First Principles Studies of Lead, Cadmium, and Selenite Adsorption at the Goethite-Water Interface

SAND2014-17098C

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Acknowledgement

Lynn Katz, Jeremiah Mangold

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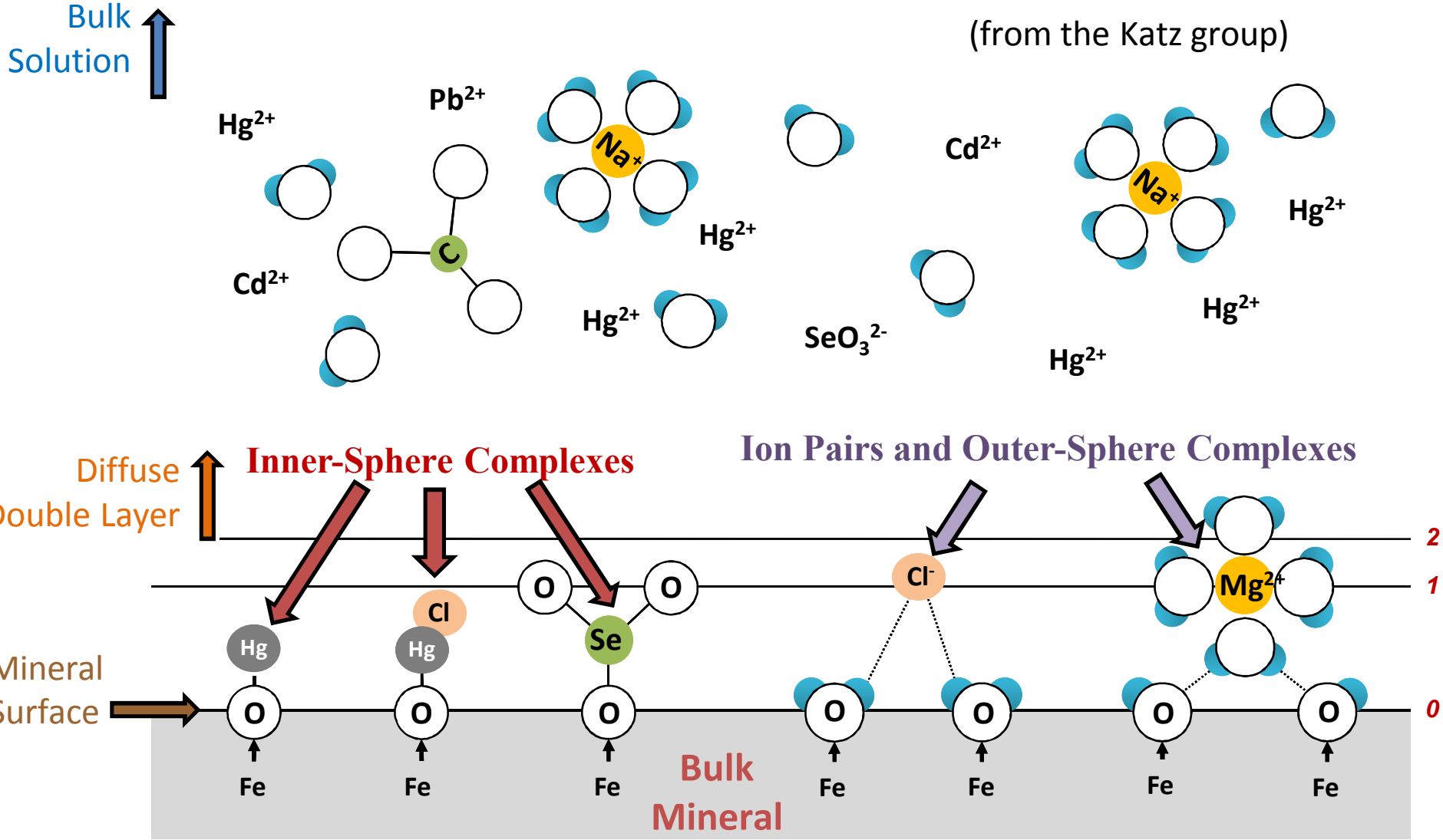
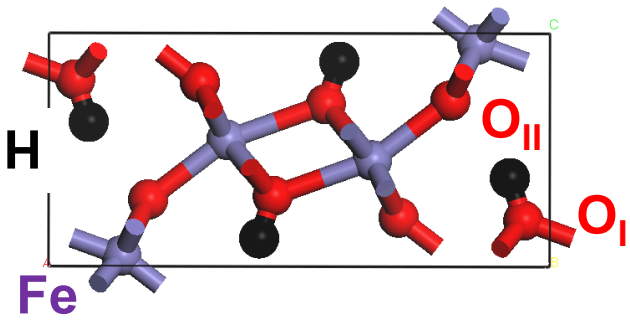
Schematic of Mineral – Water Interface

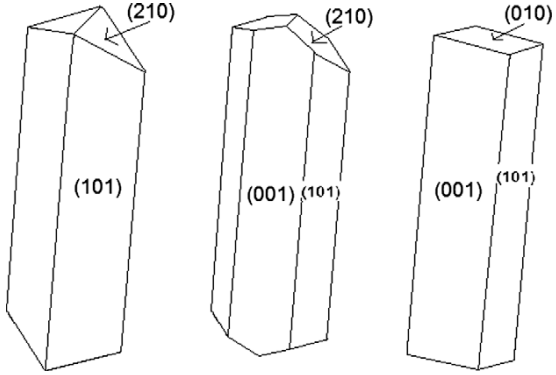


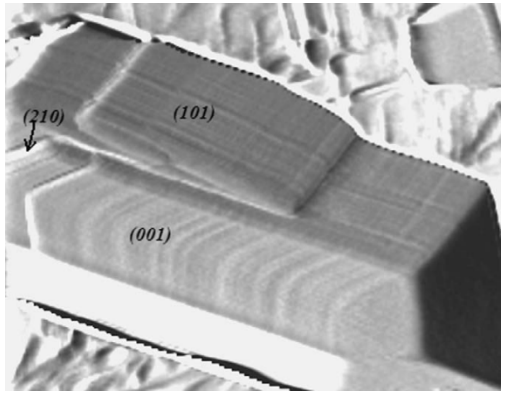
Clearly you don't want these ions near your drinking water or food supply.
Understanding how long they are retained on soil surfaces is a major DOE geochemistry goal.

Goethite: Predominant Surfaces and Surface Sites



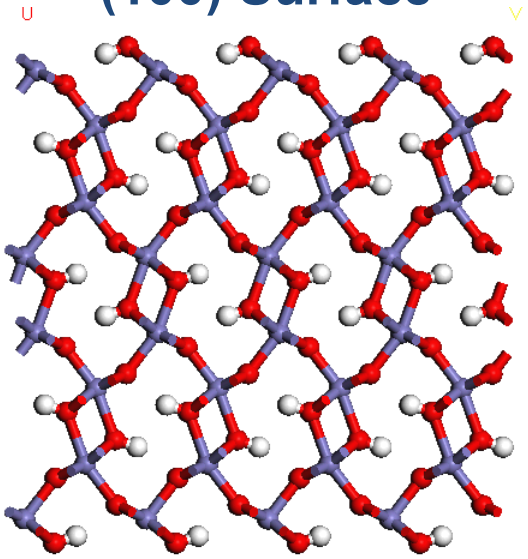
Goethite Unit Cell





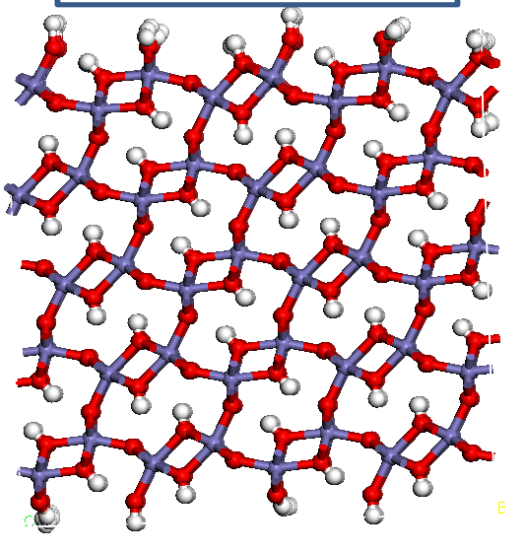
Villalobos, Cheney, Alcaraz-Cienfuegos, J. Coll. Inter. Sci. 36:412 (2009)

(100) Surface



5-fold Fe
Fe_2O_IH
Fe_3O_{II}

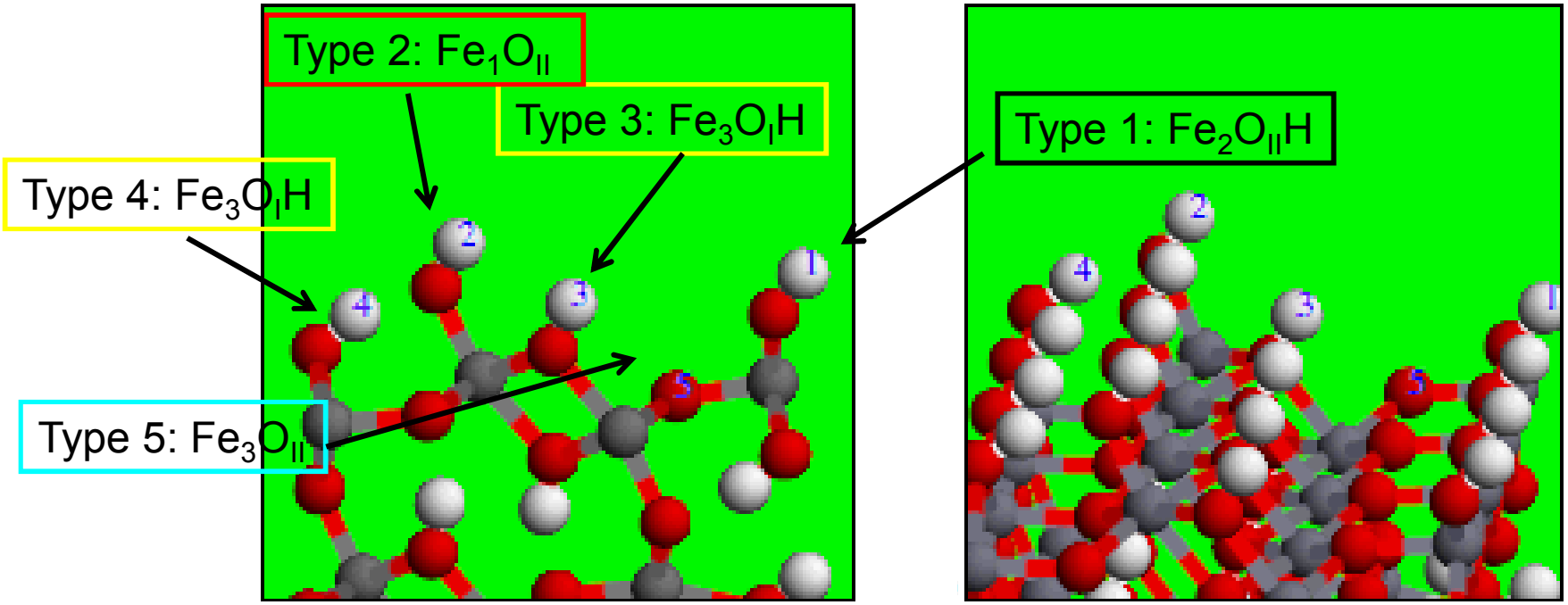
(101) Surface



$Fe_1O_{II}H$
$Fe_2O_{II}H$
Fe_3O_{II}
Fe_3O_IH

Goethite (101)/Pnma Space Group

Venema, Hiemstra, Weidler, van Riemsdijk, J. Coll. Interface Sci. 198, 2882 (1998)
Kubicki, Paul, Sparks Geochem. Trans. 9, 1 (2009)
Boily, J. Phys. Chem. C 116, 4714 (2012), Louise Criscenti ACS 2012



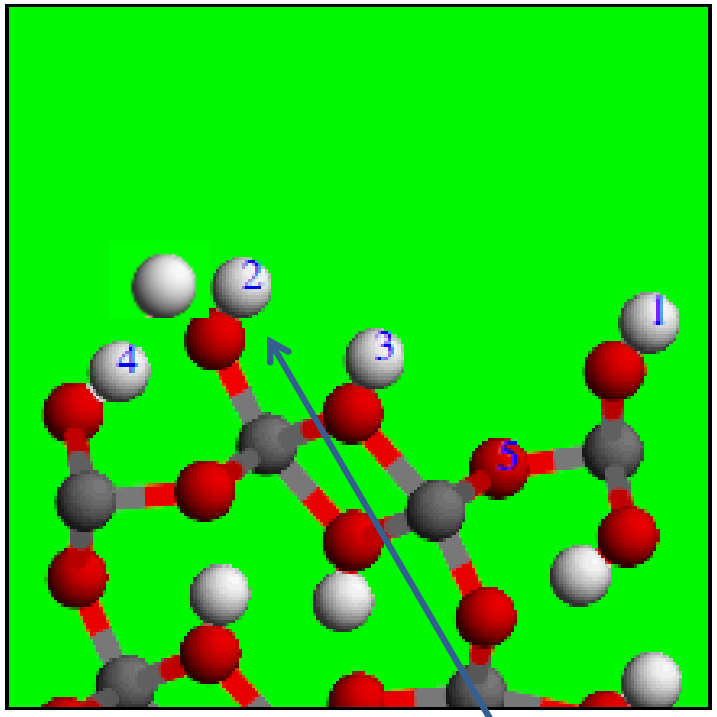
O_I = O of structural OH group
O_{II} = O alone

Fe_2O_IH: 5-fold Fe

Fe_3O_IH:
a. 3 6-fold Fe,
b. 2 6-fold, 1 4-fold Fe
FeO_{II}: 6-fold Fe
Fe_3O_{II}: 2 5-fold Fe, 1 4-fold Fe

AIMD pK_a predictions agree with MUSIC model

- "type 2" $Fe_1O_{II}H_2$ pK_a: 7.0
- protonated $FeOH_2$ accepts/donates 0.1/1.0 hydrogen bonds from/to H_2O
- deprotonated $FeOH_2$ accepts/donates 1.1/0.0 hydrogen bonds from/to H_3O^+
- involved in 2 h-bond with other FeOH



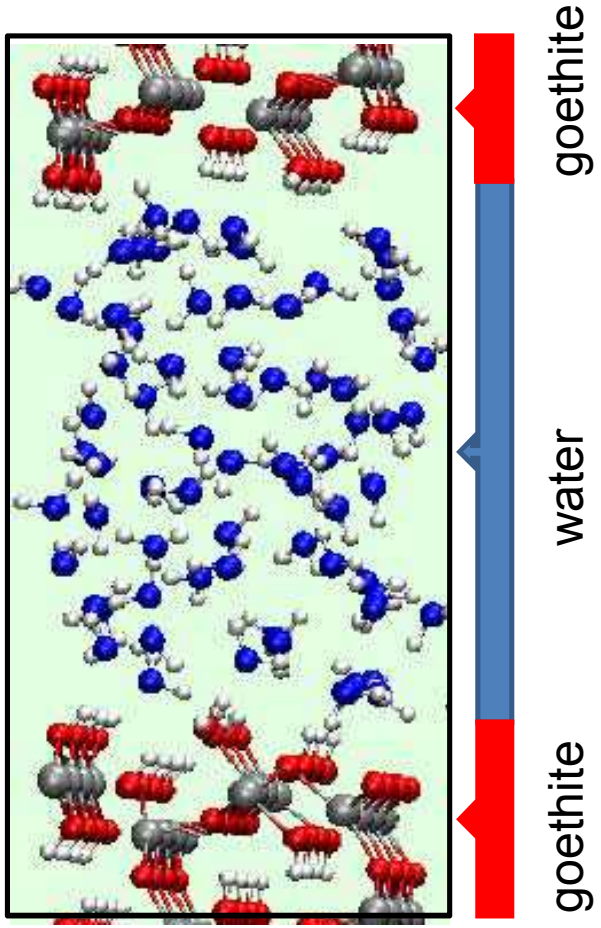
Type of group	N_S (sites/nm^2)	Bond lengths (Å)	s	m	n	log K_{H1} log K_{H2}
Fe_1O_{II}	3.03	1.946 1.767	0.610 0.194	0 0 1 1	2 2 1 1	19.6 7.7
Fe_2O_{II}	3.03	1.958 1.958	0.591 0.591	0 1	1 0	12.3 0.4
Fe_3O_{II}	3.03	1.958 1.946 1.946	0.591 0.610 0.610	0	1	−0.2
Fe_3O_I	6.06	2.092 2.103 2.103	0.411 0.399 0.399	0	1	11.7

Venema *et al.*, J. Coll. Interface. Sci 198, 282 (1998)

Our approach: *Ab initio* Molecular Dynamics (AIMD)

with potential-of-mean-force free energy calculations

Leung & Criscenti, J. Phys. Condens. Matter (2012)



AIMD shows water diffusion, hydrogen bond fluctuations

Newton: solve F = m a
in real time, finite temp

- modeling liquid requires MD (or MC)
- forces F from DFT+U
- allow bond-breaking, chemistry
- GCMC force field pre-equilibration …

all-AIMD simulations of interfaces:

- published papers: << 100
- calculating ΔG: << 20
- costly, but computers getting faster

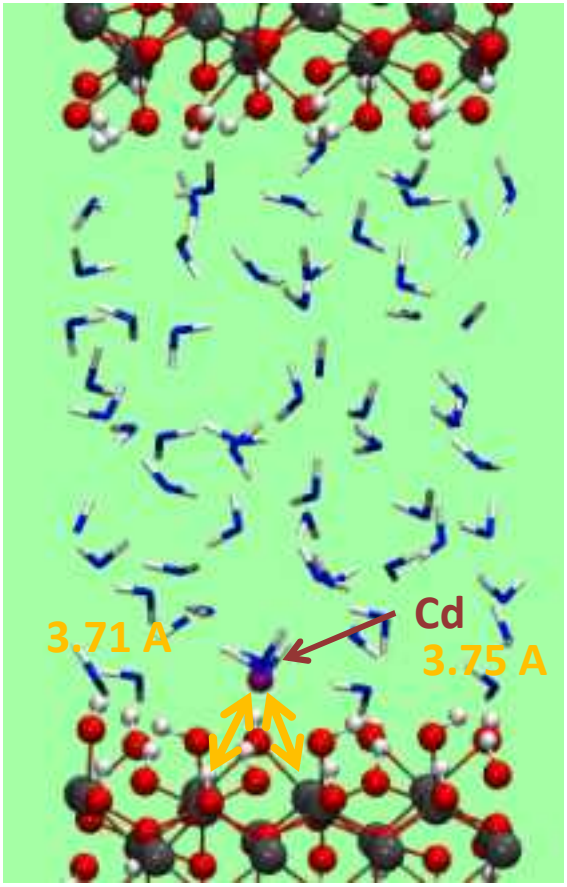
Next: add explicit ions, Cd(II) vs. Pb(II)

- compare with Pb-Fe and Cd-Fe distances derived from analyses of X-ray adsorption fine structure (EXAFS)

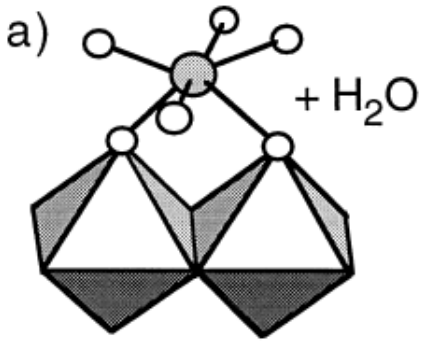
- generally performed on samples with multiple facets

Cd(II) corner-shared on FeO_6 octahedra

Front and side views



With explicit water, corner-shared Cd(II) is at least metastable



E = 0 kJ mol^{-1}

Cd-O = 2.22 Å
Cd-Fe = 3.76 Å

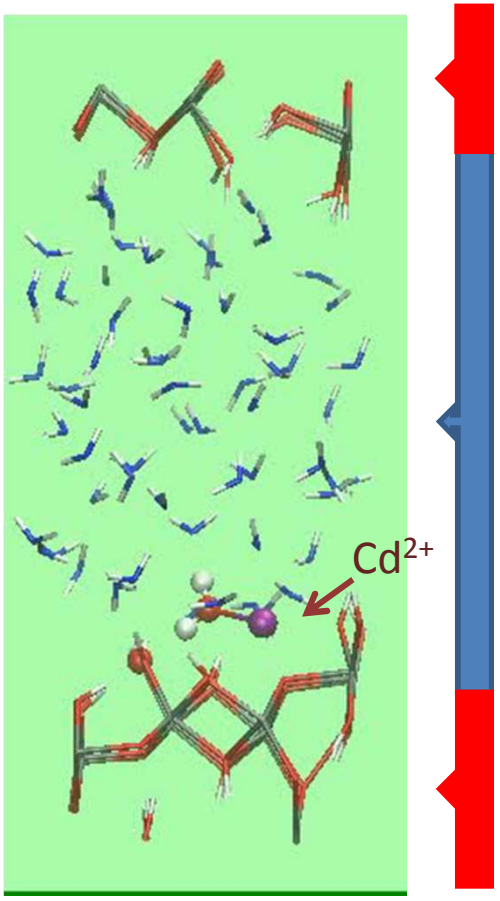
EXAFS and cluster-based DFT

The mechanism of cadmium surface complexation on iron oxyhydroxide minerals

S. R. Randall, D. M. Sherman,* K. V. Ragnarsdottir, and Clare R. Collins

Geochimica et Cosmochimica Acta, Vol. 63, No. 19/20, pp. 2971–2987, 1999

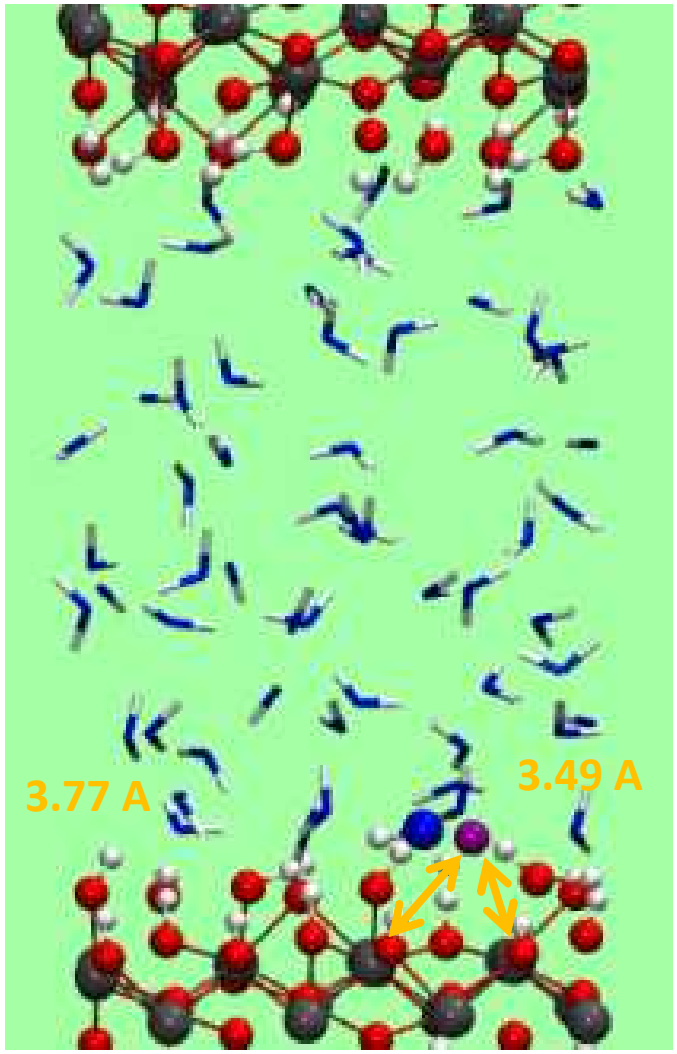
Cd(II)(OH^-) on one octabedral corner



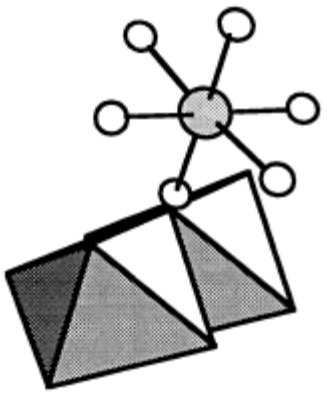
goethite

water

goethite



b)



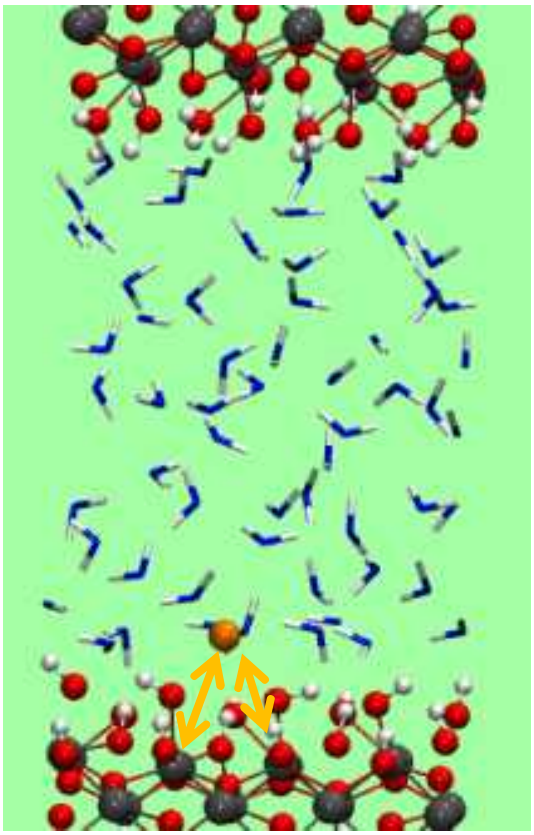
Cd-O = 2.22 Å
Cd-Fe = 3.52 Å

Single corner

- AIMD for 6 ps
- $FeOH_2$ – OH^- -- Cd^{2+}

- cluster DFT dose not have water deprotonation
- 3.52 A not seen in EXAFS
- need to compare free energies with last slide

Pb(II) corner-shared on FeO_6 octahedra



3.84 A. 3.84 A

Cannot reproduce 3.35 A distance on (101) surface yet

EXAFS: 3.35 A, 3.9 A

pH	Pb-Fe Shell* N	Pb-Fe Shell* R (Å)	Pb-Fe Shell* N	Pb-Fe Shell* R (Å)
6.0	0.6	3.34	0.7	3.92
6.0	0.9	3.36	—	—
5.0	0.8	3.36	0.6	3.93
5.0	0.4	3.33	1.4	3.89

The ~3.35 Pb-Fe EXAFS distance often attributed to minority (210) facets.

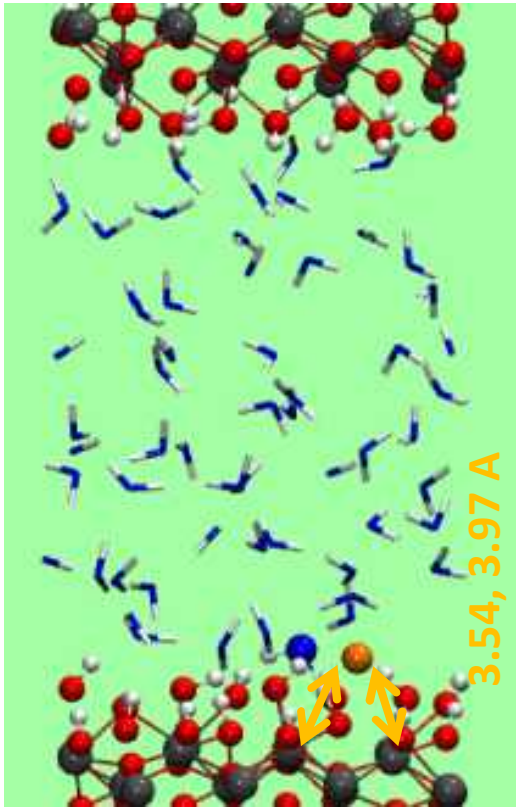
cannot rule out ~3.9 A EXAFS distance is due to majority (101) facets.

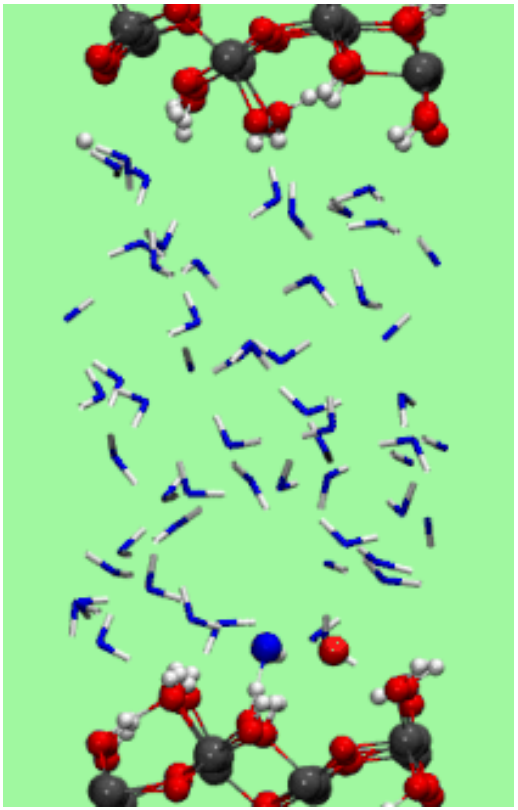
Spectroscopic studies of Pb(II)-sulfate interactions at the goethite-water interface

E. J. Elzinga[1]*, D. Peak,[1] and D. L. Sparks[1]

Geochimica et Cosmochimica Acta, Vol. 65, No. 14, pp. 2219–2230, 2001

Pb(II)(OH^-) on one octahedral corner





Pb-Fe distances are 3.54, 3.97 A.

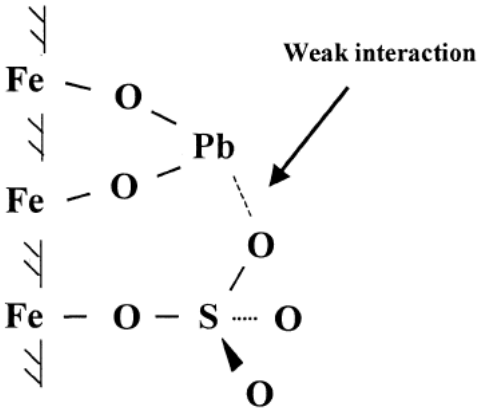
3.54 A arguably far from EXAFS

To fully analyze Pb(II) adsorption, need to model (210) surfaces

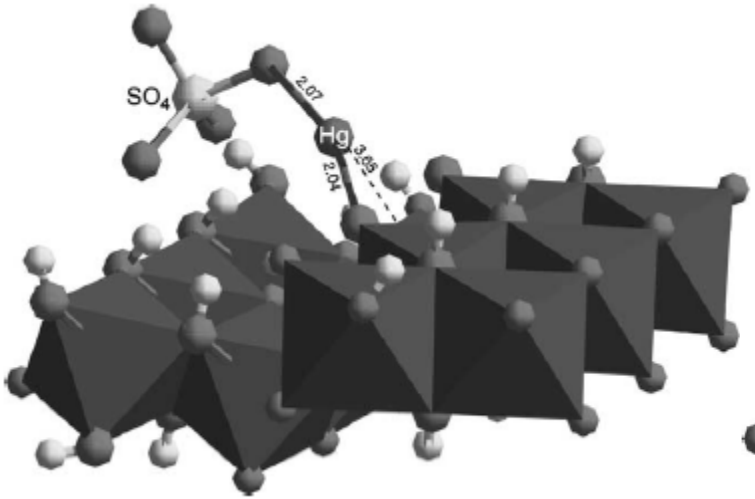
Next: add explicit ions, Pb(II)/$SeO3^{2-}$ pair

Spectroscopic Evidence supporting Ternary Complex

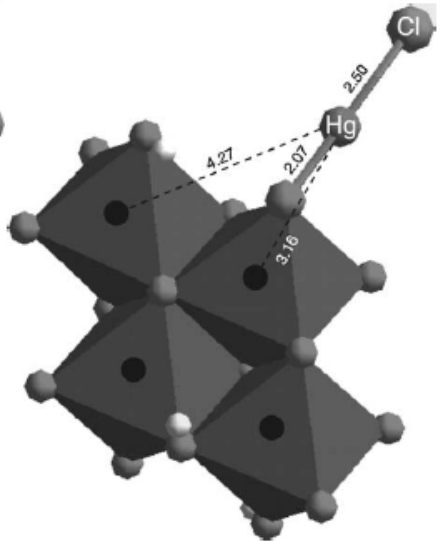
Citation	Method	Metal	Ligand
Ostergren et al. (2000a)	ATR-FTIR and EXAFS	Pb^{+2}	SO_4^{-2}
Elzinga, E.J., Peak, D., Sparks, D.L. (2001)	ATR-FTIR and EXAFS	Pb^{+2}	SO_4^{-2}
Ostergren et al. (2000b)	ATR-FTIR and EXAFS	Pb^{+2}	CO_3^{-2}
Bargar et al. (1998)	XAFS	Pb^{+2}	Cl^-
Zhang, G.Y., and Peak, D. (2007)	ATR-FTIR	Cd^{+2}	SO_4^{-2}
Kim, C. S., Rytuba, J. J. and Brown, G. E. (2004a)	EXAFS	Hg^{+2}	Cl^-



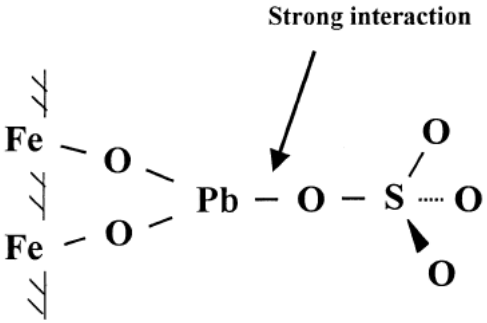
Elzinga, E.J., Peak, D., Sparks, D.L. (2001)



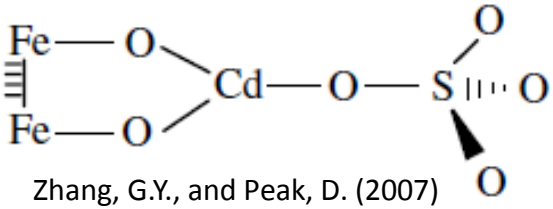
Kim et al. (2004)



Kim et al. (2004)



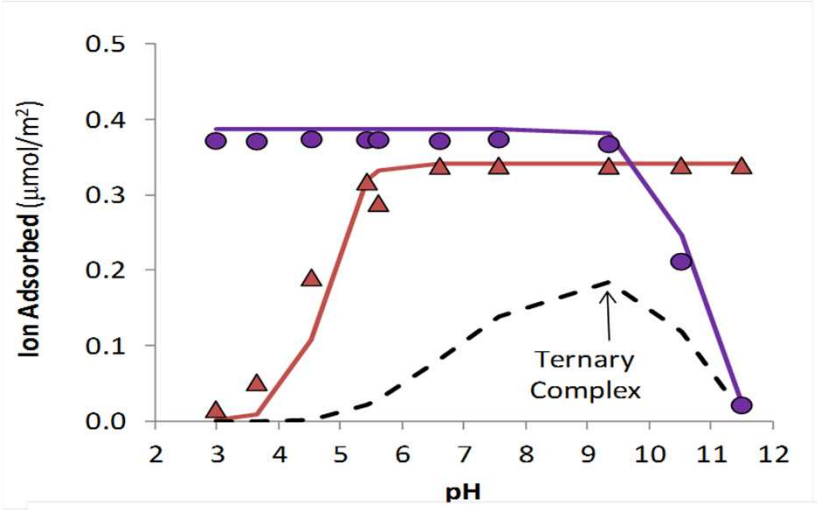
Elzinga, E.J., Peak, D., Sparks, D.L. (2001)

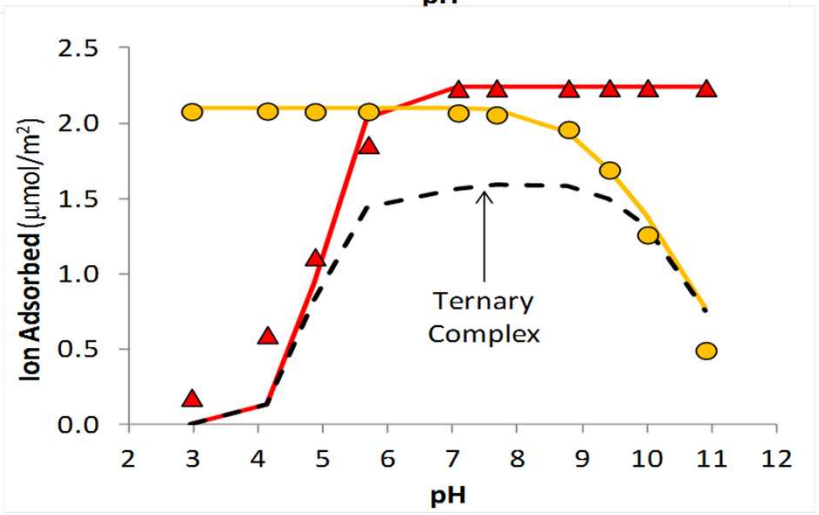


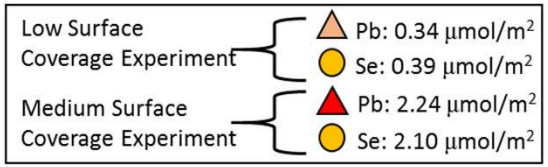
Zhang, G.Y., and Peak, D. (2007)

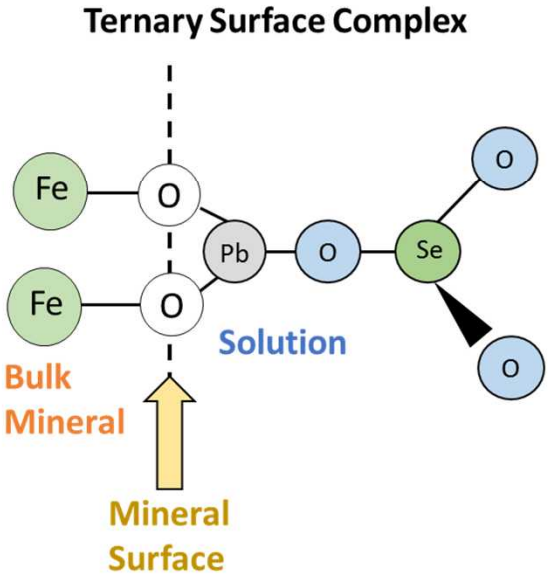
Surface Complexation Modeling of Pb^{2+} and SeO_3^{2-} on Goethite (II)

In order to fit data for the adsorption of both Pb^{2+} and SeO_3^{2-} on goethite simultaneously, the model must include a ternary surface complex.

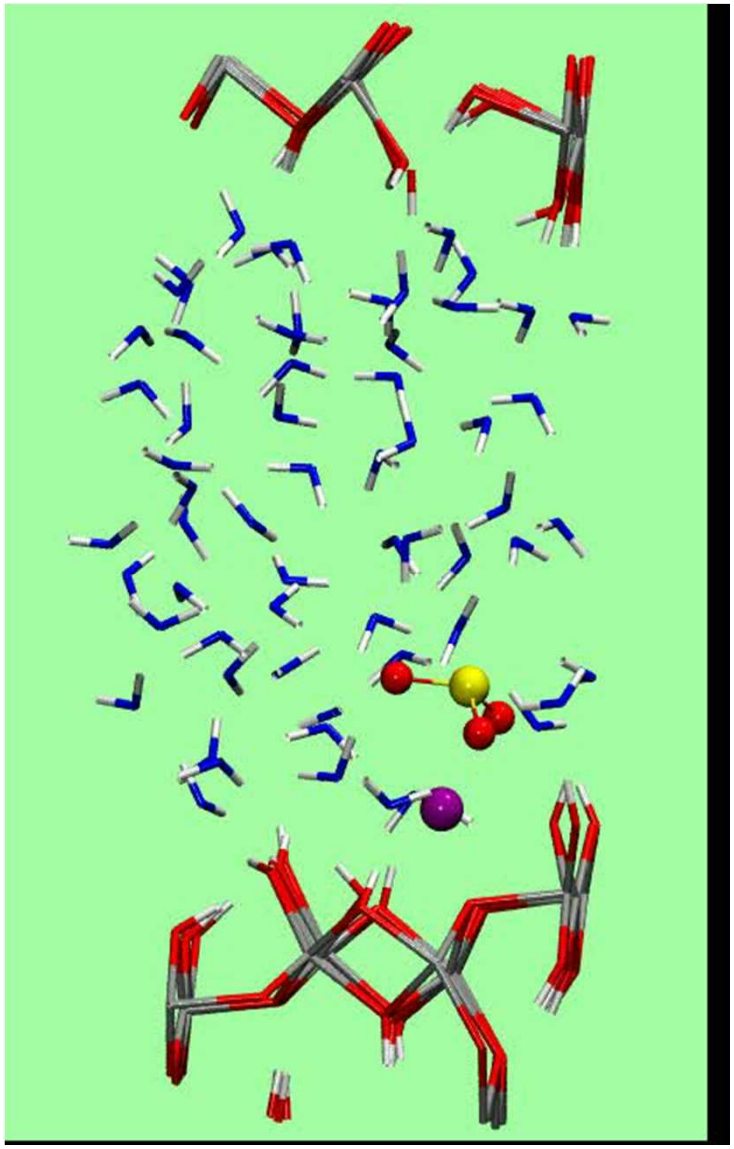




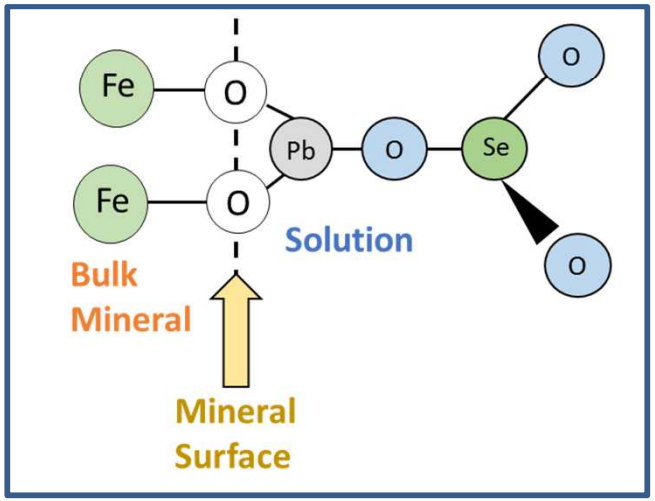




Pb/SeO_3^{2-} contact ion pair on goethite -- inconclusive



- DFT+U (for goethite) + Pb(II) + SeO_3^{2-} VASP simulations barely converges – switch to pure DFT/PBE
- Pb(II)-selenite contact ion pair (CIP) starts to detach from the surface
- Reasonable since Pb(II) dication should be strongly bound, while the CIP just have dipole moment
- Should revisit this with the (210) facet of goethite



Conclusions

- pK_a ~7.0 for $Fe_1O_{II}H_2$ group on goethite (101)
- Pb(II) on (101) (multiple protonation states) does not agree with EXAFS
- Cd(II) corner-shared on (101), Cd-Fe distances agree with EXAFS (no water deprot.)
- Pb(II) SeO_3^{2-} ion pairs on goethite simulations are inconclusive

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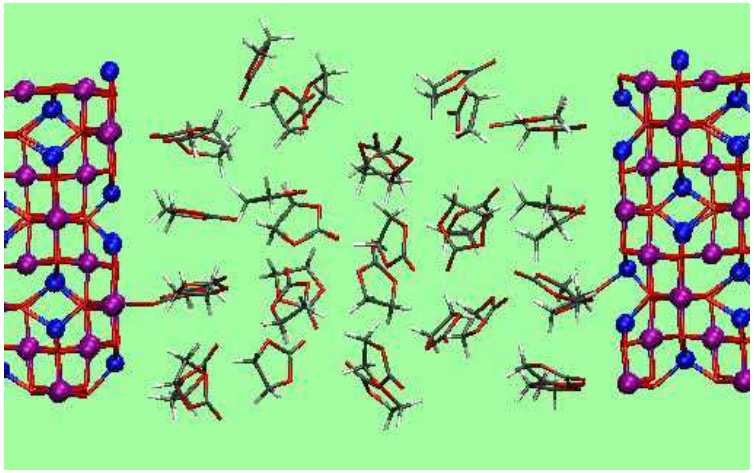
Broader Conclusions

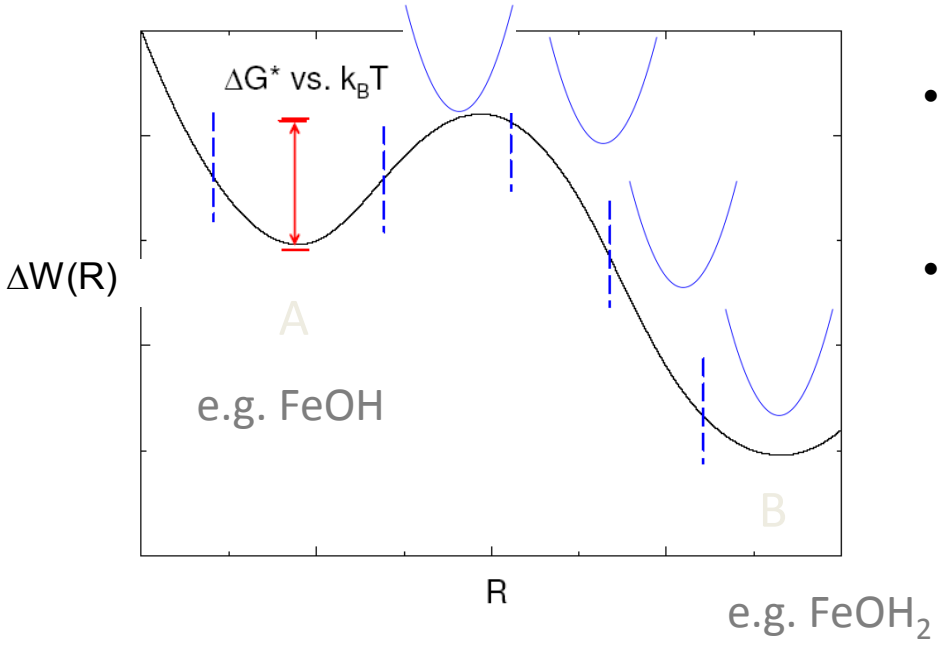
- Real material surfaces (different protonation state, surface change as pH varies)
- Proton motion, Grotthuss mechanism
- Explicit salt, not just water structure/dynamics
- Free energies of ion complexation important
- Synergy with non-aqueous systems



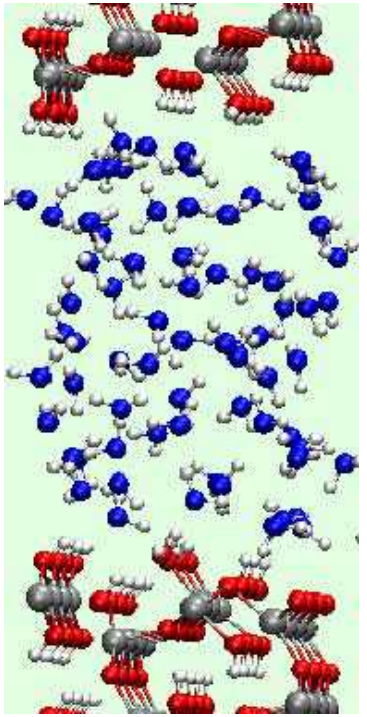
AIMD simulations of organic electrolyte breakdown at battery ($LiMn_2O_4$) surfaces

Supporting information

Deprotonation, AIMD potential of mean force (PMF)

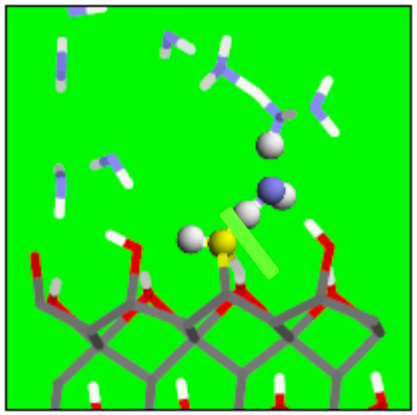


- liquid state PMF: *very* different from solid state or DFT cluster calculations
- e.g., cannot subtract energies of A & B – must trace the entire ΔW(R)

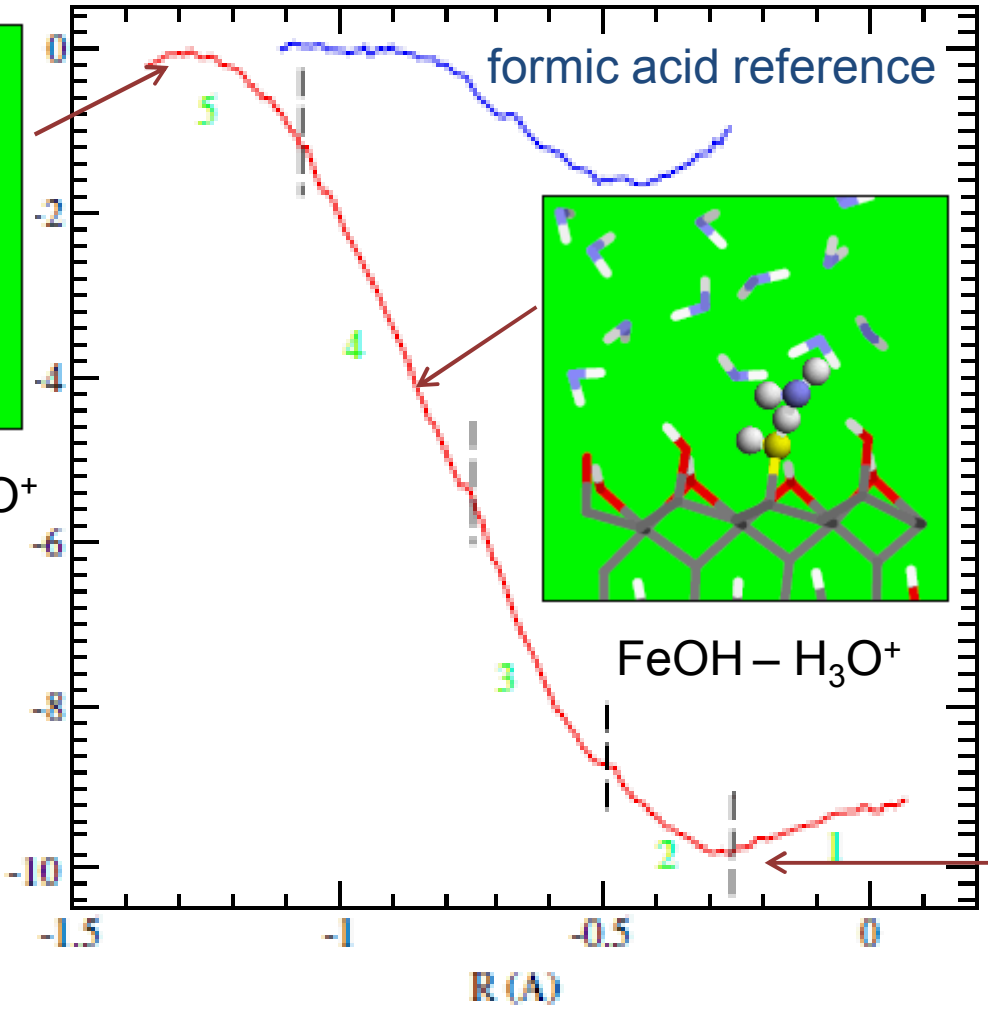


- Umbrella sampling for PMF
- AIMD using VASP, DFT+U/PBE, PAW-PP's
- MD trajectories: ~20 ps/window, NVT at T=425 K
- E_{cut} = 400 eV, 10^{-6} eV B.O. convergence, ~2 K/ps drift
- $\Delta W(R) \sim -k_B T \ln [P(R)]$; various corrections (see later)

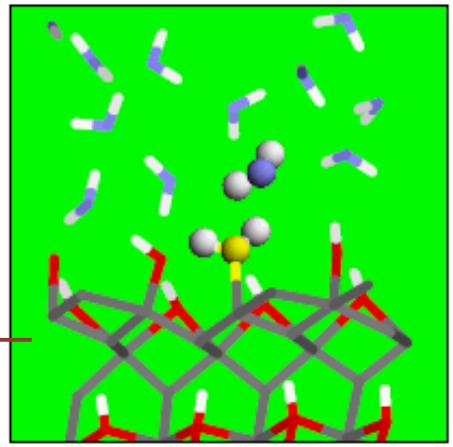
Prediction of W(R), related to pK_a



$FeOH - H_2O - H_3O^+$



$FeOH - H_3O^+$



$FeOH_2 - H_2O$

$-pK_a \times \ln(10)\, k_B T = \Delta G^{(0)} = -k_B T \ln\left\{C_0 \int_0^{R_{cut}} dR A(R) \exp[-\beta W(R)]\right\}$