

# 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  $\text{cm}^{-1}$  absorption band and causes the appearance of an additional one at 3600  $\text{cm}^{-1}$ . Subsequent deuteration with  $\text{D}_2\text{O}$  vapor shifts the 3695  $\text{cm}^{-1}$  and 3600  $\text{cm}^{-1}$  absorption bands to 2725  $\text{cm}^{-1}$  and 2650  $\text{cm}^{-1}$  respectively. The hydroxyls absorbing at 3620  $\text{cm}^{-1}$  do not interact with the acetate anion and do not readily exchange with  $\text{D}_2\text{O}$  vapor.

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

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

A comparison of the  $\nu(\text{OH})$  and  $\nu(\text{OD})$  absorption intensities for the film rotated 45° and normal to the infrared incident radiation shows that the pleochroism is more intense in the  $\nu(\text{OD})$  region than in the  $\nu(\text{OH})$  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  $\nu(\text{OH})$  stretching modes of vibration in the high frequency region ( $3750$  to  $2500\text{ cm}^{-1}$ ) and the OH sites and their bond-axis orientations in the clay lattices.

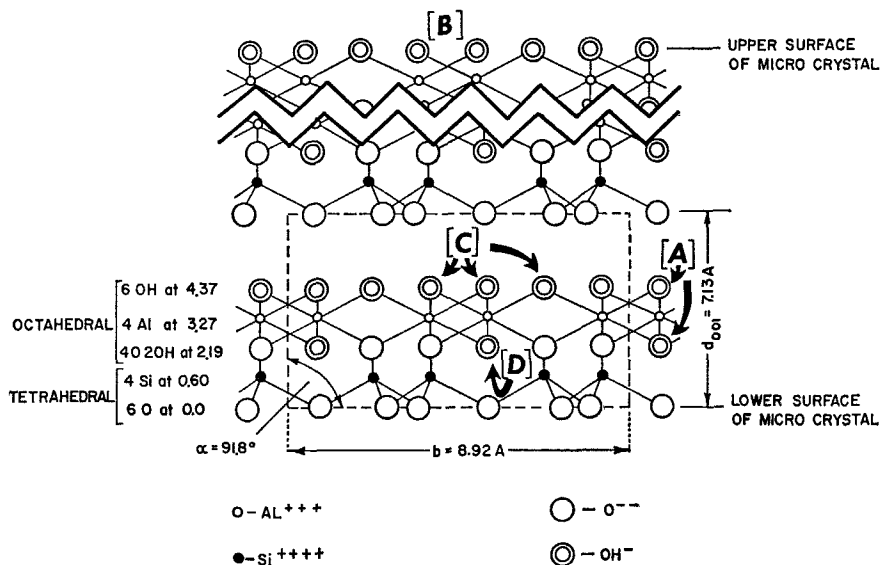


FIG. 1. Projection of the structure of kaolinite on the (100) plane showing the stacking of successive layers in a micro crystal (After Brindley). [A] and [B] indicate "outer hydroxyls"; [C] designates "inner-surface hydroxyls"; [D] indicates "inner-hydroxyls".

Most attempts to correlate the  $\nu(\text{OH})$  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  $\nu(\text{OH})$  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  $\nu(\text{OH})$  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  $\text{cm}^{-1}$ ) 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  $\text{cm}^{-1}$  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  $\text{cm}^{-1}$  and a shoulder at 3450  $\text{cm}^{-1}$ . 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 deuterioxygens 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  $\nu(\text{OH})$  band corresponding to outer OH groups should diminish and the  $\nu(\text{OD})$  band related to outer OH groups should increase more rapidly than the inner counterparts. It was also observed that the 3450  $\text{cm}^{-1}$  absorption band did not preferentially decrease as was expected if this were due to absorbed  $\text{H}_2\text{O}$ . The persistence in the sample heated to above 300°C of the 3450  $\text{cm}^{-1}$  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  $\text{cm}^{-1}$ ) 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  $\text{cm}^{-1}$ .
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  $\text{cm}^{-1}$ .
3. The 3630  $\text{cm}^{-1}$  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  $3440\text{ cm}^{-1}$  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  $3627\text{ cm}^{-1}$ . In this work, the absence of the absorption bands at  $3450$  and  $3440\text{ cm}^{-1}$  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 Schuykill dickite was advanced by Newnham (1960). The mineral was milled in Nujol and mounted between NaCl plates. Newnham observed four absorption bands located at  $3700$ ,  $3644$ ,  $3617\text{ cm}^{-1}$ . 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  $\nu(\text{OH})$  frequencies as expressed by Nakamoto *et al.* (1955), Newnham arbitrarily associated the  $3617\text{ cm}^{-1}$  frequency with  $(\text{O-H})_2 \dots \text{O}_1 = 2.97\text{ \AA}$ ,  $(\text{O-H})_4 \dots \text{O}_2 = 2.94\text{ \AA}$  and the  $1821\text{ cm}^{-1}$  frequency with  $(\text{O-H})_1 \dots (\text{O-H})_3 = 2.36\text{ \AA}$ . The proposed model placed the hydrogen atoms of  $(\text{OH})_2$ ,  $(\text{OH})_3$  and  $(\text{OH})_4$  on long hydrogen bonds that connect the hydroxyl groups to their closest neighbors in the adjacent kaolinite layer: the  $(\text{OH})_1$  was placed within the octahedral layer, i.e. in the plane common to tetrahedral and octahedral sheets. The  $(\text{OH})_1$  was said to function primarily as a free hydroxyl group, but its hydrogen interacts with the oxygen of the  $(\text{OH})_3$  along the shared edge of two octahedra to account for the weak absorption band at  $1821\text{ cm}^{-1}$ . In other words, Newnham associated the internal OH with the band at  $3700\text{ cm}^{-1}$  and assigned the absorption bands  $3644$  and  $3617\text{ cm}^{-1}$  to the interlayer OH located at  $3.12$  and  $2.95\text{ \AA}$  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  $3695\text{ cm}^{-1}$  showed a marked increase in intensity with variation of the angle of incidence. Serratosa *et al.* associated the  $3695\text{ cm}^{-1}$  absorption band with OH-bond axes showing preferred orientation with a major component perpendicular to the (001) plane. The absorption band at  $3620\text{ cm}^{-1}$  did not show any significant change with the angle of incidence of the infrared beam; hence, the  $3620\text{ cm}^{-1}$  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  $3620\text{ cm}^{-1}$  absorption band indicative of OH groups with the proton end pointing into vacant octahedral sites. Serratosa *et al.* assigned the  $3695\text{ cm}^{-1}$  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  $\text{cm}^{-1}$  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, Hidalgo and Vinas (1963) studied the infrared spectrum of hydrated and glycerated halloysite complexes and observed a considerable decrease in the intensity of the 3695  $\text{cm}^{-1}$  absorption band but no change in the intensity of the 3620  $\text{cm}^{-1}$  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  $\text{cm}^{-1}$  absorption band in halloysite.

Wolff (1963) observed that kaolinite had three absorption bands at 3704, 3663 and 3635  $\text{cm}^{-1}$ . 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  $\text{cm}^{-1}$ .

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  $\text{cm}^{-1}$  absorption bands correspond to OH groups on the upper octahedral layer, and that the 3620  $\text{cm}^{-1}$  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  $\nu(\text{OH})$  STRETCHING FREQUENCIES OF KAOLINITE AND DICKITE TO LATTICE SITES REPORTED BY VARIOUS AUTHORS (FREQUENCIES IN WAVE NUMBERS,  $\text{cm}^{-1}$ )

	Kaolinite <sup>1</sup>	Kaolinite <sup>2</sup>	Dickite <sup>3</sup>	Kaolinite <sup>4</sup>	Kaolinite <sup>5</sup>	Kaolinite <sup>6</sup>
Outer OH	3705	3698		3704 <sub>s</sub>		
		3660				
			3617	3663	3650	3710
Inner-surface OH	3665	3630			3670	
			3644	3704 <sub>s</sub> *	3695 <sub>l</sub> †	3680
Inner OH	3665	3440	3700	3704 <sub>l</sub> †	3695 <sub>l</sub> †	3620
				3635	3620	

<sup>1</sup> Auskern and Grimshaw, 1955. <sup>2</sup> Van der Marel and Zwiers, 1958. <sup>3</sup> Newnham, 1960. <sup>4</sup> Wolff, 1963. <sup>5</sup> Serratosa, Hidalgo and Vinas, 1963. <sup>6</sup> 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  $\nu(\text{OH})$  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  $2\mu$  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  $0.55\mu$ ; the distribution in the fraction less than  $2\mu$  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  $29\text{ m}^2$  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 ( $\text{CH}_3\text{COOK}$ ) 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  $\text{CH}_3\text{COOK}$  for 20 min in a Fisher mechanical mortar-and-pestle grinder and allowing the mixture to stand overnight in a 10 N solution of  $\text{CH}_3\text{COOK}$ . 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  $110^\circ\text{C}$ , 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  $2400\text{ cm}^{-1}$  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  $\text{CH}_3\text{COOK}$ -kaolinite complex was heated at  $200^\circ\text{C}$  for 2 hr to remove most of the  $\text{H}_2\text{O}$  molecules. The heated cell was immediately filled with  $\text{D}_2\text{O}$  vapor and the sample was allowed to cool in  $\text{D}_2\text{O}$  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<sub>2</sub>O at room temperature in a centrifuge; the kaolinite complex was redispersed in 3 ml. D<sub>2</sub>O and allowed to remain in contact 30 min. A 1 ml. portion of the D<sub>2</sub>O 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  $\nu(\text{OH})$  stretching absorption bands at 3695, 3670, 3650 and 3620  $\text{cm}^{-1}$ . These four absorption bands observed in the present study correspond exactly to those previously reported by Serratos, Hildago and Vinas (1963). The 3695 and 3620  $\text{cm}^{-1}$  absorption bands are very strong and have about the same intensity, whereas the 3650 and 3670  $\text{cm}^{-1}$  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  $\text{CH}_3\text{COOK}$  on an Irtran window placed in an oven at  $110^\circ\text{C}$ . 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  $25^\circ\text{C}$  and rehydrated in the laboratory atmosphere (Fig. 2b).

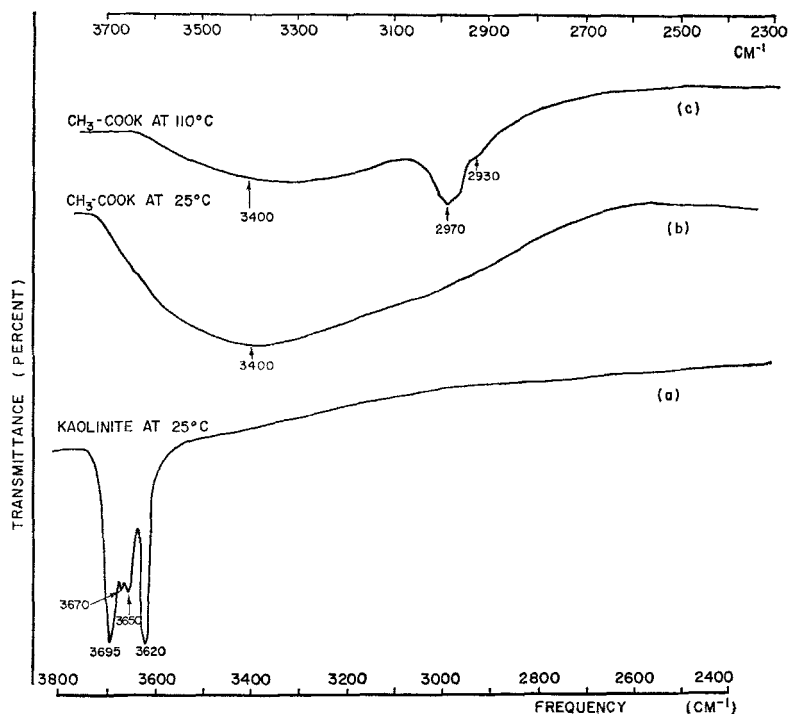


FIG. 2. Infrared spectra of (a) kaolinite at  $25^\circ\text{C}$ , (b) hydrated  $\text{CH}_3\text{COOK}$  at  $25^\circ\text{C}$ , and (c)  $\text{CH}_3\text{COOK}$  at  $110^\circ\text{C}$ .

The stretching vibration frequencies of the  $\text{CH}_3$  group of the acetate anion are responsible for the absorption bands observed at 2970 and 2930  $\text{cm}^{-1}$  (Nakamoto, 1963, p. 199).

The rehydration of the sample caused a marked increase in the intensity of the absorption band at 3400  $\text{cm}^{-1}$  that overlapped completely the 2970  $\text{cm}^{-1}$  absorption band. The wide absorption band with a transmittance minimum at 3400  $\text{cm}^{-1}$  is due to the  $\nu(\text{OH})$  stretching frequencies of adsorbed water ( $\text{H}_2\text{O}$ ) 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.

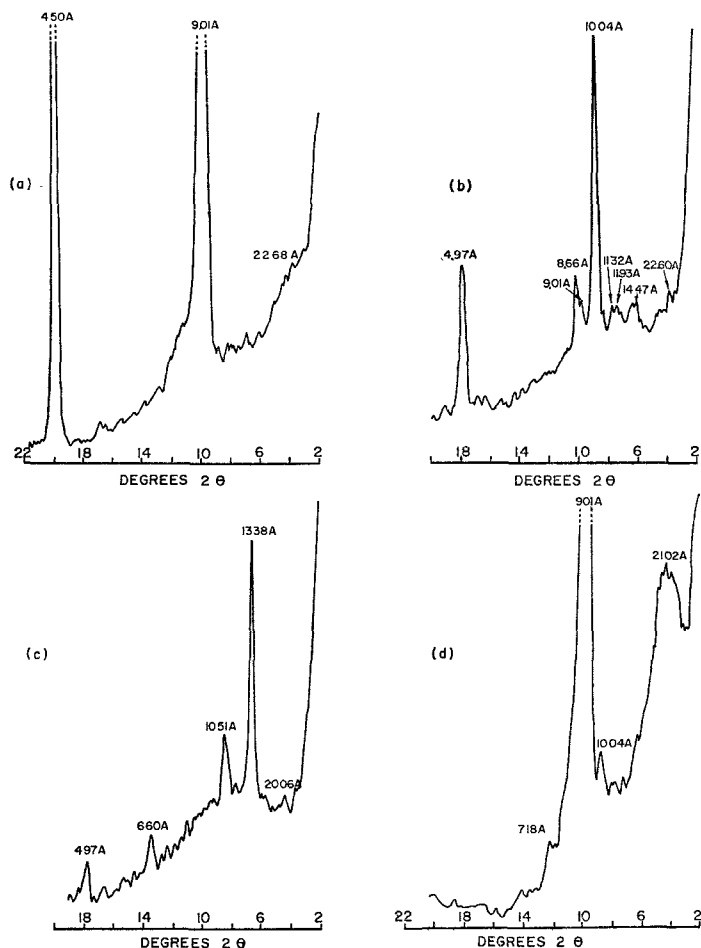


FIG. 3. X-ray diffraction patterns of  $\text{CH}_3\text{COOK}$  (a) dried 30 min at 110°C, (b) exposed 5 min at r.h. 60%, (c) exposed 10 min at r.h. 60%, and (d) reheated 10 min at 110°C.

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).

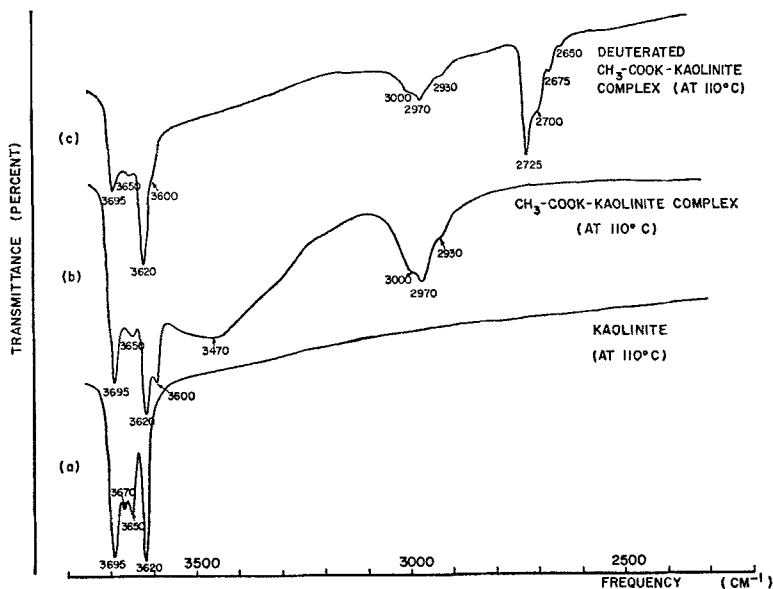


FIG. 4. Infrared spectra of (a) kaolinite at 110°C, (b) CH<sub>3</sub>COOK-kaolinite complex at 110°C, and (c) deuterated CH<sub>3</sub>COOK-kaolinite complex at 110°C.

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<sub>3</sub>COOK 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<sub>3</sub>COOK-Kaolinite Complex and its Deuteration*

The CH<sub>3</sub>COOK-kaolinite complex (Fig. 4b) shows four transmittance minima in the  $\nu(\text{OH})$  stretching region at 3695, 3650, 3620, and 3600 cm<sup>-1</sup>. Intersalation of kaolinite resulted in the disappearance of the 3670 cm<sup>-1</sup>

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

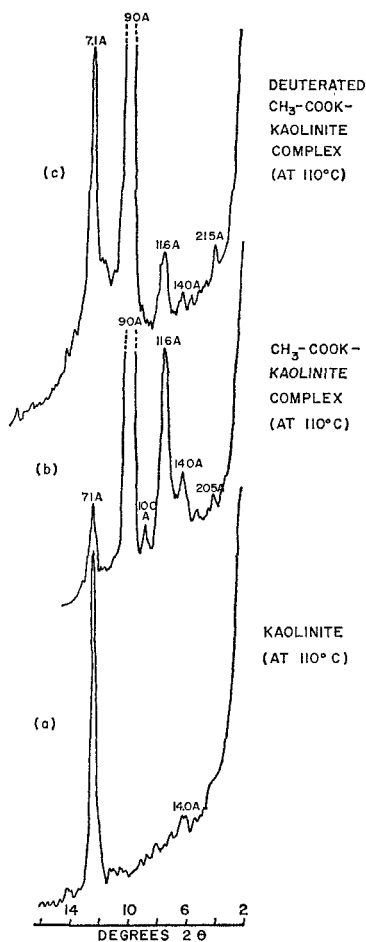


FIG. 5. X-ray diffraction patterns of (a) kaolinite at 110°C, (b)  $\text{CH}_3\text{COOK-kaolinite}$  complex at 110°C, and (c) deuterated  $\text{CH}_3\text{COOK-kaolinite}$  complex at 110°C.

In the corresponding X-ray diffraction record the peak at 11.6 Å in Fig. 5b for the  $\text{CH}_3\text{COOK}$ -kaolinite complex indicates the presence of  $\text{CH}_3\text{COOK}$  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  $\text{cm}^{-1}$  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.

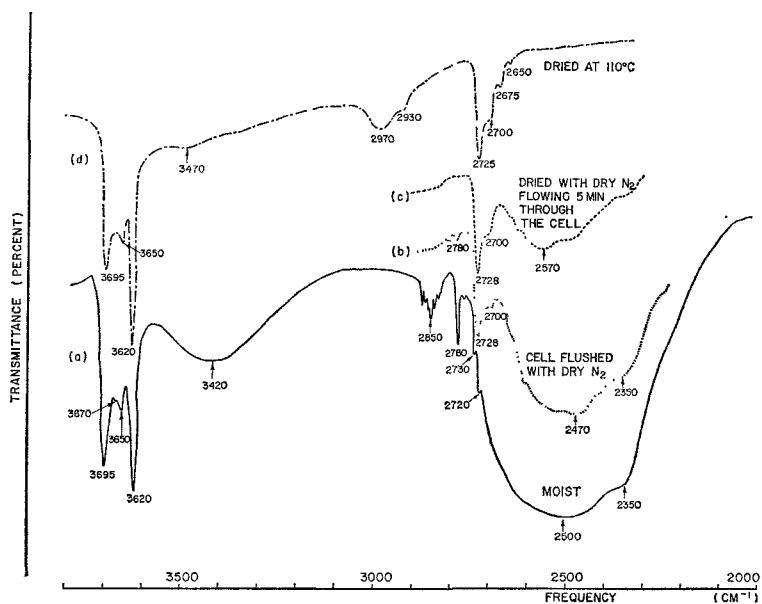


FIG. 6. Progressive drying of the deuterated  $\text{CH}_3\text{COOK}$ -kaolinite complex as revealed by infrared spectra: (a) moist, (b) cell flushed with dry  $\text{N}_2$ , (c) dried with dry  $\text{N}_2$  flowing 5 min through the cell, and (d) dried at 110°C.

The infrared spectra of the  $\text{CH}_3\text{COOK}$ -kaolinite sample that had been exposed 1 hr to  $\text{D}_2\text{O}$  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  $\text{cm}^{-1}$ , which is due to the  $\nu(\text{OD})$  stretching vibration frequencies of liquid  $\text{D}_2\text{O}$ . The  $\text{D}_2\text{O}$  vapor in the cell is responsible for the rotational structure on the 2850  $\text{cm}^{-1}$  vibrational absorption band; the 2780  $\text{cm}^{-1}$  frequency corresponds probably to HDO gas; both absorption bands at 2850 and 2780  $\text{cm}^{-1}$  disappear as the cell is filled with nitrogen gas.

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

The infrared spectrum of the deuterated  $\text{CH}_3\text{COOK}$ -kaolinite complex (Fig. 4c) shows a considerable reduction in the intensity of the  $3695$  and  $3650\text{ cm}^{-1}$  absorption bands and complete disappearance of the  $3600\text{ cm}^{-1}$  absorption band. The shift of the  $3695\text{ cm}^{-1}$  absorption band to  $2725\text{ cm}^{-1}$  caused by the substitution of protons by deuterons has resulted in a considerable decrease in the intensity of the  $3695\text{ cm}^{-1}$  absorption band.

#### *Pleochroism of the $\nu(\text{OH})$ and $\nu(\text{OD})$ 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  $\nu(\text{OH})$  and  $\nu(\text{OD})$  stretching frequencies of pure kaolinite,  $\text{CH}_3\text{COOK}$ -kaolinite complex and of deuterated  $\text{CH}_3\text{COOK}$ -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  $\theta = 0^\circ$  because the film was not rotated.

2. The oriented film was rotated by  $30^\circ$ , ( $\theta = 30^\circ$ ).

3. The oriented film was rotated by  $45^\circ$ , ( $\theta = 45^\circ$ ).

Rotation of  $30^\circ$  and  $45^\circ$  of the kaolinite film in the infrared beam (Fig. 7) produced considerable increase in the intensity of the  $3695$  and  $3650\text{ cm}^{-1}$  absorption bands but did not affect the intensity of the  $3620\text{ cm}^{-1}$  absorption band. Similar results were obtained with the  $\text{CH}_3\text{COOK}$ -kaolinite film with the exception that the intensity of the  $3695\text{ cm}^{-1}$  absorption band did not surpass that of the  $3620\text{ cm}^{-1}$ , even for  $\theta = 45^\circ$ .

Fig. 8 shows the pleochroic study of the  $\nu(\text{OD})$  absorption bands. The intensity of the  $2725\text{ cm}^{-1}$  frequency increases considerably upon rotation of the clay film (Fig. 8a), whereas the  $2700$ ,  $2675$  and  $2650\text{ cm}^{-1}$  absorption intensities are not significantly affected. Fig. 8b shows the infrared spectra in the  $\nu(\text{OD})$  region of the deuterated  $\text{CH}_3\text{COOK}$ -kaolinite sample, which had been heated at  $200^\circ\text{C}$  for 30 min. The heat treatment has favored more OH-OD exchange for the OH absorbing at  $3620\text{ cm}^{-1}$ , thus increasing the intensity of the  $2675\text{ cm}^{-1}$  absorption band. However, only the  $2725\text{ cm}^{-1}$  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  $\text{cm}^{-1}$  absorption bands supports the OH-OD shift assignment 3695 to 2725  $\text{cm}^{-1}$  previously based on the  $\nu(\text{OH}) : \nu(\text{OD})$  ratio 1.35.

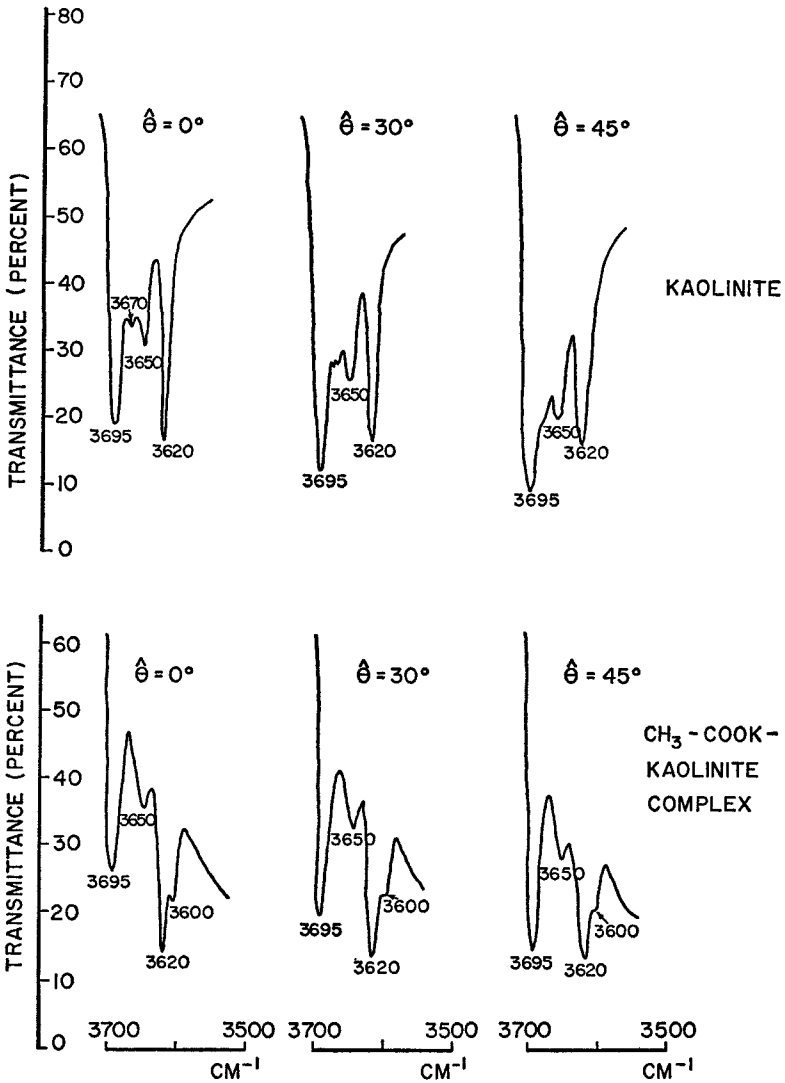


FIG. 7. Pleochroism of the  $\nu(\text{OH})$  in kaolinite and in  $\text{CH}_3\text{COOK}$ -kaolinite complex ( $\theta$  is the angle of rotation of the clay film.)

The pleochroic effect on the natural and deuterated kaolinite films indicates that the transition moment of a large proportion of OH groups absorbing at  $3695\text{ cm}^{-1}$  makes a right angle with the basal plane (001). The  $3620\text{ cm}^{-1}$  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.

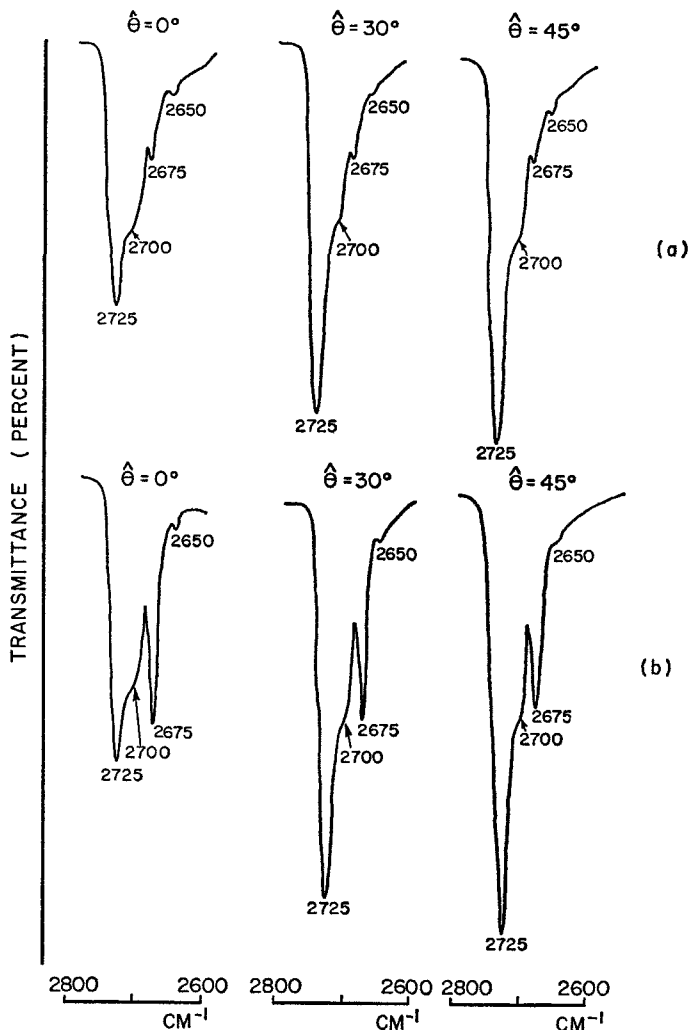


FIG. 8. Pleochroism of the  $\nu(\text{OD})$  in  $\text{CH}_3\text{COOK}$ -kaolinite: (a) heated at  $110^\circ\text{C}$ , and (b) heated at  $200^\circ\text{C}$ .

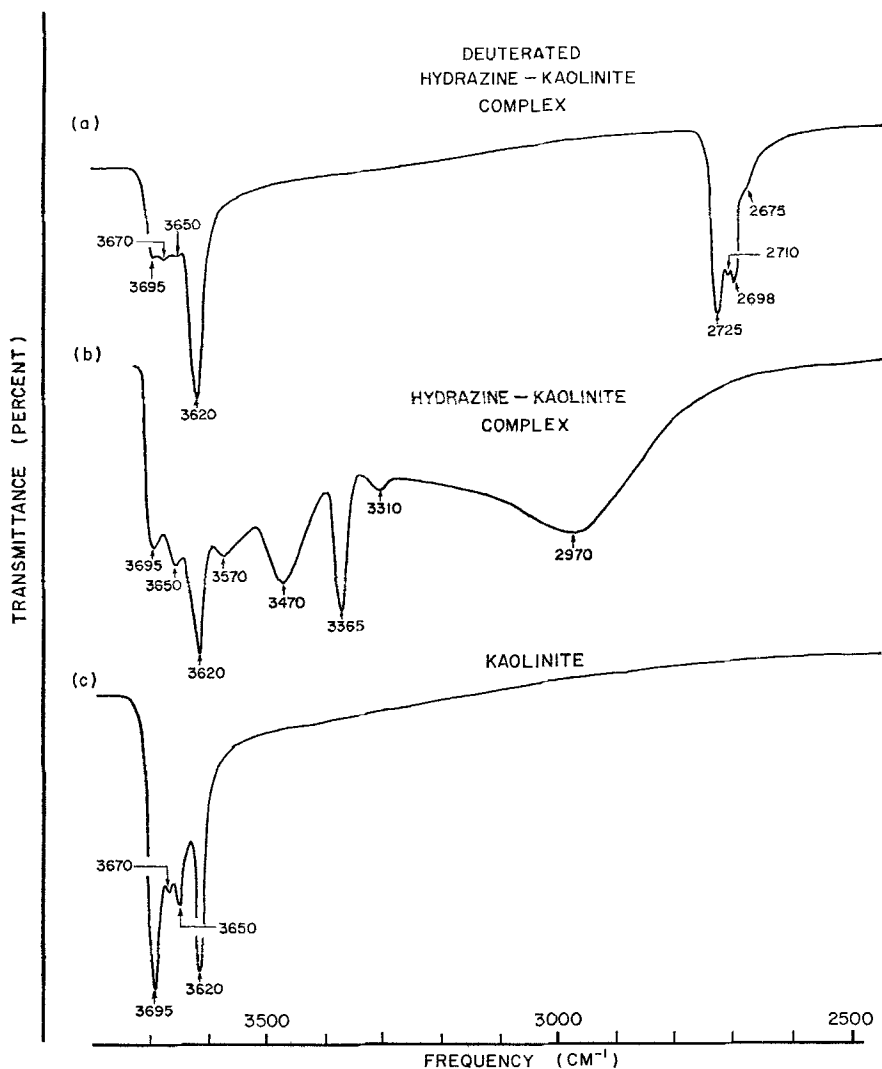


FIG. 9. Infrared spectra of (a) deuterated hydrazine-kaolinite complex heated at 110°C, (b) hydrazine-kaolinite complex heated 2 min at 110°C, and (c) kaolinite at 25°C.

*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  $\text{cm}^{-1}$  absorption bands, and the appearance of additional bands at 3570, 3470, 3365, 3310, and 2970  $\text{cm}^{-1}$ .

The expanded hydrazine-kaolinite complex (10.4 Å) was washed with  $\text{D}_2\text{O}$  and the spectra of oriented clay films were determined by X-ray diffraction and infrared spectroscopy. The X-ray pattern of the  $\text{D}_2\text{O}$ -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  $\text{D}_2\text{O}$ -treated sample. In the infrared spectrum of natural kaolinite (Fig. 9c), four  $\nu(\text{OH})$  absorption frequencies

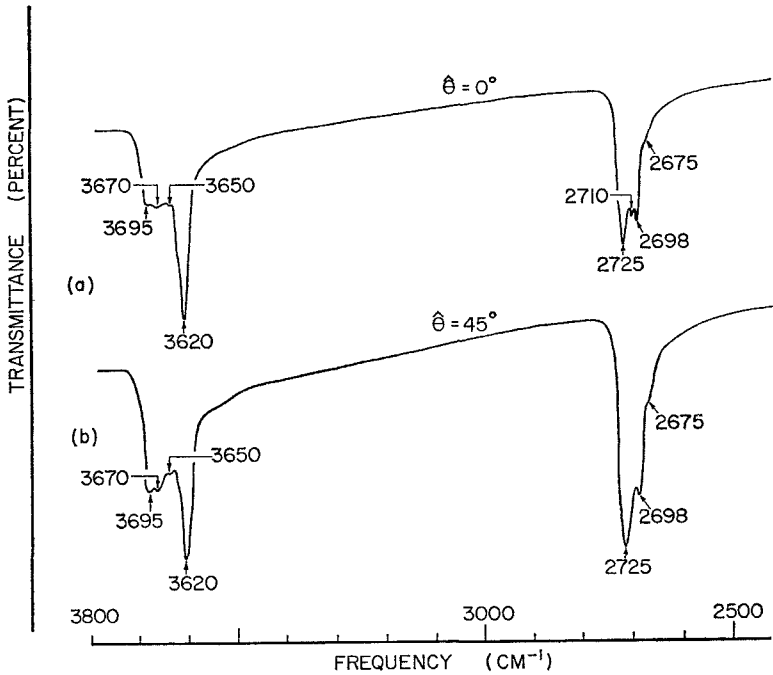


FIG. 10. Infrared spectra of deuterated kaolinite with (a)  $\theta = 0^\circ$ , and (b)  $\theta = 45^\circ$ .

are observed at 3695, 3670, 3650 and 3620  $\text{cm}^{-1}$ . Both absorptions at 3695 and 3620  $\text{cm}^{-1}$  are more intense than those at 3670 and 3650  $\text{cm}^{-1}$ . The spectrum of deuterated kaolinite (Fig. 9a) shows a reduction in the intensity of the 3695, 3670 and 3650  $\text{cm}^{-1}$  absorptions and the occurrence of strong bands at 2725 and 2698  $\text{cm}^{-1}$  and weak absorptions at 2710 and 2675  $\text{cm}^{-1}$ ; the intensity of the 3620  $\text{cm}^{-1}$  is not significantly affected by the deuteration process.

A rotation of  $45^\circ$  of the deuterated kaolinite film in the infrared beam produces considerable increase in the intensity of all the absorption bands except the  $3620\text{ cm}^{-1}$  (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  $3620\text{ cm}^{-1}$  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  $3670\text{ cm}^{-1}$  and of OD groups absorbing at  $2725$  and  $2698\text{ cm}^{-1}$  is nearly at right angles to the basal plane (001); for the  $3650$  and  $2675\text{ cm}^{-1}$  the angle is large, but less than  $90^\circ$ . The direction in dipole moment change of the OH groups absorbing at  $3620\text{ cm}^{-1}$  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 ( $\theta$  = ANGLE OF ROTATION,  $\Delta$  = DIFFERENCE BETWEEN ROTATED AND INITIAL ANGLES)

Hydroxyl				Deuteroxyl			
$\nu(\text{OH})\text{ cm}^{-1}$	$\theta = 0^\circ$	$\theta = 45^\circ$	$\Delta(45^\circ-0^\circ)$	$\nu(\text{OD})\text{ cm}^{-1}$	$\theta = 0^\circ$	$\theta = 45^\circ$	$\Delta(45^\circ-0^\circ)$
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  $3695\text{ cm}^{-1}$  absorption band and the intensity of the  $7.1\text{ \AA}$  X-ray peak of (1) the pure kaolinite, (2) the  $\text{CH}_3\text{COOK}$ -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  $3695\text{ cm}^{-1}$  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  $3650\text{ cm}^{-1}$  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  $\nu(\text{OH})$  absorption band at  $3695\text{ cm}^{-1}$  and the appearance of a new absorption band at  $3600\text{ cm}^{-1}$  in the  $\text{CH}_3\text{COOK}$ -kaolinite complex. First, the inner-surface hydroxyls form weak hydrogen bonds with the acetate anion and cause the shift of the  $3695\text{ cm}^{-1}$  to  $3600\text{ cm}^{-1}$ . This shift resulting from hydrogen bond association is comparable with that observed for the association of phenol with carbonyl compounds and ethers. The  $3600\text{ cm}^{-1}$  absorption band was shifted to  $2650\text{ cm}^{-1}$  as a result of deuteration (Fig. 4c),

indicating the formation of a similar bond type between the deuterioxylys and the acetate anions. The stretching vibration frequency of the CH group at  $2970\text{ cm}^{-1}$  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  $2650\text{ cm}^{-1}$  absorption band compared to that of the  $3600\text{ cm}^{-1}$ : (1) the possible formation of a bond O-D . . .  $\text{CD}_3\text{COOK}$  that would vibrate at a frequency lower than  $2650\text{ cm}^{-1}$  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  $11.6\text{ \AA}$  and a larger amount collapsed to  $7.1\text{ \AA}$ . When the intersalated complex was bathed in an excess of  $\text{D}_2\text{O}$  vapor, a large amount of interlayer  $\text{CH}_3\text{COOK}$  molecules was removed, and most of the particles collapsed to  $7.1\text{ \AA}$  on heating at  $110^\circ\text{C}$ . The large number of collapsed kaolinite particles would explain the strong intensity of the  $2725\text{ cm}^{-1}$  absorption band, whereas the small proportion of expanded particles at  $11.6\text{ \AA}$  would yield a weak  $2650\text{ cm}^{-1}$  absorption band. The second hypothesis assigns the  $3600\text{ cm}^{-1}$  absorption band in the  $\text{CH}_3\text{COOK}$ -kaolinite complex to occluded water molecules. This is suggested by the complete disappearance of the  $3600\text{ cm}^{-1}$  absorption band on deuteration and the shift to  $2650\text{ cm}^{-1}$ . The weakness of the  $2650\text{ cm}^{-1}$  absorption band would be due to the small amount of remaining occluded  $\text{D}_2\text{O}$  after the collapse of most of the clay particles to  $7.1\text{ \AA}$ . If this hypothesis is right, the decrease in intensity of the  $3695\text{ cm}^{-1}$  absorption band would result from strong hydrogen bonding with acetate anions, causing a shift larger than  $100\text{ cm}^{-1}$  and overlapped by the wide water band in the  $3400\text{ cm}^{-1}$  region. A study of surface reaction of OH groups of Carbosil with dimethyl vapors (McDonald, 1958) revealed a shift of the sharp  $\nu(\text{OH})$  band located at  $3750\text{ cm}^{-1}$  to a broad band at  $3290\text{ cm}^{-1}$  in the silanol-ether complexes. The  $460\text{ cm}^{-1}$  shift was interpreted as due to ether molecules approaching the silanol groups closely enough to participate in strong hydrogen bonding. Actual data on the  $\text{CH}_3\text{COOK}$ -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  $\nu(\text{COO})$  stretching band is necessary to find out about the magnitude of the shift. Nevertheless, it is evident that the inner-surface hydroxyls absorbing at  $3695\text{ cm}^{-1}$  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  $3695\text{ cm}^{-1}$  absorption band and additional absorptions at  $3570$ ,  $3470$ ,  $3365$ ,  $3310$  and  $2970\text{ cm}^{-1}$ . In the infrared spectrum of hydrazine, Giguere and Liu (1952) have observed vapor absorption bands at  $3280$ ,  $3314$ ,  $3325$  and  $3350\text{ cm}^{-1}$  and assigned these frequencies to  $\nu(\text{NH}_2)$  stretching modes of vibration; the corresponding  $\nu(\text{NH}_2)$  stretching frequencies of liquid hydrazine occurred at  $3200$  and  $3338\text{ cm}^{-1}$ . However, Catalano, Sanborn and Frazer (1963) observed in the matrix isolation spectra of  $\text{NH}_2\text{NH}_2:\text{N}_2$  the following absorption bands in the  $\nu(\text{NH}_2)$  stretching region:  $3207$ ,  $3297$ ,  $3356$  and  $3390\text{ cm}^{-1}$ ; they claimed that all the bands were

due to monomeric species except the  $3207\text{ cm}^{-1}$ . Thus, the  $\nu(\text{NH}_2)$  stretching region for hydrazine extends from  $3200$  to  $3390\text{ cm}^{-1}$ .

The infrared spectrum of hydrazine-kaolinite complex (Fig. 9b) shows two absorption bands at  $3365$  and  $3310\text{ cm}^{-1}$  located within the range of the  $\nu(\text{NH}_2)$  stretching modes of vibration of hydrazine. The strong absorption band at  $3365\text{ cm}^{-1}$  is tentatively correlated to  $\nu(\text{NH}_2)$  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  $\nu(\text{OH})$  absorption bands  $3695$ ,  $3670$  and  $3650\text{ cm}^{-1}$  of kaolinite suggests hydrogen-bonding participation with intercalated hydrazine molecules. It is postulated that the broad band located at  $2970\text{ cm}^{-1}$  corresponds to  $\text{NH}_2$  groups strongly hydrogen-bonded with the hydroxylic surface of the kaolinite mineral i.e. to  $\text{O}-\text{H} \dots \text{N}$  bond. The sharpness and the high frequency of the  $3365\text{ cm}^{-1}$  absorption band indicate hydrazine molecules not properly arranged to form hydrogen bond. The absorption band at  $3470\text{ cm}^{-1}$  is believed to result from occluded water, but no assignment is provided for the  $3570\text{ cm}^{-1}$ .

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

$\nu(\text{cm}^{-1})$		$\nu(\text{OH})$	OH-OD exchange %
OH	OD	$\nu(\text{OD})$	
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  $3650\text{ cm}^{-1}$  are largely exchanged with deuterium oxide at room temperature, whereas the OH absorbing at  $3620\text{ cm}^{-1}$  are less readily exchanged. This isotope exchange mechanism provides evidence for frequency shift assignments and for a correlation of the  $\nu(\text{OH})$  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  $3650\text{ cm}^{-1}$  suggest that they occupy identical accessible positions; they are correlated to inner-surface OH. The hydroxyls absorbing at  $3620\text{ cm}^{-1}$  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:

$$\begin{aligned} 3695 \text{ cm}^{-1} &\text{ to } 2725 \text{ cm}^{-1} \\ 3670 \text{ cm}^{-1} &\text{ to } 2710 \text{ cm}^{-1} \\ 3650 \text{ cm}^{-1} &\text{ to } 2698 \text{ cm}^{-1} \\ 3620 \text{ cm}^{-1} &\text{ to } 2675 \text{ cm}^{-1} \end{aligned}$$

A rotation of  $45^\circ$  of the deuterated kaolinite film in the infrared beam produces considerable increase in the intensity of all the absorption bands, except the  $3620 \text{ cm}^{-1}$  (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  $3620 \text{ cm}^{-1}$  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  $3670 \text{ cm}^{-1}$  and of OD groups absorbing at 2725 and  $2698 \text{ cm}^{-1}$  is nearly at right angles to the basal plane (001); for the 3650 and  $2675 \text{ cm}^{-1}$  the angle is large but less than  $90^\circ$ . The direction in dipole moment change of the OH groups absorbing at  $3620 \text{ cm}^{-1}$  makes an angle of  $16^\circ$  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  $3695 \text{ cm}^{-1}$  was interpreted as indicative of OH-bond axes at right angles to the (001) plane, whereas the nonpleochroic absorption at  $3620 \text{ cm}^{-1}$  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  $\nu(\text{CO})$  stretching mode of the peptide group has been shown experimentally and theoretically to have a transition moment making an angle of about  $20^\circ$  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  $3620 \text{ cm}^{-1}$ , 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  $3617 \text{ cm}^{-1}$ . When the above values were plotted on the correlation curve  $\nu(\text{OH})$  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  $12^\circ$  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  $\Delta(45^\circ-0^\circ)$  values (Table 2) of the  $\nu(\text{OH})$  and  $\nu(\text{OD})$  intensities clearly shows that, for the same angle of rotation, the pleochroism is more intense in the  $\nu(\text{OD})$  region than in the  $\nu(\text{OH})$  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  $\nu(\text{OH})$  region prior to deuteration. The effect is illustrated by the  $2675\text{ cm}^{-1}$  band. After deuteration it is slightly pleochroic.

It is important to point out that the difference between the high and low frequency of the  $\nu(\text{OH})$  stretching modes ( $3695-3620 = 75\text{ cm}^{-1}$ ) is larger than that in the  $\nu(\text{OD})$  region ( $2725-2675 = 50\text{ cm}^{-1}$ ). 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  $\nu(\text{OH})$  stretching frequencies of freer OH groups ( $3650\text{ cm}^{-1}$  and above) are less sensitive to the (O . . . O) distances than the lower  $\nu(\text{OH})$  frequencies corresponding to shorter (O . . . O) lengths. Thus, the shifted  $\nu(\text{OD})$  frequency ( $2675\text{ cm}^{-1}$ ) corresponding to the  $3620\text{ cm}^{-1}$  band is more affected by deuteration than the shifted frequency  $2725\text{ cm}^{-1}$ , which is related to freer OH groups absorbing at  $3695\text{ cm}^{-1}$ ; the net result is a contraction of the band width in the  $\nu(\text{OD})$  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  $2\mu$ ) 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  $3620\text{ cm}^{-1}$  and three weak absorption bands at  $3520$ ,  $3450$  and  $3370\text{ cm}^{-1}$ . The deuterated sample (Fig. 11b) shows a large reduction in the intensity of the  $3695\text{ cm}^{-1}$ , a strong absorption at  $2725\text{ cm}^{-1}$ , a shoulder at  $2680\text{ cm}^{-1}$ ,

and weaker bands at 2930 and 2850  $\text{cm}^{-1}$ . The shift of the 3695  $\text{cm}^{-1}$  to 2725  $\text{cm}^{-1}$  is identical to the observed shift in kaolinite; the 2680  $\text{cm}^{-1}$  absorption band results from the deuteration of hydroxyls absorbing at 3620  $\text{cm}^{-1}$ . The absorption band at 3520, 3450 and 3370  $\text{cm}^{-1}$  are the  $\nu(\text{OH})$  stretching frequencies of a gibbsite impurity (Frederickson, 1954). The presence of gibbsite was confirmed by the X-ray reflections at 4.79  $\text{\AA}$  and 4.39  $\text{\AA}$ .

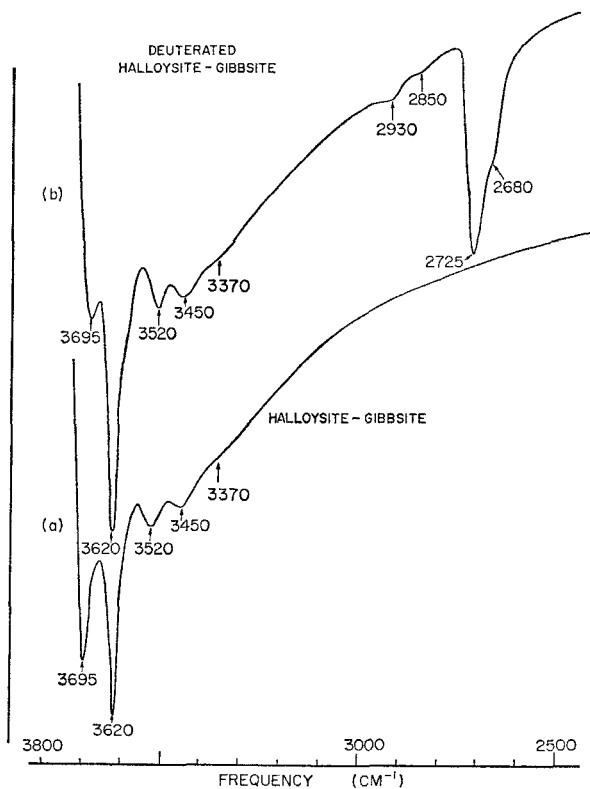


FIG. 11. Infrared spectra of (a) halloysite with gibbsite impurity, and (b) deuterated halloysite-gibbsite mixture.

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  $\text{CH}_3\text{COOK}$  remained in interlayer positions; this was indicated by weak X-ray reflection at 14.2  $\text{\AA}$ , the  $\nu(\text{CH})$  at 2930  $\text{cm}^{-1}$  and the  $\nu(\text{COO})$  at 1410 and 1560  $\text{cm}^{-1}$  (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  $\text{LiNO}_3$ -Treated Muscovite at Room Temperature*

In order to investigate more closely the weak deuteration of the inner hydroxyls absorbing at  $3620\text{ cm}^{-1}$ , we washed one sample of artificially expanded mica (White, 1956) three times with  $\text{H}_2\text{O}$  and a second sample with  $\text{D}_2\text{O}$ . After 15 hr of contact, a 1-ml portion of each suspension was evaporated

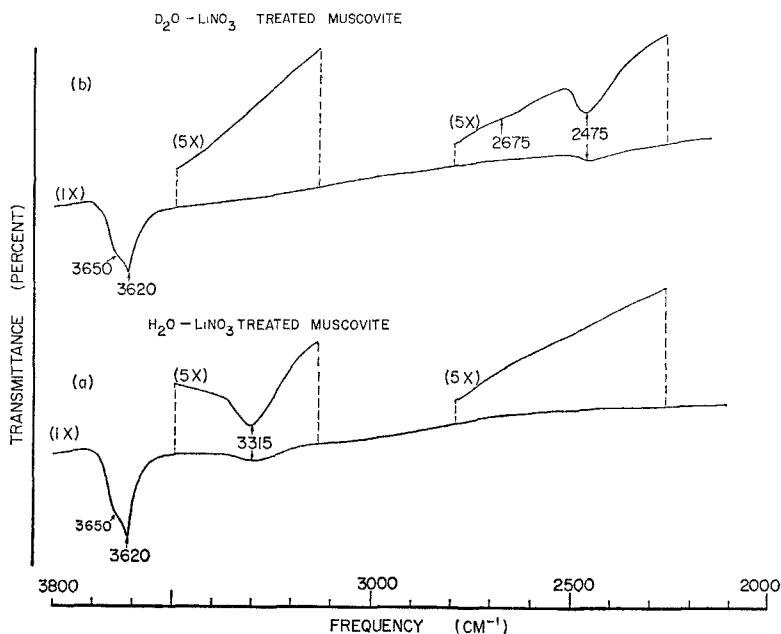


FIG. 12. Infrared spectra of artificially expanded muscovite washed with (a)  $\text{H}_2\text{O}$  and heated at  $110^\circ\text{C}$ , and (b) with  $\text{D}_2\text{O}$  and heated at  $110^\circ\text{C}$ .

on an Irtran window in an oven at  $110^\circ\text{C}$ . The infrared spectrum of the mica washed with  $\text{H}_2\text{O}$  (Fig. 12a) shows a strong absorption band at  $3620\text{ cm}^{-1}$  due to the  $\nu(\text{OH})$  stretching frequency of the inner lattice hydroxyls and a weak absorption band of  $3315\text{ cm}^{-1}$  corresponding to the  $\nu(\text{OH})$  of adsorbed water molecules. The mica washed with  $\text{D}_2\text{O}$  (Fig. 12b) shows the same absorption band at  $3620\text{ cm}^{-1}$  and a weak band at  $2475\text{ cm}^{-1}$ , which corresponds to the  $\nu(\text{OD})$  of adsorbed deuterium oxide molecules. The isotope ratio of the  $\text{OH}-\text{OD}$  shift of the adsorbed water is 1.339. If we assume that the isotope ratio of the inner lattice hydroxyls is 1.35, the  $3620\text{ cm}^{-1}$  absorption band should be shifted to  $2675\text{ cm}^{-1}$  by deuteration. The presence of a very weak

absorption band at  $2675\text{ cm}^{-1}$  (Fig. 12b) shows that the inner hydroxyls absorbing at  $3620\text{ cm}^{-1}$  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  $110^\circ\text{C}$ .

### SUMMARY

The kaolinite mineral used in this study showed four  $\nu(\text{OH})$  stretching absorption bands at 3695, 3670, 3650 and  $3620\text{ cm}^{-1}$ . Previous attempts to correlate these  $\nu(\text{OH})$  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.

Intercalation of kaolinite with  $\text{CH}_3\text{COOK}$  resulted in the reduction of the absorption intensity of the  $3695\text{ cm}^{-1}$  band and caused the occurrence of an additional absorption band at  $3600\text{ cm}^{-1}$ . The strong negative oxygens of the acetate anions formed hydrogen bonds with the inner-surface hydroxyls, thus shifting the  $3695\text{ cm}^{-1}$  frequency to lower value. Deuteration of the  $\text{CH}_3\text{COOK}$ -kaolinite complex produced considerable reduction in the intensities of the  $3695$  and  $3650\text{ cm}^{-1}$  absorption bands, complete disappearance of the  $3600\text{ cm}^{-1}$  frequency, and caused the occurrence of  $\nu(\text{OD})$  absorption bands at 2725, 2700, 2675 and  $2650\text{ cm}^{-1}$ . The hydroxyls absorbing at  $3620\text{ cm}^{-1}$  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  $3650\text{ cm}^{-1}$  absorption bands. Deuteration at room temperature of expanded hydrazine-kaolinite complex shifted the infrared stretching frequencies from  $3695\text{ cm}^{-1}$  to  $2725\text{ cm}^{-1}$ ,  $3670\text{ cm}^{-1}$  to  $2710\text{ cm}^{-1}$ ,  $3650\text{ cm}^{-1}$  to  $2698\text{ cm}^{-1}$ , and  $3620\text{ cm}^{-1}$  to  $2675\text{ cm}^{-1}$ . The OH-OD exchanges for the hydroxyls absorbing at  $3695$ ,  $3670$  and  $3650\text{ cm}^{-1}$  were 67, 60 and 62 per cent respectively and for the  $3620\text{ cm}^{-1}$  only 22 per cent. The smaller amount of OH-OD exchange for the hydroxyls absorbing at  $3620\text{ cm}^{-1}$  was also observed for halloysite,  $\text{LiNO}_3$ -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  $3670\text{ cm}^{-1}$  and of OD groups absorbing at  $2725$  and  $2698\text{ cm}^{-1}$  is nearly at right angles to the basal plane (001); for the  $3650$  and  $2675\text{ cm}^{-1}$ ; the angle is large, but less than  $90^\circ$ . The nonpleochroic behavior of the  $3620\text{ cm}^{-1}$  absorption band showed that the direction of dipole moment change of the inner OH makes an angle of about  $15^\circ$  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  $\text{cm}^{-1}$  to inner-surface hydroxyls and of the 3620  $\text{cm}^{-1}$  frequency to inner hydroxyls.

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