Molecular Structure of Dimethyl Sulfoxide in DMSO-Intercalated Kaolinites at 298 and 77 K

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The molecular structure of dimethyl sulfoxide at liquid nitrogen temperature has been obtained from the Raman spectra of dimethyl sulfoxide intercalated kaolinites by the use of Raman microprobe and a low temperature thermal stage. Raman bands at 2917 and 2935 cm^{-1} for the symmetric stretching and four bands at 2999, 3015, 3021, and 3029 cm^{-1} for the antisymmetric stretching are observed at 298 K. At liquid nitrogen temperature, five symmetric stretching frequencies at 2882, 2907, 2917, 2920, and 2937 cm^{-1} and six antisymmetric stretching frequencies at 2986, 2994, 3000, 3012, 3023, and 3032 cm^{-1} are observed for the DMSO-intercalated low defect kaolinite. Differences in the position and number of bands are observed for DMSO between the DMSO-intercalated low and high defect kaolinites. The in-plane methyl-bending region shows two Raman bands at 1411 and 1430 cm^{-1} at 298 K and 1411 and 1426 cm^{-1} at 77 K. The S═O stretching region shows bands in the 298 K spectra at 1066, 1023, and 1010 cm^{-1} and at 1010, 1023, and 1062 cm^{-1} in the 77 K spectra. These bands are assigned to the free monomeric S═O group and two different polymeric S═O groups. The C−S vibrations also show increased complexity upon obtaining spectra at 77 K. The additional bands of DMSO are attributed to the different molecular structures of DMSO in the DMSO-intercalated kaolinites.

Introduction

Kaolinites are often expanded through the insertion of molecules between the layers. This process is known as intercalation. Kaolinites may be readily intercalated with different types of molecules with consequential expansion along the *c*-axis.[1,2] Intercalation with dimethyl sulfoxide (DMSO) is often used with kaolinites is to distinguish the X-ray diffraction patterns of different types of clay minerals.[3] The reason molecules such as DMSO, acetamide, and formamide are used to expand the kaolinite layers is that these inserting molecules form stronger hydrogen bonds with the siloxane or gibbsite-like kaolinite surfaces than do the adjacent (siloxane and gibbsite-like) surfaces. Recently formamide has been used to intercalate highly ordered kaolinites with considerable success.[4,5]

Three main groups of polar organic molecules may be distinguished by their mode of intercalation. The first type of molecules (group A) are directly intercalated from the liquid, melt, or concentrated aqueous solution. Group B molecules consist of species that are indirectly intercalated by means of an entraining agent.[5] Classically, hydrazine and ammonium acetate act as entraining agents. Intercalation of organic salts such as sodium acetate and the potassium salts of glycine, alanine, and lysine can be made to intercalate kaolinite through following the hydrazine into the kaolinite. Group C molecules are those which are intercalated by displacement of previously intercalated molecules. For example, DMSO or ammonium acetate can be displaced by long chain alkylamines. Group A molecules consist of small organic molecules which are directly intercalated into the kaolinite without any pretreatment. Molecules that may act as both proton donors and acceptors such as urea, hydrazine, formamide, and acetamide easily intercalate into the kaolinite.[2] Such intercalation may be followed by both X-ray diffraction and by numerous spectroscopic methods.[6−8] However, often the kaolinite structure and the modification of the structure are followed by these methods while the changes in the molecular structure of the inserting molecule are mostly neglected. Molecules such as hydrazine and DMSO are often difficult to handle because of their volatility. In the measurement of the Raman spectra of liquids at liquid nitrogen temperatures, it is necessary to drive the water out of the system. Hence any volatile liquids are also lost in this process, making the collection of spectral data at low temperatures difficult. By using the DMSO-intercalated kaolinites, the feasibility of measurement of the changes in structure of the inserting molecule (DMSO) at liquid nitrogen temperatures is realistic. In this work we report the changes in the molecular structure of DMSO at liquid nitrogen temperatures upon intercalation of both a low and high defect kaolinite with DMSO.

Experimental Section

Kaolinite Intercalates. The kaolinites used in this study were from Kiralyhegy and Szeg in Hungary. The first kaolinite is an example of an ordered kaolinite and the second of a disordered kaolinite.[7−9] These kaolinites were intercalated by mixing 1 g of the kaolinite in anhydrous dimethyl sulfoxide in an ampule, which was sealed under nitrogen and kept at 85 °C for 7 days. Raman spectra show the presence of water in the so-called pure,

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anhydrous dimethyl sulfoxide. It should be noted that, in the preparation of the DMSO kaolinite intercalate by previous workers, water/DMSO mixtures were used.[1,2−11]

Raman Microprobe Spectroscopy. Very small 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 10×, 20×, and 50× objectives. 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) and recorded at a resolution of 2 cm^{-1} and were acquired in sections of approximately 1000 cm^{-1} for 633 nm excitation. 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. The best method of placing the kaolinites on this metal surface was to take a very small amount on the end of the spatula and then tap the crystals on to the metal surface. Further details on the spectroscopy have been published elsewhere.[8−10]

Spectra at low temperatures were obtained using a Linkam thermal stage (Scientific Instruments Ltd, Waterfield, Surrey, England). Samples were placed on a circular glass disk, 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 center of the glass disk. It was found that the best method of obtaining 77 K was to cool rapidly at 50 K/min until approximately 100 K and then cool slowly at 1 K/min 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 12 s scans for 20 min using the special short 20X (UWLD) objective. A lower Raman signal was obtained using this objective owing to the low numerical aperture of this long working distance objective. This, combined with the spherical aberration of the stage window, results in decreased signal.

Spectral manipulation such as baseline adjustment, smoothing, and normalization was performed using the Spectracalc software package GRAMS (Galactic Industries Corp., Salem, NH). 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 accordingly. Band fitting was done 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 of r^2 greater than 0.995 for the 298 spectra and 0.98 for the 77 K spectra. Graphics are presented using Microsoft Excel.

Results and Discussion

C−H Stretching Region. The Raman spectra of CH stretching region of DMSO and the DMSO intercalated kaolinites at both 298 and 77 K are shown in Figure 1. The band component analyses of the Raman spectra of the CH stretching region for DMSO and DMSO intercalated low and high defect kaolinite at 298 and 77 K are shown in Figure 2a−e, and the details of the band component analyses are reported in Table 1. Figure 1 clearly shows the increased number of the CH stretching vibrations upon intercalation of the DMSO into kaolinite. In addition, the figure displays an increased number of bands upon cooling the DMSO-intercalated kaolinites to liquid nitrogen temperature. Pure DMSO shows two degenerate Raman bands at 2911 and 2996 cm^{-1}. These bands are attributed to the symmetric and antisymmetric CH stretching vibrations of the methyl group of the dimethyl sulfoxide.[7] Upon intercalation of the low defect kaolinite, the 2911 cm^{-1} band splits into two peaks in the 298 K spectrum at 2917 and 2935 cm^{-1}. This splitting is attributed to the formation of different molecular structures of the DMSO in the intercalated kaolinite. Upon intercalation of the kaolinites with DMSO, the CH bands are no longer identical, and so different bands in the CH stretching region are observed.

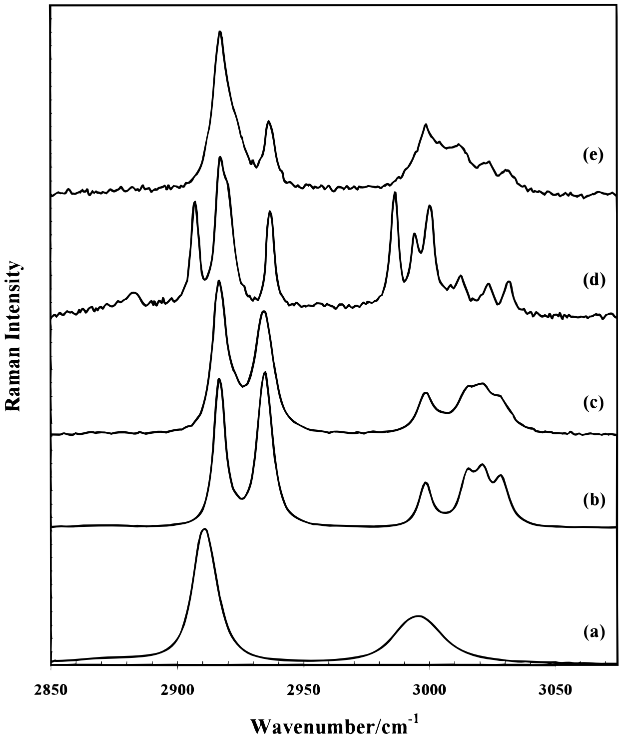

Figure 1. Raman spectra of the C−H stretching region of (a) DMSO, (b) DMSO-intercalated low defect kaolinite at 298 K, (c) DMSO-intercalated high defect kaolinite at 298 K, (d) DMSO-intercalated low defect kaolinite at 77 K, and (e) DMSO-intercalated high defect kaolinite at 77 K.

Two different methyl groups in the DMSO-intercalated kaolinite are observed, one of which is perturbed to high frequency. Johnston also reported such an observation, but the spectra show a lack of intensity in the 2935 cm^{-1} band, which is attributed to the partial intercalation of the kaolinite.[11] The 2996 cm^{-1} band splits into four bands in the 298 K spectrum at 2998, 3015, 3021, and 3029 cm^{-1} for the DMSO-intercalated low defect kaolinite. The symmetric stretching modes for the DMSO-intercalated high defect kaolinite are observed at 2917 and 2934 cm^{-1}. The two bands have the same intensities for the DMSO-intercalated high defect kaolinite. Considerable narrowing of the CH symmetric stretching vibration occurred upon intercalation of the DMSO into the kaolinite. The bands are significantly broader for the high defect DMSO-intercalated kaolinite. Upon intercalation of the low defect kaolinite with DMSO, the antisymmetric stretching vibrations at 2999, 3015, 3021, and 3029 cm^{-1} showed bandwidths of 6.7, 6.9, 7.0, and 7.5 cm^{-1}. The equivalent bands for the DMSO-intercalated high defect kaolinite have bandwidths of 8.9, 11.0, 7.9, and 14.4 cm^{-1}.

When the spectra of the CH stretching region are obtained at 77 K, greater band separation is observed (Figure 1 d,e). Both the CH symmetric and antisymmetric stretching vibrations are further resolved into component bands. For the DMSO-

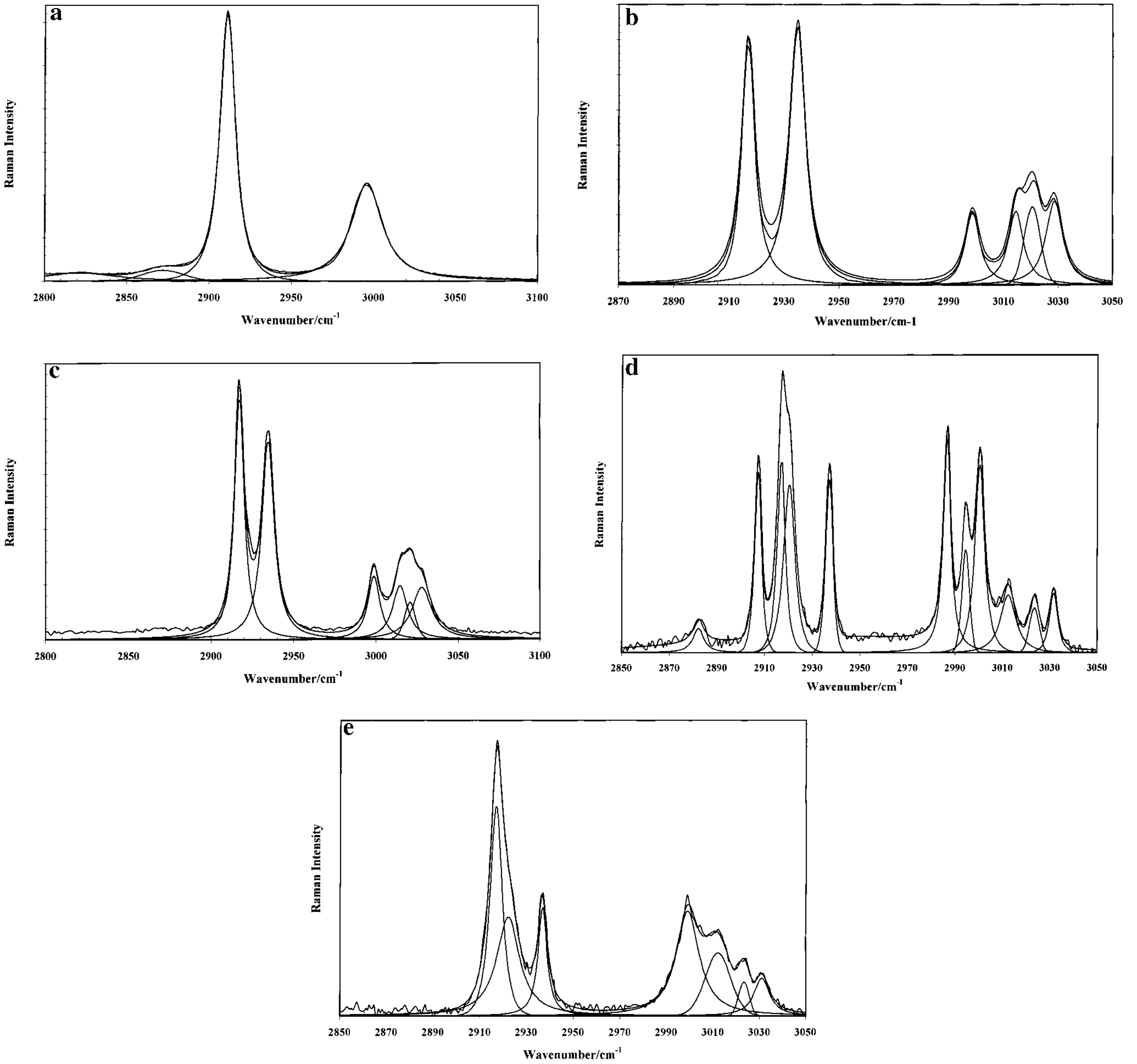

Figure 2. (a) Band component analysis of the Raman spectrum of the CH stretching region of DMSO. (b) Band component analysis of the 298 K Raman spectrum of the CH stretching region of DMSO-intercalated low defect kaolinite. (c) Band component analysis of the 298 K Raman spectrum of the CH stretching region of DMSO-intercalated high defect kaolinite. (d) Band component analysis of the 77 K Raman spectrum of the CH stretching region of DMSO-intercalated low defect kaolinite. (e) Band component analysis of the 77 K Raman spectrum of the CH stretching region of DMSO-intercalated high defect kaolinite.

intercalated low defect kaolinite, the 2911 cm^{-1} band resolves into component bands at 2882, 2907, 2917, 2920, and 2937 cm^{-1}. Thus there are five different CH symmetric stretching vibrations for the DMSO-intercalated low defect kaolinite in the spectra measured at 77 K. The antisymmetric stretching region in the 77 K spectra shows even more complexity with bands observed at 2986, 2994, 3000, 3012, 3023, and 3032 cm^{-1}. It is not known why there is one additional CH symmetric stretching vibration. The symmetric stretching C—H vibrations determined at 77 K for the DMSO-intercalated high defect kaolinite are observed at 2917, 2922, and 2937 cm^{-1}. It is noted that there are less bands observed for the CH vibrations for the DMSO-intercalated high defect kaolinite. The difference between the two sets of data rests with the less perturbed CH vibrations observed for the DMSO-intercalated low defect kaolinite but not for the DMSO-intercalated high defect kaolinite. Such less perturbed vibrations are ascribed to noninteracting DMSO molecules, which are simply occupying space within the structure. A model has been developed for the intercalation of DMSO into kaolinite on the basis of both monomeric and polymeric DMSO.[7] The behavior of the less perturbed DMSO molecules may be likened to water molecules in the interlayer space. Since the less-perturbed DMSO CH vibrations are absent for the DMSO-intercalated high defect kaolinite, this suggests that free or nonbonded DMSO is absent in this case. The ratio of these bands is 2/2/1. For the antisymmetric stretching region at 77 K, bands are observed at 2999, 3012, 3023, and 3031 cm^{-1}. The relative intensities of these bands were 26.0, 10.6, 2.5, and 7.3%.

Importantly, the measurement of the C—H stretching vibrations at liquid nitrogen temperature not only enables greater resolution with additional bands but each of the bands displays considerable narrowing. The C—H symmetric stretching bands are observed at 2882, 2907, 2917, 2920, and 2937 cm^{-1} for the

TABLE 1: Raman Spectra of the Vibrations of Dimethyl Sulfoxide, Low Defect Kaolinite Intercalated with Dimethyl Sulfoxide at 298 K, High Defect Kaolinite Intercalated with Dimethyl Sulfoxide at 298 K, Low Defect Kaolinite Intercalated with Dimethyl Sulfoxide at 77 K, and High Defect Kaolinite Intercalated with Dimethyl Sulfoxide at 77 K

assgnt	DMSO	DMSO-intercalated low defect kaolinite at 298 K	DMSO-intercalated high defect kaolinite at 298 K	DMSO-intercalated low defect kaolinite at 77 K	DMSO-intercalated high defect kaolinite at 77 K
Antisymmetric CH Stretching Vibrations					
$\nu_{\mathrm{C-H}_{\mathrm{antisym1}}}$		3029	3028	3032	3031
$\nu_{\mathrm{C-H}_{\mathrm{antisym2}}}$		3021	3021	3023	3023
$\nu_{\mathrm{C-H}_{\mathrm{antisym3}}}$		3015	3015	3012	3012
$\nu_{\mathrm{C-H}_{\mathrm{antisym4}}}$	2996	2998	2999	3000	2999
$\nu_{\mathrm{C-H}_{\mathrm{antisym5}}}$				2994	
$\nu_{\mathrm{C-H}_{\mathrm{antisym6}}}$				2986	
Symmetric CH Stretching Vibrations					
$\nu_{\mathrm{C-H}_{\mathrm{symmetric1}}}$	2911	2935	2934	2937	2937
$\nu_{\mathrm{C-H}_{\mathrm{symmetric2}}}$		2917	2917	2920	2922
$\nu_{\mathrm{C-H}_{\mathrm{symmetric3}}}$				2917	2917
$\nu_{\mathrm{C-H}_{\mathrm{symmetric4}}}$				2907	
$\nu_{\mathrm{C-H}_{\mathrm{symmetric5}}}$				2882	
Antisymmetric Bending Vibrations					
$\nu_{\mathrm{C-H}_{\mathrm{antisymbend1}}}$		1430	1430	1426	1426
Symmetric Stretching Vibrations					
$\nu_{\mathrm{C-H}_{\mathrm{symbend2}}}$	1419	1411	1411	1411	1411
Antisymmetric S═O Stretching Vibrations					
$\nu_{\mathrm{S=O}_{\mathrm{antisym1}}}$	1056	1066	1058	1062	1055
$\nu_{\mathrm{S=O}_{\mathrm{antisym2}}}$	1042		1040	1036	1036
Symmetric S═O Stretching Vibrations					
$\nu_{\mathrm{S=O}_{\mathrm{sym3}}}$	1029	1023	1026	1023	1024
$\nu_{\mathrm{S=O}_{\mathrm{sym4}}}$	1015	1010	1010	1010	1010
Methyl Rocking Vibration					
$\nu_{\mathrm{C-H}_{\mathrm{rock}}}$	951	950	951	951	950
Antisymmetric C−S Stretching Vibrations					
$\nu_{\mathbf{C-S}_{\mathrm{antisym1}}}$	699	721	720	718	718
$\nu_{\mathrm{C-S}_{\mathrm{antisym2}}}$			712	712	711
$\nu_{\mathrm{C-S}_{\mathrm{antisym3}}}$				703	705
Symmetric C−S Stretching Vibrations					
$\nu_{\mathrm{C-S}_{\mathrm{sym1}}}$	669	690	690	687	688
$\nu_{\mathrm{C-S}_{\mathrm{sym2}}}$			680	679	679
$\nu_{\mathrm{C-S}_{\mathrm{sym3}}}$				671	675
Antisymmetric C−S═O Stretching Vibrations					
$\nu_{\mathrm{S=O}_{\mathrm{antisymbend}}}$	382	387	387	384	386
Symmetric C−S═O Stretching Vibrations					
$\nu_{\mathrm{S=O}_{\mathrm{symbend}}}$	333	355	354	352	352
		334	334	334	336
Antisymmetric C−S−C Stretching Vibrations					
$\nu_{\mathbf{CSC}_{\mathrm{antisymbend}}}$	309	319	318	318	316
Symmetric C−S−C Stretching Vibrations					
$\nu_{\mathrm{CSC}_{\mathrm{symbend}}}$	302	302	310	312	305

DMSO-intercalated low defect kaolinite with bandwidths of 4.3, 3.5, 3.9, 5.7, and 3.6 cm^{-1}, respectively. These bandwidths are approximately half of that observed for the spectra at 298 K. The bands are broader for the high defect case but are less than the values measured at 298 K. The bandwidths measured at 77 K, for the DMSO-intercalated low defect kaolinite, for the antisymmetric vibrations at 2986, 2994, 3000, 3012, 3023, and 3032 cm^{-1} are 3.8, 3.7, 4.8, 7.2, 4.7, and 4.0, respectively. Again the bandwidths measure at 77 K are half the values measured at 298 K. The narrow bandwidths of the CH stretching vibrations of the DMSO-intercalated low defect kaolinite are attributed to the methyl groups being held in a well-defined crystallike structure. The broad bands of the CH stretching region of the DMSO-intercalated high defect kaolinite are ascribed to the more random orientations of the DMSO molecules in the intercalate. Such observations confirm the concept that the intercalation of the low defect kaolinite is significantly different from that of the high defect kaolinite.

A model in which DMSO and water intercalate the kaolinite has been previously proposed.[7] In this model, two types of DMSO molecules are proposed: (a) monomeric DMSO hydrogen bonded to water; (b) polymeric DMSO in which the water functions as the bonding interlinking molecule. Pronounced changes in the Raman spectrum of the inserting molecule are observed. For the symmetric vibrations, one band is observed at 2917 cm^{-1}, which may be described as an unperturbed or slightly perturbed vibration, and also there is a band at 2934 cm^{-1}, which is ascribed to a strongly perturbed vibration. There are two possibilities: First, some DMSO molecules are simply occupying the interlayer space and are not involved with any molecular interactions. Second, only half of the molecule is involved with molecular interactions. The increased complexity of the CH stretching vibrations suggests the methyl groups are locked into a rigid structure. The concept of perturbed and unperturbed DMSO molecules is supported by the observation of three S═O symmetric stretching frequencies. The frequencies of these S═O vibrations correspond to polymeric and monomeric DMSO molecules.[12] It is possible that the nonperturbed DMSO vibrations may be ascribed to the "free" or noninteracting DMSO molecules, the perturbed DMSO vibrations to monomeric DMSO, and the highly perturbed vibrations to polymeric DMSO molecules.

Upon the measurement of the Raman spectra at liquid nitrogen temperature, the CH stretching vibrations now show greater complexity. Five CH symmetric stretching vibrations are observed at liquid nitrogen temperature. These vibrations may be now divided into three groups: (a) the less perturbed vibrations at 2882 and 2907 cm^{-1}; (b) the slightly perturbed vibration at 2917 cm^{-1}; (c) the strongly perturbed vibrations at 2920 and 2937 cm^{-1}. The nonperturbed CH vibrations are attributed to the methyl groups of DMSO occupying space within the interlayer space. The slightly perturbed vibrations are attributed to monomeric DMSO molecules, as the frequencies are at positions similar to that of pure DMSO. It is possible that the strongly perturbed vibrations are due to the DMSO molecules which are in a polymeric form. Six CH antisymmetric stretching vibrations at liquid nitrogen temperature complement the six CH symmetric stretching vibrations. These antisymmetric vibrations may be also divided into three groups: (a) nonperturbed vibrations at 2986 cm^{-1}; (b) weakly perturbed vibrations at 2994 and 3000 cm^{-1}; (c) strongly perturbed vibrations at 3012, 3023, and 3032 cm^{-1}.

HCH Bending Region. DMSO spectra at 298 K display a single band at 1419 cm^{-1} with a bandwidth of 21.9 cm^{-1}. Upon intercalation of both the low and high defect kaolinites with DMSO, two bands are observed at 1411 and 1430 cm^{-1}. At liquid nitrogen temperatures, the bands are observed at 1411 and 1426 cm^{-1} with bandwidths of 5.6 and 4.8 cm^{-1}. The DRIFT spectra of the H−C−H bending region is complex with bands observed at 1438, 1428, 1408, 1404, 1392, 1374, and 1318 cm^{-1}.[7] The DRIFT spectrum of the DMSO shows two bands at 1414 and 1445 cm^{-1} only. The observation that two Raman bands yet many infrared bands are observed may be attributed to the lack of differential polarizability in the HCH bending vibrations. The changes in dipole moment of the vibrations enable the observation of the infrared spectra. The observation of multiple HCH bending vibrations fits well with the multiple bands in the stretching region.

S=O Stretching Region. The region centered on 1040 cm^{-1} is assigned to the symmetric stretching region of S=O. Details of the band component analysis of the Raman spectra of the S=O stretching region of DMSO, DMSO-intercalated low defect kaolinite, and DMSO-intercalated high defect kaolinite at both 298 and 77 K are reported in Table 1. Three Raman bands are identified for pure DMSO at 1056, 1042, and 1029 cm^{-1}. These bands are assigned to the unassociated monomer and the out-of-phase and the in-phase vibrations of the dimer.[12−16] A minor component was observed at 1015 cm^{-1}. This band is normally associated with polymeric DMSO. No Raman bands which are attributable to the linear dimer and polymeric or aggregated DMSO were observed at 1027 or 1015 cm^{-1}. A band is also observed at 951 cm^{-1}, which is assigned to the symmetric methyl rocking vibration.[12] Upon intercalation of the low defect kaolinite with DMSO, new Raman bands at 298 K are observed at 1066, 1023, and 1010 cm^{-1}. For the high defect kaolinite, bands are observed at 1058, 1040, 1026, and 1010 cm^{-1}. An additional band at 1040 cm^{-1} is observed for the DMSO-intercalated high defect kaolinite. The observation of the additional band suggests that the intercalation of the low defect kaolinite is different from that of the high defect kaolinite. The defects in the disordered kaolinite may mean that more than one polymeric type of DMSO molecules exist in the intercalate. The two bands at 1023 and 1010 cm^{-1} are assigned to two different polymeric S=O DMSO units.[12] The broad bands at 1066 and 1058 cm^{-1} are assigned to S=O of monomeric DMSO. Importantly, these results confirm that more than one type of intercalating DMSO molecule is present.[7]

For the low defect DMSO intercalation complex, 66% of the total band intensity is in the 1066 cm^{-1} band. If the differential polarizability tensors are the same for the S=O bonds in the monomer and polymer, then the relative intensity of 1066 cm^{-1} band suggests that 66% of the DMSO in the intercalate is as a monomer. The loss of weight and the pronounced endotherm observed in the DTGA patterns at 117 °C correspond to this complex. A total of 34.5% of the intensity is in the 1023 cm^{-1} band.[7] Bands for the S=O stretch of DMSO in this region are assigned to polymeric DMSO.[13,14] Therefore it is proposed that two-thirds of the DMSO is in a monomeric form and one-third is as a polymeric complex. The endotherm at 168 °C probably corresponds to the loss of this polymeric DMSO from the intercalation complex. Two bands are observed for the high defect DMSO complex at 1058 and 1040 cm^{-1}. Both bands are attributed to monomeric DMSO, and the total band area is 38%. A total of 54% of the band intensity is in the 1026 cm^{-1} band which is attributed to polymeric DMSO in the intercalate complex. Thus in both the low and high defect DMSO intercalation complexes, two types of DMSO molecules exist. In a simple analysis, these two types of molecules may be described as polymeric and monomeric. For the DMSO-intercalated low defect kaolinite spectra at 77 K, the antisymmetric stretching band is observed at 1062 cm^{-1} and the symmetric stretching frequencies are observed at 1023 and 1010 cm^{-1}. Bands are observed at 1055 and 1036 cm^{-1} for the DMSO-intercalated high defect kaolinite.

CS Stretching Region. Figure 3 shows the 275−775 cm^{-1} spectral region. Figure 4a,b shows the band component analysis of the spectral region between 640 and 740 cm^{-1} for the DMSO-intercalated low and high defect kaolinites. Details of the band component analysis are reported in Table 1. Bands are observed at 669 and 699 cm^{-1} for pure DMSO and are attributed to the symmetric and antisymmetric CS stretching vibrations. The symmetric and antisymmetric CS stretching vibrations are found at 690 and 721 cm^{-1} in the DMSO-intercalated low defect kaolinites. The bands show symmetric profiles with only one band at each frequency for the DMSO-intercalated low defect kaolinite. The bands are substantially narrower for both the antisymmetric and symmetric CS stretching vibrations for the DMSO-intercalated low defect kaolinite. There is a $\sim$21 cm^{-1} difference between the unperturbed CS stretching frequencies of pure DMSO and the perturbed stretching frequencies of DMSO in DMSO-intercalated kaolinites.

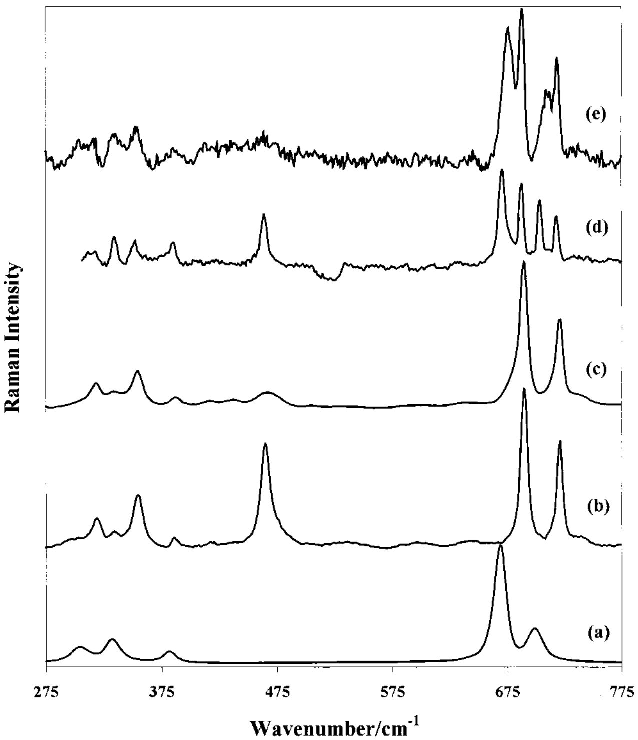

Figure 3. Raman spectra of the 300−775 cm^{-1} region of (a) DMSO, (b) DMSO-intercalated low defect kaolinite at 298 K, (c) DMSO-intercalated high defect kaolinite at 298 K, (d) DMSO-intercalated low defect kaolinite at 77 K, and (e) DMSO-intercalated high defect kaolinite at 77 K.

For the high defect kaolinite four bands are observed at 680, 690, 720, and 712 cm^{-1}. The first two bands are assigned to the symmetric stretching modes, and the second, to the antisymmetric stretching vibrations. No differences in the CS stretching frequencies between the high defect kaolinite and the low defect kaolinite were found. However, a second set of bands was observed for the DMSO-intercalated high defect kaolinite at 680 and 712 cm^{-1} with bandwidths of 15.4 and 14.6 cm^{-1}. The significance of the two sets of values for both the asymmetric and symmetric CS stretching vibrations means that two different types of molecular arrangements of the DMSO molecules are present in the intercalate. The ratio of the two types of molecules is $\sim$1:3. On the basis of DTG results, the ratio of monomer to polymeric DMSO was shown to be 1:2. The results of the ratio of the intensities of the CS vibrations fits well with the DTG results. The Raman spectra of the CS symmetric vibration at 77 K show three bands at 671, 679, and 687 cm^{-1}. These symmetric vibrations are complemented by three antisymmetric vibrations at 703, 712, and 718 cm^{-1}. The observation of three CS vibrations supports the concept of three types of DMSO molecules present at liquid nitrogen temperatures. Bands for the symmetric and antisymmetric stretching

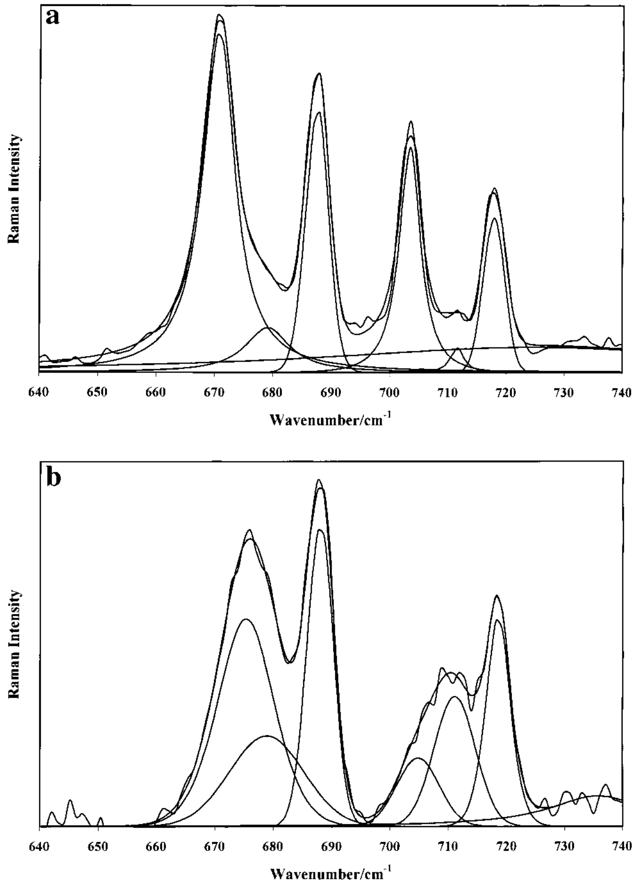

Figure 4. (a) Band component analysis of the 77 K Raman spectrum in the CS stretching region of DMSO-intercalated low defect kaolinite. (b) Band component analysis of the 77 K Raman spectrum in the CS stretching region of DMSO-intercalated high defect kaolinite.

vibrations are observed at similar frequencies for both the DMSO-intercalated high and low defect kaolinites.

C−S═O Bending Region. The bands in the Raman spectrum of DMSO at 382 and 333 cm^{-1} are assigned to the in-plane and out-of-plane C−S═O bends (Figure 3). Details of the band component analysis are reported in Table 1. The bands assigned to the C−S═O bending modes move to higher frequencies upon intercalation of the kaolinite with DMSO. The two C−S═O bends are now observed at 355 and 387 cm^{-1}. There is a very large increase in intensity of the in-plane and out-of-plane C−S═O bends relative to the intensity of the C−S−C band. This apparent increase may result from changes in symmetry of the S═O unit in the DMSO intercalation complex. The spectra in this region for the DMSO-intercalated high defect kaolinite are substantially different from that of the DMSO-intercalated low defect kaolinite. The conclusion is reached that the DMSO molecule is more perturbed for the low defect kaolinite DMSO intercalate. For the high defect kaolinite, the CSC symmetric bend is not as perturbed and so its symmetry is retained and consequently the relative intensity of this band is higher. The C−S═O symmetric bend relative intensity is 46.5% for the DMSO-intercalated low defect kaolinite and 40.2% for the high defect kaolinite. The significance of the value for the low defect kaolinite rests with the argument that the C−S═O bend is highly symmetric. Such a molecular arrangement would be possible if the S═O was linearly hydrogen bonded to the hydroxyls of the gibbsite-like surface.

The C−S═O symmetric and antisymmetric vibrations for the DMSO-intercalated low defect kaolinite are found at 334, 352, and 384 cm^{-1} at 77 K. The bandwidths of these bands are 4.8, 6.2, and 6.3 cm^{-1} respectively. These bands are narrowed by measurement of the spectra at liquid nitrogen temperatures. The C−S═O symmetric and antisymmetric vibrations at 77 K for the DMSO-intercalated high defect kaolinite are found at 336 and 352 and 386 cm^{-1}. The bandwidths have been reduced but not as much as for the DMSO-intercalated low defect kaolinite. It is considered that, for the low defect kaolinite, the kaolinite layers are stacked in a regular manner and, as a consequence, the DMSO intercalates in a regular and uniform pattern. For the disordered kaolinite, this regularity does not exist because of the large number of defect structures. Consequently the bandwidths for the C−S═O vibrations for the DMSO-intercalated high defect kaolinite are broad. It is interesting that there are two symmetric stretching vibrations and only one antisymmetric vibration. One of the symmetric stretching vibrations at 334 cm^{-1} in both the 298 and 77 K spectra is the unperturbed vibration. The 354 cm^{-1} at 298 K and 352 cm^{-1} at 77 K vibrations are the perturbed C−S═O bending vibration. The C−S═O Raman spectral data support the concept of a nonperturbed DMSO molecule and a highly perturbed DMSO molecule in the intercalation complex.

C−S−C Bending Region. Bands are observed for pure DMSO at 302 and 309 cm^{-1} in the Raman spectra measured at 298 K and are ascribed to the symmetric and antisymmetric C−S−C bending vibrations.[13−16] These bands in the 298 K spectra are observed at 302 and 319 cm^{-1} for the DMSO-intercalated low defect kaolinite and 310 and 318 cm^{-1} for the DMSO-intercalated high defect kaolinite. The bands assigned to the C−S−C bending modes move to higher frequencies upon intercalation of the kaolinite with DMSO. All the CSC stretching vibrations have decreased bandwidths upon intercalation with kaolinite. This decrease is significant in that the DMSO is being held in a more rigid "crystalline-like" structure in the intercalate. When the spectra of the DMSO-intercalated low defect kaolinite are obtained at liquid nitrogen temperatures, the two C−S−C bending vibrations are observed at 312 and 318 cm^{-1}. No splitting of these bands are observed at either 298 or 77 K. Such observations suggest that the perturbation must involve the S═O vibrations.

Refined Model. A molecular model based on the DRIFT and Raman spectroscopic results consists of DMSO in polymeric and monomeric structures in the kaolinite intercalate. Importantly, water is considered to be essential to this intercalation process and serves as the linkage molecule in the polymeric DMSO.[7] Such a model is supported by thermal analysis results.[17] Two endotherms were observed for the loss of DMSO on thermal treatment. Calculations show that the ratio of these two types of molecules ascribed to monomeric and polymeric DMSO is 2/1. The CH symmetric stretching data support the concept of a less perturbed and a strongly perturbed CH vibration which may be attributed to a monomeric and polymeric DMSO molecule. The observation of four CH antisymmetric stretching vibrations for both the DMSO-intercalated low and high defect kaolinites suggests that these vibrations are also perturbed to varying degrees. This means that the methyl groups are locked into the intercalate structure.

When the Raman spectra of the DMSO-intercalated kaolinites are obtained at liquid nitrogen temperature, substantial additional information is obtained. In particular, additional CH stretching bands are observed. The single symmetric stretching vibration for DMSO at 298 K becomes two bands for the DMSO-intercalated kaolinites at 298 K and becomes five bands for the DMSO-intercalated low defect kaolinite at 77 K. These bands may be attributed to nonperturbed, perturbed, and strongly perturbed vibrations. Thus, the proposed model requires some refinement. In particular, the monomeric DMSO molecules exist in two forms: as nonbonded DMSO and interacting DMSO molecules. At liquid nitrogen temperatures, some of the DMSO molecules are behaving as space-filling molecules in the interlayer cavity. The number of symmetric stretching frequencies and the number of DRIFT bending vibrations support the concept that the DMSO molecules are locked in a rigid structure within the intercalate. Further, the differences in the number of CH stretching frequencies between the DMSO-intercalated low and high defect kaolinites support the hypothesis that the intercalation of the low and high defect kaolinites is different.

The combination of the Raman microprobe with the low temperature thermal stage has enabled the spectra of dimethyl sulfoxide at liquid nitrogen temperature to be obtained by measurement of the DMSO-intercalated low and high defect kaolinites. Obtaining spectra at liquid nitrogen temperatures not only enabled greater band separation but resulted in different molecular structures of DMSO in the intercalated kaolinites. The single C–H symmetric stretching vibration for DMSO at 298 K became two bands upon intercalation with both the low and high defect kaolinites. When the spectra of the DMSO-intercalated low defect kaolinite was obtained at liquid nitrogen temperatures, five symmetric stretching vibrations and six antisymmetric vibrations were observed. For the DMSO-intercalated high defect kaolinite, three symmetric and four antisymmetric stretching vibrations were found. The difference in the molecular structure of the DMSO between the high and low defect kaolinites suggests that the molecular interactions of the DMSO in the low and high defect DMSO-intercalated kaolinites are different.

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