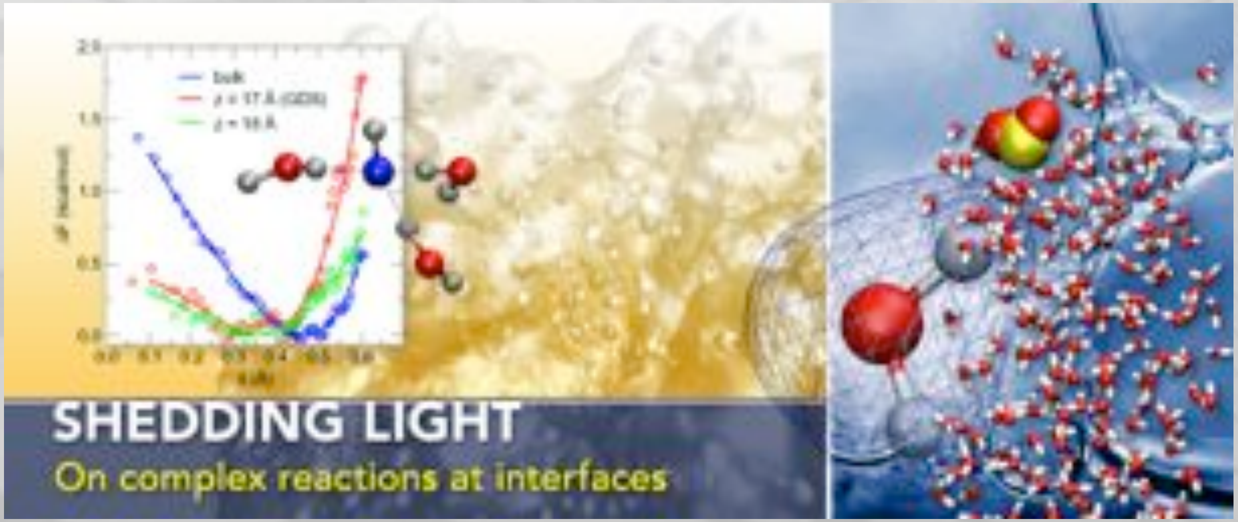
High Performance Computing in the Chemical Sciences



Christopher J. Mundy
Accelerated Computational Science

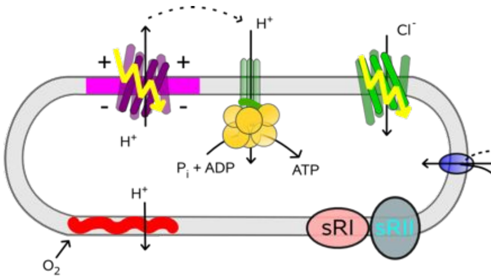
March 28-30, 2012

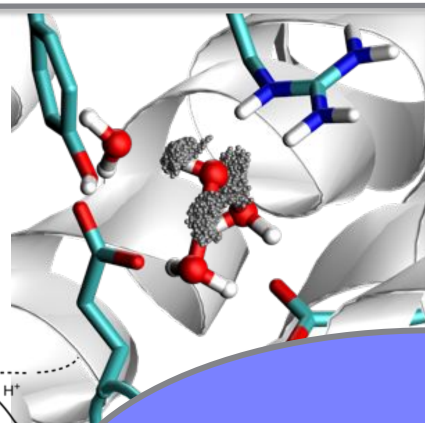
Pacific Northwest NATIONAL LABORATORY

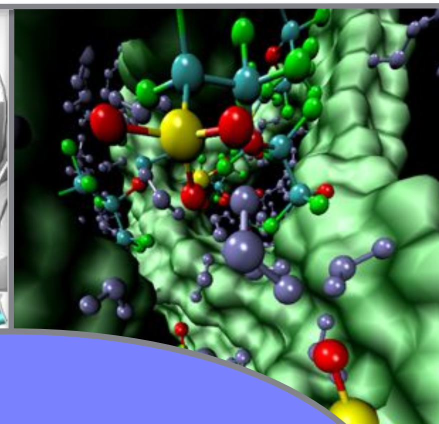
Proudly Operated by Battelle *Since 1965*

Frontiers in Chemistry: “Pimentel-Report”

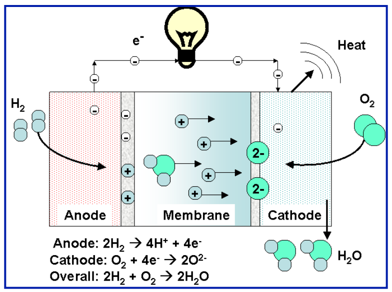
Biology





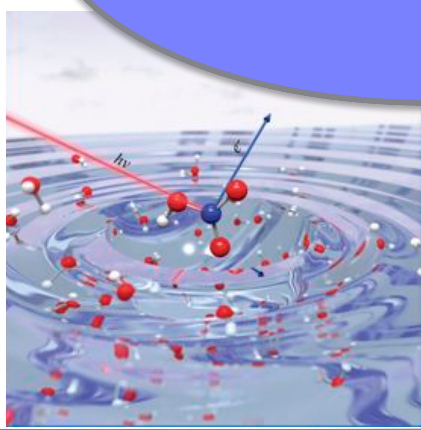


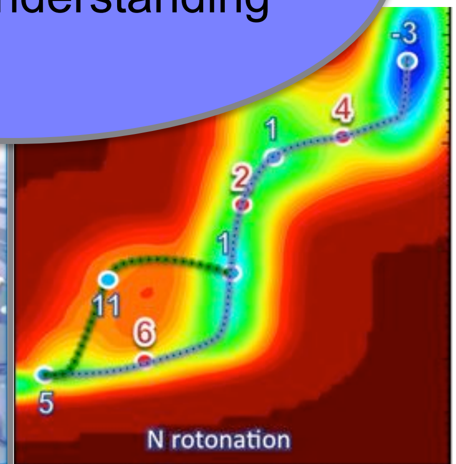
Energy

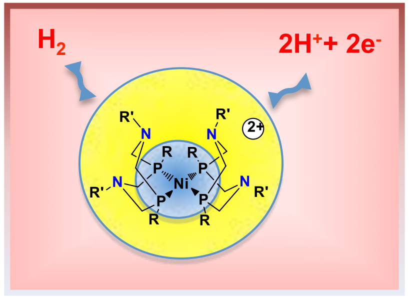


Chemistry at interfaces
needs a
molecular understanding

Atmospheric







Catalysis

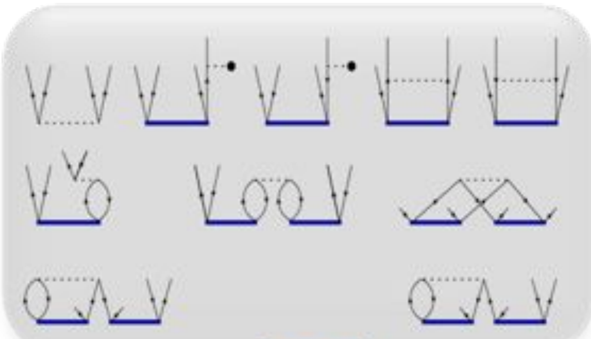
PNNL uses High Performance Computing (HPC) in Conjunction with two established DOE programs

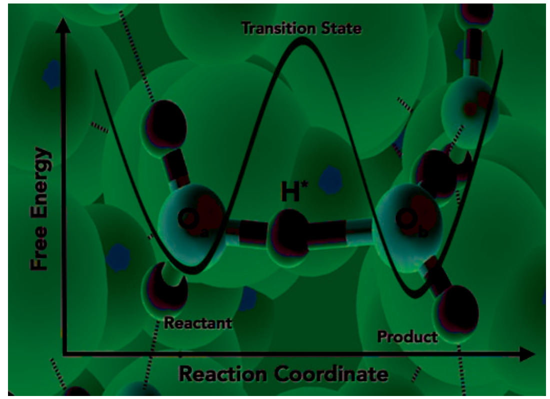
- **BES Condensed Phase and Interfacial Science (CPIMS)**
  - Mission: Provide a molecular understanding of interfacial processes
  - Legacy of Thom Dunning

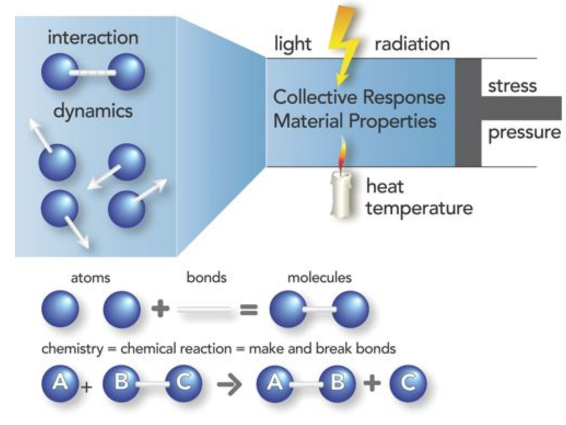
- **Energy Frontiers Research Center (EFRC) on Molecular Electrocatalysis**
  - Mission: Convert electrical energy into chemical bonds and vice-versa

- **Both programs elucidate chemical phenomena in heterogeneous environments**

HPC is Essential to PNNL Molecular Science







Simulation of Molecular Interaction **+** **Simulation of Collective Motion** **=** **Simulation of Material Properties**

What do electrons do? | What do molecules do? | What do materials do?

Validate with measurement

Computer Code: **CP2K**

Our quantum mechanical interaction = Density Functional Theory (DFT)

CP2K with our 2008-2012 INCITE award affords DFT calculations at an unprecedented scope

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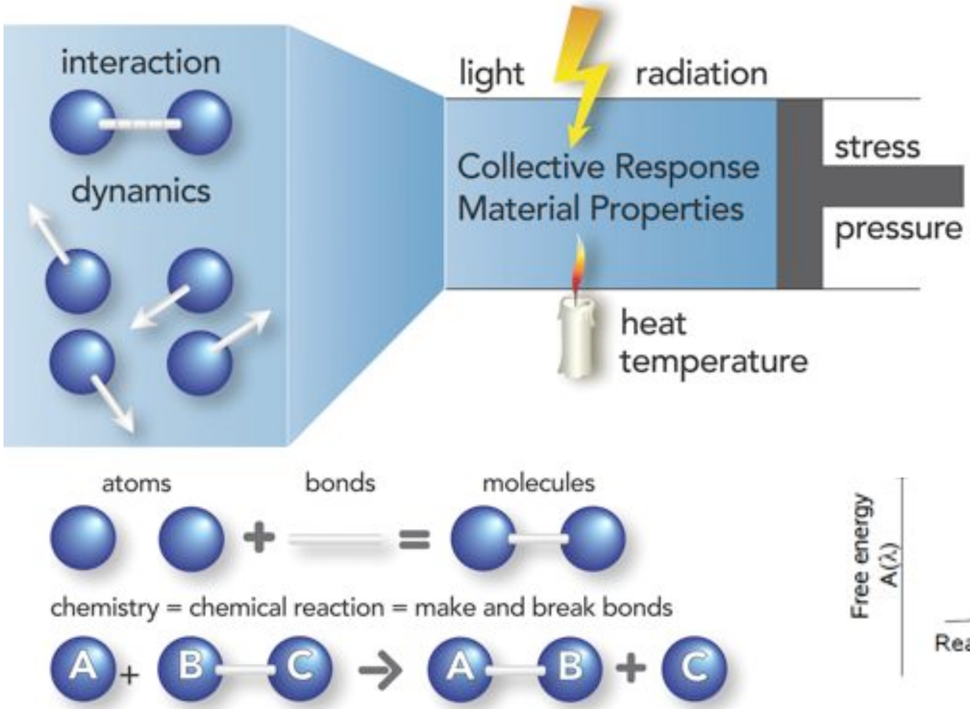
- **A wide variety of model Hamiltonians**
  - Classical
  - Semi-empirical
  - Local and non-local DFT
  - Combinations (e.g. QM/MM)
- **Various algorithms**
  - MD/MC [NVE, NVT, NpT]
  - Free energy and PES tools
  - Ehrenfest MD
- **Properties**
  - Vibrational
  - NMR, EPR, XAS, TDDFT

Statistical Mechanics is the connection between Molecular Detail and Observation

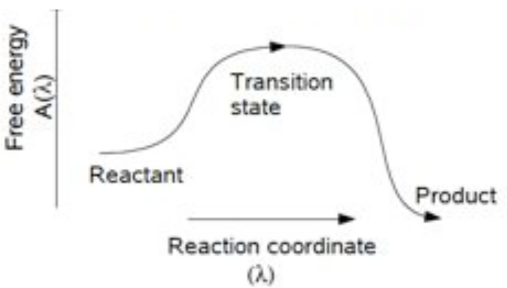
Intrinsically Parallel Methods in Molecular Simulation



❖ Sometimes good science requires embarrassingly parallel methods

- Free energy profiles
- Good statistics from independent simulation

❖ <u>Free energy</u> replaces <u>total energy</u> in complex systems at finite temperature yielding rates and affinities. Essential quantitative information for chemistry, biology, material science

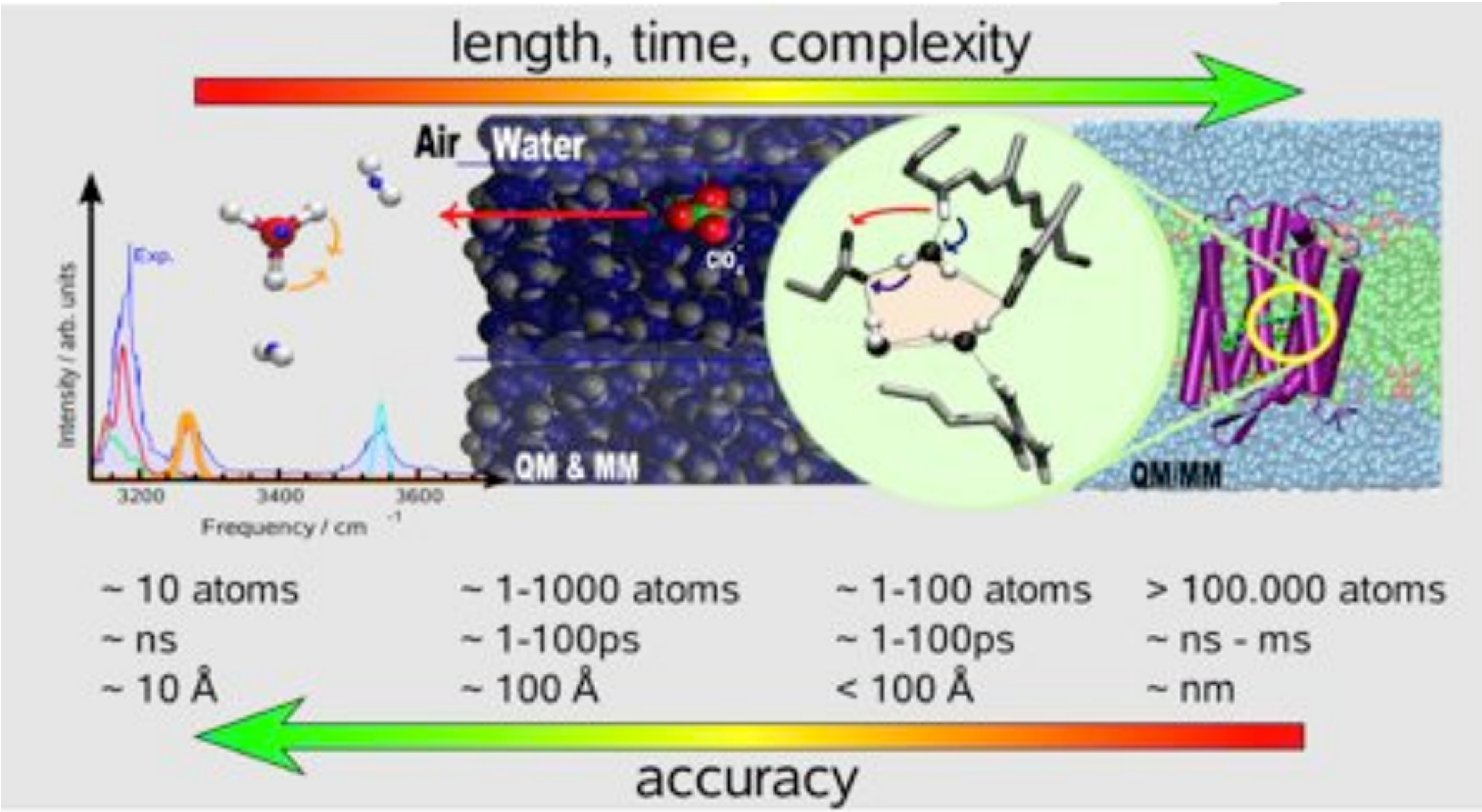


$$A_{a\to b} = \int_{\lambda_a}^{\lambda_b} \left\langle \frac{\partial H(x,p_x;\lambda)}{\partial \lambda} \right\rangle_{\lambda} d\lambda$$

❖ Parallelize over integrand and integration

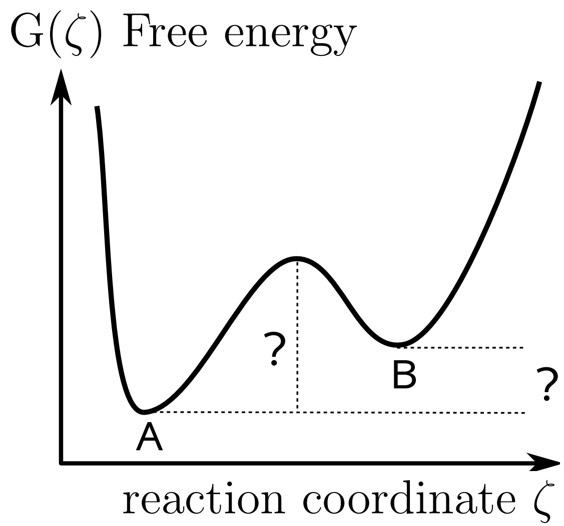
Statistical mechanics $\Rightarrow$ non-trivial results

In solving real problems no single approach will address all issues

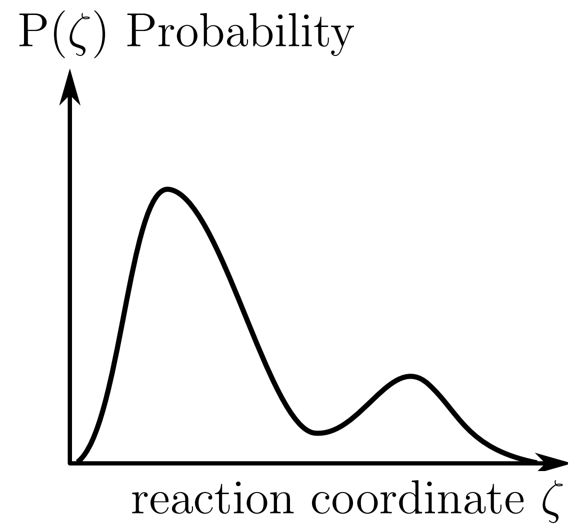


Chemistry is complex!

Reversible work theorem: We exploit one of the most important concepts in statistical mechanics

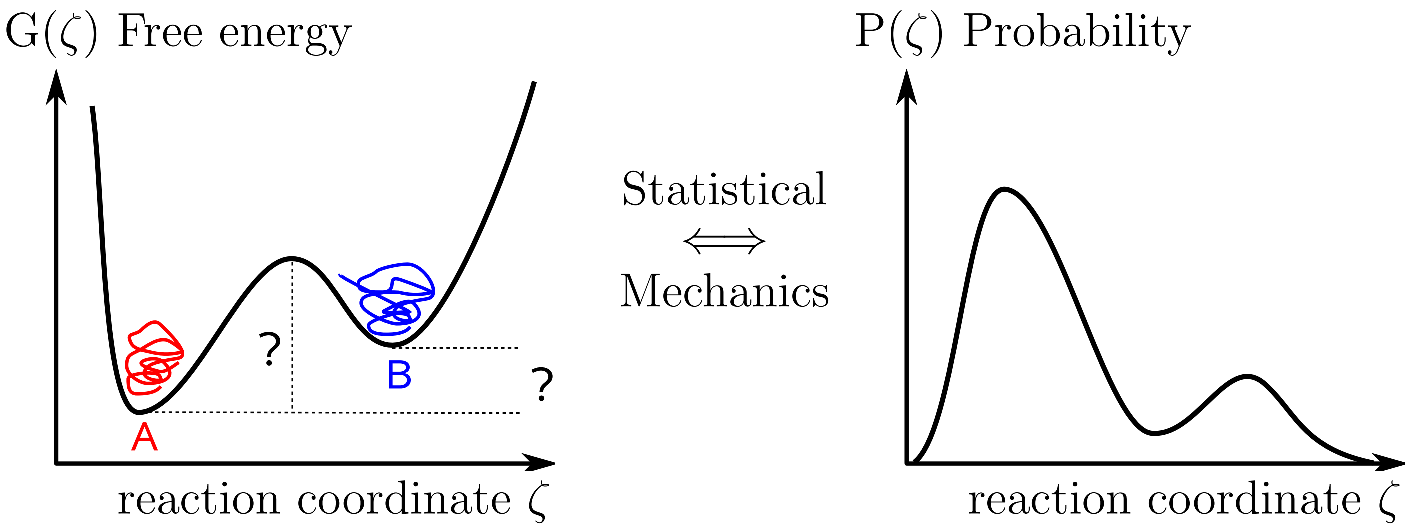


Statistical
$\Longleftrightarrow$
Mechanics



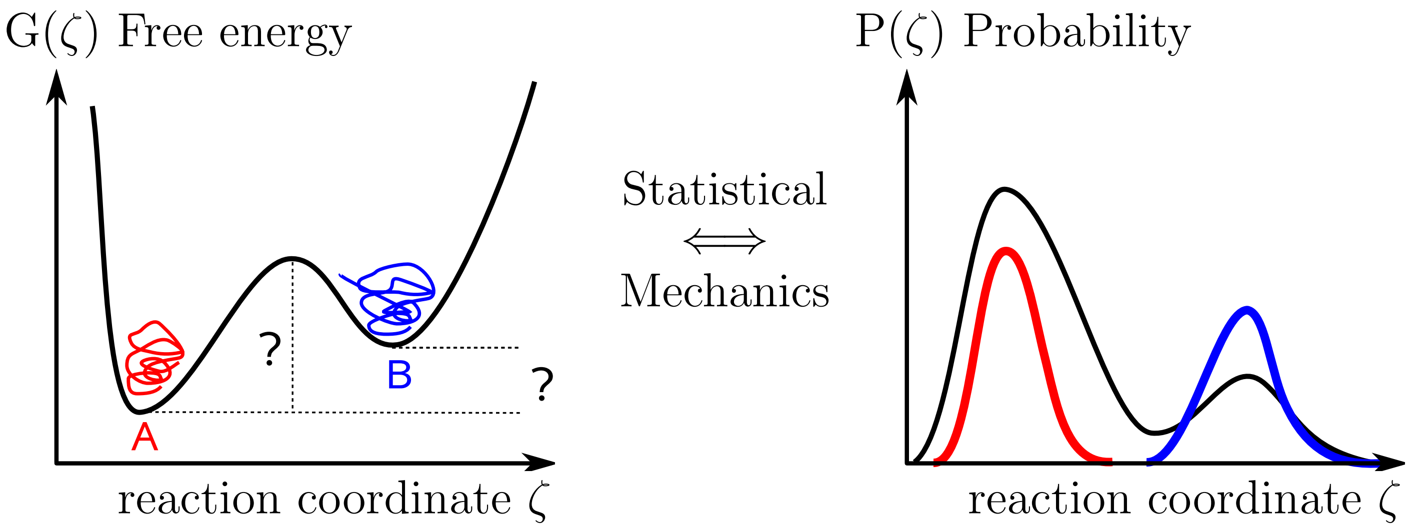
$$G(\zeta) = -k_B T \ln(P(\zeta)) + F$$

Sampling is limited in all molecular simulation techniques.



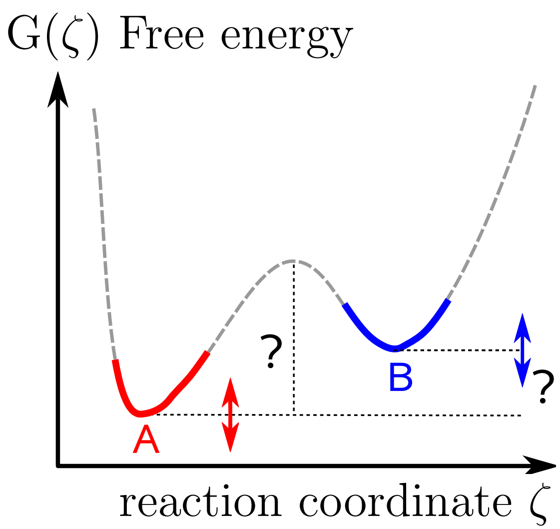
$$G(\zeta) = -k_B T \ln(P(\zeta)) + F$$

Even with powerful formula we can get the wrong answer



$$G(\zeta) = -k_B T \ln(P(\zeta)) + F$$

How do we attack the sampling problem? Umbrella-Sampling



Statistical
$\Longleftrightarrow$
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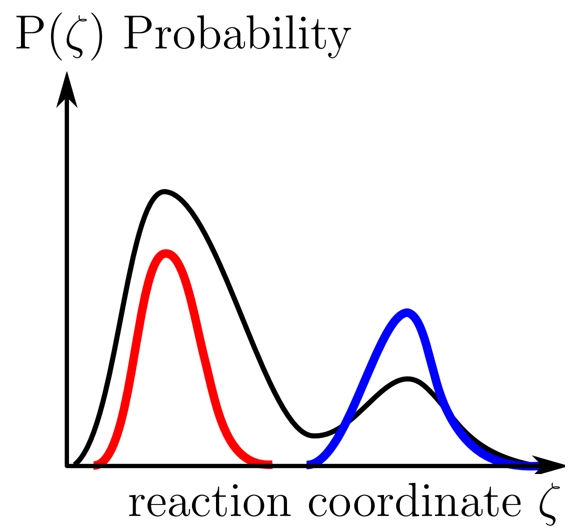
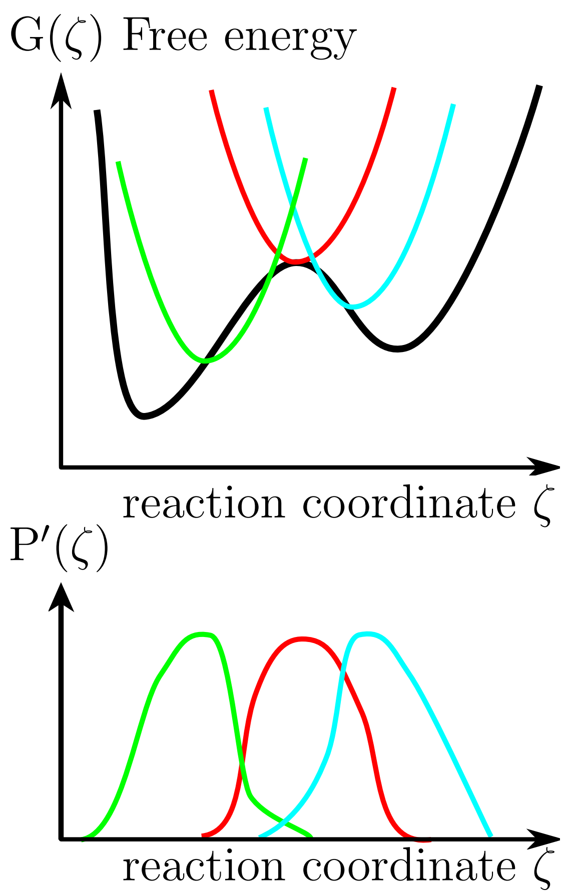


$$G(\zeta) = -k_B T \ln(P(\zeta)) + F$$

$\Rightarrow$ **Efficient sampling methods are needed!**

Umbrella-Sampling



- **idea:** add biasing potential V(ζ)

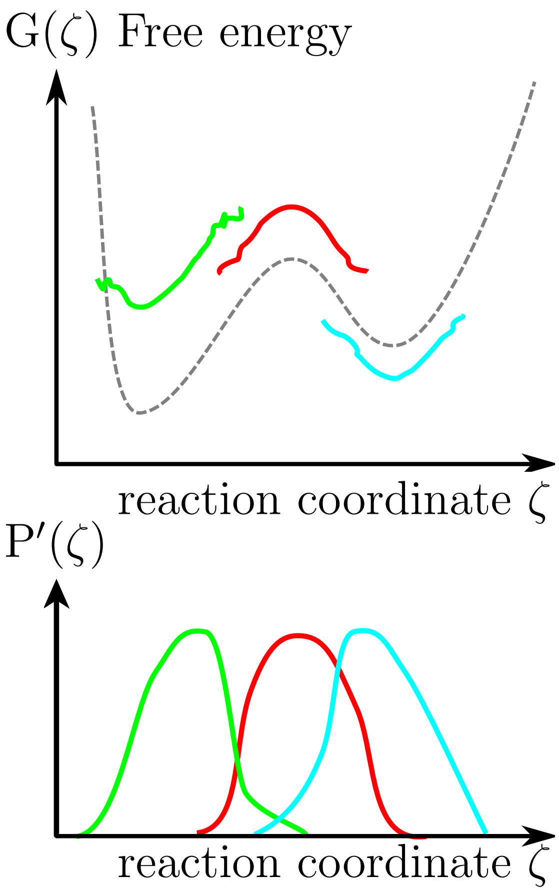
  $$V(\zeta) = \tfrac{1}{2}\,(\zeta - \zeta_0)^2$$

- compute biased probability $P'(\zeta)$
- estimate unbiased free energy G(ζ)

  $$G(\zeta) = -k_B T \ln(P'(\zeta)) + V(\zeta) + F$$

❖**We can parallelize over "umbrella" potentials**

Umbrella-Sampling



- **idea:** add biasing potential V(ζ)

  $$V(\zeta) = \frac{1}{2}(\zeta - \zeta_0)^2$$

- compute biased probability $P'(\zeta)$

- estimate unbiased free energy G(ζ)

  $$G(\zeta) = -k_B T \ln(P'(\zeta)) + V(\zeta) + F$$

$\Rightarrow$ Weighted Histogram Analysis Method for determing F in a self consistent way

We can also add this biasing potential in a clever dynamical scheme

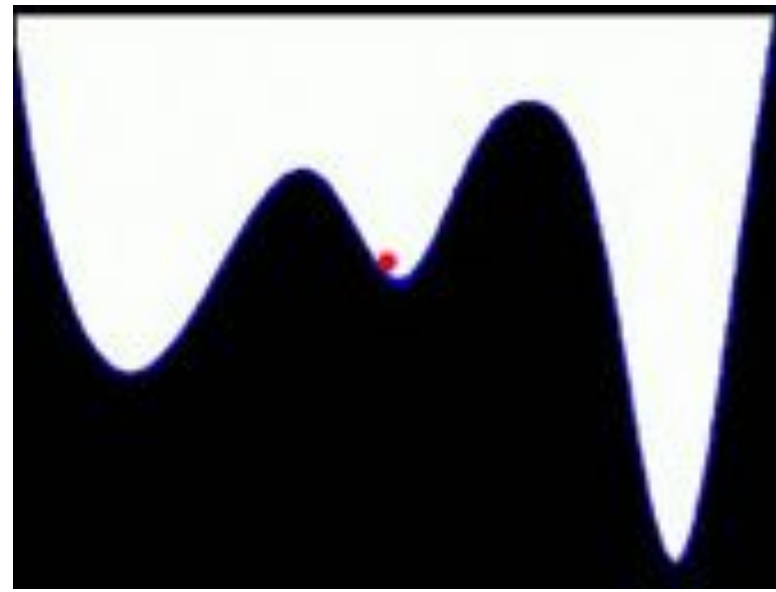
Metadynamics: History dependent potential, to cross a barrier > kT

[*Reports on Progress in Physics*, **71** (2008) 126601]

To explore $G(\zeta)$, every N time steps put a Gaussian:

$$V(\zeta,t)=\sum_{t_i<t} W \exp\left[-\frac{(\zeta-\zeta_i)^2}{2\Delta^2}\right] \Rightarrow -G(\zeta)$$

When V is flat



ζ(collective variables)

- Distance
- Torsion angle
- Coordination number

❖ Computing accurate free energy surfaces with quantum mechanical based interaction potentials requires Leadership Computing Resources

❖ **Multiple "walkers" in parallel help sample free-energy landscape**

Interfacial processes studied with DFT

Ions at interfaces are relevant to problems from atmospheric science to biology: A HPC problem

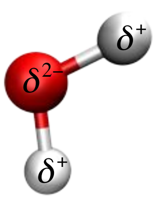
❖ **Ion specific effects**

1.Nano-assembly stability (theory of colloids important in synthesis, self-assembly, paints, etc)

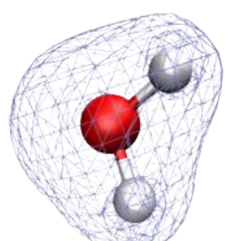
2.Protein stability (Hofmeister series)

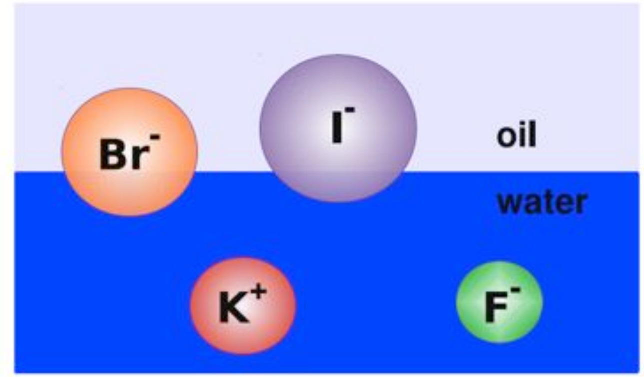
3.Heterogeneous chemistry in the atmosphere (acids, bases, halides at aqueous interfaces)

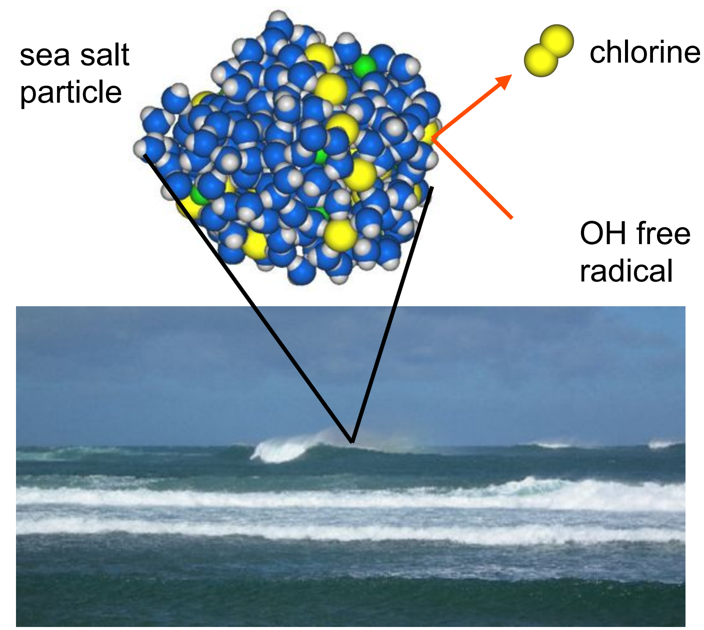
❖ **The principles of ion specific interactions are contained in a *local quantum mechanical* description of solvation**



vs.







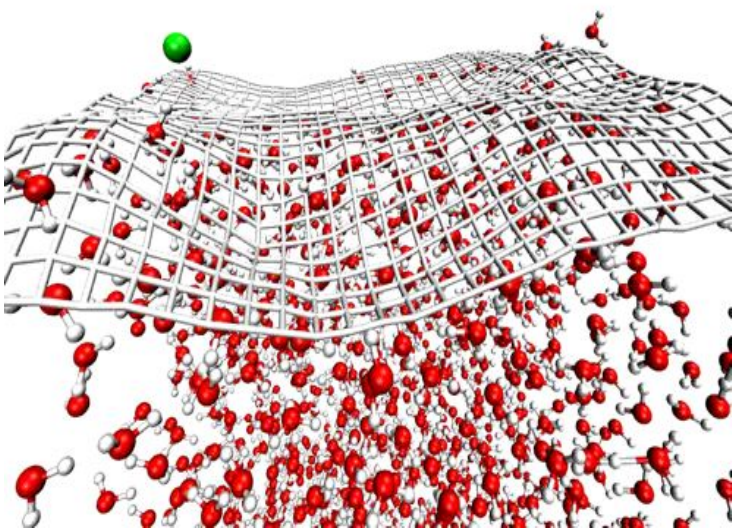
Motivation

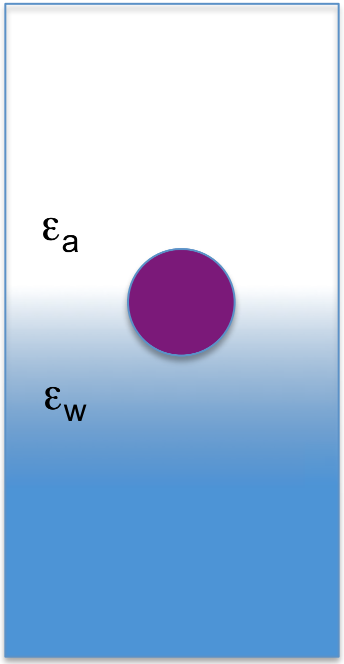
❖ **Outstanding questions:**

- Identify a theoretical model and **validate with molecular simulation to identify the principles of ion adsorption at interfaces**

We want to go from this

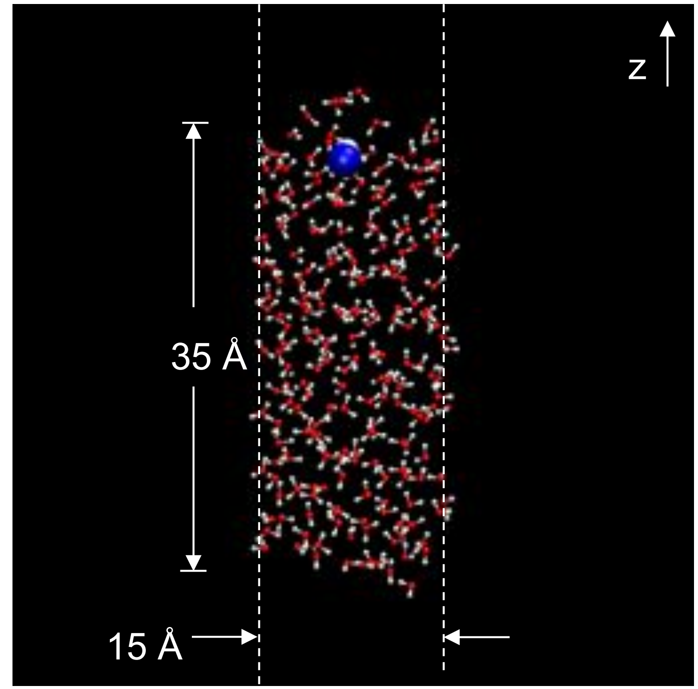
……to this





We continue to develop the protocol for large-scale DFT simulation for open aqueous systems

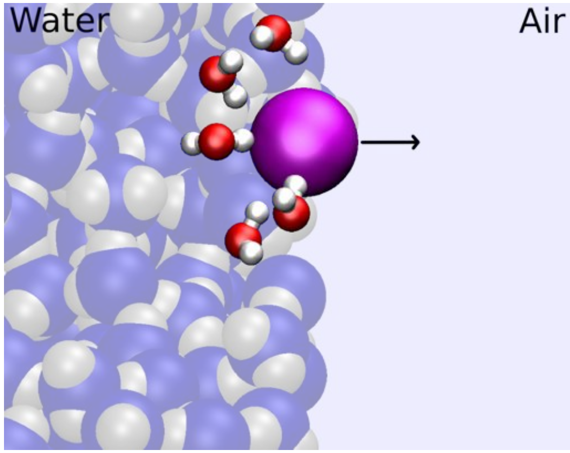
IFW Kuo and CJM, *Science* 303, 658 (2004)

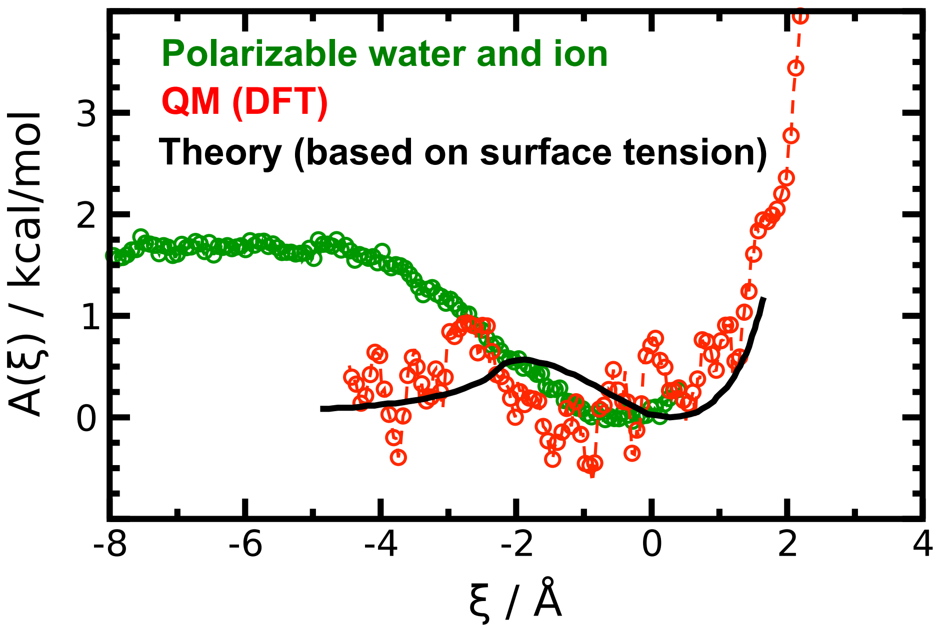


- Current system sizes of 216 waters are needed to yield a true interfacial system but larger systems are needed in order to simulate the effects of dilute salt solutions and their chemical reactions

CJM, IFW Kuo, *Chemical Reviews* 106, 1282 (2006)

Our thermodynamic calculation suggests that ion adsorption is sensitive to the local charge density





- ❖ **Quantum mechanics seems to give an answer for the potential of mean force for transfer consistent with experiments**
- ❖ **Classical empirical models with the inclusion of polarization yield too much adsorption. Results would say that the addition of salt lowers surface tension!**
- ❖ **We continue to work closely with theory and experiment to identity the microscopic principles for ion adsorption at hydrophobic interfaces**

Baer and CJM, J. Phys. Chem. Lett. 2, 1088 (2011)

Water's self-ions at the air-water interface have also generated a recent controversy

Water surface is acidic

Victoria Buch*, Anne Milet†, Robert Vácha‡, Pavel Jungwirth‡§, and J. Paul Devlin¶

7342–7347 | PNAS | May 1, 2007 | vol. 104 | no. 18

Autoionization at the surface of neat water: is the top layer pH neutral, basic, or acidic?

Robert Vácha,[a] Victoria Buch,[b] Anne Milet,[c] J. Paul Devlin[d] and Pavel Jungwirth*[a]

4736 | *Phys. Chem. Chem. Phys.*, 2007, **9**, 4736–4747

Is the liquid water surface basic or acidic? Macroscopic vs. molecular-scale investigations

Poul B. Petersen[1], Richard J. Saykally*

Chemical Physics Letters 458 (2008) 255–261

Comment on Autoionization at the surface of neat water: is the top layer pH neutral, basic, or acidic? by R. Vácha, V. Buch, A. Milet, J. P. Devlin and P. Jungwirth, *Phys. Chem. Chem. Phys.*, 2007, 9, 4736

James K. Beattie*

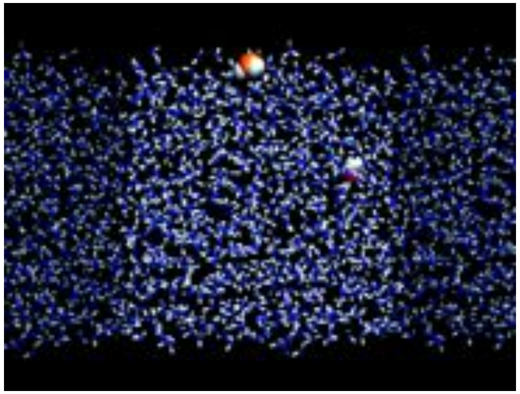
330 | *Phys. Chem. Chem. Phys.*, 2008, **10**, 330–331

PAPER 141/2 www.rsc.org/faraday_d | Faraday Discussions

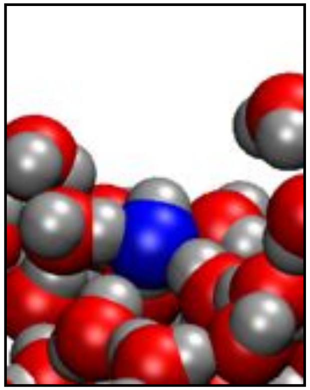
The surface of neat water is basic

James K. Beattie,* Alex M. Djerdjev and Gregory G. Warr

"Microscopic perspective" (simulation, spectroscopy): H_3O^+ adsorbs, OH^- is repelled, enhanced autoionization at interface



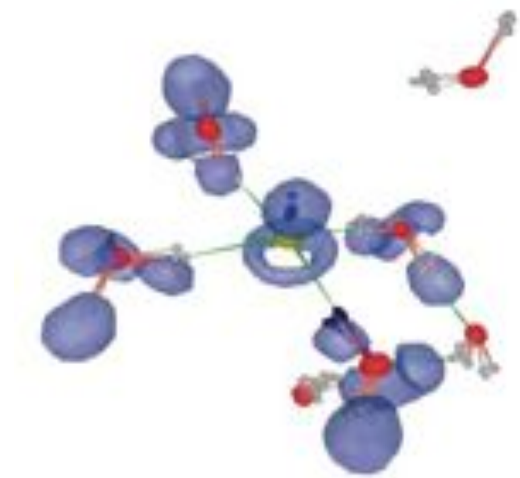
"Macroscopic perspective" (electrokinetic): water surface is negatively charged due to adsorption of OH^-



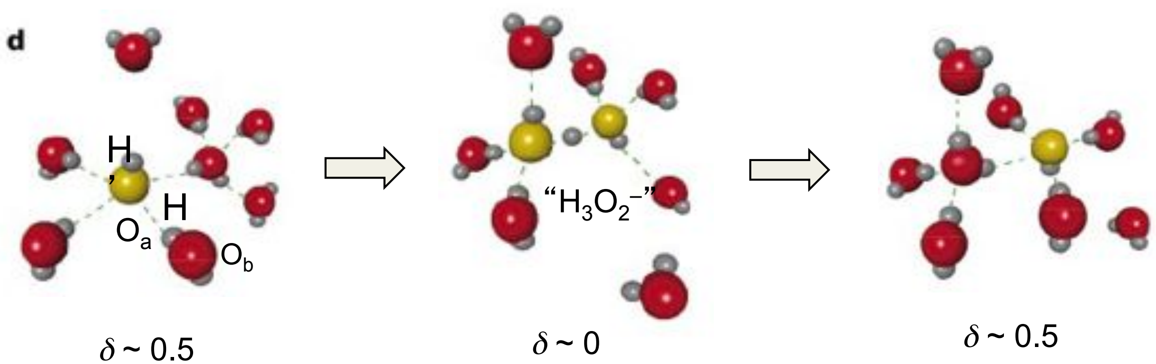
Water's self-ions produce additional challenges for molecular simulation: Chemistry!

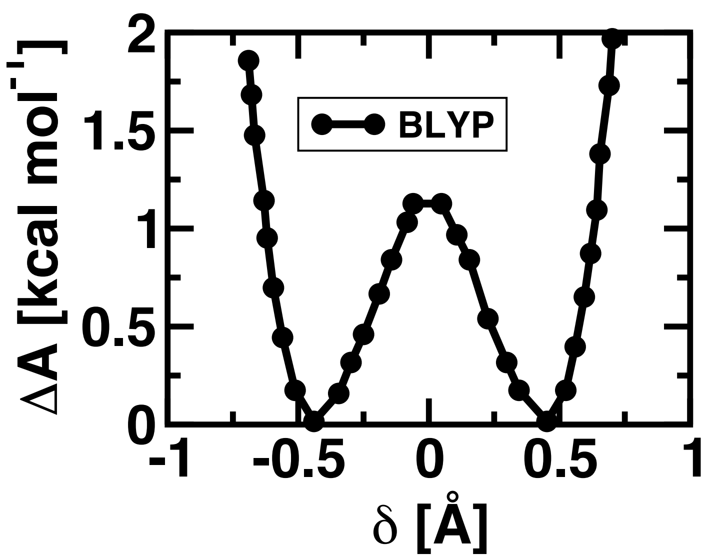
❖ Understanding water's ions requires the use of quantum mechanical charge density to:

- Capture exotic square planar arrangement of water around hydroxyl O atom (Tuckerman, Marx, Parrinello, *Nature*, 2002)
- Sample proton migration of the charge defect (*e.g.* hydroxide anion, hydronium cation)

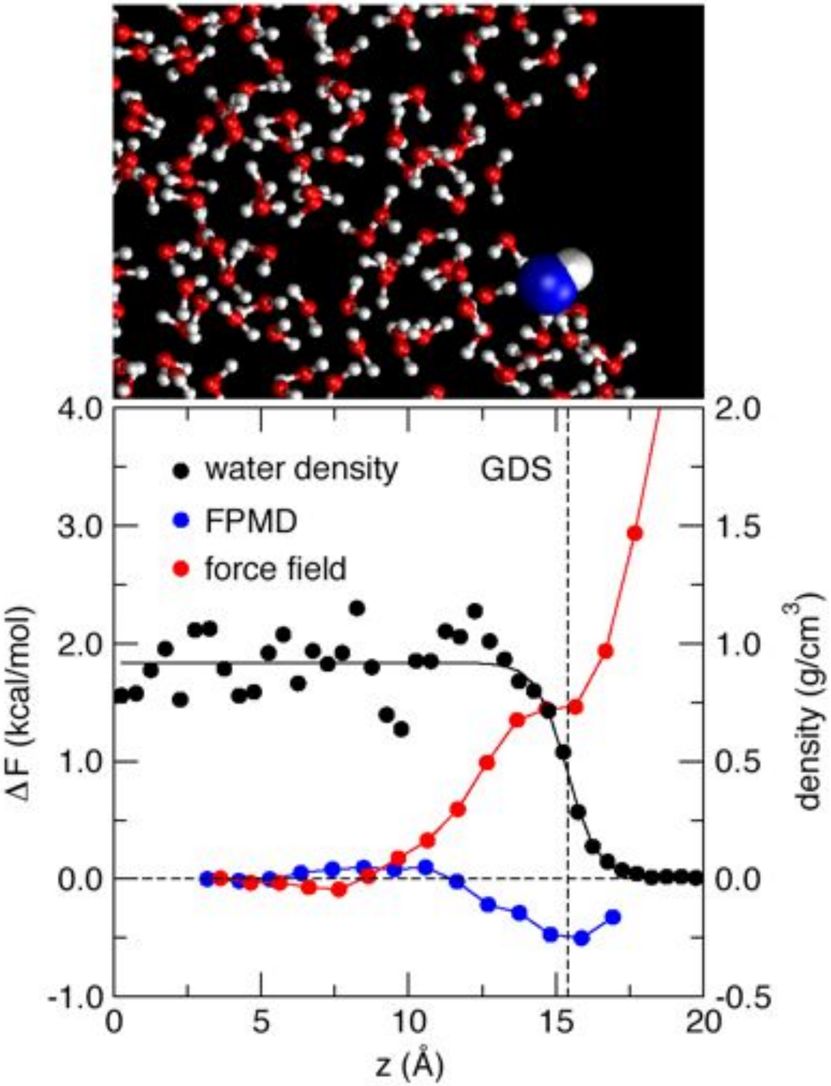


$$\delta = R(O_a\text{–}H) - R(O_b\text{–}H)$$





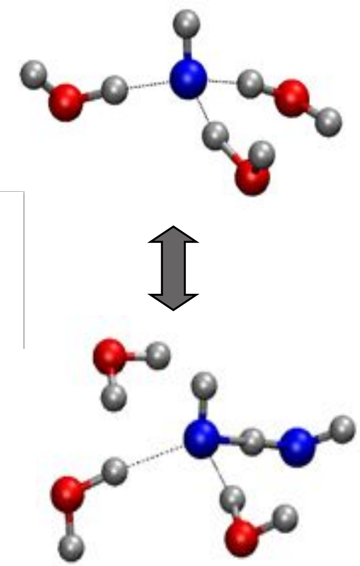
Our findings suggest that DFT provides a weakly adsorbing free energy for hydroxide



❖ H-bonded OH^- is slightly stabilized at the interface; ΔF(surface – bulk) ~ 0.5 kcal/mol

❖ Dramatic differences to the empirical force field model

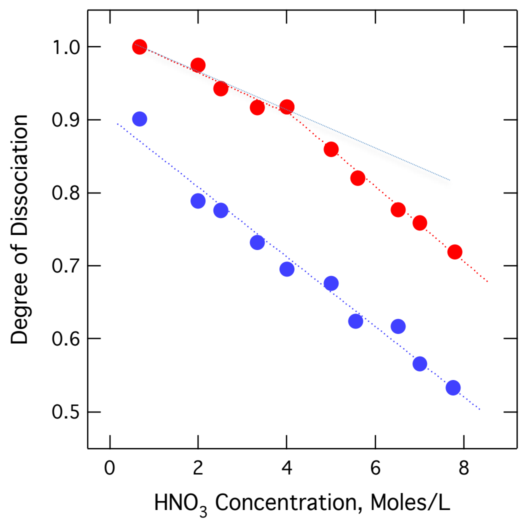
OH^- H-bonded to H_2O δ~0.45

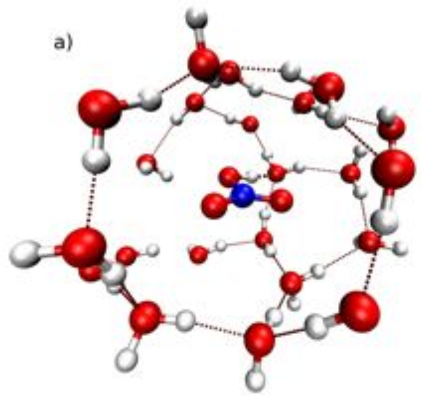


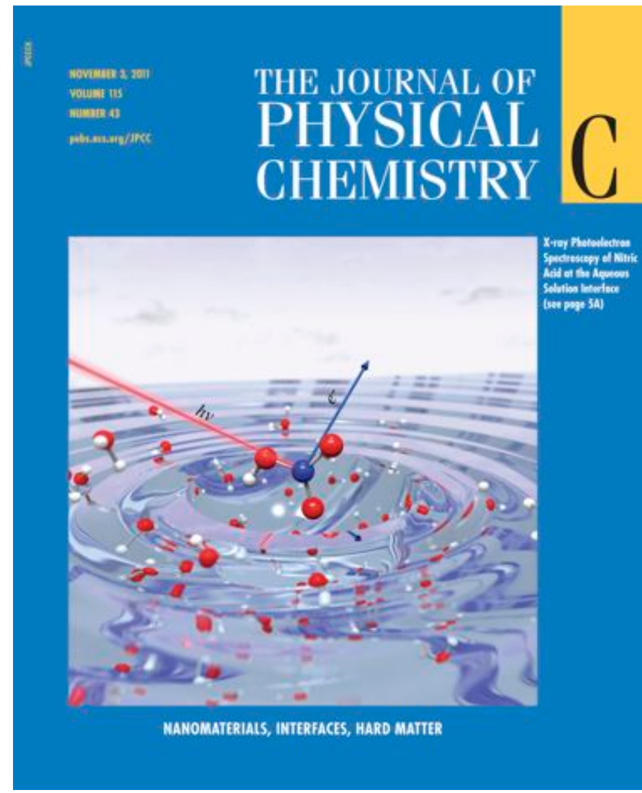
Delocalized anion "$H_3O_2^-$" δ~0.30

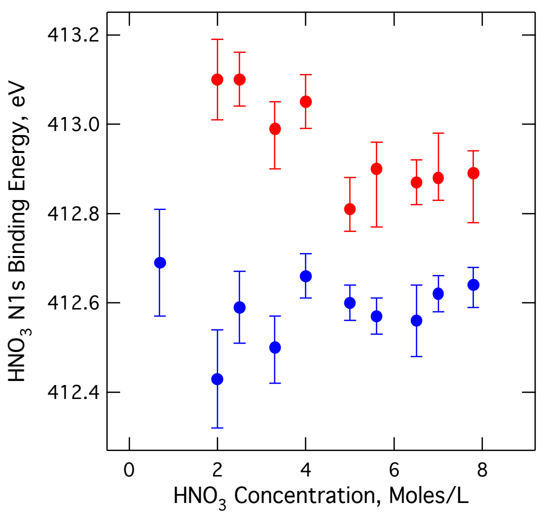
CJM, Kuo, Tuckerman, Lee, Tobias, *Chem. Phys. Letts.* 481, 2 (2009) [Frontiers Article]

We connect to state-of-the-art surface sensitive spectroscopy that measure acid dissociation at the air-water interface









❖ We correlate local solvation to1s binding energies

❖ Surface solvation of HNO_3 at low concentration similar to solvation at in bulk at high concentration

Lewis, Winter, Stern, Baer, **CJM**, Tobias & Hemminger, *J. Phys. Chem. C* **115**, *21183* (2011)

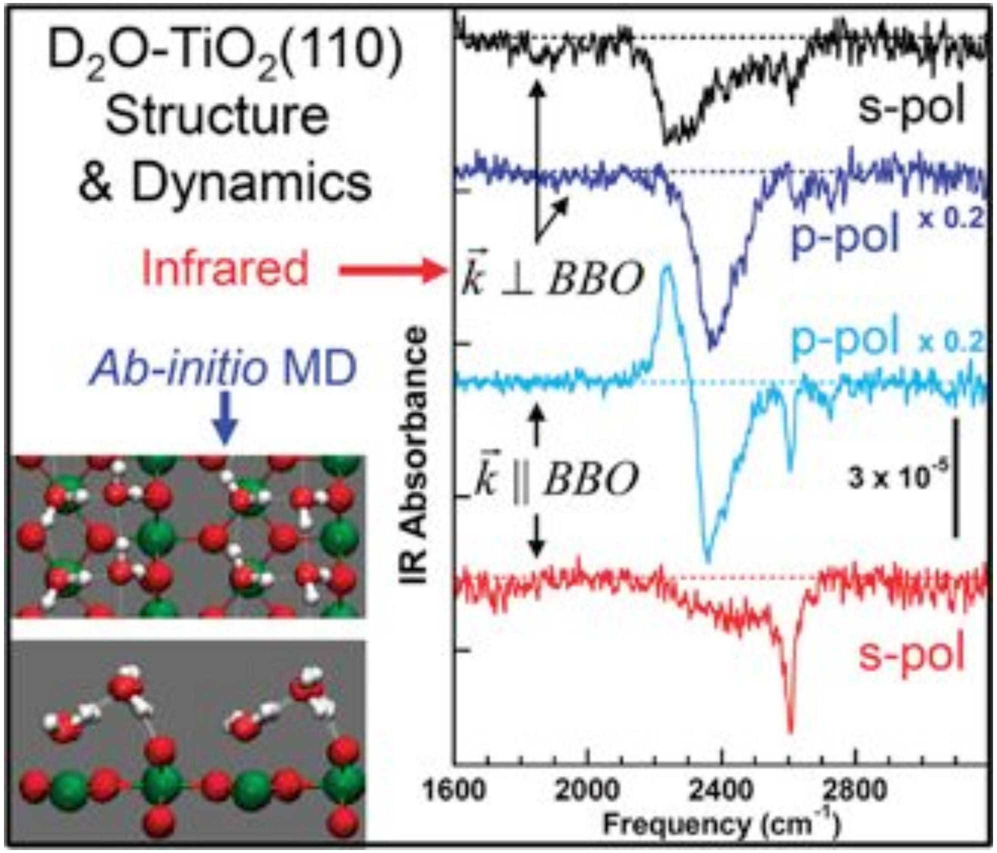
We are connecting with new experiments to study the old problem of water on TiO_2

❖ **New experiments that are both polarization and azimuth resolved give new insights to the structure of water on insulating surfaces**

❖ **Experiments are compared directly to DFT calculations**

❖ **Resolved long-standing puzzle regarding H-bonding between first and second layer**

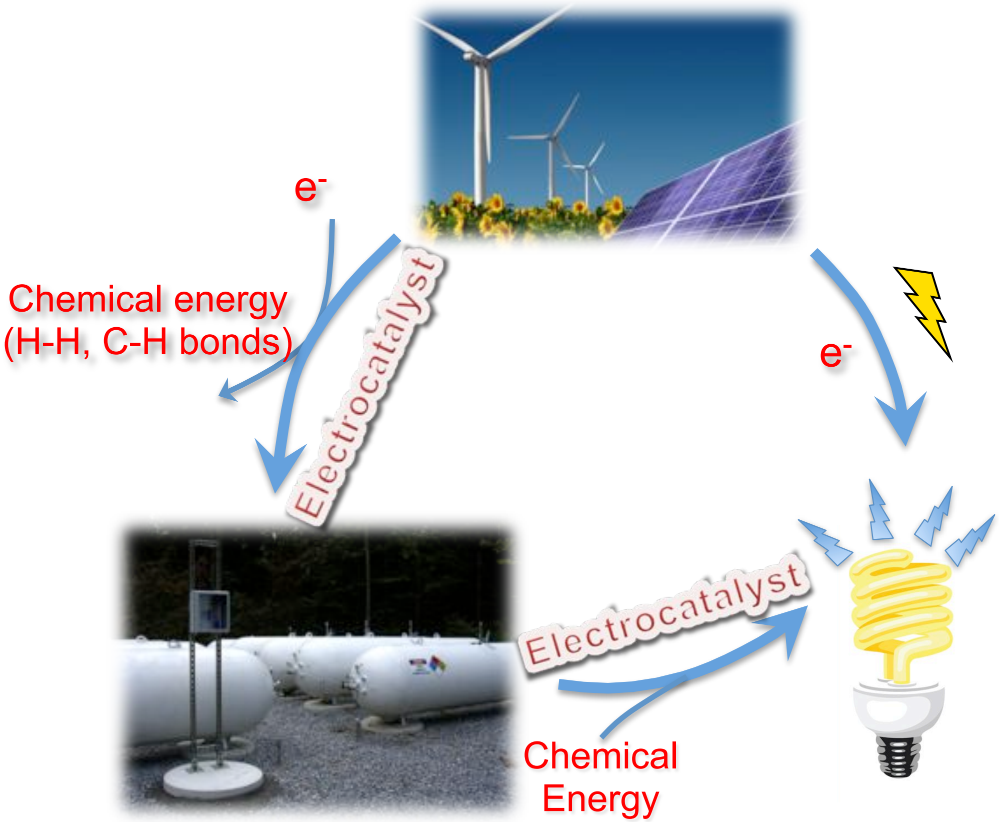
❖ **Water is not dissociated on TiO_2**



 GA Kimmel, MD Baer, ND Petrik, **JVdV,** R. Rousseau, **CJM,** *JCP-Letts* **3**, 778 (2012)

Molecular electrocatalysis

Renewable Energy



Hydrogen Oxidation

$$H_2 \rightleftharpoons 2\,e^- + 2\,H^+$$

Hydrogen Production

$$O_2 + 4\,H^+ + 4\,e^- \rightleftharpoons 2\,H_2O$$

$$N_2 + 6\,H^+ + 6\,e^- \rightleftharpoons 2\,NH_3$$

Multi-Proton multi-electron reactions

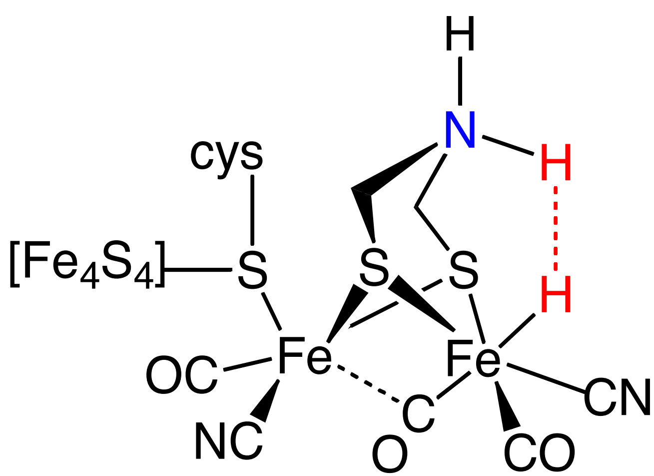
Energy is stored in chemical bonds: Interconversion between electricity and fuels will require catalysts for formation or cleavage of bonds

Use of cheap metals for noble tasks
Ni, Fe, Co but no Pt

Developing highly active, cheap metal-based catalysts for H_2 oxidation and evolution

[FeFe] Hydrogenases

- Reversible proton/dihydrogen production
- H_2 production: TOF < 10,000 s^{-1}; overpotential: 100 – 300 mV

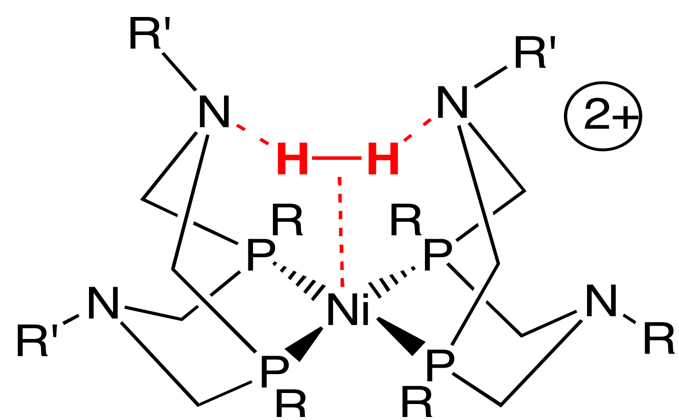


Metal-amine induce heterolytic cleavage of H_2

Fontecilla-Camps et al., *Chem. Rev*. **2007**, *107*, 4273

Ni/Phospine catalysts with proton relays

- H_2 production: TOF < 10,000 s^{-1}; overpotential: > 200 mV
- H_2 oxidation: TOF < 60 s^{-1}



Incorporate the same chemical functionalities …

Ni[P_2N_2] family of catalysts

DuBois *et al.*, *Acc. Chem. Res.* **42**, 1974 (2009)
Helm *et al.*, *Science* **333** (2011) 863

H_2 splitting elucidated with QM/MM and metadynamics

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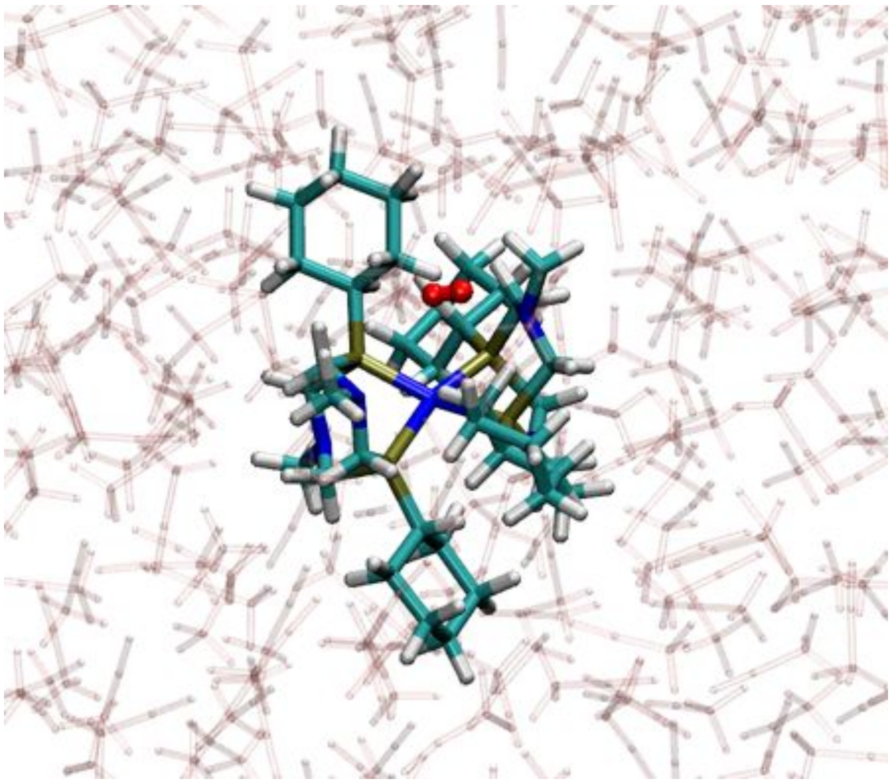
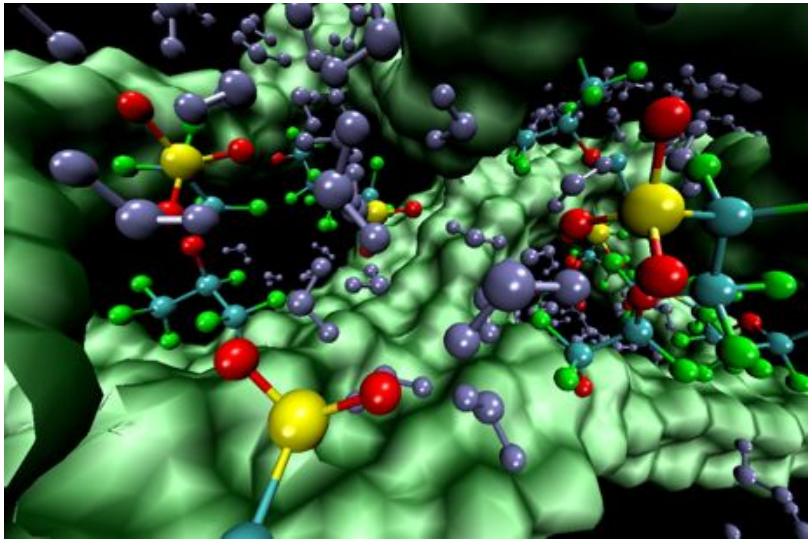


Raugei, Chen, Ho, Ginovska, Rousseau, Dupuis, DuBois, Bullock, *Chem. Eur. J.* (2012), in press

Outlook



❖ Leadership Class Computing is enabling us to simulate complex chemical systems in heterogeneous environments

❖We are computing the relevant thermodynamics functions

Future

❖ Development of other electronic structure methodologies (semi-empirical, MP2) to perform the condensed phase

❖ Proton exchange membranes for fuel cells

- Chemistry (proton transfer)
- Heterogeneous
- Large systems and times are needed to benchmark models against experiment

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