CO₂ Vibrations

Potential Changes in Temp and Precip, 2000-2099
Temperature Change, °C
Temperature Change, °C
Precipitation Change, %
Precipitation Change, %

Cyberinfrastructure Needs for Multi-disciplinary Collaborations
James D. Kubicki
Dept. of Geosciences & Earth and Environmental Systems Institute
The Pennsylvania State University

Molecular Modeling Matrix

Level of Theory = Cost of Calculation
Where does molecular modeling fit in?

- Field Geochemical Studies (Observations of Speciation and Transport)
- Laboratory Experiments (Adsorption/Desorption Kinetics)
- Characterization (e.g., IR/Raman, NMR, etc.)
- Molecular Modeling (Molecular Orbital and Molecular Dynamics Calculations)

Detailed Knowledge

Need for an Intelligent Database

- Difficult to make sense out of too much data.
- Conflicts between datasets cannot be resolved.
- Relevance of data can be hard to ascertain.
- Cannot find data you don’t know exists!

http://truong.hec.utah.edu/
Health Effects of Airborne Particulate Matter

Relative Mortality Rate

PM 2.5 microns (micro-grams/m³)

Male and Females Combined

Emphysema

Top Panel: Control– Normal gill morphology with distinct primary lamellae extending perpendicular to branchial arch and distinct secondary lamellae extending perpendicular to primary lamellae.

Bottom Panel: Gills of salmon fry after 30 d exposure to 300 µg/L aluminum. Hyperplasia of epithelial cells results in fusion of secondary lamellae.

Newman 2001

2-D structure model of hexane soot from Akhter et al. (1985)

Molecular dynamics simulation of soot for 70 of 100 ps at 300K with the COMPASS force field (Sun, 1998)

2732 atom soot model with 16 pyrene molecules after 100,000 molecular dynamics time steps with COMPASS force field in Cerius² on a SGI Octane workstation.

Layered

Curved surface

Layered

How do aerosol particles (e.g., soot) catalyze formation of acids?
Aluminum concentrations and discharge during an acid runoff episode in Powdermill Run PA

From Sharpe et al., 1987, Water Res. Bull. 23, 37

Al$_{13}$ “Keggin” cation structure


Semi-empirical model of dissolved natural organic matter with aluminum

Arsenic Groundwater Contamination

Bangladesh has an epidemic problem with arsenic.

http://www.isc.tamu.edu/PICS/OtherImages/
The number of cancers expected in Bangladesh from the exposure already undergone can be very roughly estimated by using this "default" assuming that there are 20,000,000 to 70,000,000 exposed persons at levels between 0.05 to 0.5 ppm. Estimates vary between 200,000 and 2,000,000. Even the lower estimate of cancer anticipated in Bangladesh exceeds ten fold the estimate of cancers (20,000) that might be caused worldwide by the 1986 Chernobyl catastrophe.

Source – World Health Organization

The transport of contaminants in groundwater is strongly influenced by their sorption behavior with minerals in the aquifer.

From Brown et al., 1999, Chemical Reviews

**EXAFS Model**

As-Al = 3.21 Å 3.21 Å  
As-O = 1.77 Å 1.78 Å  
(As-Al = 3.38 Å 3.28 Å  
As-O = 1.78 Å 1.77 Å  
(As-Al = 3.24 Å 3.21 Å  
As-O = 1.77 Å 1.78 Å  
(Arai et al., 2001)

**EXAFS Model**

As-Fe = 3.38 Å 3.28 Å  
As-O = 1.78 Å 1.77 Å  
(Waychunas et al., 1993)

As-O = 1.78 Å 1.77 Å  
(Farquhar et al., 2002)

Surface charging and complexation models, such as MUSIC, can be complemented by ab initio modeling of surface hydration.


Potentiometric data can be complemented by spectroscopic data particular face-specific spectra.

Ab initio molecular dynamics simulations on a large scale are necessary to model realistic surface charges and hydration at a surface.

Figure courtesy of Dr. Jorge Sofo – Dept. of Physics PSU

Mineral Dusts and Human Health

Silicate-generated radicals from crushing

Oxidation
Decomposition
Radical organic

The reaction of water with crushed silica leads to $\equiv Si + H_2O \rightarrow $SiOH + OH$^-$ and OH radicals are known to cause DNA damage

Metabolic intermediates (partially oxidized) of B[a]P are capable of forming adducts with DNA

http://www.ejbiotechnology.info/content/vol6/issue3/issues/1/
2732 atom soot model with 16 pyrene molecules after 100,000 molecular dynamics time steps with COMPASS force field in Cerius² on a SGI Octane workstation.

Layered
Curved
Compact structure and strong association of pyrene

Minimum energy configurations for PCB/soot adsorption were calculated with the COMPASS force field. Adsorption energies were then calculated using the MP2 energies based on the force field configurations.

4,4’Chloro-Biphenyl

Soot surface model

Conclusions
• Real environments are unconstrained and require understanding phenomena at multiple time and length scales.
• Accurate representation of chemical processes generally requires ab initio, quantum mechanical calculations.
• System complexity necessitates a significant number of atoms and components in molecular models of environmental chemistry.
• The combined demands of atomic-level accuracy and larger system size means that highly parallelized ab initio codes scaling as O(N) are desirable.