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Characterization of Mineral Dynamics and Adsorption through Molecular Simulation and Spectroscopy

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Sandia Geochemistry FWP

Geochemistry of Interfaces: From Surfaces to Interlayers to Clusters

Molecular Simulation and Spectroscopy of Dynamical Processes at Mineral-Aqueous Solution Interfaces. (Greathouse and Cygan)
Spectroscopic methods and molecular simulation to understand the structure and dynamics of the mineral-aqueous solution interface. ClayFF force field for classical simulations (LAMMPS code) of clays and hydrous phases.

Adsorption Equilibrium and Kinetics at Goethite-Water and Related Interfaces. (Criscenti, Leung, Allen, Katz)
Spectroscopic and molecular simulation (quantum and classical) to understand fundamental adsorption processes at the molecular level. Evaluation of surface complexation model assumptions.

Reactivity: Molecular Clusters (Nyman) and Fe(II)/Fe(III) Redox Couple in Nontronite Clay. (Ilgen)
Spectroscopic and aqueous chemical speciation methods to investigate the reactivity of the clay structural Fe(II)/Fe(III) couple towards redox transformations of inorganic contaminants, quantify the direction and kinetics of electron transfer, and develop a mechanistic model.

Sandia Geochemistry FWP

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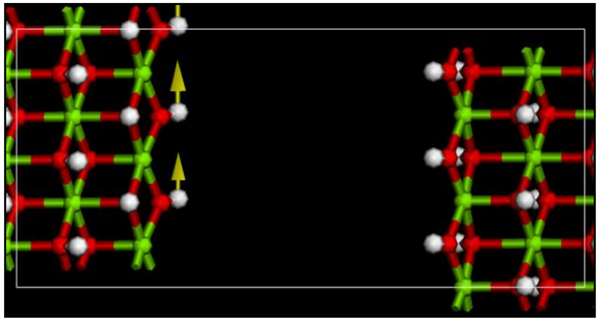
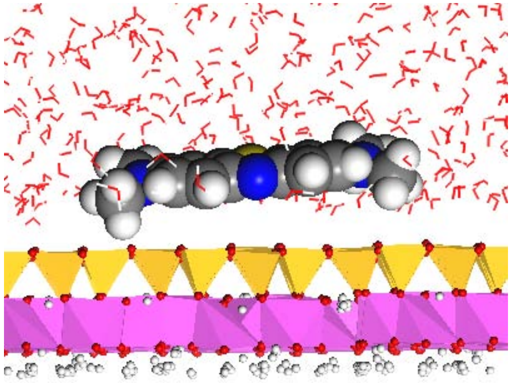
Summary of Recent and Ongoing Projects



Force field development for clay edges

Todd Zeitler (Sandia)

Parameter fitting (GULP code): Julian Gale (Curtin)



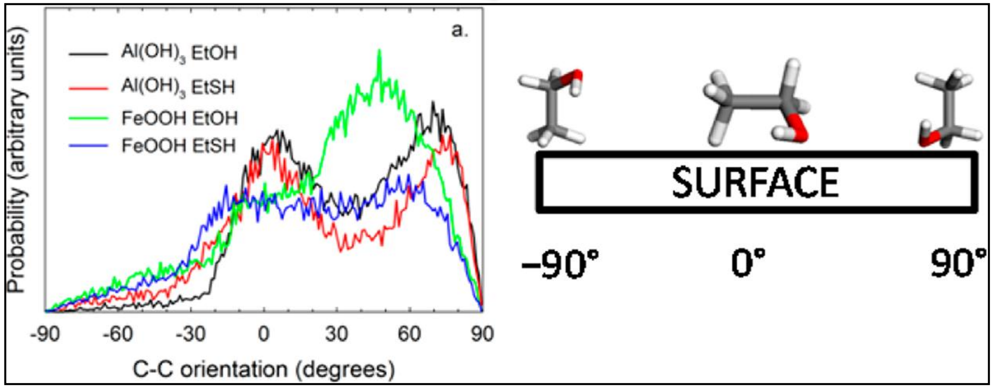
Simulation and vibrational spectroscopy of adsorbed organic molecules

Greathouse et al, *J. Phys. Chem. C* **2012**

David Hart and Margaret Ochs (Sandia)

Vibrational spectroscopy: Cliff Johnston (Purdue)

Glenn Waychnunas (LBL)

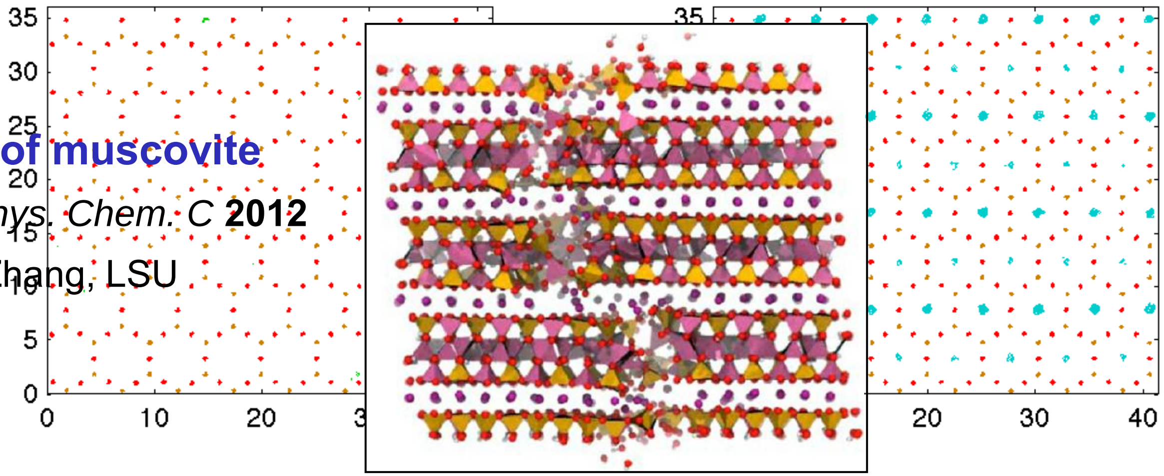


Summary of Recent and Ongoing Projects

Mechanical properties of muscovite

Teich-McGoldrick et al, *J. Phys. Chem. C* **2012**

Nanoindentation: Guoping Zhang, LSU



Ion adsorption at interlay

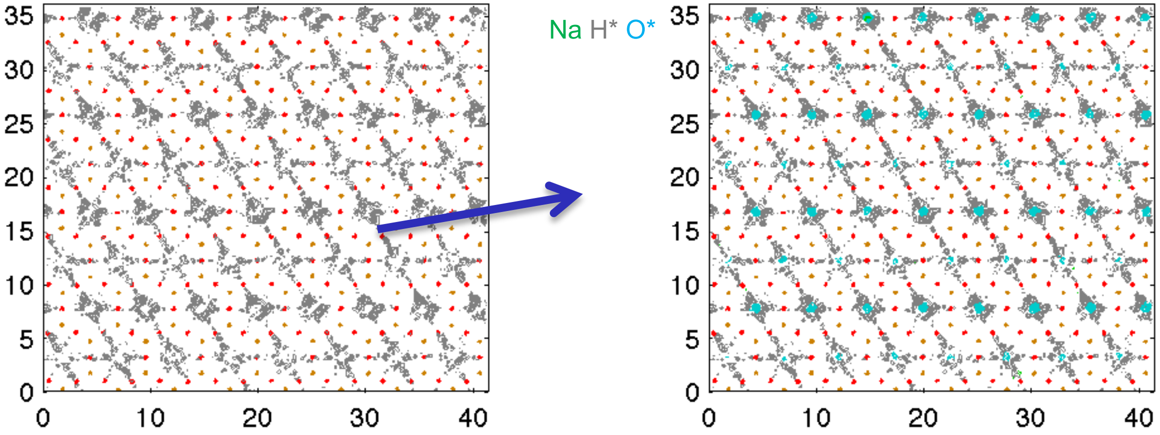
Stephanie Teich-McGoldrick ar

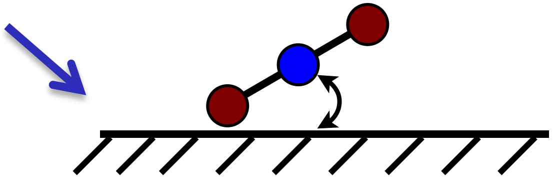
Jim Kirkpatrick (Michigan State

Simulation: Andrey Kalinichev (

NMR: Geoff Bowers (Alfred)

SHG: Sarah Gomez and Franz

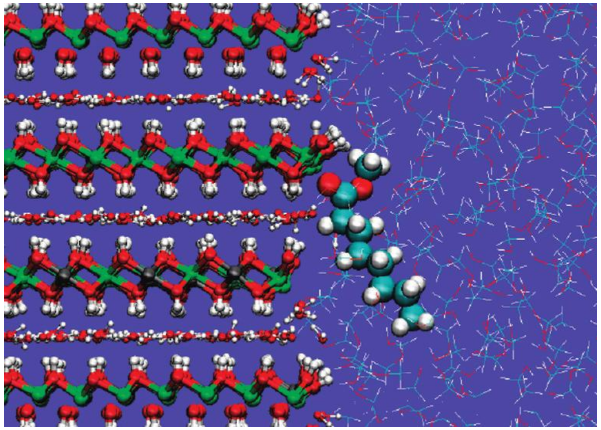




Force Field Development for Clay Edges

Recent work demonstrates that ClayFF can be modified for specific edge site applications:

- Nonbonded harmonic potential for Mg-O-H and Al-O-H angle bend.
- Parameters optimized by comparing surface vibrational modes with density functional theory (DFT).
- Prevents unbound surface hydroxyls from drifting into the aqueous region.

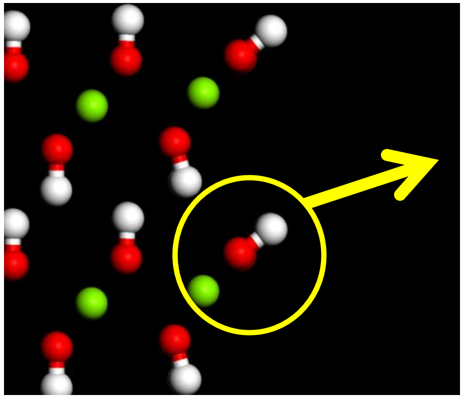


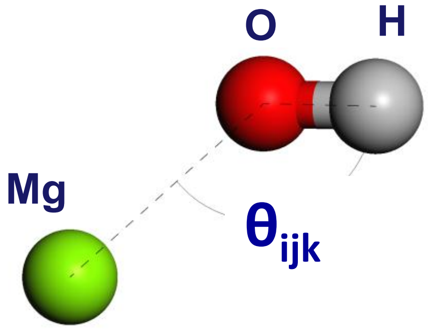
Organic molecule adsorbed on a hydrotalcite edge.
Yu and Schmidt, *J. Phys. Chem. C* **2011**.

Our goal: add M-O-H angle bending parameters to ClayFF in a transferrable way:

- Preserve flexibility of ClayFF.
- No detrimental performance compared to the original ClayFF.
- Validated with quantum calculations.
- Initial application to Mg-O-H (brucite). Al-O-H and Si-O-H to follow.

Brucite $(1\bar{1}0)$

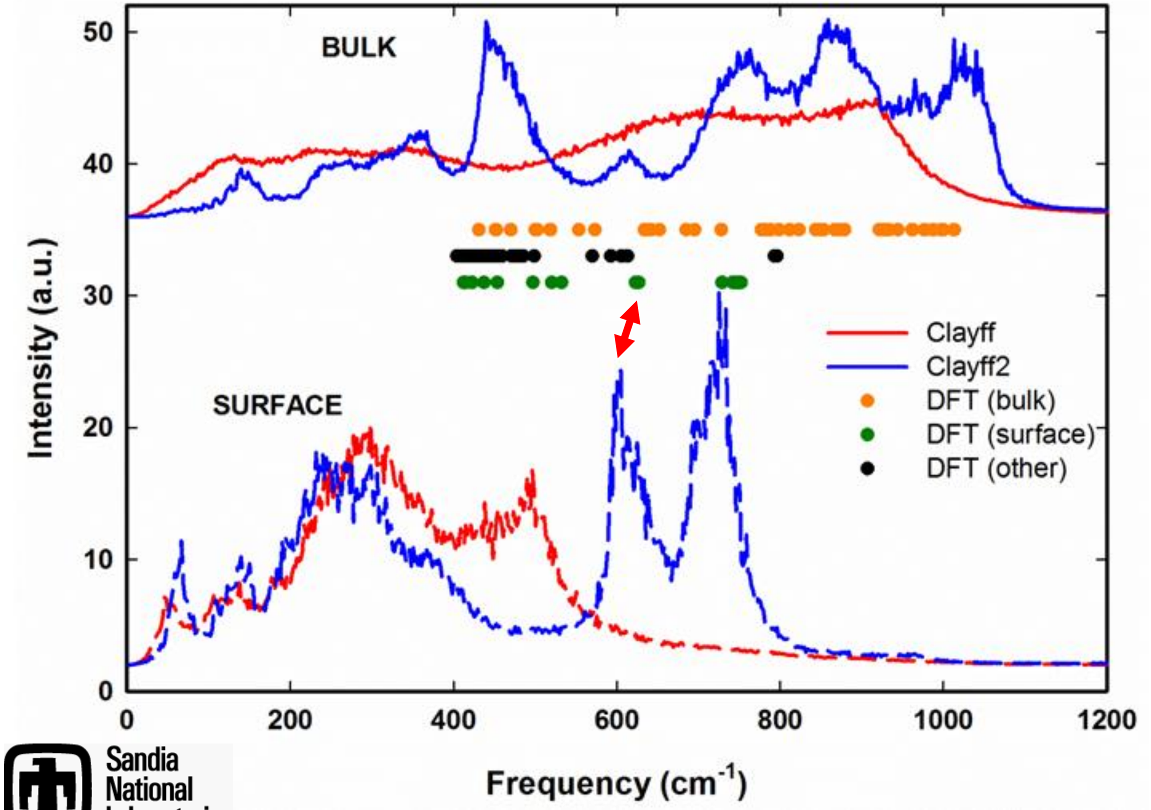




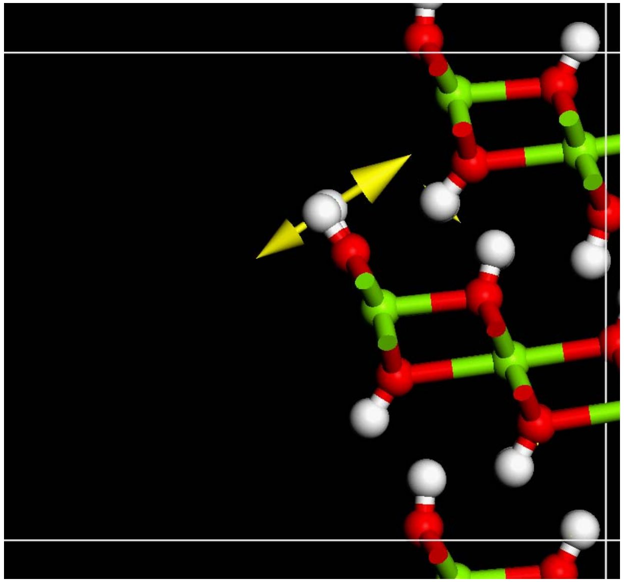
$$E_{angle\text{-}bend} = K(\theta_{ijk} - \theta_0)^2$$

Optimization of Mg-O-H Parameters

- Equilibrium angle parameter (θ = 120°) matches with DFT optimization for bulk brucite.
- Force constant (K) taken directly from Yu and Schmidt.
- Validation: vibrational power spectra from MD simulation using ClayFF (vacuum interface) compared with DFT normal modes.
- Good agreement between MD and DFT frequencies for Mg-O-H bend modes.

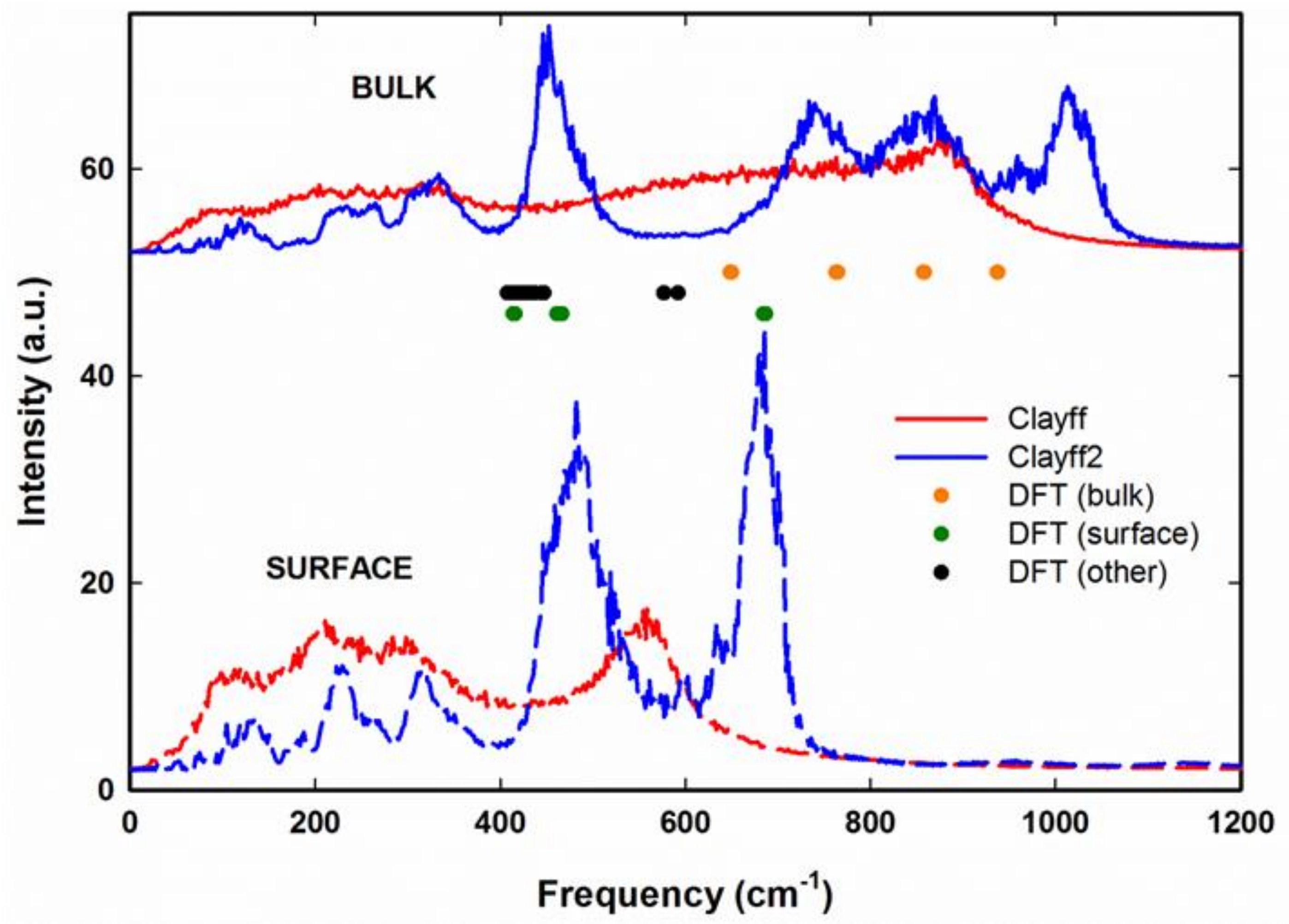


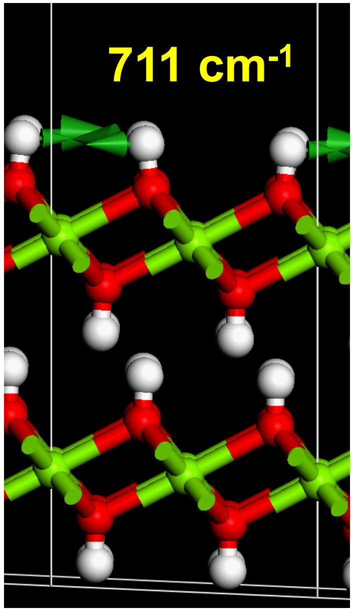
Brucite $(1\bar{1}0)$

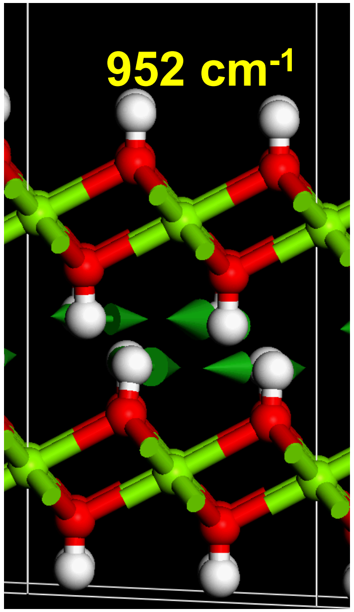


Validation: Brucite Basal Surface

Brucite (001)







Surface modes are blue-shifted in the bulk.

Calculating Mechanical Properties Using Simulation

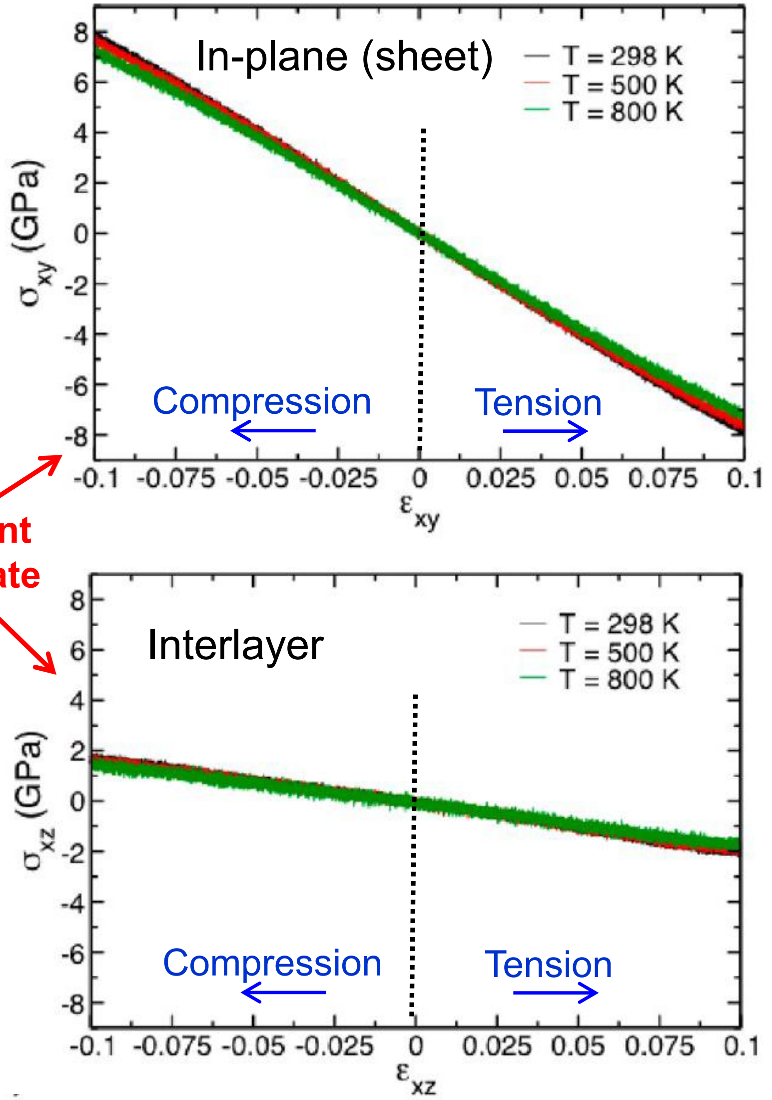
Needed for geophysical analysis and material property prediction.

Relevant to resource extraction (oil/gas) and sequestration (CO_2, nuclear waste).

Equilibrium NPT MD simulations of muscovite: hydrostatic stress / shear stress.

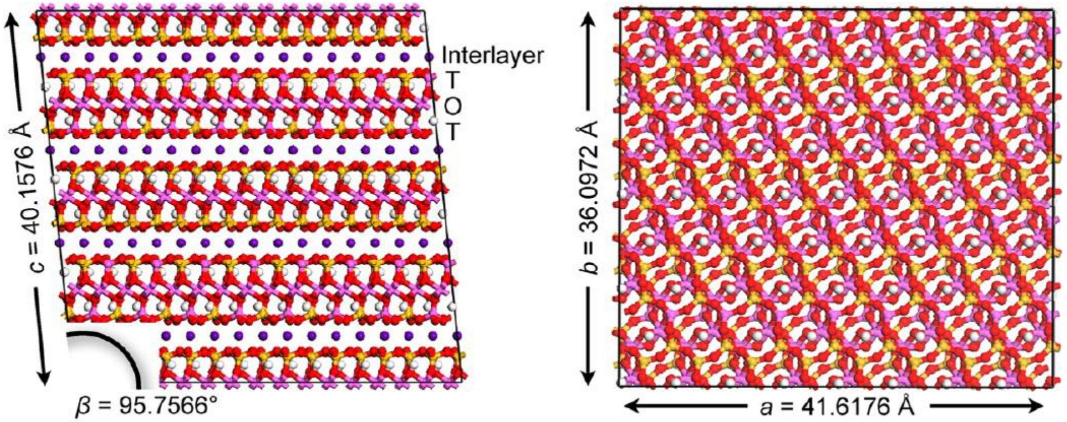
Results: moduli (bulk, Young's, shear), stress/strain curves.

Constant strain rate



Anisotropic stress-strain curves from MD simulation showing anisotropic behavior.

Teich-McGoldrick et al, *J. Phys. Chem. C* **2012**.



Muscovite 8 x 4 x 2 supercell

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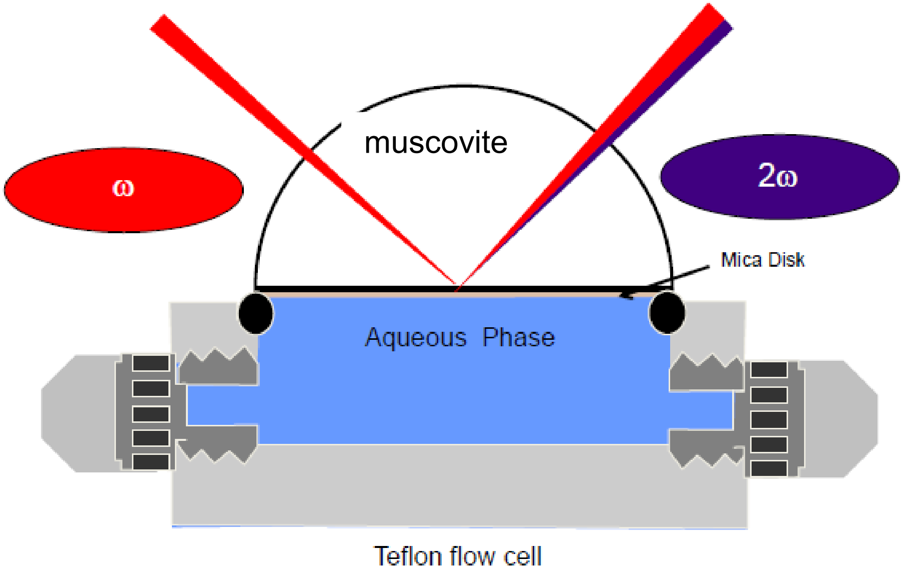
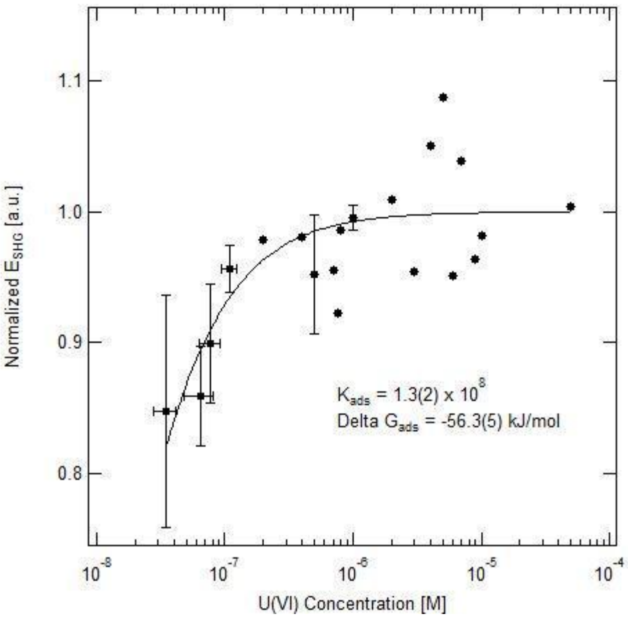
Ion Adsorption: Uranyl on Muscovite

- Examine partitioning of potassium and uranyl ions at the muscovite-interface.
- Compare simulation results on interfacial structure with second harmonic generation experiments (Franz Geiger, Northwestern).
- Strong ion adsorption: final configuration depends on initial placement of ions relative to the surface.
- MD simulations of solution-muscovite interface at different uranyl concentrations.



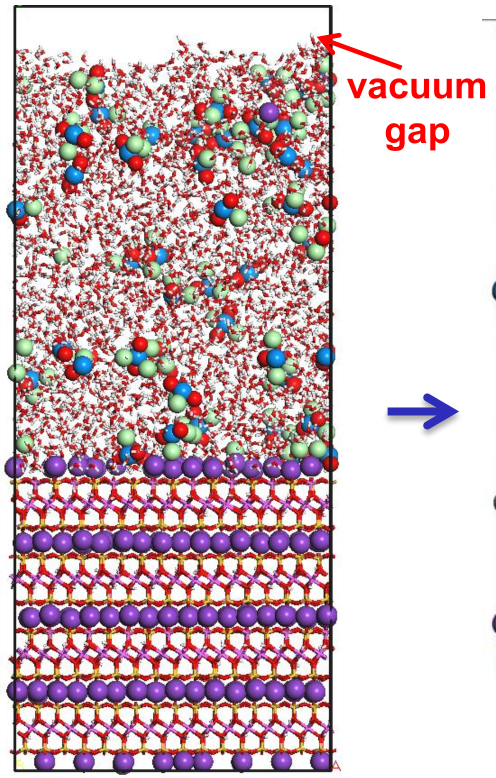
Mineral	Fused-Silica	Fused- Silica	Mica
pH	7	4	6
ΔG_{ads} (kJ/mol)	-43	-34	-56
σ_0 (C/m^2)	-0.013	-0.004	-0.020

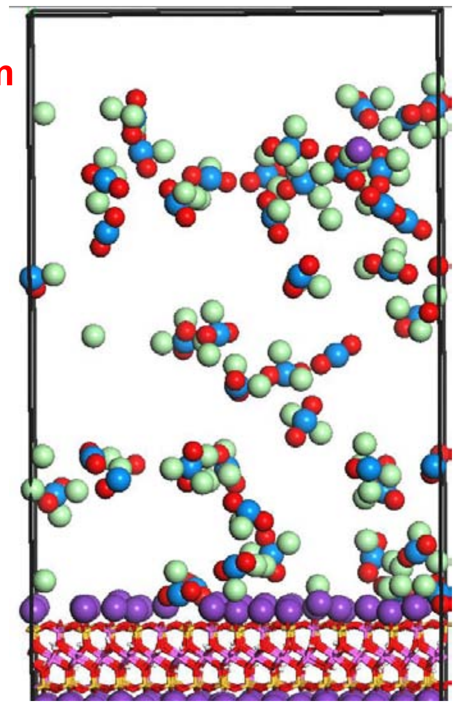
Table 1: Comparison of uranyl adsorption free energies and initial surface charge desnsities at the fused-silica and mica surfaces.

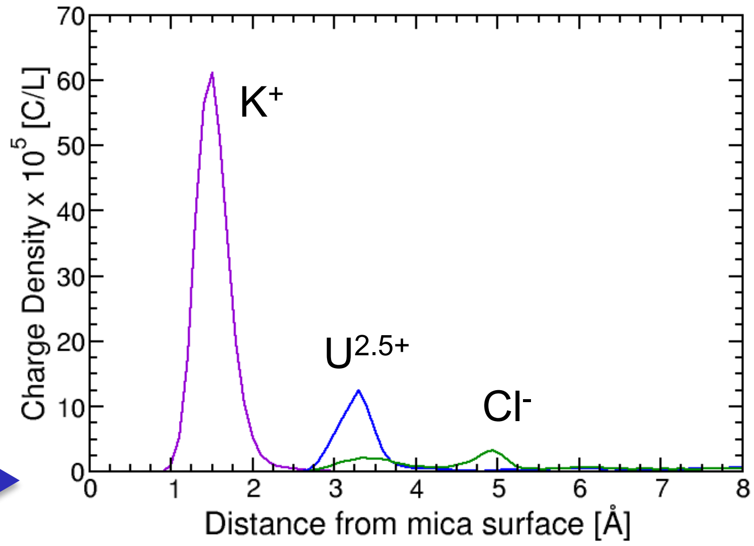


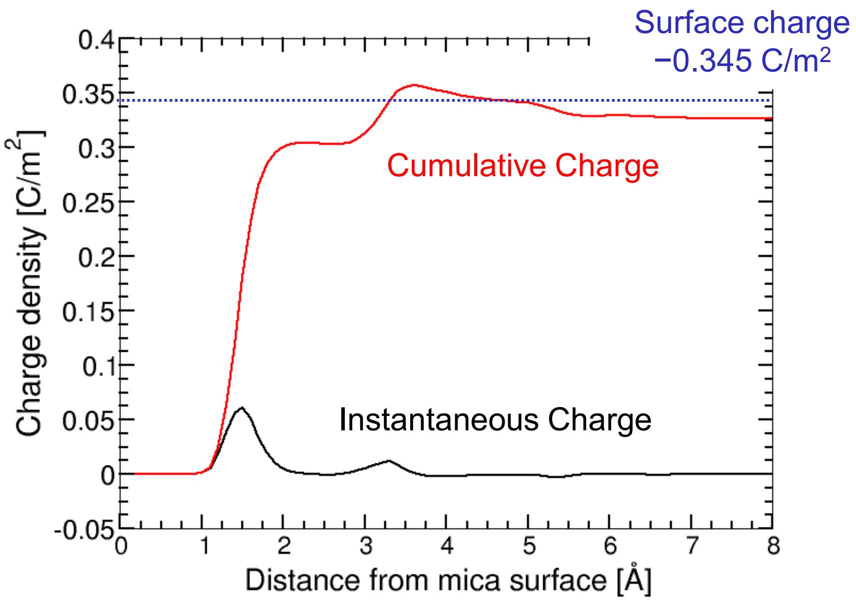
Uranyl Adsorption on Muscovite: Interfacial Structure

K-muscovite + 1.0 M $UO_2^{2+}Cl_2$







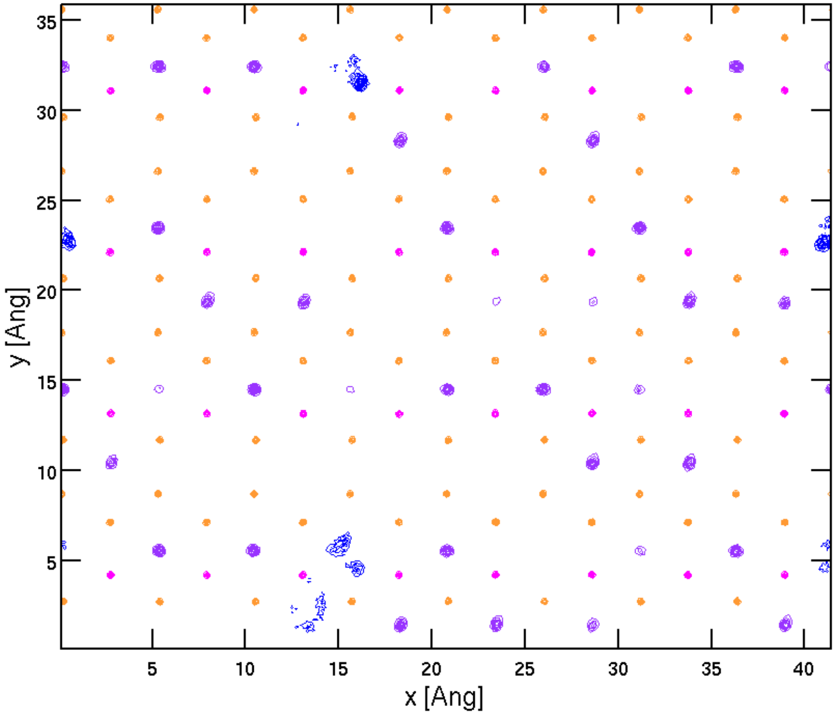


- Uranyl ions excluded from the surface due to strong binding of potassium ions.
- Uranyl ions in solution can exist as neutral or anionic species.

Uranyl Adsorption on Muscovite: Surface Structure

K-muscovite + 1.0 M $UO_2^{2+}Cl_2$

Two dimensional density profile (within 5 Å of surface)



Potassium

Aluminum

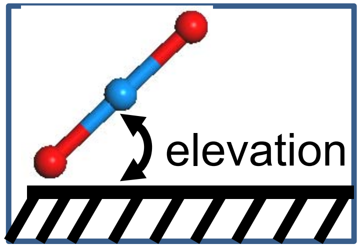
Silicon

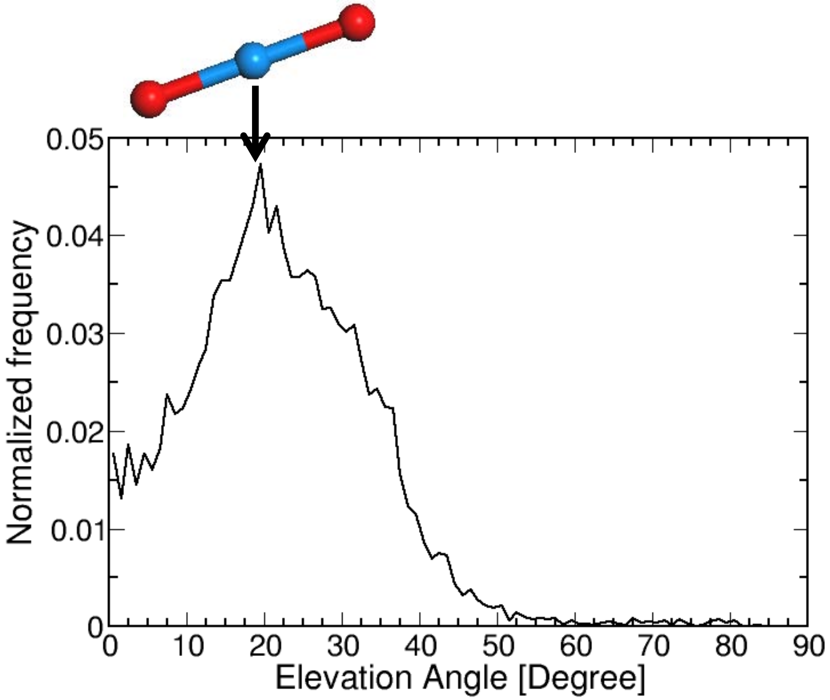
Uranyl

Potassium ions adsorb above siloxane rings near tetrahedral Al^{3+}.

Uranyl ions also adsorb near tetrahedral Al^{3+}.

No chloride ions at the surface.

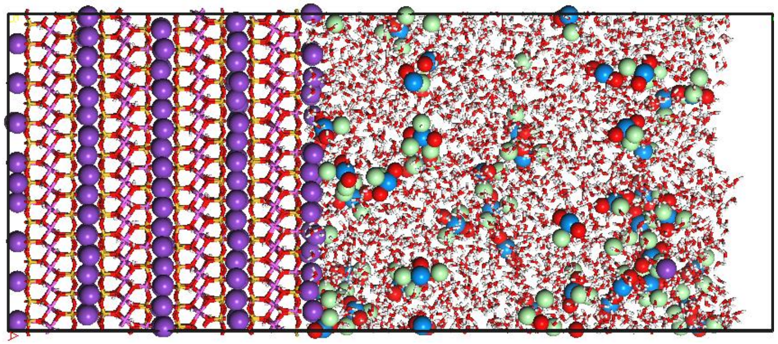




Tilted uranyl ions correspond to outer-sphere surface complexes).

Uranyl Adsorption on Muscovite: Electrolyte Effects

System	Counterion	Electrolyte	Cumulative charge at 8 Å (C/m²)	Cumulative charge at 8 Å minus surface charge (0.345 C/m²)	Uranyl ions coordinated with surface
1	K^+ (32)	--	0.326	−0.020	--
2	K^+ (32)	45 NaCl (1M)	0.345	−0.001	--
3	K^+ (32)	5 UO_2Cl_2 (~ 0.1M)	0.325	−0.020	0.78
4	K^+ (32)	45 UO_2Cl_2 (1M)	0.327	−0.185	2.40
5	UO_2^{+2} (16)	--	0.334	−0.012	15.26



- Muscovite surface charge completely neutralized.
- Slight negative cumulative charge due to associated chloride ions at the interface.
- Uranyl ions in solution can exist as neutral or anionic species with very little adsorption.

Organic Adsorption: Alcohols and Thiols on LDH Surfaces

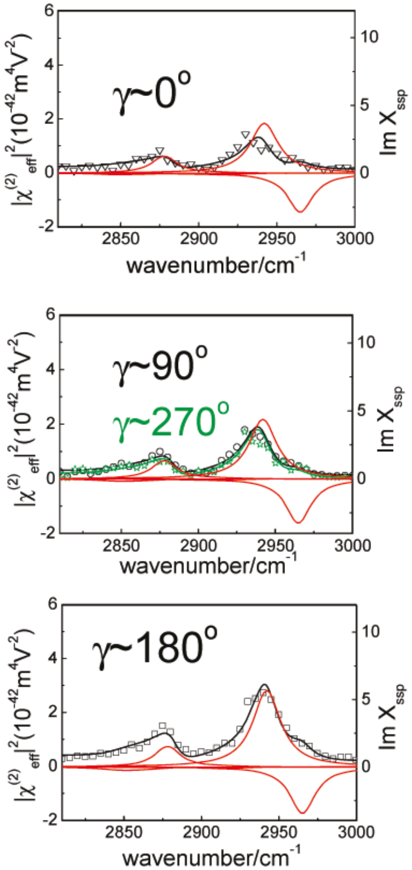
Goal: interfacial structure at the liquid-mineral interface.

Unlike adsorbed water, vibrational modes of adsorbed organics can be distinguished from surface modes.

Recent spectroscopic results suggest that strongly adsorbed organics form an ordered structure at oxide surfaces:

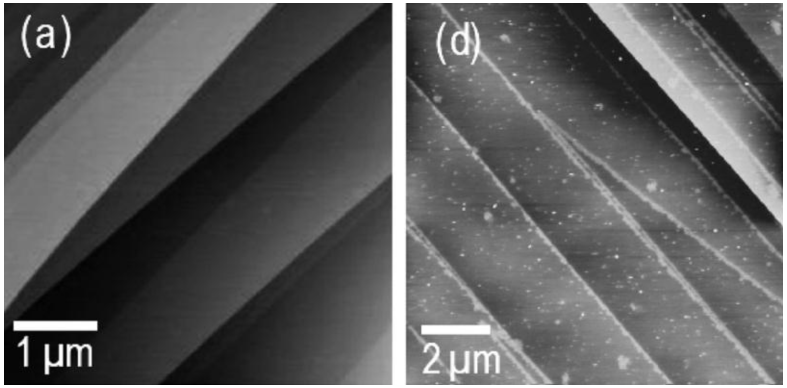
SFVS of ethanol on alumina

Comparison of CH_2 vibrational modes at different incident angles indicates two well-ordered ethanol layers on the surface.
Sung, Waychunas, and Shen, *J. Phys. Chem. Lett*. **2012**.

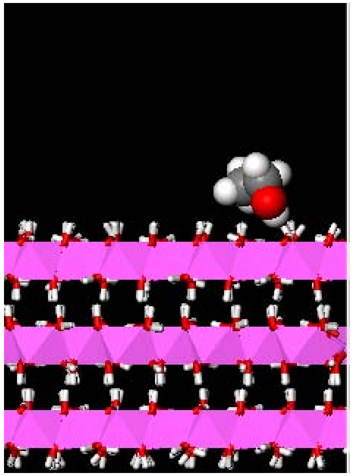


AFM of ethanol on calcite

Calcite cleaved in ethanol results in crystallization at edges and terraces.
Sand et al, *Langmuir* **2010**.



Organic Adsorption: Alcohols and Thiols on LDH Surfaces



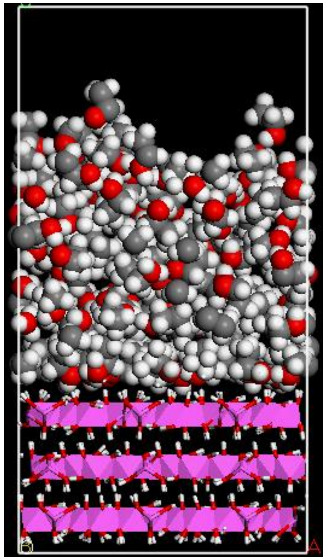
Ethanol on gibbsite

Surfaces: $Al(OH)_3$ (gibbsite), FeOOH (lepidocrocite), C (graphite), 10-15 Å thickness.

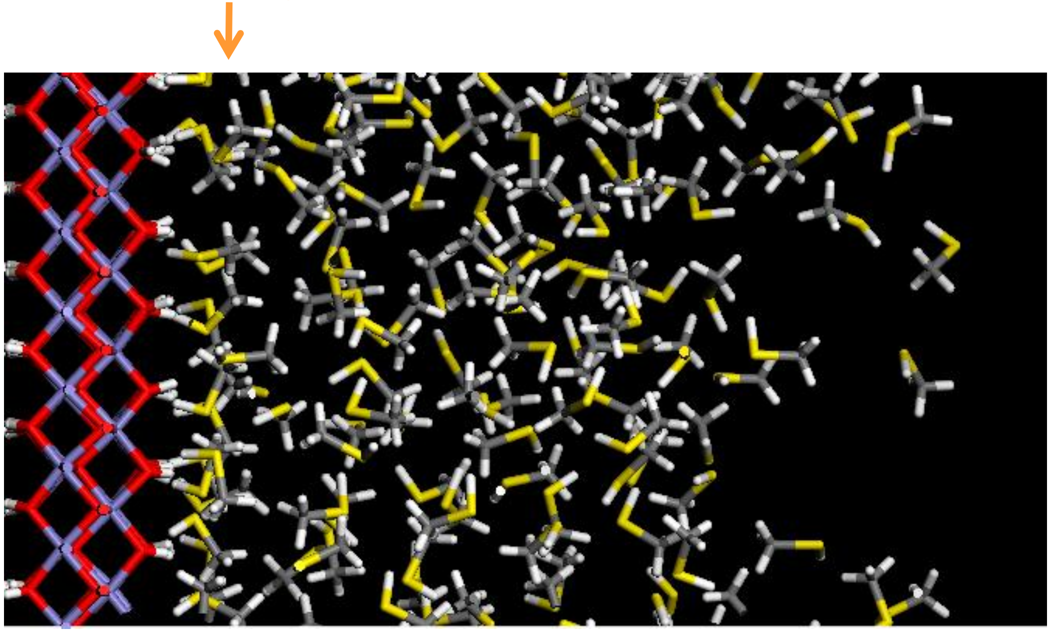
NVT simulations: ClayFF parameters for LDHs, OPLS parameters for organics and graphite.

2 adsorption regimes:

- **Infinite dilution:** adsorption enthalpy, surface complex geometry.
- **Liquid:** Structure and surface density of monolayer.



Monolayer

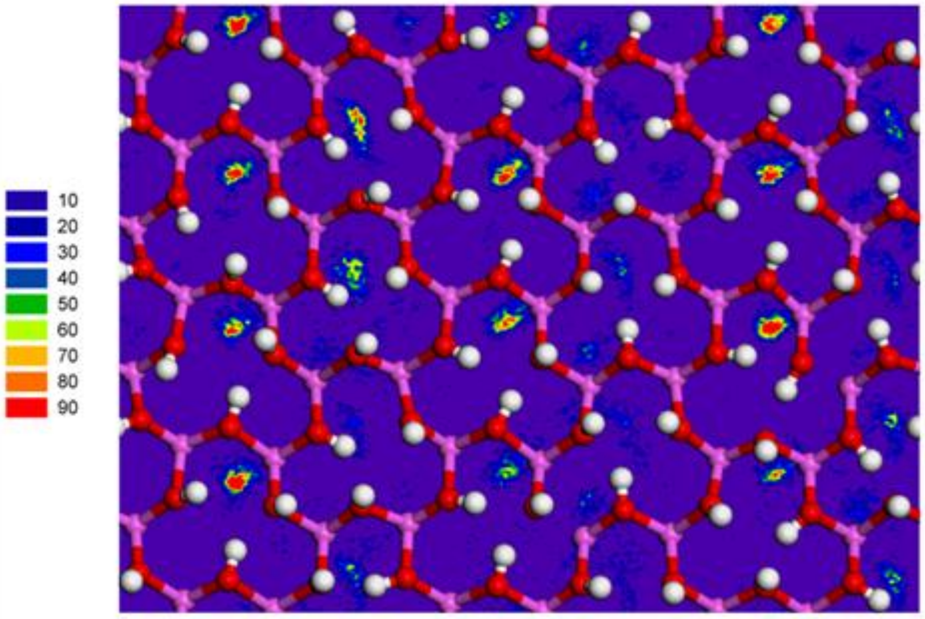


Liquid methanethiol on lepidocrocite

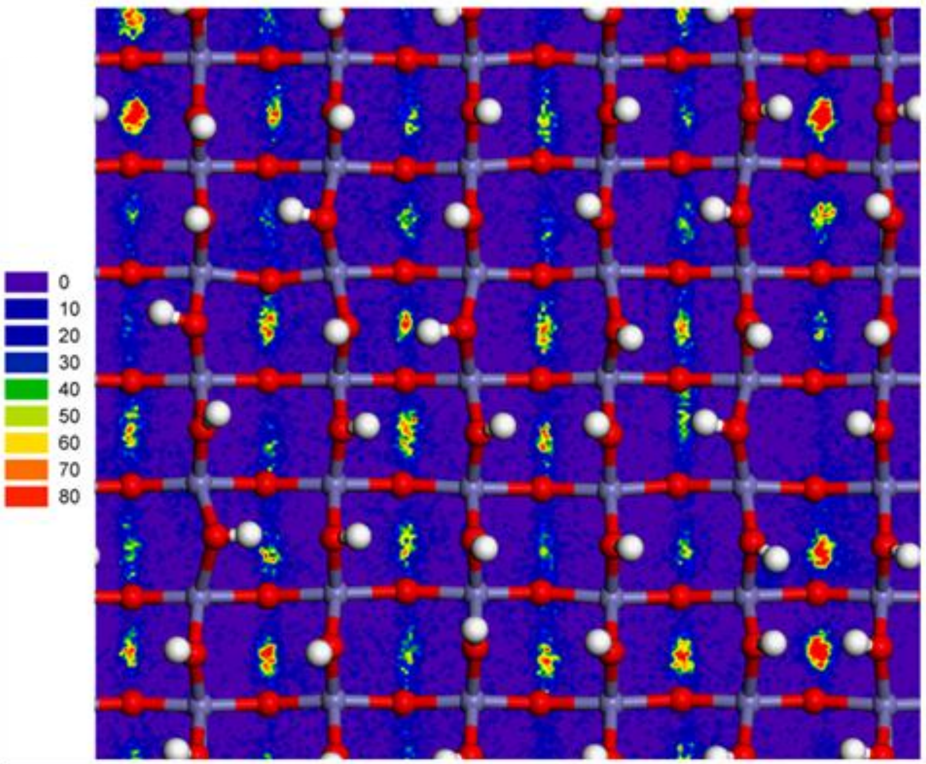
Greathouse, Hart, and Ochs
J. Phys. Chem. C **2012**.

2D Density Plots of Ethanol Adsorption

$Al(OH)_3$

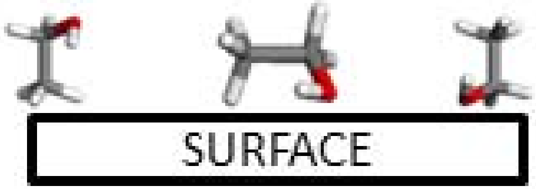


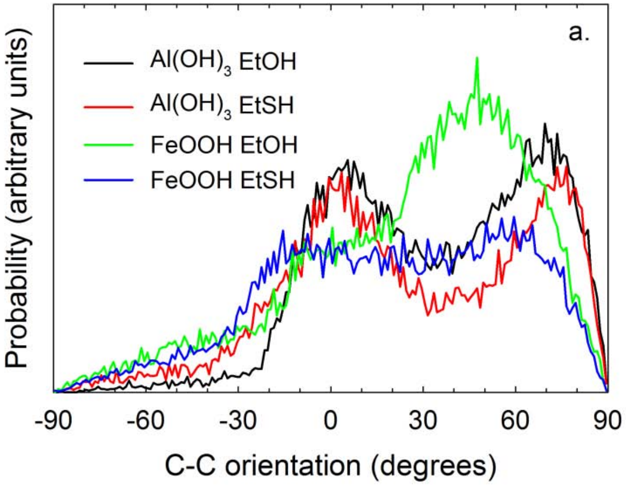
FeOOH

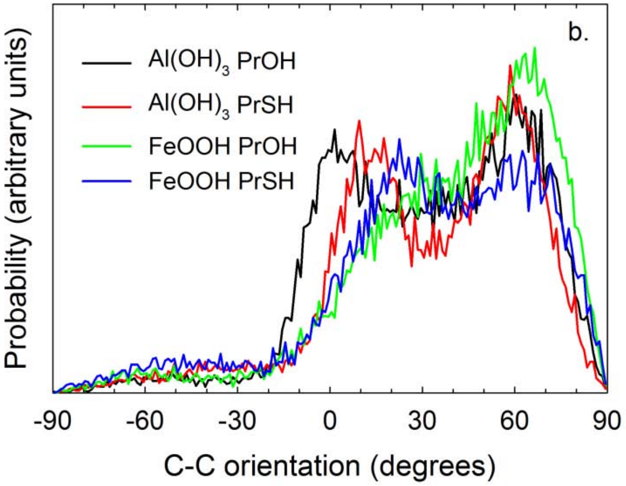


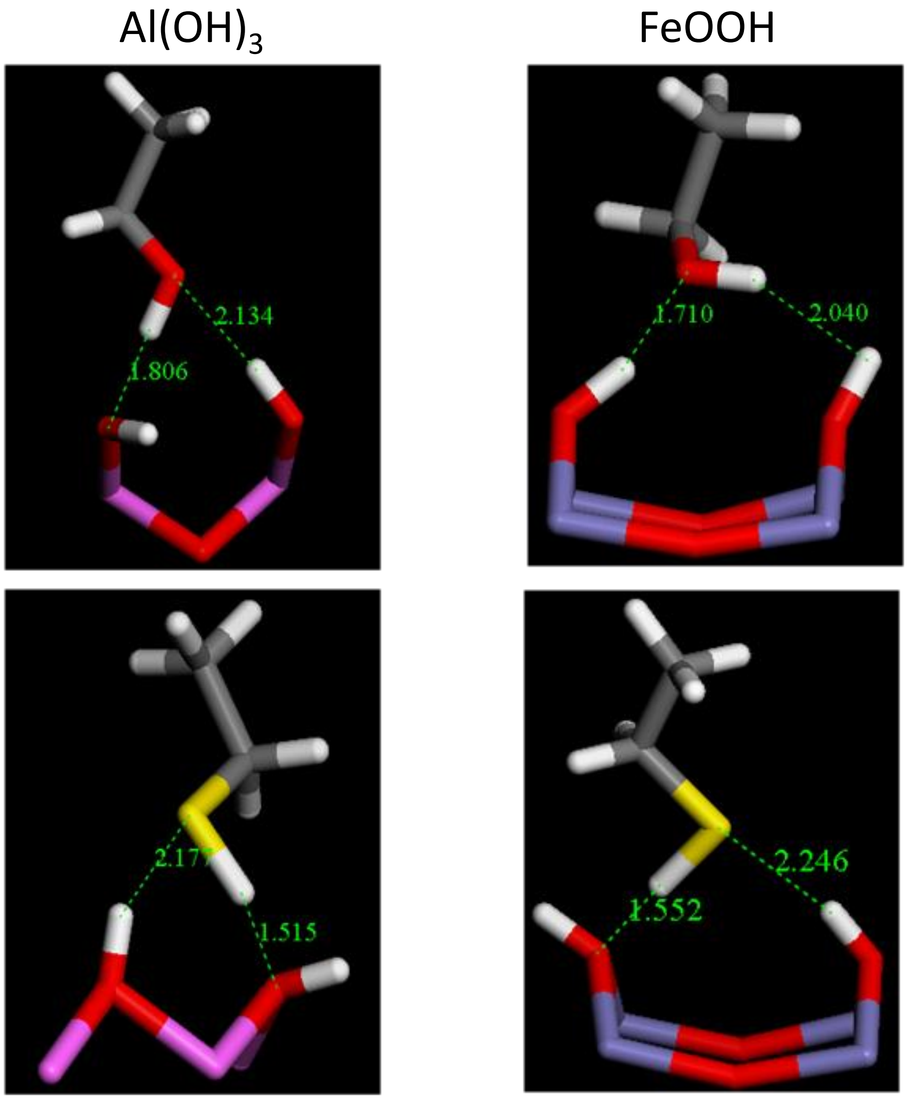
- Surface adsorption sites maximize H-bonding between O(S)H groups and surface hydroxyl groups.
- Trends in adsorption enthalpies in agreement with experimental values for alumina and activated carbon.

Adsorbate Orientation on LDH Surfaces



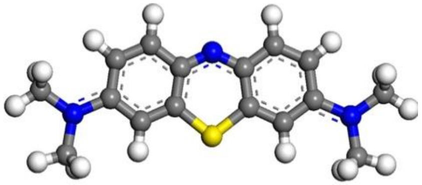




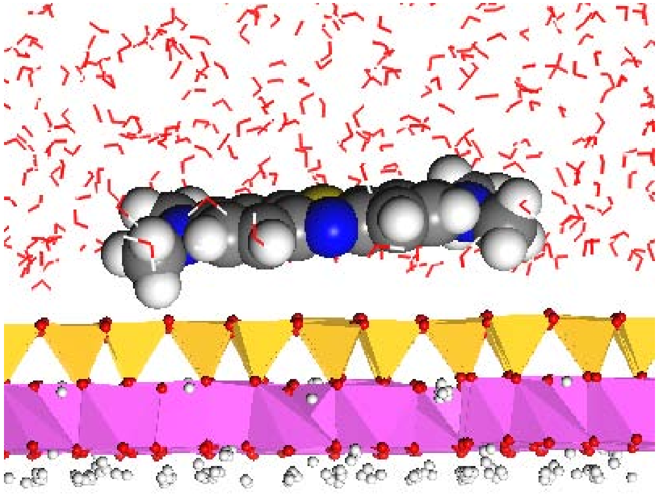


Bifurcated H-bonding with LDH surfaces.
Preferred adsorbate orientations are consistent with related DFT and SFVS results.

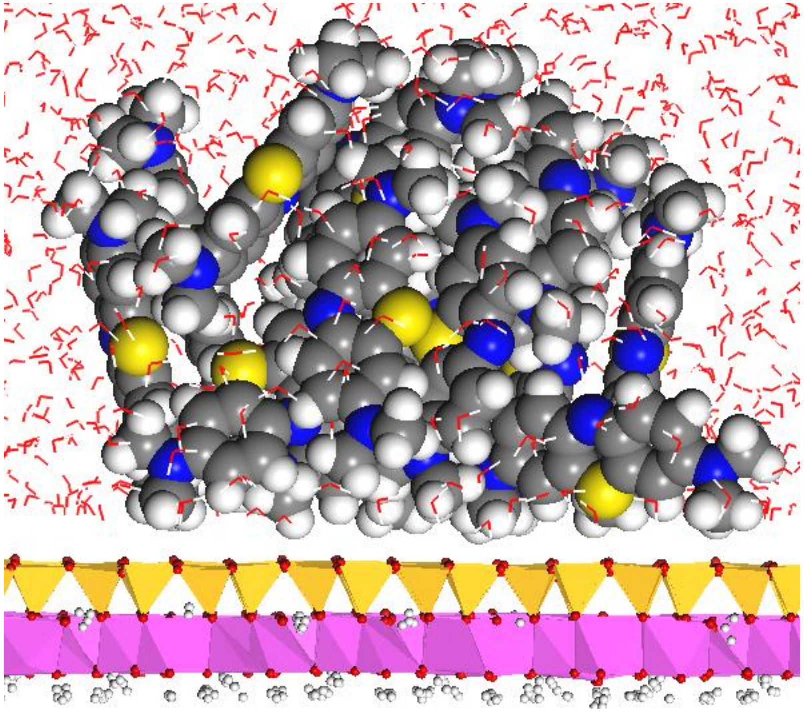
Organic Adsorption: Methylene Blue on Kaolinite



- Methylene blue is commonly used in surface area determinations.
- Compare simulated vibrational spectra of surface-adsorbed methylene blue with IR spectroscopy (Cliff Johnston, Purdue).
- MD simulations of aqueous methylene blue cation at 1) infinite dilution and 2) high concentration.
- Hydrophobic siloxane surface preferred, cation-cation interactions stronger than cation-surface interactions.
- Simulation of vibrational spectra in progress.



Infinite dilution



High concentration (12 cations)

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