Molecular Adsorption on (Oxy)hydroxide and Carbon Surfaces
Studied by Molecular Simulation and Desorption Experiments

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Objective

The adsorption of contaminant molecules on inorganic surfaces plays a central role in the fate these contaminants in the environment. Comparison of adsorption/desorption experiments with molecular dynamics (MD) simulation allows the identification of attractive surface sites for adsorption, as well as the determination of the relative strengths of these interactions. Understanding the adsorption of these compounds and the relative strength of their attraction to surfaces will allow for improved catalyst development, better materials selection for deployed surfaces, and the development of practical decontamination strategies.

MD simulations are used to compare trends in the adsorption structure and thermodynamics of small alcohols and thiols onto idealized $Al(OH)_3$ and $FeOOH$ surfaces. Simulation results are compared with experimental results on the desorption of small alcohols on aluminum hydroxide. A comparison of adsorption properties on these inorganic surfaces with a hydrophobic surface representative of activated carbon (graphite) allows us to directly determine the effect of hydrophilic surface sites and hydrogen bonding on adsorption.

Small alcohols and thiols (methyl, ethyl, n-propyl or C1 – C3) included in the present study contain functional groups found in many chemicals of industrial or technical interest, and their interactions with (oxy)hydroxide surfaces represent the likely adsorption mechanism of larger organics with similar functional groups. A comparison of alcohol/thiol adsorption thermodynamics on idealized surfaces allows us to better understand the fundamental aspects of molecular adsorption as well as the influence of functional groups on adsorption.

C1   C2   C3
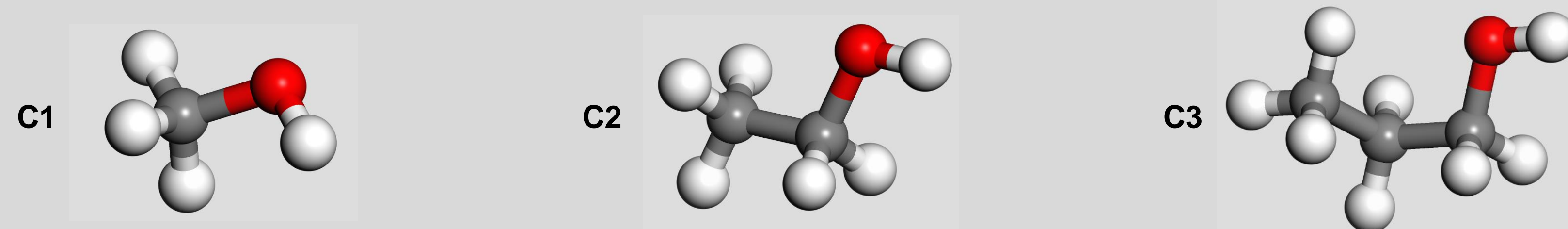
Methods

MD Simulation
- Standard force fields were used for organics[1], inorganic surfaces,[2] and graphite.[3]
- Surface coverages:
  1. Infinite dilution (single molecule) for adsorption energy calculations.
  2. Liquid layer to determine monolayer coverage, adsorption sites, and interfacial structure.
- Simulations were performed with the LAMMPS code[4] at 27 °C.
- Adsorption enthalpy ΔH_{ads} calculated from: $\Delta H_{ads} = \langle U_{gh} \rangle - \langle U_g \rangle - RT$

  Where: U_{gh} = potential energy of the adsorbed guest molecule
  U_g = potential energy of the adsorbate in the ideal gas reference state
  R = gas constant
  T = thermostat temperature
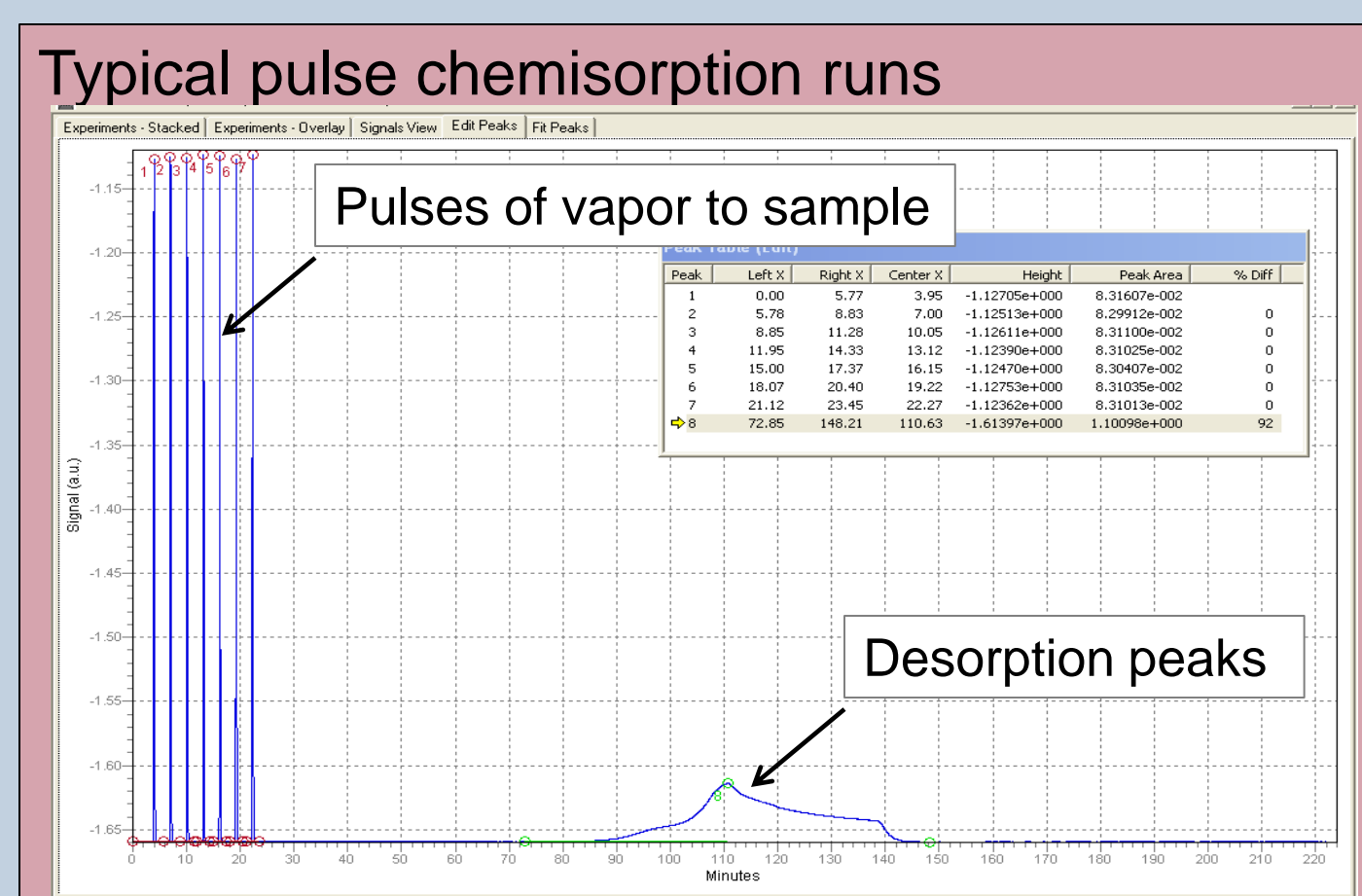
Ethanol on $Al(OH)_3$ Ethanol on $FeOOH$
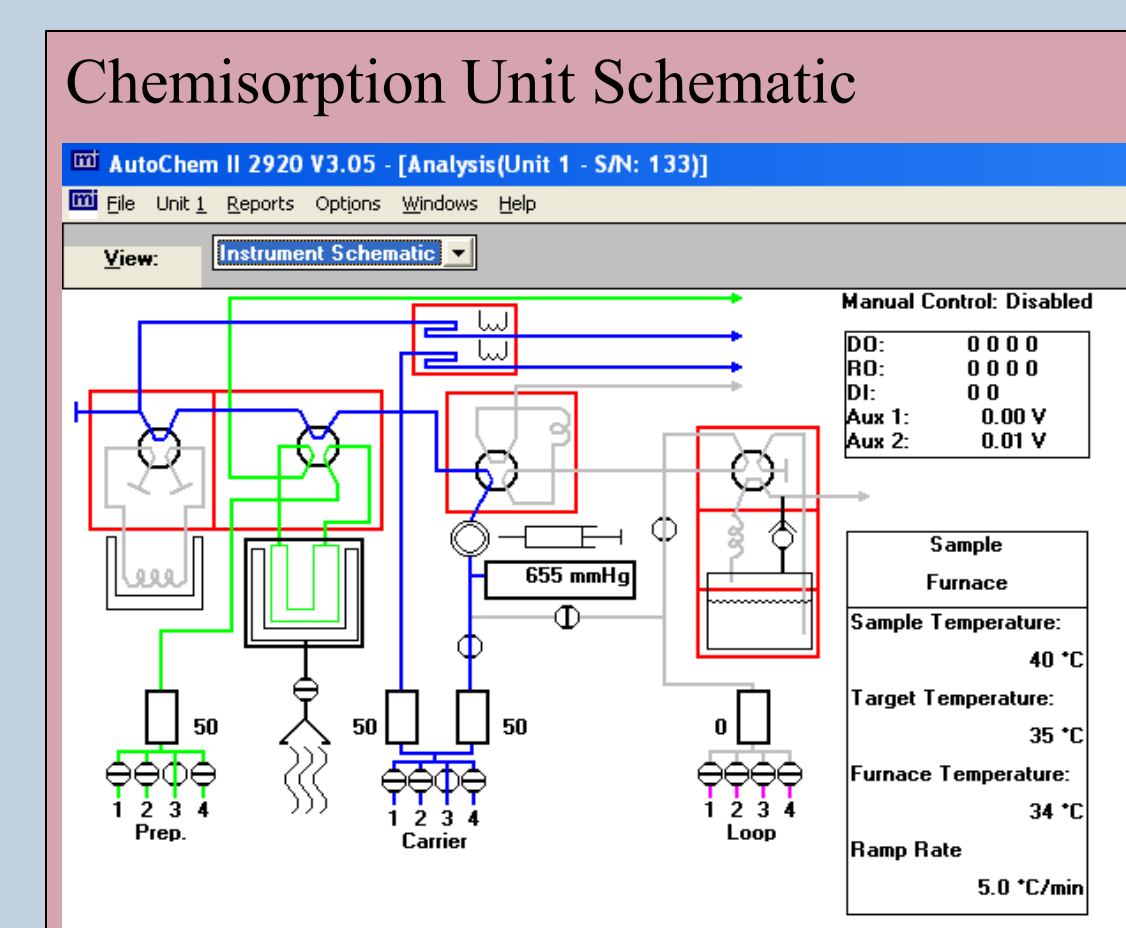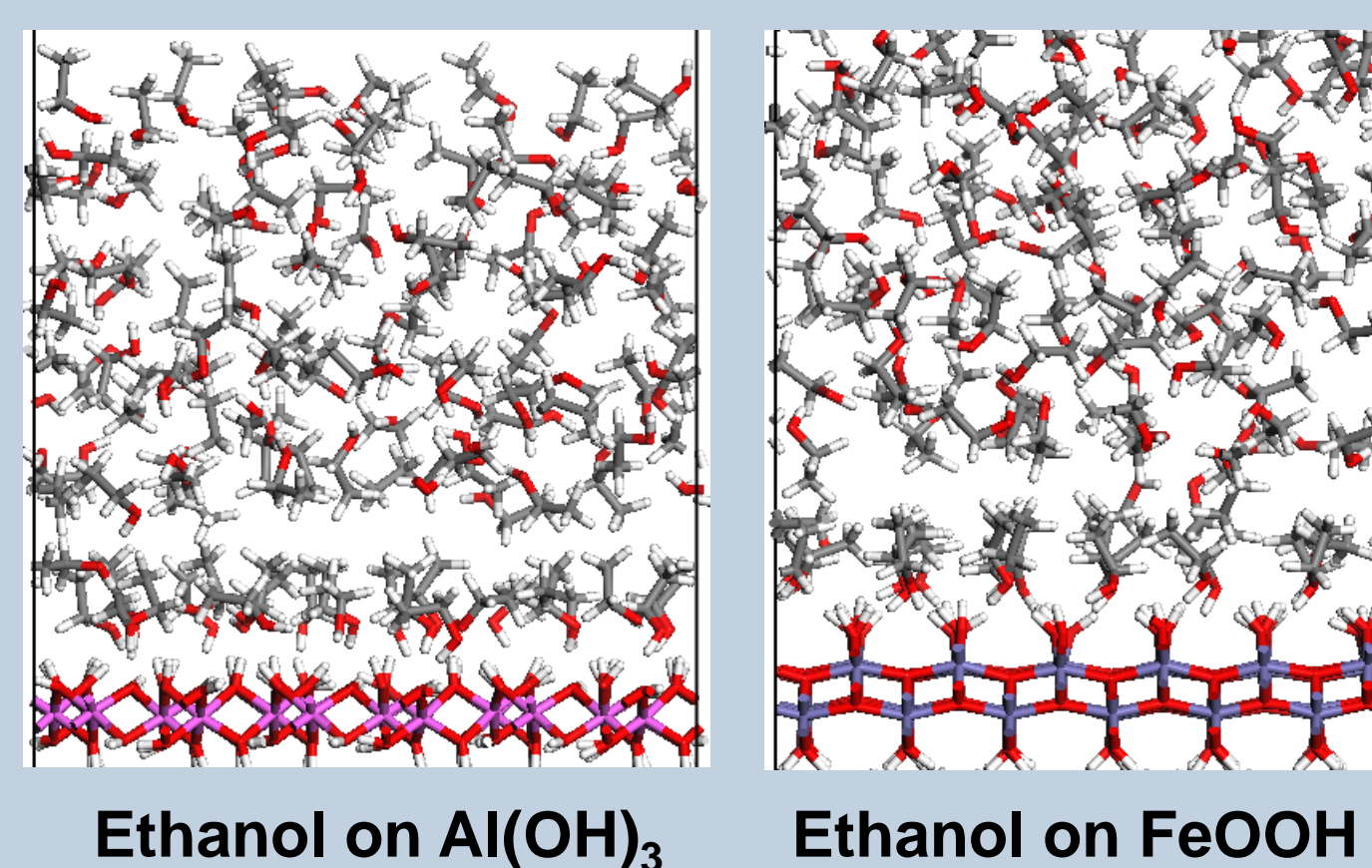
Desorption Experiments
Laboratory work employed a Chemisorption unit (Micromeritics Autochem 2920) to determine a molecule's heat of desorption, E_d (kJ/(mol·K)).

The general equation is: $\ln(\beta/T_p^2) = -E_d/RT_p + \ln(E_d A/RC)$

Where: β = ramp rate (deg/min)
T_p = Temperature at peak max (K)
E_d = Heat of Desorption (kJ/mol K)
R = gas constant
A = quantity of gas adsorbed at saturation
C = desorption rate constant

Three desorption experiments were run with different ramp rates. By plotting: $2\ln T_p - \ln \beta$ vs. $1/T_p$, the slope of the line is E_d/R.

Chemisorption Unit Schematic

Typical pulse chemisorption runs

Pulses of vapor to sample

Desorption peaks

The pulse chemisorption experiment begins with a degas step to 600 °C. The sample is cooled to room temperature, then dosed with adsorbate until saturation, which is determined by a thermal conductivity (TCD) detector. The furnace then heats the sample at a specified ramp rate, and the desorbing gas is monitored. In these experiments, the samples were heated to 600 °C between 2 and 15 deg/min.
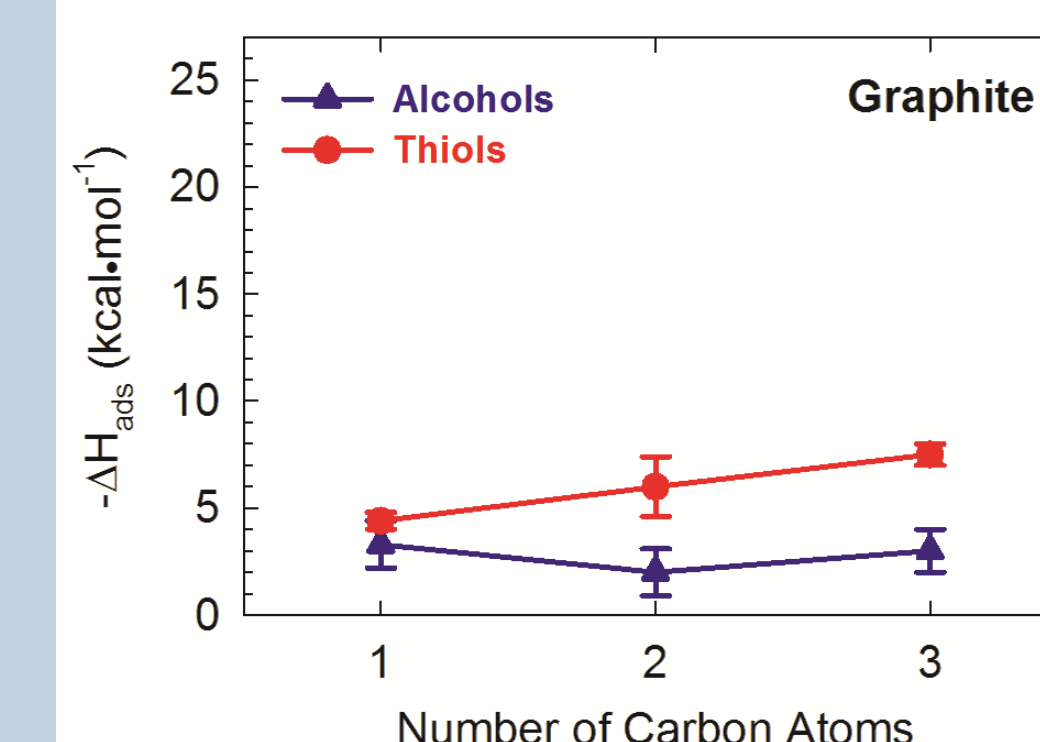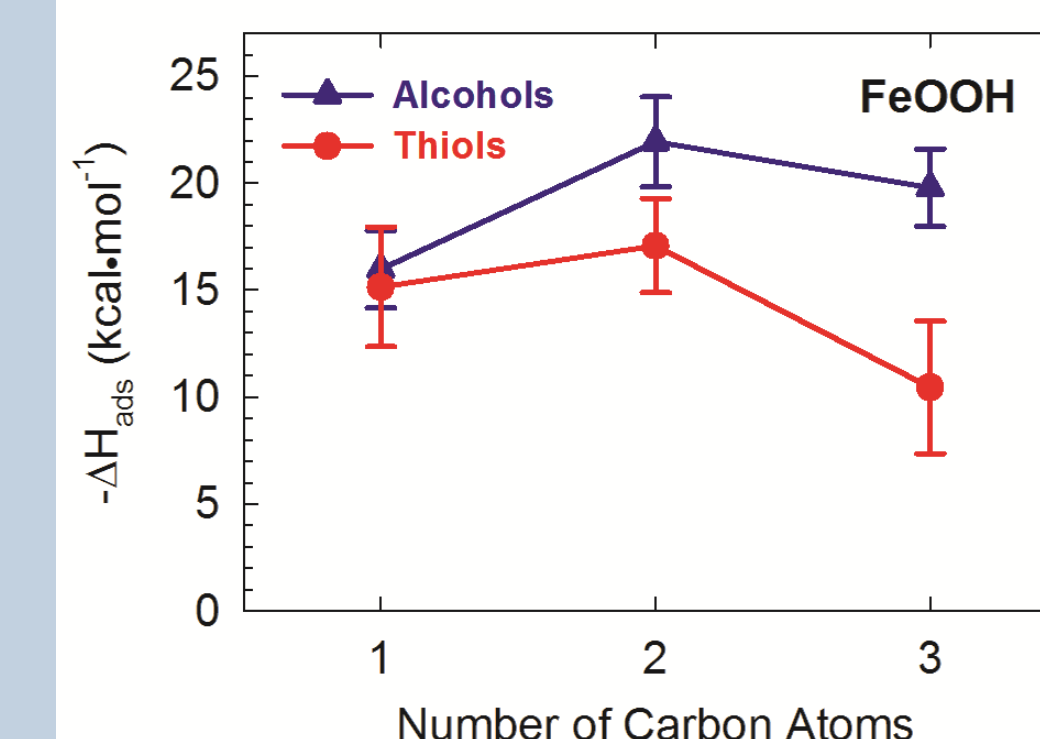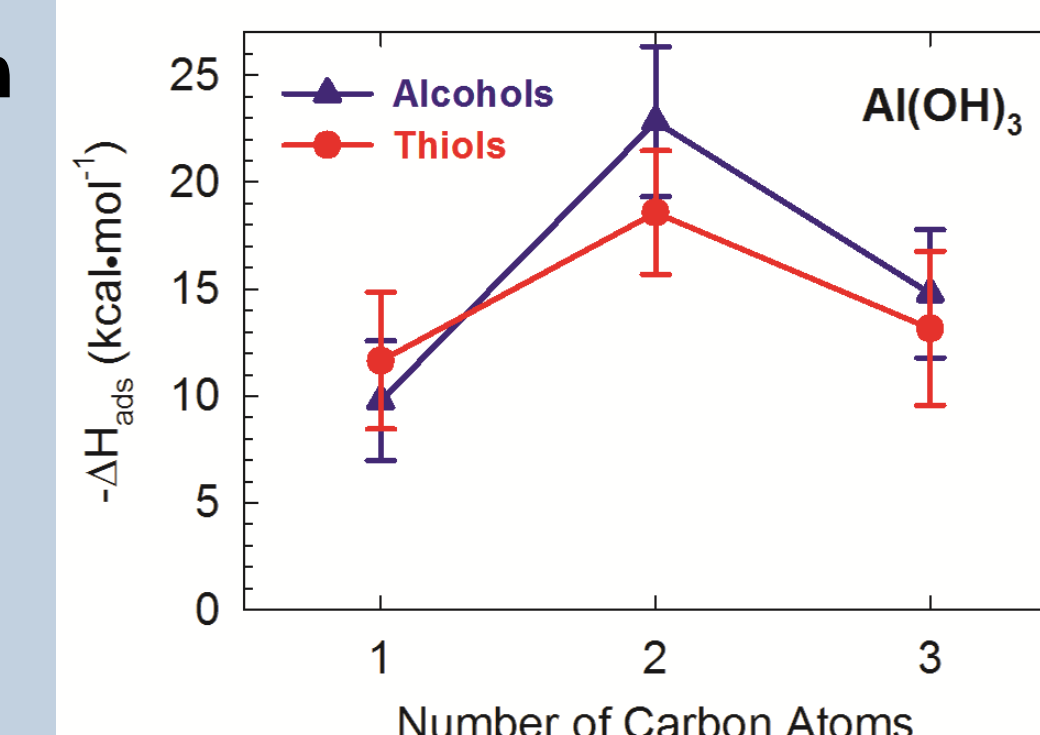
Results

Experimental Desorption Enthalpies

Ethanol on Alumina

y = -14150x - 30.619
R² = 0.9522

— $Al(OH)_3$
— Activated Carbon
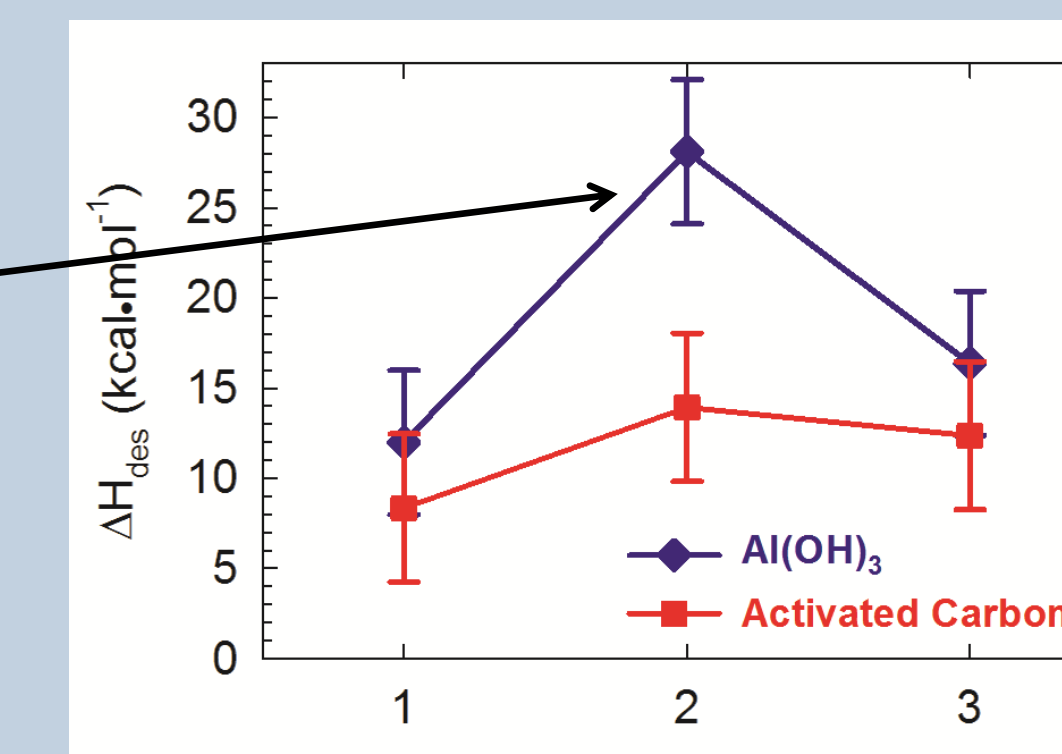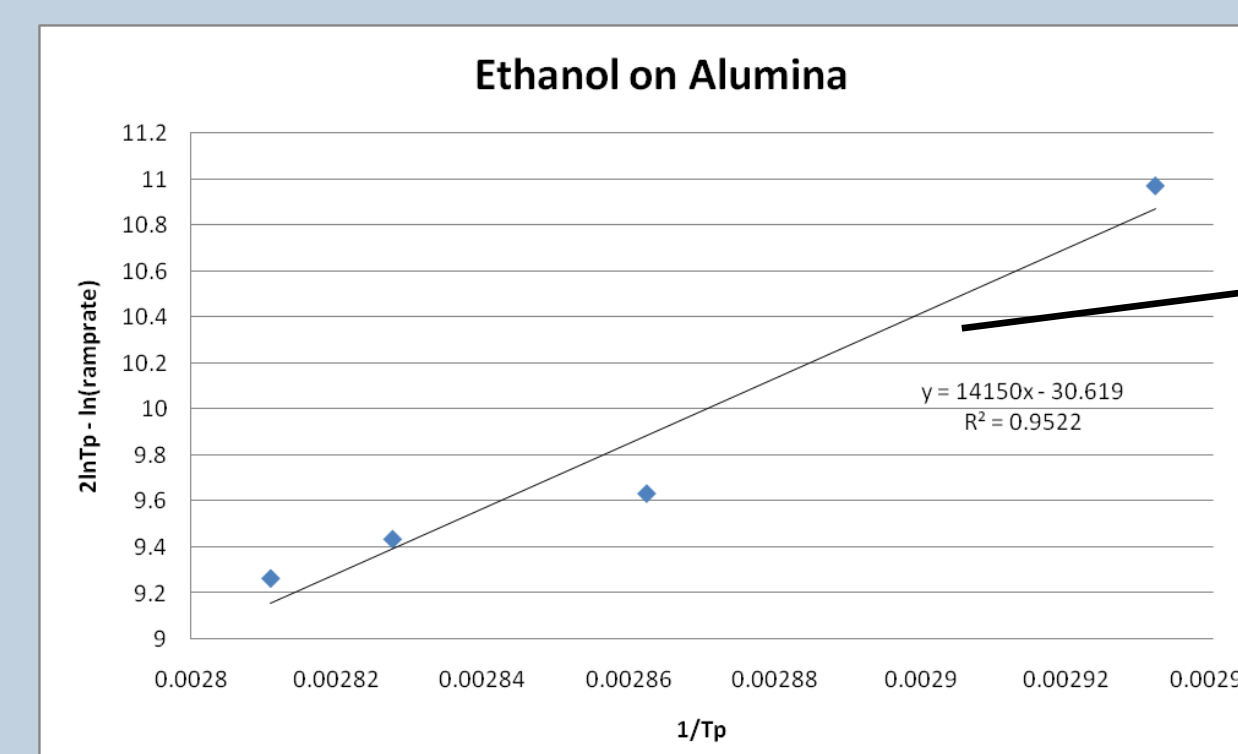
Simulated Adsorption Enthalpies

Compare with simulation

Al(OH)₃ — Alcohols / Thiols

FeOOH — Alcohols / Thiols

Graphite — Alcohols / Thiols

Comparison of adsorption/desorption enthalpies
- Excellent agreement between experimental desorption energies and simulated adsorption enthalpies.
- Experimental values for activated carbon are greater than simulated values for graphite due to the presence of functionalized adsorption sites in activated carbon.
- Adsorption of small alcohols and thiols is much more favorable on the (oxy)hydroxide surfaces than on carbon surfaces due to the presence of guest-surface hydrogen bonds in the former.
- Alcohols adsorb more strongly than thiols on (oxy)hydroxide surfaces based on the electronegativity difference between oxygen (3.4) and sulfur (2.6).
- Adsorption enthalpies on (oxy)hydroxide surfaces follow the trend C2 > C3 > C1 rather than that expected based on enthalpies of vaporization (C3 > C2 > C1).

### Monolayer Surface Densities

$Al(OH)_3$ — Alcohols / Thiols

FeOOH — Alcohols / Thiols
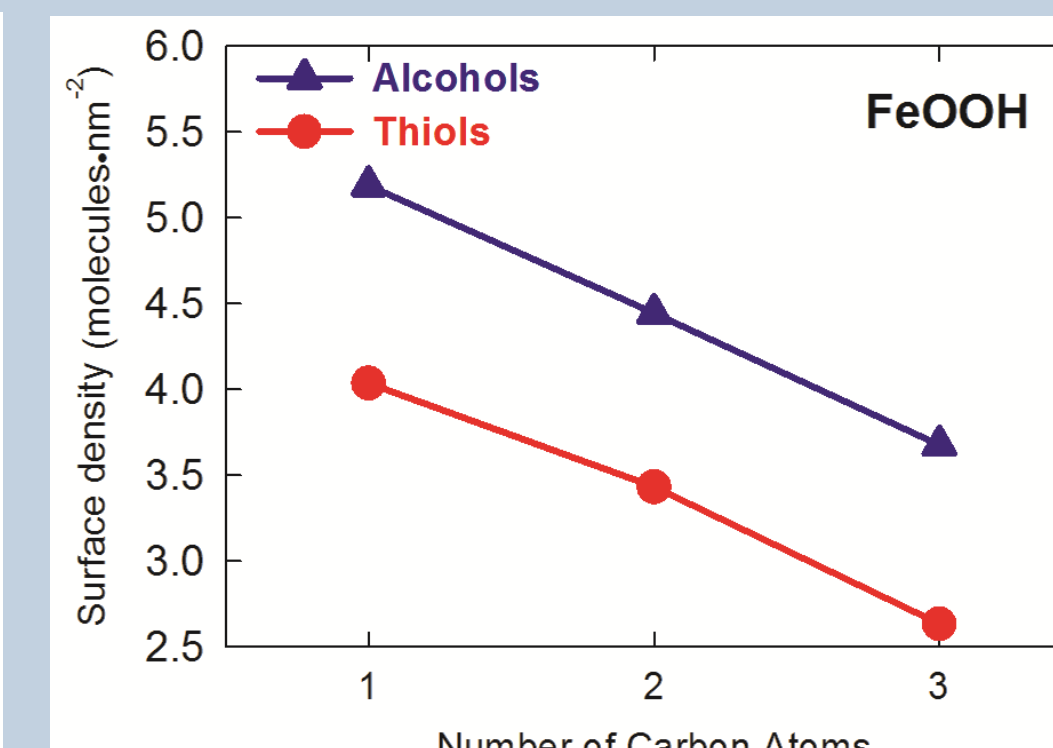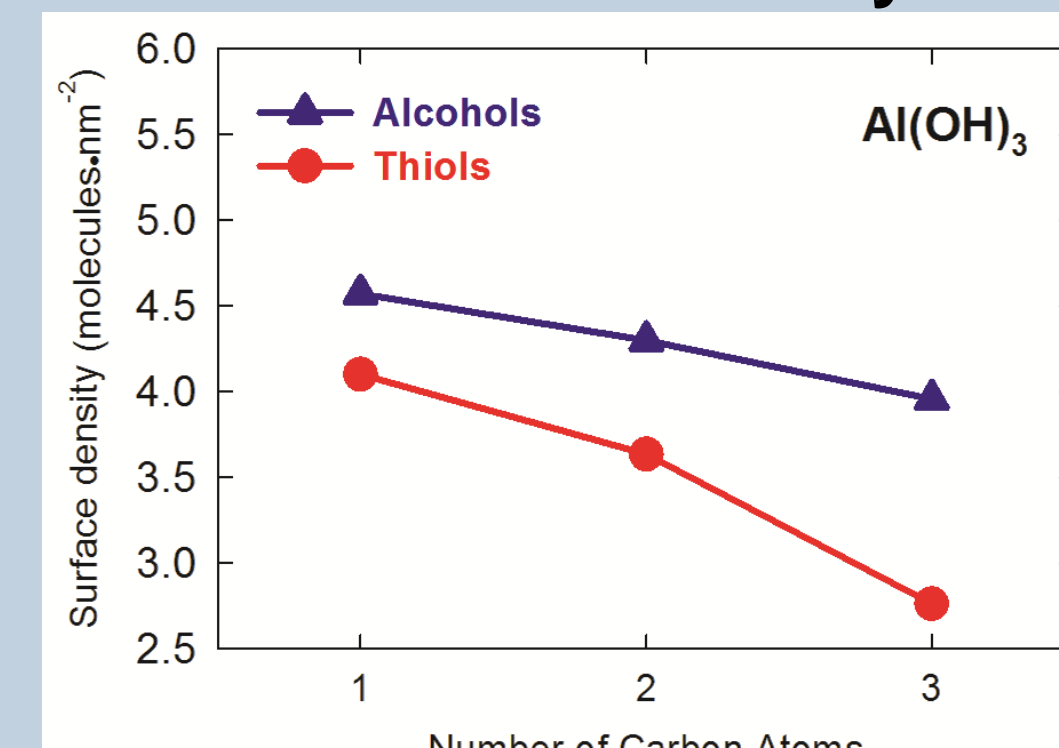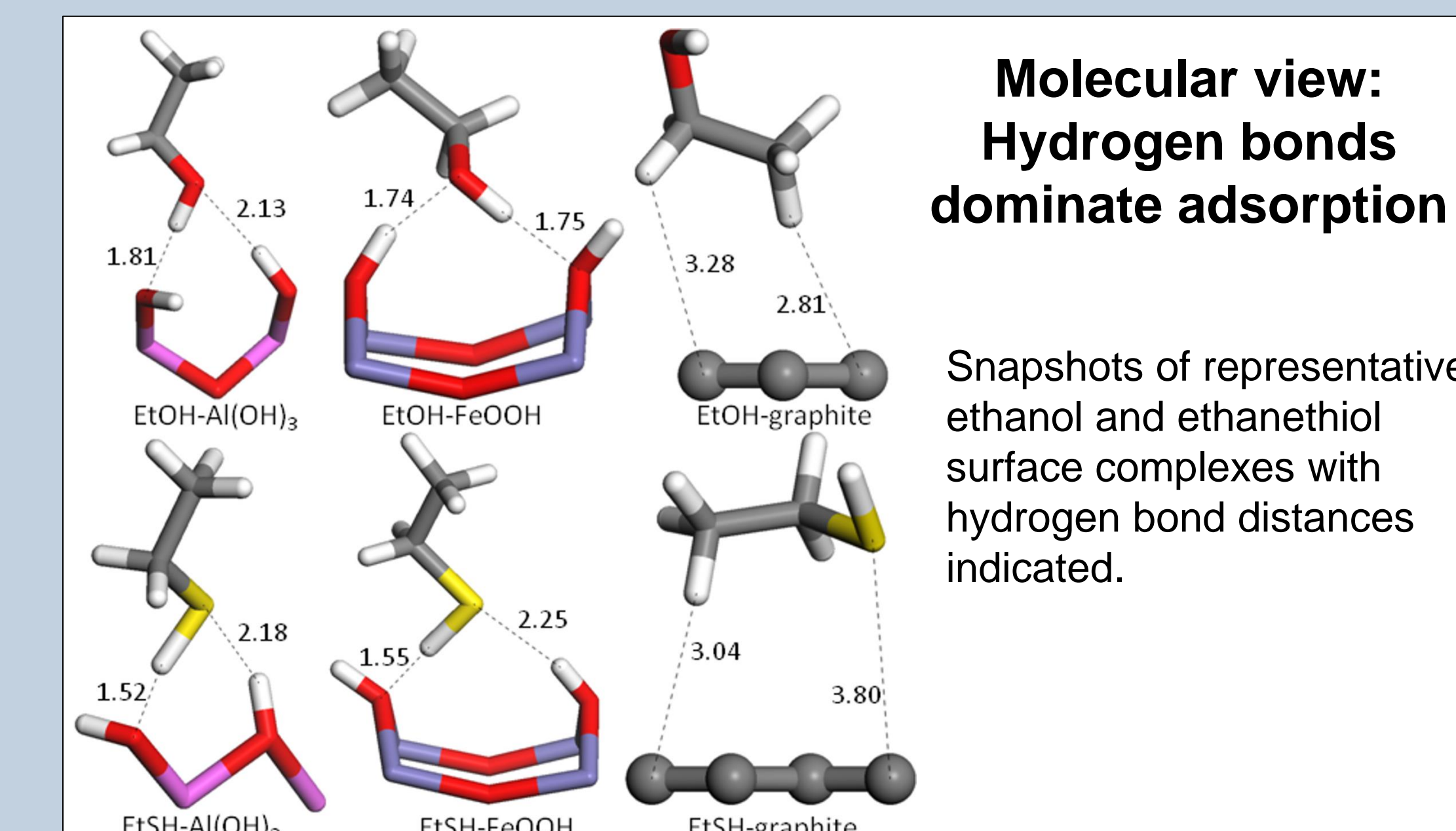
Determination of monolayer coverage from MD simulations
- Monolayer surface concentrations were determined from one-dimensional atomic density profiles.
- Monolayer densities follow the trend (C1 > C2 > C3) expected from steric and molecular size effects.
- Theoretical maximum monolayer densities are 6.8 sites/nm² ($Al(OH)_3$) and 8.3 sites/nm² (FeOOH).
- Densities are slightly higher on graphite (not shown) due to absence of strong surface-adsorbate interactions (hydrogen bonds).

Adsorption Sites

$Al(OH)_3$ FeOOH

22 Å   24 Å
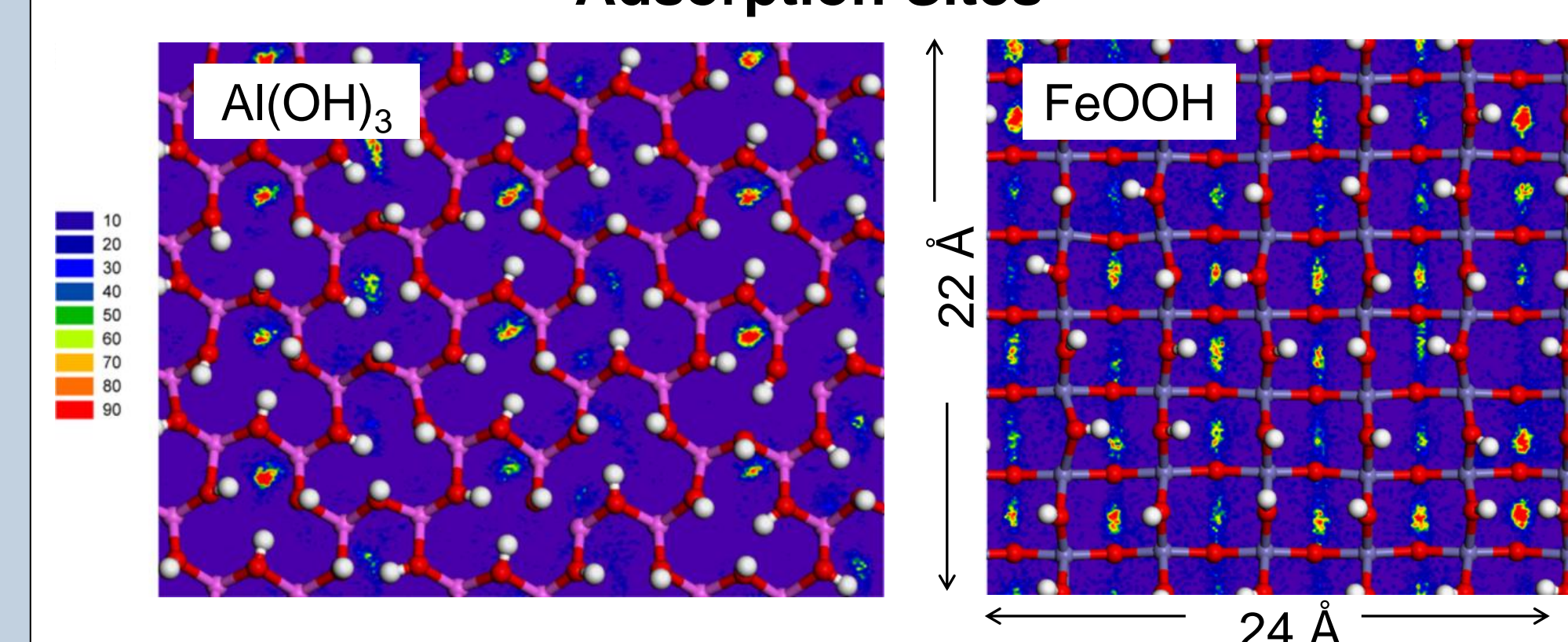
Two-dimensional probability density plots identify adsorption sites on each surface (shown for ethanol molecules). Primary adsorption sites occur over surface cavities that maximize surface-guest hydrogen bonding.

Molecular view: Hydrogen bonds dominate adsorption

1.81   2.13   1.74   1.75   3.28
2.81

EtOH-Al(OH)₃   EtOH-FeOOH   EtOH-graphite

1.52   2.18   1.55   2.25   3.04
3.80

EtSH-Al(OH)₃   EtSH-FeOOH   EtSH-graphite

Snapshots of representative ethanol and ethanethiol surface complexes with hydrogen bond distances indicated.

Conclusions
- Modeling and experimental values for the adsorption enthalpies and heats of desorption of C1-C3 alcohols are in good agreement.
- The (oxy)hydroxide surfaces display amphoteric behavior with respect to adsorbed alcohols and thiols. The increased electrostatic interaction between surface and adsorbate due to hydrogen bonding dominates the structure and energy of surface complexes.
- The large adsorption enthalpies calculated from simulations at infinite adsorbate dilution are also due to hydrogen bonding and are much larger than the adsorption enthalpies on the hydrophobic graphite or activated carbon surfaces.
- These results should inform future studies on the adsorption of polar organic onto inorganic surfaces.

References
1. Jorgensen, W. L.; Maxwell, D. S.; Tirado-Rives, J. *J. Am. Chem. Soc.* **1996**, *118*, 11225.
2. Cygan, R. T.; Liang, J.-J.; Kalinichev, A. G. *J. Phys. Chem. B* **2004**, *108*, 1255.
3. Shevade, A. V.; Jiang, S. Y.; Gubbins, K. E. *J. Chem. Phys.* **2000**, *113*, 6933-6942.
4. LAMMPS website: http://lammps.sandia.gov
5. Greathouse, J. A.; Hart, D. B.; Ochs, M. E. *J. Phys. Chem. C* **2012**, *116*, 26756.

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