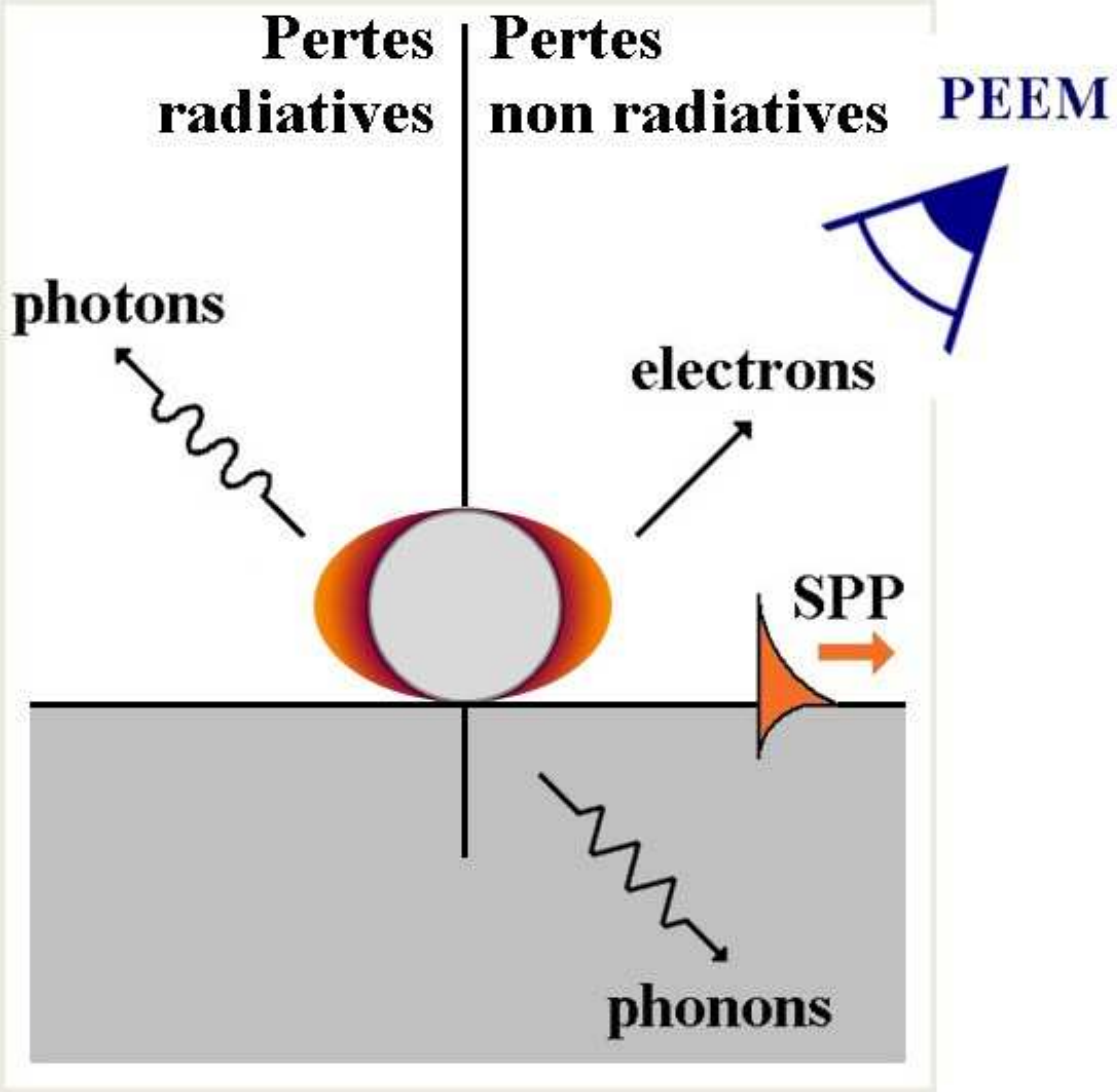
Mapping the evanescent field at the nanometre
Near field microscopies



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What is plasmonics ?

➢ "***A way to confine electromagnetic fields over dimensions on the order or smaller than the wavelength*** $\lambda_{h\nu}$***"***

S. Maier in Plasmonics: Fundamentals and Applications (2007) Springer

➢ Interaction processes between electromagnetic radiation and conduction electrons at metallic interfaces = **coherent collective charge oscillations**

➢ **Basic ingredients**

(i) *Surface plasmon-polariton* SPP - Metal / dielectric interface - Hybrid wave between a photon and a plasma oscillation - Propagative mode along the interface, evanescent in perpendicular direction

(ii) *Localised surface plasmon* LSP - Sub wavelength object - Non propagative mode

The promise of Plasmonics

- **A way to bridge the size gap between nanoelectronics and photonics**

	Working frequency	Spatial scale
Photonics	High working frequency Optical frequency 500 THz (600 nm) = 5.10^{14} Hz 500 THz = 500 000 GHz	Low spatial integration ~ $\lambda_{h\nu}$ Light wavelength ~ 600 nm in visible spectrum
Plasmonics	High working frequency Optical frequency 500 THz (600 nm) = 5.10^{14} Hz 500 THz = 500 000 GHz	Moderate - High spatial integration $\lambda_{h\nu}$ / 10 ~ 60 nm (visible)
Electronics	Low working frequency ~ 1 GHz = 1. 10^{9} Hz	High spatial integration Int. Roadmap for Devices and Sys. → MOSFET scaling 3 nm in 2022

Plasmonic near field – Experimental relevant scales

- Investigation of the full plasmonic picture requires adequate experimental resolutions in

.space
.time
.energy

- Additional degrees of freedom are

.light polarisation
.light angular momentum
.electron momentum distribution
…

Plasmonics - Physical orders of magnitude - Spatial scale

Relevant length scales of a plasmonic field

- Near field phenomena imply field spatial distribution scale << Light wavelength λ_0
- Localized surface plasmon
  - Collective coherent electron oscillation
  - Electrons perceive a static electric field amplitude (quasi static QS approximation)
  - Object dimension L << Light wavelength λ_0

- Thomas Fermi screening length ≈ 0.1 nm << Coherent charge fluctuation spatial period

- Propagation length of a surface plasmon polariton $L_{prop.}$ = 1/e plasmonic field decay length

$$L_{prop} = \frac{1}{k_x''} \qquad k_x'' = Im\left\{\frac{\omega}{c}\sqrt{\frac{\varepsilon_{Dielec}\varepsilon_{Metal}}{\varepsilon_{Dielec}+\varepsilon_{Metal}}}\right\}$$

N.A. Au/vacuum interface @ 800 nm wavelength excitation $L_{prop.}$ = 88 µm

A few tenths of a nanometer ~ 0.1 nm = 1×10^{-10} m

<

Plasmonic Spatial scale

<

A few tens of micrometers ~ 10 µm = 1.10^{-5} m

Plasmonics – Physical orders of magnitude – Time scale

Dynamics of the plasmonic near field

➢ Characteristic times of plasmonic physics

.Photon absorption time = Half-period of a Rabi oscillation ~ 1.10^{-16} s = 100 as
.Photon field oscillation ~ 1 / 500 THz ≈ 1.10^{-15} s = 1 fs
.Plasmonic field oscillation ~ 1 / 500 THz ≈ 1.10^{-15} s = 1 fs
.Plasmon coherence lifetime ~ 1.10^{-14} s = 10 fs
.Thermalisation time of a hot e^- gas ~ 1.10^{-13} s = 100 fs
.Thermalisation time of a hot e^- gas coupled to a phonon bath ~ 1.10^{-12} s = 1 ps

A few tenths of a femtosecond ~ 0.1 fs = 1×10^{-16} s
<
Plasmonic Time scale
<
One picosecond 1 ps = 1.10^{-12} s

Plasmonics – Physical orders of magnitude – Energy scale

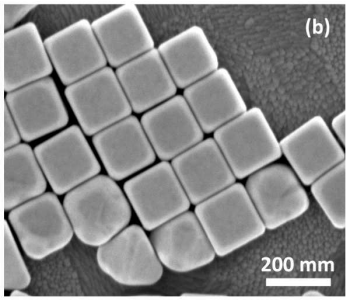
Energy of a localised surface plasmon, surface plasmon polariton

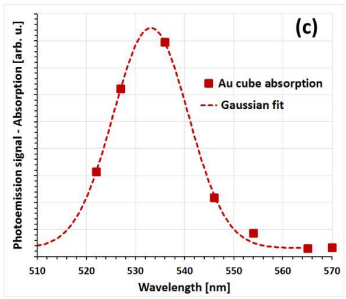
- Localised plasmon resonance energy - Full Width at Half Maximum FWHM

$$\text{FWHM} = \frac{2\hbar}{Plasmon\ coherence\ time\ T}$$

N.A. Plasmon coherence time T ≈ 10 fs = 1.10^{-14} s

FWHM ≈ 100 meV ⇔ 23 nm@530 nm





- Plasma wave in metals

Plasma oscillation quantum (volume) $\hbar\omega_V = \hbar\sqrt{\frac{\rho_e e^2}{\varepsilon_0 m_e}}$ (Surface) $\hbar\omega_S = \frac{\hbar\omega_V}{\sqrt{2}}$

m_e, e masse, resp. charge of a free electron [kg], [C],

ε_0 Vaccuum permittivity [F/m]

ρ_e nb of free electrons per unit volume [nb e^-/L^3], 1.10^{22} $e^-.cm^{-3} < \rho_e < 1.10^{24}$ $e^-.cm^{-3}$

Energy ⇒ 3.7 eV < $\hbar\omega_V$ < 37 eV, 2.6 eV < $\hbar\omega_S$ < 26 eV

A few hundredths of meV ~ 100 meV = 0.1 eV

<

Plasmonic Energy scale

<

Several eV ~ 10 eV

S. Mitiche *et al. J. of Phys. Chem.* C **121** (2017) 4517; L. Douillard *et al. Nano Lett.* **8** (2008) 935

Plasmonic near fields – Physical orders of magnitude

A few tenths of a nanometer ~ 0.1 nm = 1×10^{-10} m

<

Plasmonic Spatial Scale

<

A few tens of micrometers ~ 10 µm = 1.10^{-5} m

A few tenths of a femtosecond ~ 0.1 fs = 1×10^{-16} s

<

Plasmonic Time Scale

<

One picosecond 1 ps = 1.10^{-12} s

A few hundredths of meV ~ 100 meV = 0.1 eV

<

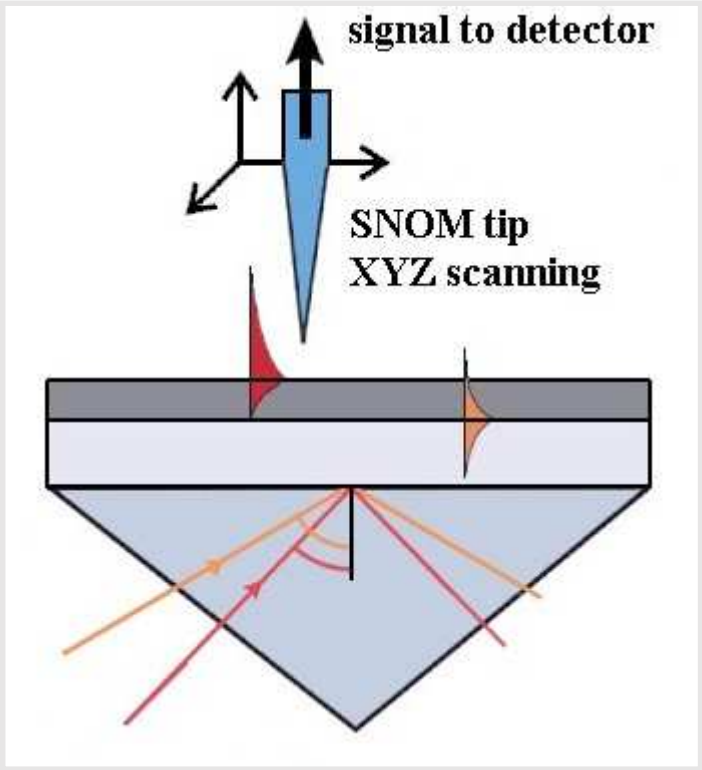
Plasmonic Energy Scale

<

Several eV ~ 10 eV

Mapping the evanescent field at the nanometre

SNOM/NSOM - *scanning near-field optical microscopy* (1984…)



➢ **Basic principle**

.scanning probe microscopy SPM. Closely related to scanning tunnelling microscopy STM

.introduction of a tip (glass fiber, metal…) in the near field of the object to be studied – **intrusive technique**

.routine resolution 50 - 100 nm

.many variants (illumination and collection modes)

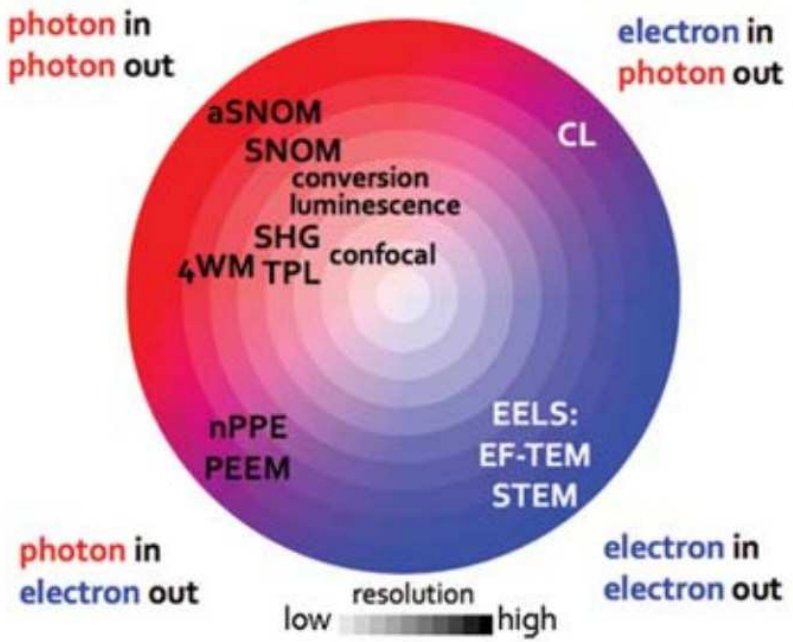
➢ **Drawbacks**

.low reproducibility of tips

.possible perturbation of the evanescent field due to LSP excitation and lightning-rod geometric effects at the tip-surface junction

Mapping the evanescent field at the nanometre

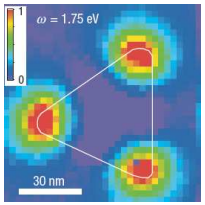
Alternative non intrusive methods (2012)



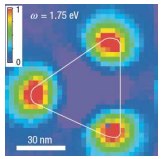
Process	Acronym	Measured quantity
	4WM – four-wave mixing **TPL** – 2-photon luminescence **SHG** – 2nd-harmonic generation **SNOM** – scanning nearfield optical microscopy **aSNOM** – apertureless SNOM	$E, \|E\|^2, \|E\|^4$
	nPPE – n-photon photoemission **PEEM** – photoemission electron microscopy	$\|E\|^{2n}$
	EELS – electron energy loss spectroscopy **TEM** – transmission electron microscopy **EF-TEM** – energy-filtered TEM **STEM** – scanning TEM	projected LDOS
	CL – cathodoluminescence	projected LDOS (partial)

- STEM EELS *scanning transmission microscopy in electron energy loss spectro. mode* (electron in, electron out) = Mapping of an electron energy loss signature
- CL *cathodoluminescence* (electron in, photon out) related to EELS
- PEEM *photoemission electron microscopy* (photon in, electron out), other acronym = n-PPE *n photon photoemission*

R. Vogelgesang *et al. Analyst* **135** (2010) 1175



Electron Energy Loss Spectrometry EELS
A tool for plasmonics



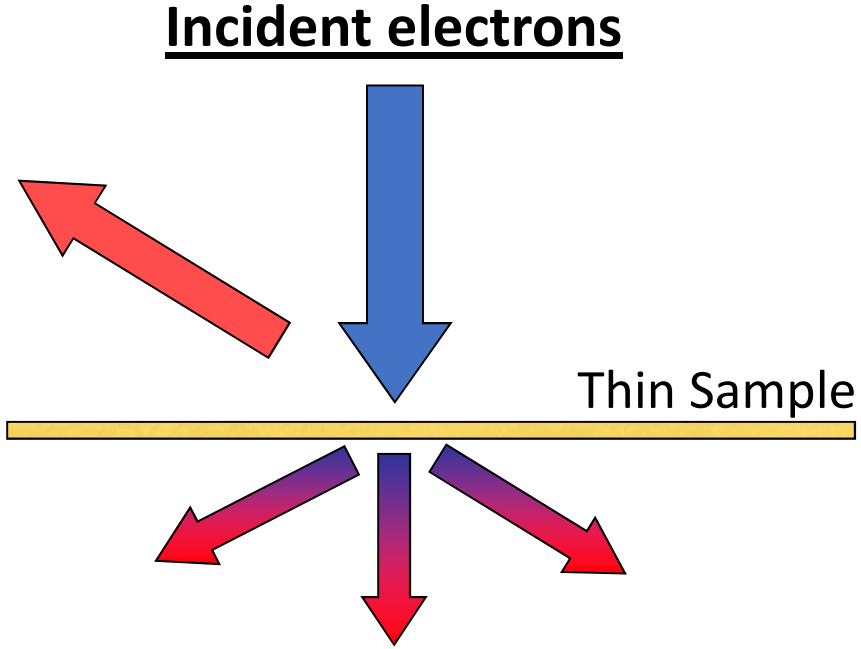
Electron energy loss spectrometry, a tool for plasmonics

Basic principle – Electron energy loss mapping

➢ To probe locally a sample (surface, thin film, particle) with a focused electron beam and investigate its excitations using the inelastically diffracted / scattered electrons

Secondary electrons
Backscattered electrons
Auger electrons

SEM, AES



Inelastically diffracted and scattered electrons

- Individual excitations
- Collective excitations

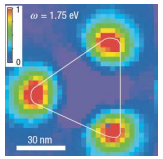
EELS Spectrometry

Transmitted electrons

TEM Bright Field Imaging

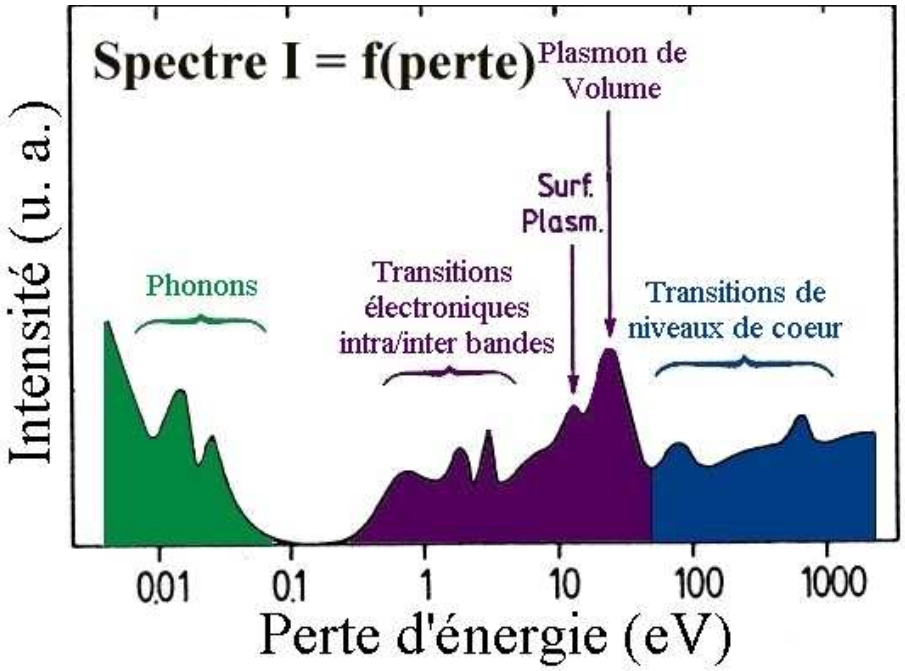
Elastically scattered and diffracted electrons - Rutherford scattered e^-

HR Diffraction (HA)ADF Imaging



Electron energy loss spectrometry, a tool for plasmonics

Basic principle – Electron energy loss spectrum



Zero loss region – Low primary energies, high energetic resolution

1 meV < ΔE < 100 meV

→ High Resolution Electron Energy Loss Spectrometry HREELS

Low loss region

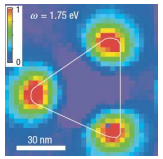
100 meV < ΔE < 50 eV

→ Electron Energy Loss Spectrometry EELS

High loss region – High primary energies

ΔE > 50 eV

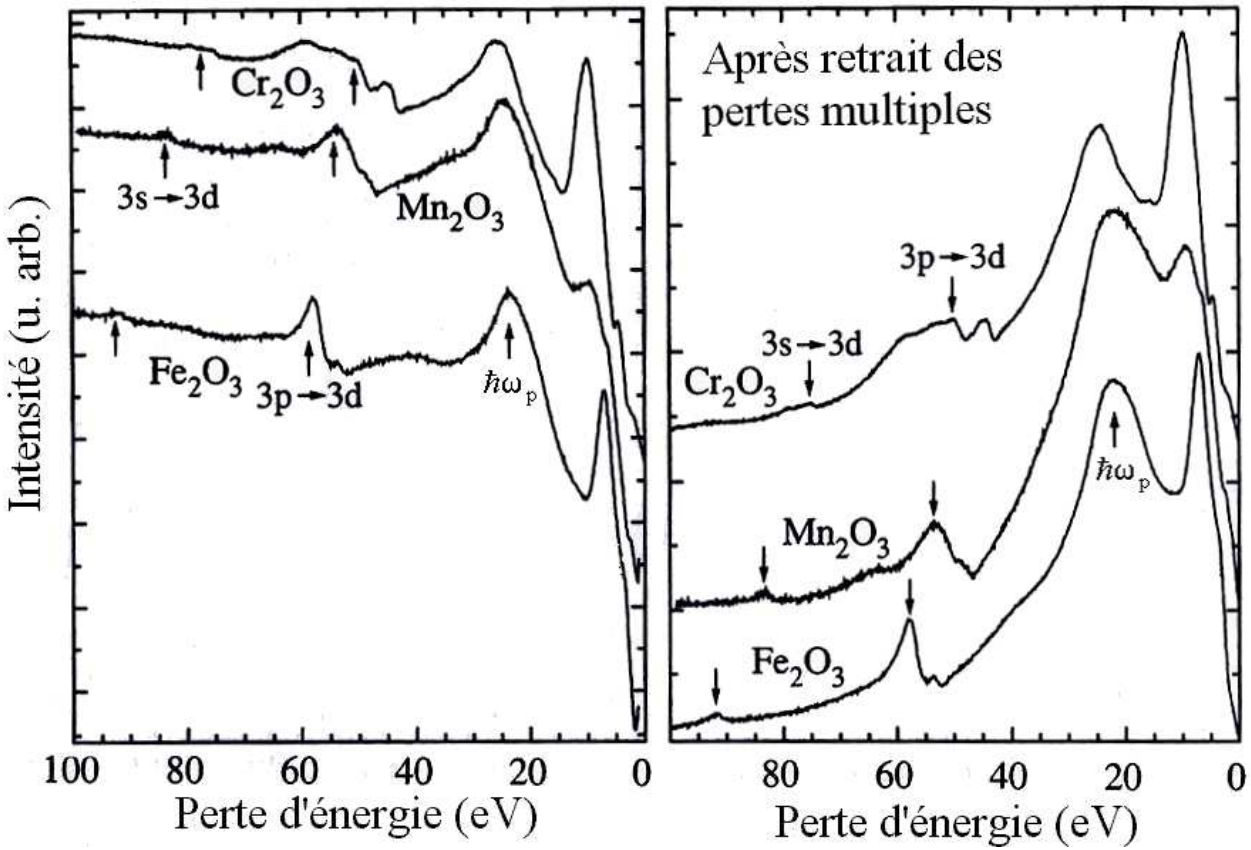
→ EXtended Electron energy Loss Fine Structures EXELFS



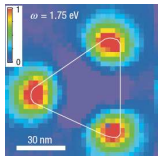
Electron energy loss spectrometry, a tool for plasmonics

Basic principle – EELS, loss region 100 meV < ΔE < 50 eV

- Excitation mechanism n°1
  - Individual excitations
  - Electronic intra-, resp. interband transitions



Electron energy loss spectra of transition metal oxides R. Zimmerman PhD (1996)



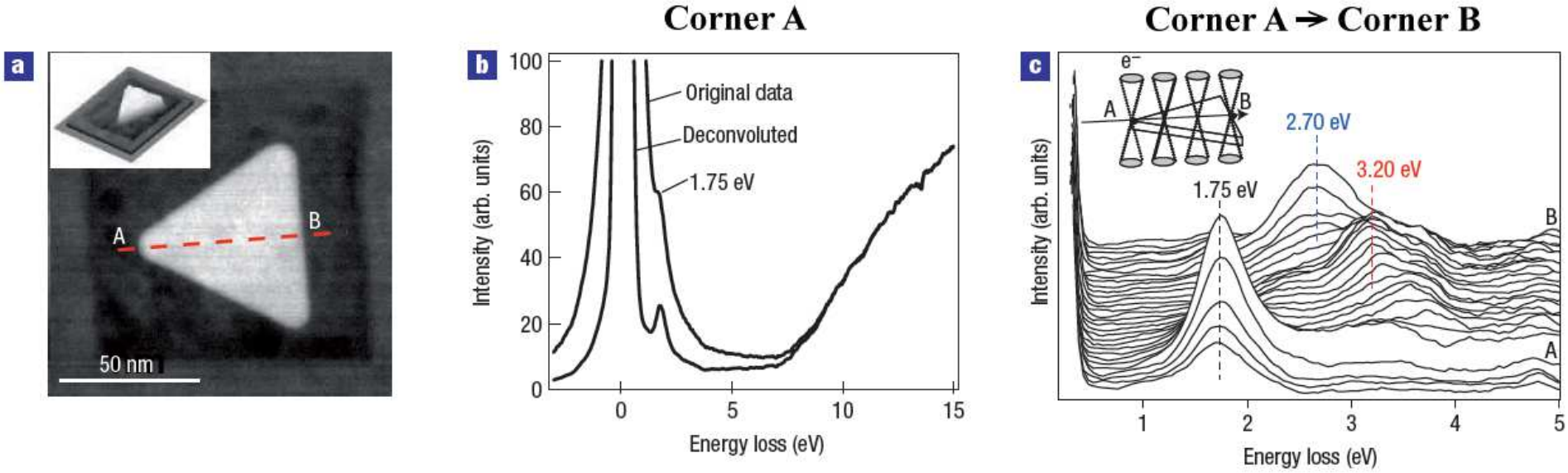
Electron energy loss spectrometry, a tool for plasmonics

Basic principle – EELS, loss region 100 meV < ΔE < 50 eV

➢ Excitation mechanism n°2

Collective excitations

Surface and bulk plasmons. Along its trajectory, an incoming electron polarizes the target, which in turn creates an induced field E_{ind}.

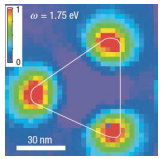


(a) Regular Au nanoprism particle. HAADF-STEM imaging

(b) EELS spectra acquired at corner A. One plasmon loss peaks at 1.75 eV

(c) A series of 32 successive low loss STEM EELS spectra acquired along the line A - B of the nanoprism. Three plasmon resonances are detected 1.75, 2.70 and 3.20 eV

J. Nelayah *et al. Nature physics* **3** (2007) 348



Electron energy loss spectrometry, a tool for plasmonics

Basic principle – EELS probability Γ_{EELS} for a small sphere a << λ

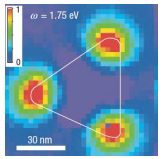
- The transient electric field associated to the e-beam is similar to a plane wave pulse of white light (at 100 keV, $\upsilon_e = 164$ nm/fs). The nanoparticle (NP) sees a pulse containing a large spectrum of frequencies. (e, e) Coulombian coupling in nature,
- All the energy absorbed or scattered by a plasmonic particle has to be provided by the incident electrons. So, full electron losses are proportional to the particle extinction cross section

$$\Gamma_{\mathrm{EELS}}^{\mathrm{sphere}}(R_\perp,\omega) = \frac{4e^2 a}{\pi\hbar v^2}\sum_{l=1}^{\infty}\sum_{m=-l}^{l}\frac{(a\omega/v)^{2l}(2-\delta_{0,m})}{(l+m)!(l-m)!}K_m{}^2\left(\frac{\omega R_\perp}{v}\right)\Im\{\alpha_l(\omega)\}$$

a Sphere diameter [m]
$R_\perp$ = (x, y) Impact parameter of the electrons traveling along the z direction at speed υ [m]
$\hbar\omega$ Loss energy [eV], ω pulsation = 2π.frequency
K_m Modified Bessel function of the second kind
$\Im$ Imaginary part
α_l Sphere polarizability for mode l [C.m²/V]
Non relativistic electrons. For relativistic electrons the Lorentz factor $\gamma = 1/\sqrt{1-\upsilon^2/c^2}$ has to be considered

- **EELS depends on all resonance modes l of the NP**

F. Garcia de Abajo *Phys. Rev. B* **59** *(1999) 3095*
M. Kociak & O. Stéphan *Chem. Soc. Rev.* **43** (2014) 3865



Electron energy loss spectrometry, a tool for plasmonics

Basic principle – EELS probability Γ_{EELS} for a small sphere a << λ

- The e-beam electric field is similar to a plane wave pulse of white light. The NP sees a pulse containing a large spectrum of frequencies
- In the quasi-static approximation, the exciting field is static, i.e. presents no spatial variation over the particle. Thus, it couples only to the $l = 1$ dipolar mode

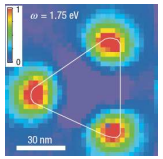
$$\Gamma_{EELS}^{sphere}(\omega, R_\perp) \propto \left(\frac{\omega}{\gamma v^2}\right)^2 \Im\left(\alpha_{\iota=1}(\omega)\right)\left(K_1^2\left(\frac{\omega R_\perp}{\gamma v}\right) + \frac{1}{\gamma^2}K_0^2\left(\frac{\omega R_\perp}{\gamma v}\right)\right)$$

$$\Gamma_{EELS}^{sphere}(\omega, R_\perp) \propto \Im\left(\alpha_{\iota=1}(\omega)\right).\exp\left(-\frac{R_\perp}{\gamma v/\omega}\right)$$

$$\sigma_{ext.} \cong \sigma_{abs.} \propto \Im\left(\alpha_{\iota=1}(\omega)\right)$$

- EELS probability of a small sphere is proportional to its extinction (absorption) cross-section as measured in far field optics, $\sigma_{ext.} \cong \sigma_{abs.} \propto \Im\left(\alpha_{\iota=1}(\omega)\right) \propto a^3$
- EELS probability is position-dependent with a quasi-exponential decay with e-beam to sphere distance $R_\perp$, attenuation length = $\gamma v/\omega \sim$ 10 - 100 nm ⇔ spatial resolution

F. Garcia de Abajo *Phys. Rev. B* **59** *(1999) 3095*
M. Kociak & O. Stéphan *Chem. Soc. Rev.* **43** (2014) 3865



Electron energy loss spectrometry, a tool for plasmonics

Basic principle – EELS probability Γ_{EELS} vs EMLDOS

➢ EMLDOS description. In quasi-static approximation

$$\Gamma_{EELS}^{sphere}\left(\omega,\vec{R}_{\perp}\right)=\frac{e^{2}}{\pi\hbar\omega^{2}}\sum_{i}\Im\left(f_{i}(\omega)\right)\left|TF_{z}(\vec{E}_{i}^{z}\left(\vec{R}_{\perp},\frac{\omega}{\upsilon}\right))\right|^{2}$$

f_i generalized polarizability, i.e. the spectral dependence of the plasmon (plasmon energies = f_i poles); TF_z is a Fourier transform along the e-beam direction at point $\vec{R}_{\perp}=(x,y)$ in real space and momentum $q_z = \omega / \upsilon$ in reciprocal space of the electron induced nearfield electric field.

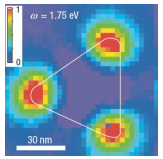
➢ Within a FT_z, EELS maps spectrally and spatially the zEMLDOS, i.e. the electromagnetic density of states in the direction along the e-beam axis

➢ EELS = Out-of-plane EMLDOS ($\vec{v}_e.\vec{E}_{ind}=\vec{v}_{e,z}.\vec{E}_{ind,z}$)

➢ Electron selection rules ≠ photon selection rules → Dark modes accessible

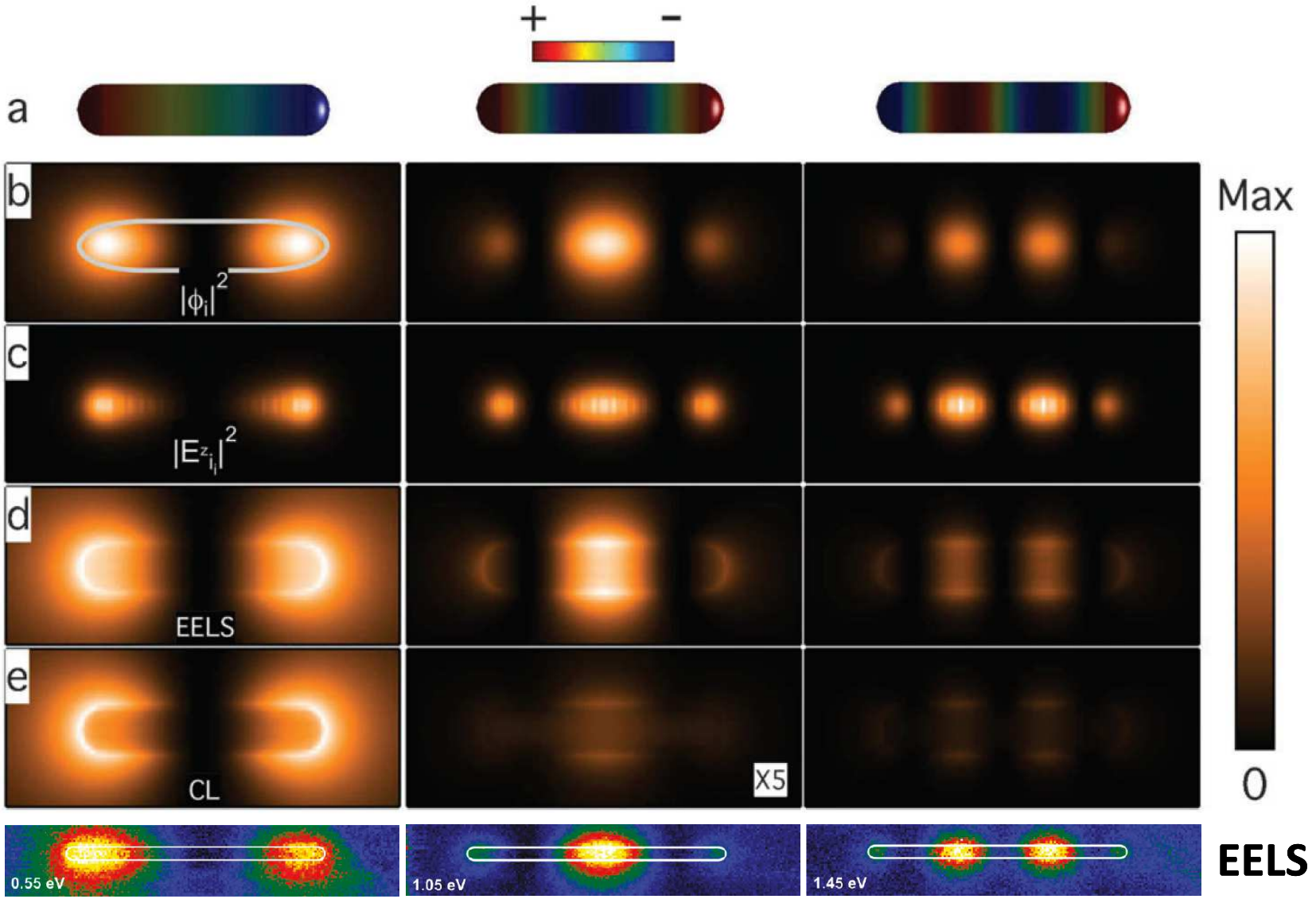
➢ Not a true optical process, so no direct control over the near field polarization

F. Garcia de Abajo *Phys. Rev. B* **59** *(1999) 3095*
M. Kociak & O. Stéphan *Chem. Soc. Rev.* **43** (2014) 3865



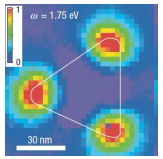
Electron energy loss spectrometry, a tool for plasmonics

Basic principle – EELS probability



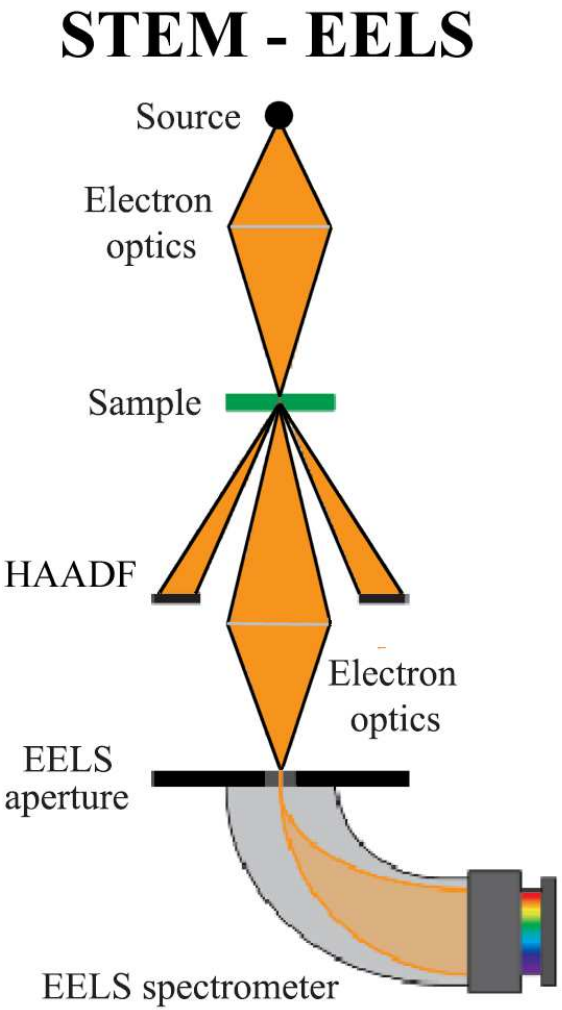
D. Rossouw *et al. Nano Lett.* **11** (2011) 1499

M. Kociak & O. Stéphan *Chem. Soc. Rev.* **43** (2014) 3865



Electron energy loss spectrometry, a tool for plasmonics

Instrumentation – STEM EELS mode



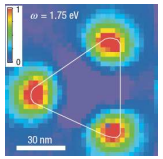
➢ Scanning transmission electron microscope in electron energy loss mode - (electron in, electron out) process

Electron source (electron field gun)
Electron optics
Energy = Hundreds of keV (TEM)

The electron beam is focused and raster scanned on the sample. Beam diameter ∅ ≤ 1 nm

EELS spectrometer for the extraction of the EELS spectrum at precise (x, y) position – Serial recording

➢ **Near field imaging through the mapping of a particular electron energy loss (plasmon energy). Spatial resolution ≈ beam diameter**



Electron energy loss spectrometry, a tool for plasmonics

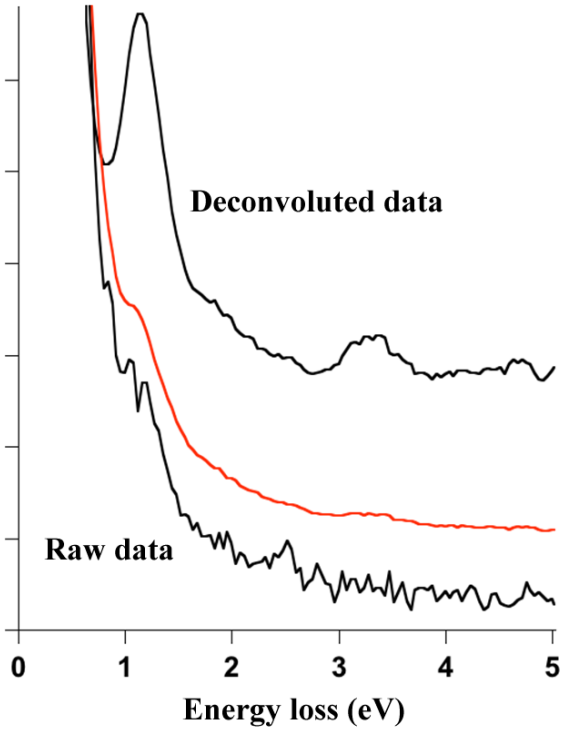
Instrumentation – STEM EELS Difficulties & Limitations

➢ How to get rid of the Zero Loss Peak ZLP

- The major experimental issue is to get at the same time both high energy- (δE = 100 meV) and high spatial- (δR = 0.1 nm) resolutions
- Thank to high brightness electron gun developments, beam monochromation (δE) is possible without too large drops of brightness (δR)
- Numerical treatments for better spectral deconvolution are now available. PSF deconvolution, Richardson-Lucy Deconvolution

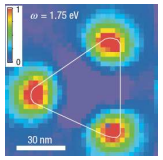
Gloter *et al.* Ultramicroscopy **96** (2003) 385

- Less noisy and faster CCD detectors are available



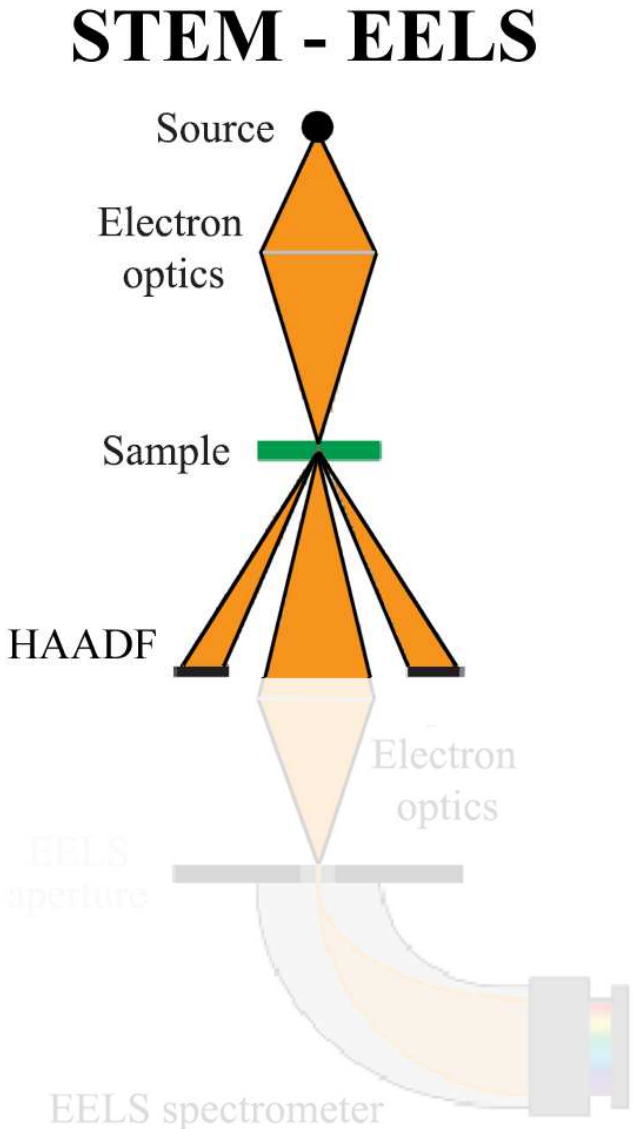
➢ Electron monochromator resolution is now down to 10 meV = 0.01 eV (2019)

E. P. Bellido *et al. Microsc. Microanal.* **20** (2014) 767
O. L. Krivanek *et al. Nature* **514** (2014) 209



Electron energy loss spectrometry, a tool for plasmonics

Instrumentation – STEM Bright Field Imaging mode



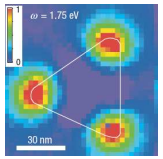
- Electron imaging

  Electron source (electron field gun)
  Electron optics

The electron beam is focused and raster scanned on the sample. Beam diameter ∅ ≤ 1 nm

- **SEM Imaging. Image is built on backscattered, secondary and/or Auger electrons**

- **TEM Imaging. Image is built on transmitted electrons**

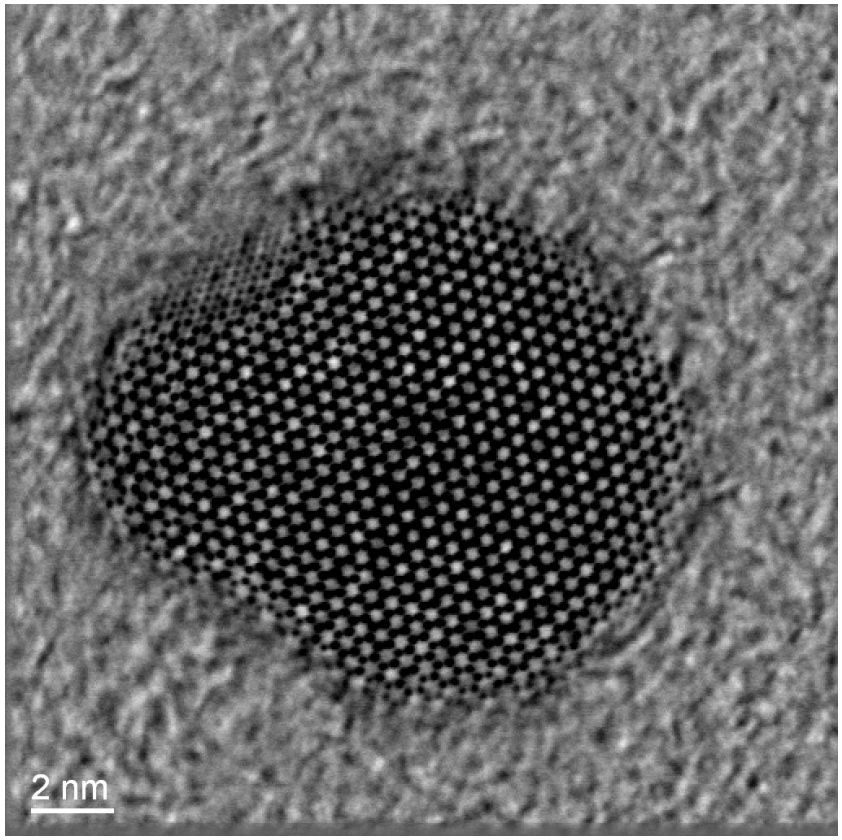


Electron energy loss spectrometry, a tool for plasmonics

Instrumentation – STEM Imaging mode

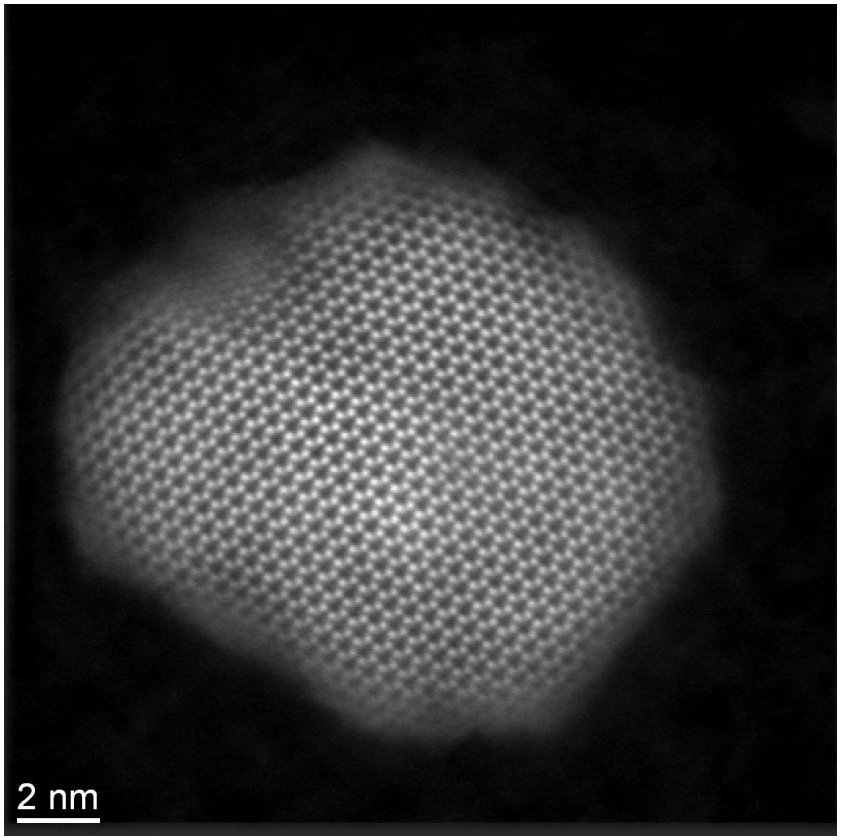
Bright field imaging mode

CdSe Platelets, courtesy B. Dubertret

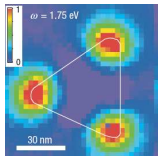


Dark Field imaging mode

CdSe Platelets, courtesy B. Dubertret

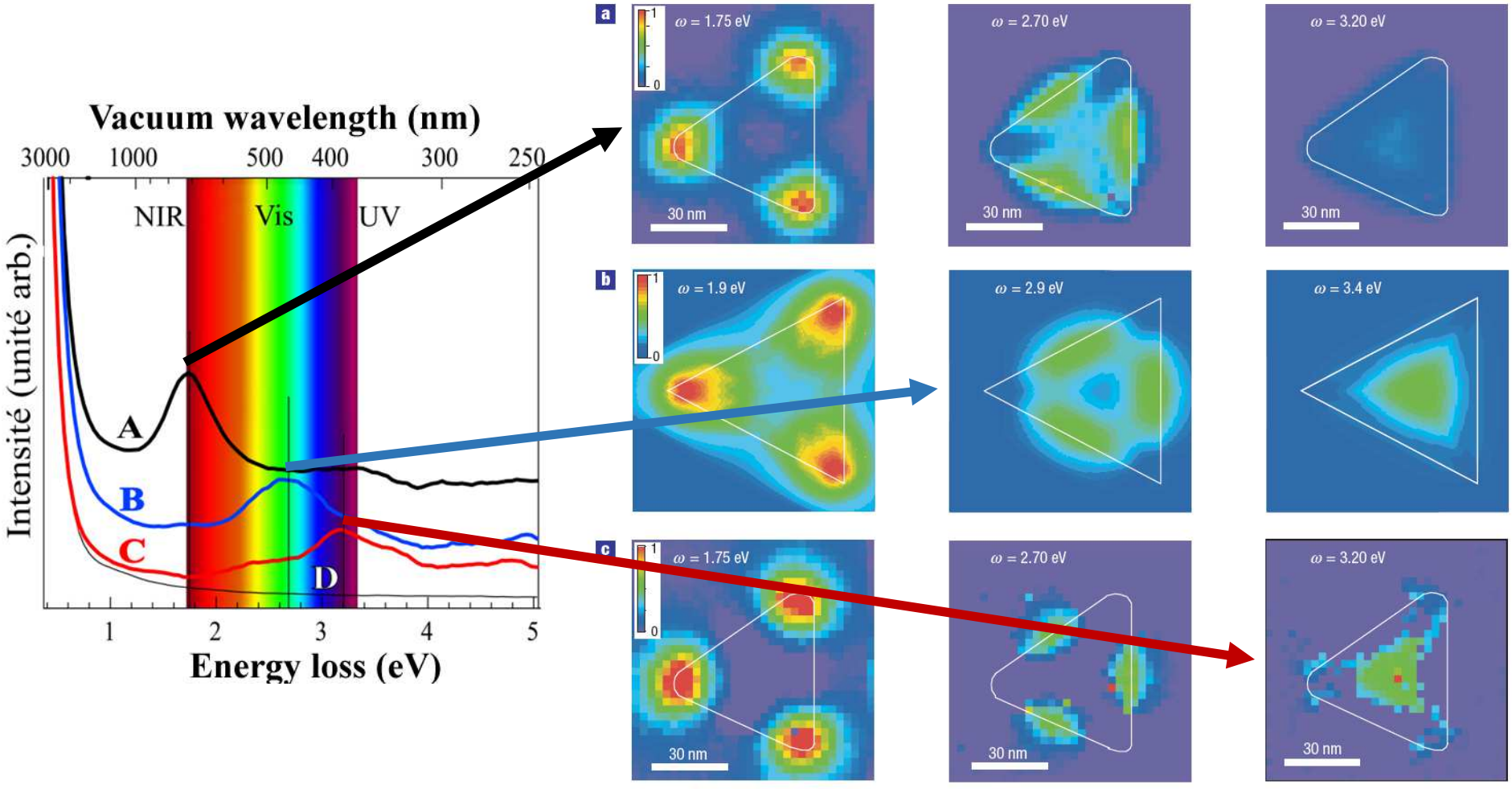


➢ **Topography imaging.** Fast electron probes can be made much smaller than the typical visible light wavelength. Atomic resolution ≈ 0.1 nm possible



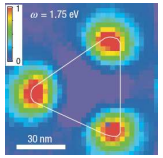
Plasmonics of 2D objects - NanoPrism D_{3h} - STEM EELS

EELS near field imaging



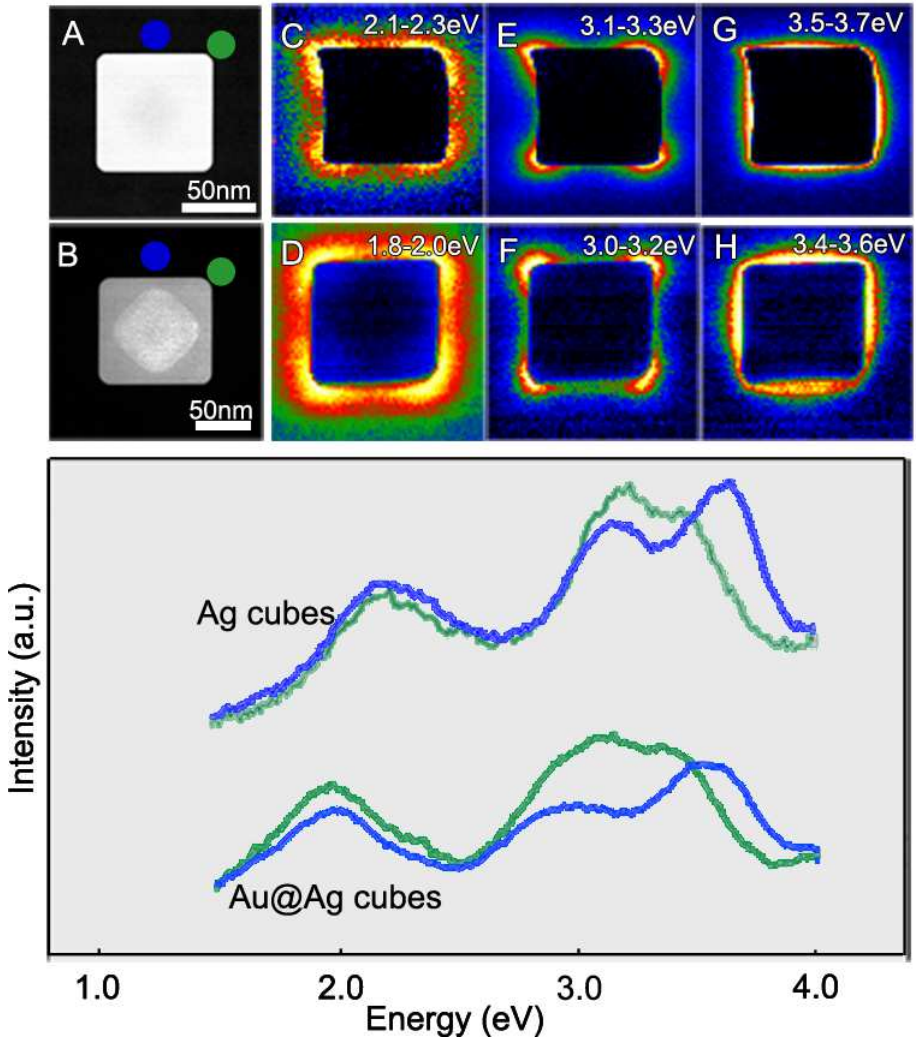
Regular nanoprism 78 nm. Near field Imaging. Resonance modes, m = {1, 2, 3} – STEM EELS
(a) Raw exp data – ZLP, (b) FDTD simulation , (c) Gaussian fitting of the exp. data

J. Nelayah *et al. Nature physics* **3** (2007) 348



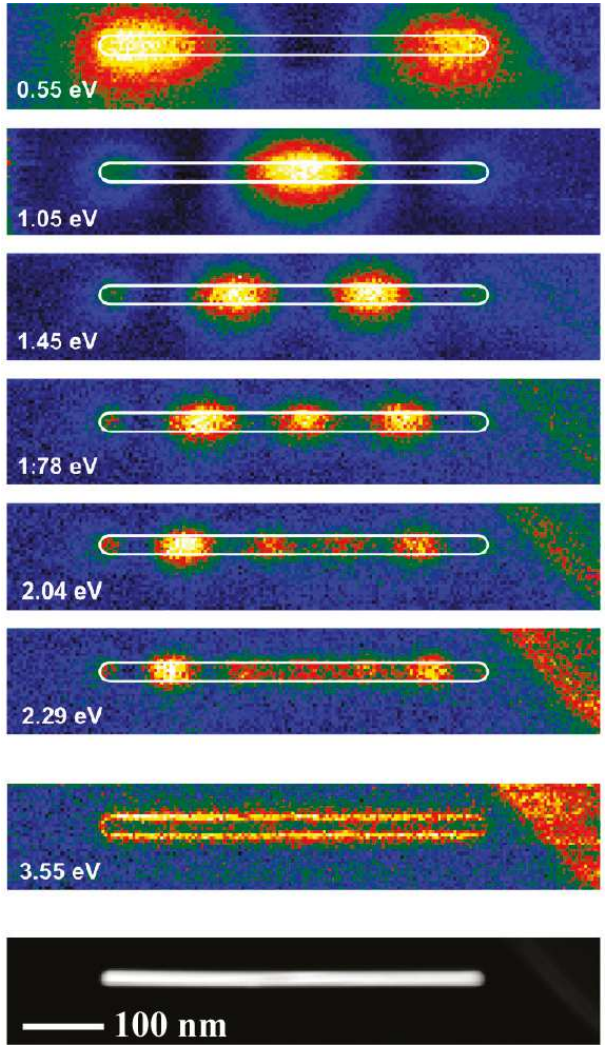
Plasmonics of Nanoobjects – Cubes & Rods - STEM EELS

EELS near field imaging



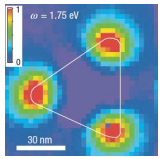
Ag and Au@Ag NanoCubes 70 nm

B. Goris *et al. J. Phys. Chem. C* **118** (2014) 15356



Ag NanoRods, 14 nm in diameter

D. Rossouw *et al. Nano Lett.* **11** (2011) 1499



Electron energy loss spectrometry, a tool for plasmonics

EELS near field imaging - Variants & Advances

- EELS 3D tomography

  → 3D mapping of plasmon resonances O. Nicoletti *et al. Nature* **502** (2013) 80; A. Hörl *et al. Phys. Rev. Lett.* **111** (2013) 076801

- Time-resolved EELS measurements in the fs time range

  → Use of a pulsed optical excitation combined with a pulsed electron probe F. Carbone *et al. Science* **325** (2009) 181

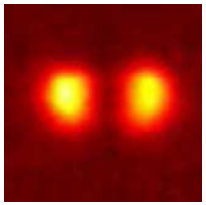
- Vortex EELS measurements

  → Use of an electron beam that carries an angular orbital momentum (diffractive phase plate, magnetic lens aberrations)

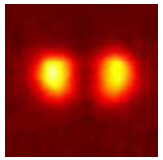
  Applications = Measurement of magnetic phenomena at the nanoscale

  Magnetic plasmon mapping Z. Mohammadi *et al. Opt. Express* **20** (2012) 15024

  Magnetic dichroism measurements in plasmonic structures X. Zambrana-Puyalto *et al. Nat. Commun.* **5** (2014) 4922



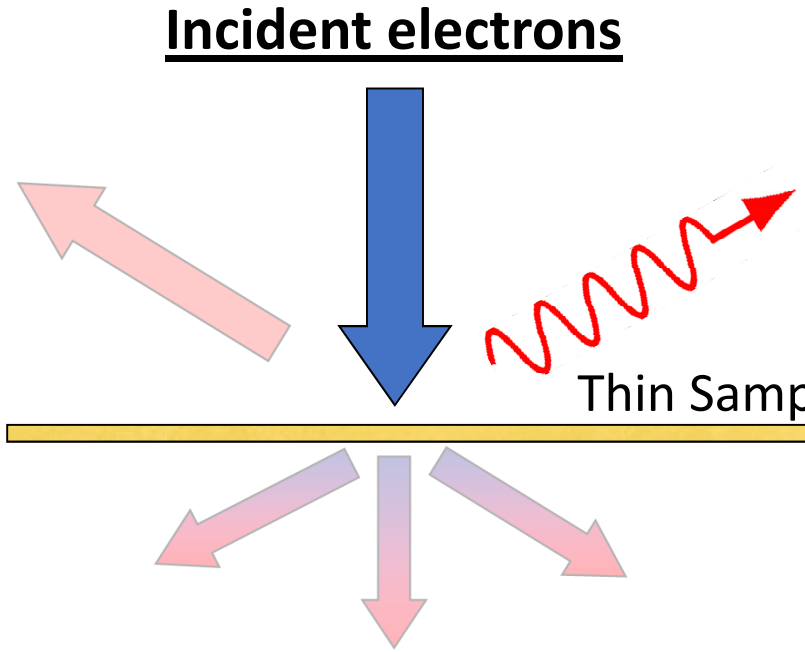
Cathodoluminescence CL
A tool for plasmonics



Cathodoluminescence, a tool for plasmonics

Basic principle – Cathodoluminescence near field imaging

➢ To probe locally a sample (surface, thin film, object) with a focused electron beam and investigate its excitations by collecting the emitted light (vis. spectrum)



Secondary electrons
Backscattered electrons
Auger electrons

SEM, AES

Photon emission
X, UV, visible, IR

Energy dispersive X-ray Spec. EDS, EDX, EDXS
CathodoLuminescence

Inelastically diffracted and scattered electrons

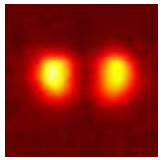
- Individual excitations
- Collective excitations

EELS Spectrometry

Transmitted electrons
TEM Bright Field imaging

Elastically scattered and diffracted electrons

HR Diffraction (HA)ADF Holography



Cathodoluminescence, a tool for plasmonics

Basic principle – Coherent CL probability Γ_{CL} of a small sphere

- The transient electric field associated to the e-beam is similar to a plane wave pulse of white light. The NP sees an EM pulse containing a large spectrum of frequencies
- In the QS approximation, the exciting field is static, i.e. presents no spatial variation over the particle size. Thus, it couples only to the $l = 1$ dipolar mode

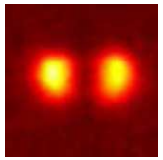
$$\Gamma_{CL}^{sphere}(\omega, R_\perp) \propto \omega^3 \left(\frac{\omega}{\gamma v^2}\right)^2 |\alpha_{l=1}(\omega)|^2 \left(K_1^2\left(\frac{\omega R_\perp}{\gamma v}\right) + \frac{1}{\gamma^2} K_0^2\left(\frac{\omega R_\perp}{\gamma v}\right)\right)$$

$$\Gamma_{CL}^{sphere}(\omega, R_\perp) \propto |\alpha_{l=1}(\omega)|^2 \exp\left(-\frac{R_\perp}{\gamma v/\omega}\right)$$

a Sphere diameter; $R_\perp$ = (x, y) Impact parameter of the electrons traveling along the z direction at speed v; $\hbar\omega$ Energy of the emitted photon; K_m Modified Bessel function of the second kind; α_l Sphere polarizability for mode l

- CL probability of a small sphere Γ_{CL} is proportional to its scattering cross section as measured in far field optics, $\sigma_{sca.} \propto |\alpha_{l=1}(\omega)|^2 \propto a^6$
- CL probability is position-dependent with a quasi-exponential decay with e-beam to sphere distance $R_\perp$, attenuation length $\gamma v/\omega \sim 10$ - 100 nm
- Radiative bright field modes accessible

A. Asenjo-Garcia, F. García de Abajo *New J. Phys.* **15** (2013) 103021; M. Kociak, O. Stéphan *Chem. Soc. Rev.* **43** (2014) 3865



Cathodoluminescence, a tool for plasmonics

Basic principle – Coherent CL probability Γ_{CL} of any particle

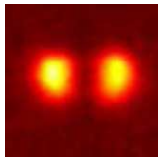
$$\Gamma_{CL}\left(\omega,\vec{R}_{\perp}\right) = \frac{\omega e^2}{4\pi^2\hbar c^3}\sum_i\sum_j f_i(\omega)\,f_j^*(\omega)\int_{\Omega_D} d\Omega\ \overrightarrow{p_{i\perp}}(\Omega).\overrightarrow{p_{j\perp}}^*(\Omega)\,.\,TF_z(\vec{E}_i^z\left(\vec{R}_{\perp},\frac{\omega}{\upsilon}\right)).TF_z(\vec{E}_j^{z^*}\left(\vec{R}_{\perp},\frac{\omega}{\upsilon}\right))$$

$$\Gamma_{CL}\left(\omega,\vec{R}_{\perp}\right) = \frac{\omega e^2}{4\pi^2\hbar c^3}\sum_i |f_i(\omega)|^2\int_{\Omega_D} d\Omega\,|\overrightarrow{p_{i\perp}}(\Omega)|^2\,.\left|TF_z\left(\vec{E}_i^z\left(\vec{R}_{\perp},\frac{\omega}{\upsilon}\right)\right)\right|^2 + \sum_i\sum_{j<i} coupled\ intermode\ terms\ (\overrightarrow{p_{i\perp}},\overrightarrow{p_{j\perp}}^*)$$

Where $f_i(\omega)$ is the generalized polarizability function introduced for the EELS description, $\overrightarrow{p_{i\perp}}(\Omega)$ is the transverse dipole of mode i (obs. dir.) and $TF_z\left(\vec{E}_i^z\left(\vec{R}_{\perp},\frac{\omega}{\upsilon}\right)\right)$ the Fourier transform along the e-beam direction at impact point $\vec{R}_{\perp}=(x,y)$ in real space and momentum $k_z = \omega/\upsilon$ in reciprocal space of the electron induced electric near field $\vec{E}_i^z$.

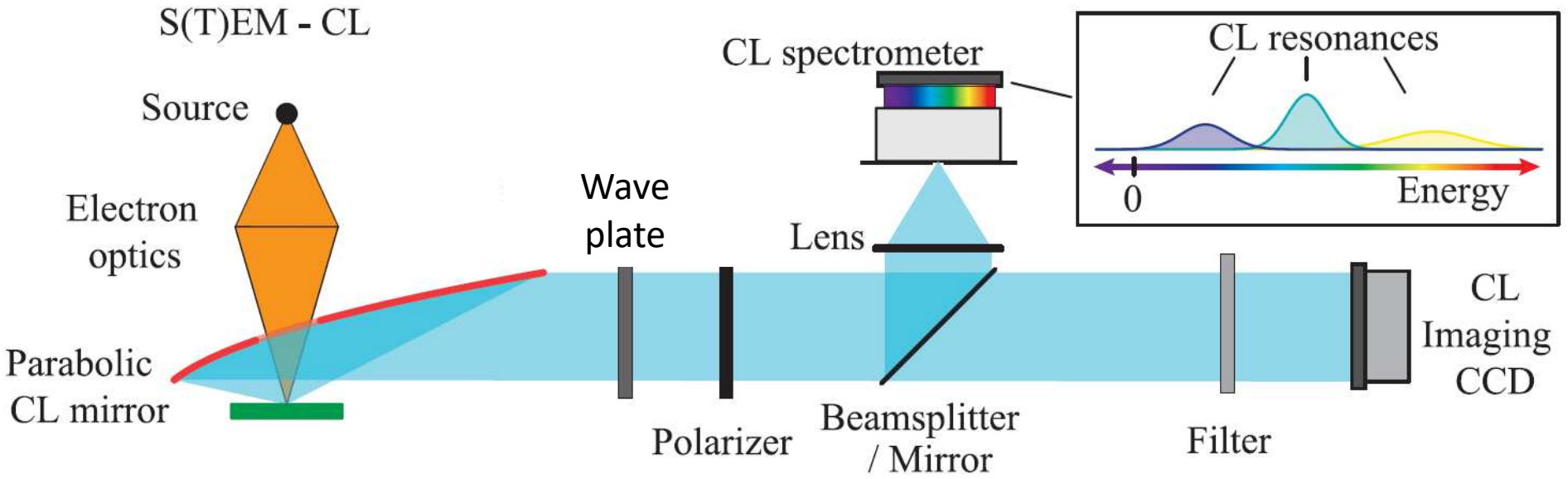
- Within a FT_z, CL maps spectrally and spatially the zEMLDOS, i.e. the electromagnetic density of states in the direction along the e-beam axis
- CL probability is proportional to the induced dipole $p_{i\perp}$ + interference terms between mode orders (i, j)

A. Losquin, M. Kociak *ACS Photonics* **2** (2015) 1619



Cathodoluminescence, a tool for plasmonics

Instrumentation – SEM CL (a few 10 kV) , STEM CL (a few 100 kV)



➢ Scanning (transmission) electron microscope in cathodoluminescence mode - (electron in, photon out) process

.Electron source (electron field gun)

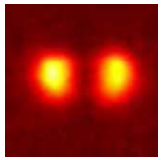
.Electron optics, Electron energy = Tens of keV for a SEM, hundreds of keV for a TEM

.The electron beam is focused and raster scanned on the sample. Beam diam. ∅ ≈ 10 nm

.The optical luminescence spectrum is collected using a parabolic mirror at each beam position (x, y)

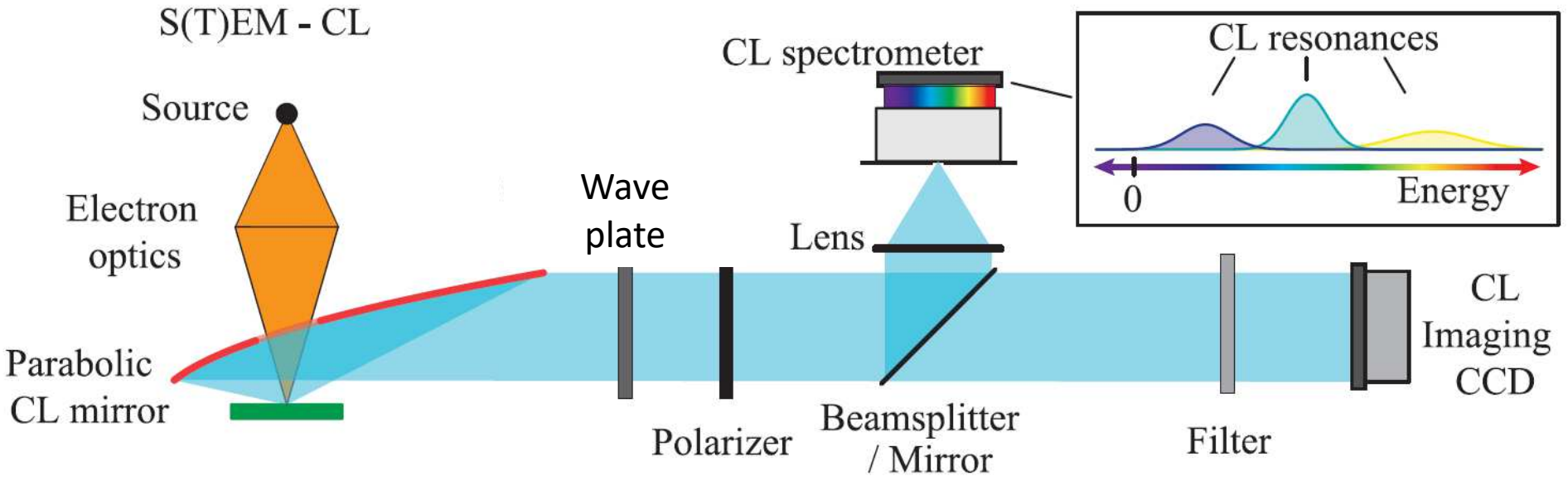
➢ **Near field imaging through the mapping of a cathodoluminescence signal**

A. Losquin, T. T. A. Lummen *Front. Phys*. **12** (2017) 127301



Cathodoluminescence, a tool for plasmonics

Instrumentation – SEM CL (a few 10 kV) , STEM CL (a few 100 kV)



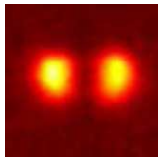
➢ Scanning (transmission) electron microscope in cathodoluminescence mode

◆ CL imaging mode. Acquisition of the spatially resolved cathodoluminescence signal at a particular optical wavelength λ. Spatial resolution $\delta R \approx$ electron beam diameter $\approx$ 10 nm

◆ CL spectrometry. Acquisition of a CL spectrum $I_{CL} = f(\lambda)$ at a fixed position (x, y)
CL signal spectral resolution 1 - 10 meV $\Leftrightarrow$ 0.3 – 3 nm @ 600 nm
Significant broad luminescence background (post treatment analysis required)

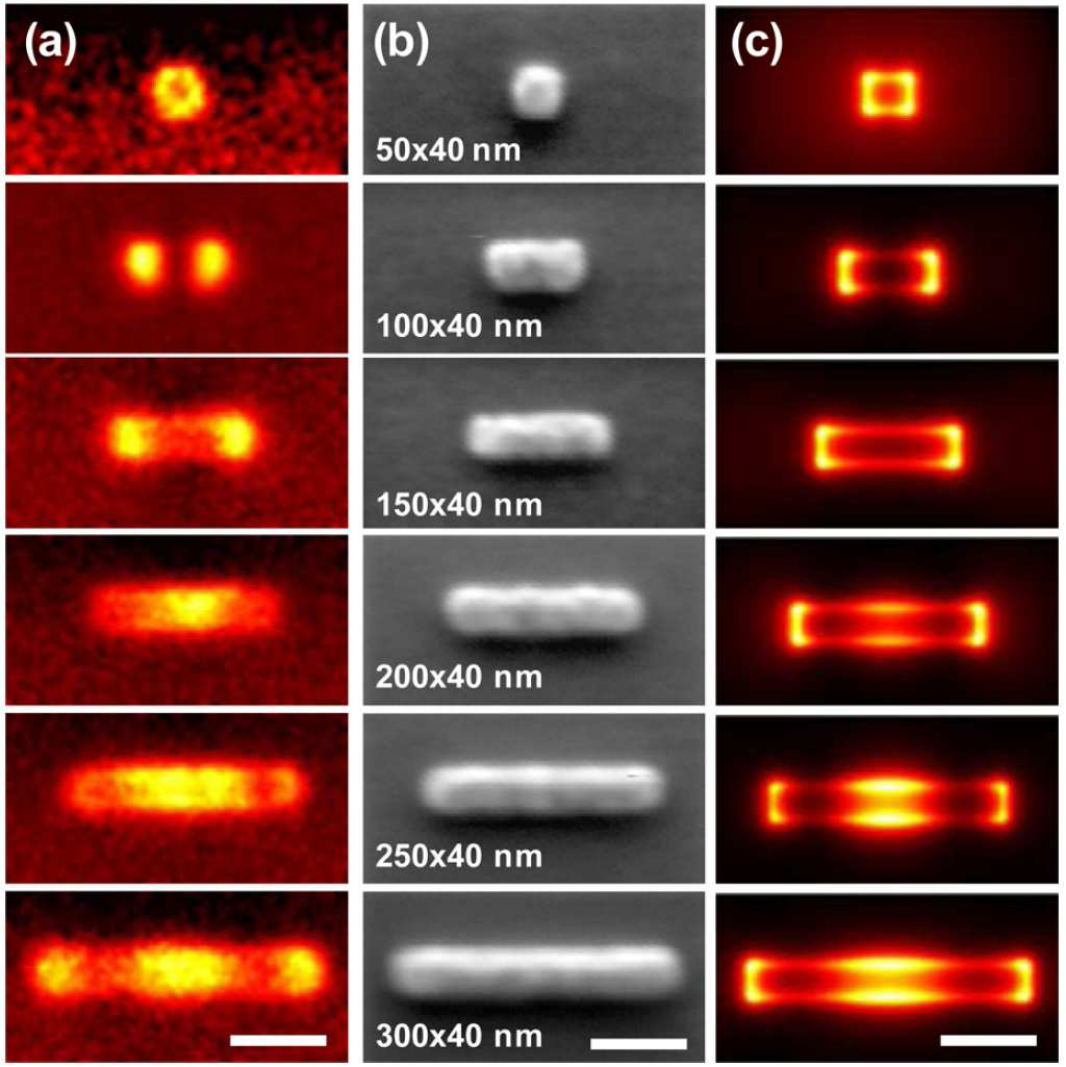
◆ Optical signal = Additional information available like the polarization of the emitted light

A. Losquin, T. T. A. Lummen *Front. Phys*. **12** (2017) 127301



Plasmonics of Nanoobjects - NanoRods

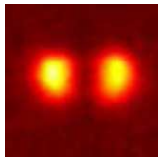
Cathodoluminescence near field imaging – STEM CL (x,y) mode



Al nanorods (a) CL near field imaging for energy range 2.5 – 3.0 eV

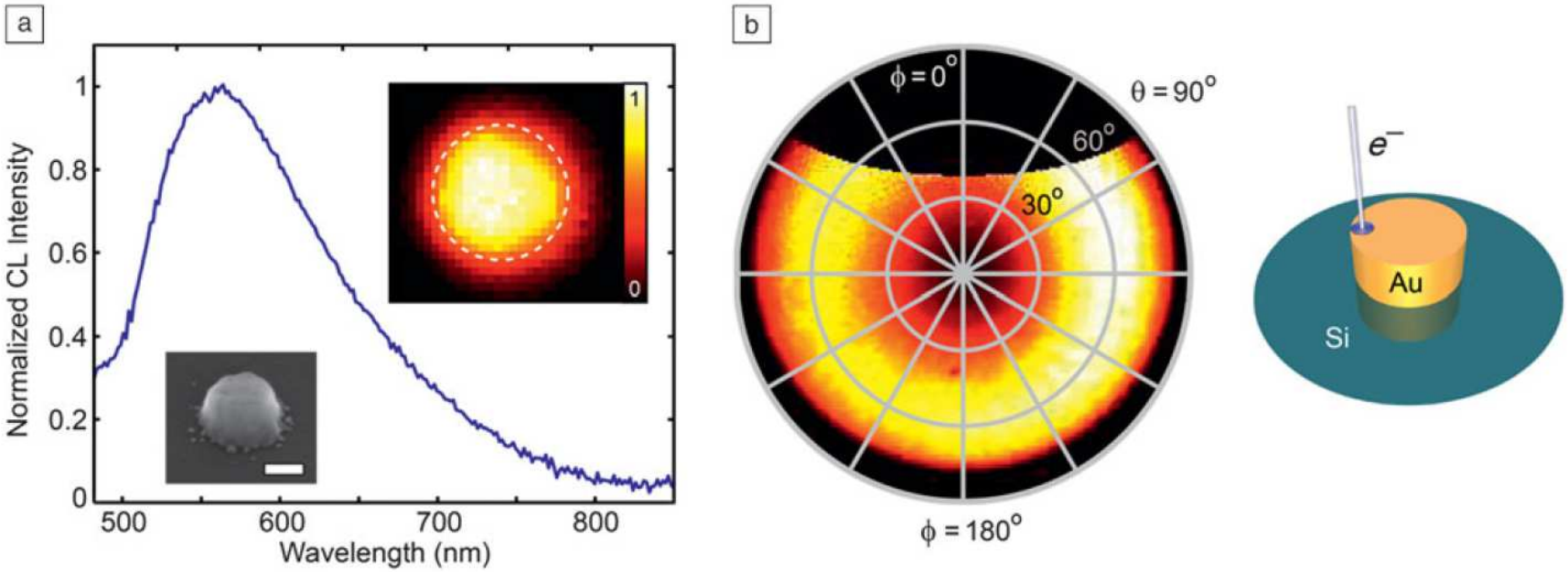
(b) SEM images (c) Calculated electromagnetic field distribution (FDTD)

M.W. Knight *et al. Nano Lett.* **12** (2012) 6000



Cathodoluminescence, a tool for plasmonics

Cathodoluminescence near field spectro. – STEM CL (λ) mode

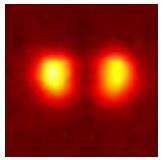


Au nanoparticle 100 nm in diameter and 80 nm in height on Si

➢ CL Spectrometry. (a) CL spectrum spatially averaged over the particle with a 5 nm resolution. A clear resonant spectrum is observed, which reflects the CL radiation of a vertically-oriented dipolar plasmon resonance in the Au NP peaking at λ = 560 nm

➢ Angle resolved CL imaging. (b) Angular distribution of the CL radiation emitted by the Au NP. Off center e^- beam excitation translates into an asymmetric intensity profile (⊥ & // dipoles)

T. Coenen *et al. MRS BULLETIN* **40** (April 2015) 359



Cathodoluminescence, a tool for plasmonics

CL near field mapping - Advances & Variants

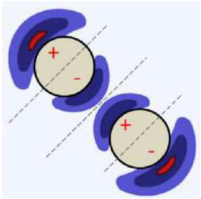
- CL 3D tomography

→ Reconstruction of 3D CL intensity maps A. C. Atre *et al. Nat. Nanotechnol.* **10** (2015) 429

- Angle resolved CL imaging polarimetry

→ Ability to characterize both directionality and polarisation characteristics of CL emission in the hemisphere above a plasmonic structure B. J. M. Brenny *et al. Appl. Phys. Lett.* **107** (2015) 201110; C. I. Osorio *et al. ACS Photonics* **3** (2016) 147

- Time resolved CL experiment, but in the ps time range (2019), not so relevant for plasmonics (1 - 10 fs time range)

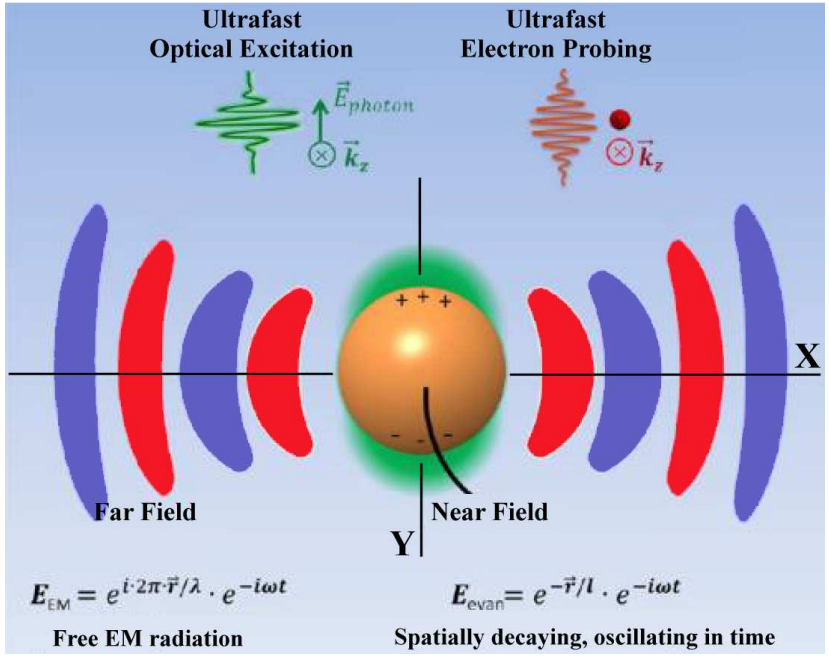


Photon-Induced Near-Field Electron Microscopy
PINEM, a tool for plasmonics

Photon-Induced Near-Field Electron Micros., a tool for plasmonics

Basic principle – PINEM near field imaging

➢ In PINEM, the plasmonic sample is excited with a photon pulse of fs duration, simultaneously, an ultrashort electron pulse images the near field induced using the optical excitation ⇨ **Three body interaction ($\hbar\omega_{ph}$ in (plasmon), e⁻ in, e⁻ out)**



➢ **Three body interaction**

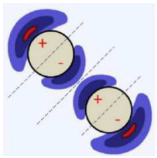
In free space, photons and electrons interact weakly because of a large momentum mismatch

e⁻ viewpt $\Delta p(e^- + n.\hbar\omega) = n.\hbar\omega/v_e$

$\hbar\omega$ viewpt $\Delta p(e^- + n.\hbar\omega) = n.\hbar\omega/c$, $c > v_e$

In solids, possible interaction between electrons and photons through a plasmon exchange, an additional source of energy and momentum - **Evanescent wave at confined sites,** $\Delta z.\Delta p \sim \hbar/2$

A. Yurtsever, A. Zewail *Nanoletter* **12** (2012) 3334

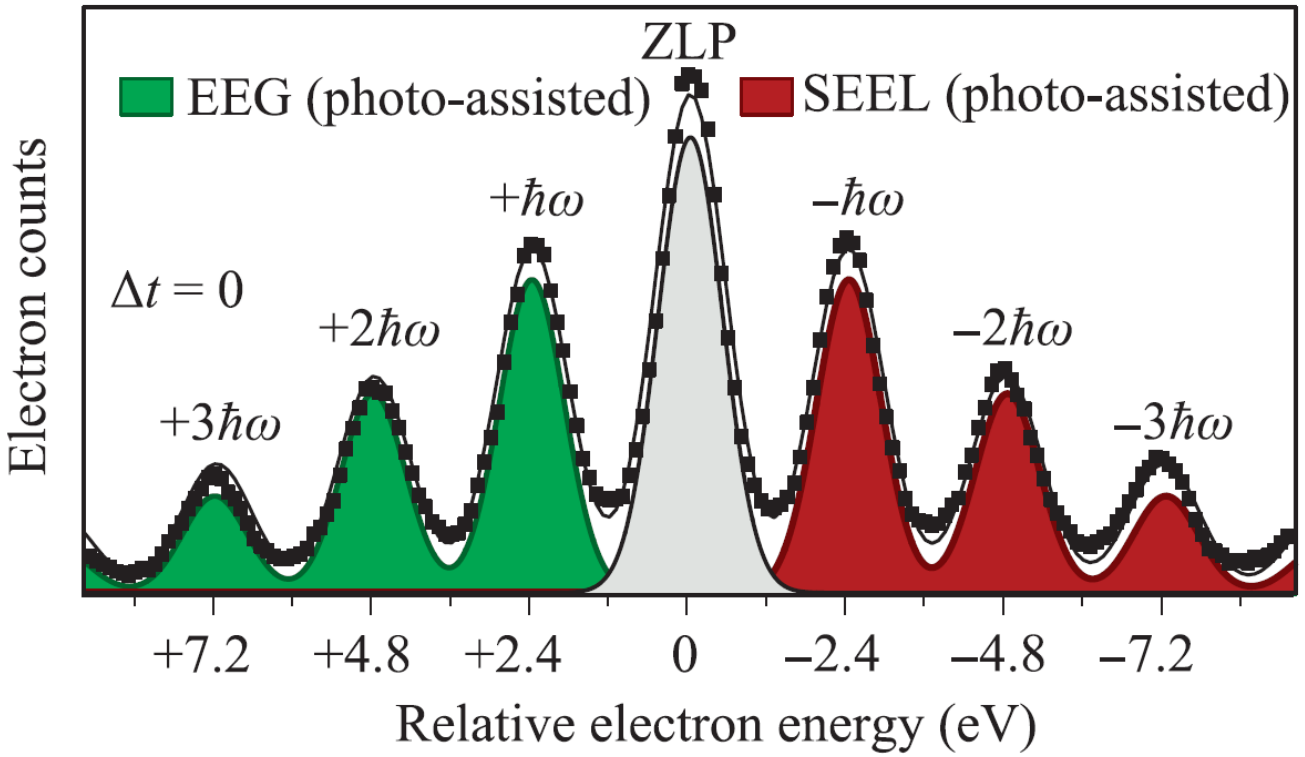


Photon-Induced Near-Field Electron Micros., a tool for plasmonics

Basic principle – PINEM near field imaging

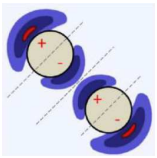
➢ Energy Electron Gain Spectrometry EEGS

In this three body interaction scheme, the electron packets **lose** and/or **gain energy** in discrete quanta of the incident photon energy $\hbar\omega$, because of the presence of a time oscillating electric field, the evanescent field associated with the resonant plasmon of the particle



Carbon nanotubes, electrons of 200 keV, fs lifetime
photons of 2.4 eV, fs lifetime
Full temporal overlap $\Delta t(\hbar\omega, e\text{-}) = 0$ s

B. Barwick, D. Flannigan, A. Zewail *Nature* **462** (2009) 902
A. Yurtsever, A. Zewail *Nanoletter* **12** (2012) 3334



Photon-Induced Near-Field Electron Micros., a tool for plasmonics

Basic principle – PINEM probability for a small sphere Γ_{EEGS}

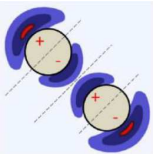
$$\Gamma_{EEGS}^{sphere}(\omega, R_\perp) \propto \left(\frac{\omega}{\gamma v^2}\right)^2 \mathrm{I}_0 \left|\alpha_{\iota=1}(\omega)\right|^2 \mathrm{K}_1^2\left(\frac{\omega \mathrm{R}_\perp}{\gamma \upsilon}\right) \delta\left(\omega - \omega_{\mathrm{ph.}}\right)$$

$$\Gamma_{EEGS}^{sphere}(\omega, R_\perp) \propto \left(\frac{\omega}{\gamma v^2}\right)^2 \mathrm{I}_0 \left|\alpha_{\iota=1}(\omega)\right|^2 \delta\left(\omega - \omega_{\mathrm{ph.}}\right) \exp\left(-\frac{R_\perp}{\gamma \upsilon/\omega}\right)$$

I_0 Intensity of the excitation laser; $\mathrm{R}_\perp$ = (x, y) Impact parameter of the electrons traveling along the z direction at speed υ; $\hbar\omega$ Loss energy; $\hbar\omega_{ph}$ photon energy; γ Lorentz factor $\gamma = 1/\sqrt{1 - \upsilon^2/c^2}$ (relativistic electrons); K_m Modified Bessel function of the second kind; α_l Sphere polarizability for mode l = 1

- PINEM probability of a small sphere is proportional to its scattering cross section as measured in far field optics, $\sigma_{sca.} \propto |\alpha_{\iota=1}(\omega)|^2 \propto a^6$
- PINEM probability is position-dependent with a quasi-exponential decay with e-beam to sphere distance $\mathrm{R}_\perp$, attenuation length $\gamma\upsilon/\omega \sim 10$ - 100 nm ⇔ spatial resolution
- PINEM proceeds by discrete quantum energy exchange $\delta(\omega - \omega_{\mathrm{ph.}})$ ⇔ well-defined energy

A. Asenjo-Garcia, F. García de Abajo *New J. Phys.* **15** (2013) 103021



Photon-Induced Near-Field Electron Micros., a tool for plasmonics

Basic principle – PINEM vs EMLDOS

➢ By energy-filtering only those electrons resulting from **one specific photon absorption**, it is possible to :

- image directly in space the electric nearfield distribution
- obtain the temporal behavior of the field on the femtosecond timescale
- map its spatial polarization dependence – **Polarisation control (bright modes)**

➢ Similar to CL and EELS, within a Fourier transform PINEM detects the near electric field component along the direction of the electron beam

$$\mathrm{I_{PINEM}(x,y,\Delta t)} = \left| \int_{+\infty}^{-\infty} E_z^{photon}(x,y,z,\Delta t) e^{-i\left(\frac{\omega}{\upsilon}\right)z} dz \right|^2$$

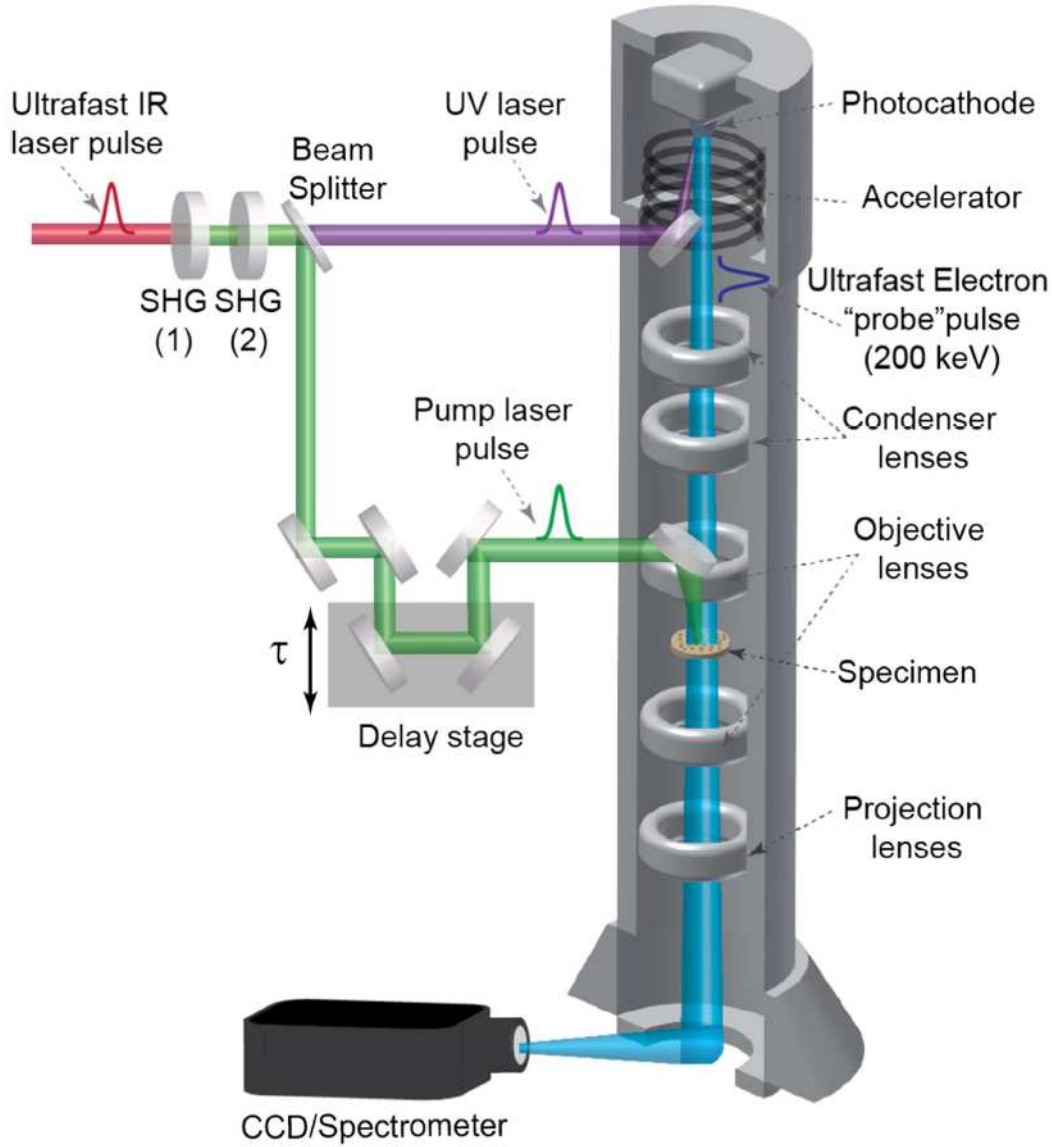
Fourier transform of the E_z^{photon} photon induced electric nearfield, along the e-beam direction at point $\vec{R}_\perp = (x,y)$ in real space, momentum value $q_z = \omega / \upsilon$ in reciprocal space and time delay Δt between electron and photon pulses (power spectrum)

Sang Tae Park *et al New J. Phys.* **12** (2010) 123028
A. Yurtsever, A. Zewail *Nano Lett.* **12** (2012) 3334

Photon-Induced Near-Field Electron Micros., a tool for plasmonics

Instrumentation – Ultrafast Electron microscope UEM

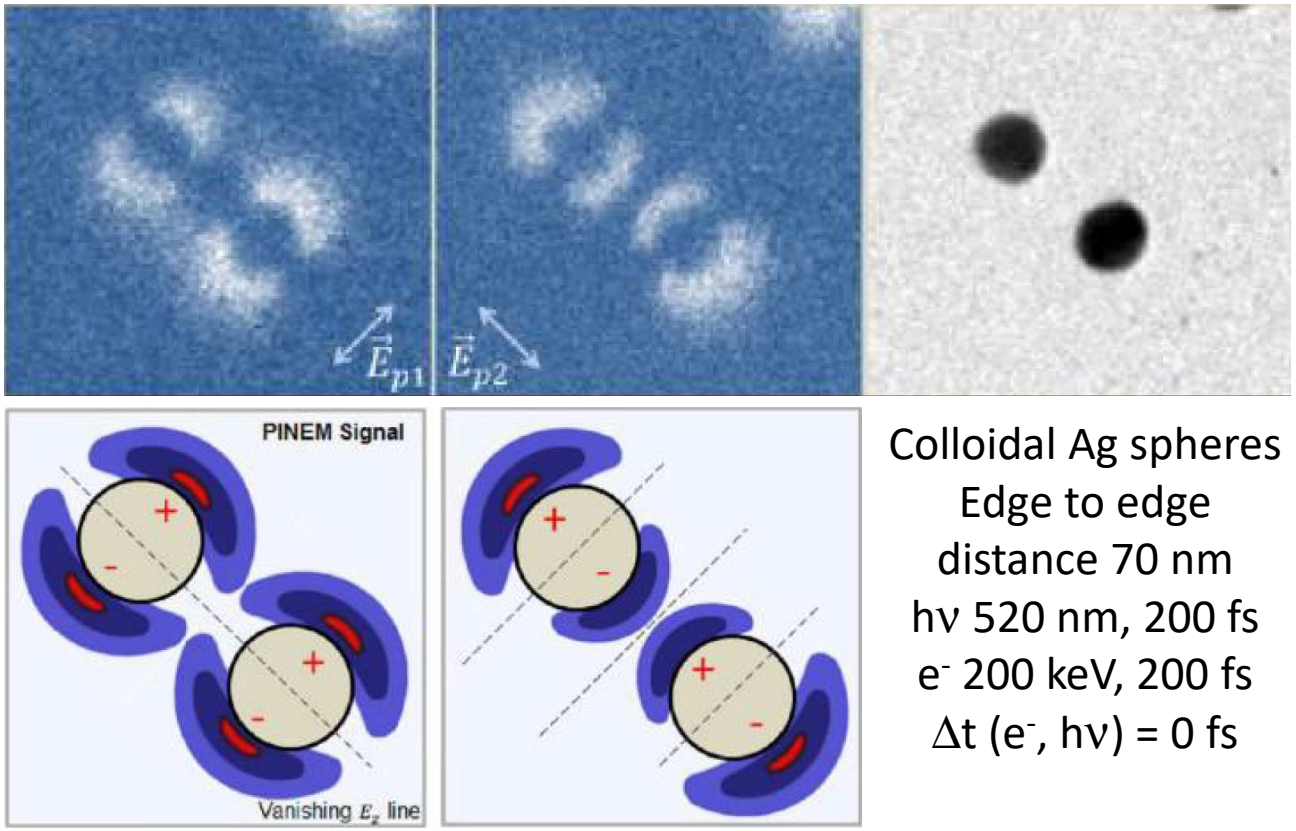
(photon in,
electron in,
electron out)
process



M. Hassan *J. Phys. B: At. Mol. Opt. Phys.* **51** (2018) 032005

PINEM near field imaging

Plasmonics of 0D objects - Au NanoSpheres



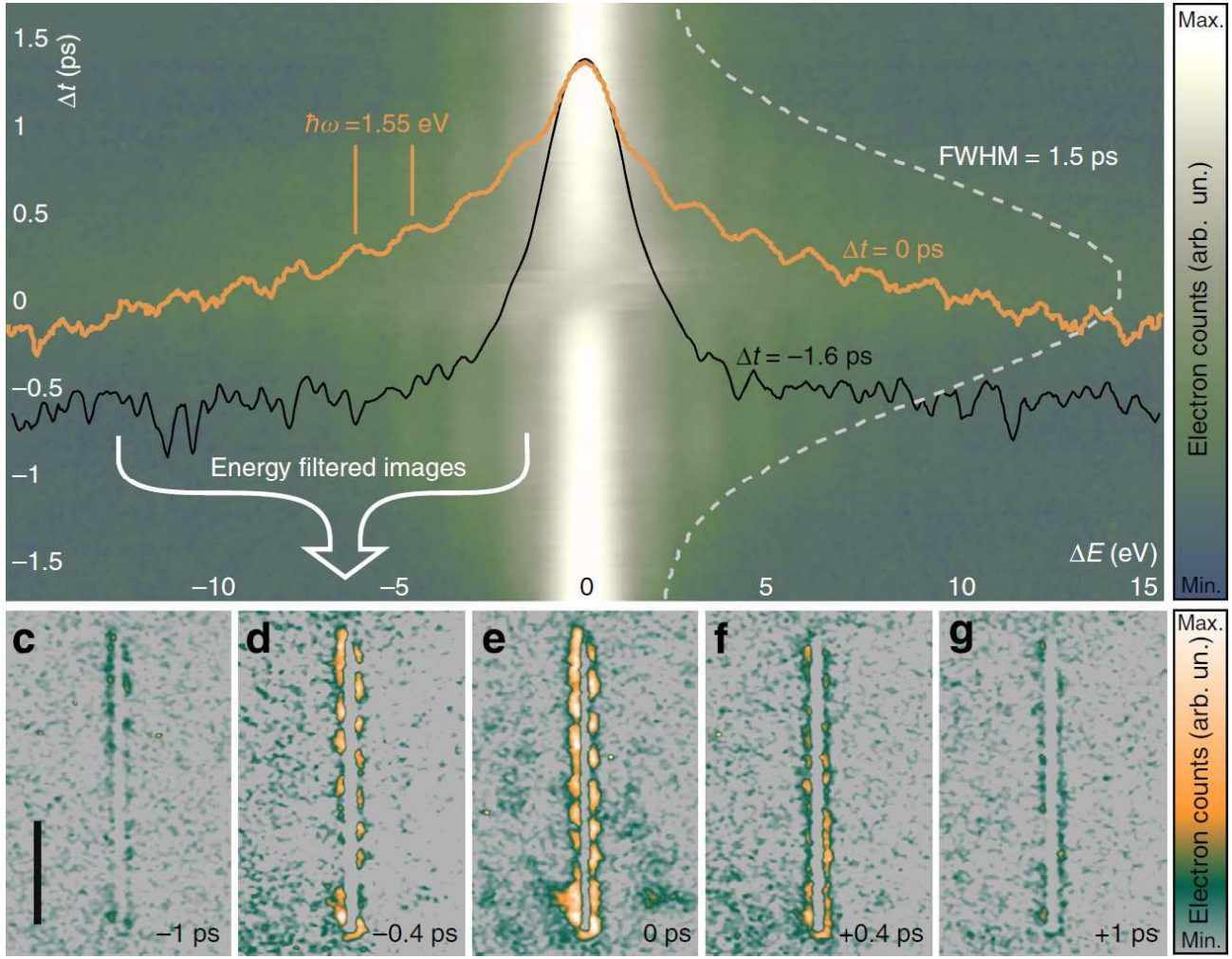
Colloidal Ag spheres
Edge to edge
distance 70 nm
hν 520 nm, 200 fs
e^- 200 keV, 200 fs
Δt (e^-, hν) = 0 fs

- Near electric field mapping along the direction of the electron beam E_z
- Spatial polarization dependence – **Optical Polarisation Control**

A. Yurtsever, A. Zewail *Nano Lett.* **12** (2012) 3334

PINEM near field imaging

Plasmonics of 1D objects – Ag Nanowires 5.7 µm x 0.134 µm

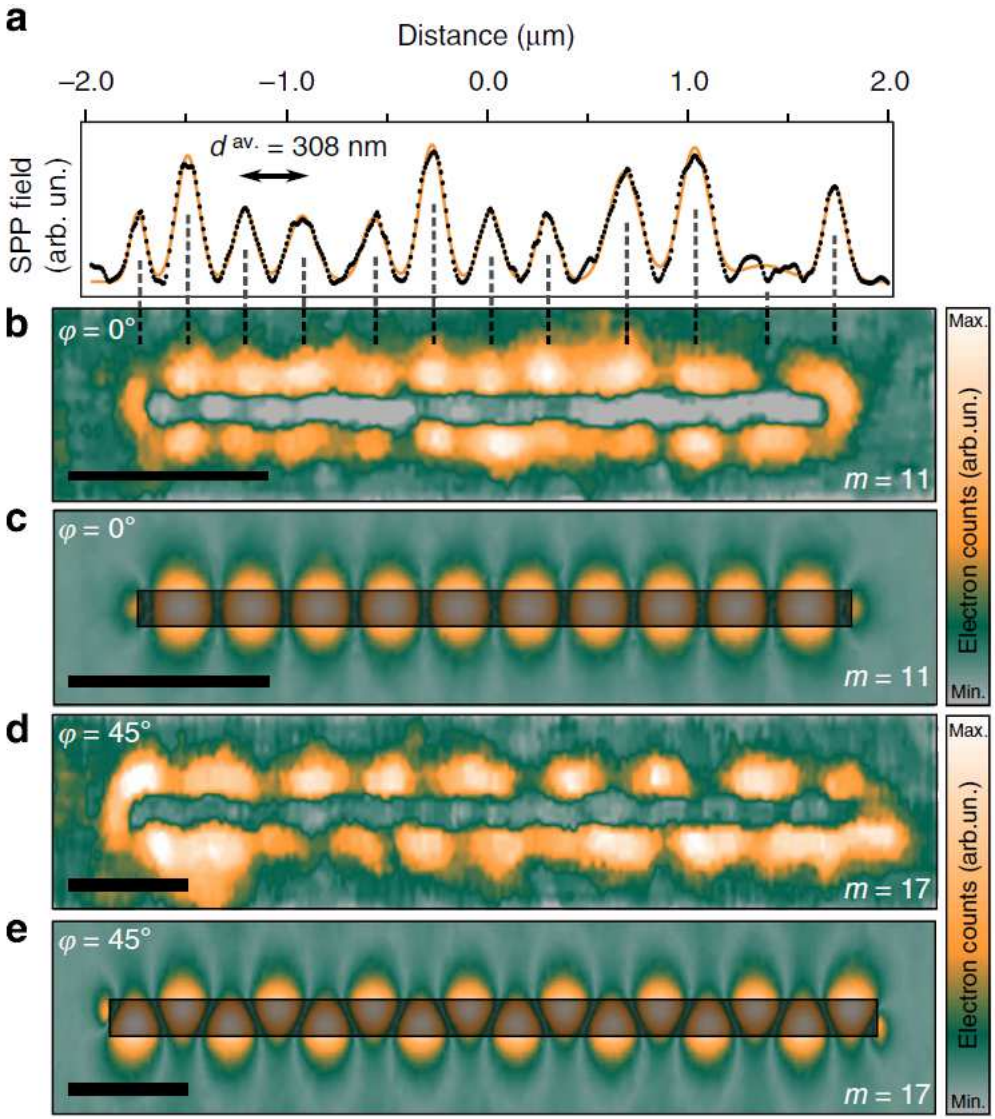


➢ Electron intensity map vs the time delay Δt between the optical pump and electron probe pulses. Wavelength 800 nm, polarization angle 45°. (c – g) Pictures of a single Ag nanowire at different Δt obtained using EEG electrons (white arrow). Scale bar 2 µm.

L. Piazza *et al. Nat. Comm.* 6:6407 (2015) 1

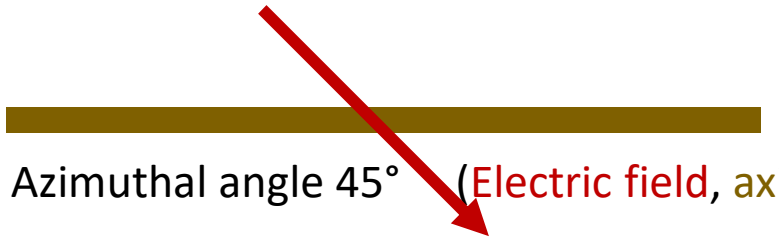
PINEM Near field imaging

Plasmonics of 1D objects - Nanowires, polarization dependence



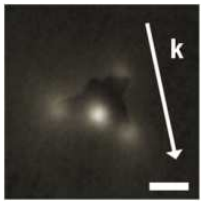
Ag Nanowire 3.4 μm in length, 90 nm in diameter. 800 nm excitation wavelength. EEG electrons at time delay $\Delta t = 0$ ps. Scale bar 1 μm.

Azimuthal angle 0° (Electric field, axis)

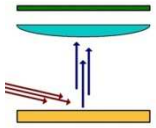


Azimuthal angle 45° (Electric field, axis)

L. Piazza *et al. Nat. Comm.* 6:6407 (2015) 1

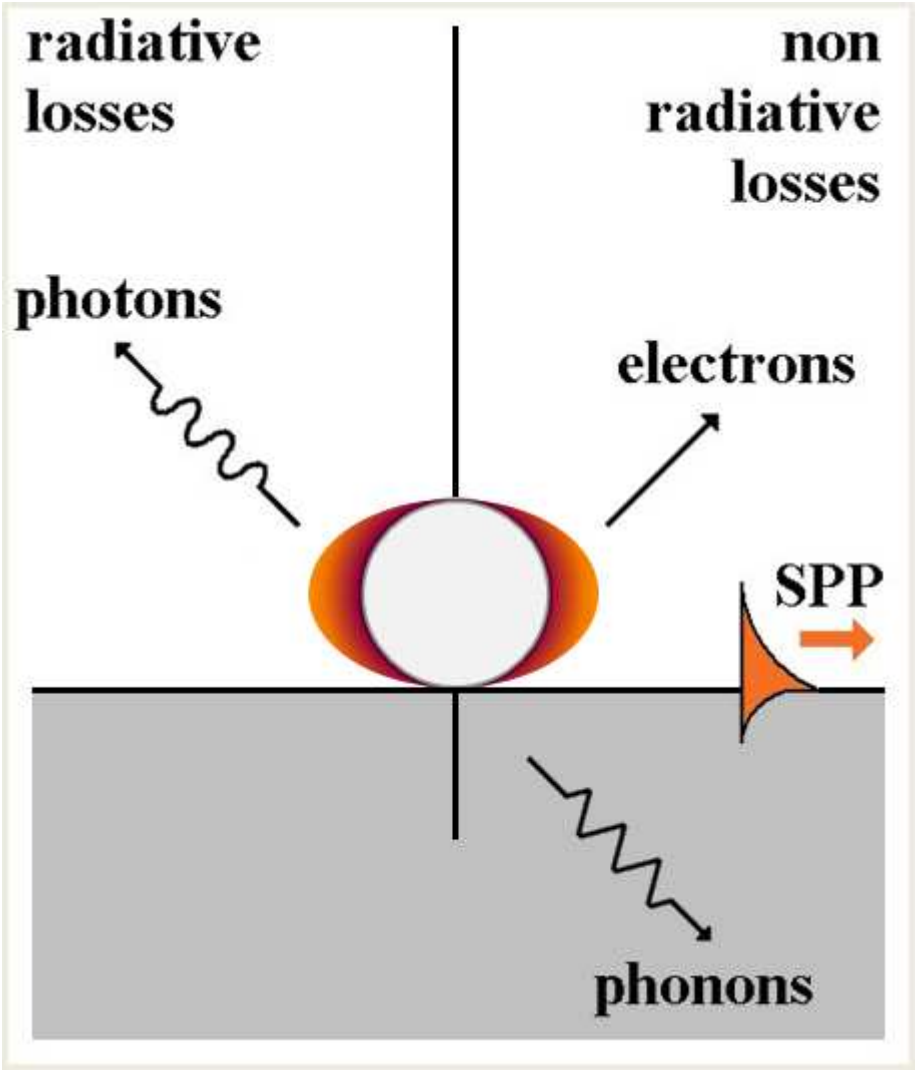


Photoemission electron microscopy PEEM
A tool for plasmonics



Photoemission electron microscopy, a tool for plasmonics

Basic principle – Plasmon decay channels



➢ **Plasmon decay channels**

.free-space radiative losses

scattering

luminescence

.non radiative losses

ohmic losses (phonons)

secondary SPP excitation

electron emission

…

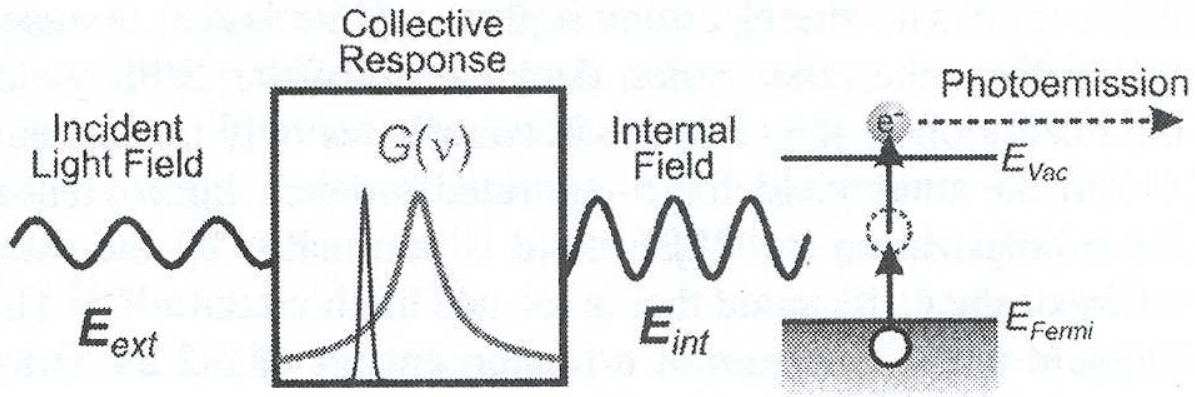
➢ **Mapping the near field at the nanoscale through electron emission - Photoelectric effect**

➢ **(photon in, electron out)**

L. Douillard, C. Charra, *J. Phys. D: Appl. Phys.* **44** (2011) 464002

Photoemission electron microscopy, a tool for plasmonics

Physical principle



(i) Plasmon excitation ⇔ Exalted photoelectric effect in plasmonic field

$$E_{\text{int.}}(\nu) = G(\nu).E_{ext.}(\nu),\ G_{Sphere} = \frac{3\varepsilon_m}{\varepsilon + 2\varepsilon_m}$$

$E_{int.}$ Internal electric field [V/m]
G Response function of the many electron system
$E_{ext.}$ Incident electric field [V/m]

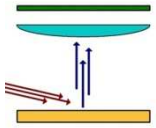
(ii) Non linear photoemission process

Plasmon res. $E_{plasmon} \approx 1{,}55$ eV (IR 800 nm)
Metal work function $\Phi_{metal} \approx 4{,}5$ eV

$$n.h\nu > \Phi_{Metal}$$

n order of non linearity,
hν photon energy [eV],
Φ_{metal} metal work function [eV]

M. Merschdorf *et al. Phys. Rev. B* **70** (2004) 193401



Photoemission electron microscopy, a tool for plasmonics

Basic principle

➢ The non linear photoemission process is proportional to the $2n^{th}$ power of the surface electric field $E_{int.}$ (electron reservoir, surface photoemission process)

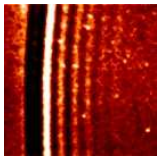
➢ Multiphotonic cascade absorption and/or coherent absorption from a hot electron gas

$$I_{e^-} \propto (\vec{p}.\vec{E}_{\text{int.}})^{2n} \propto (\vec{p}.G\vec{E}_{ext.})^{2n}$$

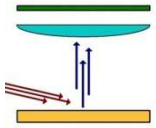
p electron momentum [kg.m/s]
$E_{int.}$ internal electric field [V/m]
n non linearity order
$E_{ext.}$ incident electric field [V/m]

➢ Bright field modes accessible (photon in)

For large objects $\geq \lambda_{h\nu}$, the internal electric field of the plasmon excitation $\vec{E}_{\text{int.}}^{SPP}(r,t)$ (group velocity v_{SPP} < c) interferes with a 2nd component linked to the incident field $\vec{E}_{\text{int.}}^{h\nu}(r,t)$ (group velocity c / refractive index).



➢ For large objects $\geq \lambda_{h\nu}$, observation of beating interference patterns between ($\vec{E}_{\text{int.}}^{SPP}(r,t)$, $\vec{E}_{\text{int.}}^{h\nu}(r,t)$)



Photoemission electron microscopy, a tool for plasmonics

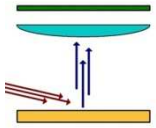
Basic principle – Photoelectron emission rate $R_{Emission}$

$$R_{Emission}^{Surface} \approx \frac{2}{\pi^2}\frac{e^2 E_F^2}{\hbar}\frac{1}{(\hbar\omega)^3}\int_{Surface}\left|E_{Surf.int.}^{\perp}\right|^{2n} dS$$

$R_{Emission}$ electron emission rate [electrons/s]
e electron charge [C]
$\hbar\omega$ energy of the incident photon [eV]
E_F Fermi level of the metallic particle [eV]
n non-linearity order, *i.e.* the number of photons absorbed to overcome the work function of the specimen []
$E_{Surf.int.}^{\perp}$ normal to the surface component of the near electric field, i.e. $EMLDOS_{\perp}$ electromagnetic density of states along the normal of the object surface [V/m]

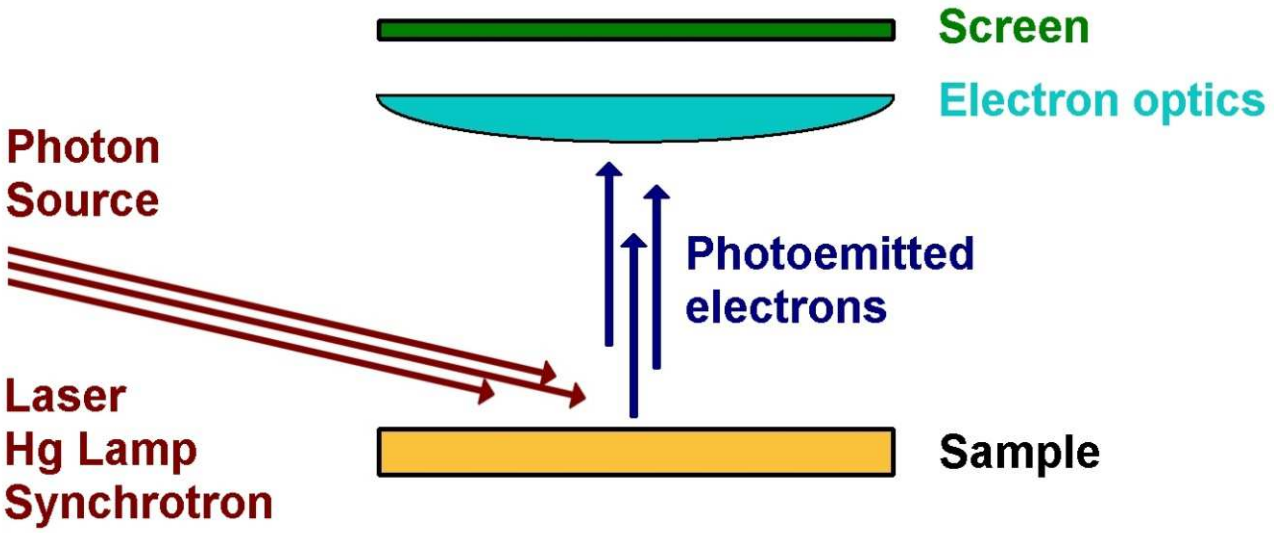
➢ PEEM signal scales with the electromagnetic density of states projected on the object surface normal.

G. Ferrini, *et al. Nucl. Inst. and Methods in Phys. Res. A* **601** (2009) 123–131



PEEM – photoemission electron microscopy (1933)

Instrumentation



➢ **Basic principle. Mapping of the photoemitted electron distribution in two dimensions** (photon in, electron out)

.standard electron optics (electrostatic, magnetic lenses)

.full field microscopy, no scanning probe

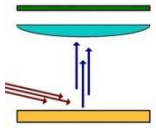
.non intrusive technique, no physical tip in the vicinity of the measuring volume (≠ SNOM)

.image contrast: work function Φ (small photon hν), photoemission lines (large photon hν)

.surface sensitivity ~ electron inelastic mean free path $\lambda_{electron}$

.lateral resolution (16 / 84 criteria) ≈ **20 nm, resp. ≤ 5 nm on AC instrument**

E. Brüche, *Z. Phys.* **86** (1933) 448; J. Pohl, *Zeitschr. f. techn. Physik* **12** (1934) 579; E. Bauer *Rep. Prog. Phys.* **57** (1994) 895



PEEM – photoemission electron microscopy (1933)

Oxidation of carbon monoxide on Pt(110)

- Oxidation reaction (445 x 445 µm²)

$$CO + * \leftrightarrows CO_{ad}$$
$$O_2 + 2* \rightarrow 2O_{ad}$$
$$CO_{ad} + O_{ad} \rightarrow CO_2 + 2*$$

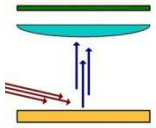
* = Free Pt(110) site

Carbon monoxide "Bright" Φ = 5.8 eV
Oxygen "Dark" Φ = 6.5 eV

Freedom degrees $P_{CO} = 4.3\ 10^{-5}$ mb, $P_{O2} = 4.10^{-4}$ mb, T = 448 K

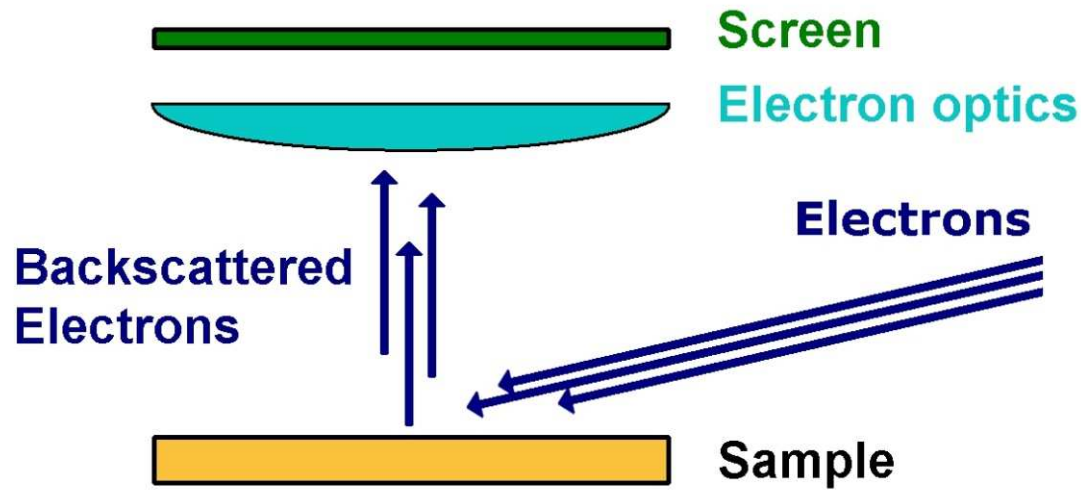
- **Spatio-temporel pattern of the surface reaction (spiral diffusion fronts)**

S. Nettesheim, A. von Oertzen, H. H. Rotermund, G. Ertl **(2007 chemistry Nobel Prize)** *J. Chem. Phys.* **98** (1993) 9977



LEEM – low energy electron microscopy

Instrumentation

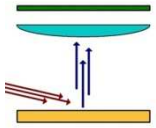


➢ **Basic principle. Mapping of the 2D backscattered electron distribution**
(electron in, electron out) - Topographic imaging LEEM = TF(LEED + phase)

.standard electron optics (electrostatic & magnetic lenses)
.full field microscopy, no scanning probe
.non intrusive technique, no physical tip in the vicinity of the measuring volume

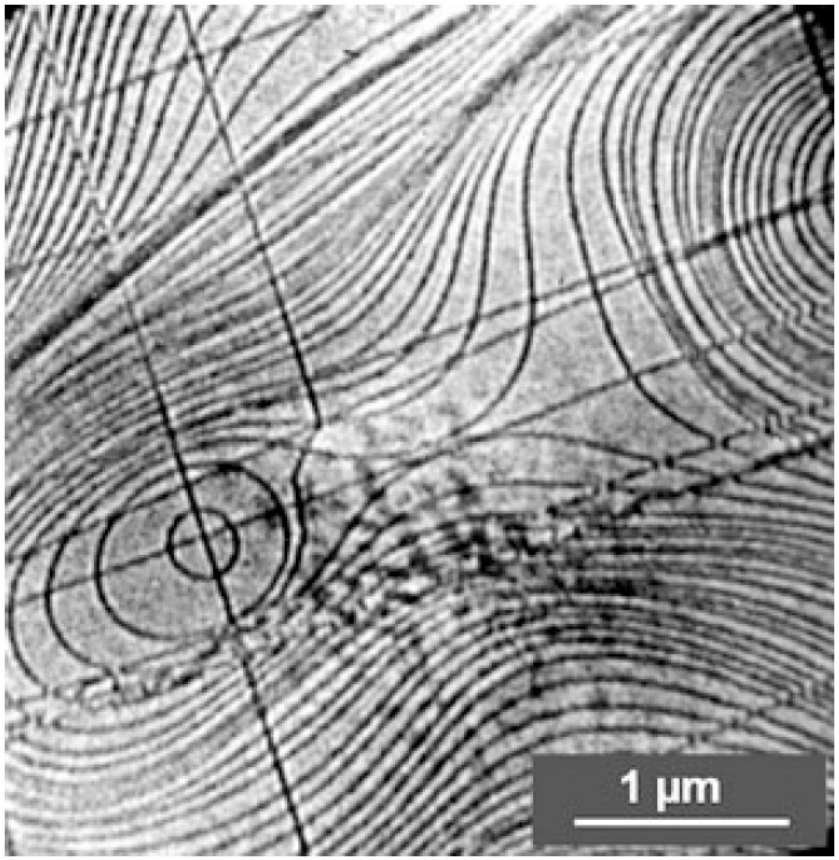
.contrast = diffraction, interferences between optical electron paths…
.vertical resolution = atomic step
.lateral resolution (16/84 criteria) ≈ **10 nm, resp. ≤ 2 nm on AC instrument**

W. Telieps, E. Bauer *Appl. Phys.* A **44** (1987) 55



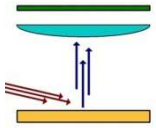
LEEM – low energy electron microscopy (1962)

Mo(100) Surface



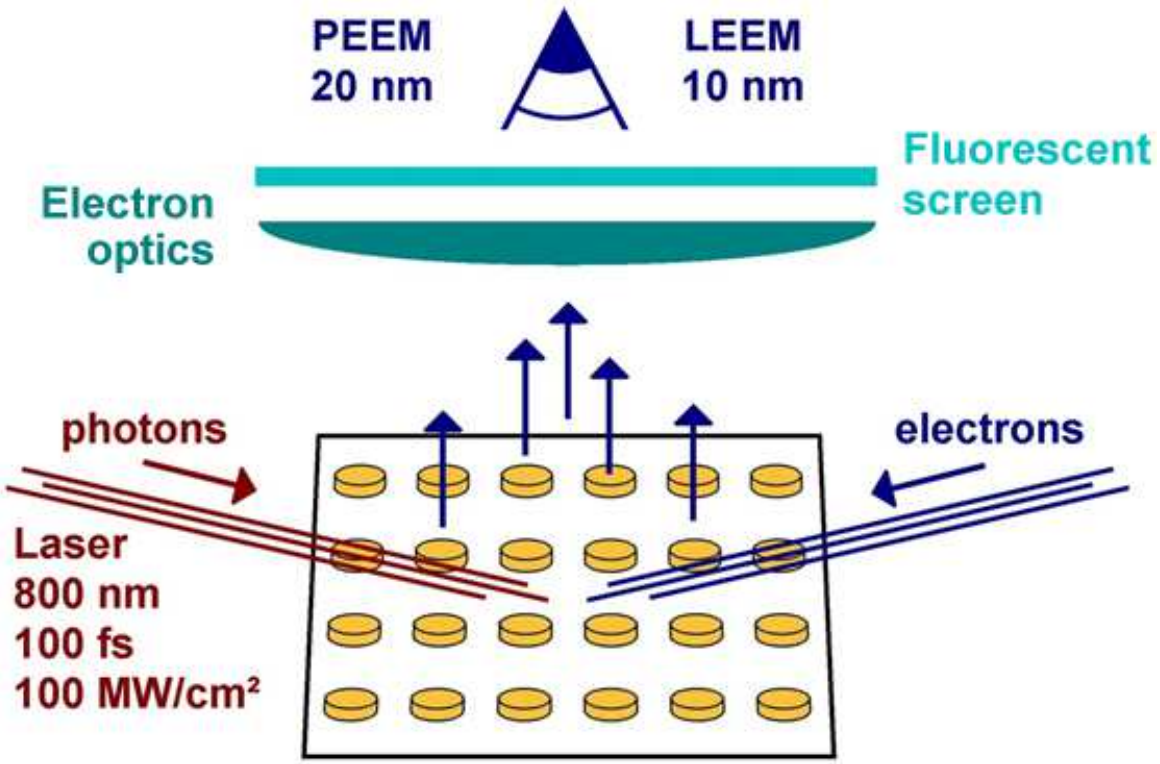
- Mo(110) Surface
  LEEM
  Electron kinetic energy 14 eV
  Monoatomic step contrast

W. Telieps, E. Bauer Ultramicroscopy **17** (1985) 57–66

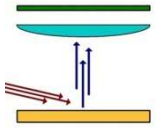


Mapping the evanescent field at the nanometre

LEEM/PEEM instrument (CEA IRAMIS Saclay)

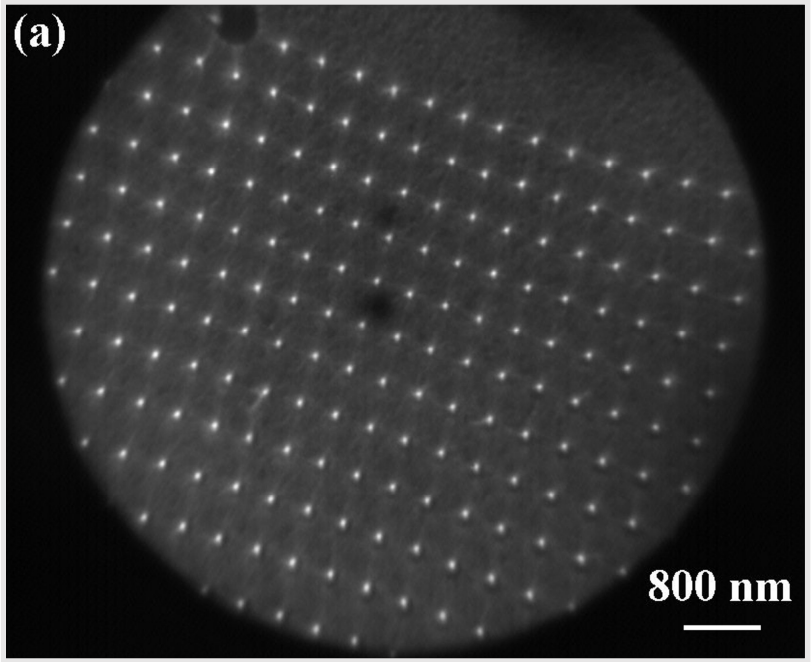


- Conductive sample (no charging effect) of low roughness
- LASER source Ti:Al_2O_3, 150 fs, wavelength [680 nm, 1100 nm] (IR) + OPO wavelength [525 nm, 650 nm], incidence angles {-90°, -45°, +3°, +15°, +90°} / sample surface plane
- LEEM / PEEM III equipped with an electron energy analyser www.elmitec-gmbh.com
  PEEM field of view 1.5 - 120 µm, 16/84 lateral resolution **20 nm** (≤ 5 nm AC)
  LEEM field of view 1.5 - 80 µm, 16/84 lateral resolution **10 nm** (≤ 2 nm AC)



Mapping the evanescent field at the nanometre - PEEM

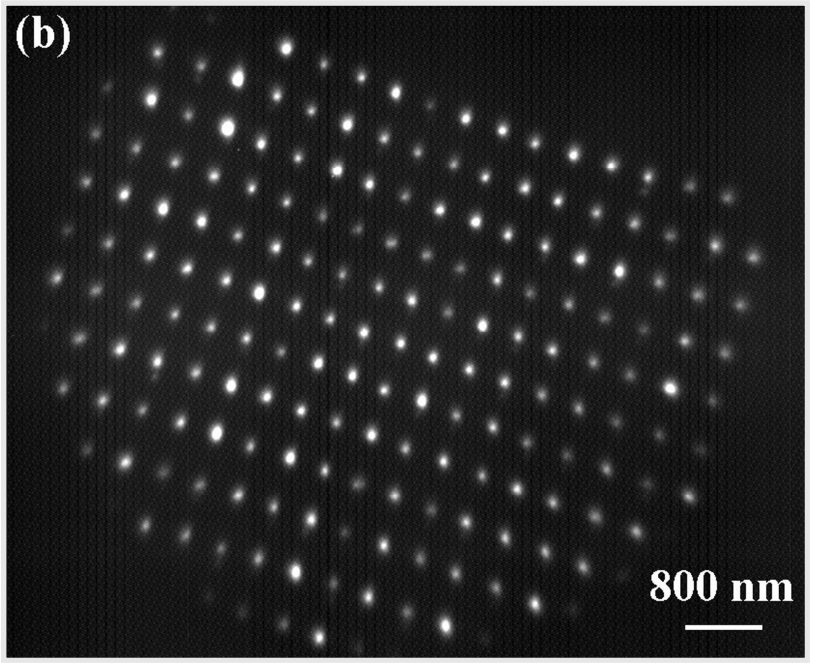
Nanoparticle assemblies - LSP



Au disks / ITO - ∅120 nm, lattice spacing 400 nm
Source UT Troyes

➢ **LEEM picture (topographic imaging mode)**

Excitation = electrons (LASER off)
Signal = backscattered electrons

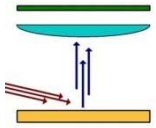


Au disks / ITO - Grazing incidence p pol. 150 MW/cm²

➢ **PEEM picture under LASER illumination**

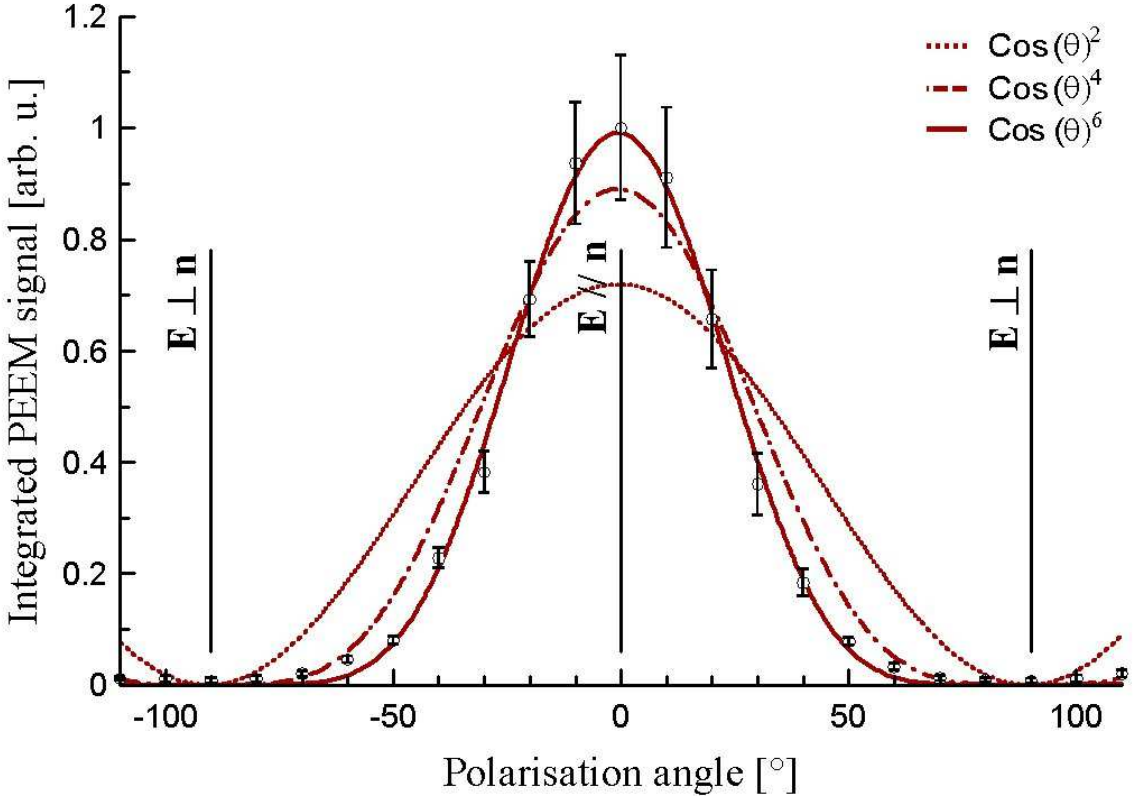
Excitation = 766 nm photons
$h\nu$ (1.62 eV) < Φ_{Au} (4.6 - 5.1 eV)
Signal = photoelectrons ! (3 $h\nu$ / e^-)
High signal to noise ratio

L. Douillard *et al. J. of Appl. Phys.* **101** (2007) 083518



Non linear photoemission – PEEM

Nano-particle assemblies – Off plane polarisation dependence



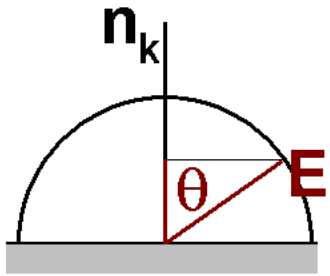
Au disks / ITO ∅120 nm

grazing incidence 17°

photon 880 nm (1.41 eV)

power dens. 140 MW/cm²

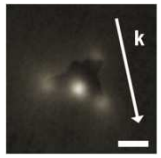
Keldysh factor 36 >> 1



➢ Dependence of the photoemission yield with the polarisation angle θ at grazing incidence ⇔ PEEM integrated signal scales as $\cos(\theta)^6$

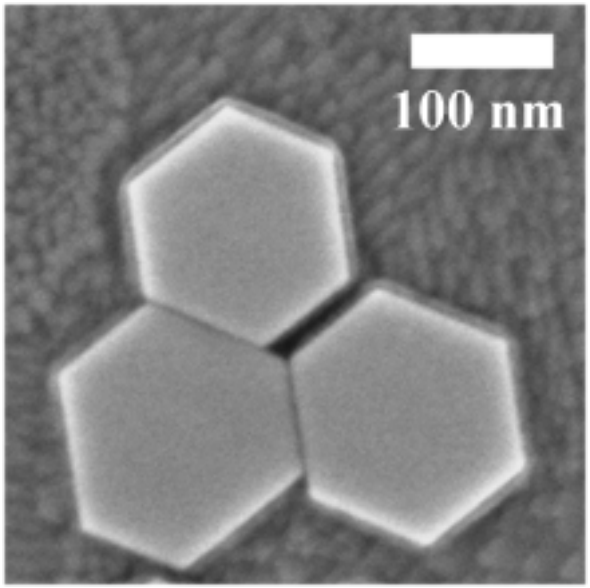
➢ **3 photon photoemission process** (3 x 1.41 eV = 4.23 eV, $\Phi_{Au} \approx 4.6 – 5.1$ eV). Probable field assisted 3-PPE emission mechanism.

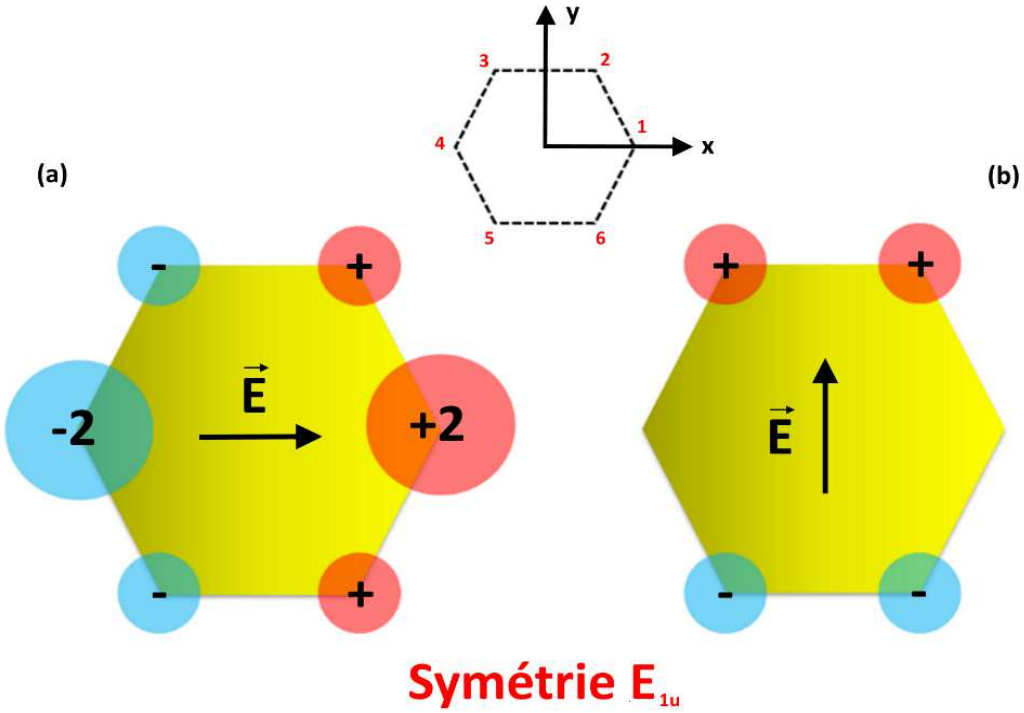
L. Douillard *et al. J. of Appl. Phys.* **101** (2007) 083518



Plasmonics of 2D objects - Nanohexagon D_{6h} - PEEM

Near field mapping - Linear polarisation





Au Hexagon - SEM

L = 150 - 200 nm

Thickness ≈ 15 nm

(Colloïdal synthesis, CEA S. Marguet)

➢ **Group Theory**

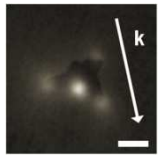
Hexagon = Object of D_{6h} symmetry

Eigenstates of the dipolar plasmon resonance for a linear polarisation excitation

S. Mitiche PhD (2018)

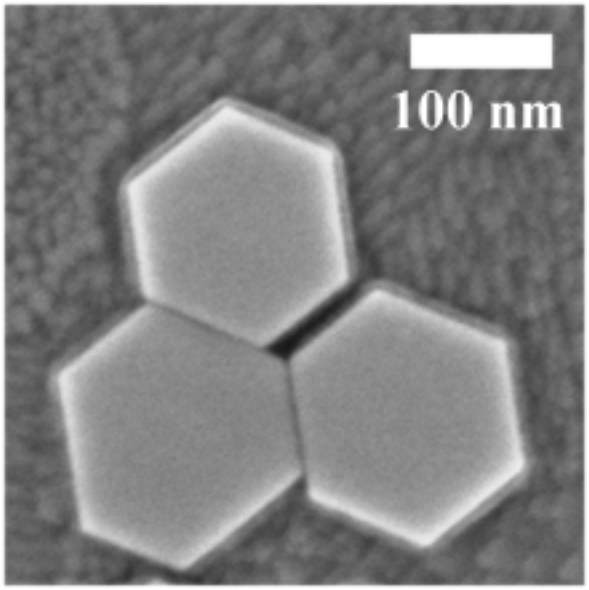
S. Mitiche, *et al. J. Phys. Chem. C* **121** (2017) 4517

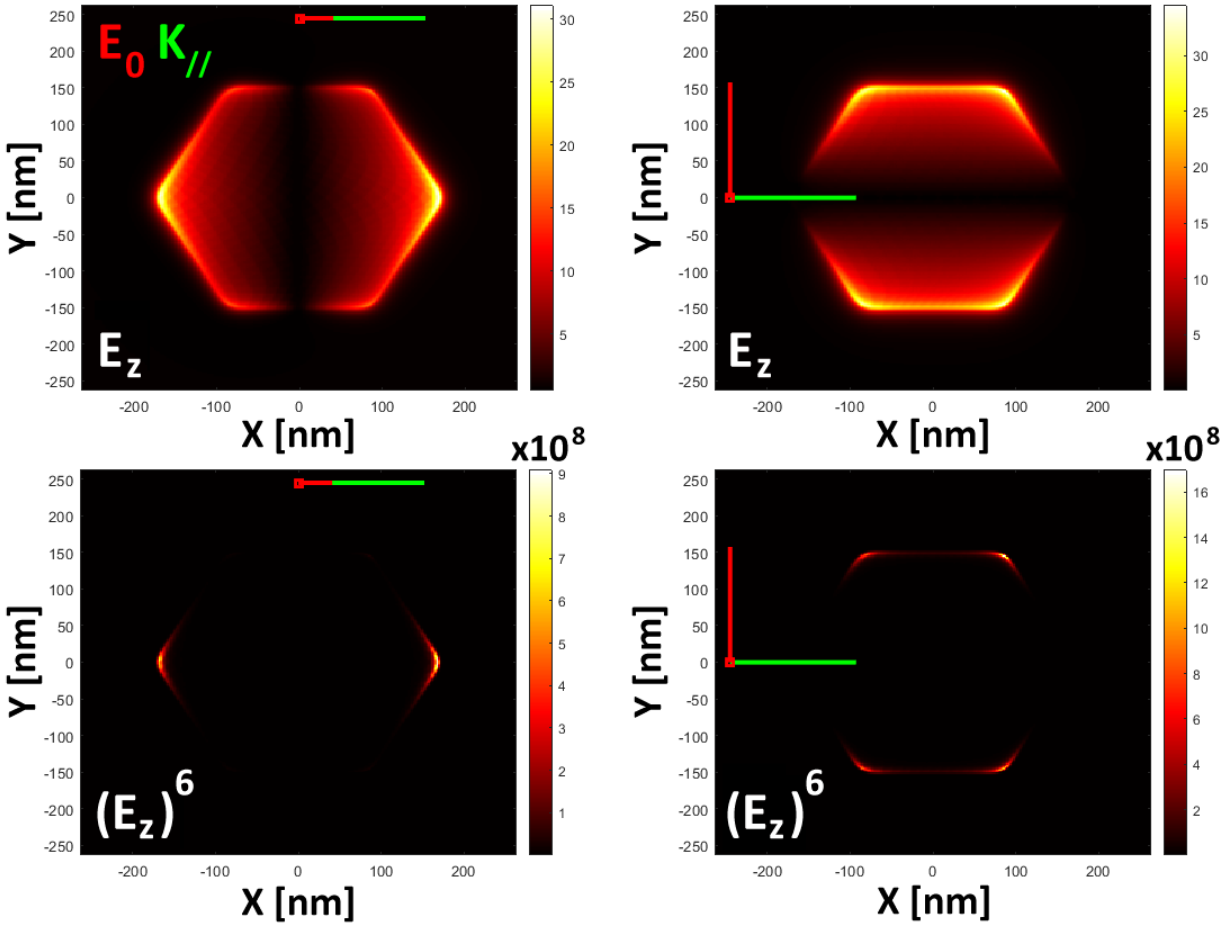
C. Awada, T. Popescu *et al. J. Phys. Chem. C* **116** (2012) 14591



Plasmonics of 2D objects - Nanohexagon D_{6h} - PEEM

Near field mapping - Linear polarisation





Au Hexagon - SEM

L = 150 - 200 nm

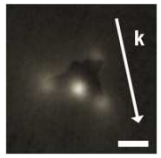
Thickness ≈ 15 nm

(Colloïdal synthesis, CEA S. Marguet)

➢ ***Boundary Element Method*** **(BEM) Simulation**

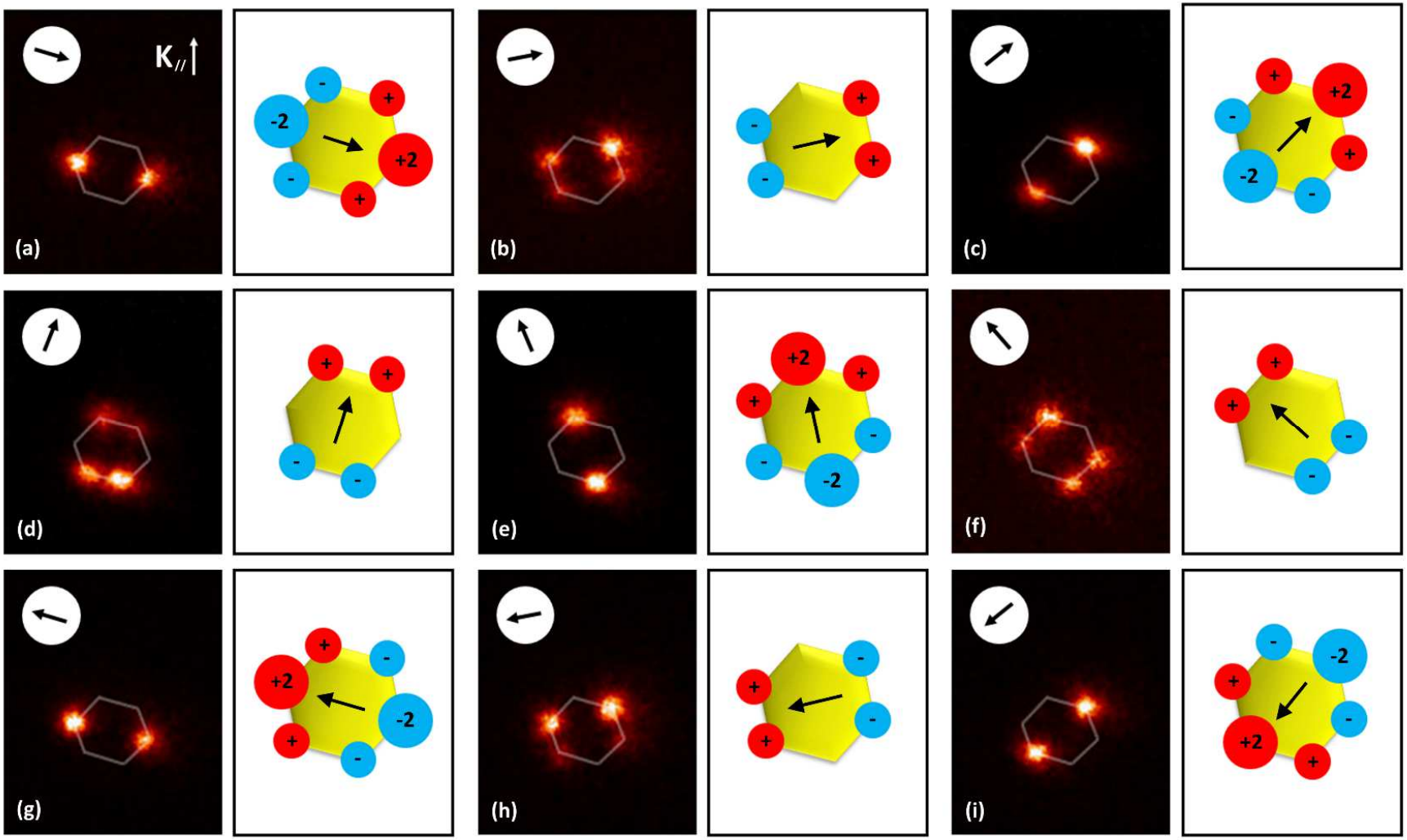
Au Hexagon

Electric field maps, z components $|E_z|$ & $|E_z|^{6 = 2x3}$



Plasmonics of 2D objects - Nanohexagon D_{6h} - PEEM

Near field mapping - Linear polarisation

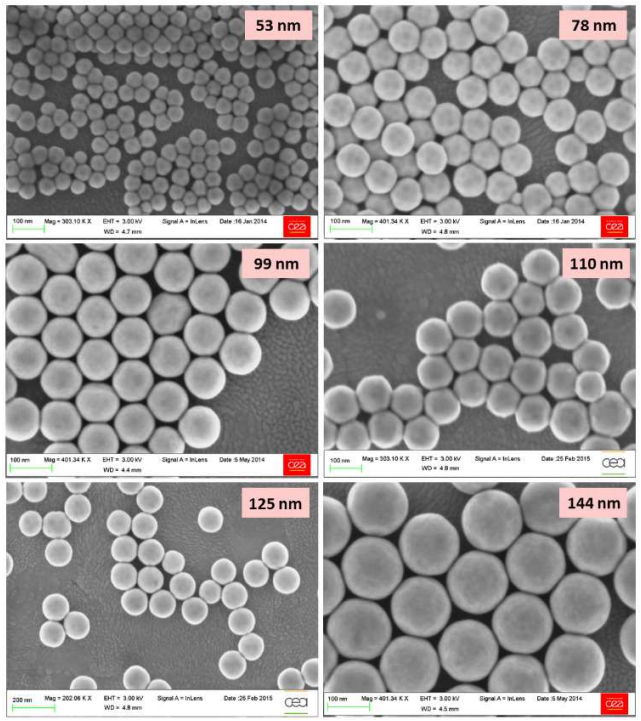


- 150 nm Au Hexagon – Dipolar resonance (λ = 850 nm) under linear pol. exc.

PEEM Imaging & Group Theory Interpretation (S. Mitiche PhD 2018)

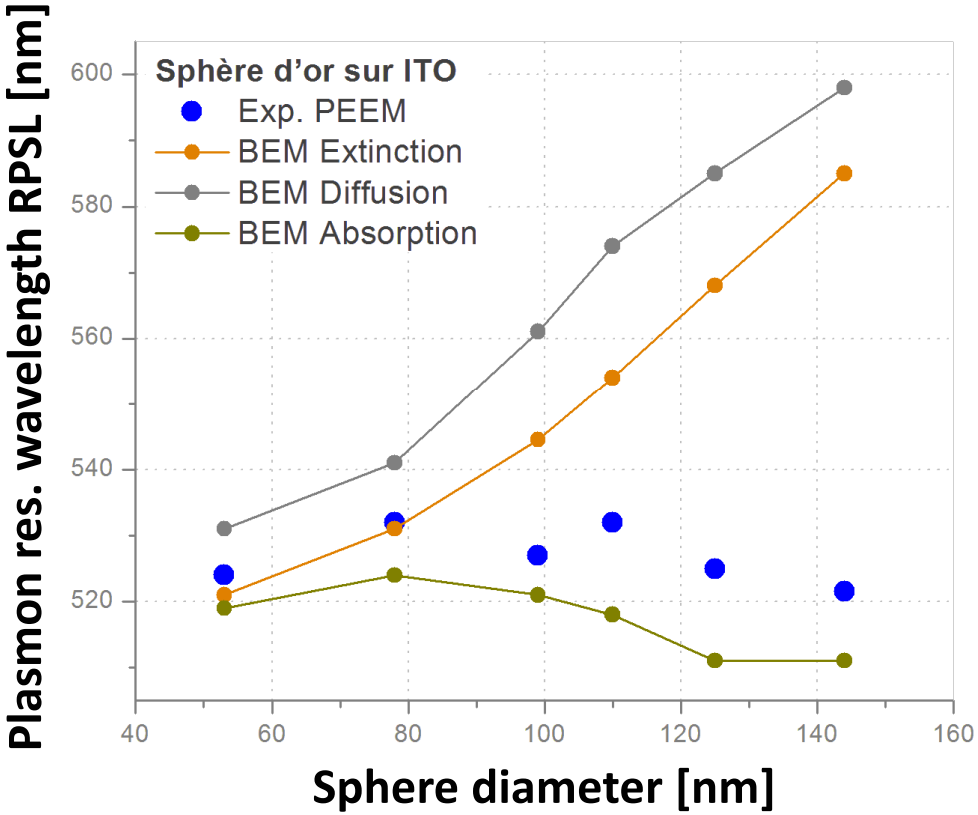
Non linear photoemission - PEEM – Absorption spectrum

Spheres - Absorption resonance = f(diameter 2R)



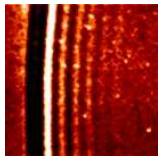
Au colloïdal spheres

(S. Marguet CEA, NIMBE)



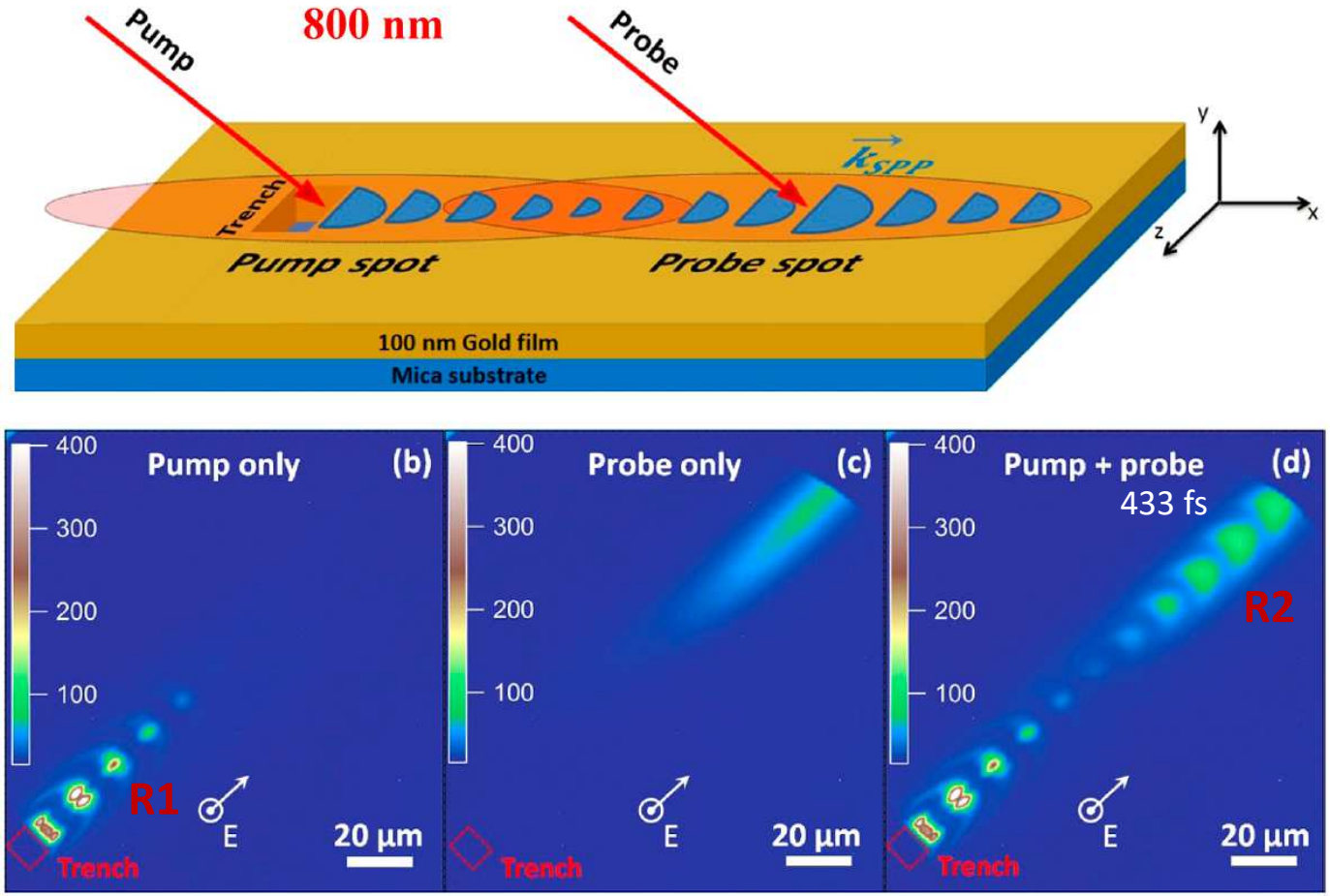
- Plasmon resonance maxima vs sphere diameter 2R
- Absorption spectrum on individual object, $I_{photoemission}$ = f(incident wavelength)
- Spectral resolution ≈ 1 nm (130 fs, 2.5 meV)

PhD S. Mitiche 2018



Propagation of plasmons-polaritons (nm, fs) – PEEM

2D Symmetry – Pump-probe experiment - Au / vide interface



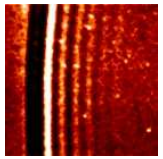
- **Plasmon polariton propagation from a trench in a Au film ($\vec{k}$ conservation)**

  Pump-probe experiment. Time resolution = 0,2 fs, spatial resolution = 20 nm

  Field propagation length δ(Au, 800 nm) = 88 µm (92 µm JC72, 89 µm Ordal87)

  Group velocity SPP = 0,95c

Y. Gong, A. Joly, D. Hu, P. El-Khoury, W. Hess *NanoLett.* ***15*** *(2015)* 3472



Propagation of plasmons-polaritons (nm, fs) – PEEM

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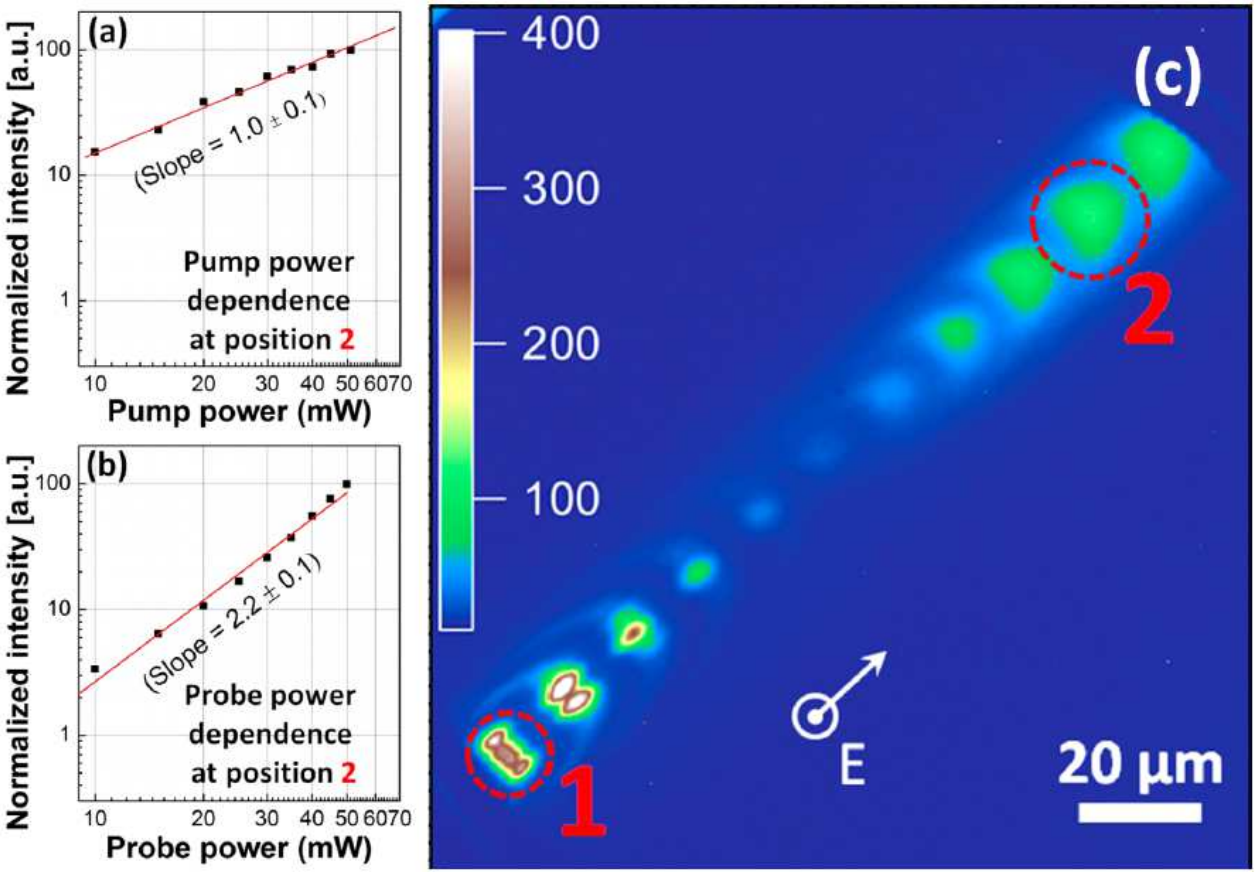
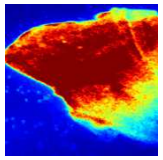


- **PEEM Region 1.** SPP signal close to the geometric launcher $I_{PEEM} \propto (E_{pump})^6$
- **PEEM Region 2.** SPP signal far away from the launcher $I_{PEEM} \propto (E_{pump})^2.(E_{probe})^4$

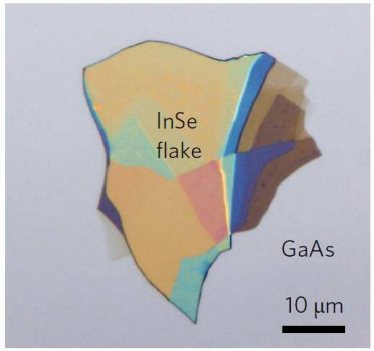
Sequential coherent photoemission process. Attenuation δ(Au, 800 nm) = 88 µm

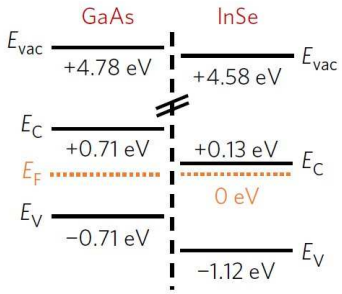
Y. Gong, A. Joly, D. Hu, P. El-Khoury, W. Hess *NanoLett.* ***15*** *(2015)* 3472

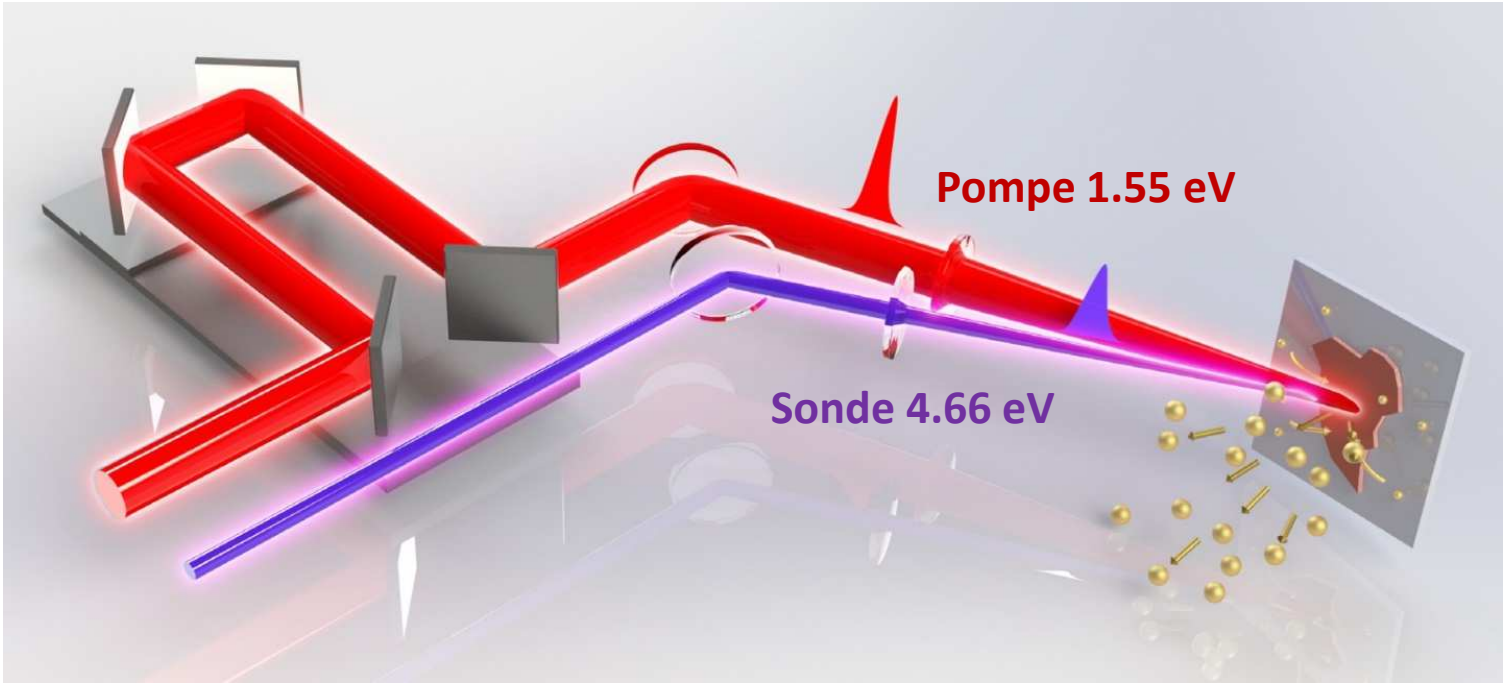


Electron dynamics in a solid - PEEM

Time-resolved PEEM variant – (space, time, energy) = (nm, fs, eV)





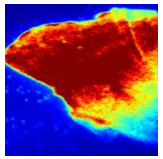


- Investigation of the electron dynamics (space, time, energy) in an elementary (p, n) junction (InSe, AsGa) = InSe flake on a AsGa substrate

Two colors Pump Probe experiment: **pump laser NIR 800 nm 1.55 eV**
probe laser UV 266 nm 4.66 eV

LEEM - PEEM III Microscope

M. Man *et al. Nature Nanotech* **12** (2017) 36



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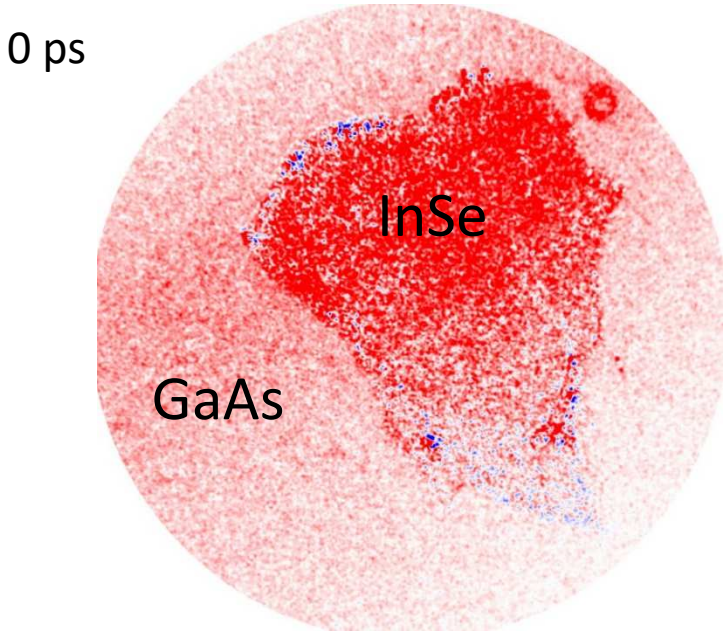
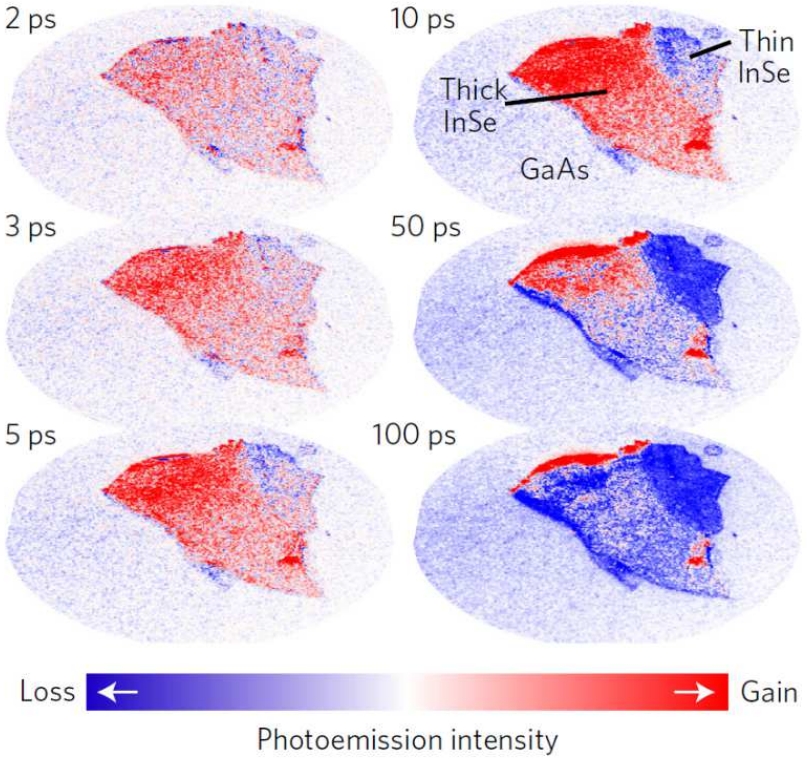




➢ **PEEM Image in energy-integrated mode @ Δt = 0 ps**

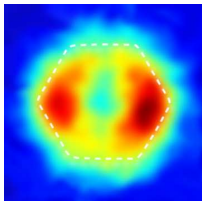
Non-equilibrium distribution of charges with high-energy electrons localized in GaAs and in available states in InSe due to a lower conduction band minimum

Electron temperature ≈ 1700 K

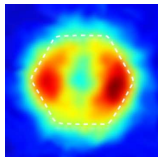
➢ **Electron transport over time in 2 steps**

(i) e^- accumulate in all parts of InSe at early time delays due to electron transfer from high-energy GaAs states

(ii) the initial rapid accumulation of charge in various parts of InSe slows down (electric field), followed by eventual recombinations

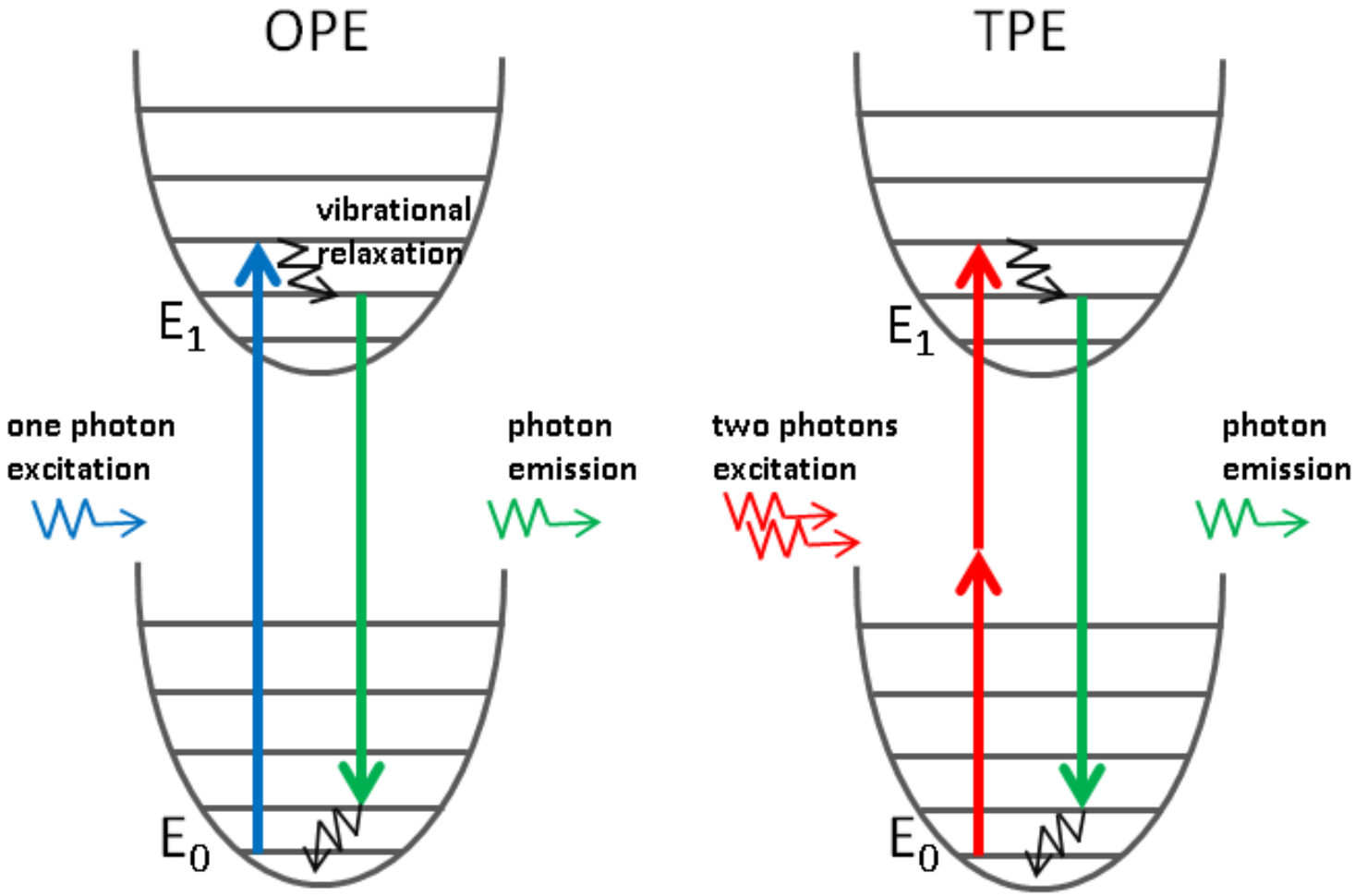


Two photon luminescence TPL
A tool for plasmonics

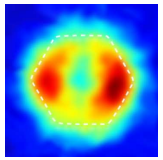


Two photon luminescence TPL, a tool for plasmonics

Two photon excitation principle (2 x photon in, 1 x photon out)



S. Carozza PhD 2017 Leiden Univ.



Two photon luminescence TPL, a tool for plasmonics

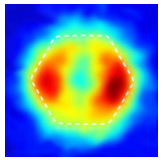
Two photon excitation signal intensity

$$I_{TPL}(\omega, \vec{R}_0) \propto \int_V |E_0(R_0, r, \omega)|^4 EMLDOS_{\parallel}^2(r, \omega) dr$$

$\hbar\omega$ energy of the incident photon
I_{TPL} two photon luminescence signal intensity
r(x, y, z) arbitrary position within the metallic particle volume V
R_0 (x_0, y_0, z_0) light beam waist center, i.e. focal point position
E_0 incident electric field
$EMLDOS_{//}(r, \omega)$ in-plane electromagnetic density of states

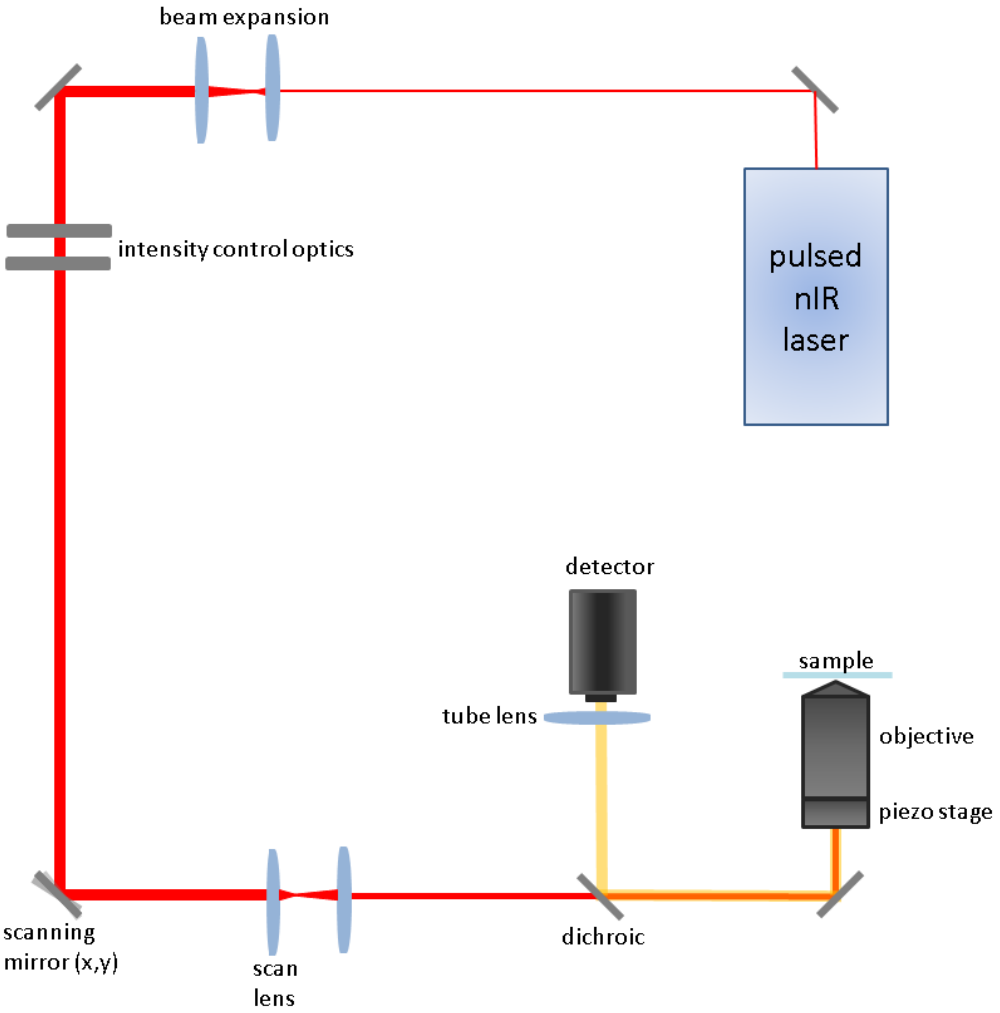
➢ TPL is proportional to the (i) squared projection of the in-plane electromagnetic density of states along the polarization direction for a linear polarization, and (ii) the squared of the in-plane electromagnetic density of states for a circular polarization

A. Teulle *et al. J. Opt. Soc. Am. B* **29** (2012) 2431
S. Viarbitskaya *et al. Nature Mat.* **12** (2013) 426

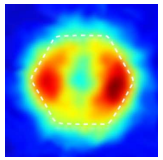


Two photon luminescence TPL, a tool for plasmonics

Instrumentation

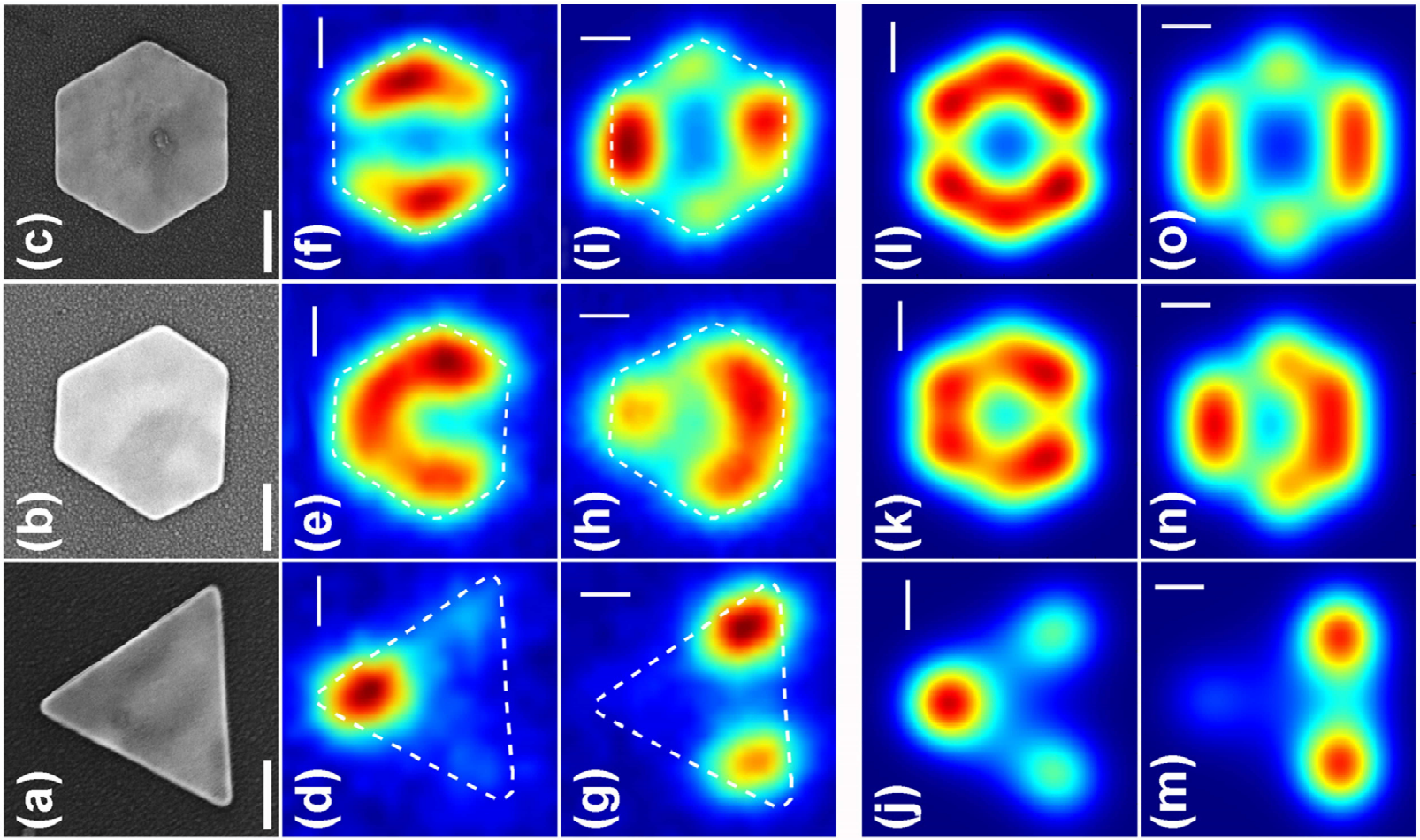


S. Carozza PhD 2017 Leiden Univ.



Two photon luminescence TPL, a tool for plasmonics

TPL near field imaging - Au nanoplatelets



(a, b, c) SEM images of triangular, truncated triangular, and hexagonal Au nanoplatelets
(d) - (i) TPL maps acquired with λ = 700 nm and linear polarization of 0° (d, e, f) and 90° (g, h, i), white bars in the upper right corners. (j, k, l, m, n, o) Simulated maps. Scale bars 200 nm.

S. Viarbitskaya *Appl. Phys. Lett.* **103** (2013) 131112

➢ Reference Reviews

A. Losquin, T. A. Lummen **Electron microscopy methods for space-, energy-, and time-resolved plasmonics** *Front. Phys.* **12** (2017) 127301, DOI 10.1007/s11467-016-0605-2

A. Merlen, F. Lagugné-Labarthet **Imaging the Optical Near Field in Plasmonic Nanostructures** *Applied Spectroscopy* **68** (2014) 1307-1326, DOI 10.1366/14-07699

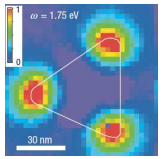
M. Kociak, O. Stéphan **Mapping plasmons at the nanometer scale in an electron microscope** *Chem. Soc. Rev.* **43** (2014) 3865, DOI 10.1039/C3CS60478K

T. Coenen *et al.* **Cathodoluminescence microscopy: Optical imaging and spectroscopy with deep-subwavelength resolution** *MRS Bulletin* **40** (April 2015) 359, DOI 10.1557/mrs.2015.64

L. Douillard, C. Charra **High-resolution mapping of plasmonic modes: photoemission and scanning tunnelling luminescence microscopies** *J. Phys. D: Appl. Phys.* **44** (2011) 464002, DOI 10.1088/0022-3727/44/46/464002

G. M. Caruso, F. Houdellier, S. Weber, M. Kociak, A. Arbouet **High brightness ultrafast transmission electron microscope based on a laser-driven cold field emission source: principle and applications** *Adv. in Phys. X* **4** (2019) 1660214 DOI 10.1080/23746149.2019.1660214

- Supplementary material



Electron Energy loss spectrometry, a tool for plasmonics

Basic principle – Electron energy loss spectrum

➢ Investigate the excitations of surfaces, thin films or objects using the inelastically diffracted / scattered electrons – Analysis of the electron energy losses

$$(E_i, k_i)_{electron} + excitation\ (fast\ electrons) \rightarrow (E_f, k_f)_{electron}$$

$\Delta E(\overrightarrow{q_{//}}) = E_f(\overrightarrow{k_f}) - E_i(\overrightarrow{k_i})$ Energy conservation

$\Delta\overrightarrow{k_{//}} = \overrightarrow{q_{//}} + \overrightarrow{G_{//}}$, $\overrightarrow{k_{//}}$ component momentum conservation

Zero loss region – Low primary energies, high energetic resolution

$E_i < 200$ eV, 1 meV $< \Delta E < 100$ meV

→ High Resolution Electron Energy Loss Spectrometry HREELS

Low loss region

$E_i < 1000$ eV, 100 meV $< \Delta E < 50$ eV

→ Electron Energy Loss Spectrometry EELS

High loss region – High primary energies

$\Delta E > 50$ eV

→ Extended Electron energy Loss Fine Structures EXELFS

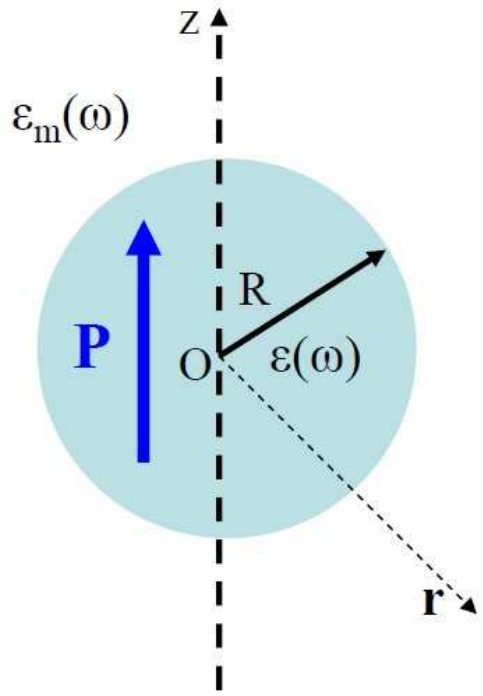
Approximation dipolaire (ou quasistatique) : λ>>Rayon (effets de retard négligeables)

$$\vec{\mathbf{E}}_0 e^{i(\vec{\mathbf{k}}.\vec{\mathbf{r}}-\omega t)} \longrightarrow \vec{\mathbf{E}}_0 e^{-i\omega t}$$

Jean Lermé
LASIM, Univ. Lyon

toutes les grandeurs ($\vec{\mathbf{E}}, \vec{\mathbf{P}}, \vec{\mathbf{D}}, V$) oscillent en ($\sim e^{-i\omega t}$)

$\vec{\mathbf{E}}(\vec{\mathbf{r}}) = -\mathbf{grad}\,[V(\vec{\mathbf{r}})]$ $\Delta V(\vec{\mathbf{r}}) = 0$ + conditions aux limites + champ à grande distance ($\mathbf{E}_0$)



Champ interne E_{int} (et donc P) uniforme

$$\vec{\mathbf{E}}_{\text{int}} = \frac{3\varepsilon_m}{\varepsilon + 2\varepsilon_m}\vec{\mathbf{E}}_0 \qquad \vec{\mathbf{P}} = \varepsilon_0 \chi \vec{\mathbf{E}}_{\text{int}}$$

Champ externe

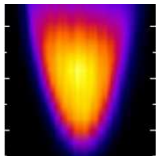
$$\vec{\mathbf{E}}_{ext} = \vec{\mathbf{E}}_0 - \mathbf{grad}\,[\frac{1}{4\pi\varepsilon_0\varepsilon_m}\frac{\vec{\mathbf{m}}.\vec{\mathbf{r}}}{r^3}]$$

⇔ champ créé par un dipôle **m** placé en O

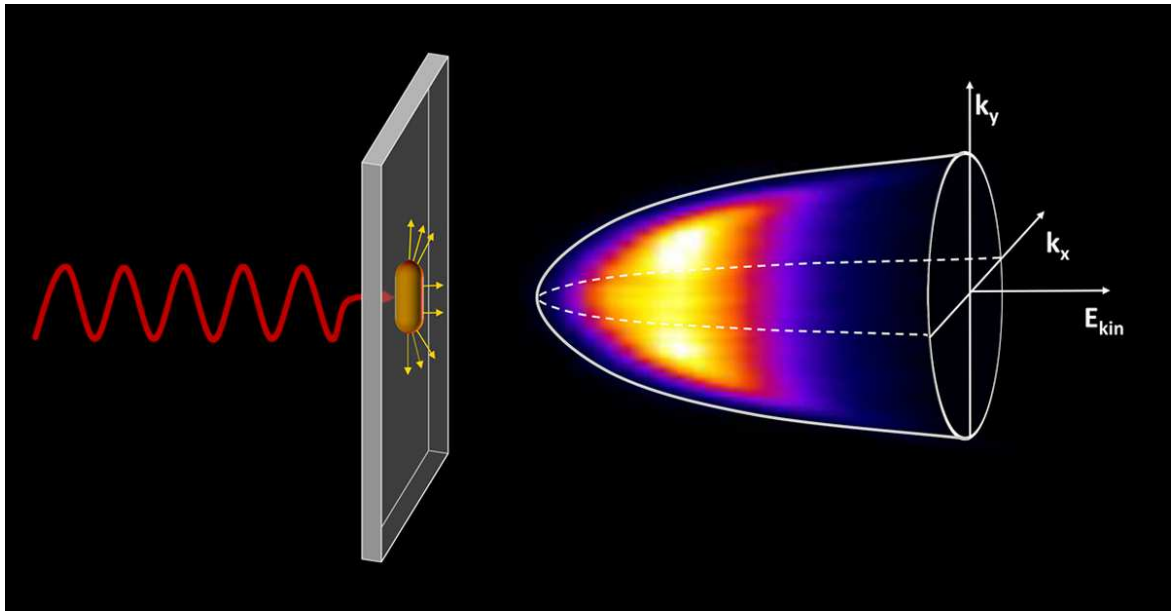
$$\vec{\mathbf{m}} = (\frac{4\pi}{3}R^3)\,3\varepsilon_0\varepsilon_m\,\frac{\varepsilon-\varepsilon_m}{\varepsilon+2\varepsilon_m}\vec{\mathbf{E}}_0$$

polarisabilité de la nanoparticule α(ω)

$$\vec{\mathbf{E}}(\vec{\mathbf{r}}) = \vec{\mathbf{E}}_0 + \vec{\mathbf{E}}_{pol}(\vec{\mathbf{r}}) \qquad \vec{\mathbf{E}}_{pol}^{(\text{int})} = \frac{\varepsilon_m - \varepsilon}{\varepsilon + 2\varepsilon_m}\vec{\mathbf{E}}_0$$



Distribution de moments des électrons chauds à l'échelle de l'objet individuel - PEEM Espace réciproque

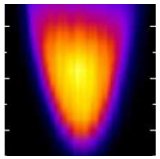


Montage Exp.

Bâtonnet Au 67 ± 2 nm x 19 ± 2 nm,
Substrat ITO / SiO_2
Résonance plasmon
λ_{Res} = 795 nm, FWHM = 41 nm, 80 meV
Illumination suivant la normale arrière
Champ électrique E_0 // k_x

- Microscopie PEEM à détection Temps de Vol dans l'espace réciproque
- Mesure de la densité d'états $\rho(k_x, k_y, E_{cin})$
- Détermination de la distribution des moments des électrons photoémis d'un bâtonnet Au à résonance plasmon

Momentum Distribution of Electrons Emitted from Resonantly Excited Individual Gold Nanorods
M. Lehr, B. Foerster, M. Schmitt, K. Krüger, C. Sönnichsen, G. Schönhense, H.-J. Elmers
Nano Lett. **17** (2017) 6606 DOI: 10.1021/acs.nanolett.7b02434



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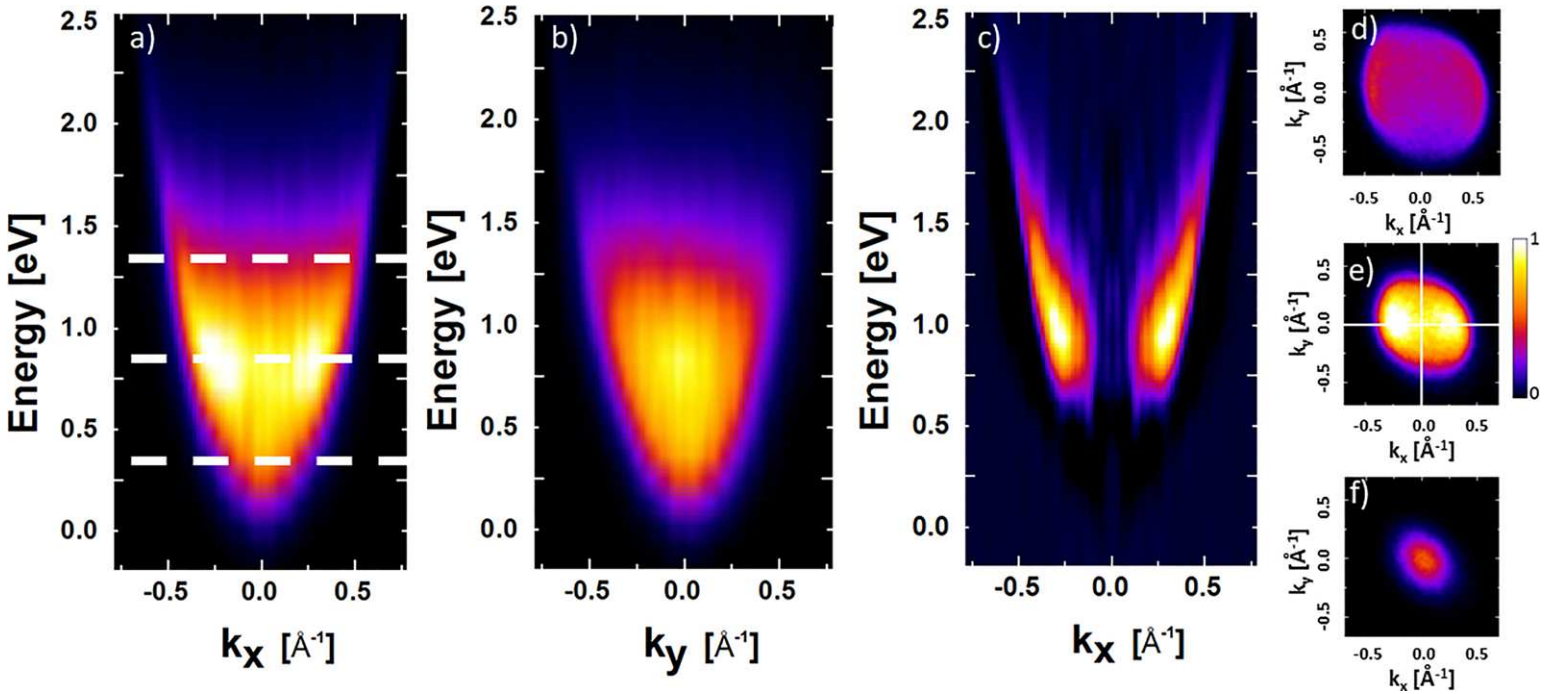
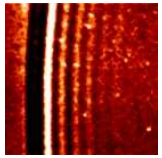


Bâtonnet Au individuel (a, b) Profils des moments suivant les directions k_x et k_y; (c) Soustraction des profils (a) et (b); (d-f) coupes transverses aux énergies cinétiques 1.3, 0.8 et 0.3 eV, cf. (a). Polarisation du champ électrique suivant la direction k_x.

- Deux composantes de moment distinctes :

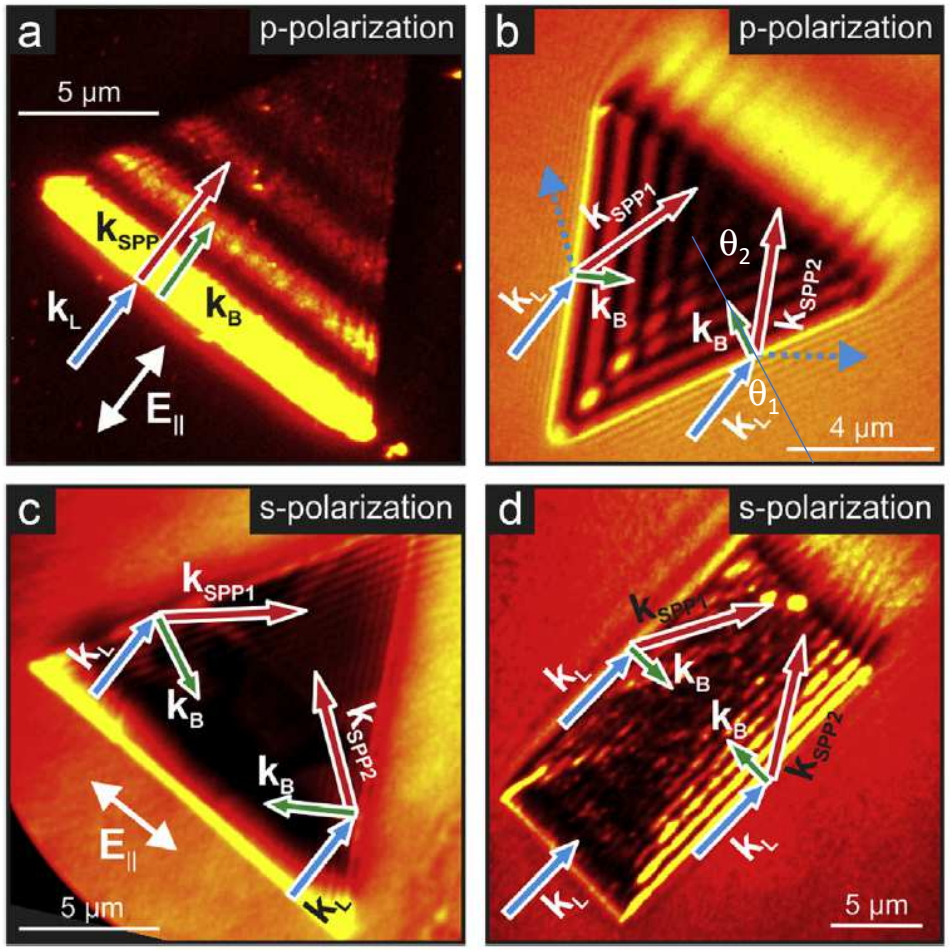
(i) Une **composante isotrope** liée à la photoémission non linéaire à partir du gaz d'électrons chauds (> 90 %, diffusion multiple),

(ii) Une **composante anisotrope** liée à l'émission de champ (effet tunnel sous champ optique) aux extrémités du bâtonnet suivant l'axe longitudinal (< 10 %). Facteur de Keldysh ~ 1 – 3. Régime de transition n.hυ vs Fowler-Nordheim



Propagation of plasmons-polaritons (nm, fs) – PEEM

Symétrie 2D – Loi Snell-Descartes - Interface Ag / vide



➢ Loi de Snell-Descartes

.Triangle Ag / Si(111)
.PEEM 2 photons

Onde incidente $k_{//}$, milieu n_{vide}
Onde SPP k_{SPP}, milieu n_{Ag}
Figure de battements k_B (Moiré)

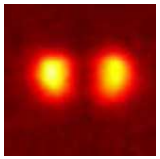
$$\overrightarrow{k_B} = \overrightarrow{k_{SPP}} - \overrightarrow{k_{//}}$$

$$k_{//} \cdot \sin(\theta_1) = k_{SPP} \cdot \sin(\theta_2)$$

➢ Validation de la loi Snell-Descartes pour la réfraction

Onde libre → Onde plasmon - polariton
Onde plasmon - polariton → Onde libre

N.M. Buckanie *et al. Ultramicroscopy* **130** (2013) 49–53



Cathodoluminescence, a tool for plasmonics

Basic principle – CL probability vs EMLDOS

In quasi-static approximation

$$\Gamma_{CL}^{sphere}\left(\omega,\vec{R}_{\perp}\right)=\frac{e^{2}}{\pi\hbar\omega^{2}}\sum_{i}\Im\left(f_{i}(\omega)\right)\left|TF_{z}(\vec{E}_{i}^{z}\left(\vec{R}_{\perp},\frac{\omega}{\upsilon}\right))\right|^{2}$$

f_i generalized polarizability, i.e. the spectral dependence variation (plasmon energies = f_i poles)
TF_z is a Fourier transform along the e-beam direction at point $\vec{R}_{\perp}=(x,y)$ in real space and momentum $q_z = \omega / \upsilon$ in reciprocal space

- For bright modes and within a FT_z, CL maps spectrally and spatially the zEMLDOS, i.e. the electromagnetic density of states in the direction along the e-beam axis
- CL = Out-of-plane EMLDOS for bright modes

- Electron selection rules ≠ photon selection rules → Dark modes accessible
- Direct control over output polarization is possible

F. Garcia de Abajo *Phys. Rev. B* **59** *(1999) 3095*
M. Kociak, O. Stéphan *Chem. Soc. Rev.* **43** (2014) 3865

➢ The electric field parallel to the electron beam is described by a temporal Gaussian wave-packet where Δp is the light pulse duration and $i\tau$ s the delay between the arrivals of the photon and the electron pulses at the position of the sample.

$$E_z(z,t) = E_z(z)\exp\left[-i\omega t - \frac{(t+\tau)^2}{\Delta_p^2}\right]$$

PINEM Echange d'impulsion suite à l'absorption (rencontre) de n photons avec un électron

(i) Point de vue de l'électron

$\Delta p = p_f - p_i$

$\Delta p = (2m(E_i \pm n.\hbar\omega))^{1/2} - (2mE_i)^{1/2})$

$\Delta p \approx n.\hbar\omega / v_e$, $E_i = 200$ keV >> $\hbar\omega = 1$ eV

(ii) Point de vue du photon

$\Delta p = p_f - p_i$

$\Delta p = n.\hbar\omega / c$, $c > v_e$

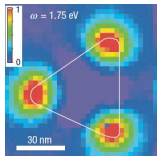
➢ EELS, EEGS, CL probabilities densities for the dipole plasmon of a sphere within the quasi static approximation

$$\Gamma_{EELS}^{sphere}(\omega, R_\perp) \propto \left(\frac{\omega}{\gamma v^2}\right)^2 \left(\mathrm{K}_1^2\left(\frac{\omega \mathrm{R}_\perp}{\gamma \upsilon}\right) + \frac{1}{\gamma^2}\mathrm{K}_0^2\left(\frac{\omega \mathrm{R}_\perp}{\gamma \upsilon}\right)\right) \Im\left(\alpha_{\iota=1}(\omega)\right)$$

$$\Gamma_{EEGS}^{sphere}(\omega, R_\perp) \propto \left(\frac{\omega}{\gamma v^2}\right)^2 \mathrm{I}_0\ \mathrm{K}_1^2\left(\frac{\omega \mathrm{R}_\perp}{\gamma \upsilon}\right) |\alpha_{\iota=1}(\omega)|^2 \delta(\omega - \omega_\mathrm{i})$$

$$\Gamma_{CL}^{sphere}(\omega, R_\perp) \propto \omega^3 \left(\frac{\omega}{\gamma v^2}\right)^2 \left(\mathrm{K}_1^2\left(\frac{\omega \mathrm{R}_\perp}{\gamma \upsilon}\right) + \frac{1}{\gamma^2}\mathrm{K}_0^2\left(\frac{\omega \mathrm{R}_\perp}{\gamma \upsilon}\right)\right) |\alpha_{\iota=1}(\omega)|^2$$

A. Asenjo-Garcia, F. García de Abajo *New J. Phys.* **15** (2013) 103021



Electron Energy loss spectrometry, a tool for plasmonics

Basic principle – EELS probability for a small sphere

- The electron electric field is similar to a plane wave pulse of white light. The NP sees a pulse containing a large spectrum of frequencies
- In the quasi-static QS approximation, the exciting field is static, i.e. presents no spatial variation over the particle. Thus, it couples only to the l = 1 dipolar mode. For non relativistic electrons, we obtain:

$$\Gamma_{\mathrm{EELS}}^{\mathrm{sphere}}(\omega,R_\perp) \propto a^3\Im(\alpha_{l=1}(\omega))(K_1{}^2(\omega R_\perp/v) + K_0{}^2(\omega R_\perp/v))$$

$$\Gamma_{EELS}^{sphere}(\omega,R_\perp) \propto a^3\Im\left(\alpha_{l=1}(\omega)\right).\exp(-\frac{R_\perp}{v/\omega})$$

$$\sigma_{ext.} \propto a^3\Im\left(\alpha_{l=1}(\omega)\right)$$

- Formally, the EELS probability of a small sphere is proportional to its absorption cross-section as measured in far field optics
- EELS probability is position-dependent with a quasi-exponential decay with e-beam to sphere distance $R_\perp$, attenuation length = $\upsilon/\omega \sim 10$ nm

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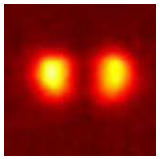

Cathodoluminescence, a tool for plasmonics

Basic principle – Coherent CL probability

- The transient electric field associated to the e-beam is similar to a plane wave pulse of white light. The NP sees a EM pulse containing a large spectrum of frequencies.
- In the quasi-static approximation, the exciting field is static, i.e. presents no spatial variation over the particle size. Thus, it couples only to the $l = 1$ dipolar mode.

$$\Gamma_{\mathrm{CL}}^{\mathrm{sphere}}(R_\perp,\omega) \propto a^6|\alpha_{l=1}(\omega)|^2(K_1{}^2(\omega R_\perp/v) + K_0{}^2(\omega R_\perp/v))$$

$$\Gamma_{CL}^{sphere}(\omega,R_\perp) \propto a^6|\alpha_{l=1}(\omega)|^2.\exp(-\frac{R_\perp}{v_e/\omega})$$

a Sphere diameter; $R_\perp$ = (x, y) Impact parameter of the electrons traveling along the z direction at speed v_e; $\hbar\omega$ Energy of the emitted photon; K_m Modified Bessel function of the second kind; α_l Sphere polarizability for mode l

- Formally, the CL probability of a small sphere is proportional to its scattering cross section as measured in far field optics, $\sigma_{sca.} \propto a^6|\alpha_{l=1}(\omega)|^2$
- CL probability is position-dependent with a quasi-exponential decay with e-beam to sphere distance $R_\perp$, attenuation length $\upsilon_e/\omega \sim 10$ nm
- Electron selection rules ≠ photon selection rules → Dark modes accessible

A. Asenjo-Garcia, F. García de Abajo *New J. Phys.* **15** (2013) 103021; M. Kociak & O. Stéphan *Chem. Soc. Rev.* **43** (2014) 3865

Vitesse d'un electron relativiste — Facteur de Lorentz

$v^2 = c^2 . (1 – 1 / (1 + E / m_e c^2)^2)$

A.N. U = 100, 200 keV, $E_0 = m_e c^2 = 511$ keV

$(v_e/c)^2 = 1 – 1 /(1 + 100 / 511)^2)$, $v_e/c = 0.548 \sim 1 / 1.82 \sim 1 / 2$ — 1.1955

$(v_e/c)^2 = 1 – 1 /(1 + 200 / 511)^2)$, $v_e/c = 0.695 \sim 1 / 1.4$ — 1.3908

Mesure EELS - Distance d'atténuation sur un TEM U = 100, 200 keV

$L = \gamma \upsilon_e/\omega = \gamma c.T /(1.82*2\pi) = \gamma/2\pi . \lambda_0/1.82$ où λ_0 désigne la longueur d'onde dans le vide du photon correspond à la perte d'énergie considérée

A.N. U = 100 keV Pour une perte de 1 eV, $\lambda_0 = 1240$ nm, L = 1.1955 x 1240 / (2π 1.82) = 130 nm

Pour une perte de 2 eV, $\lambda_0 = 620$ nm, L = 1.1955 x 620 / (2π 1.82) = 65 nm

U = 200 keV Pour une perte de 1 eV, $\lambda_0 = 1240$ nm, L = 1.3908 x 1240 / (2π 1.44) = 191 nm

Pour une perte de 2 eV, $\lambda_0 = 620$ nm, L = 1.3908 x 620 / (2π 1.44) = 95 nm

HAADF (Wikipedia) High-angle annular dark-field imaging (HAADF) is an STEM technique which produces an annular dark field image formed by very high angle, incoherently scattered electrons (Rutherford scattered from the nucleus of the atoms) — as opposed to Bragg scattered electrons. This technique is highly sensitive to variations in the atomic number of atoms in the sample (Z-contrast images).[3]

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