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Energy-Minimized Hydrogen-Atom Positions of Kaolinite

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Abstract

The H-atom positions within fixed non-H-atom structures of kaolinite have been determined using energy-minimization procedures. Our model treats all H-atom interactions as electrostatic except the intramolecular hydroxyl term which is described using a coulombic subtracted offset Morse potential. All inner-surface hydroxyl groups are found to point almost perpendicular to the layers and therefore appear to be involved in interlayer hydrogen bonding. The orientation of the inner hydroxyl is found to be directed towards the octahedral vacancy.

1. Introduction

The neutral 1:1 layers of kaolinite are held together by long-range interlayer hydrogen bonds. Although the crystal structure of the material, excepting the hydrogen positions, has been known reasonably well for a number of years from X-ray powder diffraction (Brindley & Nakahira, 1958; Brindley & Robinson, 1945, 1946) and electron diffraction techniques (Zvyagin, 1960), the positions of the H atoms are somewhat uncertain and remain controversial. It is this uncertainty which provided the motivation to study kaolinite using our energy-minimization techniques.

2. Historical background

A number of techniques have been used to locate the H atoms and understand the hydrogen bonding in kaolinite. First, infrared absorption spectroscopy has been widely employed in studying the orientations of

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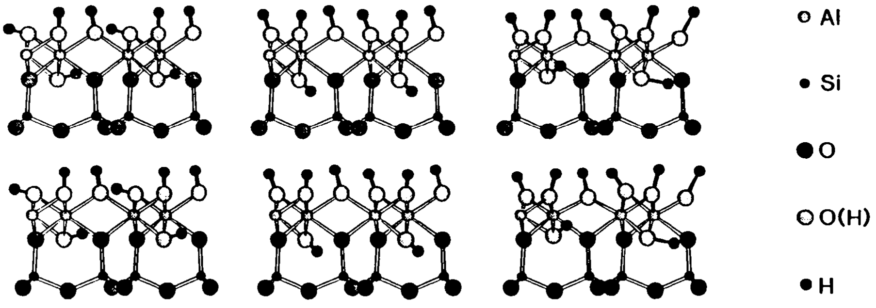
hydroxyls in kaolinite and its polytypes. A number of infrared studies have described all the *inner-surface* hydroxyl hydrogens as being involved in interlayer hydrogen bonding with the basal oxygens of the adjacent layer (Farmer, 1964; Farmer & Russell, 1964). Other IR studies report that only some of the *inner-surface* hydroxyls are involved in hydrogen bonding (Serratosa, Hidalgo & Vinas, 1962, 1963; Wolff, 1963; Ledoux & White, 1964; Wada, 1967; Kukovsky, 1968, 1969). Contrasting descriptions of the orientations of the *inner* hydroxyls using IR absorption spectroscopy have also been published. It has been suggested that the *inner* hydroxyl groups point almost perpendicular to the kaolinite layer and are directed towards the ditrigonal cavity of the tetrahedral sheet (Serratosa, Hidalgo & Vinas, 1962, 1963; Wolff, 1963). Alternative orientations have proposed that the *inner* hydroxyl groups point towards the vacant octahedral site (Ledoux & White, 1964). The contrasting interpretations of IR spectra suggest that other approaches may be needed for unambiguous elucidation of hydroxyl orientations in kaolinite.

Electrostatic calculations have been used to generate minimum-energy hydroxyl orientations in kaolinite and its polytypes (Giese, 1973; Giese & Datta, 1973). The technique was justified by the authors from the results of previous theoretical calculations which showed the hydrogen-bond interaction to be predominantly electrostatic (Coulson & Danielsson, 1954), and the interlayer forces in kaolinite to be primarily electrostatic (Cruz, Jacobs & Fripiat, 1972). The model of Giese & Datta (1973) employed formal charges on all atoms and held fixed the non-H atoms at the positions in *C*1 symmetry determined from previous studies (Zvyagin, 1960). The intramolecular O—H distance was also held fixed at 0·97 Å, while its orientation was allowed to vary. This approach, therefore, assumes the non-H positions of Zvyagin are correct and all intramolecular O—H bonds are 0·97 Å. The H-atom positions of Giese & Datta (1973), within the non-H structure of Zvyagin (1960), are shown in Fig. 1(*a*). Two of the three *inner-surface* hydroxyl groups are orientated normal to the kaolinite layer, and point towards the basal oxygens of the adjacent layer, indicating the formation of interlayer hydrogen bonds. The orientation of the third *inner-surface* hydroxyl points nearly parallel to the layers and is somewhat more difficult to interpret, as it appears not to be involved in interlayer hydrogen bonding. Calculations from IR spectra reported a similar arrangement of *inner-surface* hydroxyl groups (Wieckowski & Wiewiora, 1976). However, using a model of bent, rather than linear hydrogen bonds, the authors describe the third hydroxyl as participating in a declining interlayer hydrogen bond of very low energy.

The *inner* hydroxyl is shown to be directed towards the vacant octahedral site. Giese & Datta (1973) rationalized their orientation of the *inner* hydroxyl in terms of the repulsive forces acting on the hydrogen due to the octahedral and tetrahedral cations, with a minor stabilizing component arising from neighbouring O atoms. In order to maximize the Al—H distance, the hydroxyl group would be directed away from the octahedral sheet towards the ditrigonal cavity. Opposing this is the repulsion from the tetrahedral cations which are further away but more numerous and of higher charge. The resulting *inner* hydroxyl orientation therefore represents the balance between these two types of repulsions, and consequently points towards the vacant octahedral site.

More recently a powder neutron diffraction study (Adams, 1983) using the same non-H *C*1 framework of Zvyagin (1960) reported all three *inner-surface* hydroxyl groups to be directed normal to the kaolinite layer (see Fig. 1*b*) and therefore involved in hydrogen bonding. In contrast to the work of Giese & Datta (1973), Adams (1983) found the *inner* hydroxyl not to be directed towards the vacant octahedral site, but instead towards the ditrigonal cavity of the tetrahedral sheet.

In a combined X-ray and neutron diffraction study (Suitch & Young, 1983) a new structure of kaolinite in *P*1 symmetry was reported, see Fig. 1(*c*).



(*a*) Giese & Datta (1973) (*b*) Adams (1983) (*c*) Suitch & Young (1983)

Fig. 1. H-atom positions in kaolinite – previous work.

The authors refined all the atom positions and found that those of the non-H atoms, except the hydroxyl oxygens, were not significantly different from the atomic positions reported in *C*1 symmetry by Zvyagin (1960). It was the hydroxyl oxygen and hydrogen positions which were responsible for the removal of the *C*-centred symmetry. The structure in *P*1 symmetry therefore contains six independent *inner-surface* and two independent *inner* hydrogen positions. All six *inner-surface* hydroxyls point almost perpendicular to the kaolinite layer and are therefore involved in hydrogen bonding. The two *inner* hydroxyls, which are no longer coupled by symmetry, point in markedly different directions. One hydroxyl group is directed towards the octahedral vacancy as in the work of Giese & Datta (1973), while the other hydroxyl points towards the ditrigonal cavity as reported in the neutron study of Adams (1983). The orientations of the *inner* hydroxyls reported by Suitch & Young (1983), have, however, been questioned, as they appear not to be consistent with interpretations of NMR data (Thompson, 1984) and electron diffraction data (Thompson & Withers, 1987; Thompson, Fitzgerald & Withers, 1989). The model of Suitch & Young (1983) has also been described as incompatible with observed IR data (Brindley, Kao, Harrison, Lypsicas & Raythatha, 1986). Brindley *et al.* suggest that if the Suitch & Young (1983) structure were correct, then two *inner*-hydroxyl vibration bands or a single broad band would be observed instead of the single sharp band. Such criticism prompted yet another neutron diffraction study (Hewat & Young, 1987). After refining all atomic positions, the above authors also concluded the symmetry of kaolinite to be *P*1, with hydroxyl orientations similar to those reported by Suitch & Young (1983). Again, most non-H-atom positions were found to be consistent with *C* centring.

In view of the growing controversy as to whether kaolinite is *C* centred or primitive, a further diffraction study, using X-rays was performed (Bish & Von Dreele, 1989). As pointed out by Bish & Von Dreele (1989), there appears to be no obvious crystal chemical explanation as to why the orientations of the *inner* hydroxyl atoms should be different when all other atoms in the structure obey a *C*-centring symmetry. Moreover, Bish & Von Dreele (1989) questioned the reliability of the structures of Suitch & Young (1983) and Hewat & Young (1987) on the grounds of unrealistic bond lengths. The non-H structure reported by Bish & Von Dreele (1989) was successfully refined in space group *C*1. It is the highest precision determination of kaolinite to date [having e.s.d.'s about 20% of the value of those reported by Hewat & Young (1987)], and is generally accepted as the most reliable non-H-atom structural determination of kaolinite. The authors illustrated the importance of using a good starting model for the refinement procedure. When Bish & Von Dreele (1989) used the Suitch & Young (1983) structure as a starting model, their refinements converged to give a structure with an *R* factor of 18%, that was similar to the refinements of Suitch & Young (1983), and Hewat & Young (1987). That is, the structure exhibited *P*1 symmetry and contained a number of unrealistic bond lengths. In contrast, refinements using a starting model generated a by distance least-squares (DLS) procedure gave rise to a *C*-centred structure, with an *R* factor of 12%, that did not contain any unrealistic bond lengths. Bish & Von Dreele (1989) believe the refinements of Suitch & Young (1983) and Hewat & Young (1987) are likely to represent false-minimum structures for both X-ray and neutron data.

Thus, although the work of Bish & Von Dreele (1989) has clarified the symmetry and determined more accurately the non-H positions of the kaolinite structure, the problem of locating the H atoms remains. As yet diffraction and spectroscopic techniques have not been able to determine unambiguously the orientation of *inner* hydroxyl groups in kaolinite. Using energy-minimization procedures we have attempted to extend the theoretical work of Giese & Datta (1973).

3. Computational details

Unlike the earlier work of Giese & Datta (1973) our method applies full energy minimization to the H-atom positions. The details of our calculations are as follows.

3.1. *Description of* H-*atom interactions*

All interactions involving the H atoms are treated as electrostatic except the intramolecular hydroxyl interaction which is described using a coulombic subtracted offset Morse function (Saul, Catlow & Kendrick, 1985),

$$U_{\mathrm{O-H}} = D^{e}_{\mathrm{O-H}}\{1 - \exp[-\beta_{\mathrm{O-H}}(r_{\mathrm{O-H}} - r^{e}_{\mathrm{O-H}})]\}^{2} - q_{\mathrm{O}}q_{\mathrm{H}}r^{-1}_{\mathrm{O-H}}$$

where $D^{e}_{\mathrm{O-H}}$ is the hydroxyl bond energy, which can be directly related to parameters determined from infrared spectroscopy. $r_{\mathrm{O-H}}$ and $r^{e}_{\mathrm{O-H}}$ are the observed and equilibrium hydroxyl bond distances, respectively.

Full formal charges are assigned to all atoms, except those of the hydroxyl species ($q_{\mathrm{O}} = -1{\cdot}426$ and $q_{\mathrm{H}} = 0{\cdot}426$), whose sum equals minus one. Owing to their long-range nature, the electrostatic interactions are treated using the Ewald transformation (Ewald, 1921; Tosi, 1964).

The intramolecular hydroxyl interaction had been calculated *ab initio* and parameterized by Saul, Catlow & Kendrick (1985) so as to reproduce the structure of α-NaOH and the dipole moment of the hydroxyl group ($D^{e}_{\rm O-H} = 7{\cdot}0525$ eV, $\beta_{\rm O-H} = 2{\cdot}1986$ Å^{-1} and $r^{e}_{\rm O-H} = 0{\cdot}9485$ Å). The coulombic subtracted offset Morse function acts up to a distance of 1·2 Å; at larger separations the (O)H—O interactions are treated as electrostatic.

3.2. *Minimization procedure*

The computer code *THBREL* (Leslie, 1991) was used to energy minimize the H-atom positions. The minimization procedure employs the Newton–Raphson method, and therefore requires calculation of the second derivatives of the lattice energy with respect to atomic positions. The program allows full energy minimization of all structural parameters. In the present study, however, only the H-atom coordinates were varied.

3.3. *Structural model*

In order to investigate the influence of the non-H atom positions on the energy-minimized H-atom positions, we use the non-H-atom structures of Zvyagin (1960), Suitch & Young (1983) and Bish & Von Dreele (1989). However, we emphasize that the relaxed H-atom positions corresponding to the fixed non-H structure of Bish & Von Dreele (1989) will be the most reliable. We have also used different H-atom positions based on those of Giese & Datta (1973), Adams (1983) and Suitch & Young (1983) as initial configurations, since relaxation to the same configuration would suggest the location of a global minimum.

Table 1. *Unit-cell dimensions, non-*H*-atom positions (Bish & Von Dreele) and energy-minimized* H*-atom positions of kaolinite*

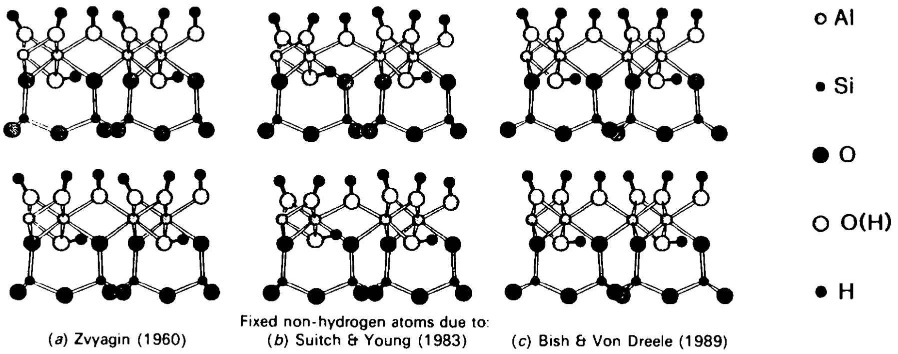
Space group $C\bar{1}$ [in the setting of Brindley & Robinson, (1946)], unit-cell dimensions are $a = 5{\cdot}1554$, $b = 8{\cdot}9448$, $c = 7{\cdot}4048$ Å, $\alpha = 91{\cdot}700$, $\beta = 104{\cdot}862$, $\gamma = 89{\cdot}822°$.

	x	y	z
Si(1)	0·9942	0·3393	0·0909
Si(2)	0·5064	0·1665	0·0913
Al(1)	0·2971	0·4957	0·4721
Al(2)	0·7926	0·3300	0·4699
O(1)	0·0501	0·3539	0·3170
O(2)	0·1214	0·6604	0·3175
O(3)	0·0	0·5	0·0
O(4)	0·2085	0·2305	0·0247
O(5)	0·2012	0·7657	0·0032
O(H1)	0·0510	0·9698	0·3220
O(H2)	0·9649	0·1665	0·6051
O(H3)	0·0348	0·4769	0·6080
O(H4)	0·0334	0·8570	0·6094
H(1)	0·1492	0·0664	0·3331
H(2)	0·0768	0·1742	0·7363
H(3)	0·0353	0·5068	0·7392
H(4)	0·0558	0·8175	0·7374

4. Results and discussion

The different initial H-atom positions generally relaxed to the same minimum energy configuration, for a particular fixed non-H structure. The most stable H-atom positions within the three fixed non-H-atom structures are shown in Fig. 2. Despite the differences in the non-H positions, the energy minimized hydroxyl orientations are similar for the three structures. All the *inner-surface* hydroxyl groups point almost perpendicular to the kaolinite layers and are therefore involved in interlayer hydrogen bonding. This is in contrast to the electrostatic calculations of Giese & Datta (1973), but is consistent with the previous diffraction studies of Adams (1983), Suitch & Young (1983) and Hewat & Young (1987), see Fig. 1. The *inner* hydroxyl groups are generally directed towards the octahedral $M(1)$ vacant sites, as in the work of Giese & Datta (1973). This is, of course, in contrast to the diffraction studies discussed above.

The relaxed H-atom positions predicted using the C-centred structures of Zvyagin (1960) and Bish & Von Dreele (1989) do obey C-centring symmetry. However, those determined using the $P1$ structure of Suitch & Young (1983) are not related by symmetry. This is particularly apparent when the orientations of



(*a*) Zvyagin (1960)

Fixed non-hydrogen atoms due to:
(*b*) Suitch & Young (1983)

(*c*) Bish & Von Dreele (1989)

Fig. 2. H-atom positions in kaolinite – this work.

Table 2. *Selected bond lengths and angles involving* H *atoms in kaolinite*

Internal O(H)—H distances (Å)		Interlayer hydrogen-bond distances (Å)		Interlayer hydrogen-bond angles (°)	
O(H1)—H(1)	0·9934				
O(H2)—H(2)	0·9948	H(2)—O(4)	2·1145	O(H2)—H(2)—O(4)	161·74
O(H3)—H(3)	0·9996	H(3)—O(3)	1·9882	O(H3)—H(3)—O(3)	161·96
O(H4)—H(4)	1·0001	H(4)—O(5)	1·9862	O(H4)—H(4)—O(5)	163·85

the *inner* hydroxyl groups are considered, although the difference is far less marked than reported in the diffraction study by Suitch & Young (1983).

The coordinates of the H atoms relaxed using the non-H structure of Bish & Von Dreele (1989), together with the non-H coordinates of the above-mentioned structure, are given in Table 1. Selected bond lengths and bond angles involving H atoms are presented in Table 2. The intramolecular hydroxyl O—H bond lengths are approximately 1 Å, the interlayer hydrogen bonds are approximately 2 Å, and interlayer hydrogen bond angles about 160°. These values are chemically realistic and consistent with those reported in previous studies of kaolinite (Adams, 1983; Suitch & Young, 1983; Hewat & Young, 1987), and the kaolin mineral polytype dickite (Adams & Hewat, 1981). We believe our predicted H-atom positions may provide a suitable starting model, in conjunction with the non-H positions of Bish & Von Dreele (1989), for the future analysis of neutron diffraction data which is needed to locate reliably the H atoms experimentally.

5. Concluding remarks

Using our electrostatic model for hydrogen bonding we conclude that in kaolinite all *inner-surface* hydroxyls are involved in interlayer hydrogen bonding and that the *inner* hydroxyls are orientated towards the vacant octahedral sites. Clearly the orientation of the hydroxyl is dependent on the positions of the surrounding atoms, which vary for different structural refinements. Therefore a full energy-minimization simulation, to relax both the H and non-H positions, is desirable. However, in order to perform such an energy-minimization simulation the description of hydrogen bonding needs to be extended. Two possible approaches include the use of multipole moments, and the introduction of a non-electrostatic contribution to augment the dominantly electrostatic model of the hydrogen bond. With models of this type it should be possible to undertake an accurate prediction of the full structure of the material using energy-minimization techniques.

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