

ON HYDRATION OF KAOLINITE SURFACES

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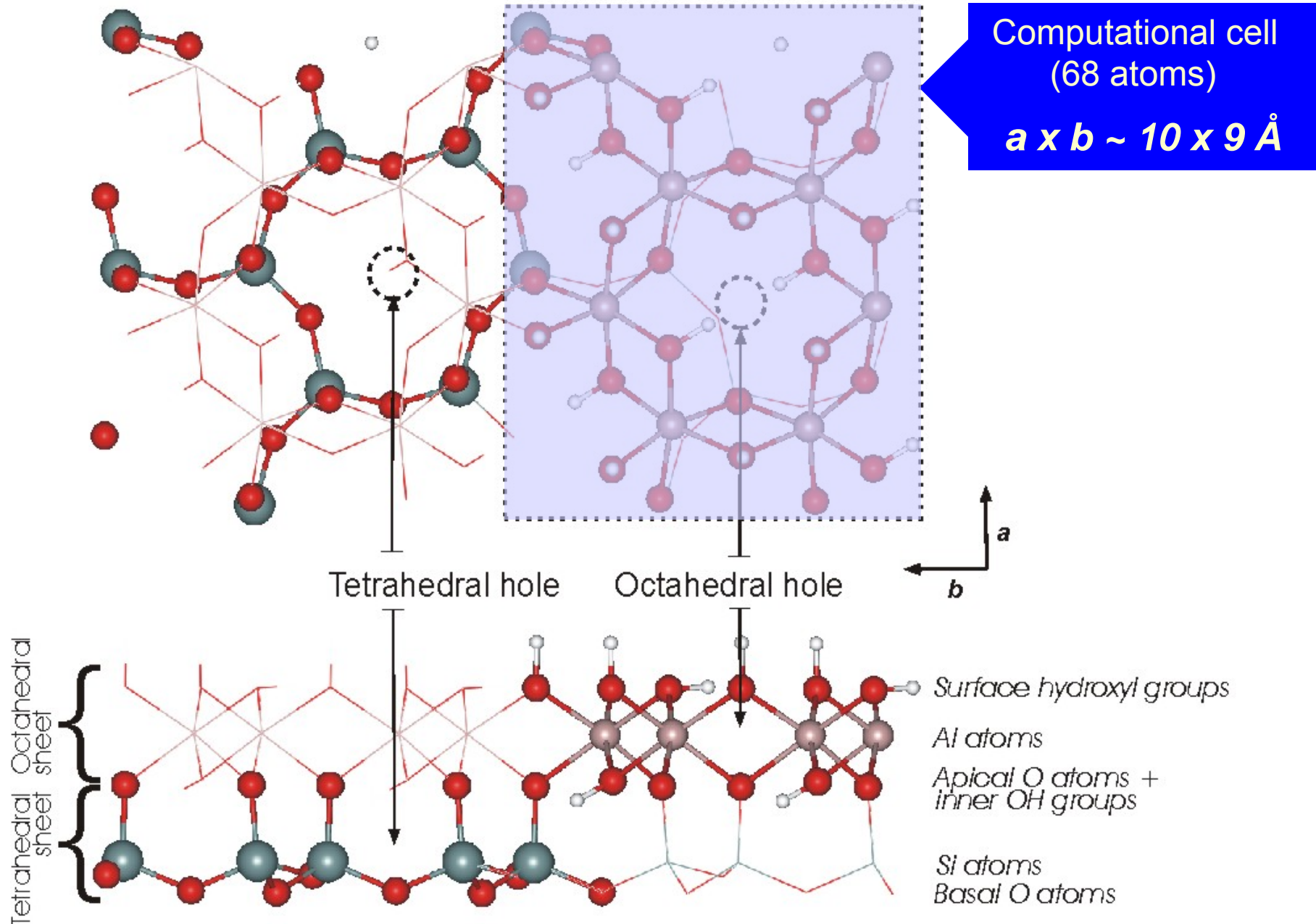
MOTIVATION

- Interactions between clay mineral surfaces and water are strongly affected by both phases.
- These interactions are controlled by the substrate structure, composition, and surface charge distribution, which vary strongly among clay minerals.
- These factors affect adsorption of molecular moieties and ions and ion exchange processes.
- These processes are, e.g., crucial for the mobility of contaminants in surface and ground water systems, mineral weathering, soil development. They are of significant interest in many geochemical, technological and/or biological systems.
- Heterogeneity and variability of clay minerals – difficulties in experimental investigations.

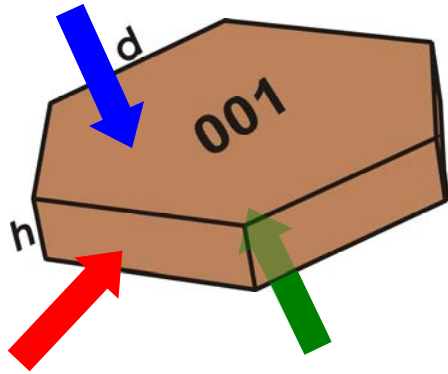
FEATURES OF KAOLINITE

GROUP:	CLAY MINERAL
TYPE:	1:1 dioctahedral
FORMULA:	$\text{Si}_4\text{Al}_4\text{O}_{10}(\text{OH})_8$
LAYER CHARGE:	0
INTERLAYER SPACE:	no
SPECIFIC SURF. AREA:	8-15 m ² /g
PARTICLE SIZE:	< 2 μm
DOMINANT SURFACE(S):	(001) - surface OH groups - basal O atoms

KAOLINITE LAYER – atomistic model



KAOLINITE – layer stacking, particle shape and surfaces



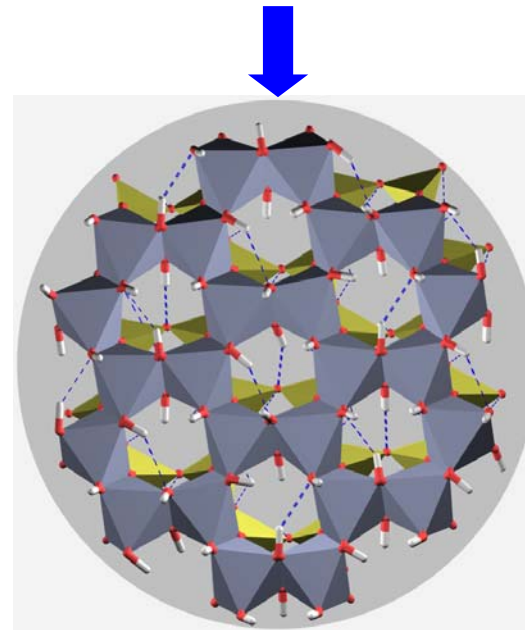
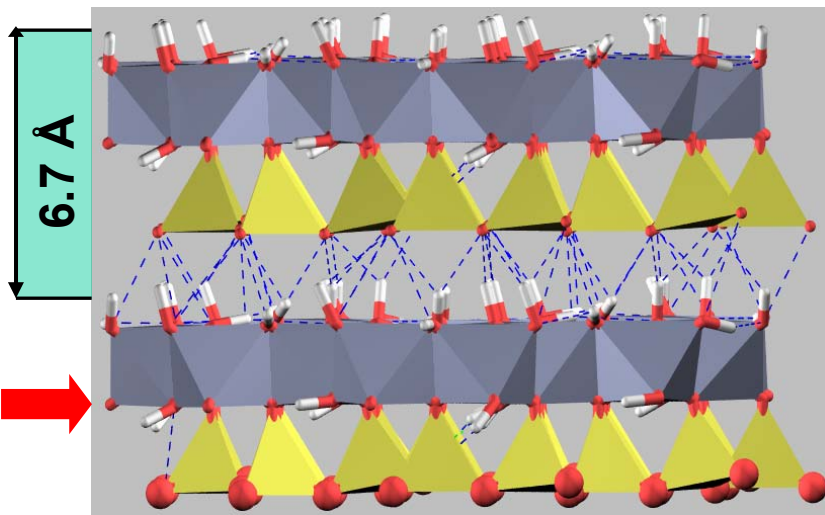
Dominant surface

0 0 1

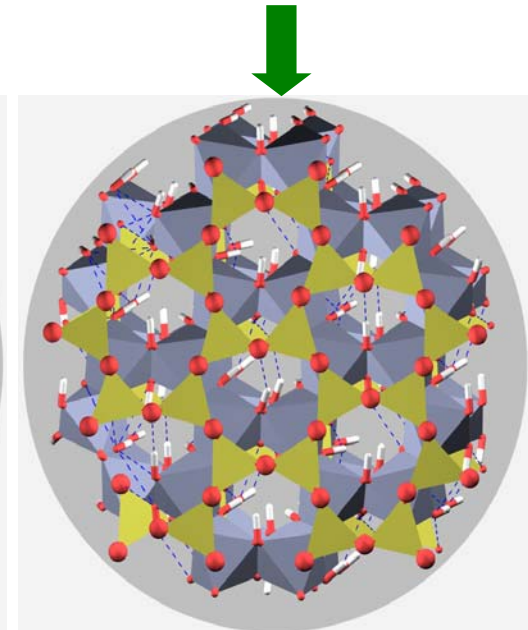
$d \sim 80 - 150 \text{ nm}$

$h \sim 10 - 30 \text{ nm}$

$S_{001} \sim 70-90 \%$

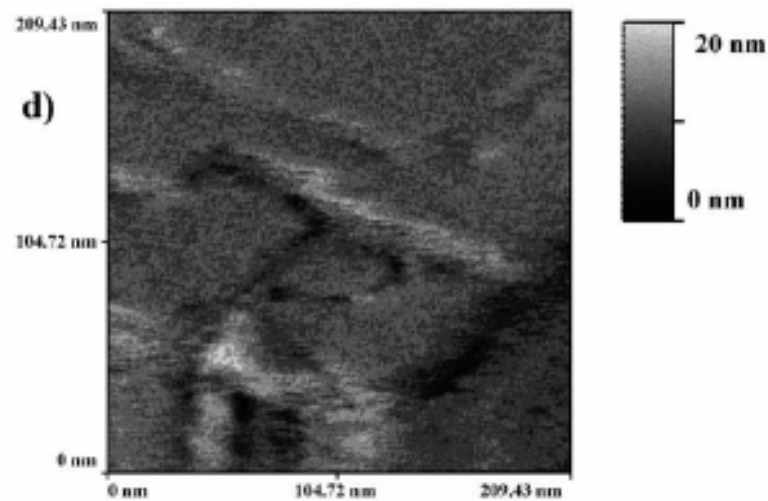
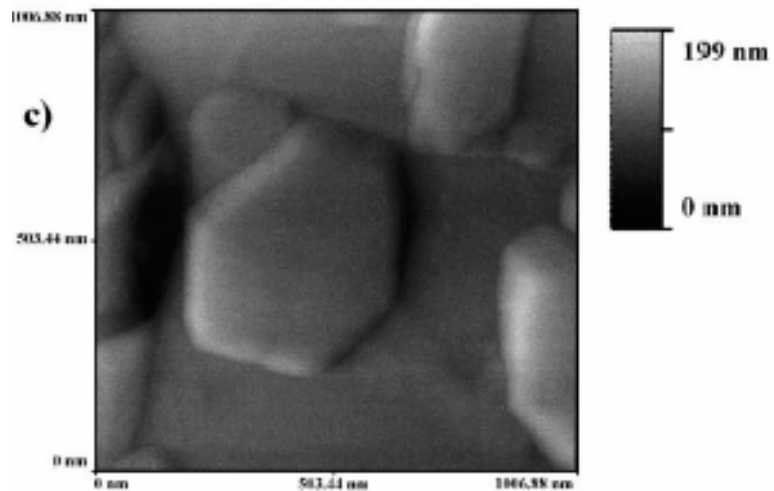
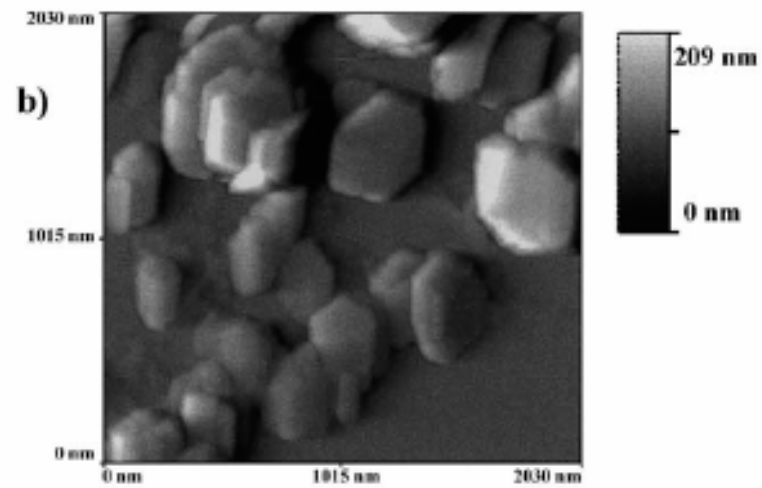
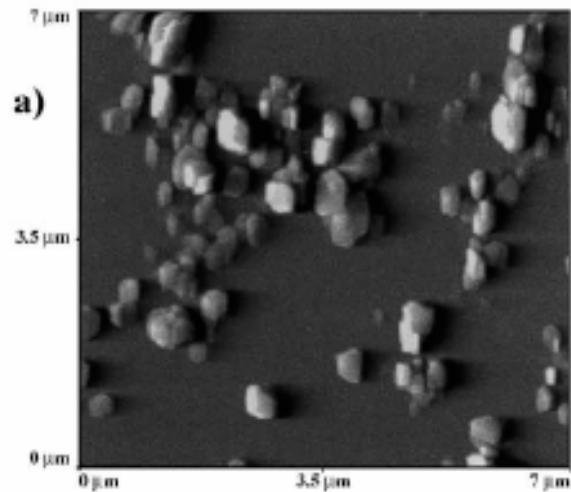


Octahedral (aluminol)
surface



Tetrahedral (siloxane)
surface

KAOLINITE - particle morphology



AFM images of kaolinite particles
(Vaz *et al.*, Powder Tech. 2002)

SIMULATION OF

sorption of water and **hydration** of kaolinite surface

- single molecule
- monomolecular H₂O layer (9 molecules)
- confined H₂O slab (15 Å, 38 molecules)

OBJECTIVES

to calculate, evaluate and compare

- structural
- energetic
- dynamical

properties of adsorbed water on kaolinite surfaces

METHODOLOGY

Ab initio simulations:

Density Functional Theory in LDA+GGA approximation (PW91);
PAW atomic pseudopotentials; plane wave (PW) basis set;
 Γ -point; periodic boundaries.

Static structural relaxation of atoms:

fixed unit cell; in 2D models : $\sim 15 \text{ \AA}$ vacuum
energy cutoff for PW – 400 eV
energetic and structural features

ab initio MD:

NVT ensemble (Nosé thermostat); fixed unit cell;
300 K; equil. phase; 5 ps MD; 1fs step; energy cutoff – 400 eV
structural, dynamical and spectroscopic properties

Program package:

Vienna **A**b initio **S**imulation **P**ackage (**VASP**);
University of Vienna



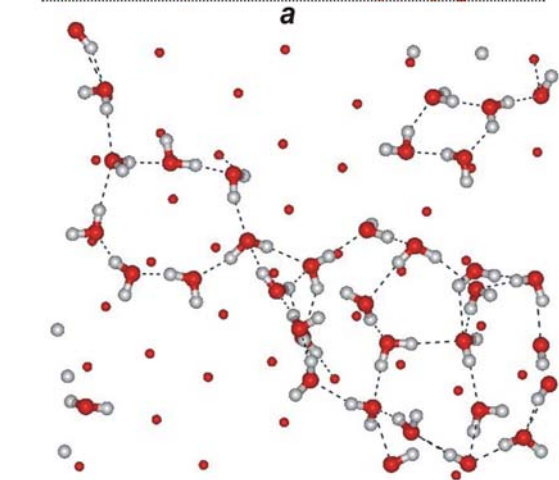
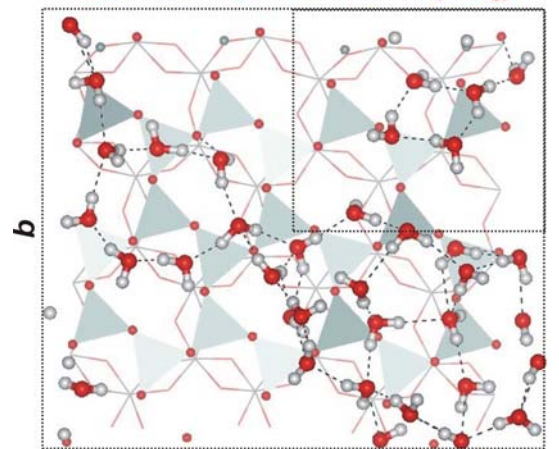
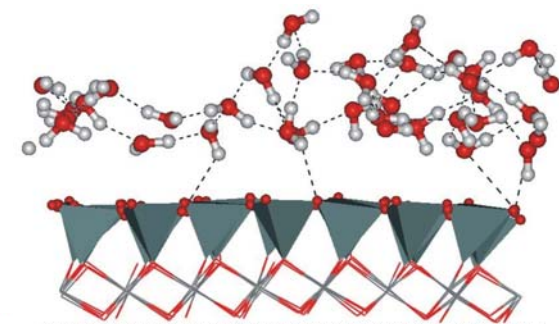
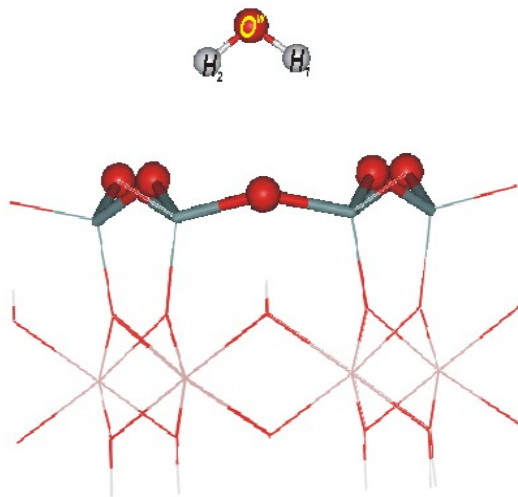
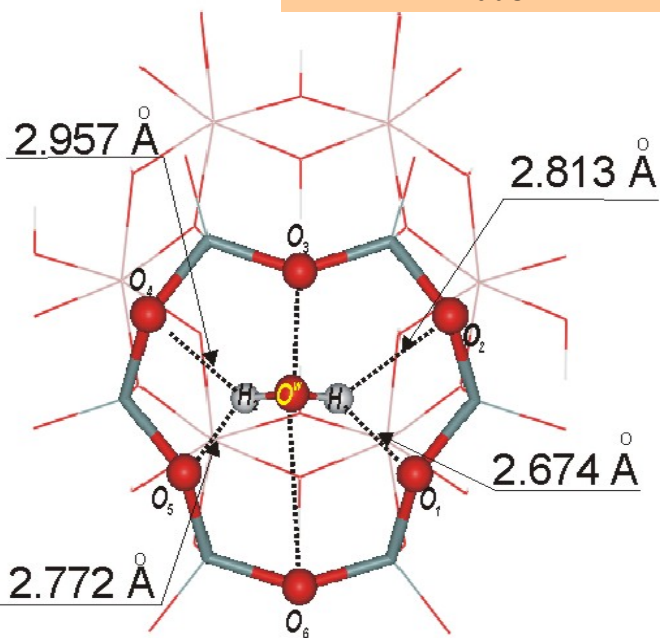
H₂O – tetrahedral surface of the kaolinite layer : H-bond structure

K(T)···water layer – MD (2ax2b)

K(T)···H₂O – static relaxation
(single molecule)

$$\Delta G_{\text{solv}}(\text{H}_2\text{O}) = -5.6 \text{ kcal/mol (PW91/SVP)}$$

$$U_{\text{ads}} = -3.6 \text{ kcal/mol (VASP)}$$



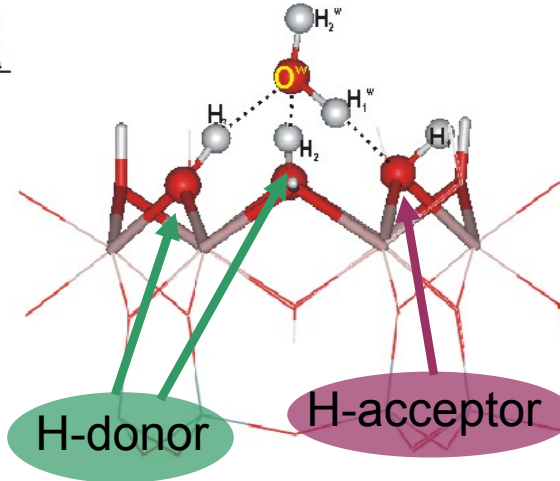
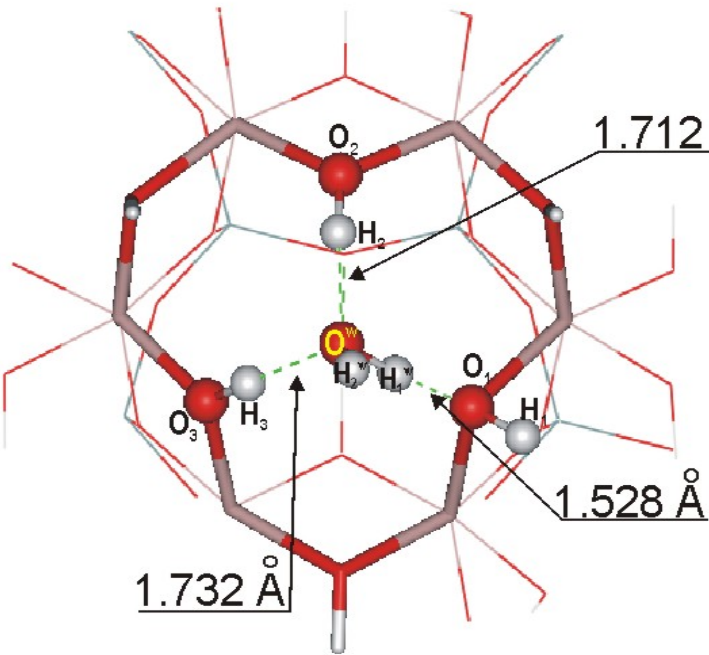
WEAK INTERACTION

H_2O – octahedral surface of the kaolinite layer : H-bond structure

$K(O)\cdots H_2O$ – static relaxation
(single molecule)

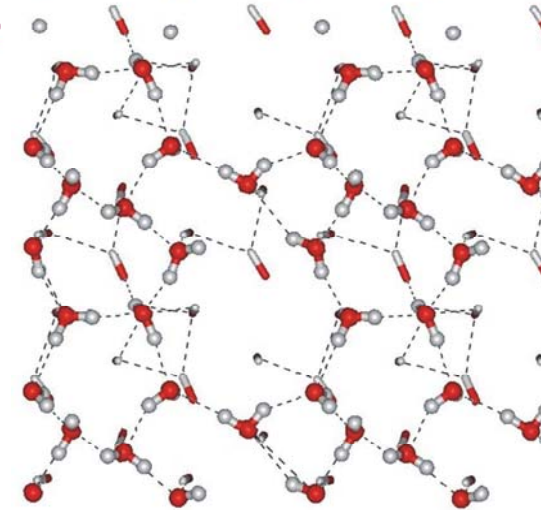
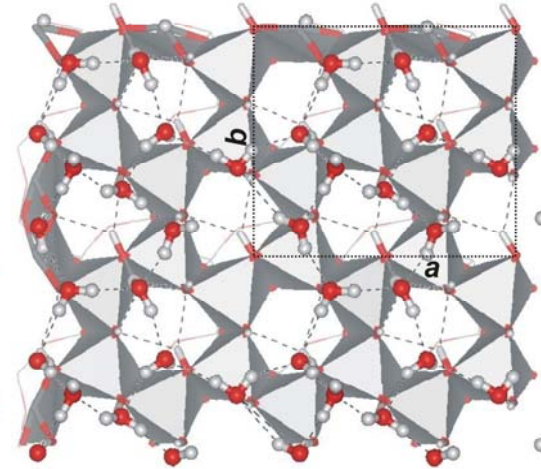
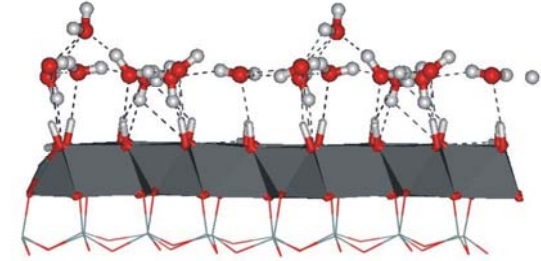
$$\Delta G_{\text{solv}}(H_2O) = -5.6 \text{ kcal/mol (PW91/SVP)}$$

$$U_{\text{ads}} = -10.3 \text{ kcal/mol (VASP)}$$



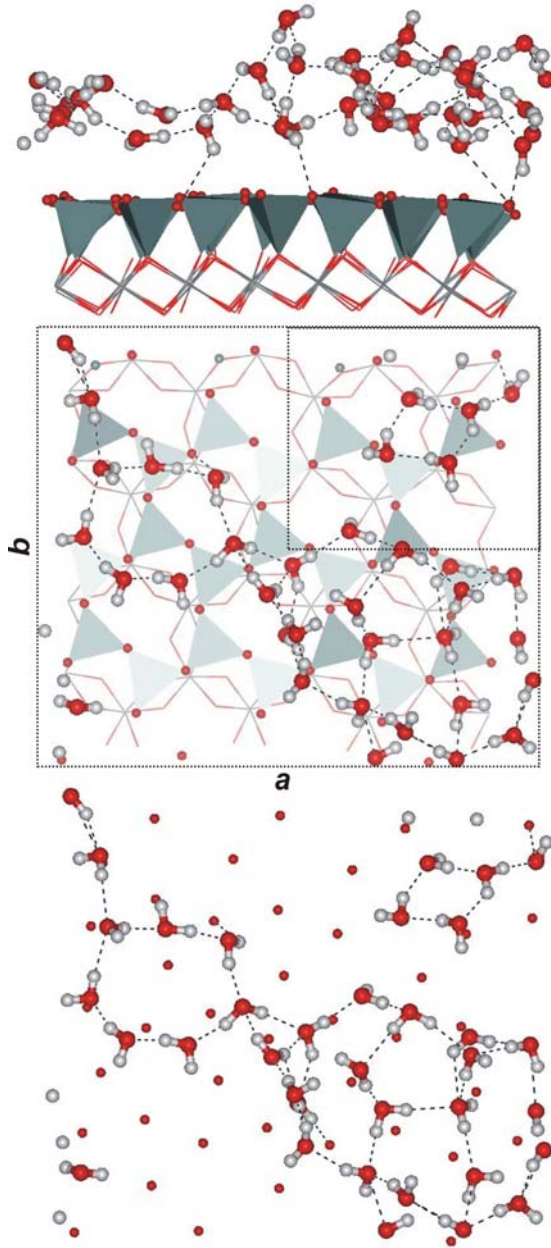
STRONG INTERACTION

$K(O)\cdots$ water layer – MD

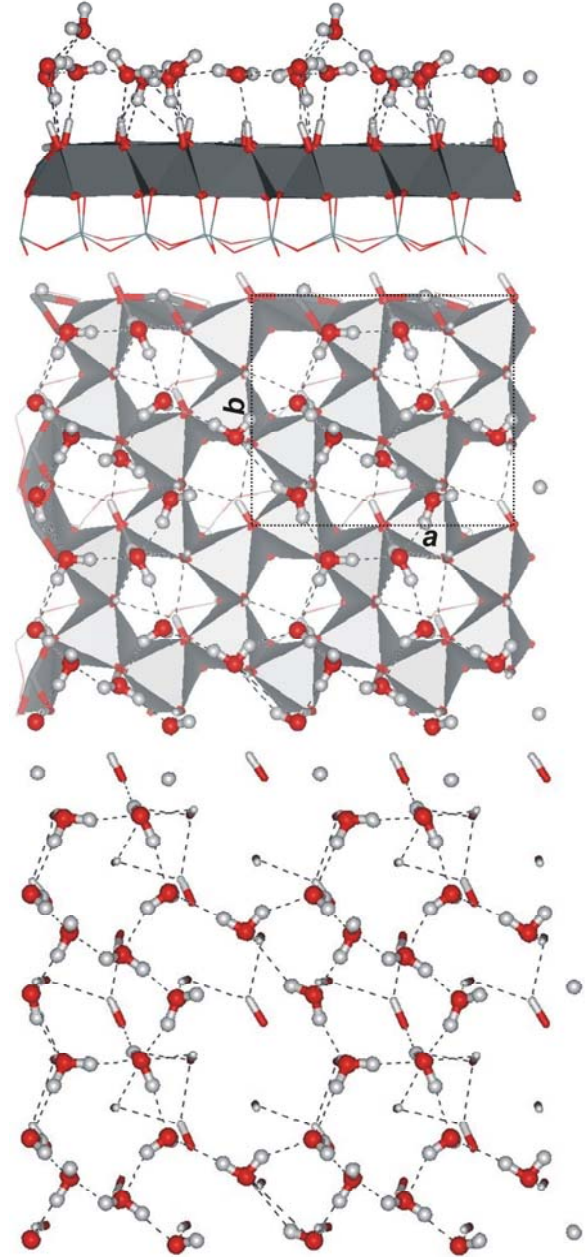


H_2O layer – both surfaces of the kaolinite layer : comparison

K(T)··water layer – MD (2ax2b)

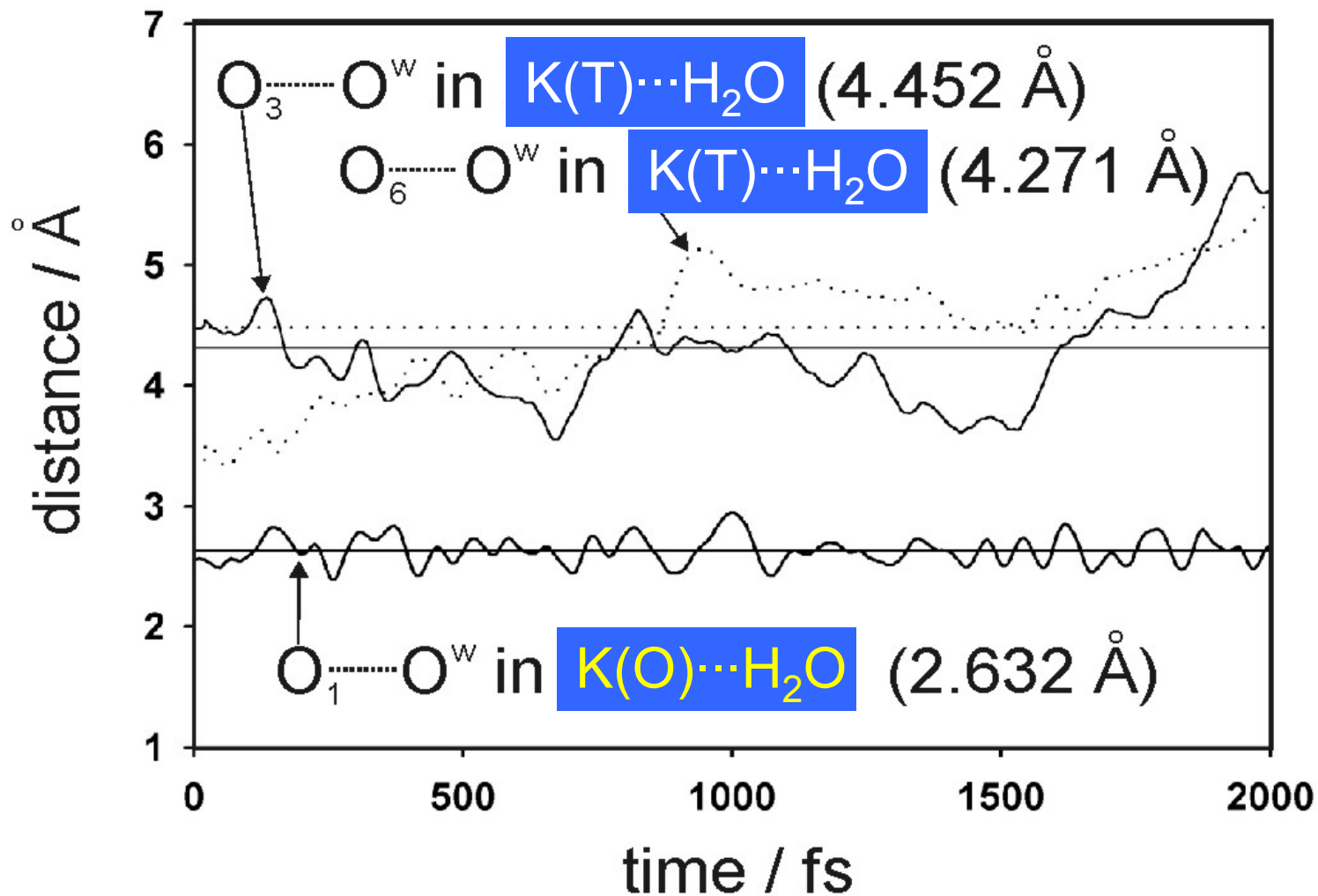


K(O)··water layer – MD



Temporal evolution of O...O distances in H-bonds

(single H₂O molecule – kaolinite surfaces: MD)



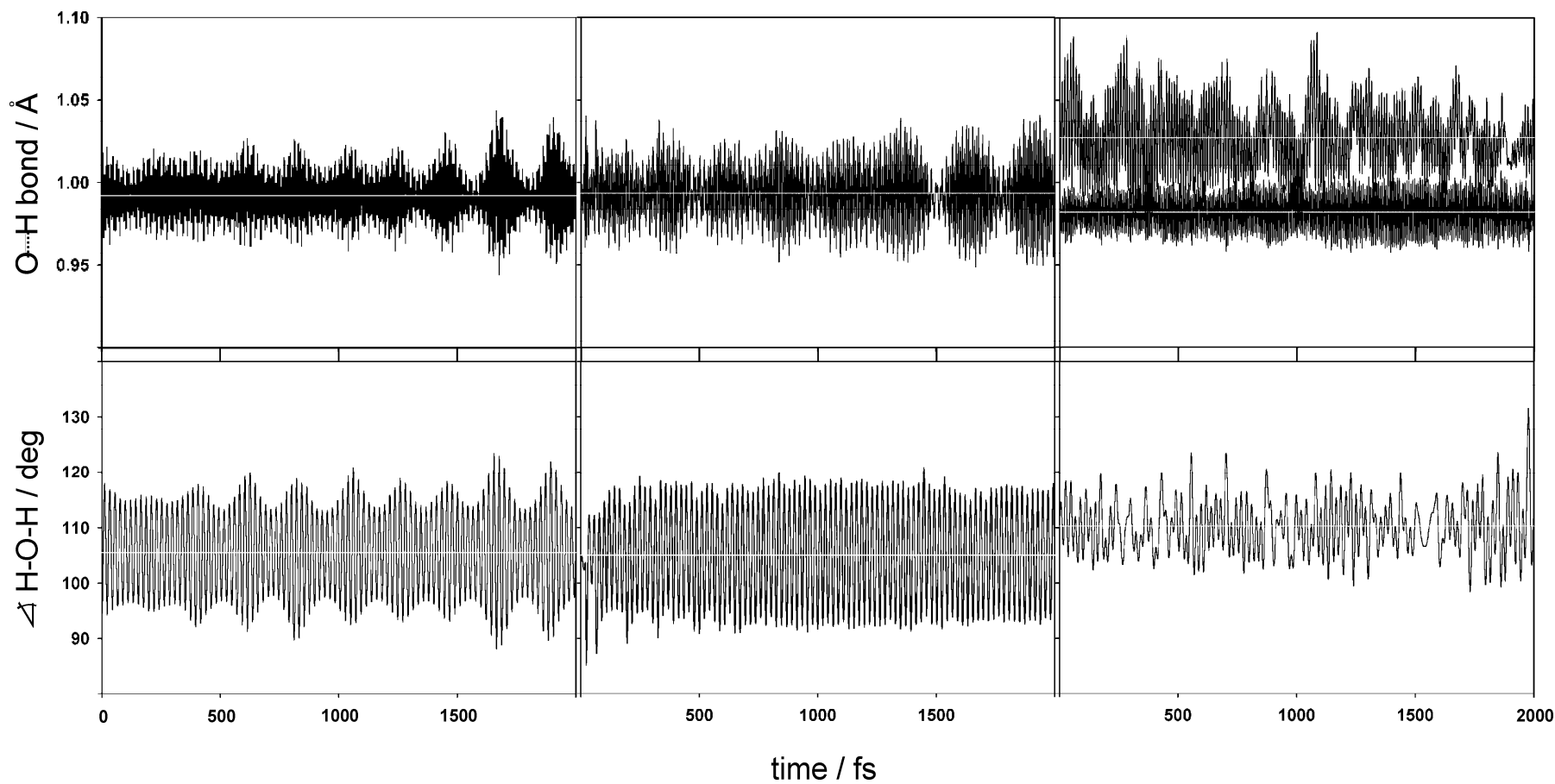
Temporal evolution of O-H bonds and H-O-H angle of H_2O

(single H_2O molecule on kaolinite surfaces: MD)

free H_2O

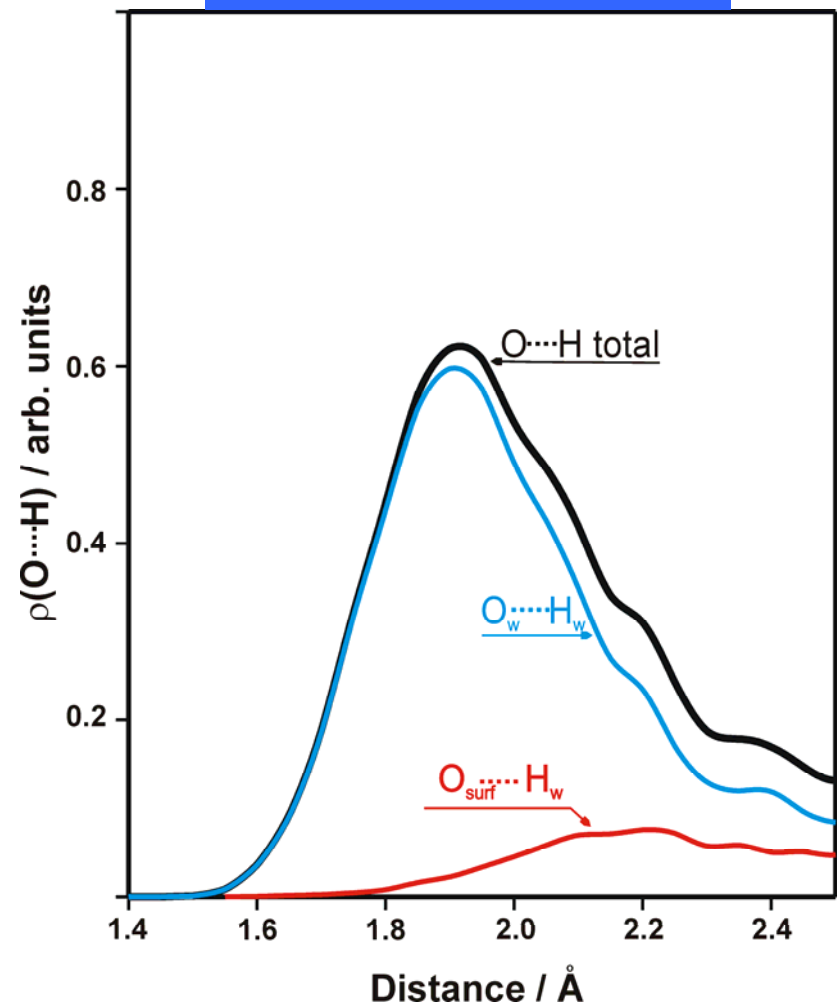
K(T)··· H_2O

K(O)··· H_2O

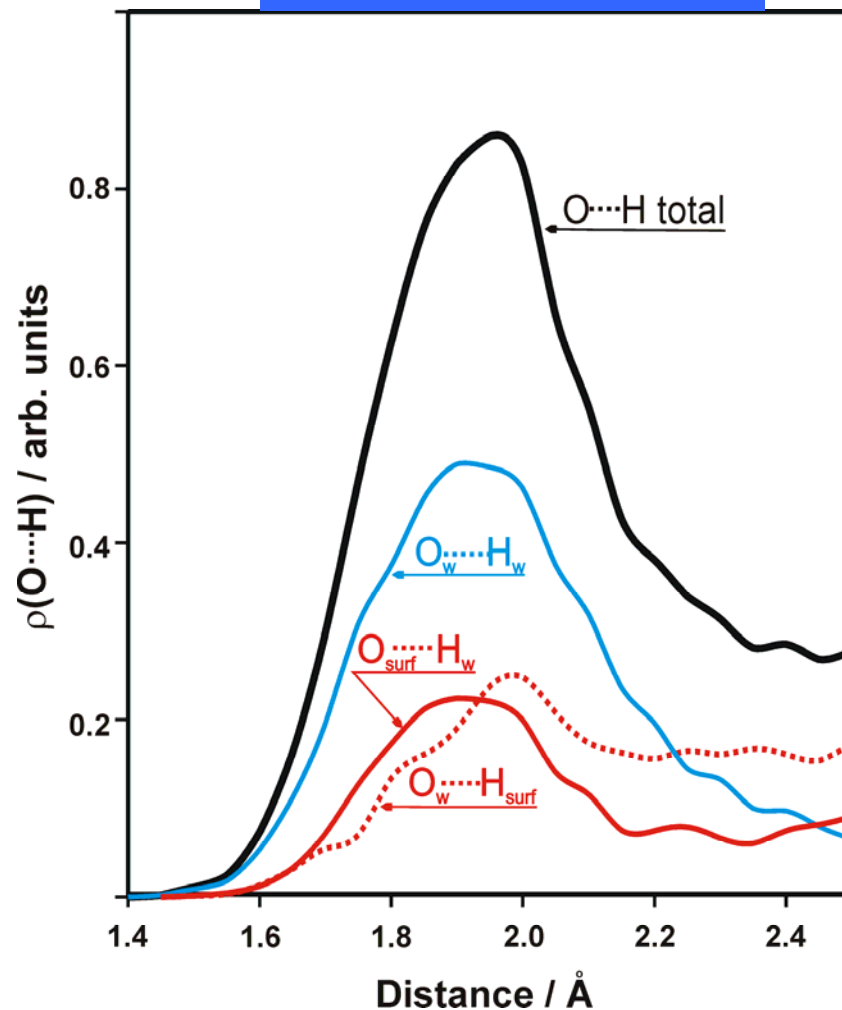


Distribution of H-bonds in kaolinite-water layer systems: MD

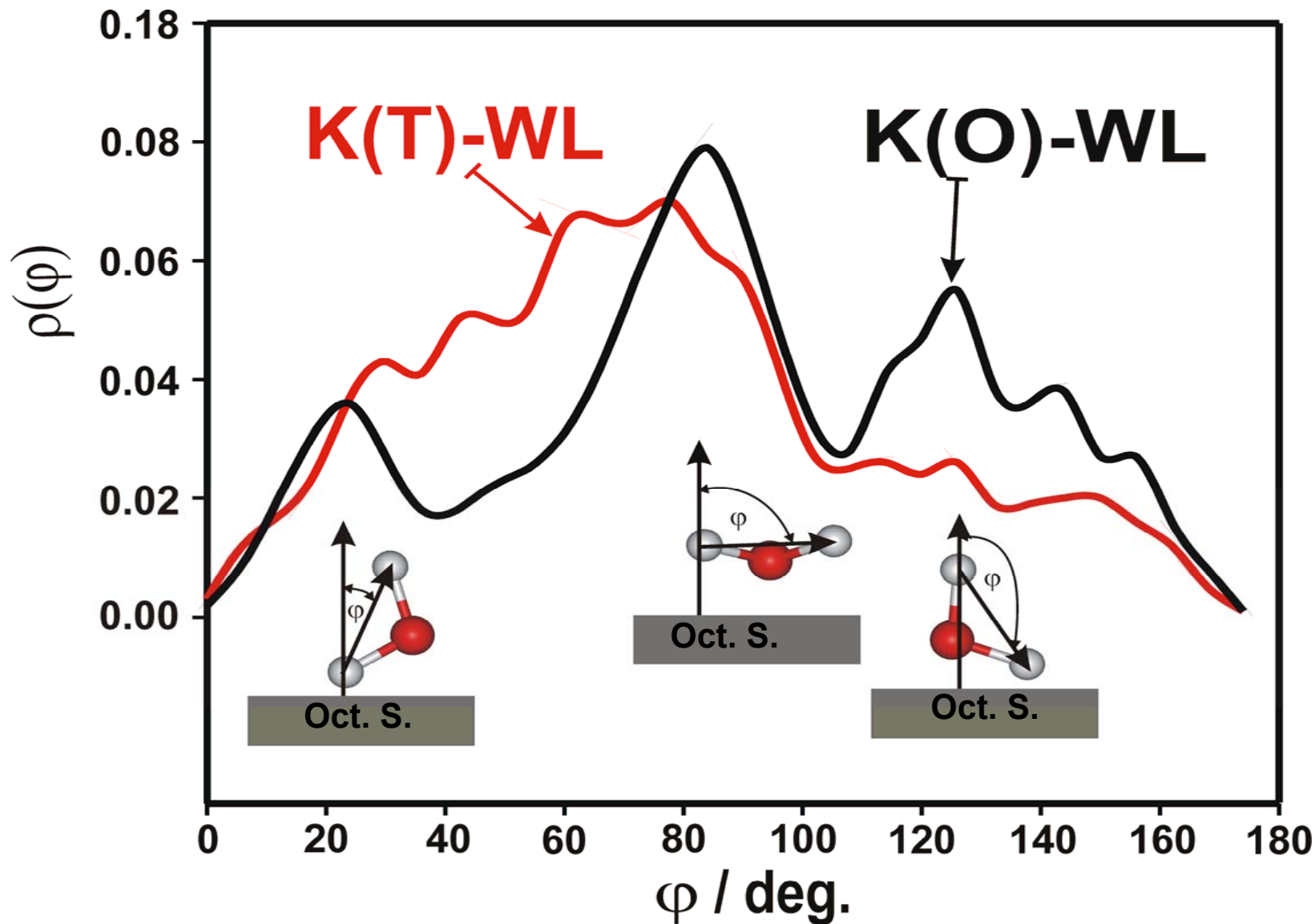
K(T)···water layer



K(O)···water layer

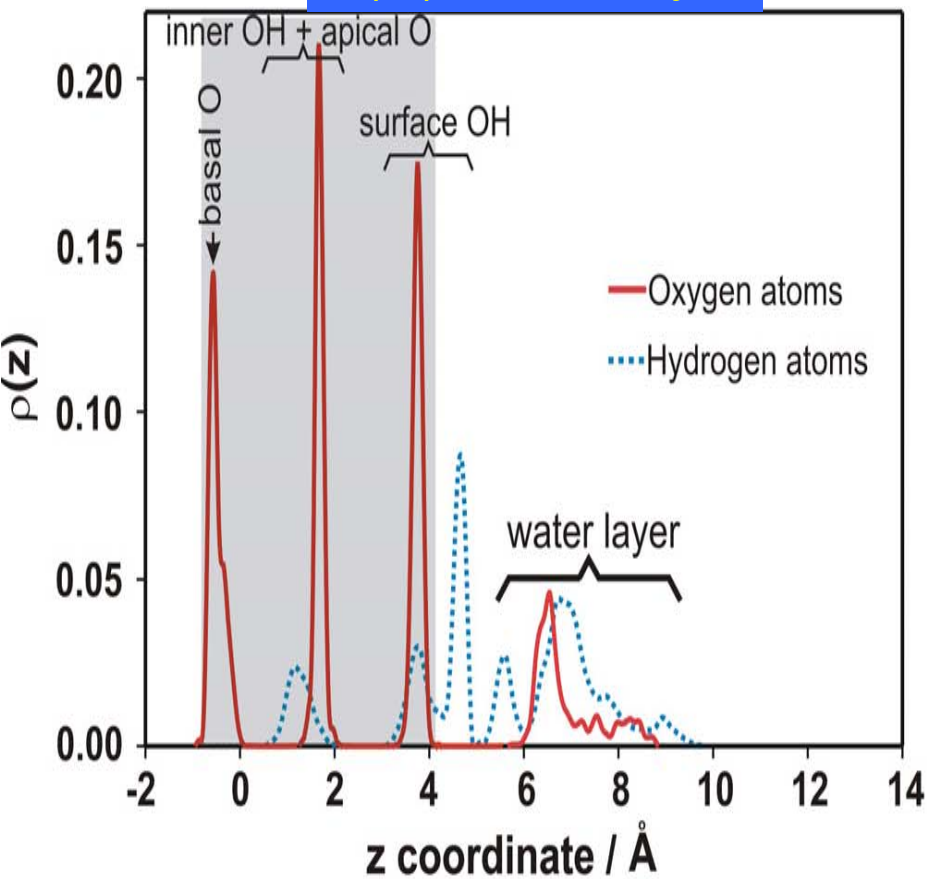


Distribution of the angle between the intraatomic HH vector and the z-coordinate: MD

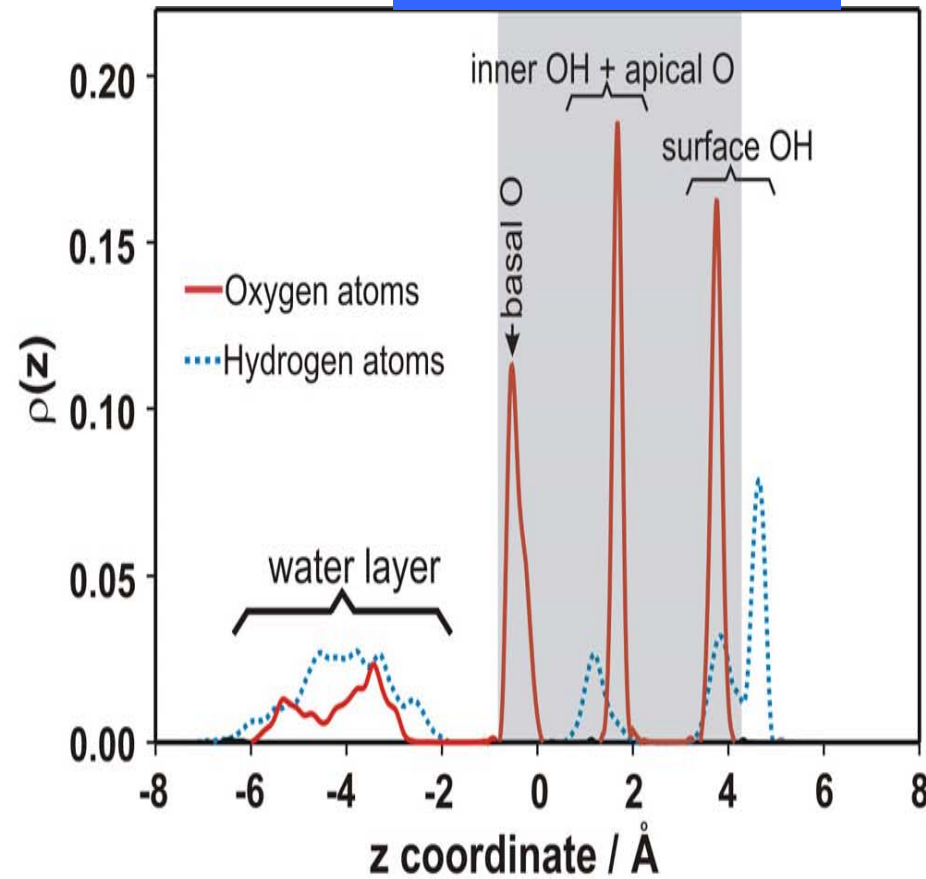


One-dimensional profiles of z-coordinate distributions of oxygen and hydrogen atoms: MD

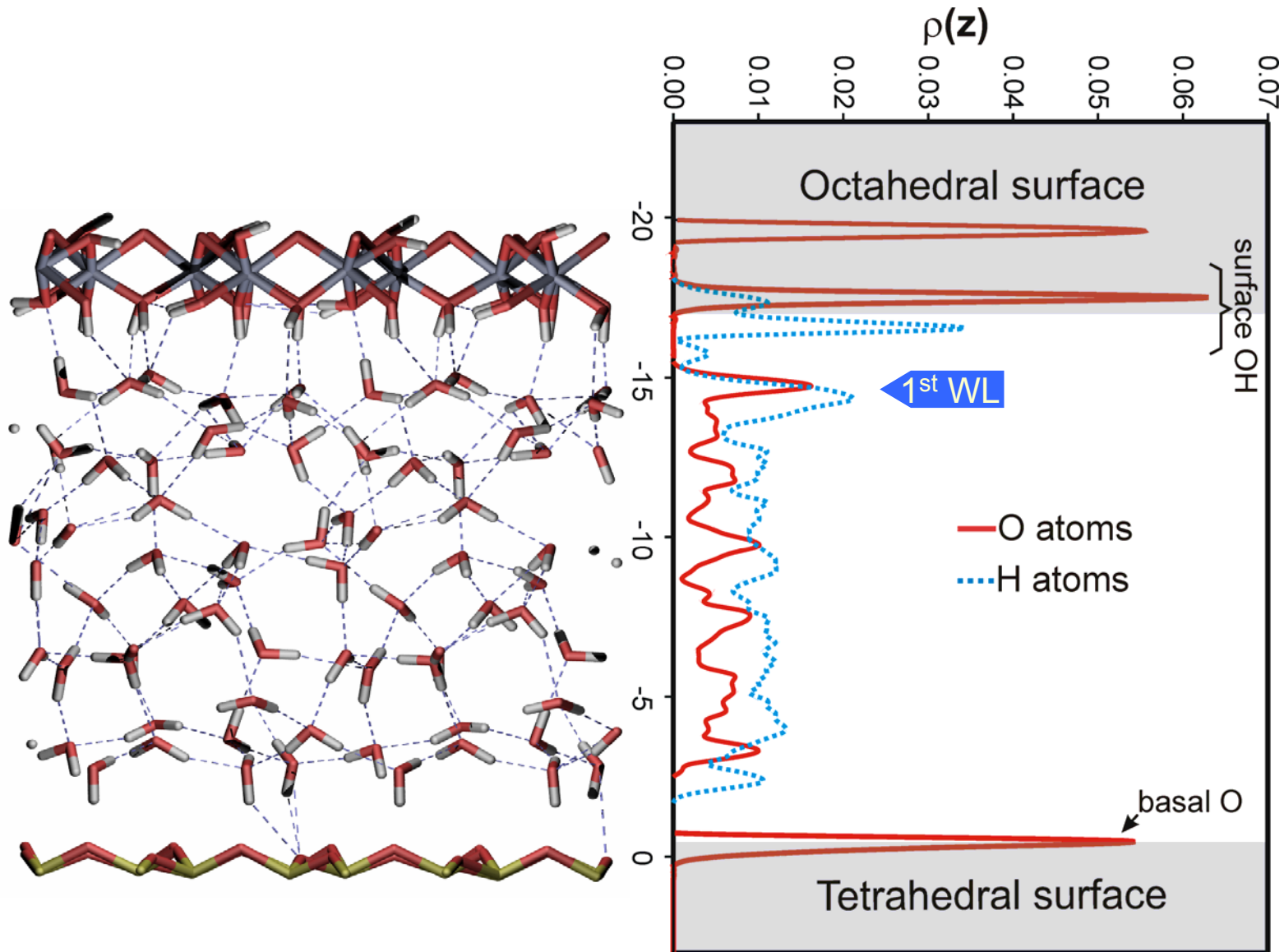
K(O)···water layer



K(T)···water layer



One-dimensional profiles of z-coordinate distributions of oxygen and hydrogen atoms – water slab: MD



Hydration energetics of kaolinite surfaces

$$\Delta E (\text{H}_2\text{O})_{\text{dimer}} = -5.6 \text{ kcal/mol (VASP,SR}^*); [-5.0 \text{ kcal/mol (MP2/TZVP)]$$

System	TET SURF.	OCT.SURF.	EDGE S.
1 H ₂ O (SR) ^a	-3.6	-10.3	
1 H ₂ O (MD) ^b	-0.8±0.5	-8.3±3.2	?
WLayer (MD) ^b	-8.3±0.4	-12.1±2.2	
WLayer (MD) ^{b,c}	-8.8±0.3 ^d	-13.5±0.3 ^e	
(energies are in kcal/mol)			

^a Static relaxation

$$\Delta U_{\text{H}} = \langle U(\text{N}) \rangle - (\langle U(0) \rangle + \text{N} \cdot \langle U(\text{H}_2\text{O}) \rangle) / \text{N}; \quad \text{N} = \text{No. H}_2\text{O}$$

^c CLAYFF: GCA 70 (2006), 562, ^d talc; ^e Al(OH)₃;

EXPERIMENTS: substantially diverse results!

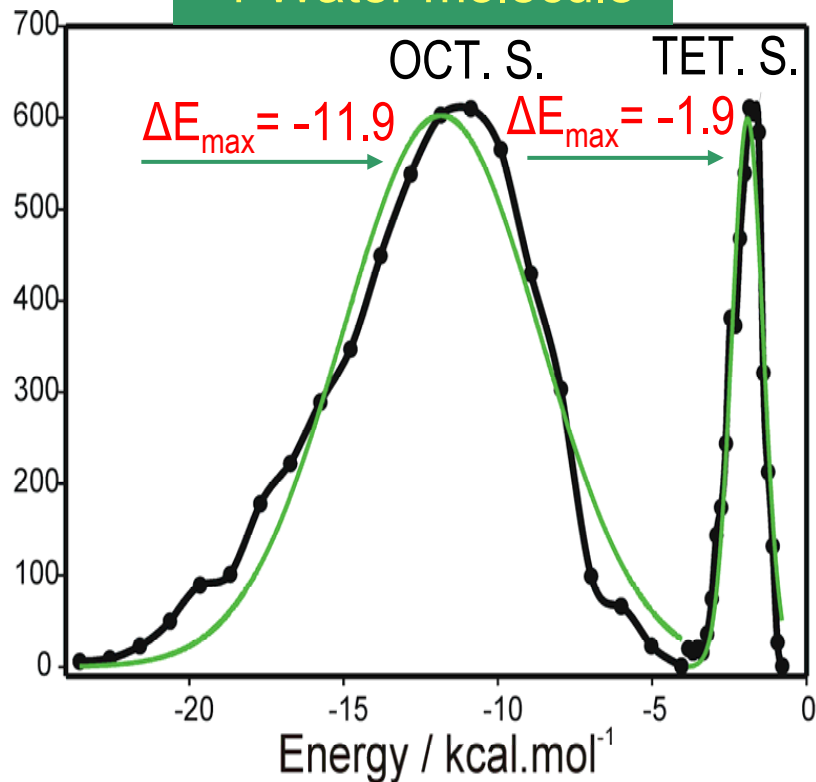
- 1) $\Delta H_{\text{hydr}} = -7.2 \text{ kcal/mol}$ (adsorption isotherm, calorimetry)
- 2) $-\Delta H_{\text{dehydr}} = -10.6 \text{ kcal/mol}$ (calorimetry)
- 3) $-\Delta H_{\text{dehydr}} = -4.1 \text{ kcal/mol}$ (desorp. isotherm)

Hydration energetics of kaolinite surfaces

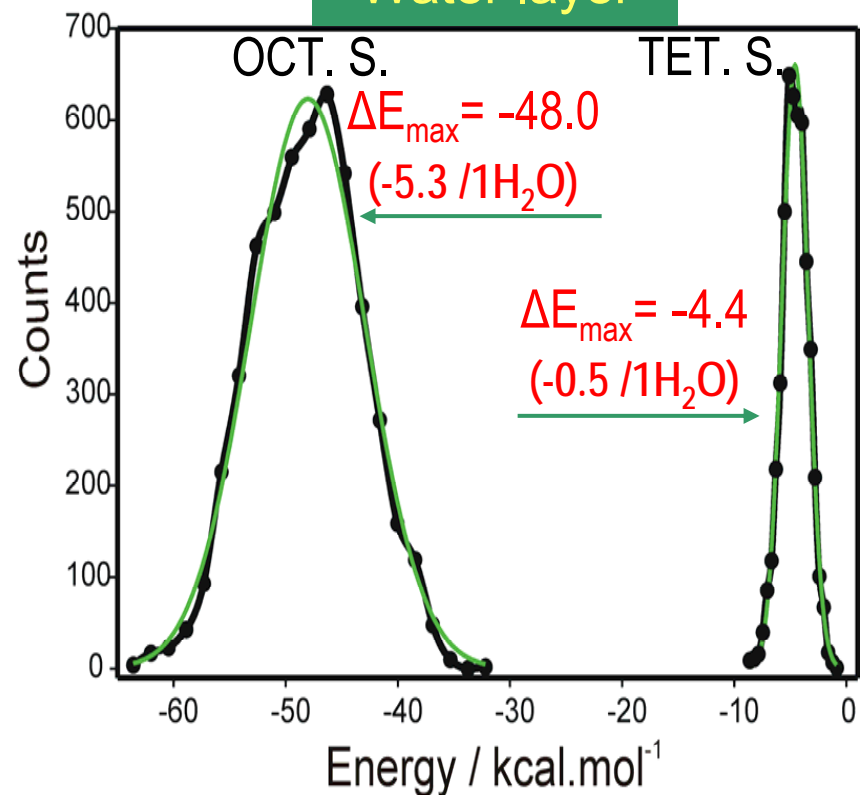
Distribution of interaction energy
calculated for 5000 MD configurations

$$\Delta E_i = E_i^{AB} - (E_i^{AB} + E_i^{AB})$$

1 Water molecule

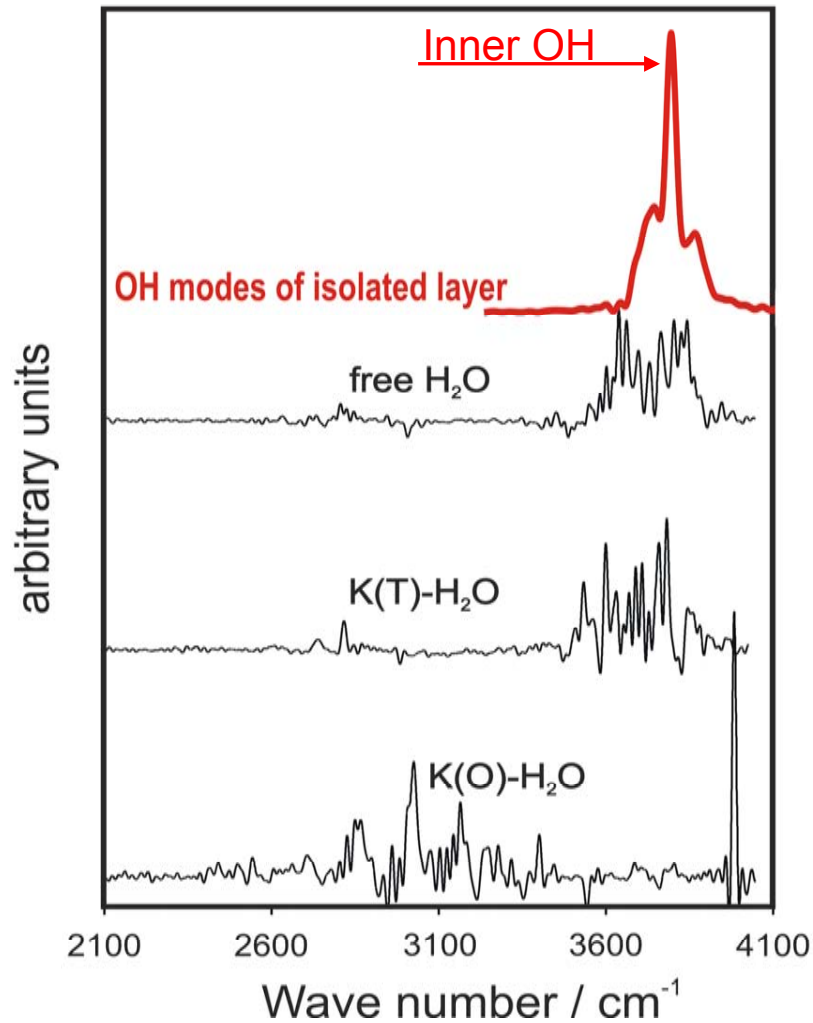


Water layer

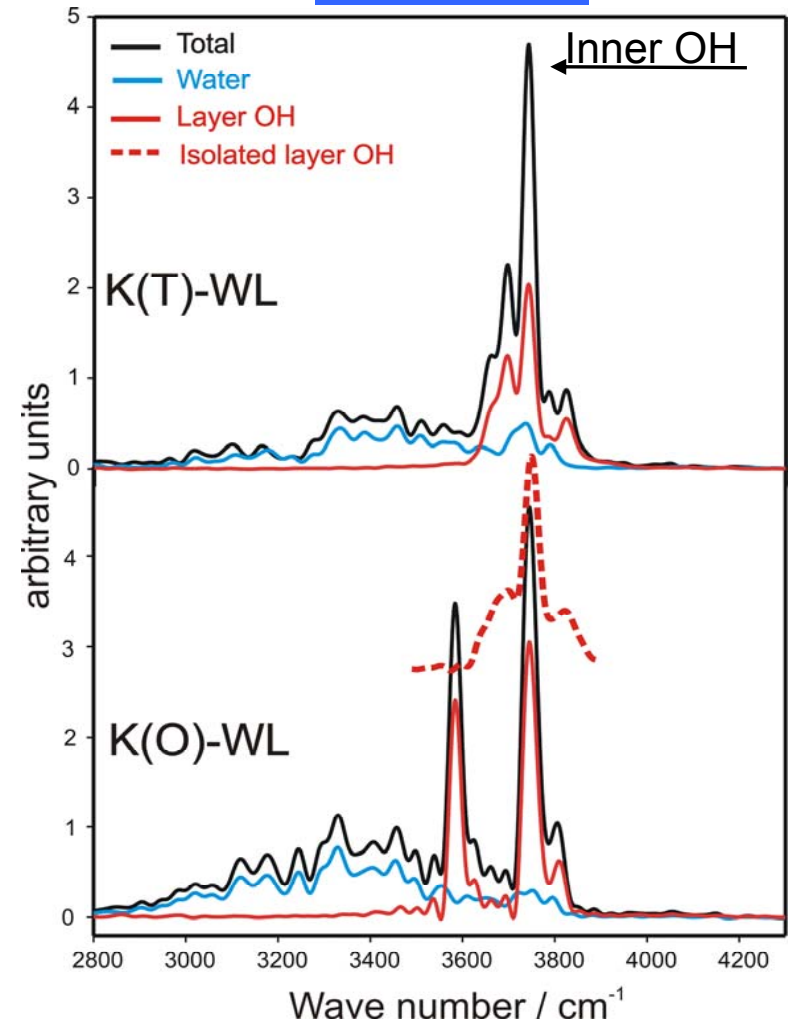


Proton dynamics – power spectra - OH stretching modes

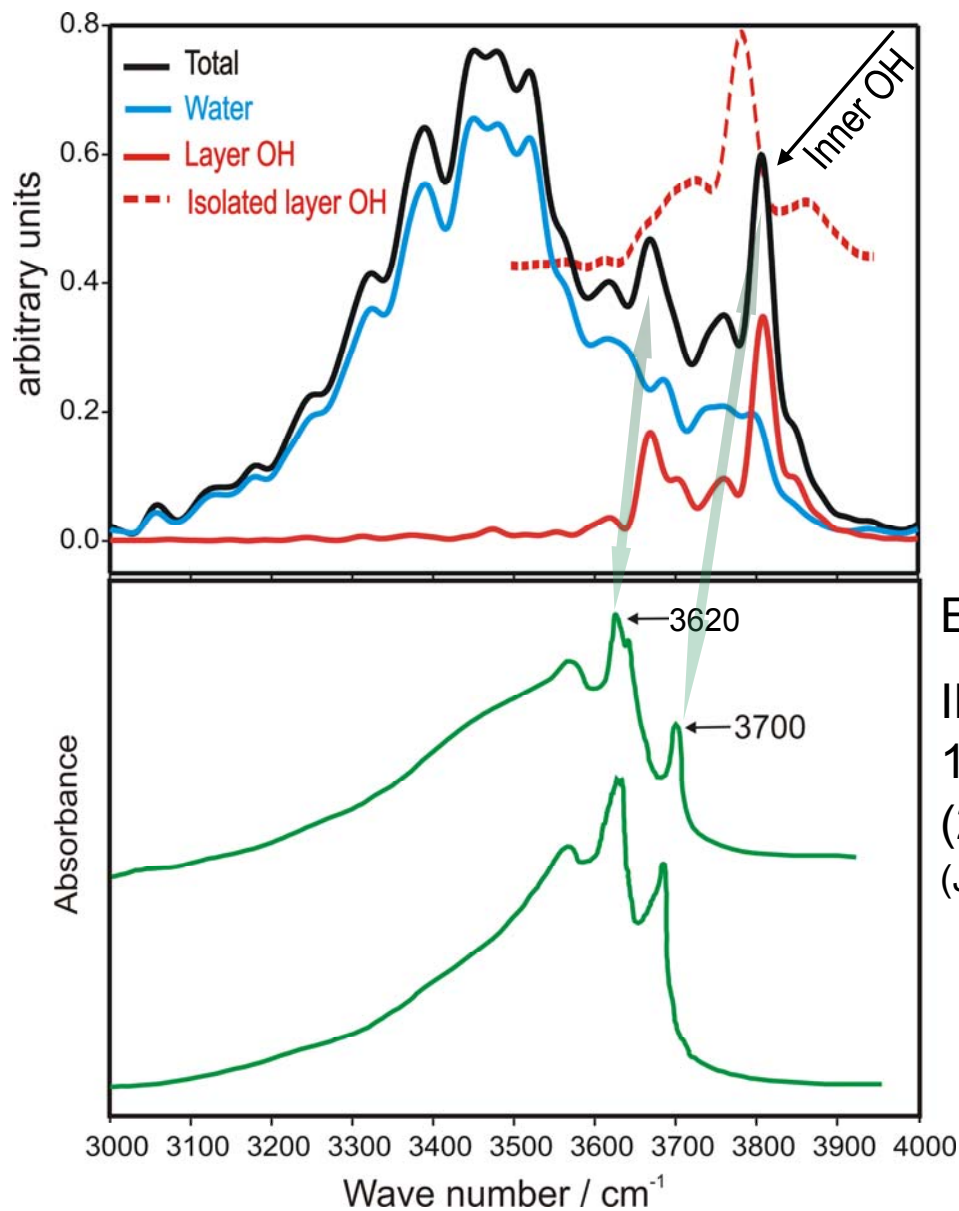
single H₂O molecule



water layer



Proton dynamics – power spectra – OH stretching modes



EXPERIMENT:

IR SPECTRA of hydrated
10 Å phase of kaolinite
(2 samples)

(J. Appl. Cryst. 33 (2000), 1075)

(001) surfaces of kaolinite layer - summary

Tetrahedral surface:

- **weak** interactions of polar molecules
- water layer – “clustering” – like in bulk (H-bonds) – weakly perturbed by layer
- **hydrophobic** tetrahedral surface
- **no adsorption** of polar molecules from polar solvent

Octahedral surface:

- Strong** interactions of polar molecules with the **octahedral** surface of kaolinite
dominant mechanism – formation of **hydrogen bonds**
- water layer – “regular” distribution affected by interactions with OH groups
 - strong mutual perturbation between water layer and OH groups
 - surface OH groups – very flexible, bifunctional character (**proton donors, proton acceptors**)
 - main contribution to the kaolinite hydration
 - **hydrophilic** surface