Edgewood Chemical Biological Center

Viewing Surface Enhanced Raman Scattering Through The Lens of Thermodynamics

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US Army Edgewood Chemical Biological Center

U.S. Army Edgewood Chemical Biological Center (ECBC)

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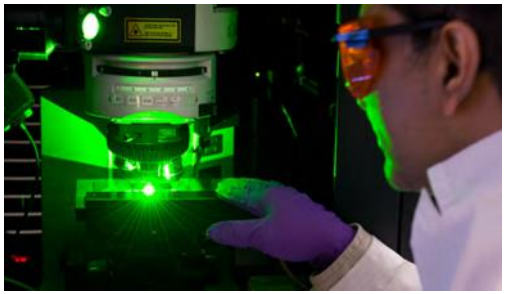
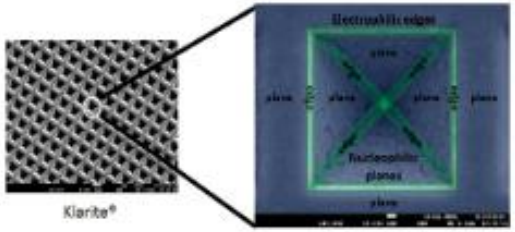
Physical Sciences Division - R&T

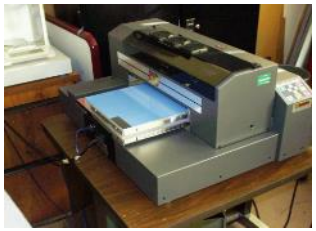
Spectroscopy Branch



Raman Spectroscopy
CBE Signature development
Surface-enhanced Raman
Surface Detection
CB Systems Test and Evaluation

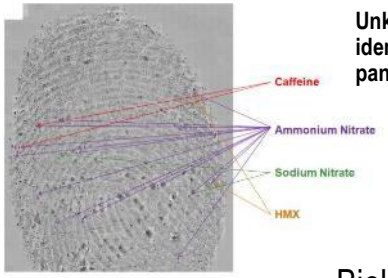
Fundamental





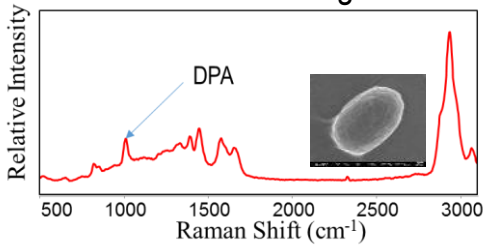
Inkjet Technology

Forensics Research

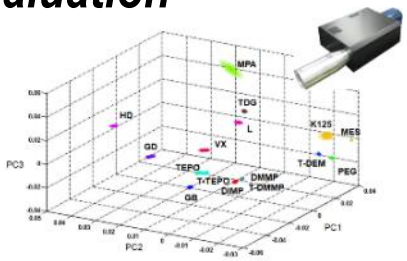


Unknown explosive identified on black car panel

Biological



CWA classification



Field test support

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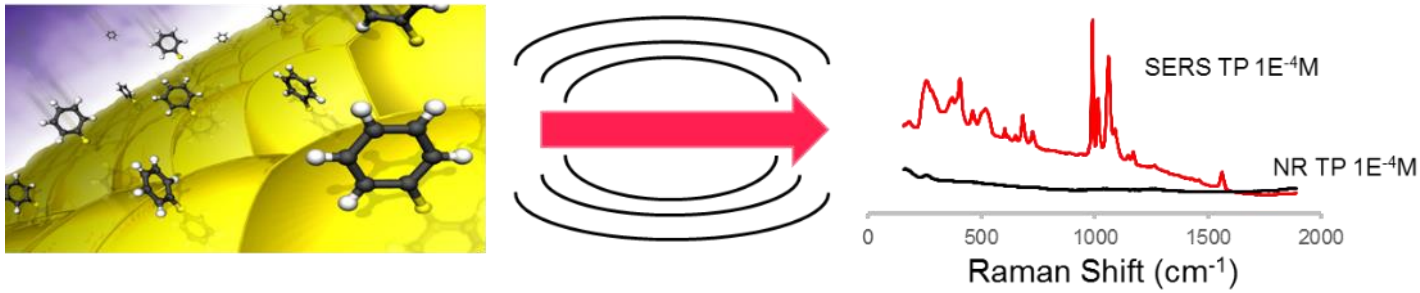
Surface enhanced Raman Scattering



- Nanometallic substrates locally amplify electromagnetic fields at or near particle surfaces providing > 10^6 enhancement over normal Raman.
- Ideal for low level detection & reduction of fluorescence
- However, real world application success has been limited!

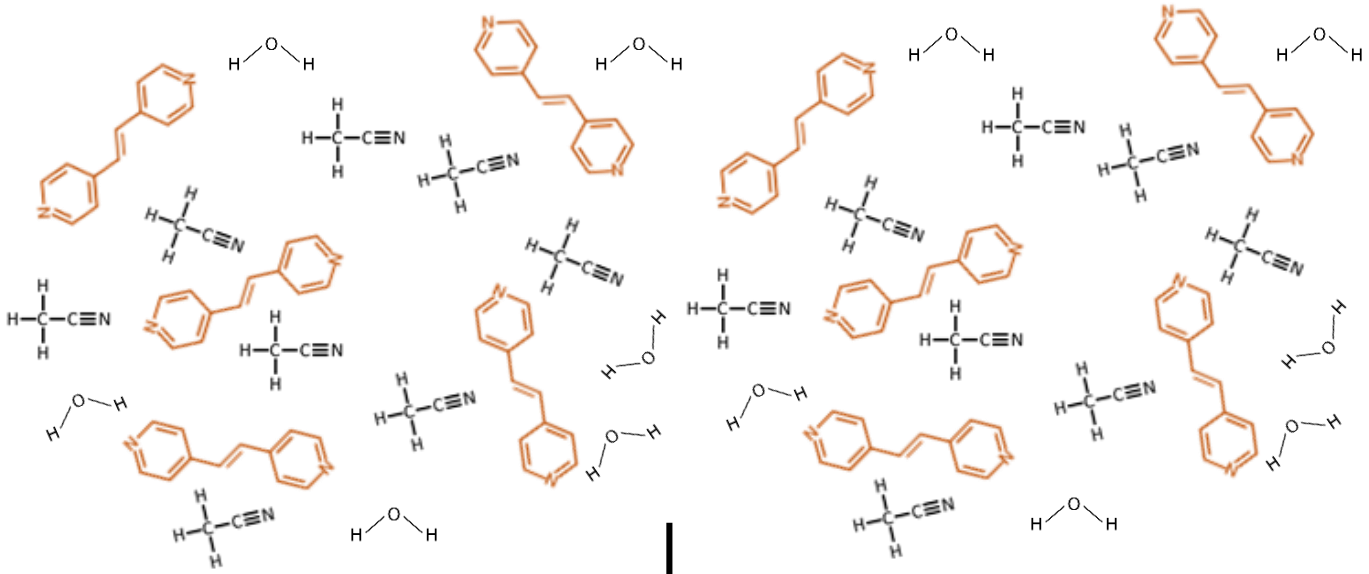
Why?

What's Missing

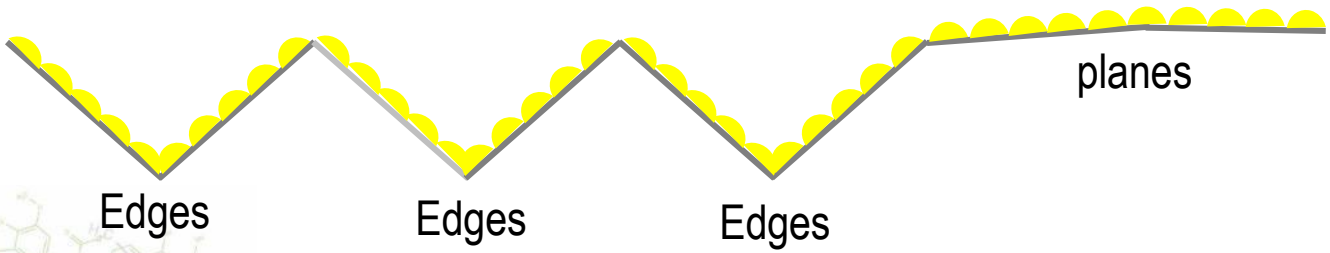
- Current theory of SERS resolves around 2 mechanisms
  - Electromagnetic enhancement drives most of signal and can be applied regardless of molecule being studied.
  - Chemical enhancement is less understood but involves charge transfer between the chemisorbed analyte & the metal surface
  - No prediction capability from theory or the traditional Enhancement Factor
- Researchers study molecules that bind well, and focus substrate manufacturing on plasmonic structures/differences.

Our work focuses on understanding the molecular properties, nano-metallic structure, and solvent factors that influence the binding of an analyte and resulting SERS response

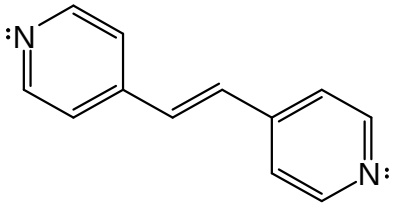
Break down of the System

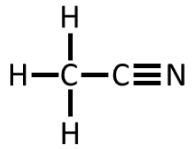


What factors drive analytes to surface



Molecules





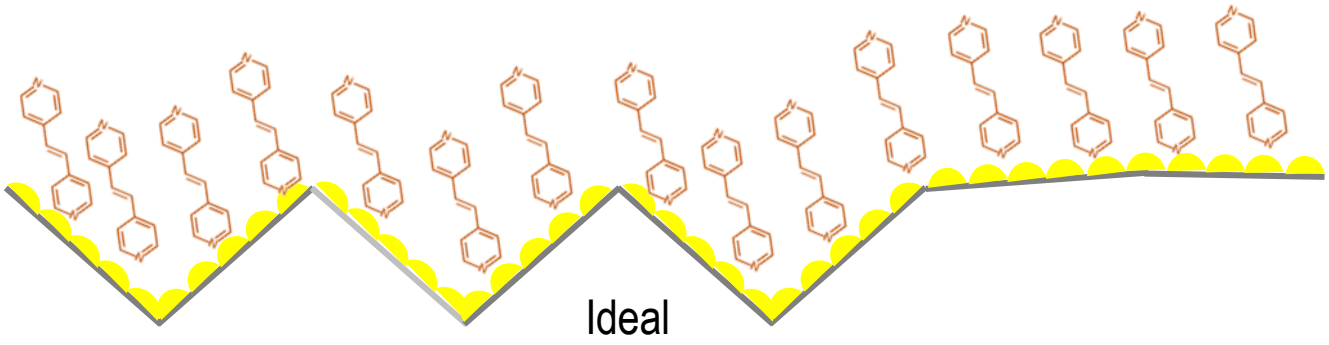
H_2O

Surface

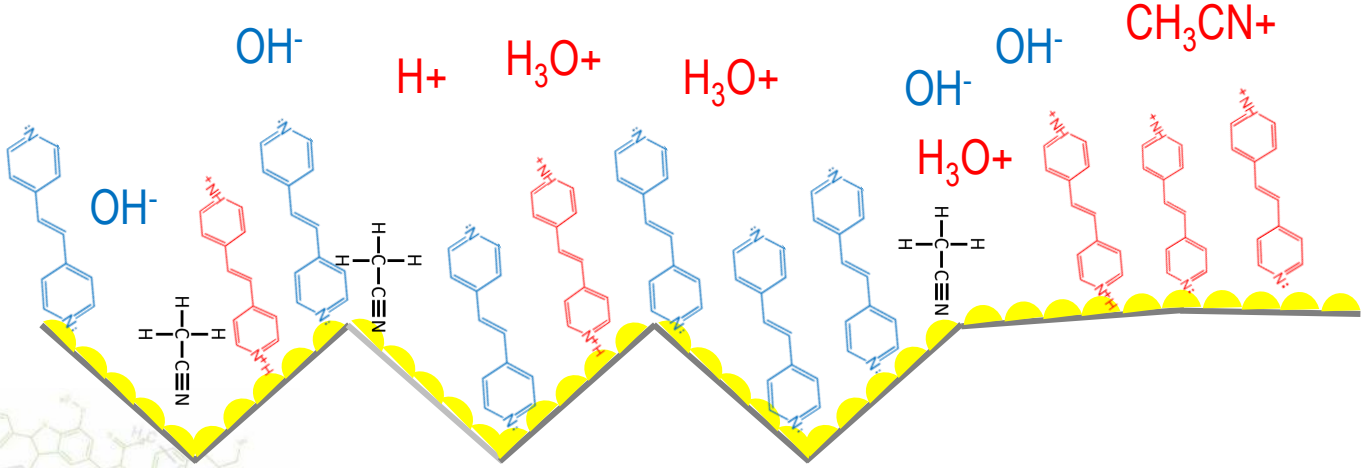
Au **Ag**

Pd, Pt, Fe, Al

Breakdown of the System

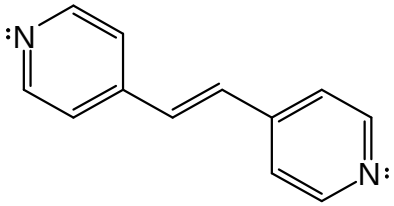


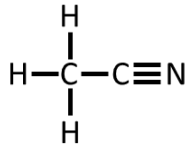
Ideal



Reality

Molecules





H_2O

Surface

Au **Ag**

Pd, Pt, Fe, Al

Attributing Thermodynamic Contributions Part I

- SERS EF (*G*): More traditional approach, based on assumption of number of adsorbed molecules per unit area. Doesn't account for differential experimental conditions
- ECBC SEV (*F*)*:* No assumptions, based on measurable and definable factors

$$G = \frac{I_S N_R}{I_R N_S} = \frac{I_S c_R V}{I_R n_S A} = \boxed{\frac{I_{S_{\max}} c_R V}{I_R n_{\max} A}}$$

- 2010 Traditional SERS EF

$$F_\alpha = \frac{c_R}{c_S} \text{ where } I_R = I_s = \alpha \times I_{S_{\max}}$$

- 2012 DARPA

Guicheteau, J., et al,. Appl. Spec. **2013**, 67(4), 396-403

$$F_\alpha = G\frac{(1-\alpha)Kn_{max}A}{V}$$

- 2014 SEV

Tripathi A. et al., *ACS Nano*, **2015**, 9(1), 584-593

Use of the SERS Enhancement Value (SEV) takes into account binding equilibrium and therefore the thermodynamics of the substrate/analyte/solvent interactions resulting in an overall more accurate measure of the sensitivity of a substrate.

Analysis Protocols

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	Drop and Dry Protocol	Constant Time and Volume Protocol	Langmuir Protocol
Thermodynamic properties	No	No	Yes
Sample volume	<100 µL	>5 ml	As high as 1 L
Time of analysis	Seconds - minutes	Minutes - hours	Days
Useful for	Determining the effectiveness of SERS substrate for a rapid response	Determining practical application of SERS substrate	Determination of binding potential properties of SERS substrate

	Drop and Dry			CTVP			Equilibrium			
Thiophenol conc	Vol (L)	Molecules	Mol/Site	Vol (L)	molecules	Mol/Site	Vol (L)	Immersion Time (hrs)	molecules	Mol/Site
5.00E-09	1.00E-05	3.01E+10	1.58E-04	0.007	2.11E+13	1.11E-01	1	500	3.01E+15	1.58E+01
5.00E-08	1.00E-05	3.01E+11	1.58E-03	0.007	2.11E+14	1.11E+00	1	250	3.01E+16	1.58E+02
5.00E-07	1.00E-05	3.01E+12	1.58E-02	0.007	2.11E+15	1.11E+01	0.05	24	1.51E+16	7.92E+01
5.00E-06	1.00E-05	3.01E+13	1.58E-01	0.007	2.11E+16	1.11E+02	0.05	24	1.51E+17	7.92E+02
5.00E-05	1.00E-05	3.01E+14	1.58E+00	0.007	2.11E+17	1.11E+03	0.05	24	1.51E+18	7.92E+03
5.00E-04	1.00E-05	3.01E+15	1.58E+01	0.007	2.11E+18	1.11E+04	0.05	24	1.51E+19	7.92E+04
5.00E-03	1.00E-05	3.01E+16	1.58E+02	0.007	2.11E+19	1.11E+05	0.05	24	1.51E+20	7.92E+05
5.00E-02	1.00E-05	3.01E+17	1.58E+03	0.007	2.11E+20	1.11E+06	0.05	24	1.51E+21	7.92E+06

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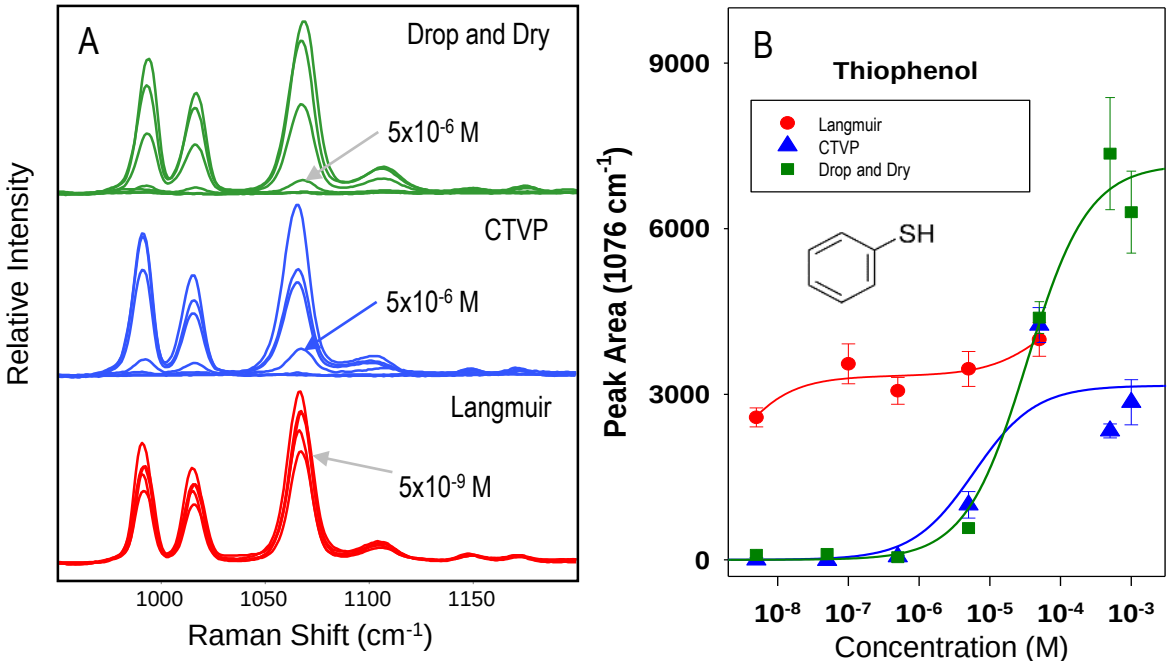
SEV



Analysis Protocol	BPE		Thiophenol	
	EF (G)	SEV (F_{90})	EF (G)	SEV (F_{90})
Drop and Dry	4.87E+06	1.36E+05	1.71E+06	1.57E+04
CTVP	5.74E+06	2.51E+06	7.55E+05	3.89E+04
Langmuir	7.29E+06	8.96E+07	9.55E+05	> 2.0E+09

$$F_{\alpha} = G\frac{(1-\alpha)Kn_{max}A}{V}$$

SEV Accounts for experimental differences which are due to contributions of the substrate/analyte/solvent interactions

Guicheteau J., et al. Faraday Discussions, DOI: 10.1039/C7FD00141J, **2017**

Attributing Thermodynamic Contributions Part II

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$$F_\alpha = G\frac{(1-\alpha)Kn_{max}A}{V}$$ **2014**

2017

$$\ln(F_\alpha) = \ln\left(\frac{G(1-\alpha)A}{V}\right) - \frac{\Delta g_{rxn}}{RT} + \left\{\frac{\Delta g_{solvation}}{RT} + \ln(n_{max} - ns_{olvent})\right\}$$

Design parameters of the SERS substrate, Spectrometer, and collection efficiency

the thermodynamics of adsorbate-substrate interaction

effect of solvent on the SERS response

Geometry and Metals

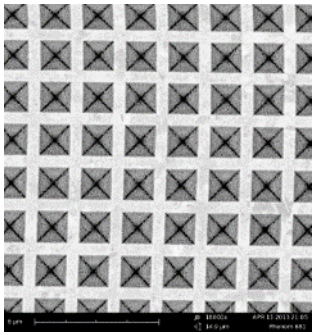
$$\ln(F_\alpha) = \ln\left(\frac{G(1-\alpha)A}{V}\right) - \frac{\Delta g_{rxn}}{RT} + \left\{\frac{\Delta g_{solvation}}{RT} + \ln(n_{max} - ns_{olvent})\right\}$$

Design parameters of the SERS substrate, Spectrometer, and collection efficiency

Geometry and Metals

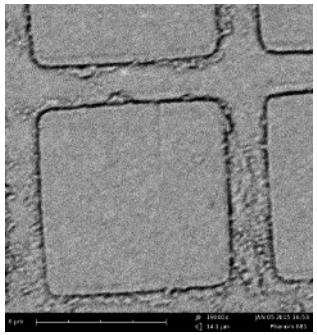
- Relationship between ln(*F*) vs. ln(*K*), yields a straight-line with a intercept proportional to $G \times n_{max}$. (SERS enhancement per unit area)

Klarite (Au and Ag)



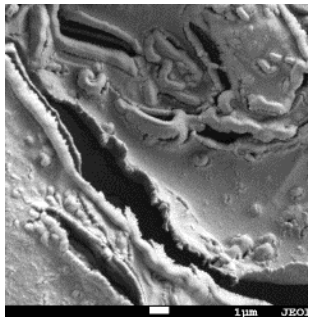
14 μm

Si Grid (Au)



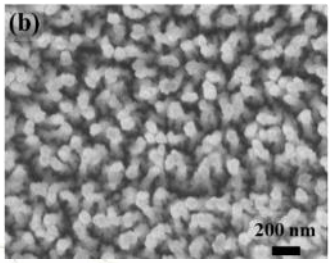
14 μm

Micro roughed (Au)



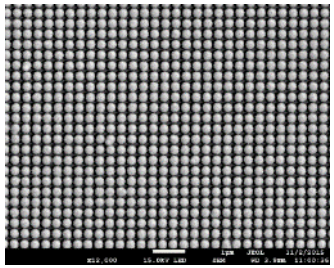
14 μm

KIMS (Au and Ag)

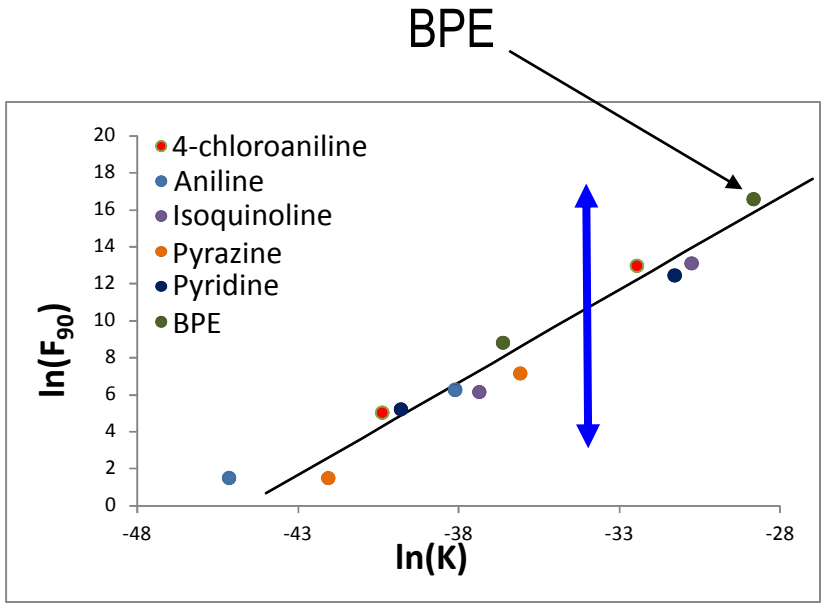


2.2 μm

K2 USCB



14 μm



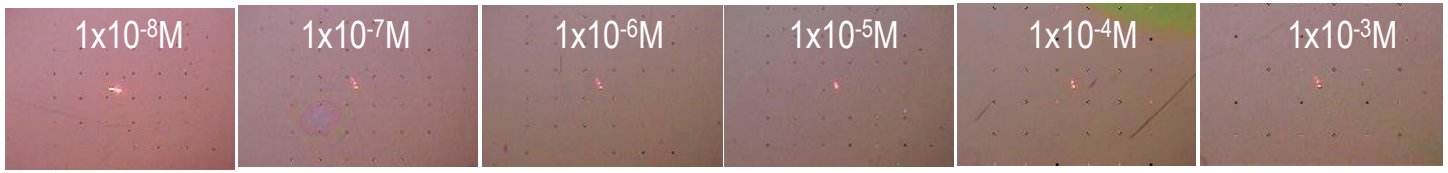
Tripathi, A.; et al. ACS Nano, **2015**, 9 (1), pp584-593

Two Paths on determining F_α relationship

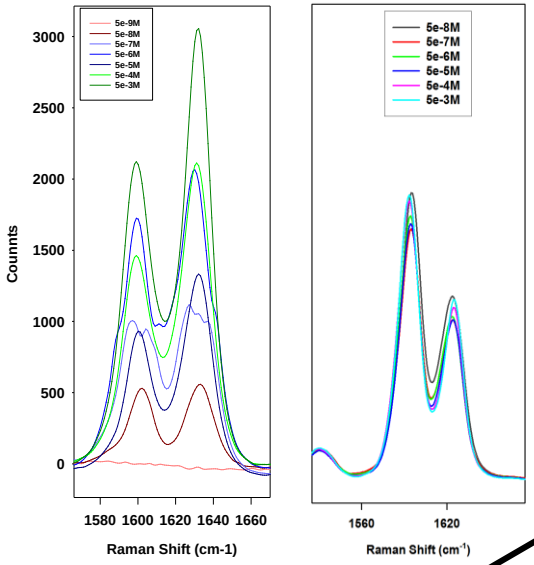
- Changing metal but keeping geometry the same
- Changing geometry but keeping metal the same
- 4 different substrates/metals combo

Geometry and Metals

BPE in H_2O



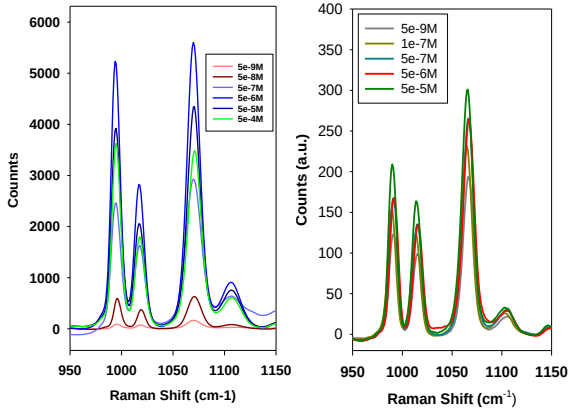
Ag-UCSB, 633nm Au-Klarite, 785nm



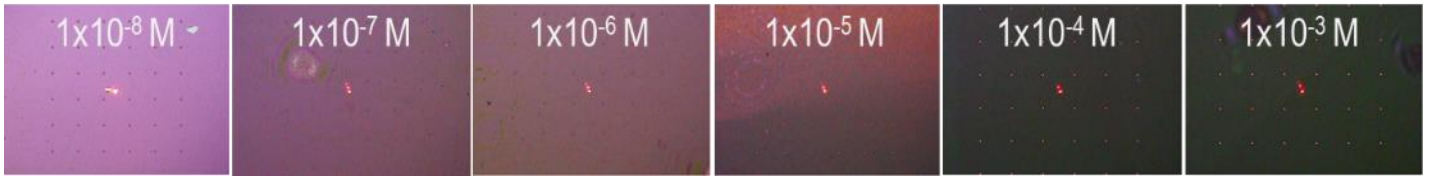
- Rearrangement of BPE molecular attachment to silver was observed as a function of concentration for Ag

TP in H_2O

Ag-UCSB, 633nm Au-Klarite, 785nm

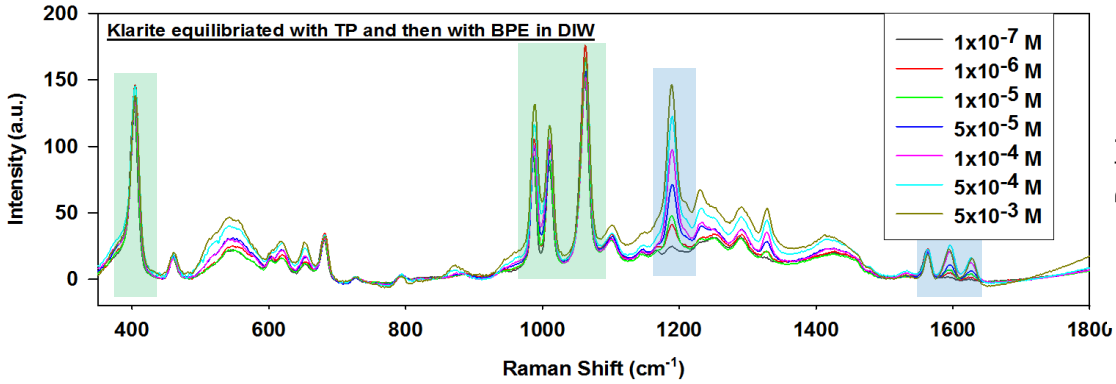


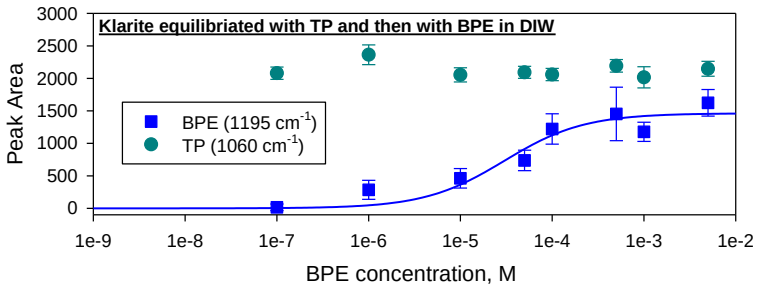
- 20 times higher response at fully formed SAM for UCSB
- Measureable equilibrium constant

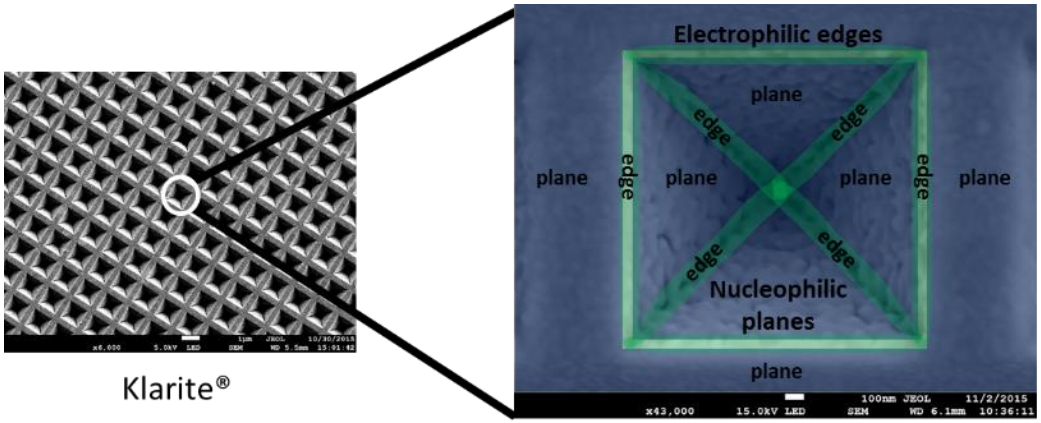


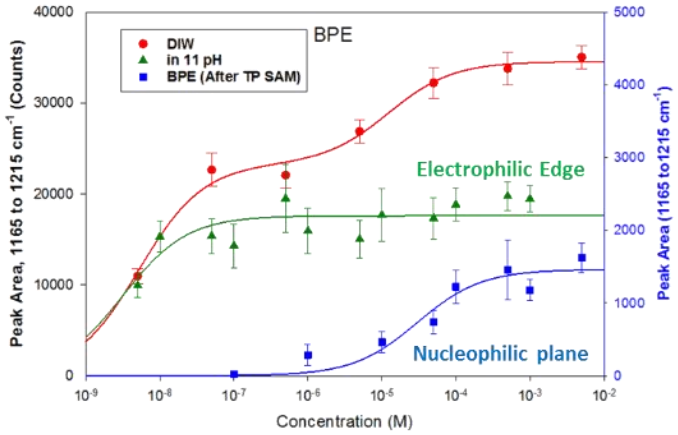
Geometry and Metals

- Identification of Nucleophilic and Electrophilic Binding Sites on SERS substrates



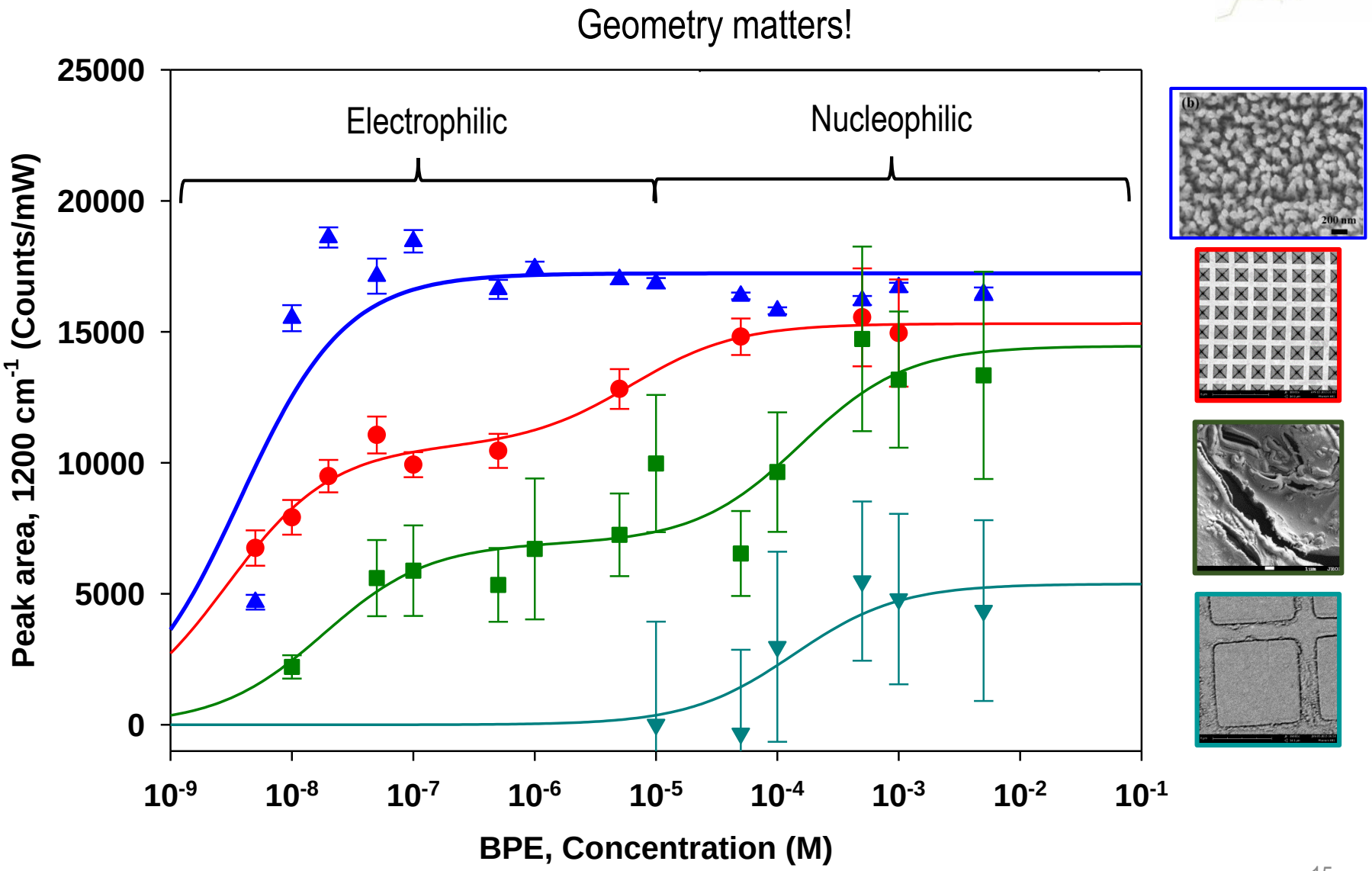






Tripathi A., et al. J. Phys. Chem. C 2016, 120, 23523−23528

Geometry and Metals



Adsorbate/Substrate Interaction

$$\ln(F_\alpha) = \ln\left(\frac{G(1-\alpha)A}{V}\right) - \frac{\Delta g_{rxn}}{RT} + \left\{\frac{\Delta g_{solvation}}{RT} + \ln(n_{max} - ns_{olvent})\right\}$$

the thermodynamics of adsorbate-substrate interaction

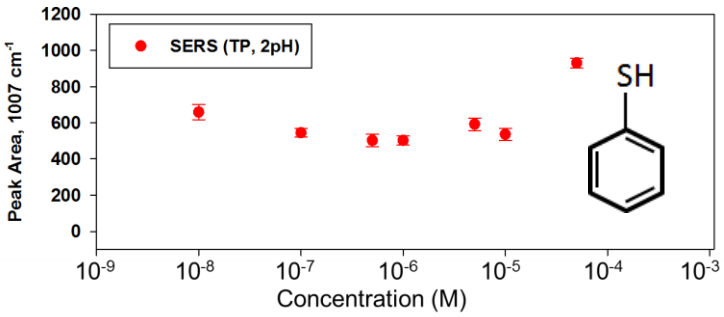
Adsorbate/Substrate Interaction

- Keeping **Substrate/Geometry** and **Solvent** the same to study influence of molecular polarity and localized charge density on binding point
- Thiophenol adsorbs very strongly to Klarite substrates such that an equilibrium constant is too large to measure.
- We selected various functional group substituted thiophenol molecules. The functional groups were selected on the basis of their ***electron donating*** (-OH, -CH3, -NH2) or ***electron withdrawing*** characteristics (-F, -Cl, -Br, -SH).

Electron Donating Groups
- $-NH_2$ (+1.53)
- -OH (+1.55)
- $-CH_3$ (+.37)

Electron Withdrawing Group
- $-NO_2$ (-4.01)
- -Cl (-1.59)
- -Br (-1.57)
- -F (-1.47)
- -SH (-1.22)

*Localized dipole moments with respect to benzene ring



Adsorbate/Substrate Interaction

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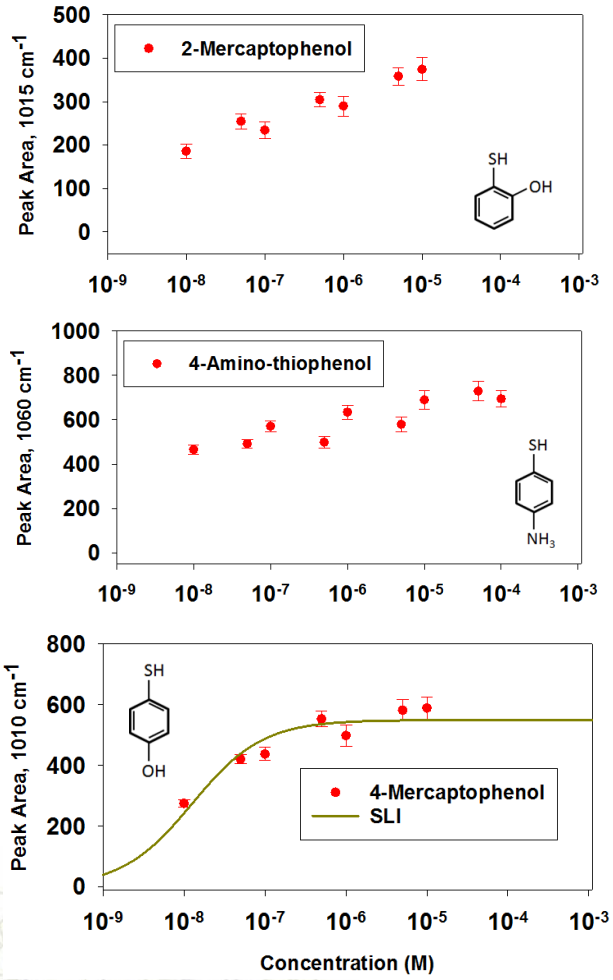
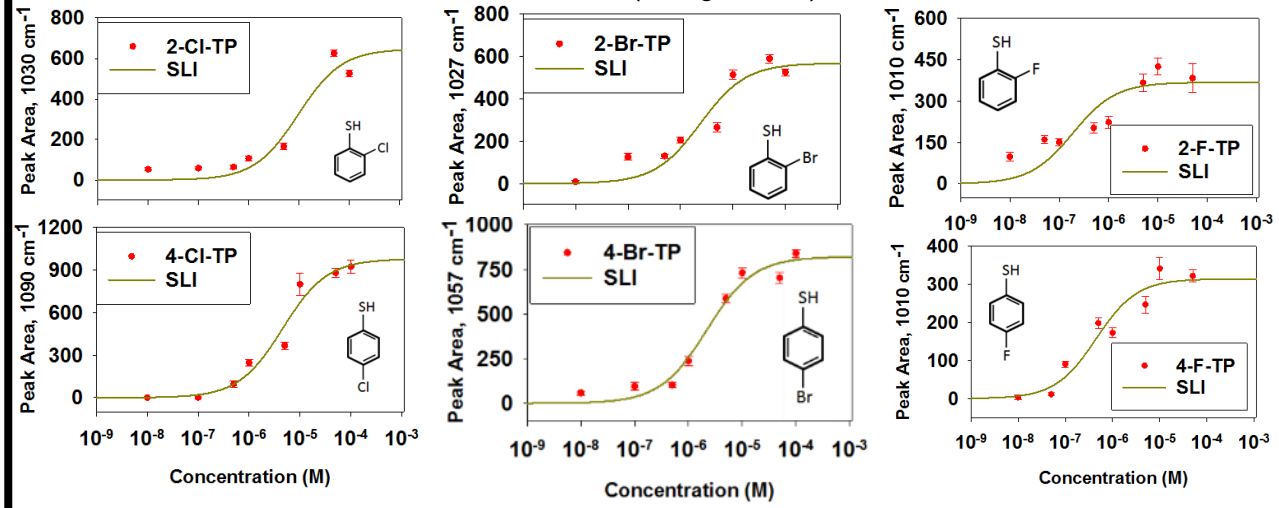
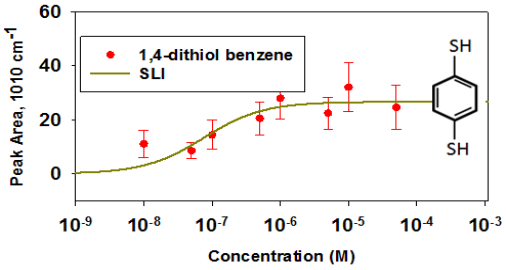
Electron donating groups



Electron withdrawing groups (halogenated)



Electron withdrawing groups (non-halogenated)

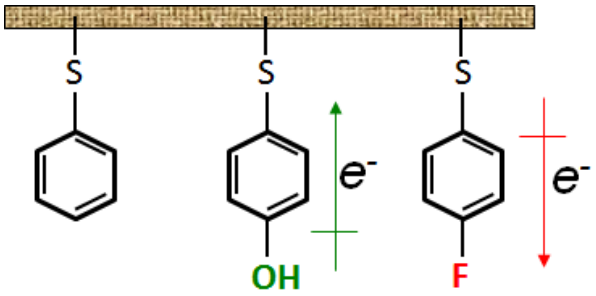


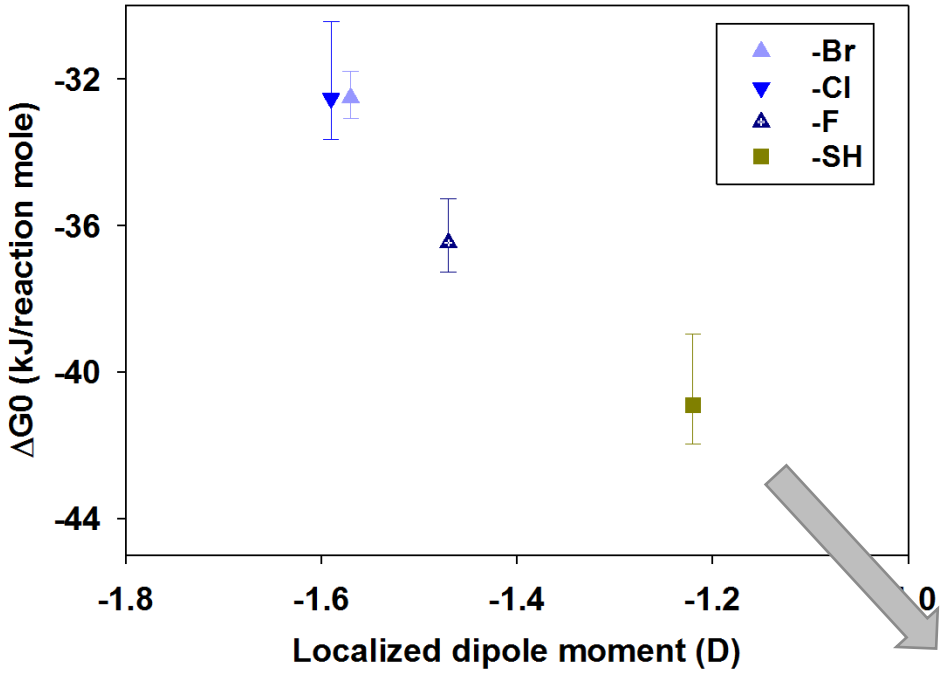
- NO2 data collection on going

Adsorbate/Substrate Interaction

A trend

- thiols with ***electron donating groups*** bind via a strong S-Au/Ag bond.
- thiols with ***electron withdrawing groups*** bind via a weaker S-Au/Ag bond.





ΔG of EDGs (–H, -CH3, -NH2) is too negative to measure

- Localized charge on sulfur affects binding

Effect of Solvent

$$\ln(F_\alpha) = \ln\left(\frac{G(1-\alpha)A}{V}\right) - \frac{\Delta g_{rxn}}{RT} + \left\{\frac{\Delta g_{solvation}}{RT} + \ln(n_{max} - ns_{olvent})\right\}$$

effect of solvent on the SERS response

Effect of Solvent

Determining the role of solvation on anlayte binding to SERS substrate: relationship to Fa

- Effect on G x n_{max}?
- Mechanism of binding?
- BPE & Thiophenol in Acetonitrile, EtoH, H_2O, dodecane, toluene

- **Three potential scenarios**
  - n_{avail} and ΔG both change
  - ΔG changes but n_{avail} is constant
  - Mechanism changes – rearrangement

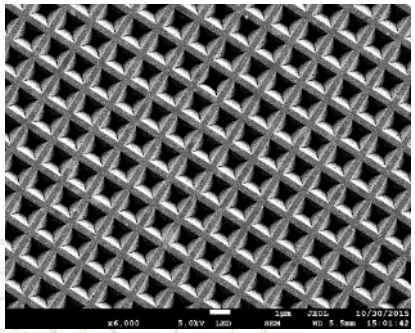
  Manuscript in preparation

$$n_{avail} = n_{max} - n_{solv}$$

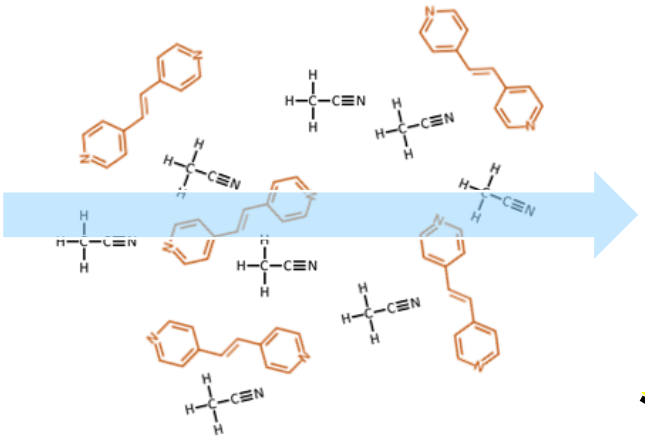
---

n_{max}

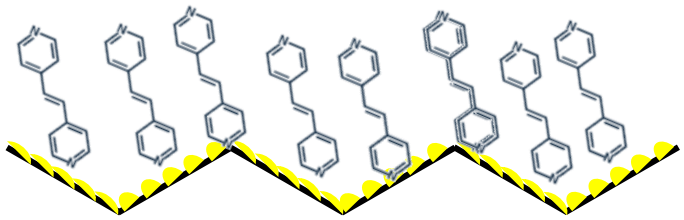
Maximum # of sites on substrate (function of substrate)



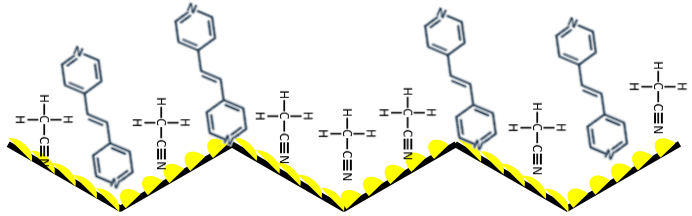
$Solvent/Analyte$



$n_{avail} = n_{max}$

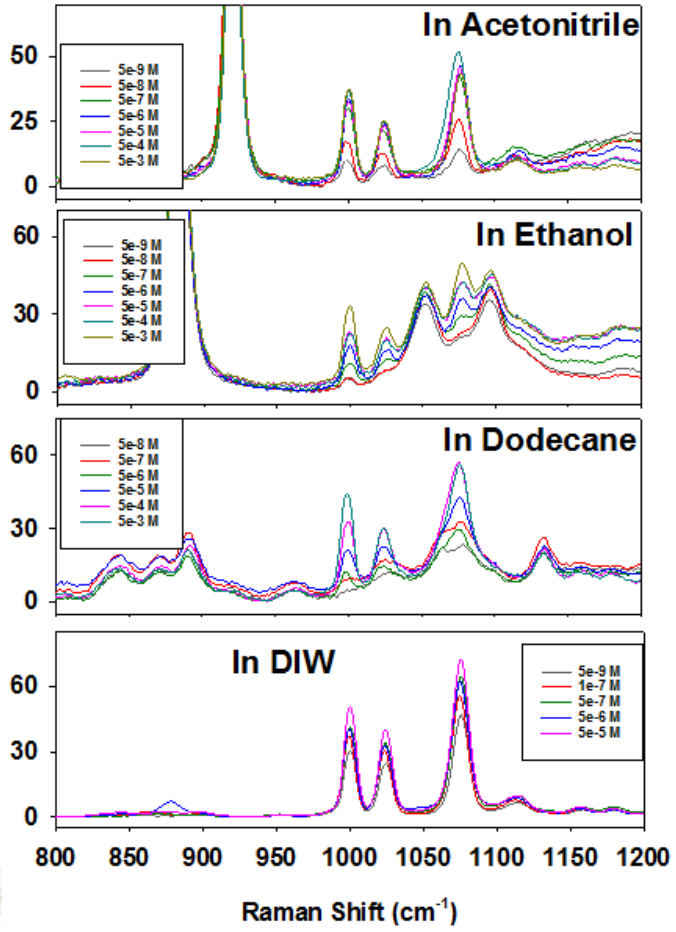


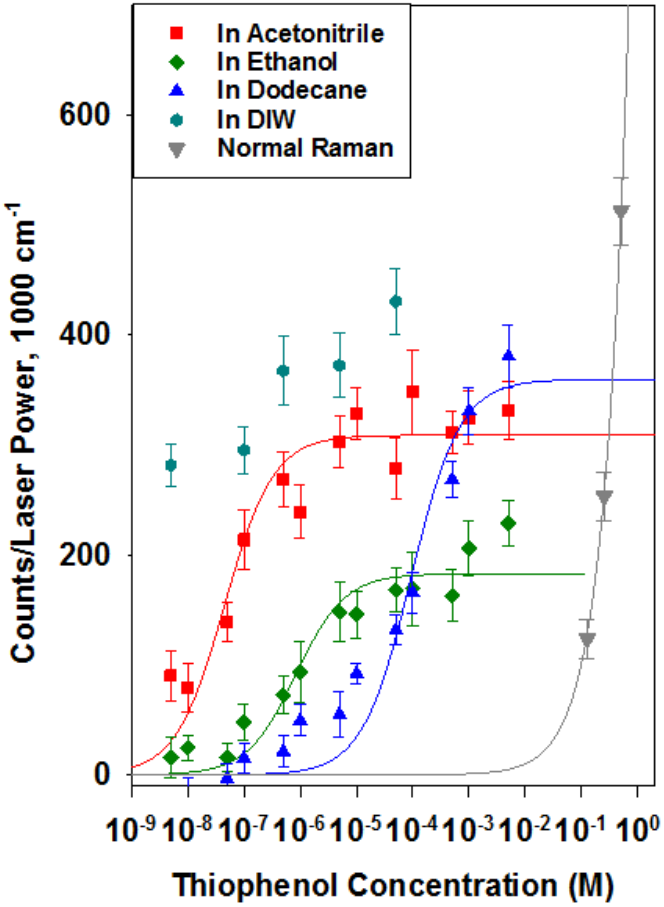
$n_{max} - n_{solv}$



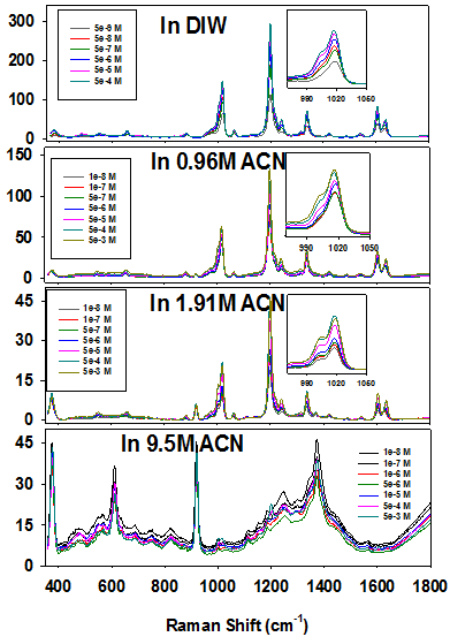
Effect of Solvent

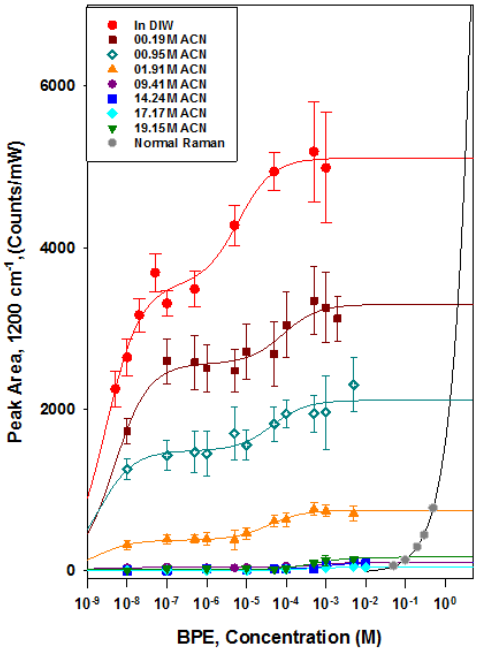
- **Solvents** can effect binding of analyte (Thiophenol example)





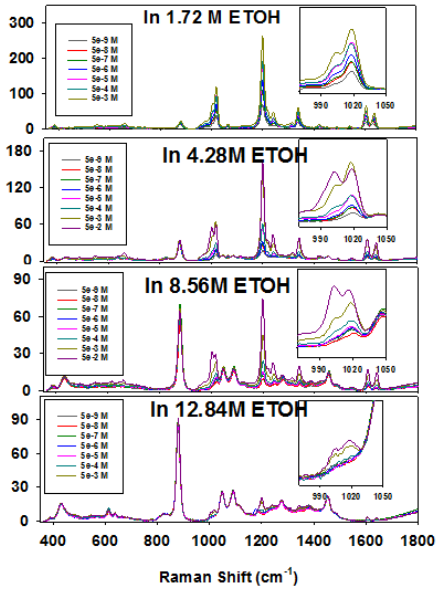
Effect of Solvent

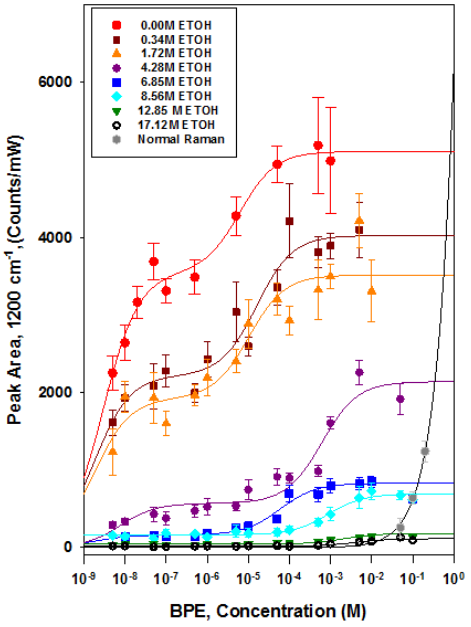




competition of available sites

Both acetonitrile and ethanol clearly influence available sites





Where to go – Application driven substrate design

$$\ln(F_\alpha) = \ln\left(\frac{G(1-\alpha)A}{V}\right) - \frac{\Delta g_{rxn}}{RT} + \left\{\frac{\Delta g_{solvation}}{RT} + \ln(n_{max} - ns_{olvent})\right\}$$

- Substrate design utilizing thermodynamic considerations
  - Increasing, decreasing electrophilic/nucleophilic nature (not just providing more sites)
  - Bridging the gap between the sites could lead to ability to bind different molecules that are not typically SERS active (threat materials, non-aromatics, etc..)

- Detection Schemes
  - Best approach to using SERS for defense detection science
  - Microfluidics (colloids/chips)
  - Swabs/test strips
  - Lab on a chip/Photonic Integrated Circuits

Questions

- Guicheteau, J. A., Tripathi, A., Emmons, E. D., Christesen, S D., Fountain III, A. W. "*Reassessing SERS Enhancement Factors: Using Thermodynamics to Drive Substrate Design*" Faraday Discussions, DOI: 10.1039/C7FD00141J, **2017**
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- Guicheteau, J. A., Farrell, M. E., Christesen, S. D., Fountain III, A. W., Pellegrino, P. M., Emmons, E. D. Tripathi, A., Wilcox, P., Emge, D. "SERS Evaluation Protocol for Nanometallic Surfaces". *Appl. Spec*. **2013**, 67(4), 396-403
- Cabalo, J., Guicheteau, J., Christesen, S. "Toward Understanding the Influence of Intermolecular Interactions and Molecular Orientation on the Chemical Enhancement of SERS". *J. Phys. Chem. A*. **2013**, 117, 9028-9038

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