Marc Chaigneau
AFM/Raman Product Manager

High-speed Tip Enhanced Raman imaging

11-10-2016

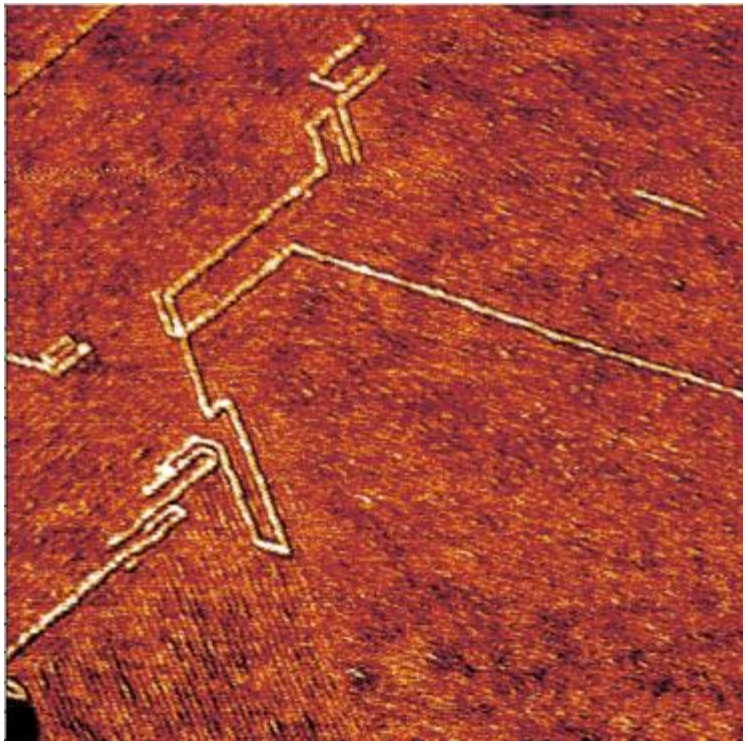
Journée Thématique - Couplage Microscopies Optiques/Microscopie à Force Atomique
Institut Pasteur de Lille

Bringing Scanning Probe Microscopies…

- SPM bring a lot of information on the physical characteristics of materials
  - *Topography*
  - *Mechanical properties*
  - *Electrical and magnetic properties*

- SPM is truly a nanoscale imaging technique…

…but it lacks ***chemical*** sensitivity



SS-DNA on HOPG functionalized with octadecylamine. 500nm frequency shift image.

... and Raman together

- Confocal Raman Microscopy is a very *specific* **chemical imaging**
  - Precise structural information, wide areas of application
  - Non-destructive technique, compatible with many environments
  - A wide spectrum of available laser sources

  (from UV to IR : possibility of resonant Raman scattering)

- **Drawbacks**
  - **Low cross-section *(~ 10^{-30})***
  - **Limited spatial resolution**

Graphene- HORIBA

- 156 x 180 = 28080 spectra (step = 0.5 µm)
- 2 min 08 (EMCCD, SWIFT; Acq. Time 2 ms + 1.5 ms)

Let’s break the Rayleigh criterion!

How?

Nano Lightning Rod

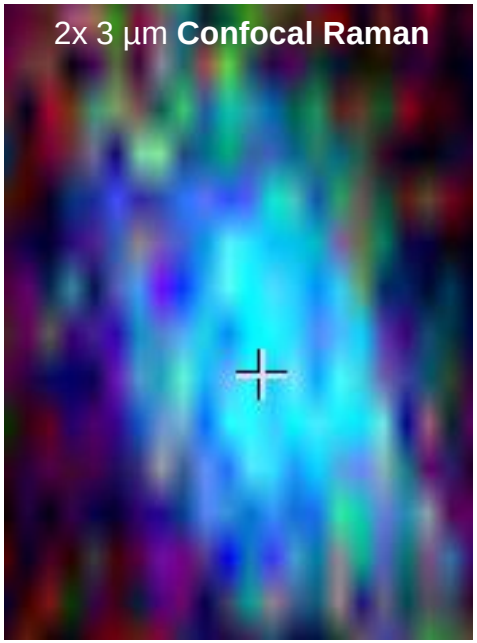
plays the role of a Nano-Antenna

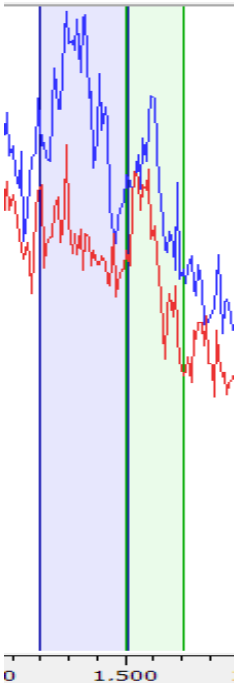
. Signal Enhancement

- *Near-Field Resolution*

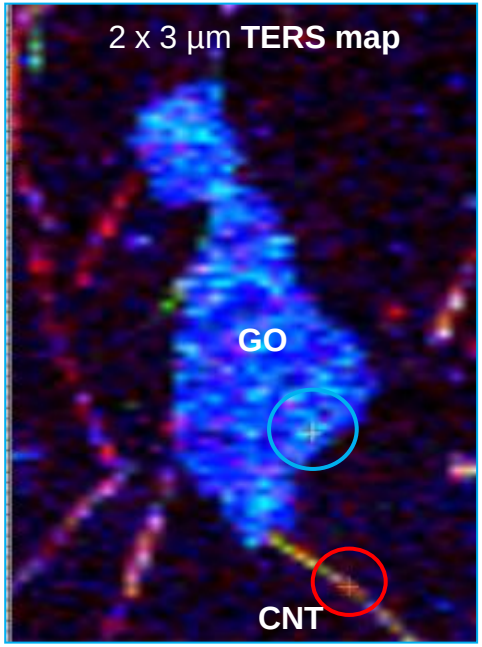
Conventional Raman VS TERS

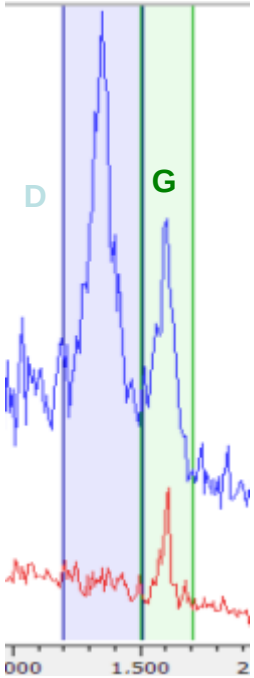
Confocal Raman and TERS of the <u>same area</u>, graphene oxide and CNTs on Au





Confocal Raman
13 mW; integration 1 s





TERS
130 µW; integration 0.2 s

I. Bringing SPM and Raman together

II. Applications of TERS in Materials and Life Sciences

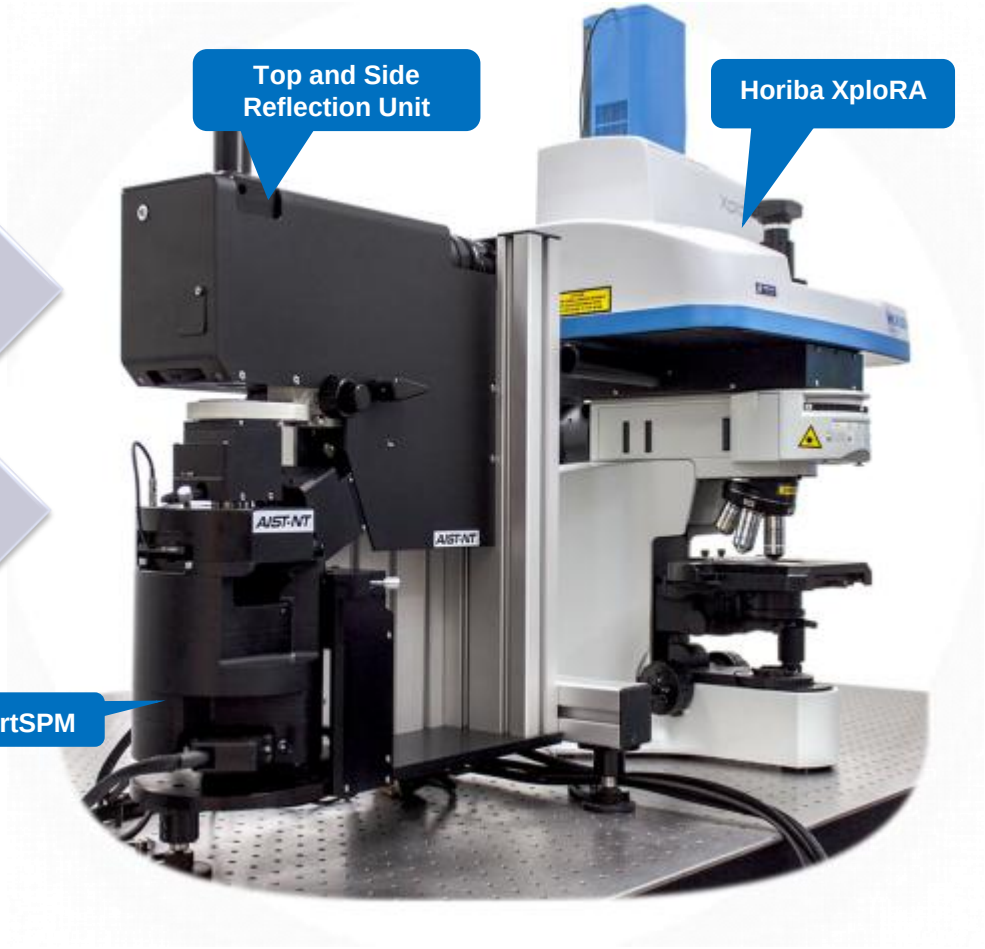
III. Stimulated Tip Enhanced Raman imaging

NanoRaman™

Bringing SPM and Raman together

High resolution Raman spectrometer → Chemical and structural analysis

Scanning probe microscope (SPM) → Nano resolved surface mapping

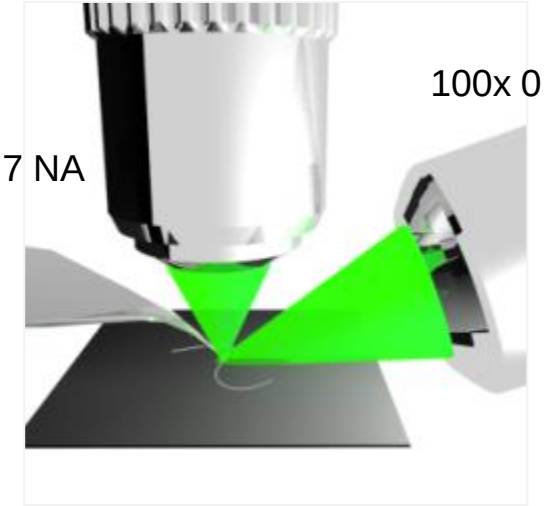


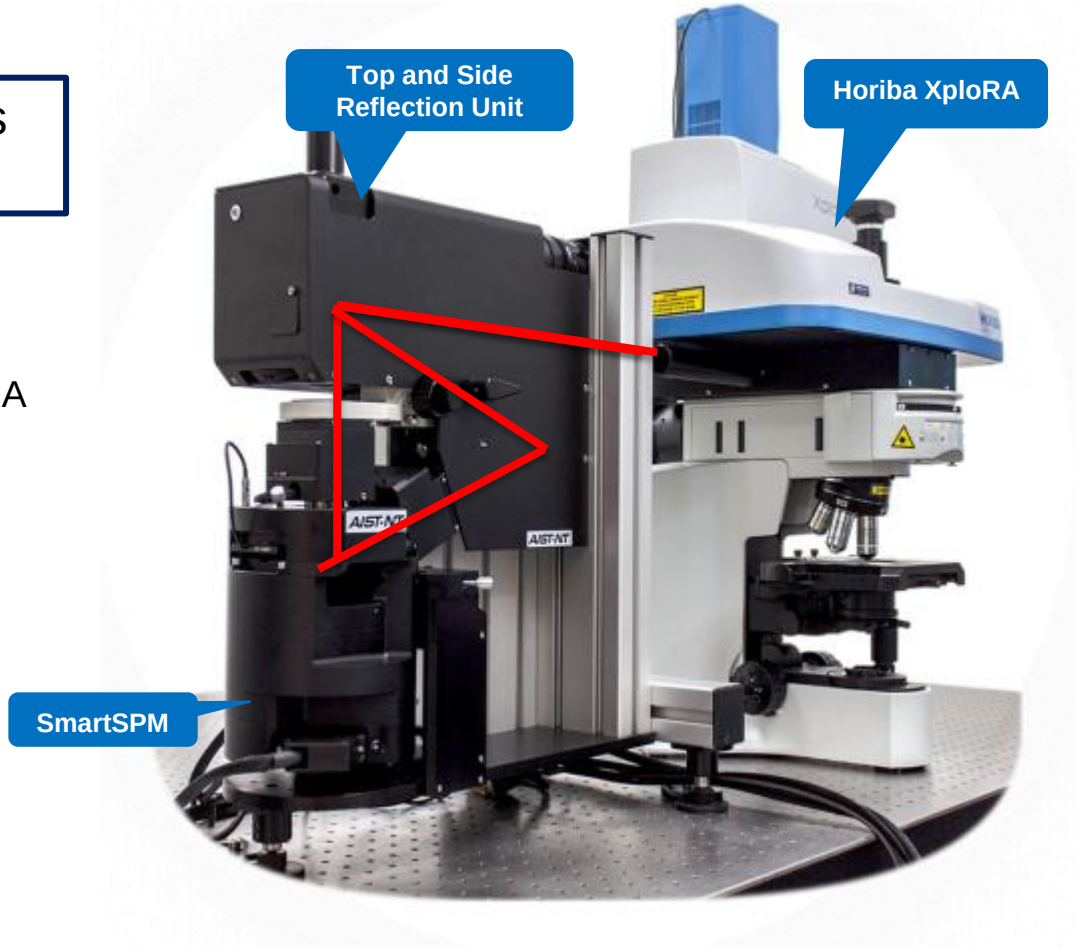
XploRA Nano

NanoRaman: Optical configurations

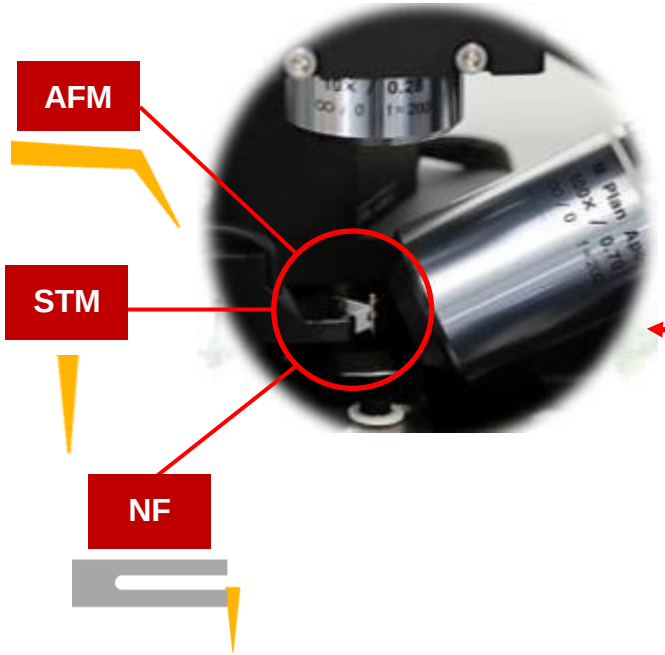
Top and Side illumination

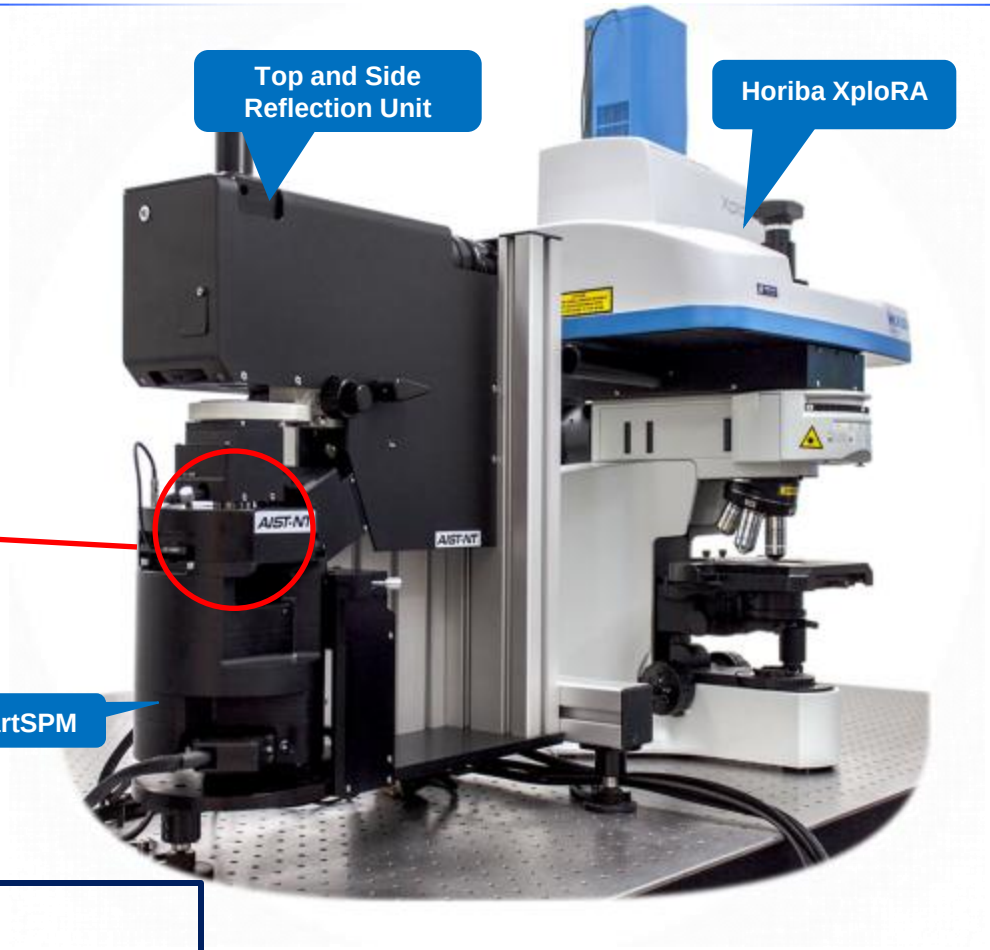
- Top: co-localized measurements
- Side: optimized for TERS





Different approaches for the SPM

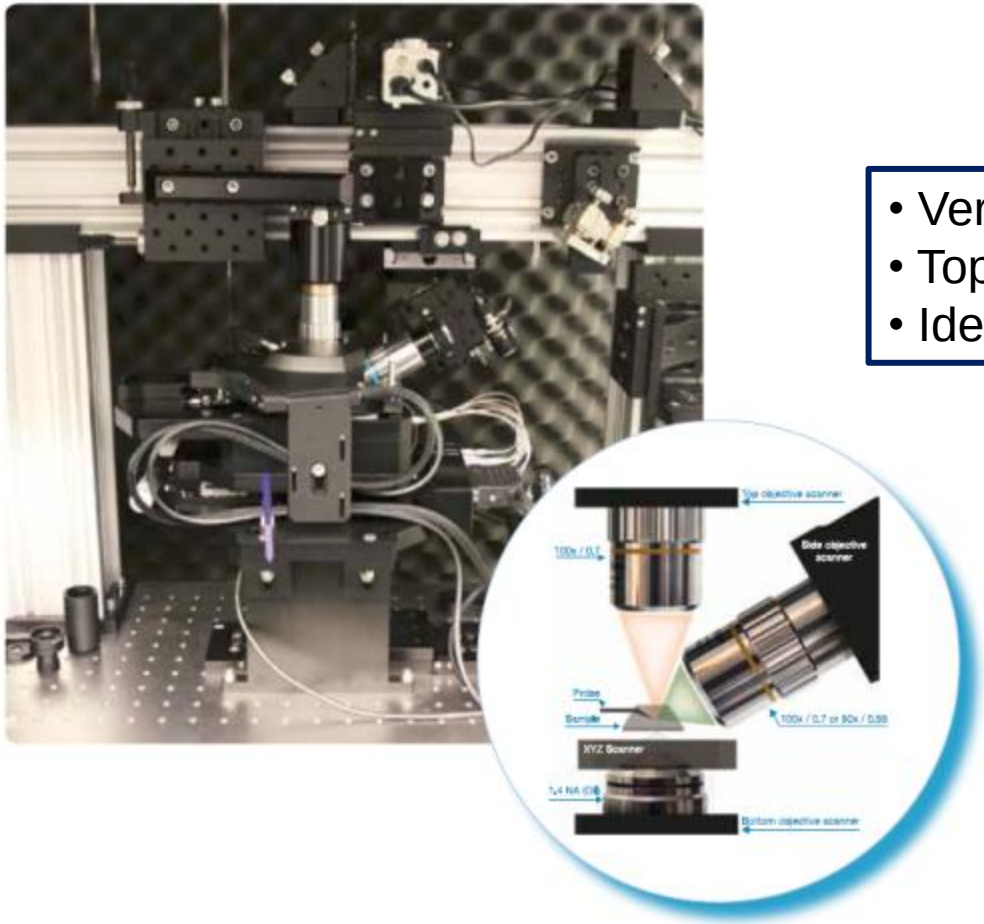




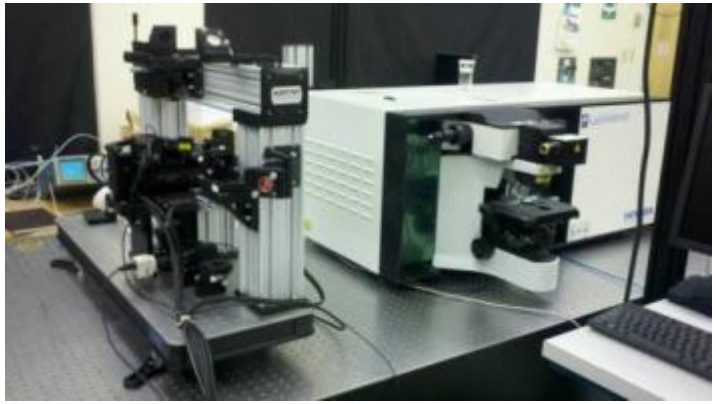
AFM: Atomic Force Microscope
STM: Scanning Tunneling Microscope
SF/NF: Shear-Force/ Normal Force Microscope
→ **HORIBA TERS tips are available**

TRIOS Platform

Transmission and Reflection optical access

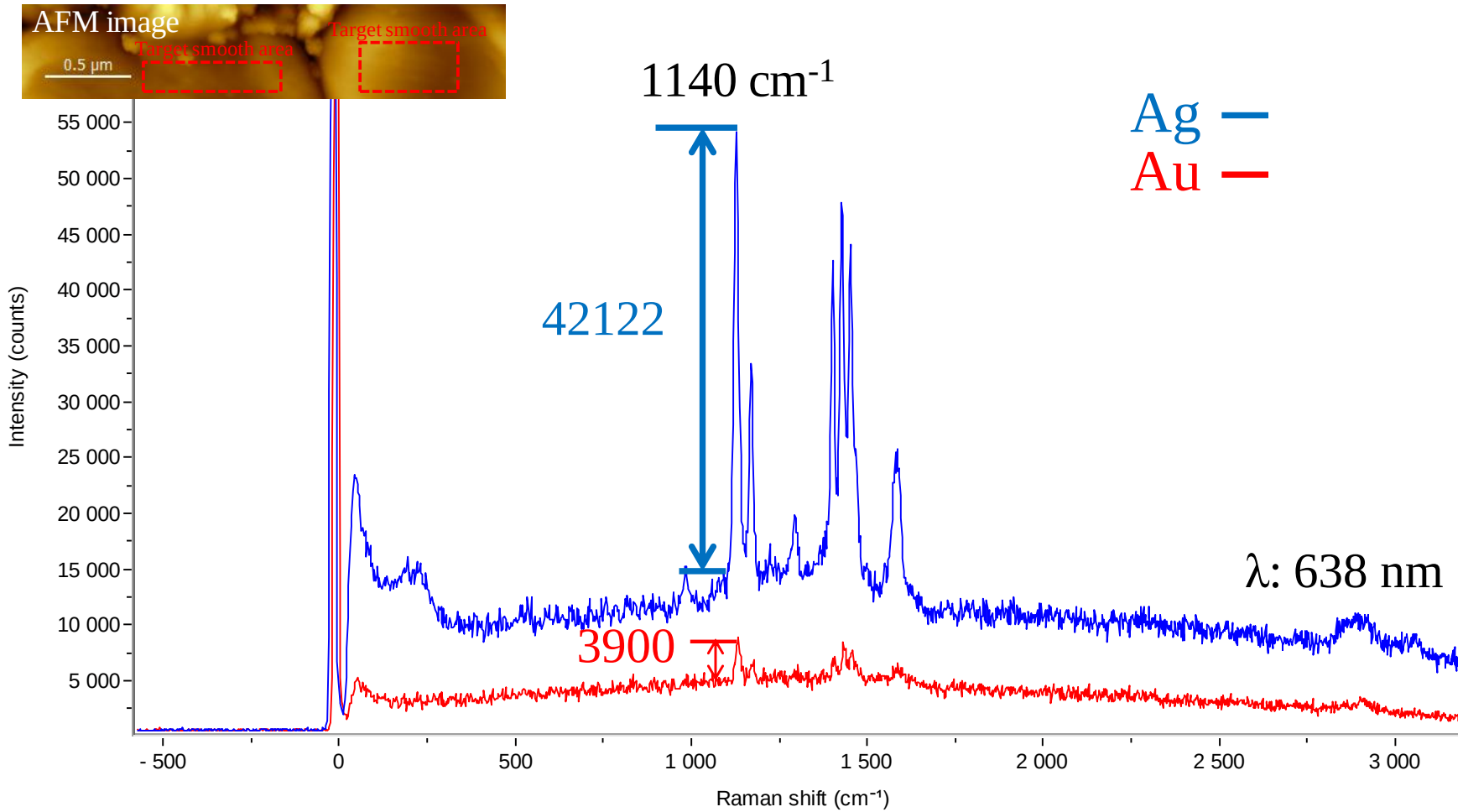


- Versatile optical coupling platform
- Top-down, side, inverted access
- Ideal for custom optical components



TER signal comparison between Ag and Au tip

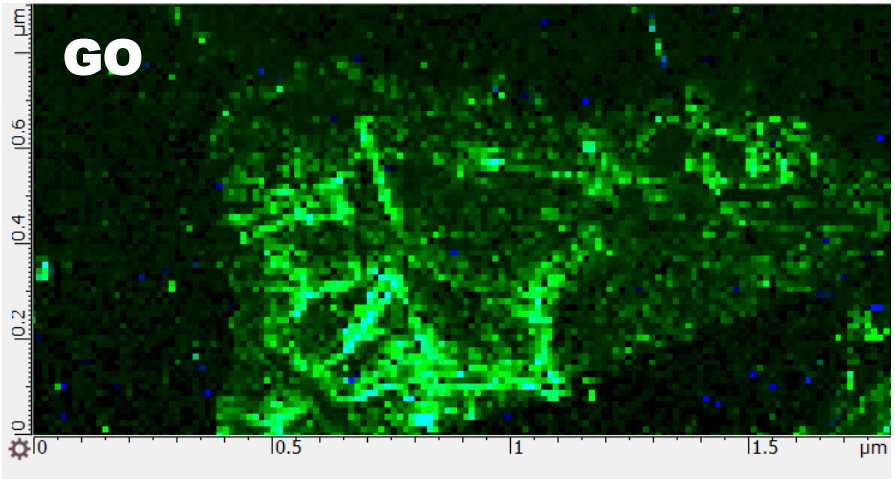
Sample: Azobenzene SAM on Au (111)

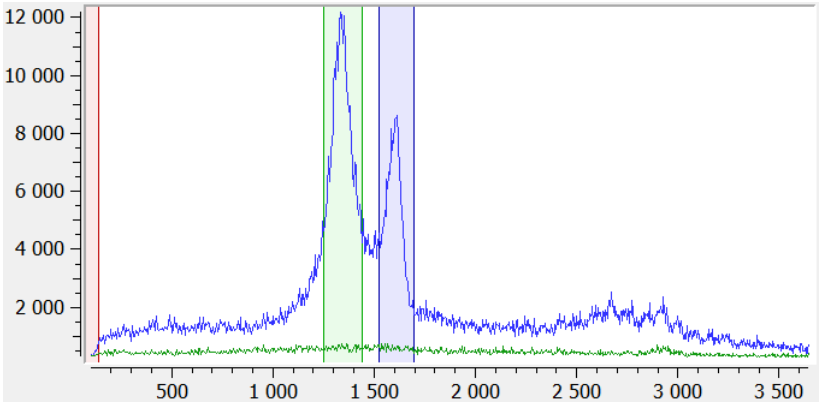


EF = 3.5 x10^5

Intensity increases ~ 10 times

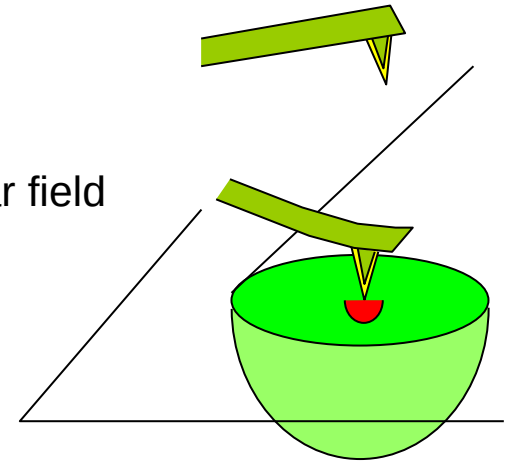
Enhancement Factor of the Ag tips





Tip OUT : Far-field

Tip IN :
Far field + Near field



Enhancement Factor

$$= \left(\frac{I_{nf} + I_{ff}}{I_{ff}} - 1 \right) \frac{V_{ff}}{V_{nf}}$$

$I_{Tip\ IN}$

$I_{Tip\ OUT}$

EF = 1.5 x10^6

A_g AFM-TERS probes

+ Innovative package to **enhance tip shelf life**

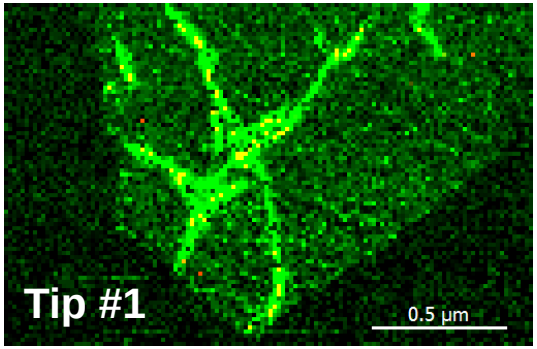
+ Raman active layer: **Ag** with protective layers

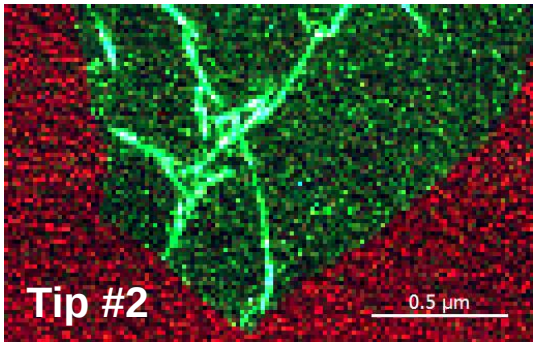
+ Great enhancement factor **EF = 10^{5-6}**

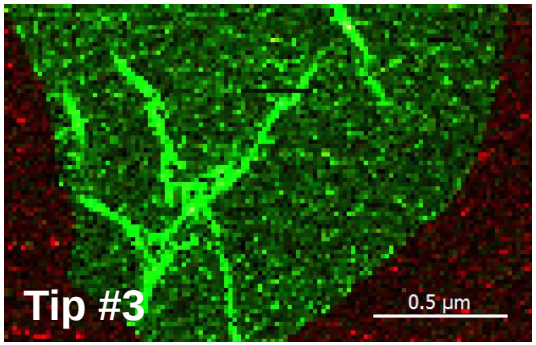
+ **Easy-of-use** thanks to the AFM regulation

+ Usable in **top/bottom** and **side** configurations

+ **9 tips out of 10 show the nanoresolution**!



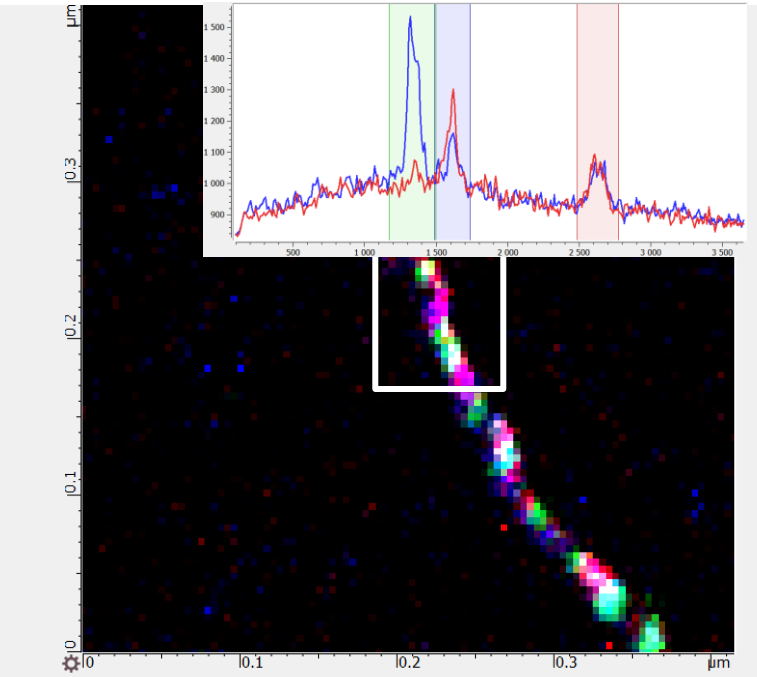




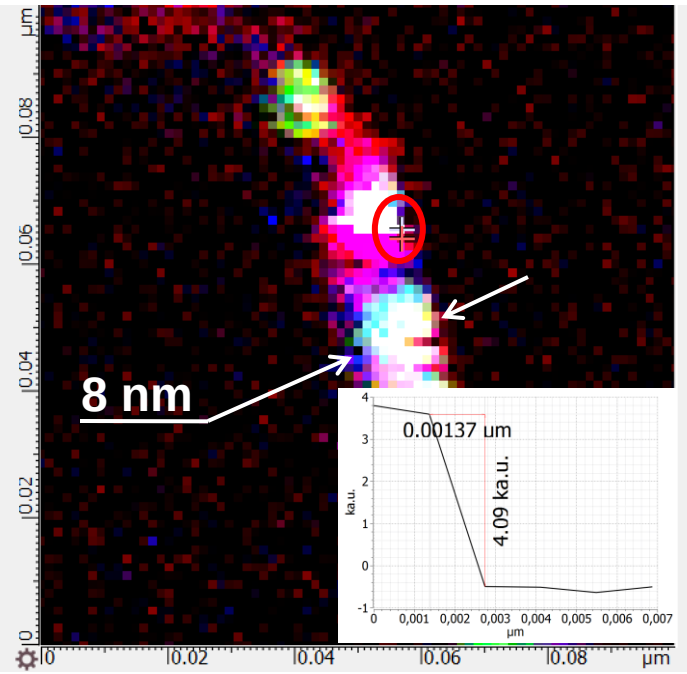
Excellent reproducibility of TERS maps

TERS: spatial resolution

CNTs maps out-of-lab conditions!



400 nm x 400 nm (100 x 100 pixels)



100 nm x 100 nm (75 x 75 pixels), 50 ms per pixel

Optical resolution capability: **8 nm**
Pixel step: **1.3 nm** → chemical sensitivity in both X and Y direction

Recorded @ SPIE San Diego, 2015

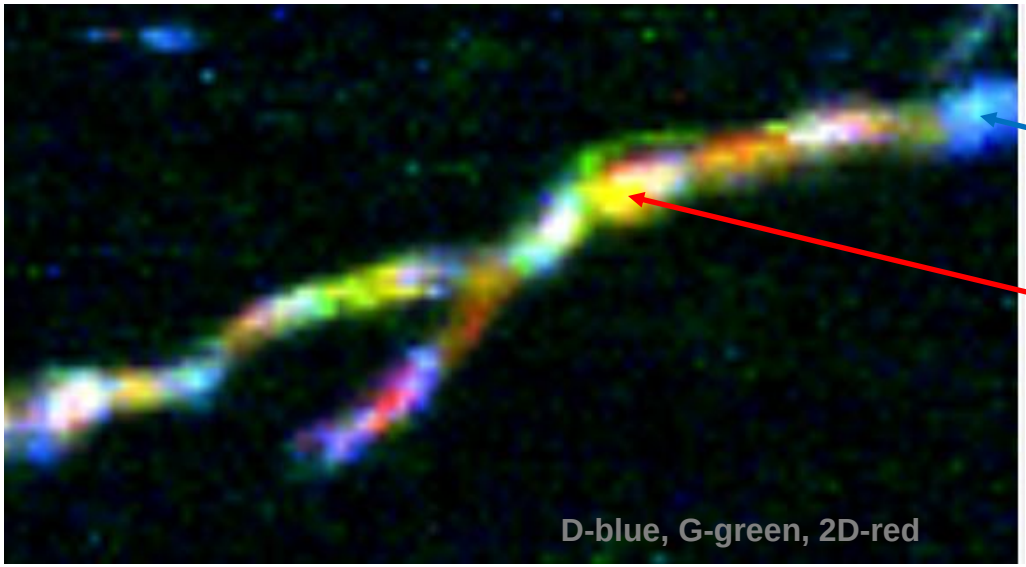
I. Bringing SPM and Raman together

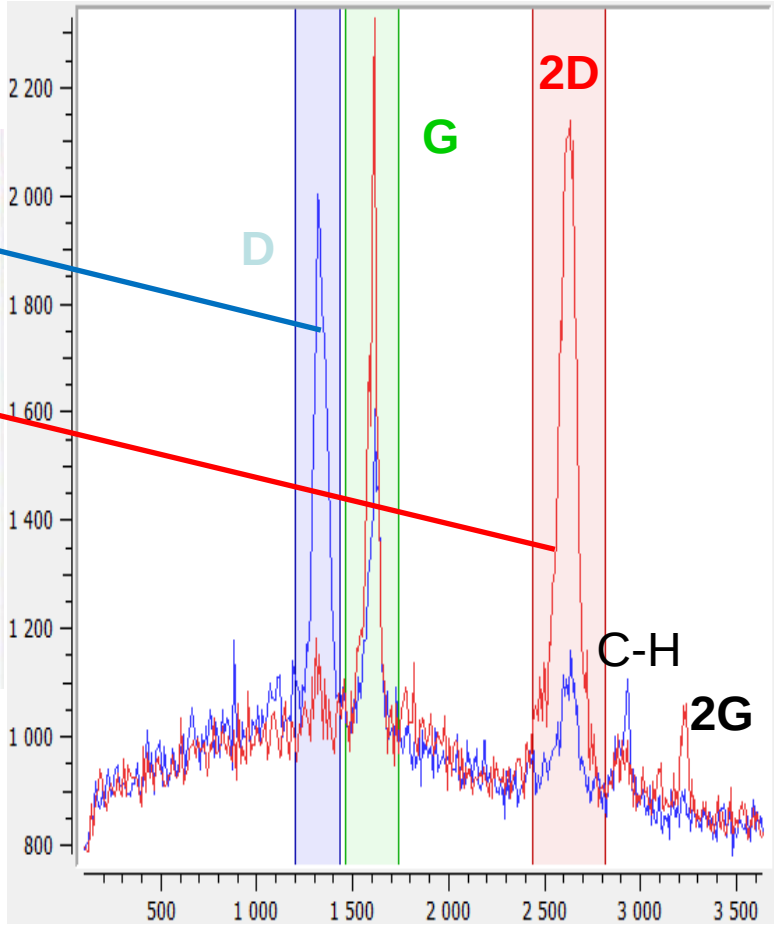
II. Applications of TERS in Materials and Life Sciences

III. Stimulated Tip Enhanced Raman imaging

1D materials: Nanotubes and Nanowires

Why TERS? → to give a fundamental insight into the **optical and electronic properties**





Chemical mapping of a single nanotube
a TERS map of a single CNT
b TER spectra of the CNT

300 x 160 nm (100 x 60 points); Excitation 638 nm; 0.13 mW; integration 0.1 s

1D materials: Nanotubes and Nanowires

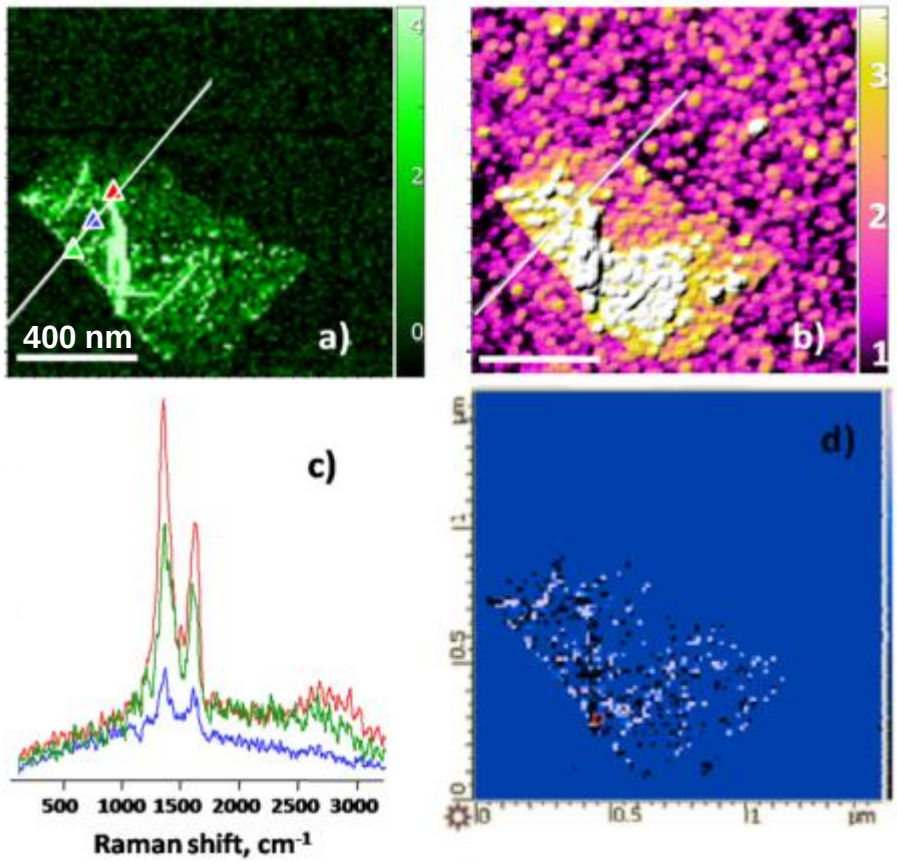
- Defect sites
- Discrimination between n- and p- doping
- Chirality variations (from the different radial breathing modes)
- Transition from semiconducting to metallic behaviour
- Pressure induced frequency shift
- Decorated nano-objects
- Test sample for TERS

Raman at the single tube level → Quality, defect density → Impact on the design of devices

CNTs, but also CdSe nanowires, Si, GaN, Ge nanowires

TERS on 2D materials

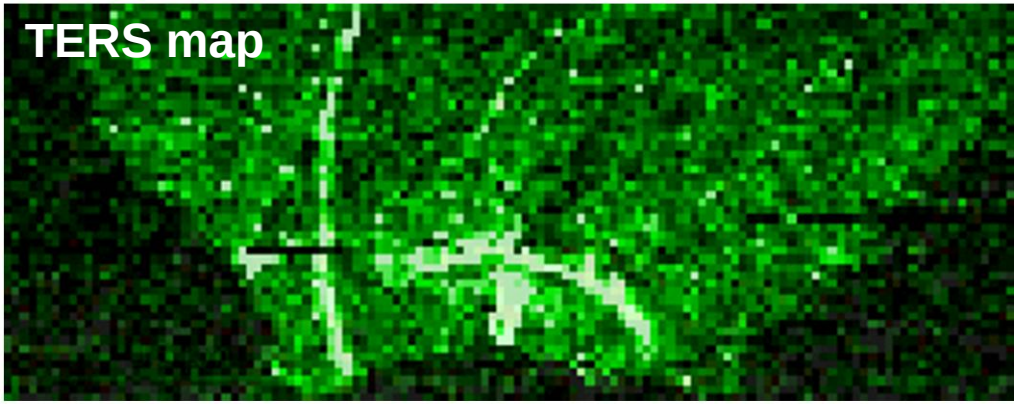
Why TERS? → to characterize **Graphene and 2D TMDCs** in terms of size, shape, **electronic properties, distribution of defects and contaminants**

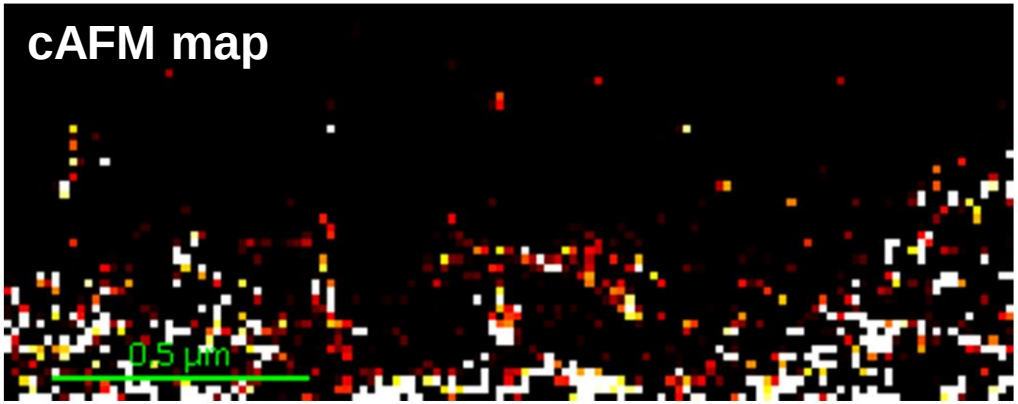


a) 100 pixels per line TERS map of D-band intensity
b) Topography image of the same flake
c) representative TERS spectra
d) distribution of the ratio of G to D band intensities

Increase of both the D and G TERS band intensities at creases and wrinkles

TERS Response of Graphene Oxide



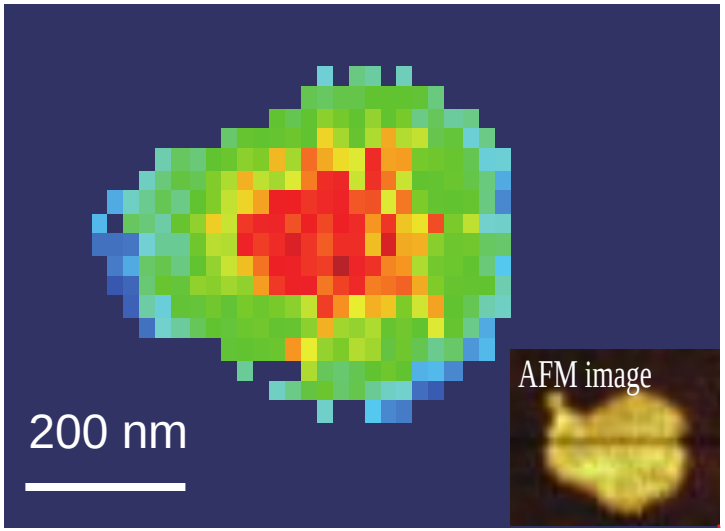


2x0.75µm (125pixels/line) TERS map of GO on gold and current map recorded during the TERS map acquisition

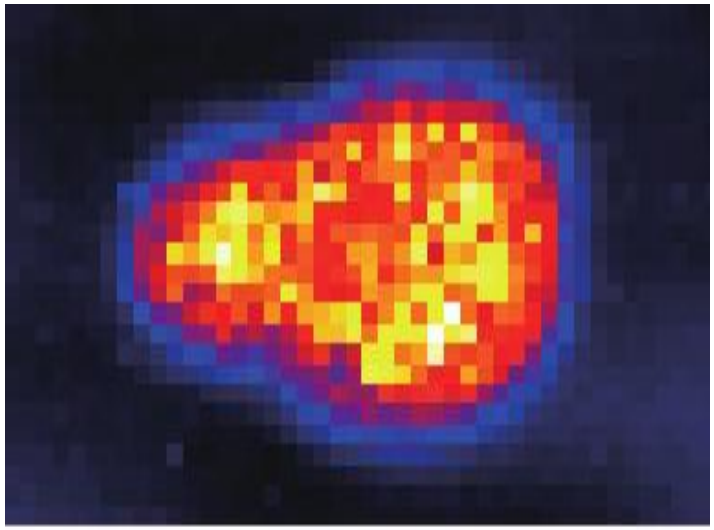
TERS on 2D materials

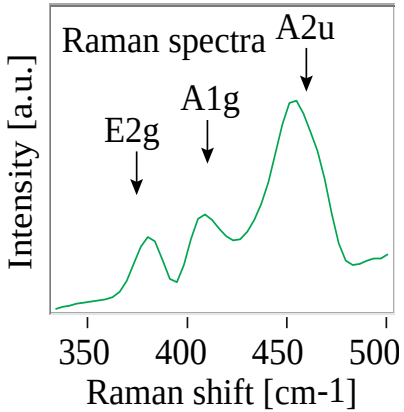
Why TERS? → to characterize **Graphene and 2D TMDCs** in terms of size, shape, **electronic properties, distribution of defects and contaminants**

TEPL



TERS





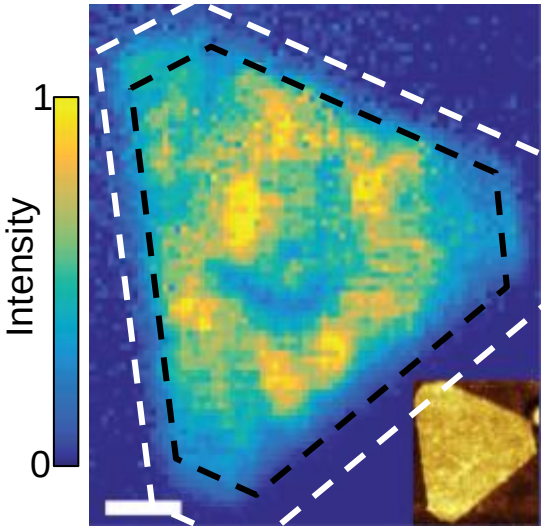
- **CVD grown MoS2 on Si substrate**
- **Ag tips**
- **Reflection configuration**

Y. Okuno, M. Chaigneau, HORIBA Scientific
F. Fabbri, IMEM (unpublished).

TERS on 2D materials

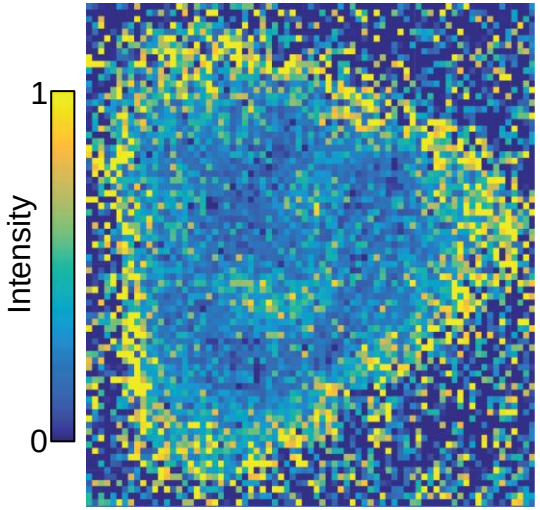
Why TERS? → to characterize **Graphene and 2D TMDCs** in terms of size, shape, **electronic properties, distribution of defects and contaminants**

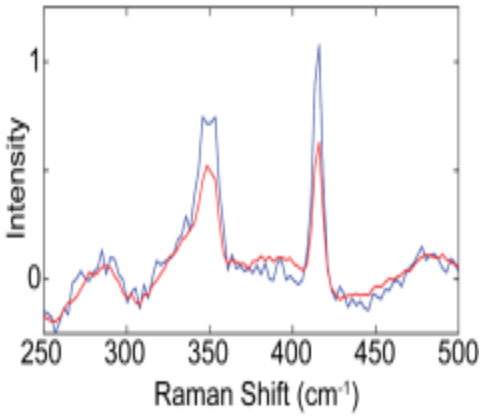
TEPL



scale bar: 250 nm

TERS





- **CVD grown WS2 on Si substrate**
- **Ag tips**
- **Reflection configuration**

Kastl, Chen, Kuykendall, Darlington,
Borys, Krayev, Schuck, Aloni & Schwartzberg (LBL), Andrey Krayez (AIST-NT) (submitted).

Novel 2D materials

- Identification of the defects
(point defects, i.e. vacancy or dopants, or grain boundaries), edges
- Hydrogen-terminaned graphene (CVD)
- Local strain distribution, inhomogeneous and unintentional doping
- Decorated 2D materials

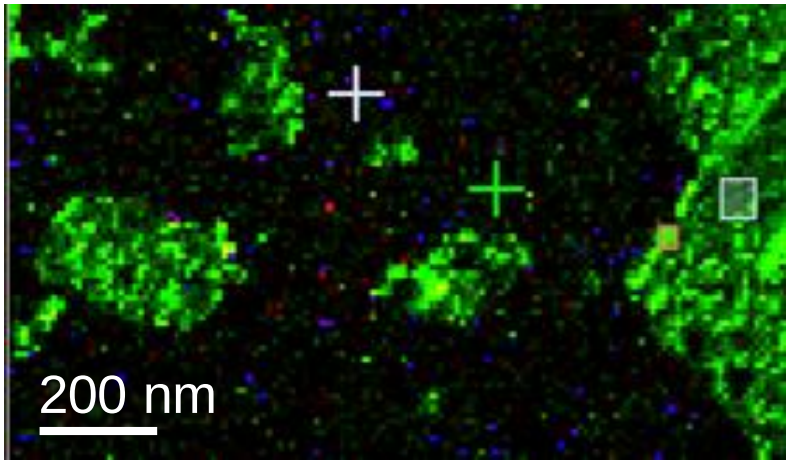
Raman at the nanoscale → defect density, strain → Impact on the design of devices

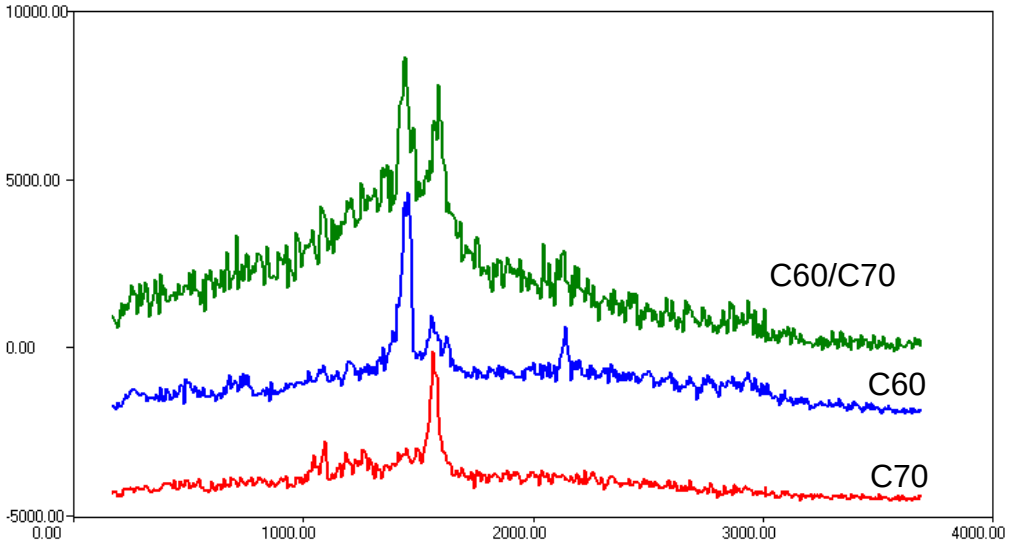
Graphene but also MoS2, WS2, WSe2, h-BN, GaSe

Just a Few Molecules

Why TERS? Single molecule spectroscopy is the **ultimate goal**!

Chemical mapping of C60 and C70 single molecules in gap mode AFM-TERS





Single molecule sensitivity in gap mode AFM-TERS

Single pixel spectra from the map showing both C60 and C70 characteristic peaks (**green**) and **spectra from only individual components** (**blue - C60**, **red- C70**)

Just a Few Molecules

- Single Molecule detection
- Organic molecules
- Polymer blends

→ distinguish nanoscopic domains with distinct chemical signatures

- Photocatalysis, plasmon induced catalysis processes

Imaging chemical species at the nanoscale

Local order / disorder

Molecular orientation

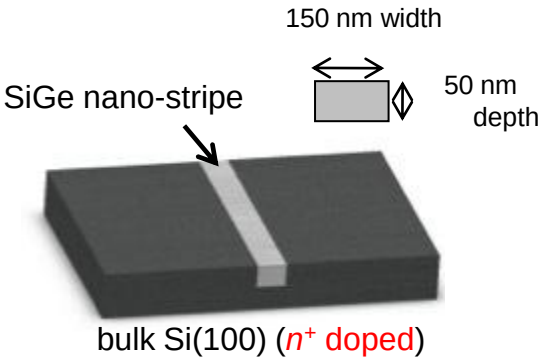
SAM grafting quality/

Phase segregation

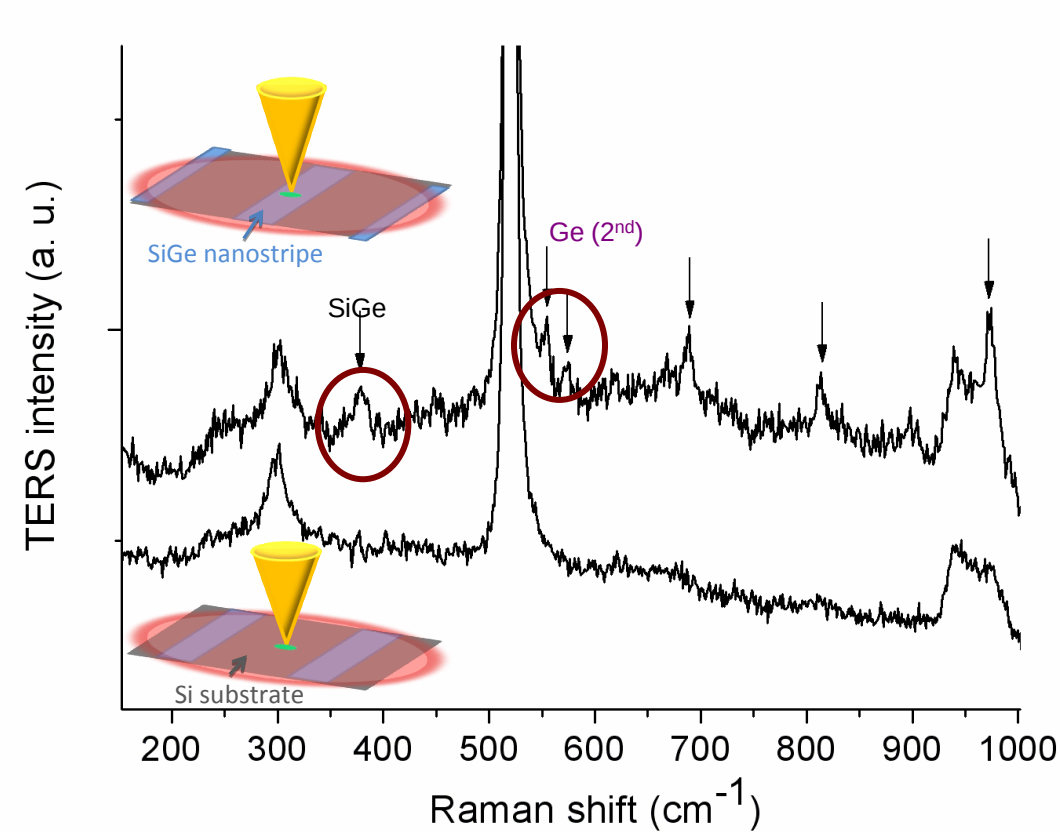
PMMA, PEDOT/PSS, Polystyrene, Dye molecules, Thiols…

Semiconducting Nanostructures

Why TERS? Monitoring the **local stress/strain** in semiconducting nanostructures and **the impact on the electronic properties**

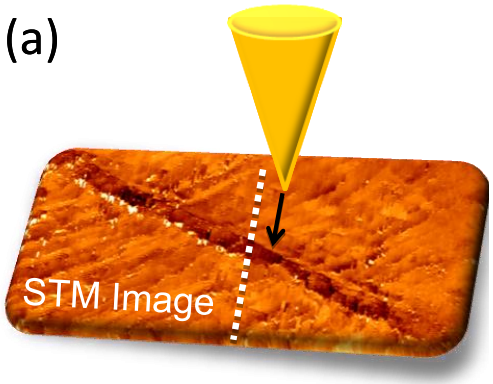


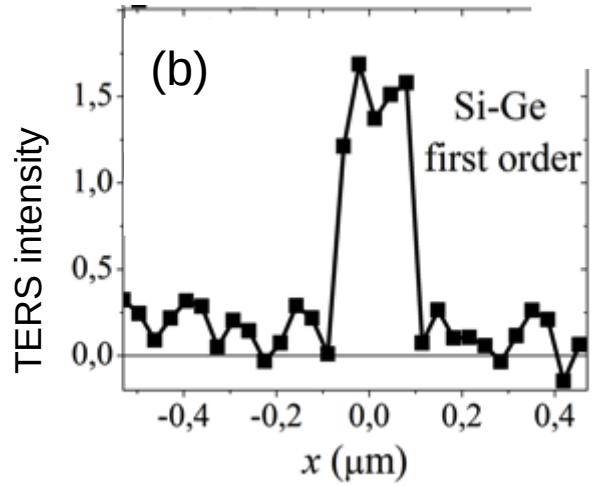
SiGe Nanostripe

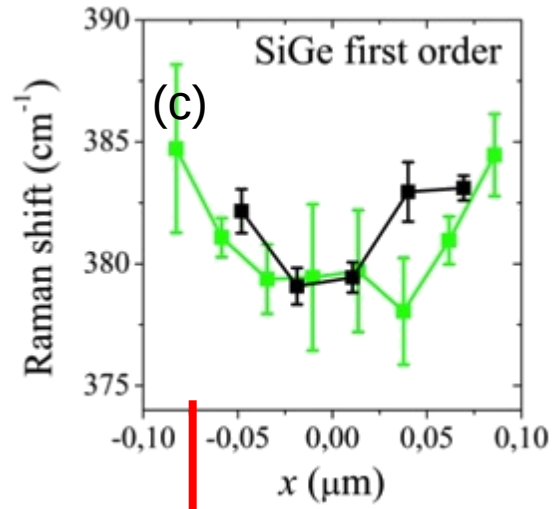


TERS spectra measured with the tip in tunneling position on the Si substrate (lower trace) and on the SiGe nano-stripe (upper trace).

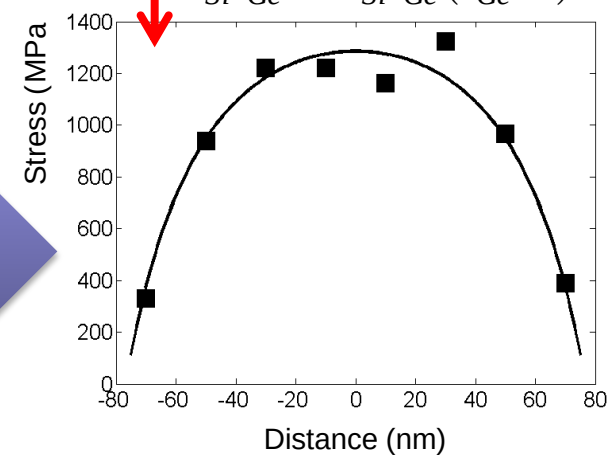
Local stress measurement in nanostructures







$$\omega_{Si-Ge} = \omega_{Si-Ge}(c_{Ge}, \varepsilon)$$



Raman enhancement in semiconducting structures → Nano-resolved Stress → Impact on the design of electronic devices

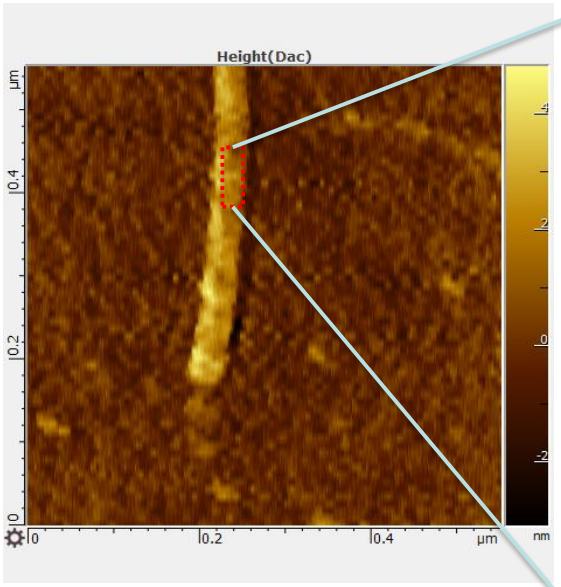
SiGe but also Si, CdS, GaN, GaAs

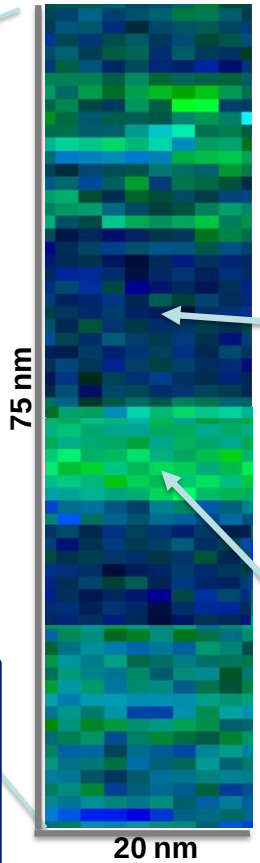
Vanacore, Chaigneau et al Physical Review B 88, 115309 (2013)

Life Sciences applications

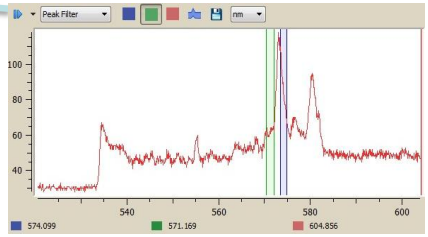
Why TERS? To investigate isolated **bio molecules** (amino acid and nucleic acid)

Sequencing of Engineered Standards

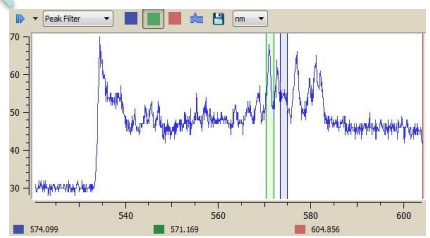




- **DNA on glass substrate**
- **Ag tips**
- **Transmission configuration**



Attr. Thymine (1395 cm-1)



Attr. Cytosine (1280 cm-1)

TERS spectral mapping of engineered DNA → clear differentiation of spectral regions of pattern and size consistent with the expected A/T and G/C homopolymeric blocks.

courtesy of RMD, Noah Kolodjieski

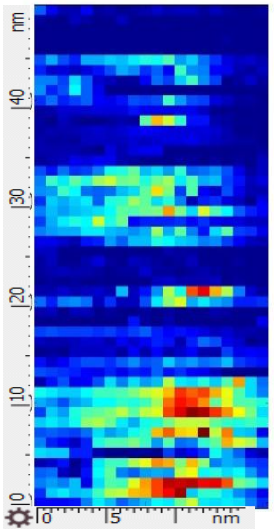
Life Sciences applications

Correlation-based reconstruction of the original sequence

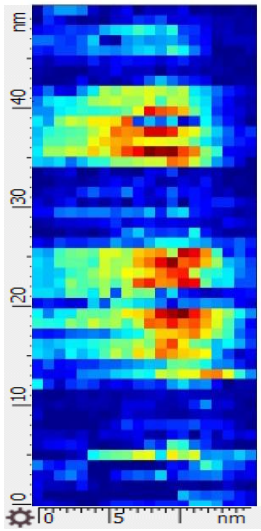
AFM of DNA

Spectral maps

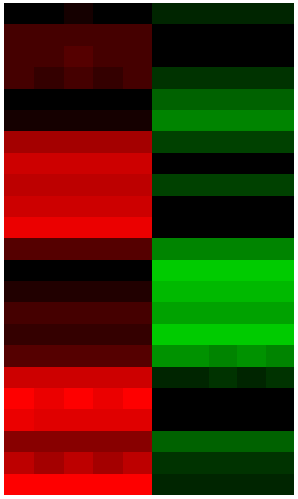
Comp. 1 (A/T)



Comp. 2 (G/C)



Horizontally averaged spectral map



Original Sequence

Sequence (image read bottom to top):

AAAATATATATAAATTAATTAAAACGGCGGGCGCGGCGGGGCGGCGCGGGCGGGAAATTTAAAATATATATAAATTAATTAAAACGGCGG
TTTTATATATATTTAATTAATTTTGCCGCCCGCGCCGCCCCGCCGCGCCCGCCCTTTAAATTTTATATATATTTAATTAATTTTGCCGCC

GCGCGGCGGGGCGGCGCGGGCGGGAAATTTAAAATATATATAAATTAATTAAAACGGCGG
CGCGCCGCCCCGCCGCGCCCGCCCTTTAAATTTTATATATATTTAATTAATTTTGCCGCC

Life Sciences applications

- Bio-molecules
- Nucleic acids → on the road to DNA sequencing.
- Amino acids (investigation of protein structures).
- Micro-organisms:
- Pathogens (bacteria, viruses) .
- Lipid membranes (cell surface).

Nanometre length-scale resolution of TERS → **Label-free measurement + fingerprint specificity** → **Identification, detection, molecular dynamics**

I. Bringing SPM and Raman together

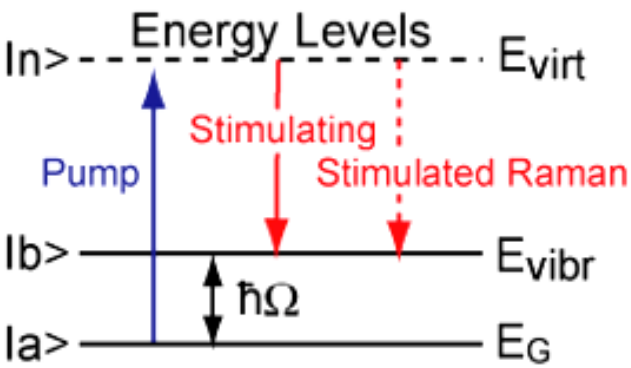
II. Applications of TERS in Materials and Life Sciences

III. Stimulated Tip Enhanced Raman imaging

Spontaneous VS stimulated TERS

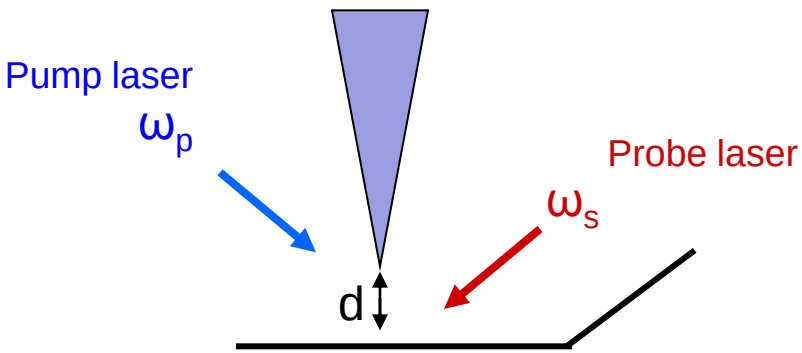
Spontaneous TERS

- Enhancement factor = $10^{5\text{-}6}$
- 100 - 1000 cts/sec
- S/N = 10 - 50



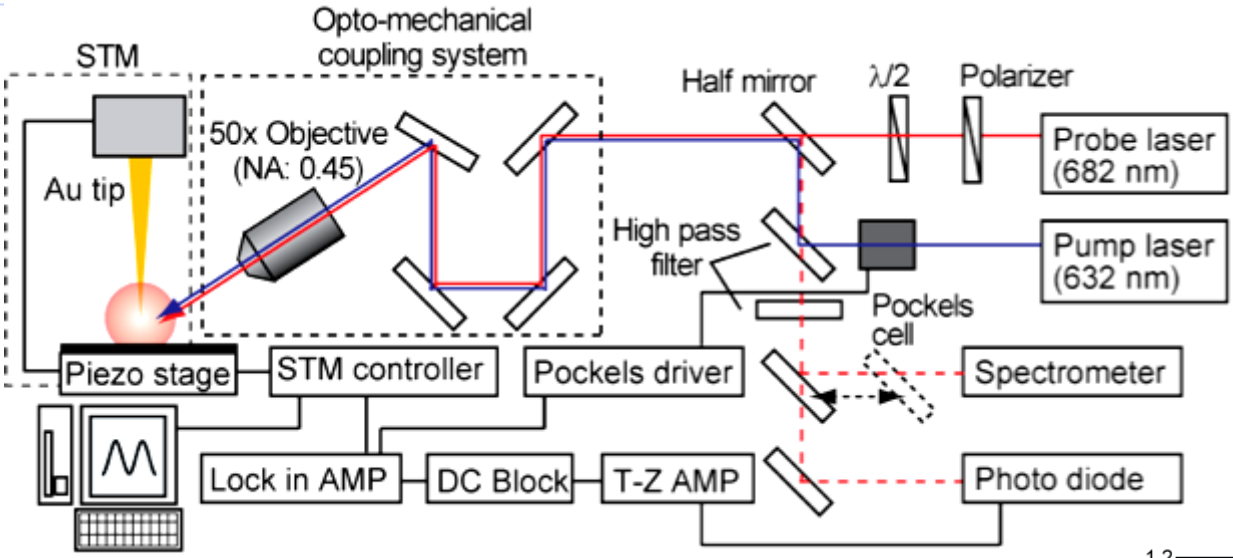
Stimulated TERS

- expected Gain = 10^9 !



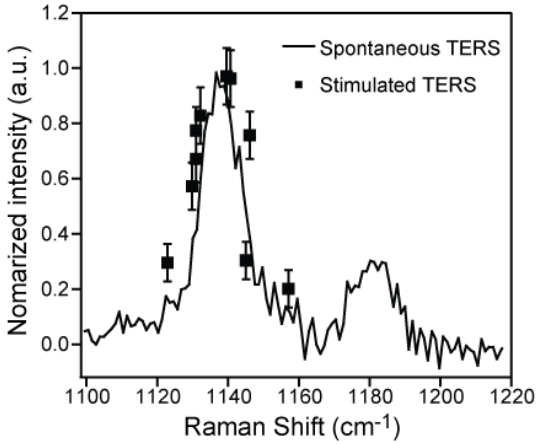
$$G = \frac{s_{STIM}}{s_{SPON}} = [32\, p^3 c^2 / w_s^2]\, F(w_s)$$

Stimulated TERS setup



Features:

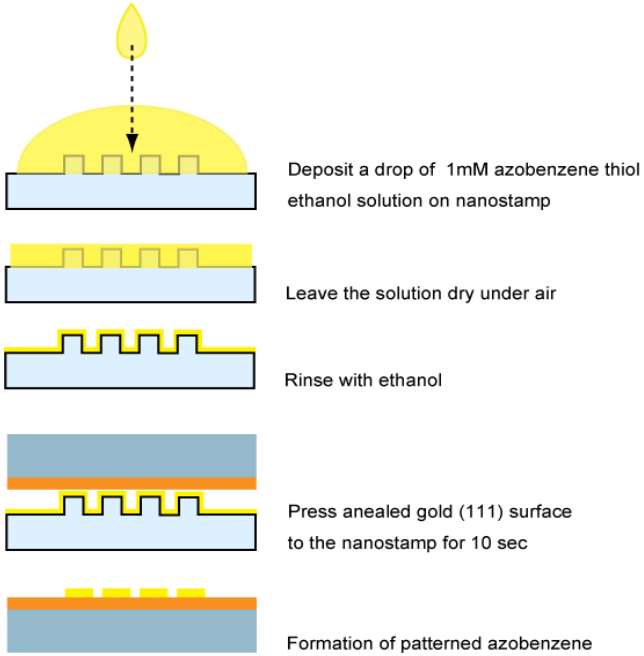
- **Polarization switching (*p* <-> *s*) of the *continuous* pump (632 nm) beam by Pockels cell (100 kHz)**
- **Tunable (10 nm) *continuous* stimulating (682 nm) beam (probe)**
- **Lock-in detection (100 kHz) on a photodiode**



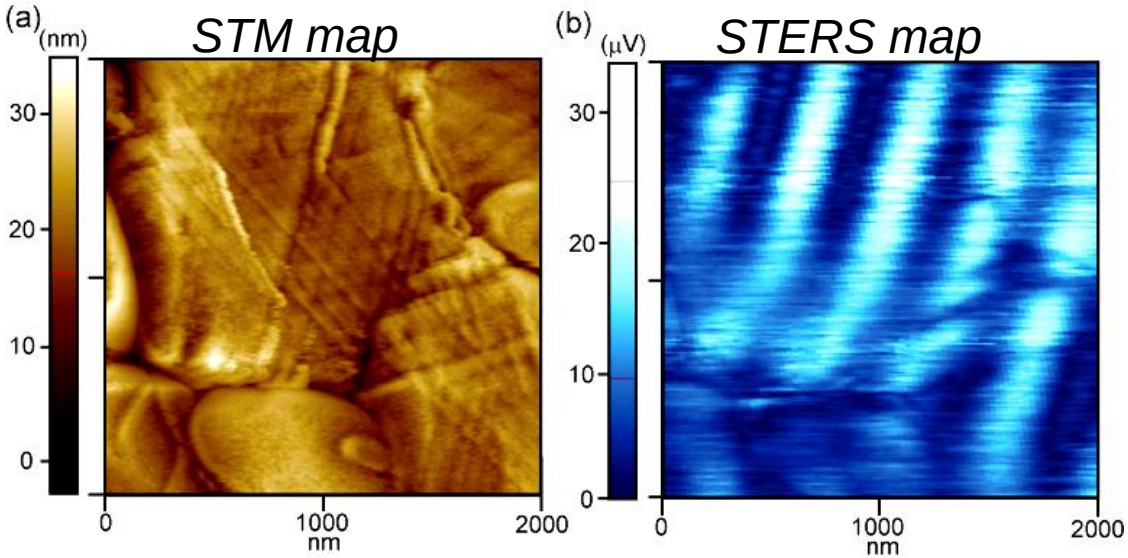
TERS spectrum and 'tuned - detuned' STERS of 1141 cm^{-1} vibration of azobenzene

Mapping of patterned azobenzene thiol SAM

Nanocontact printing



grating structure with a 300 nm width and a 300 nm spacing



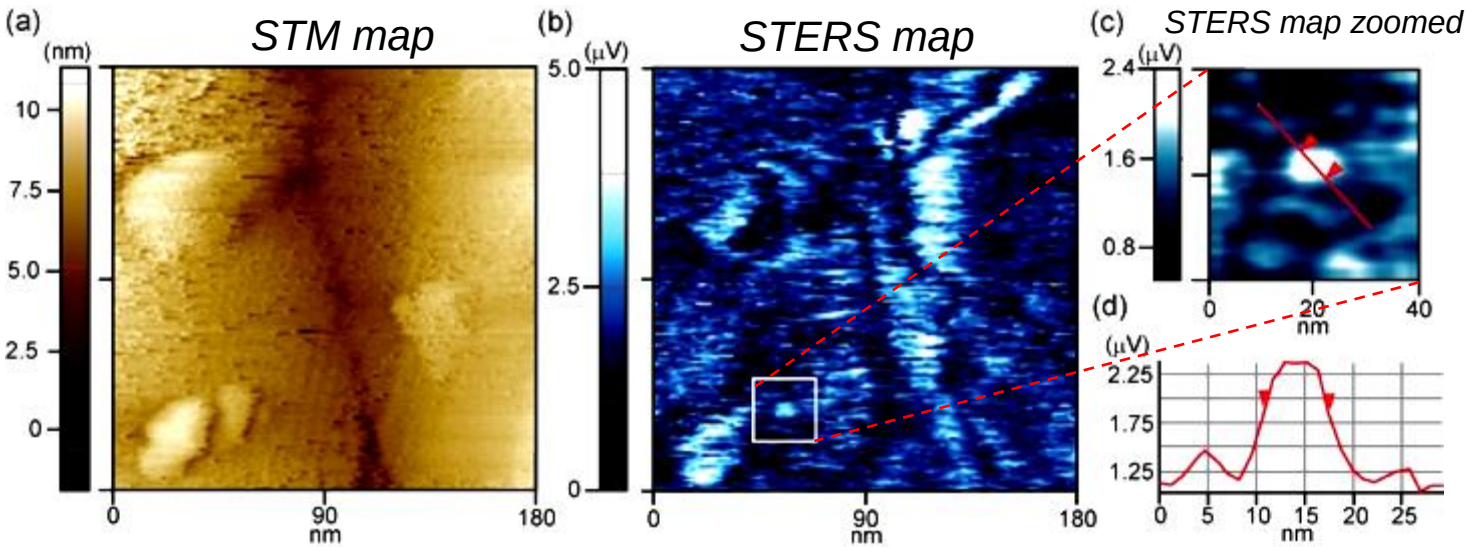
Scan rate: 0.3 Hz
Lock-in time constant: 0.1 s
Number of lines: 256
Laser power: ~ 0.5 mW (for both)
<u>Ambient conditions</u> (no UHV nor cryo)

simultaneously recorded STM and STERS images
continuous (raster scan) mapping:
14 min *vs* ***2 h*** *(theoretically) in spontaneous TERS!*

K. H. Wickramasinghe, M. Chaigneau, et al ACS Nano (2014)

STERS: spatial resolution

Azobenzene thiol SAM maps of smaller area (180 nm x 180 nm)



- Simultaneous Images @ 0.5 Hz/lines
- Optical resolution : < 6 nm
- Stimulated gain : 10^9
- S/N = 2.10^3

K. H. Wickramasinghe, M. Chaigneau, et al ACS Nano (2014)

CONCLUSIONS

- **TERS *IS READY* for real-life analytical application on number of scientifically/industrially interesting samples.**

- **Individual components in complex samples of carbon-based materials can be conventionally imaged with about 10 nm resolution and unambiguously identified based on their Raman spectra.**
- **Without detailed NANOSCALE characterization of molecules, 1-d and 2D materials their use in next generation devices is pretty much impossible. TERS can provide reliable information on peculiarities of local structure with resolution below 10 nm.**

- **The field of TERS is now rapidly advancing past technique development toward answering important scientific questions in materials science, physics, surface spectroscopy and chemistry.**

CONCLUSIONS

new trends

Non linear TERS: Stimulated TERS demonstrated

- Fast mapping capability
- Gain in SNR (with respect to TERS)
- New SPM chemical mode → potential applications

UHV TERS

TERS in liquids

Polarized Tip Enhanced Raman Scattering

ElectroChemical Tip Enhanced Raman Spectroscopy

New hybrid cantilever-based TERS tips

…

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Damien Eschimese
Ophélie Lancry
Jérémy Brites
Yoshito Okuno
Kumar Wickramasinghe
Razvigor Ossikovski
Ryohei Yasukuni
…

Thank you very much for your attention.

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