

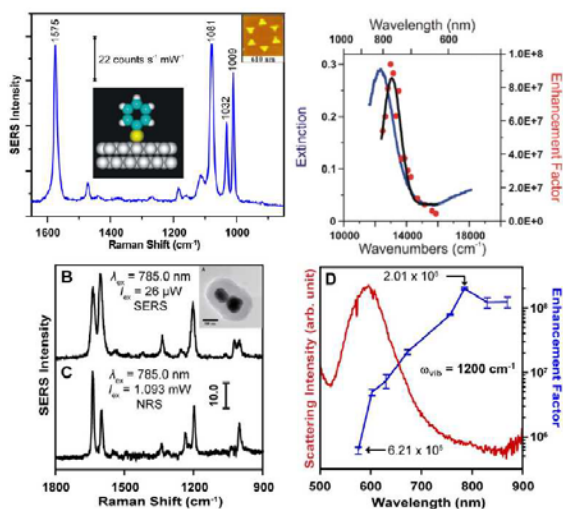
GISR2014, Parma, Italy

10:00 AM CDT (Web), Monday, June 09, 2014

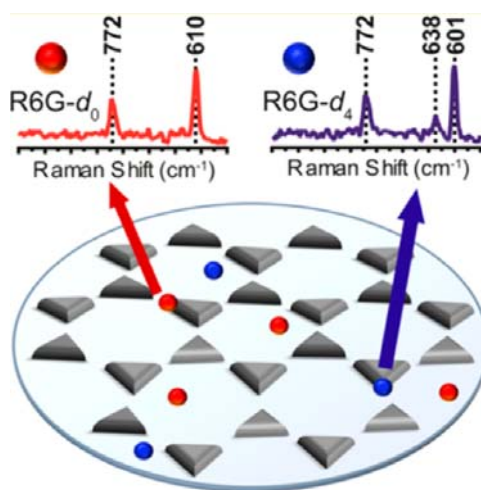
Plenary Lecture: SERS at the Single Nanoparticle, Single Molecule, and Ultrafast Levels

Richard P. Van Duyne

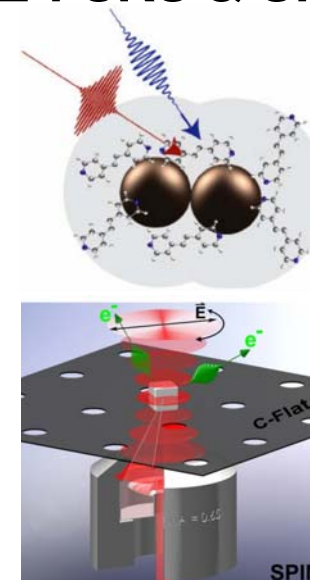
Single Nanoparticle SERS



Single Molecule SERS



Ultrafast Plasmonics: SE-FSRS & SPIM

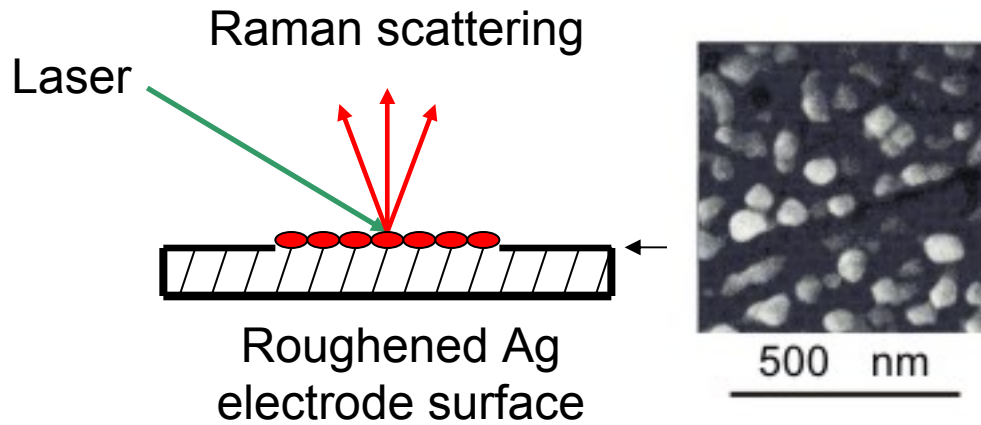


Departments of Chemistry and Biomedical Engineering & The Applied Physics Program
TECH K124, (847)-491-3561, vanduyne@northwestern.edu



Introduction

Surface Enhanced Raman Spectroscopy



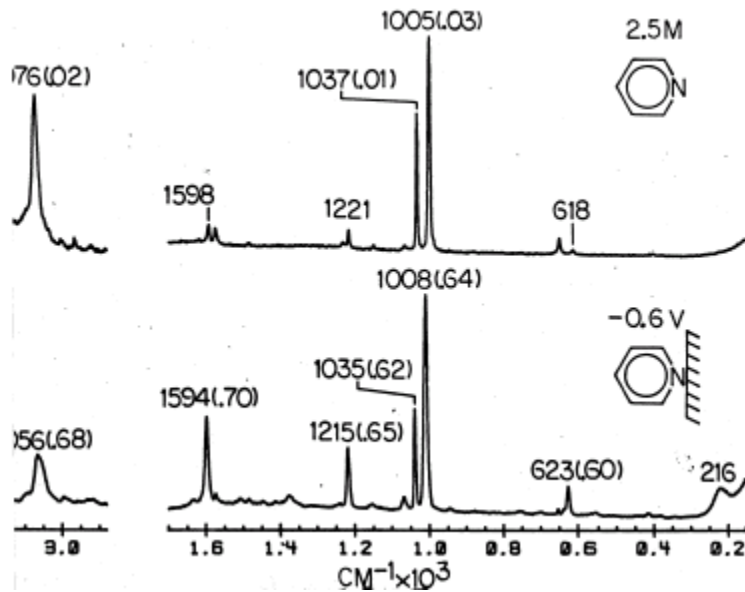
10^{5-6} Enhancement for NRS

All 27 normal modes Enhanced

Ag-N stretch at 216 cm^{-1}

10^{9-10} Enhancement for RRS

Named SERS and SERRS



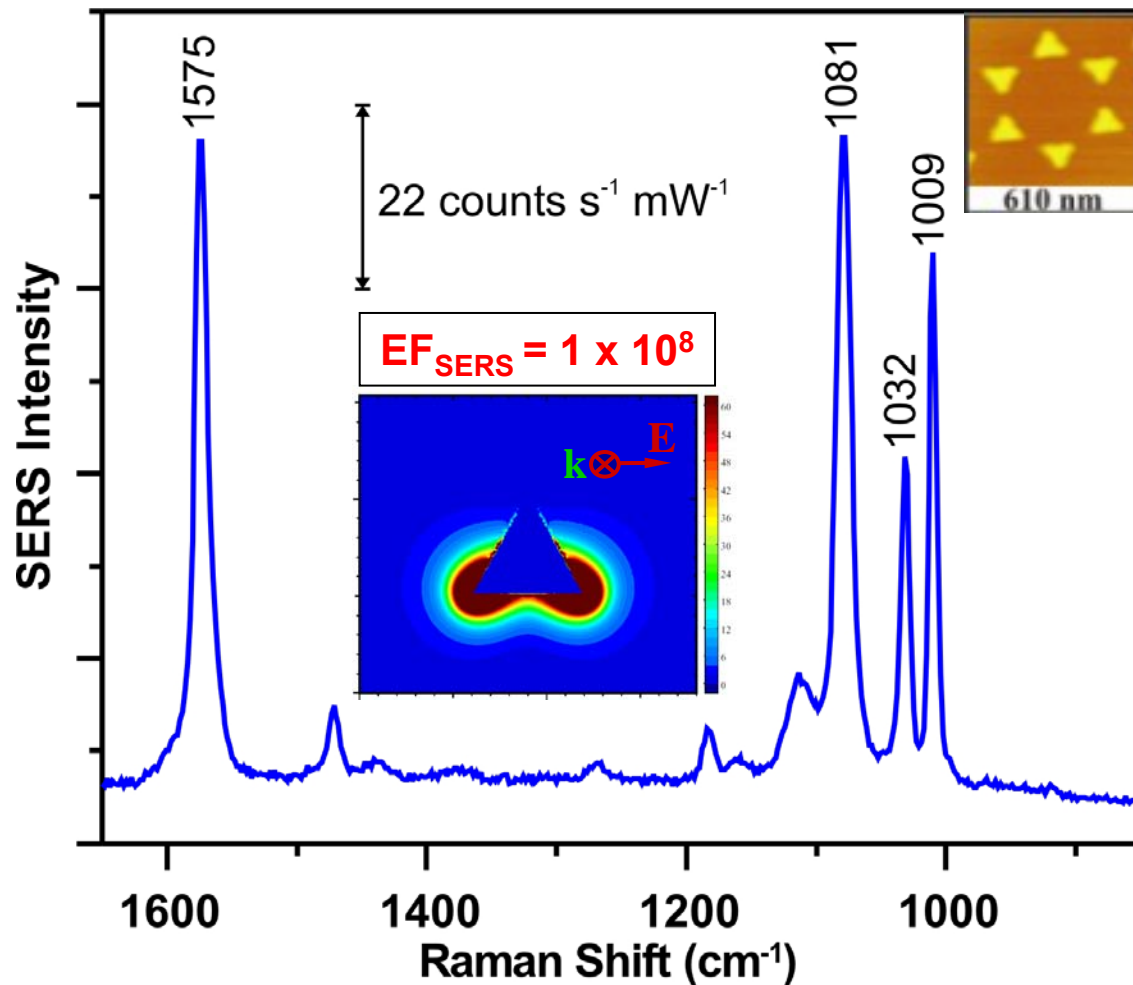
What is the Mechanism?

$$\vec{\mu} = \hat{\alpha} \vec{E}$$

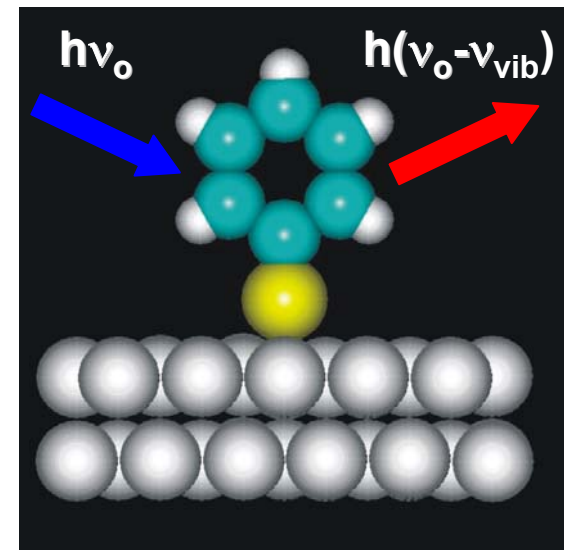
Chemical Electromagnetic

Jeanmaire & Van Duyne, *J. Electroanal. Chem.*, **84**, 1 (1977)
 Van Duyne, *J. Physique*, **38**, (C5)239-(C235)252 (1977)
 Van Duyne, *Chem. Biochem. Appl. Lasers*, **4**, 101-185 (1979)

Surface Enhanced Raman Spectroscopy (SERS)



Benzenethiol



What is the Mechanism?

$$\vec{\mu} = \hat{\alpha} \vec{E}$$

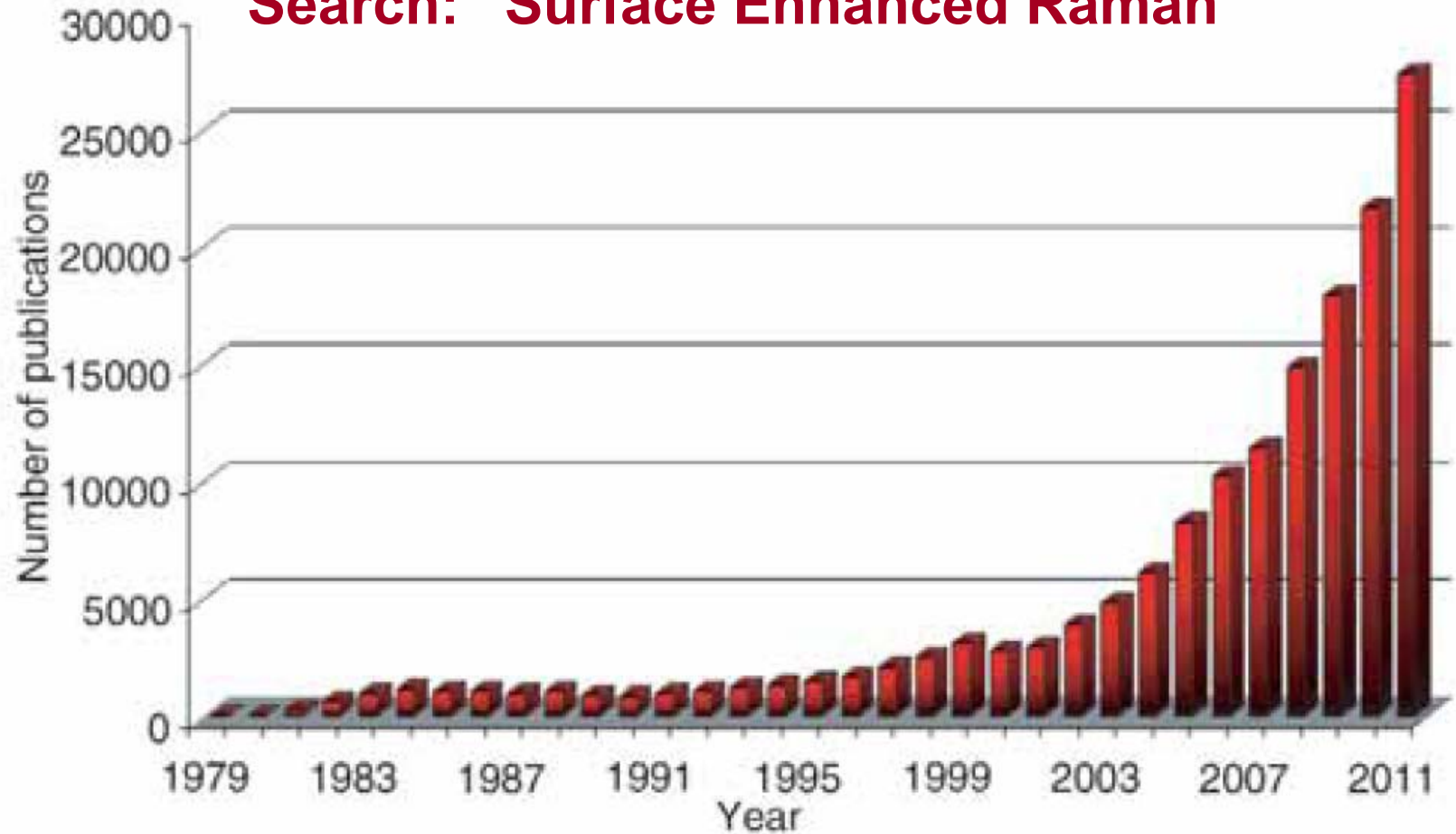
$$EF_{\text{CHEM}} \sim 10^1$$

$$EF_{\text{EM}} \sim 10^8$$

Haes, Haynes, McFarland, Zou, Schatz, and Van Duyne, *MRS Bulletin*, **30**, 368-375 (2005)
 P. Stiles, J. Dieringer, N. C. Shah, and R. P. Van Duyne, *Ann. Rev. Anal. Chem.*, **1**, 601-626 (2008)

Web of Science Citation Data

Search: "Surface Enhanced Raman"

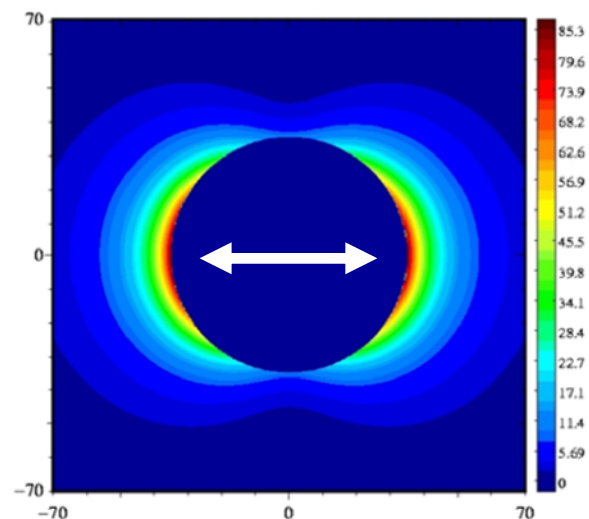
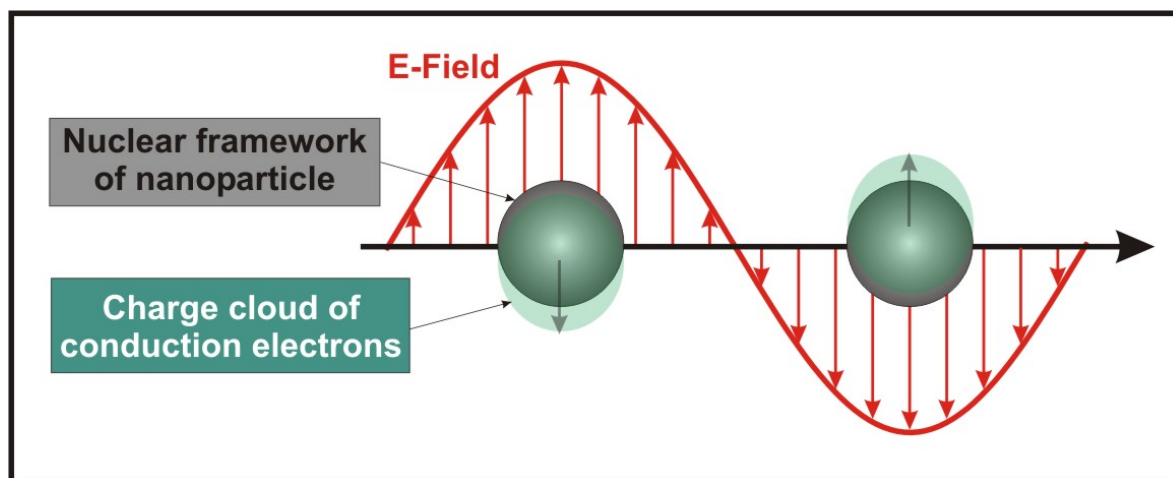


B. Sharma, R. R. Frontiera, A-I. Henry, E. Ringe, and R. P. Van Duyne,
Materials Today, 15, 16-25, January-February (2012)

The EM Mechanism of SERS

The Electromagnetic Mechanism of SERS

Principles: Amplified Electromagnetic Fields



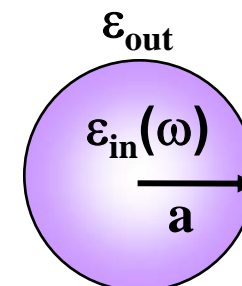
Mie theory
(1908)



$$\mathbf{E}_{\text{out}}(x,y,z) = E_0 \hat{\mathbf{z}} - \left[\frac{\epsilon_{\text{in}} - \epsilon_{\text{out}}}{(\epsilon_{\text{in}} + 2\epsilon_{\text{out}})} \right] a^3 E_0 \left[\frac{\hat{\mathbf{z}}}{r^3} - \frac{3z}{r^5} (\mathbf{x}\hat{\mathbf{x}} + \mathbf{y}\hat{\mathbf{y}} + z\hat{\mathbf{z}}) \right]$$

Dielectric Resonance \rightarrow

$$EF_{\text{SERS}}(\omega_v) = \frac{|\mathbf{E}_{\text{out}}(\omega)|^2 \left| \mathbf{E}'_{\text{out}}(\omega - \omega_v) \right|^2}{E_0^4} = \frac{[I_{\text{SERS}}(\omega_v) / N_{\text{surf}}]}{[I_{\text{NRS}}(\omega_v) / N_{\text{vol}}]}$$



The Electromagnetic Mechanism of SERS

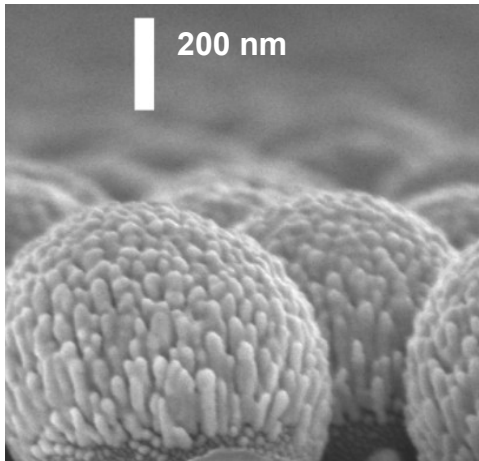
Laser excites the localized surface plasmon resonance (LSPR) and produces enhanced electromagnetic fields near nanoparticle surface.

Observables

1. Magnitude of the enhancement factor (EF) $EF_{\text{SERS, EM}} = 10^6 - 10^8$
2. Metal to molecule distance dependence $I = \left(1 + \frac{r}{a}\right)^{-10}$
3. Nanoparticle size & shape dependence
 1. very sensitive
 2. no single crystals
4. Molecular selectivity None
5. Material dielectric constants (ϵ_r , ϵ_i , ϵ_m)
 1. $\epsilon_r = -$; $\epsilon_i \sim 0$
 2. $\uparrow \epsilon_m \rightarrow$ LSPR red-shift
6. EF vs. ω_{ex} (excitation spectroscopy)
 1. narrower than LSPR
 2. blue-shifted by $1/2 \omega_{\text{Stokes}}$
7. All optically driven processes are enhanced!!! e.g. Hyper Raman

High Performance SERS Substrates: $EF \sim 10^8$

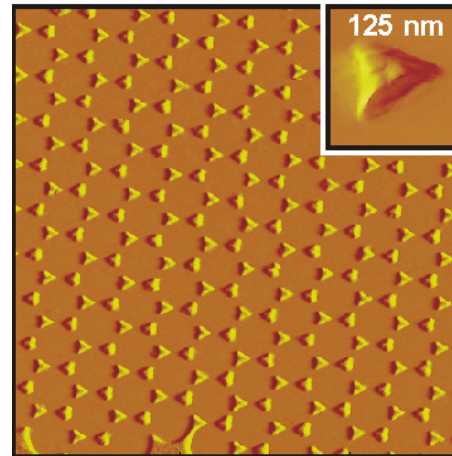
Ag Radial Rod Nanoantennas



$$EF = 1.3 \times 10^8$$

$$a_i = 2.7 \times \text{Geom.}$$

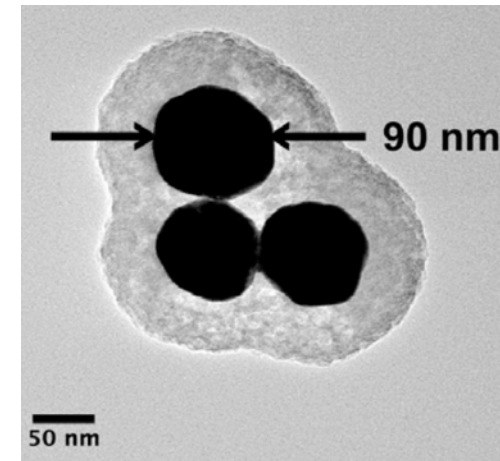
Ag Bowtie Nanoantennas



$$EF = 9.2 \times 10^7$$

$$a_i = 0.072 \times \text{Geom.}$$

Au L-Trimer Nanoantennas



$$EF = 4.8 \times 10^8$$

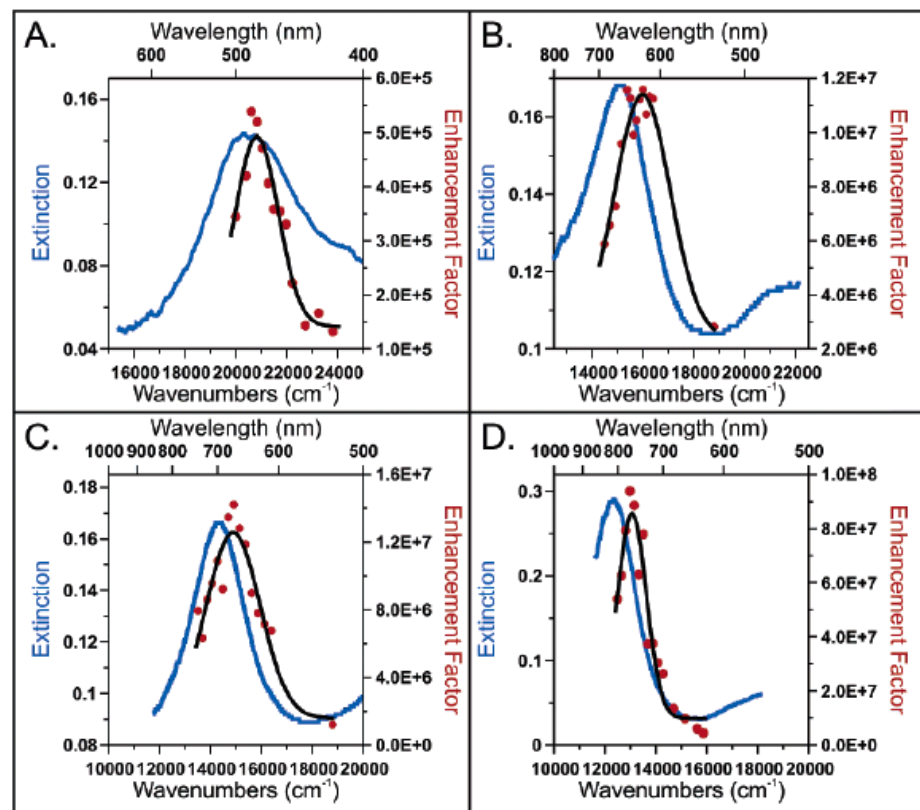
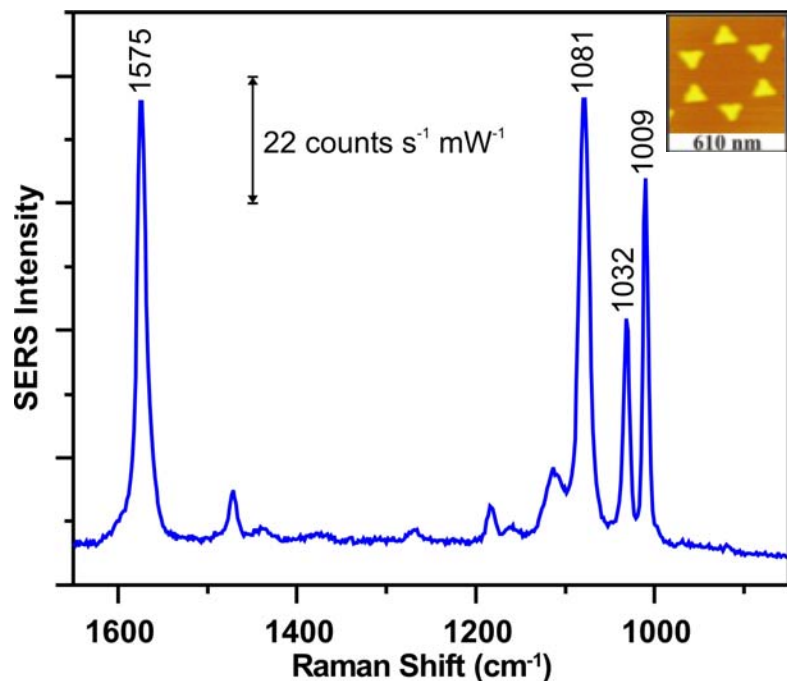
$$a_i = 0.28 \times \text{Geom.}$$

$$S_{total} \propto EF \cdot \Theta \cdot a_i$$

Enhancement Factor Coverage Surface Area

Surface Enhanced Raman Excitation Spectroscopy

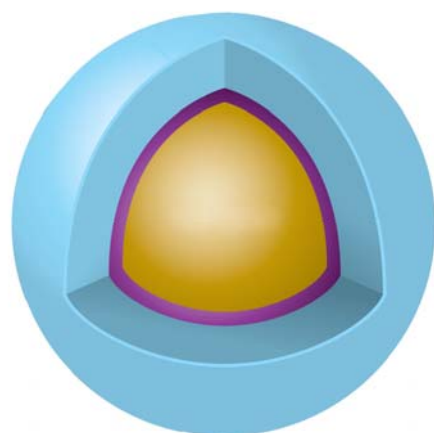
Benzenethiol on Ag NSL Nanoparticles



- EF ($\lambda_{\text{ex}} = 780 \text{ nm}$) $\sim 1 \times 10^8$
- EF ($\lambda_{\text{ex}} = 680 \text{ nm}$) $\sim 1 \times 10^7$
- EF ($\lambda_{\text{ex}} = 620 \text{ nm}$) $\sim 1 \times 10^7$
- EF ($\lambda_{\text{ex}} = 480 \text{ nm}$) $\sim 5 \times 10^5$

- SERES is narrower and **ALWAYS** blue-shifted vs. LSPR !
- $\text{EF}_{\text{SERS}} = f(\lambda_{\text{ex}}, \lambda_{\text{vib}}, \lambda_{\text{LSPR}})$

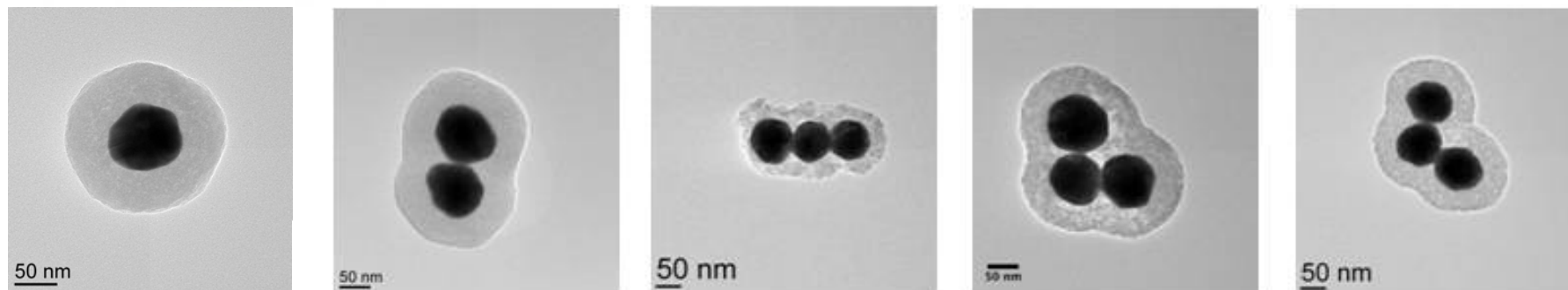
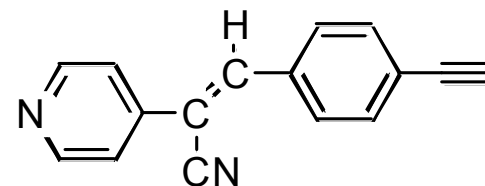
Single Nanoparticle Surface Enhanced Raman Spectroscopy: Au Nanoparticle Assemblies



 100 nm Au core

 Organic molecule

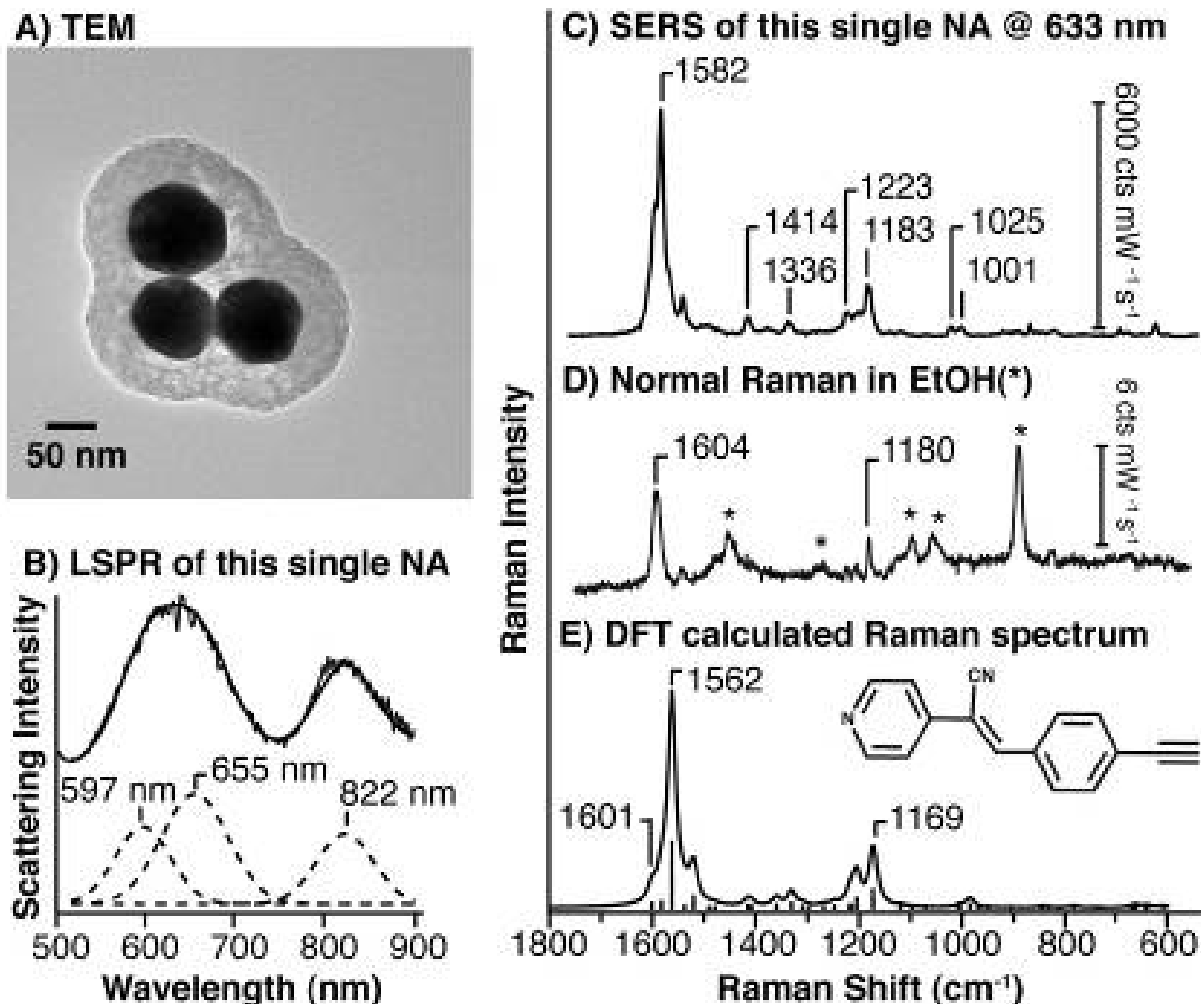
 50 nm SiO₂



- What Structure has the largest EF? Why?
- What Structural Parameter(s) Control(s) EF?

K. L. Wustholz, A-I. Henry, J. M. McMahon, R. G. Freeman, N. Valley, M. E. Piotti,
M. J. Natan, G. C. Schatz and R. P. Van Duyne, *J. Am. Chem. Soc.*, **132**, 10903-10910 (2010)

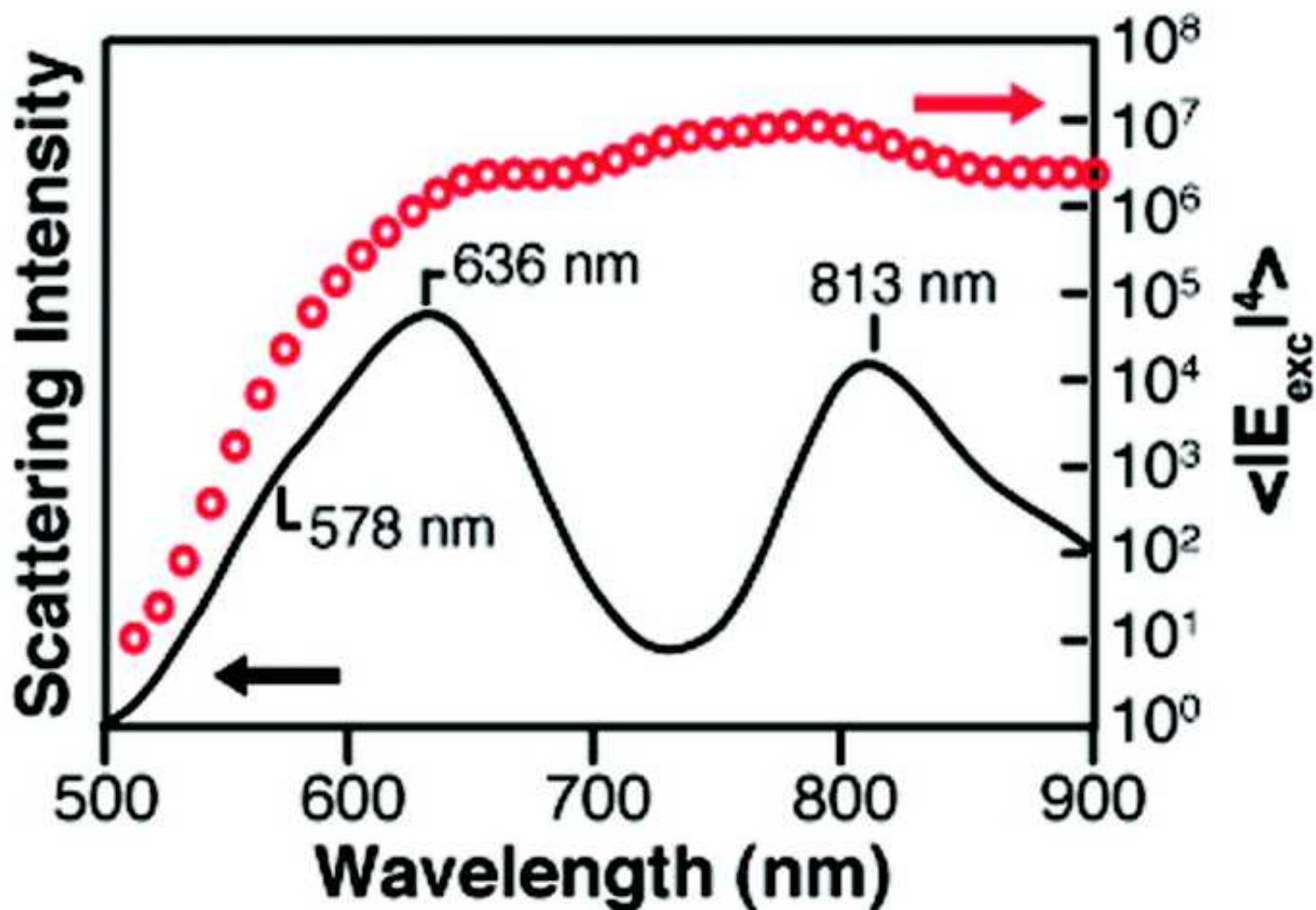
Correlated Structure, Spectroscopy & Theory of L-Au Trimer



$$EF = \frac{I_{SERS} / N_{SERS}}{I_{NRS} / N_{NRS}} = 1.7 \times 10^8$$

K. L. Wustholz, A-I. Henry, J. M. McMahon, R. G. Freeman, N. Valley, M. E. Piotti,
M. J. Natan, G. C. Schatz and R. P. Van Duyne, *J. Am. Chem. Soc.*, **132**, 10903-10910 (2010)

L-Au Trimer: $EF \sim \lambda_{\text{ex}}$ Independent (Theory)



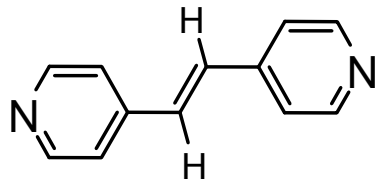
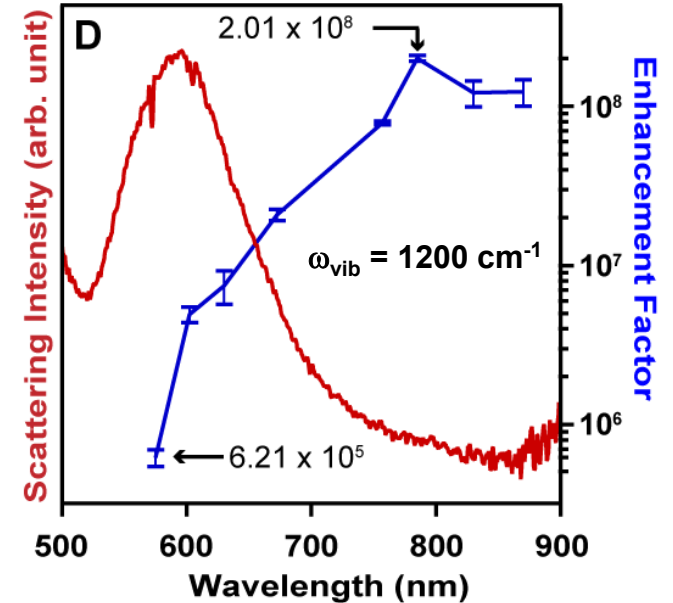
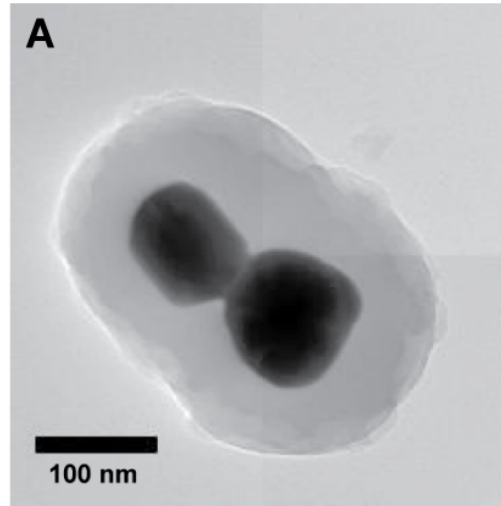
K. L. Wustholz, A-I. Henry, J. M. McMahon, R. G. Freeman, N. Valley, M. E. Piotti, M. J. Natan, G. C. Schatz and R. P. Van Duyne, *J. Am. Chem. Soc.*, **132**, 10903-10910 (2010)

SERES: Au Dimer

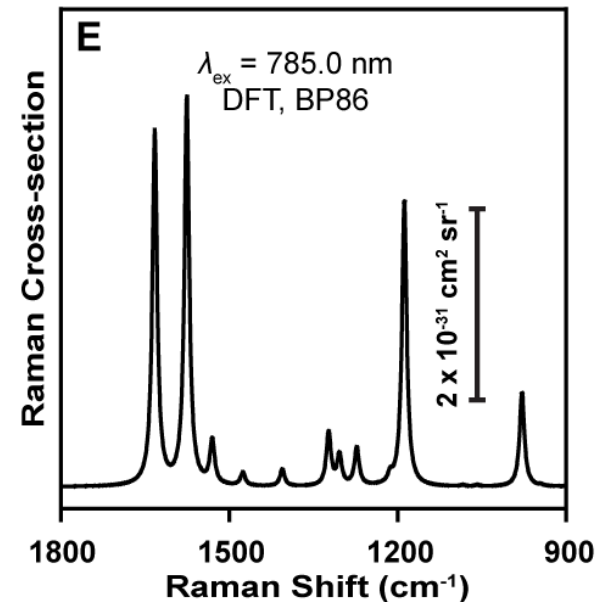
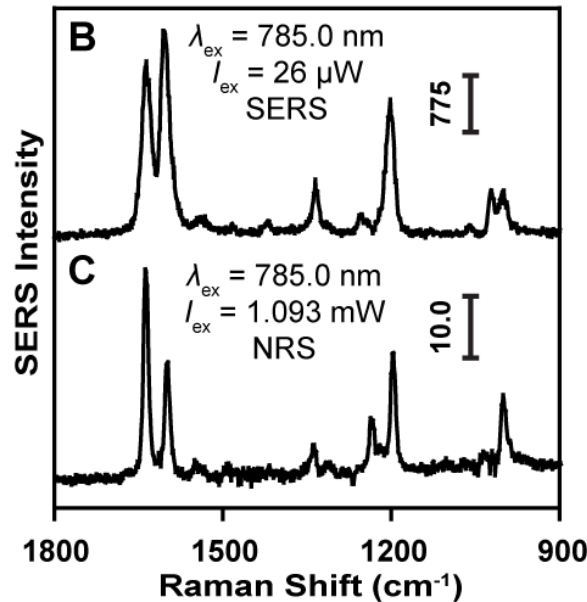
Correlated LSPR-
HRTEM-SERES

$\lambda_{\text{max,LSPR}} = 600 \text{ nm}$

$\lambda_{\text{max,EF}} = 785 \text{ nm}$



trans-1,2-bis(4-pyridyl)ethylene
BPE



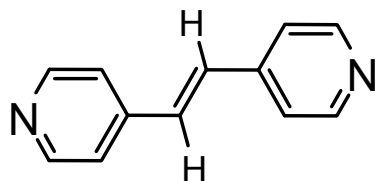
SERES: Bent-Au Trimer

Correlated LSPR-
HRTEM-SERES

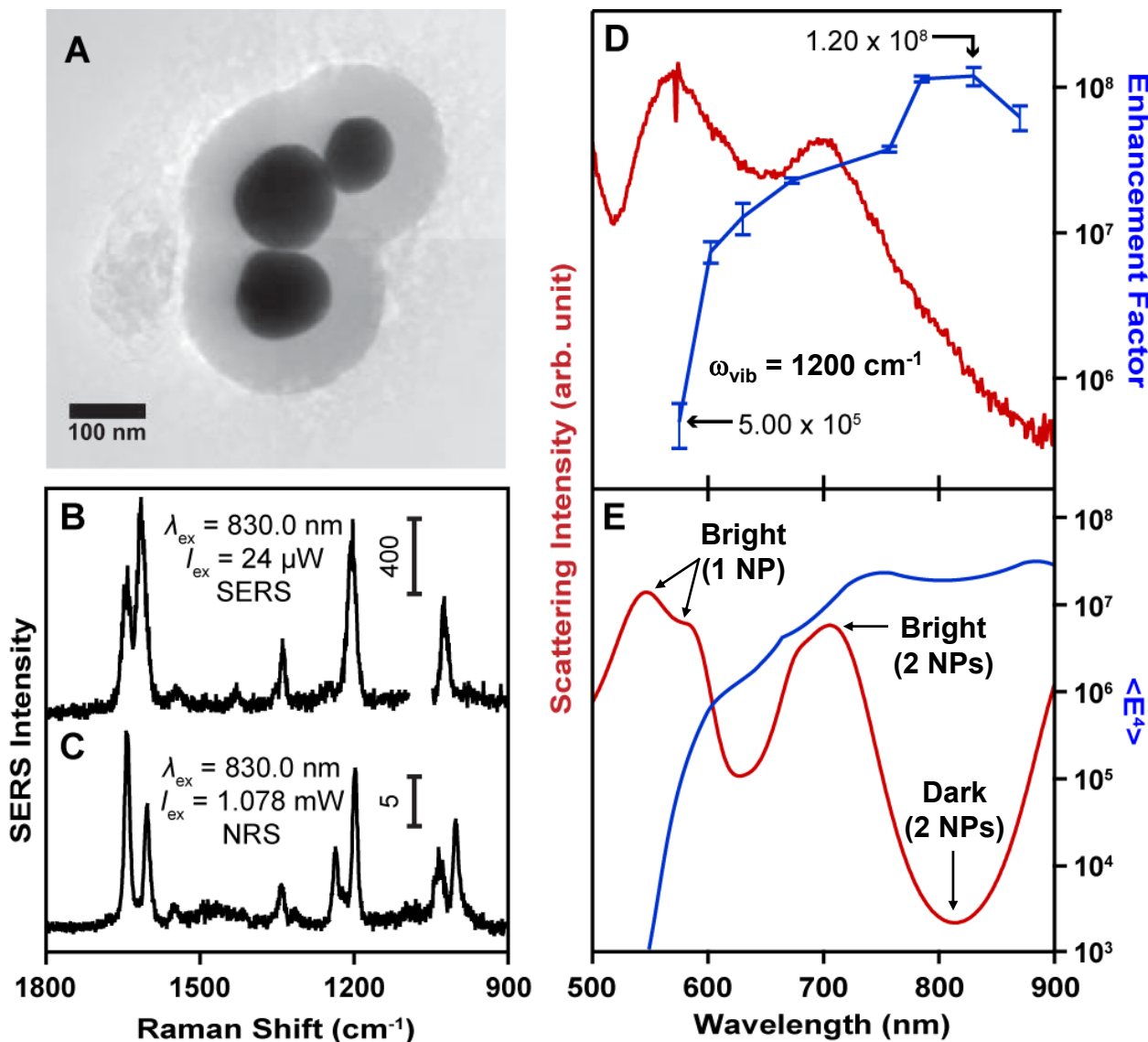
$\lambda_{\max, \text{LSPR}} = 575 \text{ nm}$

$\lambda_{\max, \text{LSPR}} = 700 \text{ nm}$

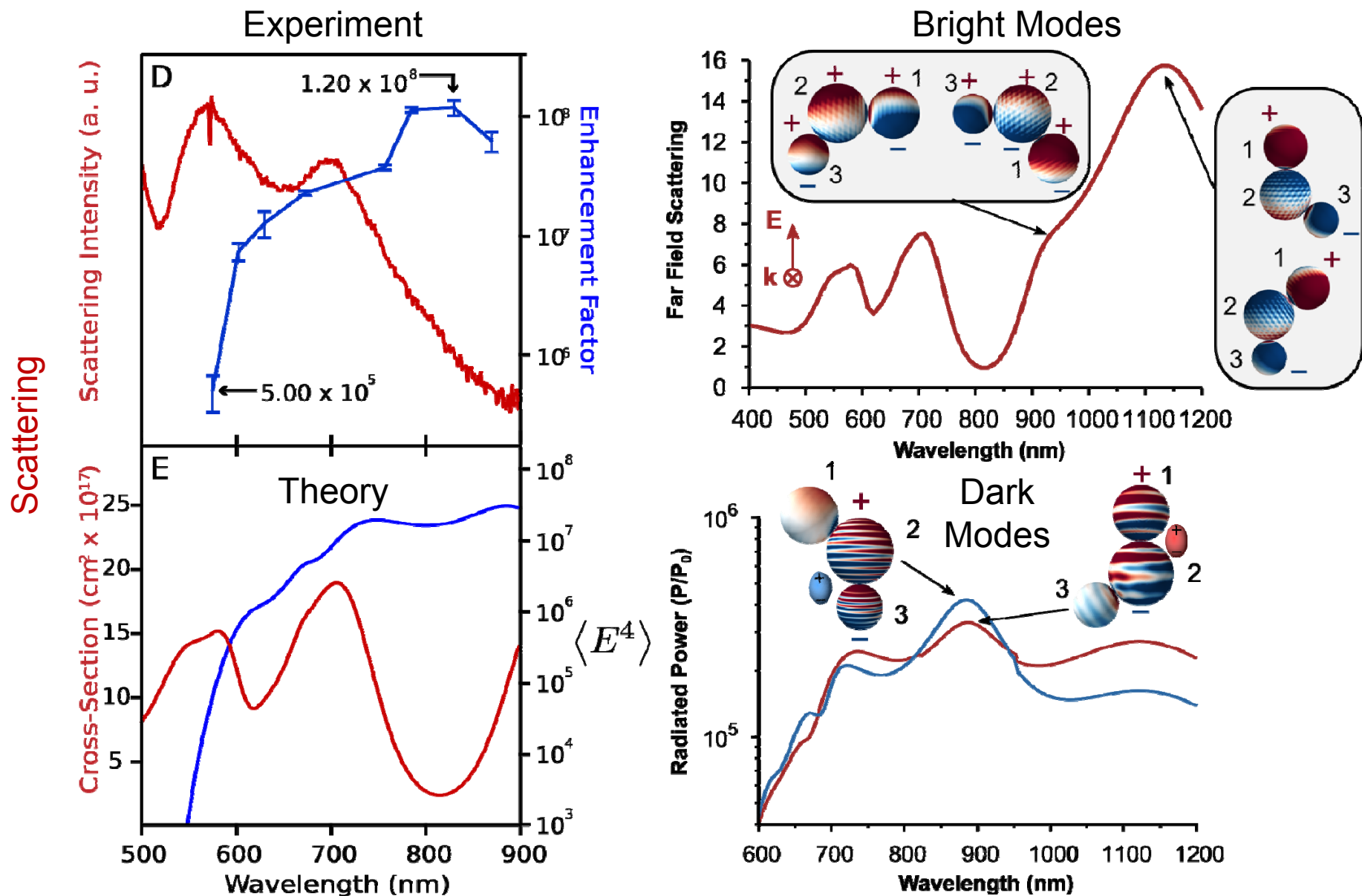
$\lambda_{\max, \text{EF}} = 830 \text{ nm}$



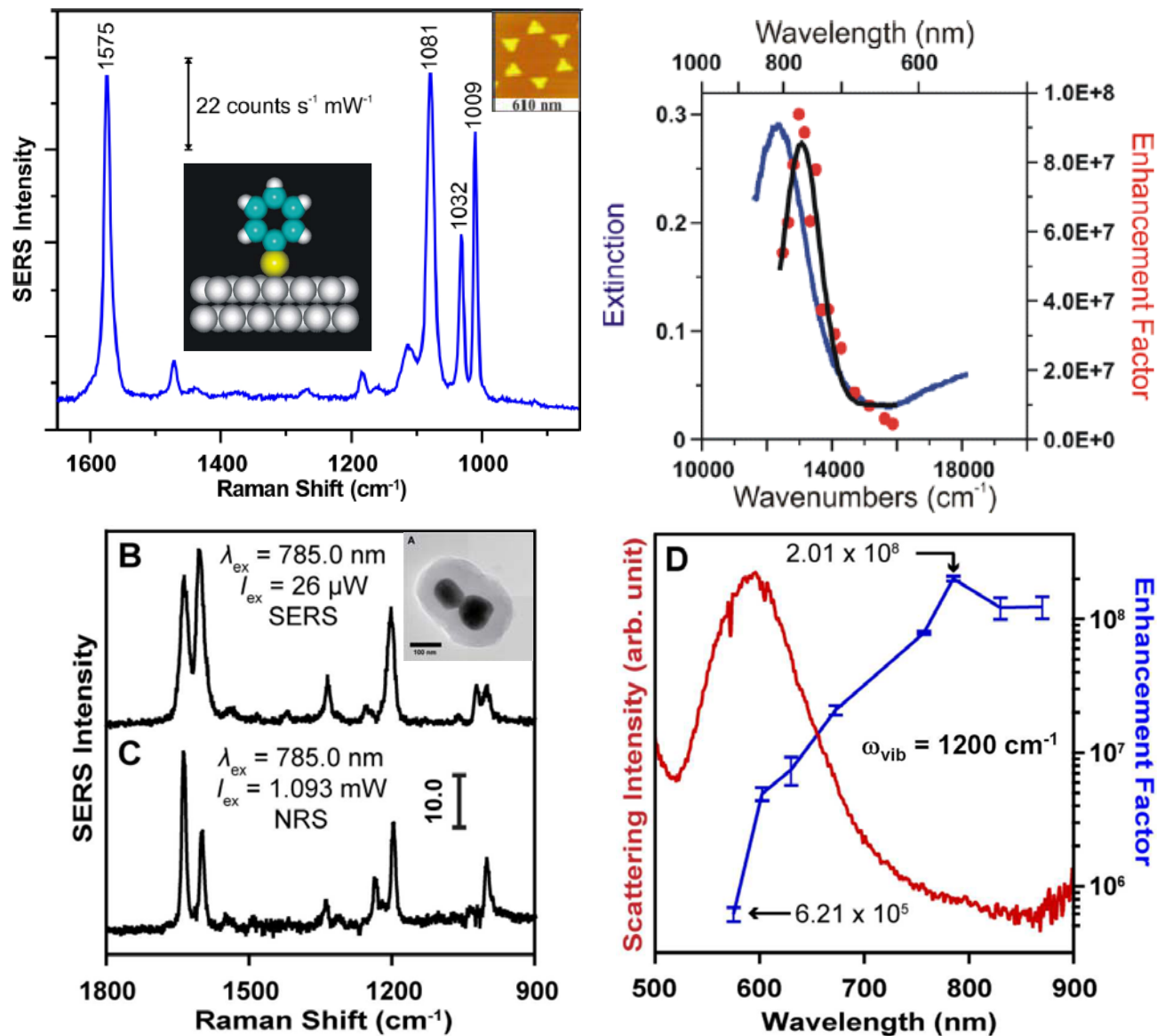
trans-1,2-bis(4-pyridyl)ethylene
BPE



SERES: Bright Modes & Dark Modes



SERS Excitation Spectroscopy



Summary: SERS Fundamentals (Single NP)

- **Au NP Dimers & Trimers: largest EF = 4.8×10^8**
- **EF NOT correlated with # cores or LSPR parameters**
- **$EF_{\text{avg}} > 10^8$: controlled by gap size in sub-nm range**
- **No Gap is REQUIRED: local radius of curvature ~ 1 nm**
- **Crevice site: local radius of curvature ~ 1 nm**
- **EF vs. ω_{ex} : \sim Independent of ω_{ex} due to near-field or dark mode excitation and re-radiation**

The Chemical Mechanism of SERS

The Chemical Mechanism of SERS

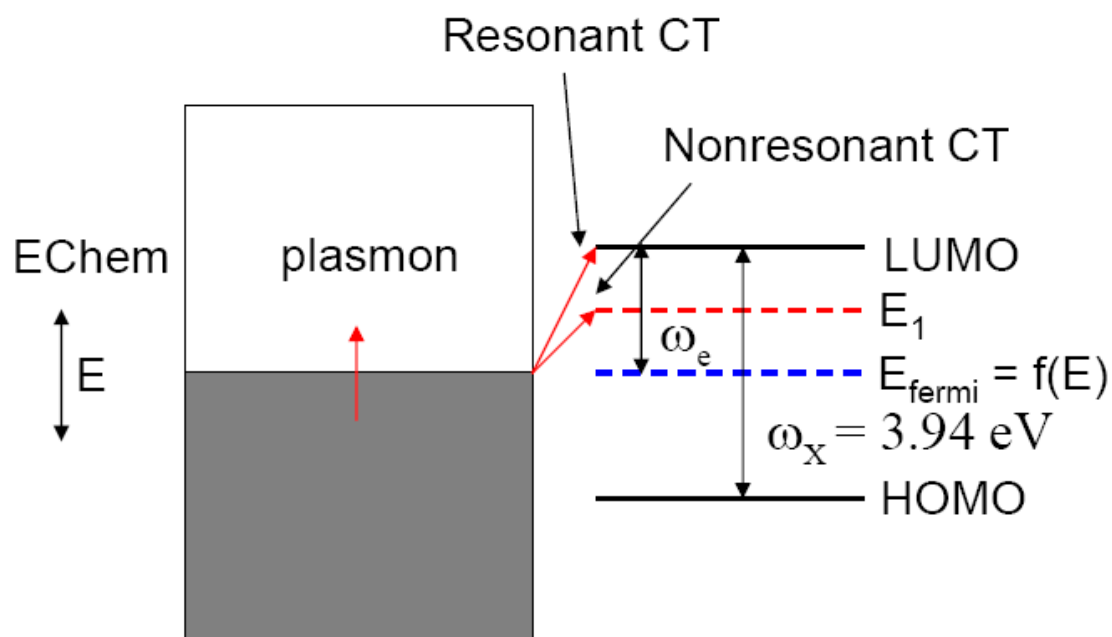
Laser excites: (a) new electronic states that arise from **chemisorption** or (b) shifted or broadened adsorbate electronic states (i.e. **resonance Raman** scattering)

Observables

1. **Magnitude of the enhancement factor (EF)** $EF_{\text{SERS, CHEM}} = 10^1 - 10^3$
2. **Metal to molecule distance dependence** No - Chemisorption only
3. **Nanoparticle size & shape dependence** None - single crystals OK
4. **Molecular selectivity** e.g. EF of CO $\sim 200 \times N_2$
5. **Material dielectric constants ($\epsilon_r, \epsilon_i, \epsilon_m$)** None
6. **EF vs. ω_{ex}** 1. No relationship to LSPR 2. dependence on E_{Fermi} vs. HOMO - LUMO gap
7. **EF vs. E (volts) resonances** Electrochemical SERS
8. **All optically driven processes are enhanced!!!** ?????

Non-Electromagnetic Contributions to SERS

1. Nonresonant charge transfer (CT) (estimated to be $1-10^3$)
2. Resonant CT (estimated to be $1-10^3$)
3. Molecular resonance Raman (determined by molecule; typically 10^2-10^4 but perhaps as high as 10^7)



$$EF_1 \propto \frac{\omega_X^4}{\omega_e^4}$$

$$\omega_e = E_{\text{LUMO}} - E_{\text{fermi}}(E)$$

$$\omega_X = \text{HOMO-LUMO}$$

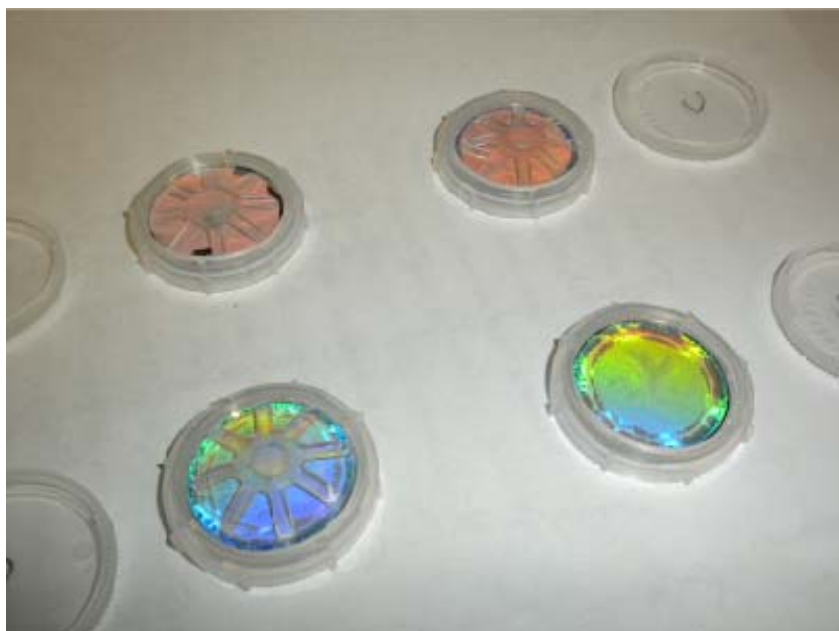
$EF_{\text{CHEM}} \sim 10^3$ for Special Cases

Table 1. Charge Transfer ($q(X \rightarrow \text{Ag})$), Bond Length ($R_{\text{Ag-N}}$), Averaged HOMO–LUMO Gap for Complex ($\bar{\omega}_{X-\text{Ag}}$), HOMO–LUMO Gap of Free Molecule (ω_X), and Integrated Raman Enhancement (EF_{int}) for Each of the Substituted Pyridines^a

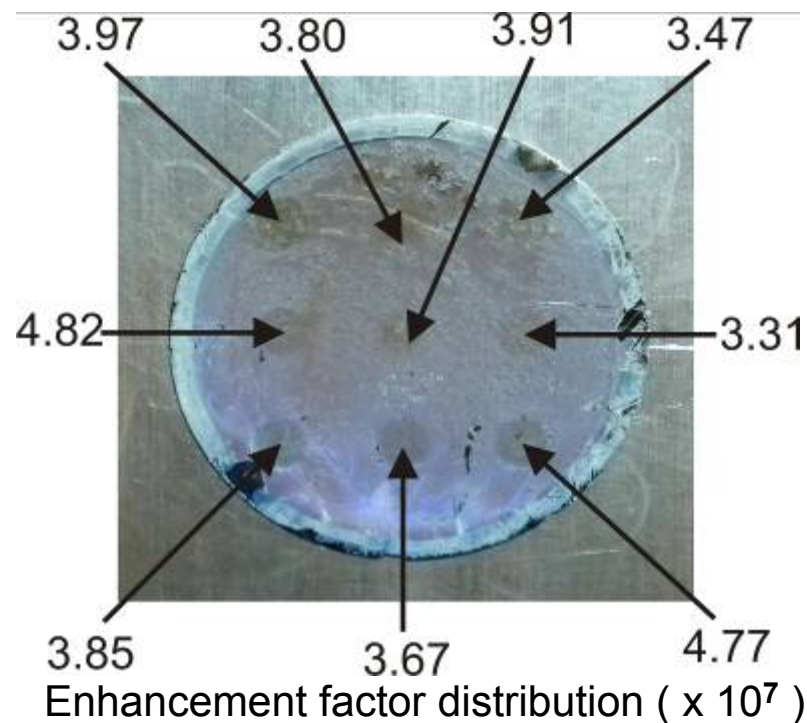
functional group	$q(X \rightarrow \text{Ag})$	$R_{\text{Ag-N}}$ (pm)	$\omega_{X-\text{Ag}}$ (eV)	ω_X (eV)	EF_{int}
<i>p</i> -C≡N	0.040e	224.9	0.077	3.500	81.47
<i>p</i> -CO ₂ H	0.060e	224.9	0.084	3.265	218.58
<i>p</i> -SO ₃ H	0.078e	225.7	0.106	3.653	1001.30
<i>m</i> -C≡N	0.093e	227.7	0.123	3.757	1135.62
<i>p</i> -CCl ₃	0.104e	226.3	0.161	3.580	4832.51
<i>m</i> -SO ₃ H	0.113e	227.3	0.177	3.861	4871.75
<i>p</i> -CCl ₂ H	0.128e	226.4	0.194	3.678	7260.90
<i>p</i> -CFCIH	0.130e	226.4	0.229	3.709	7491.35
<i>p</i> -CF ₂ H	0.130e	226.3	0.235	3.851	7055.83
<i>m</i> -Cl	0.138e	227.1	0.432	4.129	523.44
<i>p</i> -CCIH ₂	0.143e	226.5	0.329	3.741	2091.28
<i>p</i> -I	0.143e	226.3	0.482	4.119	336.73
<i>p</i> -Br	0.144e	227.0	0.487	4.172	317.82
<i>p</i> -Cl	0.145e	226.3	0.472	4.188	293.60
<i>p</i> -F	0.146e	226.5	0.706	4.028	30.27
H	0.151e	226.3	0.633	4.138	52.32
<i>m</i> -OH	0.151e	226.3	0.630	4.065	46.15
<i>p</i> -OH	0.158e	225.9	1.104	4.468	8.98
<i>m</i> -NH ₂	0.161e	226.2	0.835	3.756	9.14
<i>p</i> -CH ₃	0.163e	225.9	0.802	4.210	17.98
<i>p</i> -NH ₂	0.168e	224.5	1.227	4.082	6.74
<i>p</i> -N(CH ₃) ₂	0.181e	223.7	1.420	4.009	5.77

^a *m*- or *p*- denote the *meta* or *para*-position, respectively. Functional groups listed above H are classified as accepting and below H are classified as donating.

High Performance Substrates: **Uniform EF**

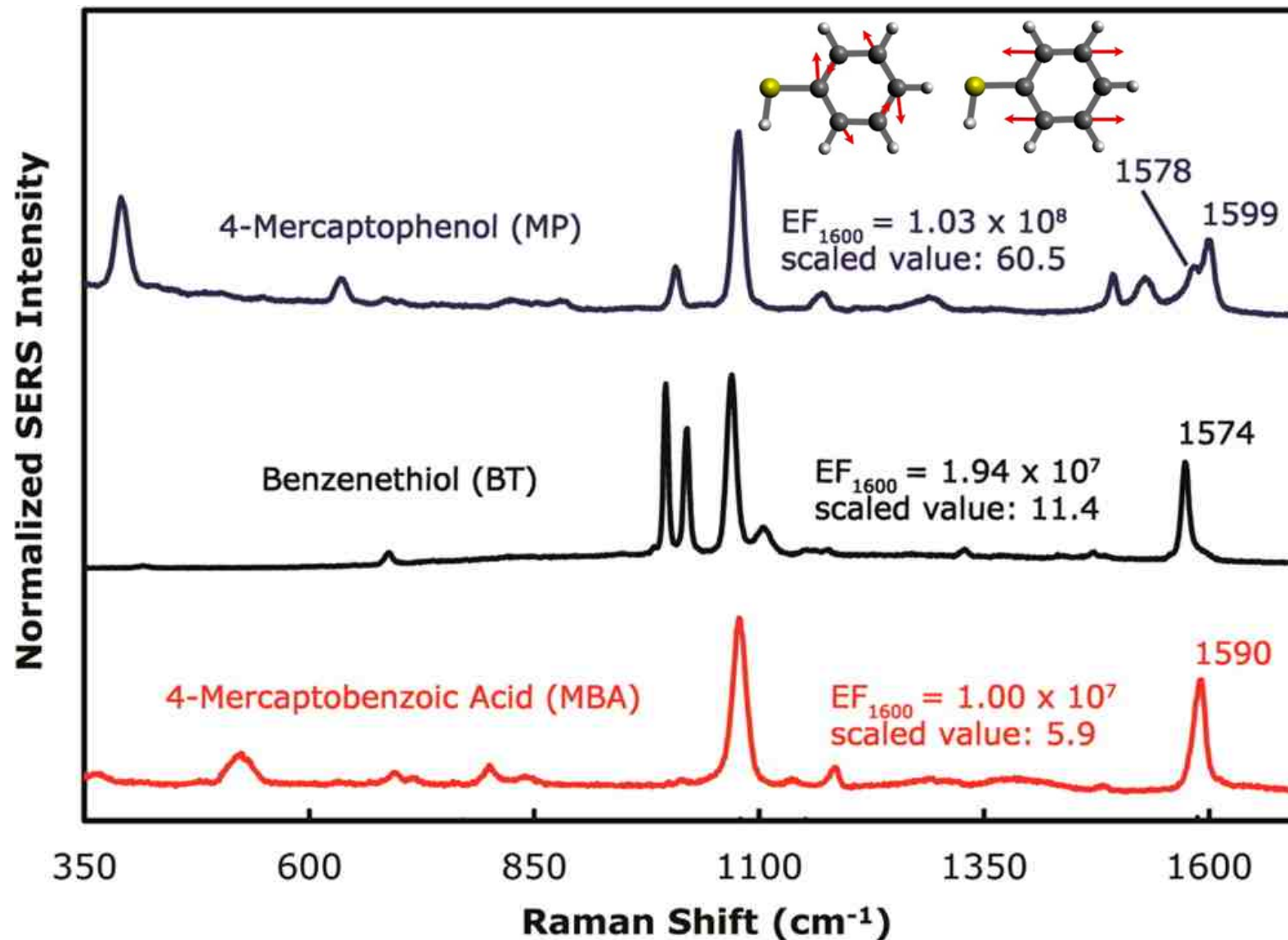


Multiple FON samples from single deposition



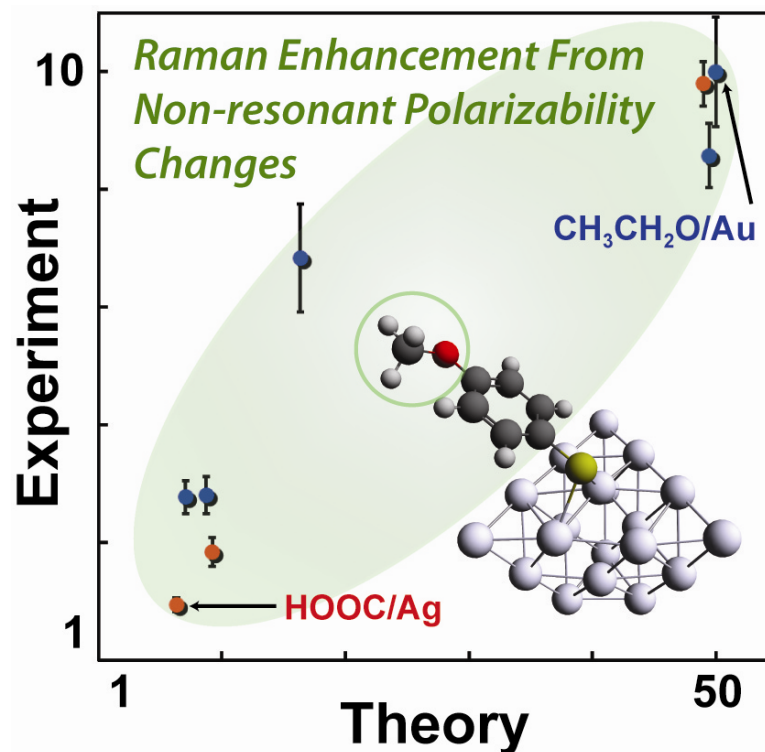
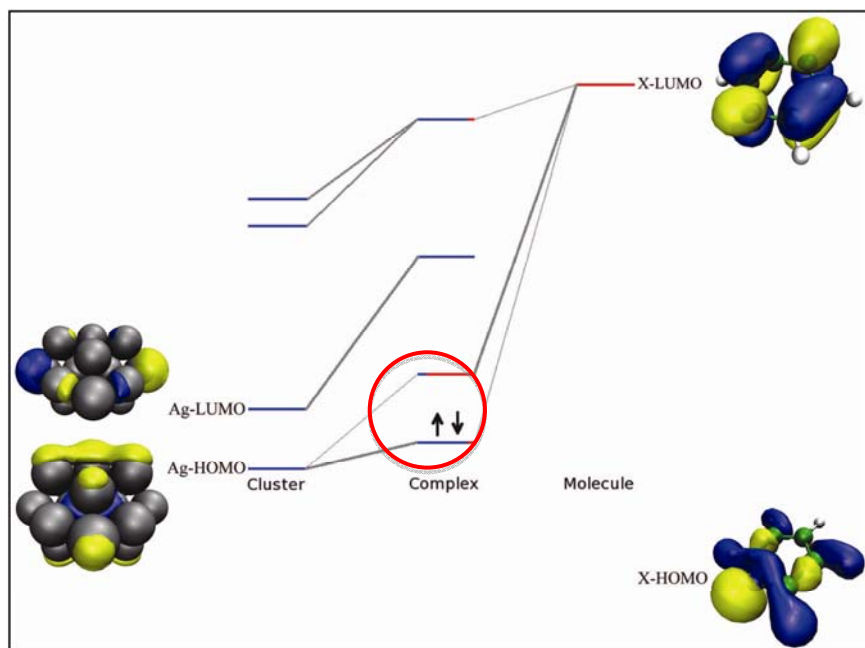
Average EF over entire 1 inch wafer is $3.95 (\pm 0.68) \times 10^7$

The CHEM Mechanism of SERS: Non-resonant Polarizability Changes in 4-Substituted Benzenethiols on Ag & Au



The CHEM Mechanism of SERS: Non-resonant Polarizability Changes in 4-Substituted Benzenethiols on Ag & Au

- **Theory (Left).** Control energy of Metal-Adsorbate complex (red circle) 8 adsorbate/surface pairs. Predicted – 50x variation in EF
- **Experiment (Right).** Demonstrated - 10x variation in EF
- (H, OH, HOOC)/Ag; (H, HOOC, CH₃O, CH₃CH₂O, NO₂)/Au



Acknowledgements: CHEM Mechanism of SERS

Van Duyne Group (Summer 2013)



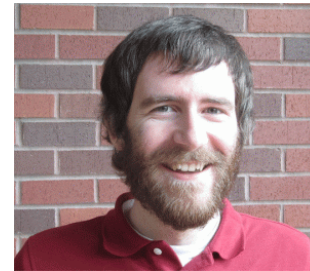
**Nathan
Greeneltch**



George Schatz



Lasse Jensen



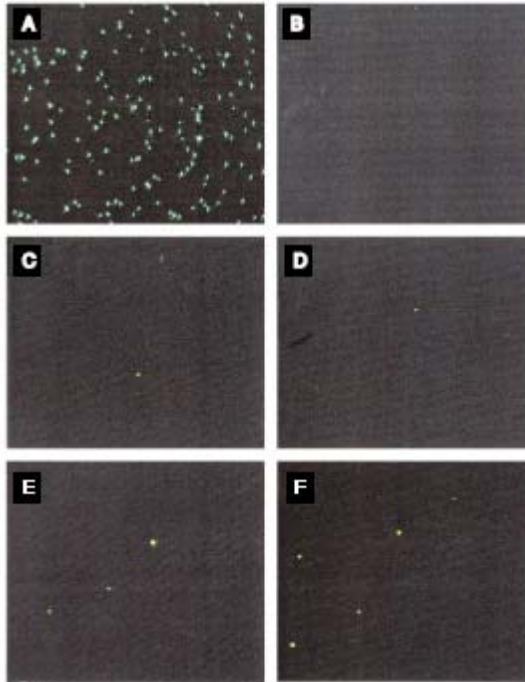
Nick Valley



Single Molecule SERS

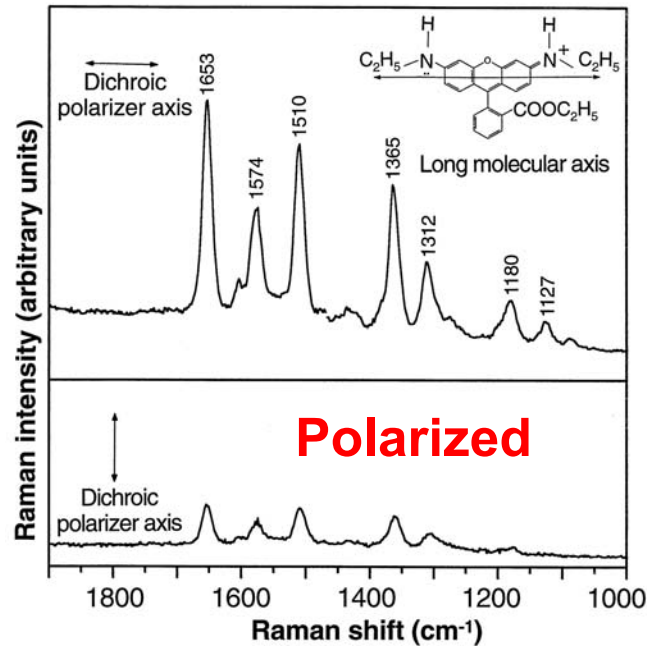
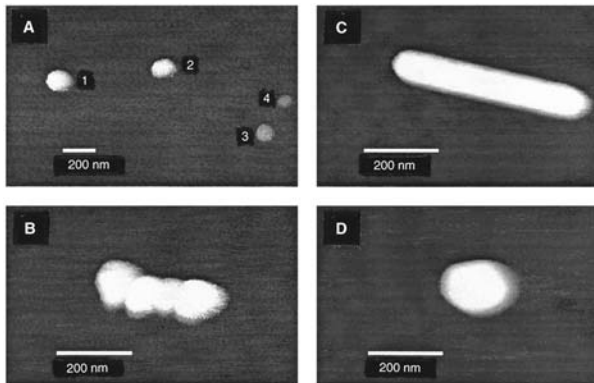
Single Molecule SERS: $EF \sim 10^{14}$!!

Few Hot Particles

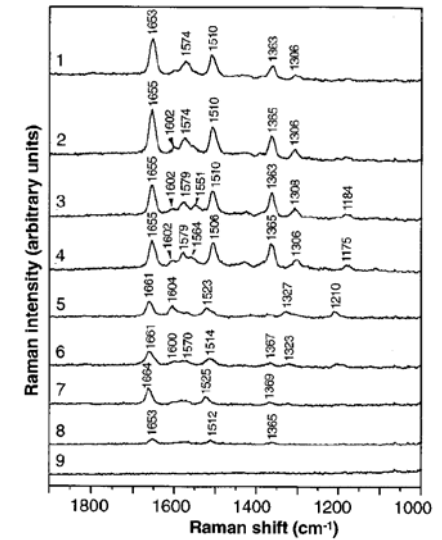


- A) Rayleigh Scattering
- B) 0 Molecules
- C) 0.5 Molecules
- D) 0.5 Molecules
- E) 5 Molecules
- F) 50 Molecules

Single or Cluster?



Spectral Wandering



0.5 molecules particle⁻¹

$\lambda_{ex} = 514.5\text{nm}$

$P_{ex} = 10\text{ mW}$

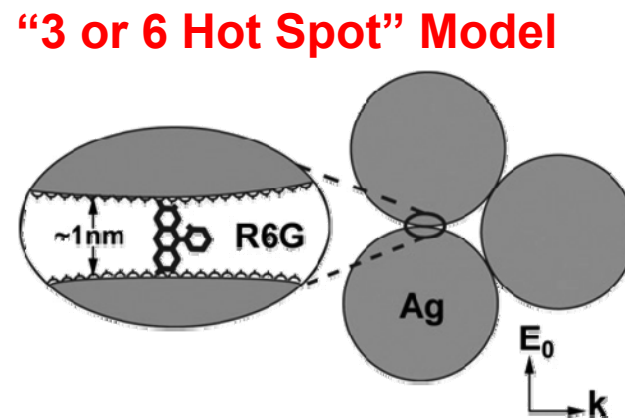
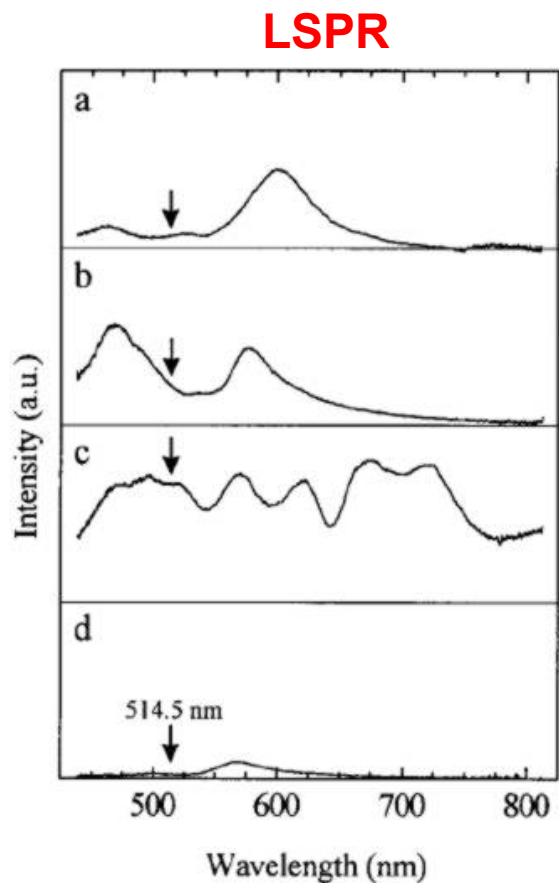
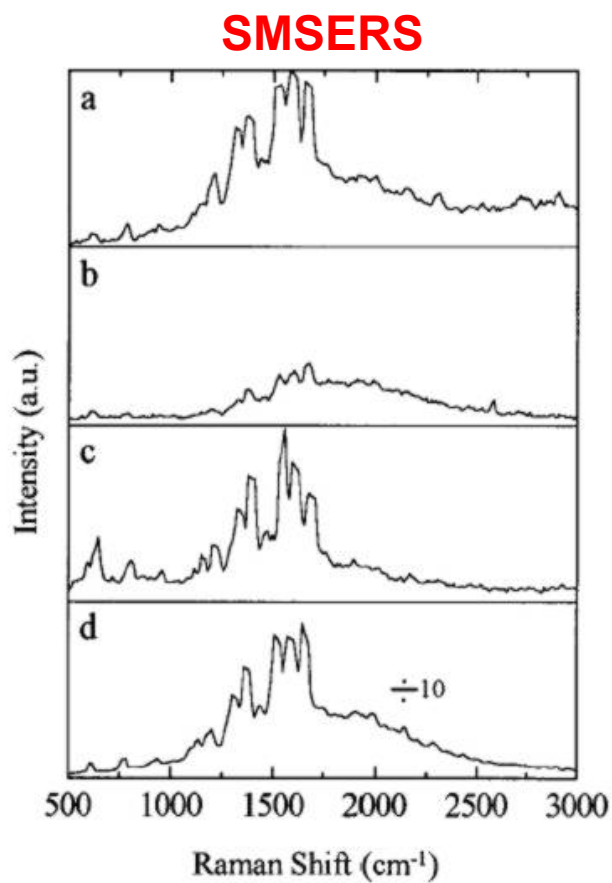
On Glass, In Air

No Relationship between SMSERS and LSPR

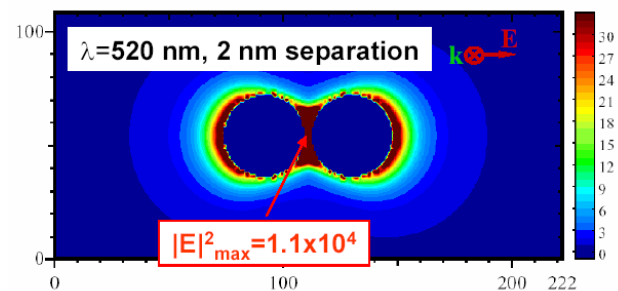
Surface Enhanced Raman Spectroscopy of Individual Rhodamine 6G Molecules on Large Ag Nanocrystals

Amy M. Michaels, M. Nirmal,[†] and L. E. Brus* *J. Am. Chem. Soc.* 1999, 121, 9932–9939

Contribution from the Department of Chemistry, Columbia University, New York, New York 10027

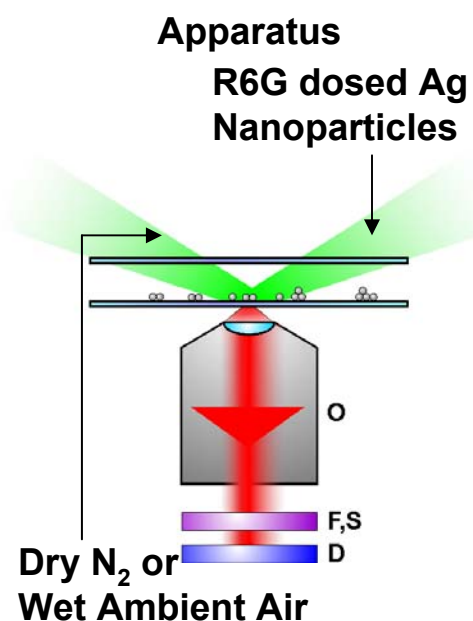
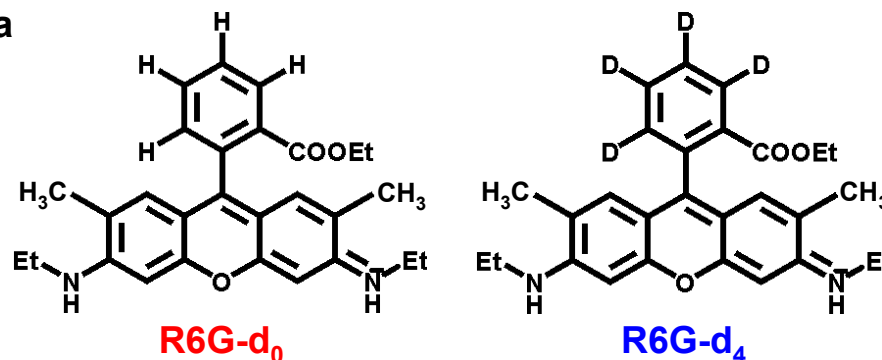


GCS Calculation

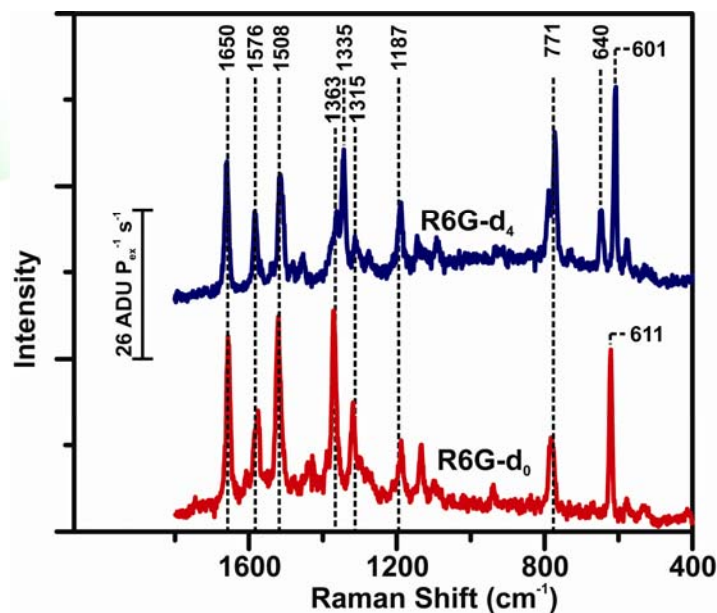


Single Molecule SERS: R6G Isotopologues

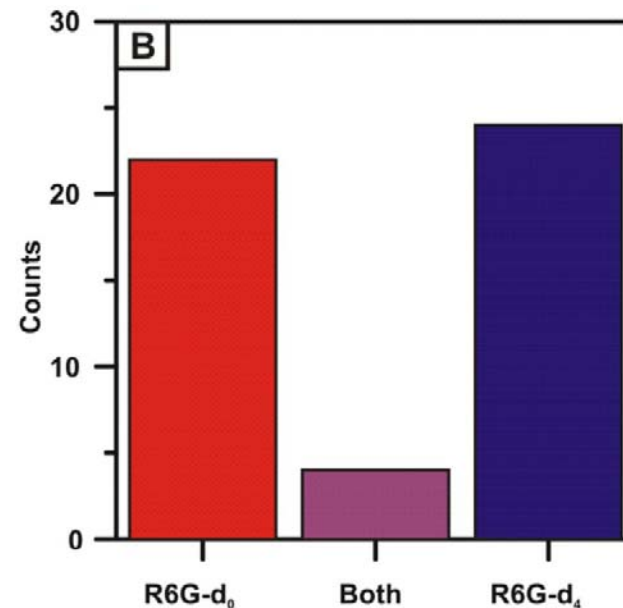
- Isotopologues have unique Raman spectra
- Ag nanoparticles dosed with 1:1 ratio R6G-d₄ and R6G-d₀
- 1 molecule per nanoparticle
- $\lambda_{\text{ex}} = 532 \text{ nm}$, 21 mW, 10 s, Dry N₂
- $\text{EF} (10^{14}) = \text{EF}_{\text{EM}} (10^8) \times \text{EF}_{\text{RRS}} (10^6)$



Single Molecule Spectra



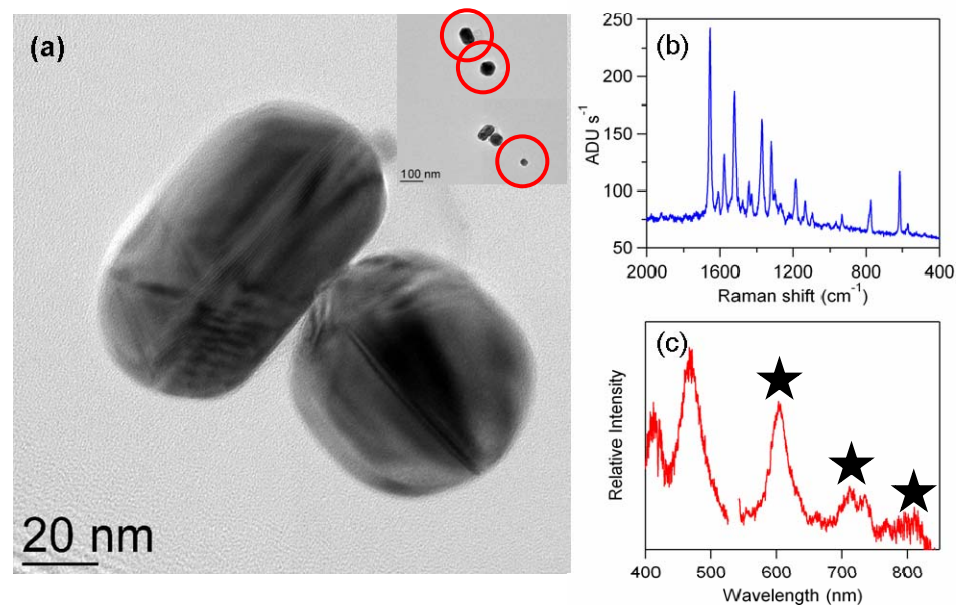
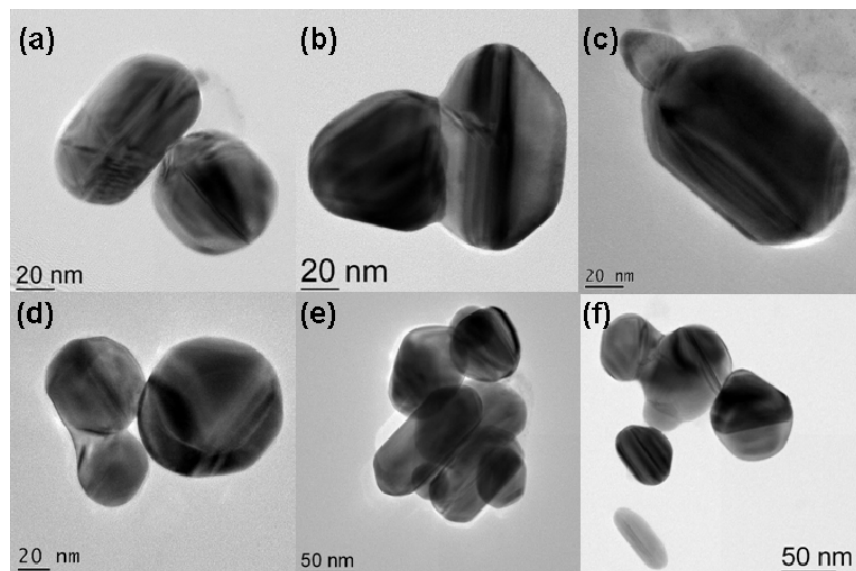
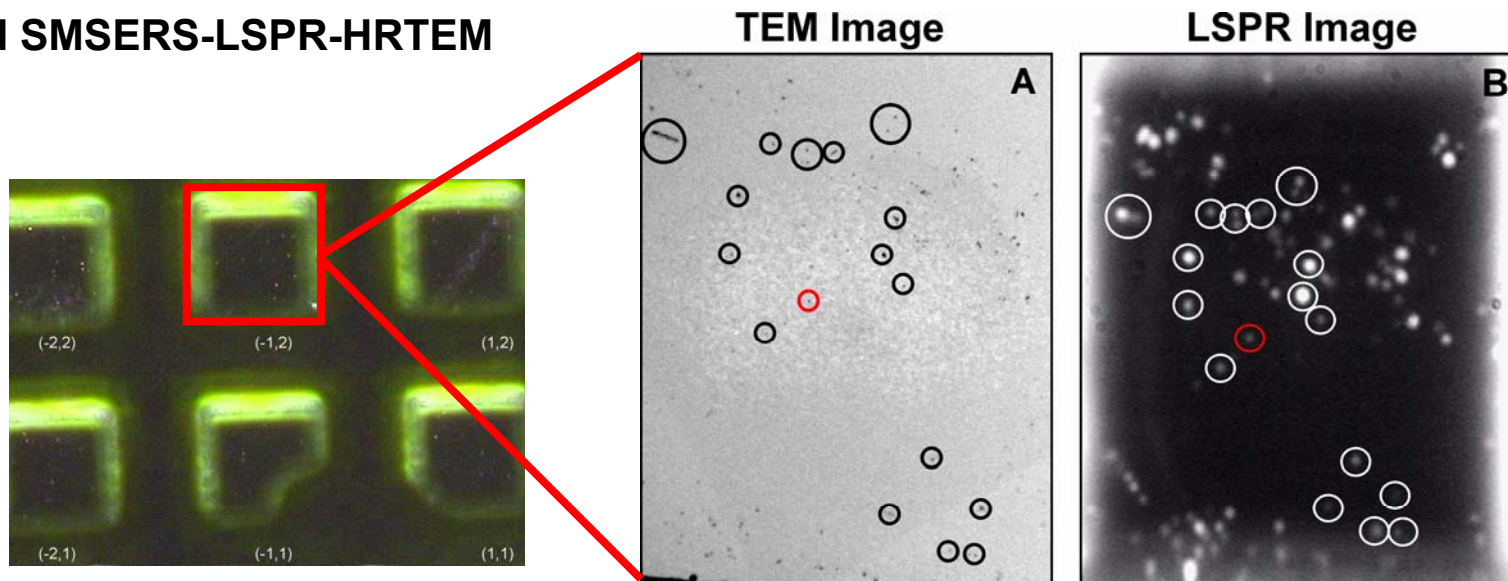
Histogram:
601 cm⁻¹; 611 cm⁻¹



Observation of d₀ OR d₄ but not both proves SMSERS

Probing the Structure of Single Molecule SERS Hot Spots

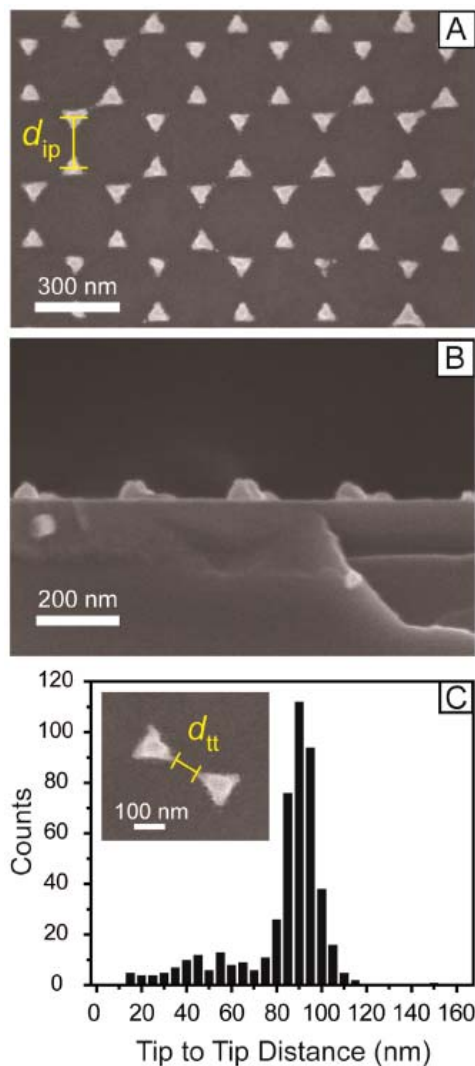
Correlated SMSERS-LSPR-HRTEM



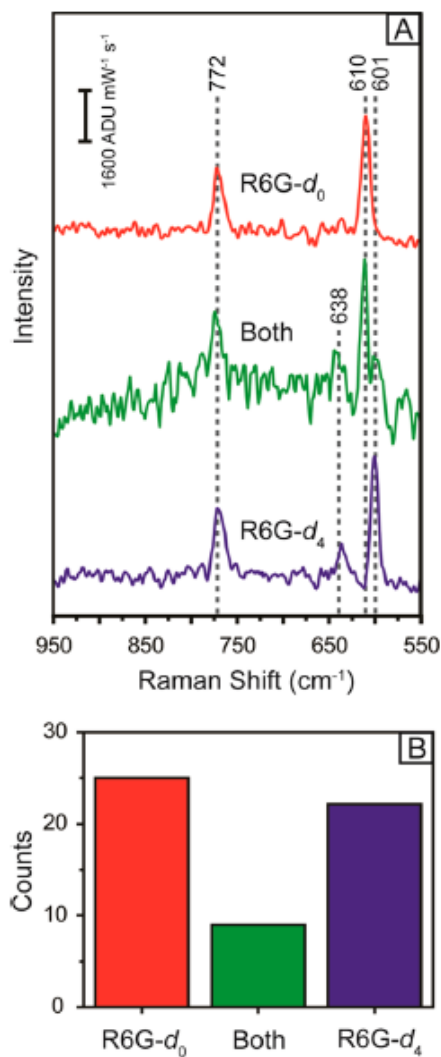
J. P. Camden, J. A. Dieringer, Y. Wang, D. J. Masiello, L. D. Marks,
G. C. Schatz, and R. P. Van Duyne, *J. Am. Chem. Soc.*, **130**, 12616-12617 (2008)

Single Molecule SERS: No Nanogaps

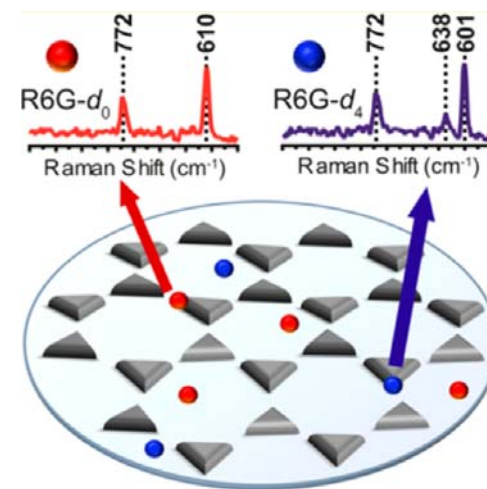
Nanosphere Lithography



SMSERS & Histogram



Conclusions



- **R6G- d_0 OR R6G- d_4 but NOT both proves SMSERS**
- **No Nanogaps**
- **Uniform, Reproducible, Tunable LSPR**

Acknowledgements: SMSERS

Van Duyne Group (Summer 2013)



Jordan Klingsporn

Alyssa Zrimsek

Anne-Isabelle Henry



George Schatz



Lasse Jensen

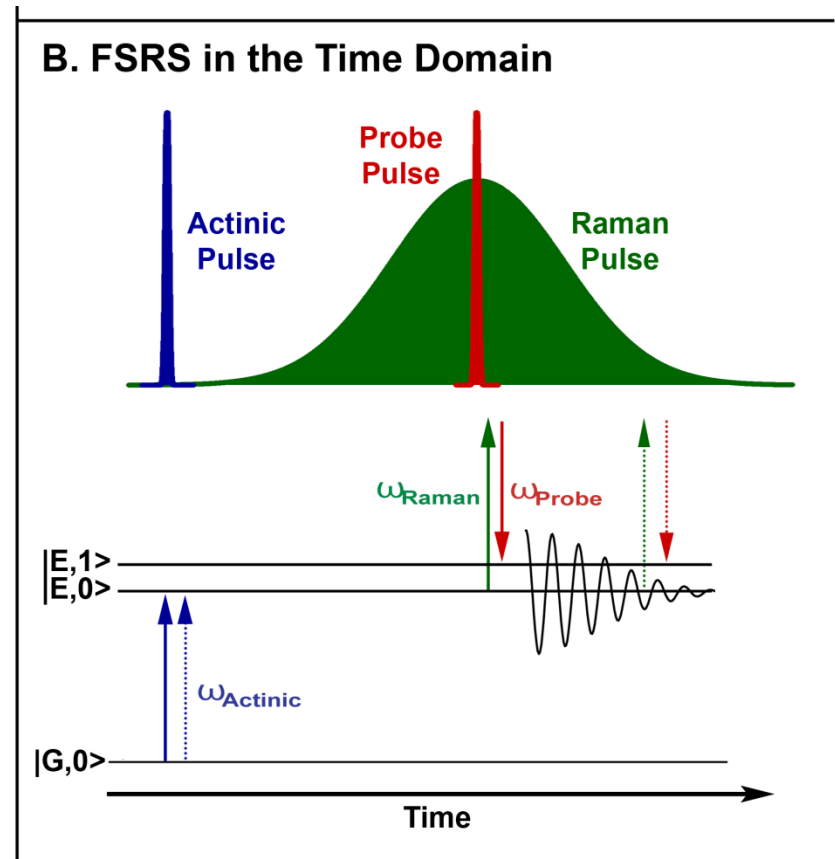
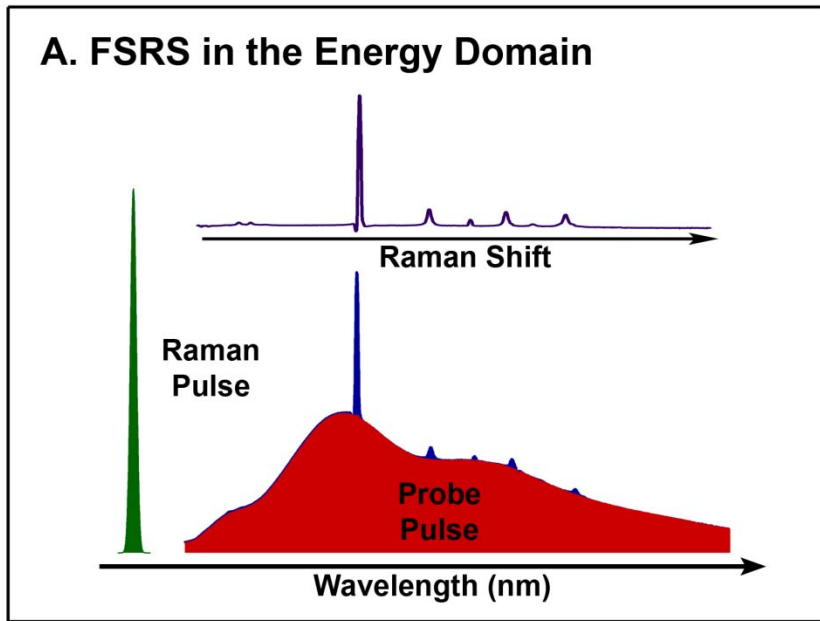


Surface-Enhanced Femtosecond Stimulated Raman Spectroscopy

Femtosecond Stimulated Raman Spectroscopy

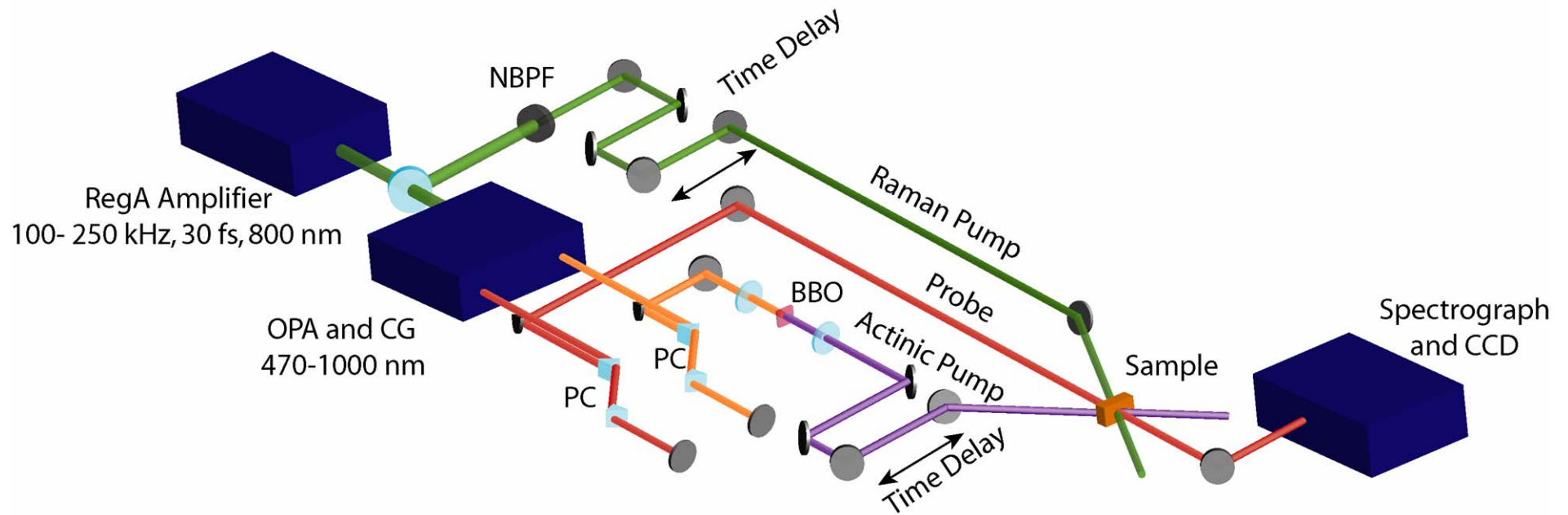
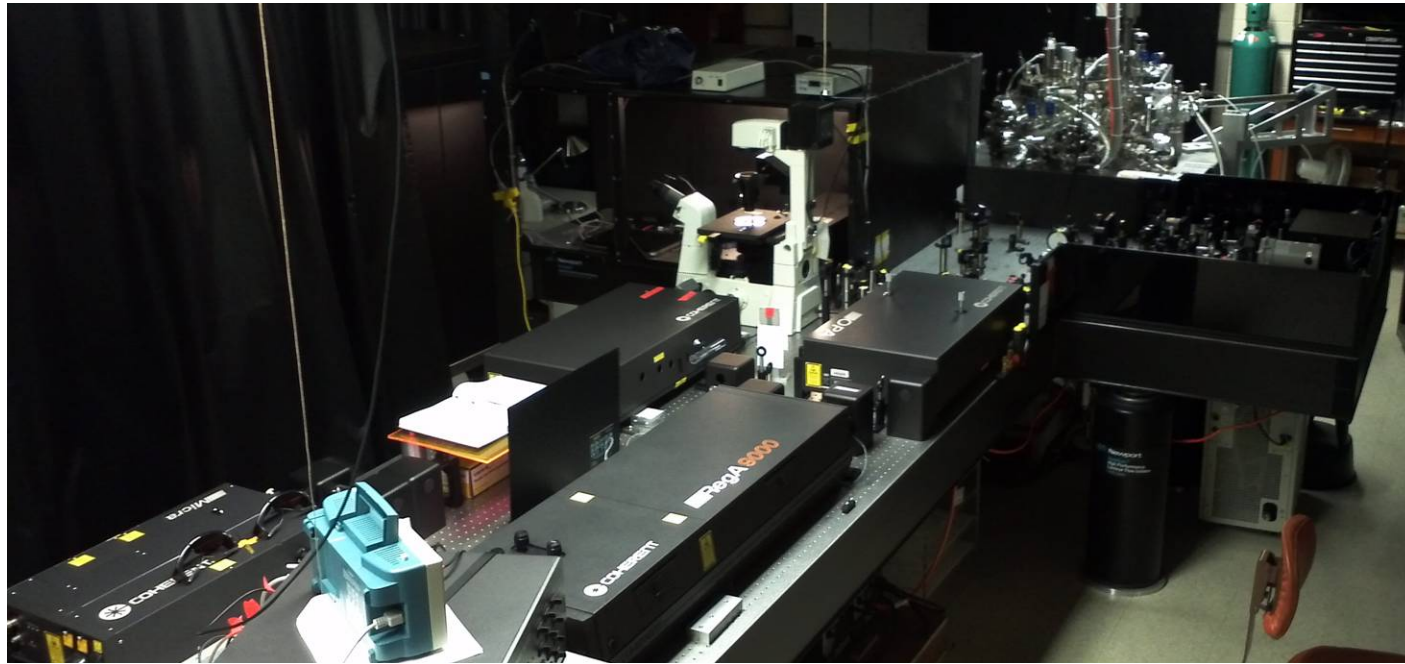
A three pulse time-resolved structural technique:

1. Actinic Pulse: 20 fs pulse excites sample
2. Raman Pulse: 3 ps pulse, narrow bandwidth at 800 nm
3. Probe Pulse: 20 fs pulse, NIR continuum

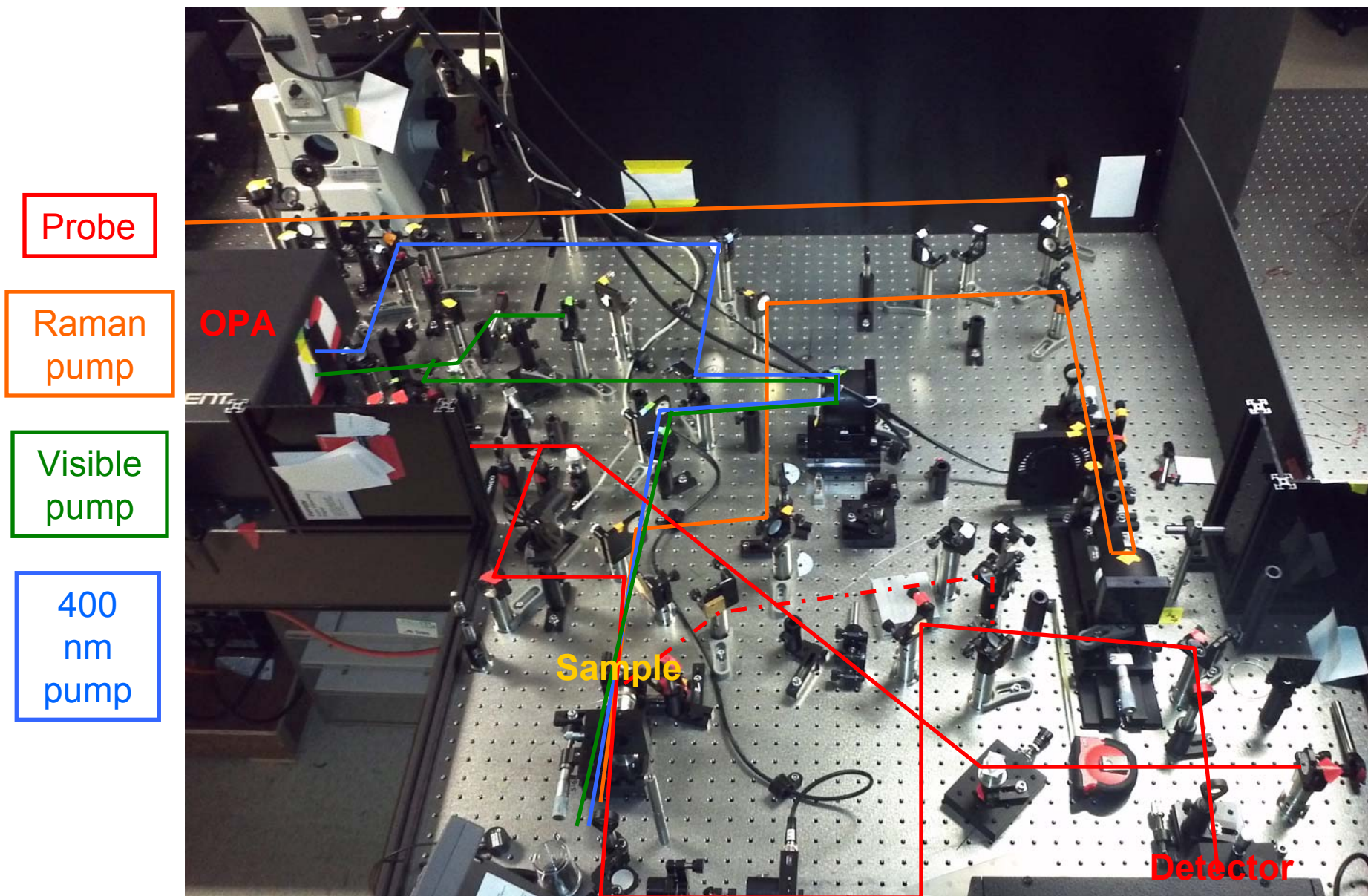


With 5 cm^{-1} spectral resolution and 50 fs temporal resolution, FSRS is a powerful technique to study ultrafast reaction dynamics

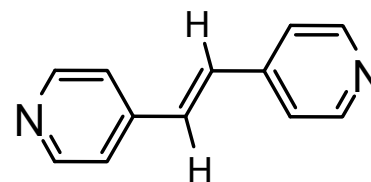
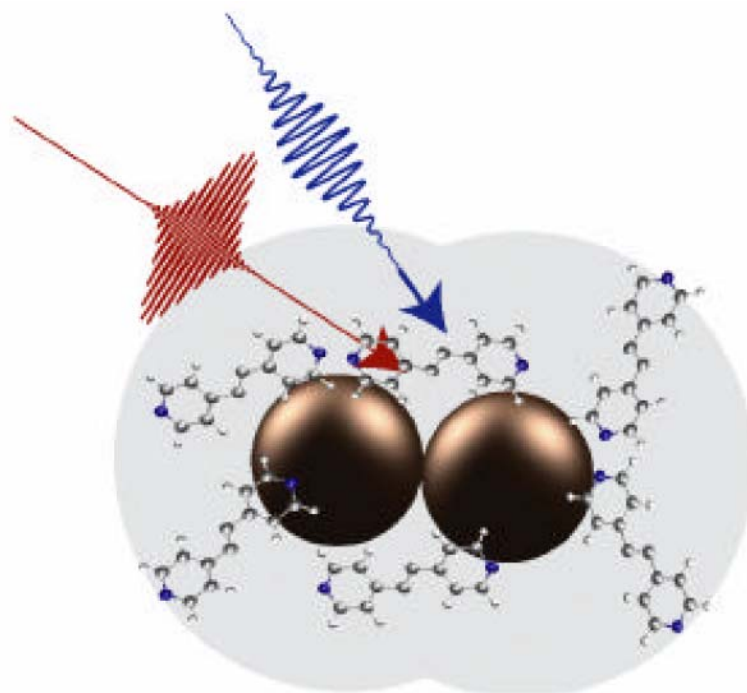
High Repetition Rate is Needed for SE-FSRS



Apparatus for SE-FSRS and ps SERS

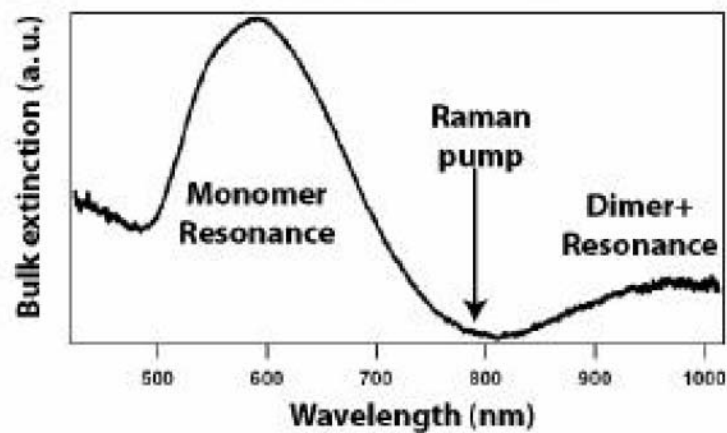


Nanoantennas for SE-FSRS

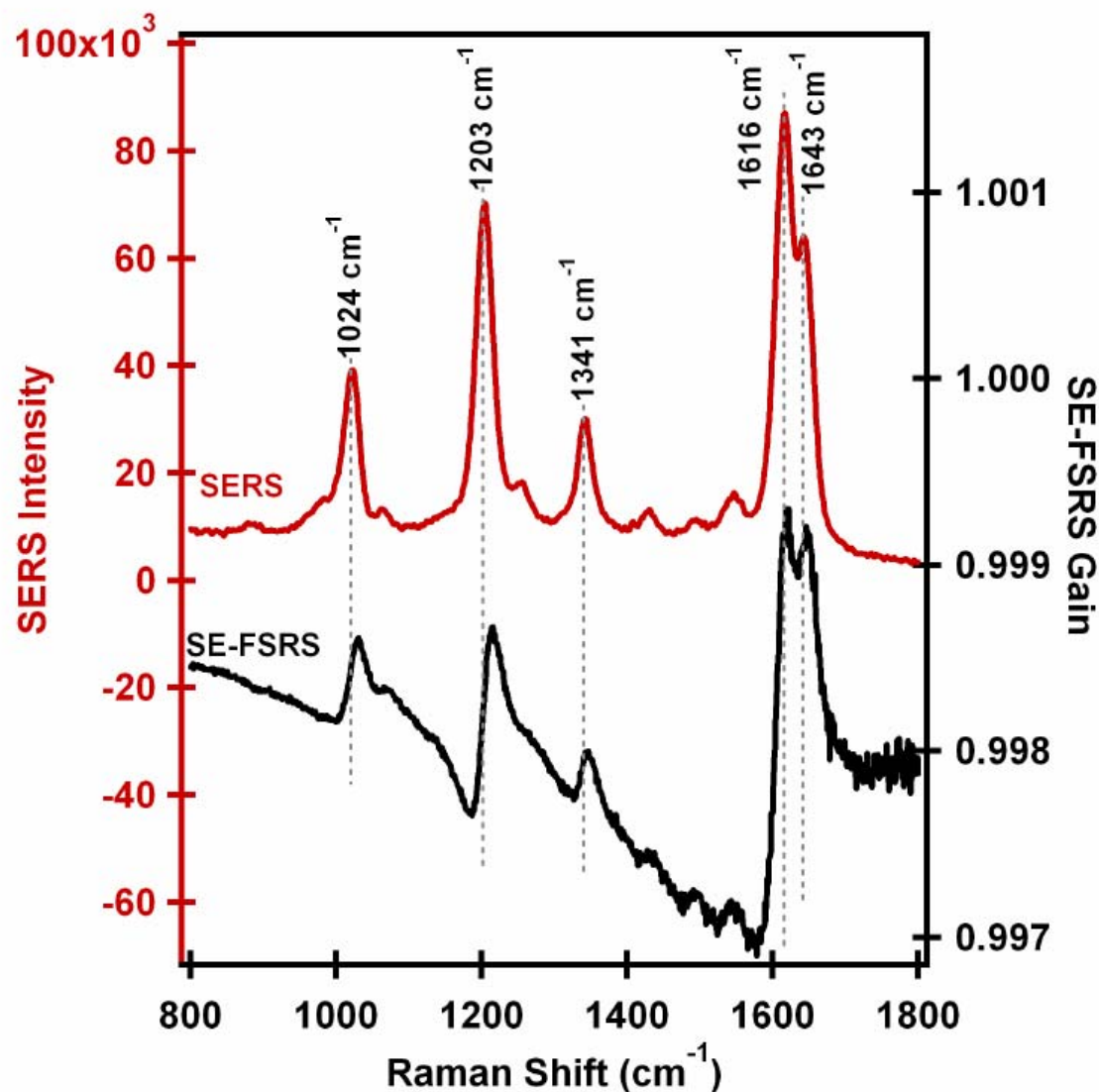


trans-1,2-bis(4-pyridyl)ethylene

BPE

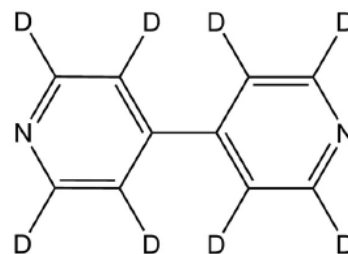
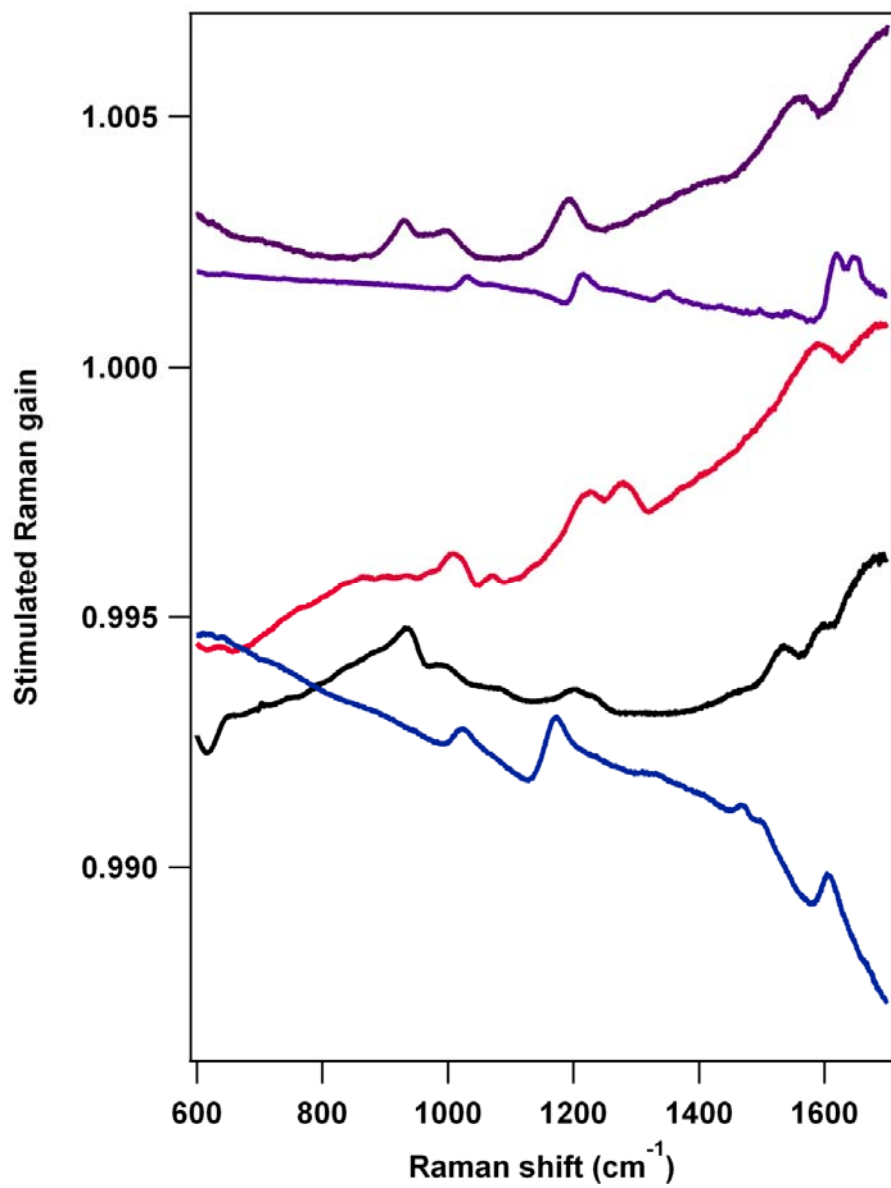


ps SERS and SE-FSRS: BPE

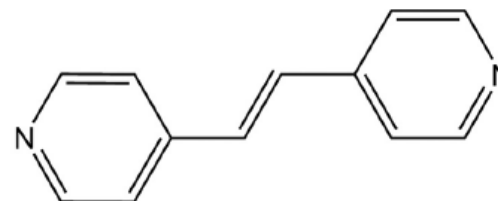


- Ps SERS & SE-FSRS show isoenergetic peaks FWHM $\Gamma = 20 \text{ cm}^{-1}$
- SE-FSRS S/N ~ 50 in 5 min.
- SE-FSRS EF $\sim 10^4$ - 10^6
- Pump: 795 nm, 2 nJ/pulse, 100 KHz, 200 μW avg. power
- Probe: 100 pJ/pulse, 100 KHz, 10 μW avg. power
- SE-FSRS Dispersive Lineshape

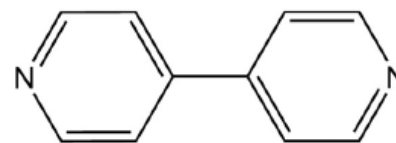
SE-FSRS works with a variety of adsorbates



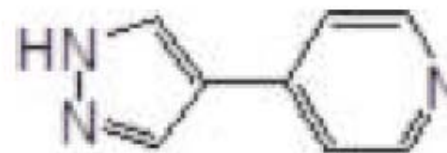
SERS421



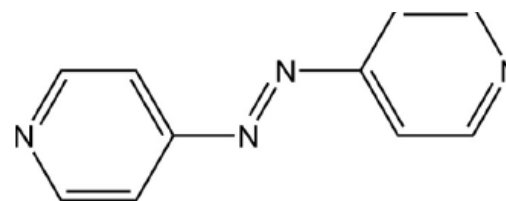
SERS440



SERS420

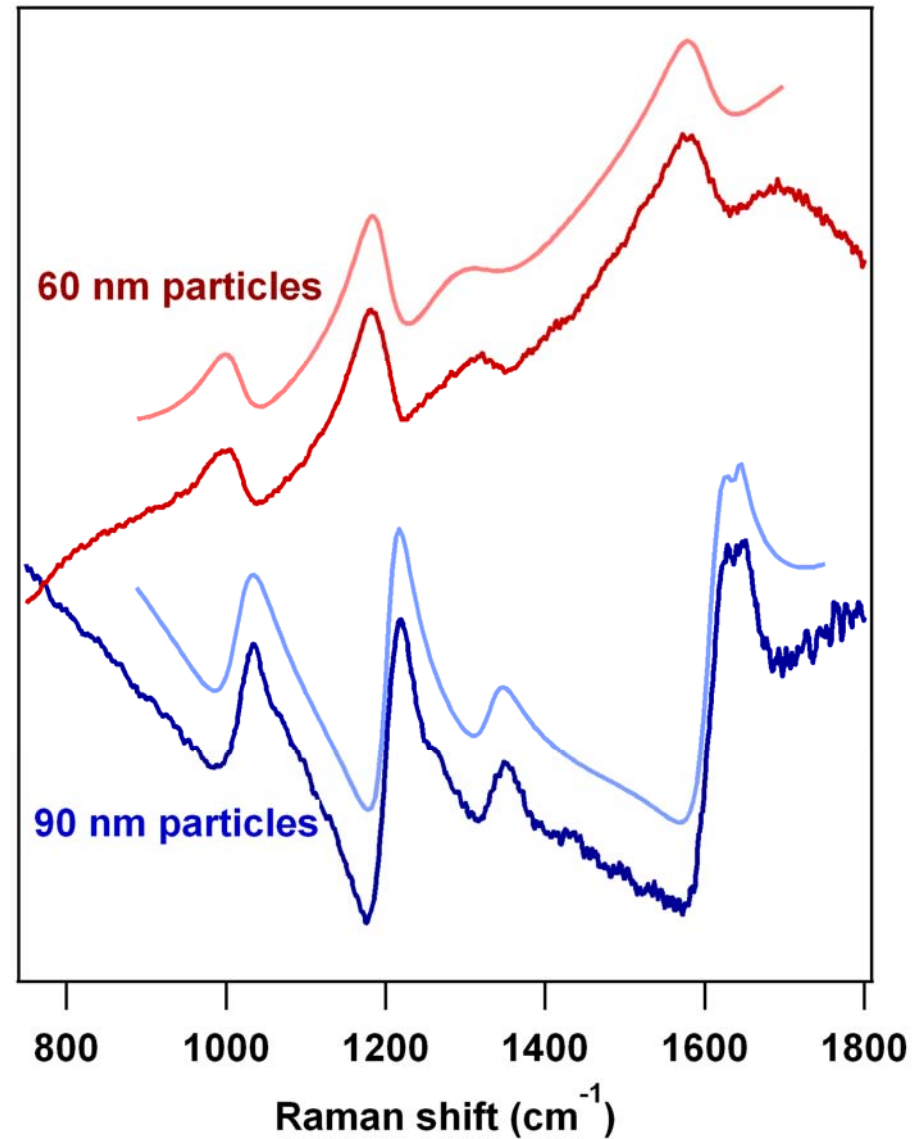
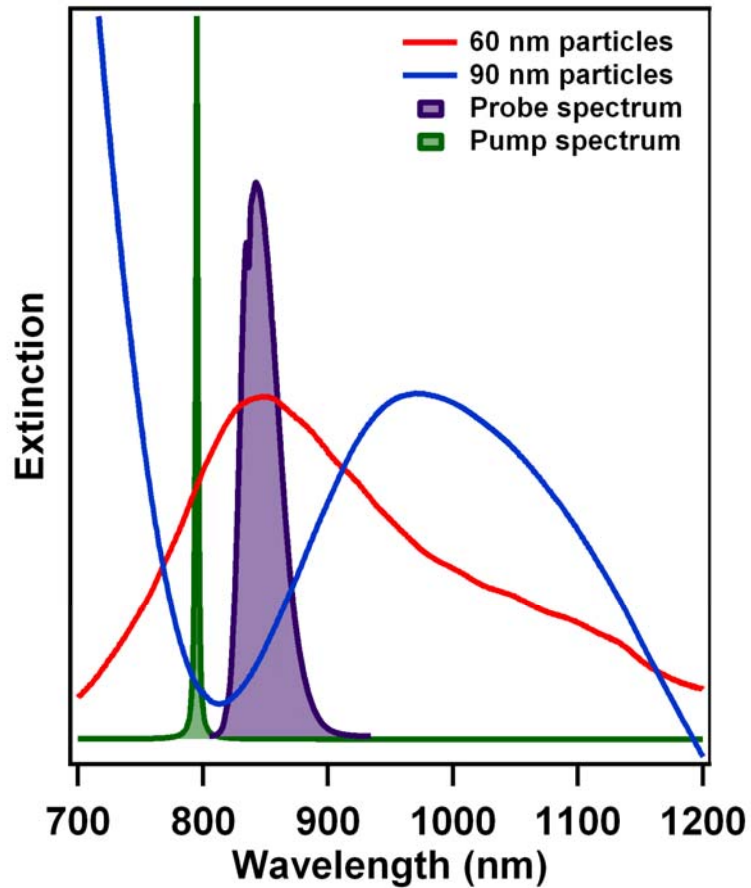


SERS411



SERS481

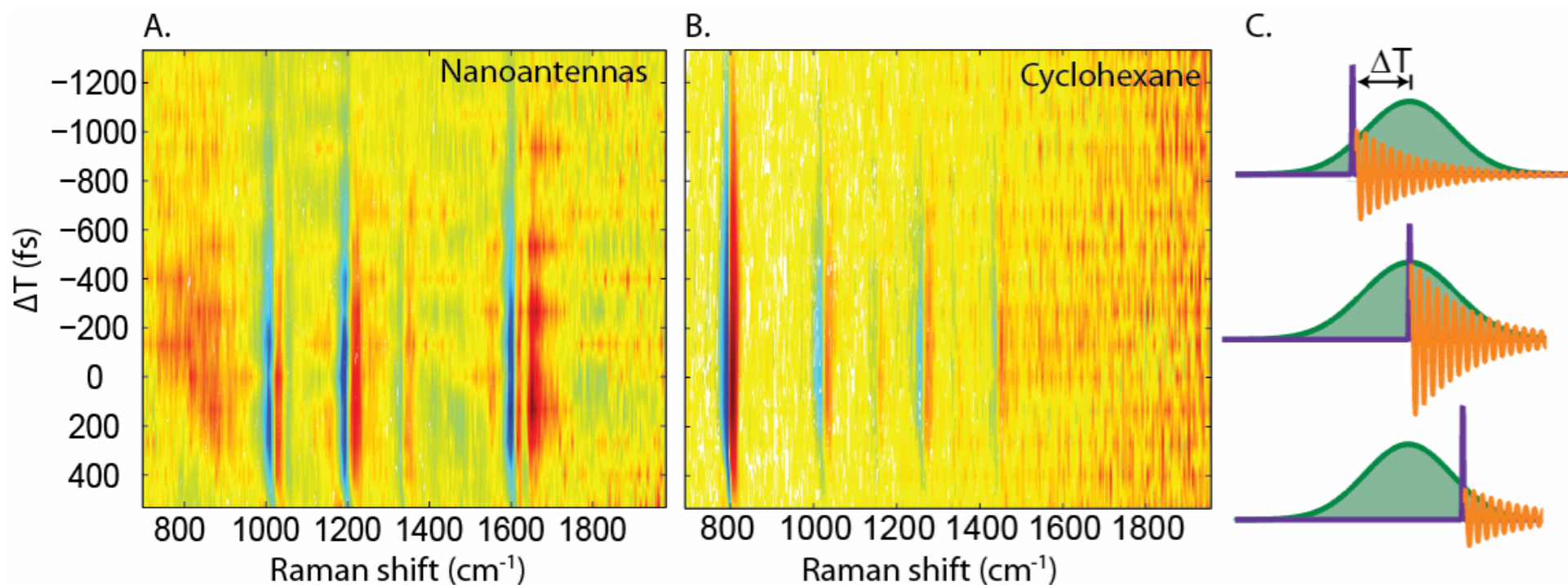
SE-FSRS plasmon dependence



● **Shifting the plasmon resonance switches the dispersion of the Fano-like lineshapes!**

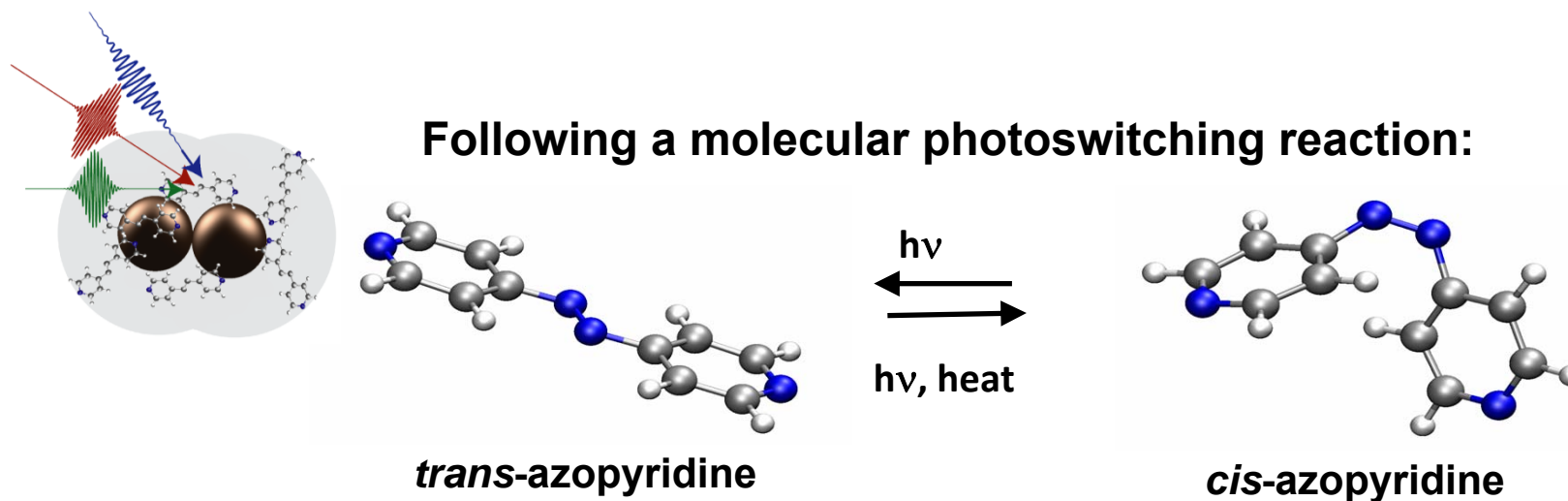
SE-FSRS: Dependence on pump-probe time delay

What is the dephasing of a vibrational coherence when strongly coupled to a nearby plasmon?

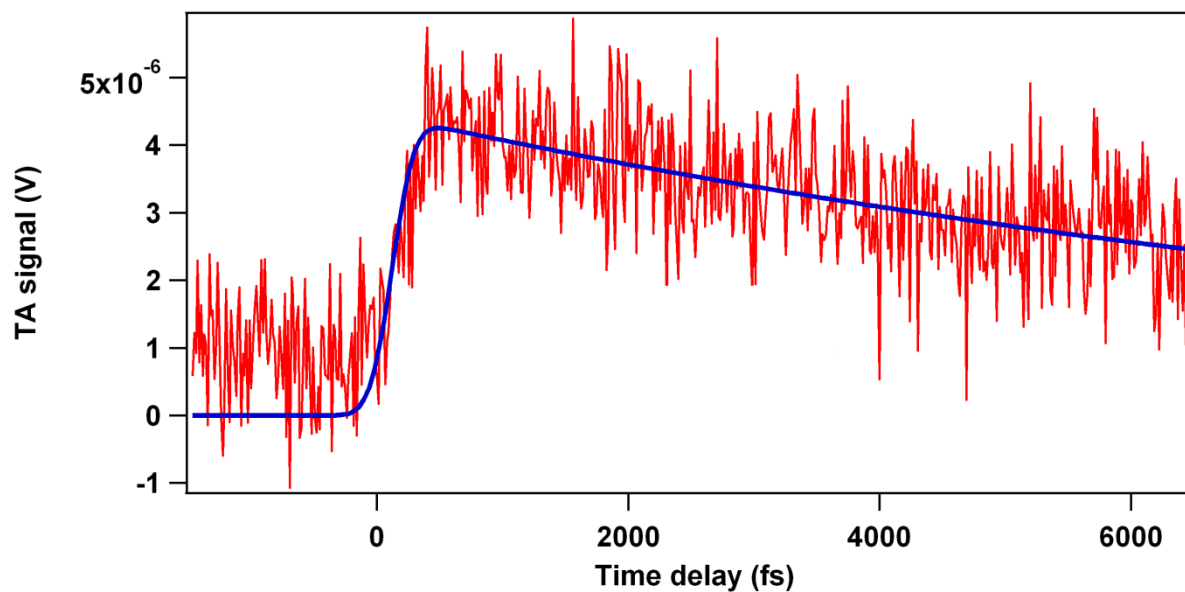


- There appears to be no additional truncation of vibrational coherence!
- Does the plasmon promote existence of long-lived coherences?

Excited State SE-FSRS: Photochemistry

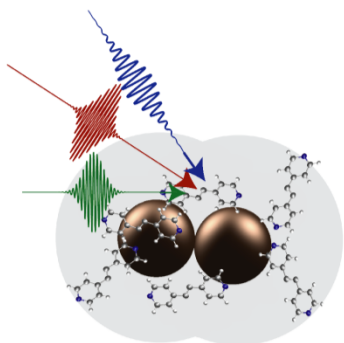


Transient response of nanoantennas + photoresponsive molecules:



R. R. Frontiera, N. L. Gruenke, and R. P. Van Duyne, in preparation (2014)

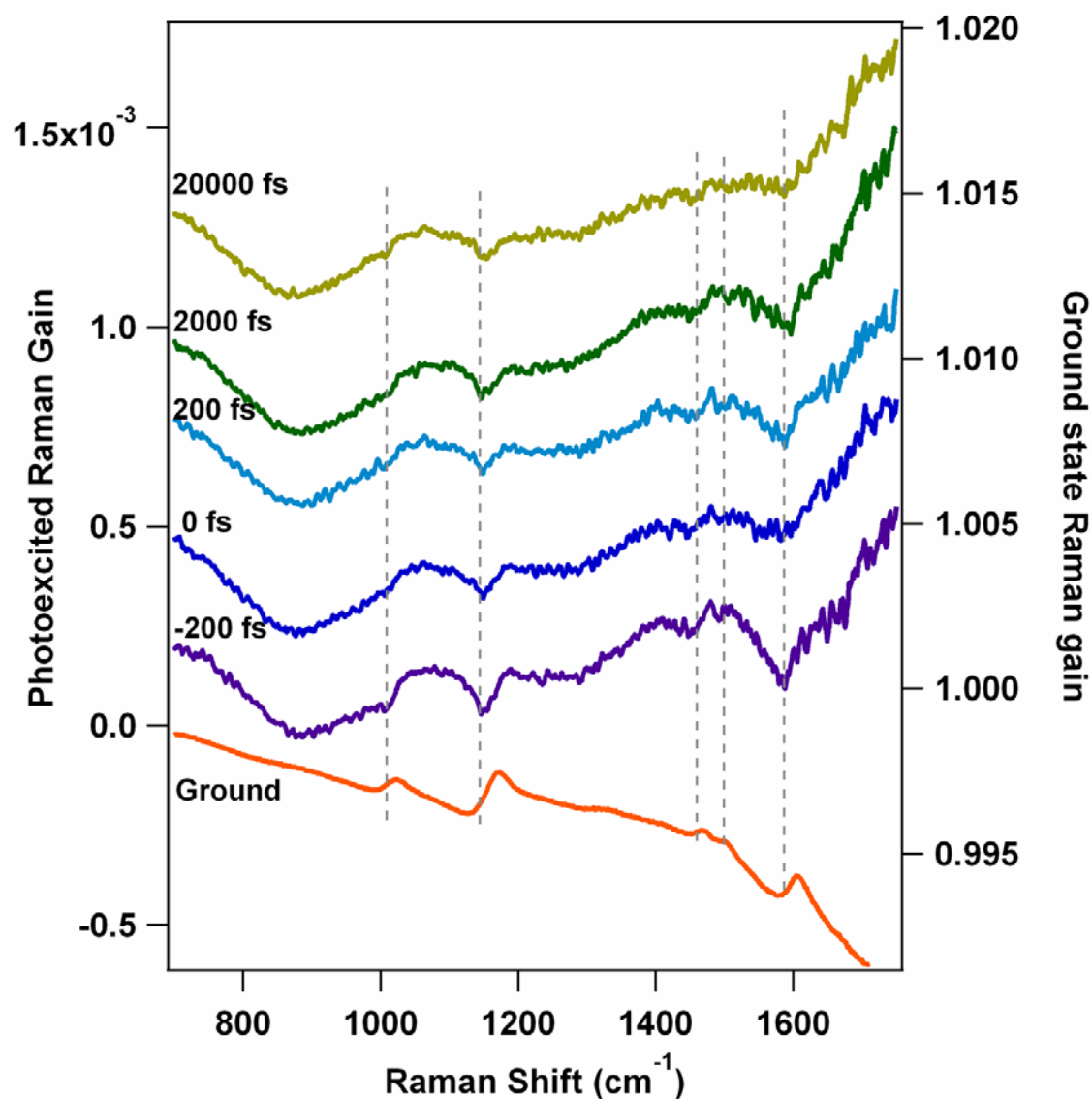
Excited State SE-FSRS: Photochemistry



-Immediate depletion
of ground state signals

-Slow ground state
recovery

-Transient saturation of
plasmon?



Conclusions: SE-FSRS

- First demonstration of SE-FSRS
- EF SE-FSRS $\sim 10^4 - 10^6$
- S/N ~ 50 in 300 s
~ 100 μW average power
- Dispersive lineshapes
Excitation of LSPR produces long-lived vibrational coherences in the adsorbate
- Time-resolved SE-FSRS can now be rationally attempted
Ultrafast dynamics of plasmonic materials

Acknowledgements: SE-FSRS

Van Duyne Group (Summer 2013)



**Bogdan
Negru**

**Natalie
Gruenke**

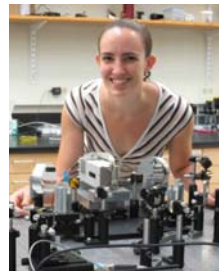
**Mike
McAnally**

**Emily
Sprague**

**Anne-Isabelle
Henry**



Renee Frontiera



Lauren Buchanan



George Schatz

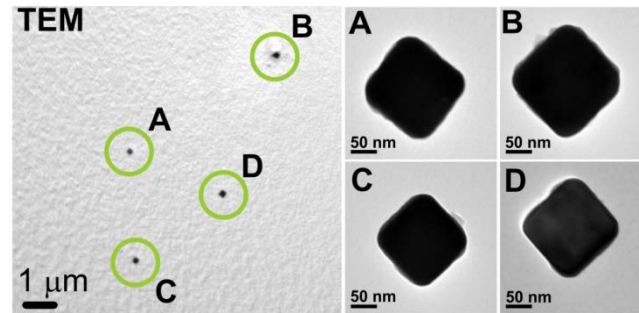
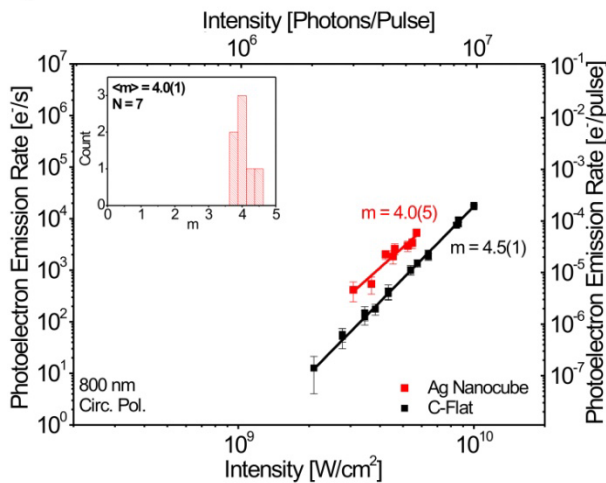
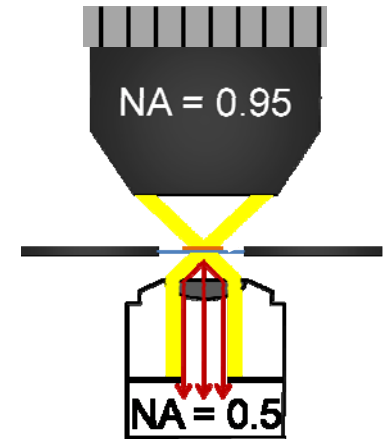
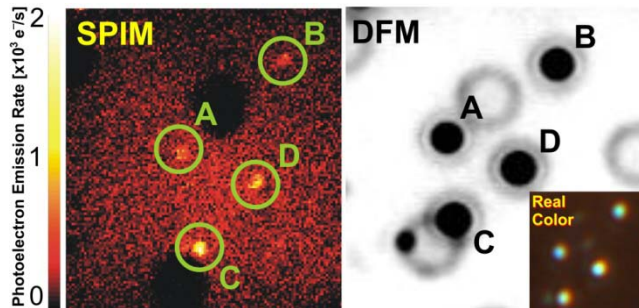
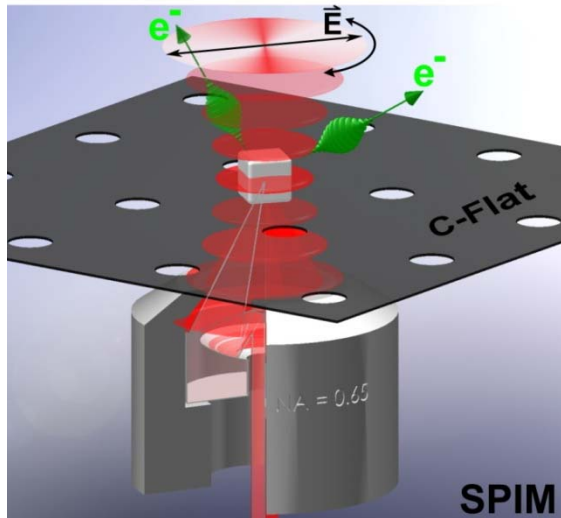


Scanning Photoionization Microscopy

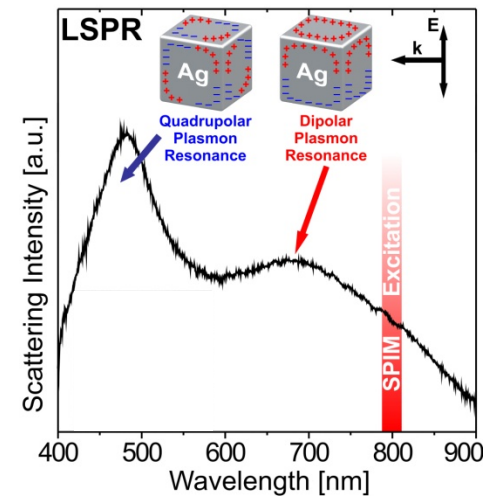
Scanning Photoionization Microscopy (SPIM)

SPIM = 4-photon photoemission
 $\lambda = 800 \text{ nm}$

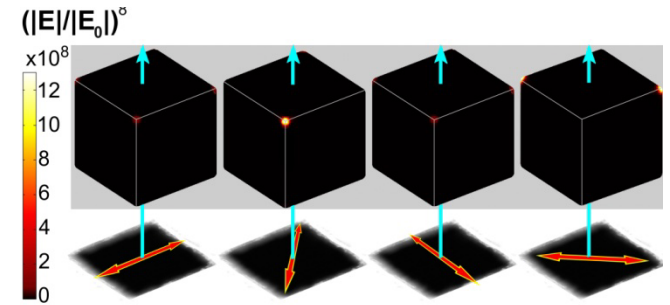
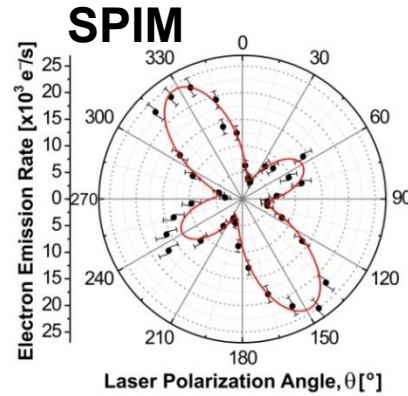
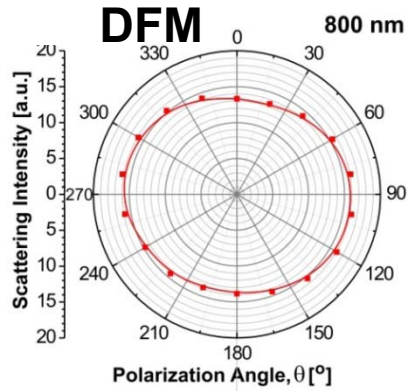
Dark field scattering:
 LSPR information



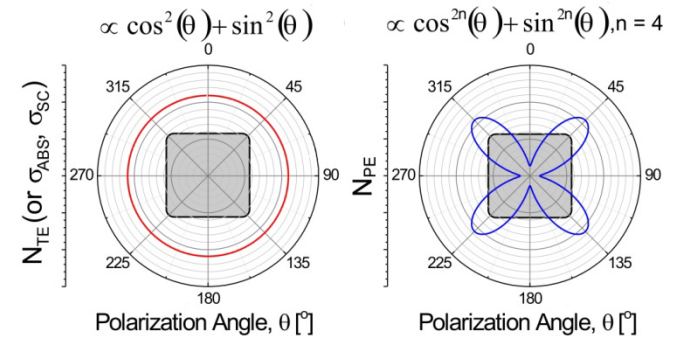
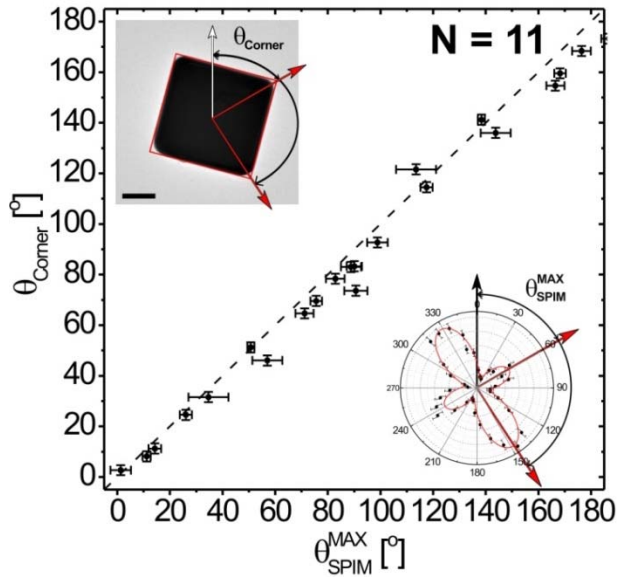
TEM:
 particle size, shape, orientation



Scanning Photoionization Microscopy (SPIM)



No polarization in DFM: symmetry
 Polarization-dependent photoelectron emission,
 aligned with corners



Emission depends on field:
 coherent multiphoton
 photoelectron emission
 NOT thermionic

Acknowledgements: SPIM

Van Duyne Group (Summer 2011)



Emilie Ringe



Younan Xia (Gattech)



Laurence Marks



David Nesbitt (UC Boulder)



RVD Giving Video Lecture
9:45 AM – 11:00 AM
Monday, June 09, 2014