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Raman Spectroscopy at Temperatures Between 298 and 423 K and at 77 K of Kaolinites Intercalated with Formamide

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Raman spectra of kaolinite and of the formamide-intercalated kaolinite were obtained at both 298 and 77 K using a Raman microprobe equipped with a thermal stage. Upon cooling to 77 K, the band attributed to the inner hydroxyl shifts by 5 cm^{-1} to lower wavenumbers and the bands assigned to the inner surface hydroxyls move to higher wavenumbers. Upon intercalation of the kaolinite with formamide, an additional Raman band attributed to the formation of a hydrogen-bonded complex between the inner surface hydroxyls and the carbonyl group of the formamide is observed at 3627 cm^{-1} at 298 K and at 3631 cm^{-1} at 77 K. Raman spectra of the deintercalation of the formamide-intercalated kaolinite are obtained by using the thermal stage to heat the intercalated kaolinite *in situ*. A decrease in intensity of the bands formed through intercalation and at the same time an increase in intensity of the inner surface hydroxyl bands are observed. A loss of intensity of the low-wavenumber region of the formamide-intercalated kaolinite is also observed.

INTRODUCTION

The kaolinite minerals have often been classified as non-expandable clays. Wada[1] introduced a new field of kaolinite research when kaolinites were expanded using potassium acetate and other organic salts. Many organic molecules of the appropriate size for insertion between the kaolinite layers have since been found and molecules such as hydrazine (NH_2NH_2), urea [($NH_2)_2CO$] and formamide ($HCONH_2$) insert between the kaolinite layers.[2,3] The interlayer bonding between kaolinite molecules arises from the hydrogen bonding between the inner surface hydroxyl groups of the octahedral gibbsite-like layer and the oxygens of the adjacent tetrahedral siloxane layer. Kaolinites are often intercalated with formamide for x-ray diffraction analysis to reveal the presence of expandable clays. In order for molecules such as formamide to penetrate between the kaolinite layers, sufficient energy must be provided for these bonding forces to be overcome.

New insights into the spectroscopy of kaolinite and the other polytypes using dispersive Raman microscopy have been forthcoming.[4–6] Raman microscopy has proven most useful for the study of the kaolin structures and for the determination of order–disorder relationships. In the work of Frost and van der Gaast,[7] kaolinites were classified according to the ratio of the two types of inner surface hydroxyls at 3685 and 3695 cm^{-1}. Correlation between the intensities of the Raman spectrum of the hydroxyl stretching vibrations and the degree of disorder using the Hinckley index showed a linear relationship between this index and the ratio of the intensities of the 3685 and 3695 cm^{-1} bands.[7] Thus Raman spectroscopy provided an innovative method for studying the defect structures of kaolinites. The application of Raman microscopy to the study of intercalated kaolinites has also proven most useful.[8–10] Upon intercalation of kaolinite with urea [($NH_2)_2CO$], considerable intensity changes in the hydroxyl stretching bands occur. Urea is a molecule which contains both the NH_2 unit and the $C=O$ unit and so chemical bonding may take place through either or both of these points of interaction. The decrease in relative intensity of the bands of the inner surface hydroxyl groups was attributed to the loss of hydrogen bonding of the inner surface hydroxyls between the adjacent kaolinite layers. The urea disrupted the interlayer hydrogen bonding between the kaolinite layers by the formation of hydrogen bonds between the silica Si—O and the N—H of the urea. This is observed by the formation of new N—H bands of increased intensity at 3392 and 3408 cm^{-1}. Formamide ($HCONH_2$) is not unlike urea in molecular structure in that it possesses both the $C=O$ and NH_2 groups,[3] the difference being that one of the NH_2 groups has been replaced by hydrogen. The formamide molecule may interact with the kaolinite surfaces through the NH_2 group. In this case the interaction would be expected to be similar to that of urea. Thus there would be no additional hydroxyl

bands found with a concomitant decrease in the inner surface hydroxyl intensities. The formamide may react with the kaolinite surface through the C=O group, in which case the interaction would be expected to be similar to that of potassium acetate and additional Raman bands at *ca.* 3605 cm^{-1} would be found. In this paper we report the alterations to the structure of a kaolinites intercalated with formamide upon thermal treatment using Raman microscopy.

EXPERIMENTAL

The kaolinite intercalates

The kaolinite used in this study was a low-defect kaolinite from Kiralyhegy, Hungary. This mineral has been characterized previously both by X-ray diffraction and by Raman spectroscopy.[5] The kaolinites were intercalated by mixing 300 mg of the kaolinite with a 50% aqueous formamide solution. The excess solution was decanted and the intercalated kaolinites were kept in a desiccator before Raman spectroscopic analysis.

Raman microprobe spectroscopy

For spectra at 298 K, kaolinite clay minerals were placed on a polished stainless-steel surface on the stage of an Olympus BHSM microscope, equipped with 5 ×, 20 × and 50 × objective lenses. For the operation of the thermal stage a special short 20 × objective lens (UWLD) was employed. No sample preparation was needed. The microscope is part of a Renishaw 1000 Raman microscope system, which also includes a monochromator, a filter system and a charge coupled device (CCD). Raman spectra were excited by a Spectra-Physics Model 127 He–Ne laser (633 nm), recorded at a resolution of 2 cm^{-1} in sections of 1000 cm^{-1} for 633 nm excitation. Repeated acquisitions using the highest magnification were accumulated to improve the signal-to-noise ratio in the spectra. For the 298 K spectra, data were collected at 20 s intervals for 10 min using the 50 × objective lens. Spectra were calibrated using the 520.5 cm^{-1} line of a silicon wafer. It should also be noted that the filters in the Renishaw spectrometer start to eliminate the Rayleigh line at about 150 cm^{-1}. This makes the determination of bands below 200 cm^{-1} difficult and without reliability. Spectra at low temperatures were obtained using a Linkam thermal stage (Scientific Instruments, Waterfield, Surrey, UK). Samples were placed on a circular glass disc which fitted over the silver plate of the thermal stage. For spectra at 77 K, nitrogen gas from liquid nitrogen passed through a small hole in this plate immediately below the centre of the glass disc. It was found that the best method of obtaining 77 K was to cool rapidly at 50 K min^{-1} until approximately 100 K and then cool slowly at 1 K min^{-1} until 77 K was obtained. Because of the increased optical path, spectra at 77 K are noisier and require longer accumulation times. Spectra were obtained using 10 s scans for 20 min using the short 20 × objective. For the thermal treatment of samples

above room temperature, samples were heated at 10 K min^{-1} until constant temperature was achieved.

Spectral manipulation such as baseline adjustment, smoothing and normalization was performed using the Spectracalc software package GRAMS (Galactic Industries, Salem, NH, USA). Band component analysis was undertaken using the Jandel Peakfit software package which enabled the type of fitting function to be selected and allowed specific parameters to be fixed or varied accordingly. Band fitting was performed using a Lorentz–Gauss cross-product function with the minimum number of component bands used for the fitting process. The Gauss–Lorentz ratio was maintained at values greater than 0.7 and fitting was undertaken until reproducible results were obtained with squared correlations $r^2 > 0.995$ for the 298 spectra and >0.98 for the 77 K spectra. Graphics are presented using Microsoft excel.

RESULTS AND DISCUSSION

Kaolinites show a complex set of overlapping bands in the Raman spectra of the hydroxyl-stretching region. Figure 1 illustrates the Raman spectrum of the low-defect kaolinite and its formamide-intercalated equivalent at room and liquid nitrogen temperatures. Essentially there are five bands labelled $\tilde{v}_1$–$\tilde{v}_5$. The bands $\tilde{v}_1$–$\tilde{v}_4$ are assigned to the inner surface hydroxyl groups. The $\tilde{v}_5$ band is assigned to the inner hydroxyl stretching vibration. The $\tilde{v}_1$ and $\tilde{v}_4$ modes have been attributed to two in-phase stretching vibrations with differing hydrogen bond symmetry.[5] One way of describing the $\tilde{v}_2$ and $\tilde{v}_3$ modes is the out-of-phase vibrations of the two $\tilde{v}_1$ and $\tilde{v}_4$ modes. Additional bands found in the hydroxyl stretching region are labelled $\tilde{v}_x$ according to the position of the additional band. Such bands are observed when the kaolinite is intercalated with various inserting molecules such as formamide. Table 1 reports the spectral characteristics of the bands upon cooling to liquid nitrogen temperature. The Raman spectrum of the low-defect kaolinite shows that the band assigned to the inner hydroxyl group $\tilde{v}_5$ moves to lower wavenumbers upon cooling to liquid nitrogen temperature. The shift observed is from 3620 to 3615 cm^{-1}, a shift of -5 cm^{-1}. The bands assigned to the inner surface hydroxyl groups shift to higher wavenumbers. All of the bands attributed to inner surface hydroxyl groups shifts to higher wavenumbers by approximately 8–10 cm^{-1}. Greater resolution of the bands is observed in the spectra obtained at 77 K.

Upon intercalation of the low-defect kaolinite with formamide, an additional Raman hydroxyl stretching band is observed at 3627 cm^{-1} in the 298 K spectrum. A broad band of low intensity is also observed at 3463 cm^{-1}. No intensity remains in the bands attributed to the inner surface hydroxyl groups $\tilde{v}_1$–$\tilde{v}_4$. The band at 3627 cm^{-1} is attributed to the inner surface hydroxyl groups which are hydrogen bonded to the C=O unit of the formamide. When the spectrum of the formamide intercalated kaolinite is obtained at 77 K, this band shifts to 3631 cm^{-1}. This shift to higher wavenumbers confirms the assignment of the band to the inner surface hydroxyl groups hydrogen bonded to the formamide molecule. The broad band at 3600 cm^{-1} in the 298 K
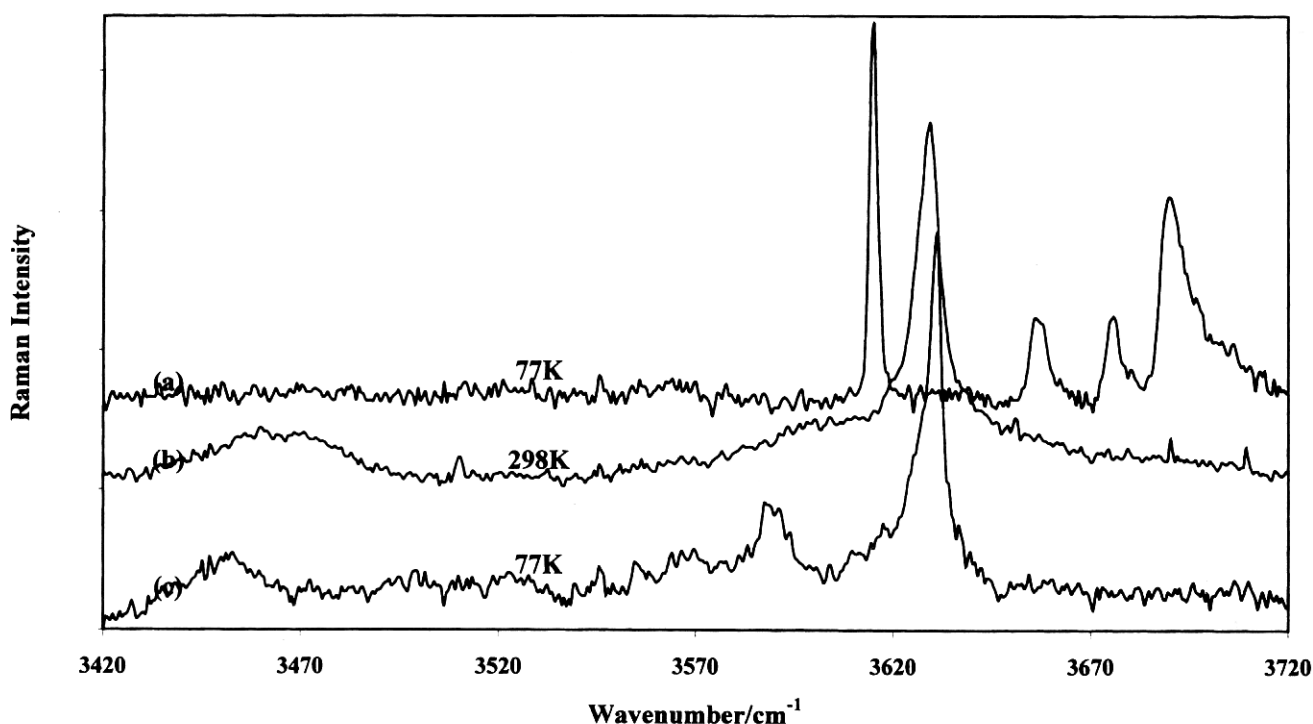
Figure 1. Raman spectra of the hydroxyl stretching region of (a) low-defect kaolinite at 77 K, (b) low-defect kaolinite intercalated with formamide at 298 K and (c) low-defect kaolinite intercalated with formamide at 77 K.
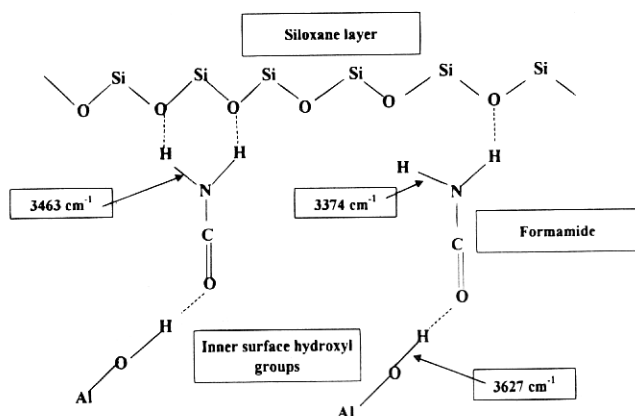
spectrum of the formamide-intercalated kaolinite is observed at 3589 cm^{-1} in the 77 K spectrum and is considerably narrower in bandwidth. This band is attributed to water molecules that are incorporated into the interlayer space when the kaolinite is intercalated with the formamide. Such a wavenumber is observed when the kaolinite undergoes some folding of the clay surface as with halloysite formation. The band observed at 3451 cm^{-1} at 77 K and 3463 at 298 K is attributed to the symmetric stretch of the N—H of the formamide that is hydrogen bonded to the siloxane surface. The $\tilde{\nu}_5$ band assigned to the inner hydroxyl group is at 3616 cm^{-1}. The exact position is difficult to determine as the peak is under the profile of the 3631 cm^{-1} band.

The bandwidth of the inner hydroxyl at 298 K is 3.3 cm^{-1} (±0.1 cm^{-1}) and is 2.3 cm^{-1} at 77 K. Such a decrease on cooling to liquid nitrogen temperature is not unexpected. A similar observation is also made for

the inner surface hydroxyl bands. The 3692 cm^{-1} band has a bandwidth of 16.3 cm^{-1} for the 298 K spectrum which becomes 17.4 cm^{-1} for the 77 K spectrum. Such an increase in bandwidth is unexpected especially when the kaolinite is cooled to liquid nitrogen temperature. The reason for this increase may be attributed to the greater resolution that is attained at low temperatures. There is an argument that this increase in bandwidth is due to the resolution of additional component bands and that there are three bands in this part of the band profile instead of two. These bands move apart upon cooling, causing an apparent broadening of the initial band profile. This argument can be sustained on the grounds that there are three different inner surface hydroxyls in the unit cell of kaolinite and that all three bands will have separate peaks at similar wavenumbers that overlap and become one broad band. It is proposed that the broad band profile centred at 3702 cm^{-1}

Table 1. Band component analysis of the hydroxyl stretching region of the low-defect kaolinite and the formamide intercalate at 298 and 77 K

| Kaolinite	Temperature K	Band characteristics, $\tilde{\nu}$/cm^{-1}	$\tilde{\nu}_{NH}$ sym	$\tilde{\nu}_7$	$\tilde{\nu}_6$	$\tilde{\nu}_6$	$\tilde{\nu}_3$	$\tilde{\nu}_2$	$\tilde{\nu}_4$	$\tilde{\nu}_1$
Low-defect kaolinite	298	Band centre/cm^{-1}			3620		3651	3668	3683	3692
		Bandwidth/cm^{-1}			3.3		11.1	9.8	11.0	16.3
		Relative area/%			24.8		17.0	5.3	30.3	22.1
	77	Band centre/cm^{-1}			3615		3659	3676	3692	3702
		Bandwidth/cm^{-1}			2.3		7.2	6.1	7.0	17.4
		Relative area/%			31.7		11.5	7.5	20.0	29.3
Low-defect kaolinite intercalated with formamide	298	Band centre/cm^{-1}	3463	3600	3620	3627				
		Bandwidth/cm^{-1}	36.8	broad	11.7	8.5				
		Relative area/%	20.9	$\sim$ 30.0	20.2	27.7				
	77	Band centre/cm^{-1}	3451	3589	3616	3631				
		Bandwidth/cm^{-1}	16.5	14.0	17.8	9.4				
		Relative area/%	14.8	23.6	20.5	41.3				

Figure 2. Molecular model of the intercalation of formamide in kaolinite.

is made up of three overlapping hydroxyl bands arising from the three different inner surface hydroxyls in the unit cell.

When kaolinite is intercalated with formamide, an additional band is observed at 3627 cm^{-1} [Fig. 1(b)]. No intensity is observed for the inner surface hydroxyl bands. This lack of intensity in the inner surface hydroxyl stretching region signifies that the kaolinite was fully intercalated. Additional bands are also observed at 3620, 3600 and 3463 cm^{-1}. The broad band at 3600 cm^{-1} is attributed to water in the interlayer space of the intercalated kaolinite. The 3620 cm^{-1} band is the inner hydroxyl band and is observed as an asymmetry on the 3627 cm^{-1} band. The band at 3463 cm^{-1} is assigned to the symmetric stretching vibration of the —N—H $\cdots$ O—Si unit. Such a band results from the interaction of the N—H of the formamide unit with the

siloxane layer of the kaolinite (Fig. 2). If the NH is not bonded to the siloxane layer a band at 3374 cm^{-1} would be expected.[11] The bandwidth of the $\tilde{\nu}_5$ band is 11.7 cm^{-1}, which is broad compared with that of the untreated kaolinite at 298 K of 3.3 cm^{-1}. The reason for this width is unclear but may be related to the difficulty of determining component bands dominated by the profile of an adjacent intense band. The bandwidth of the 3600 cm^{-1} band is large (68.6 cm^{-1}). Such a bandwidth assists in the assignment of this band to water as kaolinite hydroxyl bandwidths are narrow compared with those of water. The band at 3463 cm^{-1} is also broad with a bandwidth of 36.8 cm^{-1}.

When the spectrum of the formamide-intercalated kaolinite is obtained at 77 K, the band attributed to water shifts to 3589 cm^{-1} and sharpens considerably [Fig. 1(c)]. The band attributed to the —N—H $\cdots$ O—Si unit shifts to lower wavenumber and is observed at 3451 cm^{-1} with a considerably reduced bandwidth of 16.5 cm^{-1}. The effect of running the spectra of the formamide intercalated kaolinite at liquid nitrogen temperature is pronounced. In general, bands which originate from hydrogen-bonded complexes which may have many different molecular environments are dramatically narrowed upon cooling to 77 K. The $\tilde{\nu}_6$ band is now observed at 3631 cm^{-1} in the 77 K spectrum. This band increased in bandwidth to 9.4 cm^{-1} upon cooling to liquid nitrogen temperature. Normally on cooling to liquid nitrogen temperature it could be expected that the bandwidth would become less as per the description of the bands above. It would also be expected that the three inner surface hydroxyls in the kaolinite unit cell would bond to the formamide in an identical manner. The resulting bands will all overlap
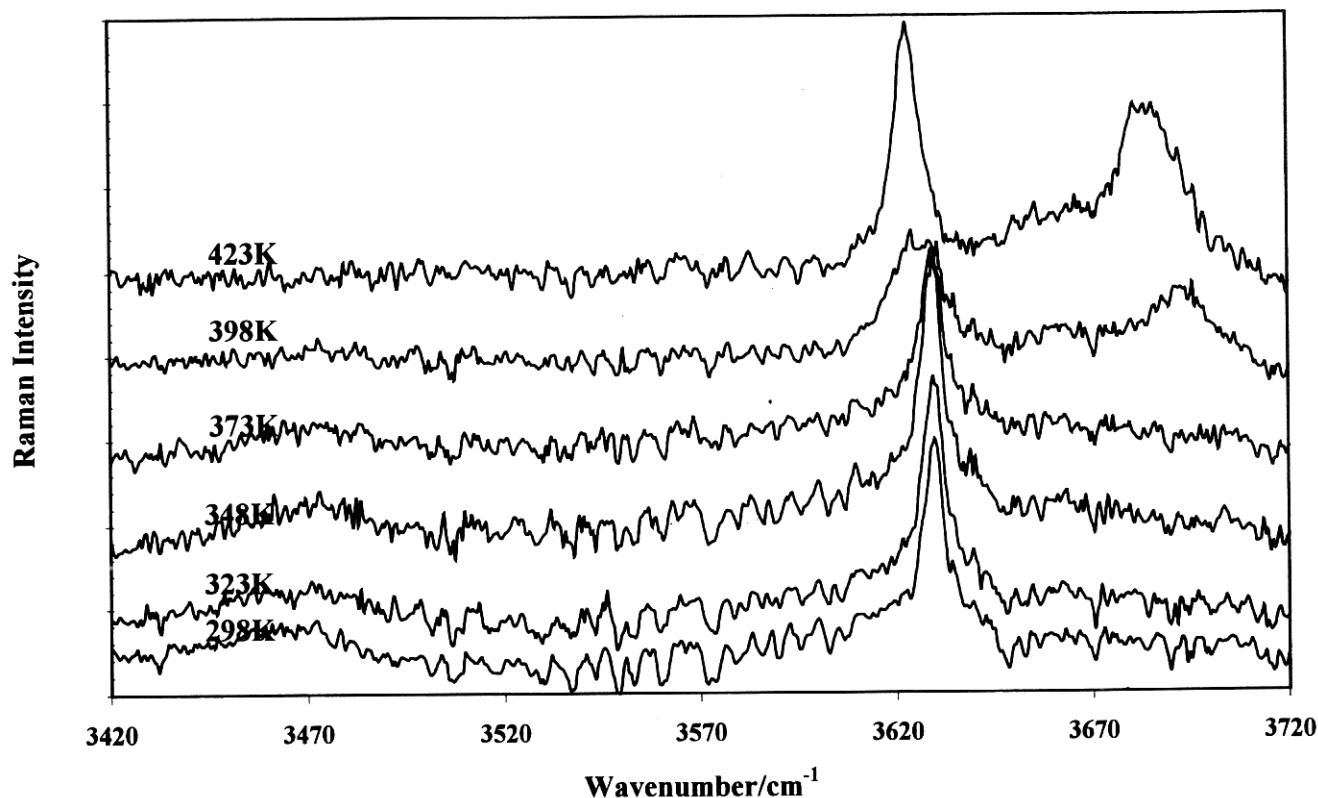
Figure 3. Raman spectra of the hydroxyl stretching region of formamide-intercalated low-defect kaolinites heated at 25 K intervals from 298 to 423 K

and will be only partially resolved by obtaining Raman spectra at liquid nitrogen temperature. Thus it is proposed that this part of the spectral profile consists of three components which move apart upon cooling. Such reasoning also assists with the assignment of this band to the formation of the hydrogen-bonded complex formed between the inner surface hydroxyls and the formamide. It is proposed that the bonding occurs between the hydrogen of the inner surface hydroxyl group and the C=O group of the formamide (Fig. 2). Such an interaction is expected to be not as strong as the interaction between an acetate ion and the inner surface hydroxyls as may be determined in the Raman spectra of kaolinites intercalated with potassium acetate.[8] In this case the additional Raman band is found at 3065 cm^{-1}. In the formamide case the interaction is weaker and is found at 3627 cm^{-1}.

Figure 3 shows the Raman spectrum of the hydroxyl stretching region of the formamide-intercalated kaolinite upon heating at 25 K intervals up to and beyond the deintercalation temperature. The deintercalation temperature is defined as the temperature at which the expanded kaolinite collapses back to its original structure. A number of observations can be made. First, at 373 K, the band attributed to the —N—H···O—Si unit at 3463 cm^{-1} has disappeared. The band shows no changes up to this temperature. At 398 K, two bands are observed at 3620 and 3627 cm^{-1} and at the same time the bands attributed to the inner surface hydroxyl groups grow in intensity as the inserting molecule is removed upon heating. In the 398 K spectrum the 3693 cm^{-1} band appears. At 423 K, the spectrum now starts to resemble that in Fig. 1(a). The spectra obtained using the thermal stage are more noisy. This is attributed to the additional optics that both the excitation and scattered radiation are required to pass.

CONCLUSIONS

In situ Raman spectroscopy at liquid nitrogen temperature was used to determine the spectral character-

istics of a low-defect kaolinite intercalated with formamide by using a Raman microprobe in conjunction with an He–Ne laser. The inner hydroxyl band was found to decrease in wavenumber to 3615 cm^{-1} and the four bands attributed to the inner surface hydroxyl groups shifted to higher wavenumbers at 77 K. All the bands showed considerable narrowing upon cooling to liquid nitrogen temperature. However, the inner surface hydroxyl band at 3692 cm^{-1} and also the 3627 cm^{-1} band of the formamide intercalate increased in bandwidth. It is proposed that the collection of spectra at liquid nitrogen temperature enabled the resolution of an additional component band to be observed. The shift of the band at 3627 cm^{-1} to 3631 cm^{-1} upon cooling to liquid nitrogen temperature assists in the assignment of this band to the inner surface hydroxyls hydrogen bonded to the formamide, most likely through the C=O of the formamide unit. The observation of a band at 3463 cm^{-1} shows that the NH unit of the formamide molecule hydrogen bonds to the oxygens of the siloxane layer.

The use of the thermal stage to heat kaolinite samples *in situ* through the deintercalation temperature allows the changes in the structure of the formamide-intercalated kaolinite to be followed as the thermal treatment occurs. The use of the thermal stage in association with the Raman microprobe offers many possibilities, not only for the study of clay minerals and their intercalated analogues but also of many other minerals. In particular, the technique allows the possibility of studying the adsorption and desorption of organics on clay minerals surfaces.

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