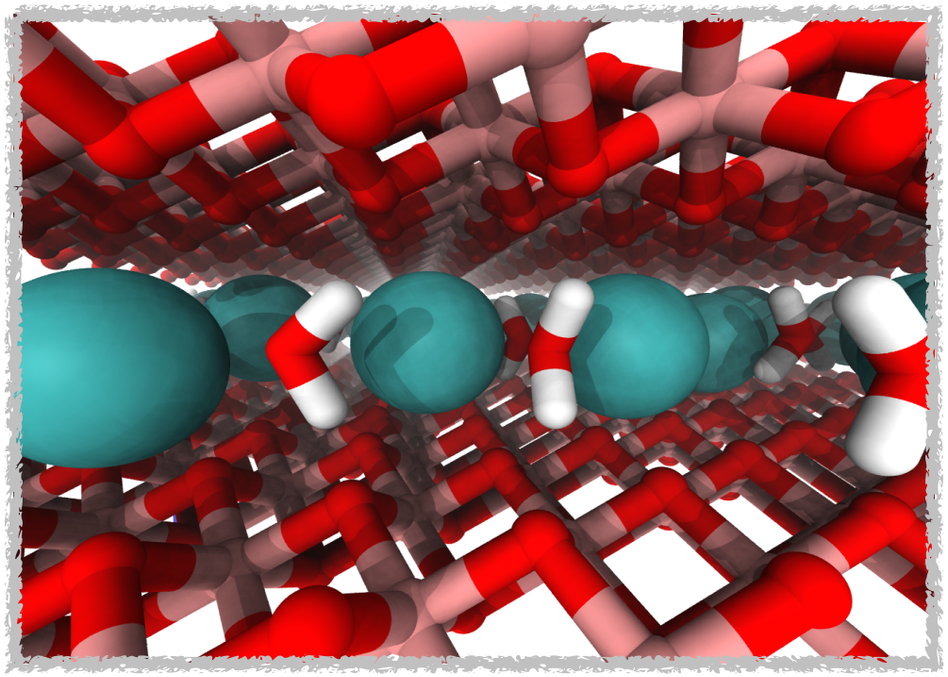
Structure and Dynamics of Water and Ions in Birnessite



Rick Remsing

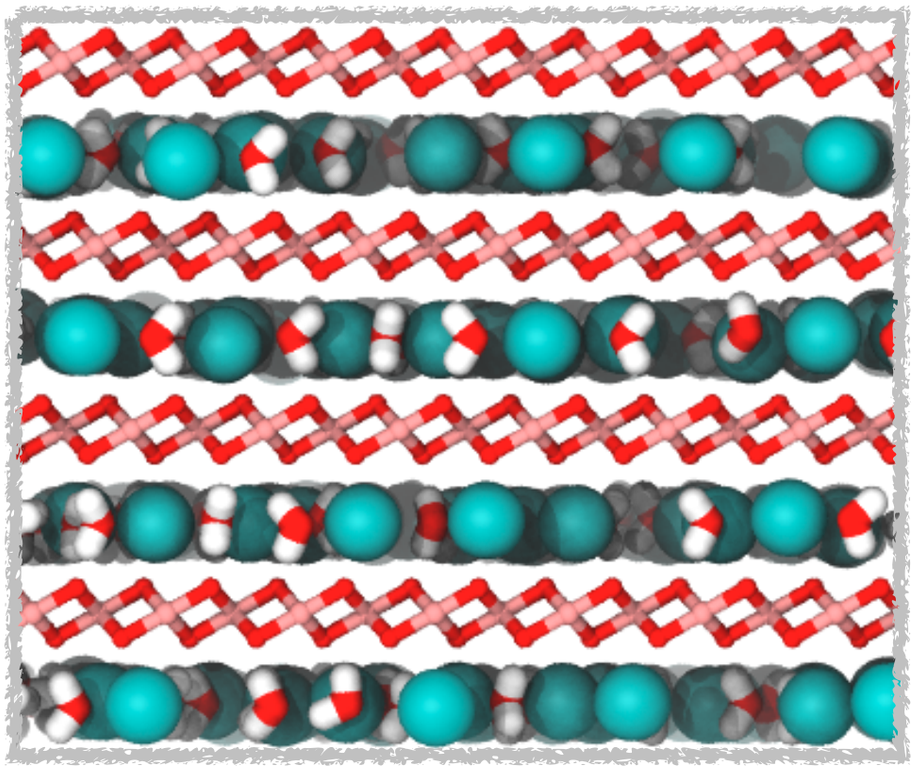
ICMS, CCDM, Temple University, Philadelphia, PA

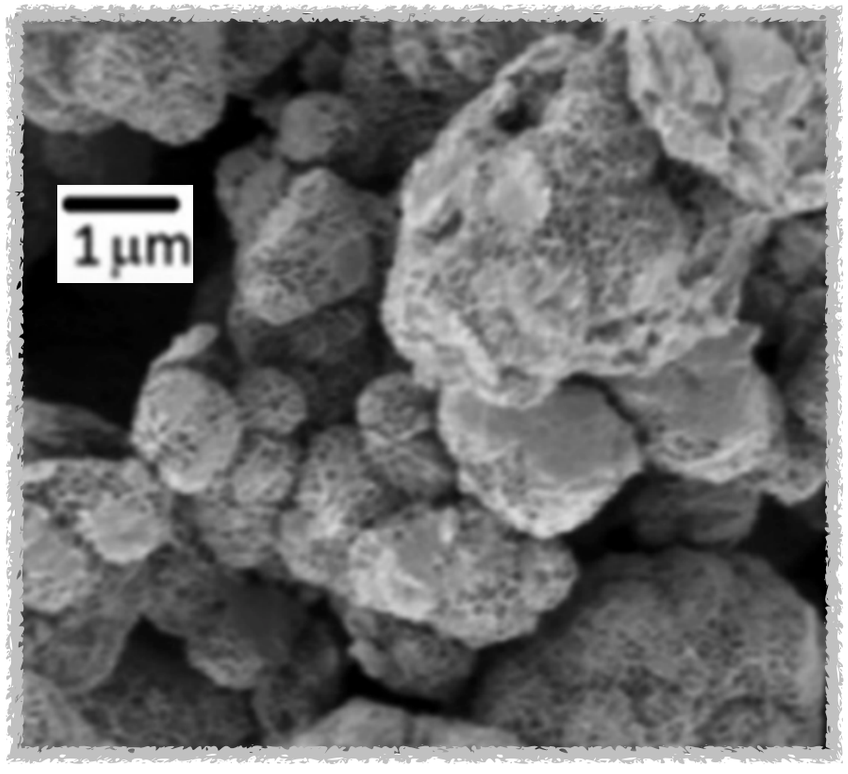
Materials for Water Splitting

- Need good catalysts for the oxygen evolution reaction (OER)

$$2\mathrm{H_2O} \overset{\mathrm{MnO_2}}{\rightarrow} \mathrm{O_2} + 4\mathrm{H^+} + 4e^-$$

- MnO_2 (Birnessite) catalyzes very effectively





- Surfaces are negatively charged; only cations intercalate

McKendry *et al.*, *Dalton Trans.*, **2015**, *44*, 12981

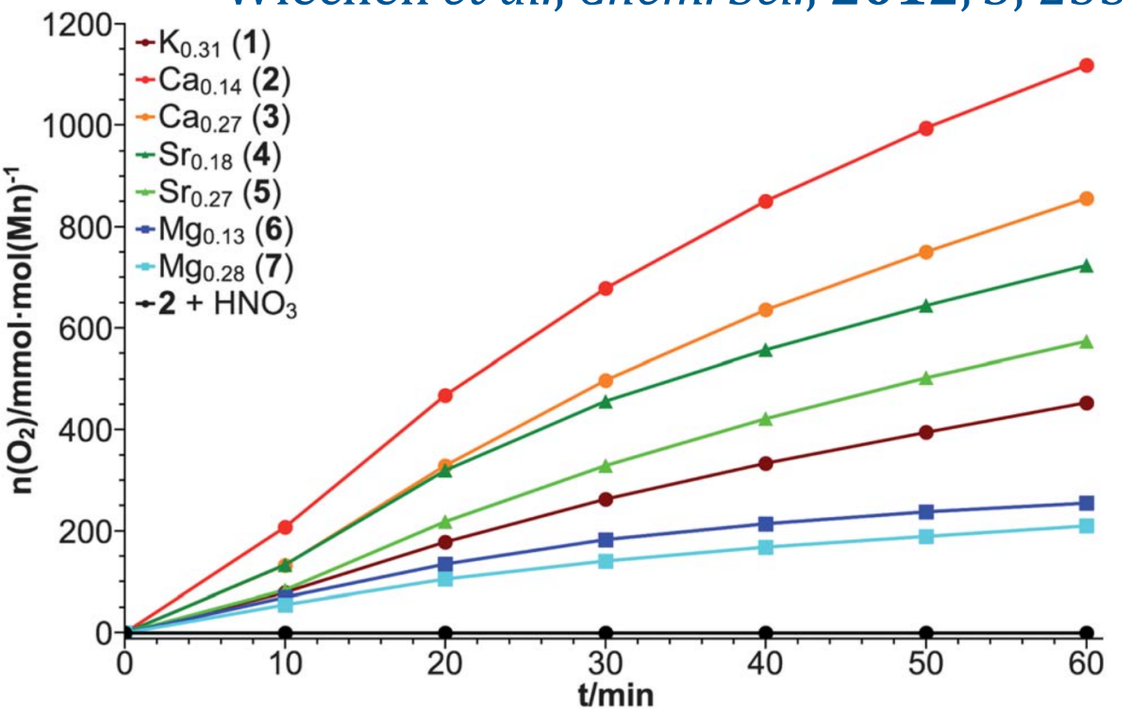
Chemistry Occurs in the Interlayer Region

- OER occurs in the confined space between two sheets

$$4M^{q} + 2H_2O \xrightarrow{MnO_2} 4M^{q-1} + 4H^{+} + O_2$$

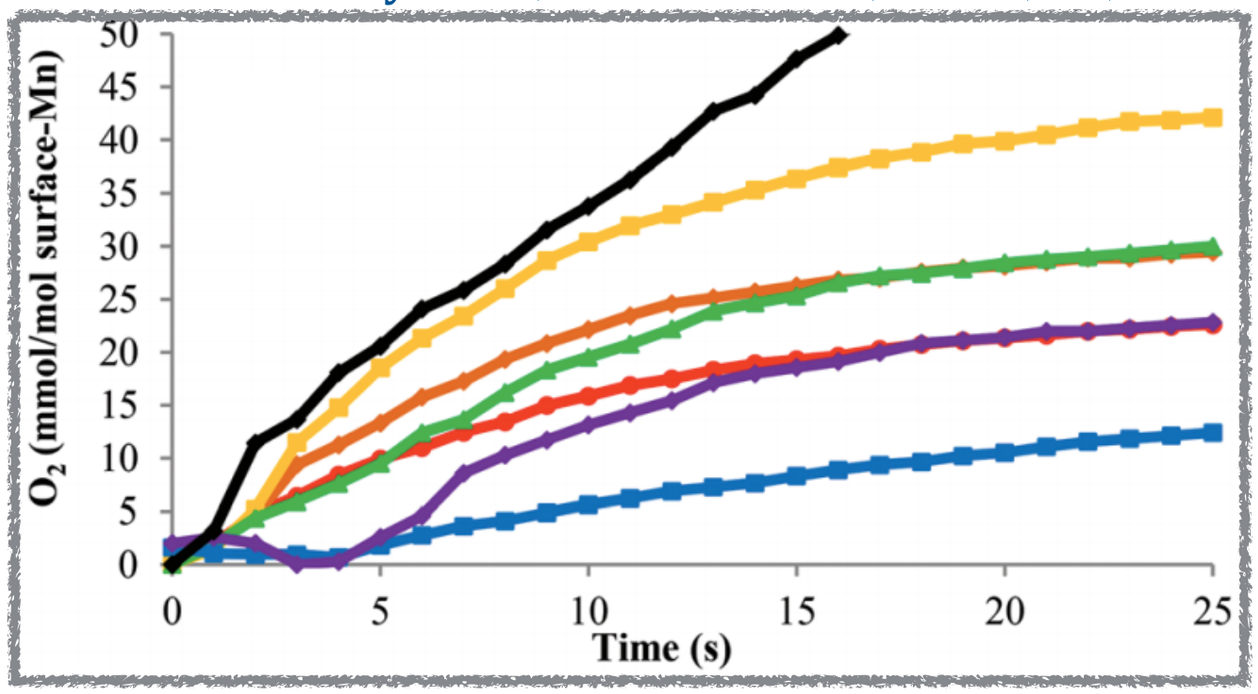
- O_2 production can be tuned with intercalants

Wiechen *et al.*, *Chem. Sci.*, **2012**, *3*, 2330



- Depends on cation charge and size…

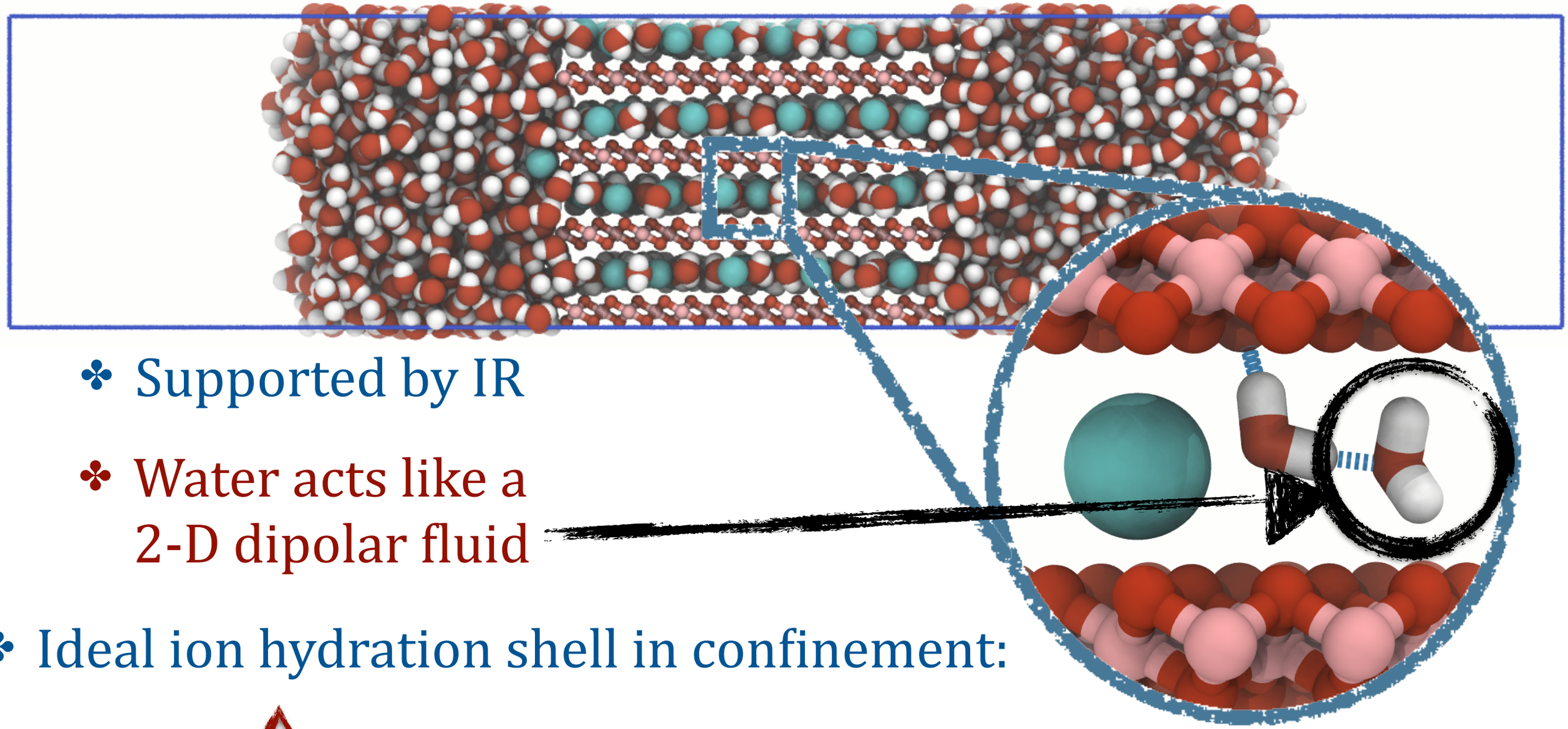
McKendry *et al.*, *Dalton Trans.*, **2015**, *44*, 12981



- …and average oxidation state
- How does confinement modify ion hydration and chemistry?

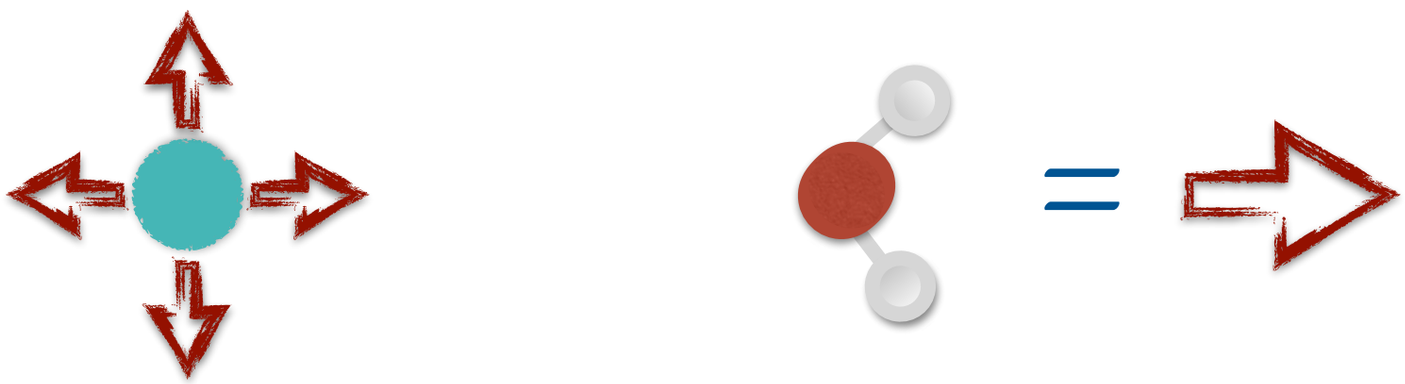
Interlayer Water is Highly Ordered

- Understand water in confinement before hydration



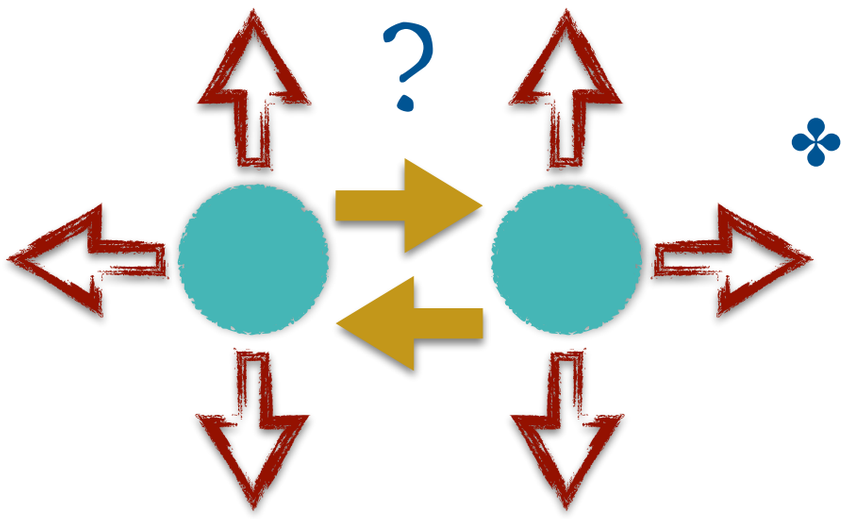
- Supported by IR
- Water acts like a 2-D dipolar fluid

- Ideal ion hydration shell in confinement:

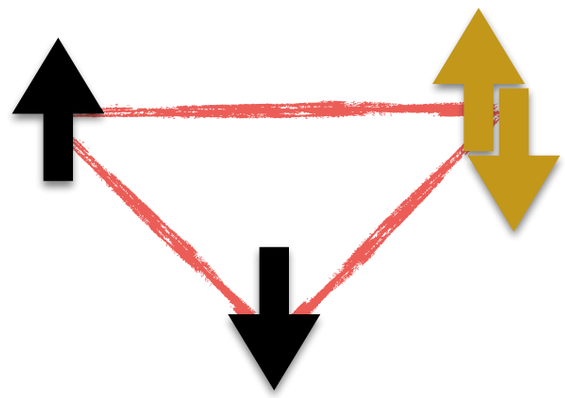


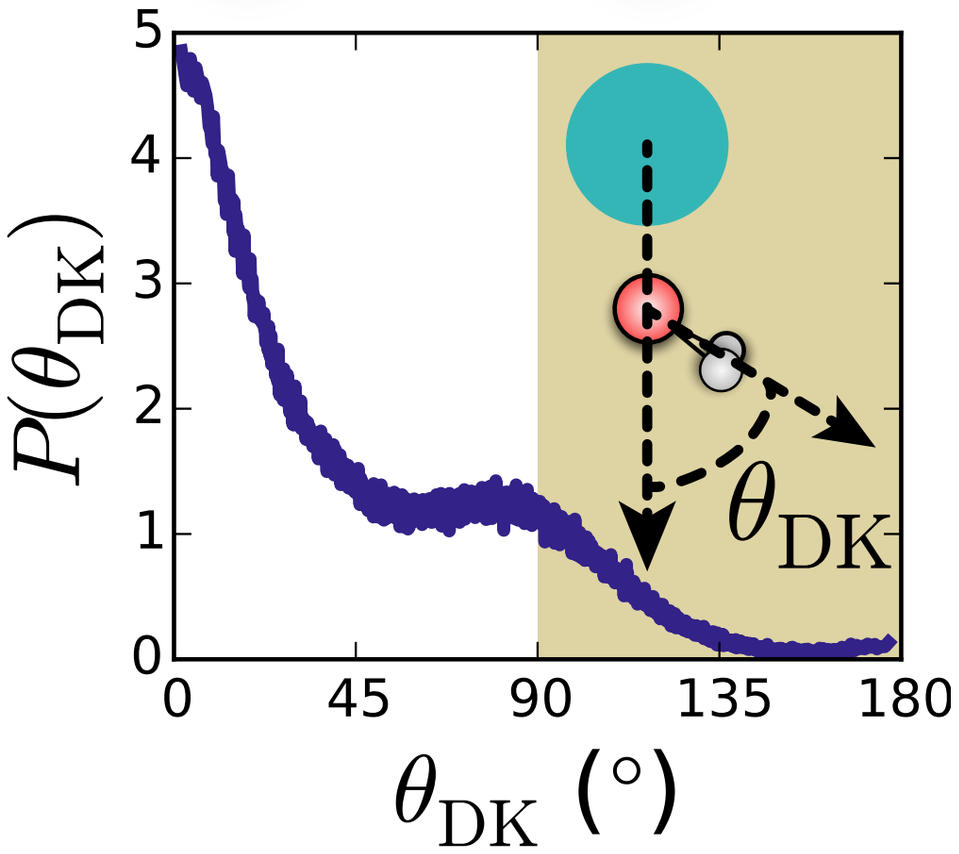
Cation Hydration is Frustrated by Ordered Water

- Frustration exists in the presence of multiple cations



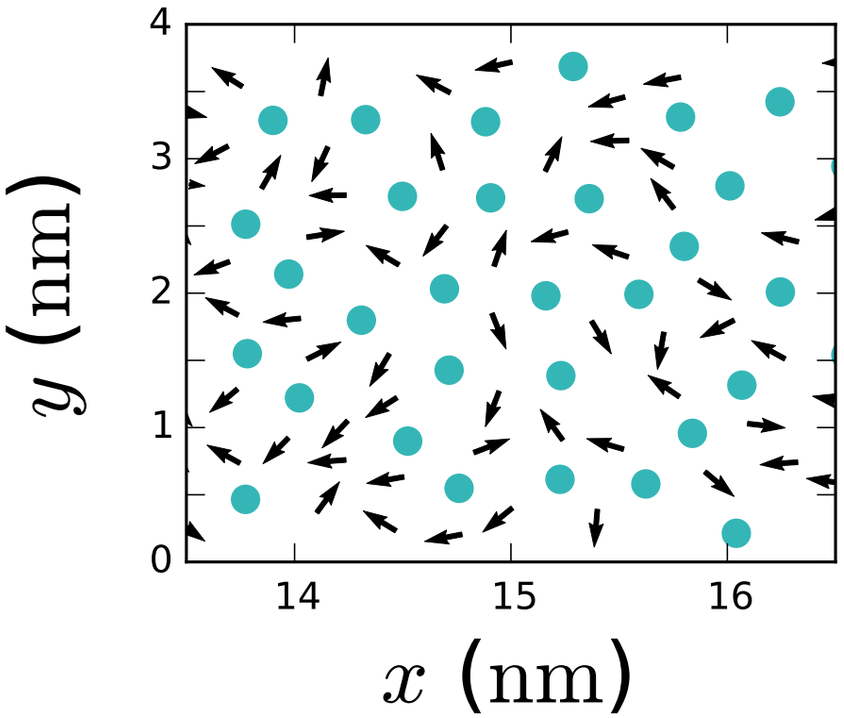
- Water between two cations never in favorable configuration



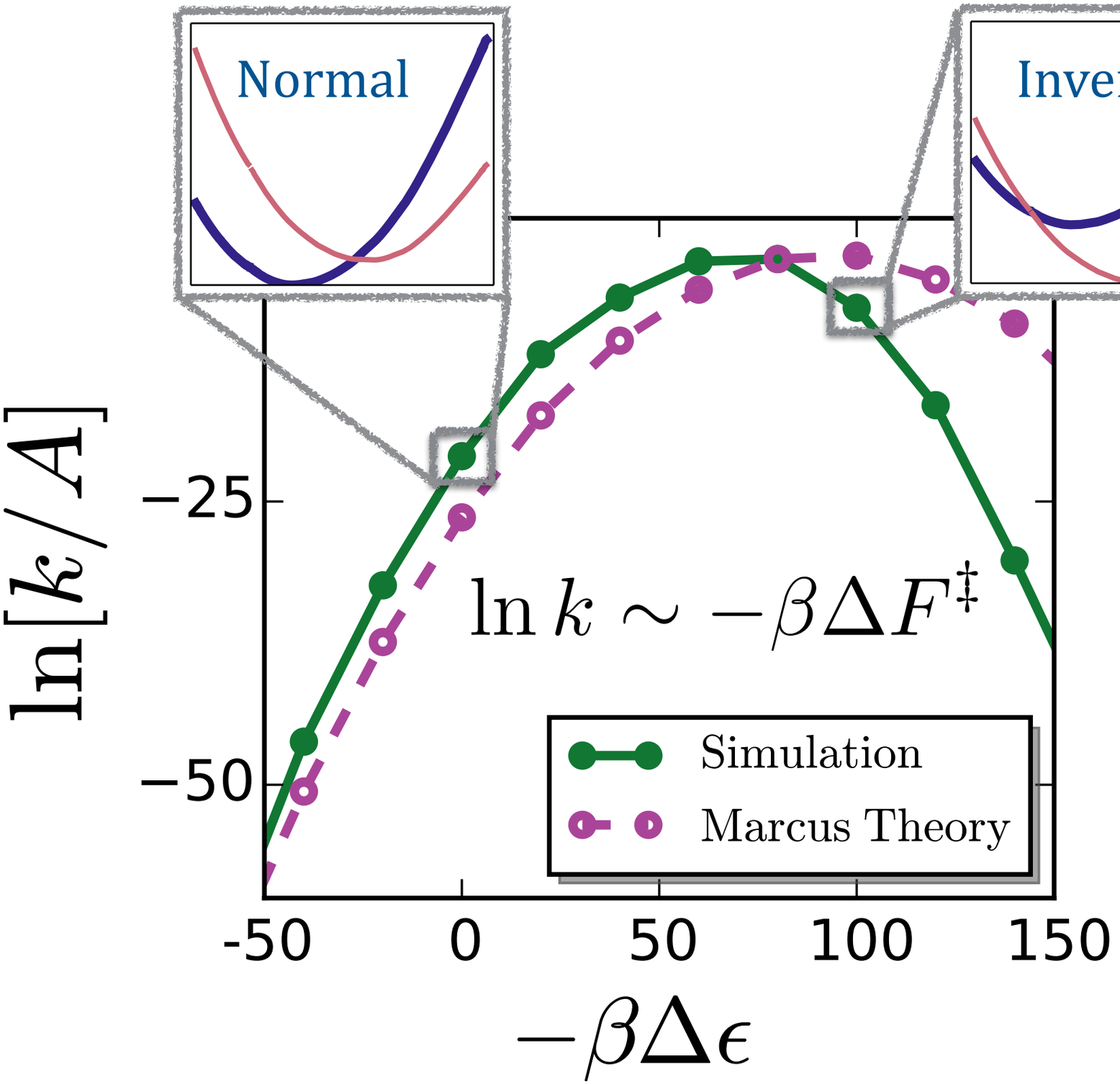


- High density of frustration
- Dynamic implications…
- Effects on chemistry?

~ 3 waters per cation



Enhanced Fluctuations Increase Rate of Electron Transfer *(in the normal regime)*



- Span range of thermodynamic driving force by shifting up and down

- Entirely due to frustration, showed with a minimal lattice model…

How does the system respond to charge transfer?

- Nonequilibrium response of solvent to charge transfer:

$$S(t) = \frac{\overline{\Delta E}(t) - \overline{\Delta E}(\infty)}{\overline{\Delta E}(0) - \overline{\Delta E}(\infty)}$$

- In linear regime, we can approx. by an equilibrium TCF:

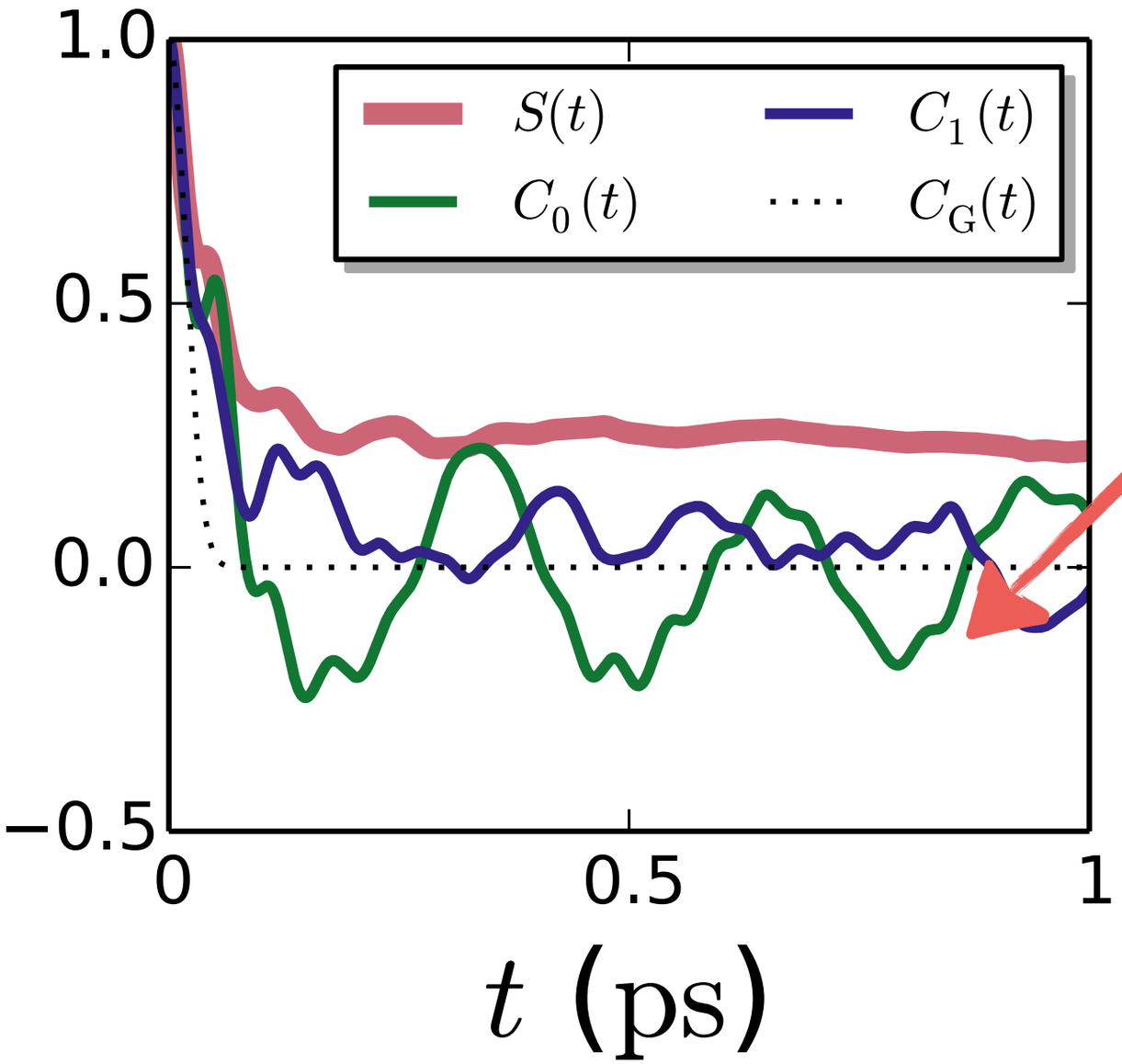
$$S(t) \approx C(t)$$

$$C(t) = \frac{\langle \delta\Delta E(t)\delta\Delta E(0)\rangle}{\langle \delta\Delta E\rangle^2}$$

- Does this hold under conditions of frustrated hydration?

Breakdown of Linear Response in Birnessite

- Linear response/fluctuation dissipation does not hold!



$$S(t) \not\approx C(t)$$

- Enhanced fluctuations due to frustration in equilibrium

- Three timescales in *S(t)*:
  $\tau_s < 1$ ps (Gaussian/Intertial)
  $\tau_i \sim 1$ ps (Local reorganization)
  $\tau_l \sim 3$ ns (Collective)

- What is origin of dynamics?
- Probe with dielectric spectroscopy?

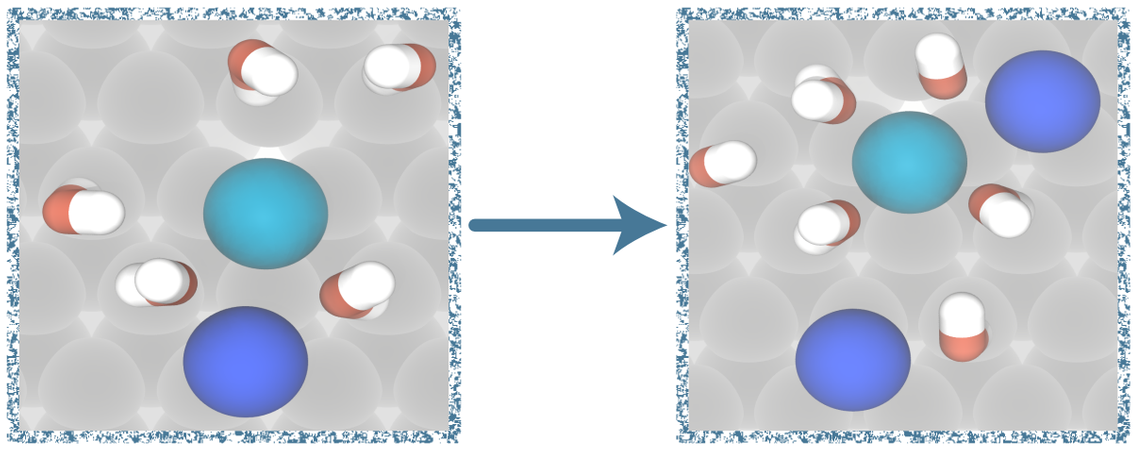
Molecular Origins of Relaxation

- TCF for orientational relaxation of hydration shell:

$$S_{\mathrm{DK}}(t) = \frac{\overline{\cos\theta_{\mathrm{DK}}}(t) - \overline{\cos\theta_{\mathrm{DK}}}(\infty)}{\overline{\cos\theta_{\mathrm{DK}}}(0) - \overline{\cos\theta_{\mathrm{DK}}}(\infty)}$$

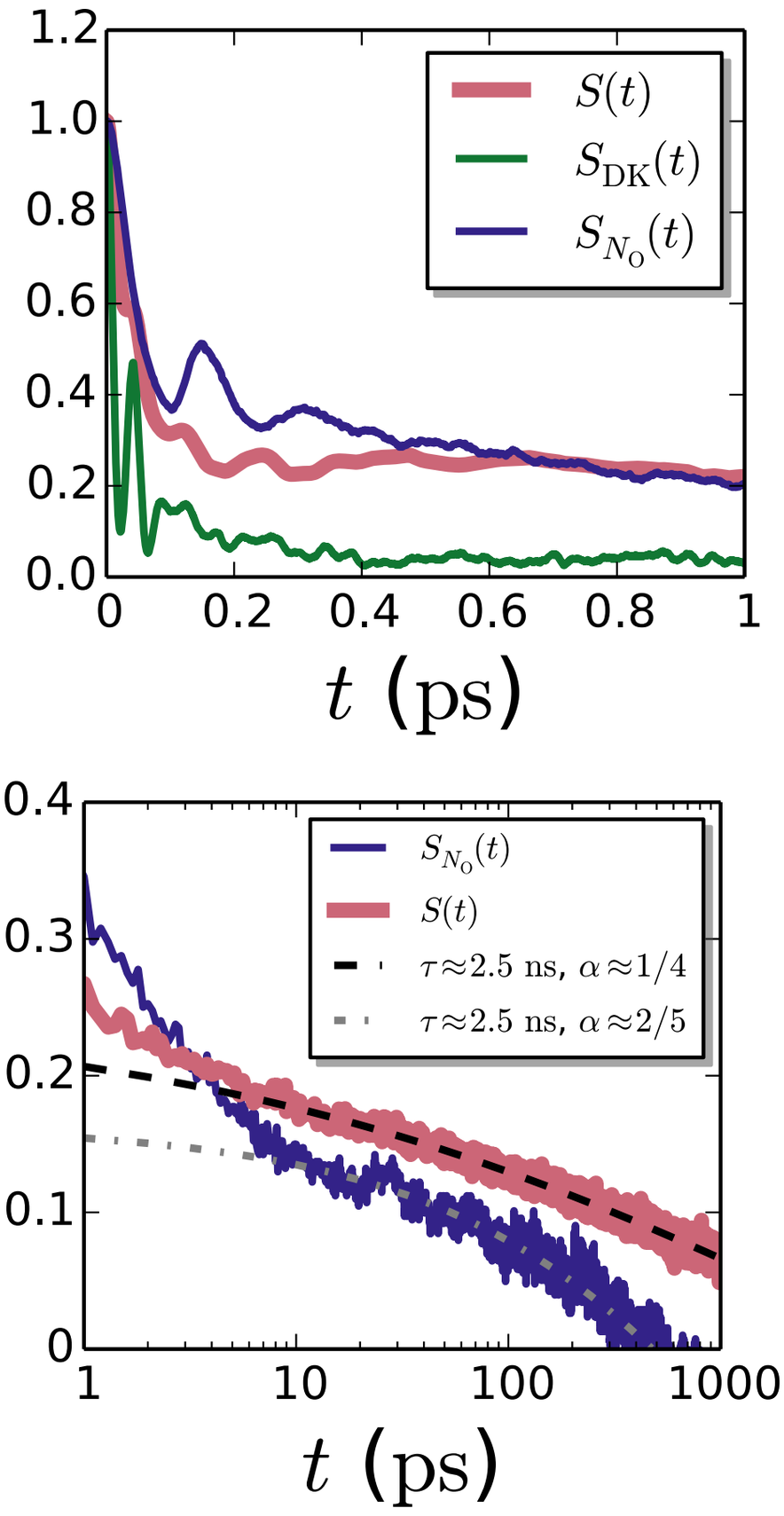
- TCF for translational relaxation of hydration shell (CN):

$$S_{N_{\mathrm{O}}}(t) = \frac{\overline{N_{\mathrm{O}}}(t) - \overline{N_{\mathrm{O}}}(\infty)}{\overline{N_{\mathrm{O}}}(0) - \overline{N_{\mathrm{O}}}(\infty)}$$

$N_{\mathrm{O}}^{(0)} \approx 3$  $N_{\mathrm{O}}^{(1)} \approx 4$

- Both are descriptions of **local** relaxation only

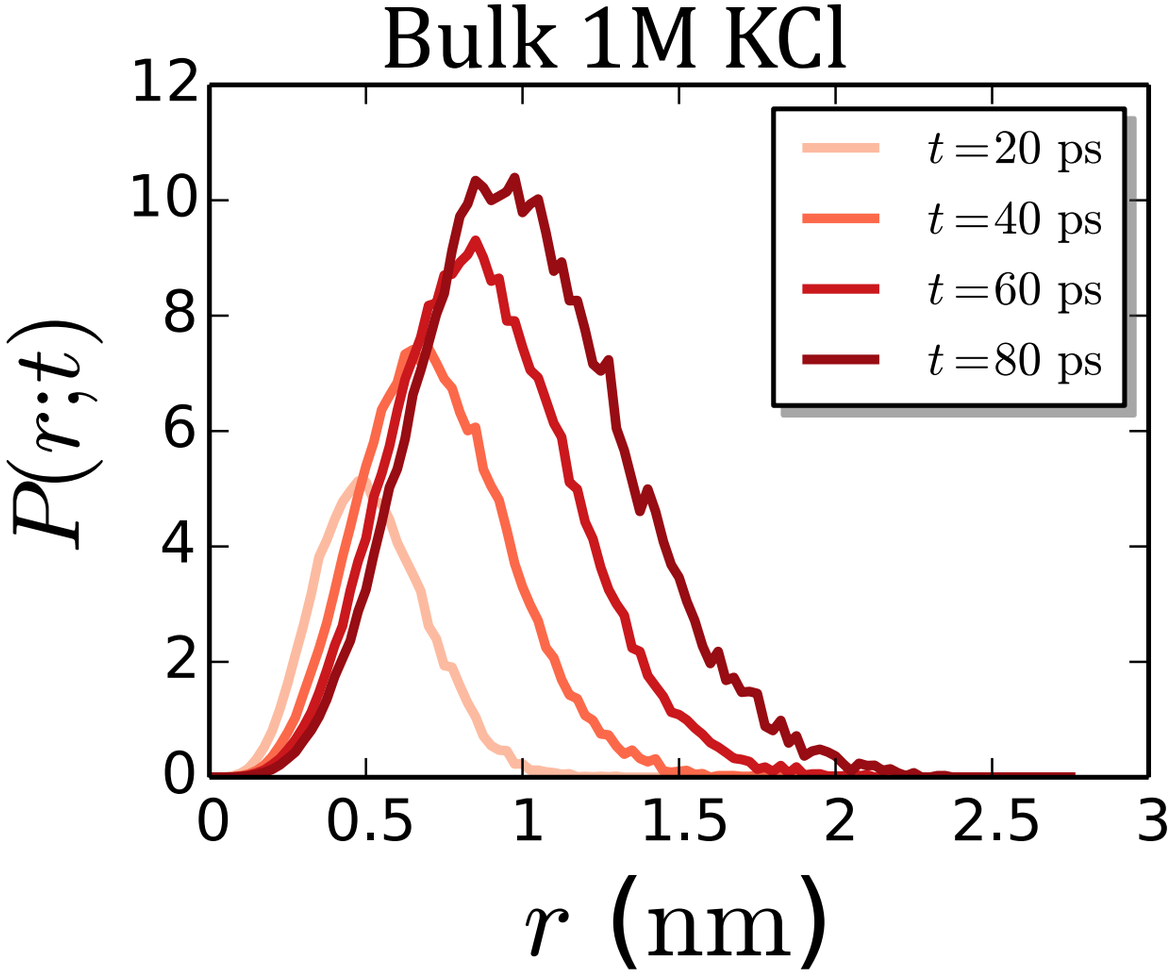
Molecular Origins of Relaxation

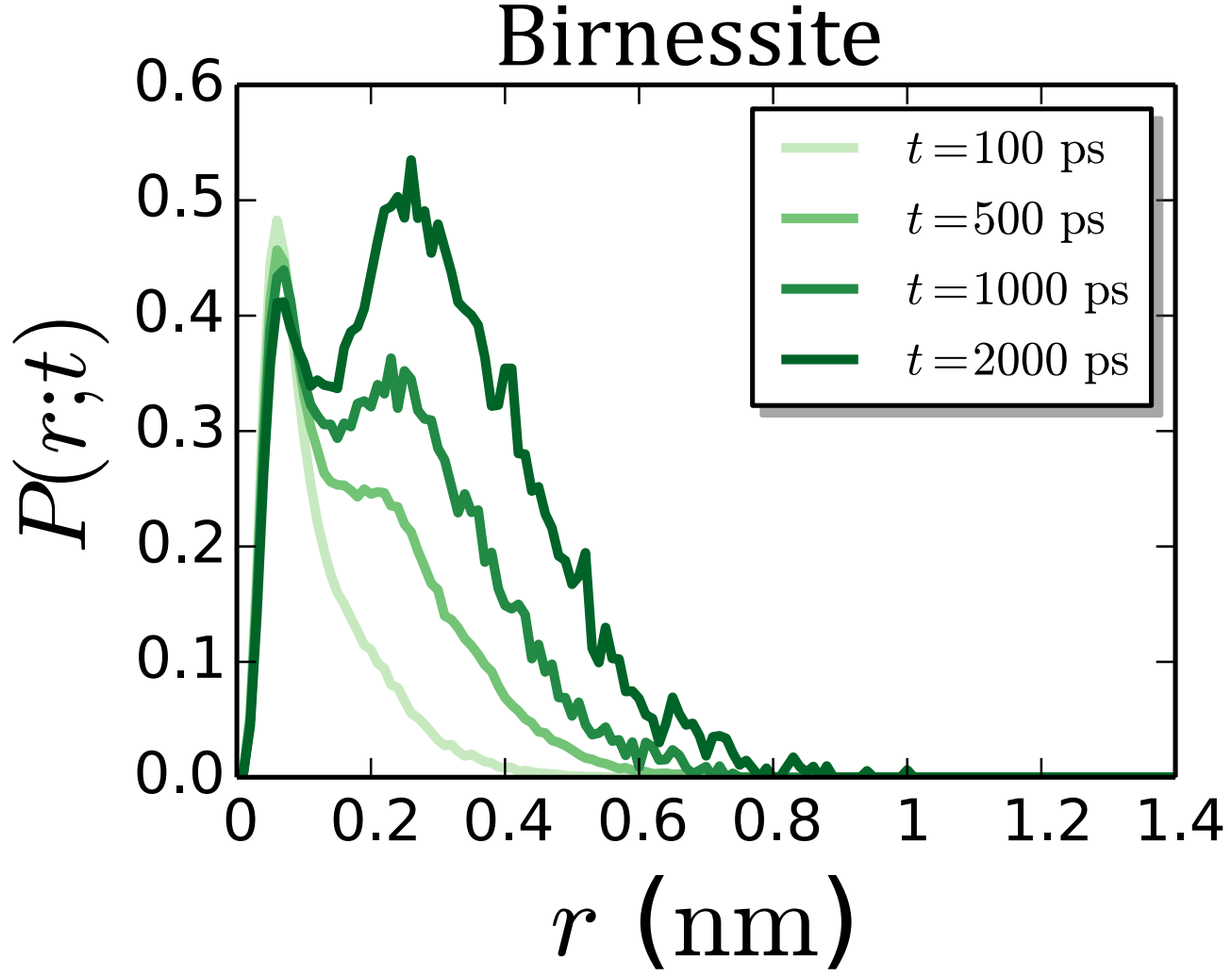


- Hydration shell dynamics account for features of S(t), peaks/valleys in registry
- Orientational relaxation is faster than translational
- Stretched exponential at long times: collective (glassy) dynamics
- Implications for chemical reactions occurring on ns timescales…

Signatures of Collective Dynamics in Equilibrium

- *P(r,t)*: Probability K^+ moves a distance *r* in a time *t*
- $P(r,t) = 4\pi r^2 G(r,t)$; *G(r,t)* self van Hove Function





- Gaussian in a "normal" liquid

- Diffusion proceeds by hopping between sites

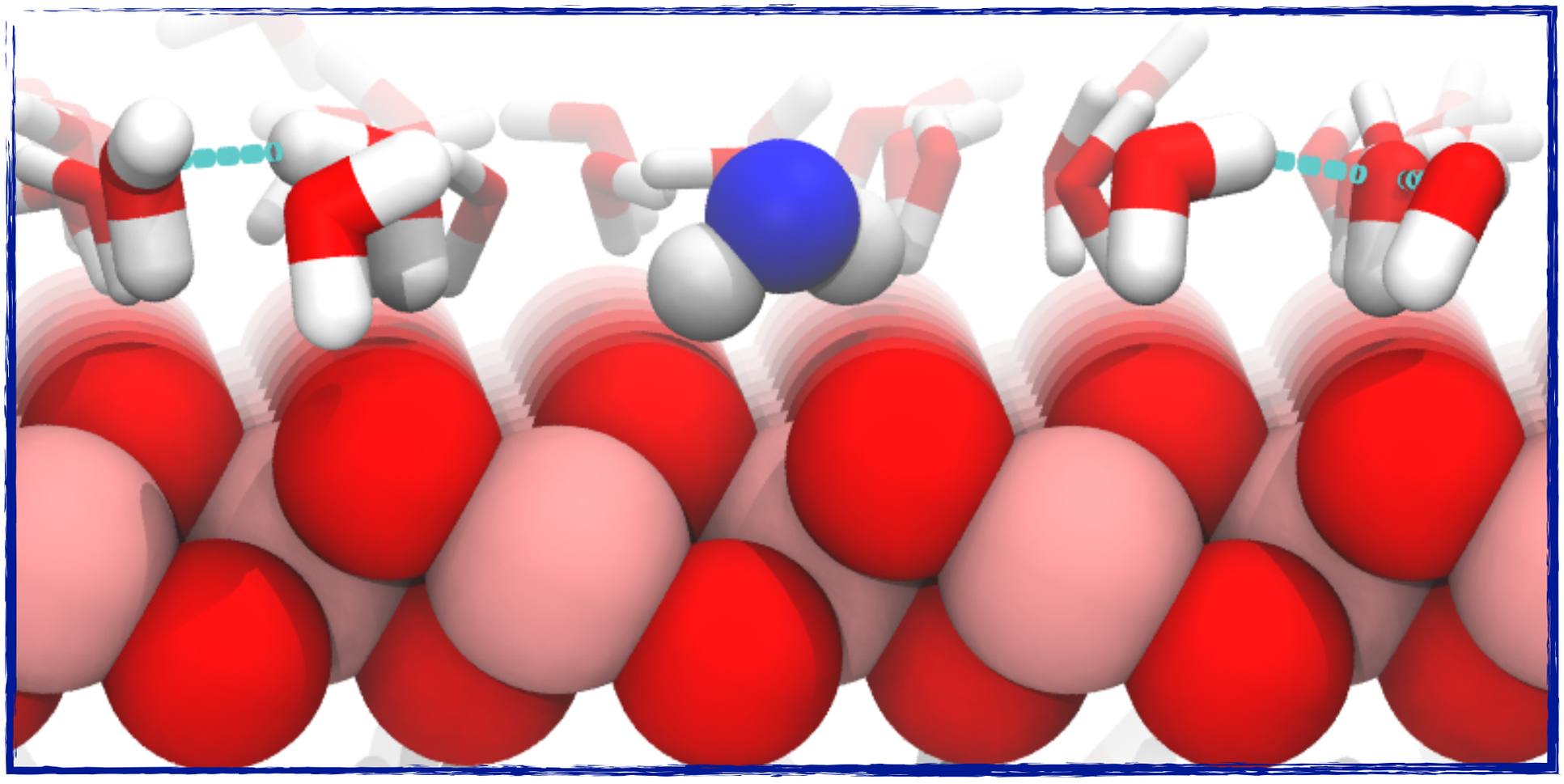
Ion Adsorption to Nanosheets

- Let's consider OER at nanosheets/bilayers
- Water oxidation correlates with ion hydration energies
- Does this also correlate with adsorption?

- First, what does water structure look like at nanosheet?

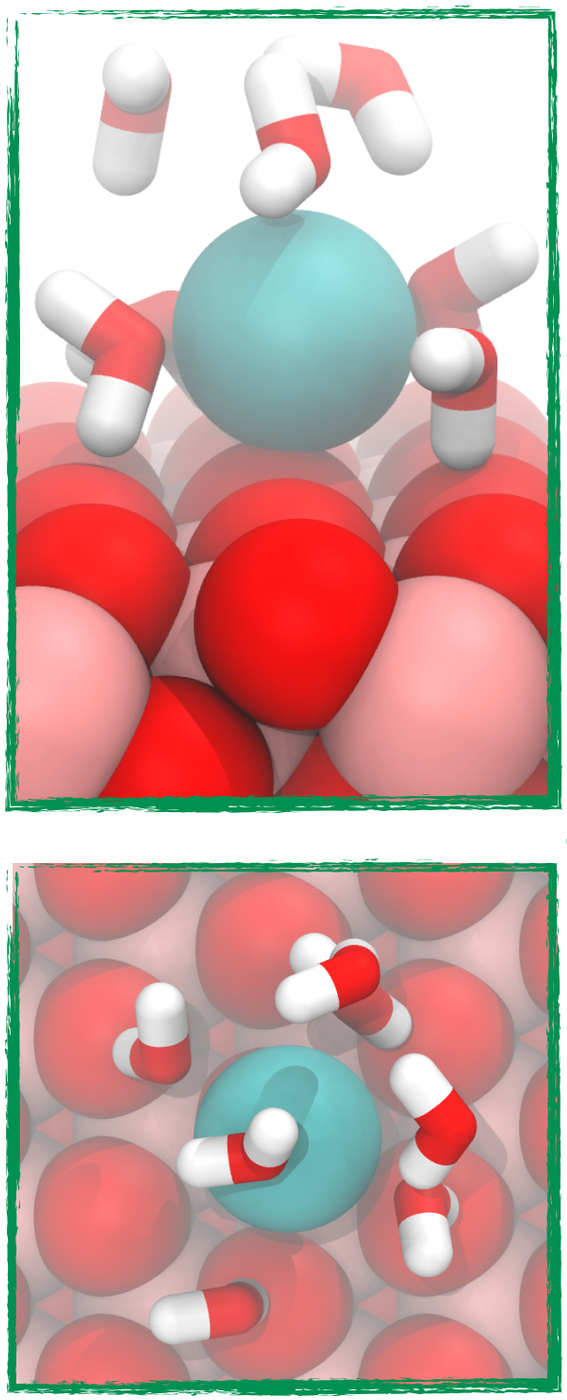
Water Structure at Nanosheets

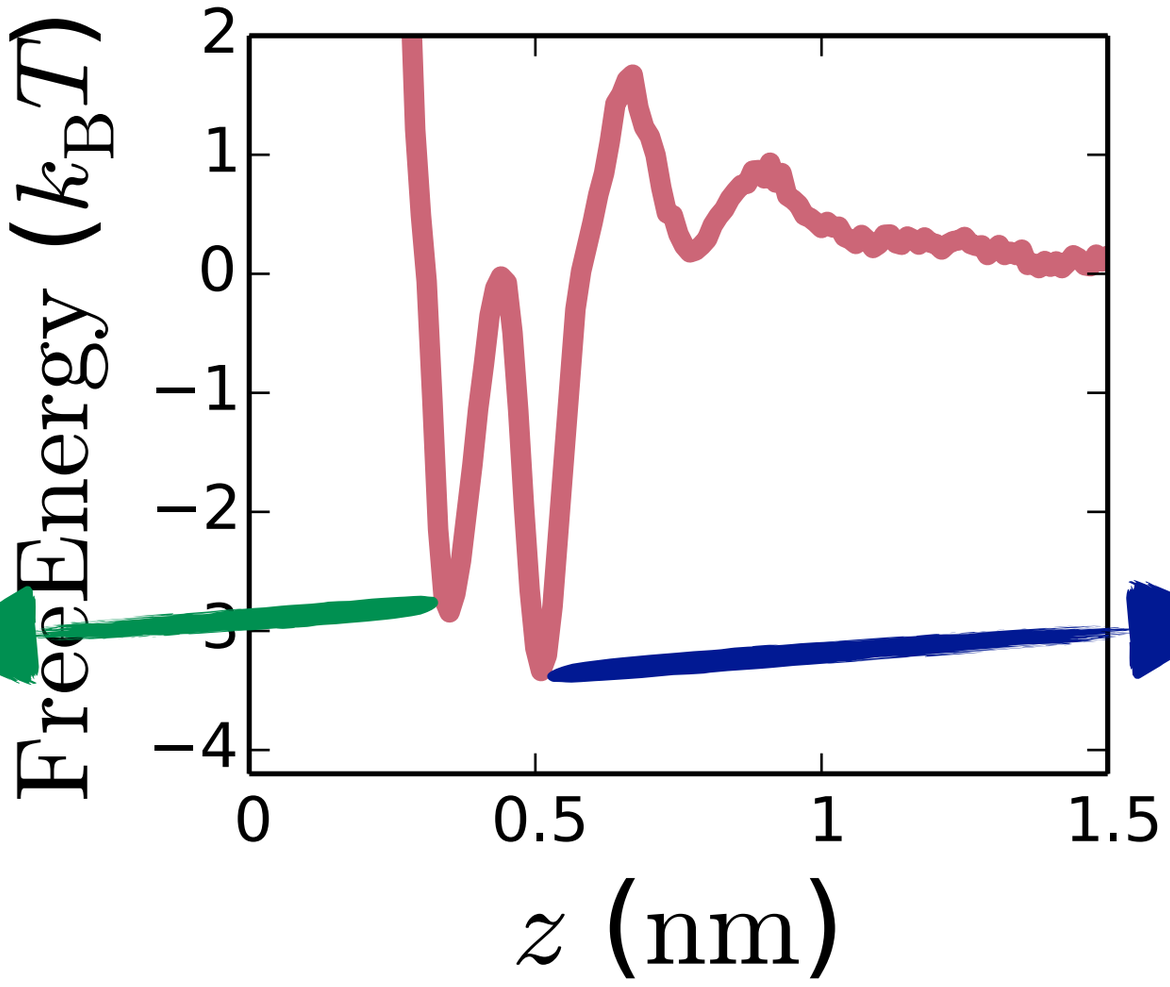
- Water oxidation correlation with ion hydration energies
- Does this also correlate with adsorption?

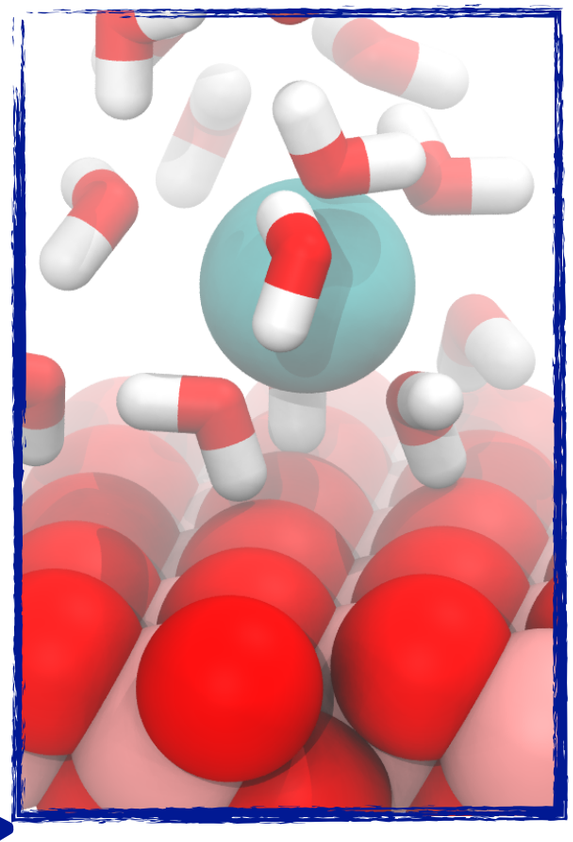


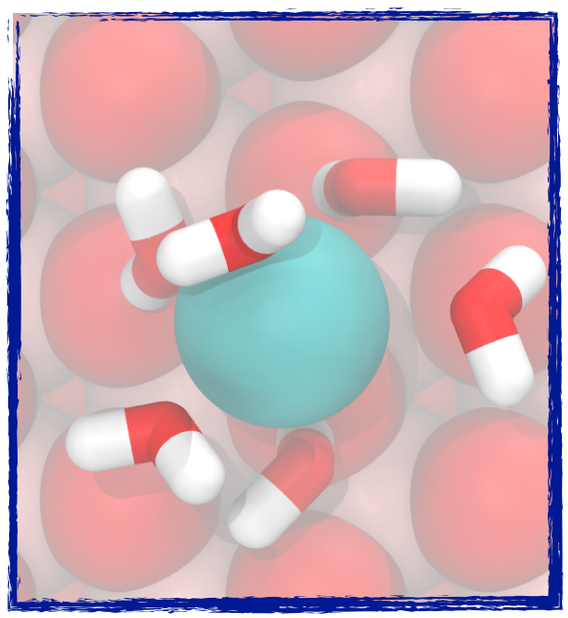
- Single and Double H-bonded (absent in birnessite)
- Quantified by detailed analysis

Na^+ Adsorption to Nanosheets



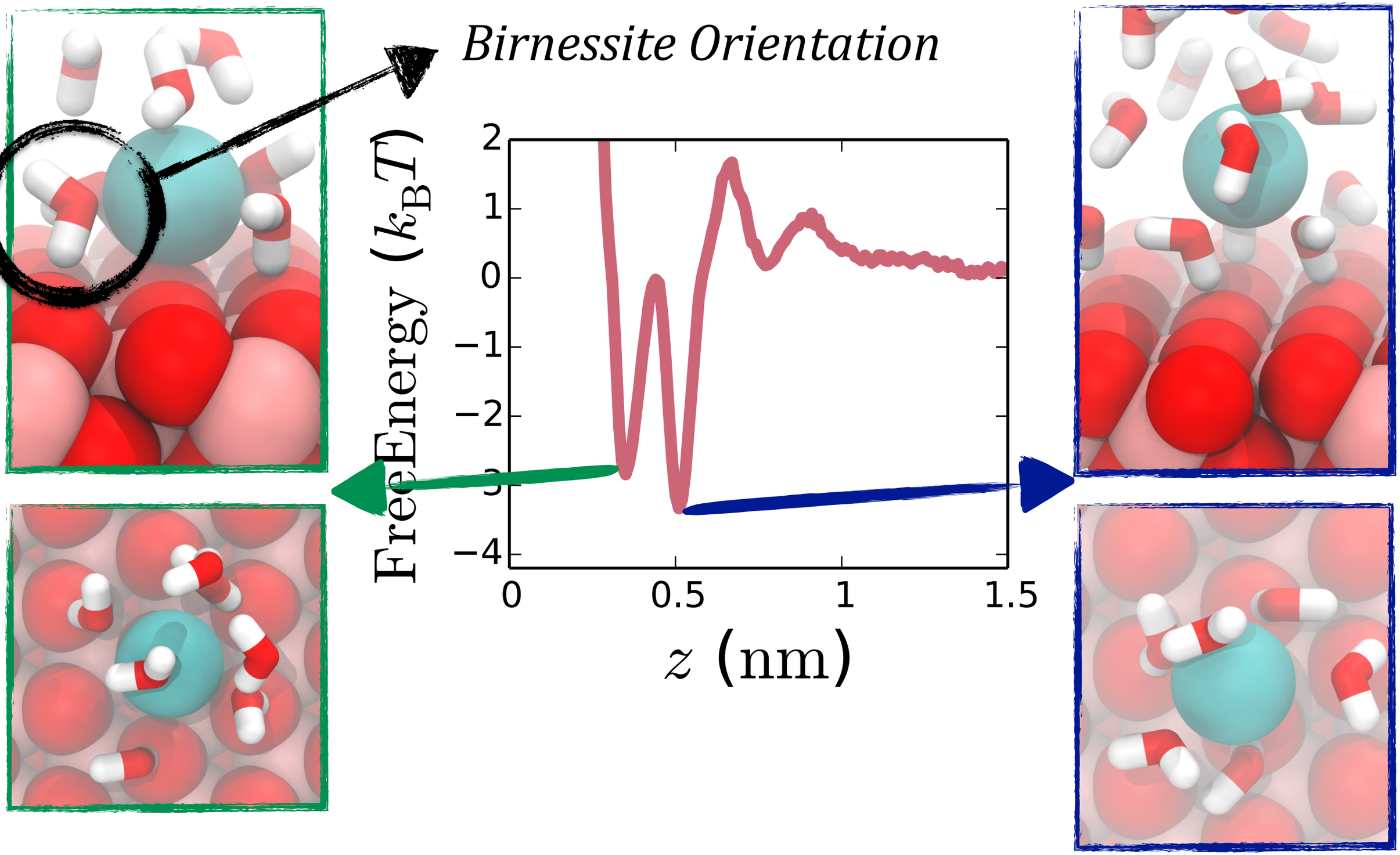






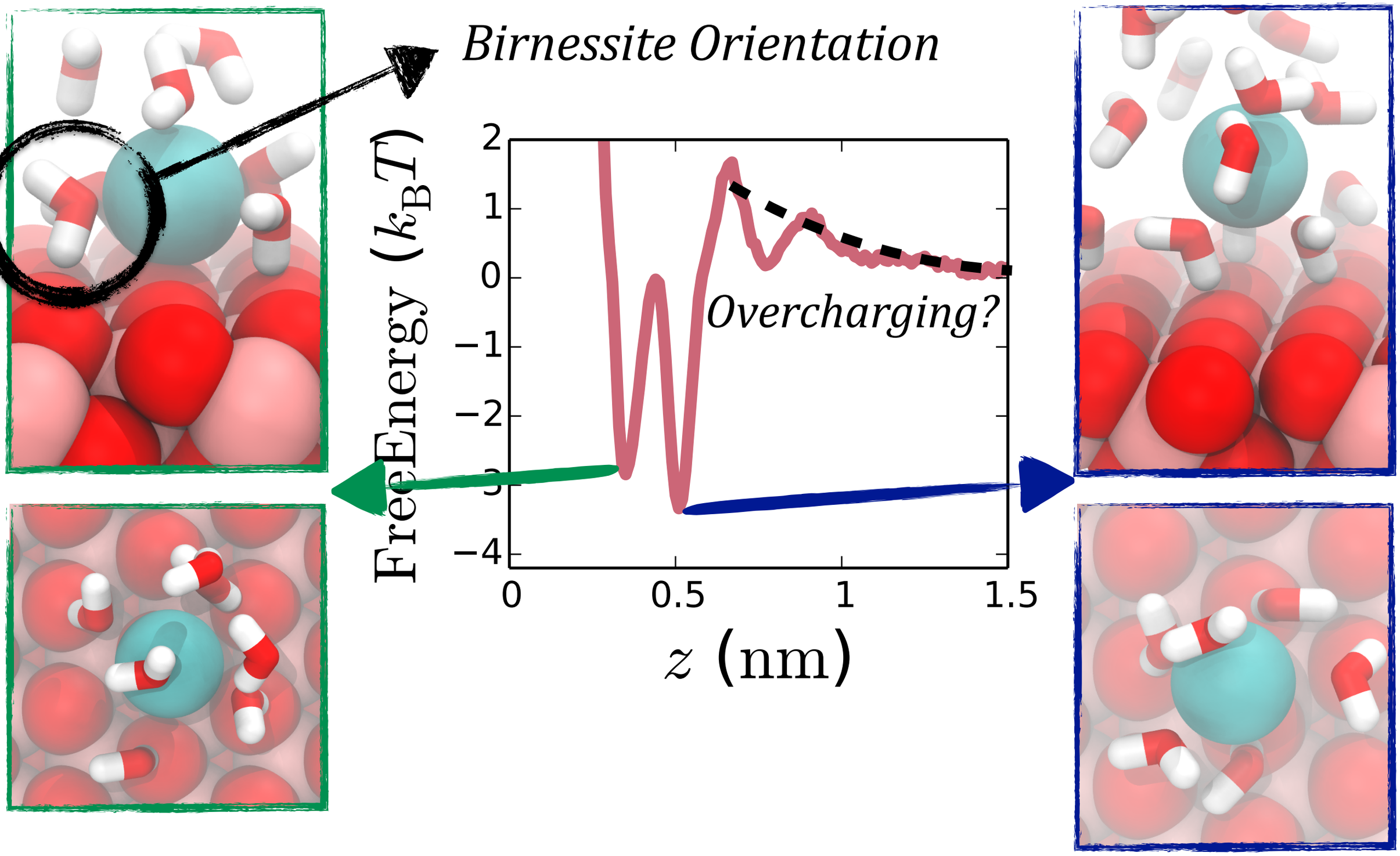
- Adsorbed ions interact directly or as entire hydration shell

Na^+ Adsorption to Nanosheets



- Adsorbed ions interact directly or as entire hydration shell

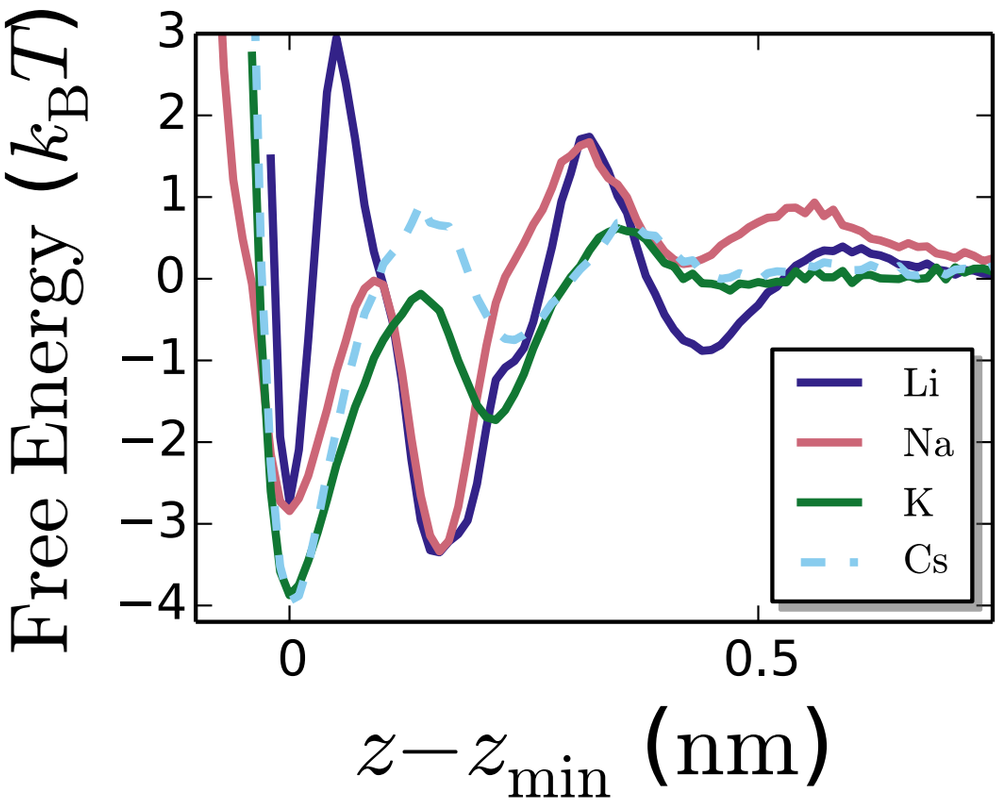
Na^+ Adsorption to Nanosheets

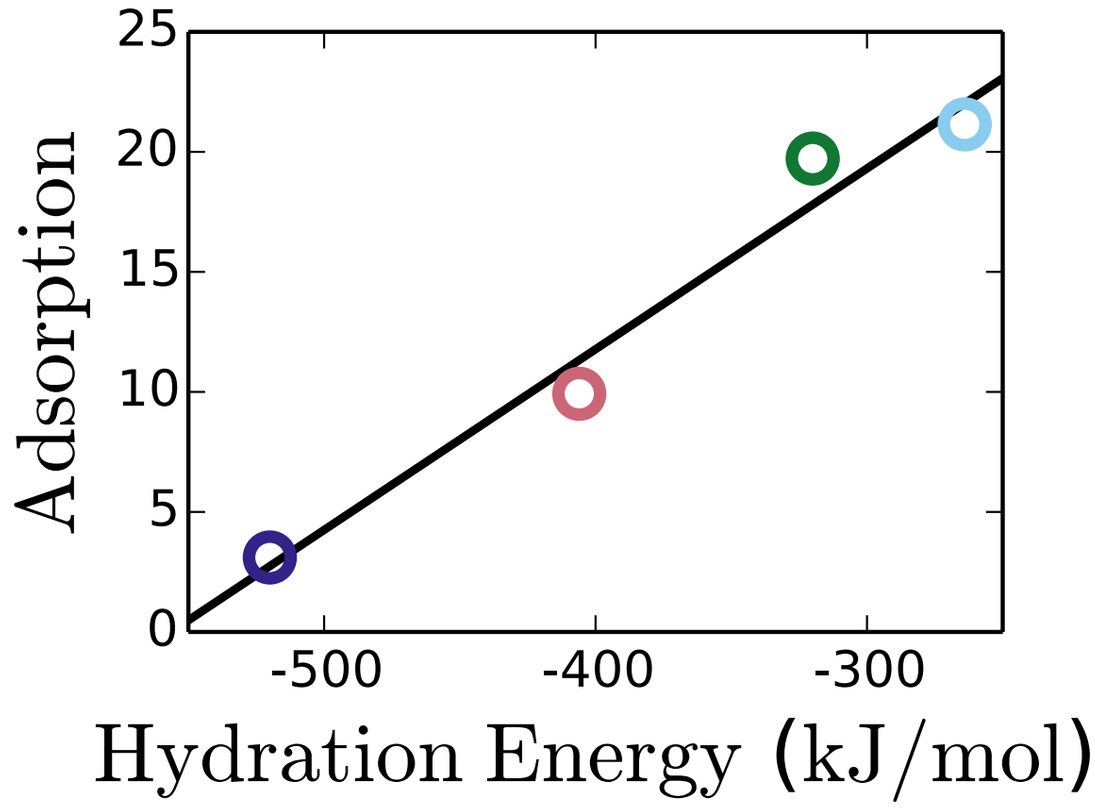


- Adsorbed ions interact directly or as entire hydration shell

Ion Adsorption to Nanosheets

- Water oxidation correlates with ion hydration energies
- Balance of interactions (bulk/interface hydration, water-surface, ion-surface)



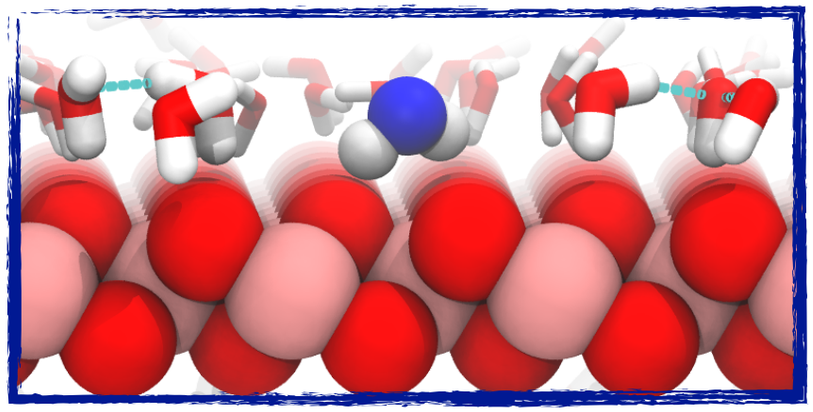


- $Li^+ < Na^+ < K^+ < Cs^+$
- $Ba^{2+} < Ca^{2+}$
- Adsorption correlates with reactivity
- Why? Water, Electronic structure, …?

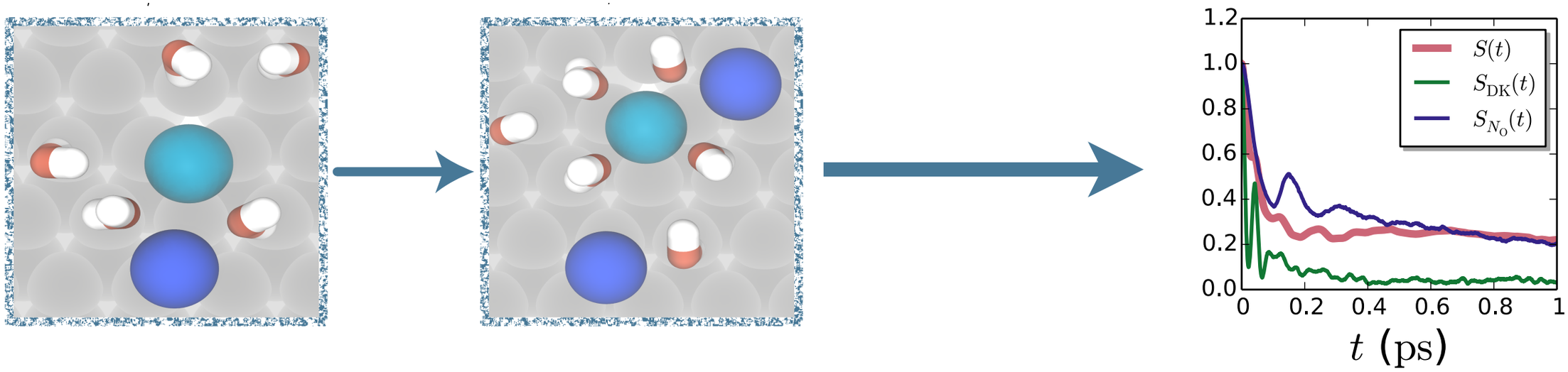
Future Work: Large Scale Structure and Dynamics

- Confinement effects: Birnessite vs. Buserite vs. Nanosheets

- Experimentally probe interfacial structure and dynamics (SFG, VER, Dielectric Spectroscopy)



- Understand dynamics in conjunction with experiments

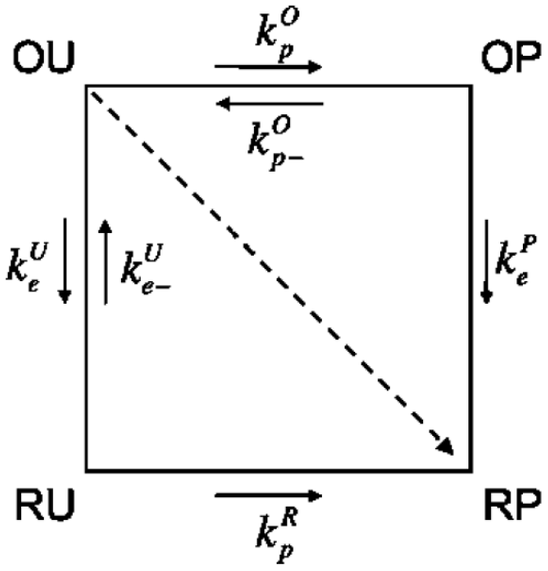


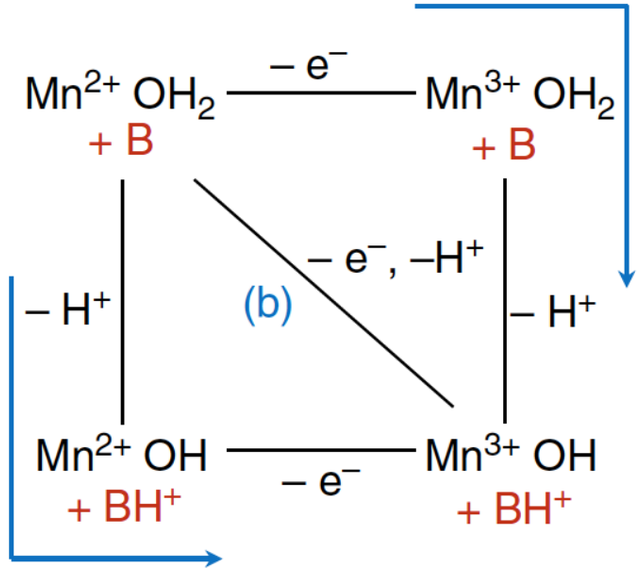
Future Work: Chemical Dynamics

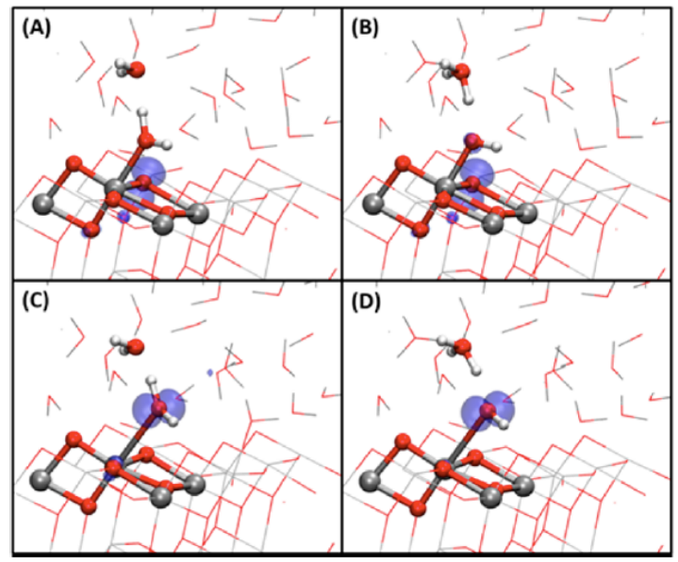
- Frustration is good for electron transfer, *but what about the rest of the water oxidation process*?

$$2\mathrm{H_2O} \rightarrow \mathrm{O_2} + 4\mathrm{H^+} + 4e^-$$

- Proton-coupled electron transfer?



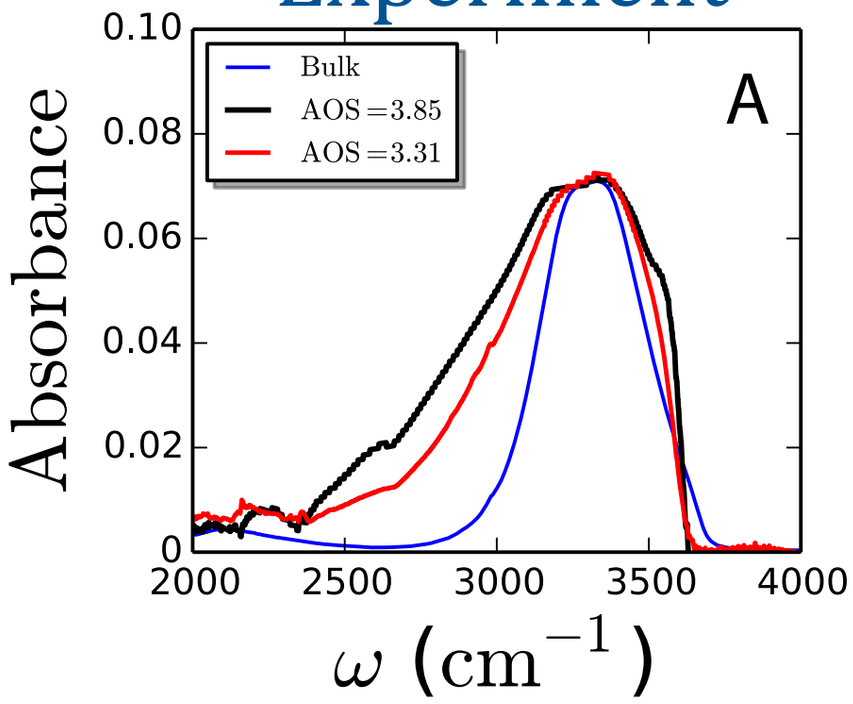




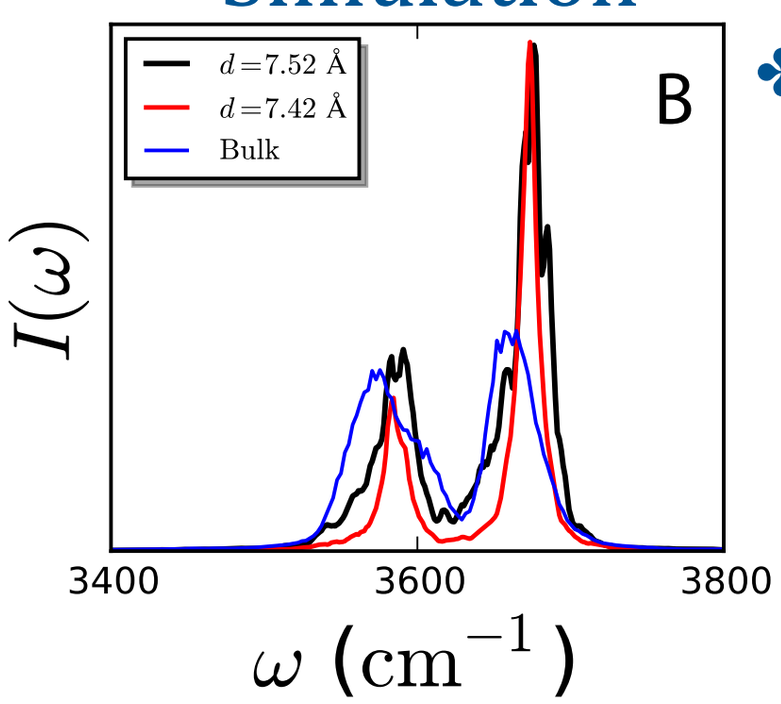
- Quantum dynamics and thermodynamics of ET (tunneling)
- Model water oxidation:
  - What structures are best for oxidation?
  - Collective/confinement effects?
  - Mechanism?

Evidence of Ordered Waters in IR Spectra

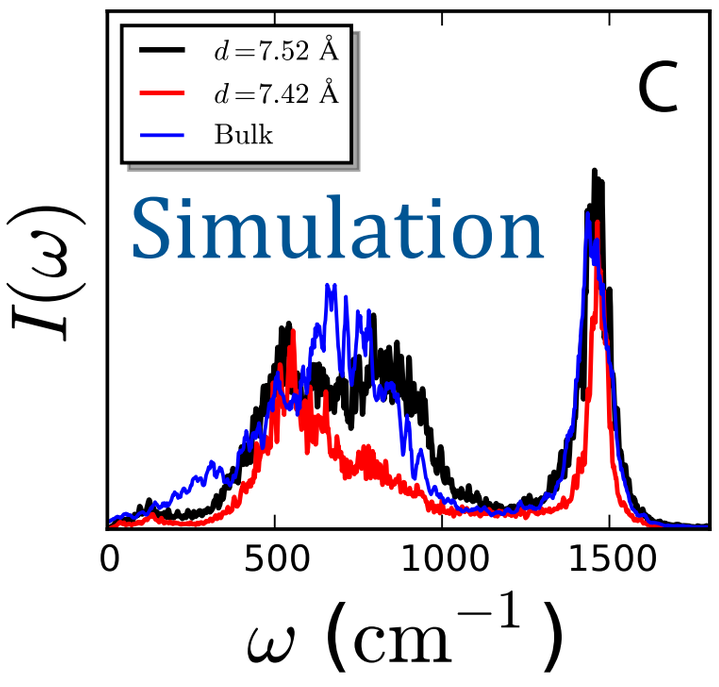
Experiment

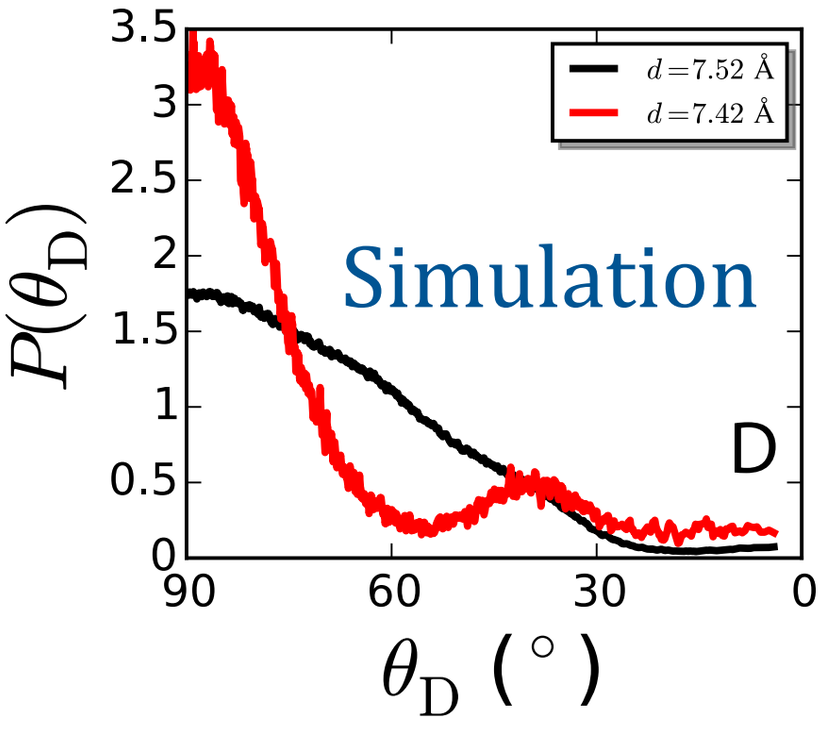


Simulation



- Shoulder at high frequency disappears when water structure is increased





- Low frequency librational modes shift to lower frequencies: slow dynamics

Let's get to the Chemistry…

…well half of it

- Impact of hydration structure on electron transfer?

$$\underline{\lambda = 0} \qquad\qquad \underline{\lambda = 1}$$

$$\mathrm{M}^{q-1} \xrightarrow{\mathrm{MnO_2}} \mathrm{M}^{q} + e^{-}$$

- Free energy landscape with energy gap as order parameter:

$$\Delta E(\mathbf{R}) \equiv \mathcal{H}_1(\mathbf{R}) - \mathcal{H}_0(\mathbf{R})$$

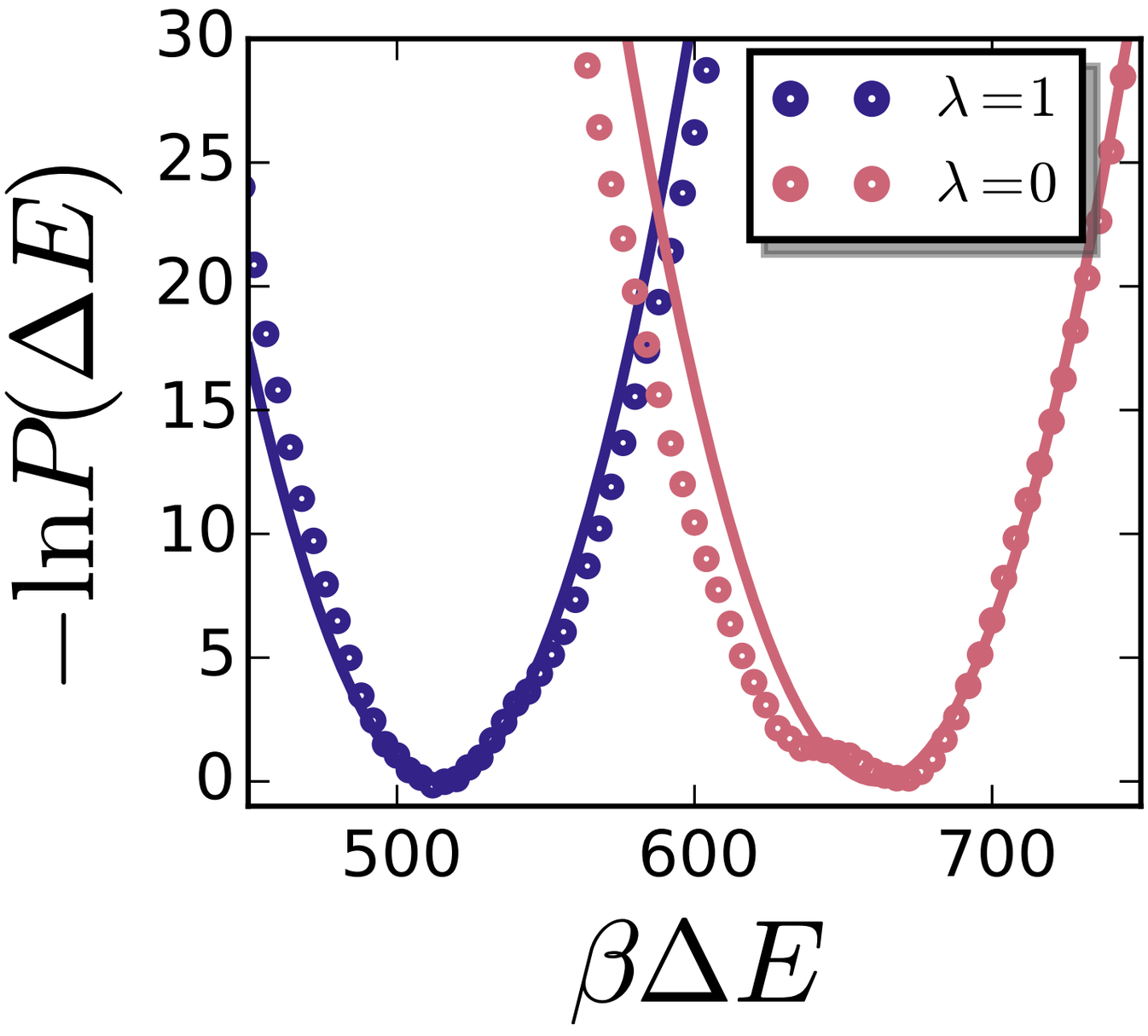
- Compare with highly successful Marcus theory
  (linear response, Gaussian fluctuations, parabolic free energies…)

R. A. Marcus, *Ann. Rev. Phys. Chem.*, **1964**

D. Chandler, *Classical and Quantum Dynamics in Condensed Phase Simulations.*, **1998**

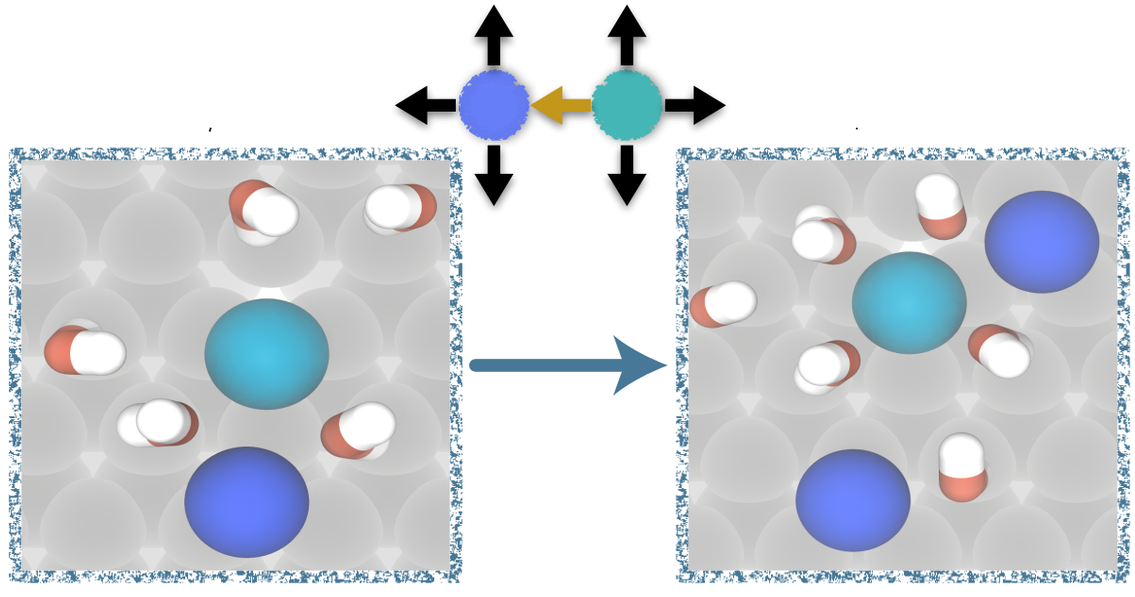
Frustration Leads to Deviations From Marcus Theory

- Impact of hydration structure on electron transfer?



$$\underset{\lambda = 0}{\mathrm{M}^{q-1}} \xrightarrow{\mathrm{MnO_2}} \underset{\lambda = 1}{\mathrm{M}^{q}} + e^-$$

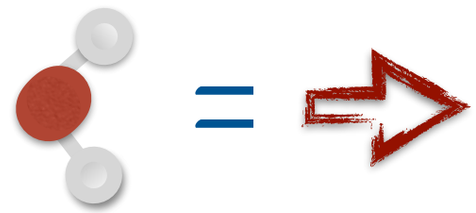
- Non-Gaussian energy gap fluctuations



- What about kinetics?

The Charge Frustrated XY Model

$$\mathcal{H} = \mathcal{H}_{\mathrm{XY}} + \mathcal{H}_q + \mathcal{H}_{\mathrm{I}}$$



The Charge Frustrated XY Model

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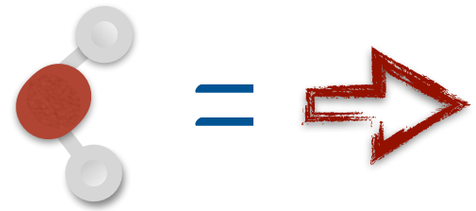
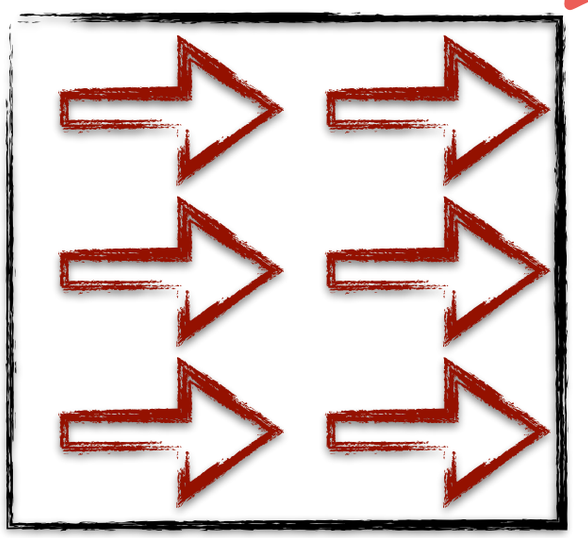
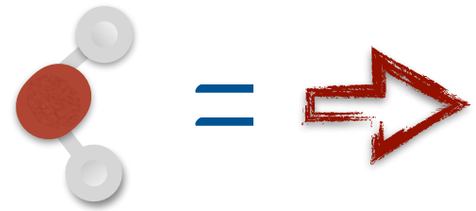


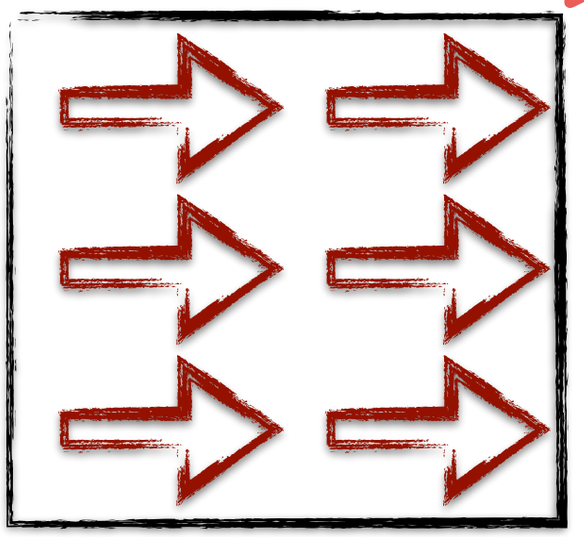


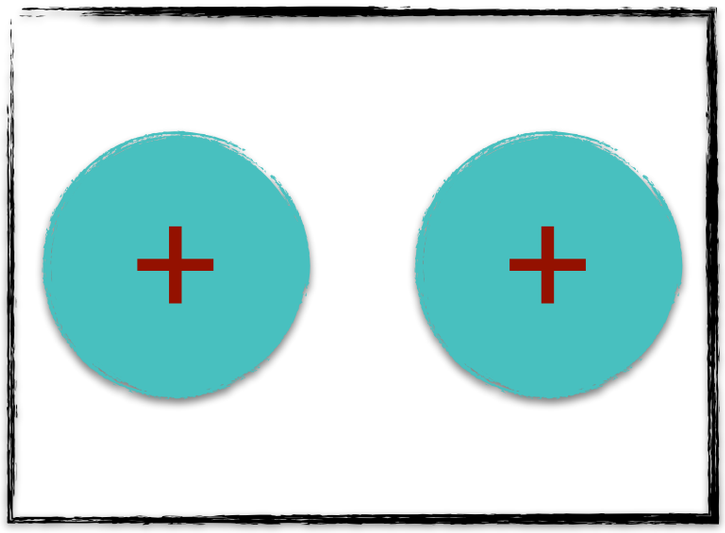
- Dipole (spin) alignment

The Charge Frustrated XY Model

$$\mathcal{H} = \mathcal{H}_{\mathrm{XY}} + \mathcal{H}_q + \mathcal{H}_{\mathrm{I}}$$



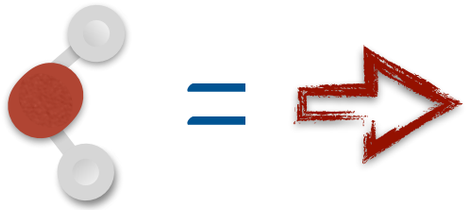


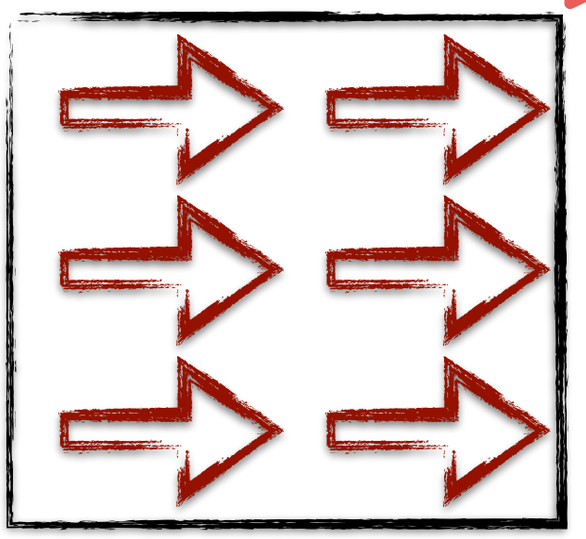


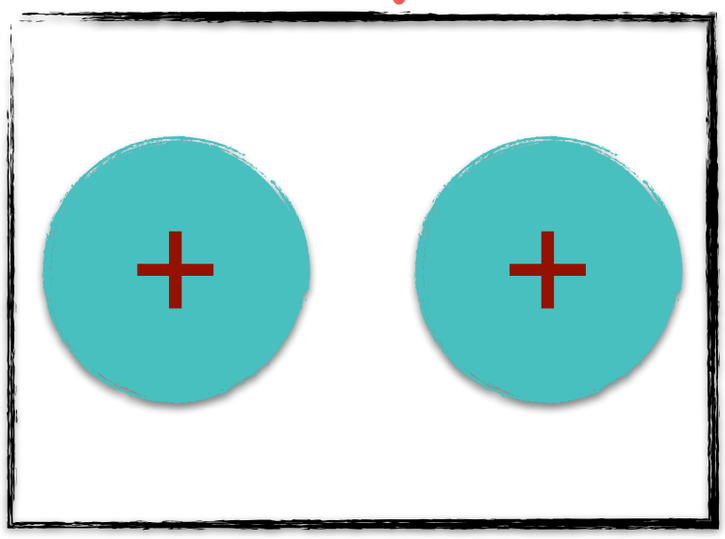
- Dipole (spin) alignment
- Coulomb like-charge repulsion

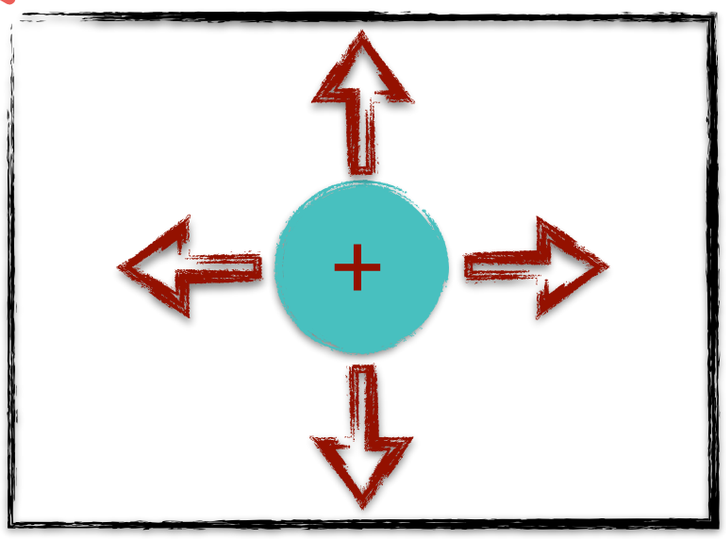
The Charge Frustrated XY Model

$$\mathcal{H} = \mathcal{H}_{\mathrm{XY}} + \mathcal{H}_q + \mathcal{H}_{\mathrm{I}}$$









- Dipole (spin) alignment
- Coulomb like-charge repulsion
- Ion hydration (defect formation)

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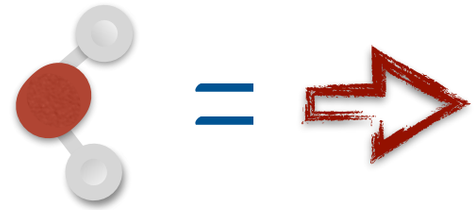

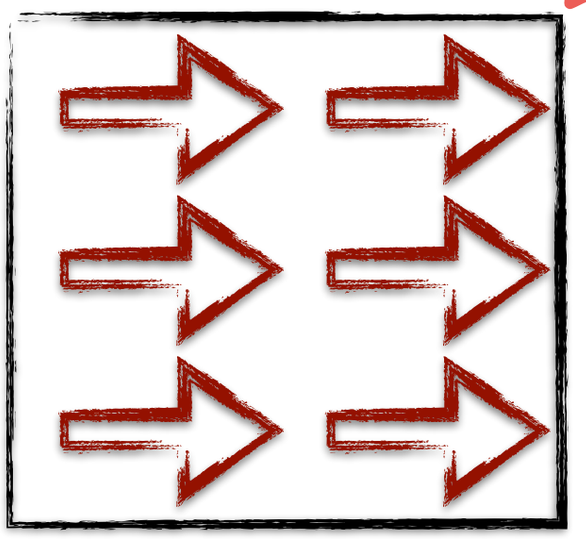

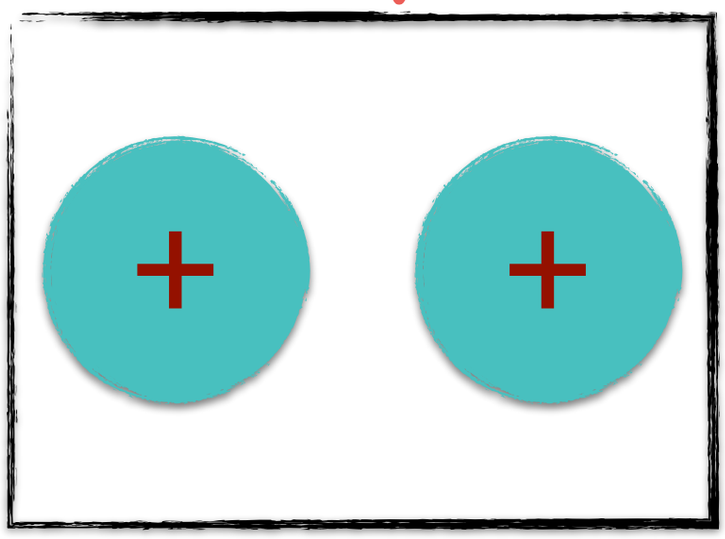

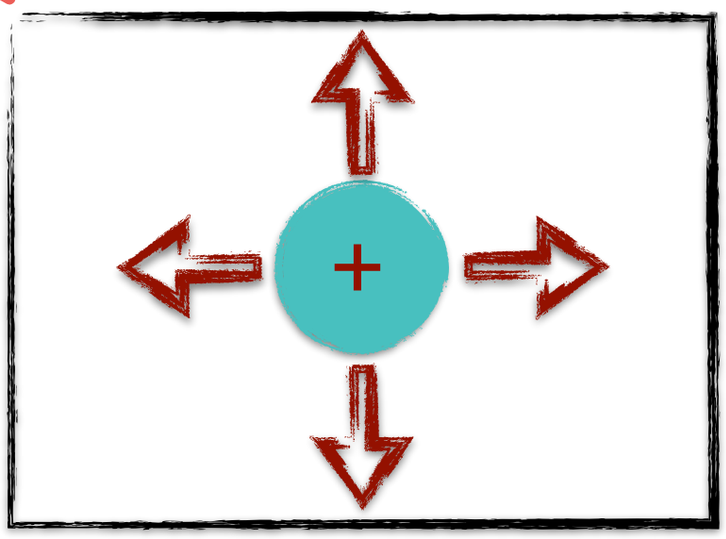

- Dipole (spin) alignment
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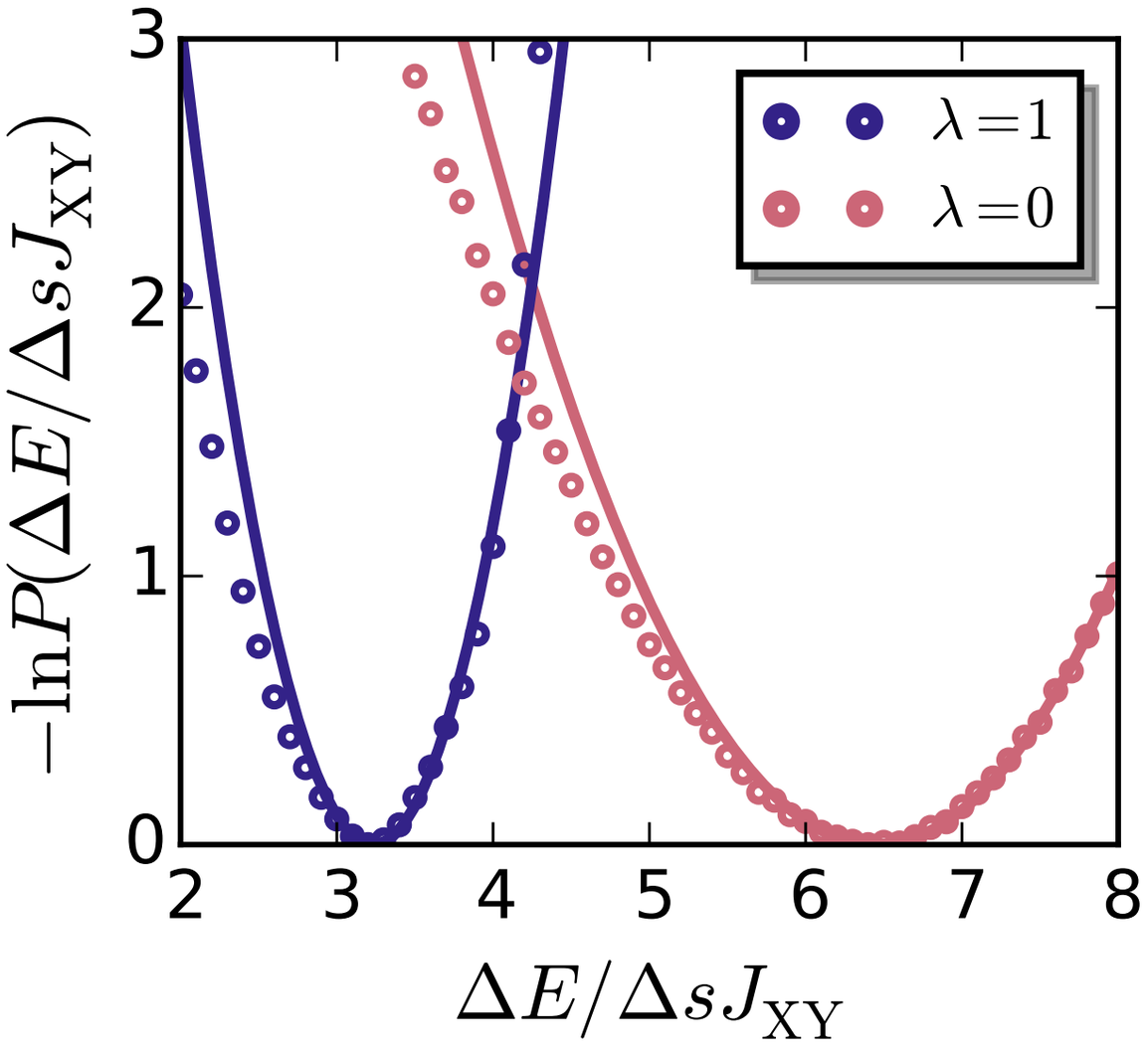
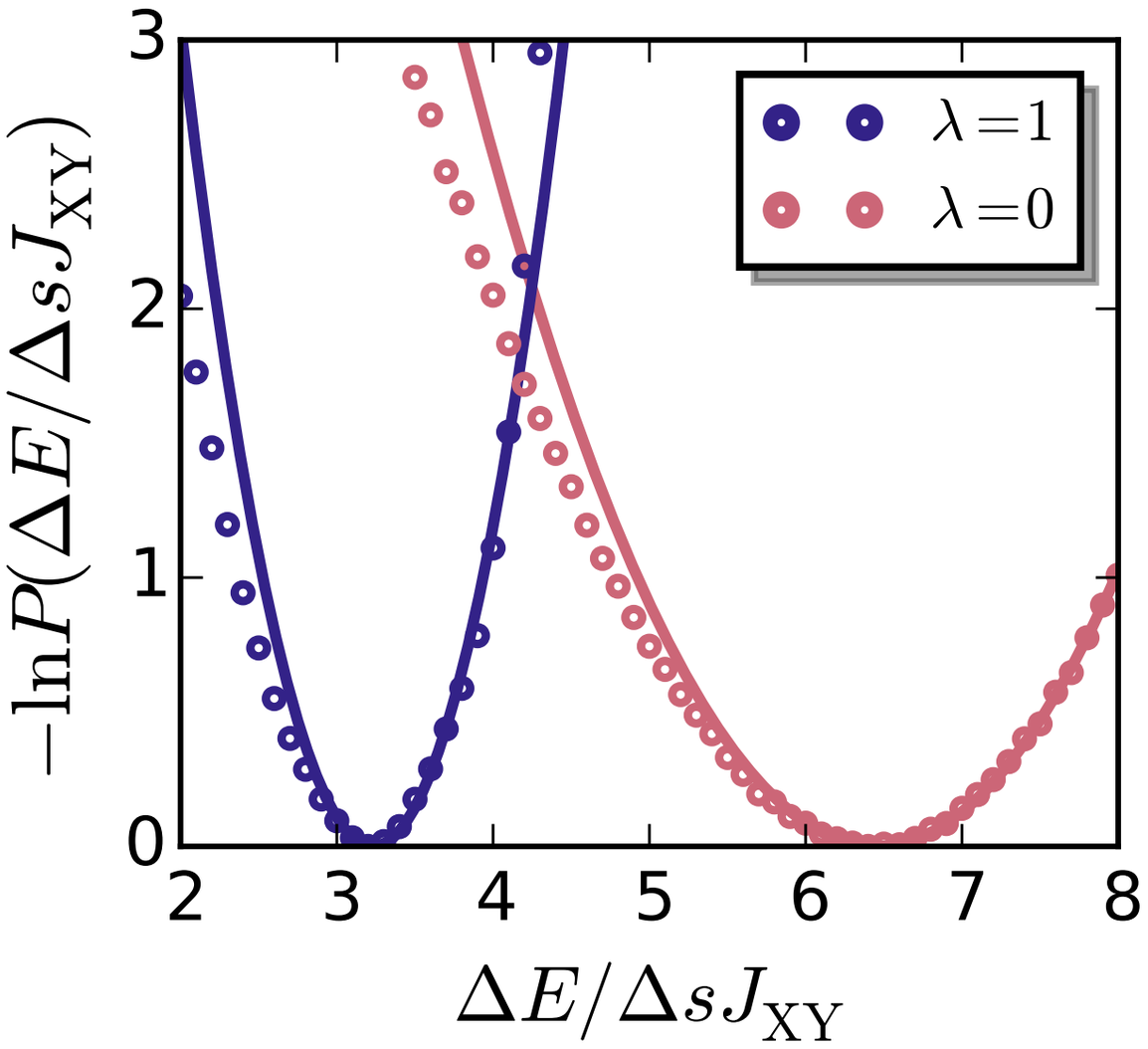
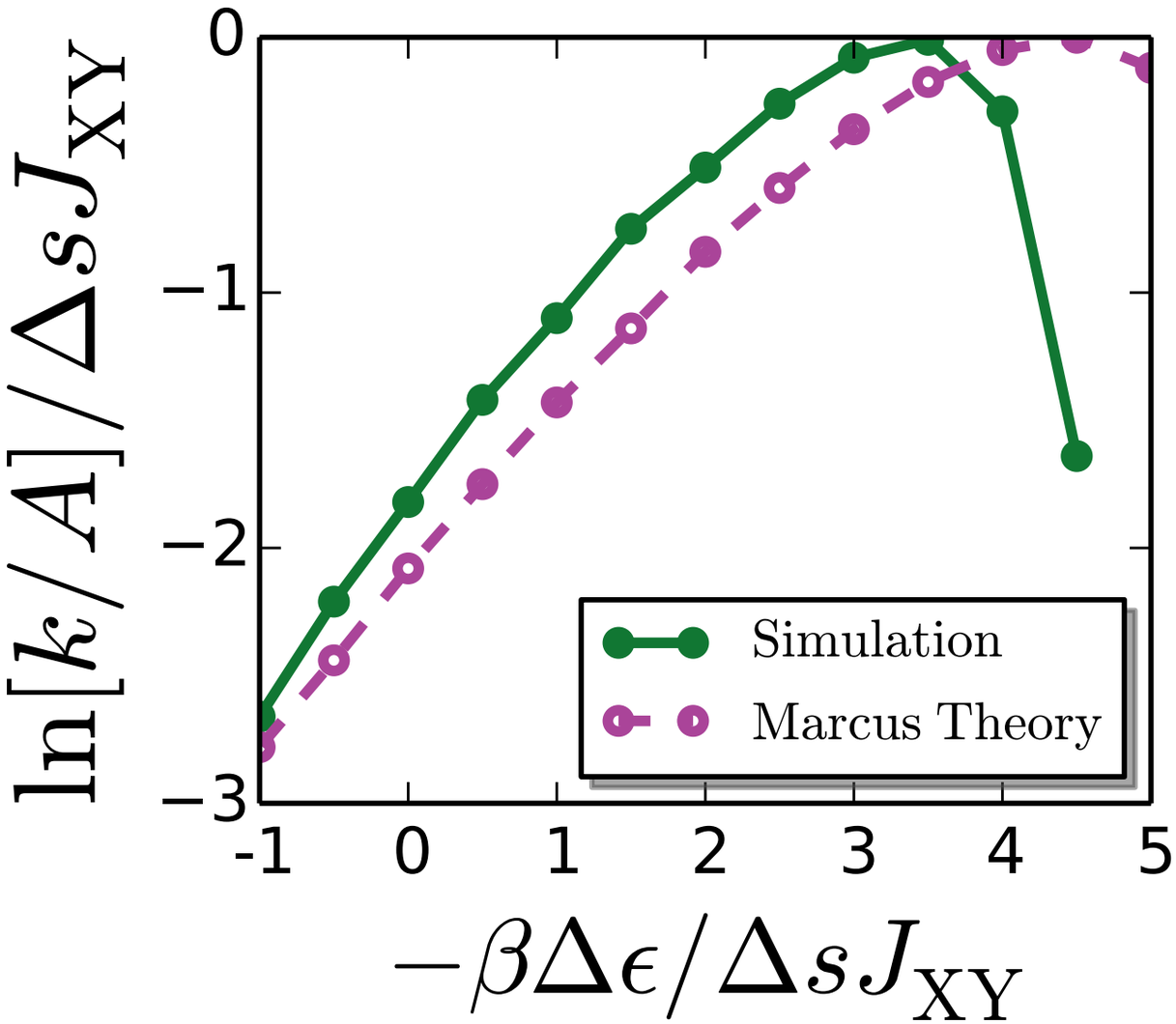
- Does this minimal model capture the relevant physics?
- What does it predict for electron transfer?

Frustrated Solvation can Enhance Electron Transfer Rates



Frustrated Solvation can Enhance Electron Transfer Rates





- Enhanced electron transfer rates are due to frustration!
- Can we use this for anything else?

Cation Charge and Electron Transfer

- Experiments: increasing charge increases oxidation rates.
- Let's do this in our simple model…

Cation Charge and Electron Transfer

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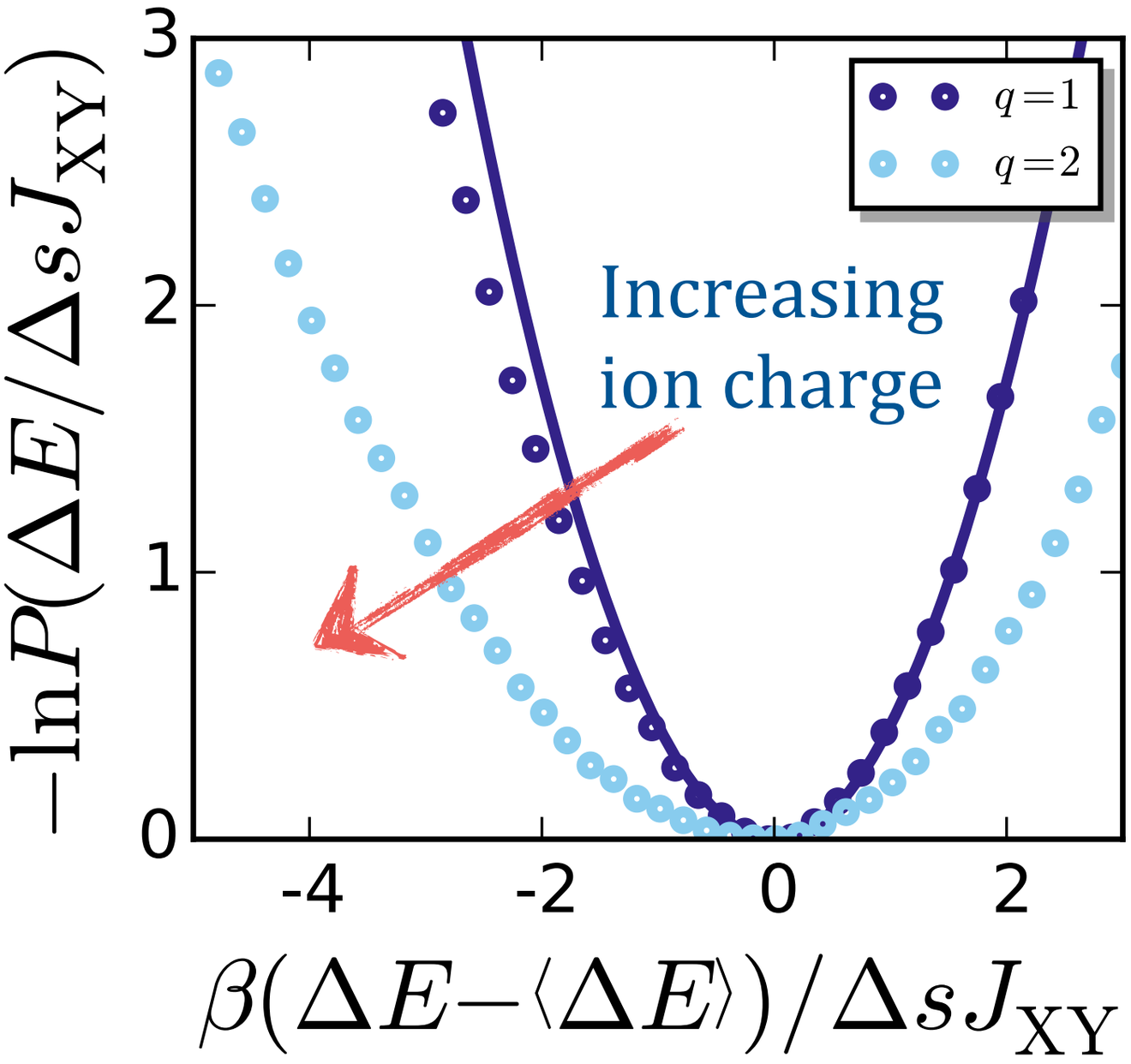
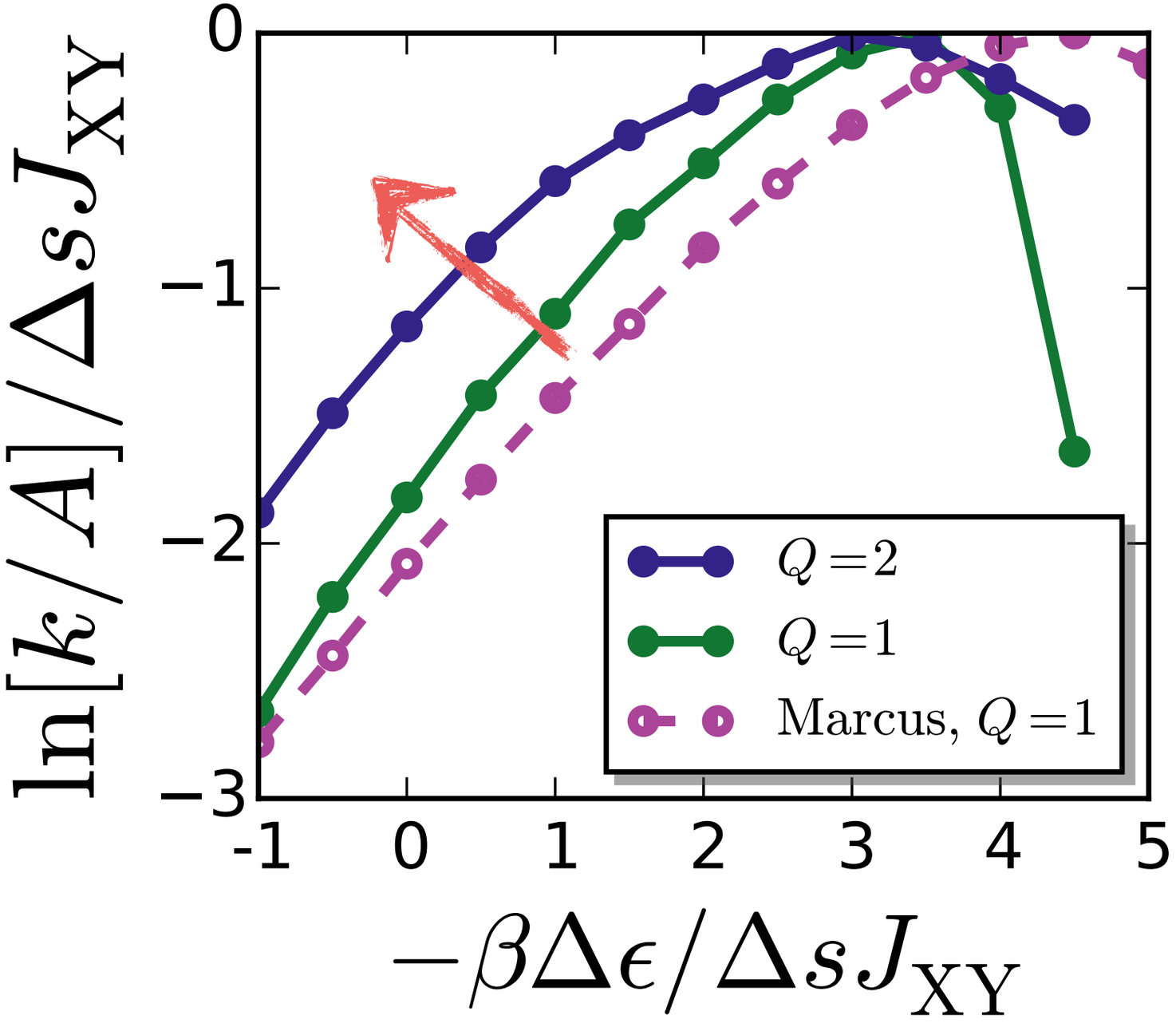


- Fluctuations are enhanced with increasing charge
- Result of increasing frustration

- *What about rates?*

Cation Charge and Electron Transfer

- Experiments: increasing charge increases oxidation rates.
- Let's do this in our simple model…



- Rates increased further by increasing charge on ion
- Agrees with experimental results

- *Can use these ideas to design better catalysts?*