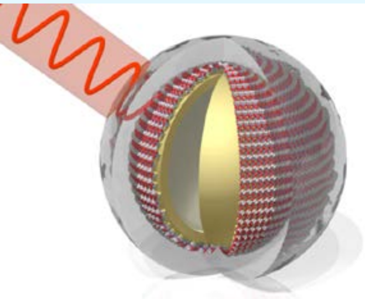
UNIVERSITÄT DUISBURG ESSEN

Open-Minded

Raman Workshop@ETHZ
13th June 2018

CENIDE
CENTER FOR NANOINTEGRATION DUISBURG-ESSEN

Surface-enhanced Raman Spectroscopy and Imaging with Molecularly Functionalized Noble Metal Nanoparticles

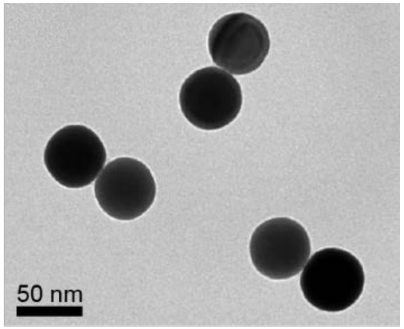


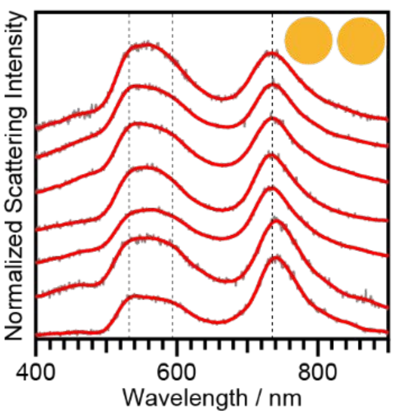
J.-H. Yoon, L. Langolf, W. Xie,
R. Grzeschik, E. Stepula,
X. Wang, Y. Zhang,
<u>Sebastian Schlücker</u>

University Duisburg-Essen

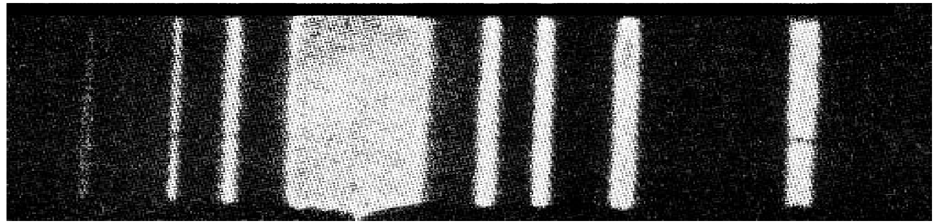
Department of Chemistry

www.uni-due.de/schluecker-lab

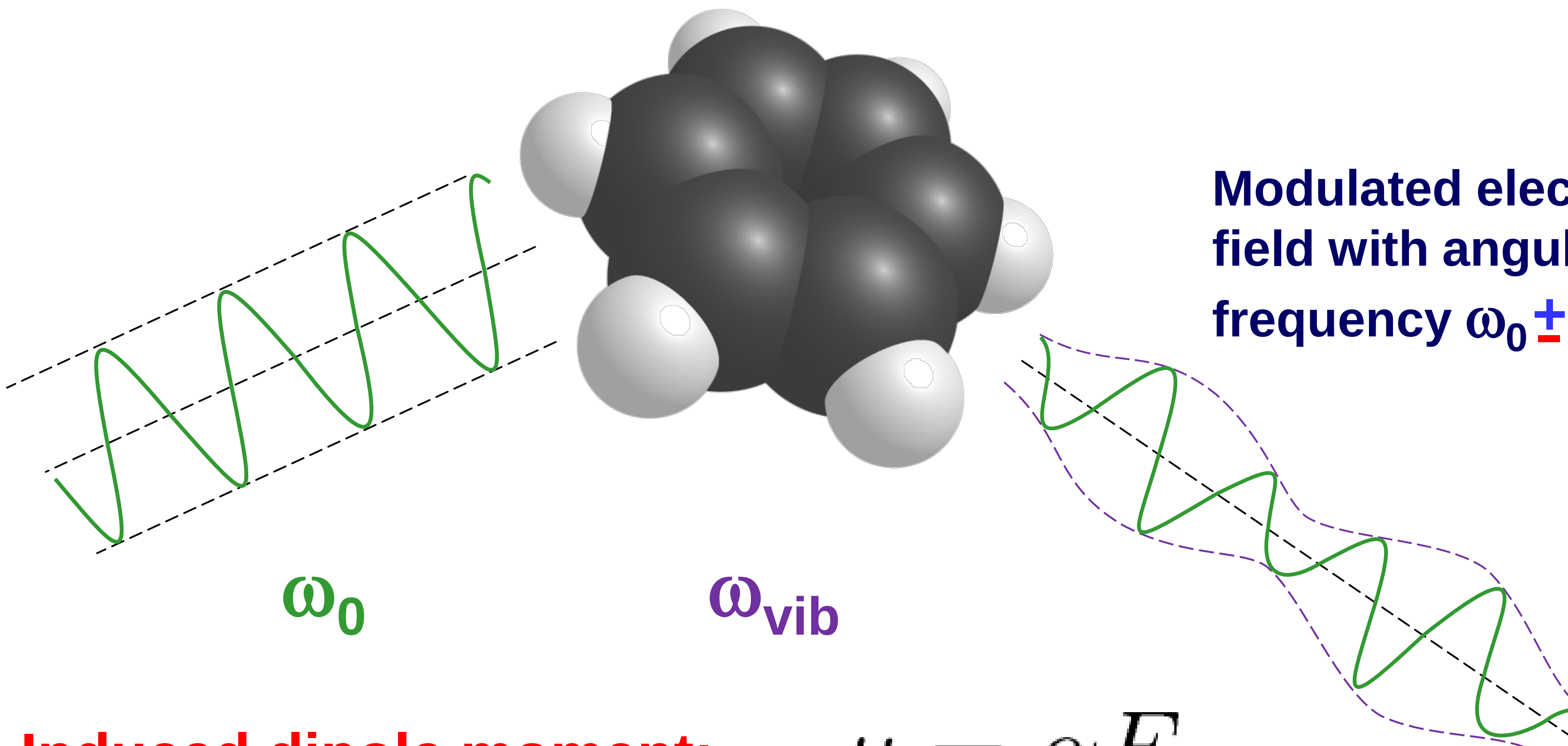




Classical Description of Raman Scattering



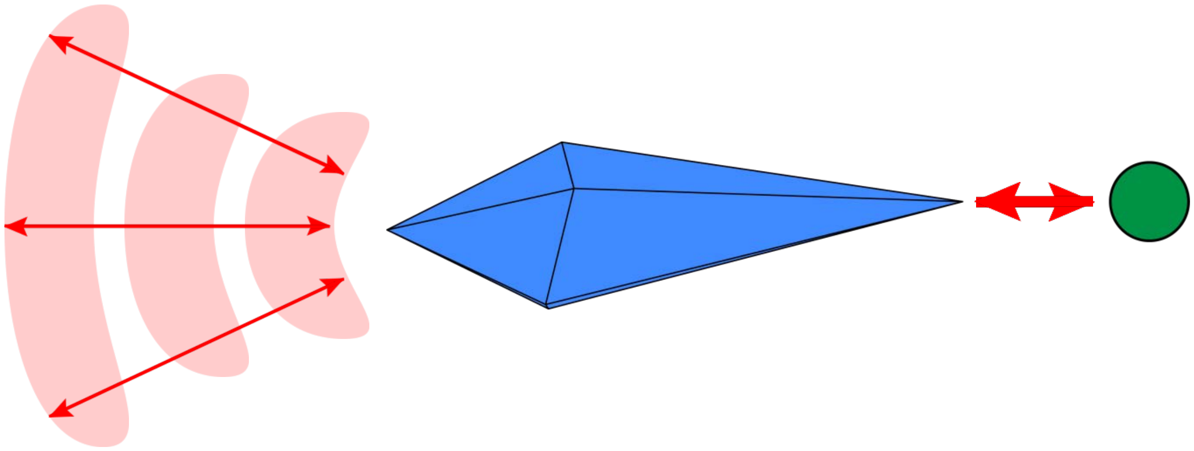
$\omega_0 + \omega_{vib}$ ω_0 $\omega_0 - \omega_{vib}$



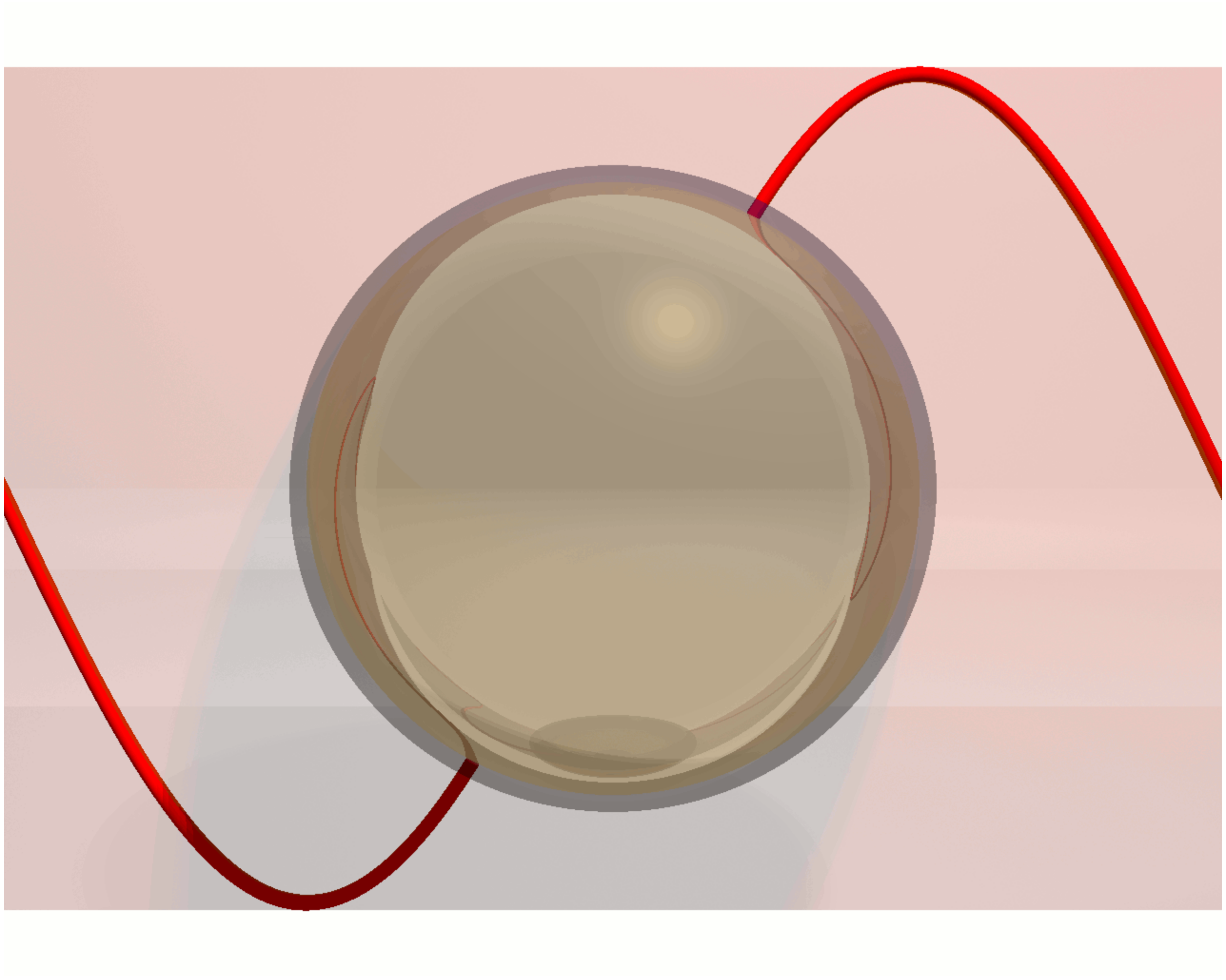
Modulated electric field with angular frequency $\omega_0 \pm \omega_{vib}$

Induced dipole moment: $\mu = \alpha E$

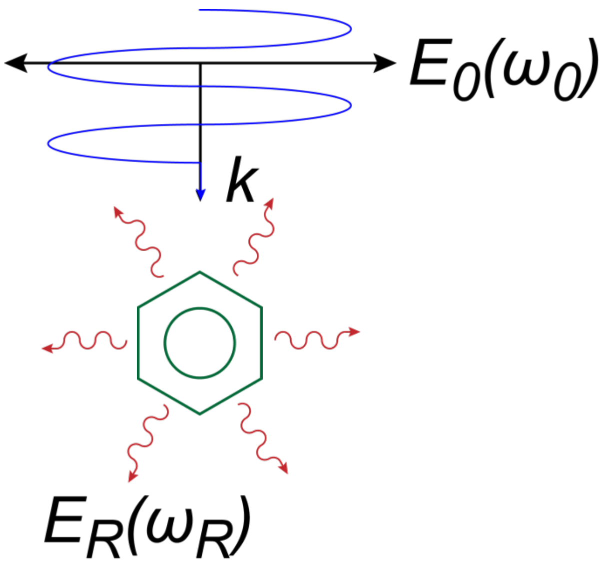
Nano-Antenna: Receiver and Transmitter



Localized Surface Plasmon Resonance (LSPR) Excitation on AuNP



Normal versus Surface-Enhanced Raman Scattering (SERS)

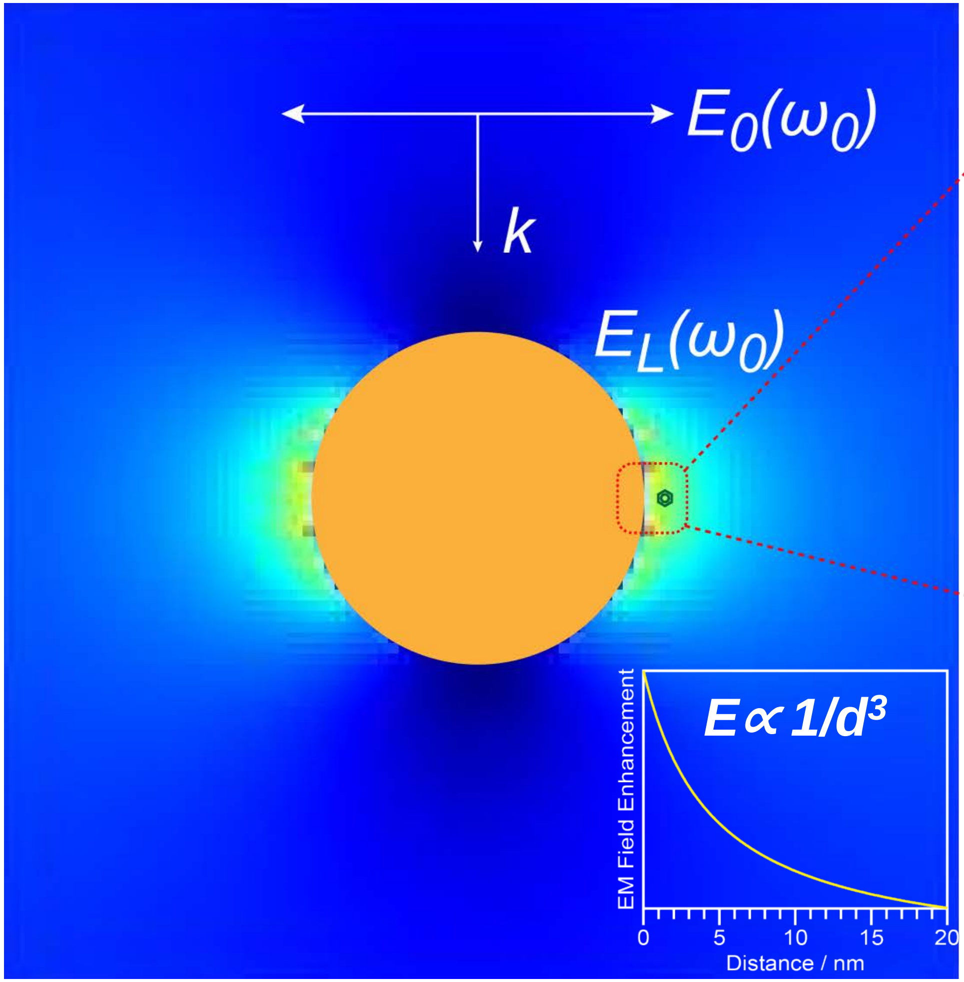


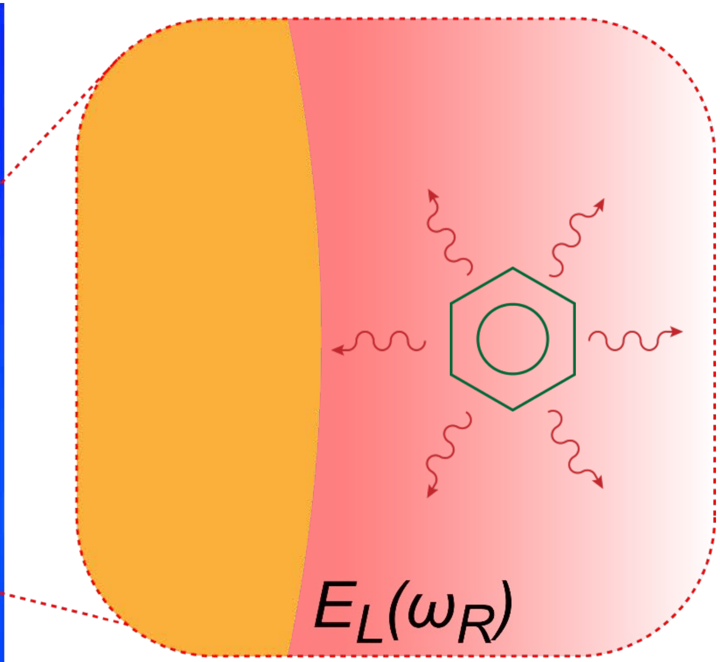
Normal Raman:

$I_R \propto E^2$

Normal versus Surface-Enhanced Raman Scattering (SERS)

The Electromagnetic Enhancement (EM) Contribution





SERS:

$$I_{SERS} \propto |E_L(\omega_0)|^2 \cdot |E_L(\omega_R)|^2 \approx E^4$$

$$\propto 1/d^{12}$$

Sensitivity

Surface selectivity

A Short History of Surface-enhanced Raman Scattering (SERS)

1973 - First observation (Fleischmann)

1977 - First explanation & quantitative measurement (Van Duyne)

1978 - Electromagnetic model for SERS (Moskovits)

1997 - First observation of single-molecule SERS (Nie, Kneipp)

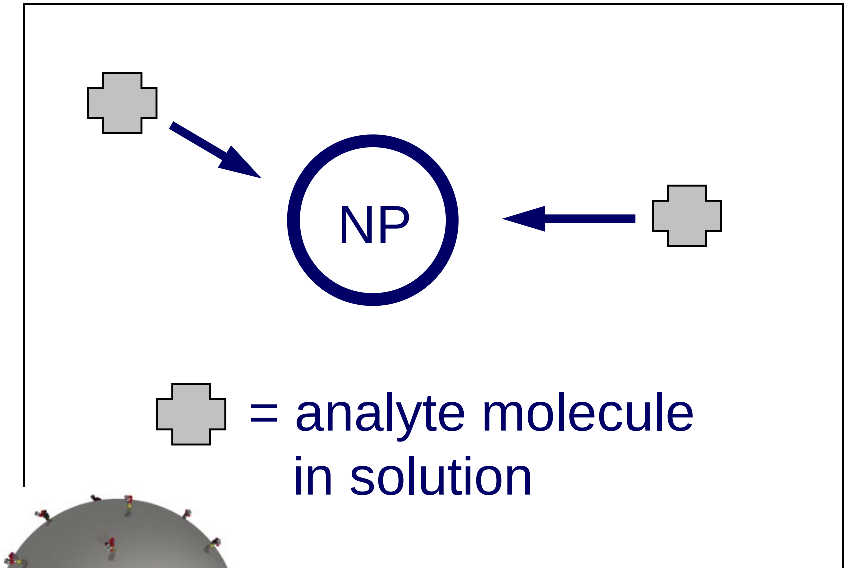
SERS Enhancement Factor (EF):

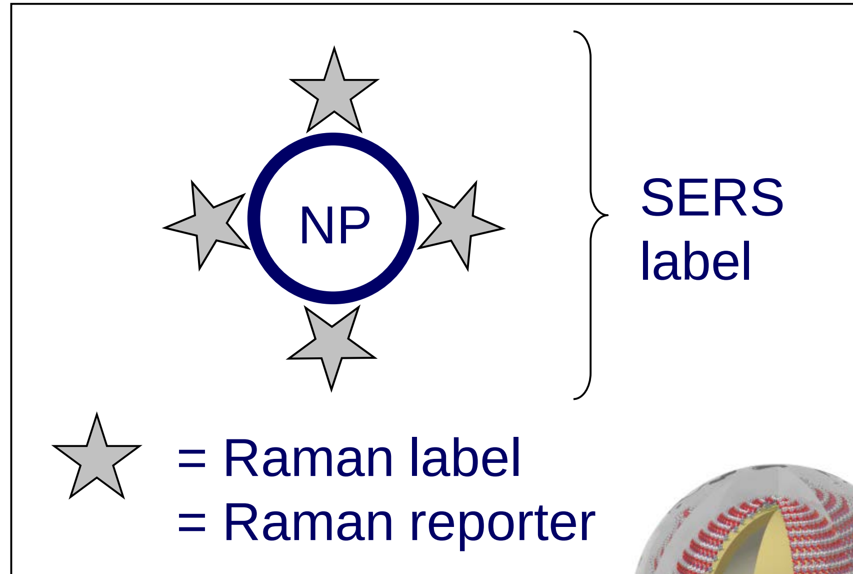
$$\frac{\text{SERS Signal/Number of Molecules on Surface}}{\text{Normal Raman Signal/Number of Molecules in Solution}}$$

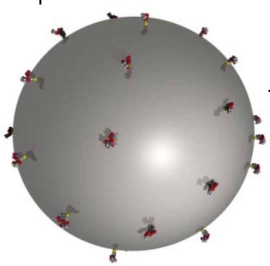
EM = plasmonic (up to ~10^{11}) × CM (non-plasmonic up to ~$10^{2\text{-}3}$)

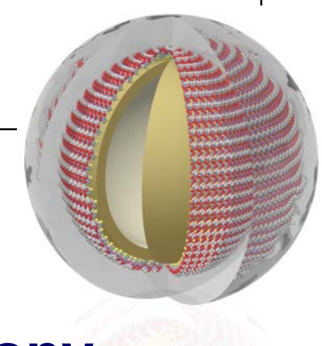
SERS Applications with Noble Metal Colloids

Label-free vs. SERS labels (nanotags)







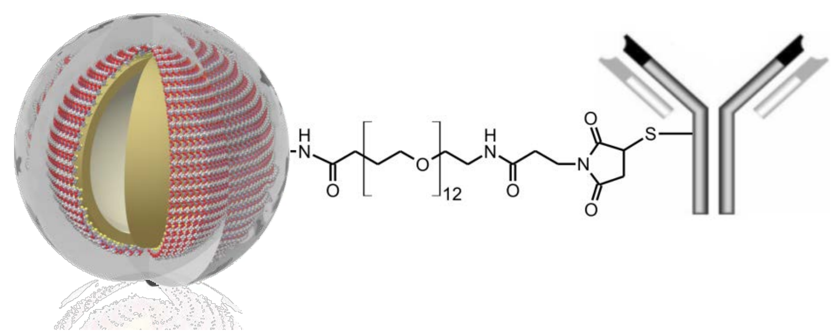


- **Detection of Analytes**

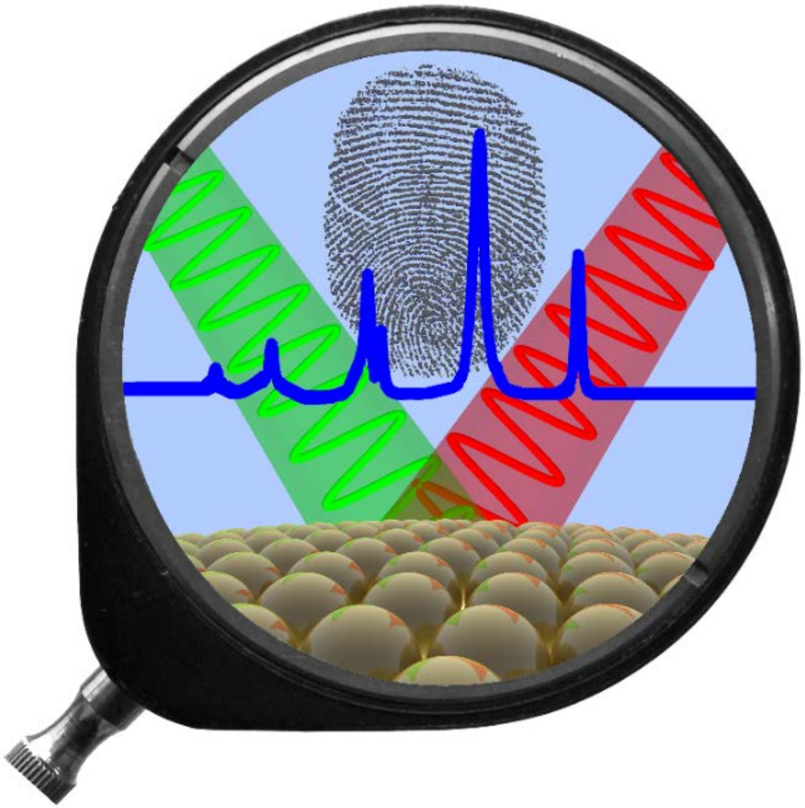
biomolecules, drugs, explosives, food components, pharmaceuticals, pigments (e.g., in paintings)

- **Chemical Reaction Monitoring**

- **Immunoassays**
- **iSERS Microscopy**



SERS Literature: From Fundamentals to Applications



Angewandte Reviews

Spectroscopic Methods

Surface-Enhanced Raman Spectroscopy: Concepts and Chemical Applications
Angew. Chem. Int. Ed. **2014**, 53, 4756-4795.

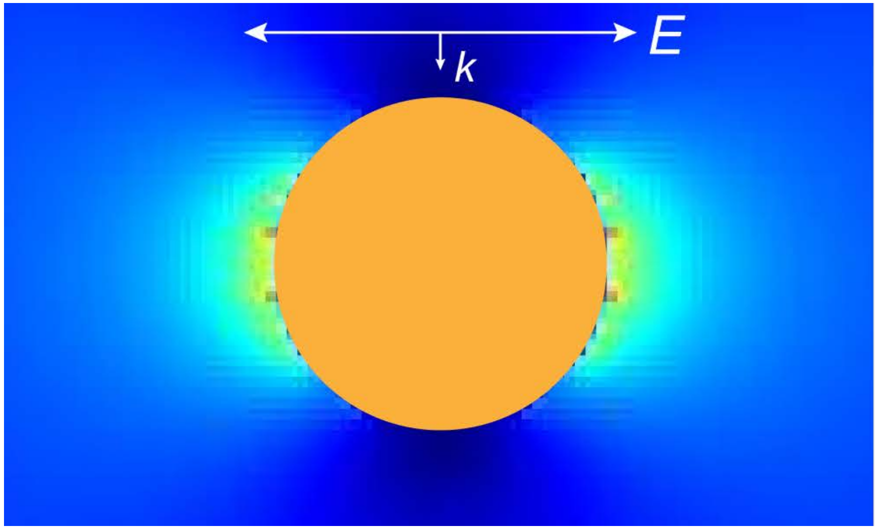
WILEY-VCH

Surface Enhanced
Raman Spectroscopy

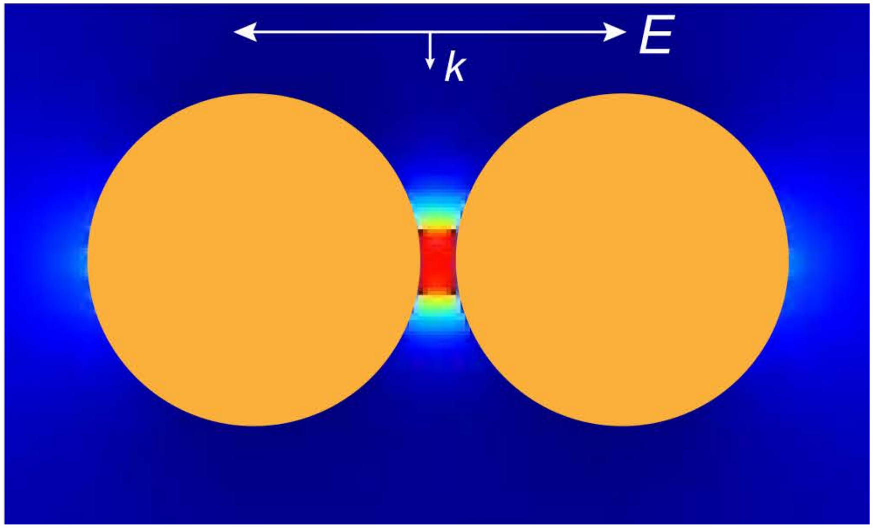
Analytical, Biophysical and Life Science Applications

Maximum Signal Enhancement: Dimers for Ultrasensitive SERS

Monomer



Dimer

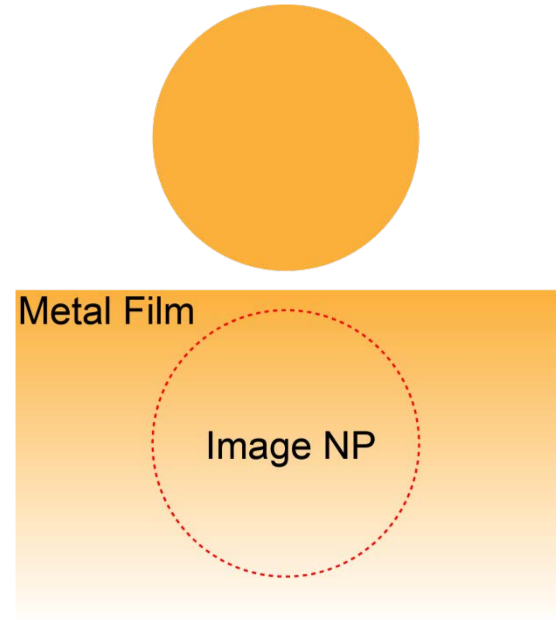


Hot Spot

Dependent on Gap Distance

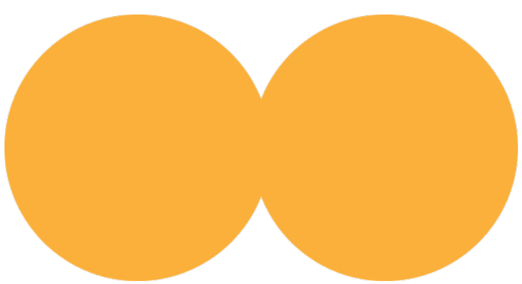
Dimers: Generating a HOT SPOT

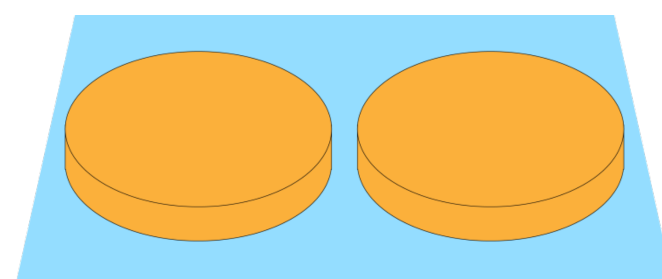
Inter-gap



Intra-gap

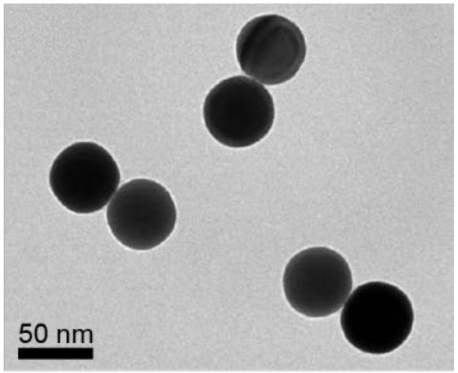
Crevice

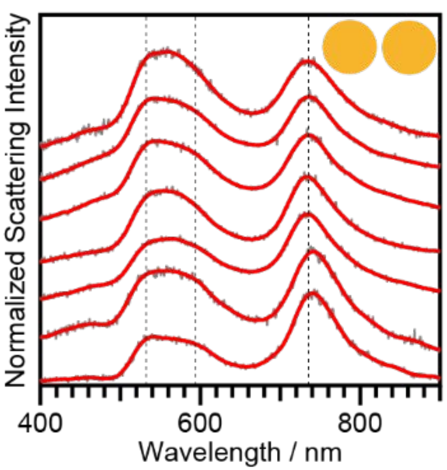




Physical Chemistry I @ UDE

Precision Plasmonics

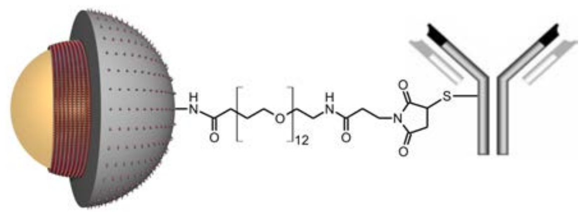




Small **2018**

Anal. Chem. **2018**

SERS nanotags/labels immuno-SERS (iSERS)



Angew. Chem. **2009**

Small **2010**

Small **2011**

Chem. Comm. **2012**

Nanoscale **2013**

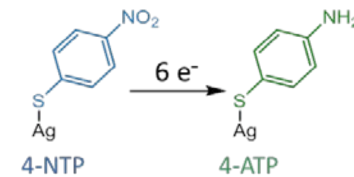
Chem. Comm. **2014**

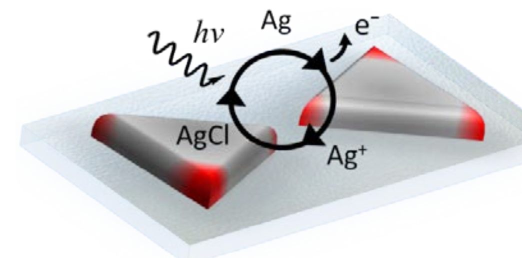
PCCP **2015**

Analyst **2016**

Anal. Chem. **2017**

Chemical Energy Conversion





JACS **2011**

JACS **2013**

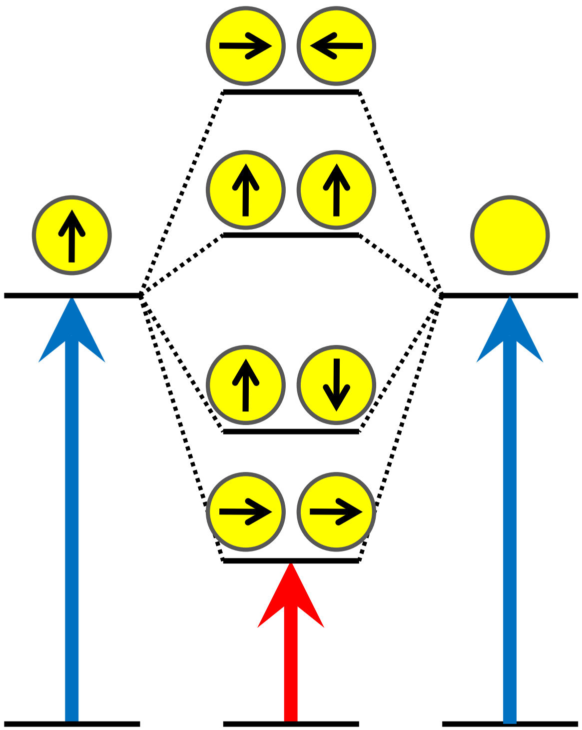
Nature Comm. **2015**

Angew. Chem. **2016**

Nature Comm. **2017**

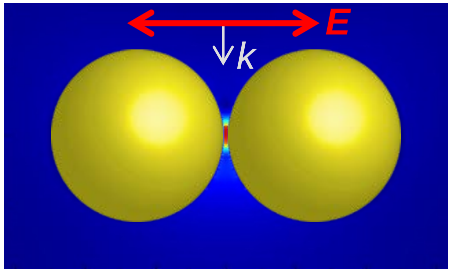
Theory: Ideal Dimers of Gold Nanospheres

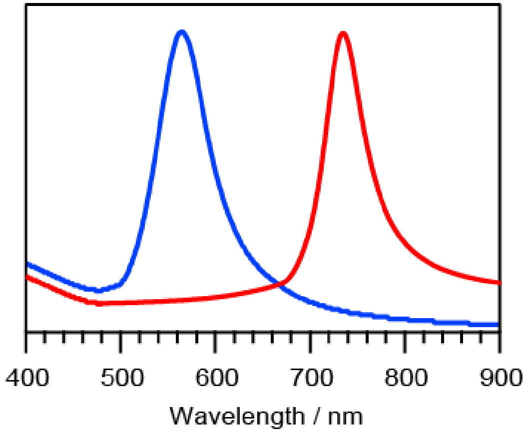
Plasmon Hybridization (cf. LCAO theory)



Nordlander *et al*.

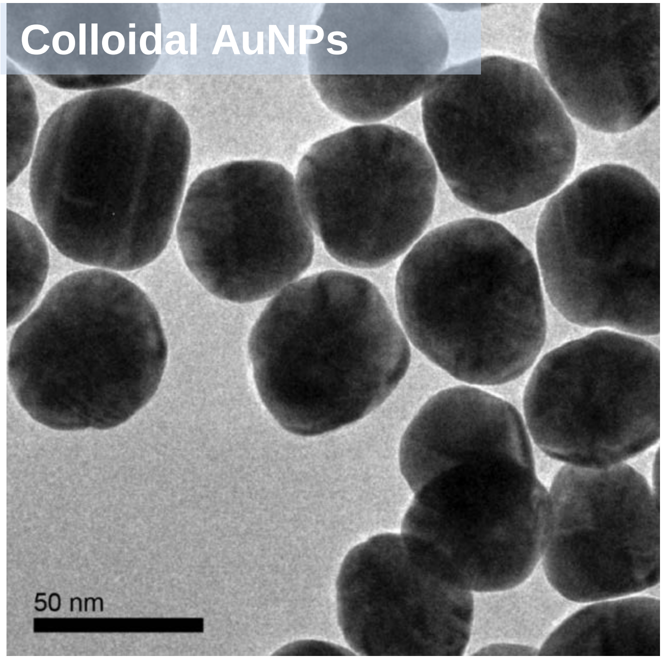
Two spheres separated by a very small defined gap



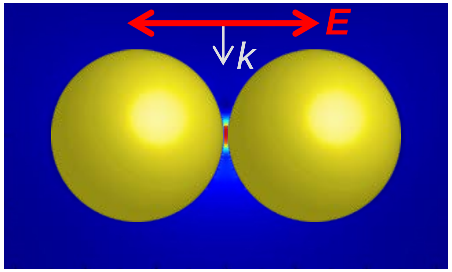


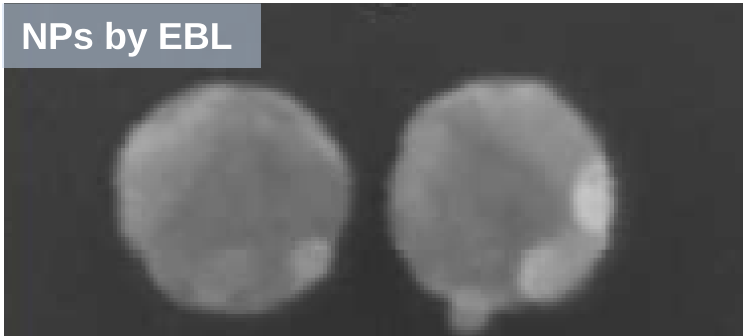
Towards Ideal Dimers: Experimental Challenges

Gold nanoparticles are not perfectly spherical but are nanocrystals



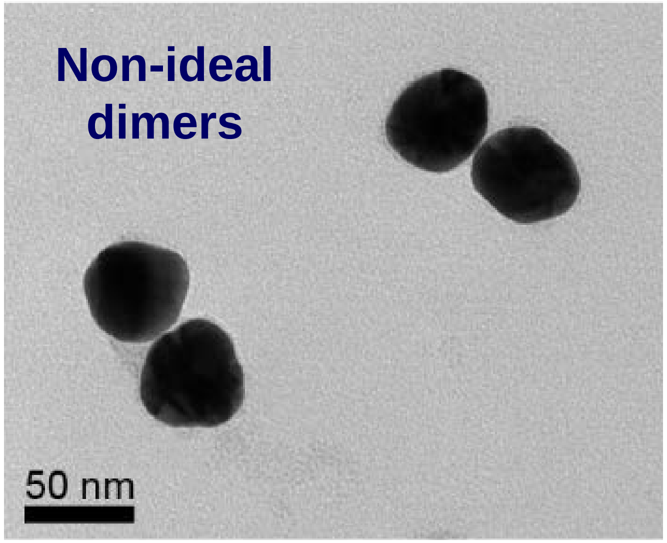
Two <u>spheres</u> separated by a <u>very small defined gap</u>

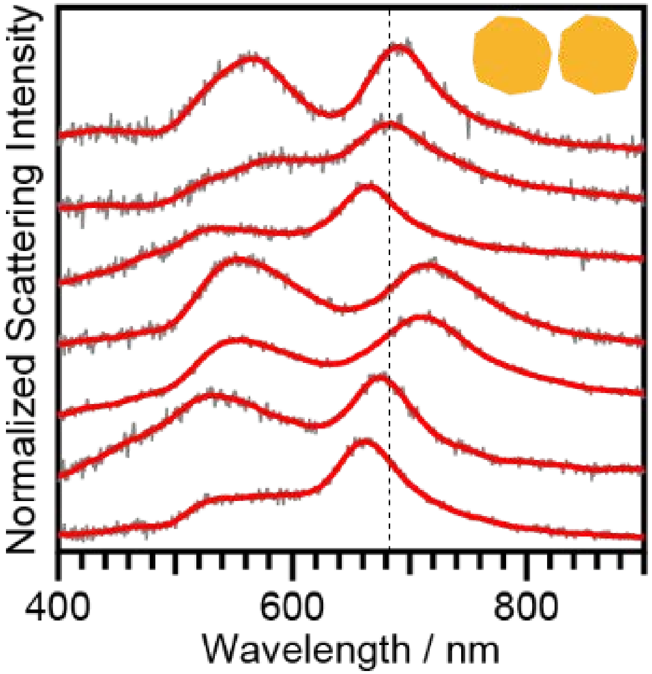




Halas *et al*. *Nano Lett.* **2013**, *13*, 3281.

Non-Spherical Particles with Controlled Gap Distance

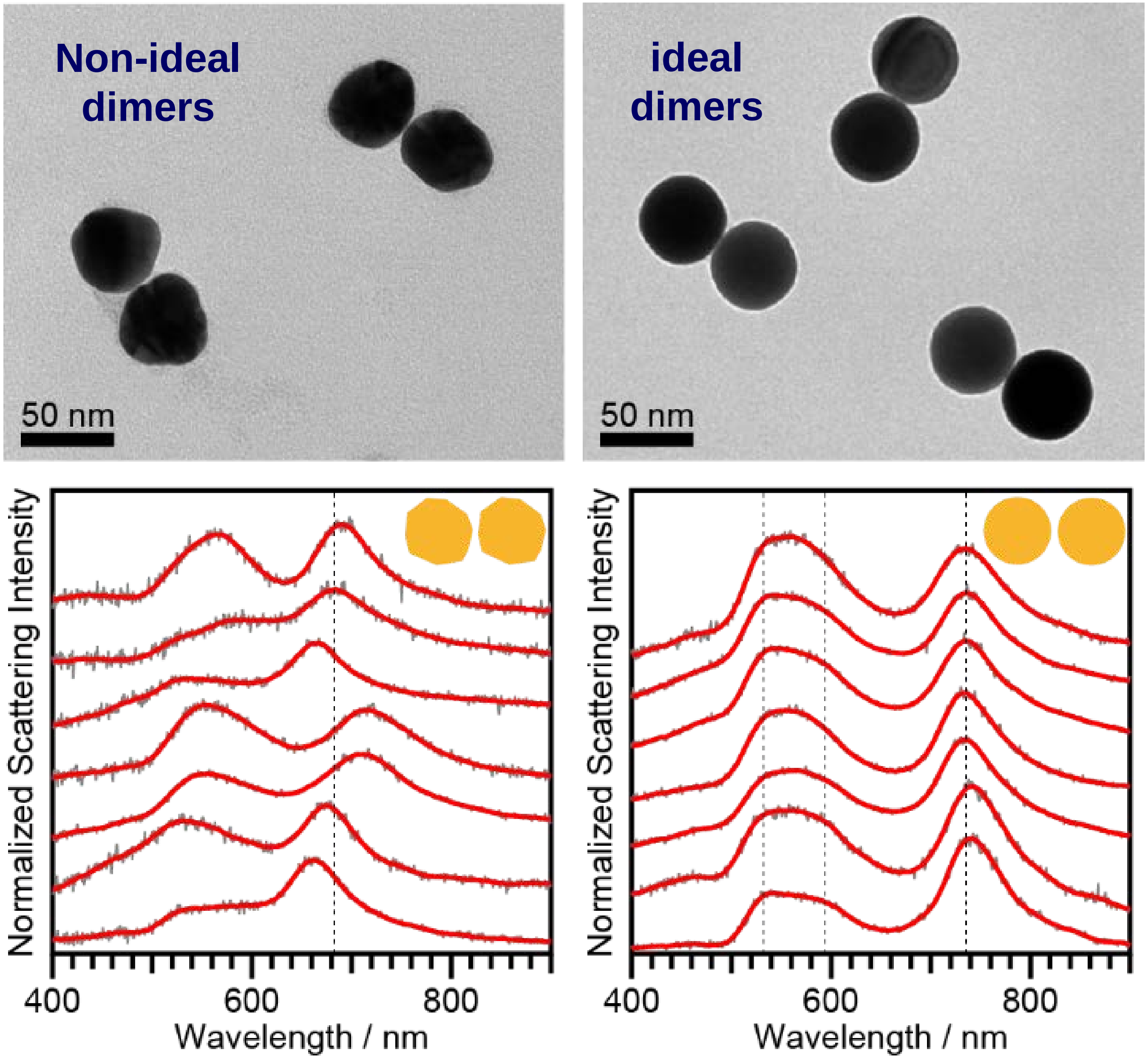




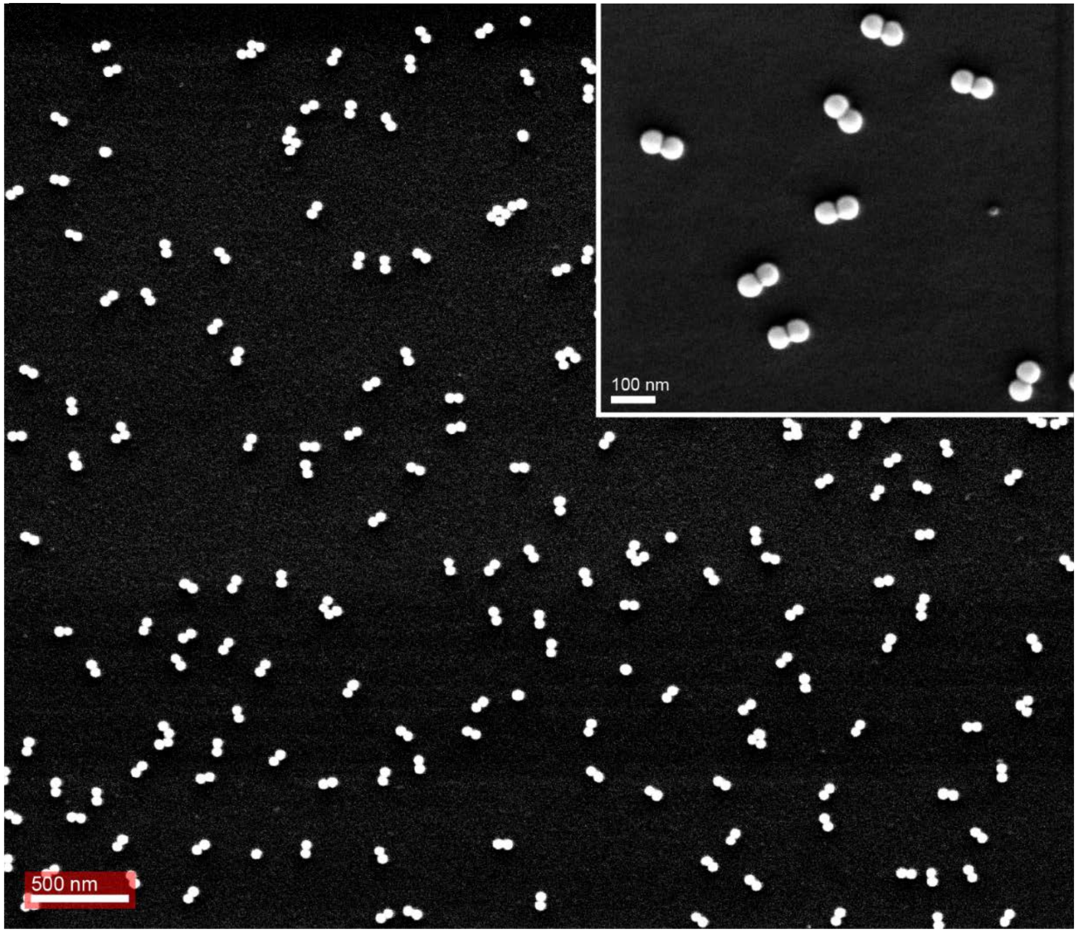
Controlled short gap distance: C8 dithiol (ca. 1.3 nm)

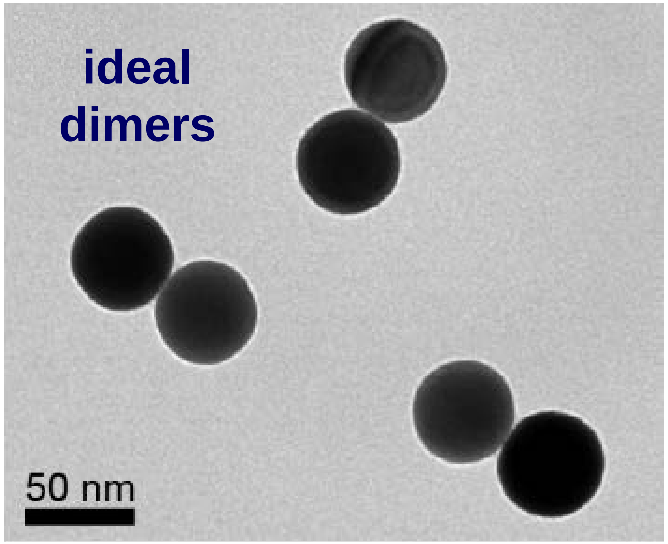
Single particle dark field scattering spectra

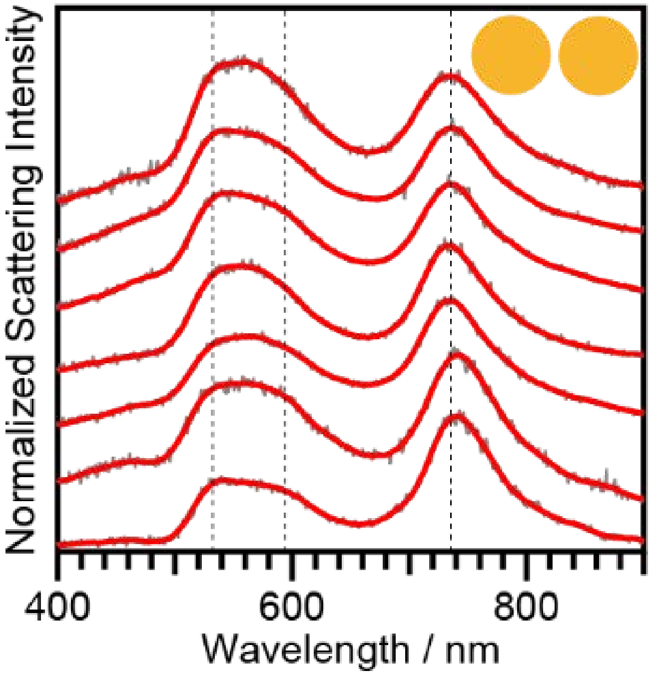
Precision Plasmonics: Ideal Dimers of Gold Nanospheres



Precision Plasmonics: Ideal Dimers of Gold Nanospheres

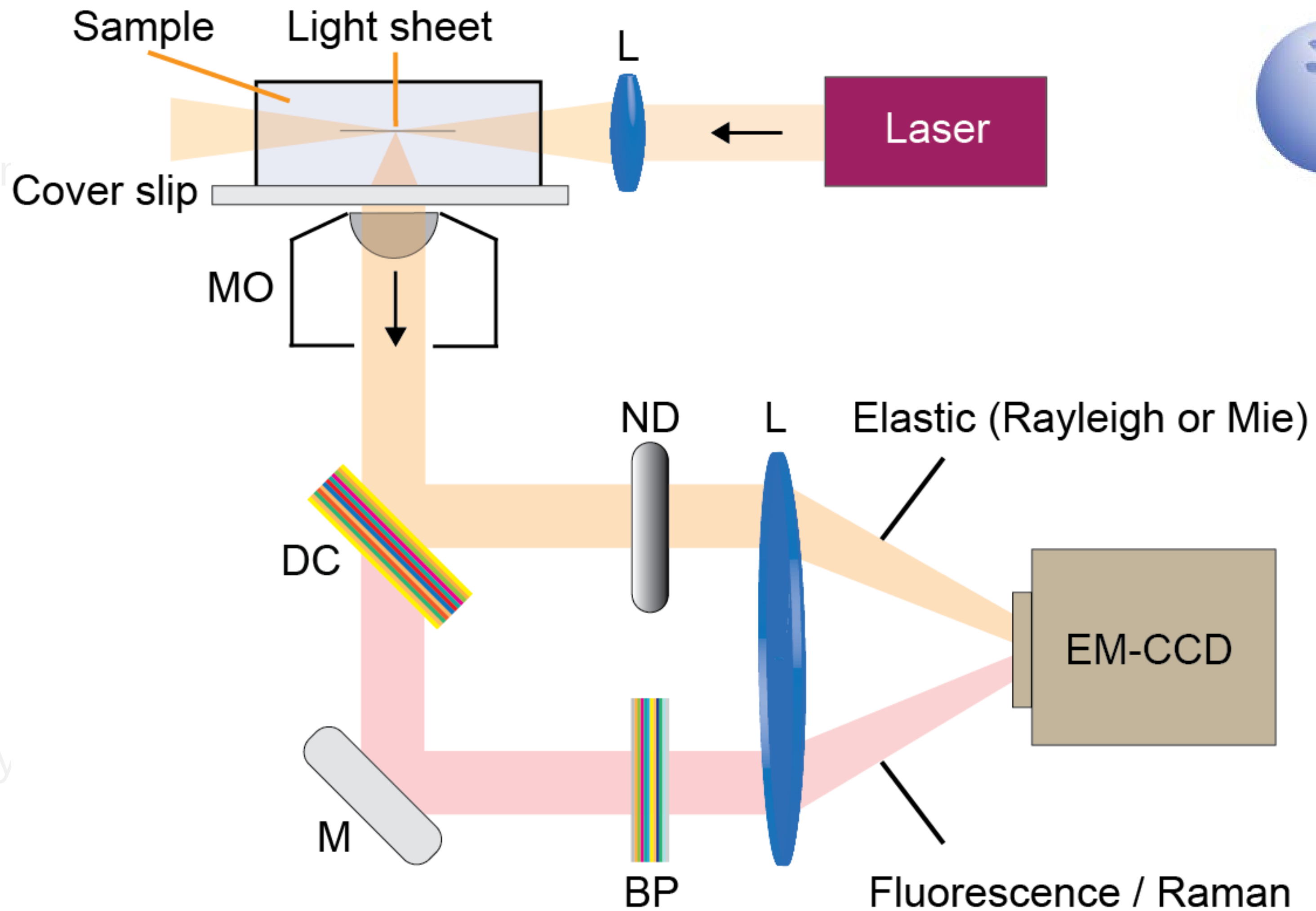






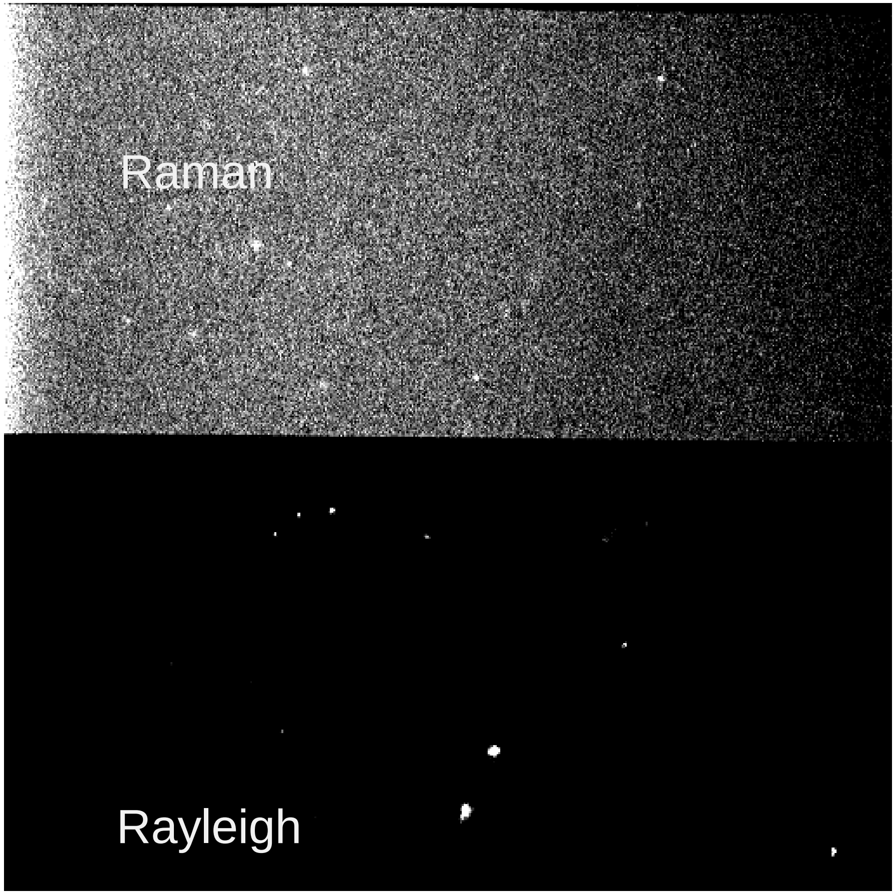
Small **2018**

Correlative Single-Particle Rayleigh/SERS Imaging in Suspension

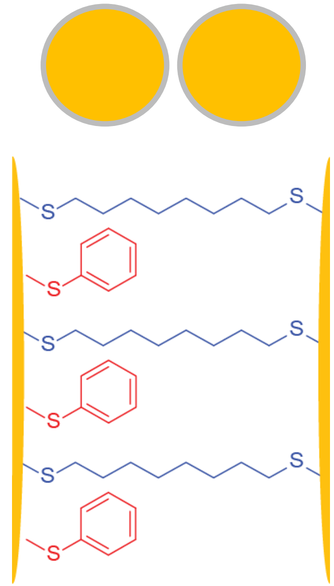


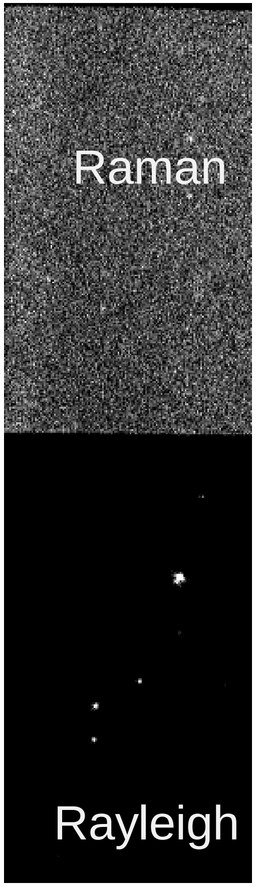
Anal. Chem. **2018**

Single-Particle SERS of Dimers in Suspension



100 ms / frame



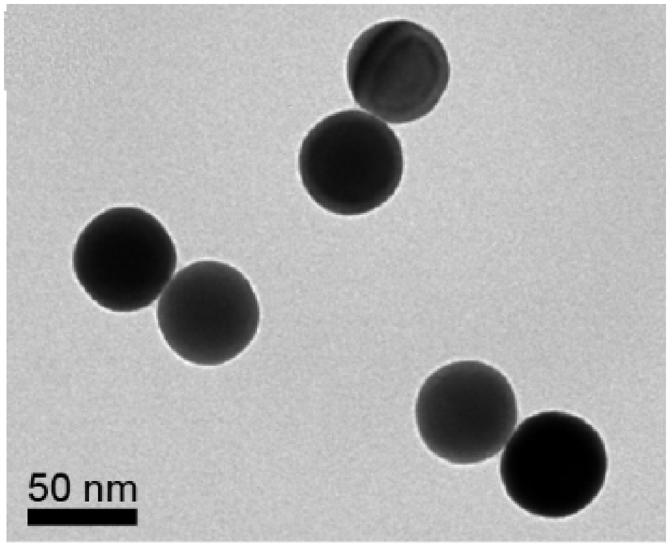


10 ms / frame

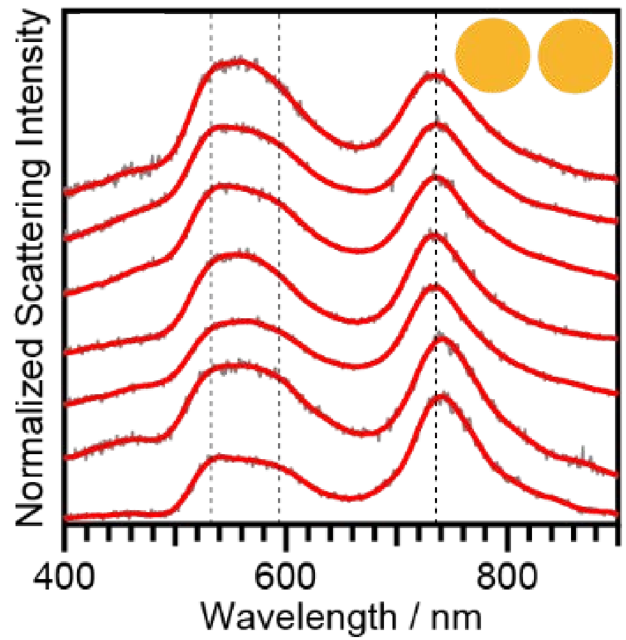
Anal. Chem. **2018**

Summary 1: Precision Plasmonics with AuNP Dimers

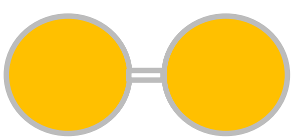
uniform **structure (gap morphology)**

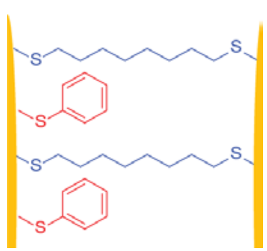


uniform **scattering spectra**



Correlative Rayleigh/SERS video rate imaging of *single* NPs in suspension

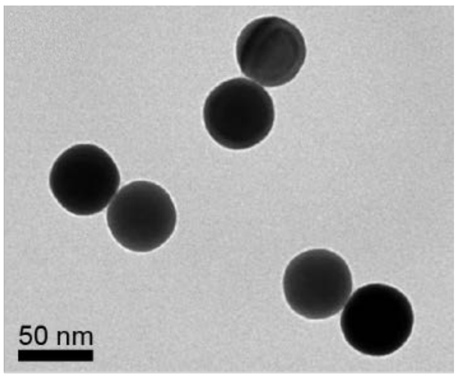


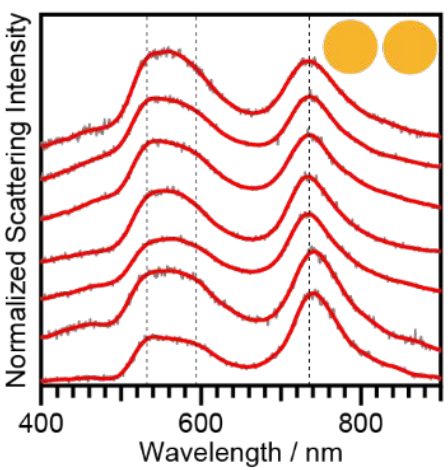


1: Raman or Fluorescence	**x % (?!)**
2: Rayleigh/Mie	**100 % (Ref.)**

Physical Chemistry I @ UDE

Precision Plasmonics

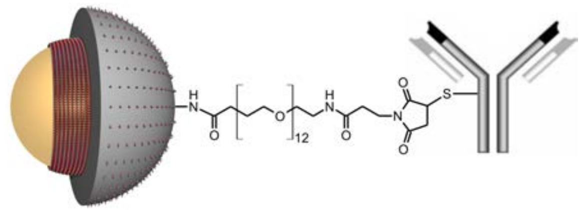




Small **2018**

Anal. Chem. **2018**

SERS nanotags/labels immuno-SERS (iSERS)



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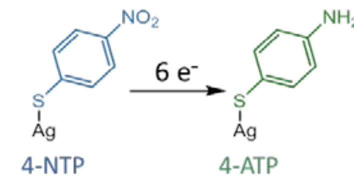
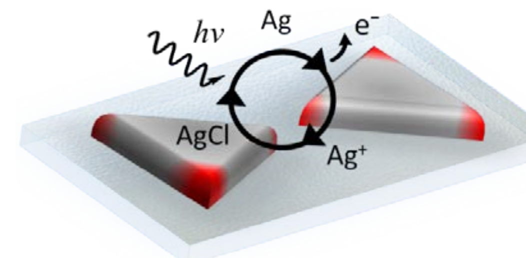




JACS **2011**

JACS **2013**

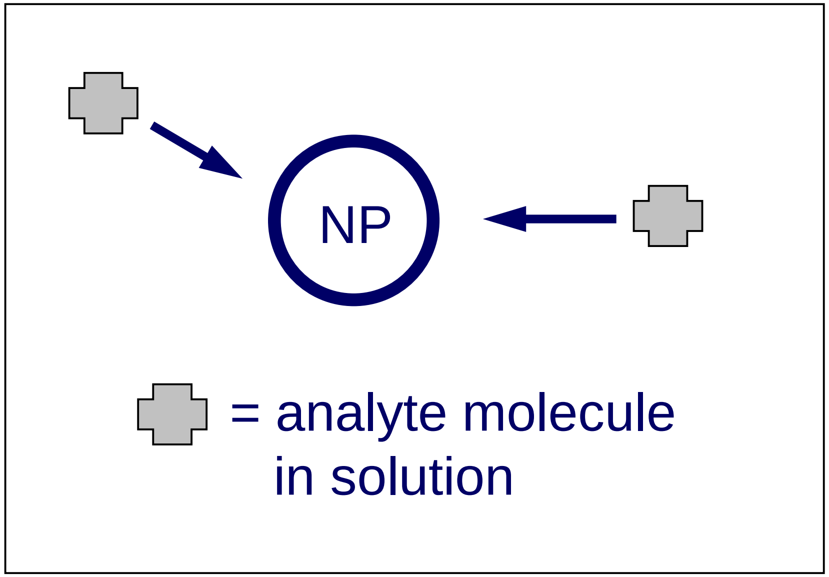
Nature Comm. **2015**

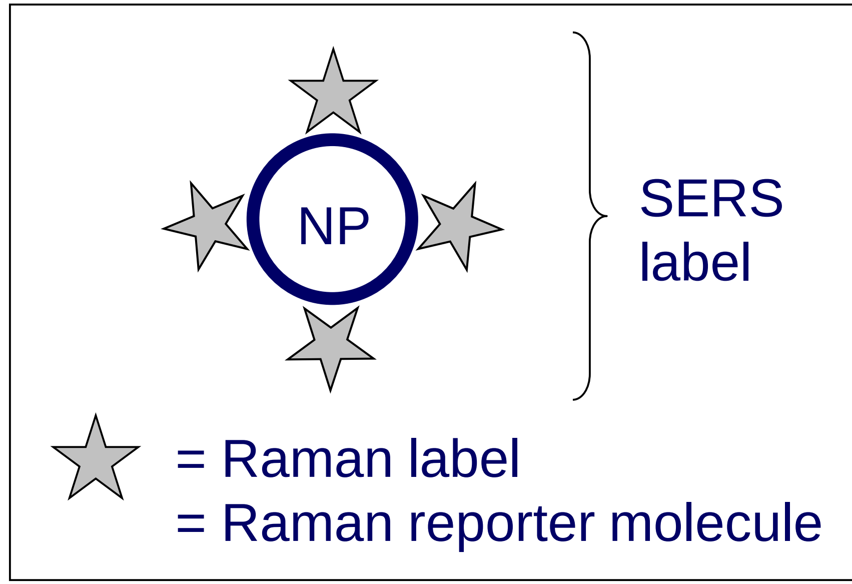
Angew. Chem. **2016**

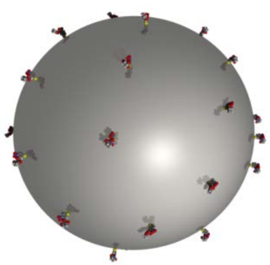
Nature Comm. **2017**

Applications of SERS with Plasmonic Nanoparticles

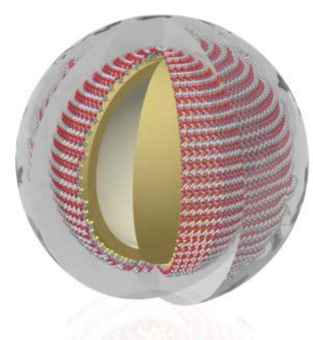
Label-free SERS vs. SERS NP labels = Nanotags



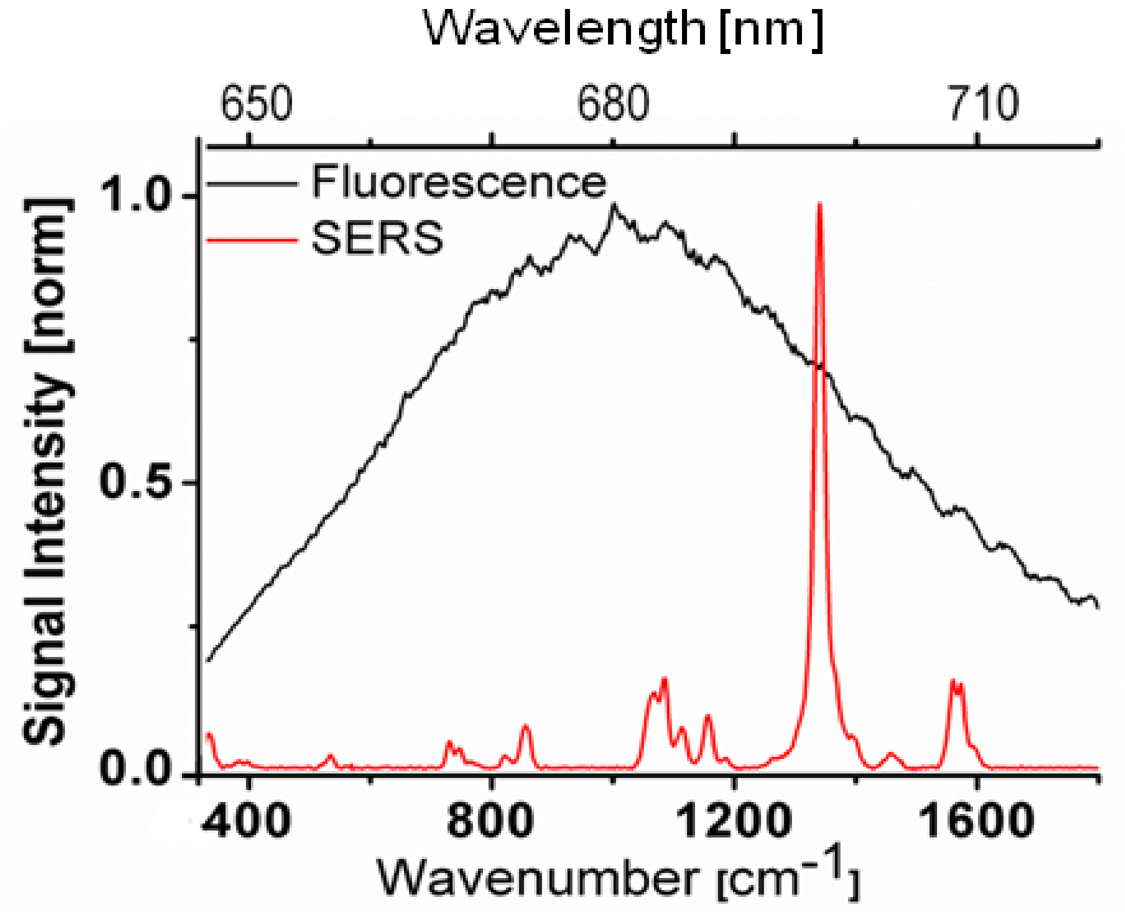




vs.

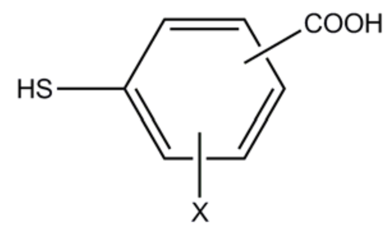


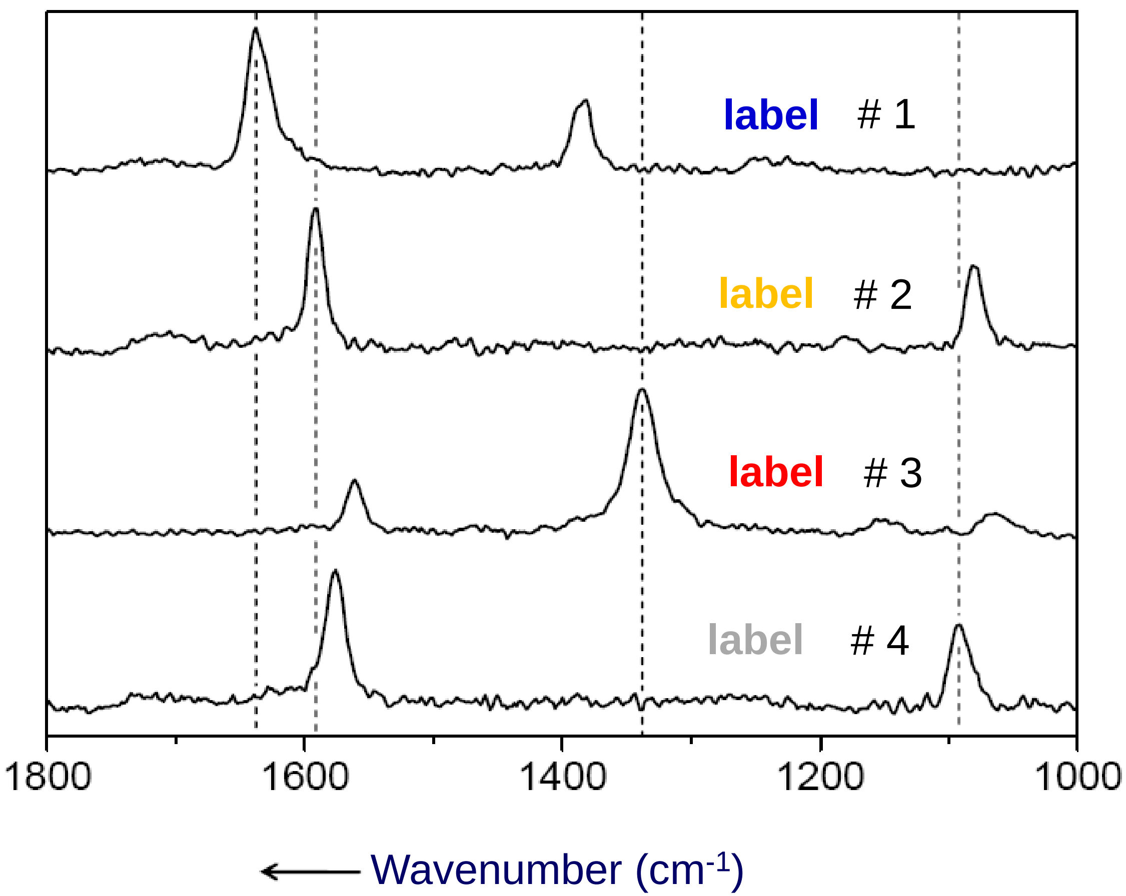
Spectral Multiplexing: Small Width of Raman Peaks

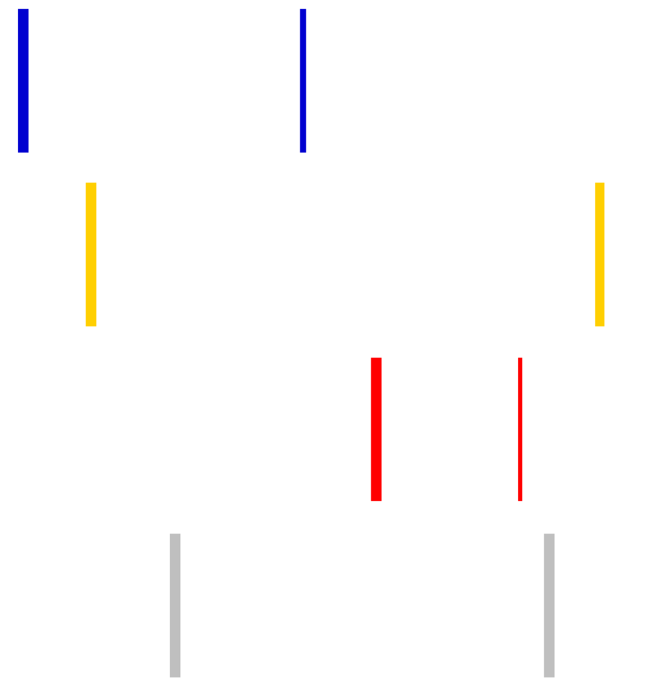


Nanoscale **2014**

Spectral Multiplexing with SERS Labels

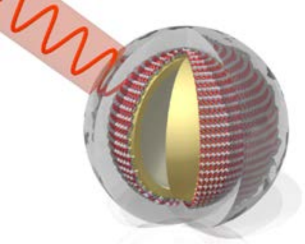






Detection of multiple labels in a single measurement!

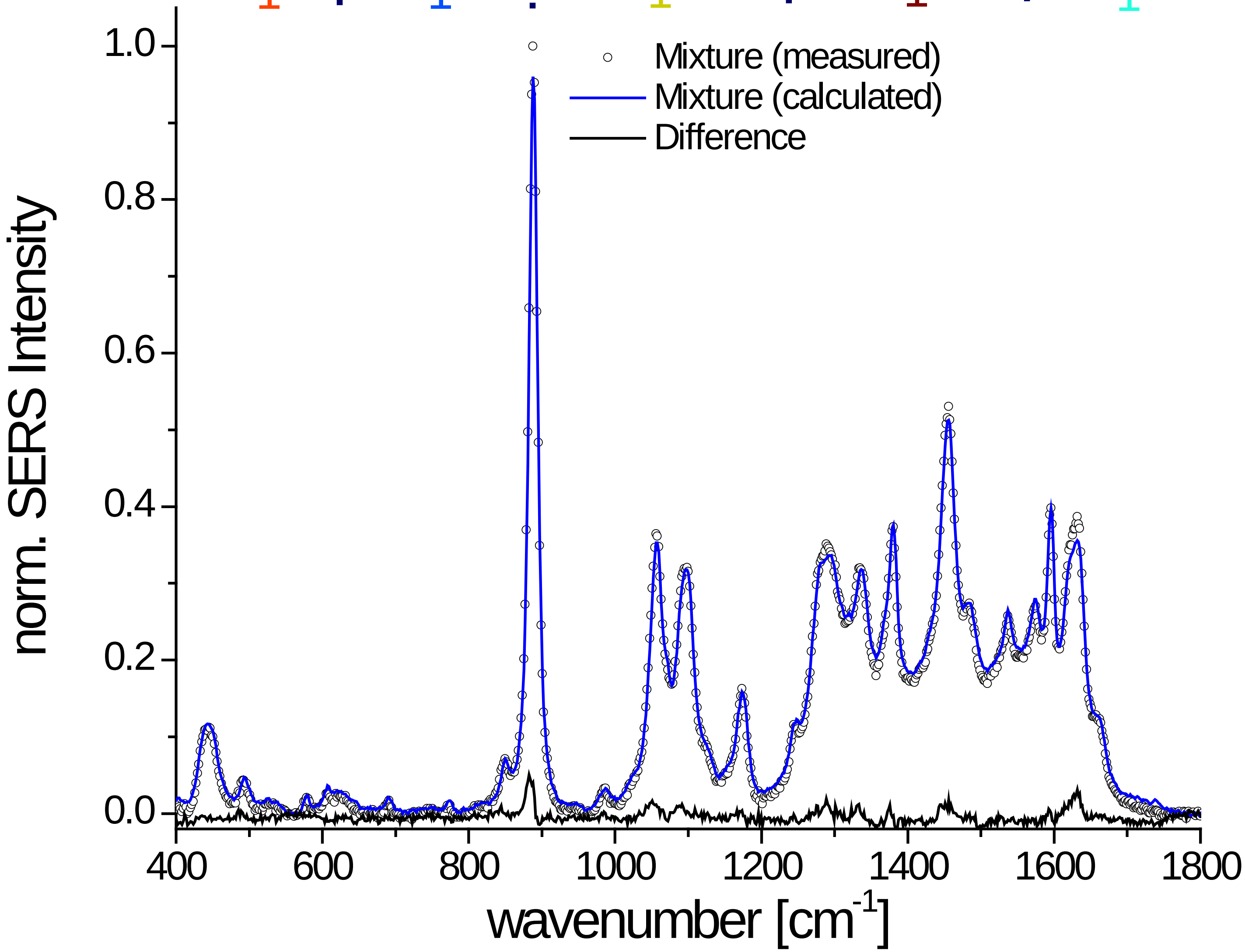
Anal. Bioanal. Chem. **2009**



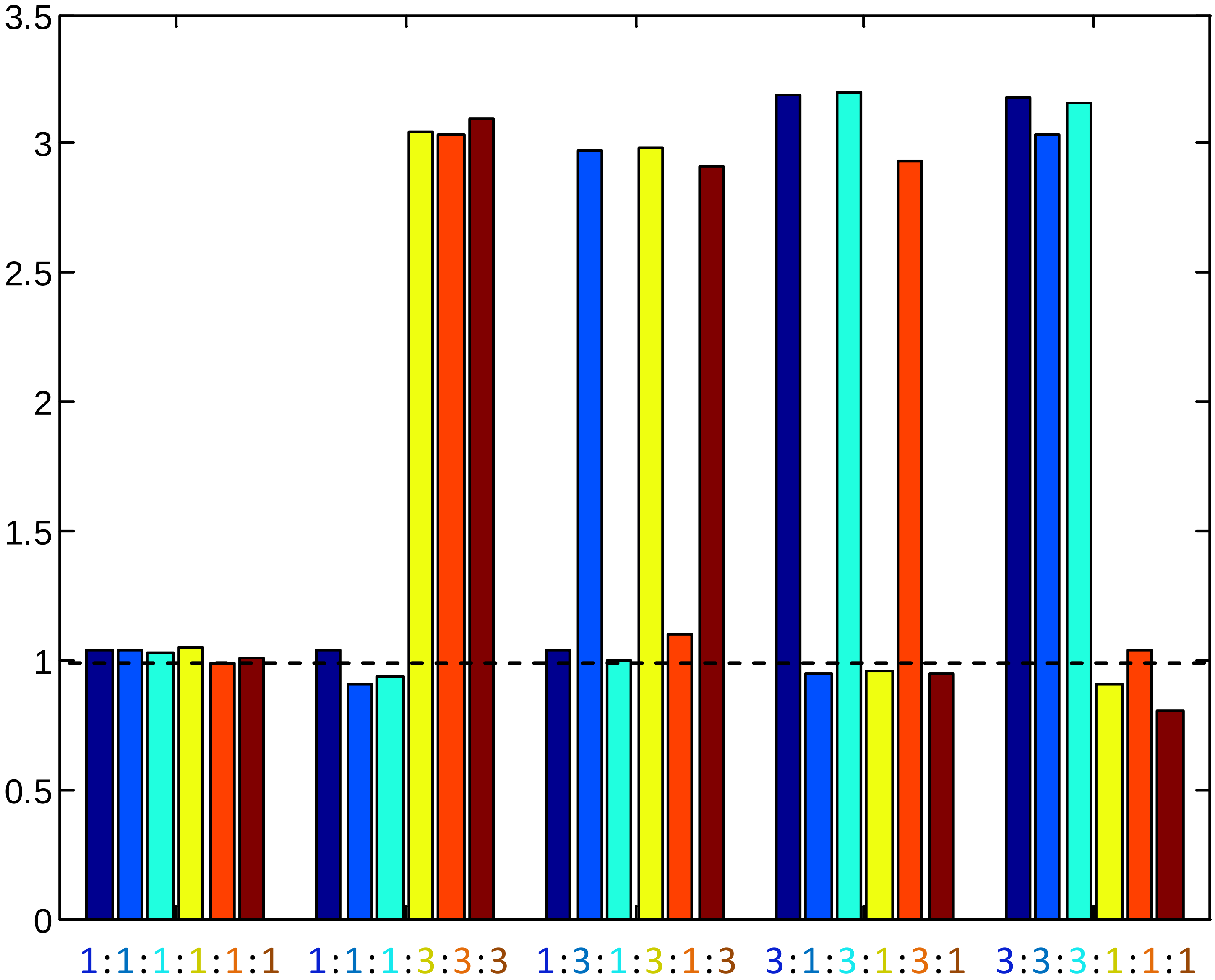
SERS Multiplexing: Quantitative 6-plex

TN + MMC + MMTAA + TFMBA + MNBA + BMBA

1 : 1 : 1 : 1 : 1 : 1



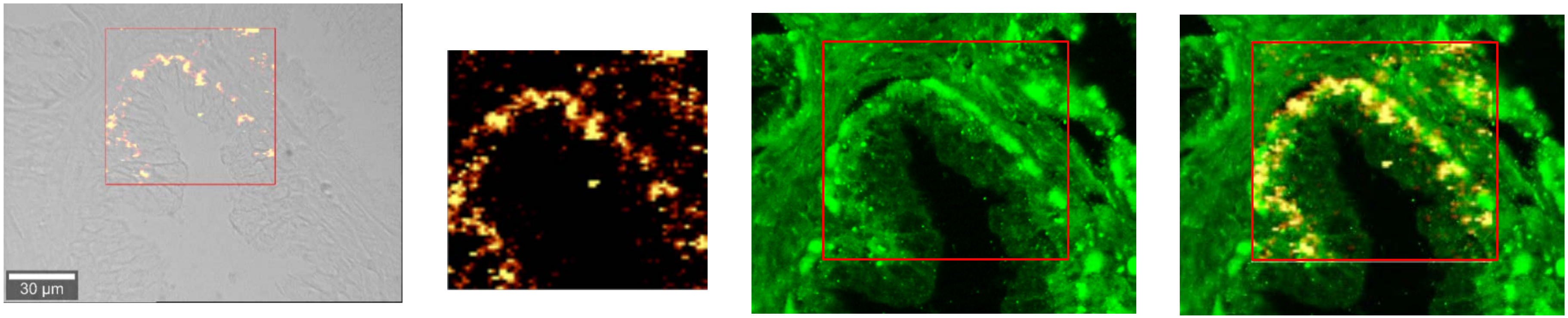
Quantitative 6-Color SERS Experiments (Cuvette)



J. Raman Spectrosc. **2016**

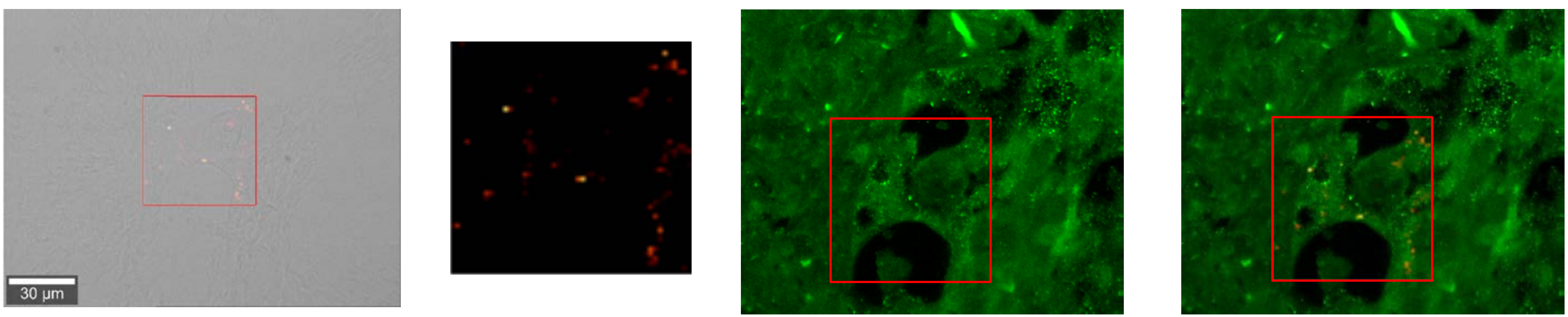
Example: Benign vs. Cancerous Prostate Biopsies

Benign: (+)-P63 (tumor suppressor; cancer-specific)

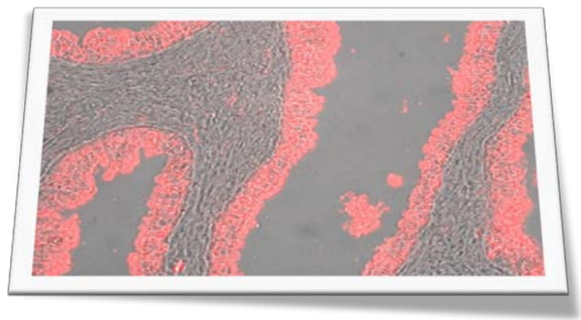
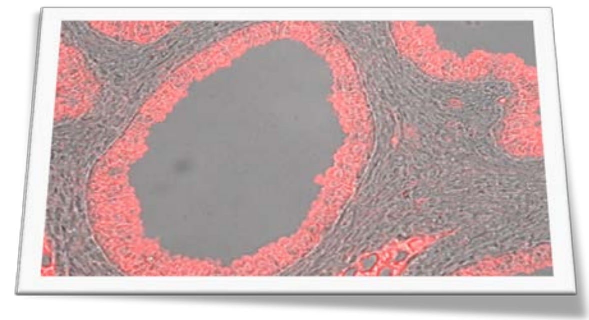


BF & iSERS **iSERS** **iF** **iF & iSERS**

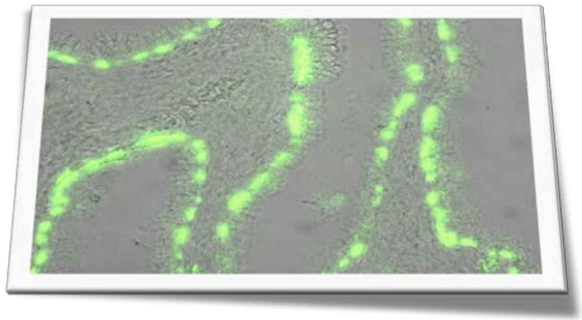
Cancerous: (-)-P63

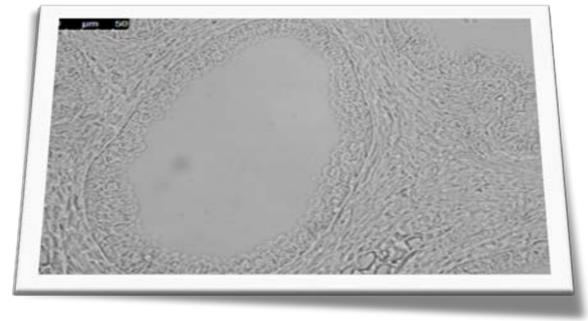


2-Color-iSERS: Benign vs. Cancerous Prostate Biopsies

	Benign	Cancerous
		
PSA	+	+
P63	+	-

2-Color-iSERS: Benign vs. Cancerous Prostate Biopsies

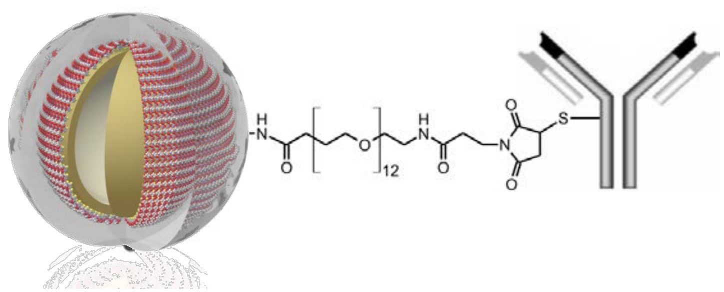


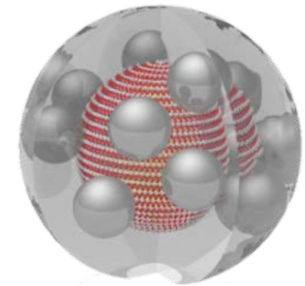


	Benign	Cancerous
PSA	+	+
P63	+	-

Summary 2: SERS nanotags for iSERS microscopy & assays

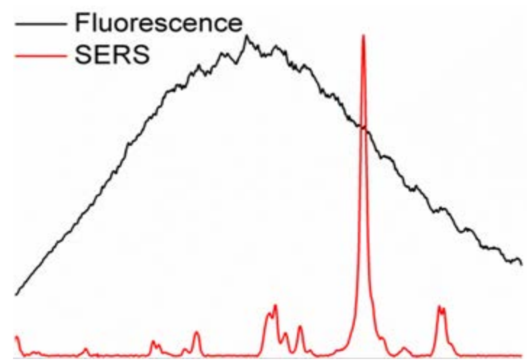
SERS label
= plasmonic NP
& Raman reporter
& shell (optional)

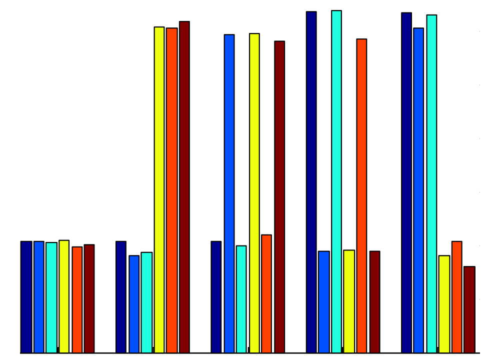




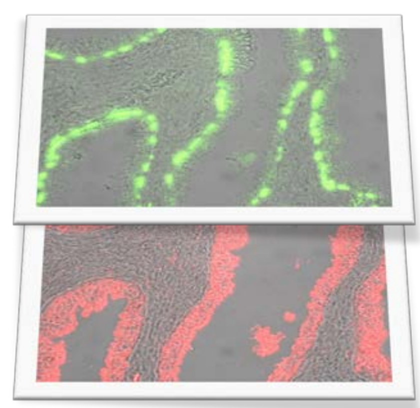
Multiplexing (colours) & Quantification

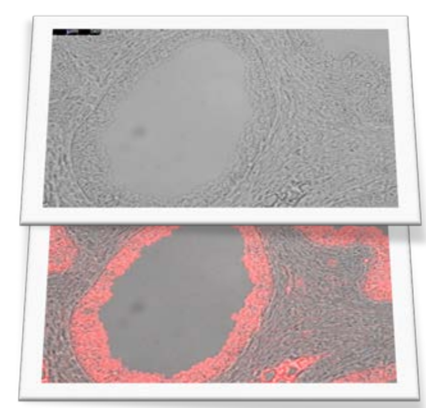
photostable
& bright (single NPs!)





iSERS
= immuno-SERS microscopy

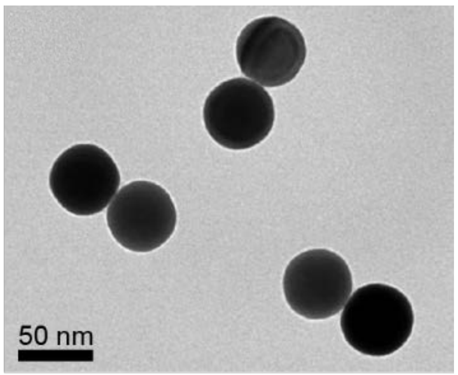


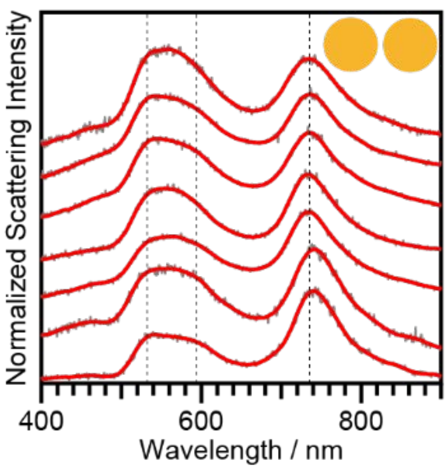


Long term goal:
Personalized diagnostics
(quantitative, multi-marker)

Physical Chemistry I @ UDE

Precision Plasmonics

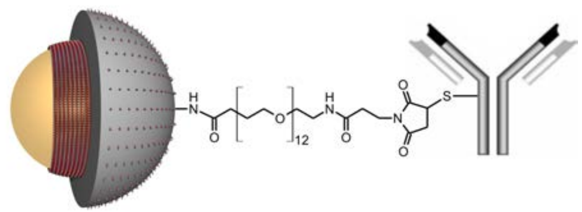




Small **2018**

Anal. Chem. **2018**

SERS nanotags/labels immuno-SERS (iSERS)



Angew. Chem. **2009**

Small **2010**

Small **2011**

Chem. Comm. **2012**

Nanoscale **2013**

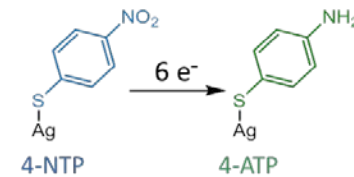
Chem. Comm. **2014**

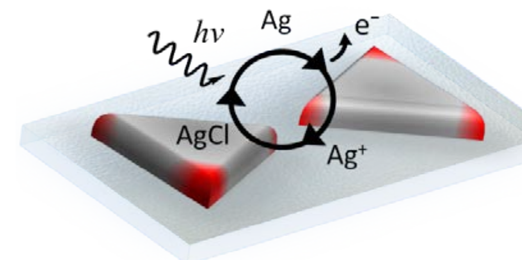
PCCP **2015**

Analyst **2016**

Anal. Chem. **2017**

Chemical Energy Conversion





JACS **2011**

JACS **2013**

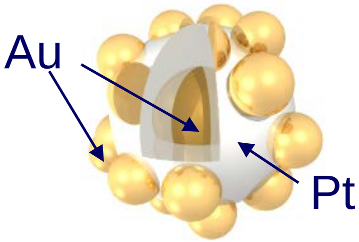
Nature Comm. **2015**

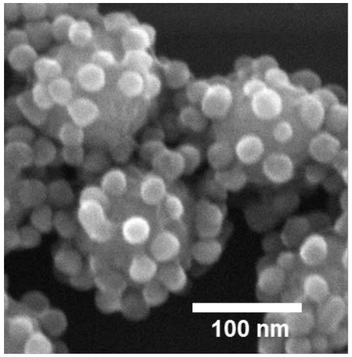
Angew. Chem. **2016**

Nature Comm. **2017**

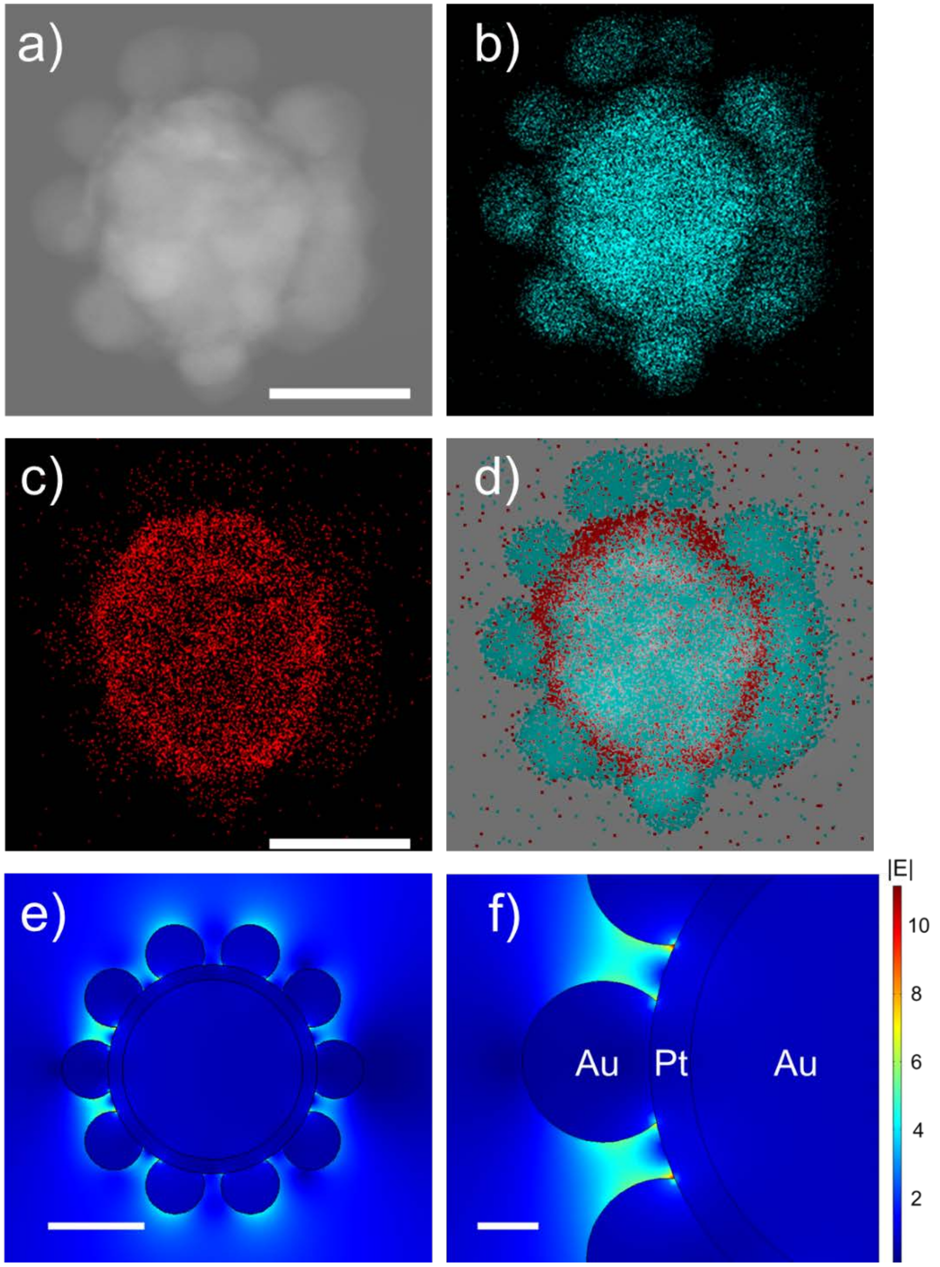
Plasmonic NPs for Chemical Energy Conversion

Bifunctional Au/Pt/Au nanoraspberries

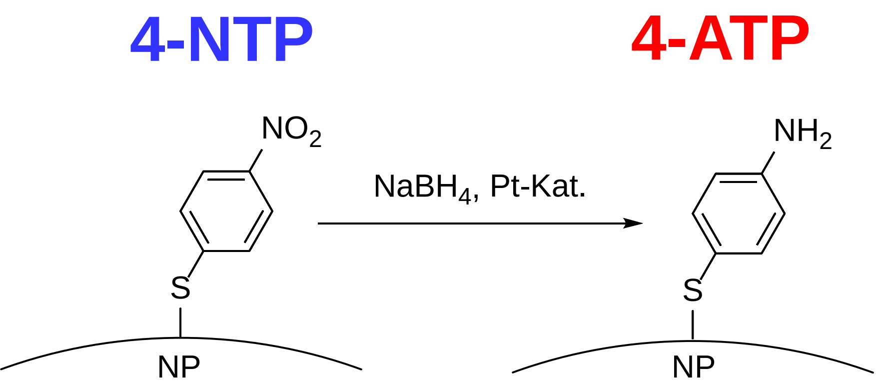


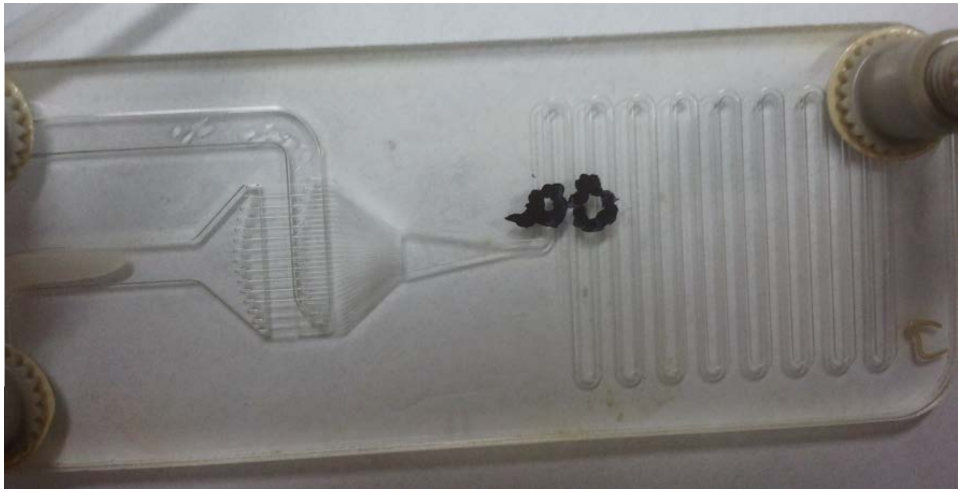


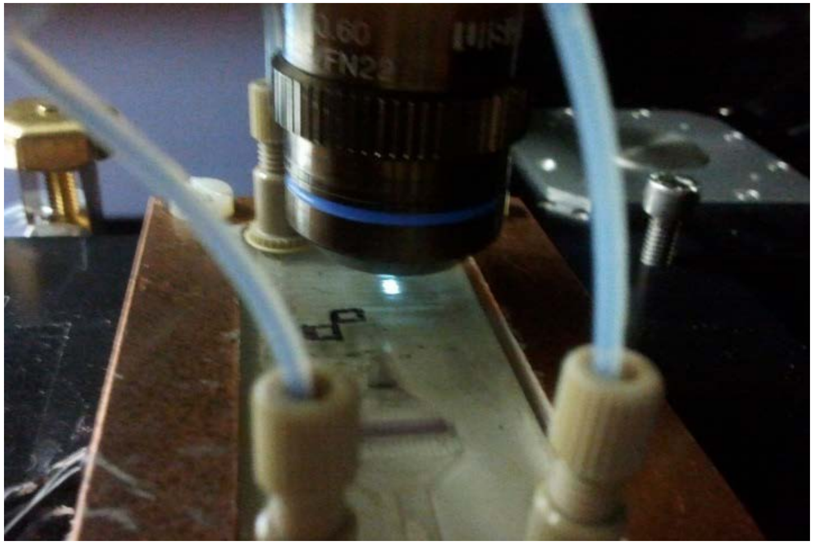
J. Am. Chem. Soc. **2011**

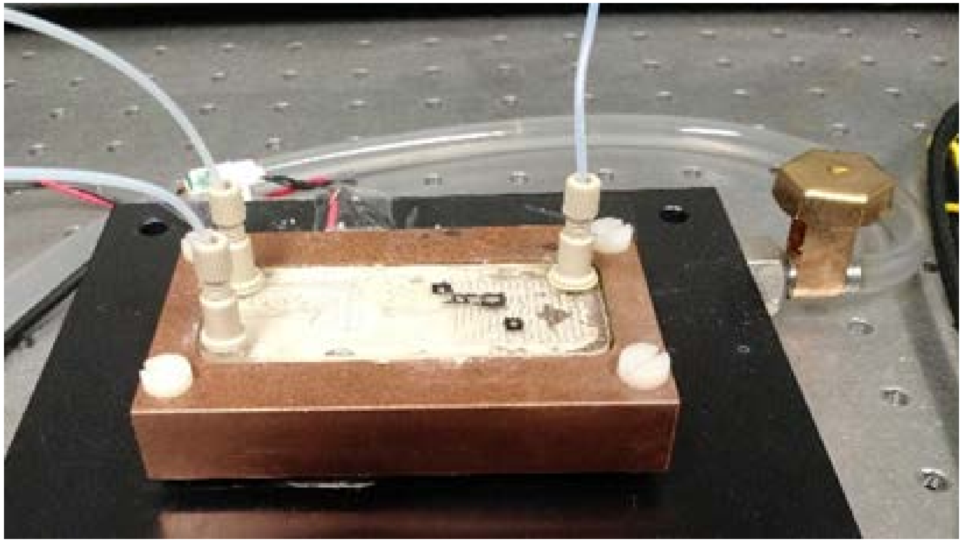


Microfluidic SERS: Label-free Kinetic Reaction Monitoring



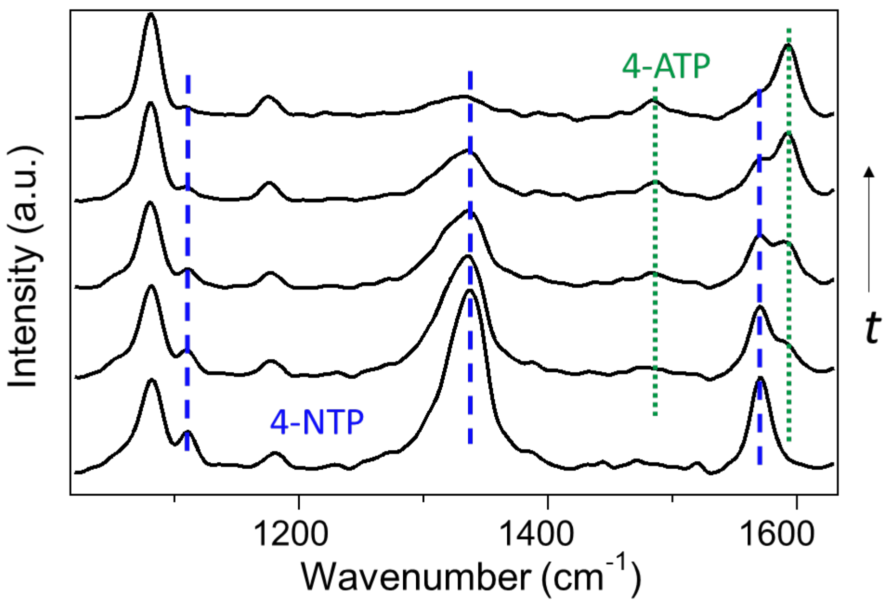




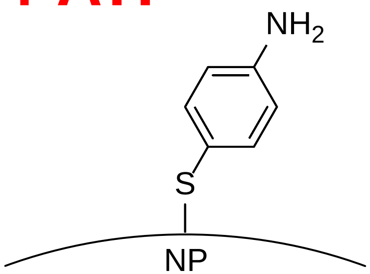


Angew. Chem. Int. Ed. **2016**, *55*, 13729.

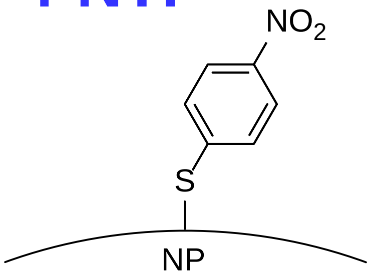
Model Reaction: Nitro to Amino Reduction ($NaBH_4$, Pt-cat.)



4-ATP

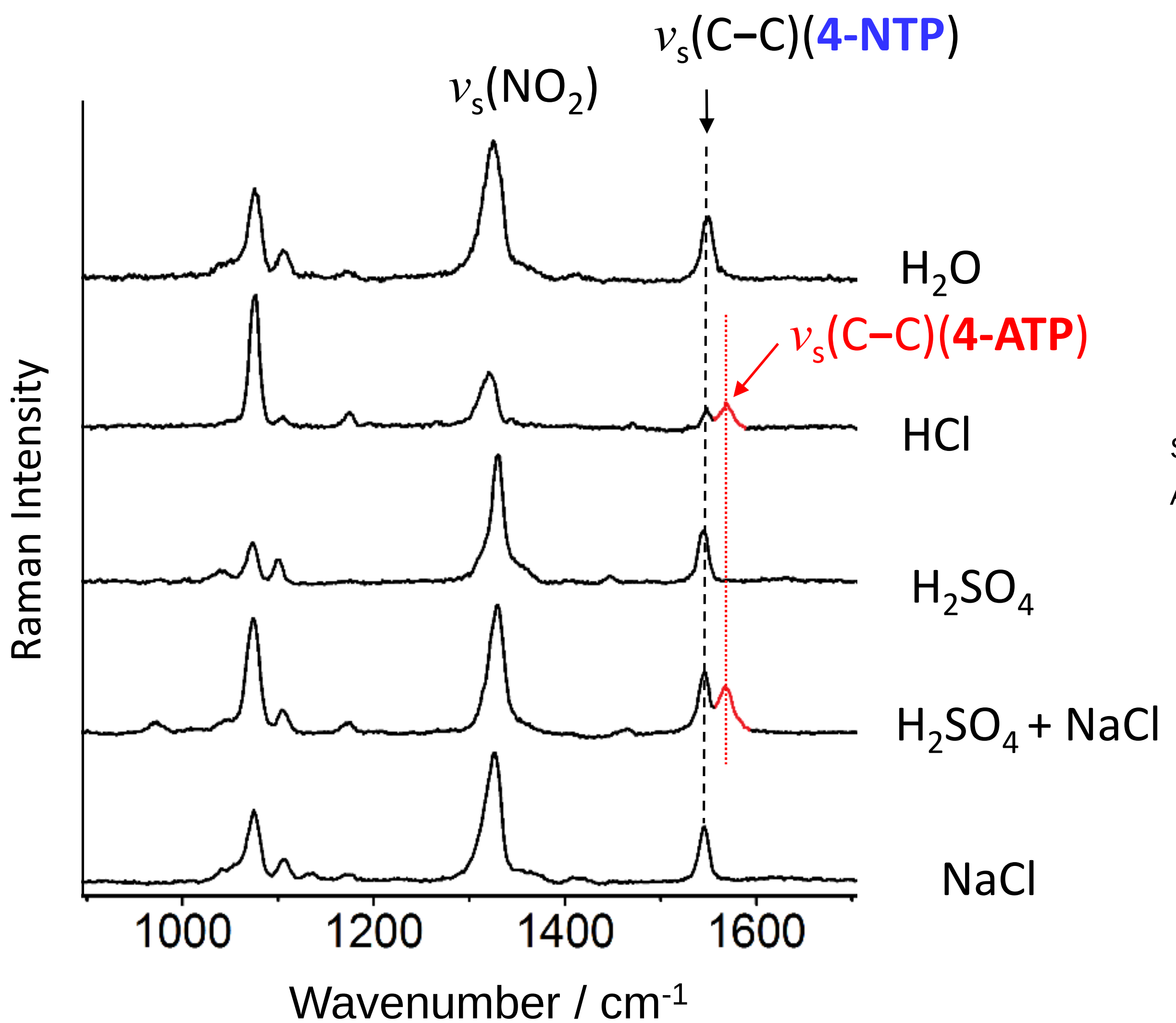


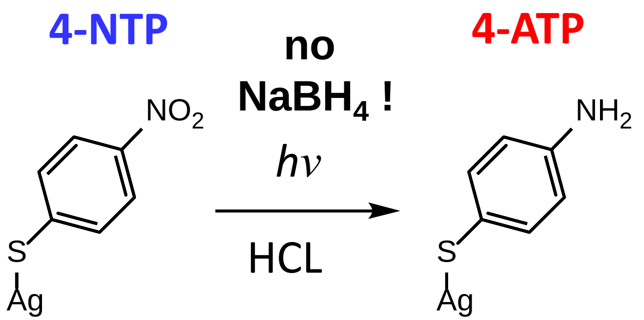
4-NTP



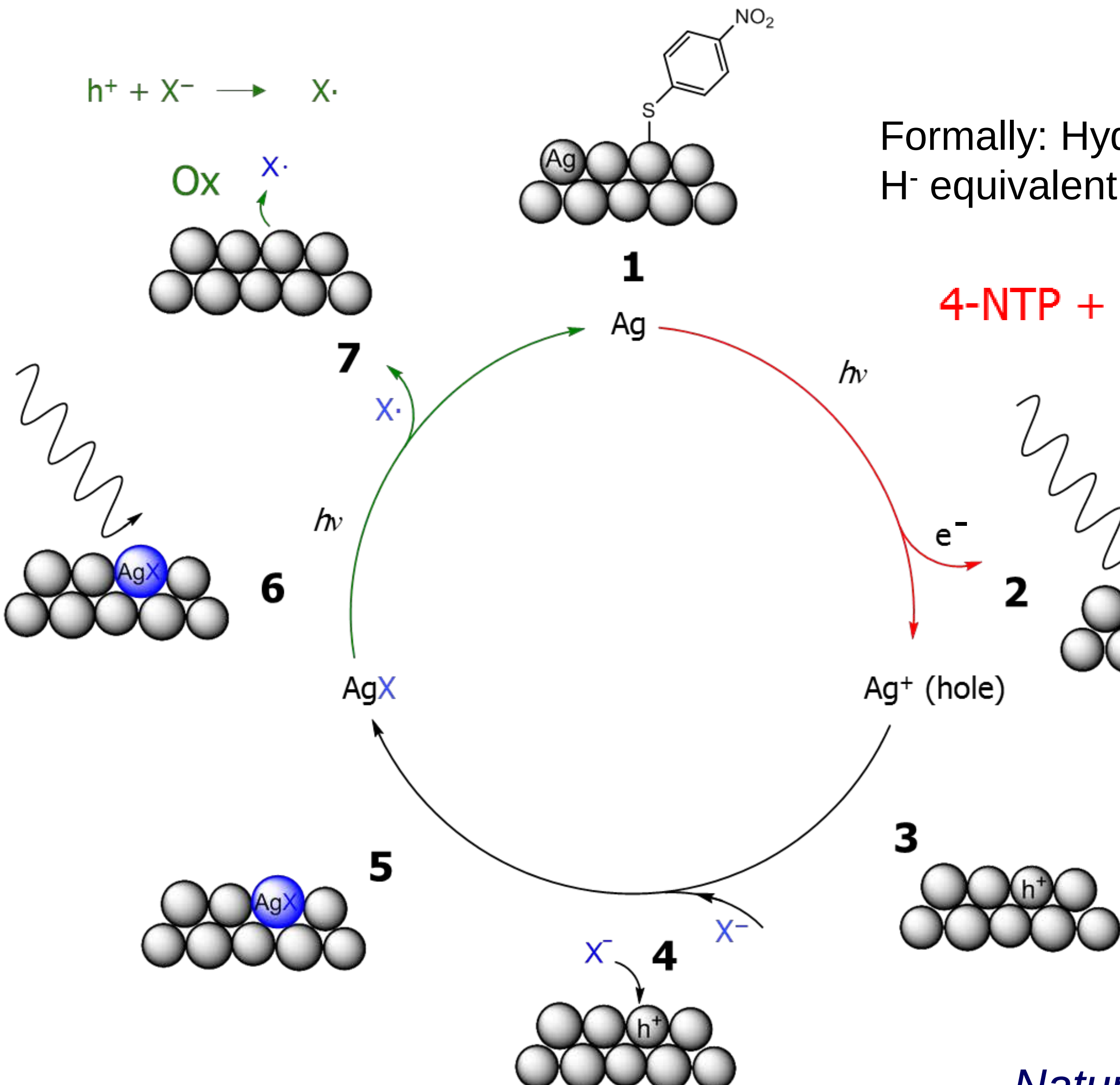
Surprise: Hydride Reduction *without* Hydride Reagents!

Ag core/Ag satellite NPs



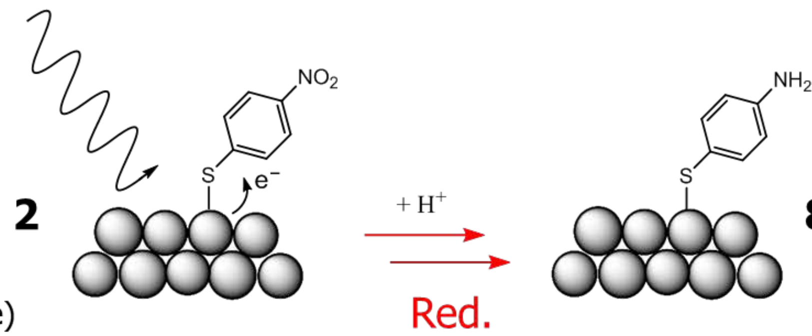


Hot Electrons & Photorecycling (AgX)



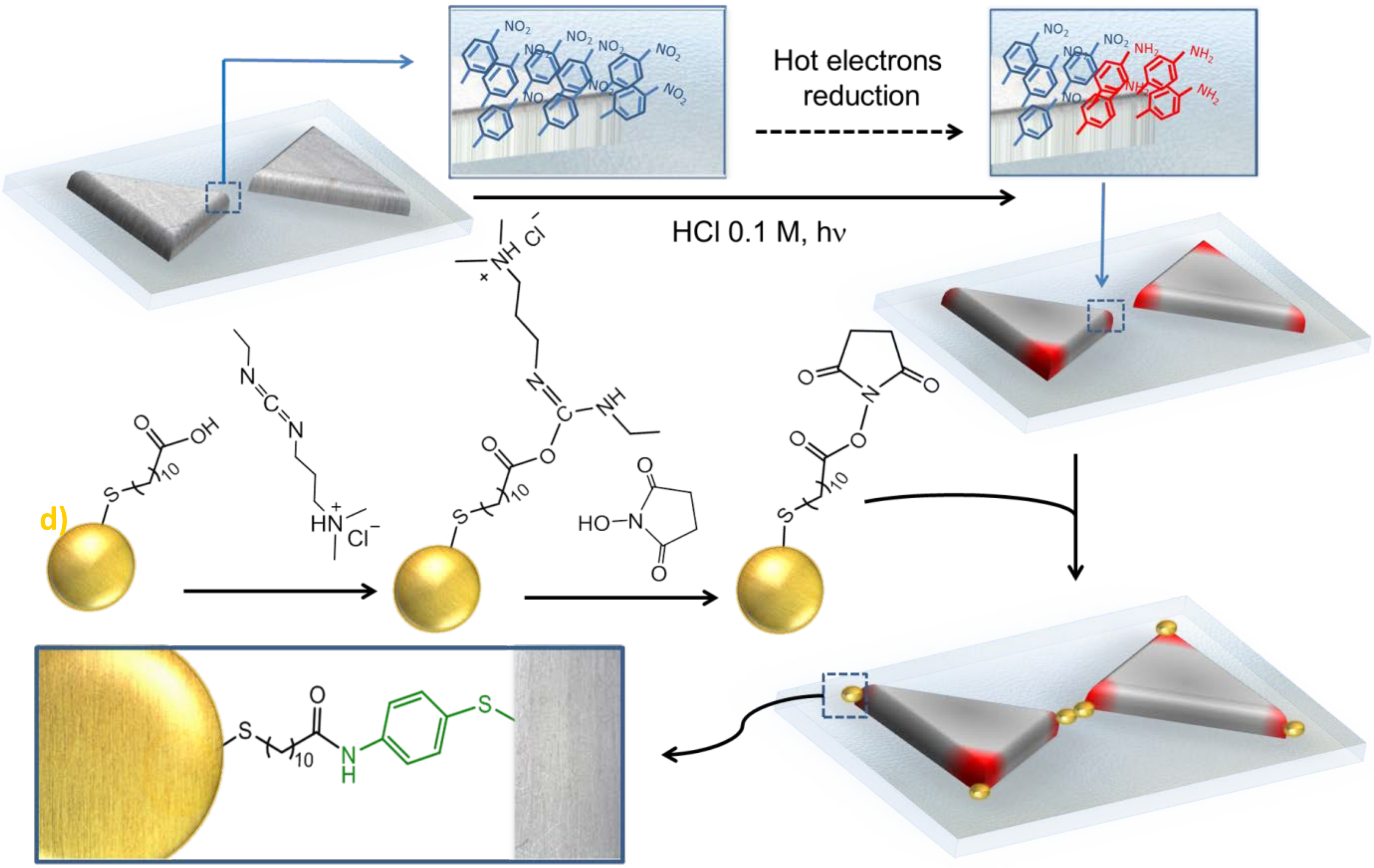
Formally: Hydride reduction without hydrides
H^- equivalent in protic environment: $H^- = H^+ + 2e^-$

$$\text{4-NTP} + 6e^- + 6H^+ \longrightarrow \text{4-ATP} + 2H_2O$$



Nature Comm. **2015**

Hot Electrons Drive Nano-Localized Chemistry



Nature Comm. **2017**

Summary 3: from label-free SERS to plasmonic chemistry