



Surface-Enhanced Raman Scattering (SERS)

Victor Ovchinnikov

Aalto Nanofab
Aalto University
Espoo, Finland

Alvar Aalto was a famous Finnish architect and designer



Outline

- Bulk Raman spectroscopy
- SERS principles
- Plasmonics
- SERS substrate – nanoengineering
- Instrumentation
- Applications



Pros and cons of Raman (SERS)

- **Advantages**

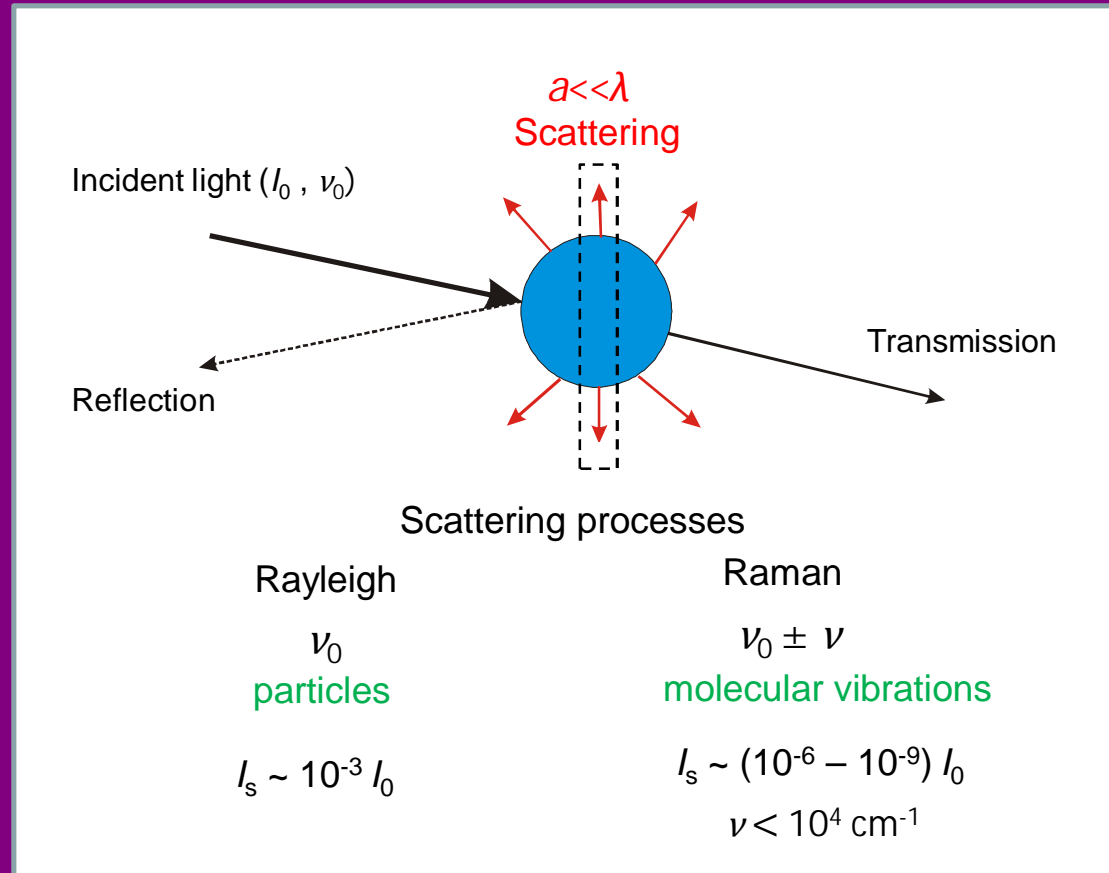
- Can be used with solids, liquids or gases
- No sample preparation needed (KBr, nujol)
- Non-destructive, non-invasive
- Works *in-situ* and *in-vitro* for biological samples
- No vacuum needed
- Works under a wide range of conditions (temperature, pressure)
- Short time scale
- Can work with aqueous solutions
- Glass vials can be used
- Can use down fibre optic cables for remote sampling
- Very small analyzing volume – till single molecule (SERS)
- Extremely high spatial resolution (SERS)

- **Disadvantages**

- Cannot be used for metals or alloys
- Very low sensitivity (Raman)
- Can be swamped by fluorescence from some materials

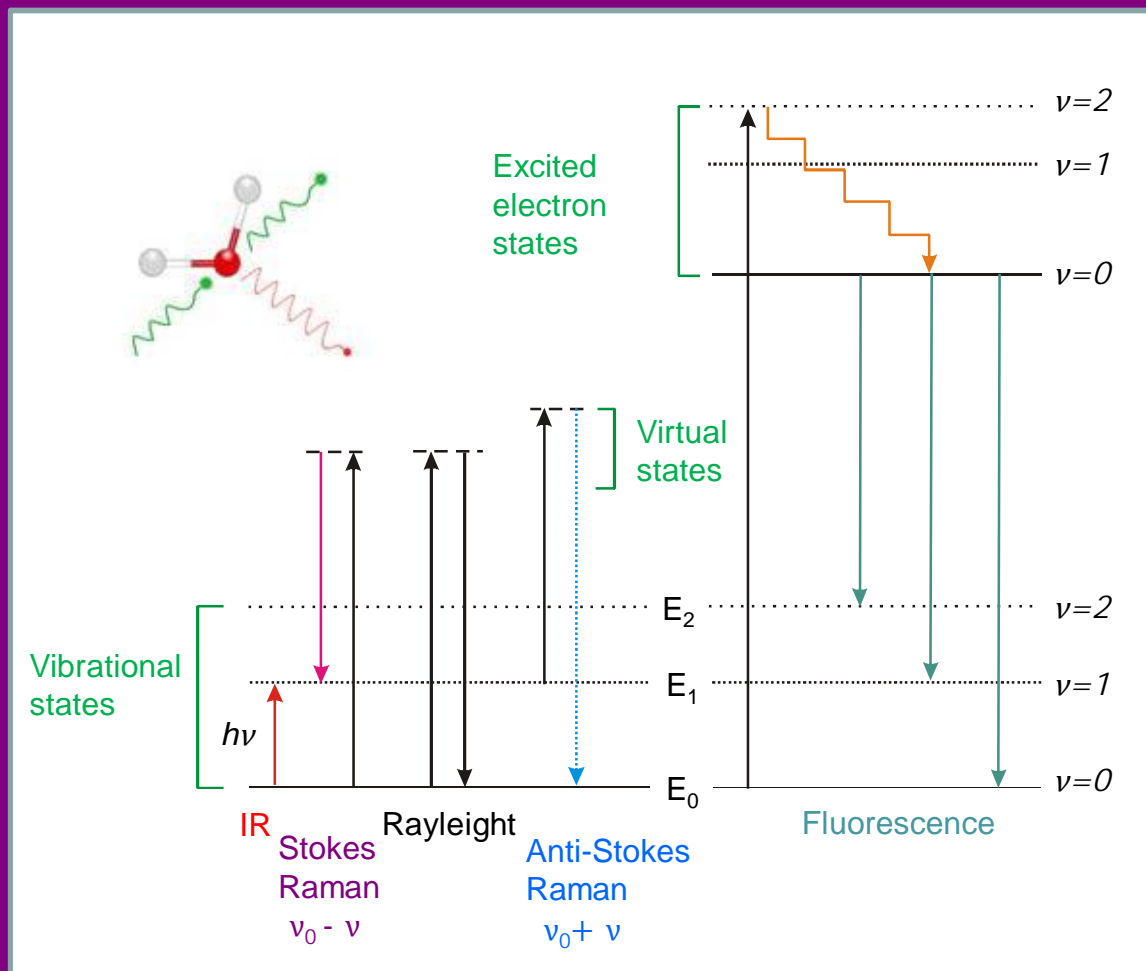


Scattered radiation



A!

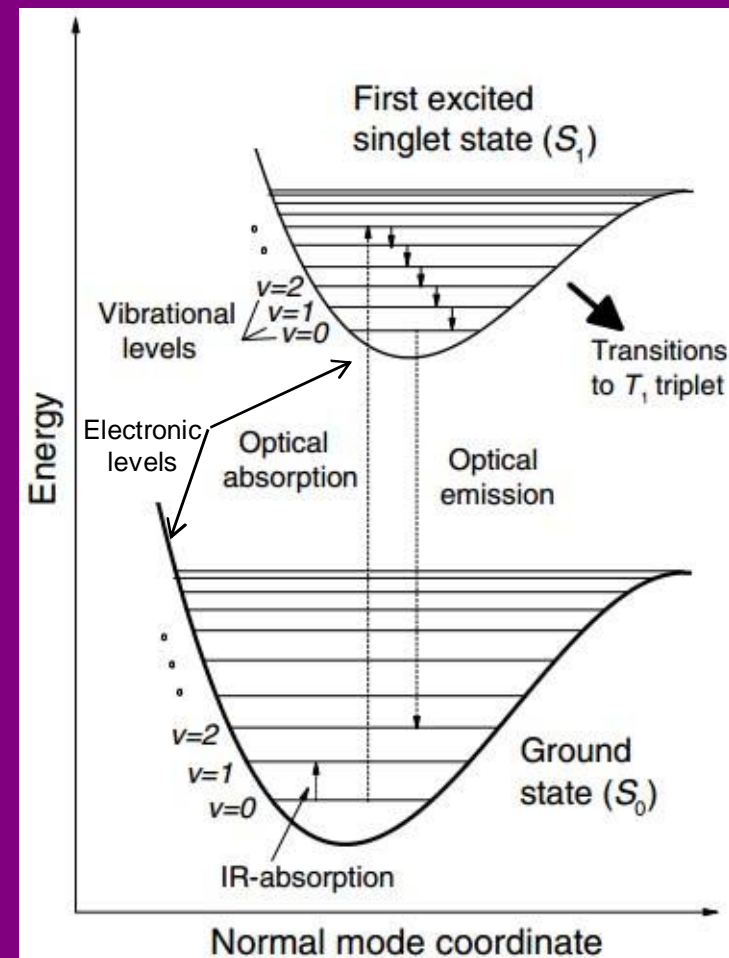
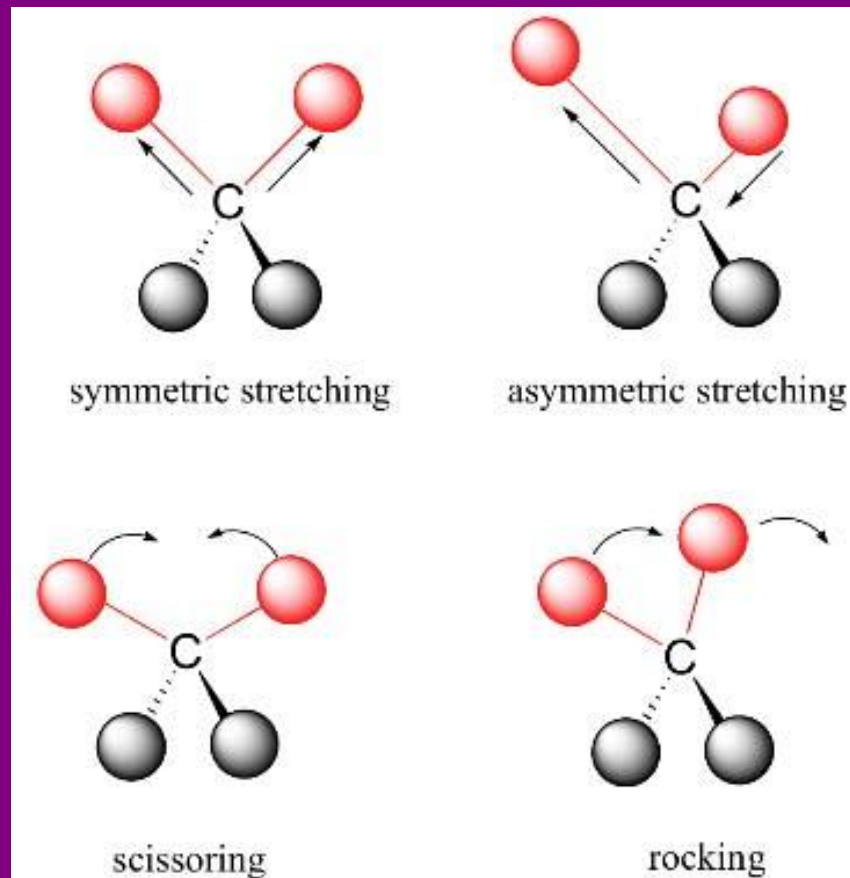
Energy levels



ν is independent of ν_0

A!

Molecular vibrations



E.C. Le Ru and P. G. Etchegoin, Principles of Surface-Enhanced Raman Spectroscopy and related plasmonic effects, Elsevier, 2009
<http://chemwiki.ucdavis.edu>



Dipole moment in a molecule

$$p = \alpha E$$

p - induced (not permanent) electric dipole moment of a molecule

α - polarizability

E - electric field

$$\alpha = \alpha_0 + \left(\frac{\partial \alpha}{\partial r} \right) \Delta r$$

$$\Delta r = r_{max} \cos(2\pi \nu t)$$

$$E = E_0 \cos(2\pi \nu_0 t)$$

$$p = \alpha_0 E_0 \cos(2\pi \nu_0 t) + \frac{E_0 r_{max}}{2} \left(\frac{d\alpha}{dr} \right) (\cos(2\pi t(\nu_0 + \nu)) + \cos(2\pi t(\nu_0 - \nu)))$$

α_0 - molecule equilibrium polarizability

E_0 - maximum electric field

ν_0, ν - excitation and vibrational frequency, respectively

r_{max} - maximum vibrational amplitude

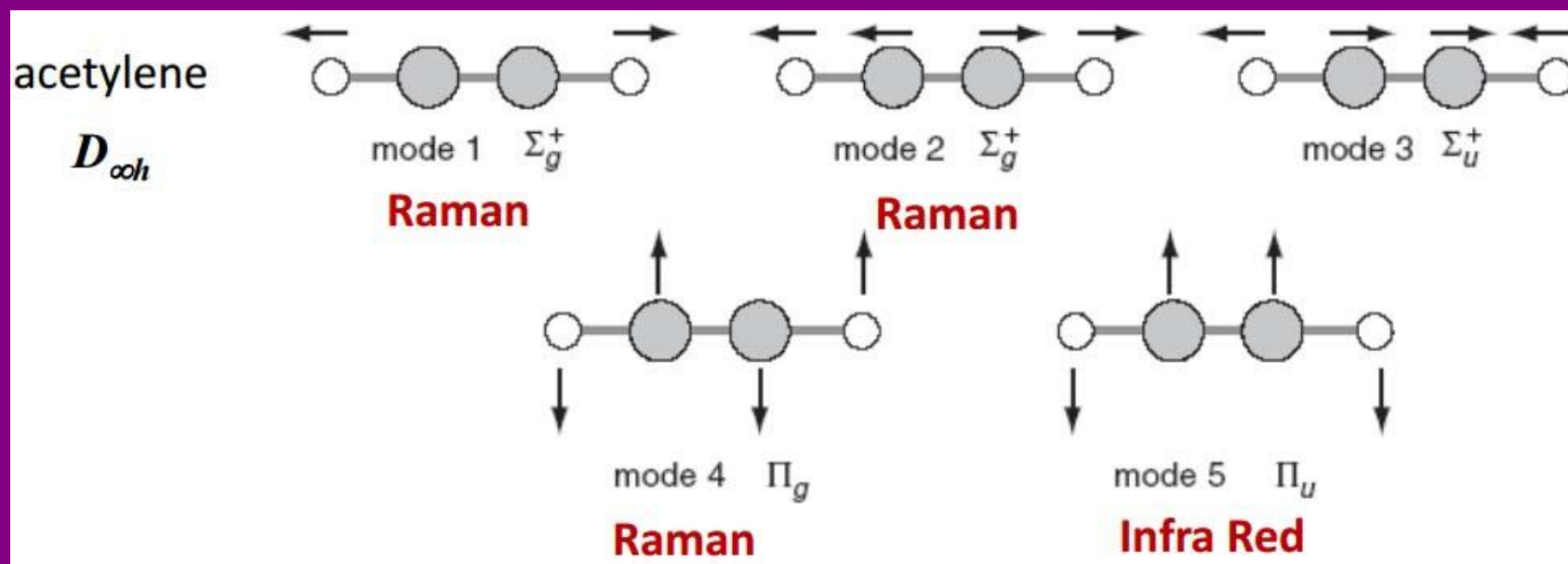
'Modulation' of linear optical polarizability due to presence of internal vibrations

Spectroscopy 16(11), 2001, p.32

A!

Selection rules

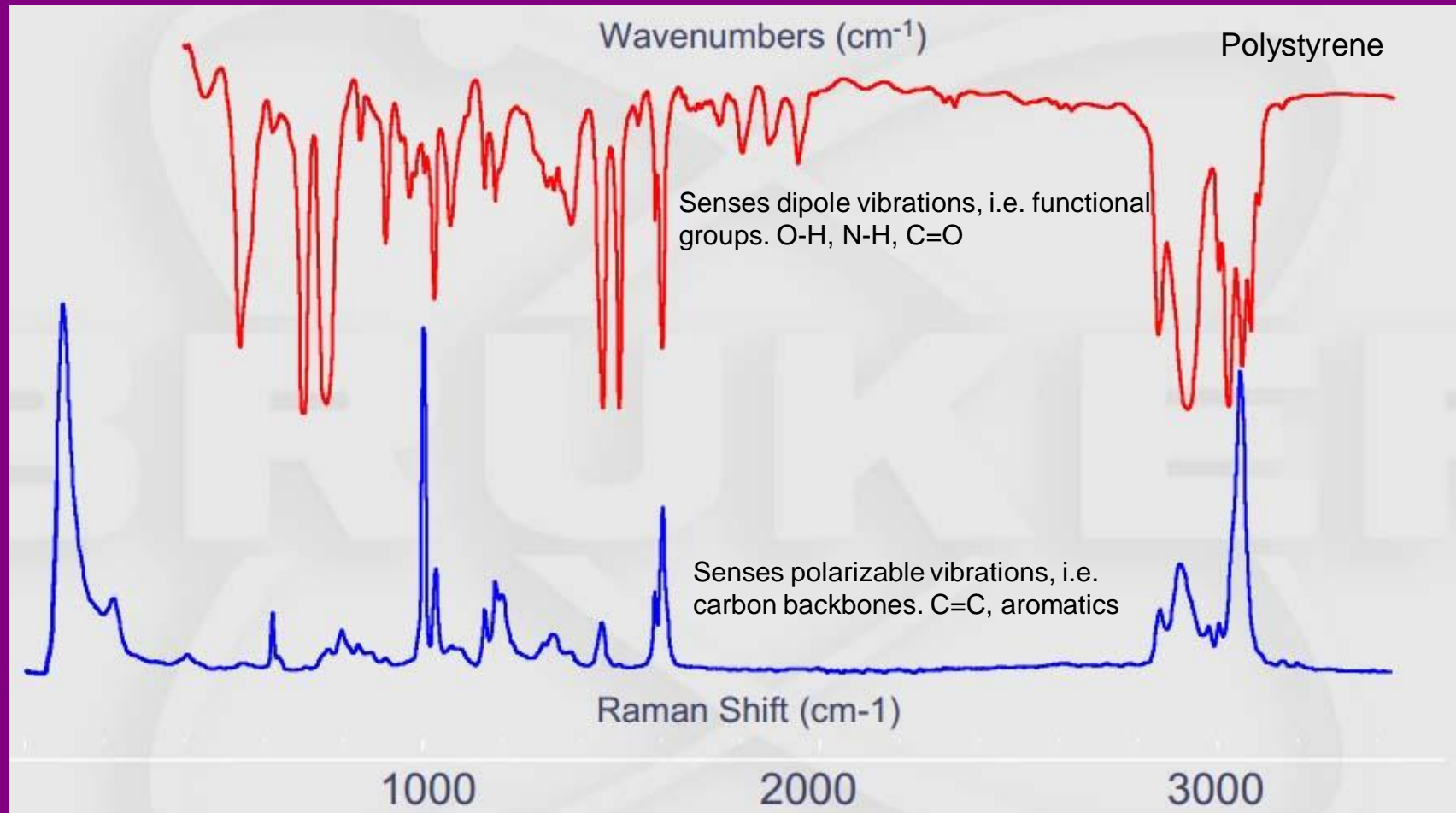
- The polarizability must change during the vibration
- In a centrosymmetric molecule (i.e., one with a centre of inversion symmetry) a vibrational mode may be either IR active or Raman active, but not both.



mackenzie.chem.ox.ac.uk/teaching/Raman%20Scattering.pdf

A!

IR vs Raman



<http://www.brukeroptics.com/senterra-overview.html>



Raman intensity

$$I_S \propto N \left(\frac{\partial \alpha}{\partial r} \right)_{\Delta r=0}^2 (\nu_0 - \nu)^4 E_0^2$$

N – volume density of scattering molecule

Raman shift (wave-number)

$$\bar{\nu}[\text{cm}^{-1}] = \frac{10^7}{\lambda[\text{nm}]}$$

λ - wavelength

Anti-Stokes to Stokes ratio for k mode

$$\rho_k = A e^{-\frac{\hbar \omega_k}{k_B T}}$$

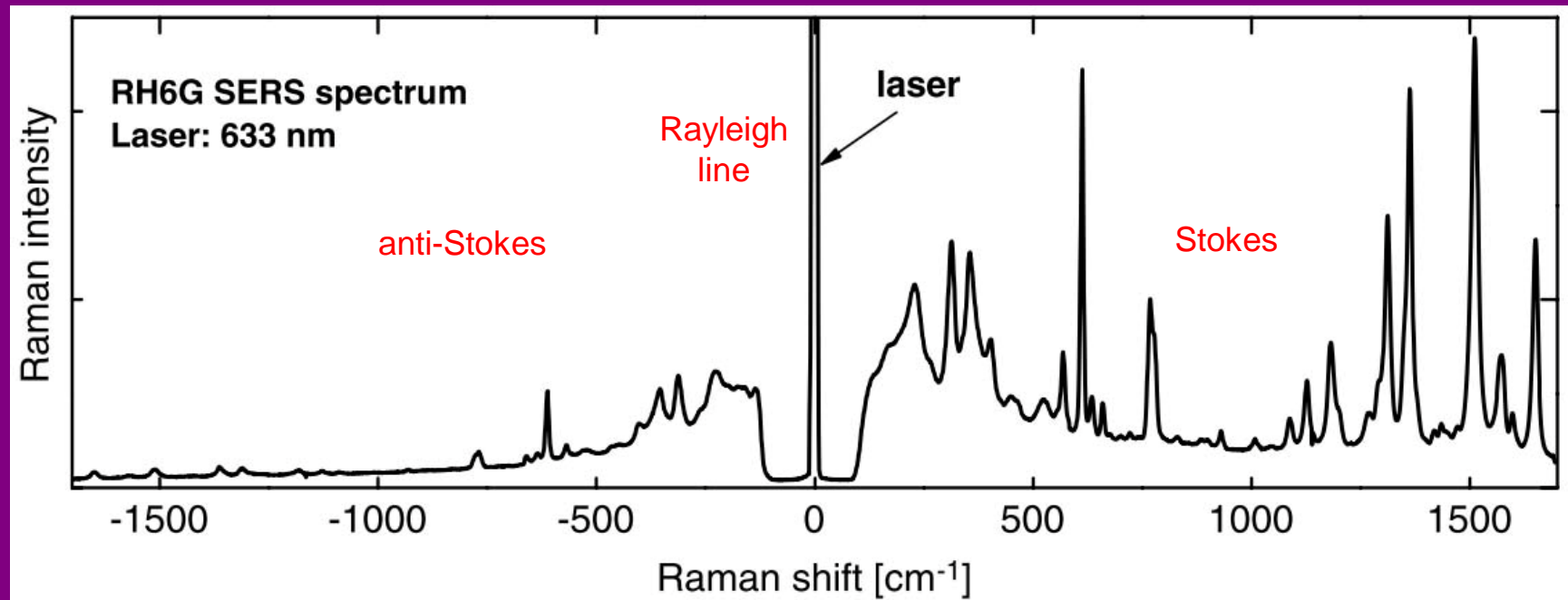
$$A = \frac{\nu^4_{aS}}{\nu^4_S}$$

Krafft et al., Journal of Biomedical Optics, 17, 2012, p.040801-15

E.C. Le Ru and P. G. Etchegoin, Principles of Surface-Enhanced Raman Spectroscopy and related plasmonic effects, Elsevier, 2009.

A!

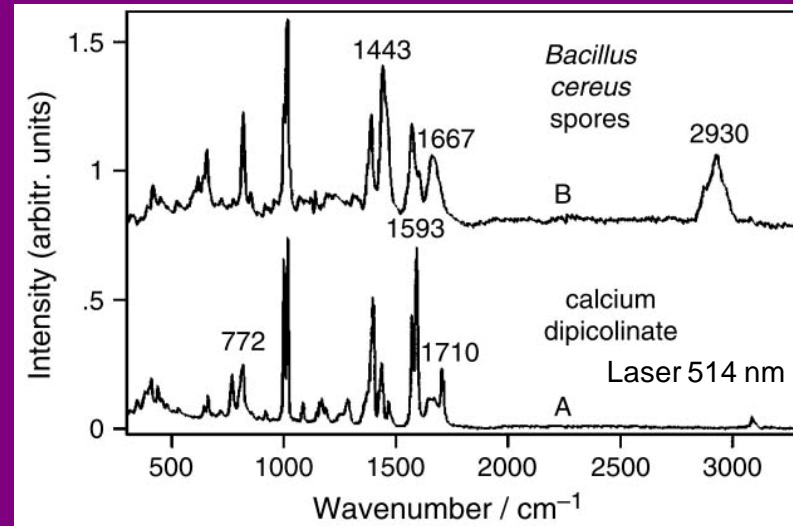
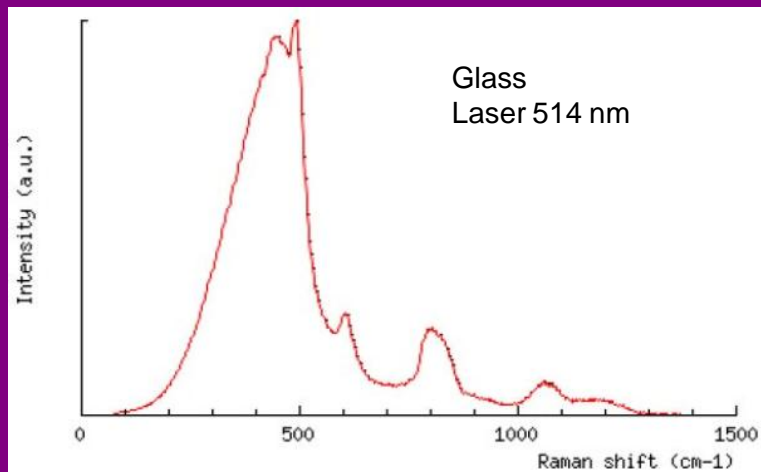
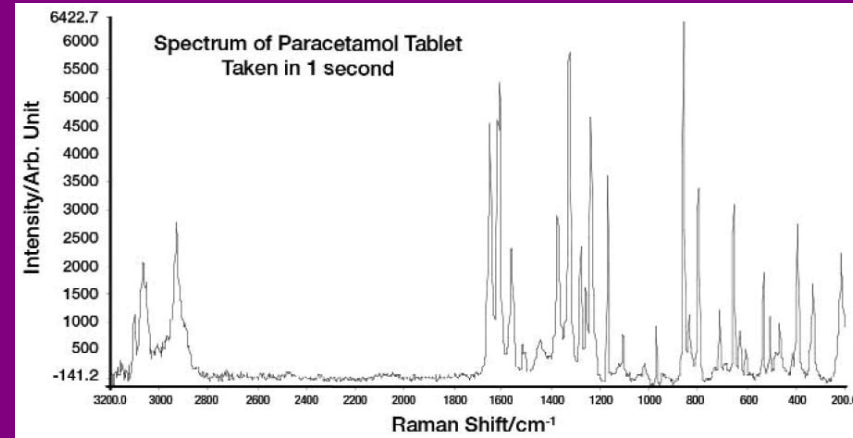
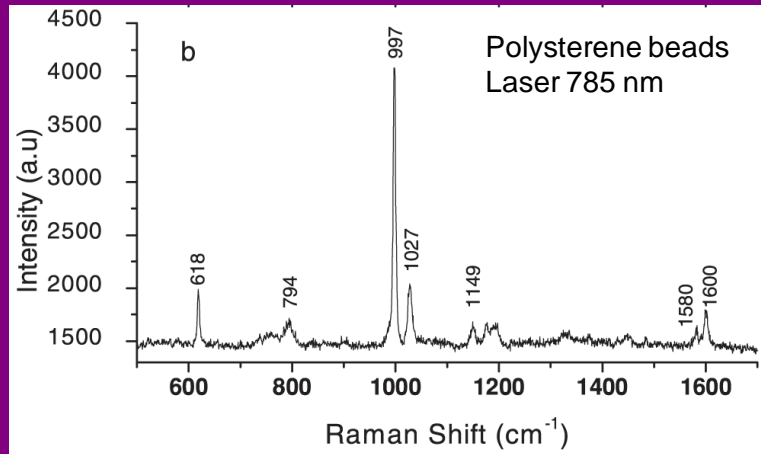
Stokes vs anti-Stokes



E.C. Le Ru and P. G. Etchegoin, Principles of Surface-Enhanced Raman Spectroscopy and related plasmonic effects, Elsevier , 2009

A!

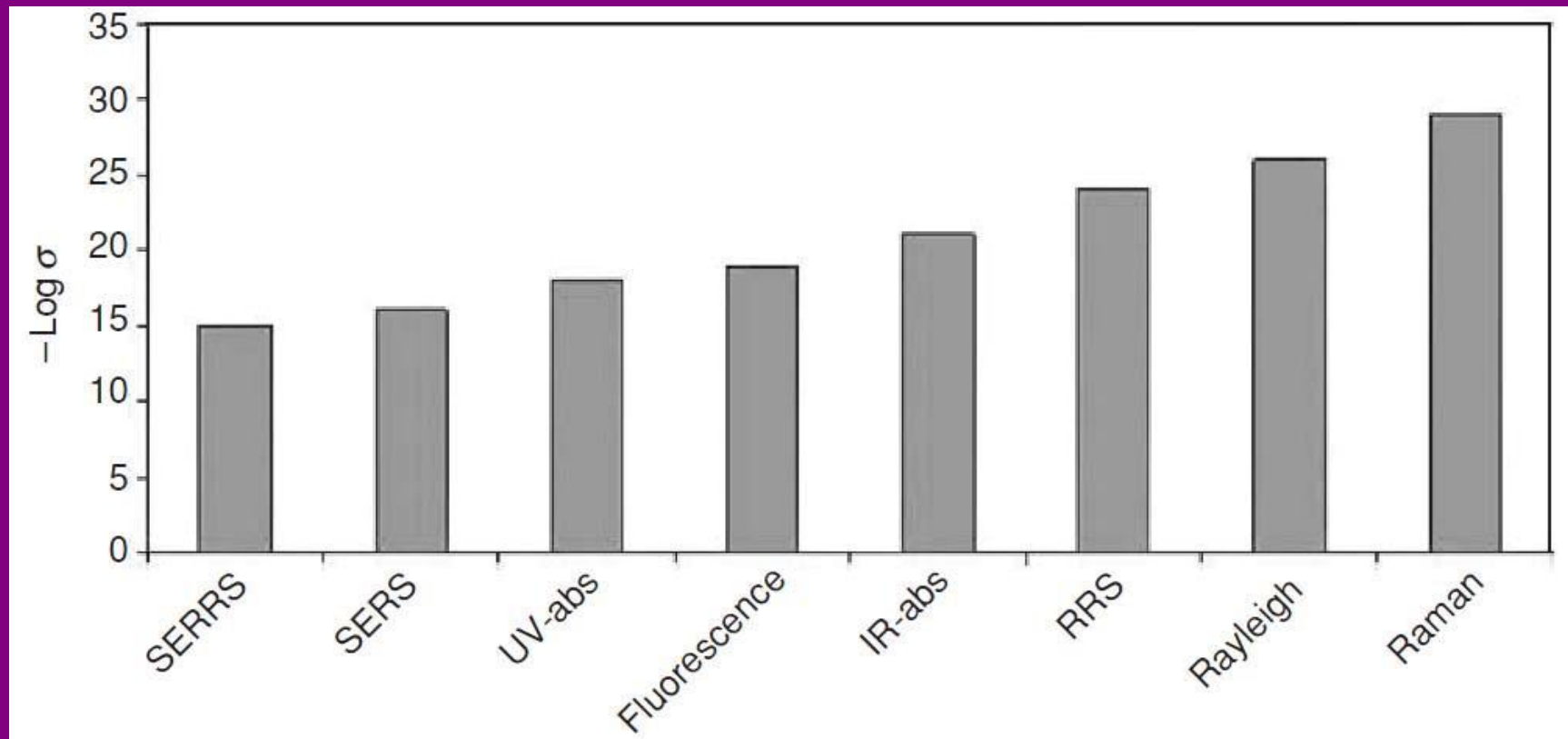
Spectrum examples



Bankapur A et al, (2010) .PLoS ONE 5(4): e10427.
doi:10.1371/journal.pone.0010427.
Laboratoire de Sciences de la Terre ENS-Lyon

www.perkinelmer.com , Introduction to Raman Spectroscopy
J. Raman Spectrosc. 2004; 35: 82–86

A! Cross-sections of the optical processes



R. Aroca, Surface-Enhanced Vibrational Spectroscopy, J. Wiley & Sons Ltd, 2007



Intermediate conclusion I

- Raman spectroscopy provides ‘fingerprint’ of molecular bonds and crystalline structure (phonons) in dependence on environment conditions (temperature, pressure ...) through non-resonance excitation of any vibrational transitions
- At the same time method applications in real life are hindered by very low cross-section of Raman scattering



Steps of Raman development

- **Laser application**
 - dramatically improved power of excitation and Raman signal
- **SERS effect**
 - Enhanced method sensitivity up to 10^{14}
- **Raman microscope**
 - Decreased probe volume (light spot diameter below $1 \mu\text{m}$)
- **Portable SERS**
 - Mobility of analyses

C. Douketis et al., J. Chem. Phys. 2000, **113**, 11315-23

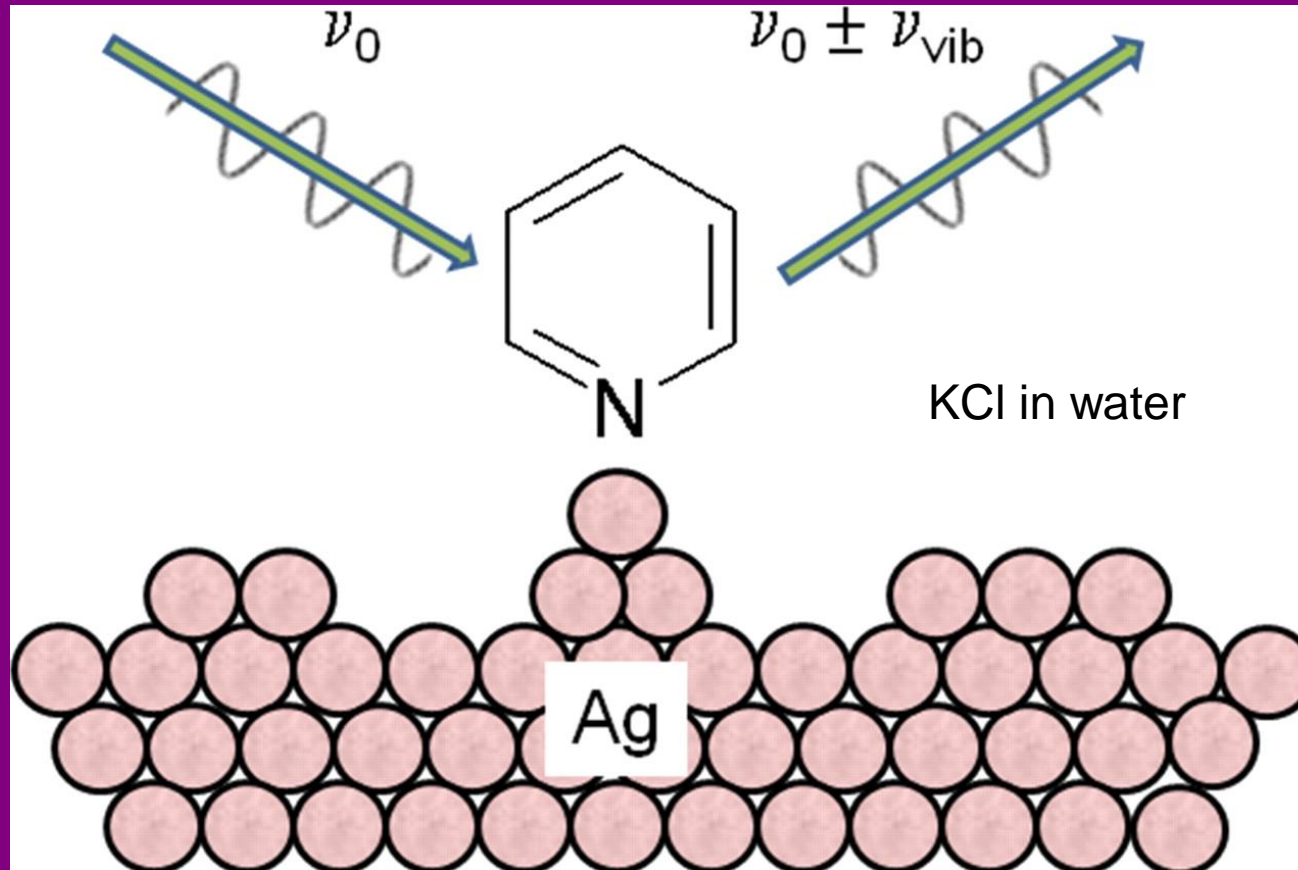
A!

SERS discovery

- M. Fleischmann, P. J. Hendra, and A. J. McQuillan. “Raman spectra of pyridine adsorbed at a silver electrode.” *Chem. Phys. Lett.*, **26**, 1974, p.163–66
- Jeanmaire D.L. and Van Duyne R.P., “Surface Raman spectroelectrochemistry, part 1: heterocyclic, aromatic, and aliphatic amines adsorbed on the anodized silver electrode.” *J. Electroanal. Chem.*, **84**, 1977, p.120
- Albrecht and Creighton, “Anomalously intense Raman spectra of pyridine at a silver electrode.” *J. Am. Chem. Soc.*, **99**, 1977, p.5215-17

A!

SERS experiment with pyridine adsorbed on silver



McQuillan A J Notes Rec. R. Soc. 2009;63:105-109

A!

SERS definitions

- SERS is a phenomenon associated with the enhancement of the electromagnetic field surrounding small objects optically excited near an intense and sharp plasmon resonance. The enhanced fields excite the adsorbate (probe) and the scattered radiation will again be enhanced.
- *Surface-enhanced Raman scattering (SERS)* consists in using the large local field enhancements that can exist at metallic surfaces (under the right conditions, typically by profiting from localized surface plasmon resonances) to boost the Raman scattering signal of molecules at (or close to) the surface.

E.C. Le Ru and P. G. Etchegoin, Principles of Surface-Enhanced Raman Spectroscopy and related plasmonic effects, Elsevier , 2009

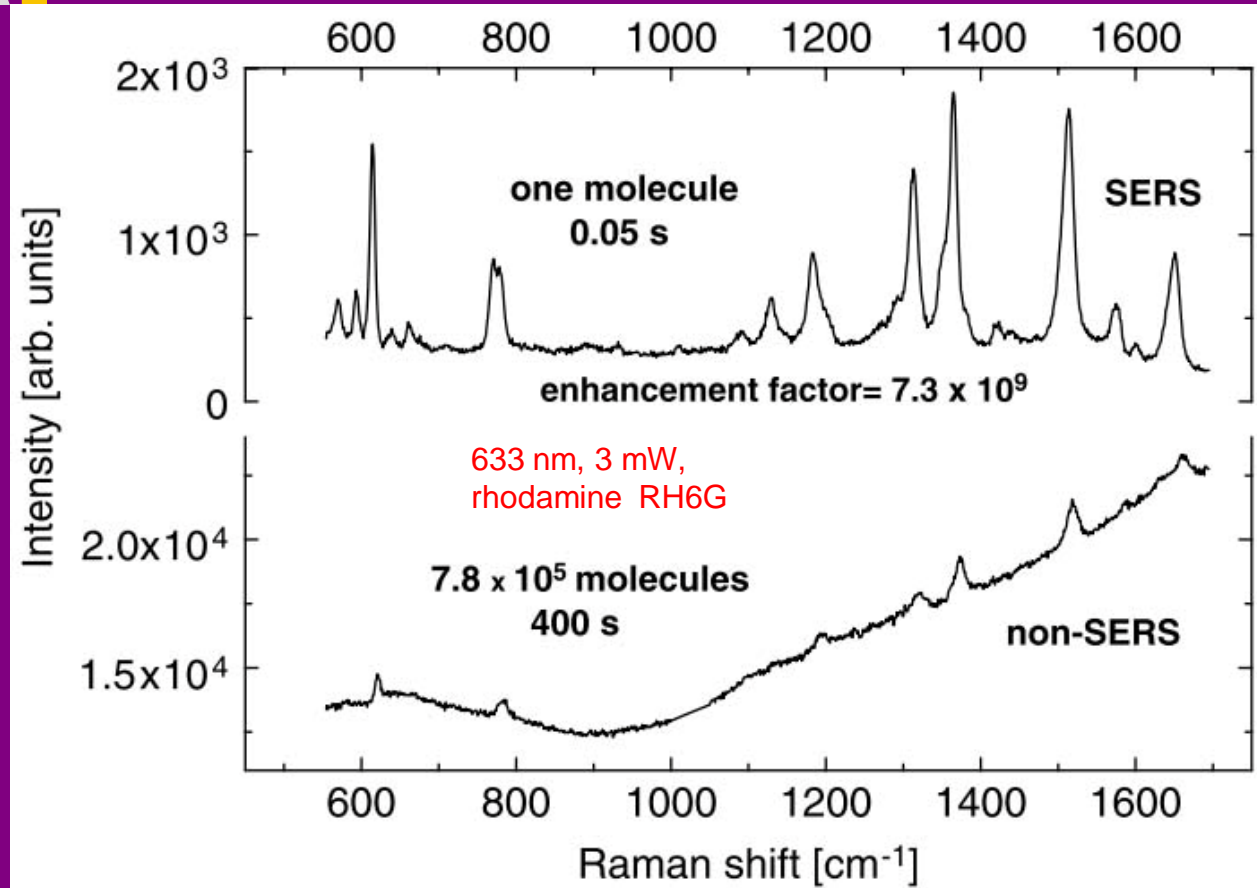
A!

First experience

- **SERS conditions:**
 - specific metals (e.g. Au, Ag, Cu, Pt, ...)
 - surfaces with roughness on the nanometer scale
 - proper wavelength of excitation
- **SERS results:**
 - no enhancements observed for water, methanol, etc - most solvents...
 - certain molecules provided much higher Raman intensities (mostly molecules with carbon double-bonds)

A!

Bulk Raman versus SERS



Surface selection rules

Bottom spectrum: 100 μM solution in a 13 μm^3 scattering volume, $\times 100$ immersion objective with 400 s integration time. Top: signal from a single molecule under the same experimental conditions, but with 0.05 s integration time.

E. C. Le Ru et al., J. Phys. Chem. C, 111, 2007, p.13794–803



Dielectric function of metals

$$\varepsilon(\omega) = \varepsilon_{\infty} \left(1 - \frac{\omega_p^2}{\omega^2 + i\gamma_0\omega} \right)$$

γ_0 - damping term

ε_{∞} - optical response of the positive ions

ω_p - plasma frequency

$$\omega_p = \sqrt{\frac{ne^2}{m\varepsilon_0\varepsilon_{\infty}}}$$

n, m - concentration of free electrons

m - effective mass of electron

e - charge of electron

ε_0 - vacuum permittivity

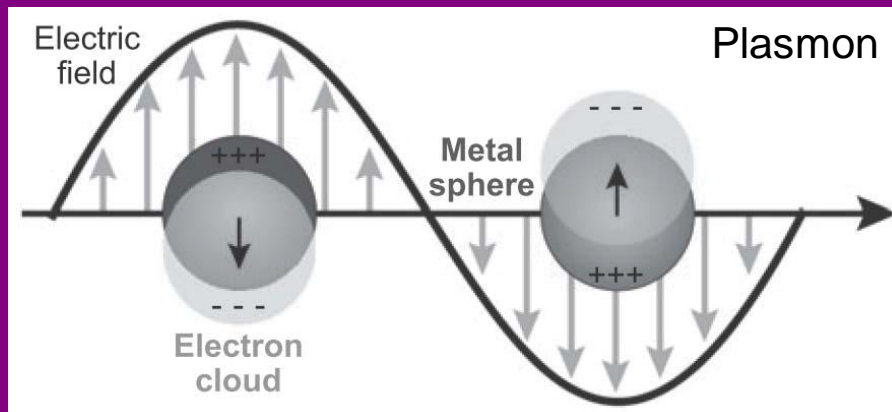
E.C. Le Ru and P. G. Etchegoin, Principles of Surface-Enhanced Raman Spectroscopy and related plasmonic effects, Elsevier , 2009.

A! Localized surface plasmon resonance (SPR) in metal sphere

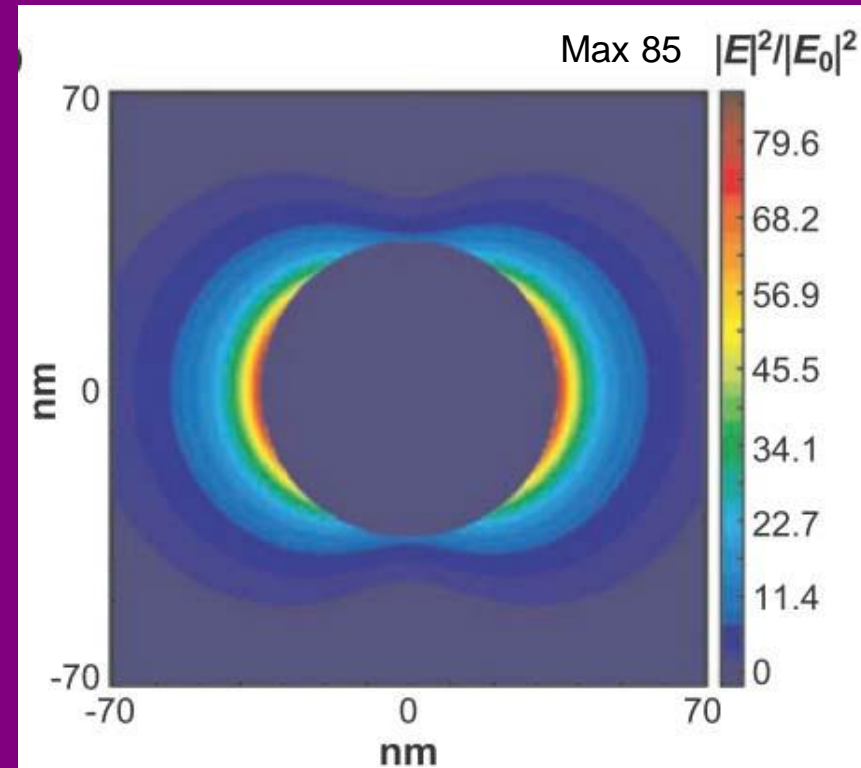
The (complex) electric field inside the sphere is constant

$$E_{in} = \frac{3\epsilon_M}{\epsilon(\omega) + 2\epsilon_M} E_0$$

ϵ_M - relative dielectric constant of medium



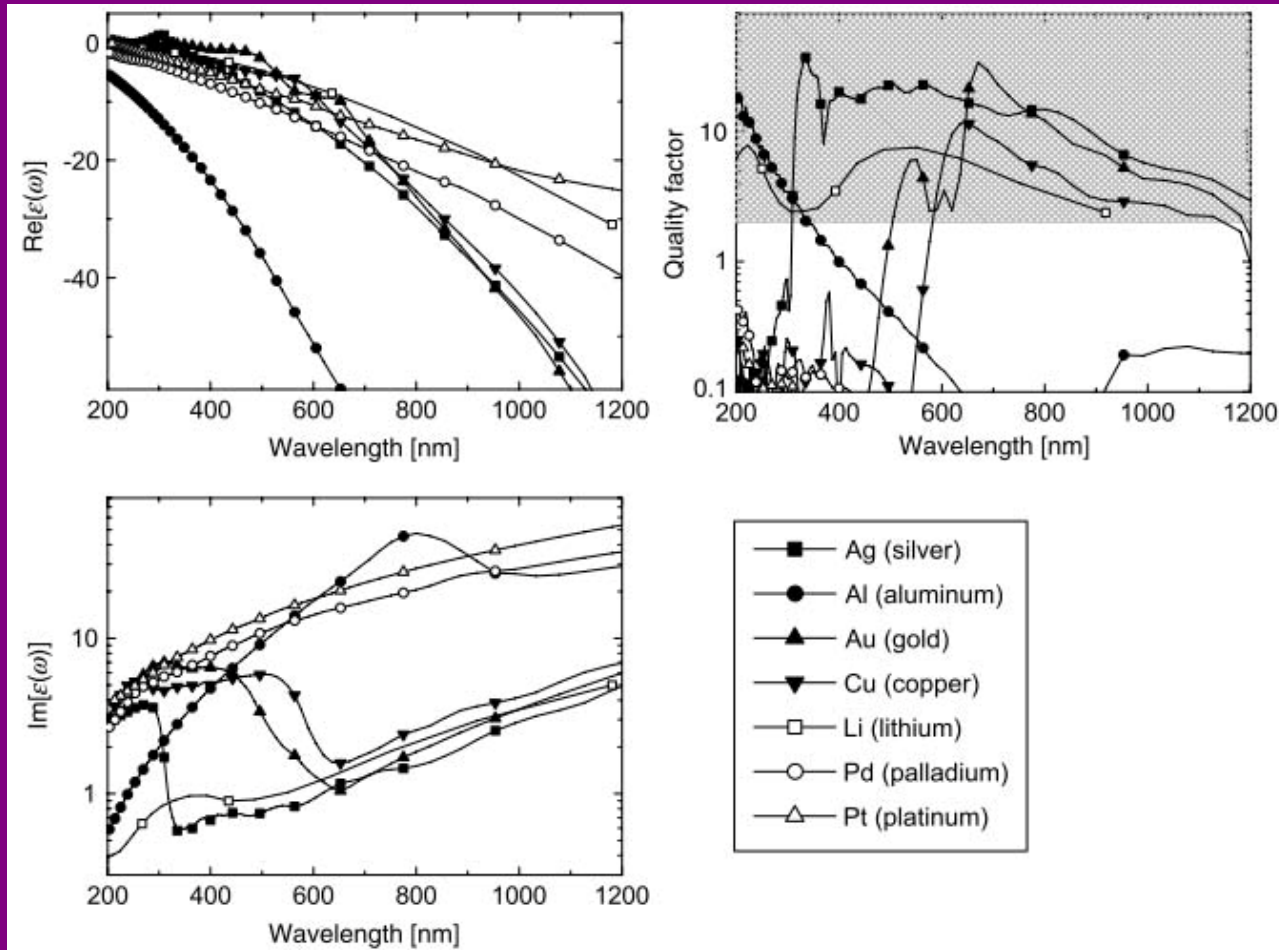
Ag sphere (35nm) in vacuum,
at resonance wavelength 370 nm



E.C. Le Ru and P. G. Etchegoin, Principles of Surface-Enhanced Raman Spectroscopy and related plasmonic effects, Elsevier , 2009.
Stiles P.L. *et al*, Annual Review of Analytical Chemistry, 1, 2008, p.601-26

A!

Optical properties of metals



$$Q = \frac{\omega(d\epsilon'/d\omega)}{2(\epsilon''(\omega))^2}$$

$$\begin{aligned}\epsilon' &= \text{Re}(\epsilon), \\ \epsilon'' &= \text{Im}(\epsilon)\end{aligned}$$

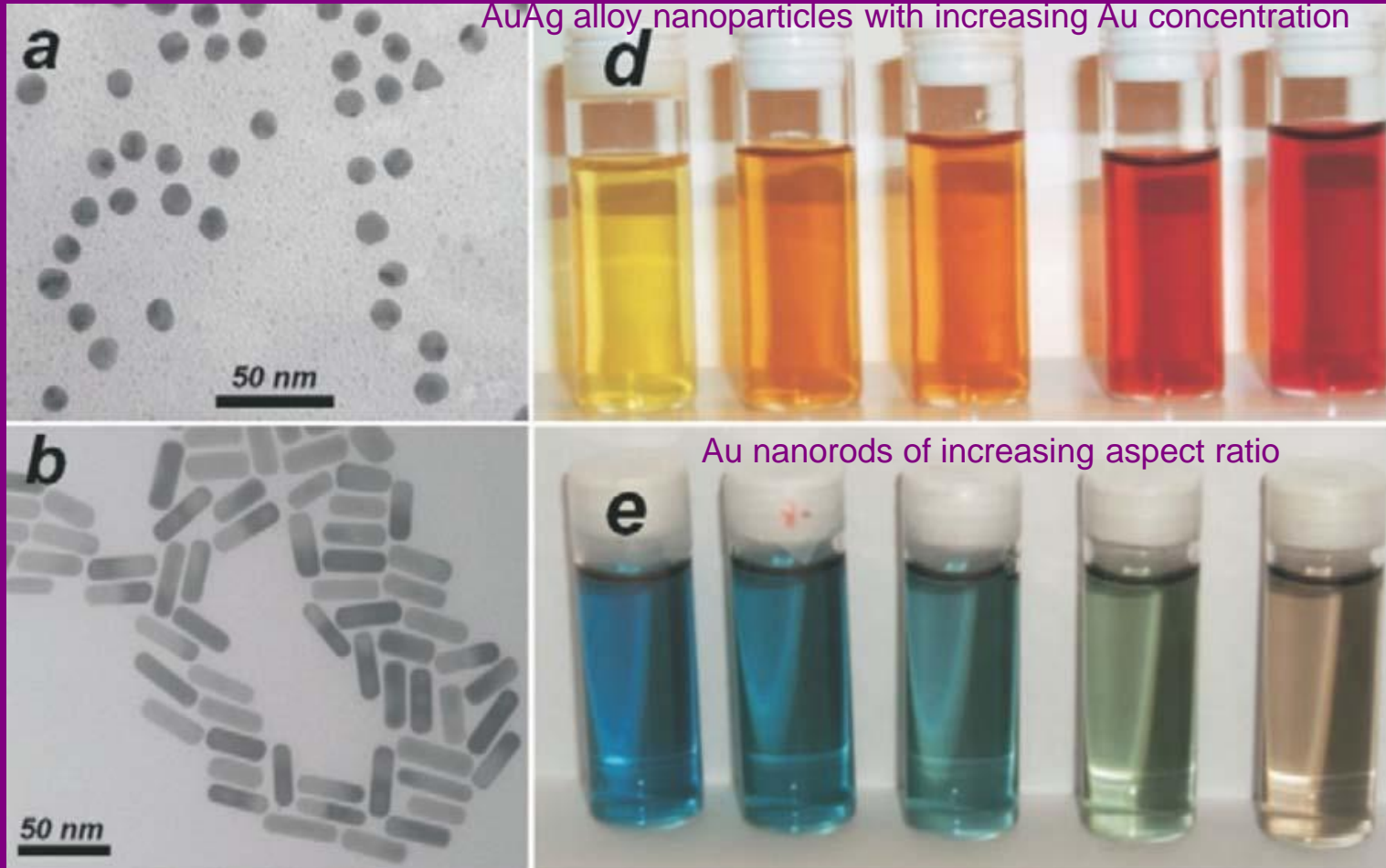
$\text{Re}(\epsilon)$ is negative, -20...-1
 $\text{Im}(\epsilon)$ is small, $Q > 2$

E. D. Palik, editor. Handbook of optical constants of solids III. Academic Press, New York, 1998.

E.C. Le Ru and P. G. Etchegoin, Principles of Surface-Enhanced Raman Spectroscopy and related plasmonic effects, Elsevier, 2009

A!

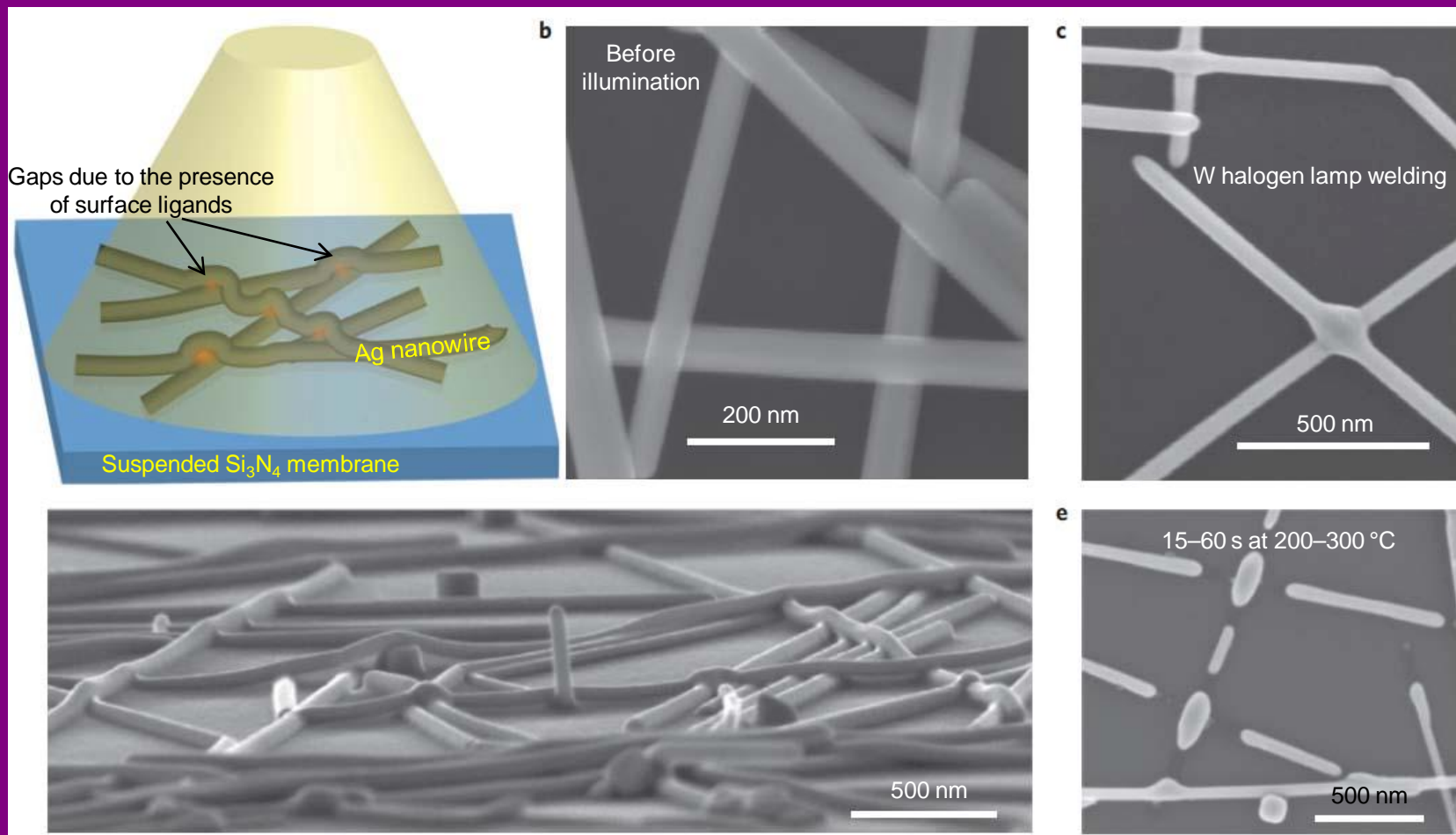
Material and size effect in plasmon resonance



Materials Today, Feb 2004, p. 26-31

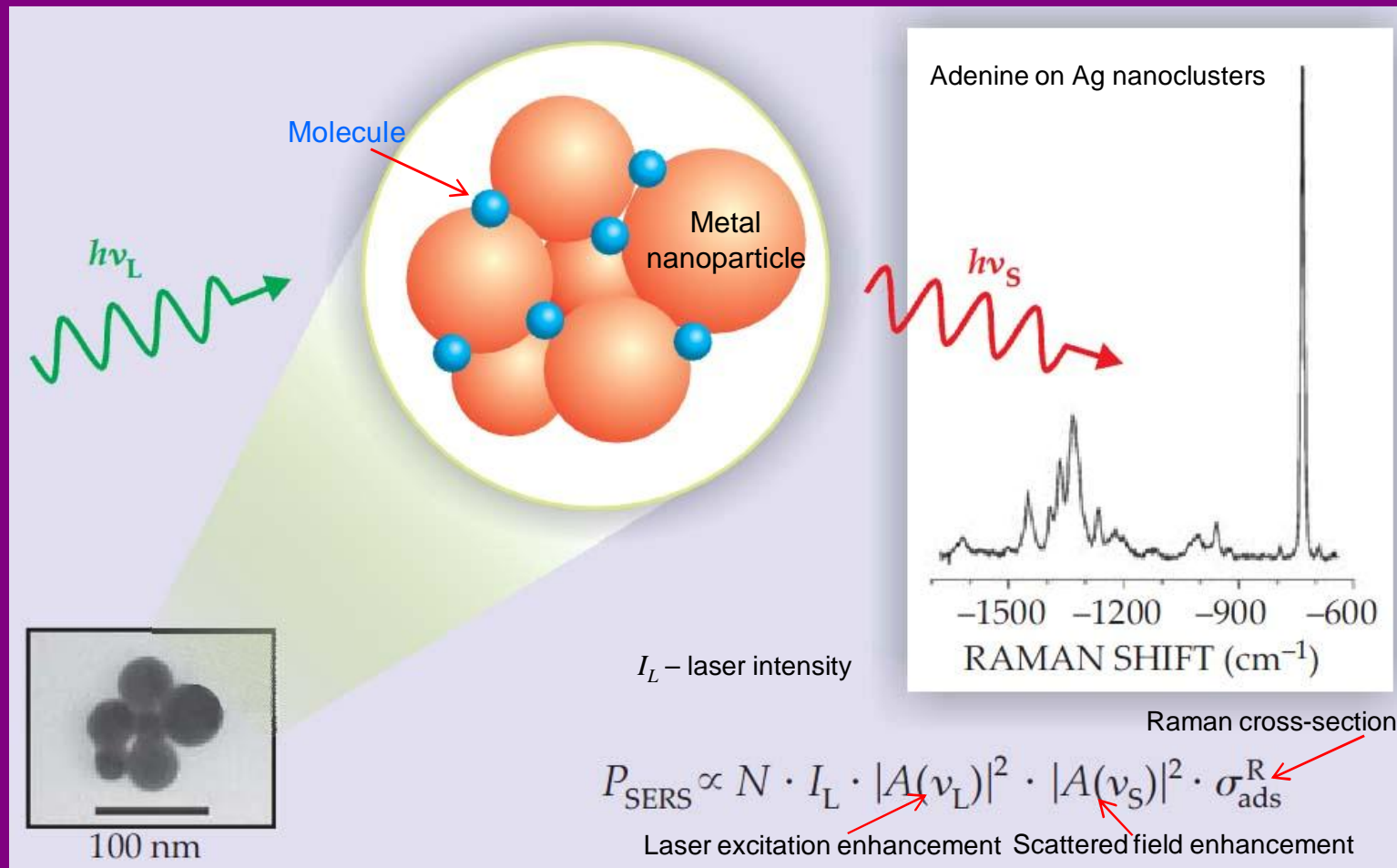
A!

Plasmonic welding



E. C. Garnett, *Nature Materials* 11, 241–249 (2012)

A! Electromagnetic enhancement in near-field



K. Kneipp, *Physic Today*, **60**(11), 2007, p. 40-46

A! Electric field outside of metal sphere

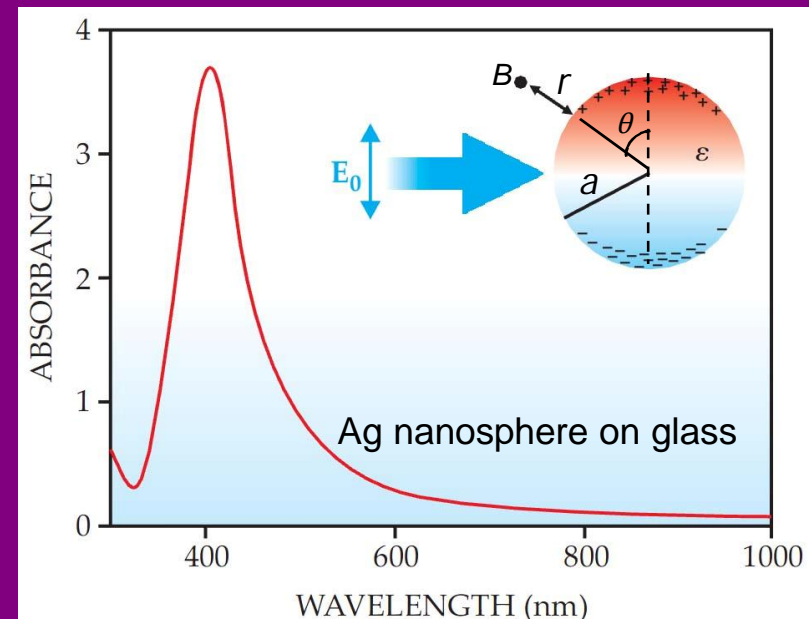
$$\mathbf{E}_{out}(x, y, z) = E_0 \hat{\mathbf{z}} - \alpha E_0 \left[\frac{\hat{\mathbf{z}}}{r^3} - \frac{3z}{r^5} (x\hat{\mathbf{x}} + y\hat{\mathbf{y}} + z\hat{\mathbf{z}}) \right]$$

x, y, z – Cartesian coordinates,
 r – radial distance from sphere to the point $B(x, y, z)$
 $\hat{\mathbf{x}}, \hat{\mathbf{y}}, \hat{\mathbf{z}}$ – Cartesian unit vectors

$$\alpha = ga^3$$

a – radius of the sphere

$$g = \frac{\varepsilon(\omega) - \varepsilon_M}{\varepsilon(\omega) + 2\varepsilon_M}$$



K. Kneipp, *Physic Today*, **60**(11), 2007, p. 40-46

Stiles P.L. *et al*, *Annual Review of Analytical Chemistry*, **1**, 2008, p.601-26



E^4 enhancement of outside field

Electric field at the surface of nanosphere

$$|\mathbf{E}_{out}|^2 = E_0^2 [|1 - g|^2 + 3\cos^2\theta(2\text{Re}(g) + |g|^2)]$$

Maximum E_{out} at $\theta=0^\circ$

$$|\mathbf{E}_{out}|^2 = 4E_0^2 |g|^2$$

Enhancement factor

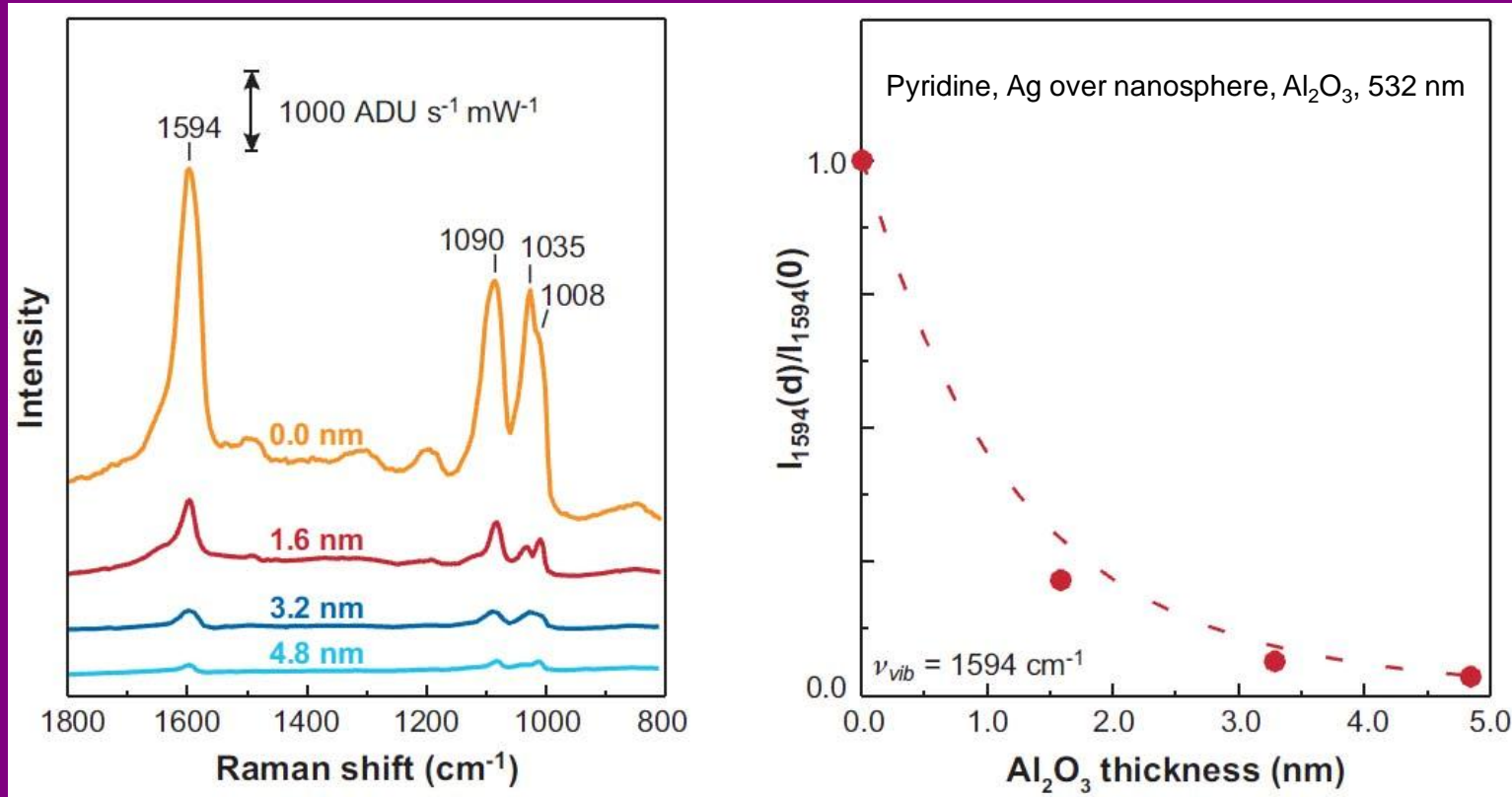
$$EF = \frac{|\mathbf{E}_{out}|^2 |\mathbf{E}'_{out}|^2}{|\mathbf{E}_0|^4} = 4|g|^2 |g'|^2$$

Stiles P.L. *et al*, Annual Review of Analytical Chemistry, 1, 2008, p.601-26

A!

Distance dependence

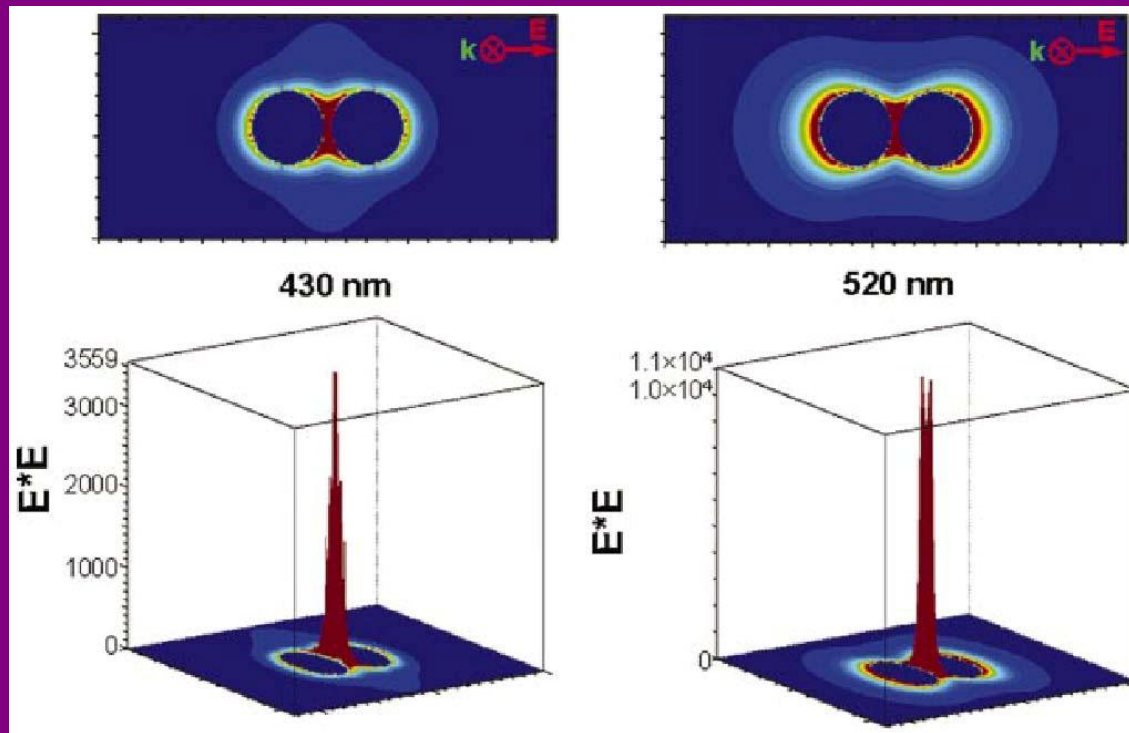
$$I_{SERS} = \left(\frac{a+r}{a} \right)^{-10}$$



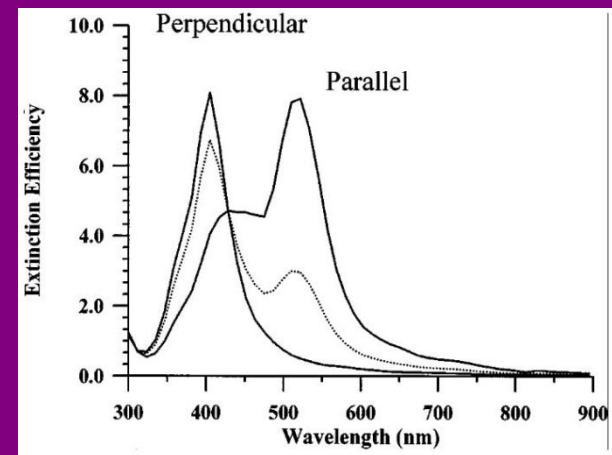
Stiles P.L. *et al*, Annual Review of Analytical Chemistry, 1, 2008, p.601-26

A!

Ag dimer enhancement



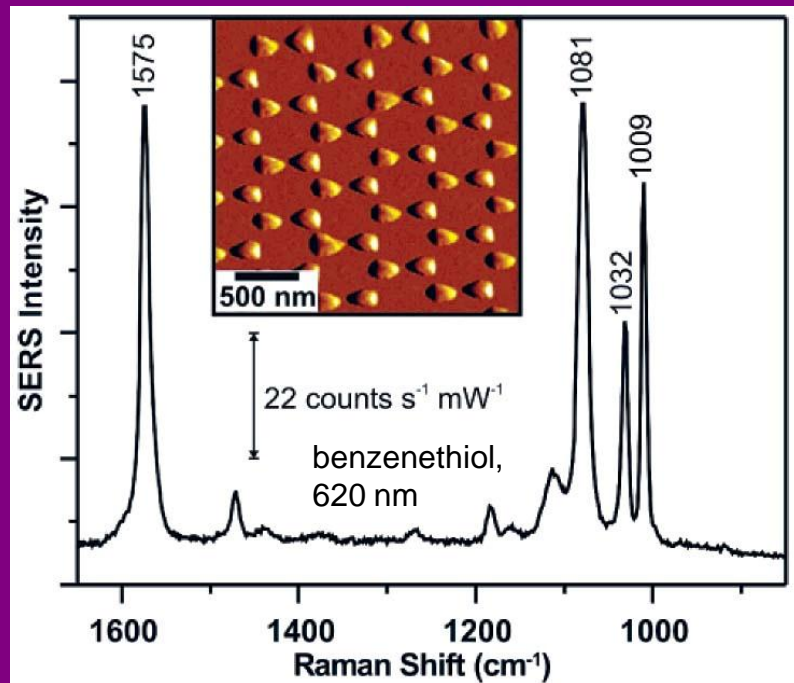
36 nm spheres separated by 2 nm gap
For sphere is 85, slide 22



E. Hao and G. C. Schatz, J. Chem. Phys., Vol. 120, No. 1, 1 January 2004

A!

Wavelength dependence

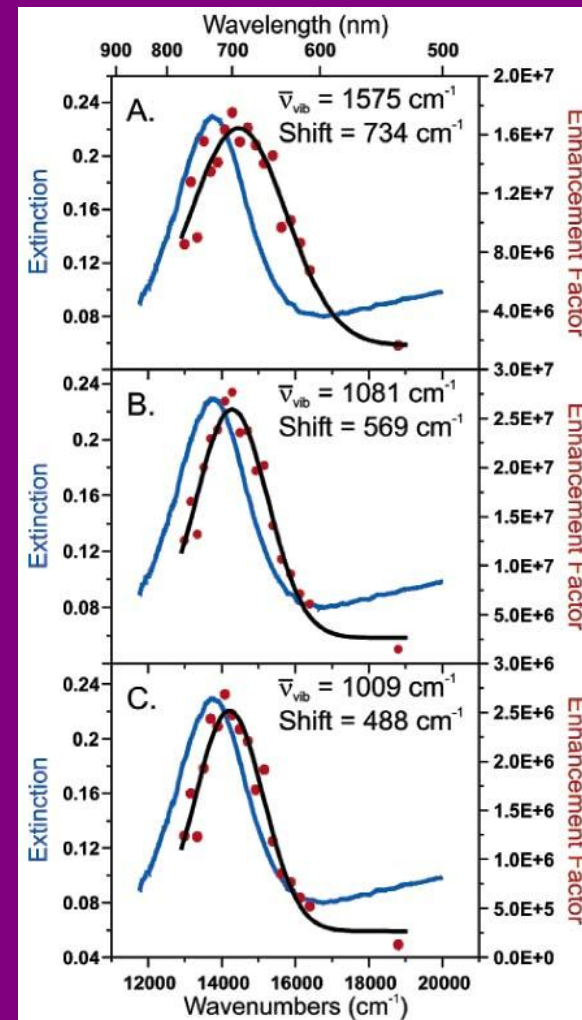


NSL with 450nm spheres, 55 nm Ag on glass

SERES – surface enhanced excitation spectroscopy

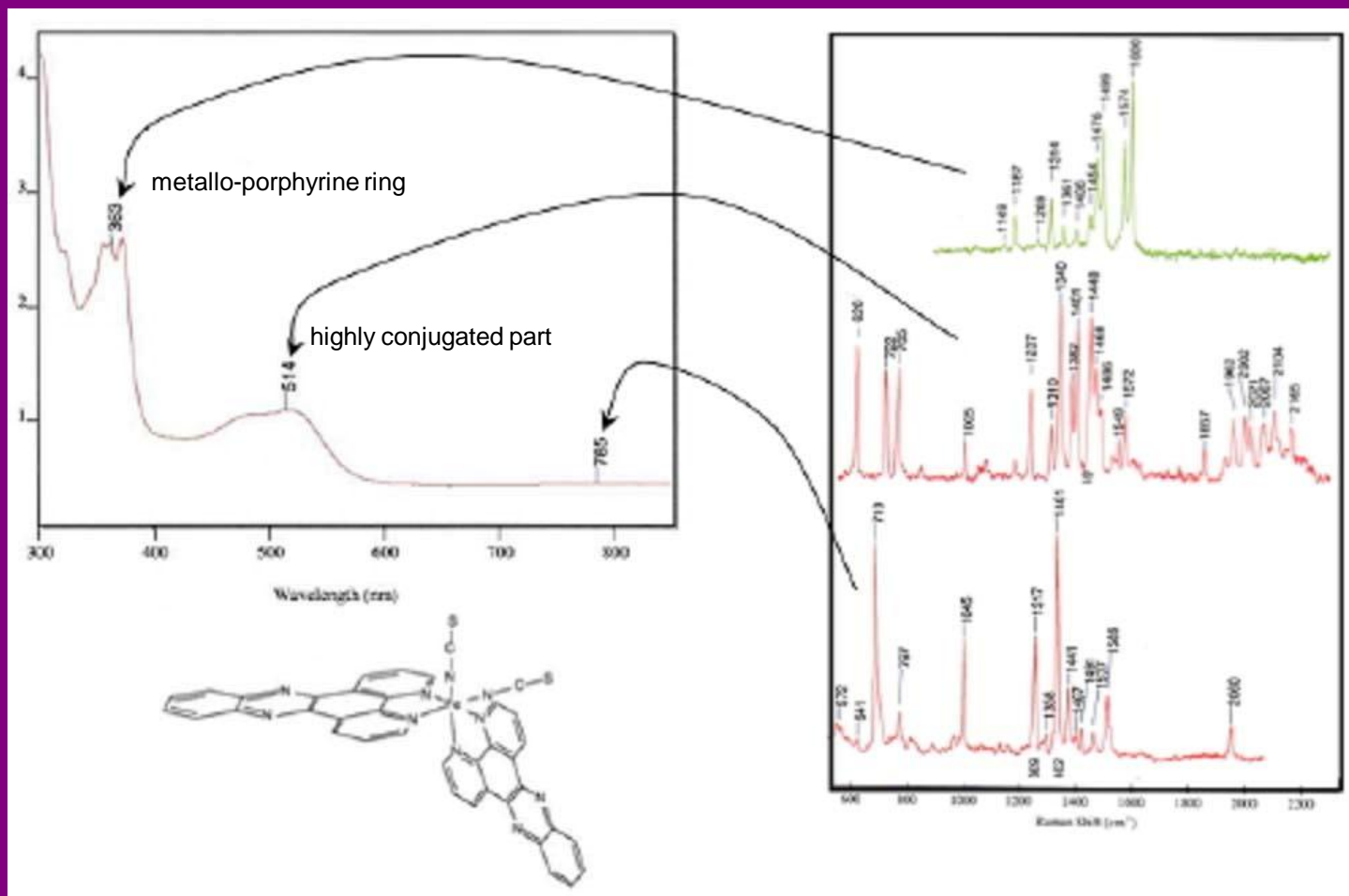
SERS is maximum when laser excitation is between SPR and the analyzed spectrum line

J. Phys. Chem. B **2005**, *109*, 11279-11285



A!

SERRS



RRS provides additional $EF = 10^2-10^6$

Resonance

Resonance

No resonance

©2011 www.raman.de • Dr. Bernd Dippel

Due to matching of excitation to absorption of a specific part of the molecule, the Raman spectrum associated with this part of the molecule is selectively enhanced

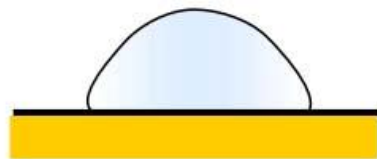


SERRS

- The energy of the incoming laser is adjusted such that it or the scattered light coincide with an electronic transition of the molecule or crystal
- The main advantage of RR spectroscopy over traditional Raman spectroscopy is the large increase in intensity of the peaks in question
- The main disadvantage of RR spectroscopy is the increased risk of fluorescence and photo-degradation of the sample due to the increased energy of the incoming laser light

A! Delivering molecules to metal structures

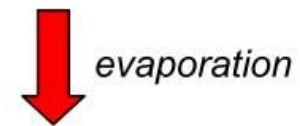
Aqueous solutions
no surface chemistry



Aqueous solutions
with surface chemistry



Volatile solutions
no surface chemistry



Droplet formation depends on nature of solution, surface material and surface nanopattern (pillars...)

Molecule attachment may be strong or weak depending on molecule affinity to metal and surface chemistry

www.d3technologies.co.uk - www.renishawdiagnostics.com/en/klarite-sers-substrates

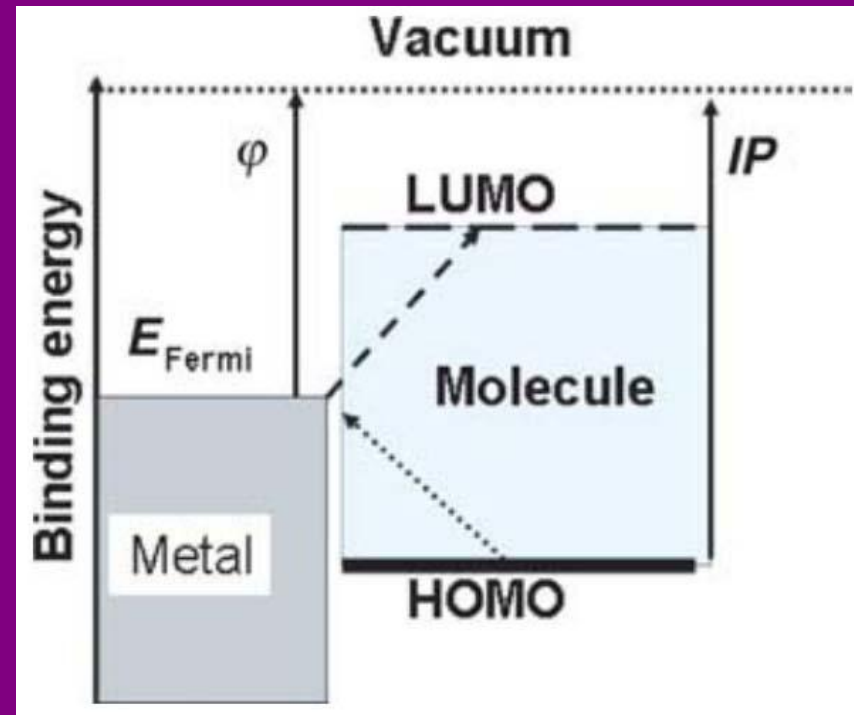
A!

Chemical enhancement

$$EF = EF_{EM} \cdot EF_{CE}$$

EF_{EM} , EF_{CE} – electromagnetic and chemical enhancement factors, respectively

- Charge transfer (CT) through metal-molecule complex
- Up to 10^2 contribution theoretically, up 100 practically
- CT is a special case of resonant Raman scattering

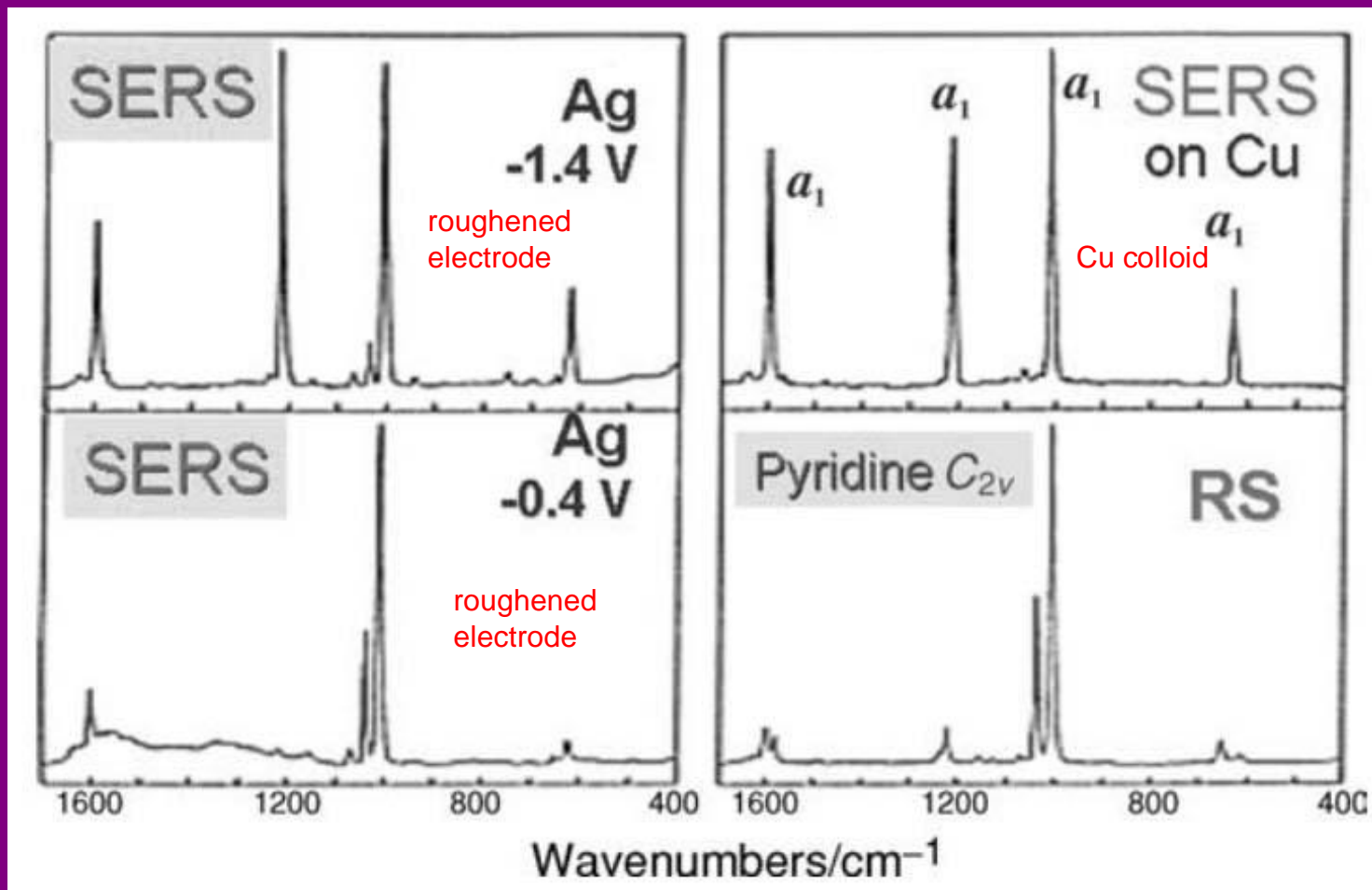


IP – ionization potential,
 ϕ – work function of the metal

A!

Chemical enhancement

647 nm





SERS enhancement factor

Analytical enhancement factor

$$AEF = \frac{I_{SERS}/c_{SERS}}{I_{RS}/c_{RS}}$$

I_{SERS} , I_{RS} – intensities of SERS and Raman signals, respectively
 c_{SERS} , c_{RS} – molecule concentrations for SERS and Raman, respectively

SERS substrate enhancement factor

$$SSEF = \frac{I_{SERS}/N_{surf}}{I_{RS}/N_{vol}}$$

$N_{vol} = c_{RS}V$ – number of molecules in the scattering volume V



SERS aspects

- Maximum SERS *EF* occurs at specific positions on the surface ('hot spots'): nanosphere 10^6 , nanogap 10^{11} (SERRS)
- Average SERS *EF* (averaged over all possible positions on the metallic surface) 10 - 10^3 for non-optimized conditions, 10^7 - 10^8 for very good SERS substrates.
- Adsorption efficiency of the probe
- Sample transfer on 2D SERS substrate

A!

Intermediate conclusion II

- High local electromagnetic field near the plasmon nanostructures provides very high enhancement of Raman scattering (SERS)
- SERS effect depends on metal-molecule affinity and resonance conditions in molecule
- The highest EF is reached in random 'hot spots', if the probe molecule has got at this 'spot'



SERS substrates

- SERS substrate is any metallic structure (nano-structure) that produces the SERS enhancement:
 - Metallic nano-particles in solution (colloids)
 - ‘Planar’ metallic structures or arrays of metallic nano-particles supported on a planar substrate (glass, silicon)
 - Metal electrodes in electrochemistry (roughed electrodes)



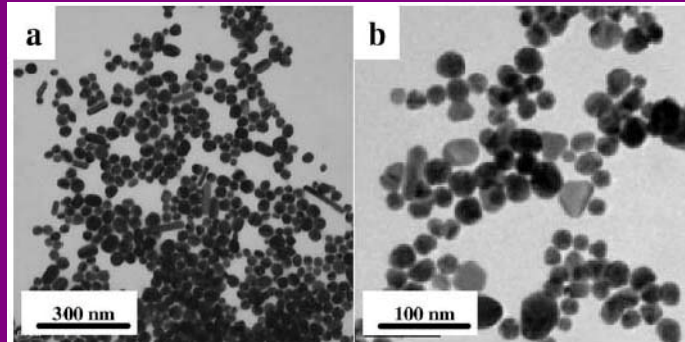
Metal colloids for SERS

- Mainly Au, Ag or Cu nanoparticles (diameter 10 – 80 nm) in water
- Produced by:
 - Chemical reduction. Process depends on:
 - Kind of metal
 - Reducing reagent AgNO₃, K(AuCl₄)
 - Temperature (boiling 1 h)
 - Stabilizing agents
 - Metal ion concentration
 - Laser ablation
 - Photoreduction
- The best SERS is provided by highly aggregated colloids
- Cube, triangle, nanorod shapes of particle
- The background SERS – water 3100 – 3600 cm⁻¹, 'cathedral peaks' around 1360 and 1560 cm⁻¹ (amorphous carbon), low-frequency signals (150 – 250 cm⁻¹) metal complexes Ag-O, Ag-Cl
- Enhancement up to 10¹⁴ (SMD possible)

A!

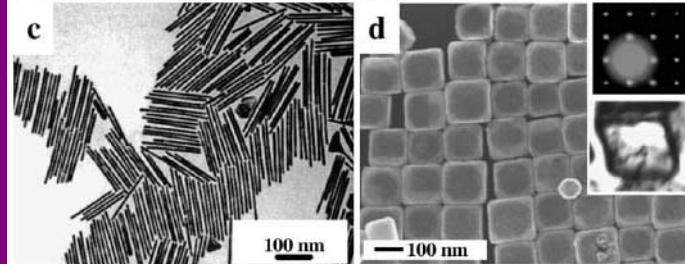
Colloids images

TEM of Ag citrate colloid
 $\lambda_{\max} = 406 \text{ nm}$



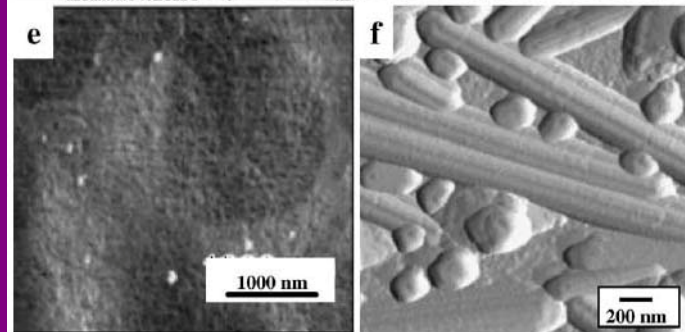
TEM of Au borohydride colloid,
Au particles 20-70 nm,
 $\lambda_{\max} = 535 \text{ nm}$

TEM of Au nanorods,
 $\lambda_{\max} = 525 \text{ nm}$ and 885 nm



TEM of Au nanosquares

AFM of Au nanospheres embedded
in film of biopolymer chitosan
(inert organic matrix)



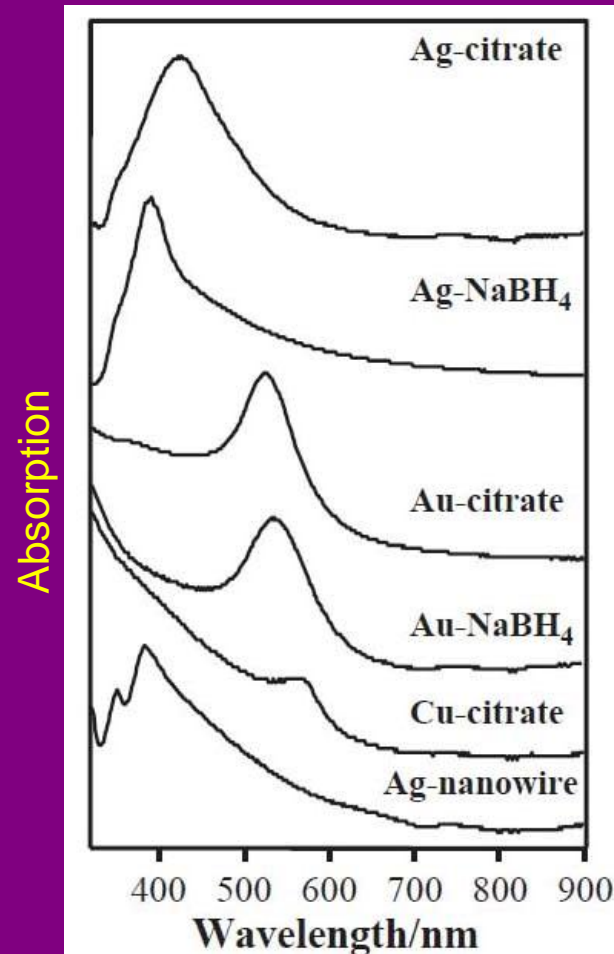
AFM of Ag nanowires
in dendrimer matrix

R.F. Aroca et al. / Advances in Colloid and Interface Science 116 (2005) 45–61

A!

SPR of colloids

Observed effects are due to particle size, concentration, aspect ratio.

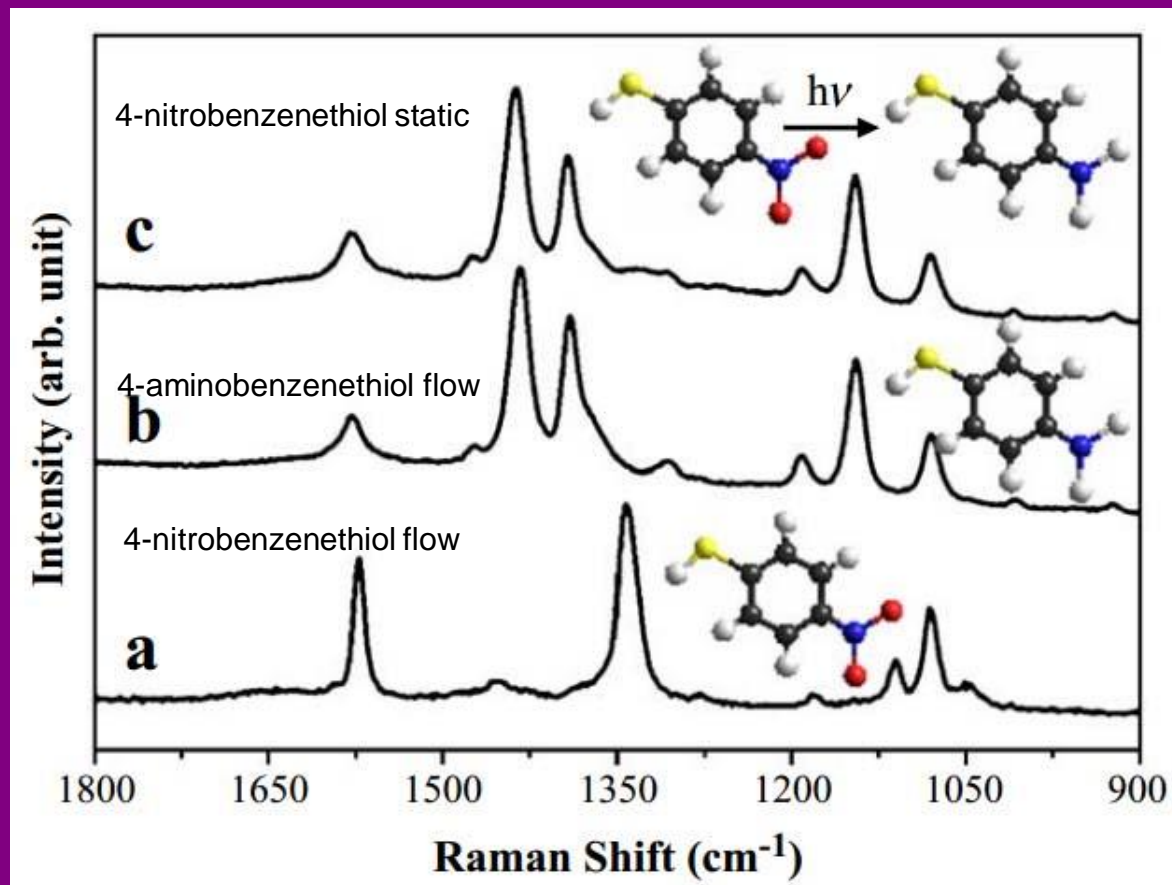


Partical surface charge deterns stability, adsorbivity, electrokinetic properties

R.F. Aroca et al. / Advances in Colloid and Interface Science 116 (2005) 45–61

A!

Laser induced photo-reaction



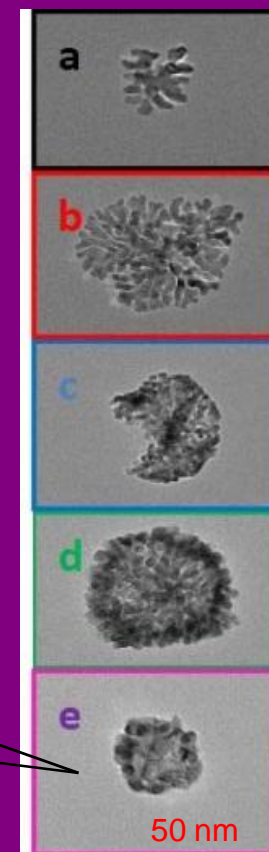
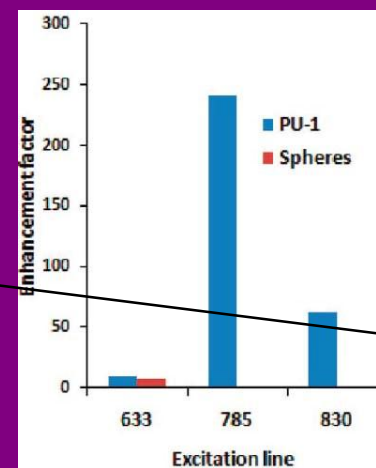
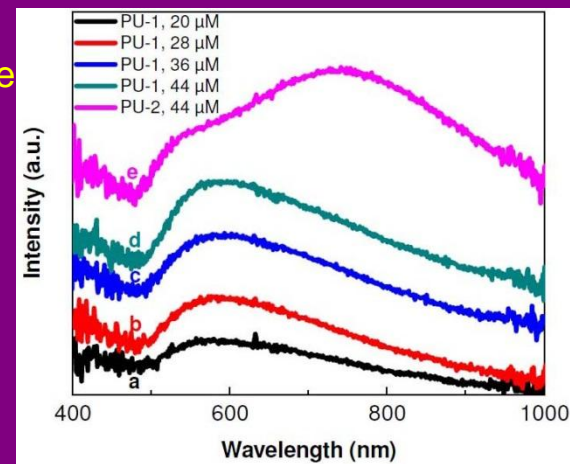
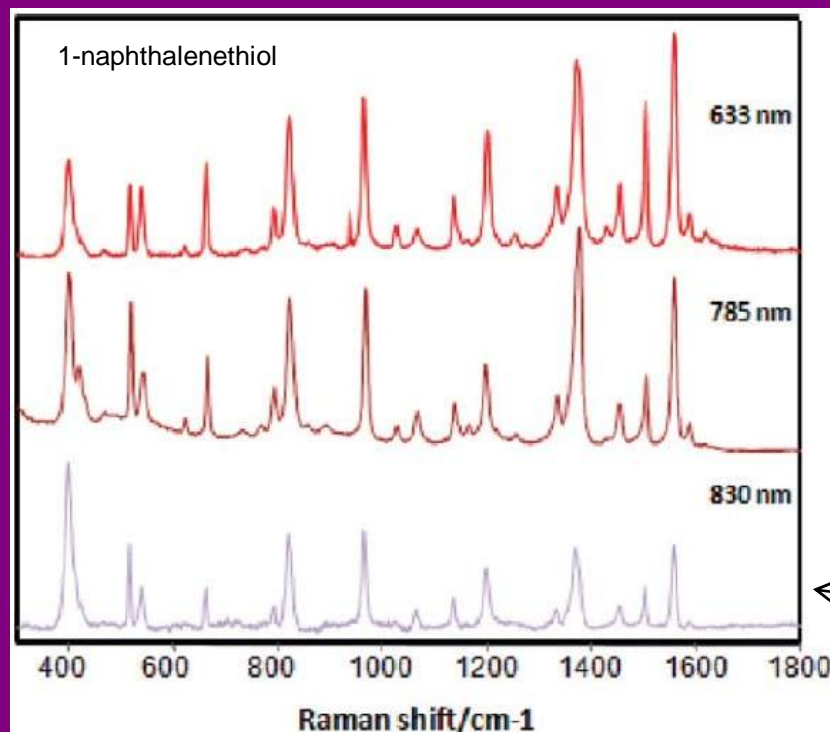
Ag colloid, 514 nm

R.F. Aroca et al. / Advances in Colloid and Interface Science 116 (2005) 45–61

A!

Gold Lace Nanoshells

PU means amphiphilic polyurethane template

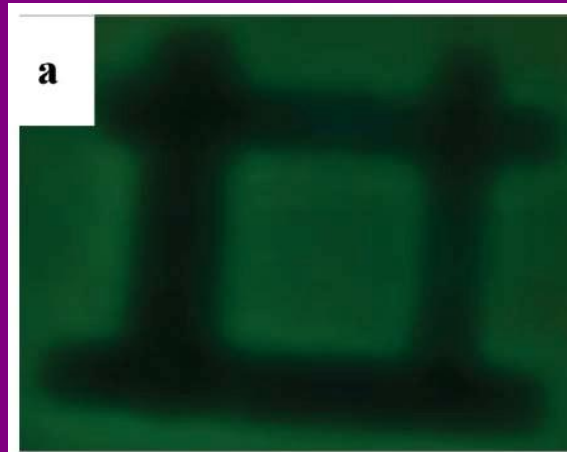


M. Yang et al., SERS-Active Gold Lace Nanoshells with Built-in Hotspots, *Nano Lett.* 2010, 10, 4013–4019

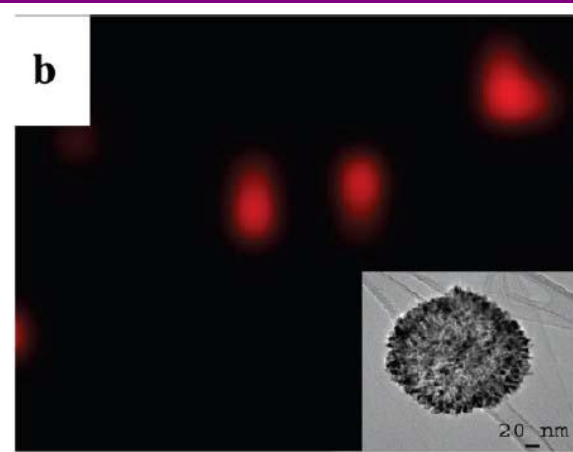
A!

Images of single lace nanoparticle

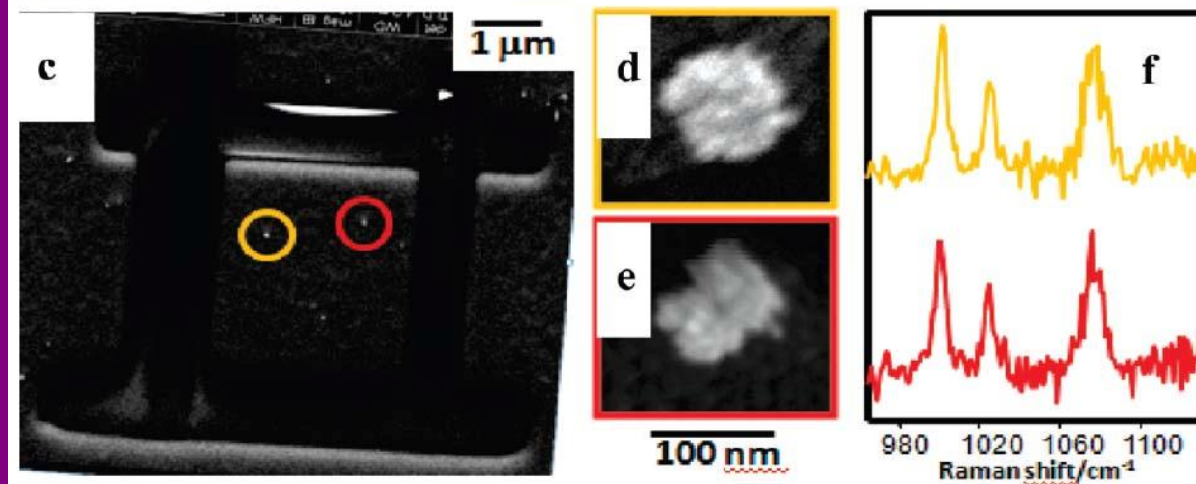
Optical



Raman



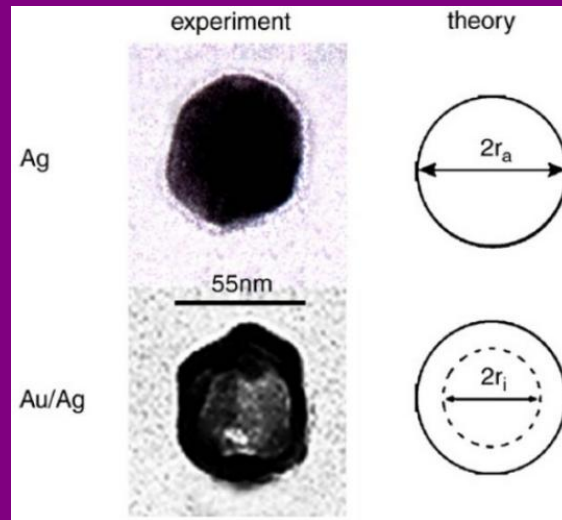
SEM



M. Yang et al., SERS-Active Gold Lace Nanoshells with Built-in Hotspots, *Nano Lett.* 2010, 10, 4013–4019

A!

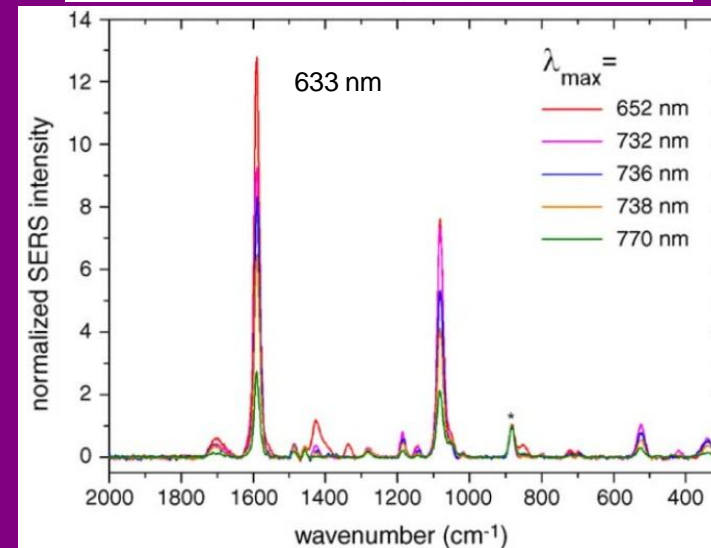
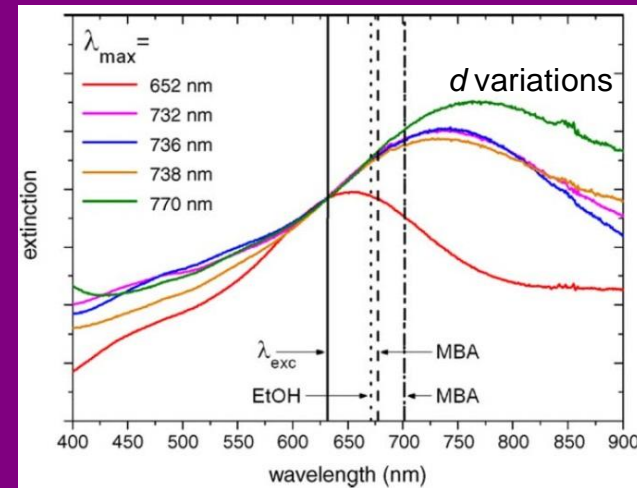
Nanoshells



$$d = (r_a - r_i)$$

- additional degree of tunability of SPR by changing the thickness d of shells
- more uniform signal (less fluctuations)

4-mercaptobenzoic acid (MBA)



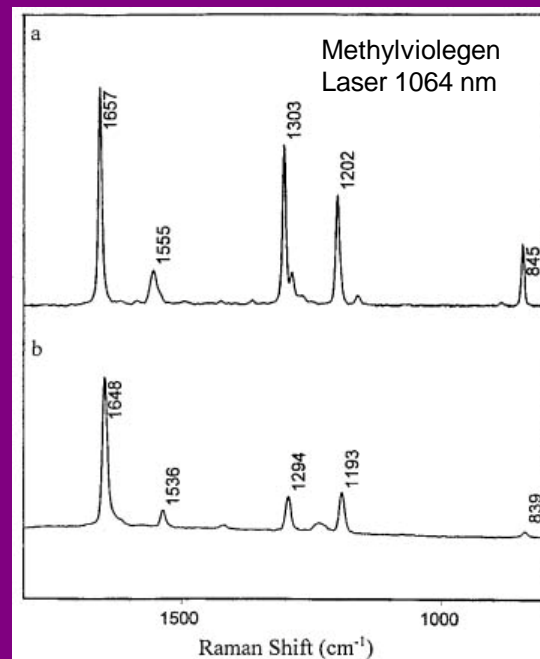
M. Gellner et al. / Vibrational Spectroscopy 50 (2009) 43–47

A!

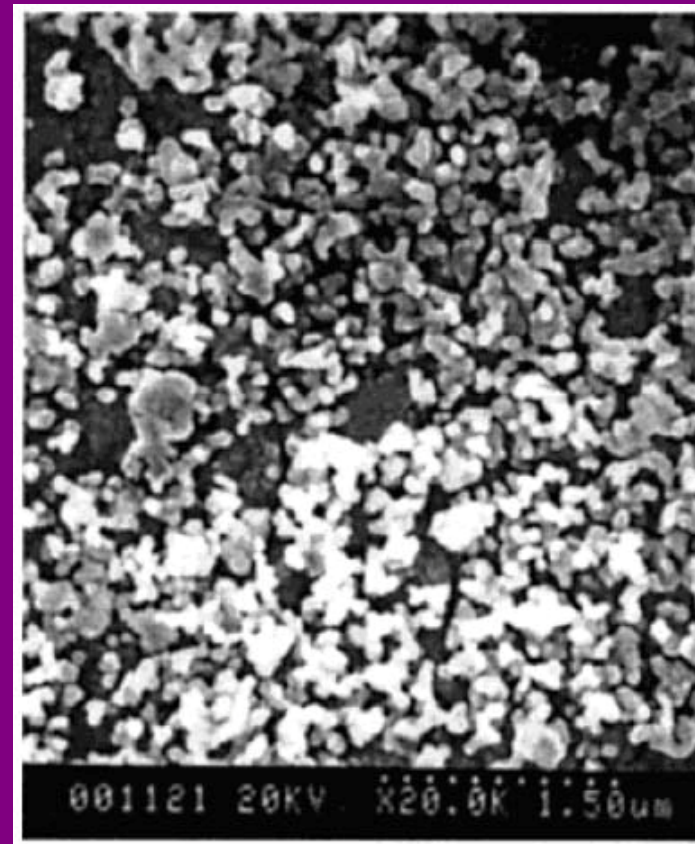
Metal electrodes

- Surface protrusions 25-500 nm
- Ag in KCl electrolyte
- Oxidation-reduction cycles

SERS



bulk Raman



Zheng et al., J. Phys. Chem. B, Vol. 106, No. 5, 2002, p.1019-23

A! 'Planar' substrates - metal island films

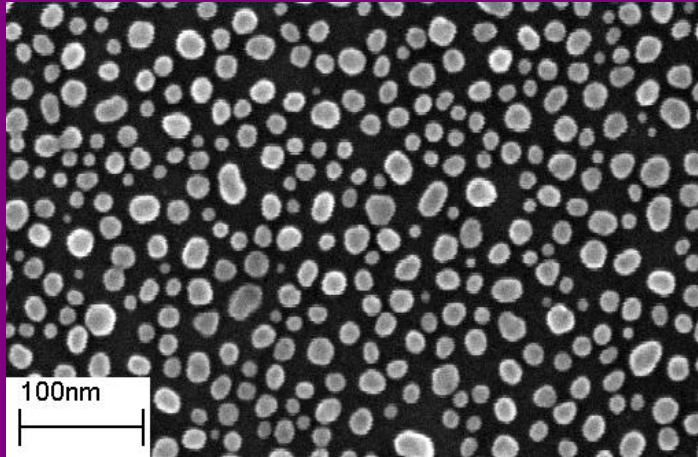
- Prepared by PVD – physical vapor deposition
- Applicability to any substrate
- High purity
- Structure can be controlled by deposition rate (0.5 Å/s), substrate roughness, temperature, mass thickness (6 nm), annealing
- Cold-deposited (-100 °C) Ag (pore, voids, cavities)

A!

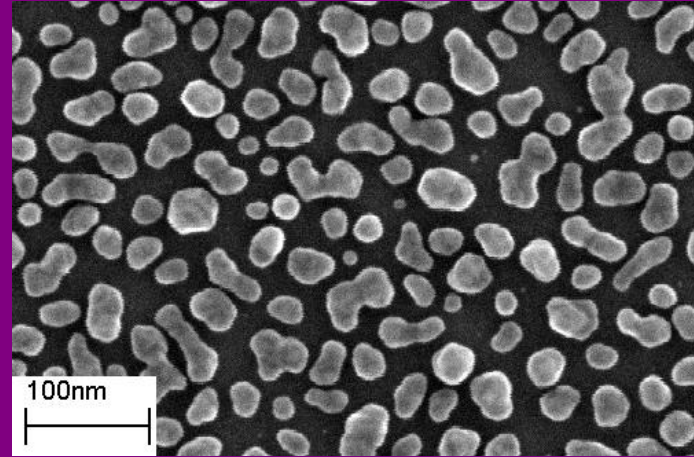
As deposited silver films

Room temperature

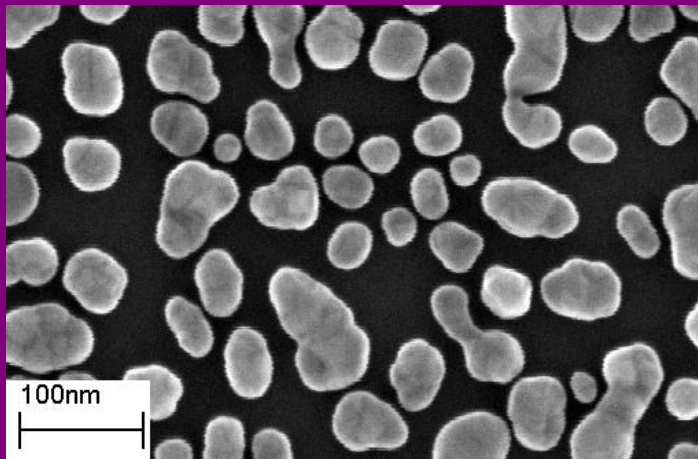
4 nm
0.2 Å/s



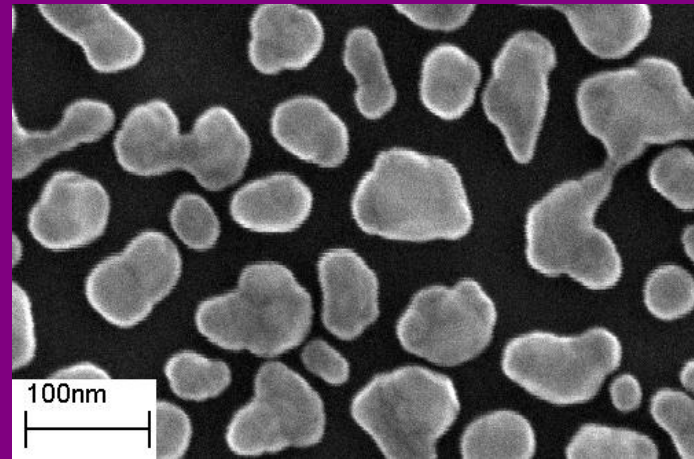
5.5 nm
0.5 Å/s



10 nm
2.0 Å/s



12 nm
0.2 Å/s

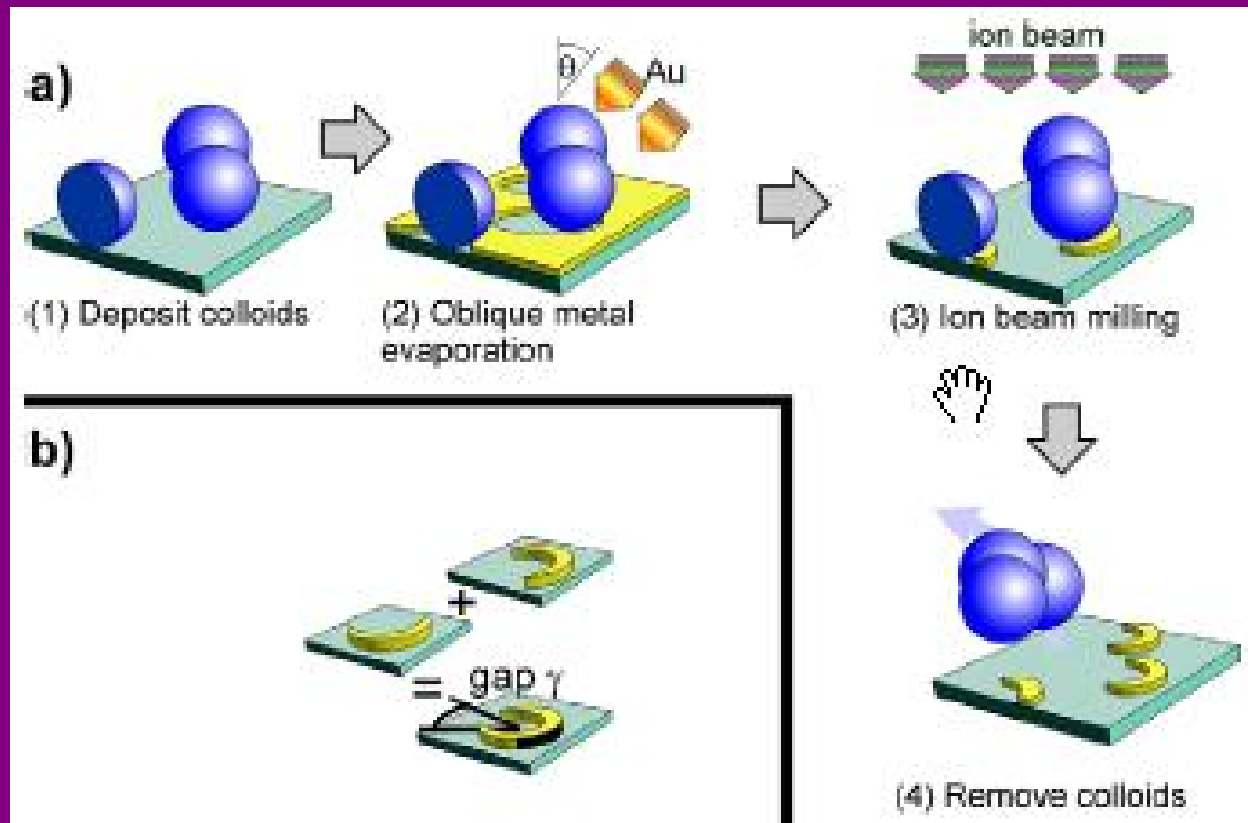


A! 'Planar' substrates - nanoengineered surfaces

- The aim is optimization (to obtain high EF) and reproducibility
- Nanosphere based
 - Ag on top of spheres (AgFON)
 - Nanosphere lithography (NSL)
- Fabricated with self-organized metal islands
- E-beam lithography (ring, crescent, dimer...)
- Temperature controlled (nano-particle monolayer on a thermo-responsive polymer film)

A!

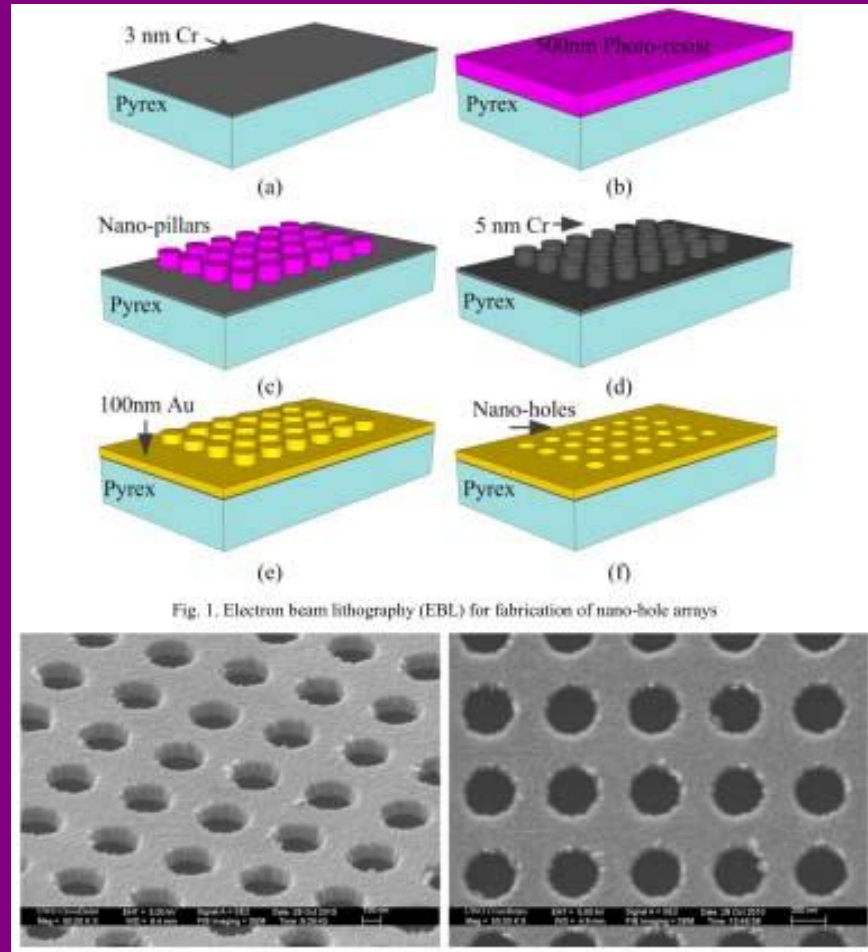
Nanocrescents fabricated by nanosphere lithography



H. Rochholz *et al.*, *New Journal of Physics*, **9** (2007) 53

A!

Nanohole array



100 nm thick Au
200 nm holes



Optimal SERS substrate

$$I(\omega_S) = NA\Omega \frac{d\sigma(\omega_S)}{d\Omega} P_L(\omega_L) \varepsilon(\omega_L)^{-1} Q(\omega_S) T_m T_0 EF$$

$I(\omega_S)$ – SERS intensity at Stokes frequency ω_S

N – molecular surface density

A – excitation area

Ω – solid angle of photon collection

$\sigma(\omega_S)$ – Raman scattering cross section

$P_L(\omega_L)$ – radiant flux at excitation frequency

$\varepsilon(\omega_L)$ – energy of incident photon

$Q(\omega_S)$ – quantum efficiency of the detector

T_m – transmissiton efficiency of the spectrometer

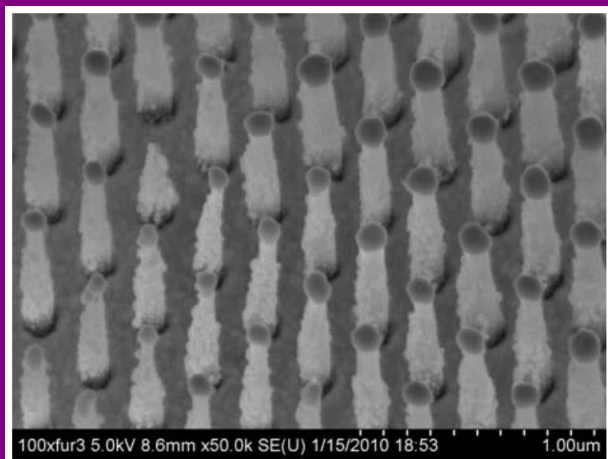
T_0 – transmissiton efficiency of the collection optics

EF – enhancement factor

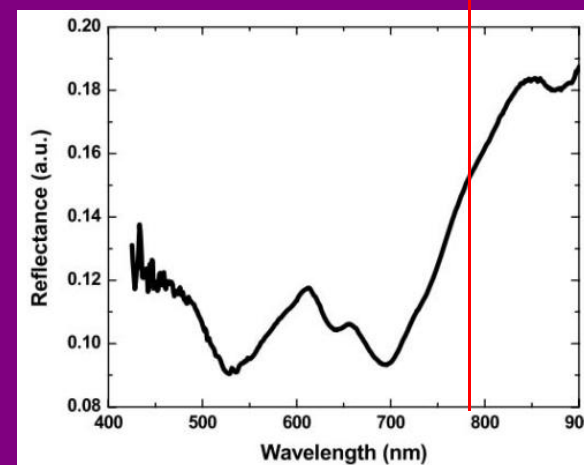
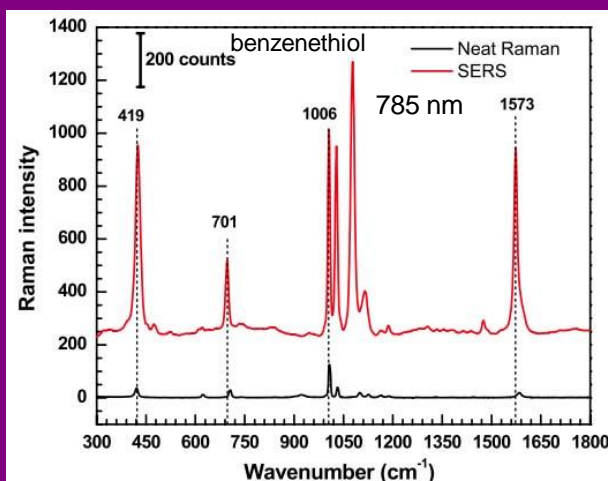
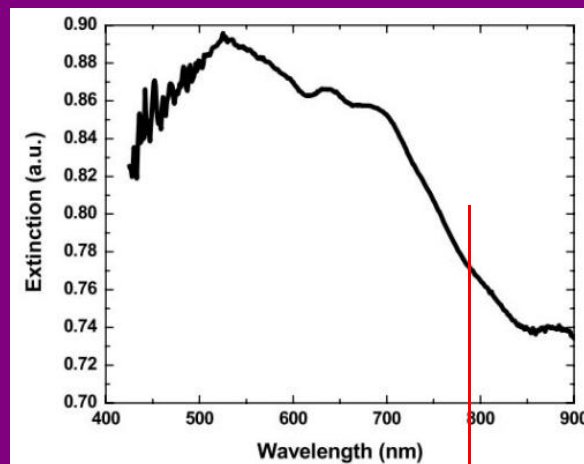
Stiles P.L. *et al*, Annual Review of Analytical Chemistry, 1, 2008, p.601-26

A!

Pillar based substrate



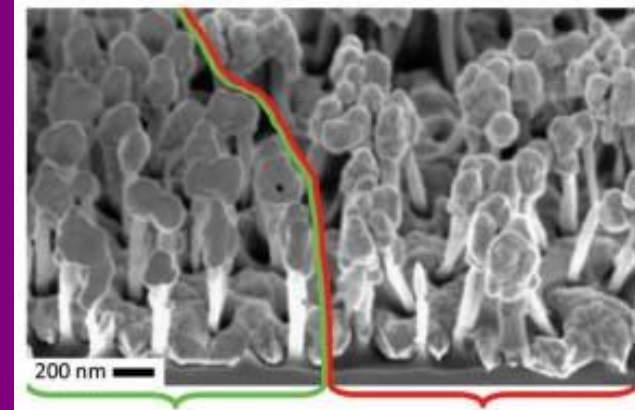
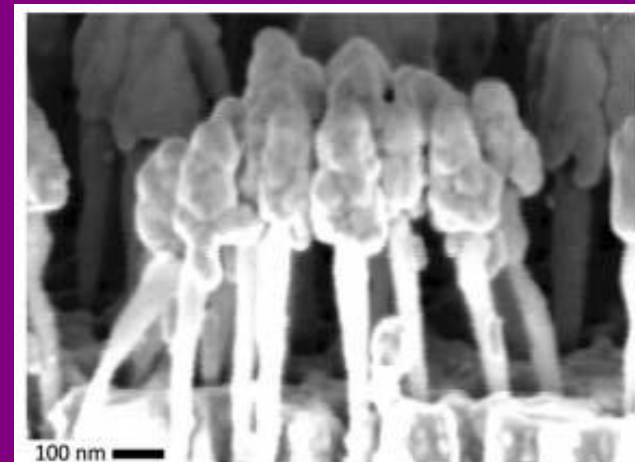
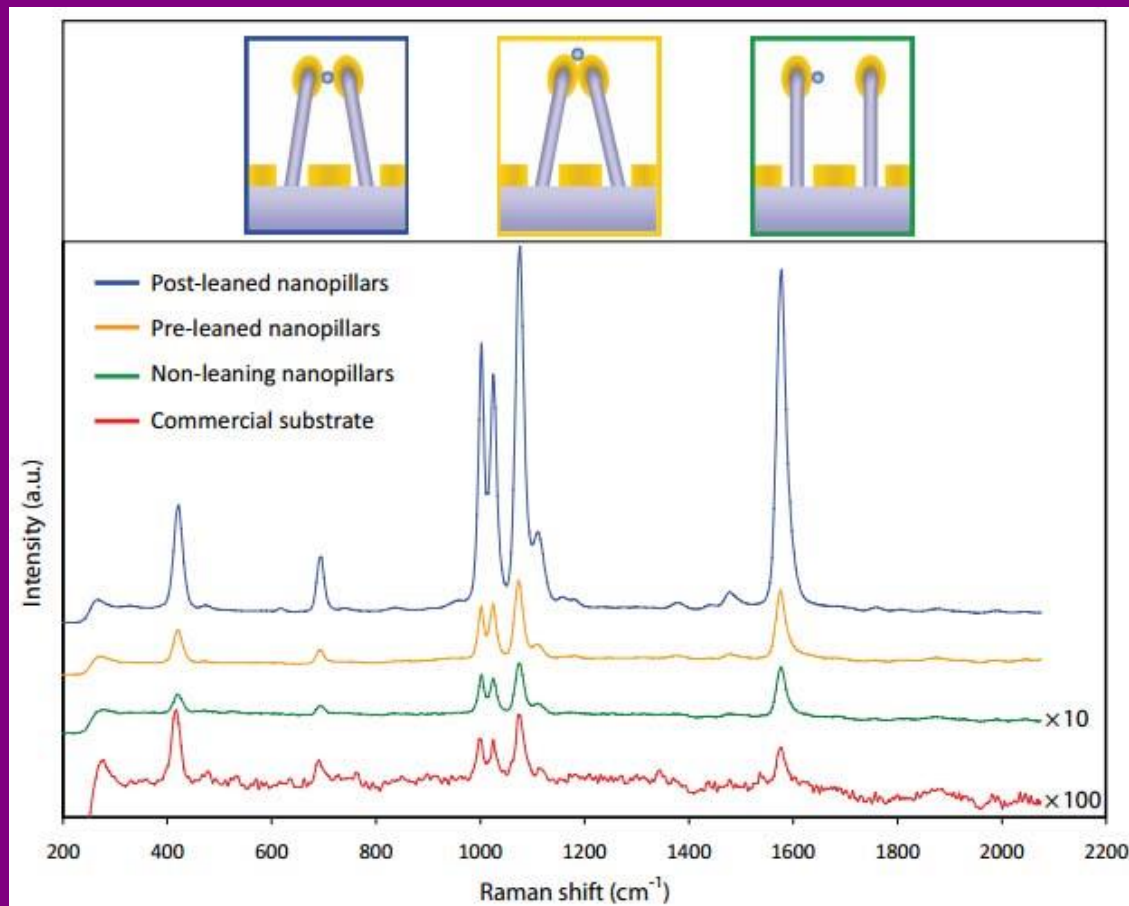
SiO₂
d=150nm
gap 350 nm
h=500nm
Ag 80nm
 $EF=5 \cdot 10^7$



M. R. Gartia et al., Rigorous surface enhanced Raman spectral characterization of large-area high-uniformity silver-coated tapered silica nanopillar arrays, *Nanotechnology*, 21(2010) 395701 (9pp)

A!

Leaning Si pillars



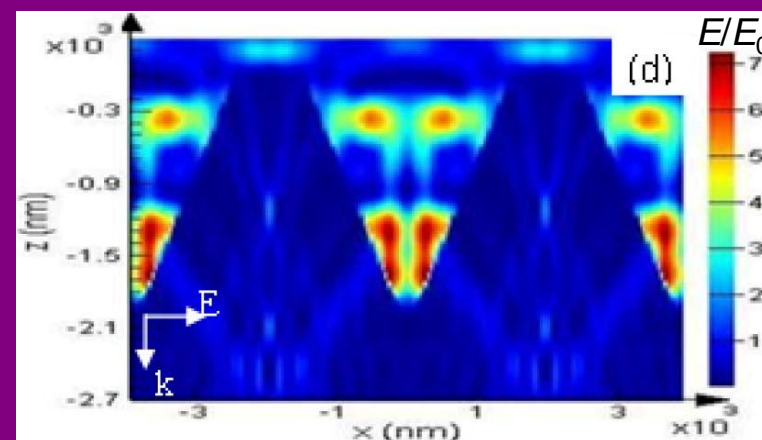
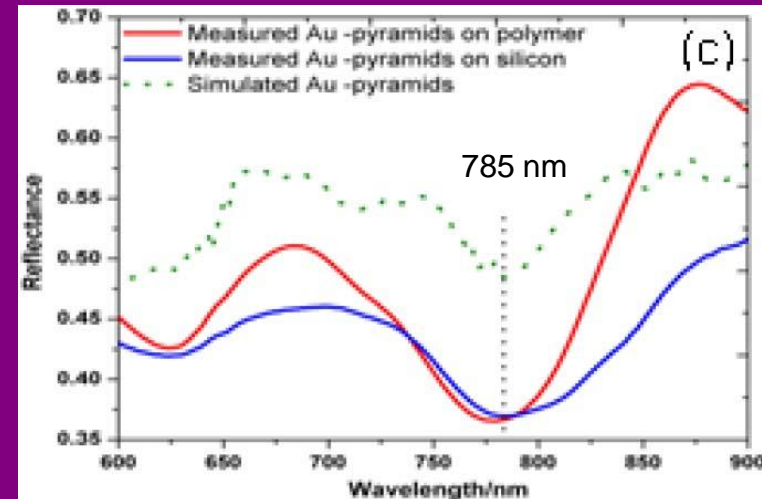
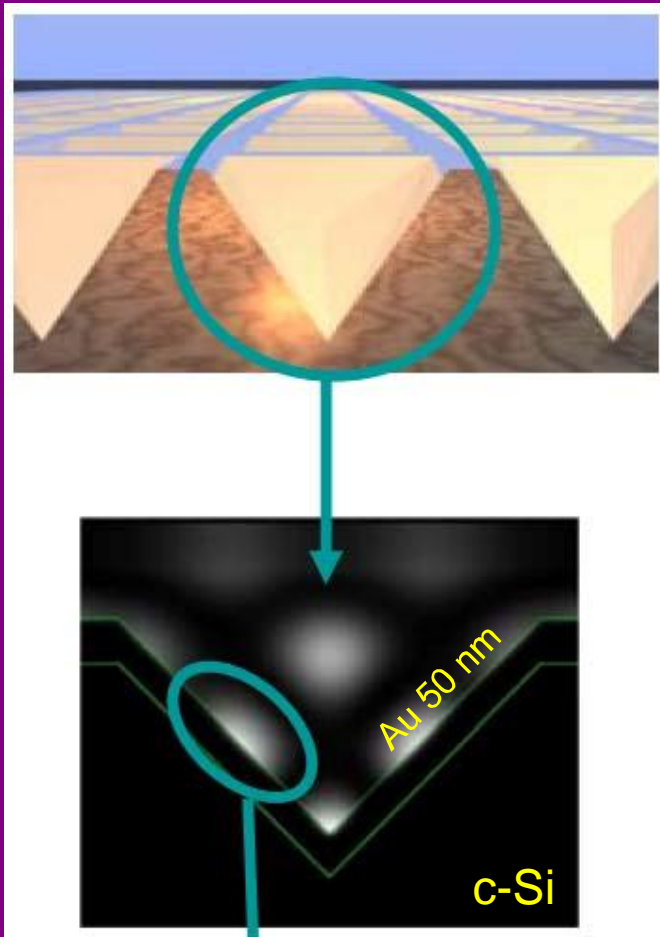
no leaning

leaning

M.S. Schmidt et al., *Adv. Mater.* 2012, 24, OP11–OP18

A! Commercial SERS substrate (Klarite)

Very high enhancements are 'sacrificed' in favor of homogeneity and reproducibility



www.d3technologies.co.uk - www.renishawdiagnostics.com/en/klarite-sers-substrates

ZHIDA XU, Master Thesis, University of Illinois at Urbana-Champaign, 2011

A!

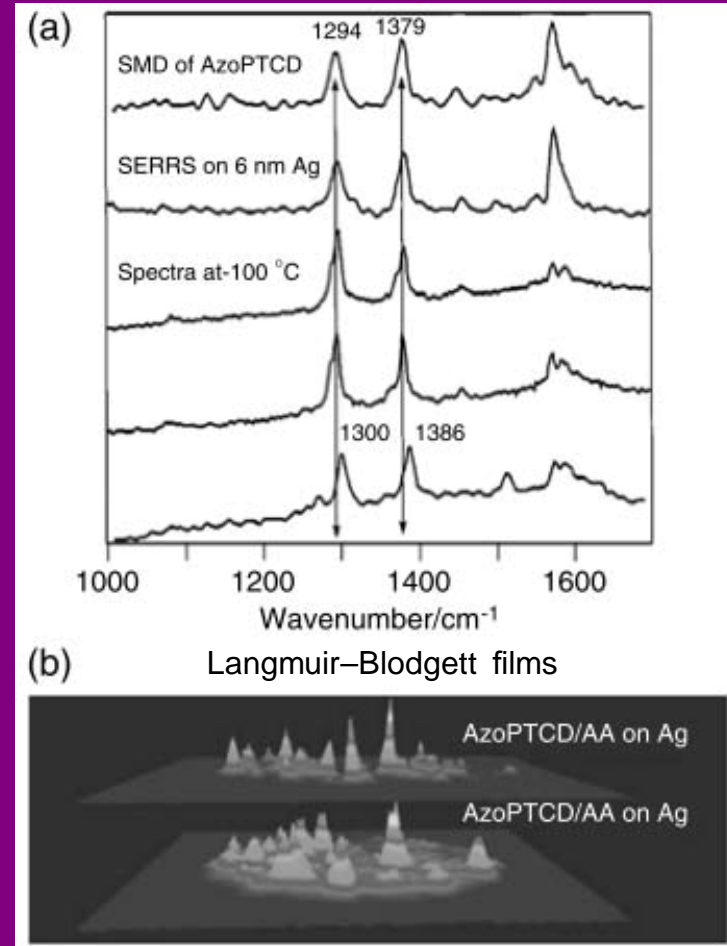
SMD –why?

- To push analytical tools to their ultimate resolution limits
- The understanding of unique single-molecule phenomena that are potentially washed out by ensemble averages
- Early single-molecule emission was inferred from indirect evidence
- Ultra-low concentration studies – statistical result, but they provide hint of possibility SMD

A!

Single-molecule detection

- Competitive to fluorescence
- Rhodamine 6G like pyridine for average SERS
- SMD SERS was possible only for molecules situated between Ag nanoparticles
- The higher surface EF , the more localized are hot spots
- At low concentrations single particle enhancement occurs only in SERRS, not SERS, allowing lower concentrations to be detected
- The highest the enhancements (SMD) are the most uncontrollable from the experimental point of view

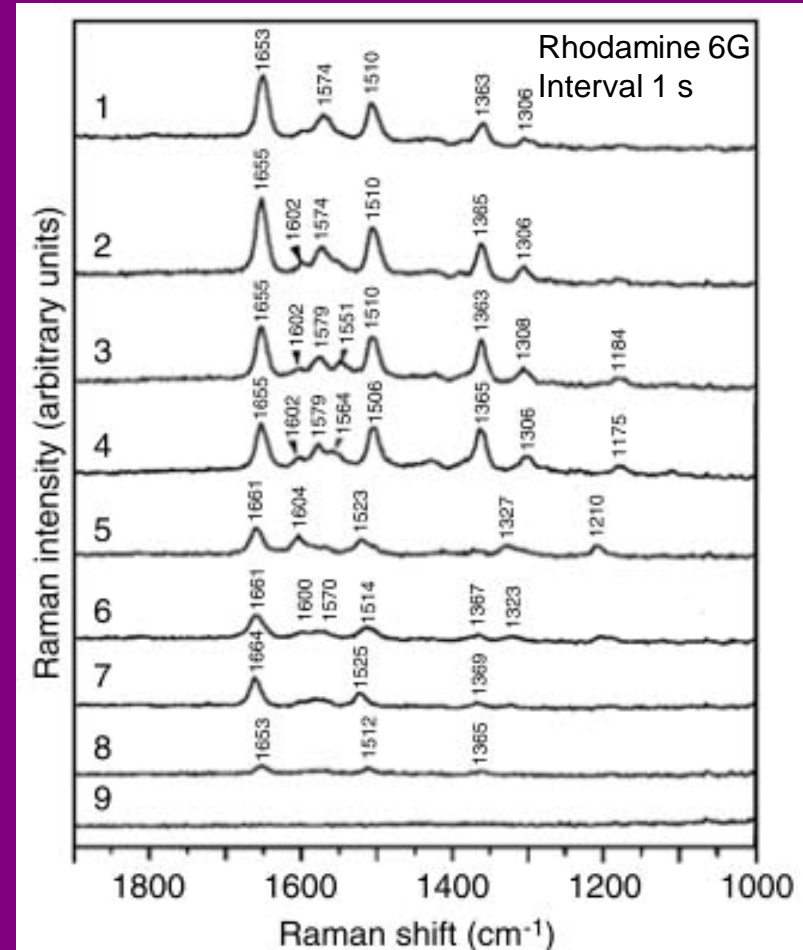


C. J. L. Constantino et al., *J. Raman Spectrosc.*, 36:574–580, 2005

A!

SERS fluctuations

- Intensity fluctuations with possible blinking or complete disappearing
- Spectral shape fluctuations, in either the relative intensities of the peaks, or the peak positions (Raman shifts) and widths, random peak appearance
- Evidence of SMD, because average SERS stable, SMD – no



E.C. Le Ru and P. G. Etchegoin, Principles of Surface-Enhanced Raman Spectroscopy and related plasmonic effects, Elsevier , 2009



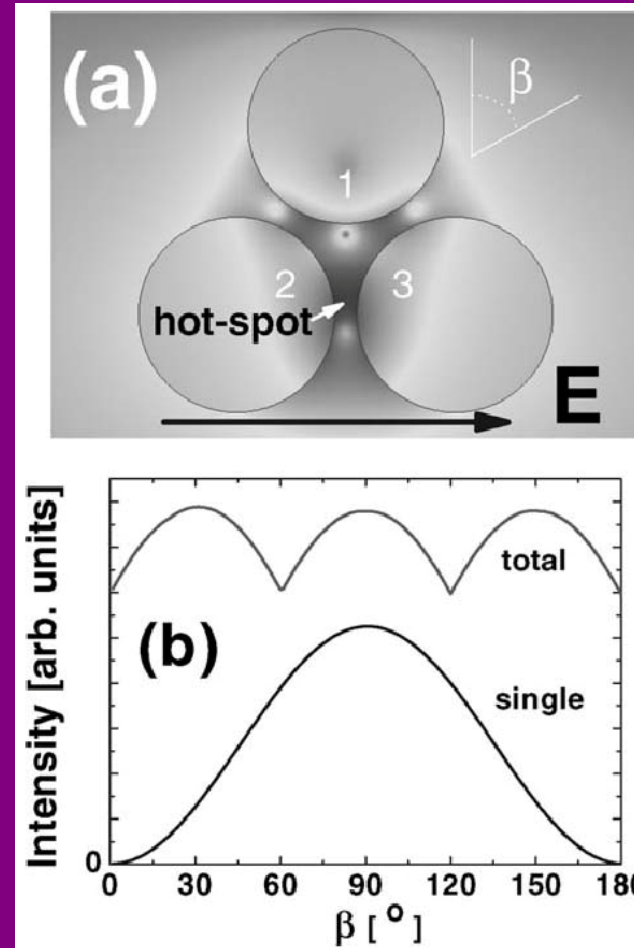
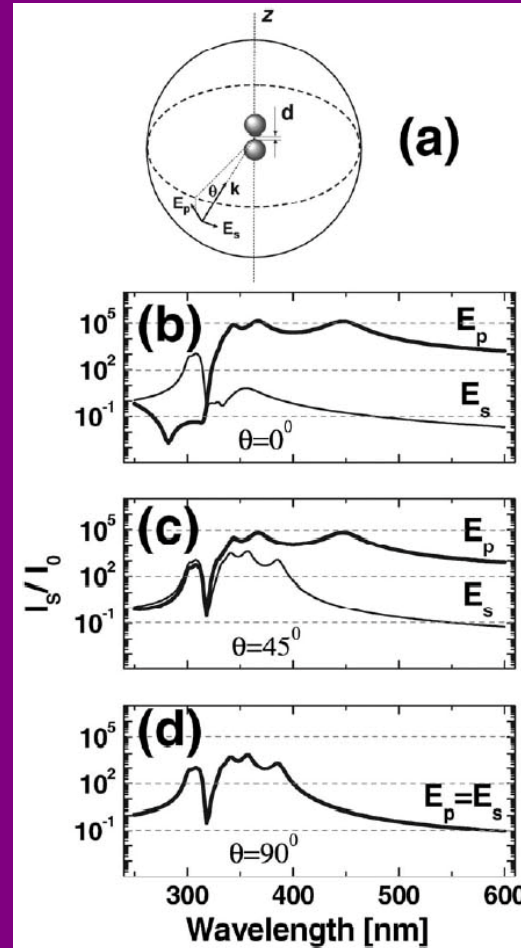
SERS fluctuation sources

- Photo-induced and site dependent – variation of the local field enhancement
- Submonolayer coverage of hot spots
- Photo-induced and spontaneous dynamics – chemistry change for long scans
- Photo-bleaching of dyes, photo-desorption, photo-induced surface diffusion,
- Substrate heating, and possibly substrate morphology changes (through photo-oxidation for example)
- Surface diffusion of a single molecule in-and-out of a hot-spot (for SMD)

A!

Polarization dependence

Dimer is polarization sensitive

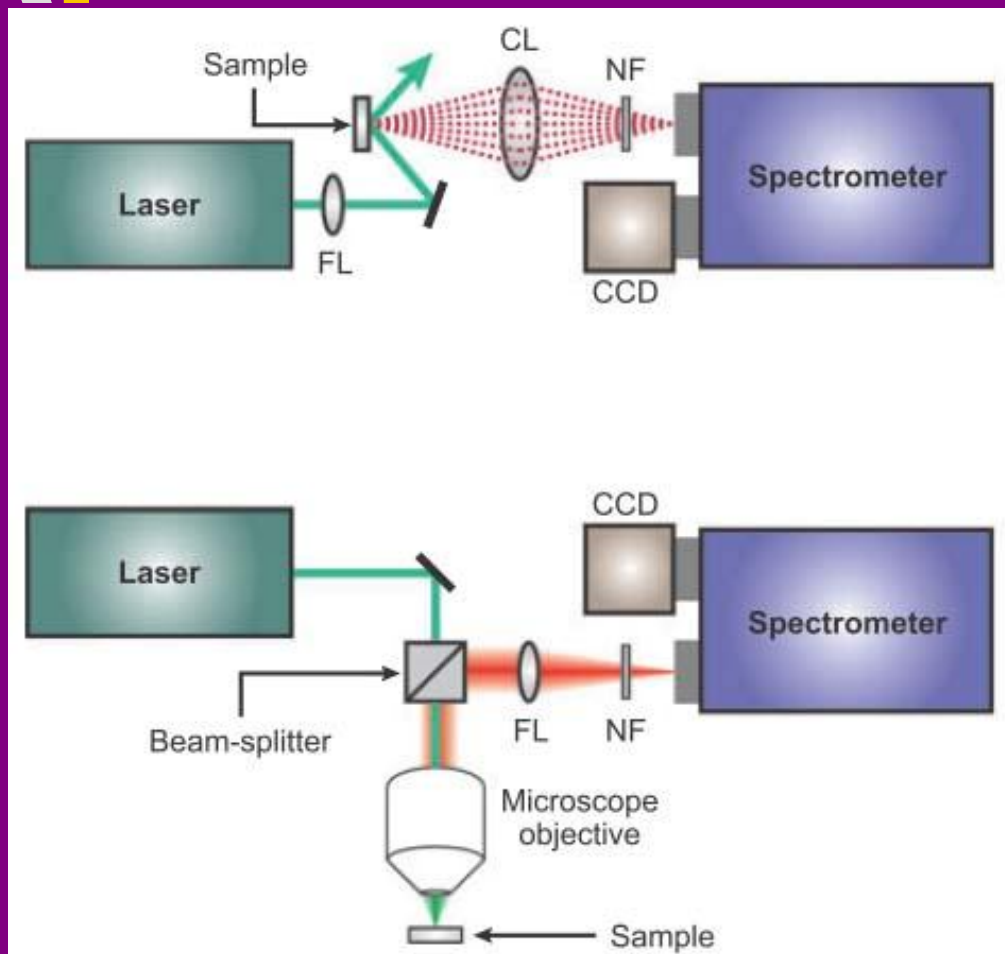


Practically isotropic

P. G. Etchegoin et al., Polarization-dependent effects in surface enhanced Raman scattering (SERS) *Phys. Chem. Chem. Phys.*, 2006, 8, 2624–2628

A!

Raman instrumentation



Excitation and Raman are spatially separated

The same optical way for excitation and Raman

Diameter of airy disk

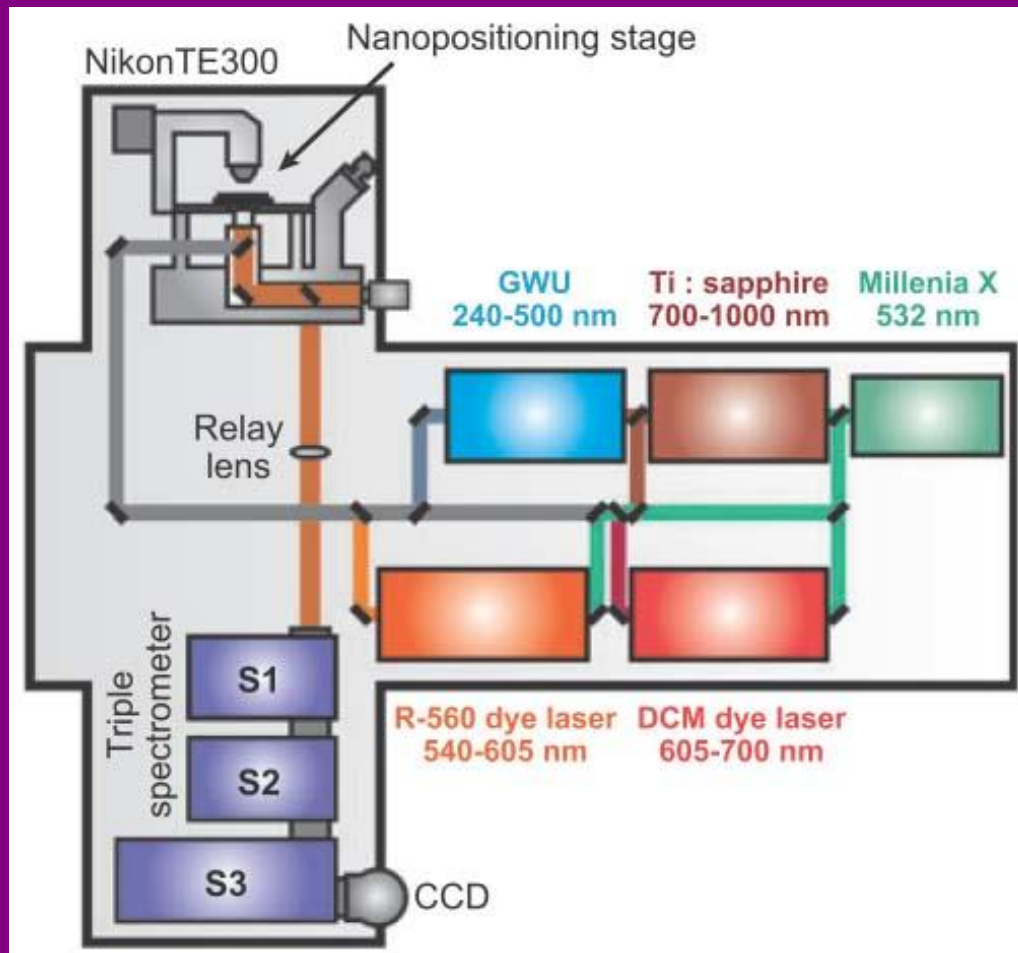
$$d = 1.22 / N.A.$$

N.A. - numerical aperture

Stiles P.L. *et al*, Annual Review of Analytical Chemistry, 1, 2008, p.601-26

A!

Multilaser Raman instrumentation



To avoid photogenerated processes

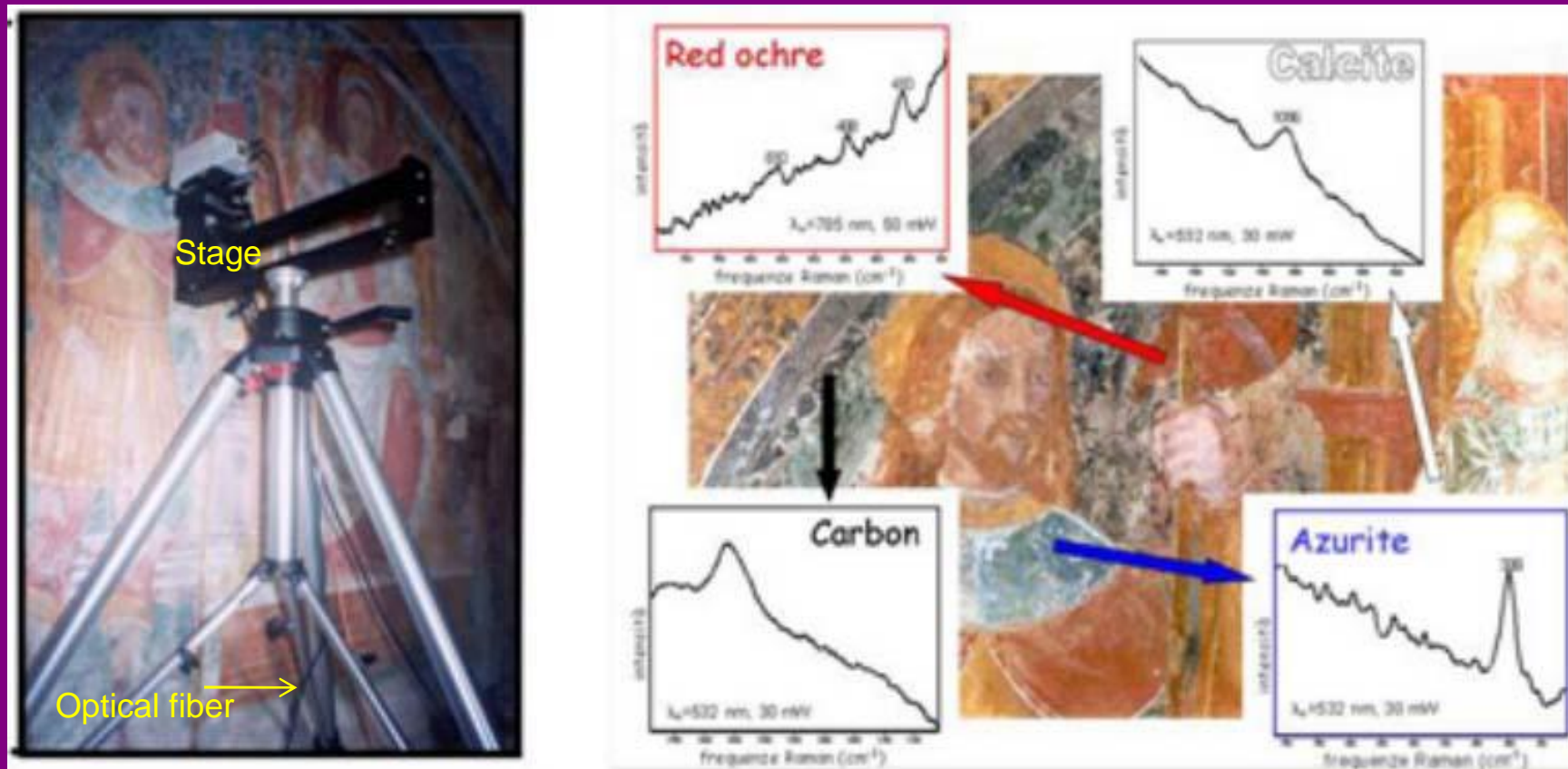
To decrease continuous Raman

To realize SERRS

Stiles P.L. *et al*, Annual Review of Analytical Chemistry, 1, 2008, p.601-26

A!

Portable Raman



www.jascoinc.com, RMP-300 Portable Raman Spectrometer

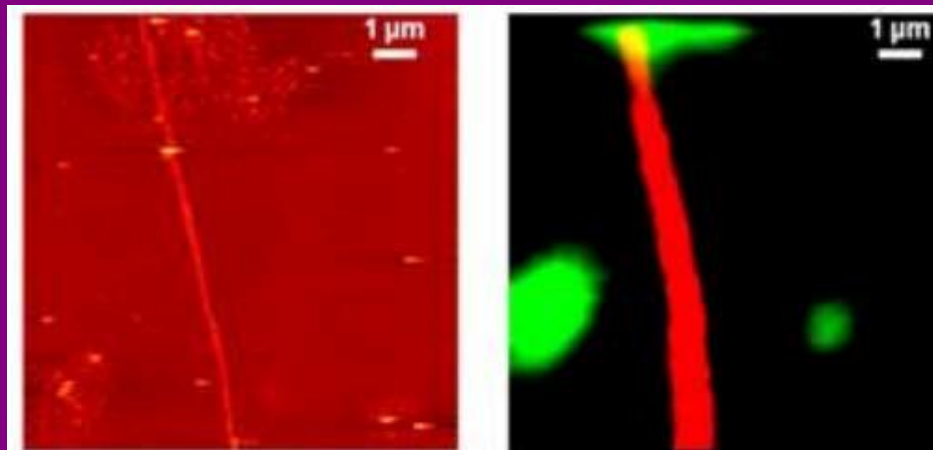


Applications

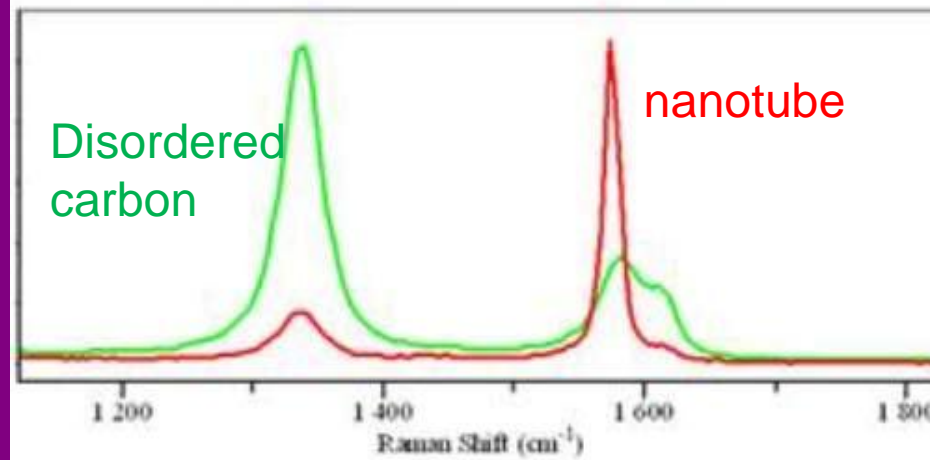
- Chemical identification (bonds)
- Physical identification (crystallinity, phases, graphene)
- Stress and diameter measurements (carbon nanotubes)
- Trace analysis (explosives and drug detection)
- Process monitoring (in-situ measurements)
- Uncovering painting
- Biology (DNA) and medicine (glucose *in-vivo*)
- Pharmacology

A! Single walled carbon nanotube on Si

AFM
10 x 10 um



Raman, step 250 nm
Time per point 5s



<http://www.horiba.com/scientific/products/raman-spectroscopy/raman-imaging/image-gallery/swcnt/>

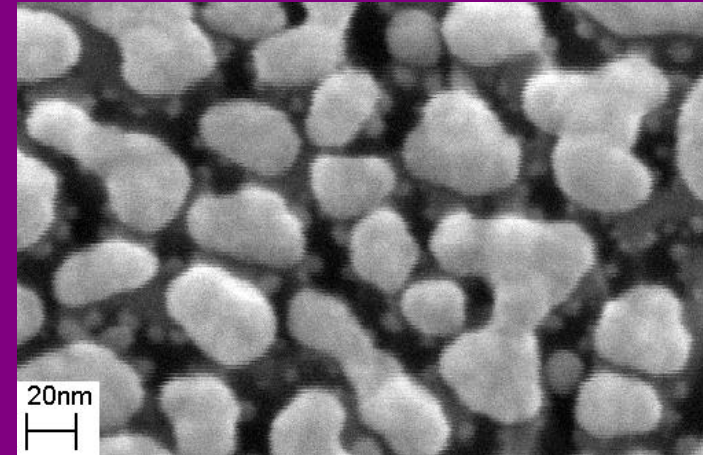
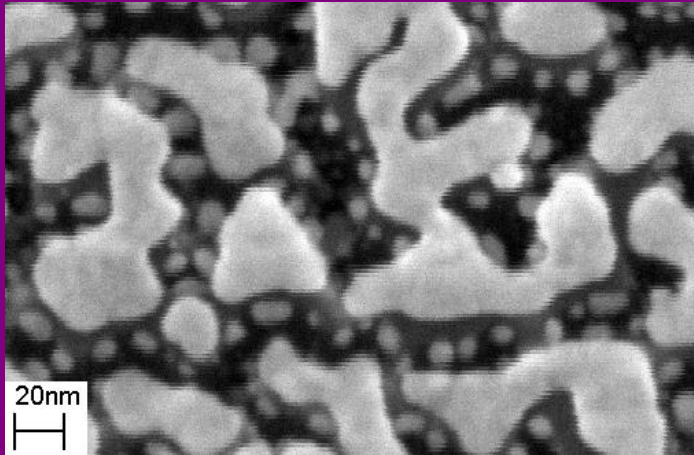
A!

SERS substrates with adhesion layer

Normal evaporation

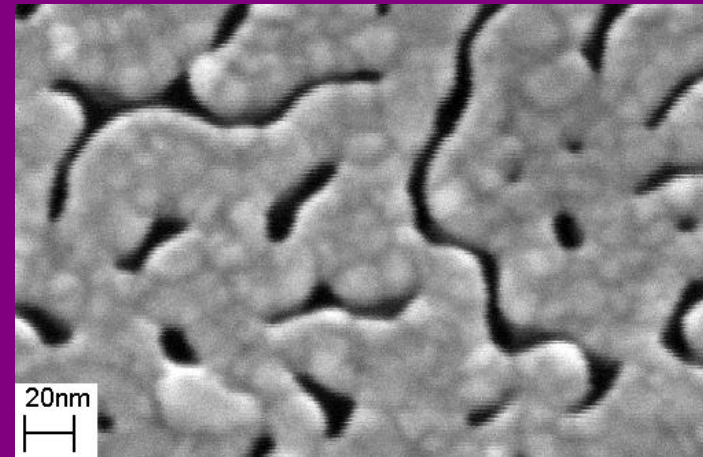
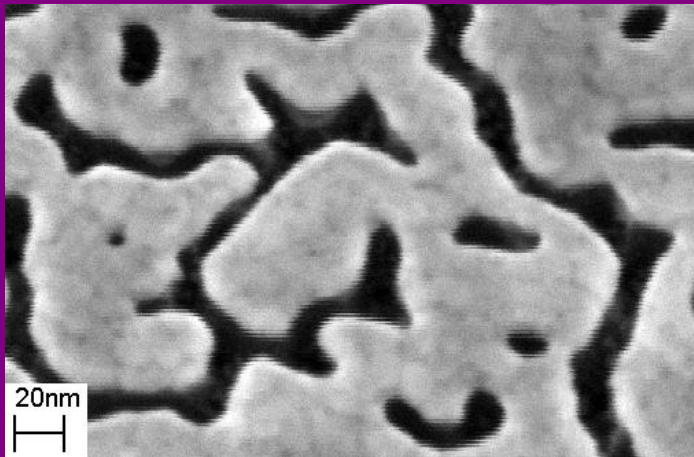
Evaporation angle 70°

Au=8nm,
tilted 30°



Ag=8nm,
tilted 30°

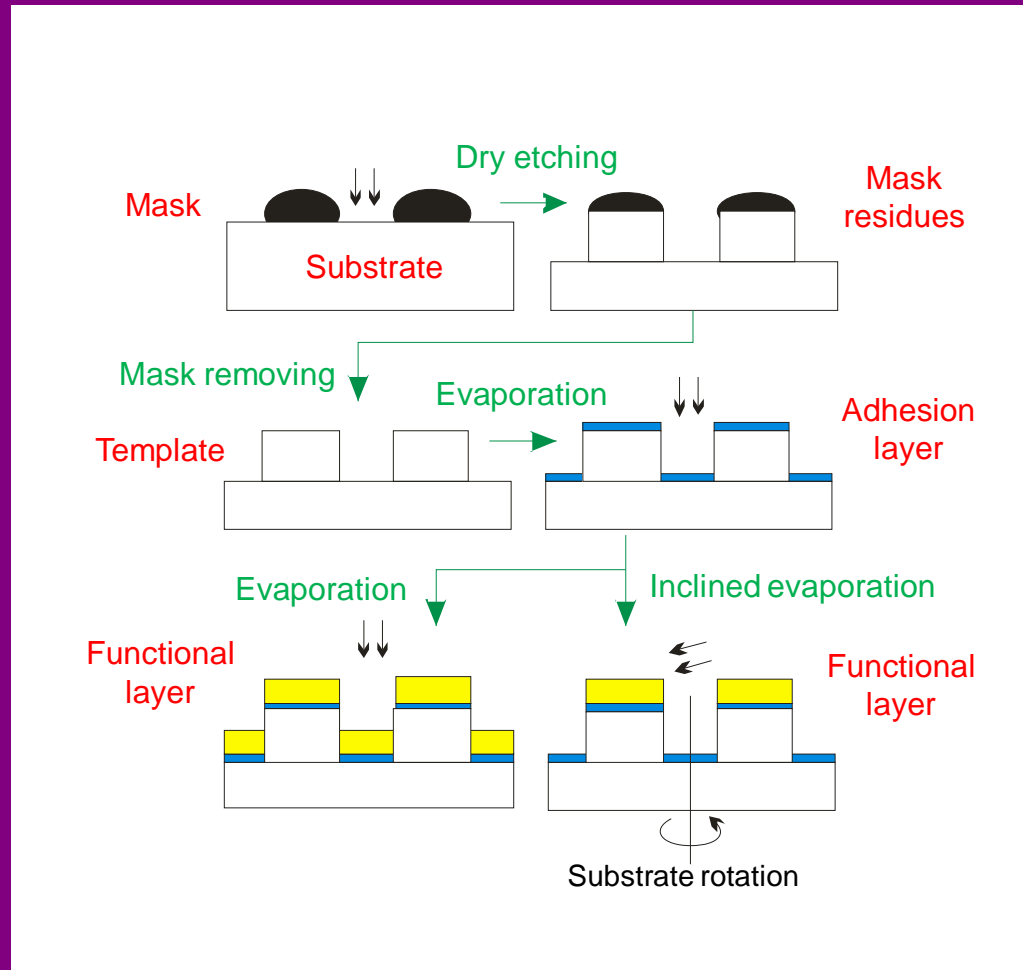
Ti=1 nm
Au=8nm,
tilted 30°



Ti=1 nm
Ag=8nm,
tilted 30°

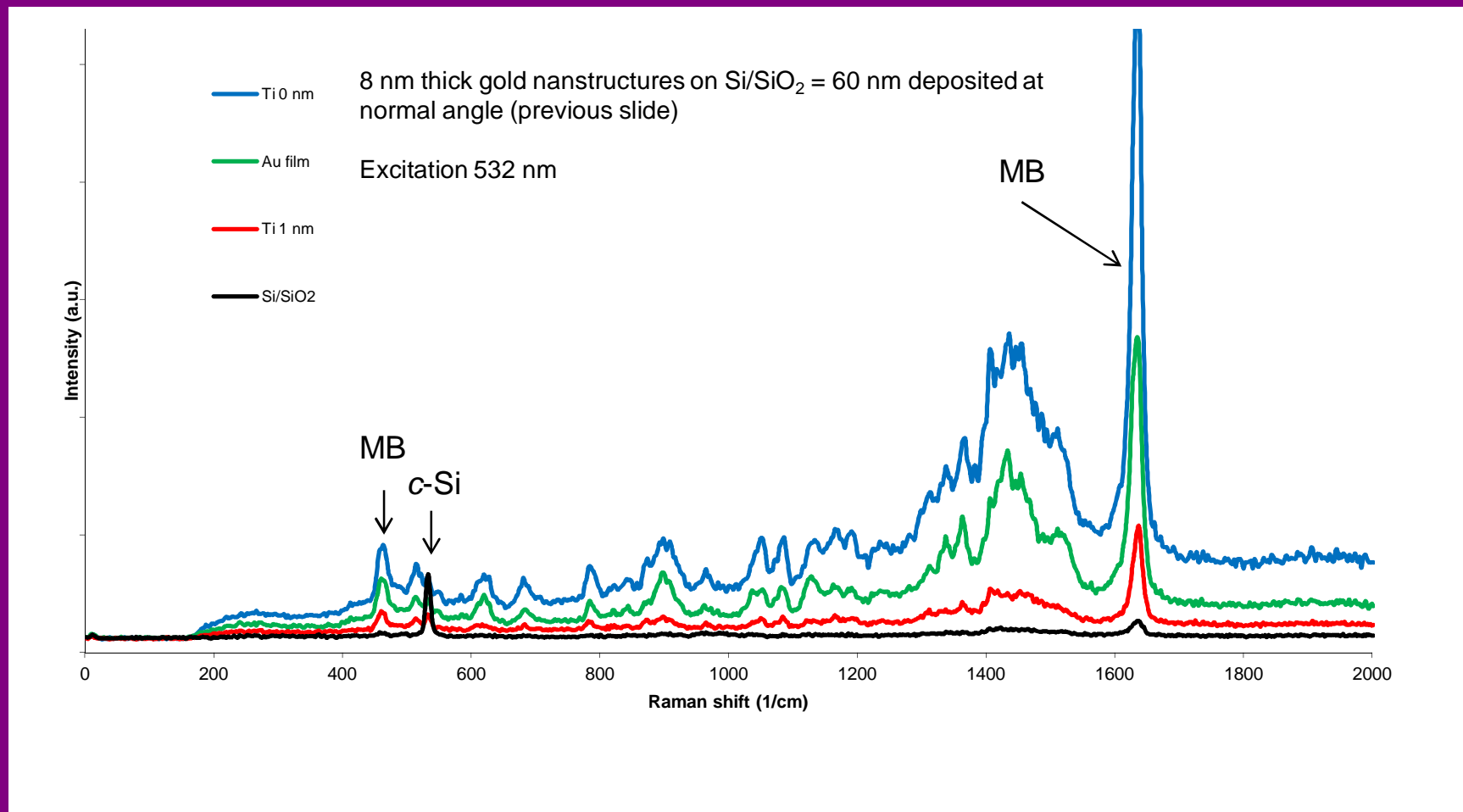
A!

Fabrication method of metal nanostructures on a template

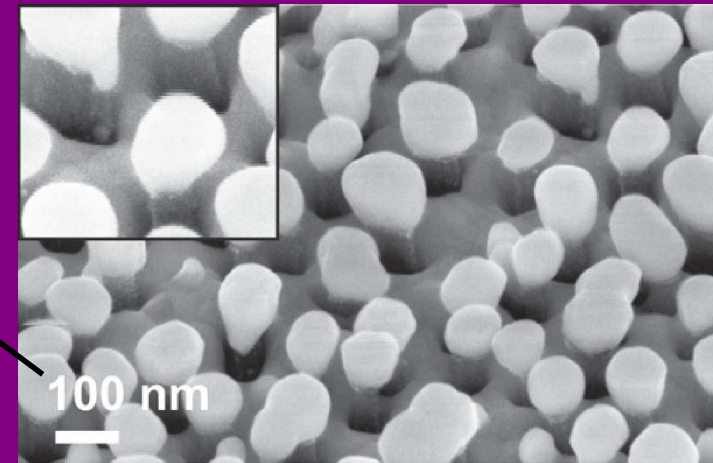
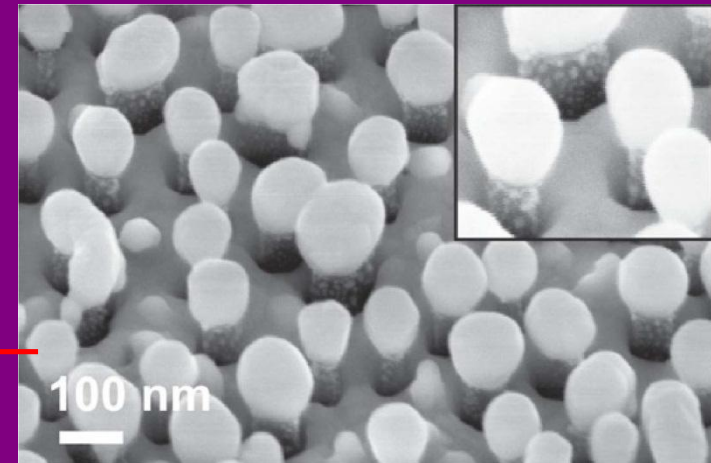
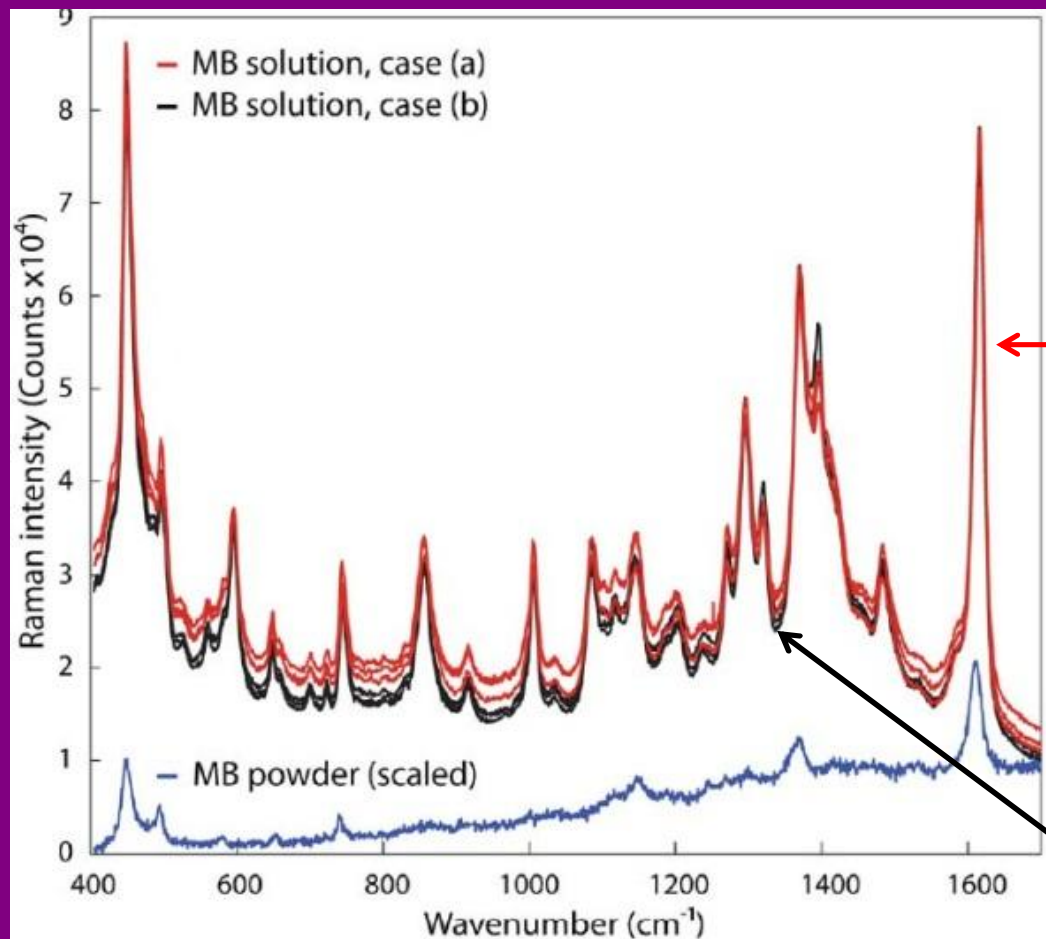


A!

SERS spectra of methylene blue for the gold nanostructures



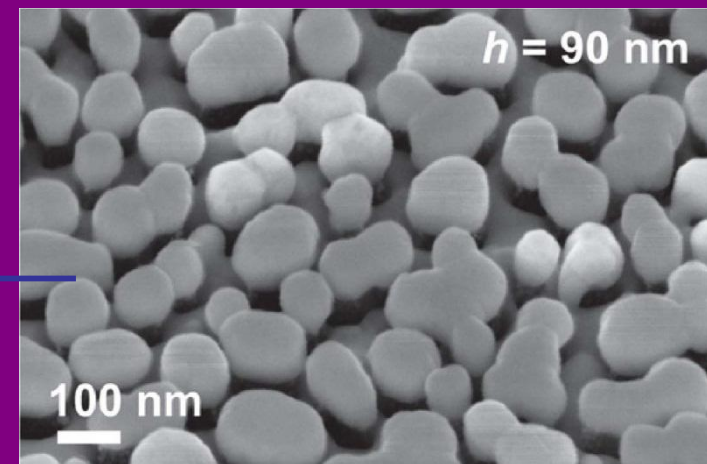
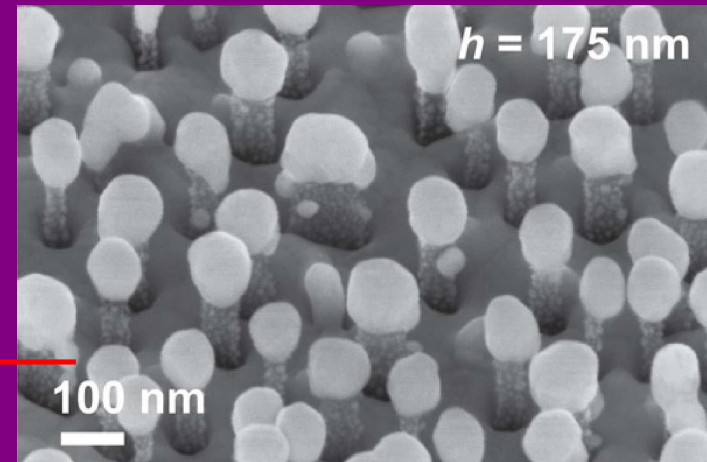
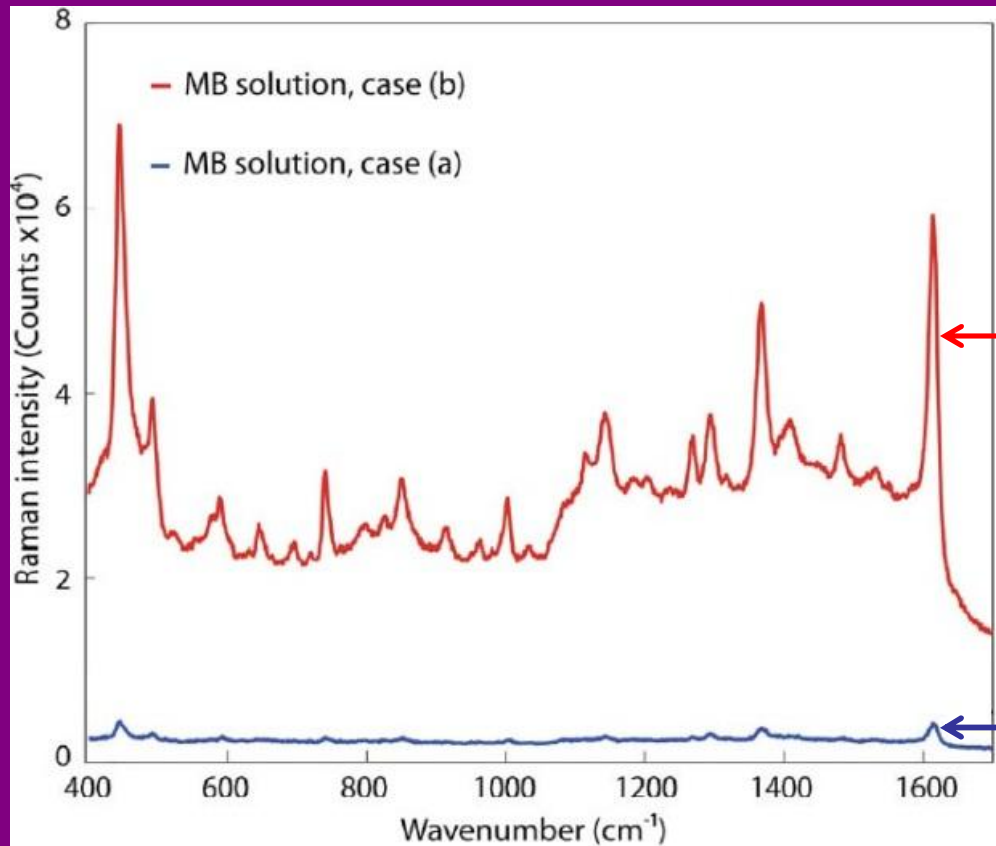
A! Large and small particles on the same SERS substrate



A. Shevchenko et al., *Appl. Phys. Lett.* 100, 171913 (2012)

A!

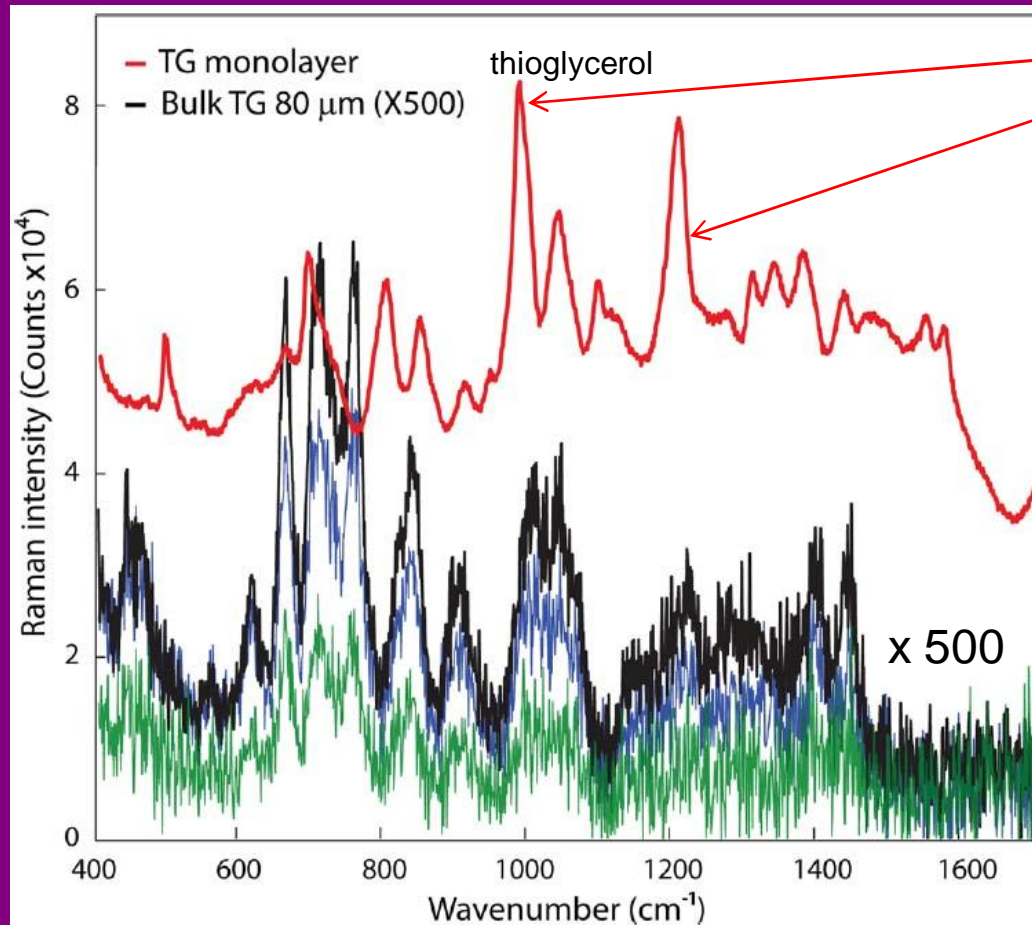
Effect of pillar height



A. Shevchenko et al., Appl. Phys. Lett. 100, 171913 (2012)

A!

EF measurement



Used for *EF* estimation

Thickness of thioglycerol layer is 80 μm (black), 48 μm (blue) and 25 μm (green)

A. Shevchenko et al., *Appl. Phys. Lett.* 100, 171913 (2012)

A! SERS vs fluorescence spectroscopy

- Fluorescence is very efficient – SMD
- Fluorescence is currently a well-established technique
- SERS has high specificity, providing a unique ‘fingerprint’ – background distinguish, multiplexing
- SERS is applied directly to the molecule, no fluorophore
- Any excitation wavelength for SERS
- Higher spectral specificity
- Infrared excitation

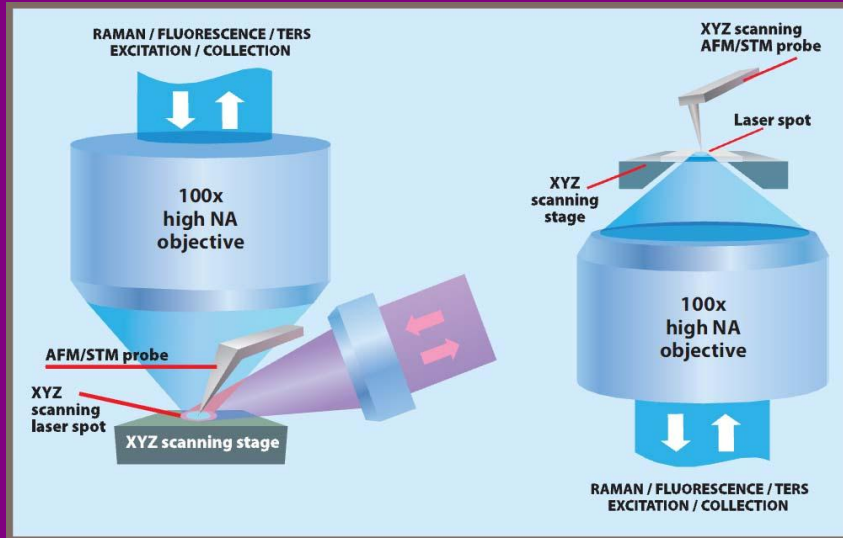


Biological applications of SERS

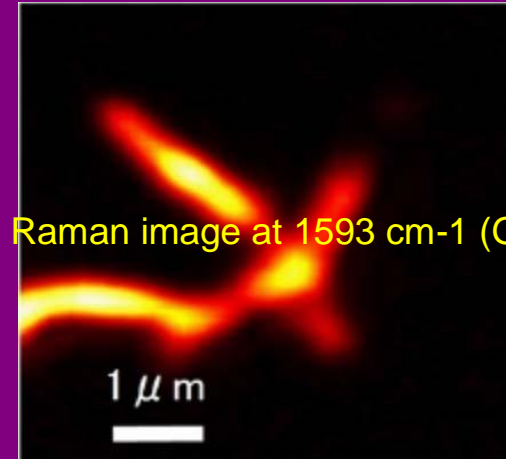
- Intracellular measurements
- SERS images (optical bioimaging)
- SERS labels for biomolecule identifying
- Biocompatible nanosensors
- Glucose measurement in vivo
- Characterization of bacteria
- DNA detection

A!

TERS

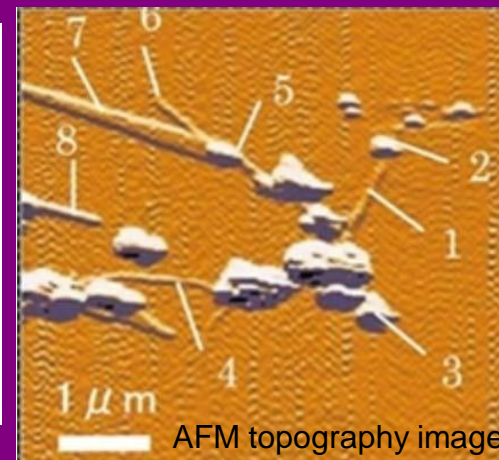
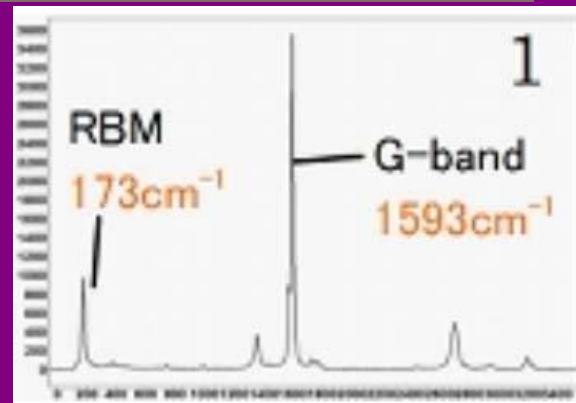


Single-walled Carbon Nanotubes



Raman image at 1593 cm⁻¹ (G-band)

TERS problem is experimental difficulties
TERS is aimed at creating a hot-spot on demand at a specific location on a substrate, because we cannot put the probe exactly in 'hot spot' of SERS array



AFM topography image

www.ntmdt.us, NTEGRA Spectra: Nano-Raman Imaging
www.tokyoinst.co.jp, Nanofinder@30



Summary

- Metal nanostructures provide huge *EF* of the Raman scattering, making possible single molecule detection
- The enhancement happens due to SPR and requires nanotechnology and simulations to produce nanoengineered SERS substrate
- High informativity and sensitivity of SERS bursted multiple applications of the method in different areas
- SERS substrate fabrication, distribution and reproducibility are still main problems for SERS



SERS future

- Commercial production of reproducible and chip SERS substrate
- Wide application of SERRS with improvement of tunable lasers
- Application of new plasmonic materials (graphene, semiconductors)
- Standardization and data bases for spectrum interpretation



Questions

- Is it possible to do SERS of metals?
- What is about SERS of mixer of compounds?
- Is Raman qualitative or quantitative?
- Does Raman require any sample preparation?
- Is Raman destructive?
- Is fluorescence a problem for SERS?
- Why we have fluctuations in SERS?
- What is surface selection rules?



Thank you for attention