Title: Surface-Enhanced Raman Spectroscopy and its Progeny

Date: Nov 29, 2007 04:00 PM

URL: http://pirsa.org/07110059

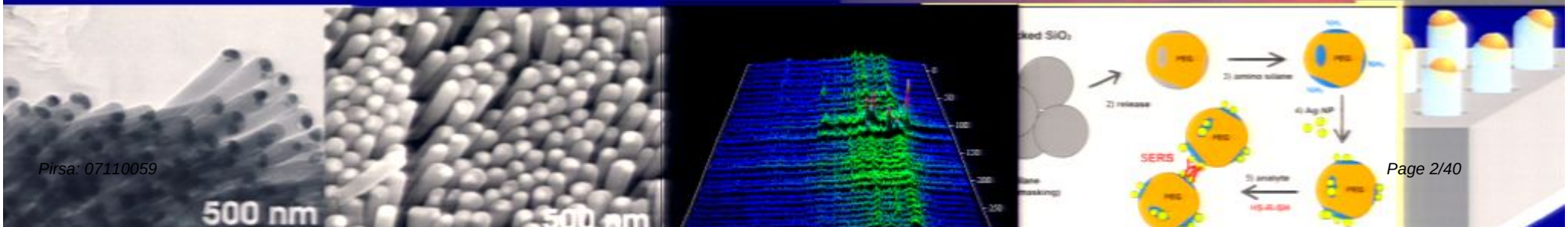
Abstract: Some thirty years ago surface-enhanced Raman (SERS) was discovered. In a nutshell, molecules positioned near roughened silver and gold surfaces were found to produce Raman spectra some 6 orders more intense than what an equivalent number of solution-phase molecules did. A large number of mechanisms were proposed to account for this spectacular effect, among which the one that seems to account for most of the observations essentially ascribes SERS to the concentration of the optical field in appropriately structured, interacting nanoscale features which operate both on the incident and Raman-scattered light. This concentration is to be appreciable only for features in which strong and narrow localized surface plasmons were excited. This Â“plasmonicÂ” model not only accounted for many of SERS seminal features but also gave birth to the research fields of plasmonics and so-called metamaterials most of which achieve the necessary conditions governing the electrical permittivity and magnetic susceptibility of metamaterials in wavelength regions where plasmons are excited.
SERS was again in the news approximately 10 years ago when a number of groups pointed out that SERS from individual molecules could be observed leading some to speculate that this observation challenged the plasmonic origin of SERS. The discovery of single-molecule SERS, coincident with the intense interest of the research community in nanoscience and technology, produced a renaissance of interest in SERS that is still with us. The work of the past half dozen years reaffirmed SERS as ultimately a plasmonic effect wherein most SERS-active systems are actually rather heterogeneous with most of the enhancement originating from Â“hot spotsÂ” where the enhancement could top 10 orders of magnitude averaged over territory where the enhancement is rather low. The major current challenge in the field is to devise nanostructures where the hot spots dominate, leading to systems with an inordinate ability to focus electromagnetic fields so as to produce not only extraordinarily intense SERS (presumably as a super-sensitive chemical analysis tool) but also as loci where other unusual photo-induced physical and chemical processes occur when the system is illuminated with rather banal light sources. The talk will illustrate some of the most recent advances in this field.

Surface Enhanced Raman and its progeny

Gary Braun, SeungJoon Lee, Brian Piorek, Martin Schierhorn, Dwight Seferos, Blanka Vlckova (Charles University, Prague)

Norbert Reich, Carl Meinhart and Martin Moskovits

Perimeter Institute and the Guelph-Waterloo Graduate Institute, November 2007



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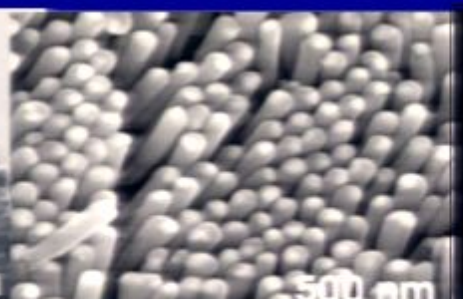
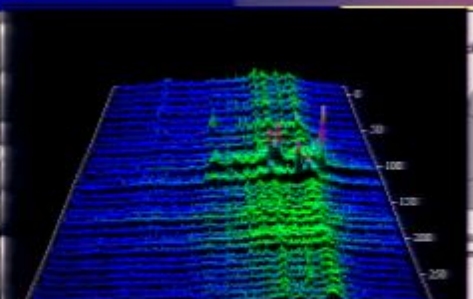


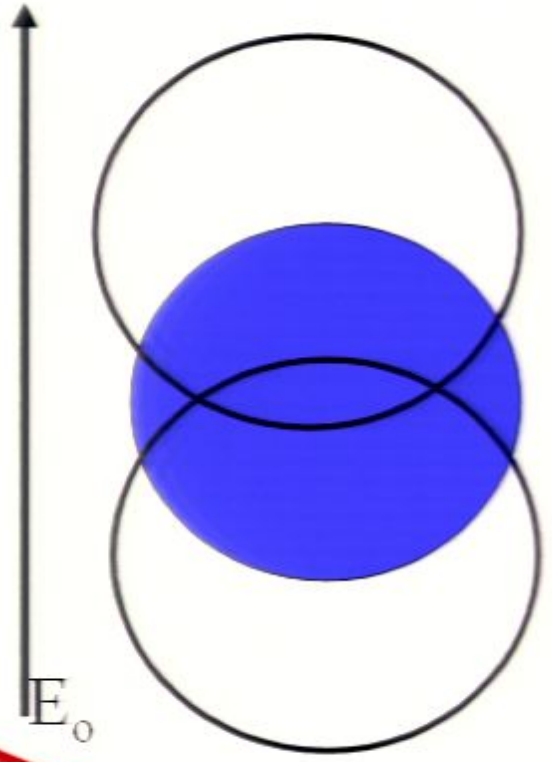


SERS was first observed in 1974, "discovered" in 1977, explained in terms of localized surface plasmons in 1978, re-discovered as single-molecule SERS in 1996 and re-explained in terms of "hot spots" due to coupled surface plasmons in 1999, rediscovering an effect predicted in 1980.

Quick summary

$$\alpha = R^3 \frac{\varepsilon - 1}{\varepsilon + 2} \qquad \varepsilon = \varepsilon_b + 1 - \frac{\omega_p^2}{\omega^2 + i\omega\gamma}$$

$$\alpha = \frac{R^3(\varepsilon_b \omega^2 - \omega_p^2) + i\omega\gamma\varepsilon_b}{((\varepsilon_b + 3)\omega^2 - \omega_p^2) + i\omega\gamma(\varepsilon_b + 3)}$$

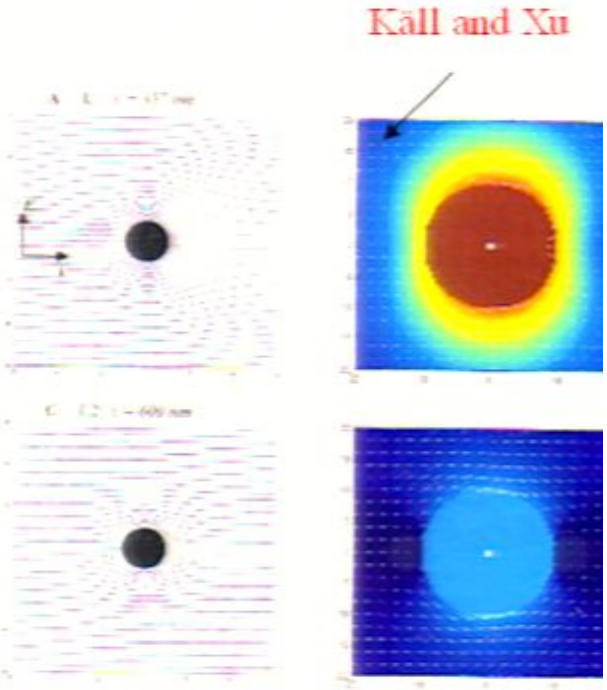


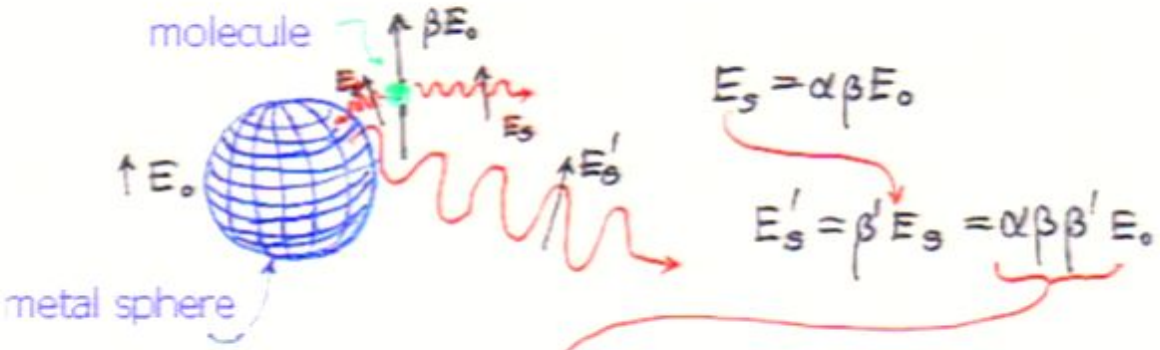
$$\omega_R = \frac{\omega_p}{\sqrt{\varepsilon_b + 3}}$$

All else being equal, this term predicts which metals will show the most intense SERS and their rank as enhancers.

Surface-plasmon resonance

The one-two enhancement punch





$$E_s = \alpha\beta E_0$$

$$E_s' = \beta' E_s = \alpha\beta\beta' E_0$$

$$I_{SERS} \propto |E_s'|^2 = |\alpha|^2 |\beta\beta'|^2 |E_0|^2$$

$$I_{SERS} \tilde{\propto} |\alpha|^2 |\beta|^4 I_0$$

$$I_{Raman} \propto |\alpha|^2 I_0$$

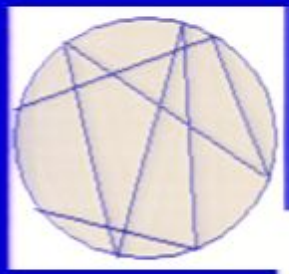
The SERS scattering comes from the metal and not the molecule

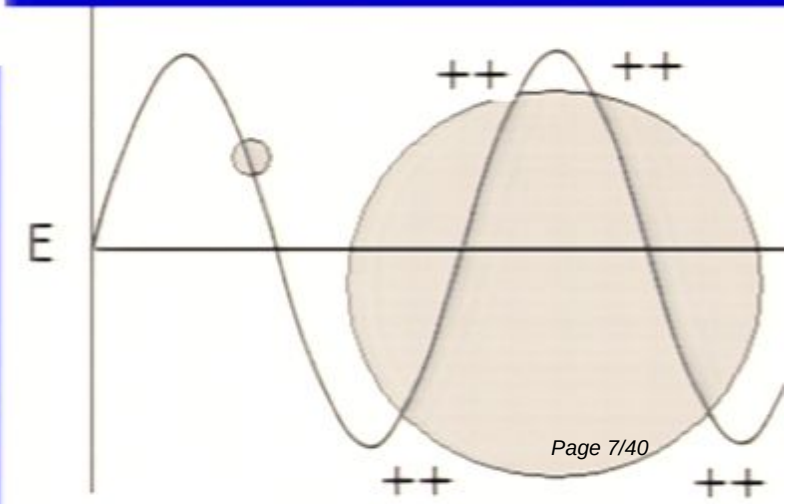
Enhancement, $G = I_{SERS}/I_{Raman} \sim \beta^4$ for small Stokes shift and $\sim \beta^{2-4}$ for very large Stokes shifts.

An effect that works well ONLY at the nanoscale.

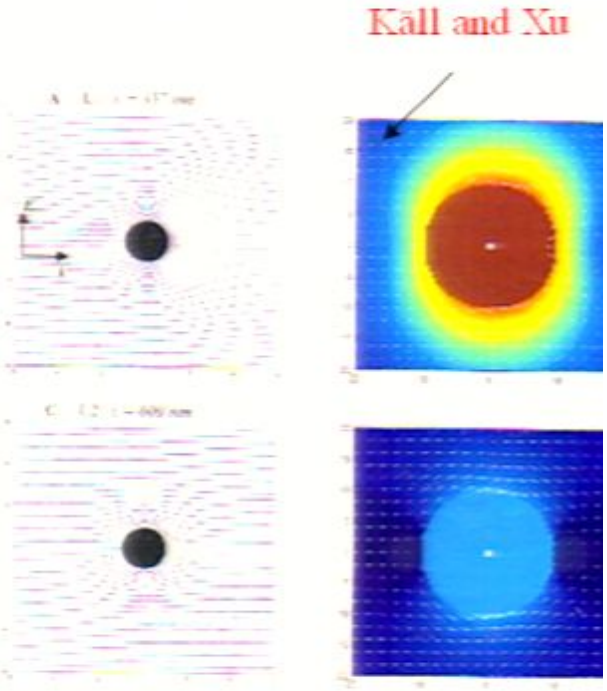
Too big: dissipation of optically pumped energy into heat (excitation of multipoles)

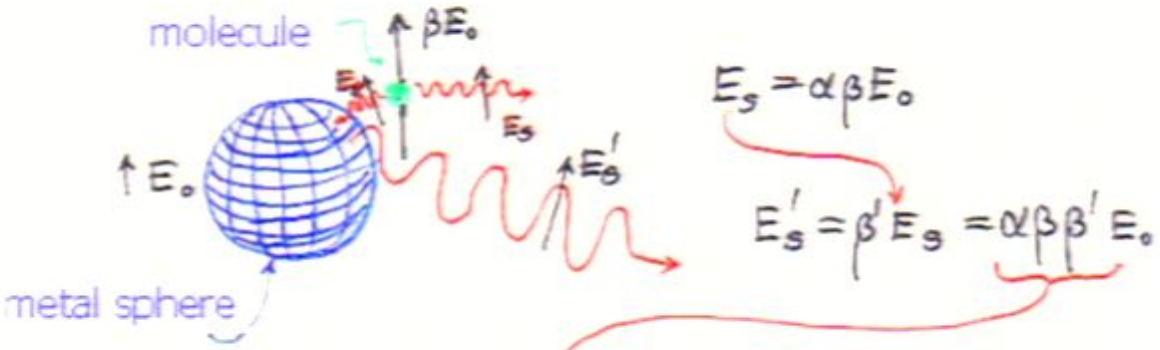
Too small: the conductivity of the metal is reduced (electron scattering at the nanostructure's surfaces) and hence the quality factor of the surface plasmon resonance





The one-two enhancement punch





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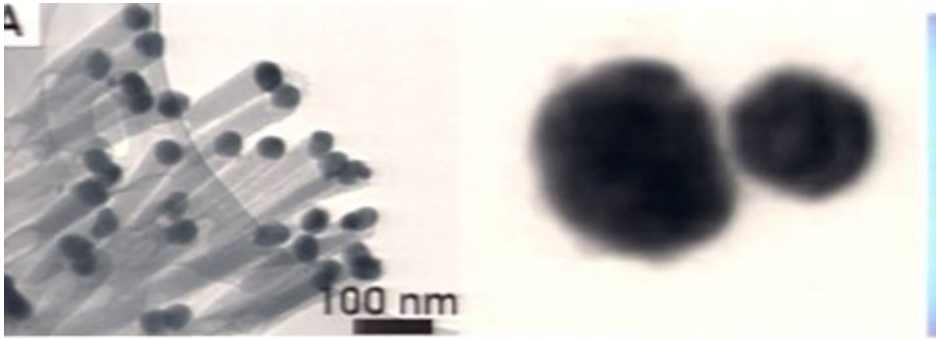
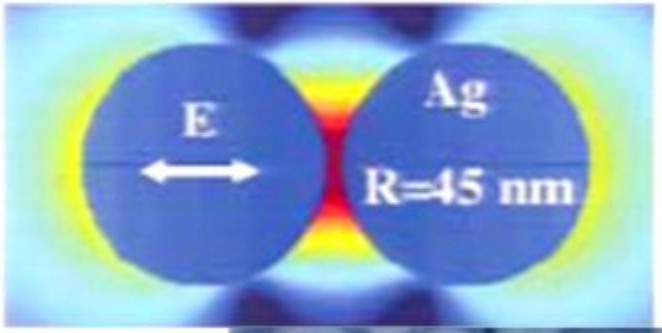
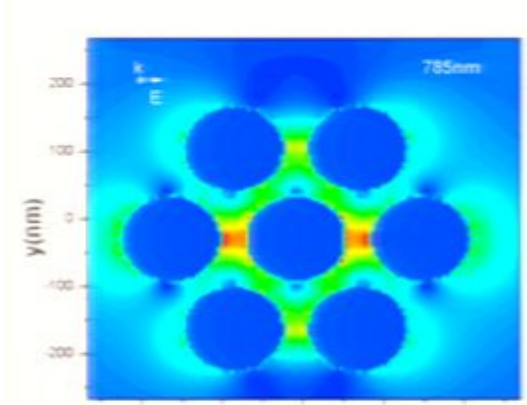
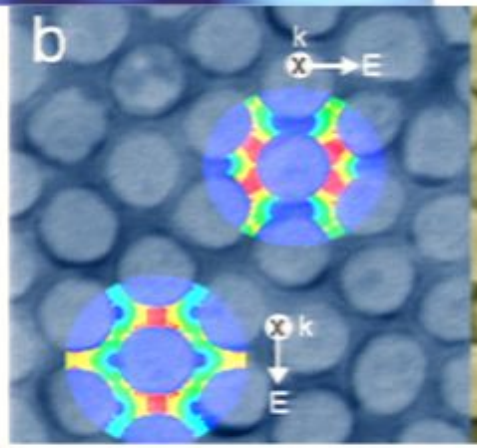
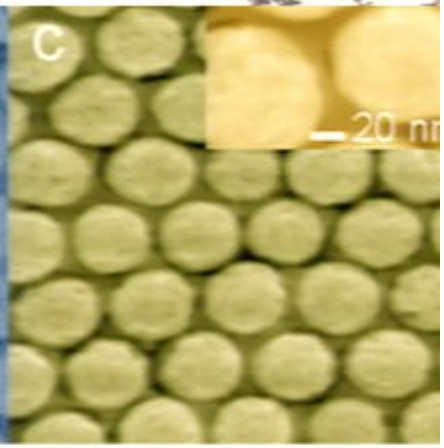
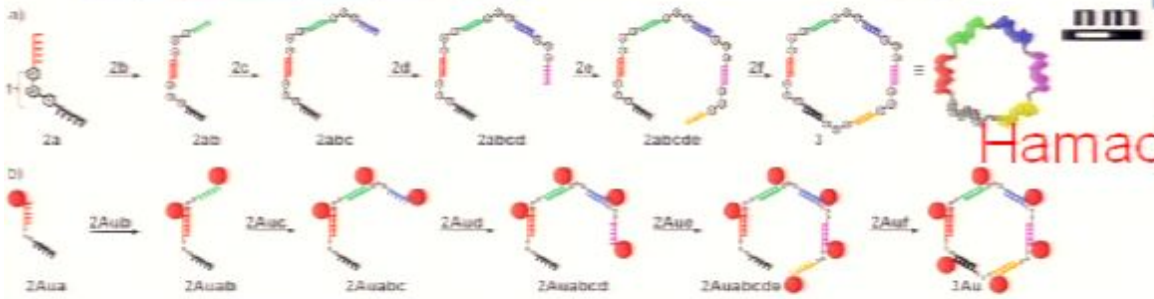






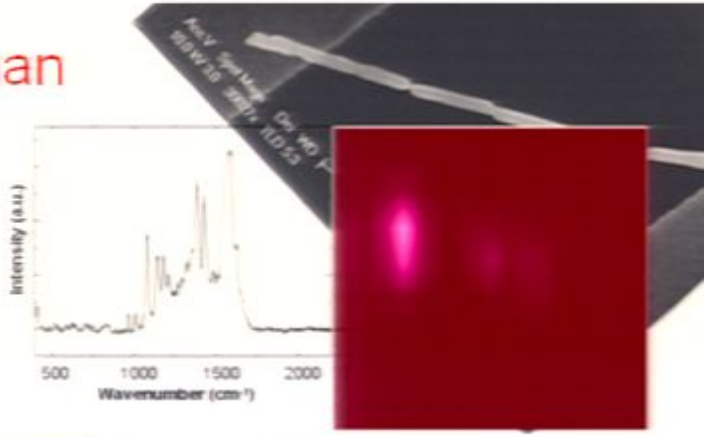




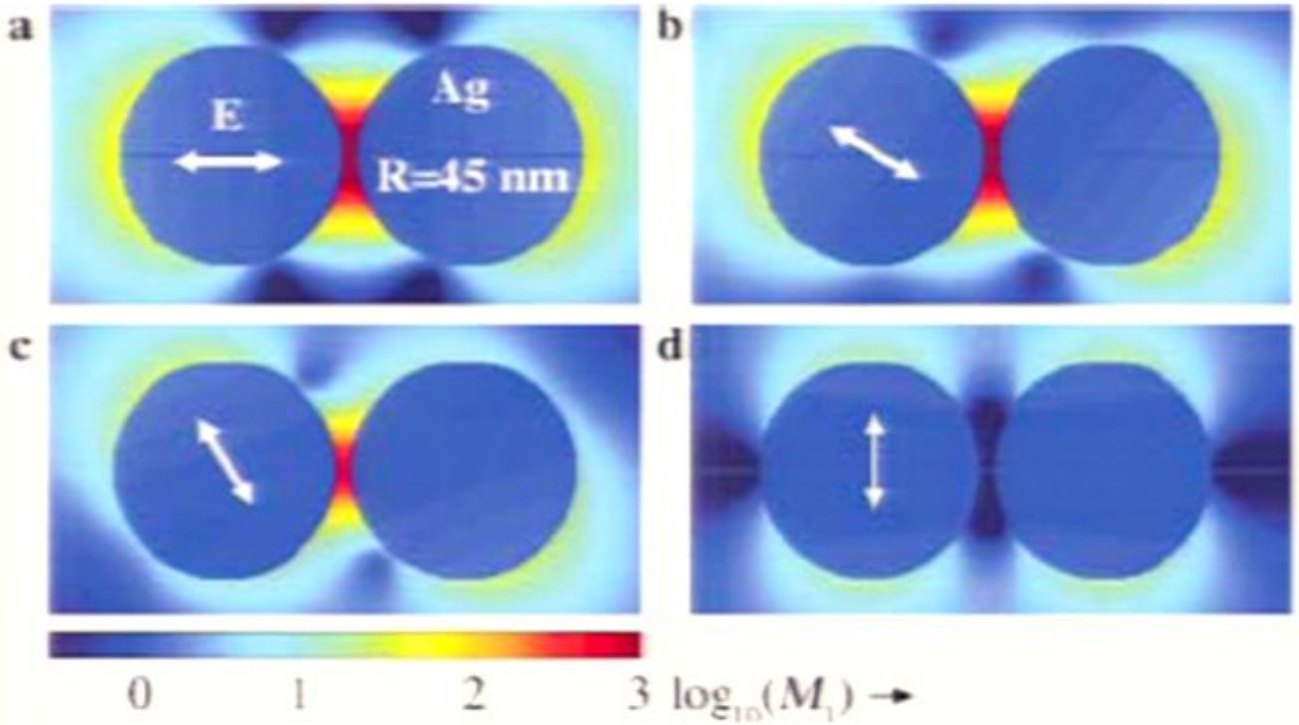


nm

Hamadi Sleiman



But the most intense SERS was always observed in systems of coupled particles

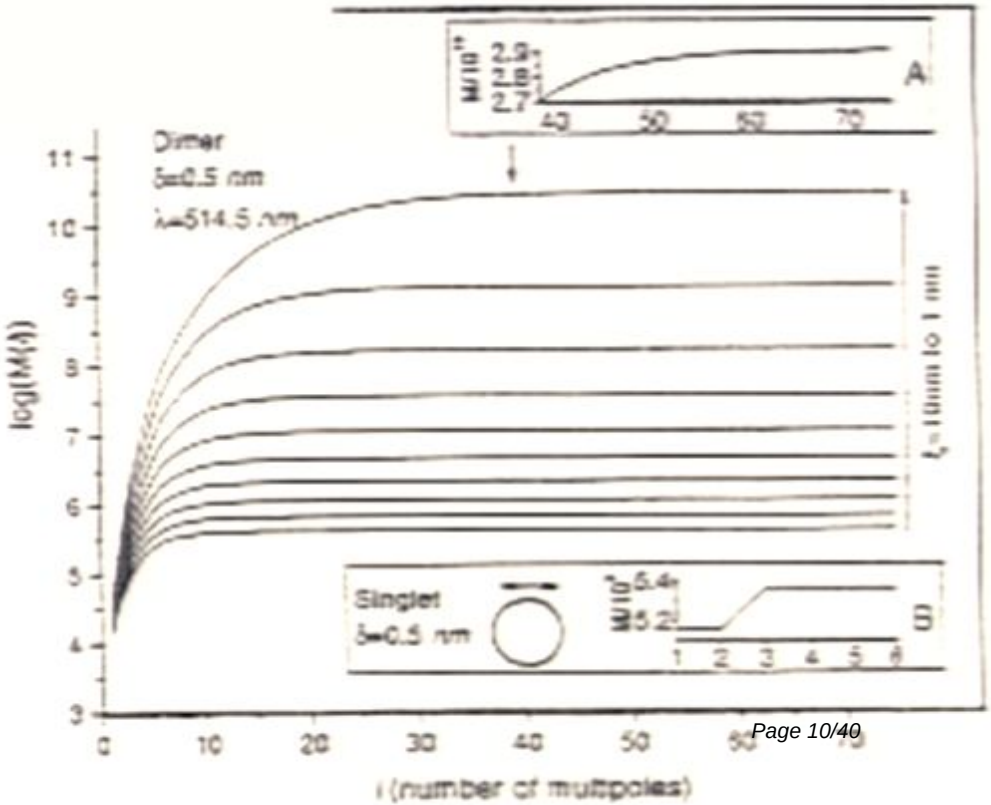


Formation of em
hot spot in inter-
particle site

(predicted by Metiu
in 1980)

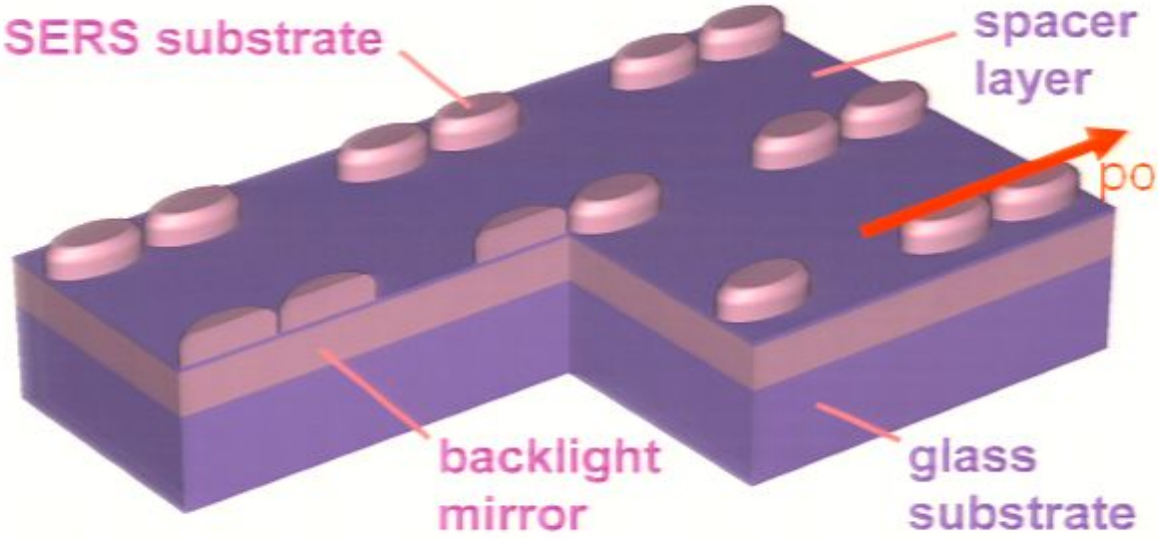
Xu and Käll

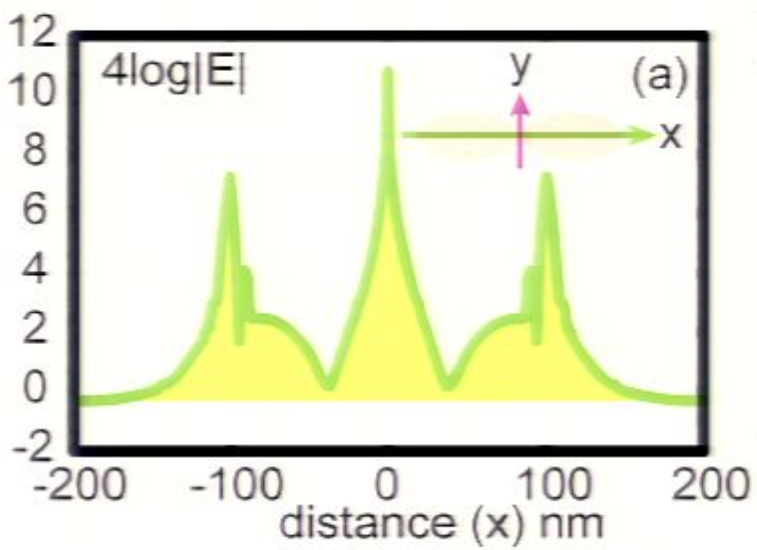
SERS signal is normally an average over a greatly inhomogeneous system

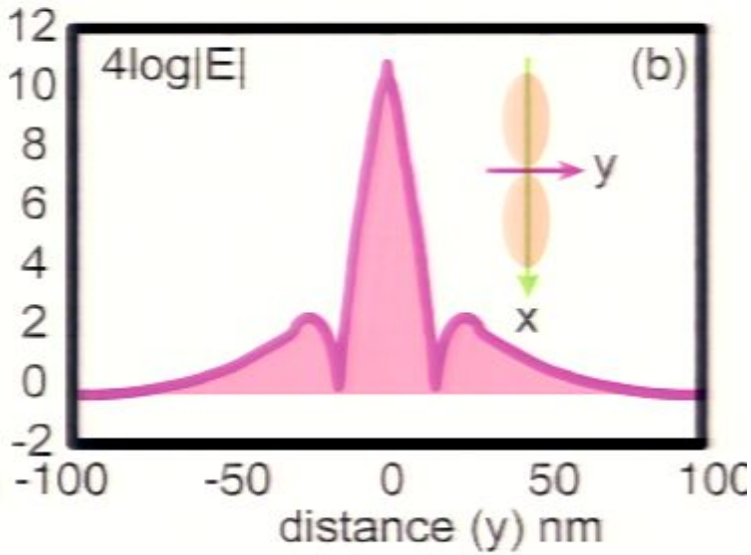


Nanoantennas

Shalaev et al

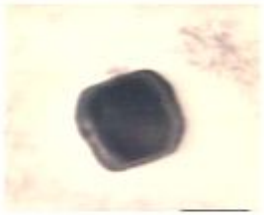


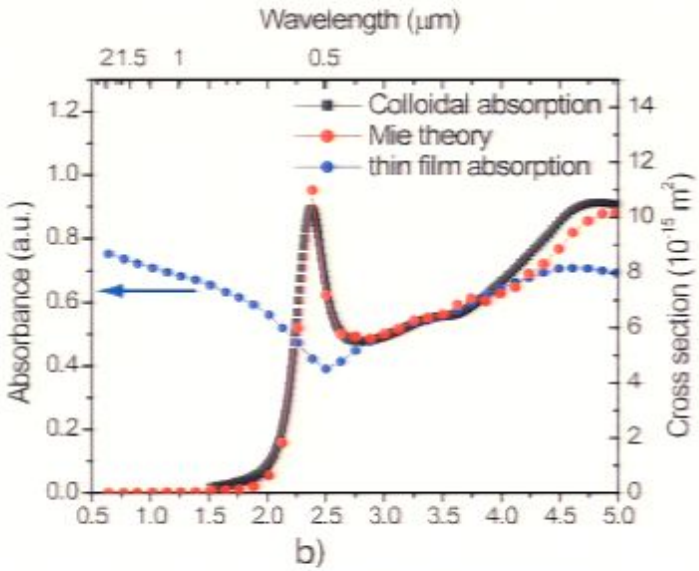


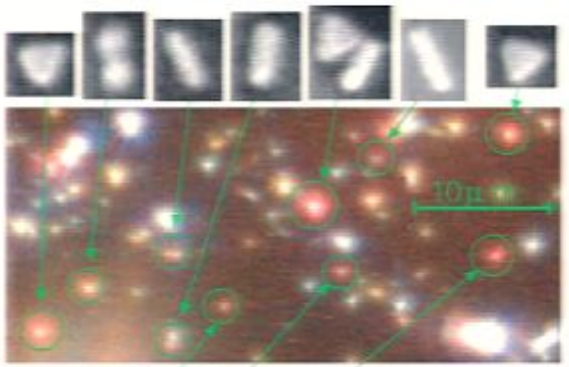


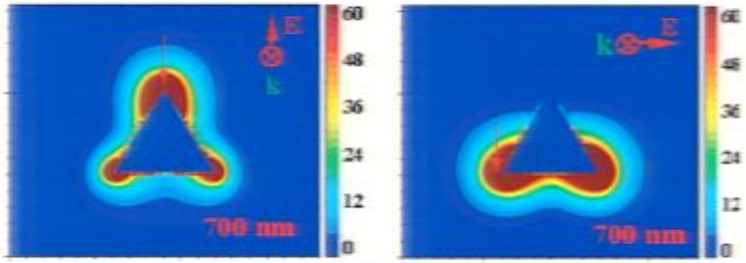
Computed log "SERS enhancement" along two trajectories of a nanoantenna illuminated in the SP region

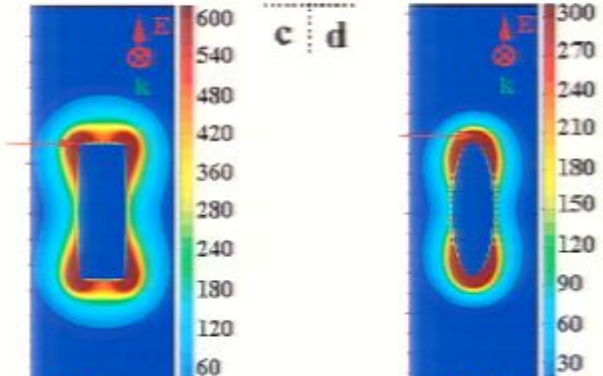
An entire new field of optical physics – plasmonics – was born as a result



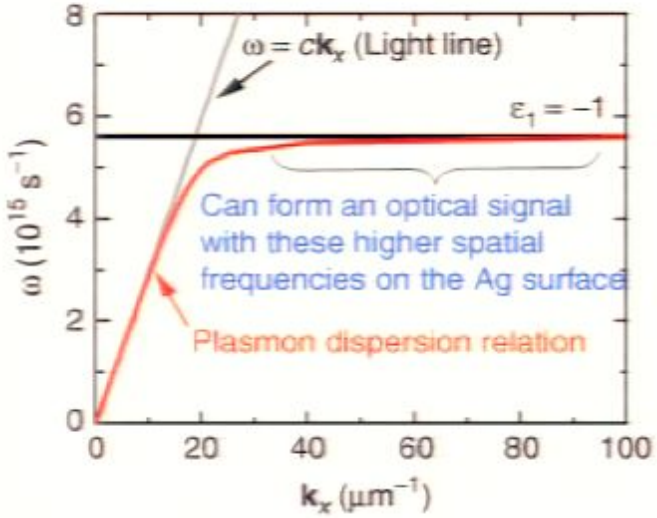


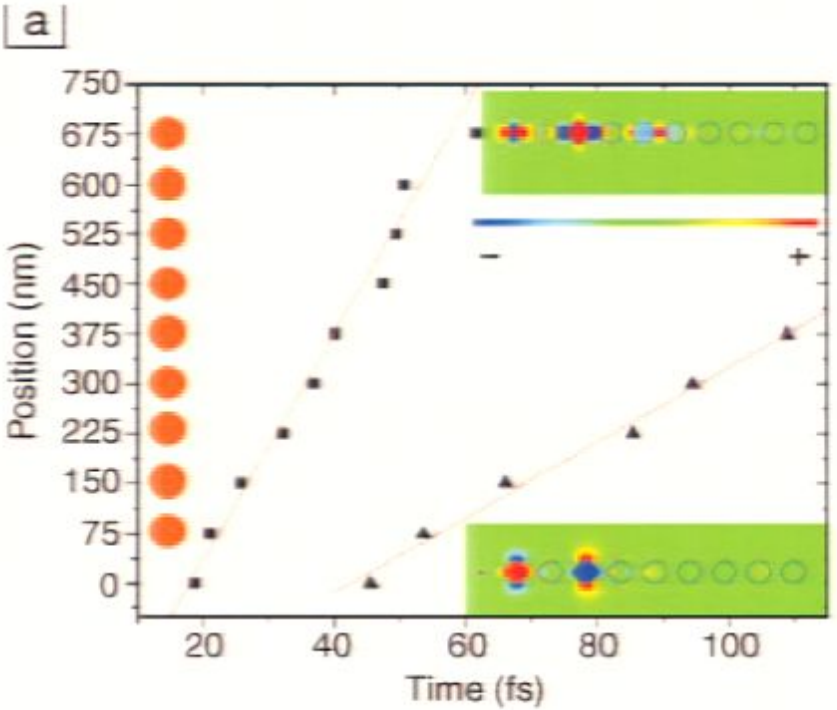


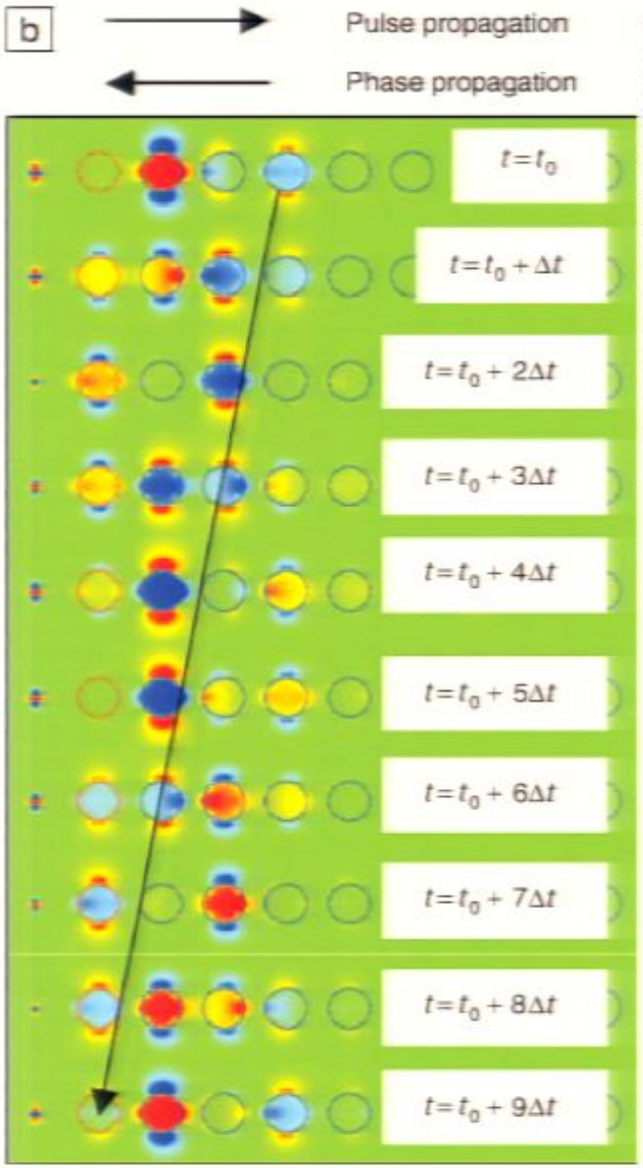




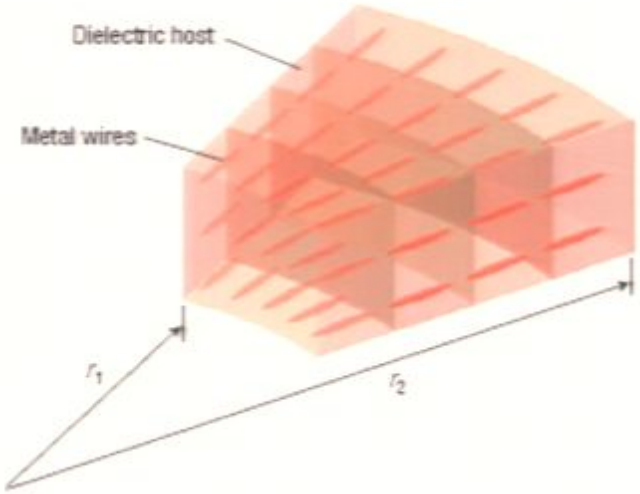
54E. Hao and G. C. Schatz, J. Chem. Phys. **120**, 357 2004



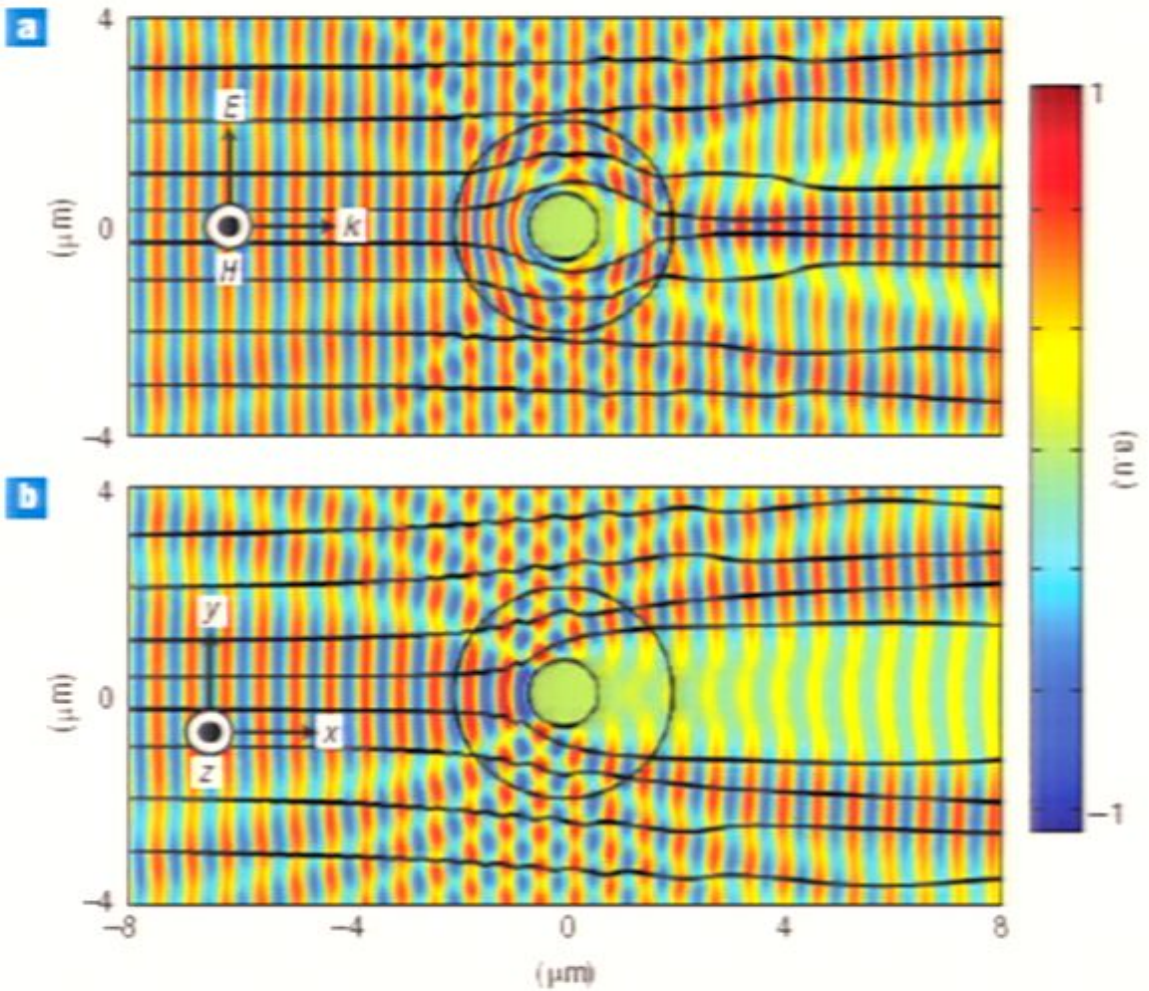




(a) Pulse peak positions over time in a plasmon waveguide consisti of spherical particles with a diameter 50 nm for both longitudinal (solid squares) and transverse (solid triangles) polarization. The solid circles along th ordinate indicate the position of the A nanoparticles. A snapshot of the x component of the electric field in the xy plane for longitudinal polarization i shown in the upper inset; similarly, a snapshot of the y component for transverse polarization is shown in th lower inset. (b) Time snapshots of the electric field for transverse pulse propagation show a negative phase velocity with an antiparallel orientatio of the phase and group velocities

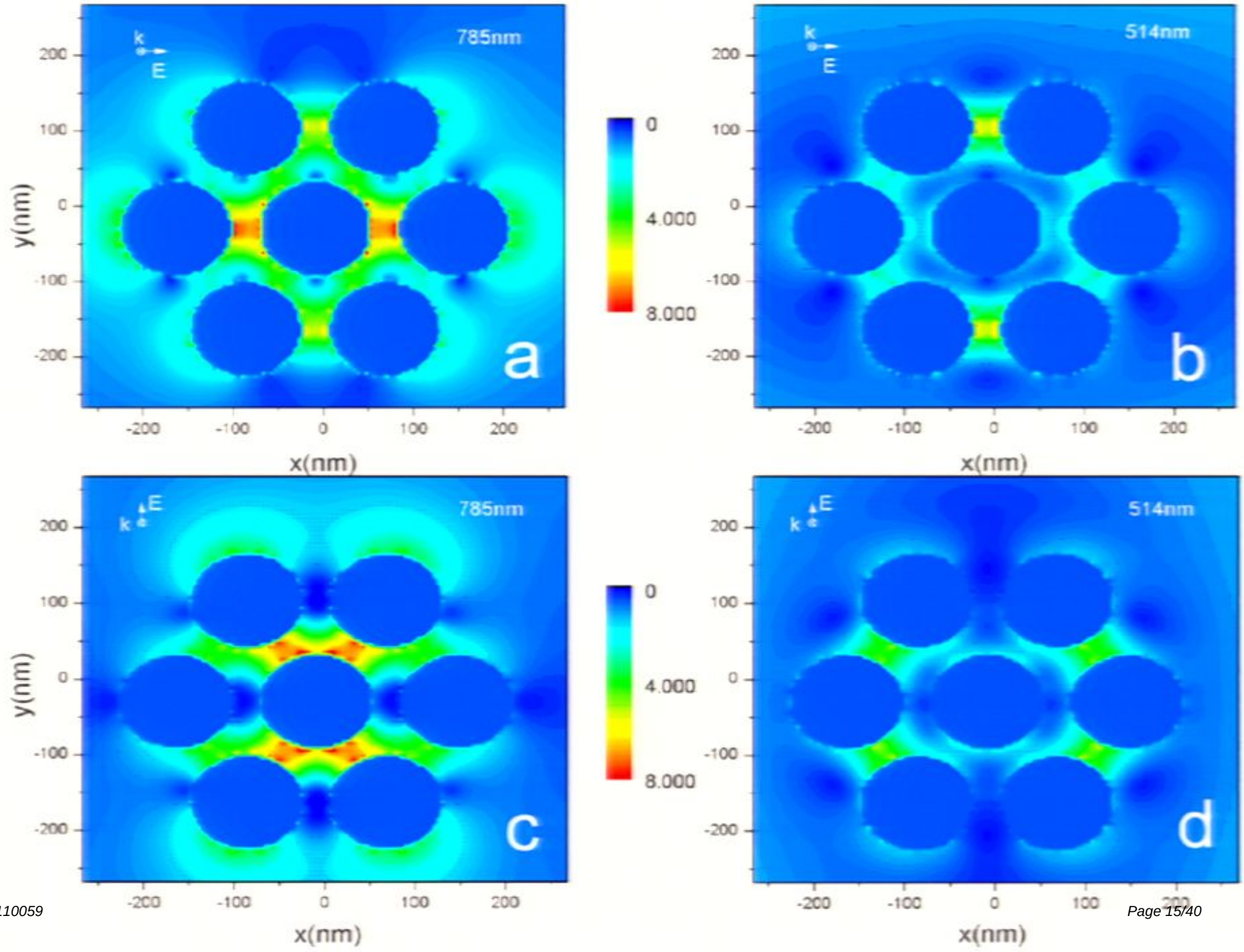


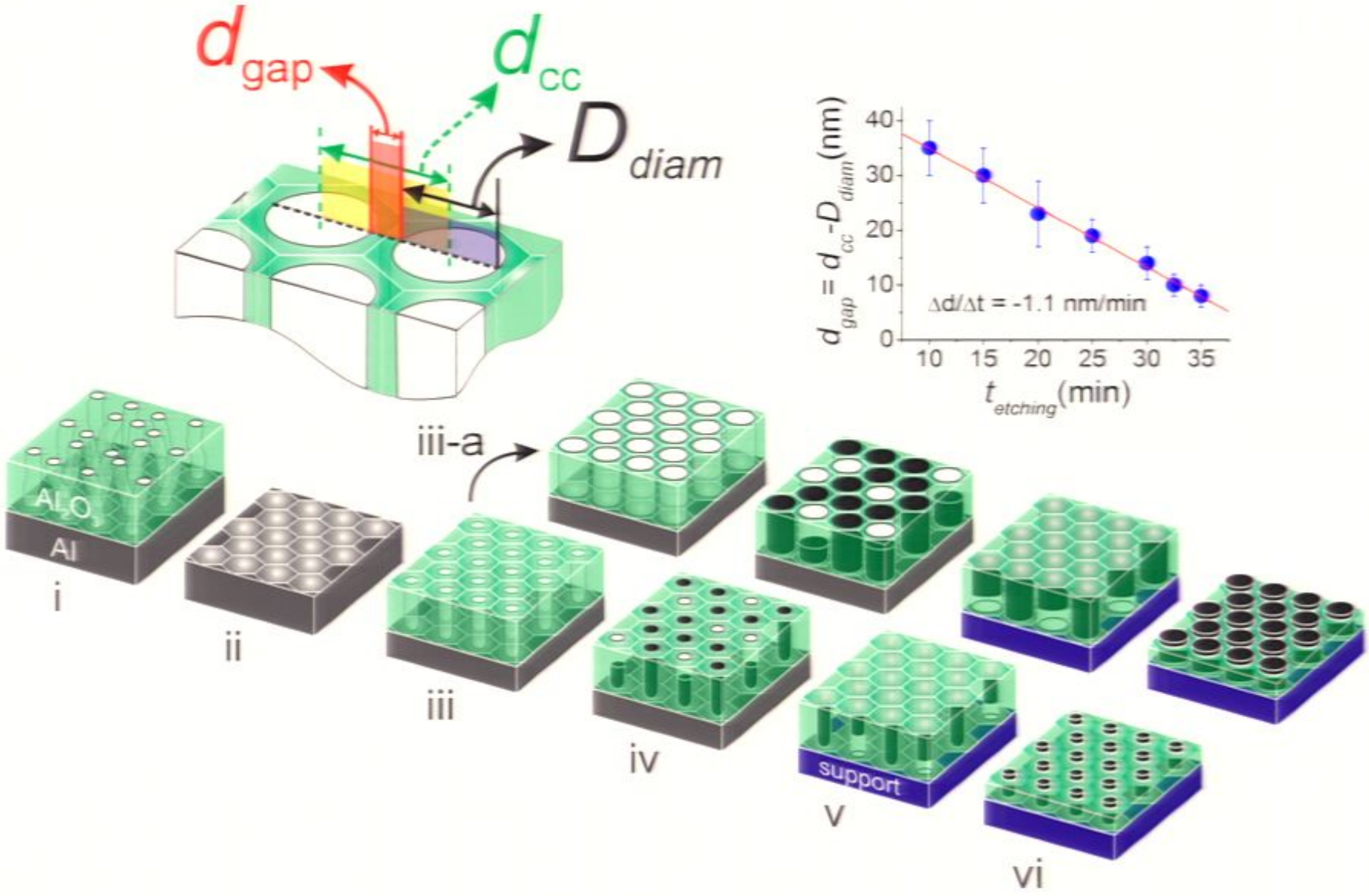
Optical Cloaking using a nanowire-based metamaterial

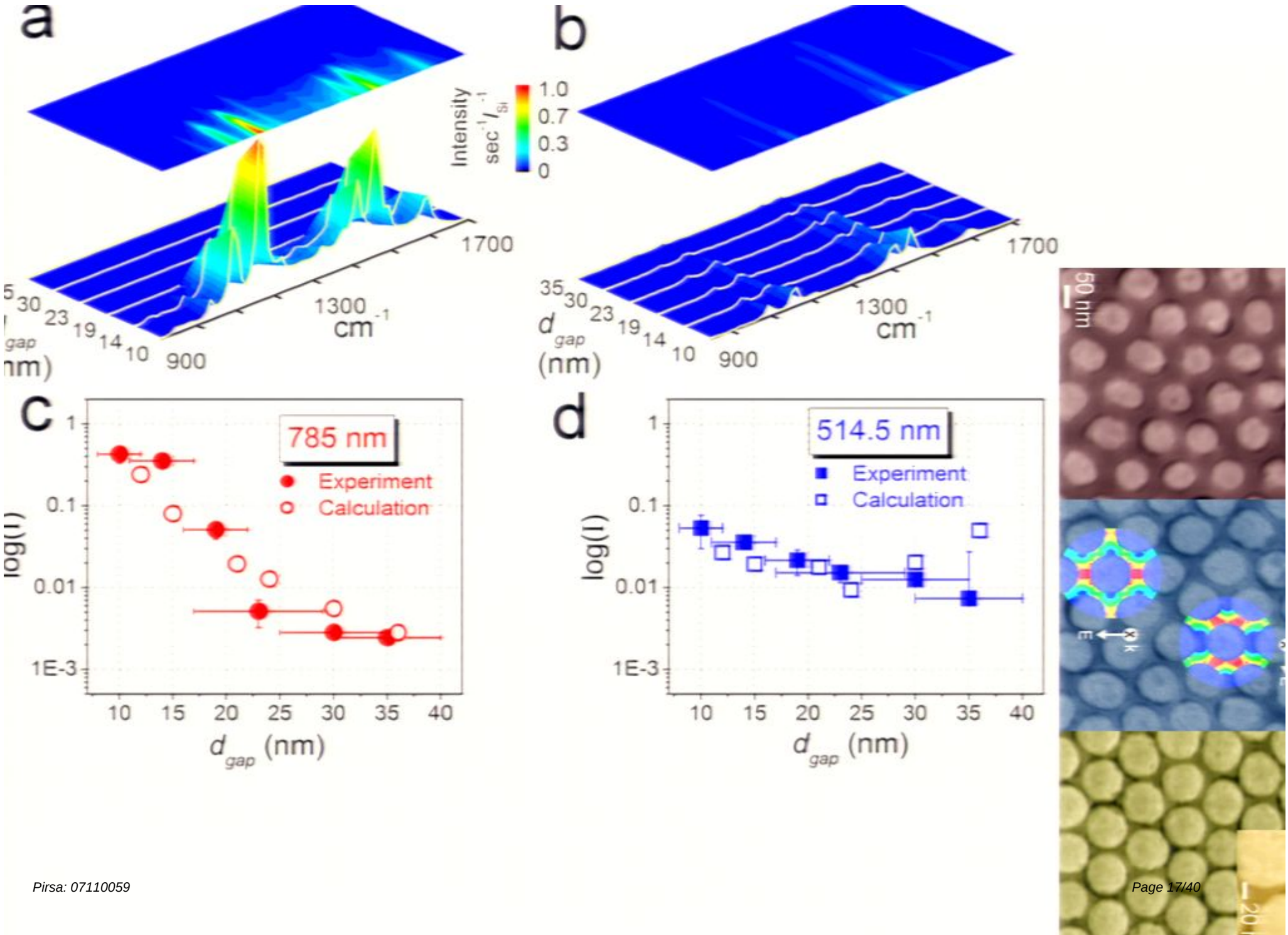


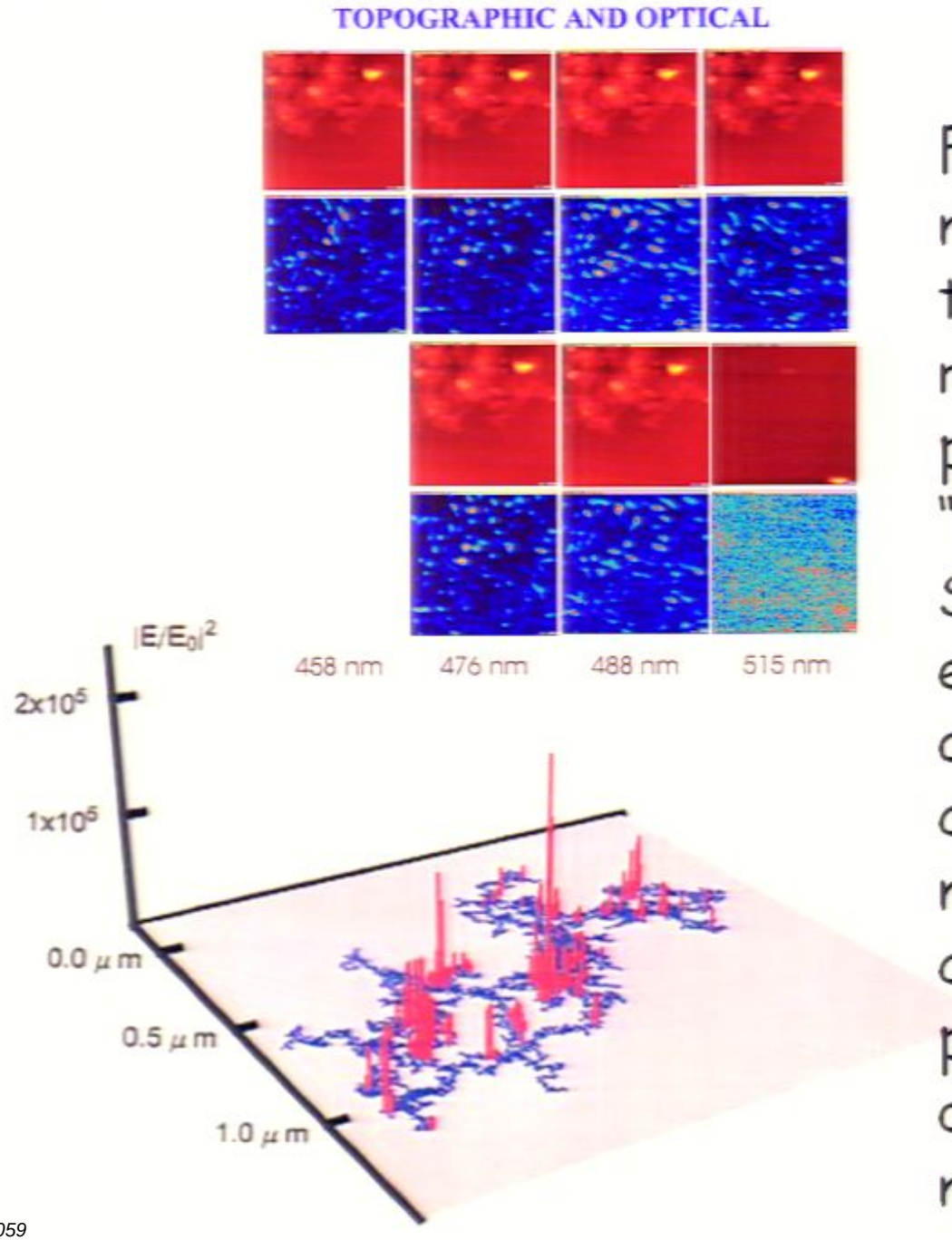
Interest in metamaterials (materials for which the phase velocity counter-propagates with the group velocity) also owes its resurgence to plasmonics

MENSHAN CAI, UDAY K. CHETTIAR, ALEXANDER V. KILDISHEV AND VLADIMIR M. SHALAEV* Nature 2007


785nm
514nm
k
E
a
b
c
d
0
4.000
8.000
y(nm)
x(nm)
200
100
0
-100
-200


d_{gap}
d_{cc}
D_{diam}
$d_{gap} = d_{cc} - D_{diam}$ (nm)
40
30
20
10
0
10
15
20
25
30
35
$t_{etching}$ (min)
Δd/Δt = -1.1 nm/min
iii-a
Al_2O_3
Al
i
ii
iii
iv
support
v
vi

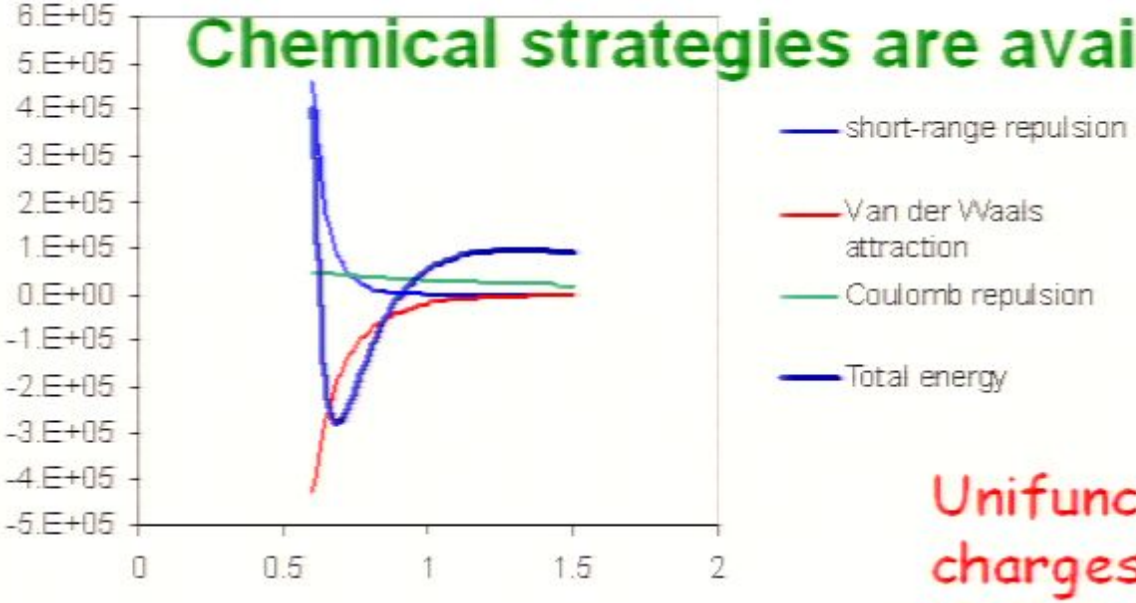

a
b
Intensity
sec^{-1} I_{Si}^{-1}
1.0
0.7
0.3
0
1700
1300
cm^{-1}
900
d_{gap}
(nm)
35
30
23
19
14
10
c
785 nm
Experiment
Calculation
log(I)
1
0.1
0.01
1E-3
10
15
20
25
30
35
40
d_{gap} (nm)
d
514.5 nm
Experiment
Calculation
50 nm
E
k



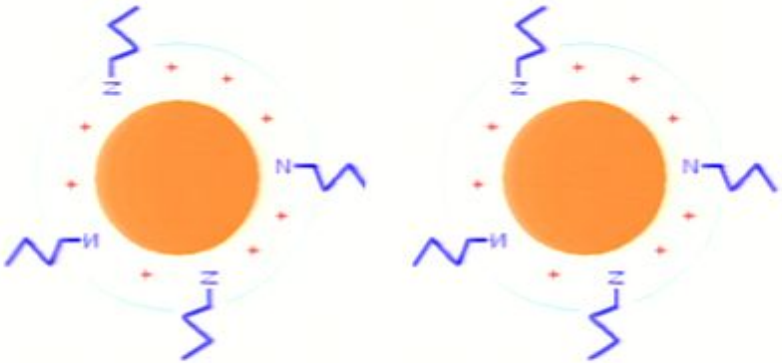
Fractal clusters of nanoparticles excited in the surface plasmon region are also predicted to possess "hot spots" where the SERS enhancement is expected to be as large as 10^{11}. These hot spots correspond to localized normal modes of coupled, dipolar surface plasmons, each oscillator resident on a nanoparticle.

Shalaev et al

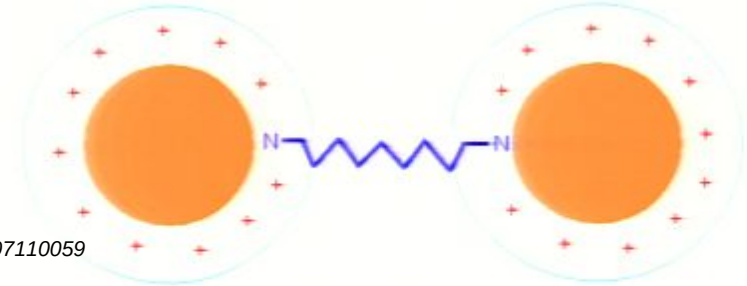
Chemical strategies are available for making hot spots

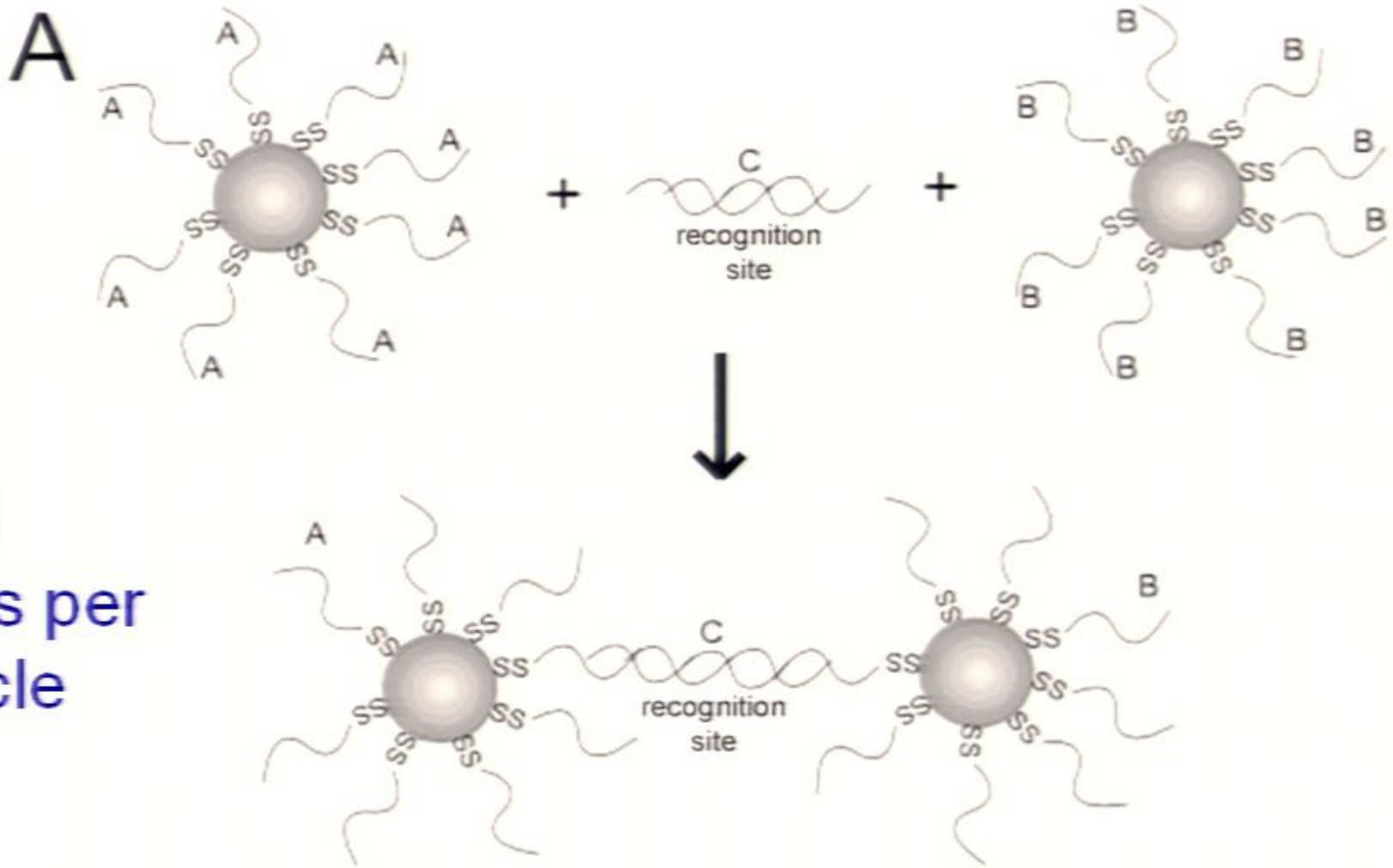


Unifunctional ligands displace surface charges allowing Coulomb repulsion to be overcome which leads to aggregation by Van der Walls attraction. BUT only if ligand concentration is above a threshold so that enough charges are displaced.

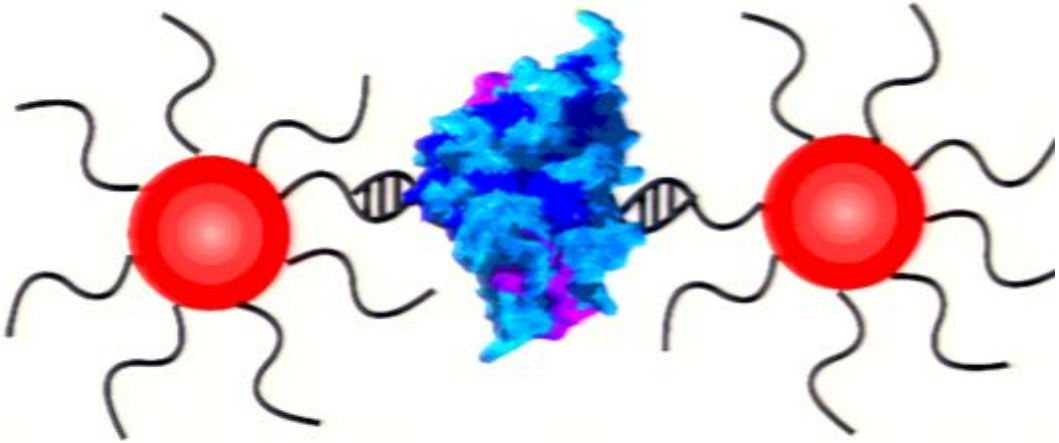


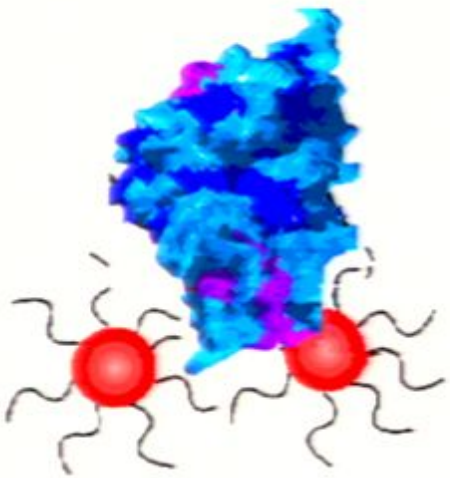
But a bi-functional ligand can overcome the coulomb repulsion even at low ligand concentrations provided that the surface chemical bonds are strong enough.

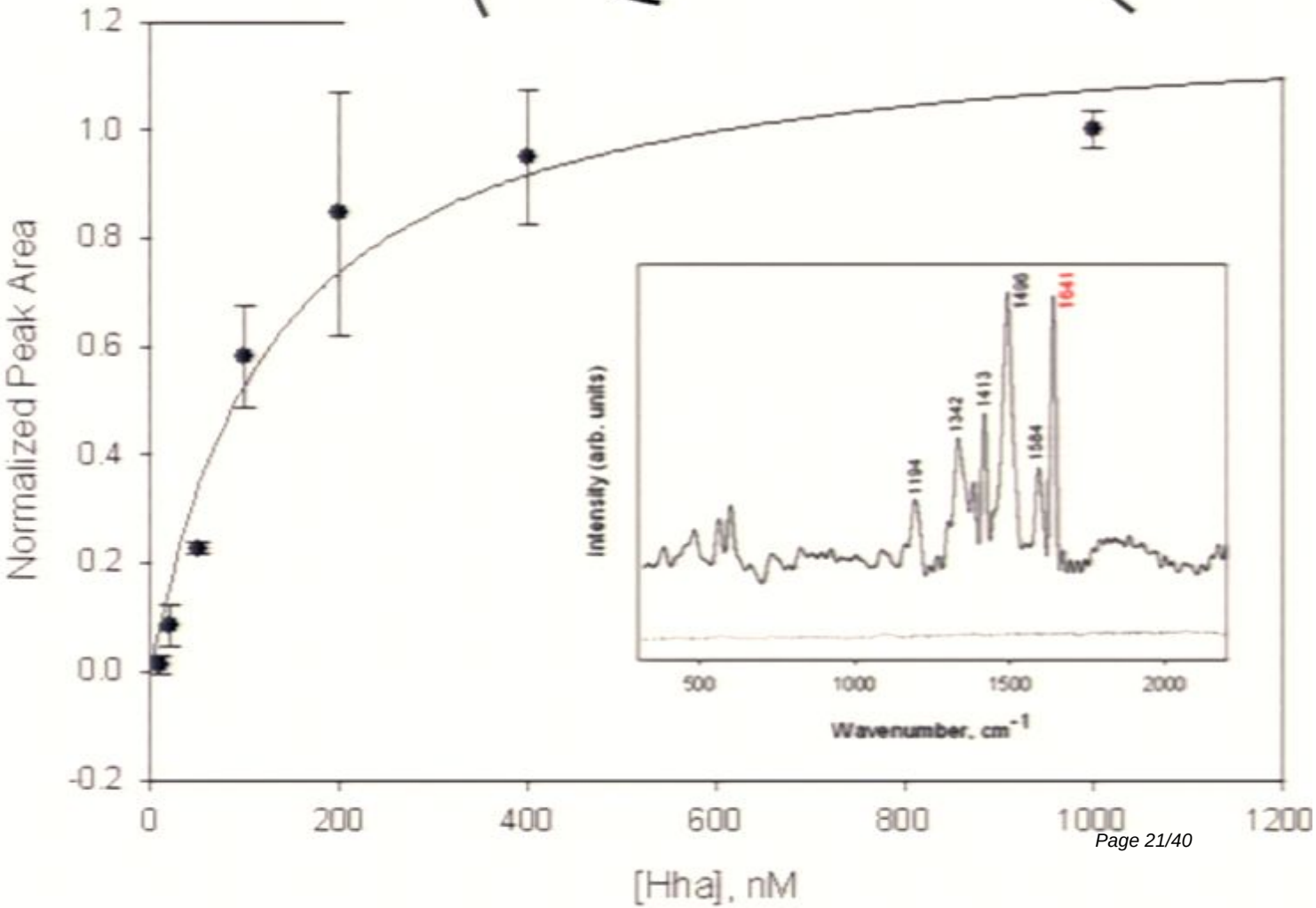



A
A
A
A
A
A
A
A
SS
+
C
recognition
site
+
B
B
B
B
B
B
B
B
B
~180
oligos per
particle
A
C
recognition
site
B
B
C
D
100 nm
100 nm
100 nm

Sequence-specific DNA binding proteins: cytosine-C5-methyltransferase (CGCG); and TATA binding protein, a eukaryotic transcriptional regulator

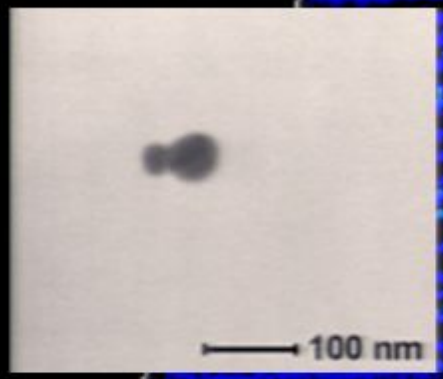




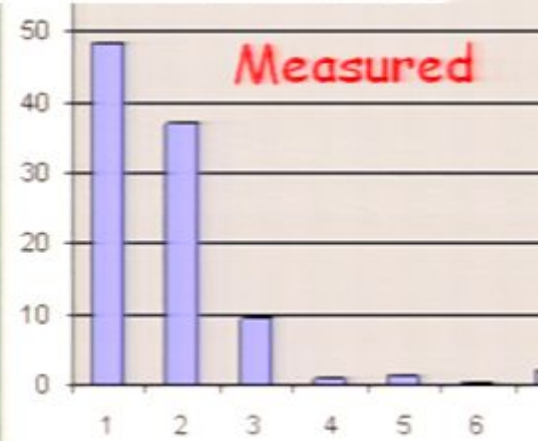


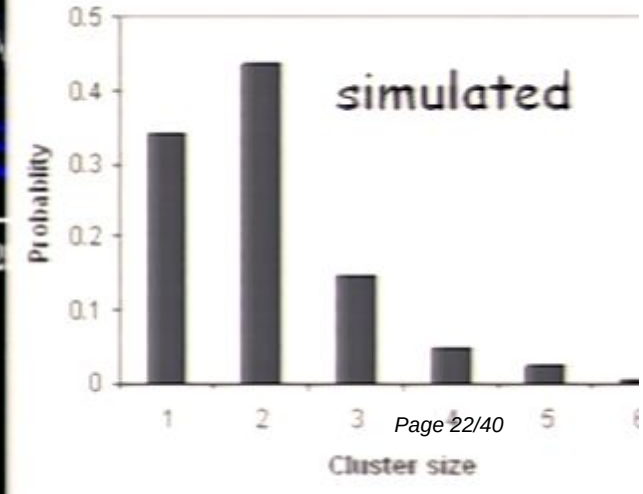
And placing a single molecular linker reliably in the hot spot by self-assembly produces single-molecule spectra routinely.

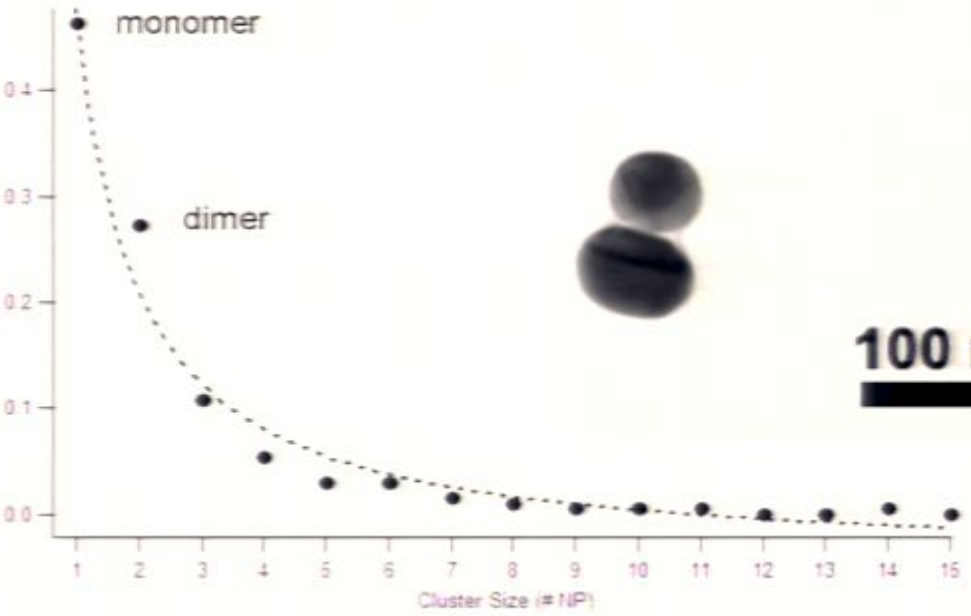
Vlčkova et al.

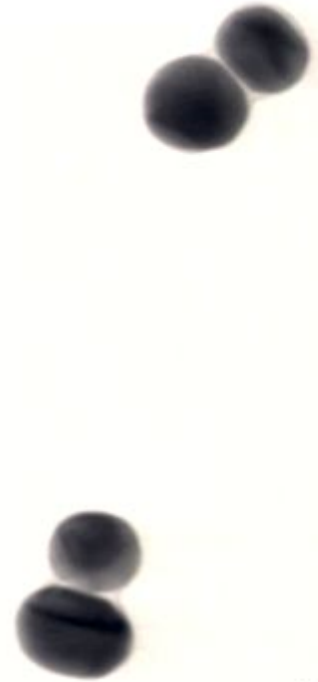


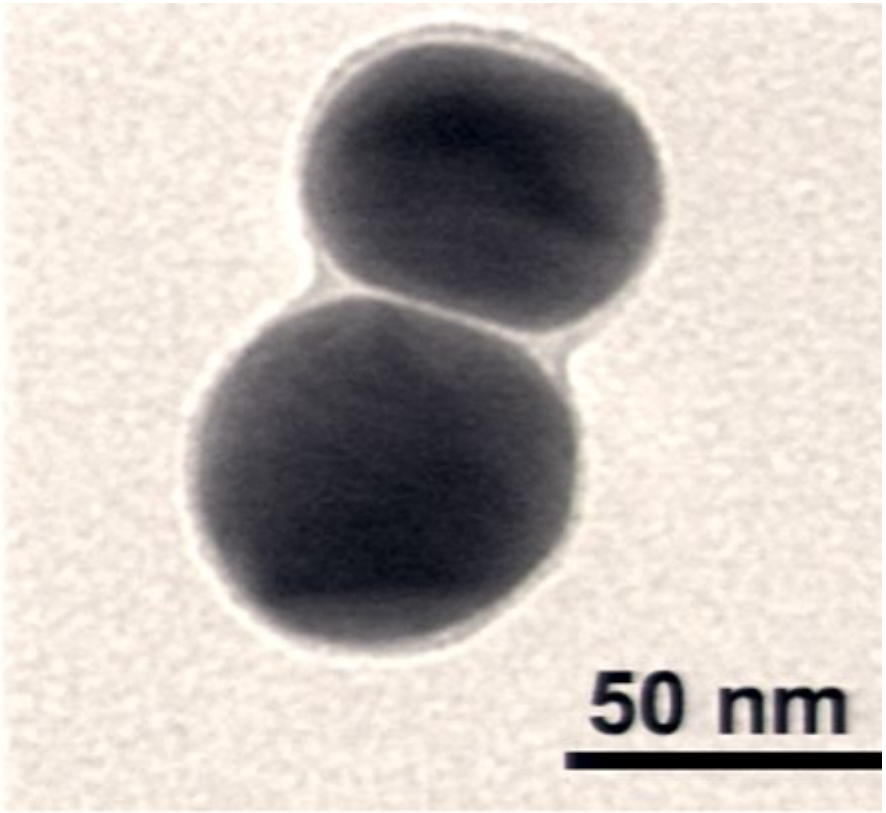
Time evolution of the SERS signal from a 4,4'-diaminoazobenzene-bridged dimer or small aggregate

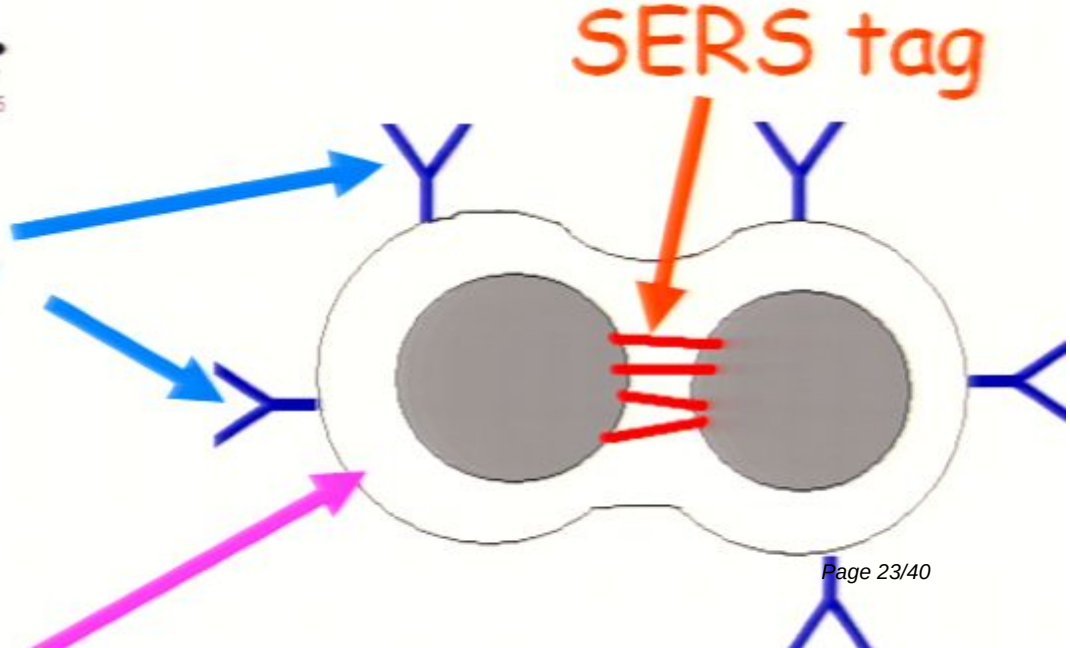


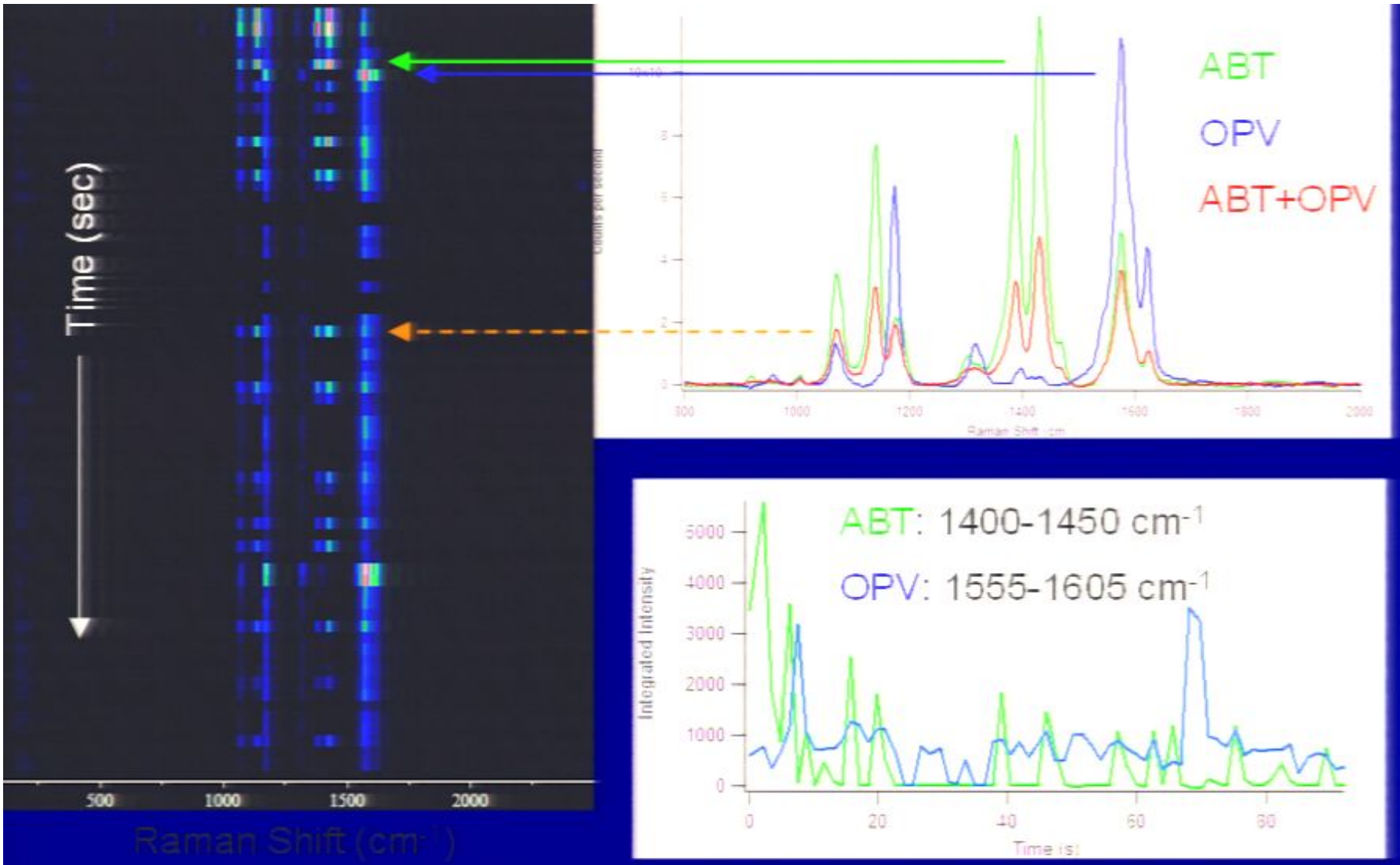



monomer
dimer
0.4
0.3
0.2
0.1
0.0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
Cluster Size (# NP)


100 nm

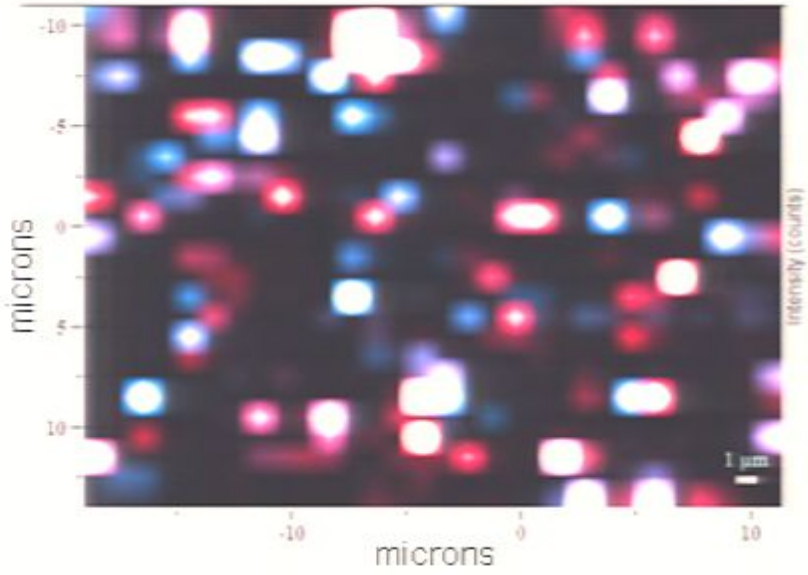

50 nm

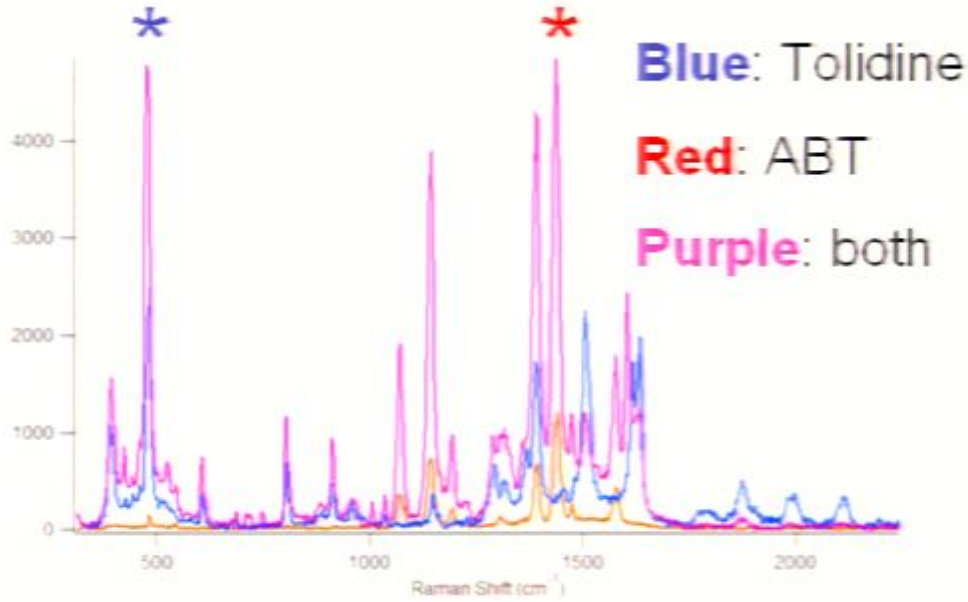

SERS tag
Antibody



SERS-Clusters on two independently labeled beads flowing through a microchannel. Peak value at 1434 cm^{-1} is due to the ABT tag, the 1575 cm^{-1} band is due largely to OPV

Mapping: Multiplexing Two Clusters

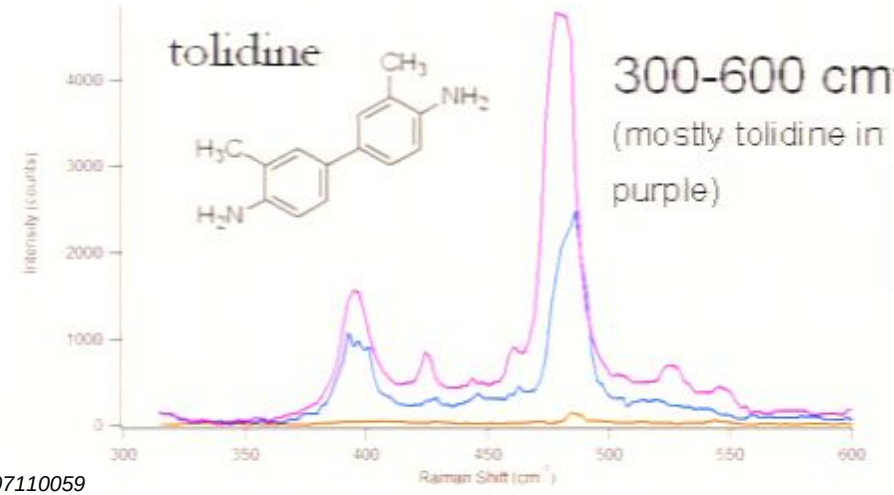




Blue: Tolidine

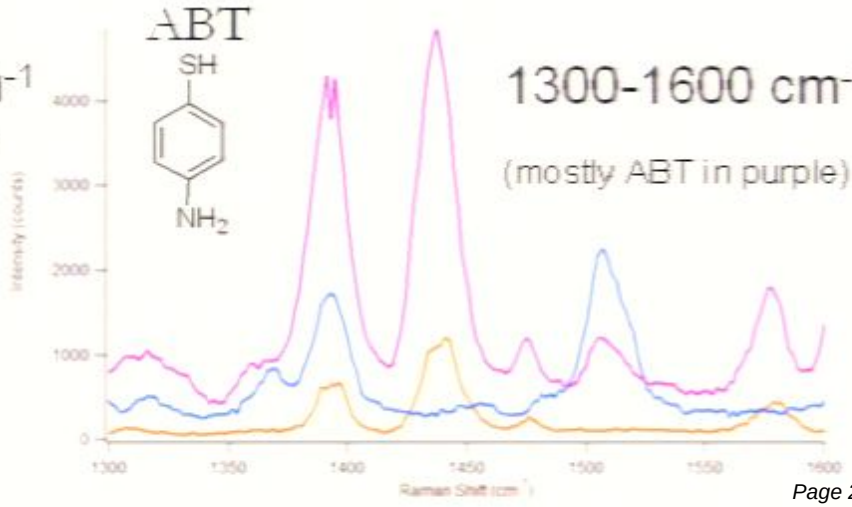
Red: ABT

Purple: both



300-600 cm^{-1}

(mostly tolidine in purple)



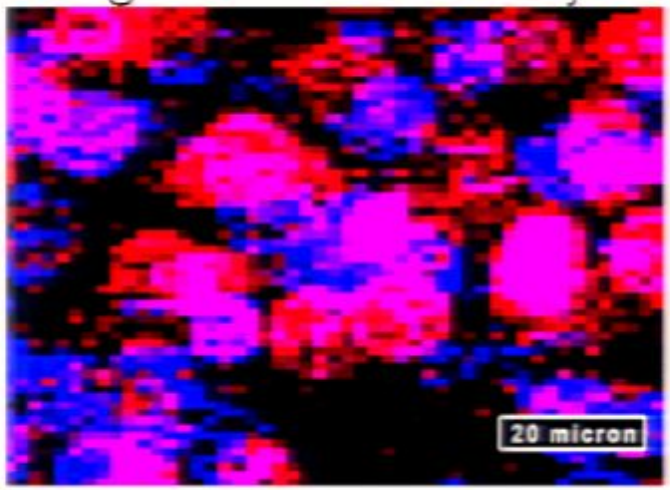
1300-1600 cm^{-1}

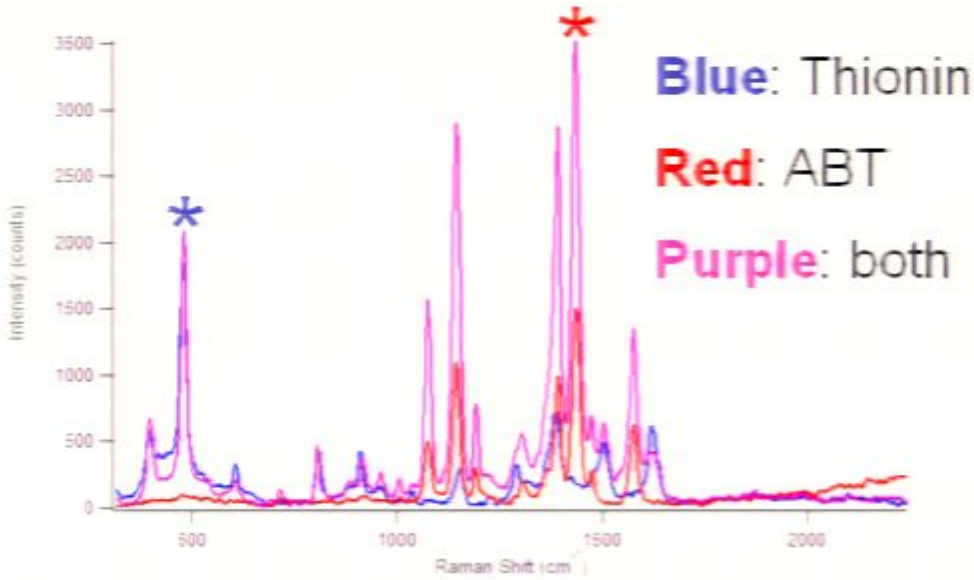
(mostly ABT in purple)

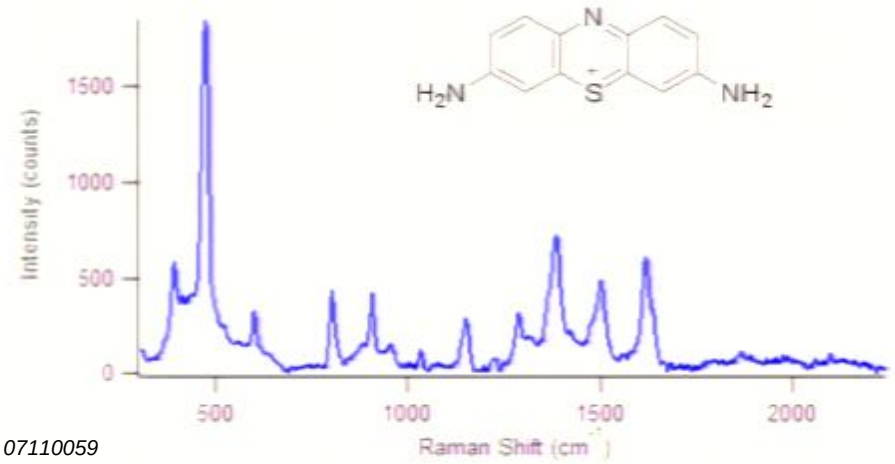
B-Cell Labeling Using Ab-SERS Clusters (ABT tag)

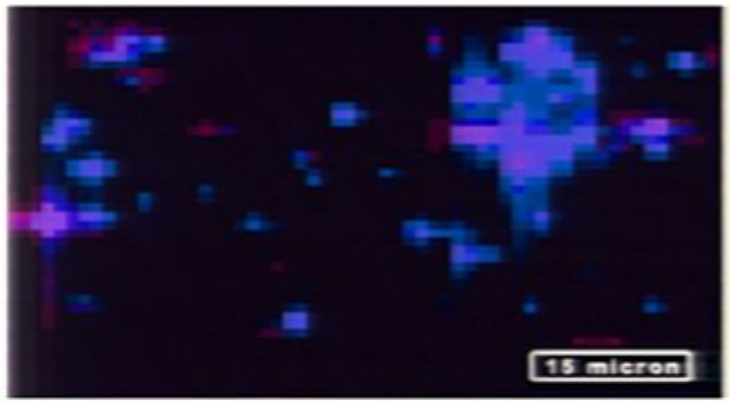
CD19+/CD49e+ cells labeled with thionin-Mab49e and ABT-Mab19 SERS Clusters

Integrated and overlayed





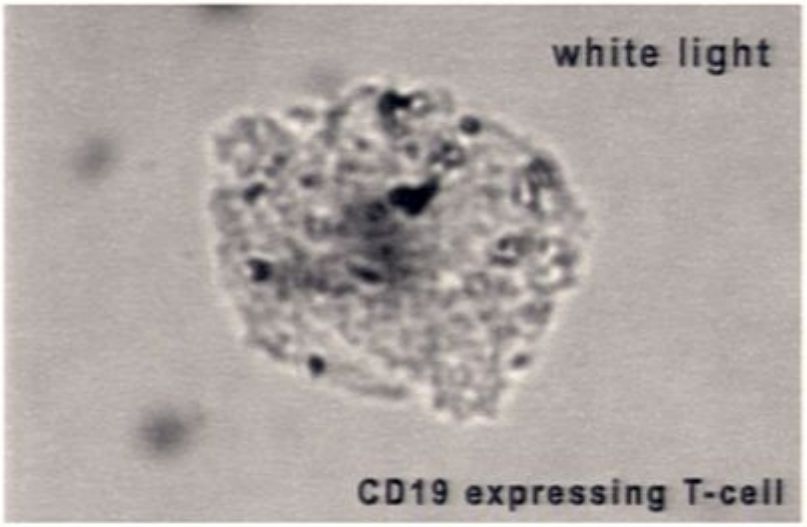


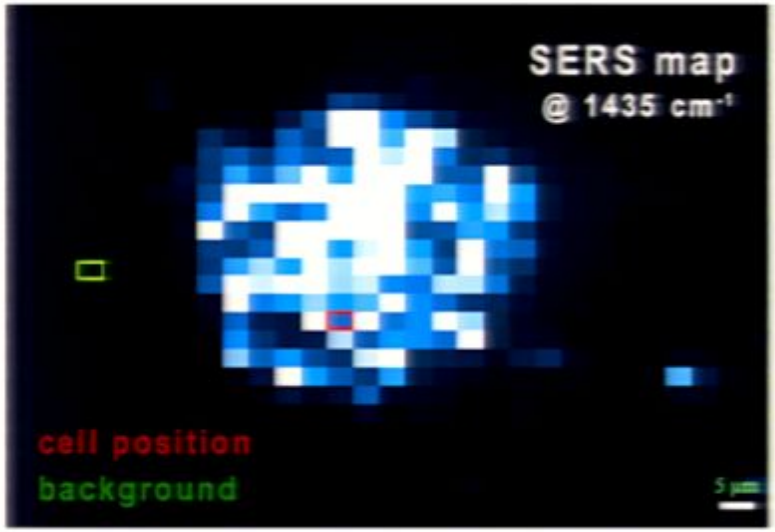


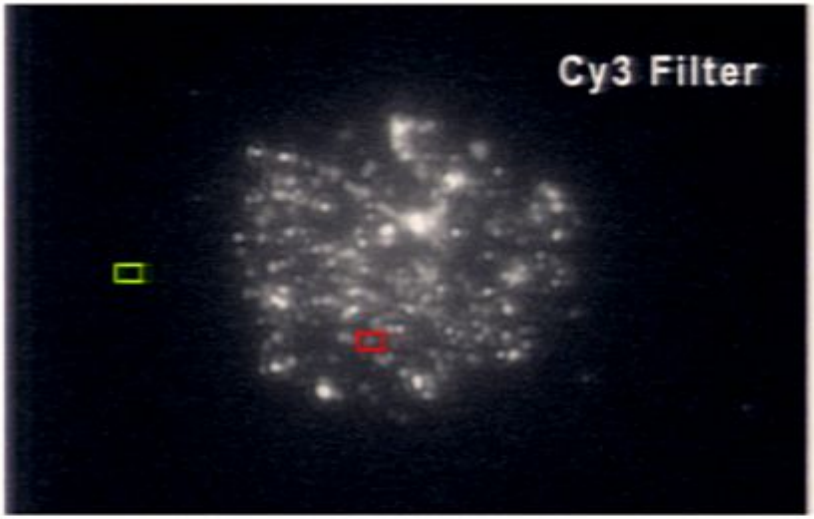
Control: CD38+/CD49e+ w/ same Cluste

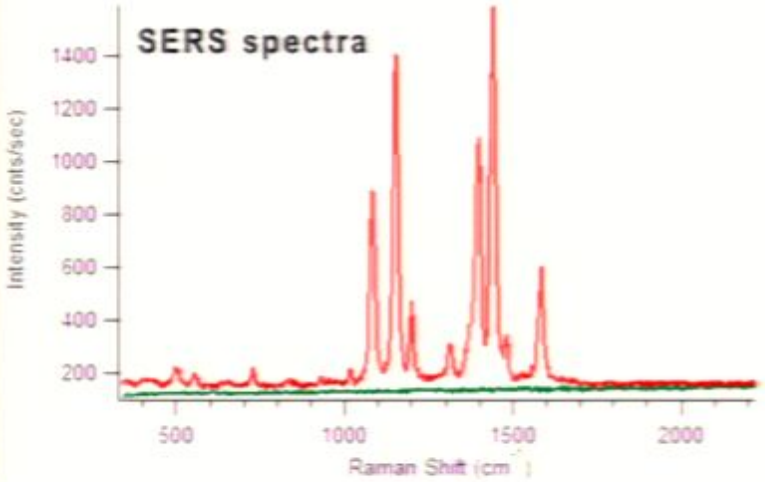
B-Cells Labeling Using Ab-SERS Clusters (ABT tag)

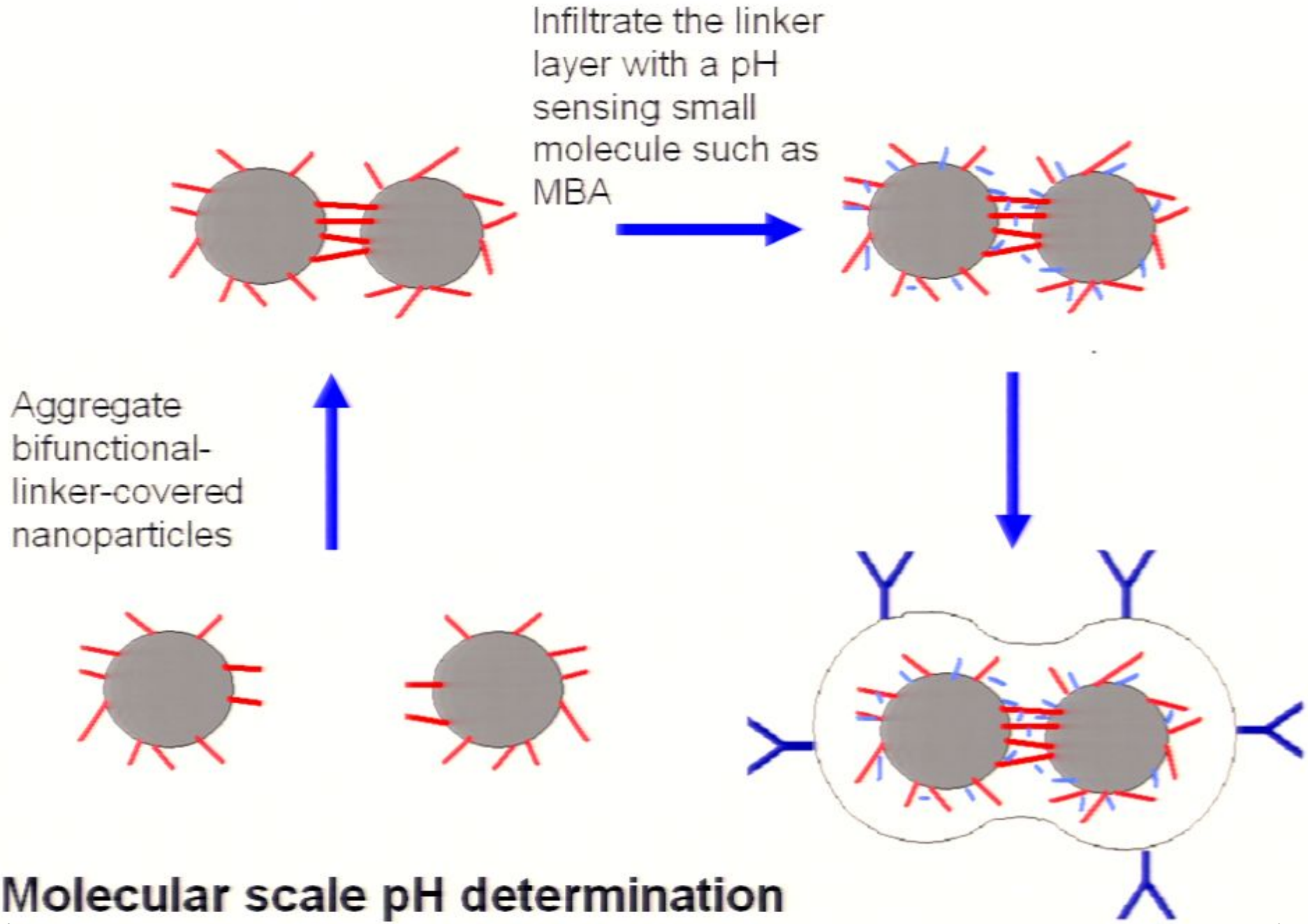
Brighter than commercial fluorescence label



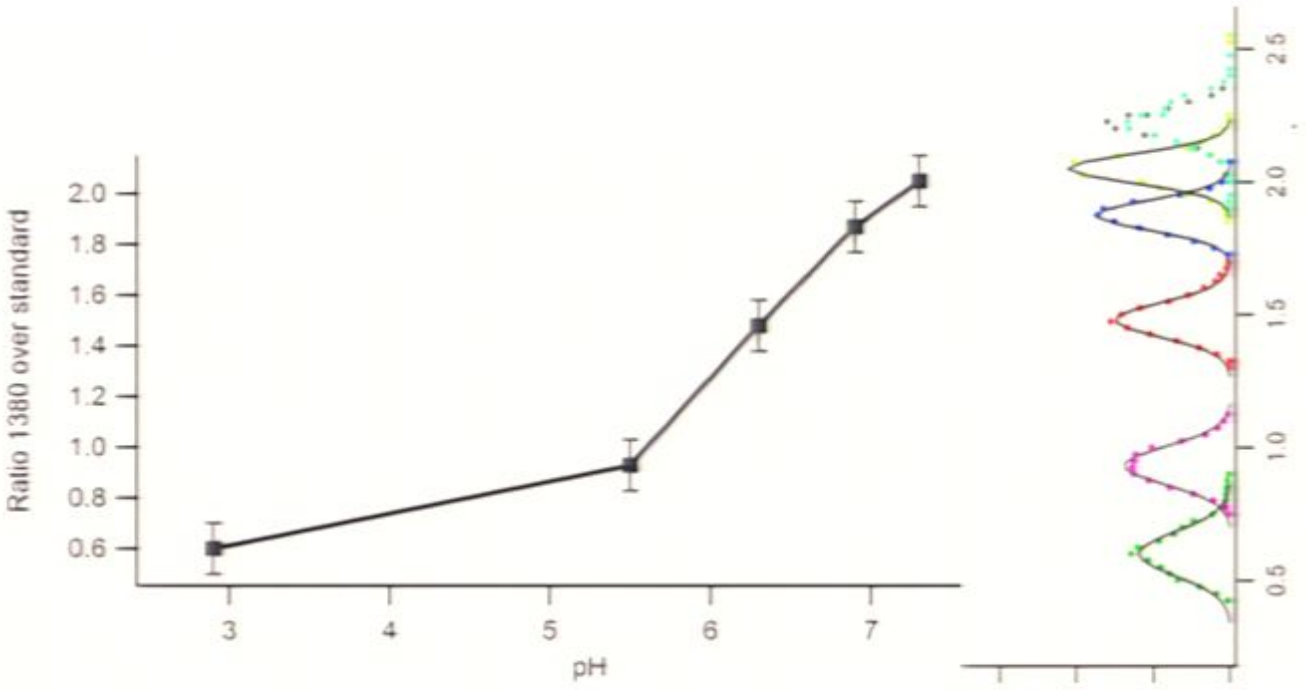


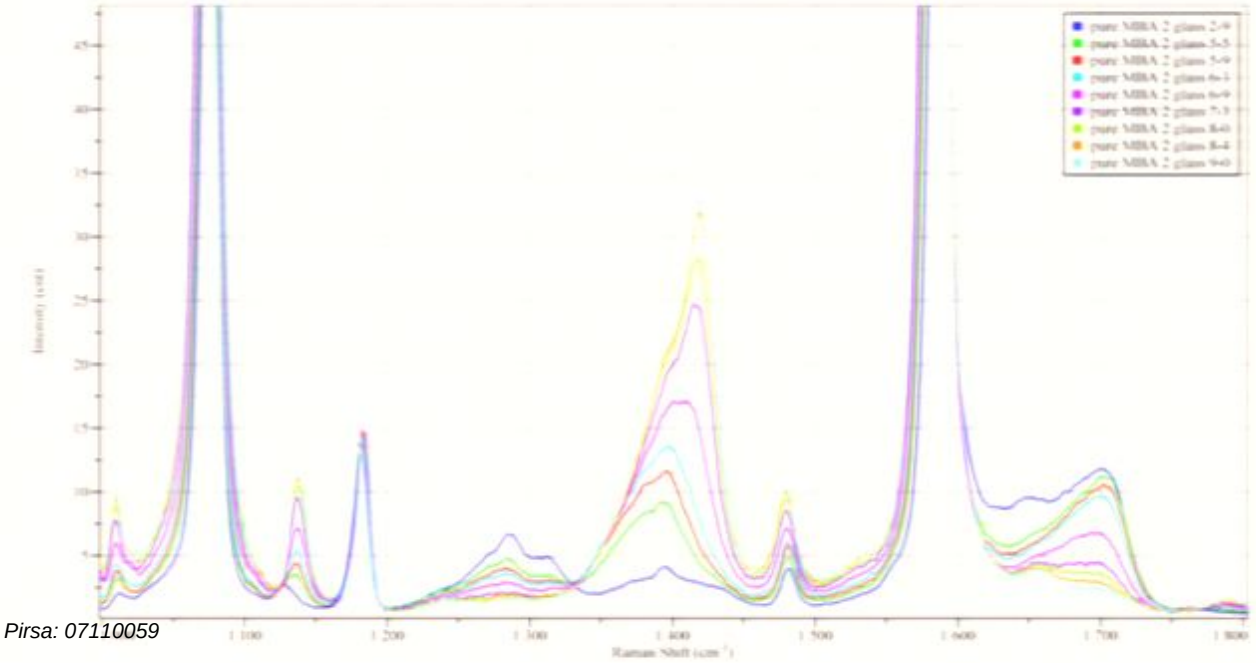




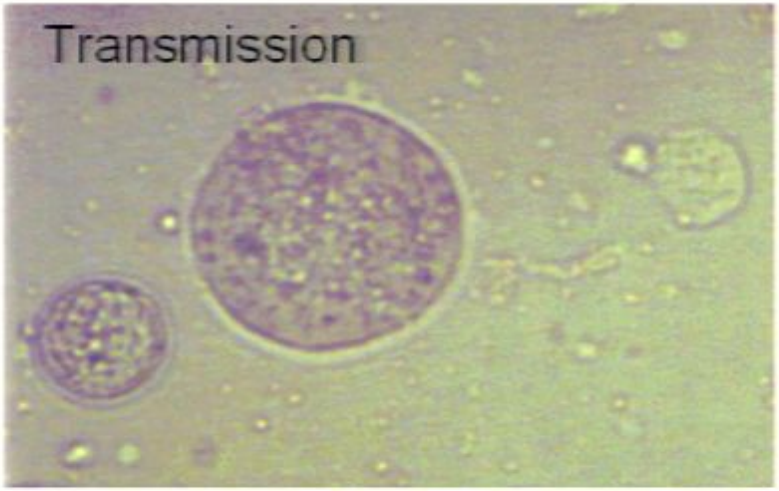


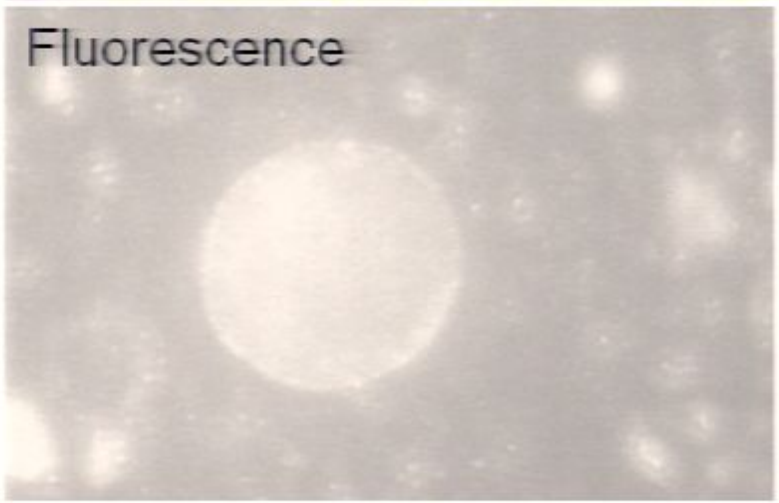
Molecular scale pH determination



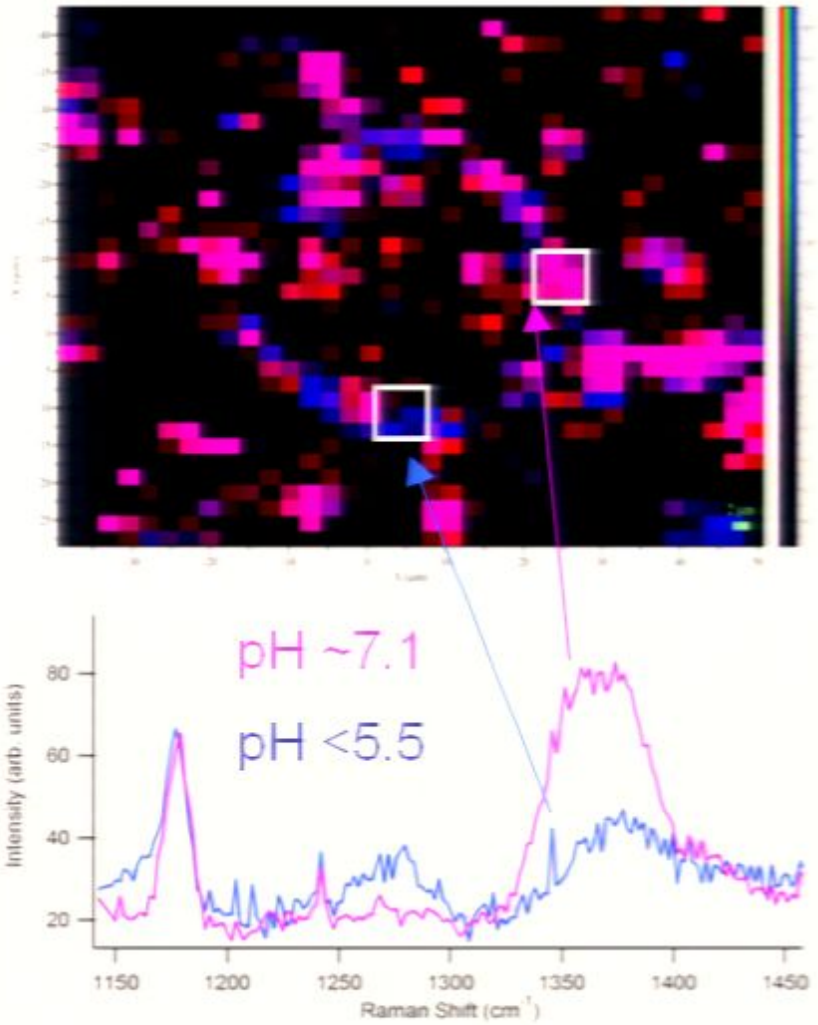


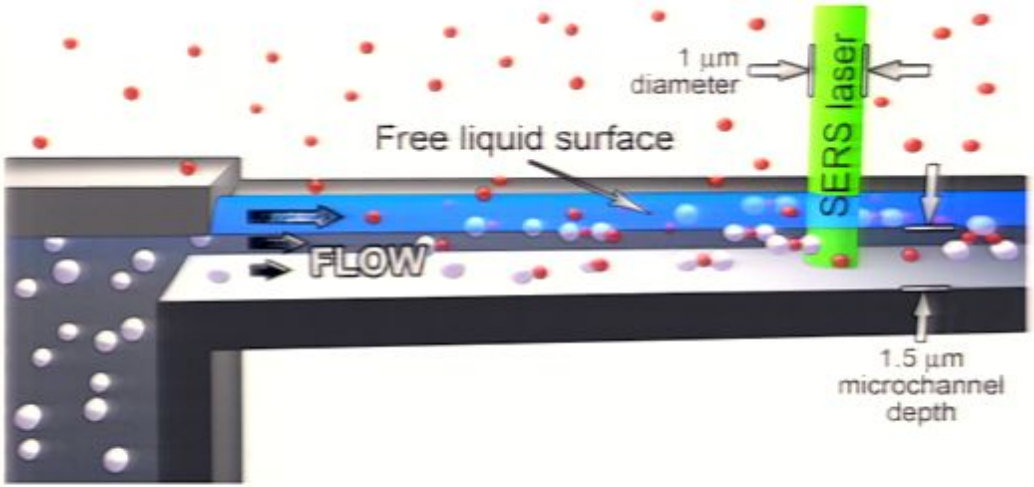
Calibration indicates that pH can be determined with ±0.5 pH units in volume ~ a few nm^3

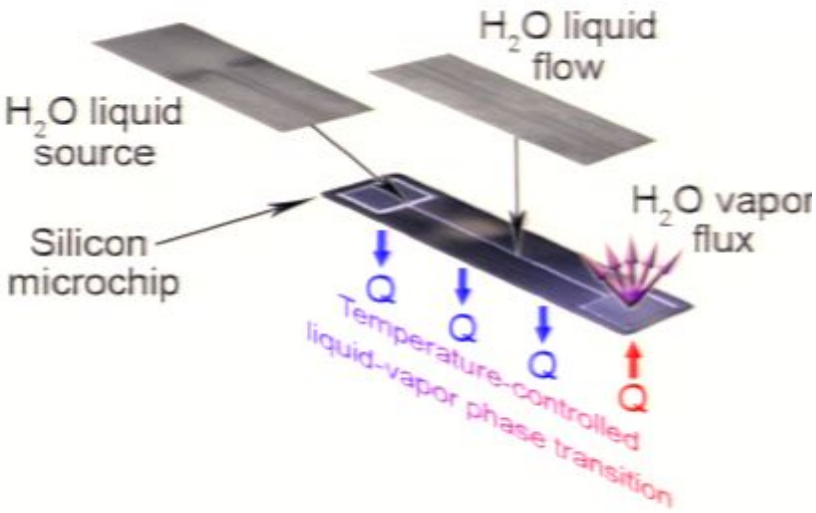


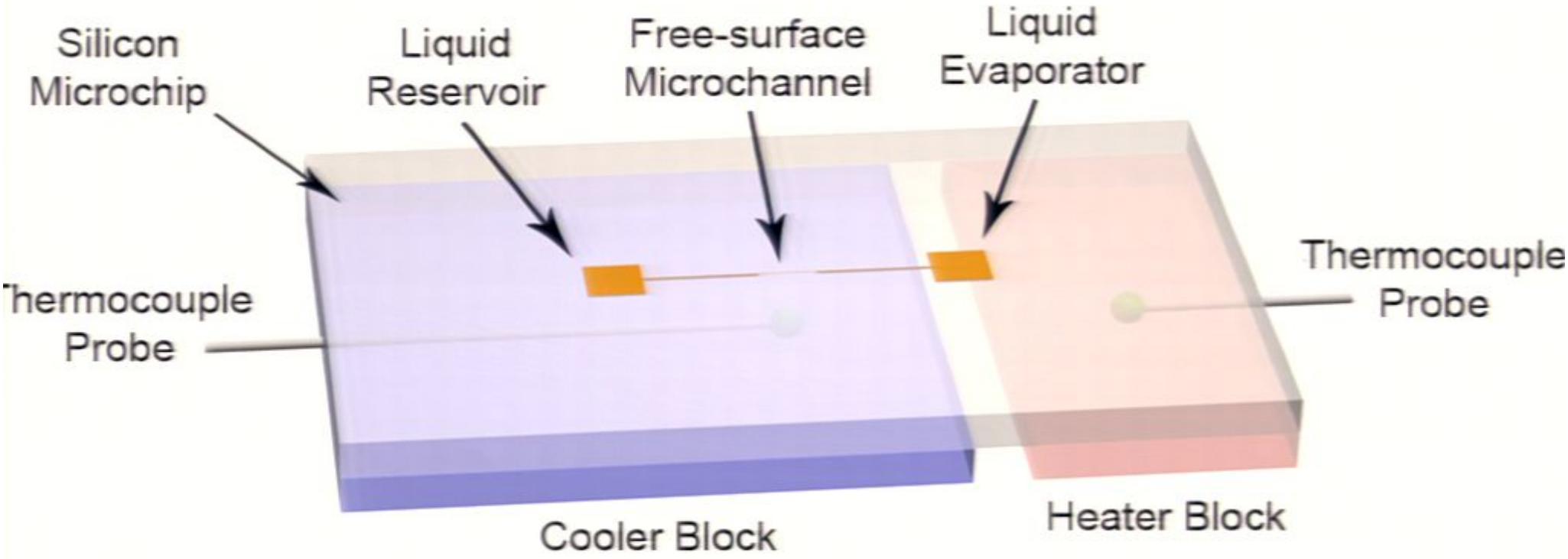


Raman overlay of **ring** vs.
COO- stretches

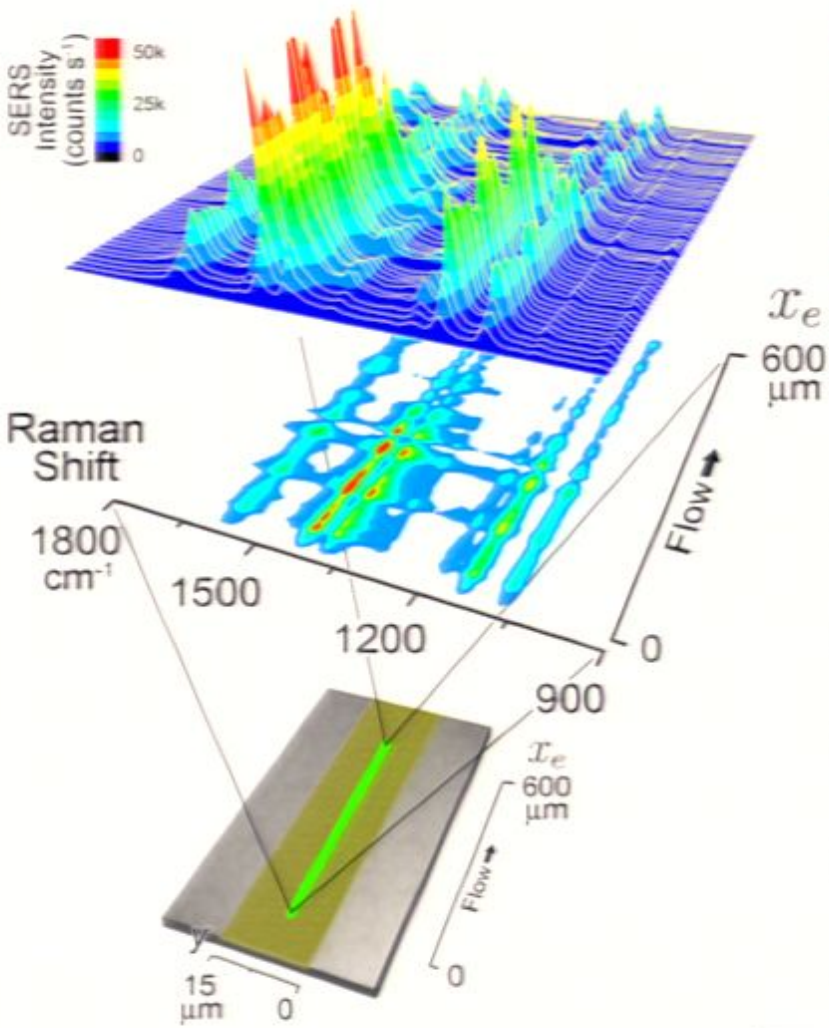


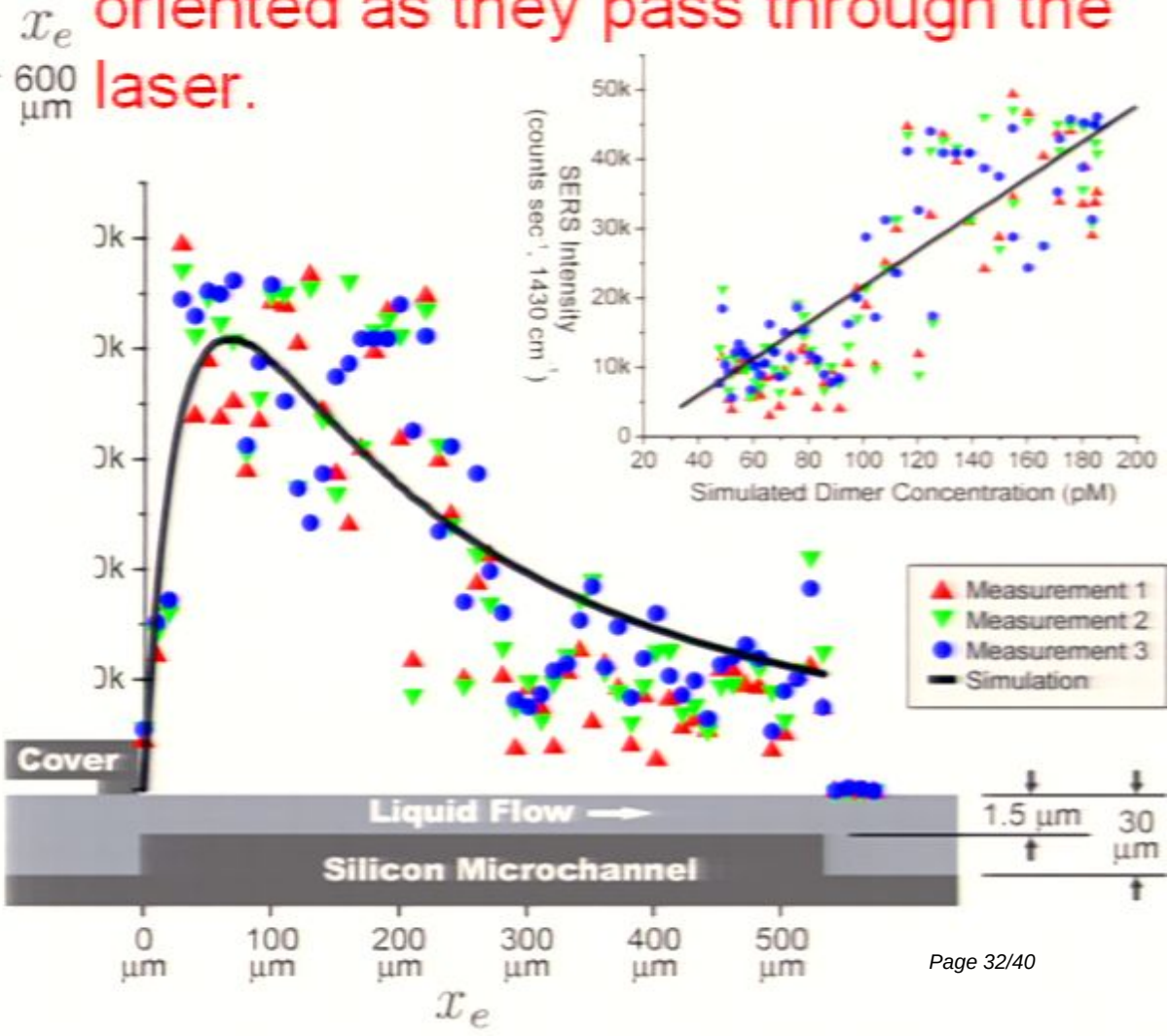

1 μm
diameter
SERS laser
Free liquid surface
FLOW
1.5 μm
microchannel
depth


H2O liquid
flow
H2O liquid
source
H2O vapor
flux
Silicon
microchip
Q
Q
Q
Q
Temperature-controlled
liquid-vapor phase transition

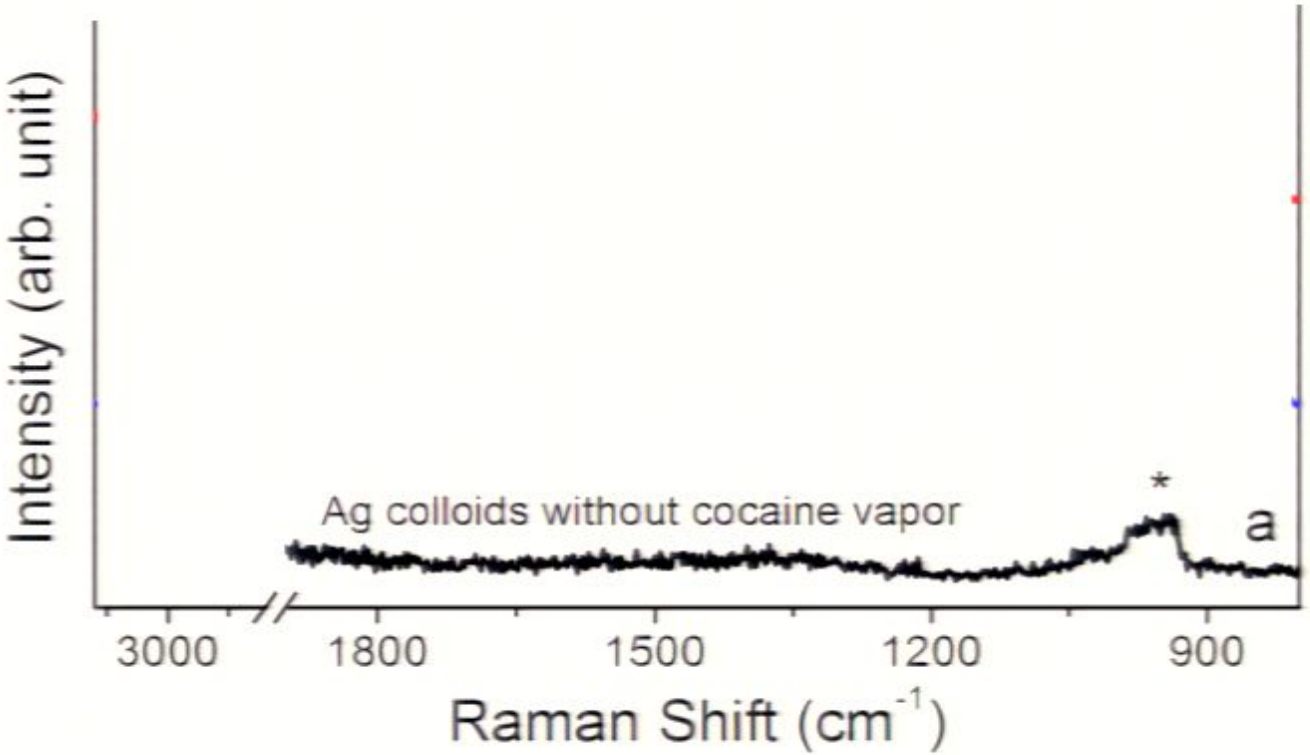

Silicon
Microchip
Liquid
Reservoir
Free-surface
Microchannel
Liquid
Evaporator
Thermocouple
Probe
Thermocouple
Probe
Cooler Block
Heater Block

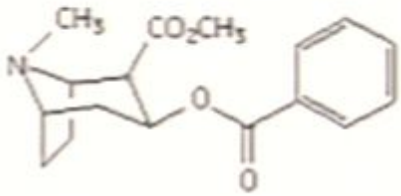
The intensity fluctuations are due both to small number statistics (6 dimers on average) and the fact that the particles are randomly oriented as they pass through the laser.





Detection of cocaine vapor at room temperature

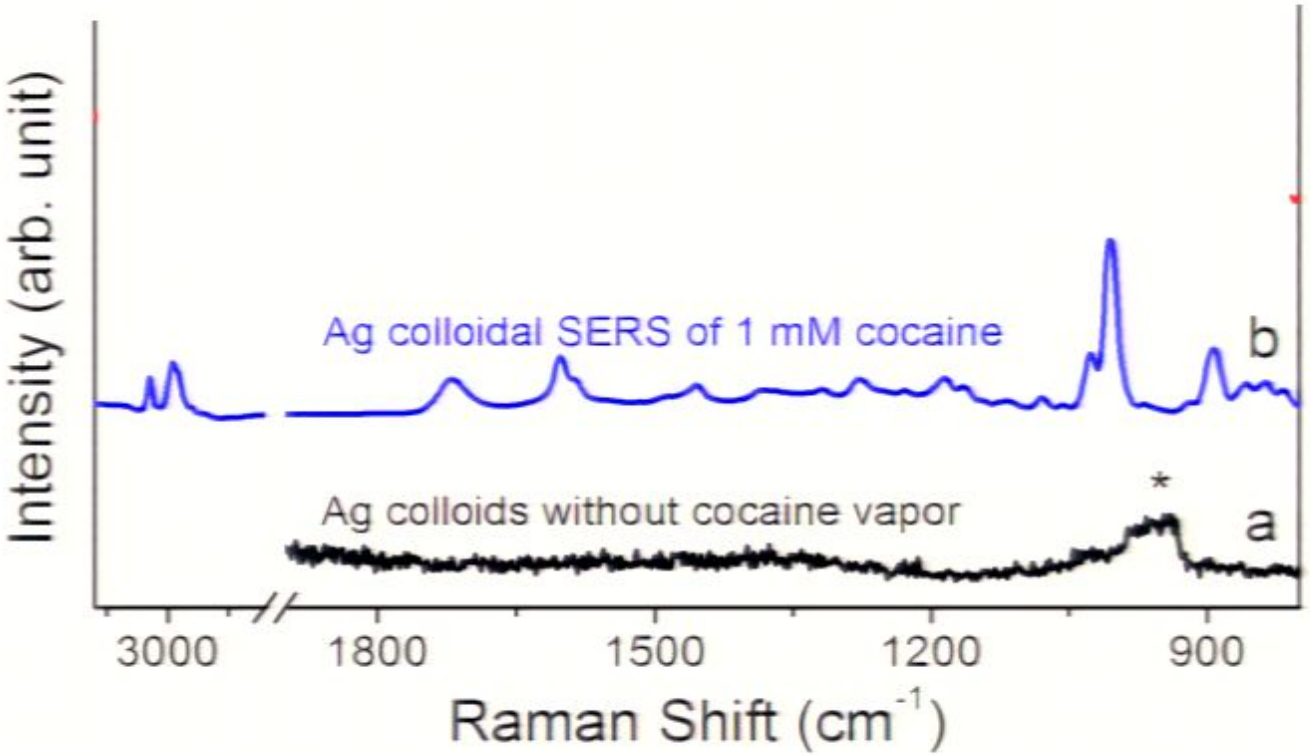


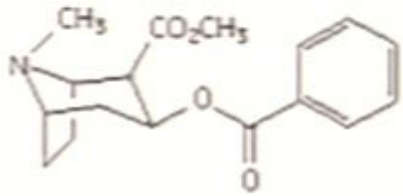


cocaine

30 s of exposure

Detection of cocaine vapor at room temperature

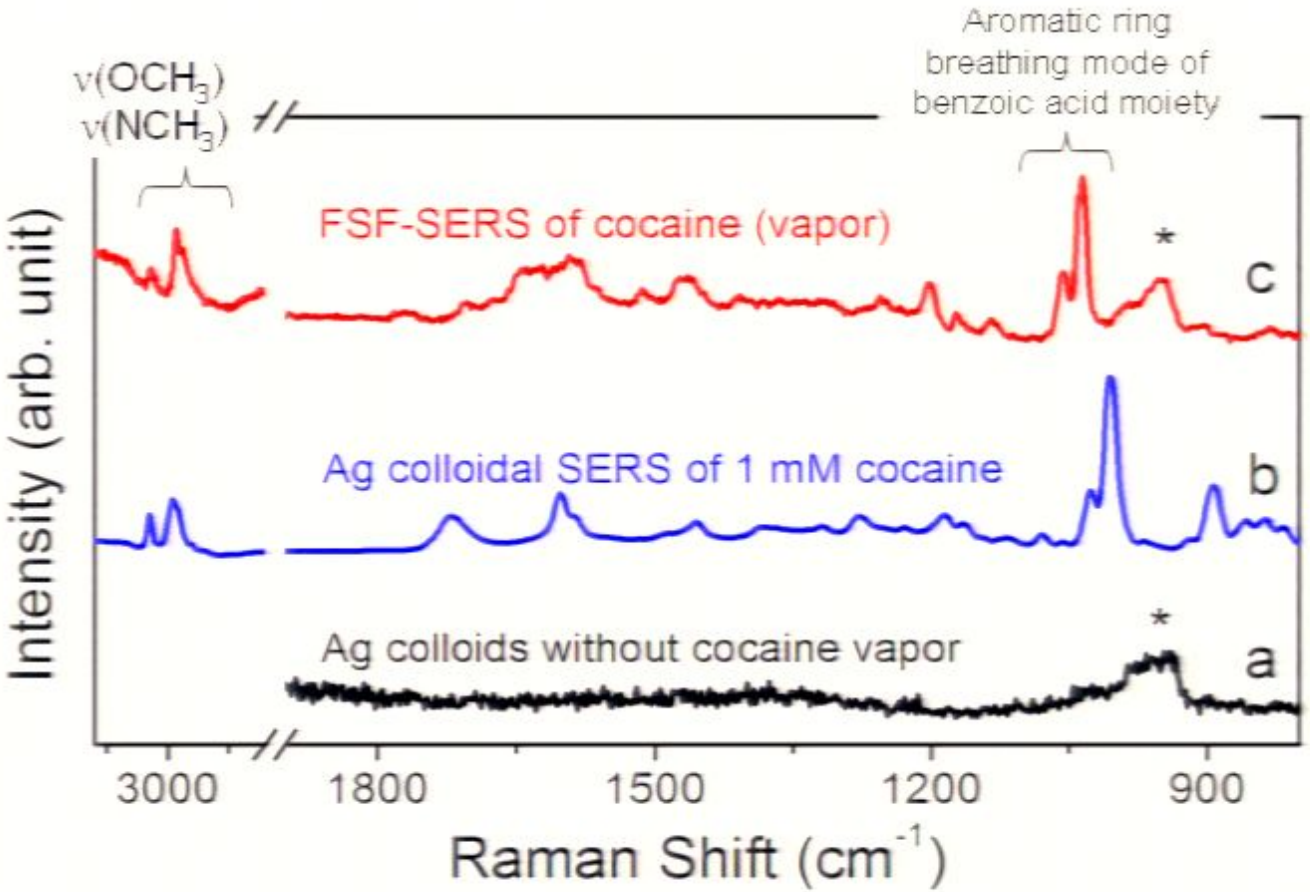


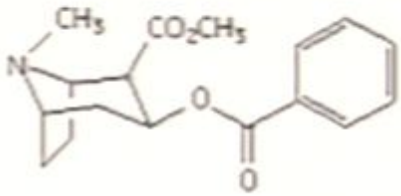


cocaine

30 s of exposure

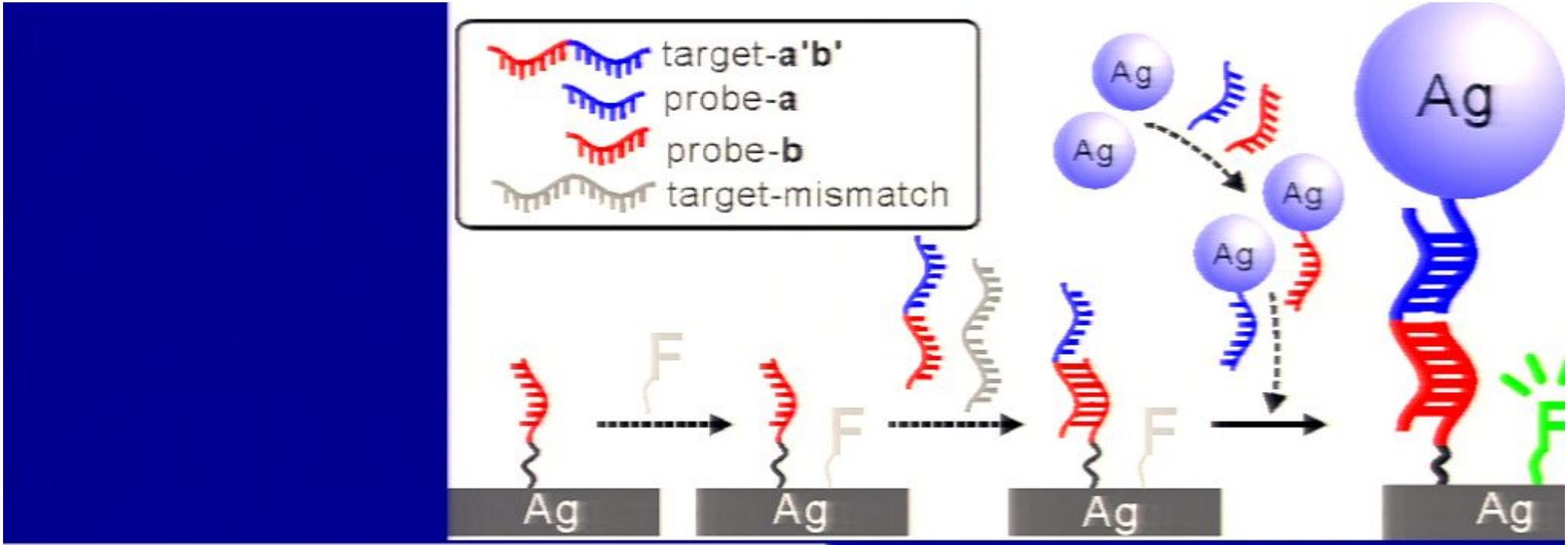
Detection of cocaine vapor at room temperature

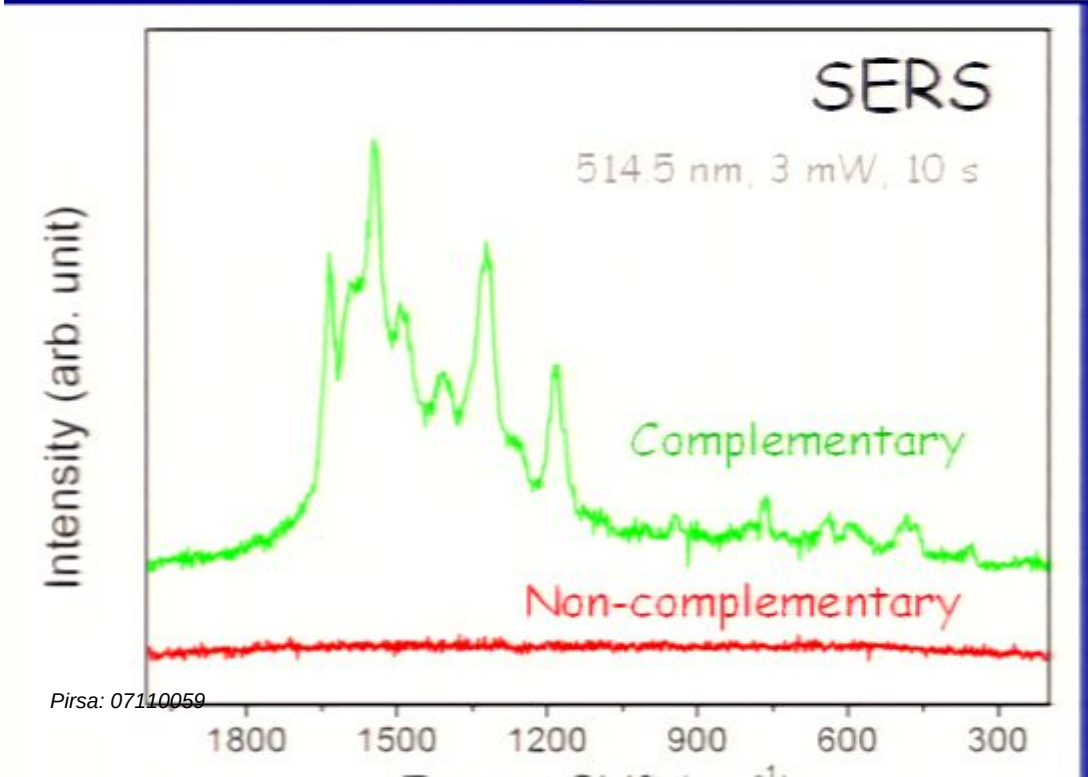




cocaine

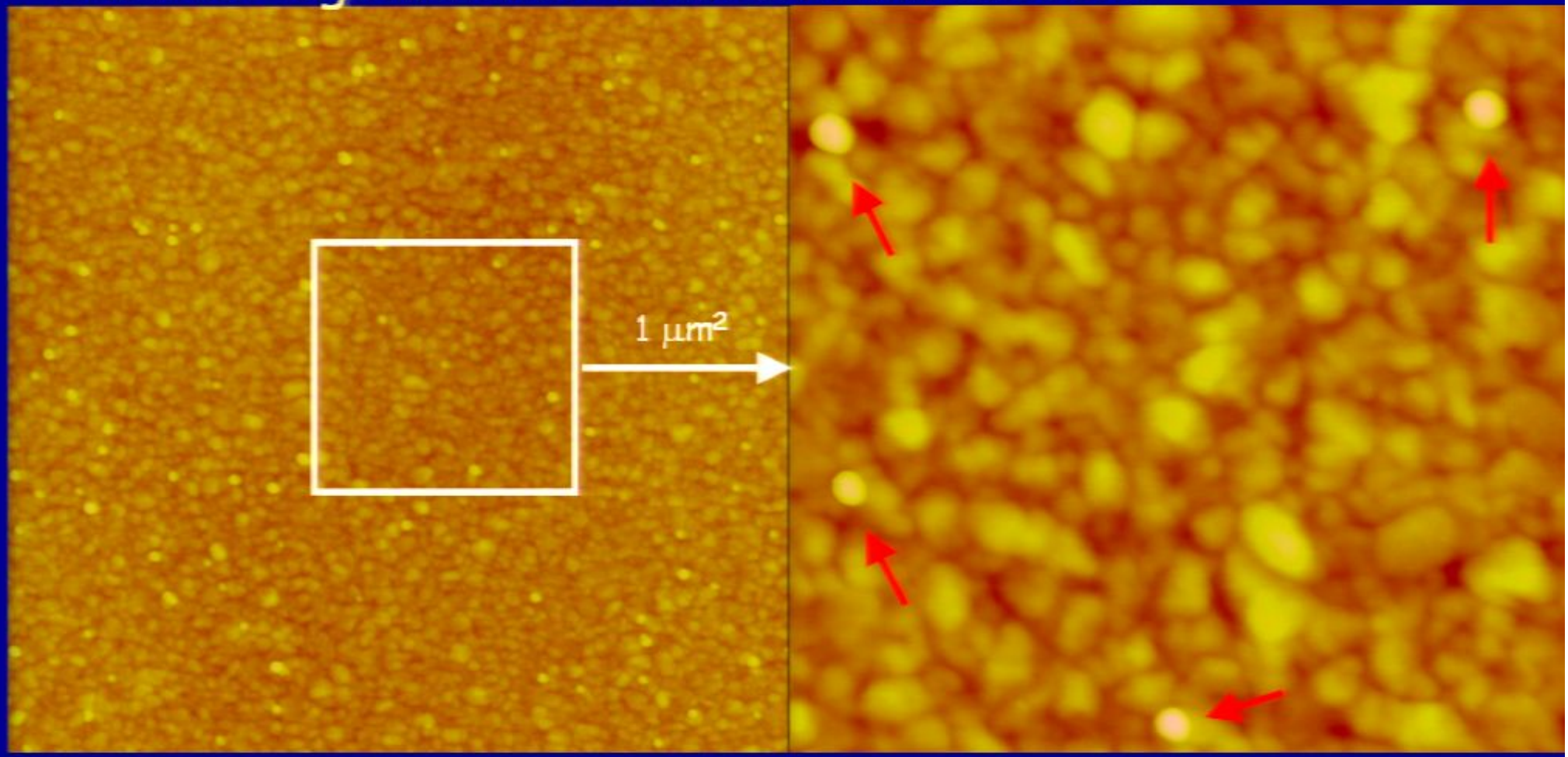
30 s of exposure

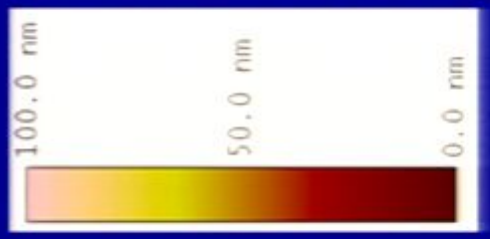




Molecular recognition at the near single- molecule level. (Molecular sensing functionality is collocated with hot spots, and the rest of the surface is passivated.)

All that signal comes from a few molecules





Density of AgNP per laser spot (~1 μm²) = ~3-5

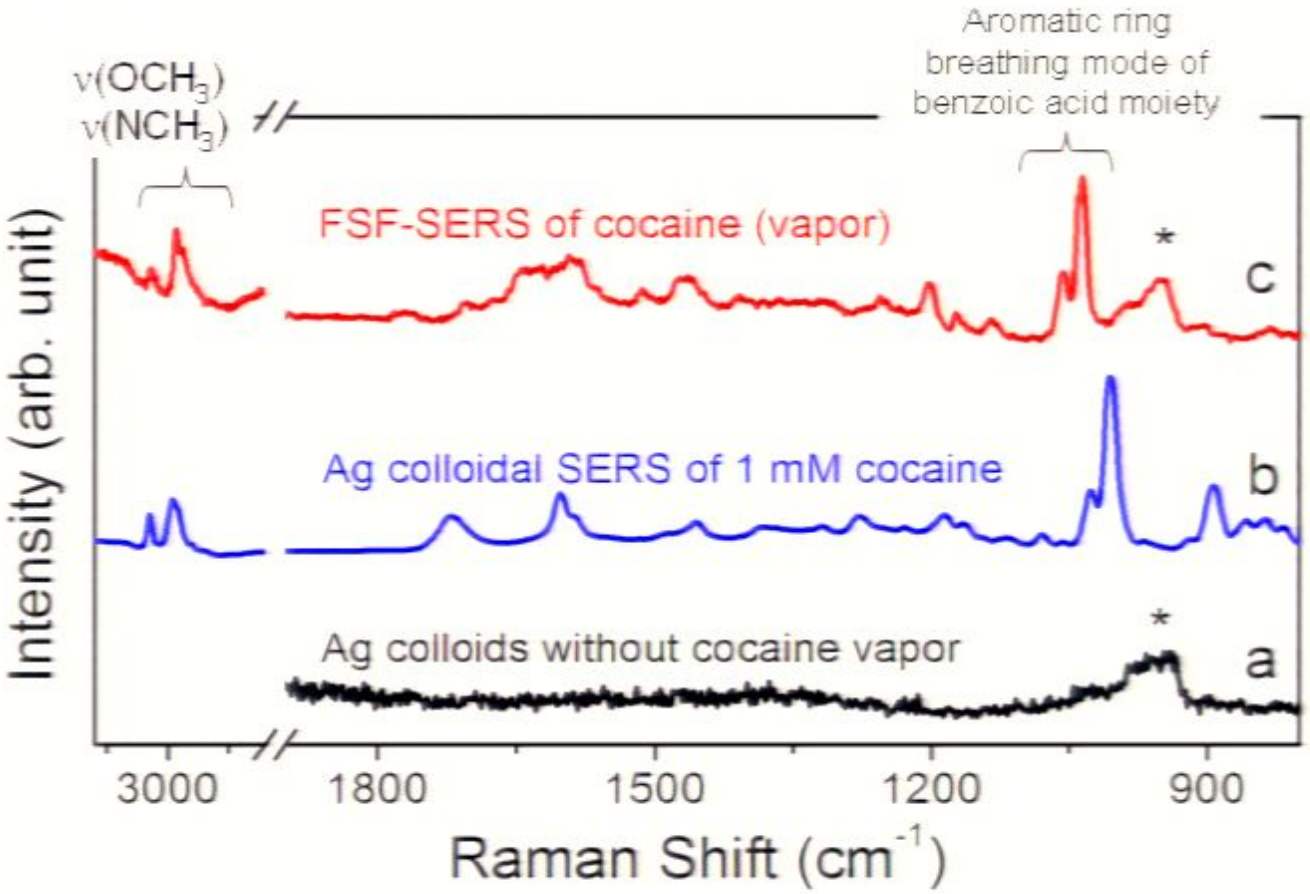
AFM images

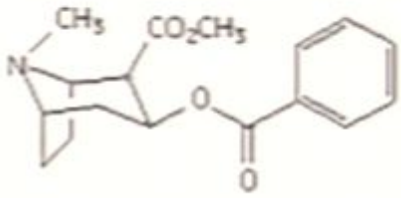
Summary

- SERS is primarily a plasmonic phenomenon
- Its discovery gave birth to the field of plasmonics and to the current resurgence of interest in metamaterials
- The phenomenon is entering its “engineering” phase
- A good quantum mechanical treatment of many plasmonic effects is still unavailable, including a good treatment of the conversion of a plasmon (a multi-electron dynamical effect) into single-electron excitations

End of slide show, click to exit.

Detection of cocaine vapor at room temperature





cocaine

30 s of exposure