



IIT ROORKEE



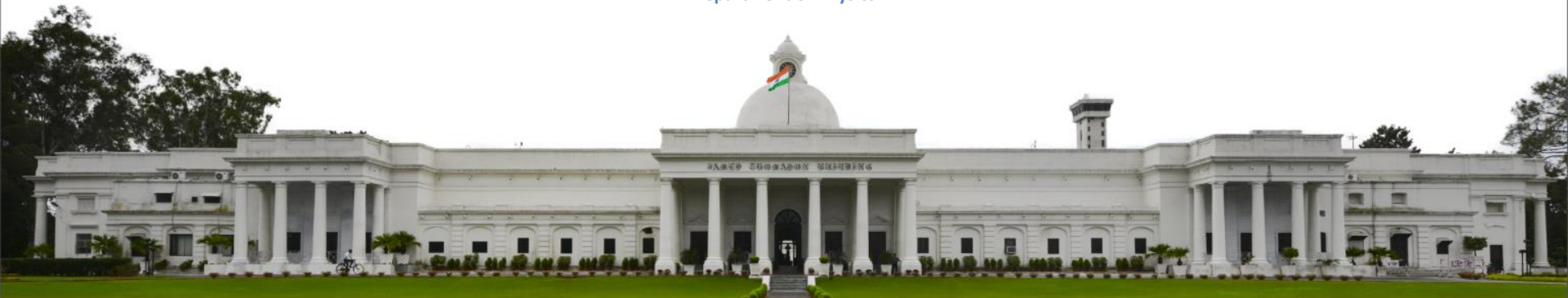
NPTEL ONLINE
CERTIFICATION COURSE

Lecture 16: Multiple Optical Sensors of Different Mechanisms

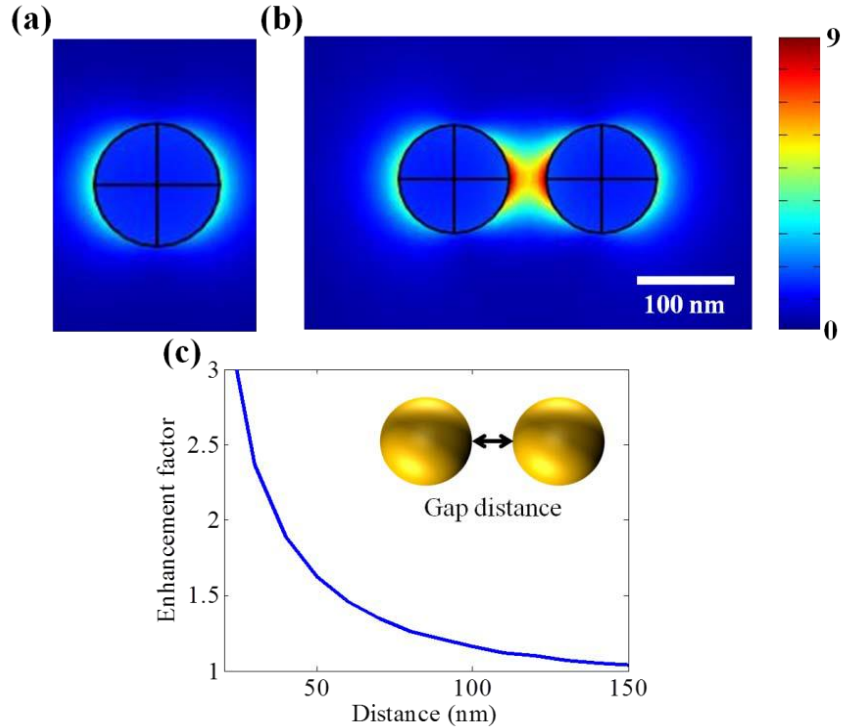
Optimum Field Enhancement in LSPR, Fluorescence, SEF, SEIRA, ESP-LSP Coupling, Colorimetric and CARS based Sensors

Sachin Kumar Srivastava

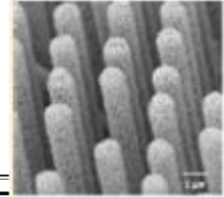
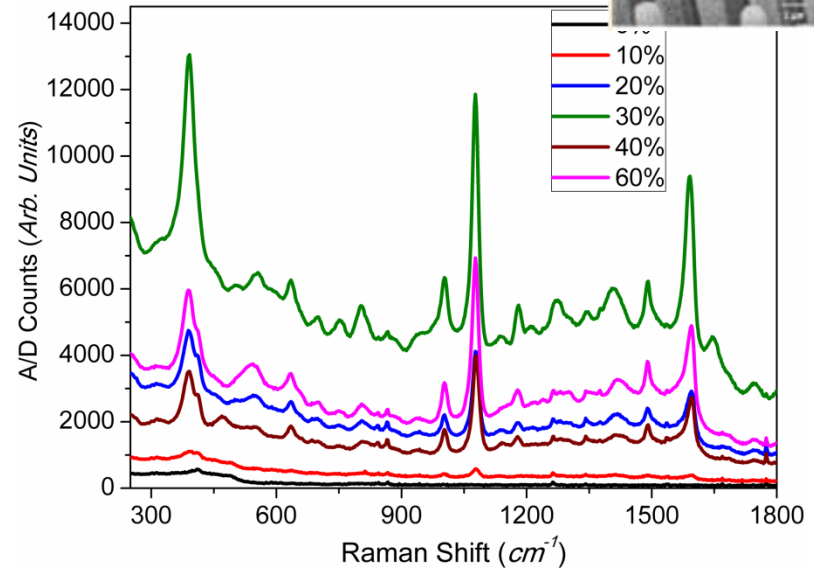
Department of Physics



Optimum Enhanced EM Fields in Plasmonic Configurations



A porous film of nanorods

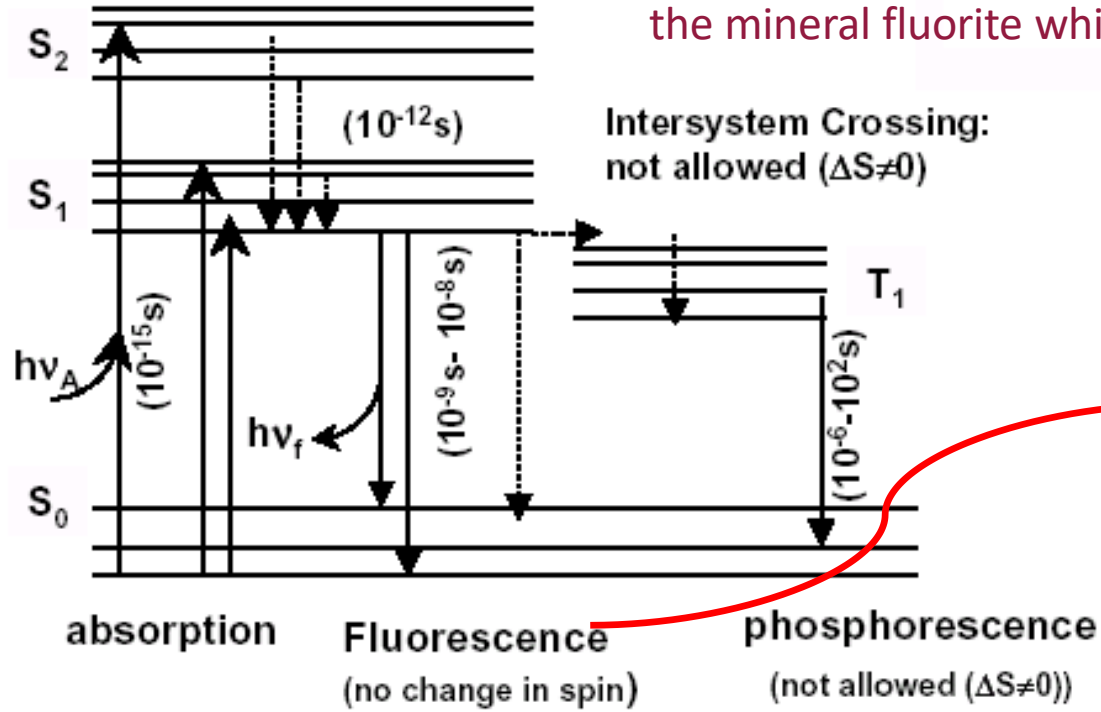


Chung et al, Sensors, **11**, 10907 (2011)

Srivastava et al., Small, **10**, 3579 (2014)

Fluorescence

Jablonski Diagram



“fluorescence”: named by George Gabriel Stokes (1852) after the mineral fluorite which lights up when illuminated with UV

Characteristic Times

Absorption: 10^{-15} s

Vibrational Relaxation: $10^{-12} - 10^{-10} \text{ s}$

Lifetime of S_1 : $10^{-10} - 10^{-7} \text{ s}$

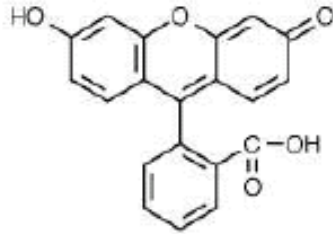
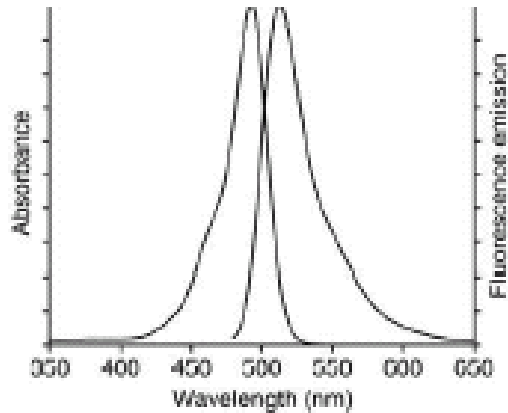
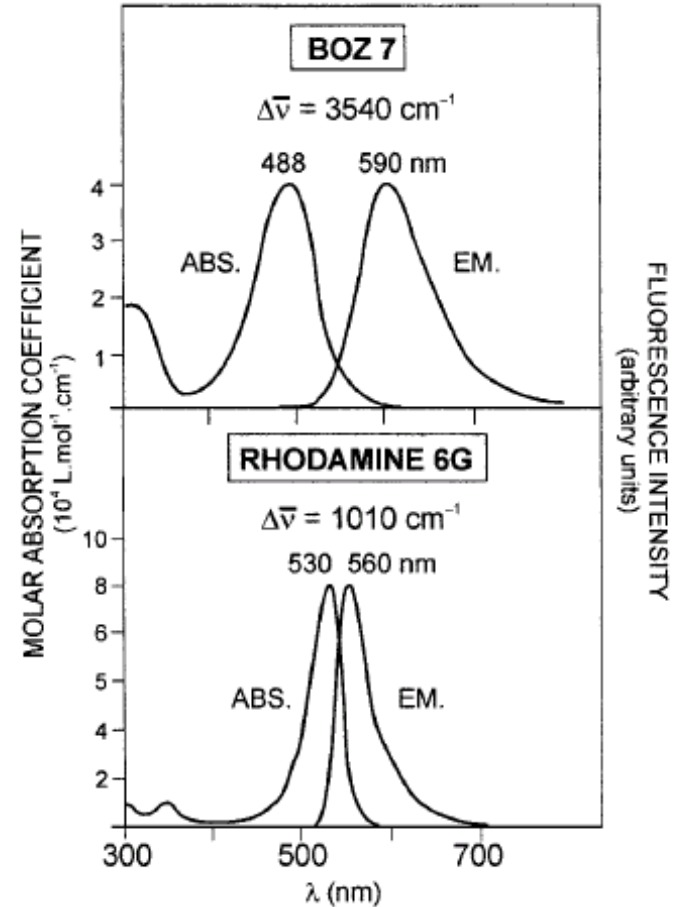
Inter-system Crossing: $10^{-10} - 10^{-8} \text{ s}$

Internal Conversion: $10^{-11} - 10^{-9} \text{ s}$

Lifetime of T_1 : $10^{-6} - 1 \text{ s}$

Some Common Fluorophores

Fluorescein

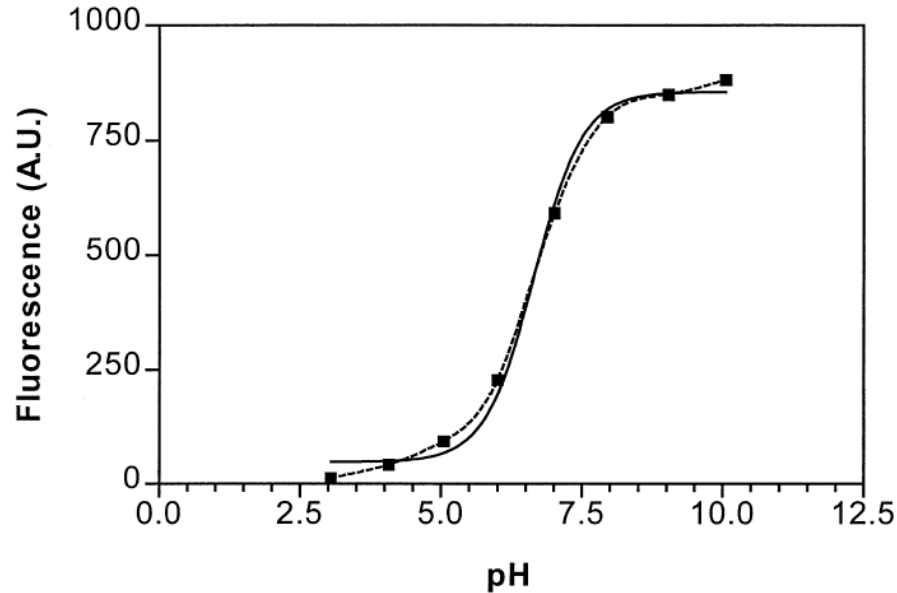


Intrinsic Fluorescence of Natural Proteins and Peptides

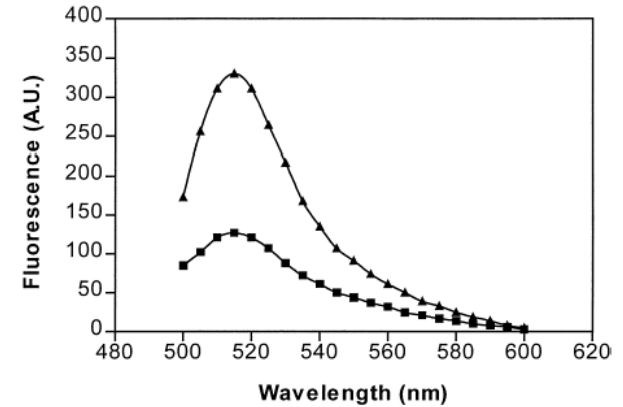
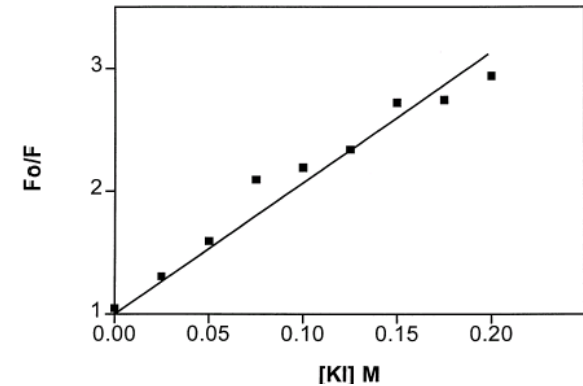
		Absorption		Fluorescence			Sensitivity
Substance	Condition	$\lambda_{\max}$ (nm)	$\epsilon_{\max}$ $\times 10^{-3}$	$\lambda_{\max}$ (nm)	ϕ_F	τ_F (nsec)	$\epsilon_{\max} \phi_F$ $\times 10^{-2}$
Tryptophan	H ₂ O, pH 7	280	5.6	348	0.20	2.6	11
Tyrosine	H ₂ O, pH 7	274	1.4	303	0.14	3.6	2.0
Phenylalanine	H ₂ O, pH 7	257	0.2	282	0.04	6.4	0.08
Adenine	H ₂ O, pH 7	260	13.4	321	2.6×10^{-4}	<0.02	0.032
Guanine	H ₂ O, pH 7	275	8.1	329	2.6×10^{-4}	<0.02	0.024
Cytosine	H ₂ O, pH 7	267	6.1	313	0.8×10^{-4}	<0.02	0.005
Uracil	H ₂ O, pH 7	260	9.5	308	0.4×10^{-4}	<0.02	0.004
NADH	H ₂ O, pH 7	340	6.2	470	0.019	0.40	1.2

Fluorescence Based Sensing

pH Sensor



Quenching Effect based Sensing



Fluorescence Biosensor

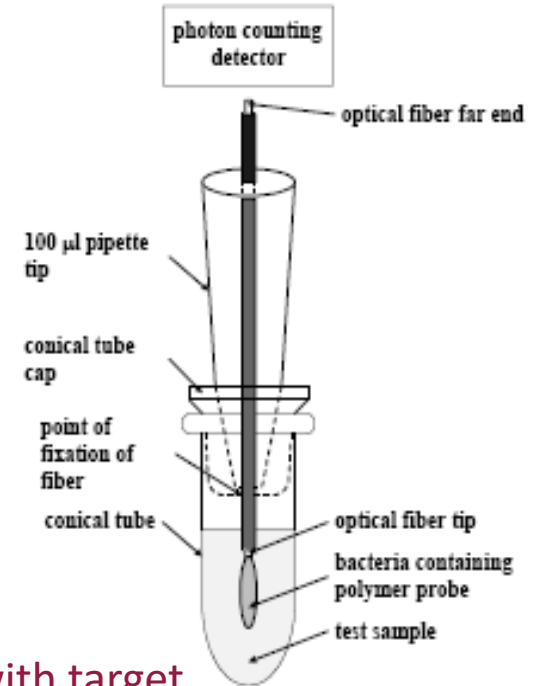
Fluorescent biosensor design

The fundamental design of a fluorescent biosensor consists of a receptor binding site and a fluorophore connected by a linker.



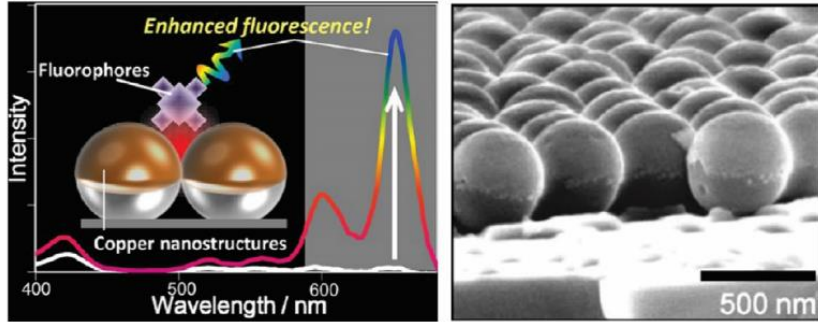
The linker provides a means for triggering a change in the fluorescence of the attached fluorophore.

Bissel et al. Topics in Current Chemistry, Vol. 168 , Springer Verlag (1993), pp. 223-261



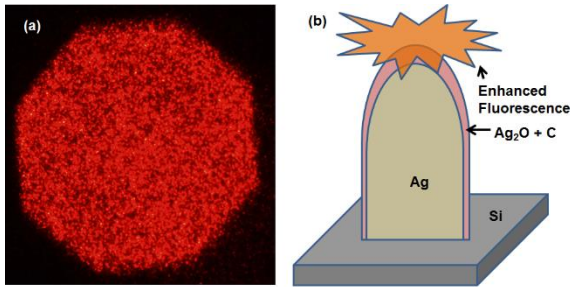
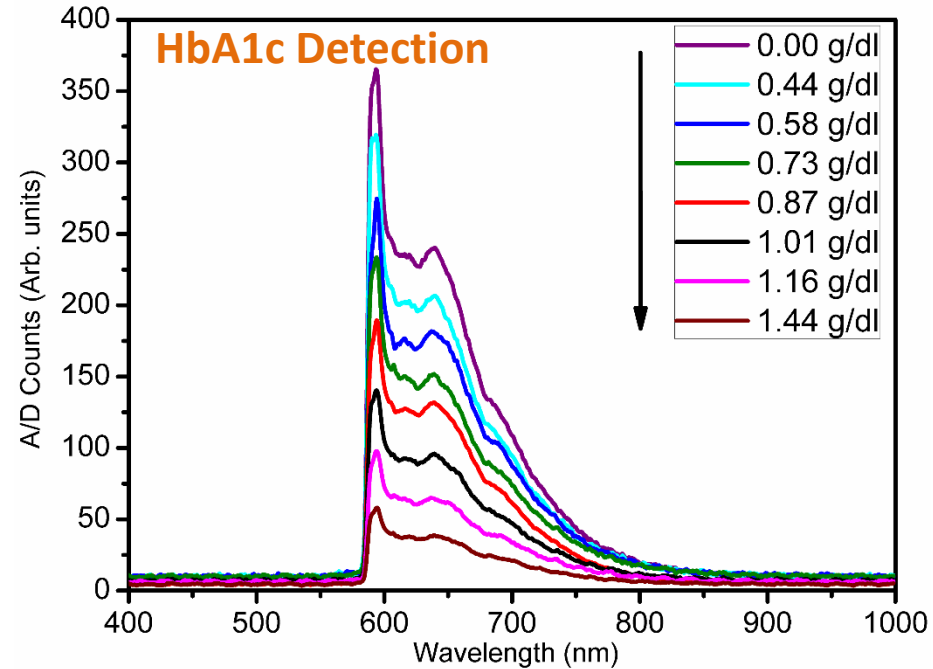
- Genetically engineered bacteria that glow when interacting with target.

Surface Enhanced Fluorescence (SEF)



Sugawa et al., ACS Nano 11, 9997 (2013)

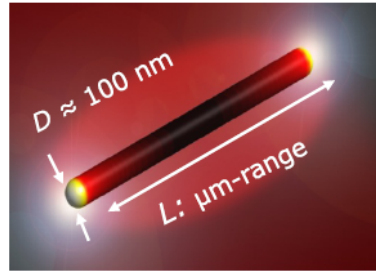
Enhanced Intrinsic Fluorescence



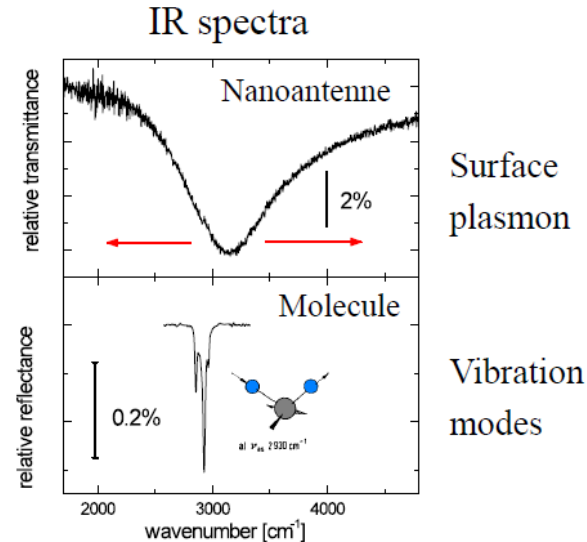
Srivastava et al., Optics Express, 25, 4761 (2017)

Surface Enhanced IR Absorption (SEIRA)

Principle: Exploitation of near – field enhancement in the vicinity of plasmonic nanoantenna



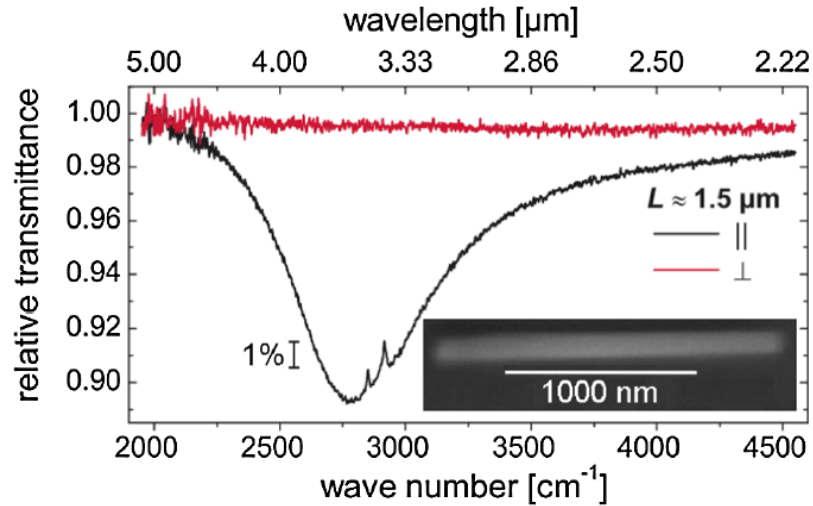
Nanoantenna
- Micrometric length
- Nanometric width



Coupling between molecular vibrations and surface plasmons

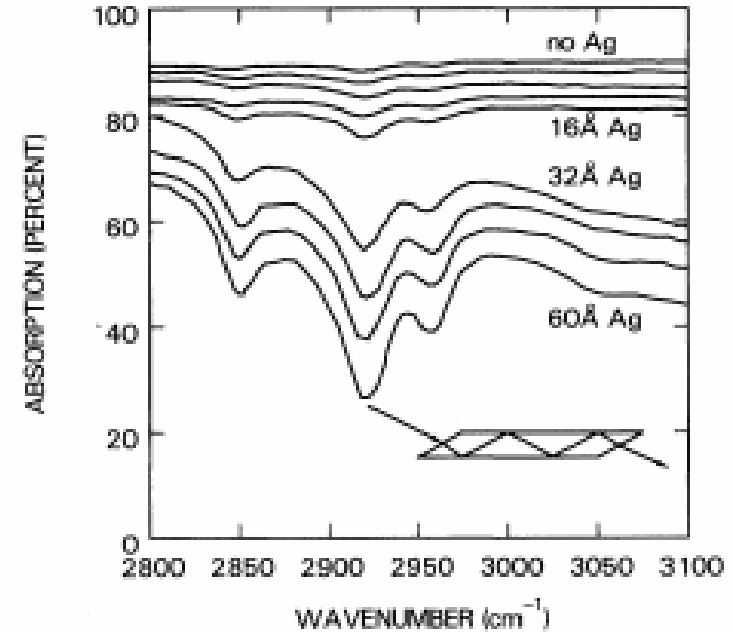
SEIRA Based Sensing

Gold nanowires on CaF_2 , Electrochemistry on membrane, Diameter = 100 nm
Monolayer of OctaDecaThiol (ODT, $\text{C}_{18}\text{H}_{37}\text{SH}$)



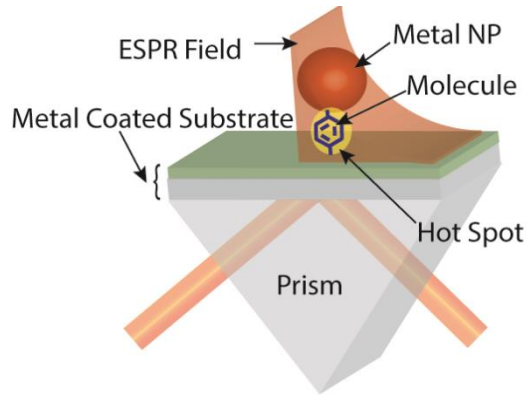
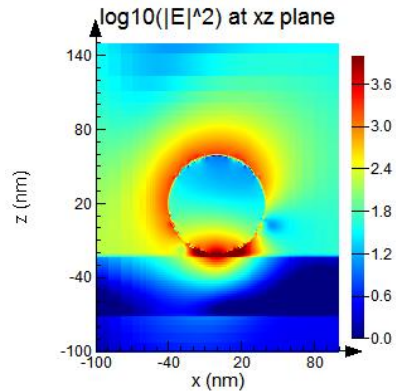
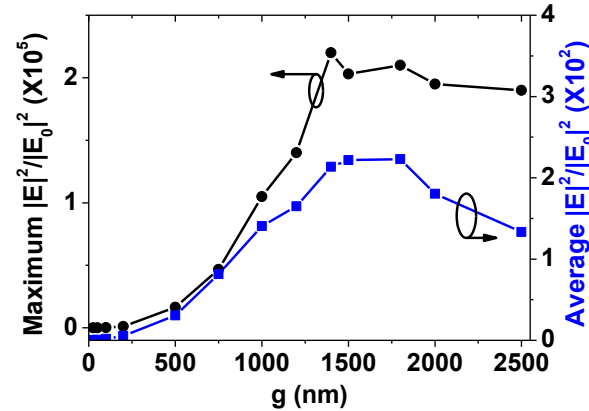
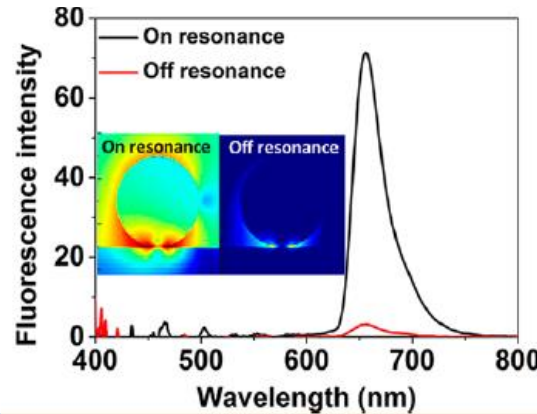
⇒ Enhancement factor around 300 000

F. Neubrech, et al., Phys. Rev. Lett. 101, 157403, 2008



Tsang et al. Phys. Rev. Lett. 1980, 45, 201

ESP-LSP Coupling Based Ultra-high Enhancement of EM Field

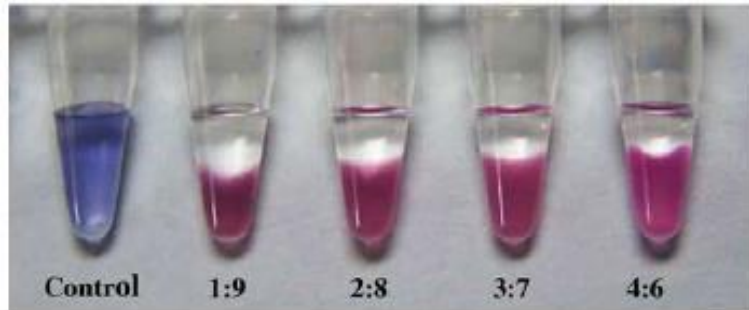
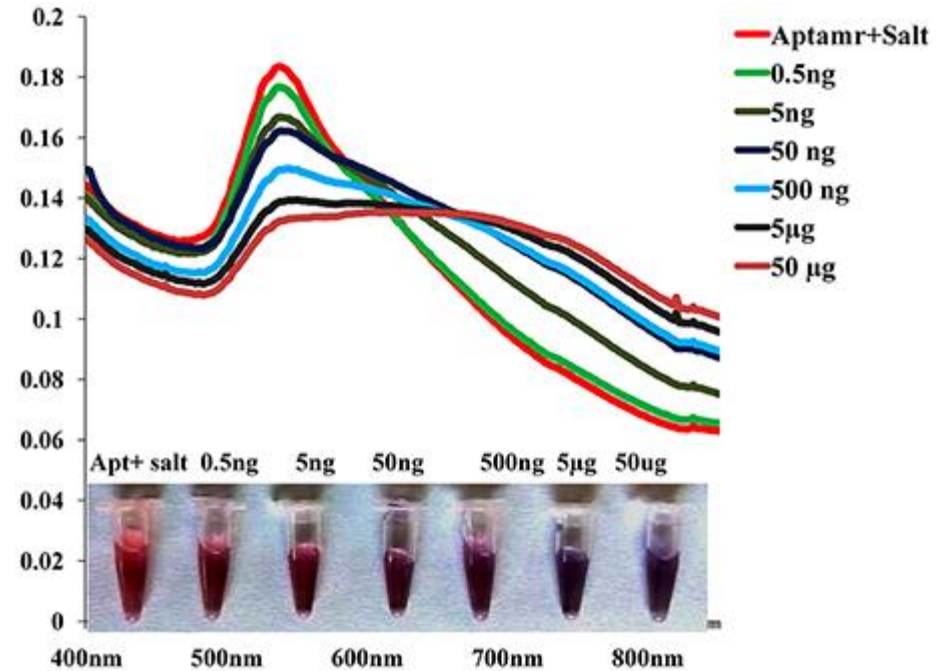


Li, et al. J. Phys. Chem. C **119**, 19382 (2015)

Li, et al. Nanoscale **8**, 15658 (2016)

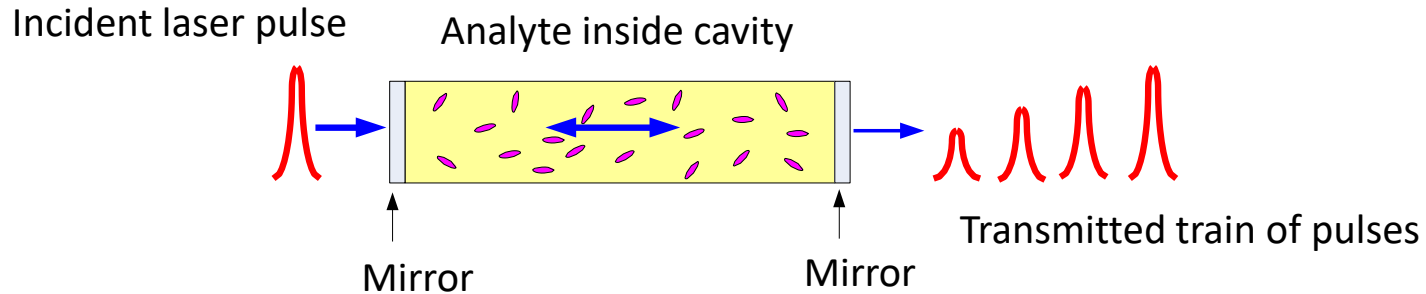
Colorimetric Sensors

- Change of color when interaction occurs.
- Mostly Qualitative but sometimes Quantitative



Mondal et al., Front. Microbiol. 9 179 (2018)

Cavity Ring Down Absorption Spectroscopy Sensors



For uniform absorbers the peaks decay exponentially:

$$\tau = l / \{c(1 - R + Y + \alpha l)\}$$

← Mirror loss

$$I = I_0 \exp(-t / \tau)$$

For a cavity length of 1 m, the 100-ppm/roundtrip precision translates to a minimum detectable absorbance of $\approx 10^{-6} \text{ cm}^{-1}$

$$A = -\log_{10} T$$

$$A = \frac{l}{2.303c} \left(\frac{1}{\tau} - \frac{1}{\tau_e} \right)$$

← decay time when the cavity is without the analyte.

Summary

1. Optimum nanoplasmonic structures for highest enhanced EM Fields were discussed
2. Basics of fluorescence and its use in sensing was presented
3. SEF, SEIRA, ESP-LSP coupling, colorimetric and CARS based sensing were discussed.

Thank You