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Structural and Vibrational Properties of Clay Minerals from Classical and *ab initio* Molecular Dynamics Simulations

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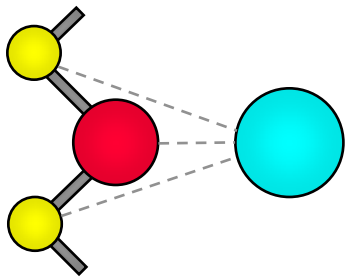
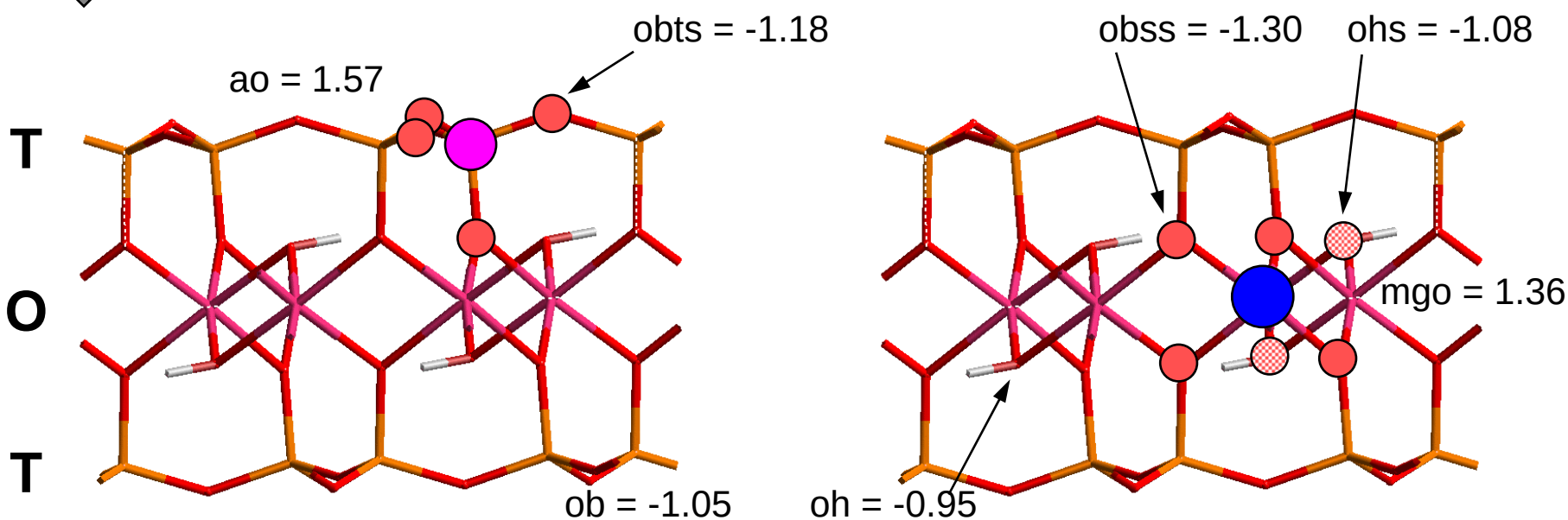
Acknowledgements

U.S. Department of Energy, Basic Energy Sciences

Nonbonded clay force field



Fully **flexible** model for exchange of momentum and energy among all species



$$E = \sum_i \sum_j \left[\left(\frac{A_{ij}}{r_{ij}} \right)^{12} - \left(\frac{B_{ij}}{r_{ij}} \right)^{6} + \frac{q_i q_j}{\varepsilon r_{ij}} \right]$$

van der Waals Coulombic

Cygan et al, *J Phys Chem B* **2004**

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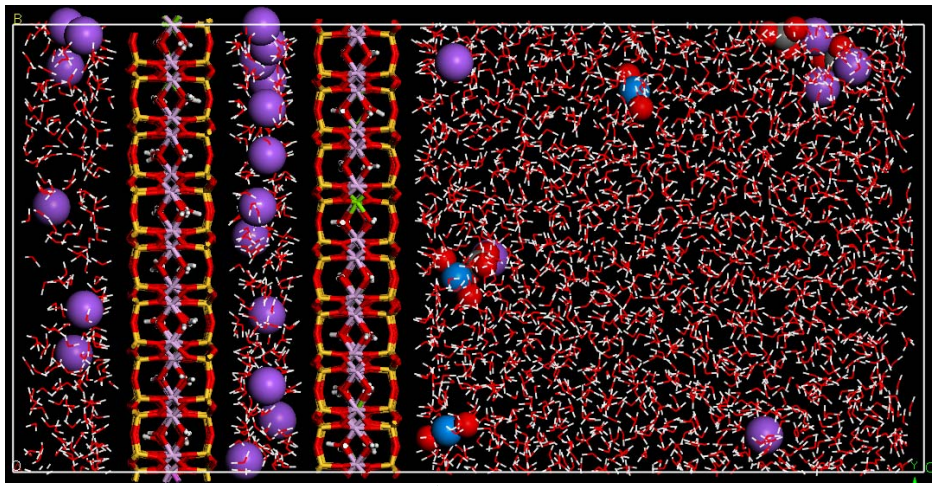
Summary of recent BES research

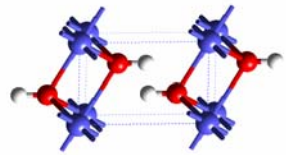
Montmorillonite
UO_2^{2+}/Na^+ sorption
42 Å x 36 Å x 72 Å
10k atoms, 0.027 M



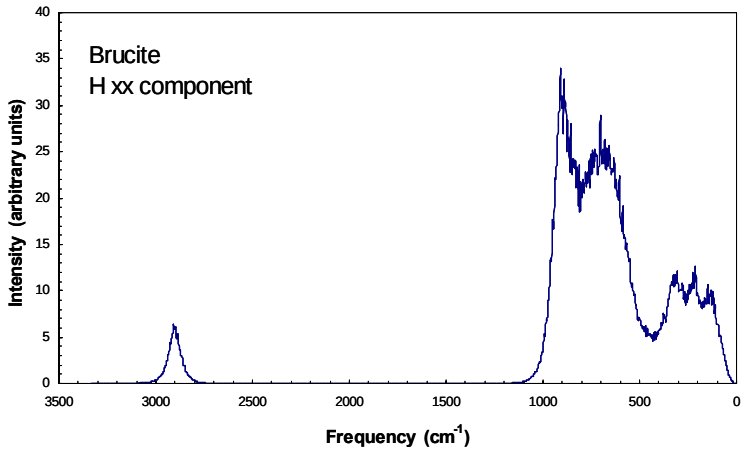
Sorption Layer

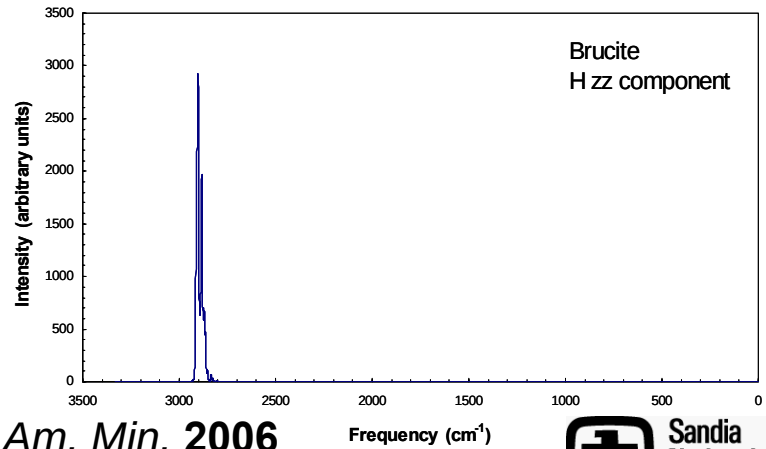
Greathouse and Cygan, *PCCP* **2005**
Greathouse and Cygan, *ES&T* **2006**

Brucite, $Mg(OH)_2$
Anisotropic OH vibrations
26 Å x 19 Å x 14 Å



H Power Spectra





Braterman and Cygan, *Am. Min.* **2006**

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Collaborators

Andrey Kalinichev and James Kirkpatrick, University of Illinois
Spectroscopic and simulation studies of clays, LDH's

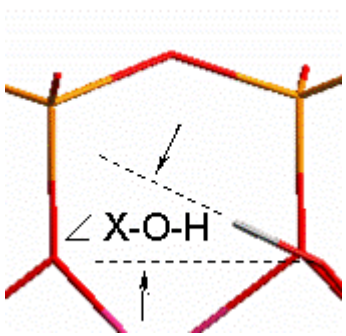
Jeffrey Post, Smithsonian Institution
Diffraction and spectroscopic studies of birnessite

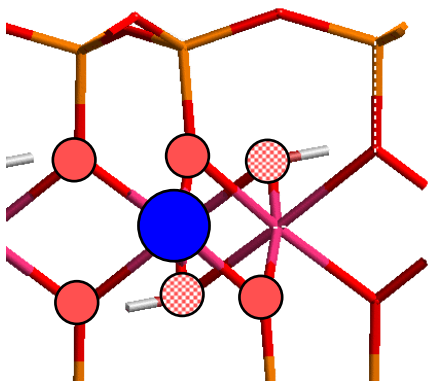
Cliff Johnston, Purdue University
Vibrational spectroscopy of clays and clay interlayer species

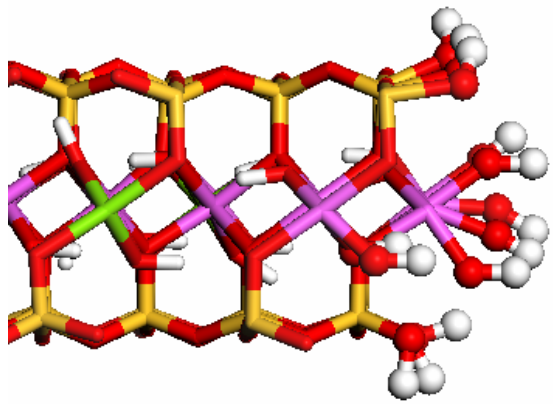
Melissa Denecke, FZK Karlsruhe
Synchrotron X-ray absorption studies of radionuclide sorption
EXAFS studies of Hf adsorption onto mica edge sites

Reductionism

- Simplify a complex problem
- Compare quantum calculations with classical
- Increment the level of complexity in the classical force field
- Accuracy (quantum) vs. system size (classical)







Uncharged clay

Charged clay

Edge sites

Computational Resources

BES Capital Equipment

- 34 CPU cluster + 34 CPU cluster + 32 CPU = **100 CPU**

  Greathouse/Cygan Criscenti Shared
- 14 terabytes data storage

Classical (force field) molecular dynamics

- LAMMPS software
- **> 1M atoms** possible
- **> 1 ns time** scale

ab initio molecular dynamics

- VASP software
- SNL institutional cluster (Thunderbird) for **256-CPU jobs**
- **160 atoms, 2 clay layers**
- **25 ps** time scales (< 10 ps times in the literature)

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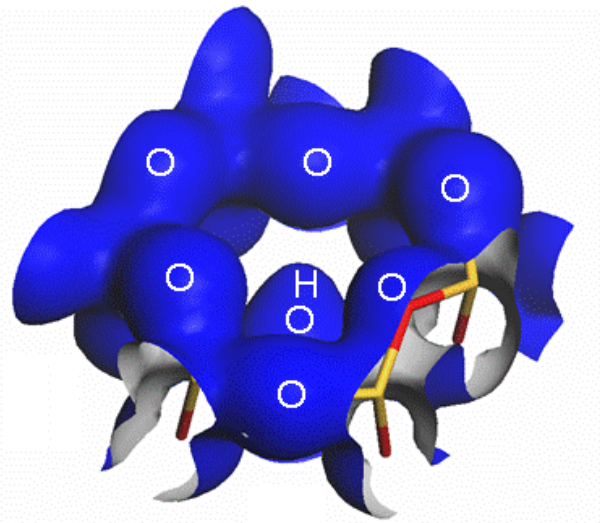
Molecular Dynamics

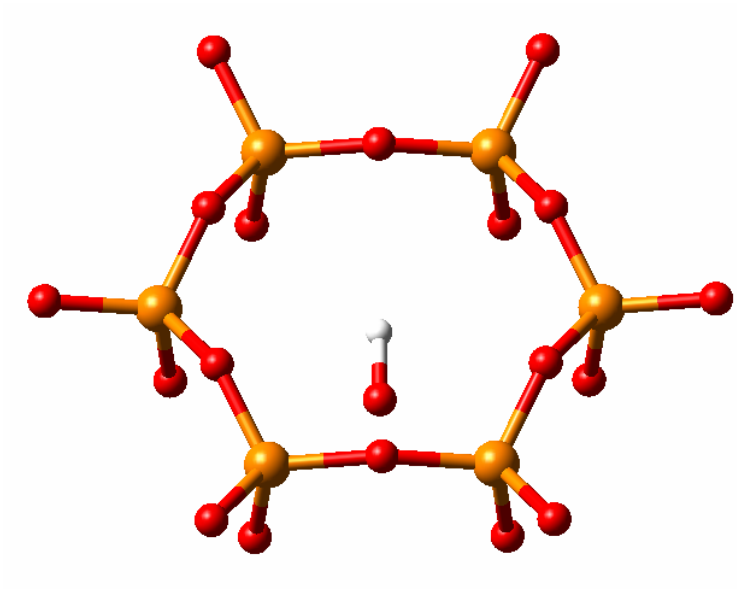
***ab initio* Molecular Dynamics**

- PAW pseudopotentials with plane-wave basis set
- Exchange-correlation treated through GGA
- Gamma point calculations
- Constant pressure optimizations
- 2 x1x2 supercell (160 – 168 atoms)
- 25 ps NVT production simulations
- 0.5 fs timestep
- 256 processors – 8 days

Classical Molecular Dynamics

- CLAYFF force field
- 8x4x3 supercell (3840 – 4032 atoms)
- 1.0 ns NVT production simulations
- 0.5 fs timestep
- 4 processors – 1.5 days





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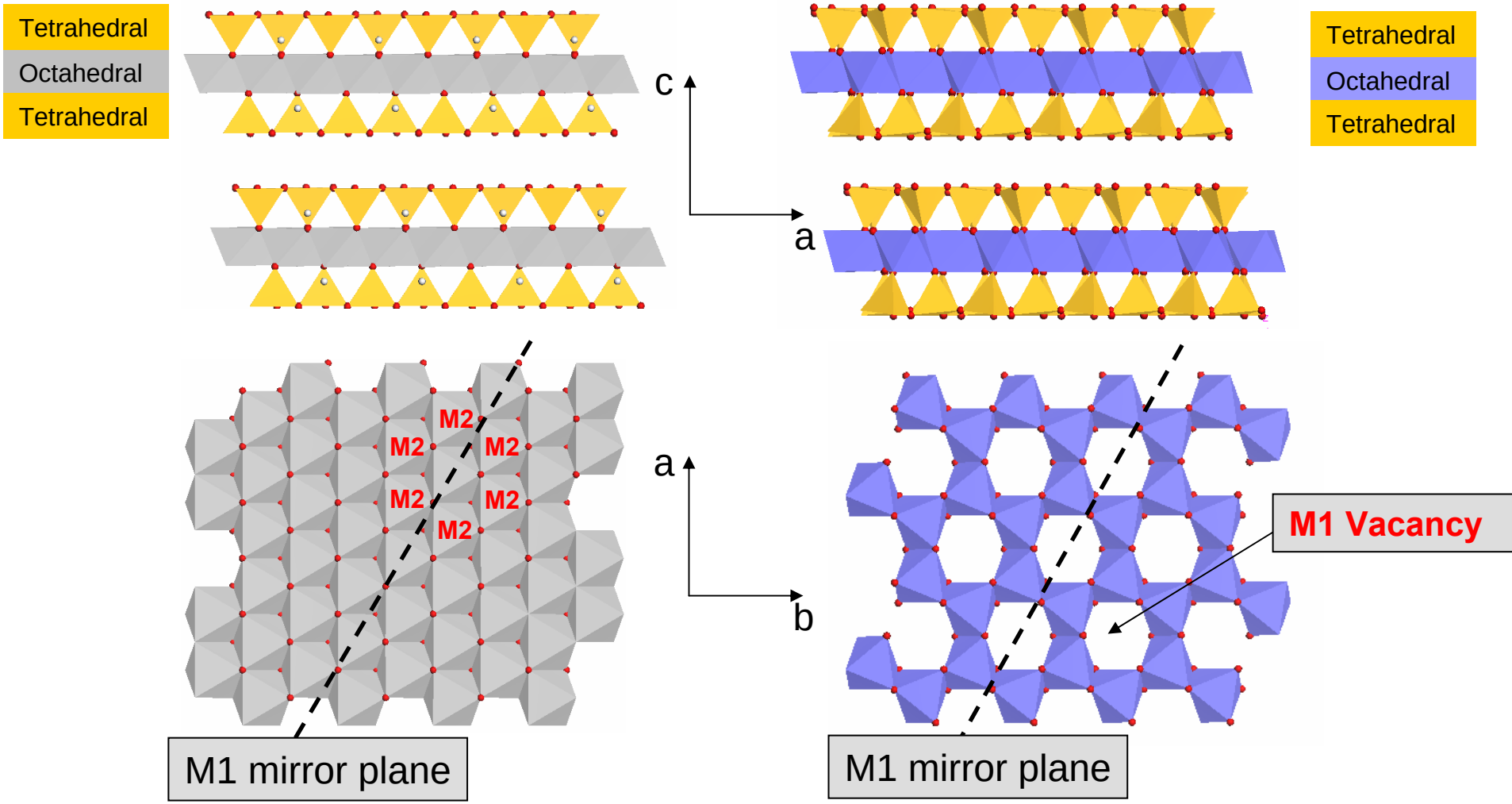
Geometry of 2:1 Layered Clays

Talc

$Mg_3(OH)_2(Si_4O_{10})$

Pyrophyllite

$Al(OH)(Si_2O_5)$



Perdikatsis, *Z. Kristallogr.*, **1981**

Lee and Guggenheim, *Am. Mineral.*, **1981**

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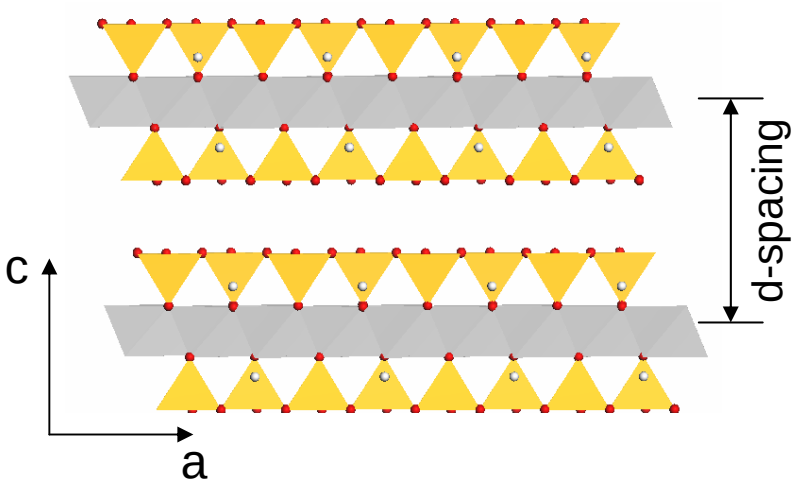
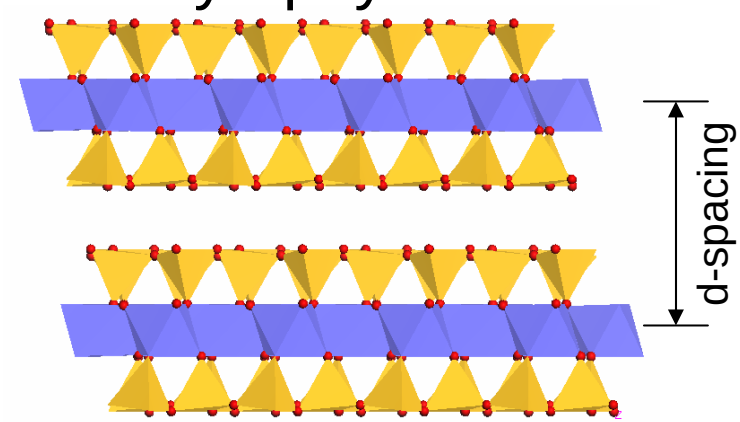
Initial Results (Larentzos et al, J. Phys. Chem. C, submitted)

Talc



Pyrophyllite



	DFT	CLAYFF	Expt.
d-spacing	9.128 Å	9.13 Å	9.351 Å
O-H bond	0.96 Å	1.03 Å	
O-H stretch	3669 cm^{-1}	3750 cm^{-1}	3677 cm^{-1}

	DFT	CLAYFF	Expt.
d-spacing	8.900 Å	9.31 Å	9.190 Å
O-H bond	0.97 Å	1.03 Å	
O-H stretch	3658 cm^{-1}	3750 cm^{-1}	3675 cm^{-1}

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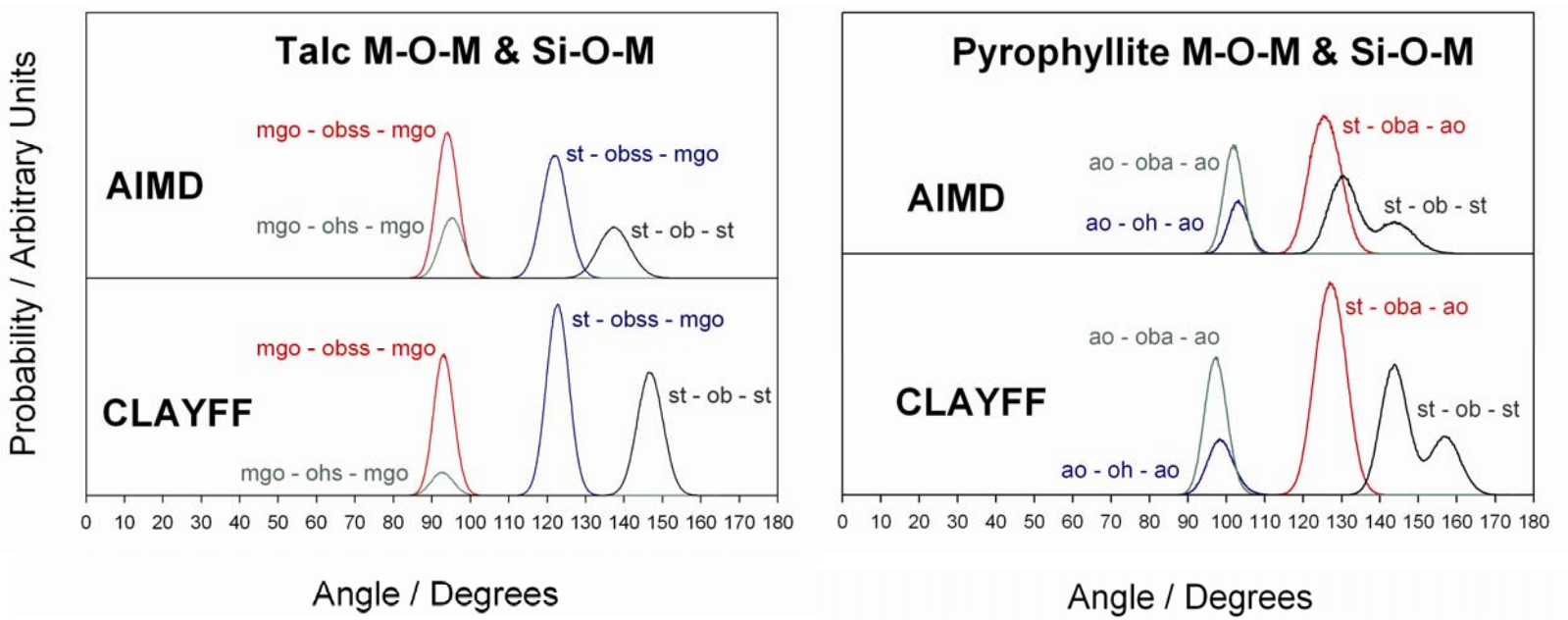
Angle Distributions



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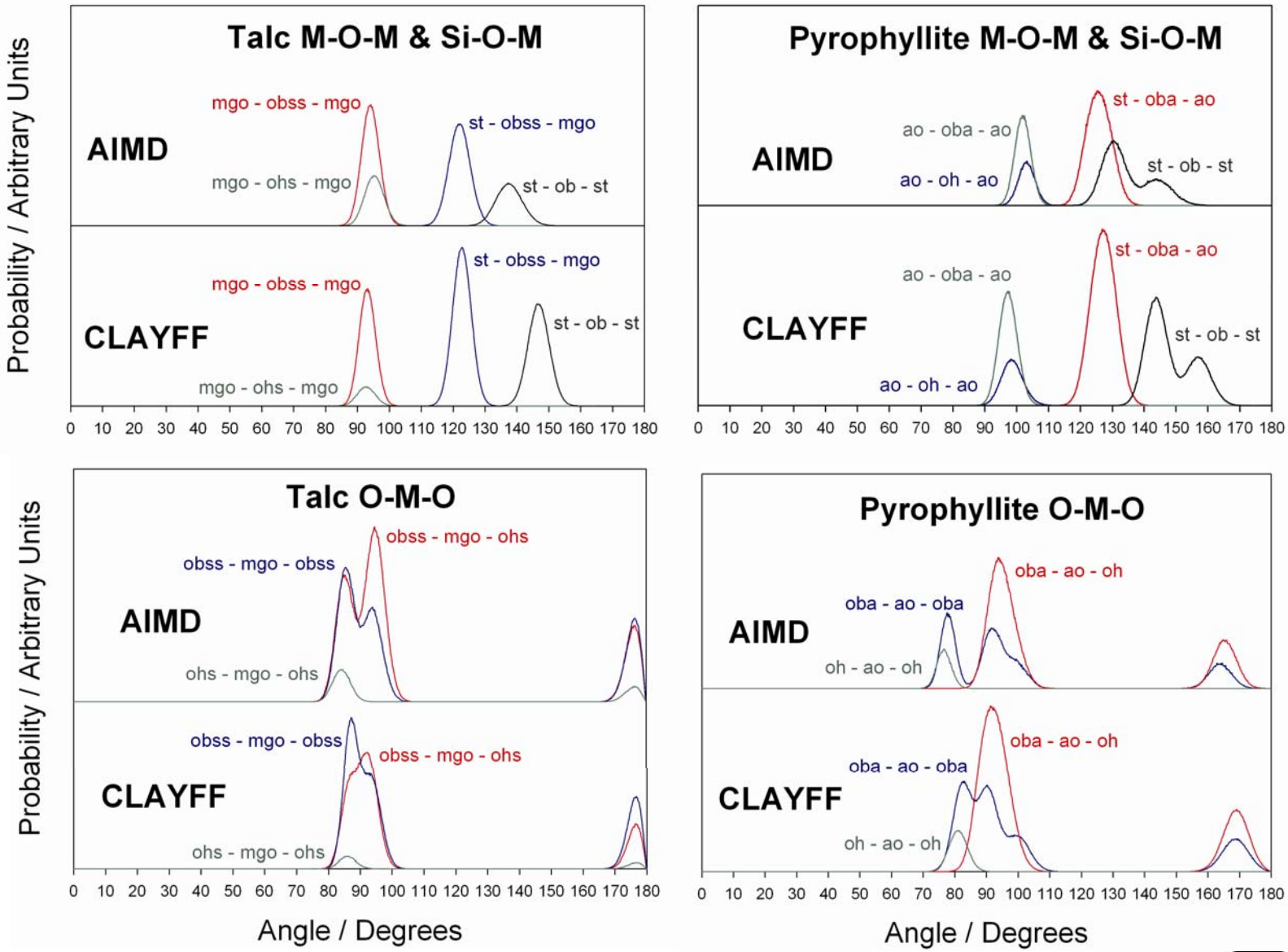
Angle Distributions



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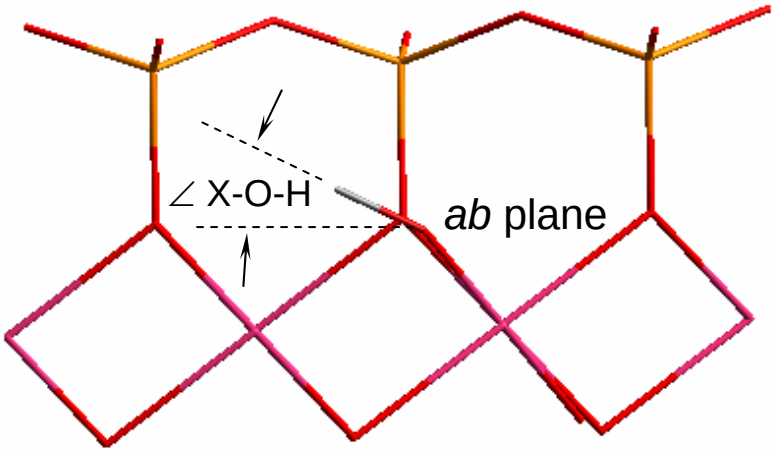
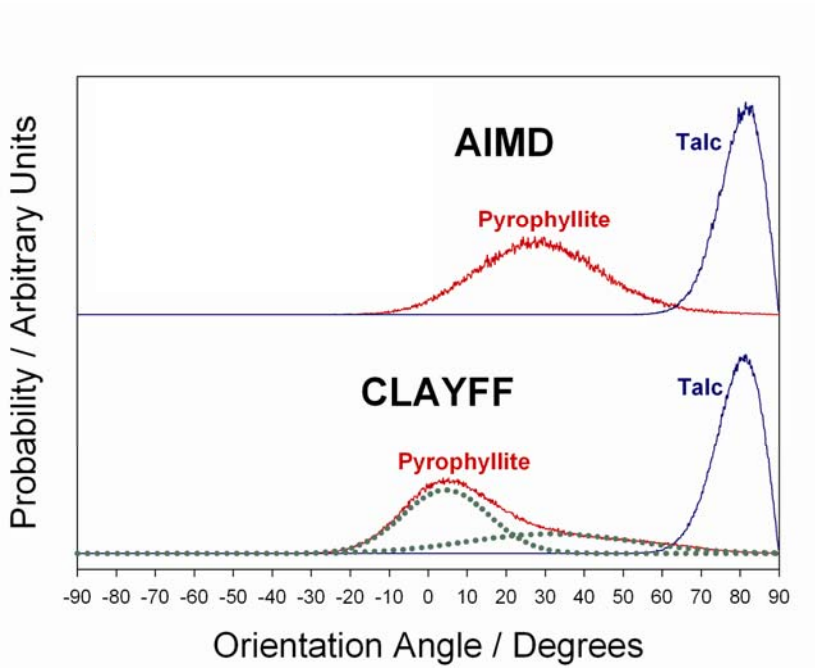
Hydroxyl orientation





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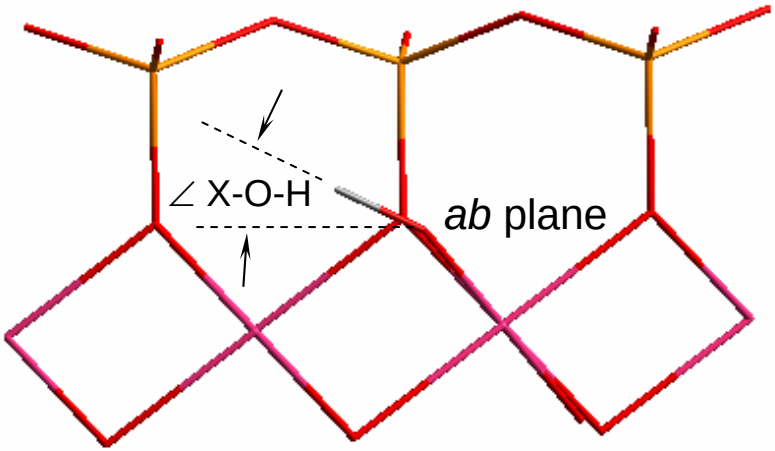
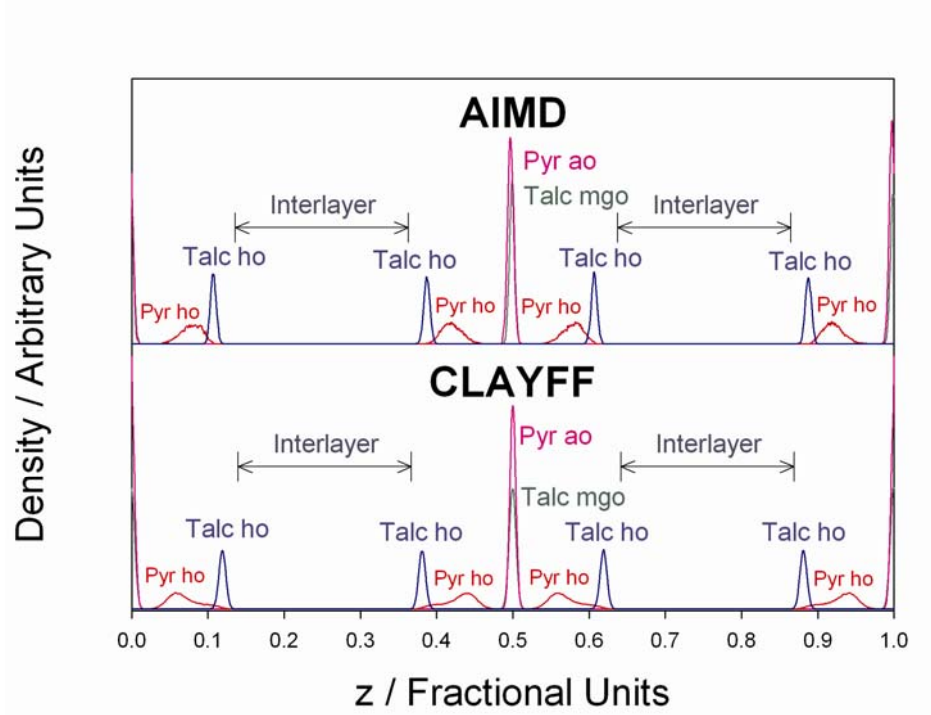
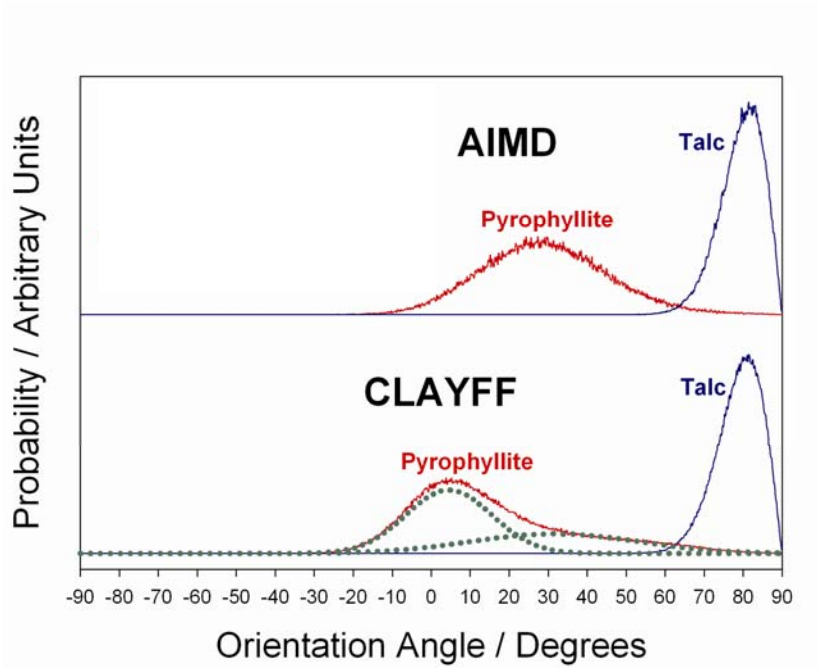
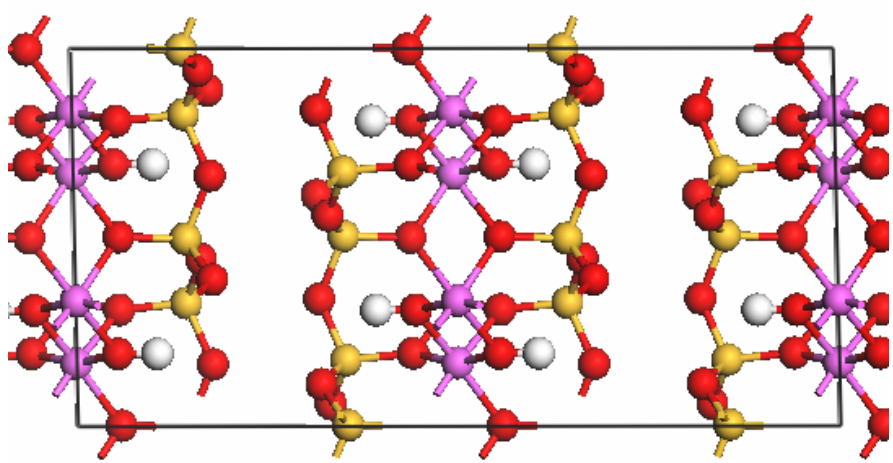
Hydroxyl orientation









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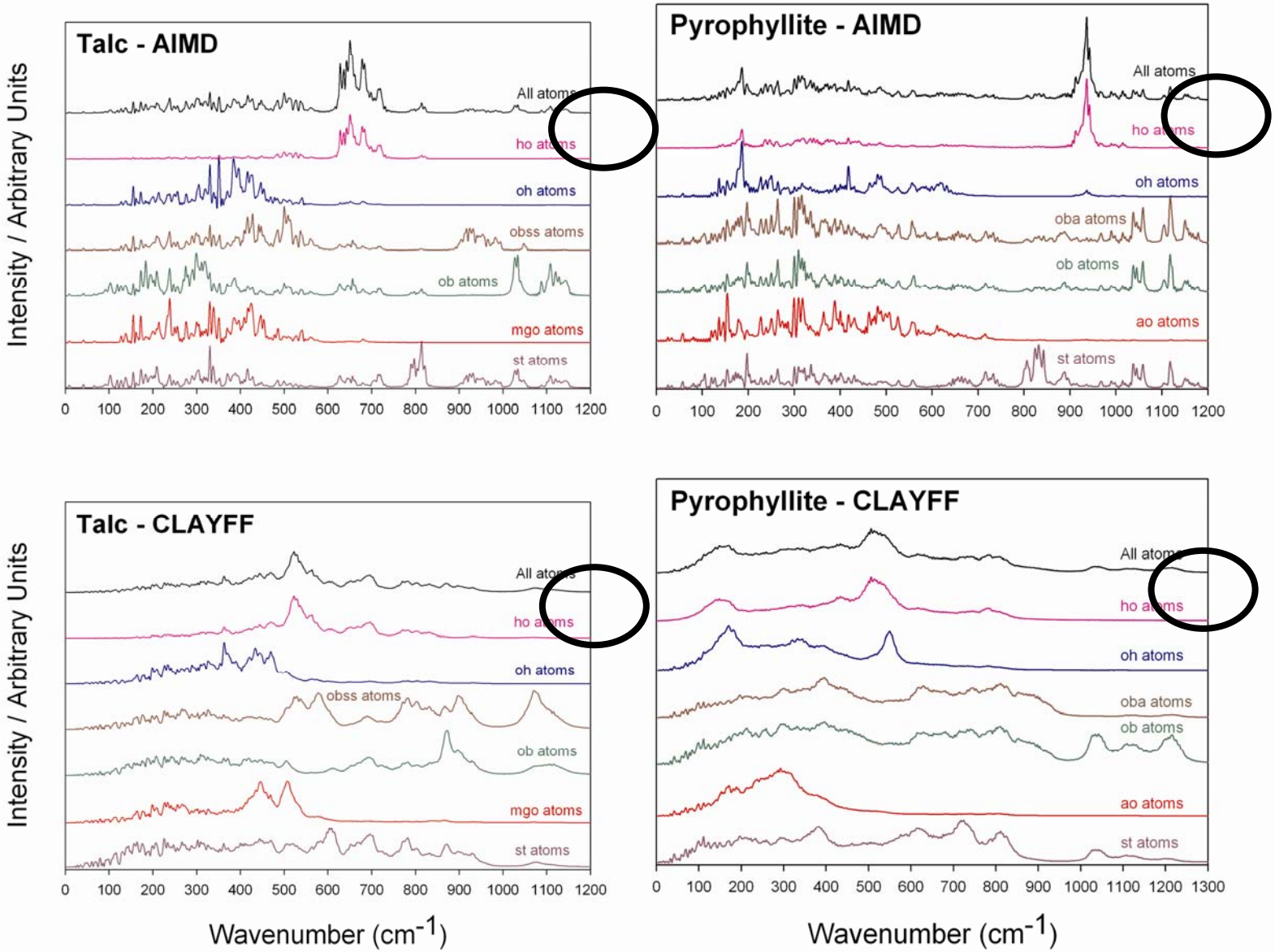
Vibrational Spectra - Pyrophyllite



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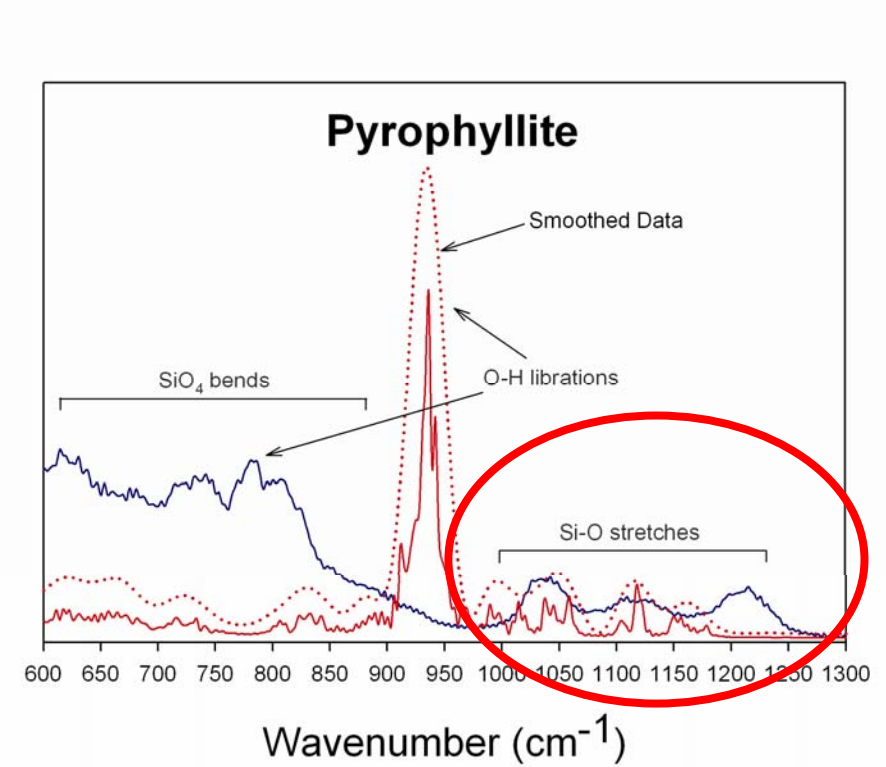
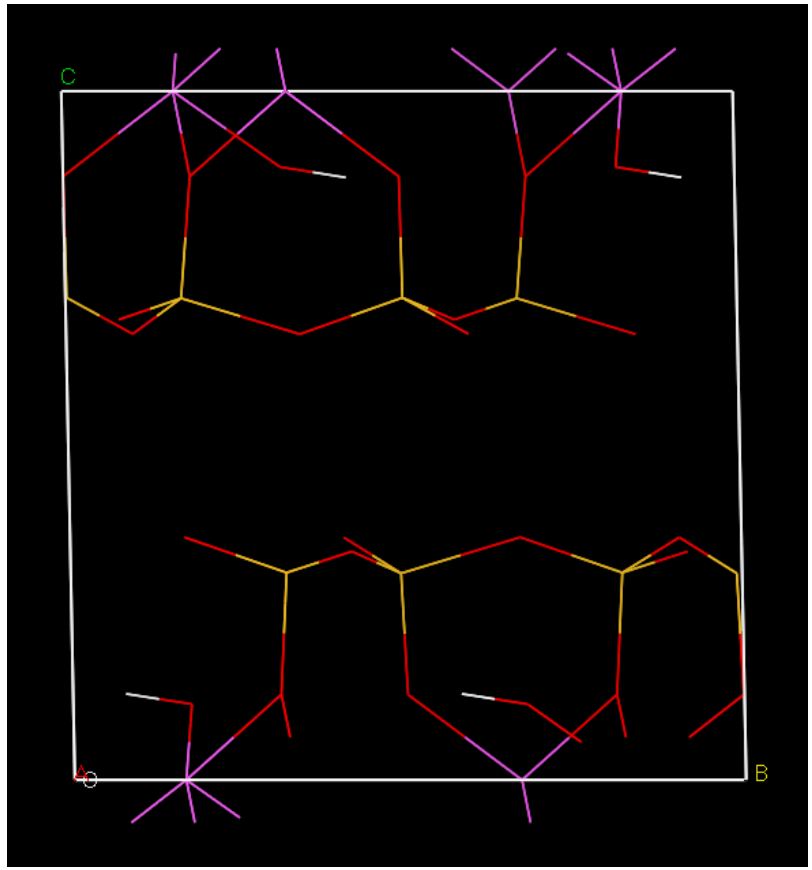
Pyrophyllite Si-O(ob) stretch at 1085 cm^{-1}





Blue = CLAYFF

Red = AIMD

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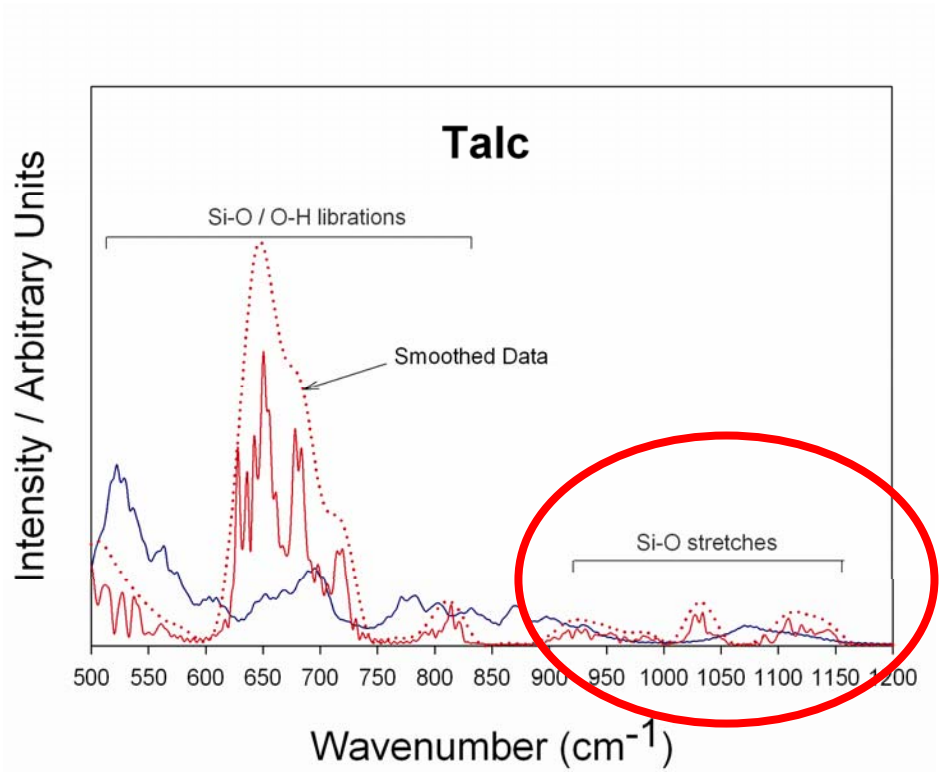
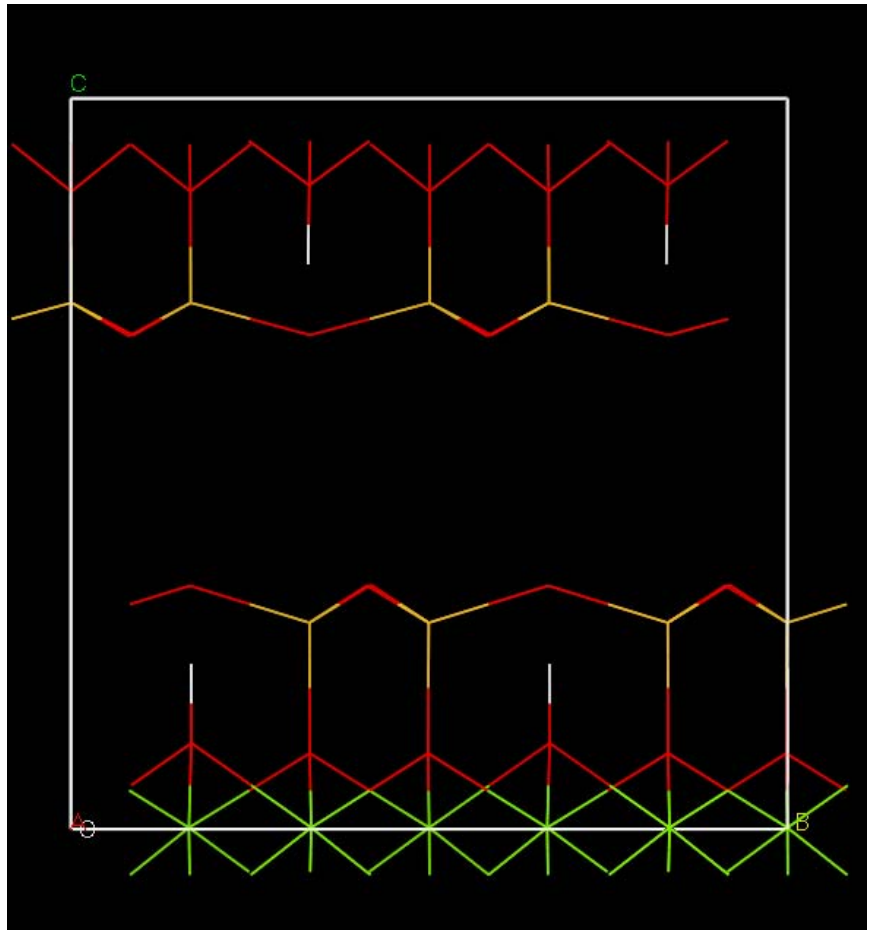
Talc Si-O(obss) stretch at 1044 cm^{-1}





Blue = CLAYFF

Red = AIMD

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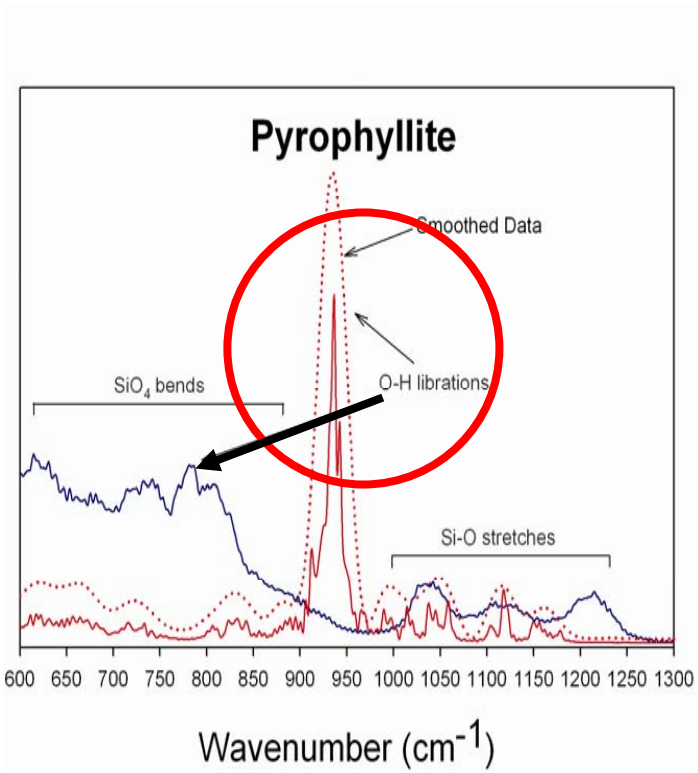
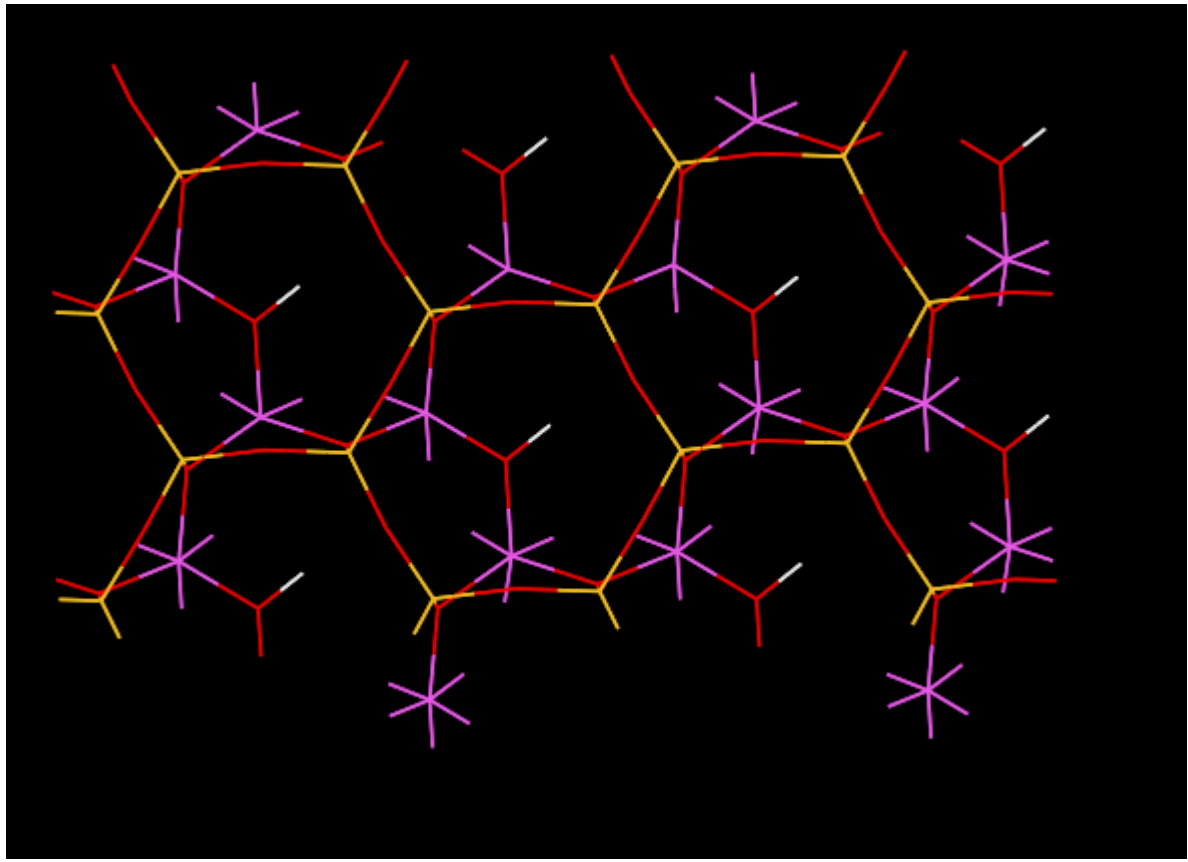
Pyrophyllite O-H Libration at 745 cm^{-1}





Blue = CLAYFF

Red = AIMD

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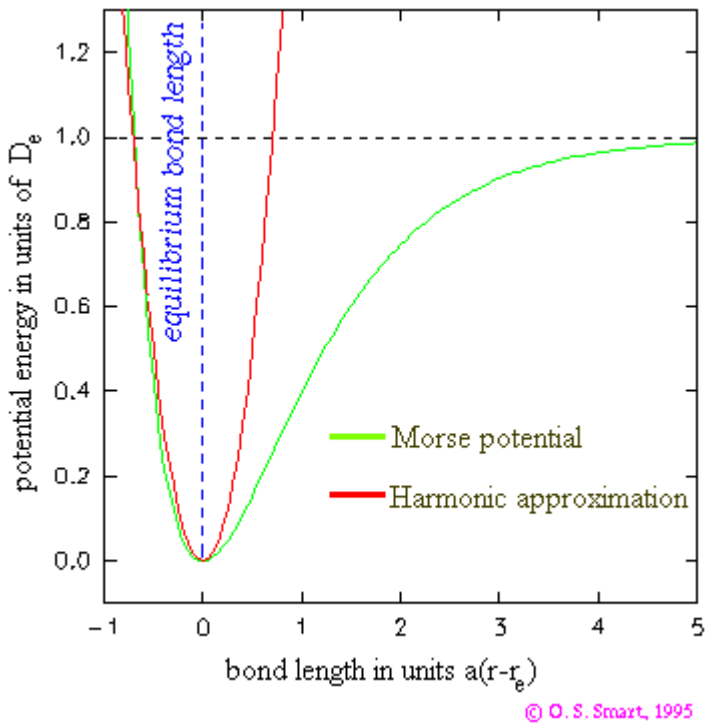
Considerations for CLAYFF

- O-H bond: harmonic → Morse
  - tune O-H stretch frequency
  - O-H bond length
  - O-H libration mode
  - O-H angle orientation
- Add Si-O-Si angle bend term
- Add M-O-H angle bend term
  - O-H angle orientation
  - Possibly needed for edge sites



Future Directions

- Charged dioctahedral and trioctahedral clays (M1 and M2 sites)
- Cations and water
- Edge sites

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