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HYDROXYL DEFORMATION IN KAOLINS

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Abstract—The hydroxyl deformation modes of kaolins have been studied by Fourier transform (FT) Raman spectroscopy. Kaolinites showed well-resolved bands at 959, 938 and 915 cm^{-1} and an additional band at 923 cm^{-1}. For dickites, well-resolved bands were observed at 955, 936.5, 915 and 903 cm^{-1}. Halloysites showed less-resolved Raman bands at 950, 938, 923, 913 and 895 cm^{-1}. The first 3 bands were assigned to the librational modes of the 3 inner-surface hydroxyl groups, and the 915-cm^{-1} band was assigned to the libration of the inner hydroxyl group. The band in the 905 to 895 cm^{-1} range was attributed to "free" or non-hydrogen-bonded inner-surface hydroxyl groups. The 915-cm^{-1} band contributed ~65% of the total spectral profile and was a sharp band with a bandwidth of 11.8 cm^{-1} for dickite, 14.0 cm^{-1} for kaolinites and 17.6 cm^{-1} for halloysites. Such small bandwidths suggest that the rotation of the inner hydroxyl group is severely restricted. For the inner-surface hydroxyl groups, it is proposed that the hydroxyl deformation modes are not coupled and that the 3 inner-surface deformation modes are attributable to the three OH2-4 hydroxyls of the kaolinite structure. For intercalates of kaolinite and halloysite with urea, a new intense band at ~903 cm^{-1} was observed with concomitant loss in intensity of the bands at 959, 938 and 923 cm^{-1} bands. This band was assigned to the non-hydrogen-bonded hydroxyl libration of the kaolinite–urea intercalate. Infrared reflectance (IR) spectroscopy confirms these band assignments.

Key Words—Deformation Mode, Dickite, FT Raman, Halloysite, Hydroxyl, Infrared, Intercalation, Kaolinite, Libration, Reflectance.

INTRODUCTION

The vibrational spectroscopy of kaolins has attracted considerable interest due to its application to the structural study of kaolin minerals. The hydroxyl bands are very sensitive probes for distinguishing between kaolin clay minerals and determining their structure (Frost 1997). The assignment of the hydroxyl stretching bands remains under constant review, and differing viewpoints concerning the position and orientation of both the inner and inner-surface hydroxyl groups exist (Giese 1988). FT Raman spectroscopy has already proven a very powerful technique in the study of kaolin minerals (Frost et al. 1993; Frost 1995). Kaolinite, as with the other kaolin clay minerals, contains 2 types of hydroxyl groups: 1) the outer hydroxyl groups or so-called "inner-surface hydroxyls", designated OuOH, and 2) the inner hydroxyl groups, designated InOH. The OuOH groups are situated in the outer upper, unshared plane, whereas the InOH groups are located in the plane shared with the apical oxygens of the tetrahedral sheet. In an ordered sample such as the Georgia kaolinite (KGa-1), the 4 distinct IR bands are observed as follows: the 3 higher-frequency vibrations (ν_1, ν_2, ν_3) are assigned to the 3 outer (OuOH) and the ν_5 band at 3620 cm^{-1} is assigned to the inner hydroxyl (InOH) (Farmer 1974; Johnston et al. 1990). The latter assignment is based on selective deuteration studies (Ledoux and White 1964; Wada 1967; White et al. 1970; Rouxhet et al. 1977). The commonly accepted view is that the ν_1 and ν_2 bands are the coupled antisymmetric and symmetric vibrations (Brindley et al. 1986; Michaelian 1986). The assignment of the ν_3 band is open to question but the suggestion has been made that the band is due to symmetry reduction of the OuOH hydroxyl (Farmer and Russell 1964). These hydroxyl groups have deformation modes in the 915 to 960 cm^{-1} range which have been assigned to the inner and inner-surface hydroxyl modes, respectively, based on the selective deuteration made possible by the formation of interlayer complexes (Wada 1967). While there have been several IR studies of the hydroxyl deformation modes, no detailed studies of the Raman spectra of the hydroxyl deformation modes have been reported. Further, studies of halloysite hydroxyl vibrations are few, as are studies of the intercalation of halloysites with urea and potassium acetate. In this paper, Raman spectroscopy is applied to study of the aluminium hydroxyl deformation vibrations of kaolins, often termed "hydroxyl librations" because the rotation of the hydroxyl group is restricted due to hydrogen bonding. The basis of this research is to determine if the hydroxyl deformation vibrations are coupled or, if not, if the hydroxyl deformation vibrations represent discrete hydroxyl groups.

EXPERIMENTAL

A suite of kaolinites dickites and halloysites as shown in Tables 1 and 2 were analyzed by FT Raman spectroscopy, using the Perkin-Elmer 2000 series FT spectrometer. The latter was fitted with a Raman accessory comprising a Spectron Laser Systems SL301

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Table 1. Raman spectral analysis of the hydroxyl librational region of kaolinites and dickites.

		Kaolinites						Dickites	
		Keokuk	Mesa Alta	Birdwood	Lal-lal	Williamstown	Mt. Hope	San Juanito dickite	Sainte Claire dickite
Band 1	Band center	957	959	956	959	956	955		966
(ν_{L1})	Full width	19.4	11.8	20.3	19	18.7	19	—	15.3
	Band area	9%	5.3%	7.8%	6%	3%	2.1%		1.6%
Band 1	Band center	935	938	935	939	937	933.5	954	954
(ν_{L2})	Full width	22.5	18.5	6.7	15.3	7.8	7.3	18.7	17.7
	Band area	28.5%	24.4%	3.1%	15.5%	7.7%	5.5%	13.2%	11%
Band 2	Band center	925	923.7	924	924	923.5	919	936.5	936.5
(ν_{L3})	Full width	19.1	11.5	15.1	18.4	12.2	17.8	12.4	13.4
	Band area	15.9%	12.9%	20.8%	26.4%	22%	46.8%	6.7%	10.4%
Band 3	Band center	914.5	913.6	913.4	913.5	912.5	912	915	915.3
(ν_{L4})	Full width	19.1	14.2	14.0	15.4	11.6	10.9	11.8	11.7
	Band area	58.5%	57%	68.4%	57%	65.6%	47%	69.8%	64.5%
Band 4	Band center	895	901	891	891	902	895	901	904
(ν_{L5})	Full width	28.6	19.6	24	7	4.8	4.0	19.7	19.7
	Band area	2.3%	1.25%	1.3%	0.9%	4.7%	0.65%	10.3%	12.3%

Nd-YAG laser operating at a wavelength of 1064 nm, and a Raman sampling compartment incorporating 180-degree optics (Frost et al. 1993; Frost 1995; Frost 1997).

Experimental procedures for the intercalation of kaolinite and halloysites have been reported (Frost et al. 1997). The urea intercalate was prepared by simply mixing 300 mg of kaolinite with 30 mL of a 10-*M* urea solution. The urea solution is maintained at concentrations less than saturation, thus ensuring that no urea was mixed in with the kaolinite–urea intercalate. Three hundred milligrams of kaolinite or halloysite were treated with 30 mL of 7.2 *M* potassium acetate solution. The samples were shaken for 80 h in a constant temperature bath at ambient temperature for potassium acetate. The excess solution on the clay was removed by centrifugation. The intercalated kaolinite or halloysite was allowed to dry in air for 5 d before Raman spectroscopic analysis. The halloysite or kaolinite urea complex was dried in a desiccator above anhydrous calcium chloride. The degree of intercalation was determined by the ratio of the intensity of the 001 peak before and after intercalation.

Diffuse reflectance Fourier transform infrared spectroscopy (commonly known as DRIFT) analyses were undertaken using a Bio-rad 60A spectrometer. A total of 512 scans were obtained at a resolution of 2 cm^{-1}. Spectral processing such as baseline adjustment, smoothing and normalization was performed using the Spectracalc software package GRAMS (Galactic Industries Corporation, New Hampshire). Band component analysis was carried out using the peakfit soft-

Table 2. Raman spectral analysis of the hydroxyl librational region of halloysites and kaolinite and halloysite urea intercalates.

		Halloysite			Birdwood kaolinite–urea intercalate	Szeg halloysite–urea intercalate
		Szeg	NZ	Belgium		
Band 1	Band center	951	950	950		
(ν_{L1})	Full width	26	27.5	17.5	—	—
	Band area	14%	15%	12.3%		
Band 2	Band center	934	934	938	939	935
(ν_{L2})	Full width	23.7	22.9	22.9	12.7	14.6
	Band area	12.1%	12.2%	8%	2%	2%
Band 3	Band center	922	922	923	925	922
(ν_{L3})	Full width	19.1	19.1	19	14	18
	Band area	2.05%	2.75%	2.7%	2.5%	1.5%
Band 4	Band center	914	913	910	912.5	915
(ν_{L4})	Full width	17.8	17.6	21.5	12.6	15
	Band area	62.5%	58%	60.2%	17.4%	22.2%
Band 5	Band center	890	904	895	903	903
(ν_{L5})	Full width	18.5	19.7	29.5	15.8	19
	Band area	10.8%	10.7%	11.3%	75%	70%

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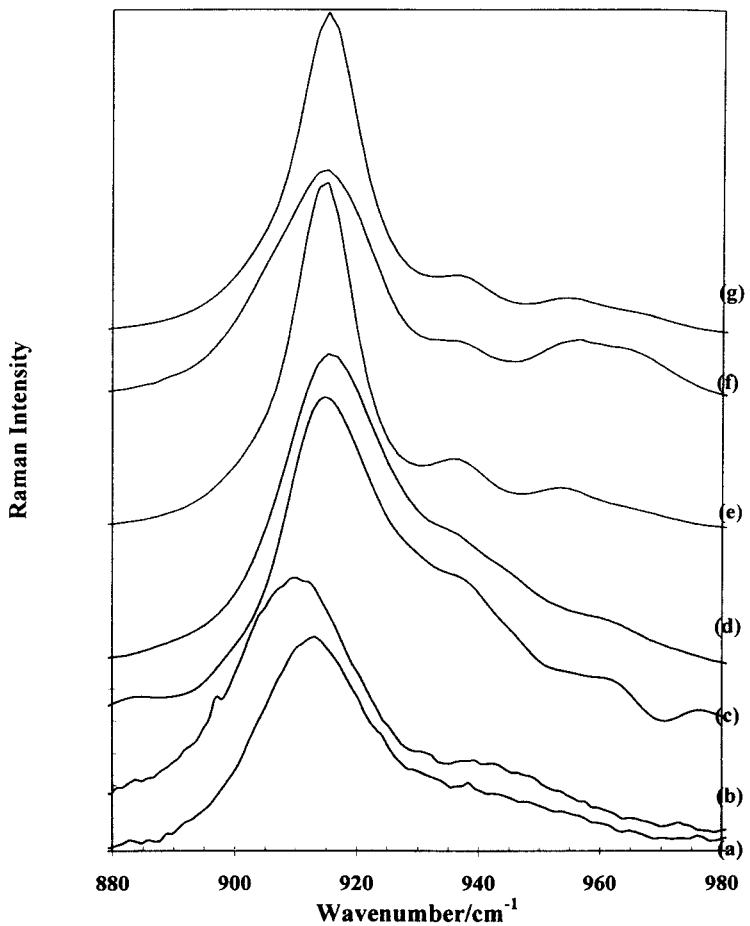


Figure 1. Raman spectra of the hydroxyl deformation region of: a) halloysite (New Zealand); b) halloysite (Belgium); c) kaolinite (Lal-lal Australia); d) kaolinite (Kiralyhegy) Hungary); e) dickite (Sainte Claire); f) dickite (Sainte Claire); g) dickite (San Juanito).

ware package by Jandel Scientific. Lorentz-Gauss cross product functions were used throughout and peak fitting carried out until the squared correlation coefficients with $r^2 > 0.995$ were obtained.

RESULTS AND DISCUSSION

Kaolinites

The inner and inner-surface OH deformation vibrations at 914 and 935 cm^{-1} were assigned by Wada using selective deuteration studies (Wada 1967). Only 2 IR bands were observed for kaolinite, but 3 at 960, 933 and 913 were observed for dickite. The bands at 960 and 935 cm^{-1} were shifted upon selective deuteration to 720 cm^{-1}. The band at 914 cm^{-1} remained unchanged in this process. The FT Raman spectra of the Al-OH-Al deformation modes have been reported by Frost (1997). Significant differences in the spectral region of the deformation modes were observed but the quality of the spectra was such that further analysis could not be undertaken. With the improvement in technology of the spectrometer, chiefly in detector response, the vibrational bands of the low-frequency region can now be measured with an improvement of a factor of 10 compared with that published (Frost 1997). The Raman spectra of the Al-OH librations of several kaolins are shown in Figure 1. The halloysite (Figures 1a and 1b) spectra are broad and of a weak intensity compared to that of the other kaolin polytypes. Spectra of kaolinites show greater resolution (Figures 1c and 1d). Spectra for dickites show further resolution with resolvable component bands (Figures 1e to 1f). Differences in the hydroxyl deformation spectra between the kaolinite clay minerals are attributed to differences in the kaolin polytype structures. The broad spectra without well-defined bands of the halloysites suggest considerable variation in the orientation of the hydroxyl groups. As this random variation in orientation of the hydroxyls is reduced from halloysite through kaolinite to dickite, the orientation of the hydroxyl groups is becoming more well defined, resulting in more highly resolved Raman spectra.

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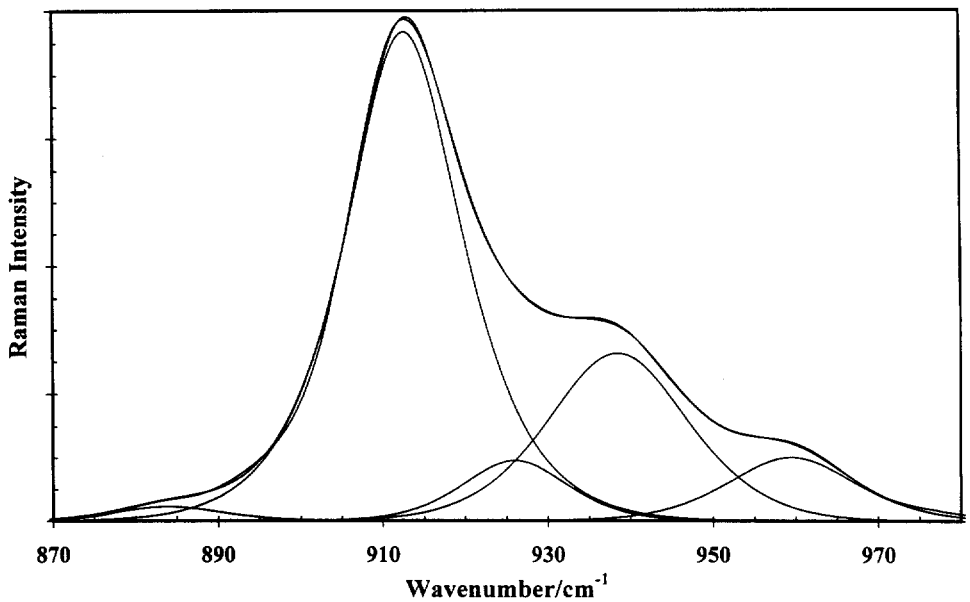


Figure 2. Band component analysis of the Raman spectrum hydroxyl deformation region of Keokuk kaolinite.

The intensity of the Al-OH bending vibrations of kaolins is weak, but is sufficient for band component analysis. The reason for this lack of Raman intensity may be attributed to the lack of symmetry of the deformation vibration. These deformation vibrations show much greater intensity in the IR because the restricted rotations of the hydroxyl groups show large changes in dipole moment. Raman spectra depend on changes in the polarizability of a bond. The results of the band component analyses of the Raman spectra of the AlOH librations for kaolinites are reported in Table 1 and illustrated by the spectra shown in Figures 2 to 4. Clearly each of the experimental band profiles shows resolution in the spectra with several component bands. For each kaolinite, 5 bands were found, with band centers at ~959, 936, 924, 914 and 895 cm^{-1}. Table 1 reports the results of the band component analysis and shows the band centers, bandwidths

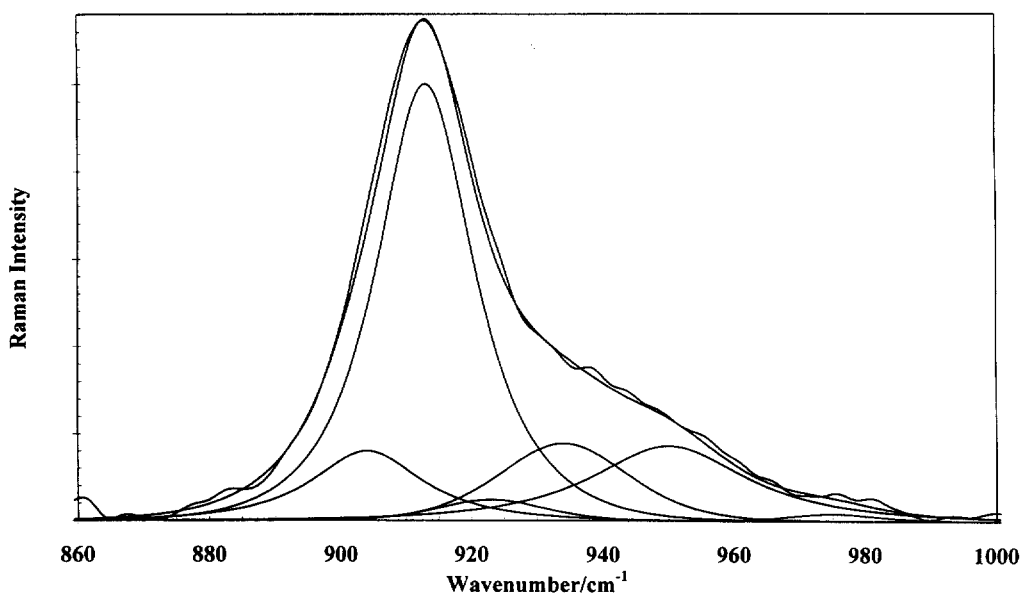


Figure 3. Band component analysis of the Raman spectrum hydroxyl librational region of halloysite from New Zealand.

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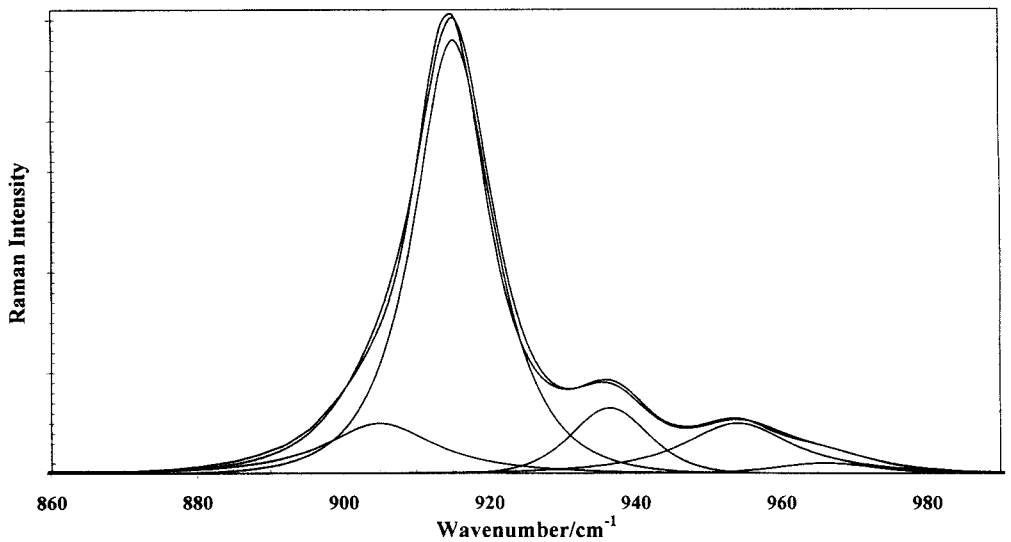


Figure 4. Band component analysis of the Raman spectrum hydroxyl librational region of San Juanito dickite.

and the intensities of these bands as percentage normalized areas for a series of kaolinites and 2 dickites. For the Keokuk kaolinite, the band at ~935 cm^{-1} has a bandwidth (as full width half maxima, FWHM) of 22.5 cm^{-1} and a percentage normalized area of 28.5%. The band centered at 925 cm^{-1} has a bandwidth of 19.1 cm^{-1} and an area of 15.9%. The band centered at 914.5 cm^{-1} which makes up ~58.5% of the total band area, is considerably sharper with a width of ~19.1 cm^{-1}. The data for the Mesa Alta, Lal-lal and Birdwood kaolinites are similar in values. Variation may reflect differences in the structure of the kaolinite hydroxyls. Alternatively, the variation may simply be a function of the band component analysis methodology. The X-ray diffraction (XRD) patterns of the Williamstown and Mt. Hope kaolinites show high-defect structures, and variation in the band component analysis data from that of the ordered kaolinites is to be expected. For example, the 933.5-cm^{-1} band of the Williamstown kaolinite has a bandwidth of 7.8 cm^{-1} and an area of 5.5%. The 919-cm^{-1} band has a width of 17.8 cm^{-1} and an intensity of 46.8%. The band centered at 912.5 cm^{-1} makes up 65.6% of the total intensity and has a bandwidth of 11.6 cm^{-1}. In the band component analysis of all the experimental profiles, a band with low intensity was found in the 890–895 cm^{-1} region. This band comprised ~2–3% of the total band area. The kaolinite with the highest intensity in the 890–895 cm^{-1} region is the most disordered kaolinite, the Williamstown kaolinite. This is not unexpected, as the increased disordering would result in the formation of fewer hydrogen bonds. As a consequence, more non-hydrogen-bonded hydroxyl groups would be found, resulting an increase in the intensity of the 890–895 cm^{-1} region.

The hydroxyl stretching and deformation vibrational modes have been shown to strongly correlate with the degree of disorder (Barrios et al. 1977) and interlayer bonding (Wieckowski and Wiewióra 1976; Giese 1988; Johnston and Stone 1990). The variation in the hydroxyl deformation modes reported in Table 1 may be due to differences in crystallinity and hydrogen bonding among the kaolinites. One commonly accepted view is that the hydroxyl stretching bands at ~3695 and 3685 cm^{-1} are the coupled and uncoupled stretching vibrations. One possibility is that the bands at 3670 and 3655 cm^{-1} are the out-of-phase vibrations of the 2 in-phase vibrations at 3695 and 3685 cm^{-1}. Now the question that arises is: do the hydroxyl deformation modes couple in a manner similar to that of the hydroxyl stretching vibrations, or are the deformation vibrations determined using Raman spectroscopy simply due to the 3 inner-surface hydroxyl groups with different orientations? For vibrations to couple, the motion of the vibration would need to be in the same direction. This is unlikely, as the hydroxyl librations are probably random in motion. The hydroxyl deformation is a restricted bending vibration and these rotations are in all directions; consequently, the coupling of these motions is unlikely. A modified model of the structure of kaolinite based on the theoretical studies of Hess and Saunders (Hess and Saunders 1992) is shown in Figure 5. This figure illustrates the position of the hydroxyl groups in relation to the gibbsite and siloxane layers and shows the rotation of the hydroxyl groups, illustrated by the circular line. Since the hy-

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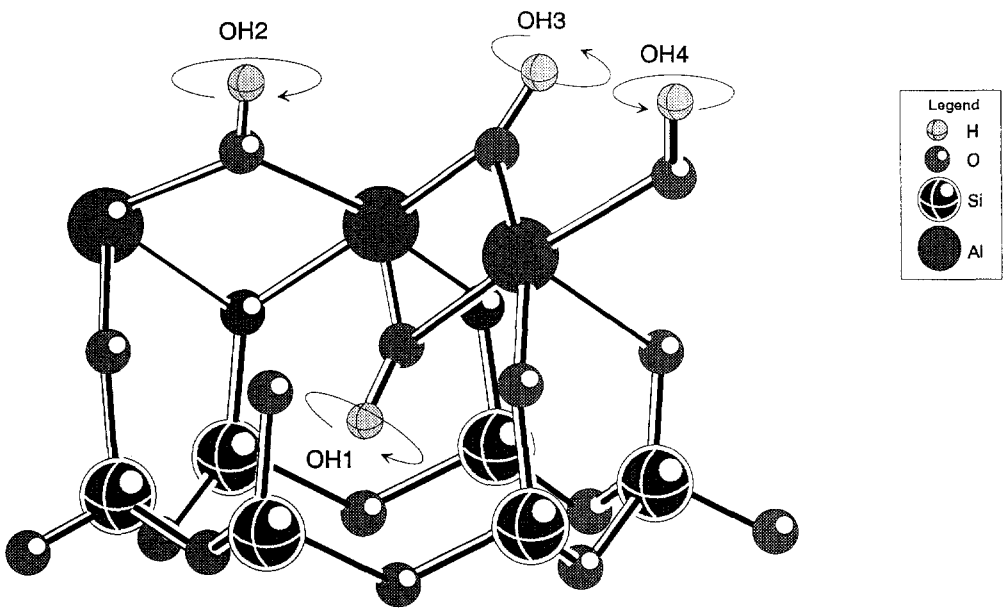


Figure 5. Model of kaolinite and the hydroxyl deformations.

droxyl group is strongly hydrogen-bonded to the adjacent silica layer, this rotation is restricted. The model further shows the possibility that the inner-surface hydroxyl groups are rotating in varying directions. Again, it is unlikely that the hydroxyl deformation modes are coupled. The lack of intensity of the hydroxyl deformation modes in both the IR and Raman spectroscopy supports this concept. Further, the model in Figure 5 shows the hydroxyl rotations as being circular, but this may not necessarily be the case: the restricted rotation of the hydroxyl groups could occur in one plane. It is envisaged that the hydroxyl deformations are occurring in a random manner.

Infrared bands centred at 935 and 915 cm^{-1} have been assigned to the inner-surface and inner Al-OH-Al bending vibrations, respectively (Farmer and Russell 1964; Wada 1967; Farmer 1974; Johnston et al. 1990). Normally for kaolinites 2 Raman bands are found at 936 and 924 cm^{-1} and may be attributed to 2 types of inner-surface hydroxyls. For ordered kaolinites, a third band is observed at ~957 cm^{-1}. The total band area of these 2 bands is ~30%, which is noteworthy as the percentage of the total band area for the inner-surface hydroxyls would be expected to approach a value of 75%. In kaolinite structure, the 4 types of hydroxyl groups referred to as OH1, OH2, OH3 and OH4 are present (Giese 1988). The 3 observed inner-surface hydroxyl deformation modes can be attributed to the 3 inner-surface hydroxyl groups OH2–4. These are the 3 hydroxyl groups that point away from the 001 plane, as may be observed in Figure 5. The OH1 hydroxyl group is the hydroxyl group contained within the kaolinite structure. The 903-cm^{-1} band may be assigned to a nonbonded inner surface hydroxyl group.

The differences in the band positions of the deformation modes of these inner-surface hydroxyl groups may be attributed to the strengths of the hydrogen bonding. The bands with the highest frequencies are assigned to the hydroxyls involved in the strongest hydrogen bond. The strongest hydrogen bond is the bond with the shortest H-bond distance. Hydroxyl bond distances and angles have been reported (Young and Hewatt 1988; Giese 1988; Hess and Saunders 1992). However, the positions of the hydroxyl groups' hydrogens are not well defined. Both experimental and theoretical results show agreement in the bond angles of the hydroxyl groups with the *ab* plane. The consensus is that the inner-surface hydroxyl groups are at angles of between 50 and 75 degrees to the *ab* plane. The exact position of the hydrogens is not known and the position depends on whether the Al-O-H bonds are linear or bent. If the hydroxyl group is waging, then it is very difficult to determine the exact position of the hydrogen using static techniques such as XRD and neutron activation methods. Raman spectroscopy is determining positions of the hydroxyl groups on the picosecond time scale. This means that for a band of width 20 cm^{-1}, the hydroxyl group is changing position every 0.53 ps.

Raman spectra of the hydroxyl stretching region of halloysites show 3 bands at 3616.5, 3623.4 and 3629.7 cm^{-1} (Frost and Shurvell 1997). The third band at 914 cm^{-1} is assigned to the inner hydroxyl group and

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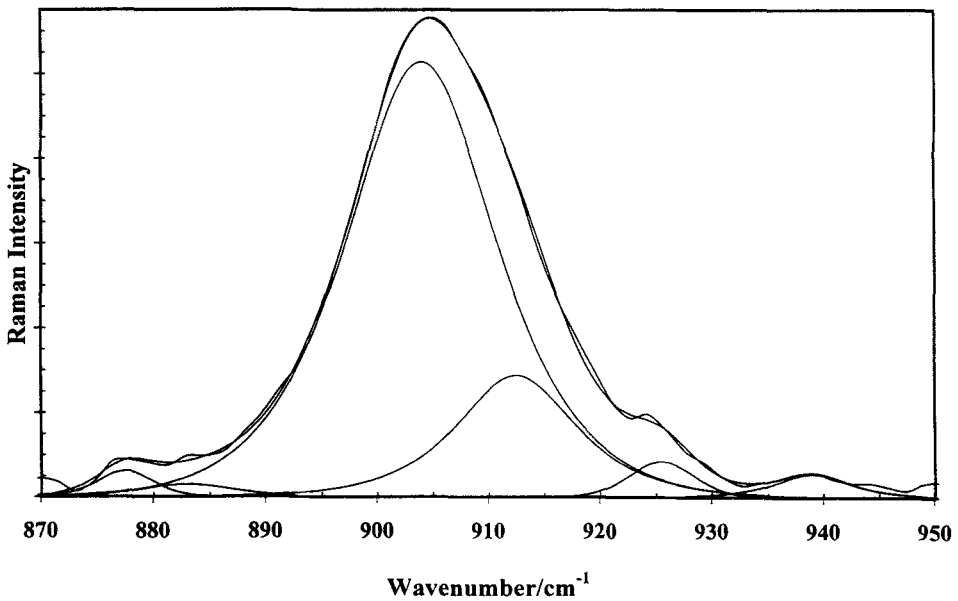


Figure 6. Band component analysis of the Raman spectrum hydroxyl deformation region of kaolinite–urea intercalate.

makes up ~65% of the total band area in the band component analysis. This band is sharp and, hence, the bending of the Al-OH group is restricted due to the positioning of the inner hydroxyl group pointing toward the dioctahedral vacancy (Hess and Saunders 1992). There are 2 possible positions for the inner hydroxyl groups in the kaolinite lattice: 1) the hydroxyl group points toward the dioctahedral vacancy in the aluminium layer (Hess and Saunders 1992) or 2) the hydroxyl group points toward the inner ditrigonal space of the siloxane layer. It is possible that the inner-surface hydroxyl group is oscillating between these 2 positions. One way of assigning the 2 AlOH libration bands at 914 and 895 cm^{-1} is to suggest that the first band is due to the hydroxyl group taking up position (1) and the second band is the inner hydroxyl group taking up position (2). An alternative suggestion for the band found at ~895 cm^{-1} is that it is the librational band of a non-hydrogen-bonded inner-surface hydroxyl group. This latter assignment is the more likely.

When an ordered kaolinite is intercalated with urea, the deformation region of the Raman spectrum of the kaolinite is altered dramatically, as is illustrated in Figure 6. The effect of insertion of the urea is to delaminate the kaolinite and remove the hydrogen bonding between the adjacent layers. Clearly, 2 bands are now present at 912.5 and 904 cm^{-1} with widths of 12.6 and 15.9 cm^{-1} and areas of 17.4 and 75%. The bands which were at 959, 938 and 923 cm^{-1} have been reduced in intensity to 0, 2 and 2.5%. These bands represent the deformation modes of the inner-surface hydroxyls which, after intercalation, have been reduced to a minimum in intensity. The band at 904 cm^{-1} now represents almost all of the intensity of the librational modes of the inner-surface hydroxyl groups. Such observations for deformation modes of the intercalated kaolinite confirm the band assignments above. The 905-cm^{-1} band now makes up 75% of the total band intensity, which is the expected value.

The Raman values reported in this paper are in good agreement with the IR deformation modes reported by Ledoux and White (1966). In this work, IR bands were found at 935, 910 and 895 cm^{-1}. The 895-cm^{-1} IR band was only found in the spectrum of the kaolinite–urea intercalates. However, no assignment of the new band was made. The IR reflectance spectra of the librational region of kaolinite, its potassium acetate intercalate and the washed and heated kaolinite–potassium acetate intercalate are illustrated in Figure 7. The major IR peaks for kaolinite are observed at 913 and 937 cm^{-1}. DRIFT spectra are less resolved than the FT Raman bands and component bands are observed at 923 and 877 cm^{-1}. The latter band is very weak. In the potassium acetate–kaolinite intercalate, the band at 935 cm^{-1} is absent but a new band at 897 cm^{-1} is formed (Figure 7b). There is some intensity (~5%) remaining in the band at 923 cm^{-1}. After washing of the kaolinite intercalate, the band at 937 cm^{-1} reappears with concomitant loss of intensity for the 897-cm^{-1} band (Figure 7c). Some intensity of the band at 897 cm^{-1} remains; however, on heating the kaolinite at 125 °C for 24 h, this band also disappears (Figure 7d). Simultaneously, the band at 923 cm^{-1} has increased in intensity. Upon intercalation of the kaolinite, the acetate ion has formed hydrogen bonds with the inner-surface hydroxyl groups with the consequen-

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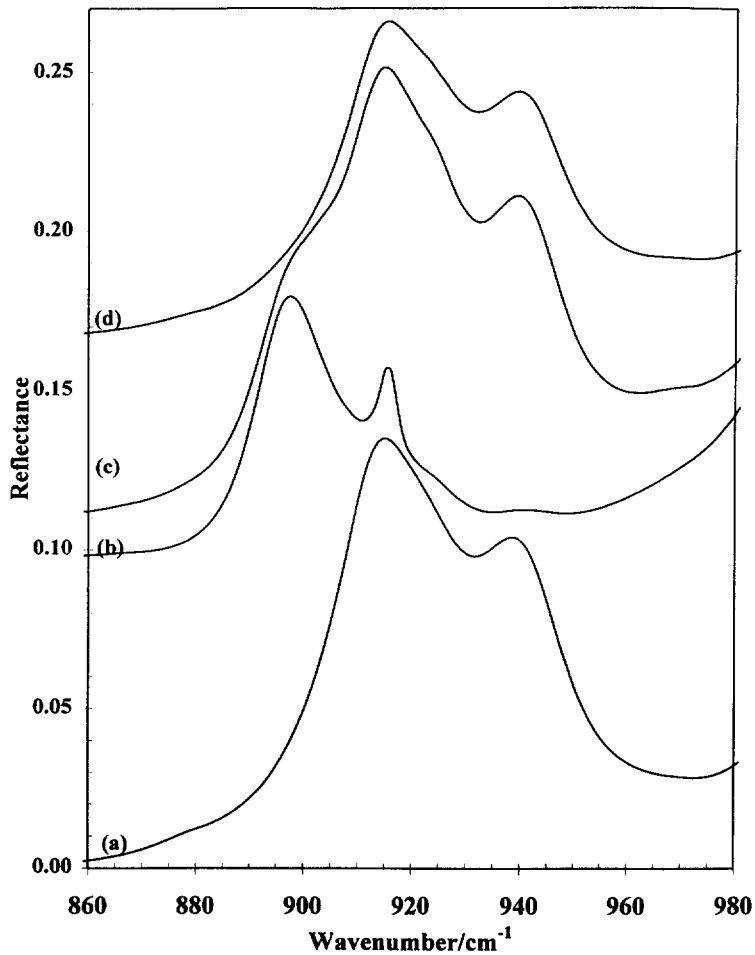


Figure 7. DRIFT spectra of the librational region of a) kaolinite; b) kaolinite–potassium acetate intercalate; c) washed kaolinite–potassium acetate intercalate; d) heated and washed kaolinite–potassium acetate intercalate.

tial loss of the hydrogen bonds between the siloxane layer and the hydroxyl groups. Consequently, the intensity of the bands in the 923 and 937 cm^{-1} region decreases to zero. On washing of the kaolinite with water, the deintercalated kaolinite now shows intensity on these bands. This means that the inner-surface hydroxyl groups are no longer bonded to the acetate but now can reform hydrogen bond linkages to the siloxane layer. Some intensity in the 897-cm^{-1} band remains even after washing for 10 min. Subsequent heating of the kaolinite then removes the last of the intercalated kaolinite. The spectrum as in Figure 7d now resembles that of the untreated kaolinite (Figure 7a). The IR reflectance results strongly support the conclusions made from the study of the Raman spectroscopy of the librational region of kaolinites: in particular, the assignment of the component bands of the hydroxyl deformation region. Five bands are proposed based on 3 OuOH groups at 959, 936, 924; an InOH group at 914 cm^{-1}; and a non-hydrogen-bonded OuOH at 895 cm^{-1}.

Dickites

Dickites have been well studied by IR microscopy, and IR vibrational modes at 911, 937 and 952 cm^{-1} were reported (Johnston et al. 1990). FT Raman spectroscopy has been used to show that when all of the crystals of a kaolinite deposit are aligned over large distances, then 3 different spectra may be obtained from 3 orthogonal axes (Frost 1997). Variation in the FT Raman spectra of the hydroxyl deformation region is also observed. The results are reported for dickites in Table 1. Again, as for the Williamstown kaolinite (Frost 1997), because groups of dickite crystals show some alignment, different spectra may be obtained depending on the relationship of the incident laser beam and the alignment of the clay crystals (even though the laser spot size is 100 μm in diameter). The spectra

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are obviously dependent on the orientation of the dickite crystals. Five bands are observed at 966, 955, 936.5, 915 and 903 cm^{-1}. The first 4 bands are well resolved. The bands at 966, 955 and 936 cm^{-1} are identified with the inner-surface hydroxyl groups and the band at 915 cm^{-1} is assigned to the InOH groups. The band at 903 cm^{-1} may be assigned to non-hydrogen-bonding OuOH groups. In the dickite structure, the 4 types of hydroxyl groups are referred to as OH1, OH2, OH3 and OH4 (Giese 1988). The model in Figure 5 is appropriate for the dickite structure as well as for kaolinite. The three observed inner-surface hydroxyl deformation modes can be attributed to the 3 inner-surface hydroxyl groups OH2–4. The band at 955 cm^{-1} has a width of 18.7 cm^{-1} for the dickite from San Juanito and 17.7 cm^{-1} for the dickite from Sainte Claire. The intensity of the band as determined by the normalized band areas, varies among the spectra but is between 11 and 16%. The band at 936.5 cm^{-1} is sharper with a width of 12.4 cm^{-1}. The area of this band varies considerably with each spectrum. The ν_{13} band at 915 cm^{-1} is well defined with a width of 11.8 cm^{-1}; the band intensity varies from 58 to 70%. This band is attributed to the InOH inner hydroxyl groups. The band centered at 903 cm^{-1} has a width of ~20 cm^{-1} and makes up the order of 10 to 14% of the total area. This band is attributed to non-hydrogen-bonded InOH groups that point toward the ditrigonal cavity of the siloxane sheet. The ratio of the intensities of the 903-cm^{-1} to the sum of the intensities of the 938- and 923-cm^{-1} bands is ~1/30. This value may well represent a measure of the number of Si-O-Si units of the siloxane sheet not involved in hydrogen bonding with the next adjacent layer.

Halloysites

Halloysites have been shown to have 3 bands in the InOH region, which result from the folding of the layers (Frost and Shurvell 1997). While resolved bands for the ν_1 and ν_5 modes of halloysite can be obtained, the ν_2 and ν_3 bands are not clearly resolved and are best described as a broad continuum. It would not be expected that well-resolved bands for the librational region would be obtained. Nevertheless, the experimental band profiles in the hydroxyl librational region do show some resolution, even though the collection of Raman spectral data is not easy for this region for halloysites. Table 2 reports the results of the band component analyses of the hydroxyl deformation vibration for 3 halloysites from Hungary, New Zealand, and Belgium. The table further reports the results of analyses for a kaolinite–urea intercalate and an halloysite–urea intercalate. The continuum of the hydroxyl stretching region for halloysites is reflected in the hydroxyl librational region. Six component bands are required to fit the experiment band profile. The OuOH librational bands were found at 950 and 938 cm^{-1} with widths of 27 and 23 cm^{-1}. These large bandwidths reflect the range of different orientations of the halloysite hydroxyl groups. The total area of these 2 bands is ~23%, which is again low. The InOH librational bands are centered at 913 and 895 cm^{-1} and have widths of 17.6 and 19.7 cm^{-1}. The deformation bands for halloysites are much broader than that for the other kaolinites. The band area of the 914-cm^{-1} band is ~60% with the total band area of these 2 bands being 70%. There is an additional band centered on 923 cm^{-1} which is required to fit the experimental band profile. This band is also assigned to the InOH group. The band has a width of 19 cm^{-1} but only makes up 2.75% of the total area.

The Raman spectrum of the hydroxyl deformation region of the Szeg halloysite intercalated with urea shows 2 major bands at 912.5 and 903 cm^{-1} with areas of 22.2 and 70%. The remaining intensity is in the bands at 938 and 923 cm^{-1}. The broad profile in the 920 to 950 cm^{-1} region has been lost. Upon intercalation, the peak position of the OuOH hydroxyl deformation modes moves to 903 cm^{-1}. This observation confirms the assignment of the bands in halloysite at 950, 938 and 923 cm^{-1} to the inner-surface hydroxyls, because these vibrations are lost upon intercalation. The 903-cm^{-1} bandwidth was 19 cm^{-1}, which is considerably greater than the value for the non-hydrogen-bonded hydroxyl deformation mode of kaolinite. DRIFT spectra show similar although less well-defined spectra. The broad spectral profile similar to the Raman spectrum of this region, in the 920 to 950 cm^{-1} region, is observed with the band at 913 cm^{-1} being the major feature of the spectrum. A low-intensity band at 879 cm^{-1} is also observed. This band is of substantially increased intensity compared with the equivalent band in kaolinite. On intercalation, the broad spectral profile in the 920–950 cm^{-1} region is reduced in intensity with the new band at 897 cm^{-1} formed. There is some intensity remaining in the 923-cm^{-1} band and the band at 897 cm^{-1} appears to have shifted to 863 cm^{-1}. Upon washing of the intercalated halloysite, the spectral profile resembles that of the untreated halloysite. On heating of the washed intercalate, the spectral profile remains unchanged. As with the results for kaolinites, the analysis of the halloysite IR spectra supports the proposition that the 3 bands at 950, 938 and 923 cm^{-1} are assigned to the 3 hydrogen-bonded OuOH groups. The 913-cm^{-1} band is attributed to the InOH groups and the 895-cm^{-1} band to the non-hydrogen-bonded OuOH groups.

CONCLUSIONS

FT-Raman spectroscopy has proven to be a very useful technique for the study of the vibrational spectra of the kaolin minerals, particularly for the observation of the hydroxyl deformation modes. In this paper, the FT-Raman spectra of a series of kaolinites of

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different orders, dickites of different complexity and halloysites have been measured in the hydroxyl deformation region. The spectra are strongly influenced by the sample orientation. Kaolinites are shown to have 4 principal hydroxyl deformation modes centered at 956, 938, 923 and 914 cm^{-1}, with a minor component at ~903 cm^{-1}. The first 3 bands are assigned to the 3 inner-surface hydroxyl groups and the fourth band at 914 cm^{-1} to the inner hydroxyl group. The band at ~903 cm^{-1} is assigned to the inner-surface hydroxyl group that is not involved in hydrogen bonding.

The hydroxyl deformation modes of dickites are orientation-dependent and show bands at 955, 936.5, 915 and 903 cm^{-1}. The first 3 bands are in a position similar to that of kaolinite, and may attributed to the OH2–4 groups in the dickite structure. The dickite deformation bands are considerably sharper than for kaolinite. It appears that the hydroxyls take a more well-defined position so that the hydrogen bonding restricts the libration of the inner-surface hydroxyl groups. Halloysites show 4 bands at 950, 934, 913 and 895 cm^{-1}. The bands are again assigned to the 3 inner-surface hydroxyl groups and the inner hydroxyl group. The area of the band at 895 cm^{-1} is ~12% and is due to non-hydrogen-bonded hydroxyl groups. When kaolinite and halloysite are intercalated with urea, the intensity of the inner-surface hydroxyl deformation modes is reduced and a new intense band at ~903 cm^{-1} is formed. This band is assigned to the hydroxyl deformation vibrations of "free" inner-surface hydroxyls. These observations assist in the confirmation of the band assignments.

Bands in the IR reflectance spectra of the kaolinite and halloysite are found in positions similar to the Raman spectra. Intercalation causes reduction in intensity of the inner-surface hydroxyl groups with concomitant increase in intensity of the inner-surface hydroxyl that is hydrogen-bonded with the acetate group at 895 cm^{-1}. Washing of the kaolins causes the removal of the acetate group, with the consequential removal of the 895-cm^{-1} band. After washing, the spectral profile of the librational region resembles that of the untreated kaolins. The IR data support the proposition that the librational region is composed of 5 bands at ~950, 936, 923, 914 and 895 cm^{-1}. The first 3 bands are assigned to the 3 inner-surface hydroxyl groups, the band at 914 cm^{-1} is assigned to the inner hydroxyl group and the bands in the 870 to 890 cm^{-1} region are assigned to the non-hydrogen-bonded inner-surface hydroxyl group.

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