SERS and SEIRA
Signal optimisation and applications

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Plan du cours

1. SERS signal optimisation
2. SERS sensor
3. SEIRA
4. SERS/SEIRA coupling

Signal optimisation in SERS

SERS principle

$$\vec{P} = \alpha . \vec{E}$$

Chemical Effect

Charge transfert…

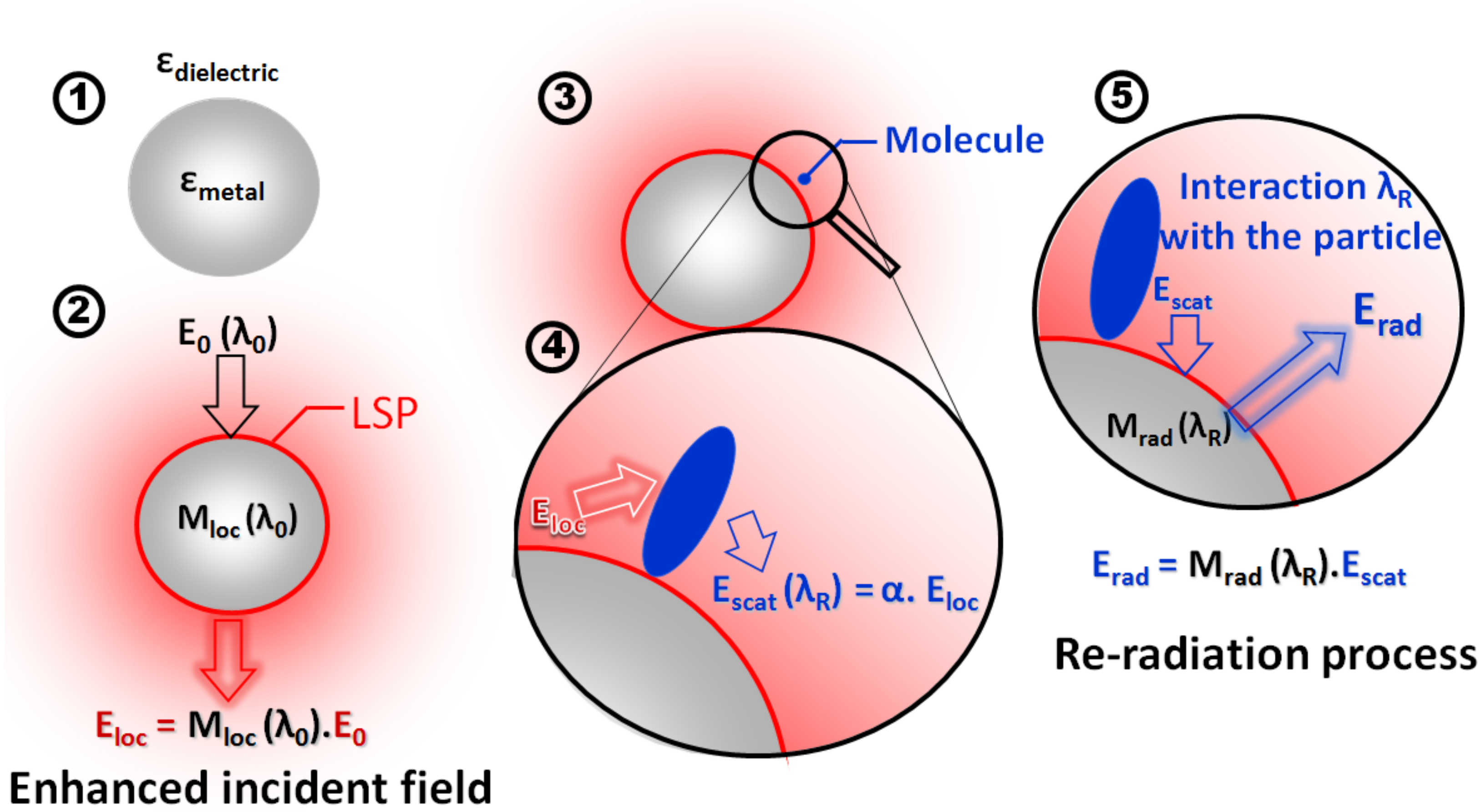
Enhancement ≈ 10^2

Electromagnetic Effect

Electromagnetic field enhancement

Enhancement ≈ 10^8

SERS principle: Electromagnetic effect



$$I_{SERS} = [M(\lambda_R).M(\lambda_0)]^2.\alpha^2.E^2$$

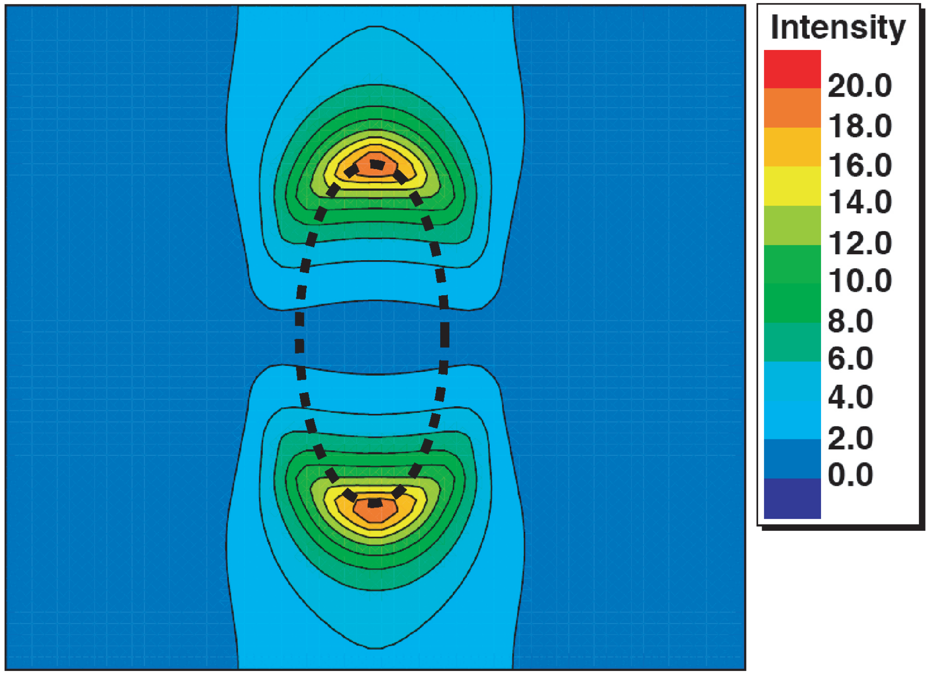
$$I_{SERS} = [M(\lambda_R).M(\lambda_0)]^2.I_{Raman} \approx M(\lambda_0)^4 I_{Inc}$$

⇒ Giant Raman enhancement up to 10^{10}

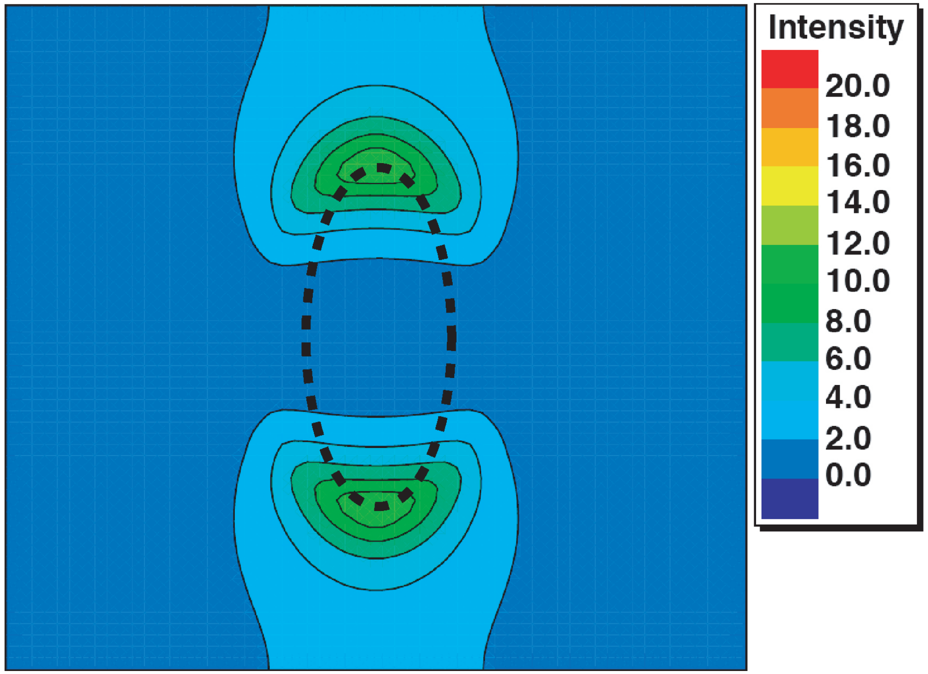
N. Guillot *et al. JQSRT* **113,** 2321, 2012, N. Guillot et al., *J. of Nanophotonics,* **6(1)**, 64506, 2012

Near field enhancement

Gold nanowire : long axis = 150 nm



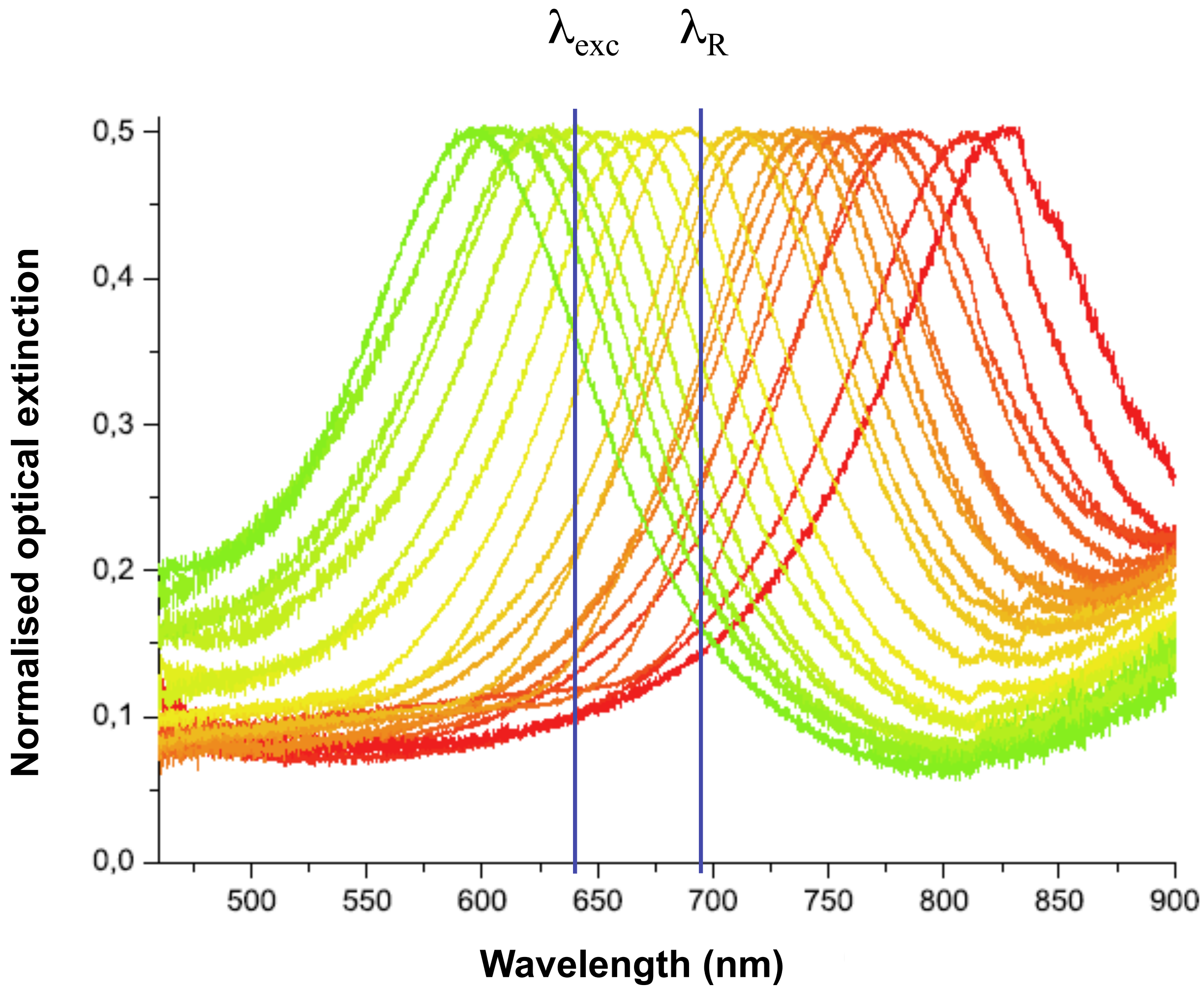
Intensity map at 712 nm



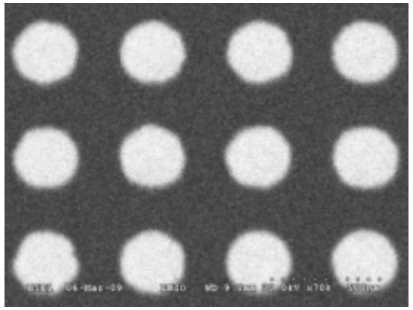
Intensity map at 800 nm

A.S. Grimault et al. Appl. Phys. B 84, 111, 2006

SERS Experiments

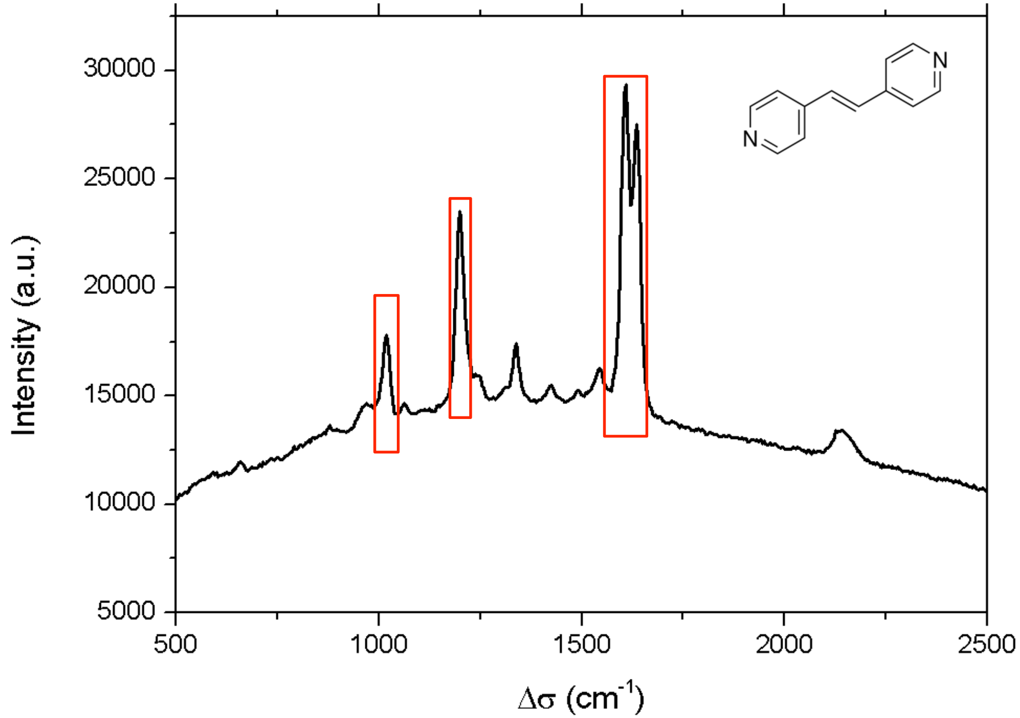


SERS Experiments



Nanocylinders :
100 nm < Ø < 200 nm,
height = 50 nm

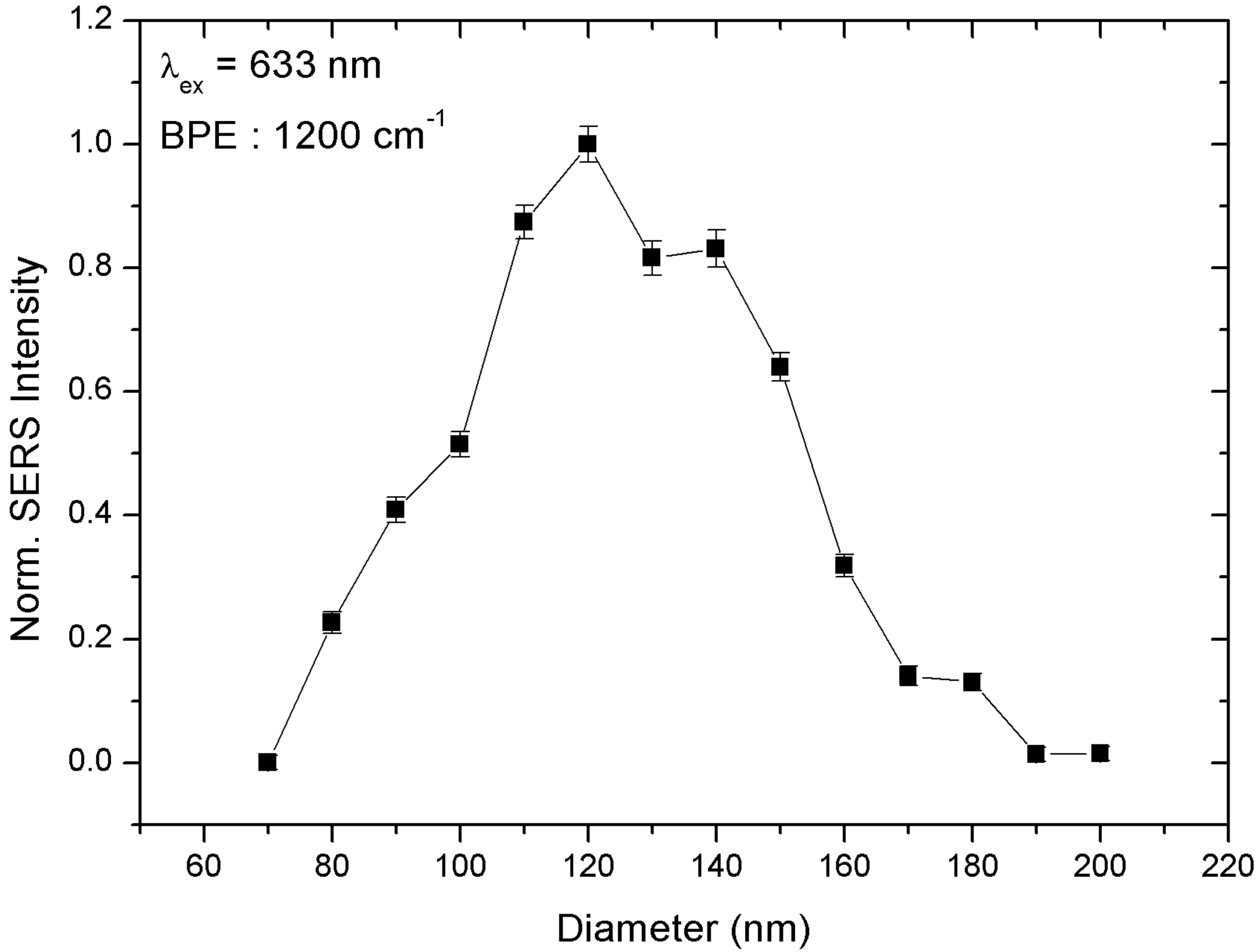
λ_{exc}= 633 nm
λ_{exc}= 660 nm
λ_{exc}= 691 nm
λ_{exc}= 785 nm



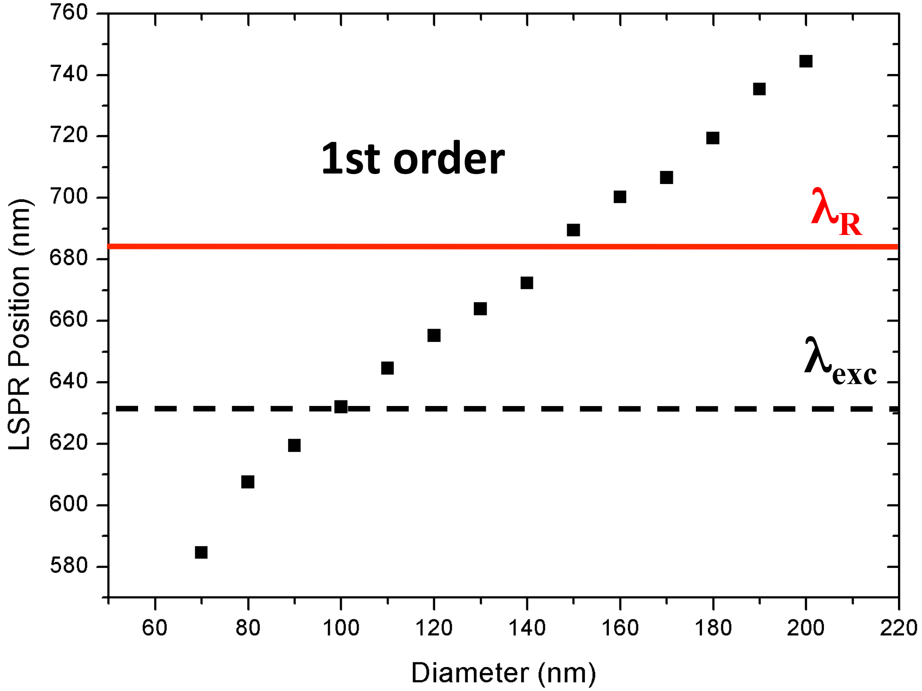
trans-1,2-bis(4-pyridyl)ethylene (BPE)

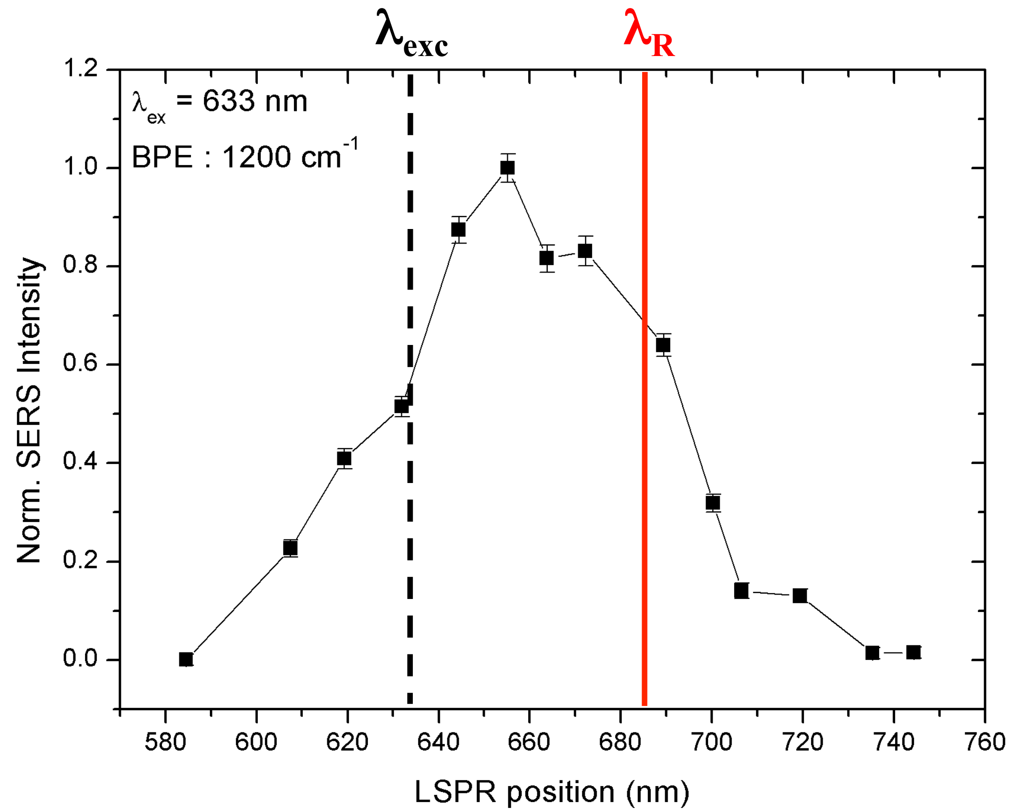
1007 cm^{-1}: pyridine ring breathing mode
1200 cm^{-1} : C=C stretching mode
1606 cm^{-1}: pyridine ring C=C stretching mode
1636 cm^{-1}: whole pyridine ring stretching mode

SERS vs diameter



SERS vs LSPR





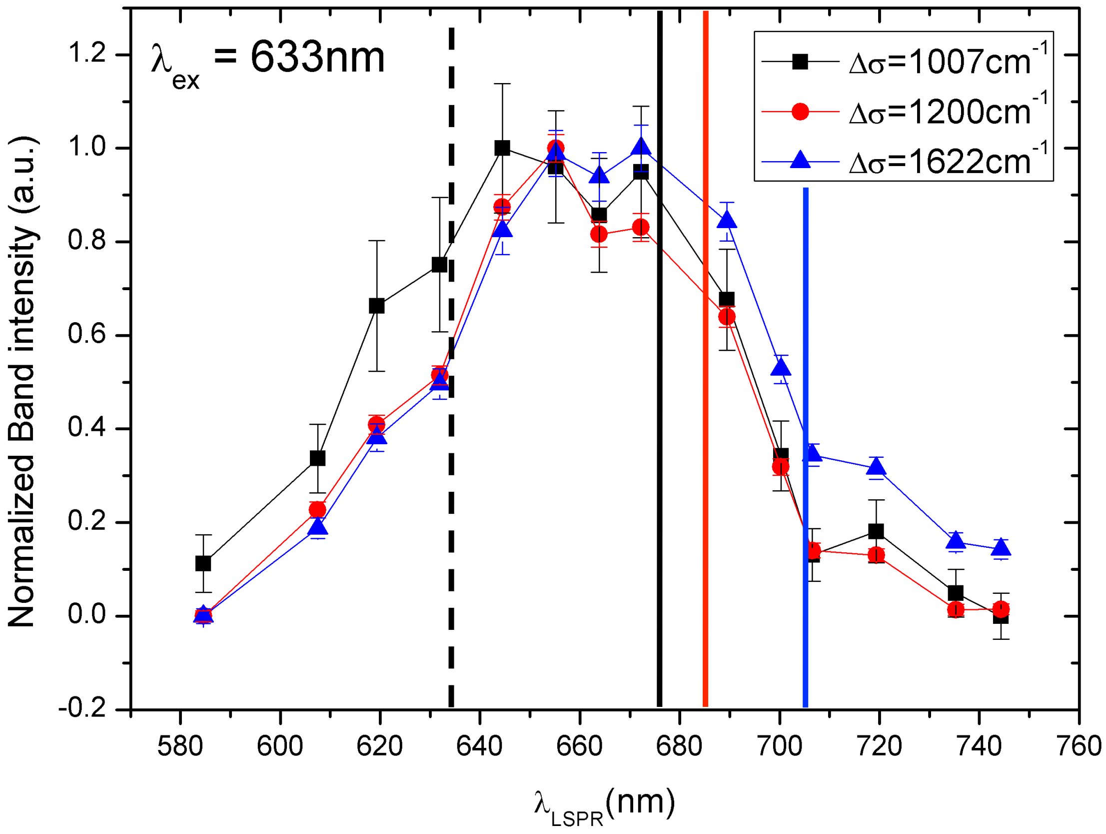
$$G_{SERS} = | f(\lambda_{exc}).f(\lambda_R) |^2$$

$$G_{SERS}\ \mathbf{Max} \Rightarrow \lambda_{exc} < \lambda_{LSPR} < \lambda_R$$

A.Wokaun *et al.*, *Solid State Phys.* 38, 1984

N. Guillot *et al. JQSRT* **113,** 2321, 2012, N. Guillot et al., *J. of Nanophotonics,* **6(1)**, 64506, 2012

SERS Experiments



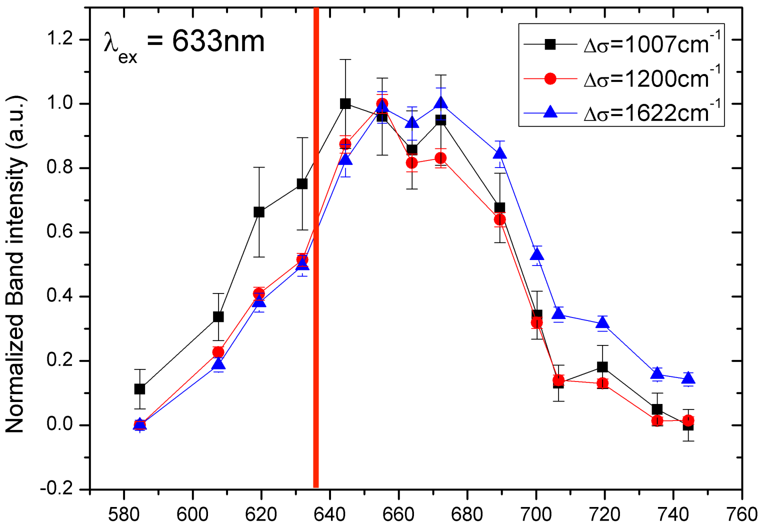
λ_R = 676 nm

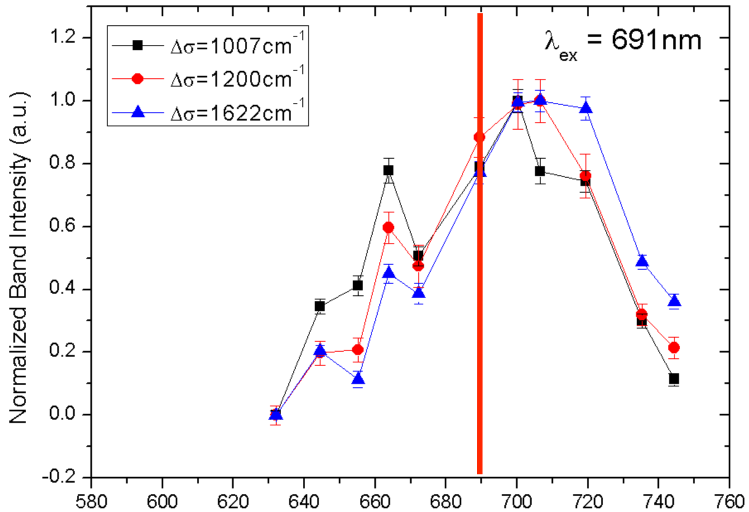
λ_R = 685 nm

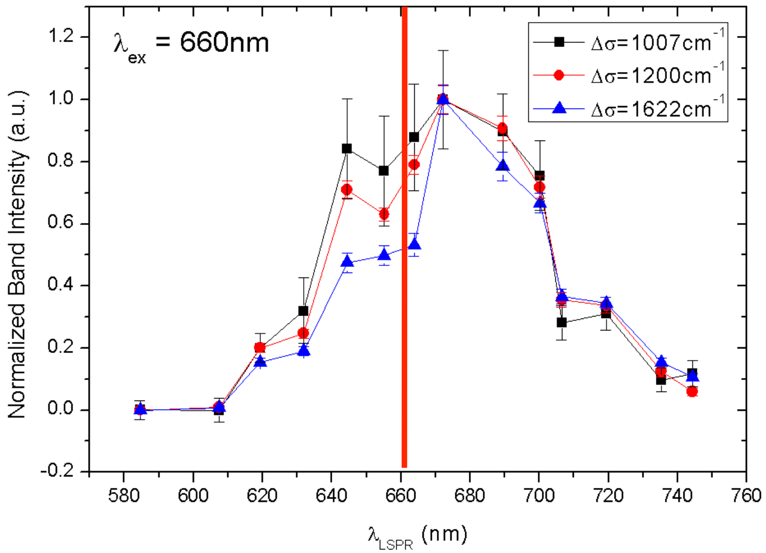
λ_R = 705 nm

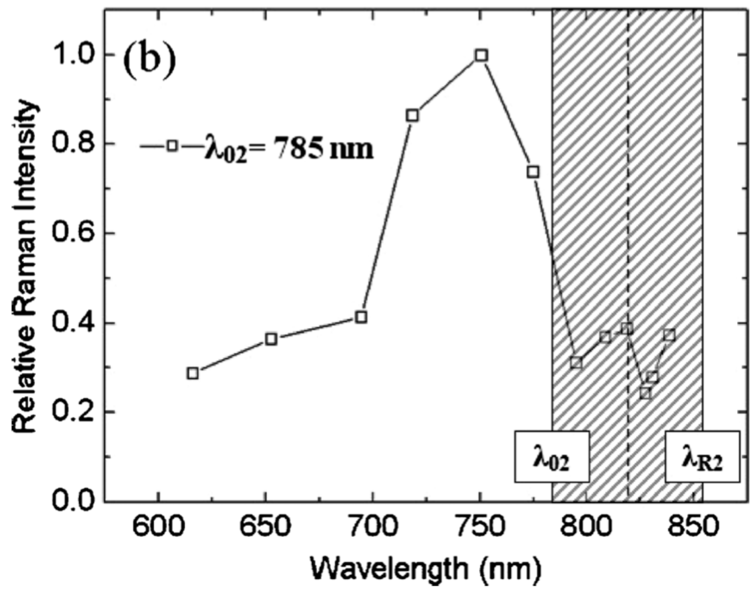
F. Colas *et al*., *J. Phys. Chem. C* accepted

SERS Experiments



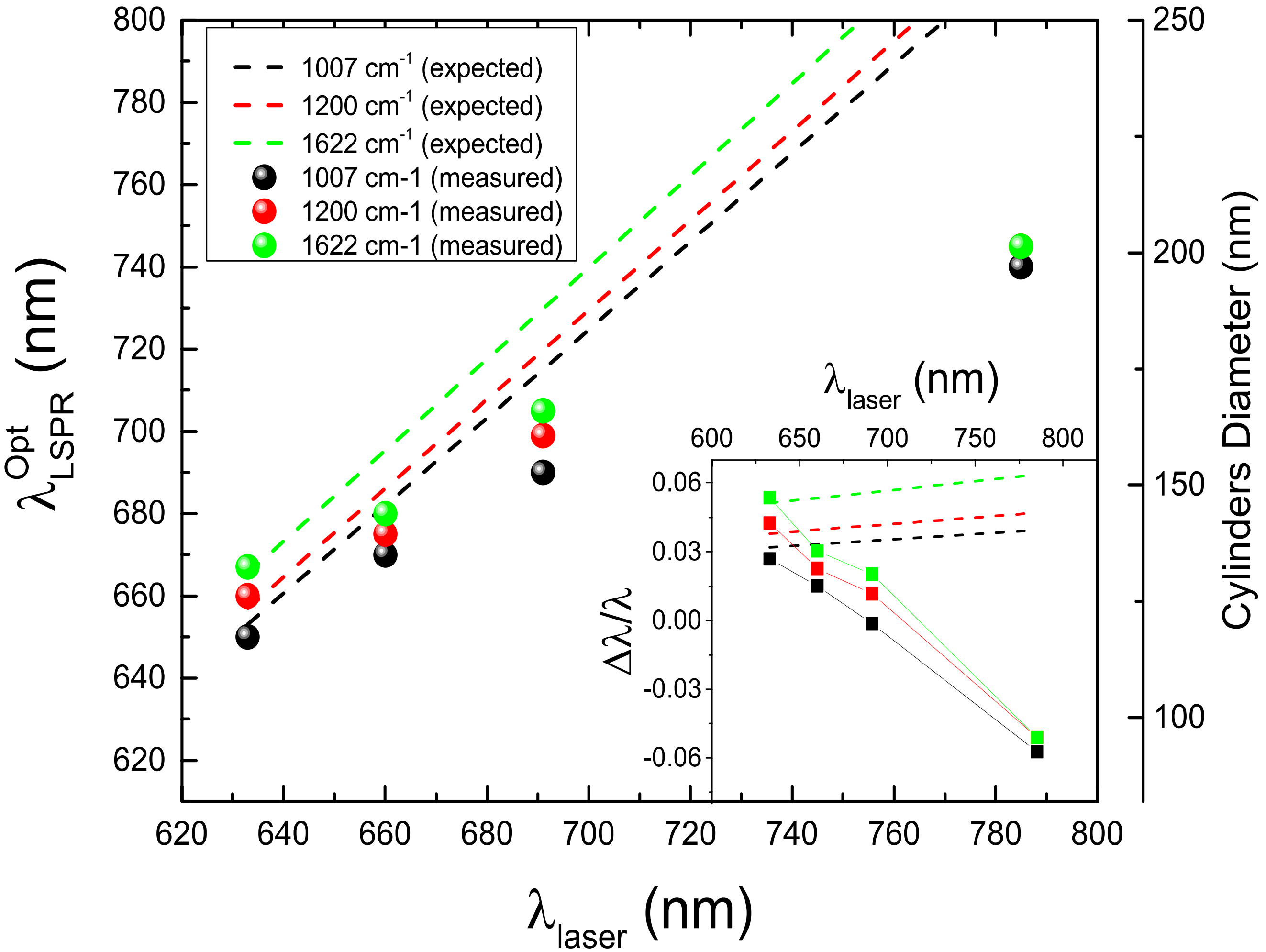






N. Guillot, *Appl. Phys. Lett.* 97, 023113 (2010)

SERS vs LSPR



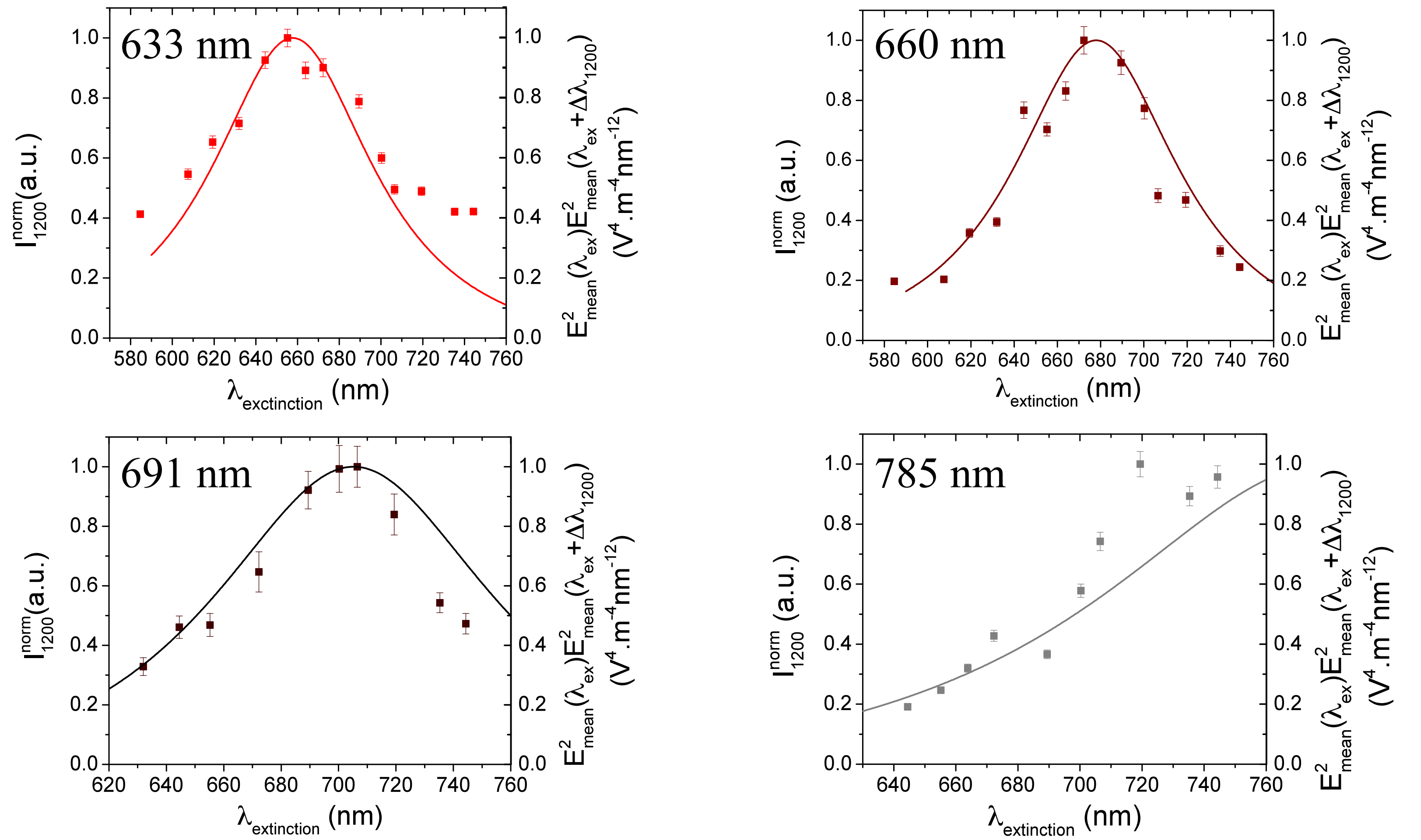
⇒ **Shift between the expected LSPR position and the effective one**

⇒ **Near-field / Far-field shift ?**

Comparison DDA - Experiments

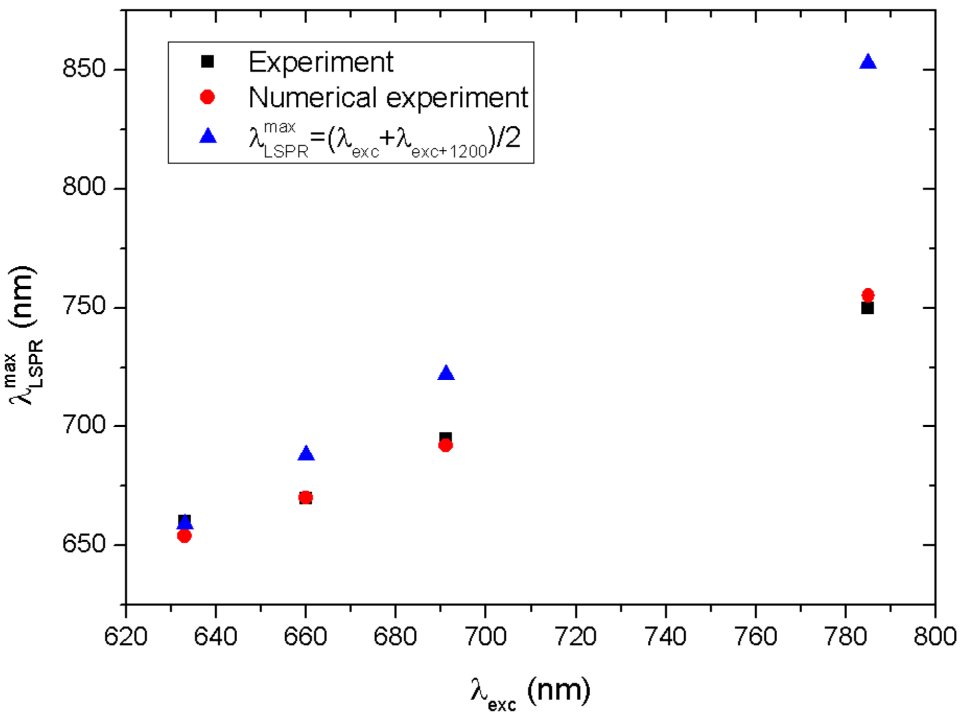
Discrete Dipole Approximation (DDSCAT 7.3)

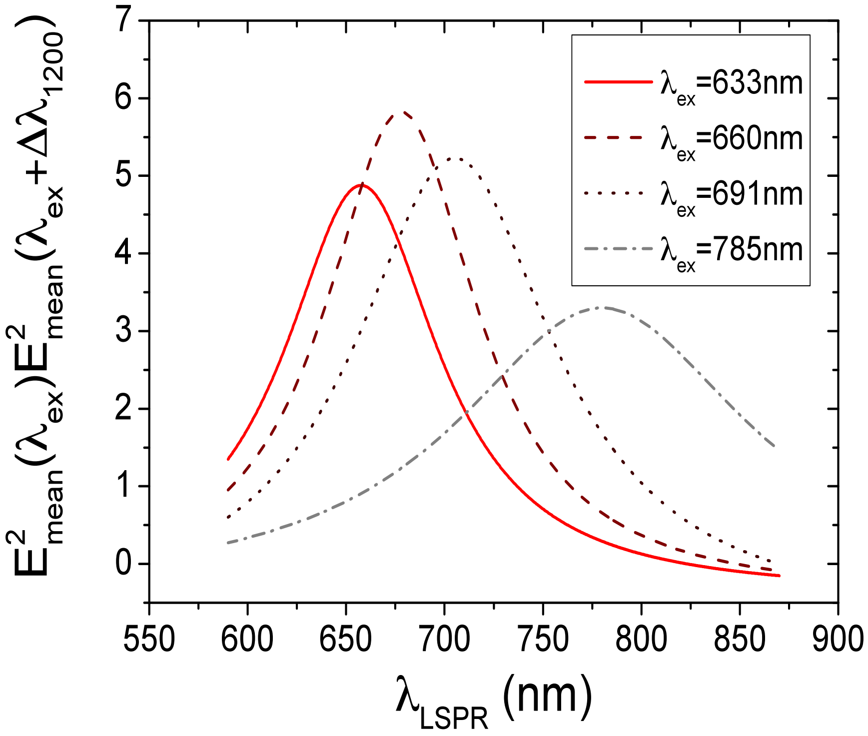
B. Draine, P. Flatau, *JOSA A*, 1994, 11(4)1491-1499



⇒ **Good agreement between DDA calculations and experiments**

Comparison DDA - Experiments





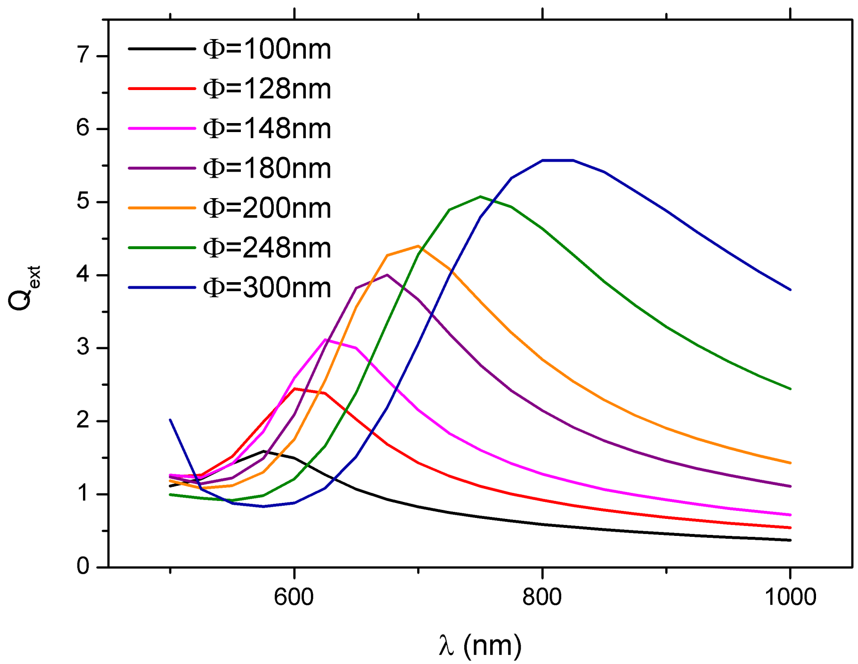
⇒ **Observation of the shift between the expected and the observed LSPR**

⇒ **Change in the relative intensity of the enhancement**

Near-field/Far-field discrepancy

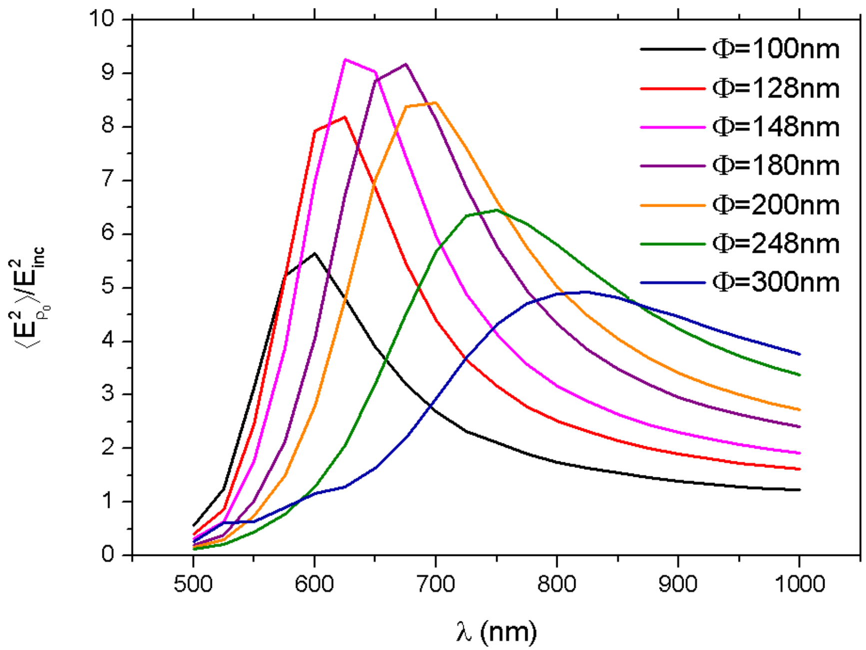
LSPR

Far field measurement



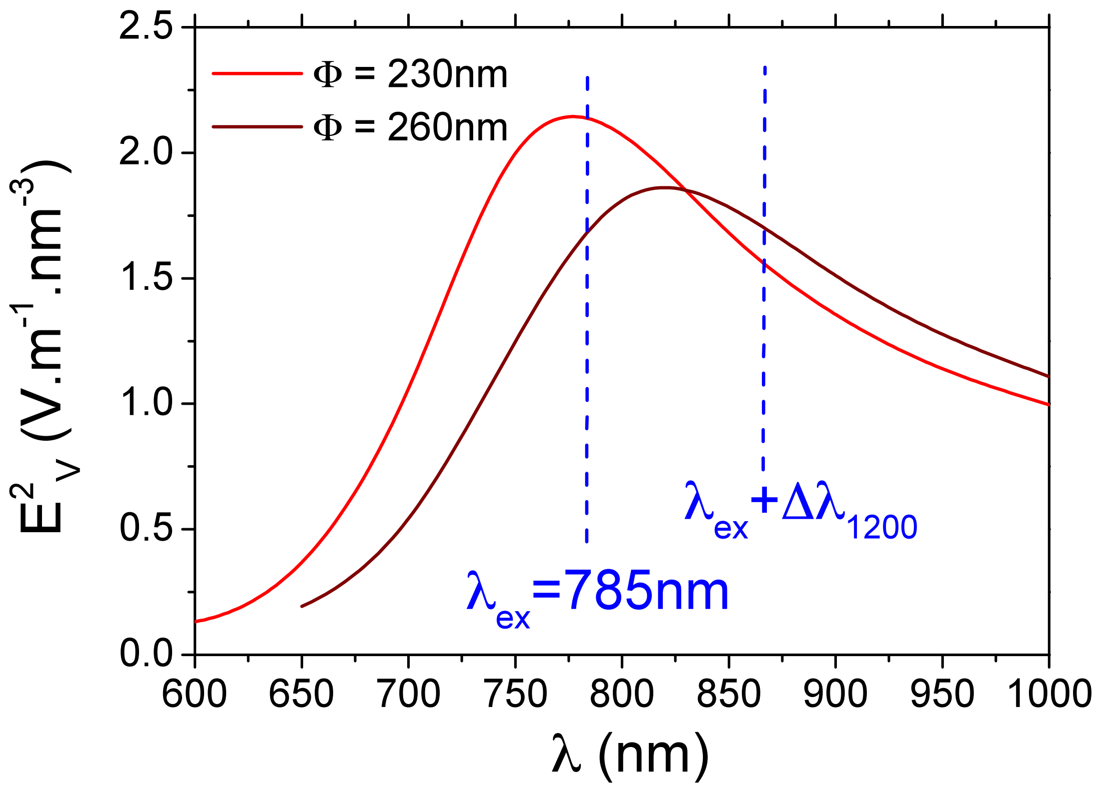
SERS

Near field measurement



⇒ Broadening and decrease of the intensity of the near-field enhancement

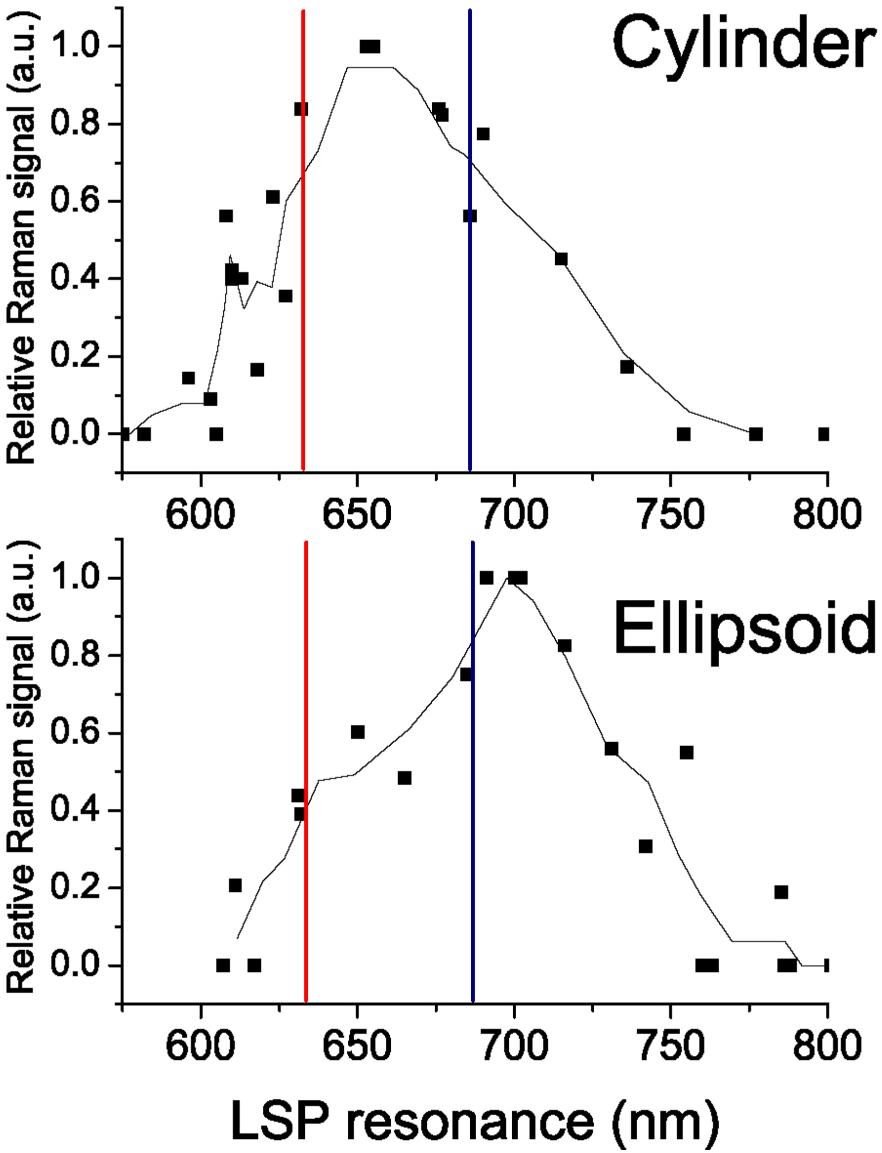
Near-field/Far-field discrepancy



⇒ **Best SERS enhancement for a lower diameter and thus for a blueshifted LSPR**

F. Colas *et al.*, *J. Phys. Chem. C* accepted

SERS vs LSPR



Nanocylinders : 50 nm < diameter < 200 nm
Nano-ellipses : 50 nm < major axis < 200 nm

Excitation Wavelength

$$\lambda_{exc} = 632.8\text{nm}$$

BPE Raman mode: 1200cm^{-1}

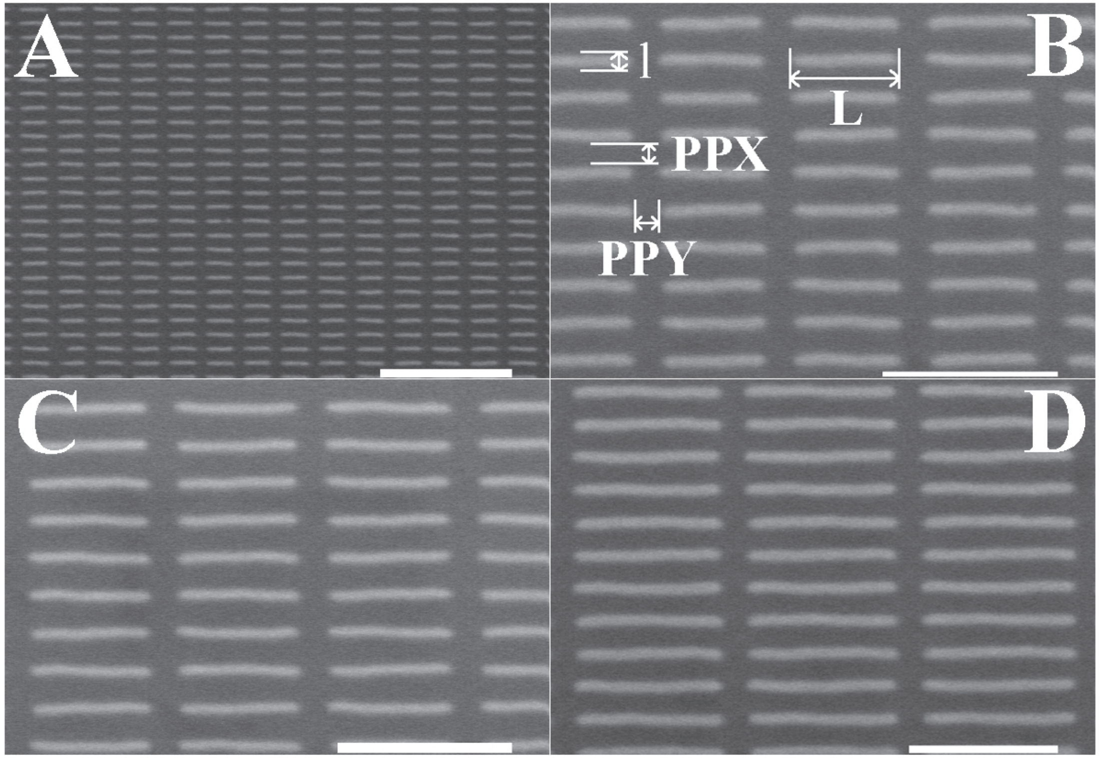
$$\lambda_R = 685\text{nm}$$

$$G_{SERS} = |f(\lambda_{exc}).f(\lambda_R)|^2$$

$$G_{SERS}\ \text{Max} \Rightarrow \lambda_{exc} < \lambda_{LSPR} < \lambda_R\ ?$$

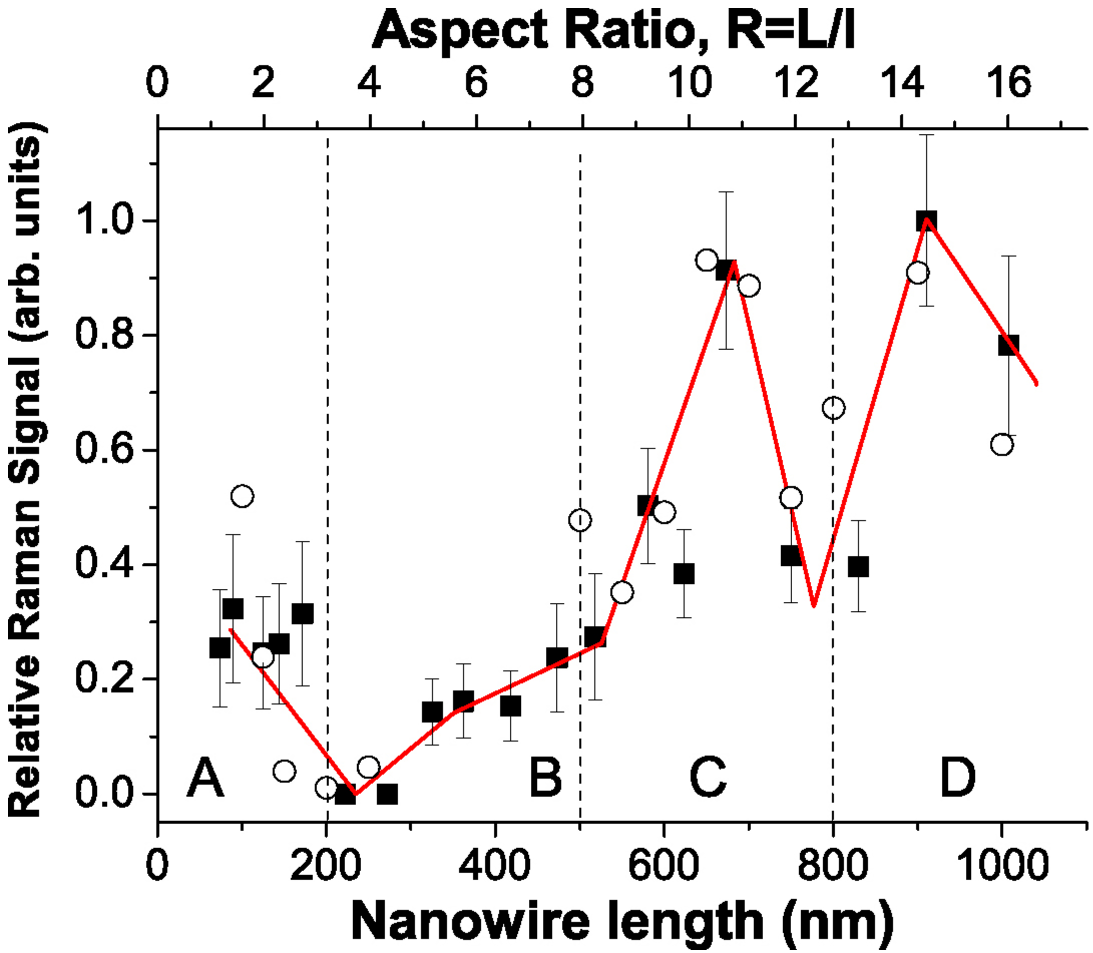
J. Grand. *et al.*, *PRB* **72**, 33407, 2005

Gold Nanowires



L = from 50 nm to 1000 nm, l = 60 nm, height = 50 nm, PPX = PPY = 200 nm

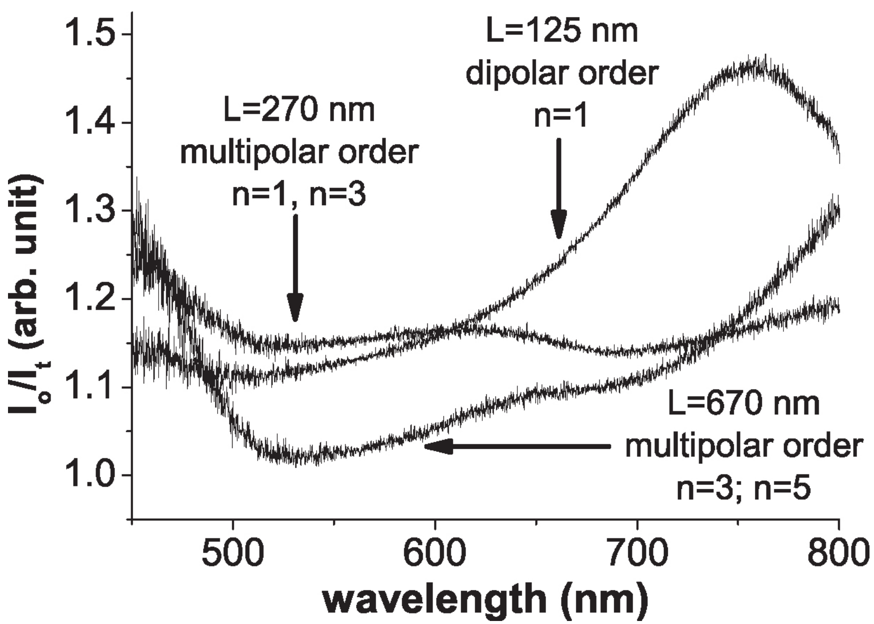
Gold Nanowires : SERS

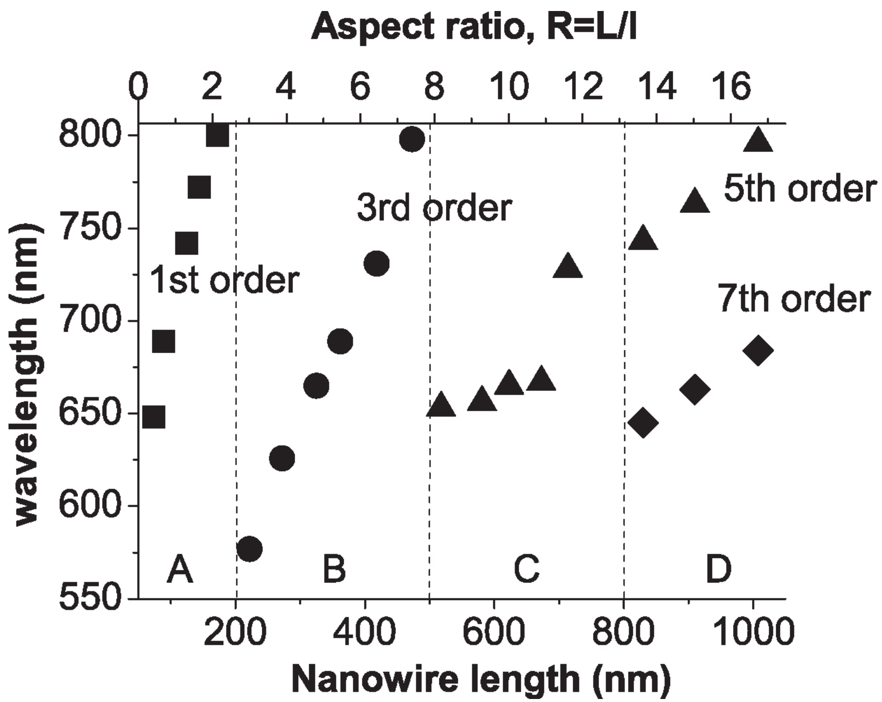


⇒ **Raman enhancement maximum for one optimum length**

(L. Billot *et al.*, *CPL* **422**, 303, 2006)

Gold Nanowires : LSPR

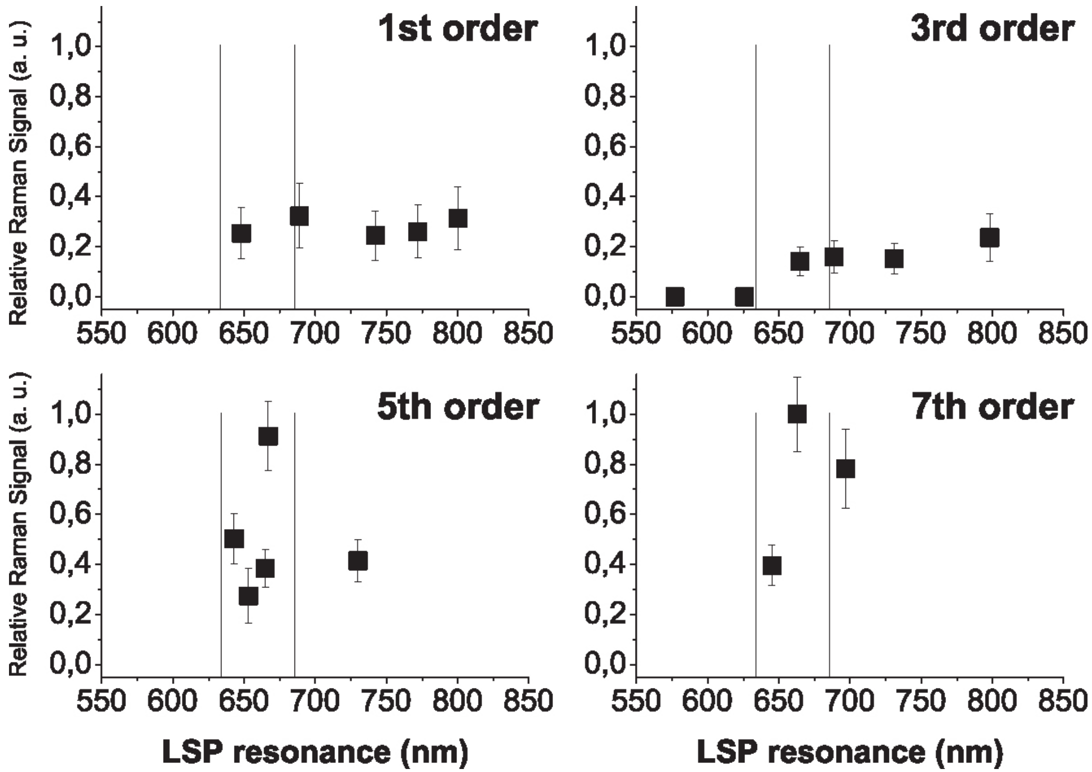




⇒ Observation of odd multipolar LSPR

(G. Schider *et al.*, *PRB* **68**, 155427, 2003)

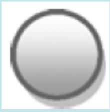
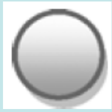
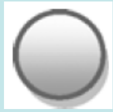
Gold Nanowires : LSPR



⇒ **Best enhancement for LSPR close to 675 nm, ≈ λ_R**

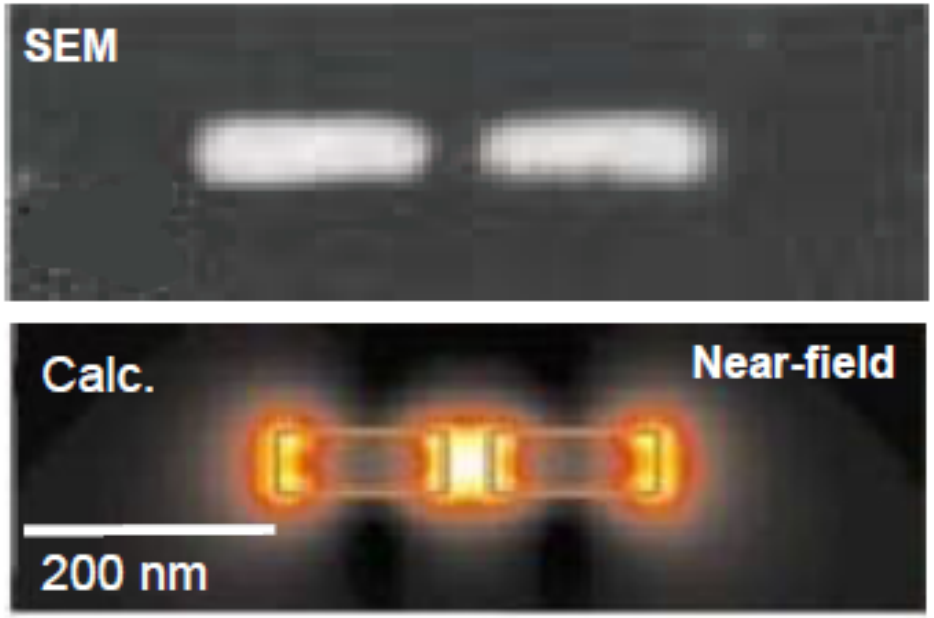
⇒ **Some multipolar LSPR have better enhancement than dipolar LSPR**

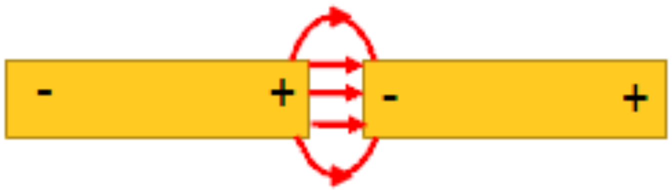
LSPR rules

					
λ_{Exc}	633	660	785	633, 676	514, 532 633
λ_{LSPR} rules	$= (\lambda_0 + \lambda_R)/2$	$\approx \lambda_0$	$< \lambda_0$	$\approx \lambda_R$	$\lambda_0 < \lambda_{LSPR} < \lambda_R$

⇒ **The LSPR rules depend on the shape of the nanostructures and on the excitation wavelength**

Electromagnetic Coupling

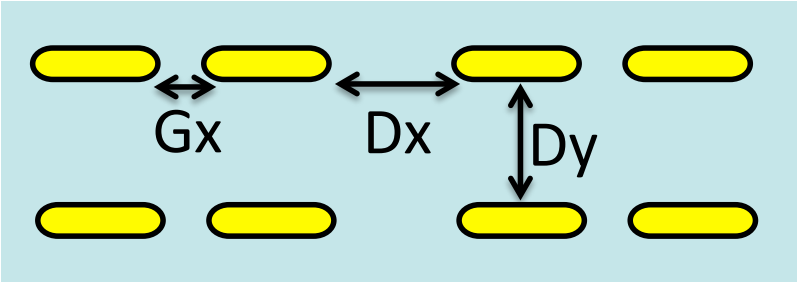


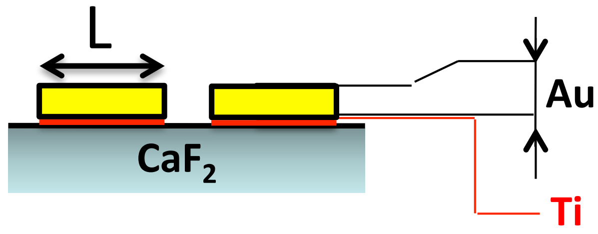


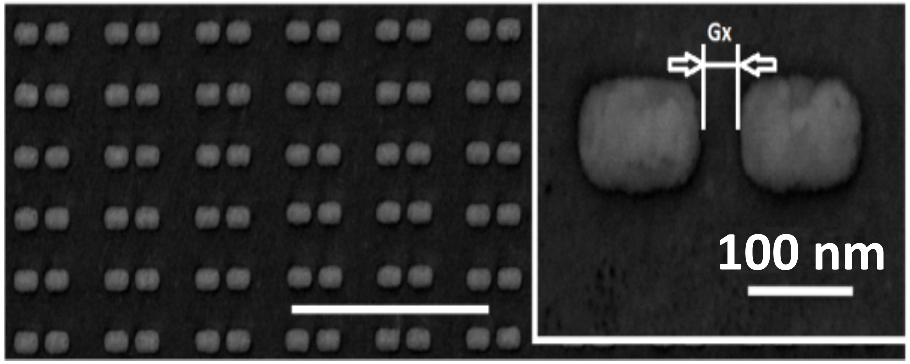
Systematic study to measure the consequences of coupling on LSPR and on SERS

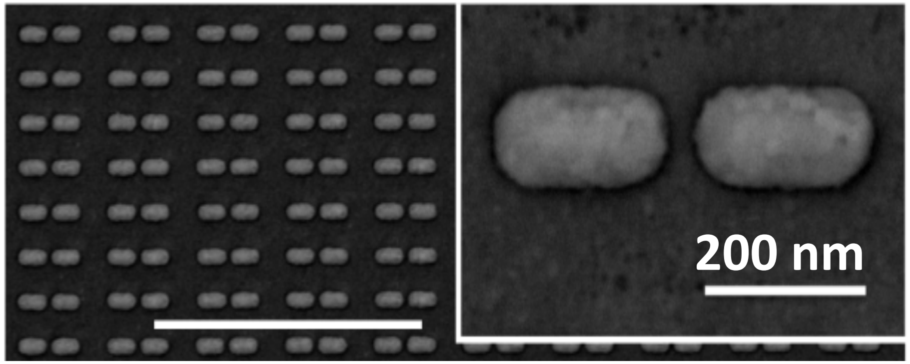
P. Mühlshlegel *et al.*, *Science* **308**, 1607, 2005

Electromagnetic Coupling



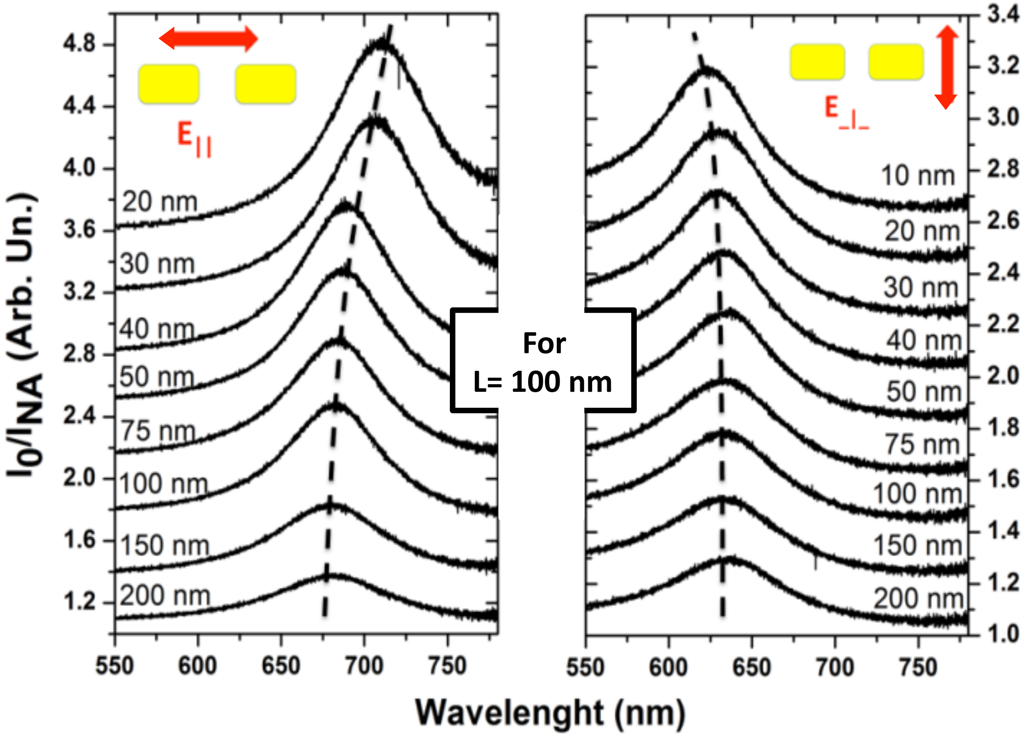


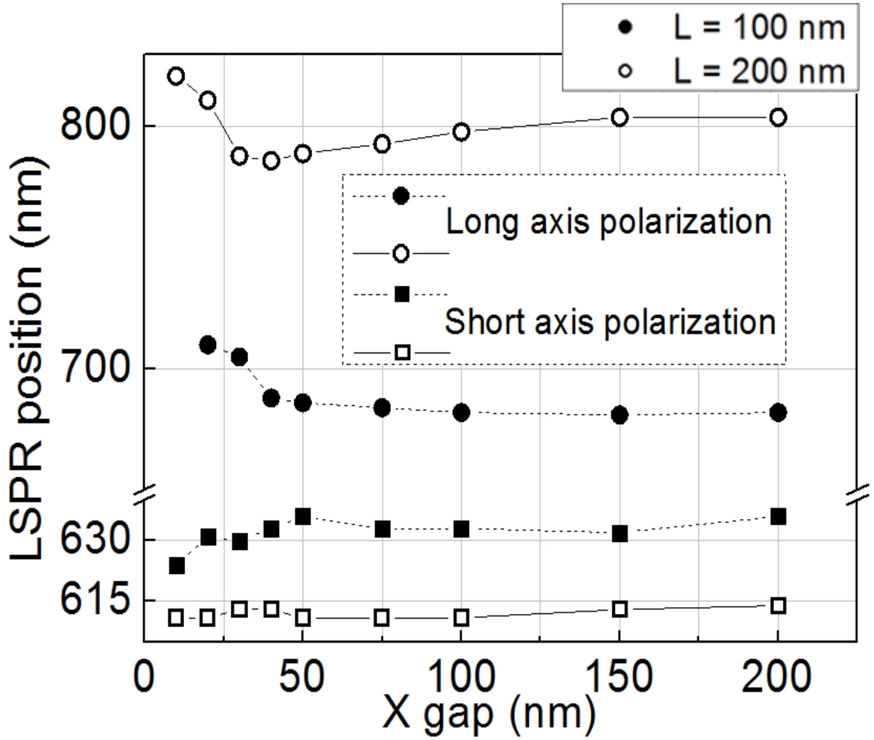




Gx (nm)	Length L (nm)	Height=Width (nm)	Dy=Dy
10,20,30,40,50, 75,100,150,200	**100**	60	200
10,20,30,40,50, 75, 00,150,200	**200**	60	200

Electromagnetic Coupling: LSPR

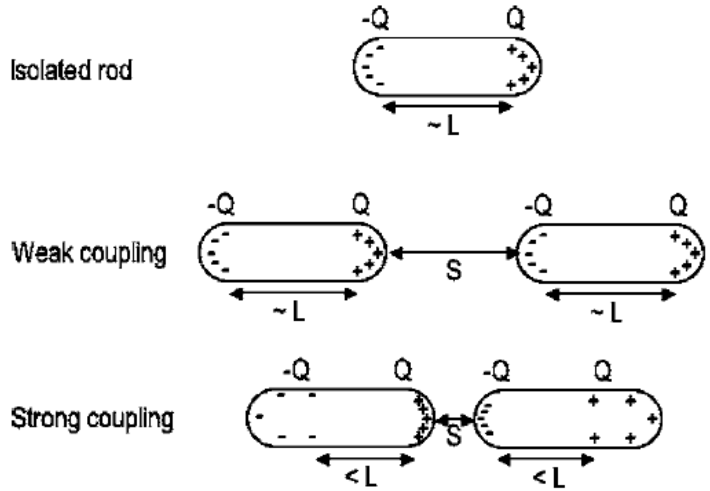




$E_{||}$ field polarization = LSPR Redshift

$E_{\_|\_}$ field polarization = LSPR Blueshift

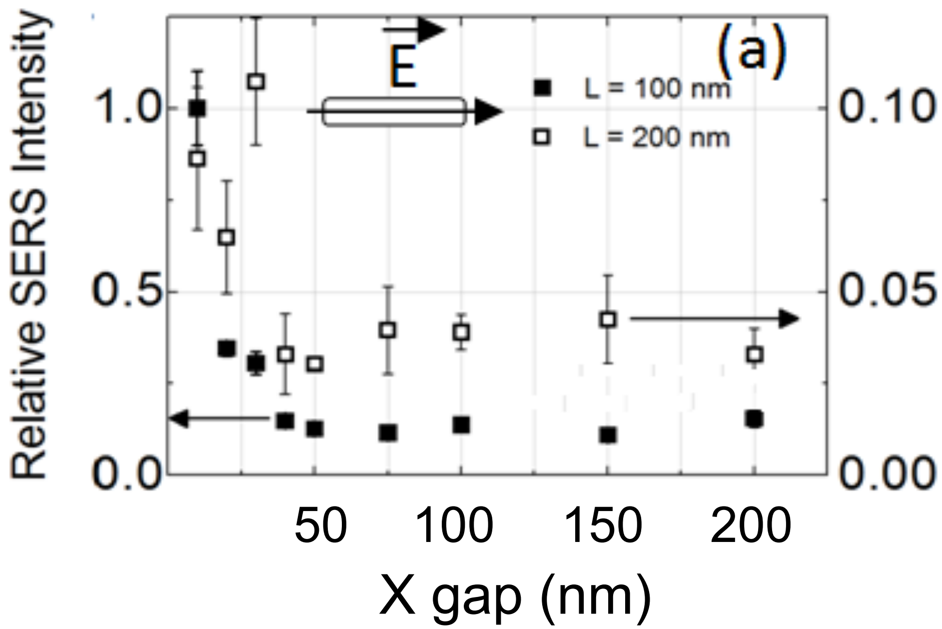
Typical of a coupling effect



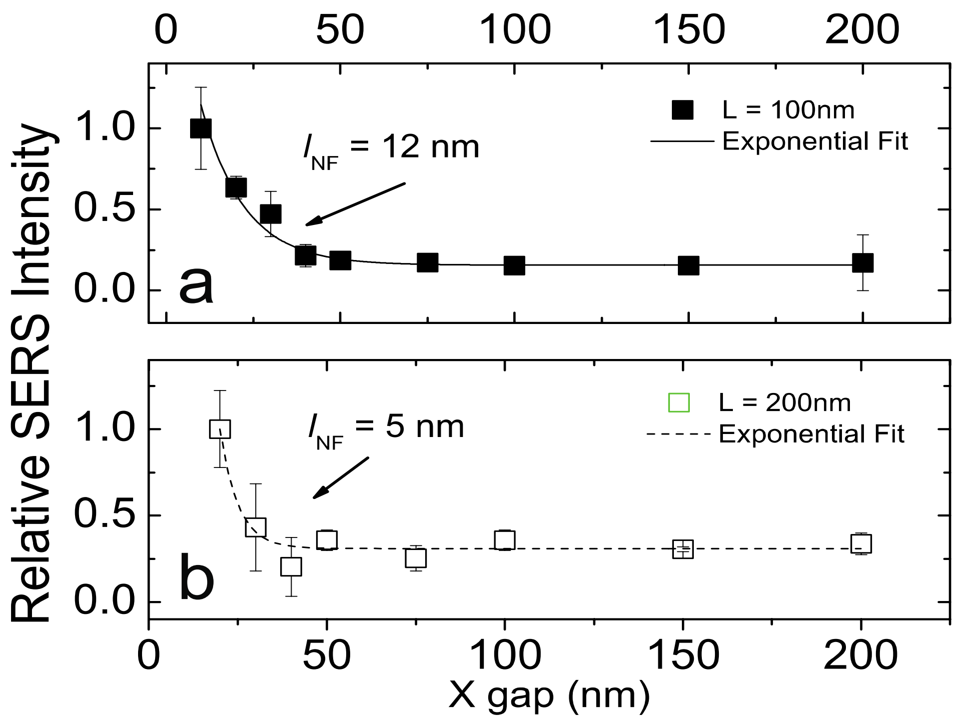
J. Aizpurua *et al, PRB 7***1, 2005, 235420**

Electromagnetic Coupling: SERS

BPE (10^{-3} M)



Methylen Blue (10^{-3} M)

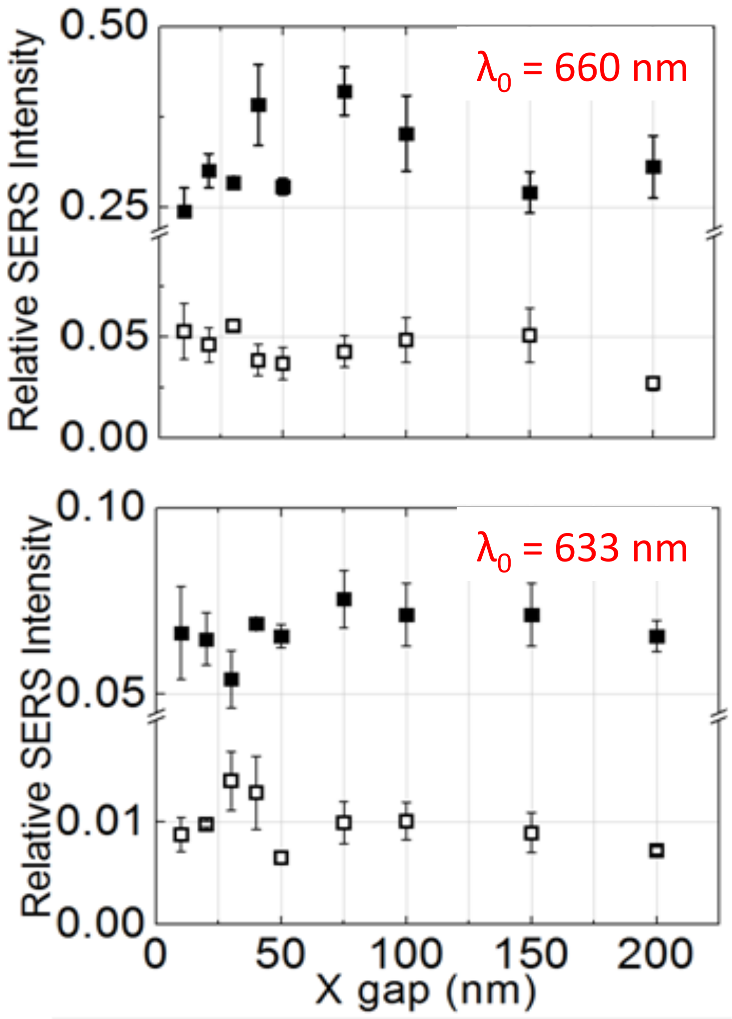


⇒ **Coupling for a lower gap and lower SERS intensity for L=200 nm**

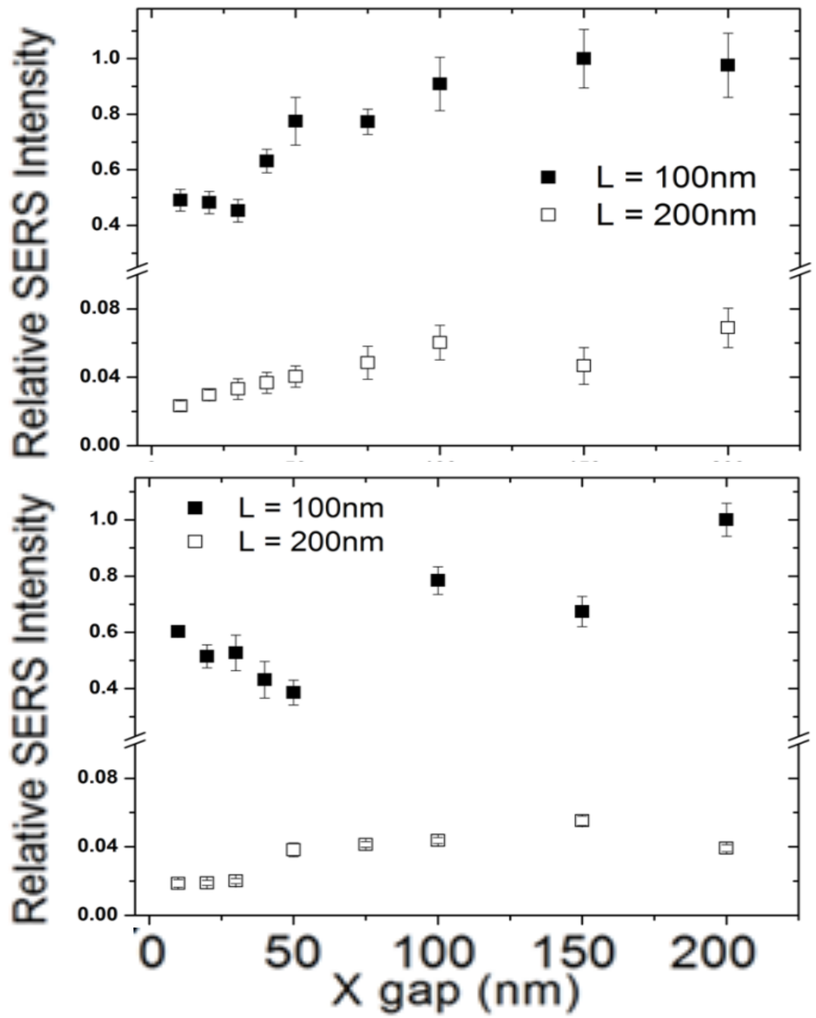
S. Kessentini *et al.*, *J. Phys. Chem. C* **118**, 3209, 2014

Electromagnetic Coupling: SERS

BPE (10^{-3} M)

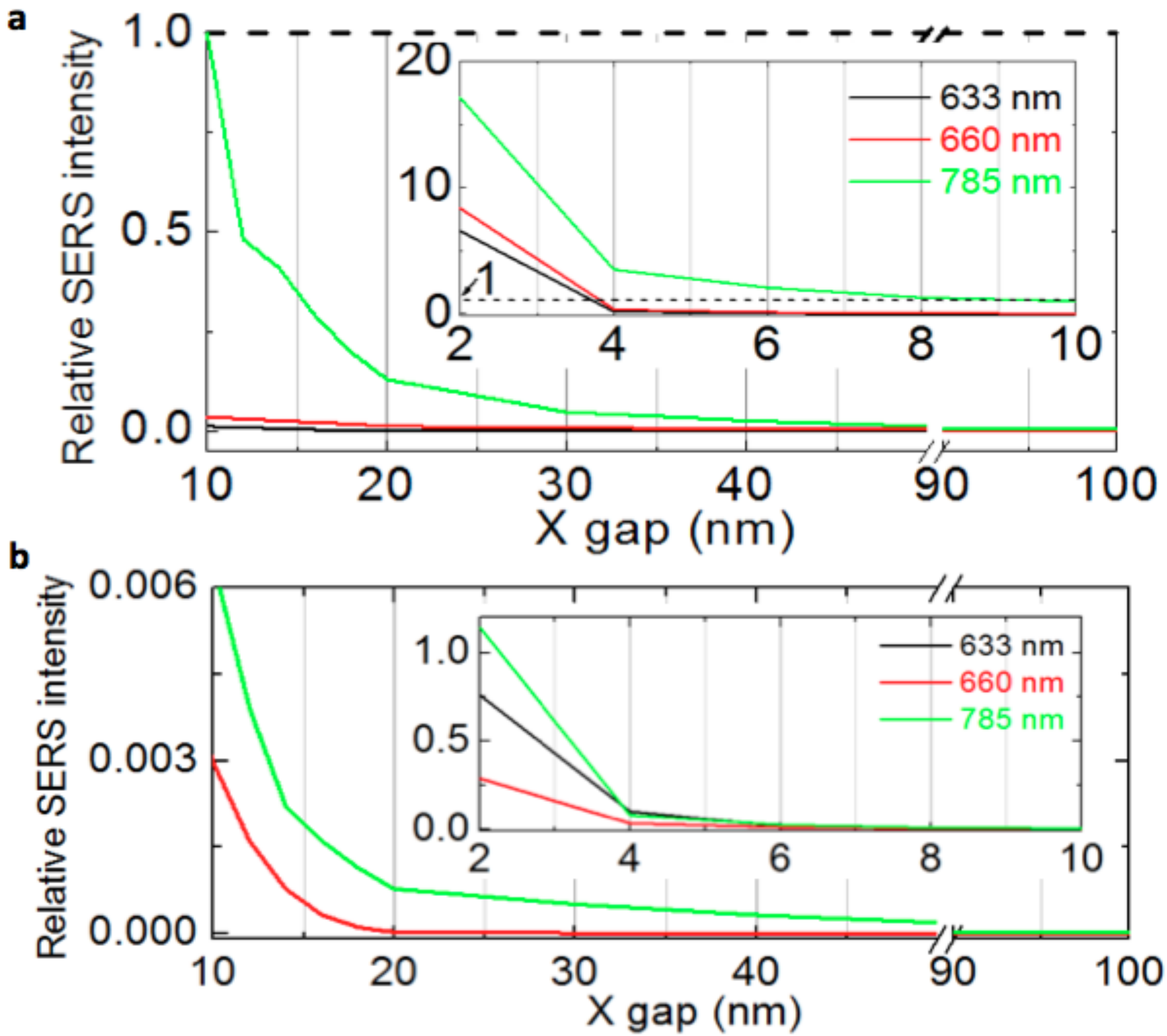


Methylen Blue (10^{-3} M)



⇒ **No coupling for excitation wavelength at 633 and 660nm**

Electromagnetic Coupling: simulation

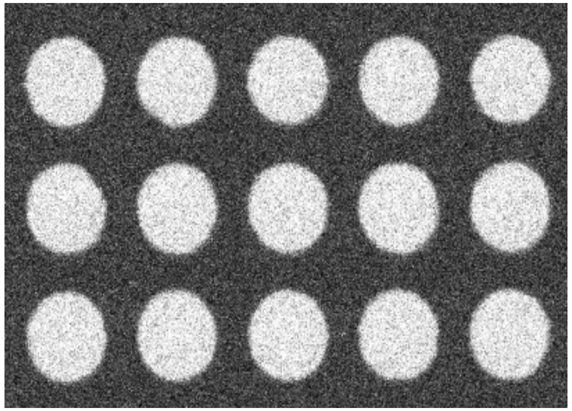


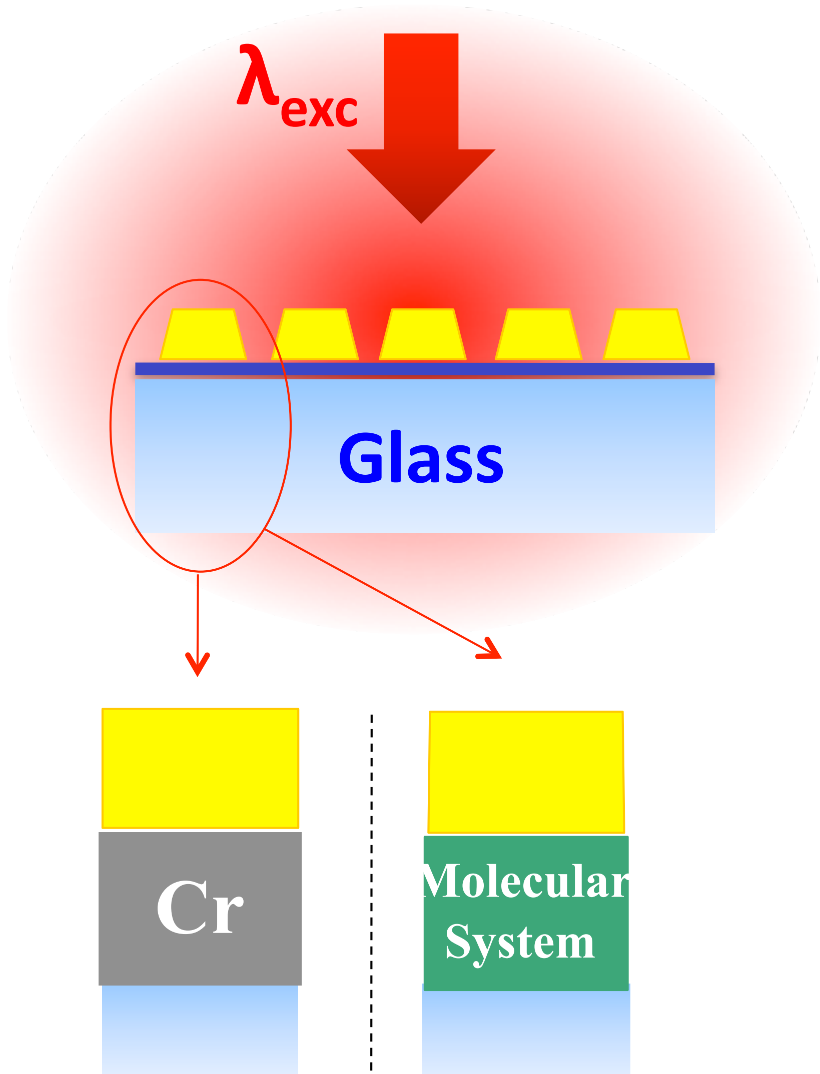
L=100 nm

L=200 nm

⇒ **Confinement of few nm for L=200 nm**

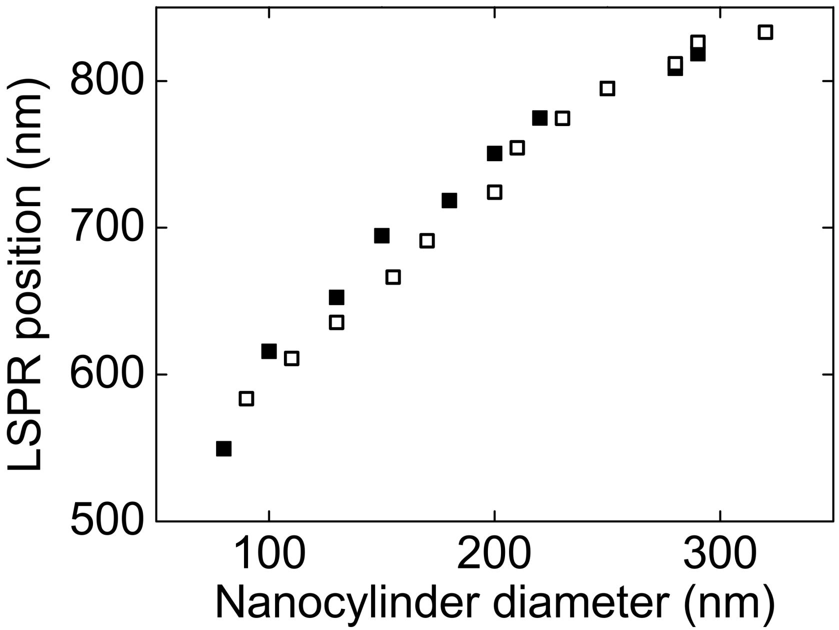
Adhesion layer

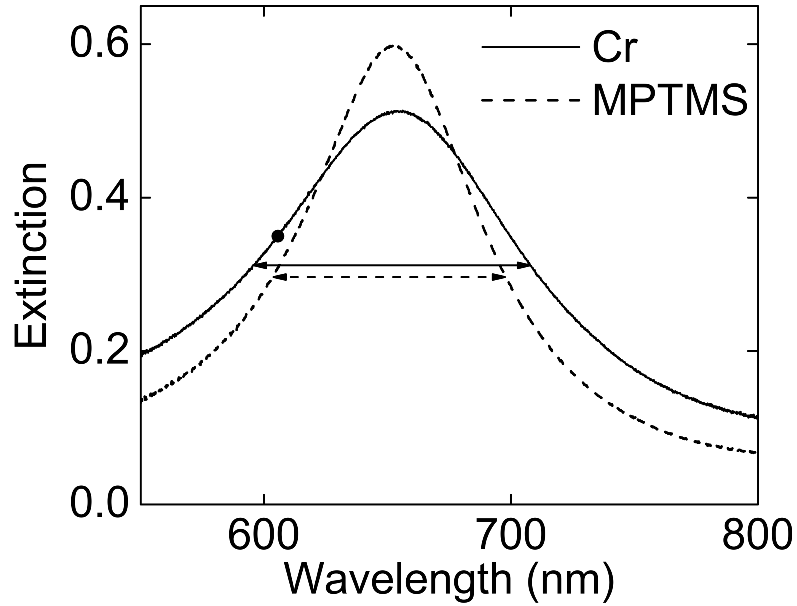


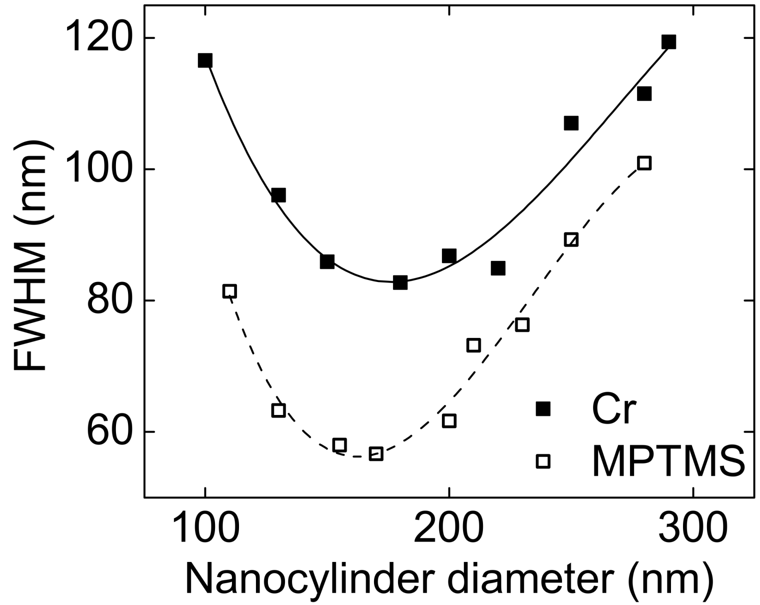


Adhesion layer
between glass and gold
⇒ Cr or MPTMS

Adhesion layer: LSPR





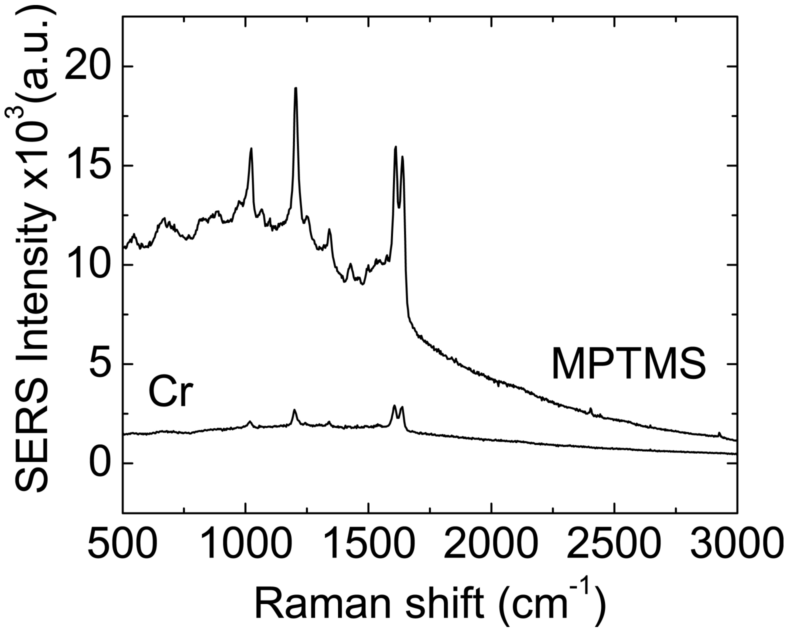


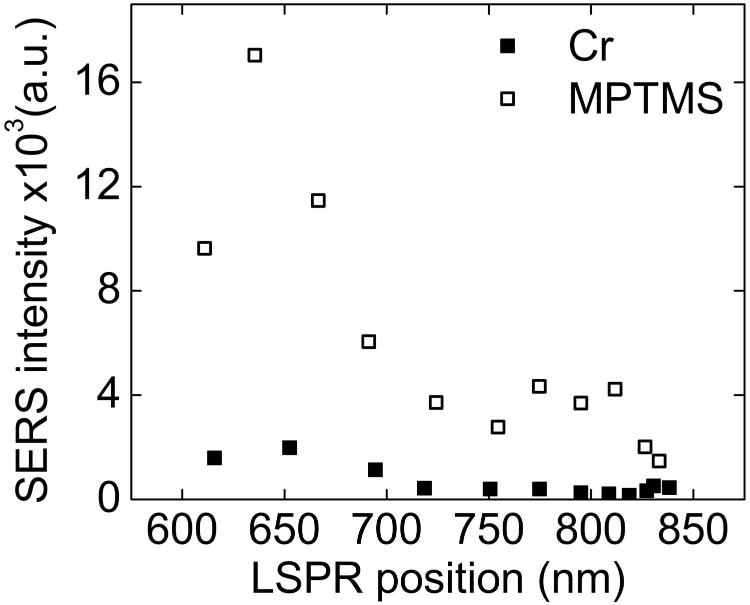
⇒ **No modification of the LSPR position**

⇒ **Improvement of the Q factor of the LSPR**

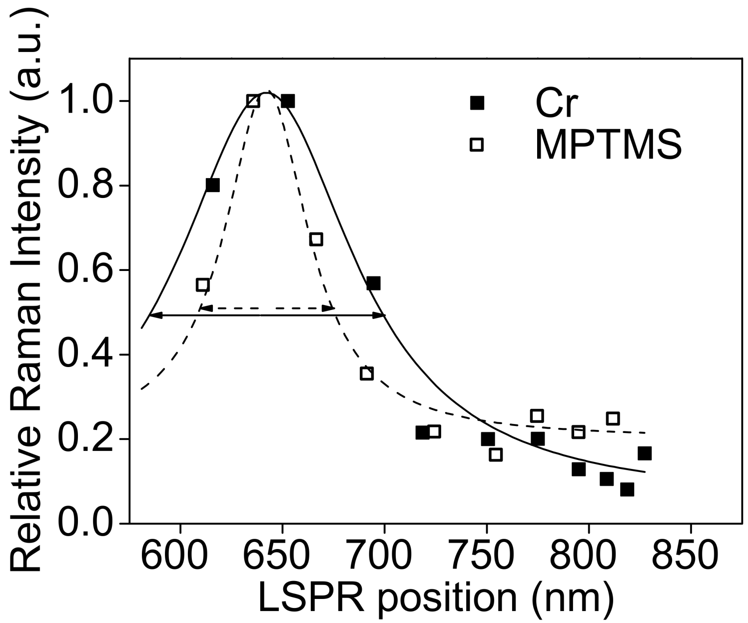
M. Lamy de la Chapelle *et al.*, *Plasmonics,* **8**, 411, 2013

Adhesion layer: SERS



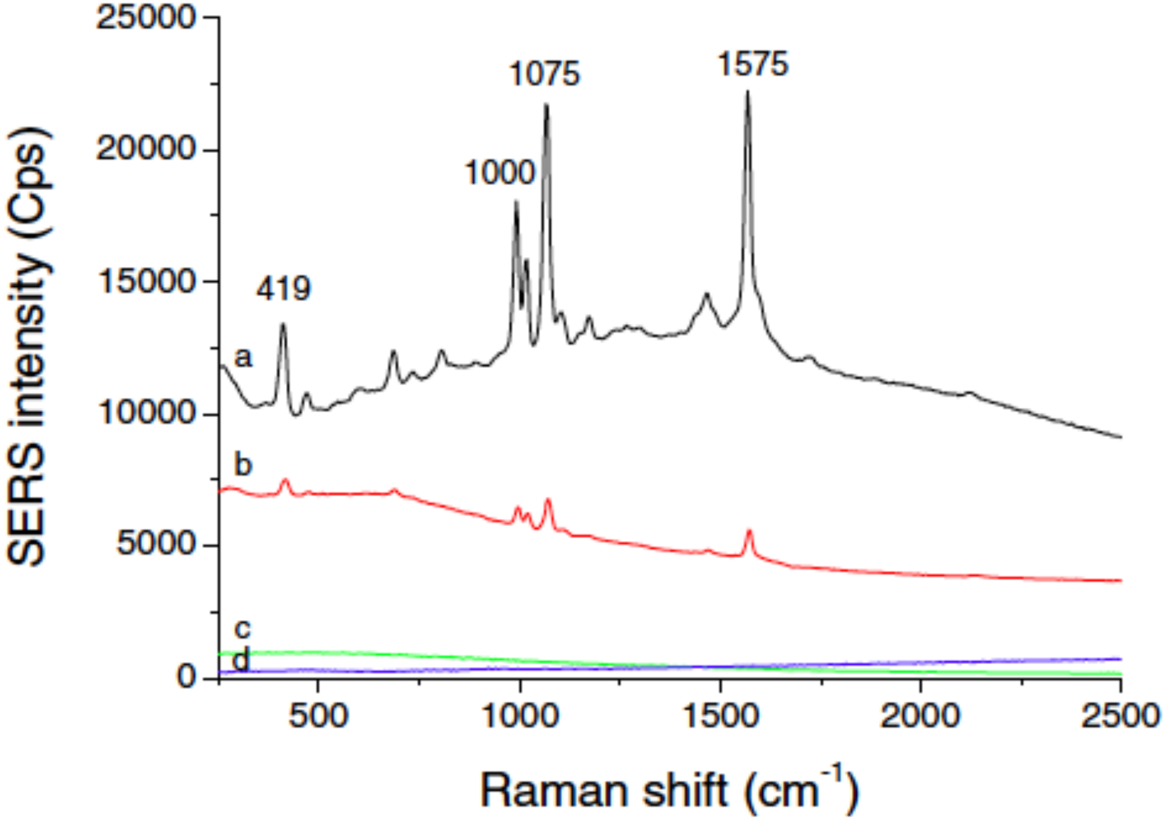


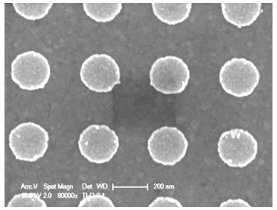
⇒ **Improvement of the SERS signal by one order of magnitude**



H. Shen *et al.*, *Optics Express* **20**, 21278, 2012

Influence of the substrate : SERS





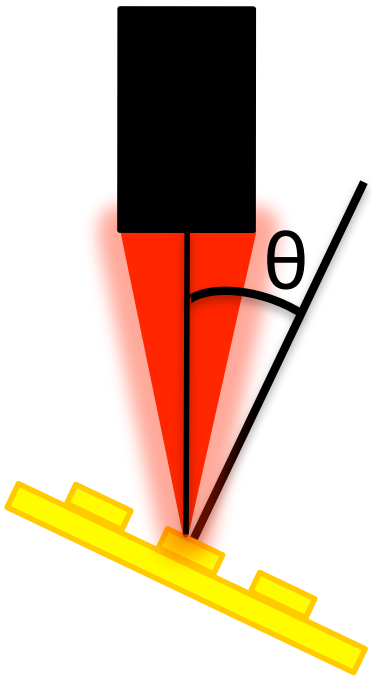
P = 400 nm
Ø = 200 nm

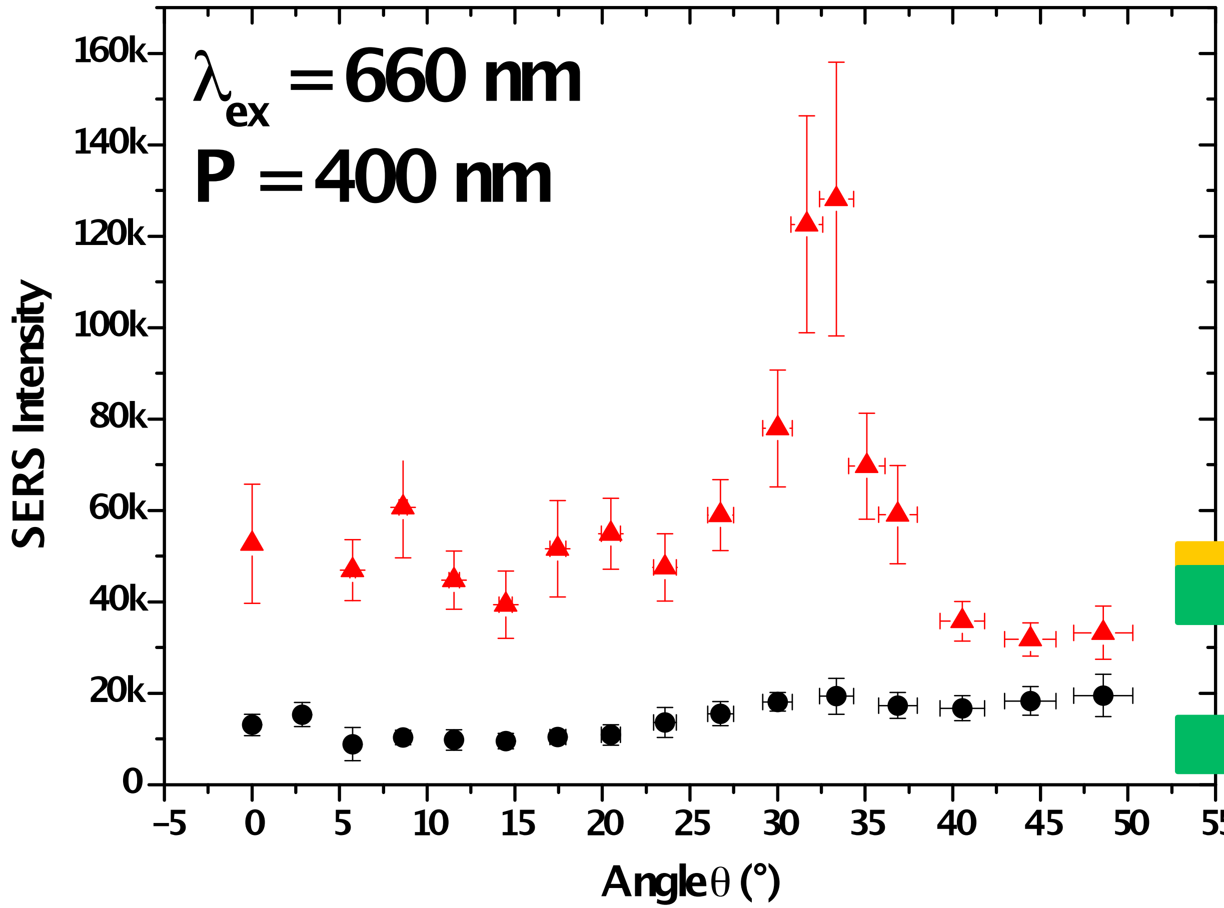
⇒ **SERS intensity one order of magnitude higher with gold film**

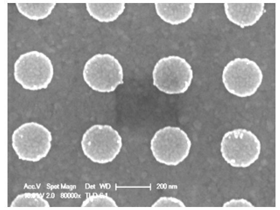
J.F. Bryche *et al.*, *Plasmonics* **11**, 601, 2016

Influence of the substrate : SERS

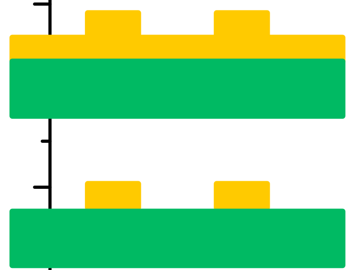
10x Obj.
N.A. = 0.25







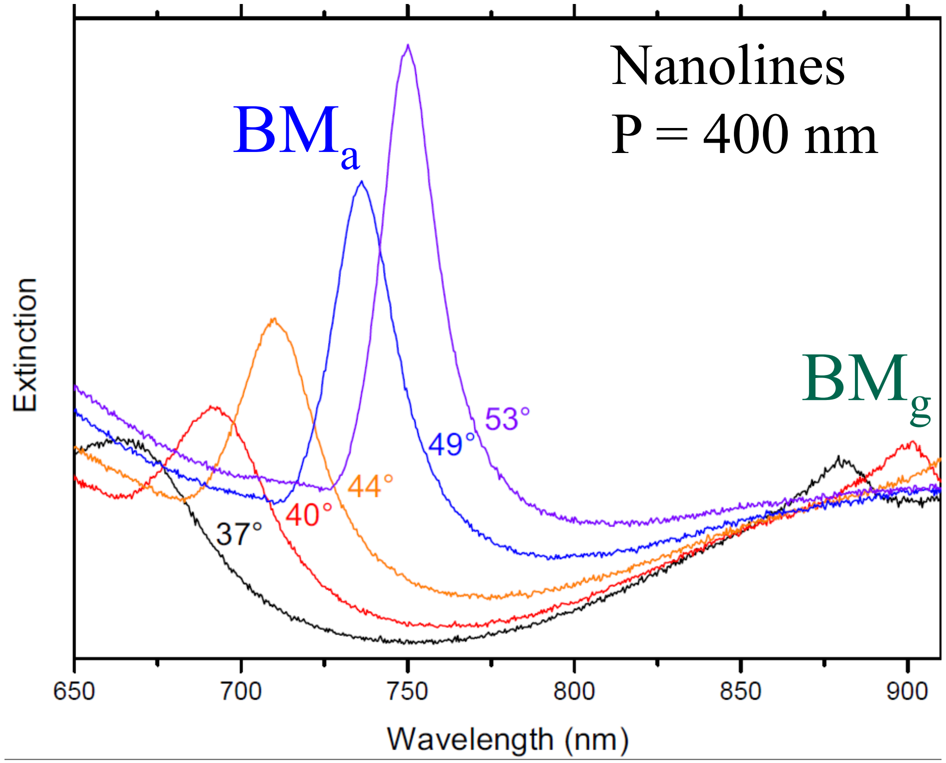
Ø = 200 nm
1075 cm^{-1}

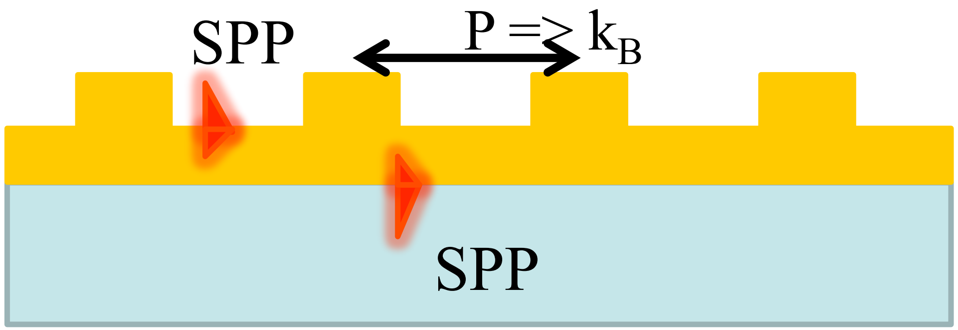


Gold film => angular dependence
Without gold film => no dependence

R. Gillibert *et al.*, *Nanotechnology* **27**, 115202, 2016

Influence of the substrate : Plasmon





$$k_{BM} = k_{spp} \pm k_B$$

$$= k_0 \sin\theta \left\{ \text{Bragg conditions} \right\}$$

$k_{spp}^{a,\,g}$ Gold/Air or Gold/Glass

⇒ **Constructive interferences when** $k_{spp} \pm k_B = k_0 \sin\theta$

⇒ **Excitation of a Bragg Mode (BM$_a$ and BM$_g$)**

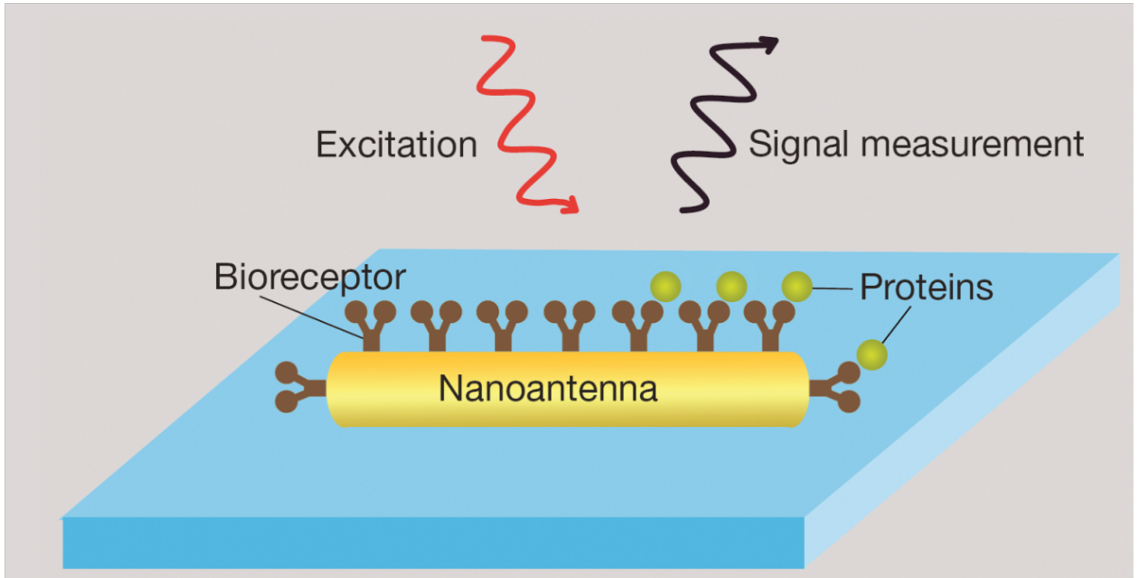
Conclusions

1. Optimization of the gold nanostructure
   I. LSPR rules depends on shape and excitation wavelength
      - Far field / Near field
      - Tip effect
   II. Coupling
   III. Nanostructure environment

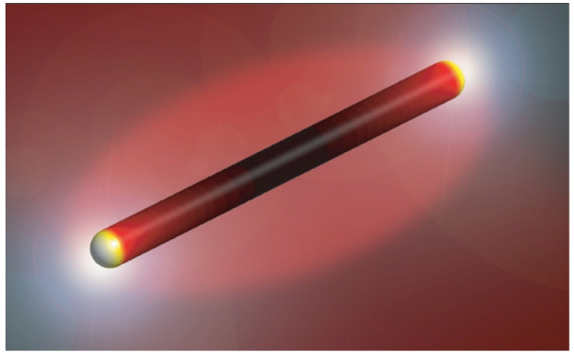
2. Gold nanostructure arrays
   ⇒ Reproducible SERS nanosensor
   ⇒ Sensorchip

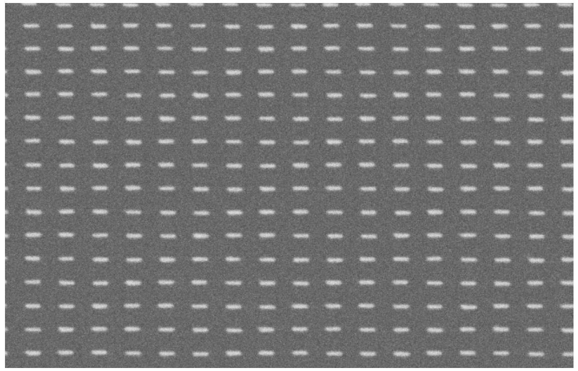
SERS sensor

Sensor principle



Nanosensor principle applied to protein detection

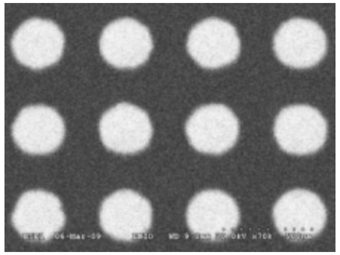




4 steps approach

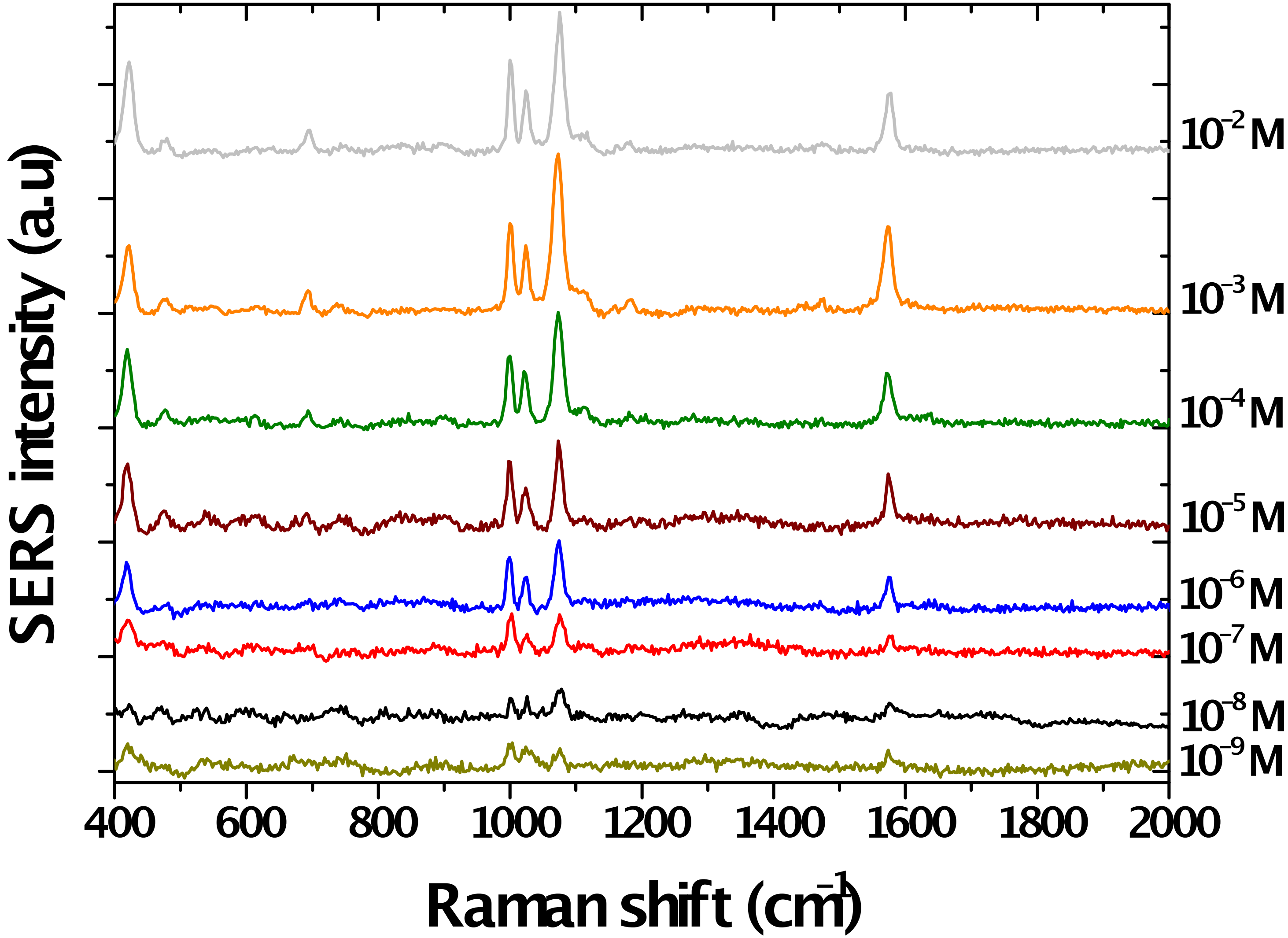
- 1. Raman spectrocopy: **Label Free detection**
- 2. Nanoparticle: **High sensitivity**
- 3. Bioreceptor: **High molecular selectivity**
- 4. Nanoparticle array: **High reproducibility**

Sensor limit of detection



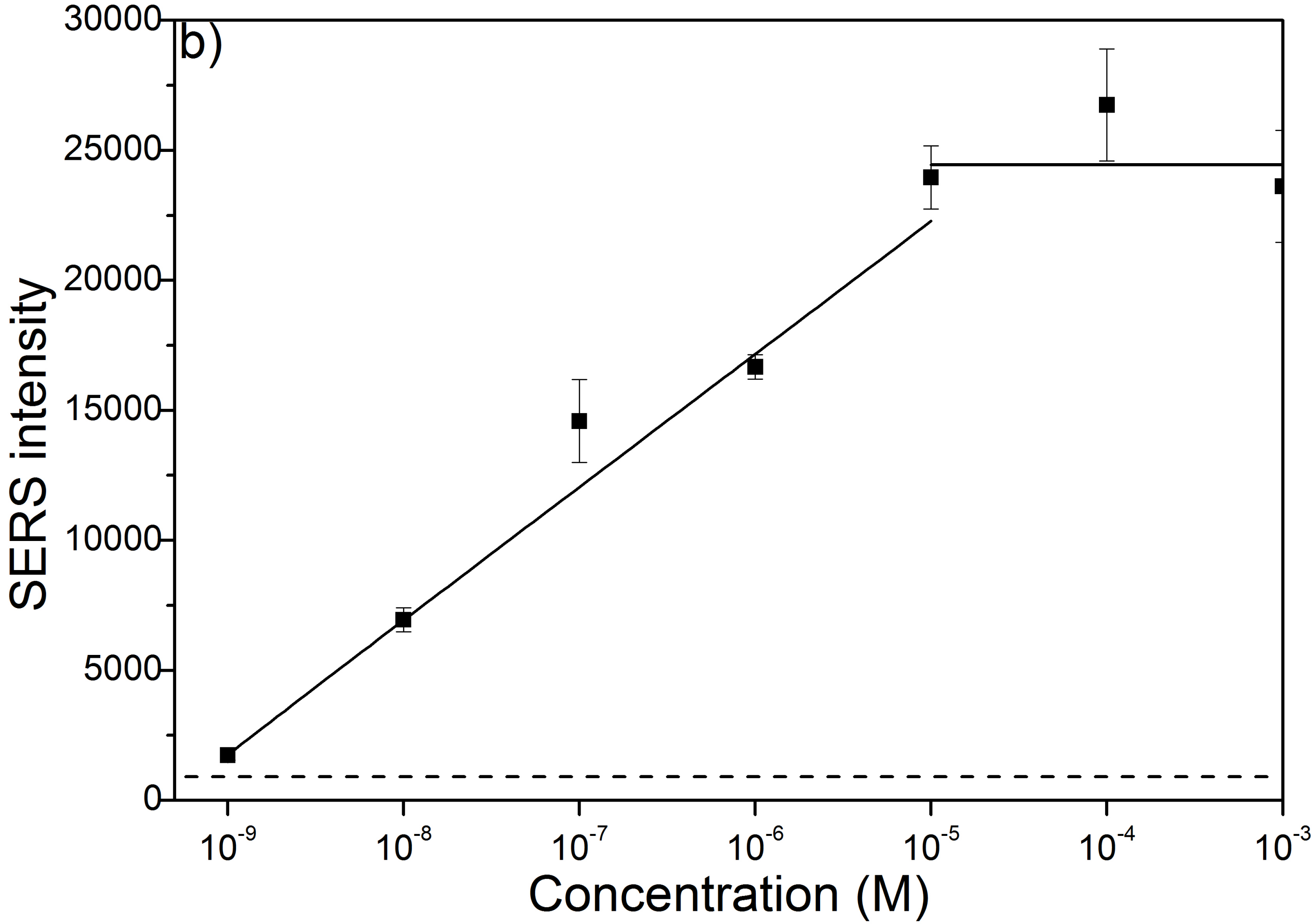
Ø = 190 nm

Benzenethiol
λ_{exc} = 785nm



Sensor limit of detection

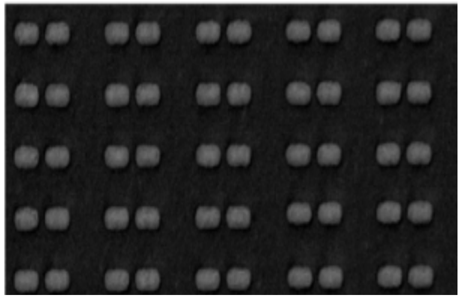
λ=785nm

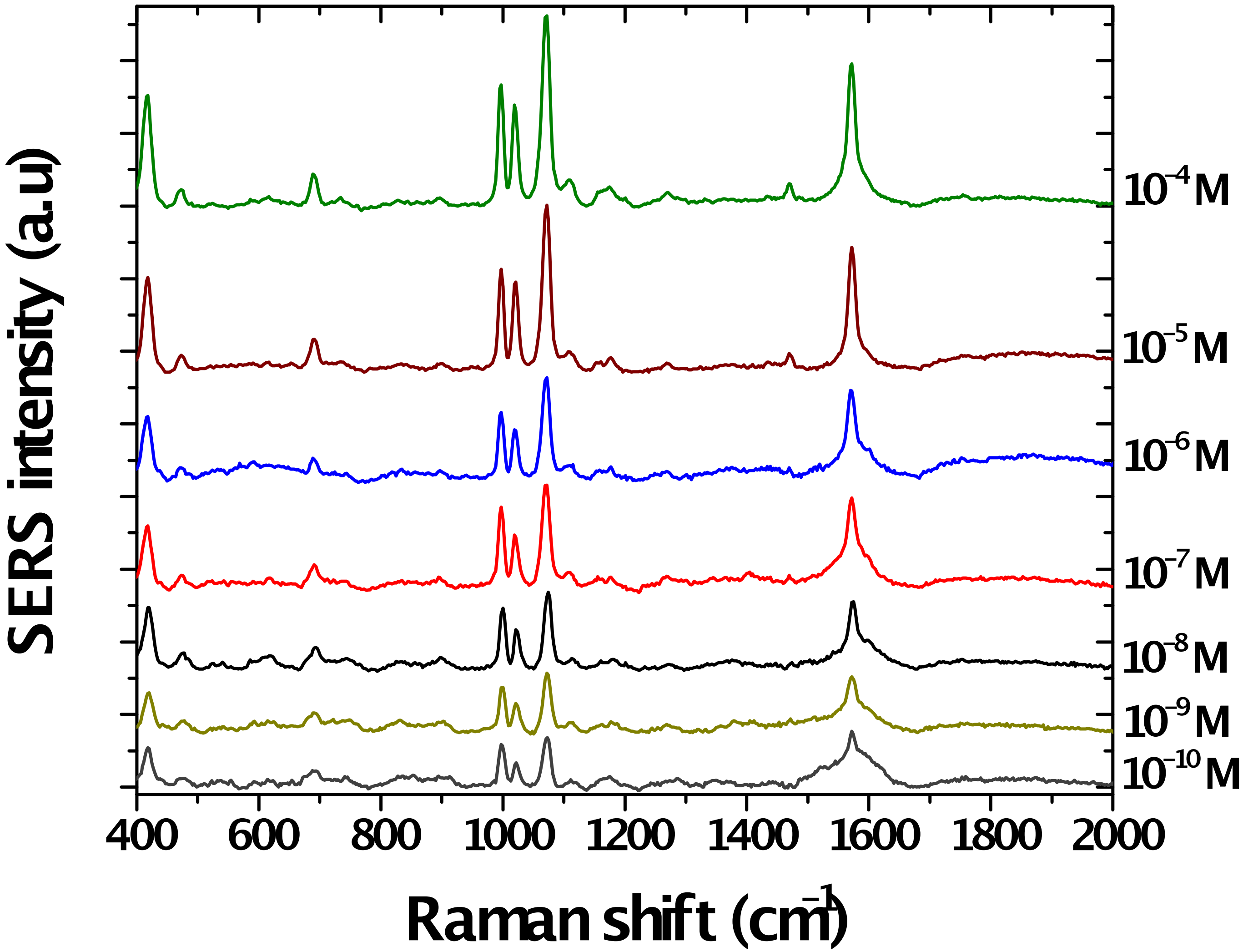


⇒ **Surface saturation at 10 µM/L**

⇒ **At 785 nm, LOD = 1 nM/L**

Sensor limit of detection

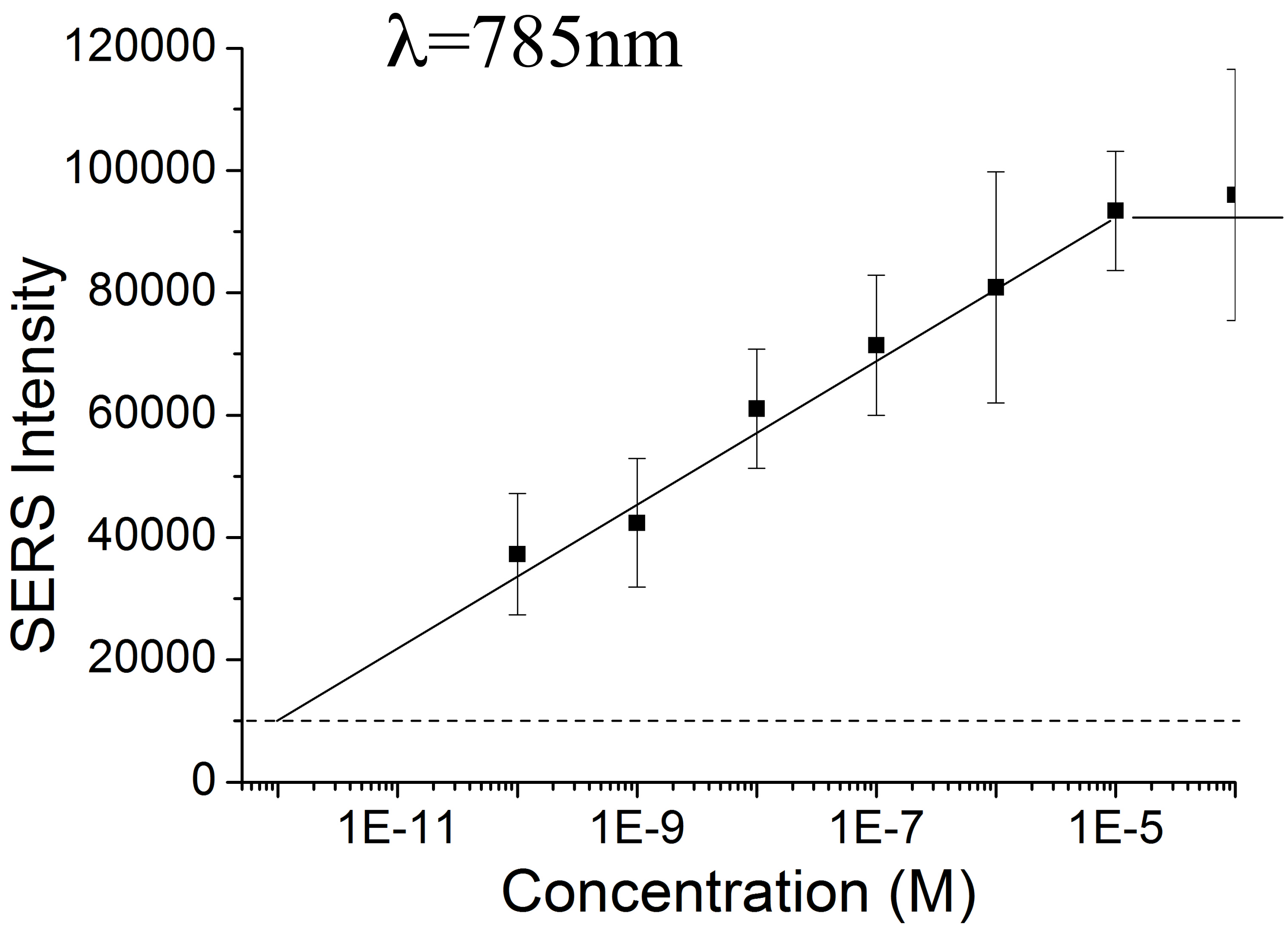




Length = 100 nm
Gap = 20 nm

Benzenethiol
λ_{exc} = 785nm

Sensor limit of detection

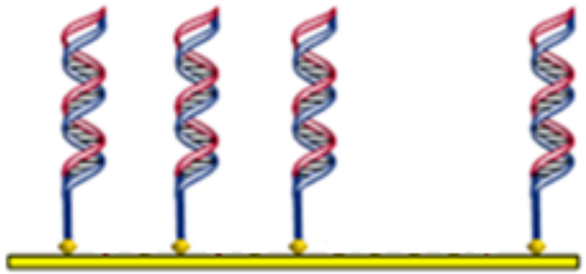


⇒ **At 785 nm, LOD = 1 pM**

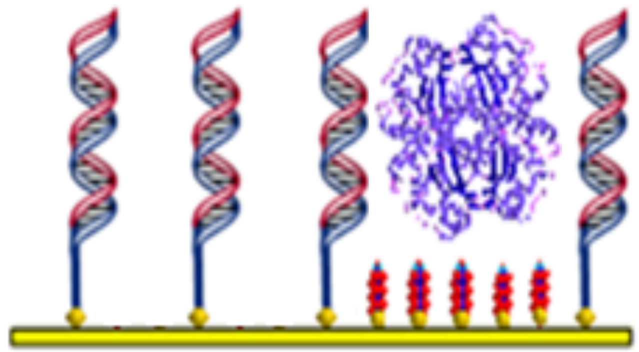
⇒ **Dimers are two orders of magnitude more sensitive**

MnSOD Detection

- Cleaning samples with UV ozone and ethanol
- Aptamer:
  deposit **1h** of **c=100 ng/µL**
  wash with KCl buffer **2x5 min**



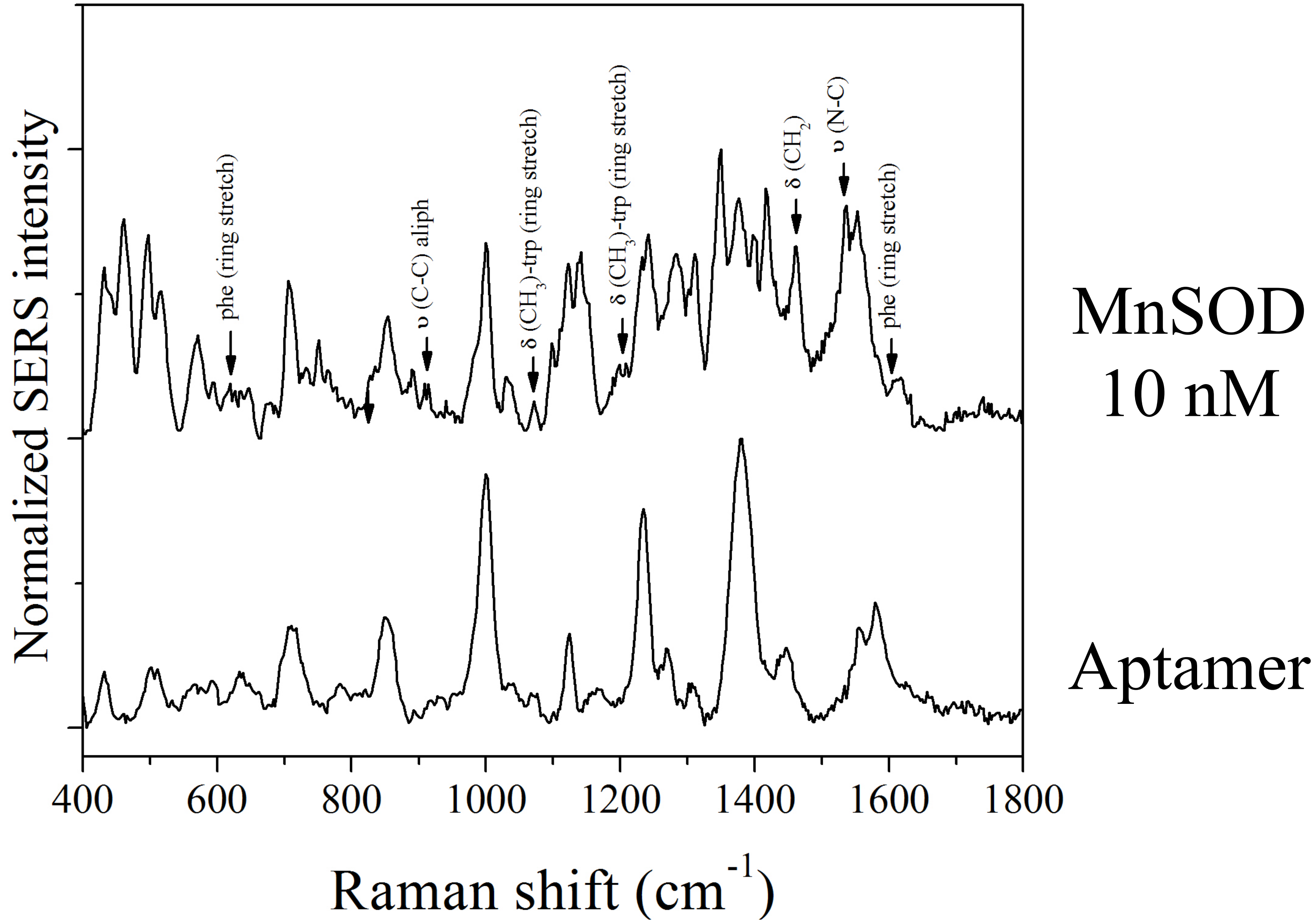
- Blocking molecule :
  6-Mercapto-1-hexanol
  incubation **1h** of **c=2 mM**
  wash with ethanol



- MnSOD sample: incubation **1h**
  Wash with PBS buffer

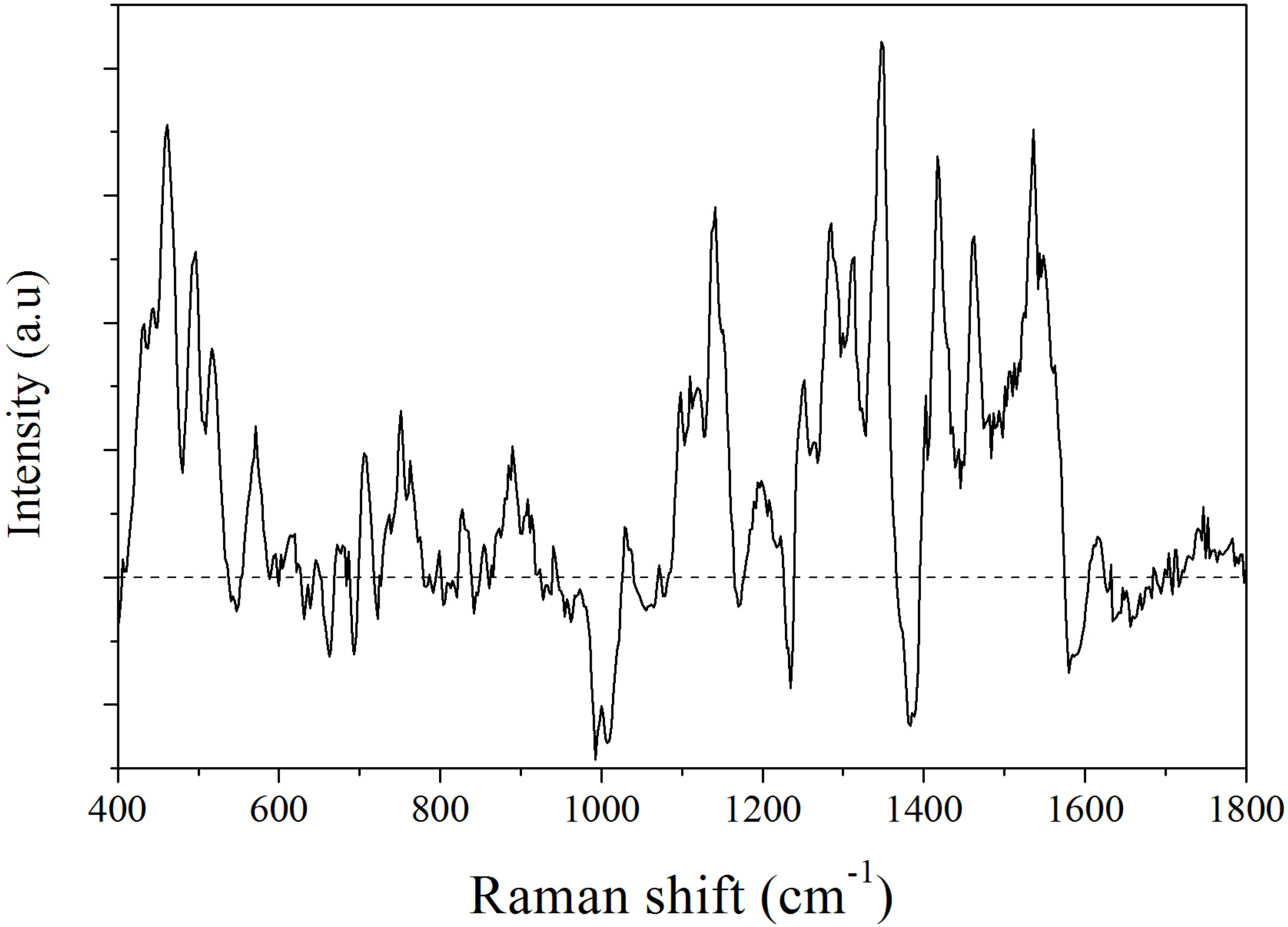
MnSOD Detection: SERS

Laser : **660** nm for ϕ=**140** nm (10s, 0,1 mW)



MnSOD Detection: SERS

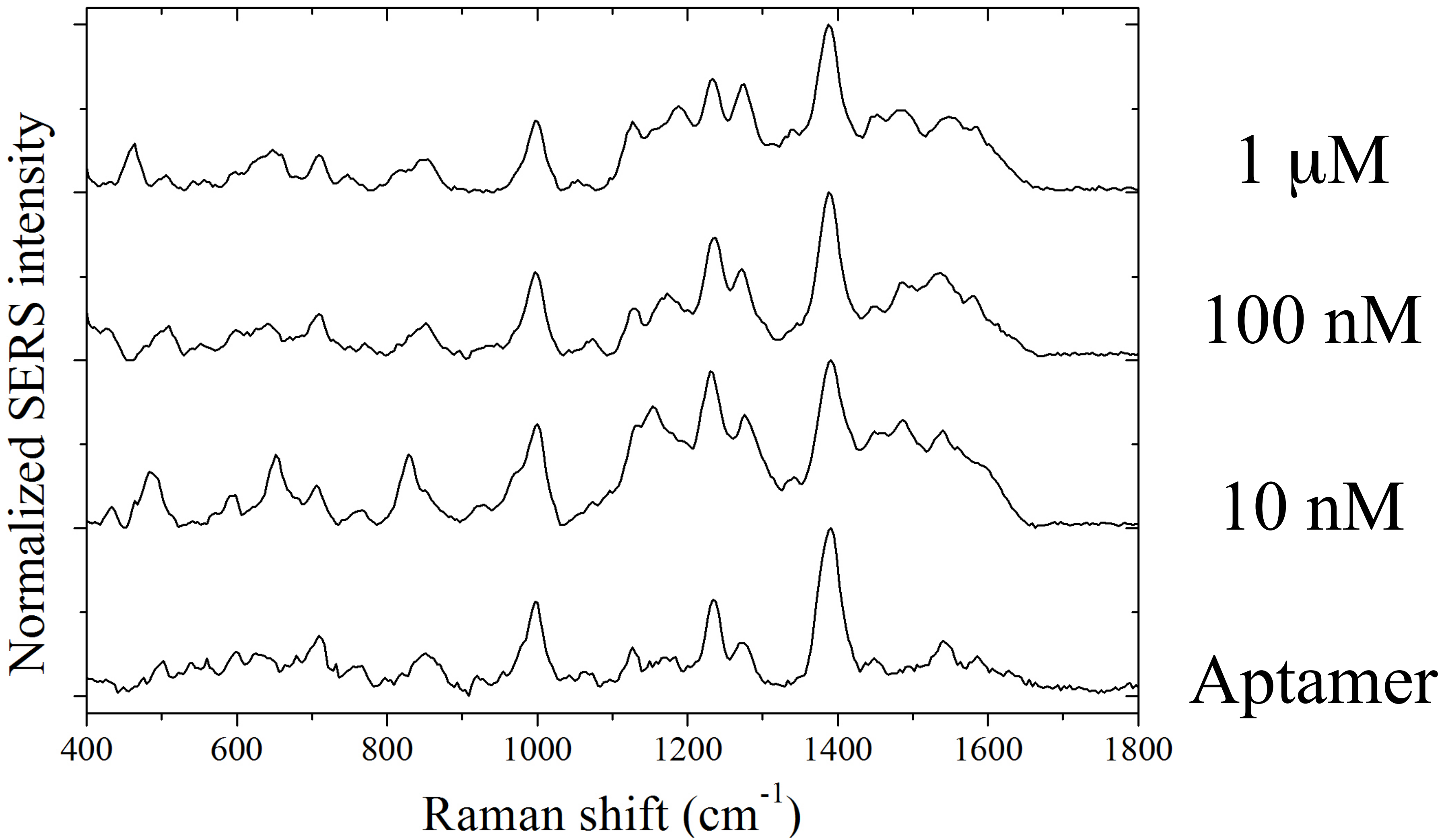
Laser : **660** nm for ϕ=**140** nm (10s, 0,1 mW)



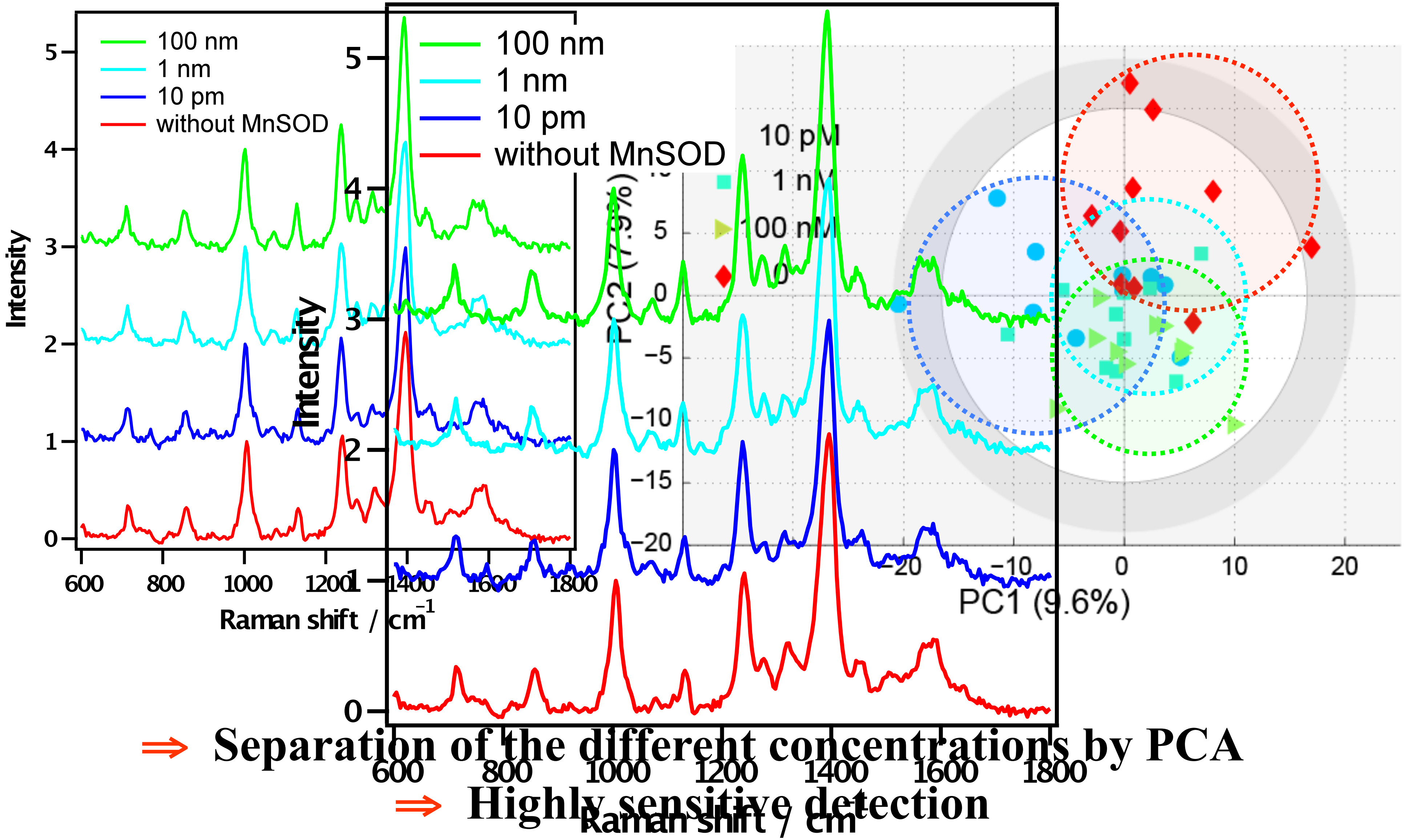
C.David *et al.*, *Vib. Spect.* **62**, 50, 2012

MnSOD Detection: SERS

Laser : **660** nm for ϕ=**140** nm (10s, 0,1 mW)



MnSOD Detection: PCA

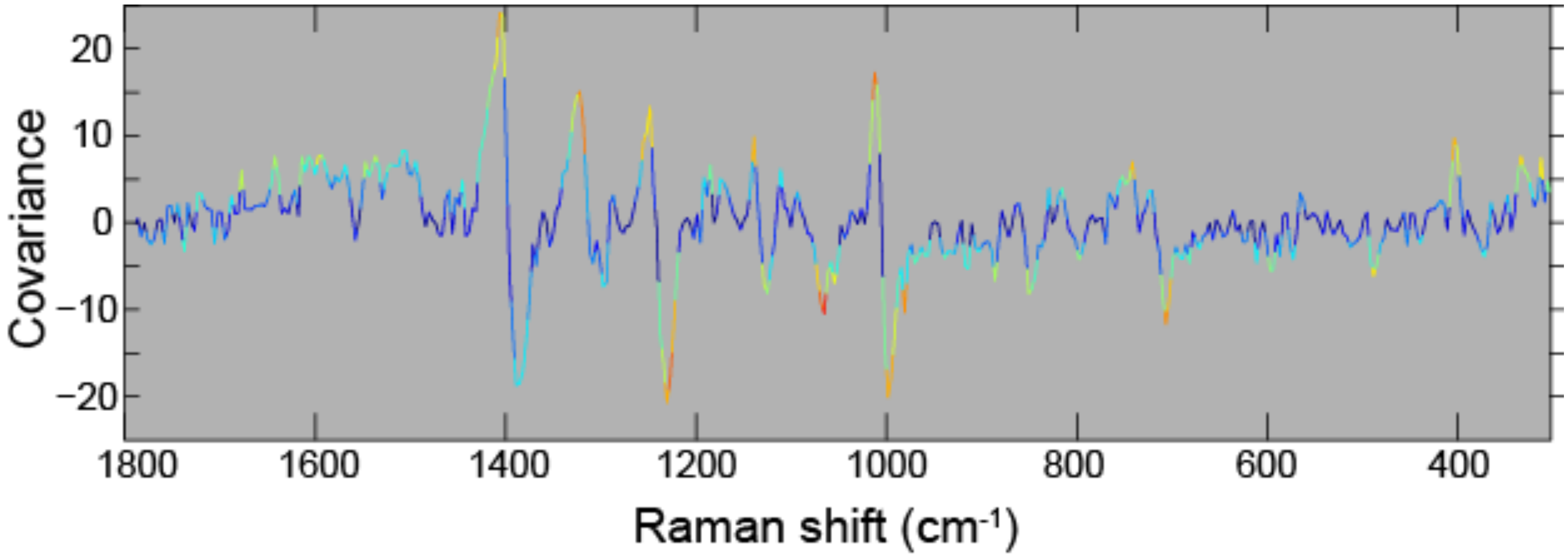


⇒ **Separation of the different concentrations by PCA**

⇒ **Highly sensitive detection**

MnSOD Detection: PCA

Observation of the spectral variation after the MnSOD deposition

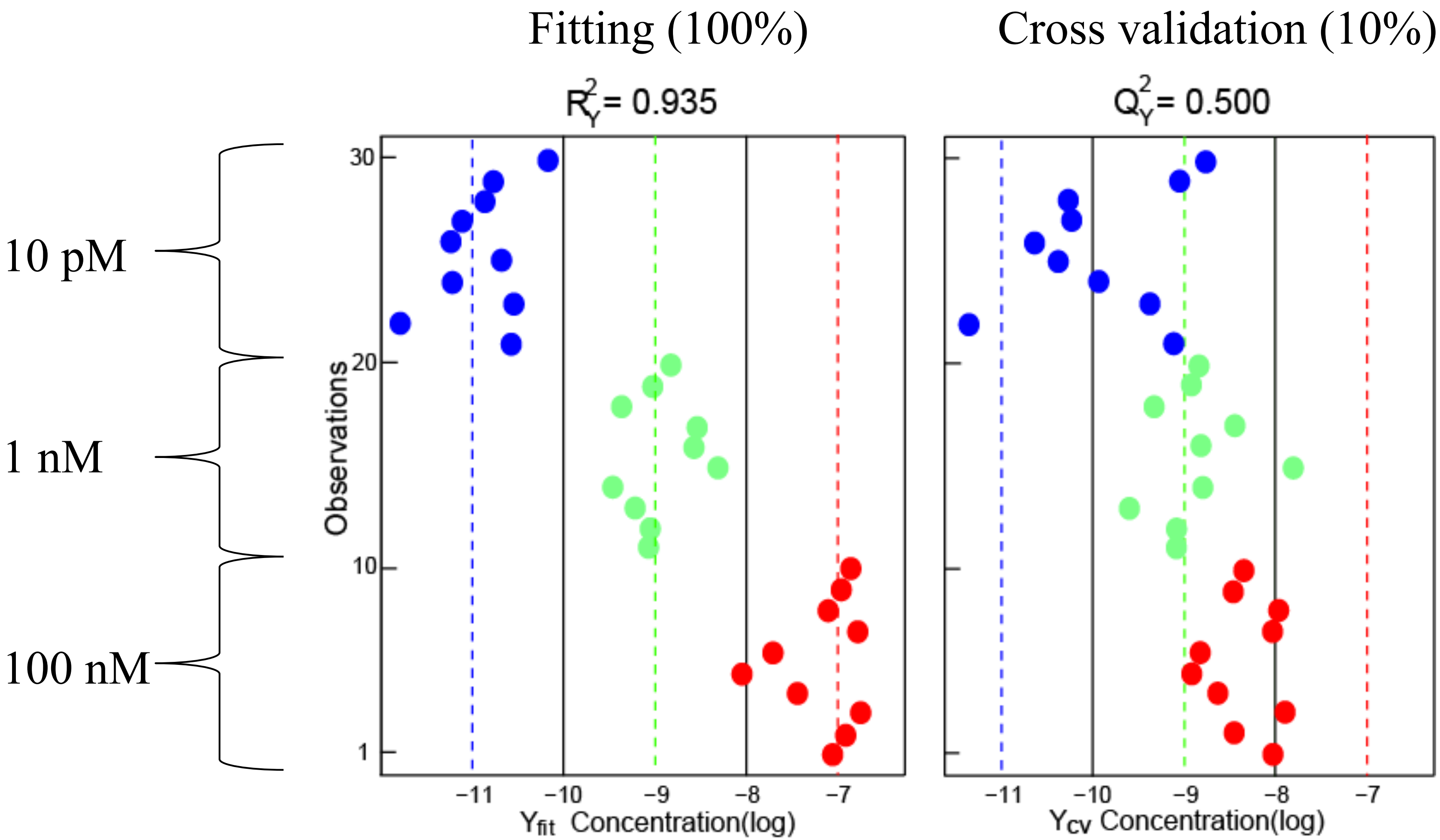


⇒ **Shift of the aptamer bands**

⇒ **Modification of the aptamer conformation with MnSOD interaction**

MnSOD Detection: PLS

Partial Least Square regression: 30 spectra / 10 per concentration



⇒ **Discrimination of the different concentrations**

Conclusions

1. Detection limit at the picomolar level

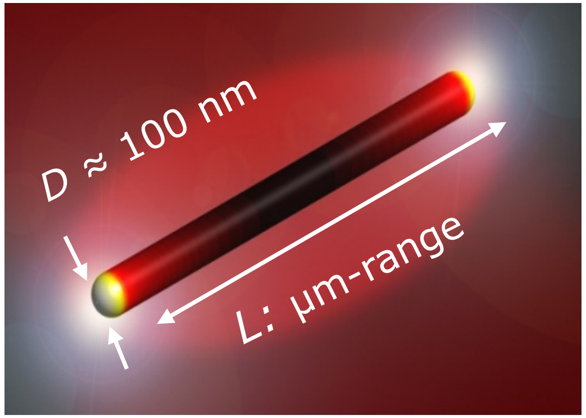
2. Detection of proteins at low concentration

3. Reproducible SERS nanobiosensor

Surface Enhanced IR Absorption

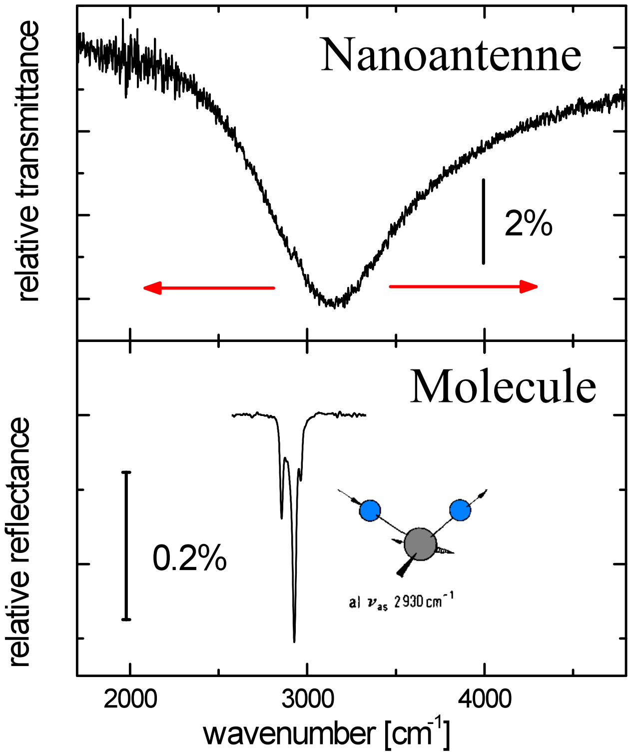
Surface Enhanced IR Absoprtion

Principle : Exploit the near field enhancement created at the nanoantenna vicinity



Nanoantenna
- Micrometric length
- Nanometric width

IR spectra



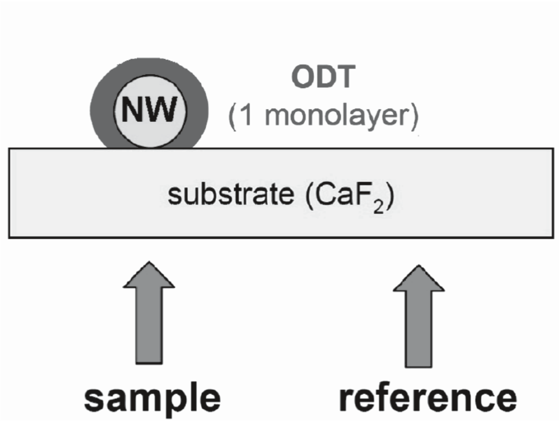
Surface plasmon

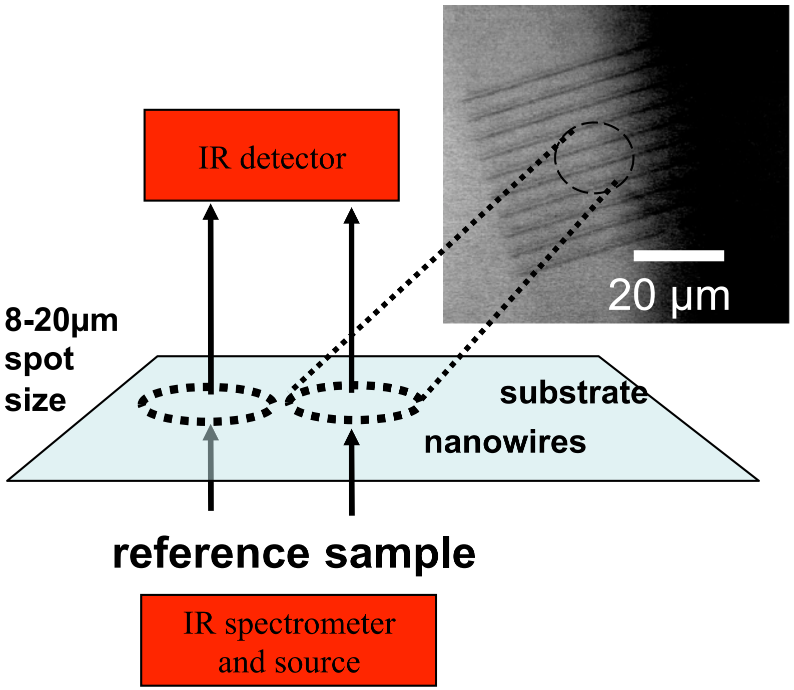
Vibration modes

⇒ **Coupling between the molecular vibration and the surface plasmon**

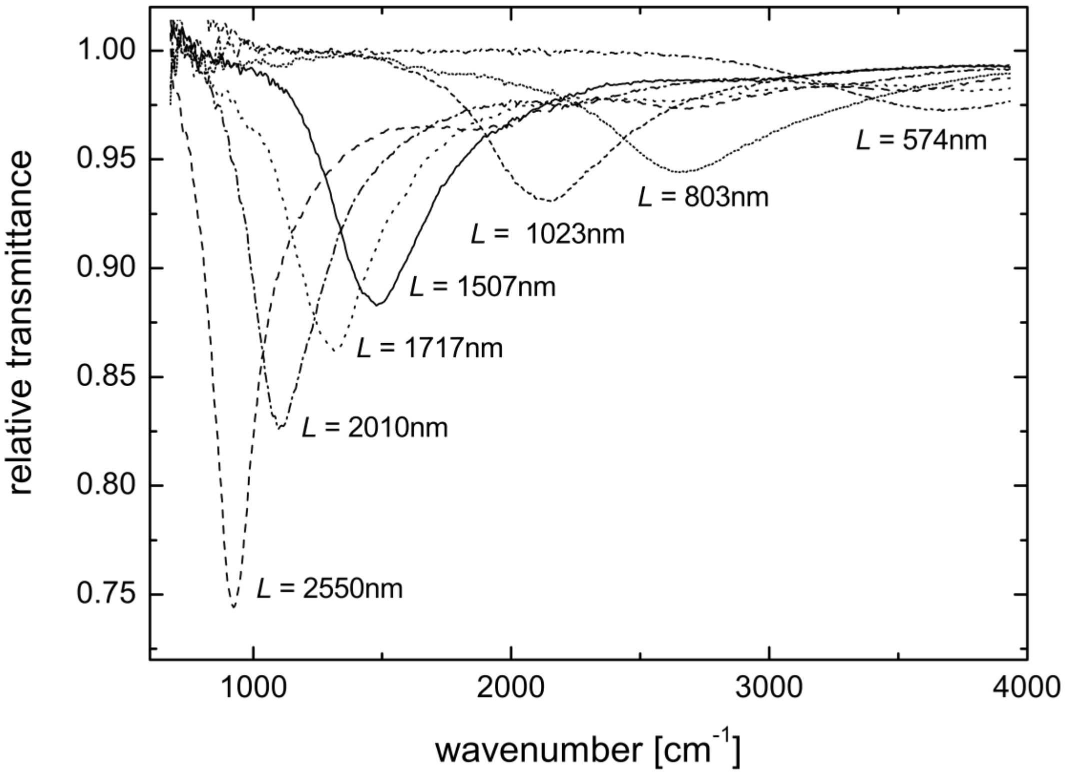
Surface Enhanced IR Absoprtion

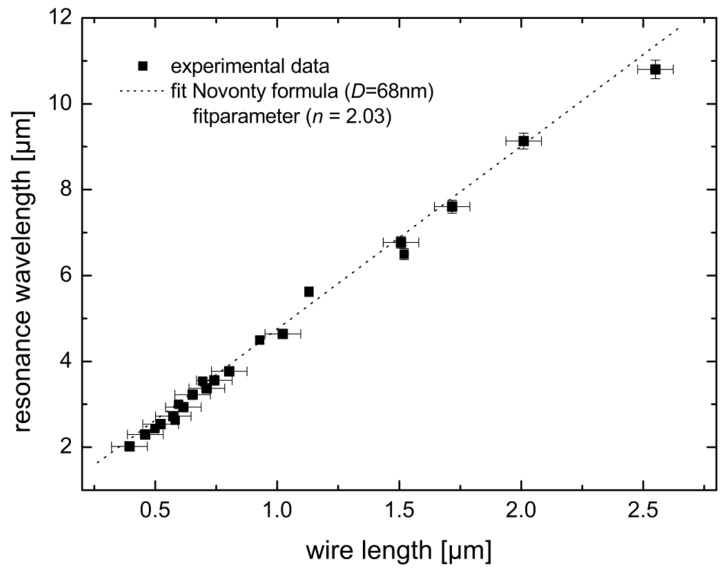
Measurement in transmission with an IR microscope





Surface plasmon in IR





$$2L = a(D, n_{eff}, \lambda_P) \cdot \lambda_{res} \cdot l$$

λ_{res} : *resonant wavelength*

l : *order of modes*

n_{eff} : *effective refractive index*

λ_p : *plasma wavelength*

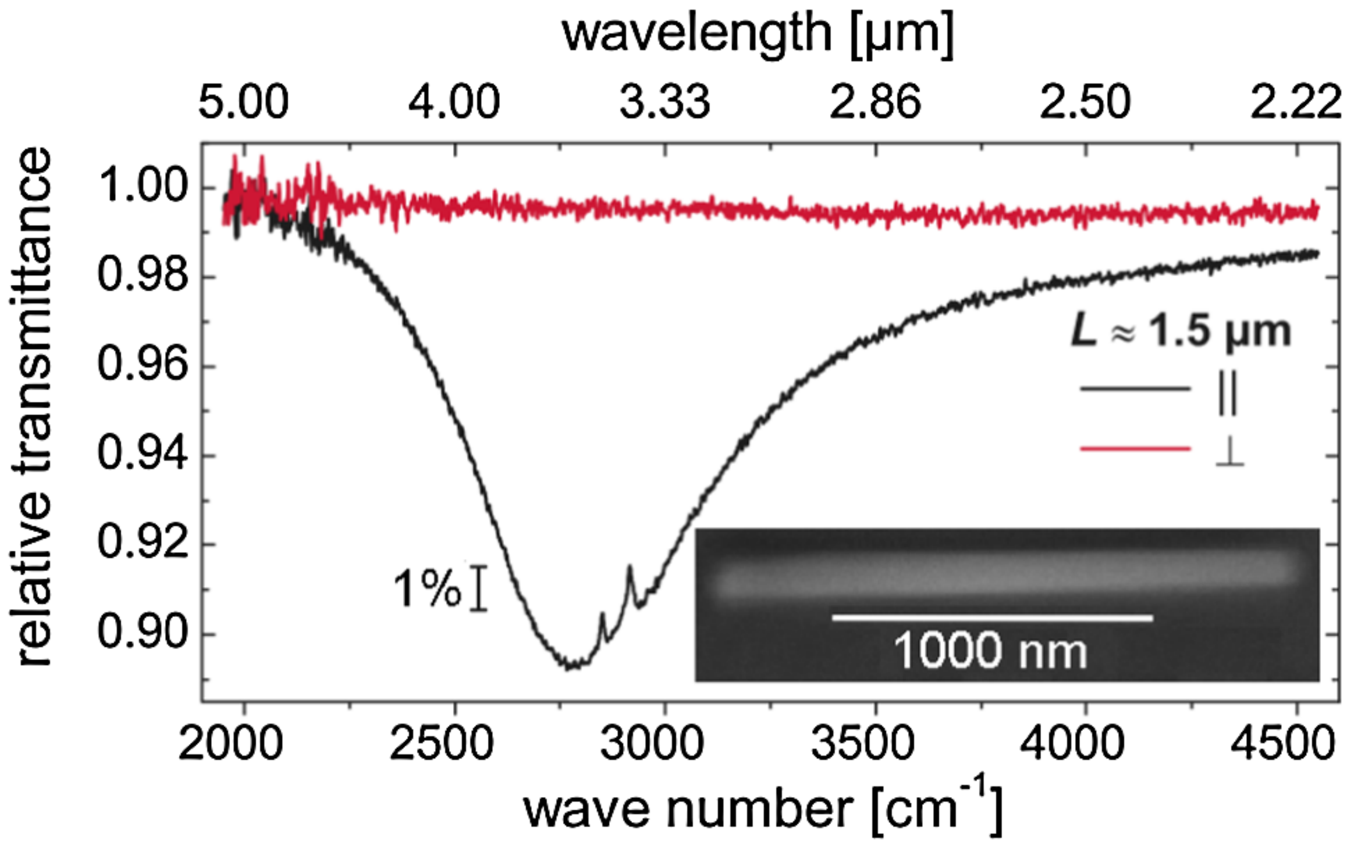
Gold nanowires on ZnS (EBL)
Width and height = 60 nm
Gap = 73 nm

F. Neubrech, et al, Appl. Phys. Lett. 93, 163105, 2008

L. Novotny, PRL 98, 266802 (2007)

Detection by SEIRA

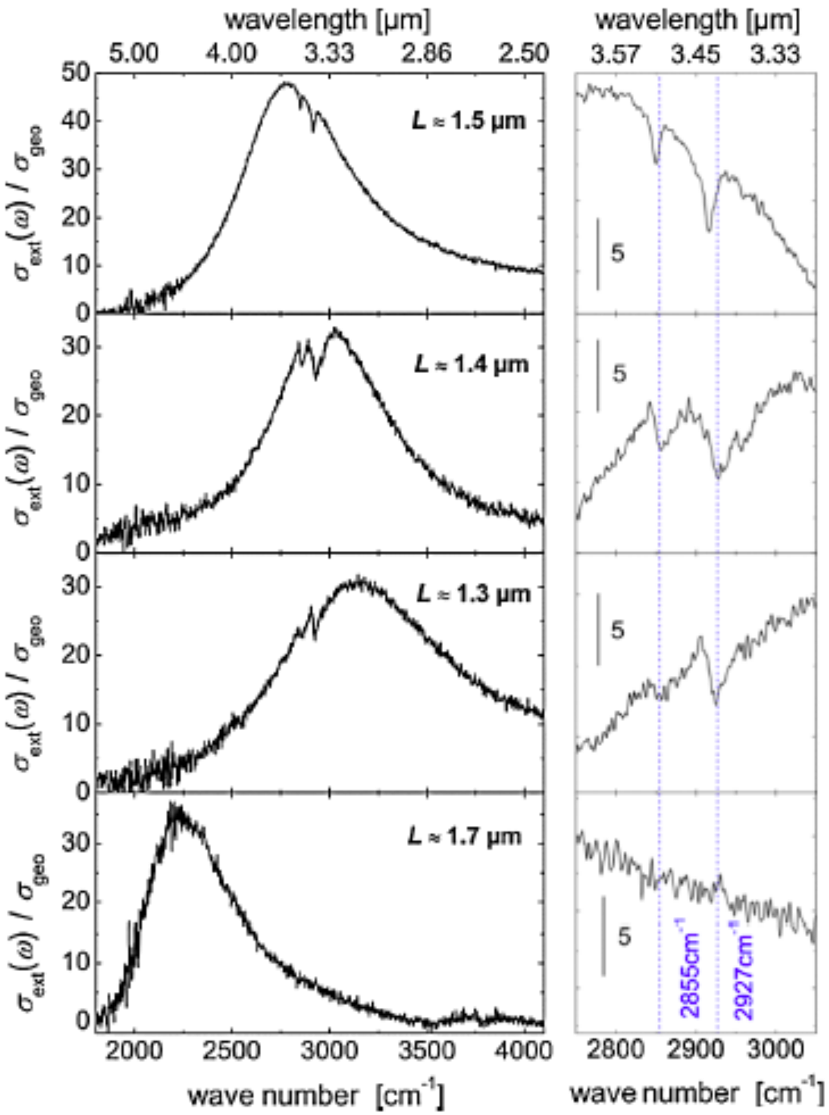
Gold nanowires on CaF_2, Electrochimistry on membrane, Diameter = 100 nm
Monolayer of OctaDecaThiol (ODT, C18H37SH)



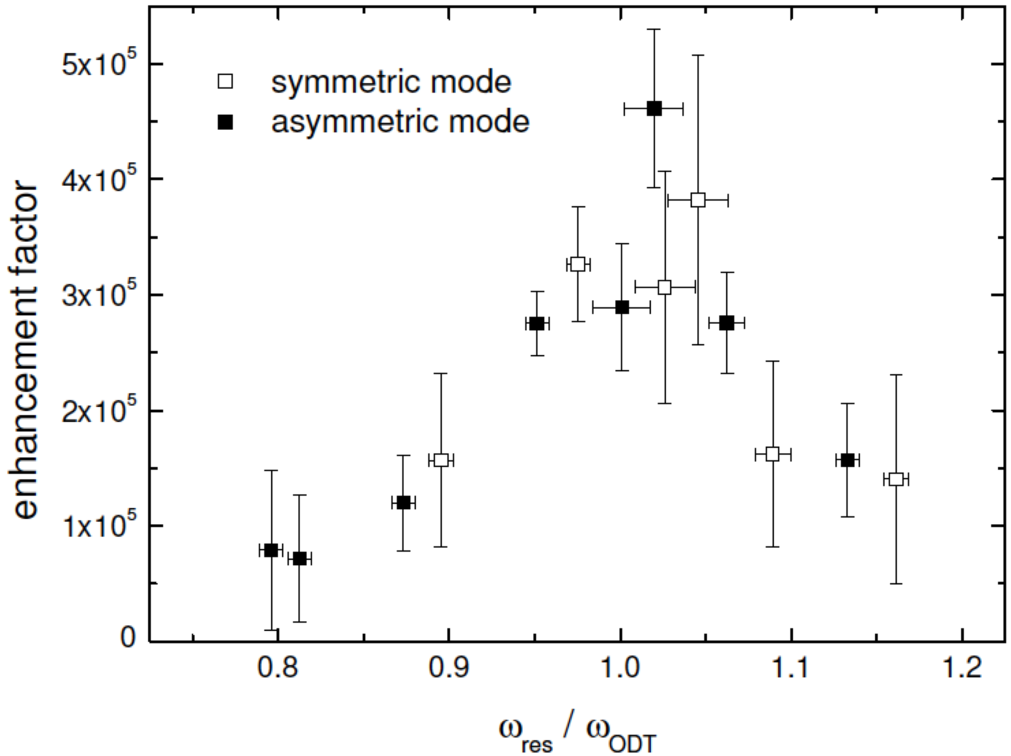
⇒ **Enhancement factor around 300 000**

F. Neubrech, et al., Phys. Rev. Lett. 101, 157403, 2008

Detection by SEIRA: influence of the LSPR



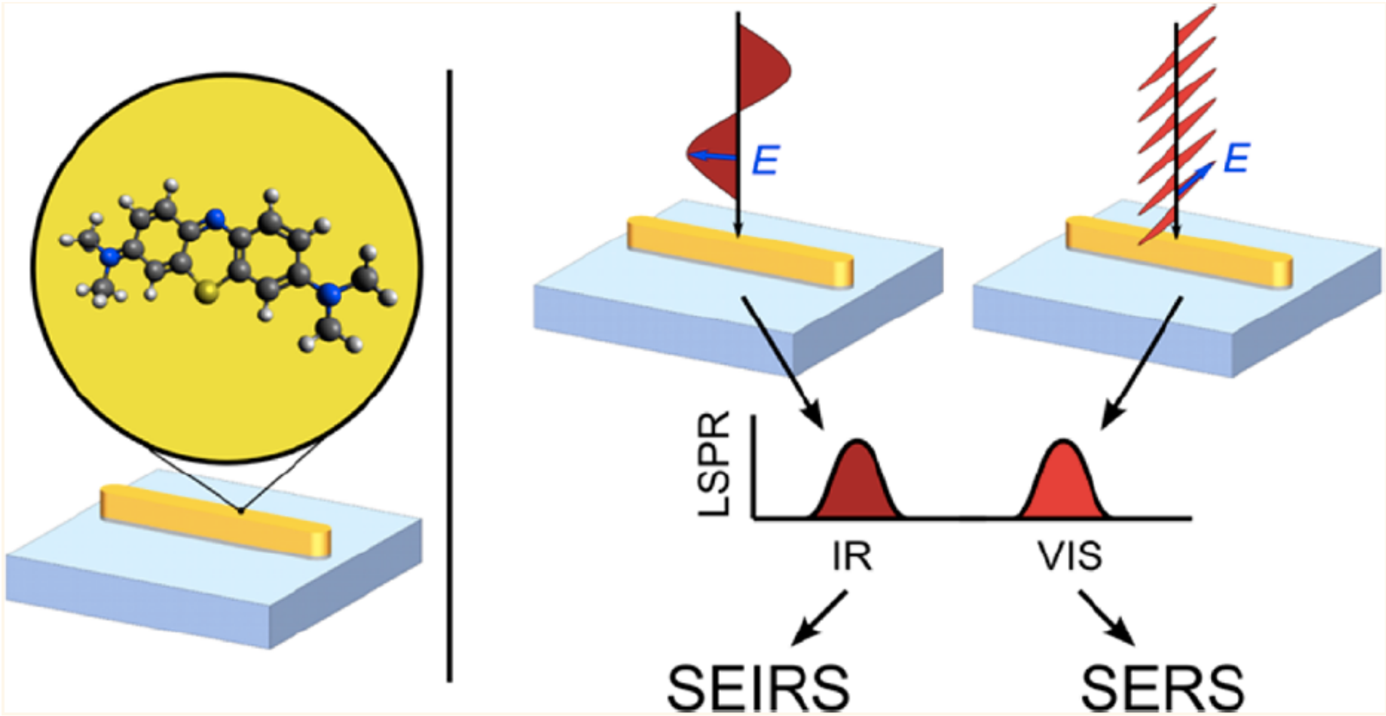
⇒ **Fano behaviour**



⇒ **Optimal IR signal for $\lambda_{SPR}=\lambda_{Vib}$**

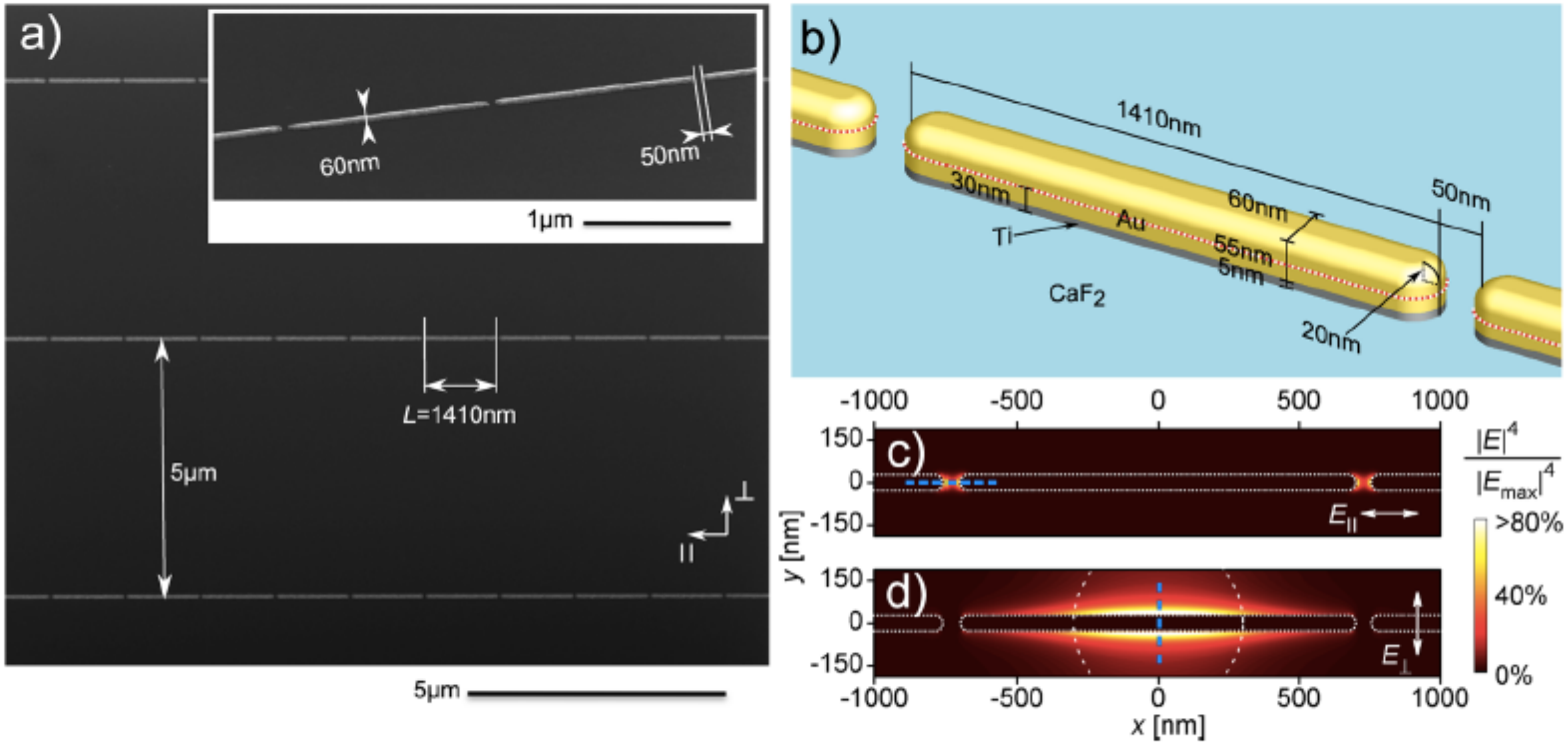
SERS/SEIRA coupling

SERS/SEIRA: principle



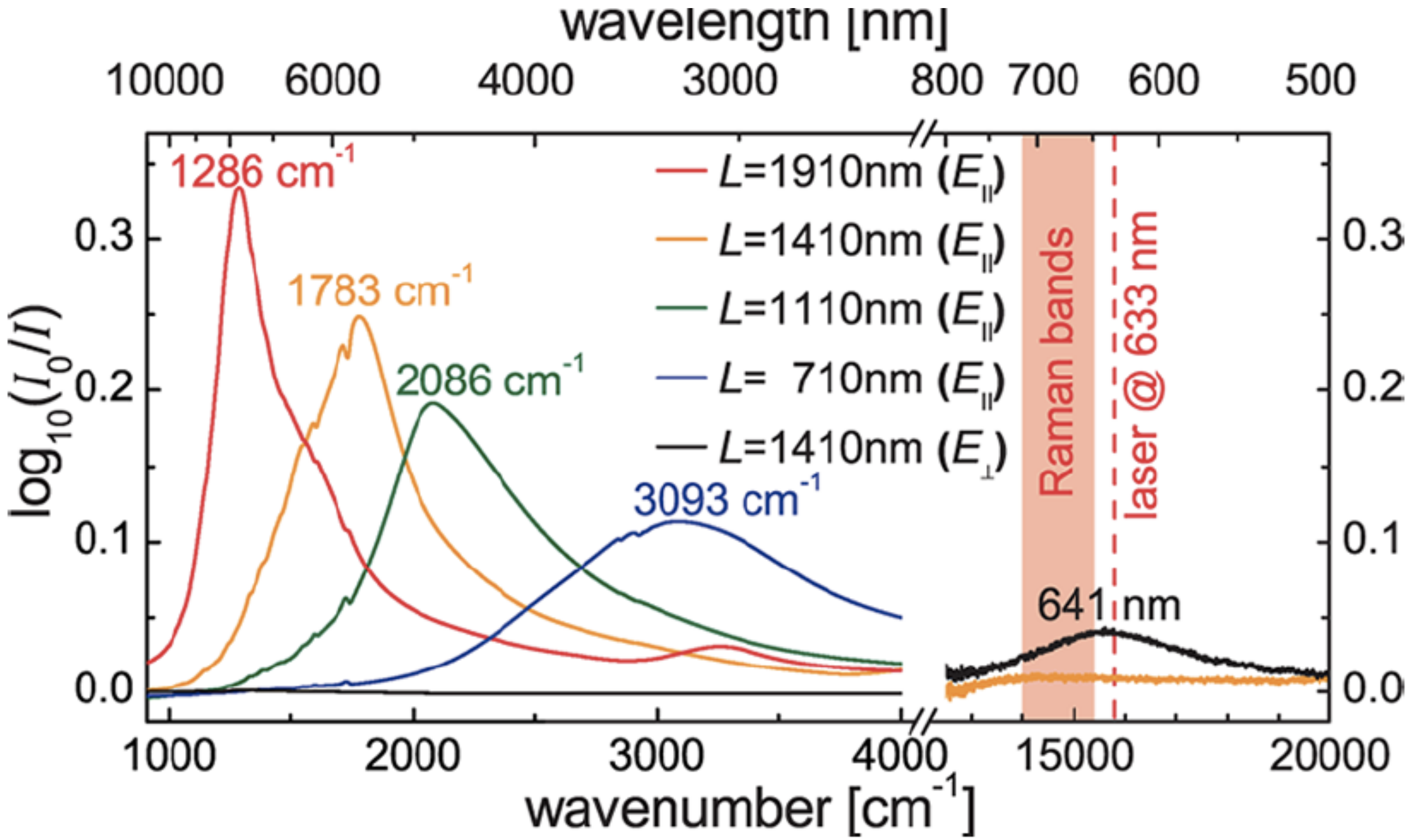
C. D'Andrea, et al., ACS Nano, 7(4), 3522, 2013

SERS/SEIRA: nanostructures



Methylene blue: 10^{-4} M

SERS/SEIRA: LSPR

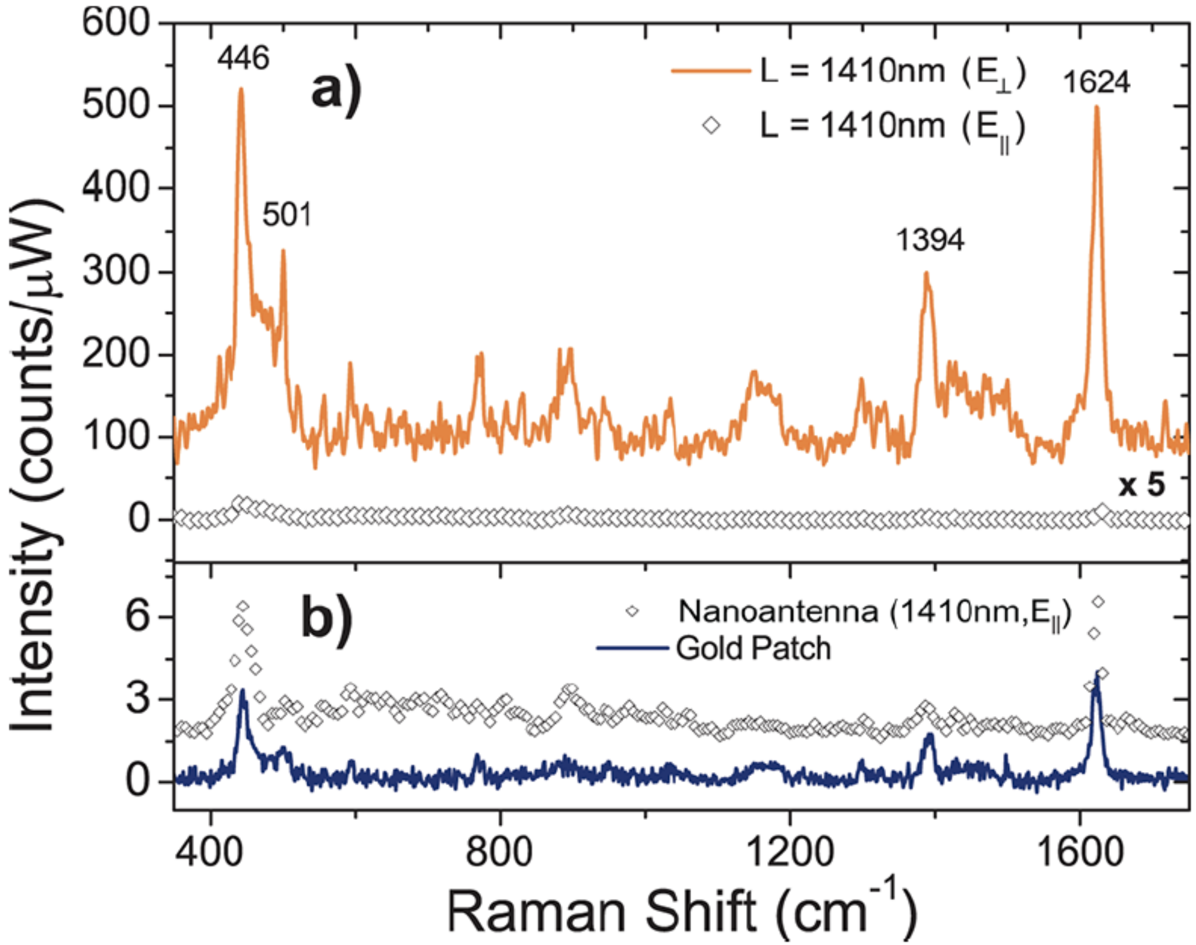


⇒ E_{Para} : **Plasmon resonance in IR / SEIRA**

⇒ E_{Perp} : **Plasmon resonance in the visible / SERS**

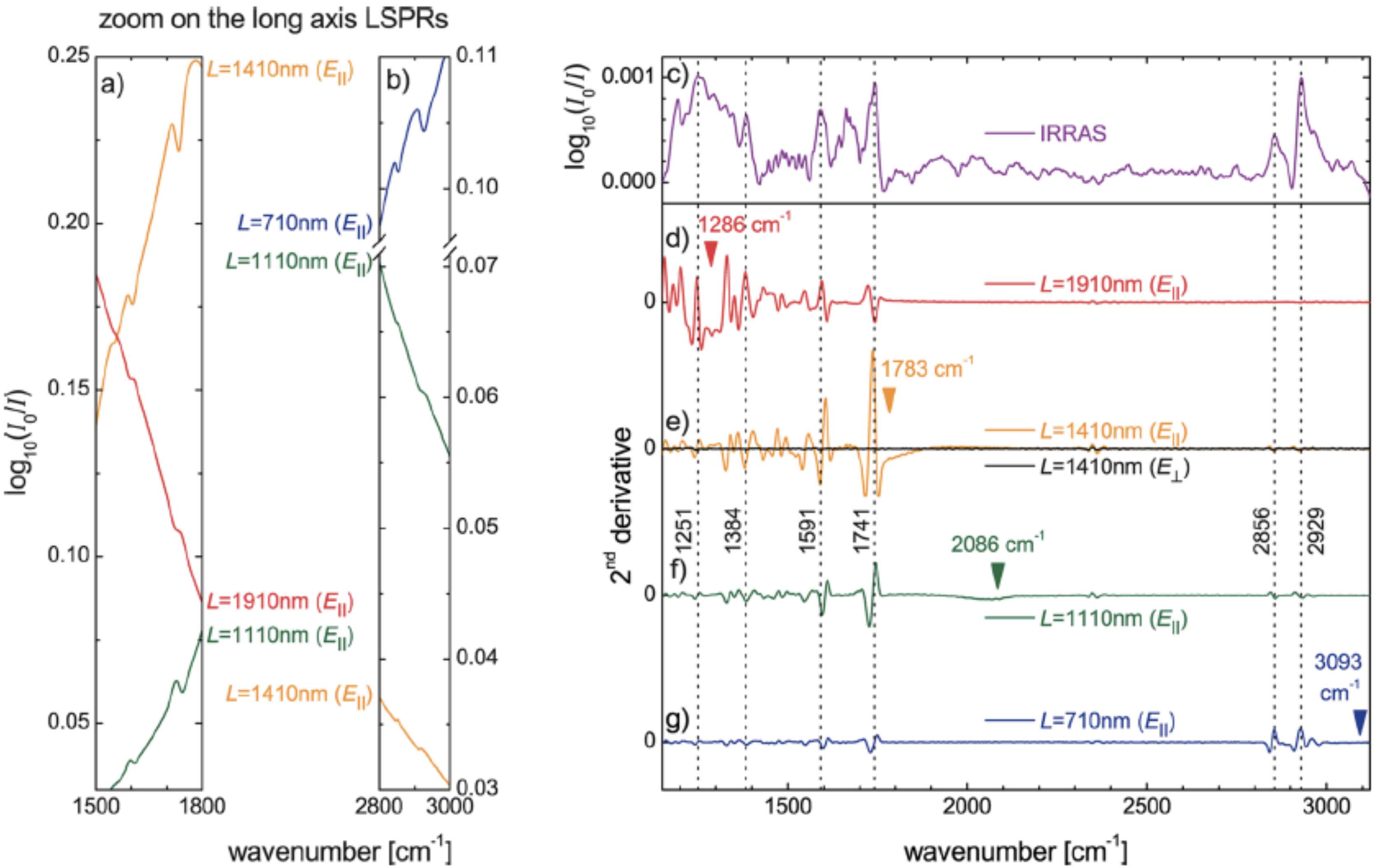
SERS/SEIRA: SERS

HeNe laser : λ = 633 nm, x100 objective : NA = 0.9



⇒ **Enhancement factor = 5.10^2**

SERS/SEIRA: SEIRA



⇒ **Enhancement factor = 6.10^5**

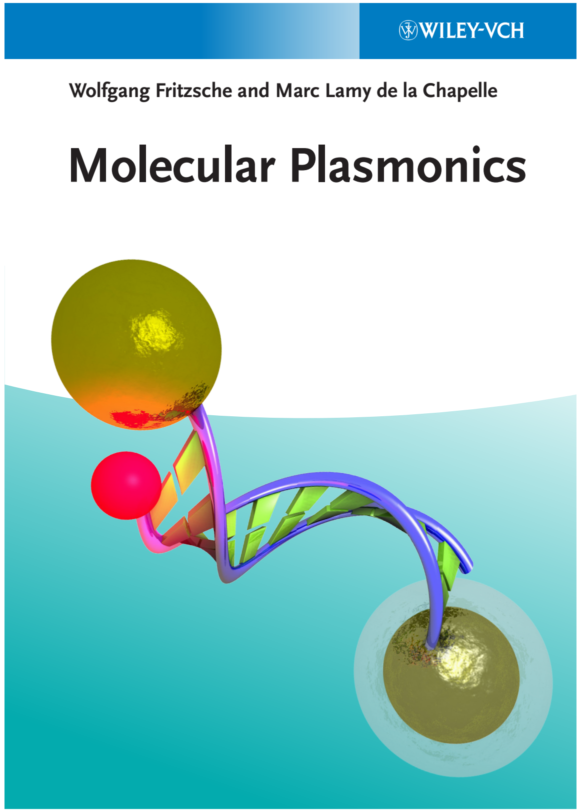
Conclusion

1. Large enhancement factor in SEIRA with nanoantenna

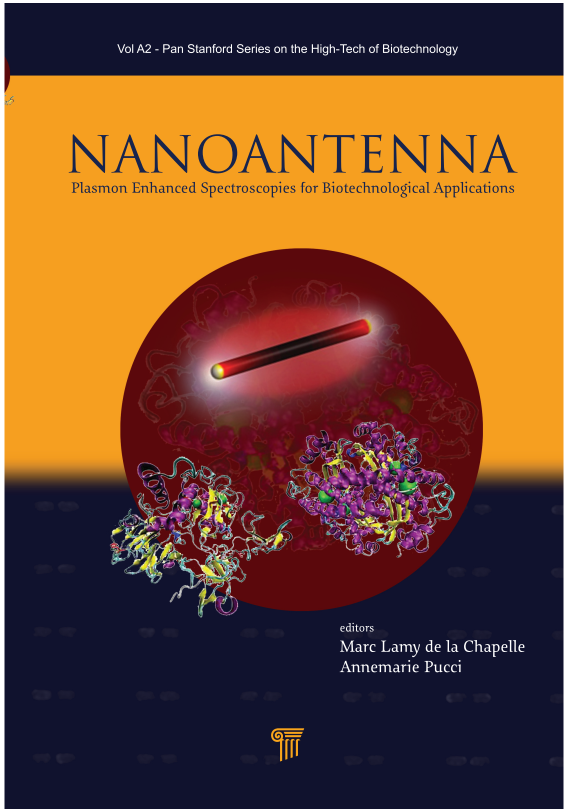
2. Optimisation of the signal in SEIRA

3. SERS and SEIRA coupling with individual nanoantenna

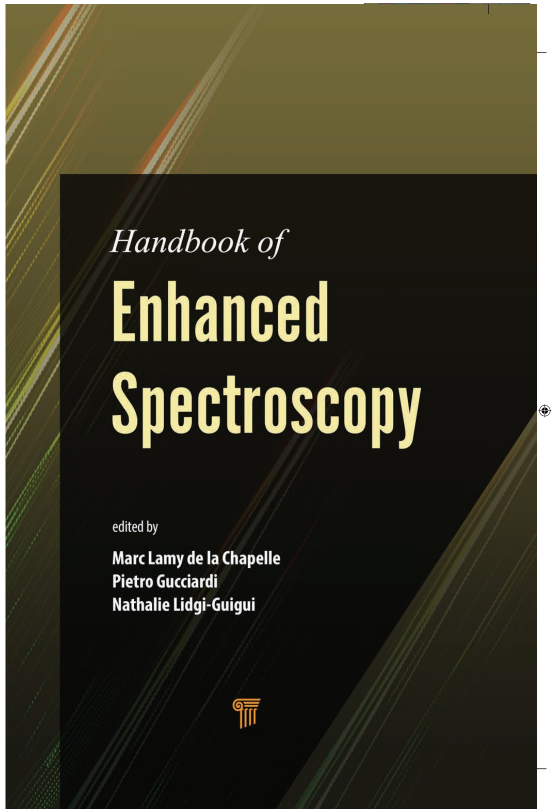
References



Molecular Plasmonics
W. Fritzsche
M. Lamy de la Chapelle
Wiley VCH Verlag, 2014



Nanoantenna
M. Lamy de la Chapelle,
A. Pucci
Pan Stanford Publishing, 2013



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P. Gucciardi,
M. Lamy de la Chapelle,
N. Lidgi-Guigui
Pan Stanford Publishing, 2016

Special issue on surface-enhanced Raman spectroscopy
Journal of Optics, Volume 17, Numéro 11, Novembre 2015

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HEALTH-F5-2009-241818

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