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Raman spectroscopy of urea and urea-intercalated kaolinites at 77K

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Abstract

The Raman spectra of urea and urea-intercalated kaolinites have been recorded at 77K using a Renishaw Raman microprobe equipped with liquid nitrogen cooled microscope stage. The NH₂ stretching modes of urea were observed as four bands at 3250, 3321, 3355 and 3425 cm⁻¹ at 77K. These four bands are attributed to a change in conformation upon cooling to liquid nitrogen temperature. Upon intercalation of urea into both low and high defect kaolinites, only two bands were observed near 3390 and 3410 cm⁻¹. This is explained by hydrogen bonding between the amine groups of urea and oxygen atoms of the siloxane layer of kaolinite with only one urea conformation. When the intercalated low defect kaolinite was cooled to 77K, the bands near 3700 cm⁻¹ attributed to the stretching modes of the inner surface hydroxyls disappeared and a new band was observed at 3615 cm⁻¹. This is explained by the breaking of hydrogen bonds involving OH groups of the gibbsite-like layer and formation of new bonds to the C=O group of the intercalated urea. Thus it is suggested that at low temperatures two kinds of hydrogen bonds are formed by urea molecules in urea-intercalated kaolinite.

Key Words: Intercalation, Kaolinite, Urea, Liquid Nitrogen Temperature, Raman Microscopy,

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1. Introduction

In recent papers, Raman spectra of kaolinite hydroxyls at room temperature [1] and at 77K [2] have been reported. Raman spectra of urea-intercalated kaolinite at room temperature have been reported recently [3-5]. The present paper reports the Raman spectra of urea-intercalated kaolinite (ordered and disordered) at 77K.

1.1 Kaolinite

Kaolinite, $\text{Al}_4[\text{Si}_4\text{O}_{10}](\text{OH})_8$ is a naturally occurring inorganic polymer with a layer structure consisting of siloxane and gibbsite-like layers. The siloxane layer is composed of SiO_4 tetrahedra linked in a hexagonal array. The bases of the tetrahedra are approximately coplanar and the apical oxygen atoms are linked to a second layer containing aluminum ions and OH groups (the gibbsite-type layer). Kaolinite has been described as a non-expandable clay. However, when treated with aqueous solutions containing molecules such as urea, formamide, or potassium acetate, kaolinite undergoes expansion through the insertion of the molecules between the kaolinite layers [6-10]. Such a process is known as intercalation.

The structure and vibrational spectroscopy of kaolinite and other layer silicates has been reviewed by Farmer [11]. Kaolin clay minerals contain two types of hydroxyl groups (i) the outer hydroxyl groups, or so-called inner surface hydroxyls and (ii) the inner hydroxyl groups. These hydroxyl groups were designated OuOH and InOH respectively by Frost and van der Gaast [1]. The OuOH groups are situated in an outer, unshared plane, whereas the InOH groups are located in the plane shared with the apical oxygen atoms of the tetrahedral sheet. Four distinct bands are observed in the infrared spectrum of kaolinite at 3697, 3669, 3652 and 3620 cm^{-1} [11]. The three higher frequency bands (designated ν_1 , ν_2 and ν_3) are assigned to OH stretching modes of the three inner surface hydroxyl groups (OuOH) [1]. The band at 3620 cm^{-1} is designated ν_5 and is assigned to the stretching mode of an inner hydroxyl group (InOH) [12,13].

The Raman spectrum in the OH stretching region of kaolinite contains five [1] features. In addition to the four frequencies noted above, an infrared inactive feature is observed at 3685 cm^{-1} . This is designated ν_4 and is observed as a component of an unresolved doublet of medium intensity at 3695/3685 cm^{-1} . The relative intensities of the components of this doublet depend on the orientation of the kaolinite crystal [1]. The 3669 and 3652 cm^{-1} bands (ν_2 and ν_3) are weak, while the 3620 cm^{-1} band (ν_5) is strong and sharp. The intensity of the OH stretching bands depends on the defect structure of the kaolinite. In highly ordered kaolinites ν_4 has been detected in the infrared spectrum at 3684 cm^{-1} when band resolution was carried out [14]. The assignment of the hydroxyl stretching bands remains under discussion, and differing viewpoints concerning the position and orientation of the inner surface hydroxyl groups exist [1,12].

Intercalation involves the breaking of some hydrogen bonds between the kaolinite layers and the formation of new hydrogen bonds with the inserting molecule. These new bonds usually involve the inner surface hydroxyl groups (OuOH) and changes are observed in the intensities of bands assigned to vibrations of these groups. This is observed for intercalated molecules such as potassium acetate, where hydrogen bonding occurs between the carboxylate group of the acetate anion and the inner surface hydroxyls of the gibbsite-like layer. In this case a decrease in the intensity of the corresponding OH stretching bands is observed and additional bands due to new hydrogen-bonded OH groups are observed between 3595 and 3605 cm^{-1} [15,16].

1.2 Urea

The vibrational spectra of urea in the solid and gas phase and in solution have been reviewed recently [17]. In this comprehensive review article, 95 references are given to papers on urea, including the microwave spectrum, infrared and Raman spectra and band assignments, normal coordinate analysis and other theoretical calculations and structure determination by X-ray and neutron diffraction methods.

For the purposes of the present study, we are interested in the molecular structure of urea and the solid state Raman spectra at normal and low temperatures. Urea was shown to be a planar molecule belonging to the point group the C_{2v} in the solid state by polarized infrared studies of oriented single crystals [18,19]. The planarity of the urea molecule in the solid state is mainly due to a network of hydrogen bonds. It should be noted that the planar structure of urea only exists in the solid state. In solution or as a dilute phase, one or more conformations of the NH units exist.

The 18 normal vibrations of the planar NH_2CONH_2 molecule are distributed among the irreducible representations of the C_{2v} point group as: $7A_1+2A_2+3B_1+6B_2$ modes. The skeletal modes comprise a C=O stretch (A_1), symmetric and anti-symmetric NCN stretches (A_1+B_2), an NCN bend (A_1), and a NCO bend (B_2). There is also a CN_2 out of plane wag (B_1). There are twelve vibrations involving the hydrogen atoms. These comprise two symmetric (A_1+B_2) and two anti-symmetric stretching modes (A_1+B_2), two HNH bending modes (A_1+B_2), two NH_2 rocking modes (A_1+B_2), and in-plane and out-of-plane NH_2 wagging and twisting modes ($2A_2+2B_1$).

1.3 Urea-intercalated kaolinite

Early infrared studies of hydrogen-bonding in the urea-kaolinite intercalate were reported by Ledoux and White in 1966 [6]. In recent Raman studies at room temperature [4,5], evidence was found for hydrogen bonding involving the NH_2 groups, rather than the C=O group of urea. Large shifts in the NH stretching bands of urea were observed, but there was little change in the intensity of the bands attributed to vibrations of the inner surface hydroxyl groups. This indicated that at room temperature molecular interactions are formed between the amine hydrogen atoms of urea and oxygen atoms of the siloxane layer of kaolinite, while hydrogen bonding of the hydroxyl groups of the gibbsite-like layer of kaolinite are not involved. Molecular interactions between the urea and the siloxane layer may involve van der Waals forces.

In molecules such as urea and amino acids which contain both C=O and NH_2 groups the possibility exists for two types of hydrogen bonds to be formed. The first involves the hydrogen atoms of the amine groups and the oxygen atoms of the siloxane layer and the second involves the C=O group and hydroxyl groups of the Gibbsite-like layer. The objective of the work described in this paper was to investigate this possibility by extending Raman spectroscopic studies of the intercalation of kaolinite with urea to low temperatures.

2. Experimental

2.1 The kaolinite intercalates

The kaolinites used in this study are a low defect kaolinite from Kiralyhegy and a high defect kaolinite from Szeg, in Hungary. These minerals have been previously characterised both by X-ray diffraction and by Raman spectroscopy [4,5]. The kaolinites

were intercalated by mixing 300 mg of the kaolinite with a 9.0M urea aqueous solution at 65 °C for 80 hours. The excess solution was decanted and the solids removed from the solution by centrifugation. The intercalated kaolinites were kept in a desiccator before Raman spectroscopic analysis. The intercalation of the kaolinites was checked by X-ray diffraction [4,5].

2.2 Raman Microprobe Spectroscopy

For room temperature studies, milligram amounts of the kaolinite or the intercalated clay mineral were placed on a polished metal surface on the stage of an Olympus BHSM microscope, equipped with 10x, 20x, and 50x objective lenses. 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), as detector. Raman spectra were excited by a Spectra-Physics model 127 He/Ne laser (633 nm) and recorded at a resolution of 4 cm⁻¹. Repeated acquisitions using the highest magnification, were accumulated to improve the signal to noise ratio. Spectra were calibrated using the 520.5 cm⁻¹ line of a silicon wafer. Further details of the technique have been published elsewhere [2,4,5].

Spectra at low temperatures were obtained using a Linkam thermal stage (Scientific Instruments Ltd, Waterfield, Surrey, England) [2,20]. Samples were placed on a circular quartz disc, which fitted over a cooled silver plate. For spectra at 77 K, nitrogen gas from liquid nitrogen passed through a small hole in this plate immediately below the centre of the quartz disc. Samples were cooled rapidly to 77K at 50 K per minute. It was possible to mount three samples in small aluminum cups on the quartz disc. Raman spectra were obtained using a special 50X long working distance objective. The low numerical aperture of this objective gave rise to weaker spectra than those obtained with the usual 50X objective. Also, spectra recorded using the low temperature device are noisier than those obtained at room temperature. Hence longer accumulation times are required. In the present case one hundred 20-second scans were accumulated to record each spectrum.

Spectral manipulation such as baseline adjustment, smoothing and normalisation was performed using the GRAMS32[®] software package (Galactic Industries Corporation, 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 allows specific parameters to be fixed or varied. Band fitting was done using a Lorentz-Gauss 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 of r² greater than 0.995 for the 298K spectra and 0.98 for the 77K spectra. Graphics are presented using Microsoft EXCEL.

3. RESULTS AND DISCUSSION

3.1 Raman spectra of urea at 298K and 77K

The Raman spectra of urea at 298 and 77K are shown in Figure 1a-d. Table 1 lists the observed NH stretching frequencies of urea and the urea-intercalated low and high defect kaolinites at 298 and 77K. In Figure 1a it is seen that the Raman spectrum of urea at 298K contains bands at 3435, 3357 and 3242 cm⁻¹ with a shoulder at 3323 cm⁻¹. These frequencies are close to those reported by Ferraro et al. [21] and are assigned to the anti-symmetric and symmetric NH₂ stretching vibrations of urea. Band resolution of the NH₂ stretching band

envelope gave the relative intensities of the four components listed in Table 1. On cooling urea to liquid nitrogen temperature, the shoulder at 3323 cm^{-1} becomes a resolved peak at 3321 cm^{-1} with increased intensity. Small shifts are observed in the other three bands and the resolved bandwidths are reduced (see Table 1).

Some other urea bands also show significant changes when the spectra are recorded at low temperatures (reference [17] and Figure 1b). Table 2 reports the spectral characteristics of urea bands occurring below 3000 cm^{-1} . A detailed discussion of the infrared and Raman spectra of solid urea at room temperature and at low temperatures is given in reference [17]. In this paper it was shown by isotopic substitution studies that the fundamentals in the $1700\text{--}1400\text{ cm}^{-1}$ region all involve NH_2 bending, $\text{C}=\text{O}$ stretching and NCN stretching. It is suggested that the two bands observed at 1649 and 1581 cm^{-1} in the 298K Raman spectrum of urea involve stretching modes of the free and hydrogen bonded $\text{C}=\text{O}$ group. The relative intensities of these bands is 5:1 and the bandwidths are 17.3 and 24.9 cm^{-1} respectively. This suggestion is supported by the bandwidth and wavenumber of the higher frequency band, which remains unchanged upon cooling to liquid nitrogen temperatures, while the 1581 cm^{-1} band shifts to 1590 cm^{-1} and becomes broader. A strong band is observed at 1542 cm^{-1} in the 298K spectrum. This band shifts to 1537 cm^{-1} in the 77K spectrum (Figure 1b) and is attributed to an NH_2 bending mode. A weak band is observed at 1474 cm^{-1} in the 298 K spectrum with a bandwidth of 15.0 cm^{-1} . At 77K the peak shifts to 1485 cm^{-1} with a bandwidth of 8.9 cm^{-1} . This band is attributed to the antisymmetric NCN stretching mode. Bands observed at 1176 and 1047 cm^{-1} in the 298K spectrum are attributed to the two NH_2 rocking vibrations. The former is unshifted at 77K , while the latter shifts up to 1055 cm^{-1} . A very strong band (Figure 1c) attributed to the NCN symmetric stretching mode is observed at 1012 cm^{-1} at 298K and at 1017 cm^{-1} at 77K . Bands at 565 and 548 cm^{-1} are assigned to the NCO and NCN bending modes. Two additional very weak Raman bands are observed at 373 and 211 cm^{-1} in the 77K spectrum. These two bands are probably external (lattice) modes of crystalline urea

3.2. The OH stretching region of urea-intercalated kaolinites at 77K

Kaolinites are described as having low and high defect structures depending on the stacking of the kaolinite layers. Low defect (ordered) kaolinites have a regular stacking sequence whereas high defect (disordered) kaolinites show disordered stacking. Figure 2 displays the Raman spectrum of the hydroxyl-stretching region of the urea-intercalated low and high defect kaolinites at 77K . Raman spectra of urea-intercalated kaolinites at 298K have been reported previously [3-5]. Table 3 reports the band component analysis of the Raman spectra of the hydroxyl-stretching region of the untreated kaolinites and the urea-intercalated kaolinites at 298 K and 77K . Previous studies have reported the Raman spectra of untreated kaolinites in the hydroxyl stretching region at 77K [2,20].

The Raman spectra of urea-intercalated kaolinites recorded at 77K show differences from those recorded at room temperature (Figure 2). No intensity remains in the inner surface hydroxyl stretching bands (ν_1 , ν_2 and ν_4) for the ordered kaolinite at 77K and the 3621 cm^{-1} room temperature band is split into two components at 3622 and 3615 cm^{-1} . This suggests that the inner surface hydroxyl groups are hydrogen bonded (through the $\text{C}=\text{O}$ group) to the inserting molecule. There is also the possibility that the 3621 cm^{-1} band coincides with that of the inner hydroxyl vibration ($\sim 3620\text{ cm}^{-1}$ in the 298 K spectrum) and it is only when the spectra are recorded at liquid nitrogen temperature that the two bands are separated

For the urea-intercalated disordered kaolinite at 77K, similar results are obtained. However, in this case significant intensity remains in the ν_1 band at 3711 cm^{-1} attributed to the inner surface hydroxyl groups. The ν_2 , ν_3 , and ν_4 bands all shift to higher frequencies at liquid nitrogen temperature. This is also consistent with previous observations on untreated kaolinite [2,20]. The observation that significant intensity remains in the bands attributed to the inner surface hydroxyl groups of the urea-intercalated high defect kaolinite implies that the kaolinite was only partially intercalated. This conclusion is confirmed by X-ray diffraction studies. Differences in the intensities of bands in the hydroxyl stretching region of the urea-intercalated kaolinites indicates that the low and high defect kaolinites are intercalated differently. Intuitively, it might be expected that the high defect kaolinite would be more extensively intercalated. This appears not to be the case as both the X-ray diffraction and vibrational spectroscopic techniques indicate that the low defect kaolinite is more fully intercalated than the high defect kaolinite. The band at 3602 cm^{-1} is attributed to a hydroxyl stretching vibration of water molecules in the interlayer structure. The bandwidth of 17.2 cm^{-1} supports this assignment.

3.3 *The NH stretching region of urea-intercalated kaolinites at 77K*

Upon intercalation of the kaolinite with urea at 298K, the anti-symmetric and symmetric NH_2 stretching vibrations of urea are found at 3408 and 3391 cm^{-1} for the ordered urea intercalate and at 3410 and 3387 cm^{-1} for the disordered urea intercalate (Table 1 and Figure 3). It is noted that the four bands observed for urea become two bands in the urea-intercalates. These bands are attributed to urea amine groups hydrogen bonded to the siloxane layer. The relative intensities of the two bands are the same.

On cooling to liquid nitrogen temperatures, the antisymmetric and symmetric stretching vibrations are found at 3421 and 3382 cm^{-1} for the low defect urea-intercalate and at 3418 and 3382 cm^{-1} for the high defect urea-intercalate. An additional band is observed at 3373 cm^{-1} in the spectrum of the low defect urea-intercalate. Thus the anti-symmetric stretching vibration shifts to a higher frequency, while the symmetric stretching mode shifts to a lower frequency upon cooling to liquid nitrogen temperatures. The 3410 and 3387 cm^{-1} bands broaden from 14 cm^{-1} at 298K to 20 cm^{-1} at 77K. The increased bandwidth on cooling to liquid nitrogen temperature may be due to the presence of new unresolved bands

The low temperature Raman spectrum of intercalated urea between 1700 and 1100 cm^{-1} is too weak to be observed, but a significant change is observed in the strong 1017 cm^{-1} band. This band is attributed to the symmetrical NCN stretch and it shifts to 1014 cm^{-1} and develops a broad shoulder at about 1004 cm^{-1} . When band resolution is carried out these two components have about equal areas for the urea-intercalated low defect kaolinite. For the urea-intercalated high defect kaolinite, the high frequency component occurs at 1016 cm^{-1} and its area is about three times larger than the shoulder at 1006 cm^{-1} . These observations suggest that due to interaction of urea with the kaolinite, there is a perturbation of the NCN stretch of the interacting urea molecules, which gives rise to the broad shoulder.

3.4 *A Proposed model for urea intercalation.*

A model is proposed in which the C=O group of urea is hydrogen bonded to the inner surface hydroxyls. At the same time one of the two NH_2 groups is hydrogen bonded to the siloxane layer with the second NH_2 unit being free. This model of molecular interaction

differs from that proposed at 298K [5]. In the Raman spectra of urea intercalated kaolinites measured at 298 K, significant intensity remains in the bands attributed to the inner surface hydroxyl groups. Thus the interaction at 298 K is believed to occur only between the NH₂ groups and the siloxane layer. On cooling to 77K, the urea and hydroxyl surfaces are brought closer together so that hydrogen bonding between the hydroxyls of the gibbsite-like layer and the C=O group can occur. The observation of changes in the symmetric NCN stretching band in the 77K spectrum of the urea-intercalated kaolinites supports this model. This vibration is observed at 1009 cm⁻¹ for the urea-intercalated low defect kaolinite at 298K [5]. At 77K, this band shifts to 1014 cm⁻¹ and a broad shoulder develops at 1004 cm⁻¹. The observation of two NCN stretching frequencies again suggests that one of the amine groups is bonded to the kaolinite surface while the second remains non-bonded.

4. Conclusions

The Raman spectra of polycrystalline urea and urea-intercalated low and high defect kaolinites have been recorded at liquid nitrogen temperature. Significant changes were observed in the spectra of both the inserting urea molecule and the host kaolinite. In particular a new band attributed to the inner hydroxyl groups hydrogen bonded to the C=O group of urea was observed at 3615 cm⁻¹. At 77K, no intensity remained in the bands attributed to the inner surface hydroxyls of the untreated low defect kaolinite. This indicates that all of the inner surface hydroxyls are involved in hydrogen bonding with the urea C=O group. A broad band observed at ~3600 cm⁻¹ in both the low and high defect kaolinites is assigned to water in the intercalate.

Significant changes also occur in the spectrum of the inserting urea molecule. Four bands corresponding to the two sets of antisymmetric and symmetric NH₂ stretching modes were observed for urea at 77K. Upon intercalation of the kaolinites with urea, only one set of NH₂ stretching bands was observed. It is assumed that one of the NH₂ groups is involved in hydrogen bonding with the oxygen atoms of the siloxane layer. A shoulder develops at 1004 cm⁻¹ on the low wavenumber side of the symmetric NCN stretching mode. This is also attributed to the formation of hydrogen bonds by one of the NH₂ groups.

A model based upon a change of the points of interaction of the urea molecules with the kaolinite surfaces is proposed. At 298K, urea forms hydrogen bonds to the oxygen atoms of the siloxane surface. It is suggested that at 77K, the layers are closer together and this results in the carboxyl group forming additional hydrogen bonds to the hydroxyls of the gibbsite-like surface.

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Figure 1d Raman spectra of the low frequency region of urea at 298 and 77K.

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