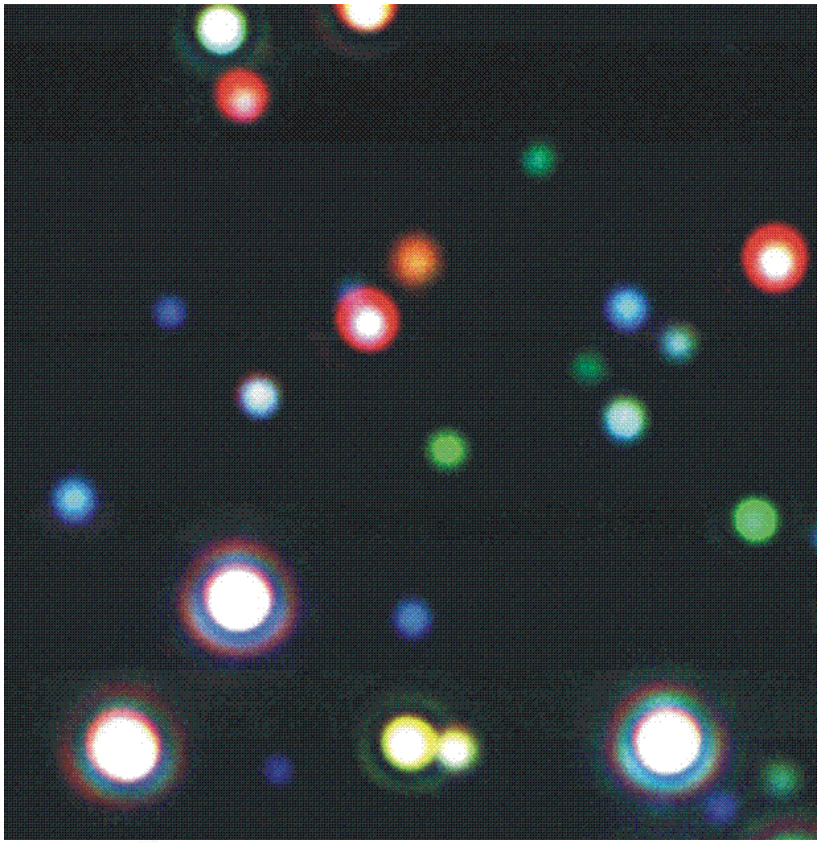
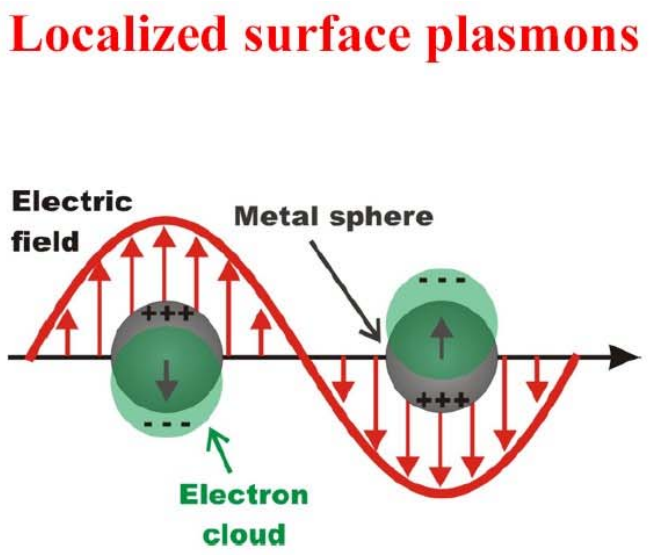
Research Seminar for New Graduate Students

Ryan 4003, 10:45 - 11:00 AM Tuesday September 15, 2015

Molecular Plasmonics: Nanoscale Spectroscopy & Sensing

Richard P. Van Duyne



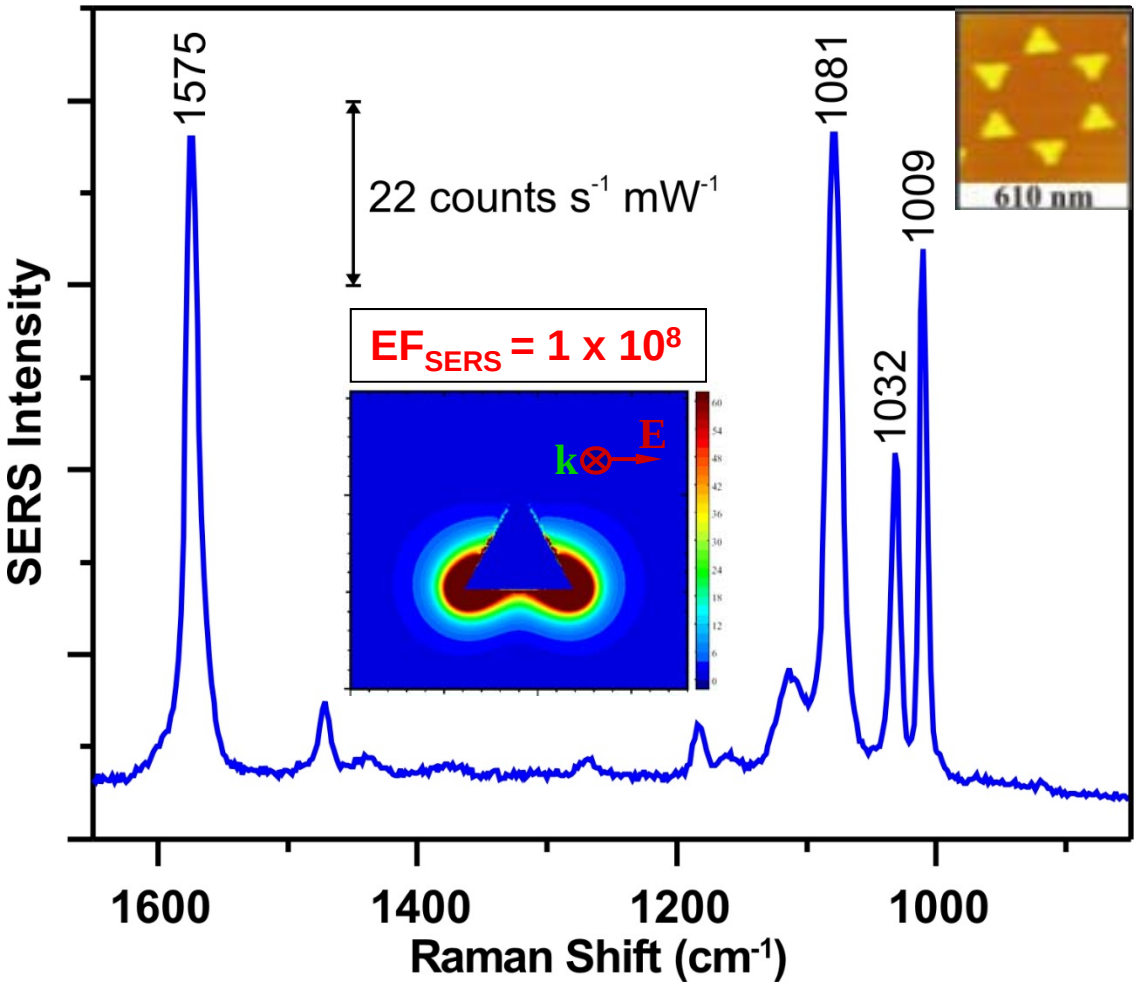


- Particle size << λ
- Plasmon is localized
- $l_d \sim 5$ nm

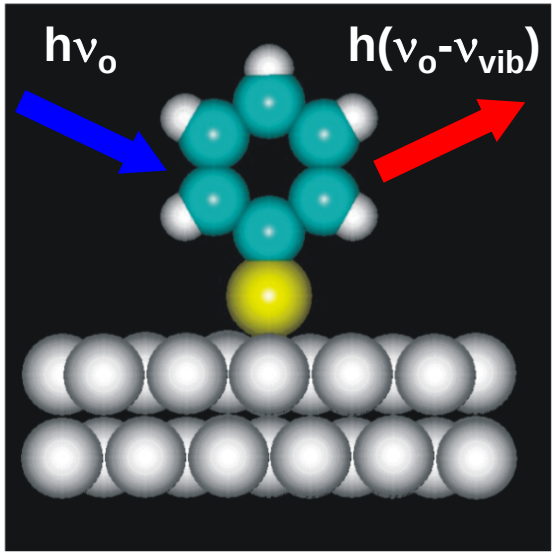
Departments of Chemistry and Biomedical Engineering & The Applied Physics Program

TECH K124, (847)-491-3561, vanduyne@northwestern.edu

Surface Enhanced Raman Spectroscopy (SERS)



Benzenethiol



What is the Mechanism?

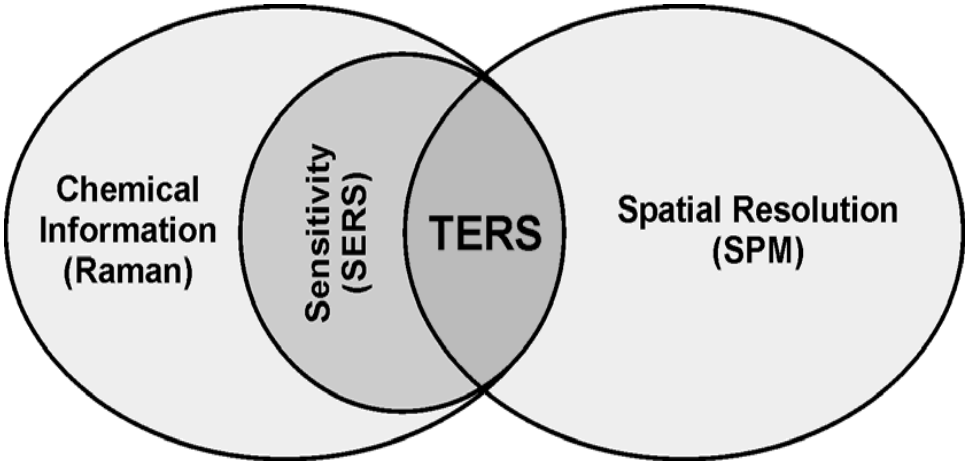
$$\vec{\mu} = \hat{\alpha}\vec{E}$$

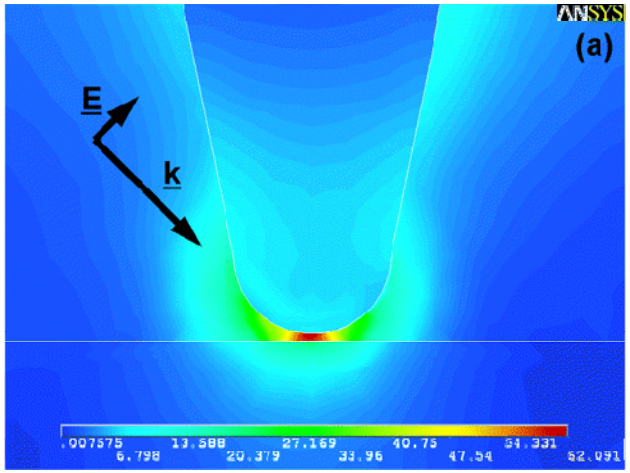
$EF_{CHEM} \sim 10^1$ $EF_{EM} \sim 10^8$

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)

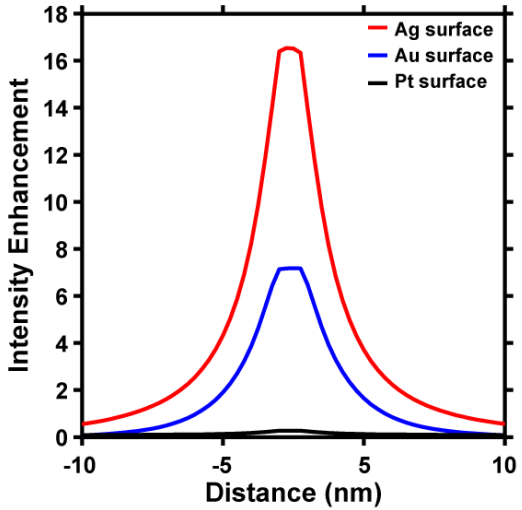
Tip-Enhanced Raman Spectroscopy (TERS)





$$EF_{TERS} = \frac{I_{engaged}}{I_{retracted}} \times \frac{r_{focus}^2}{r_{tip}^2}$$

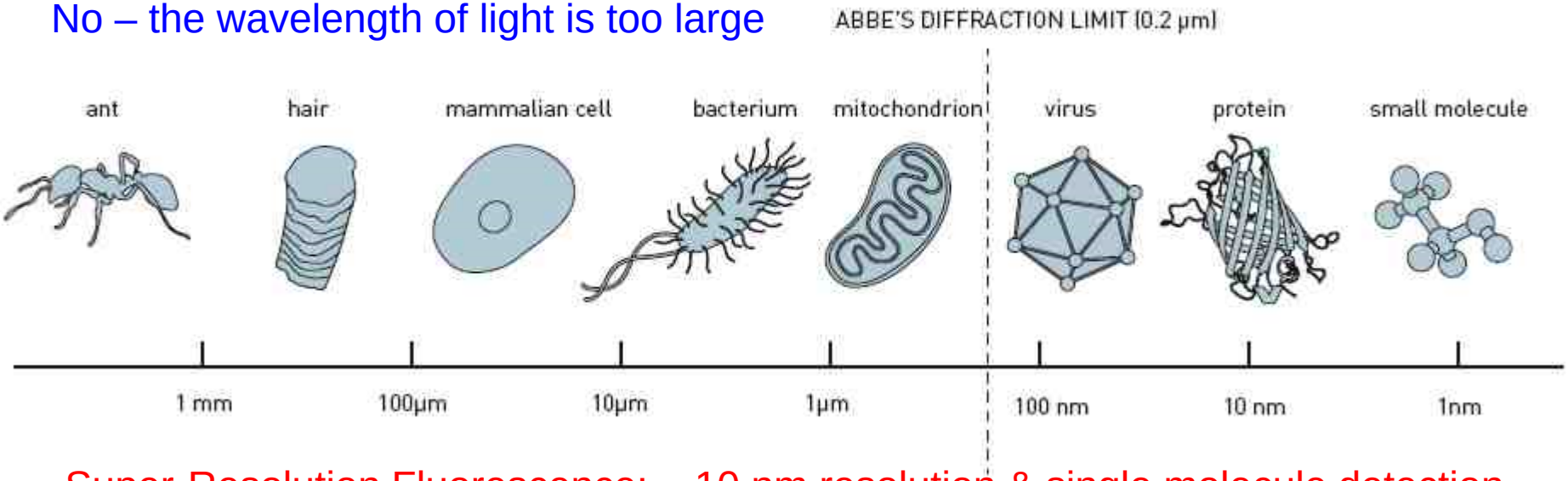
$$EF_{TERS} = 10^4\text{-}10^8$$



TERS: ~ 1-2 nm resolution & single molecule identification

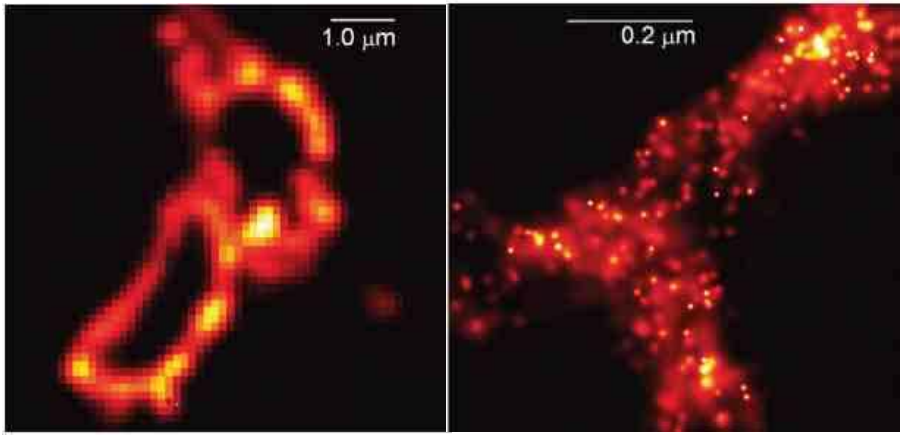
Nanoscale Imaging with Light

No – the wavelength of light is too large



Super-Resolution Fluorescence: ~ 10 nm resolution & single molecule detection

2014 Nobel Prize in Chemistry
E. Betzig, S. Hell, W. E. Moerner



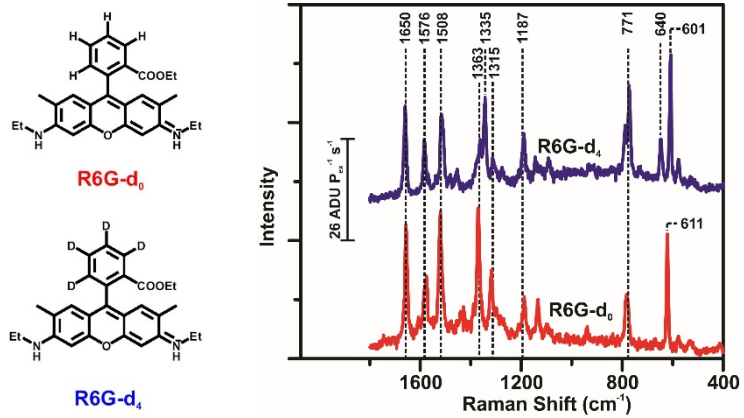
Conventional Fluorescence Microscopy

Super-Resolution Fluorescence Microscopy

Van Duyne Group Research Portfolio #1

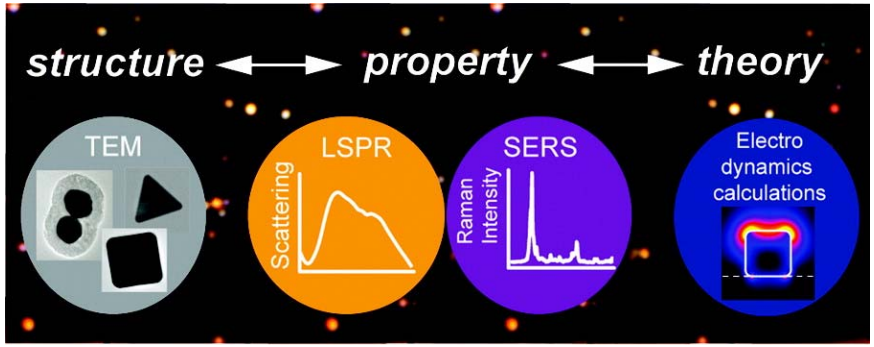
Grand Challenge: Control light on the 1-100 nm Length Scale

Single Molecule Spectroscopy



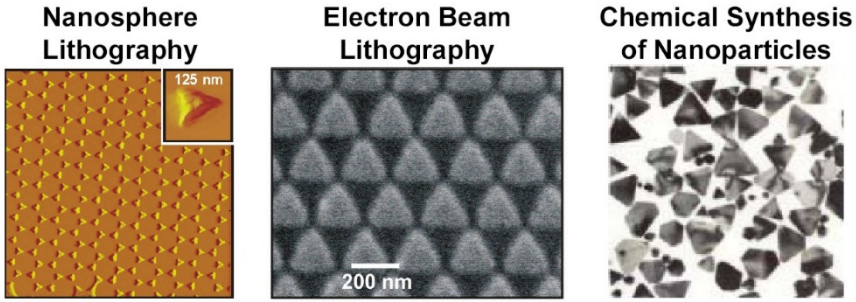
JACS, 129, 16249-16256 (2007)

Single Particle Spectroscopy



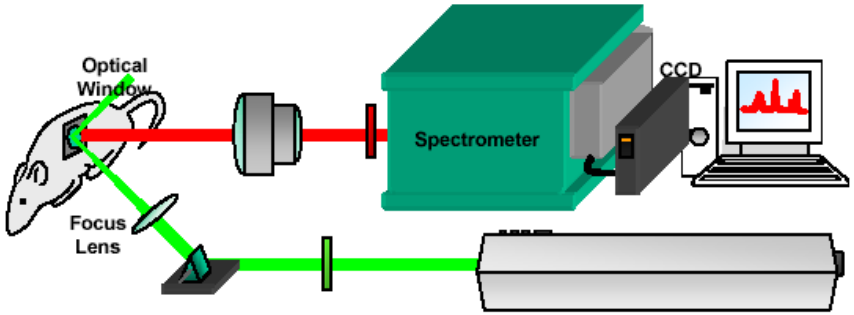
JPCC, 116, 393-403 (2012)

Plasmonic Materials



MRS Bulletin, 30, 368 (2005)

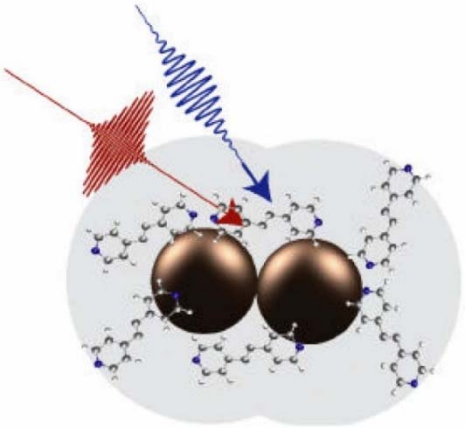
Plasmonic Biosensors

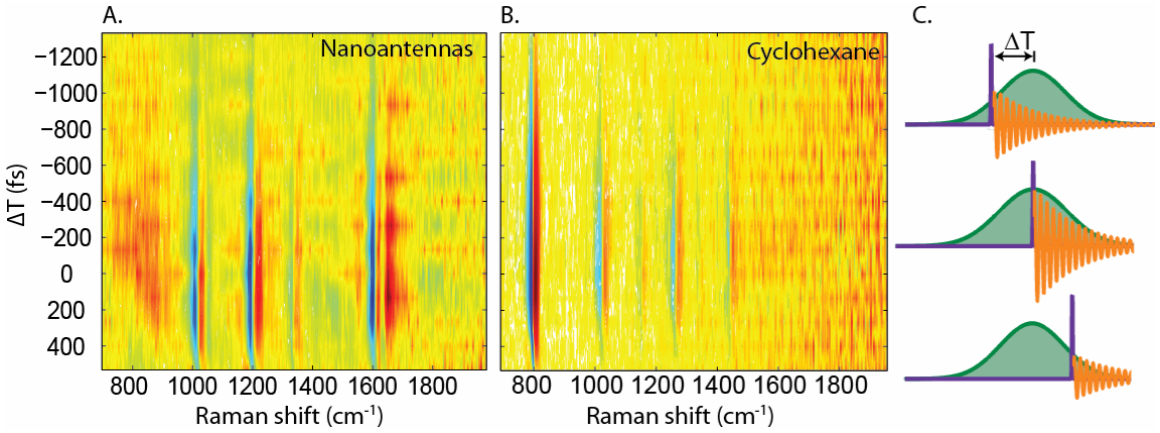


Nature Materials, 7, 442 - 453 (2008)

Van Duyne Group Research Portfolio #2

Surface Enhanced Femtosecond Stimulated Raman Spectroscopy

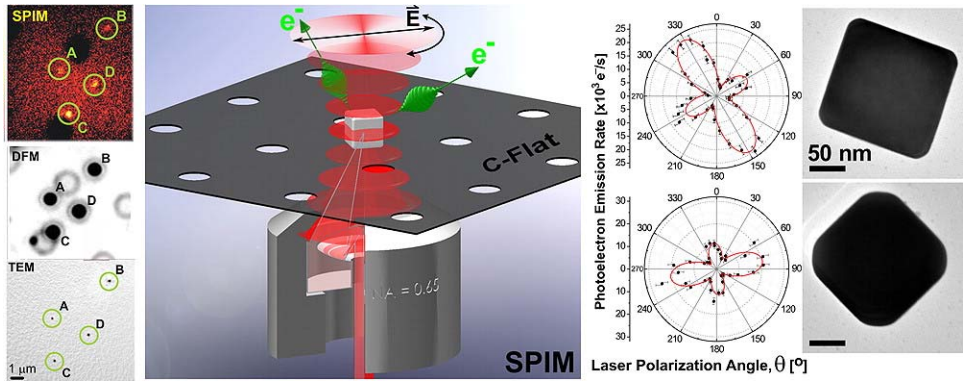


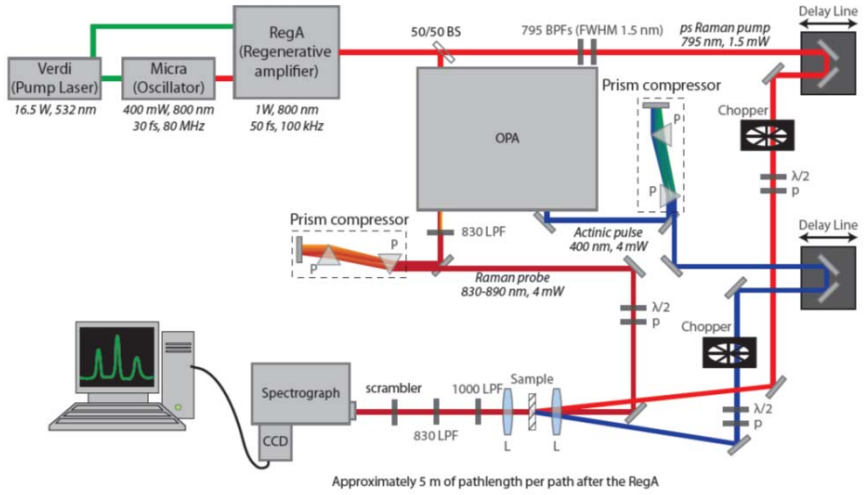


JPCL, 2, 1193-1203 (2011)

Nano. Lett., 12, 5989-5994 (2012)

Ultrafast Photoionization Microscopy



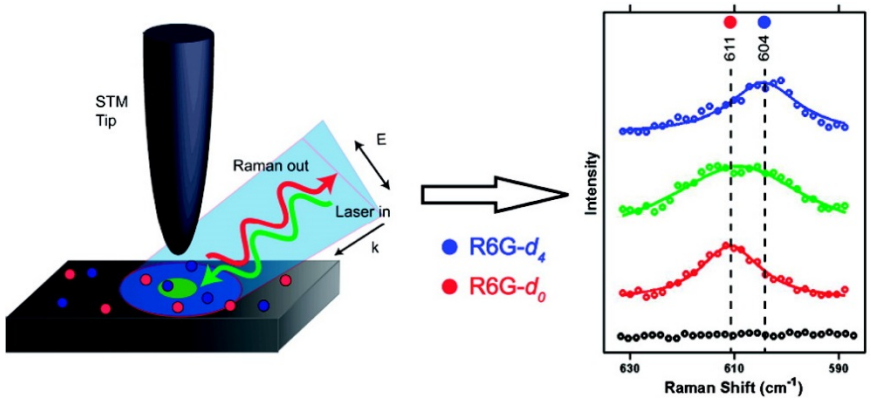


Nano. Lett. 12, 4823-4829 (2012)

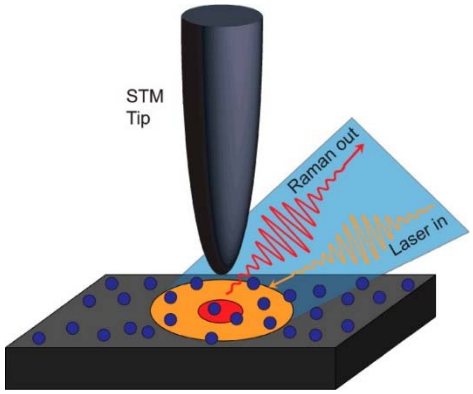
Nano. Lett. Submitted (2015)

Van Duyne Group Research Portfolio #3

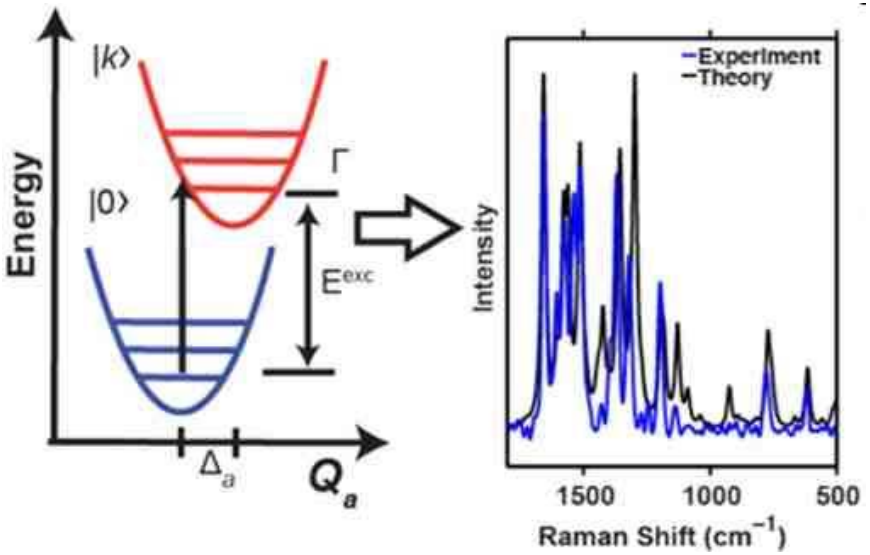
Tip Enhanced Raman Spectroscopy



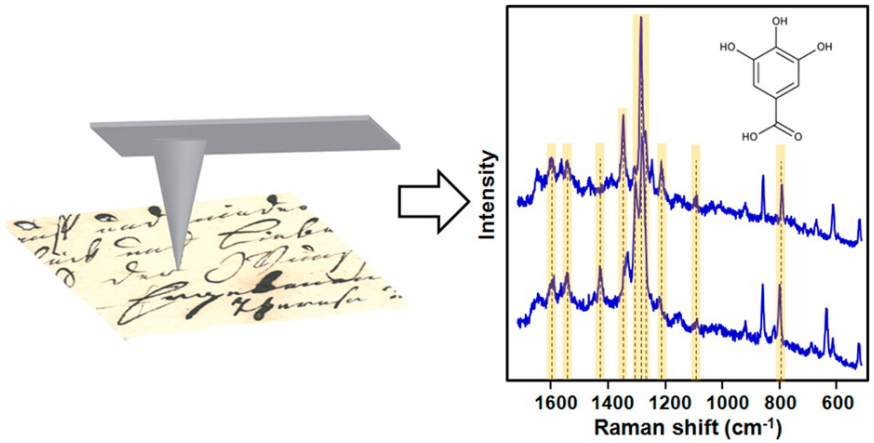
Single Molecule TERS
J. Phys. Chem. C, 116, 478-483 (2012)



Picosecond TERS in Ambient
JPCL, 5, 106-110 (2014)



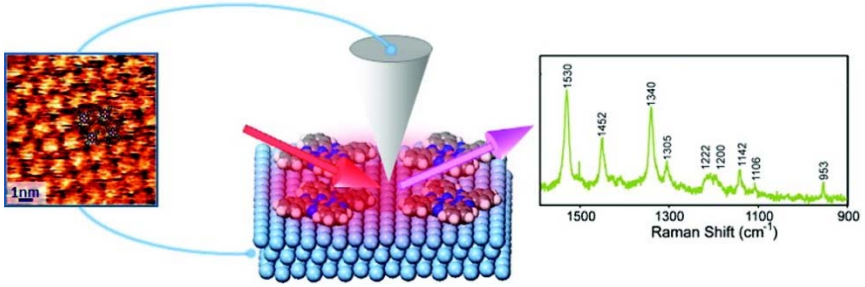
Relative Intensity Fluctuation in SMTERS
JACS, 135, 17187-17192 (2013)



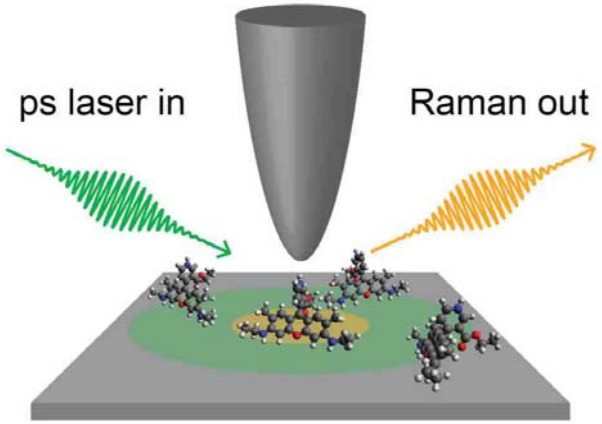
TERS for Identification of Indigo and Iron Gall Ink on Paper
JACS, 136, 8677-8684 (2014)

Van Duyne Group Research Portfolio #3 (cont'd)

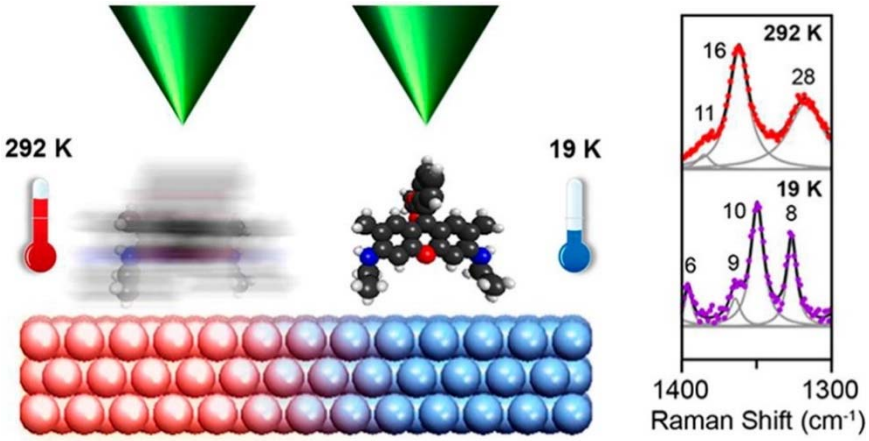
Ultrahigh Vacuum Tip Enhanced Raman Spectroscopy



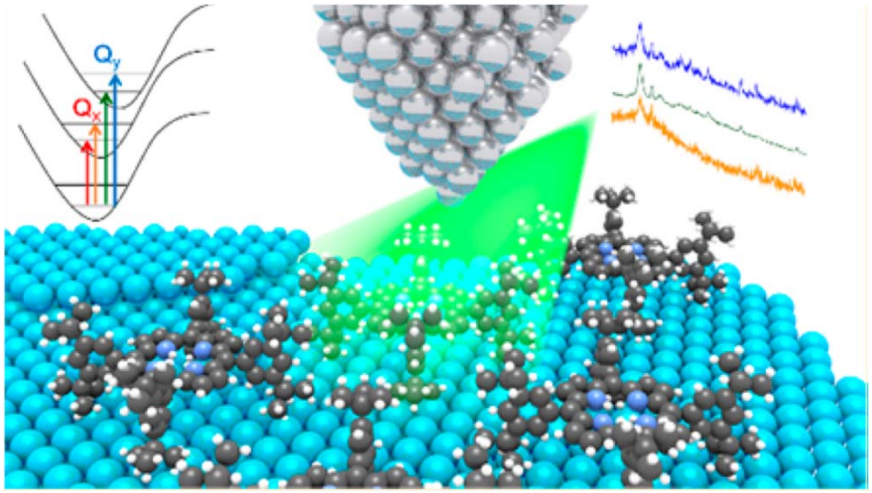
UHV-TERS Combined with Molecular-Resolution STM
Nano Lett.,12, 5061-5067 (2012)



Picosecond TERS in UHV
JPCL, 5, 2657-2661 (2014)



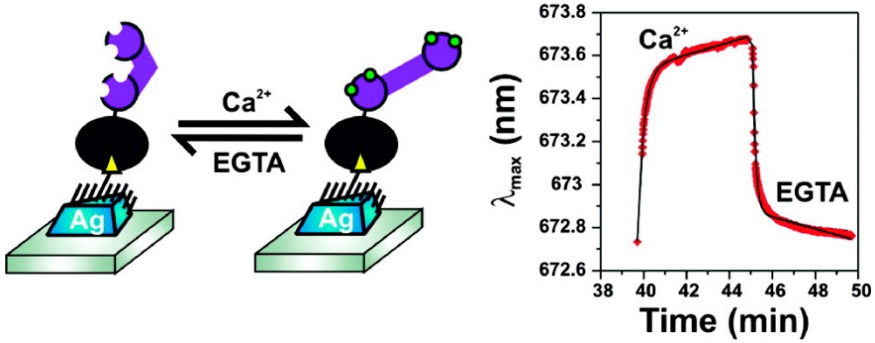
LT(19K)-UHV-TERS
JACS, 136, 3881-3887 (2014)



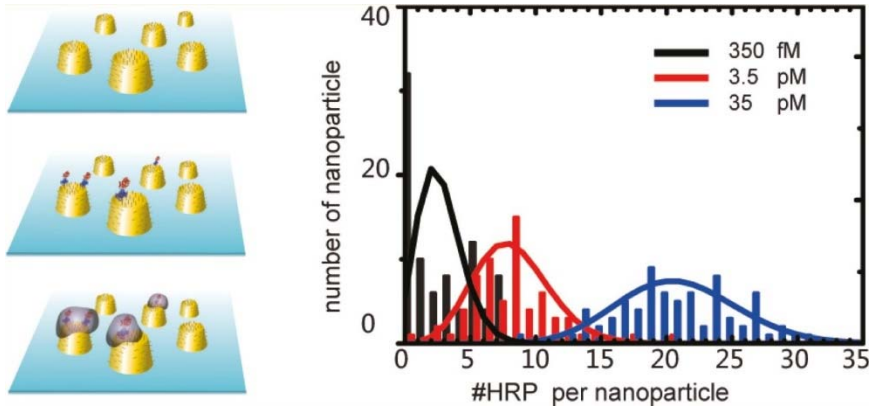
UHV-TERS/TEF of Porphyrin
Nano. Lett., 15, 4114-4120 (2015)

Van Duyne Group Research Portfolio #4

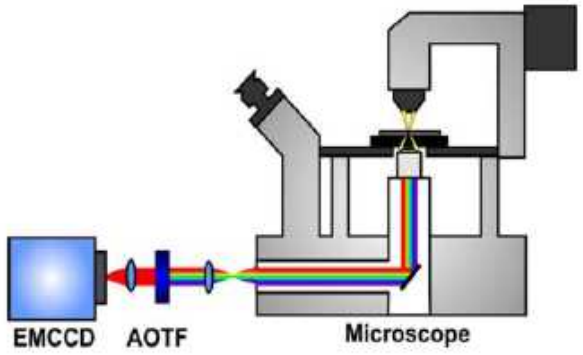
High Resolution Plasmonic Sensors

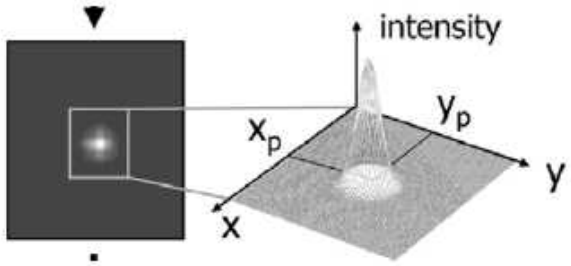


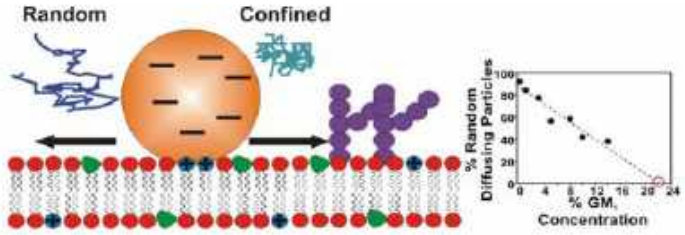
HR-LSPR Sensor: Calmodulin
JACS, 130, 5836-5837 (2008)
Nano Lett,11,1098-1105 (2011)



Single Molecule LSPR
Nano Lett., 11, 1826-1830 (2011)



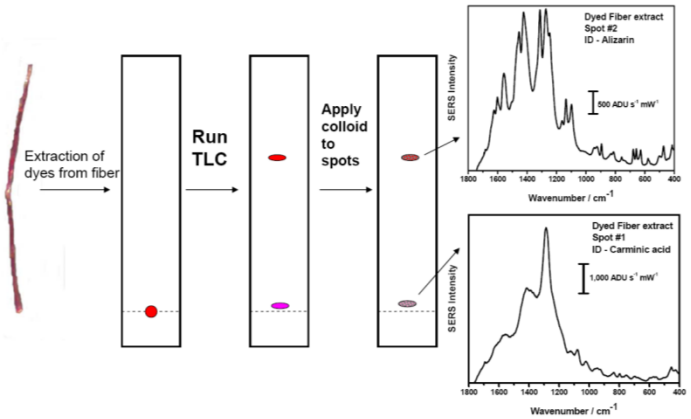




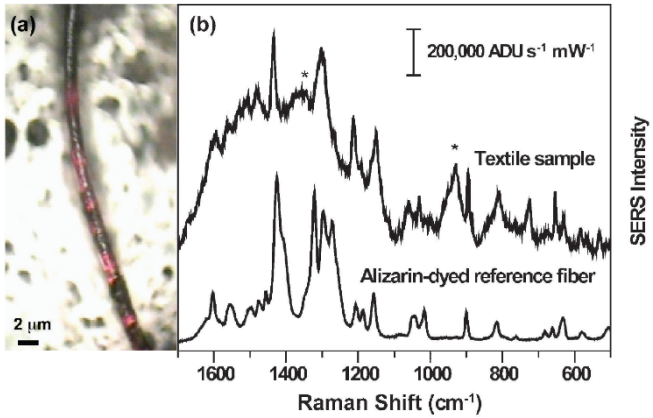
Super-Resolution LSPR Microscopy
JACS, 134, 15832–15839 (2012)

Van Duyne Group Research Portfolio #5

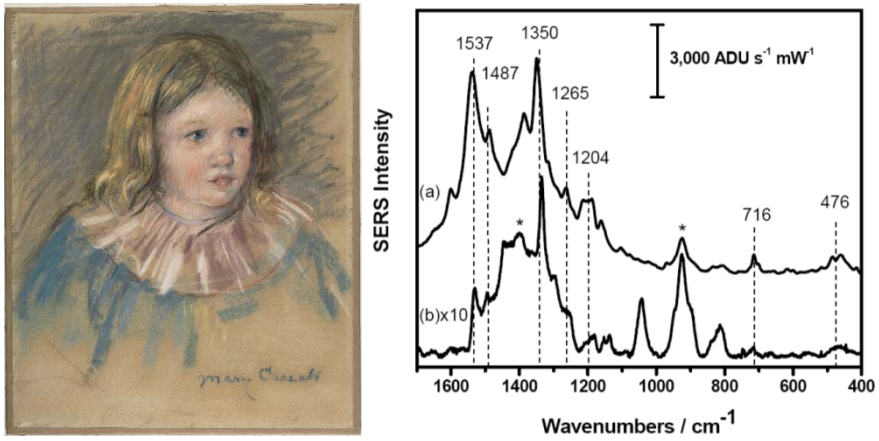
SERS for Art Conservation Science



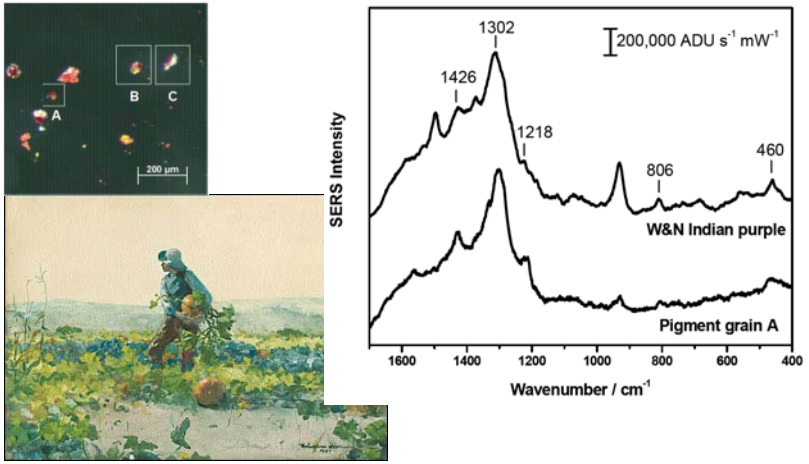
TLC-SERS for Fiber Analysis
Anal. Chem. 81, 3056-3062 (2009)



SERS for Fiber Analysis
PCCP, 11, 7350-7359 (2009)



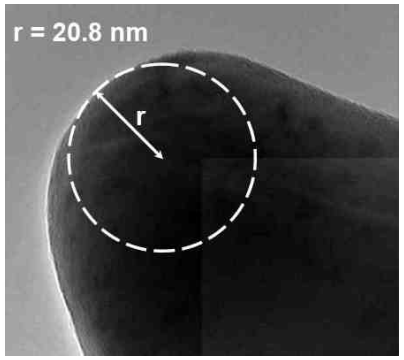
SERS to Identify of Color in Mary Cassatt's Pastels, Anal. Chem. 81, 7443-7447 (2009)

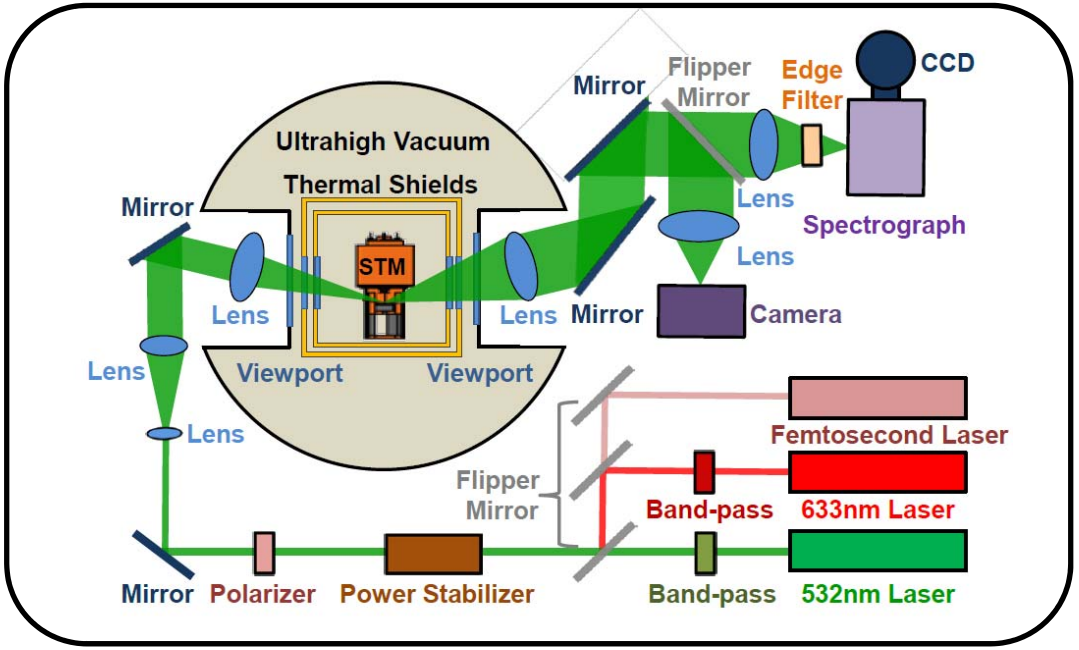


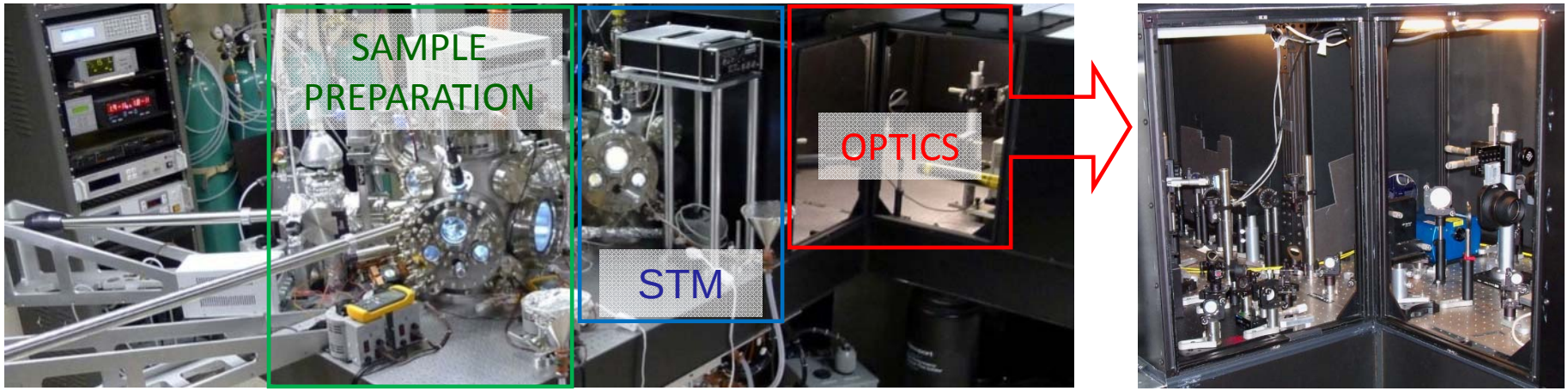
SERS to Identify Color in Winslow Homer's Watercolors, JRS 42, 1305-1310 (2011)

Ultrahigh Vacuum Tip-Enhanced Raman Spectroscopy

- All external optics
- < 2 x 10^{-11} torr
- Cryostat: 7K; 19K



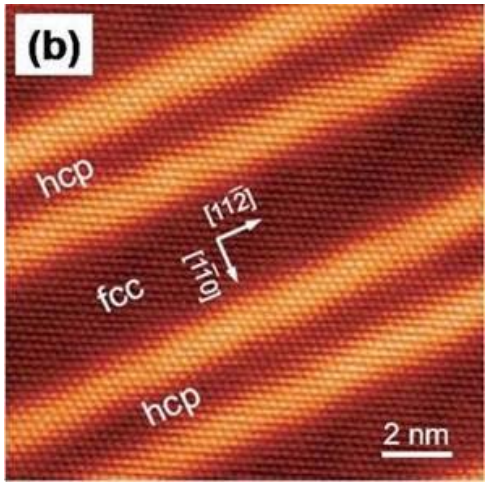




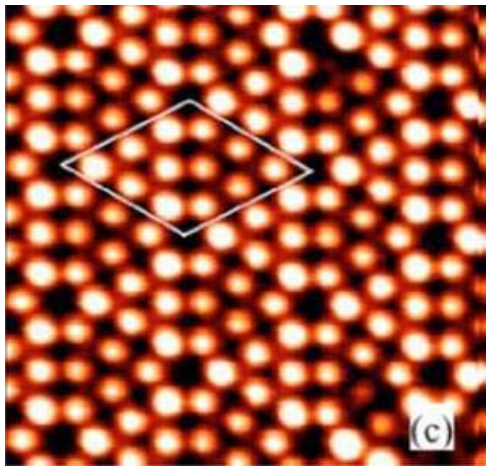
E. Foley, N. Jiang, A. McFarland, J. Klingsporn, M. Sonntag, J. Dieringer, M. Hersam, and RVD, *in preparation* (2015)

LT-UHV-STM: Examples of High Resolution Images

Atomic Resolution

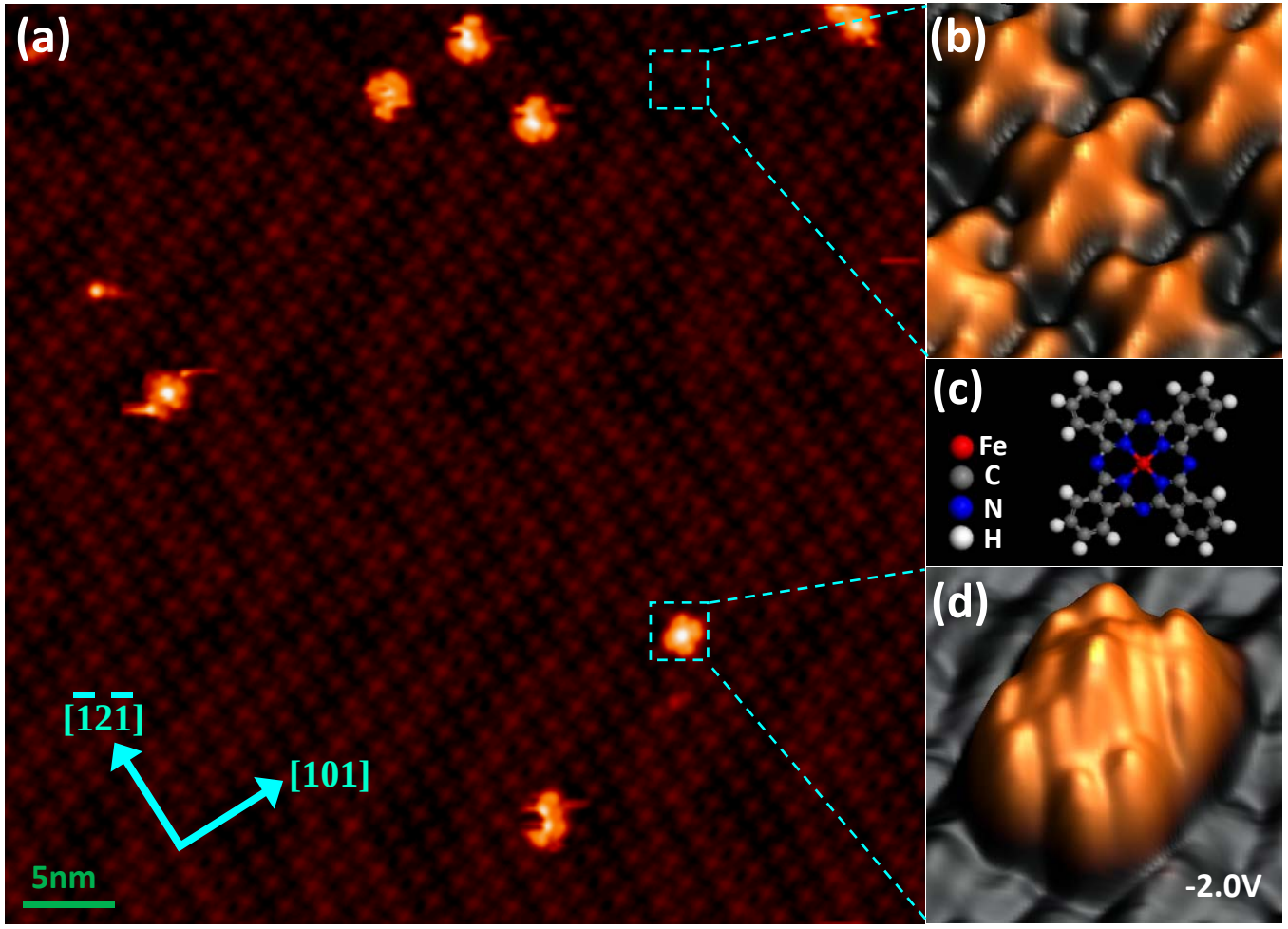


Au(111)



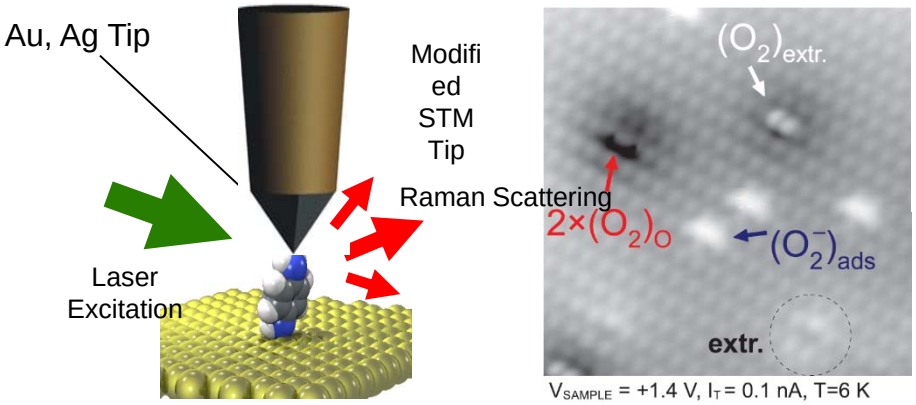
Si(111)

Sub-molecular Resolution

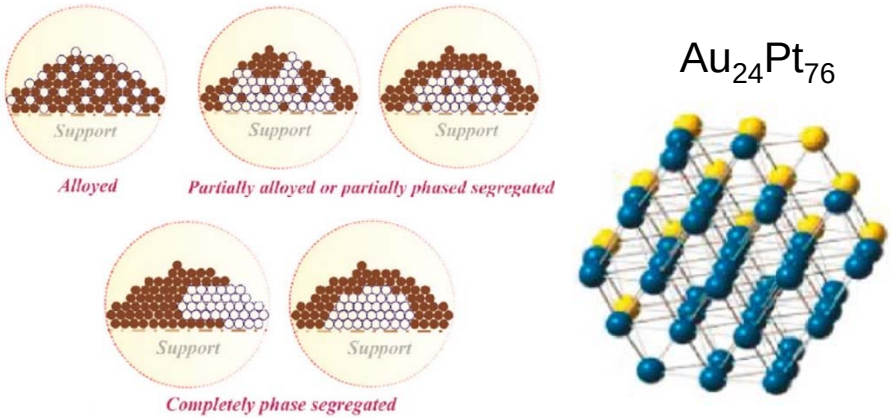


FePc on Au(111)

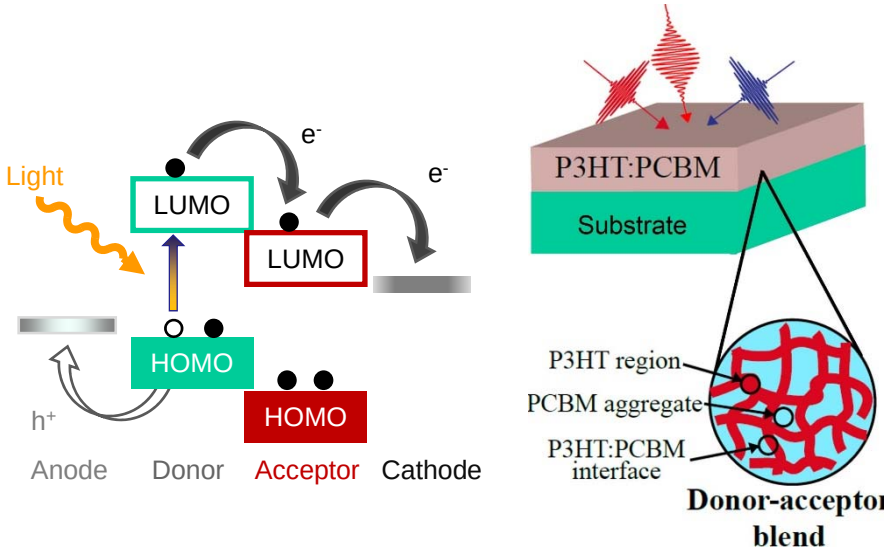
Motivation: Nanoscale Raman Spectroscopy



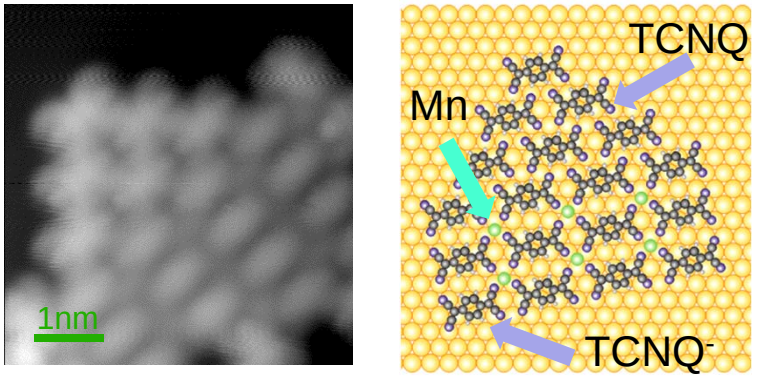
Single Site Catalysis
Science 341, 988 (2013)



Nanocrystalline alloys
Chem. Mater., 22, 4283 (2010)



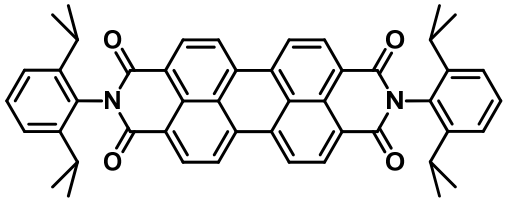
Organic Photovoltaic Materials
Nature, 414, 338 (2001)



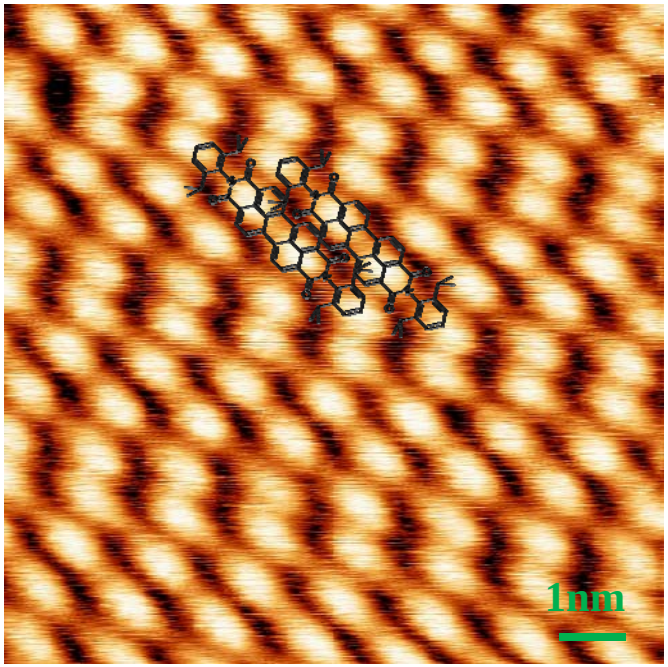
Surface segregation of adsorbates
JPCC 116, 24558 (2012)

RT-UHV-TERS: Ag Tip/PDI/Ag(111)

PDI

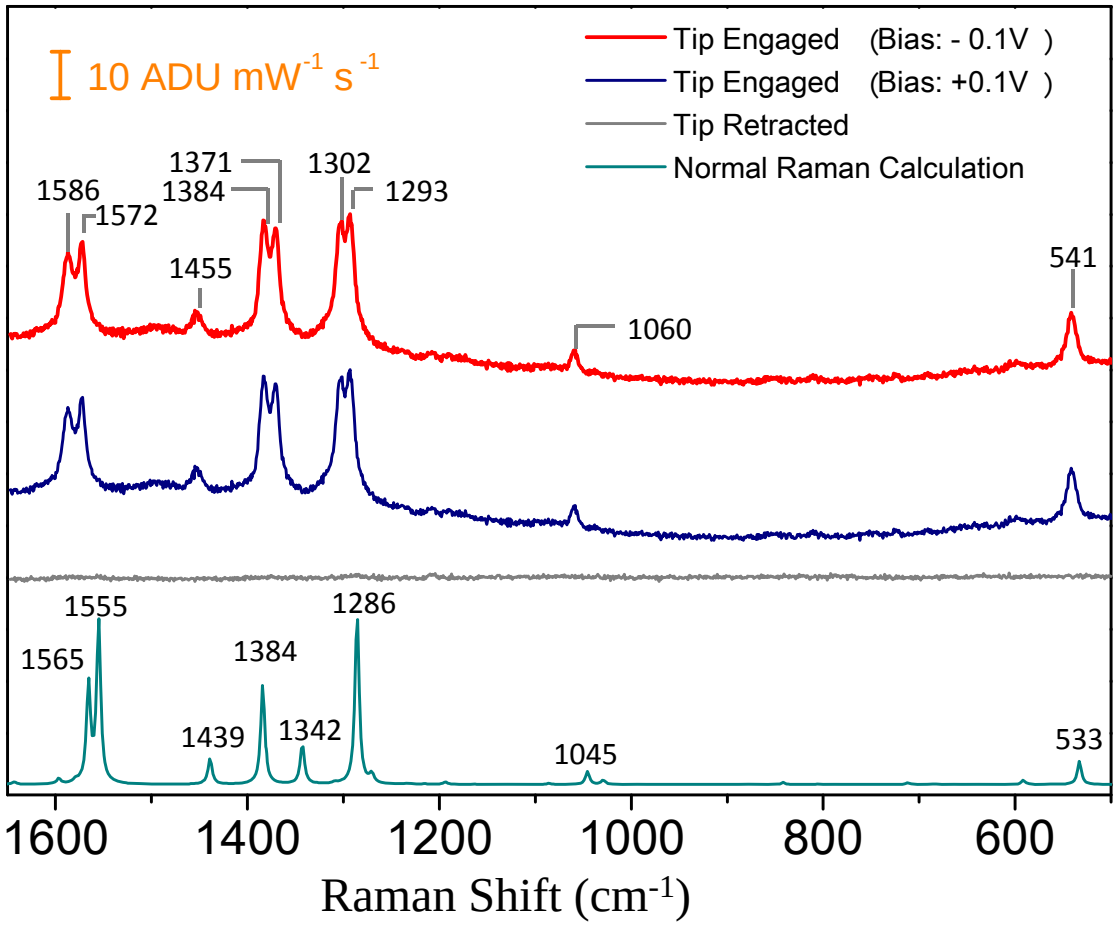


- Sublimed in UHV ~ 0.5 ML
- Electrochemically-etched Ag probe
- λ_{ex} = 532 nm, 0.5 mW, 30 s, 6 accums

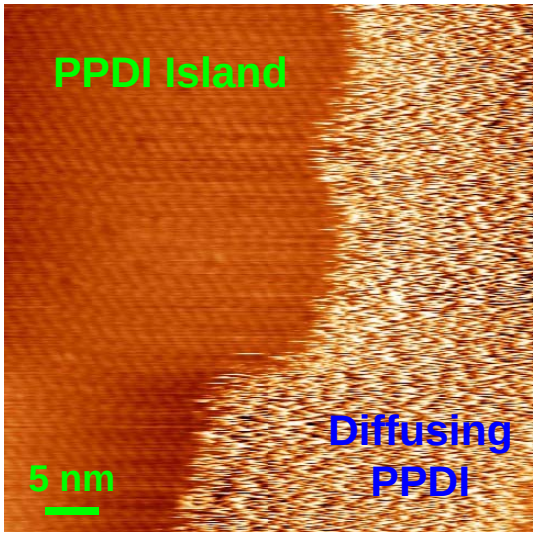


PDI Island

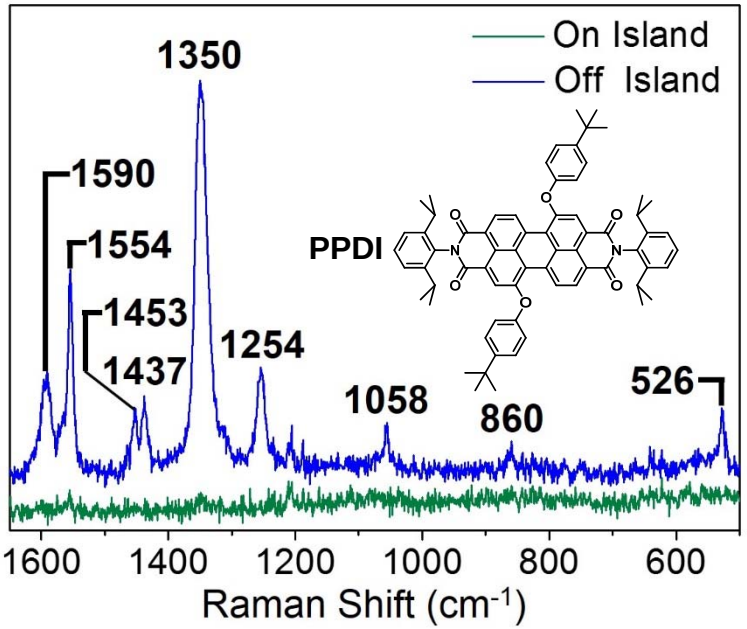
2.5V, 0.1nA, Pt/Ir Tip

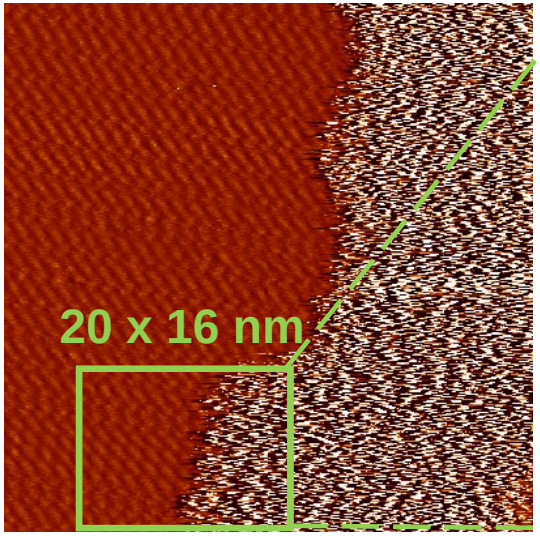


4.3 nm Resolution in RT-UHV-TERS: Ag Tip/PPDI/Ag(100)

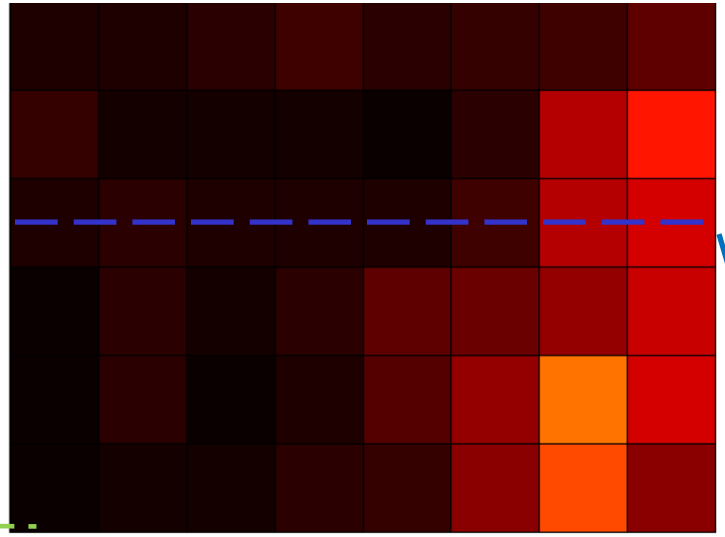


1.0V, 0.3nA, Ag Tip

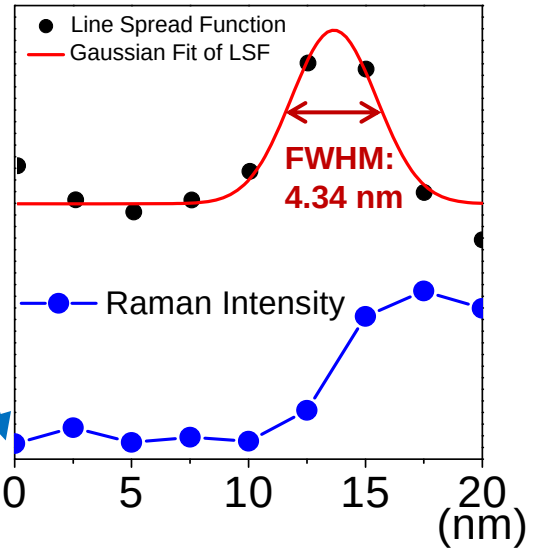




Current Image, Ag Tip



1350 cm^{-1} TERS Map, Ag Tip

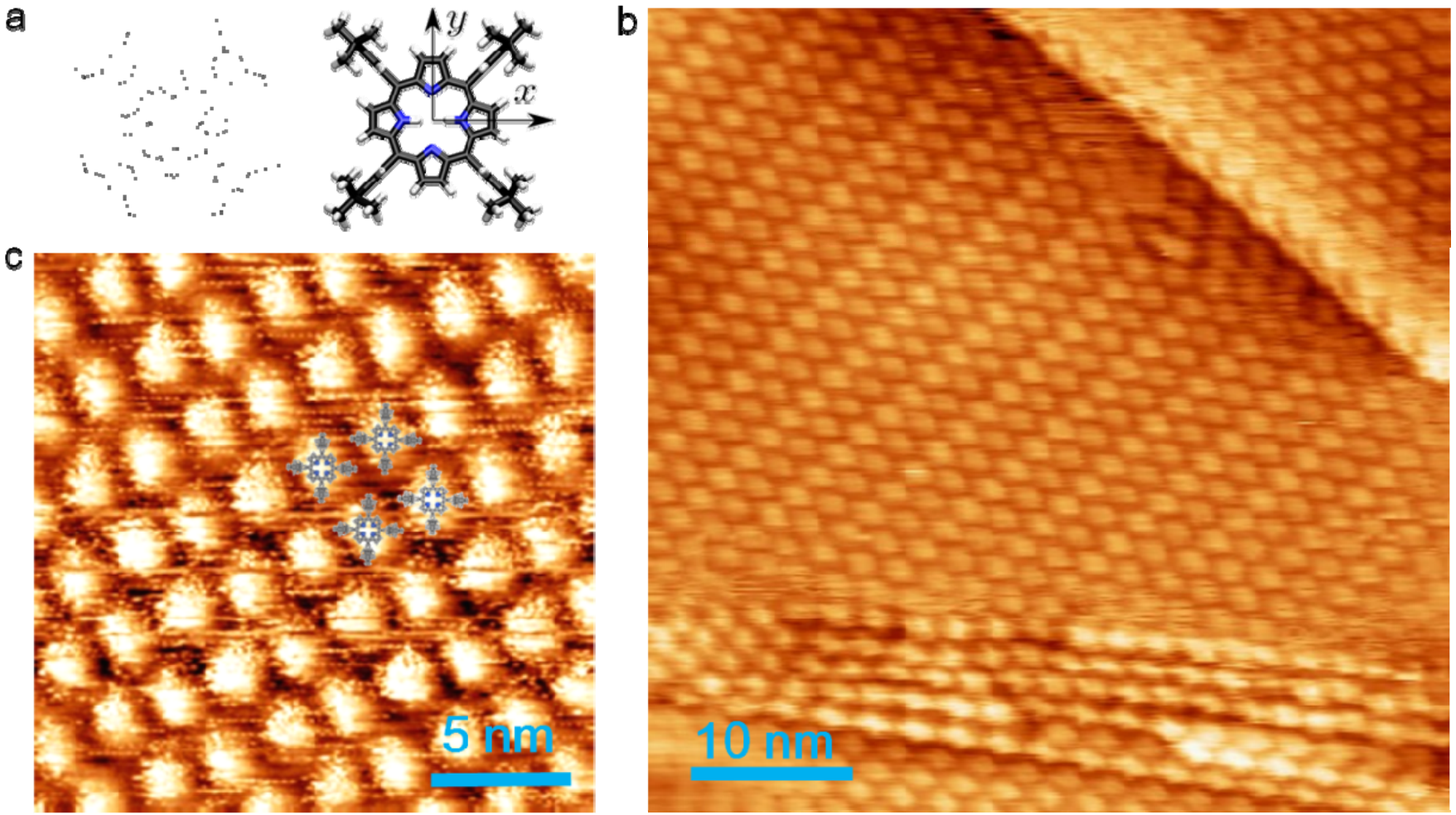


1350 cm^{-1} TERS Line Scan

N. Jiang, N. Chiang, E. Pozzi,, L. Madison, G. Schatz, M. Hersam, and R. P. Van Duyne, submitted (2015)

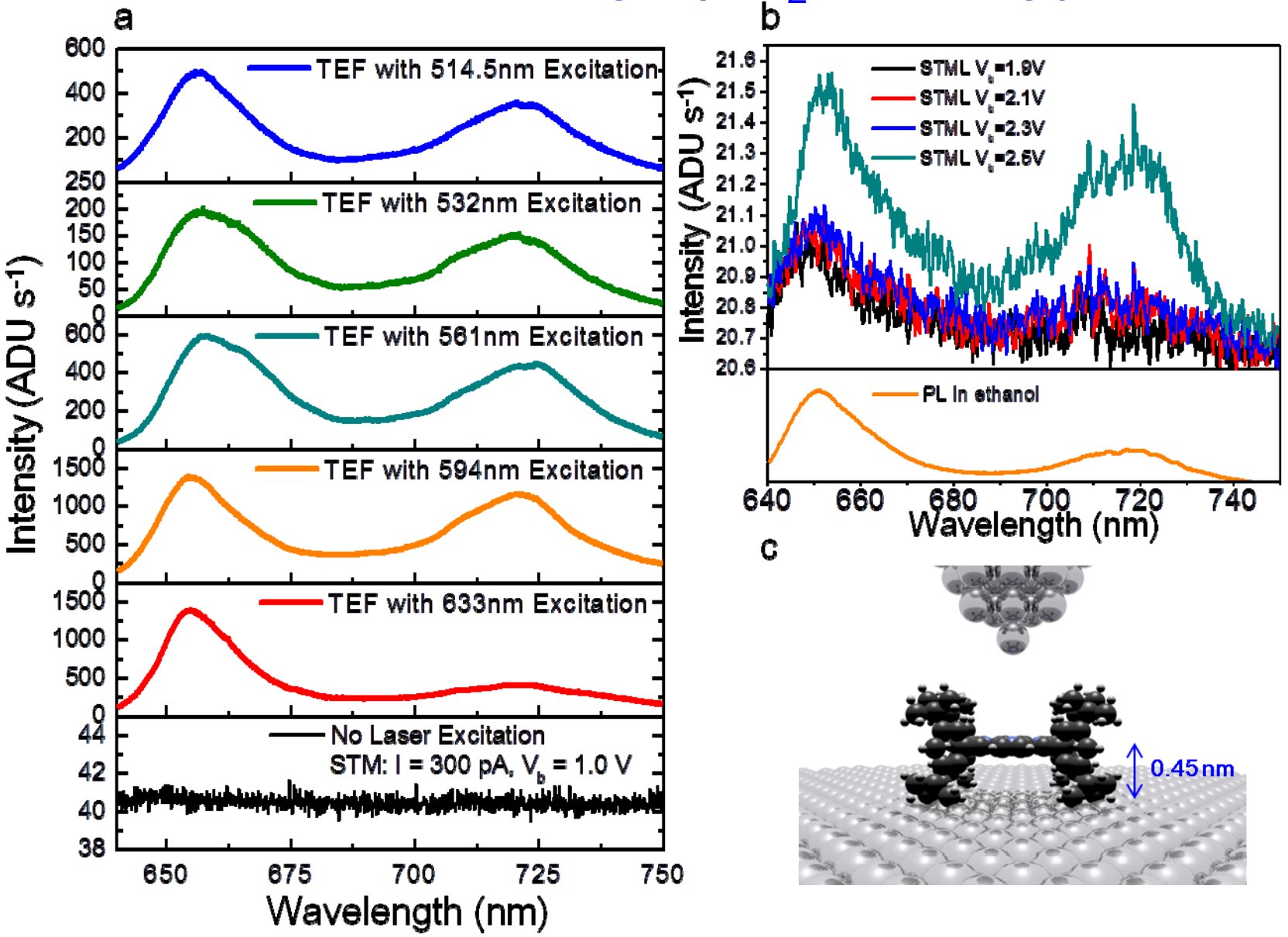
RT-UHV-STM: Ag Tip/H_2TBPP/Ag(111)

H_2TBPP



Chiang, Jiang, Pozzi, Chulhai, Jensen, Hersam, Seideman, & RVD, Nano. Lett., 15, 4114-4120 (2015)

RT-UHV-TEF: Ag Tip/H_2TBPP/Ag(111)



Chiang, Jiang, Pozzi, Chulhai, Jensen, Hersam, Seideman, & RVD, Nano. Lett., 15, 4114-4120 (2015)

Van Duyne Group & Collaborators Summer 2015

2nd Row: Dmitry Kurouski, Naihao Chiang, Sicelo Masango, Emma Vander Ende, Lauren Buchanan, Mike Mattei, Cassie George, Natalie Gruenke, Kathleen Clark, Eric Pozzi, Mike McAnally, Ryan Hackler, Guillaume Goubert

1st Row: Bogdan Negru, Alyssa Zrimsek, Betty Peng, Toby Singer, Anne-Isabelle Henry, RPVD, Xu Chen, Hannah Mayhew, Stephanie Zaleski, Emily Sprague, Fernanda Cardinal

Not shown: Nolan Wong

NU, Chemistry
Harris, Hupp, Mirkin, Mrksich, Ratner, Schatz, Scheidt Seideman, Stair, Weitz

NU, MS&E
Hersam, Marks

UCI, CaSTL
Apkarian, Ho

AIC, Art Conserv.
Casadio

PSU, Chemistry
Jensen

International
Mikael Käll (Chalmers)
Bill Barnes (Exeter)
Besenbacher (Aarhus)
Pileni (Paris VI)
Vallee (Lyon)
Liz-Marzan (Spain)

AFOSR MURI
Bard (UT), White (Utah), Willets (Temple), Zhang (U Wash.)

Van Duyne Group: Placement

Graduate Students

Christy L. Haynes	1998-2003	Ph.D.(2003)	University of Minnesota (Faculty)
Amanda J. Haes	1999-2004	Ph.D.(2003)	University of Iowa (Faculty)
Adam D. McFarland	1999-2004	Ph.D.(2004)	Res. Scientist, Eli Lily
Xiaoyu Zhang	2001-2006	Ph.D.(2006)	Res. Scientist, Eli Lily
Chanda Ranjit Yonzon	2001-2006	Ph.D.(2006)	Res. Scientist, Schering Plough
Alyson V. Whitney	2002-2007	Ph.D.(2007)	Chemist, British Petroleum
Leif J. Sherry	2002-2007	Ph.D.(2007)	Chemistry Instructor, Bossier Parish Community College (Faculty)
Matthew A. Young	2002-2007	Ph.D.(2007)	Hillsdale College (Faculty)
Erin C. McLellan	2002-2007	Ph.D.(2007)	IBM, Albany, NY (Scientist)
Jiha Sung	2002-2007	Ph.D.(2007)	Dongkuk University (Faculty)
Jing Zhao	2003-2008	Ph.D.(2008)	University of Connecticut (Faculty)
David Q. Andrews	2003-2008	Ph.D.(2008)	Senior Scientist, EWG
Jenny Roden	2006-2008	M.S.(2008)	Teacher, Chicago Public Schools
Kevin Biggs	2004-2009	Ph.D.(2009)	Scientist III, US Pharmocpieal
Paige Hall	2005-2010	Ph.D. (2010)	University of Portland (Faculty)
Kathryn Kosuda	2005-2010	Ph.D. (2010)	Vaxess Technologies
Julia Bingham	2005-2010	Ph.D. (2010)	Postdoc, NU (Van Duyne Group)

Van Duyne Group: Placement

Graduate Students #2

Emilie Ringe	**2008-2012**	**Ph.D.(2012)**	**Rice University (Faculty, Mat. Sci.)**
Samuel Kleinman	**2007-2012**	**Ph.D.(2012)**	**Postdoc, NU (Van Duyne Group)**
Matt Sonntag	**2009-2013**	**Ph.D.(2013)**	**Albright College, (Faculty)**
Lauren Kreno	**2009-2013**	**Ph.D.(2013)**	**ExxonMobil (Research Scientist)**
Nathan Greeneltch	**2009-2013**	**Ph.D.(2013)**	**Intel**
Natalie Ray	**2009-2013**	**Ph.D.(2013)**	**British Petroleum (Chemist)**
Ke Ma	**2009-2013**	**Ph.D.(2013)**	**MedSphere Corp. (Biomed. Engineer)**
Jordan Klingsporn	**2010-2014**	**Ph.D.(2014)**	**Intel**
Laura Ruvuna	**2008-2013**	**Ph.D.(2013)**	**Abbott**
Alex Peroff	**2009-2014**	**Ph.D.(2014)**	**Postdoc, SUNY Albany (Lednev Group)**
Natalie Gruenke	**2010-2015**	**Ph.D.(2015)**	**Postdoc, UC Berkeley (Fleming Group)**

Van Duyne Group: Placement

Postdoctoral Fellows

Douglas A. Stuart	**2003-2006**	**University of West Georgia (Faculty)**
Katherine A. Willets	**2005-2007**	**Temple University, Austin (Faculty)**
Paul L. Stiles	**2005-2007**	**ZEV Capital Research (Analysis & Design)**
Rebecca L. Stiles	**2007-2008**	**Avon (Program Manager)**
Jeffrey N. Anker	**2006-2008**	**Clemson University (Faculty)**
Jon P. Camden	**2006-2008**	**University of Tennessee (Faculty)**
Christa Brosseau	**2007-2009**	**Saint Mary's University (Faculty)**
Nilam Shah	**2008-2010**	**Northwestern University (Res. Faculty)**
Kristin Wustholz	**2007-2010**	**College of William & Mary (Faculty)**
Faith Boman	**2009-2011**	**Stepan Company (Research Scientist)**
Julia Ruemelle	**2009-2011**	**Illinois Toolworks (Research Scientist)**
Julia Bingham	**2010-2011**	**St. Xavier College (Faculty)**
Dragos Seghete	**2010-2011**	**Intel (Research Scientist)**
Jon Yuen	**2010-2012**	**Washington University, St. Louis (Postdoc)**
Jon Dieringer	**2008-2011**	**Northwestern University (Senior Res. Assoc.)**

Van Duyne Group: Placement

Postdoctoral Fellows #2

Laura Sagle	**2009-2012**	**University of Cincinnati (Faculty)**
Renee Frontiera	**2010-2013**	**University of Minnesota (Faculty)**
Samuel Kleinman	**2012-2013**	**Research Scientist, (OndaVia, Inc.)**
Bhavya Sharma	**2011-2015**	**University of Tennessee (Faculty)**
Nan Jiang	**2010-2015**	**University of Illinois, Chicago (Faculty)**
Nilam Shah	**2009-2015**	**Lake Forest College (Faculty)**

Van Duyne Group

Group Meetings:

Time: Thursdays 4-5 pm

Place: TECH K140

Open House:

Date: 09/30/15

Time: 4:00 – 6:00 pm

Place: Pancoe 2nd floor (Near Einstein's)

Meet the group, see our work, enjoy free FOOD and DRINKS

Van Duyne Travel Schedule
September - November

09/27/15 – 09/30/15: **SciX**

10/15/15 – 10/17/15: **Univ. Iowa**

10/27/15 – 10/31/15: **Osaka, Japan**

Van Duyne Group Project Summary (2015-2016)

New Students = (1 full, 1 full + 1 joint, or 2 joint)

- **NSF (CHE):** Single Molecule & Ultrafast Spectroscopy
- **NSF (MRSEC):** Plasmonics, Materials for TERS, HRTEM
- **NSF (CCI):** Ultrafast TERS, Ultrafast Raman, electron transfer
- **DOE (SISGR):** Ultrafast TERS, Photocatalysis, Solar (Pending)
- **AFOSR MURI:** Nanoscale Electrochemistry – SECM/TERS
- **AFOSR COE:** Bioprogrammable plasmonic sensors for human performance biomarkers
- **Baxter:** SERS Sensors – Critical Care Analytes
- **NSF (SCIART):** TERS in Art Conservation (Pending)
- **DARPA MakeIt:** Automated Platform for Organic Synthesis (Pending)

Questions