



Relationship between infrared spectra and isomorphous substitution in smectites: A computer simulation study

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Smectites, members¹ of the 2:1 layer silicate family, share the common feature that two tetrahedral sheets sandwich a sheet of octahedrally coordinated metal ion. The diversity of the members of the 2:1 layer silicates occurs because of their capacity for isomorphous substitution of various cations in the octahedral or tetrahedral sheets. Substitution of a divalent metal ion (such as Mg^{2+}) for the trivalent Al^{3+} or a trivalent metal ion (such as Al^{3+}) for the tetravalent silicon results in a net negative charge, which then undergoes interaction with positive ions (the exchangeable cations) to form an interlayer hydrated phase. Local density functional (LDF) calculations were employed to model isomorphous substitution of Al^{3+} by Na^+ , K^+ , Mg^{2+} , Fe^{2+} , and Fe^{3+} in the octahedral layer of a dioctahedral smectite clay such as montmorillonite. The energies of the isomorphous substitution were then compared with the experimental observation. The ordering for successful substitution is $Al^{3+} > Fe^{3+} > Mg^{2+} > Fe^{2+} > Na^+ < K^+$. This ordering is consistent with experimental observation. The vibrational frequencies for the isomorphous substituted systems were calculated by LDF calculation and were compared with the experimental IR results. The results match very well with experiment. This understanding will help in successful prediction of the catalytic activity of smectite clays. © 1996 by Elsevier Science Inc.

Keywords: smectite, isomorphous substitution, LDF calculation, vibrational frequency, IR.

INTRODUCTION

Smectites and other related hydrous phyllosilicate clay minerals belong to the 2:1 class of clay minerals, in which two tetrahedral silicate sheets sandwich a single octahedral metal (usually aluminum or magnesium) sheet. Clays can act as both Lewis and Brønsted acids and are a naturally occurring source of inorganic catalysts that facilitate a number of organic reactions.¹ Clays are also important in areas of environmental concern, for example, in controlling migration of pesticides through soil.² The valuable catalytic and adsorptive properties of clays provide ample reason for establishing a firm theoretical understanding of their structure and behavior. Computer simulation studies can contribute significantly in achieving an understanding of structure–property relationships by the synthesis of current understanding and data, and by their perspicacity in revealing critical conceptual issues whose resolution demands additional experimentation. The theoretical approach for complex clay systems, however, has been a classic one, as exemplified by the work of Giese³ on the expandability of 2:1 clays. Monte Carlo simulation is the most used simulation technique in the case of clays to determine the water content in the interlayer as a function of interlamellar distance.^{4,5} There are classic mechanical simulations of adsorption of hydrocarbons on the surfaces of clay minerals.⁶ There are few quantum chemical calculations to correlate structure and property in the case of clay materials.^{7,8} Aronowitz et al. used extended Hückel theory to model the isomorphous substitution of Al^{3+} by other cations in the octahedral layer of a dioctahedral smectite. The diversity of the members of the 2:1 layer silicates occur because of their capacity for isomorphous substitution of various cations in the octahedral or tetrahedral sheets. Substitution of a divalent metal ion (such as Mg^{2+}) for the trivalent Al^{3+} or a trivalent metal ion (such as Al^{3+}) for the tetravalent silicon results in a net negative charge, which undergoes interaction with positive

Color Plates for this article are on pages 285 and 286.

ions (the exchangeable cations) to form an interlayer hydrated phase. In this context we have used local density functional calculations to (1) determine the applicability of this approach in predicting the preference of isomorphous substitution among various elements and (2) compare the vibrational frequency obtained by the calculation with the experimental infrared (IR) spectra with a special emphasis on montmorillonite clays.

METHOD AND MODEL

The ideal formula of the clay montmorillonite, a member of the 2:1 dioctahedral smectite family, is $(\text{Na}^+_x, n\text{H}_2\text{O})(\text{Al}_{4-x}\text{Mg}_x)\text{Si}_8\text{O}_{20}(\text{OH})_4$. The model of montmorillonite was generated from the well-defined crystal structure of pyrophyllite, having the formula $\text{Si}_8\text{Al}_4\text{O}_{20}(\text{OH})_4$ as mentioned elsewhere.⁹ The $\text{Al}_2\text{Si}_6\text{O}_{24}\text{H}_{18}$ cluster generated from the clay is shown in Figure 1. Figure 1 displays a top view of one tetrahedral and one octahedral sheet, showing the hexagonal cavities at the oxygen surface of the silicon layers. In Figure 1 the silicons (lightly shaded) are bonded to aluminum (black) through oxygen (white) bridges. The hydrogens (darkly shaded) are connected to oxygens (white). The two aluminums and the oxygens attached to them were labeled. The dangling bonds were saturated by hydrogen atoms (not drawn in Figure 1). The hydroxyl at the center of the hexagonal cavity is parallel to the clay surface and pointing in the direction of the vacancy of the octahedral network. Of the two octahedral aluminums, one is more stable than the other, as mentioned in our earlier study.⁹ Therefore the isomorphous substitution calculations were performed on a cluster model with formula $\text{AlSi}_4\text{O}_{14}\text{H}_{10}$ generated from the

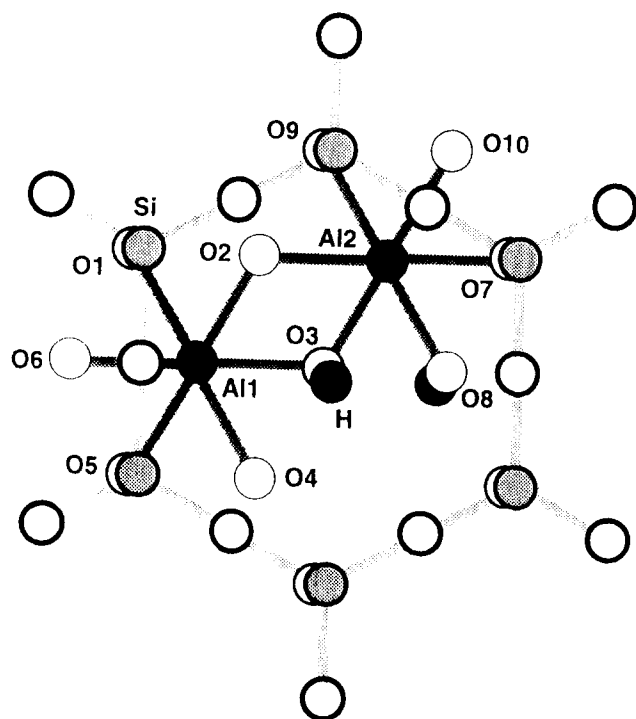


Figure 1. The top view of the cluster model of montmorillonite with six tetrahedral silicons and two octahedral aluminums, having the formula $\text{Al}_2\text{Si}_6\text{O}_{24}\text{H}_{18}$.

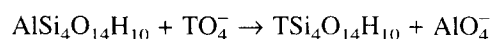
above-mentioned cluster centered on the less stable aluminum site (Al 1 in Figure 1) in the cluster.

The local density functional (LDF) calculations have been performed with the DMOL¹⁰ program, which is based on the work of von Barth and Hedin.¹¹ DMOL uses numerically tabulated functions for its orbital basis set. We employ a double numeric with polarization (DNP) basis set and extra fine grid (equals 6 000 points per atom). We determined the harmonic frequencies and the corresponding normal modes by diagonalizing the Cartesian-Hessian matrix constructed by numerical differentiation of the analytic gradients obtained at the equilibrium geometry. We used a small (usually 0.008 eV) smear value to avoid energy convergence problems during the vibrational calculations, which means a small excitation for these systems; however, this procedure does not introduce considerable error in the vibrational spectra. The calculated energies are not free from the basis set superposition error, but this error is minimized by the quality of basis set used in the calculations.

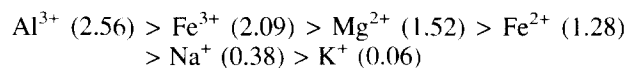
RESULTS AND DISCUSSION

Isomorphous substitution of octahedral aluminum

Isomorphous substitution of an Al^{3+} ion at an octahedral site by Na^+ , K^+ , Mg^{2+} , Fe^{2+} , and Fe^{3+} was treated as in the case in which the octahedral site was initially occupied by Al^{3+} , followed by substitution by the above metal ions at that site. In each case the cluster was totally optimized. The initial and final optimized configuration of the $\text{FeSi}_4\text{O}_{14}\text{H}_{10}$ cluster is shown in Color Plate 1. The optimized structure shows that Fe^{3+} moves away from the plane of the silica tetrahedrons. The substitution energy values are shown in Table 1. The substitution energy has been calculated by the following equation:



The substitution energy shows that the preference in aluminum substitution in an octahedral layer of montmorillonite is of the order $\text{Fe}^{3+} > \text{Mg}^{2+} > \text{Fe}^{2+} > \text{Na}^+ > \text{K}^+$. It is noted below that the magnitude of electron density (numbers in the parentheses) transferred to the metal ion is



Thus, rather than the formal charges associated with the various cations, the calculated in situ net charges are given by 0.44+, 0.91+, 0.48+, 0.72+, 0.62+, and 0.94+, where the

Table 1. Local density functional study on $\text{AlSi}_4\text{O}_{14}\text{H}_{10}$ cluster to calculate substitution energy for different substituents in place of octahedral Al^{3+}

| Substituted metal ion | Substituted cluster | Substitution energy (a.u.) |
|-----------------------|--|----------------------------|
| Na^+ | $[\text{NaSi}_4\text{O}_{14}\text{H}_{10}]^{2-}$ | -42.68 |
| K^+ | $[\text{KSi}_4\text{O}_{14}\text{H}_{10}]^{2-}$ | -42.54 |
| Mg^{2+} | $[\text{MgSi}_4\text{O}_{14}\text{H}_{10}]^-$ | -42.81 |
| Fe^{2+} | $[\text{FeSi}_4\text{O}_{14}\text{H}_{10}]^-$ | -42.73 |
| Fe^{3+} | $[\text{FeSi}_4\text{O}_{14}\text{H}_{10}]$ | -42.92 |

same cation order as in the above set of inequalities has been kept. This ordering agrees with the proposal of Goldschmidt.¹² His proposal was based on the approximate relative sizes of metal ions in their appropriate valences. It is observed that insertion of Na⁺ or K⁺ in place of Al³⁺ in the octahedral layer is a less favorable process.

The effect of isomorphous substitution on the charge density of the oxygens that are in direct contact with the octahedral Al³⁺ is of interest. Irrespective of the cations substituted for Al³⁺ ion, it is observed that the charge on these oxygens, which are the boundary of the interlayer region, does not change much. As with varying charge on the metal cations the negative charge on the system will be different, which leads to a conclusion that the excess negative charge is dispersed throughout the crystal and that it is not obvious where the exchangeable cation would be located.

The nature of the highest occupied molecular orbitals (HOMOs) does not change much regardless of the specific cation in the octahedral site. These topmost orbitals are centered on the framework oxygens (octahedral layer). It is observed that the filled orbitals are pushed up with respect to the valence band for all the isomorphous substitution cases considered. Similarly, the lowest unoccupied molecular orbitals (LUMOs) are interspersed in a conduction band. It seems that the montmorillonite clays behave as a semiconductor.

Molecular electrostatic potential (MESP) maps yield information on the molecular regions that are preferred or avoided by an electrophile or nucleophile. The MESP is evaluated with neglect of the contribution of two center charge distributions, an approximation that is common in semiempirical methods. The MESP maps in this study are generated from wave functions obtained by LDF study. The MESP maps around the FeSi₄O₁₄H₁₀ cluster are shown in Color Plate 2. The potential map shows the central iron has a positive potential smeared inside the range of negative potential. The Fe³⁺ that is away from the plane of the silica tetrahedrons has a positive potential zone, which results in a high activity of the iron in the isomorphously substituted clay materials. This fact is supported by the substitution energy values as mentioned above.

Comparison of vibrational frequency with infrared

Farmer¹³ has shown that the vibrations of layer silicates can be approximately classified into those of the constituent units, i.e., the hydroxyl groups, the silicate anion, the octahedral cations, and the interlayer cations. This classification is essentially complete for the high-frequency OH stretching vibrations, lying in the 3400- to 3750-cm⁻¹ regions, but is less complete, although still useful, for OH bending frequencies, lying in the 600- to 950-cm⁻¹ region. The Si-O stretching vibrations lying in the 700- to 1200-cm⁻¹ region are only weakly coupled with other vibrations of the structure but Si-O bending vibrations, around 150 and 600 cm⁻¹, are strongly coupled with vibrations of octahedral cations and with translational vibrations of hydroxyl groups. Infrared spectroscopic studies of smectites having variable octahedral site compositions have shown related shifts in the spectral features at 4 500 cm⁻¹ and in the 950- to 850-cm⁻¹

range, owing to structural O-H species.¹⁴ The infrared absorption due to structural OH in montmorillonite includes the O-H stretching vibration at 3632 cm⁻¹.¹⁴ Vibrational frequency calculations have been performed on montmorillonite with different isomorphous substitution in the octahedral layer. The results have been compared with the available experimental data.

The results of vibrational frequency determined by LDF calculations are shown in Table 2. The results match well with the experimental data, with a little broadening in the signals. This broadening probably occurs because of computational limitations: the set of atoms used in this study is significantly less than that found in real clay particles. Therefore, the conclusions must be viewed as correlative and predictive in nature. Since the vibrational frequencies reported appear to agree with experimental observations, future studies are warranted. Again, in the case of the H-O-Al band, first, when the amount of Mg²⁺ in the octahedral sites increases, the H-O-Al adsorption band at 935 cm⁻¹ decreases in intensity. Second, the frequency and the intensity of the Si-O-Al band at 535 cm⁻¹ decrease as a result of substitution; this matches well with the observation of Stubican and Roy.¹⁵ The polarizing power of the interlayer cations forms a trend that is consistent with, in general, the vibrational energies of bending vibrations. The stronger the polarizing power of the cation, the more the cation hinders the bending vibration. Therefore, higher vibrational frequencies of all bending bonds are observed in the case of interlayer Mg²⁺- and Fe³⁺-exchanged montmorillonites relative to the Na⁺-, K⁺-, and Fe²⁺-exchanged montmorillonites.

CONCLUSION

This study is the first to see how a local density functional (LDF) study matches experimental observations. The order of preference of isomorphous substitution by different metal ions at the octahedral position of montmorillonite clays has been predicted. The order of preference calculated by LDF calculation is Fe³⁺ > Mg²⁺ > Fe²⁺ > Na⁺ > K⁺. This result matches well the order predicted by Goldschmidt and Aronowitz et al. The topmost orbitals in all cases of isomorphous substitution are centered on oxygens composing the octahedral layer framework. The lowest empty orbitals are interspersed in a conduction band. The filled orbitals are

Table 2. Local density functional study on vibrational frequency calculation of isomorphously substituted clusters and comparison with infrared data

| Vibration | Wavenumber (cm ⁻¹) | |
|---------------------------------------|--------------------------------|------------|
| | Experimental | Calculated |
| Al ₂ -OH stretch + bend | 4 535 ^a | 4 522 |
| AlFe ³⁺ -OH stretch + bend | 4 510 ^a | 4 498 |
| AlMg ²⁺ -OH stretch + bend | 4 480 ^a | 4 473 |
| Al ₂ -OH bend | 918 ^a | 911 |
| AlFe ³⁺ -OH bend | 890 ^a | 879 |
| AlMg ²⁺ -OH | 851 ^a | 837 |

^aFrom Bishop et al.¹⁴

pushed up with respect to the valence band for all isomorphous substituents. Thus montmorillonite behaves like a semiconductor. Vibrational frequency results match well with experimental observations, with a little broadening of the spectra, mainly due to CPU limitations (the set of atoms used in this study is significantly less than that found in real clay lattice). Since vibrational frequencies agree with the experimental IR values, future study is warranted.

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