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## Molecular Modeling in Environmental Sciences: Applications for Mineral-Water-Organic Matters Systems

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An attempt to develop a program and potential models for large-scale molecular simulations of clay-water-organic matters systems is in progress by the authors in order to investigate diffusion and/or adsorption processes of organic pollutants on clay mineral surfaces. We suppose here polycyclic aromatic hydrocarbons (PAHs) and dioxins as actual target pollutants.

Clay minerals are common matters in the Earth surface environment, which can be found as main components of soils, sediments and eolian dusts. Surfaces of some clay minerals have high affinity for water and organic matters. Such minerals interact with a variety of inorganic and organic pollutants and are expected to be responsible for diffusion and stabilization of pollutants.

Understanding diffusion and adsorption processes of pollutants on mineral surfaces in molecular level is important for predicting macro-scale behavior of pollutants in environments, as fundamental parameters which would be introduced to macro-scale simulation. On developing the simulation program and the force field, we deal with three types of clay minerals, water, and benzene in calculations. Benzene is interesting because of its prototypical character for PAHs, and such simple molecule is favorable as a test case in developing methodology.

Developing a method for the large-scale simulations leads two subjects. Crystals of clay minerals have plate-like morphology and their edge structures are not completely investigated. The first subject is to establish a set of structural models adoptable for all directions of edge faces. In spite that reasonable edge models of clay minerals are indispensable to understand surface process, they have not been studied as well as the basal plane because of its experimental difficulty. Theoretical approaches like the first principle calculation could compensate a lack of experimental data in such a case.

Edge models proposed by previous workers can not cover all directions of edge face. The previous edge models are based on the Periodic Bond Chains (PBC) theory, which can be adoptable to for all edge faces. Such a set of edge models leads to clay particles with ideal hexagonal morphologies bordered by edge faces with reasonable structures (Fig. 1). It is of essential interest to compare diffusion and adsorption properties of many molecules between on the basal surface and on the edge surface of clays.

The other subject is to implement a routine to deal with organic molecules into the MXDORTO, a molecular dynamics program developed by one of the authors, which has gave good results, for example, in simulation of expansion of clay minerals by water. In order to profit these results, the MXDORTO was improved to simulate organic molecules, and simultaneously appropriate force field is under developing. A full-flexible model was adopted to deal with organic molecules, which results

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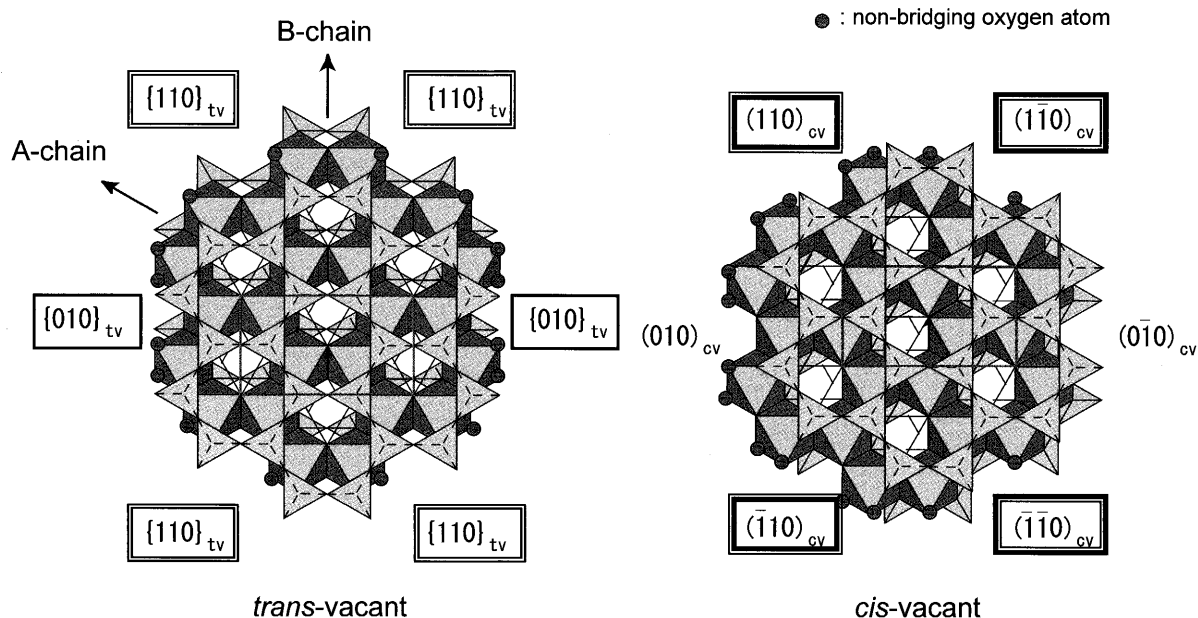


Fig. 1. Structural models of 2:1 clay edges based on the PBC theory. There are two and four symmetrically nonequivalent edge faces respectively in *trans*-vacant layer and in *cis*-vacant layer.

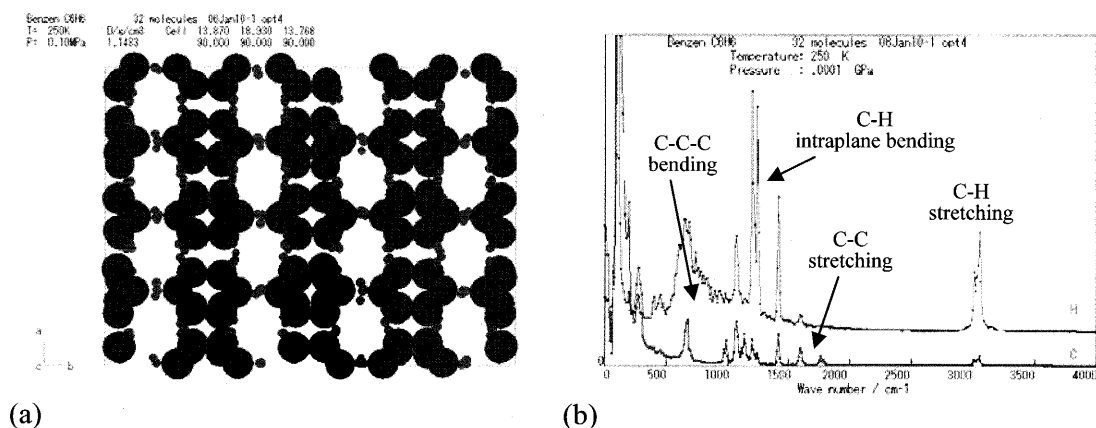


Fig. 2. Classical molecular dynamics of benzene crystal in NPT ensemble (250 K, 0.1 MPa) started from benzene-I structure by Bacon et al. (1964). (a) Snapshot after relaxation of 4 ps, 10,000 steps. (b) Atomic vibrational spectra calculated from 10,000-steps sampling after 10,000-steps relaxation.

in simple program coding and more realistic models than constrained models like a rigid molecule and the SHAKE method Fig. 2 shows a test run of benzene crystal using the MXDORTO. We have obtained good intramolecular geometry (bond distances and angles) and vibrational spectra in the test. The initial structure of benzene-I transformed to benzene-I', a low temperature phase of benzene-I, during relaxation. This is inconsistent with experimental results, and implies that intermolecular potential parameters which control molecular packing configurations should be refined further to reproduce features of experimental crystal structures.

A test run for a system consisting of infinite-slabs of clay, water, and benzene molecules is processing. To obtain meaningful results for such systems, parameters for benzen-water and benzene-clay interactions are also to be optimized. First principle calculations for the latter case are discussed in the other paper by the same authors.