In situ Raman Spectroscopy: Fundamentals and Applications

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Plan

Fundamentals

- Vibronic spectroscopies
- Introduction to Raman spectroscopy
- A few words about instrumentation

Applications to surface science

- Raman spectroscopy at interfaces
- SERS
- TERS

Conclusions/Outlook

I. Fundamentals

Vibronic spectroscopies

Type of VS,
virtues

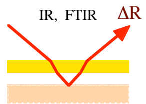
Introduction to Raman spectroscopy

Basics
General applications

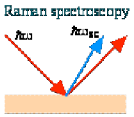
A few words to Instumentation of RS

• Vibronic spectroscopies

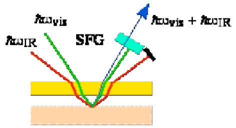
at interfaces



Infrared spectroscopy IR, FTIR, SNIFTIRS, ...



Raman spectroscopy RS, RRS, CARS, ..., SERS, TERS



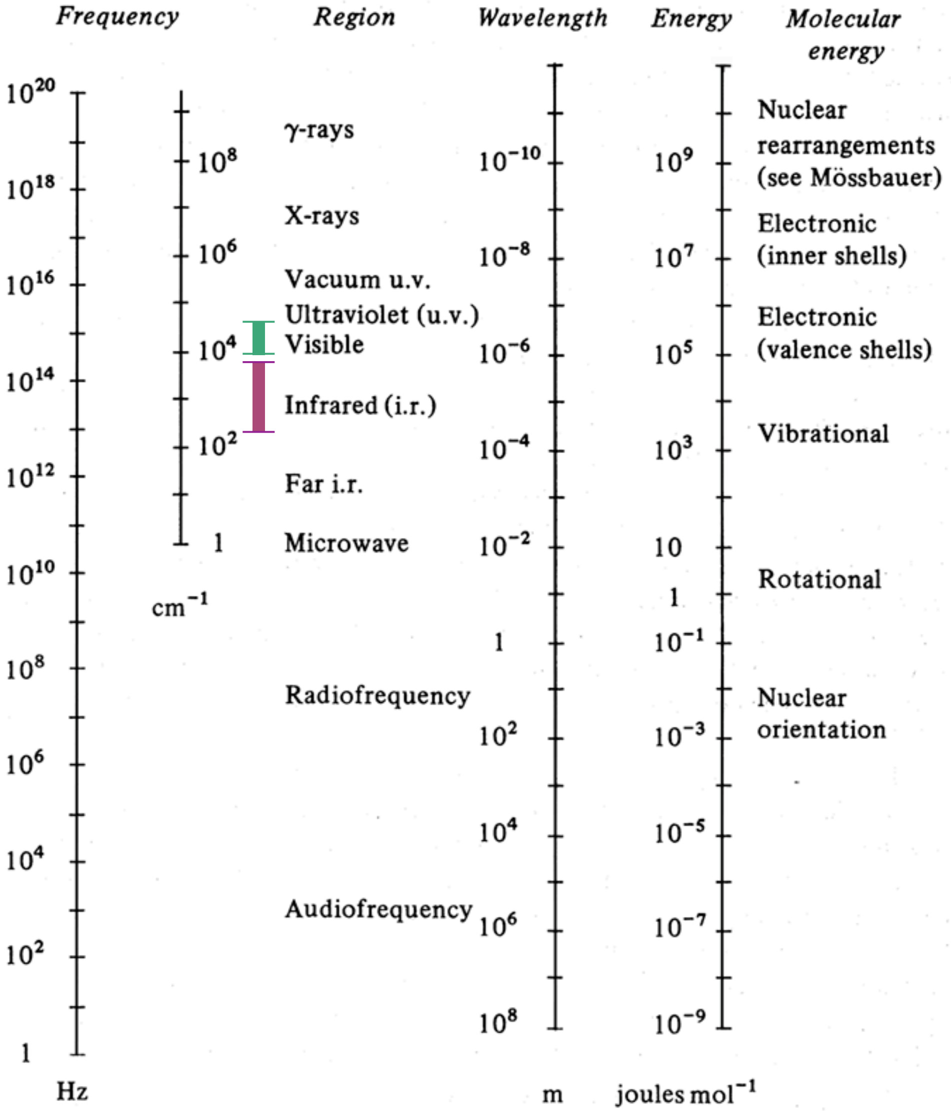
Sum frequency generation SFG, DFG

Inelastic neutron scattering

Electron energy loss spectroscopy EELS

I. Fundamentals: EM frequency regions

Regions of the electromagnetic spectrum and associated molecular energies

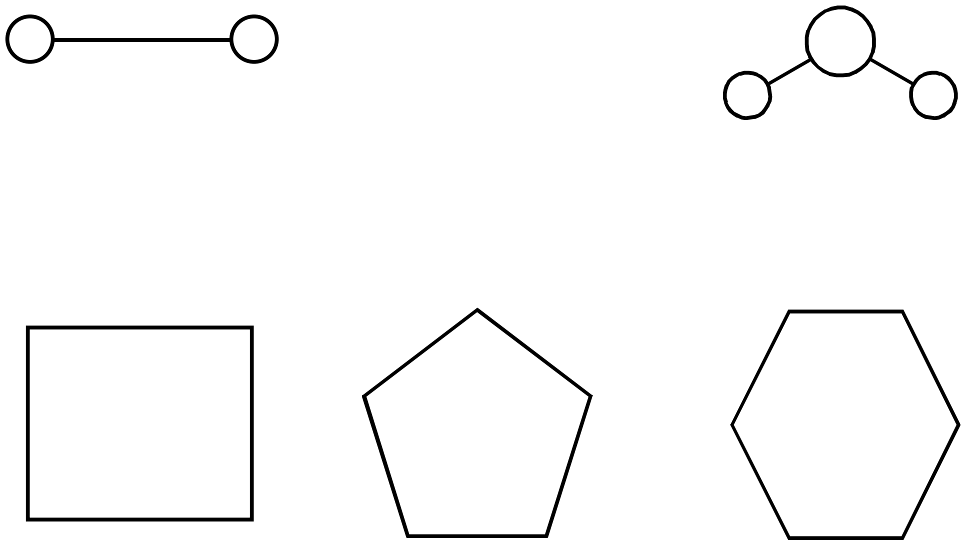


Useful approximations: $1\ \text{cm}^{-1} \approx 10\ \text{J mol}^{-1}$

$\approx 3 \times 10^{10}\ \text{Hz}$

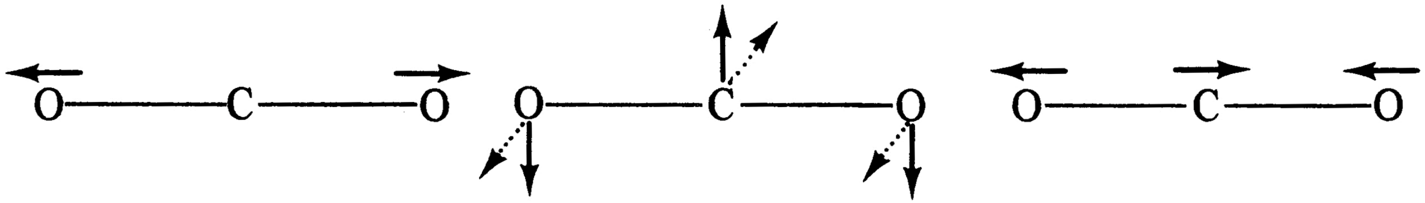
$1\ \text{eV} \approx 8000\ \text{cm}^{-1} \approx 100\ \text{kJ mol}^{-1}$

Selection Rules



It's the molecular symmetry and the particular optical process, which determine what can be "seen"

Raman and IR activity of CO_2



(a) (b) (c)

a) is the symmetrical stretching mode ν_1

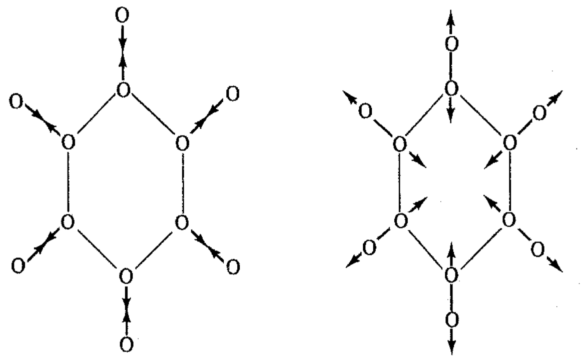
b) is a deformation mode ν_2 (degenerated)

c) is the antisymmetrical stretching mode ν_3

For a linear molecule, the number of normal modes is n_{nm} = (3N-5), thus for CO_2 n_{nm} = 4; i.e, one for (a) , two for (b) and one for (c).

Normal modes of C_6H_6

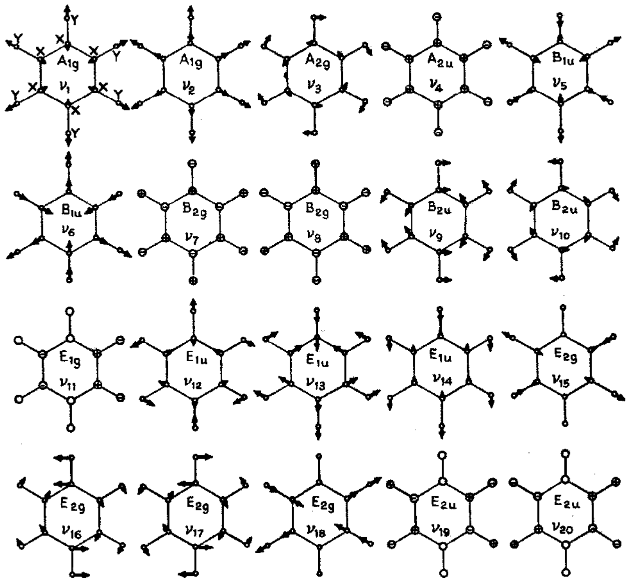
The symmetrical stretching mode of benzene



One of the breathing modes ν_2 (A_{1g})

[the other is ν_6 (B_{1u})]

The 20 normal modes of vibration of benzene
(there are (3N-6) normal modes, some are degenerated)



10 are degenerated (10 E_g and 10 E_u)

10 A and B modes

Virtues of Vibrational Spectroscopies

Rich information on

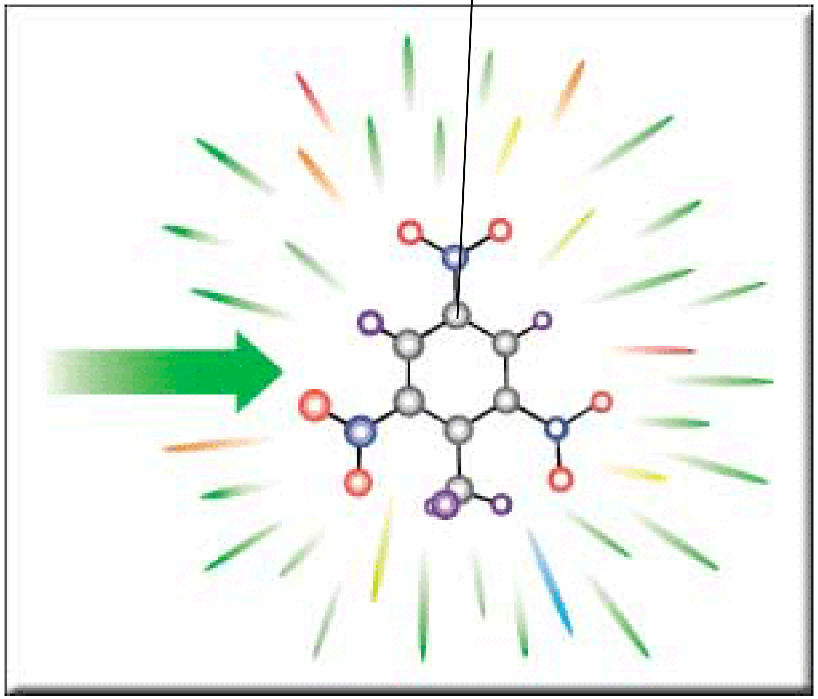
- the kind of species, intermediate
- internal structure
- environment

• Introduction to Raman spectroscopy

Basics

General applications

Inelastic Light Scattering



seen
by CV Raman

1930 Nobel Prize in physics for his discovery of the Raman effect.

Polarizability , Dipole Moment

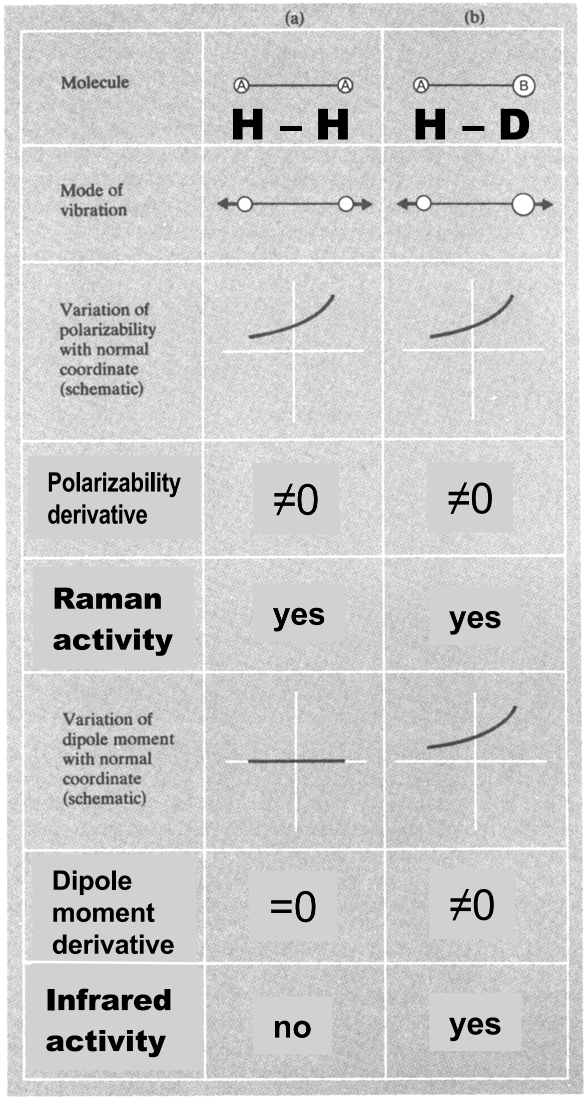


Fig. 3.7 Comparison of polarizability and dipole moment variations in the neighbourhood of the equilibrium position and vibrational Raman and infrared activities for (a) an A_2 and (b) an AB molecule

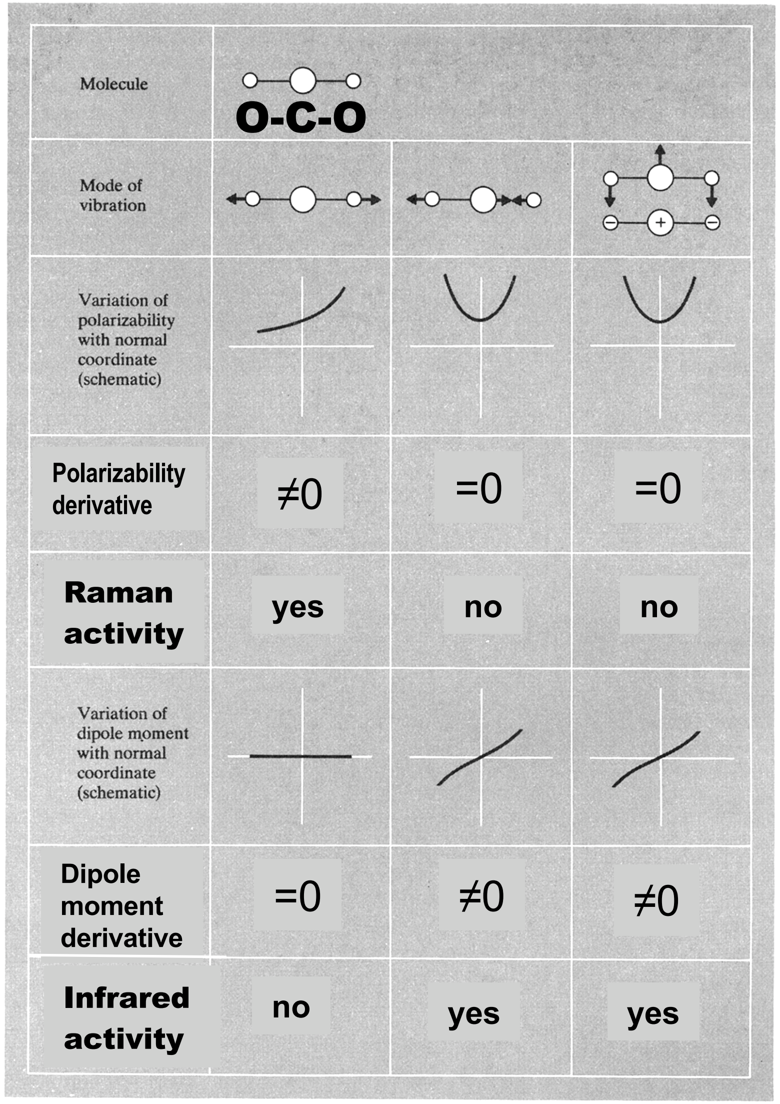
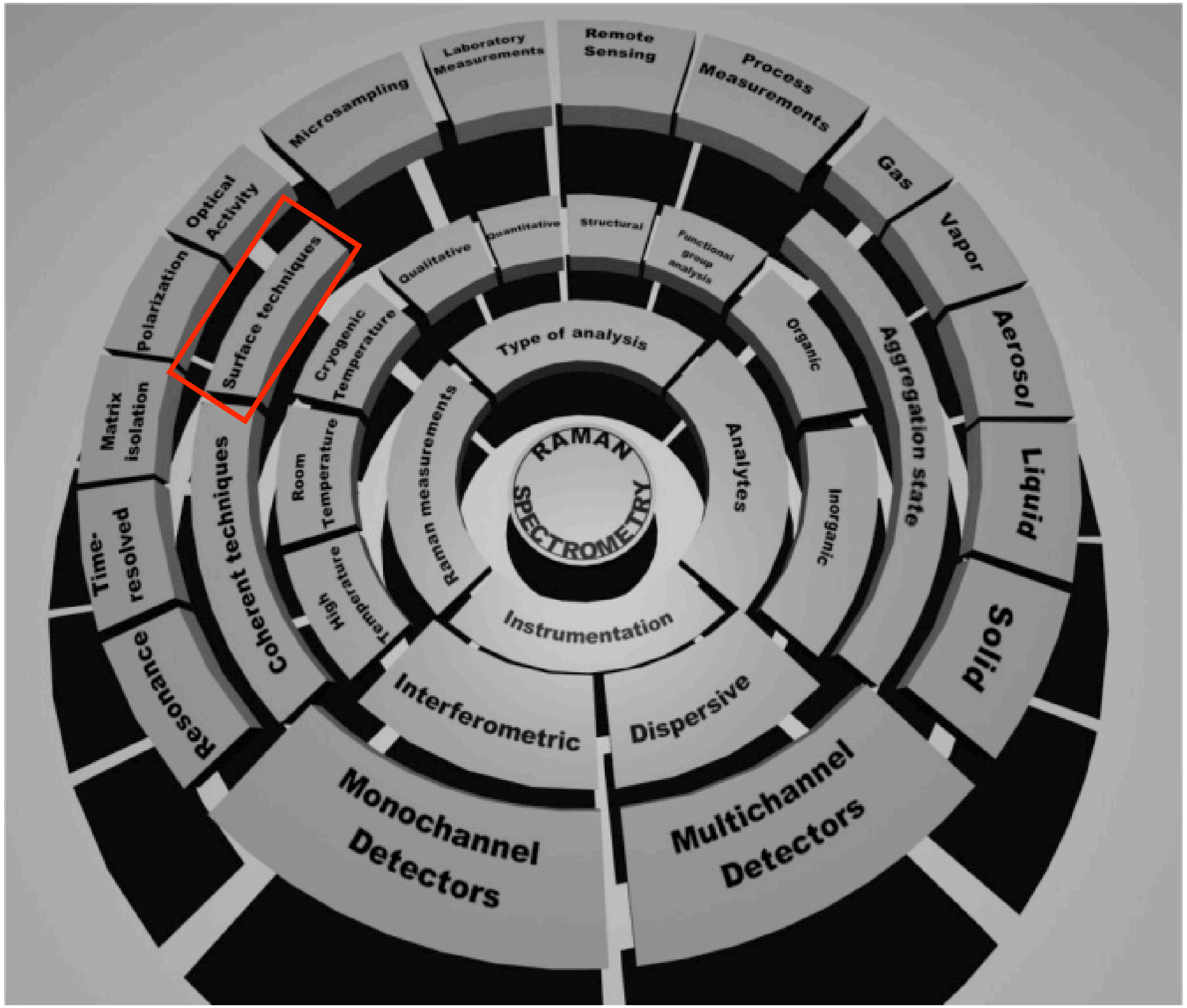


Fig. 3.8 Polarizability and dipole moment variations in the neighbourhood of the equilibrium position and vibrational Raman and infrared activities for a linear ABA molecule

D.A. Long, Raman spectroscopy

Fields of Raman spectroscopy



• A few Words about Instrumentation

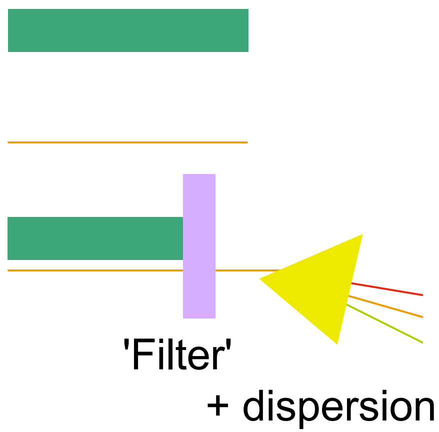
Earlier setups

Modern spectrographs

'Technical' Problem: Incident intensity: 0.001 - 10 W

scattered intensity: $10^{-15} – 10^{-10}$ W

separation efficiency >> 10^{-15}



Double Grating Spectrometer

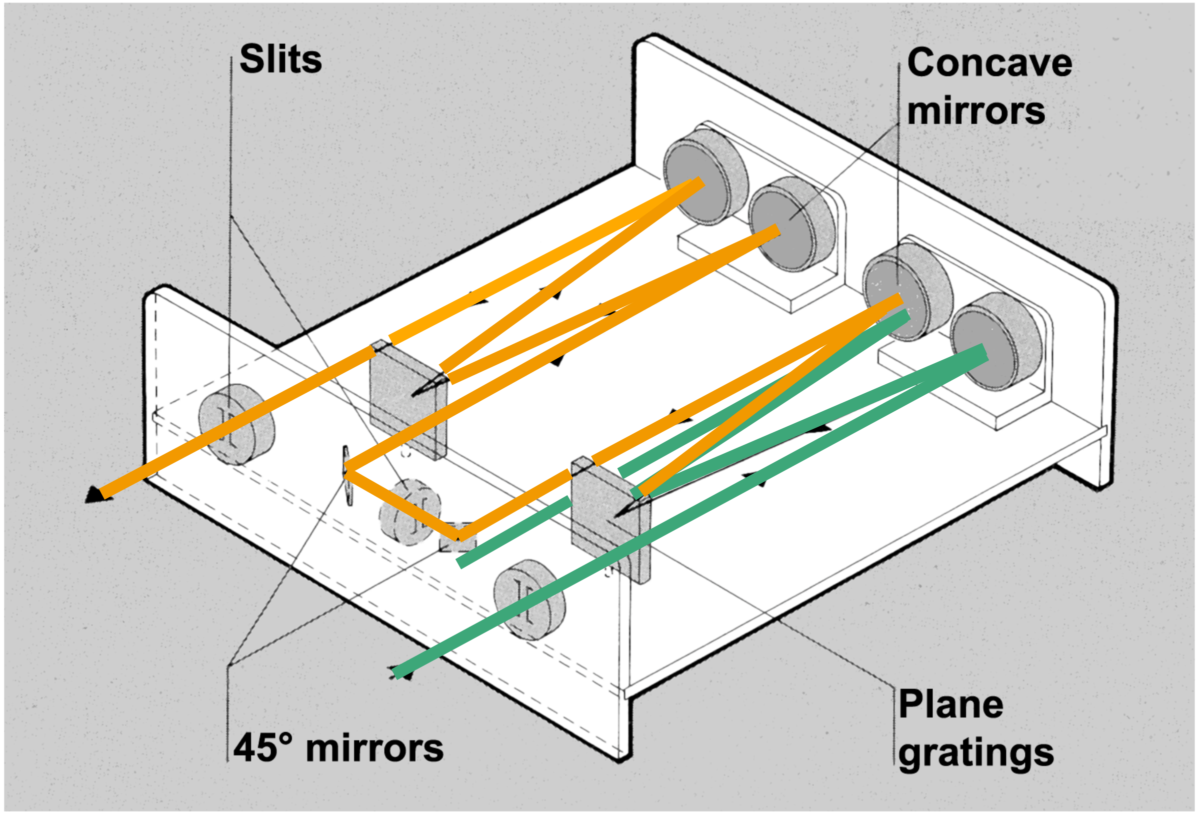


Fig. 6.6 Typical double monochromator grating dispersing system for the study of vibrational Raman spectra under medium resolution

- Laser+Raman
- Its 1st path
- A single frequency is passed thourgh the double mono-chormator

Sample illumination

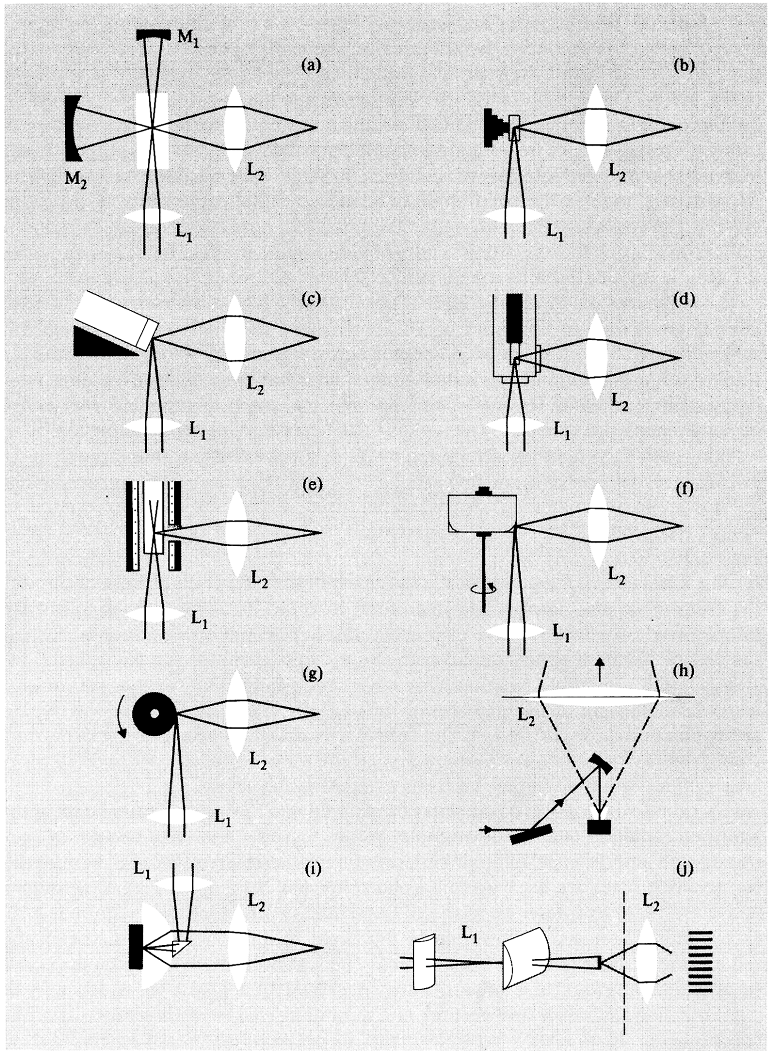
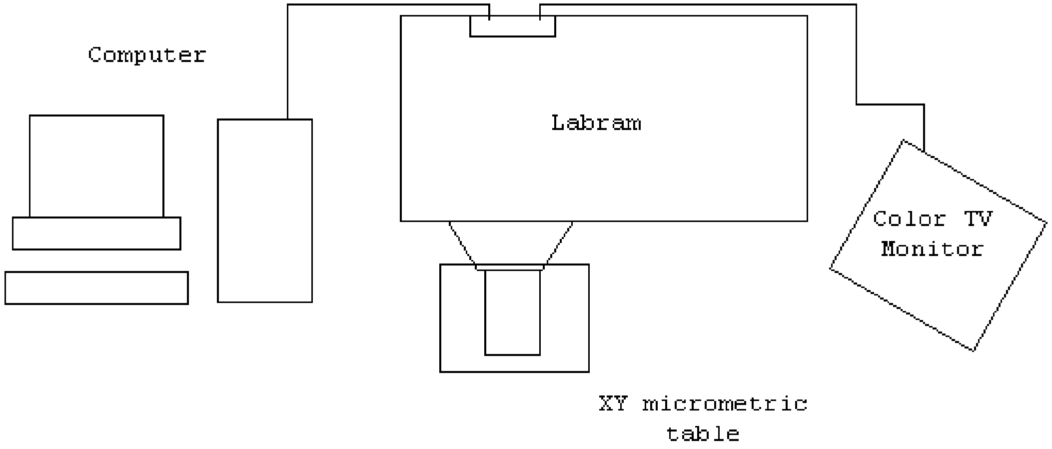
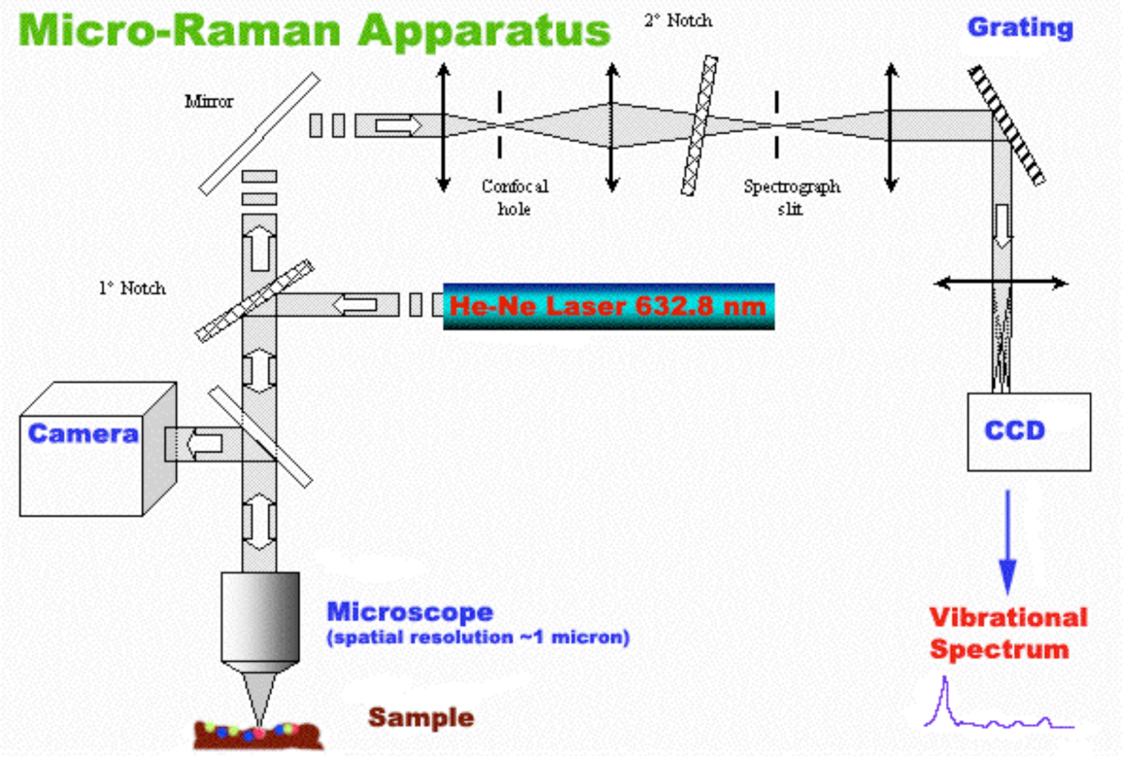


Fig. 6.3 Various arrangements for sample illumination: (a) sample extra-cavity, (b) single crystal mounted on a goniometer, (c) powdered solid, (d) low-temperature cryostat, (e) high-temperature cell, (f) spinning sample cell (liquids), (g) spinning reel for fibres, (h) diamond anvil for high pressure studies of crystals, (i) 180° scattering geometry, and (j) 0° scattering geometry

Raman Setup for Interfacial Studies





II. Applications to Surface Science

- **Raman Spectroscopy at interfaces**

  Problems, solutions

- **Surface -Enhanced Raman Spectroscopy (SERS)**

  HT SERS, SERS fluctuations, SERS at colloids

- **Tip -Enhanced Raman Spectroscopy (TERS)**

  How does a fine needle boosts Raman spectroscopy ?

  TERS concept, Setup, Tips, TERS at Me(hkl), giant EM enhancement

• Raman Spectroscopy at Interfaces

Advantages

Problems

Solutions

Advantages of Raman Scattering at Surfaces

Though the expected intensities are low, there are a number of advantages for RS:

1. Working with visible light (in general)
2. Full spectral range (~0 cm^{-1} to > 4000 cm^{-1})
3. High spectral resolution (0.1 cm^{-1} to 4 cm^{-1})
4. Vibronic spectra are sensitive to

    the kind of substrate and bonding

    the bonding sites

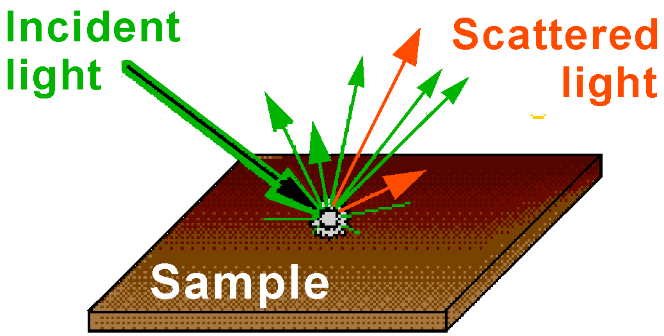
    the surface coverage, molecular orientation

    the coadsorption

    the interfacial field ← **(electrode potential)**

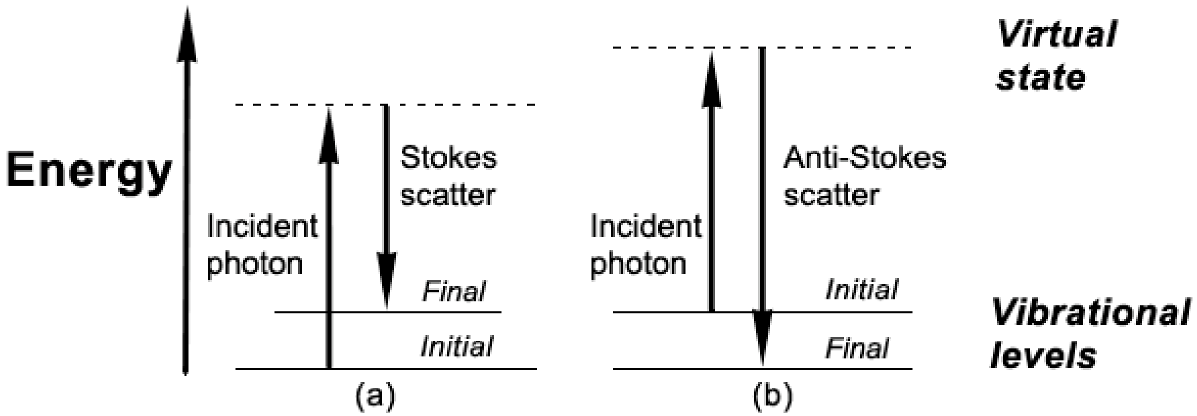
    ....

Raman Spectroscopy by Adsorbates



Extremely low intensities exspected (< 1 cps)

Enhancement necessary !

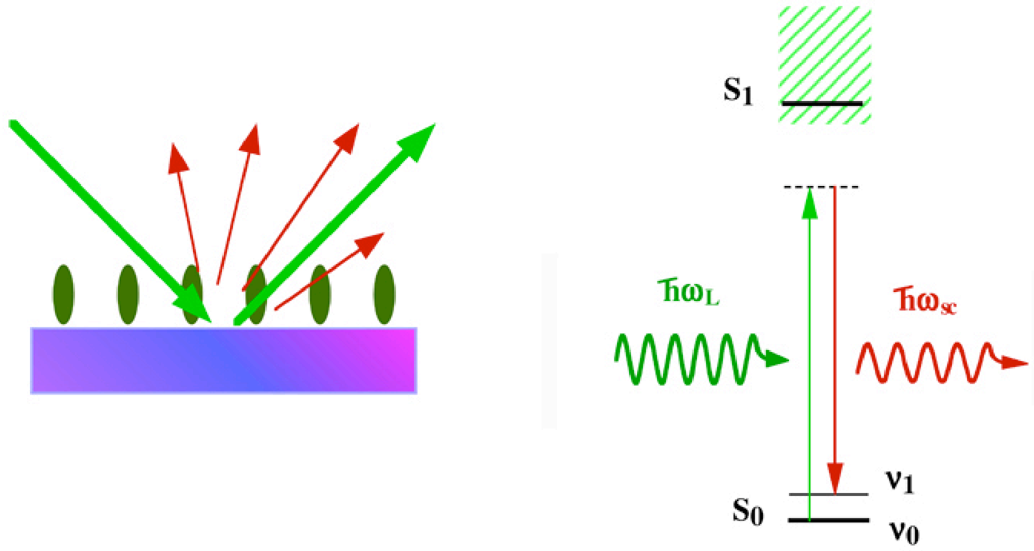


Raman processes: Stokes and Anti-Stokes scattering

Normal Raman scattering (NRS): $(d\sigma / d\Omega) \sim 10^{-31} - 10^{-28}\ cm^2\ sr^{-1}$

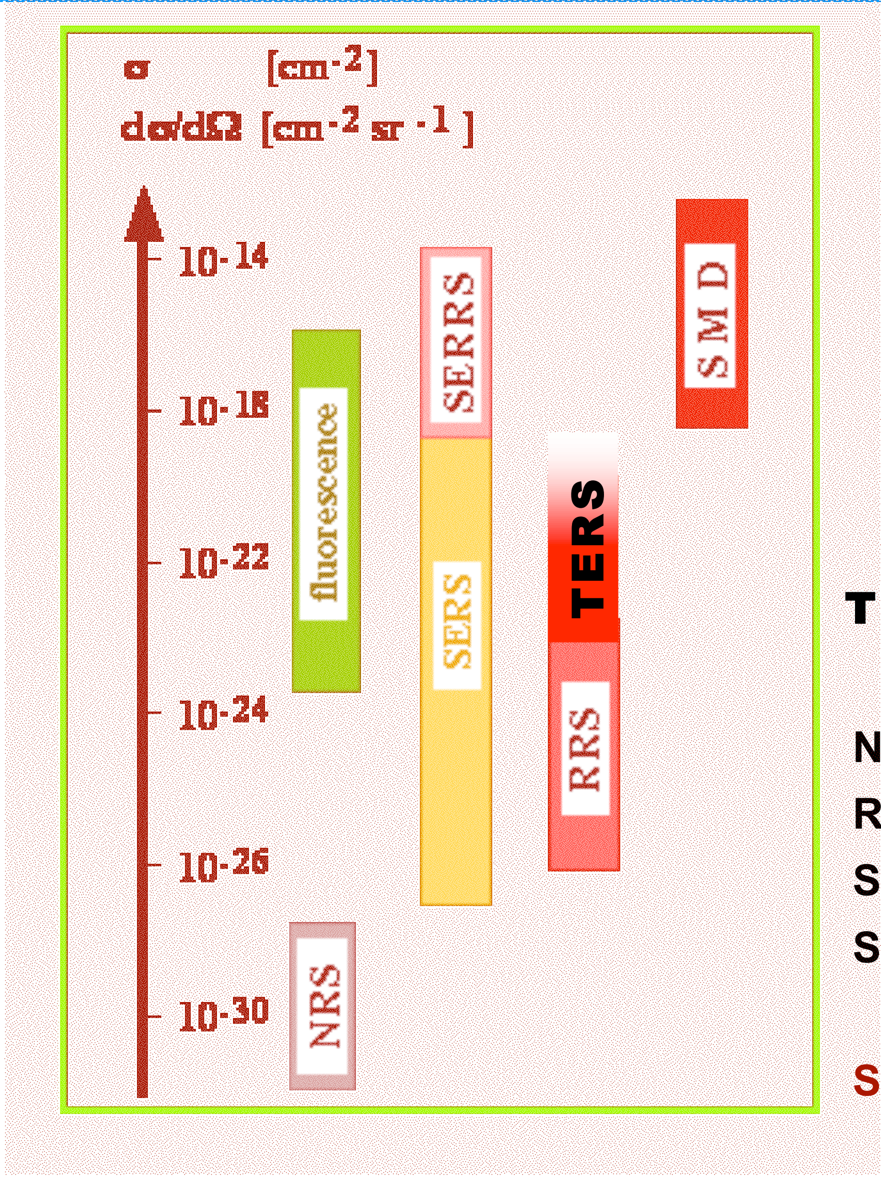
More on Scattering Yield

The yield of the Raman process at a surface



differential cross section	$d\sigma / d\Omega = 10^{-29}\ cm^2$
flux of photons:	$10^{18}\ s^{-1}$
number of scatterers:	$10^{15}\ cm^{-2}$
detector system (opt. losses):	10^{-4}
expected intensity:	< 1 c.p.s.

Cross Sections of Optical Processes



TERS	tip–enhanced Raman spectroscopy
NRS	normal Raman scattering
RRS	resonance Raman scattering
SERS	surface enhanced Raman scattering
SERRS	surface enhanced resonance Raman scattering
SMD	single molecule detection

• Surface – Enhanced Raman Spectroscopy (SERS)

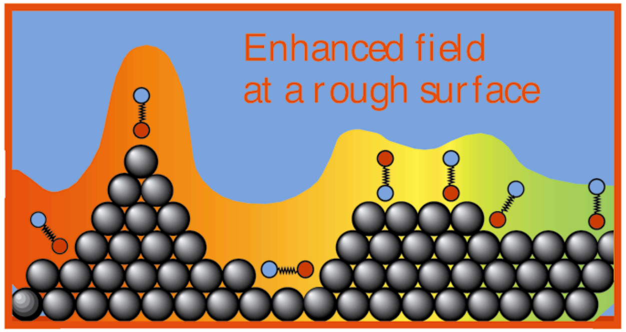
A few words about SERS

HT SERS

SERS fluctuations

SERS at colloids

Surface-Enhanced Raman Spectroscopy (SERS)



Roughened surfaces:

>>> excitation of localized surface plasmons

>>> locally enhanced fields

Intense SERS only for Ag, Cu, Au. Weaker signals from transition metals.

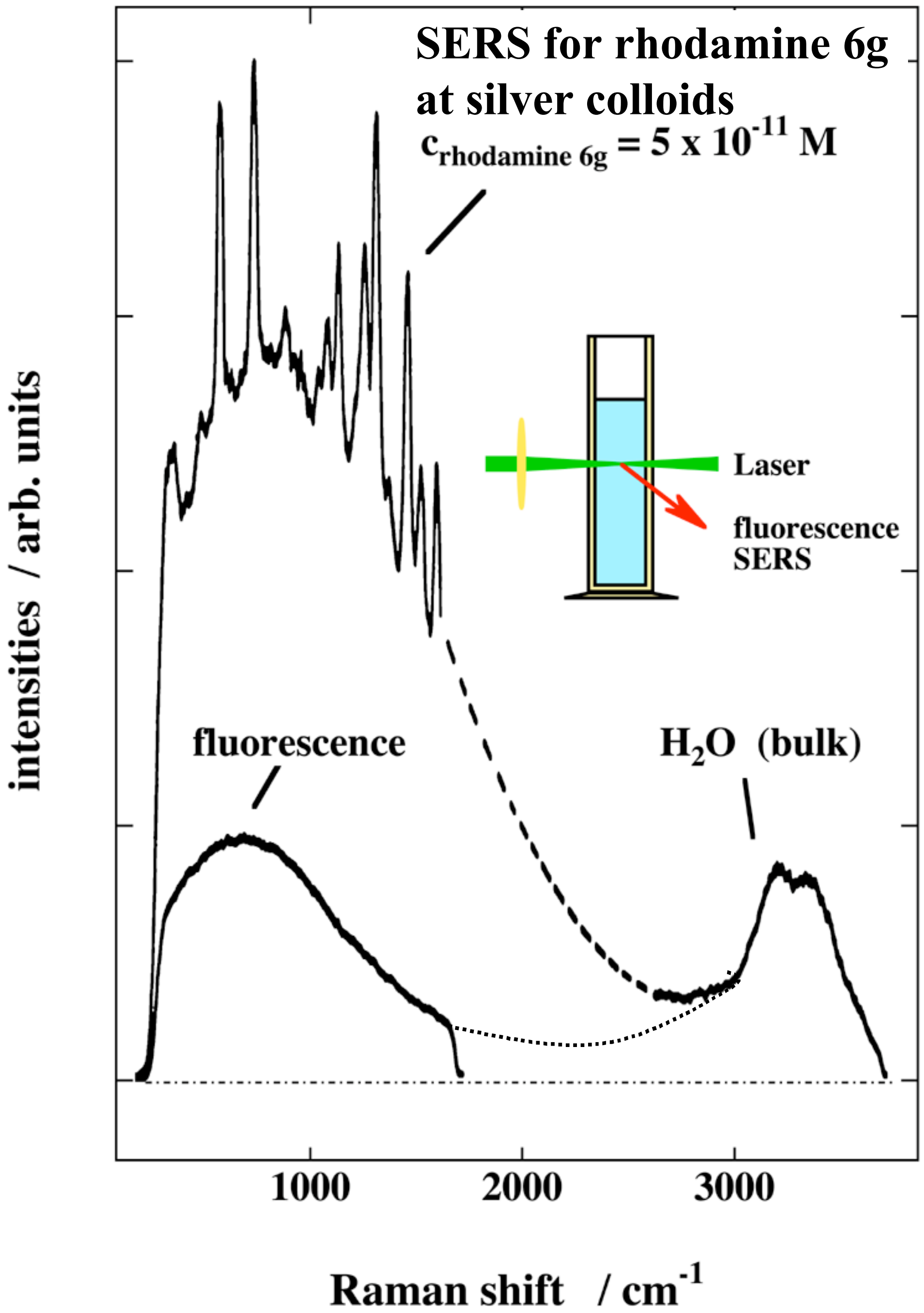
Roughness required

Not for all molecules

Surface enhancements reported:

Often F ~ 10^6 ;

F ranges from ~ 10^2 to > 10^{12} !

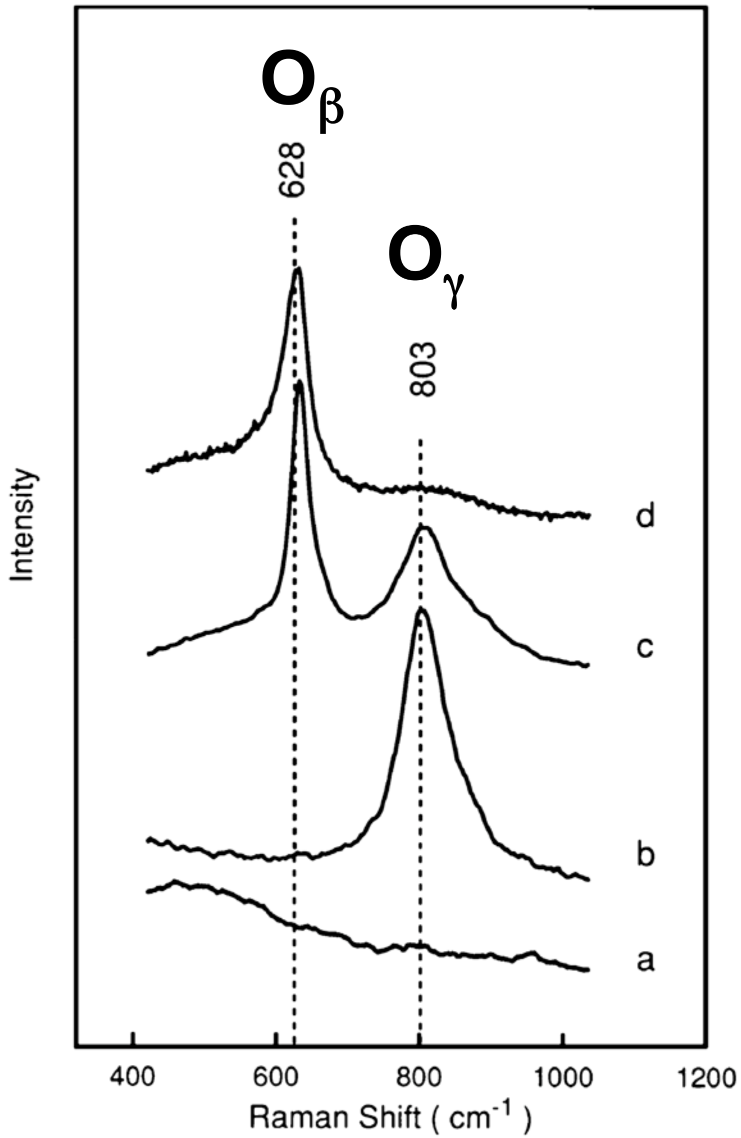


1. Dye in aqueous solution fluorescence

2. silver sol added:
   No of Ag-particles **=**
   No of dye molecules, i.e,
   in average 1 dye molecule at 1 Ag-particle

Single Molecules **3**(5-6), 285 (2002)

Raman Spectroscopy of O_γ and O_β on Ag(111) at high T



0.8 bar N_2 + 0.2 bar O_2

d) T = 920 K

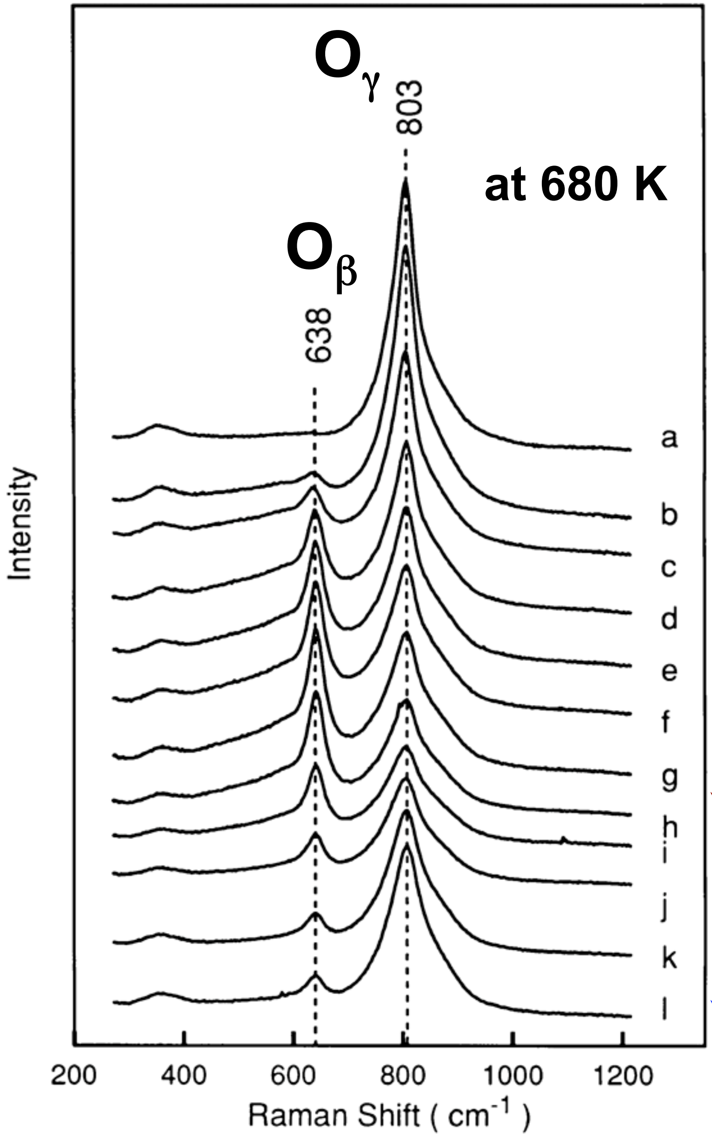
c) T = 830 K

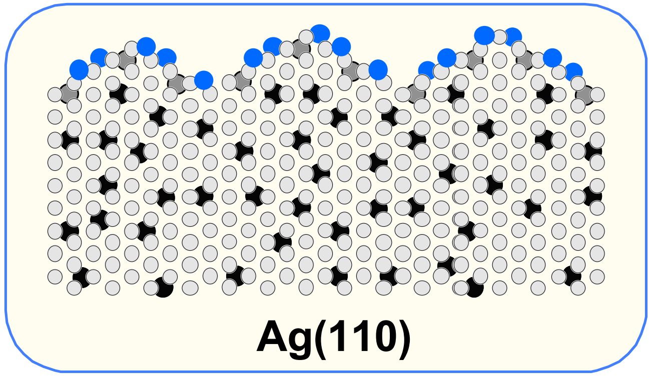
b) T = 780 K

a) T = 620 K

PRL 72 1561 (1994)

Raman Spectroscopy of O_γ and O_β on Ag(110) at hight T





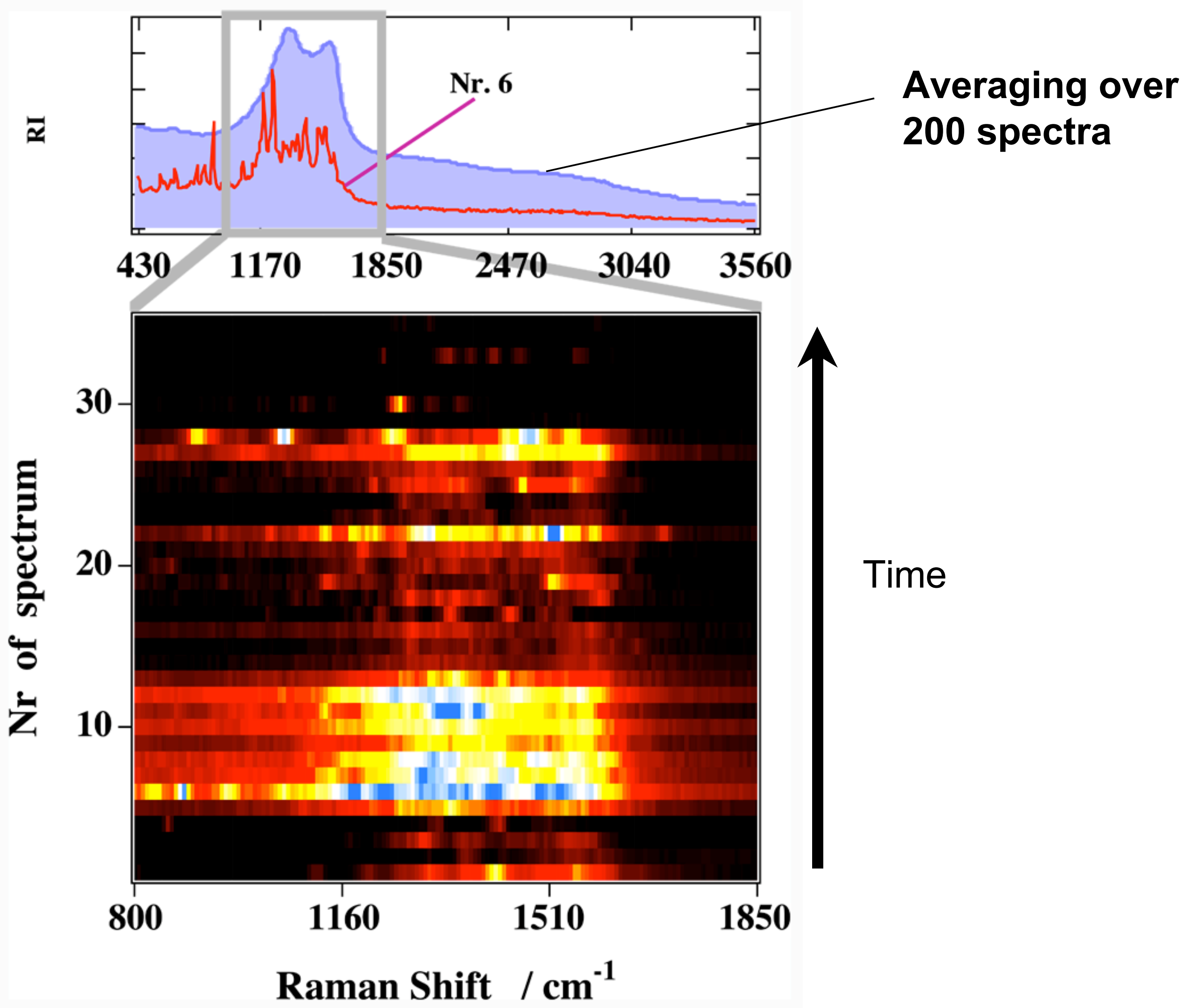
0.8 bar N_2 + 0.2 bar O_2

Switch to 1 bar N_2

back to 0.8 bar N_2 + 0.2 bar O_2

PRL 72 1561 (1994)

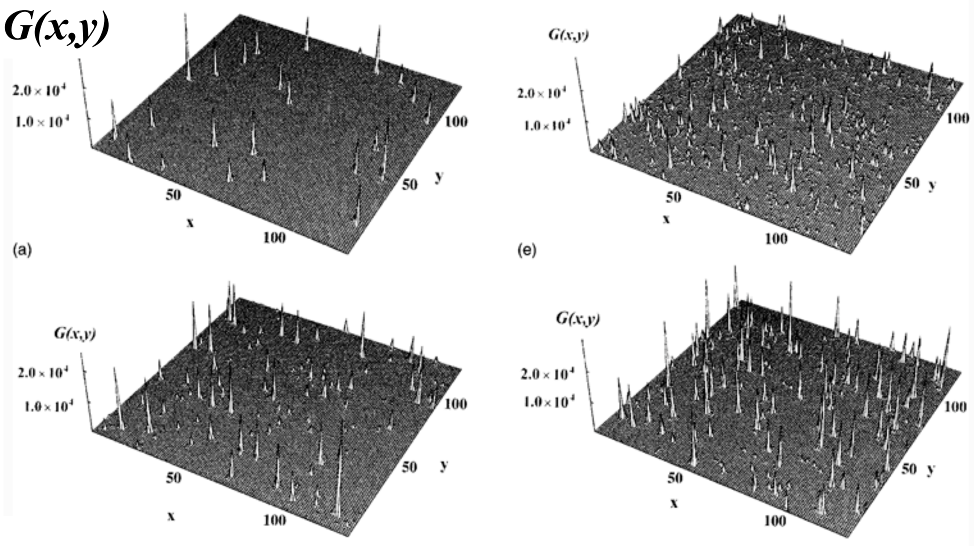
Spectral fluctuations for amorphous carbon at Ag



Electrochemistry (jp.) **68**, 942 (2000)

Shalaev's "hot spots" in a fractal surface

Shalaev et al., PRB, 57 (1998) 13265.



G(x,y) = enhancement of the EM field

roughness is aproximated

by a fractal stucture

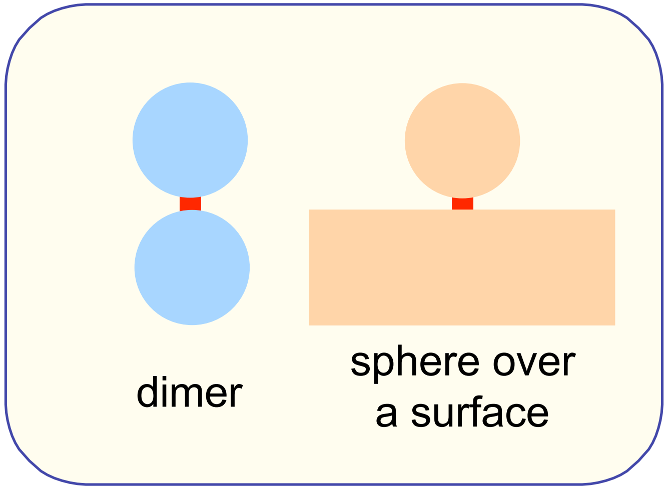
At some locations,

huge enhancements

are found in calculations

→ **"hot spots"**

Because F_{TERS} ~ g^4 , a few hot spots can produce most of SERS



• Tip -Enhanced Raman Spectroscopy (TERS)

Concept

TERS setup

STM tips

First experiments at Ag and Au

Experiments at single crystalline surfaces

a) small optically non-resonant molecules at Au(111), Au(110), Pt(110)

b) resonant dye (Malachite Green Isothiocyanate) at Au(111), Pt(110)

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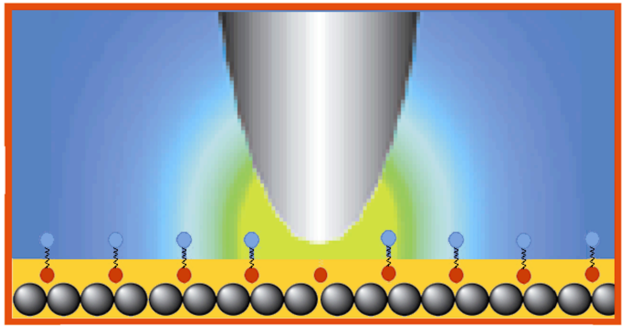
How to Move from SERS to TERS ?

Tip+metal:

>>> Localized
- surface plasmons

Locally, high EM-fields

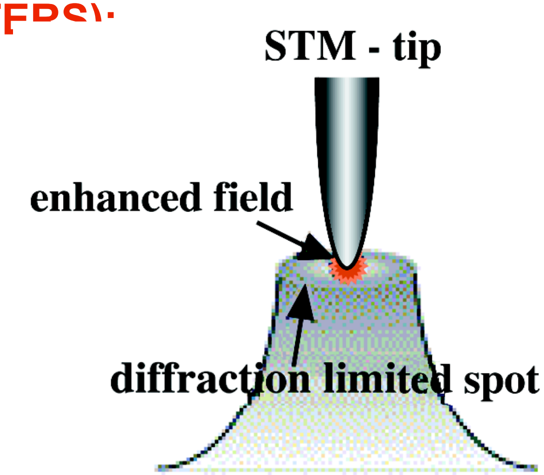


Instead of many internal hot spots of a rough surface (= SERS)
use a single external hot spot over a smooth surface (= TERS):

i.e., use a STM tip of Ag or Au

as an **near-field enhancer**

having sub-wavelength resolution



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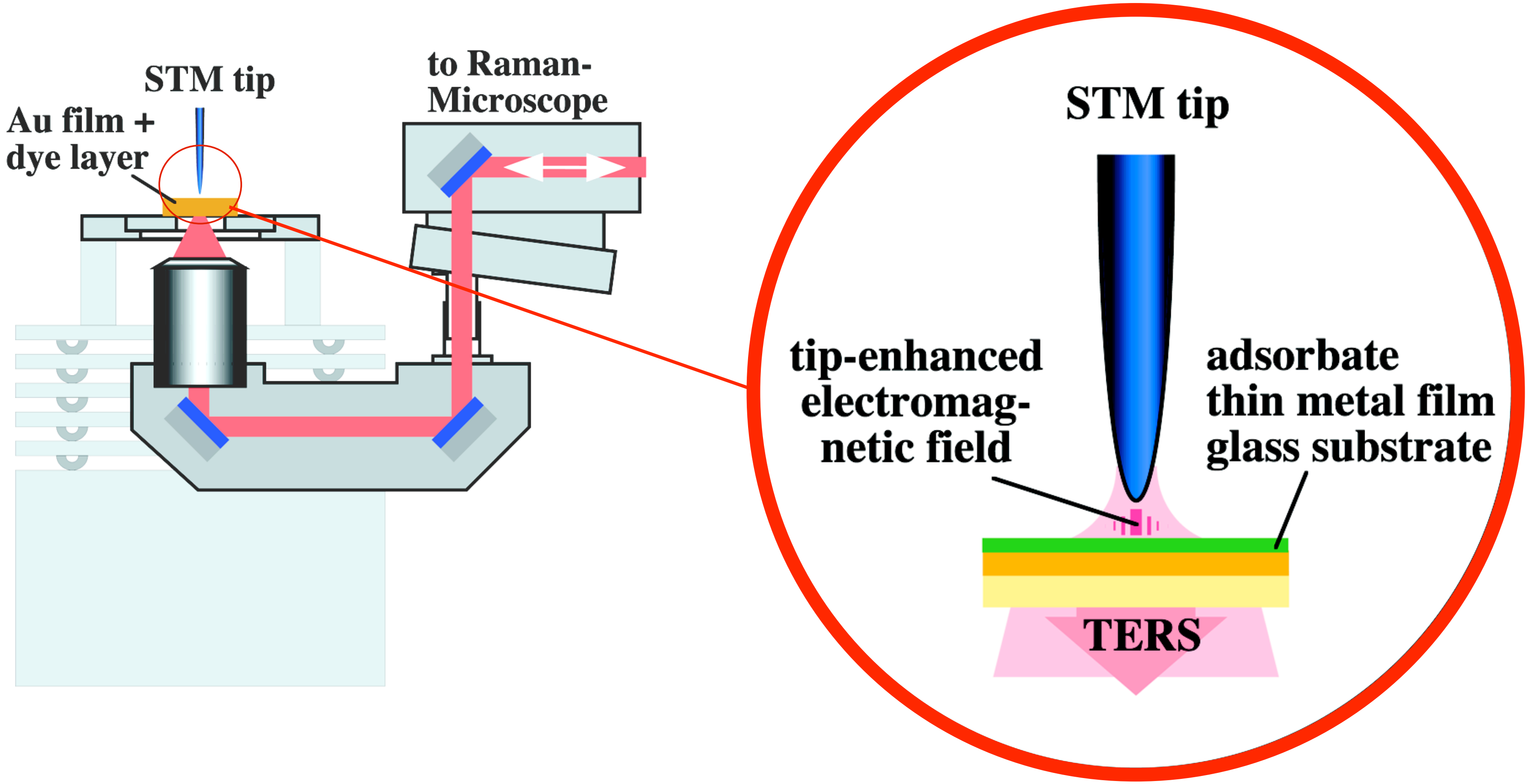
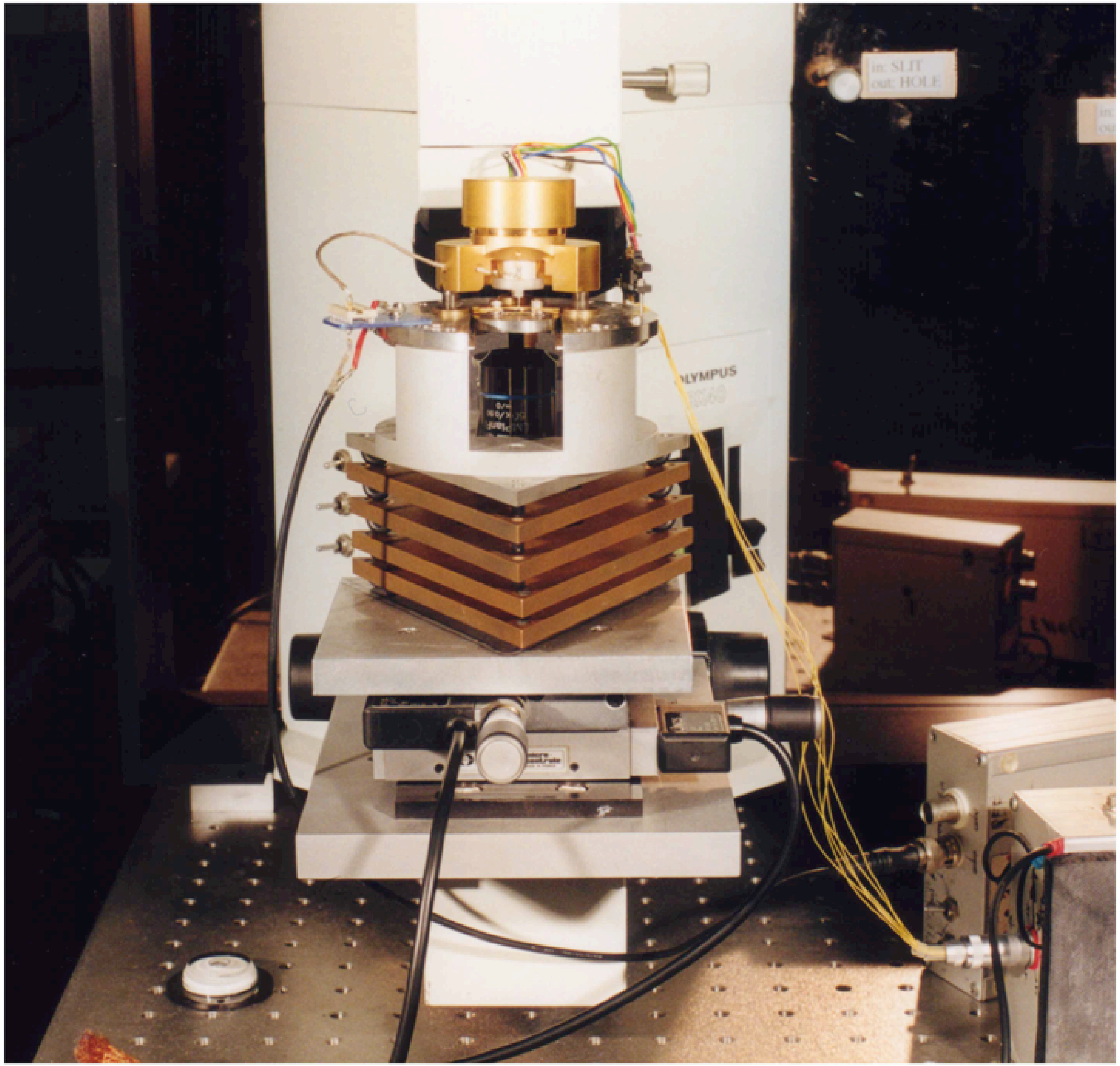
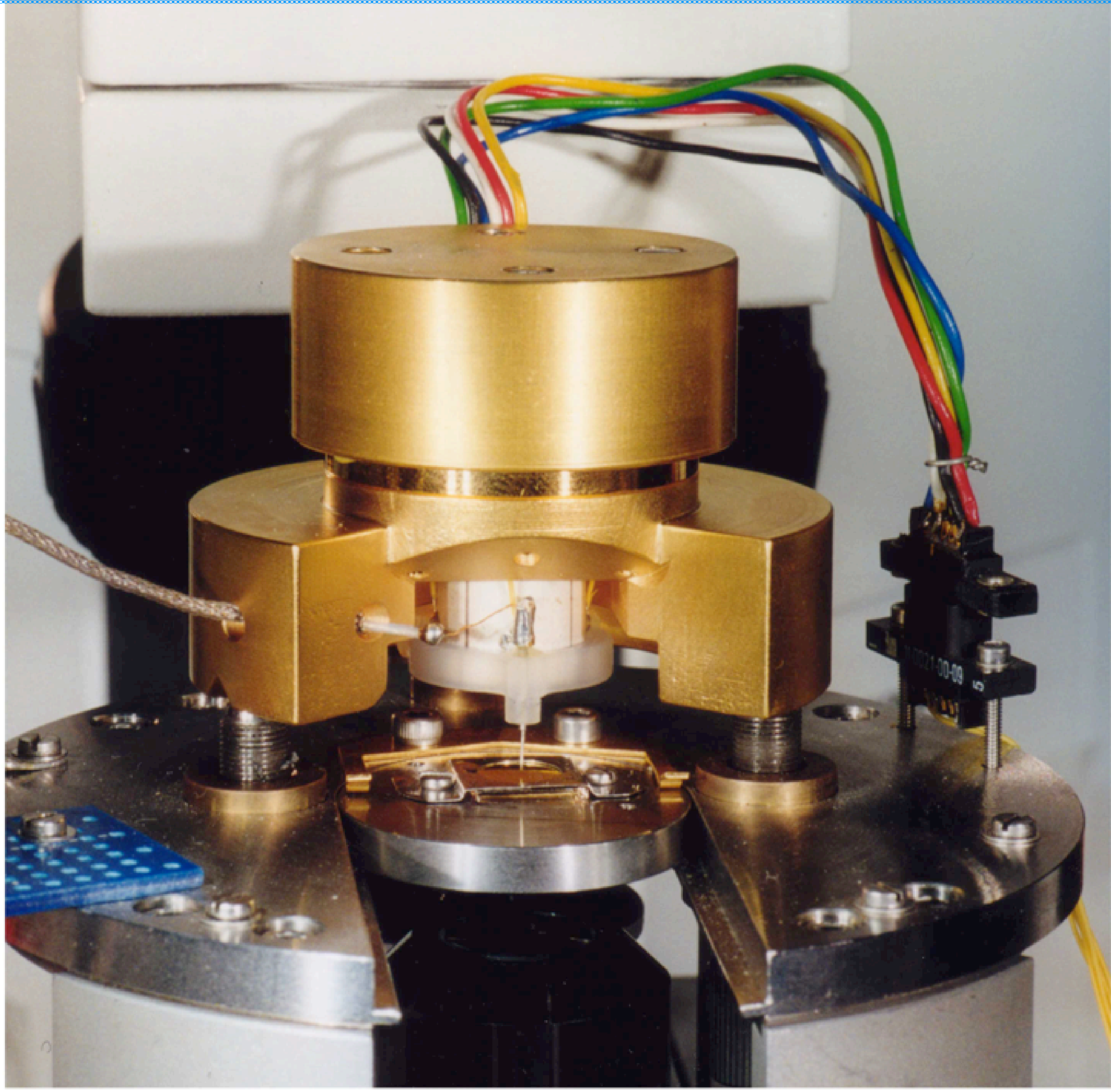
Setup A: The inverted Raman–Microscope



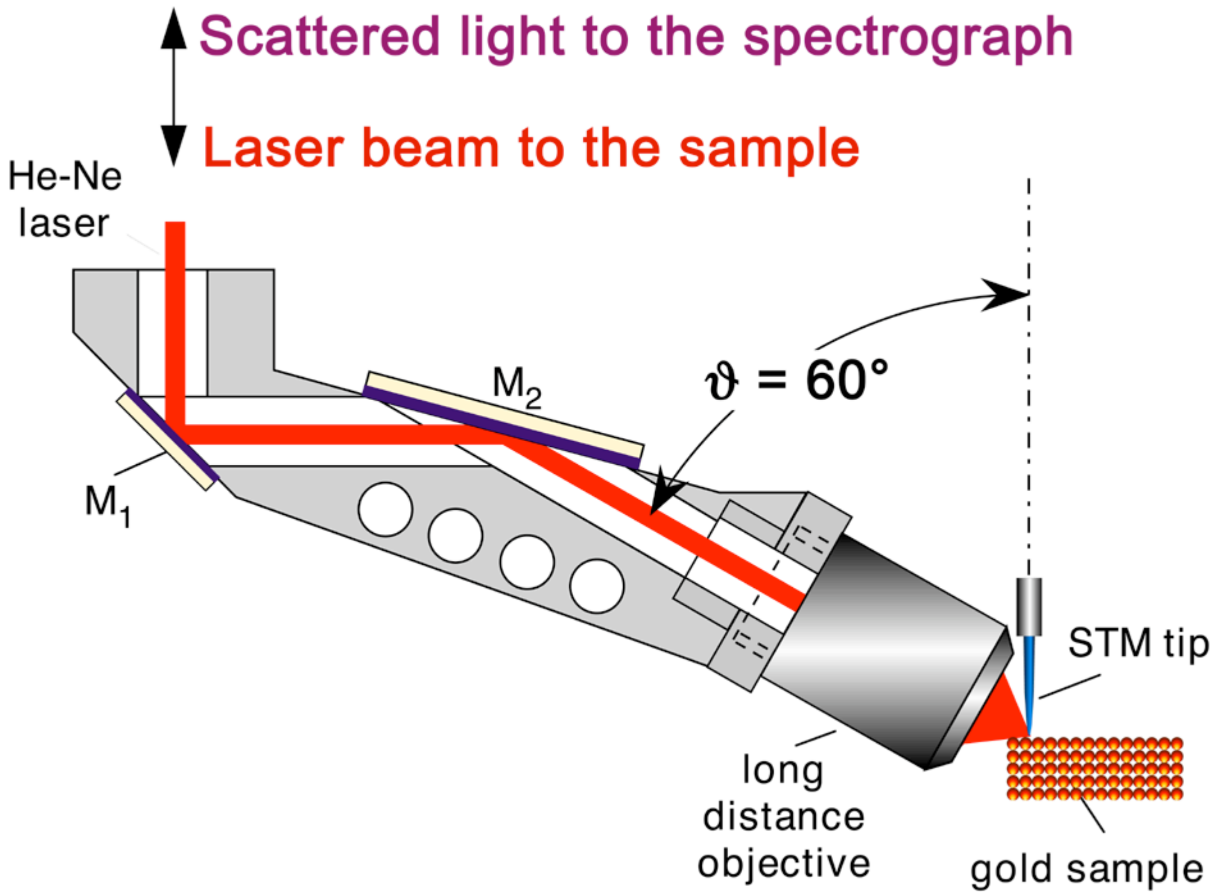
Tip-enhanced Raman spectrosocopy (TERS) using an inverted microscope



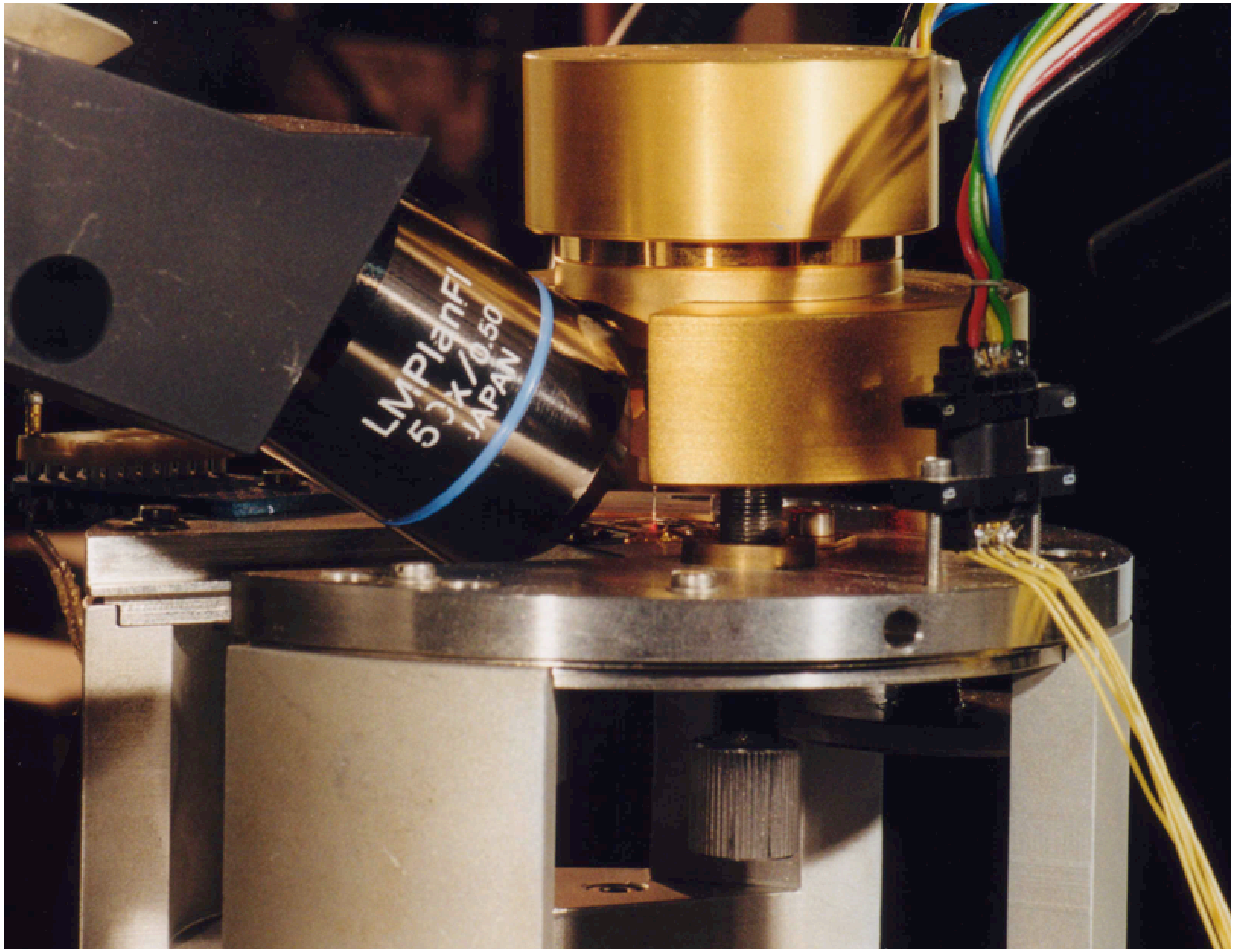
**STM head, Ag-tip above a thin Au-film (12 nm) on a glass slide.
Objective focusses the laser beam through the metal film on the tip
and collects the inelastically scattered light in backscattering mode.**



Setup B: Side illumination, TERS and Light–Emission



Setupu B: Side illumination (60°)



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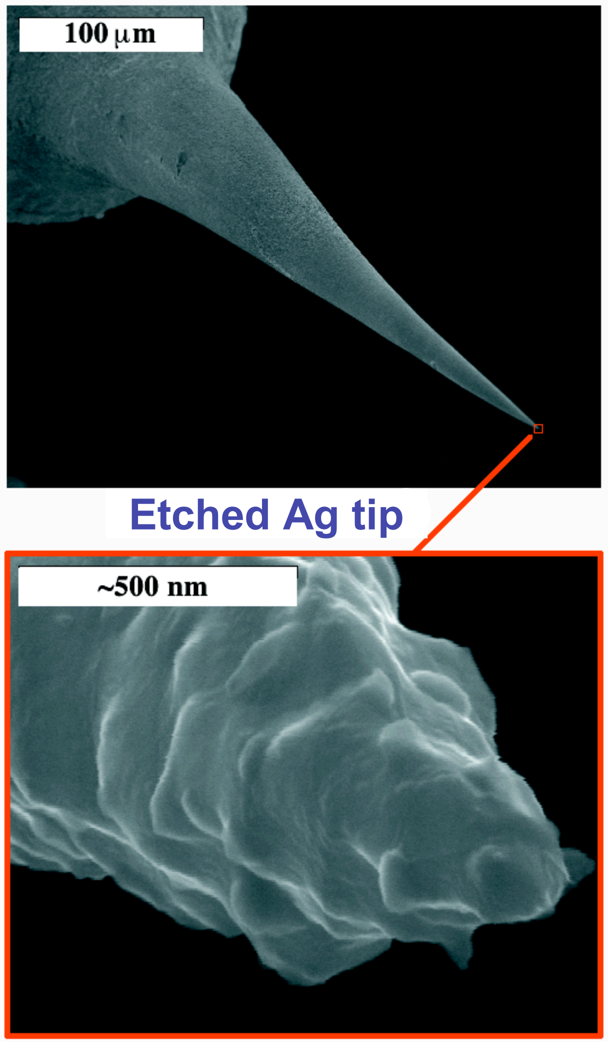
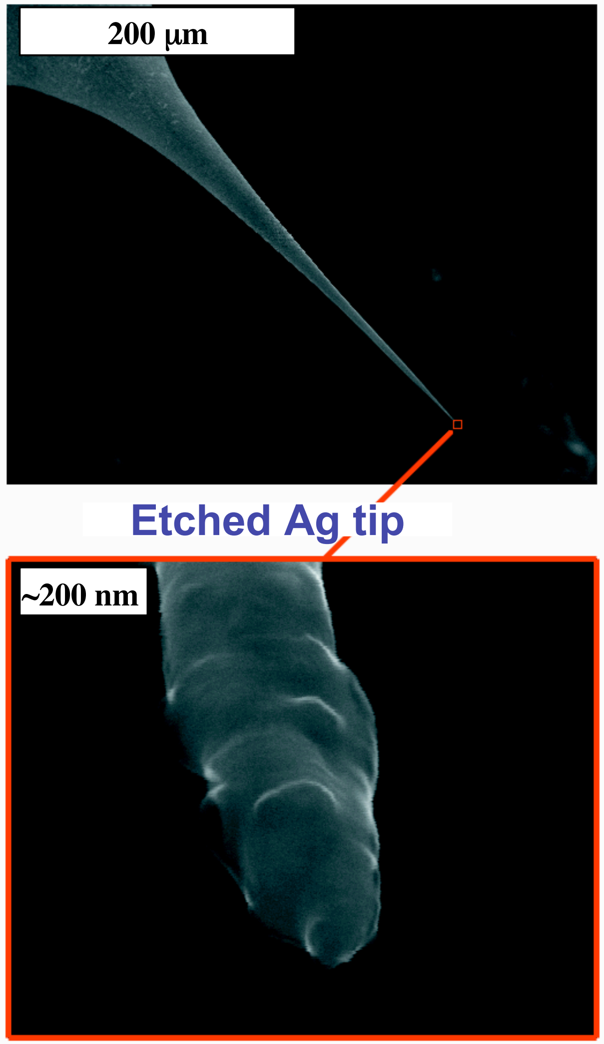
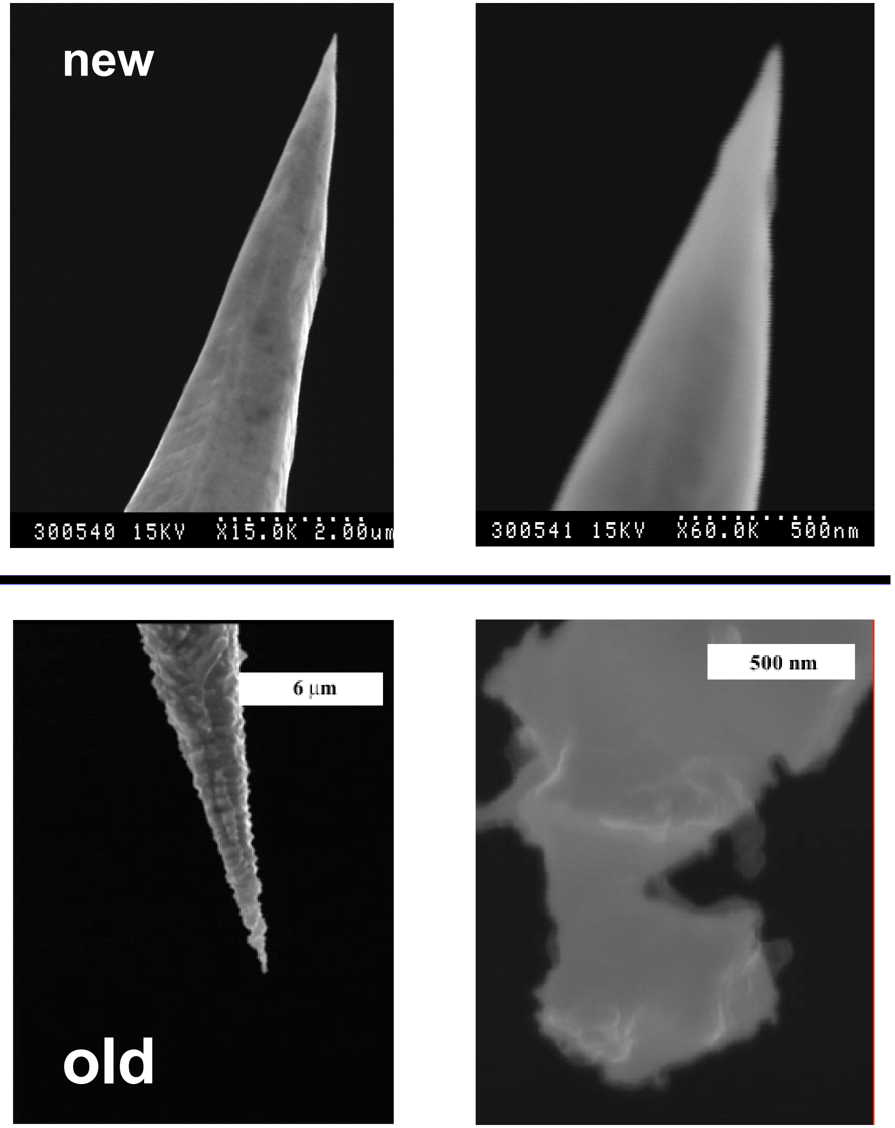




A new, easy Method for Preparation of STM Tips

Applied Voltage: ~2.4 V



Electro-

chemical etching of a gold wire (0,125 mm)

in a solution of 1:1 ethanol and conc. HCl.

Toward sharp Tips

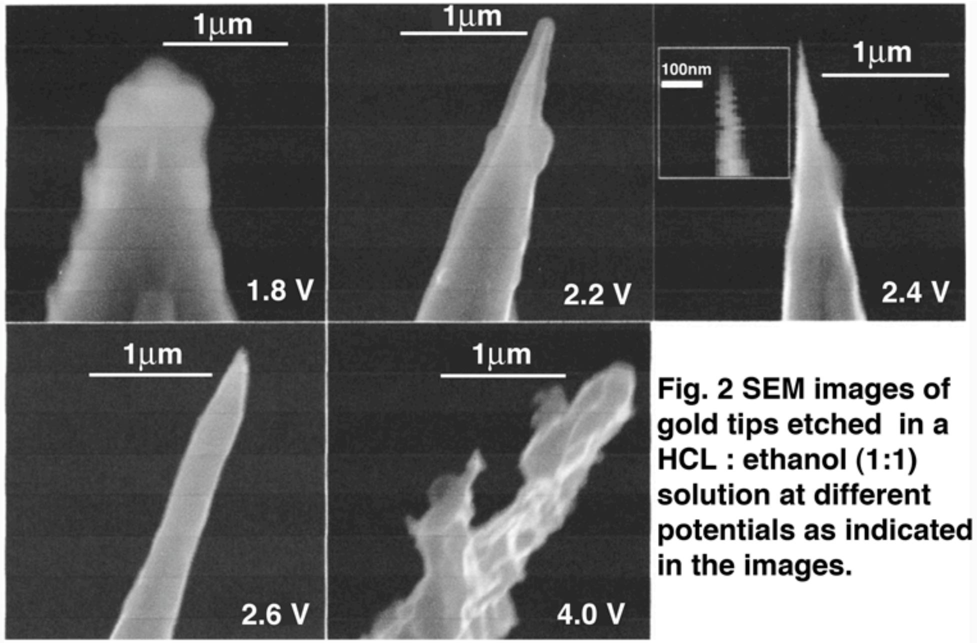


Fig. 2 SEM images of gold tips etched in a HCL : ethanol (1:1) solution at different potentials as indicated in the images.

Variation of the potential

Variation of the mixture

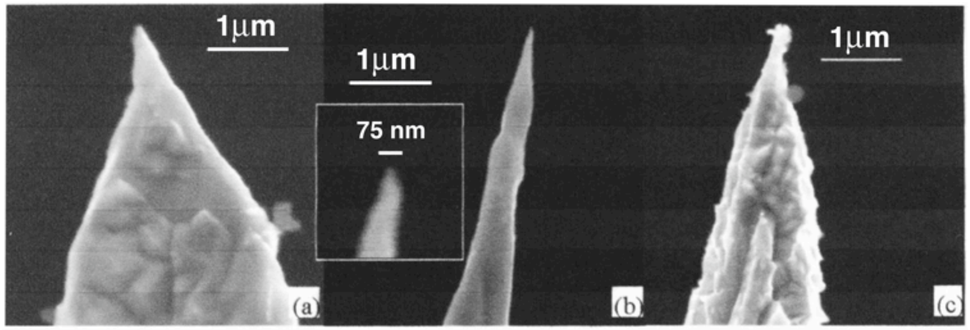


Fig. 3: SEM images of gold tips etched at 2.4 V in HCL : ethanol solutions with different contents: (a) 1:2, (b) 1:1, and (c) 2:1.

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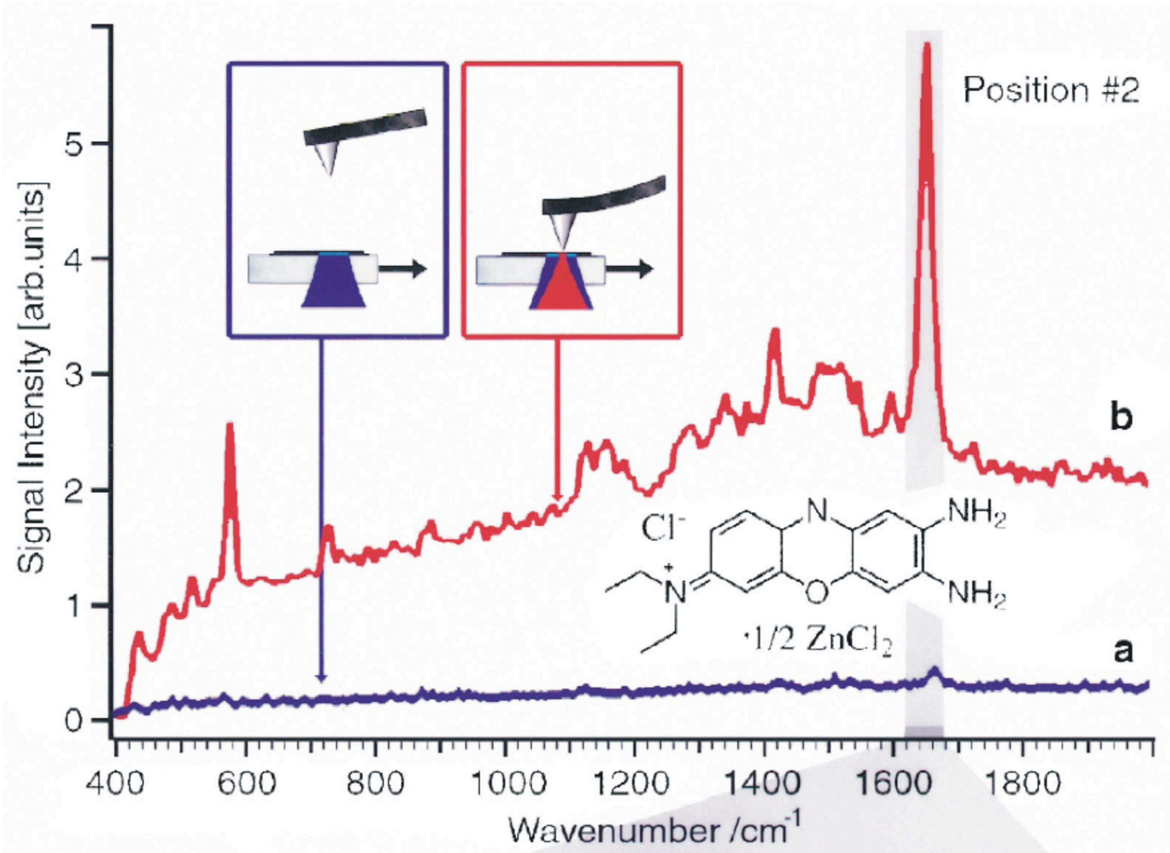
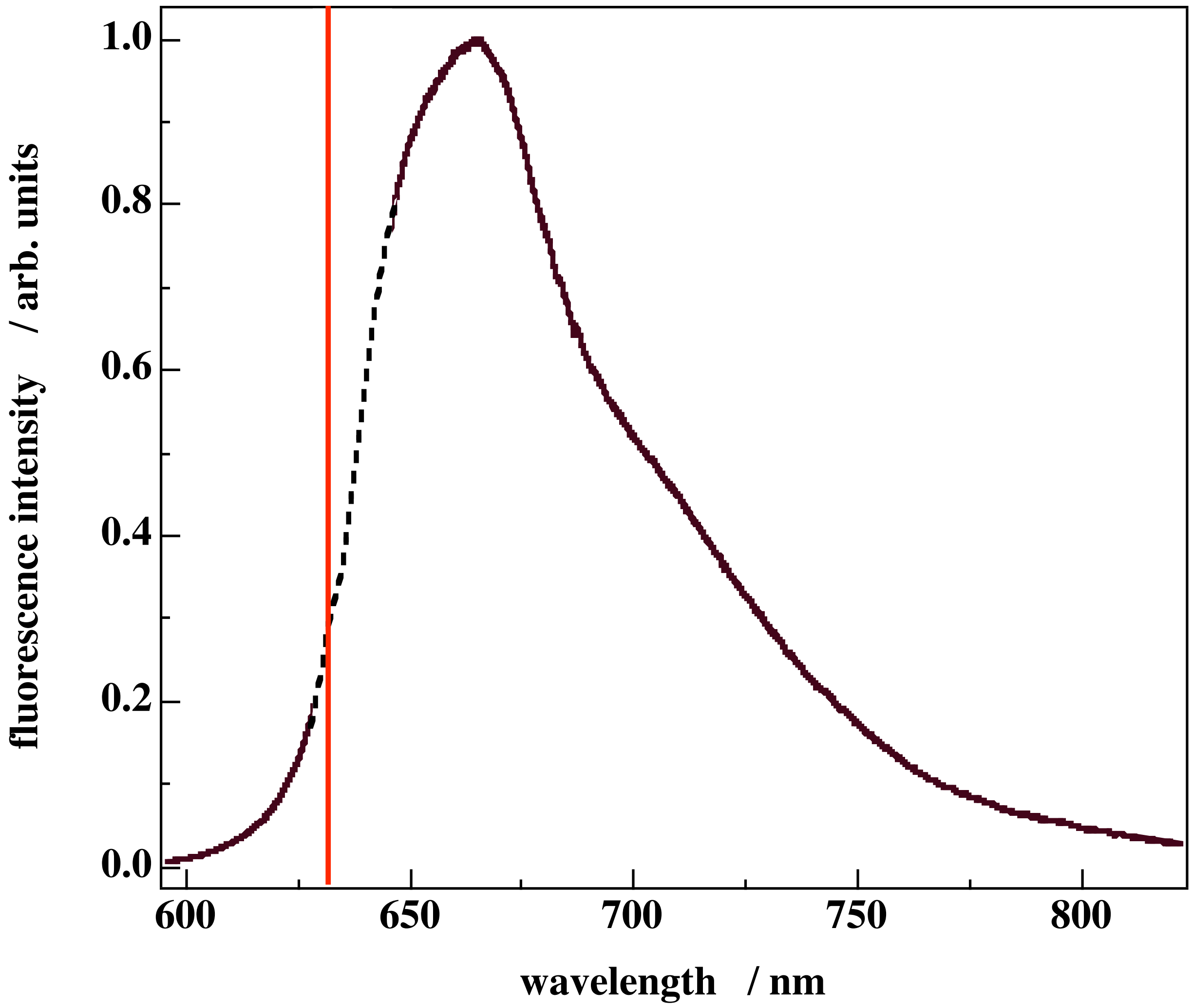
Stöckle: Tip–Enhanced Raman Scattering — AFM



TERS spectra of brilliant cresyl blue (BCB) dispersed on a glass support measured with a silver-coated AFM probe. The two Raman spectra were measured with the tip retracted from the sample (a) and with the tip in contact with the sample (b). FEF: 2000.

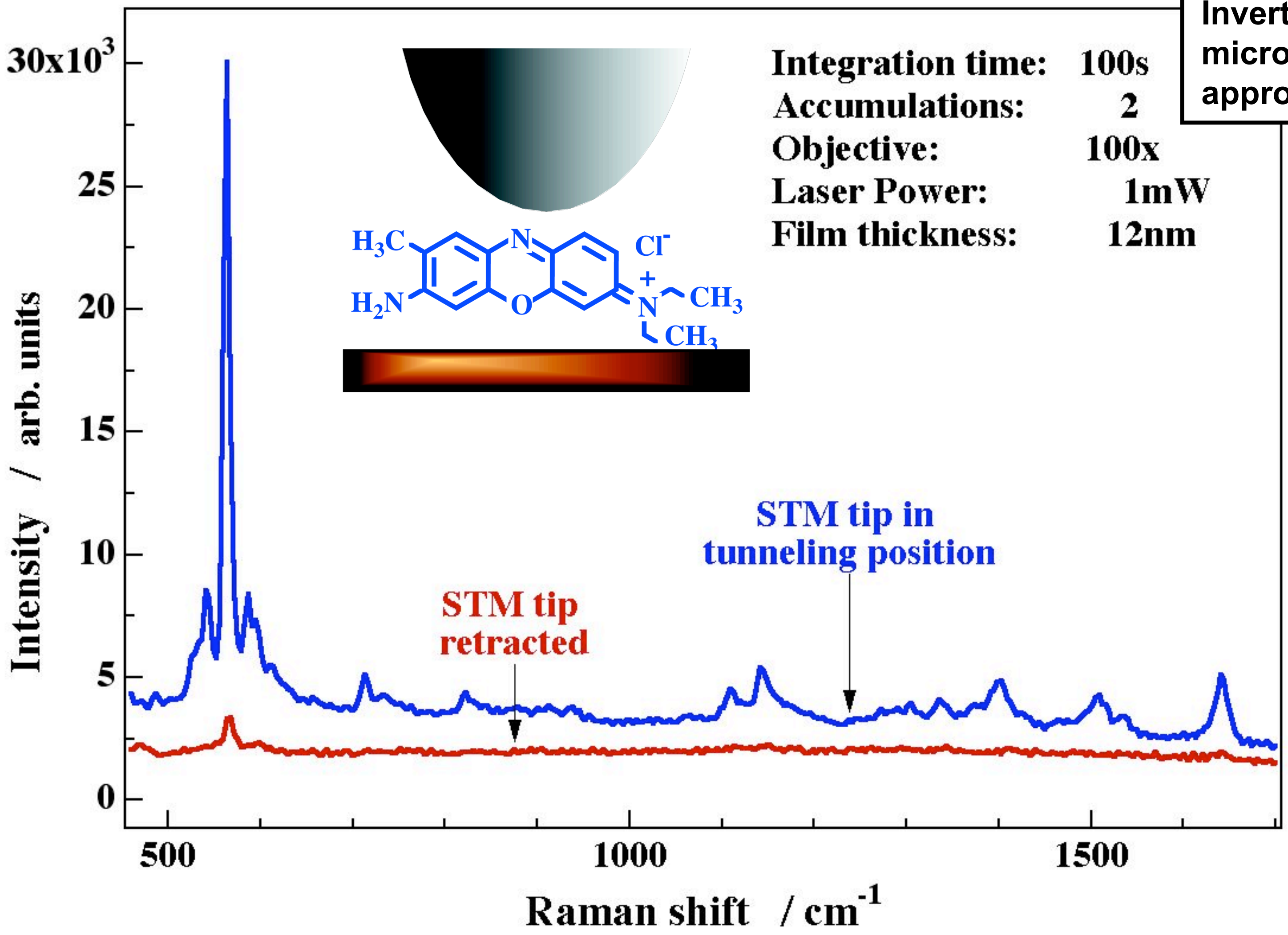
From: R.M. Stöckle et al.: Chem. Phys. Lett 318 (2000) 131-136

TERS: Fluorescence of BCB



Brilliant Cresyle Blue (BCB) at a smooth Au Surface

Inverted microscope approach



_TERS at Single Crystalline Surfaces

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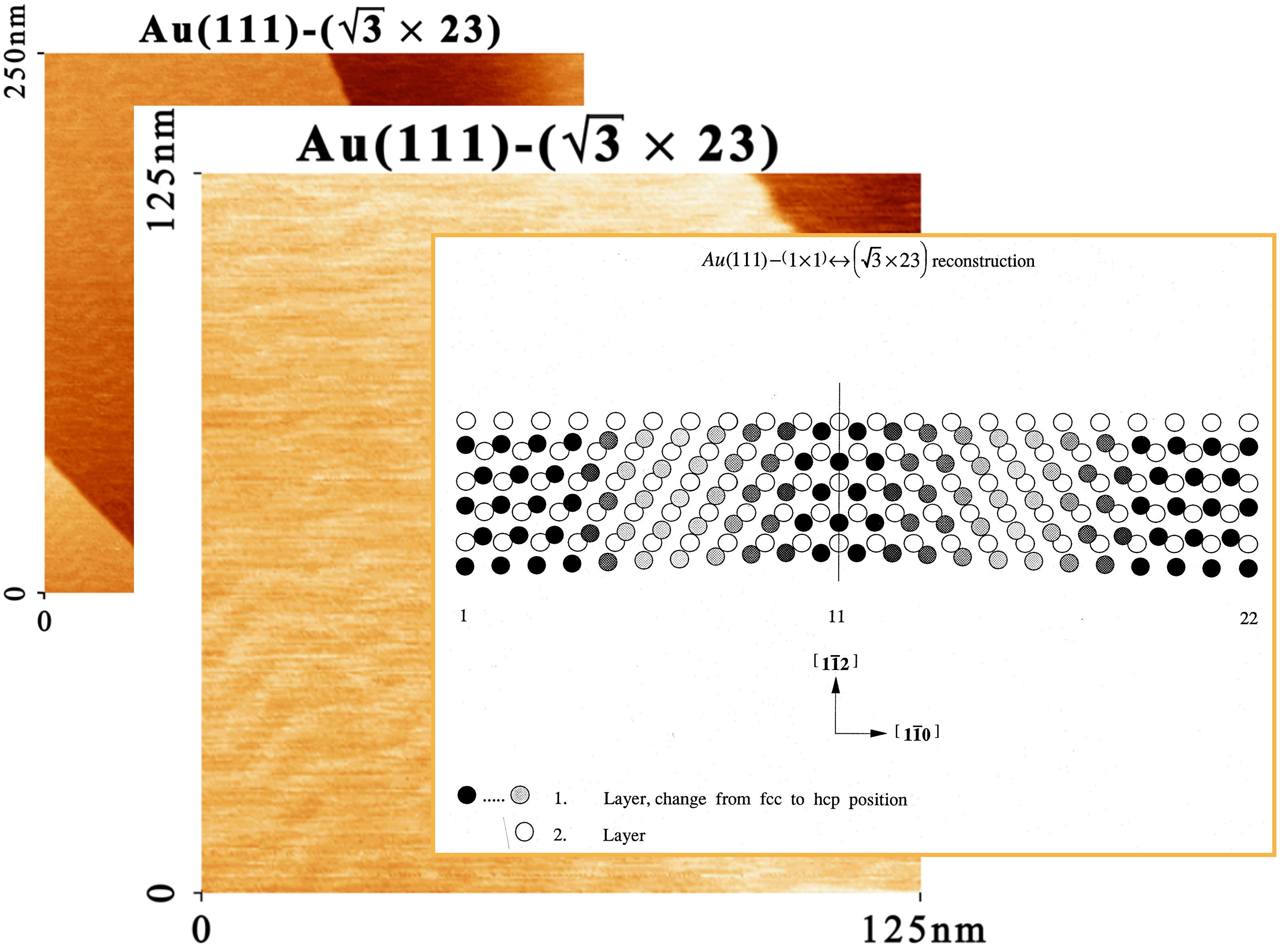
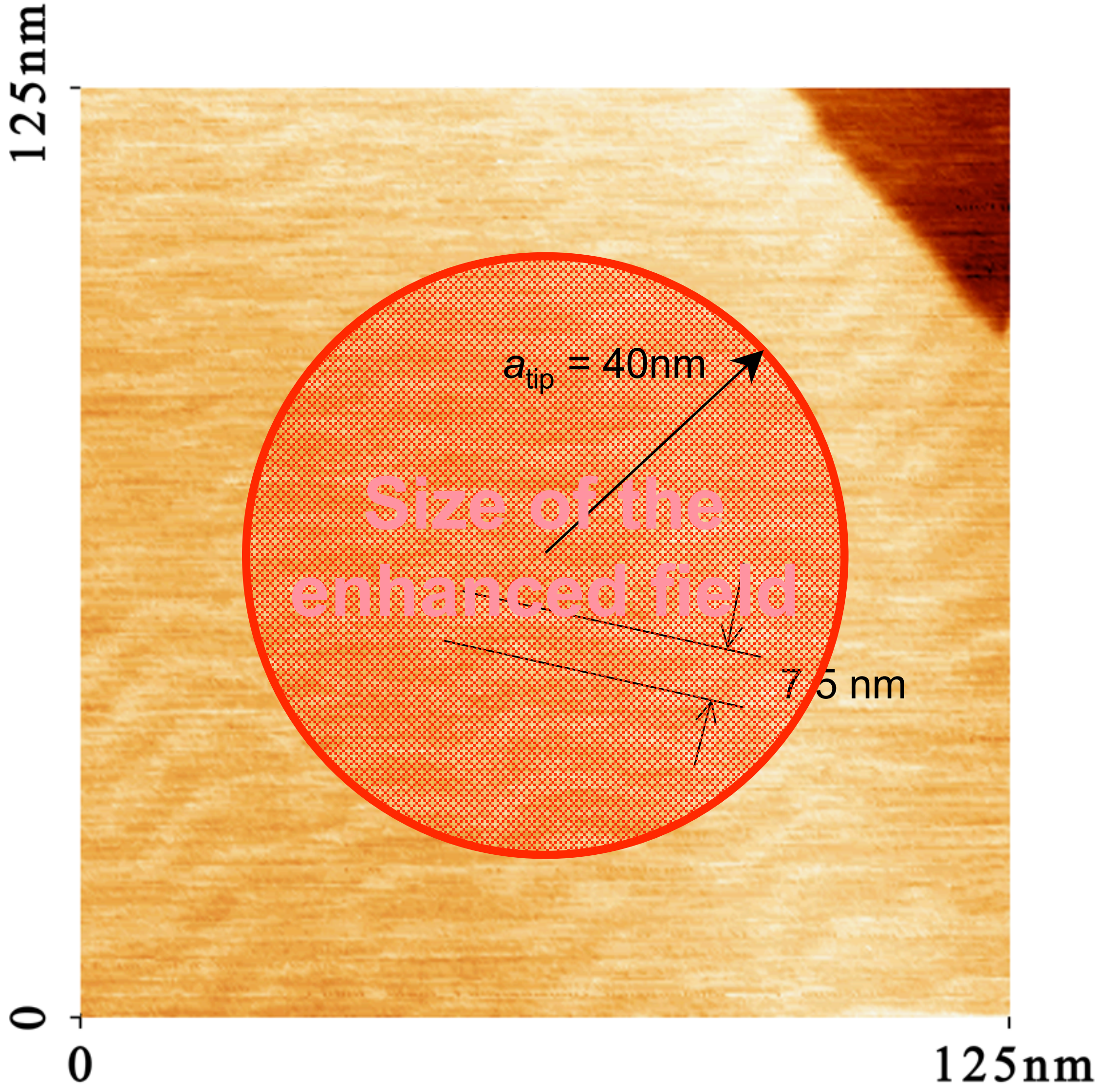
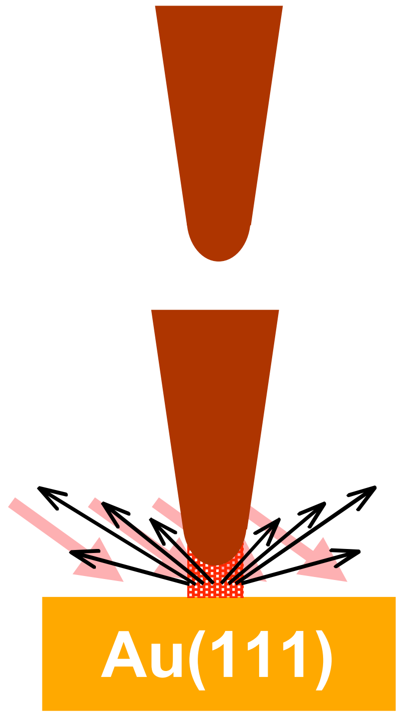
Gold(111) and surface reconstruction

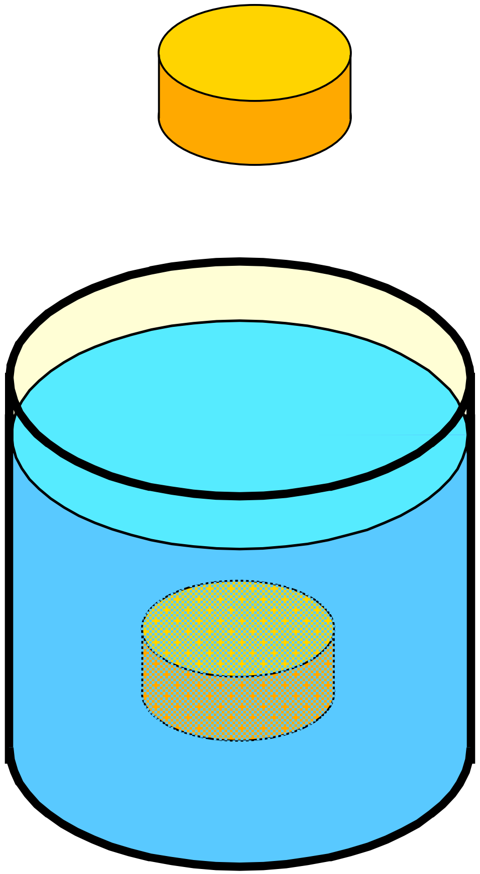


The size of the Laser focus and of the enhanced field





Crystal Preparation and Cyanide–Adsorption

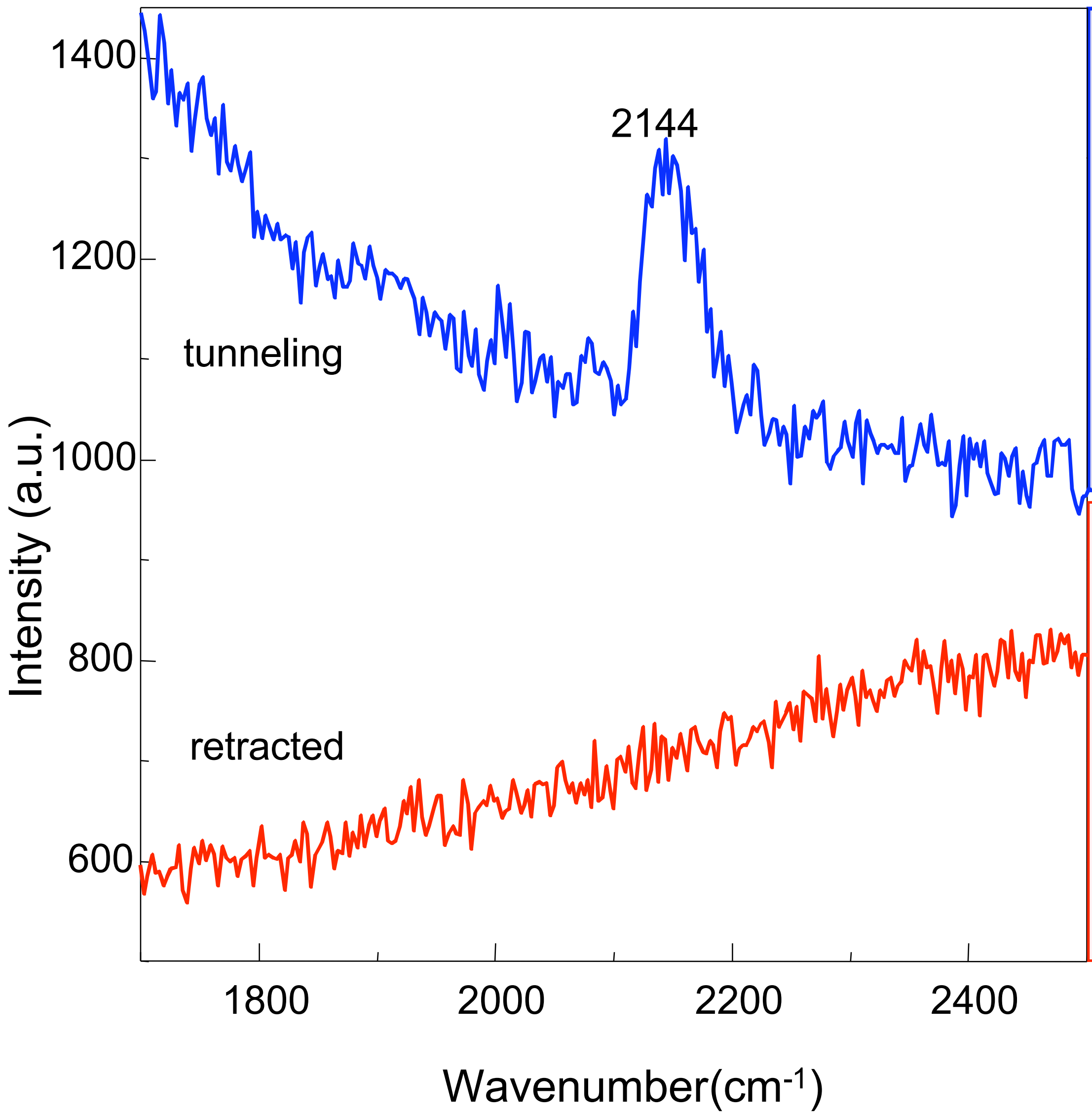


Au(111) flame annealed

Au(111) emersed and placed into the spectrometer

Au(111) immersed, i.e., dipped into 0.1 mM NaCN+0.1 M $NaClO_4$ with potential controlled at -0.75 V vs SCE

CN^- at Au(111)



$$I_{TERS} \approx I_{RRS}\, g^4 \left(a_{field}^2 / R_{focus}^2\right) \approx 200 \text{ cps}$$

$$\Rightarrow g^4 \approx 4.5 \times 10^5$$

$a_{field} \approx 40$ nm; $R_{focus} \approx 1000$ nm

$$I_{RRS} \approx N_{CN^-} \left(\frac{d\sigma}{d\Omega}\right)_{RS} I_{Laser}\, \eta_{Raman\ system}$$

$$\approx 0.25 \text{ cps}$$

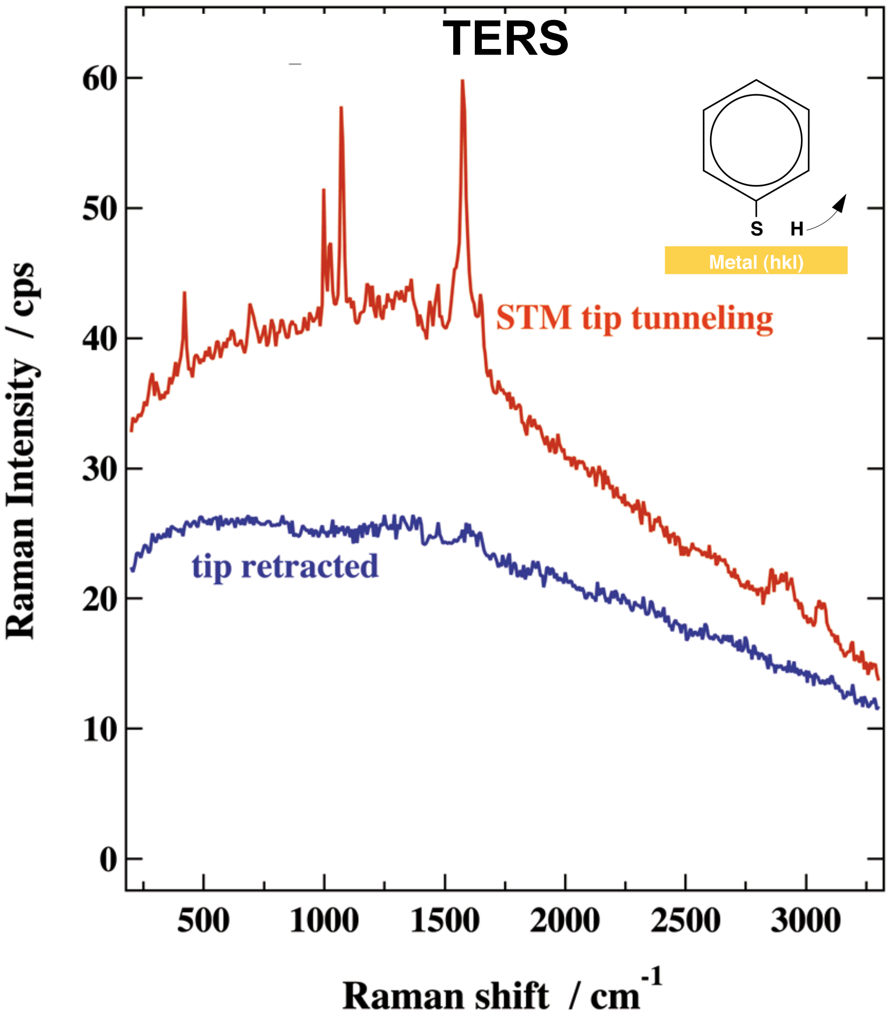
$\left(\frac{d\sigma}{d\Omega}\right)_{RS} \approx 4 \times 10^{-30}$ cm^2 sr^{-1} molecules^{-1}

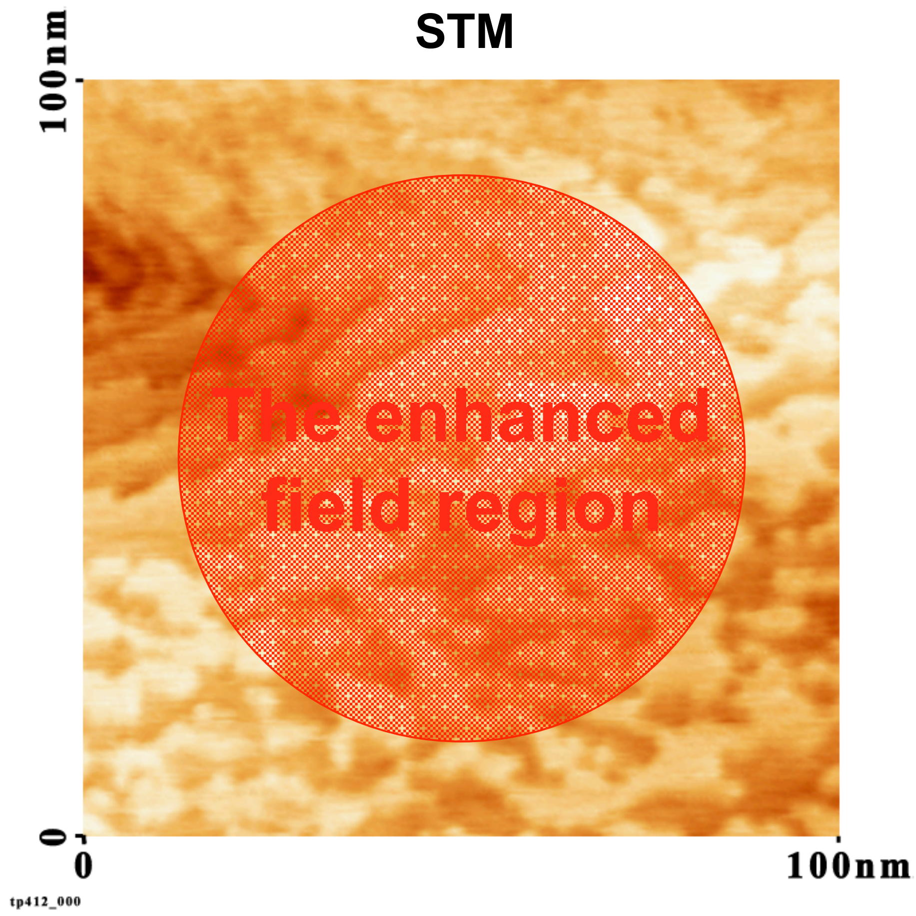
$N_{CN^-} \approx 8 \times 10^{14}$ molecules cm^{-2}

$I_{Laser} \approx 1.6 \times 10^{16}$ photons

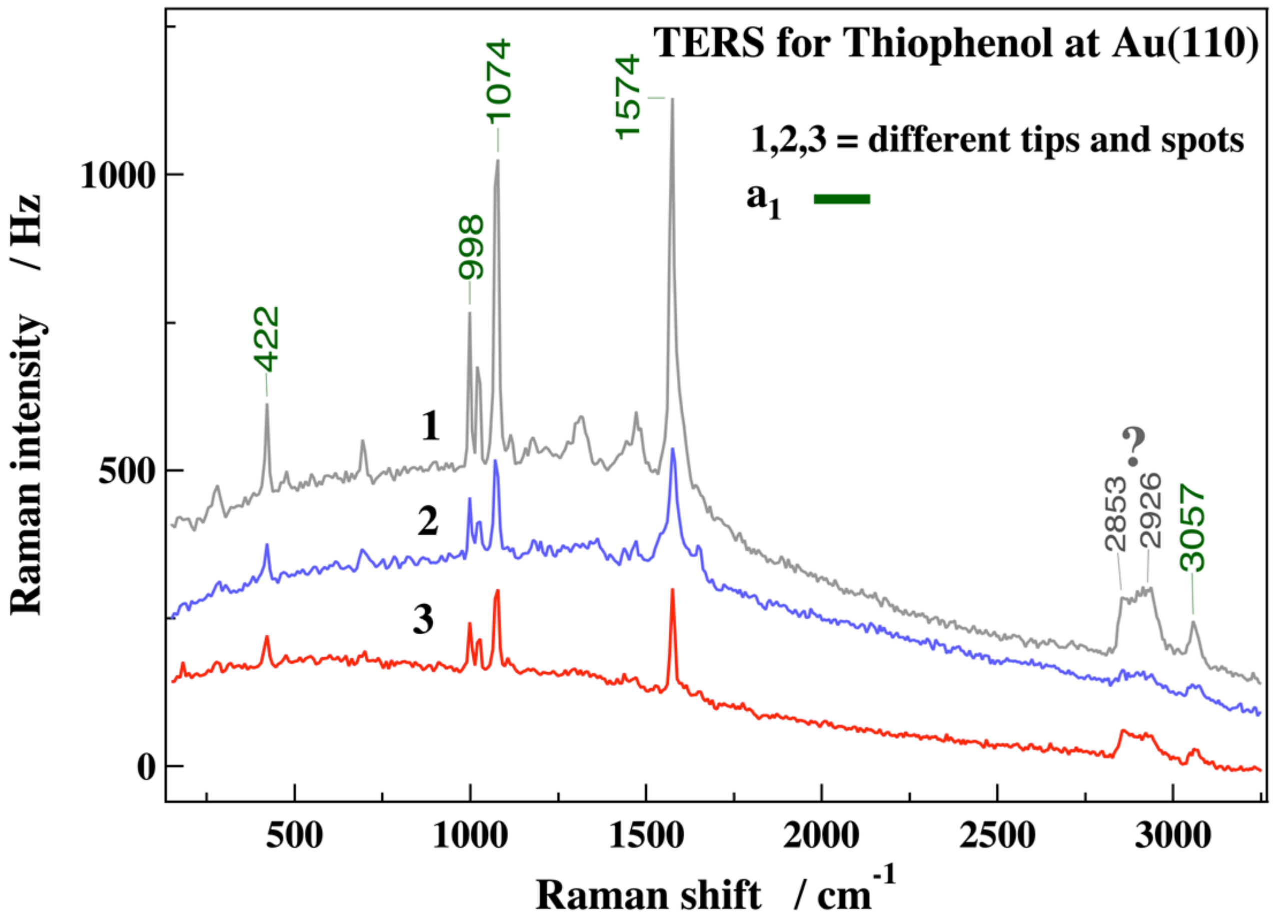
$\eta_{Raman\ system} \approx 0.005$

TERS and STM at the Air/Thiophenol/Au(110) Surface





Comparison of different TERS–Experiments

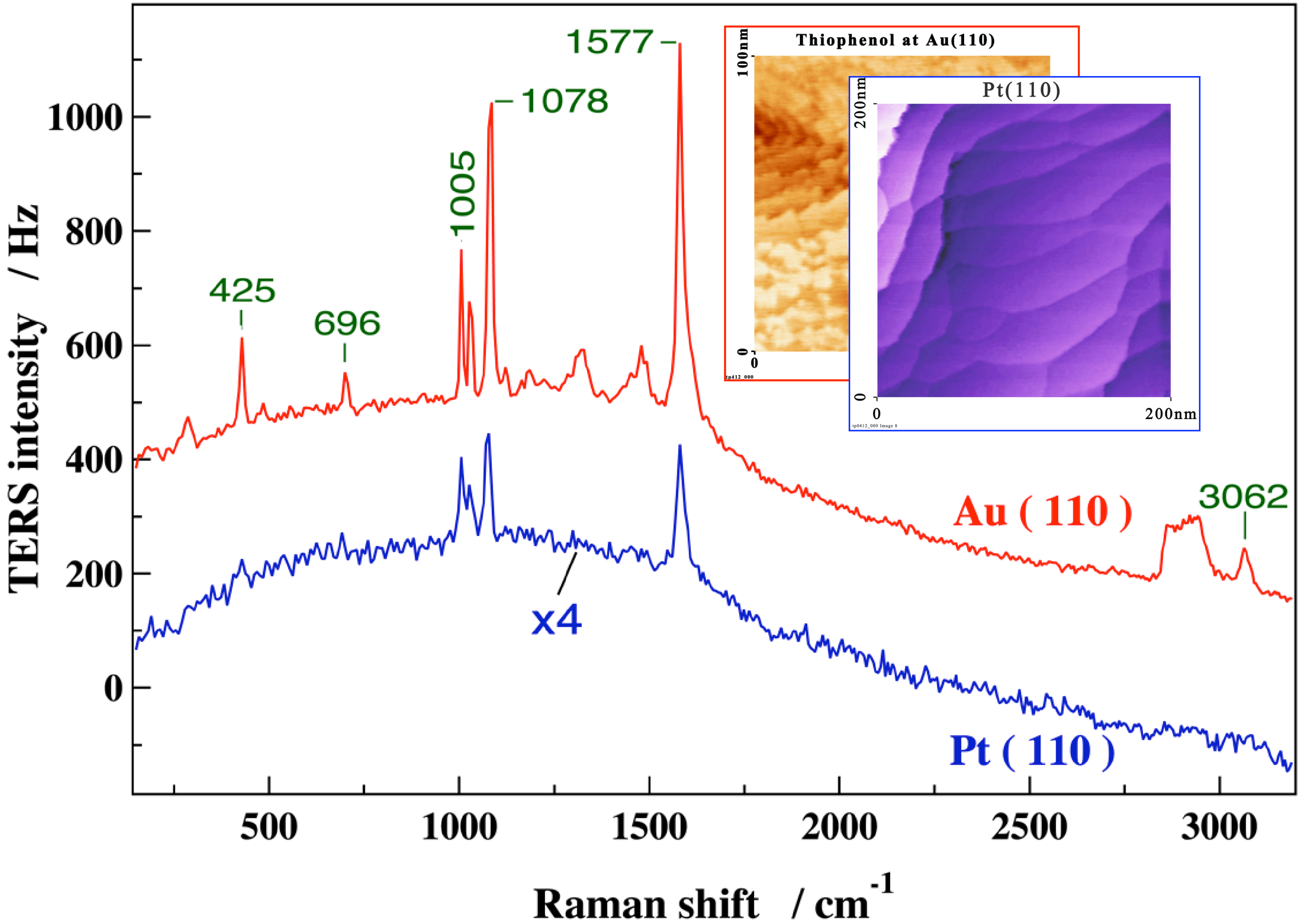


For thiophenol the TERS frequencies are close to ordinary Raman frequencies of this molecule

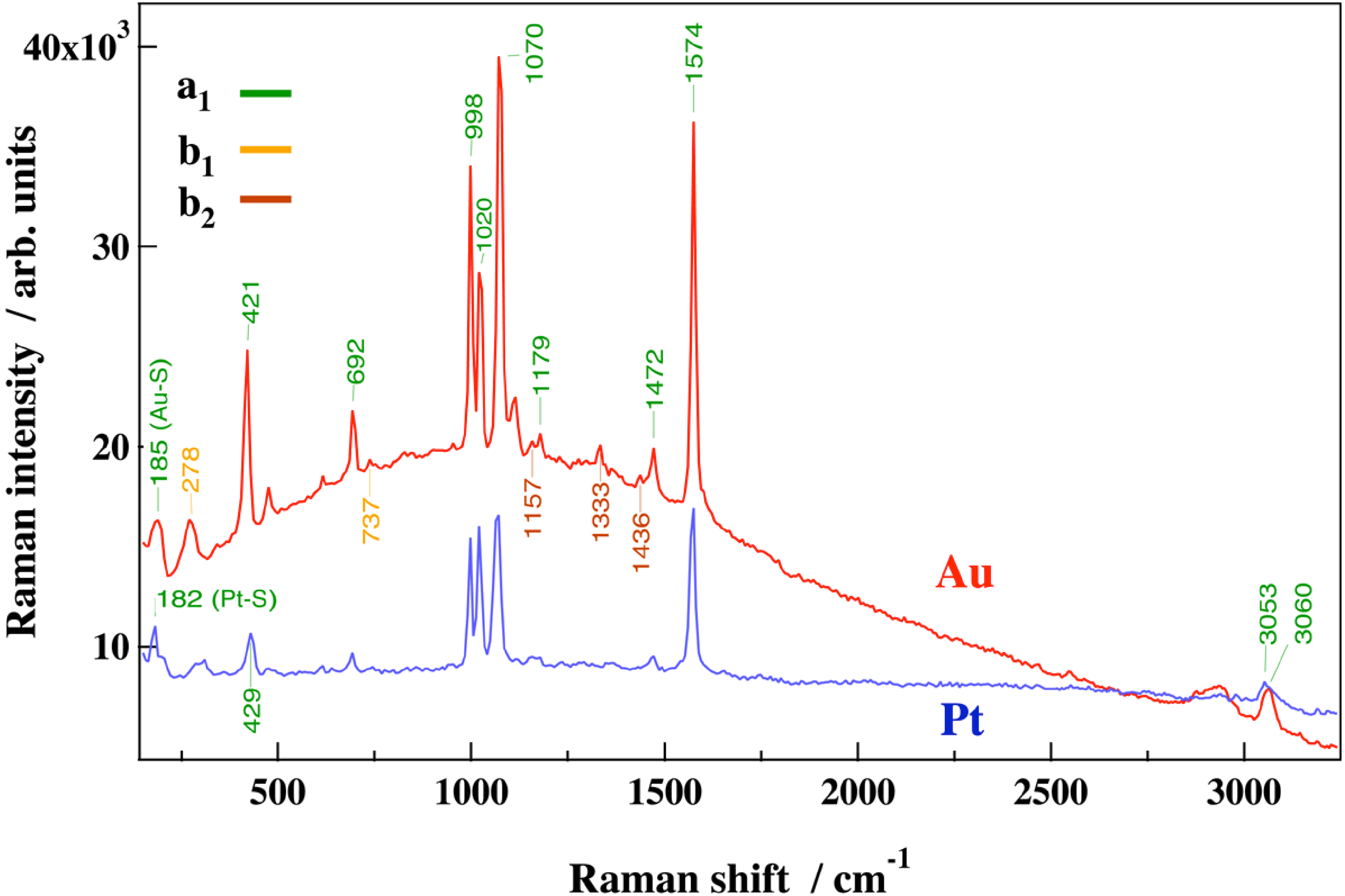
Unknown bands at 180, 270, 2850-2950 cm^{-1}

Different experiments: Strong variation in intensity, half widths, background.

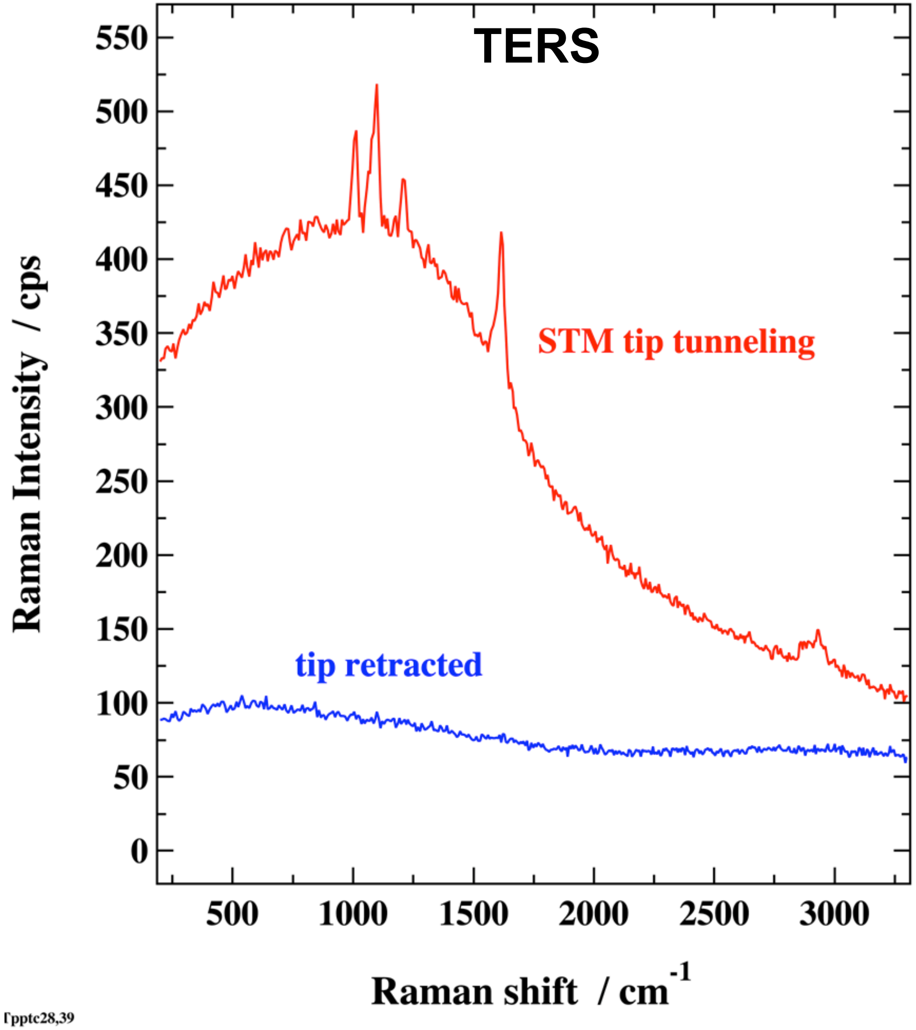
TERS for Thiophenol at smooth Au(110) and Pt(110)

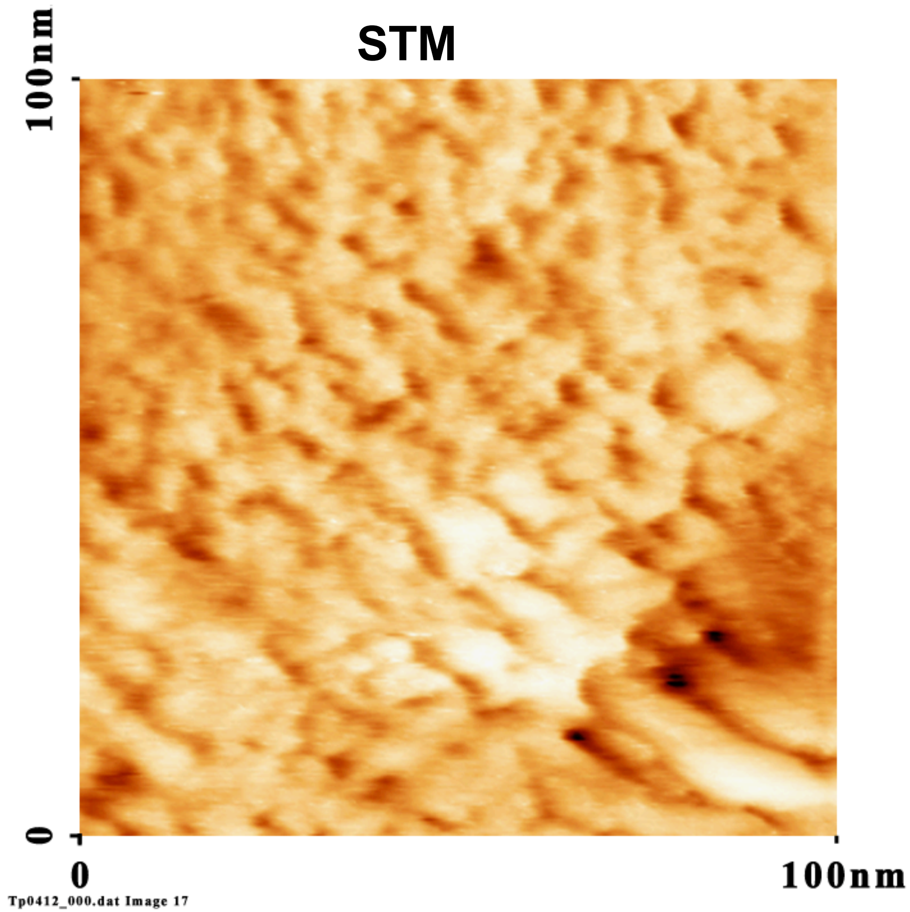


SERS (!) for Thiophenol at roughened Au und Pt



TERS and STM for Mercaptopyridine at Au(110)



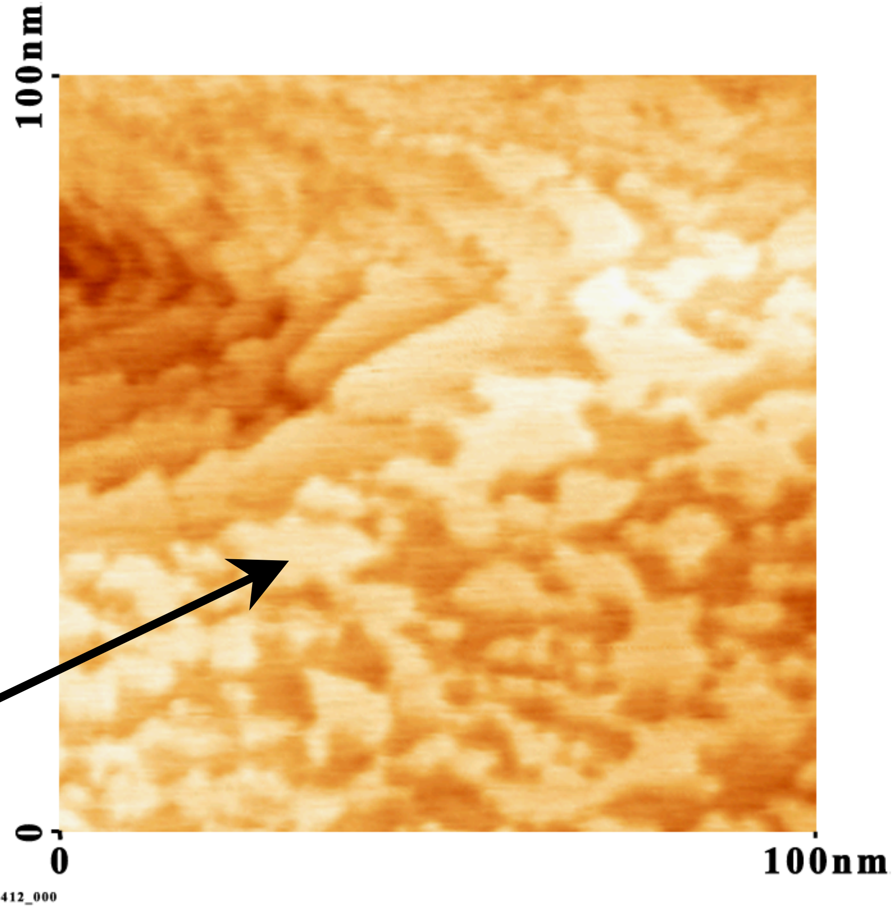


Reason of Restructuring

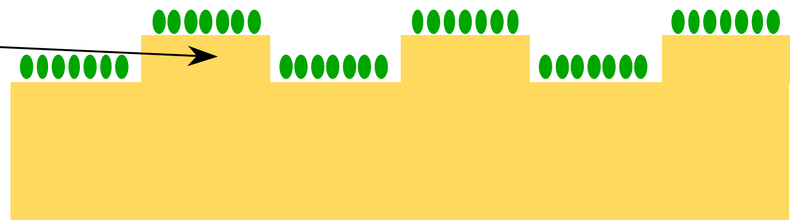
Surface restructuring can occur due to

a) surface chemistry during adsorption of the species from solution (local electrochemistry)

b) tip induced restructuring



The small structures have all one atomic step height



_TERS / Dyes under Optical Resonance

Concept

TERS setup

STM tips

First experiments at Ag and Au

Experiments at single crystalline surfaces

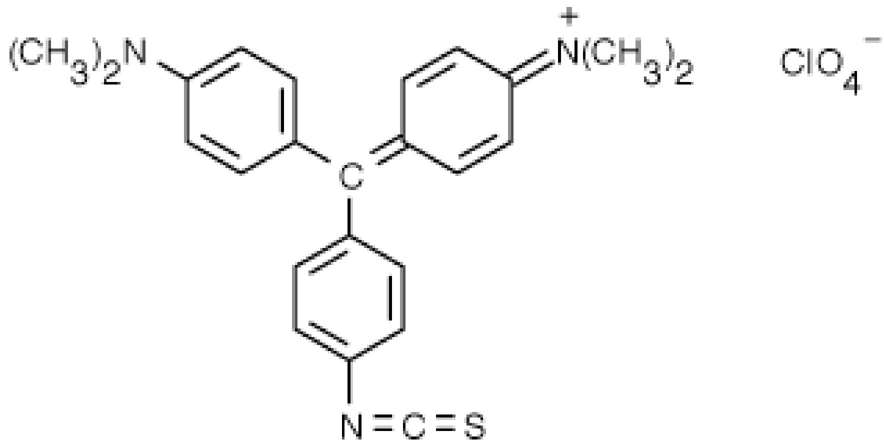
a) small optically non-resonant molecules at Au(111), Au(110), Pt(110)

b) resonant dye (Malachite Green Isothiocyanate) at Au(111), Pt(110)

Discussion

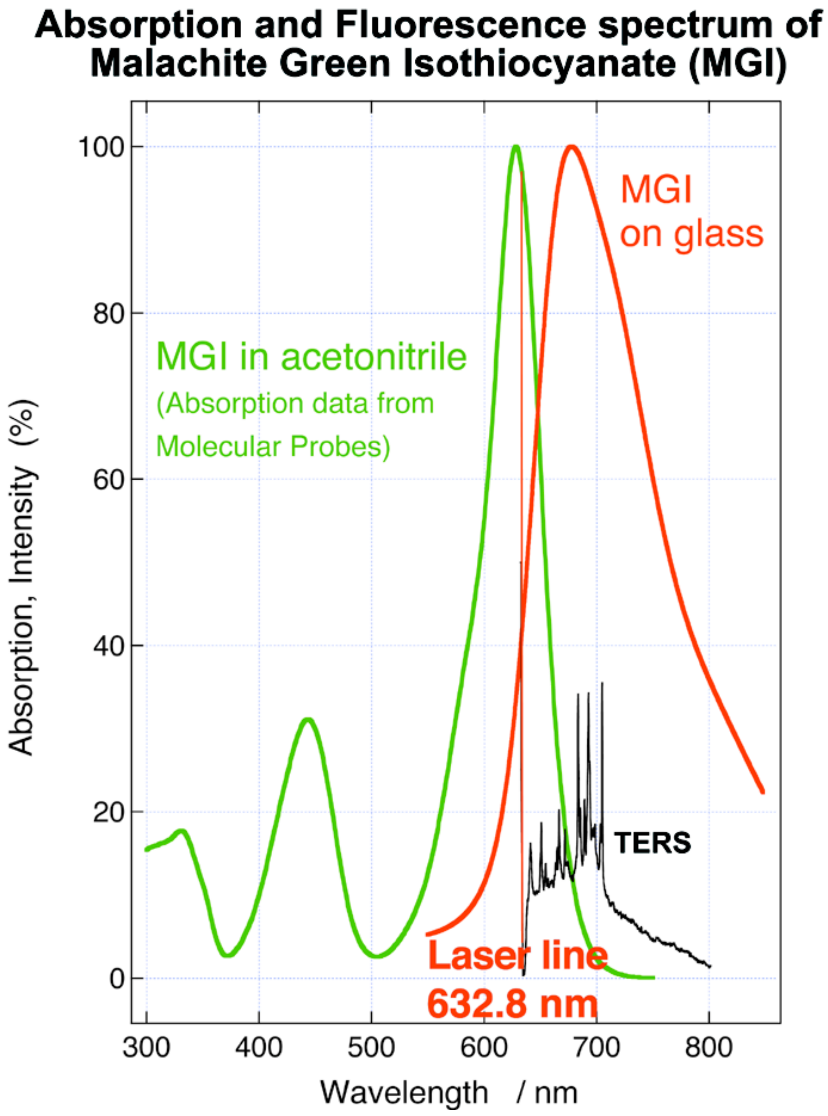
Conclusions/Outlook

Malachite Green Isothiocyanate (MGITC)



The sulfur atom of the isothiocyanate end interacts strongly with the Au surface

Malachite Green Isothiocyanate at Au(111)



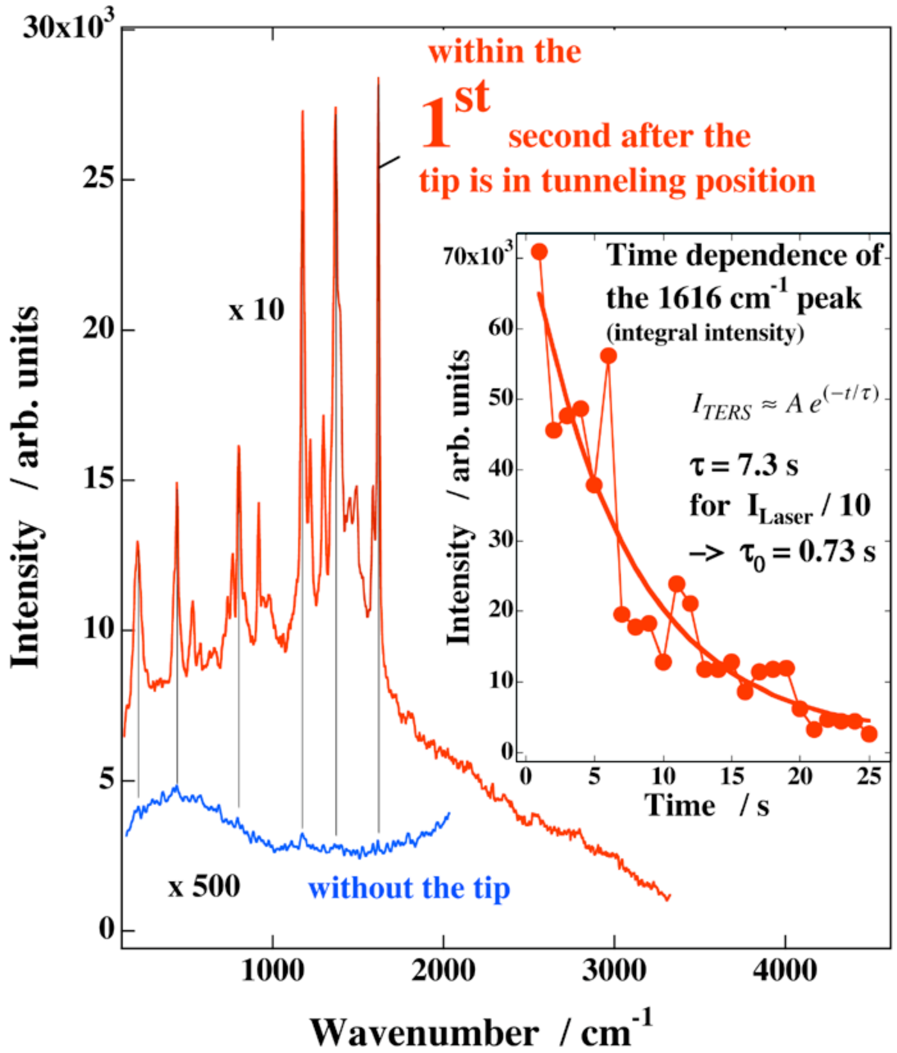
- The laser line (632.8 nm) is close to the absorption maximum <u>and</u>
- the Raman spectrum is also well located in the fluorescence region

- Optimal resonance conditions

But fluorescence quenching is needed (RRS is weak)!

Easy <u>and</u> efficient for dyes at metal surfaces

Raman for Malachite Green Isothiocyanate at Au(111)



Tip retracted: I_{RRS} = 2 cps

Tip tunneling: I_{TERS} = 30000 cps

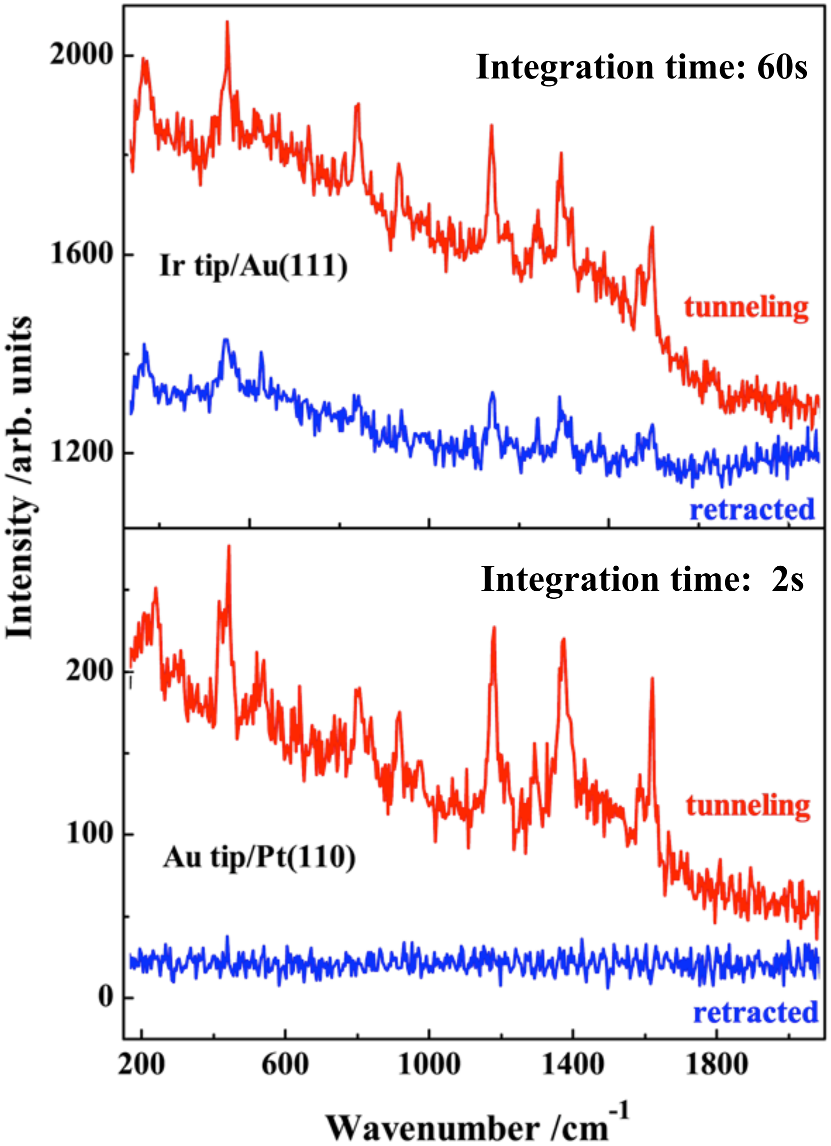
Net-gain: q = 15000 !

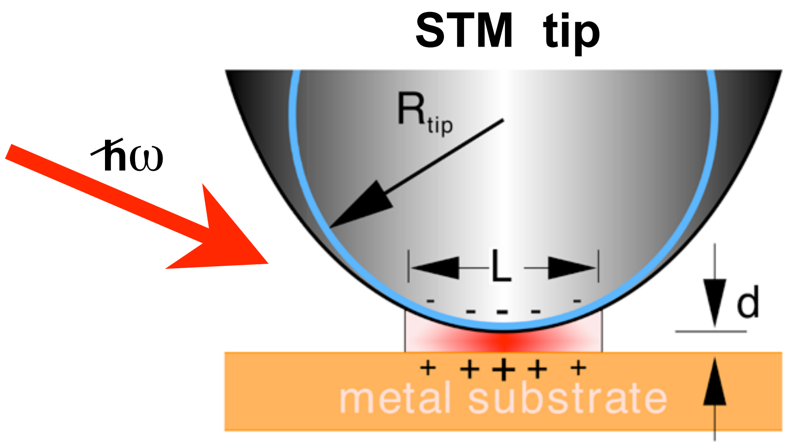
Field enhancement: g ~ 50

TERS enhancement: $g^4 \sim 6 \times 10^6$

Radius of enhanced field: a ~ 50 nm

Further Experiments with MGITC



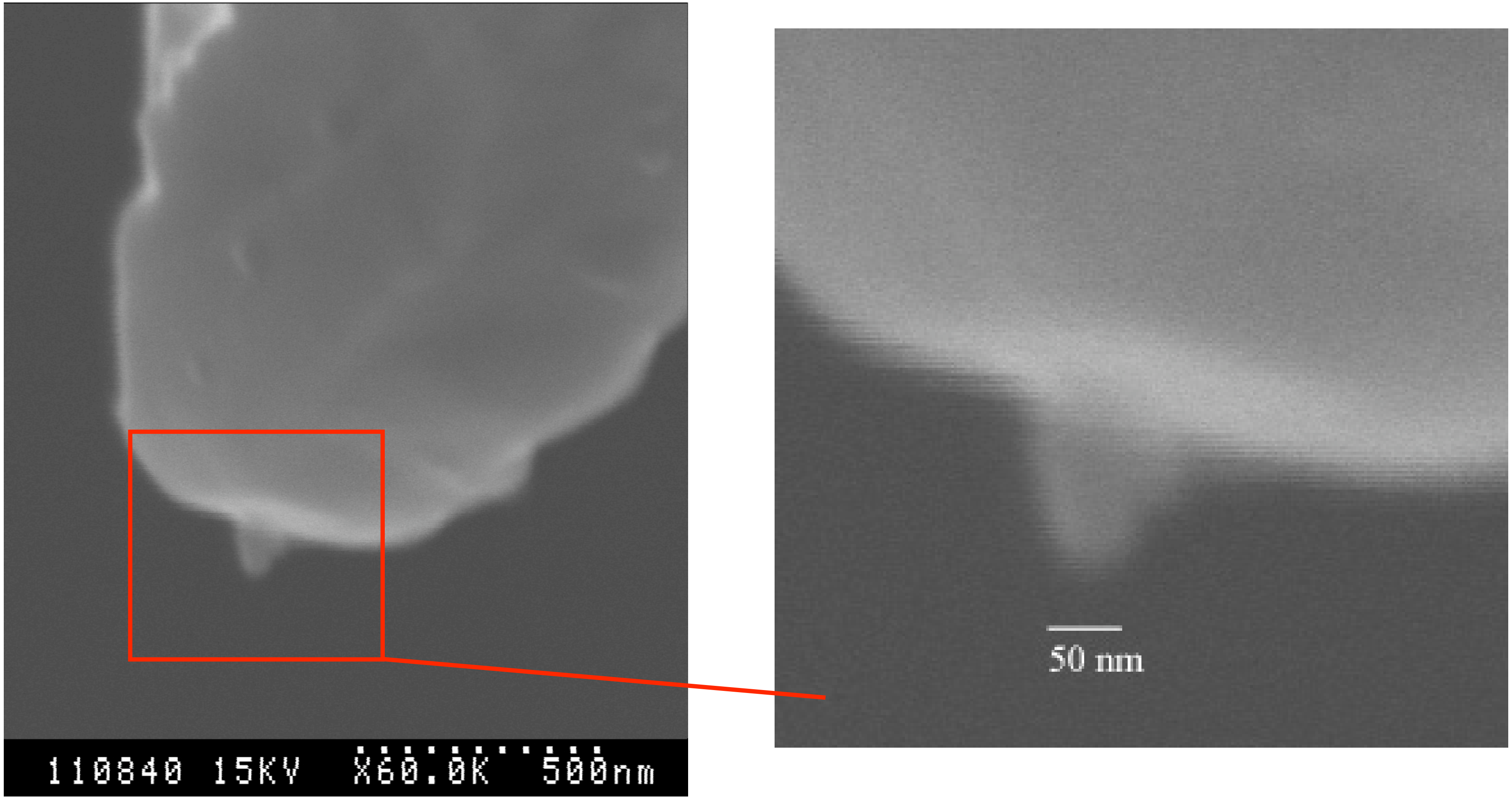


Both, tip and metal-substrate form the cavity for the localized surface plasmons (LSP) and both influence the strength of the optical resonance.

Strength of LSP fields:

Au-tip / Au(111) >> Au-tip / Pt(110) > Ir-tip / Au(111)

The Shape of the Tip



Concept

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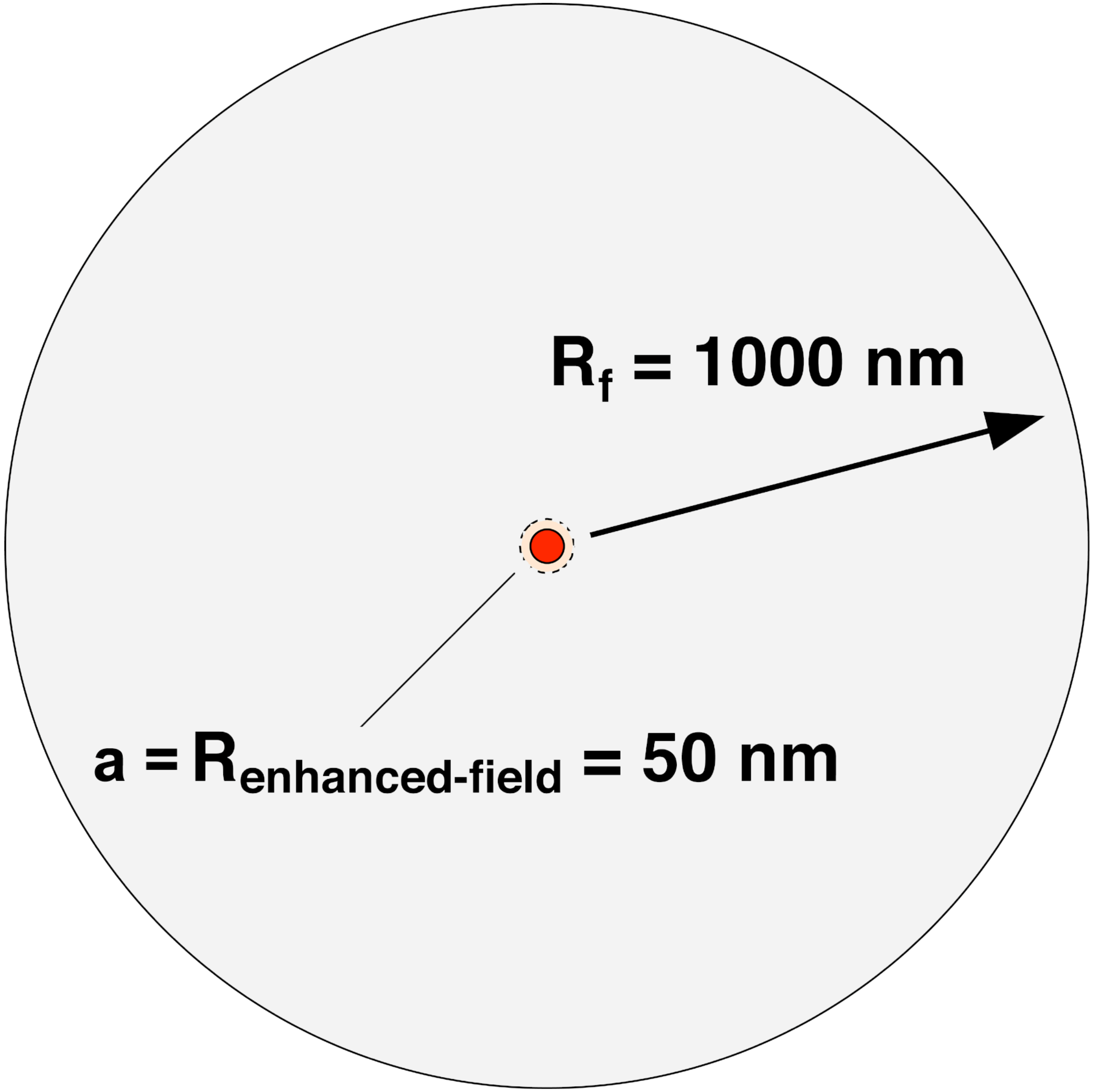
a) small optically non-resonant molecules at Au(111), Au(110), Pt(110)

b) resonant dye (Malachite Green Isothiocyanate) at Au(111), Pt(110)

Discussion

Discussion: R_{Focus} and $R_{enhanced\ field}$



Toward Single Molecule–Spectroscopy

I_{TERS} =

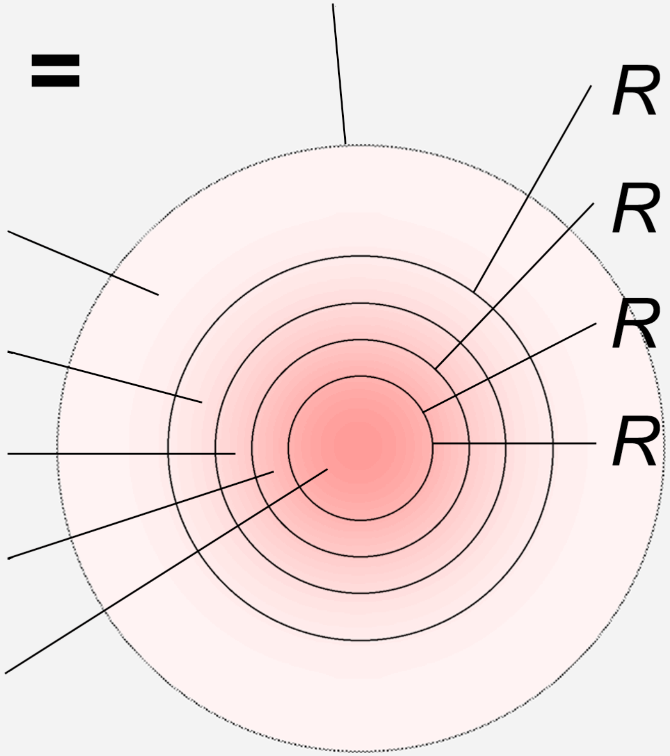
99 %

80 %

60 %

40 %

20 %



$R_{enhanced\text{-}field}$ = 5 nm	26 molecules
R = 3,2 nm	10,5 "
R = 2,4 nm	6,0 "
R = 1,8 nm	3,4 "
R = 1,2 nm	1,5 "

Let us approximate the radial distribution of the tip-enhanced field by a Gaussian profile

$$g \sim g_0\, e^{-r^2/a^2} \qquad I_{TERS} \propto g^4$$

Toward to Single Molecule Spectroscopy

Then, for keeping the TERS intensity level

the TERS enhancement must rise to: $g^4 \sim 10^9$ **or larger**

and for dyes (in optical resonance)

the bleaching time constant should be: $\tau < 0{,}07$ s !

Single Molecule Spectroscopy ?

There are a number of reports on **SERS** for single molecules (such as for rhodamine 6g) with a SERS enhancement of $g^4 \gg 10^9$; thus, we expect in these cases $\tau \ll 0{,}07$ s !

Why is there no (fast) bleaching ?

III.a. Conclusions

★ **Surface – enhanced Raman scattering (SERS) for**

A) Oxygen at catalytically active Ag(111)

B) amourphous carbon at Ag (fluctuations -> "hot spots")

C) huge Raman intensities for dyes adsorbed at Ag-colloids

★ STM-tip enhanced Raman scattering (TERS) for

Adsorbates at smooth single crystalline samples

a) optically non-resonant molecules

CN^- / Au(111),

Thiophenol / Au(111) , Au(110) und Pt(110)

Mercaptopyridine / Au(110)

b) optically resonant molekules **(Malachite Green Isothiocyanate = MGITC)**

Au-tip / MGITC / Au(111) : **TERS enhancement > 10^6**

Ir-tip / MGITC / Au(111)

Au-tip / MGITC / Pt(110)

III.c. Outlook

★ **For dyes and for radii of the confined EM-fieldes of about R_{field} ~ 50 nm the TERS signal originates from a few thousand molecules.**

In other words, we have the prospect for

Single–Molecule–Raman–Spectroscopy

(B. Pettinger et al., Electrochemistry (Jp.) 12, 942, 2000;
dito, Single Molecules, 3(5-6) 285, 2002;
dito, J. Electroanal. Chem., 554-555C, 293, 2003;
dito, Phys. Rev. Lett., 92, 096101, 2004
dito, Angewandte Chemie, int. Ed., in press 2004)

See also the papers

R.M. Stöckle, Y.D. Suh, V. Deckert and R. Zenobi, Chem. Phys. Lett., 318, 131, 2000.
M. S. Anderson, Appl. Phys. Lett., 73, 21, 2000.

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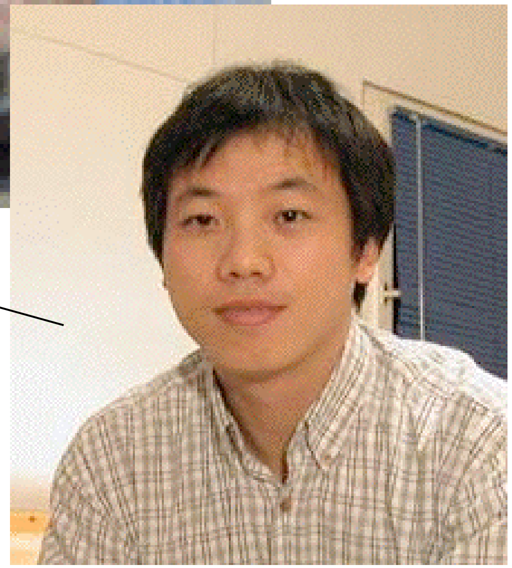
Bin Ren	
Rolf Schuster,	*STM specialist*
Gerhard Ertl	*scientific*
+	**+**
Max-Planck-Gesellschaft	*financial support*



Thanks for your attention !