SAND2022-3363C

Enhanced Cu^{2+} Dimerization on Mineral Surfaces – an ab initio Molecular Dynamics Free Energy Study

Kevin Leung and Jeffery Greathouse

Sandia National Laboratories

Thanks: Anastasia Ilgen, Andrew Knight

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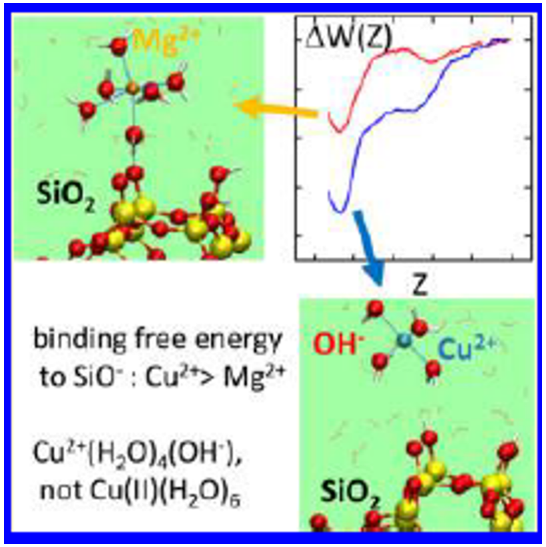
Motivations

- adsorption of metal cations on mineral surfaces is a main stay of geochemistry
- toxic/radioactive ion trapping

- At high metal cation concentrations, heterogeneous nucleation/precipitation occurs



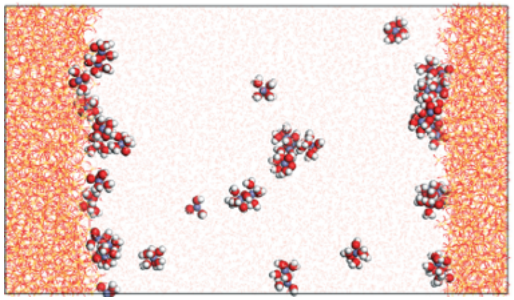
binding free energy to SiO^- : $Cu^{2+} > Mg^{2+}$

$Cu^{2+}(H_2O)_4(OH^-)$, not $Cu(II)(H_2O)_6$

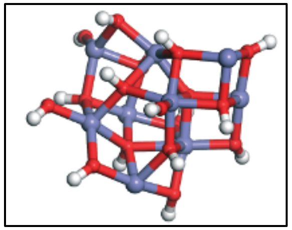
Concerted Metal Cation Desorption and Proton Transfer on Deprotonated Silica Surfaces

Kevin Leung,* Louise J. Criscenti, Andrew W. Knight, Anastasia G. Ilgen, Tuan A. Ho, and Jeffery A. Greathouse *J. Phys. Chem. Lett.* 2018, 9, 5379–5385

higher $[M^{q+}]$



MD snapshot: Fe(II) hydroxide cluster on silica surface in water



Enlarged snapshot of Fe(II) hydroxide cluster

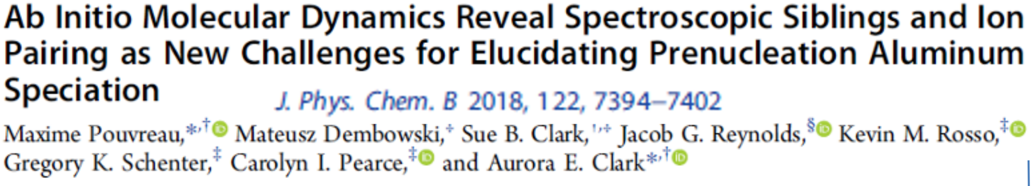
Effects of nanoconfinement and surface charge on iron adsorption on mesoporous silica†

Jeffery A. Greathouse, *[a] Tyler J. Duncan,[a] Anastasia G. Ilgen, [a] Jacob A. Harvey, [a] Louise J. Criscenti[a] and Andrew W. Knight[b]

Environ. Sci.: Nano, 2021, **8**, 1992–2005

- What happens in between? dimerization, polymerization …
- Much less studied

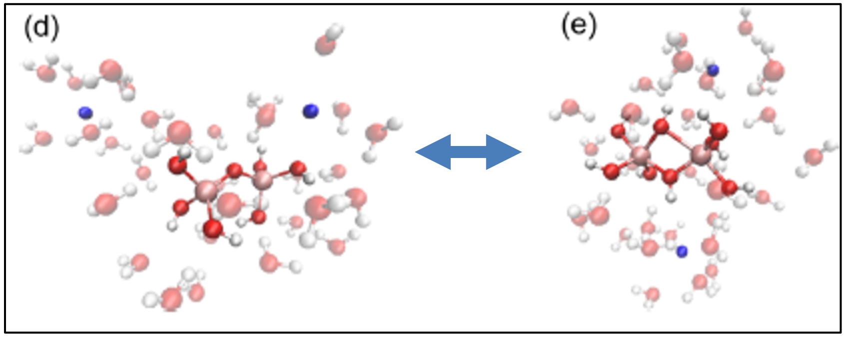
Metal cation dimers in water/on surface



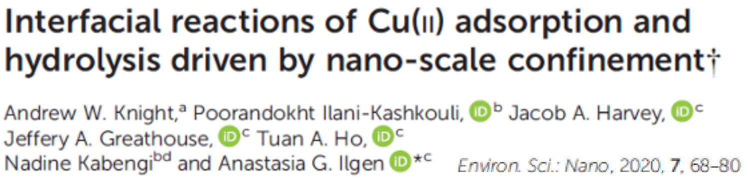
Ab Initio Molecular Dynamics Reveal Spectroscopic Siblings and Ion Pairing as New Challenges for Elucidating Prenucleation Aluminum Speciation

J. Phys. Chem. B 2018, 122, 7394–7402

Maxime Pouvreau,[*,†] Mateusz Dembowski,[‡] Sue B. Clark,[†,‡] Jacob G. Reynolds,[§] Kevin M. Rosso,[‡] Gregory K. Schenter,[‡] Carolyn I. Pearce,[‡] and Aurora E. Clark[*,†]



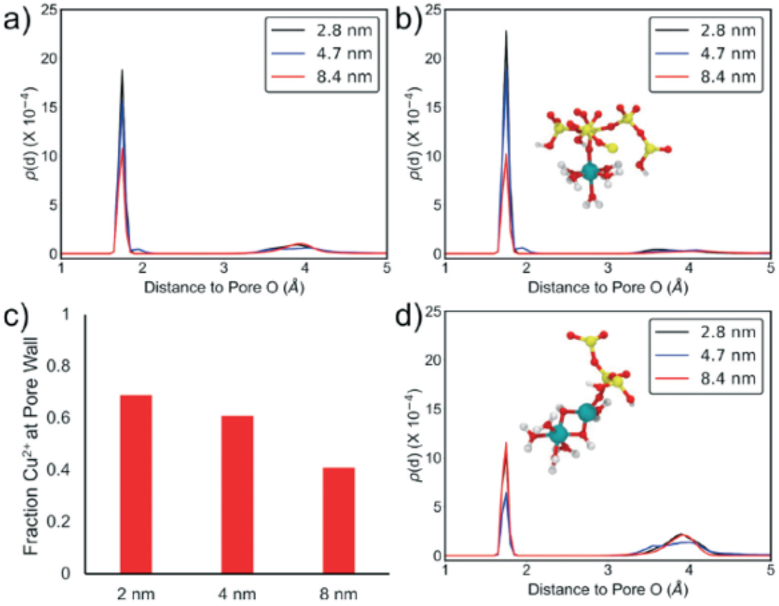
Al hydroxo- or oxo- dimers most studied



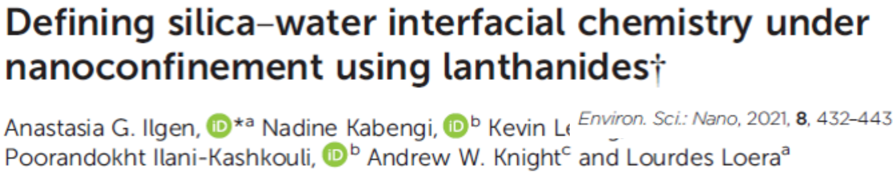
Interfacial reactions of Cu(II) adsorption and hydrolysis driven by nano-scale confinement†

Andrew W. Knight,[a] Poorandokht Ilani-Kashkouli,[b] Jacob A. Harvey,[c] Jeffery A. Greathouse,[c] Tuan A. Ho,[c] Nadine Kabengi[bd] and Anastasia G. Ilgen[*c]

Environ. Sci.: Nano, 2020, **7**, 68–80



Cu dimers reported, simulated (MD)

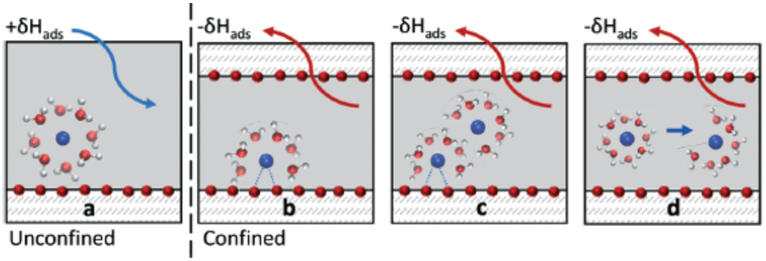


Defining silica–water interfacial chemistry under nanoconfinement using lanthanides†

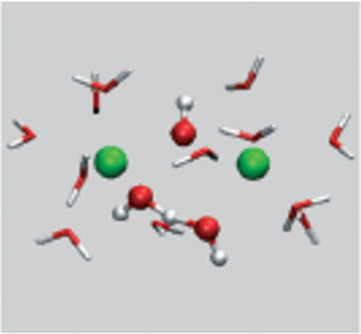
Anastasia G. Ilgen,[*a] Nadine Kabengi,[b] Kevin L

Environ. Sci.: Nano, 2021, **8**, 432–443

Poorandokht Ilani-Kashkouli,[b] Andrew W. Knight[c] and Lourdes Loera[a]



- Experimental evidence of Nd(III), other REE dimerization in silica nanopores



- Corroborated using gaussian DFT/BP86 calculations, but overestimate dimerization tendency

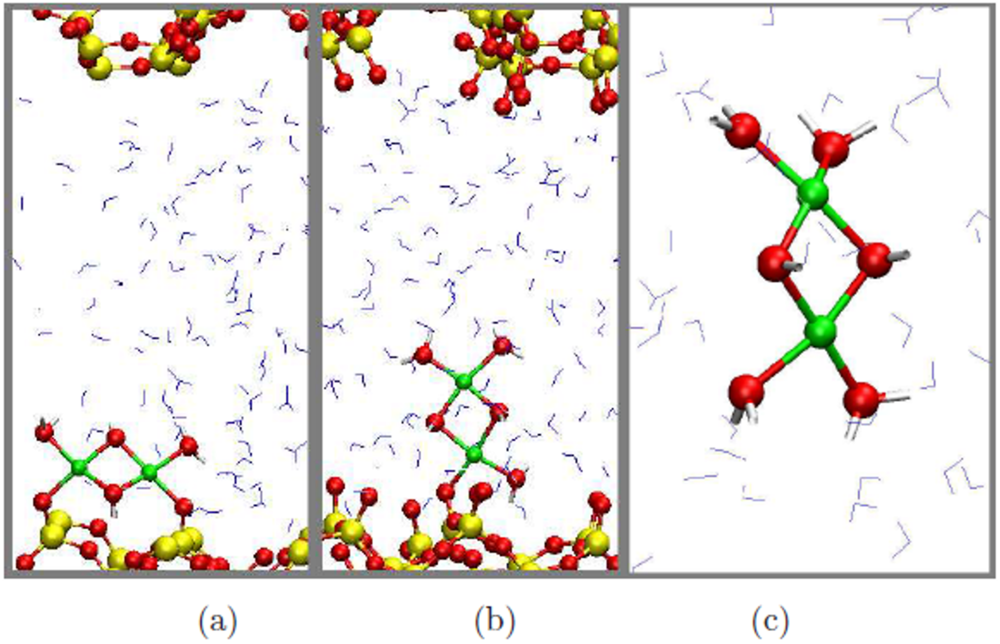
Here, focus on Cu-dimerization via AIMD free energy

Compare
free energy of:

dimer on
silica

dimer on
silica

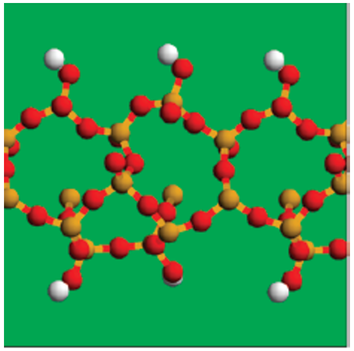
dimer in
water



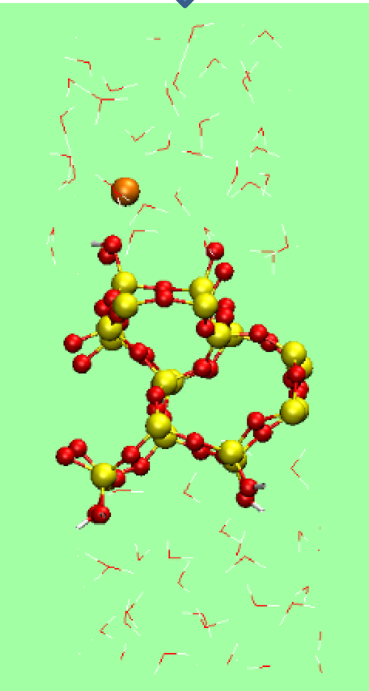
These structures motivated by classical force field studies, bridged by two OH^-

Computational Model and method: AIMD/PMF

reconstructed (001)



add water, cation



- focus on silica, use model with single binding site as benchmark
- use our previous reconstructed β-cristobalite (001), pKa = 7.0 – 8.1

J. Am. Chem. Soc., **2009**, *131*, 18358

*important to have only one unique binding site; most mineral surfaces have cation multiple binding sites, hard to get clean results, e.g., Leung & Criscsenti, J. Phys. Condens. Matter 29, 365101 (2017)

- Sulpizi and Gaigeot groups found lower pKa SiOH on amorphous silica but multiple binding site complicates analysis

Bimodal Acidity at the Amorphous Silica/Water Interface

Morgane Pfeiffer-Laplaud,[†] Dominique Costa,[‡] Frederik Tielens,[§] Marie-Pierre Gaigeot,[∥,⊥]
and Marialore Sulpizi[*,#]

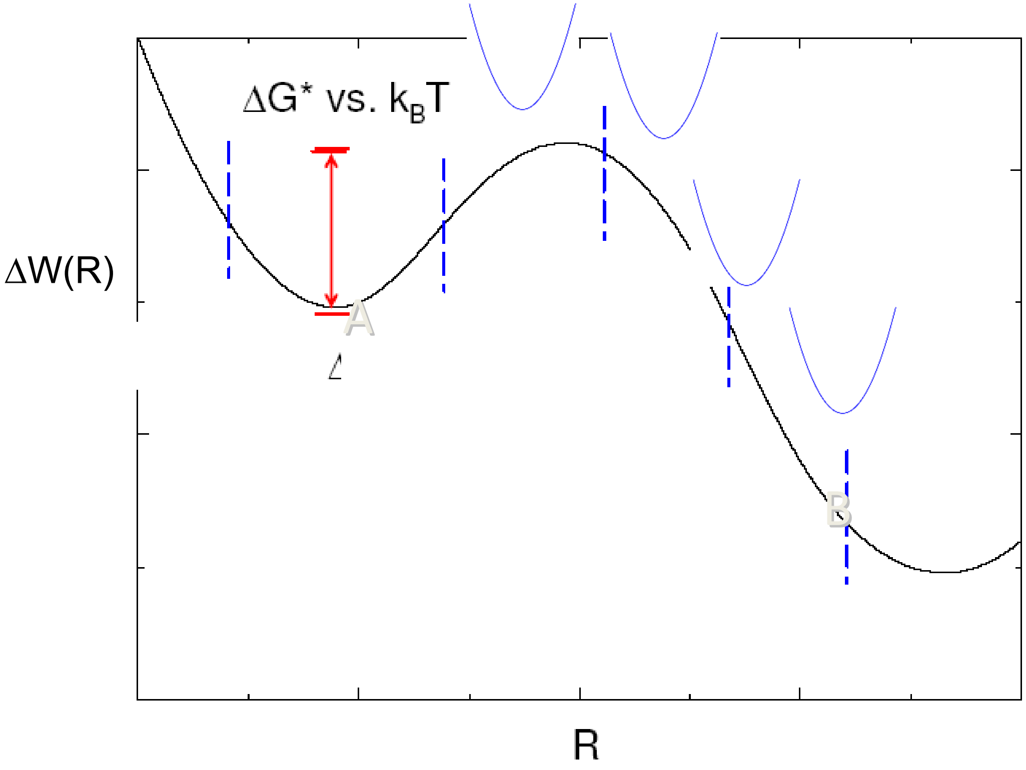
- ~4 SiOH groups per nm^2, higher than our experimental SiOH density
- DFT/PBE, 14x14x26 A^3 simulation cell, Γ-point sampling

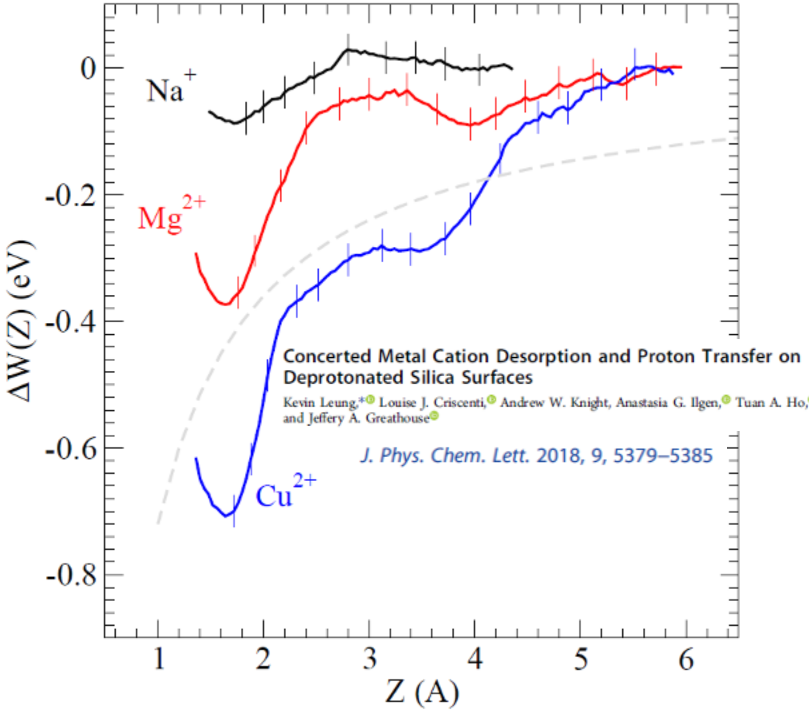
(larger cell than our previous work)

- T=400 K, umbrella sampling
- One RE^{3+} in each simulation cell, ~350 ps total each
- 3 SiO$^-$ group to keep charge neutrality
- Qualitatively compare with measurements

Potential of Mean Force is the way to calculate barriers/exothermicity in liquids

$\Delta W(R) \sim -k_BT \ln [P(R)]$

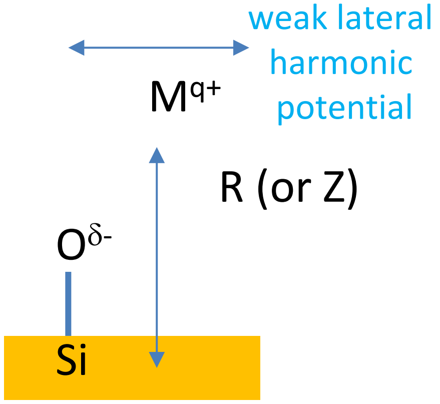




Concerted Metal Cation Desorption and Proton Transfer on Deprotonated Silica Surfaces

Kevin Leung,* Louise J. Criscenti, Andrew W. Knight, Anastasia G. Ilgen, Tuan A. Ho, and Jeffery A. Greathouse

J. Phys. Chem. Lett. 2018, 9, 5379–5385


weak lateral harmonic potential

M^{q+}

R (or Z)

$O^{\delta-}$

Si

desorption free energy: $\Delta G_{\rm ads}/k_{\rm B}T = -\log\{\int_\Omega d\Omega \exp[-\Delta W(Z)/k_{\rm B}T]/(V_o)\}$

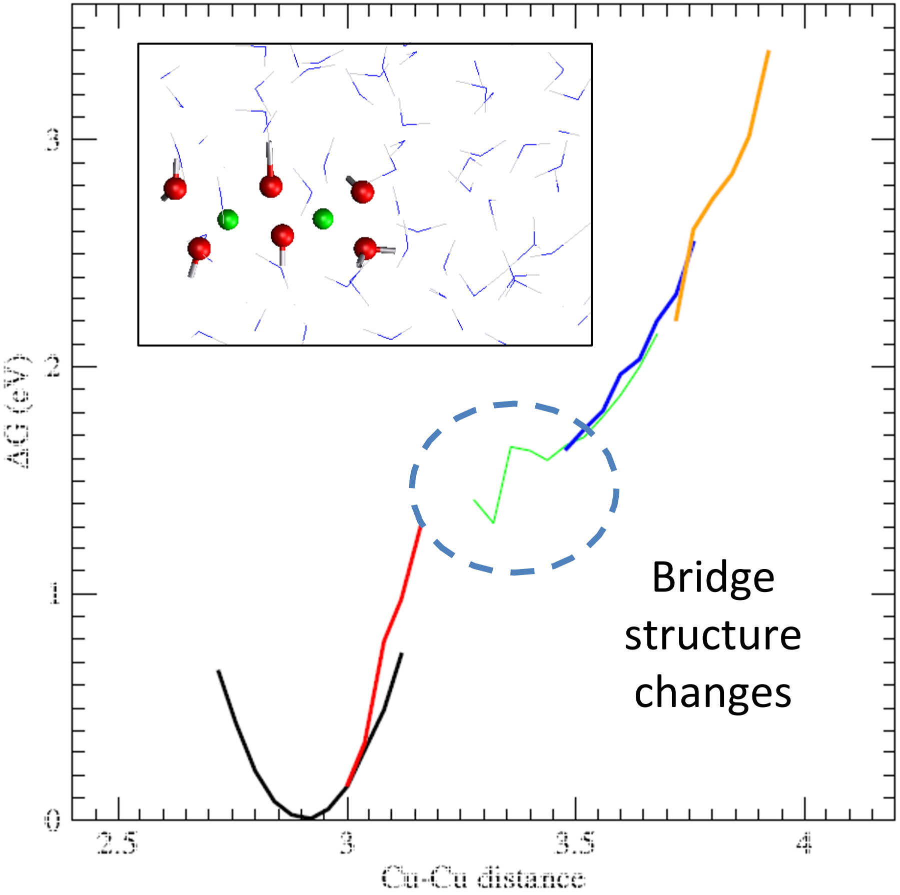
Na^+: +0.13 +/- 0.03 eV (unbound)

Mg^{2+}: -0.14 +/- 0.05 eV

Cu^{2+}: -0.47 +/- 0.07 eV

First try: Cu-Cu distance as reactive coordinate

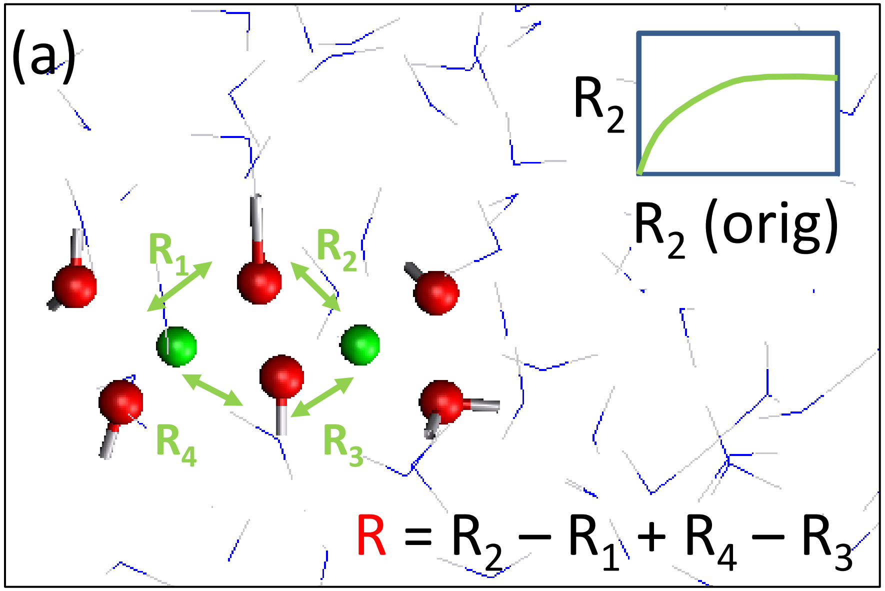
$[Cu(II)(OH^-)_2]_2$ in water



Bridge structure changes

PMF does not converge with umbrella sample, see discontinuities

Second try: 6-body reaction coordinate to break Cu-O



R_n (orig), n=1,4: original Cu-O distances

~1.9 < R_n (orig) < infinity

R_n , n=1,4: rescaled.

~1.9 < R_n (orig) < ~ 4 A

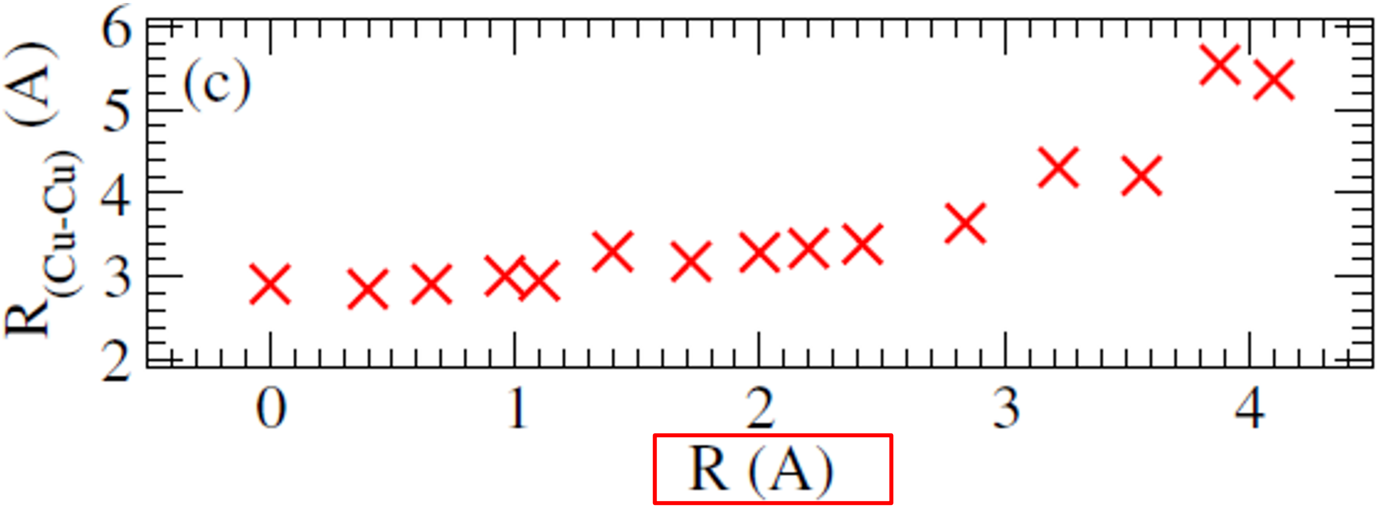
R_n ~ R_n (orig) for small R_n (~ 2 A)

~ 4 A as Rn (orig) >> 4 A, so **R** starts to control breaking of second Cu-O bond

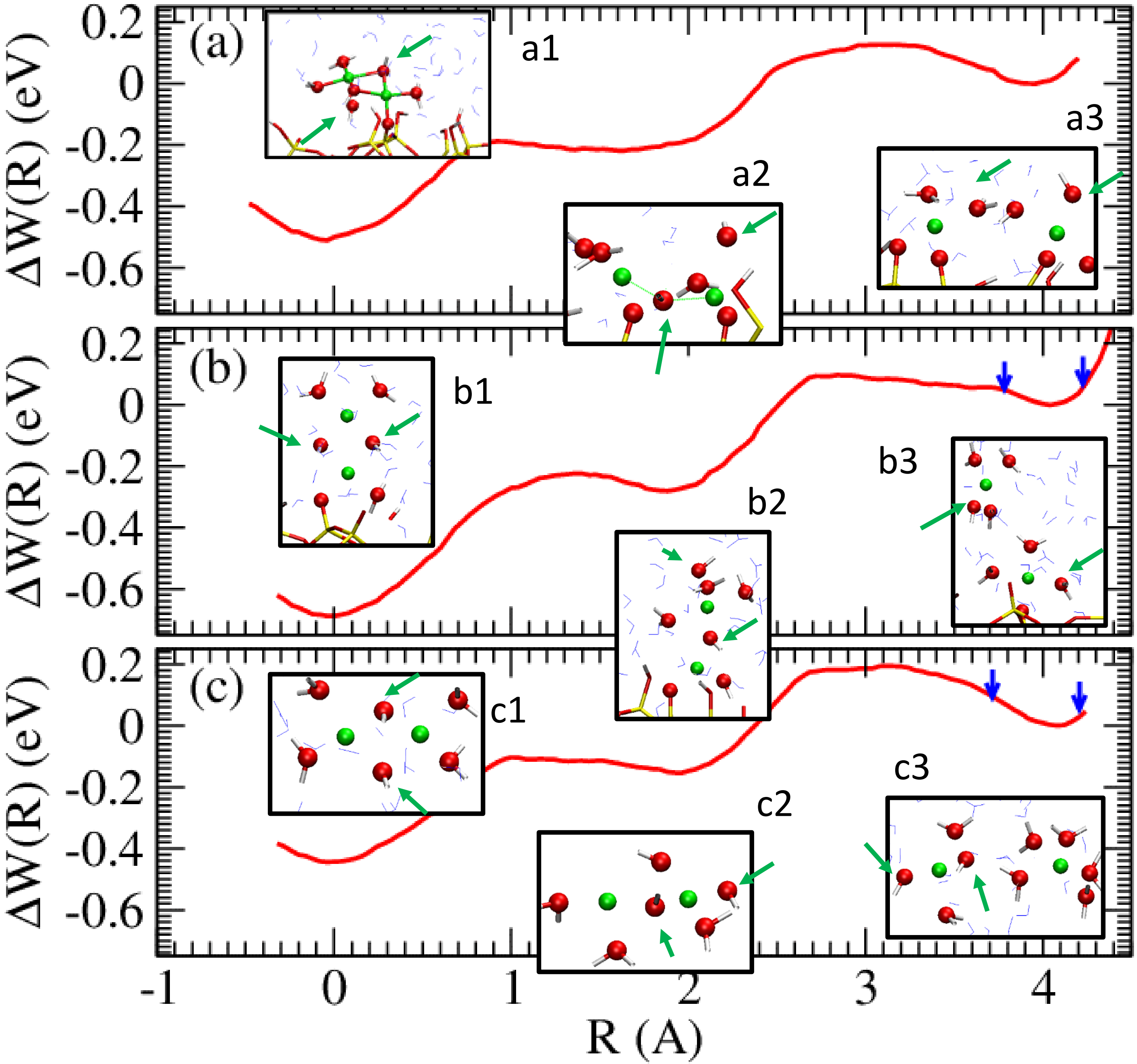
$$R_n = R_B + [R_n(\text{orig}) - R_B]/\{1 + [R_n(\text{orig}) - R_A]^4\}$$

R independent of $R_{(\text{Cu-Cu})}$

explains why $R_{(\text{Cu-Cu})}$ doesn't work



Results



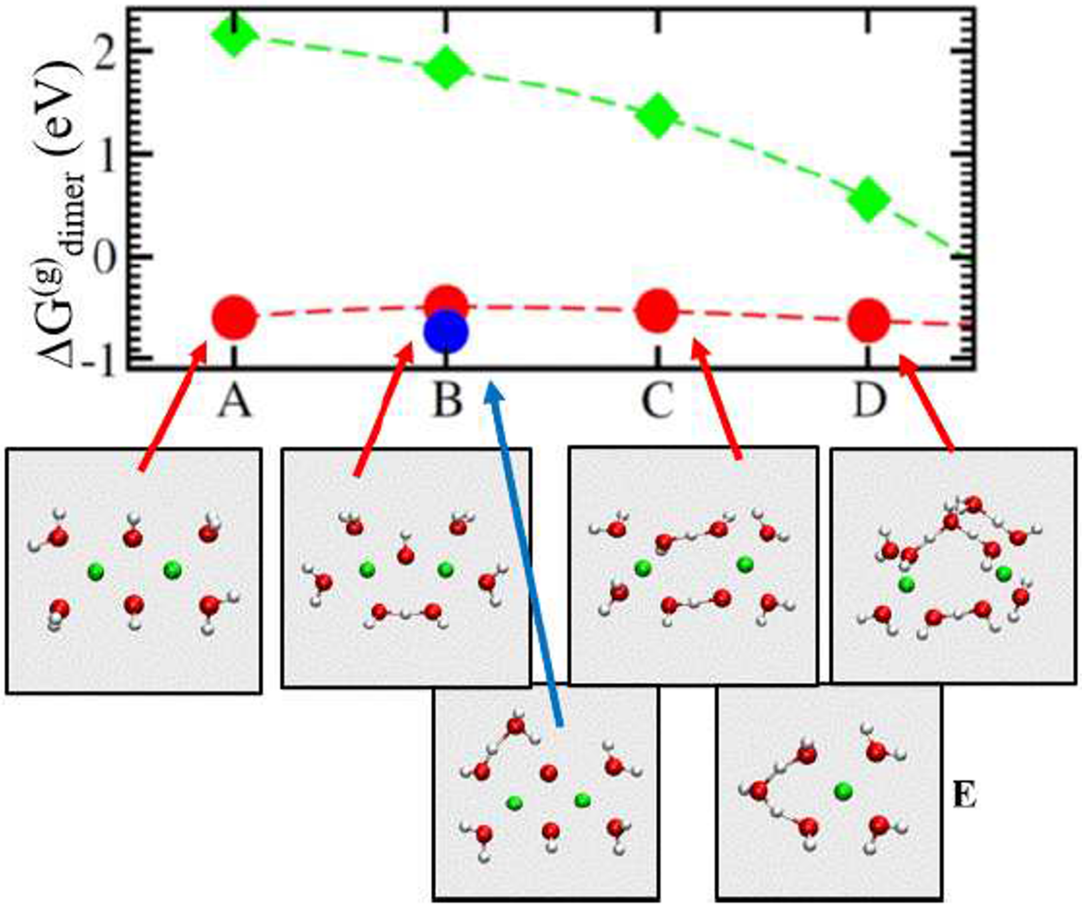
horizontal
ΔG_{dimer} =-0.51 eV

vertical
ΔG_{dimer} =-0.59 eV
(CMD predictions)

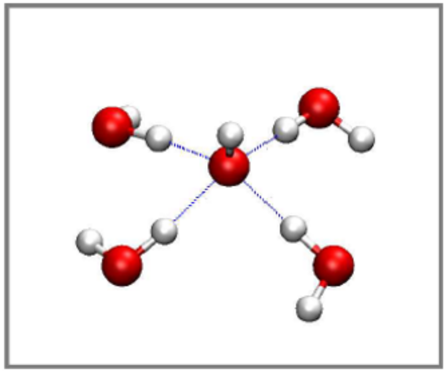
In water
ΔG_{dimer} =-0.38 eV
(PHREEQC:-0.33 eV)

Green arrow: OH^-

Why are our gaussian results inaccurate?



- No PCM: results reasonable, Cu(II) dimer unbound, repulsion decreases with distance/more H_2O
- default PCM: Cu(II) always bound regardless of distance – wrong!
- Compared $OH^-(H_2O)_4$ vs OH^- energetics in PCM -> discrepancy due to inaccurate PCM solvation of exposed OH^- groups



Conclusions

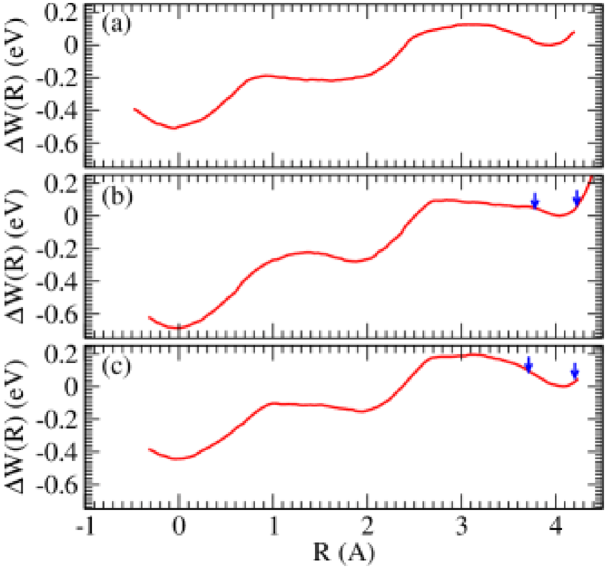
- AIMD potential-of-mean-force calculations show Cu(II) dimerization more favorable on silica surfaces than in water

- Vertical dimers more favorable than horizontal ones

- Energy landscape implies desorption takes ~ seconds, easily reaches equilibrium

- Needs to devise new reaction coordinate, not perfect, future research needed

- Gaussian (DFT cluster + implicit solvent) calculations inaccurate if implicit solvation of OH^- is not well treated.



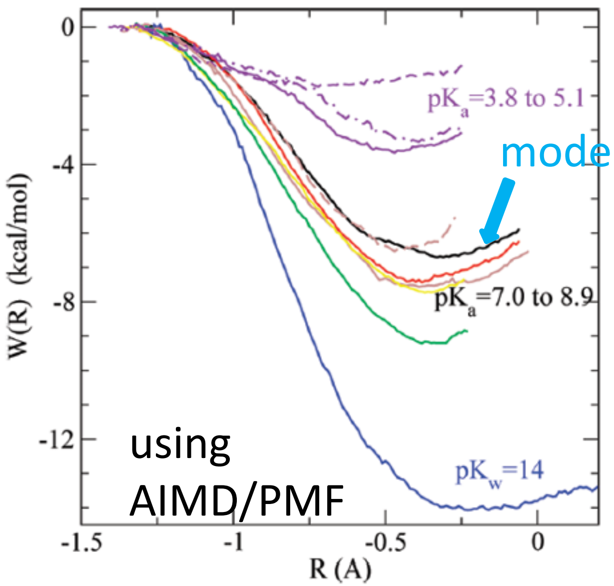
Supporting slides

pH- and pK_a -dependence

Elucidating the Bimodal Acid–Base Behavior of the Water–Silica Interface from First Principles

Kevin Leung,*,† Ida M. B. Nielsen,‡ and Louise J. Criscenti†

J. AM. CHEM. SOC. 2009



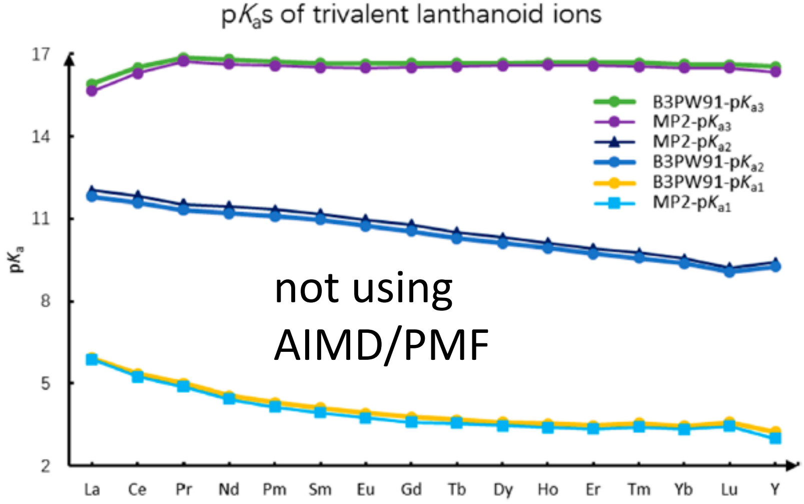
model silica pK_a

using AIMD/PMF

What is pK_{a1} of $Ln(III)(H_2O)_n$ complexes?

Theoretical Study of pK_a Values for Trivalent Rare-Earth Metal Cations in Aqueous Solution *J. Phys. Chem. A* 2018, 122, 700–707

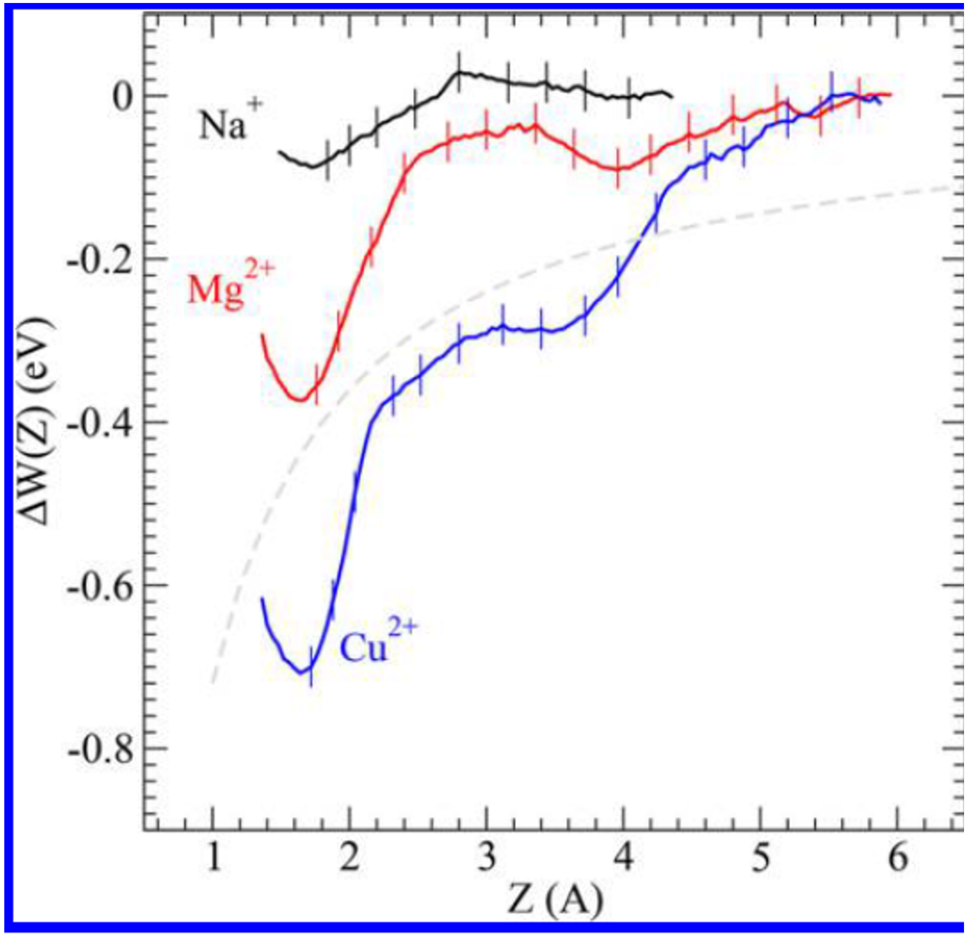
Donghai Yu,†,§ Ruobing Du,† Ji-Chang Xiao,*,† Shengming Xu,*,‡ Chunying Rong,† and Shubin Liu*,∥



not using AIMD/PMF

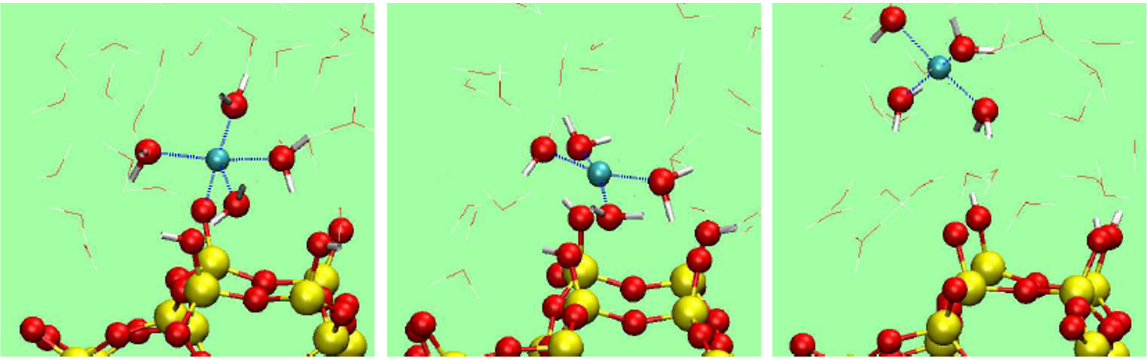
- Yu et al suggests pK_{a1} ~ 3-4
- thermodynamic data suggests Ln(III) pK_{a1} ~ 7-8 (courtesy of Louise Criscenti)
- both values consistent with proton exchange seen between SiOH and Ln(III) in AIMD
- higher pH (>6) creates SiO^-, favors Ln(III) adsorption but also Ln hydroxide precipitation
- suggests local high pH may help Ln(III) selectivity without precipitation

Our previous work on other cations on silica



Much larger effects due to hydrolysis: Cu(II) has it, Mg(II) not

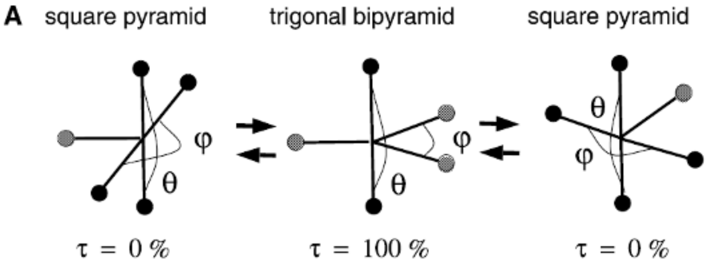
Cu(II) in water is always an outlier

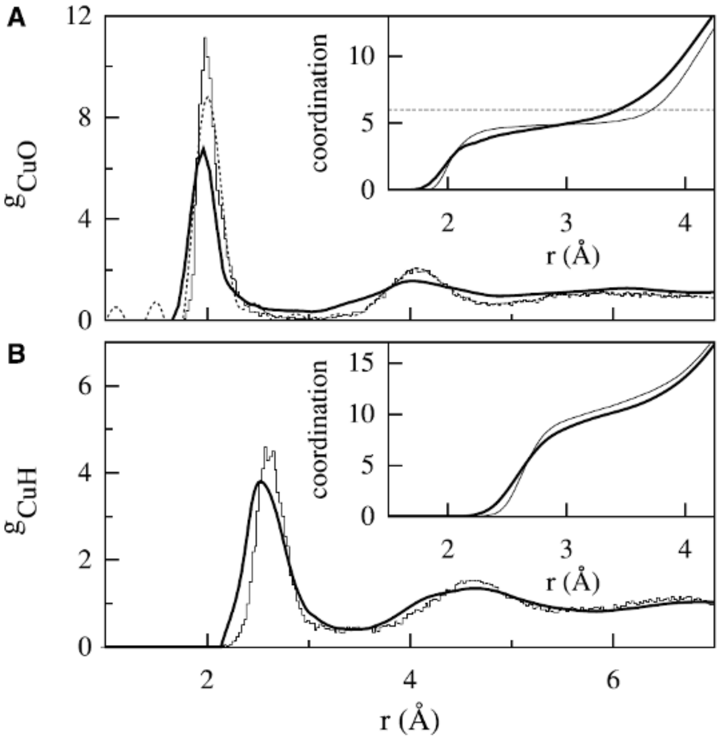


First Solvation Shell of the Cu(II) Aqua Ion: Evidence for Fivefold Coordination

Alfredo Pasquarello,[1,2]* Ingrid Petri,[3] Philip S. Salmon,[3]
Olivier Parisel,[1,2] Roberto Car,[1,4] Éva Tóth,[5] D. Hugh Powell,[6]
Henry E. Fischer,[7] Lothar Helm,[5] André E. Merbach[5]

2 FEBRUARY 2001 VOL 291 SCIENCE





PMF statistics