Spectroscopie exaltée par effet de pointe (TERS) : principe et instrumentation

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PMSE GDR 3430

Ecole Thématique "Plasmonique Moléculaire et Spectroscopies Exaltées"

Cours, ateliers pratiques, visites, posters, table ronde

20-24 juin 2016 Toulouse (France)

Outline

Introduction

I. 15 years of TERS

II. Principle

III. Instrumentation

IV. Simulation et modeling

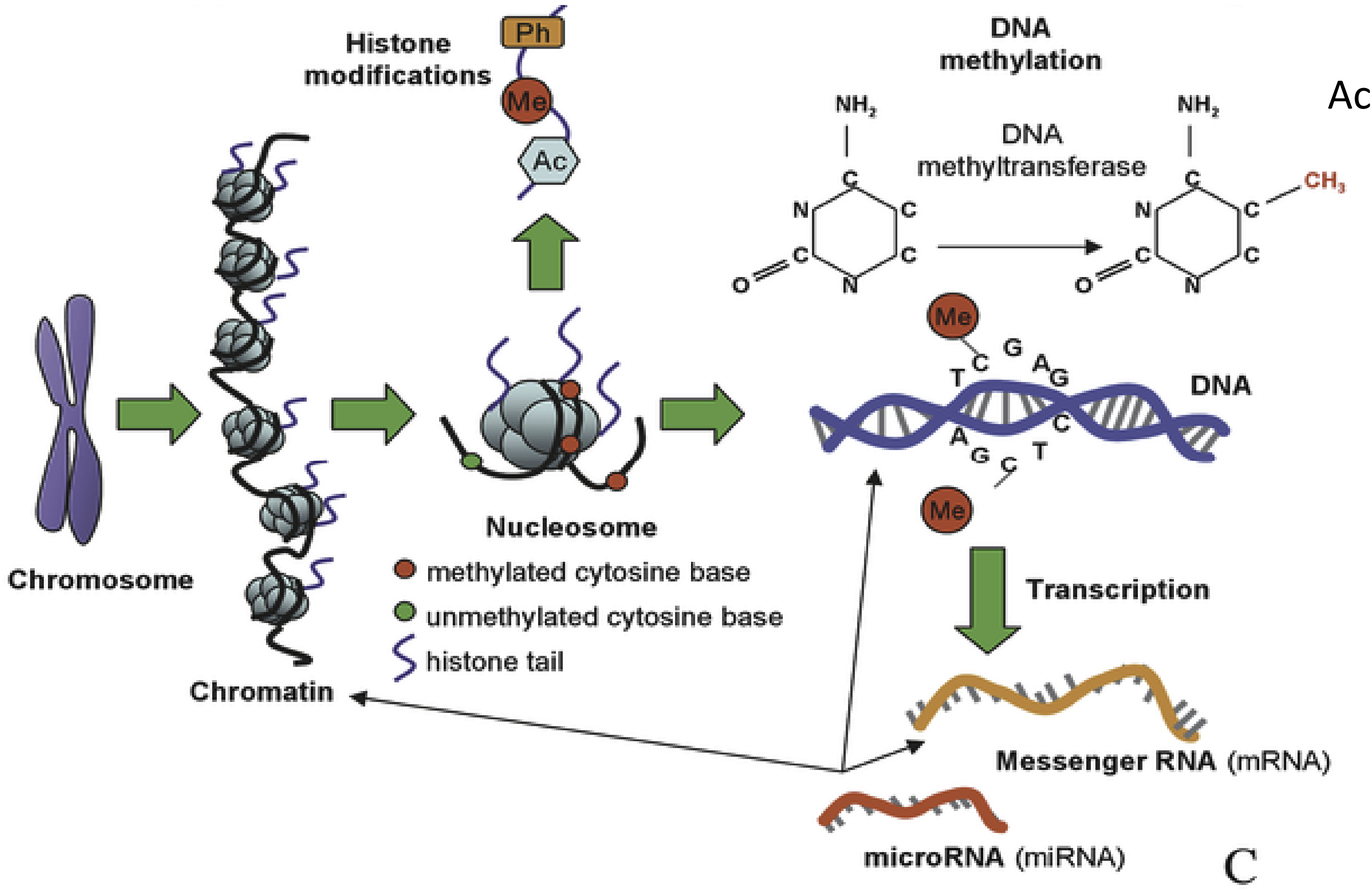
V. Applications

Conclusion

Marques épigénétiques
(“mémoire” de l’environnement)

⇩

Activité génétique



Gómez-Díaz E, Jordà M, Peinado MA, Rivero A (2012) Epigenetics of Host–Pathogen Interactions: The Road Ahead and the Road Behind. PLoS Pathog 8(11): e1003007. doi:10.1371/journal.ppat.1003007
http://journals.plos.org/plospathogens/article?id=info:doi/10.1371/journal.ppat.1003007

PLOS | PATHOGENS

Introduction

- Nanosciences → sondes locales
  - TEM, SPM, XPS, EELS, …

  info: structure, élément, valence, environnement chimique, mécanique, surface, …

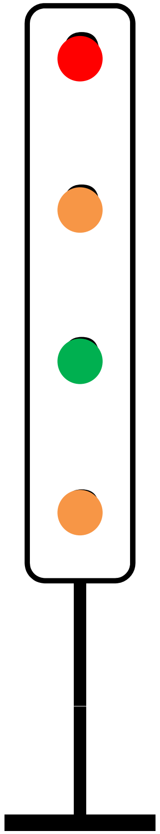
  limites : information moléculaire et supramoléculaire, conditions environnementales, …

- Chimie analytique → sondes qualitatives ET quantitatives
  - IRTF, Raman, …

  Info : chimique, orientation, transferts de charges, stress, cinétique, in-situ, on-line, …

  limites : résolution, sensibilité*, marqueurs (fluo), …

Probing vibrations



Inelastic neutron scattering ($\sigma \approx 10^{-xx}$-10^{-xx} cm^2/molecule)

IR spectroscopy ($\sigma \approx 10^{-xx}$-10^{-xx} cm^2/molecule)

Raman scattering ($\sigma \approx 10^{-31}$-10^{-23} cm^2/molecule)

Inelastic electron scanning spectroscopy

JC1

$\Rightarrow$ sensibilité ET résolution spatiale ?

Slide 5

JC1 Terme exact
JCV 4; 08/06/2016

Micro-Raman : Advantages *versus* Disadvantages

Advantages :

1) **Very rich information** about molecular vibrations and structures of materials

2) **No sample preparation required** (≠ FTIR or TEM)

3) **Non-destructive** techniques and **in-situ** experiments

Disadvantages :

1) Very low cross section

$$\frac{d\sigma}{d\Omega} \sim 10^{-28}\ \mathrm{cm}^{-2}\ \mathrm{sr}^{-1}$$

⇒ low **sensitivity**

2) Poor spatial **resolution** $\Rightarrow \cong \lambda/2$

$$\Delta x \sim \frac{1.22\,\lambda}{NA} \sim 250\ \ nm$$

3) Not usable for pure metals

⇒ sensitivity AND spatial resolution ?

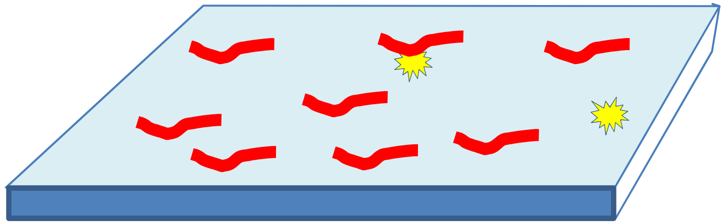
Introduction

Diffusion Raman

Exaltation localisée

“Nano-Raman”

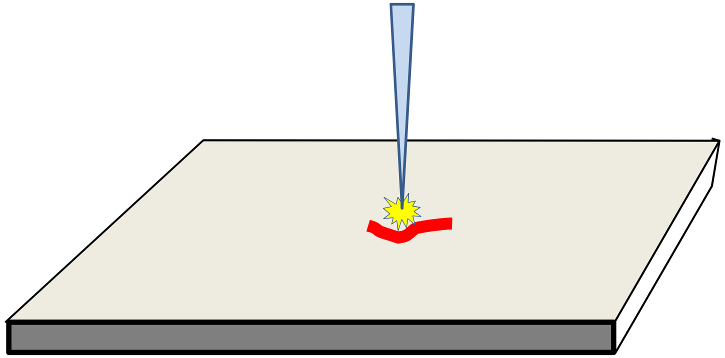
field **enhancement**



SERS

a “***very few***”
“***very hot****” spots
randomly distributed

Localized field **enhancement**

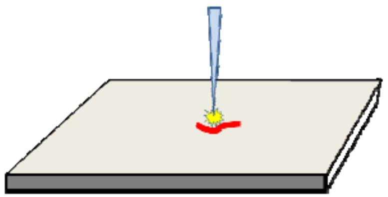


TERS

a “***single very hot***” spots
with a nanoscale
controlled position

Introduction

Localized field enhancement



TERS

a "***single very hot***" spots
with a nanoscale
controlled position

Flexible configurations

- Light excitation
- Substrate
- Light detection
- Probe Molecule
- Tip (material, geometry, …)

⇒ Emerging technique which is considered as ***the first label-free technique*** able to provide the ***single-molecule detection spatially resolved*** in the near future.

Part. I : 15 years of TERS

1984 : 1st near field scan using visible light (SNOM) [Pohl D.W. *et al. APL* 1984, Lewis *Ultramicroscopy* 1984]

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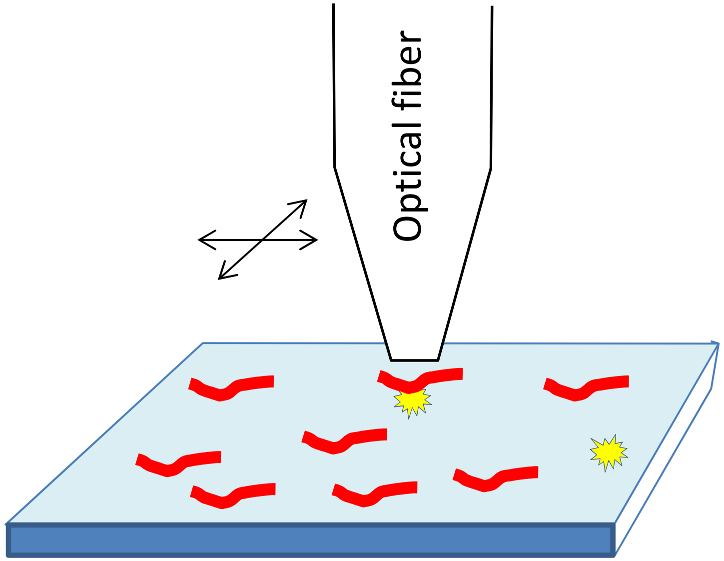
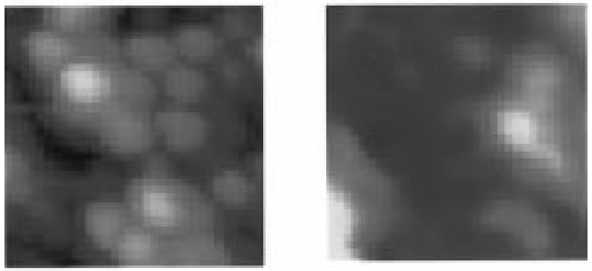
Beginning of **near field Raman** …



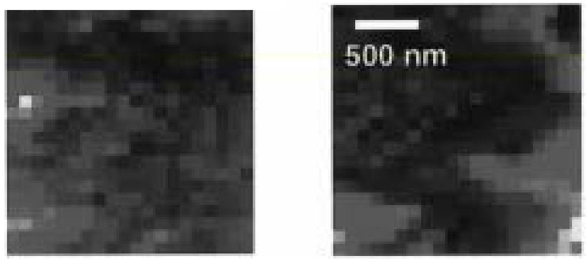
SNOM on SERS substrate

15 years of TERS

Beginning of the **near field Raman** …

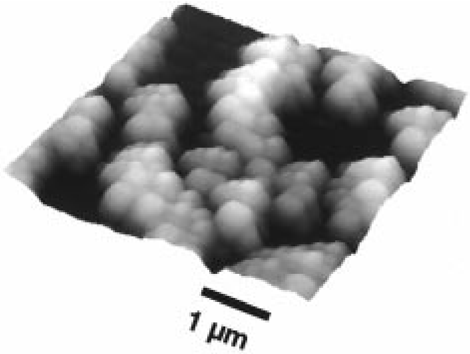

Topography

Near field reflectivity

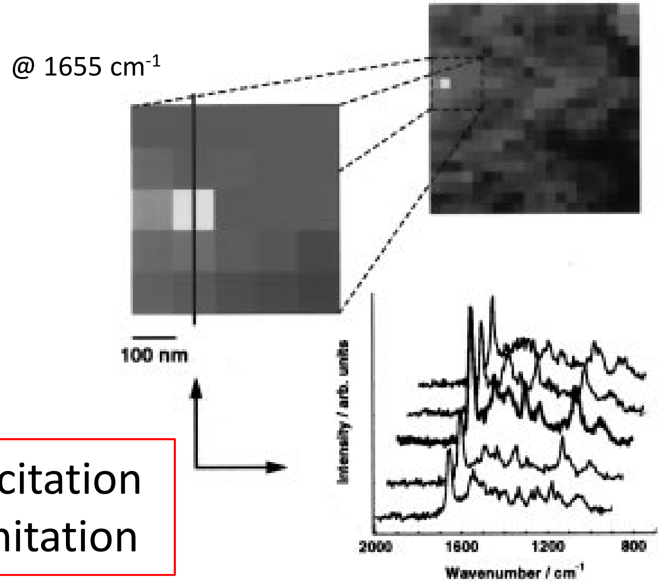

Raman @ 1524 cm^{-1}

Raman @ 800 cm^{-1} (silica)

Deckert, V., Zeisel, D., Zenobi, R. and Vo-Dinh, T.
Near-field surface-enhanced Raman imaging of
dye-labeled DNA with 100-nm resolution.
Anal. Chem., 70, pp. 2646–2650 (1998)



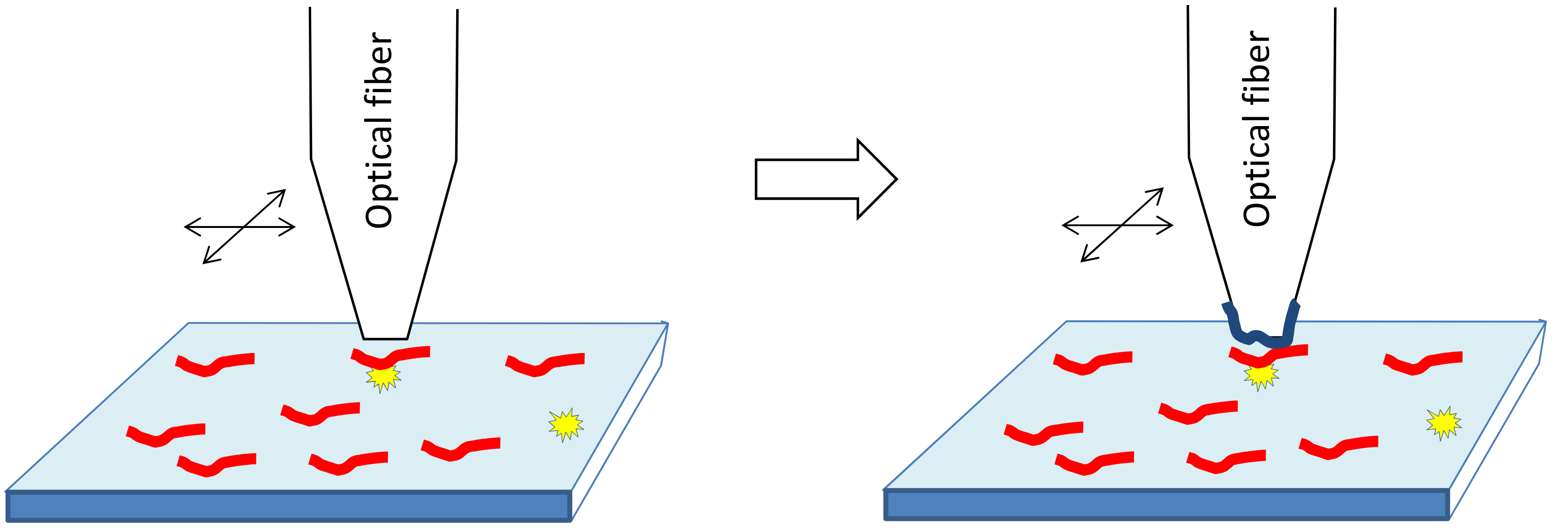
Ag **SERS substrate** / **SNOM**
Analyte :BCB label-DNA
Excitation : 488 nm (near field – fiber with 80-100nm res.)
Collection : Far field


@ 1655 cm^{-1}

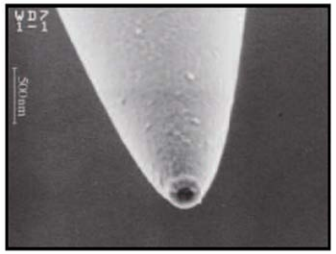
☹ Low intensity excitation
☹ Aperture size limitation

15 years of TERS

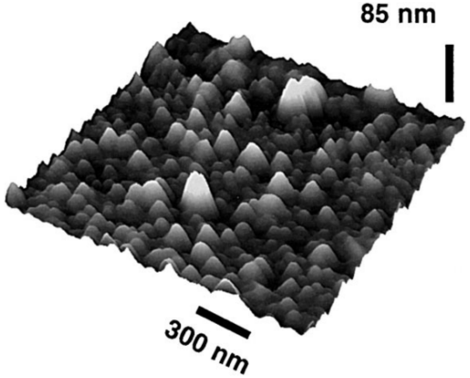
How to increase the signal from near field … ?



Beginning of the **near field Raman** …

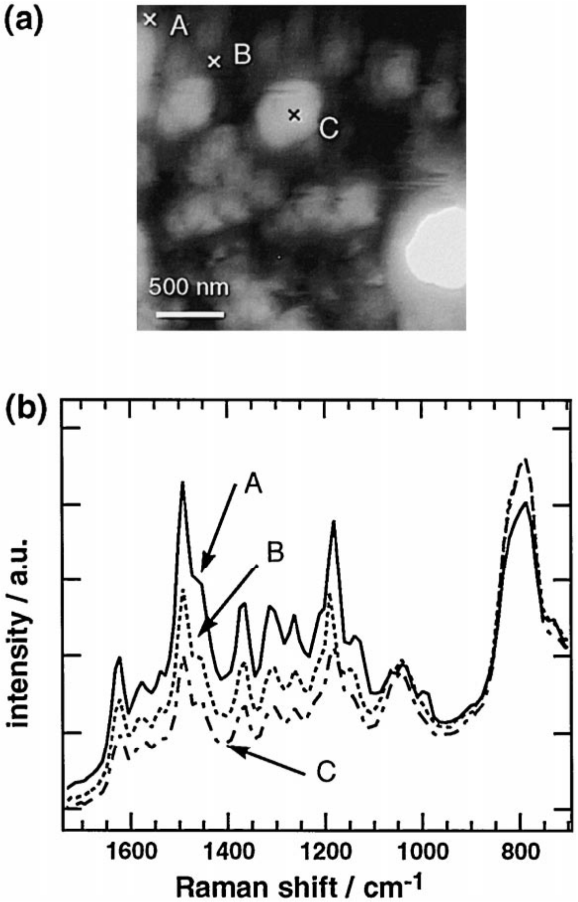


+



Ag SERS substrate / **SNOM with Ag coated fiber**
Analyte :R6G
Excitation : 514 nm (near field)
Collection : Far field

- Limited amount of excitation power
- → Needs very efficient samples for imaging in reasonable times !!!

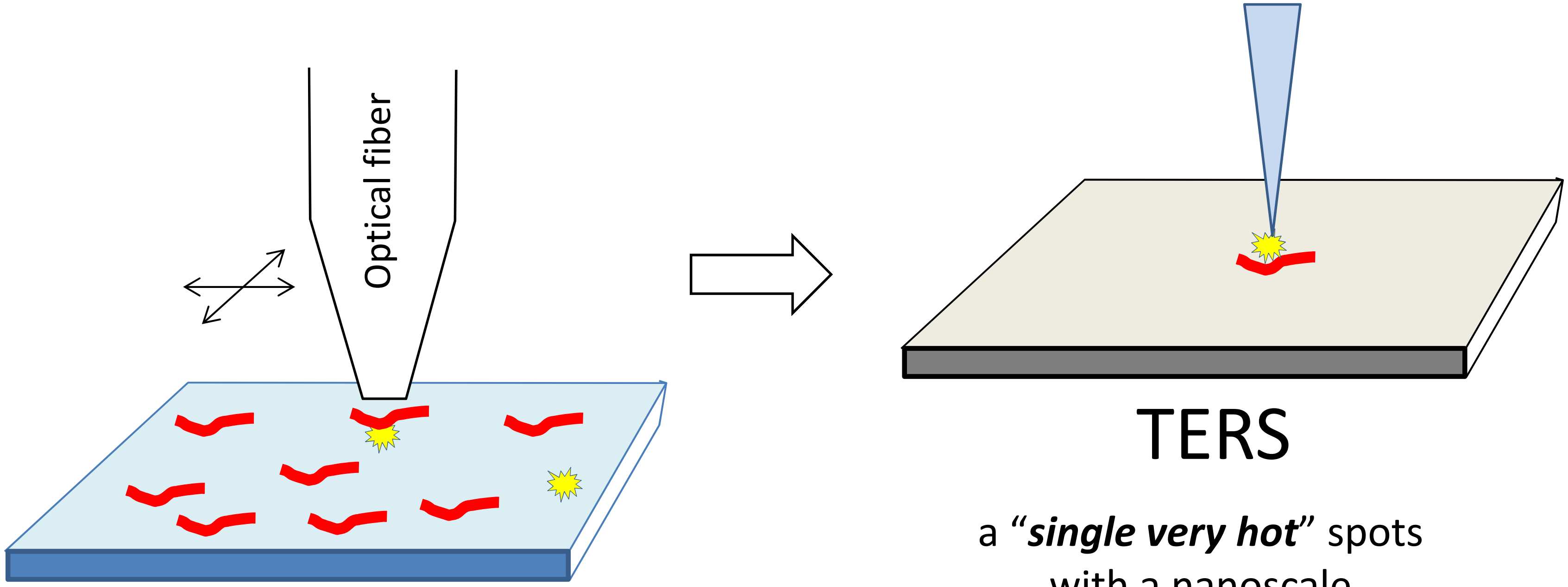


Zeisel, D., Deckert, V., Zenobi, R. and Vo-Dinh, T.
Near-field surface-enhanced Raman spectroscopy of dye molecules adsorbed on silver island films *CPL 283, pp. 381-385 (1998)*

15 years of TERS

Aims :

1- Avoid critical the dependence of SERS enhancement on the substrate
2- Use any substrate (non plasmonic)
3- Overcome the fiber output limitation
4- **Increase the spatial resolution**



TERS

a “***single very hot***” spots
with a nanoscale
controlled position

(apertureless SNOM)

A brief history …

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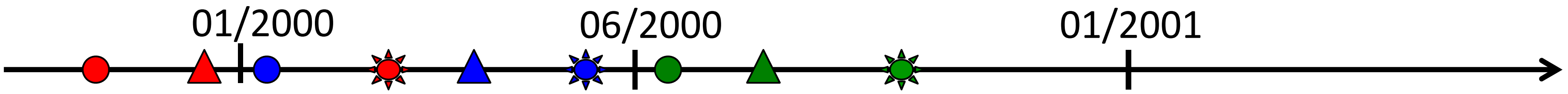
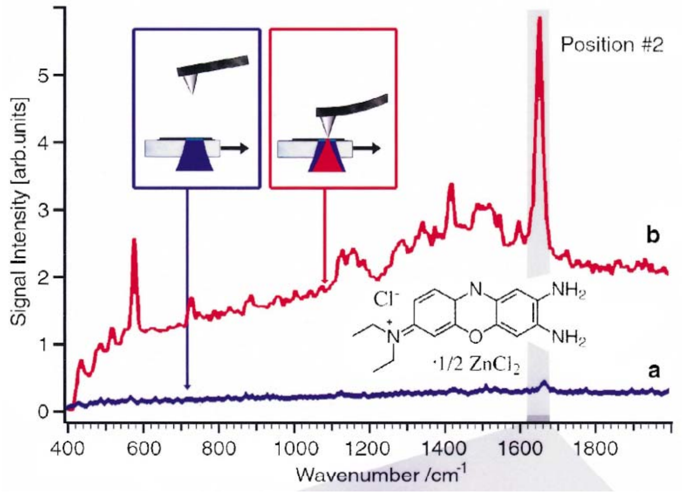


R. Zenobi (R. M. Stöckle *et al.* *CPL* 318, 131 2000) BCB Ag 488 nm
M.S. Anderson (*APL* 76-3130 2000) Sulphur Au 785 nm
S. Kawata (N. Hayazawa *et al.* *Opt. Commun.* 183, 333 (2000) R6G Ag 488 nm

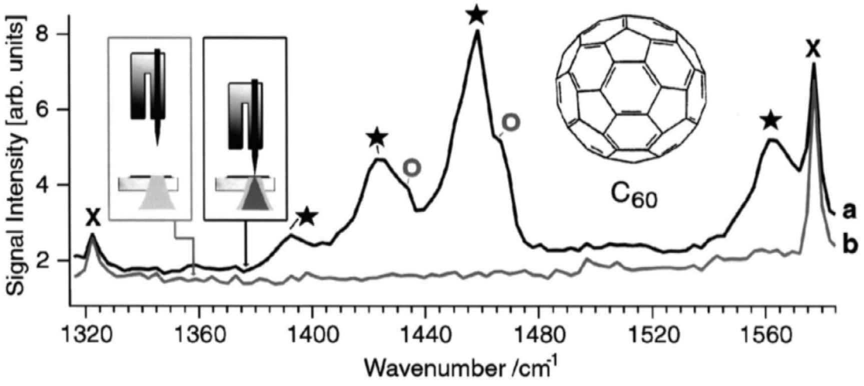
Tip enhanced Raman scattering / ETHZ

Stöckle, R. M., Suh, Y. D., Deckert, V. and Zenobi, R. (2000). *Chem. Phys. Lett., 318* (2000)



Ag coated AFM tip
Analyte : BCB on glass substrate
Excitation : 488 nm (Far field – inverted microscope NA 1.4)
Collection : Far field
EF ≈ 2000

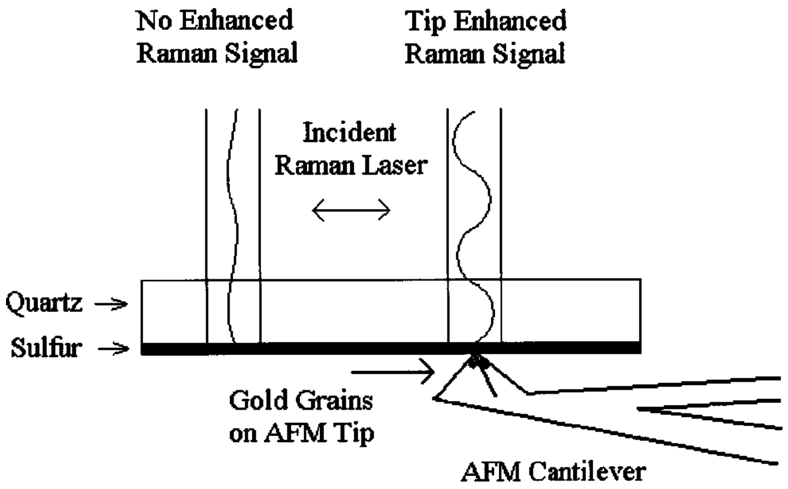
○ Raman modes of C_{60}
★ Charge transfer with Au gold tip

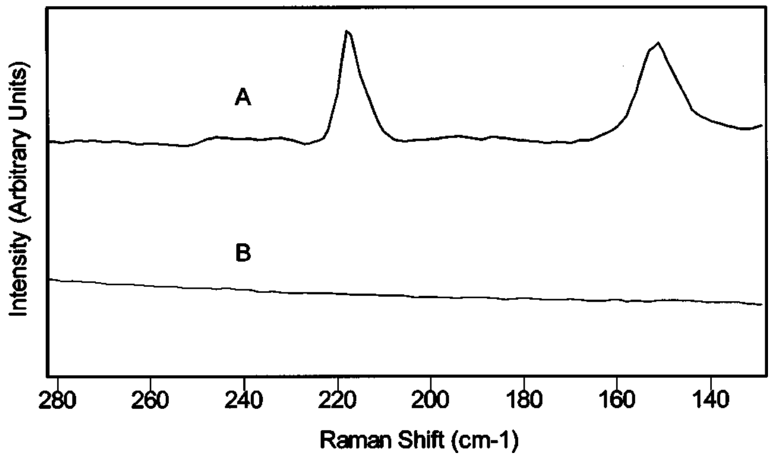


Etched Au gold wire – tuning fork set-up
Analyte : C_{60} on glass substrate
Excitation : 488 nm (Far field – inverted microscope NA 1.4)
Collection : Far field
EF ≈ 40 000

Tip enhanced Raman scattering / CalTech

Anderson,M. S. *Appl. Phys. Lett. 76* (2000)

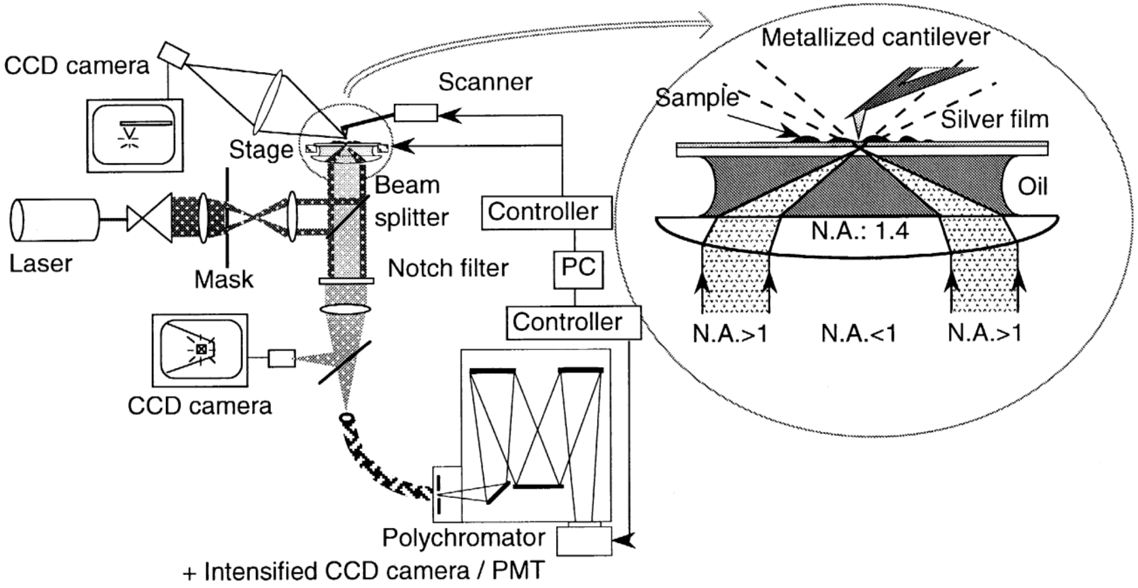


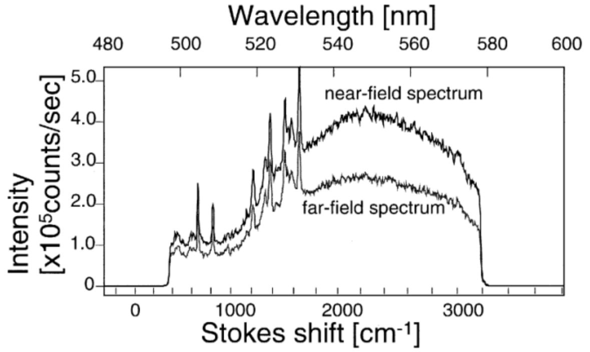


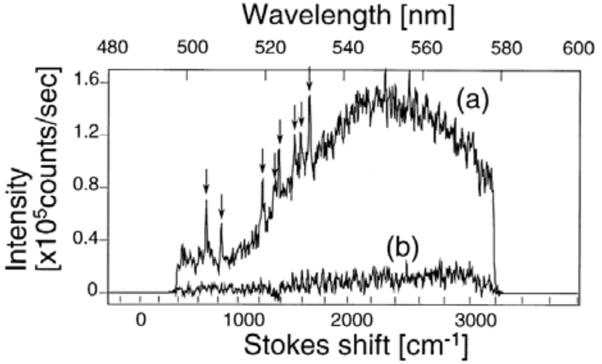
Au coated AFM tip
Analyte : Sulphur on quartz substrate
Excitation : 785 nm, Far field
Collection : Far field
EF ≈ 1000

Tip enhanced Raman scattering / Osaka University

Hayazawa, N., Inouye, Y., Sekkat, Z. and Kawata, S.
Metallized tip amplification of near-field Raman scattering, *Opt. Commun., 183,* pp. 333–336 (2000)

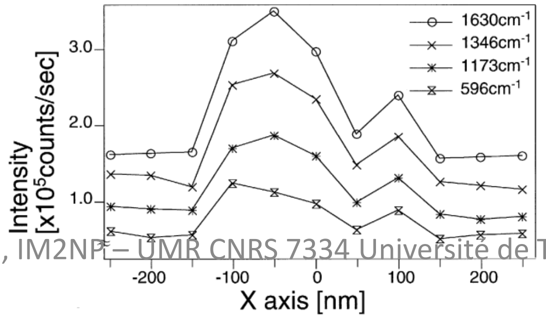






a. The subtraction of the far-field from the near-field spectrum
b. same as a. but with a silicon cantilever.

Ag coated AFM tip
Analyte : R6G on glass substrate
Excitation : 488 nm (Far field – inverted microscope NA 1.4)
Collection : Far field
EF ≈ 40



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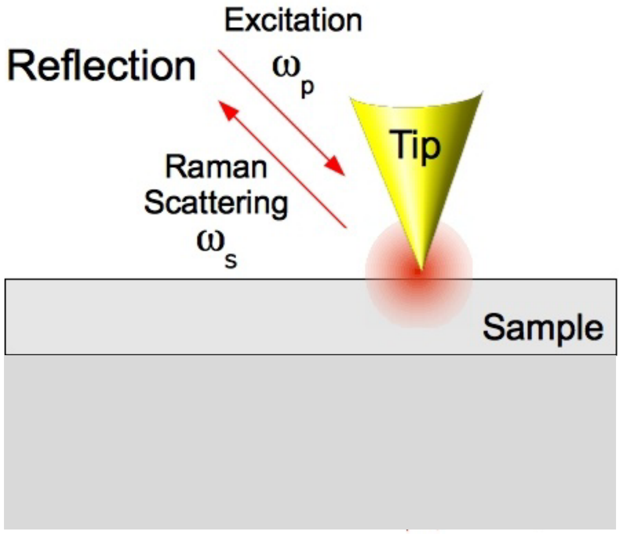
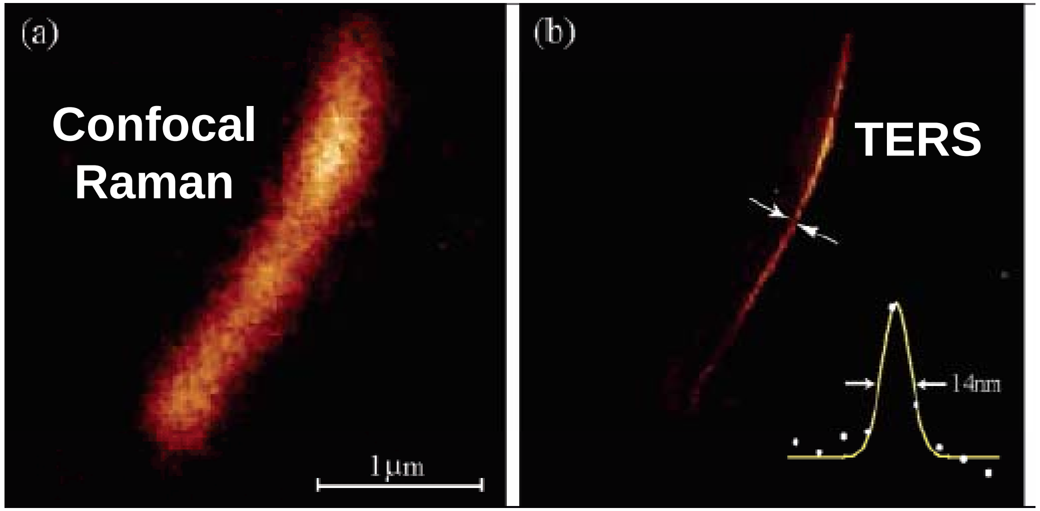
2001-2004 : Top illumination TERS [Sun *et al. Mater. Phys. Mech.* 2001, Anderson *et al. RSI* 2002, Hartschuh *et al. Int. J. Nanoscale* 2004]

Top illumination TERS





FWHM: 275 nm

FWHM: 14 nm

Hartschuh *et al*. ***Int. J. Nanoscale 3***, 371 (2004)

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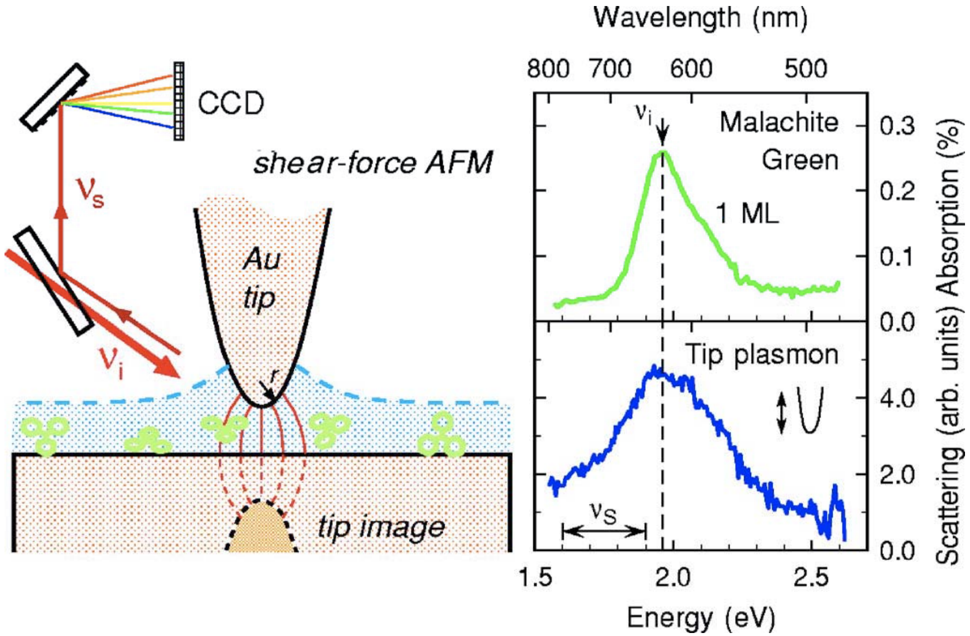
2004 : Tip enhanced CARS [Ishimura *et al. PRL* 2004]

2006 : Single molecule TERS [Neascu C.C. et al. PRB 2006]

Single molecule TERS

Neacsu, C. C., Dreyer, J., Behr, N. and Raschke, M. B.
Scanning probe Raman spectroscopy with single-molecule sensitivity PRB *73, p. 193406 (2006)*

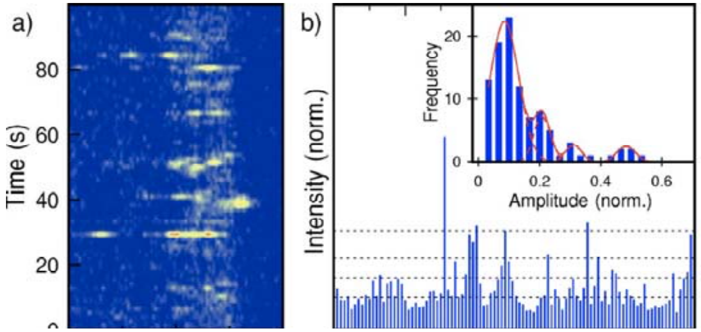


Au coated tip / gold substrate : **Gap Mode**

Ambient atmosphere, shear force AFM

Analyte : submonolayer of triarylmethane dye malachite green (MG)

Excitation : 633 nm / Top illumination



Confirmed by different groups:
Zhang *et al. JPCC* 111, 1733 (2007)
Sonntag *et al. JPCC* 116, 478 (2012).

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2004 : Tip enhanced CARS [Ishimura *et al. PRL* 2004]

2006 : Single molecule TERS [Neascu C.C. et al. PRB 2006]

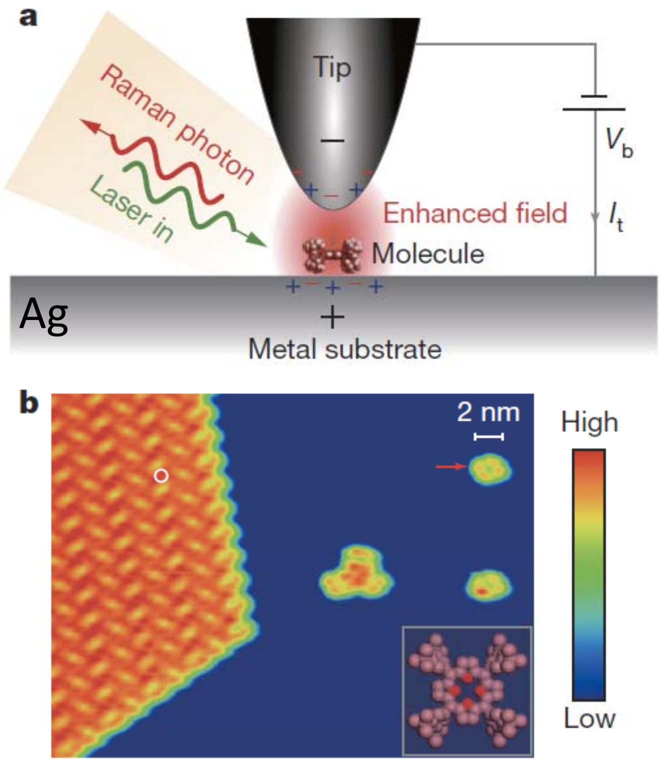
2009 : UV-TERS [Poborchii *et al. JRS* 2009]

2013 : Molecular inner structure resolution [Zhang et al. *Nature* 2013]

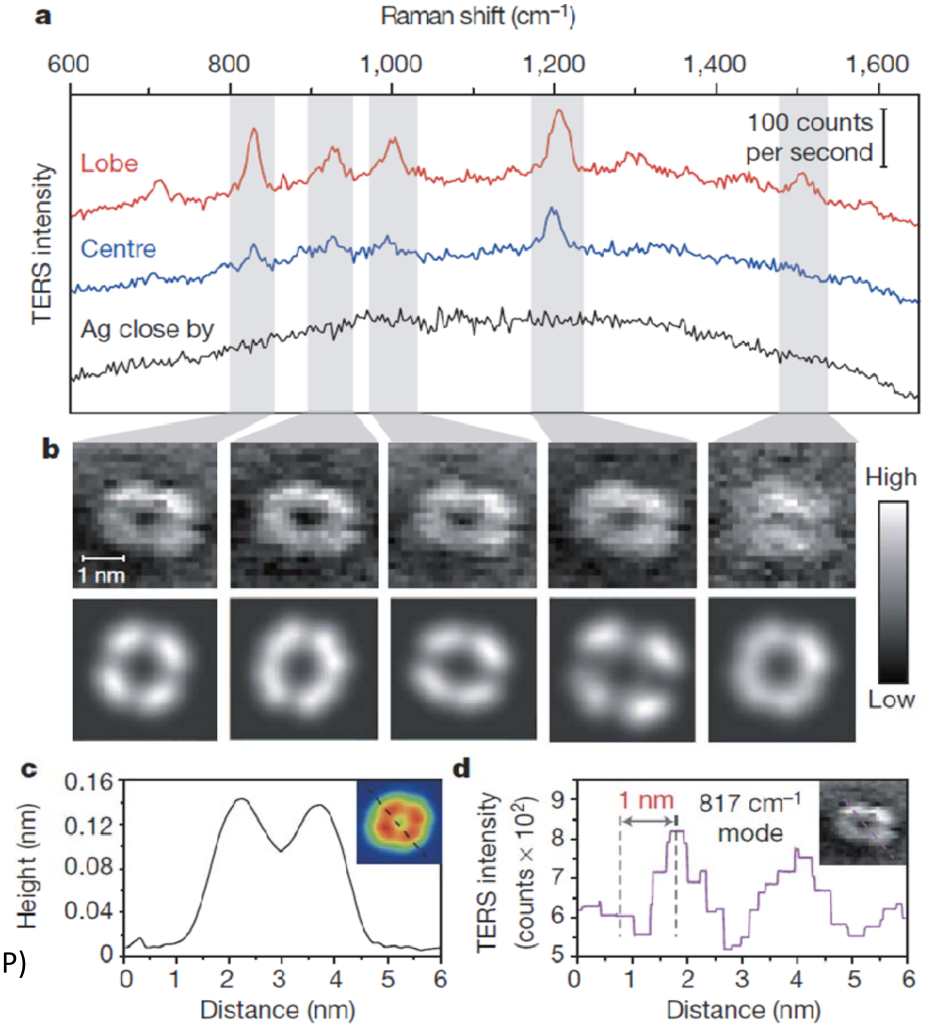
Molecular inner structure resolution

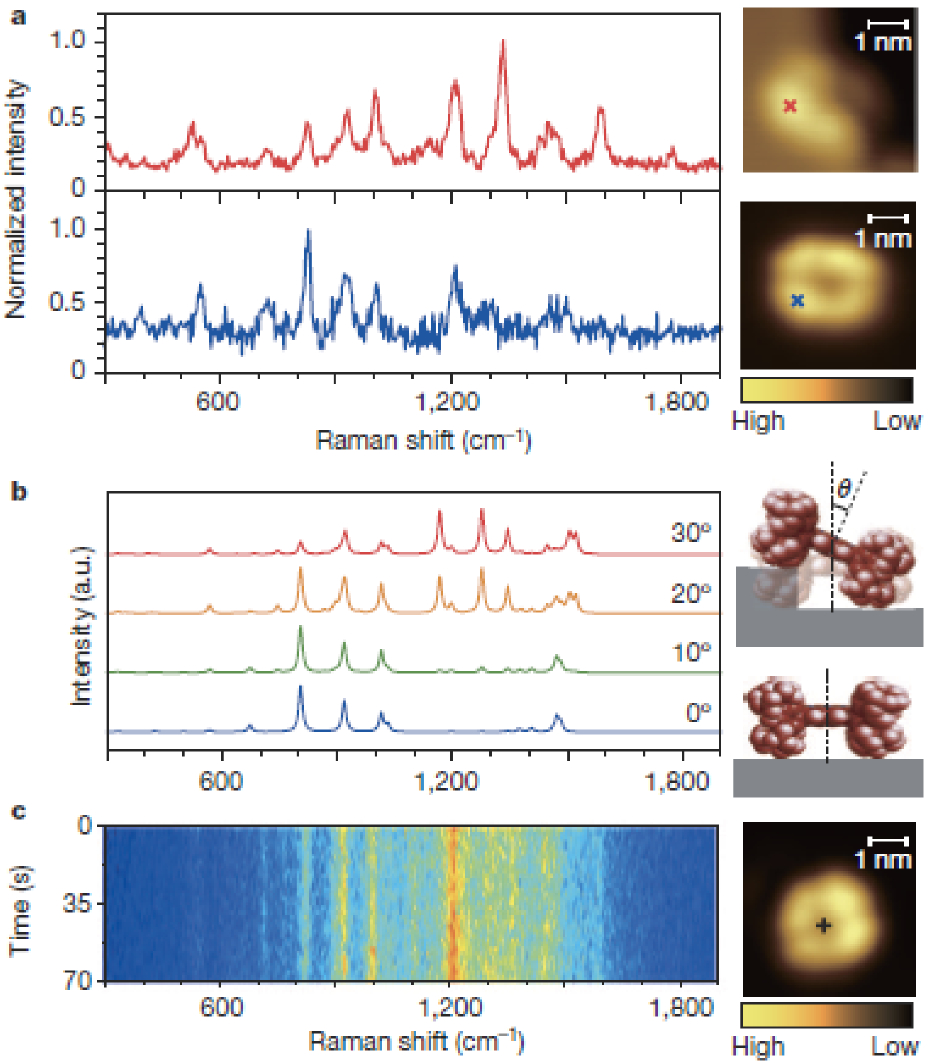
Zhang, R., Zhang, Y., Dong, Z. C., Jiang, S., Zhang, C., Chen, L. G., Zhang, L., Liao, Y., Aizpurua, J., Luo, Y., Yang, J. L. and Hou, J. G. Chemical mapping of a single molecule by plasmon-enhanced Raman scattering, *Nature, 498, pp. 82–86 (2013)*

Cryo-UHV-TERS STM



meso-tetrakis(3,5-di-tertiarybutylphenyl)-porphyrin (H2TBPP)



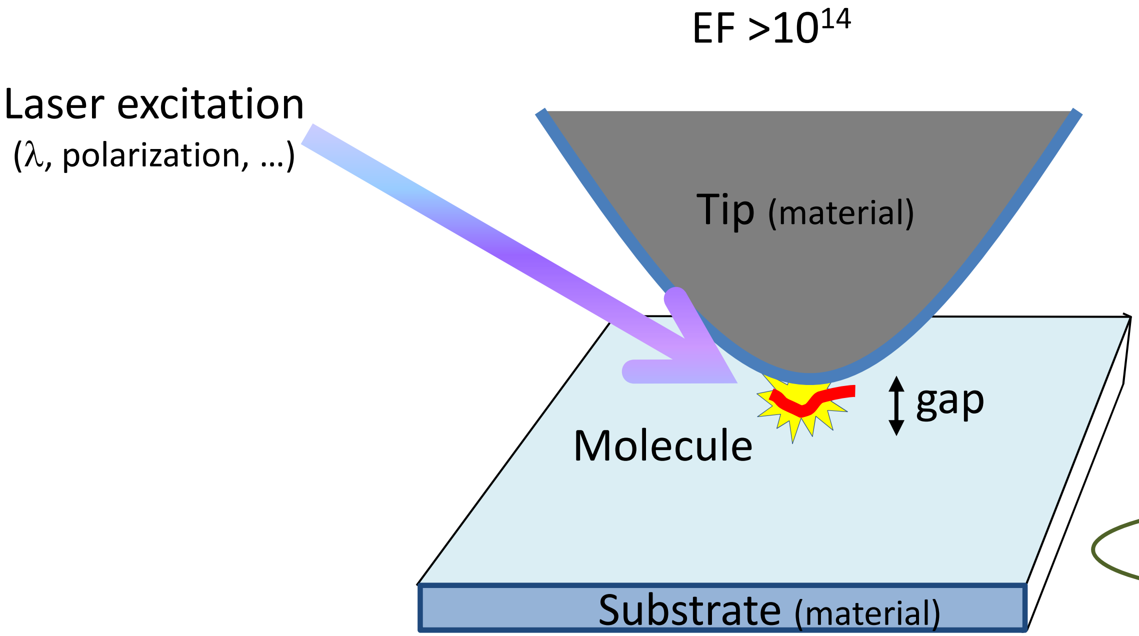


from Zhang, R. Et al. *Nature* *2013*

II- Principle of TERS

⇒ Localized and efficient resonance for excitation + Raman scattering

EF >10^{14}



Matched resonance :

- λ_{exc}
- Tip
- Substrate
- Tip/substrate distance
- $\lambda_{Raman\ mode}$

⇒ Scattered light collection

spectrally matched resonance of the nanocavity
plasmon to the molecular vibronic transitions

How to define EF factor ?

TERS : far field (FF) excitation / collection …

… but nanoscale information is near field (NS) !

$I_{NF} = \underset{\text{Approached}}{\boxed{I_{FF} + I_{NF}}} - \underset{\text{Withdrawn}}{\boxed{I_{FF}}}$ … *shadowing by tip (!)* → the net gain is $G_{net} = I_{NF} / I_{FF}$

in 2000s $G_{net} \approx 1.5 - 40$

EF / illuminated area, volume ??? → $\mathrm{EF} = G_{\mathrm{net}} \left(\frac{r_{\mathrm{foc}}}{r_{\mathrm{tip}}} \right)^2$ *in 2000s* $EF_{exp} \approx 10^2\text{-}10^4 \ll EF_{Theor}$

<u>Memo</u> : $I_{\mathrm{scat}} = E^2_{\mathrm{inc}}\,(\lambda_{\mathrm{inc}}) \cdot E^2_{\mathrm{rad}}\,(\lambda_{\mathrm{rad}})$

↳ blue- or red-shift … from a few nm to 100 nm!

Case of “sharp resonance”

Key parameter for TERS : tailoring the resonance

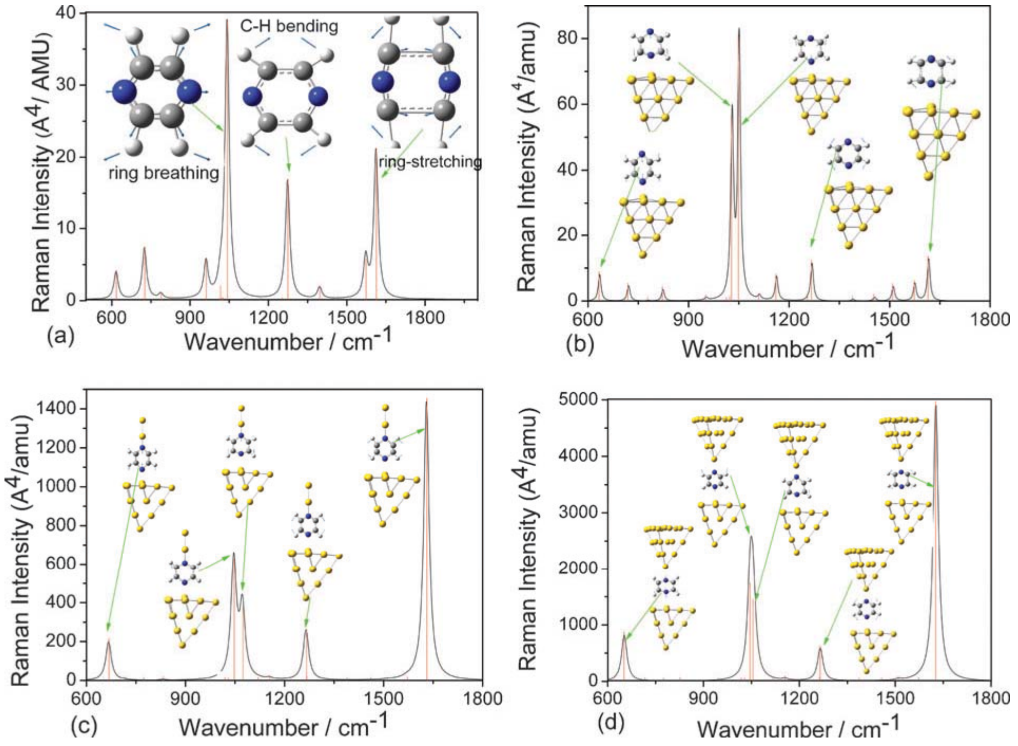
EM *vs* chemical enhancement

see "SERS section" …

Theoretically reveal the nature of the
chemical enhancement on TERS vs SERS

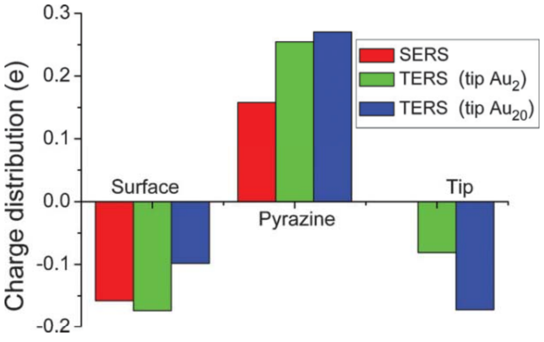
Example 1 : Sun et al. PCCP 2009

A few selected references :
Billmann, J., Kovacs, G. & Otto,A. *Surf. Sci.* 1980, 92, 153–173
Lippitsch, M. E. et al. *PRB* 1984, 29, 3101–3110
M. Moskovits, *Rev. Mod. Phys*., 1985, 57, 783.
A. Otto et al. *J. Phys.: Condens. Mater* 1992, 4, 1143.
H. X. Xu et al. *PRL* 1999, 83, 4357.
K. Kneipp et al. *Chem. Rev*., 1999, 99, 2957.
R. M. Stöckle et al. *CPL* 2000, 318, 131.
B. Pettinger et al. *PRL* 2004, 92, 096101
H. Watanabe et al. *PRB* 2004, 69, 155418.
K. F. Domke et al. *JACS* 2006, 128, 14721.
Perez-Gonzalez et al. *New J. Phys*. 2011, 13, 083013



Calculation of charge density in four kinds of CT

(1) CT tip → molecule
(2) CT surface → molecule,
(3) CT tip and surface → molecule simultaneously
(4) Tunneling CT between tip and surface

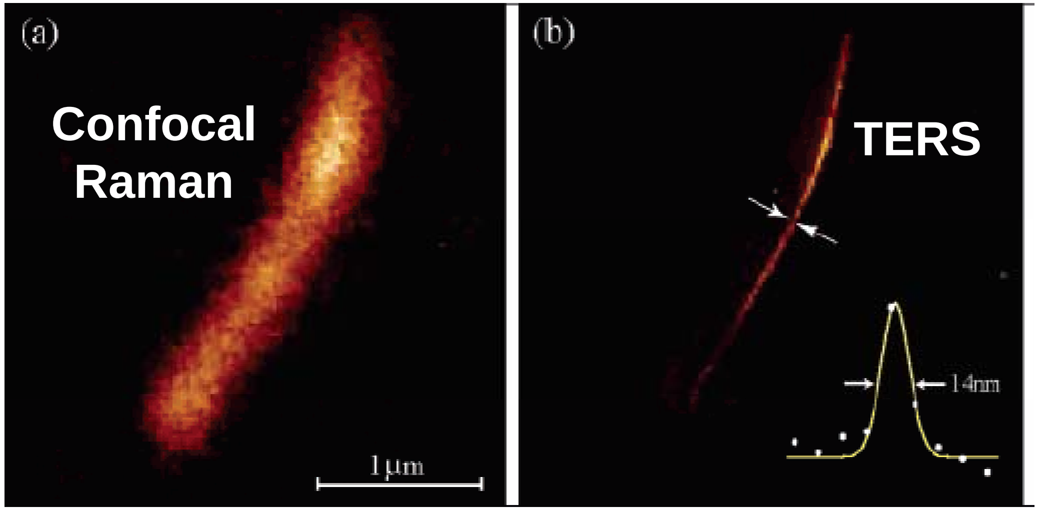


Methods : DFT (cluster and NRS), 3D-FDTD (electric field)

The $EF_{calc.}$ for pyrazine modes varies for from 2 to 140

Static electronic polarizability components calculated in TERS are larger than those calculated in SERS

Principle of TERS



FWHM: 275 nm

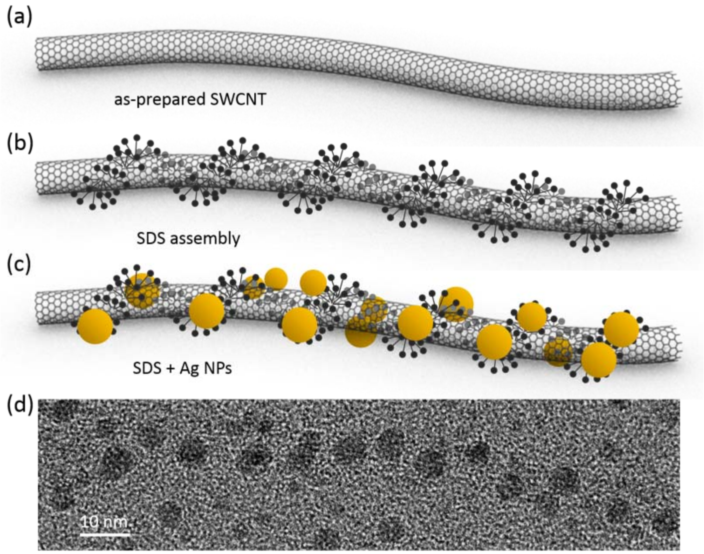
FWHM: 14 nm

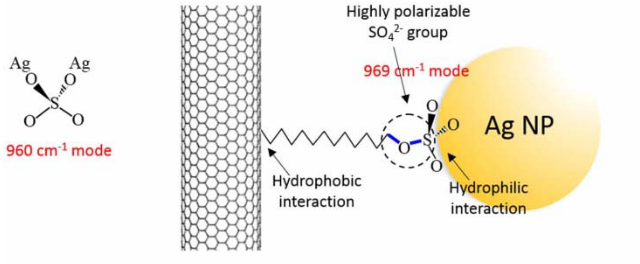
Hartschuh *et al*. ***Int. J. Nanoscale 3***, 371 (2004)

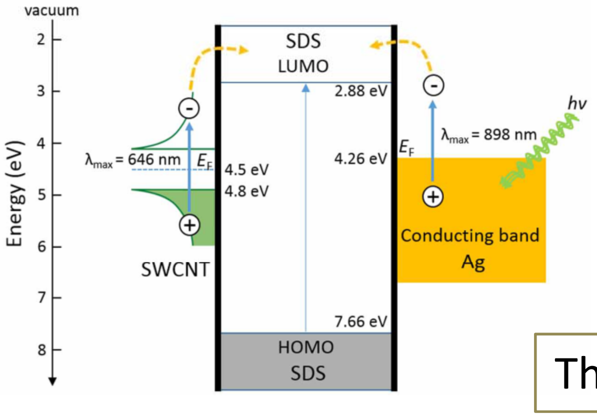
Principle of TERS

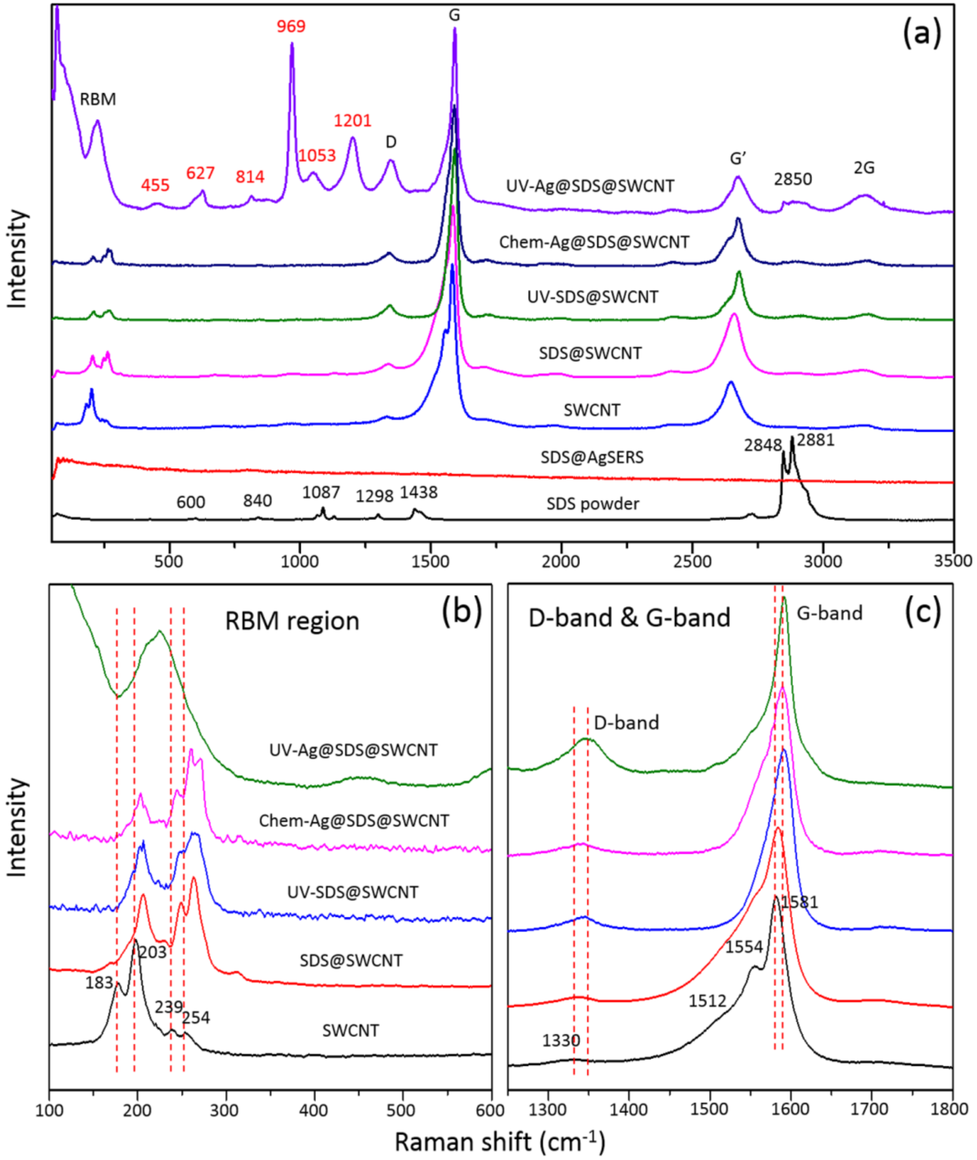
Example 2 : Light induced CT in CNT-SDS-Ag system

Valmalette *et al.* Sci. Reports 2012









The insight of the “chemical effect” is still limited

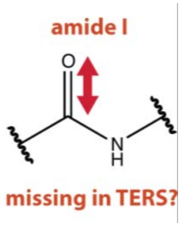
Modification of Raman modes, TERS *vs* NRS

- ☐ Width (lower density of state)
- ☐ Position (metallic bonding to tip and/or substrate)
- ☐ Relative intensities (orientation, electric field lines)
- ☐ Selection rules (CT, field gradient, ...)
- ☐ Time fluctuation
- ☐ Photo-bleaching (EF^2 law*)

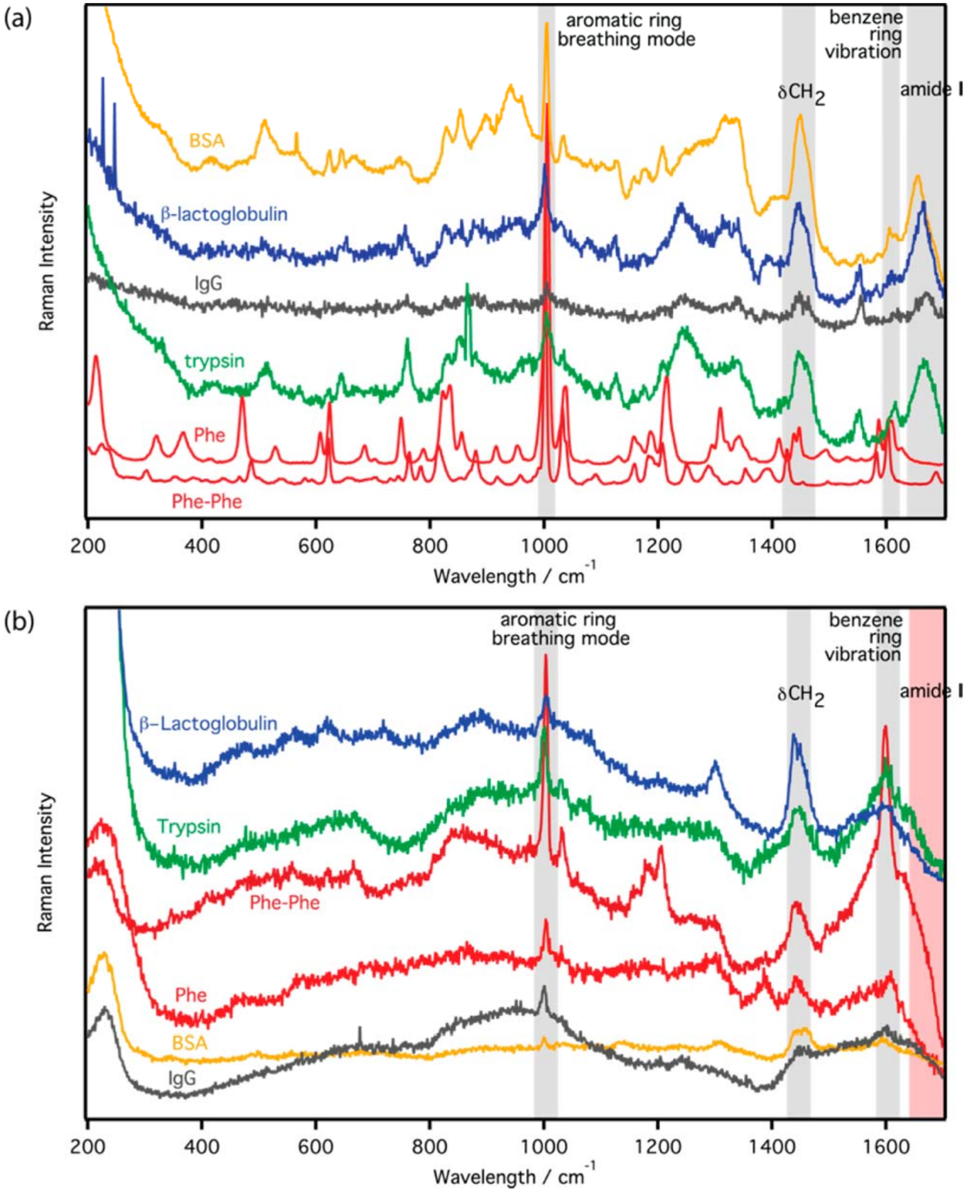
* Pettinger *et al*. JRS 2005

Principle of TERS

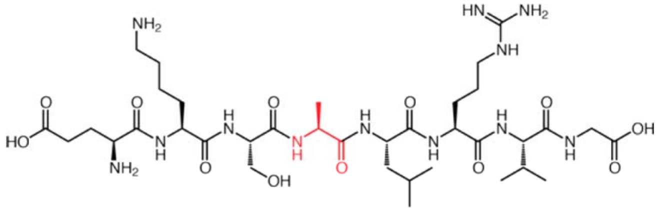
Example : the missing amide I mode in GM-TERS



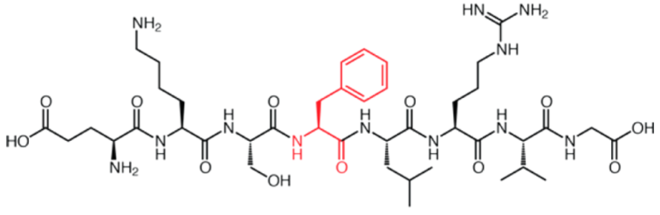
Blum et al. JPCC 2012



- ➢ NRS : amide I mode of proteins is widely used to identify secondary structure motifs of proteins
- ➢ GM-TERS : not visible* !



(1) Ala-Octapeptide: Glu-Lys-Ser-Ala-Leu-Arg-Val-Gly



(2) Phe-Octapeptide: Glu-Lys-Ser-Phe-Leu-Arg-Val-Gly

αPeptides differ at only one position in their sequences Glu-Lys-Ser-Xaa-Leu-Arg-Val-Gly, where Xaa = Ala (1), Phe (2).

* however, aromatic modes are prominent and can be used as reliable marker bands for imaging of proteins in a complex environment.

III- Instrumentation

Environment

- Air
- Liquid
- UHV
- inert

Light excitation

Positioning
Polarization
Incident angle
Wavelength
…

Nanoscale control of the environment of the **probe molecule**

Tip

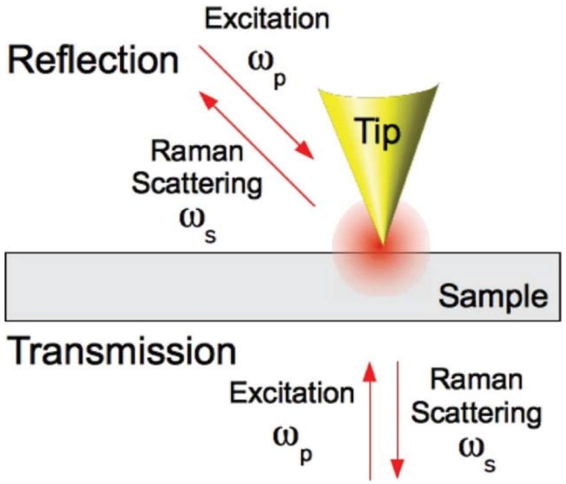
Positioning (TF, AFM, STM)
Material (Ag, Au, coating, …)
Shape
Reliability
…

Substrate

Material (transparent, opaque)
Morphology

Instrumentation

Configuration



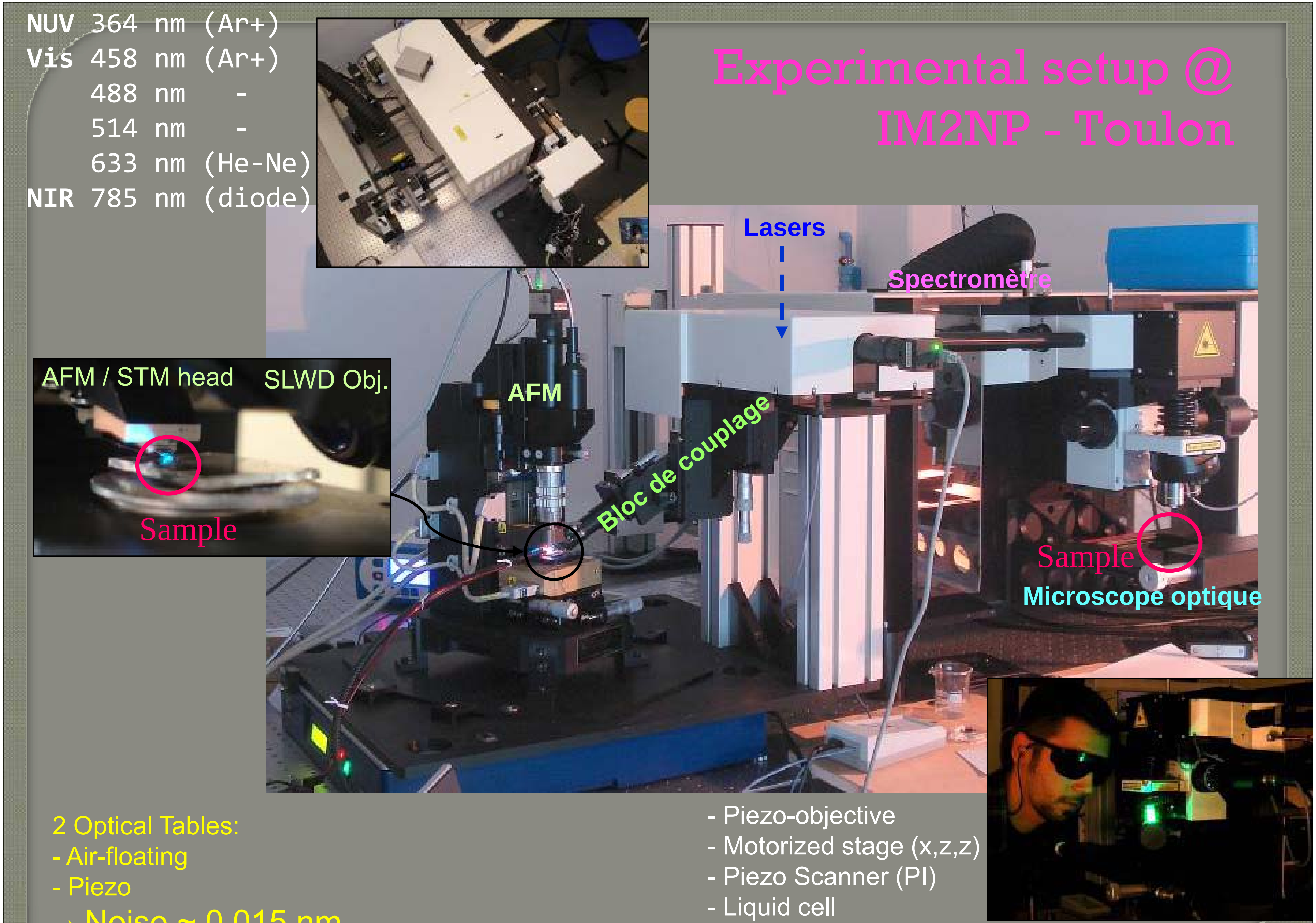
- AFM-based inverted microscope (transparent substrates) – *Transmission TERS*
- AFM-based top illumination (opaque substrates) – *Reflection TERS*
- STM : ***matching of the nanocavity plasmon resonance*** to the molecular transition with extremely precise tuning capability and large variety of single-molecule photochemical phenomena
- HV-TERS for monolayers and and submonolayers
- UV-TERS using Al tips
- TECARS (Tip Enchanced CARS)

Alignment procedure :

1. Scanning the tip / laser beam → intensity map
2. Positioning laser beam at the highest EF
3. Moving sample only

Experimental setup @ IM2NP - Toulon

NUV 364 nm (Ar+)
Vis 458 nm (Ar+)
488 nm -
514 nm -
633 nm (He-Ne)
NIR 785 nm (diode)

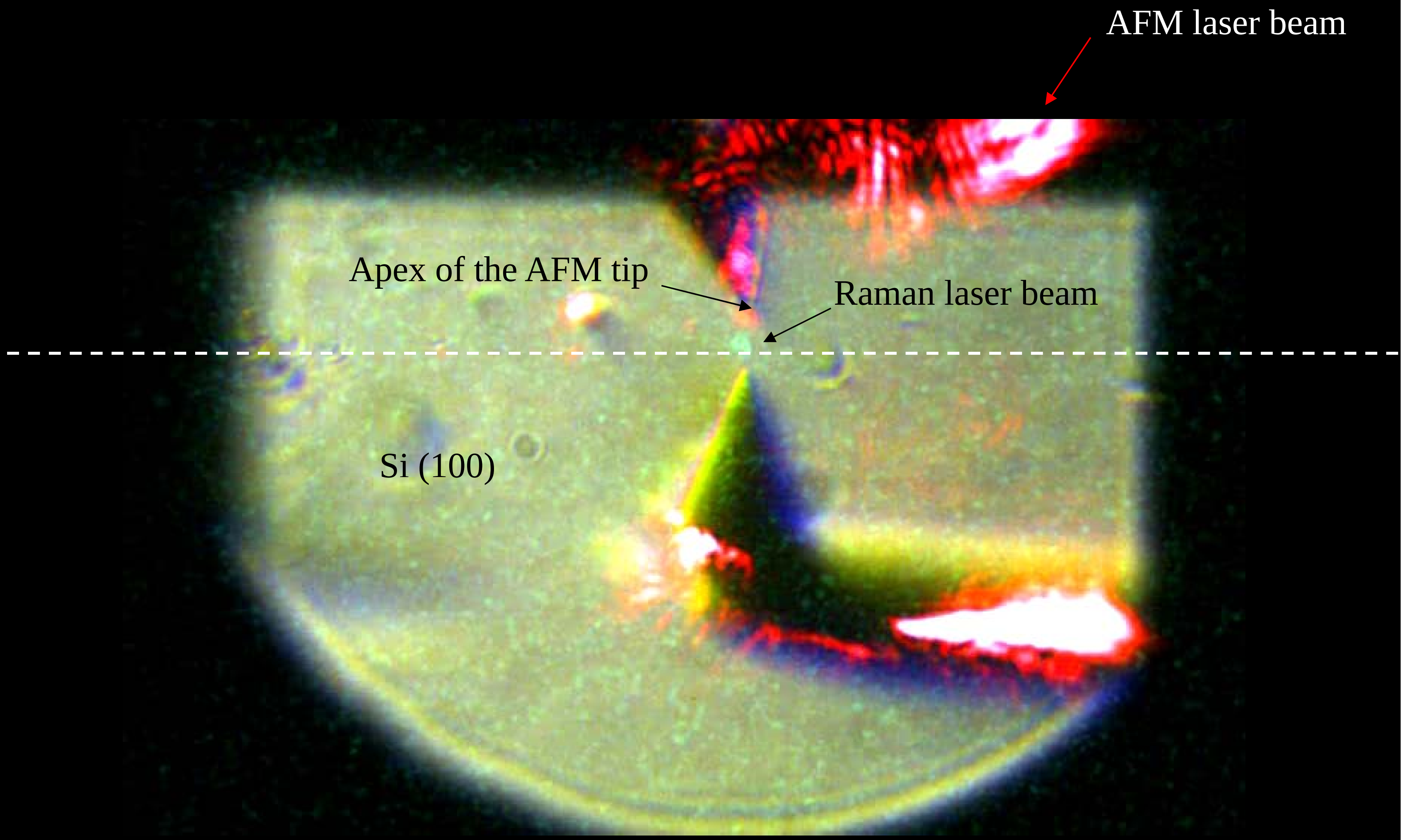


2 Optical Tables:
- Air-floating
- Piezo

→ Noise ~ 0.015 nm

- Piezo-objective
- Motorized stage (x,z,z)
- Piezo Scanner (PI)
- Liquid cell
- Environmental cell liq N_2 to 600°C

Approche – retrait d'une pointe TERS sur Si (100)



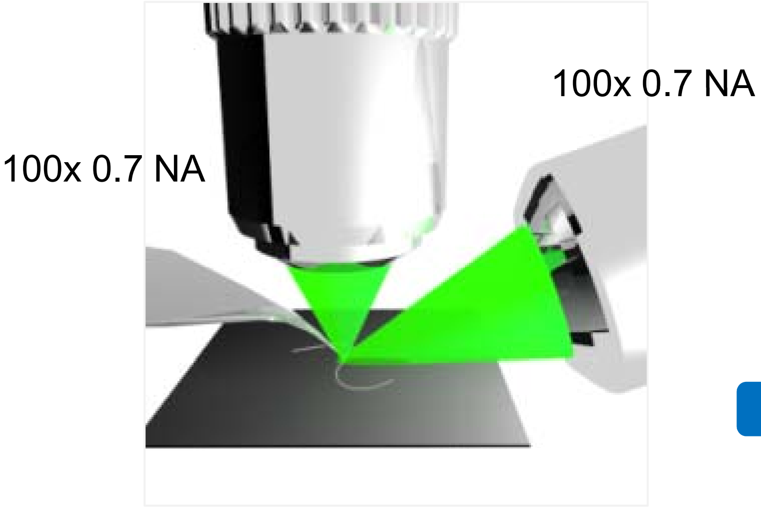
Valmalette J.C. "Handbook of Enhanced Spectroscopy:
TERS, Principles and Applications",
Ed. M. Lamy de la Chapelle, ***Pan Standford Publishing*** 2015

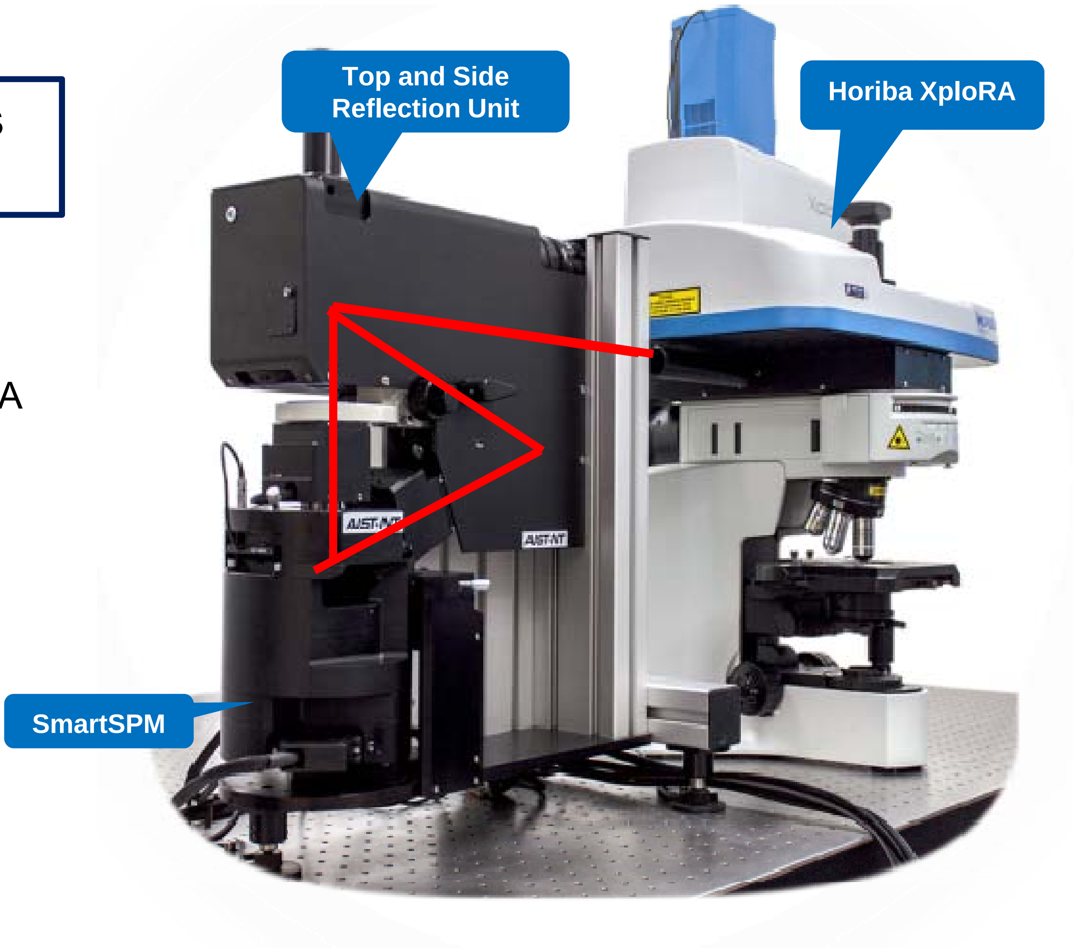
CRC press

NanoRaman: Optical configurations

Top and Side illumination

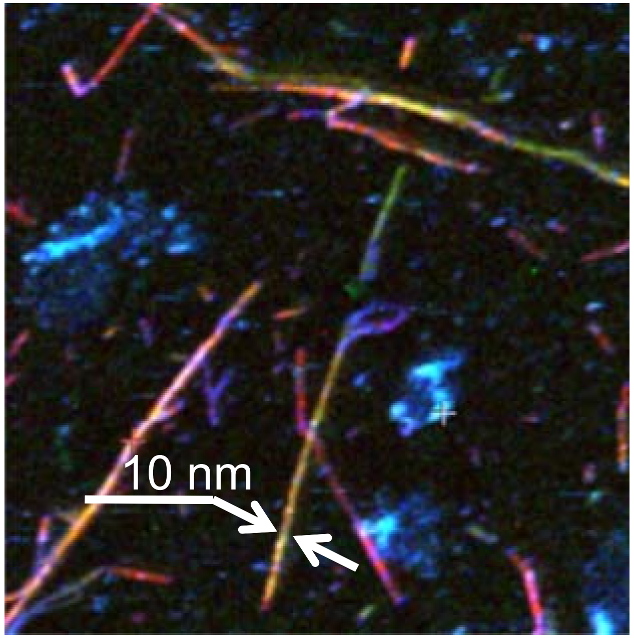
- Top: co-localized measurements
- Side: optimized for TERS

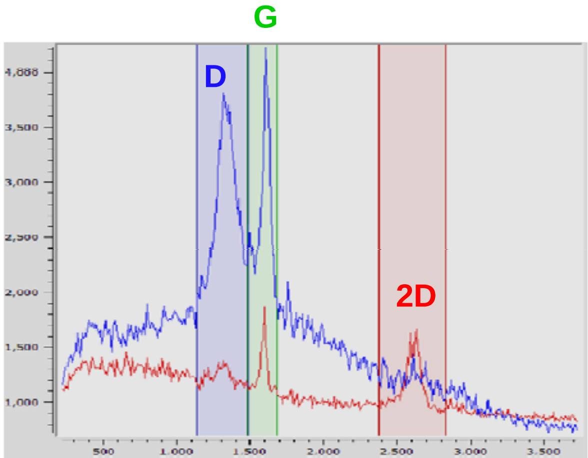




Probing Nano-Objects at the nanoscale

2 x 2 µm (200 x 200 points) NF / TERS images.
Excitation 638 nm; 6 mW; integration time 8 ms
Total map time: 8 min 9 sec





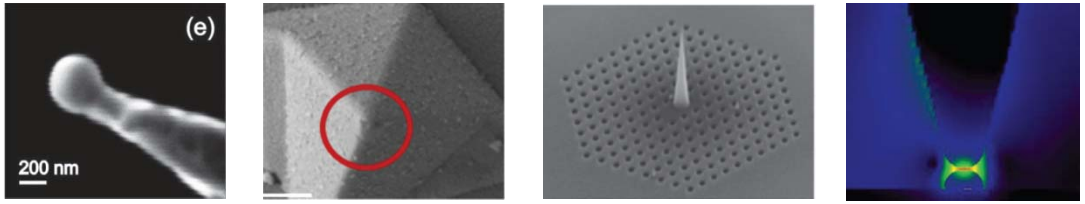
TERS spatial resolution ~ 10 nm (< λ / 60)

Raman at the single tube level

Local Defect sites

Amorphous Carbon structures/ Contaminants

Tips preparation



AFM tips : ☺ high versatility, materials, complex geometry and structures, coating
☹ high cost

STM and ***TF tips*** : ☺ low cost
☹ low versatility

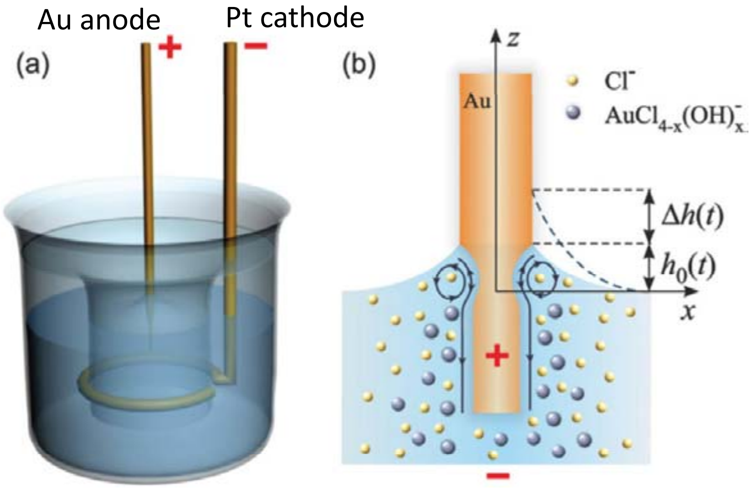
But for all … a poor reliability.

Sun PCCP 2009 There are two kinds of TERS, as illustrated in Fig. 1. For conventional TERS the surface is flat5 while, for double-tip TERS, a fixed nanoprotrusion (i.e., a gold nanoparticle made using an aerosol technique) is placed on a flat gold surface.7 Comparing this to the case of a gold tip on a flat gold surface, Chen et al. found that a larger Raman enhancement can be obtained using the double-tip configuration.7

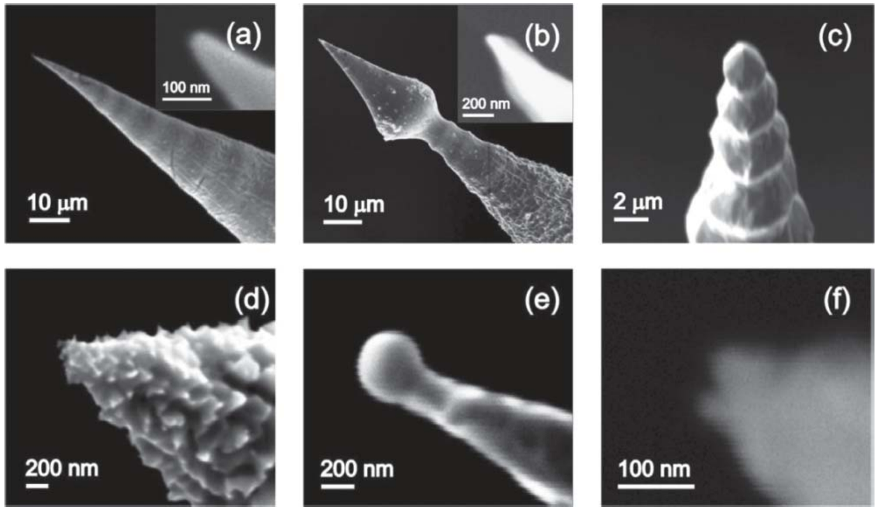
Tips preparation

Electrochemical etching

Two steps
1. Fast (HCl/H2SO4 mixture)
2. Slow (water/MeOH)



from Kharintsev *et al. JPD* 2013



from Kharintsev *et al. JPD* 2013

Etching mechanism at an electric field–driven liquid meniscus

References :

- Ren, B., Picardi, G. and Pettinger, B. (2004). *Rev. Sc. Instrum., 75 (4), pp. 837–841.*
- Billot, L., Berguiga, L., De La Chapelle, M. L., Gilbert, Y. and Bachelot, R. (2005). *Eur. Phys. J. Appl. Phys., 31, p. 139*
- Lopes M., Toury, T., de La Chapelle, M. L., Bonaccorso, F. and Gucciardi, P. G. (2013). *Rev. Sc. Instrum., 84 (7), p. 073702.*

(for Ag coated W wires, see Yi K, *et al RSI* 2008)

Instrumentation

Tips preparation

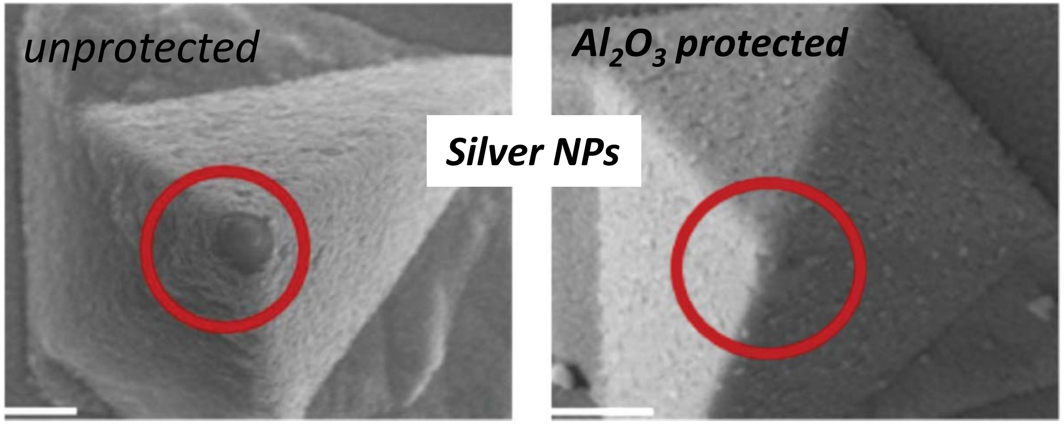
Dielectric coating

Prevent contamination and/or oxidation ⇒ **protective layer**
Tuning of the plasmonic response
Using $\neq \varepsilon_r$ ↗ EF

$Si_3N_4 \rightarrow$ Al ultra-thin coating $\rightarrow Al_2O_3$ dense coating

Life time of AFM tips

after six scans on a standard silicon grid



Si_3N_4 AFM tip

Real EF ?

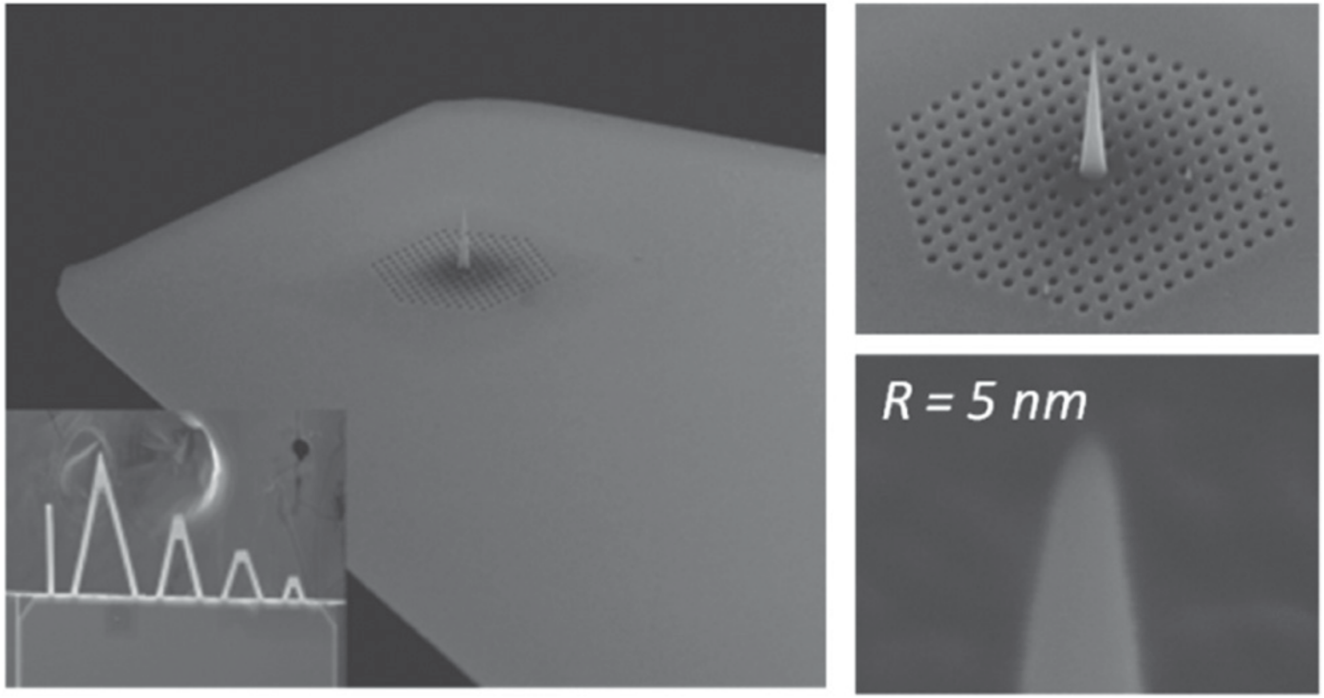
Im H *et al. ACSNano* 2010

But still controversy on protective layer …

Tips preparation

Plasmonic-photonic device architectures

Waveguide on a silicon nitride AFM cantilever with a conical shape and radius of curvature at the apex of 5 nm



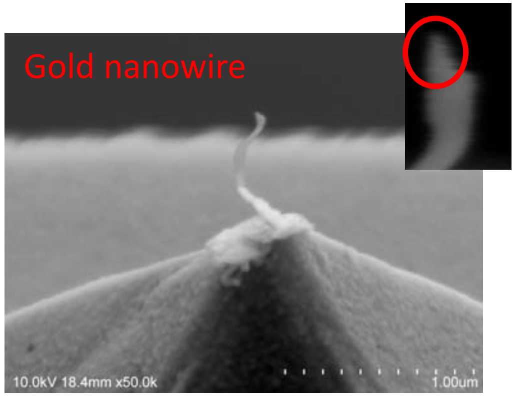
De Angelis *et al. Nature Nanotechnology* 2010

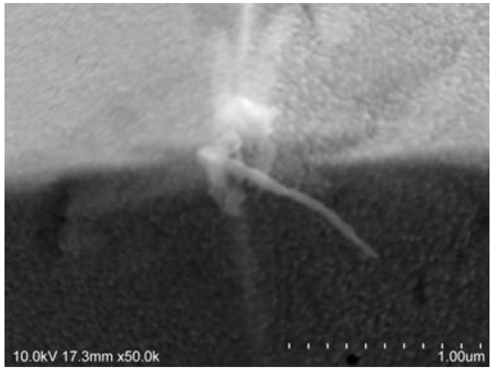
Instrumentation

Tips preparation

- ➢ Gold nanowire on Si AFM tip

Radius ~25nm

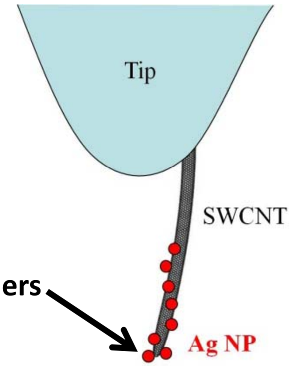




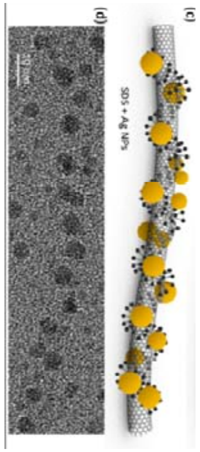
Limitation :
mechanical properties
of nanowires

Valmalette J.C. 2011 (comm.)

- ➢ Ag-SWCNT antenna



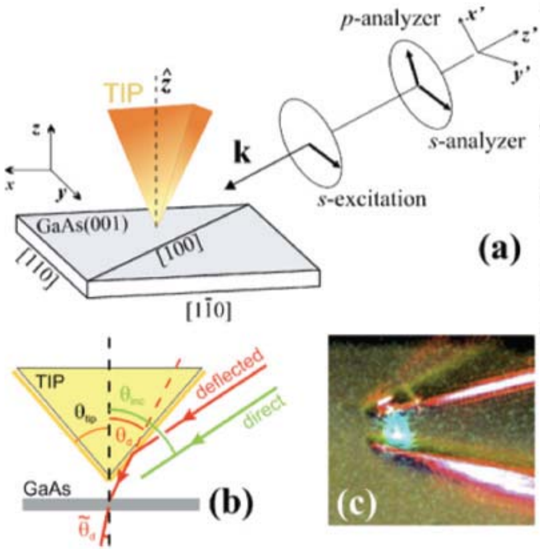
Ag nanoparticles **dimers**

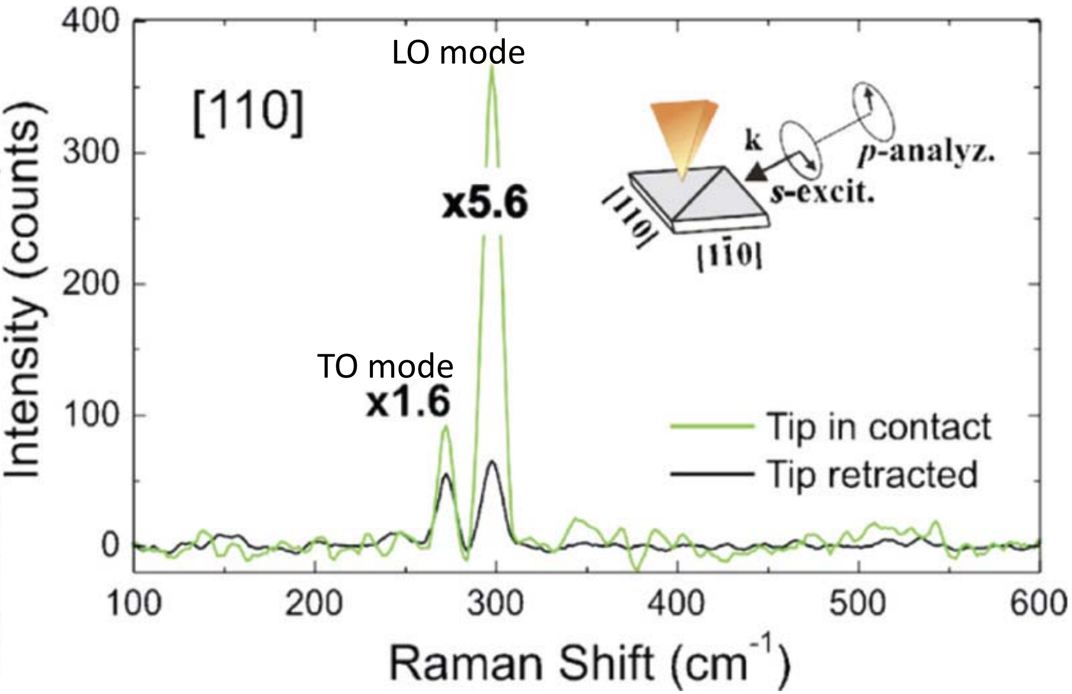


Valmalette et al. Sci. Reports (2014)

Polarization effect

Example : TERS on GaAs single crystal

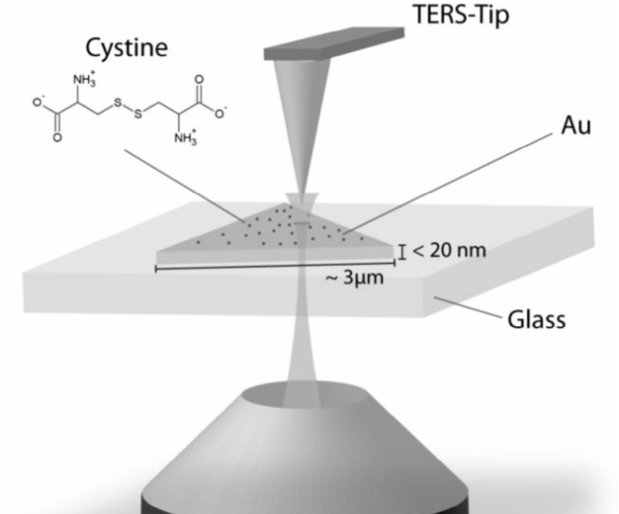




Gucciardi & Valmalette APL 2010

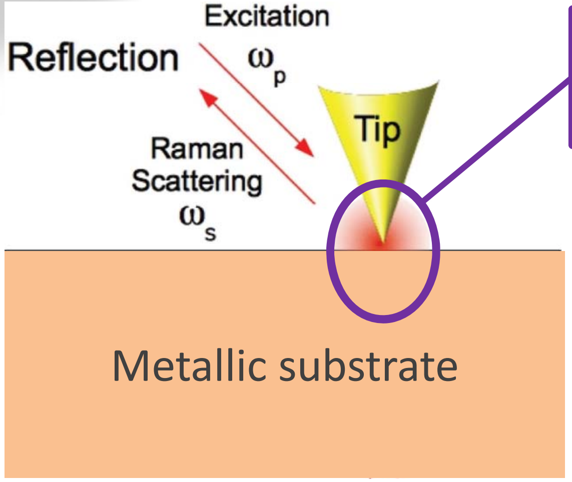
Differential LO-TO signal increase
⇒ ***fingerprint*** of tip-induced ***depolarization***

Gap-mode TERS



→ Metallic substrates :

- Very flat and thin surface Au, Ag, …
- Graphene
- SERS active ?
- …



Broadband of **nanocavity** plasmon field

⇩

Obtain on-resonance very sharp Raman modes

⇒ UHV-TERS

UHV-TERS

✓Tip and sample surface can be cleaned up easily and maintained clean ⇒ **Stable EF**

✓ Controlled coverage by molecules ⇒ **Single molecule TERS**

✓**Feedback-controlled TERS spectra** with and “without” tunneling currents

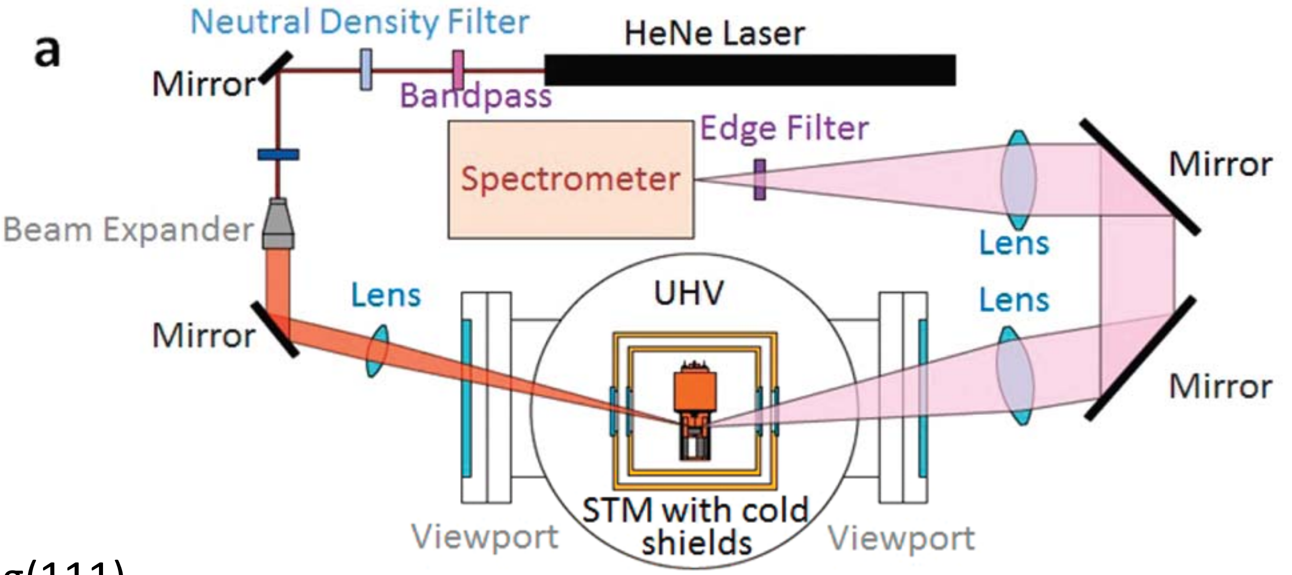
✓ UHV experimental advantages :

- ↘ desorption of molecules
- ↘ diffusion of molecules
- ↘ photo-degradation
- ↗ thermal stability (∼0.15 nm/min)

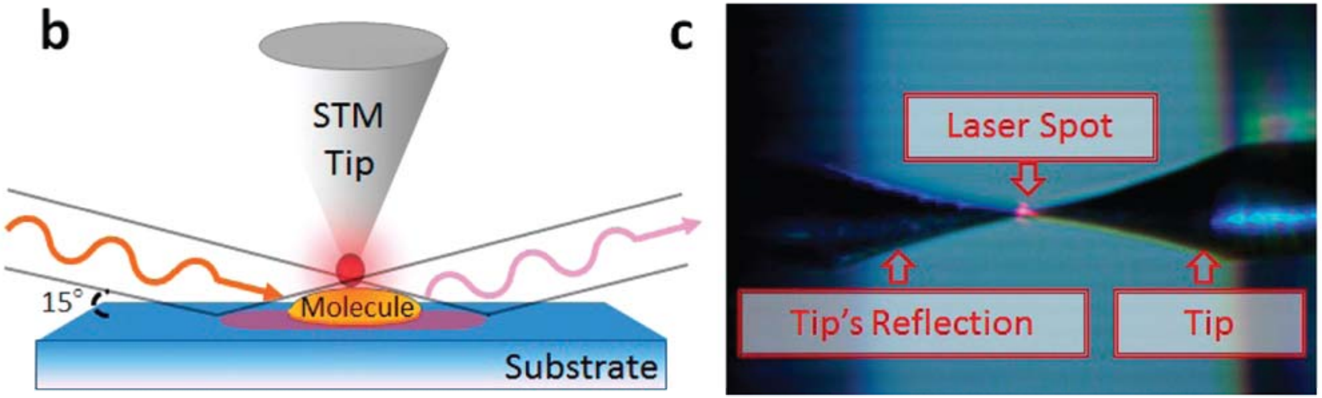
✓ Single **photophysics - photochemistry** mechanisms

Van Duyne’s group, Northwestern University on CuPc (Jiang N. et al. *NanoLetters* 2012)

UHV-TERS

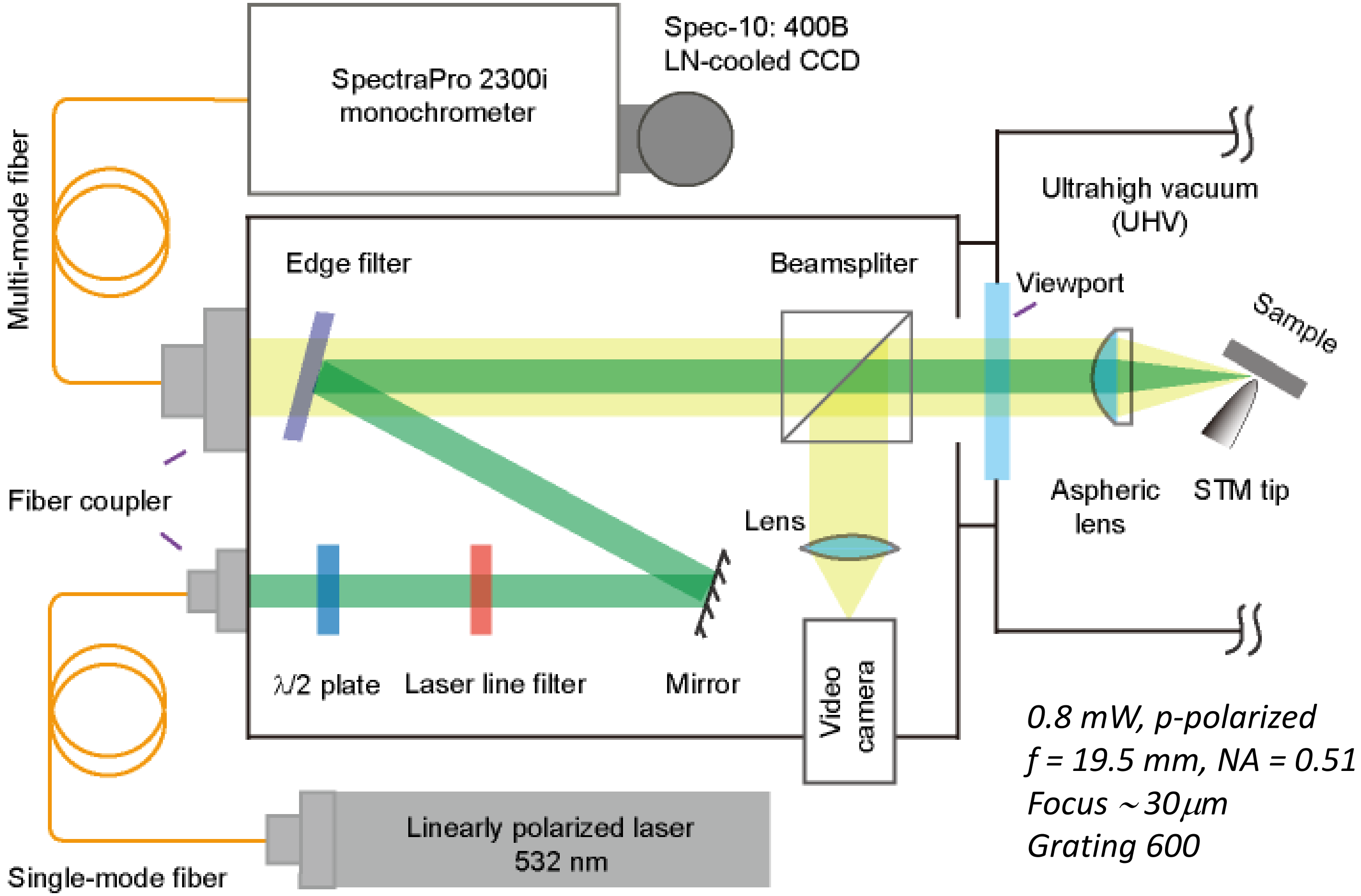


CuPc on Ag(111)



Jiang N. et al. *NanoLetters* 2012

UHV-TERS

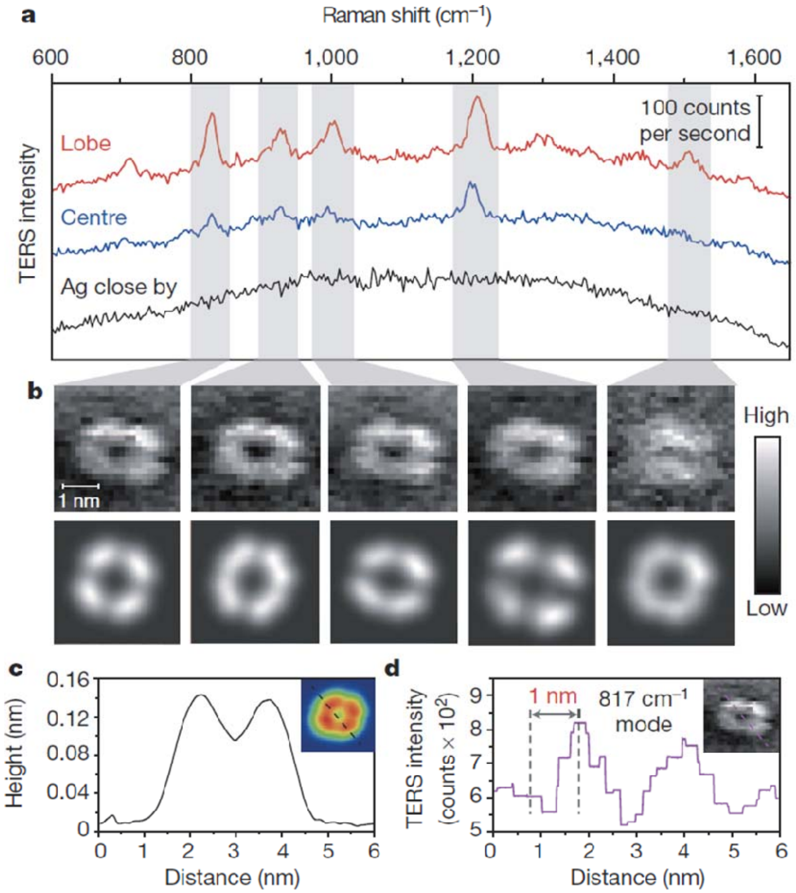


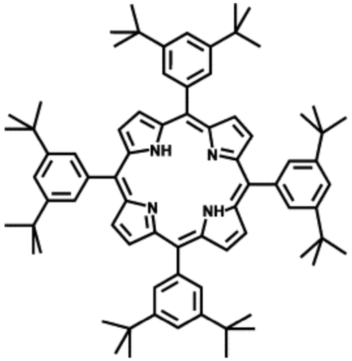
0.8 mW, p-polarized
f = 19.5 mm, NA = 0.51
Focus ~30μm
Grating 600

Zhang *et al*. Nature 2013

Feedback-controlled TERS spectra with and “without” tunneling currents

UHV-TERS

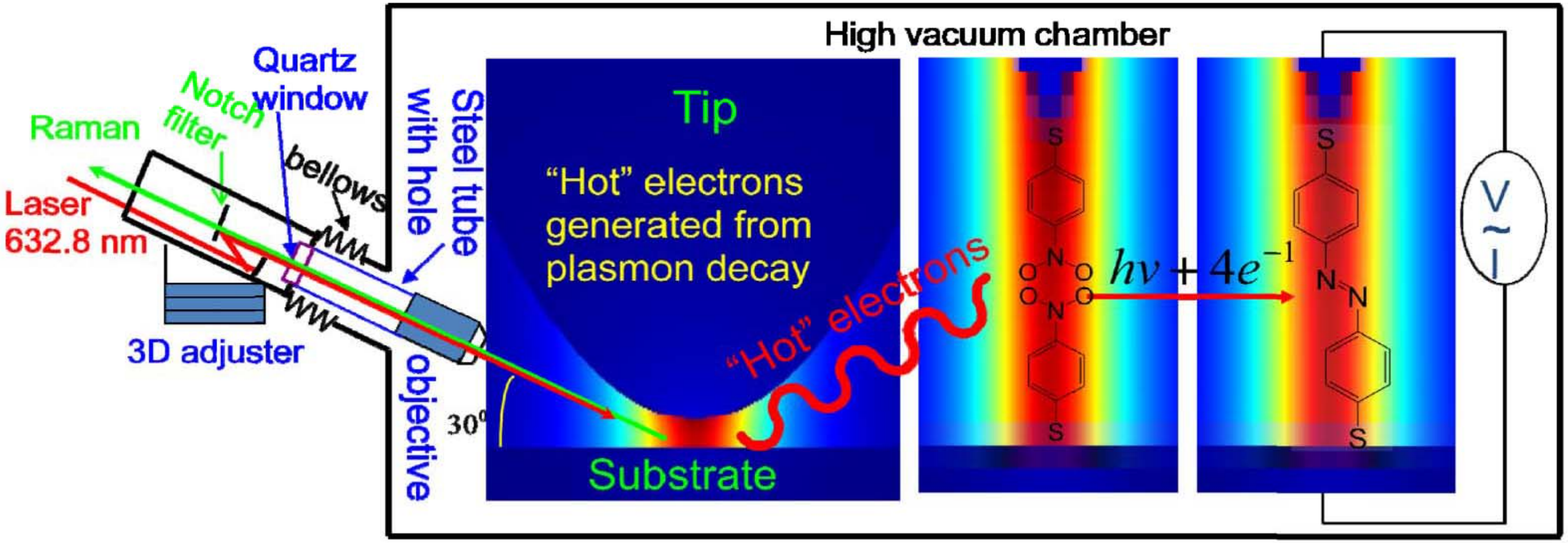


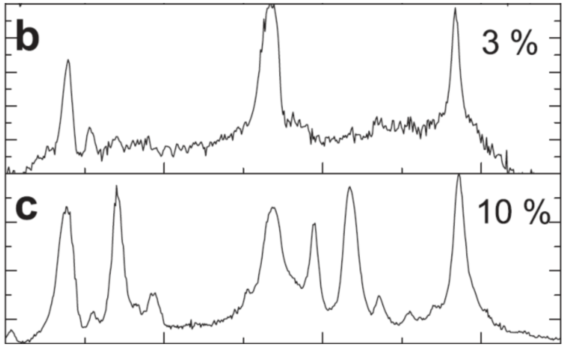


H_2TBPP

Zhang *et al*. Nature 2013

In-situ plasmon-driven chemical reactions





Sun M. et al. Sc. Reports 2012

dimerization

4-nitrobenzenethiol ⇨ dimercaptoazobenzene

Towards the simultaneous ***Single Chemical Detection …***

and ***Single Chemical Reaction*** ?

Other related techniques

- ☐ TE-CARS (Ishimura T. et al. PRL 2004)
- ☐ TEIR (Keilmann and Hillenbrand *PTRSLA* 2004, Raschke et al. *CPC* 2005)
- ☐ TEF (Hartschuh et al. *PTRSLA* 2004)
- ☐ …

IV- Simulation et modeling

- Essential tool to push-up the limit of the local field enhancement before testing new configurations

Incident wave
⊗
Tip/Substrate
⊗
Molecule

Δ position a few 0.1 nm $\Rightarrow$ EF changes a few orders of magnitudes !

Dipole discrete approximation (**DDA**) : Local field as a function of (***E***, ***k***), ε_r, geometry,

Tip in air $\Rightarrow$ EF max with polarization // tip

Finite-difference time-domain (**FDTD**) : solving Maxwell's equations in complex geometries

Longitudinal electric field:

$$E_z(\rho,z) = 2iA\int_0^\alpha P(\theta)\cos^{1/2}(\theta)\sin^2(\theta)J_0(\kappa\rho\sin\theta)\times\exp(i\kappa z\cos\theta)\,d\theta, \qquad (1)$$

Transverse electric field:

$$E_{tr}(\rho,z) = A\int_0^\alpha P(\theta)\cos^{1/2}(\theta)\sin(2\theta)J_1(\kappa\rho\sin\theta)\times\exp(i\kappa z\cos\theta)\,d\theta, \qquad (2)$$

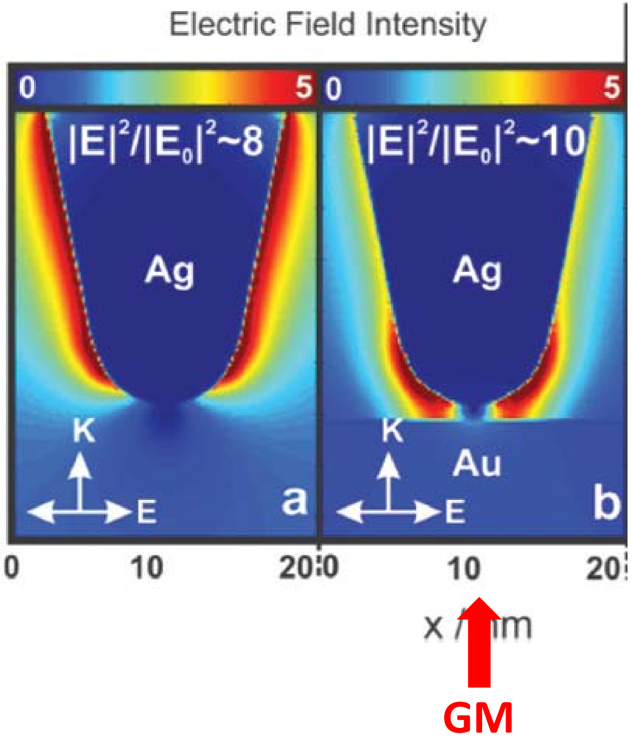
α : maximum focusing angle
J_0 and 1 J_1 : Bessel functions
$P(\vartheta)$: pupil function of a Bessel Gaussian beam.

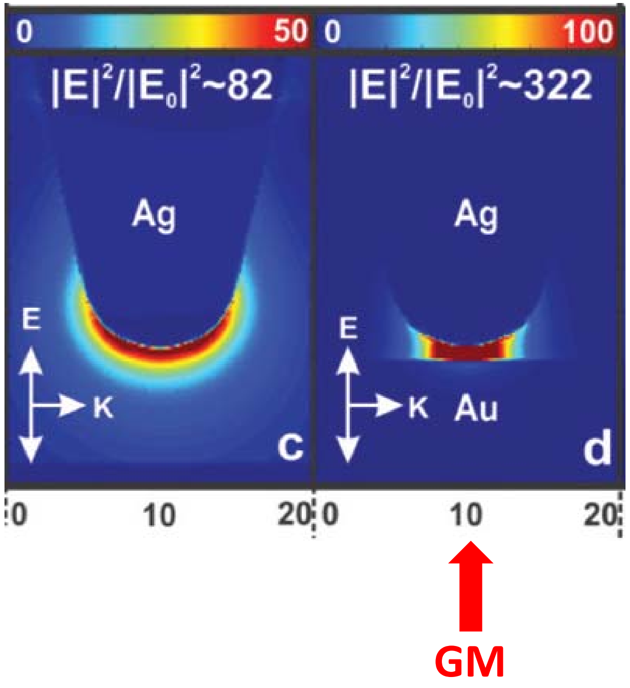
For more details, see Section modeling

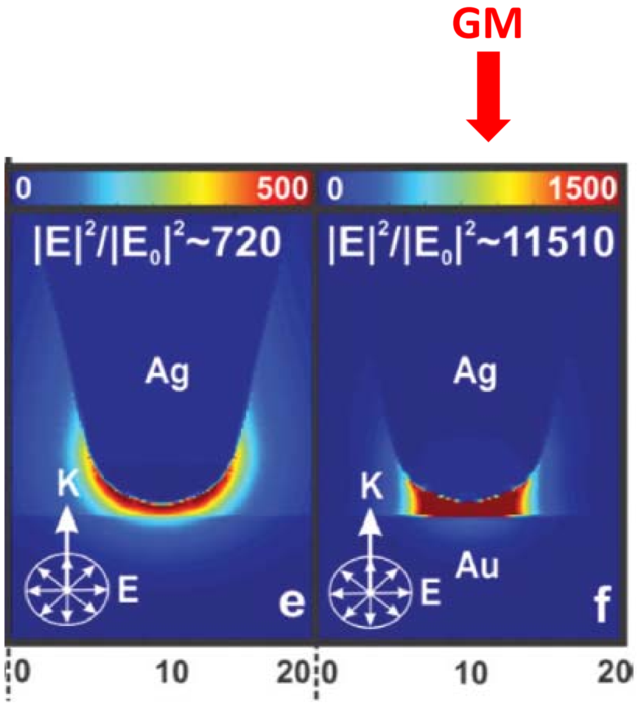
Comparison N-/GM-modes

Tip: radius 10 nm, cone 25°
Substrate: thickness 5 nm
Excitation: 532 nm
Gap: 1 nm

Kazemi-Zanjani et al *Opt. Expr.* 2013







FDTD controversy for TERS

Reliability to solve nano-optics problems ?
Converge to the true solution* ?
For very small radius ⇒ discontinuous Galerkin (DG)**

⇩

Mesh generation with element sizes
varying several orders of magnitude

⇩

Ultra large linear system !

Current challenge to overcome in a near future

*staircasing approximation in curved geometry even with negligible voxel size

** variant of finite elements methods

5- Applications

- Material science
  - CNT bundles or individual CNT, graphene, and 6H-SiC with graphene adlayers, imaging the locally induced strain distribution in CNTs.
  - Other inorganic compounds: semiconductors (InN, Si(001), GaAs(001), oxides $BaTiO_3$, TiO_2 and silicone
  - Surfaces and interfaces: local interactions at the interface of styrene-butadiene rubber/MWCNT nanocomposites, surface bonding on silicon, single surface states in inorganic semiconductors, such as Nb dopedTiO_2. Interaction between large polyatomic molecular adsorbates and specific binding sites on solid surfaces.
  - Catalysts and heterogeneous catalytic reactions
  - Stress measurement

5- Applications

- Molecular electronics
  - Molecular monolayers: Cu porphyrin , CuPc, thiol compounds
  - Singlemolecule TERS imaging
  - Electron transport processes in molecular junction
  - Electron transport from donor molecules to acceptor molecules (in organic photovoltaic is deduced from TERS / photoluminescence
  - (PL) measurements of correlation between
  - polymer blends segregation and PL quenching efficiency

- Biotechnology
- Photophysics

5- Applications

Biotechnology

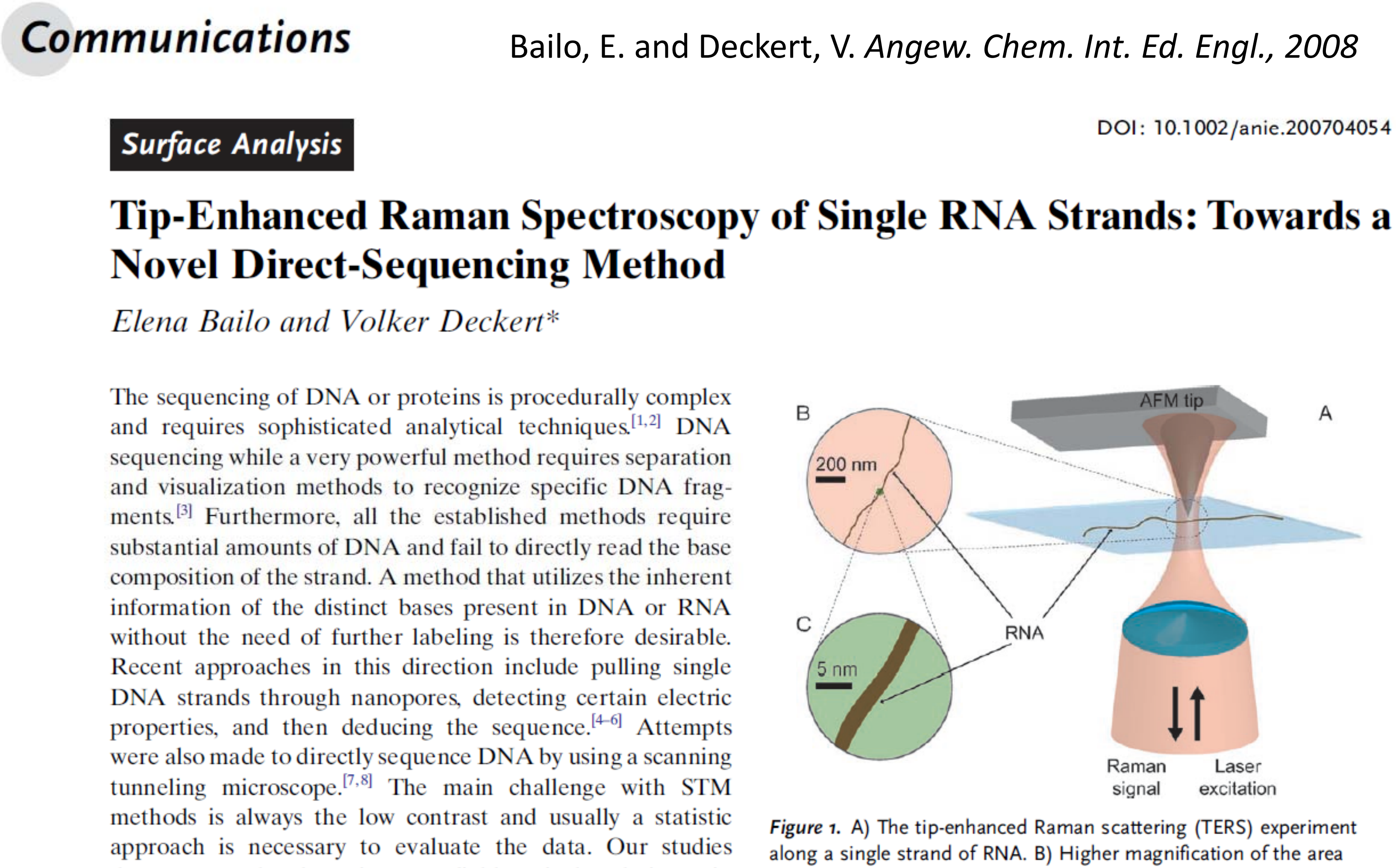
biological units: proteins

- peptides
- single RNA strands
- cytochrome
- lipid domains
- alginate biofilms
- insulin amyloid fibrils

biological mechanisms:

- Interactions of proteins with biocrystal
- protein–ligand binding
- in vivo characterization of protein uptake by yeast cell envelope

Bailo, E. and Deckert, V. *Angew. Chem. Int. Ed. Engl., 2008*



Surface Analysis

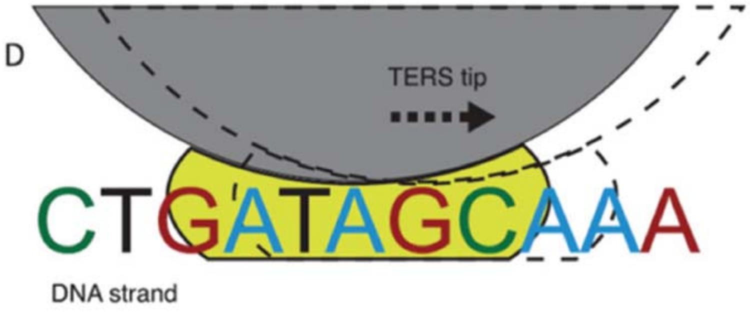
DOI: 10.1002/anie.200704054

Tip-Enhanced Raman Spectroscopy of Single RNA Strands: Towards a Novel Direct-Sequencing Method

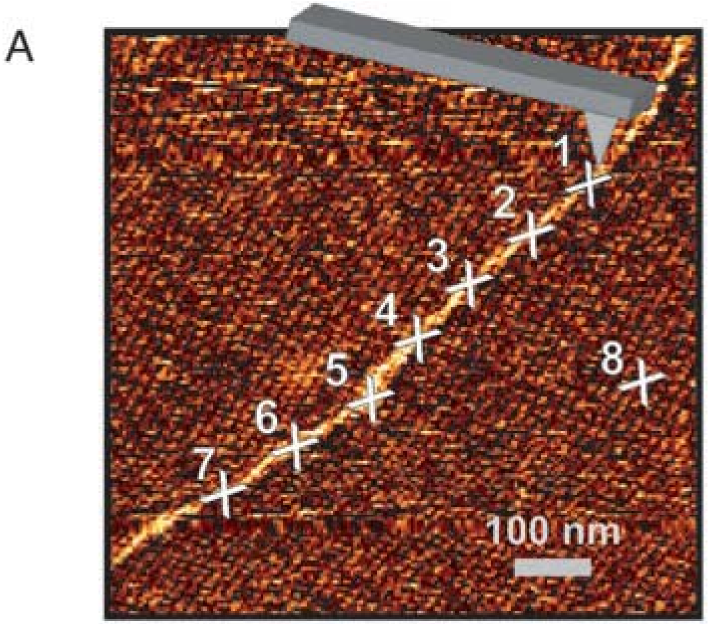
*Elena Bailo and Volker Deckert**

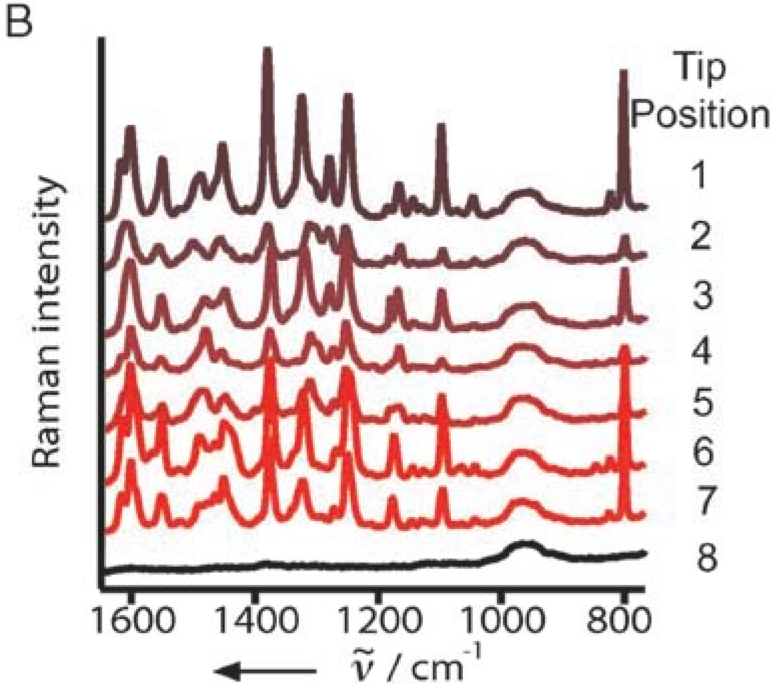
The sequencing of DNA or proteins is procedurally complex and requires sophisticated analytical techniques.[1,2] DNA sequencing while a very powerful method requires separation and visualization methods to recognize specific DNA fragments.[3] Furthermore, all the established methods require substantial amounts of DNA and fail to directly read the base composition of the strand. A method that utilizes the inherent information of the distinct bases present in DNA or RNA without the need of further labeling is therefore desirable. Recent approaches in this direction include pulling single DNA strands through nanopores, detecting certain electric properties, and then deducing the sequence.[4–6] Attempts were also made to directly sequence DNA by using a scanning tunneling microscope.[7,8] The main challenge with STM methods is always the low contrast and usually a statistic approach is necessary to evaluate the data. Our studies demonstrate that by using near-field optical techniques in

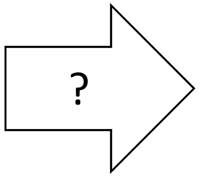
Figure 1. A) The tip-enhanced Raman scattering (TERS) experiment along a single strand of RNA. B) Higher magnification of the area approximately corresponding to the size of the laser spot. C) Magnification corresponding to the interaction area of the TERS probe tip.

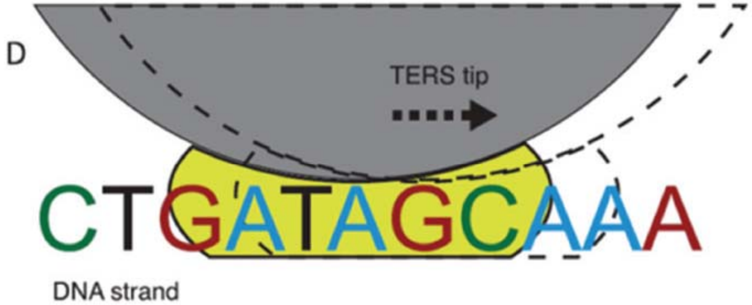


l Deckert, V. *Angew. Chem. Int. Ed. Engl., 2008*









- Les limitations majeures
  - Milieu liquide (systèmes biologiques, conditions environnementales …)
  - Reproductibilité
  - Contamination

Conclusion

- Analysis with nanometric accuracy
- Wide diversity of systems
- Probe other physical effects (tunneling current, PL, light induced electron transfer, …)
- …

but TERS is not yet a mature technique

Perspectives

- UV-TERS $\rightarrow$ fundamental knowledge
- Substrates for GM excitation (graphene, …)
- Modeling λ- and space-dependence of nanocavity
  - mesh generation with element sizes varying several orders of magnitude, discontinuous Galerkin (DG)
  - Calculation from density functional density (DFT) of the "*chemical effect*"
- Laser excitation tuning to fit nanocavity plasmon resonance