Quantum Mechanics of Water Adsorption

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Plan

A case study of first principles molecular dynamics used to study the adsorption of water on an oxide surface.

- A brief reminder of the underlying theory
    DFT, plane waves and pseudopotentials

- TiO_2 (110)
    bulk electronic structure – expectations for the surface

- Water adsorption !
    What do we know from experiment ?
    Structural model
    The use of molecular dynamics

Write the density in terms of a set of N non-interacting orbitals…

$$\rho(\mathbf{r}) = \Sigma |\phi_i(\mathbf{r})|^2$$

The non interacting kinetic energy and the classical Coulomb interaction

$$T_s[\rho] = -\frac{1}{2}\sum_i^N \left\langle \phi_i \left| \nabla^2 \right| \phi_i \right\rangle \qquad E_H[\rho] = \frac{1}{2}\int \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2$$

Allow us to recast the energy functional as:

$$E[\rho] = T_s[\rho] + E_{ext}[\rho] + E_H[\rho] + E_{xc}[\rho]$$

Where we have introduced

$$E_{xc}[\rho] = (T[\rho] - T_s[\rho]) + (E_{ee}[\rho] - E_H[\rho])$$

Variation Theorem => Kohn Sham Equations

Vary the energy with respect to the orbitals and ….

$$\left[-\frac{1}{2}\nabla^2 + v_{ext}(\mathbf{r}) + \int \frac{\rho(\mathbf{r'})}{|\mathbf{r}-\mathbf{r'}|}d\mathbf{r'} + v_{xc}(\mathbf{r}) \right]\phi_i(\mathbf{r}) = \varepsilon_i\phi_i(\mathbf{r})$$

$$V_{xc}(\mathbf{r}) = \frac{\partial E_{xc}[\rho]}{\partial\rho(\mathbf{r})}$$

No approximations, So…

If we knew $E_{xc}[\rho]$ we could solve for the *exact* ground state energy and density !

Cost – N^3 ….. in principle but O (N) if locality of chemistry recognised.

Accuracy: Atomisation Energies

	Kurth - m.r.e % 20 molecules	Adamo m.a.e (max) kcal/mol G2 set of 148 molecules
LDA	22%	
BLYP	5%	
PBE	7%	17 (51)
HCTH	3%	-
VS98	2%	3 (12)
PKZB	3%	5 (38)
Hybrid	-	3 (20)

Solving the Single Particle Equations

To solve the single particle equations…

- Select a representation for $\psi(r)$

- Build the secular equations

- Solve by minimisation or diagonalisation

- Iterate to self consistency…

A Representation for ψ(r)

Alternatives

1. Direct representation on a grid - $\psi(r_i)$
   Potentially very accurate but huge grids required – expensive

2. Expansion in a basis set
   Compact representation, potential for high accuracy, efficient, choose functions for computational convenience. Solve by iteration and diagonalisation or direct minimisation.

   - Linear combination of atomic orbitals
     – eg: Gaussians, Muffin-Tin Orbitals (LMTO), Atomic Orbitals…

   - Expansion in plane waves

   - Mixed schemes (PAW, FLAPW, …)

Here we consider the LCAO (Gaussian's) and the plane-wave method.

Plane Waves

$$\psi_j^{\vec{k}}(\vec{r}) = \sum_K^{(\vec{k}+\vec{K})^2 < E_{cut}} C_{j,\vec{K}}^{\vec{k}} e^{-i(\vec{k}+\vec{K}).\vec{r}}$$

- Systematic improvement with increasing E_{cut}

- Direct minimisation of the total energy

- Analytic gradients via Helman-Feynman – forces are accurate and cheap

- Pseudopotentials must be used

- Large number of basis functions $N \sim 10^6$ (especially for heavy atoms).
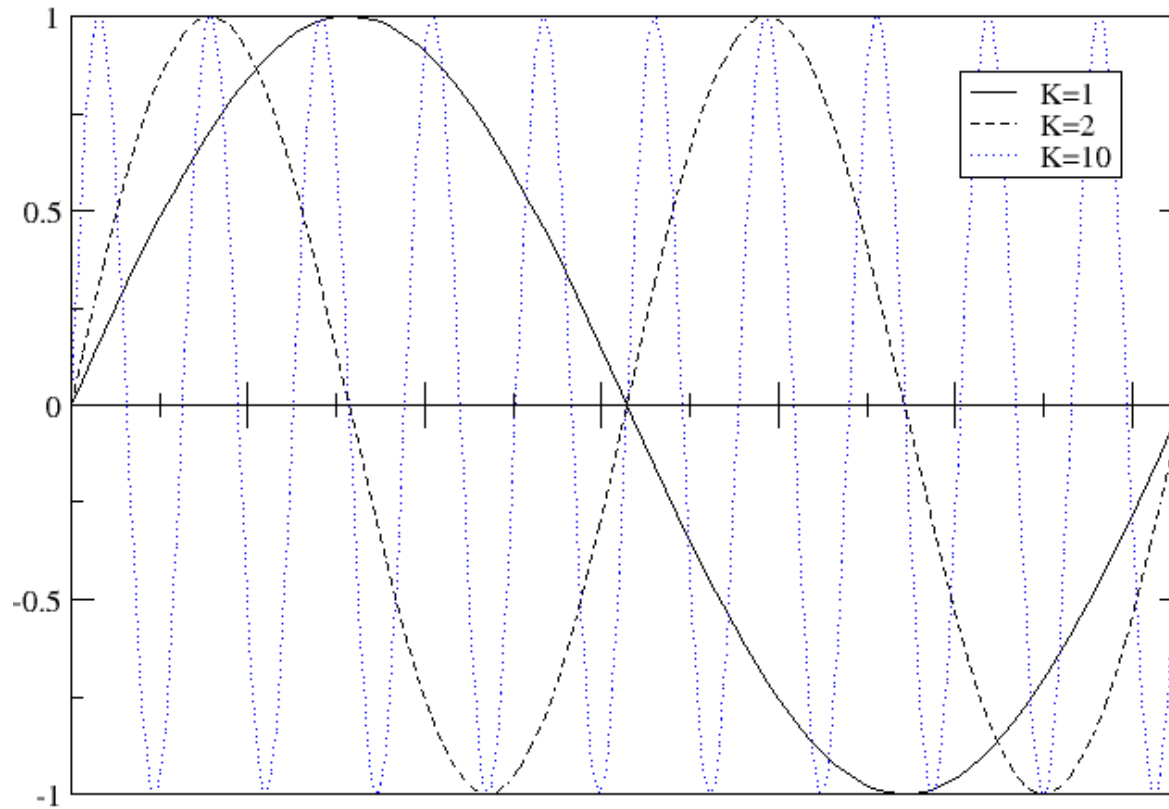

For example: CASTEP, VASP
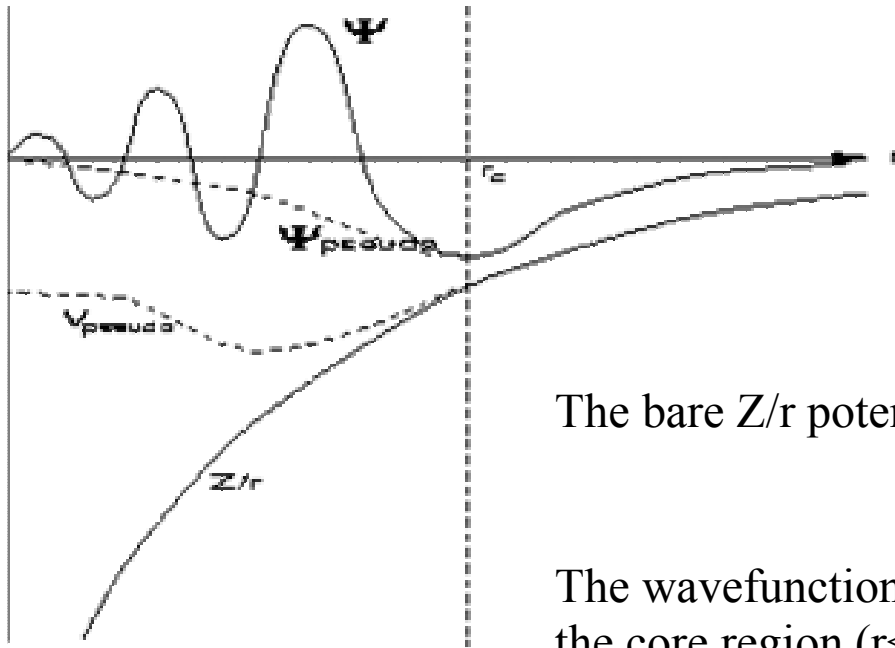
The bare Z/r potential is replaced by V_{pseudo}

The wavefunction, ψ, is replaced by ψ_{pseudo}. They differ inside the core region ($r<r_c$) but match in value and gradient at r_c and so are the same outside the core.

V_{pseudo} is chosen to make ψ_{pseudo} as smooth as possible ie: it can be expanded in a plane waves.

$$\sum_{\mathbf{K}'} \left[|\mathbf{k} + \mathbf{K}|^2 \, \delta_{\mathbf{K}\mathbf{K}'} + V(\mathbf{K} - \mathbf{K}') \right] C_{i,\mathbf{k}+\mathbf{K}'} = \varepsilon_{i,\mathbf{k}+\mathbf{K}} C_{i,\mathbf{k}+\mathbf{K}'}$$

Diagonalisation of $[H_{KK'}]$ of order $10^6 \times 10^6$ intractable

=> direct minimisation

$$E = \min E(\{\psi_i\})$$

With the constraint,

$$\int \psi_i^*(\vec{r}) \psi_j^*(\vec{r}) d\vec{r} = \delta_{ij}$$

The Problem: Water on TiO$_2$

TiO$_2$

- d^0 transition-metal oxide, 3 eV band gap, rutile structure
- Widely used as pigment and opacifier (powder), also catalyst and catalyst support

Motivation and background

- Photoelectrolysis of water (Fujishima and Honda, Nature **238** 37 (1972))
- Microcrytalline powders exposed to air
- Water used as experimental probe of the surface
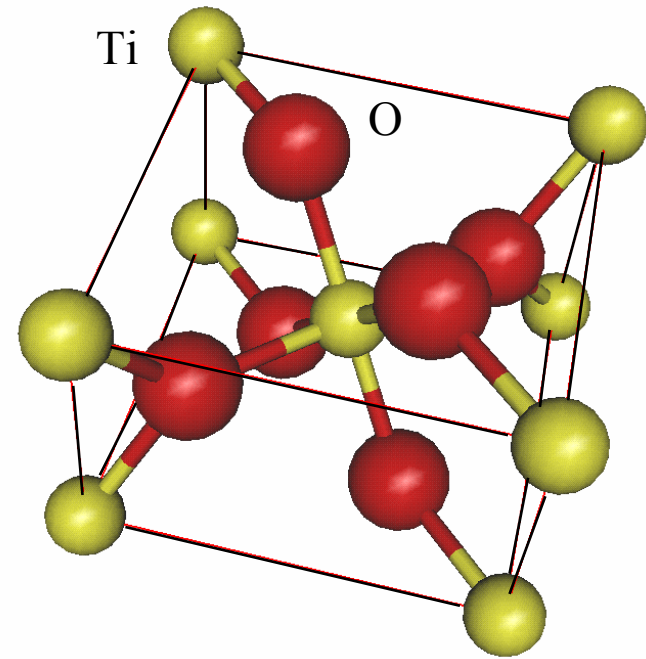
Ti^{4+} (d^0)

O^{2-} (s^{2}p^6)

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a 4.594

c 2.958

u 0.305
```
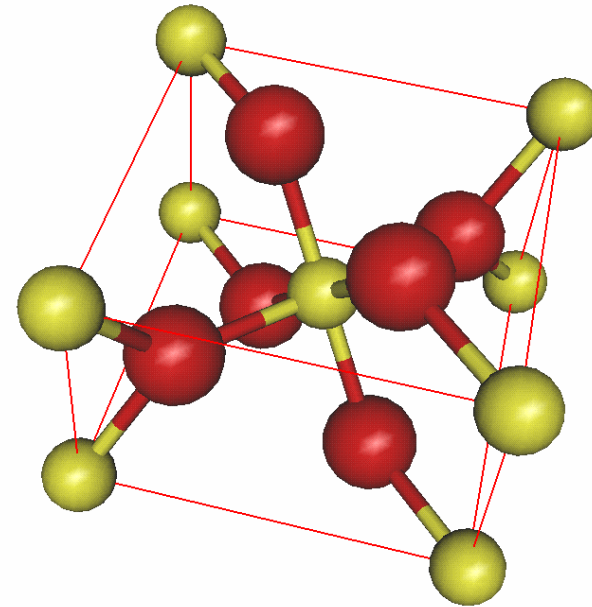

- **Rutile-6, Anatase-6, Columbite-6, Baddeleyite-7 … Fluorite-8**

- **Cottunite – the hardest known oxide (*Nature, April 2001*)**

- **Ti$_x$O$_y$ $\rightarrow$ TiO, Ti$_2$O$_3$, Ti$_4$O$_7$, - Magnelli-Phases**

- **Surfaces - (100) 1x3, (110) soft vibrations, water chemistry**
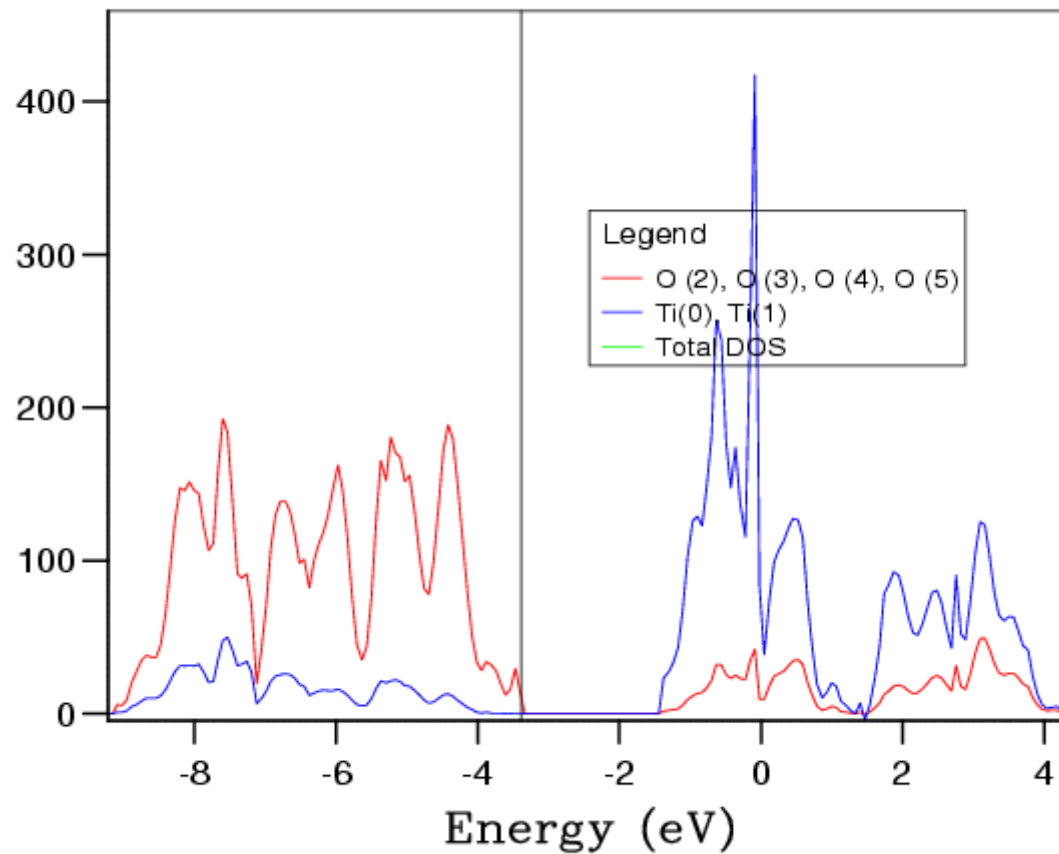
Expect a strongly ionic oxide:

Ti $^{4+}$: $1s^2\, 2s^2p^6\, 3s^2p^6d^0$

O^{2-} : $1s^2\, 2s^2p^6$
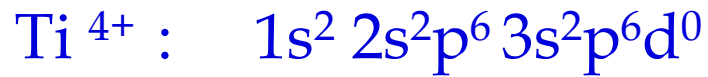
In the solid state these energy levels broaden to form bands.

The energy levels can be summarised as a density of states.

TiO2 Density of States

Legend
- O (2), O (3), O (4), O (5)
- Ti(0), Ti(1)
- Total DOS

Energy (eV)

Fermi energy marked as a vertical line

Valence band O-2p

Conduction band Ti-d

Ionic expectations realised
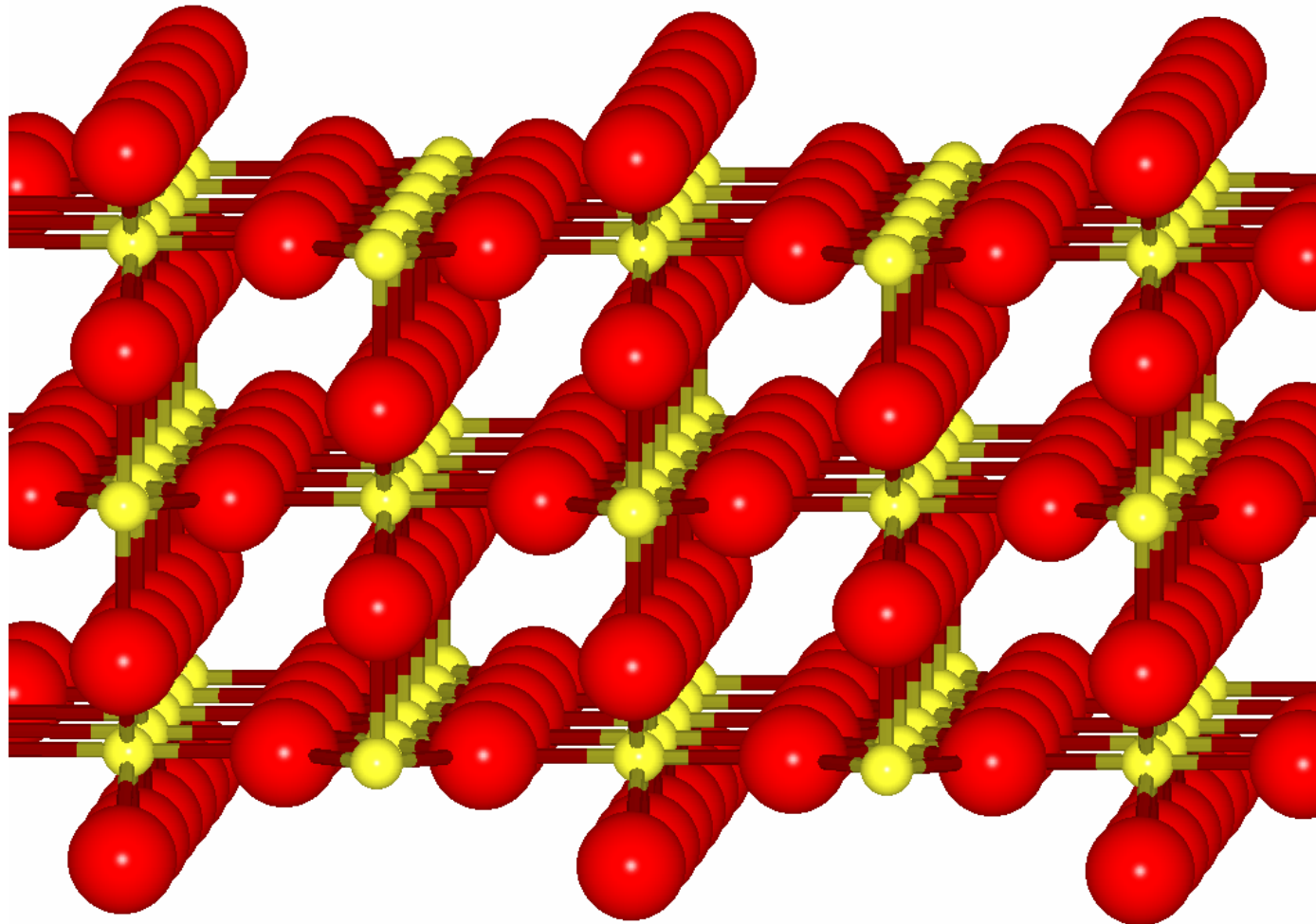
Water on TiO$_2$ (110): Interpreting Experiment

Experiment (UPS, TPD, HREELS)

- Dissociation at low coverage
- Predicts presence of molecular H$_2$O at monolayer coverage ($\Theta=1$)
- No more than 25% of water is dissociated at $\Theta=1$
- Most workers believe defects cause dissociation

and Theory

- Dissociation at <u>all</u> coverages on <u>defect-free</u> surface
- But notably, previous first-principles studies have symmetry constraints and limited structural relaxation
- Little contact with experiment

...were in conflict
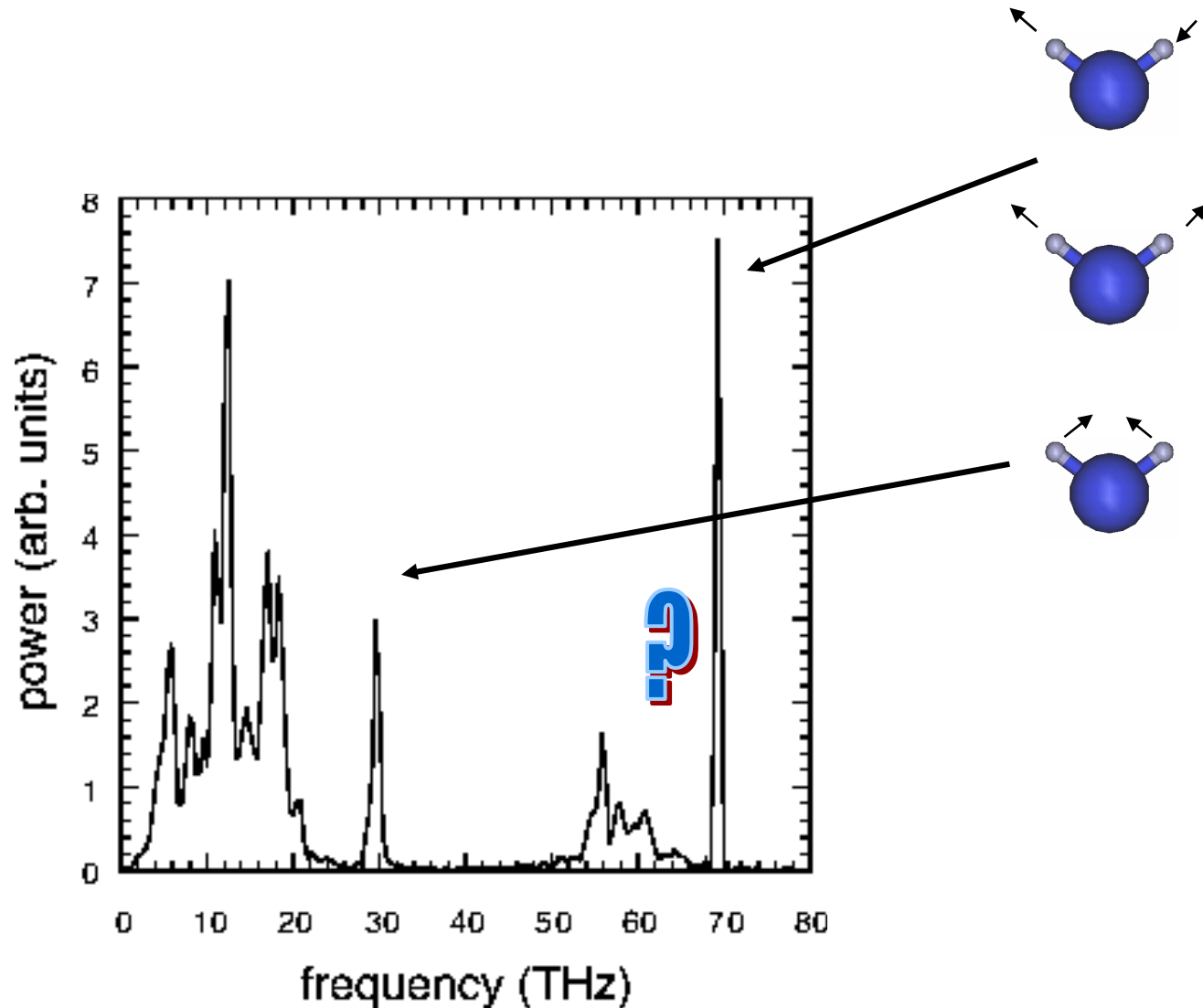
The Plan

Half-coverage (Θ=0.5)

- MD to explore adsorption site and mechanism
- Relate to experiment at "low coverage"

Θ=1

- Use 2x1 cell and 2 molecules to investigate the effect of intermolecular interactions
- More MD for adsorption site
- Static calculations for adsorption energies
- Consistent with experiment?

Using Molecular Dynamics for Kinetics

Quantum mechanical molecular dynamics allows one to "see" the time evolution of the atomic positions. This is very nice but it is in general **not** an efficient way to study reaction kinetics.

The MD time step is typically 1 femtosecond. Usually energy barriers are high enough that it takes many vibrations before the transition state is reached – the MD is then mostly watching harmonic vibrations for many time steps before the rare event of a reaction.

Usually better to map out the energy surface using a technique like Nudged Elastic Band…

Techniques

DFT Plane-wave pseudopotential method
- Big systems + strong pseudopotentials (Transition-metal + first row) => parallel computers
- Need forces for MD and structural relaxation
- GGA: accurate for H-bond energetics

Molecular Dynamics
- Good for exploring configuration space of a small molecule on a surface, because
  - few degrees of freedom
  - small energy barriers
- Use to calculate vibrational spectra
  - H-bonded molecules => anharmonic potential
  - Can relate to HREELS

KB-pseudopotentials, PW II GGA

- TiO_2 calculated (expt) values:
  a=4.69 (4.594) c=2.99 (2.959) Å,
  u=0.306 (0.3050)

- H_2O: r=0.967 (0.957) Å,
  θ = 105.1° (104.5)

ν_1 = 111 (109.6) THz
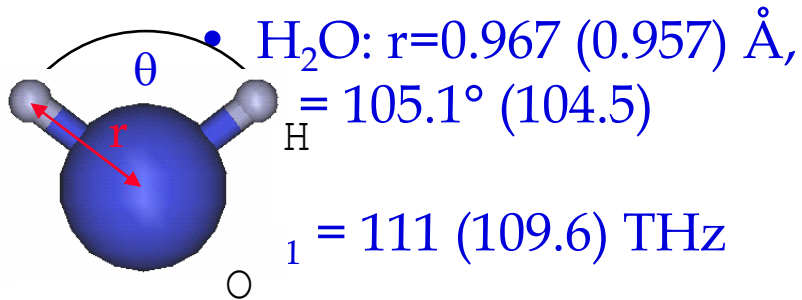
ν_2 = 114 (112.6) THz

ν_3 = 46.6 (47.82) THz
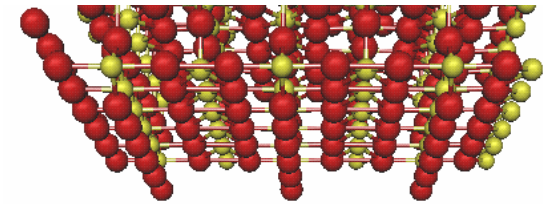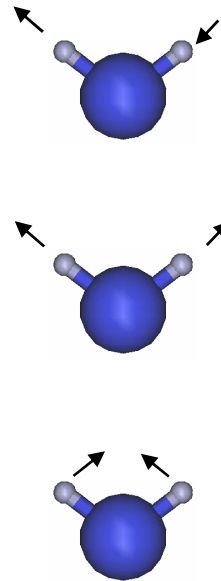
Slab
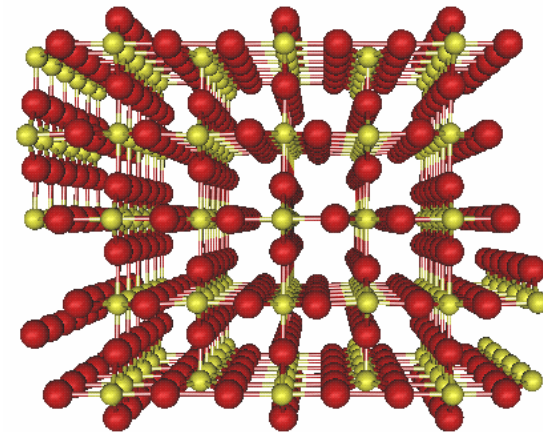
Geometry
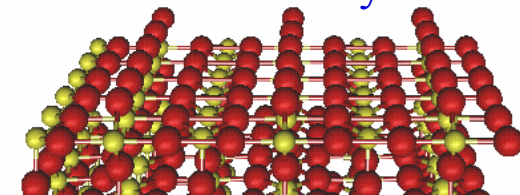
MD Details

MD: two kinds

- Adsorption simulations
  - Molecule positioned above surface, no initial velocity
  - Allowed to react with surface
- Equilibrium runs
  - Used to calculate frequency spectra
  - System relaxed and equilibrated
  - Low T (150 K), 3ps

All MD runs

- H mass 3 amu <=> timestep 1.5 fs
- Does not alter equilibrium quantities (e.g. MSD)
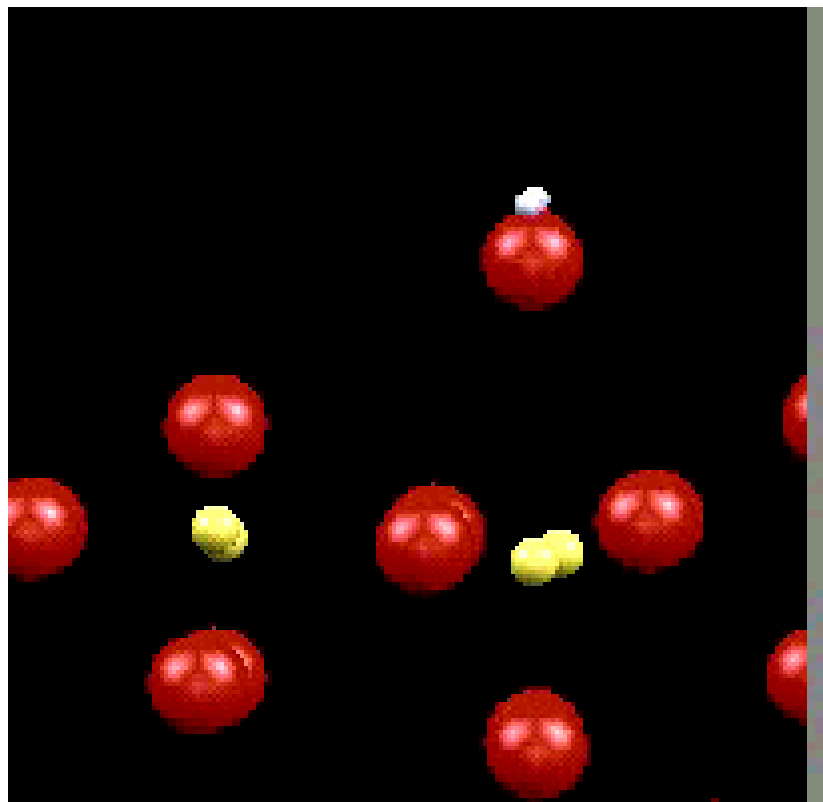- Shift in frequencies (v'_3 = 29 THz) must be corrected in comparisons

Clean Surface

- 2x1 supercell
- Bridging Oxygen (BO) ridges along [001]
- Fivefold- and sixfold-coordinated Ti (5f, 6f)
- $E_s = 0.69\ Jm^{-2}$
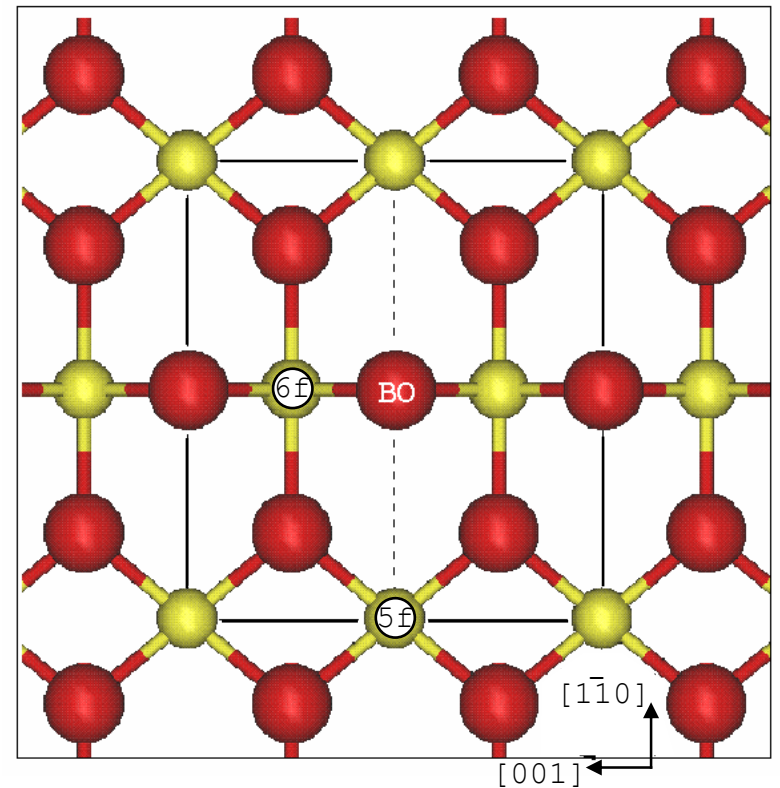
**Water adsorption
at the 5-fold
titanium site**

Water adsorption above the bridging oxygen row
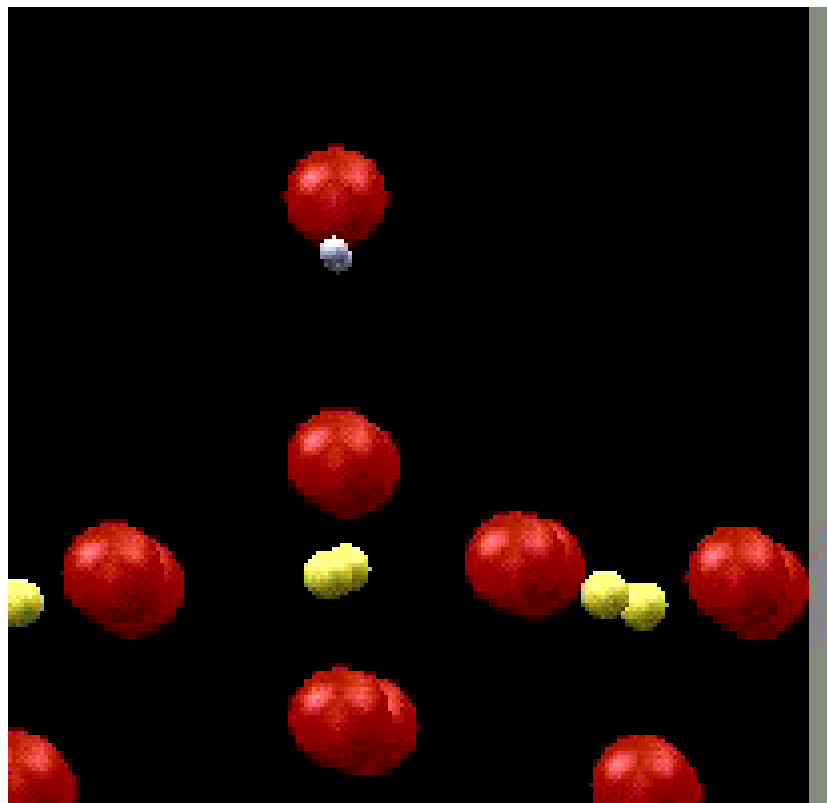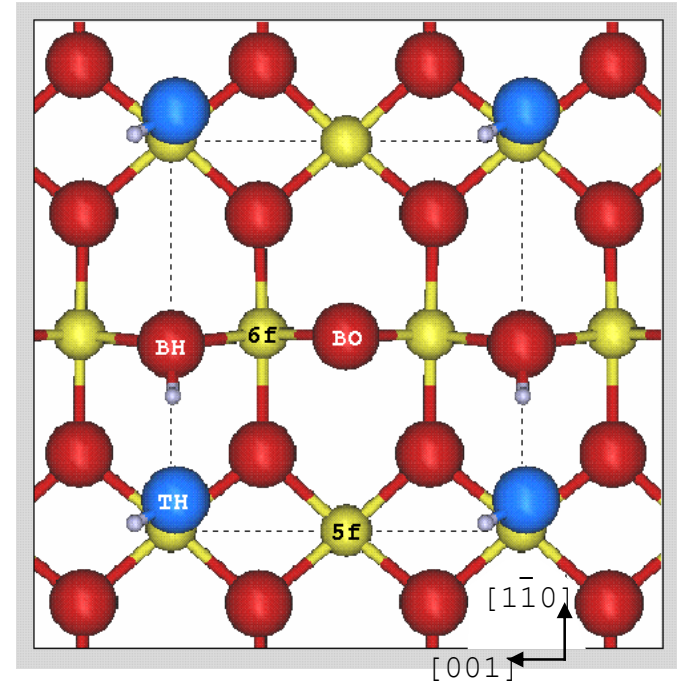
Half-monolayer water in equilibrium with the surface
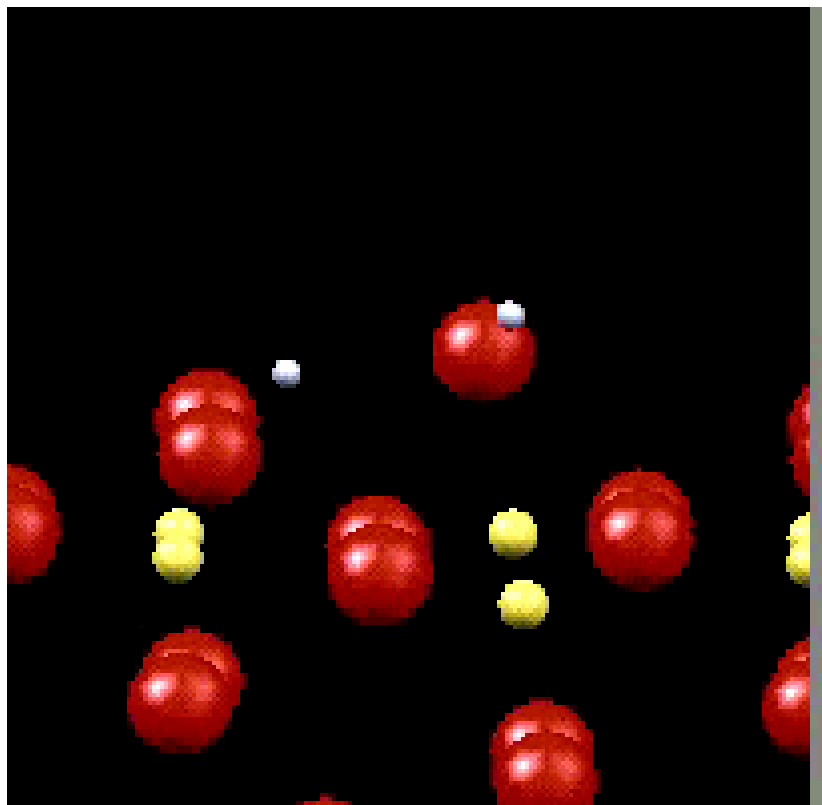
Adsorption of 1 molecule in the 2x1 cell

- Several initial configurations tried but adsorption only at the 5f site

- Lowest-energy state is <u>dissociated</u>, adsorption energy $E_{OH}=0.91$ eV

  - BH = bridging OH
  - TH = terminal OH

- Metastable <u>molecular</u> state E_M = 0.87 eV
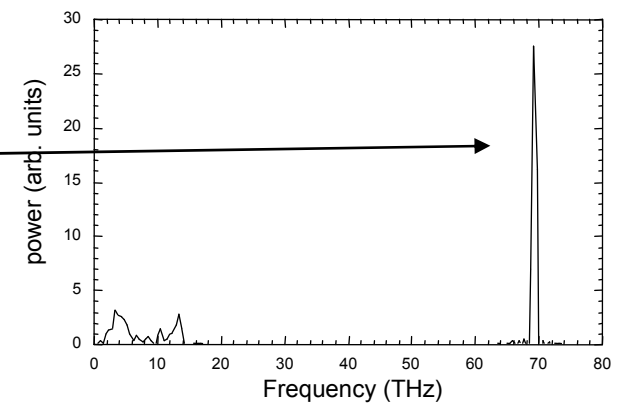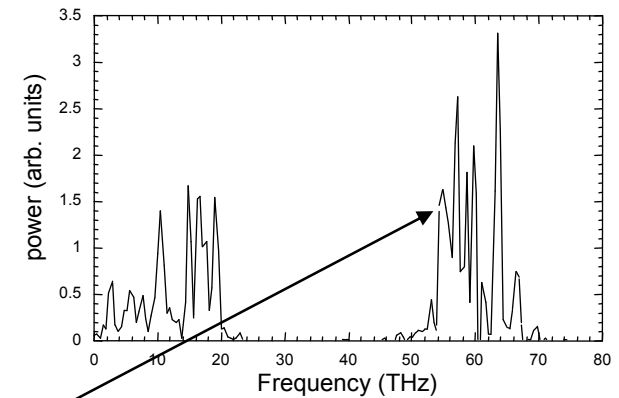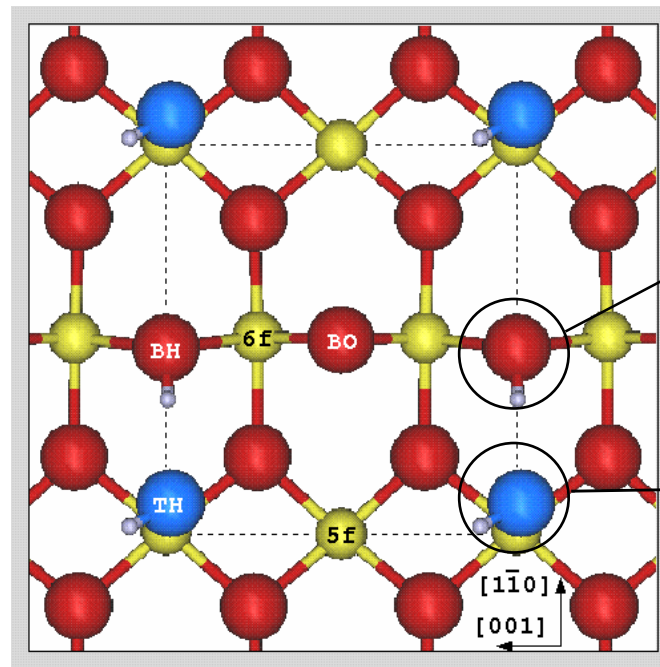
Equilibrium MD for H vibrations

- H-bonding broadens the BH signal
- Only one sharp high-frequency peak: usual to predict two for dissociated H_2O
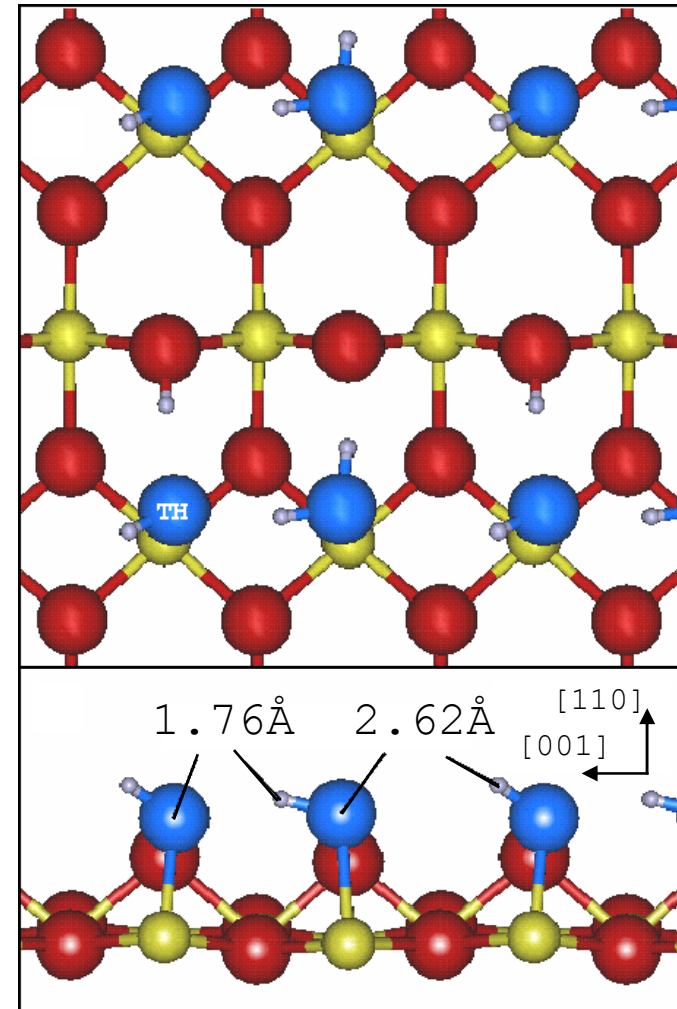
Θ=1: Lowest-Energy State

From the 3 MD runs, adsorption occurs
only at the 5f site

- Mixed dissociative and molecular
  adsorption!
- Strong H-bonding:
    - Pulls adsorbates off the 5f sites
    - Displaces bridging-O's
    - Breaks symmetry
    - Stabilises the molecule
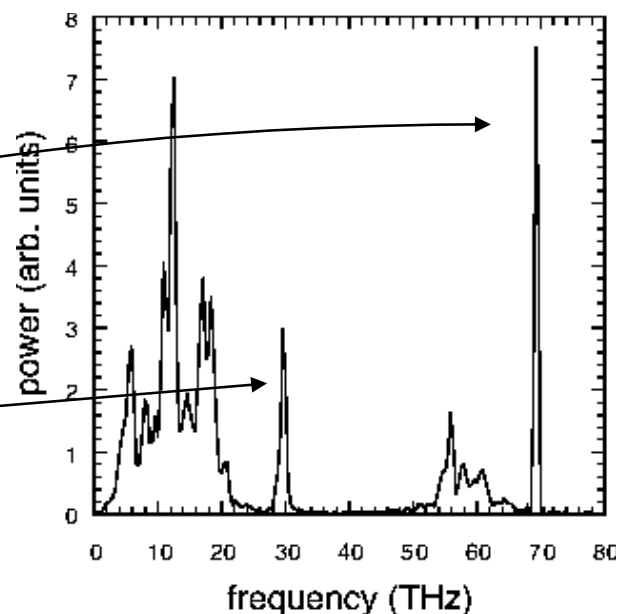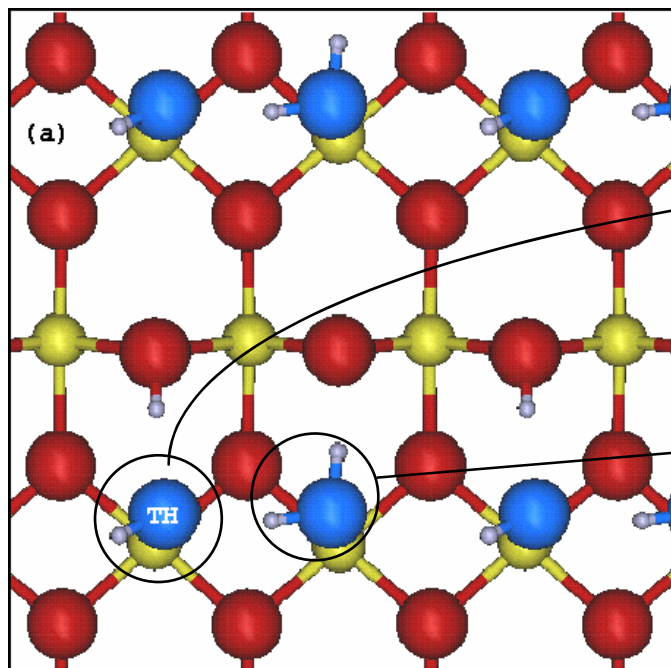- Adsorption energy
  E_{mix} = 1.01 eV

$\Theta=1$: Energetics of Metastable States

- **All water dissociated**
    - Adsorption energy $E_{2OH} = 0.91$ eV identical to E_{OH} ($\Theta=0.5$)
    - Implies zero interaction between OH groups

- **All water molecular**
    - Adsorption energy $E_{2M} = 0.99$ eV
    - <u>Very</u> close to E_{mix}, at limit of theory
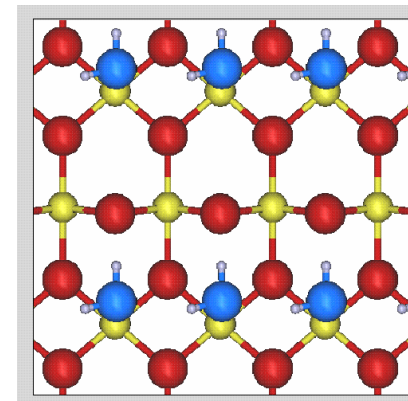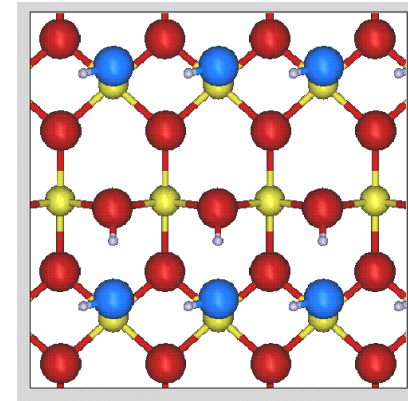
Mixed State: Good vibrations

All features of HREELS spectrum reproduced. Molecules stable at high coverage due to H-bonds.

- Molecule gives bond-bending signal
- TH gives sharp high-frequency peak
  - Therefore it is not H-bonded
- All other high-frequency modes broadened by H-bonding

Competing States: a Delicate Balance

- All water dissociated
  - No H-bonding
  - 0.04 eV gained by dissociating from molecular state (ignoring H-bonding)
- All water molecular

  $2 \times (E_{OH} - E_M) = 0.24$ eV
  - 0.12 eV per H-bond
  - Verified by calculations on the "net" of molecules
- Mixed State

  $2 \times E_{mix} - (E_M + E_{OH}) = 0.24$ eV
  - 0.24 eV per H-bond (only one bond)

This is why only one molecule dissociates — there is no advantage in losing all H-bonding interactions

Conclusions

Theory of water chemistry on TiO_2 (110)

- At $\Theta = 0.5$
  - Dissociation favourable
  - H-bonding between the resultant OH groups yields a broadened vibrational spectrum
- At $\Theta = 1$
  - Molecules stabilised by H-bonds
  - Water in both dissociated and molecular forms?
  - Complete HREELS spectrum reproduced

The consequences of intermolecular interactions <u>must be explored</u> — in previous work, failure to do this led to the wrong conclusions

More Conclusions

- The energetics are delicately balanced
    - For other materials the conclusions may be different: SnO2 has same rutile structure, lattice parameters 6% bigger. What happens there?
    - Caution with small energy differences
- Interpreting experiments: new framework
- Need more experiments, and more comparisons