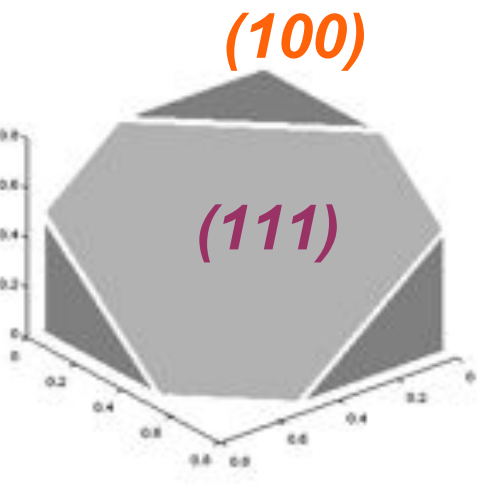
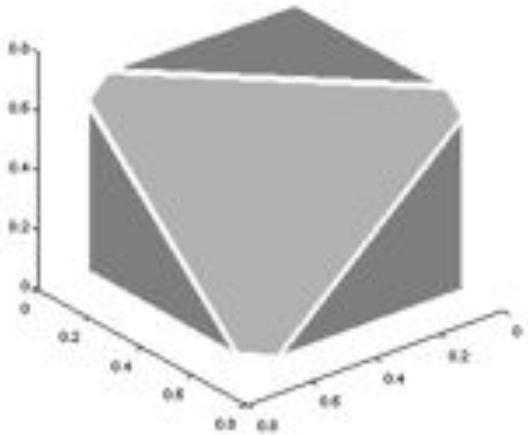
RST-PRINCIPLES PREDICTIONS UNDER REALIST ELECTROCHEMICAL CONDITIONS

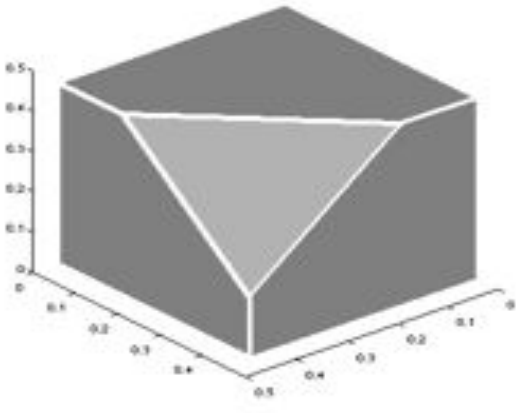
MARZARI, THEORY AND SIMULATION OF MATERIALS, E



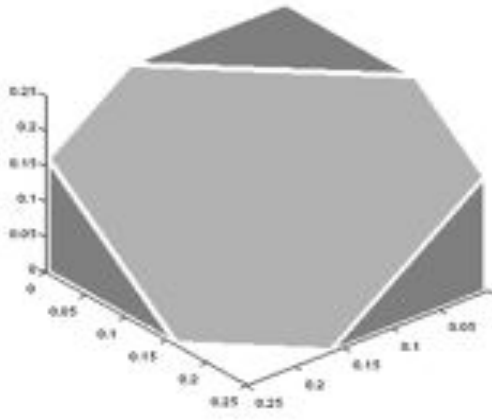
V = 0.4 V/SHE



V = 0.5 V/SHE



V = 0.6 V/SHE



V = 1.0 V/SHE

Credits (continued)

- Damian Scherlis (Universi of Buenos Aires)
- Oliviero Andreussi (University of Pisa)
- Celine Dupont (Universite Bourgogne)
- Matteo Cococcioni (EPFL)

Crowns (Crown Chemist)

Ismaila Dabo (Penn State)

Nicephore Bonnet (AIST Tsukuba)

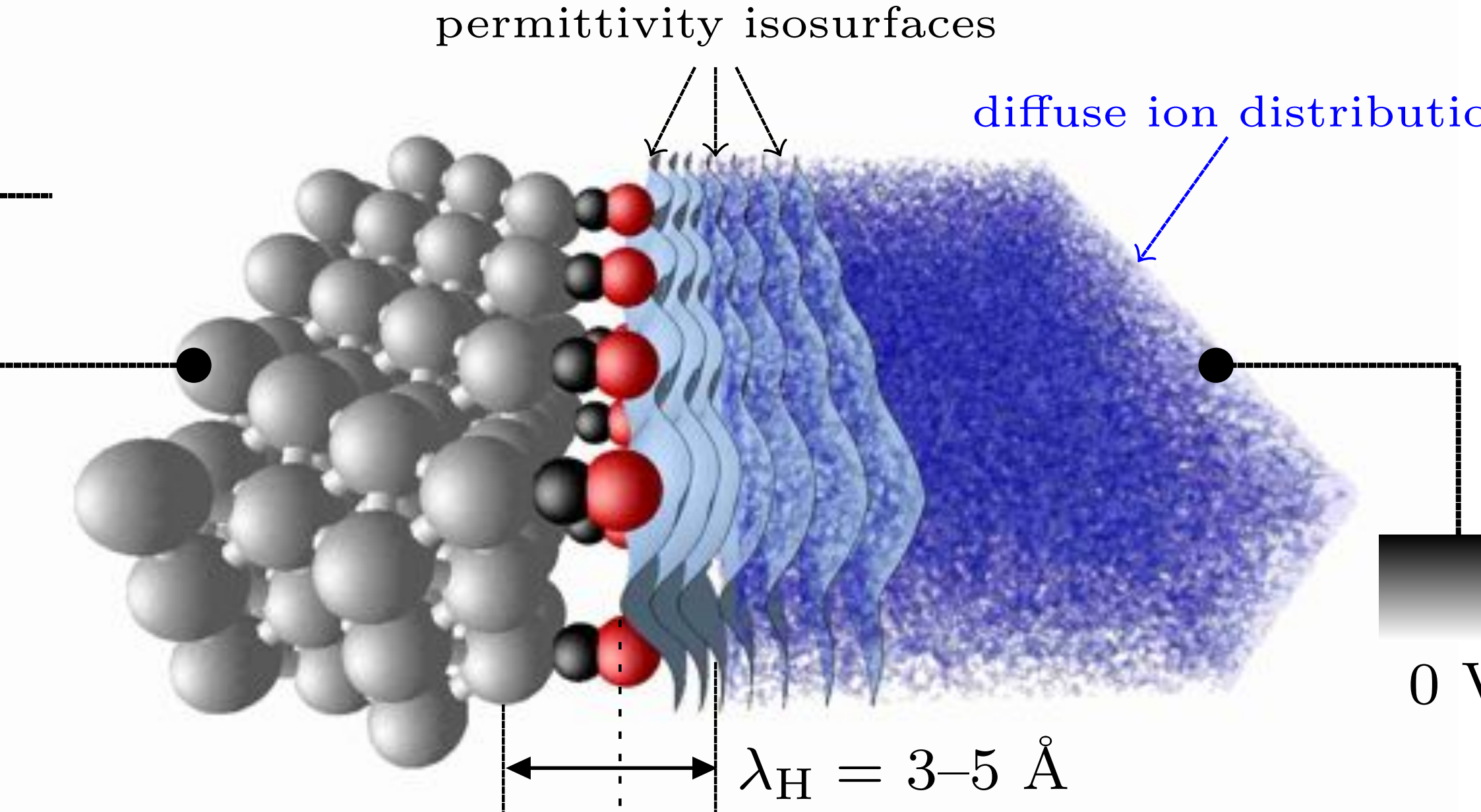
First principles simulations in realistic electrochemical environments

- **Biology:** Many processes take place in salty, watery environments
- **Technology:** Key industrial reactions take place in aqueous solutions or solvents
- **Synthesis:** Growth of nanoparticles and crystals by wet chemistry is strongly influenced by the solvent

First principles simulations in realistic electrochemical environments

- **Energy:** Electrified solid-liquid interfaces are key to harvesting, storing, and converting energy:
  - Photocatalysis in a dye-sensitized solar cell
  - Electrolyte chemistry in a lithium-ion battery
  - Fuel-into-electricity in a fuel cell

First principles simulations in realistic electrochemical environments



Water and solvation

What's wrong with water?

It's a liquid! (need long ab-initio md)

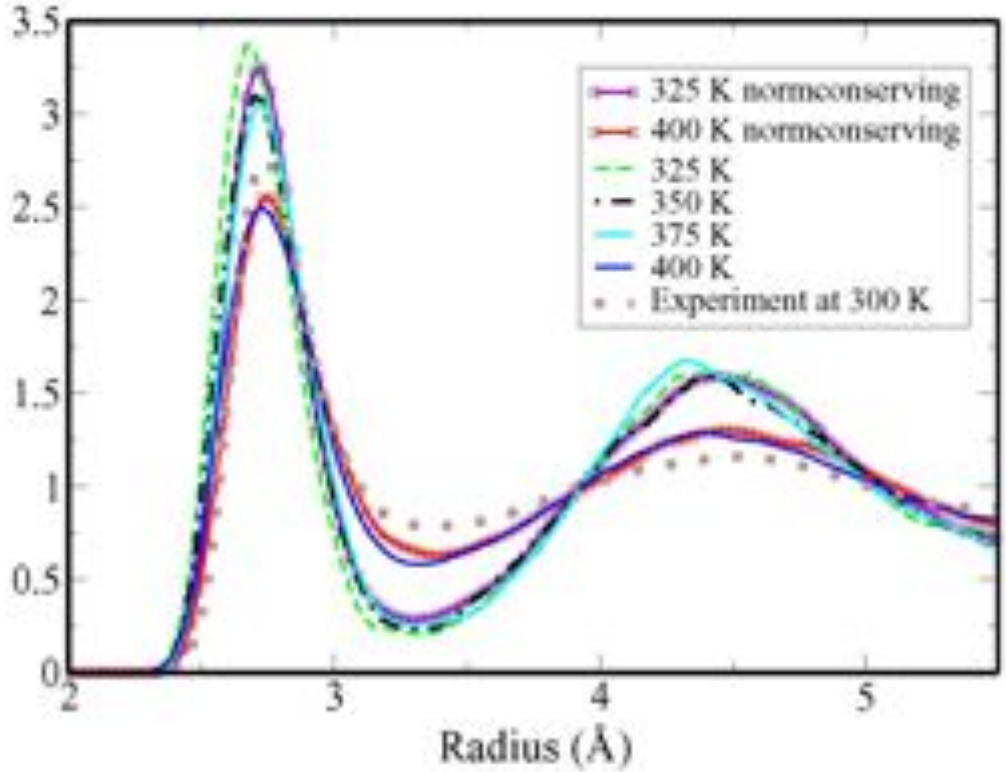
Even its structure is challenging in DFT

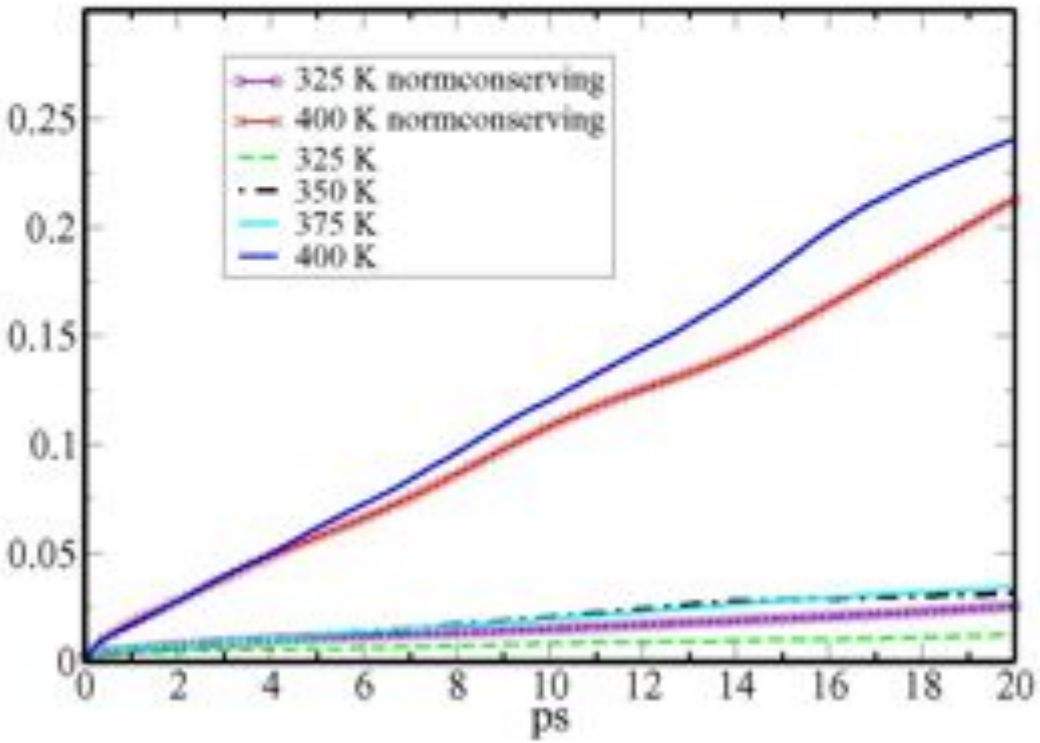
At what temperature does it melt/freeze

What is its dielectric constant?

H is light - tunnelling, Bose-Einstein sta

Water, ice, or glass?

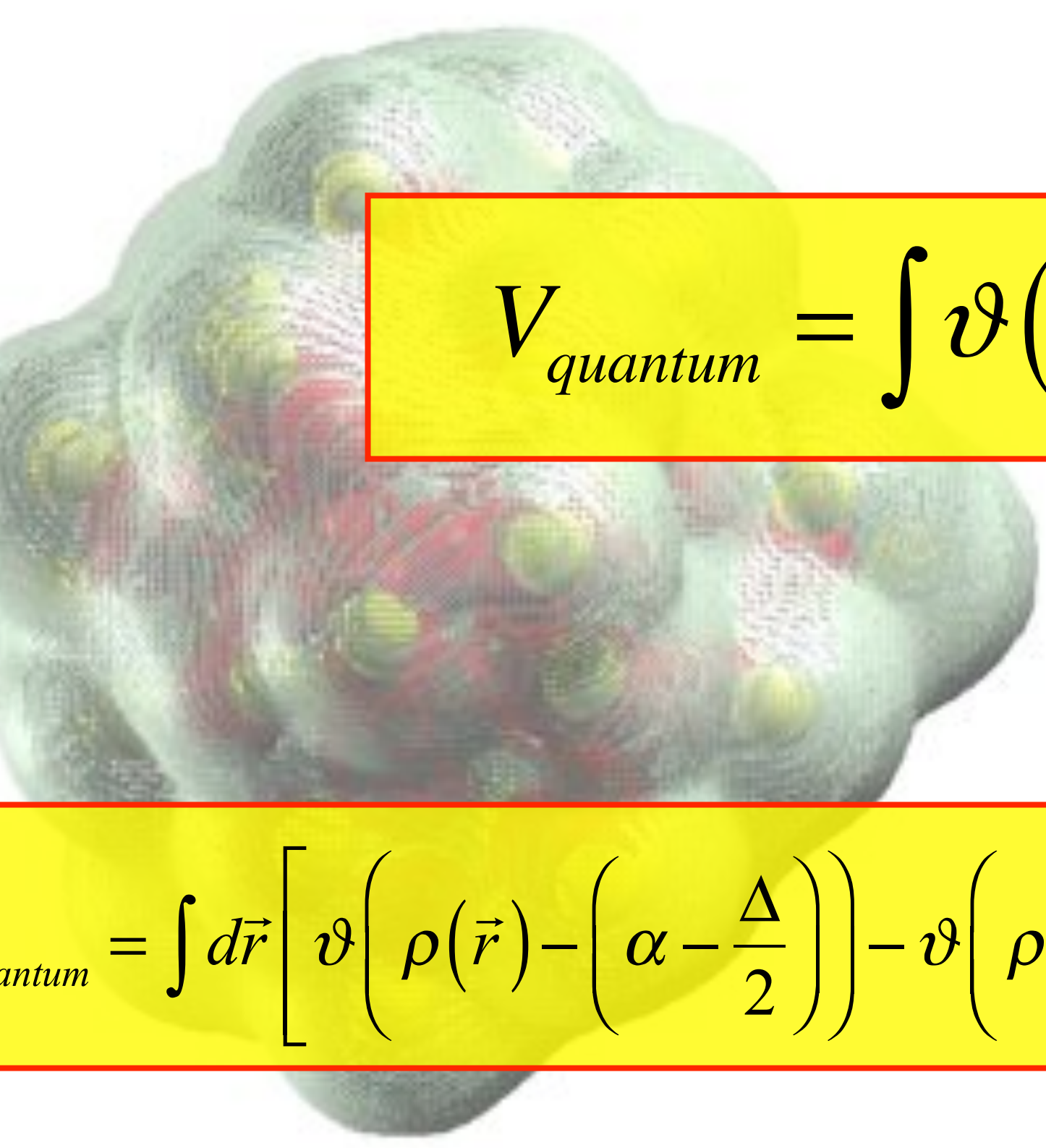




BE water is overstructured

Galli's group, JCP 2004, 2005)

It melts at 400K… (Sit and Marzari, JCP 2005)



$$V_{quantum} = \int \vartheta\left(\rho(\vec{r}) - \alpha\right) d\vec{r}$$

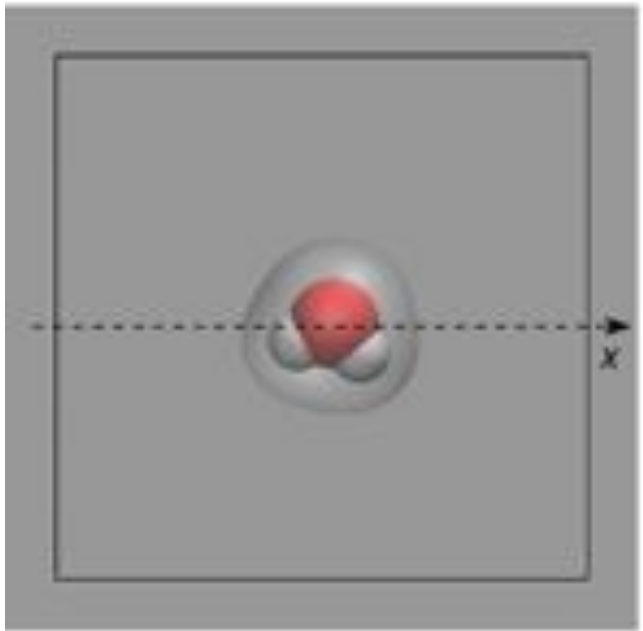
$$\text{antum} = \int d\vec{r}\left[\vartheta\left(\rho(\vec{r}) - \left(\alpha - \frac{\Delta}{2}\right)\right) - \vartheta\left(\rho(\vec{r}) - \left(\alpha + \frac{\Delta}{2}\right)\right)\right]\frac{\left|\vec{\nabla}\rho\right(}{\Delta}$$

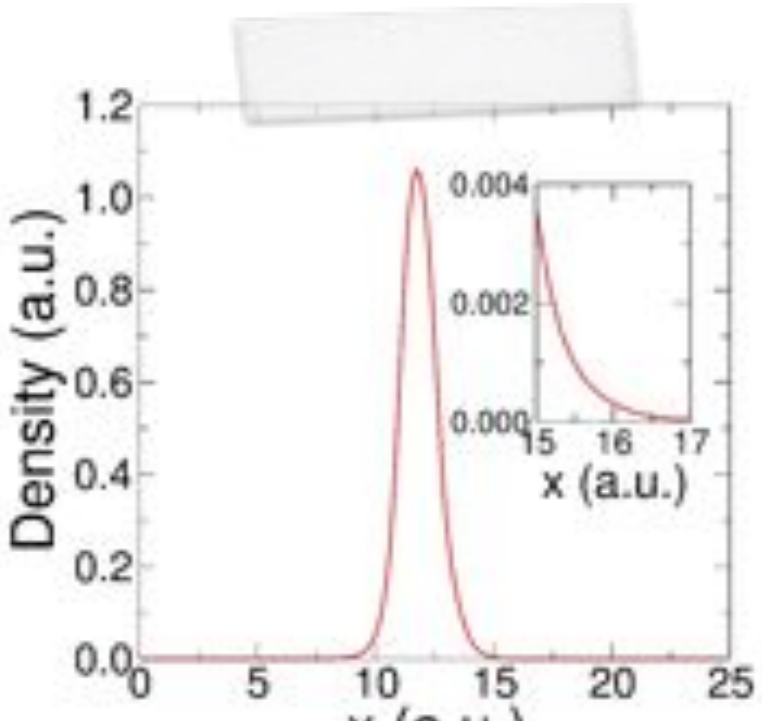
self-consistent continuum solvation mod

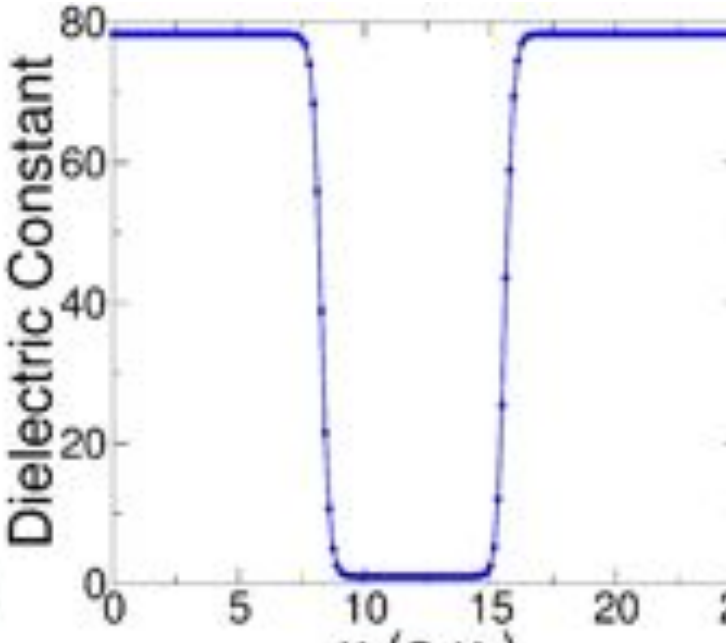
Electrostatics: Poisson equation in a dielectric medium

$$\nabla^2 V(\vec{r}) = -4\pi\rho(\vec{r}) \quad \rightarrow \quad \vec{\nabla}\cdot\left(\varepsilon\left[\rho(\vec{r})\right]\vec{\nabla}V(\vec{r})\right) = -4\pi\rho(\vec{r})$$

J.-L. Fattebert and F. Gygi, Int. J. Quantum Chem. 93, 139 (2003)







self-consistent continuum solvation mod

Electrostatics: Poisson equation in a dielectric medium

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J.-L. Fattebert and F. Gygi, Int. J. Quantum Chem. 93, 139 (2003)

Non-electrostatics (cavitation, etc…)

$$E \rightarrow E + \alpha S^{\left[\rho(\vec{r})\right]}_{quantum} + \beta V^{\left[\rho(\vec{r})\right]}_{quantum}$$

D.A. Scherlis, J.-L. Fattebert, F. Gygi, M. Cococcioni, and N. Marzari JCP 124, 074103 (2006)

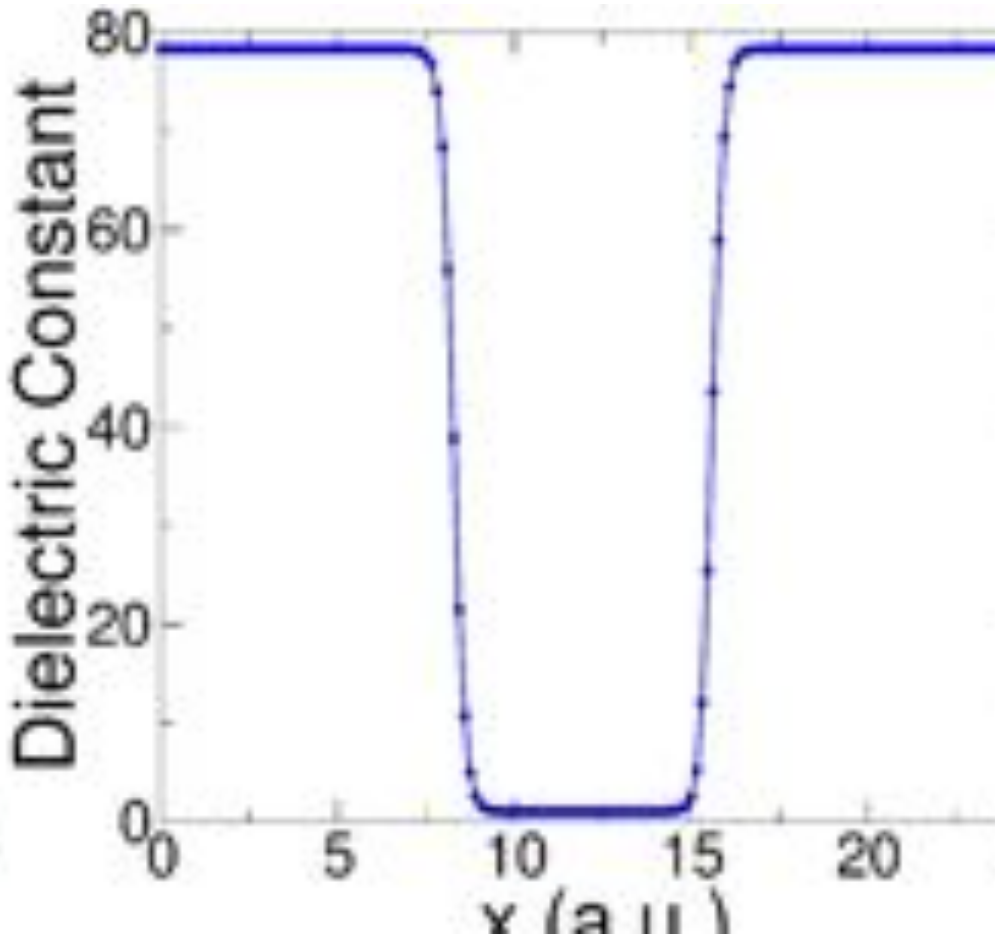
O. Andreussi, I. Dabo, and N. Marzari, JCP 136, 064102 (2012)

Parameters in the model

$$E \rightarrow E^{\left[\varepsilon\left(\rho\left(\vec{r}\right)\right)\right]} + \alpha S^{\left[\rho\left(\vec{r}\right)\right]}_{quantum} + \beta V^{\left[\rho\left(\vec{r}\right)\right]}_{quantum}$$

ree/four parameters:

- **2 parameters for dielectric function**
- **1 or 2 parameters for non-electrostatic terms (proportional to quantum volume and quantum surface)**



Generalized Poisson equation: from multigrid to iterative

$$\nabla \cdot \epsilon\left(\rho^{elec}\left(\mathbf{r}\right)\right) \nabla \phi^{tot}\left(\mathbf{r}\right) = -4\pi\rho^{solute}\left(\mathbf{r}\right)$$

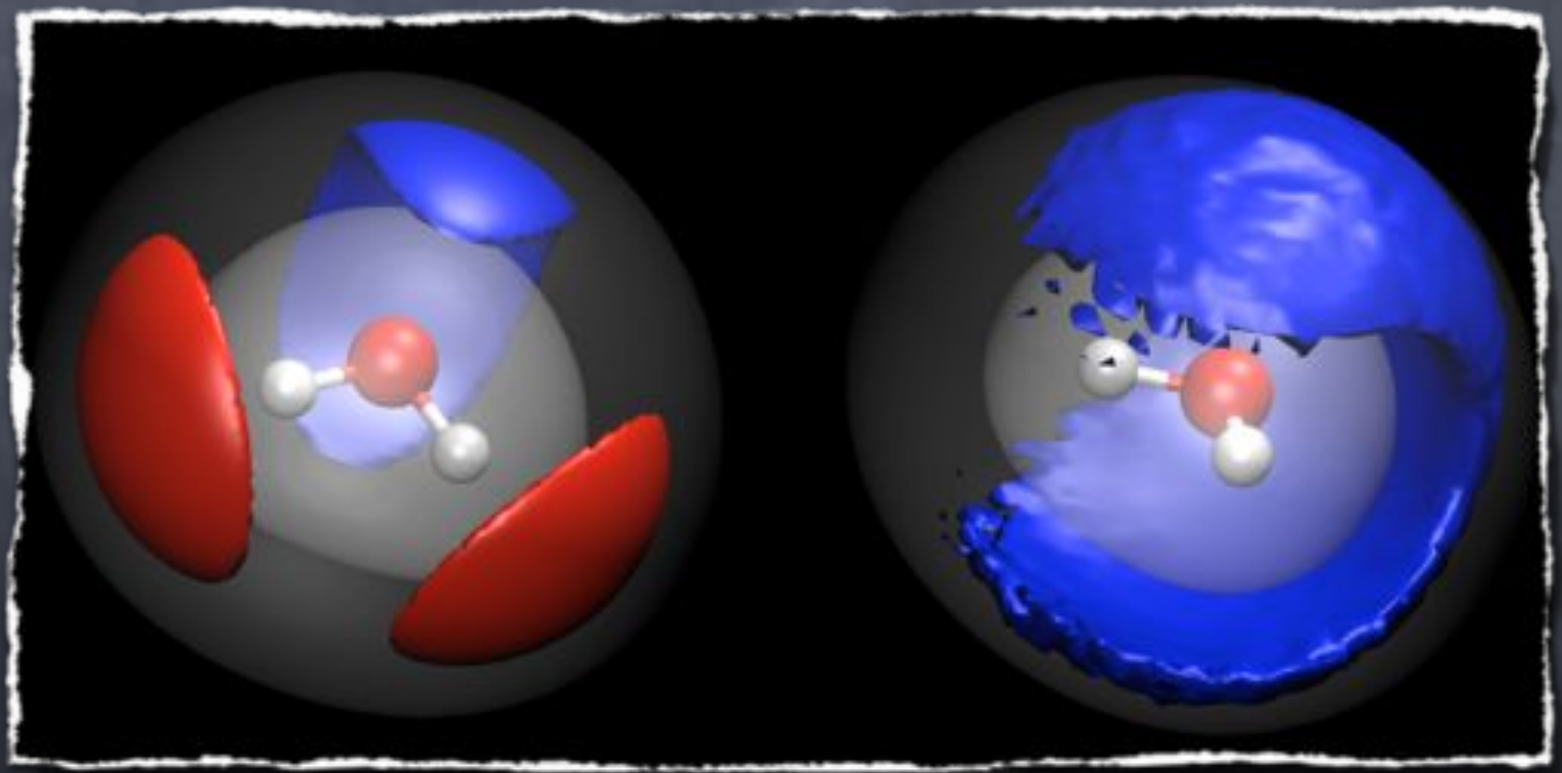
$$\rho^{pol}\left(\mathbf{r}\right) \equiv -\nabla \cdot \mathbf{P}\left(\mathbf{r}\right) = \nabla \cdot \left(\frac{\epsilon\left(\rho^{elec}\left(\mathbf{r}\right)\right) - 1}{4\pi} \nabla \phi^{tot}\left(\mathbf{r}\right) \right)$$

$$\nabla^2 \phi^{tot}\left(\mathbf{r}\right) = -4\pi\left(\rho^{solute}\left(\mathbf{r}\right) + \rho^{pol}\left(\mathbf{r}\right)\right)$$

Polarization charges

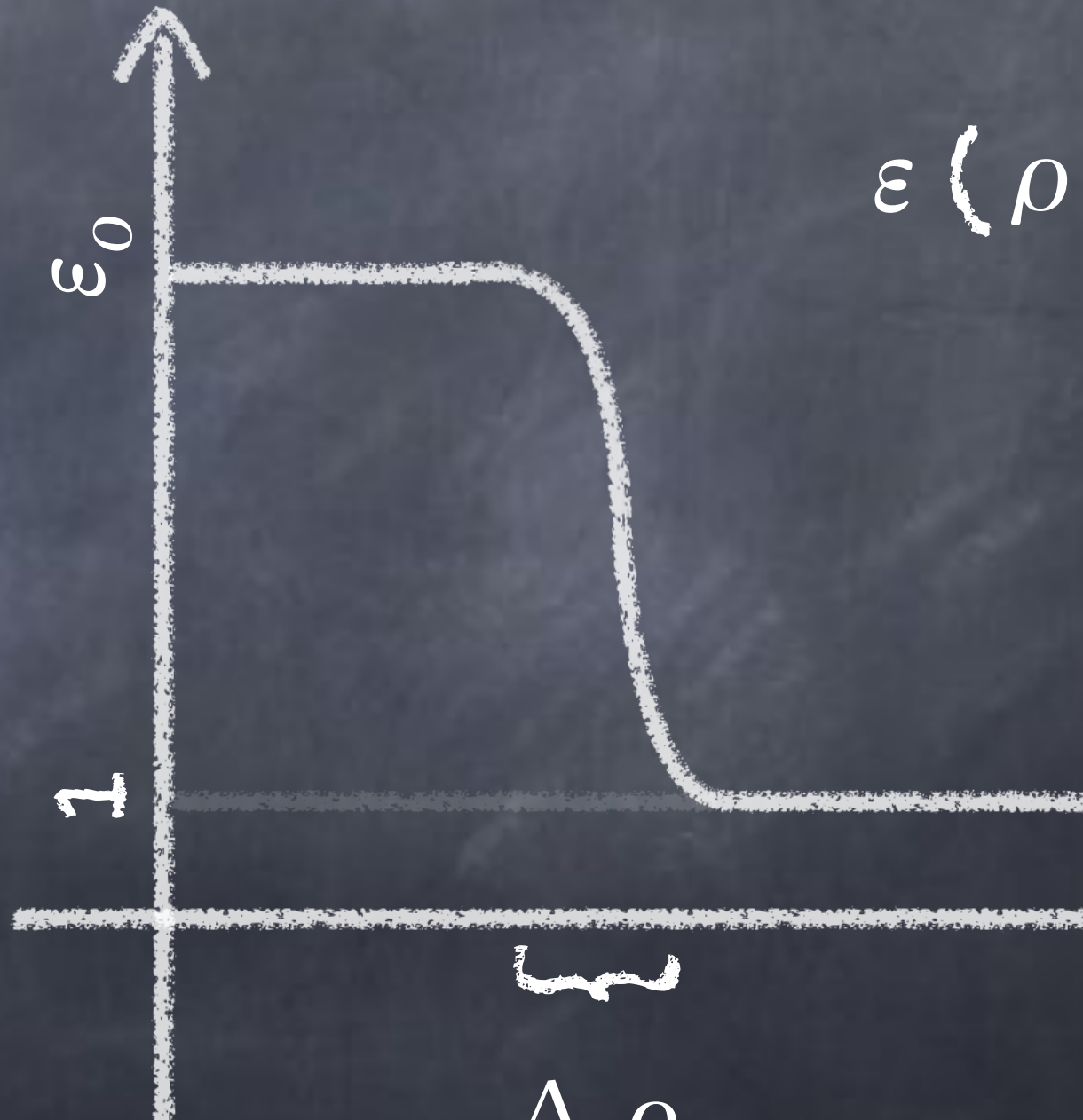
wo contributions

$$\rho^{pol}(\mathbf{r}) = \frac{1}{4\pi}\nabla \ln \epsilon\left(\rho^{elec}(\mathbf{r})\right) \cdot \nabla \phi^{tot}(\mathbf{r}) - \frac{\epsilon\left(\rho^{elec}(\mathbf{r})\right) - 1}{\epsilon\left(\rho^{elec}(\mathbf{r})\right)} \rho^{solute}(\mathbf{r})$$



Which dielectric function?

- Extrema: $1, \varepsilon_0$
- Flat in the solute
- Flat in the bulk dielectric
- Smooth

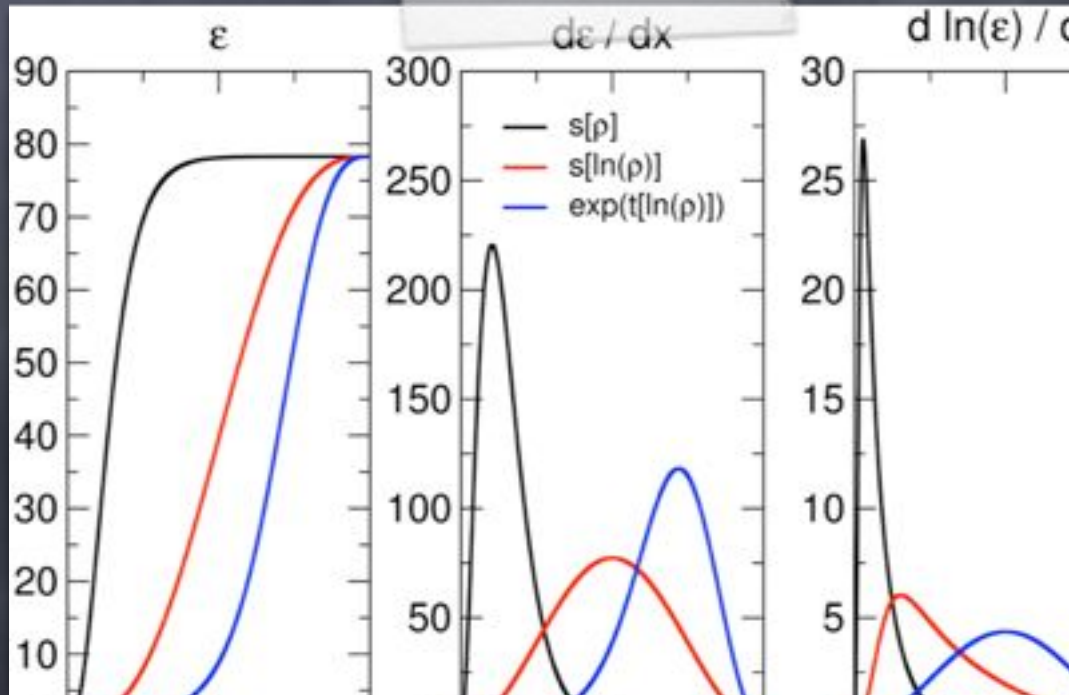


Avoid numerical instabilities

- Smooth piece-wise definition
- But: Electronic density decays exponentially
- Polarization charge is a function of the gradient of the logarithm of epsilon

$$\epsilon_{\epsilon_0,\rho_{min},\rho_{max}}\left(\rho^{elec}\right) = \begin{cases} 1 & \rho^{elec} > \rho_{max} \\ \exp\left(t\left(\ln \rho^{elec}\right)\right) & \rho_{min} < \rho^{elec} < \\ \epsilon_0 & \rho^{elec} < \rho_{min} \end{cases}$$

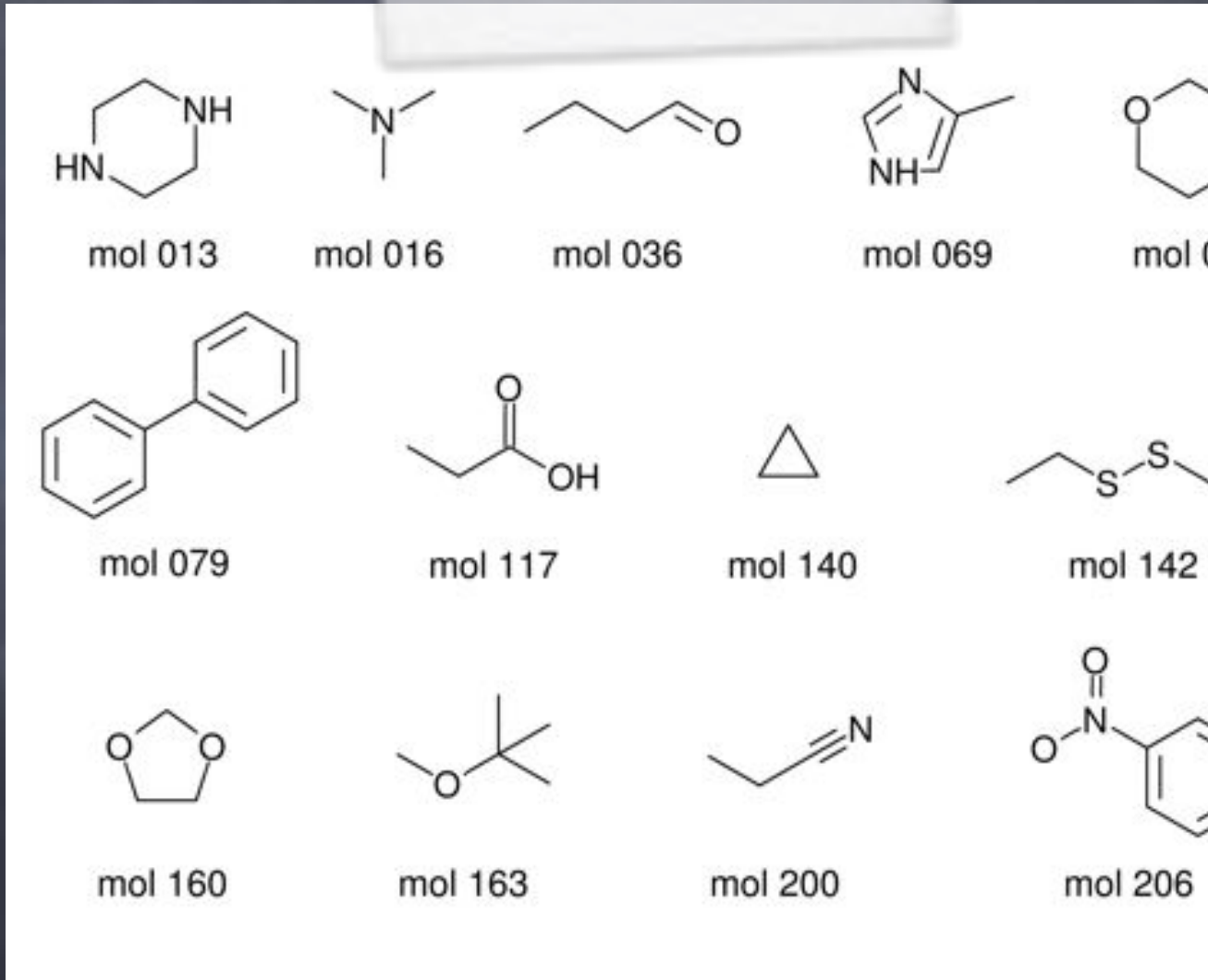
$$t\left(x\right) = \frac{\ln \epsilon_0}{2\pi}\left[2\pi\frac{\left(\ln \rho_{max} - x\right)}{\left(\ln \rho_{max} - \ln \rho_{min}\right)} - \sin\left(2\pi\frac{\left(\ln \rho_{max} - \right.\right.\right.$$



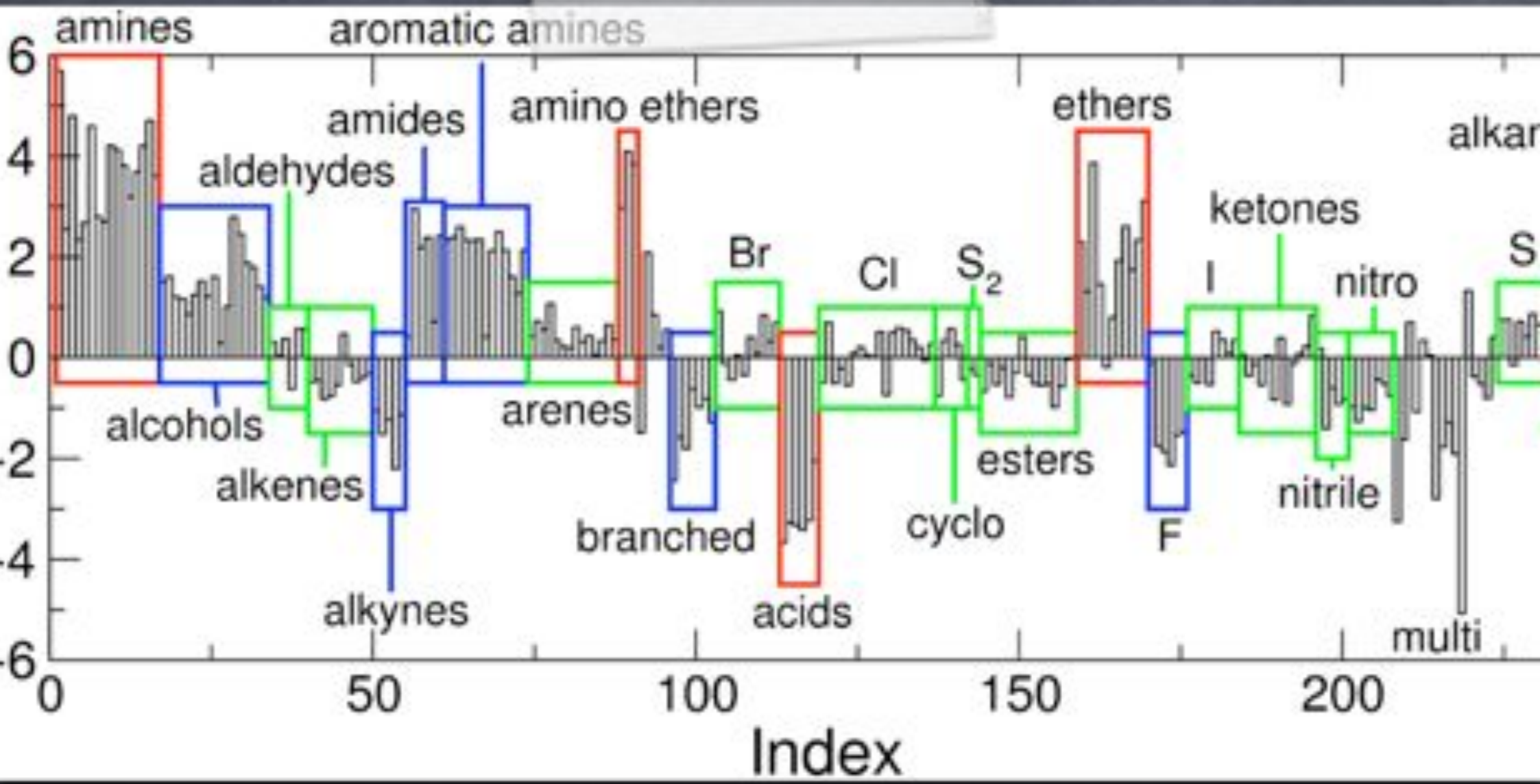
Parameter fitting

Cavity parameters to reproduce electrostatic solvation energy of PCM

Non-electrostatic parameters to reproduce total solvation free energies



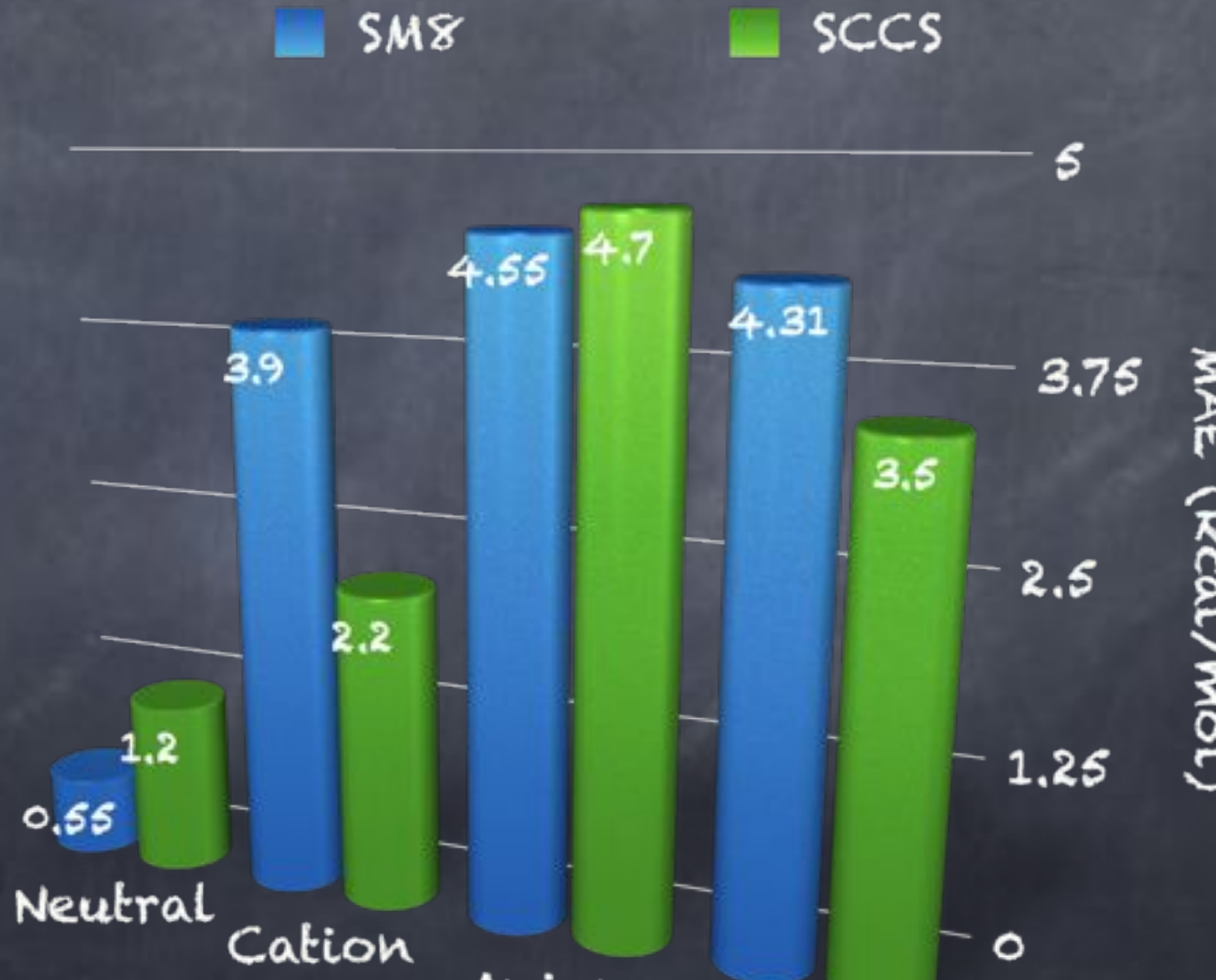
on 240 solvation energies)



charged systems

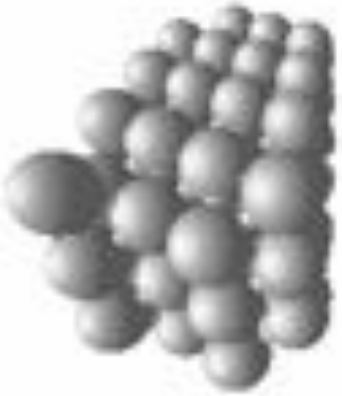
xcellent results
or cations (MAE
2.2 kcal/mol)

ery good results
or anion, with
parametrization
IAE ~4.7 kcal/
ol)



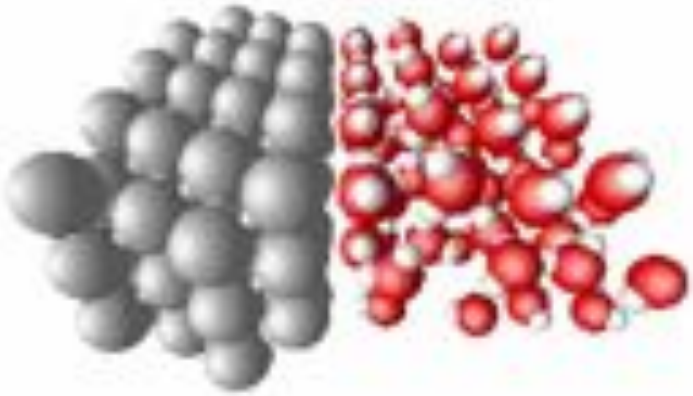
Multiscale electrochemical model

(a) Work function Φ



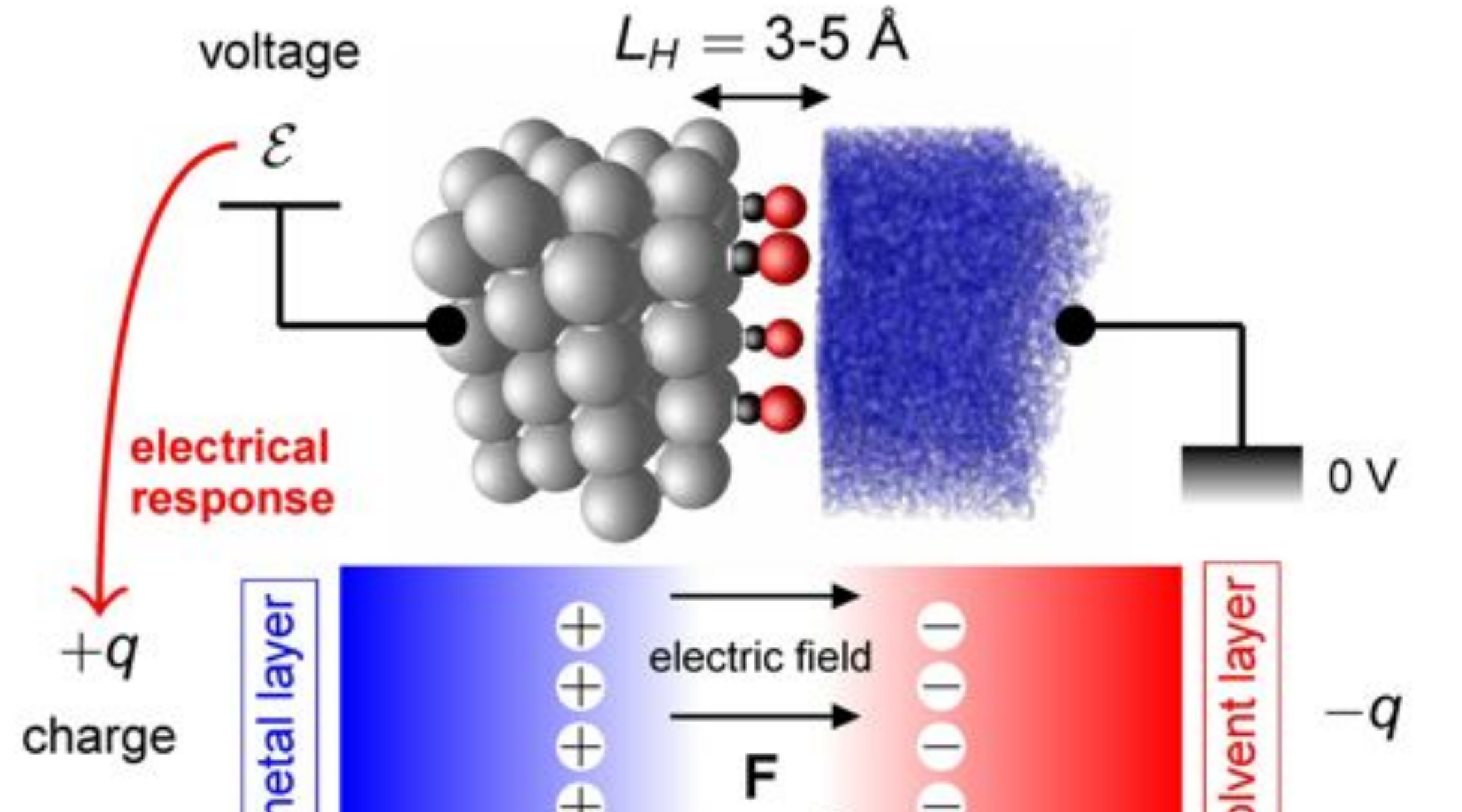
vacuum

(b) Electrode potential $\mathcal{E}$



1. **Work Function**: Difference between the Fermi energy and the vacuum reference energy ($q = 0$ only)
2. **Electrode Potential**: Difference between the Fermi energy and

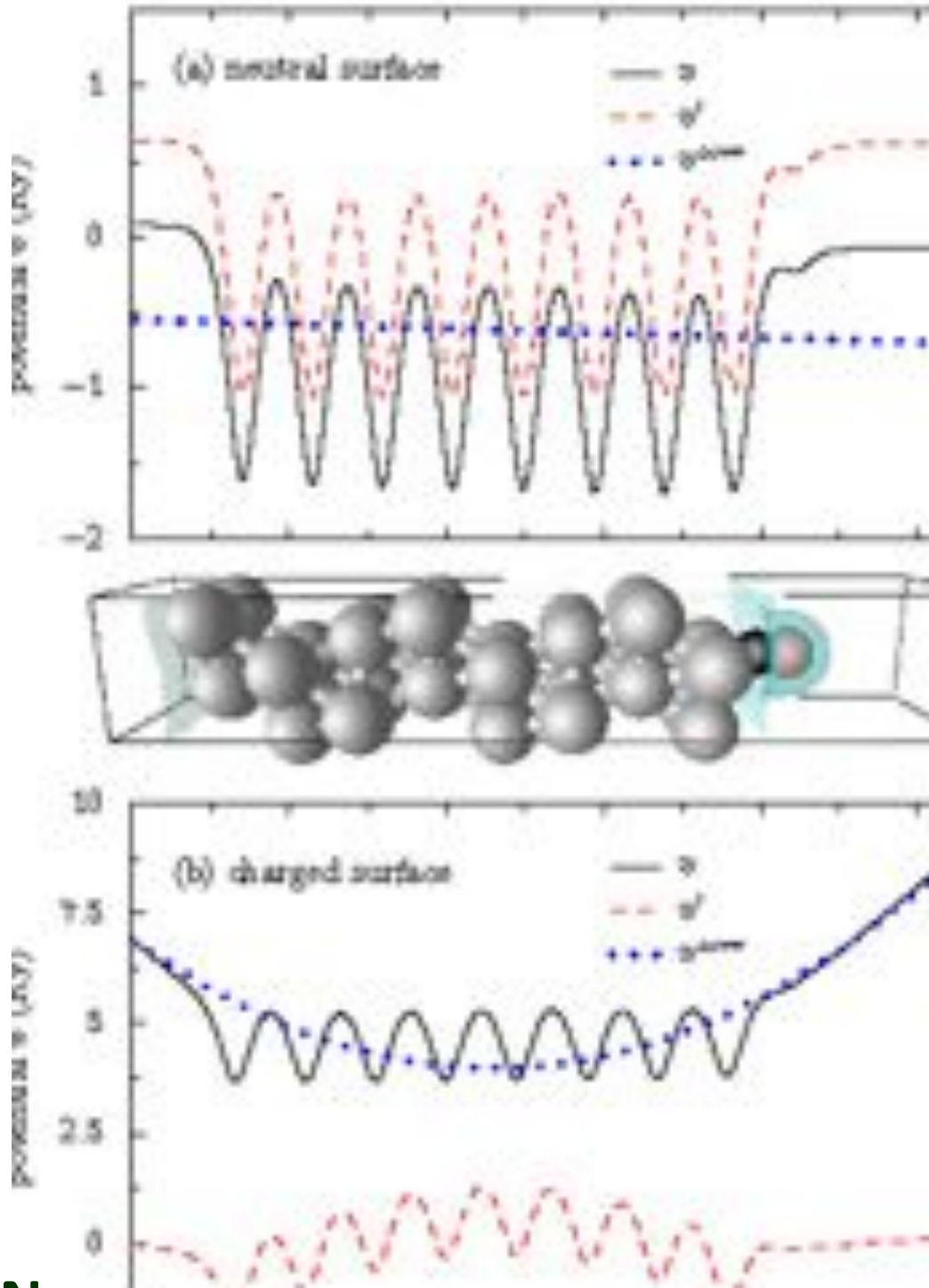
he electrode potential is measured from the screened respo
to charging coming from the quantum, solvent, and counteri
fields (also the opposite could be done – at fixed potential

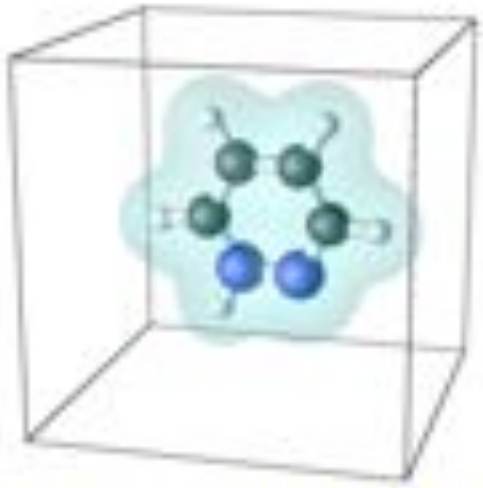


$$d^2v/dz^2 = -4\pi\rho$$

$$- \quad d^2v'/dz^2 = -4\pi(\rho - \langle\rho\rangle)$$

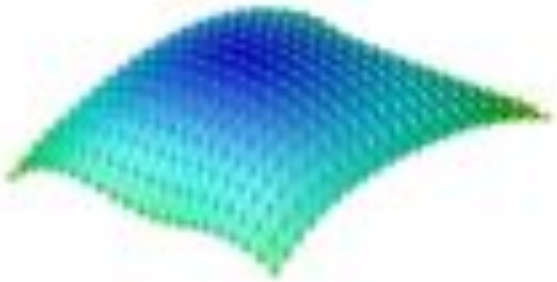
$$d^2v^{corr}/dz^2 = -4\pi\langle\rho\rangle$$

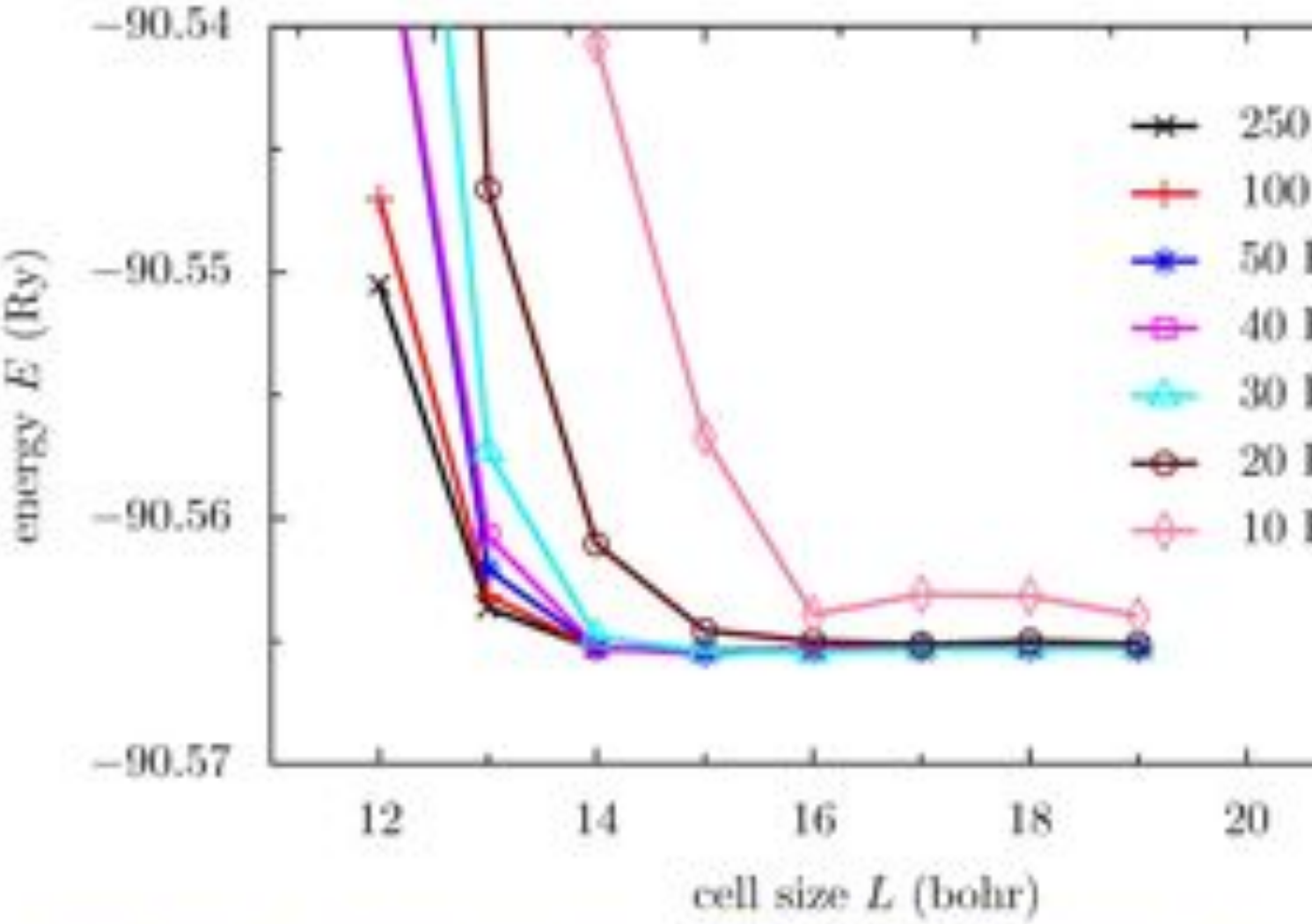




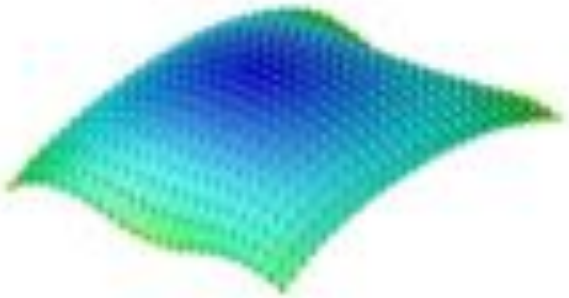
E^{cont} = 10 Ry (13 × 13 × 13)

E^{cont} = 20 Ry (21 × 21 × 21)

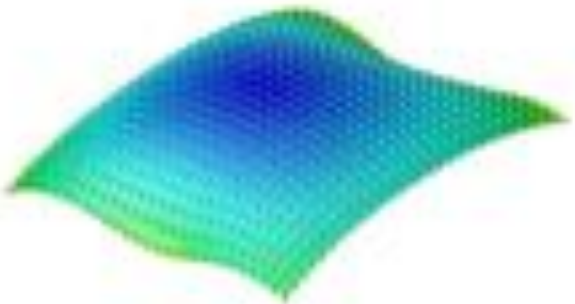




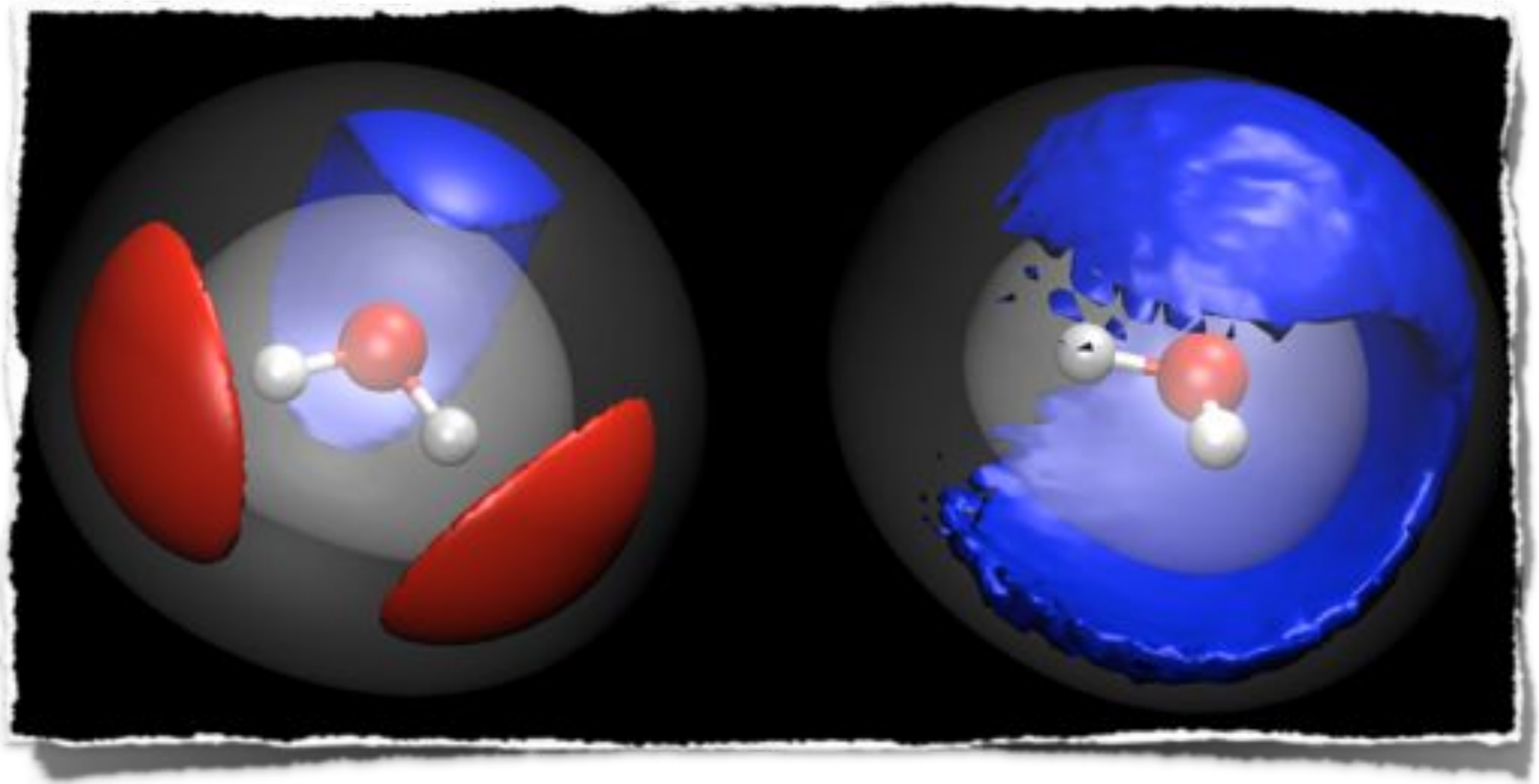
E^{cont} = 30 Ry (25 × 25 × 25)



E^{cont} = 40 Ry (29 × 29 × 29)



Second ingredient: SCCS (self-consistent continuum solvation)



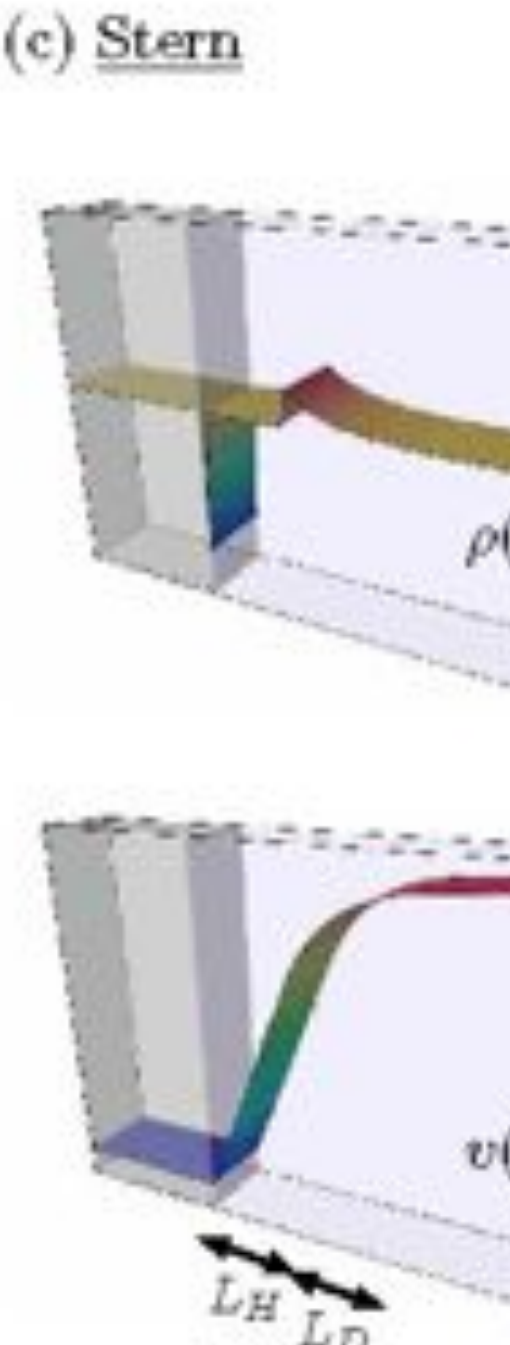
d ingredient: self-consistent field of counteri (Guoy-Chapmann-Stern)

$$\nabla \cdot \epsilon \nabla v^{corr} = -4\pi(\langle \rho \rangle + \rho'_p + \rho_d)$$

$$\rho'_p = \nabla \cdot \chi \nabla v'$$

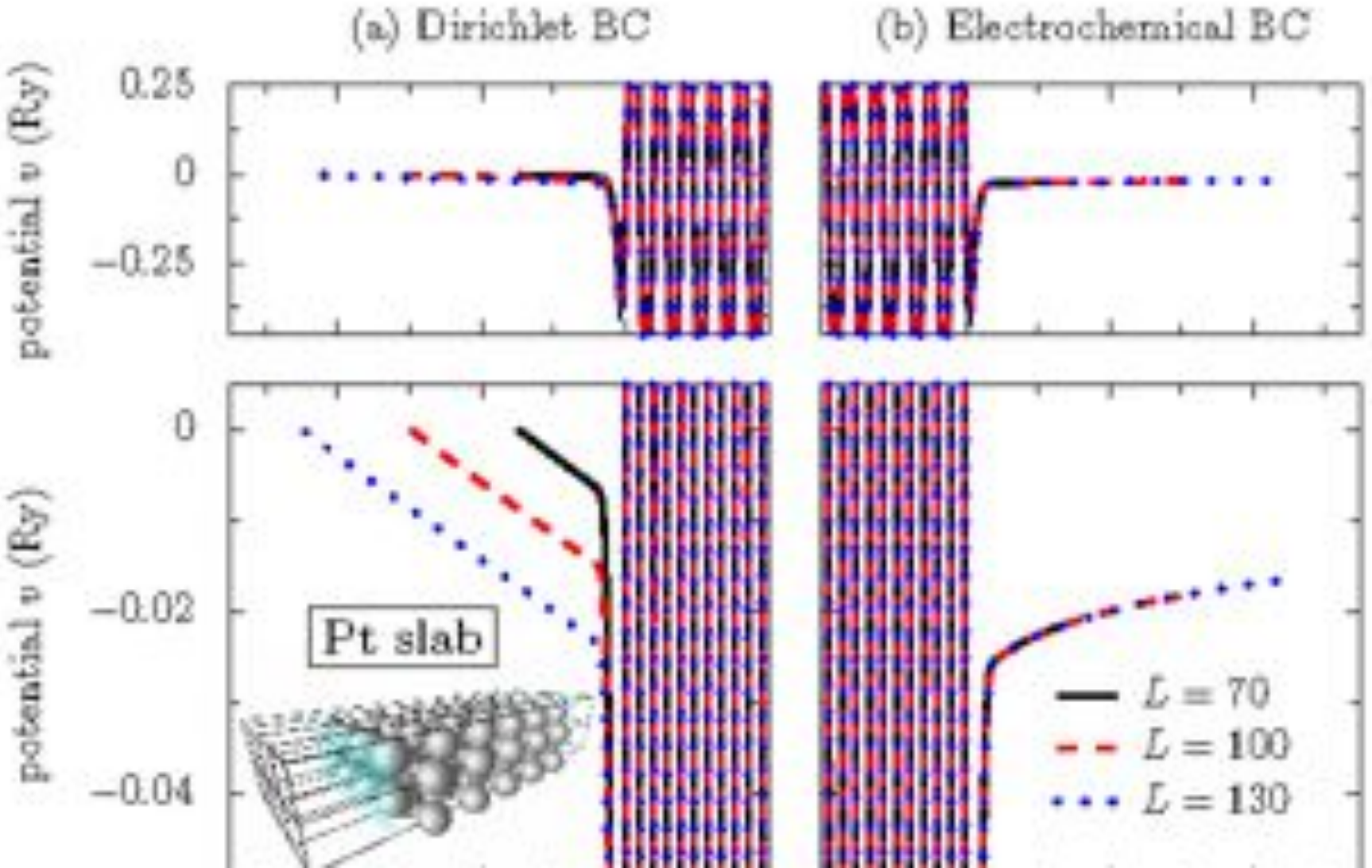
$$\rho_d = z_d c_d \left(e^{-\frac{z_d v}{k_B T}} - e^{+\frac{z_d v}{k_B T}} \right) \text{ if } \rho < \rho_1$$

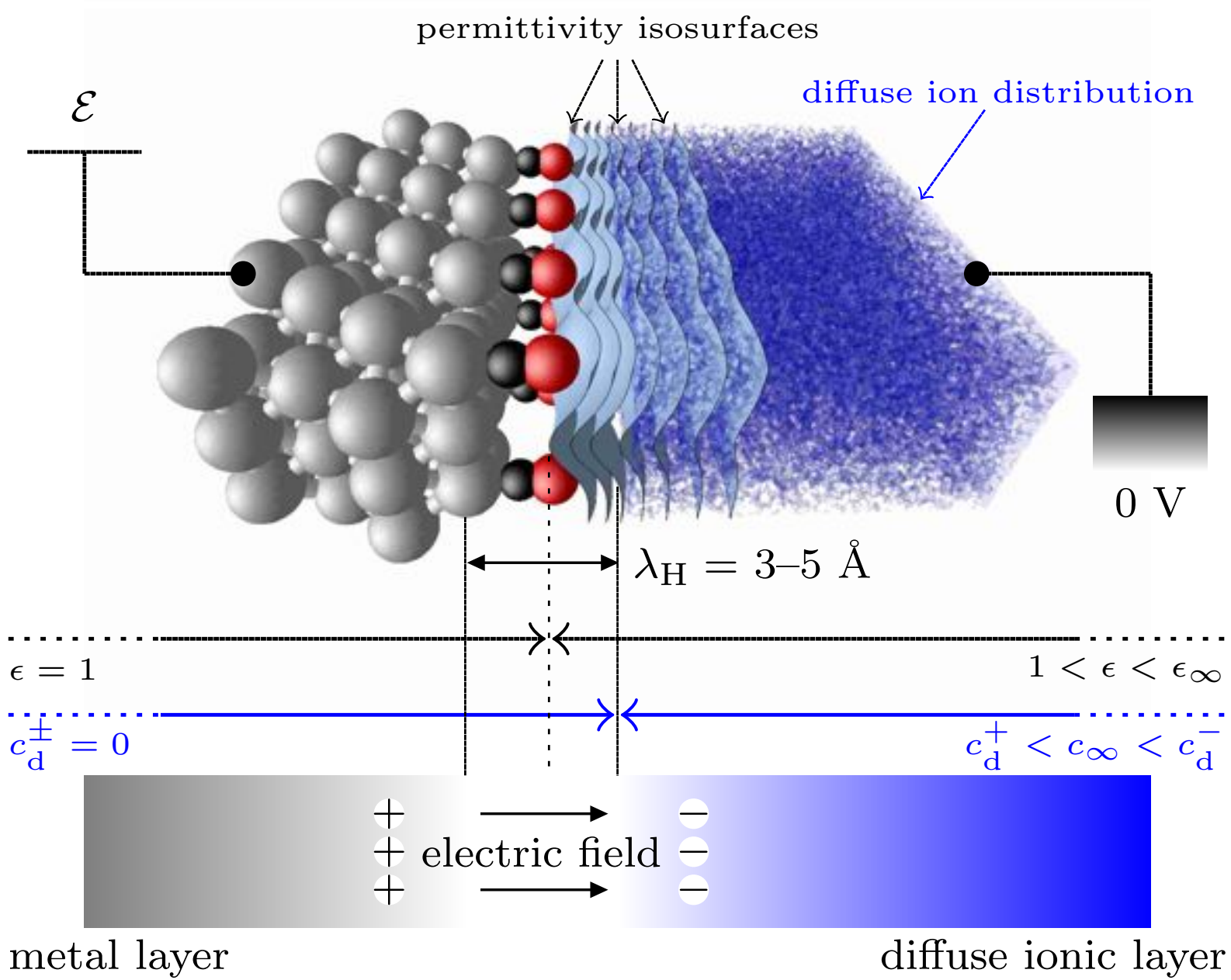
$\Rightarrow$ ionic solvent reaction field



Electrochemical Boundary Conditions

$$\frac{dv}{dz}(z) = -\left(\frac{36\pi c_d k_B T}{\epsilon_S}\right)^{\frac{1}{2}} \sinh\frac{z_d v(z)}{2k_B T} \quad \text{at } z = \pm L/2$$



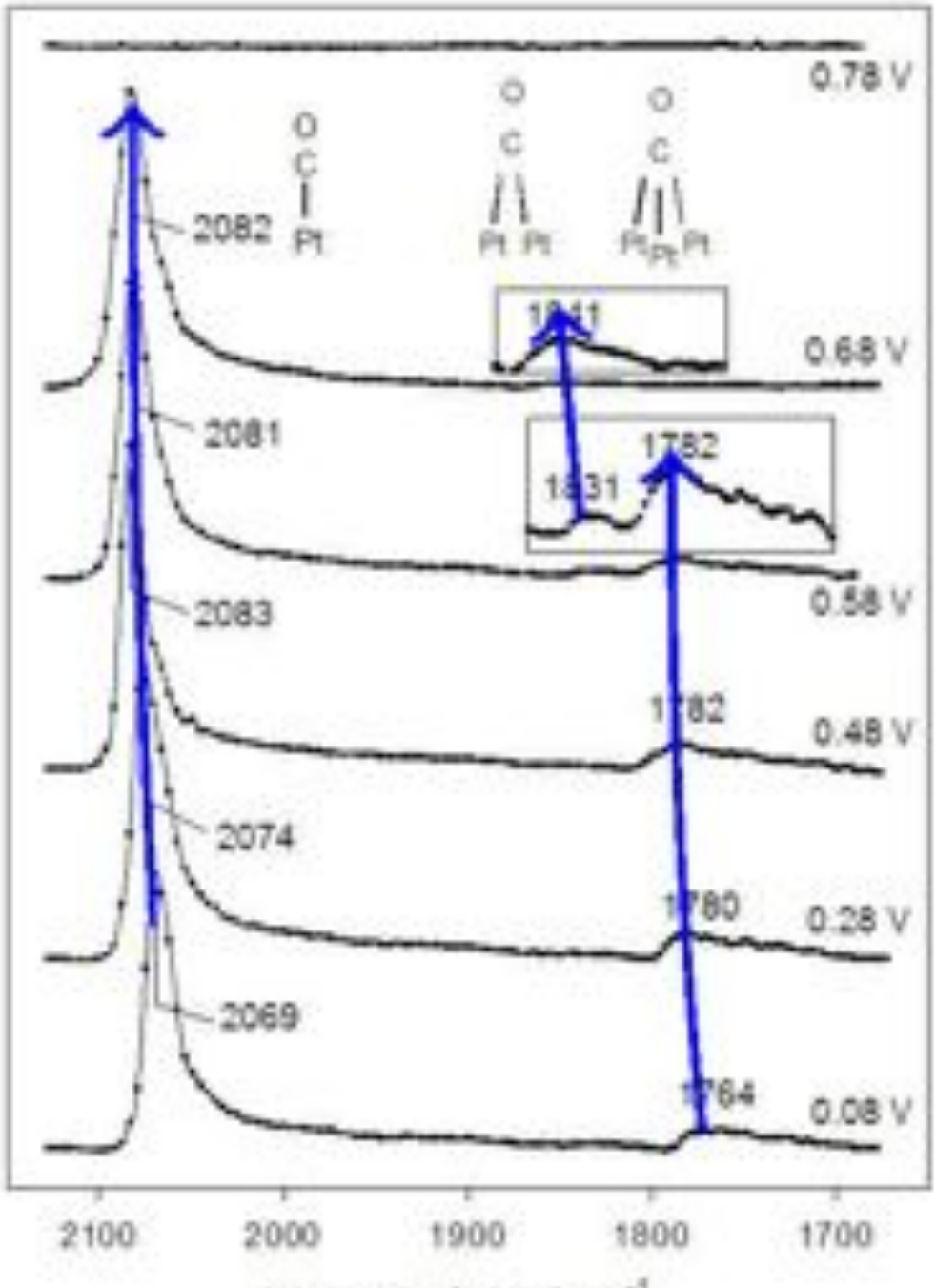


I. Dabo, PhD, MIT (2007)

I. Dabo, E. Cances, Y. L. Li, and N. Marzari, arXiv:0901.0096v2 (2009)

Application: Stark tuning

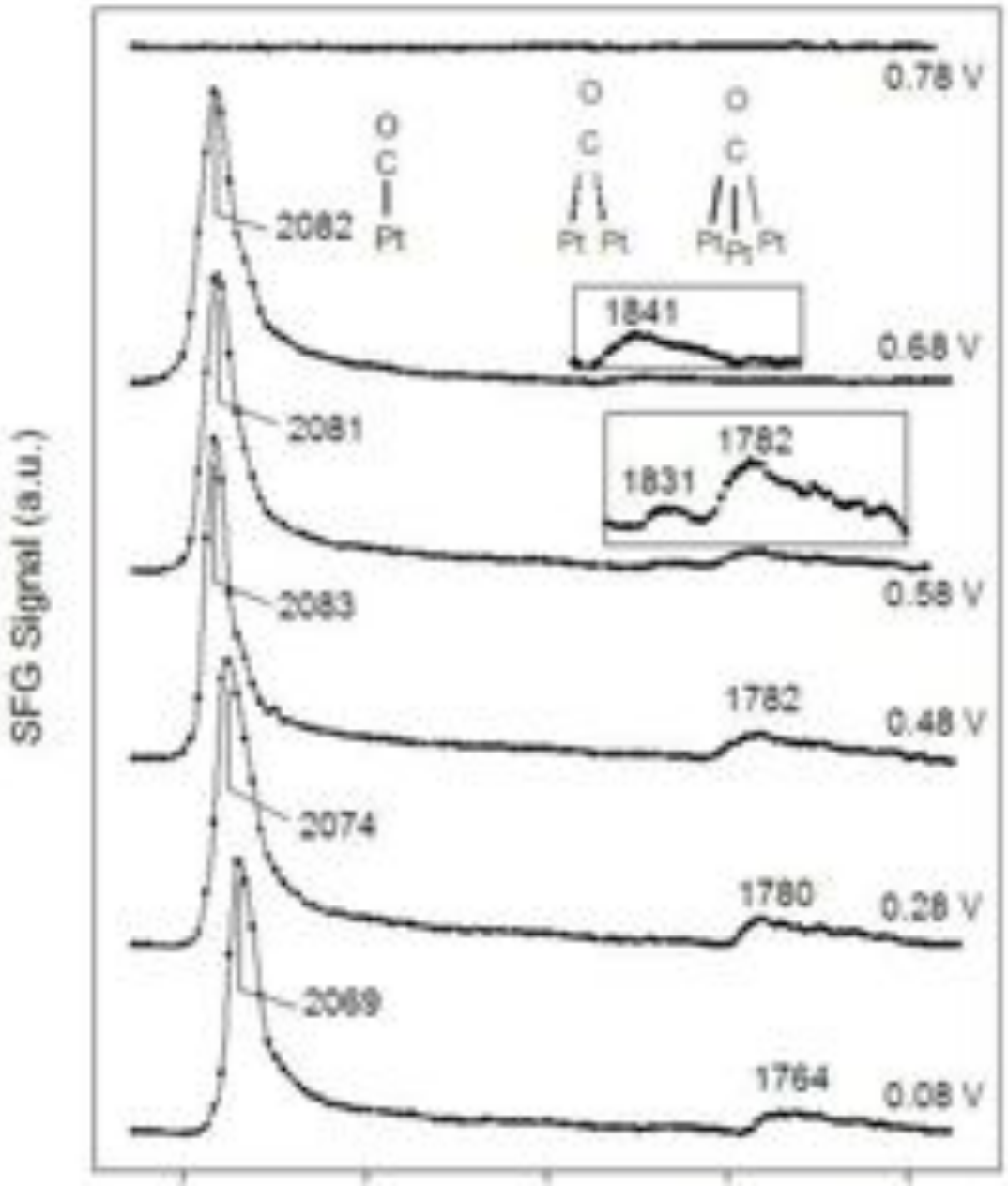
Stark tuning slope



$$\frac{d\nu(\mathrm{C{-}O})}{d\mathcal{E}} = 28\text{-}32\ \mathrm{cm}^{-1}\cdot\mathrm{m}^{2}$$

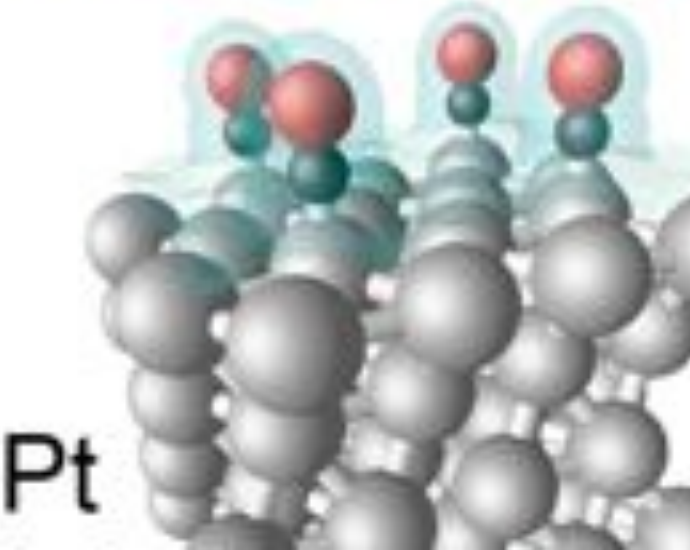
- Technogically important system (CO poisoning).
- Accurate experimental da
- Highly sensitive to electrochemical condition
- No comprehensive first-principles model.

I. Dabo, A. Wieckowski, N. Marzari, JACS 129, 11045-11052 (2007)



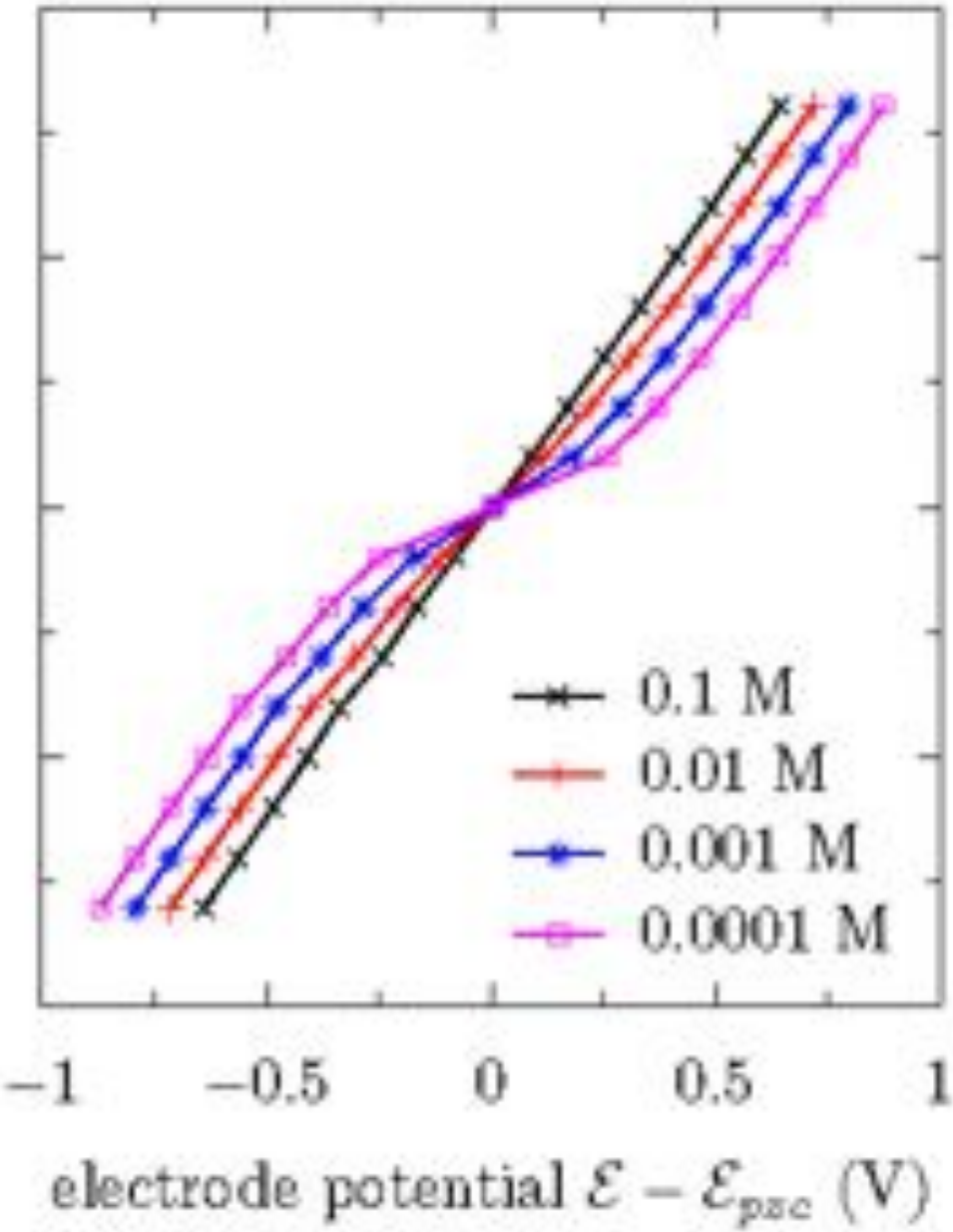
$\nu(C-O)$

	DFT	(Exp.)
atop	2050 cm^{-1}	(2070 cm
bridge	1845 cm^{-1}	(1830 cm
hcp	1752 cm^{-1}	(1760 cm
fcc	1743 cm^{-1}	(1760 cm

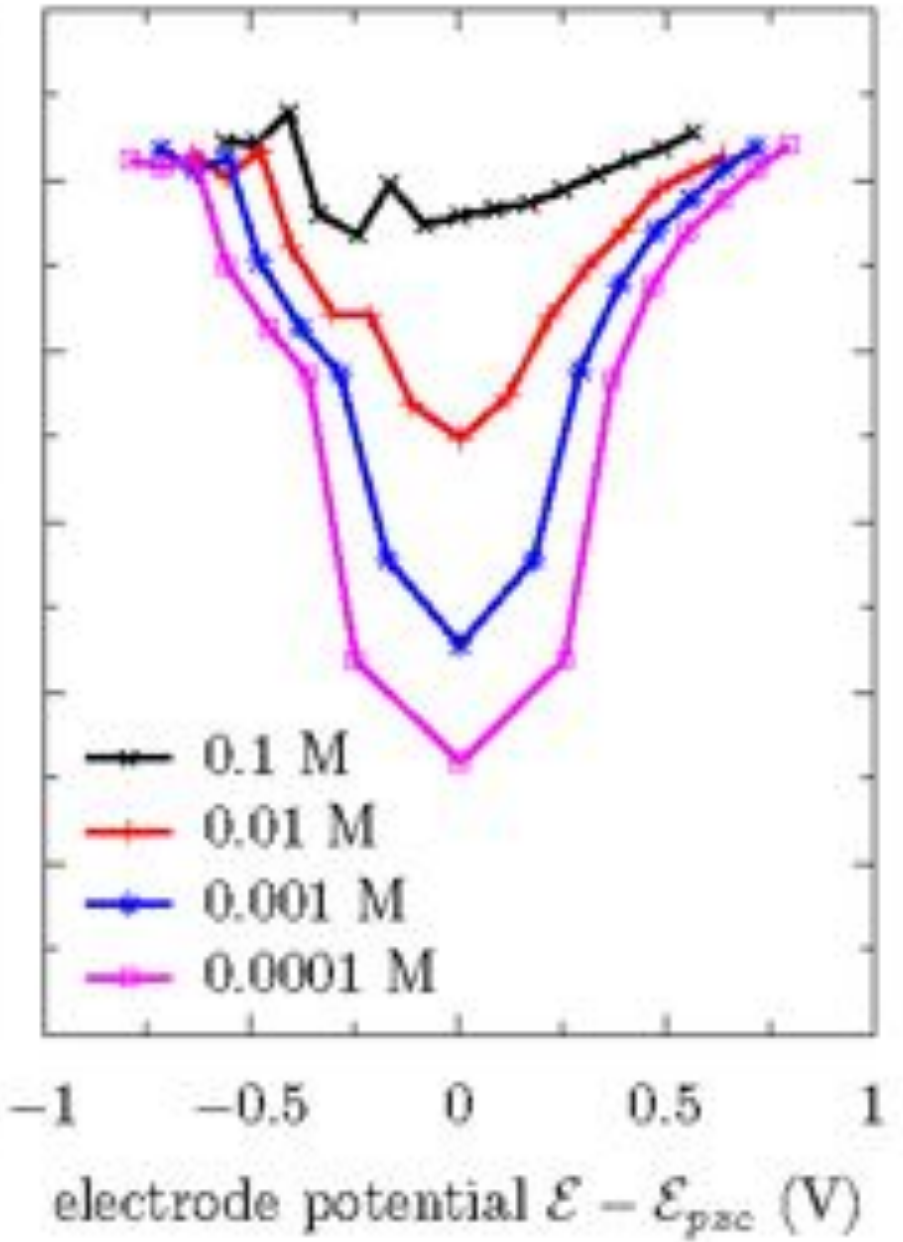


Charge and capacitance as a function of potential

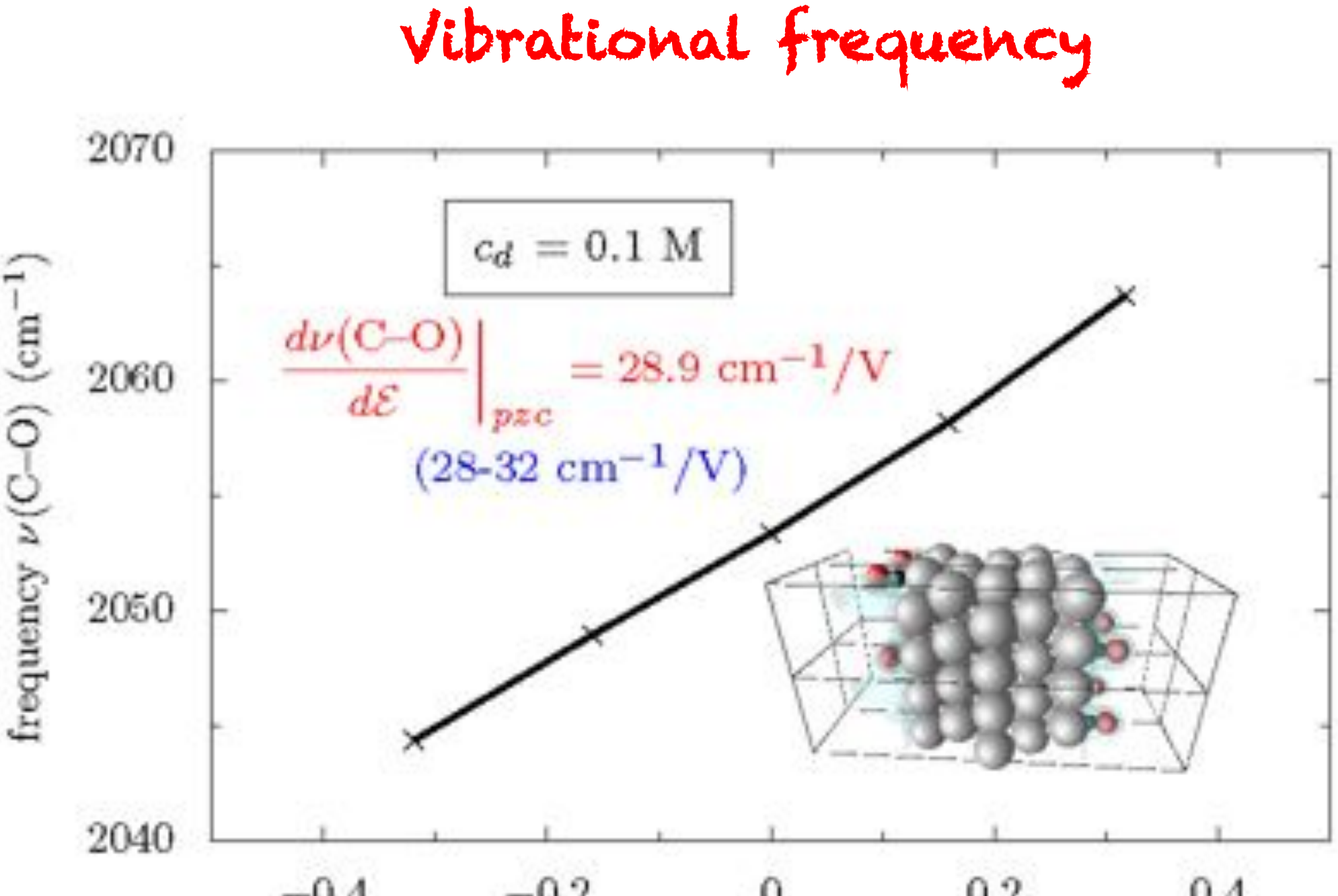
Surface charge



Capacitance



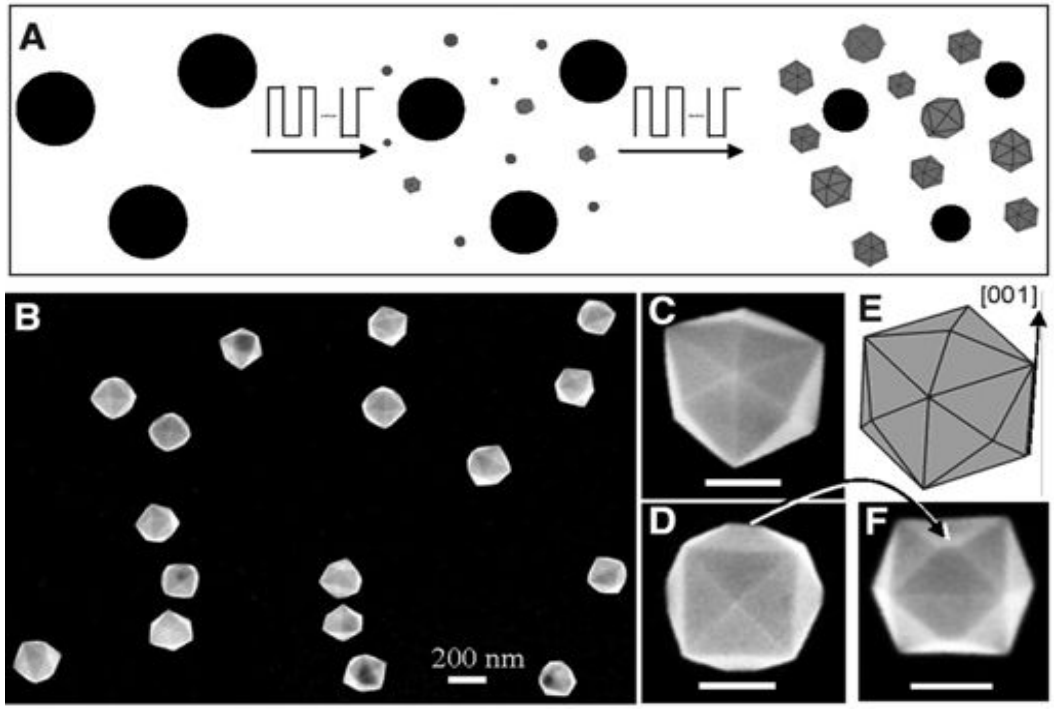
Electrochemical vibrational Stark effect



Application: Equilibrium shapes of nanoparticles (potential, pH)

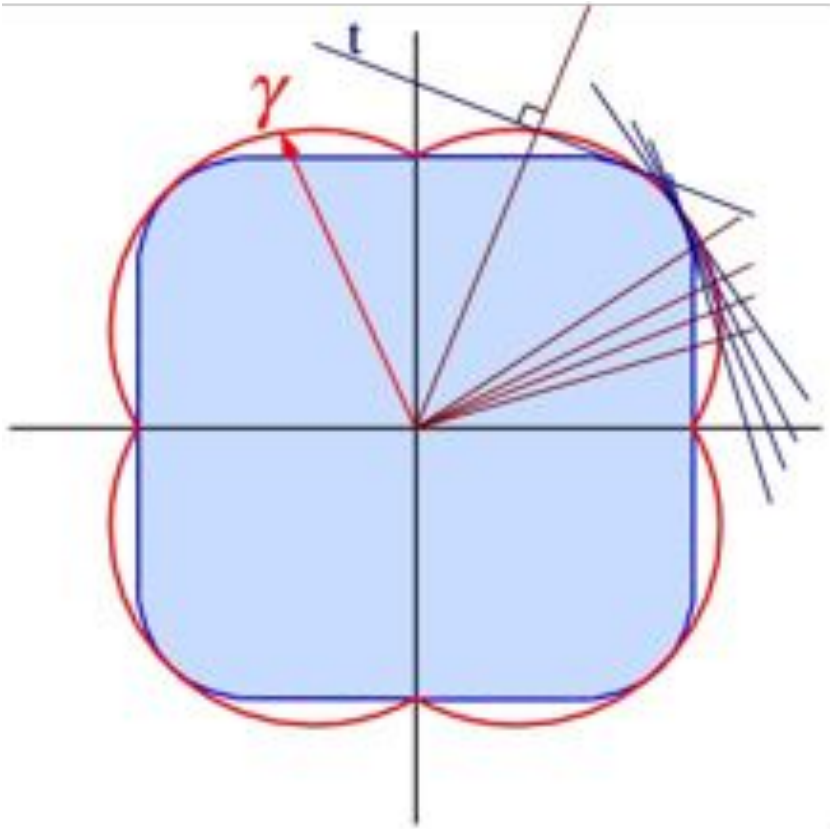
Surface energies at applied potential, pH

Possible potential-shape relationship evidence



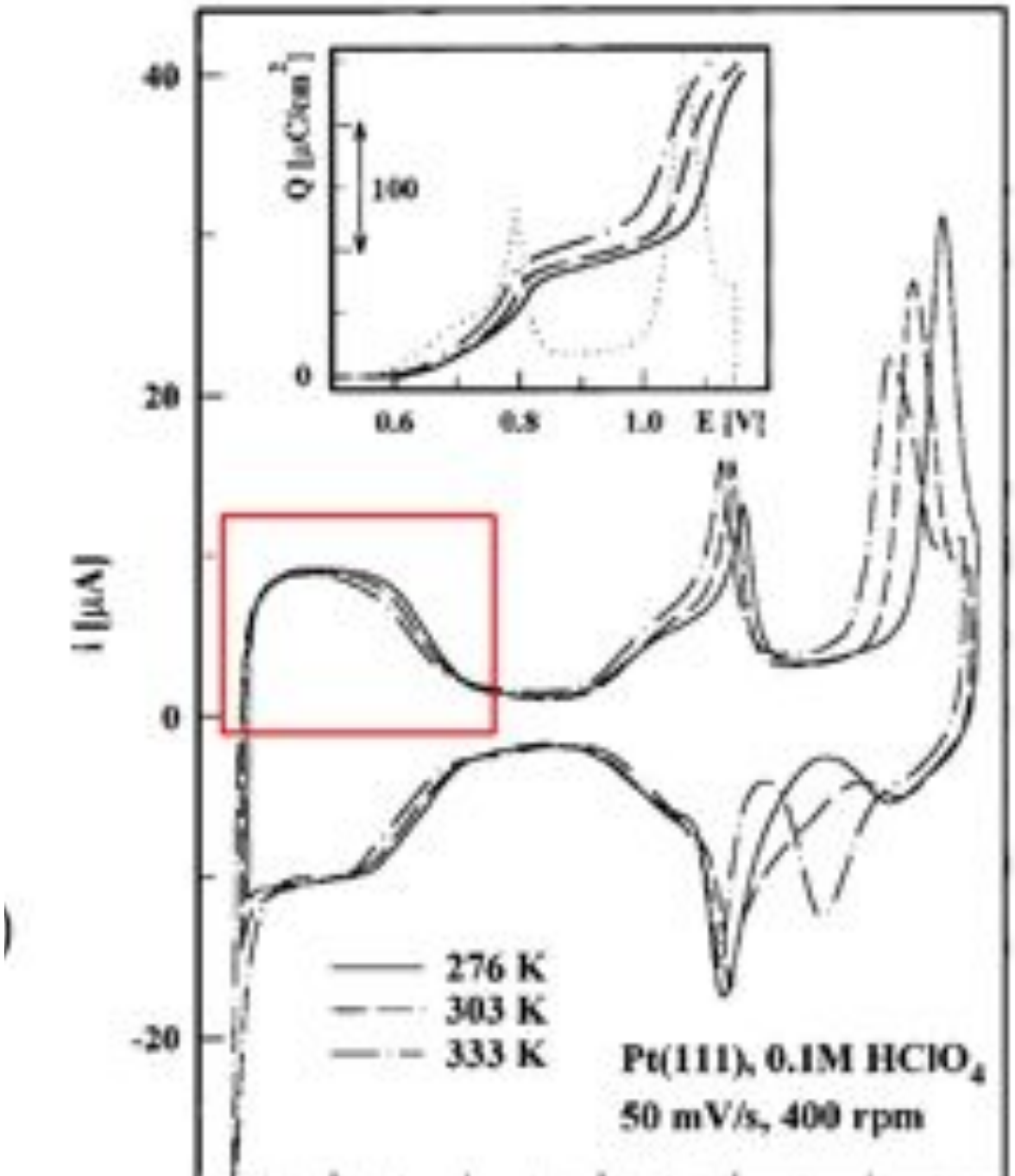
[Tian, Science 2007]

The Wulff constructior



$$\gamma \longleftrightarrow V$$

Hydrogen underpotential deposition



Electrosorption of a proton (Norskov et al.)

$$H_{aq}^{+} + e^{-} \longrightarrow H^{*}$$

$$H_{aq}^{+} + e^{-} \longrightarrow 1/2\ H_2\ (g)$$

(at equilibrium for the RHE)

$$1/2\ H_2\ (g) \longrightarrow H^{*}$$

Electrosorption of a proton (Norskov et al.)

At a potential U measured with respect to RHE:

$$\Delta G_{tot} = eU + \Delta G(\theta) + kT \ln(\theta/(1-\theta))$$

$$\Delta G(\theta) = \Delta E + ZPE + 0.20eV$$

Effect of pH

tandard vs reference hydrogen electrode

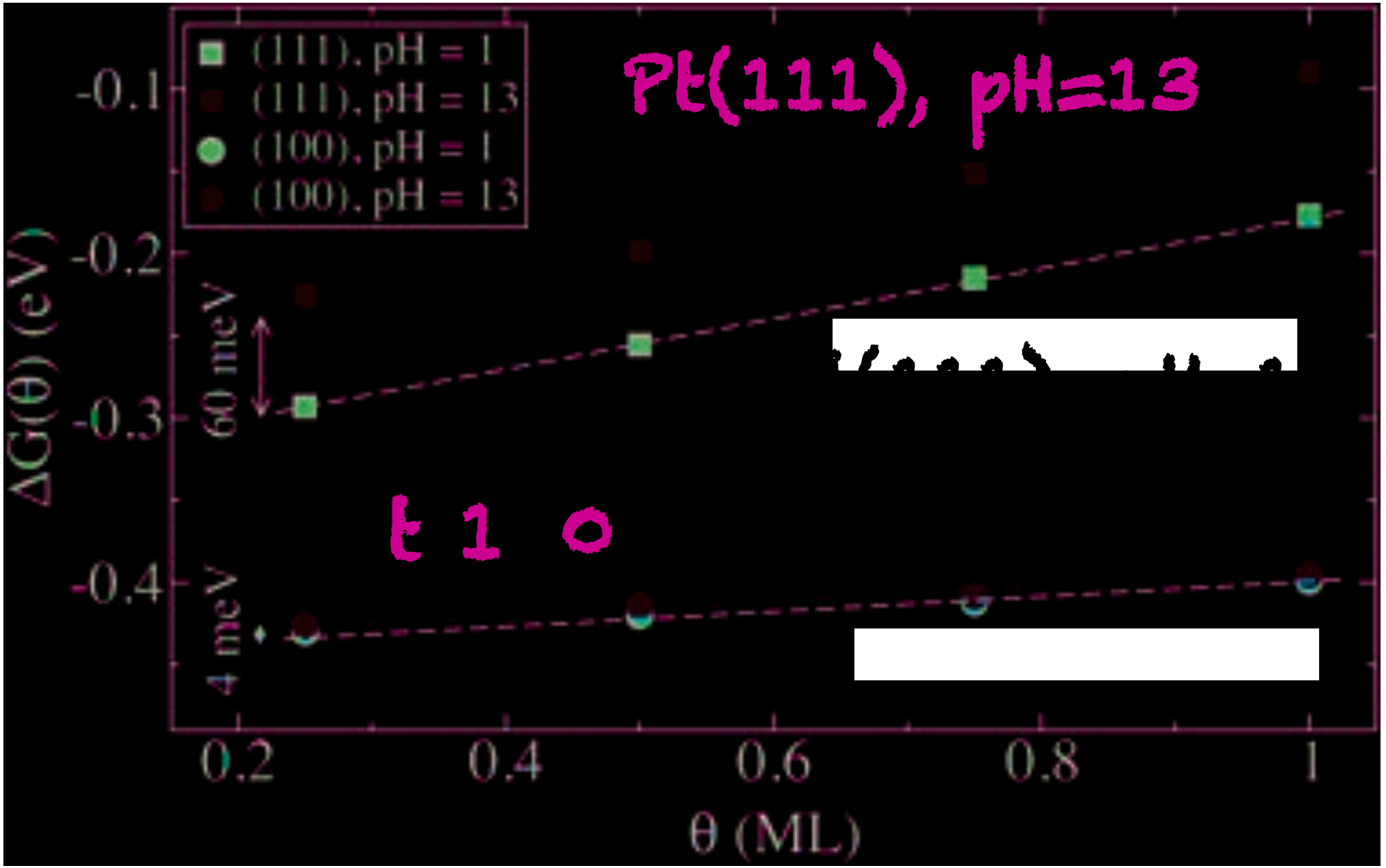
$\Phi_{RHE} = \Phi_{SHE} + kT \ln [H^+] = \Phi_{SHE} - 0.059 \times pH$

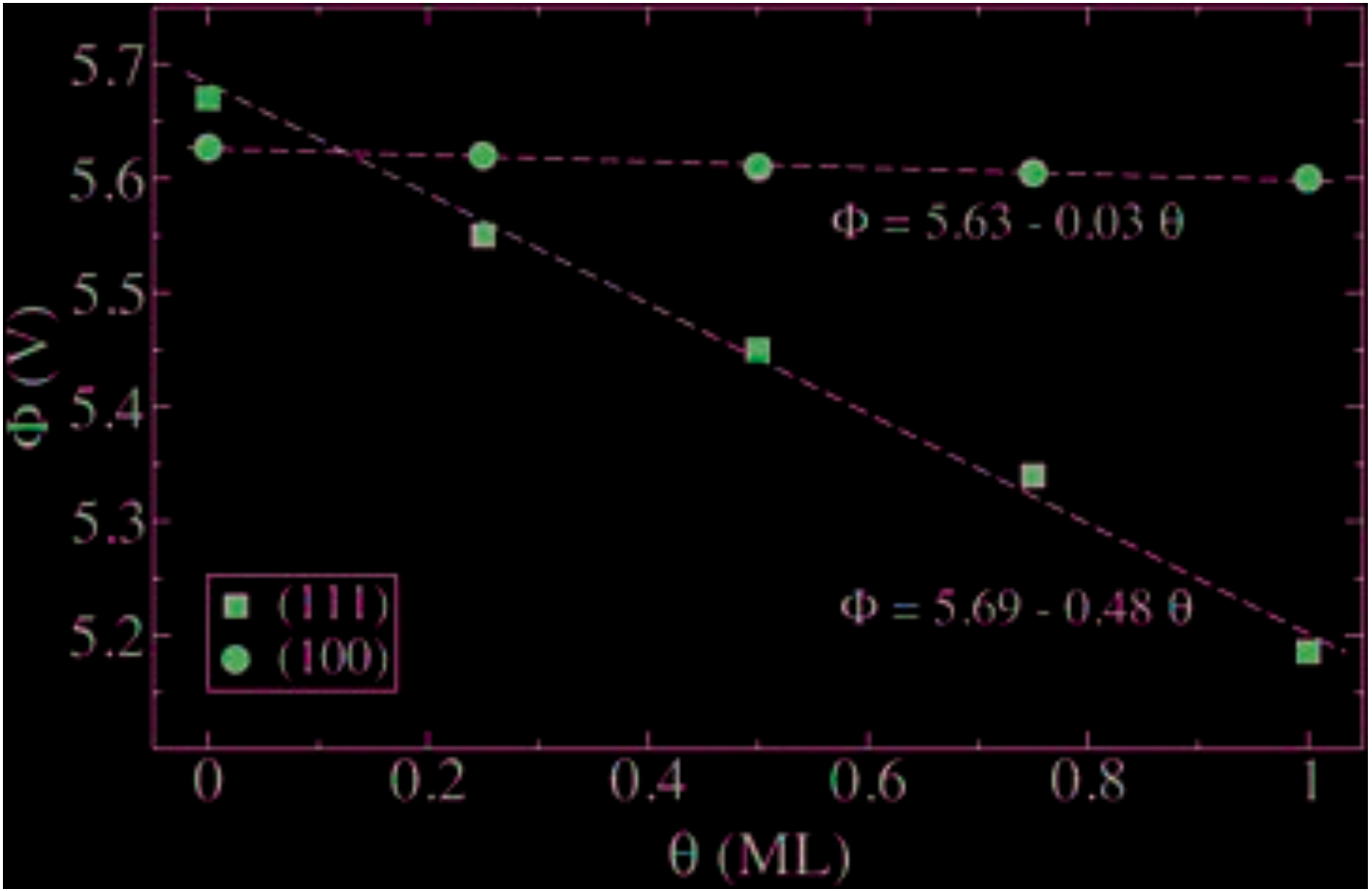
Assumption from expts:
PZC at 0 pH is 0.3V/RHE

t any other pH the charge on the surface

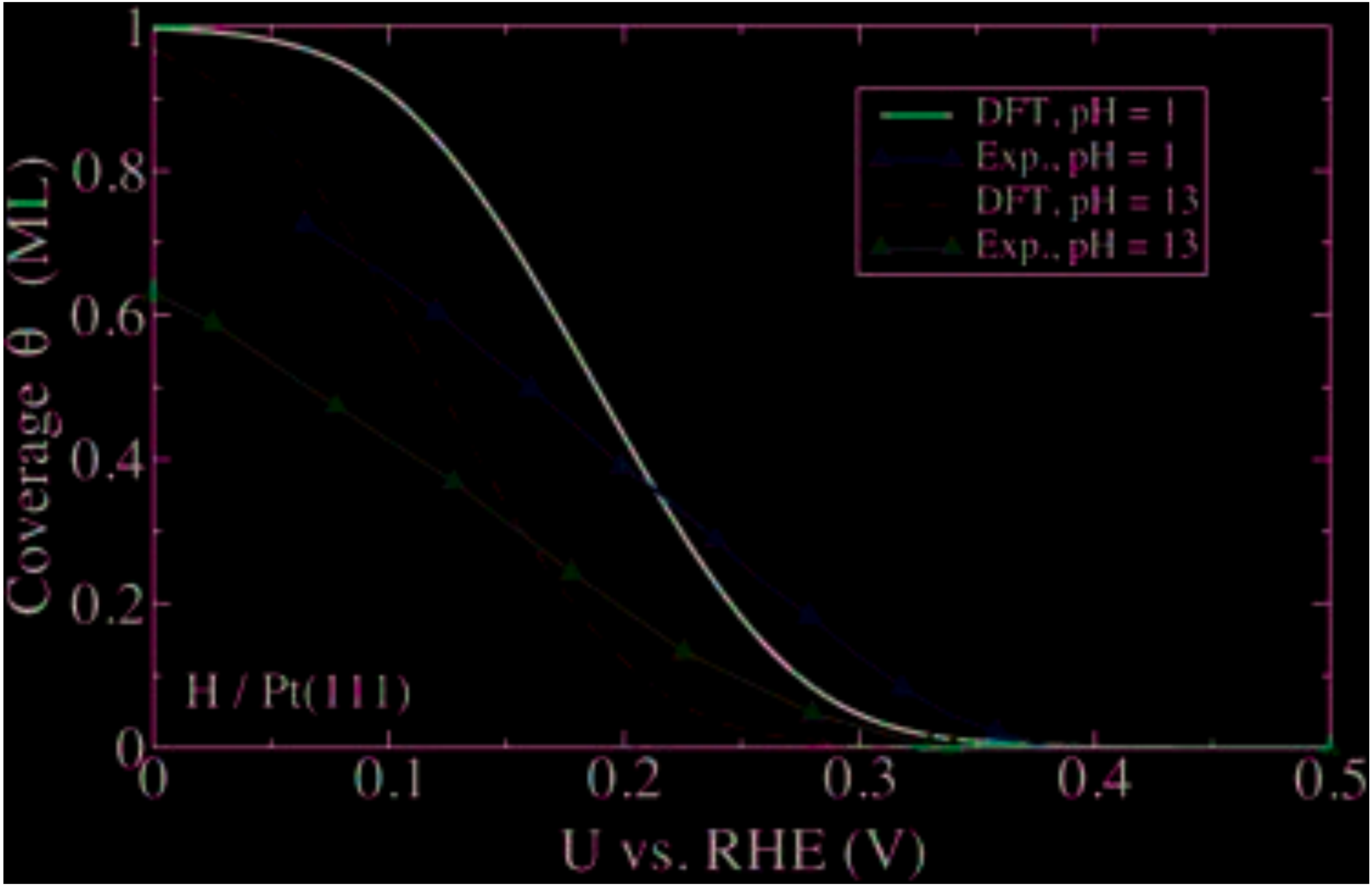
$\sigma = - 0.059 \times pH \times c_{dl}$

Assumption from expts:

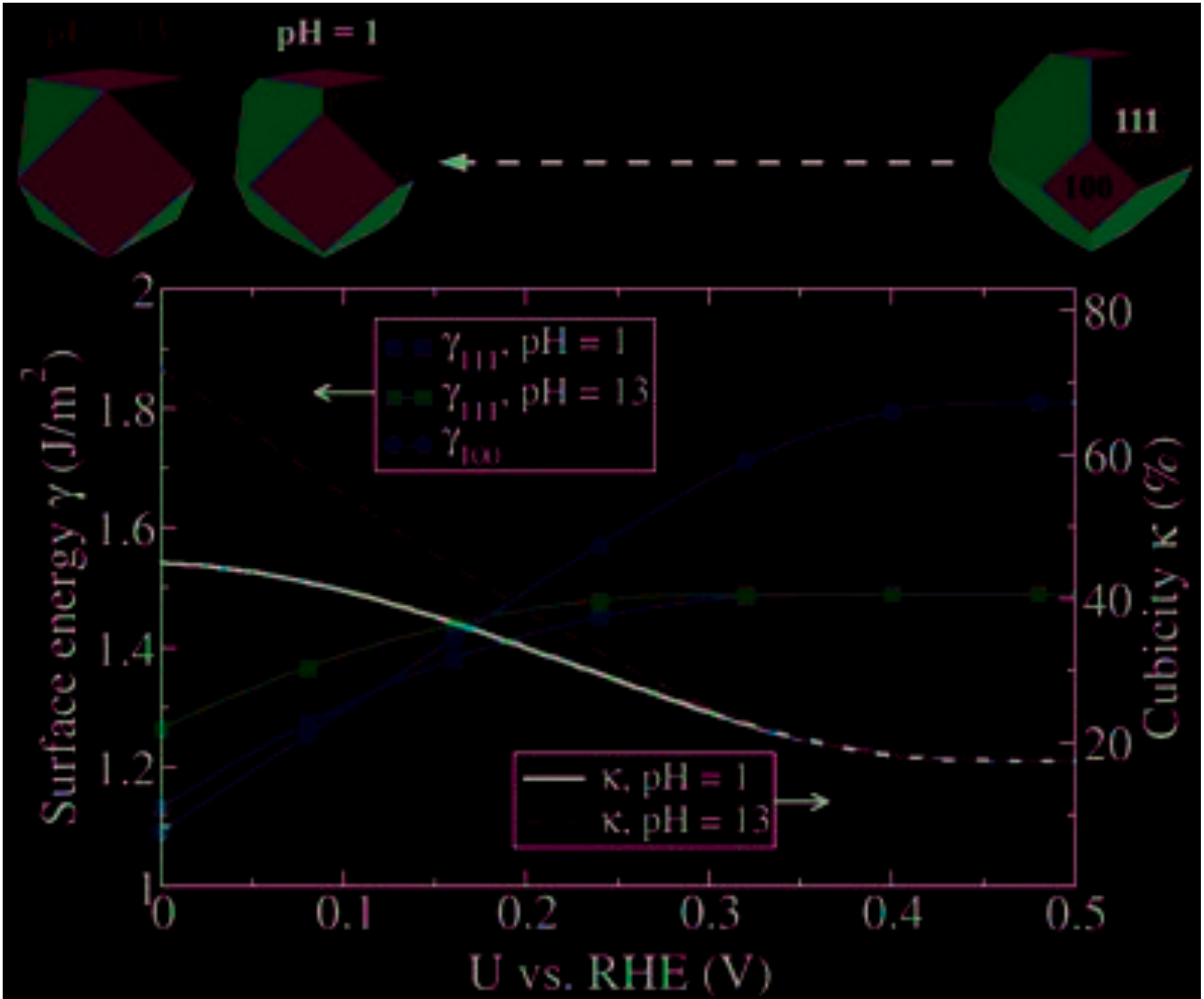

(111), pH = 1
(111), pH = 13
(100), pH = 1
(100), pH = 13
Pt(111), pH=13
-0.1
-0.2
-0.3
-0.4
ΔG(θ) (eV)
60 meV
4 meV
0.2
0.4
0.6
0.8
1
θ (ML)


5.7
5.6
5.5
5.4
5.3
5.2
Φ (V)
0
0.2
0.4
0.6
0.8
1
θ (ML)
Φ = 5.63 - 0.03 θ
Φ = 5.69 - 0.48 θ
(111)
(100)

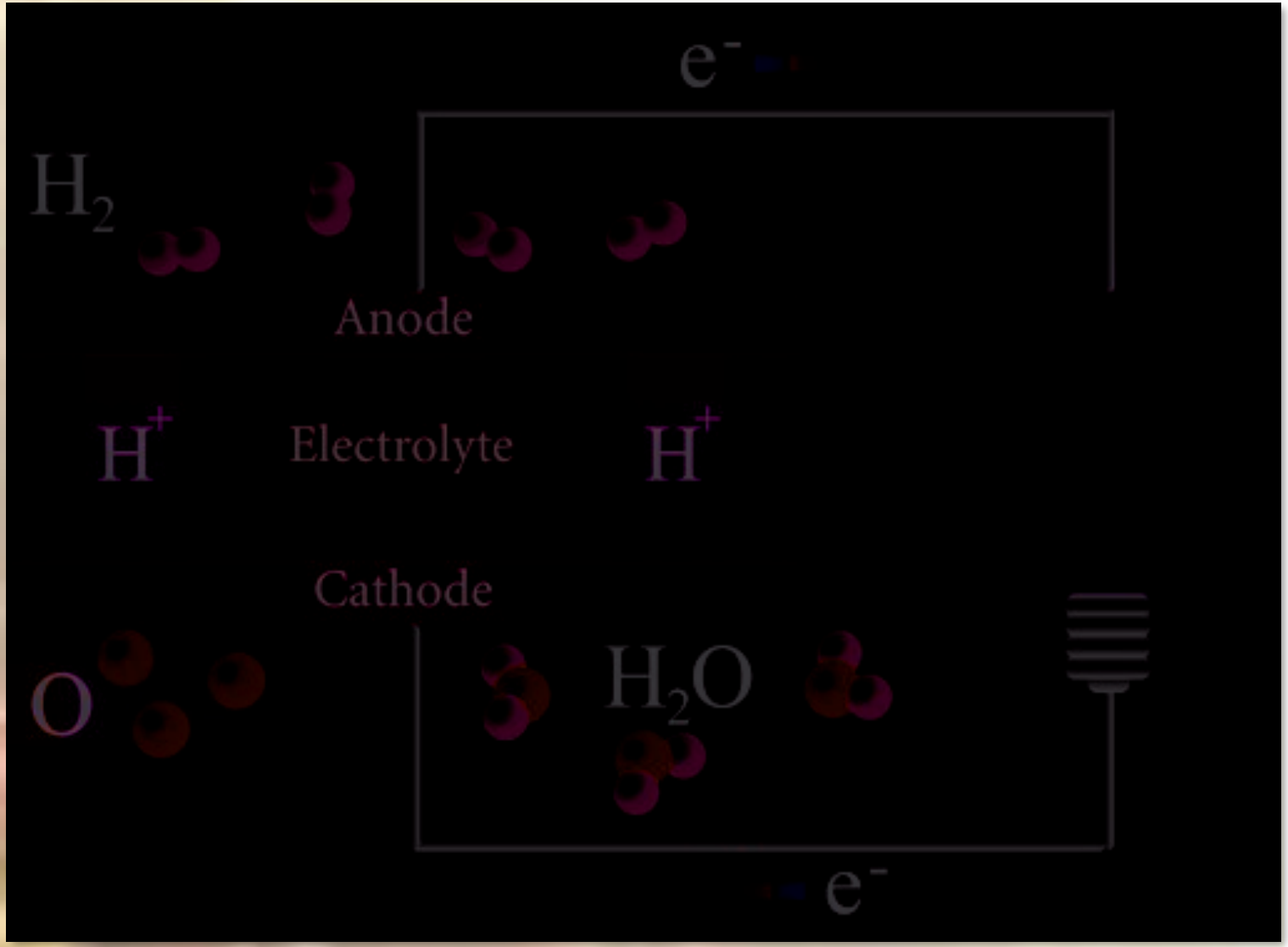
Hydrogen deposition curves: ΔG(pH,U)=0

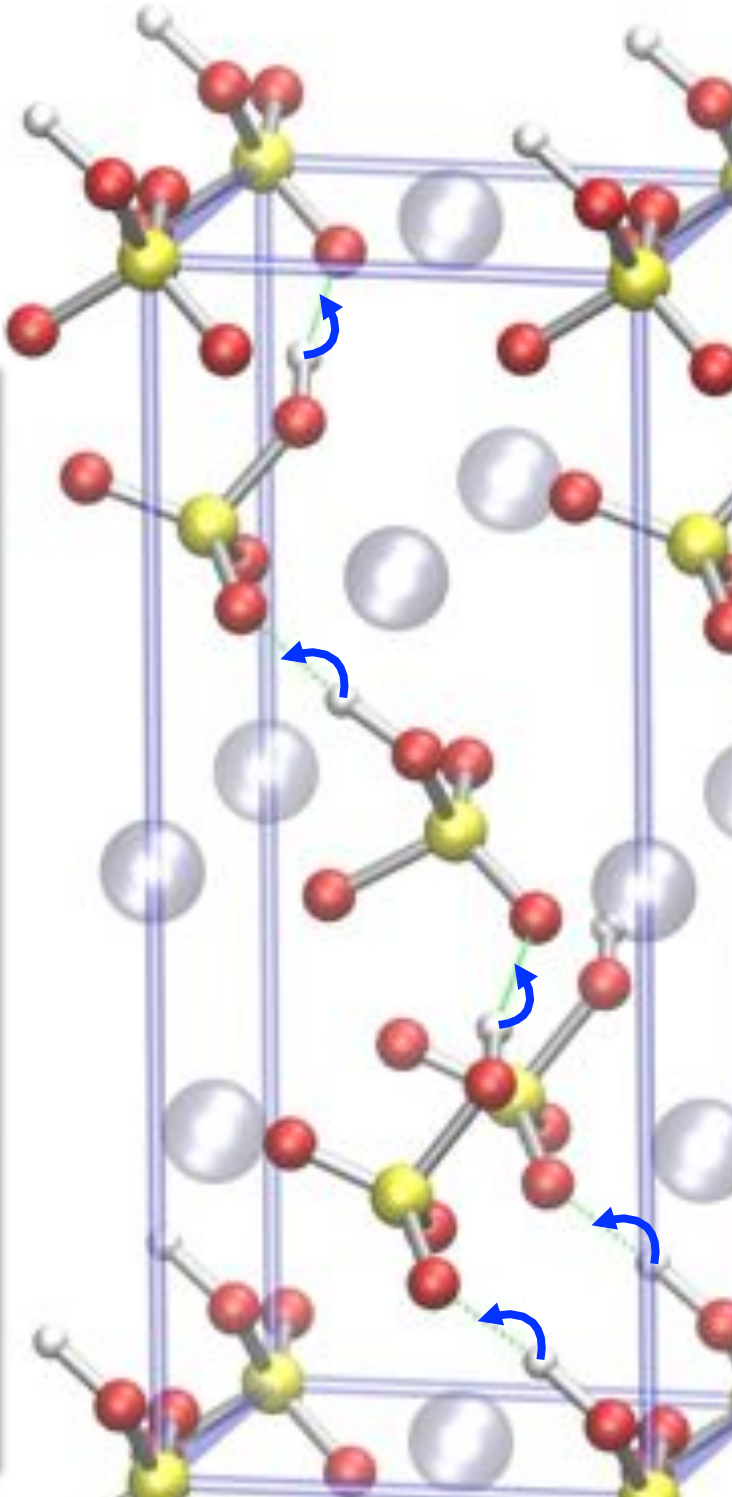


Wulff construction: nanoparticle shape



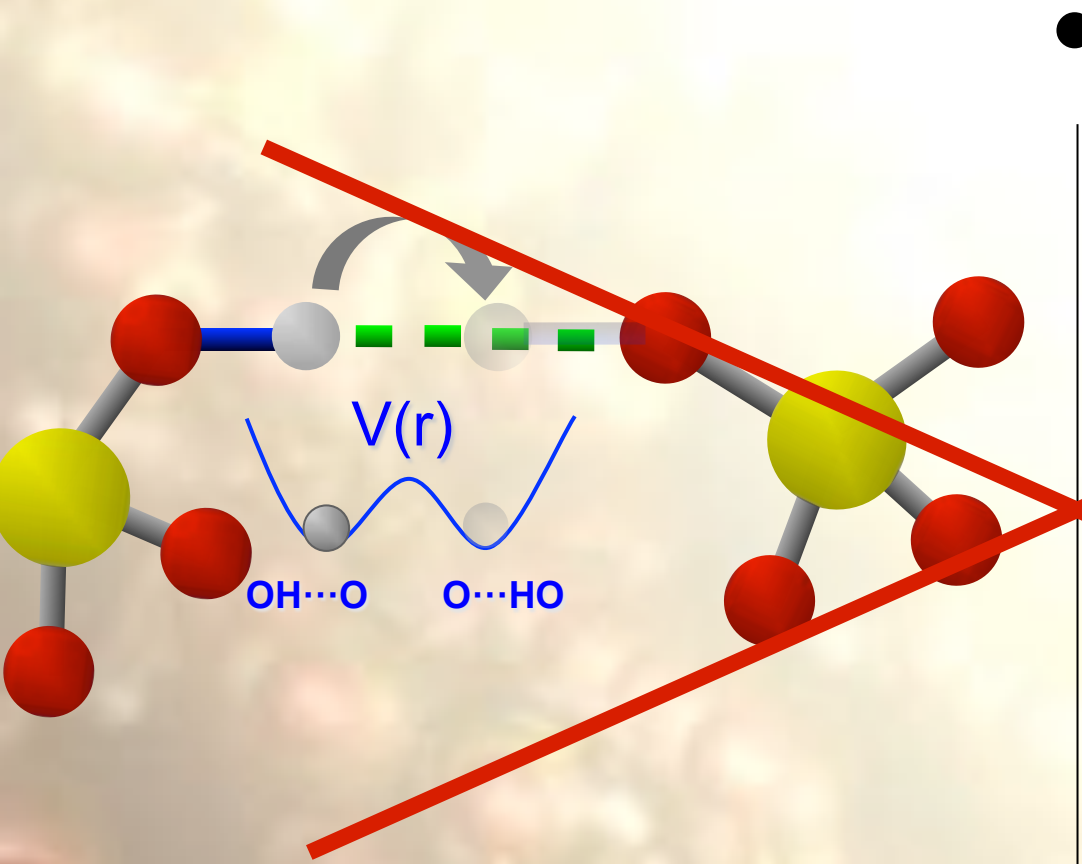
Haile et al., *Nature* **410**, 910 (2001)

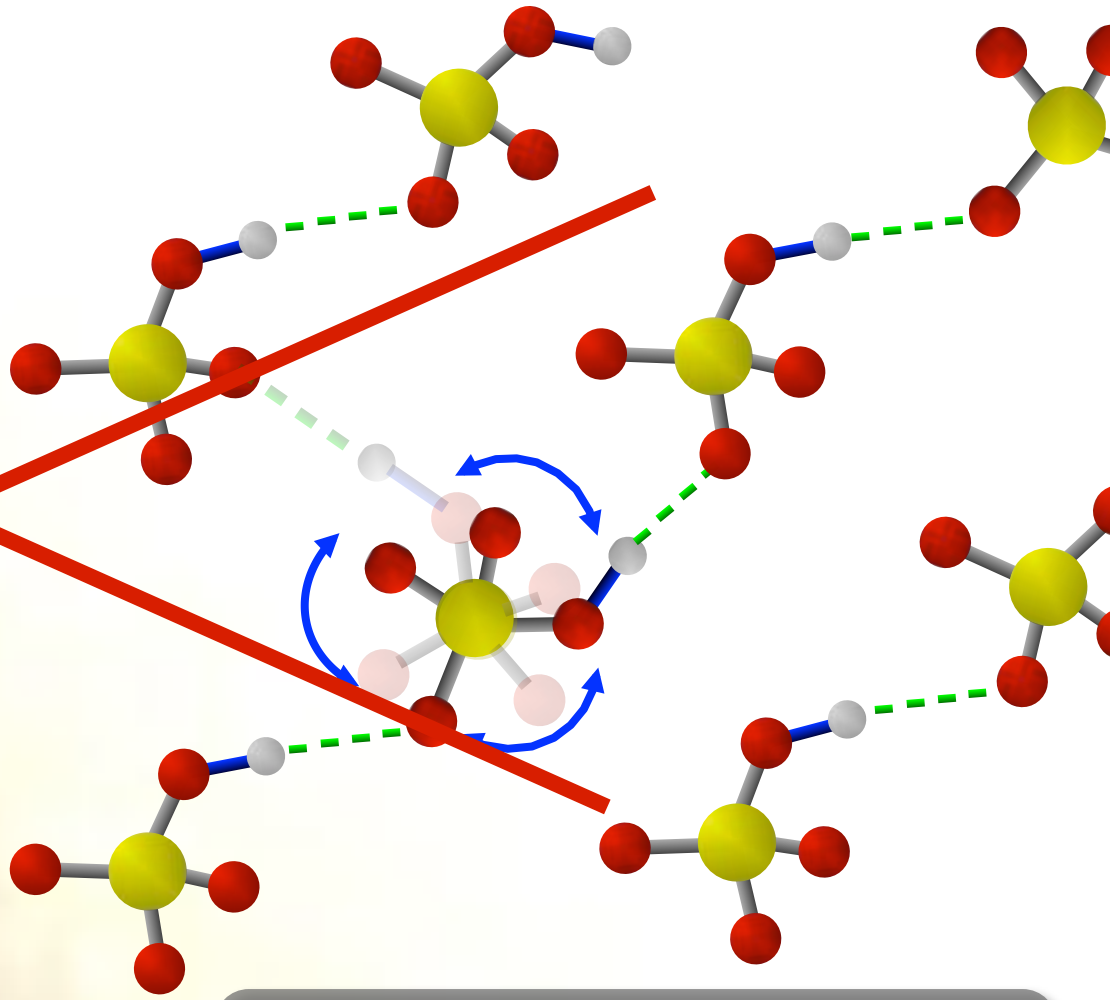




Two independent processes

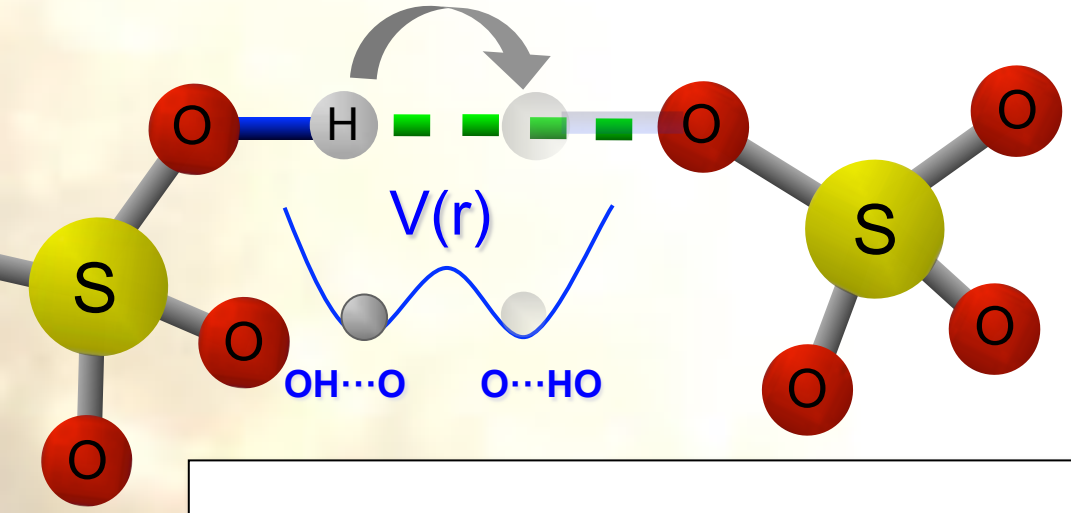
Proton hopping ? SO_4 rotation



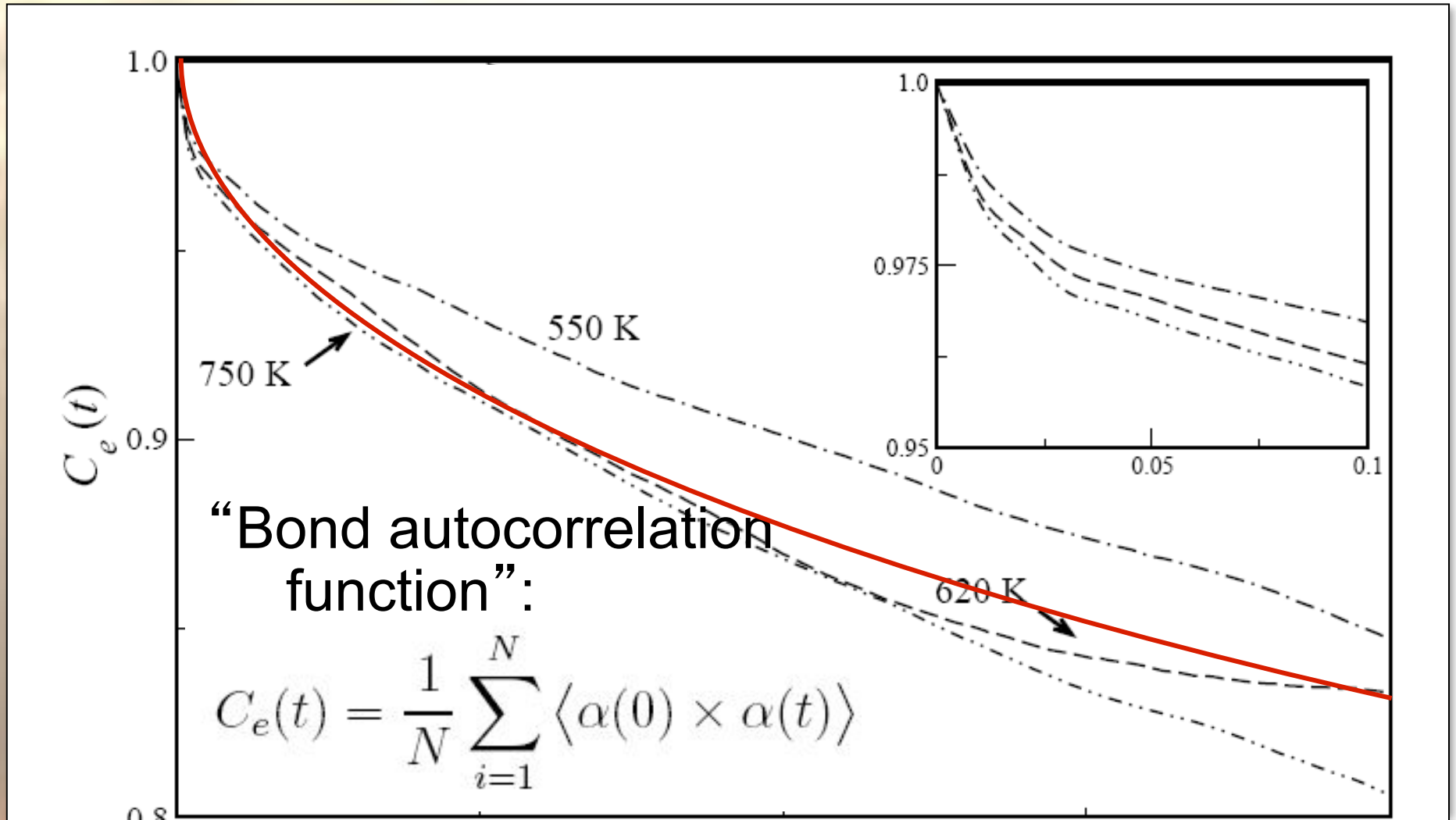


Slow (10^9 s-1)?

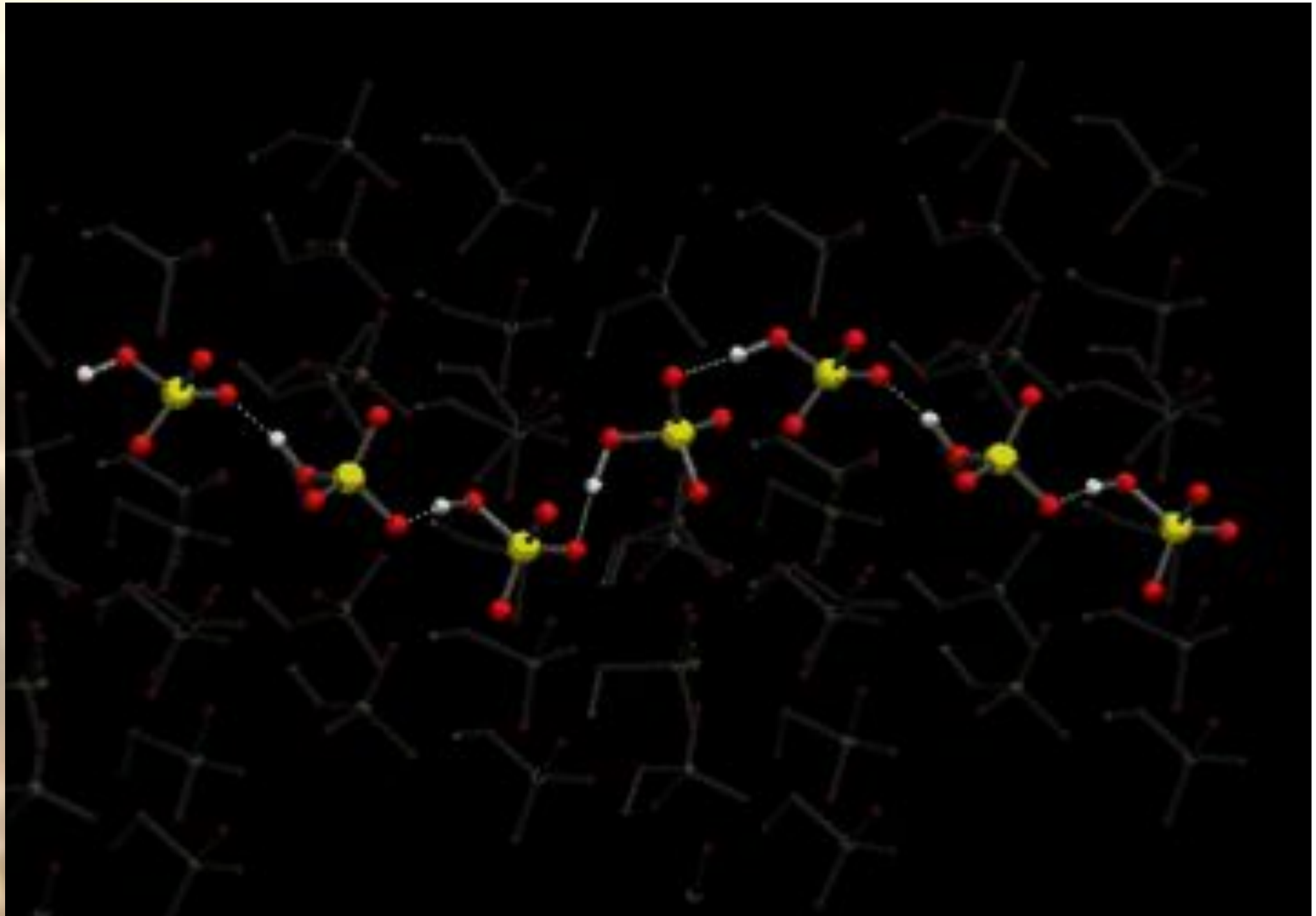
Fast (10^{11} s-1)?



- *Frequent (every 1.1 – 1.7 p*
- *High (85%) reversal rate*

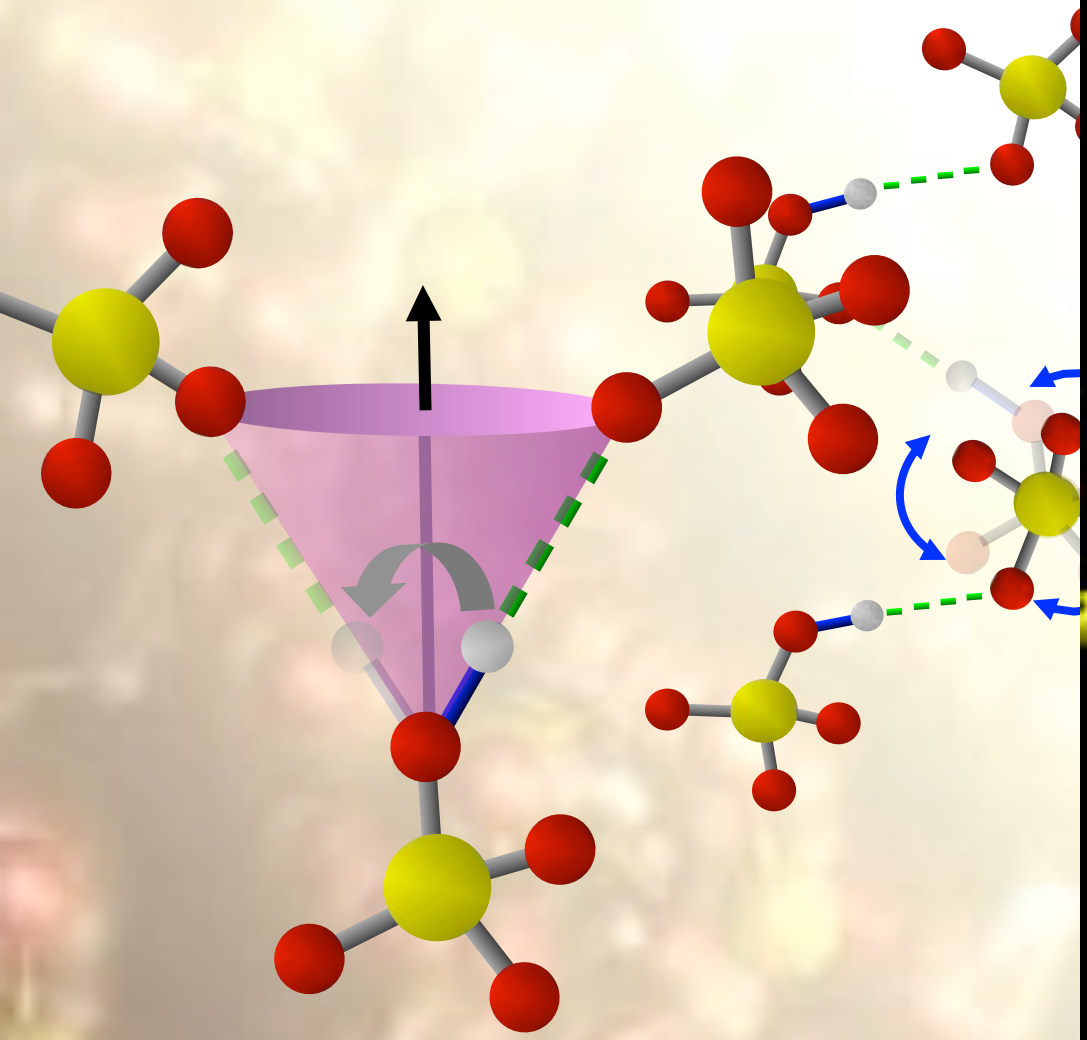


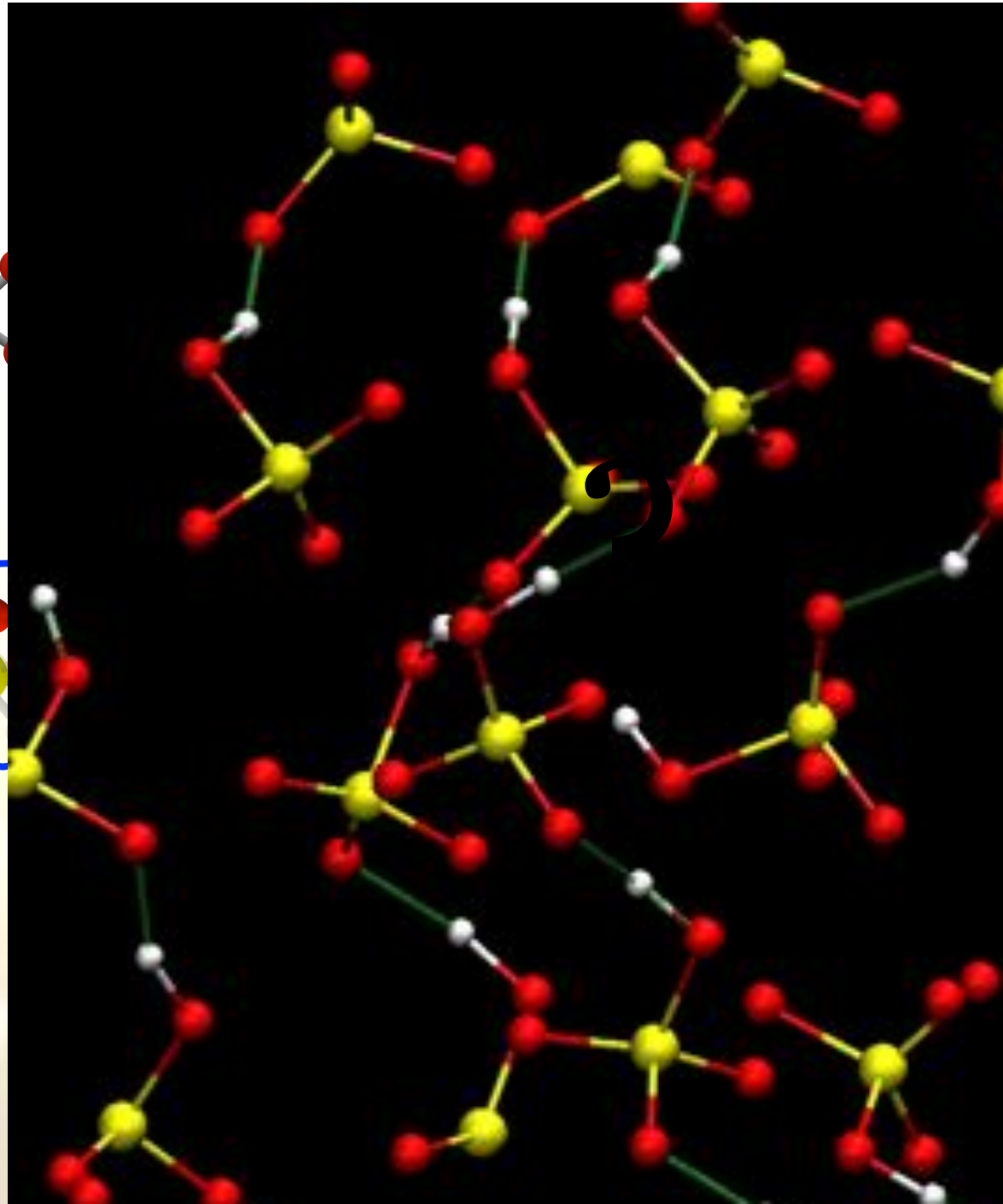
Tim



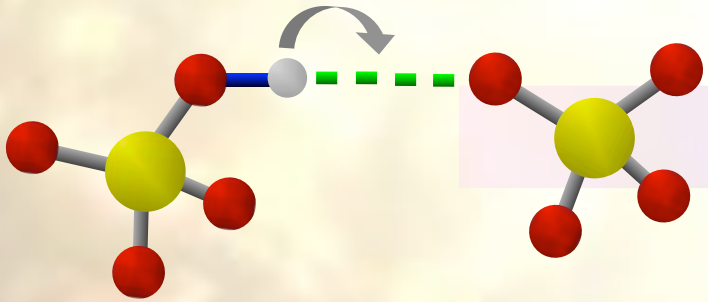
requent (every 0.25 – 1.0 ps!)

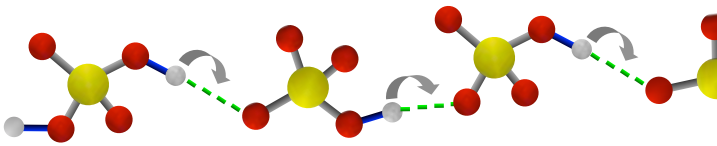
40% reversal rate

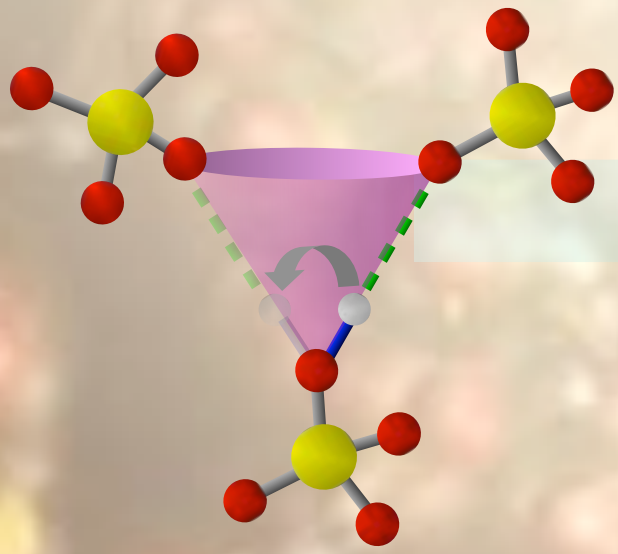




	Proposed	*This work*
Chemical-bond dynamics	10^{9} s $^{-1}$	10^{12} s $^{-1}$ (limited by reversa to 10^{11} s $^{-1}$)*
ydrogen-bond dynamics	10^{11} s $^{-1}$	10^{12} s $^{-1}$

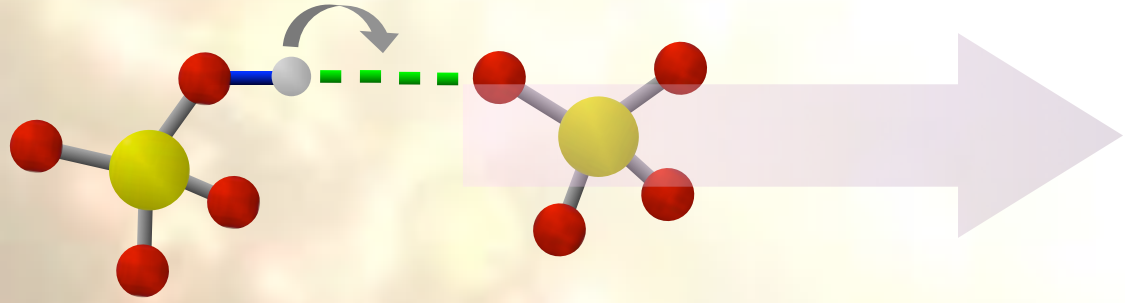






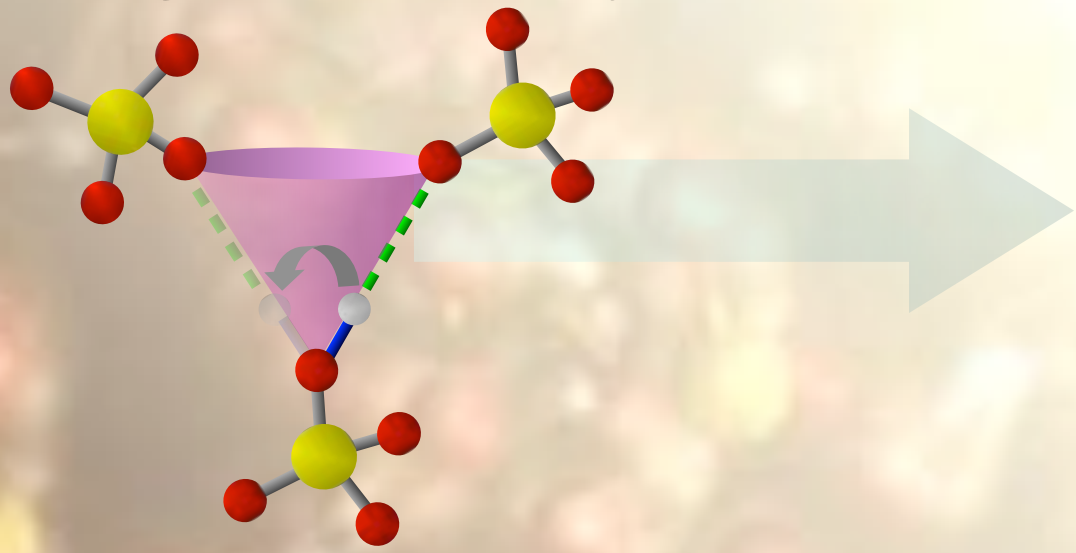
No significant $CsHSO_4$ / $CsDSO_4$ isotope effect

Chemical-bond dynamics



SO_4 controls attempt frequency

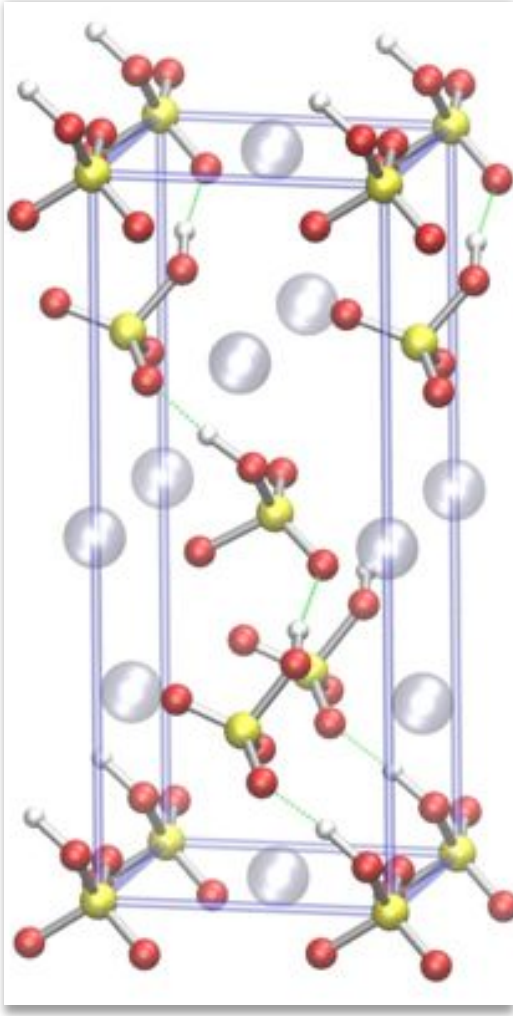
Hydrogen-bond dynamics

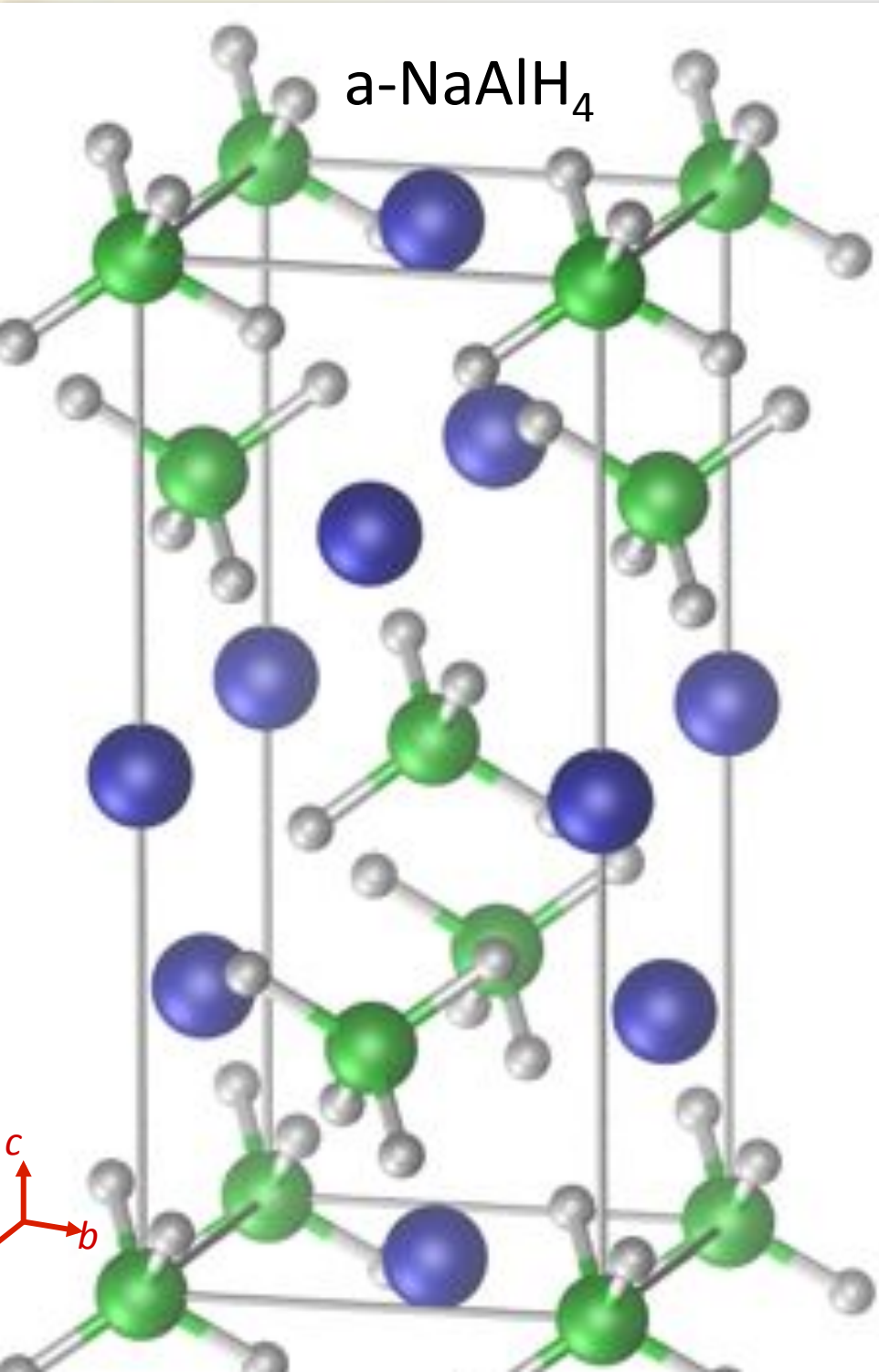


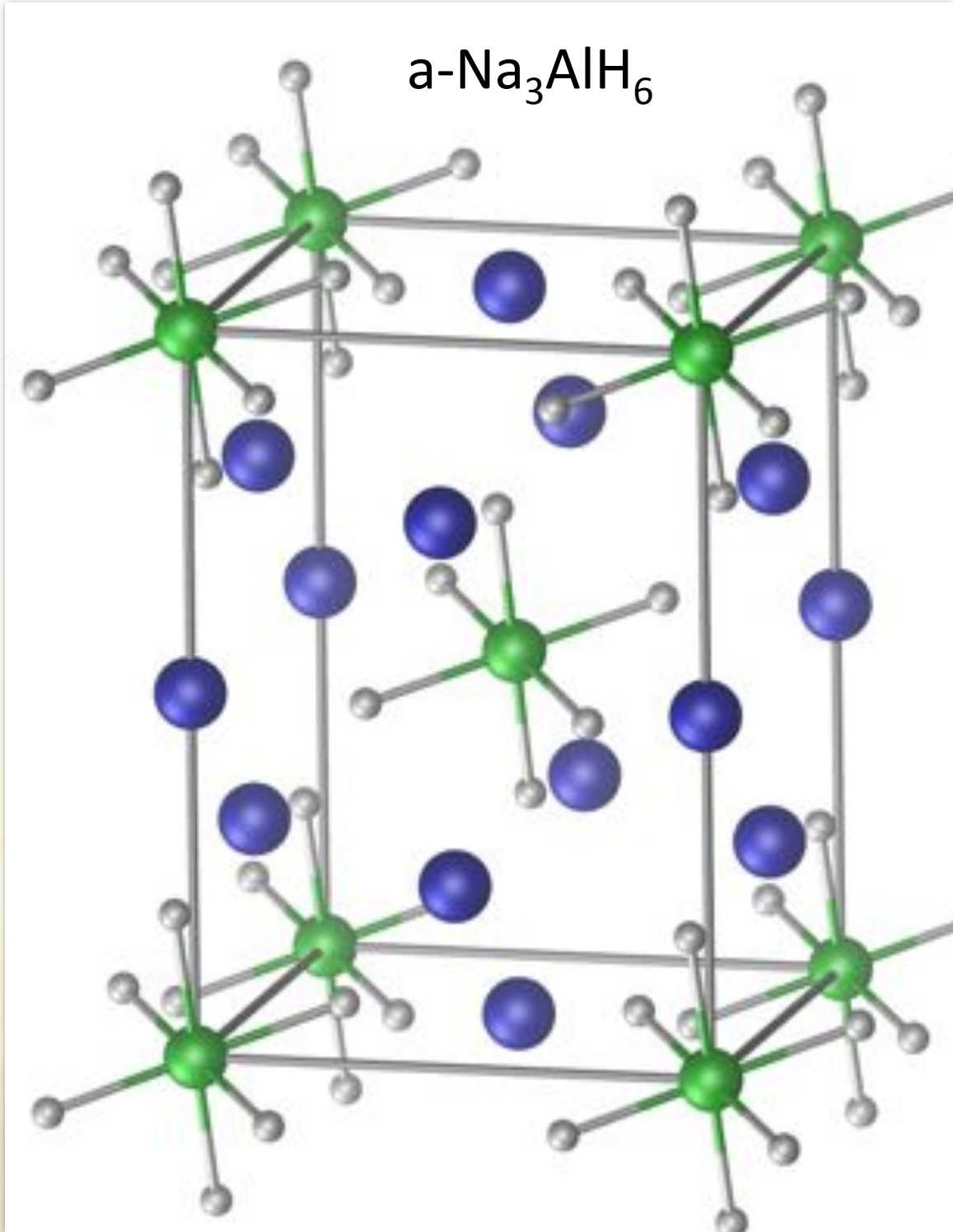
SO_4 controls reversal rate

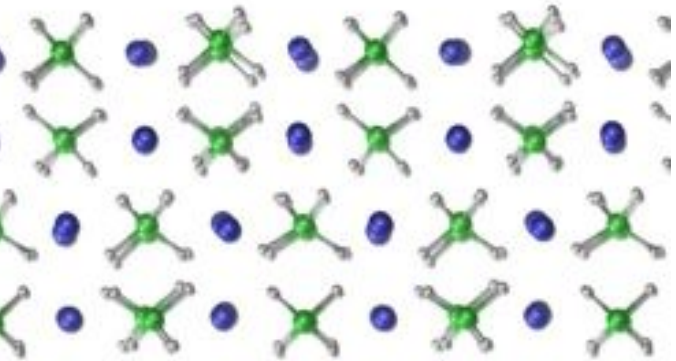
$sHSO_4$:

- New picture of hydrogen bond dynamics
- SO_4 rotation controls attempt frequency of chemical bond dynamics and reversal rate of hydrogen bond dynamics
- SO_4 rotation (not chemical bond dynamics!) is rate limiting
- Topological analysis shows chains increase jump likelihood

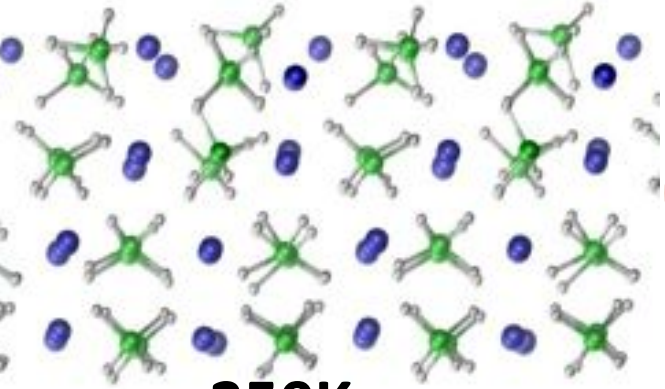



a-NaAlH4
c
b

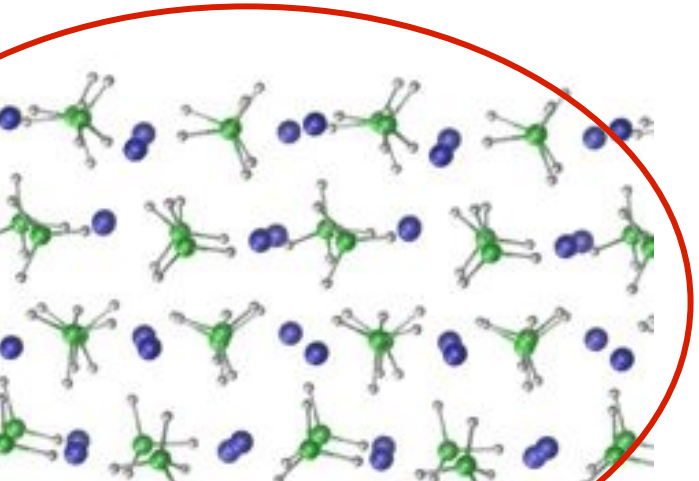

a-Na3AlH6

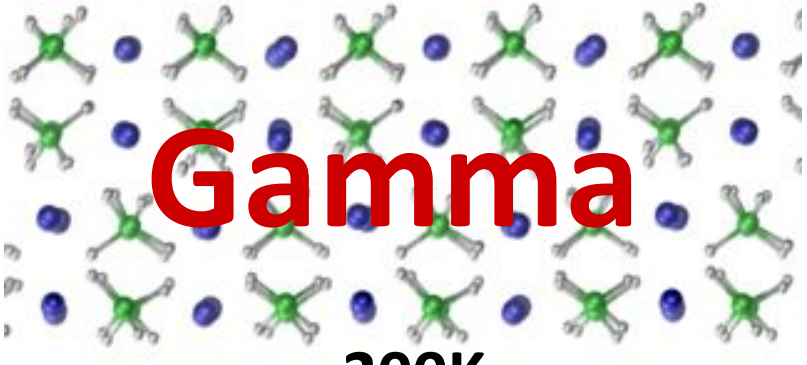


150K



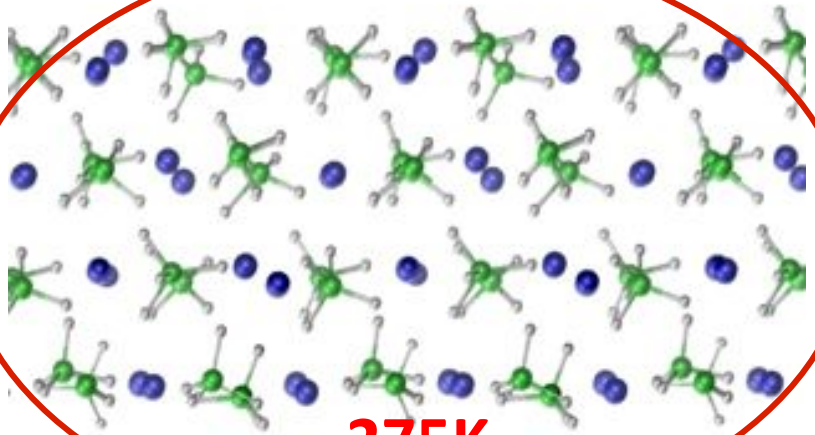
250K



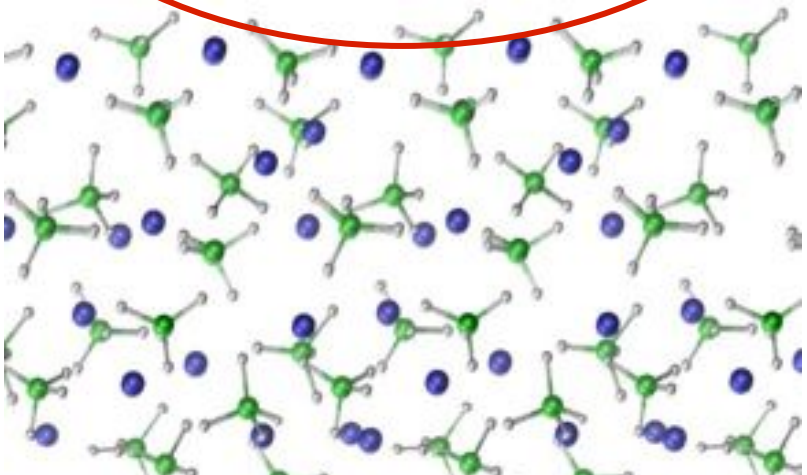


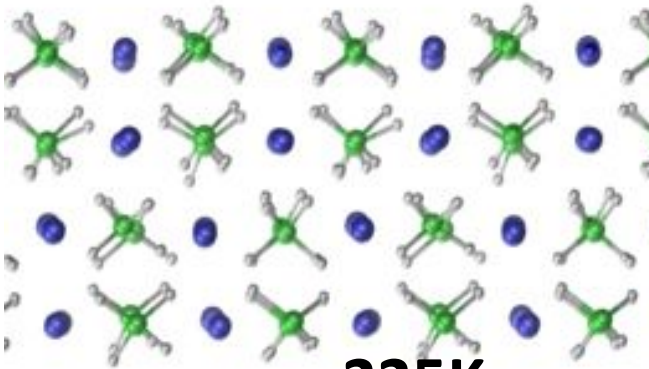
Gamma

200K

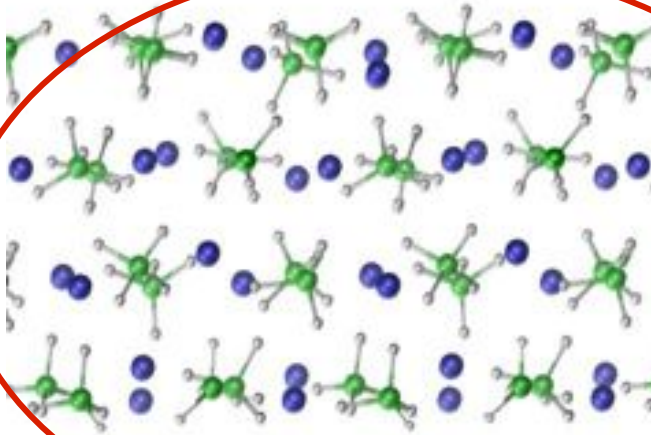


275K

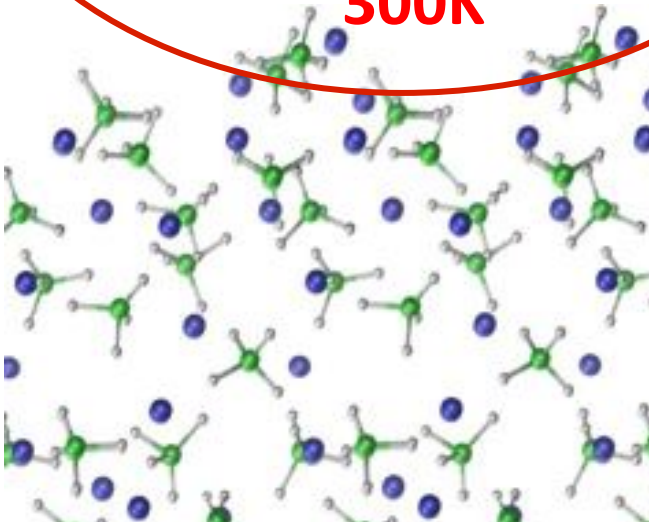


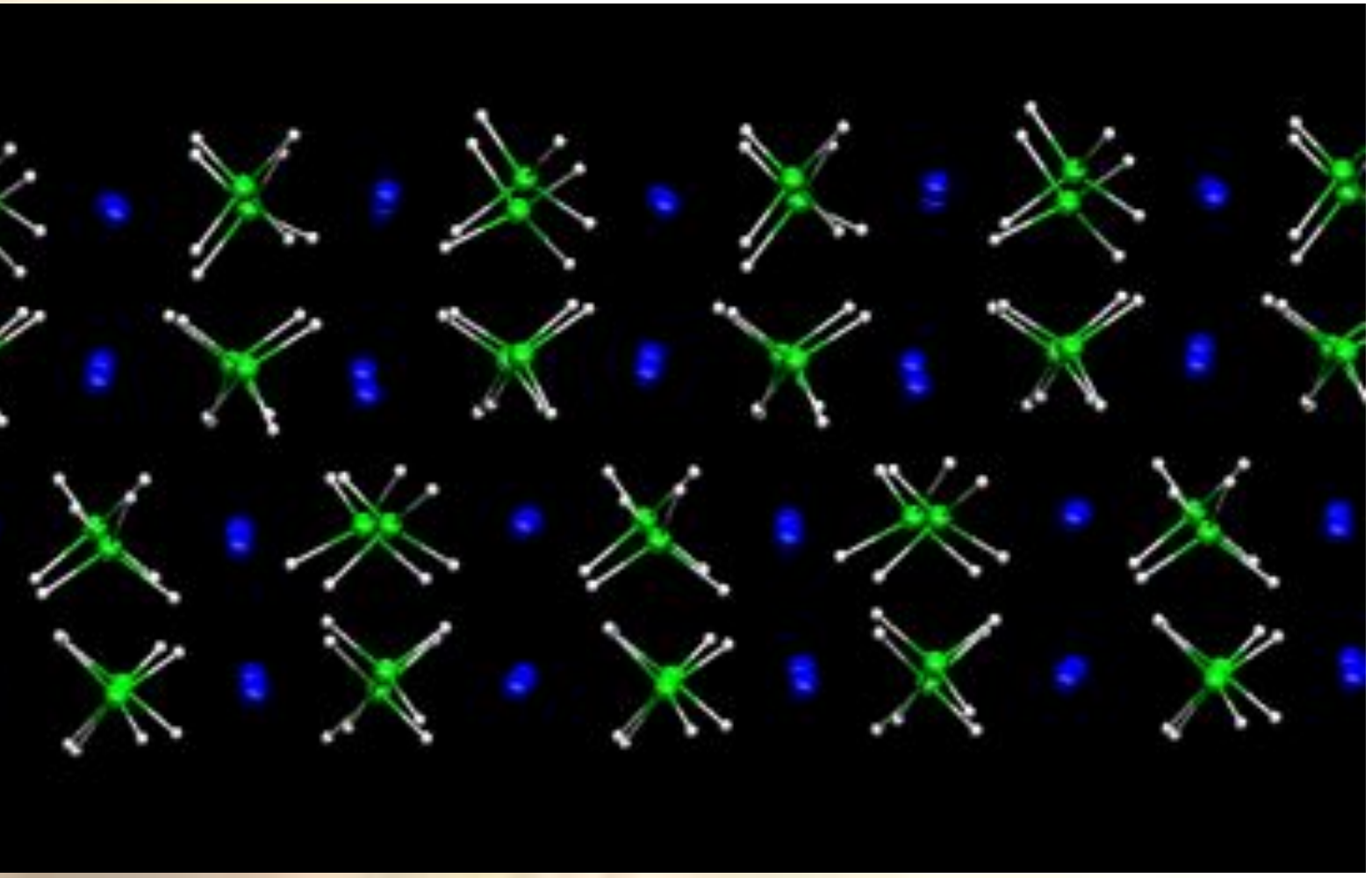


225K



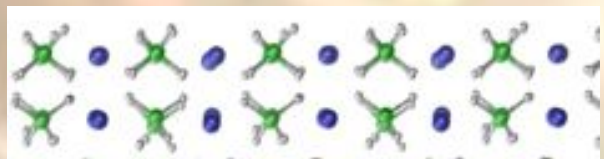
300K

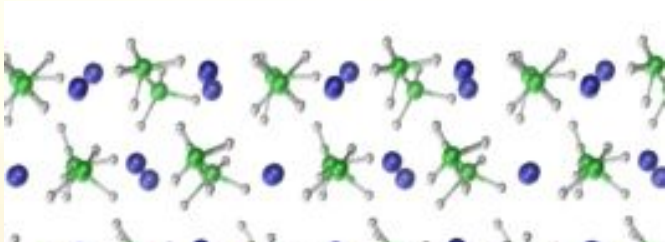


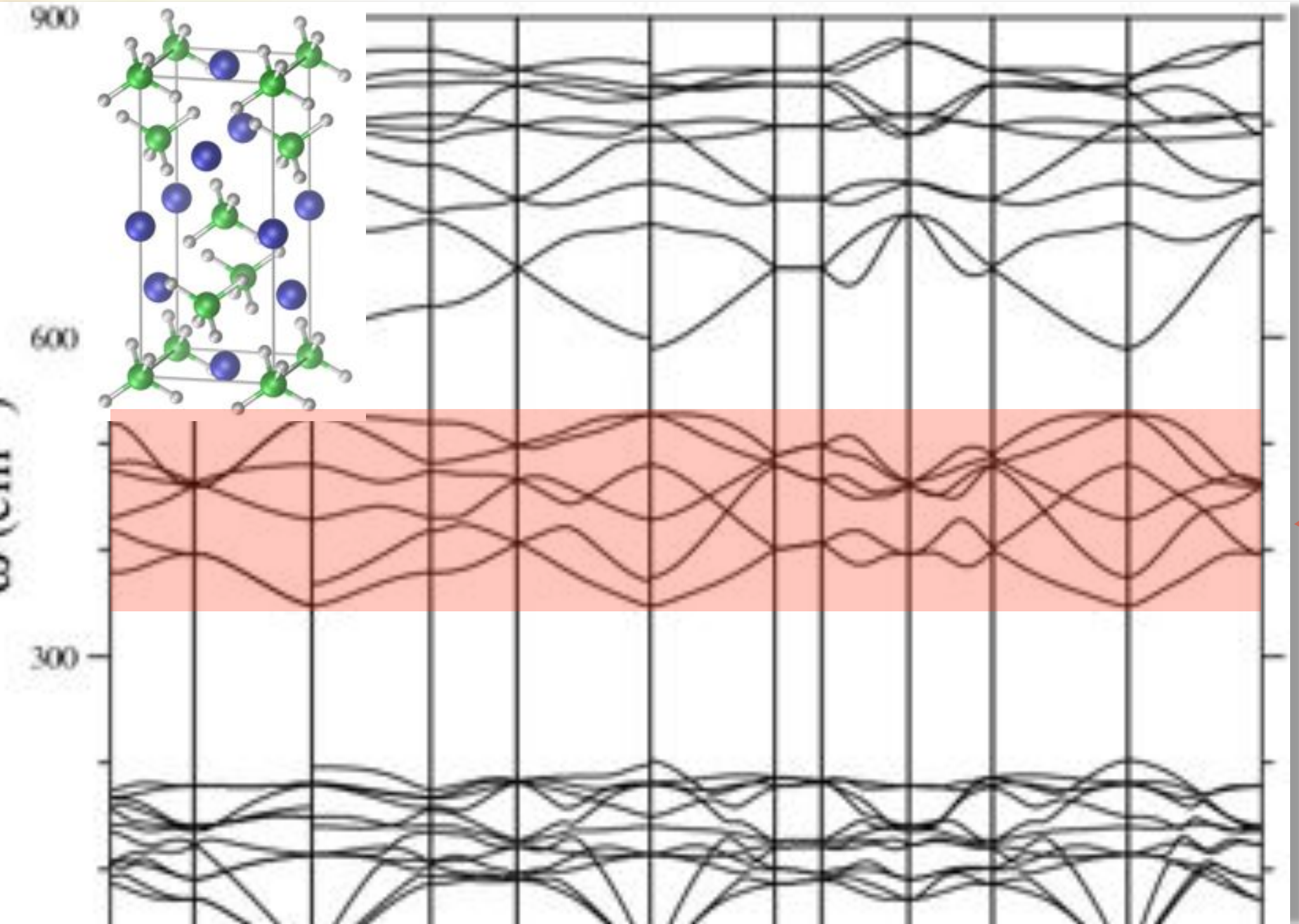


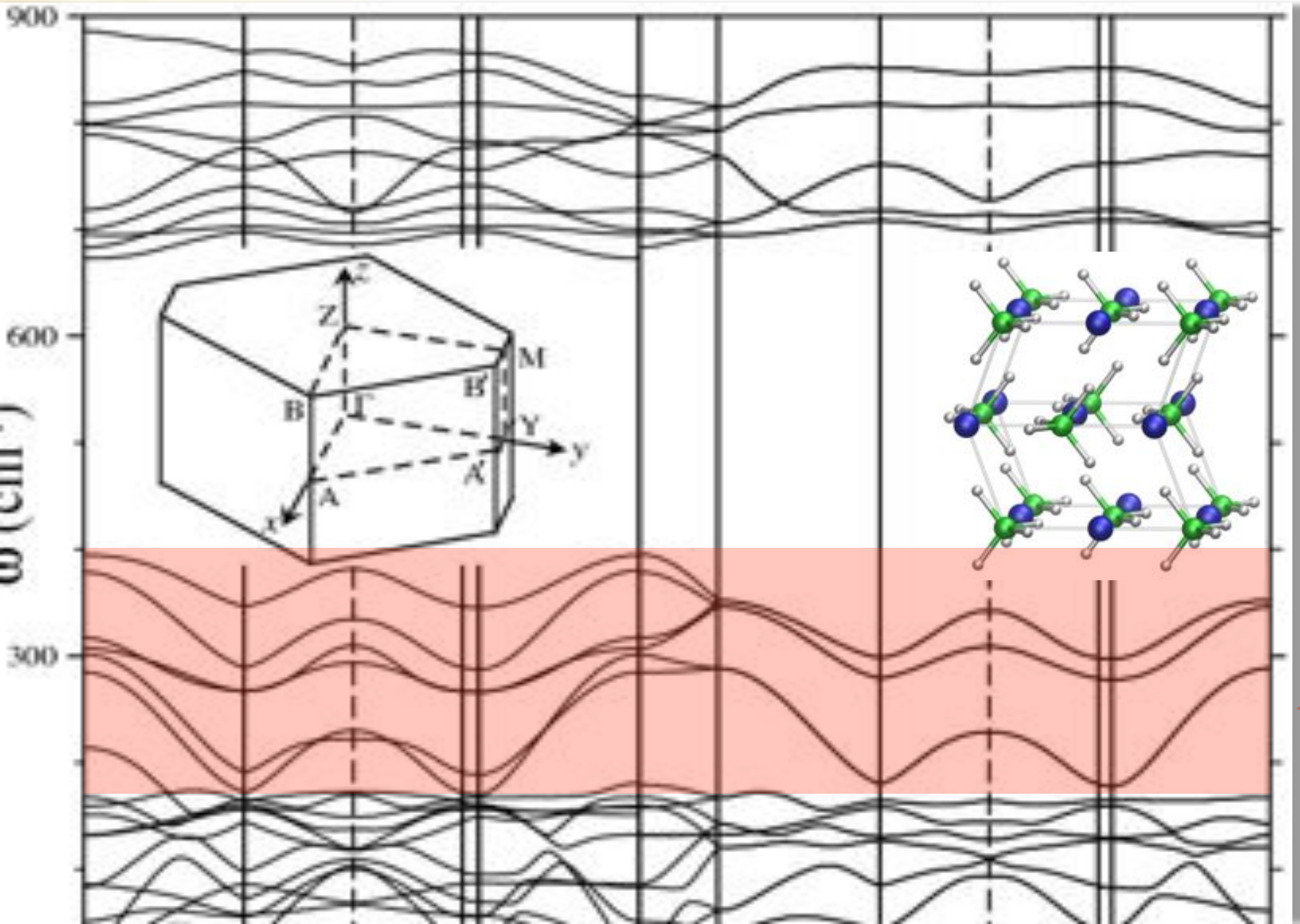
1. Rotation of AlH tetrahedra at surf
2. Expansion alon lattice parameter
3. Shear of surfac planes

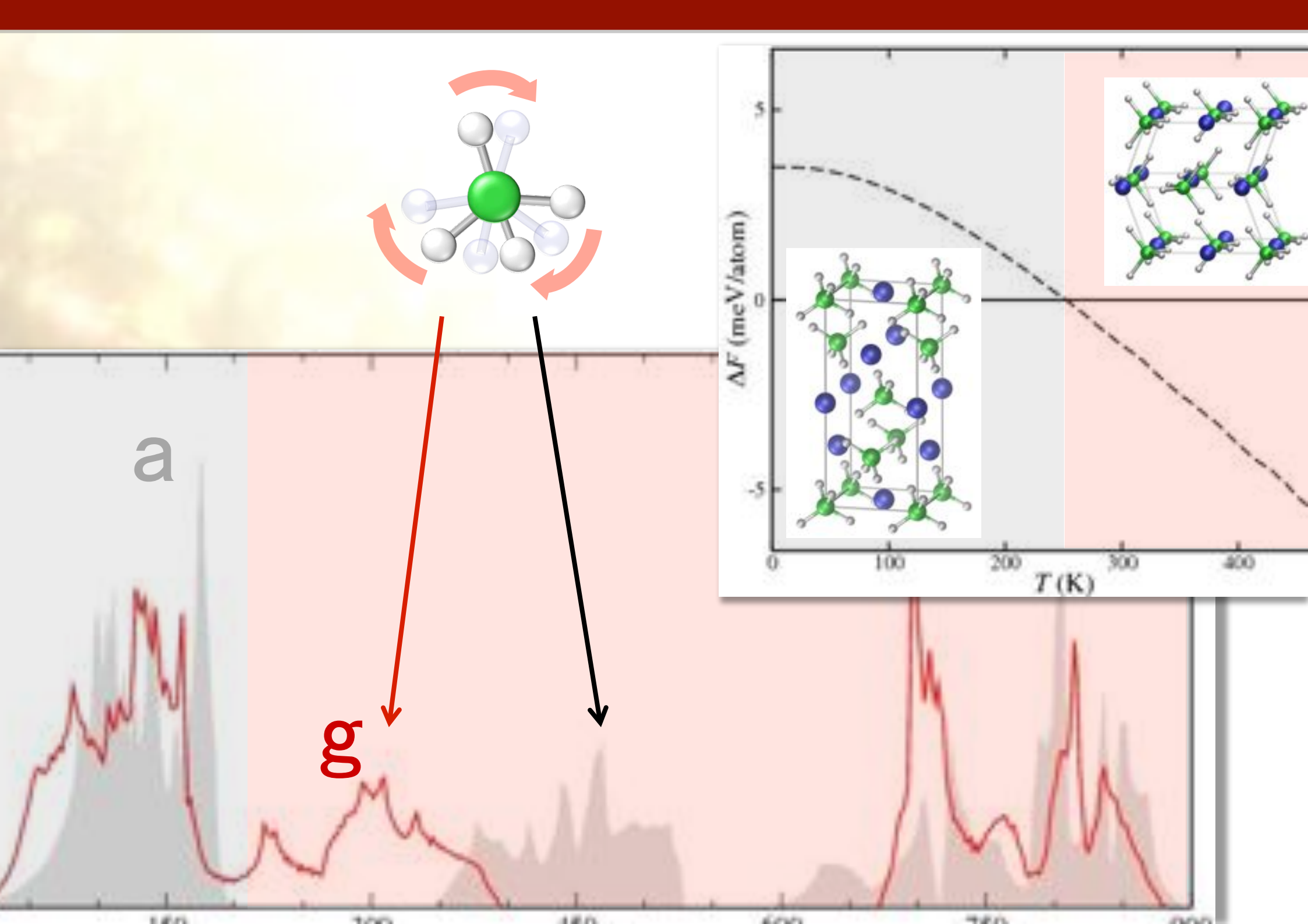
(001) Surface slab @ 275K

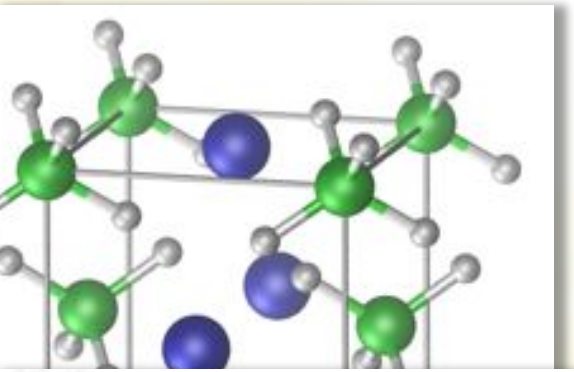


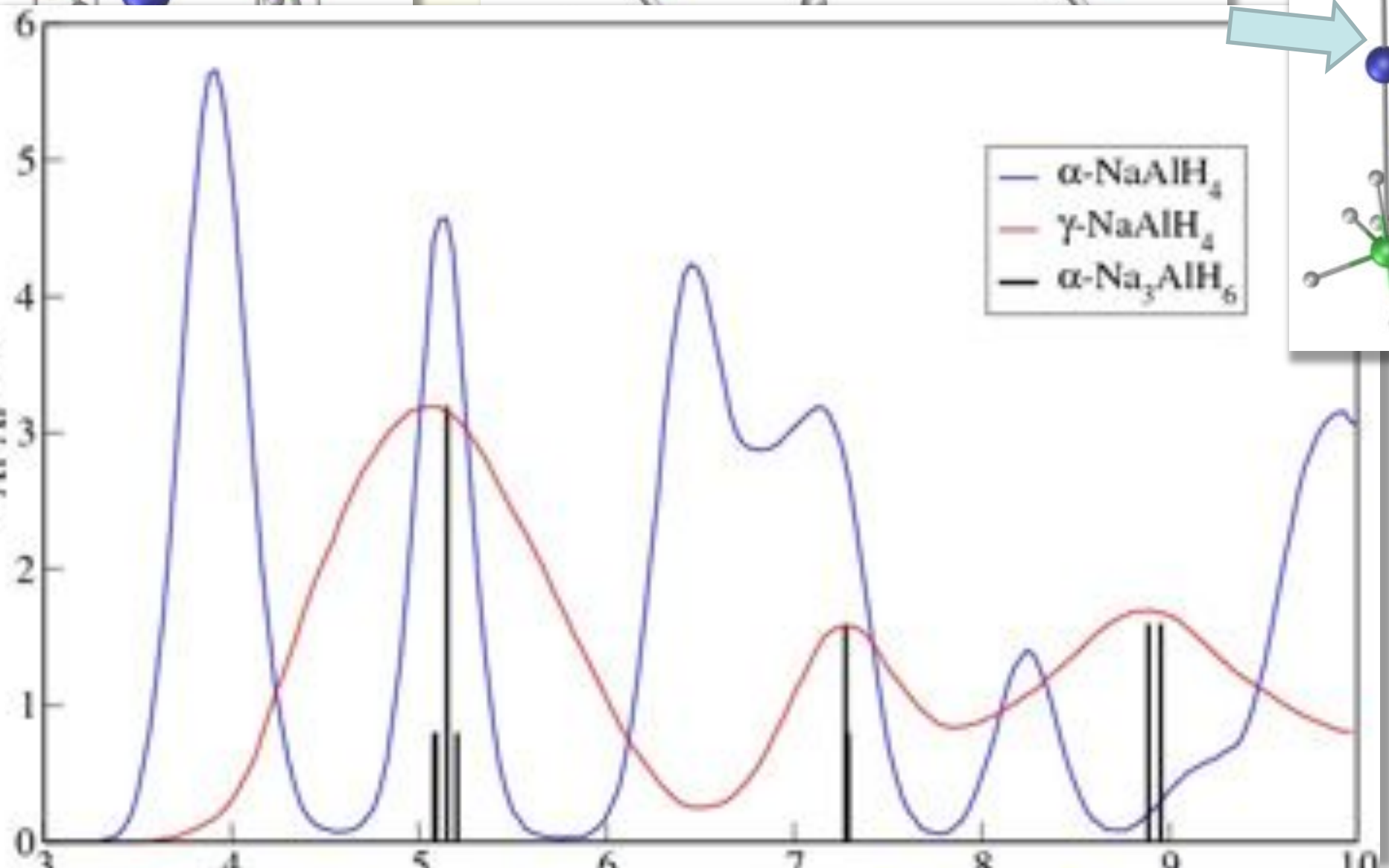



900
600
300

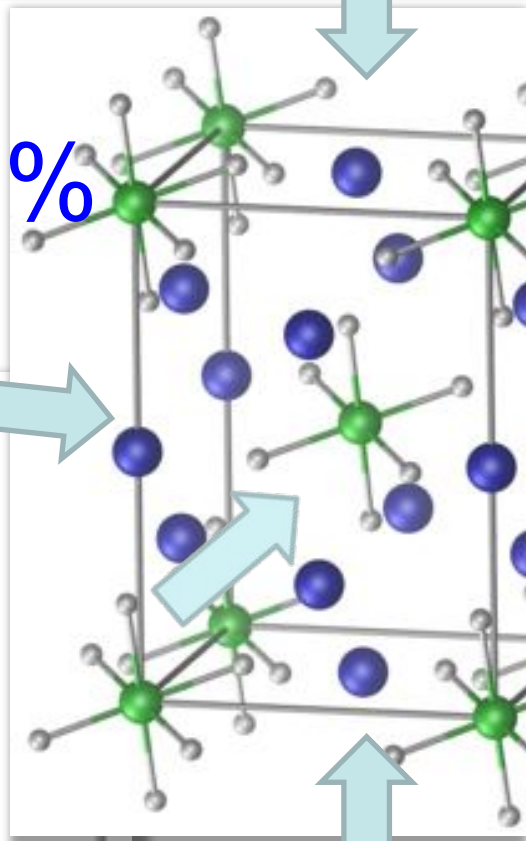

900
600
300
Z
M
B'
B
Γ
Y
y
A'
A
x


a
g
ΔF (meV/atom)
T (K)
5
0
-5
0
100
200
300
400

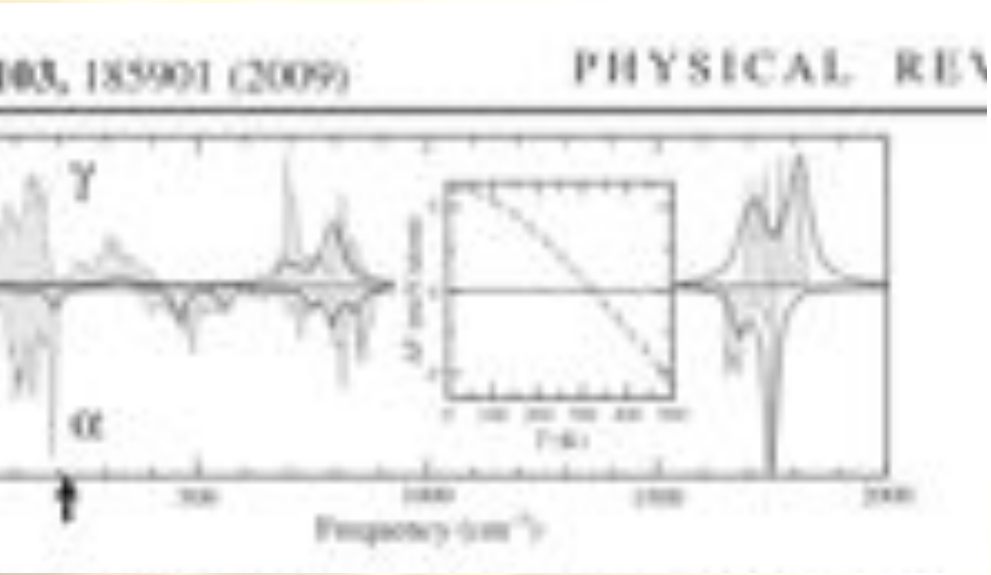




10%



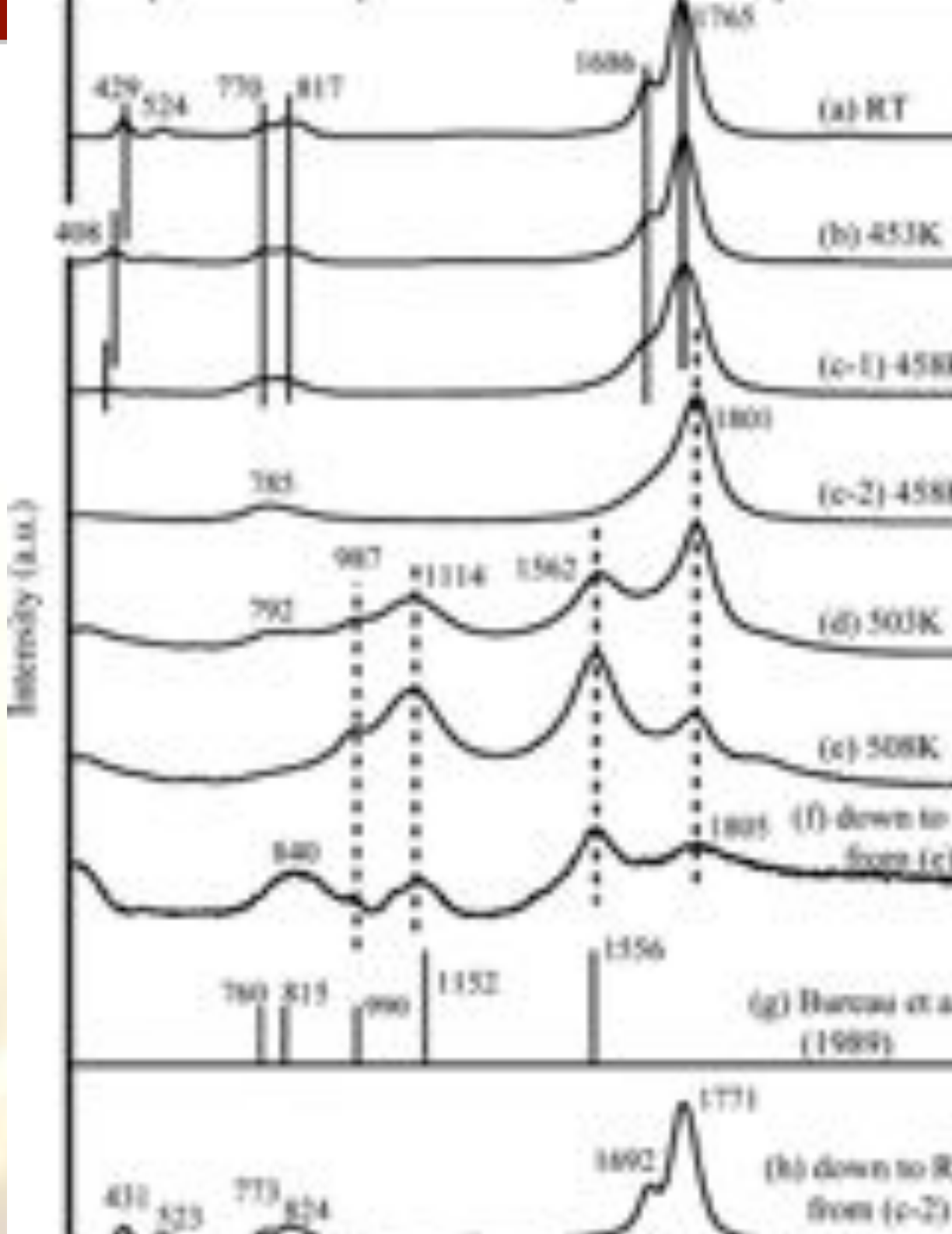
a-Na_3AlH_6



***Yukawa et al., J. Alloys Comp. 46&447, 242 (2007)*:**

- Stable at room T
- Intact AlH_4 units with little constraint from lattice
- Appearance of new vibrational peak at 1800 cm^{-1}

Anton, J. Alloys Comp. 356&357, 400 (2003):



Conclusions

- First-principles electrochemistry is a novel challenge for our field – we need to understand the accuracy of our predictions, but especially to find novel ways to calculate experimentally relevant properties
- If we succeed, we can leverage the power of quantum simulations for characterization and design of novel materials/processes/devices.

Thank you for listening!