

# First Principle Calculations of Clay-Benzene and Clay-Naphthalene Interaction Energies

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# First Principle Calculations of Clay-Benzene and Clay-Naphthalene Interaction Energies

Koichi SHIRAKI<sup>a</sup>, Katsuyuki Kawamura<sup>b</sup> and Kazue Tazaki<sup>c</sup>

(a) Department of Earth Sciences, Kanazawa University, Kakuma-machi, Kanazawa, Ishikawa 920-1192, JAPAN

(b) Department of Earth and Planetary Sciences, Tokyo Institute of Technology, 2-12-1 Ookayama, Meguro-ku, Tokyo 152-8551, JAPAN

(c) Graduate School of Natural Science and Technology, Kanazawa University, Kakuma-machi, Kanazawa, Ishikawa 920-1192, JAPAN

Clay-polycyclic aromatic hydrocarbons (PAHs) interaction energies are estimated by first principle calculation with the SIESTA, a Linear Combination of Atomic Orbitals-Density Functional Theory (LCAO-DFT) program. The results will be referred to in optimization of force field parameters for large-scale classical simulation of clay-water-PAHs system. The background of this study is related with the other paper by the same authors.

Three models of clay minerals were calculated for clay-PAHs interaction energies, which are a pyrophyllite ( $\text{Si}_2\text{Al}_4\text{O}_{10}(\text{OH})_2$ ) as a prototype model for cation substitutions, a beidellite-type model ( $\text{X}_{0.33}(\text{Al}_2)(\text{Al}_{0.33}\text{Si}_{3.67})\text{O}_{10}(\text{OH})_2$ ) with tetrahedral substitution by Al, and a montmorillonite-type model ( $\text{X}_{0.33}(\text{Al}_{1.67}\text{Mg}_{0.33})(\text{Si}_4)\text{O}_{10}(\text{OH})_2$ ) with octahedral substitution by Mg (Fig. 1). The calculations were made with DZP basis set in 3-dimensional periodic condition which leads infinite-slab model of clay. Adsorption sites of benzene, naphthalene on the clay basal planes were searched plotting potential curves as a function of the intermolecular distance (Fig. 2 shows the cases of clay-benzene), and further structural optimizations were made at the adsorption sites.

The counterpoise method (Boys and Bernardi, 1970) was used for correction of basis set superposition error (BSSE) to obtain precise interaction energies which is necessary for precise interaction energy in LCAO method. The results are listed in Table 1. Tetrahedral substitution resulted in a remarkable increase of interaction energy (see  $\Delta E_{\text{BSSE}}$ ). All values of interaction energies are much larger than the mean translational energy of a molecule (c.a. 0.04 eV at 300 K).

Table. 1. Interaction energies calculated with BSSE correction for clay-benzene and clay-naphthalene systems.

Benzene	E1	E2	E3	E4	E5	BSSE (eV)	$\Delta E$ (eV)	$\Delta E_{\text{BSSE}}$ (eV)	Re (Ang)
	$E_{\text{clay+benz.}}$	$E_{\text{claydummy+benz.}}$	$E_{\text{clay+benz.dummy}}$	$E_{\text{benz.}}$	$E_{\text{clay}}$				
Non Sub	-27453.24	-1023.87	-26428.99	-1023.73	-26429.24	-0.10	-0.27	-0.38	3.156
Oct. Sub	-27384.31	-1023.88	-26360.08	-1023.73	-26359.97	0.26	-0.60	-0.35	3.027
Tet. Sub	-27366.64	-1023.89	not converged	-1023.73	-26342.15	-	-0.76	-	2.919

Naphthalene	$E_{\text{clay+naph.}}$	$E_{\text{claydummy+naph.}}$	$E_{\text{clay+naph.dummy}}$	$E_{\text{naph.}}$	$E_{\text{clay}}$	BSSE (eV)	$\Delta E$ (eV)	$\Delta E_{\text{BSSE}}$ (eV)	Re (Ang)
	Non Sub	-28104.03	-1674.66	-26429.09	-1674.44				
Oct. Sub	-28035.53	-1674.64	-26360.23	-1674.43	-26359.97	0.46	-1.12	-0.66	3.030
Tet. Sub	-28017.86	-1674.66	not converged	-1674.43	-26342.15	-	-1.27	-	3.031

Re: Distance between clay basal oxygen and PAHs

$$\begin{aligned} \Delta E &= E1 - (E4 + E5) \\ \Delta E_{\text{BSSE}} &= E1' - (E4 + E5) \\ &= E1 + \text{BSSE} - (E4 + E5) \\ &= E1 + (E4 + E5 - E2 - E3) - (E4 + E5) \end{aligned}$$

<sup>a</sup> Electronic Address: shiraki@earth.s.kanazawa-u.ac.jp

<sup>b</sup> Electronic Address: katsu@geo.titech.ac.jp,

<sup>c</sup> Electronic Address: kazuet@kenroku.kanazawa-u.ac.jp

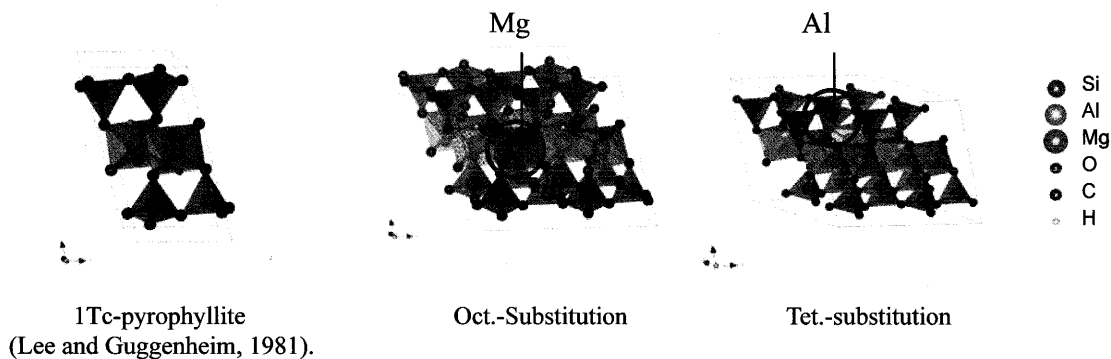


Fig. 1. Structural models of 2:1 clays used in this study. Pyrophyllite has a simple chemical composition. Substitution of octahedral Al for Mg leads montmorillonite-type layer. Substitution of tetrahedral Si for Al leads beidellite-type layer.

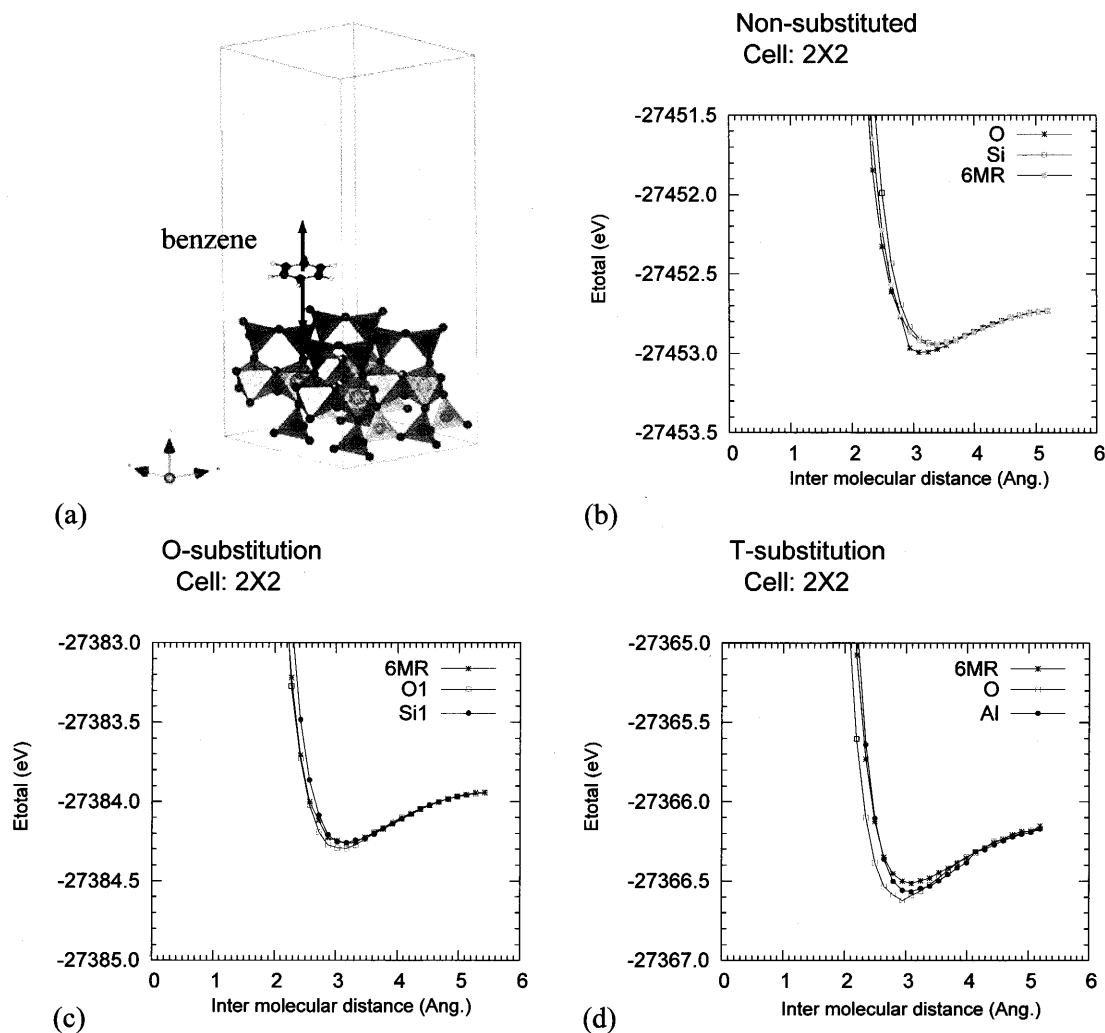


Fig. 2. Simulation model and calculated intermolecular potential curve in the clay-benzene systems. (a) Illustration of simulation model. An example of the pyrophyllite-benzene system. (b) Pyrophyllite. The horizontal axis indicates distance from basal plane to benzene molecule. (c) Montmorillonite-type layer. (d) Beidellite-type layer.

The energies estimated here are not converged in relation to basis set size. These values may be unsuitable for referential data to which the force field parameters for the large-scale simulation are fitted. Higher precision could be obtained by introducing an extrapolation technique (Feller, 1992) to calculate interaction energies at basis set limit.