Water Study at Surface and Interface

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Water — an enduring mystery

Yet another theory of liquid water structure raises questions about interdisciplinarity, drug design, astrobiology, molecular biology, geochemistry and more.

Philip Ball

No one really understands water. It's embarrassing to admit it, but the stuff that covers two-thirds of our planet is still a mystery. Worse, the more we look, the more the problems accumulate: new techniques probing deeper into the molecular architecture of liquid water are throwing up more puzzles.

This guilty secret has myriad ramifications. Water defines the terrestrial environment. It is central to Earth and atmospheric sciences, to biology and to many technologies. The common assumption that water is well characterized has led to explanatory edifices built on shaky ground. The situation is unsatisfactory intellectually and hazardous in practice.

Everyone is agreed that one aspect of water's molecular structure sets it apart from most other liquids: fleeting hydrogen bonds[1]. These feeble bonds that link the molecules constantly break and form above water's melting point, yet still impose a degree of structure on the molecular jumble.

That's where the consensus ends. The

K. HOKUSAI (1790–1849)/BRIDGEMAN

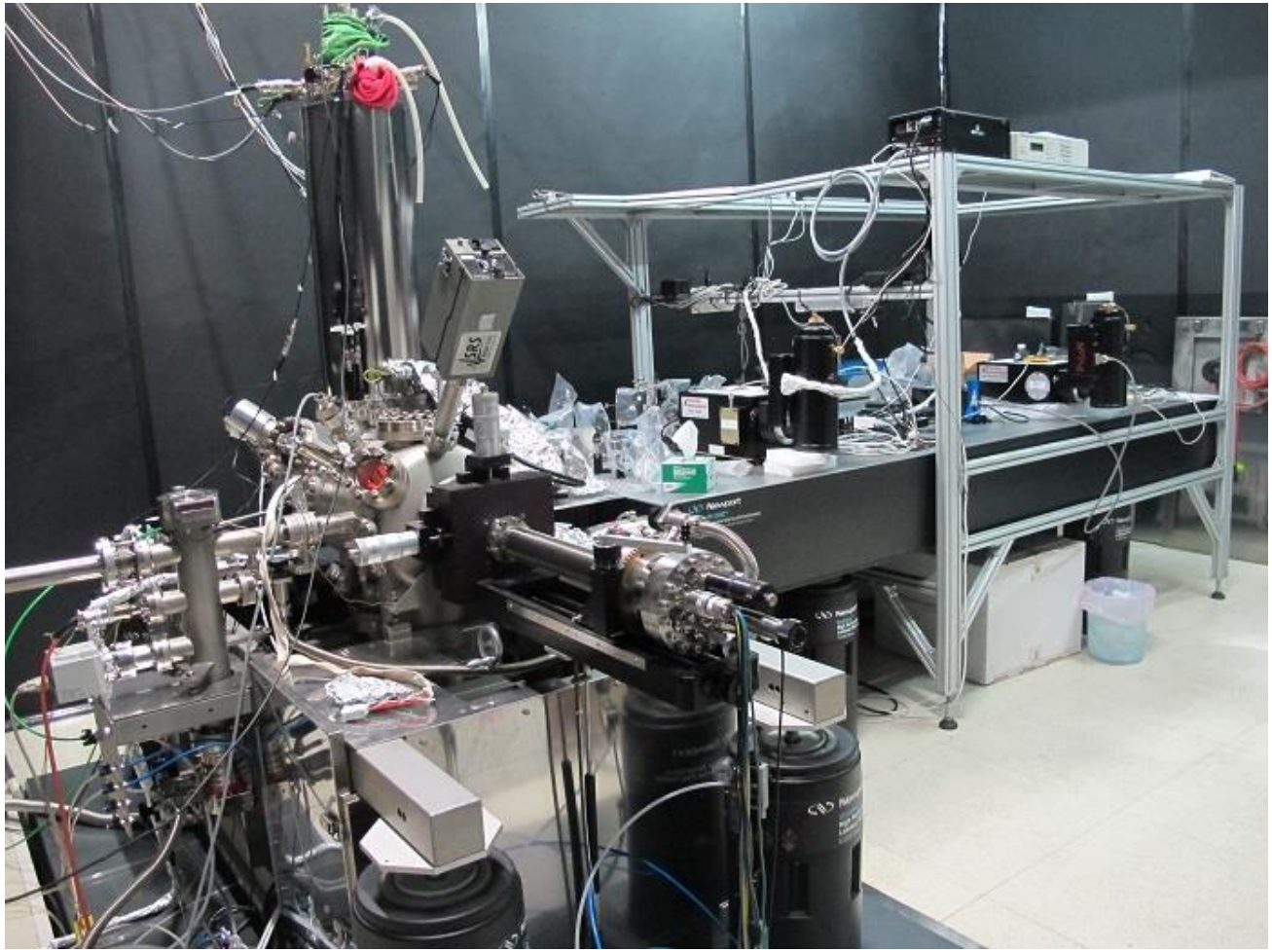
Why mystery?

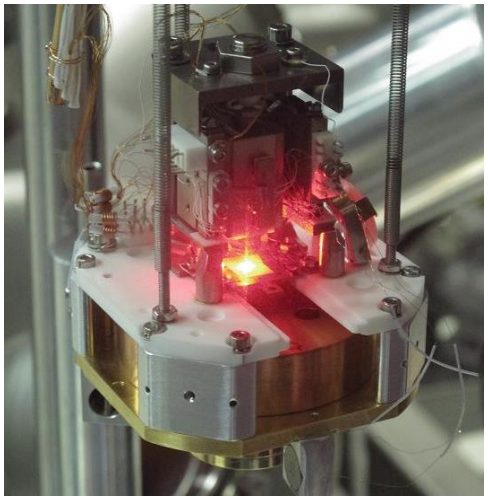
- Theoretically:
  - Electronic structure accurate (more complex weak interaction)
  - Ergodicity
  - Nuclear quantum effects (NQEs), statistically still fine, dynamically problematic
- Experimentally:
  - Atomic level resolution: What does a water molecular look like?

Why mystery?

- Theoretically:
  - Electronic structure accurate
  - Ergodicity
  - Quantum nuclear effects, statistically still fine, dynamically problematic
- Experimentally:
  - Atomic level resolution
- Method we use:
  - Low temperature STM + first principle methods

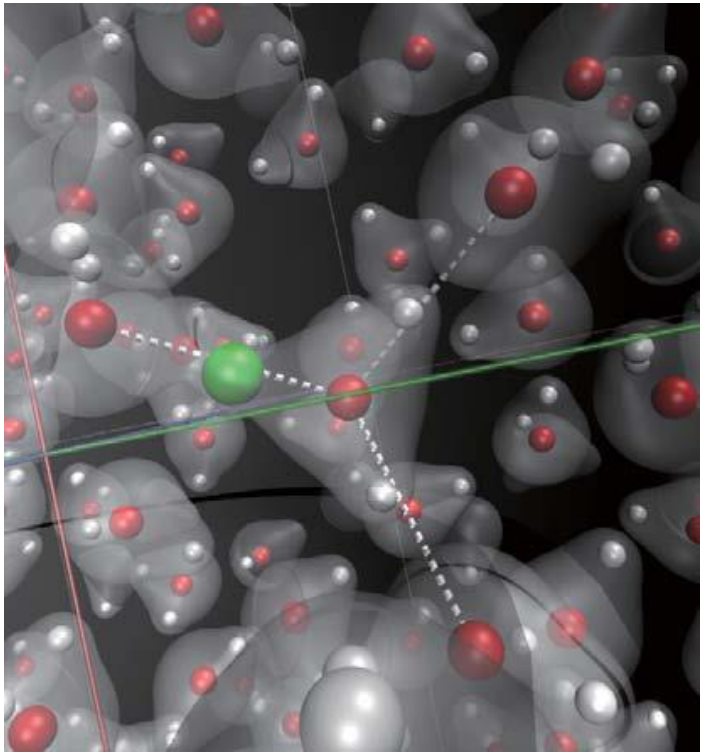
Scanning Tunneling Microscope (STM)

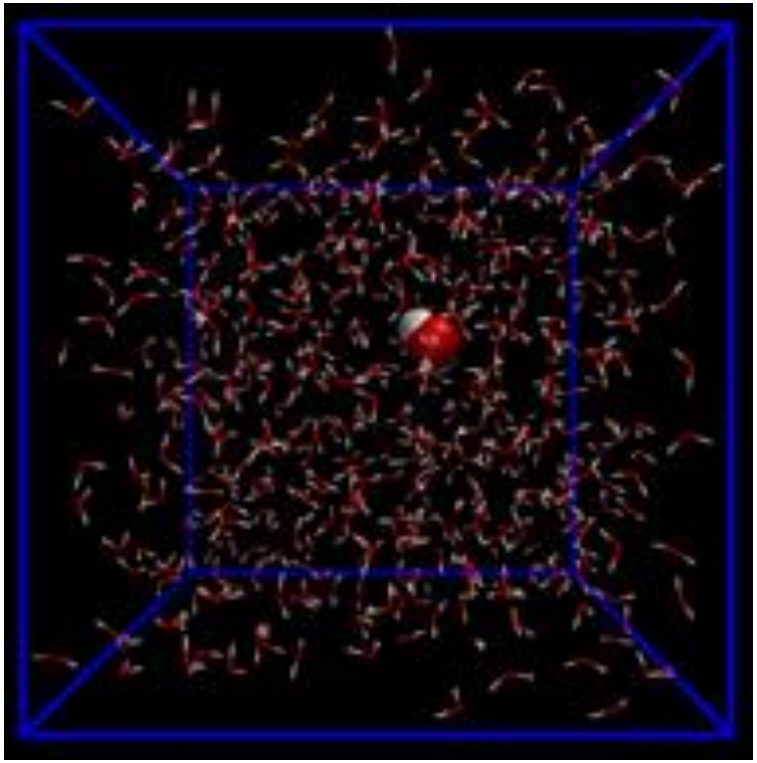




-lowest T: 5K±5mK
-xy drift: <0.01Å/min
-He cost: <1 L/day
-Minimum I: 100fA
-Freq resolution: 20mHz
-Q factor: >200,000
-In situ evaporation
-Optical
-Time resolution: 100fs

Home-made Laser-combined LT-STM/AFM system (Ying Jiang @PKU)





Classical Mechanics

Classical Particle

Quantum Mechanical Path Integral

Ring Polymer

Outline

- Introduction of an order parameter
  - Pan, … …, EGW , ***Phys. Rev. Lett***. (2008); Sun, … …, EGW， ***PNAS*** (2012)

- Submolecular imaging of water on NaCl(001)
  - Guo, … …, EGW and Jiang, ***Nature Mater.*** (2014)

- Clustering of water on NaCl(001)
  - Chen, … …, EGW, ***Nature Commun.*** (2014)

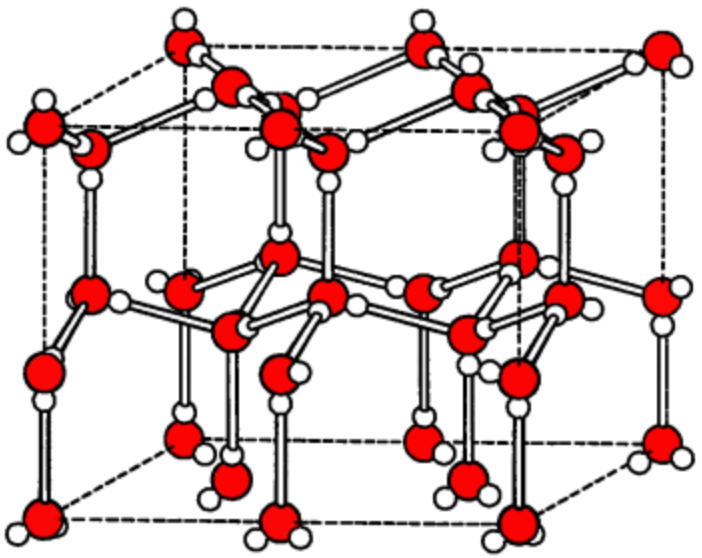
- Full quantum tunneling of protons
  - Meng , … …, EGW and Jiang, ***Nature Phys.*** (2015)

- Full quantum effect of hydrogen bond
  - Guo, … …, EGW and Jiang, ***Science*** (2016)

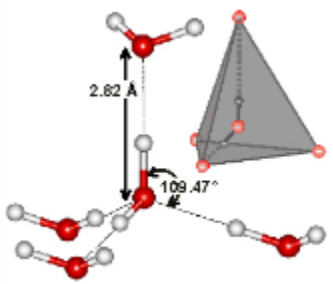
Outline

- Introduction of an order parameter
  - Pan, … …, EGW , ***Phys. Rev. Lett***. (2008); Sun, … …, EGW， ***PNAS*** (2012)

Bulk Ice Ih:
A Proton Disordered Solid



Bernal-Fowler ice rules:



(1) Each oxygen atom has two OH bonds.
(2) There is exactly one hydrogen atom between each two nearest neighbour oxygen atoms.

J. D. Bernal and R. H. Fowler, J. Chem. Phys. 1, 515 (1933).

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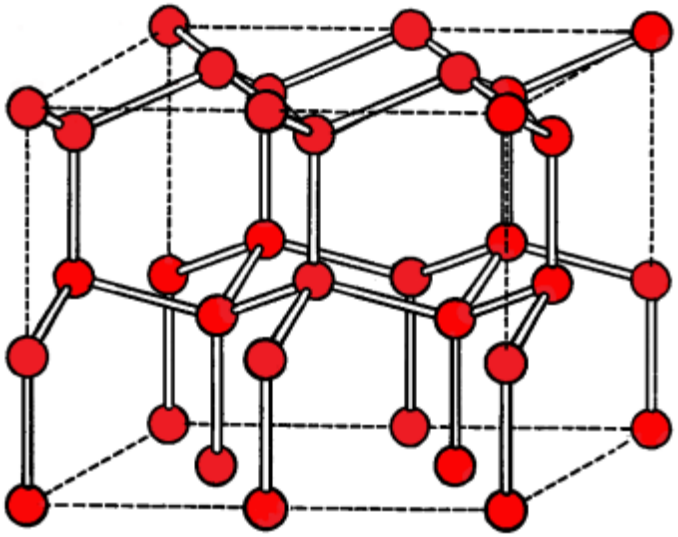
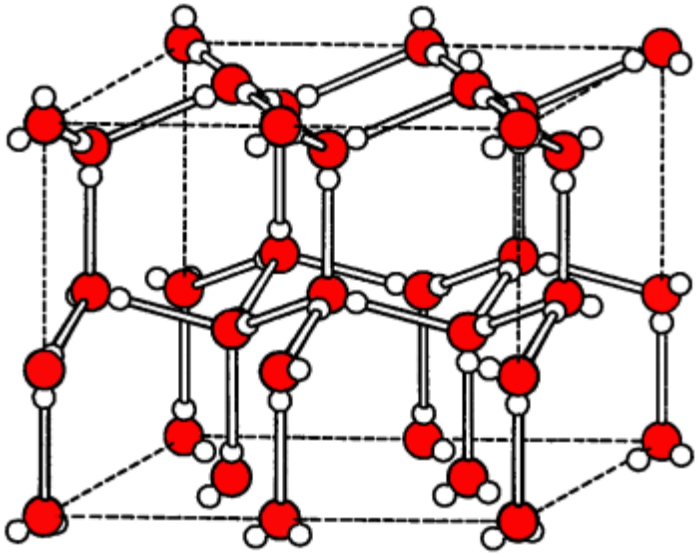
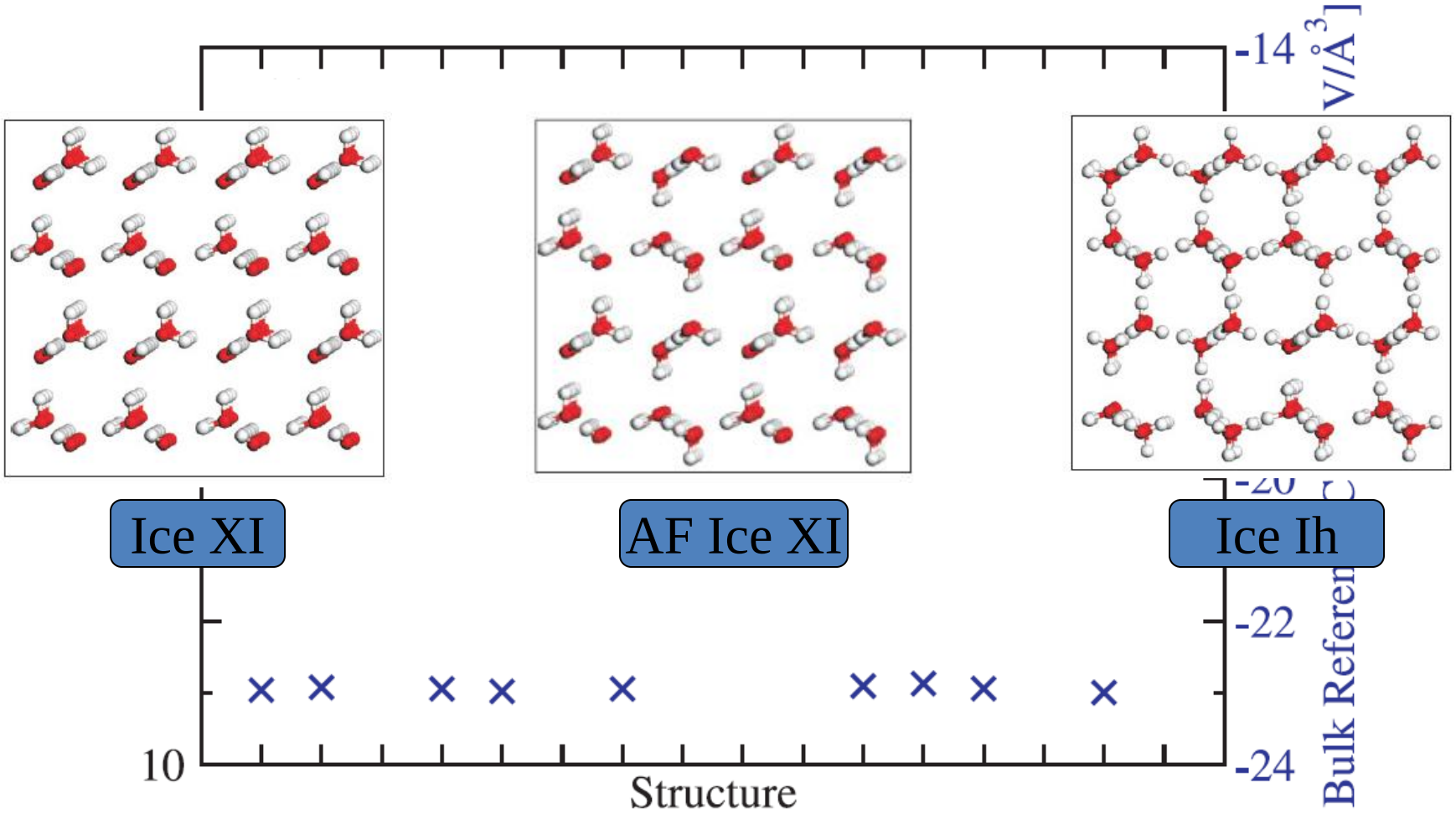




The cohesive energy of ice Ih



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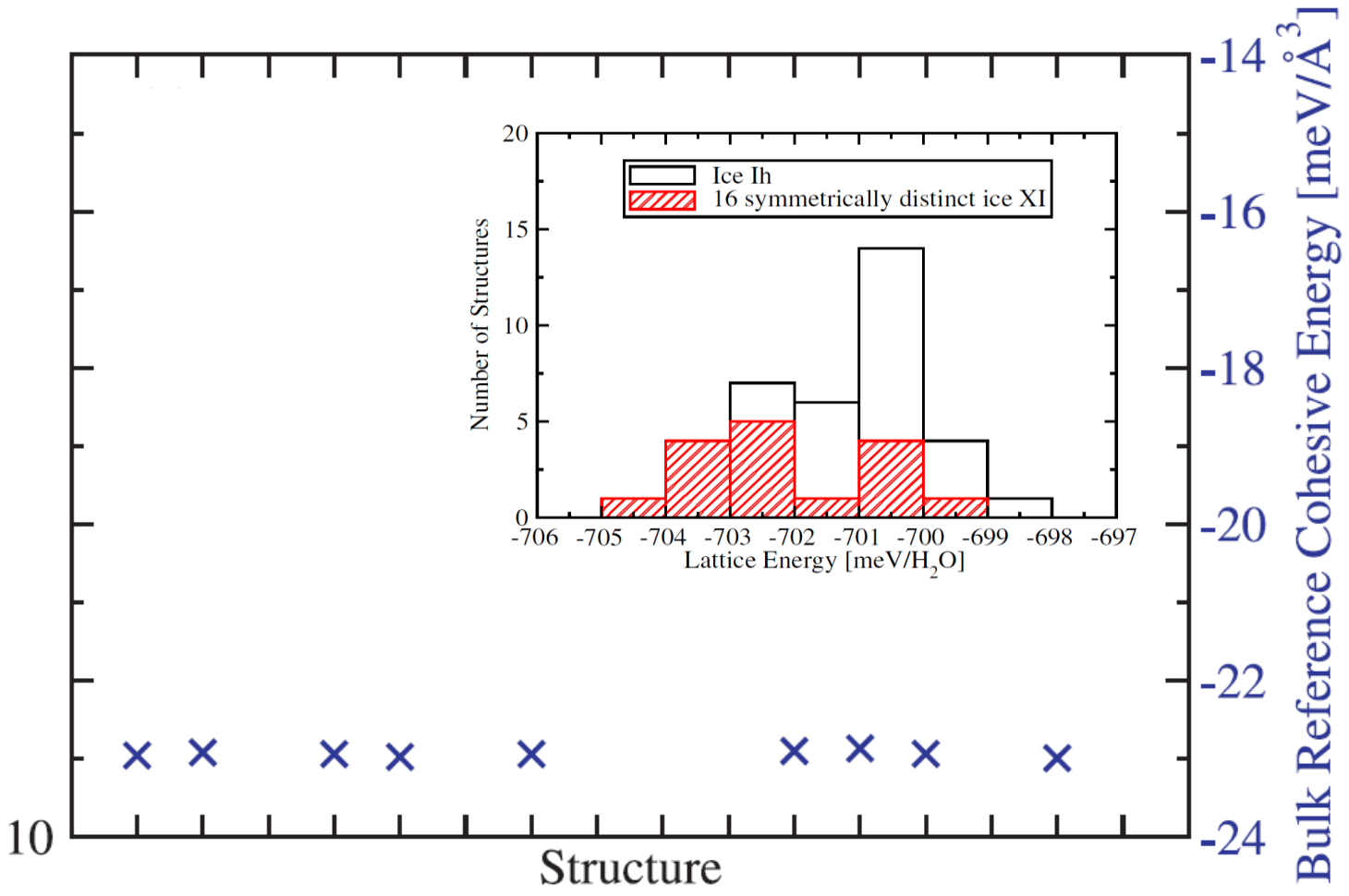
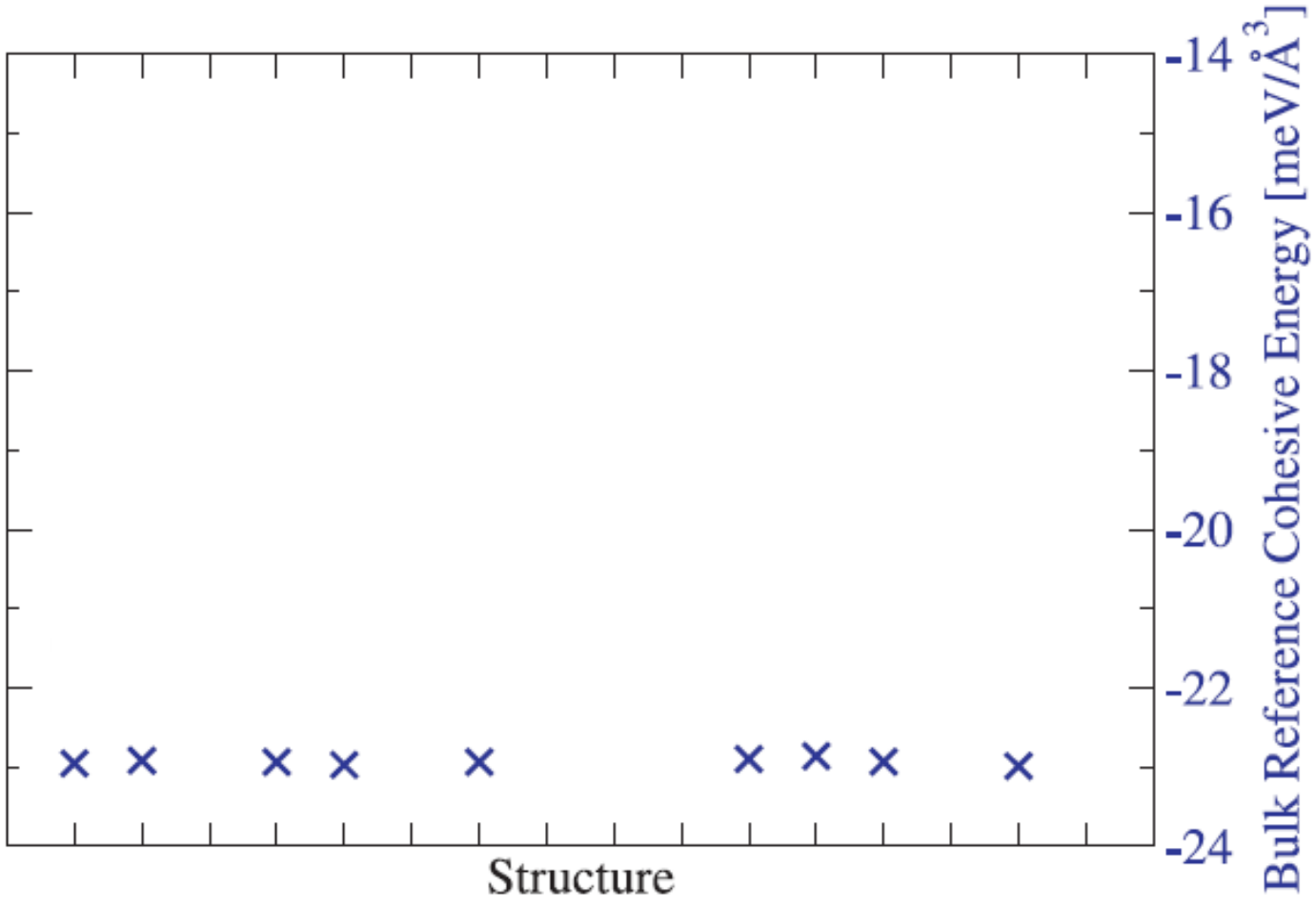


The bulk phase transition of ice XI/Ih: 72 K (K_BT ~ 6 meV/H_2O)

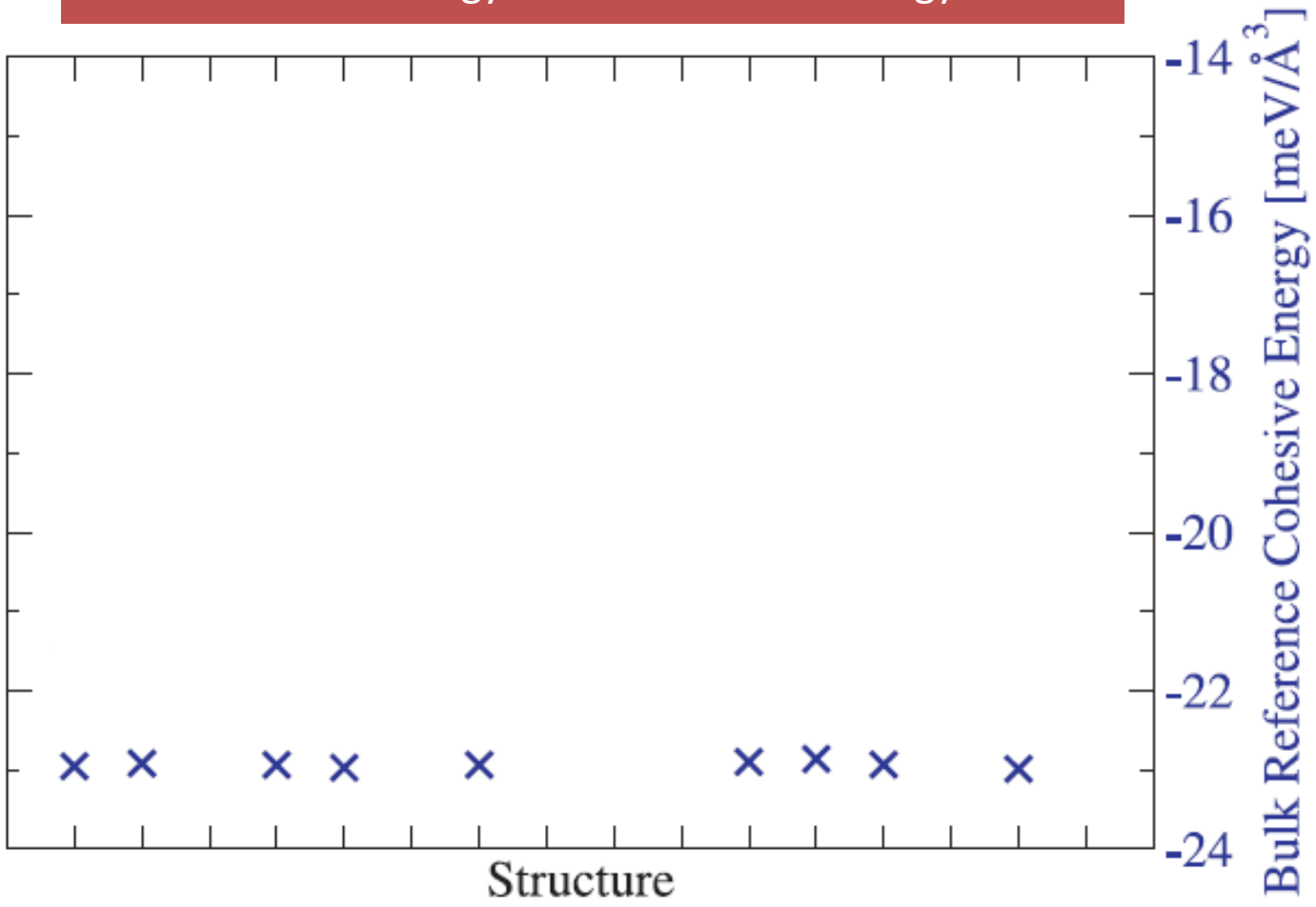
The energy changes on proton disorder in bulk: ~ 6 meV/H_2O

The surface energy of ice Ih



$$\gamma = \frac{E_{\text{tot}}^{\text{slab}}(n) - n E_{\text{tot}}^{\text{bulk}}}{2A}$$

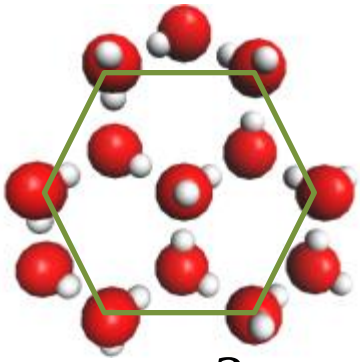
Surface Energy vs Bulk Cohesive Energy



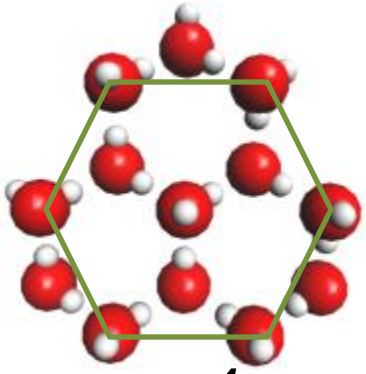
Bulk variation influenced by proton distribution ~ 6 meV/H_2O
Surface variation influenced by proton distribution >100 meV/H_2O

Order Parameter

New order parameter on basal plane surfaces of ice Ih



$c_i=3$



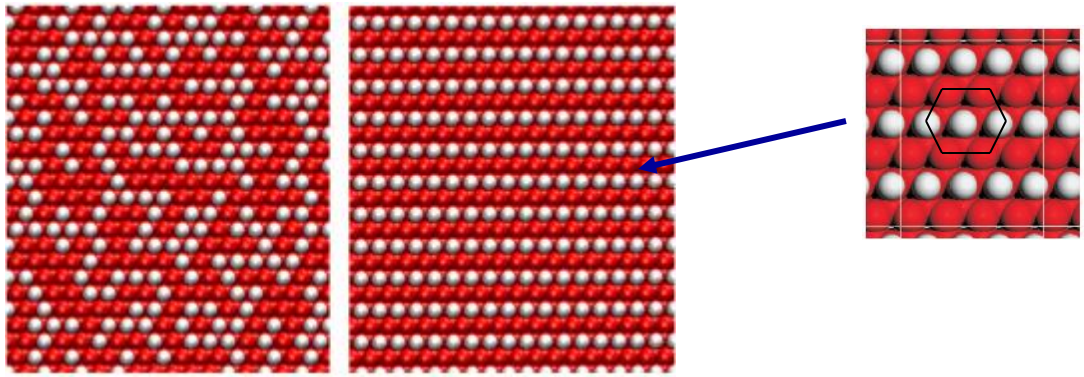
$c_i=4$

Order parameter:

$$C_{OH} = \frac{1}{N_{OH}} \sum_{i=1}^{N_{OH}} c_i,$$

C_{OH} : [2, 6)

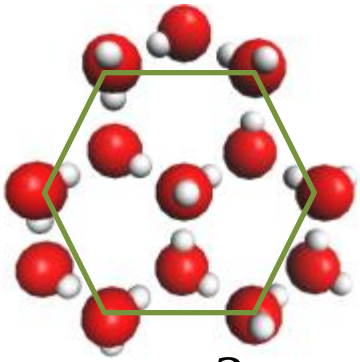
The larger the order parameters, the more inhomogeneous the proton distribution.



C_{OH} ~ 3 C_{OH} = 2

Order Parameter

New order parameter on basal plane surfaces of ice Ih



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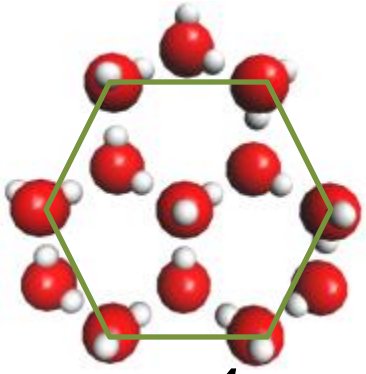

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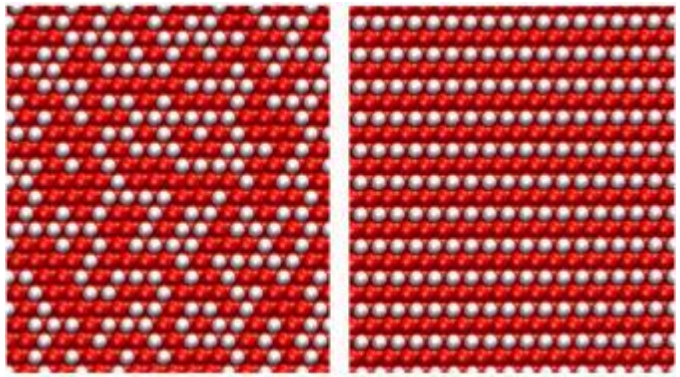
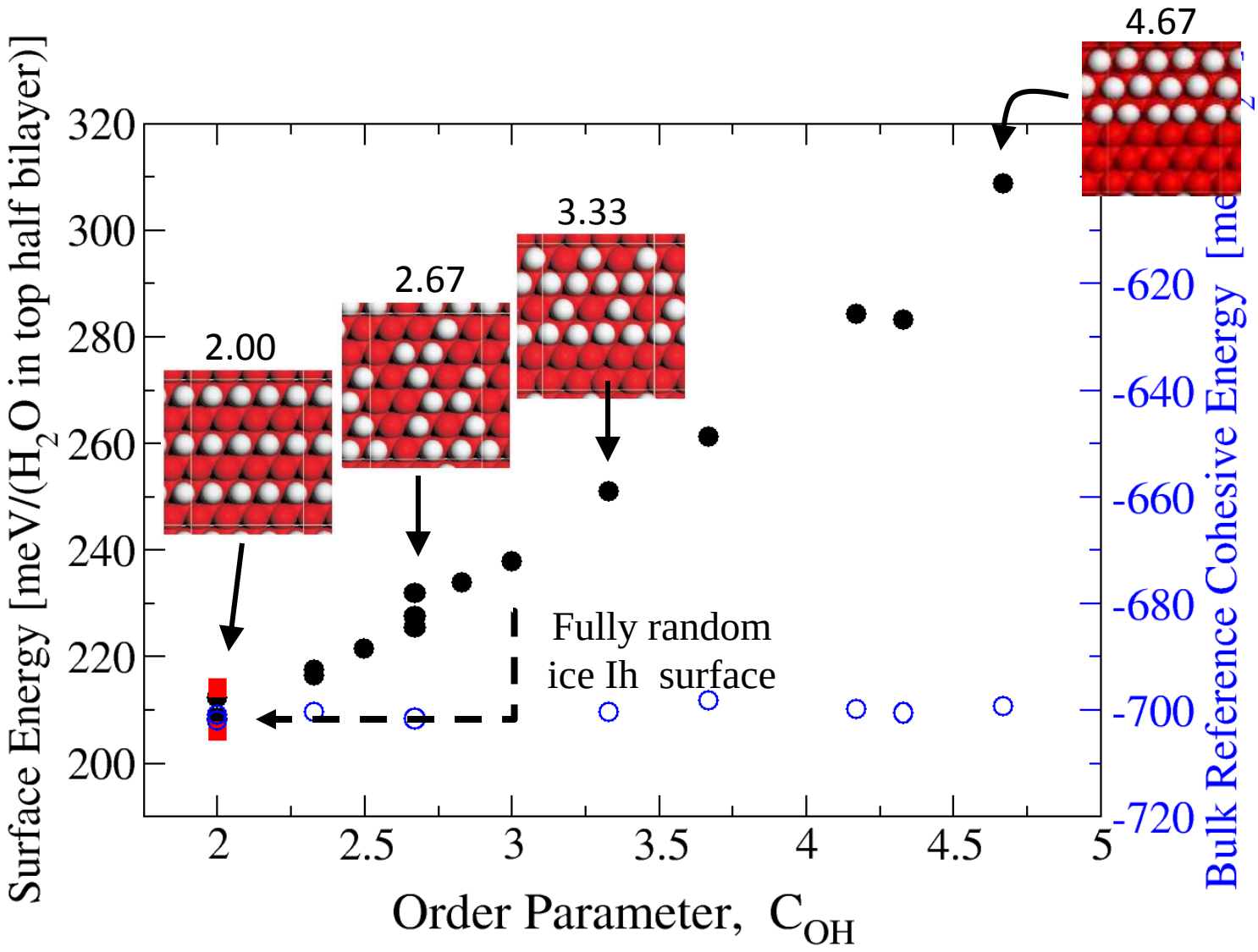
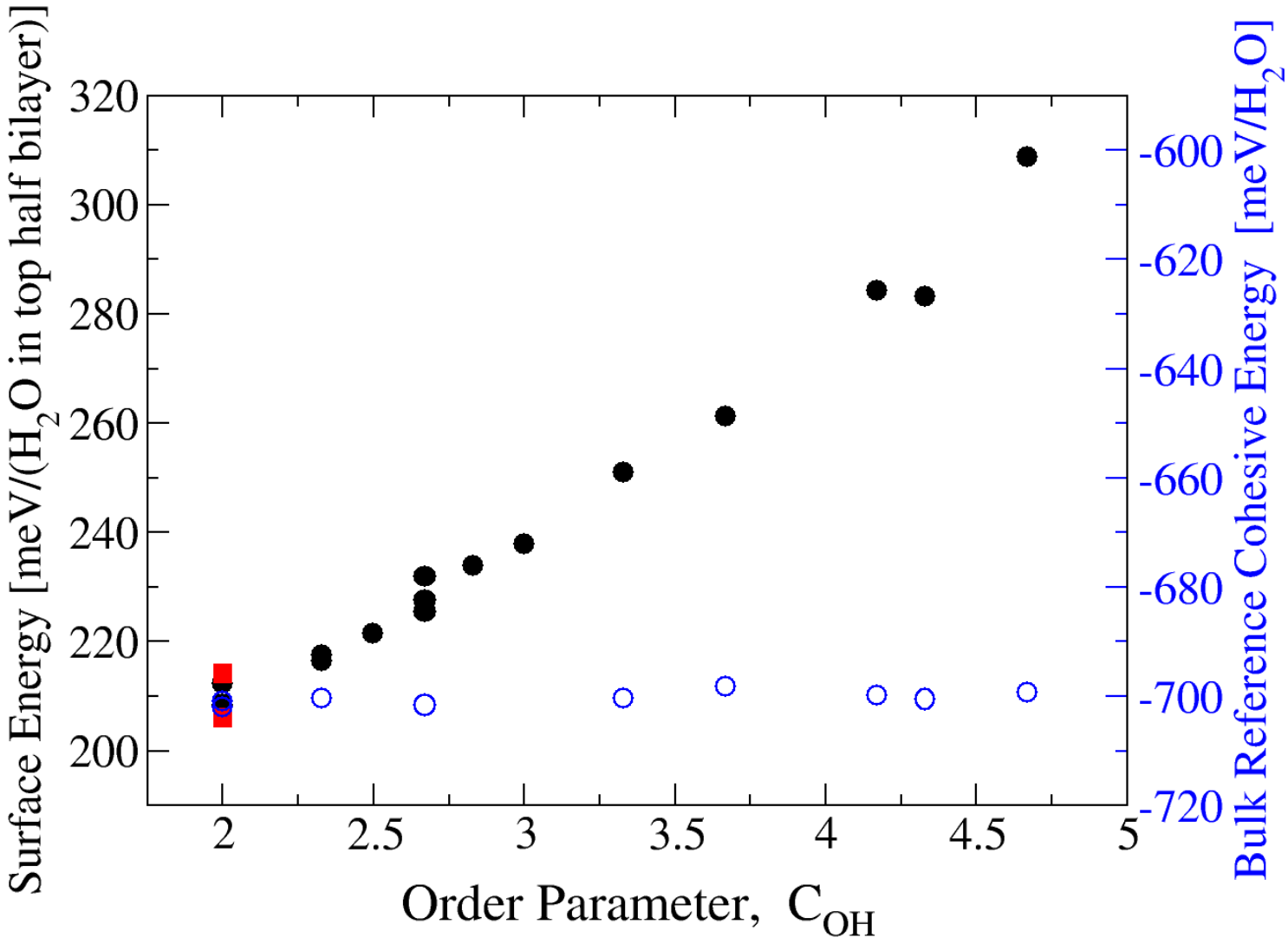


$C_{OH} \sim 3$ $C_{OH} = 2$

Basal plane surface energies depend on the order parameters, C_{OH}



Basal plane surface energies depend on the order parameters, C_{OH}



In a classical electrostatic model, we write the surface energy for various ice I*h* surfaces as

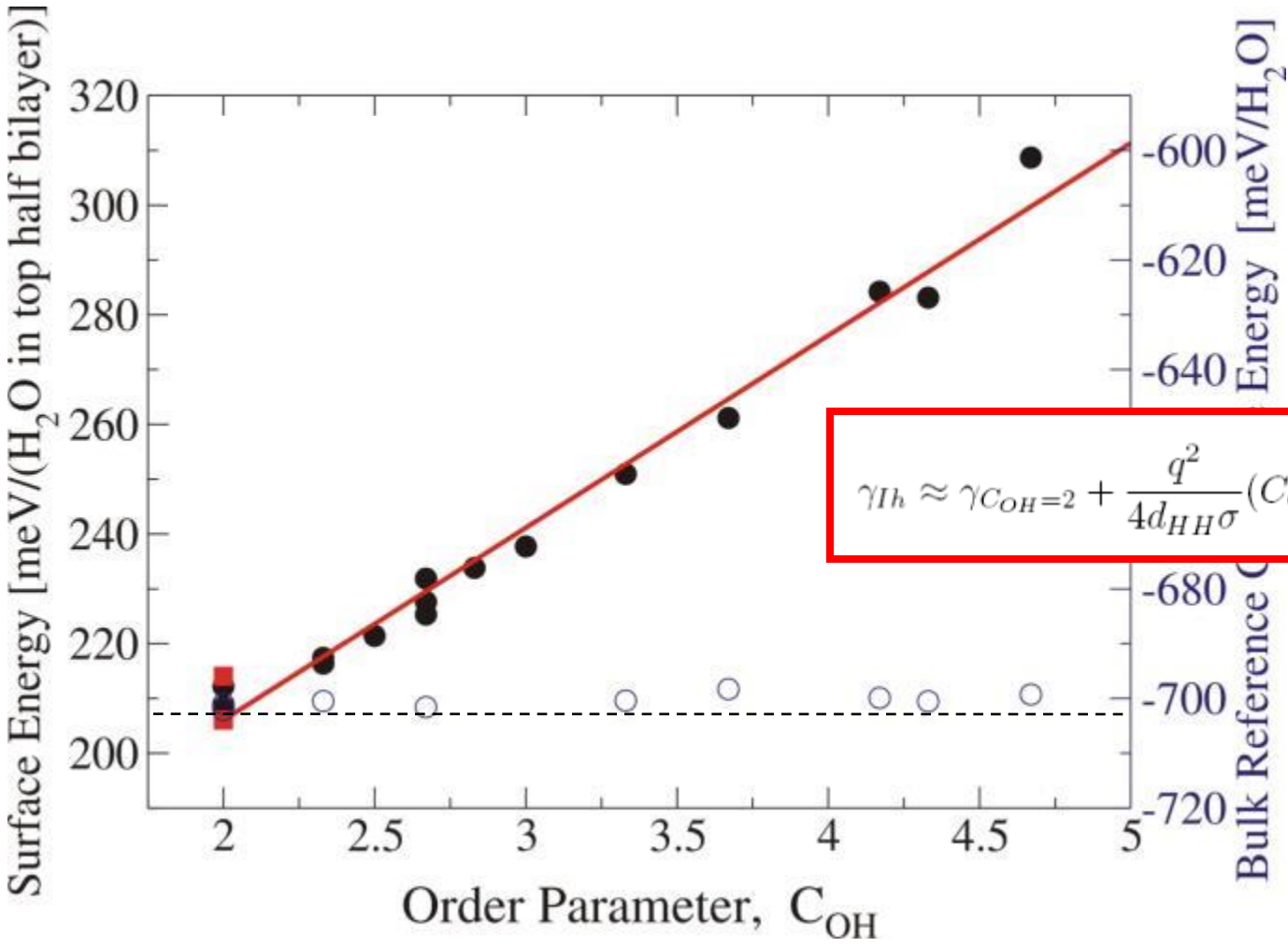
$$\gamma_{Ih} \approx \gamma_{C_{OH}=2} + \frac{\Delta E_{HH}}{A},$$

where $\gamma_{C_{OH}=2}$ s the surface energy of surfaces with C_{OH}=2 and $\Delta\, \boldsymbol{E}_{HH}$ a surface excess energy which C_{OH}>2 surfaces have due to the additional repulsion between dangling OH groups brought about by their on average closer proximity to each other. We express the total repulsion between dangling $\boldsymbol{E}_{HH}$ groups through a screened Coulomb interaction, which leads to

$$\gamma_{Ih} \approx \gamma_{C_{OH}=2} + \frac{q^2}{4 d_{HH} \sigma}(C_{OH} - 2),$$

It depends linearly on $\boldsymbol{C}_{OH}$ with a slope proportional to $\boldsymbol{q}^2$. $\boldsymbol{q}$ is the "effective charge" on the H atoms of the dangling OH groups. If $\boldsymbol{d}_{HH}$=4.42A and σ=16.92A^2, then the best fit for the charge $\boldsymbol{q}$=0.21e based on our DFT PBE and BLYP results.

Basal plane surface energies depend on the order parameters, C_{OH}

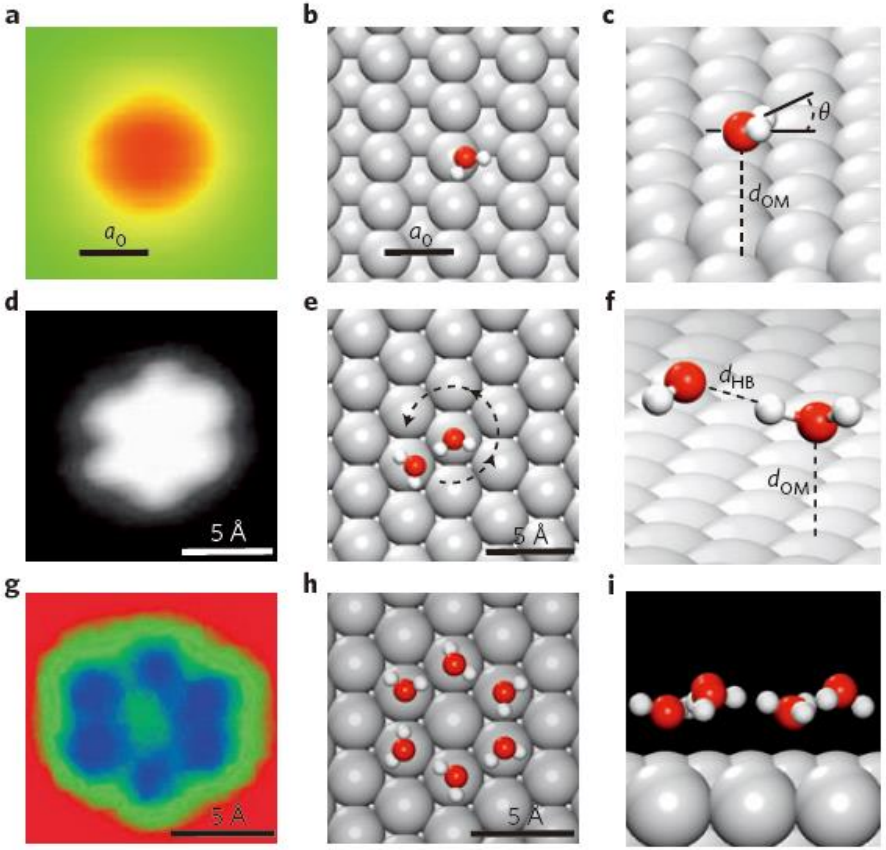


On dangling OH bonds, effective charge: q

Outline

- Submolecular imaging of water on NaCl(001)
  - Guo, ……, EGW and Jiang, ***Nat. Mater.*** (2014)

Previous STM studies of water



Carrasco, Hodgson, & Michaelides *Nat. Mater.* **11**, 667 (2012)

T. Mitsui, *et al.* Science 297, 18501852 (2002).
A. Verdaguer, *et al.* Chem. Rev. 106, 1478 (2006)
A. Michaelides and K. Morgenstern, Nat. Mater. 6, 597601 (2007)
A. Hodgson and S. Haq, Surf. Sci. Rep. 64, 381 (2009)
P. J. Feibelman, Science 295, 99 (2002)
T. Kamagai, et al. Nat. Mater. 11, 167 (2012)

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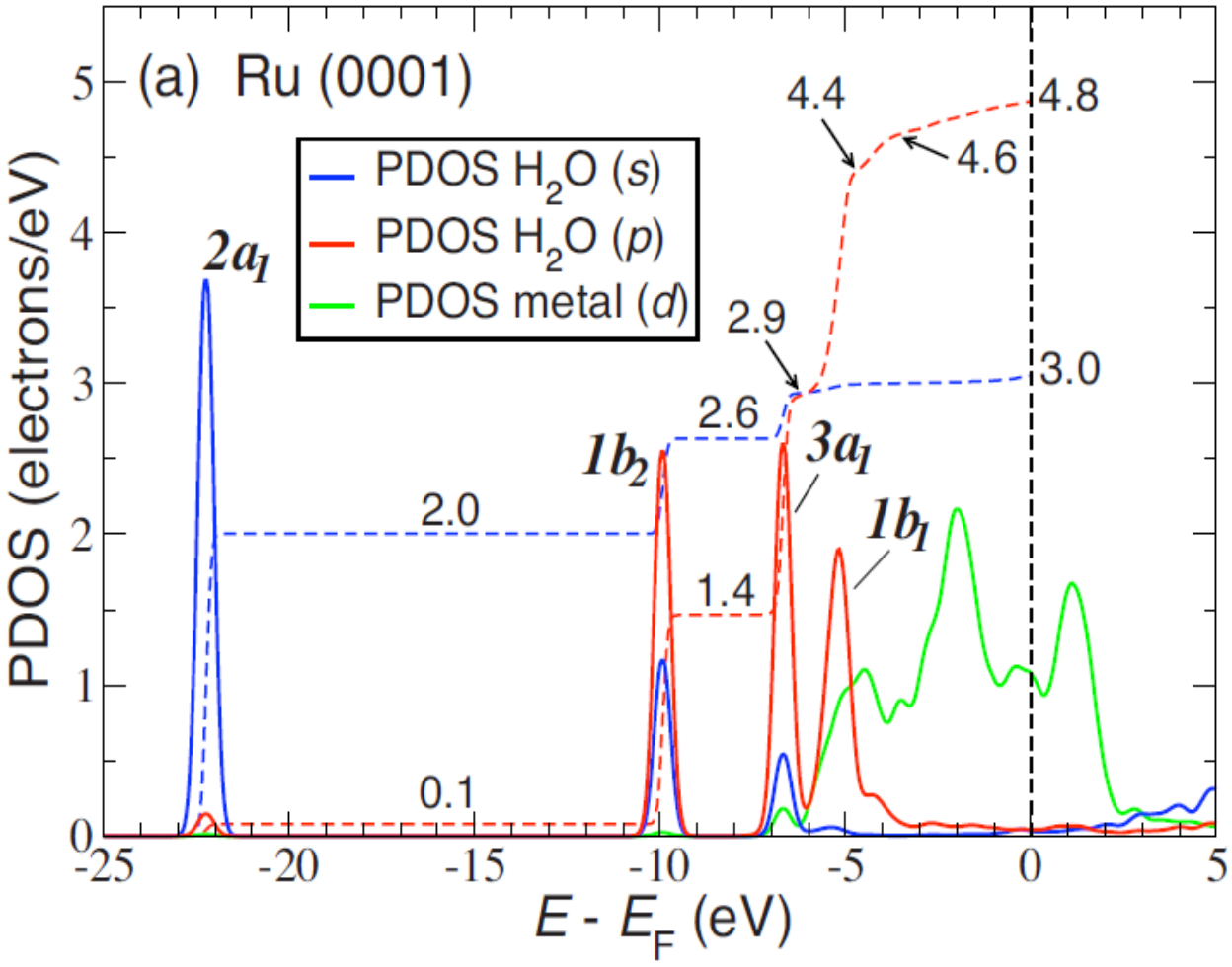


Carrasco, Michaelides, & Scheffler *J. Chem. Phys.* **130**, 18470 (2009)

Our experimental setup

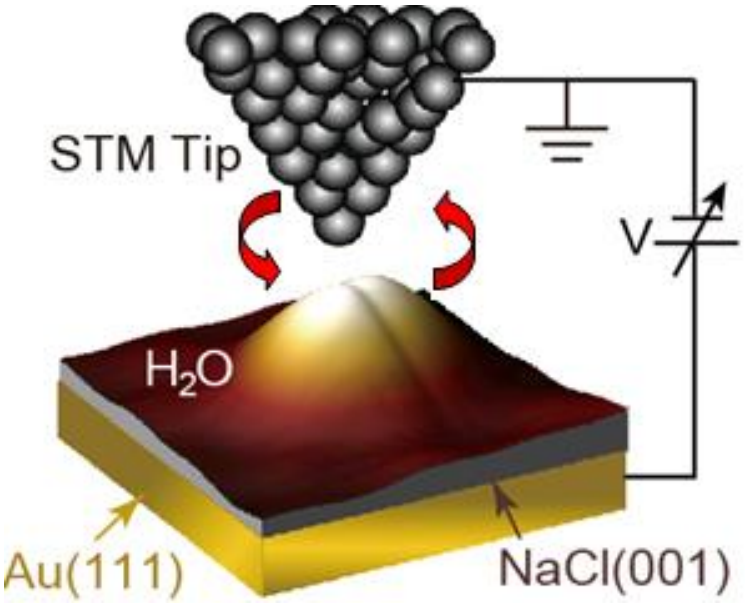
Why no orbital structure of water?

1. Water-substrate hybridization

   - Insulating film

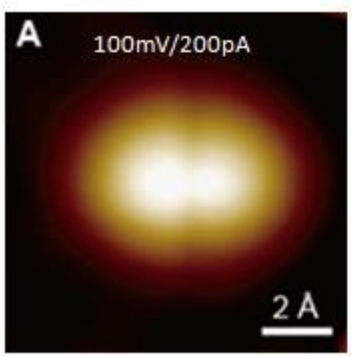
2. Molecular orbitals far from E_F

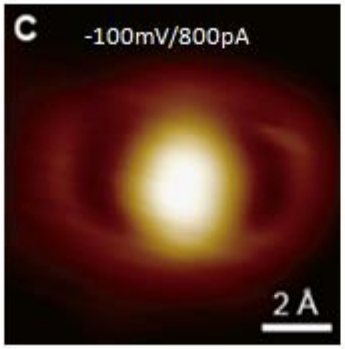
   - Tip-molecular coupling

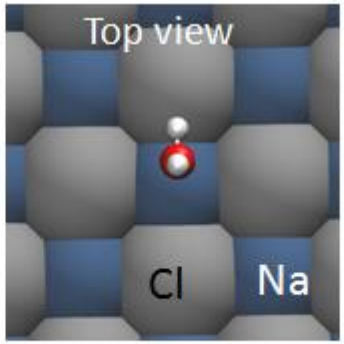


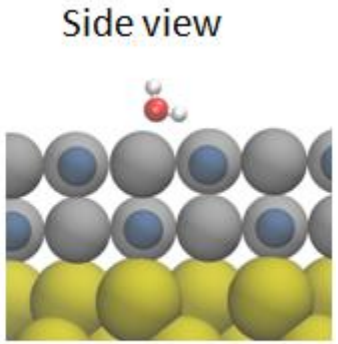
Orbital imaging of monomer

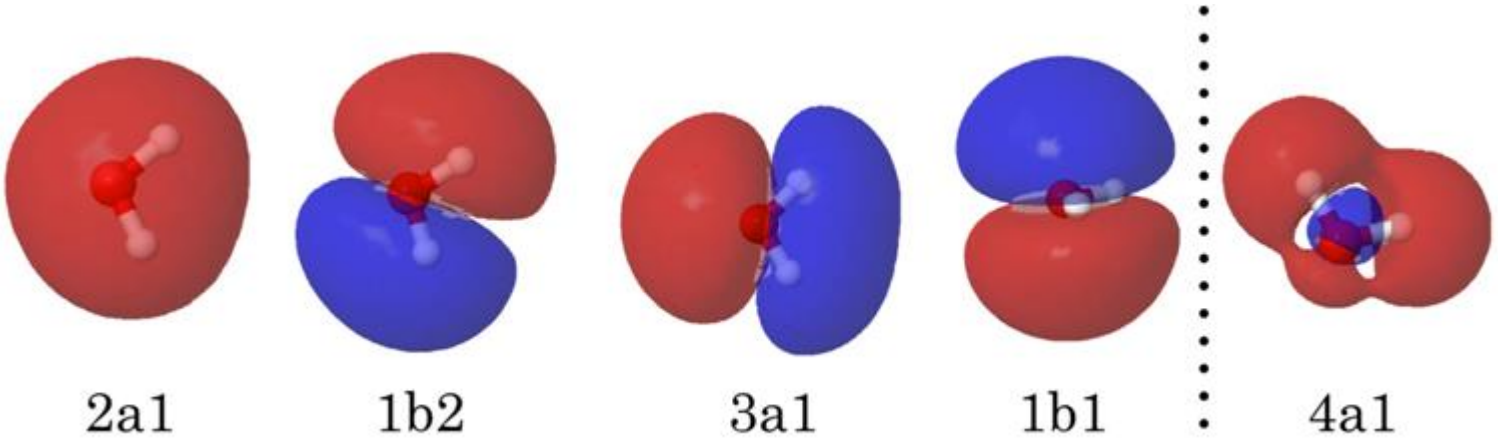
Guo, … EGW*, Jiang* , ***Nat. Mater.*** 13, 184 (2014)











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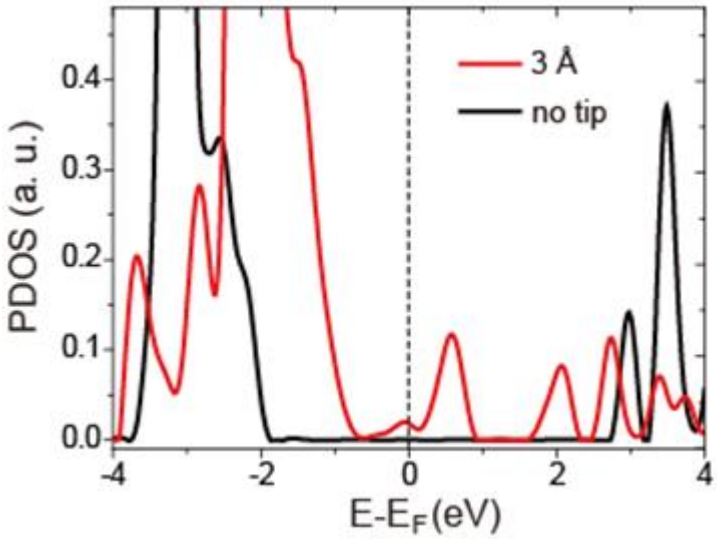
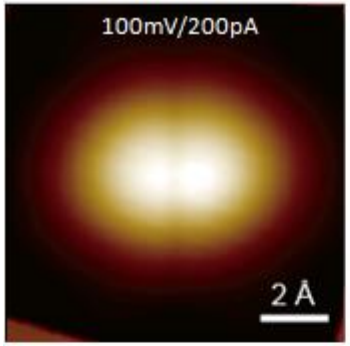
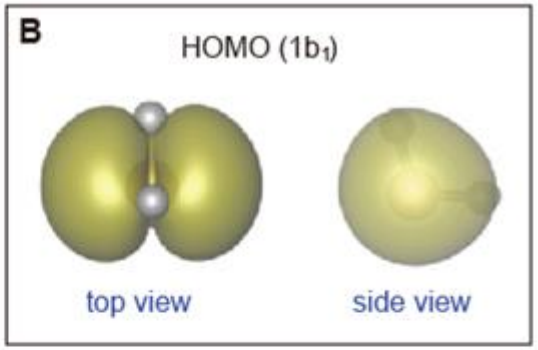
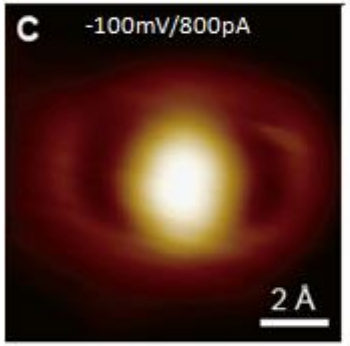
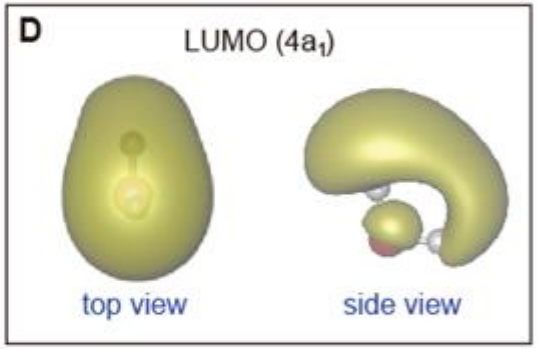
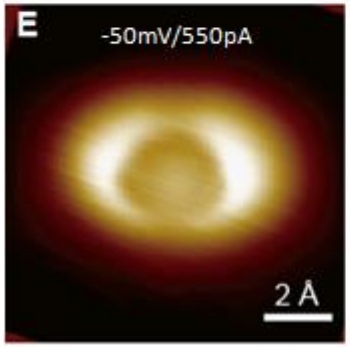


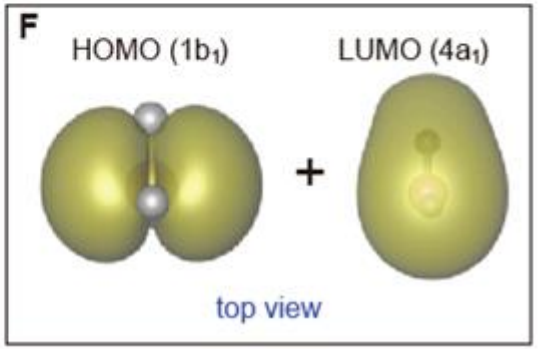




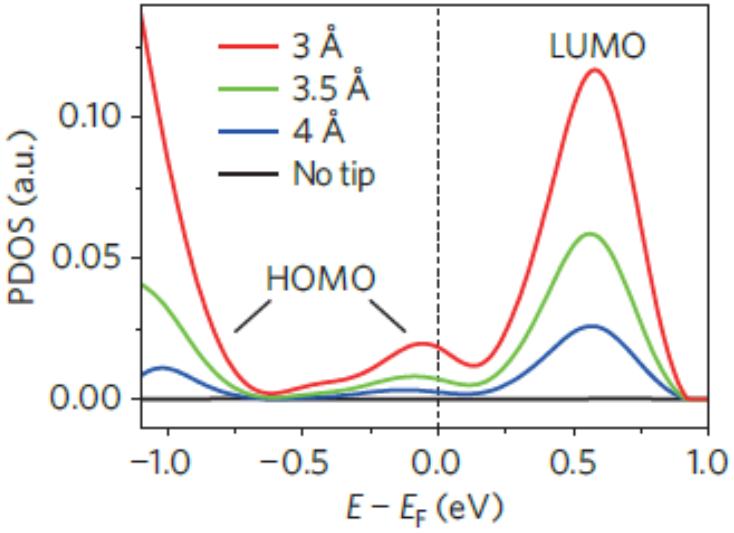


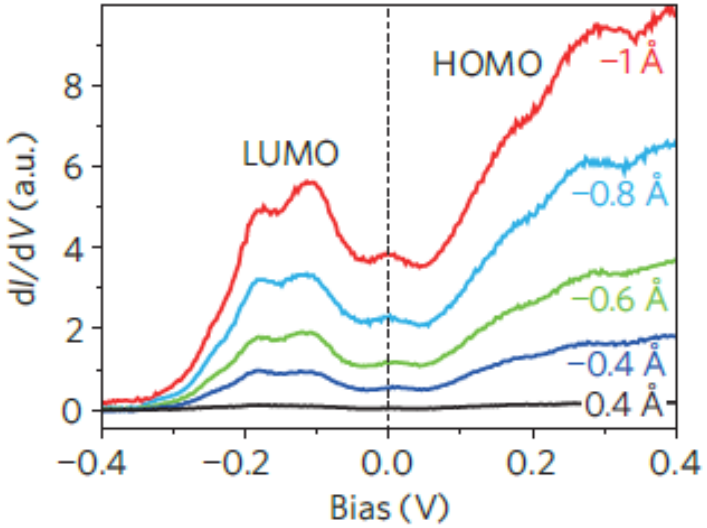


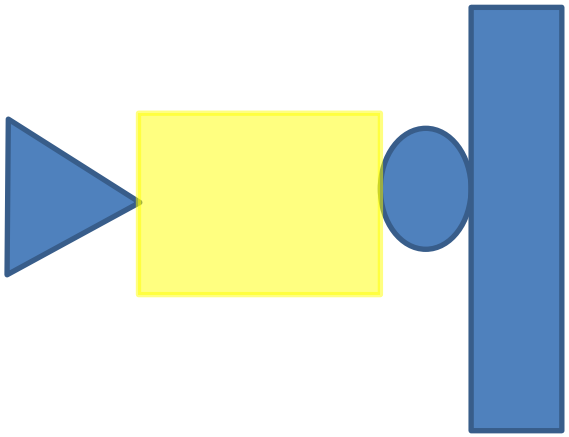


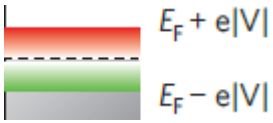


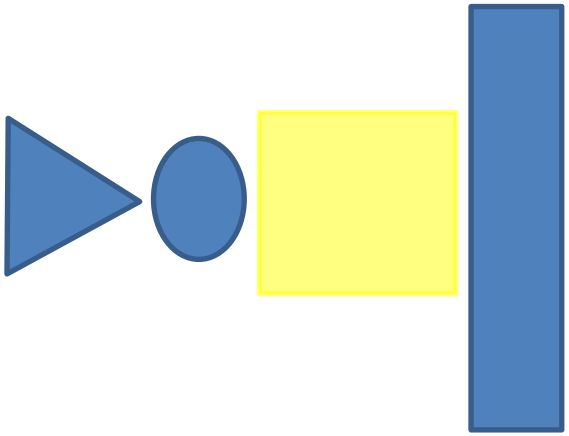
Orbital imaging of monomer

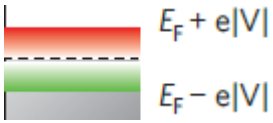




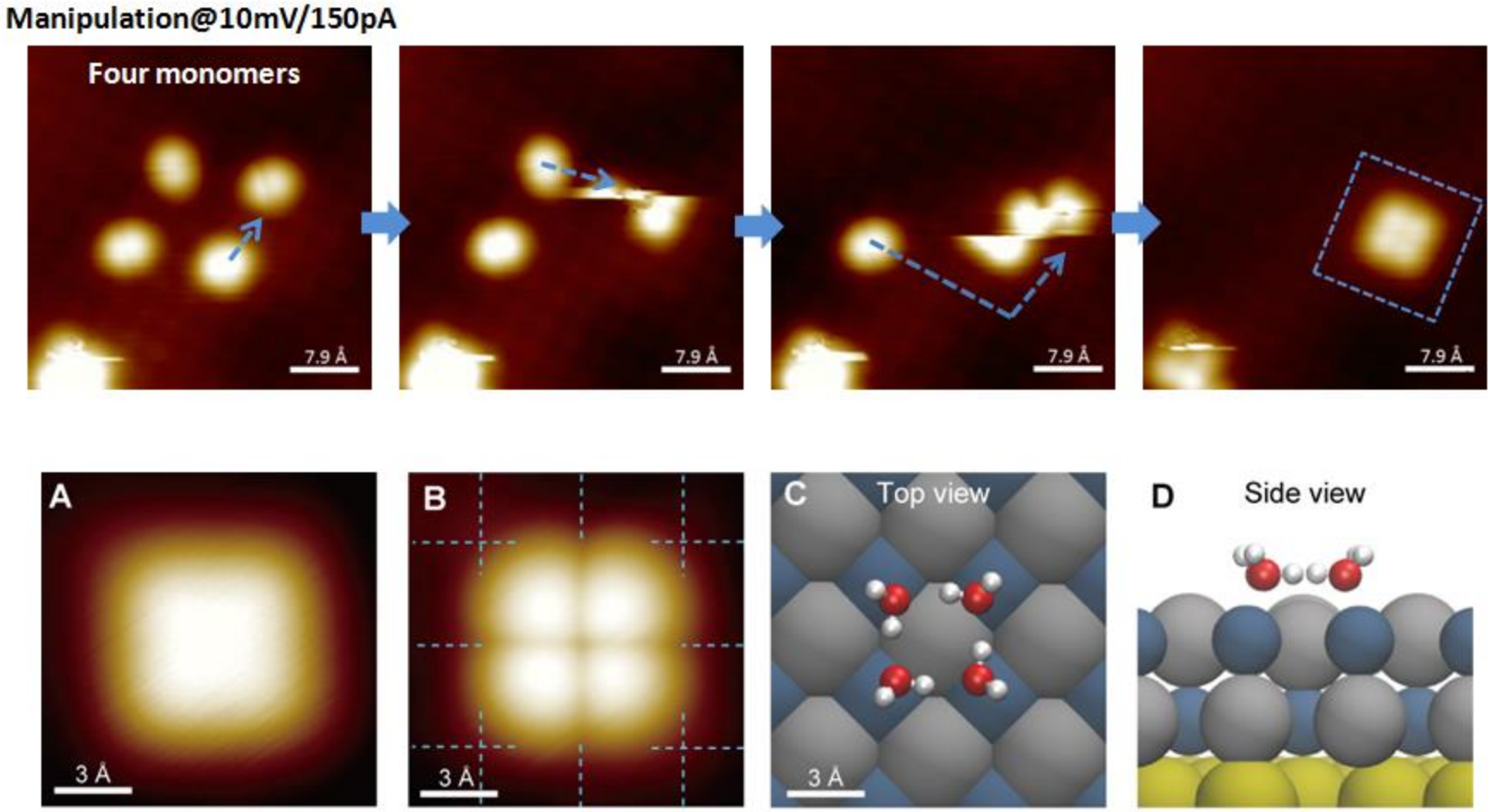


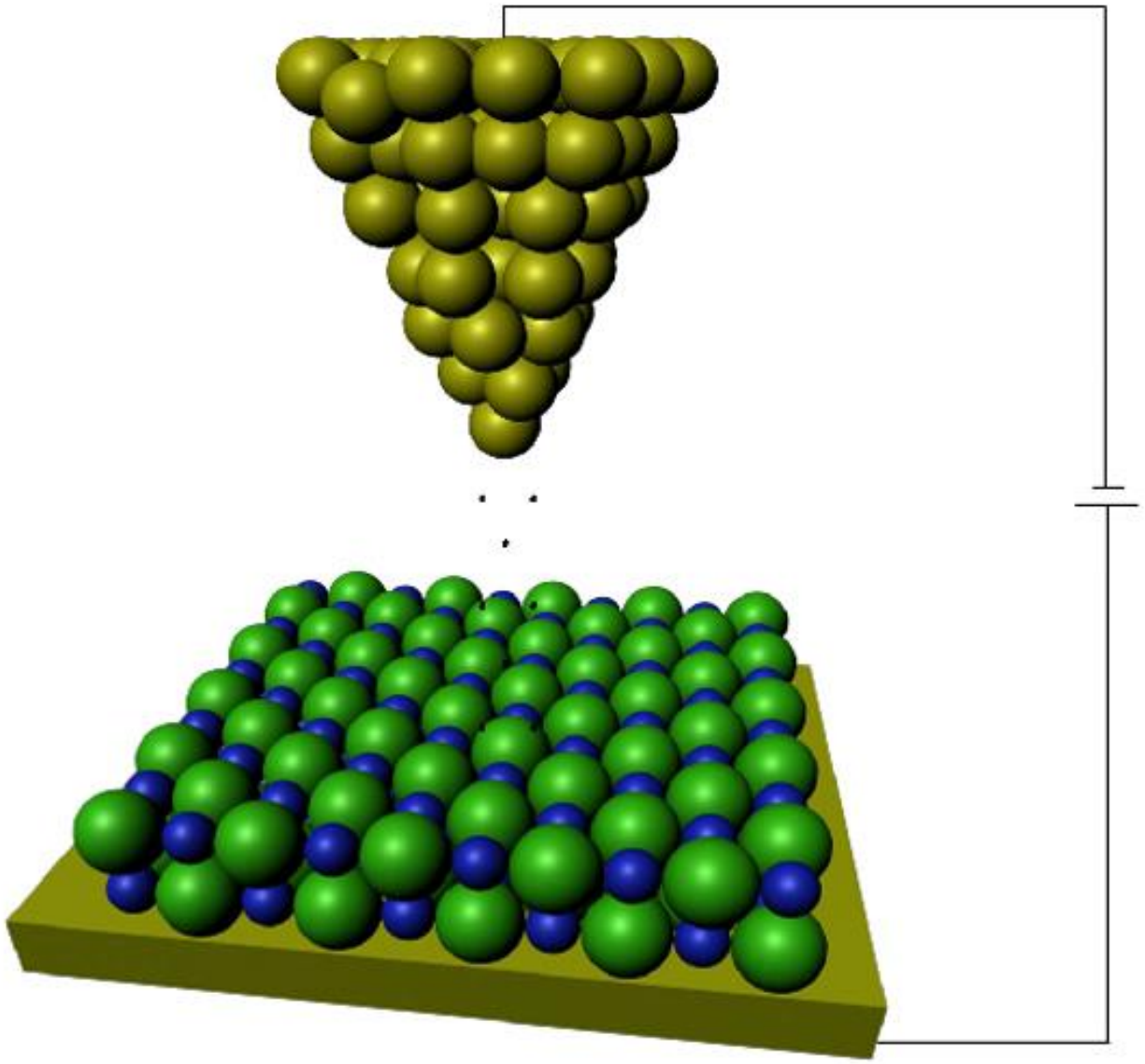




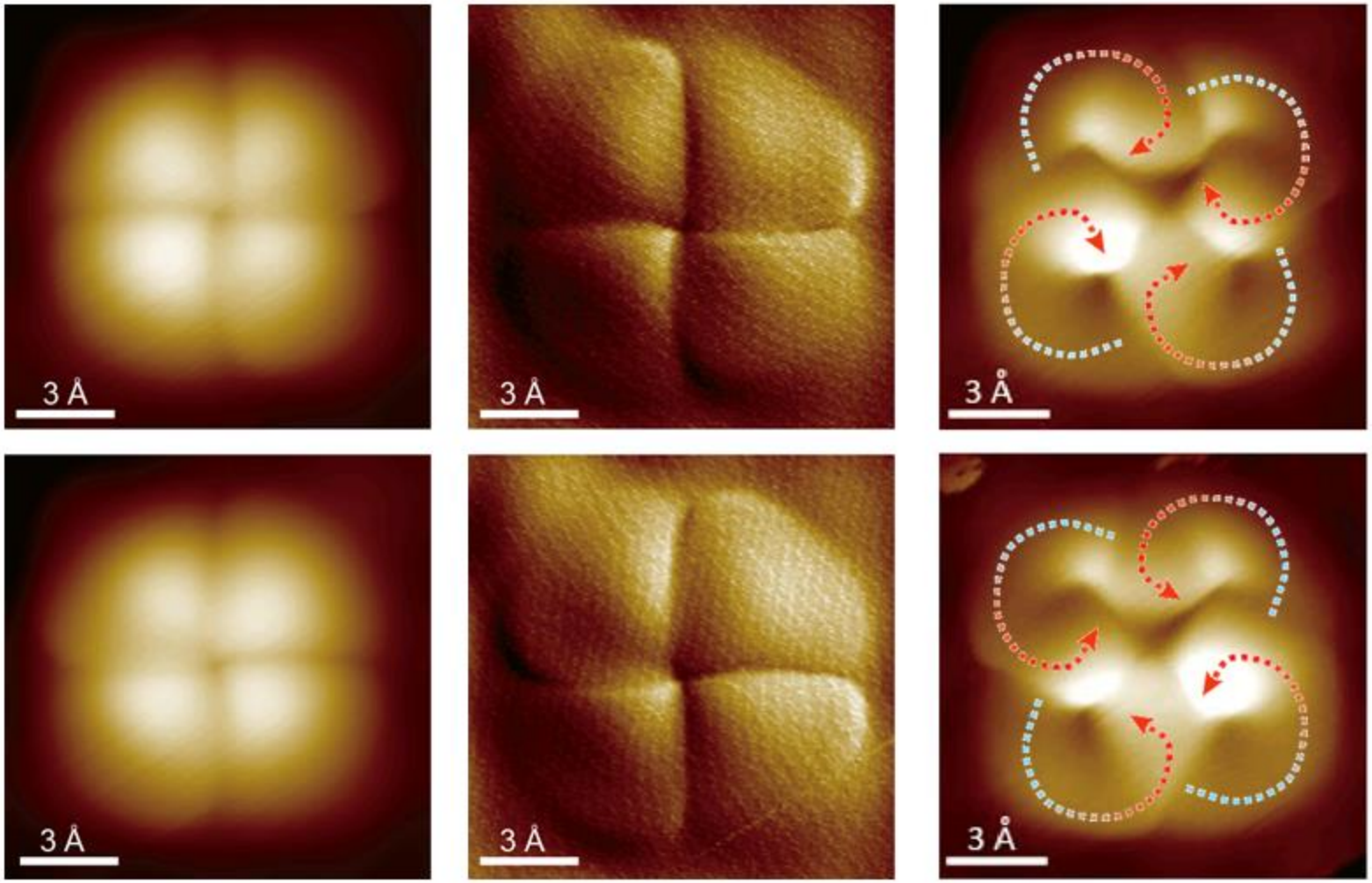


Constructing water tetramer at 5K



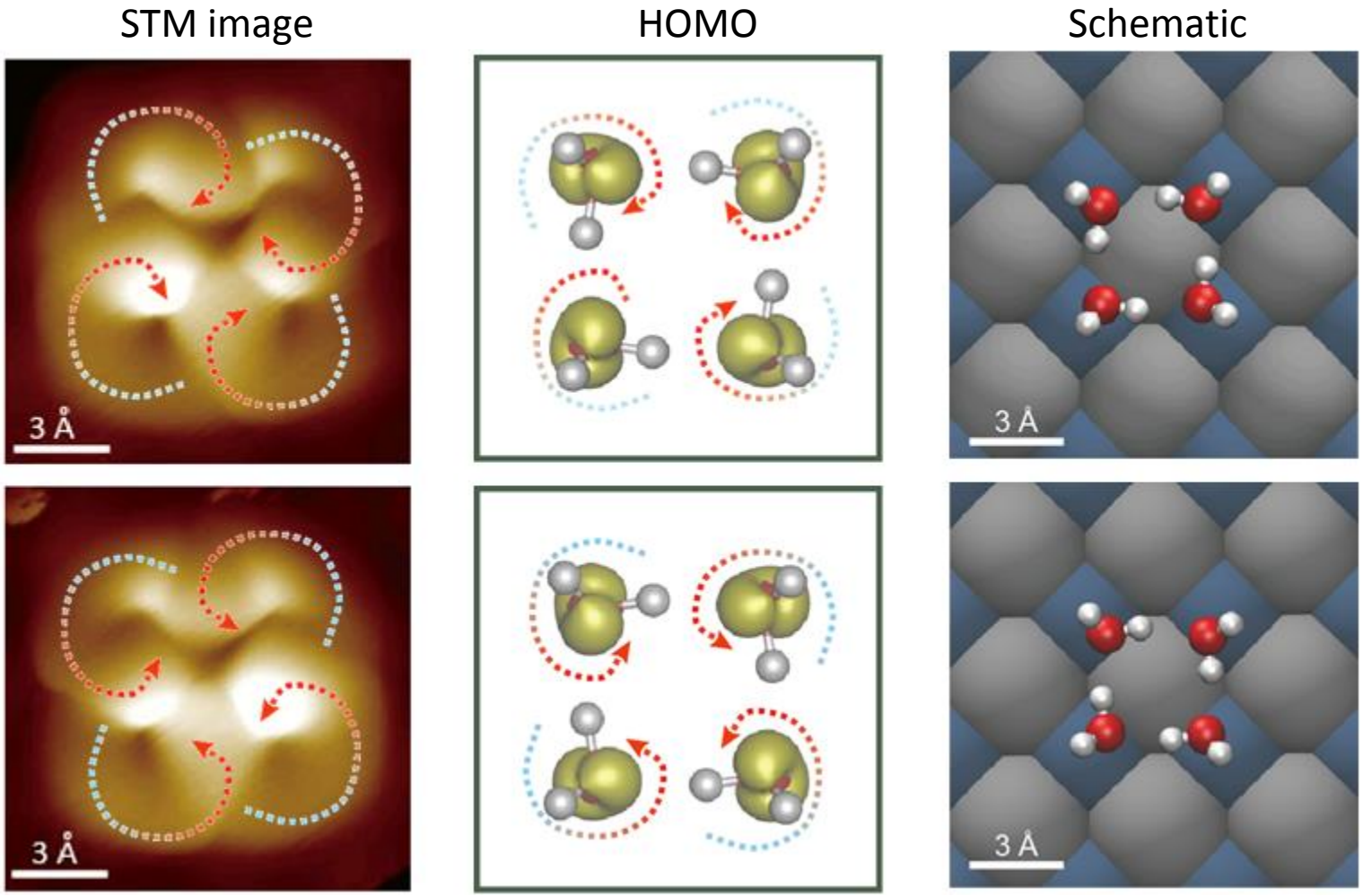


Two types of states of a water tetramer



Guo, … EGW*, Jiang* , ***Nat. Mater.*** 13, 184 (2014)

Orbital imaging of tetramer



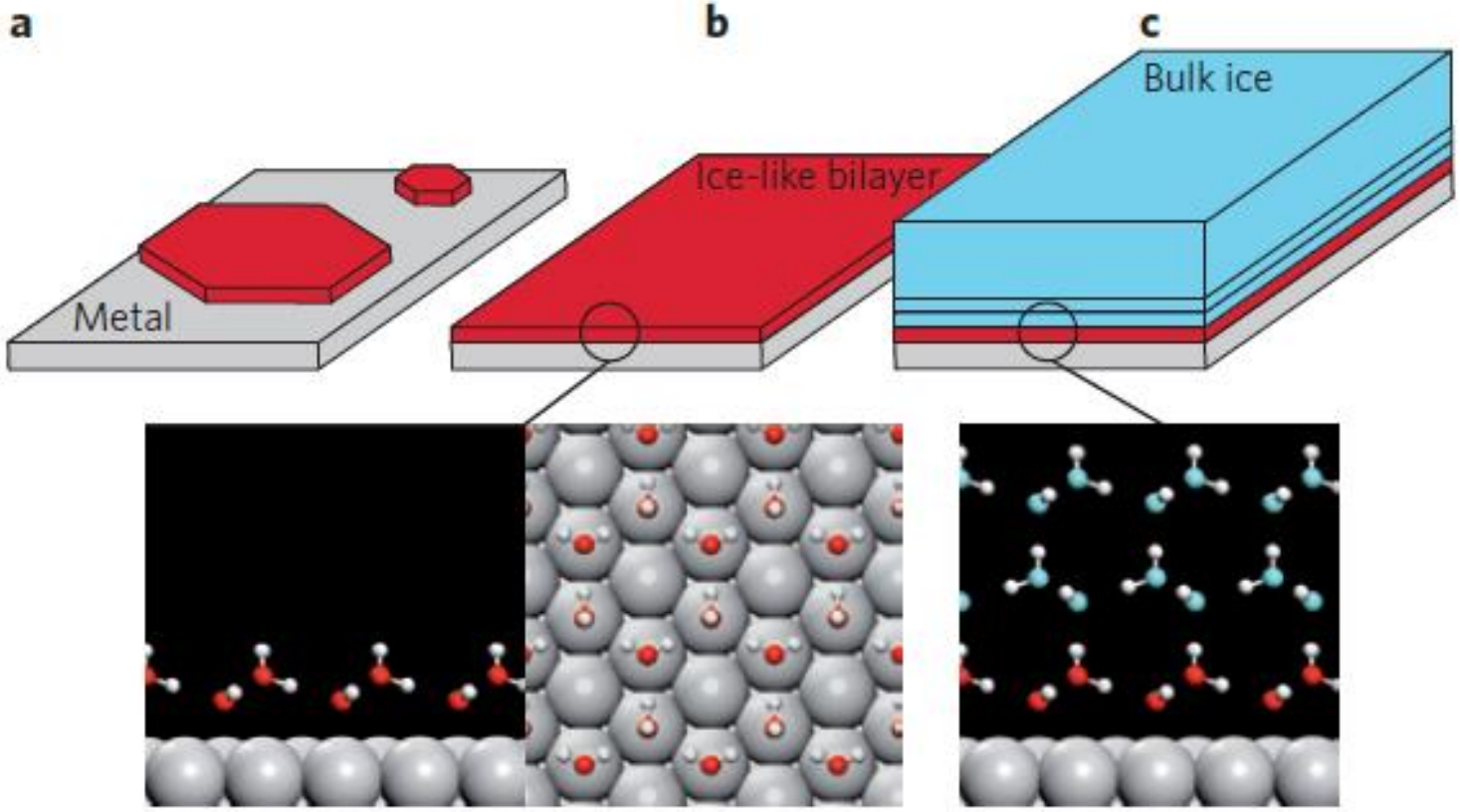
Guo, … EGW*, Jiang* , ***Nat. Mater.*** 13, 184 (2014)

Outline

- Clustering of water on NaCl(001)
  - Chen, Li, … …, EGW*, **Nat. Commun.*** (2014)

Water on solids

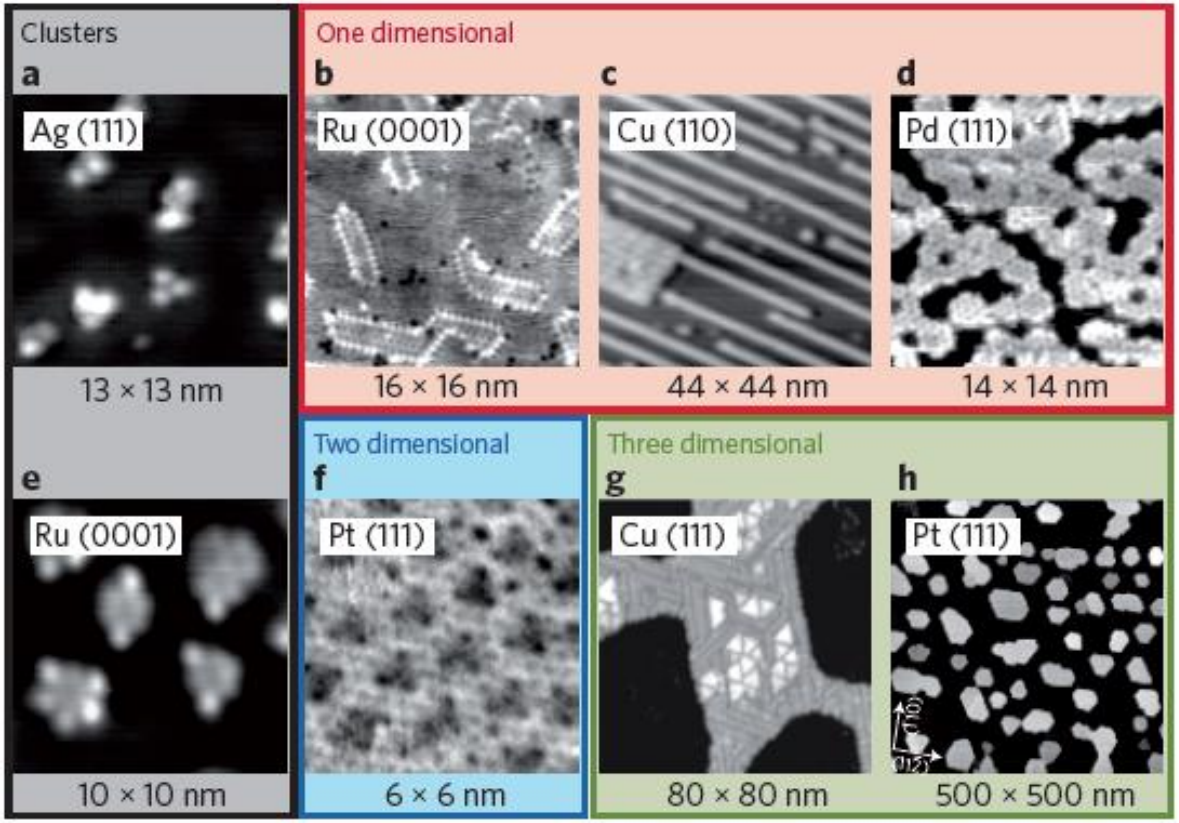
- Conventionally dominated by the hexagonal bilayer model based on the Bernal-Fowler-Pauling ice rule



Carrasco, Hodgson, & Michaelides *Nat. Mater.* **11**, 667 (2012)

Water on solids

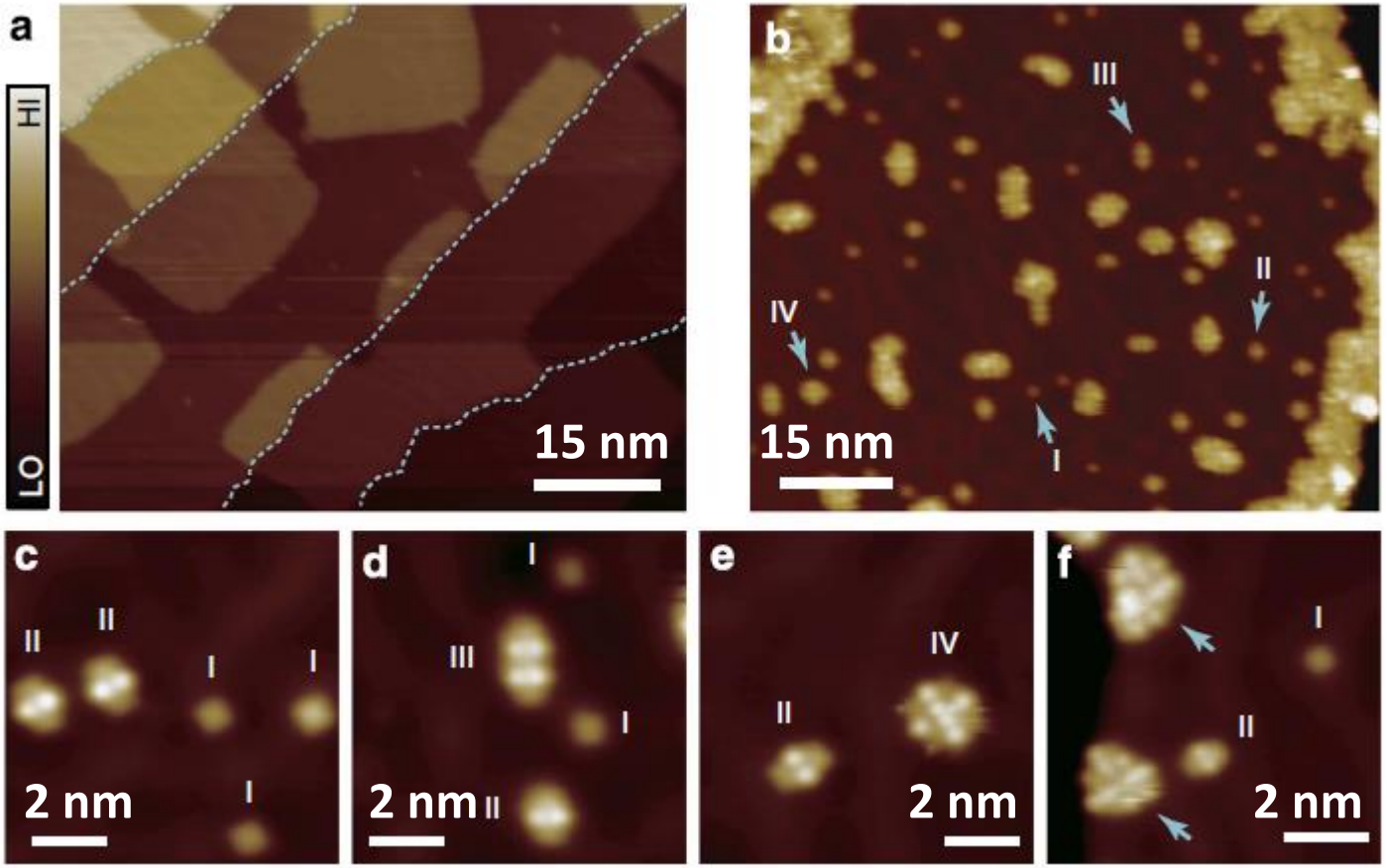
- More detailed pictures appear on different metal surfaces



Carrasco, Hodgson, & Michaelides *Nat. Mater.* **11**, 667 (2012)
Gawronski *et al. Phys. Rev. Lett.* **101**, 136102 (2008)
Nie *et al. Phys. Rev. Lett.* **105**, 026102 (2010)
Yamada *et al. Phys. Rev. Lett.* **96**, 036105 (2006)
Salmeron *et al. Faraday Discuss.* **141**, 221 (2009) ……

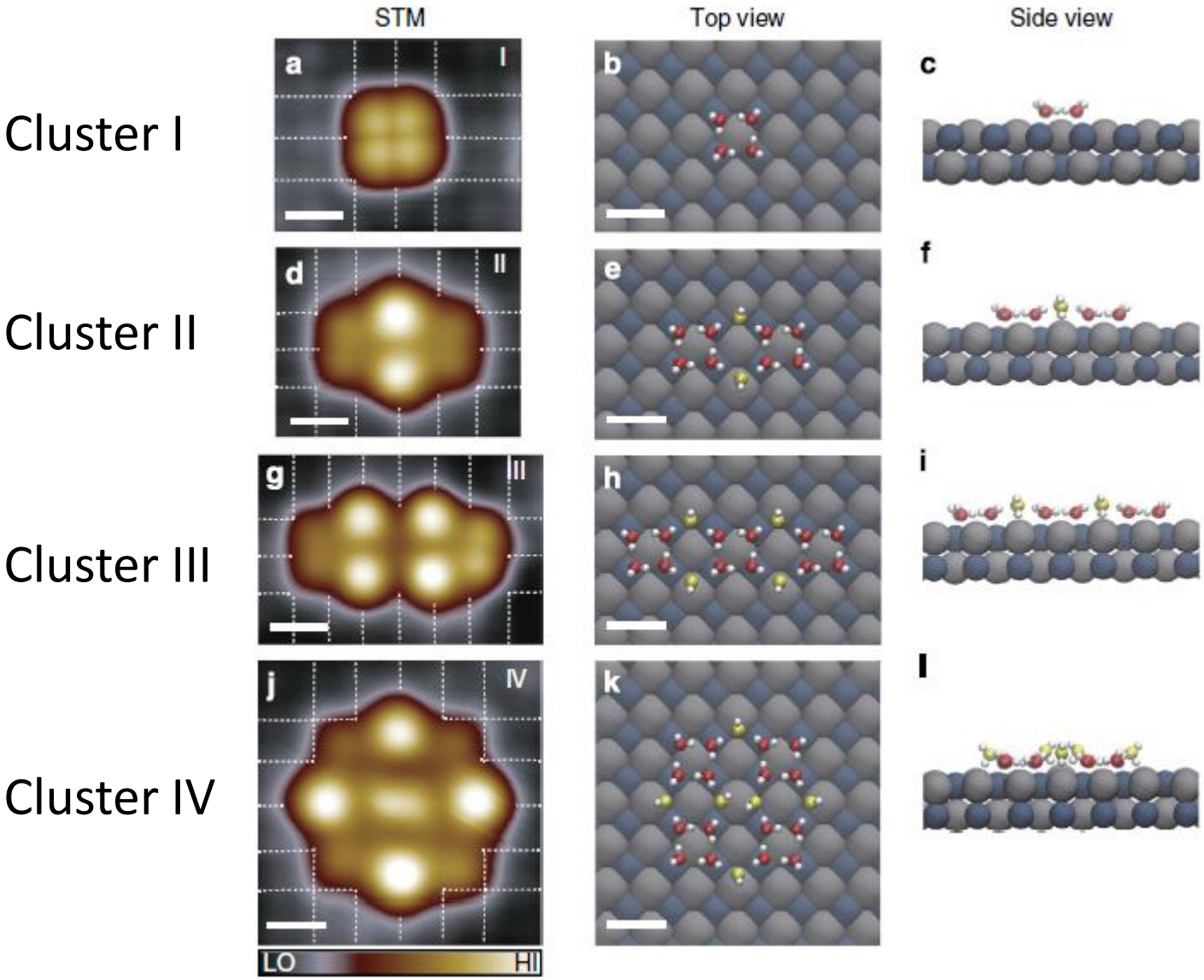
Water on salt (001)

- After dosing 0.1 bilayer water at 77 K.



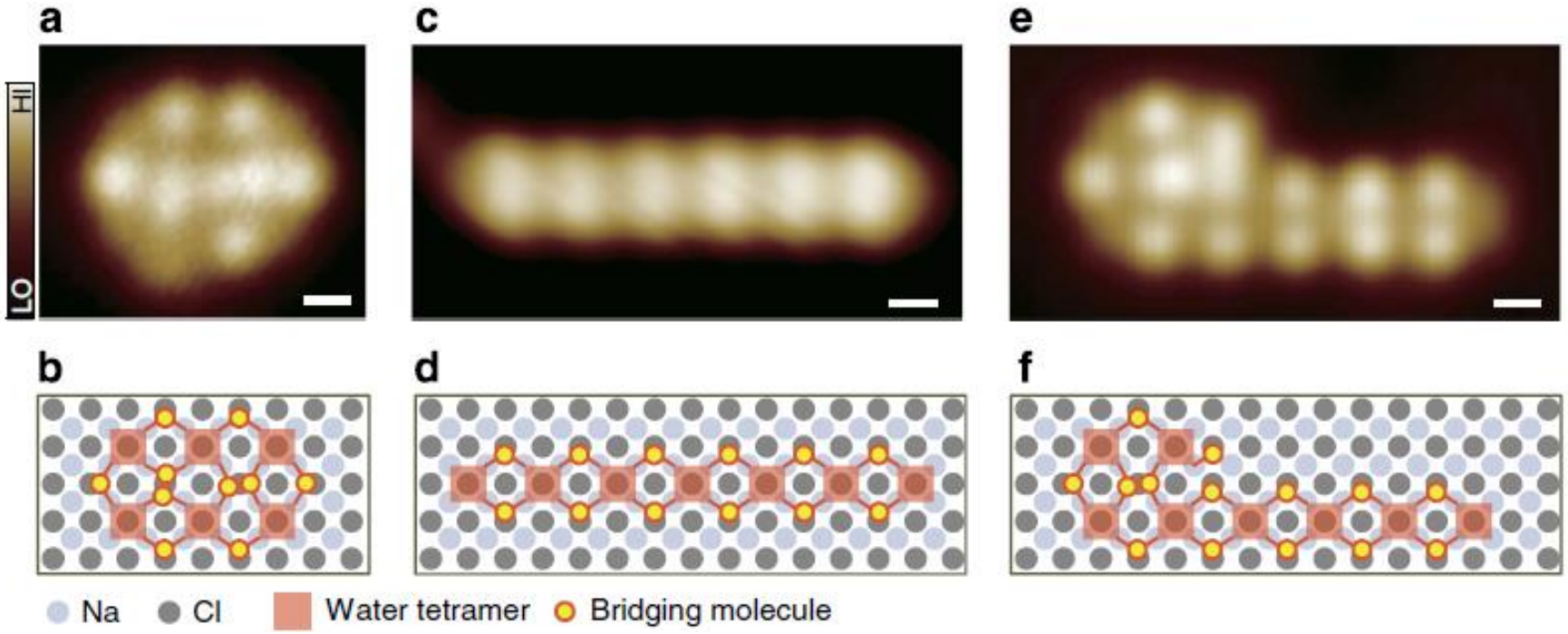
Chen, Li*…, EGW*, *Nat. Commun.* **5**, 4056 (2014)

Water on salt (001)



Water on salt (001)

- Larger clusters



1) Tetramer is the basic building block;
2) The larger clusters formed by minimizing the numbers of bridging water moleculae.

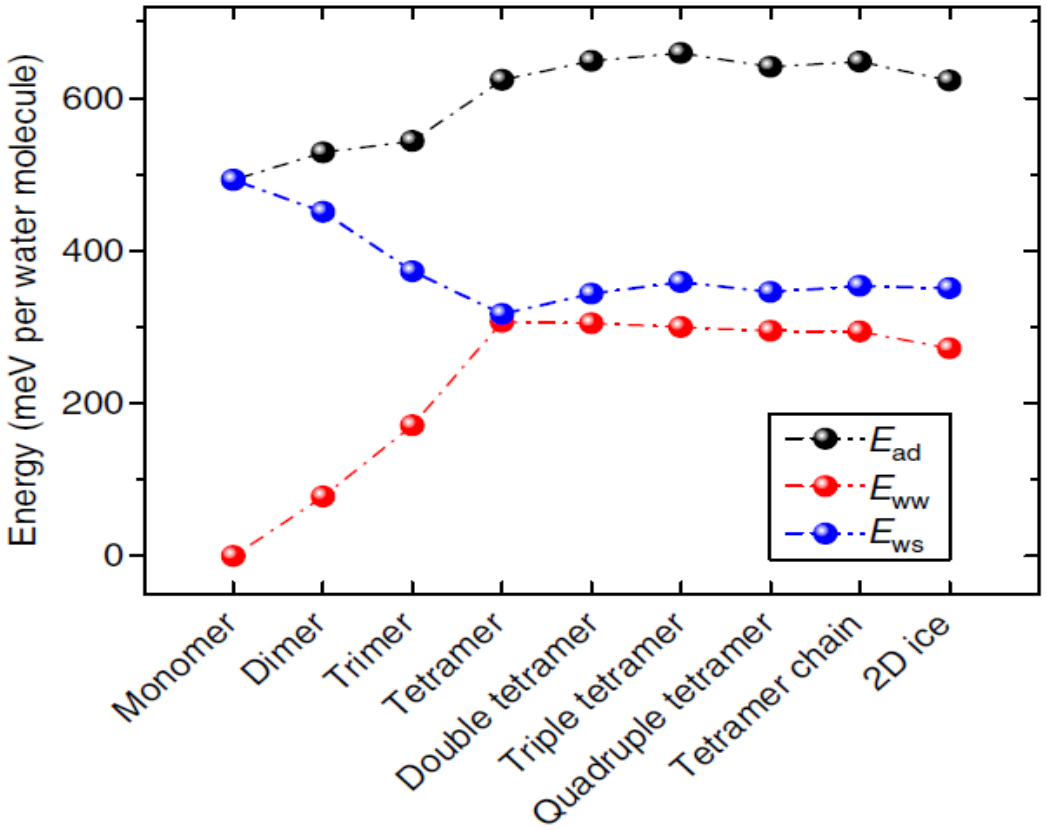
Water on salt (001)

- Why tetramer?

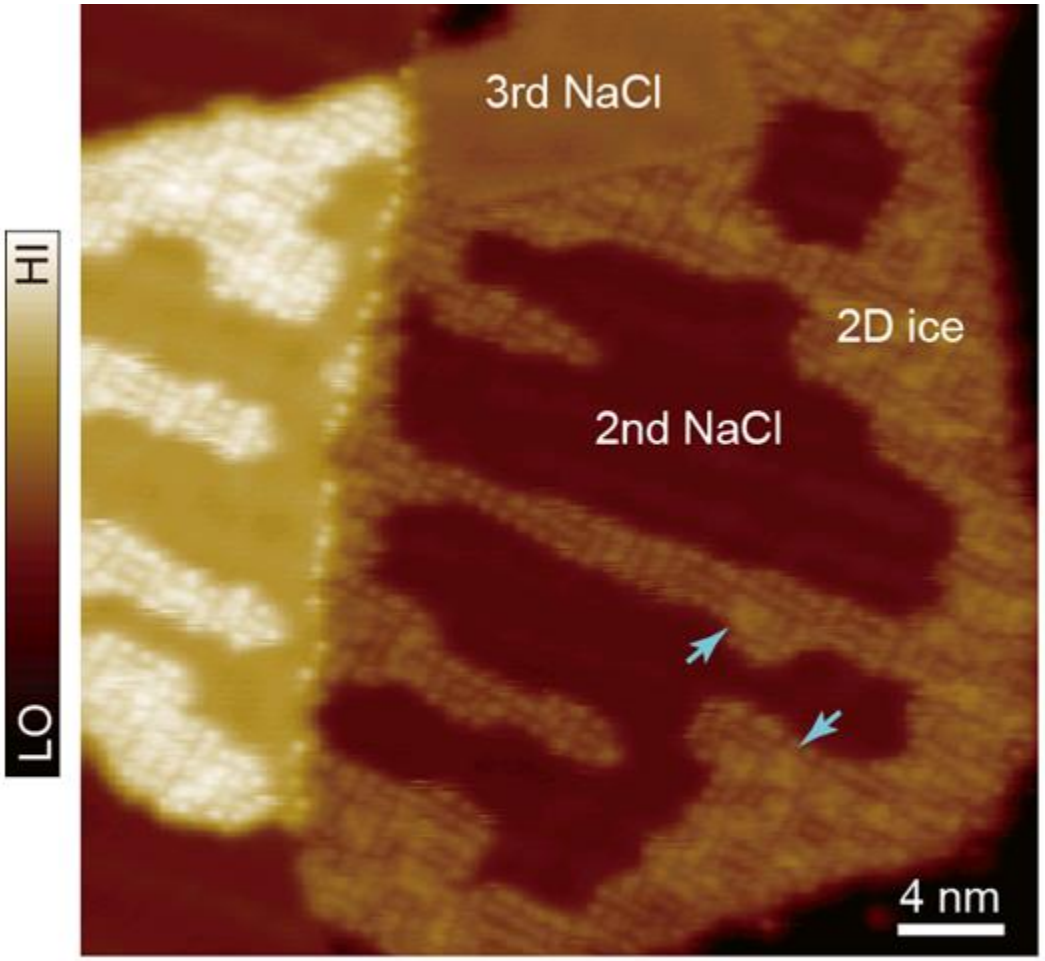
$$E_{\mathrm{ads}} = \frac{1}{n}\left\{E\left[(\mathrm{NaCl}(001))_{\mathrm{relaxed}}\right] + n \times E\left[(\mathrm{H_2O})_{\mathrm{gas}}\right] - E\left[(\mathrm{NaCl}(001) + n\mathrm{H_2O})_{\mathrm{relaxed}}\right]\right\}$$

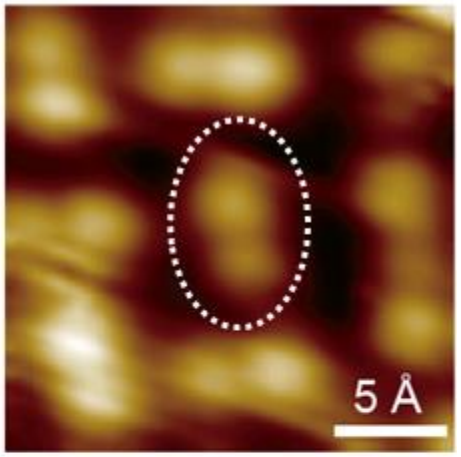
$$E_{\mathrm{ww}} = \frac{1}{n}\left\{n \times E\left[(\mathrm{H_2O})_{\mathrm{gas}}\right] - E\left[(n\mathrm{H_2O})_{\mathrm{network}}\right]\right\}$$

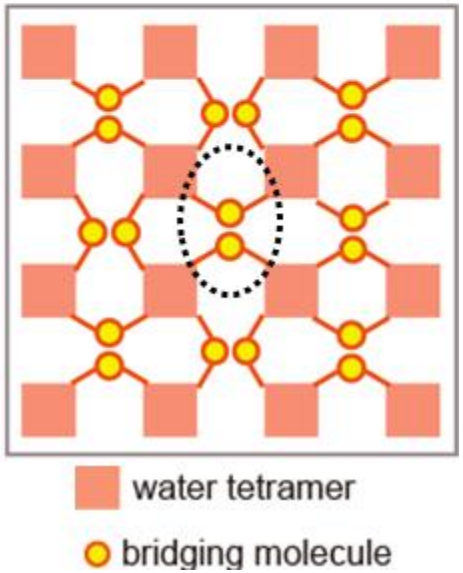
$$E_{\mathrm{ws}} = E_{\mathrm{ads}} - E_{\mathrm{ww}}$$



2D ice growth



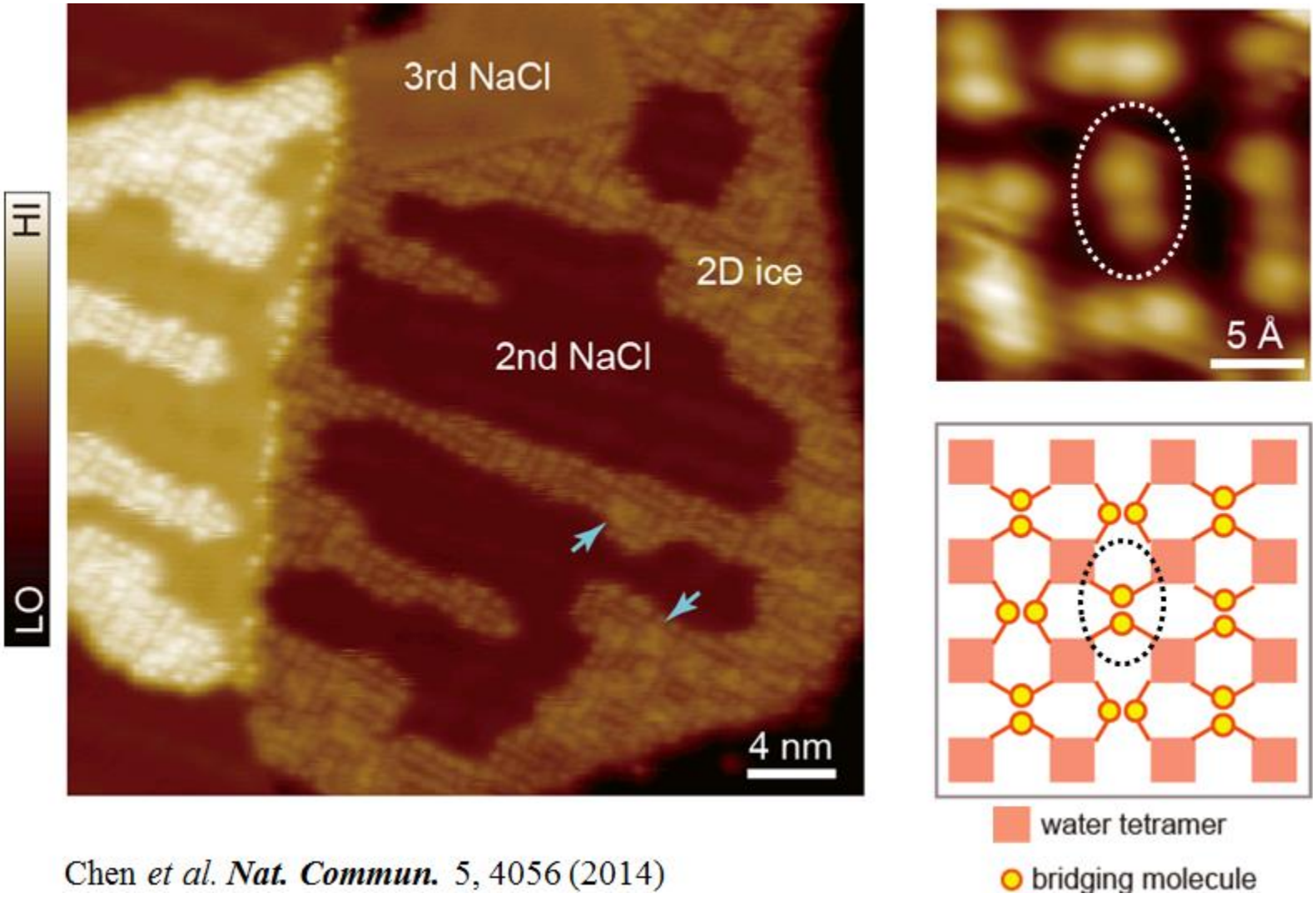




Chen *et al.* ***Nat. Commun.*** 5, 4056 (2014)

Order Parameter: Pan, … …, **EGW**, ***Phys. Rev. Lett.*** 101, 155703(2008);
Sun, … …, **EGW**， ***PNAS*** 109, 201206879(2012)

2D ice growth

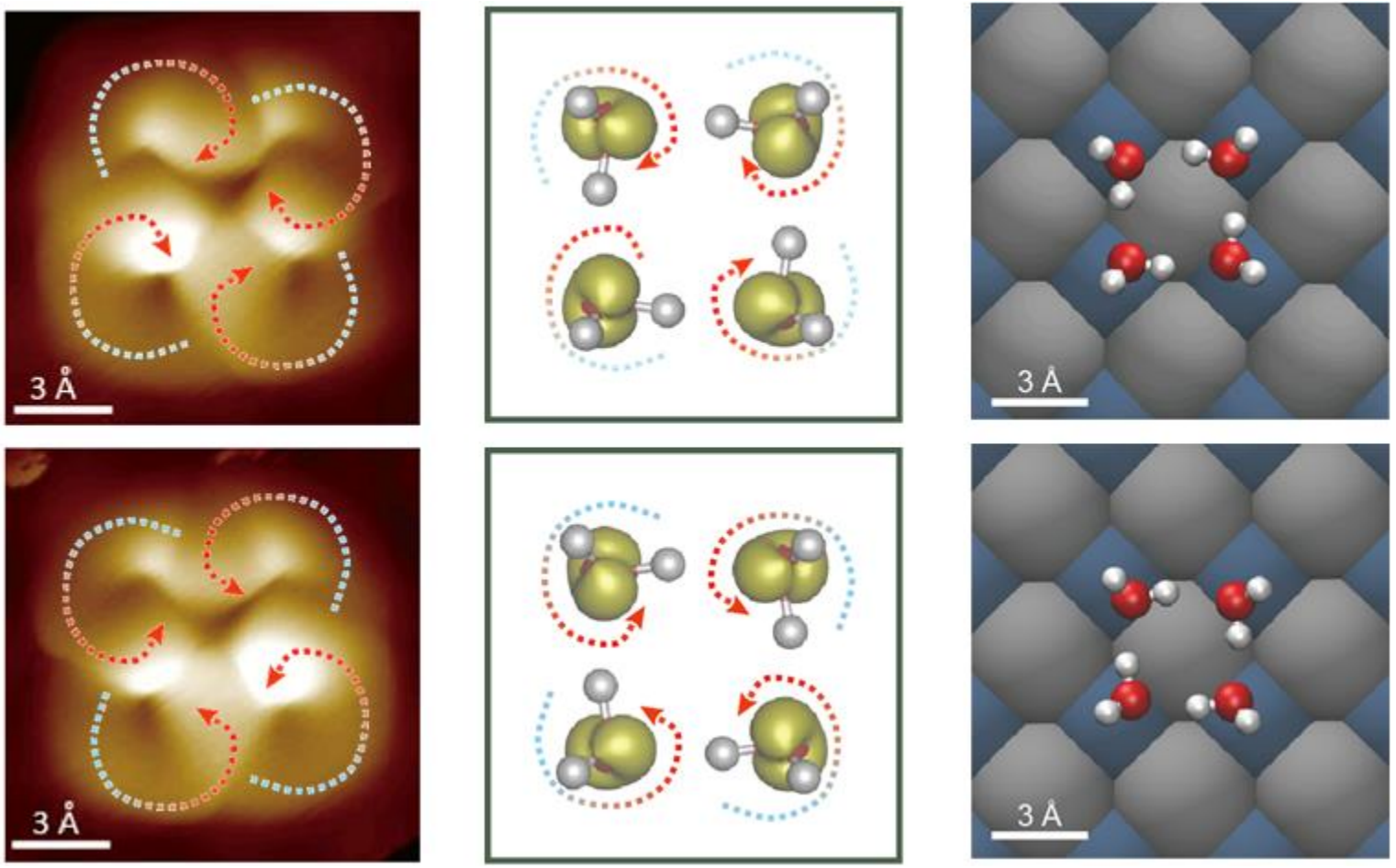


Chen *et al.* ***Nat. Commun.*** 5, 4056 (2014)

Chen, Li*…, EGW*, *Nat. Commun.* **5**, 4056 (2014)

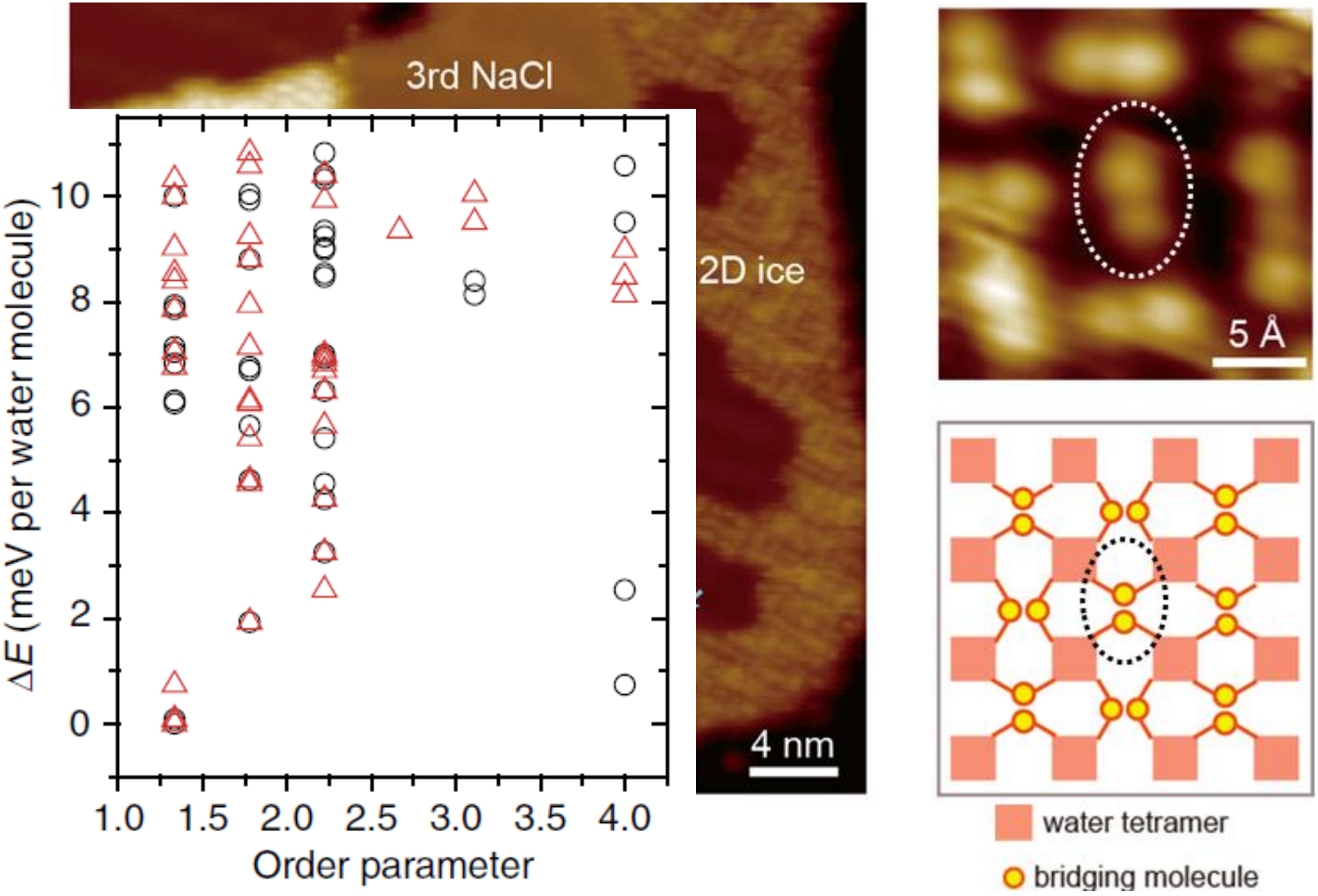
Orbital imaging of tetramer

STM image | HOMO | Schematic



Guo, … EGW*, Jiang* , ***Nat. Mater.*** 13, 184 (2014)

2D ice growth



Chen, Li*…, EGW*, *Nat. Commun.* **5**, 4056 (2014)

Outline

- Full quantum tunneling of the protons
  - Meng, … …, EGW and Jiang, ***Nat. Phys. (2015)***

Schrodinger is the first person who realized that a real material can be viewed as a poly-atomic system, which is a intermixture of two coupled subsystems, one is nuclei and the other is electrons.

Schrodinger equation (1926) :

$$\hat{H} = -\sum_{i=1}^{N} \frac{1}{2}\nabla_i^2 + \frac{1}{2}\sum_{i\neq i'} V(\mathbf{r}_i - \mathbf{r}_{i'}) - \sum_{j=1}^{M} \frac{1}{2M_j}\nabla_j^2 + \frac{1}{2}\sum_{j\neq j'} V(\mathbf{R}_j - \mathbf{R}_{j'}) + \frac{1}{2}\sum_{i,j} V(\mathbf{r}_i - \mathbf{R}_j)$$

Born-Oppenheimer approximation (1927) :

$$\hat{H}_{\mathrm{e}} = -\sum_{i=1}^{N} \frac{1}{2}\nabla_i^2 + \frac{1}{2}\sum_{i\neq i'} V(\mathbf{r}_i - \mathbf{r}_{i'}) + \frac{1}{2}\sum_{i,j} V(\mathbf{r}_i - \mathbf{R}_j)$$

《*Computer Simulations of Molecules and Condensed Matters: from Electronic Structures to Molecular Dynamics*》(2015)

Xinzheng Li and Enge Wang

Schrodinger equation（1926）：

$$\hat{H} = -\sum_{i=1}^{N}\frac{1}{2}\nabla_i^2 + \frac{1}{2}\sum_{i\neq i'}V(\mathbf{r}_i-\mathbf{r}_{i'}) - \sum_{j=1}^{M}\frac{1}{2M_j}\nabla_j^2 + \frac{1}{2}\sum_{j\neq j'}V(\mathbf{R}_j-\mathbf{R}_{j'}) + \frac{1}{2}\sum_{i,j}V(\mathbf{r}_i-\mathbf{R}_j)$$

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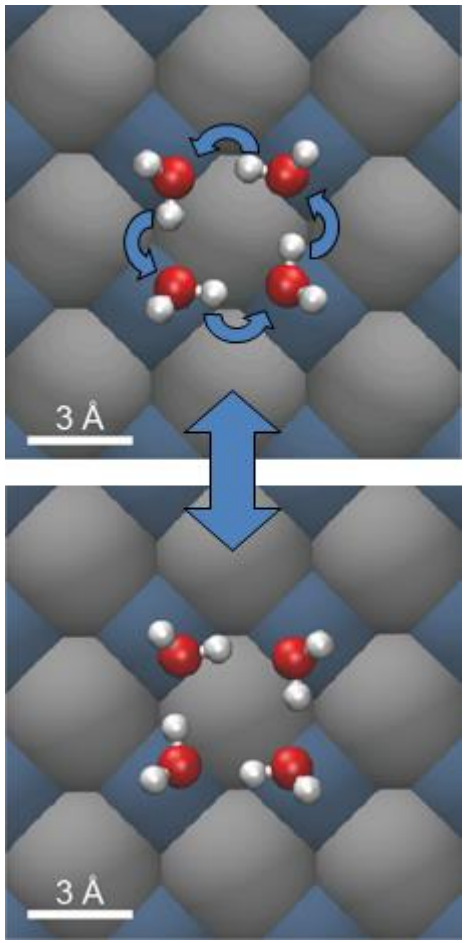
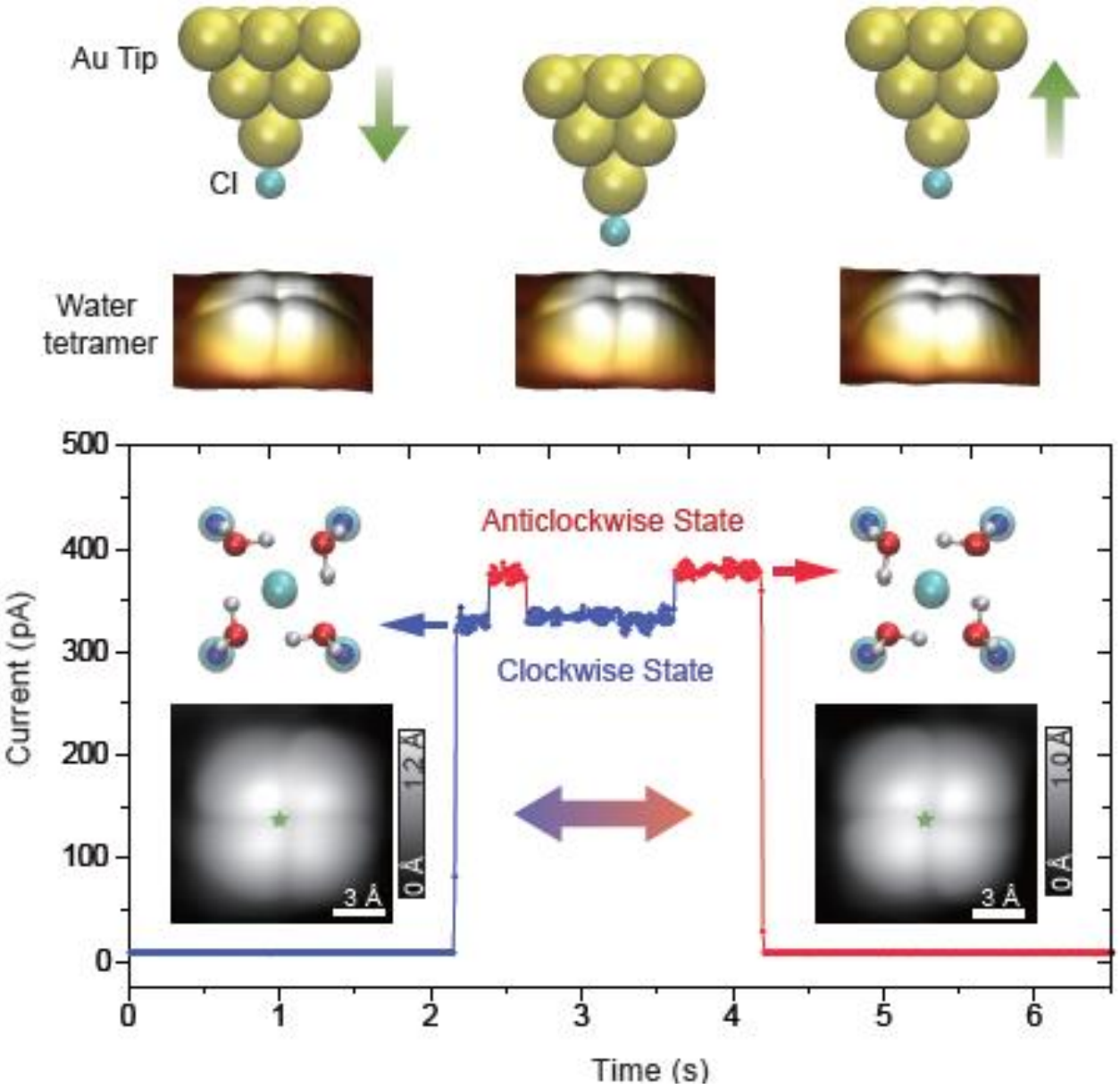
问题：

1. 忽略原子核本身的量子效应(NQEs)
2. 忽略原子核的量子化对电子态的影响（非绝热效应）

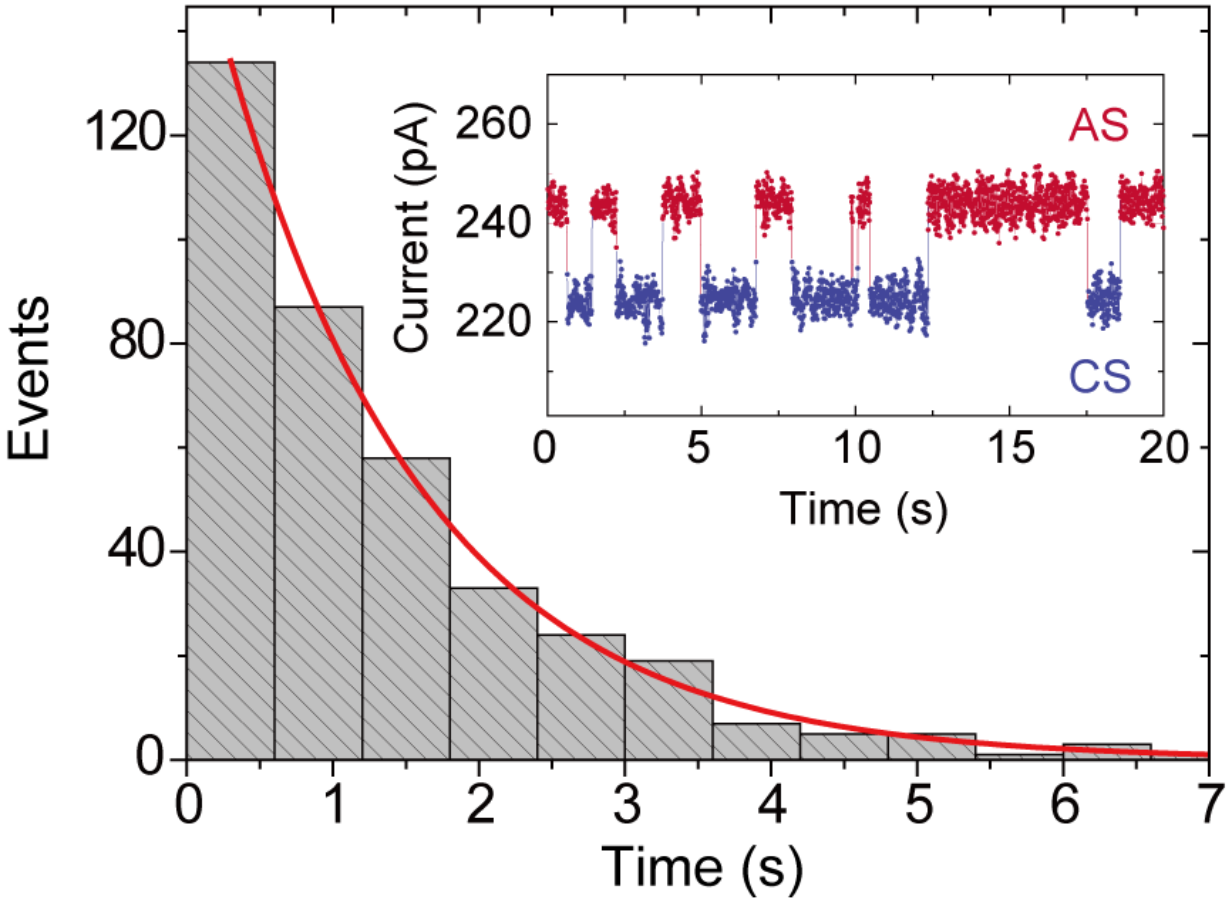
对于轻元素体系，这种处理将会变得不准确甚至失效。

Chirality switching



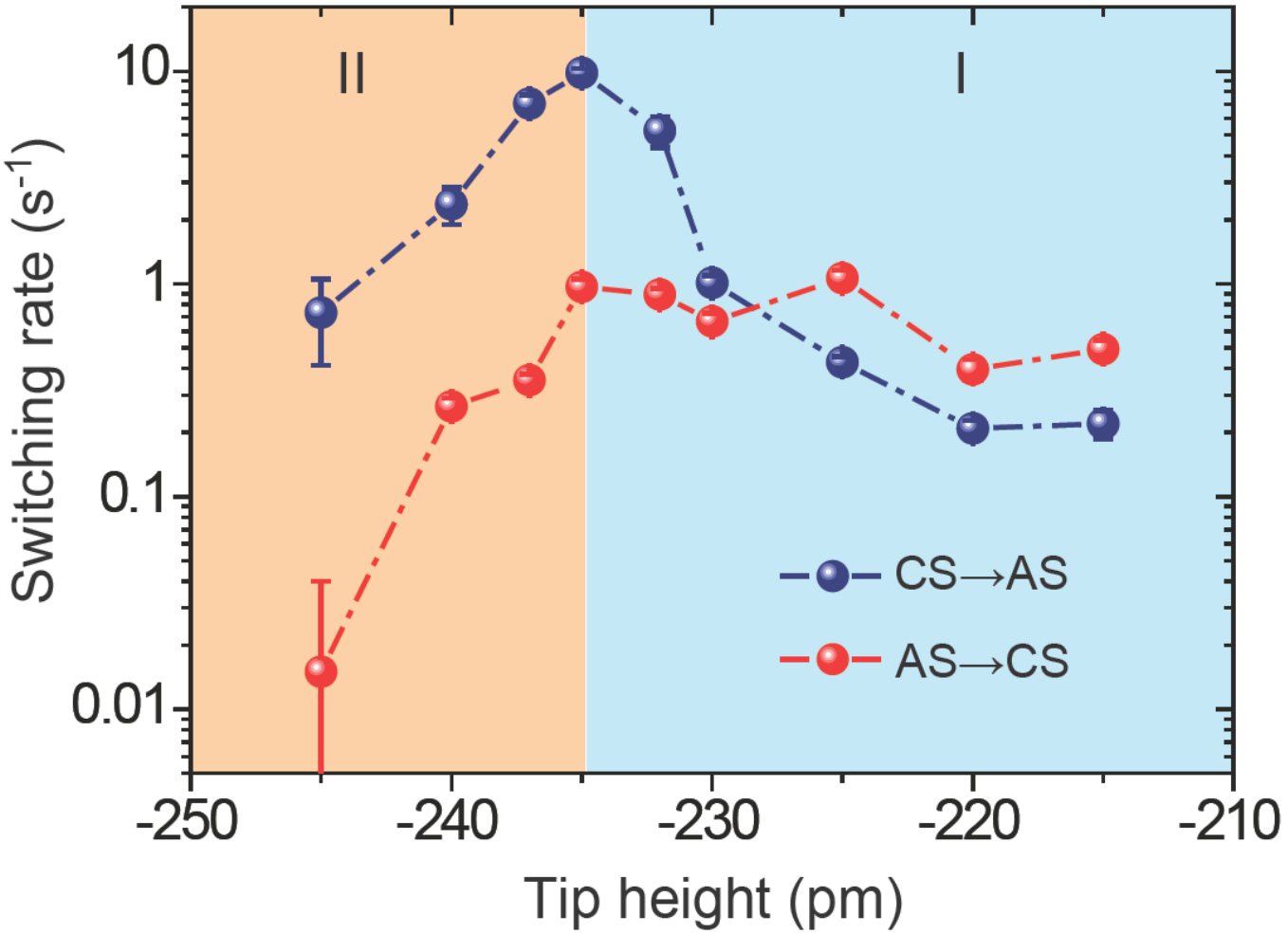


Switching rate

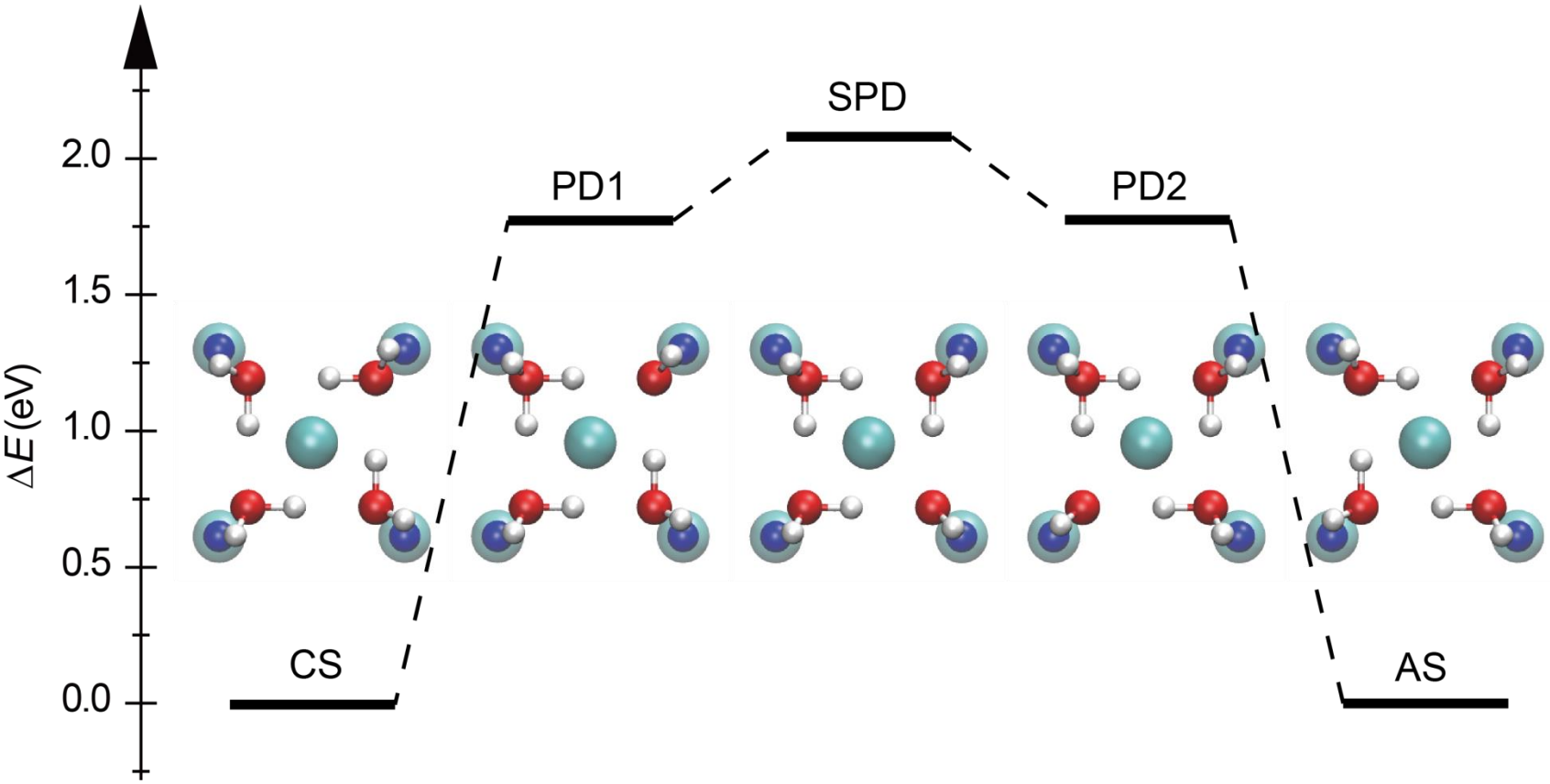


$y=Ae^{-t/\tau}$. Inverse of τ just means the switching rate from the clockwise state to the anti-clockwise state.

Switching rate dependence on tip height

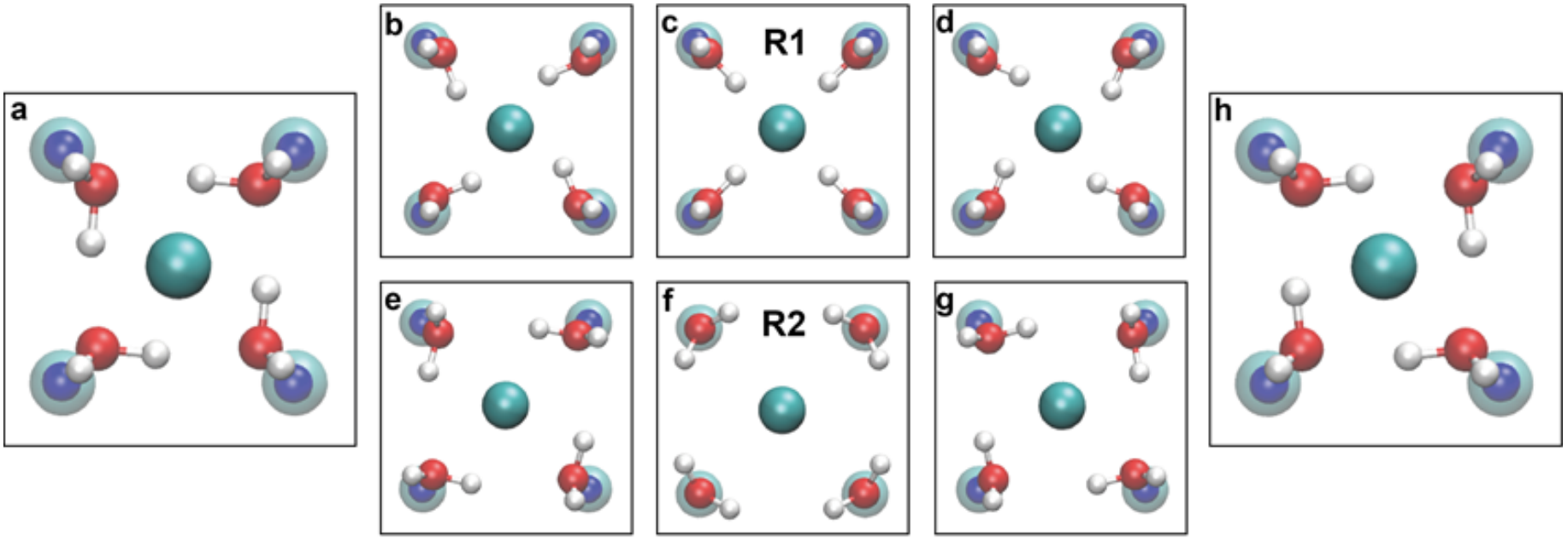


Stepwise proton transfer

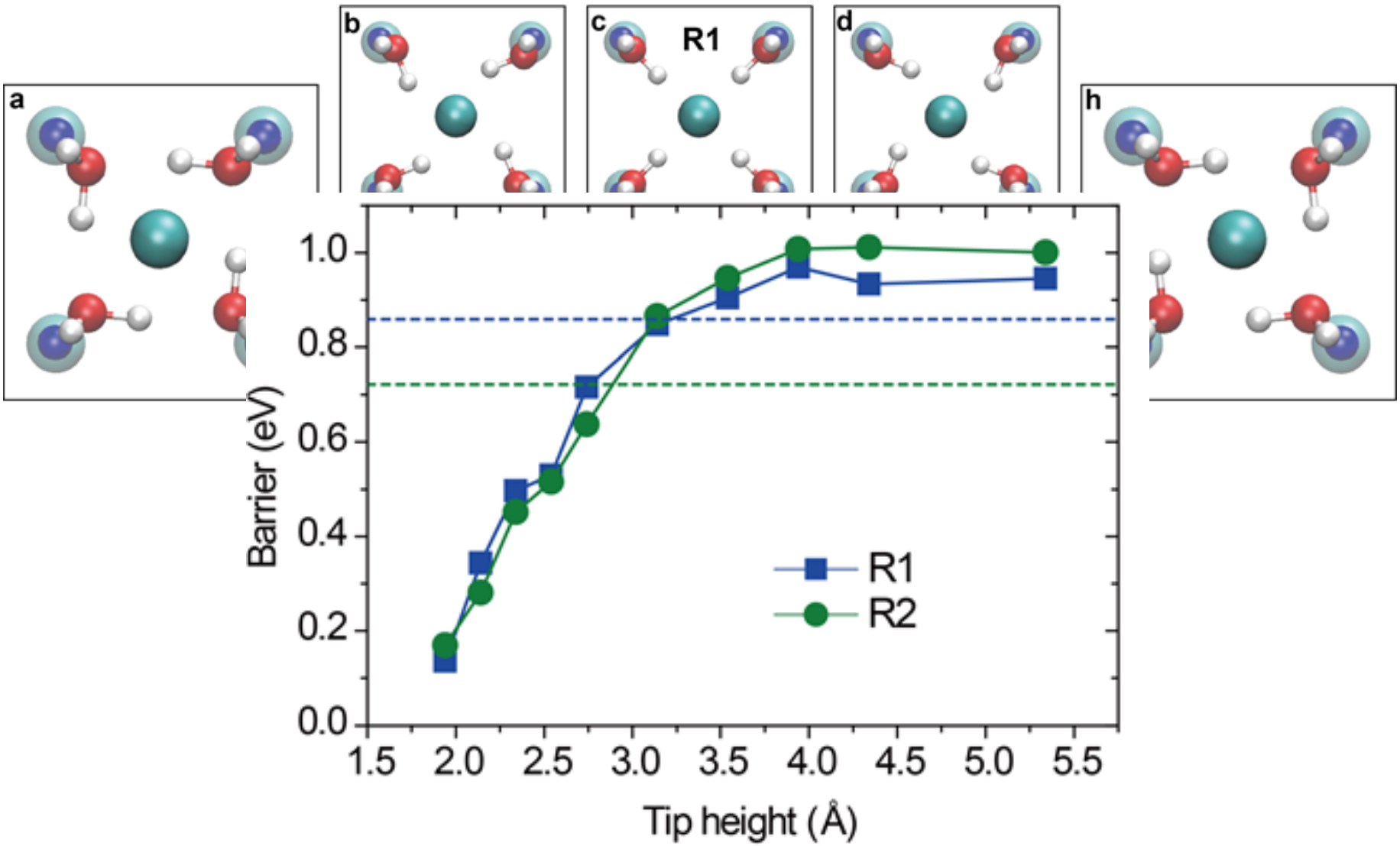


Climbing image Nudged Elastic Band: Barrier too high

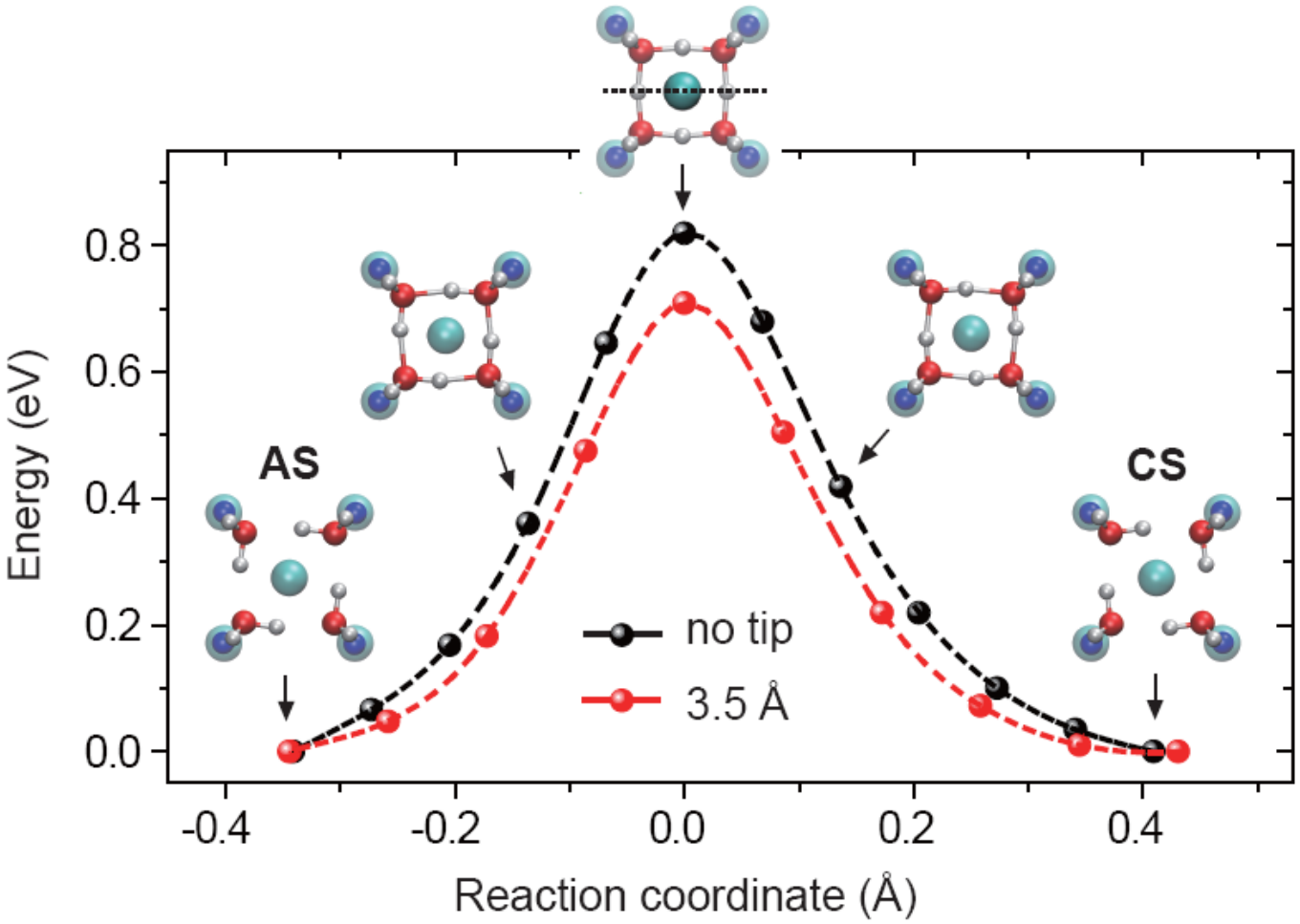
Rotation of the water molecules



Rotation of the water molecules

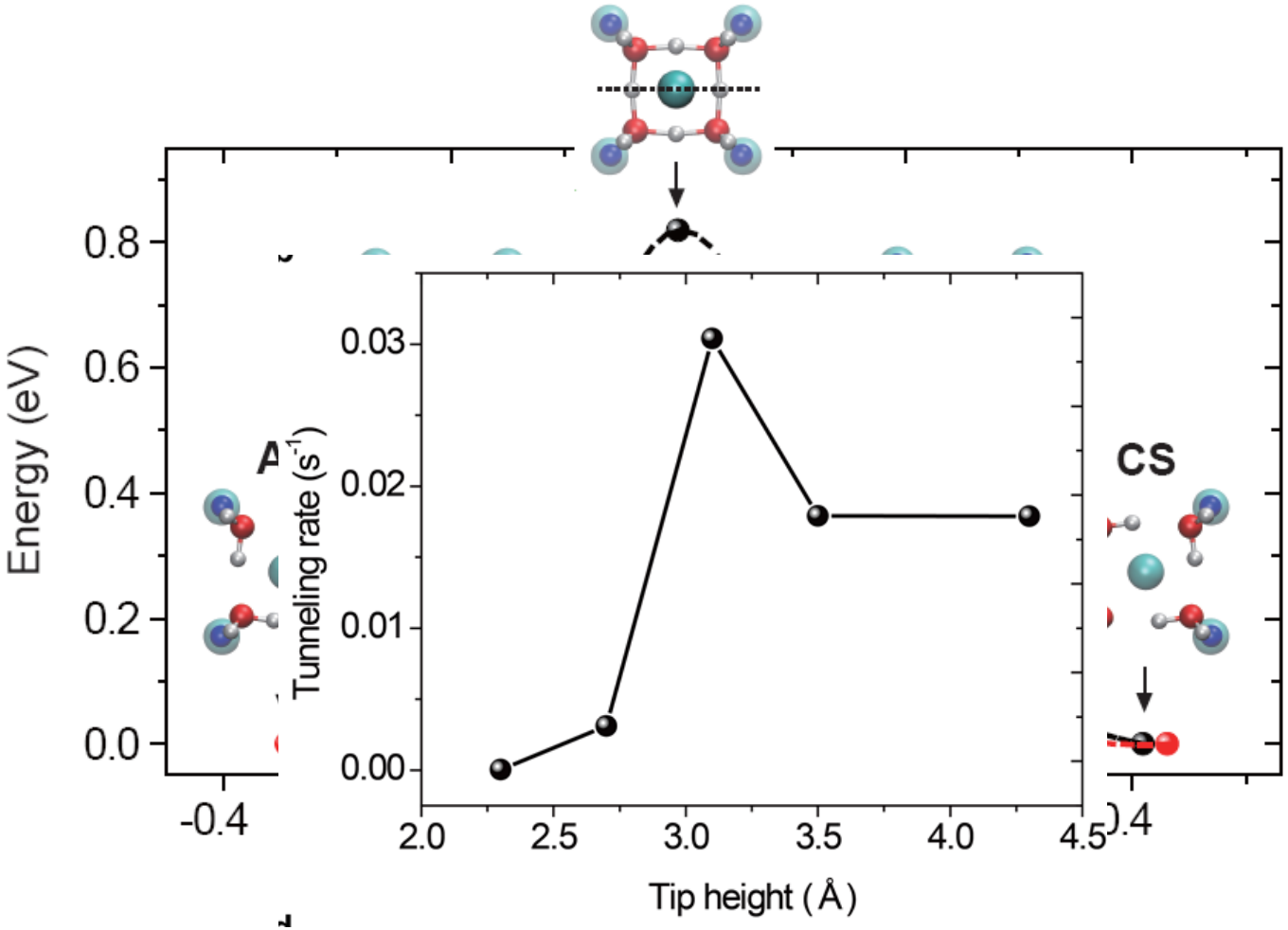


Phonon-assisted concerted proton transfer



Trakhtenberg & Klochikhin, *Chem. Phys.* *232*, 175 (1998)
Spahr et al. *Phys. Rev. Lett.* 102, 077506 (2009)
Drechsel-Grau & Marx, *Phys. Rev. Lett.* 112, 148302 (2014)

Phonon-assisted concerted proton transfer

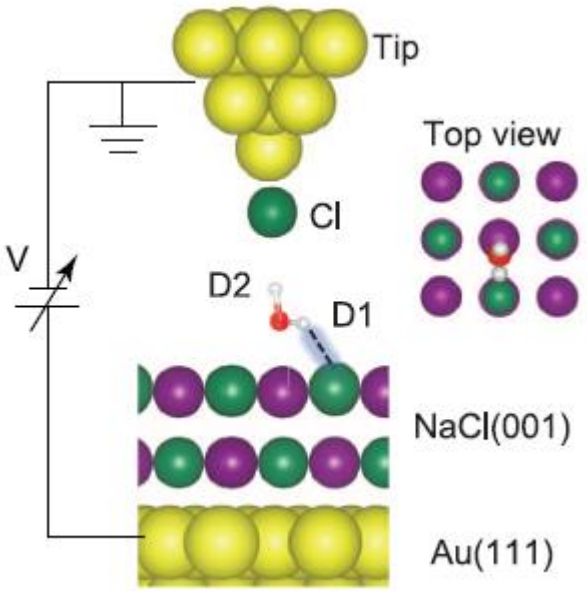


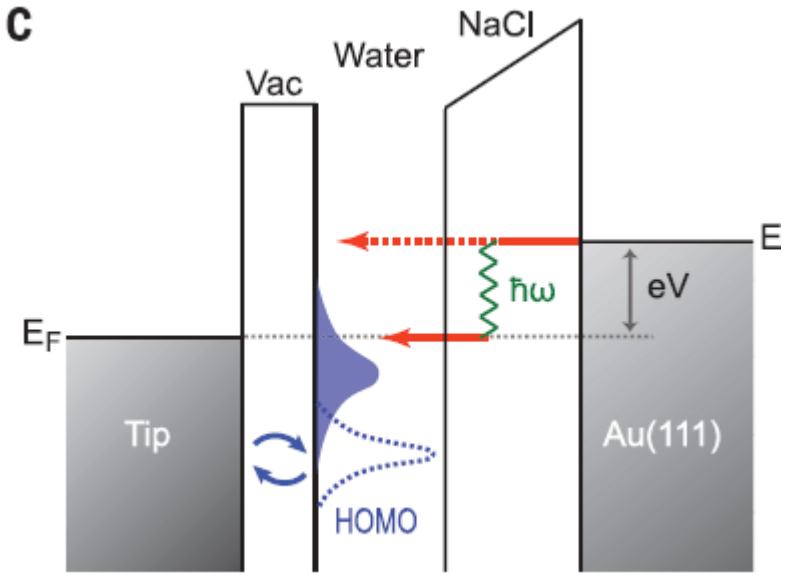
Trakhtenberg & Klochikhin, *Chem. Phys. 232*, 175 (1998)
Spahr et al. *Phys. Rev. Lett.* 102, 077506 (2009)
Drechsel-Grau & Marx, *Phys. Rev. Lett.* 112, 148302 (2014)

Outline

- Full quantum effect of hydrogen bond
  - Guo, … …, EGW and Jiang, ***Science*** (2016)

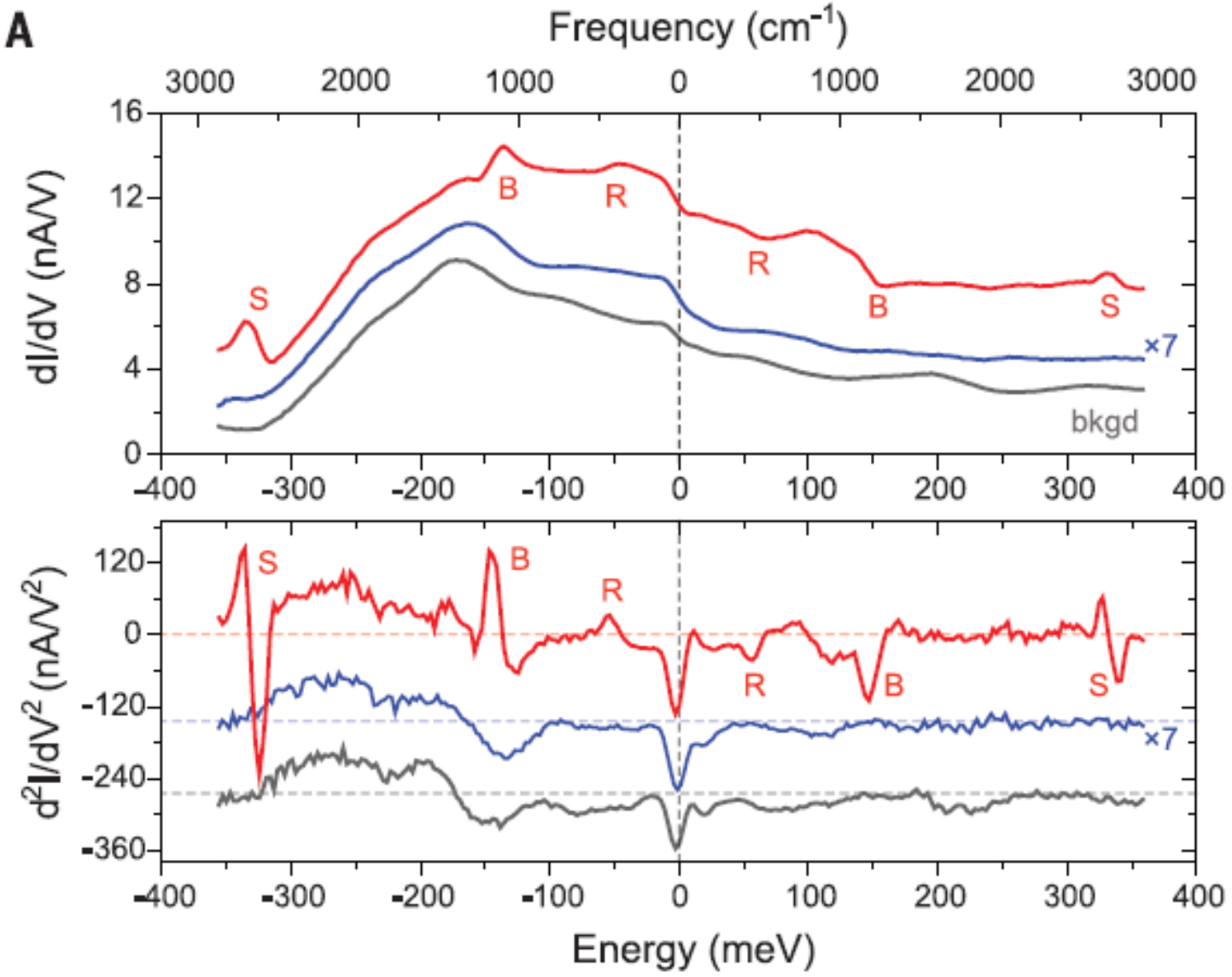
Inelastic tunneling spectroscopy and NQEs of HB



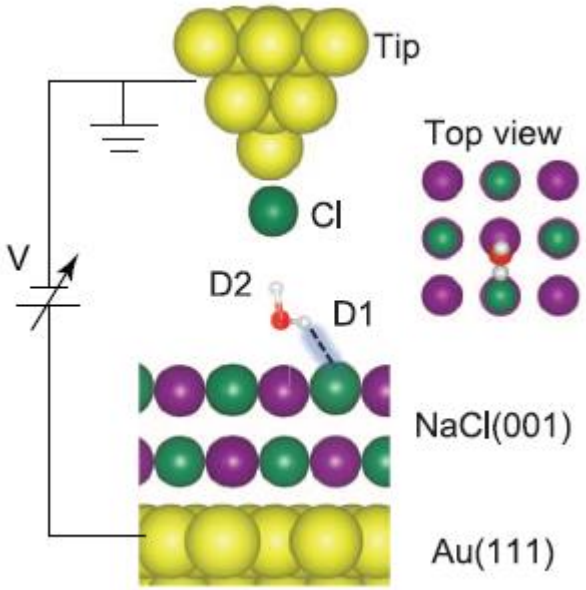


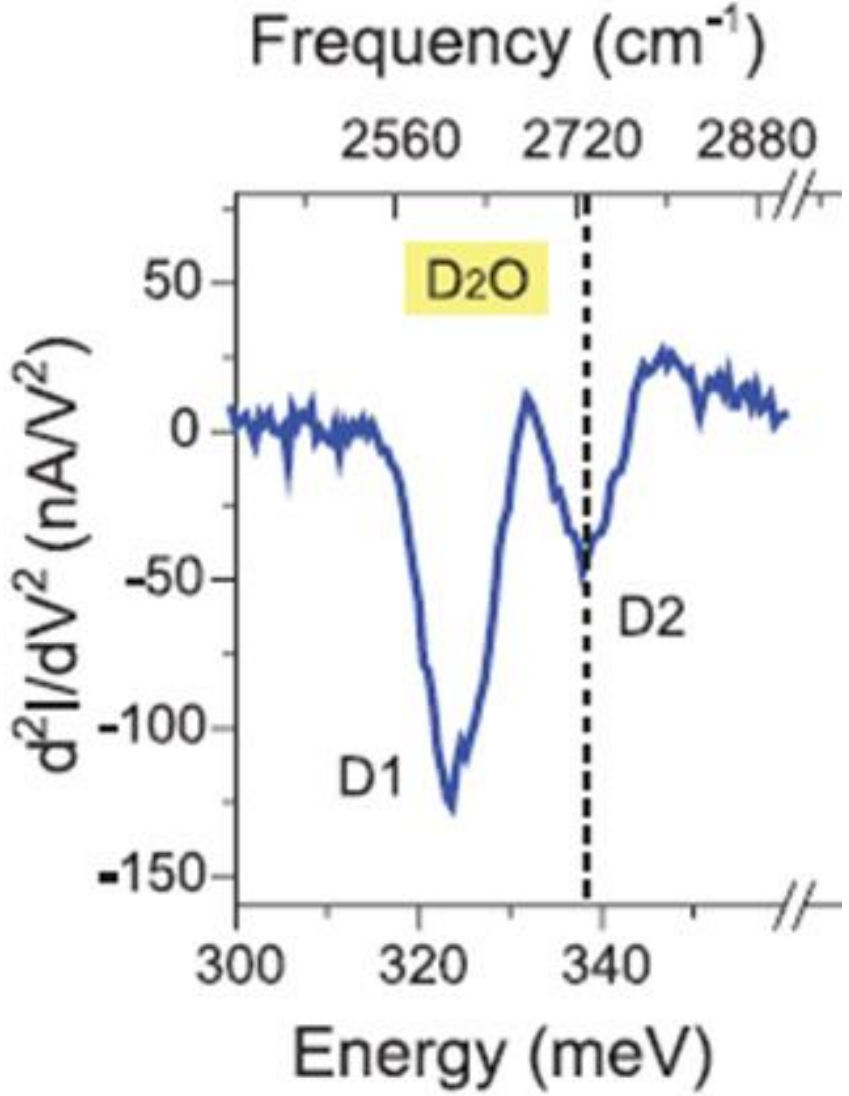
D_2O monomer

Inelastic tunneling spectroscopy and NQEs of HB

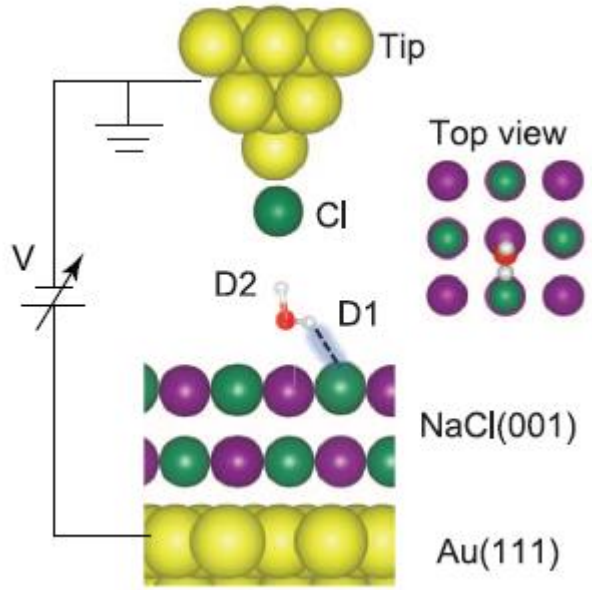


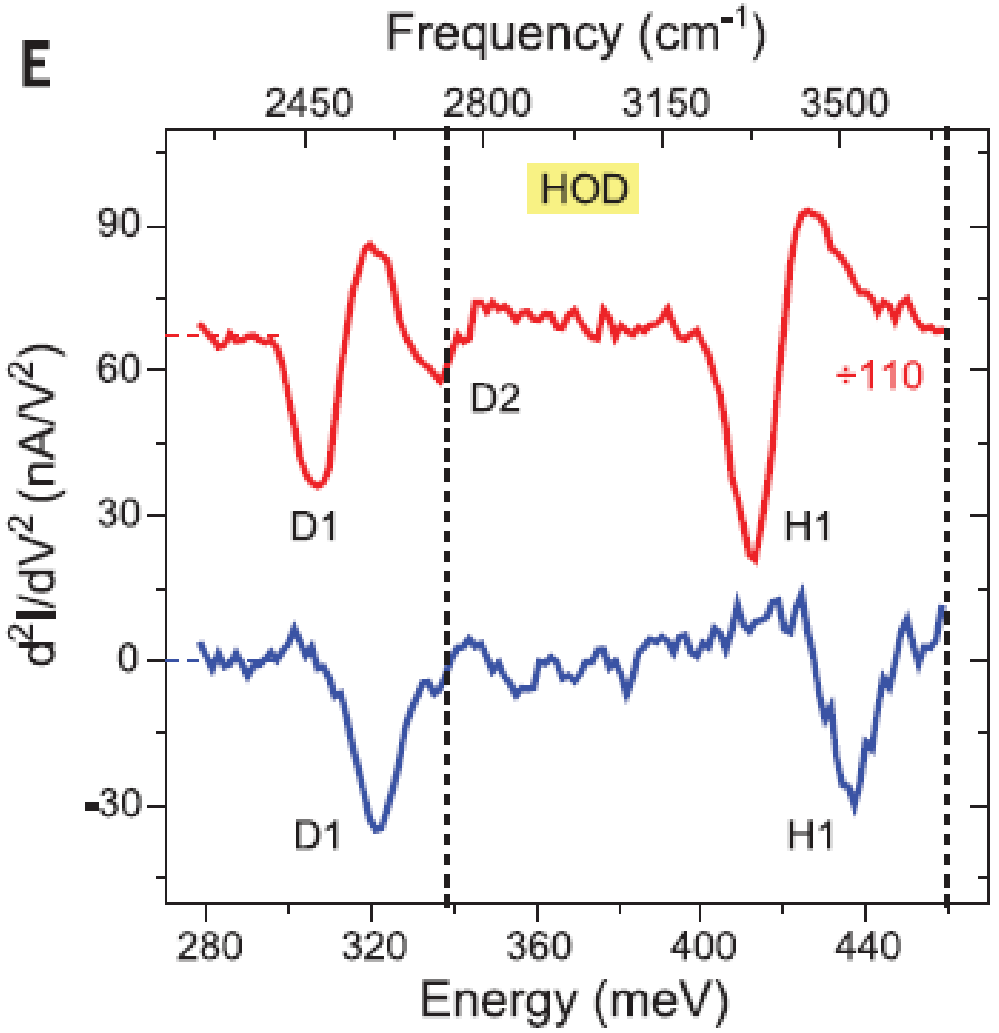
Inelastic tunneling spectroscopy and NQEs of HB



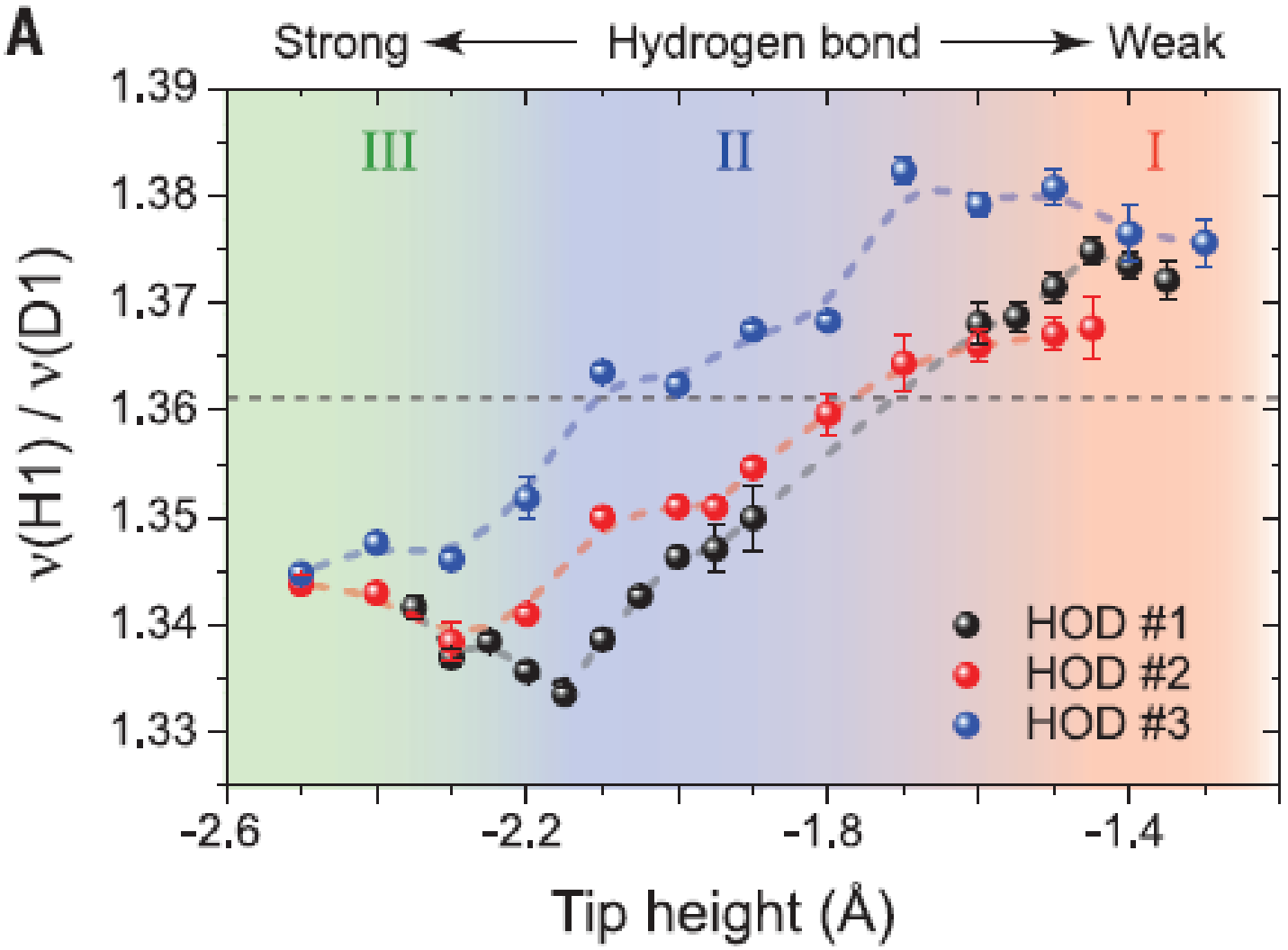


Inelastic tunneling spectroscopy and NQEs of HB

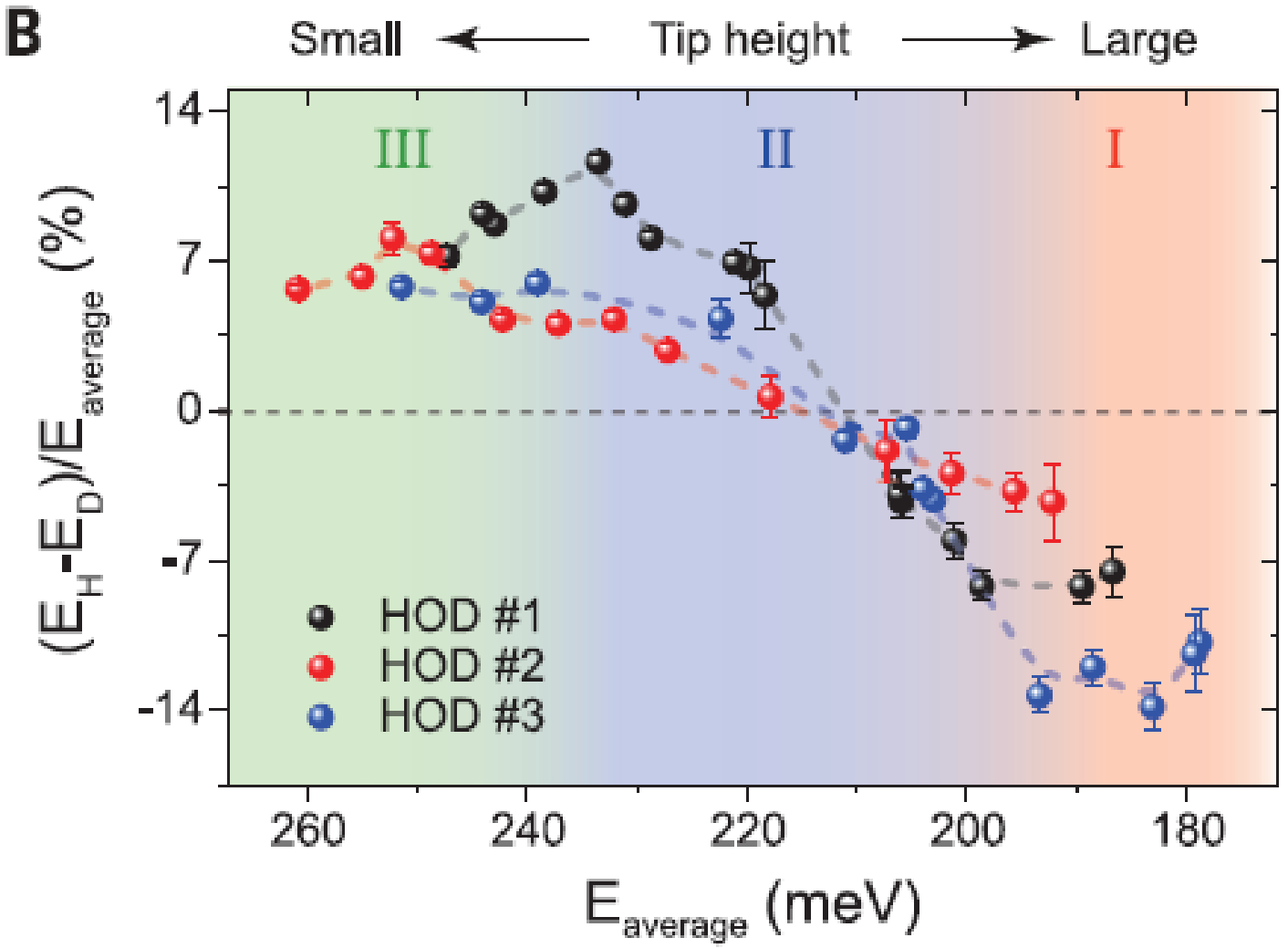




Inelastic tunneling spectroscopy and NQEs of HB



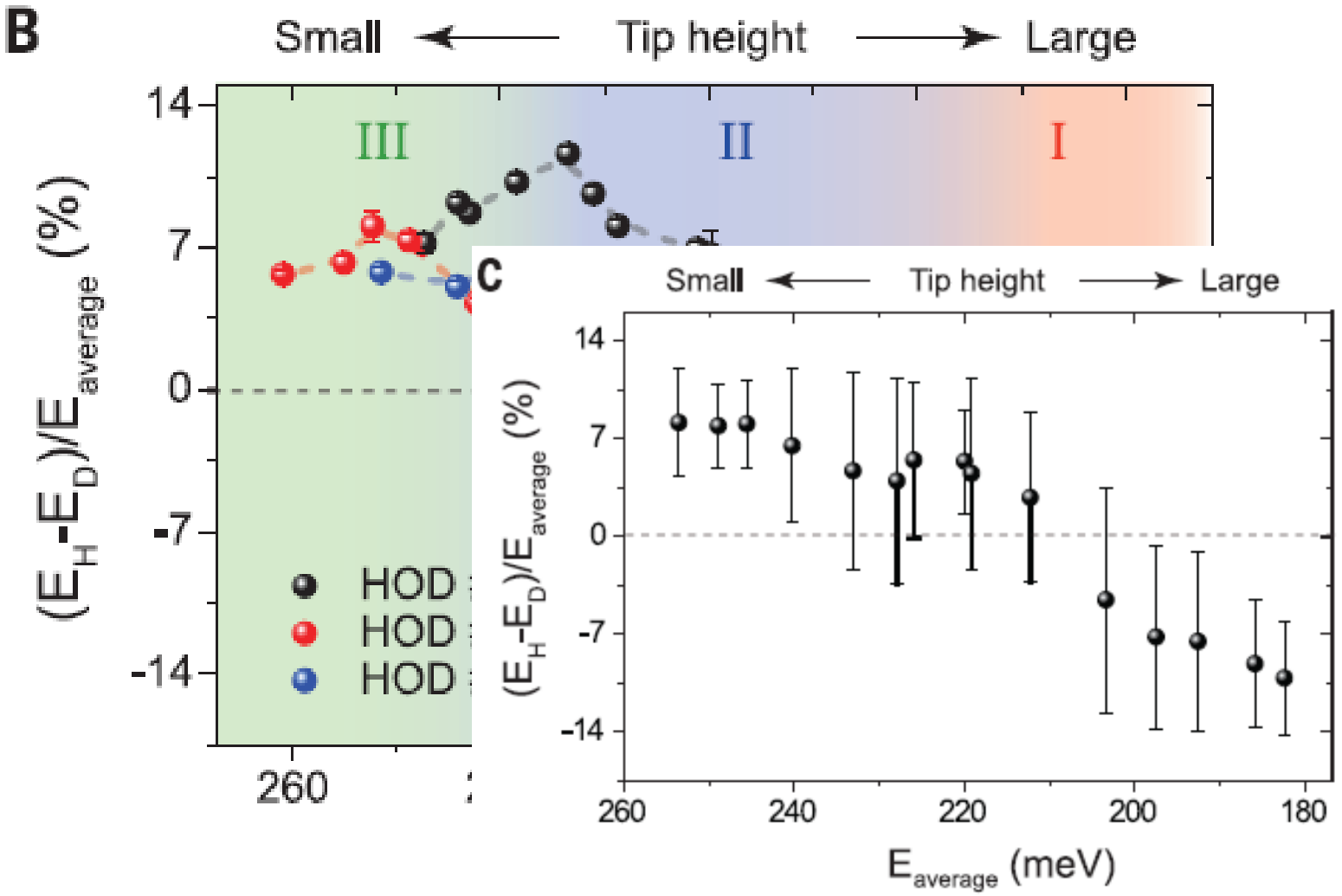
Inelastic tunneling spectroscopy and NQEs of HB



$$\Delta H = 1.3 \times \sqrt{\Delta \nu}$$

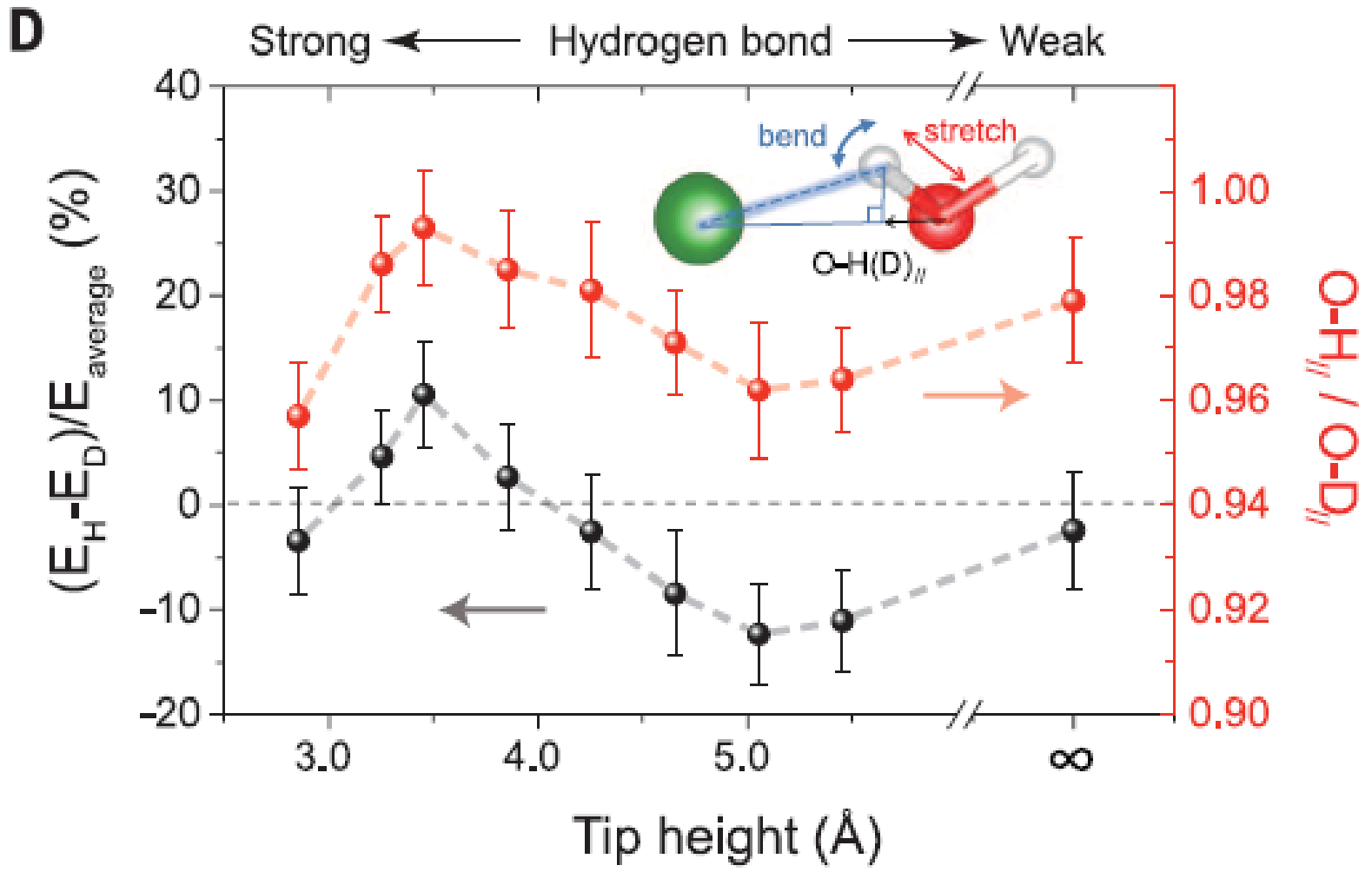
Li, *et al.* ***PNAS* 108**, 6369 (2011)

Inelastic tunneling spectroscopy and NQEs of HB



$$\Delta H = 1.3 \times \sqrt{\Delta \nu}$$

Inelastic tunneling spectroscopy and NQEs of HB



Guo, *et al.* ***Science*** 352, 321 (2016)

Summery

- For the first time, I have shown you the inside structure of a single water molecular and the directionality of H-bonds of water clusters in real space.

- Furthermore, for the first time, I have shown you how important of nuclear quantum effects (NQEs) in the dynamic study of a real material system, for example of water on salt.

Acknowledgements

The people behind the work:

Ying Jiang (*Professor@PKU*) Exp

Xinzheng Li (*Professor@PKU*) Theo

Students *@PKU* Exp and Theo


Thank you !