

ORIENTATION OF HEXANEDIAMINE IN SYNTHETIC FLUORHECTORITE

WILLIAM HERTL AND ROGER F. BARTHOLOMEW

Corning Inc., Research & Development Division (SP-FR-6)
Corning, New York 14831

Abstract—Fourier-transform infrared (FTIR) spectroscopic studies were carried out on 1,6-hexanediamine hydrochloride (HDA)-treated synthetic fluorhectorite to determine the orientation of functional groups within the structure. Oriented crystal layers were prepared by flocculating the smectite slurry with glass fibers to obtain a 100- μm -thick paper. Orientations were determined by measuring integrated IR band intensities at various incident beam angles ($\leq 60^\circ$), inasmuch as absorption occurred only if the oscillating dipole of the functional group interacted with the electric vector of the incident radiation. The H-N-H plane in amine groups was aligned parallel to the lamellar plane. The H-O-H plane of the small amount of sorbed water was inclined 45° or more to the interlamellar layer, and the OH groups were inclined 45° to this layer.

Even with the incorporation of HDA in the interlamellar structure, at high humidity, additional water sorbed. The sorbed water competed with and displaced amine groups from the surface, resulting in randomly oriented amine groups. Many of the amine groups were ionized, whereas the additional sorbed water showed little orientation.

This study demonstrated that the orientation of intercalated amines in fluorhectorite can be determined by following the intensity changes in infrared-active bands as a function of the incident beam angle. With intercalated HDA, the orientations were influenced by the presence of interlayer water.

Key Words—Adsorption, Fluorhectorite, Fourier-transform infrared spectroscopy, Functional group orientation, Hexanediamine, Infrared Spectroscopy.

INTRODUCTION

Pillaring in phyllosilicates has become of great interest because of the many potential uses of these materials in chromatography (Mingelgrin *et al.*, 1985), adsorption (Odom, 1984), and as effective petroleum-cracking catalysts (Adams *et al.*, 1987). Synthetic fluorhectorites, because of their controlled composition and purity, can be used as binder systems in a glass fiber paper for printed circuit boards (Hoda, 1986). Epoxy-filled ceramic paper laminates are superior to the conventional circuit-board substrate material (FR-4) in thermal, electrical and dimensional stabilities. Naturally occurring layered silicates have been used as binders to make paper, but because of impurities, electrical properties are well below the required specifications. In particular, to minimize the sensitivity of the dielectric properties to humidity arising from the hydrophilic nature of the fluorhectorite, the paper can be treated with different chemicals prior to resin impregnation. Treatment of the paper with amines, such as hexanediamine hydrochloride, has been found to improve the water resistance of epoxy-impregnated paper (Hoda, 1986). The present study was undertaken to aid in optimizing the pillaring process, with the object being to understand the way the amine is oriented between the silicate layers, how the pillaring affects the water structure in the inner layers, and the effect of variable ambient humidity on these interlayer structures.

Infrared spectra of oriented clay films, using either

polarized light or varying incidence angles of the IR beam with respect to the film, can be used to determine the orientation of functional groups in the interlamellar structure. Light absorption occurs if the oscillating dipole of a functional group interacts with the electric vector of the incident radiation. If the molecules are oriented, the intensities of several of the bands change intensity with changes in polarization angle or angle of incidence. If the molecules are not oriented, the band intensities do not change.

Several studies have dealt with the orientation of OH groups in lawsonite (Labotka and Rossman, 1974), kaolinite (Serratosa *et al.*, 1962), oxidized and unoxidized biotite (Juo and White, 1969), and vermiculite (Hougardy *et al.*, 1970). Comparative studies of various micas (Serratosa and Bradley, 1958; Rouxhet *et al.*, 1966; Fripiat *et al.*, 1984) have also been made. Generally the orientations of the OH groups, with respect to the cleavage planes, have been determined. Often the orientation of interlayer water molecules could also be determined.

The incorporation of organic molecules into layered silicates has been widely studied. Several infrared techniques have been used to determine the molecular orientations. Attenuated total reflectance spectra with polarized light has been used to compare ornithine and aminohexanoic acid in vermiculite (Raupach and Janik, 1976). This system has also been studied using X-ray diffraction (Slade *et al.*, 1976). Changes in the

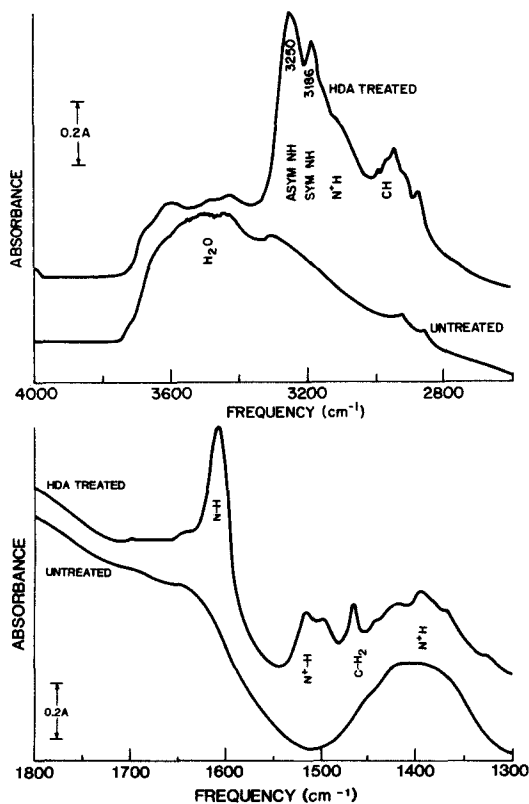


Figure 1. Spectra of fluorhectorite paper (upper) before and (lower) after hexanediamine (HDA) treatment.

dichroism of specific absorption bands showed that neutral or charged pyridine can be incorporated in clay complexes either vertically or flat (Serratosa, 1964) and that octyl-ammonium complexes differently with vermiculite in the expanded and collapsed phases (Serratosa *et al.*, 1970). Perturbations in absorption band frequencies corroborated the conformations of highly ordered dimethyl sulfoxide-kaolinite complexes (Johnston *et al.*, 1984).

The present paper describes an IR study of the reactions between interlayer 1,6-hexanediamine hydrochloride and synthetic fluorhectorite. The synthetic fluorhectorite was prepared as thin sheets by a papermaking process that oriented the fluorhectorite plates. Spectra were recorded over a range of incident-beam angles which allowed intensity changes arising from the orientation of the hexanediamine, the hydroxyl groups, and the water in the interlamellar spaces to be observed. Changes in molecular orientation with changes in the ambient humidity were also observed.

EXPERIMENTAL

Fluorhectorite synthesis

Fluorhectorite was synthesized by preparing a glass of composition $\text{NaMg}_{2.5}\text{Si}_4\text{O}_{10}\text{F}_2$ from silica sand, so-

dium carbonate, magnesium oxide, and sodium silicofluoride. The melt was covered to minimize fluorine loss. The glass was then heat treated at 925°C to nucleate and grow the crystalline fluorhectorite (Beall *et al.*, 1980). The synthetic fluorhectorite that was produced was charge deficient; this is a major requirement for water swelling in layered silicates. When exposed to water, it readily swelled and self-delaminated. The delaminated material was then ion exchanged in KCl solution, which formed a flocculated suspension in water containing about 6 wt. % solids. The suspension was further treated in a Kady Mill to reduce the size of the particles to about 1 μm in length and 3 or 4 molecular layers thick. The resultant slurry was used to make paper.

Papermaking process

The slurry was used to prepare paper using either handsheet equipment (Williams Company, Watertown, New York), or a Fourdrinier process (University of Miami (Oxford, Ohio)). No difference was noted between the paper made by hand or by machine. The paper contained 25 wt. % of E-Glass fiber (C-1/4"-636) and 75% fluorhectorite. To improve the drainage of the paper and to maximize the solids retention, 0.5 g of polyethylene imine to 100 g of fluorhectorite was used as a retention aid. The paper weighed 85 g/m^2 , and was 0.004 inches (100 μm) thick.

Paper treatments

Sheets of the paper were cut into about 15-cm squares and treated in an aqueous solution of 1,6-hexanediamine hydrochloride. Ion exchange of the monovalent hexanediamine cation was generally complete in < 15 min. The sheets were soaked for 20 min and then washed in reverse osmosis-treated water to remove the excess chloride. Two washings of about 10-min duration were sufficient to reduce the chloride level to < 0.1 wt. %. The treated sheets were air dried for 10 min and then dried in an oven at 155°C for 1 hr.

Spectroscopic measurements

All spectra were taken with a Perkin-Elmer model 1800 FTIR double-beam spectrophotometer. The paper was sufficiently thin (100 μm) to transmit IR radiation over the greater part of the spectral range (\approx 0.5% transmittance at 4000 cm^{-1} , increasing to about 15% transmittance at low frequencies).

The spectra were acquired using a deuterated triglycine sulfate (DTGS) detector operating at ambient temperature. Typical instrument operating parameters were 30 sample scans at 4- cm^{-1} resolution using a 0.10- cm/s interferometer mirror speed. The peak-to-peak signal-to-noise ratio, measured on the background in the interval 2600–2700 cm^{-1} , was \geq 800:1.

For the band intensity vs. beam incidence-angle studies the paper was mounted in a variable-angle

Table 1. NH-band frequencies of 1,6-hexanediamine (HDA) dispersed in various media.

Medium	NH-stretching bands	N ⁺ H-stretching bands	Frequency shift ¹
CCl ₄	3387, 3320	—	0 (ref.)
	3298, 3191		-89
Aqueous (pH = 12)	3374, 3308		-13
Aqueous (pH = 2)		3070	
Ether	3360, 3300	3080	-27
	3250, 3192		-137
KBr	3338		-49
	3338	3080	-49
Solid HDA	3330		-57
Fluorlube	3250, 3170		-137
	3250, 3186	3080	-137

¹ Frequency shift in cm⁻¹ of asymmetric NH-band measured with respect to band frequency of hexanediamine dispersed in CCl₄.

holder, which could be adjusted to the nearest 0.5°. The paper sample was sufficiently large so that the entire beam area was intercepted at all angles. For a given sample, about 12 spectra were taken, in random order, over a range of beam-incidence angles of 7° to 60°. If possible, integrated band areas were measured using the software provided with the spectrophotometer; otherwise, optical densities (absorbances) were measured. If both could be measured, similar behavior was observed for the CH (2900-cm⁻¹), NH (3240-cm⁻¹), and OH (3600-cm⁻¹) bands.

RESULTS AND DISCUSSION

Spectral features of fluorhectorite paper

Figure 1 shows spectra of untreated fluorhectorite paper and paper that was treated with hexanediamine hydrochloride (HDA). Changes due to the treatment include a reduction in sorbed water (broad absorption near 3400 cm⁻¹ and band at 1640 cm⁻¹) and an appearance of the NH- and CH-bands due to the sorbed HDA.

Several OH-stretching bands were also apparent in the 3600-cm⁻¹ region, which partially overlapped the strong water stretching band. To improve the resolution of these OH bands by removing a large fraction of the water, untreated fluorhectorite paper was heated in air at 475°C for 2 hr. With most of the water removed, discrete, but weak (absorbances = 0.03–0.04) OH bands were observed at 3730, 3666, and 3590 cm⁻¹. These probably arose from some hydroxylation resulting from the various aqueous solution treatments used in the papermaking process. After the HDA treatment, a broader, more prominent OH band appeared near 3600 cm⁻¹ (Figure 1, upper), which probably was due to coordinated water. An OH-stretching band near 3635 cm⁻¹, arising from coordinated water in Mg-hectorite, was reported by Farmer and Russell (1971). Because -N⁺H groups were also observed, the forma-

Table 2. Ratio of hexanediamine NH/CH-band intensities.

Medium	A _{NH} /A _{CH}
CCl ₄	0.07–0.2
Fluorlube	0.65
KBr	2.0
In fluorhectorite	6.90–11.4

tion of RNH₃OH could also have contributed to the appearance of the OH bands.

Spectra were taken of HDA in polar and non-polar solvents and in the solid state. The NH-band frequencies for HDA in the media are listed in Table 1 along with the frequency shifts ($\Delta\nu$) measured with respect to HDA dispersed in CCl₄.

Spectra of dilute solutions of alkyl amines in non-polar solvents showed the asymmetric NH-stretching band at 3398–3381 cm⁻¹ and the symmetric NH-stretching band at 3344–3324 cm⁻¹. These bands showed small frequency shifts with changes in solvent polarity and larger shifts in concentrated solutions if intermolecular association occurred. Intramolecular bonding also lowers the frequencies (Bellamy, 1975).

HDA adsorbed in the interlamellar spaces gave rise to predominantly lower frequency NH-bands ($\Delta\nu = 137$ cm⁻¹), showing that the NH groups interacted with the fluorhectorite or that the amine molecules were self-associated under the constraints of the interlayer space. In addition, weak bands due to N⁺H were observed for some samples and arose from the presence of moisture reacting with the amino groups.

In addition to the NH-frequency shifts, the distribution of CH-stretching band intensities also changed, indicating an interaction with the hectorite surface. Table 2 gives the ratios of the NH- to CH-integrated band intensities for HDA in several of the systems. The ratios of NH/CH band intensities varied over a wide range and was highest for HDA sorbed in the interlamellar spaces.

Relative intensity changes for methylated phenol CH₃-stretching modes in solution and chemisorbed on Al₂O₃ have been ascribed to methyl group interaction with the surface (Taylor and Ludlam, 1972). Profound reductions in CH-band intensities of methylene groups have also been reported (Raupach and Janik, 1976) as being due to the closeness of these groups to surface oxygen atoms of the silicate layer, which exert van der Waals forces on these groups. For this reduction to occur, at least some of the carbons must be within 3.4 Å of the silicate surface oxygens.

Oriented structures

A vibration is said to be infrared active if a change in dipole moment occurs during the vibration. For a vibrational excitation to occur, the oscillating dipole and the electric vector of the radiation must interact.

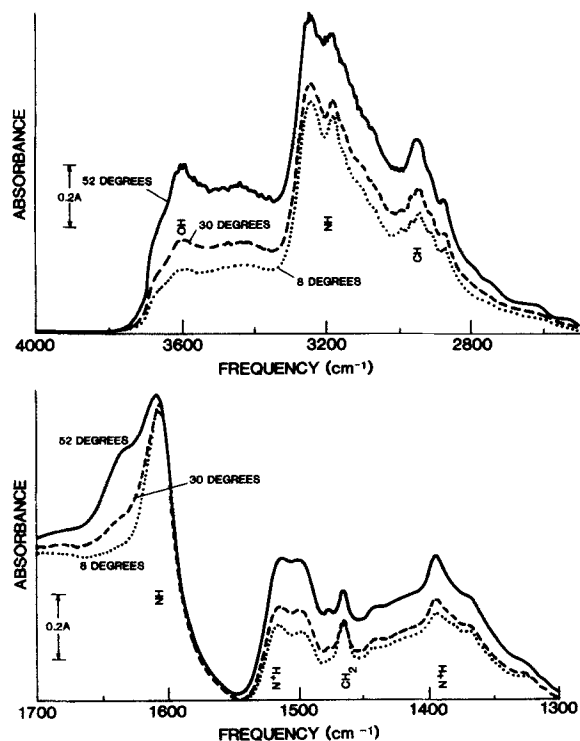


Figure 2. Spectra of hexanediamine-treated fluorhectorite paper taken at several beam incidence angles. Paper was desiccated for three days prior to taking spectra.

If the oscillating dipole is perpendicular to the electric vector, no interaction occurs; if the oscillating dipole is parallel to the electric vector, maximum interaction occurs. In gases and liquids the molecules are randomly oriented, and all infrared active vibrations give rise to absorption bands. This phenomenon has been used to study the orientation of subunits in stretched polymer films by polarized radiation (Jasse and Koenig, 1979) and adsorbed molecules in phyllosilicates by varying the incidence angle of the radiation.

The papermaking process produced plates for which the probability of fluorhectorite layers being parallel to the plane of the paper is high. Spectra were recorded and band intensities were measured over a 7°–60°-range of beam-incidence angles; selected spectra are shown in Figure 2. Particularly prominent were the intensity changes in the bands near 3600 cm⁻¹ (-OH), 3450 cm⁻¹ (H₂O), and 1640 cm⁻¹ (H₂O).

The path length through the sample increased with increasing incidence angle. To normalize the data to constant path length (Lambert's law), the band areas and peak absorbances were multiplied by the cosine of the incidence angle. The data are plotted in Figures 3a–3d, with the lines drawn to guide the eye.

Amine groups. The changes in dipole moments for both the NH-stretching and NH₂-bending vibrations of the

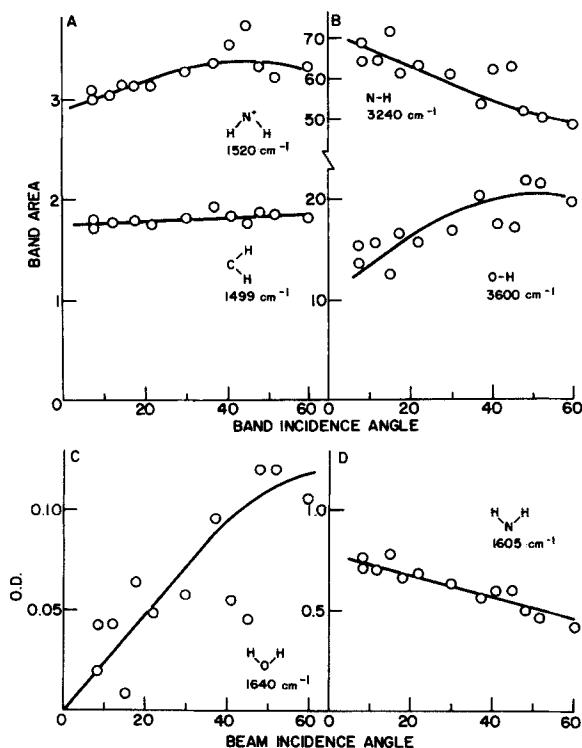


Figure 3. Band intensities measured on desiccated fluorhectorite, from spectra taken at various beam incidence angles. Band intensities were corrected for increasing path length through sample with increasing angle. Lines were drawn to guide the eye.

-NH₂ group occur in the H-N-H plane. Figure 3 shows that the behavior of the stretching vibrations near 3240 cm⁻¹ (Figure 3b) was essentially the same as the bending vibration at 1605 cm⁻¹ (Figure 3d), i.e., that the H-N-H plane was nearly parallel to the surface.

Methylene groups. The intensities of the CH₂-bending vibrations at 1469 cm⁻¹ (Figure 3a) from the hexane chain were nearly constant. The NH/CH band-intensity ratios indicated that at least some of the carbons were within 3.4 Å of the surface oxygens. For this flat configuration the CH₂ bending dipoles were oriented randomly within the *a-b* plane.

Ammonium groups. The band at 1520 cm⁻¹ arose from the bending vibration mode of the -N⁺H₃ group. This group showed some small preferential orientation near 45° incidence (Figure 3a).

Hydroxyl groups. The change in dipole moment of the OH group vibration at 3600 cm⁻¹ was along the O-H bond axis. This band increased in intensity with increasing angle of incidence (Figure 3b) and showed a maximum in the range 37°–47°, indicating that the OH groups were inclined to the interlamellar plane. Farmer and Russell (1971) showed that the appearance of a

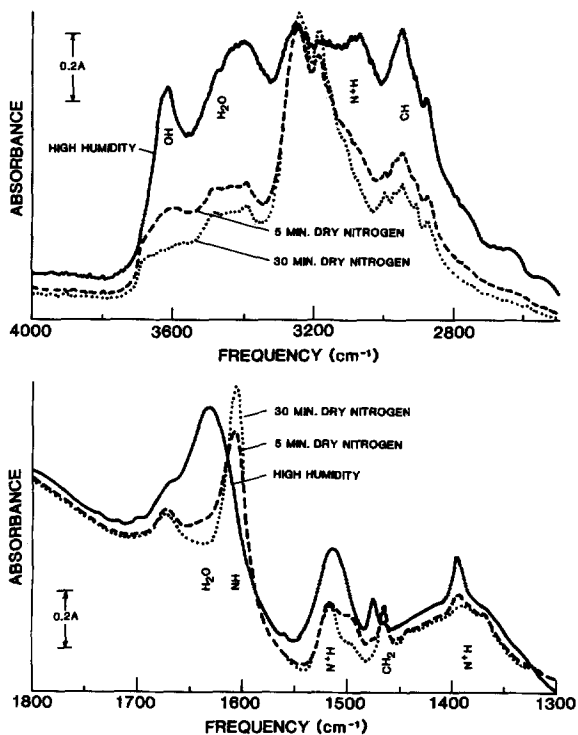


Figure 4. Spectra of hexanediamine-treated fluorhectorite paper (a) in high humidity atmosphere, (b) after 5 min in dry nitrogen, and (c) after 30 min in dry nitrogen.

high-frequency OH band near 3620 cm^{-1} arises from water in layer silicates, specifically from OH groups directed at a high angle to the silicate sheets. The OH-band intensity changes observed here are consistent with this explanation.

Molecular H_2O . The bending mode of water at 1640 cm^{-1} is an in-plane H–O–H vibration, with the dipole moment change along the molecular axis. The weak band intensity at low incidence angles (Figure 3c), along with the intensity increases with increasing angle indicate that the H–O–H plane was oriented at a large angle to the plane of the fluorhectorite paper.

Large oscillating absorbance changes were obvious from a visual inspection of the spectra. The same behavior was shown by the water-stretching band at 3400 cm^{-1} , the magnitude of which was much greater than the 10–15% scatter obtained from measurements of the other functional groups. The reason for the apparent oscillating absorbance is not clear, although the behavior is suggestive of an interference effect.

Effect of adsorbed water on structure

Water adsorbed reversibly on fluorhectorite. The spectra of HDA-treated fluorhectorite paper (a) immediately after exposure to a relative humidity close to 100%, (b) after 5 min in a dry nitrogen atmosphere, and (c) after 30 min in a dry nitrogen atmosphere are

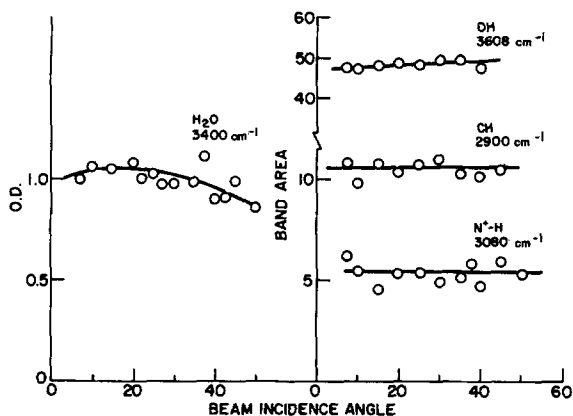


Figure 5. Band intensities measured on fluorhectorite at ambient humidity, from spectra taken at various beam incidence angles. Band intensities were corrected for increasing path length through sample with increasing angle. Lines were drawn to guide the eye.

shown in Figure 4. The change in sorbed water is readily seen from the intensity changes in the water bands near 3400 and 1640 cm^{-1} . The sorbed water interacted with the amine groups because additional ionized N^+H_3 groups were apparently present (3080 , 1395 , and 1516 cm^{-1}). A substantial increase in OH band intensity at 3614 cm^{-1} was also observed, due to the additional water or water interaction with HDA.

Changes were also observed in the bands associated with the randomly oriented methylene groups. If moisture was sorbed, the intensities of the CH vibrations (2900-cm^{-1} region) increased 2.6 times and the CH-bending vibration at 1465 cm^{-1} shifted to 1476 cm^{-1} (Figure 4). Band intensity decreases have been ascribed to interactions with the van der Waals force field from the surface (Raupach and Janik, 1976), as mentioned above, suggesting that if water was sorbed, the CH groups were displaced from the surface.

The orientation of the functional groups was determined, as described above, for fluorhectorite paper in equilibrium with the ambient atmosphere (50%–60% RH). The integrated band areas or absorbances at various incidence angles are plotted in Figure 5. As for the dry sample, the methylene CH ($2800\text{--}3000\text{ cm}^{-1}$) and ionized N^+H (3080 cm^{-1}) stretching bands showed little change in intensity at various incidence angles.

The additional OH groups at 3608 cm^{-1} were also essentially random. Accurate amine-group measurements could not be obtained due to the strong intensity of the overlapping water-vibration band. The average band intensity due to the adsorbed molecular water indicated a nearly random water arrangement.

CONCLUSIONS

These data suggest that HDA molecules were taken into the fluorhectorite interlayer spaces in such a man-

ner that the $-NH_2$ groups were aligned with the H-N-H planes parallel to the basal surfaces. The methylene groups showed no particular orientation. The few ionized amine groups present showed little orientation. The adsorbed water H-O-H plane was oriented at a large angle to the basal surfaces with the hydroxyl groups inclined 45° to the interlamellar planes.

If additional water was taken up, it competed with the amine groups for the fluorhectorite sites. Many of the amine groups became ionized. This additional sorbed water showed little orientation.

The methylene groups showed no particular spatial orientation. During adsorption of water the methylene group band intensity increased, indicating that the methylene groups were adjacent to the surface plane in the dry state, but became displaced as the adsorption of water increased.

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