SAND2011-6252C

Exceptional service in the national interest

Sandia National Laboratories

Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

Sandia National Laboratories

Sulfate Adsorption to Goethite (100) and (101)

Kelly Theel

Dr. Louise Criscenti

U.S. DEPARTMENT OF ENERGY | NNSA

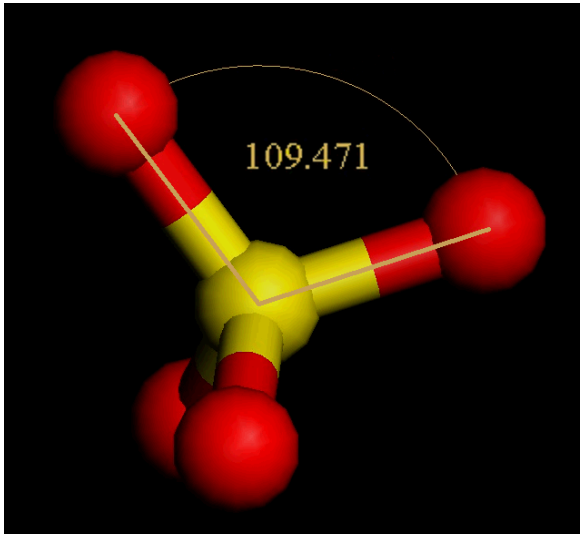
Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

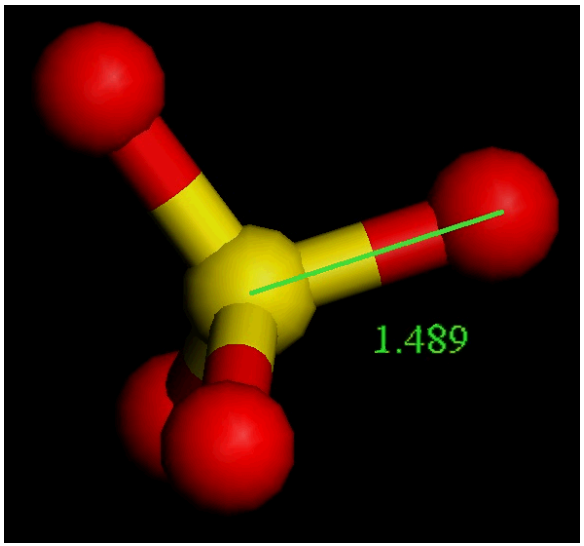
Motivation

- Lynn Katz (UT-Austin) experimental work with sulfate at (100) and (101) surfaces of goethite
- Difficulties modeling cation and anion on the surface
- Cation and anion total available surface sites are different!
- Proposed: steric factor to account for the lower number of available sites for sulfate
  - Is that physical?

Cannon Sulfate Model

- Optimized at HF 6-31+G(d)
  - Rigid model
- Found lowest energy conformations with rigid TIP3P H2O at HF 6-31+G(d)
  - 2 models
    - Used CHELPG to fit charges at atom centers
      - (O=-1.10 S=2.40)
    - Used -1.00 on O and 2.00 on S
- Started with OPLS thiol LJ parameters
  - Matched calculated binding energies SO_4^{2-}-H2O
- Validated with free energy transform (Xe => SO_4^{2-})
  - -260.5 kcal/mol experimental
  - -275.4 kcal/mol theoretical



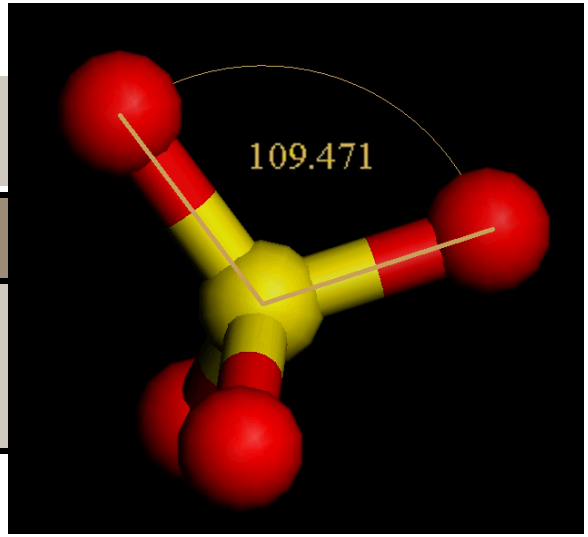


Cannon, et. al, J. Phys. Chem. 1994,98, 6225-6230

Kalinichev Sulfate Model

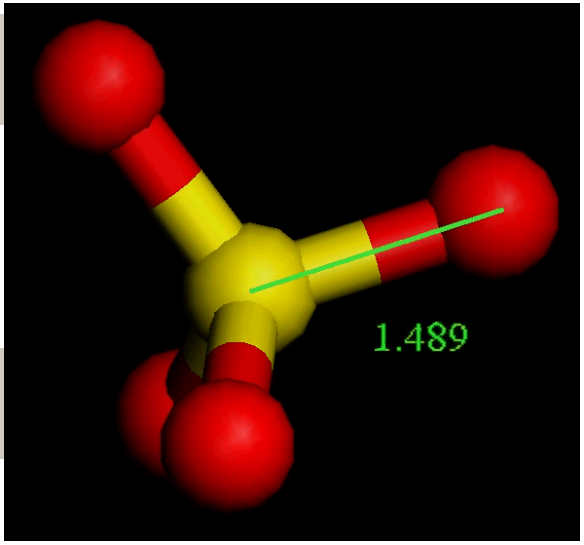
$$U_{\text{Lennard-Jones}} = 4\varepsilon\left(\sigma^{12}/R^{12} - \sigma^{6}/R^{6}\right)$$

Sulfate S (charge = 2.00)	Sulfate O (charge = -1.00)
Sigma = 3.55	Sigma = 3.15
Epsilon = 0.25	Epsilon = 0.20



$$U_{\text{bond stretch}} = K_{\text{stretch}}\,(R - R_0)^2$$

- Bond stretch force constant = 625.00

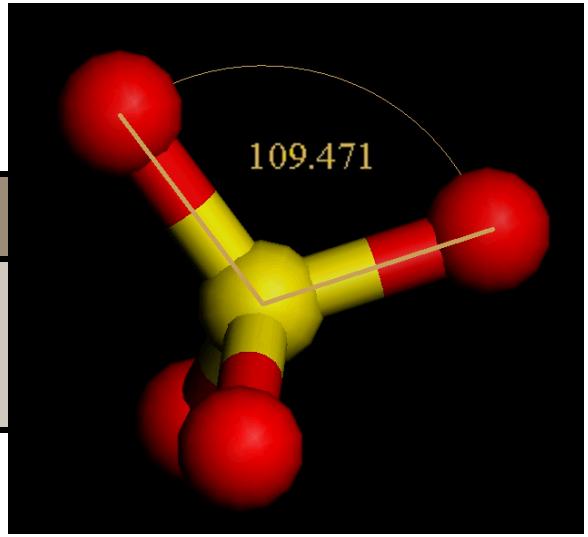


$$U_{\text{angle bend}} = K_{\text{bend}}\,(\theta - \theta_0)^2$$

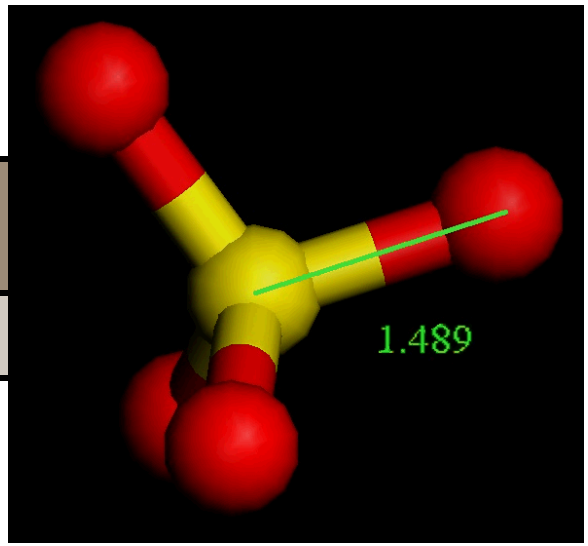
- Angle bend force constant = 102.50

Kalinichev Sulfate Model

IR in aqueous solution	Kalinichev in gas phase
Bend = 451 cm^{-1}	Bend = 482 cm^{-1}
Stretch = 1104 cm^{-1}	Stretch = 1273 cm^{-1}



Cannon Rigid TIP3P Interaction Energy	Kalinichev Flexible SPC Interaction Energy
-225.26 kcal/mol	-248.55 kcal/mol



Experimental values from: Kloprogge et al., American Mineralogist, Volume 87, pages 623–629, 2002

Kalinichev Sulfate Model

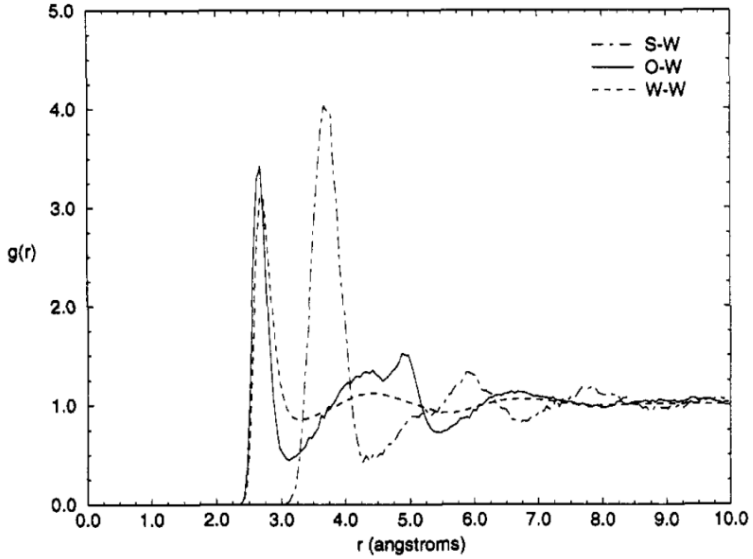
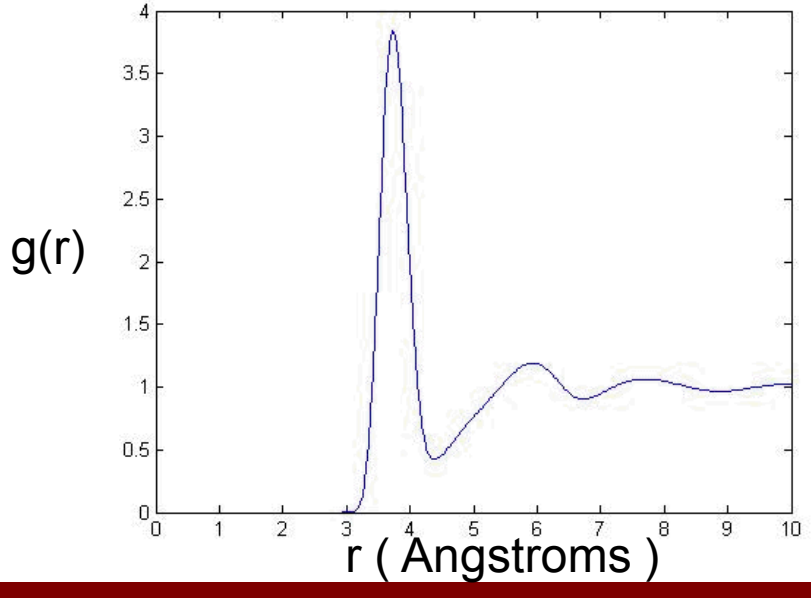
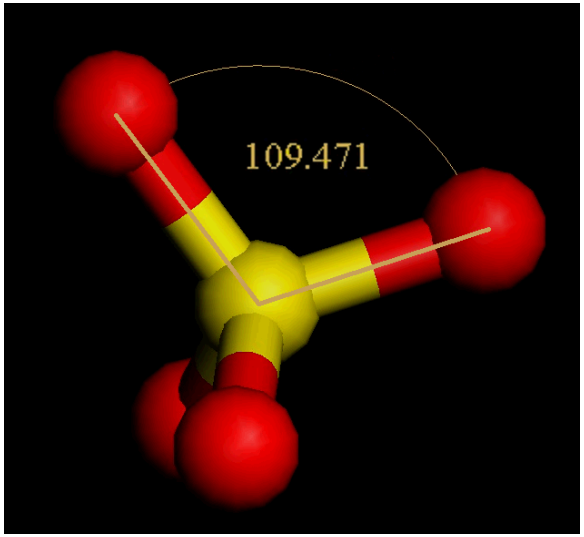
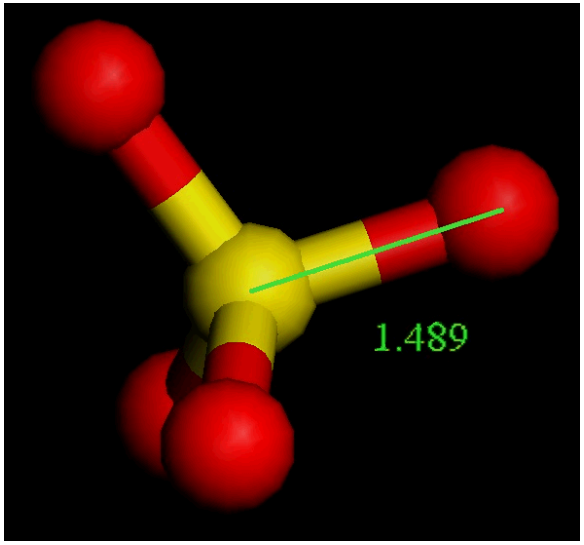


Figure 3. Pair correlation functions for S–O_w, O_s–O_w, and O_w–O_w pairs.

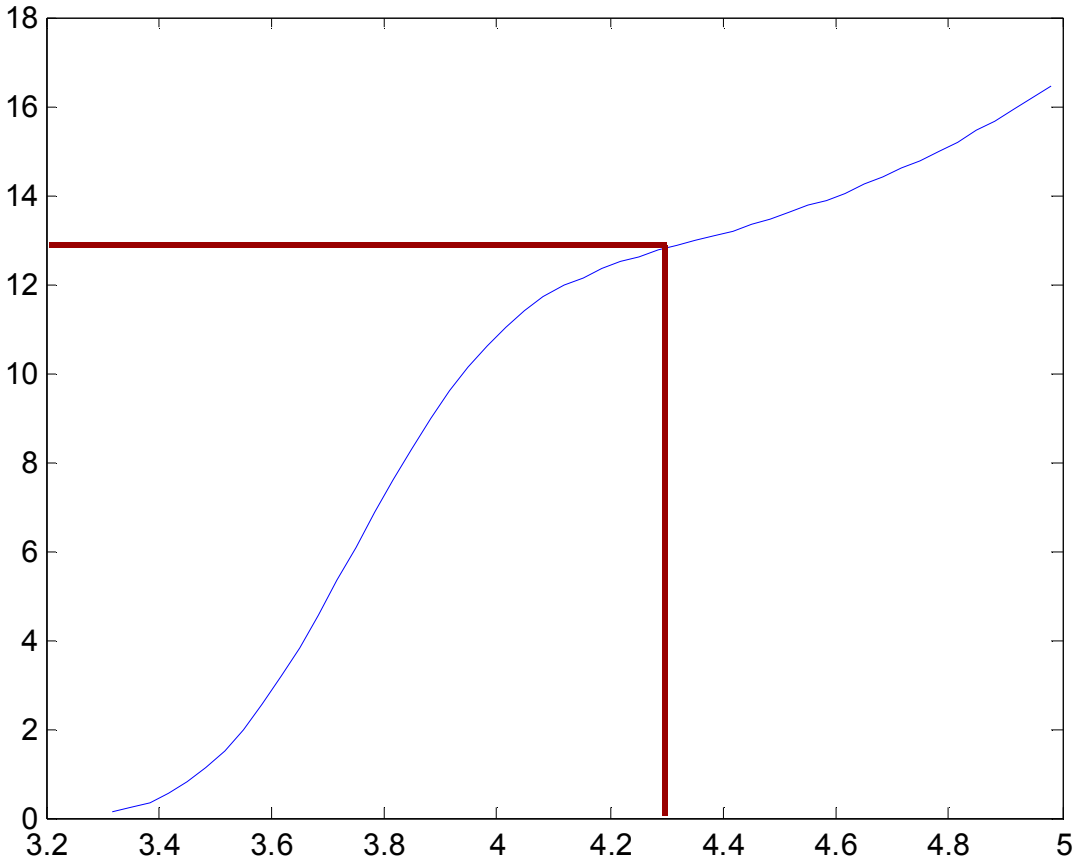


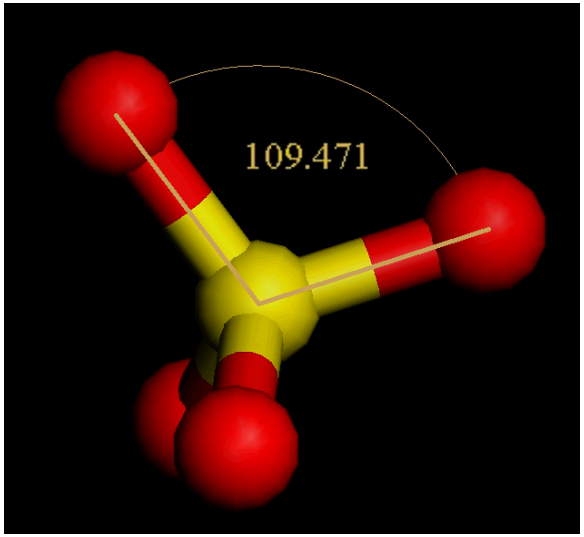


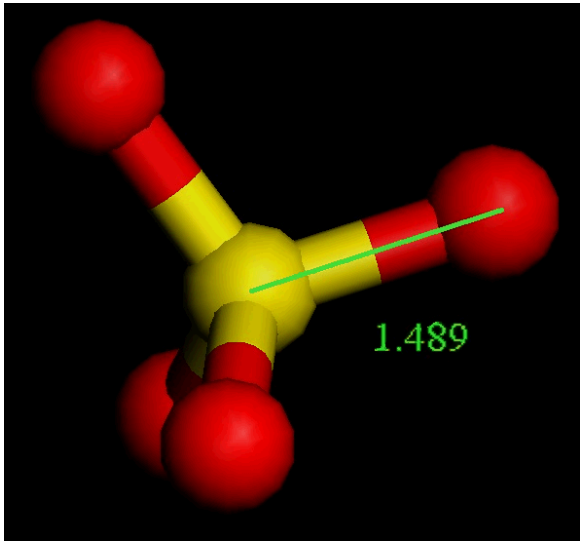


Kalinichev Sulfate Model

- Cannon model: approx 13 waters in complex
- Experimental: varies from 6 to 14
- Good agreement with Cannon



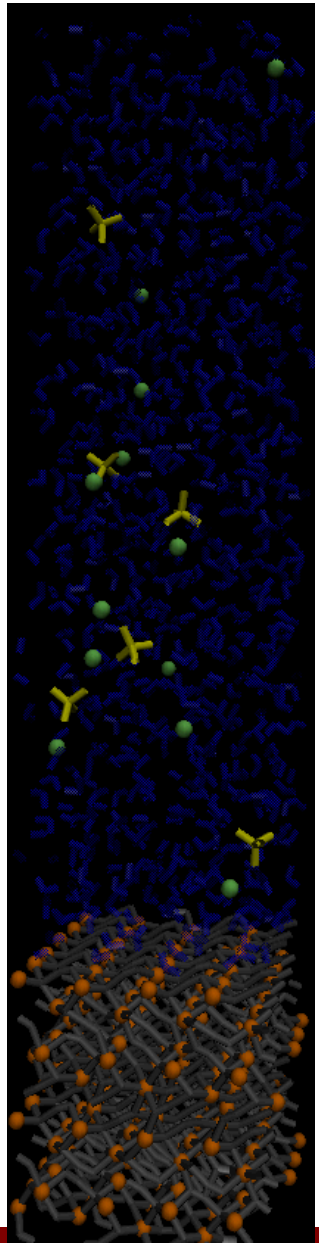




Na_2SO_4 on Goethite (100)

- Complexation as a function of concentration
  - 0.46 molal
  - 1.00 molal
  - 1.46 molal

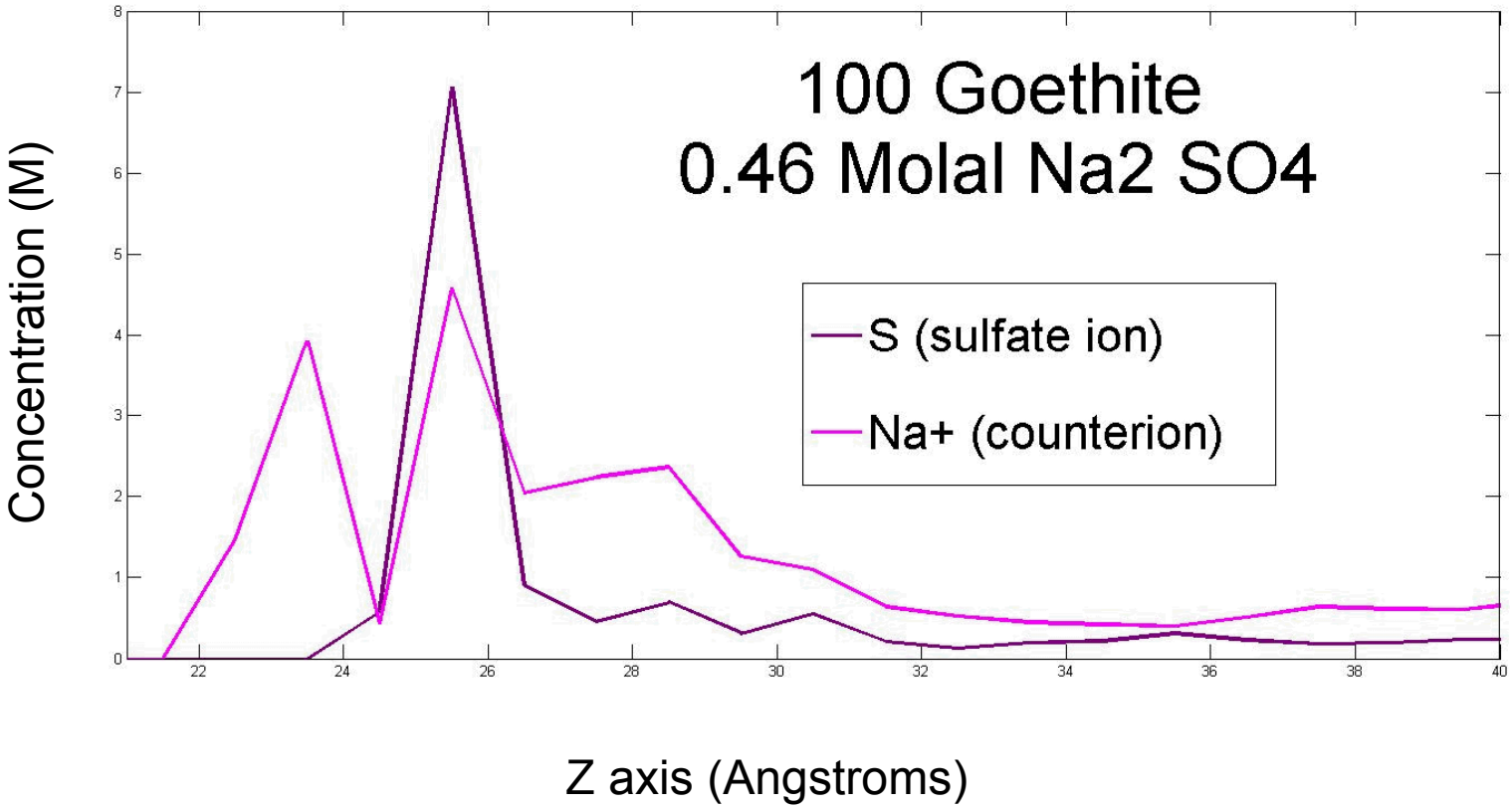
- 3 vacuum boxes above
- L-J potential at top to enforce vacuum
- 1 iron atom held stationary
- 50 picoseconds to equilibrate NVE
- 10 nanoseconds production NVT
  - (300K, Nose-Hoover thermostat)

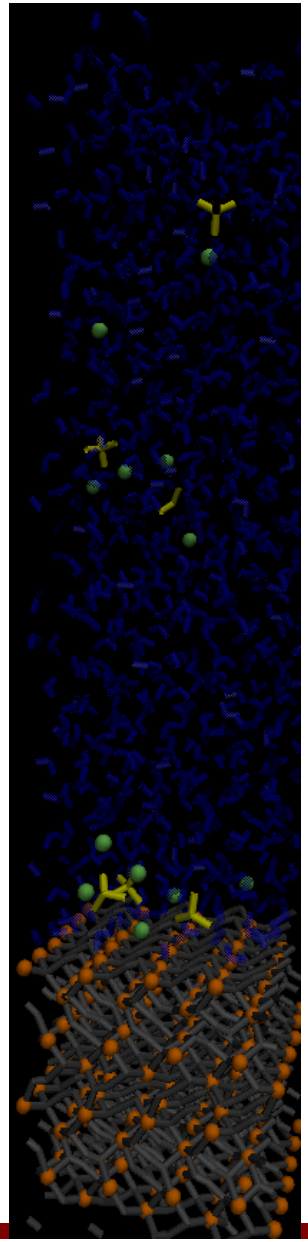


Na_2SO_4 on Goethite (100)

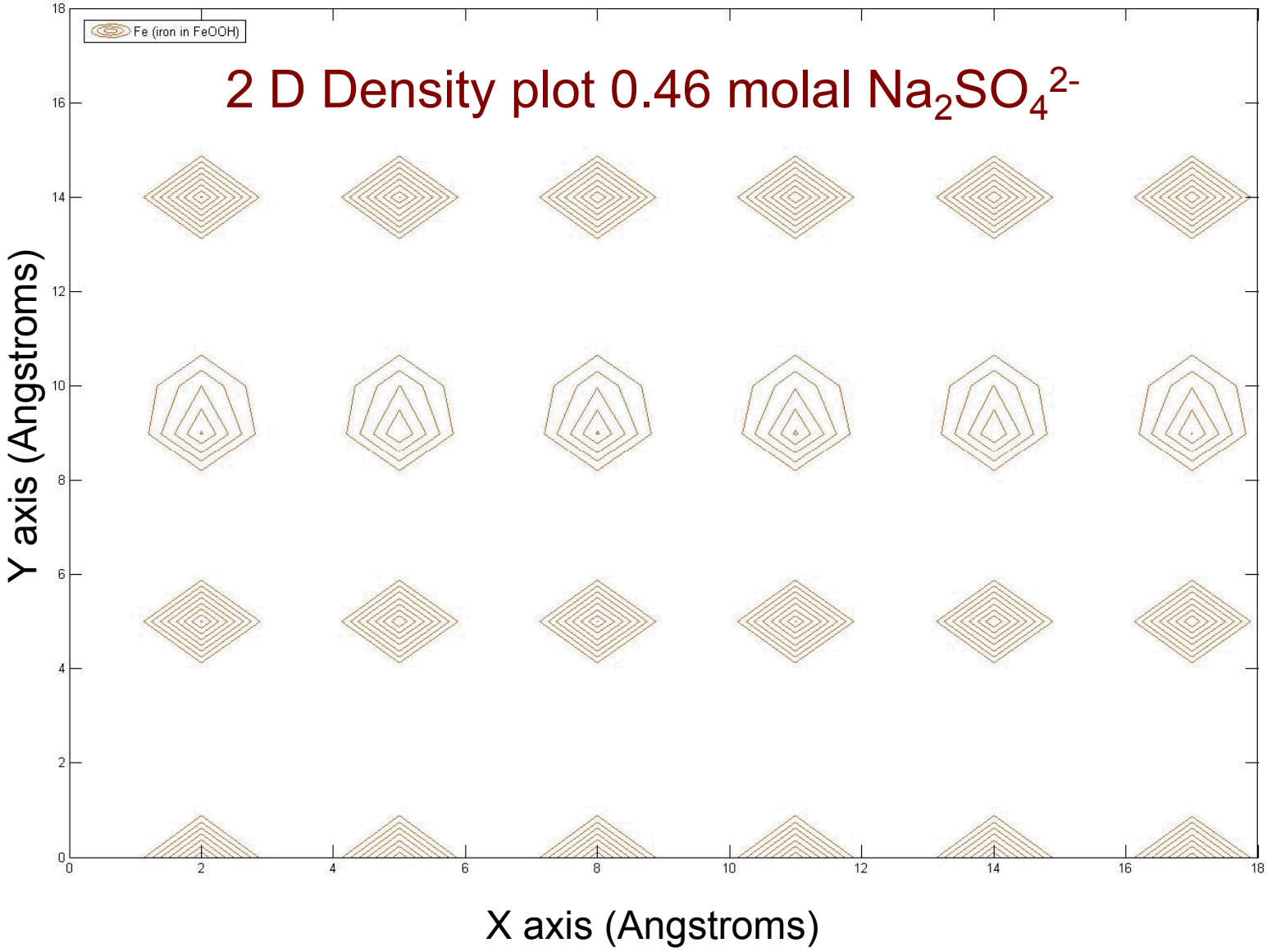
Sandia National Laboratories

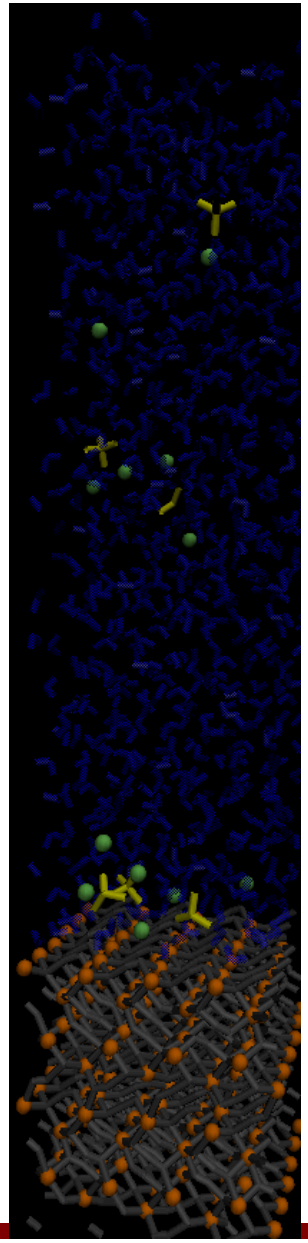
1 D Density plot



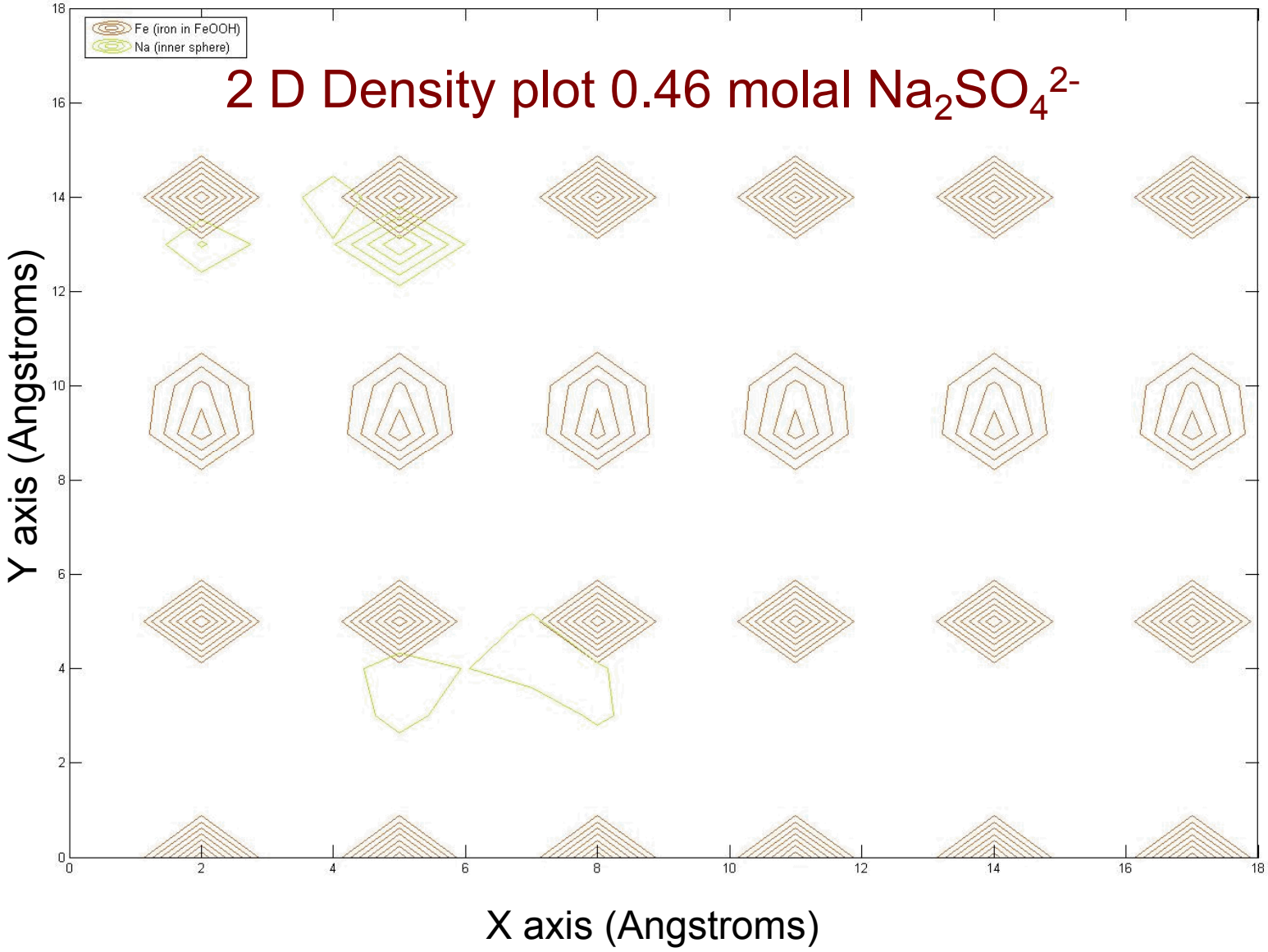


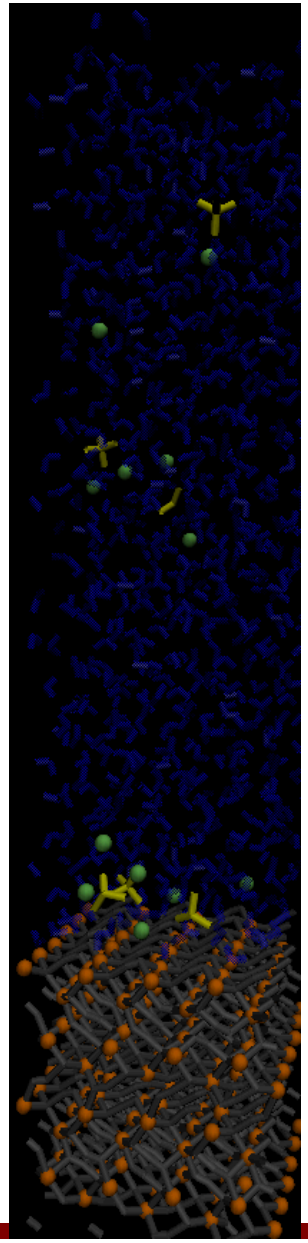
Na_2SO_4 on Goethite (100)





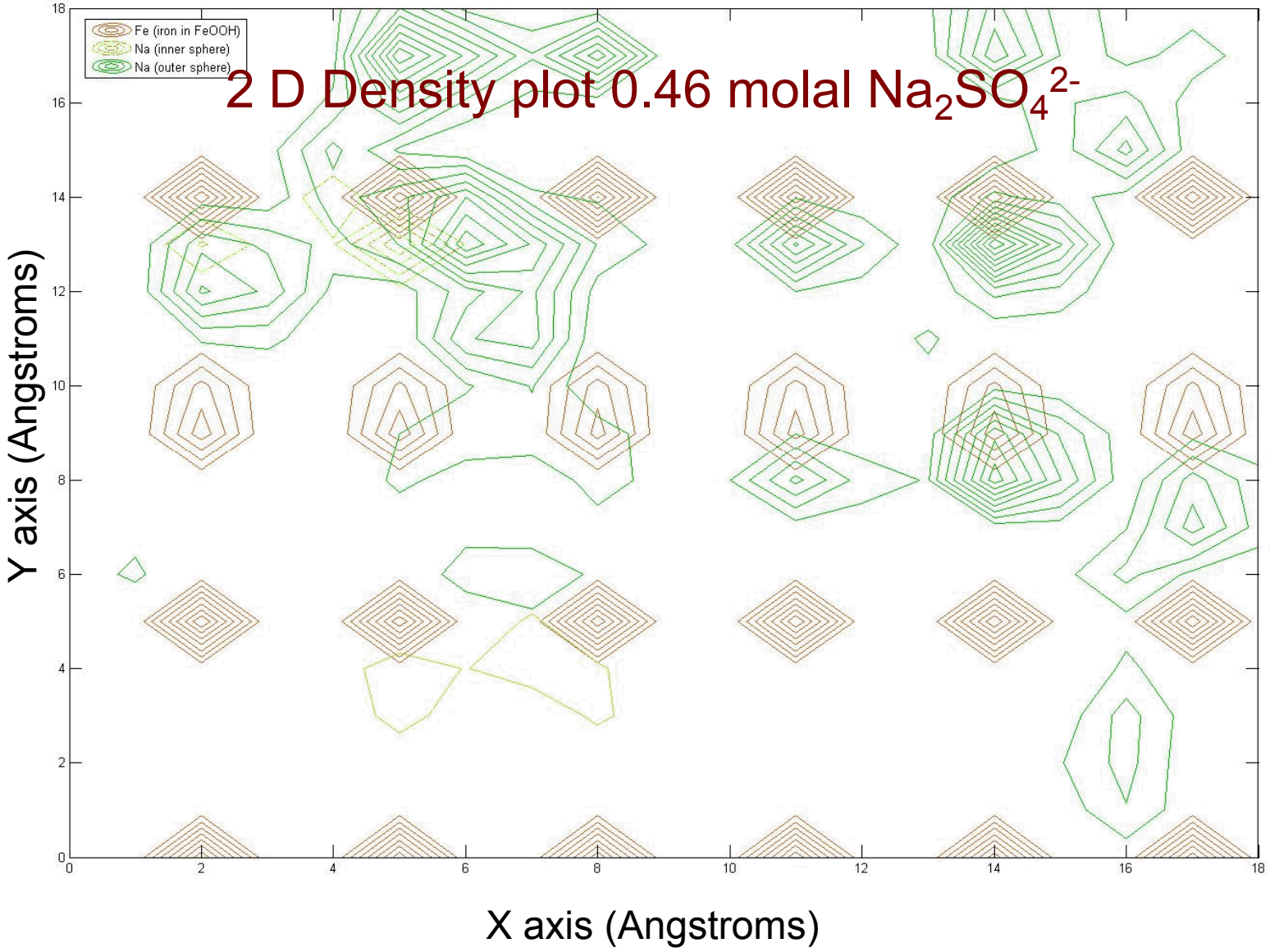
Na_2SO_4 on Goethite (100)

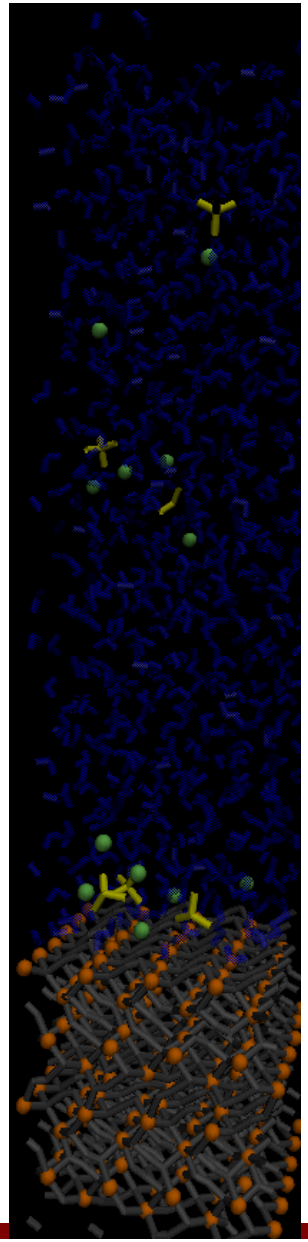




Na_2SO_4 on Goethite (100)

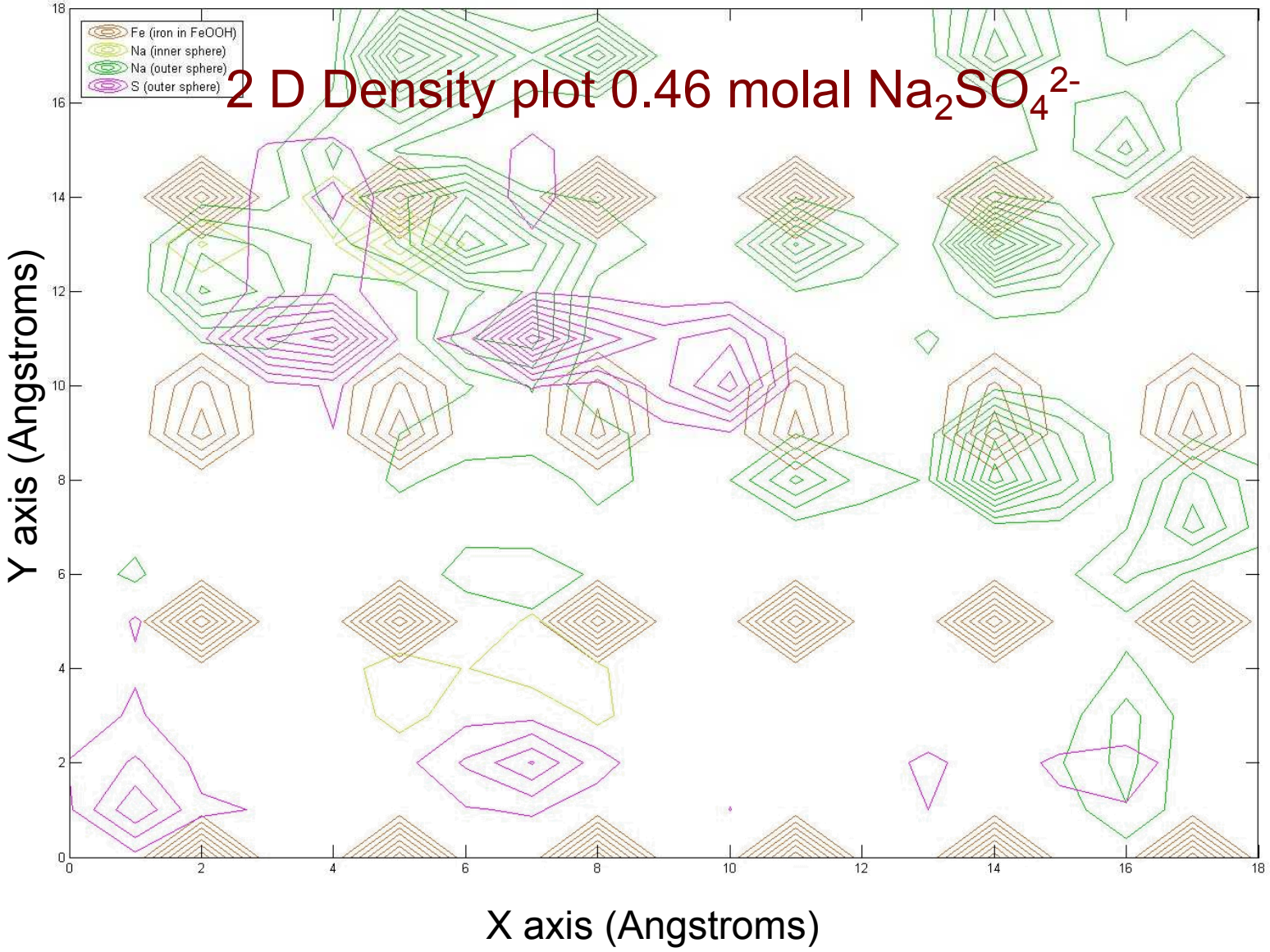
Sandia National Laboratories

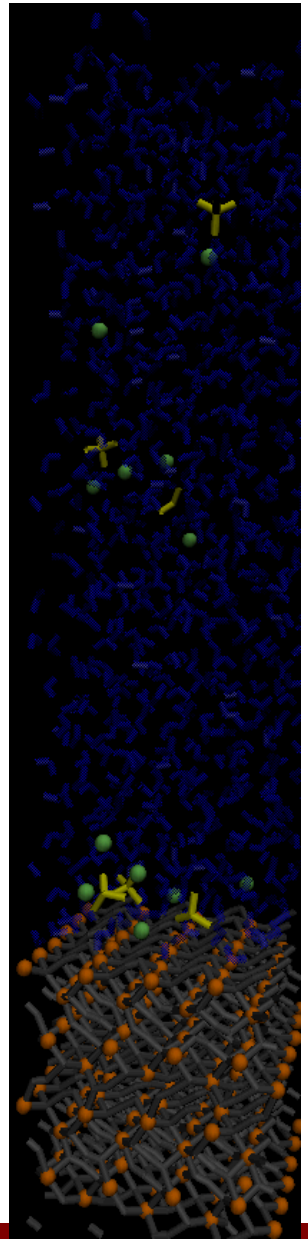




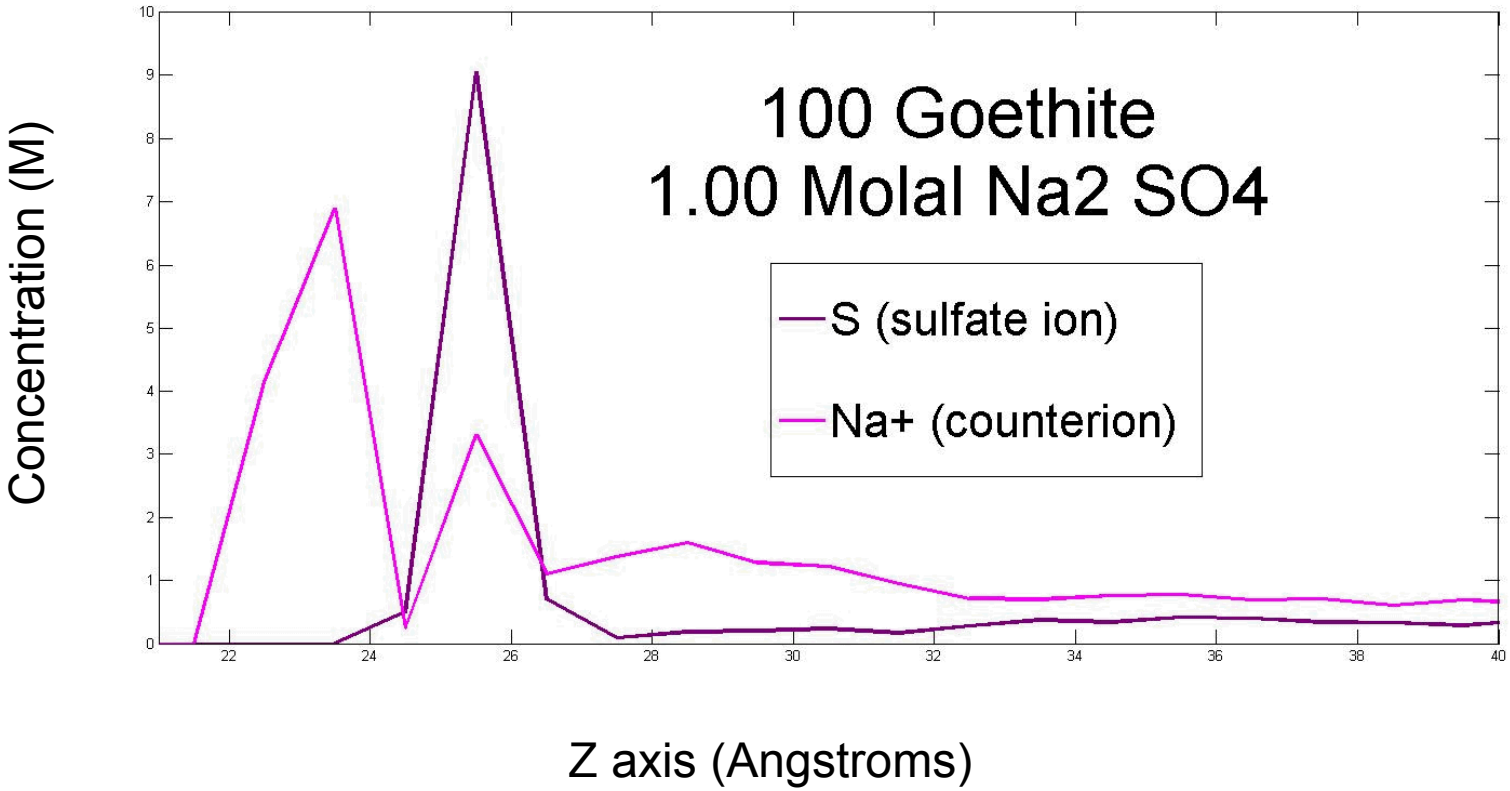
Na_2SO_4 on Goethite (100)

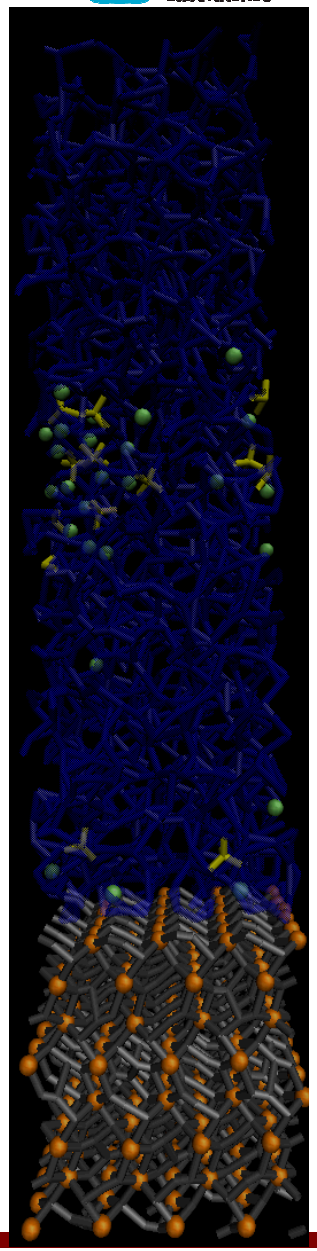
Sandia National Laboratories



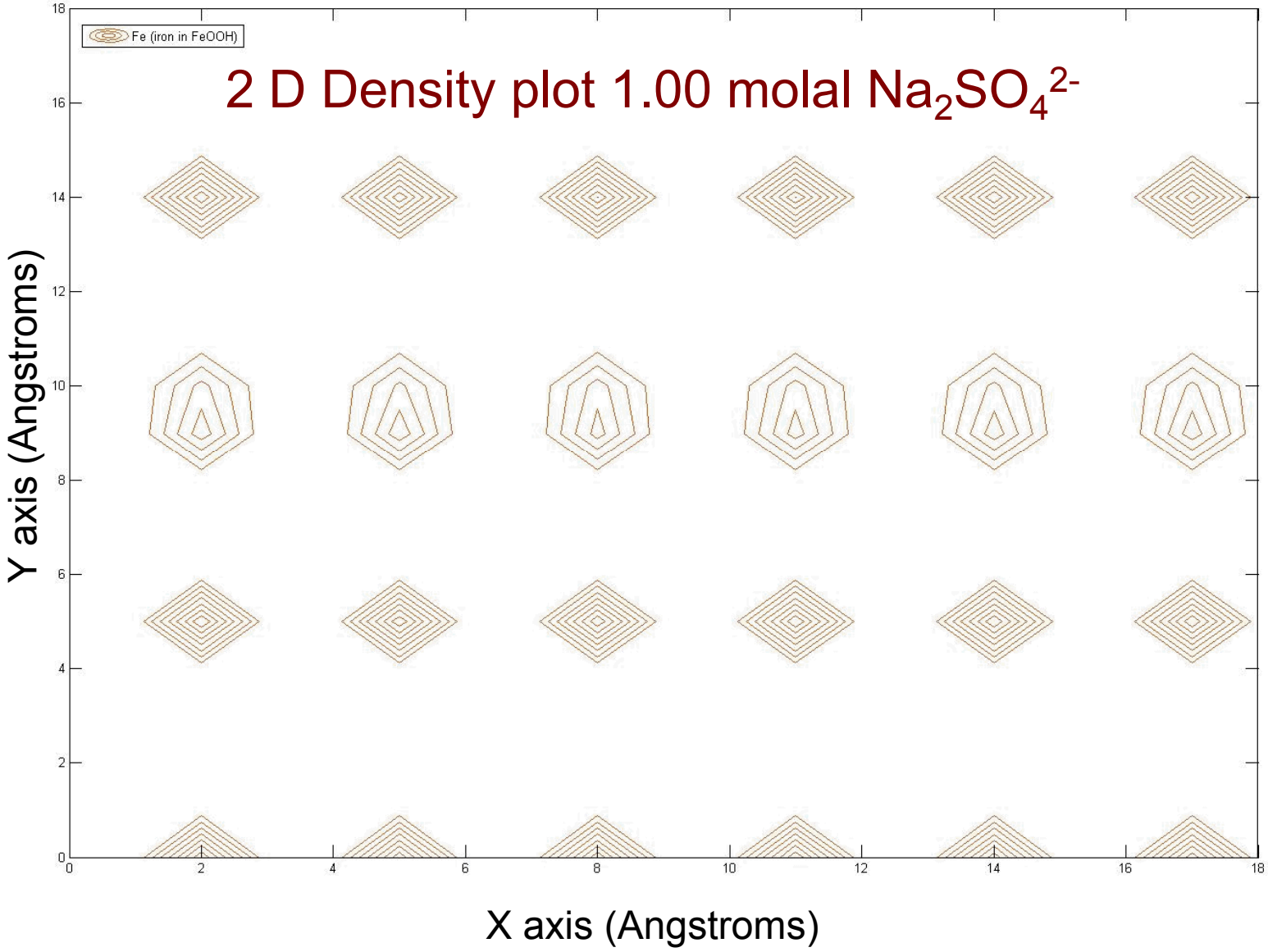


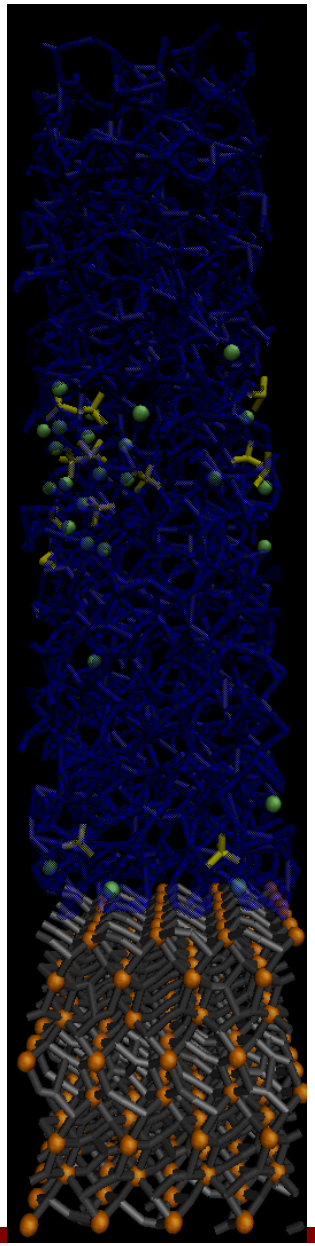
1.00 molal Na_2SO_4 on (100)



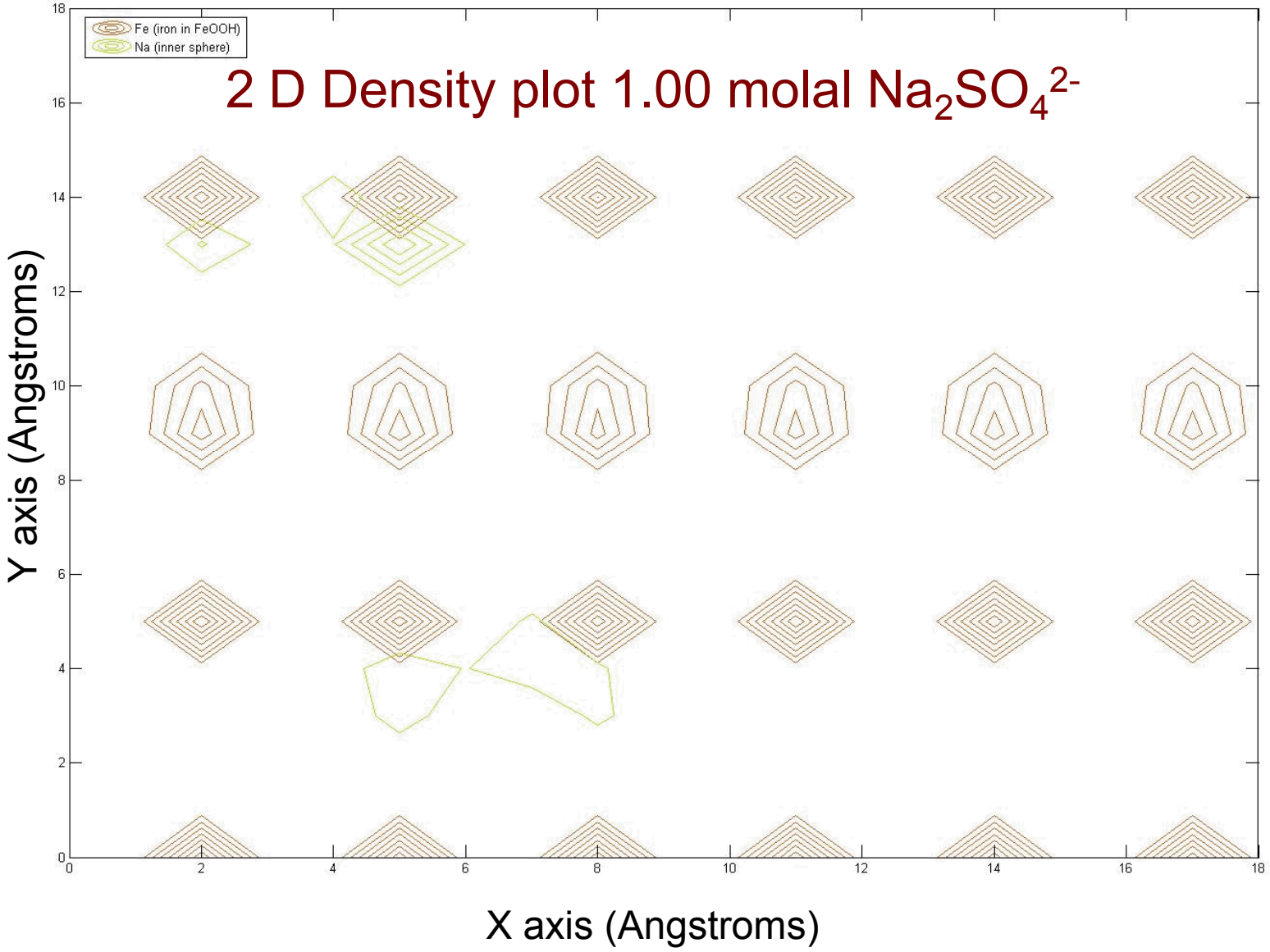


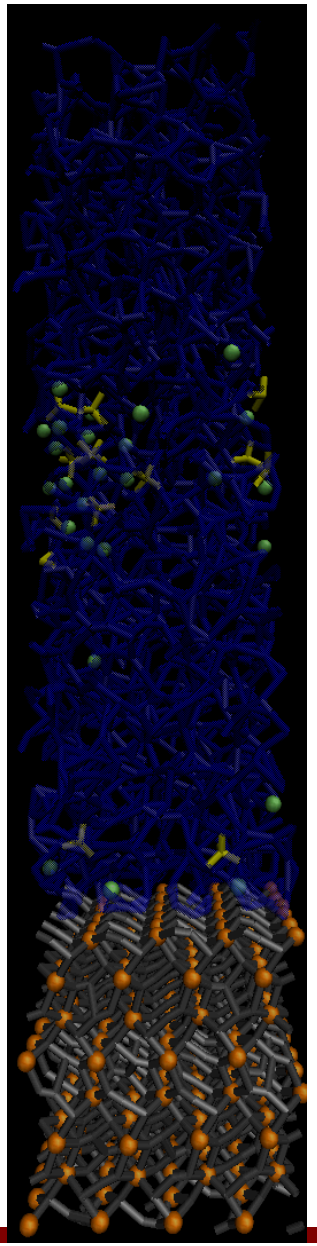
Na_2SO_4 on Goethite (100)





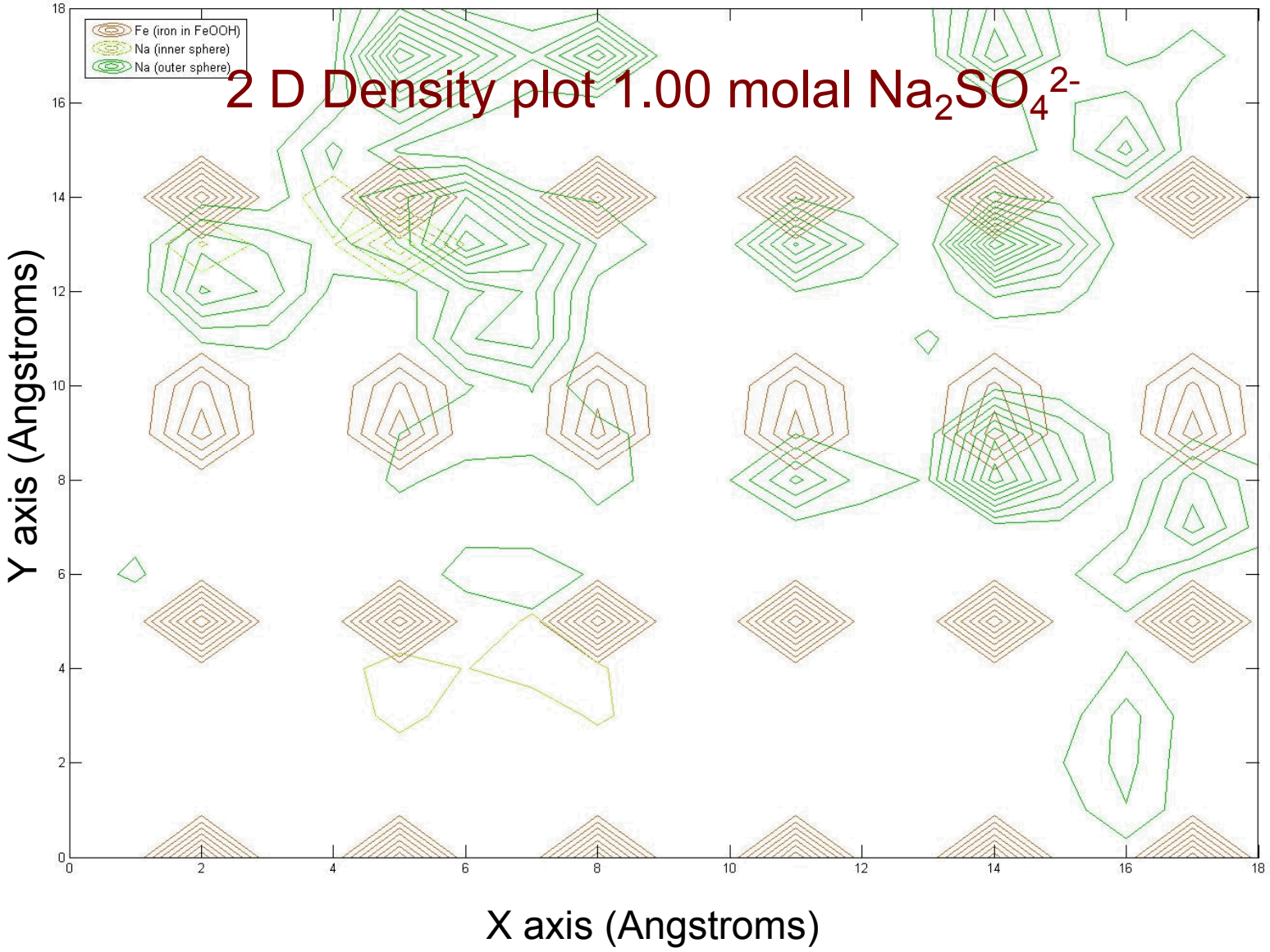
Na_2SO_4 on Goethite (100)

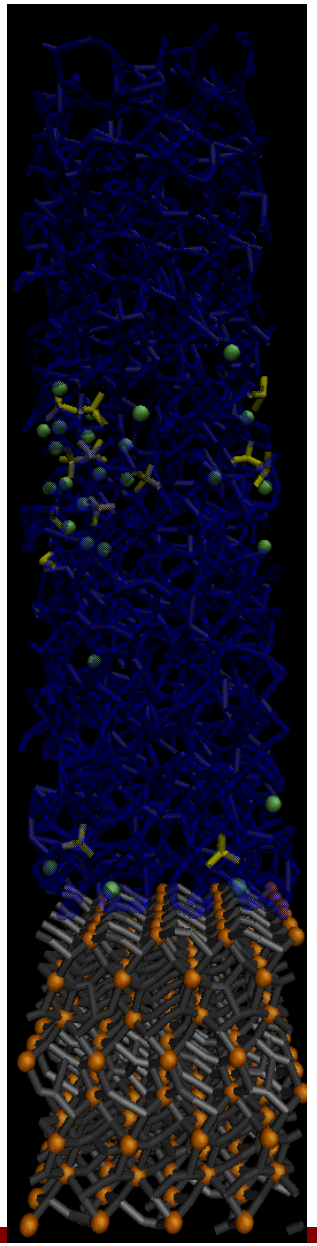




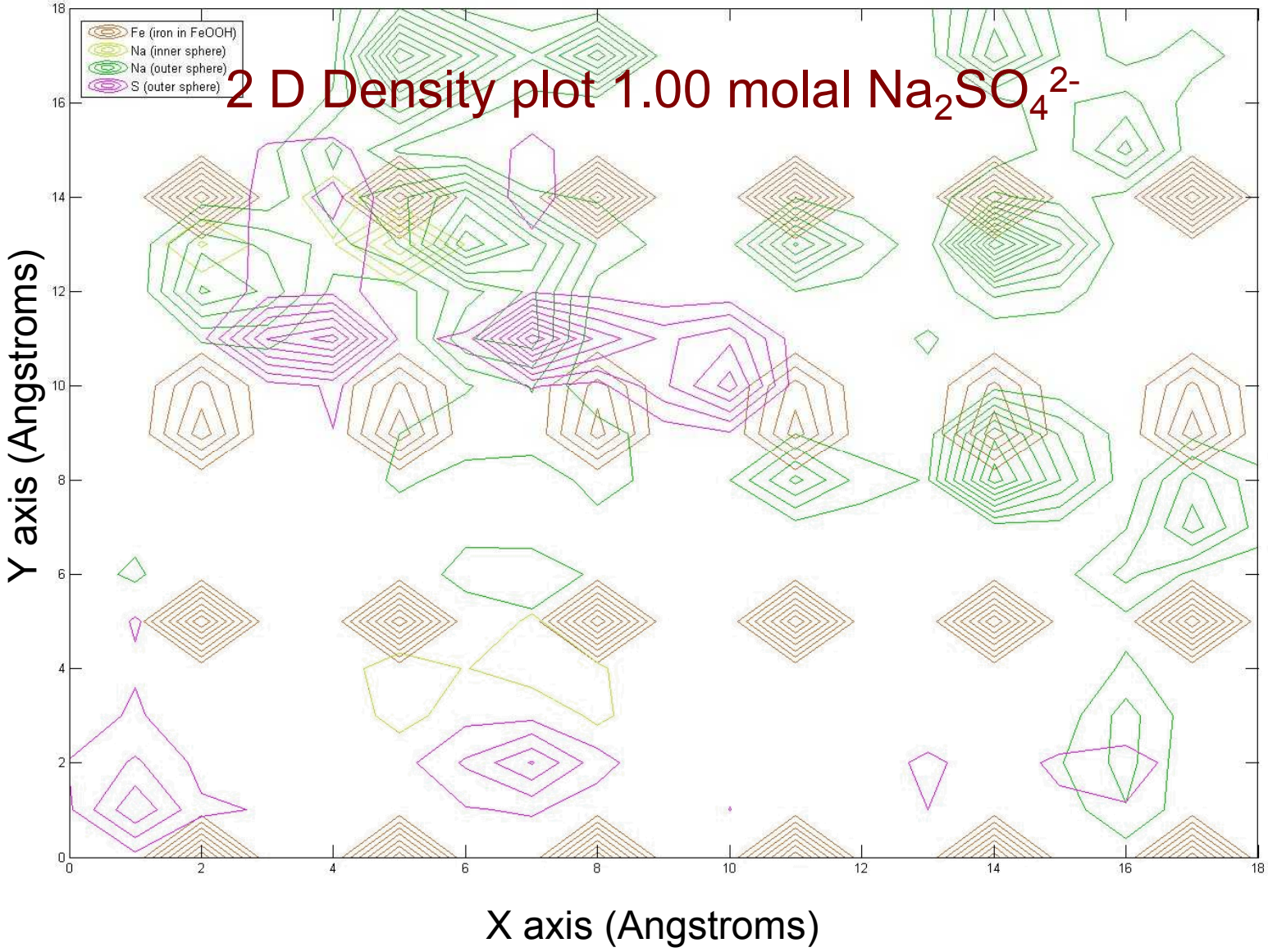
Na_2SO_4 on Goethite (100)

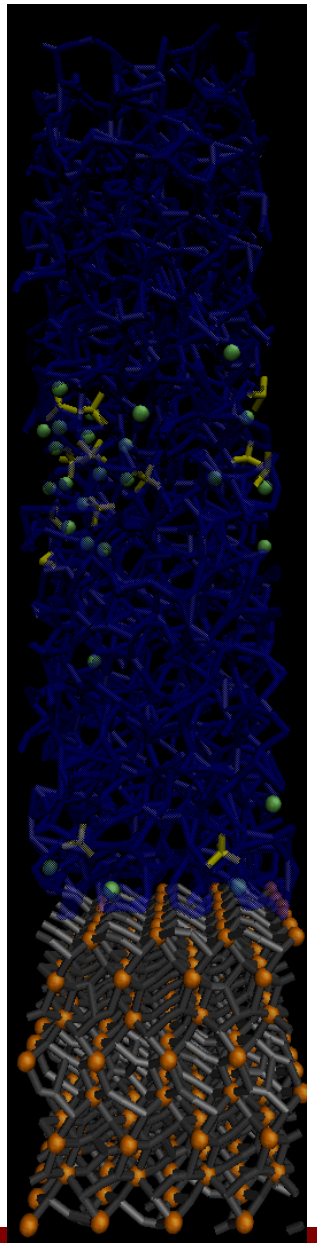
Sandia National Laboratories



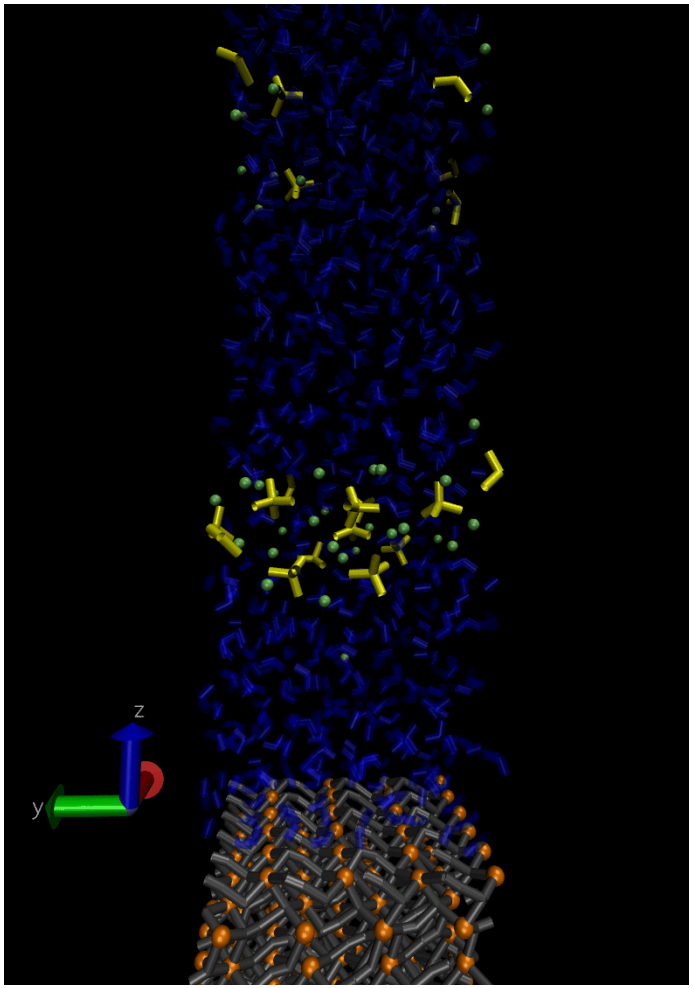


Na_2SO_4 on Goethite (100)



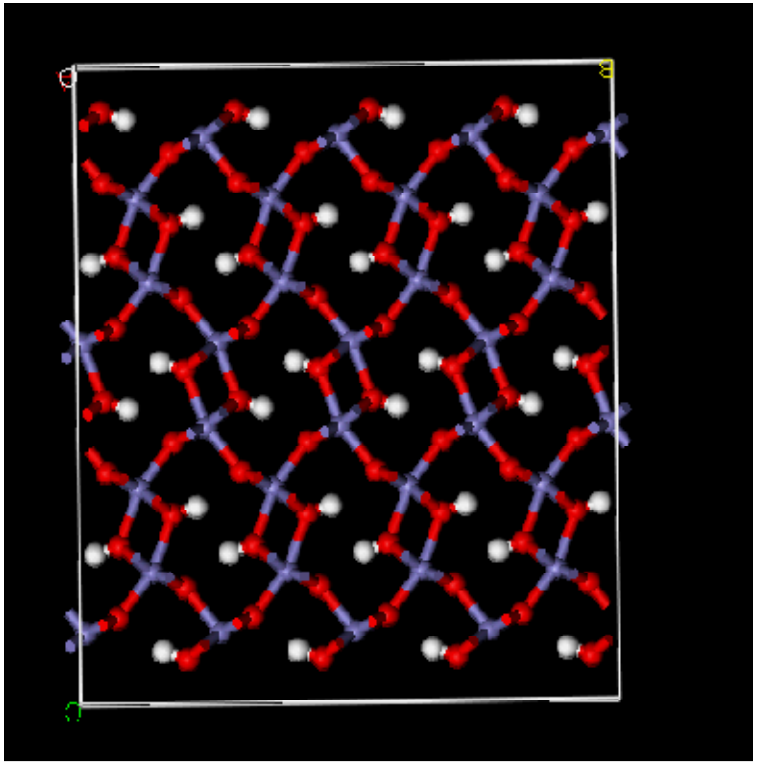


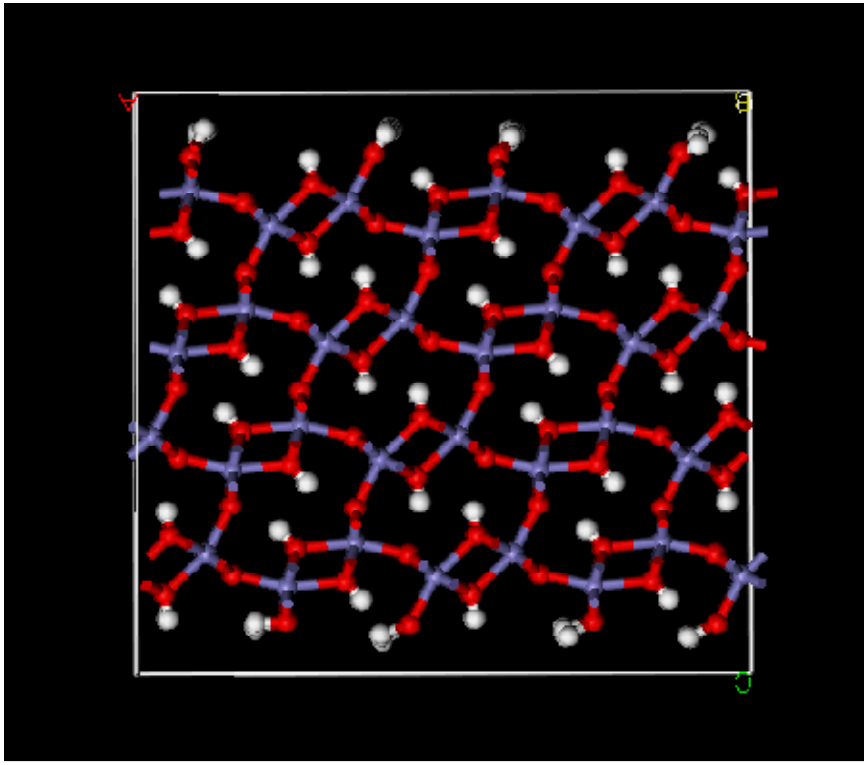
1.46 molal Na_2SO_4 on (100)



Goethite (100) and Goethite (101)

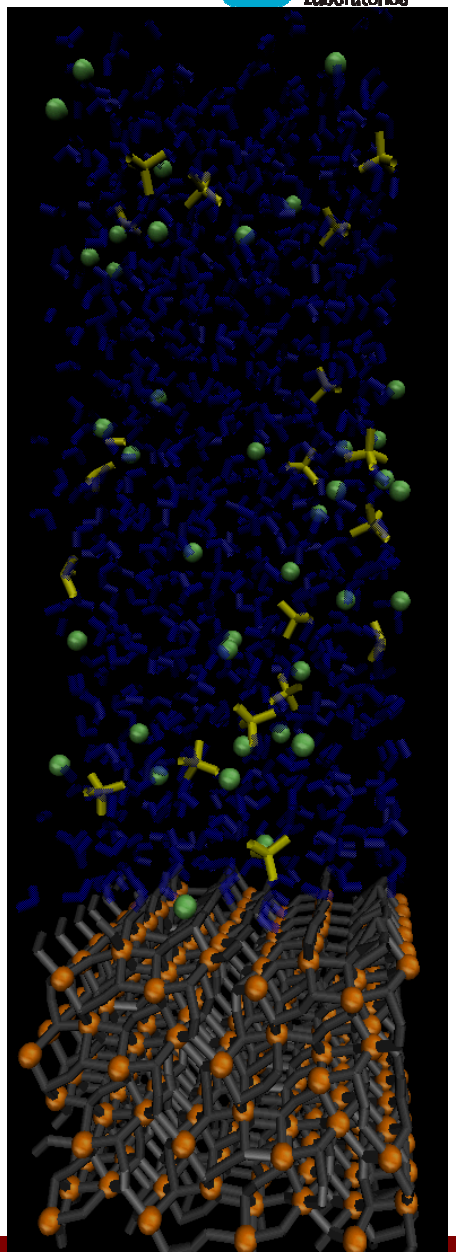
Sandia National Laboratories





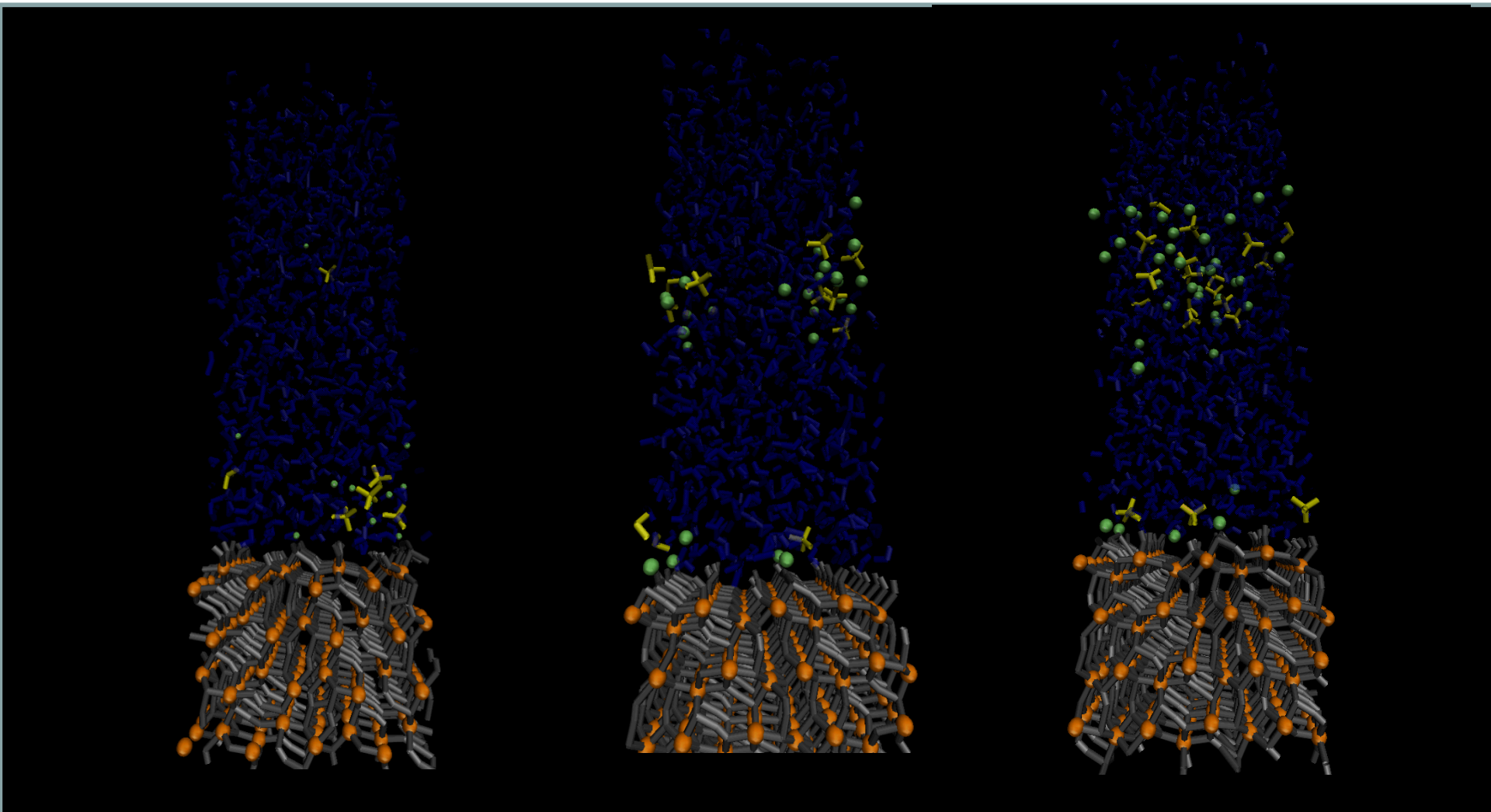
Na_2SO_4 on Goethite (101)

- Complexation as a function of concentration
  - 0.46 molal
  - 1.00 molal
  - 1.46 molal



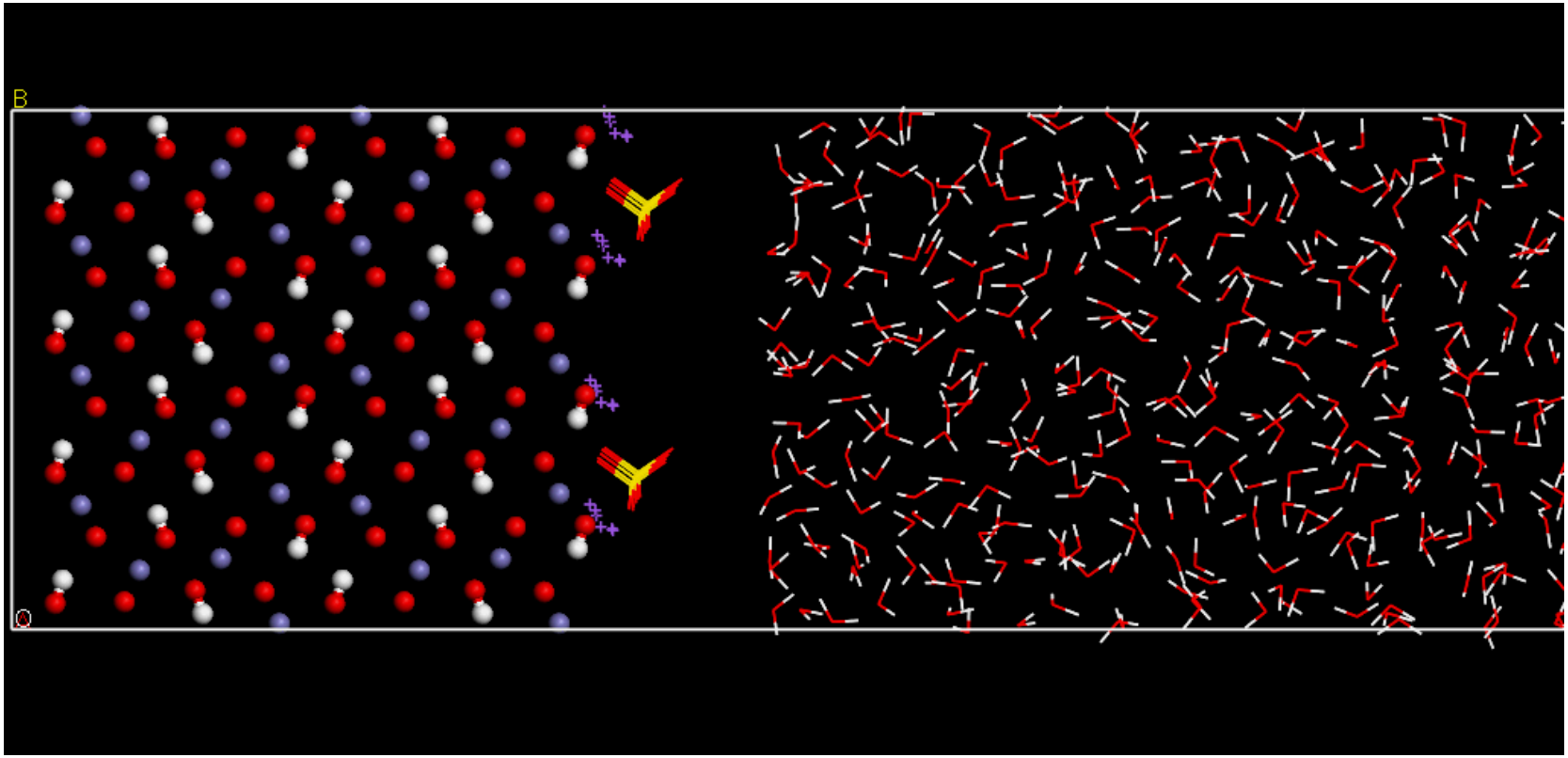
(101)
0.46 molal - 1.00 molal - 1.46 molal

Sandia National Laboratories



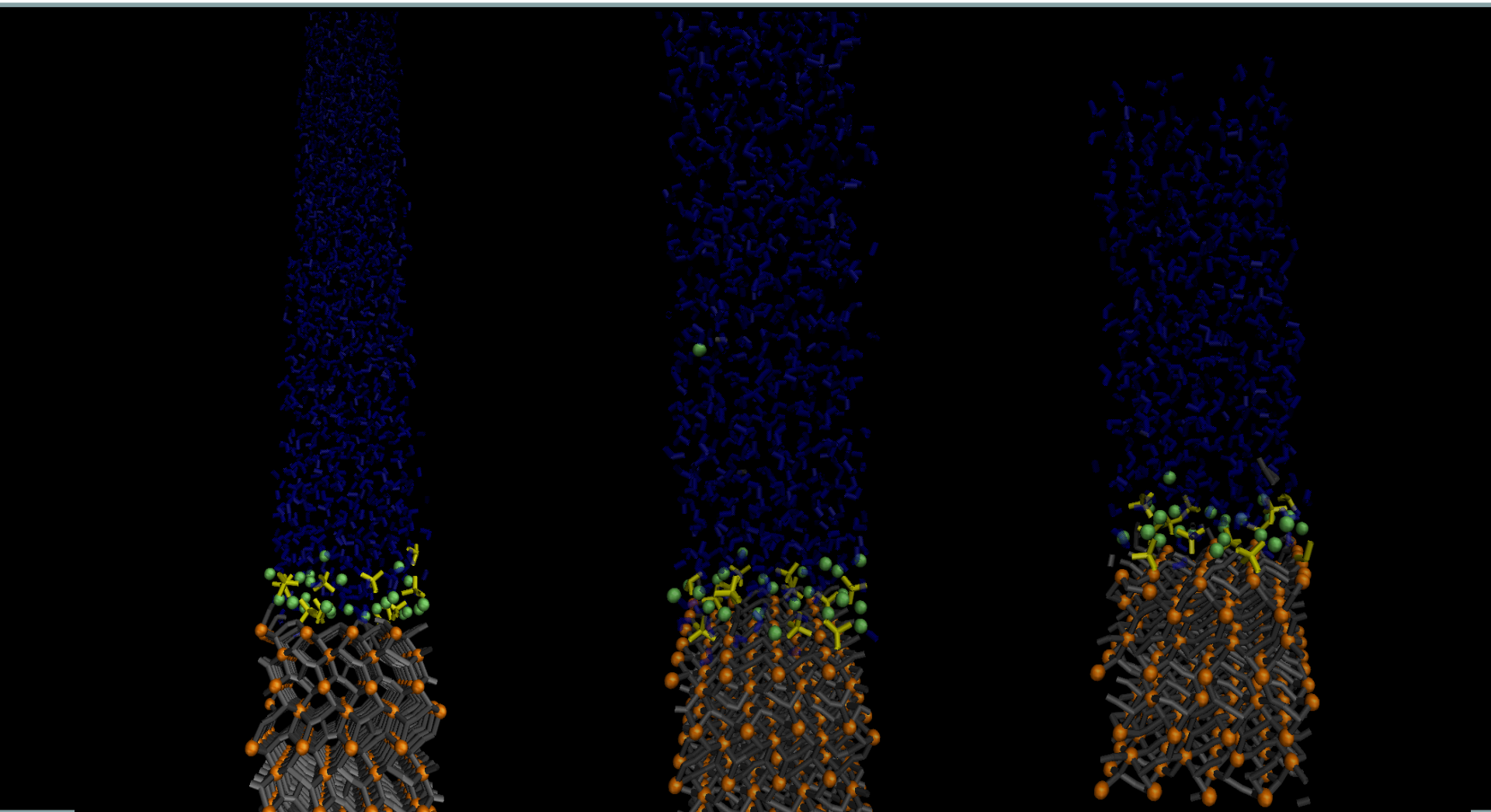
Loaded Goethite (100) and (101)

- 0.50 molal, 1.00 molal, 1.5 molal
- Complexation as a function of concentration



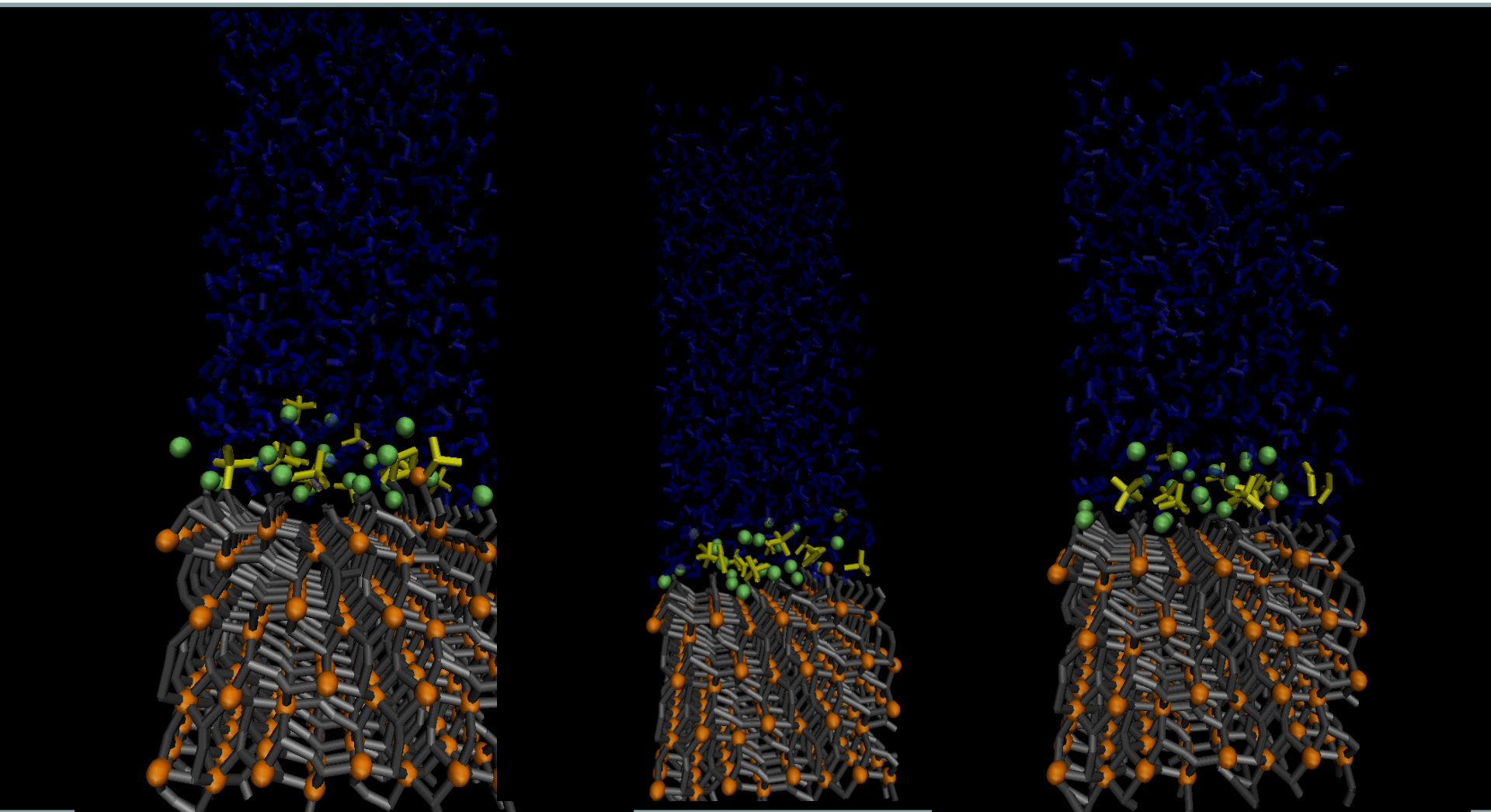
(100)
0.50 molal - 1.00 molal - 1.50 molal

Sandia National Laboratories



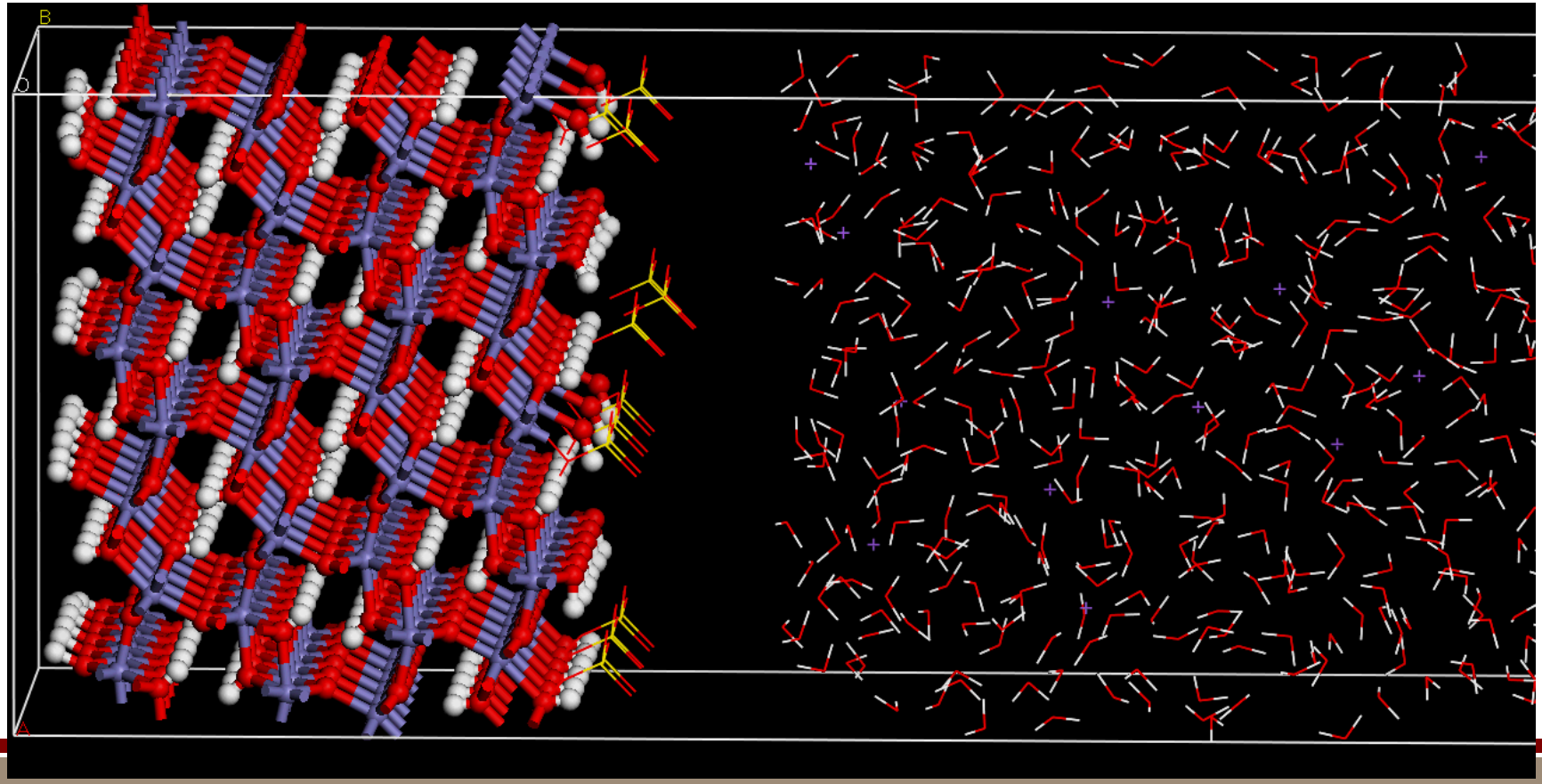
(101)
0.50 molal - 1.00 molal - 1.50 molal

Sandia National Laboratories



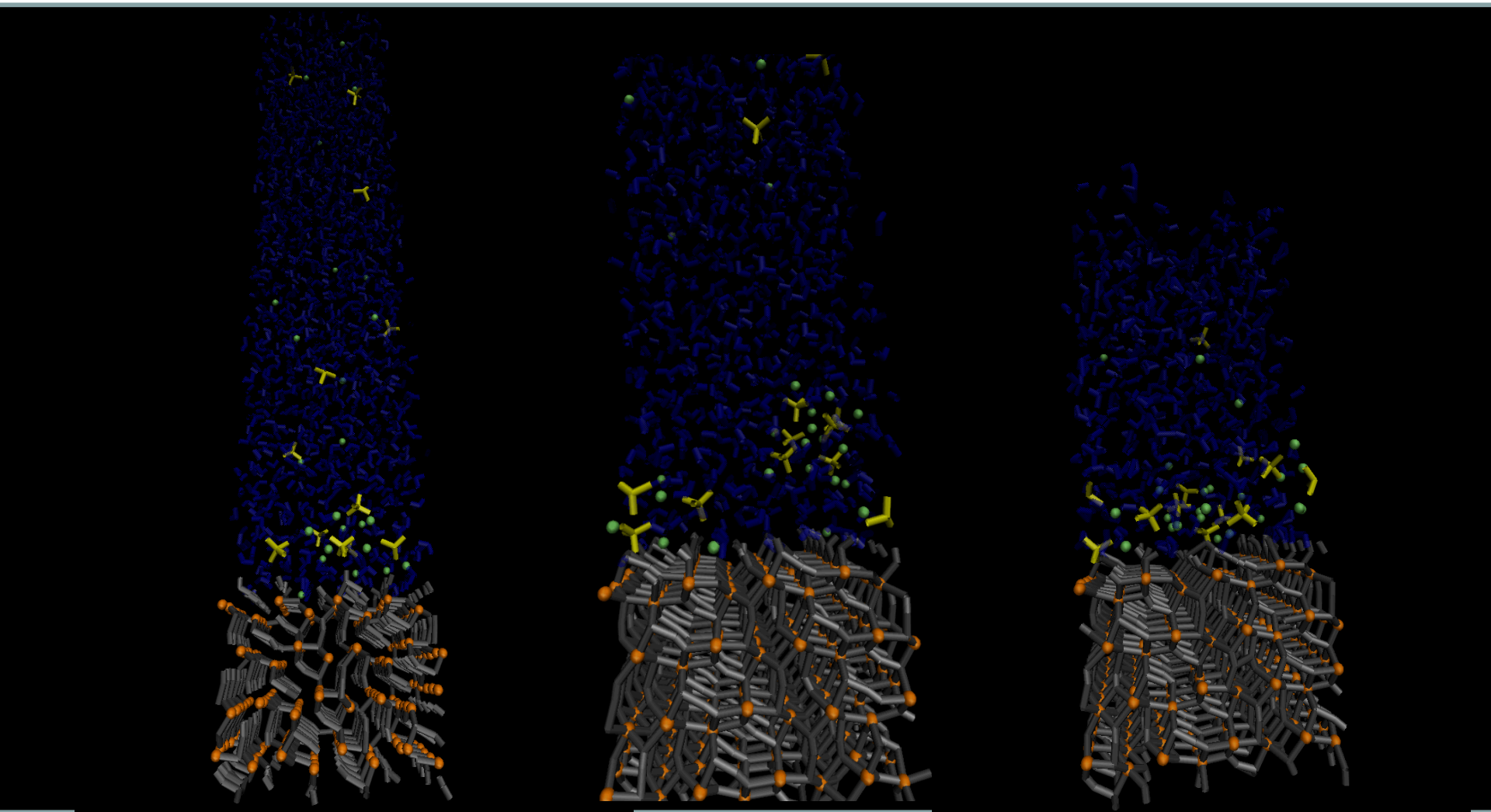
De-Hydroxylated (101)

- 0.50 molal, 1.00 molal, 1.5 molal
- Complexation as a function of concentration



De-Hydroxylated (101)
0.50 molal - 1.00 molal - 1.50 molal

Sandia National Laboratories



Conclusions, Future Work

Sandia National Laboratories

- Why isn't the sulfate binding as much as the cation? Is a steric factor physically reasonable?
- Two explanations
  - Steric hindrance from large surface complexes
  - Lower pH induced de-hydroxylation
- Both of these explanations deserve further investigation

Sandia National Laboratories

THANK YOU!