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# ESTIMATION OF ADSORPTION ENERGIES OF SOME SIMPLE MOLECULES ON CLAY SURFACES: A PRELIMINARY RESEARCH FOR THE CLAY-ORGANIC INTERACTION

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## ABSTRACT

Adsorption behavior of four small molecules on clay mineral surfaces was investigated using first principles quantum chemistry calculation. The self consistent density functional theory (DFT) method based on a linear combination of atomic orbitals (LCAO) basis set implemented in the SIESTA program was applied to calculation of intermolecular potentials between water, H<sub>2</sub>O, hydrogen sulfide, H<sub>2</sub>S, ammonia, NH<sub>3</sub> and methane, CH<sub>4</sub>, and clay mineral surfaces. The generalized gradient approximation (GGA) was used for the better description of weak intermolecular bonding.

H<sub>2</sub>O molecule has the largest adsorption energy among the four kinds of molecule, and CH<sub>4</sub> molecule has the smallest adsorption energy. This result gives some important implications on the clay-organic interaction.

## INTRODUCTION

Clay minerals are regarded as interesting materials in chemical industries and environmental researches, because of its flexible physico-chemical properties, e.g.

cation exchangeability, surface acidity. Expandability of interlayer region is one of such features typical for smectite group. The smectite group is characterized by its small layer charge in a range from 0.0 to 0.25. This small layer charge causes hydrophylicity and organophylicity of smectite group. These delicate properties are controlled by complex interactions between clay surfaces, water molecules, interlayer cations, and organic molecules, and would be applicable to remediation of spilled oil.

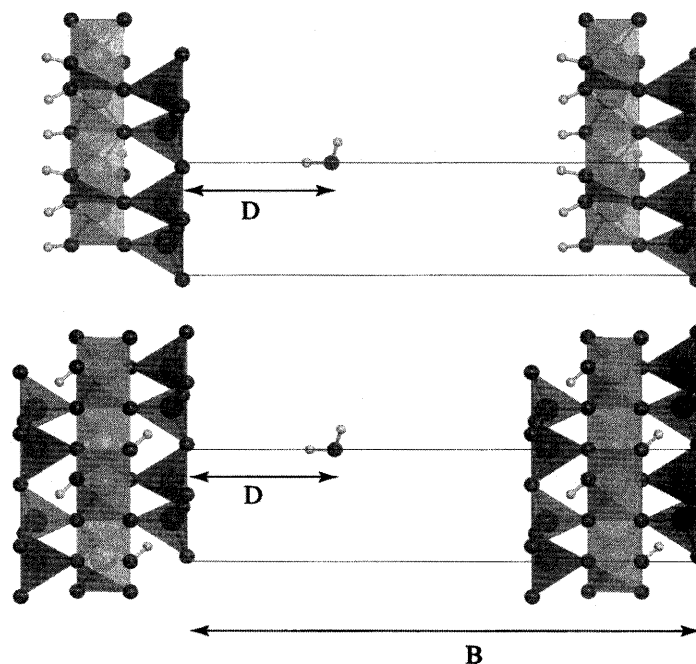
Recently a variety of simulation methods is applicable to investigation of atomistic mechanisms in material sciences. Although the authors have been trying to investigate clay-water interaction by means of molecular dynamics (MD) simulation based on model potentials developed empirically from crystal structures and spectroscopies (Shiraki *et al.*, 2002), essential success could not be achieved because direct observation of intermolecular force is very difficult. How to model the interaction between mineral surface and water or organic molecules is unsolved and important problem. In this study, the SIESTA program (Soler *et al.*, 2002), which is a first principles quantum chemical code, was applied to estimation of adsorption energy of some simple molecules onto clay mineral surfaces.

## SIMULATION METHOD

### Structural models

*Ab initio* calculations were done using periodic condition as illustrated in Figure 1. The structural models are developed by three dimensionally repeated unit cell which include one clay layer and one molecules of H<sub>2</sub>O, H<sub>2</sub>S, NH<sub>3</sub>, CH<sub>4</sub>. Two types of clay layer, dioctahedral 1:1 layer (kaolinite) and dioctahedral 2:1 layer (pyrophyllite), were used as layer models.

The structural models of clay layer were taken from previous works of crystal structure refinements. The structure of dioctahedral 1:1 layer (kaolinite) is based on the result of Rietveld analysis of neutron diffraction data by Bish (1993) which includes hydrogen positions. The atomic coordinates of dioctahedral 2:1 layer (pyrophyllite) refined by Wardle and Brindley (1972) are available only for non-hydrogen atoms. Hydrogen position of pyrophyllite structure is based on a theoretical result of electrostatic energy minimization calculated by Giese (1973) for non-hydrogen atom positions by Wardle and Brindley (1972). There is also more recent refinement by Lee



**Figure 1** Two simulated models including clay layers and water molecules are illustrated. The upper model contains 1:1 layer (kaolinite), and the lower has 2:1 layer (pyrophyllite). Rectangle boxes are showing unit cells described by pseudo-hexagonal cell which include minimum number of atoms. D is a distance from the oxygen of H<sub>2</sub>O molecule to the basal plane. B indicates a basal distance which was adjusted to 2 nm for both models.

and Guggenheim (1981), but hydrogen positions were not analyzed in their analysis. Thus the data by Wardle and Brindley was chosen considering concordance between hydrogen and non-hydrogen atomic coordinates.

A pseudo-hexagonal cell was used to describe clay mineral structures in order to minimize number of atoms to be included in a unit cell. In pseudo-hexagonal cell, lengths of a and b axes are nearly equal, lattice angles are in a condition of  $\alpha = \beta = 90^\circ$  and  $\gamma \approx 120^\circ$ . Atomic coordinates were converted by transformation of basis to be described by the pseudo-hexagonal cell. Number of atoms in a unit cell becomes half of the original one by this conversion.

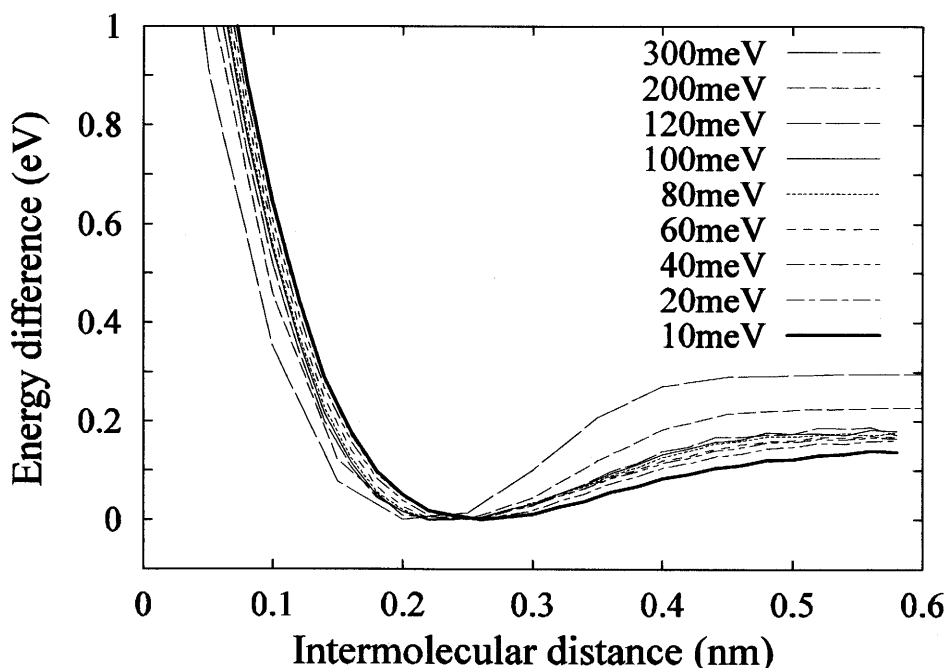
### Calculating method

The *Ab initio* program SIESTA-0.15 (Soler *et al.*, 2002) was used to calculate total

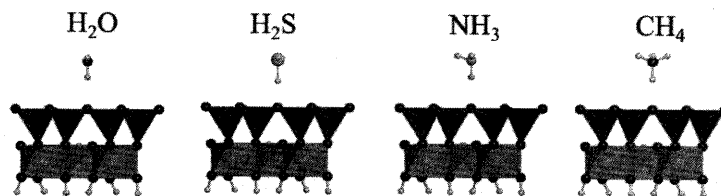
energies for different configurations of small several molecules such as H<sub>2</sub>O, H<sub>2</sub>S, NH<sub>3</sub>, CH<sub>4</sub> on clay surfaces. The self consistent density functional theory (DFT) method based on a linear combination of atomic orbitals (LCAO) basis set implemented in the SIESTA program. The generalized gradient approximation (GGA) was used so that weak intermolecular bonding could be better described. The basis set used in this study is DZP set. A k-grid cutoff parameter and a mesh cut-off parameter were set to 15 Å and 150 Ry respectively. An energy shift parameter which determines cutoff radii of atomic orbitals was set to 100 meV.

## RESULTS

### Convergency of potential curve depending on the energy shift value



**Figure 2** Clay-H<sub>2</sub>O intermolecular potential curves between a H<sub>2</sub>O molecule and 1:1 layer surface calculated by DFT. Differences of total energies from minimum of each curve were plotted as a function of distance between the oxygen of H<sub>2</sub>O and a basal plane. Convergency of potential curve was checked in a range from 300 meV to 10 meV of the energy shift. See text for further details.



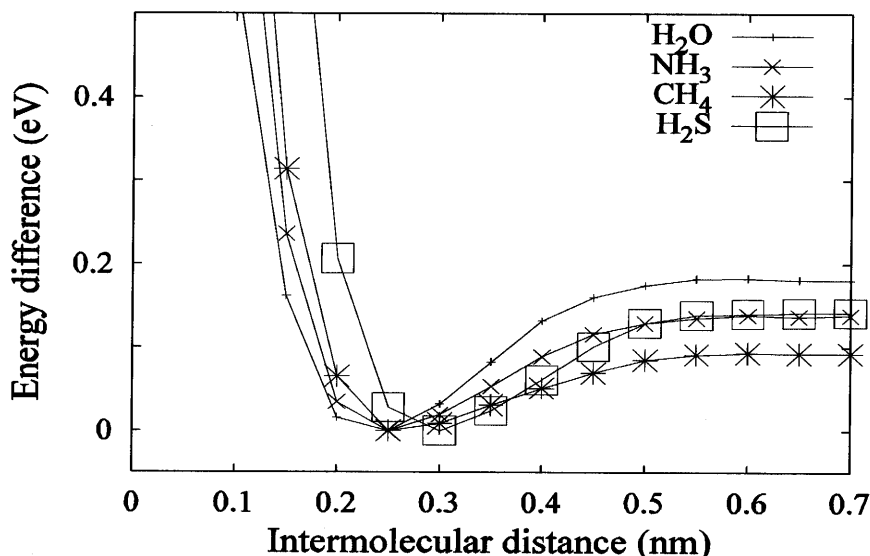
**Figure 3** Schematic representation of four types of models exhibiting small molecules placed on the 1:1 clay surface. All molecules have one hydrogen atom down to the clay surface. Distances from the molecules to the clay surface were changed to evaluate potential curves (Figure 4), but intermolecular structures and directions of molecules were remained.

The energy shift is a parameter which controls the cutoff radius of atomic orbitals. A specific value of energy shift results in different cutoff radii depending on chemical species. Potential curves of interaction between kaolinite surface and a H<sub>2</sub>O molecule for a variety of energy shift values were calculated (Figure 2). In Figure 2, the energies are plotted as difference from the minima of each curve.

Decreasing the energy shift results in an increment of the cutoff radius of atomic orbitals. A small value of the energy shift is favorable for better precision, but a computational cost becomes higher. Thus it is necessary to find an appropriate value of the energy shift which would give an acceptable precision and an executable job size.

The calculated potential curves have minima in the range from 0.20 to 0.25 nm of distance and flat planes in a range of larger distance. A difference between two energy levels at the minimum and the flat plane is regarded as the adsorption energy. Decreasing the energy shift resulted in a displacement of the minimum position from 0.2 nm to 0.25 nm and decreasing the energy gap.

As shown in Figure 2, even the smallest value of energy shift (10 meV) does not seem to give a converged curve. But an energy shift of 100 meV, which is thought as a standard value for an enough precision, was chosen for the studies hereafter in order to save computational costs.

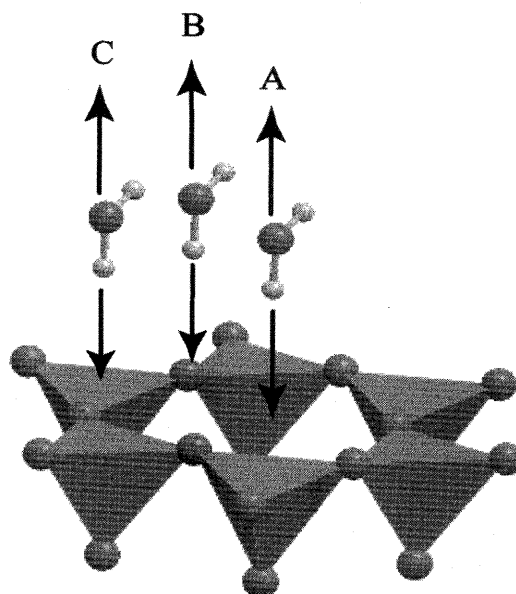


**Figure 4** Intermolecular potential curves as a function of distance from a center atom of each molecule to basal plane of clay minerals. Total energies for different intermolecular distance were plotted as differences from the minimum values of each potential curve.

### Interaction between small molecules and 1:1 layer surface

Four small molecules, H<sub>2</sub>O, H<sub>2</sub>S, NH<sub>3</sub> and CH<sub>4</sub>, were placed on the tetrahedral surface of kaolinite (Figure 3), in an arrangement in which one hydrogen atom is directed to the clay surface. Total energies were calculated for different distances between clay surface and the molecules. The molecules were moved with stepwise manner along a line perpendicular to the surface (Figure 1). The perpendicular line crosses the basal plane of clay layer at the center of six-membered ring. Moving molecules step by step with increment of 0.05 nm, total energies of system were calculated for each molecular position. The energies are plotted in Figure 4 as a function of distance between the central atoms, O, S, N and C, of the molecules and the basal plane of clay minerals (oxygen plane at the surface). The energies are represented as differences from the minimum value in a potential curve.

The four potential curves are similar in shape, which have minima at 0.25-0.30 nm and flat planes in a range of distance larger than 0.5 nm. An energy gap between



**Figure 5** Three paths on 2:1 phyllosilicate along which potential curves were calculated . All paths are normal to the basal plane. The path A intersects the basal plane at the center of six-membered ring. The path B and the path C pass through the oxygen labeled O3 and the silicon labeled Si1, respectively.

these two energetic levels can be regarded as adsorption energy. A potential curve for  $\text{H}_2\text{O}$  shows the largest energy gap of 0.18 eV. Curves for  $\text{H}_2\text{S}$  and  $\text{NH}_3$  have gaps of 0.14 eV. The smallest gap, 0.9 eV, is obtained for  $\text{CH}_4$ .

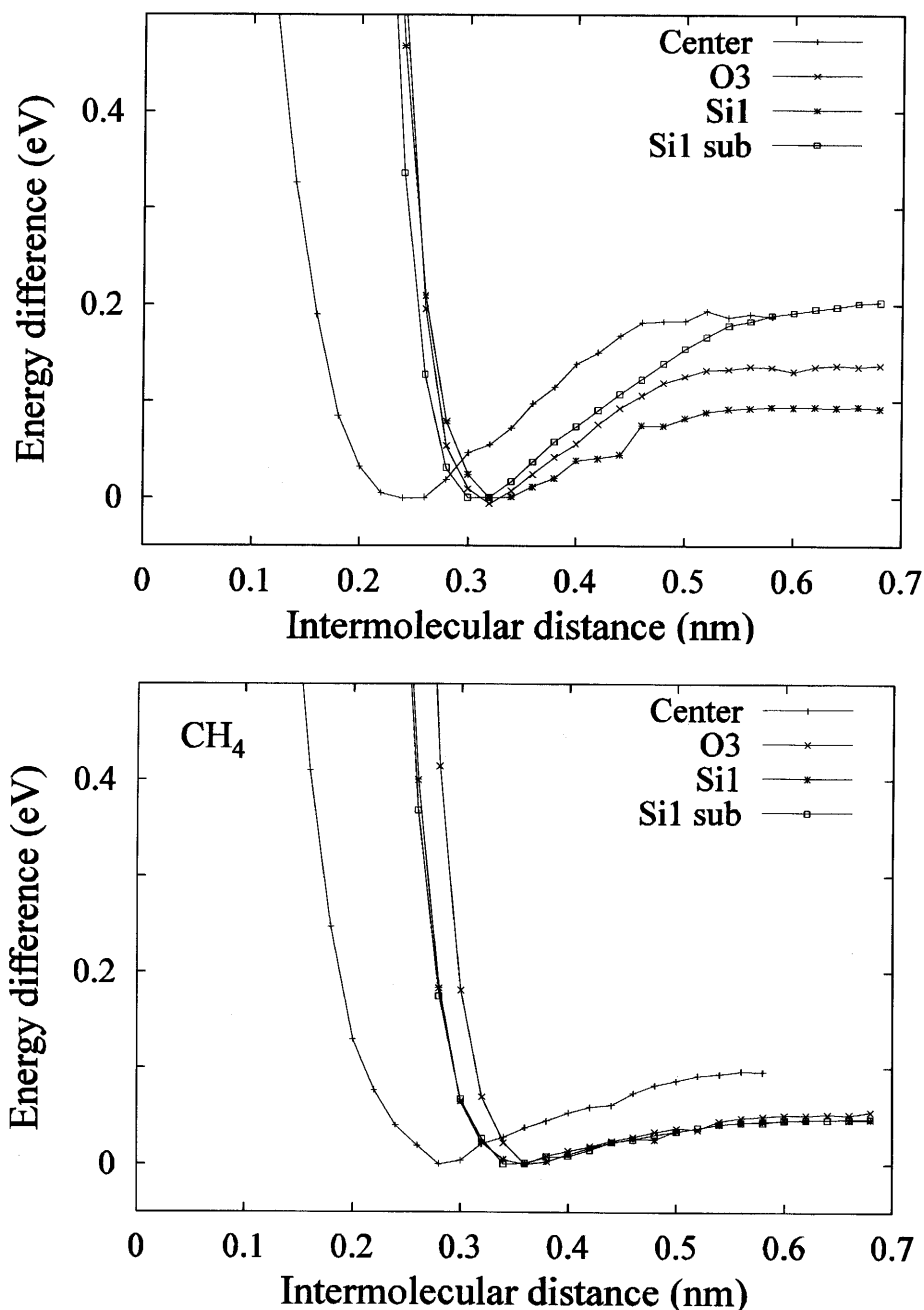
### Interaction between $\text{H}_2\text{O}$ , $\text{CH}_4$ molecules and 2:1 layer surface

Calculations on the adsorption of  $\text{H}_2\text{O}$  and  $\text{CH}_4$  by the surface of 2:1 phyllosilicate layer were also made. Figure 5 illustrates three paths along which molecules are moved in a stepwise manner with increment of 0.02 nm more in detail than the case of 1:1 layer surface.

Four potential curves are shown for both of  $\text{H}_2\text{O}$  and  $\text{CH}_4$  molecules in Figure 6. The curves labeled "center" is calculated along the path A in Figure 5. The ones labeled "O3" and "Si1" are along the paths B and C respectively. The other labeled "Si1\_sub" is along the path C, but the Si1 site in the pyrophyllite structure is substituted by Al.

The potential curves labeled "O3", "Si1" and "Si1\_sub" have equilibrium (minimum) points at about 0.3 nm for  $\text{H}_2\text{O}$ , at about 0.35 nm for  $\text{CH}_4$ . These minima are more distant than those of "center" which are placed at 0.24 nm for  $\text{H}_2\text{O}$  and at 0.28 nm





**Figure 6** Potential curves showing adsorption energies of  $\text{H}_2\text{O}$  and  $\text{CH}_4$  molecules on dioctahedral 2:1 layer. Differences of energy from the minima of each potential curve are plotted as a function of molecular distance from the basal plane. The curve labeled "center" is calculated along the path A. "O3" and "Si1" are along the paths B and C respectively. "Si1\_sub" is along the path C but with the Si1 site substituted by Al.

for  $\text{CH}_4$ . It is caused by repulsion from oxygen atoms on the basal plane. No matter along which path,  $\text{H}_2\text{O}$  molecule show potential gap larger than  $\text{CH}_4$ . This implies that

adsorption energy of H<sub>2</sub>O molecule on clay surface is larger than CH<sub>4</sub>.

## DISCUSSION

The results provide keys to consider mechanisms of interaction between large organic molecules and clay surface. Alkane molecules are nonpolar and have no significant interaction each other neither with other molecules like H<sub>2</sub>O. This property is derived from its almost pure covalent bonding between C-C and C-H bonds, which leads to hydrophobic property of alkanes (Hart *et al.*, 1999). Thus alkanes have little interaction with H<sub>2</sub>O molecules, is not soluble in water. In contrast, water molecule has a significant dipole moment. This polarity causes hydrogen bond in bulk water and with other kinds of molecules. Some molecules, like alcohols, which have OH groups show hydrophylicity. These descriptions are concordant with the results in the present study.

In consequence, saturated hydrocarbons (alkanes) are expected to have weak interaction with other molecules and clay surfaces, comparing with H<sub>2</sub>O molecule. In considering the intercalation of alkanes into smectite, it is anticipated that alkane molecules would not be able to separate the bonding between interlayer water and smectite layer and that intercalation of alkanes will not be achieved.

This preliminary study shows a possibility of predictions on interaction between various kinds of molecules and clay minerals. In order to realize it, model potentials fitted to *ab initio* calculations like the present study should be introduced to the classical molecular dynamics method to understand behaviors of large-scale systems and effects of dynamics.

## CONCLUSION

*Ab initio* calculations were done in order to determine adsorption energy of small molecules such as H<sub>2</sub>O, H<sub>2</sub>S, NH<sub>3</sub>, CH<sub>4</sub>, on clay surface. The results are meaningful and might explain some intercalation phenomena. In addition, the results can be introduced to the classical molecular dynamics method which can deal with large-scale systems composed of many atoms and dynamical characters of system.

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