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Effects of Defect Doping on the Kaolinite (001) with H_2O Adsorption

Dr. Jian Zhao

State Key Laboratory of Geomechanics and Deep Underground Engineering

China University of Mining and Technology, Beijing

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SUBJECTS

- **Introduction**
- **Structure of kaolinite in clay minerals**
- **Mechanism of adsorption of H_2O on kaolinite**
- **Effects of defects on kaolinite with H_2O adsorption**
- **Conclusions**

Large-deformation damage of soft rock

Roof falling
50% clay minerals

Deformation of roof and sides
90% clay minerals

Floor heaving of the deep roadways
50% clay minerals

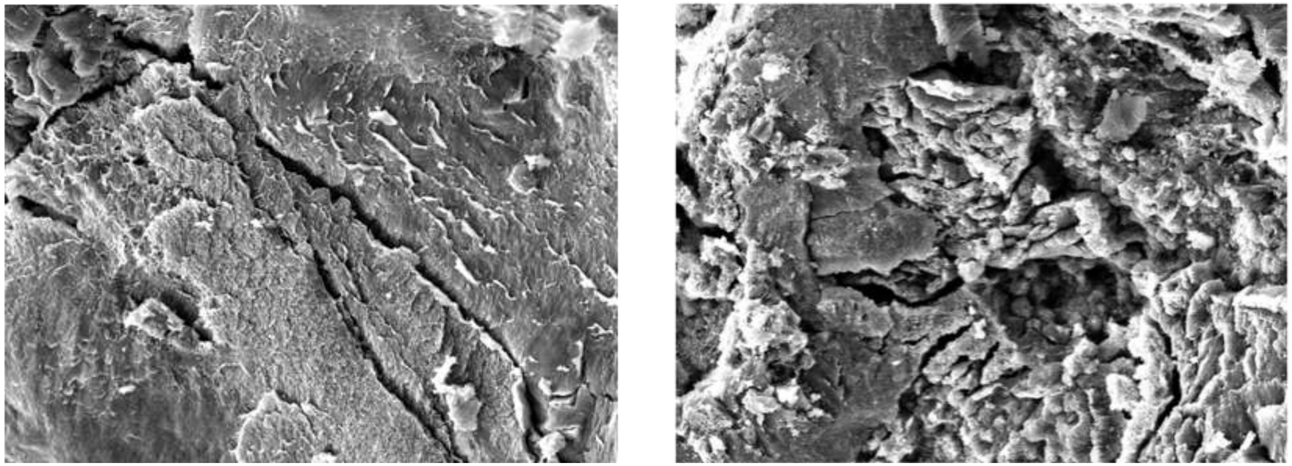
Failures of the supported systems
90% clay minerals

INTRODUCTION

- **Dealing with large-scale deformations in soft-rock tunnels is a very important issue in soft-rock tunnel engineering.**

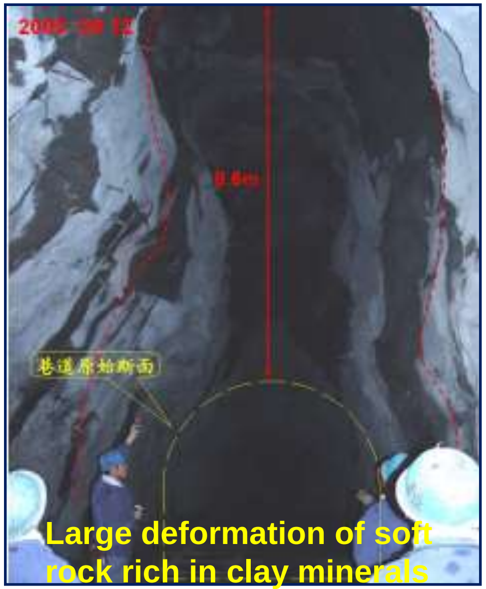
- **The mechanism of this large-scale deformation is closely related to the interaction of water molecules with soft rocks rich in clay minerals.**

- **In the last few decades, considerable amount of experimental efforts have been devoted to the mechanism of deformation of soft rock.**



SEM image of mudstone before and after water adsorption

Introduction

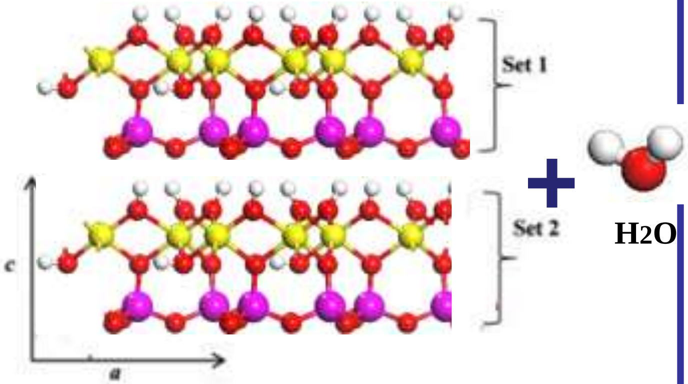


Large deformation of soft rock rich in clay minerals

Closely related interaction between clay minerals and water

microscopic mechanism of interaction between water and clay minerals are not well understood yet

Kaolinite and montmorillonite are most abundant clay minerals



Kaolinite
$(Al_4[Si_4O_{10}](OH)_8)$

★ **In order to gain a better predictive understanding of the governing principles associated with large-scale deformation of clay minerals, the microscopic mechanism of interaction of water with kaolinite was investigated.**

Calculation Methods

The interaction of water with solid surfaces：

The interaction of water with solid surfaces: Fundamental aspects

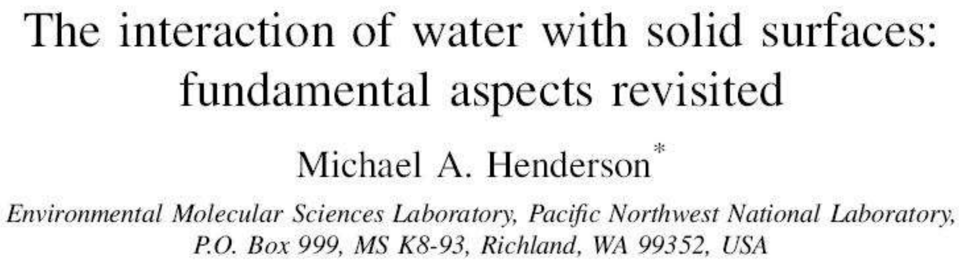
Patricia A. Thiel*

Department of Chemistry and Ames Laboratory, Iowa State University, Ames, IA 50011, USA

Theodore E. Madey

Surface Science Division, National Bureau of Standards, Gaithersburg, MD 20899, USA

Surf. Sci. Rep. **7**, 211 (1987)

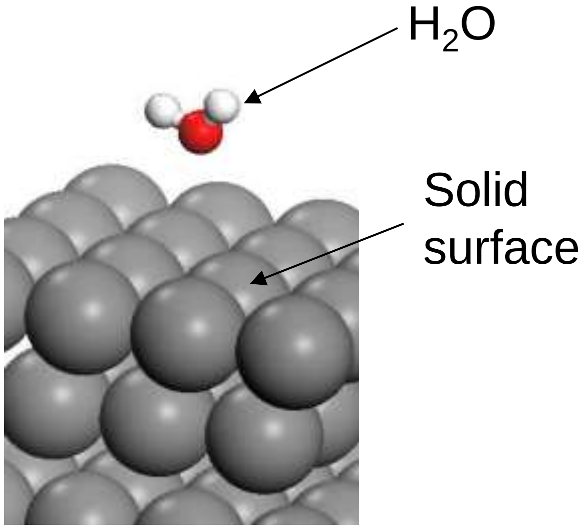


The interaction of water with solid surfaces:
fundamental aspects revisited

Michael A. Henderson*

Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory,
P.O. Box 999, MS K8-93, Richland, WA 99352, USA

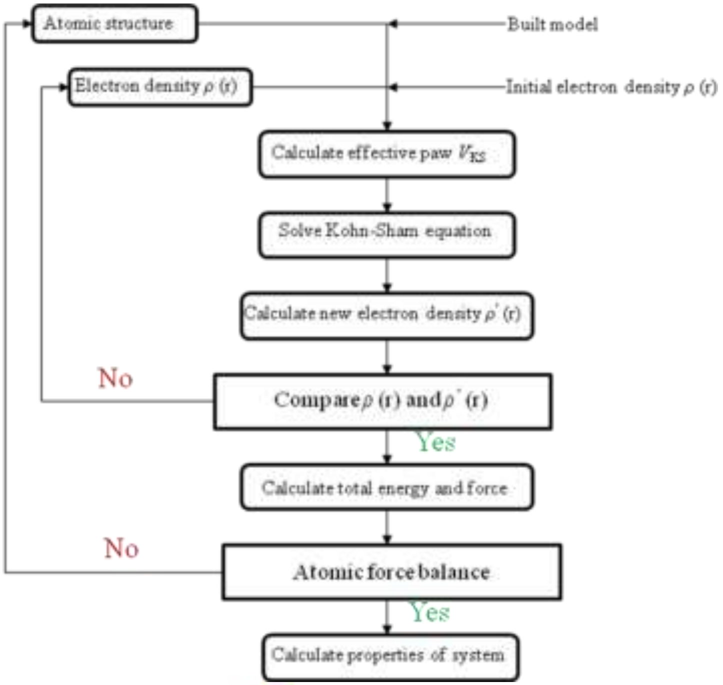
Surf. Sci. Rep. **46**, 1 (2002)



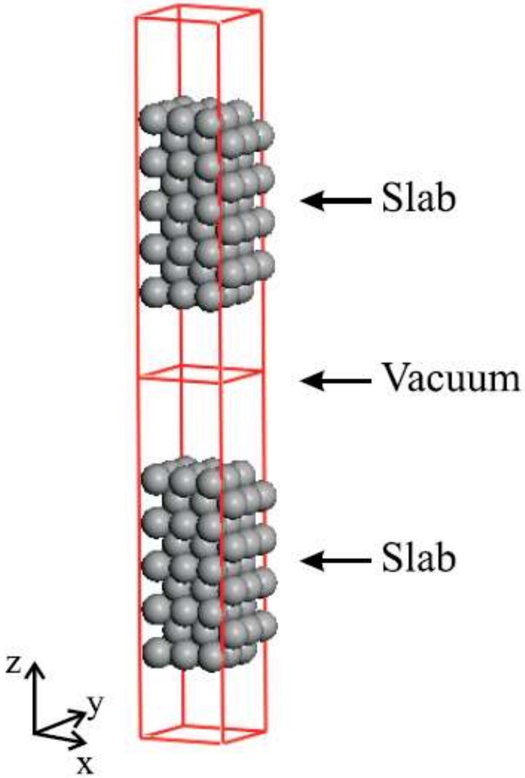
Computer simulation (Vienna Abinitio Simulation Package referred to as VASP) based on the density-functional theory (DFT) has been proven to be a powerful and reliable tool to study water-solid interfaces at the molecular level.

Calculation Methods

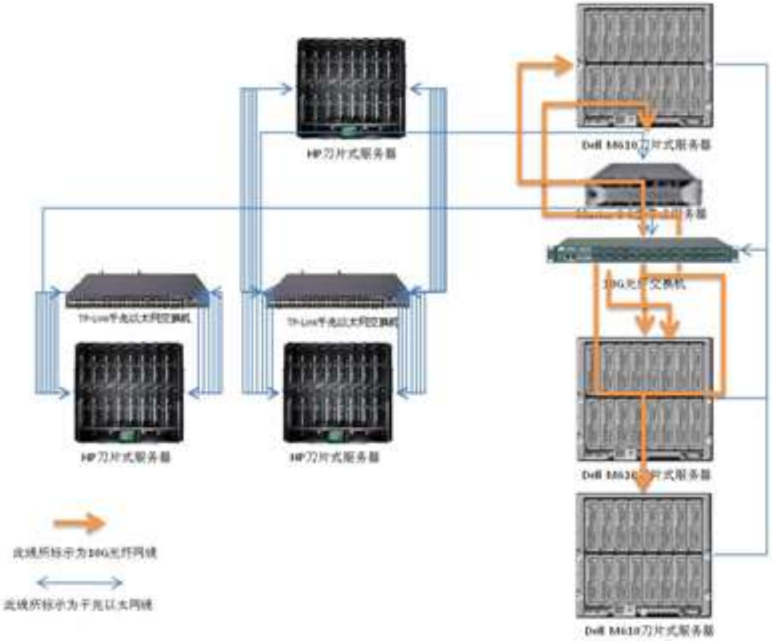
The calculation steps of first principle calculation methods:



Slab model



Calculation Condition



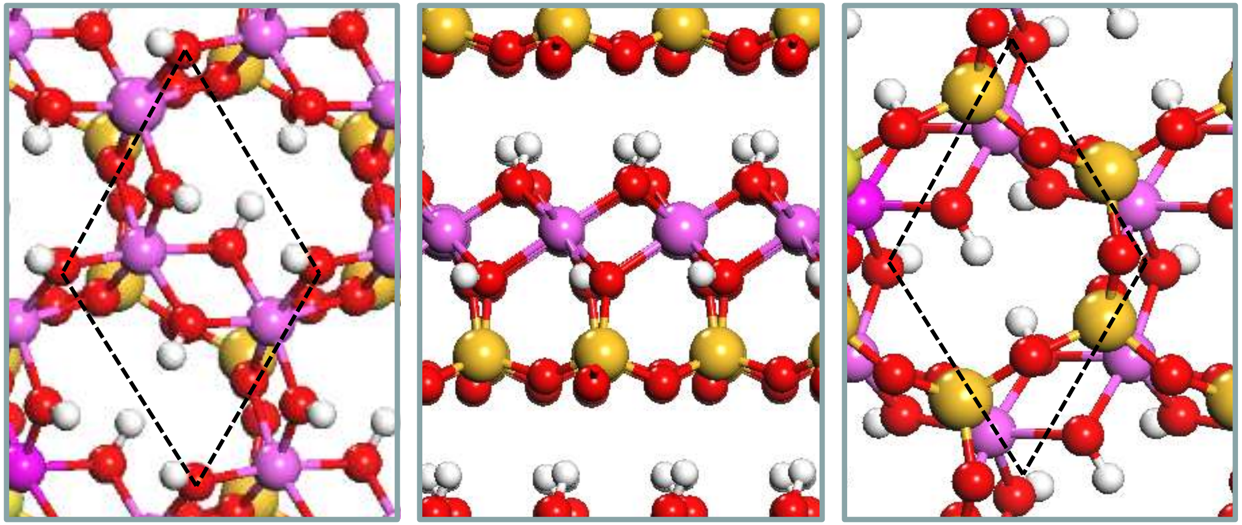
Basic parameters of the High-performance computing cluster

Dell blade server (128)

Linux and Windows operating systems

A top speed of 30.7 trillion math operations per second

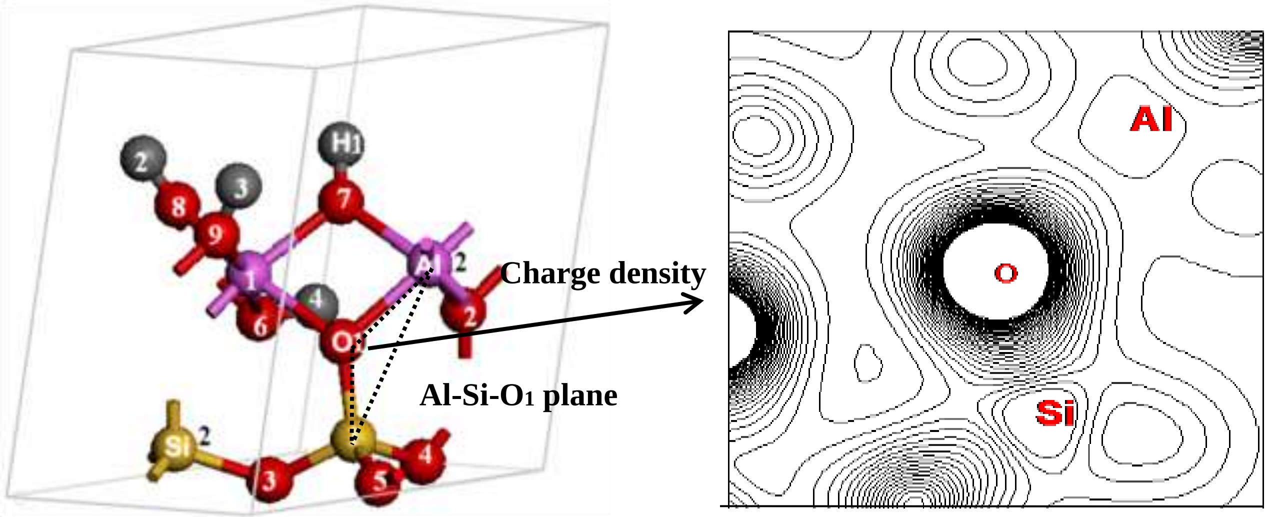
Atomic and electronic structure of kaolinite



Unit cell of kaolinite $Al_2Si_2O_9H_4$ containing 17 atoms

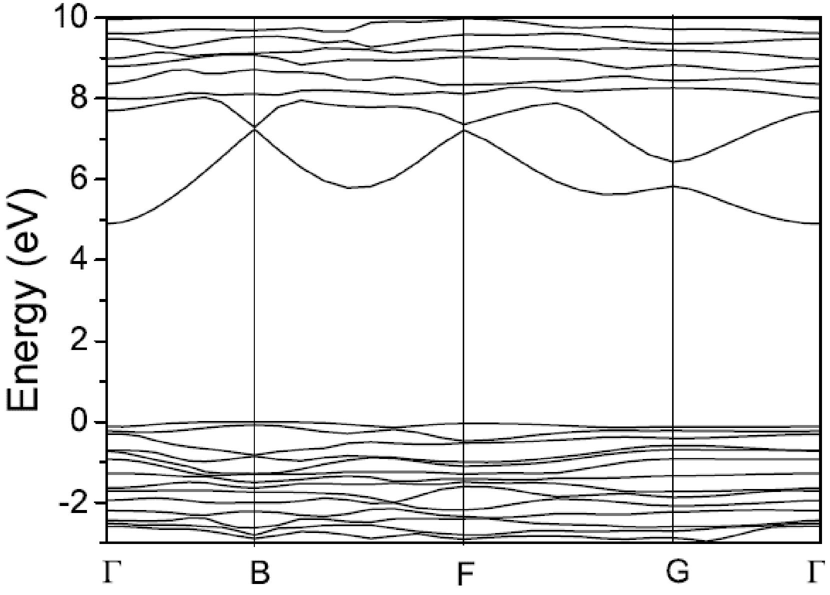
Parameters	Calculated	Experimental	Different radio%
a	5.160 Ǻ	5.155 Ǻ	0.9
b	5.160 Ǻ	5.155 Ǻ	0.9
c	7.602 Ǻ	7.405 Ǻ	2.5
α	81°	75.14°	7.2
β	89°	84.12°	5.4
γ	60.18º	60.18°	0

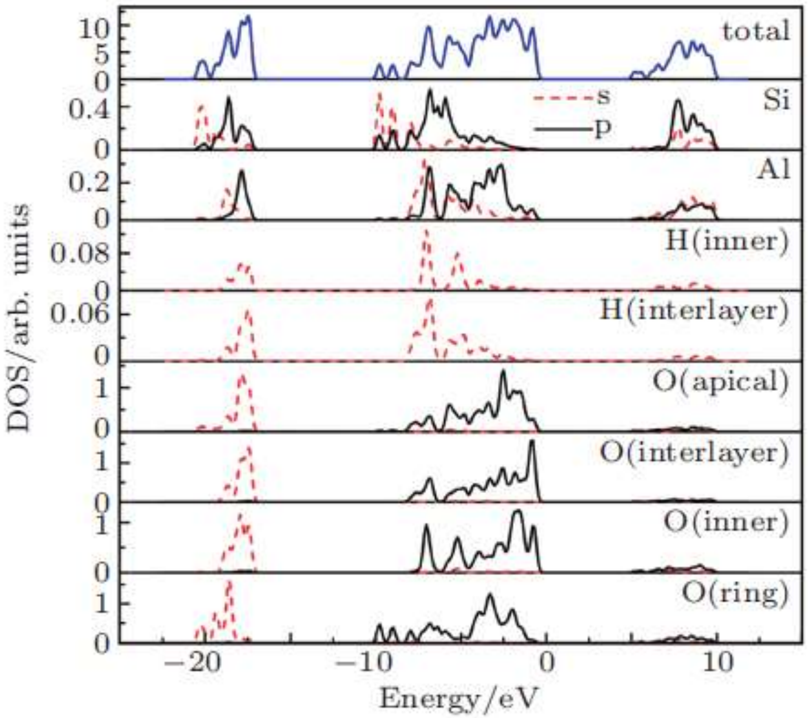
Atomic and electronic structure of kaolinite



Bonds	distances(Å)	Bonds	distances(Å)
Si1-O1	1.607	Si2-O2	1.609
Si1-O3	1.630	Si2-O3	1.634
Si1-O4	1.608	Si2-O4	1.609
Si1-O5	1.635	Si2-O5	1.630
Al1-O1	1.957	Al2-O1	1.970
Al1-O2	1.970	Al2-O2	1.954
Al1-O6	1.908	Al2-O6	1.906
Al1-O7	1.864	Al2-O7	1.874
Al1-O8	1.869	Al2-O8	1.870
Al1-O9	1.869	Al2-O9	1.868
H1-O7	0.987	H3-O9	0.981
H2-O8	0.987	H4-O6	0.981

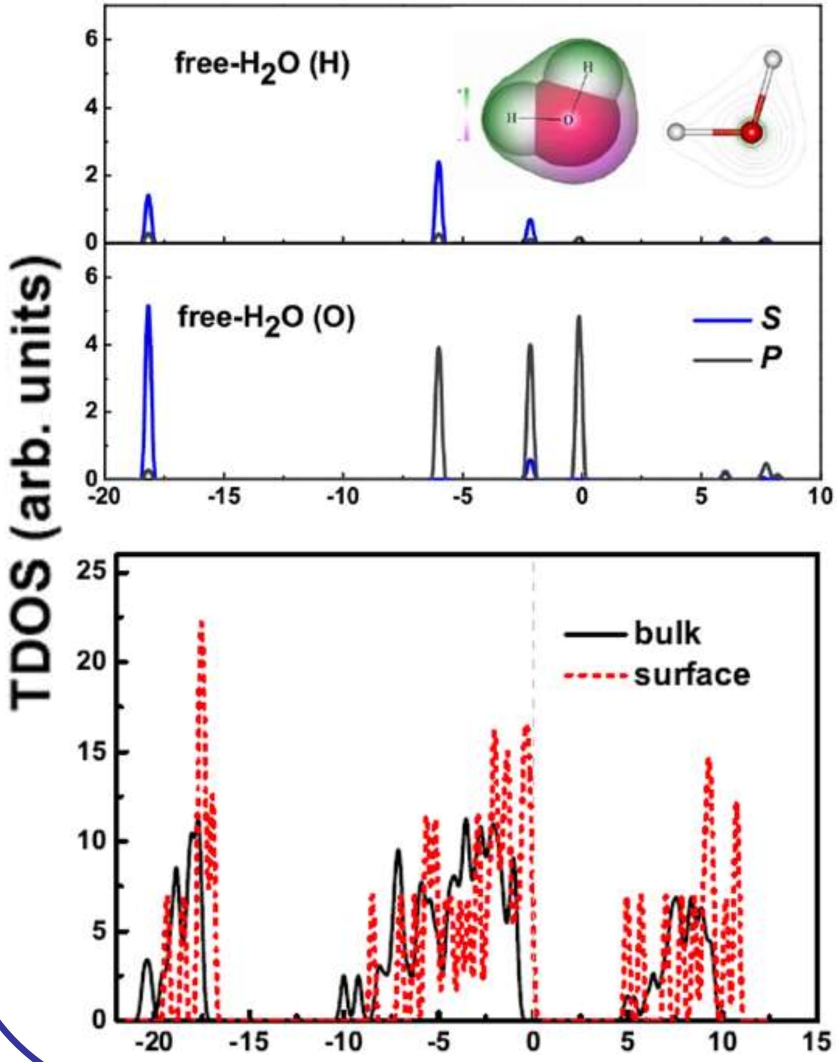
Atomic and electronic structure of kaolinite





- ●Band structure of kaolinite along the highsymmetry lines of the Brillouin zone. The Fermi energy is set at zero. The kaolinite has an indirect band gap with a gap width of 4.89 eV.
- ●The PDOS of the different kinds of oxygen atoms are similar to each other. This similarity is due to the high ionicity of the oxygen.

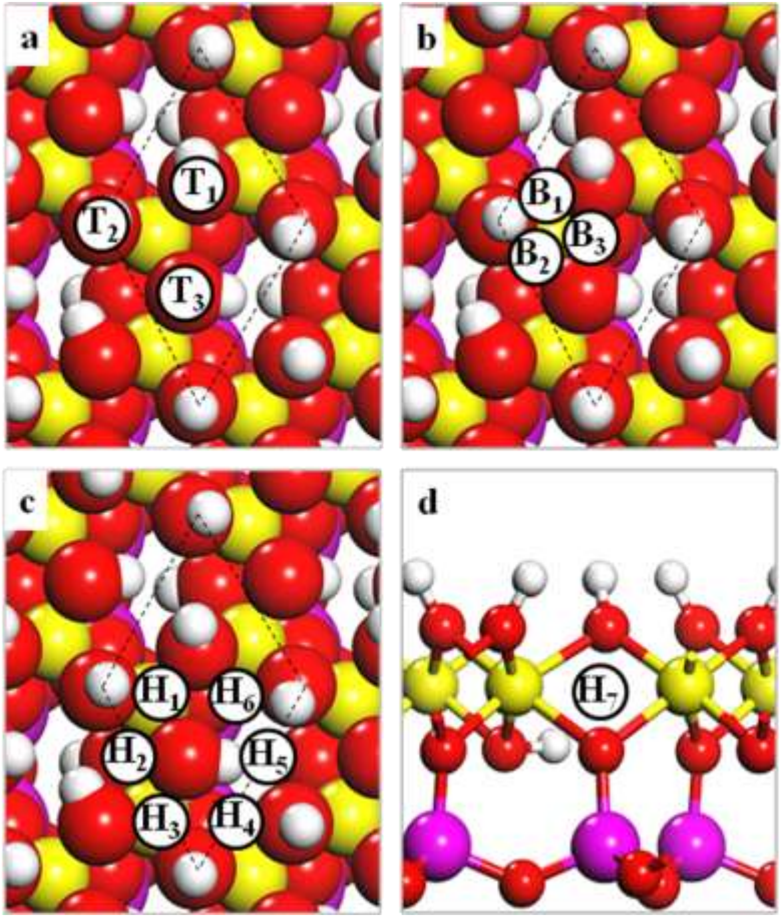
Mechanism of interaction between kaolinite and water molecules



•The bond length and the HOH internal angle of a free H_2O molecule are 0.97Å and 104.6^O, respectively.

• It is clear that the distribution form of the total DOS is similar for the bulk and surface kaolinite. This means that our constructed surface keeps the basic properties with the bulk kaolinite.

Adsorption of H_2O on the kaolinite(001)



- **We consider the four kinds of high-symmetry adsorption sites for H_2O including on-surface (three one-fold top sites (T_1-T_3), three twofold bridge sites (B_1-B_3), and six threefold hollow sites (H_1-H_6) and Al-surface (one six-fold hollow site H_7) of kaolinite.**

- **Adsorption energy of the adsorbed H_2O molecule on kaolinite substrate：**

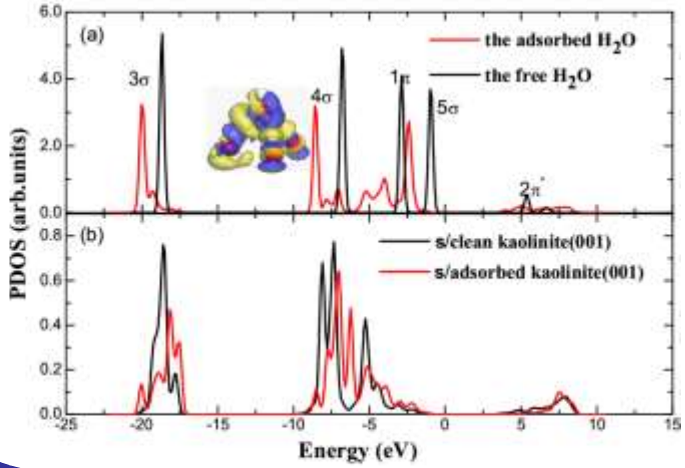
$$E_{ad} = E_{H_2O/kao(001)} - E_{H_2O} - E_{kao(001)}$$

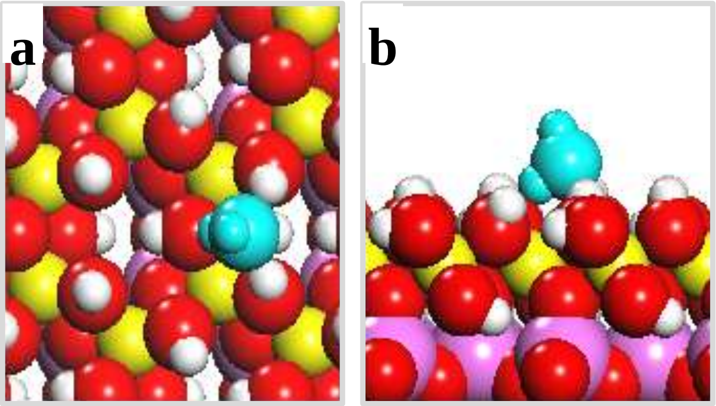
Adsorption of H_2O on the kaolinite(001)

- The calculated energetics and geometries for the monomer adsorption on six hollow adsorption sites of kaolinite (001)

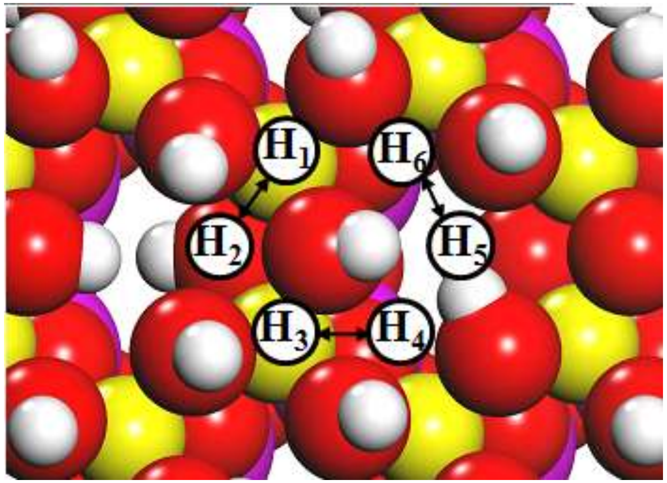
Site	E_{ads} (eV)	$d_{\mathrm{O-H_1}}$ Å	$d_{\mathrm{O-H_2}}$ Å	∠HOH(deg)
H_2O	-	0.97	0.97	104.6
H_1	1.15	0.97	1.04	109.6
H_2	1.07	0.97	1.03	109.9
H_3	1.07	0.97	1.03	110.1
H_4	1.06	0.97	1.03	110.5
H_5	1.10	0.97	1.03	111.2
H_6	1.06	0.97	1.03	110.5

●It is found that the preferred adsorption sites on the kaolinite(001) surface for H2O are the threefold hollow sites.



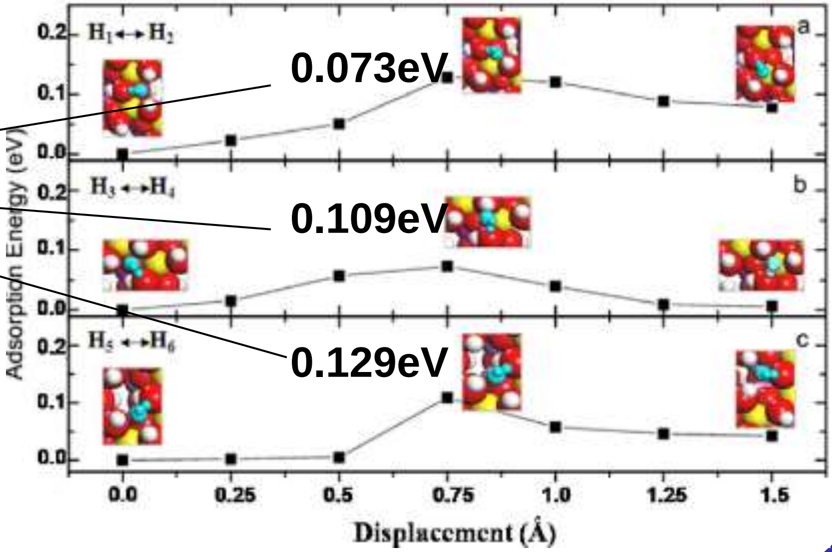


Diffusion of H_2O on the kaolinite(001)



Given a H_2O monomer at a hollow site we then investigate how it would negotiate its way across the (001) surface. Since we find that H_2O does not adsorb at atop and bridge sites, only diffusion energetics between hollow and adjacent hollow sites is examined.

It is clear therefore that the three diffusion paths encounter slightly different activation barriers.



0.073eV

0.109eV

0.129eV

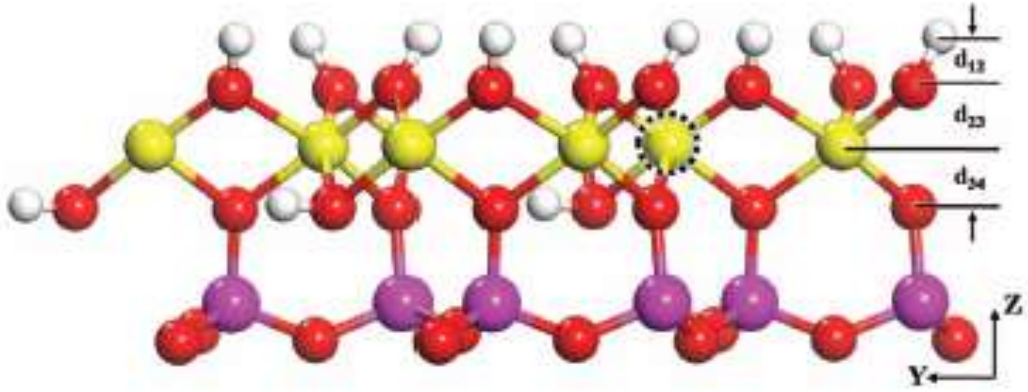
Dissociation of H_2O on kaolinite(001)

- **Our simulation proves that no dissociation state exists for the H_2O on kaolinite(001) surface under room temperature.**
- **This is confirmed by our first-principles static as well as quantum molecular dynamics simulations.**

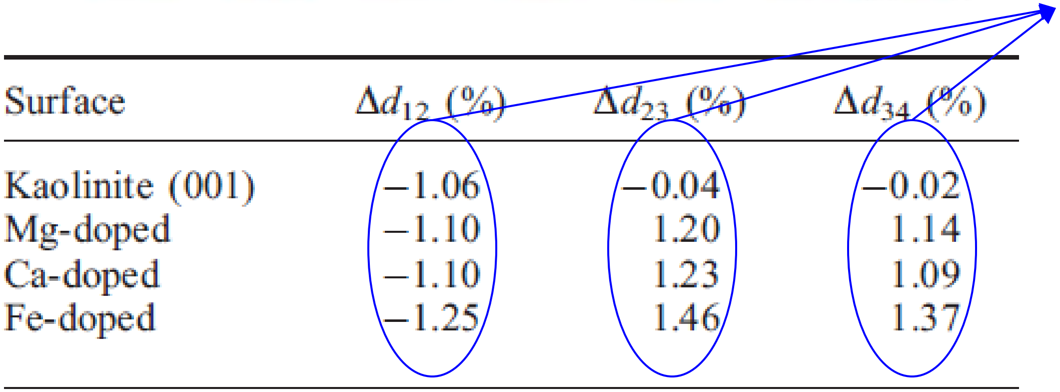
Effects of defects on structures of kaolinite

- **The primary contaminant defects and the concentration ranges**

Mg	Ca	Fe
0.07–0.71 wt.%	0.14–0.54 wt.%	0.07–0.31 wt.%



$$\Delta d_{ij} = \frac{d_{ij} - d_0}{d_0}$$

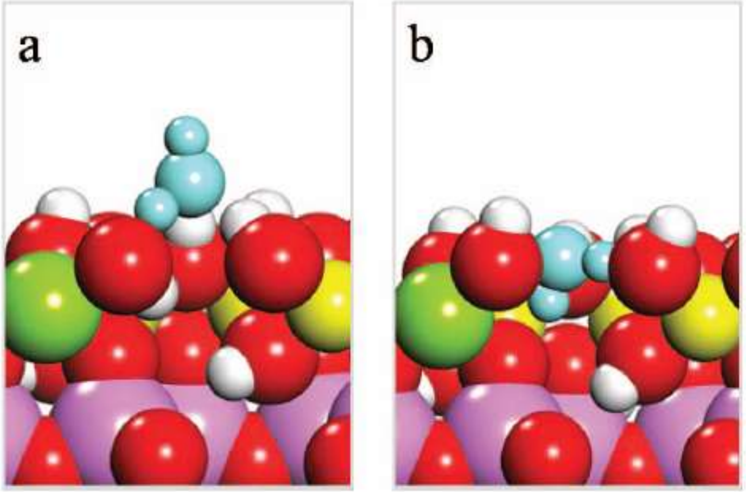


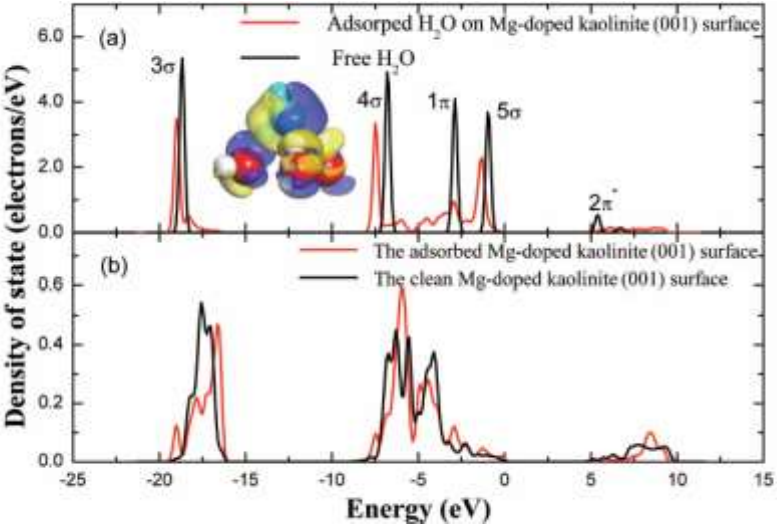
Surface	Δd_{12} (%)	Δd_{23} (%)	Δd_{34} (%)
Kaolinite (001)	−1.06	−0.04	−0.02
Mg-doped	−1.10	1.20	1.14
Ca-doped	−1.10	1.23	1.09
Fe-doped	−1.25	1.46	1.37

●**The results showed that for the Mg-, Ca-, and Fe(II)-doped kaolinites (001), the surface relaxation around the doping layer changed from contraction to expansion, due to the redistribution of electrons.**

Effects of defects on kaolinite(001) with H_2O adsorption

- **Side view of: an adsorbed water molecule on the surface of the hollow site (a); and the Al-surface hollow site (b) of defect-doped kaolinite**



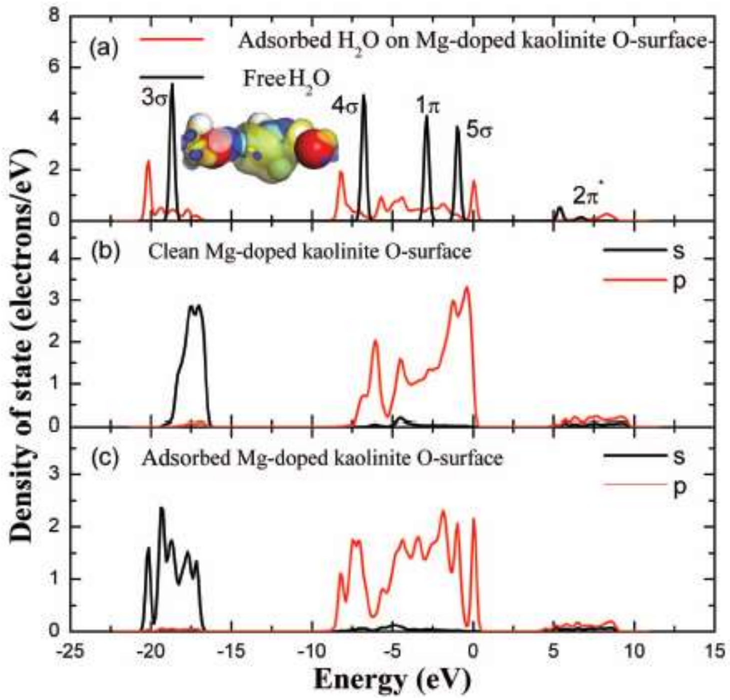


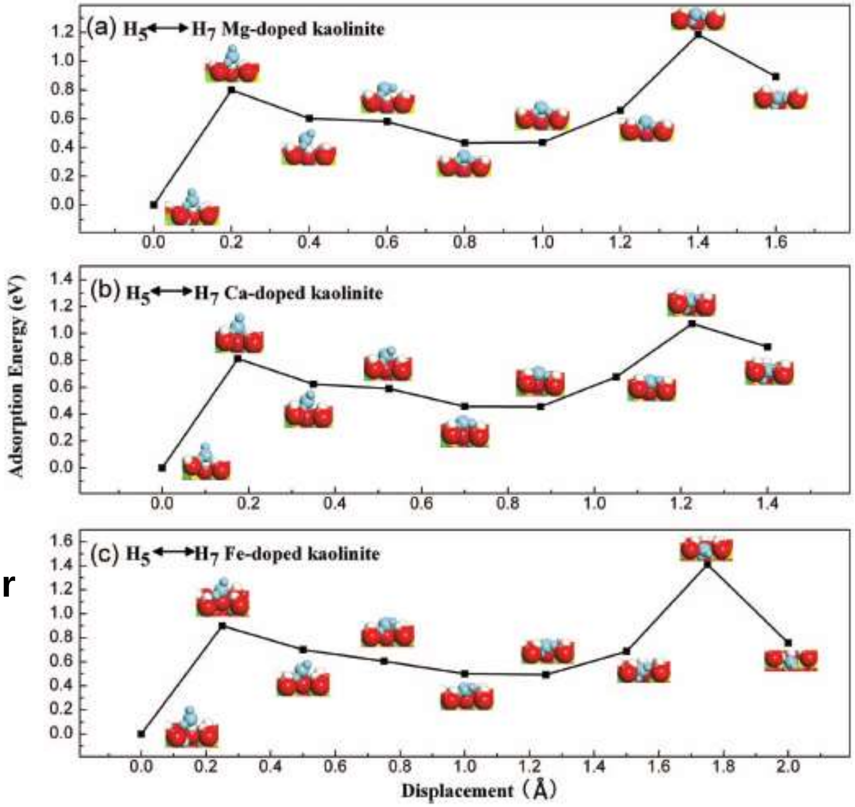
- **Calculated energies for monomer adsorption on six hollow adsorption sites on the surface and one hollow adsorption site on the Al surface of Mg-, Ca-, and Fe-doped kaolinite (001).**

E_{ads} (eV)	H_1	H_2	H_3	H_4	H_5	H_6	H_7
Undoped	1.07	1.06	1.10	1.06	1.15	1.07	–
Mg-doped	0.95	1.04	1.08	0.99	1.10	1.08	0.28
Ca-doped	0.83	0.96	0.85	0.90	1.03	0.90	0.26
Fe-doped	1.01	1.07	1.02	1.03	1.08	1.00	0.20

Effects of defects on kaolinite(001) with H_2O adsorption

- The energetic barriers for penetration of H2O from the adsorption site on the surface to an adsorption site on the O surface of doped kaolinites, implied that the effects of doping make it easier for water molecules to penetrate from the on-surface site to the O-surface site.





- Electronic partial density of states plots for the H_2O molecule and the top-layer H ions bonded to H_2O at the stable threefold hollow adsorption site on the surface.

Conclusions

- We have studied the atomic and the electronic structures of kaolinite through first-principles DFT-LDA calculations. The calculated indirect band gap is 4.89 eV. Based on above results, we study the mechanism of interaction between kaolinite and water molecules in the following.

- We have found that H_2O adsorbs preferentially at threefold hollow site on surface with the adsorption energies ranging from 1.06 to 1.15 eV. The activation energies barrier ranging from 0.073 to 0.129 eV. Finally, no dissociation states of water molecule are found for the ideal kaolinite (001) surface.

Conclusions

- **The results showed that after Mg, Ca, and Fe(II) doping, the surface atomic structure was changed. Due to redistribution of electrons, the surface relaxation changed from contraction to expansion around the doping layer.**

- **The results showed that H_2O adsorbs preferentially on the surface three-fold hollow sites of Mg-, Ca-, and Fe-doped kaolinites (001), which are less than undoped kaolinite. However, the H_2O molecule cannot adsorb on the undoped kaolinite O surface.**

- **The energetic barriers for penetration of H_2O from the adsorption site on the surface to an adsorption site on the O surface of doped kaolinites, implied that the effects of doping make it easier for water molecules to penetrate from the on-surface site to the O-surface site.**

ACKNOWLEDGMENTS

The research above was supported by the National Natural Science Foundation of China (No 40972196 and 41172263) and Youth Talent Support Project

Thank you for your attention!