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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 clusters 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 Al^{3+}, Fe^{3+}, and Mg^{2+} 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 ν(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.