



# Field-Enhanced Scanning Near Field Optical Microscopy

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## How to retrieve optical spectroscopic information on the nanoscale?

**ISOLATE**

Confocal  
Microscopy



Photo: A. Mahmoud  
Eric Betzig



Photo: A. Mahmoud  
Stefan W. Hell

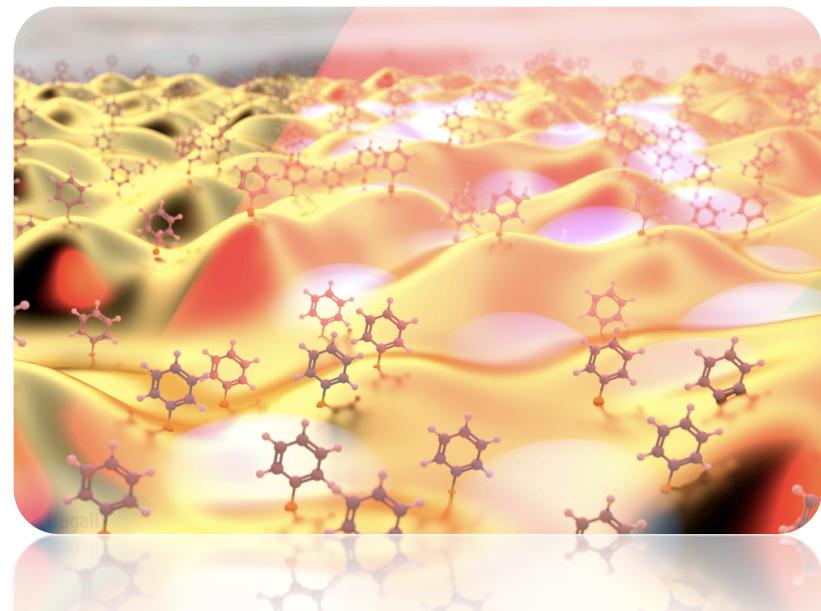


Photo: A. Mahmoud  
William E. Moerner

Difficulty: weak interaction cross-sections  $\sigma = 10^{-15} \rightarrow 10^{-30} \text{ cm}^2$   
→ need for field amplification

**TEXTURED  
METAL  
SURFACES**

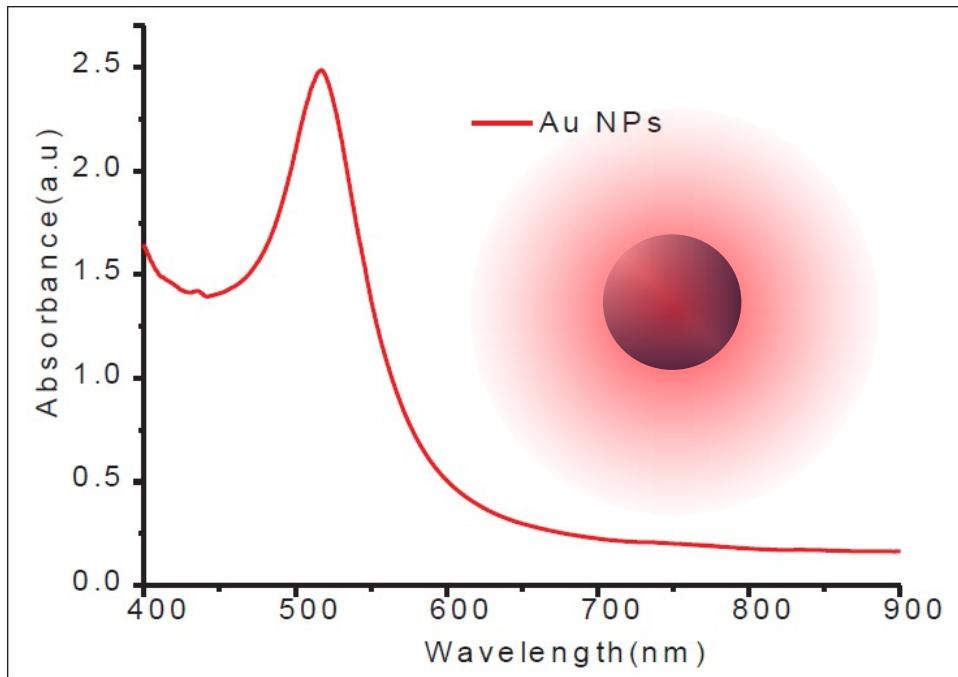
SERS  
SHG



Review of the principle & applications behind field enhanced optical microscopy/spectroscopy

Some outside-the-box optical applications

## –Localized Surface Plasmon excitation –



The polarizability of a small sphere

$$\alpha = 4\pi a^3 \frac{\epsilon - 1}{\epsilon + 2}$$

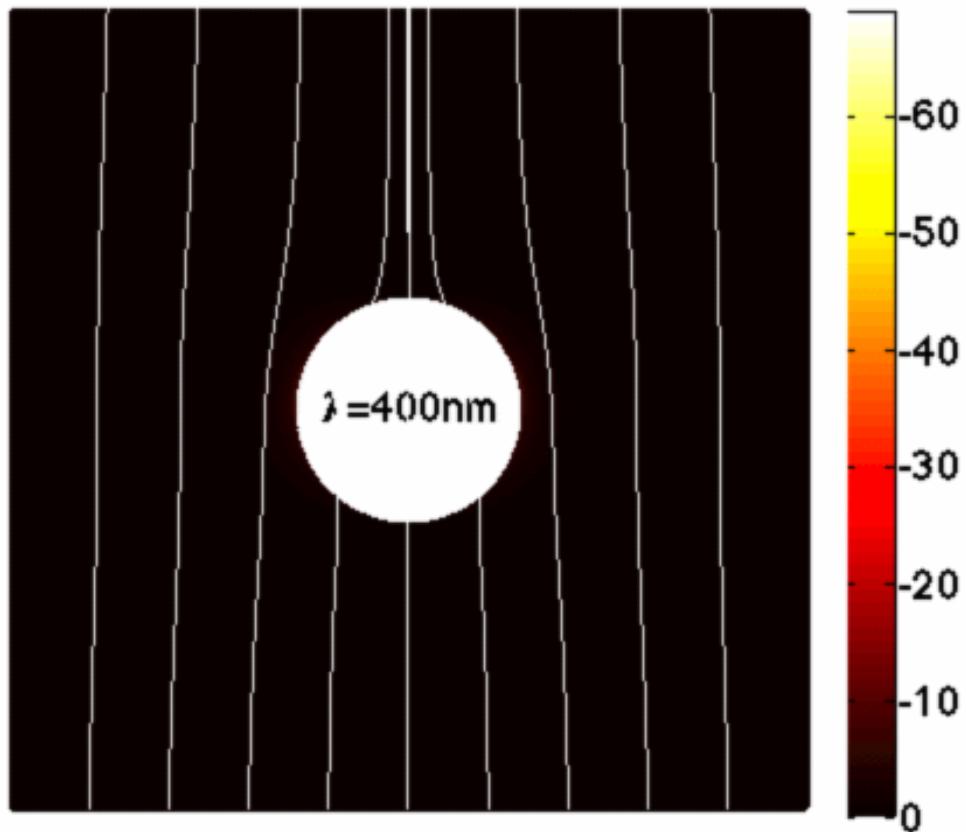
$\alpha$  diverges (resonance) for  $\epsilon = -2$

The total field near the nanoparticle

$$E_t = E_{inc} + E_{loc} = E_{inc} + 4\pi a^3 \frac{\epsilon - 1}{\epsilon + 2} E_{inc}$$

Local field enhancement

## – Surface Plasmon excitation –

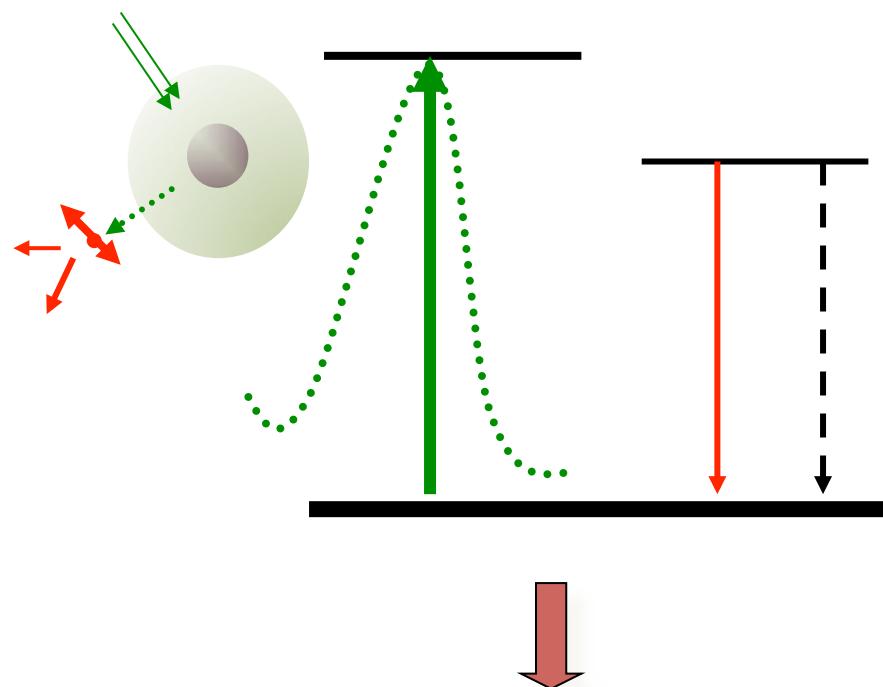


Sensitive to:

- materials
- shape & size
- polarization

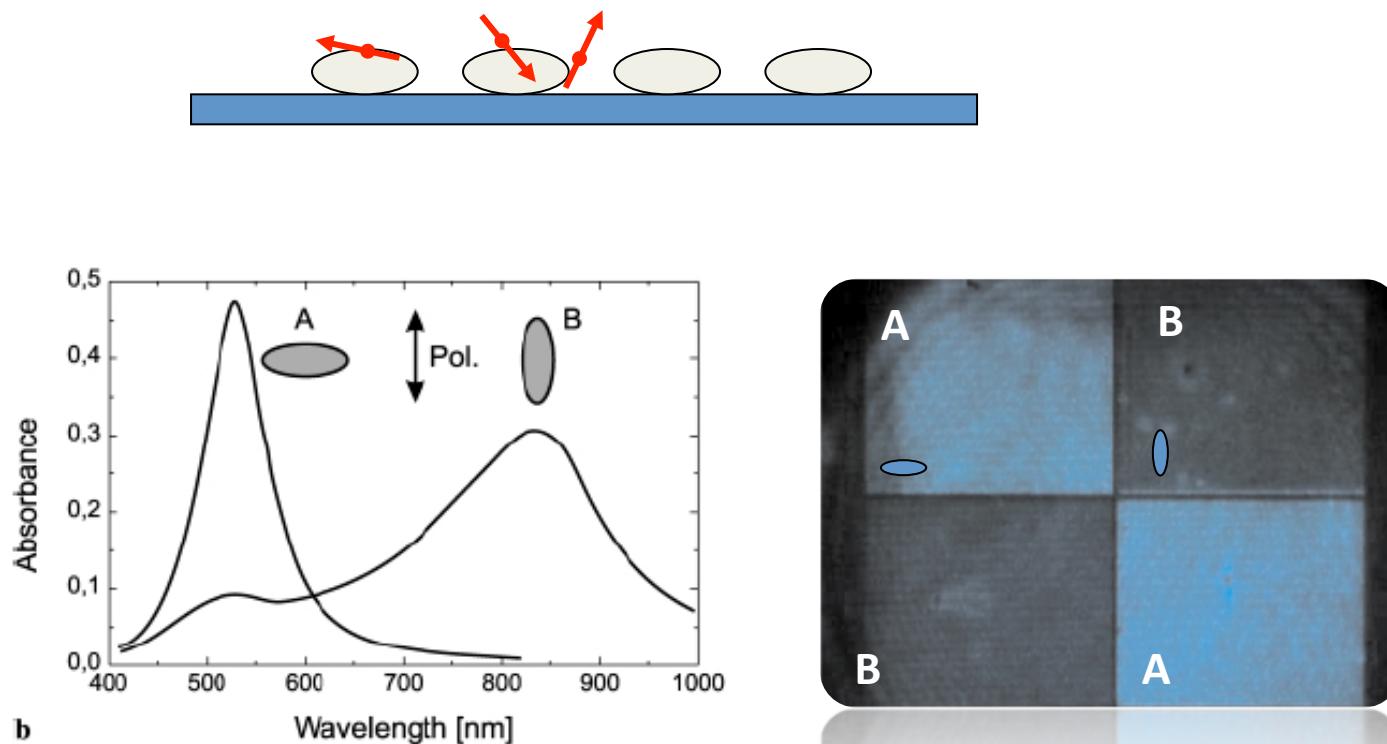
## - Fluorescent enhancement–

The resonance can be tuned to match either **the absorption maximum** or **the emission maximum**

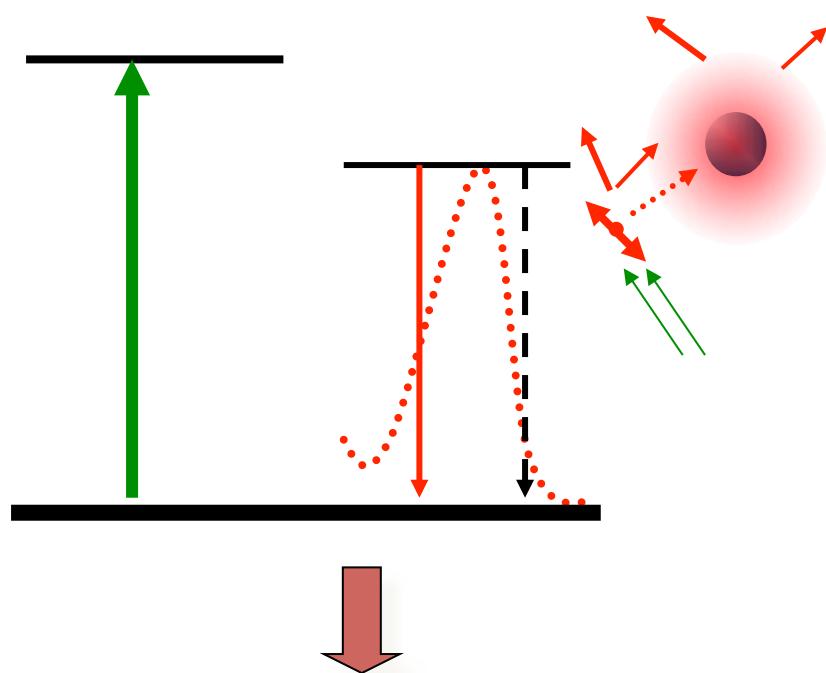


Enhancement of the excitation

Excitation resonant with the short axis and the absorption maximum



Ditlbacher *et al.*, *Appl. Phys. B.* **73**, 373 (2001)



$$F_p = \frac{3}{4\pi^2} \left( \frac{\lambda}{n} \right)^3 \frac{Q}{V_{eff}}$$

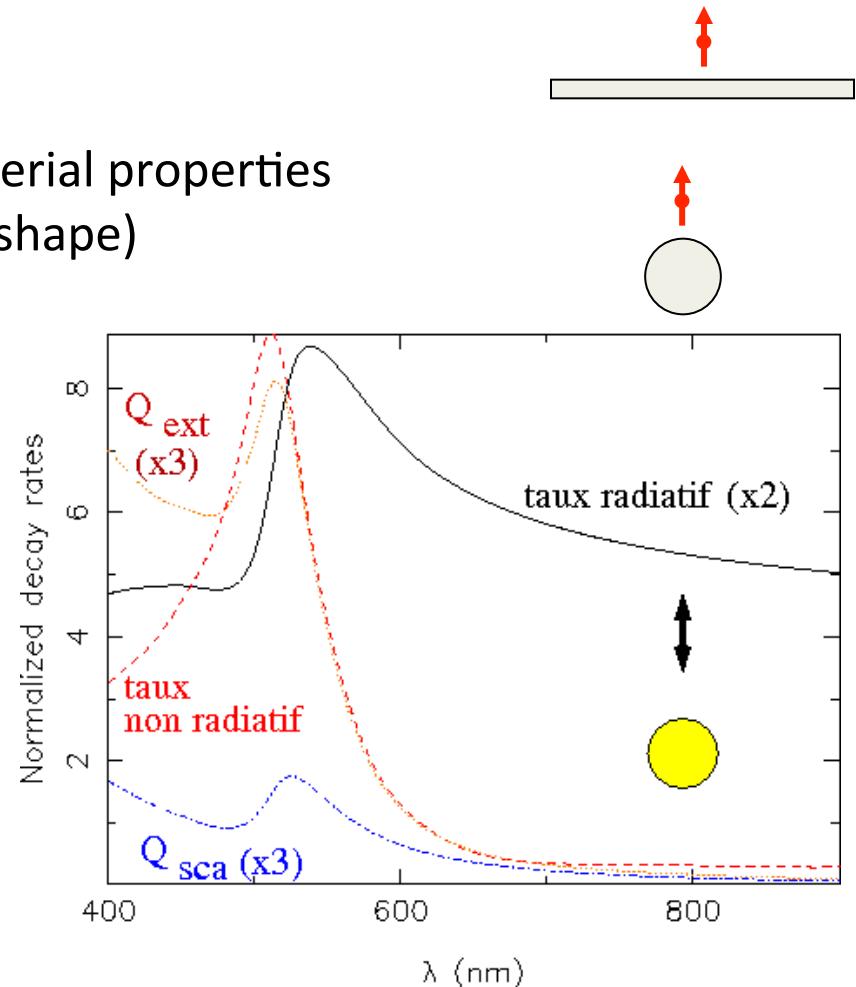
Modification of the decay rates (Purcell)

Radiative and non-radiative decay rates have different spectral maxima

- At small distance  $\gamma_{nr}$  depends on material properties
- $\gamma_r$  depends on  $\epsilon$  and  $\alpha$  (material and shape)

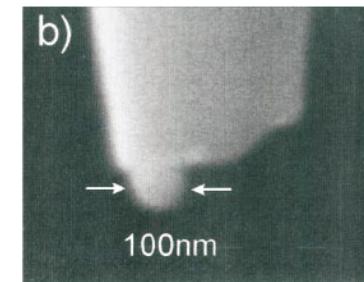
And this is distance-dependent !

Surface plasmon resonances are broad and there's spectral overlap between absorption and emission

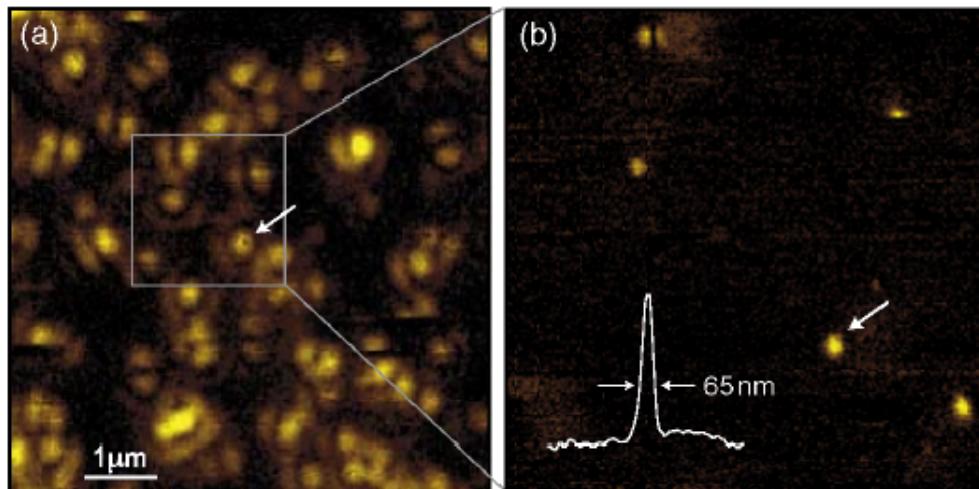


Courtesy of G. Colas des Francs (uB)

Attachment of single metal nanoparticle  
at the extremity of a scanning probe

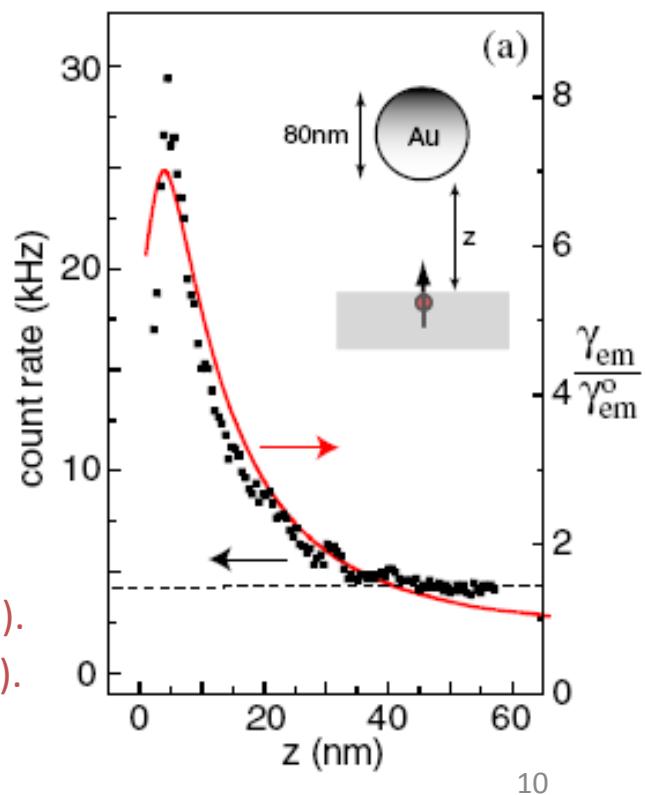


Th. Kalkbrenner et al., *J. Microsc.* **202**, 72 (2000).



P. Anger et al., *Phys. Rev. Lett.* **96**, 113002 (2006).

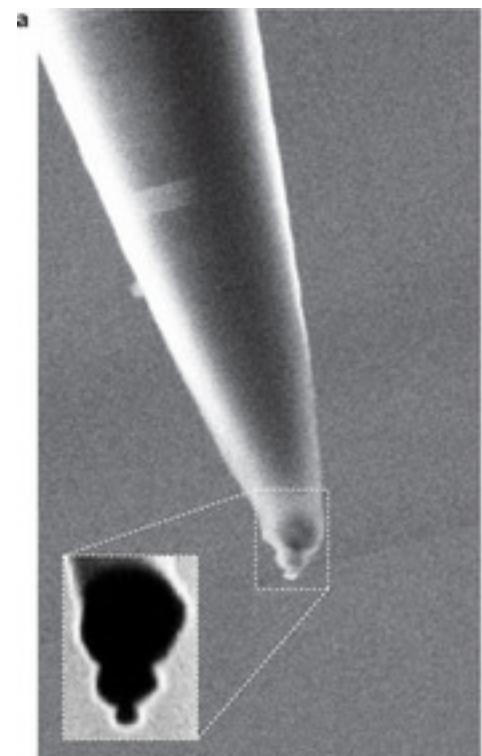
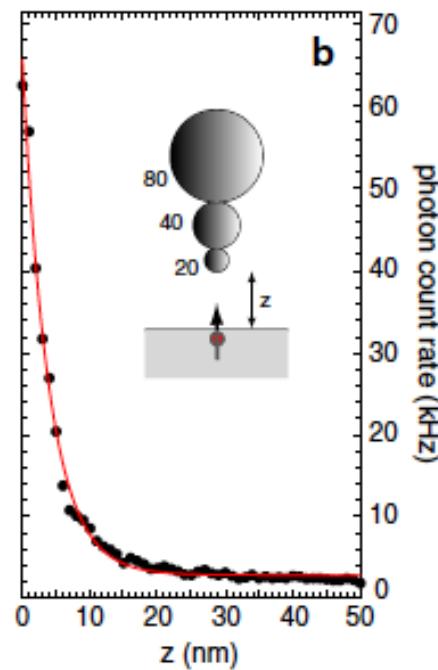
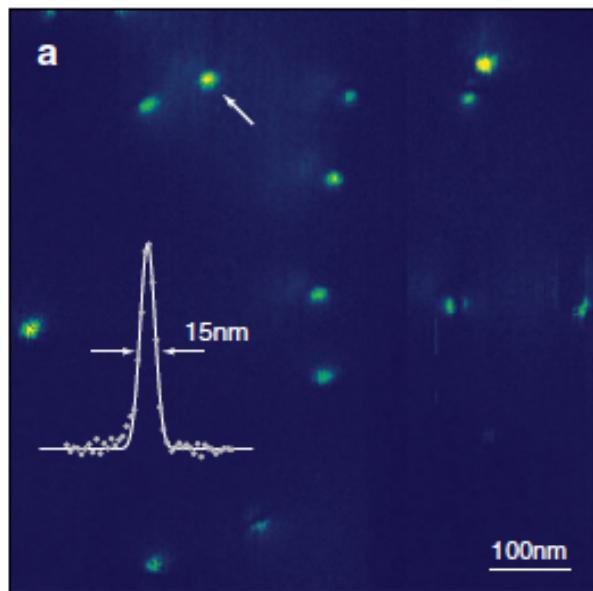
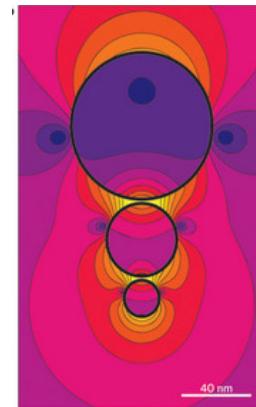
S. Kühn et al., *Phys. Rev. Lett.* **97**, 017402 (2006).



## Attachment of three metal nanoparticles at the extremity of a scanning probe: cascade effect

Large particle: interaction with incident field

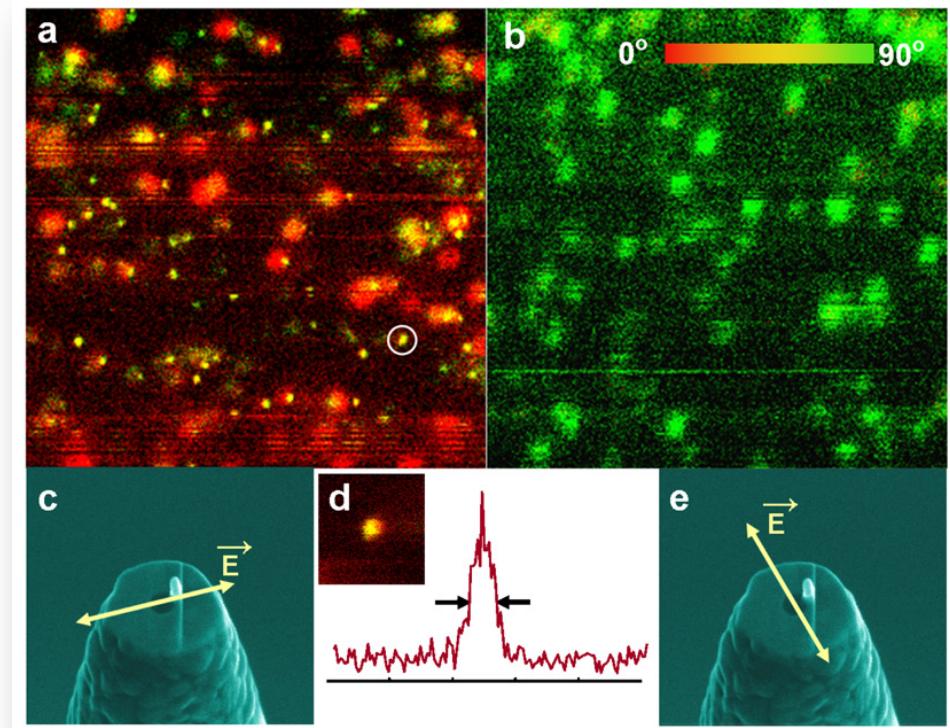
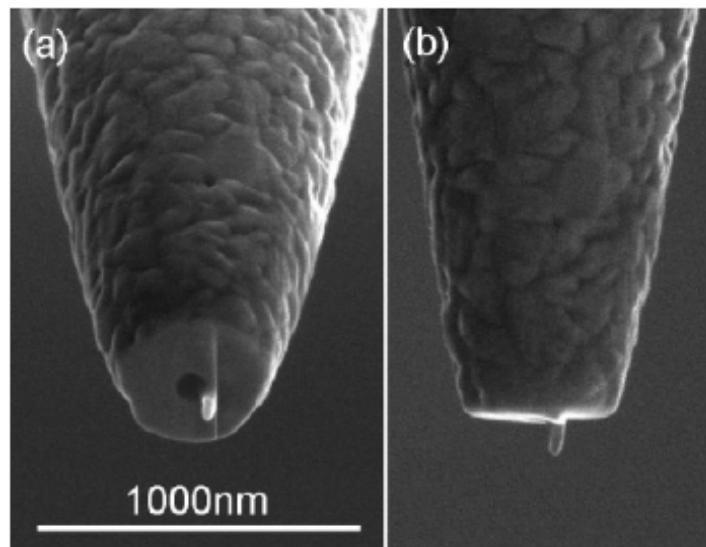
Small particle: field localization



P. Anger et al., *Phys. Rev. Lett.* **96**, 113002 (2006).

## Fabrication of a resonant antenna to efficiently funnel the field into a localized source

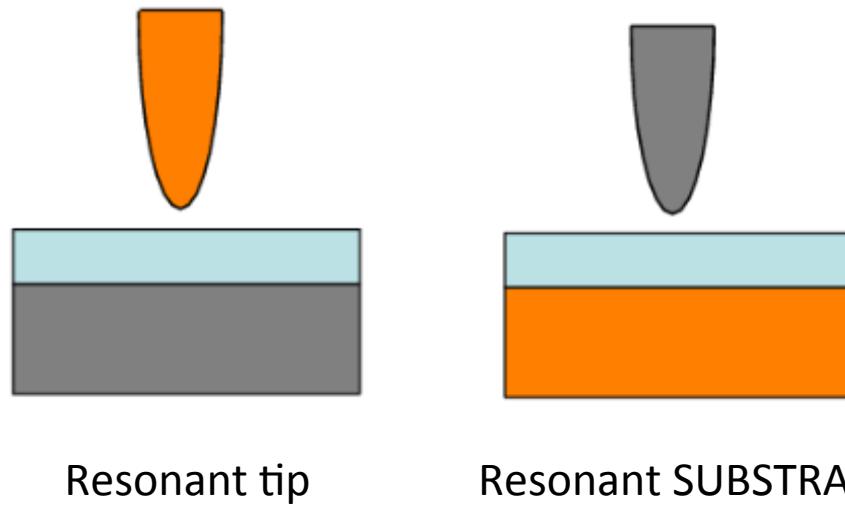
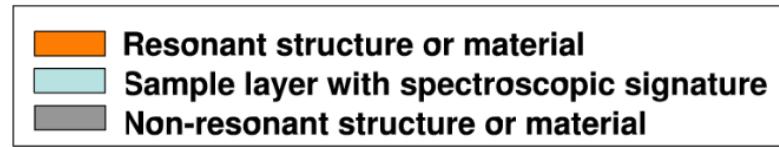
*In situ* growing of a monopole antenna at the end to an optical fiber probe



T. Taminiau, et al. *Nano Lett.* 7, 28 (2007)

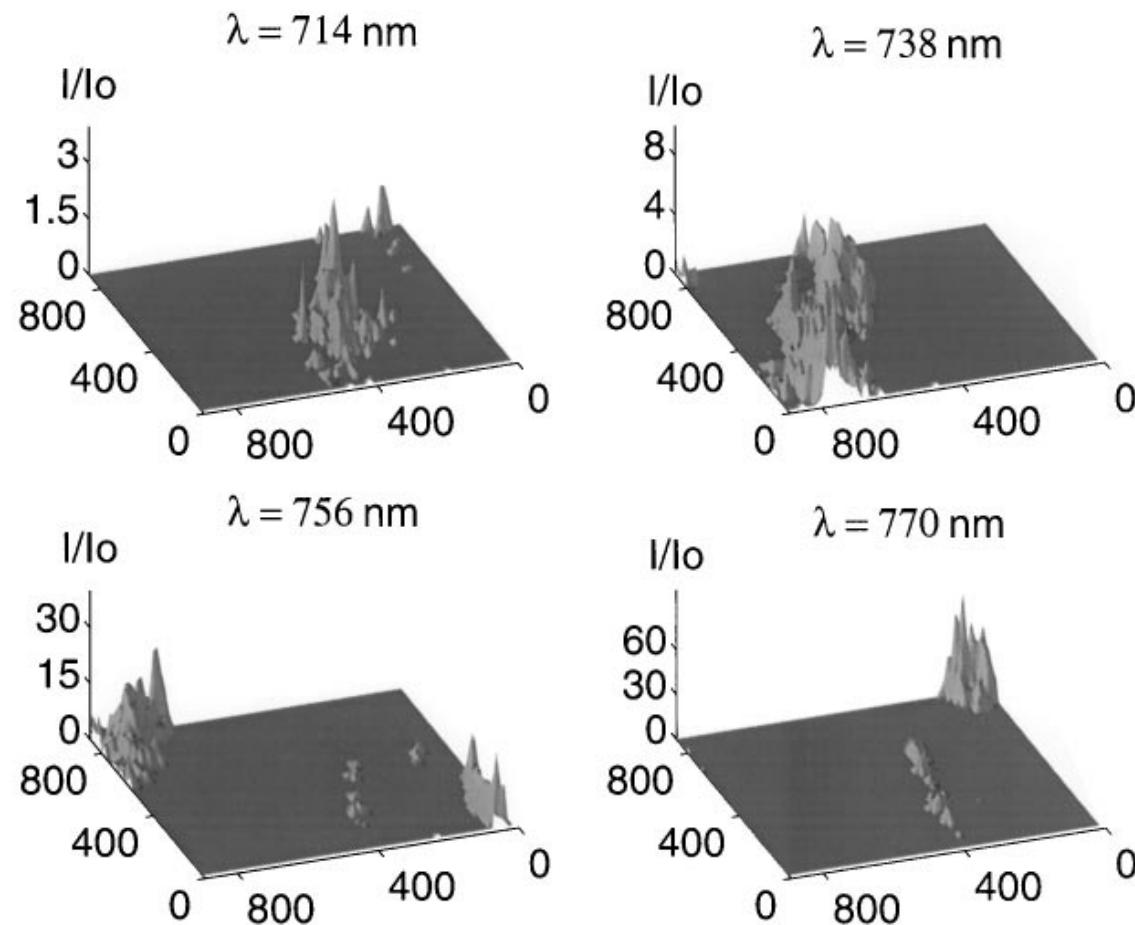
POSTER # 11 par C. Hubert

# Resonant substrate

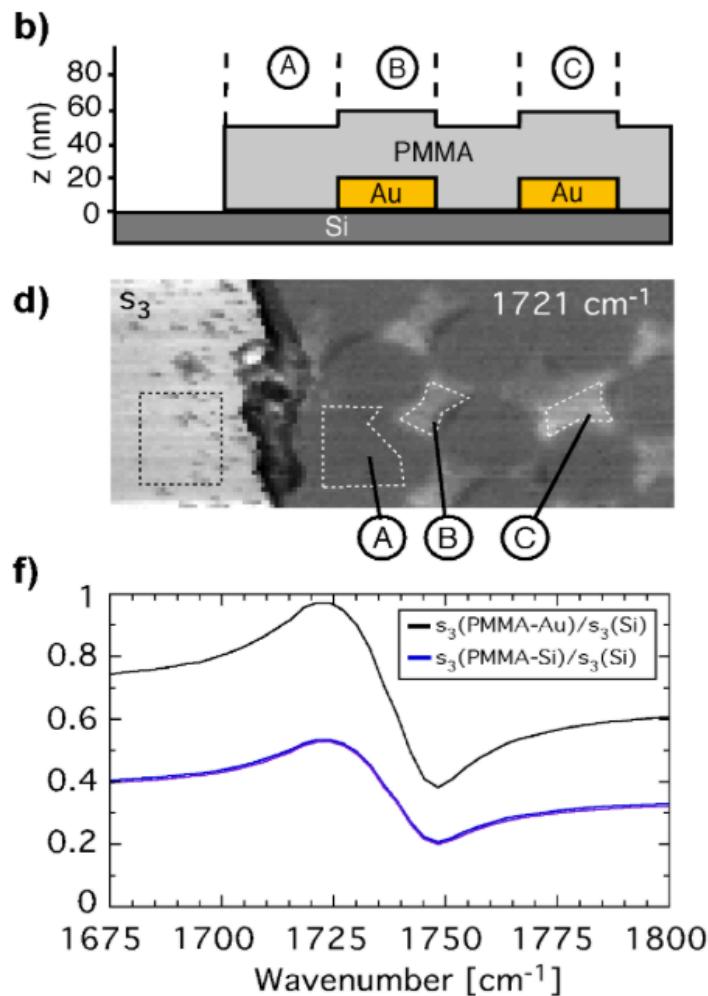


# Resonant substrate

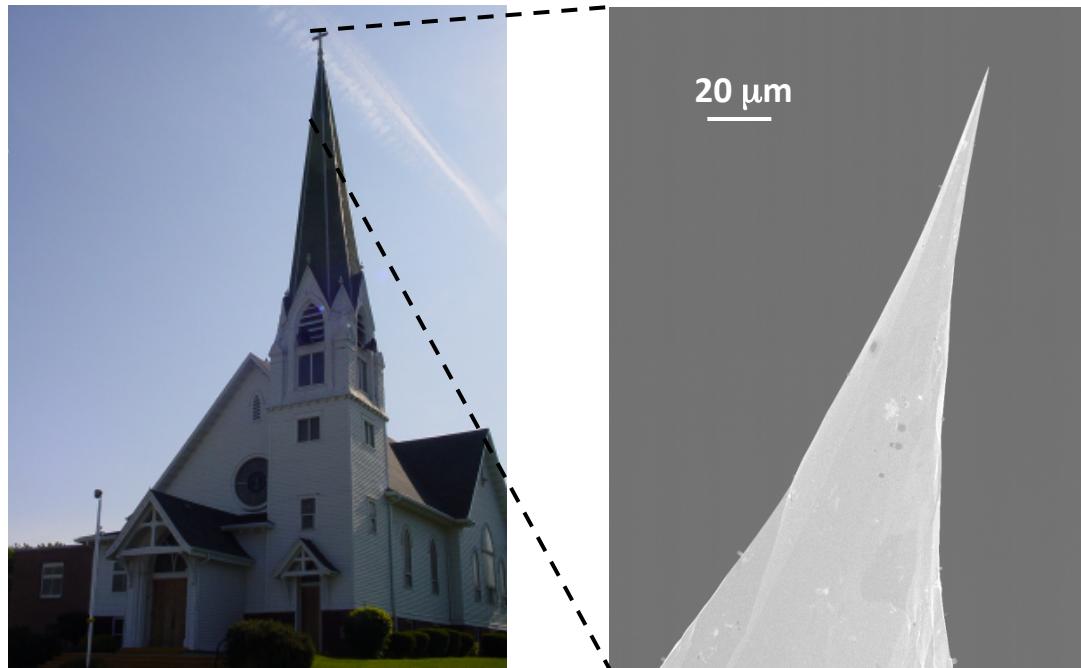
(a)



# Resonant substrate

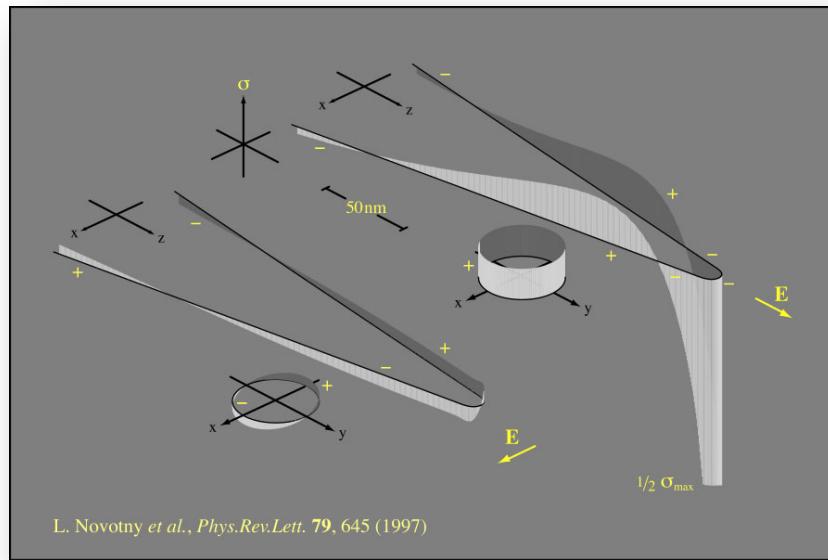


## – Lightning rod effect –

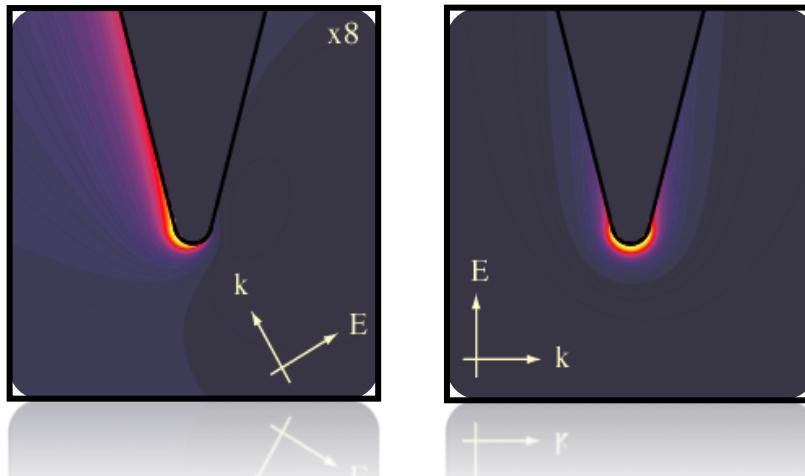


- Lightning rod effect  
*Needs:*
  - Geometric singularity
  - Good conductor
  - Proper polarization

## Electric field must be aligned on axis!



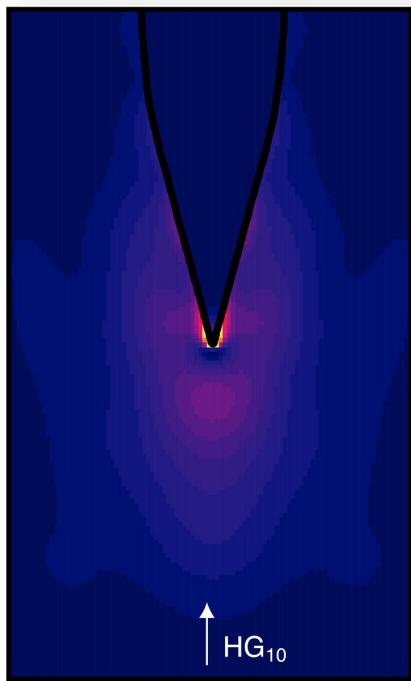
- Surface charge density increases at the apex



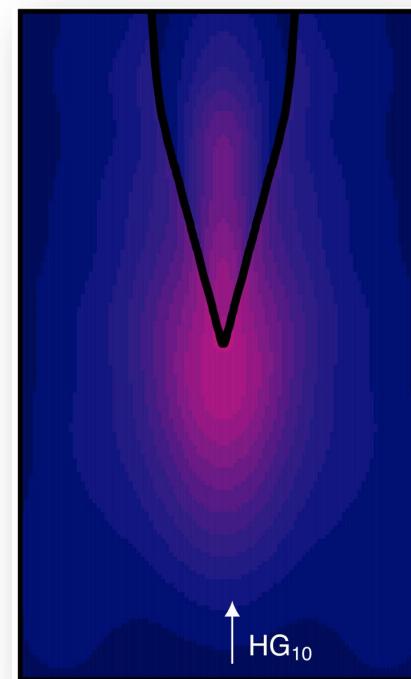
- Electric field intensity around a 10 nm radius Au tip

L. Novotny et al., *Ultramicroscopy* **71**, 21, (1998).

- Intensity of the field for focused illuminations on a Au and glass tip

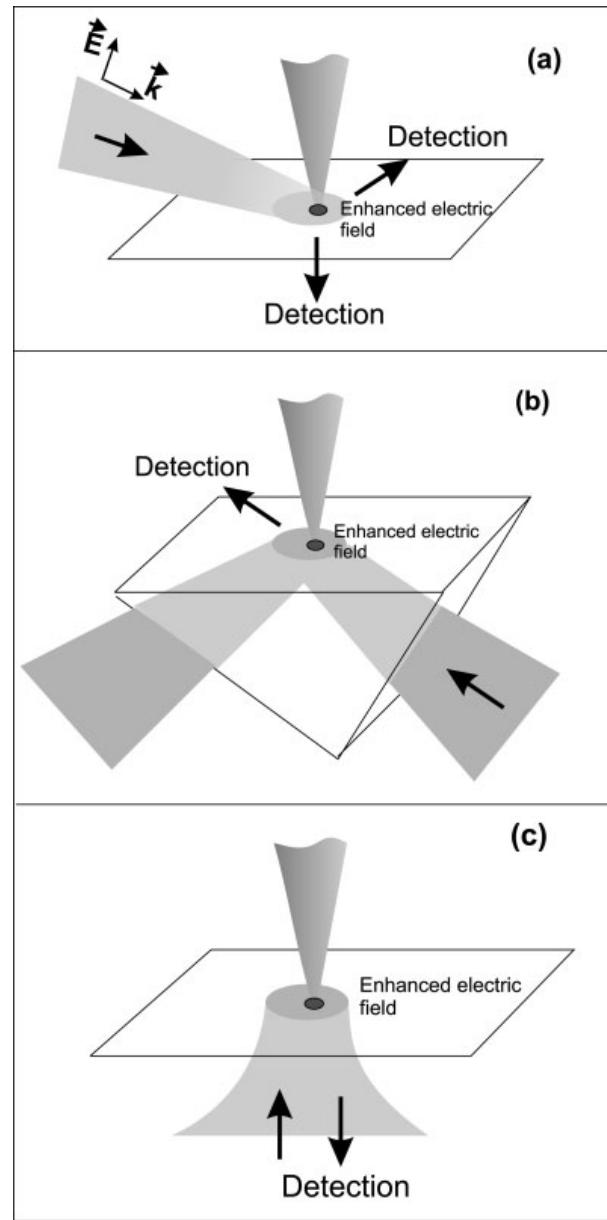


**Au tip**



**$SiO_2$  tip**

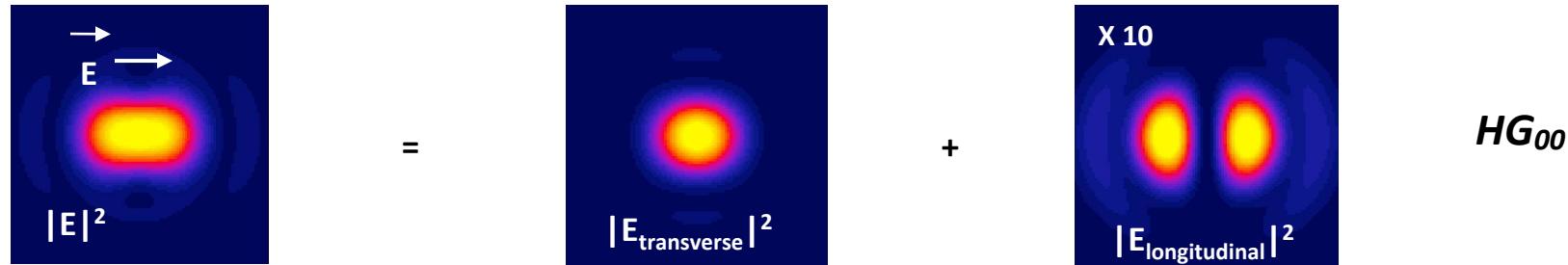
- Side illumination
- Evanescent TM field
- In highly focused laser beams, a longitudinal field is created in the focus.



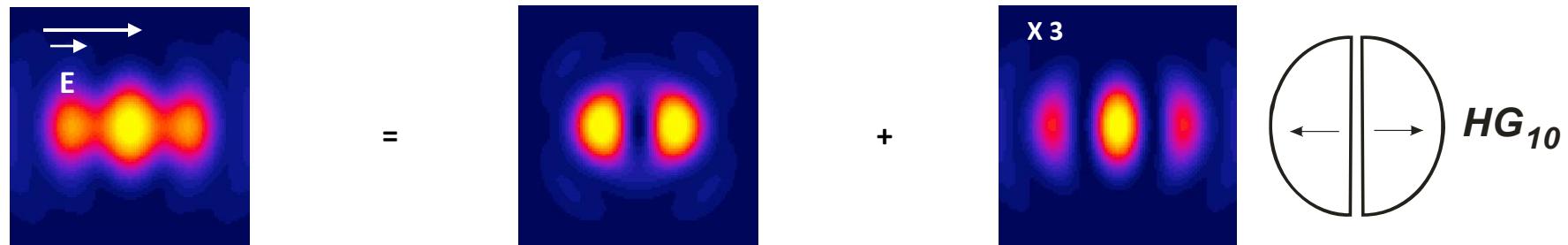
# Implementation

In tightly focused laser beams (high NA objective), the tip must be placed in a z-oriented lobe to generate an enhancement

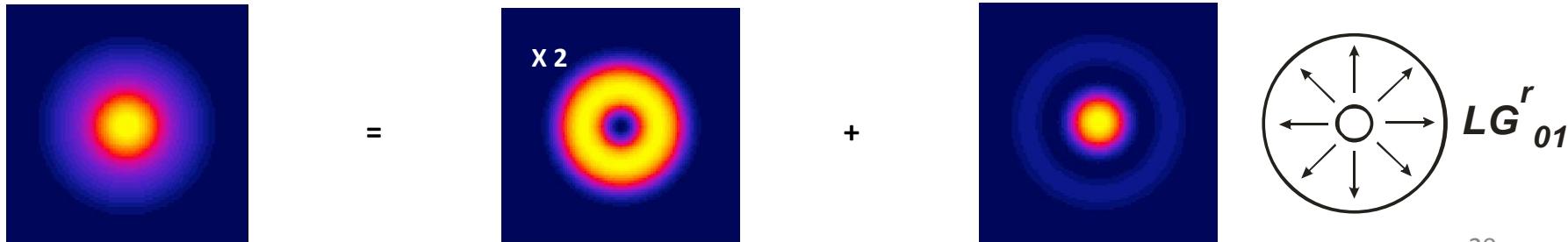
- Gaussian mode



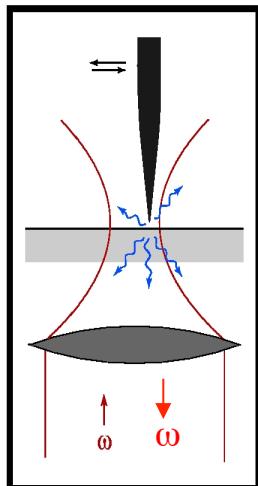
- Hermite-Gaussian mode



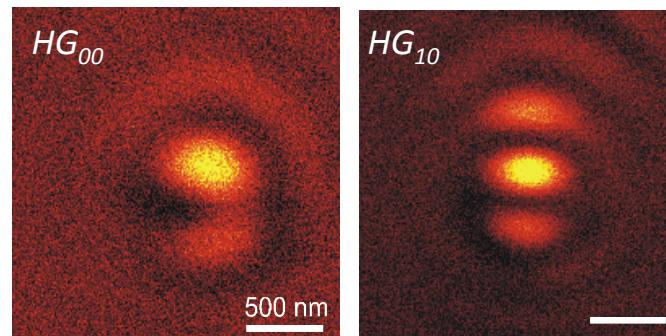
- Radial mode (doughnut mode)



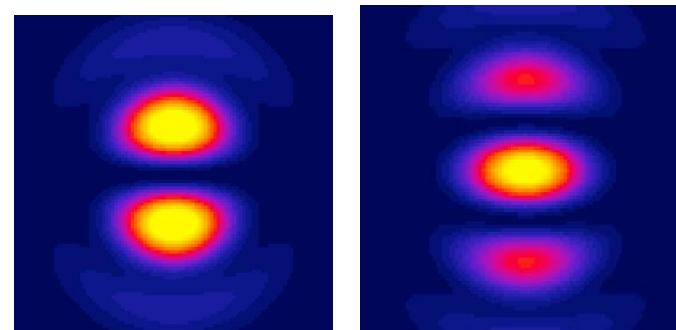
# Longitudinal sensitivity of the tip's response

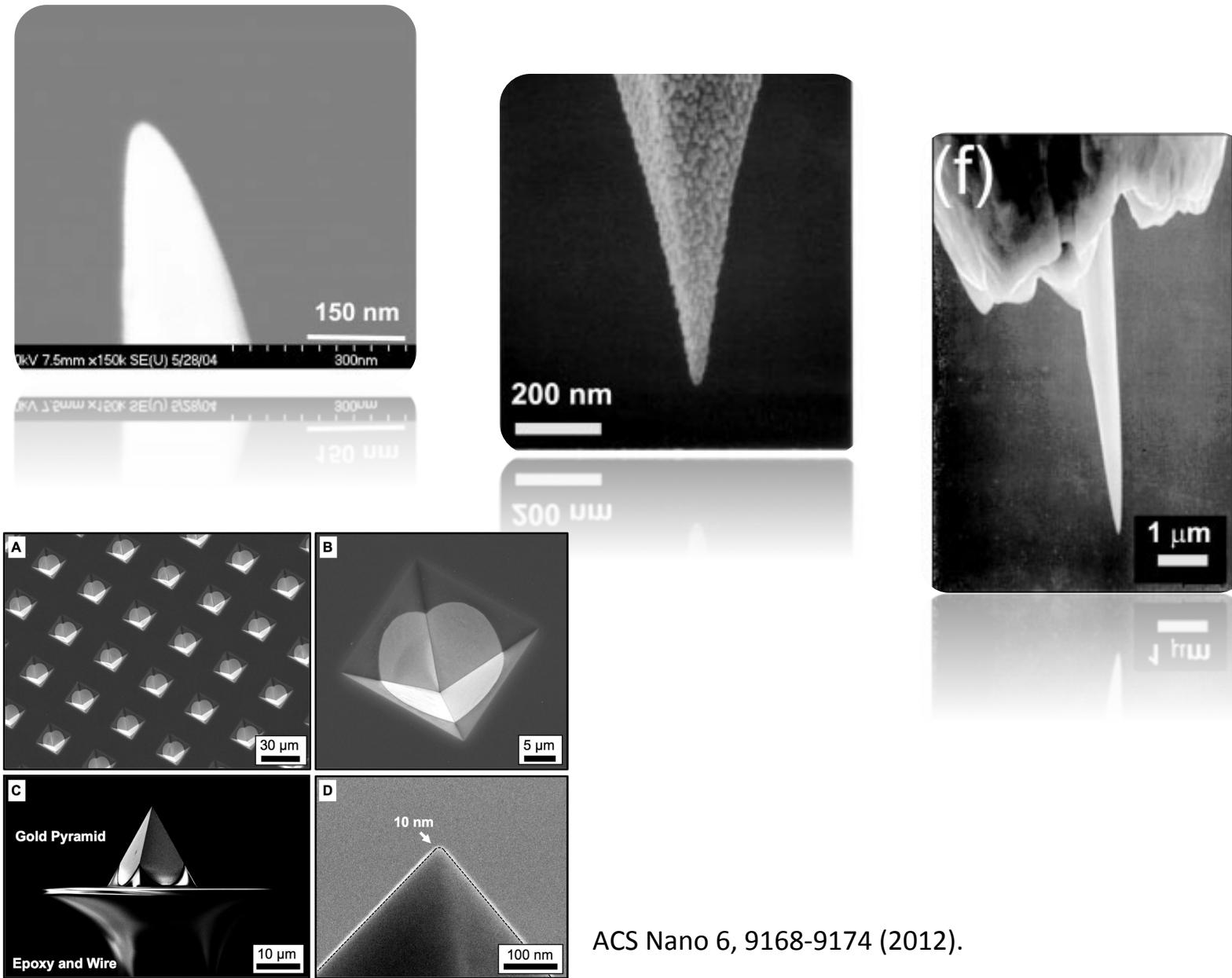


Signal scattered by a gold tip

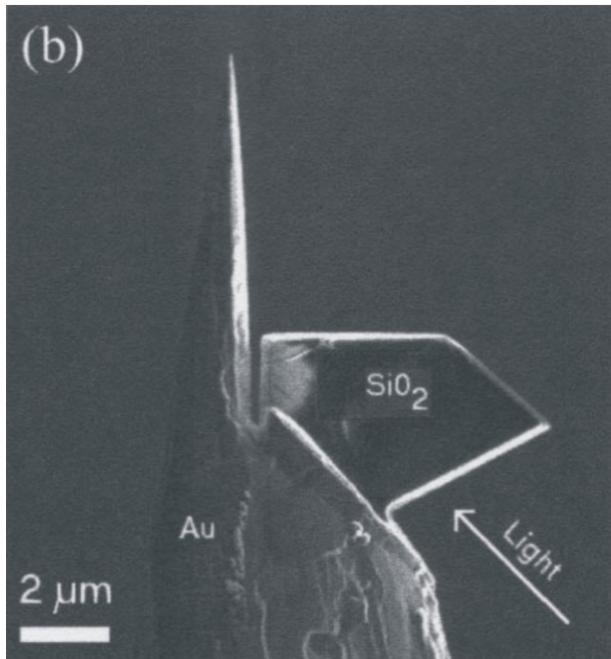


Scattered signal is stronger for  
the field aligned along the tip axis  
Field enhancement effect!



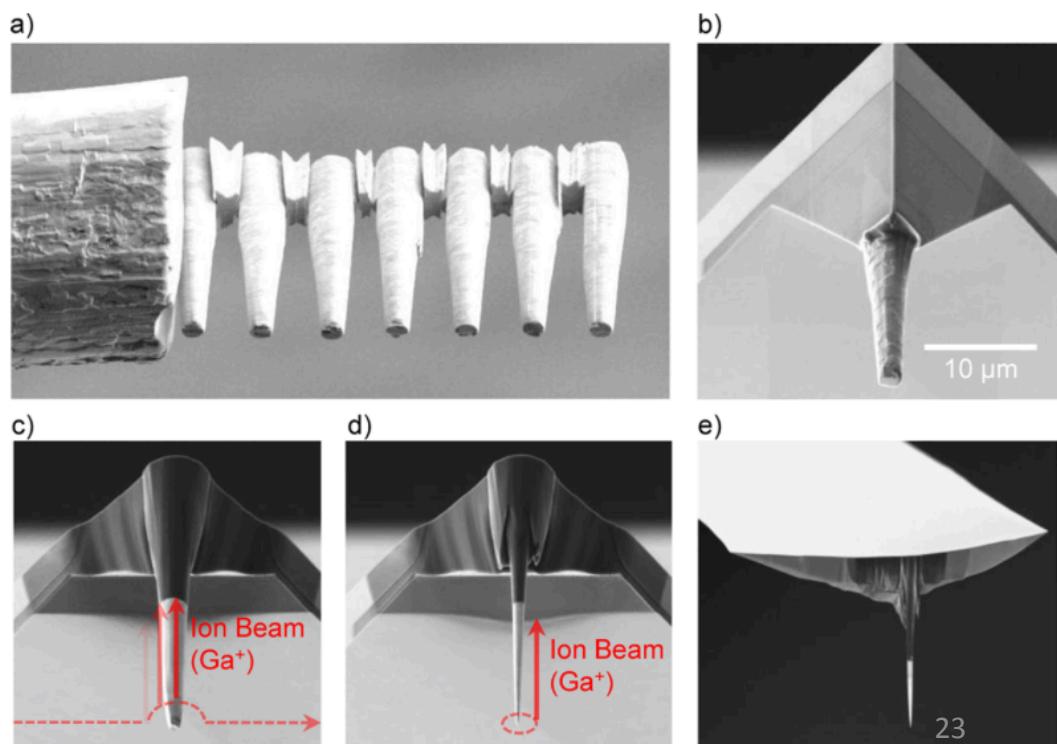


## FIB craftsmanship



E. Sanchez et al *Rev. Sci. Instrum.* 73, 3901 (2002)

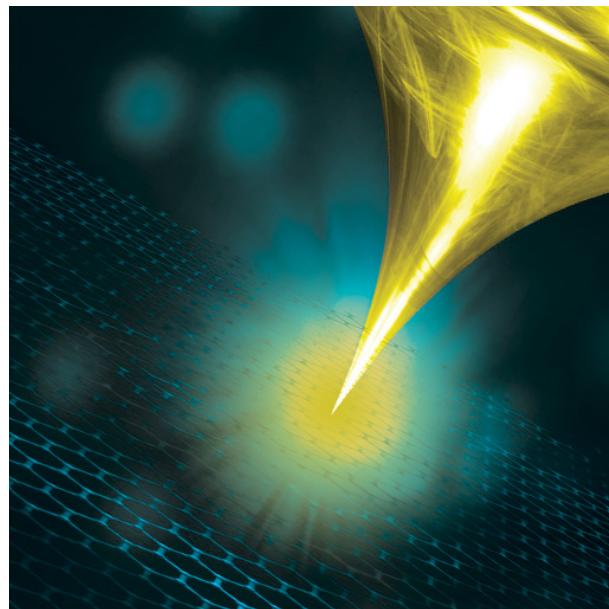
F. Huth et al. *Nano Lett.* 13, 1065 (2013)



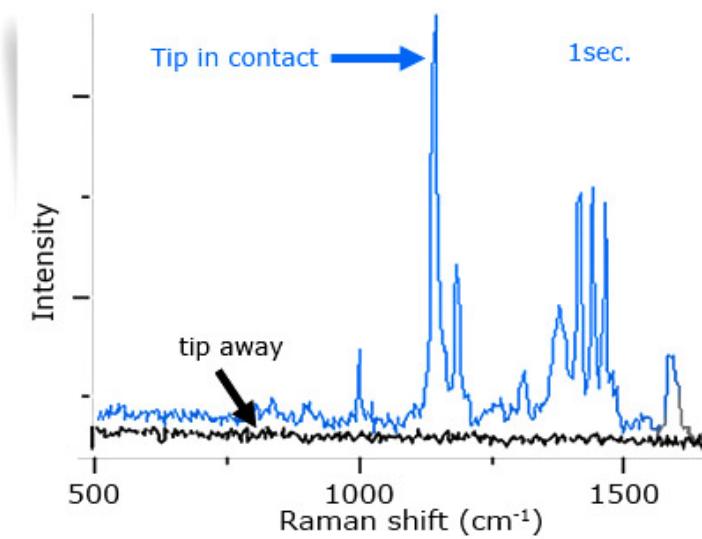
# The hall of fame: TERS imaging

*TERS imaging provides a means to chemically characterize the heterogeneous distribution of adsorbates across a surface at the nanometer length scale.*

R. P. Van Duyne *J. Phys. Chem. Lett.* **5**, 3125 (2014)

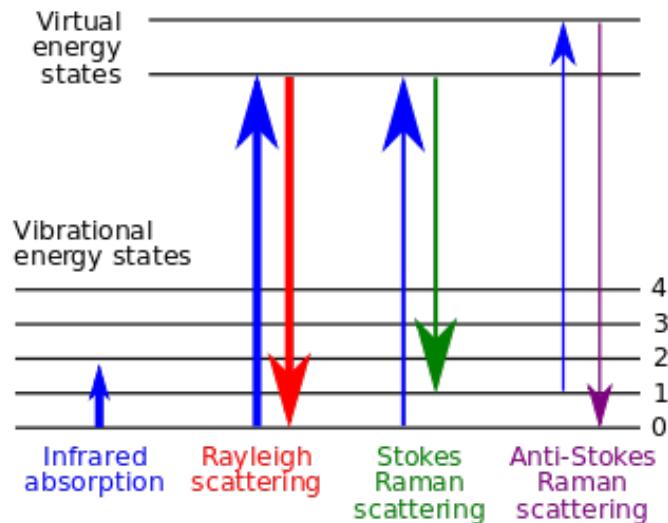


NPL, Teddington, UK



**HORIBA**  
Scientific

# (tip-enhanced) Raman spectroscopy



$$\sigma_{Raman} \approx 10^{-30} \text{ cm}^2$$

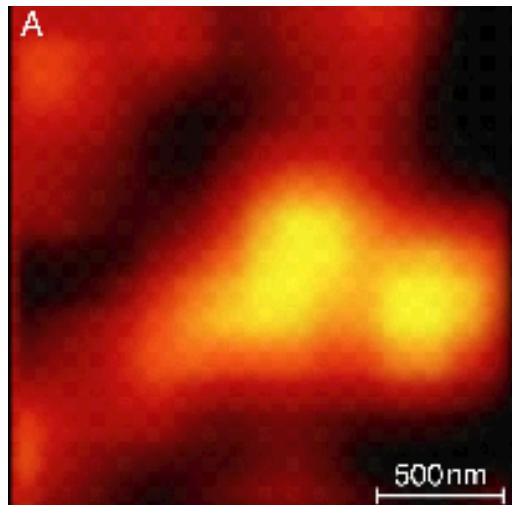
Very weak cross-section

Collected signal can be increased by introducing a surface plasmon amplification **twice**:  
Field enhancement magnifies the incident field, then the scattered Raman photons are also amplified by the plasmon during the process

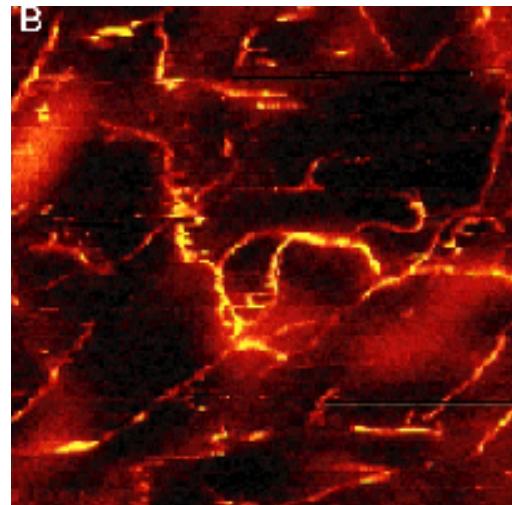
# The hall of fame: TERS imaging

- Comparison between confocal and field-enhanced carbon nanotubes vibrational imaging

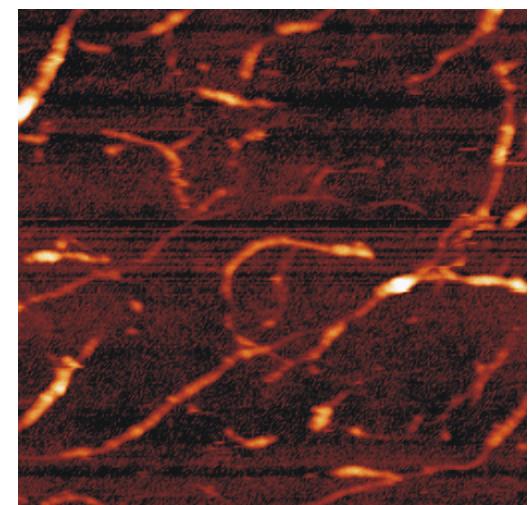
Image size: 1500x1500 nm<sup>2</sup>



*Confocal Raman  
G band*



*Near field Raman  
G band*



*Topography*

# The hall of fame: TERS imaging

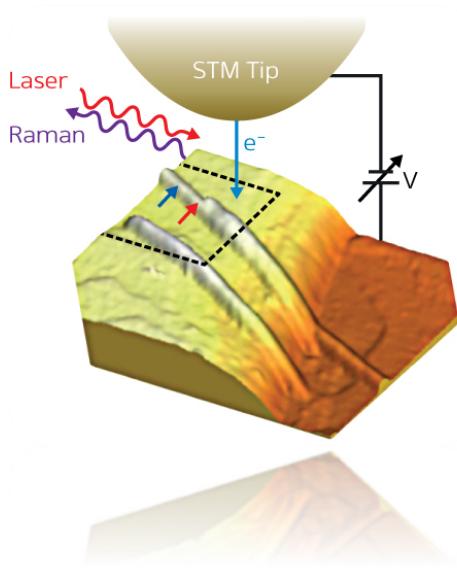
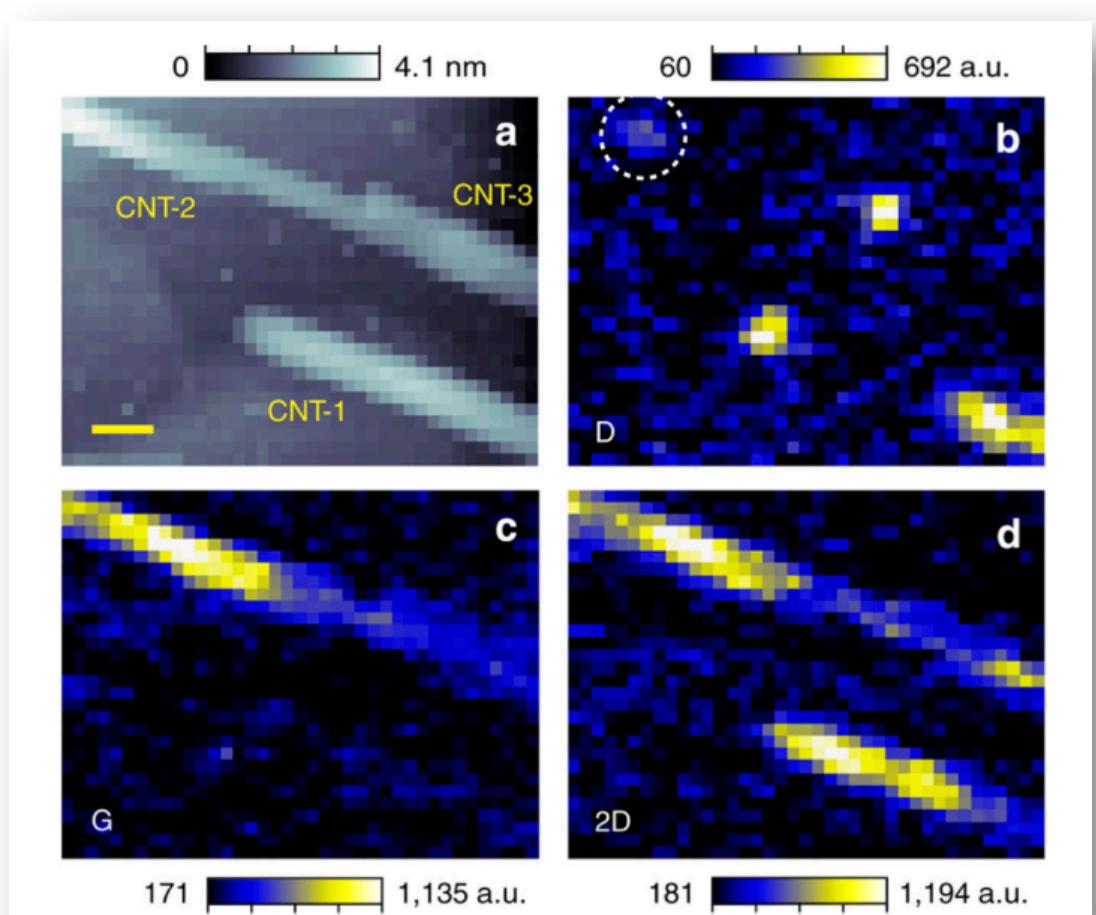


Image size: 39x30nm<sup>2</sup>

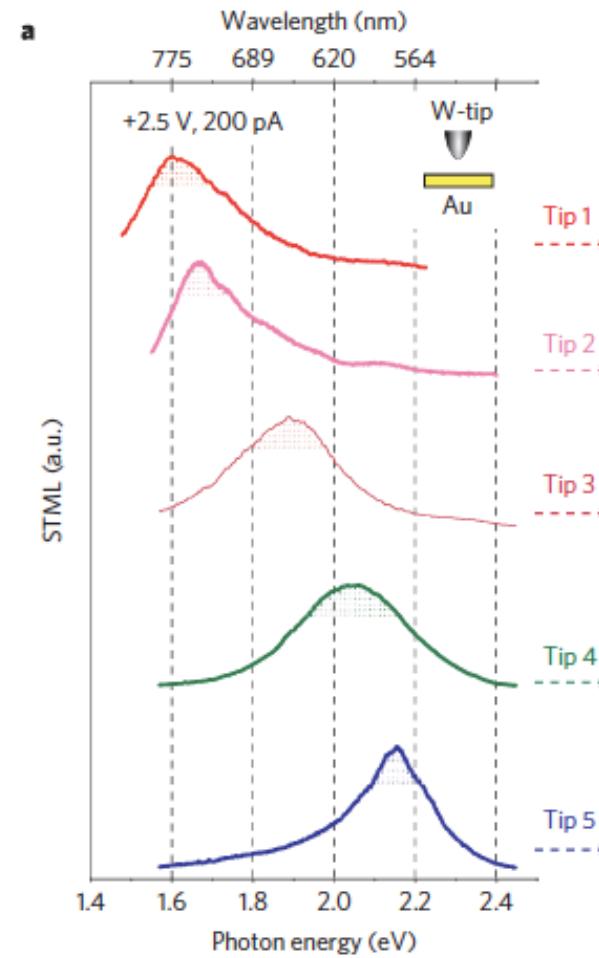
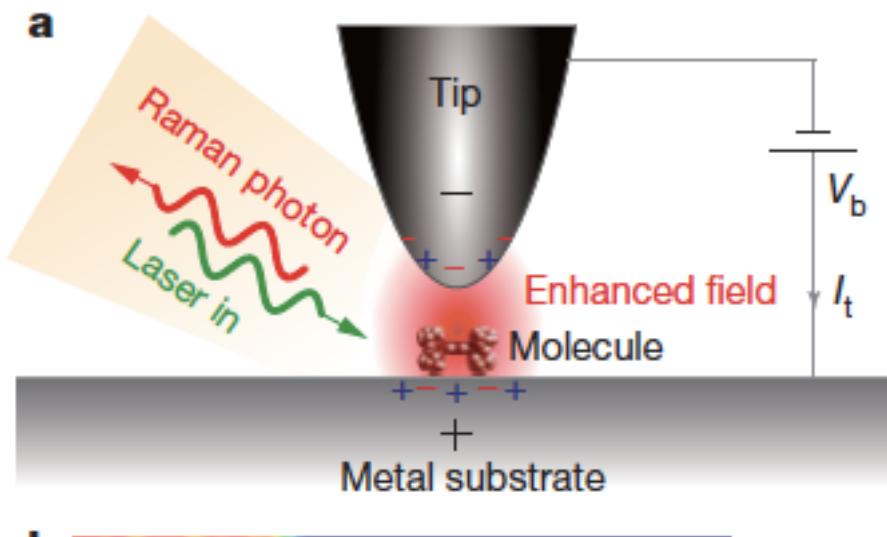
Resolution at the dimension of the NT diameter

Effect from bundling, defect can be interrogated

A Raman spectra is measured at pixel then the maps are reconstructed by integrating the light scattered in the D (defect), G (NT structure) and 2D (overtone) Raman peaks

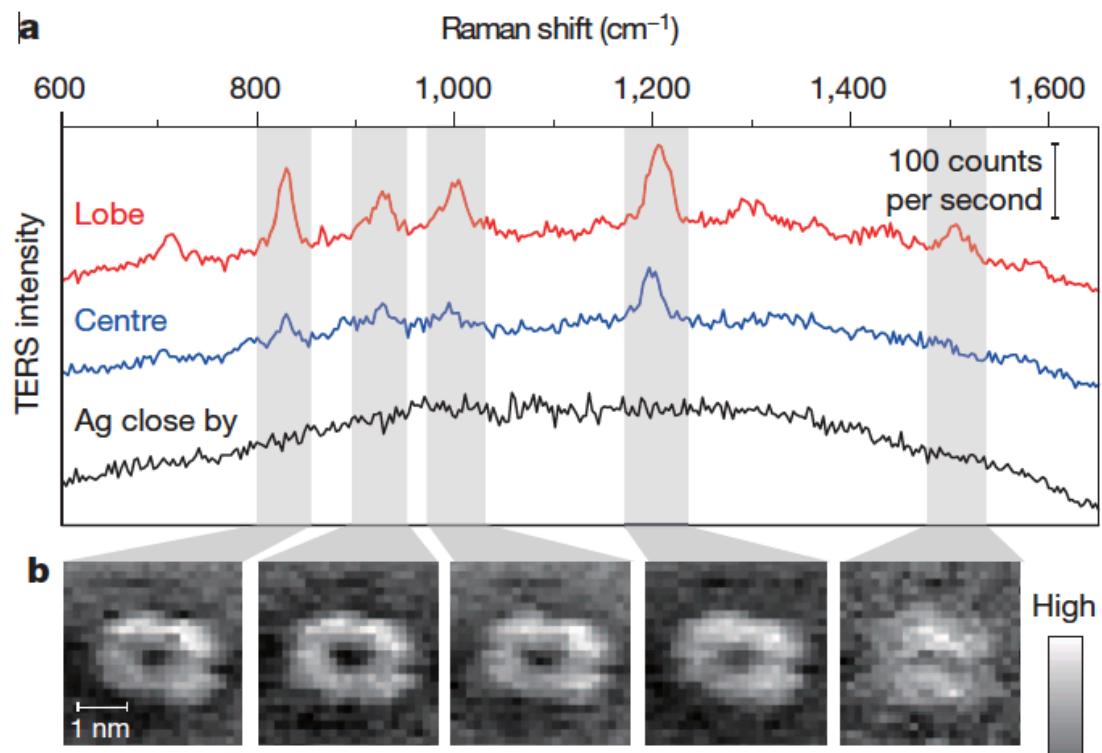


Spectrally matching the resonance of the nanocavity plasmon to the molecular vibronic transitions to improve the resolution

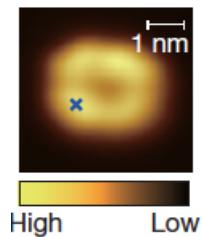


# The hall of fame: TERS imaging

Image size:  $3.6 \times 3.6 \text{ nm}^2$



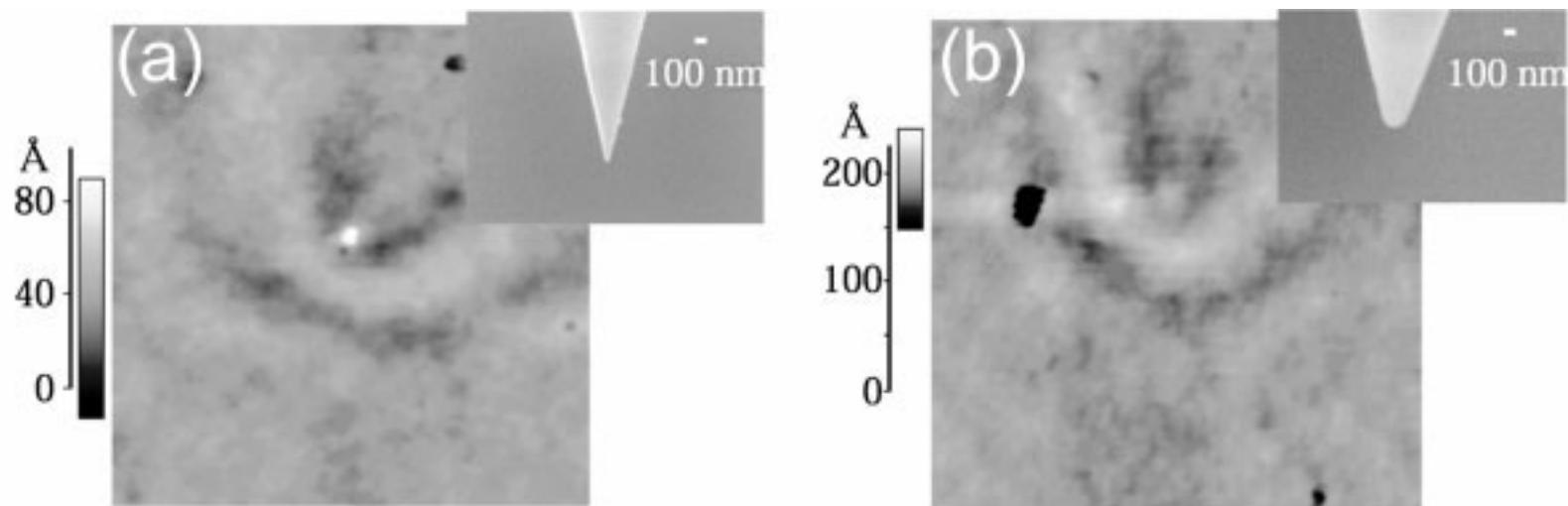
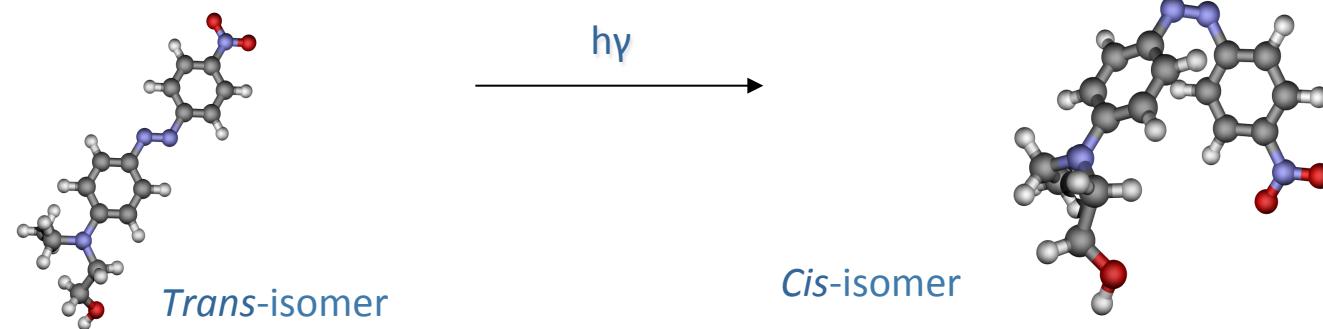
Chemical recognition with submolecular resolution!  
Correlation of the Raman signal with a molecule's local environment



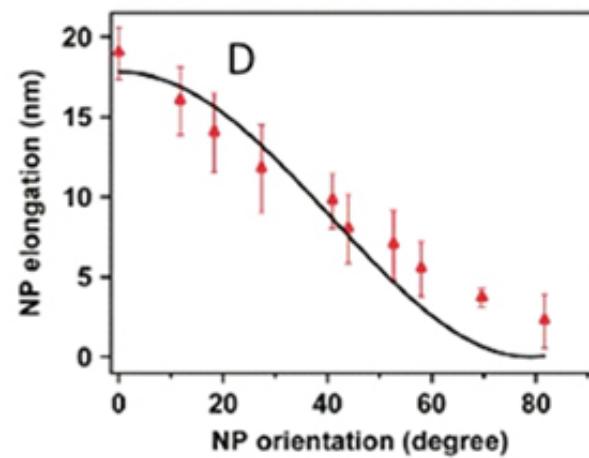
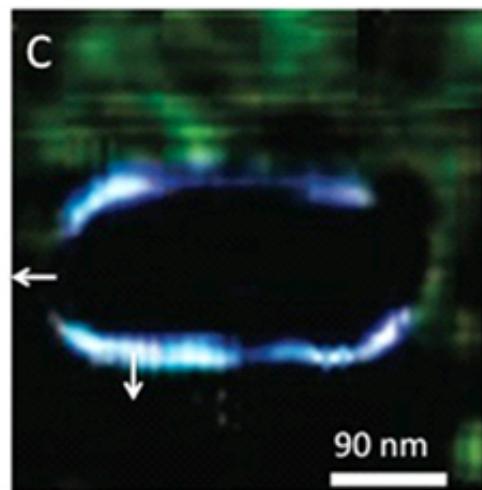
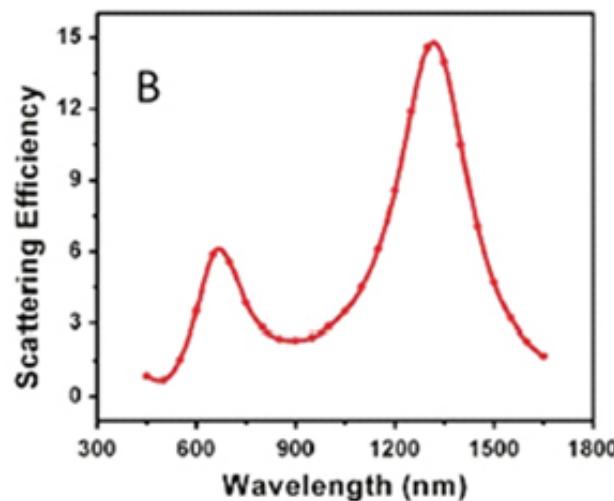
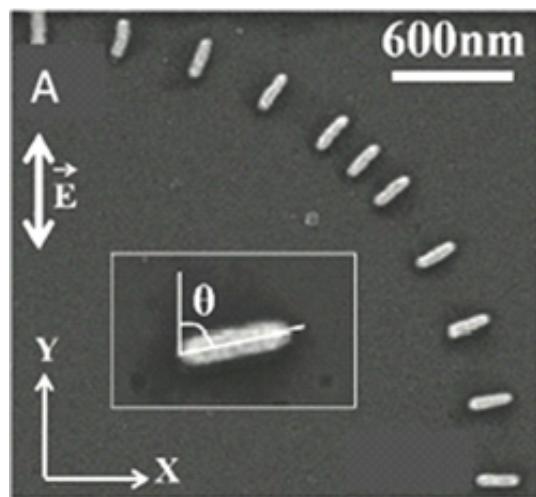
Review of the principle & applications behind field enhanced optical microscopy/spectroscopy

Some outside-the-box applications

- Local photo-isomerization of an azo-polymer

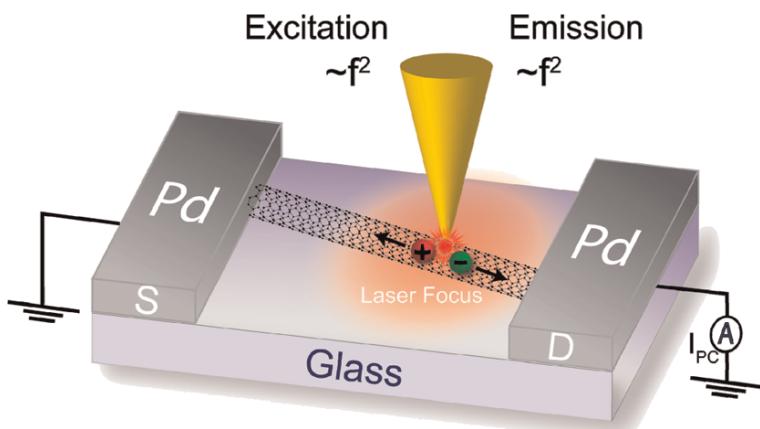


# Field enhancement beyond inelastic imaging

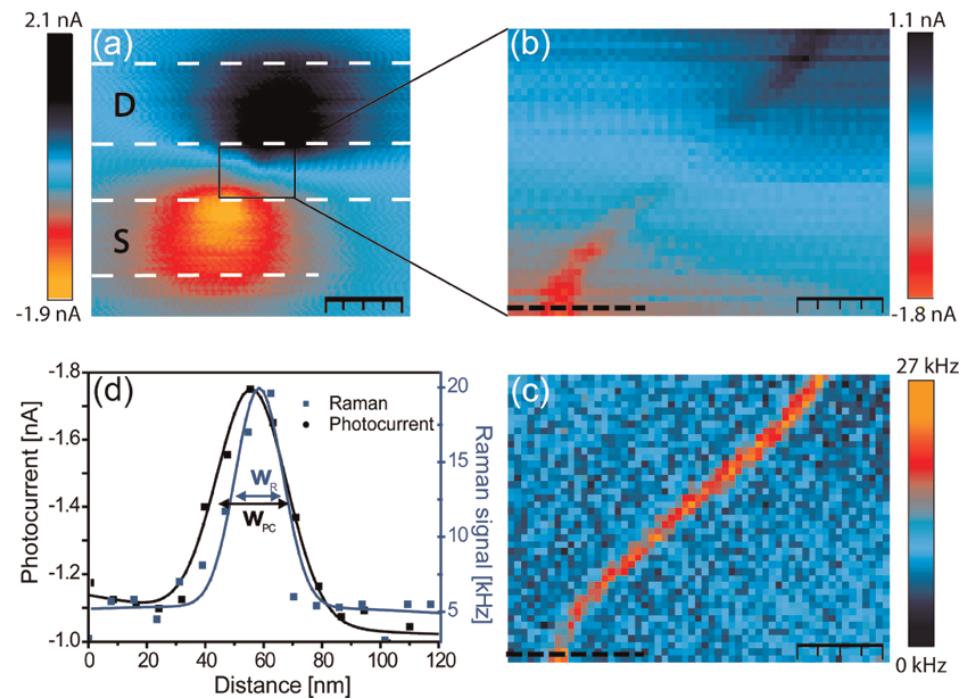


# Field enhancement beyond inelastic imaging

- Enhancing the performance of nanoscale device

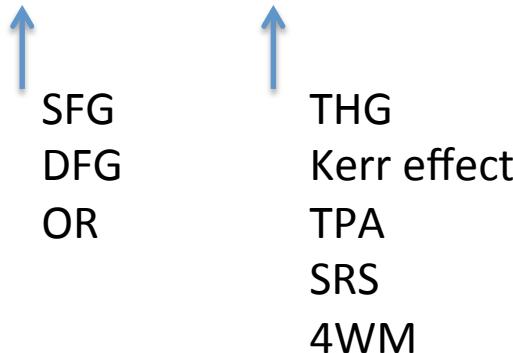


zero-bias photocurrent caused by charge separation in local built-in electric fields at the contacts



- Other processes benefiting from a field enhancement mechanism are nonlinear responses

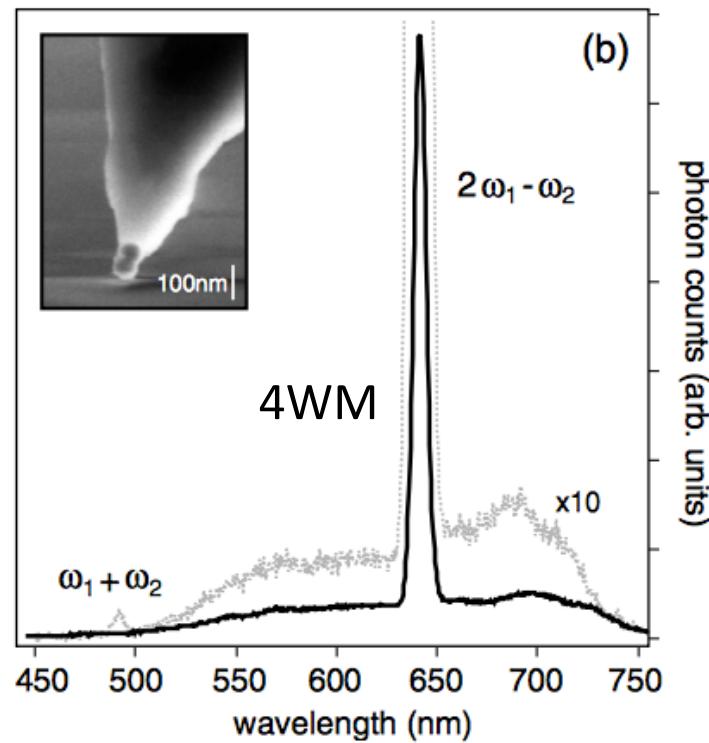
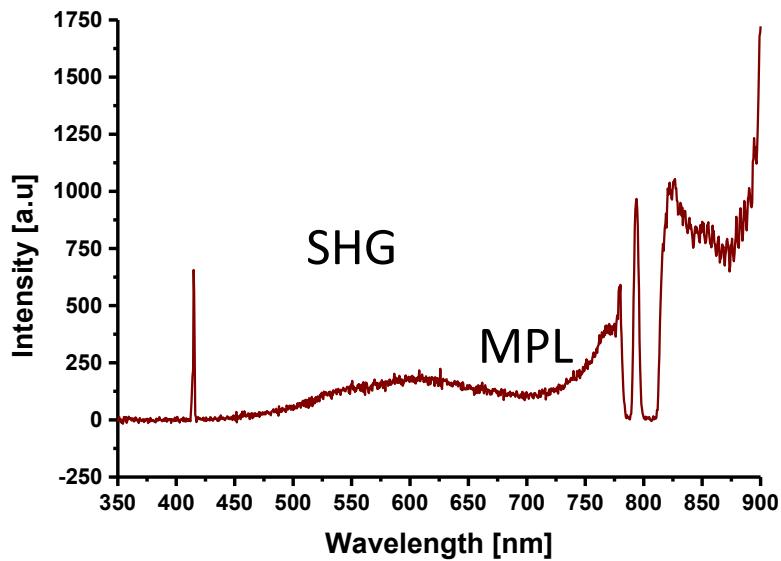
$$P(t) = \varepsilon_0 \left( \chi^{(1)} E(t) + \chi^{(2)} E^2(t) + \chi^{(3)} E^3(t) + \dots \right)$$



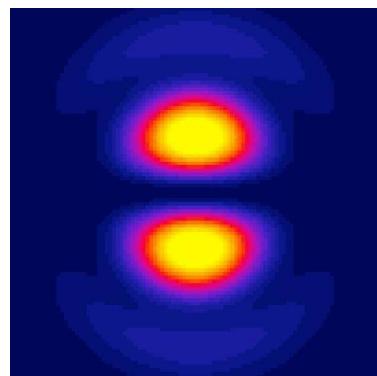
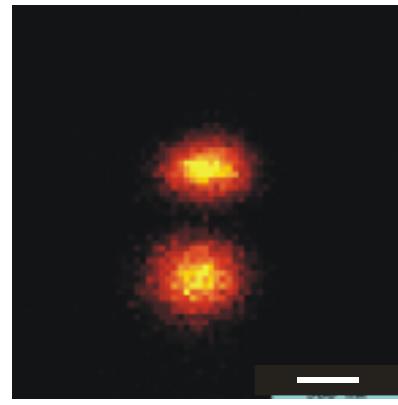
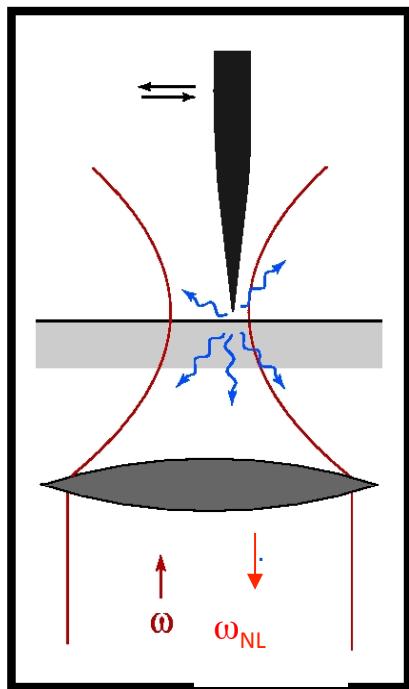
Time-domain:  
Concentration of the same average power  
into the high peak power with low duty cycle

Space-domain: Concentrate the high peak power into higher local power density to increase the efficiency

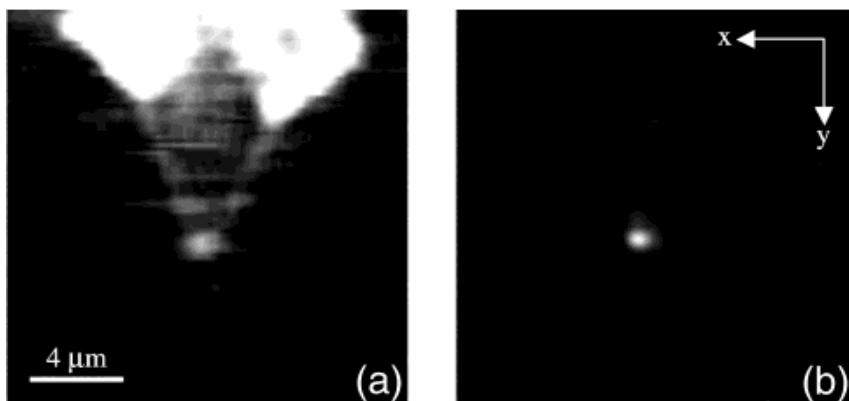
- Interestingly, the metal itself can be the source of nonlinearity!



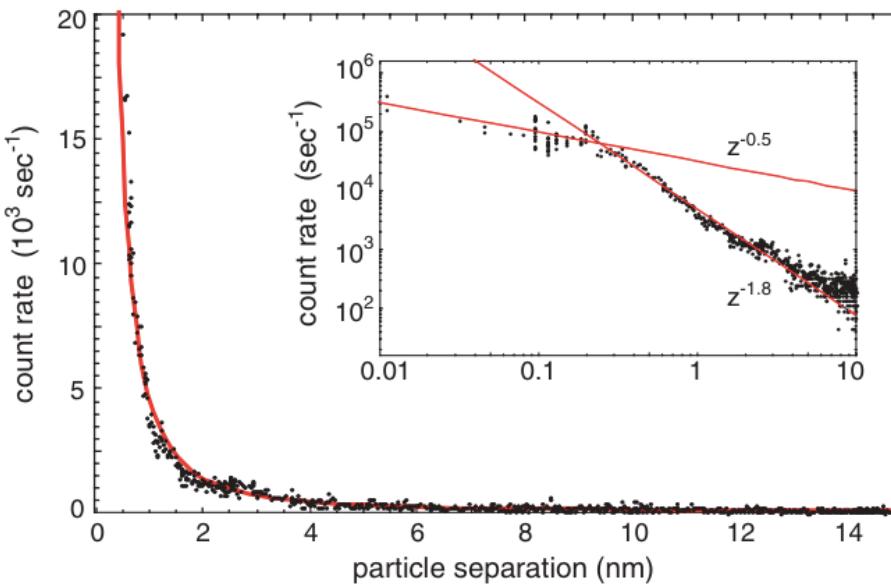
SHG



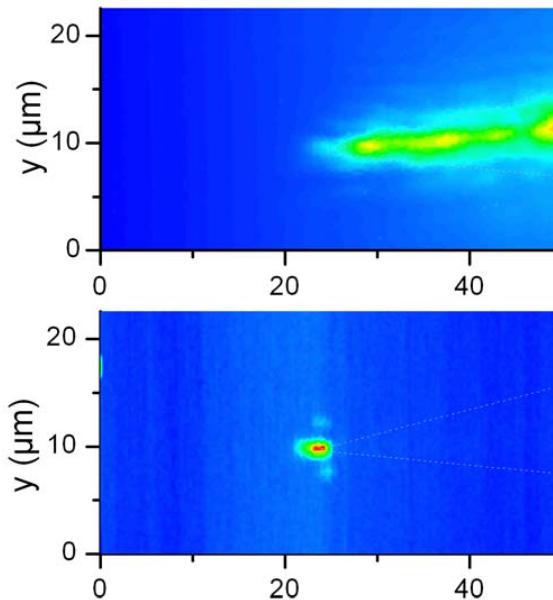
# Local source of nonlinear radiation



M. Labardi et al, *Opt. Lett.* **29**, 62 (2004).

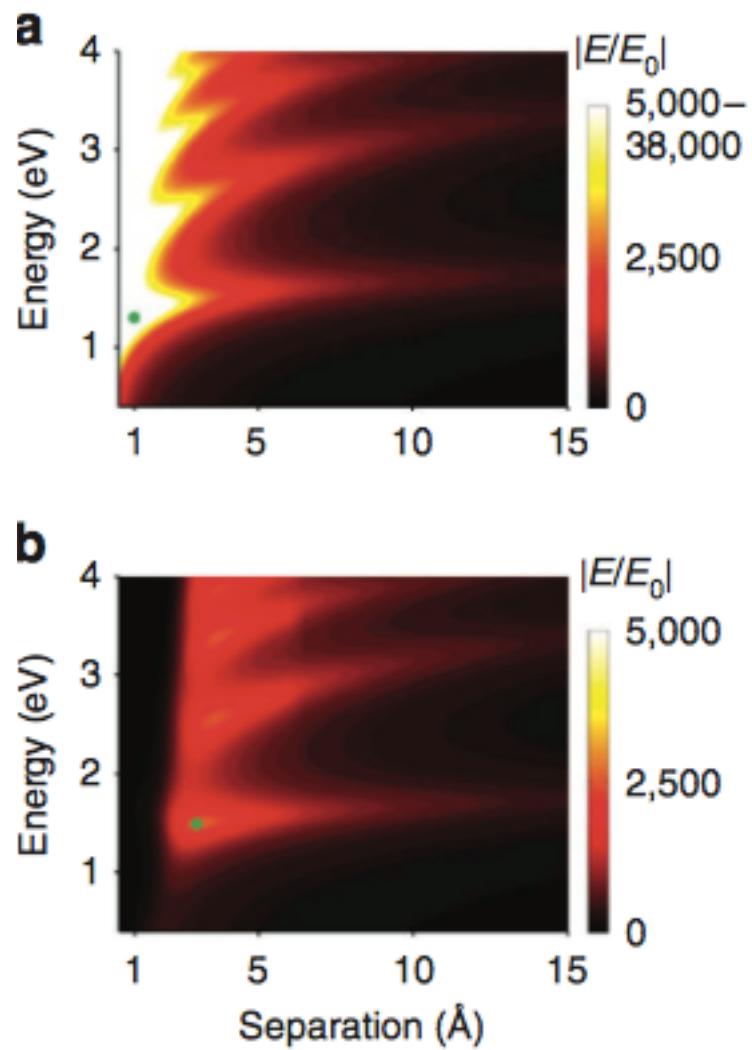
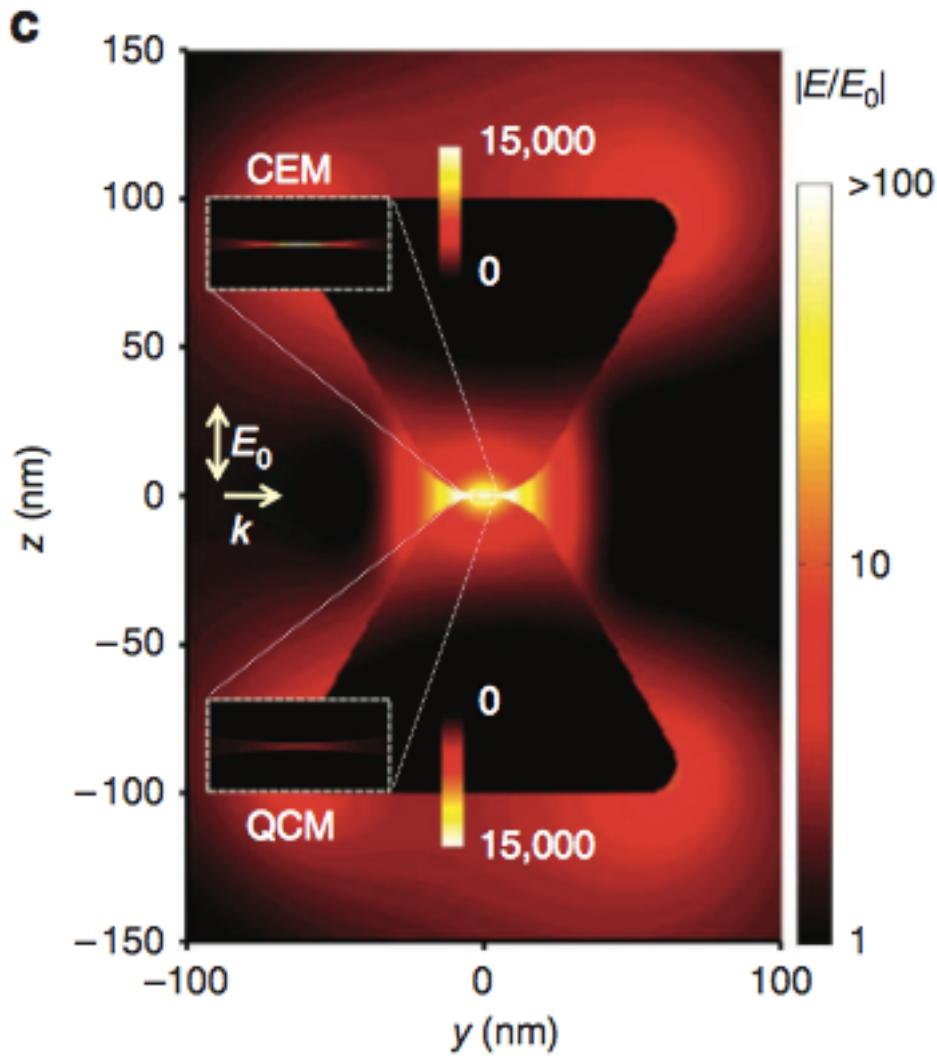


M. Danckwerts et al , *Phys. Rev. Lett.* **98**, 026104 (2007).

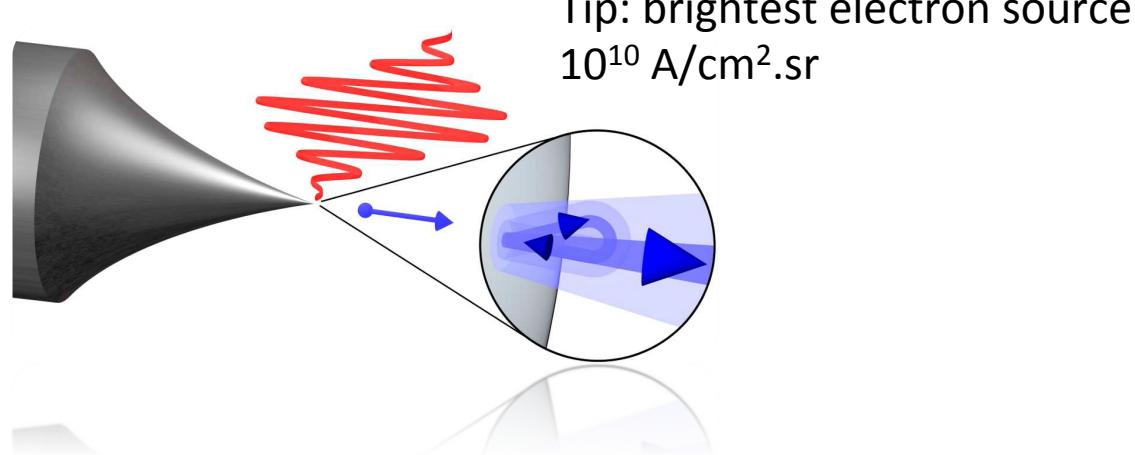


C. Ropers et al , *Phys. Rev. Lett.* **98**, 043907 (2007).

# Where's the limit?



Using the field enhancement of a metallic tip to efficiently extract electron pulses



Light-wave electronics:  
Time-resolved electron microscopy  
Ultrafast A/D converters  
Novel laser accelerators  
Ultrafast X-ray sources

# Electron emission

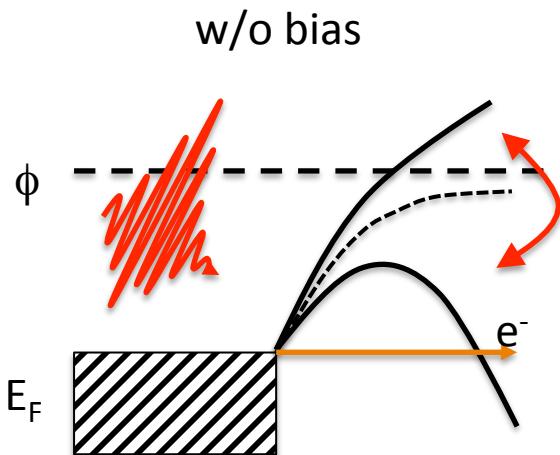
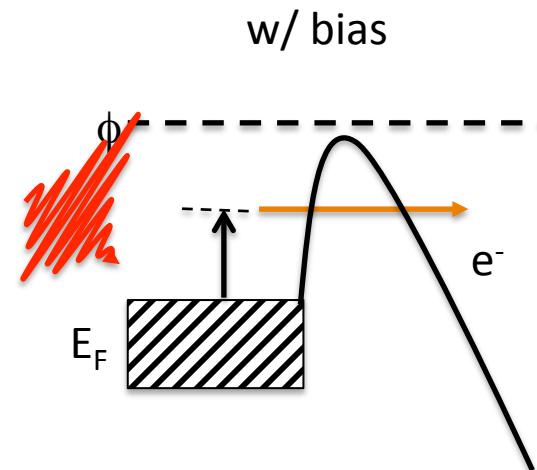
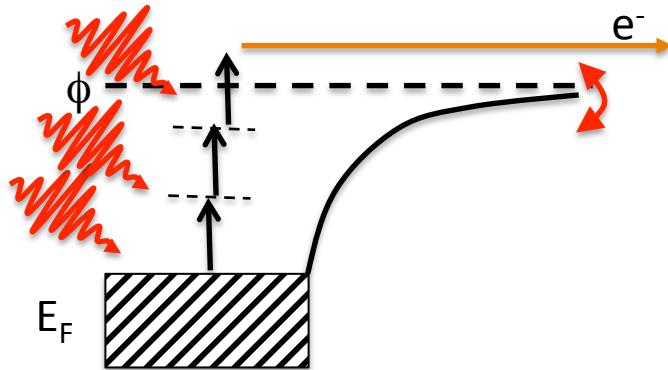


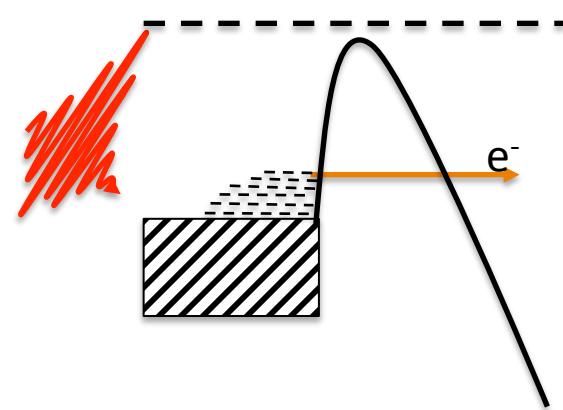
Photo-assisted tunneling



Tunneling of excited electrons

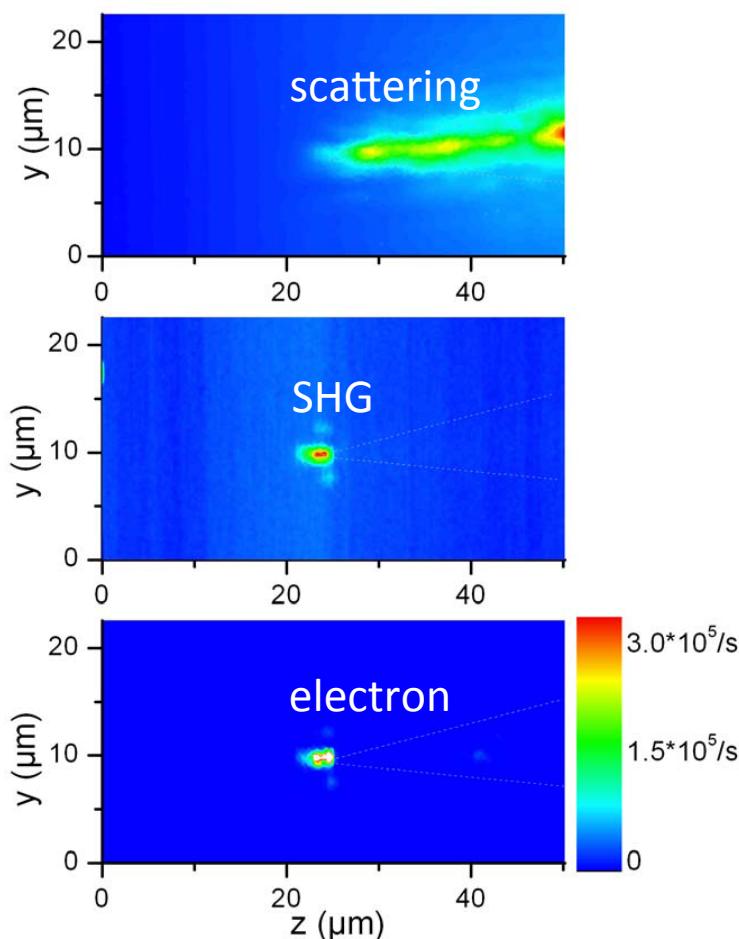


Multiphoton photoemission

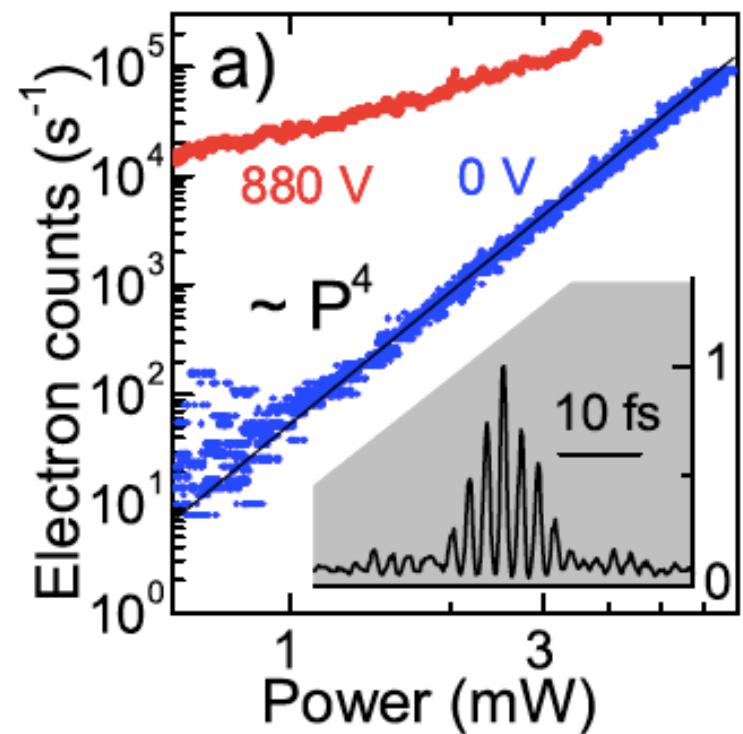


Thermally-assisted field emission

# Tip-enhanced electron emission

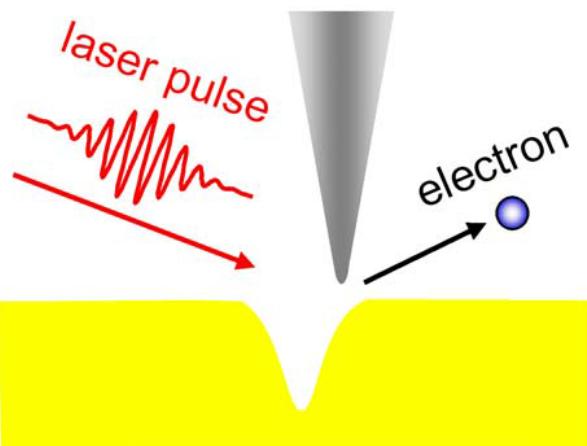


For null bias: multi-photon emission  
With applied bias: tunneling of excited e-

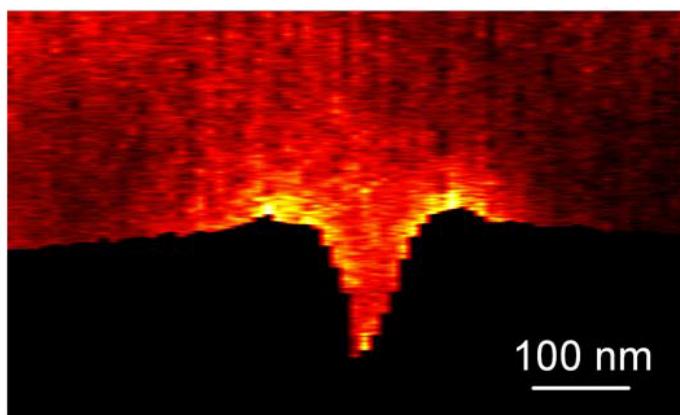


Field enhancement plus strong nonlinearity is  
essential for free electron generation

# Tip-enhanced electron microscopy

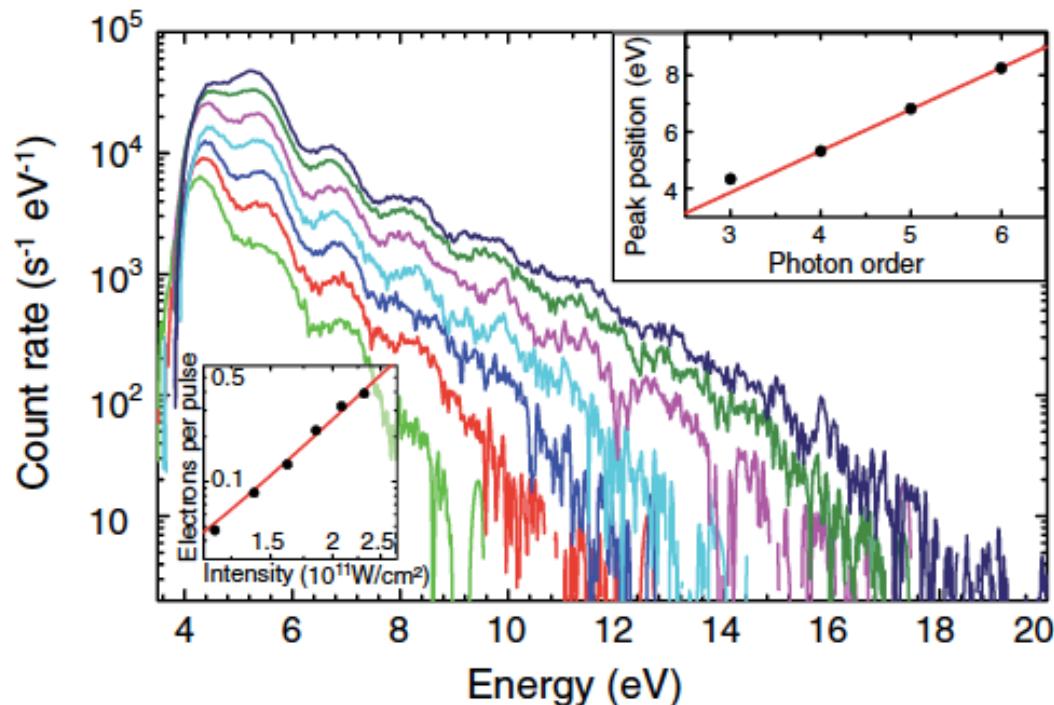


Imaging via the change of electron yield



C. Ropers et al , *Phys. Rev. Lett.* **98**,  
043907 (2007).

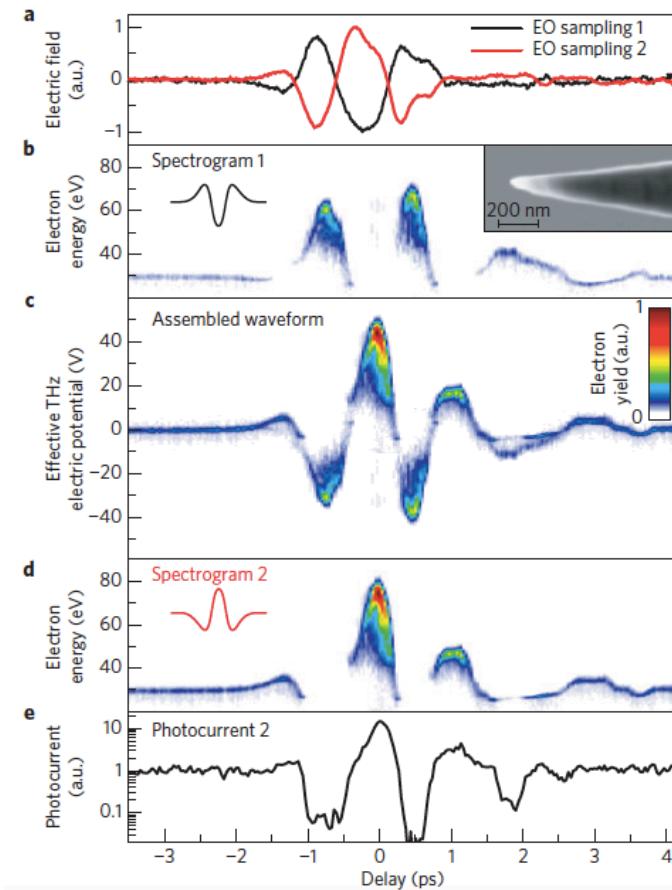
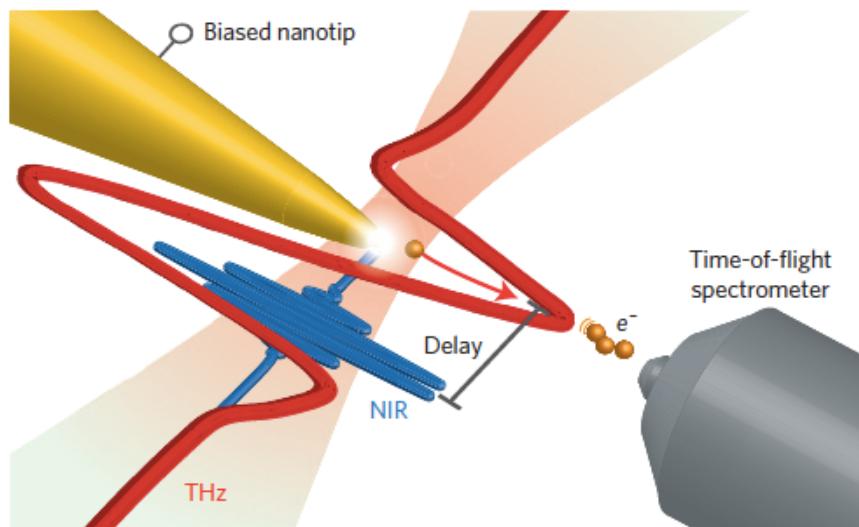
# Broad band kinetic energy spectrum



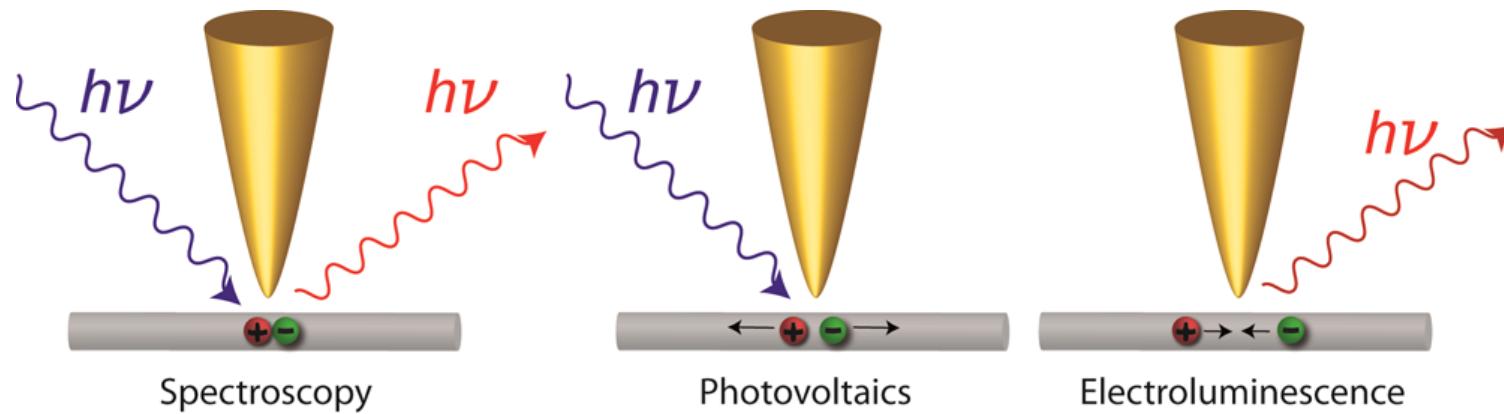
M. Shenk et al , *Phys. Rev. Lett.* **105**,  
257601(2010).

# Gating electron emission

nonlinear photoelectron emission from the tip apex, which is gated and streaked by locally enhanced single-cycle terahertz fields



Wimmers et al., *Nature Phys* **10**, 432 (2014).



- Optical microscopy/spectroscopy at sub-molecular resolution level
- Variety of linear and nonlinear processes triggered at the nanoscale
- Point-like source of fs-electron pulses