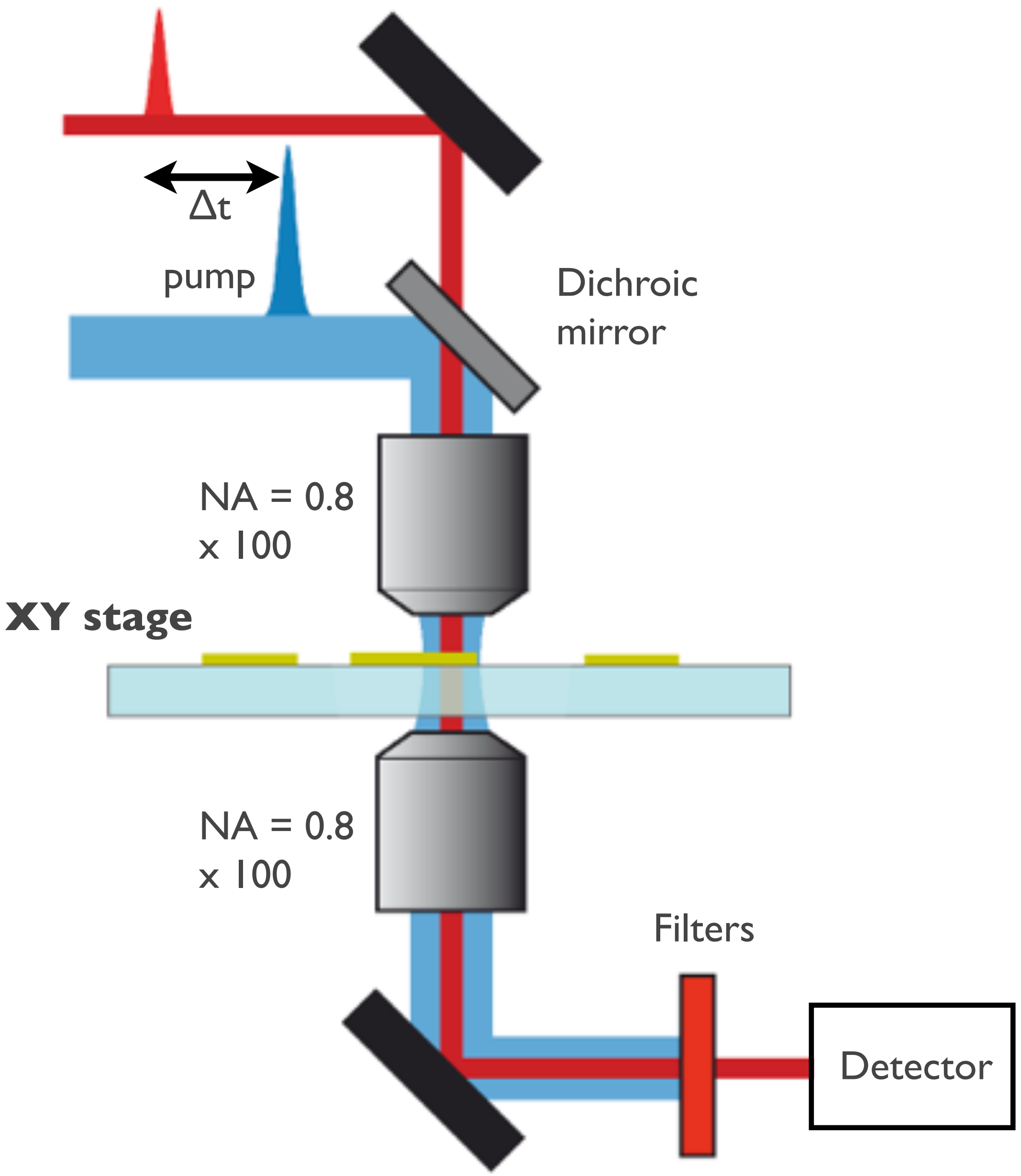
→ Influence of environment

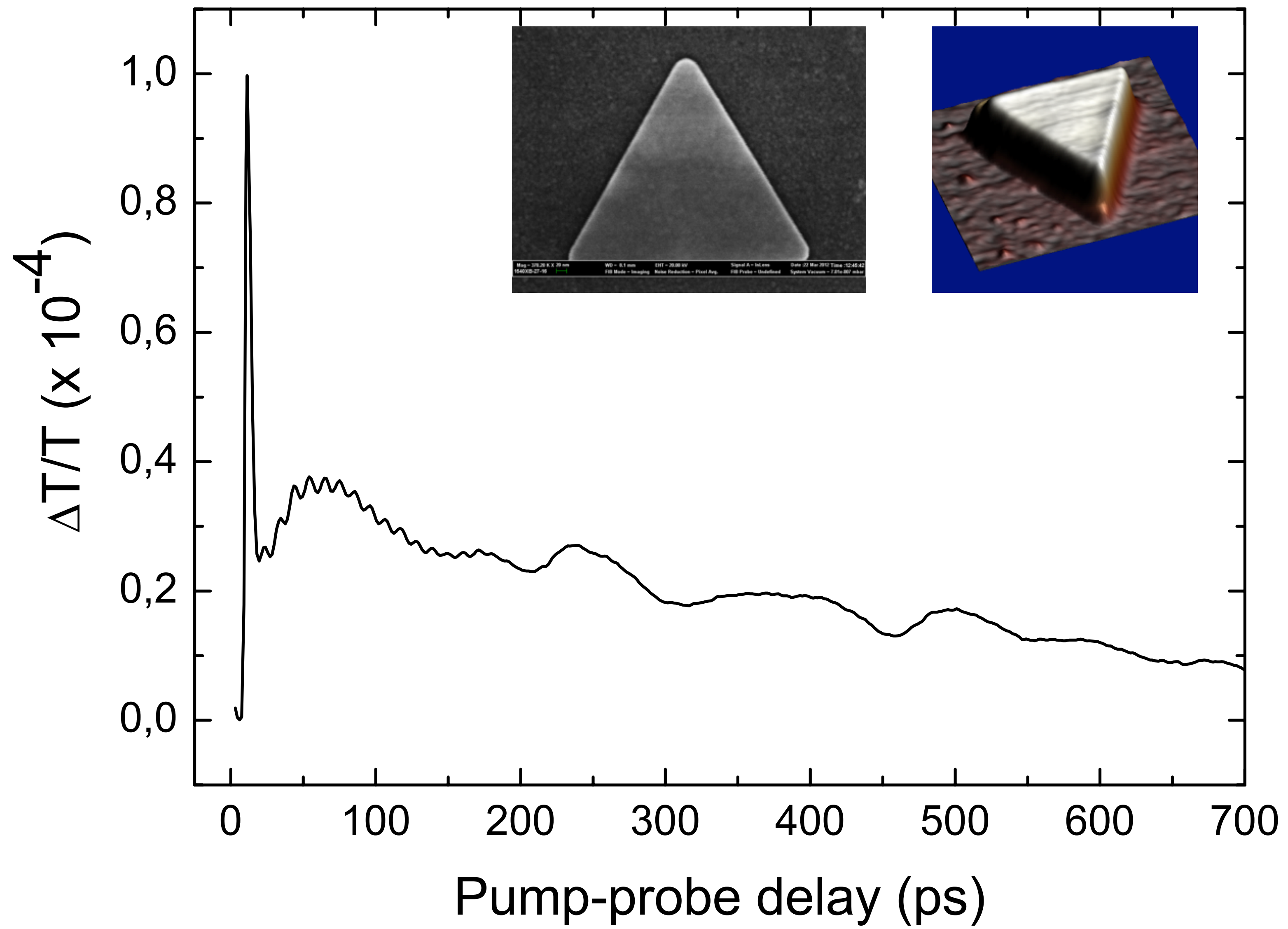
→ Large dispersion of damping time

→ Coupling to **substrate**

Marty et al, Nanoletters, 11(8), 3301–3306, **2011**

Transient absorption spectroscopy of large crystalline gold nanoparticles

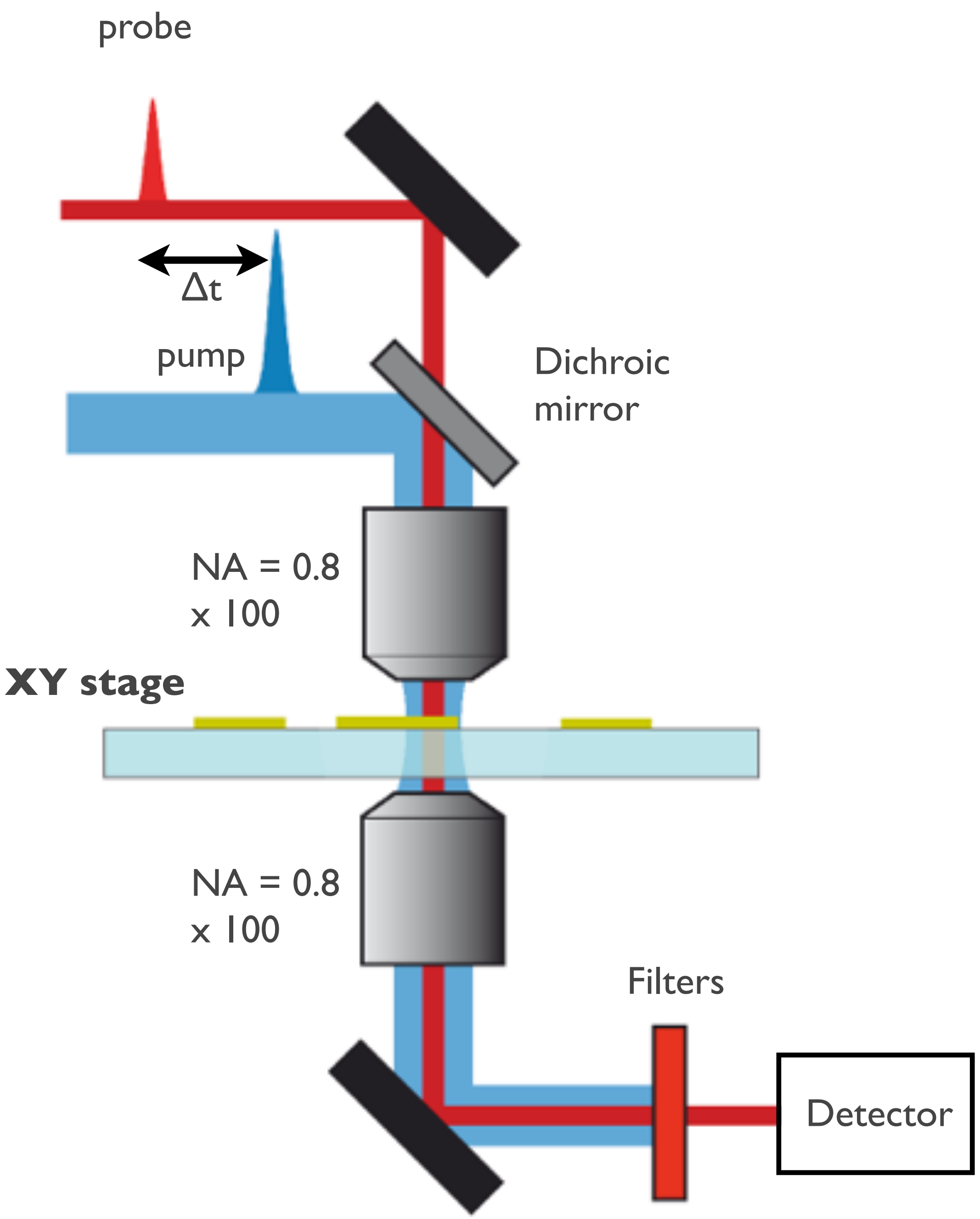


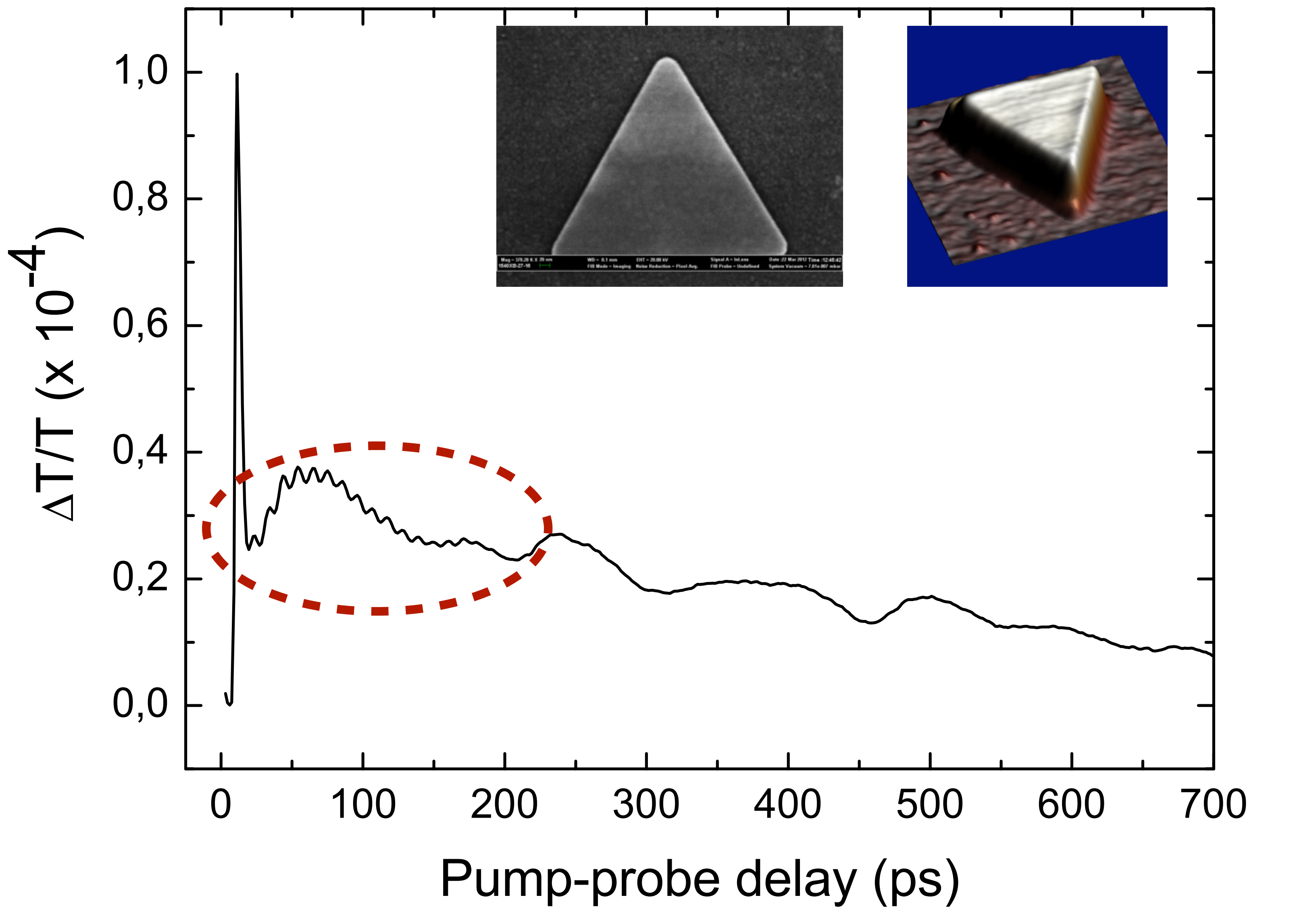


Detection limit : **$\Delta T/T \sim 10^{-7}$**

⇒ Several **acoustic vibration modes** visible

Transient absorption spectroscopy of large crystalline gold nanoparticles





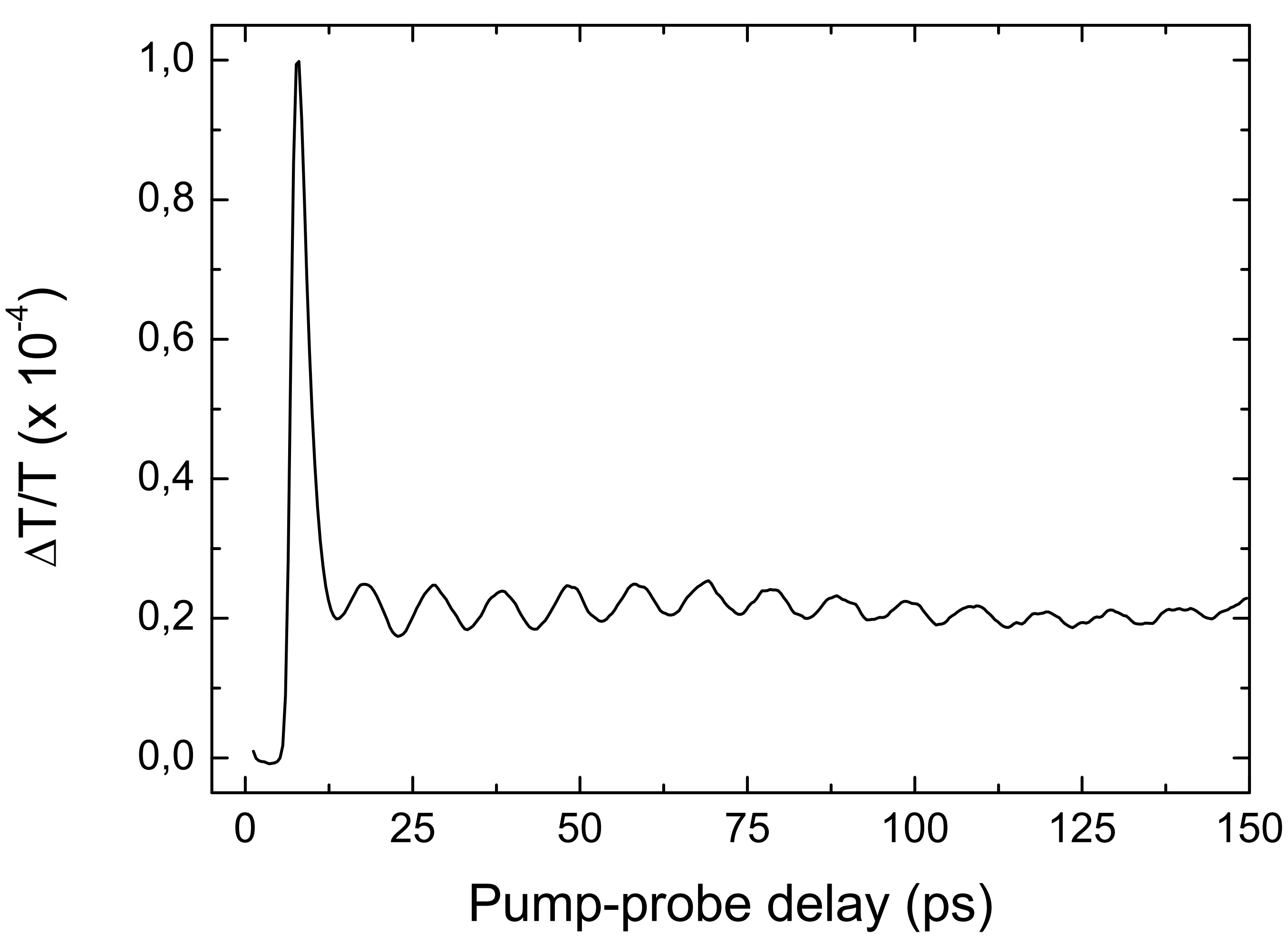
<u>**Detection limit :**</u> **$\Delta T/T \sim 10^{-7}$**

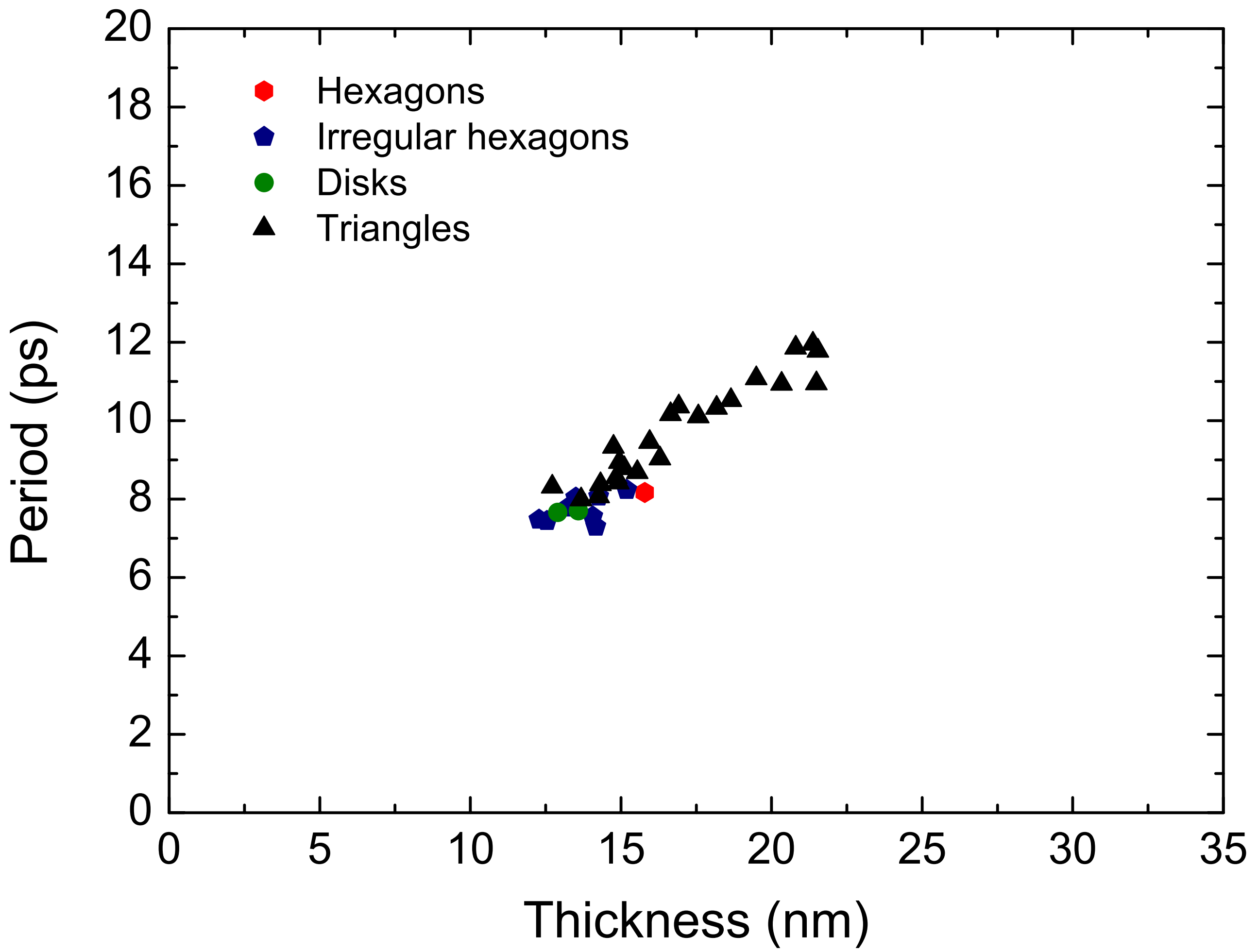
⇒ Several **acoustic vibration modes** visible

⇒ Focus on the **high frequency** mode

Thickness vibration mode

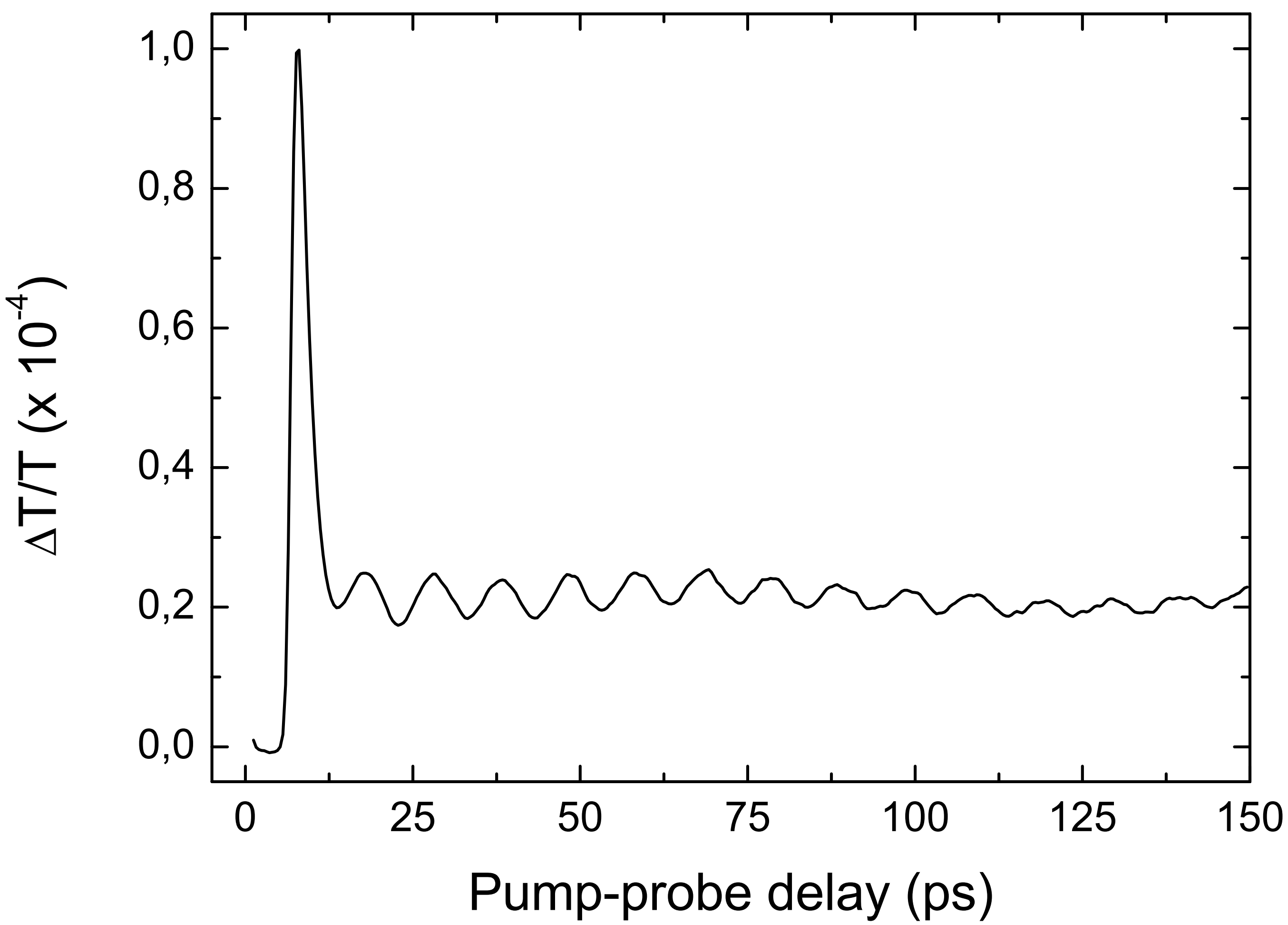
Systematic experiments on 40 different MNPs

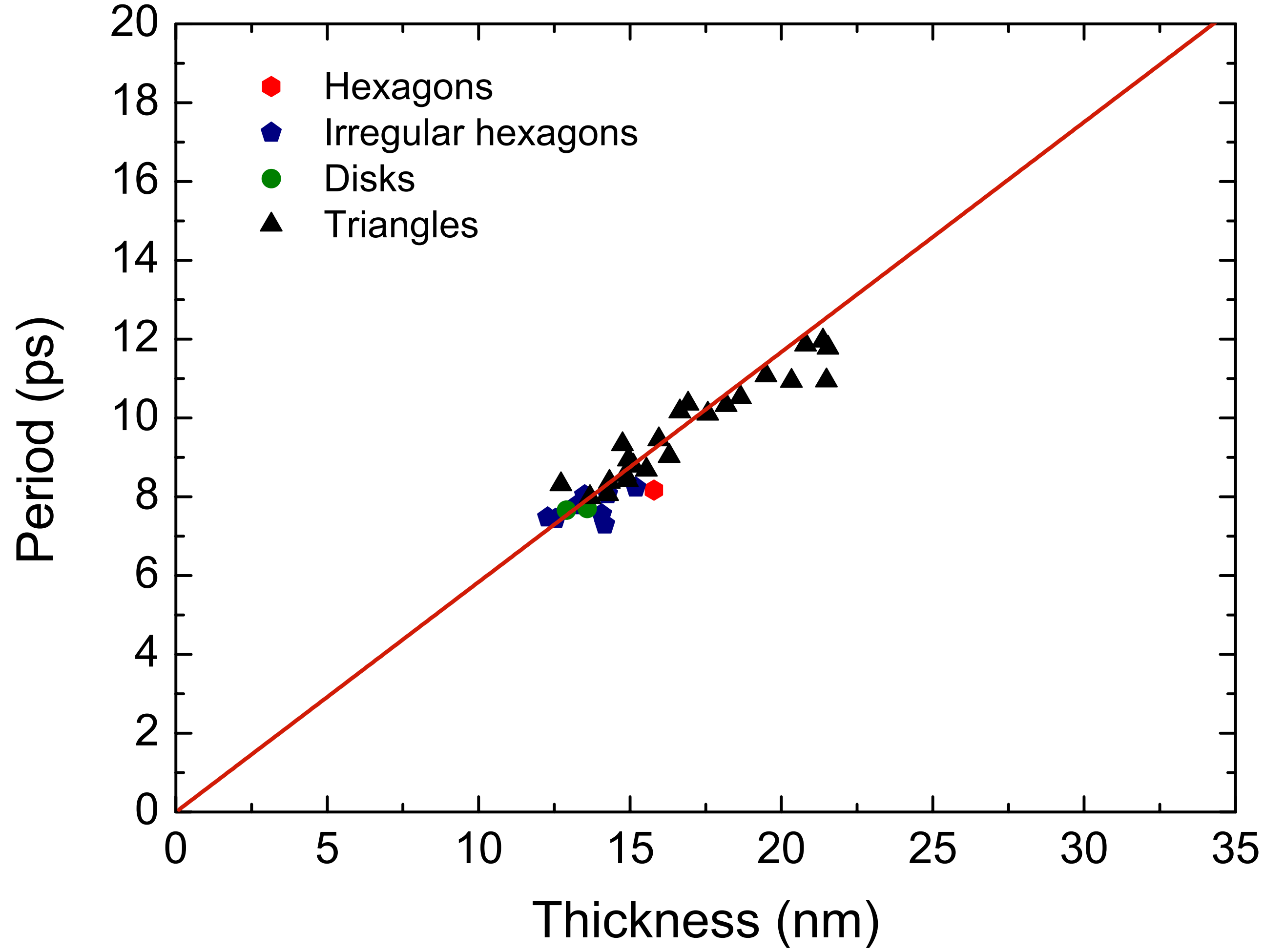




Thickness vibration mode

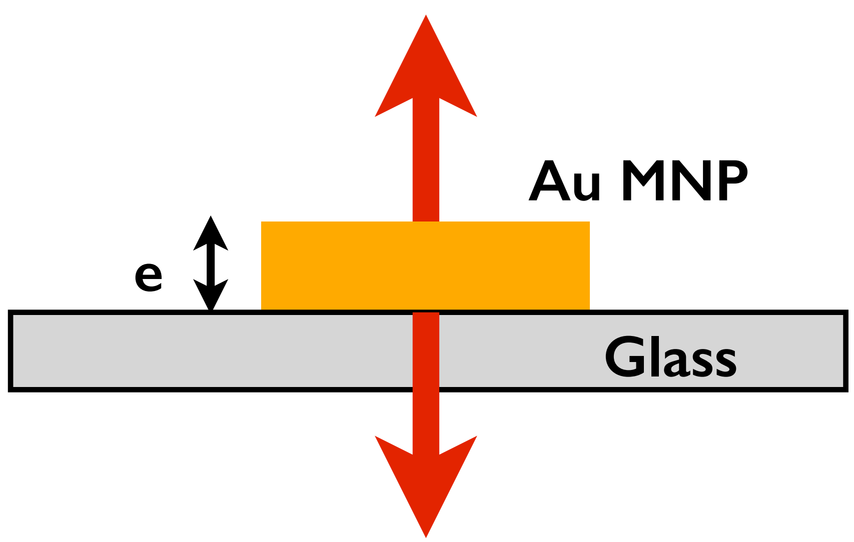
Systematic experiments on 40 different MNPs





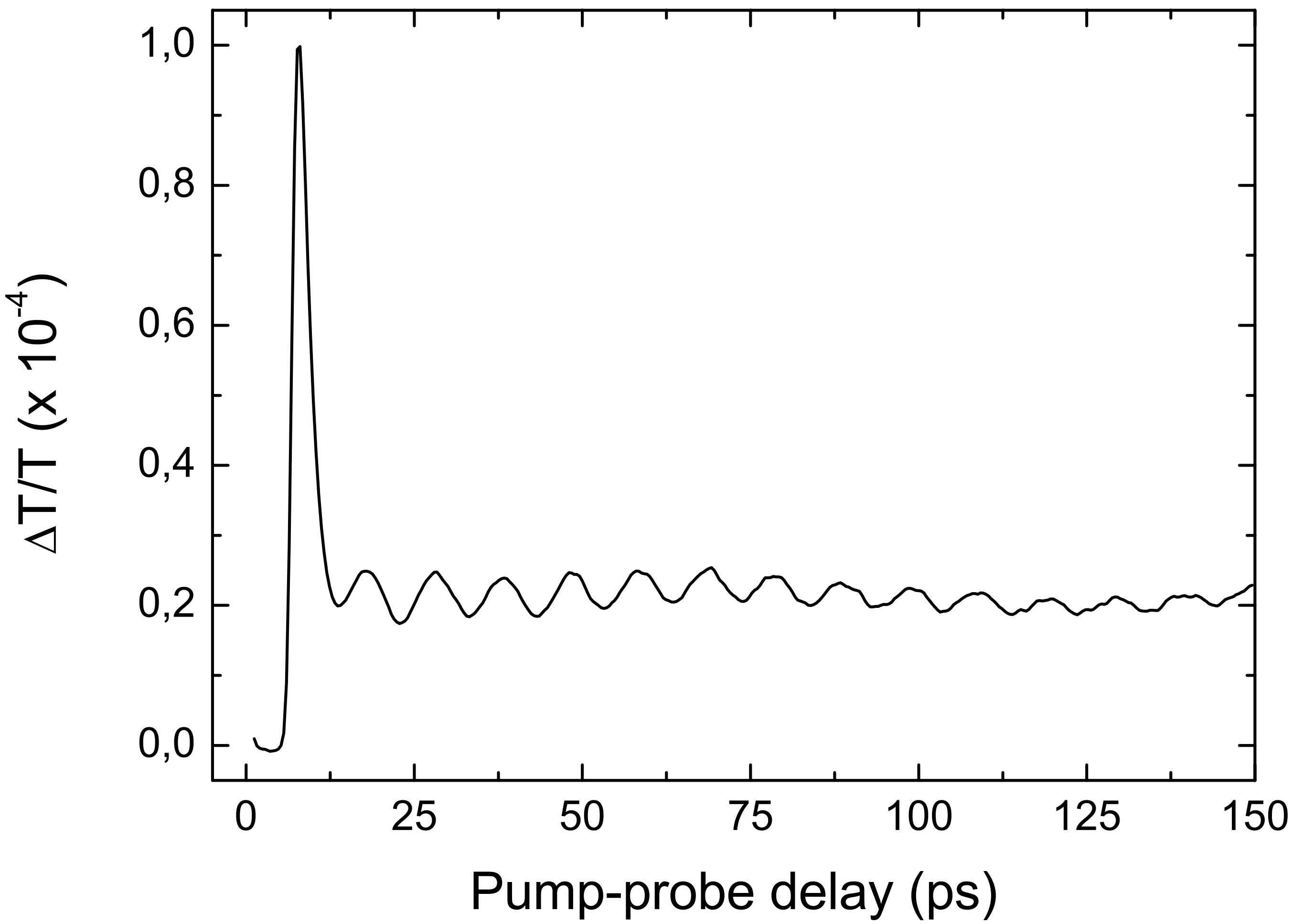
Thickness vibrations of a free plate :

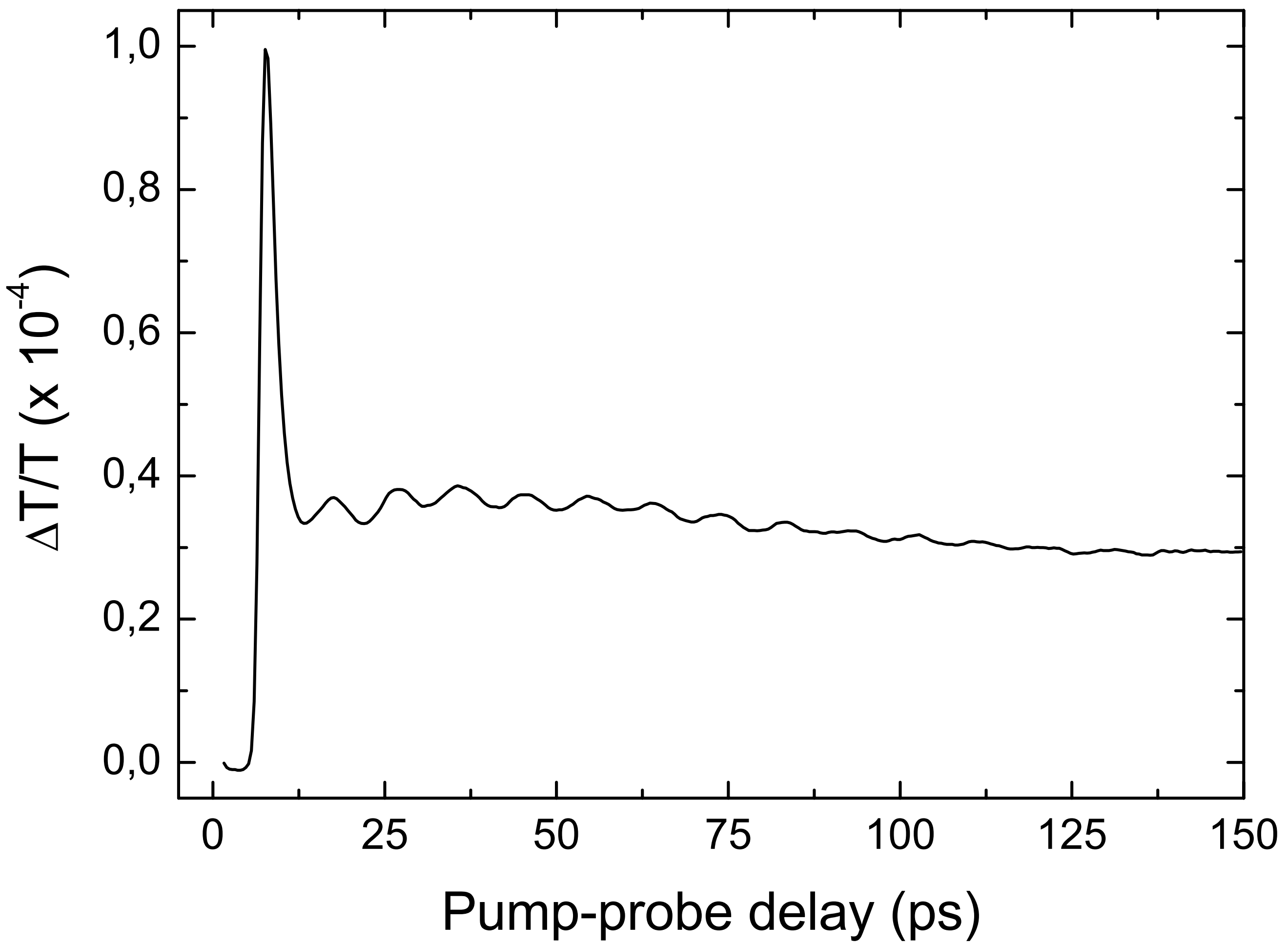
$$T = \frac{2\,e}{v_{l2}}$$



Fedou et al, Phys. Chem. Chem. Phys., 15, 4205-4213, (**2013**)

Damping time of the thickness vibrations





Damping very different from one particle to the other

Numerical fitting by damped cosine :
$$Ae^{-\gamma t}\cos(\frac{2\pi t}{T}+\varphi)$$

⇒ **Damping rate & damping time :**
$$\gamma = \frac{1}{\tau}$$

⇒ To compare oscillators with different frequencies : **Quality factor**
$$Q = \pi \nu \tau$$

Energy dissipation to environment : a basic model

$$\frac{1}{Q} = \frac{1}{Q_{intr}} + \frac{1}{Q_{env}}$$

Intrinsic damping :

anharmonicity - crystalline defects .....

Au nanorods (25x60 nm) : f = 80 GHz - $\langle Q_{intr} \rangle$= 84
Au nanospheres (80 nm) : f = 40 GHz - $\langle Q_{intr} \rangle$= 40
Ruijgrok et al, Nanoletters., 12, 1063−1069 (**2012**)

Coupling to environment :

Sound radiation

Energy dissipation to environment : a basic model

$$\frac{1}{Q} = \frac{1}{Q_{intr}} + \frac{1}{Q_{env}}$$

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Ruijgrok et al, Nanoletters., 12, 1063−1069 (**2012**)

Coupling to environment :

Sound radiation

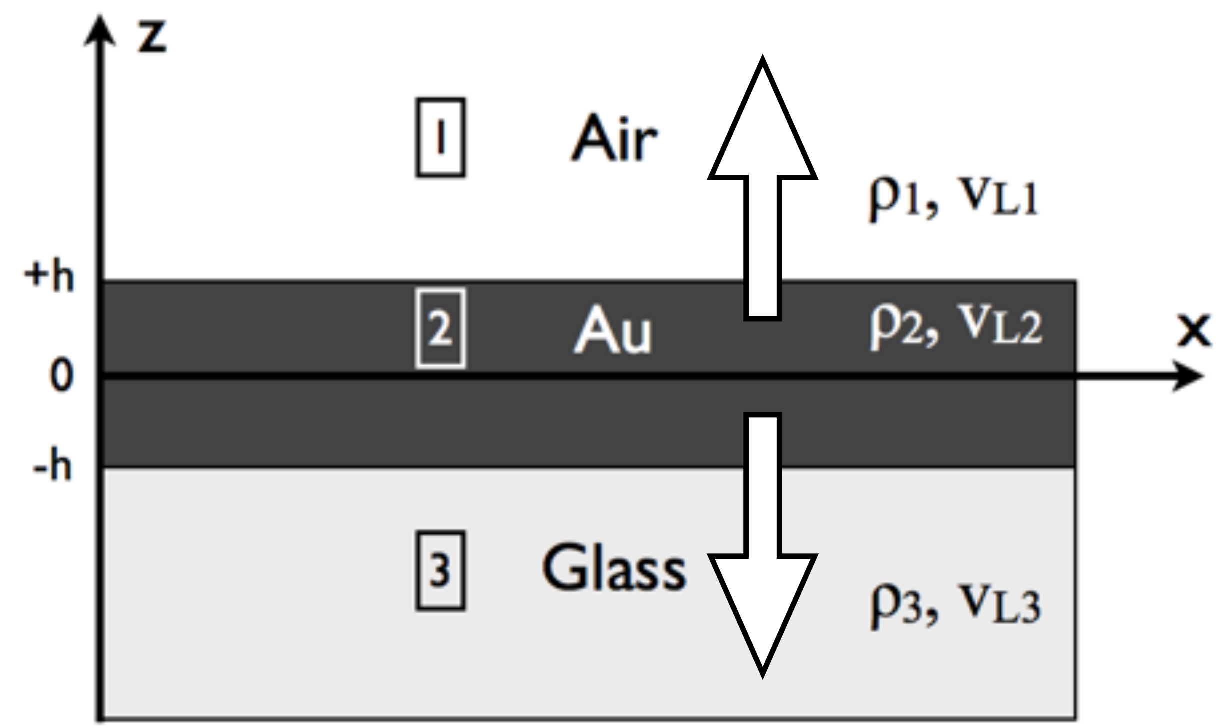
Sound radiation from flat metal particles :

Simple 3-layer model

Unidimensional sound propagation

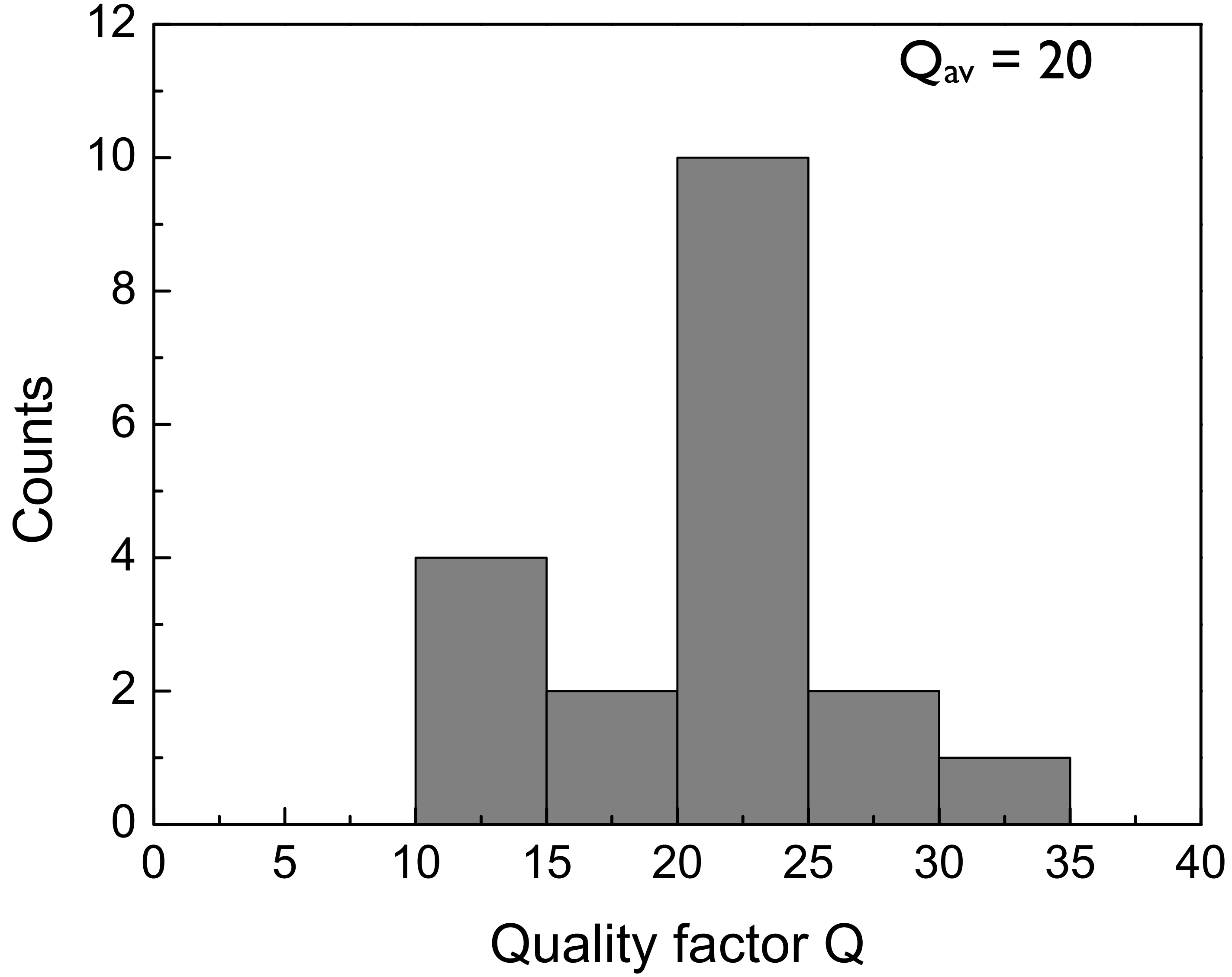
Boundary conditions at each interface

Complex frequencies : $\tilde{\omega} = \omega + i\gamma_{env}$



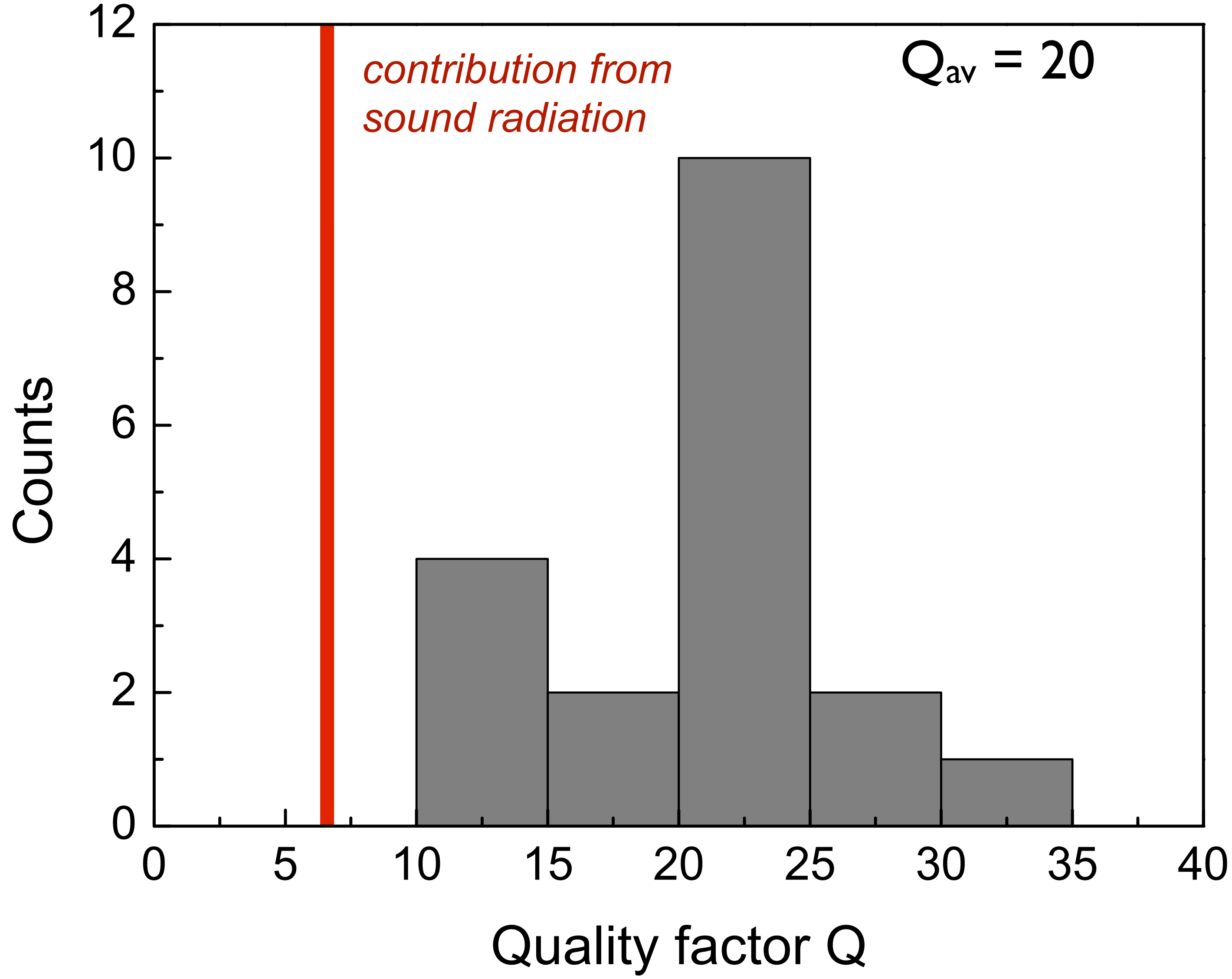
Quality factor for air/Au/SiO_2 : $Q_{env} \approx 7$

Experimental distribution of quality factors



Strong dispersion of measured Q

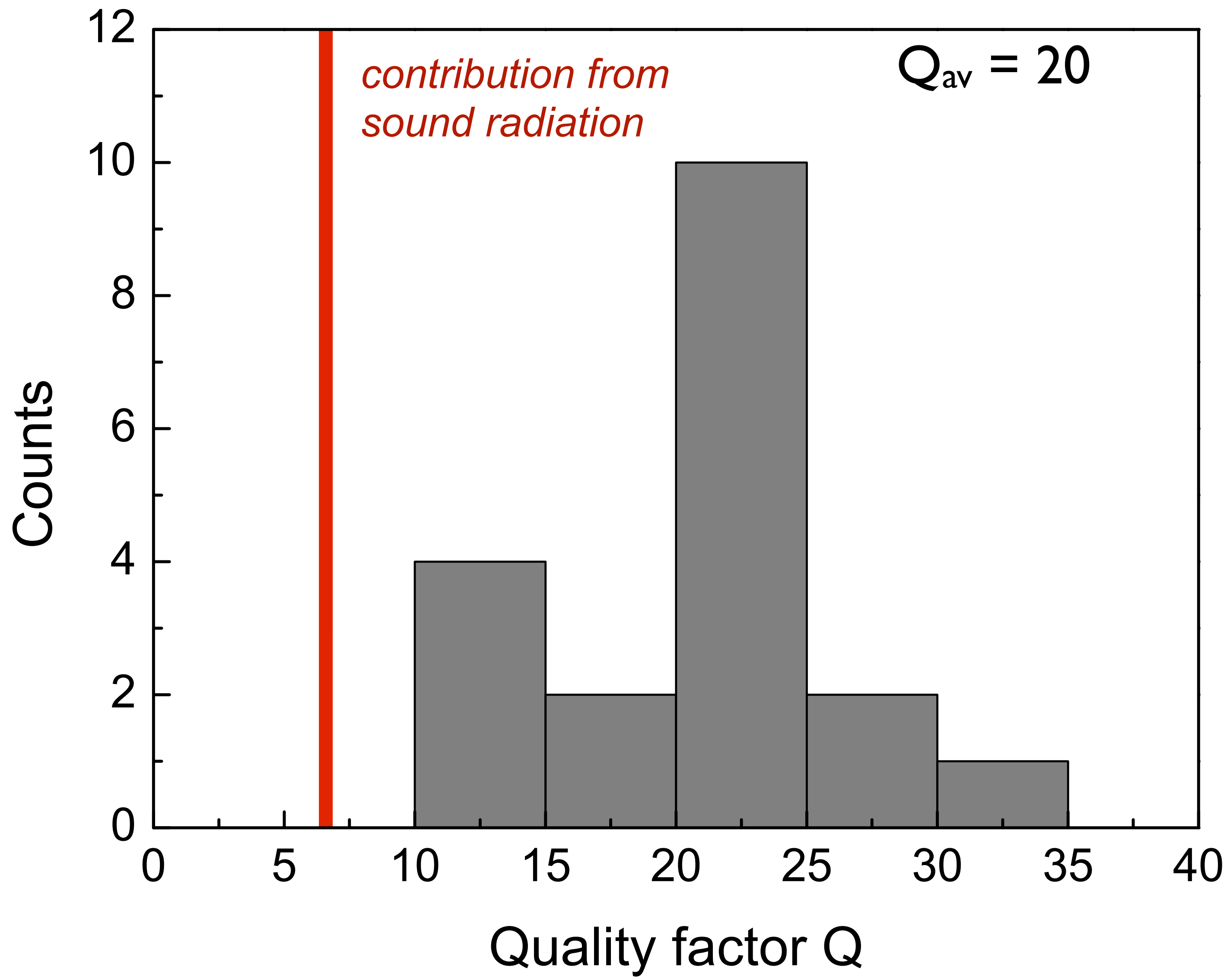
Experimental distribution of quality factors



Strong dispersion of measured Q

Quality factor always higher than predicted w/o intrinsic contribution

Experimental distribution of quality factors



Strong dispersion of measured Q

Quality factor always higher than predicted w/o intrinsic contribution

Mechanical decoupling MNP/substrate

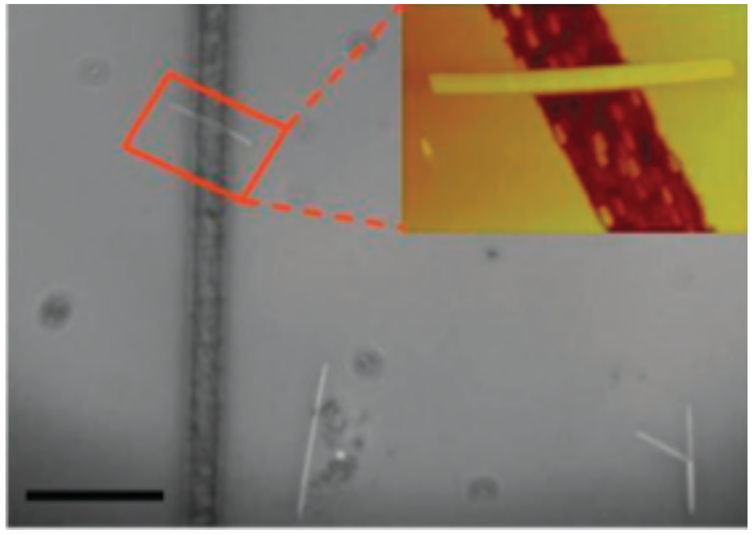
Residual interfacial PVP layer

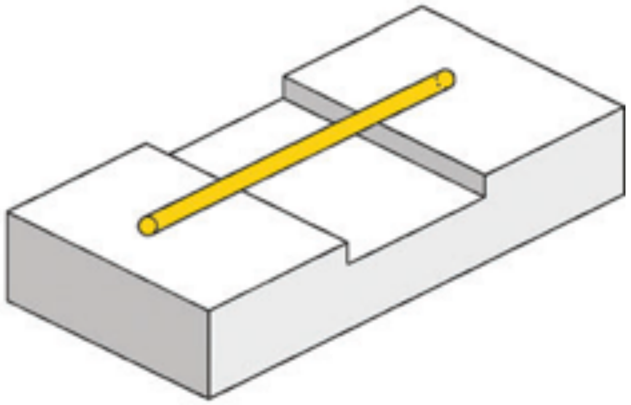
Intrinsic contribution ?

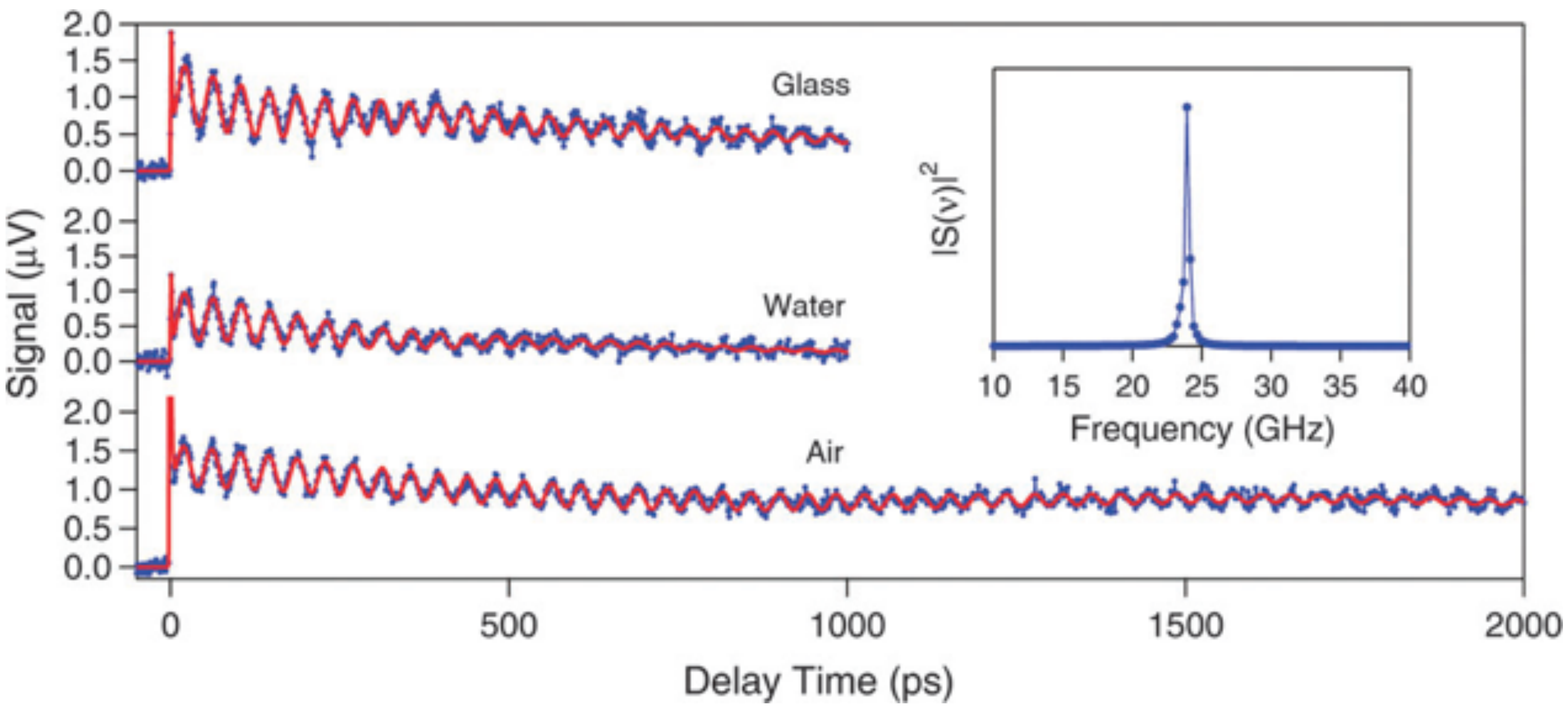
Fedou et al, Phys. Chem. Chem. Phys., 15, 4205-4213, (**2013**)

Substrates have an influence on the damping of the acoustic vibrations of MNPs

→ Need to get rid of substrate to address **intrinsic damping** mechanisms



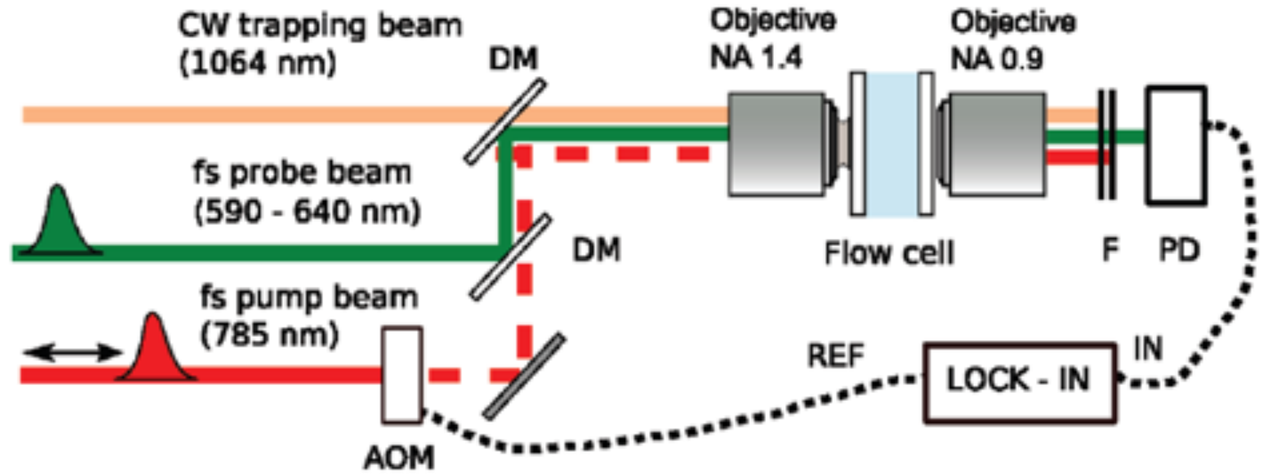


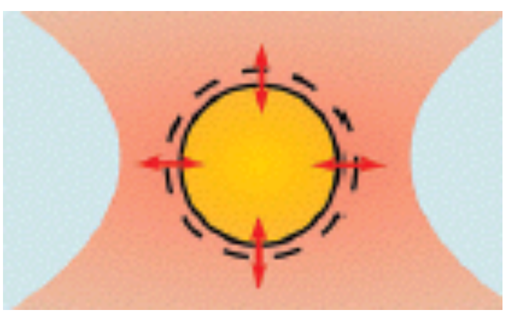


Major et al, Phys.Chem. Chem. Phys.,15, 4169, **2013**

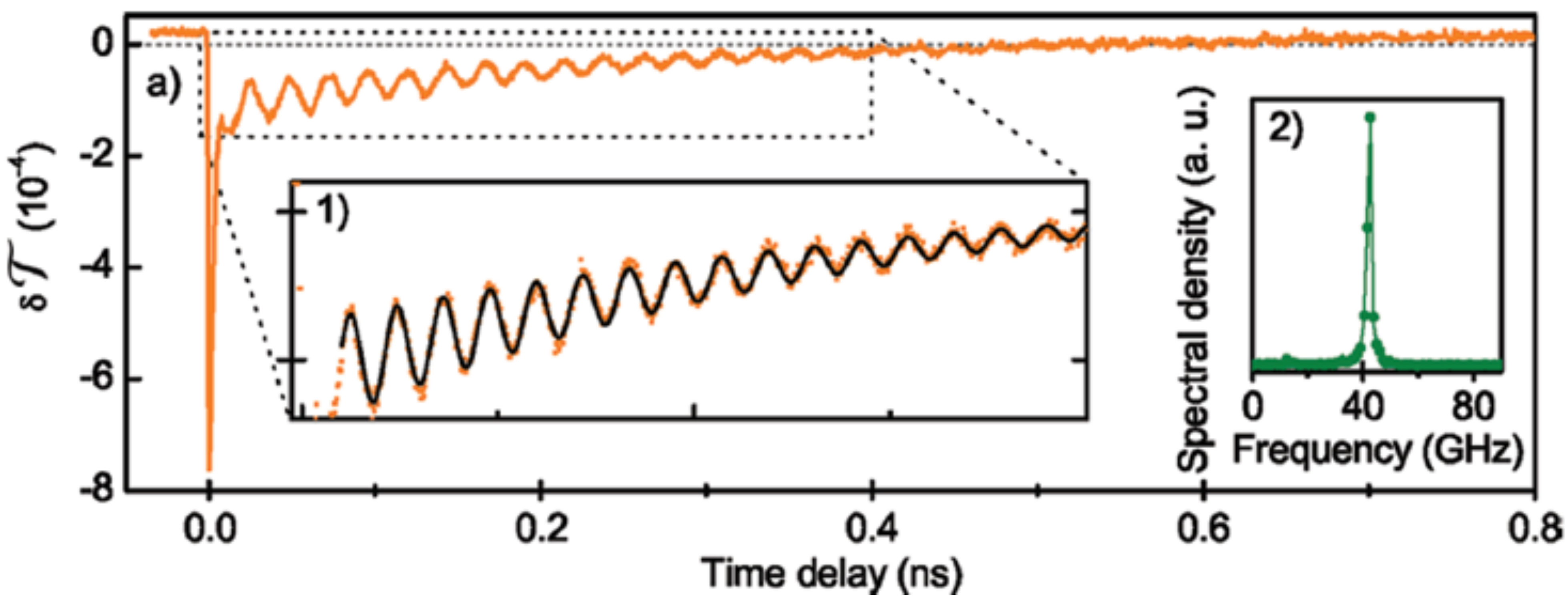
Damping of Acoustic Vibrations of Optically Trapped Single Gold Nanoparticles

Ultrafast pump-probe spectroscopy + Optical trapping





Au NS - D=80nm



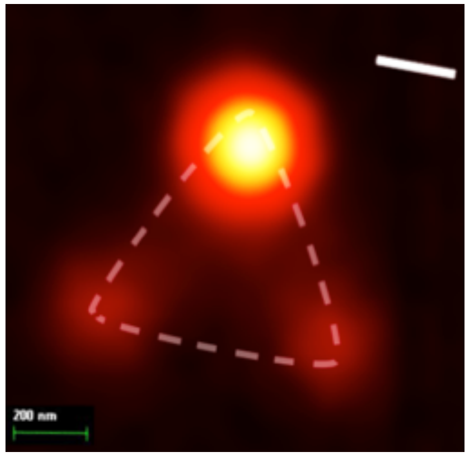
→ **Particle-to-particle variation in damping times**

→ Vibrational damping not only by dissipation into the liquid, but also by **intrinsic** **mechanisms**

→ Experiments on gold nanorods suggest that **crystal structure** is **important**

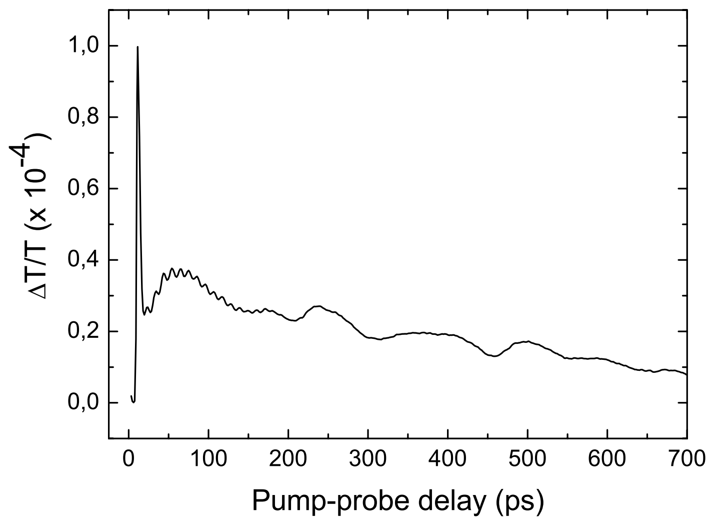
Ruijgrok, et al, Nanoletters., 12, 1063, **2012**

Conclusion



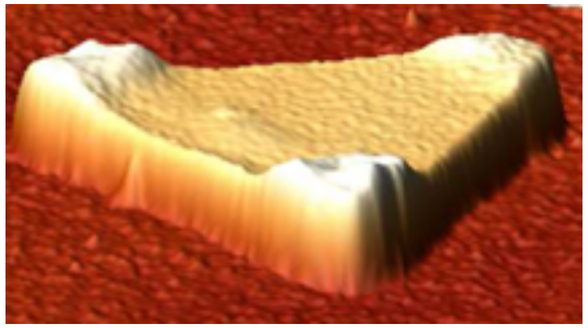
Ultrafast dynamics of metallic nano-objects:

→ Complex sequence of relaxation processes
→ Timescales from <u>a few fs</u> to <u>several hundreds ps</u>



Enhancement of optical response by Surface Plasmons:

→ Ultrafast Time-Resolved Studies on **<u>individual</u>** nano-objects
→ Selective investigation of the different processes
→ Size effects evidenced on electronic and vibrational dynamics



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