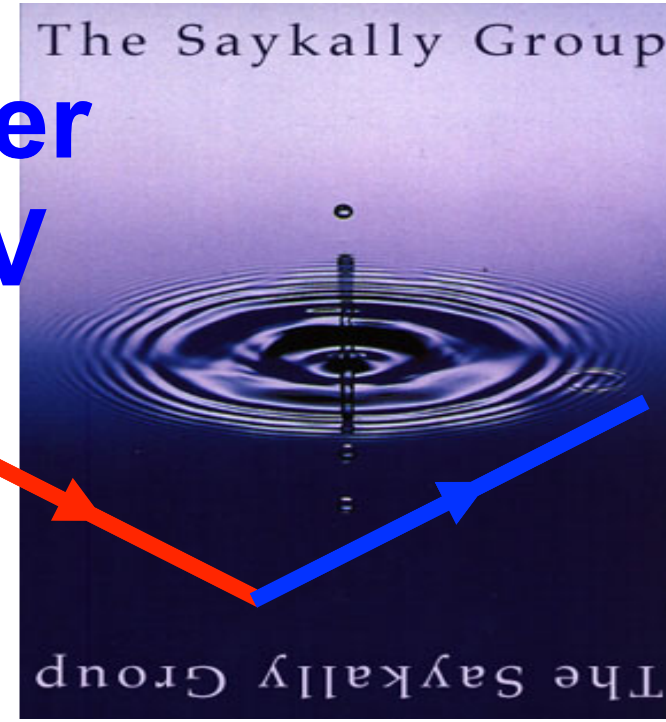
Adsorption of Ions to Aqueous Interfaces and its Effects on Water Evaporation Rates

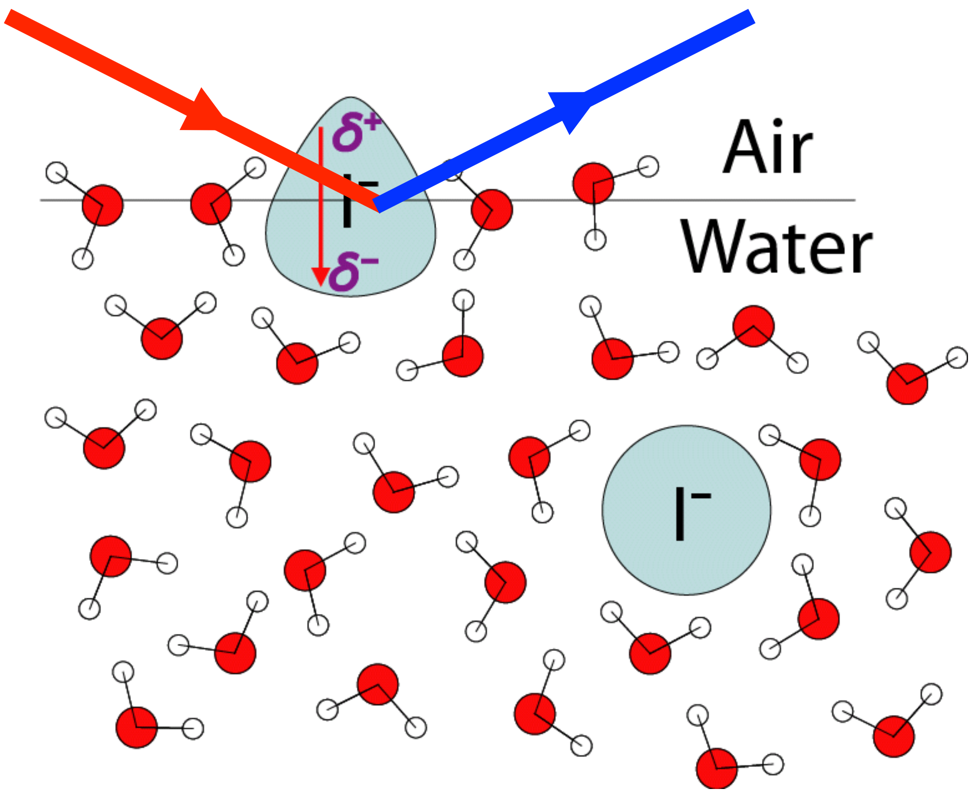
67 TH INT. SPECTROSCOPY CONFERENCE
COLUMBUS, OH

JUNE 19, 2012

The Saykally Group

Ions at the Liquid Water Surface Probed by UV Second Harmonic Generation





Prof. Poul Petersen(Cornell)
Dr. Abigail Miller
Dr. Rob Onorato
Dr. Dale Otten
Dr. Lei Shen
Debra McCaffery
Greg Dallinger
Tony Rizzo
Dr. Ali Eftekhari
Department of Chemistry. University of California, Berkeley, Ca 94720

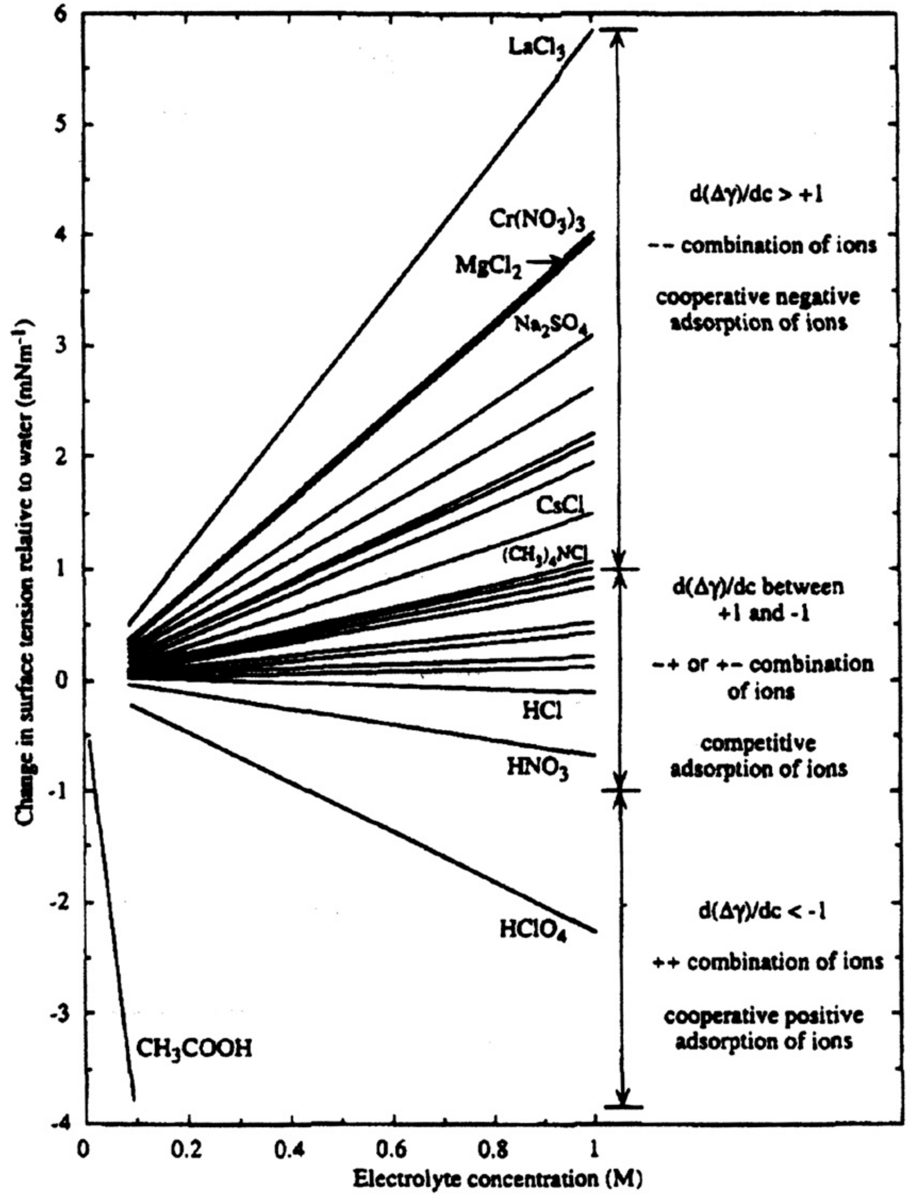
Ions at the Water Surface?

- Textbooks: surface devoid of ions!

- Surface tension increases with salt concentration
- Thermodynamics: Gibbs adsorption equation

$$-d\gamma = \Gamma d\mu$$

- Ions depleted at the surface



Weissenborn, P. K.; Pugh, R. J. *Langmuir* **1995**, 11, 1422

Continuum Models: Image Charge Repulsion

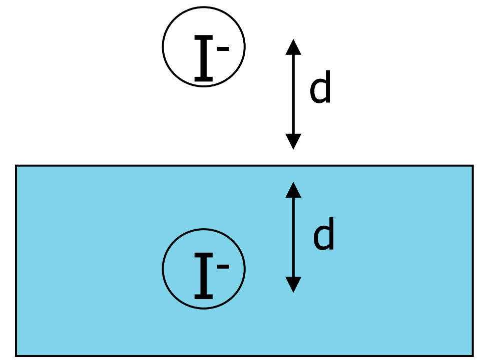


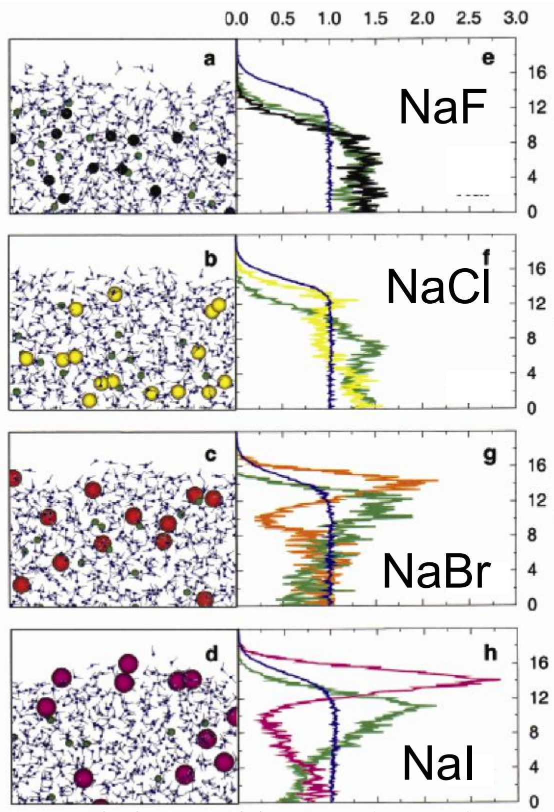
Image Charge Potential

- First modeled by Onsager and Samaras[1]
- Interface as sharp boundary between continuous dielectric media
- Ions as hard spheres
- "Outermost liquid layer is ion-free"

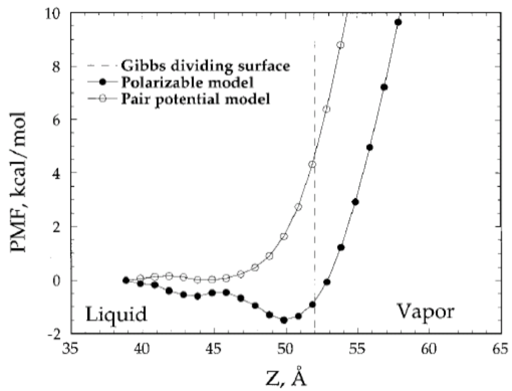
[1])Onsager, L.; Samaras, N. N. T. *J. Phys. Chem.* **1934**, 2, 528

New Picture Emerging….

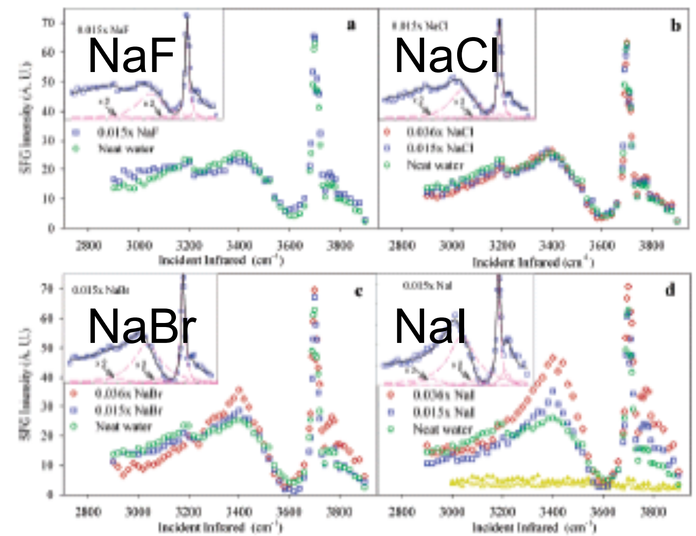
- Theory
- Experiment



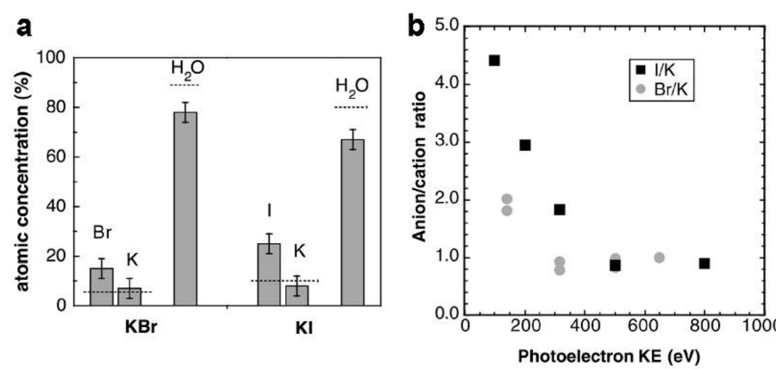
Jungwirth & Tobias *J. Phys. Chem. B.* **105**, 10468 (2001)



Dang & Chang *J. Phys. Chem. B* **106**, 235 (2002)



Liu et al. *J. Phys. Chem. B,* **108**, 2252 (2004)



Ghosal et al. *Science,* **307**, 563 (2005)

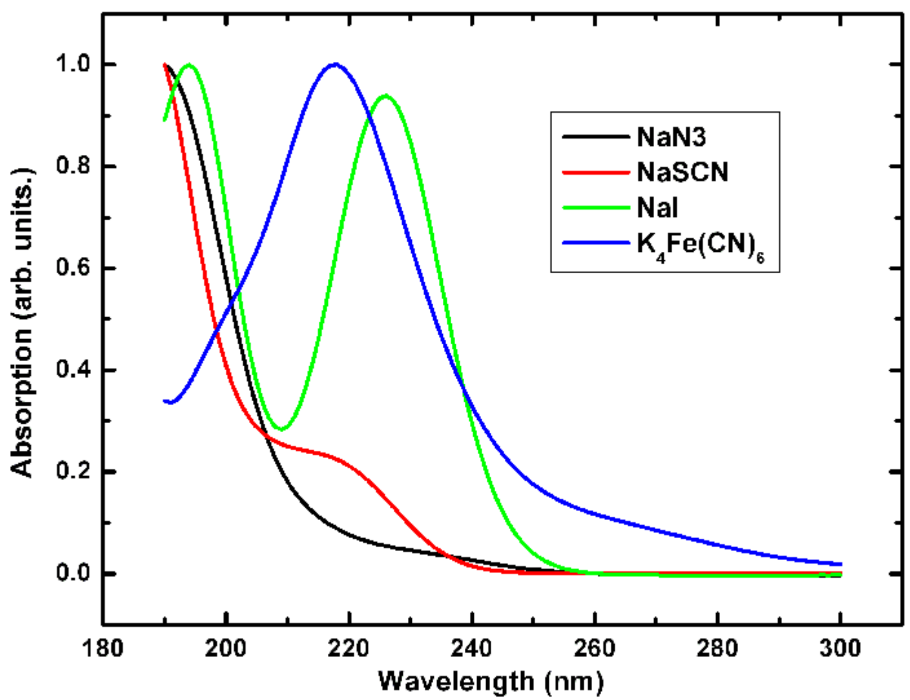
Petersen & Saykally *Annu. Rev. Phys. Chem*. **57**, 333 (2006)
Jungwirth & Tobias *Chem. Rev.* **106**, 1259 (2006)
Gopalakrishnan et al. *Chem. Rev*. **106**, 1155 (2006)
Chang & Dang *Chem. Rev*. **106**, 1305 (2006)
Verdaguer et al. *Chem. Rev.* **106**, 1478 (2006)

Probing Surface Ions: Our Approach.

Highly surface-specific technique

- Direct probe of anions

- Second harmonic generation (SHG) resonant with anion charge-transfer-to-solvent (CTTS) transitions

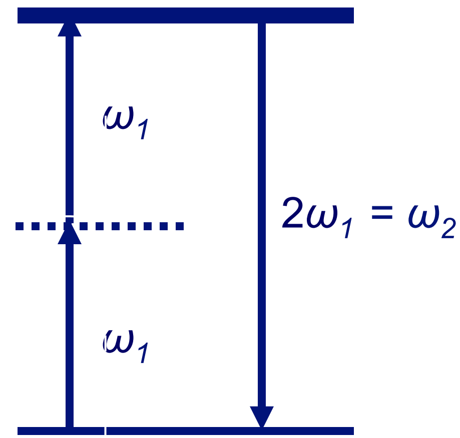


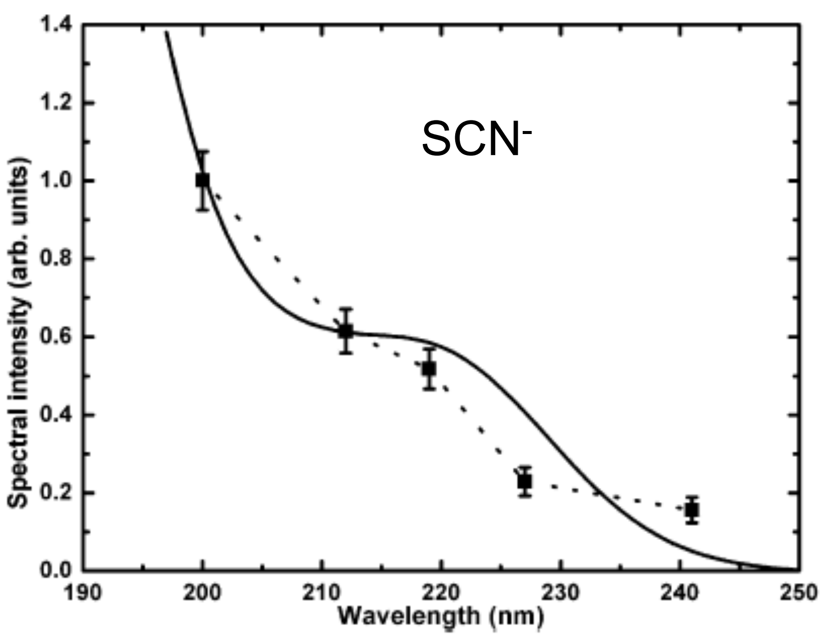
CTTS SHG at an interface

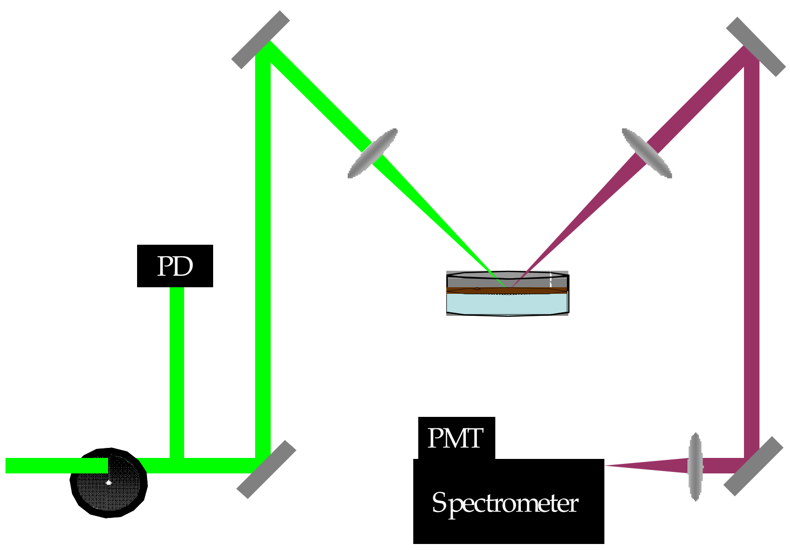
the Saykally Group

$$I_{SHG} \propto \left|\chi^{(2)}\right|^2 I_{fund}$$

$$\chi^{(2)}_{ion} = N_S \langle \beta \rangle_{orientation}$$

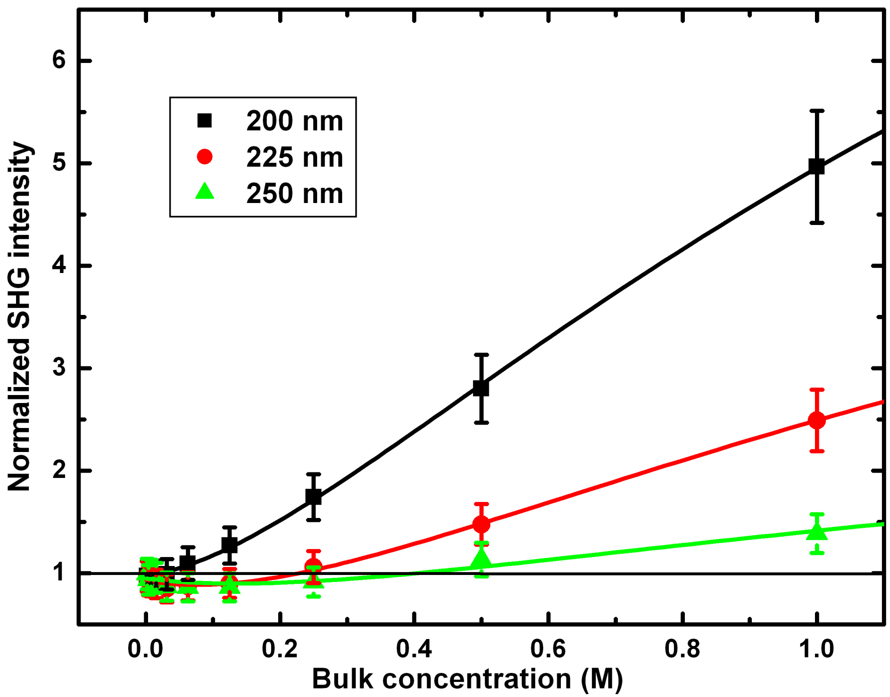




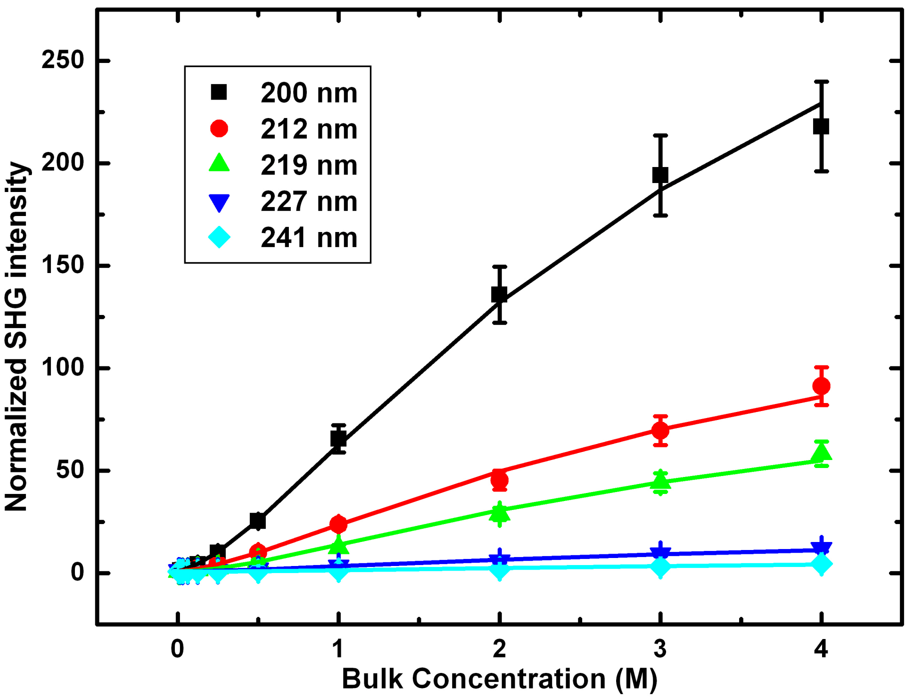


Molar Concentration Range

NaN_3



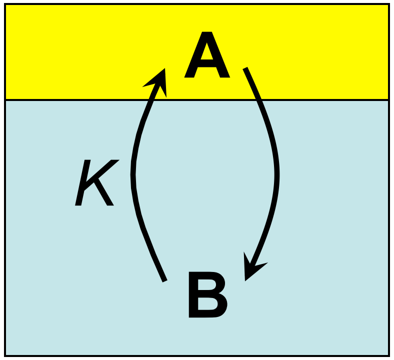
NaSCN



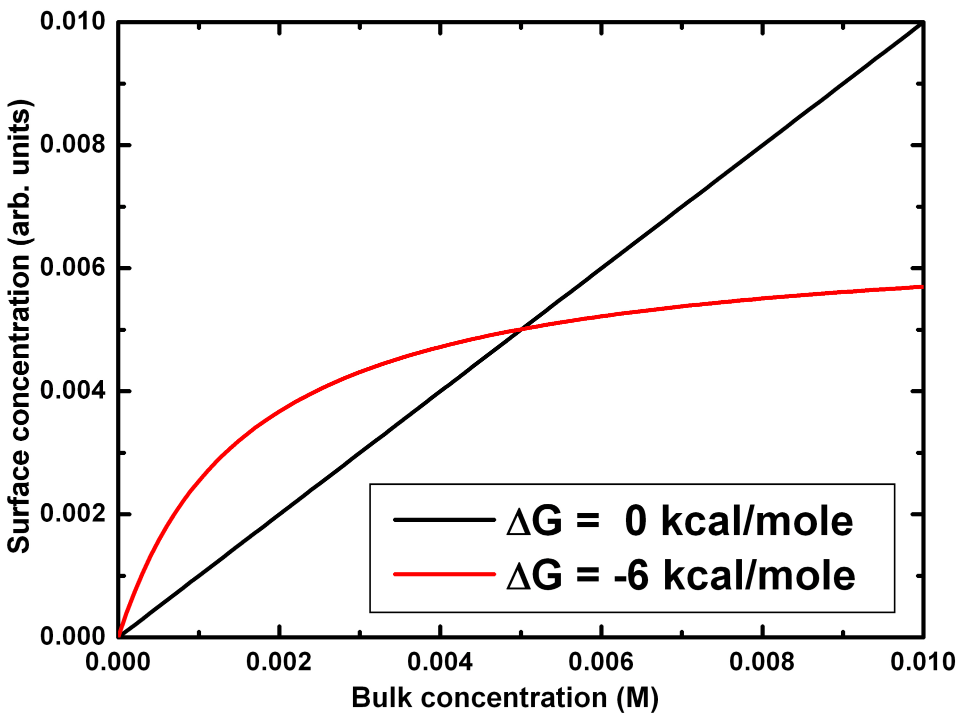
Petersen, Saykally *Chem. Phys. Lett*. **397**, 51 (2004)

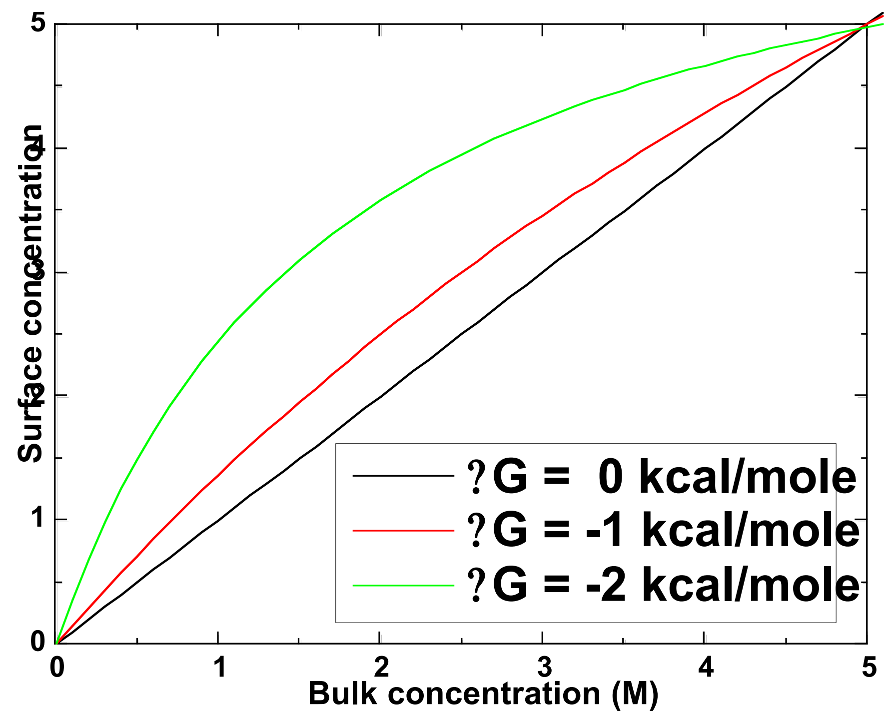
Petersen, Saykally *J. Phys. Chem. B,* **109**, 10915 (2005)

Langmuir Isotherm



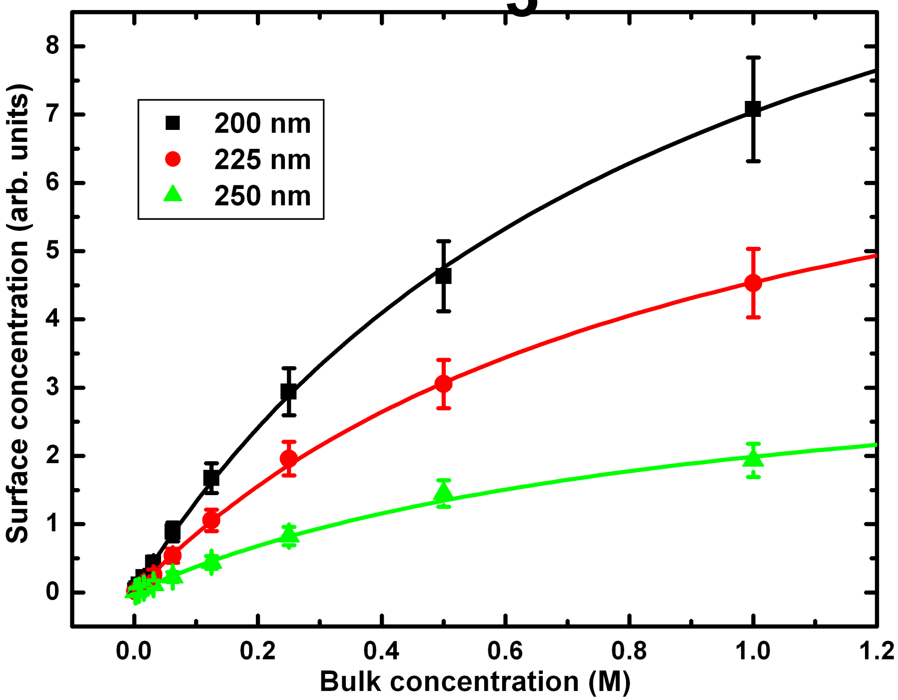
$$N_S = \frac{N_S^{\max} \; x}{x + 55.5 moles/liter \; \exp(\Delta G_{Ads}/RT)}$$



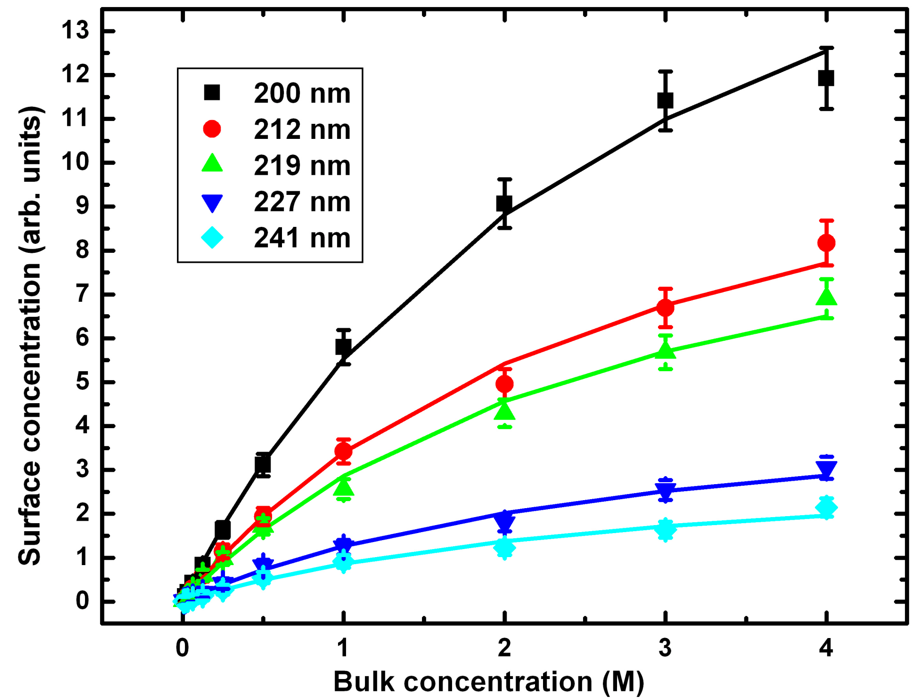


Molar Concentrations

NaN_3



NaSCN



- Langmuir isotherms with a Gibbs free energies of -9.8 +/- 0.4 and -7.4 +/- 0.1 kJ/mole, respectively
- Supports predictions from atmospheric chemistry and MD simulations

Petersen, Saykally *Chem. Phys. Lett*. **397**, 51 (2004)

Petersen, Saykally *J. Phys. Chem. B,* **109**, 10915 (2005)

Summary: Selective Ion Adsorption (Berkeley UV SHG Experiments)

	High concentration			Low concentration		
anion	lower limit	ΔG_{ads} (kJ/mol)	upper limit	lower limit	ΔG_{ads} (kJ/mol)	upper limit
SCN^-	-7.6	-7.5	-7.4			
I^-	-3.3*	NA	0*	-25.6	-25.5	-25.4
NO_3^-	-2	15	NA			
Br^-	-4.1	-1.4	NA	-36.4	-34.7	-20.0
Cl-				-29.9	-28.7	-26.2
OH^-	-4	NA	NA			

N_3^- -9.8 ***old

Prof. Poul Peterson-Cornell

J Phys Chem B 21July 2006

FEATURE ARTICLE

Probing the Interfacial Structure of Aqueous Electrolytes with Femtosecond Second Harmonic Generation Spectroscopy

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Department of Chemistry, University of California, Berkeley, California 94720
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Ann Rev Phys Chem 6 Dec 2005

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AR REVIEWS IN ADVANCE10.1146/annurev.physchem.57.032905.104609
(Some corrections may occur before final publication online and in print)

REVIEWS IN ADVANCE

Annu. Rev. Phys. Chem. 2006. 57:12.1–12.32
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ON THE NATURE OF IONS AT THE LIQUID WATER SURFACE

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Mechanism of Ion Surface Enhancement ??

Expectation is that entropy (volume exclusion) drives surface adsorption, and enthalpy (electrostatics) resists it.

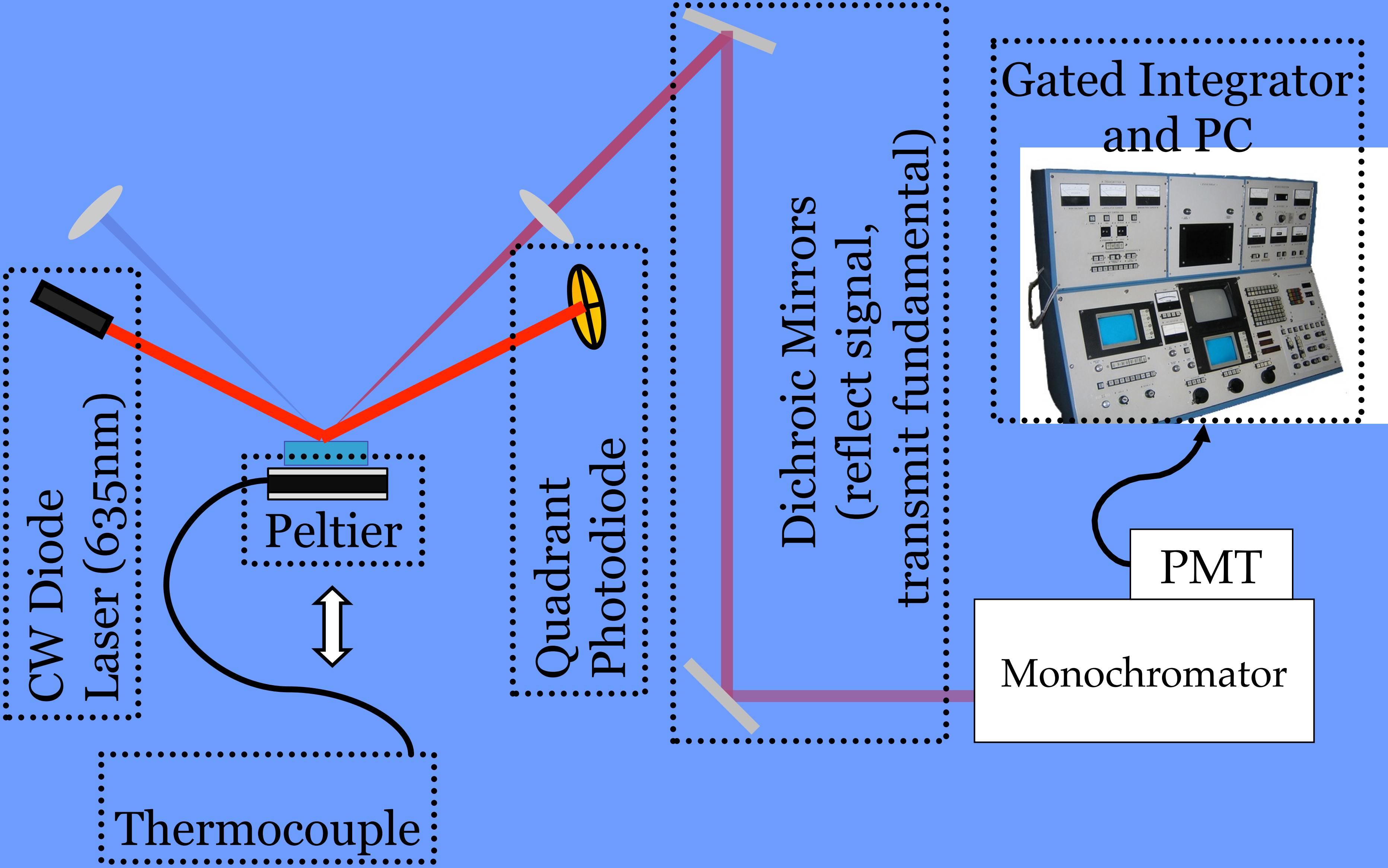
Ion selectivity

Polarizability? (Jungwirth, Tobias, Dang,..)

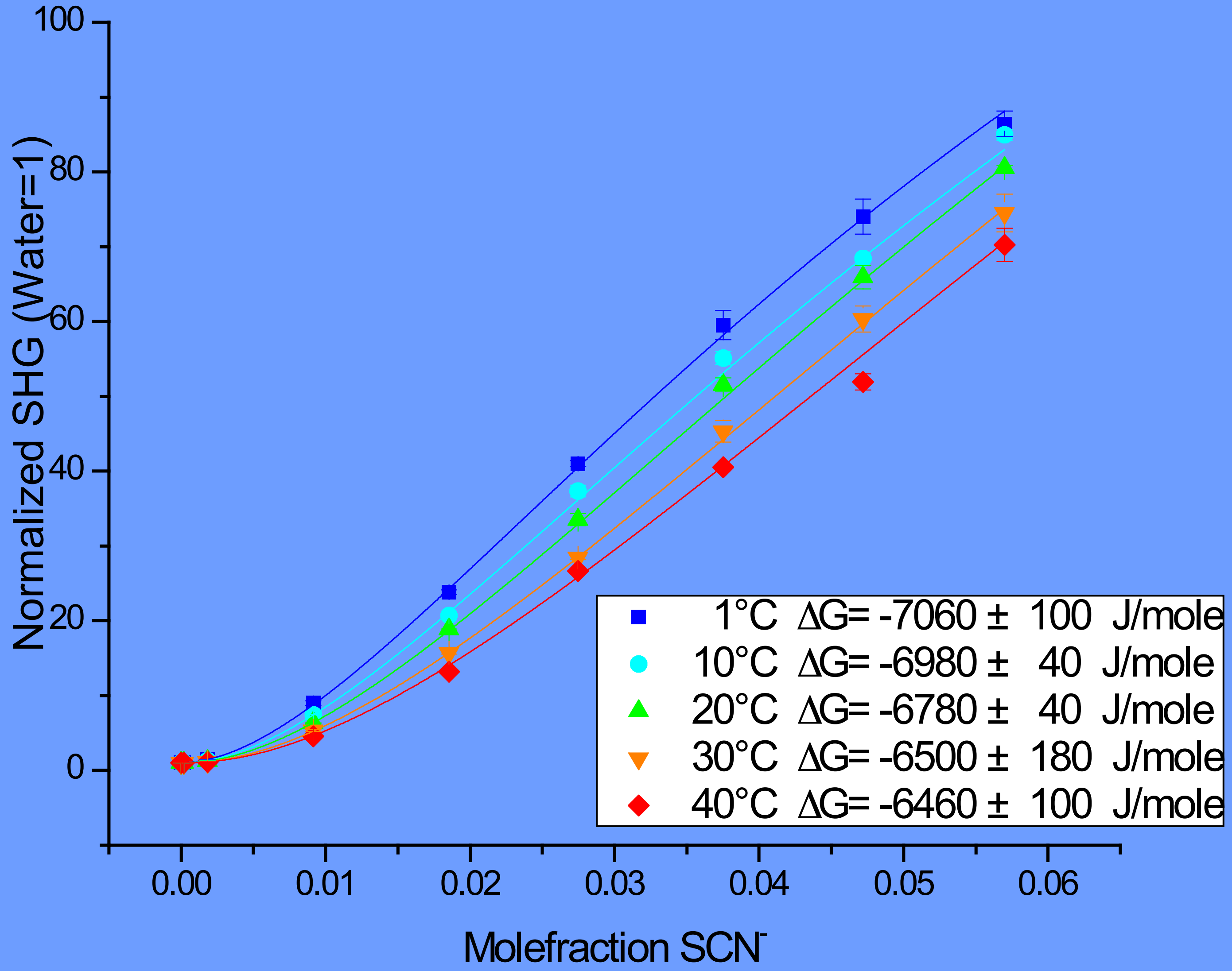
Size?(Netz, Geiger…)

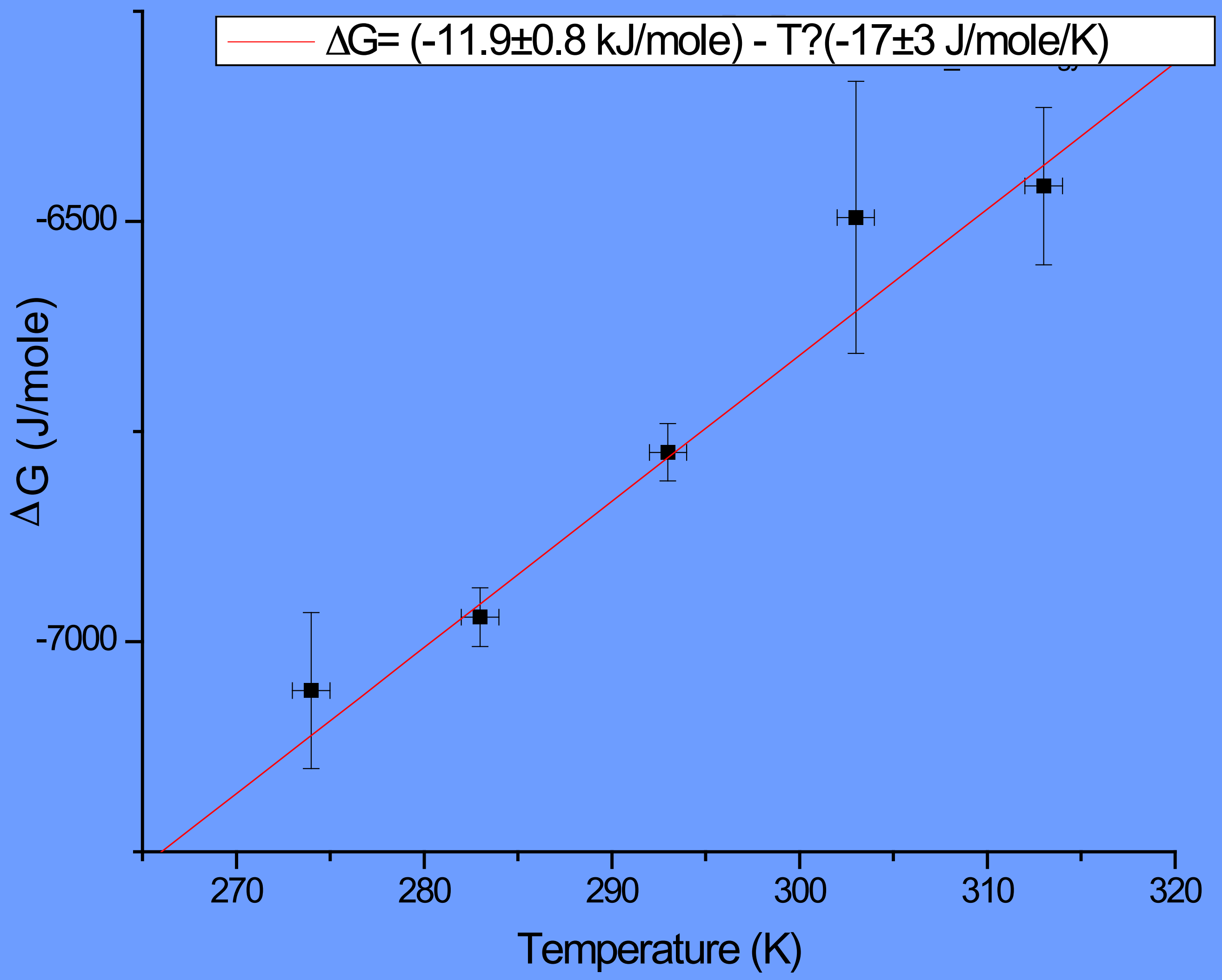
Desolvation Free Energy? (Collins, Record,…)

T-dependence Experiment



SCN$^-$: Temperature dependent SHG




ΔG= (-11.9±0.8 kJ/mole) - T?(-17±3 J/mole/K)
-6500
-7000
ΔG (J/mole)
270
280
290
300
310
320
Temperature (K)

RESULTS

- Measure free energy as a function of temperature

$$\Delta G = \Delta H - T\Delta S$$

- Extract the enthalpy and entropy for this process

Expectation is that positive entropy (cavitation) drives surface adsorption, and positive enthalpy (electrostatics) resist it.

But…experiment shows that both enthalpy and entropy changes are **large** and **negative** ??????

????

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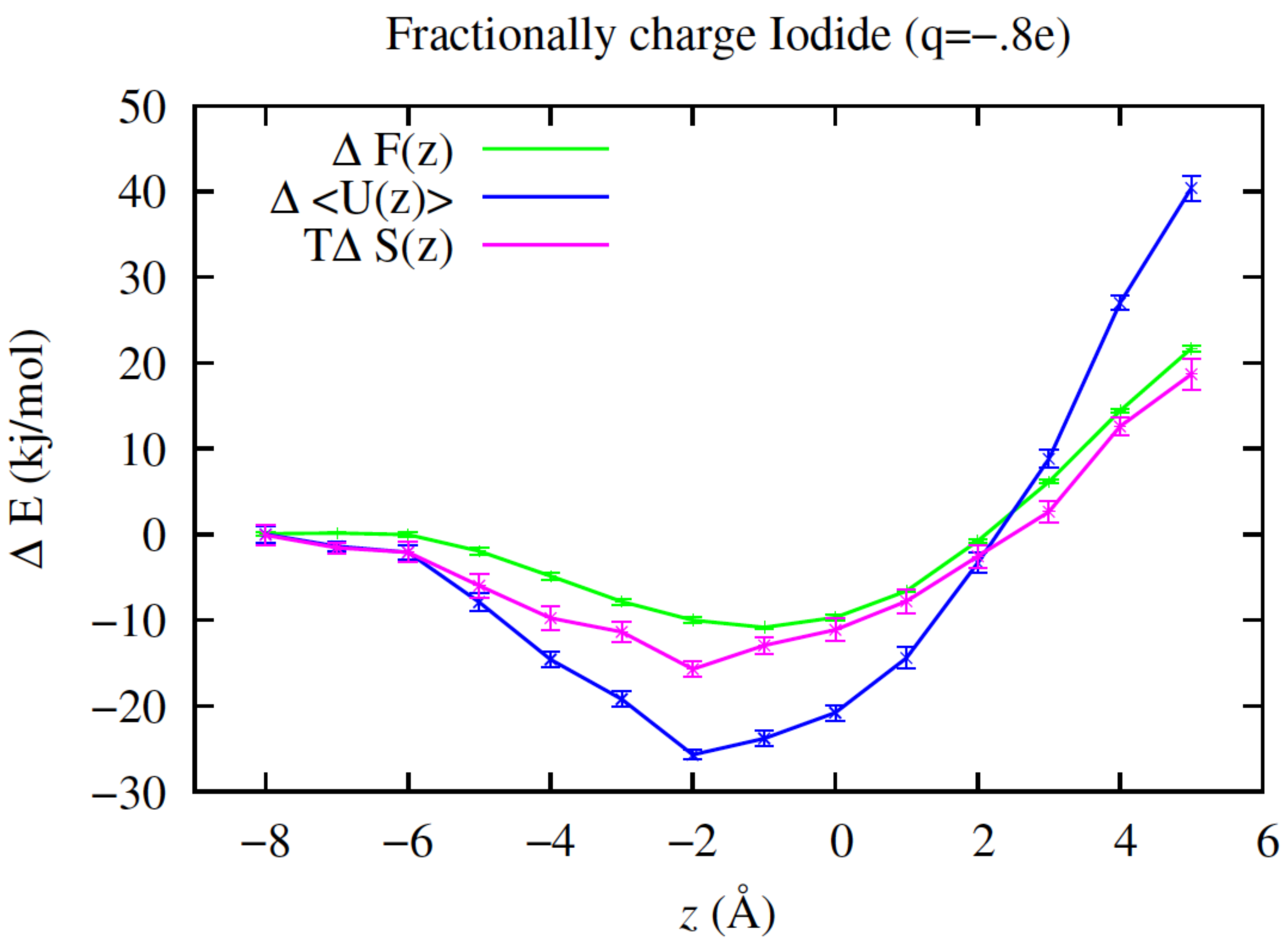
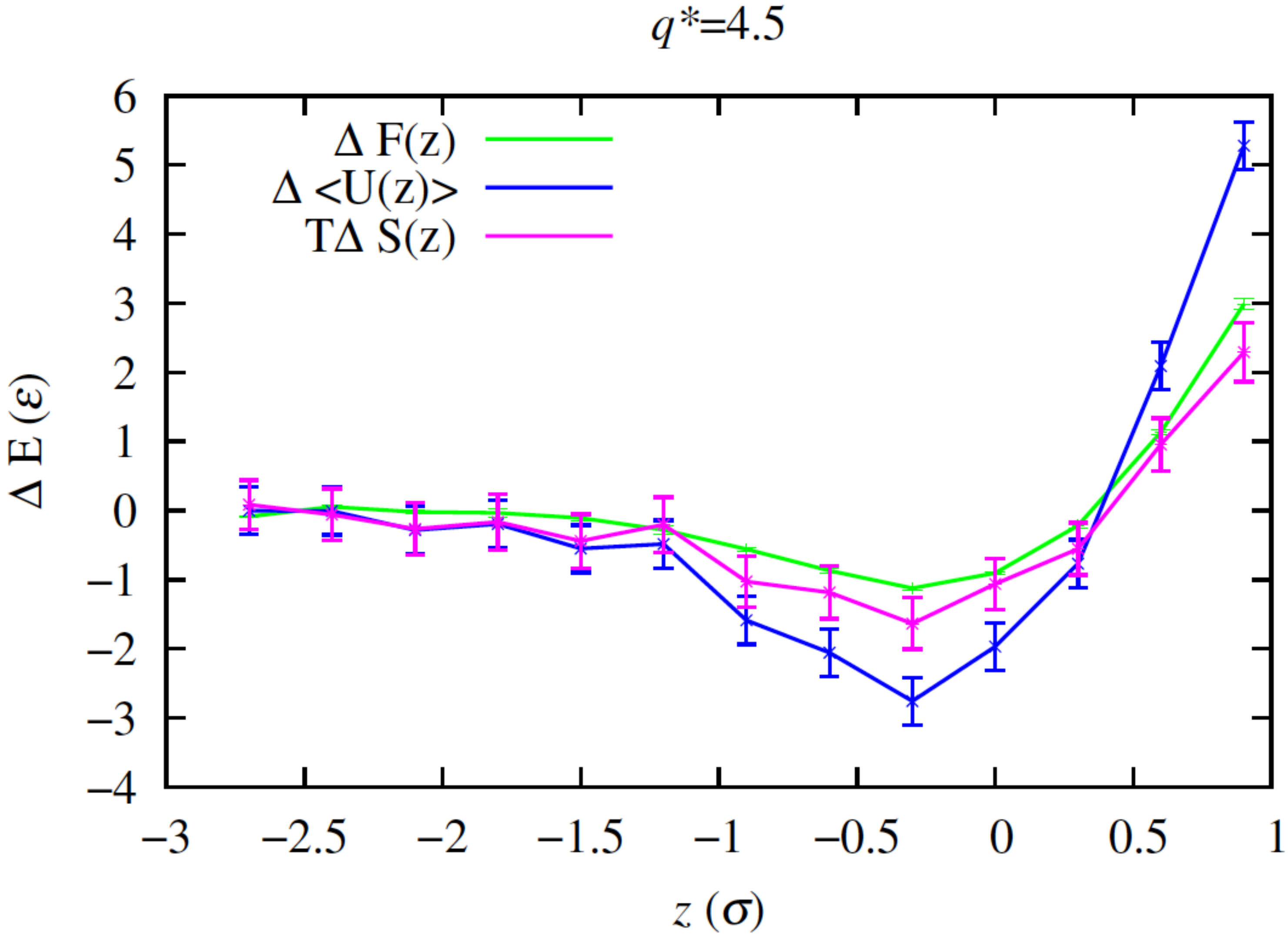
Pat Shaffer

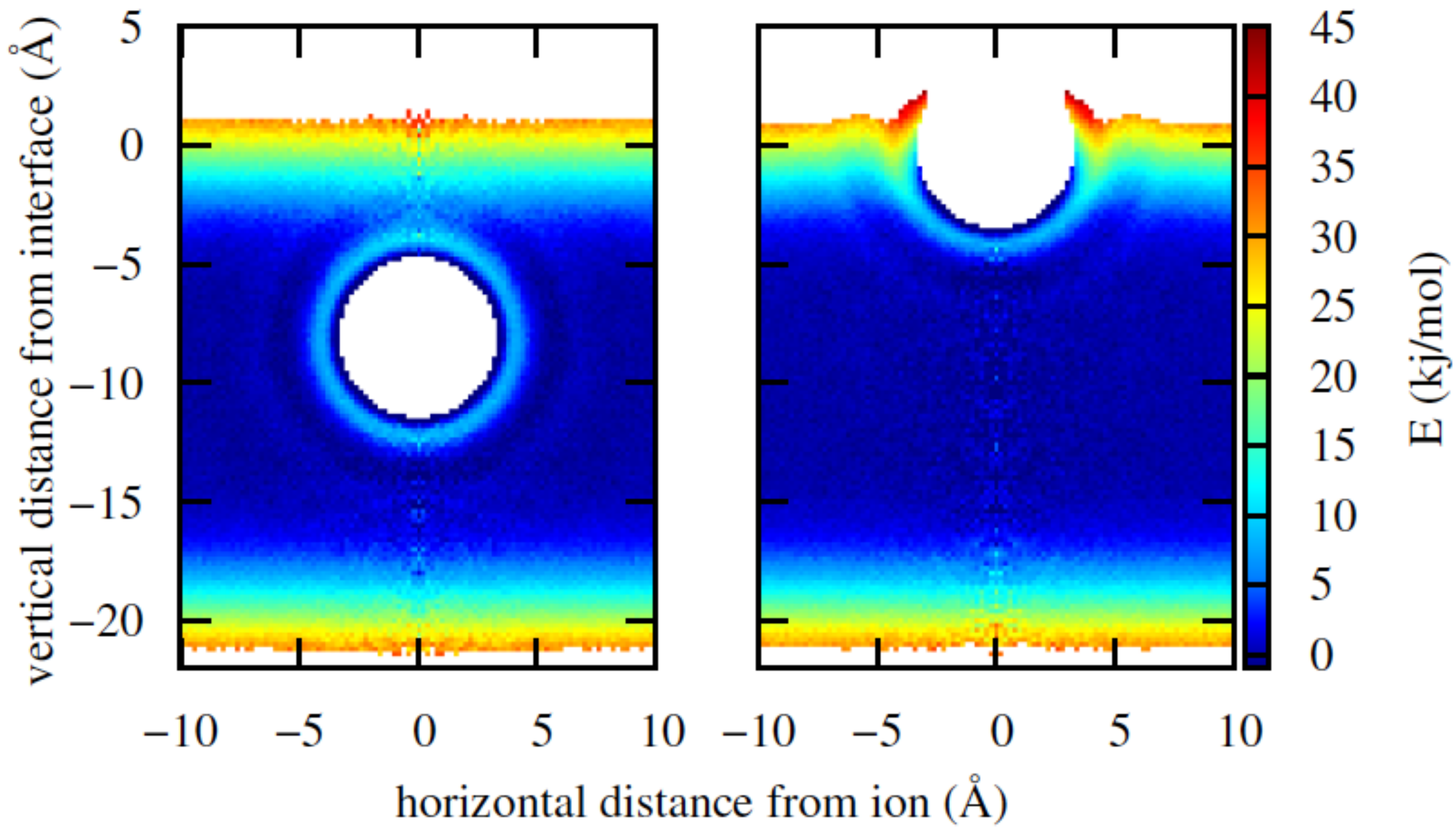
Ion adsorption supported by simulations of SPC/E water(GDS=0)



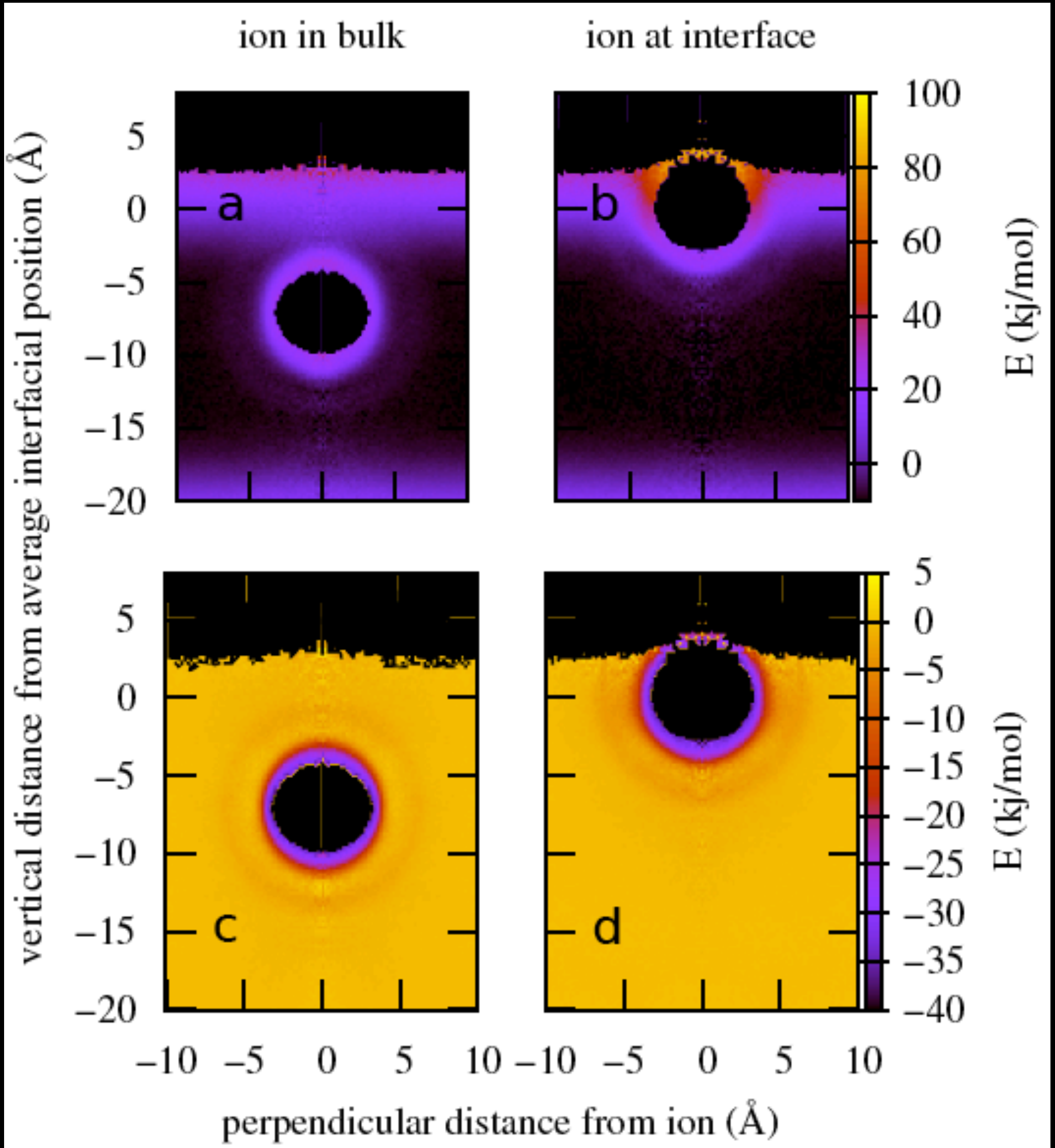
Generality: Ion adsorption in simulations of a Stockmayer fluid



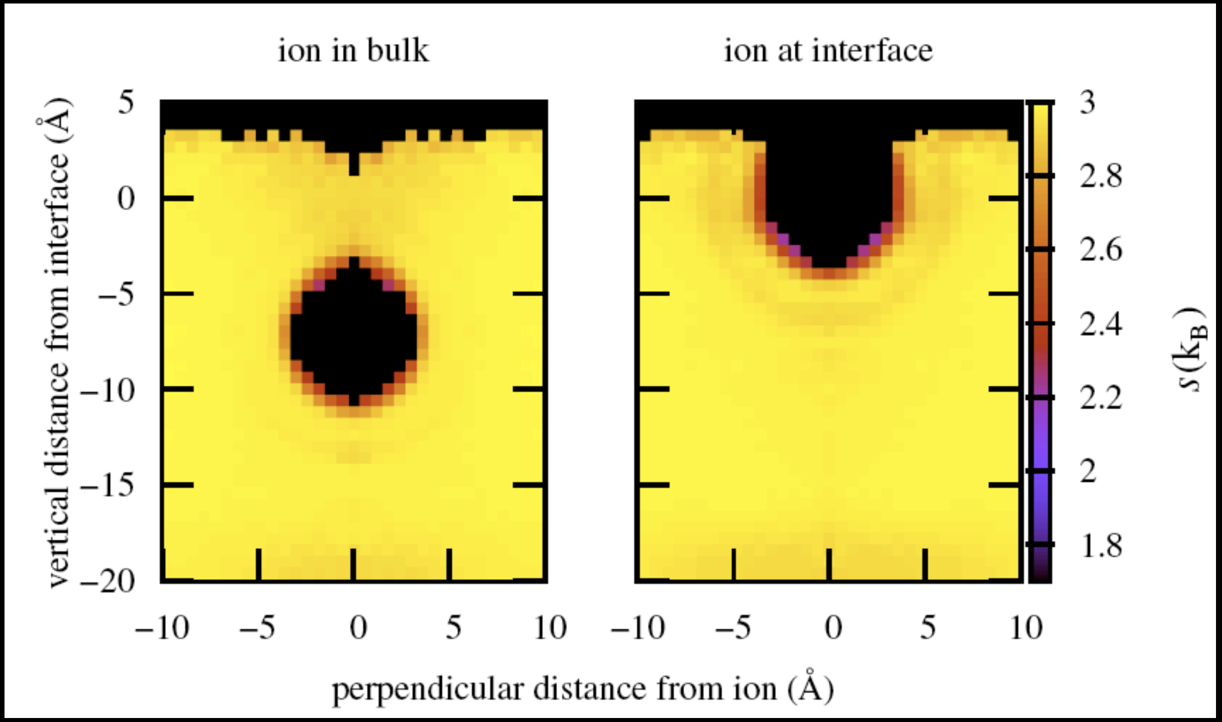
Enthalpy: Weakly hydrated surface ions release some waters which return to the bulk, where they experience stronger interactions



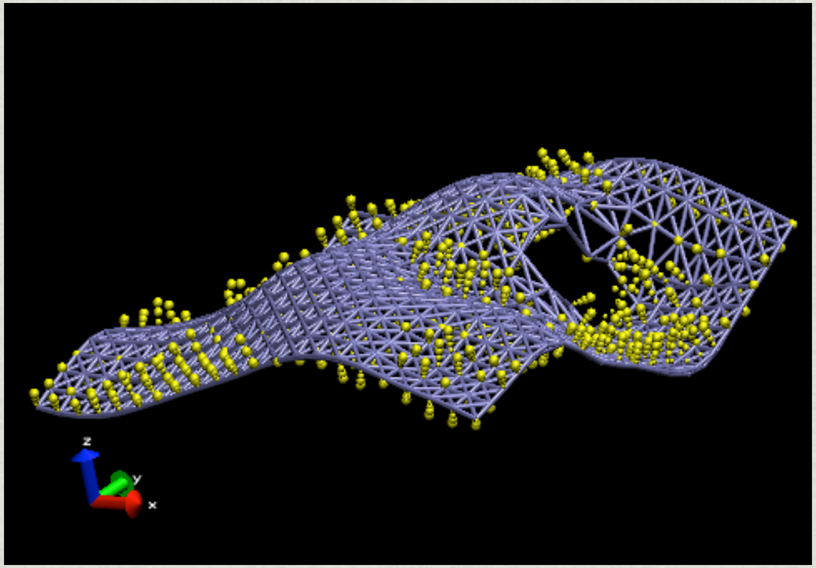
Enthalpic interactions are very *local*

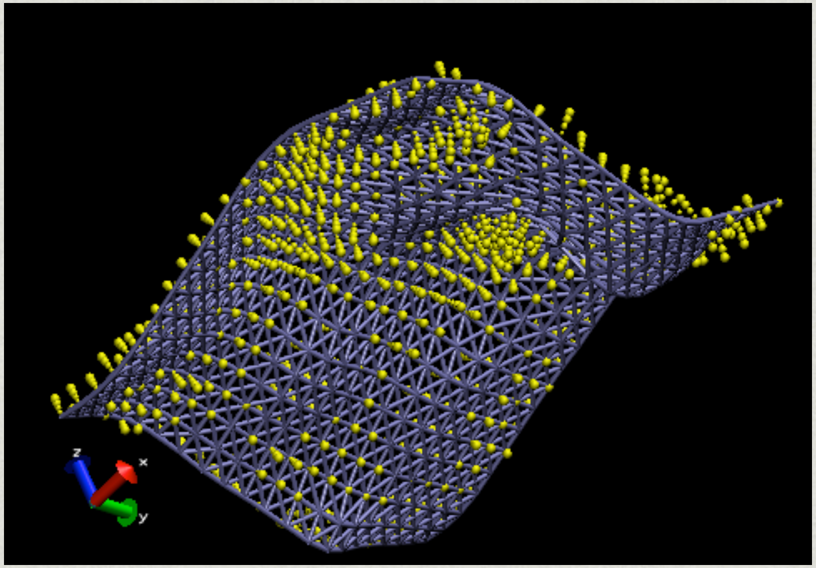


Local orientational entropy change is *favorable(as expected).* but *small*

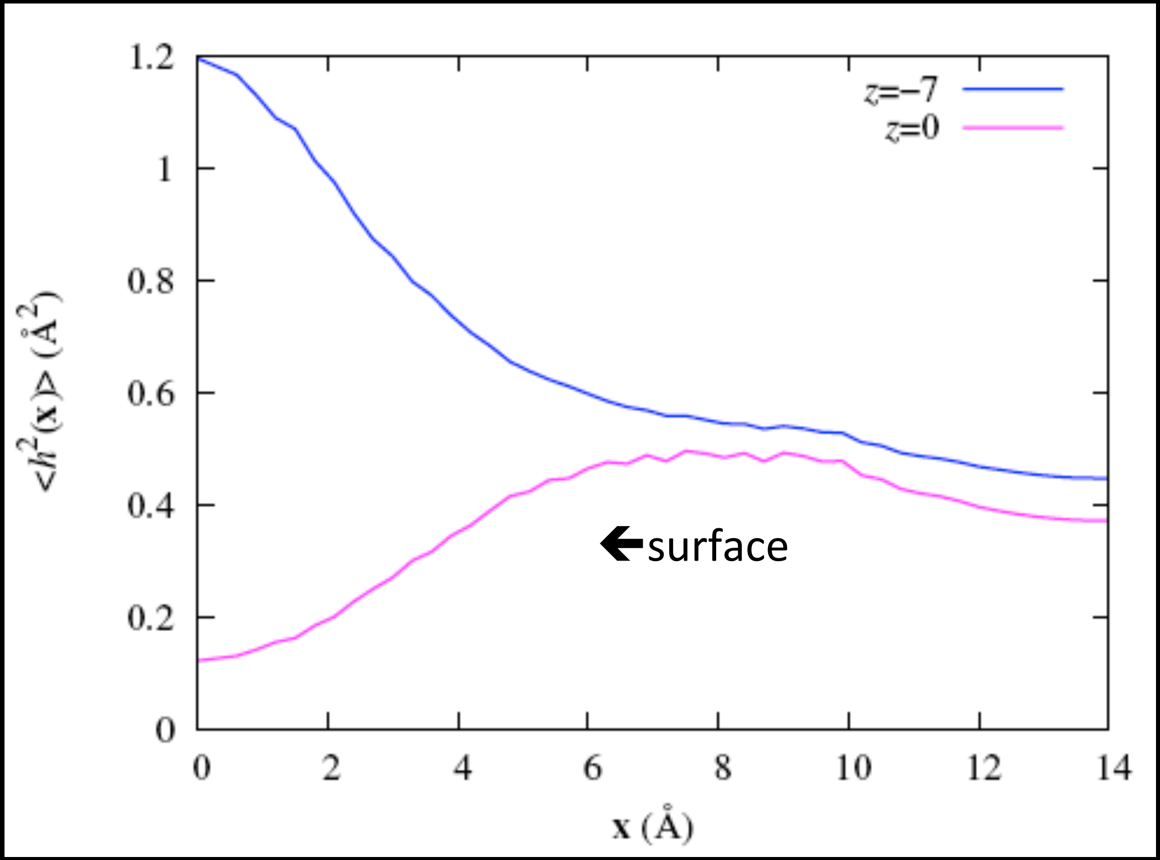


Dominant entropy change: suppression of capillary waves !

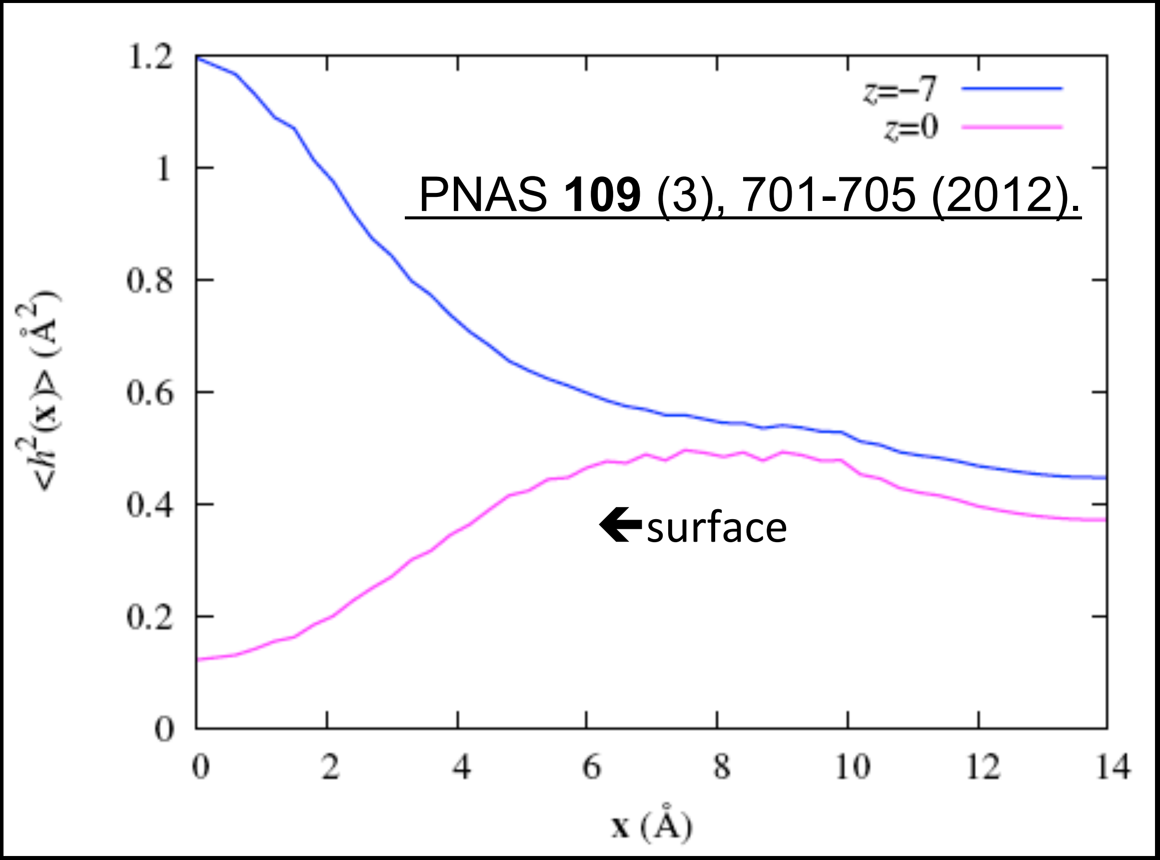




Dominant entropy change is *unfavorable*: **Nonlocal** capillary wave suppression on the instantaneous interface



Dominant entropy change is unfavorable**: Nonlocal** capillary wave suppression on the instantaneous interface

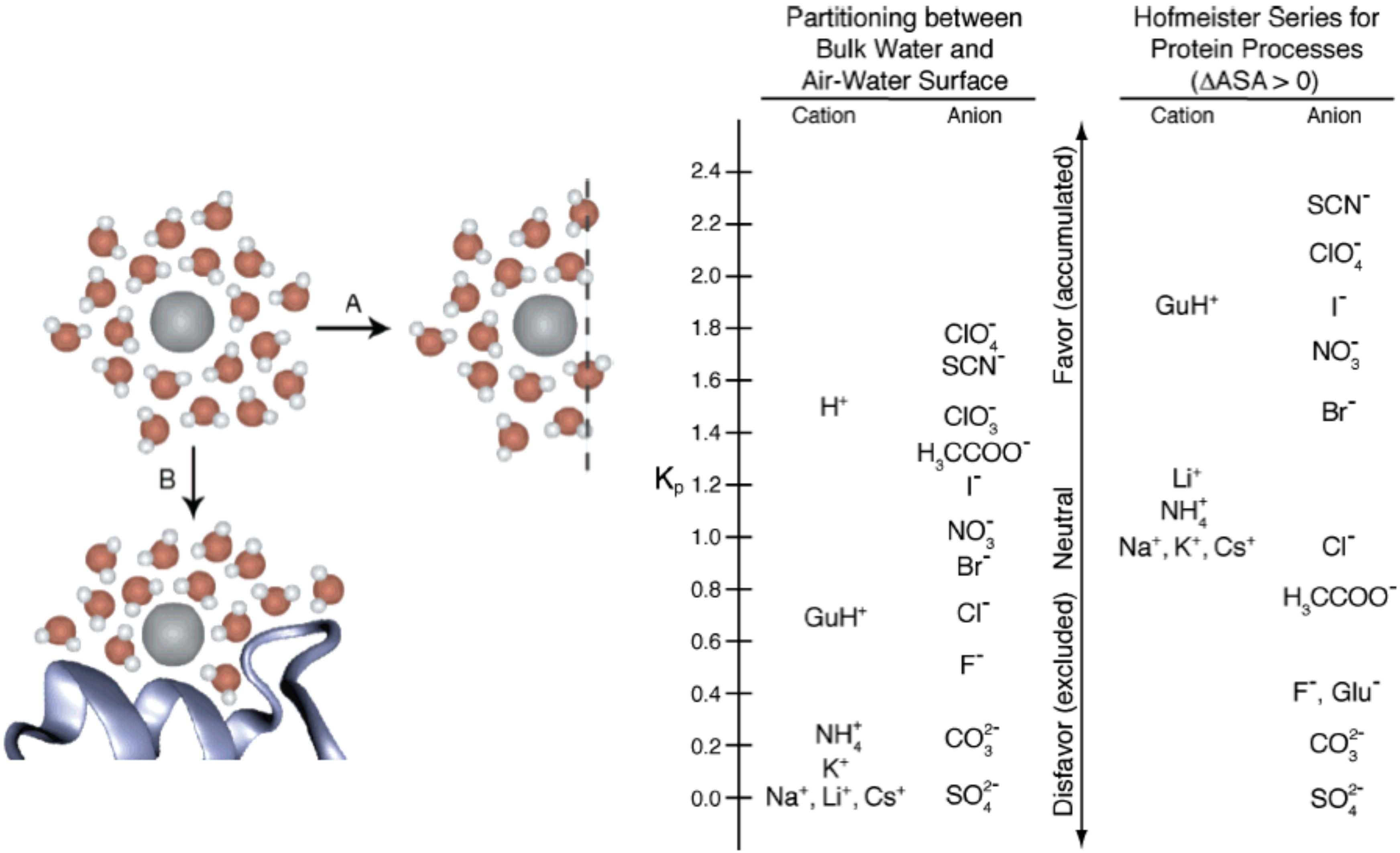


D.E. Otten, P. Shaffer, P. Geissler, R.J. Saykally

"Elucidating the Mechanism of Selective Ion Adsorption to the Liquid Water Surface," PNAS **109** (3), 701-705 (2012).

"SACRIFICES AT THE SURFACE" EDITORS'CHOICE, Science **335**,504(3Feb 2012)

Hofmeister effects correlate with ion adsorption at the air-water interface



Pegram and Record *J. Phys. Chem. B* **2007**, *111*, 5411−5417

~ 40 Phenomena Follow Hofmeister Ordering

K.Collins and M. Washabaugh, *Quarterly Review of Biophysics* 18, 4 (1985).

<u>e.g</u>. ionic partial molar volume at infinite dilution
partial molal compressibilities
thermal conductivity
potential of zero charge for a Hg electrode in aqueous electrolyte
dielectric relaxation time of water
dielectric constant
reaction rates and thermodynamic activation parameters
charge-transfer band of I-
protein solubility
protein denaturation temperature
degree of protein aggregation
EVAPORATION RATES??

Adsorption of Ions to Aqueous Interfaces and its Effects on Water Evaporation Rates

Joint project with Prof. Ron Cohen

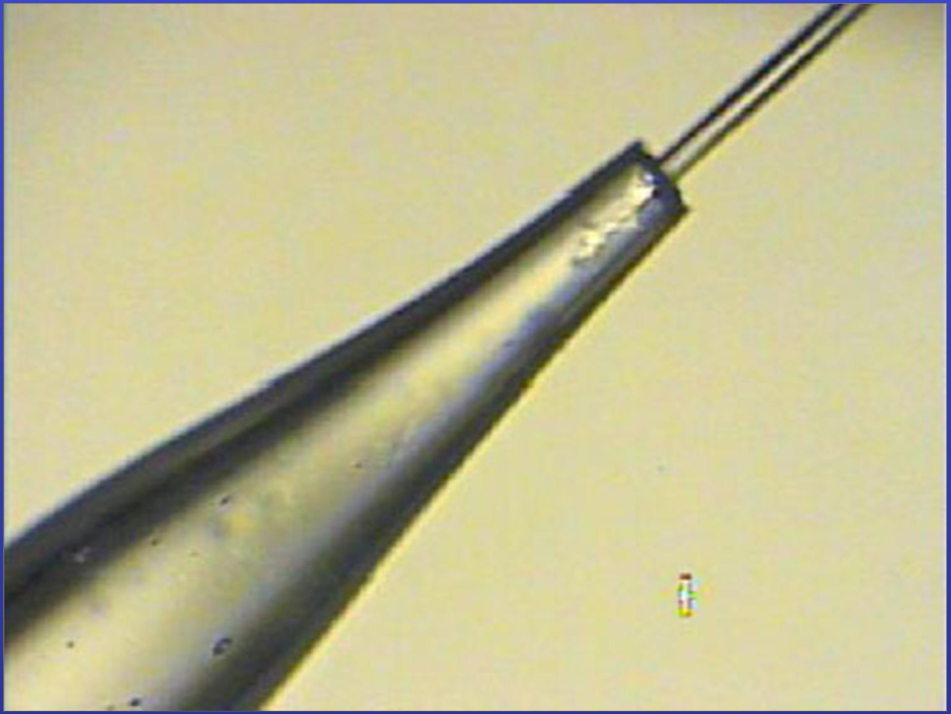
Prof.Chris Cappa(UC-Davis)
Dr. Jared Smith
Dr. Walter Drisdell
Orion Shih
Kaitlin Duffey

The Saykally Group

Water Evaporation

$$J = \gamma_e \frac{p_{sat}}{\sqrt{2\pi mkT}}$$

- Experimental values of evaporation coefficient (γ_e) span 3 orders of magnitude
- Liquid microjets - evaporation without condensation



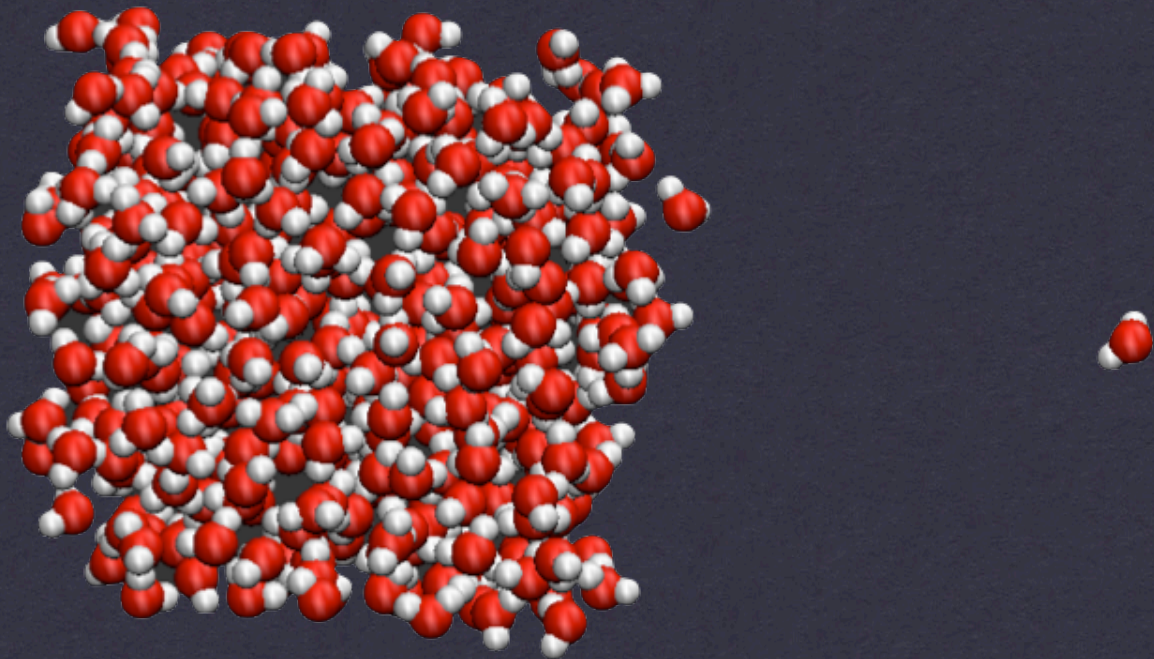
H_2O: $\gamma_e = 0.62 \pm 0.09$

D_2O: $\gamma_e = 0.57 \pm 0.06$

3M $(NH_4)_2SO_4$: $\gamma_e = 0.58 \pm 0.05$

4M $NaClO_4$: $\gamma_e = 0.47 \pm 0.02$

~25% decrease



Towards a molecular mechanism of water evaporation

Evaporation is a Rare Event

- In Molecular terms:
  - *~1 evaporation event / 10 nm^2 / 10 ns……A very rare event!!*
- Essential Question: Molecular Mechanism ???

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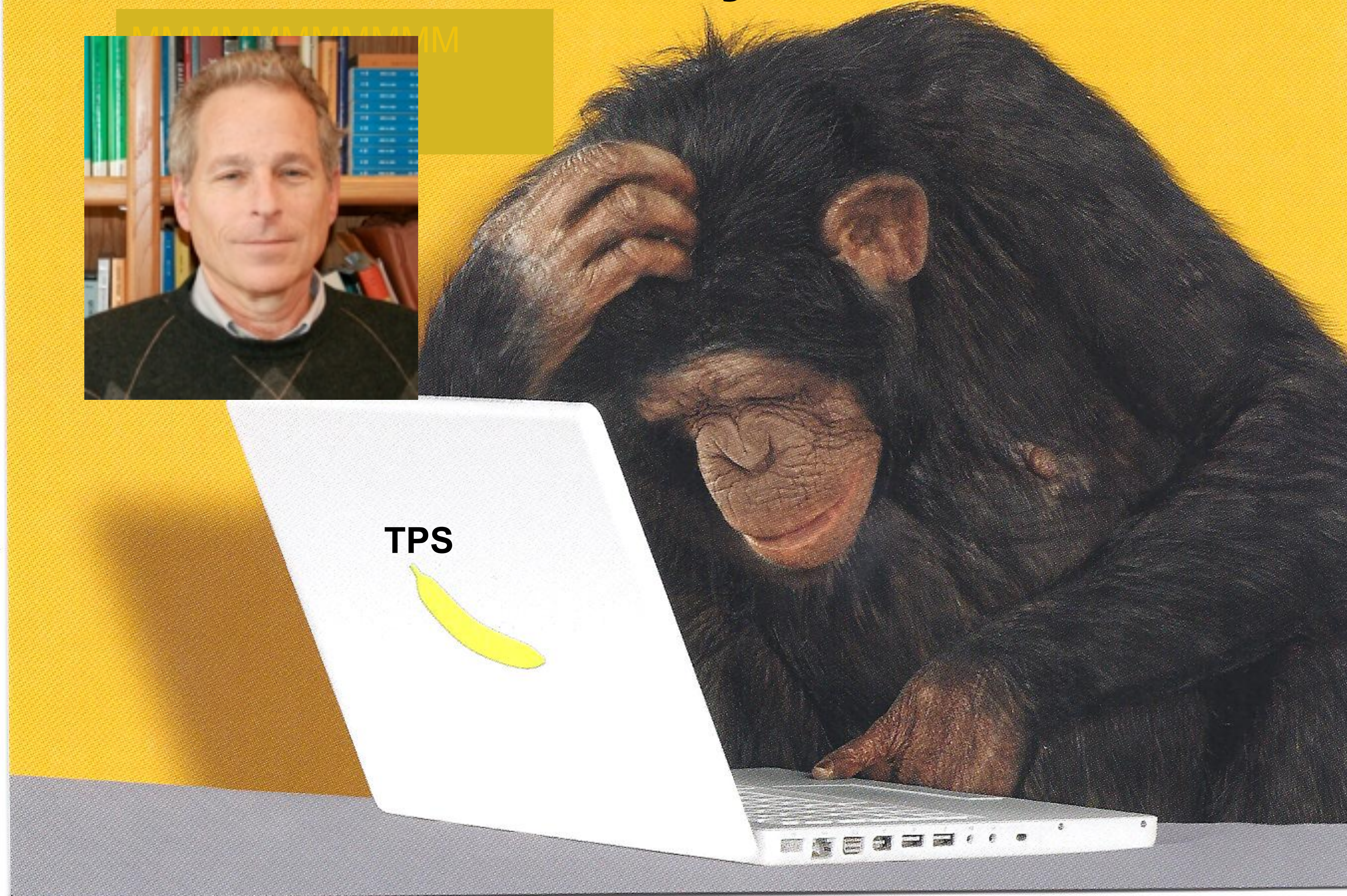
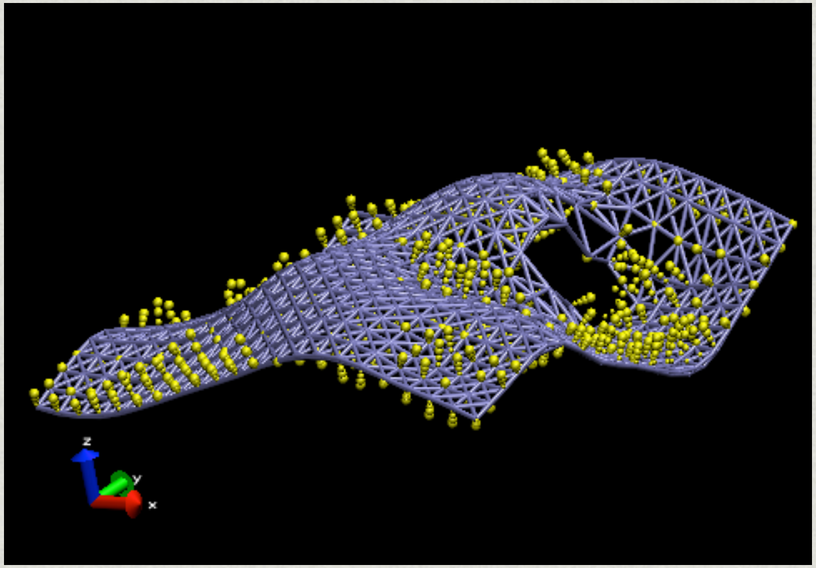
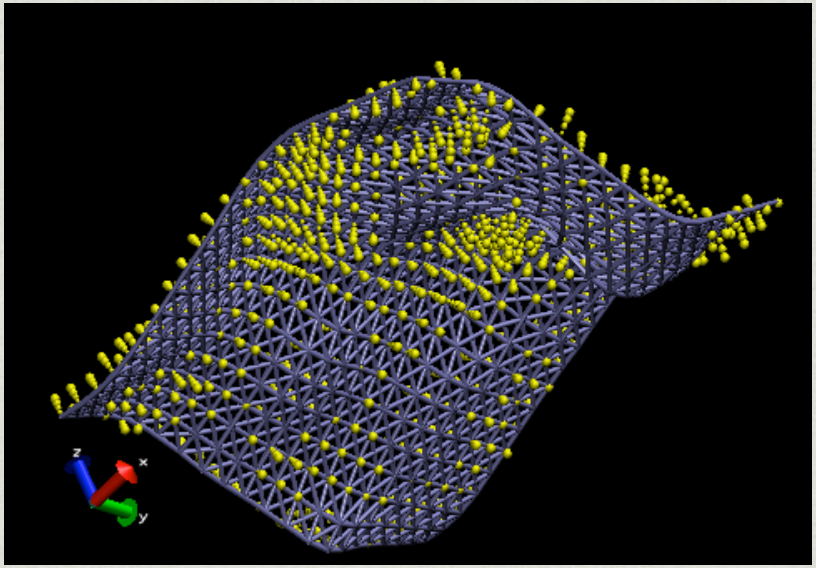


Dr. Patrick Varilly(postdoc-Cambridge)

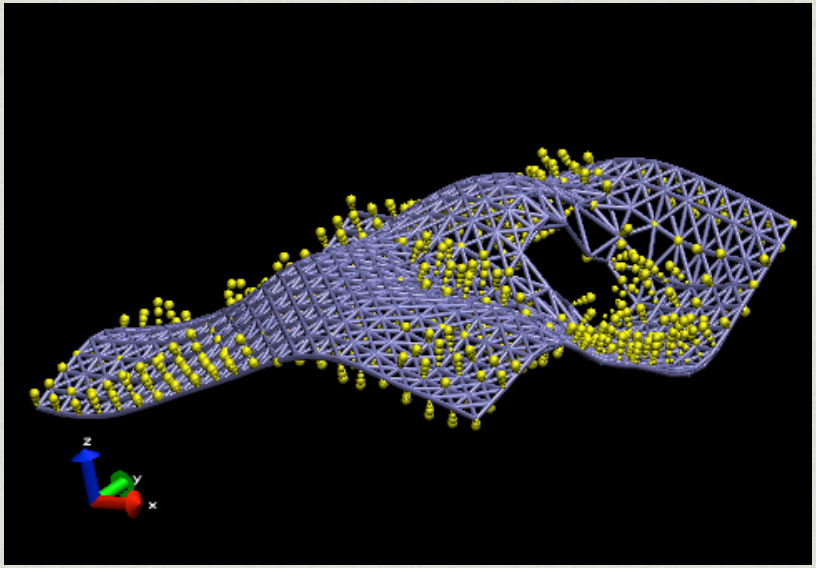
Critical feature: fluctuations of the instantaneous interface ("capillary waves")

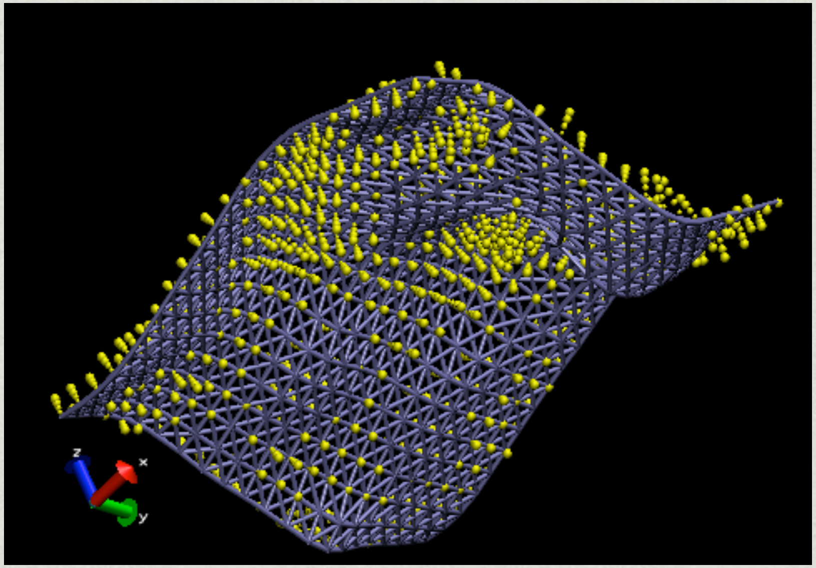




:

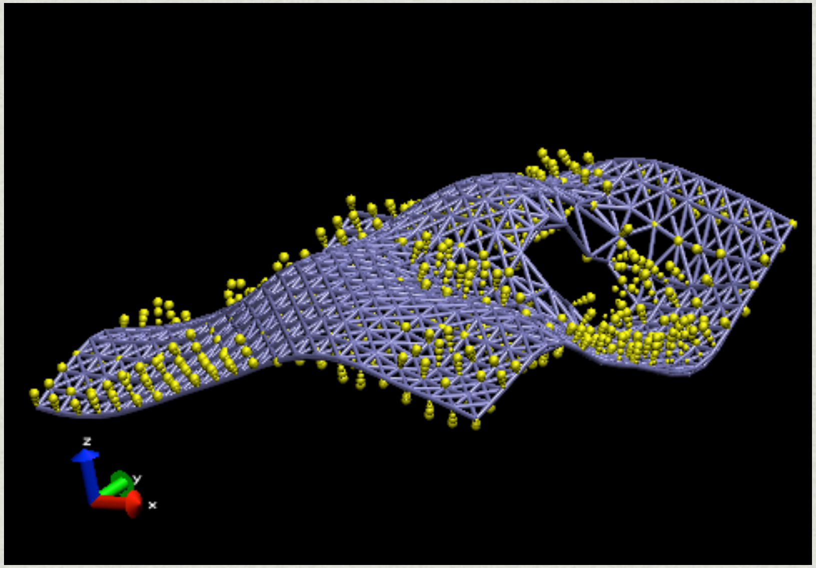
Critical feature: curvature of the instantaneous interface

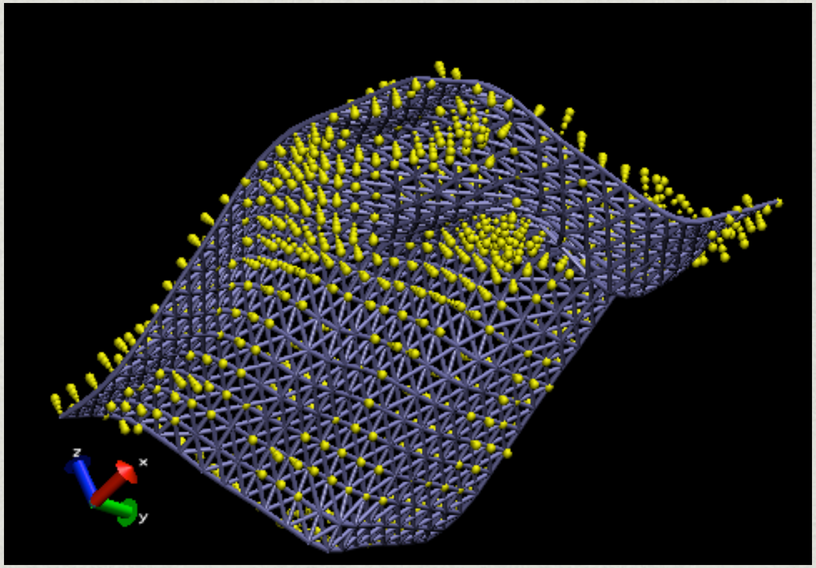




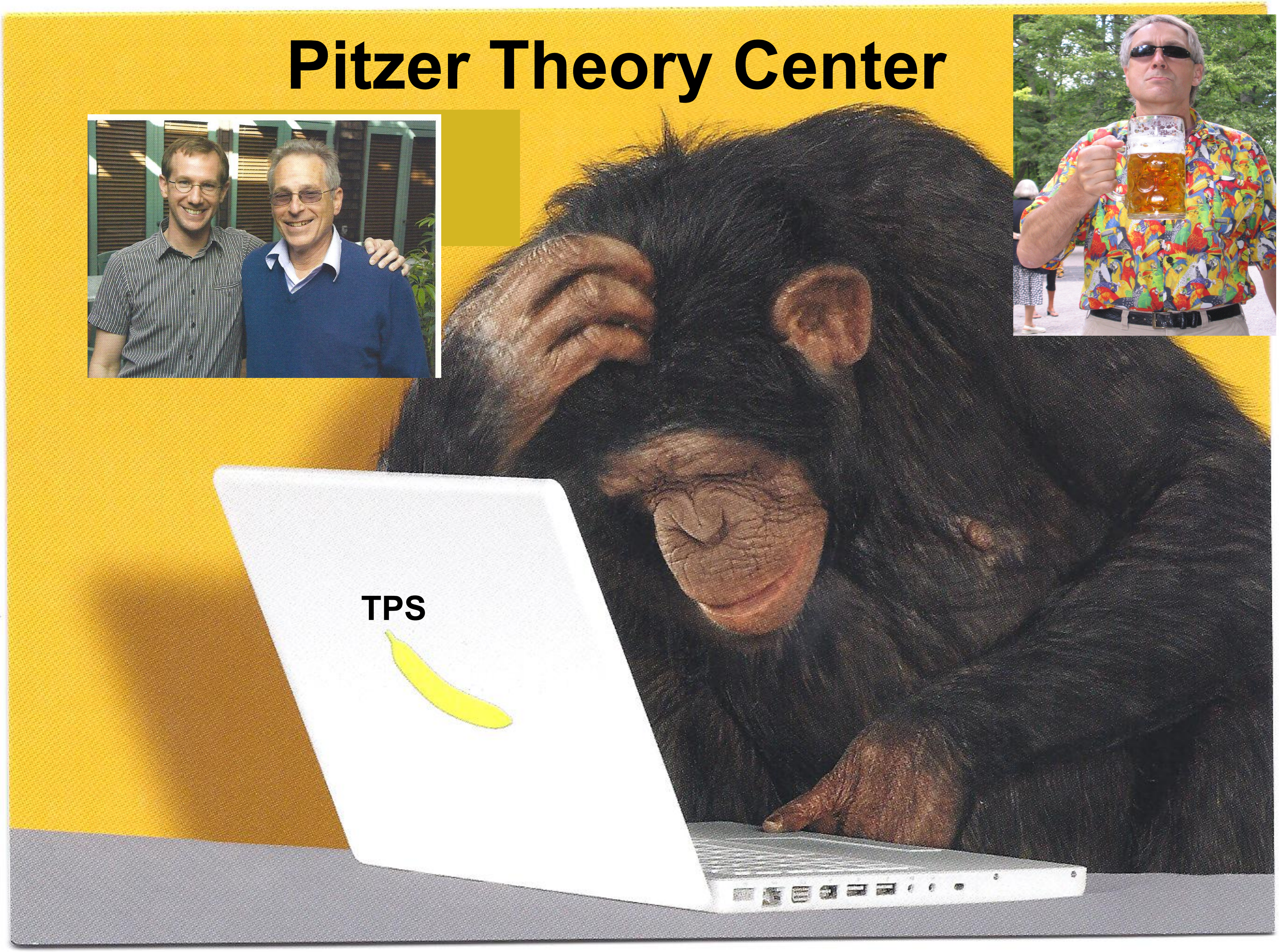
TPS Result: $\gamma_e = 1$???????

Critical feature: suppression of capillary waves for $NaClO_4^-$????





-25% reduction in evap coefficient


Pitzer Theory Center
TPS

Thank$$$ to BE$-DOE for funding thi$$ work!!