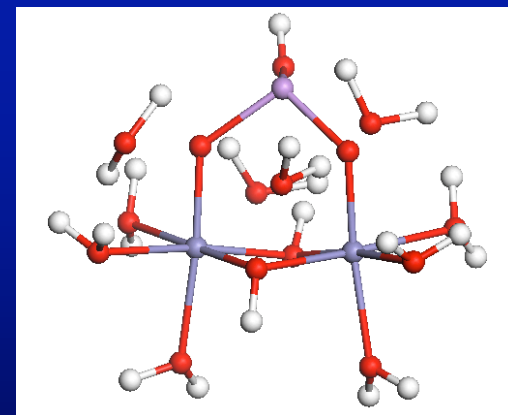
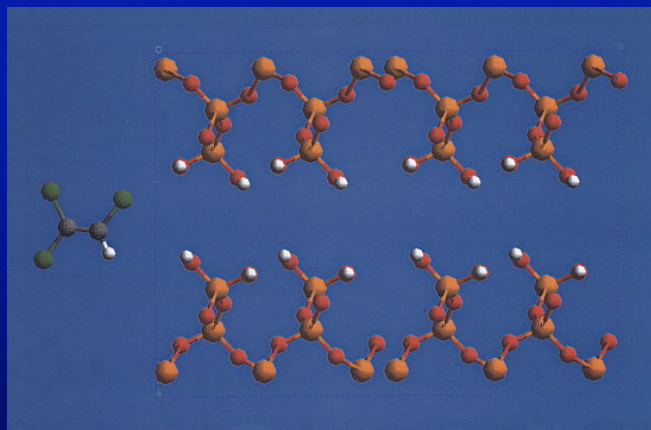
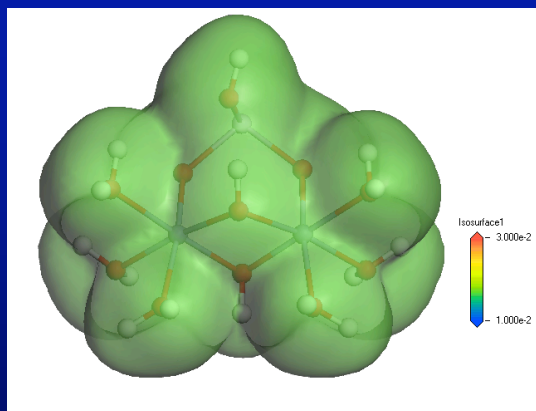
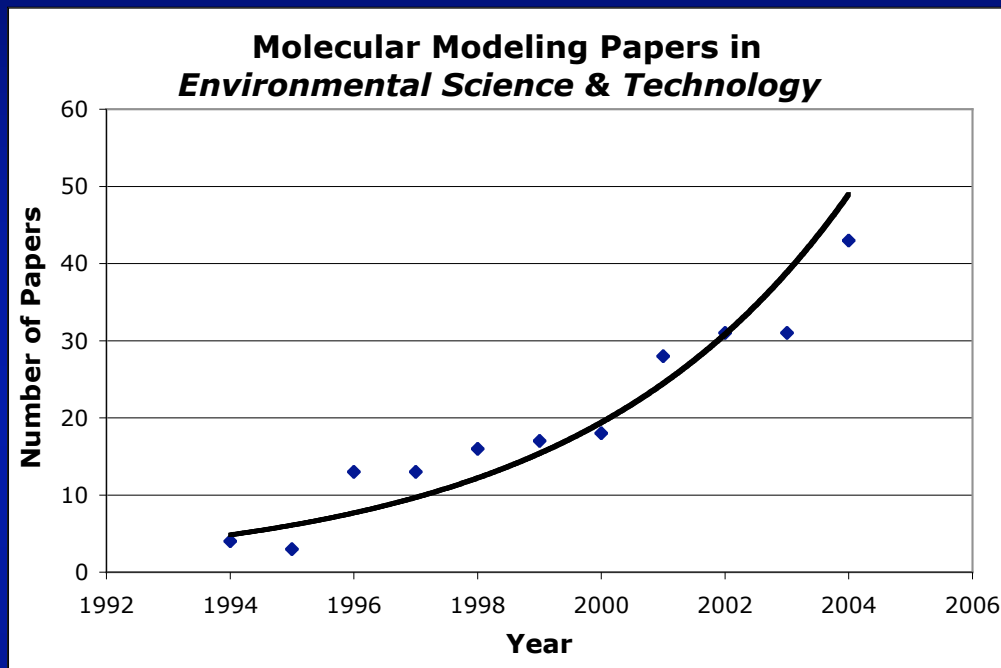


Ab Initio and Force Field Modeling of Sorption Phenomena Associated with Water Treatment

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Molecular Modeling



- Quasi-exponential growth in modeling.
- Will replace i-Pod as the latest fad by 2009*.

*estimation based on current trends

Outline

- **Computational methods**
- **TCE adsorption in adsorbent micropores**
- **Chemisorption of TCE and PCE on iron surfaces**
- **Complexation of H_3AsO_3 with ferric hydroxides**

Computational Methods

All are based on energy minimization or conformance with a Boltzmann distribution of energies.

Molecular Mechanics - Empirical Force Fields (physical interactions)

Monte Carlo Methods (MC)

Canonical Monte Carlo

Grand Canonical Monte Carlo

Molecular Dynamics (MD)

Quantum Mechanics Methods (QM) - Ab Initio (chemical reactions)

Molecular Orbital (MO)

Density Functional Theory (DFT)

Properties Accessible by Calculation

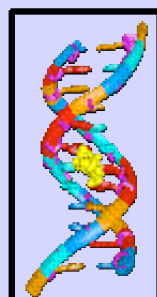
- **molecular properties:** bond lengths, bond angles, bond energies, vibrational spectra, partial atomic charges, dipole moments
- **arrangements of molecular systems:** crystal structure, associations in solution, identification of adsorption or enzyme binding sites
- **thermodynamic properties:** heat capacities, equilibrium constants and activation energies for reactions, Henry's law constants, solubilities, enthalpies and Gibbs energies of formation, reaction and adsorption
- **transport properties:** diffusion coefficients, viscosities
- **time evolution of molecular systems**

Methods Comparison



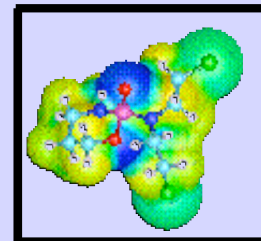
**Molecular
Mechanics**

**100,000
atoms**



**Semi-Empirical
Quantum Mechanics**

**1000
atoms**



***ab initio*
Quantum Mechanics**

**100
atoms**

**Use Empirically-Derived
Potential Function**

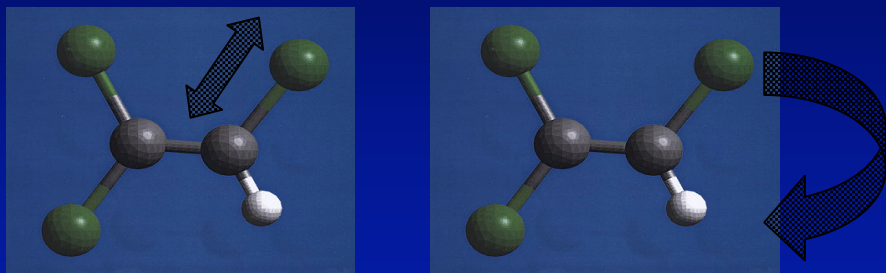
**Solve Approximate
Schrodinger Equation**

**Solve Exact
Schrodinger Equation**

Empirical Parameters Needed

Computationally Demanding

Molecular Mechanics Force Field



Parameters for each **atom type** may be empirically measured or determined from *ab initio* calculations.

$$E_P = \underbrace{E_B + E_A + E_T + E_I}_{\text{bonded}} + \underbrace{E_{\text{vdW}} + E_{\text{Elec}}}_{\text{nonbonded}}$$

E_B = bond stretch energy

E_A = angle bending energy

E_T = dihedral angle torsion energy

E_{op} = out of plane bending energy

E_{vdW} = van der Waals energy

E_{elec} = electrostatic energy

$$E_p(\mathbf{r}^N) = \sum_{\text{bonds}} \frac{k_i}{2} (l_i - l_{i,o})^2 + \sum_{\text{angles}} \frac{k_i}{2} (\theta_i - \theta_{i,o})^2 + \sum_{\text{torsions}} \frac{V_n}{2} [1 + \cos(n\omega - \gamma)] + \sum_{\text{op-angles}} \frac{k_i}{2} \theta_i^2$$

$$+ \sum_{i=1}^N \sum_{j=i+1}^N \left(4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] + \frac{q_i q_j}{4\pi\epsilon_o r_{ij}} \right)$$

Quantum Mechanics - Molecular Orbital Theory

Schrödinger Equation $\hat{H}\psi = E\psi$ $\langle E \rangle = \int \psi^* \hat{H}\psi \, d\mathbf{r}$

$\psi(\mathbf{r}) =$ N electron wave function for the system

$$\hat{H} = -\sum_A \frac{1}{2M_A} \nabla_A^2 - \sum_i \frac{1}{2} \nabla_i^2 + \sum_{i,j>i} \frac{1}{r_{ij}} - \sum_{i,A} \frac{Z_A}{r_{iA}} + \sum_{A,B>A} \frac{Z_A Z_B}{R_{AB}}$$

The diagram illustrates the components of the Hamiltonian operator \hat{H} in the equation above. The terms are annotated as follows:

- $-\sum_A \frac{1}{2M_A} \nabla_A^2$: Kinetic energy of nuclei (labeled as **neglected**)
- $-\sum_i \frac{1}{2} \nabla_i^2$: Kinetic energy of electrons
- $\sum_{i,j>i} \frac{1}{r_{ij}}$: Electron-Electron repulsion
- $-\sum_{i,A} \frac{Z_A}{r_{iA}}$: Nucleus-Electron attraction
- $\sum_{A,B>A} \frac{Z_A Z_B}{R_{AB}}$: Nucleus-Nucleus repulsion (labeled as **constant**)

Red brackets group the first two terms as **Kinetic energy** and the last three terms as **Potential**.

ψ is unknown but can be **approximated** as a product of one electron wave functions.

Single electron wave functions can be approximated as a linear combination of single electron atomic orbital functions.

Variational Principle

- Iterative solution required - best approximate wave function (ψ_{trial}) is the one that gives the lowest energy.
- Goal is to minimize the calculated energy (E_{trial}) by changing the weighting coefficients in the linear combination of atomic orbitals (LCAO).
- Energy given by the approximate wave function (E_{trial}) will be \geq true ground state energy (E_0).

$$\langle \psi_{\text{trial}} | \hat{H} | \psi_{\text{trial}} \rangle = E_{\text{trial}} \geq E_0 = \langle \psi_0 | \hat{H} | \psi_0 \rangle$$

Quantum Mechanics - Density Functional Theory

$$\left[-\frac{1}{2} \nabla_i^2 - \sum_A \frac{Z_A}{r_{iA}} + \int \frac{\rho(\vec{\mathbf{r}}_2)}{r_{i2}} d\vec{\mathbf{r}}_2 + V_{xc} \right] \psi_i(\mathbf{r}_i) = \varepsilon_i \psi_i(\mathbf{r}_i)$$

Kohn Sham Equation

$\psi_i(\mathbf{r}_i)$ = single electron orbital function

$\psi_i(\mathbf{r}_i) \sim$ probability density function for electron i

$$\rho(\mathbf{r}) = \sum_{i=1}^N |\psi_i(\mathbf{r}_i)|^2$$

- For the same level of accuracy, DFT is much faster than MO methods.
- Hamiltonian is not exact: V_{xc} is unknown and must be approximated.
- LCAO used to approximate ψ_i for each electron.
- Iterative solution based on optimizing the coefficients in the LCAO.
- Best set of coefficients gives the lowest energy for each set of atomic positions.
- Energy (E_{trial}) given by the approximate electron density (ρ_{trial}) will be \geq or \leq true ground state energy (E_0) due to errors in V_{xc} .

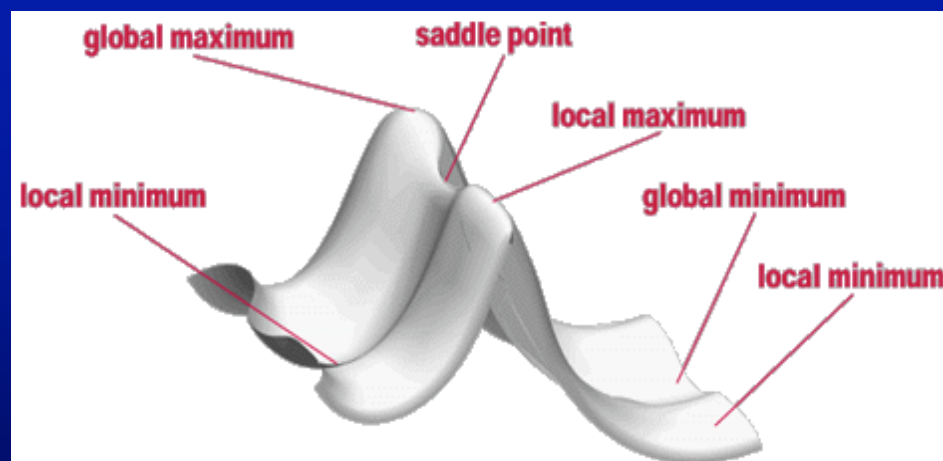
$$E_{\text{trial}}[\rho_{\text{trial}}] \geq \text{or} \leq E_0[\rho_0]$$

Approximation Errors for Quantum Methods

- **Correlation error:** LCAO approximation of ψ averages the electric field arising from the electrons and ignores instantaneous electron-electron repulsion. Electrons may get too close (**Coulomb hole**).
- **Exchange error:** Pauli exclusion principle results in electrons of the same spin being depleted near electrons with the same spatial orbitals. Not a problem with MO theory but DFT uses an empirical function for approximating the exchange energy (**Fermi hole**).
- Different QM methods use different ways of correcting for these errors.

DFT Geometry Optimization

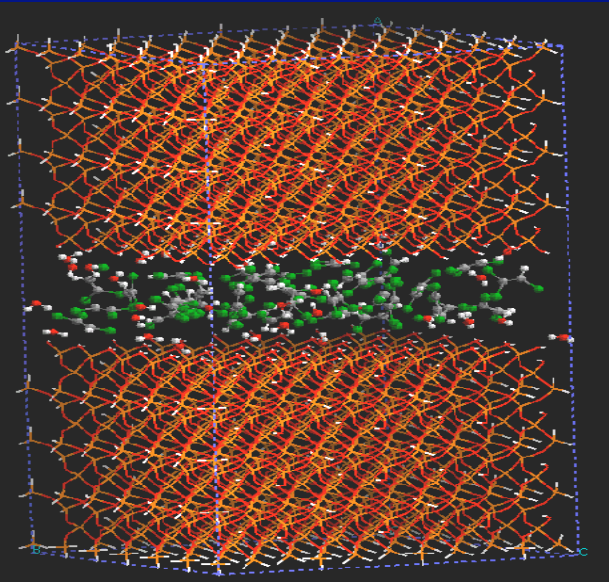
- Evaluate the energy of the system for different positions of the atoms (nuclei). For each set of atomic positions, determine the set of ψ_i that yield the lowest energy.
- Calculate the gradient of the potential energy with respect to the atomic positions.
- Set the gradient equal to zero and use standard root finding techniques to determine the atomic coordinates for the stationary points.
- Evaluate second derivatives of the potential energy at the stationary points to find the global minimum.
- Activation energies can also be determined from the potential energy surface.



Potential Energy Surface

Canonical Monte Carlo Simulations

Constant: NVT



1. Evaluate the energy of the system (E_p) for any initial configuration of the molecules.
2. Randomly choose 1 molecule to move (translation, rotation).
3. Evaluate the new energy of the system after the move (E'_p)
4. Accept the move if: $E'_p \leq E_p$ or if $\exp\left[\frac{-(E'_p - E_p)}{kT}\right] \geq \text{random}_{0 \rightarrow 1}$
5. Reject move if $\exp\left[\frac{-(E'_p - E_p)}{kT}\right] \leq \text{random}_{0 \rightarrow 1}$
6. Repeat steps 2 through 5 until the energy of the system reaches a stable value. Stabilized value not the minimum energy.

- Final configuration is a balance between energy minimizing configuration and randomized positions due to thermal energy (Boltzmann distribution).
- Molecules are usually held rigid and bonds do not stretch or bend.
- Moves are not physical and time evolution of the system is meaningless.
- Displacement distance scaled such that $\sim 50\%$ of the moves are accepted.

Grand Canonical Monte Carlo

Constant: μVT

The number of each type of molecule (N_i) may change over time.

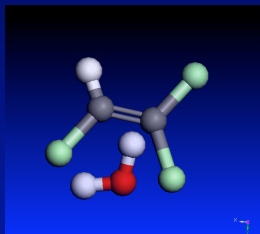
1. Evaluate the energy of the system (E_p) for any initial configuration of the molecules.
2. Randomly choose 1 molecular move, insertion or deletion.
3. Evaluate the energy of the system after the molecular move, insertion or deletion (E'_p).
4. For molecular moves, acceptance criteria same as NVT
5. If molecule is inserted, accept if: $E'_p \leq E_p$ or if $\exp\left[\frac{-(E'_p - E_p)}{kT} - \ln\frac{(N_i + 1)kT}{f_i V}\right] \geq \text{random}_{0 \rightarrow 1}$
5. If molecule is deleted, accept if: $E'_p \leq E_p$ or if $\exp\left[\frac{-(E'_p - E_p)}{kT} + \ln\frac{(N_i)kT}{f_i V}\right] \geq \text{random}_{0 \rightarrow 1}$

Molecular Dynamics

- Molecules follow Newton's 2nd Law: $\mathbf{F}=\mathbf{ma}$
- $\mathbf{F}=-dE_p/d\mathbf{r}$
- All molecules move at the same time
- Molecules are flexible and bonds may stretch and bend
- Captures true time evolution of the system
- Velocity scaling often used to control temperature
- Time steps of $\sim 10^{-15}$ s (fs) constrain simulations to very short time spans (up to 10^{-9} s)

Molecular Mechanics Solvation Effects

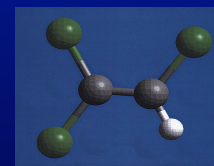
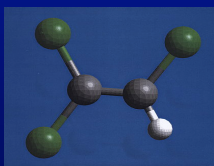
Explicit water molecules:



Dielectric constant:

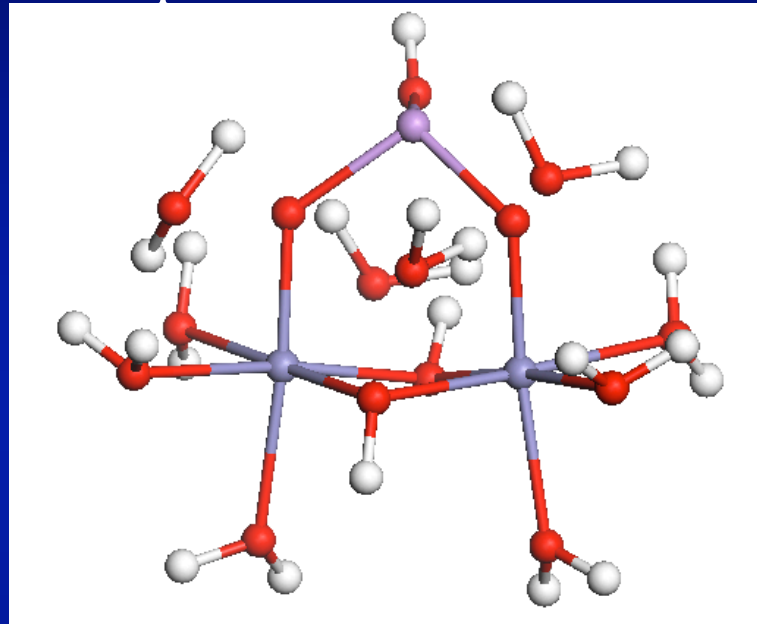
$$E_p(\mathbf{r}^N) = \sum_{\text{bonds}} \frac{k_i}{2} (l_i - l_{i,o})^2 + \sum_{\text{angles}} \frac{k_i}{2} (\theta_i - \theta_{i,o})^2 + \sum_{\text{torsions}} \frac{V_n}{2} [1 + \cos(n\omega - \gamma)] + \sum_{\text{op-angles}} \frac{k_i}{2} \theta_i^2 + \sum_{i=1}^N \sum_{j=i+1}^N \left(4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] + \frac{q_i q_j}{4\pi\epsilon_o r_{ij}} \right)$$

Useful for interactions at distances \gg the size of a water molecule ($\sim 2.5 \text{ \AA}$).



Quantum Mechanical Solvation Effects

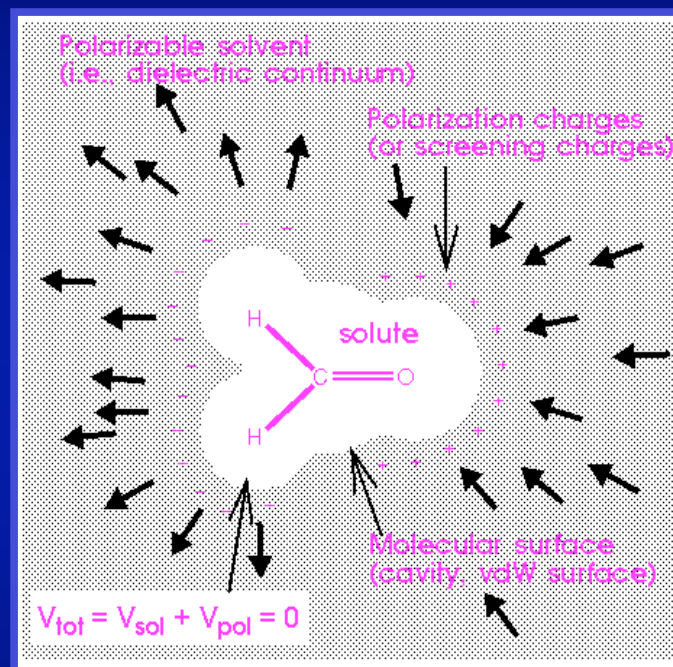
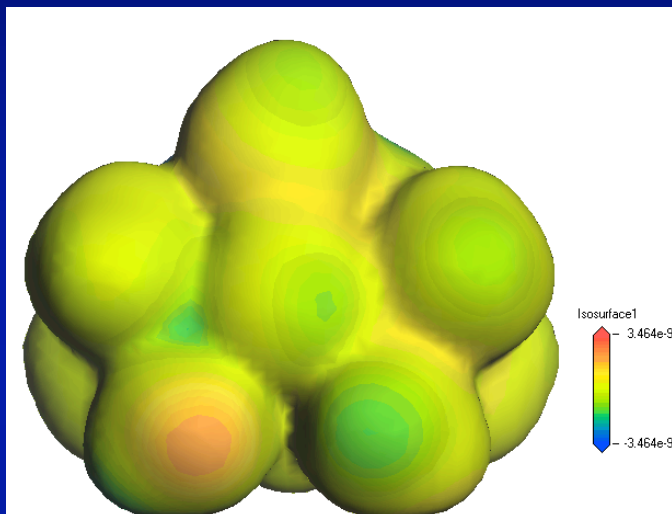
Explicit Water Molecules



- Convergence problems arise since potential energy surface becomes flattened because many different positions of the water molecules are nearly isoenergetic.
- Greatly increases computational time.

Quantum Mechanical Solvation Effects

Self Consistent Reaction Field Polarized Continuum Models



The electrostatic potential is calculated at the van der Waals surface of each solute and solvent molecule.

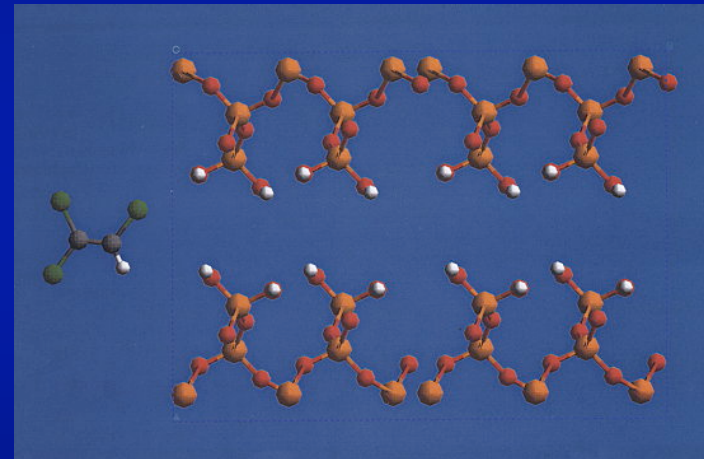
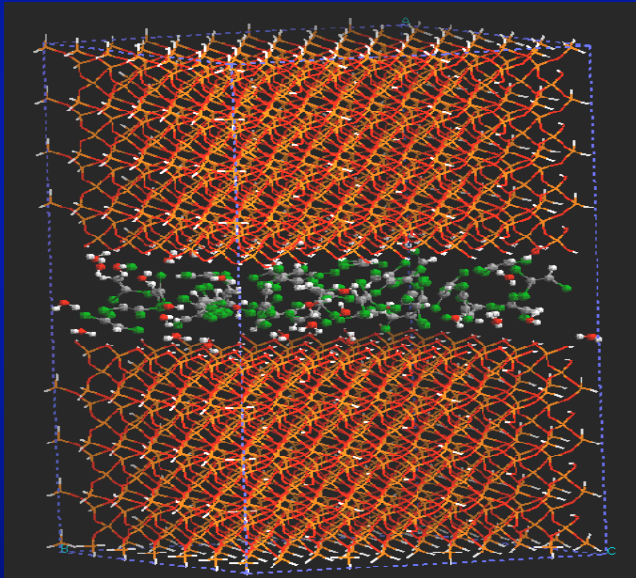
$$\Delta G_{sol} = \Delta G_{elec} + \Delta G_{cav} + \Delta G_{vdw}$$

$$\Delta G_{cav} + \Delta G_{vdw} = \gamma A + b$$

Example Applications

Competitive adsorption of water and TCE in mineral micropores

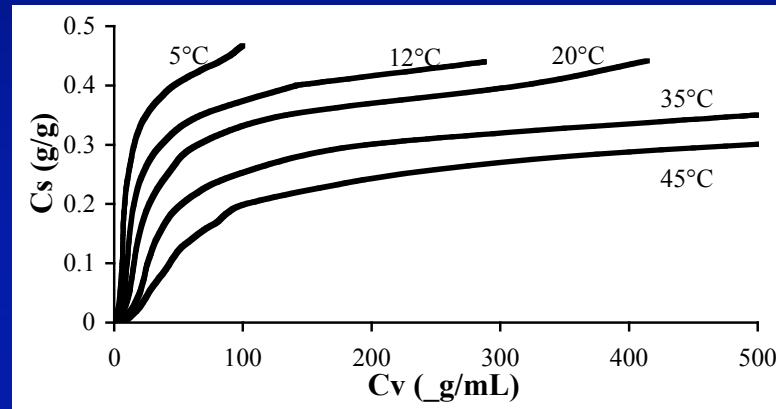
- High energy adsorption in mineral micropores leads to slow desorption of contaminants from sediments.
- Slow diffusion through molecular-sized pores leads to slow desorption rates.



How does the strength of TCE-micropore interactions depend on the pore size and surface properties?

Experimental Approach

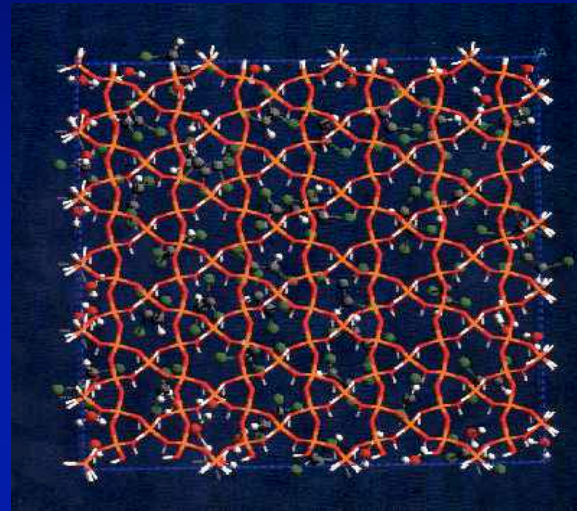
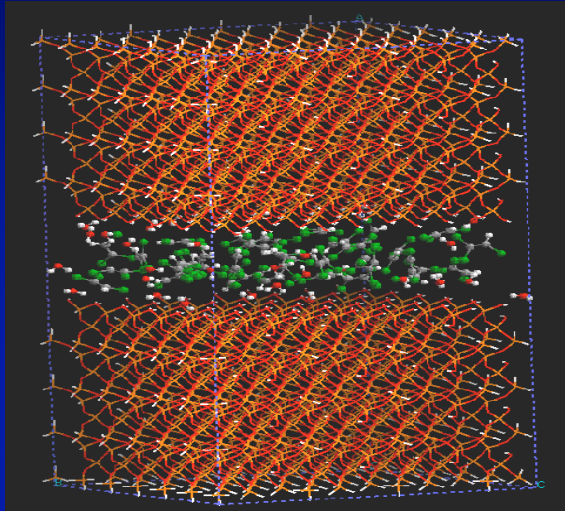
TCE Adsorption Isotherms on Zeolite H-Y



Measure the temperature dependence of adsorption isotherms to determine the isosteric heat of adsorption for a range of solids.

$$Q_{iso} = \Delta h_i^{ads} = -RT^2 \left[\frac{\partial \ln f_i}{\partial T} \right]_{n_i, n_j}$$

Modeling Approach



- GCMC simulations: water fugacity = f_w^{pure} and TCE fugacity = $0.01 f_{\text{TCE}}^{\text{pure}}$.
- $30 \times 30 \text{ \AA} \times 6\text{-}20 \text{ \AA}$ cell was generated from a silica crystal.
- Periodic boundary conditions eliminate edge effects.
- Silica framework was held rigid.
- Simulations run with different silica surface charges to simulate a range in hydrophilicity. Surface charge controlled by removing H from Si-OH.
- Simulations performed with COMPASS forcefield (Accelrys, Inc.)

Validating the Force Field Parameters for TCE and Water

Constant NPT MD simulations used to calculate the enthalpies of condensation and pure phase liquid densities for TCE and water.

Compound	ΔH° (kJ/mole)		Liquid Density (g/ml)	
	Calculated	Actual	Calculated	Actual
Water	-44	-45	1.01	0.997
TCE	-39	-34	1.51	1.46

Force field parameters give reasonable results for TCE and water.

NVT Simulation of Water Adsorption

Characterizing the pore hydrophilicity.

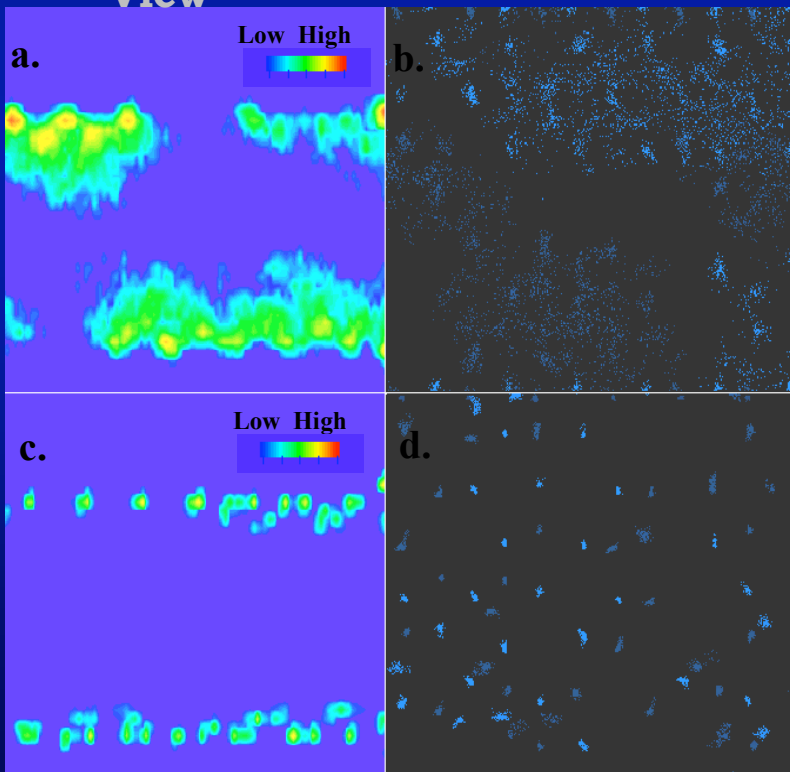
Experimental Values

silica $Q_{\text{iso}} = -42$ to -52 kJ/mol

Monolayer coverage: $N=77$ molecules

Side
View

Top
View



Uncharged Pore

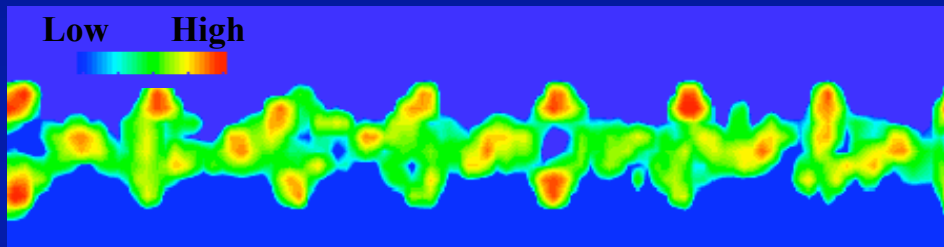
Charged
Pore

- $Q_{\text{iso}} = -36$ kJ/mol
- less hydrophilic than real mineral pores

- $Q_{\text{iso}} = -146$ kJ/mol
- more hydrophilic than real mineral pores

μ VT Simulation of Water Adsorption

Adsorption density plot for water adsorption in a silica pore with a 8 Å pore width.

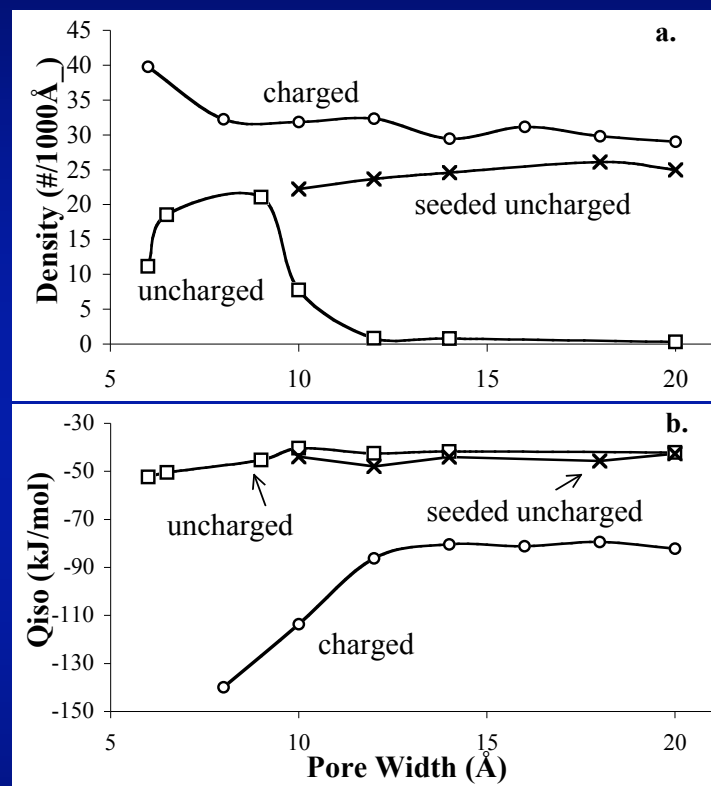


$$Q_i^{\text{iso}} = \frac{\langle UN_i \rangle - \langle U \rangle \langle N_i \rangle}{\langle N_i^2 \rangle - \langle N_i \rangle^2} - kT$$

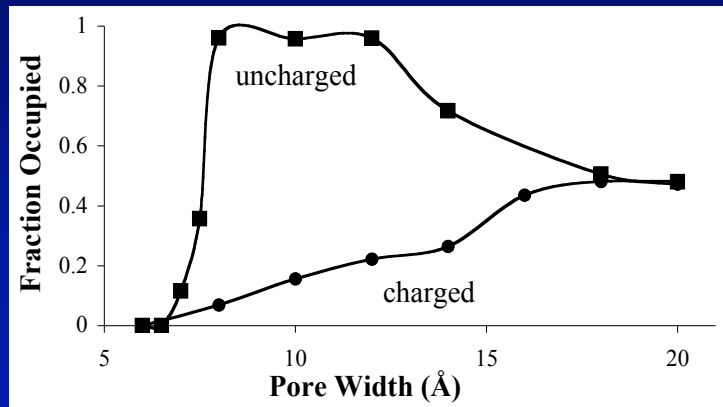
$\langle U \rangle$ = system internal energy averaged over a large number of system configurations

$\langle N_i \rangle$ = number of molecules of type i over averaged over a large number of system configurations

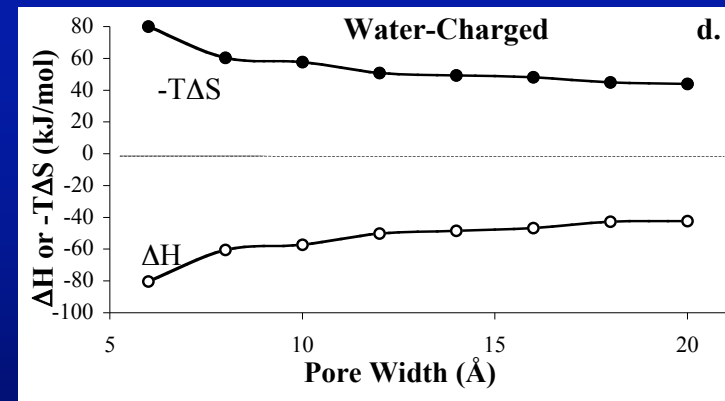
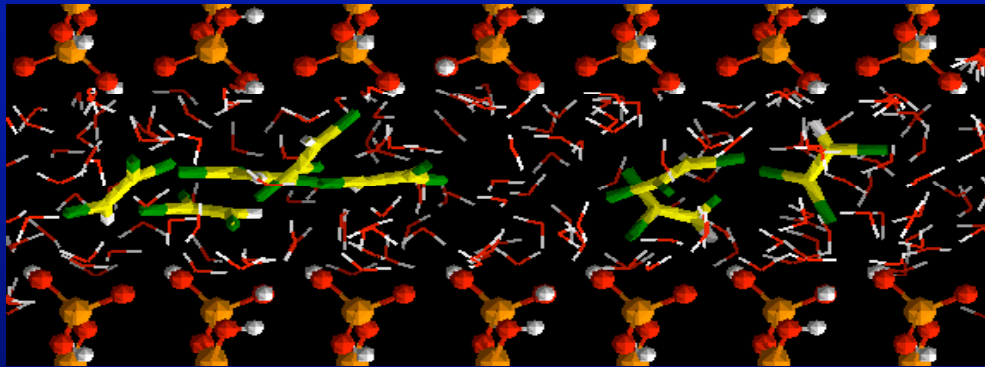
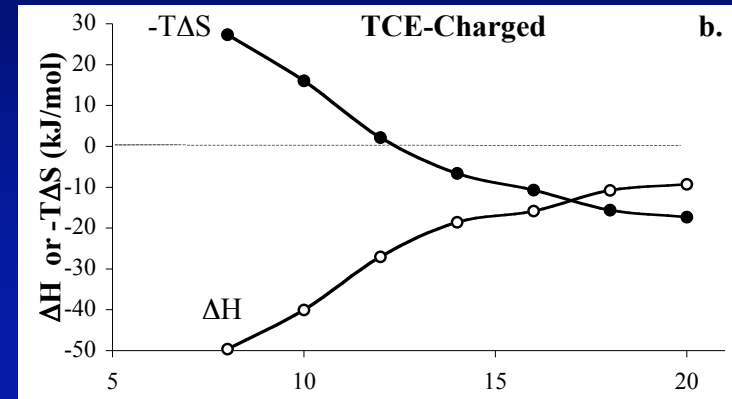
k = Boltzmann's constant = $R/6.022 \times 10^{23}$



μ VT Simulation of TCE & Water Adsorption

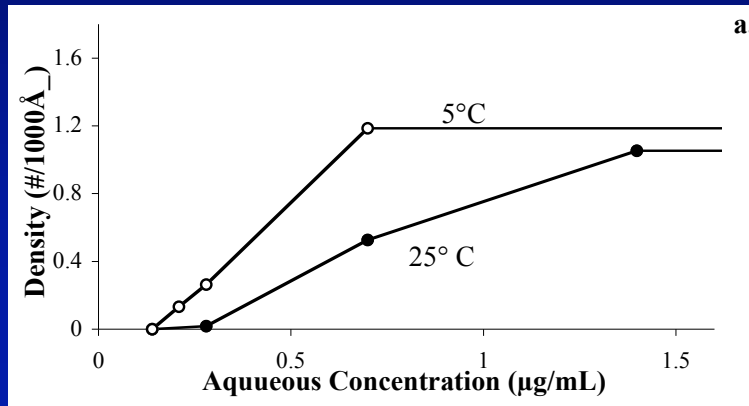


Volume fraction occupied by TCE



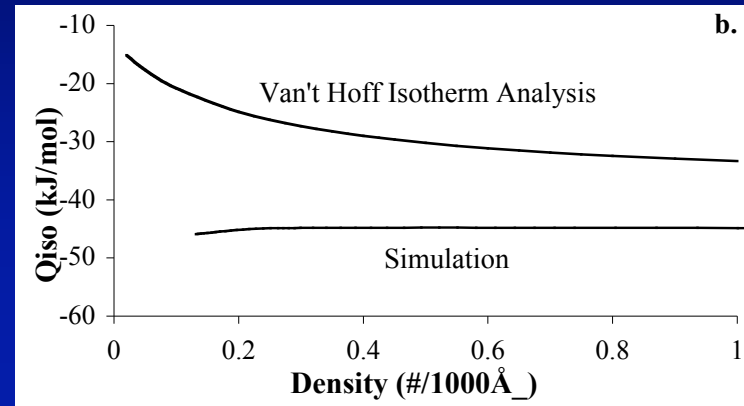
TCE at a liquid phase mole fraction of 2×10^{-6} (1% x_{sat}) can displace water from both mildly hydrophobic and very hydrophilic micropores.

Isosteric Heats of Adsorption



TCE adsorption isotherms in a charged 10 Å pore.

$$Q_{iso} = -RT^2 \left[\frac{\partial \ln f_i}{\partial T} \right]_{n_i, n_j}$$



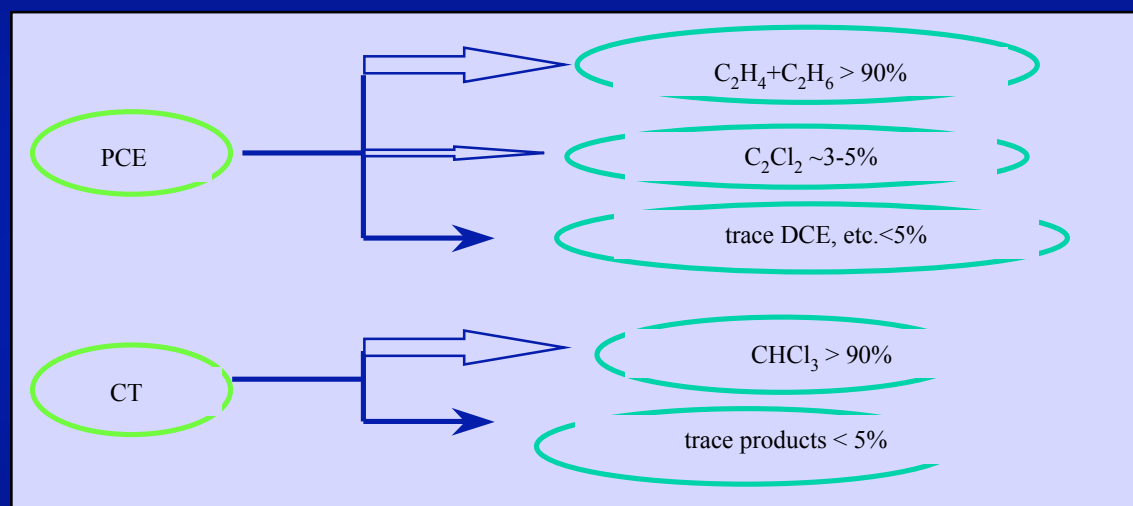
Heats of TCE adsorption

$$Q_i^{iso} = \frac{\langle UN_i \rangle - \langle U \rangle \langle N_i \rangle}{\langle N_i^2 \rangle - \langle N_i \rangle^2} - kT$$

- Van't Hoff method for evaluating adsorption energies underestimates the true adsorption energies due to ignoring the effects of water adsorption.
- Contaminant-sediment interactions may be stronger than previously believed.

Background Reductive Dechlorination

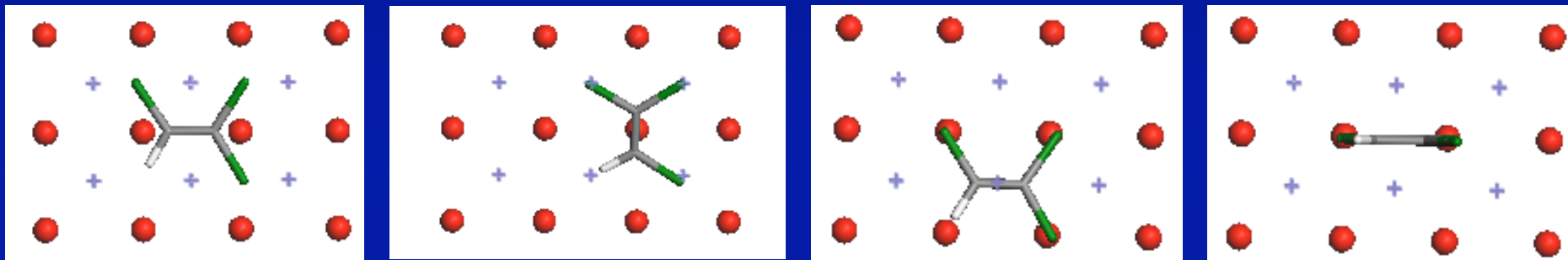
- Zerovalent iron filings are used for reductive dechlorination of solvents in water.
- Complete dechlorination of chloroethenes but sequential dechlorination of chloroethanes.
- Reaction rates for chloroethenes are much faster than those for analogous chloroethanes.
- Evidence of an inner-sphere electron transfer mechanism associated with chloroethenes.



Do trichloroethylene (TCE) and tetrachloroethylene (PCE) chemically adsorb on iron surfaces?

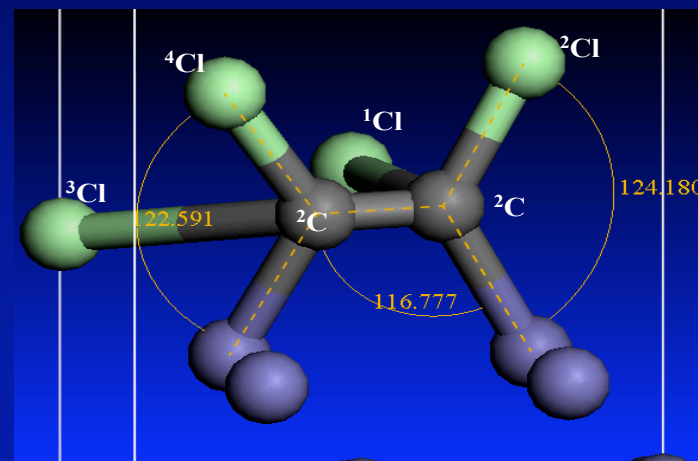
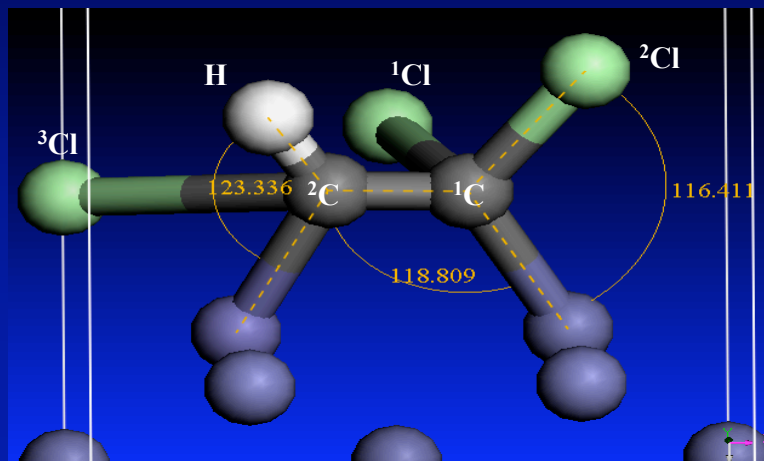
Investigate surface complex formation of TCE and PCE with iron slabs using periodic density functional theory

Starting geometries

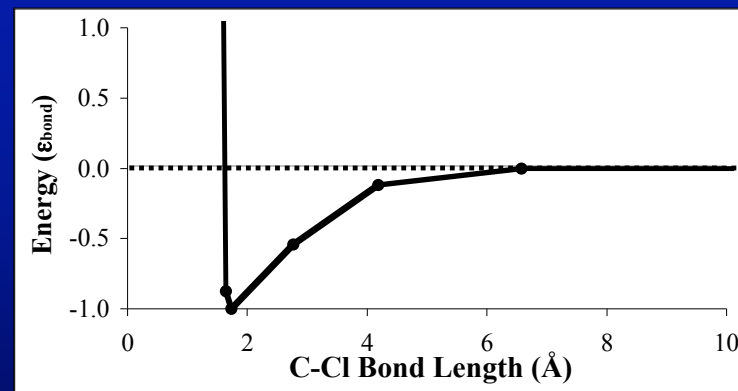


- iron modeled as a periodic 5 x 5 x 5 layer Fe[100] slab

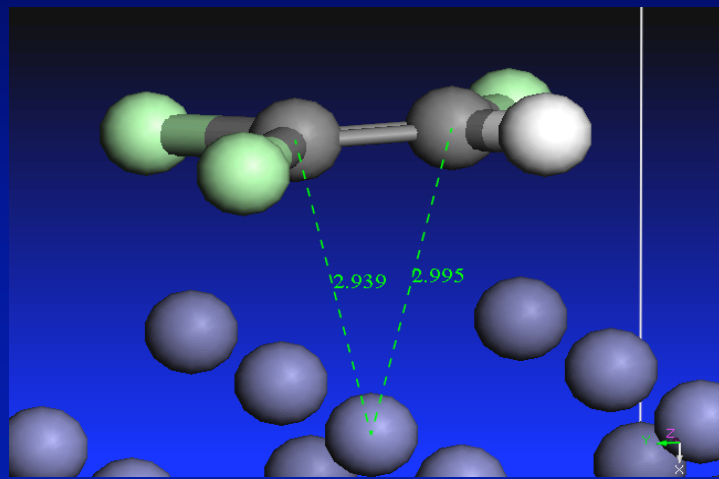
Di-sigma Complex Formation



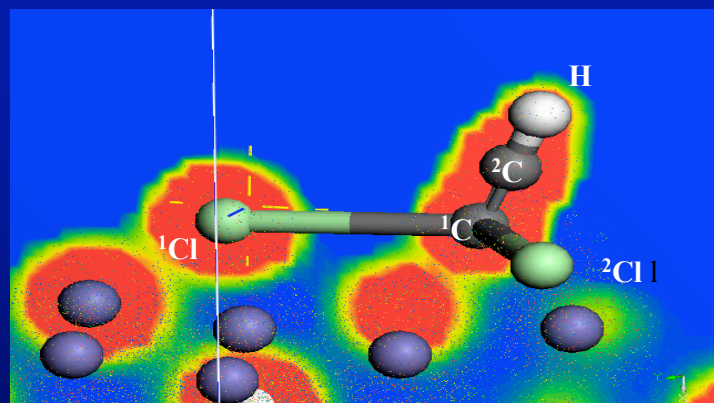
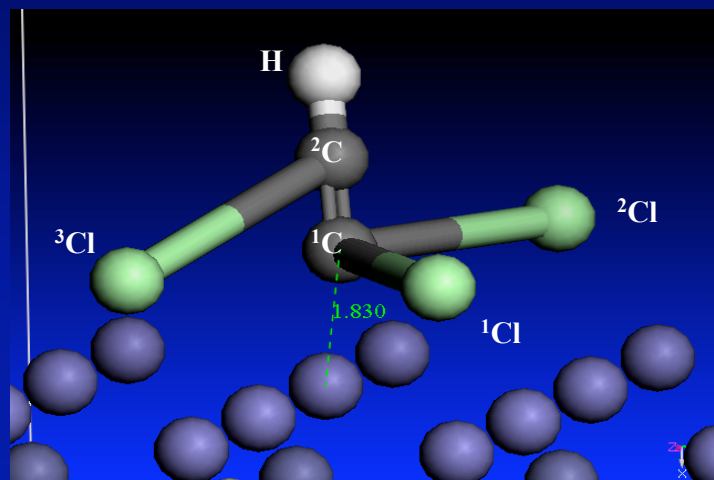
- Activation of 2 C-Cl bonds to $>3 \text{ \AA}$.
- C bond angles and C-C bond lengths indicates sp^2 hybridization.



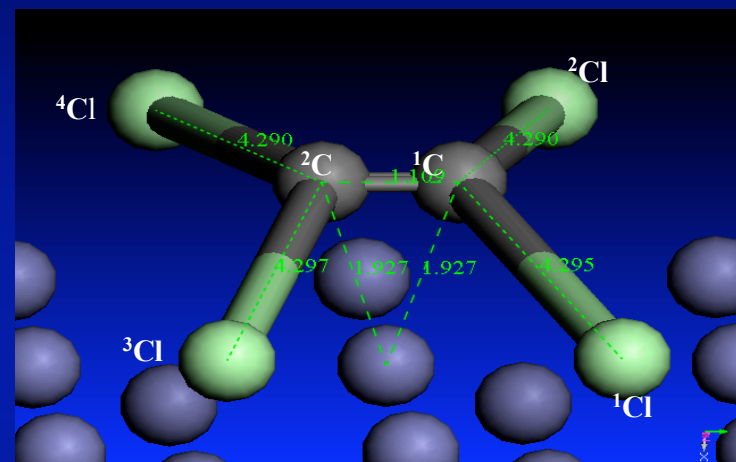
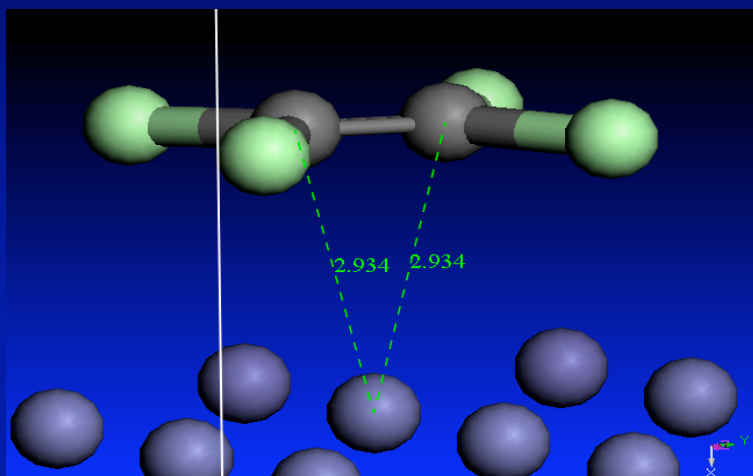
Sigma Bonded TCE



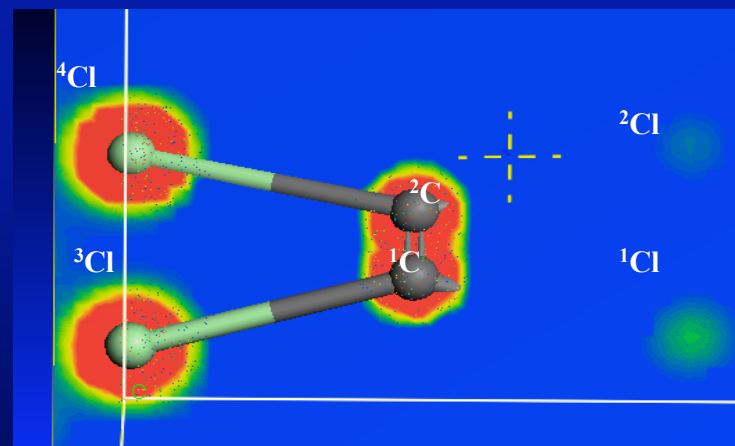
- All 3 C-Cl bonds broken to ~ 4.3 Å.
- C-Fe bond length similar to di-sigma complex.
- Reduction in C=C bond length by 0.14 Å, consistent with conversion of double to triple bond.



PCE Pi-Complex Formation



- All 4 C-Cl bonds broken to ~ 4.3 Å.
- Fe-Cl bond distances close to those in FeCl_2 crystal.



Bindings Energies

Compound	Binding Energy (kJ/mol)	Structure
PCE	-915.67	pi
TCE	-805.21	sigma
PCE	-609.56	di-sigma
TCE	-568.93	di-sigma

- Lower energies of pi and sigma complexes are consistent with complete dechlorination that is most often observed.
- Formation of di-sigma complexes and the breaking of 2 C-Cl bonds is consistent with observations of trace amounts of chloroacetylene and dichloroacetylene*.

*Arnold & Roberts, *Environ. Sci. Technol.* **2000**, 34, 1794.

Chemical Adsorption of As(III) on Ferric hydroxides

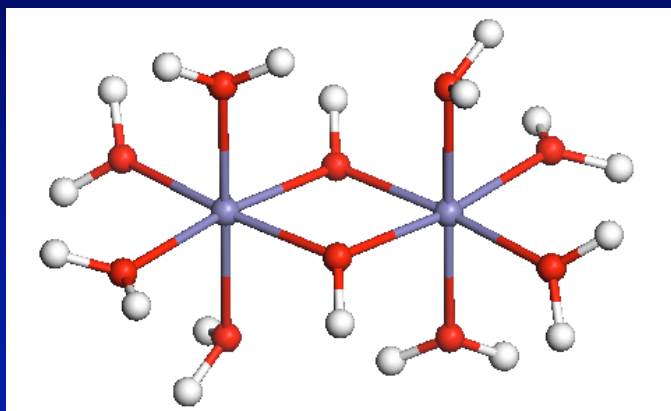
Motivation

- Iron oxides are being used as adsorbents for removing arsenic from potable water.
- There is very little experimental information on As(III) complexes with ferric hydroxides.
- Conflicting experimental results on As(III) interactions with ferric hydroxides.
- Unusual hysteretic effects are difficult to resolve experimentally.

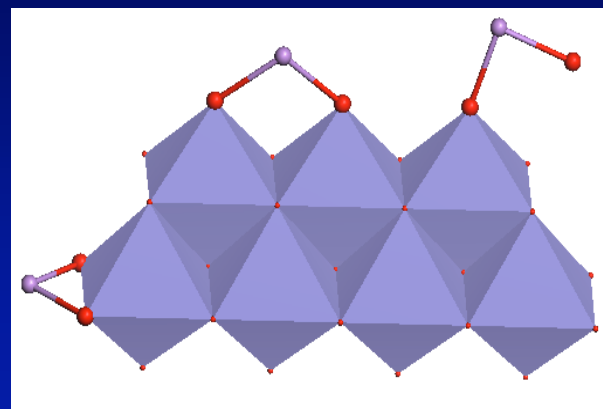
Questions to Address

- Why do some studies show oxidation of As(III) upon adsorption to ferric hydroxides and other studies do not?
- How do impurities in the ferric hydroxides affect the binding strength?
- What products form when H_3AsO_3 and HAsO_2 bind to ferric hydroxides?

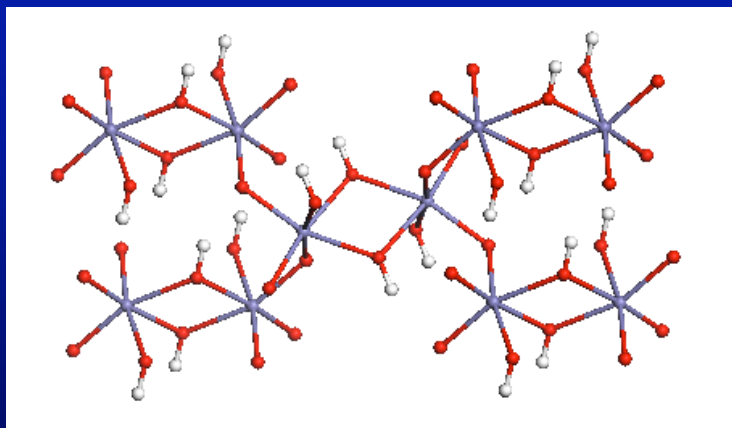
Chemical Adsorption of As(III) on Ferric hydroxides



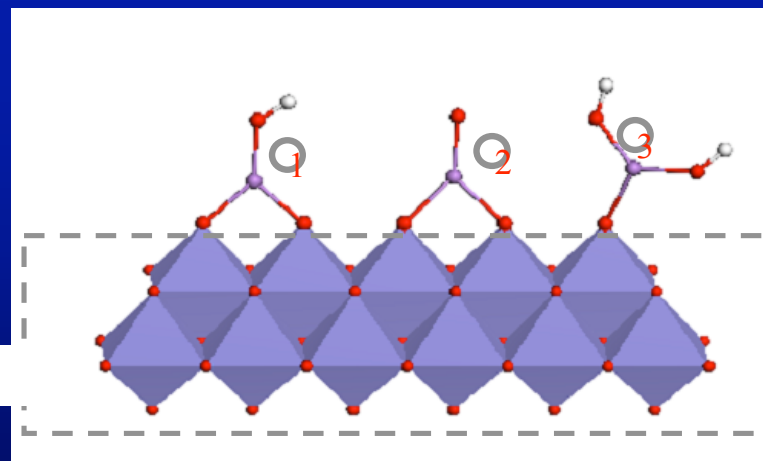
Octahedral clusters used to simulate ferric hydroxides.



Binding energies calculated for edge and corner sites and mono- and bi-dentate complexes.

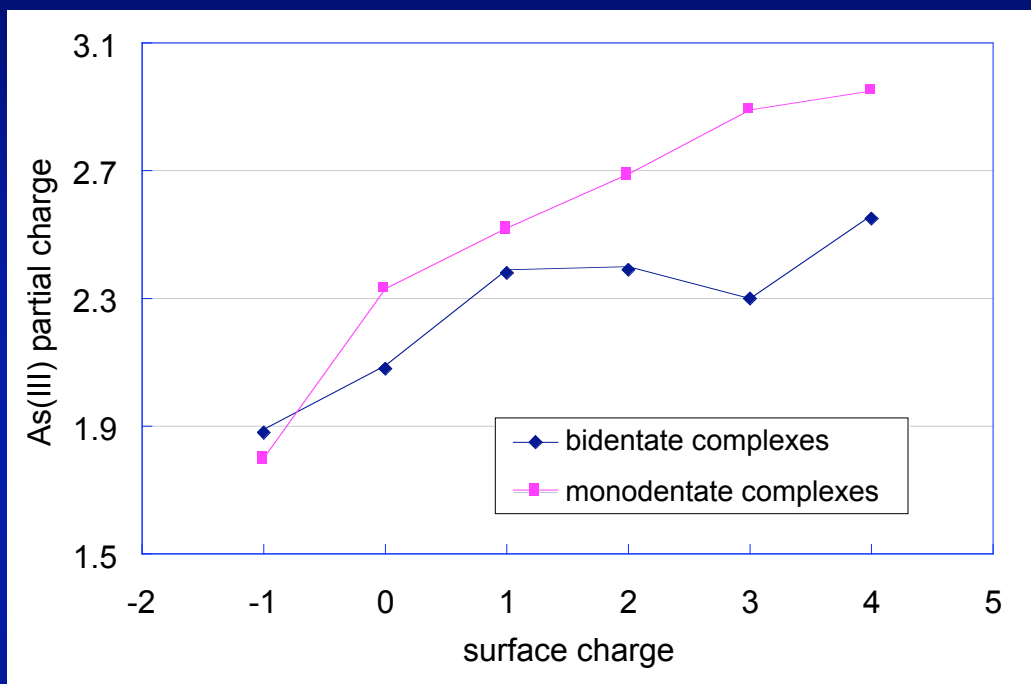


Goethite (α -FeOOH)

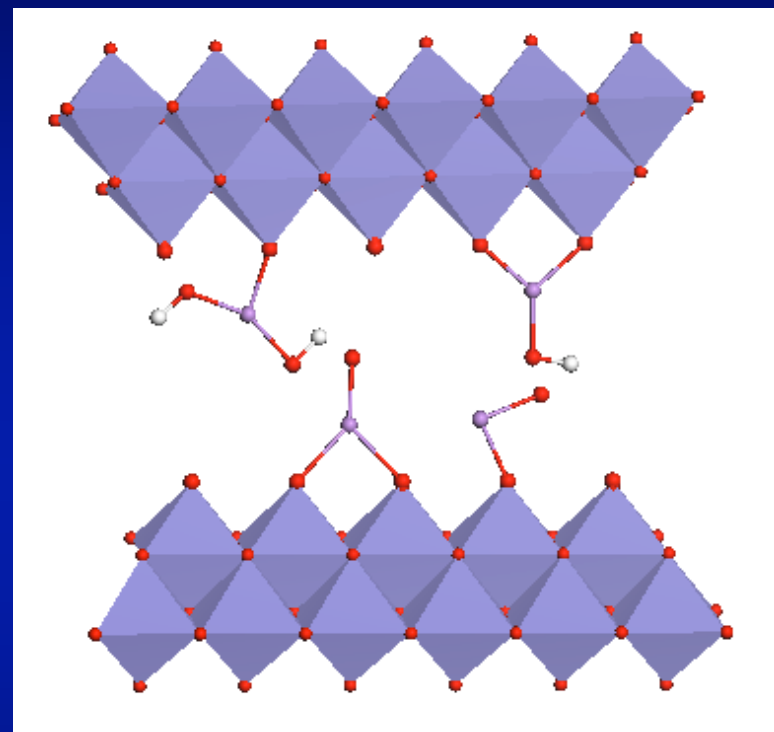


Determined the effects of hydration and protonation on binding energies.

Chemical Adsorption of As(III) on Ferric hydroxides

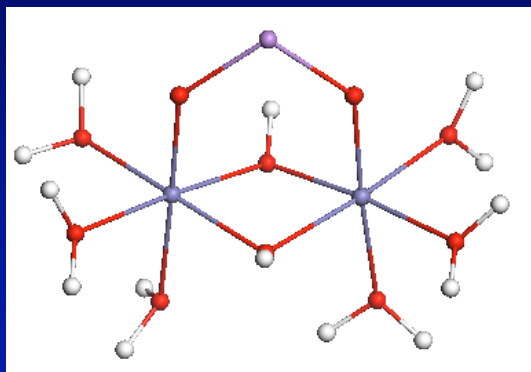


Effects of pH on binding energies and As(III) oxidation investigated by varying the surface charge.

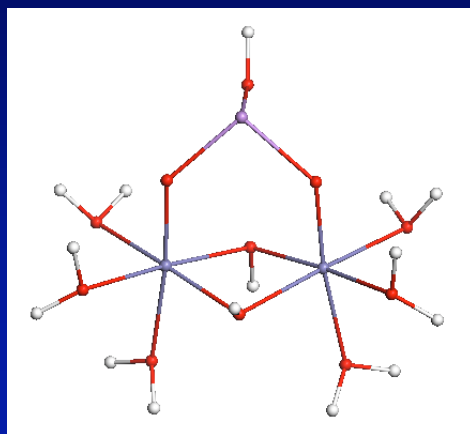


Effects of porosity and As(III) loading on binding energies investigated using molecular mechanics simulations.

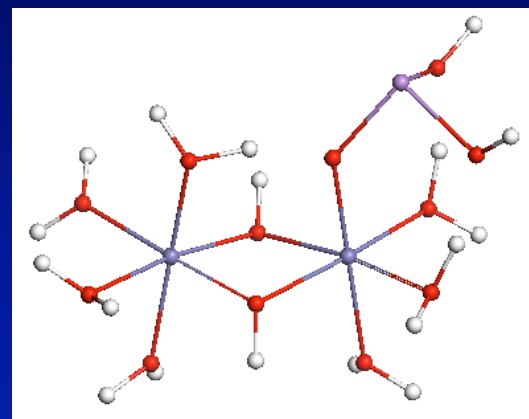
Energetically Favorable Binding Modes



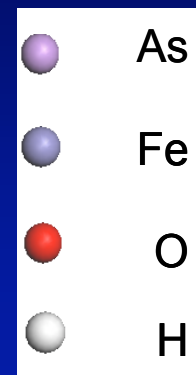
Complex A



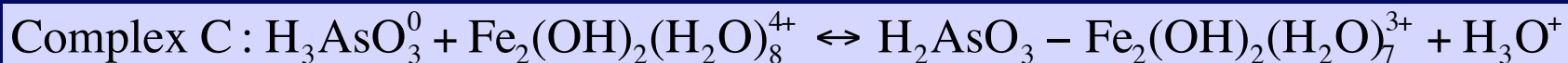
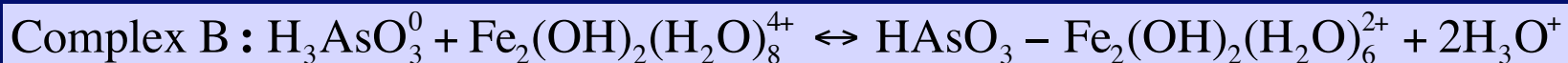
Complex B



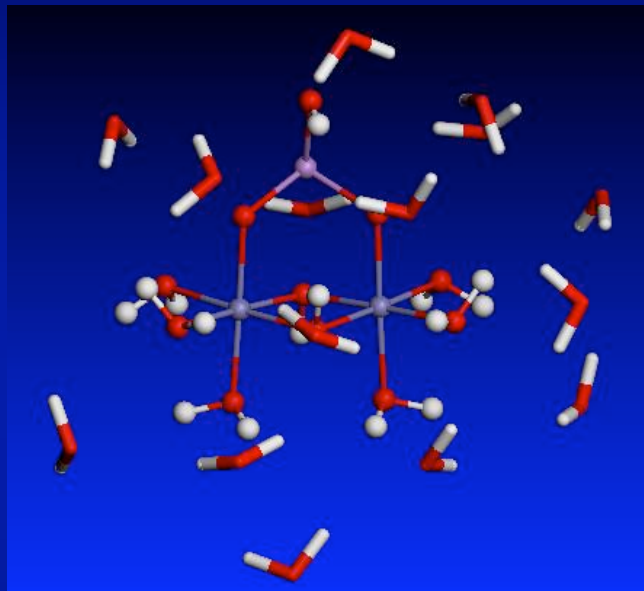
Complex C



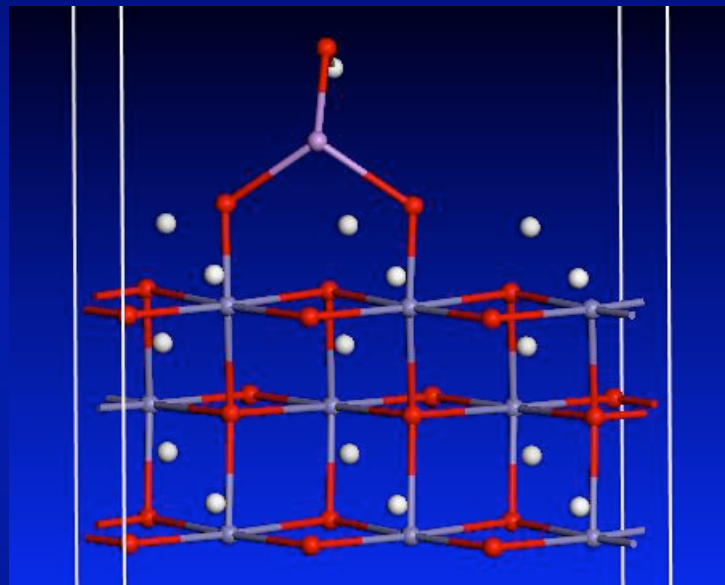
Complex	in vacuo		in solution	
	ΔE	ΔE	ΔH° (298 K)	ΔG° (298 K)
A	-814	-629	-629	-667
B	-1208	-349	-337	-366
C	-919	-727	-712	-699



New Approaches May be Needed

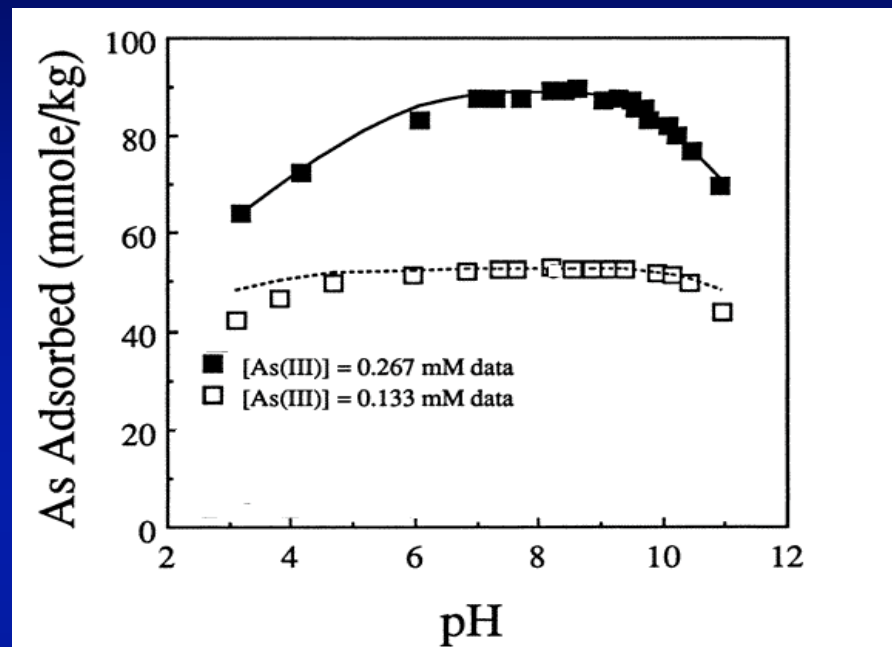
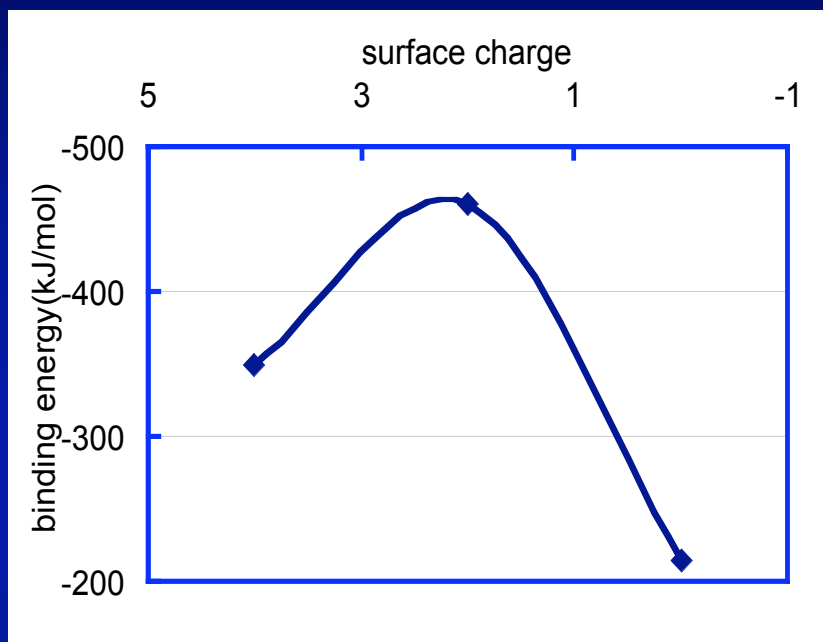


Use QM/MM methods
to better account for
hydration.

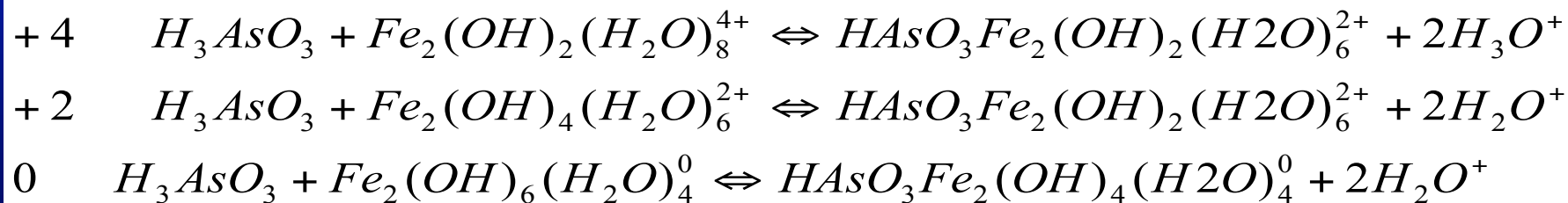


Use more constrained
adsorbents such as
lepidocrocite.

Comparison with Experiments



Dixit, S.; Hering, J. G. *Environ. Sci. Technol.* **2003**, 37, 4182-4189.



Joys of Modeling

- Can obtain information that is not experimentally accessible.
- Vary properties of the system as desired.
- Inexpensive compared to experimentation. Commercial software packages for PCs typically cost from \$500 to \$10,000.
- With commercial software, don't need a PhD in computational chemistry (any fool can be a modeler).
- Fast compared to experimentation (high research productivity).
- High repeatability between runs (improves sleep habits of PI).
- Good way to make friends (collaborators always welcome).

Woes of Modeling

- Only certain aspects of any system can be modeled at one time.
- The relationship between the model and reality can be difficult to establish.
- A thorough understanding of the system is needed to select which aspects of the system to model.
- Modeling is best used to explain previously collected data.
- Convergence problems for large systems and bad initial guesses.
- Incorporation of solvation effects can be difficult. Convergence problems with too many explicit water molecules.

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