

ABSTRACT

In order to predict the Surface Enhanced Raman Scattering (SERS) activity of relevant toxic compounds, it is important to understand the nature of the analyte binding to the noble metal surface. In this effort we have studied the binding of several nitrogen containing aromatic chemicals to nanostructured gold surfaces from aqueous media.

These studies have revealed that a complex equilibrium state exists between the molecules and the gold surface that cannot be explained by a simple Langmuir isotherm.

OBJECTIVES

- ❑ Investigate the nature of two equilibrium state: Dual Site or Dual Arrangement?
- ❑ If dual site:
 - The charge states of the two site
 - Geometrical location

MATERIALS AND METHODS

All chemicals were purchased from Sigma-Aldrich and used without further purification. Klarite was obtained from Renishaw Diagnostics. JASCO NRS2000 Raman microscope with 785nm excitation laser at 4.5mW was used to acquire Raman spectra.

Three types of Langmuir isotherms...

Single Langmuir Isotherm (SLI)

$$I_{CS} = I_{max} \left(\frac{KC_S}{1 + KC_S} \right) \quad (1)$$

Where: 'K' is the equilibrium constant, 'Cs' is the analyte concentration, 'ICS' is peak area of a spectral feature at the concentration 'Cs', and 'Imax' is the maximum observed peak area of that spectral feature.

Dual Site Langmuir Isotherm (DSLII)

Two binding sites with β_1 and β_2 the fractions representing each of these sites:

$$I_{CS} = I_{max} \left(\frac{\beta_1 K_1 C_S}{1 + K_1 C_S} + \frac{\beta_2 K_2 C_S}{1 + K_2 C_S} \right) \quad (2)$$

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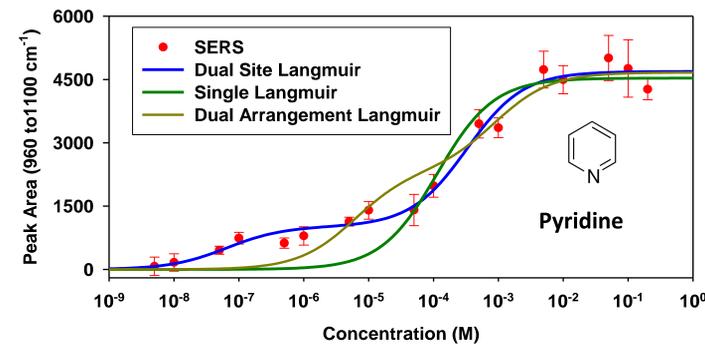
Dual Arrangement Langmuir Isotherm (DALI)

Rearrangement of molecules result in a higher packing density at higher concentrations:

$$I_{CS} = I_{max} \left(\frac{K_1 C_S + 2K_1 K_2 C_S^2}{1 + K_1 C_S + K_1 K_2 C_S^2} \right) \quad (3)$$

OBSERVED ISOTHERMS

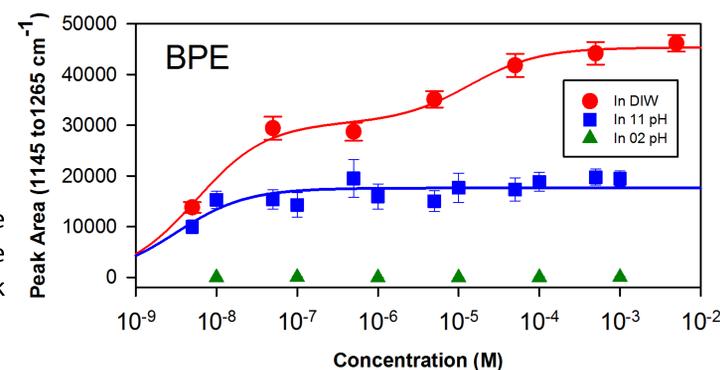
We acquired SERS based adsorption isotherms for five azarenes and four anilines with Klarite as the substrate and DI water as solvent (Tripathi et al, *ACS Nano*, 2015, 9 (1), pp 584–593).



The Single Langmuir Isotherm does not explain the observed phenomenon.

Clearly, Dual Site Langmuir Model fits the best. But DSLI has one more fitting parameter than does DALI.

Dual Site or Dual Arrangement?



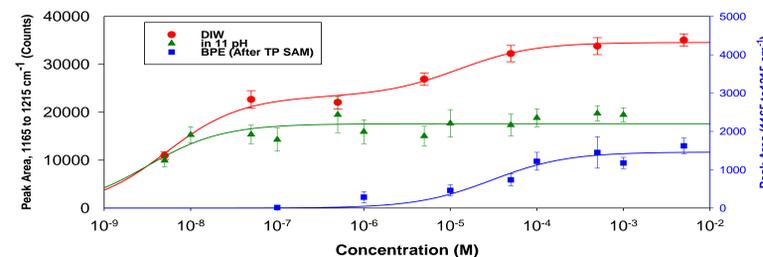
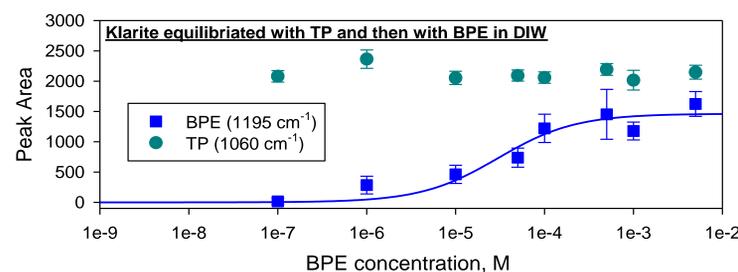
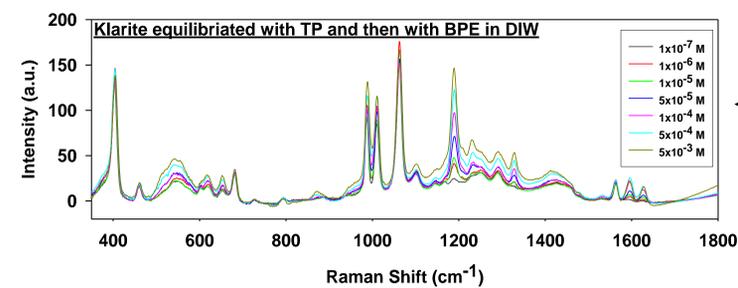
Solvent	protonated BPE	1 st ΔG (kJ/m)	2 nd ΔG (kJ/m)
DIW	10 % (pkb ~ 6)	-47.40	-27.94
11 pH NaOH	0.001 %	-48.33	--
2 pH HCl	99.99 %	--	--

Crowding of adsorbed BPE molecules should have caused the rearrangement but did not. We attribute the observed isotherms to existence of two types of sites

Chemical Nature of the Dual Sites

The adsorption study of BPE in 11 pH suggest that the one of the sites accepts non-ionized BPE molecules and is most likely electrophilic in nature.

We saturated a Klarite substrate with 1e-4M thiophenol solution. This Klarite substrate was then equilibrated with BPE solution (1e-7M to 1e-3M) in DIW.

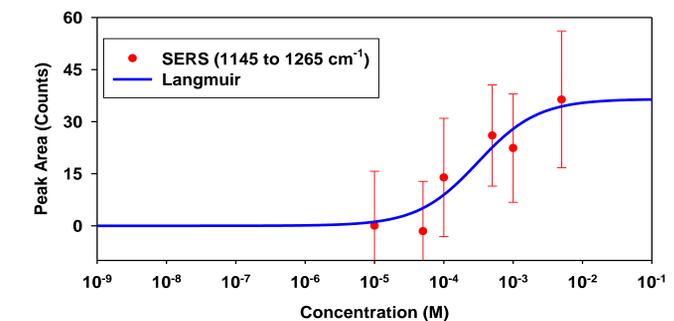
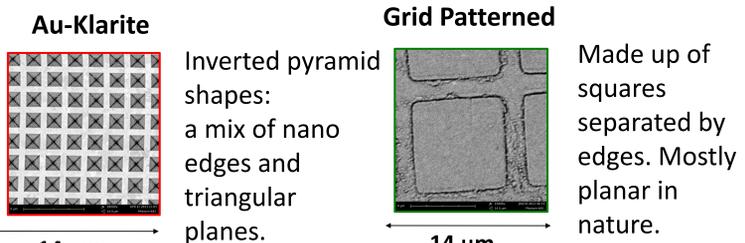


Solvent	protonated BPE	1 st ΔG (kJ/m)	2 nd ΔG (kJ/m)
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11 pH NaOH	0.001 %	-48.33	--
BPE on TP coated klarite		--	-25.96

The adsorption isotherm of BPE on Klarite pre-saturated with thiophenol is well explained by SLI model. It is clear that BPE attachment is not due to detachment of adsorbed thiophenol because thiophenol signal strength does not change. Thus, attachment of BPE is occurring at sites that could not be occupied by thiophenol. A similar experiment with BPE in 11 pH did not show BPE spectral response. This suggests that non-ionized BPE molecules are not binding to a thiophenol pre-saturated substrate. These two experiments strongly suggest that only the protonated BPE ions can bind to a thiophenol saturated substrate. Thus, the second site is nucleophilic in nature.

Geometrical Nature of the Dual Sites

The electrophilic and nucleophilic site may have specific geometrical location. Consider two different types of planar Au-SERS substrate.

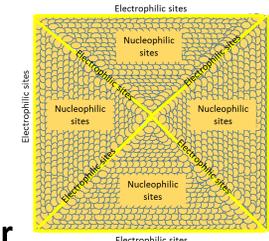


Grid Patterned

The adsorption isotherm of BPE on grid patterned Au-substrate is well explained by SLI model. The free energy of binding is estimated to be -20 kJ/mole. This compares well with the second binding energy observed in Klarite (related to nucleophilic sites). Thus, we hypothesize that the planar surface may be responsible for nucleophilic attachment.

Based on our observations, we hypothesize that the observed isotherms of various nitrogenous based compounds on Klarite are due to dual sites:

Nucleophilic (on the planar surface) and electrophilic (on the edges).



Acknowledgements

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