Isomorphous substitution effect on the vibration frequencies of hydroxyl groups in molecular cluster models of the clay octahedral sheet

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ABSTRACT

The geometrical features and electronic structure of molecular cluster models of two octahedrally coordinated cations in edge-sharing octahedra were studied by means of Hartree-Fock ab initio molecular orbital calculations at LANL2DZ and 6-31+G* levels. These models represent the different cation pairs among Al3+, Fe3+, and Mg2+ of the octahedral sheet of clays. These models reproduce the experimental values of the main geometrical features in the corresponding minerals. The vibrational frequencies of the bridging hydroxyl groups (M-OH-M') were calculated and compared with experimental data. A good agreement between theoretical and experimental results was found. The relative differences of υ(OH) and δ(OH) frequencies calculated among these (M-OH-M') cation pairs are similar to the experimental behavior in clays. Theoretical γ(OH) frequencies were also calculated and presented as an estimation of the experimental. Correlations between the atomic weights and the atomic Mulliken charges of the cations with the experimental and theoretical OH vibration frequencies have been also determined and a similar behavior was found.

INTRODUCTION

Smectites and other related 2:1 phyllosilicate clay minerals share the common structural feature that two tetrahedral layers sandwich a sheet of octahedrally coordinated cations. The great diversity of these silicates occurs because of their capacity for isomorphous substitution of various cations in octahedral and tetrahedral sheets, providing different properties in the interlayer space (Güven 1988). In dioctahedral clays, isomorphous substitution Al3+ by Mg2+ in the octahedral sheet, or Si4+ by Al3+ in the tetrahedral sheet results in a net negative charge, which is compensated by additional cations in the interlayer space. The valuable catalytic and adsorptive properties of clays motivate theoretical study of their structure and behavior. Such studies can also be useful to understand some mineral transformations and some industrial applications of clays, like catalysis, and nuclear waste and pollutant disposal barrier component.

The interlayer space and cation distribution in the tetrahedral sheet of these minerals were studied previously (Güven 1988; Karaborni et al. 1996 and references therein), but the properties of the octahedral sheet have received scant attention. The cation ordering of the octahedral sheet of these minerals is important in natural transformations and dehydroxylation processes. The cations of this layer are octahedrally coordinated with six anions, at least two of which are hydroxyl groups. Most properties of these OH groups will depend on the nature of the cations joined to them.

Many XRD studies of 2:1 clay structures are reported, but these give no indication of the proton positions within the hydroxyl groups. IR studies of muscovite (Vedder 1964) and electrostatic calculations (Giese 1979) have suggested that the orientation of these hydroxyl groups is sensitive to the structure of the octahedral sheet. The study of the structure and properties of these hydroxyl groups is interesting, because they can play a major role in the catalytic activity of these minerals, in their interactions with water, other molecules and cations. Additionally, the octahedral cations can play a significant role in sorption and dissolution phenomena in many minerals, where OH groups can have varying effects on the reactivity of mineral surface (Schindler and Stumm 1987).

Spectroscopic methods are especially useful for studying clay structure, because they probe local atomic environments and have the potential to determine indirectly short-range cation ordering. IR data exists for stretching (3700–5000 cm−1) (Besson and Drits 1997; Madejová et al. 1994) and bending (700–1000 cm−1) (Cuadros and Altear 1998) OH vibrations in clays. However, it is difficult to obtain experimentally an accurate identification and quantitative study of the cation distribution in these systems. Hence, computer simulations can play a critical role, such as, Reverse Monte Carlo simulations (Cuadros et al. 1999).

Some modeling of clays have been reported applying empirical interatomic potentials (Collins and Catlow 1992; Bleam 1993). However, clay structures are difficult to treat using empirical forcefield methods. Hydrogen bonding, low symmetry and relatively weak interactions in the interlayer space require at least the more sophisticated and exact methods provided by the molecular orbital theory. To study the chemical-physical properties of solids by means of quantum mechanical theory, two main models can be considered: a semi-infinite model and a local model. The first one studies the mineral crystal in its whole extension, the electrons can be described by plane waves (Payne et al. 1992) or LCAO (Orlando et al. 1994; Sanchez-Portal et al. 1997) approaches and the unit cell is extended by a translation periodicity of the crystal. There are different approaches and applications in this model giving important re-