

All-atom ab initio energy minimization of the kaolinite crystal structure

J. DAVID HOBBS,¹ RANDALL T. CYGAN,² KATHRYN L. NAGY,² PETER A. SCHULTZ,¹ AND MARK P. SEARS¹

¹Computational Material Sciences Department, Sandia National Laboratories, Albuquerque, New Mexico 87185-1111, U.S.A.

²Geochemistry Department, Sandia National Laboratories, Albuquerque, New Mexico 87185-1111, U.S.A.

ABSTRACT

Calculations that minimize the energy and optimize the geometry of all atomic coordinates for two proposed kaolinite crystal structures were performed using a first-principles, quantum chemical code based on local density functional theory. All calculations were performed using published unit-cell parameters. Inner- and interlayer H atom positions agree well with those determined by Bish (1993) from neutron diffraction data and confirm a unit cell with *C*1 symmetry.

INTRODUCTION

Accurate interpretation of high-quality crystal-structure refinements and spectroscopic data on adsorption at the molecular or atomistic scale would benefit from independent calculations of mineral structures and surfaces based on quantum-chemical approaches. One approach has been to use empirical or partial ab initio determinations of crystal structures and surface molecular configurations (Sherman 1991; Hess and Saunders 1992; Kubicki et al. 1996). However, the recent evolution in high-performance computers and ab initio quantum chemistry codes offers new, accurate, and inexpensive routes to understanding mineral structures (Winkler et al. 1995a; Brodholt et al. 1996; Smrcok and Benco 1996) and mineral surface-contaminant interactions such as those of interest in radioactive and chemical-waste remediation. The purpose of this study is to evaluate the local density functional computational method for accurate reproduction of structure and bonding in a sheet aluminosilicate mineral as a foundation for future study of surface relaxation phenomena for the extended mineral, water, and adsorbate complex. Typically, layered sheet structures, such as those representing clay minerals, are difficult to treat using the simpler empirical forcefield methods. Low symmetry, hydrogen bonding, and large localized charge separations require the more sophisticated and exact methods provided by the molecular orbital approach.

Here, we report the first all-atom geometry optimization of kaolinite, $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$, using a periodic density functional method that was developed to run on massively parallel (MP) computers. The kaolinite Al octahedral sheet contains both interlayer OH groups that form hydrogen bonds with the adjacent Si tetrahedral sheet and inner OH groups associated with vacant octahedral Al sites. The interlayer and inner OH groups have been suggested (Giese and Costanzo 1986; Cygan et al. 1997b) to be significant in the surface electrostatics that influence the formation of host-guest complexes and thus may play

an important role as a model in evaluating the transport of hazardous wastes. Numerous studies, both experimental (Adams 1983; Young and Hewat 1988; Bish and Von Dreele 1989; Bish 1993) and theoretical (Giese and Datta 1973; Giese 1982; Hess and Saunders 1992), have addressed the heavy atom positions and proton orientations in kaolinite; however, no optimization calculations involving all atoms of the unit cell in a periodic structure have been conducted.

Detailed and accurate quantum mechanical studies of the adsorption of small molecules onto hydrated mineral surfaces requires calculation of extended periodic surfaces. The alternative approach, using truncated clusters containing sites of interest, does not accurately represent the long-range interactions in the crystal. Boundary effects can lead to calculated adsorption energies that depend on cluster size and thus are not comparable with experimentally determined energies. The main purpose of the present study is to establish that the first-principles, periodic, density functional method is useful in reproducing the bulk structure and bonding in layered aluminosilicate minerals. Ultimately, we plan to apply the methods developed in simulating the bulk structure of kaolinite to the surface structure, and then to bulk and surface structures of other important layered aluminosilicate minerals.

METHODS AND RESULTS

The first-principles periodic bulk calculations used the local density approximation (Kohn and Sham 1965) to density functional theory (Hohenberg and Kohn 1964) in a Gaussian-based linear combination of atomic orbitals (LCAO) basis. The calculations were performed using the QUEST (quantum electronic structure) code, designed and written (Sears and Schultz, unpublished manuscript) for massively parallel, distributed-memory computer architectures. QUEST has been used successfully in bulk (Nelson et al. 1995), surface (Feibelman 1987), and molecular (Jennison et al. 1997) applications. Local density

functional (LDF) molecular orbital codes are superior to standard Hartree-Fock (HF) methods in their computational scaling for two- and three-dimensional periodic systems (i.e., the computation problem scales as $\sim n^{1.5}$, where n is the number of basis functions employed). QUEST uses the Perdew-Zunger (1981) parameterization of the Ceperley-Alder electron gas results for the exchange correlation functional in fully self-consistent calculations. The core-valence interactions were treated using standard, norm-conserving, non-local forms of ab initio pseudopotentials (Hamann et al. 1989). The basis set consisted of atom-centered sets of Gaussian functions contracted to give "double-zeta + polarization" quality bases: two radial degrees of freedom each for s and p orbitals plus a d orbital for all atoms except H, which has only a single p and no d orbital. This method reproduces well the results of highly converged plane calculations (see Nelson et al. 1995) but has the advantage of being particularly well-suited to systems with atoms having strong potentials (e.g., O). This full-potential method makes no empirical approximations about the shape of the charge density or potential beyond the use of pseudopotentials to remove explicit treatment of the chemically inert core electrons. In the LCAO calculations, the gamma point and a two-point sampling of the Brillouin zone according to the method of Monkhorst and Pack (1976) were used. The periodic boundary conditions considered two lattice images for each a , b , and c direction of the unit cell. The total number of lattice images is thus 125 because they are arranged symmetrically in each direction. No symmetry operators were used; therefore the 34-atom unit cell was adjusted to reflect $P1$ symmetry despite the determination of $C1$ symmetry for kaolinite (Bish 1993). A convergence tolerance of 10^{-5} Ryd (2 Rydberg = 1 Hartree = 627.5 kcal/mol = 27.21 eV) was set within the QUEST program. Force calculations incorporated the Pulay (1977) corrections necessary to account for the dependence of the LCAO basis orbitals on atomic positions. Optimization of the atomic positions was achieved using a modified Broyden's method (Johnson 1988). This modified Newton-Raphson method uses the atomic positions and calculated gradients of the exact converged LDF energies to calculate new atomic positions that minimize atomic forces. All QUEST calculations were performed on an 1824-processor Intel Paragon computer.

Full-geometry optimization was accomplished starting with atomic coordinates from two recent refinements of X-ray and neutron diffraction data (Suitch and Young 1983; Young and Hewat 1988; Bish 1993). The initial energies (see Fig. 1) for these starting structures were also compared to a recent empirical model calculation that used Coulombic and Buckingham-type potentials implemented in the GULP computer software (Gale 1993; Cygan et al. 1997a). Geometry optimizations were unconstrained for all atomic coordinates; however, experimental unit-cell parameters were not adjusted relative to new atomic positions during the minimizations. Although con-

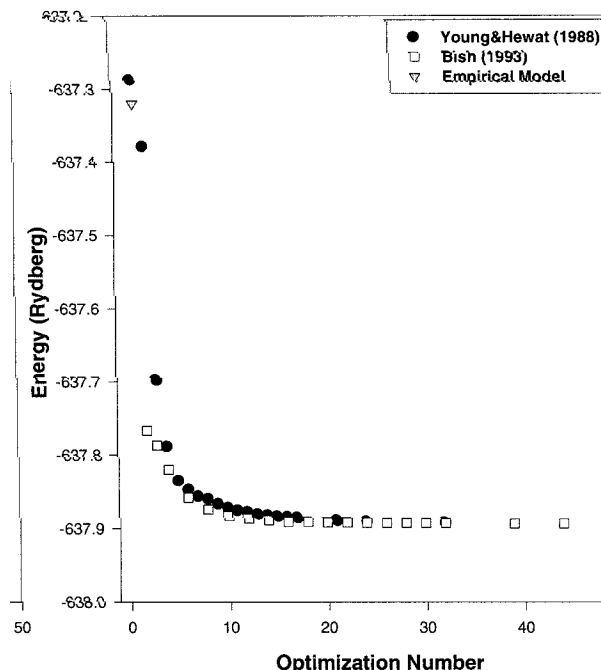


FIGURE 1. Plot of converged LDF energies vs. optimization number for kaolinite structures: Bish (1993) (open squares), Young and Hewat (1988) (solid circles), and empirical (Cygan et al. 1997a) (inverted triangle). Optimization number refers to the number of the iteration in the energy-minimization scheme.

stant pressure LDF calculations are expected to compress the unit cell because of the under prediction of bonds by approximately 0.02 Å (Hehre and Huang 1995; Winkler et al. 1995a), the reduction in individual lattice parameters is typically no more than about 4% unless more sophisticated and costly techniques, such as gradient-corrected calculations are performed (Winkler et al. 1995b). Additionally, fixing the unit-cell parameters is not expected to influence the observed results significantly in this case because starting cell parameters are derived from low-temperature (1.5 K) neutron diffraction data (Bish 1993) and structural studies of temperature effects (Bish and Von Dreele 1989) on the c dimension suggest minimal ($\leq 1\%$) changes over significant temperature ranges (1.5–300 K).

Because QUEST cannot yet perform a constant-pressure minimization (i.e., having cell parameters and atomic positions simultaneously optimized), we explored the effect of changing the "fixed" c dimension on the energy calculations. The c dimension was varied while maintaining the optimized internal structure of kaolinite (i.e., only the interlayer spacing was changed). As is usual for density functional theory calculations, our results under predict the c dimension by approximately 1–2% (Fig. 2). However, the observed energy change is only 3.19×10^{-3} Ryd. Thus, the energy change for the unit cell is less than 9.38×10^{-5} Ryd/atom. This small energy per atom indicates that if the complete structure were energy-opti-

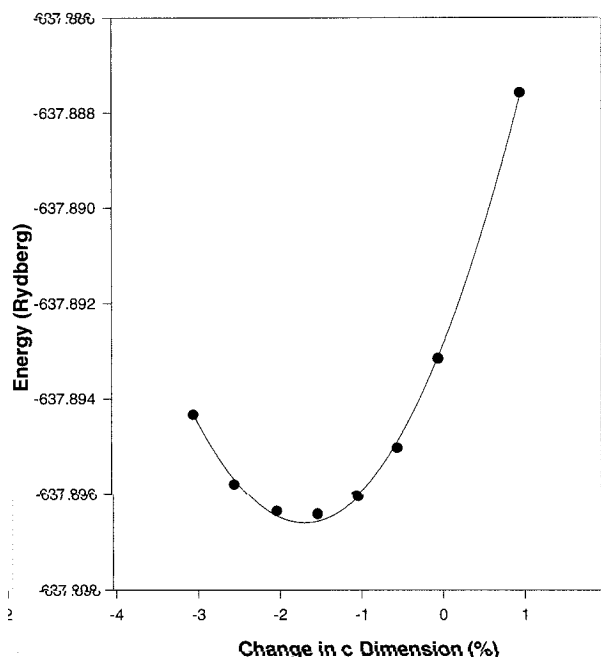


FIGURE 2. Plot of converged LDF energies vs. percent change from the experimentally determined c dimension.

mized there would be no significant change to the c dimension, nor would we expect changes to the general bonding and symmetry.

For comparison with a recent HF calculation (Hess and Saunders 1992), an H-atom-only optimization was also performed by fixing the heavy atoms to the positions previously reported by Bish and Von Dreele (1989) and minimizing the energy relative to only inner and interlayer H atom positions. Data from this minimization are included in Table 1.

Figure 1 plots the LDF-calculated energies vs. optimization experiment number for the Bish (1993) and Young and Hewat (1988) structures. The empirically based constant-pressure structure of kaolinite obtained by Cygan et al. (1997a) was not optimized using the LDF method but provides a single-point energy that is close to the energy calculated for the Young and Hewat (1988) structure. This third structure provides an independent and theoretical comparison with the two experimentally based structural models. Although the initial energies of the two refined structures differ significantly (0.339 Ryd), while having slightly different lattice parameters (unit-cell lengths agree within 0.01 Å; unit-cell volumes are within 0.2%), they converged rapidly to similar energies and structures. Symmetries of the resulting calculated structures were determined using a symmetry-finding algorithm (Molecular Simulations Inc.) and are consistent with the unit cell possessing overall $C1$ symmetry. All heavy-atom positions (Al, Si, and O) produce an excellent mapping and reduction of the $P1$ -based LDF structure to a $C1$ symmetry structure. The interlayer H atoms positions exhibit $C1$ symmetry to a tolerance of 0.018 Å,

TABLE 1. Comparison of calculated and experimental average bond distances (Å) in kaolinite

Bonds	Calculated	Observed*	
Si-O (apical)	1.6130	1.618(5)	
Si-O (basal)	1.6401	1.616(6)	
Si-O (all)	1.6317	1.615(8)	
HF (6-31G**)	1.6291	—	
Al-OH (interlayer)	1.8556	1.880(6)	
Al-OH (inner)	1.9191	1.926(7)	
Al-O (apical)	2.0128	1.967(8)	
Al-O (all)	1.9259	1.908(15)	
HF (6-31G**)	1.9335	—	
O-H (interlayer)	0.9873	0.9810†	0.978(4)
O-H (inner)	0.9937	0.9922†	0.975(4)
O-H (all)	0.9905	—	0.977(8)
HF (6-31G**)	0.9488	—	—

* Bish (1993).

† H-atom-only DFT optimization.

whereas the inner H atoms of kaolinite agree within 0.064 Å. Both H position tolerances are similar to the offsets expected from the standard deviations obtained for the atomic positions from the neutron diffraction data (Bish 1993).

A qualitative picture of the agreement between the calculated structure and that proposed by Bish (1993) can be seen in Figure 3, and structural details are reported in Table 1 and Table 2. For general comparison, HF calculations at the 6-31G** basis-set level were performed using the Spartan program (Hehre and Huang 1995) on two model kaolin structural subunits: an Al atom hexacoordinated by H_2O , $Al(H_2O)_6^+$, and a tetrahedrally coordinated Si atom, $Si(OH)_4$. Results of these calculations are included in Table 1.

Overall structural agreement between heavy atoms and protons of the energy-optimized structure and a recent Rietveld refinement (Bish 1993) is excellent. Bond lengths (Table 1) and bond angles (see Fig. 3) are generally consistent with experimental results for kaolinite

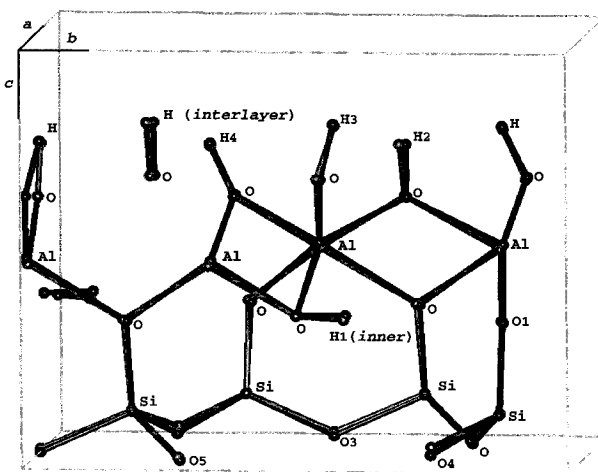


FIGURE 3. Comparison of the calculated (solid) and the Bish (1993) experimental (shaded) kaolinite structures. Note the good agreement of bond lengths and bond angles.

TABLE 2. Comparison of calculated and experimentally determined OH orientations and H-bond distances in kaolinite

Atom	Angle of OH with (001) (°)	Hydrogen bond	Distance (Å)
H1	3.76 (0.46)*	H1...O1	2.571 (2.577)*
H2	91.16 (87.15)	H2...O4	1.998 (2.145)
H3	78.24 (74.33)	H3...O3	1.955 (2.039)
H4	64.58 (65.01)	H4...O5	1.921 (2.041)

* Observed values (Bish 1993) shown in parentheses.

(Bish and Von Dreele 1989; Bish 1993) and dickite (Bish and Johnston 1993). Furthermore, bonding trends for particular Al-O and O-H pairs are accurately reproduced. For example, Al-O bond distances associated with interlayer OH groups, Al-O bonds involving the inner OH groups (adjacent to vacant octahedral sites), and apical Al-O bonds joining the Si tetrahedral sheet, all have distinct bond lengths in the reported X-ray crystal-structure refinements (Bish and Von Dreele 1989; Bish 1993). From Table 1, it can be seen that this trend is replicated in the calculated structures. Apical Al-O bonds (i.e., those that connect to an Si-O bond) are observed to be longer than Al-O bonds involving OH groups, whereas Al-O bonds that involve interlayer OH groups are shorter than Al-O bonds associated with the inner OH group. The calculated Si-O bond distances also show heterogeneity between the apical and basal Si-O bond. The apical Si-O bonds are significantly shorter (~ 0.03 Å) than their basal counterparts. Structural heterogeneity for the Si-O bond system was not reported in the experimental data.

Differences in O-H bond distances are also found for the inner and interlayer OH groups (Table 1). These differences are on the order of 0.01 Å and exist for both the fully optimized and H-atom-only optimized structures. Significant differences in O-H bond distances were not observed in the Rietveld refinement data at 1.5 K (Bish 1993). The orientations of OH groups in the geometry-optimized structures (Table 2) are also similar to those determined through model fitting of the neutron diffraction data. Only minor differences ($<0.5^\circ$) were observed between the full and H-atom-only optimized structures. Moreover, the two inner OH positions of the *P1* symmetry unit cell used for all calculations are identical. Thus, there is no evidence for breaking of the proposed *C* centering of the crystal.

For comparison with previous HF calculations (Hess and Saunders 1992), the energies associated with a range of inner OH positions were investigated (Fig. 4). In these calculations, only the OH angles relative to the adjacent Al-O-Al plane were evaluated. The two adjacent Al-O-H angles have values of 107.4 and 107.0°, respectively, in the geometry-optimized structure and values of 109.1 and 109.5° in the refined structure of Bish (1993). The OH angle to the Al-O-Al plane was allowed to vary while keeping the O-H bond distance and the rest of the kaolinite structure constant. The energy minimum for this

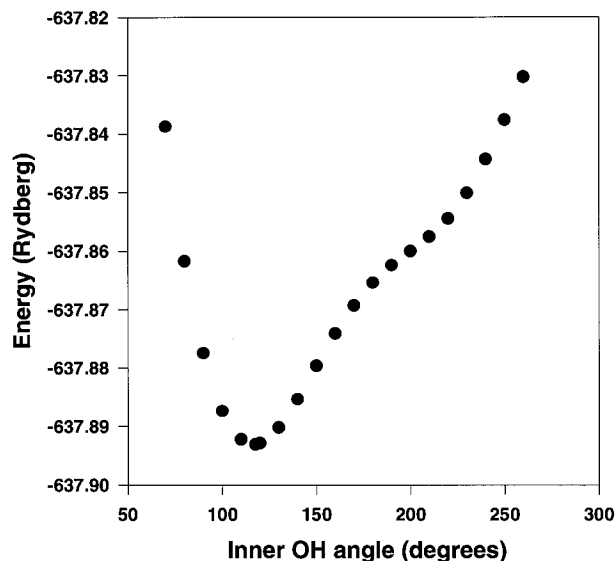


FIGURE 4. Plot of the LDF-based energy vs. inner OH angle for kaolinite. The inner OH angle is that between the inner OH and the adjacent Al-O-Al plane. See text for more detail.

calculation corresponds to an angle of 117.7°. The corresponding angle is 121.0° in the experimental structure (Bish 1993). Decreasing this angle (i.e., insertion of the proton into the Al octahedral layer) produces a rapid increase in the total converged energy. Increasing this angle also increases the total LDF energy, but in addition it produced an inflection point centered near 200°. The presence of this inflection point will be discussed in the next section.

Finally, the calculated neutron powder diffraction intensities based upon coordinates from the energy-optimized and observed (Bish 1993) structures are in excellent agreement (Fig. 5). The calculated diffraction pattern for kaolinite was generated from the unit cell obtained for the all-atom LDF optimization. The Diffraction software (Molecular Simulations Inc.) using a neutron wavelength of 1.91 Å provided Gaussian-shaped diffraction peaks in the range 6–115° 2θ. All major, and almost all minor, peak positions and their relative intensities are comparable for both structures. In a similar fashion, we examined the X-ray diffraction pattern associated with the LDF-based structure. No peaks violating *C1* symmetry were observed at 9.9° or within the range 15.5–19.0° 2θ. In contrast, the *P1*-based kaolinite structure of Young and Hewat (1988) produced significant diffraction intensities in these forbidden 2θ regions, although none is observed in the experimental data obtained for the Keokuk kaolinite (Bish 1993). These results support the conclusions of Bish (1993) that the kaolinite structure can be characterized by a crystal lattice that is nonprimitive and possesses *C* centering. The most convincing aspect of these results is that our LDF calculations were performed on a unit cell with *P1* symmetry (no unit-cell symmetry), which

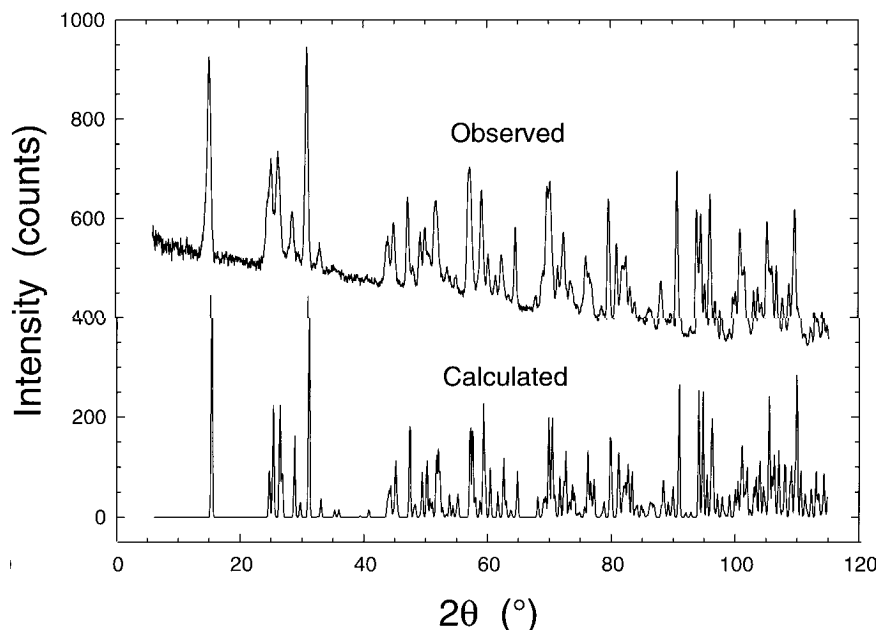


FIGURE 5. Comparison of neutron powder diffraction patterns obtained for the Keokuk kaolinite (observed) with that calculated for the LDF-optimized kaolinite structure. The difference in intensities between the two patterns is related to the background counts associated with the neutron diffraction experiment. No background correction was made so as to preserve the offset between patterns.

ultimately energy optimized (regularized) to the higher symmetry $C1$ unit cell.

DISCUSSION

The results in Table 1 demonstrate that the LDF molecular orbital method can reproduce the general features of kaolinite. The average calculated Si-O bond distance of 1.632 Å is in good agreement with that observed in the crystal (1.615 Å) and in excellent agreement with the HF result (1.629 Å) using a comparable level of basis set. Differences between the calculated and experimental values might reflect either a structural relaxation in the basal Si-O bonds because of electronic delocalization within the homogeneous Si-O network or to soft constraints used in the Rietveld refinement. The latter possibility could be tested by using different starting values for the apical and basal Si-O bonds in future refinements.

Trends in the typical Al-O bond distances are well reproduced. On average, Al-O bond lengths are accurate within approximately 0.01 Å, and differences in particular bonds may also result from external factors such as temperature and pressure. Of course, such deviations also may be related to the assumptions of the theoretical model, in particular, to the limitation of the calculations to a constant-volume configuration.

The OH orientations in kaolinite have been the subject of the widest debate. Our results, like the previous HF results, support the general C centering and $C1$ symmetry in the pure crystal. However, our specific results for the inner H-atom-only optimization appear to differ from those obtained using a minimal STO-3G basis set (Hess and Saunders 1992), which does not reproduce molecular

structures and energies as accurately. In calculating the energies associated with rotation of the inner OH group, Hess and Saunders (1992) reported a “broad transition state” between 190 and 220°. In our results (Fig. 4), an inflection point occurs over this angular range, but no minimum is observed. Analysis of the data suggests that this lowering in the rate of change in the total energy with respect to inner-OH position occurs because of interaction of the inner H atom (OH...O distance = 2.5 Å) with a nearby basal O atom. This interaction distance is similar to that found for the OH group at its optimized position (see Table 2) and is also similar to the model for hydrogen bond stabilization suggested by Adams (1983).

The OH orientations in the interlayer region are also in good agreement with those found by Bish (1993) [interlayer OH positions were not optimized in the ab initio study of Hess and Saunders (1992)]. Furthermore, the calculated O-H bond lengths and hydrogen bonds correlate well with observed single-crystal infrared spectra of kaolinite (Johnston et al. 1990) that show four distinct O-H stretching frequencies at 3620, 3652, 3668, and 3695 cm^{-1} . Therefore, the calculated longer O-H bond distance is consistent with its assignment as the lowest frequency mode. The three higher frequency modes can be assigned on the basis of the observed hydrogen bonding distance; however, other factors, such as small differences in O-H bond length, may more directly influence the relative vibrational energies.

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