INFRARED STUDIES OF THE HYDROXYL GROUPS IN INTERCALATED KAOLINITE COMPLEXES*

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ABSTRACT

EXPANSION of kaolinite with potassium acetate reduces the intensity of the 3695 cm^{-1} absorption band and causes the appearance of an additional one at 3600 cm^{-1}. Subsequent deuteration with D_2O vapor shifts the 3695 cm^{-1} and 3600 cm^{-1} absorption bands to 2725 cm^{-1} and 2650 cm^{-1} respectively. The hydroxyls absorbing at 3620 cm^{-1} do not interact with the acetate anion and do not readily exchange with D_2O vapor.

Deuteration of expanded hydrazine–kaolinite complex at room temperature shifts the infrared stretching frequencies 3695, 3670, 3650 and 3620 cm^{-1} to 2725, 2710, 2698 and 2675 cm^{-1} respectively. The OH-OD exchanges for the hydroxyls absorbing at 3695, 3670 and 3650 cm^{-1} are 67, 60 and 62 per cent respectively, and for the 3620 cm^{-1} only 22 per cent. The 3695, 3670 and 3650 cm^{-1} absorption bands are correlated predominantly to inner-surface hydroxyls and the 3620 cm^{-1} to inner hydroxyls located below the holes in the silica tetrahedral layer.

The ν(OH) absorption bands at 3695, 3670 and 3650 cm^{-1}, and the ν(OD) at 2725, 2698, and 2675 cm^{-1} are pleochroic, whereas the 3620 cm^{-1} absorption band is non-pleochroic. The direction of the dipole moment change of OH groups absorbing at 3695 cm^{-1} and 3670 cm^{-1}, and of OD groups absorbing at 2725 cm^{-1} and 2698 cm^{-1}, is nearly at right angles to the basal plane (001); for the 3650 cm^{-1} and 2675 cm^{-1} bands, the angle is large, but less than 90°. The inner hydroxyls absorbing at 3620 cm^{-1} have their dipole moment change inclined at about 15° to the " ab " cleavage plane.

A comparison of the ν(OH) and ν(OD) absorption intensities for the film rotated 45° and normal to the infrared incident radiation shows that the pleochroism is more intense in the ν(OD) region than in the ν(OH) region. This indicates that partial deuteration perturbs the direction of dipole moment change of the " hydrogen bond " with respect to the initial orientation prior to deuteration; the net result is the formation of larger angles between the direction of the OD dipole moment changes and the basal plane (001) than existed for OH prior to deuteration.

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INTRODUCTION

INFRARED spectroscopy has found an increasing number of applications in the field of mineral research. The attention given in recent years to the infrared study of clay minerals has improved our understanding of their structural properties. However, there continue to be differences in opinion about the correlation between the ν(OH) stretching modes of vibration in the high frequency region (3750 to 2500 cm^{-1}) and the OH sites and their bond-axis orientations in the clay lattices.

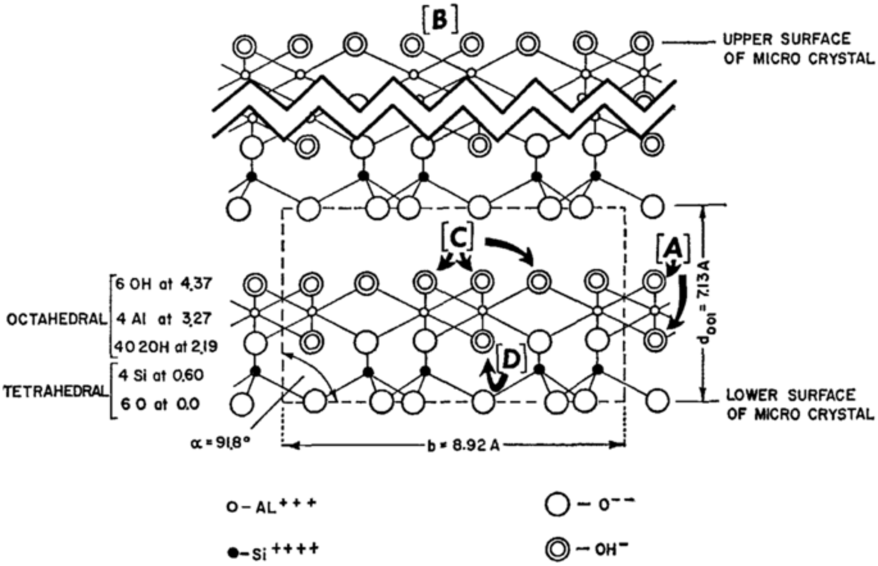

FIG. 1. Projection of the structure of kaolinite on the (100) plane showing the stacking of successive layers in a micro crystal (After Brindley). [A] and [B] indicate " outer hydroxyls "; [C] designates " inner-surface hydroxyls "; [D] indicates " inner-hydroxyls ".

Most attempts to correlate the ν(OH) stretching frequencies of kaolinite to corresponding OH lattice sites have been based entirely on the ideal structural model of kaolinite. This approach is hazardous because the structure of kaolinite cannot be studied by the X-ray single crystal methods, and, consequently, it cannot be refined beyond the idealized arrangement.

In the present work we attempted to produce frequency shifts by selectively deuterating the OH groups of expanded kaolinite according to the accessibility of the sites for exchange reaction, and also to induce perturbations of the ν(OH) stretching frequencies by promoting interaction between the lattice OH groups of kaolinite and intercalated substances containing structural groups susceptible to form hydrogen bonding. Therefore, the correlation between the ν(OH) frequencies and the OH lattice sites will be based on direct evidences obtained from band shifts and perturbations and not on inference of O–H . . . O distances in an ideal structural model of kaolinite.

There have been several attempts to associate absorption bands appearing in the OH stretching region (3750 to 3000 cm^{-1}) with structural OH groups in the lattice of kaolinite.

The structure of kaolinite is represented by the (100) projection shown in Fig. 1. The terminology used to designate the OH groups in the kaolinite model is as follows: " outer hydroxyls " are indicated by [A] and [B]; " inner-surface hydroxyls " are designated by [C]; " inner hydroxyls " are marked [D].

Roy and Roy (1957) tested the assumption made by Auskern and Grimshaw (1955) and Wadsworth, Mackay and Cutler (1955) that the doublet in the absorption band of kaolinite in the 3700 cm^{-1} region corresponds to " inner " and " outer " hydroxyls in the kaolinite structure. Roy and Roy used the KBr preparatory technique and observed two absorption maxima for kaolinite at 3705 and 3665 cm^{-1} and a shoulder at 3450 cm^{-1}. Assuming that deuteration would replace, first, the proton of outer OH followed by the substitution of the inner OH, they attempted the isotopic exchange. However, as deuteroxyls substituted for hydroxyls the maxima decreased, maintaining their original intensity ratios, and the OD frequencies increased according to a similar intensity pattern. This was considered as evidence that the major absorption frequencies cannot be correlated with the inner and outer hydroxyls since the ν(OH) band corresponding to outer OH groups should diminish and the ν(OD) band related to outer OH groups should increase more rapidly than the inner counterparts. It was also observed that the 3450 cm^{-1} absorption band did not preferentially decrease as was expected if this were due to absorbed H_2O. The persistence in the sample heated to above 300°C of the 3450 cm^{-1} frequency was claimed to result from hydrogen-bonded hydroxyls in the structure.

Van der Marel and Zwiers (1958) have studied kaolinite mounted in KBr pellets and observed four distinct OH absorption bands. They emphasized the correspondence of four OH absorption bands (3698, 3660, 3630 and 3440 cm^{-1}) to four different locations of the OH groups in Gruner's model of kaolinite. The absorption band of highest frequency was assigned to the structural OH farthest removed from neighboring oxygens and the decreasing frequencies were correlated according to the proximity of the OH groups to the oxygens. Van der Marel and Zwiers arrived at the following suggestions:

1. The free OH groups situated at the sides of the crystals and at their surface of fractures caused the absorption band at 3698 cm^{-1}.
2. The OH groups situated at the surface of the micro crystals and bonded to the external octahedral layer produced the absorption band at 3660 cm^{-1}.
3. The 3630 cm^{-1} absorption band was credited to the OH groups within the octahedral layer, i.e. in the plane common to the octahedral and the tetrahedral layers.

4. The 3440 cm^{-1} absorption band was due to OH groups situated at the surfaces between the neutral kaolinite layers, i.e. the OH groups located within the micro crystals on the surface of the octahedral sheets opposite to tetrahedral oxygens of the adjacent 1 : 1 unit.

Fripiat and Toussaint (1960) examined oriented clay films of kaolinite and observed only three transmission minima at 3700, 3663 and 3627 cm^{-1}. In this work, the absence of the absorption bands at 3450 and 3440 cm^{-1} observed by Roy and Roy (1957), and Van der Marel and Zwiers (1958) respectively indicates that these absorption bands were due to hygroscopic water in the KBr pellet itself and not to lattice hydroxyls.

An attractive interpretation of the infrared spectrum of Schuylkill dickite was advanced by Newnham (1960). The mineral was mulled in Nujol and mounted between NaCl plates. Newnham observed four absorption bands located at 3700, 3644, 3617 cm^{-1}. Using his data obtained from the X-ray Fourier synthesis of the single crystal of dickite and the correlation curve between O–H . . . O distances and the υ(OH) frequencies as expressed by Nakamoto *et al.* (1955), Newnham arbitrarily associated the 3617 cm^{-1} frequency with $(O{-}H)_2 \ldots O_1 = 2.97$ Å, $(O{-}H)_4 \ldots O_2 = 2.94$ Å and the 1821 cm^{-1} frequency with $(O{-}H)_1 \ldots (O{-}H)_3 = 2.36$ Å. The proposed model placed the hydrogen atoms of $(OH)_2$, $(OH)_3$ and $(OH)_4$ on long hydrogen bonds that connect the hydroxyl groups to their closest neighbors in the adjacent kaolinite layer: the $(OH)_1$ was placed within the octahedral layer, i.e. in the plane common to tetrahedral and octahedral sheets. The $(OH)_1$ was said to function primarily as a free hydroxyl group, but its hydrogen interacts with the oxygen of the $(OH)_3$ along the shared edge of two octahedra to account for the weak absorption band at 1821 cm^{-1}. In other words, Newnham associated the internal OH with the band at 3700 cm^{-1} and assigned the absorption bands 3644 and 3617 cm^{-1} to the interlayer OH located at 3.12 and 2.95 Å respectively from opposite oxygens.

Serratosa, Hidalgo and Vinas (1962, 1963) compared the infrared spectra of an oriented kaolinite film on an Irtran window taken at different incidence angles with an unoriented specimen mounted in a KBr pellet. In the oriented specimen, the absorption band at 3695 cm^{-1} showed a marked increase in intensity with variation of the angle of incidence. Serratosa *et al.* associated the 3695 cm^{-1} absorption band with OH-bond axes showing preferred orientation with a major component perpendicular to the (001) plane. The absorption band at 3620 cm^{-1} did not show any significant change with the angle of incidence of the infrared beam; hence, the 3620 cm^{-1} absorption frequency was assigned to OH groups pointing toward the unoccupied octahedra. The latter assignment was based on the studies made by Serratosa and Bradley (1958) and Bassett (1960) in which it was observed that dioctahedral micas and clays have a nonpleochroic 3620 cm^{-1} absorption band indicative of OH groups with the proton end pointing into vacant octahedral sites. Serratosa *et al.* assigned the 3695 cm^{-1} absorption frequency to " free " OH groups located below the 6-membered open oxygen ring of the tetrahedral sheet, i.e.

in the plane common to tetrahedral and octahedral sheets. Since the 3695 cm^{-1} absorption band is the widest and the most intense and there are only two corresponding OH groups per unit cell, other OH groups had to be invoked to contribute to this absorption band. Serratosa *et al.* selected the OH groups at the surface of the layers pointing to the same tetrahedral holes of the adjacent layer. They explained the band width as resulting from two unassociated OH groups with not quite equivalent energies.

Serratosa, Hildalgo and Vinas (1963) studied the infrared spectrum of hydrated and glycerated halloysite complexes and observed a considerable decrease in the intensity of the 3695 cm^{-1} absorption band but no change in the intensity of the 3620 cm^{-1} absorption band. These results supported their assumption that OH groups located on the basal octahedral layer opposite the oxygens of the adjacent 1 : 1 unit contribute to the 3695 cm^{-1} absorption band in halloysite.

Wolff (1963) observed that kaolinite had three absorption bands at 3704, 3663 and 3635 cm^{-1}. His assignments were essentially identical to those proposed by Serratosa, Hidalgo and Vinas (1963) with the exception that OH groups located at the edges and in the fractures of plates would contribute to the intensity of the high frequency absorption band 3704 cm^{-1}.

Fripiat and Toussaint (1963) made an infrared study of the dehydroxylation of kaolinite, and, in order to explain the frequency shifts that appeared when the temperature was raised to 400°C, they formulated the hypothesis that the 3710 and 3680 cm^{-1} absorption bands correspond to OH groups on the upper octahedral layer, and that the 3620 cm^{-1} absorption band which does not change with film orientation is related to OH groups in the plane common to the tetrahedral and octahedral sheets.

TABLE 1.—ASSIGNMENTS OF THE ν(OH) STRETCHING FREQUENCIES OF KAOLINITE AND DICKITE TO LATTICE SITES REPORTED BY VARIOUS AUTHORS (FREQUENCIES IN WAVE NUMBERS, cm^{-1})

	Kaolinite[1]	Kaolinite[2]	Dickite[3]	Kaolinite[4]	Kaolinite[5]	Kaolinite[6]
		3698				
Outer OH	3705			3704$_s$		
		3660				
			3617	3663	3650	3710
Inner-surface OH	3665	3630			3670	
			3644	3704$_s$*	3695$_l$†	3680
				3704$_l$†	3695$_l$†	
Inner OH	3665	3440	3700			3620
				3635	3620	

[1] Auskern and Grimshaw, 1955. [2] Van der Marel and Zwiers, 1958. [3] Newnham, 1960. [4] Wolff, 1963. [5] Serratosa, Hidalgo and Vinas, 1963. [6] Fripiat and Toussaint, 1963.

* s = small contribution to the intensity of the absorption band.

† l = large contribution to the intensity of the absorption band.

Table 1 shows a comparison of the various assignments of the ν(OH) stretching frequencies of kaolinite and dickite to lattice sites.

EXPERIMENTAL

Kaolinite Sample

The kaolinite used in this study was commercial grade Hydrite No. 10 obtained from Georgia Kaolin Company. The d_{001} spacing is 7.13 Å and a small amount of quartz is present. The particles less than 2μ in size exist as thin flat hexagonal plates; in the larger size fractions they are found as stacks firmly bound together. The average particle size is 0.55μ; the distribution in the fraction less than 2μ is: 2.0 to $1.0\mu = 15.5$ per cent; 1.0–$0.2\mu = 40.1$ per cent and less than $0.2\mu = 8.0$ per cent. The total surface area, determined by the procedure proposed by Diamond and Kinter (1958), is 29 m^2 per g and the cation-exchange capacity is 3.1 meq per 100 g.

Preparation of Expanded Kaolinite and Deuteration

Andrew, Jackson and Wada (1960) expanded kaolinite from 7 to 14 Å simply by grinding and hydrating a mixture of potassium acetate (CH_3COOK) and kaolinite, and proposed the term "intersalation" for the phenomena of entrance of such salts between lattice layers of clay minerals. The intersalated kaolinite for our study was prepared by grinding a 1 g sample of the mineral (Hydrite No. 10, Georgia Kaolin Company) with 15 mM of CH_3COOK for 20 min in a Fisher mechanical mortar-and-pestle grinder and allowing the mixture to stand overnight in a 10 N solution of CH_3COOK. The supernatant liquid was removed by centrifugation followed by decantation, and a small portion of the sediment was dispersed in distilled water. A film specimen was immediately prepared by evaporating in a desiccator 1 ml. of suspension that had been placed on a cover glass (Corning 22 mm circle, No. 2 thickness).

The X-ray diffraction pattern of the oriented thin film, heated at 110°C, and recorded while a stream of dry nitrogen was passed through the sample chamber in order to prevent rehydration, indicated that a large proportion of the kaolinite micro crystals was expanded to 11.6 Å, although a significant amount remained in the unexpanded state at 7.13 Å. The same film specimen mounted on the cover glass was inserted as a window into a cylindrical stainless steel infrared cell with the specimen surface inside the cell. Compensation was obtained between 4000 and 2400 cm^{-1} by use of four matched windows in the reference and sample cells. The cell was filled with dry nitrogen while the infrared spectrum was being recorded.

In order to deuterate the kaolinite mineral in this experiment, the cell containing the expanded CH_3COOK–kaolinite complex was heated at 200°C for 2 hr to remove most of the H_2O molecules. The heated cell was immediately filled with D_2O vapor and the sample was allowed to cool in D_2O vapor for 1 hr.

Weiss *et al.* (1963a, 1963b) used hydrazine to expand kaolinite from 7.1 to 10.4 Å. In the present study the expanded hydrazine-kaolinite complex was prepared by dispersing a 0.1 g sample of kaolinite in 10 ml. of Eastman 95 per cent hydrazine. The suspension was shaken frequently and allowed to stand in contact 10 days at room temperature. A 1 ml. portion of the hydrazine–kaolinite mixture was pipetted on an Irtran window placed inside a desiccator, and the sample dried while the hydrazine vapor was continuously aspirated. X-ray diffraction data indicated that nearly all of the clay particles were expanded to 10.4 Å. The specimen was also used for infrared measurements.

A small portion (2 ml.) of the expanded hydrazine–kaolinite complex ($d_{001} = 10.4$ Å) was washed twice with 1 ml. D_2O at room temperature in a centrifuge; the kaolinite complex was redispersed in 3 ml. D_2O and allowed to remain in contact 30 min. A 1 ml. portion of the D_2O suspension was evaporated at 110°C on an Irtran window for infrared and X-ray measurements of the oriented deuterated clay film.

Instruments

The X-ray diffraction patterns were recorded on a General Electric XRD-5 diffractometer with a No. 2 SPG detector and a Speedomax SPG chart recorder. The diffractometer was used under the following operating conditions: copper target X-ray tube at 40 kV and 16 mA; nickel filter; goniometer scan speed 2° per min; 1° defining slit width and medium resolution Soller slit; counting range 100–5000 c/s; time constant, 2; and recording chart speed of 30 in. per hr. Rehydration was prevented by passing a stream of dry nitrogen through a sample chamber.

All the infrared absorption spectra were recorded with a double-beam infrared spectrophotometer, Perkin-Elmer Model 421. This instrument uses the optical null principle with a diffraction grating as the dispersing element and automatically records transmittance versus frequency. In the present work, the spectra were recorded at both 1 × and 5 × expansion scale, depending on the nature of the sample or the degree of resolution desired.

RESULTS

Infrared and X-Ray Spectra of Kaolinite and Potassium Acetate

The infrared spectrum of the kaolinite film mounted on an Irtran window (Fig. 2a) shows four ν(OH) stretching absorption bands at 3695, 3670, 3650 and 3620 cm^{-1}. These four absorption bands observed in the present study correspond exactly to those previously reported by Serratosa, Hildago and Vinas (1963). The 3695 and 3620 cm^{-1} absorption bands are very strong and have about the same intensity, whereas the 3650 and 3670 cm^{-1} absorption bands are much less intense. The X-ray diffraction pattern (see Fig. 5a) shows a strong reflection at 7.1 Å.

The infrared absorption spectra of a thin layer of potassium acetate crystals are shown in Fig. 2. The specimen was prepared by evaporating 1 ml. 0.02 N solution of CH_3COOK on an Irtran window placed in an oven at 110°C. The infrared spectra of the sample were recorded (1) immediately after the sample was removed from the oven, while a stream of dry nitrogen was passed over the sample to prevent rehydration (Fig. 2c) and (2) after the sample had cooled to 25°C and rehydrated in the laboratory atmosphere (Fig. 2b).

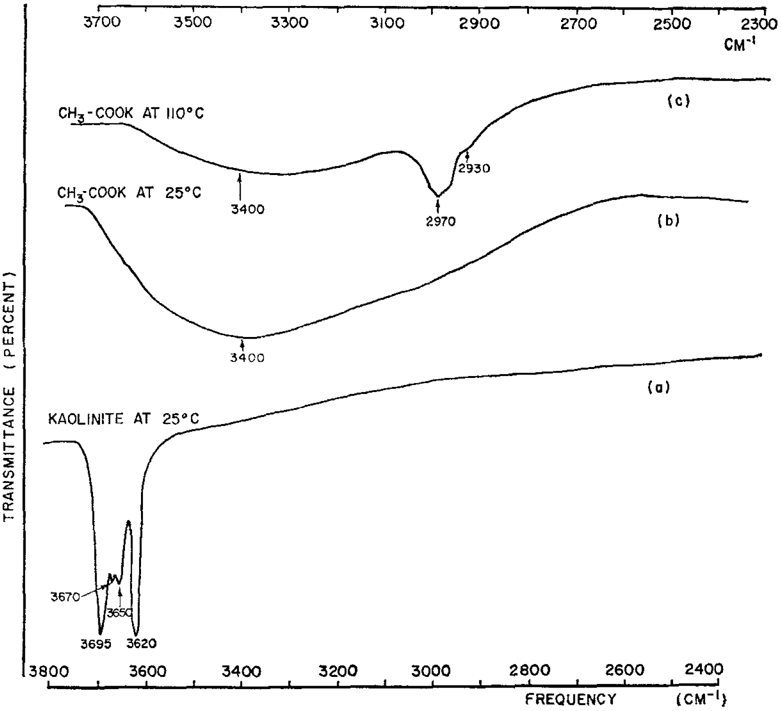

FIG. 2. Infrared spectra of (a) kaolinite at 25°C, (b) hydrated CH_3COOK at 25°C, and (c) CH_3COOK at 110°C.

The stretching vibration frequencies of the CH_3 group of the acetate anion are responsible for the absorption bands observed at 2970 and 2930 cm^{-1} (Nakamoto, 1963, p. 199).

The rehydration of the sample caused a marked increase in the intensity of the absorption band at 3400 cm^{-1} that overlapped completely the 2970 cm^{-1} absorption band. The wide absorption band with a transmittance minimum at 3400 cm^{-1} is due to the $\nu(OH)$ stretching frequencies of adsorbed water (H_2O) in the acetate salt.

Fig. 3a represents the X-ray diffraction pattern of the sample heated at

110°C and recorded while a stream of dry nitrogen was passed through the sample chamber in order to prevent rehydration. The dried sample shows two sharp reflection peaks at 9.01 and 4.50 Å, and a weak reflection at 22.68 Å. The sample chamber was removed, and the sample allowed to rehydrate in the laboratory atmosphere. Fig. 3b shows the X-ray diffraction pattern of the sample that had been rehydrated 5 min in the laboratory atmosphere; the 9.01 and 4.50 Å reflections have shifted to 10.04 and 4.97 Å respectively.

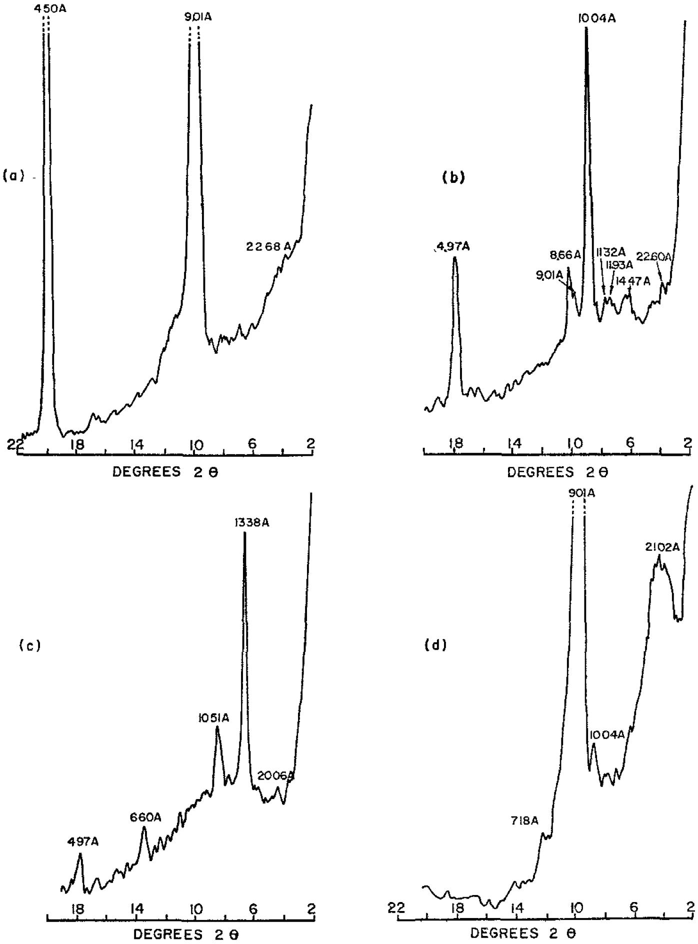

FIG. 3. X-ray diffraction patterns of CH_3COOK (a) dried 30 min at 110°C, (b) exposed 5 min at r.h. 60%, (c) exposed 10 min at r.h. 60%, and (d) reheated 10 min at 110°C.

Fig. 3c represents the sample that had rehydrated 10 min; the most intense peak occurs at 13.38 Å. Prolonged exposure of the sample in the laboratory air rapidly decreased the intensity of the 13.38 Å reflection without shifting this peak to a larger spacing. The sample was then allowed to dry 5 min at 110°C and the X-ray diffraction pattern was recorded while the sample was protected against rehydration; the 9.01 Å reflection was regenerated and an additional peak appeared at 21.02 Å (Fig. 3d).

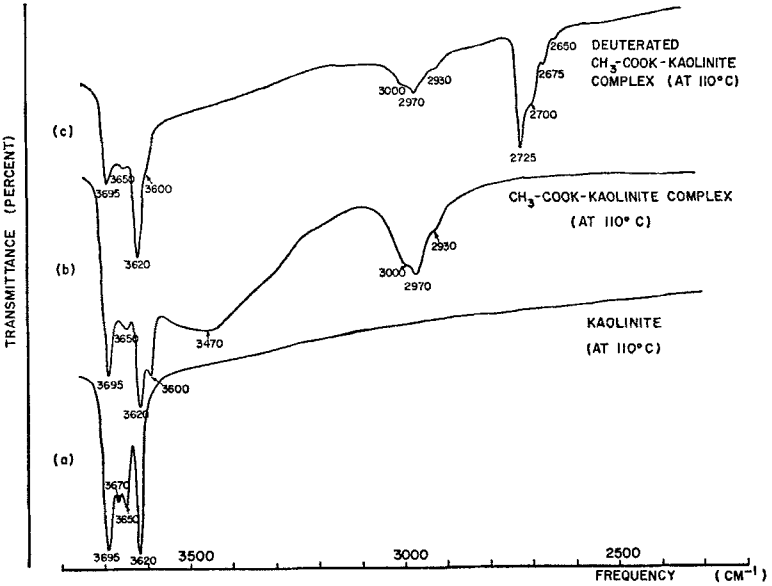

Fig. 4. Infrared spectra of (a) kaolinite at 110°C, (b) CH_3COOK–kaolinite complex at 110°C, and (c) deuterated CH_3COOK–kaolinite complex at 110°C.

A search of the literature failed to disclose any study pertaining to the crystal structure of the potassium acetate salt; however, the results described above indicate that the CH_3COOK salt has a layered structure and the hydration of the crystals causes the interlayer spacing 9.01 Å to increase by 4.37 Å.

Infrared and X-Ray Spectra of CH_3COOK–Kaolinite Complex and its Deuteration

The CH_3COOK–kaolinite complex (Fig. 4b) shows four transmittance minima in the ν(OH) stretching region at 3695, 3650, 3620, and 3600 cm^{-1}. Intersalation of kaolinite resulted in the disappearance of the 3670 cm^{-1}

absorption and the occurrence of additional bands at 3600, 3470, 2970, and 2930 cm^{-1}. The absorption intensities of the 3695 and 3650 cm^{-1} bands were considerably reduced, whereas that of the 3620 cm^{-1} absorption band was not significantly affected. The 3470 cm^{-1} frequency is attributed to remaining interlayer water molecules. The ν(CH) stretching vibration frequencies of the acetate anion are responsible for absorption at 3000, 2970 and 2930 cm^{-1}.

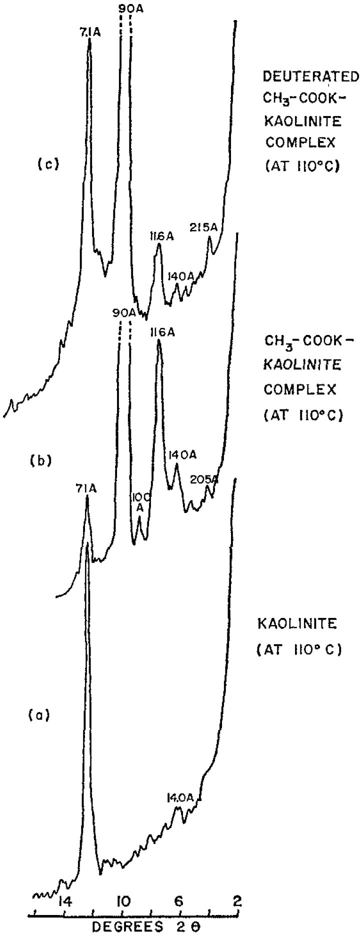

FIG. 5. X-ray diffraction patterns of (a) kaolinite at 110°C, (b) CH_3COOK–kaolinite complex at 110°C, and (c) deuterated CH_3COOK–kaolinite complex at 110°C.

In the corresponding X-ray diffraction record the peak at 11.6 Å in Fig. 5b for the CH_3COOK–kaolinite complex indicates the presence of CH_3COOK molecules in interlayer positions (Wada, 1961). When the acetate anion is situated in an interlayer position, there is a decrease in intensity of the 3695 cm^{-1} absorption band; the strong negative oxygens of the acetate anions would form hydrogen bonds with inner-surface hydroxyls, thus shifting their frequencies toward lower values. Improvement in the orientation of the clay particles would produce a similar effect, but deuteration and treatments with hydrazine show that expansion and interlayer compounds are responsible for the decrease in intensity.

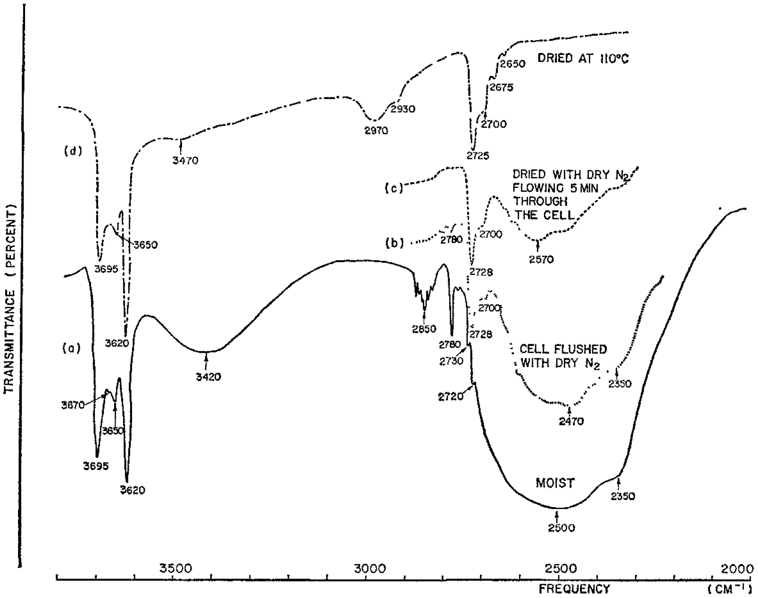

Fig. 6. Progressive drying of the deuterated CH_3COOK–kaolinite complex as revealed by infrared spectra: (a) moist, (b) cell flushed with dry N_2, (c) dried with dry N_2 flowing 5 min through the cell, and (d) dried at 110°C.

The infrared spectra of the CH_3COOK–kaolinite sample that had been exposed 1 hr to D_2O vapor were recorded while the cell was flushed with dry nitrogen gas (Fig. 6a, b and c), and finally heated at 110°C for 30 min (Fig. 6d). The infrared spectrum of the moist sample (Fig. 6a) shows a strong absorption band at 2500 cm^{-1}, which is due to the ν(OD) stretching vibration frequencies of liquid D_2O. The D_2O vapor in the cell is responsible for the rotational structure on the 2850 cm^{-1} vibrational absorption band; the 2780 cm^{-1} frequency corresponds probably to HDO gas; both absorption bands at 2850 and 2780 cm^{-1} disappear as the cell is filled with nitrogen gas.

As the sample was successively dried, the 2500 cm^{-1} absorption band decreased gradually, but a strong asymmetrical band appeared between 2750 and 2625 cm^{-1}. The absorption bands at 2725, 2700, 2675 and 2650 cm^{-1} correspond to OH-OD shifts as indicated by their stability at 110°C and by the isotopic ratios of ν(OH) : ν(OD) of 1.35.

The infrared spectrum of the deuterated CH_3COOK–kaolinite complex Fig. 4c) shows a considerable reduction in the intensity of the 3695 and 3650 cm^{-1} absorption bands and complete disappearance of the 3600 cm^{-1} absorption band. The shift of the 3695 cm^{-1} absorption band to 2725 cm^{-1} caused by the substitution of protons by deuterons has resulted in a considerable decrease in the intensity of the 3695 cm^{-1} absorption band.

Pleochroism of the ν(OH) and ν(OD) Absorption Bands

The observed intensity of an infrared absorption band depends on the angle between the direction of the alteration of the dipole moment and the direction of vibration of the radiation. If the direction of dipole moment change is parallel to the direction of " propagation " of the infrared light, no absorption takes place; if they lie at right angles to one another, maximum absorption occurs; between the two cases there is a gradual transition. Bassett (1960) has clearly described the interaction of the infrared beam with the hydroxyls of micas. We have studied the pleochroism of the ν(OH) and ν(OD) stretching frequencies of pure kaolinite, CH_3COOK–kaolinite complex and of deuterated CH_3COOK–kaolinite. Three sets of spectra were recorded with the following arrangements of the oriented clay film:

1. The oriented clay film occupied the usual position for infrared determination, i.e. at right angle to the direction of the incident infrared radiation. It is designated by $\theta = 0°$ because the film was not rotated.
2. The oriented film was rotated by 30°, ($\theta = 30°$).
3. The oriented film was rotated by 45°, ($\theta = 45°$).

Rotation of 30° and 45° of the kaolinite film in the infrared beam (Fig. 7) produced considerable increase in the intensity of the 3695 and 3650 cm^{-1} absorption bands but did not affect the intensity of the 3620 cm^{-1} absorption band. Similar results were obtained with the CH_3COOK–kaolinite film with the exception that the intensity of the 3695 cm^{-1} absorption band did not surpass that of the 3620 cm^{-1}, even for $\theta = 45°$.

Fig. 8 shows the pleochroic study of the ν(OD) absorption bands. The intensity of the 2725 cm^{-1} frequency increases considerably upon rotation of the clay film (Fig. 8a), whereas the 2700, 2675 and 2650 cm^{-1} absorption intensities are not significantly affected. Fig. 8b shows the infrared spectra in the ν(OD) region of the deuterated CH_3COOK–kaolinite sample, which had been heated at 200°C for 30 min. The heat treatment has favored more OH-OD exchange for the OH absorbing at 3620 cm^{-1}, thus increasing the intensity of the 2675 cm^{-1} absorption band. However, only the 2725 cm^{-1} absorption band was significantly dependent on the orientation of the clay film with respect to the direction of incidence of the infrared radiation.

The strong pleochroism exhibited by the 3695 and 2725 cm^{-1} absorption bands supports the OH-OD shift assignment 3695 to 2725 cm^{-1} previously based on the ν(OH) : ν(OD) ratio 1.35.

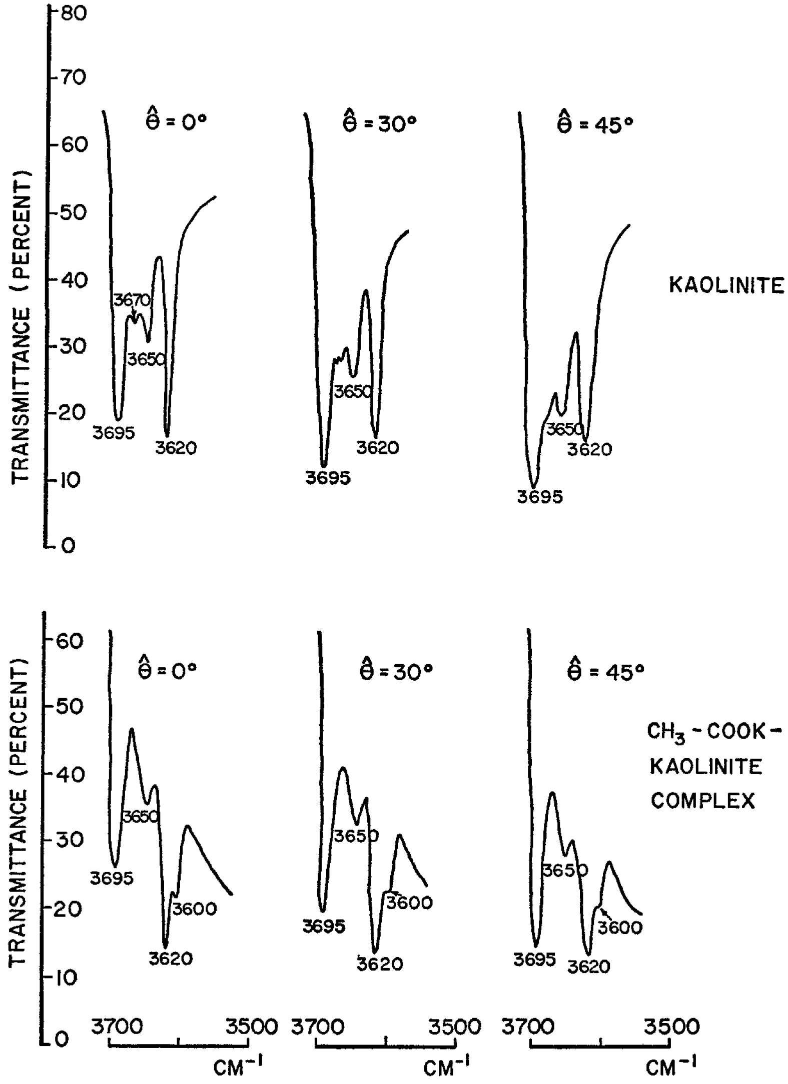

FIG. 7. Pleochroism of the ν(OH) in kaolinite and in CH$_3$COOK–kaolinite complex (θ is the angle of rotation of the clay film.)

The pleochroic effect on the natural and deuterated kaolinite films indicates that the transition moment of a large proportion of OH groups absorbing at 3695 cm^{-1} makes a right angle with the basal plane (001). The 3620 cm^{-1} absorption band that is not affected by the rotation of the clay film must correspond to OH dipoles making a low angle with the " *ab* " cleavage plane.

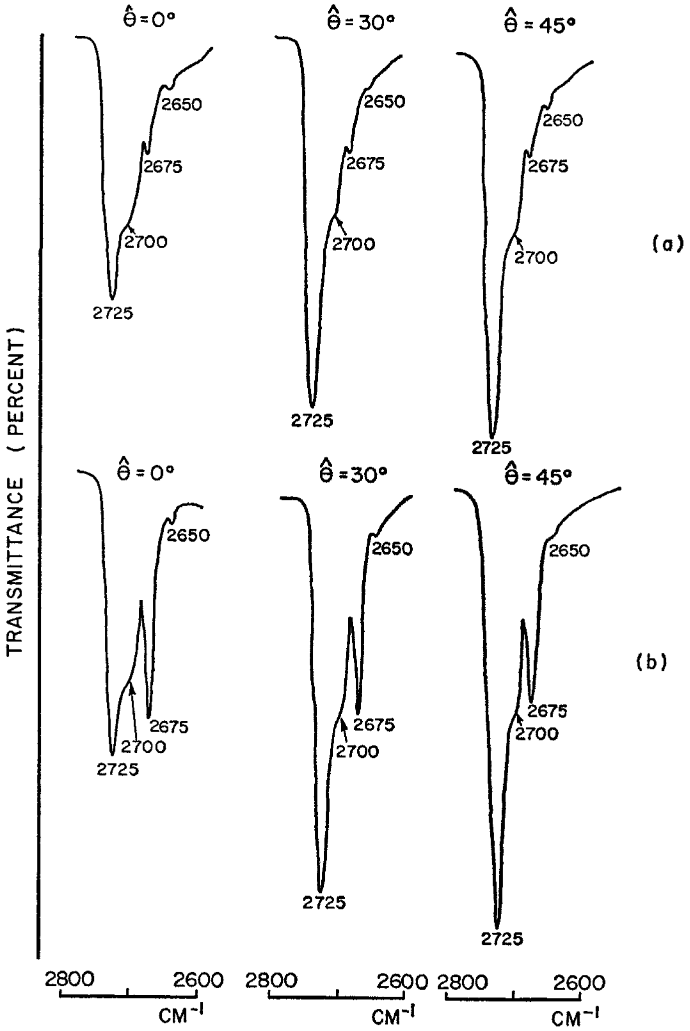

FIG. 8. Pleochroism of the ν(OD) in CH_3COOK–kaolinite: (a) heated at 110°C, and (b) heated at 200°C.

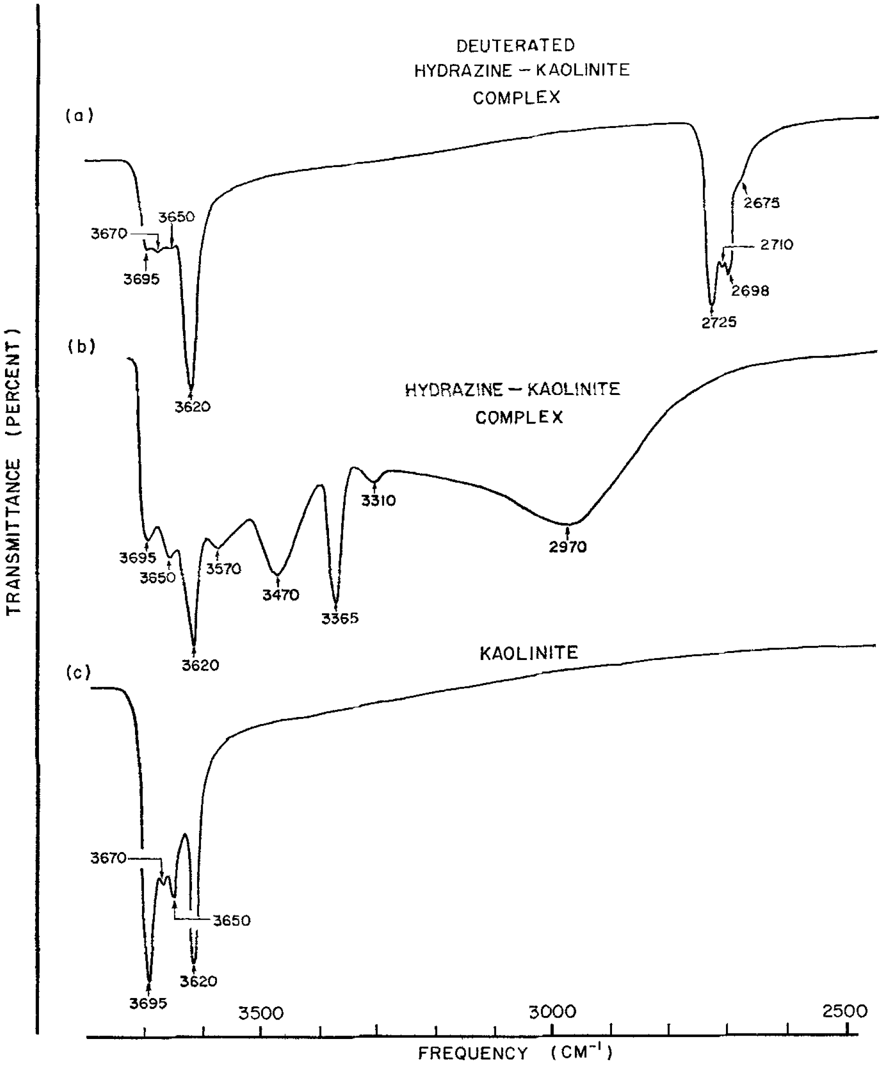

Fig. 9. Infrared spectra of (a) deuterated hydrazine–kaolinite complex heated at 110°C, (b) hydrazine–kaolinite complex heated 2 min at 110°C, and (c) kaolinite at 25°C.

Infrared Spectra of Hydrazine–Kaolinite Complex and its Deuteration

The infrared spectrum of the hydrazine–kaolinite complex dried in the desiccator at room temperature is shown in Fig. 9b. The striking features of the spectrum when compared to that of pure kaolinite (Fig. 9c) is the large reduction in the intensity of the 3695, 3670 and 3650 cm^{-1} absorption bands, and the appearance of additional bands at 3570, 3470, 3365, 3310, and 2970 cm^{-1}.

The expanded hydrazine–kaolinite complex (10.4 Å) was washed with D_2O and the spectra of oriented clay films were determined by X-ray diffraction and infrared spectroscopy. The X-ray pattern of the D_2O-treated kaolinite shows that the mineral has collapsed to its original spacing, 7.13 Å. Fig. 9 shows a comparison of the infrared spectra of natural kaolinite with the hydrazine–kaolinite complex and the D_2O-treated sample. In the infrared spectrum of natural kaolinite (Fig. 9c), four ν(OH) absorption frequencies are observed at 3695, 3670, 3650 and 3620 cm^{-1}. Both absorptions at 3695 and 3620 cm^{-1} are more intense than those at 3670 and 3650 cm^{-1}. The spectrum of deuterated kaolinite (Fig. 9a) shows a reduction in the intensity of the 3695, 3670 and 3650 cm^{-1} absorptions and the occurrence of strong bands at 2725 and 2698 cm^{-1} and weak absorptions at 2710 and 2675 cm^{-1}; the intensity of the 3620 cm^{-1} is not significantly affected by the deuteration process.

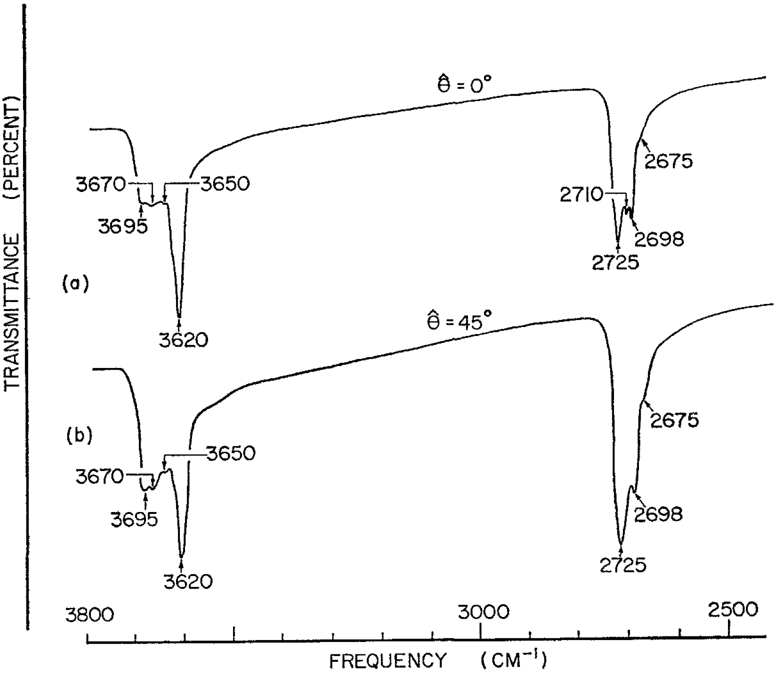

FIG. 10. Infrared spectra of deuterated kaolinite with (a) $\theta = 0°$, and (b) $\theta = 45°$.

A rotation of 45° of the deuterated kaolinite film in the infrared beam produces considerable increase in the intensity of all the absorption bands except the 3620 cm^{-1} (Fig. 10). The differences between the background line absorption and the minimum transmittance (Table 2) indicate no change at all in the intensity of the 3620 cm^{-1} absorption band. The pleochroic effect on the oriented kaolinite film indicates that the direction of the change of the dipole moment of OH groups absorbing at 3695 and 3670 cm^{-1} and of OD groups absorbing at 2725 and 2698 cm^{-1} is nearly at right angles to the basal plane (001); for the 3650 and 2675 cm^{-1} the angle is large, but less than 90°. The direction in dipole moment change of the OH groups absorbing at 3620 cm^{-1} makes a low angle with the " ab " cleavage plane.

TABLE 2.—INTENSITIES OF THE HYDROXYL AND DEUTEROXYL STRETCHING FREQUENCIES OF KAOLINITE OBTAINED FROM THE DIFFERENCE BETWEEN THE BACKGROUND ABSORPTION LINE AND THE MINIMUM PERCENTAGE OF TRANSMITTANCE (θ = ANGLE OF ROTATION, Δ = DIFFERENCE BETWEEN ROTATED AND INITIAL ANGLES)

Hydroxyl				Deuteroxyl			
ν(OH) cm^{-1}	$\theta = 0°$	$\theta = 45°$	$\Delta(45°–0°)$	ν(OD) cm^{-1}	$\theta = 0°$	$\theta = 45°$	$\Delta(45°–0°)$
3695	16.0	26.0	10.0	2725	32.5	48.5	16.0
3670	17.0	26.5	9.5	2710	—	—	—
3650	16.5	23.0	6.5	2698	27.5	37.0	9.5
3620	41.5	41.5	0.0	2675	11.5	18.0	6.5

DISCUSSION

The correlation between the intensity of the 3695 cm^{-1} absorption band and the intensity of the 7.1 Å X-ray peak of (1) the pure kaolinite, (2) the CH_3COOK–kaolinite complex and (3) the hydrazine–kaolinite complex favors the interpretation that expansion and interaction of interlayer materials with hydroxyls are the factors primarily responsible for the decrease in intensity of the 3695 cm^{-1} absorption band, and suggests that the explanation based on reorientation of clay particles must be disregarded. The strong decrease in intensity of the 3695, 3670 and 3650 cm^{-1} absorption bands indicates that the corresponding OH are highly reactive groups in the presence of interlayered potassium acetate, hydrazine or deuterium oxide molecules.

Two hypotheses are proposed to explain the decrease in intensity of the ν(OH) absorption band at 3695 cm^{-1} and the appearance of a new absorption band at 3600 cm^{-1} in the CH_3COOK–kaolinite complex. First, the inner-surface hydroxyls form weak hydrogen bonds with the acetate anion and cause the shift of the 3695 cm^{-1} to 3600 cm^{-1}. This shift resulting from hydrogen bond association is comparable with that observed for the association of phenol with carbonyl compounds and ethers. The 3600 cm^{-1} absorption band was shifted to 2650 cm^{-1} as a result of deuteration (Fig. 4c), indicating the formation of a similar bond type between the deuteroxyls and the acetate anions. The stretching vibration frequency of the CH group at 2970 cm^{-1} is still present after deuteration and indicates that protons remain in the acetate anions. Two reasons are advanced to explain the weak intensity of the 2650 cm^{-1} absorption band compared to that of the 3600 cm^{-1}: (1) the possible formation of a bond O-D . . . CD_3COOK that would vibrate at a frequency lower than 2650 cm^{-1} and be located beyond the observed range; (2) the X-ray diffraction pattern of the deuterated complex (Fig. 5c) indicates only a small portion of expanded kaolinite at 11.6 Å and a larger amount collapsed to 7.1 Å. When the intersalated complex was bathed in an excess of D_2O vapor, a large amount of interlayer CH_3COOK molecules was removed, and most of the particles collapsed to 7.1 Å on heating at 110°C. The large number of collapsed kaolinite particles would explain the strong intensity of the 2725 cm^{-1} absorption band, whereas the small proportion of expanded particles at 11.6 Å would yield a weak 2650 cm^{-1} absorption band. The second hypothesis assigns the 3600 cm^{-1} absorption band in the CH_3COOK–kaolinite complex to occluded water molecules. This is suggested by the complete disappearance of the 3600 cm^{-1} absorption band on deuteration and the shift to 2650 cm^{-1}. The weakness of the 2650 cm^{-1} absorption band would be due to the small amount of remaining occluded D_2O after the collapse of most of the clay particles to 7.1 Å. If this hypothesis is right, the decrease in intensity of the 3695 cm^{-1} absorption band would result from strong hydrogen bonding with acetate anions, causing a shift larger than 100 cm^{-1} and overlapped by the wide water band in the 3400 cm^{-1} region. A study of surface reaction of OH groups of Carbosil with dimethyl vapors (McDonald, 1958) revealed a shift of the sharp ν(OH) band located at 3750 cm^{-1} to a broad band at 3290 cm^{-1} in the silanol–ether complexes. The 460 cm^{-1} shift was interpreted as due to ether molecules approaching the silanol groups closely enough to participate in strong hydrogen bonding. Actual data on the CH_3COOK–kaolinite complex do not permit any definite conclusion whether the shift is of the order of one hundred or of a few hundred wave numbers. A close examination of the ν(COO) stretching band is necessary to find out about the magnitude of the shift. Nevertheless, it is evident that the inner-surface hydroxyls absorbing at 3695 cm^{-1} are reactive groups in the presence of an acetate salt.

The infrared spectrum of the hydrazine–kaolinite complex (Fig. 9b) shows the largest decrease in intensity of the 3695 cm^{-1} absorption band and additional absorptions at 3570, 3470, 3365, 3310 and 2970 cm^{-1}. In the infrared spectrum of hydrazine, Giguere and Liu (1952) have observed vapor absorption bands at 3280, 3314, 3325 and 3350 cm^{-1} and assigned these frequencies to $\nu(NH_2)$ stretching modes of vibration; the corresponding $\nu(NH_2)$ stretching frequencies of liquid hydrazine occurred at 3200 and 3338 cm^{-1}. However, Catalano, Sanborn and Frazer (1963) observed in the matrix isolation spectra of $NH_2NH_2 : N_2$ the following absorption bands in the $\nu(NH_2)$ stretching region: 3207, 3297, 3356 and 3390 cm^{-1}; they claimed that all the bands were due to monomeric species except the 3207 cm^{-1}. Thus, the $\nu(NH_2)$ stretching region for hydrazine extends from 3200 to 3390 cm^{-1}.

The infrared spectrum of hydrazine–kaolinite complex (Fig. 9b) shows two absorption bands at 3365 and 3310 cm^{-1} located within the range of the $\nu(NH_2)$ stretching modes of vibration of hydrazine. The strong absorption band at 3365 cm^{-1} is tentatively correlated to $\nu(NH_2)$ stretching of the intercalated hydrazine molecules. If this is correct, the intercalation of hydrazine causes the shift of the characteristic absorption bands of the liquid to a higher frequency, and this is accompanied by depolymerization of the liquid.

The large reduction in intensity of the $\nu(OH)$ absorption bands 3695, 3670 and 3650 cm^{-1} of kaolinite suggests hydrogen-bonding participation with intercalated hydrazine molecules. It is postulated that the broad band located at 2970 cm^{-1} corresponds to NH_2 groups strongly hydrogen-bonded with the hydroxylic surface of the kaolinite mineral i.e. to O—H . . . N bond. The sharpness and the high frequency of the 3365 cm^{-1} absorption band indicate hydrazine molecules not properly arranged to form hydrogen bond. The absorption band at 3470 cm^{-1} is believed to result from occluded water, but no assignment is provided for the 3570 cm^{-1}.

TABLE 3.—RATIOS OF HYDROXYL TO DEUTEROXYL STRETCHING FREQUENCIES AND PERCENTAGES OF OH–OD EXCHANGE OBTAINED FROM DEUTERATION OF THE HYDRAZINE–KAOLINITE COMPLEX

$\nu(cm^{-1})$		$\nu(OH)$	OH–OD exchange
OH	OD	$\nu(OD)$	%
3695	2725	1.3559	66.8
3670	2710	1.3542	59.6
3650	2698	1.3528	62.2
3620	2675	1.3532	22.0

In the present study, it has been shown that expansion of kaolinite with potassium acetate or hydrazine greatly facilitates the deuterium exchange with hydroxyls. The OH absorbing at 3695, 3670 and 3650 cm^{-1} are largely exchanged with deuterium oxide at room temperature, whereas the OH absorbing at 3620 cm^{-1} are less readily exchanged. This isotope exchange mechanism provides evidence for frequency shift assignments and for a correlation of the $\nu(OH)$ stretching frequencies of kaolinite to lattice sites because it selectively deuterates the hydroxyls according to their accessibility for exchange reaction. The high percentages of the OH-OD exchange at room temperature (Table 3) for the hydroxyls absorbing at 3695, 3670 and 3650 cm^{-1} suggest that they occupy identical accessible positions; they are correated to inner-surface OH. The hydroxyls absorbing at 3620 cm^{-1} are less completely deuterated; they should therefore be located in inner positions.

This selective deuteration of inner-surface and inner hydroxyls suggests the following OH-OD shift assignments:

3695 cm^{-1} to 2725 cm^{-1}
3670 cm^{-1} to 2710 cm^{-1}
3650 cm^{-1} to 2698 cm^{-1}
3620 cm^{-1} to 2675 cm^{-1}

A rotation of 45° of the deuterated kaolinite film in the infrared beam produces considerable increase in the intensity of all the absorption bands, except the 3620 cm^{-1} (Fig. 10). The differences between the background line absorption and the minimum transmittance (Table 2) indicate no change at all in the intensity of the 3620 cm^{-1} absorption band. The pleochroic effect observed for the oriented kaolinite film indicates that the direction of the dipole change of OH groups absorbing at 3695 and 3670 cm^{-1} and of OD groups absorbing at 2725 and 2698 cm^{-1} is nearly at right angles to the basal plane (001); for the 3650 and 2675 cm^{-1} the angle is large but less than 90°. The direction in dipole moment change of the OH groups absorbing at 3620 cm^{-1} makes an angle of 16° with the " ab " cleavage plane; this conclusion is based on an analogy with muscovite in which the OH occupy positions comparable with inner OH in kaolinite (Vedder and McDonald, 1963).

Similar observations were previously reported by Serratosa and Bradley (1958), Serratosa, Hidalgo and Vinas (1963) and Wolff (1963), but the pleochroic absorption band at 3695 cm^{-1} was interpreted as indicative of OH-bond axes at right angles to the (001) plane, whereas the nonpleochroic absorption at 3620 cm^{-1} was associated with OH groups in which the proton end was pointing into vacant octahedral sites. The measurements in pleochroic studies indicate only the direction of the dipole moment change and not essentially the direction of the vibrating bond. The direction of the dipole moment change and the bond axis may not be parallel because of crystalline perturbations or because of intramolecular interactions with other parts of the molecule. For instance, the ν(CO) stretching mode of the peptide group has been shown experimentally and theoretically to have a transition moment making an angle of about 20° with the axis of the (C—O) bond (Krimm, 1963). Thus, caution must be exercised in making structural deductions from pleochroic studies. According to Huggins and Pimentel (1956), the interpretation of the pleochroism in terms of bond orientations is acceptable only for linear hydrogen bonds, for which the stretching modes are enhanced by the dipole change induced along the bond.

In the present study an attempt was made to relate the average (O–H . . . O) distance 3.02 Å reported by Radoslovich (1960) for muscovite and the usually observed absorption frequency at 3620 cm^{-1}, and also the (O–H . . . O) values obtained by Newnham (1960) for dickite, 3.12, 2.97, and 2.94 Å with the absorption frequencies 3700, 3644 and 3617 cm^{-1}. When the above values were plotted on the correlation curve ν(OH) frequencies versus

(O . . . O) distances as proposed by Lippincott and Schroeder (1955) for a one-dimensional model of the linear hydrogen bond, it was found that the values for muscovite and dickite fall considerably below the curve. The most probable interpretation is that the (O–H . . . O) bonds are of the bent type. It has been shown by neutron diffraction (Busing and Levy, 1958) that in diaspore the H atom in (O–H . . . O) lies 12° off the O–O axis of the hydrogen bond. Since the linearity of the (O–H . . . O) bonds in kaolinite has not been established, the parallelism of the direction of the dipole moment change and the OH-bond axis is uncertain.

A comparison of the $\Delta(45°–0°)$ values (Table 2) of the ν(OH) and ν(OD) intensities clearly shows that, for the same angle of rotation, the pleochroism is more intense in the ν(OD) region than in the ν(OH) region. This indicates that partial deuteration perturbs the direction of the OD dipole moment change with respect to the initial OH orientations; the net result is the formation of larger angles between the direction of the OD dipole moment changes and the basal plane (001) with respect to the angles that existed in the ν(OH) region prior to deuteration. The effect is illustrated by the 2675 cm^{-1} band. After deuteration it is slightly pleochroic.

It is important to point out that the difference between the high and low frequency of the ν(OH) stretching modes ($3695–3620 = 75$ cm^{-1}) is larger than that in the ν(OD) region ($2725–2675 = 50$ cm^{-1}). Hallan (1963) reported that the lower frequency of the deuteration band decreases the zero-point energy of the vibrational ground state which, accordingly, gives rise to (1) a slight contraction of the OD bond distance, (2) a diminished dipole moment and (3) a potential barrier to transfer which is higher for D than for H atoms.

Since the OD distance is shorter than the OH length, the (O . . . O) distance in (O–D . . . O) bond is longer than it was in the (O–H . . . O) bond prior to deuteration; thus deuteration implies a weakening of the " hydrogen bond ". It was shown by Nakamoto *et al.* (1955) that the ν(OH) stretching frequencies of freer OH groups (3650 cm^{-1} and above) are less sensitive to the (O . . . O) distances than the lower ν(OH) frequencies corresponding to shorter (O . . . O) lengths. Thus, the shifted ν(OD) frequency (2675 cm^{-1}) corresponding to the 3620 cm^{-1} band is more affected by deuteration than the shifted frequency 2725 cm^{-1}, which is related to freer OH groups absorbing at 3695 cm^{-1}; the net result is a contraction of the band width in the ν(OD) region.

Selective Deuteration of the Hydrazine–Halloysite Complex at Room Temperature

A sample of halloysite (A.P.I., no. H-12, Bedford, Indiana, less than 2μ) was deuterated by the procedure used for kaolinite. The infrared spectrum of the natural halloysite (Fig. 11a) shows two strong absorption bands at 3695 and 3620 cm^{-1} and three weak absorption bands at 3520, 3450 and 3370 cm^{-1}. The deuterated sample (Fig. 11b) shows a large reduction in the intensity of the 3695 cm^{-1}, a strong absorption at 2725 cm^{-1}, a shoulder at 2680 cm^{-1}, and weaker bands at 2930 and 2850 cm^{-1}. The shift of the 3695 cm^{-1} to 2725 cm^{-1} is identical to the observed shift in kaolinite; the 2680 cm^{-1} absorption band results from the deuteration of hydroxyls absorbing at 3620 cm^{-1}. The absorption band at 3520, 3450 and 3370 cm^{-1} are the ν(OH) stretching frequencies of a gibbsite impurity (Frederickson, 1954). The presence of gibbsite was confirmed by the X-ray reflections at 4.79 Å and 4.39 Å.

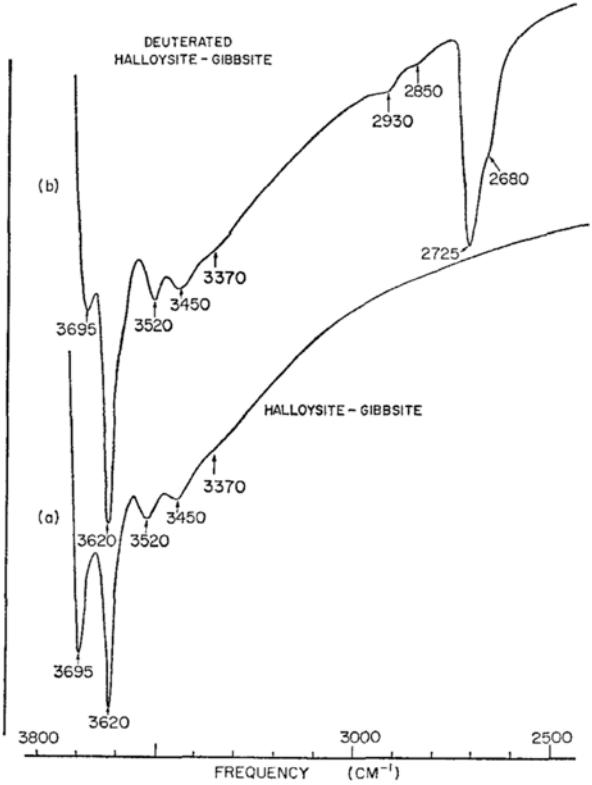

FIG. 11. Infrared spectra of (a) halloysite with gibbsite impurity, and (b) deuterated halloysite–gibbsite mixture.

Intersalation, followed by hydrazine treatment, has expanded halloysite but did not form complexes with gibbsite. The micro crystals of gibbsite were not expanded and consequently no OH–OD exchange took place. Although the intersalated halloysite has been washed three times with hydrazine, a small amount of CH_3COOK remained in interlayer positions; this was indicated by weak X-ray reflection at 14.2 Å, the ν(CH) at 2930 cm^{-1} and the ν(COO) at 1410 and 1560 cm^{-1} (Nakamoto, 1963, p. 199). Because of the tubular crystal habit of halloysite, the rotation of the deuterated clay film did not produce the pleochroic effect observed in kaolinite.

Deuteration of $LiNO_3$-Treated Muscovite at Room Temperature

In order to investigate more closely the weak deuteration of the inner hydroxyls absorbing at 3620 cm^{-1}, we washed one sample of artificially expanded mica (White, 1956) three times with H_2O and a second sample with D_2O. After 15 hr of contact, a 1-ml portion of each suspension was evaporated on an Irtran window in an oven at 110°C. The infrared spectrum of the mica washed with H_2O (Fig. 12a) shows a strong absorption band at 3620 cm^{-1} due to the ν(OH) stretching frequency of the inner lattice hydroxyls and a weak absorption band of 3315 cm^{-1} corresponding to the ν(OH) of adsorbed water molecules. The mica washed with D_2O (Fig. 12b) shows the same absorption band at 3620 cm^{-1} and a weak band at 2475 cm^{-1}, which corresponds to the ν(OD) of adsorbed deuterium oxide molecules. The isotope ratio of the OH–OD shift of the adsorbed water is 1.339. If we assume that the isotope ratio of the inner lattice hydroxyls is 1.35, the 3620 cm^{-1} absorption band should be shifted to 2675 cm^{-1} by deuteration. The presence of a very weak

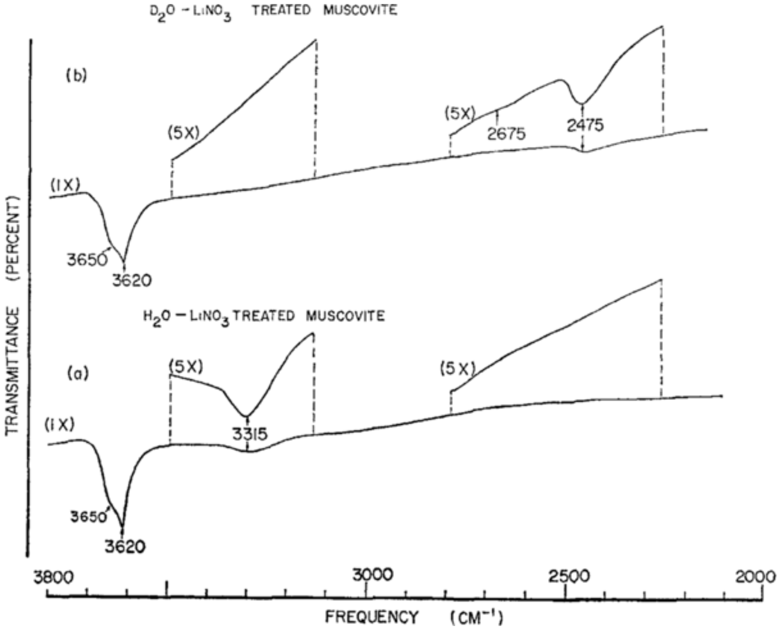

FIG. 12. Infrared spectra of artificially expanded muscovite washed with (a) H_2O and heated at 110°C, and (b) with D_2O and heated at 110°C.

absorption band at 2675 cm^{-1} (Fig. 12b) shows that the inner hydroxyls absorbing at 3620 cm^{-1} are not readily exchangeable at room temperature. Rosenqvist (1963) has observed in hydrous micas that the inner hydroxyls undergo a very slow exchange reaction; even for fine clay material, equilibrium is not attained after two years at 110°C.

SUMMARY

The kaolinite mineral used in this study showed four ν(OH) stretching absorption bands at 3695, 3670, 3650 and 3620 cm^{-1}. Previous attempts to correlate these ν(OH) stretching frequencies of kaolinite to corresponding OH lattice sites were based entirely on the ideal structural model. In the present work the assignments of the hydroxyl absorption bands to definite positions in the crystal lattice of kaolinite were essentially based on the hydrogen bonding interaction between the lattice OH ions and the structural groups of intercalated substances and on OH–OD shifts produced by selective deuteration.

Intersalation of kaolinite with CH_3COOK resulted in the reduction of the absorption intensity of the 3695 cm^{-1} band and caused the occurrence of an additional absorption band at 3600 cm^{-1}. The strong negative oxygens of the acetate anions formed hydrogen bonds with the inner-surface hydroxyls, thus shifting the 3695 cm^{-1} frequency to lower value. Deuteration of the CH_3COOK–kaolinite complex produced considerable reduction in the intensities of the 3695 and 3650 cm^{-1} absorption bands, complete disappearance of the 3600 cm^{-1} frequency, and caused the occurrence of ν(OD) absorption bands at 2725, 2700, 2675 and 2650 cm^{-1}. The hydroxyls absorbing at 3620 cm^{-1} were not perturbed by the presence of the acetate anions in interlayer positions.

Intercalation of hydrazine in kaolinite produced a large reduction in the intensities of the 3695, 3670 and 3650 cm^{-1} absorption bands. Deuteration at room temperature of expanded hydrazine–kaolinite complex shifted the infrared stretching frequencies from 3695 cm^{-1} to 2725 cm^{-1}, 3670 cm^{-1} to 2710 cm^{-1}, 3650 cm^{-1} to 2698 cm^{-1}, and 3620 cm^{-1} to 2675 cm^{-1}. The OH–OD exchanges for the hydroxyls absorbing at 3695, 3670 and 3650 cm^{-1} were 67, 60 and 62 per cent respectively and for the 3620 cm^{-1} only 22 per cent. The smaller amount of OH–OD exchange for the hydroxyls absorbing at 3620 cm^{-1} was also observed for halloysite, $LiNO_3$-treated muscovite.

The pleochroic effect observed for the oriented kaolinite film indicated that the direction of the dipole moment change of OH groups absorbing at 3695 and 3670 cm^{-1} and of OD groups absorbing at 2725 and 2698 cm^{-1} is nearly at right angles to the basal plane (001); for the 3650 and 2675 cm^{-1}; the angle is large, but less than 90°. The nonpleochroic behavior of the 3620 cm^{-1} absorption band showed that the direction of dipole moment change of the inner OH makes an angle of about 15° with the " ab " cleavage plane.

All these considerations derived from this infrared spectroscopic study of

kaolinite complexes and their deuteration strongly suggest the assignments of the absorption bands 3695, 3670 and 3650 cm^{-1} to inner-surface hydroxyls and of the 3620 cm^{-1} frequency to inner hydroxyls.

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REFERENCES

ANDREW, R. M., JACKSON, M. L., and WADA, K. (1960) Intersalation as a technique for identification of kaolinite from chloritic materials by X-ray diffraction, *Soil Sci. Soc. Am., Proc.* **24,** 422–4.

AUSKERN, A , and GRIMSHAW, R. W. (1955) Differences between the infrared absorption spectra of some clays and related minerals (abstract), Program of the Fourth National Clay Conference, Pennsylvania State University.

BASSETT, W. A. (1960) Role of hydroxyl orientation in mica alteration, *Bull. Geol. Soc. Am.* **71,** 449–56.

BUSING, W. R., and LEVY, H. A. (1958) A single crystal neutron diffraction study of diaspore, AlO(OH), *Acta Cryst.* **11,** 798–803.

CATALANO, E., SANBORN, R. H., and FRAZER, J. W. (1963) On the infrared spectrum of hydrazine matrix-isolation studies of the system $NH_2NH_2 : N_2$ (1), *J. Chem. Phys.* **38,** 2265–72.

DIAMOND, S., and KINTER, E. B. (1958) Surface area of clay minerals as derived from measurements of glycerol retention, *Clays and Clay Minerals*, Nat. Acad. Sci.—Nat. Res. Council, Publ. 566, pp. 334–7.

FREDERICKSON, L. D. (1954) Characterization of hydrated aluminas by infrared spectroscopy; application to study of bauxite ores, *Anal. Chem.* **26,** 1883–5.

FRIPIAT, J. J., and TOUSSAINT, F. (1960) Pre-dehydroxylation state of kaolinite, *Nature* **186,** 627.

FRIPIAT, J. J., and TOUSSAINT, F. (1963) Dehydroxylation of kaolinite, II, Conductometric measurements and infrared spectroscopy, *J. Phys. Chem.* **67,** 30–6.

GIGUERE, P. A., and LIU, I. D. (1952) Infrared spectrum of hydrazine, *J. Chem. Phys.* **20,** 136–40.

HALLAN, H. E. (1963) *Infra-Red Spectroscopy and Molecular Structure* (Edited by M. Davies), p. 418, Elsevier, New York.

HUGGINS, C. M., and PIMENTEL, G. C. (1956) Systematics of the infrared spectral properties of hydrogen bonding systems: frequency shift, half width, and intensity, *J. Phys. Chem.* **60,** 1615–19.

KRIMM, S. (1963) *Infra-Red Spectroscopy and Molecular Structure* (Edited by M. Davies), p. 287, Elsevier, New York.

McDONALD, R. S. (1958) Surface functionality of amorphous silica by infrared spectroscopy, *J. Phys. Chem.* **62,** 1168–78.

NAKAMOTO, K. (1963) *Infrared Spectra of Inorganic and Coordination Compounds*, John Wiley, New York.

NEWNHAM, R. E. (1960) A refinement of the dickite structure and some remarks on polymorphism in kaolin minerals, Massachusetts Inst. Technology, Lab. Insulation Res., Tech. Rep. 148, pp. 1–30.

ROSENQVIST, TH. (1963) Studies in position and mobility of the H atoms in hydrous micas, *Clays and Clay Minerals*, 11th Conf. [1962], pp. 117–35, Pergamon Press, New York.

ROY, D. M., and ROY, R. (1957) Hydrogen-deuterium exchange in clays and problems in the assignment of infrared frequencies in the hydroxyl region, *Geochim. Cosmochim. Acta* **11,** 72–85.

SERRATOSA, J. M., and BRADLEY, W. F. (1958) Determination of the orientation of OH bond axes in layer silicates by infrared absorption, *J. Phys. Chem.* **62,** 1164–7.

SERRATOSA, J. M., HIDALGO, J. M. A., and VINAS, J. M. (1962) Orientation of OH bonds in kaolinite, *Nature*, **195,** 486–7.

SERRATOSA, J. M., HIDALGO, J. M. A., and VINAS, J. M. (1963) Infrared study of the OH groups in kaolin minerals, *International Clay Conference, Sweden* (Edited by Th. Rosenqvist and P. Graff-Petersen), pp. 17–26, Pergamon Press, New York.

VAN DER MAREL, H. W., and ZWIERS, J. H. L. (1958) OH stretching bands of the kaolin minerals, *Silicates Ind.* **24,** 359–68.

VEDDER, W., and MCDONALD, R. S. (1963) Vibrations of the OH ions in muscovite, *J. Chem. Phys.* **38,** 1583–90.

WADA, K. (1961) Lattice expansion of kaolin minerals by treatment with potassium acetate, *Am. Mineralogist* **46,** 78–91.

WADSWORTH, M. E., MACKAY, T. L., and CUTLER, I. B. (1955) Surface and internal structure of clay minerals as indicated by infrared spectra, *Am. Ceram. Soc. Bull.* **33,** 15–20.

WEISS, A., THIELEPAPE, W., GORING, G., RITTER, W., and SCHAFER, H. (1963a) Kaolinite-einlagerungs-verbindungen, *International Clay Conference*, Sweden (Edited by Th. Rosenqvist and P. Graff-Petersen), pp. 287–301, Pergamon Press, New York.

WEISS, A., THIELEPAPE, W., RITTER, W., SCHAFER, H., and GORING, W. (1963b) Zur Kenntnis von hydrazin-kaolinit, *Z. Anorg. Allgem. Chem.* **320,** 183–204.

WHITE, J. L. (1956) Reactions of molten salts with layer-lattice silicates, *Clays and Clay Minerals*, Nat. Acad. Sci.—Nat. Res. Council, Publ. 456, pp. 133–46.

WOLFF, R. G. (1963) Structural aspects of kaolinite using infrared absorption, *Am. Mineralogist* **48,** 390–9.