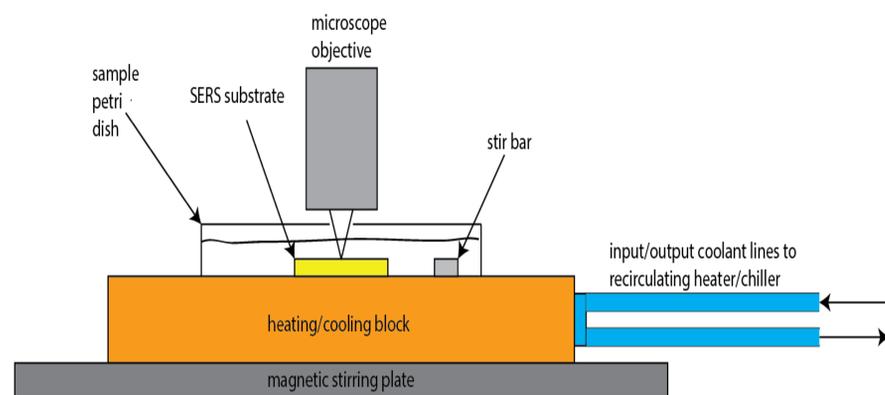


Abstract

Adsorption of molecules on surfaces plays an important role in many different technical applications, and can be influenced by many factors. Molecular parameters such as polarity and solubility are expected to play an important role in adsorption. We are studying the effect of polarity and solubility on the adsorption of aromatic molecules on noble metal surfaces using the technique of surface-enhanced Raman spectroscopy (SERS). Detection of low concentrations of analytes of interest such as explosives and toxic chemicals is possible using SERS, but only if the molecule adsorbs to the surface. To reduce the relative lack of information on what causes molecules to adsorb, we have studied different series of aromatic thiol and nitrogen-containing molecules with different substituents that lead to varying levels of overall molecular polarity and solubility. These factors have been showed to have an effect on adsorption rates, equilibrium constants, and binding energies. These measurements show trends which can provide predictive power for determining the SERS response.

Experimental Technique

The SERS measurements were performed with a JASCO Raman microscope system using 785 nm excitation. Klarite SERS substrates were used due to their reproducible SERS enhancement properties. The Raman spectra and reaction kinetics were measured in solution. The solution and substrates were maintained at constant, controlled temperatures inside a Petri dish that served as a reaction vessel.



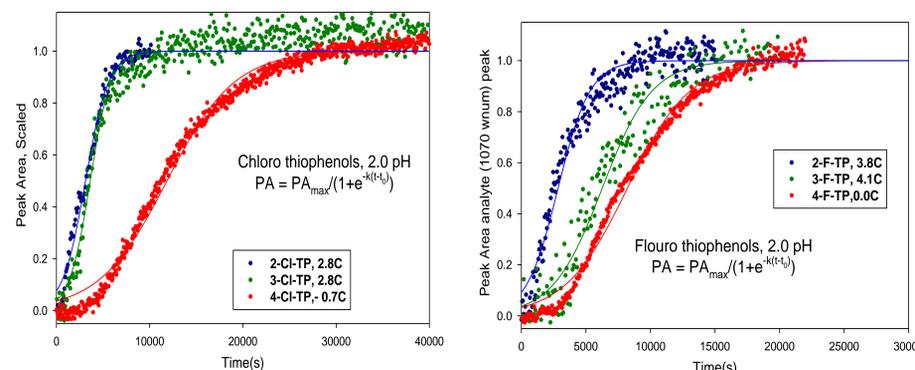
Aromatic Thiol Reaction Rates

Reaction rates different series of aromatic thiols were measured to determine the effect of overall molecular polarity. The kinetic profiles were determined at pH 2, at a concentration of 5×10^{-7} M, where the thiol groups were protonated. Under these circumstances, our group previously determined that thiophenol exhibits an autocatalysis-like behavior described by the Prout-Tompkins model, via a physisorbed precursor.

For the halogen substituted thiophenols, it was found that placing the halogen atom in the para position led to significantly smaller rate constants than the other positions, indicating the effect of the overall dipole moment.

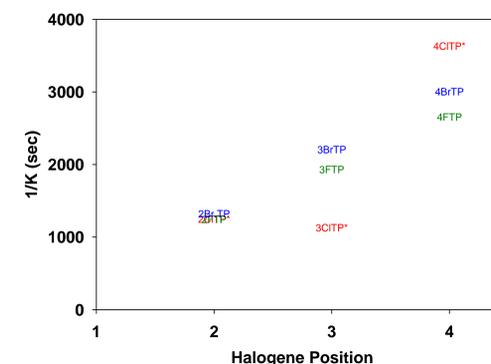
Kinetic Profiles

The kinetic profiles for the halogen substituted thiophenols at low pH show s-shaped Prout-Tompkins curves. The rates shows trend with the substitution position, or alternatively the overall molecular dipole moment.



Rate Constants as a Function of Molecular Dipole Moment

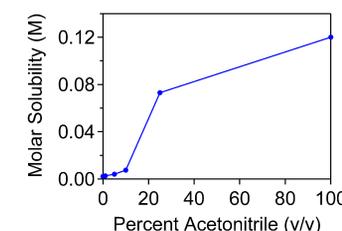
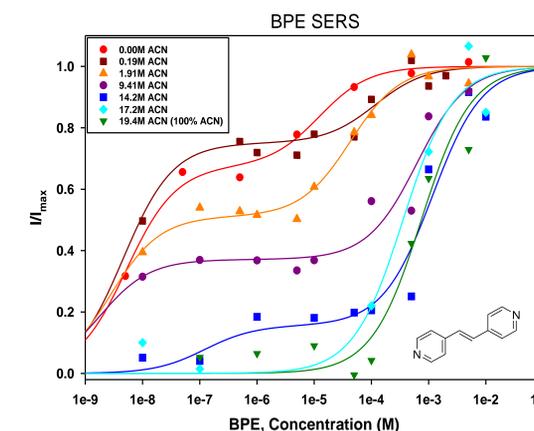
Literature Dipole Moments	
2-CITP:	1.98 D
3-CITP:	1.56 D
4-CITP:	1.16 D
2-BrTP:	1.96 D
3-BrTP:	1.51 D
4-BrTP:	1.14 D



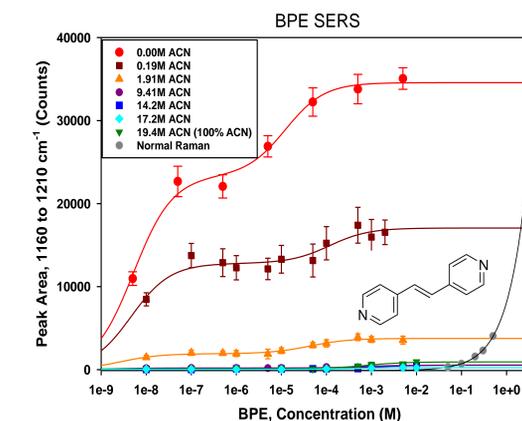
Nitrogen Containing Aromatic Molecule Equilibrium Measurements

Equilibrium adsorption isotherm measurements were performed for the double ringed nitrogen-containing molecule BPE, 1,2-di(4-pyridyl)ethylene. These measurements were performed in mixed acetonitrile/water solvents. BPE is more soluble in acetonitrile than in water. As a result, the equilibrium is shifted. In addition, we believe acetonitrile is taking up some sites on the Klarite substrates, leading to decreased intensity in solvents containing acetonitrile.

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



percent acetonitrile (v/v)	molar solubility (M)
0	0.0022
1	0.0026
5	0.0040
10	0.0074
25	0.073
100	0.12



Acknowledgements

We would like to acknowledge U.S. Army funding provided through the Edgewood Chemical Biological Center's in-house laboratory independent research (ILIR) (PE 0601101A) and Surface Science programs (PE 0601102A Project VR9). The opinions, interpretations, conclusions and recommendations are those of the authors and are not necessarily endorsed by the U.S. Government.