

## RAMAN SPECTROSCOPIC STUDY OF KAOLINITE IN AQUEOUS SUSPENSION

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**Abstract**—The vibrational modes of clay minerals in aqueous suspension are uniquely accessible to Raman spectroscopy, but this potentially powerful approach has not been applied heretofore to study clays in aqueous samples. In this paper, Raman spectra in the 100- to 4000-cm<sup>-1</sup> region were obtained for kaolinite in aqueous suspension and in air-dry samples. Contact with water perturbed the low-wavenumber Raman spectrum (100 to 1000 cm<sup>-1</sup>) significantly with respect to relative band intensities and resulted in a pH dependence of the integrated intensity in the OH-stretching region. Comparison of the Raman and infrared (IR) spectra of air-dry kaolinite samples confirmed five Raman-active OH-stretching modes at 3621, 3652, 3668, 3688, and 3696 cm<sup>-1</sup>, in contrast to four IR-active modes at 3621, 3652, 3668, and 3695 cm<sup>-1</sup>. The Raman spectra of two kaolinites of different origin showed differences in band positions and intensities. These results suggest that Raman spectroscopy may provide a useful method to study clay mineral-water interactions, colloidal behavior in clay suspensions, and variations in clay mineral structure.

**Key Words**—Aqueous suspension, Infrared spectroscopy, Kaolinite, pH, Raman spectroscopy.

### INTRODUCTION

The structural features of kaolinite, particularly those of its hydroxyl groups, remain the subject of continuous investigation and controversy (Giese, 1982; Adams, 1983; Suitch and Young, 1983; Prost, 1984). Until the details of the kaolinite structure are understood fully, the application of diverse experimental approaches which provide complementary information about the mineral seems prudent. Within the realm of optical absorption spectroscopy, the principal complementary techniques for investigating the vibrational modes of kaolinite are infrared (IR) and Raman spectroscopy. Inasmuch as the vibrational state transitions probed by IR spectroscopy must involve changes in dipole moment, whereas those probed by Raman spectroscopy must involve changes in polarizability (Wilson *et al.*, 1955), each technique can, in principle, give a different picture of the vibrational spectrum. Hence, more complete characterization of the modes of atomic motion in the kaolinite structure should result from applying both methods.

One of the attractive aspects of Raman spectroscopy, insofar as its application to clay minerals is concerned, results from the fact that liquid water is much less Raman-active than IR-active. Water possesses this property because the fundamental vibrations of the water molecule induce a large change in its dipole moment but only a small change in its polarizability. As

a result, Raman spectroscopy is uniquely suitable for studying the vibrational spectra of clay minerals in aqueous suspension, which better simulates natural conditions than the sample presentation techniques used in IR studies of clay minerals (Farmer, 1974).

To illustrate the utility of Raman spectroscopy in investigations of kaolinite, this paper presents a method for obtaining kaolinite spectra in aqueous suspension. The resulting spectrum of a “wet” kaolinite is also compared with the Raman and IR spectra of air-dry kaolinite samples.

### MATERIALS AND METHODS

#### *Kaolinite samples*

The samples studied were KGa-1 kaolinite from Washington County, Georgia, obtained from the Source Clays Repository of The Clay Minerals Society, and American Petroleum Institute reference kaolinite (API #9) from Mesa Alta, New Mexico, obtained from Ward's Natural Science Establishment, Rochester, New York. A description and some characterization of these minerals were given by van Olphen and Fripiat (1979) for the KGa-1 kaolinite and by Kerr (1951) for the Mesa Alta material.

#### *Na-kaolinite suspension*

Two hundred grams of the untreated KGa-1 clay were placed in 1 liter of distilled water and dispersed for size fractionation by adjusting the pH of the suspension to 9.5 by the addition of small aliquots of 0.01 M NaOH. The kaolinite suspension was size-fractionated immediately by centrifugation and the fraction

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having an equivalent-spherical-diameter of  $<2.0 \mu\text{m}$  was collected. The suspension then was flocculated by the addition of 1 liter of 0.001 M HCl in 1.0 M NaCl. To separate the supernatant solution from the flocculated clay, the suspension was divided into six samples, and each was centrifuged for 10 min at a relative centrifugal force of 700. The supernatant solution then was decanted and its pH measured. The kaolinite samples were redispersed manually into 1 liter of the 0.001 M HCl/1.0 M NaCl solution, and the washing procedure was repeated until the pH of the supernatant solution equaled that of the washing solution (pH 3). This objective typically required five washes. The clay then was redispersed into 1 liter of 0.001 M NaCl, and the above washing procedure was repeated five more times. This treatment was adequate to raise the pH of the supernatant solution to 5.5. The final step of procedure consisted of redispersing the clay into 0.01 M NaCl and adjusting the volume of the flocculated suspension such that a clay concentration of 20% (w/w) was obtained.

#### Raman and infrared spectroscopy

The Raman spectra were obtained on a computer-controlled Spex Industries Ramalog 6 spectrometer equipped with a thermoelectrically cooled Hamamatsu R955 photomultiplier tube and a photon-counting detection system. The 488.0-nm line of an argon ion laser (Spectra Physics model 164-05) was used at an incident power output of 100 mW. The spectral slit width ranged from 2 to 4  $\text{cm}^{-1}$  for all of the spectra reported in this paper.

Sample presentation of the Na-kaolinite in aqueous suspension ("wet" kaolinite) consisted of placing 30 ml of clay suspension in a 50-ml Pyrex beaker. The Pyrex beaker showed no spectral interference in the 100–4000- $\text{cm}^{-1}$  region. The relatively large volume of the beaker provided greater homogeneity in the suspension than that afforded by the conventional glass capillary sample presentation. A preliminary experiment showed that the signal-to-noise ratio in the Raman spectrum of kaolinite in aqueous suspension increased as the clay concentration increased to a maximum value at a clay concentration of 20% (w/w). This clay concentration was chosen for the present study. Sample presentation of air-dry KGa-1 kaolinite involved placing a loosely packed powder of the purified clay in a sample holder. Presentation of the air-dry Mesa Alta kaolinite consisted of mounting a hard consolidated nodule of the clay directly as received in the sample illuminator.

The illumination geometry involved scattered light collected at an angle of  $90^\circ$  to the incident light source. Raman spectra of kaolinite in the OH-stretching region were obtained by using a  $0.5\text{-cm}^{-1}$  step size and a counting time of 5 sec at each step. For a scan range of 3600 to 3725  $\text{cm}^{-1}$ , 250 data points were collected.

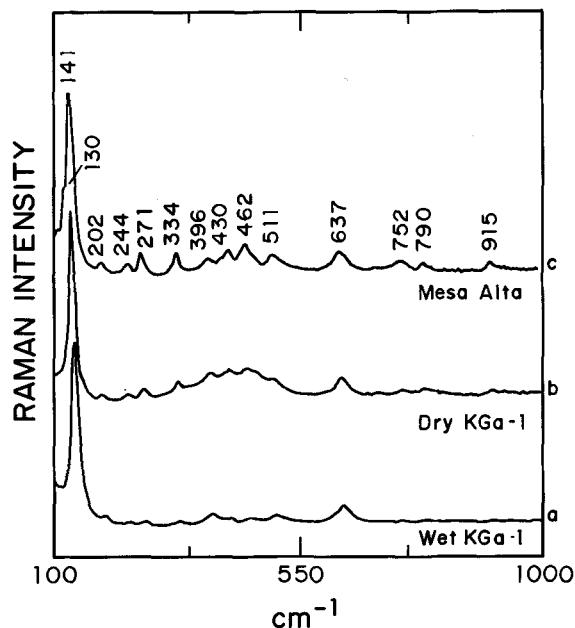


Figure 1. Raman spectra of (a) KGa-1 in aqueous suspension, (b) dry KGa-1, and (c) dry Mesa Alta kaolinite in 100–1000- $\text{cm}^{-1}$  region.

An individual scan required about 20 min. The same counting time was used in obtaining spectra in other regions, but with a different step size. The step size for the low-wavenumber scans was  $1.0 \text{ cm}^{-1}$  and for the 100–4000- $\text{cm}^{-1}$  scans,  $4.0 \text{ cm}^{-1}$ . The Raman spectrometer was calibrated with a low-pressure neon lamp.

Infrared spectra were recorded using a Perkin Elmer 621 filter-grating double-beam instrument. Samples were prepared for IR analysis by deposition from aqueous suspension onto thin AgCl plates and stored in a desiccator over  $\text{P}_2\text{O}_5$  prior to spectral analysis.

#### Data analysis

To determine quantitatively the positions, widths, and integrated intensities of the OH-stretching bands in the Raman spectrum of kaolinite, a computer program was written to assist in deconvoluting the spectra. The fitting function consisted of five Lorentzian curves plus a quadratic polynomial background correction. A Lorentzian line-shape was chosen to represent individual bands in the spectra because both IR bands and homogeneously broadened Raman bands closely approximate Lorentzian lineshapes (Maddams and Mead, 1982). The algorithm minimized iteratively the  $\chi^2$  value of a least-squares adjustment of the fitting function (Bevington, 1977). The output of the deconvolution program consisted of a calculated position, width, and intensity value for each of the five Lorentzian curves plus three parameters that described the quadratic baseline.

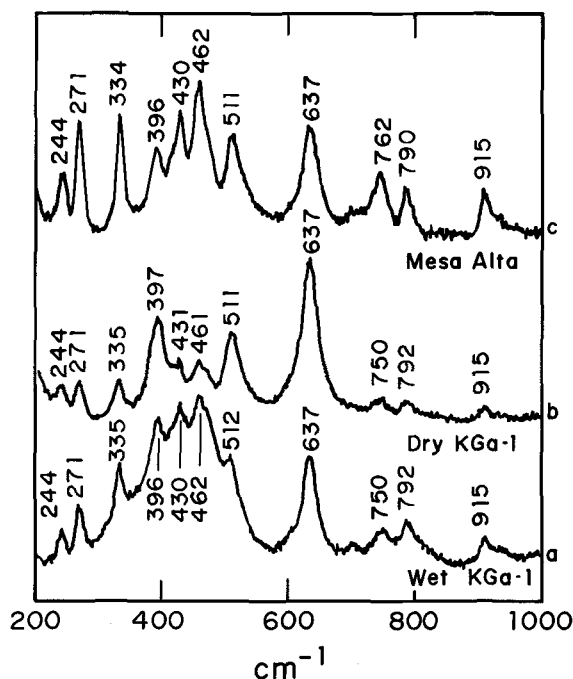


Figure 2. Raman spectra of (a) KGa-1 in aqueous suspension, (b) dry KGa-1, and (c) dry Mesa Alta kaolinite in 200–1000-cm<sup>-1</sup> region.

## RESULTS AND DISCUSSION

### Low-wavenumber region

Raman spectra of the dry KGa-1 and Mesa Alta kaolinites in the 100–1000-cm<sup>-1</sup> region are shown in Figures 1 and 2. A corresponding IR spectrum of the dry KGa-1 kaolinite is shown in Figure 3. The band at 141 cm<sup>-1</sup> in Figure 1 was not observable by IR spectroscopy, but is, by a factor of ten, the most intense band in the Raman spectrum of kaolinite. The position, width, and relative intensity of this band are similar among the spectra in Figure 1, and the same band appeared in the Raman spectrum of dry Keokuk kaolinite published by Wiewiora *et al.* (1979). This band has not yet been assigned to a vibrational mode; however, its very large Raman intensity could occur only as a result of a mode which induces a very large change in polarizability.

Although the number and positions of the bands in Figure 2 are similar in the spectra of the dry KGa-1 and Mesa Alta kaolinites, there is little correspondence among the relative intensities. The 637-cm<sup>-1</sup> band in the Mesa Alta spectrum appears to be the only band of lower intensity than those in the spectrum of the dry KGa-1 clay. In the spectrum of the Mesa Alta clay, the relative intensities of the 462-, 430-, 334-, and 271-cm<sup>-1</sup> bands are significantly larger than those in the spectrum of the dry KGa-1 clay. The sharp, distinct bands of the low-wavenumber Raman spectrum of the

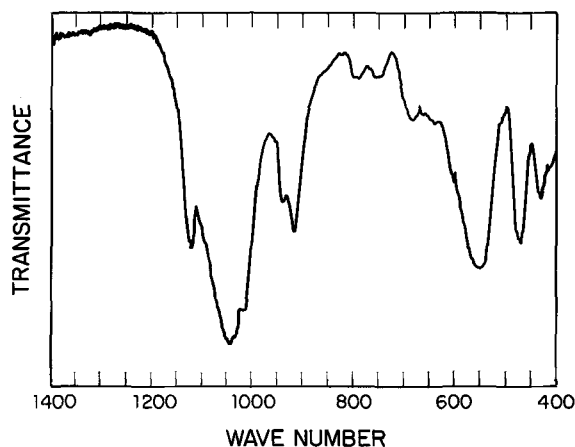


Figure 3. Infrared spectrum of dry, thin film sample of KGa-1 kaolinite deposited on AgCl window in 400–1400-cm<sup>-1</sup> region.

Mesa Alta kaolinite underscore the utility of Raman spectroscopy to study the vibrational modes in clay minerals with little or no sample preparation.

The complementary nature of Raman and IR spectroscopy is illustrated by significant differences between the low-wavenumber Raman and IR spectra of dry kaolinite (Figures 2 and 3). The 692-, 555-, and 470-cm<sup>-1</sup> bands were observed only in the IR spectrum, whereas the 512-, 396-, and 140-cm<sup>-1</sup> bands were unique to the Raman spectrum. Even though the 637-cm<sup>-1</sup> band appeared in both the Raman and IR spectra, it was relatively weak in the latter (Figure 3). The positions of the 940-, 915-, 792-, and 750-cm<sup>-1</sup> bands correspond well in the Raman and IR spectra; however, the relative intensities of the 940- and 915-cm<sup>-1</sup> bands are much less in the Raman spectrum. A numerical comparison of band positions in the two kinds of spectra is given in Table 1.

The Raman spectrum of "wet" KGa-1 kaolinite in the low-wavenumber region also is shown in Figures 1 and 2. This spectrum, except for the 141-cm<sup>-1</sup> band, differs significantly from the Raman spectrum of dry KGa-1 kaolinite. For example, the intensities of the 637-, 512-, and 396-cm<sup>-1</sup> bands are substantially weaker in the spectrum of the "wet" kaolinite (Figure 2). On the other hand, the relative intensities of the 462- and 430-cm<sup>-1</sup> bands are greater in the spectrum of the "wet" kaolinite. Band assignments for the low-wavenumber spectrum of kaolinite can not yet be made, but the results demonstrate nonetheless that Raman spectroscopy can probe the vibrational modes of kaolinite in aqueous suspension and that the Raman spectrum of kaolinite is altered significantly by the presence of water. Thus, Raman spectroscopy may prove to be a sensitive tool with which to study perturbations induced in the vibrational modes of clay minerals by the

Table 1. Band positions ( $\text{cm}^{-1}$ ) in the Raman and infrared (IR) spectra of kaolinities.

IR <sup>1</sup>	Raman		
	Washington County, Georgia (KGa-1)	Mesa Alta, New Mexico	Keokuk, Iowa <sup>2</sup>
3695	3695	3696	3692
	3688	3688	3682
3668	3668	3668	3668
3652	3652	3652	3650
3620	3651	3621	3620
1120	—	—	—
1101	—	—	1105
1040	—	—	1048
1018	—	—	—
941	940	941	935
918	915	915	916
799	—	—	—
792	790	790	791
754	750	752	749
692	700	—	—
638	637	637	—
555	—	—	—
—	512	511	—
470	—	—	—
—	461	462	461
440	431	430	434
—	—	—	420
405	397	396	—
366	—	—	—
352	—	—	—
338	335	334	338
268	271	271	272
—	244	244	248
—	—	—	215
190	201	202	200
—	141	141	—
130	130	130	132
			120

<sup>1</sup> Data compiled from Farmer (1974), Ledoux and White (1964), Wada (1967), Ishii *et al.* (1967), Estep *et al.* (1968), Larson *et al.* (1972), and Rouxhet *et al.* (1977).

<sup>2</sup> Wiewiora *et al.* (1979).

presence of interfacial water and intercalated compounds (Johnston *et al.*, 1984).

#### OH-stretching region

Raman spectra in the OH-stretching region ( $3500\text{--}3800\text{ cm}^{-1}$ ) of "wet" KGa-1, dry KGa-1, and dry Mesa Alta kaolinite are shown in Figure 4. These spectra are in good overall agreement with the Raman spectrum of the OH-stretching vibrations in the spectrum of dry Keokuk kaolinite published by Wiewiora *et al.* (1979). For comparison, the IR spectrum of dry KGa-1 kaolinite is shown in Figure 5. In contrast with the lack of correspondence between the low-wavenumber IR and Raman spectra of kaolinite, the two spectra are generally similar in the OH-stretching region. The principal difference between the IR and Raman spectra in this region is the appearance of five bands in the Raman spectrum and only four bands in the IR spectrum.

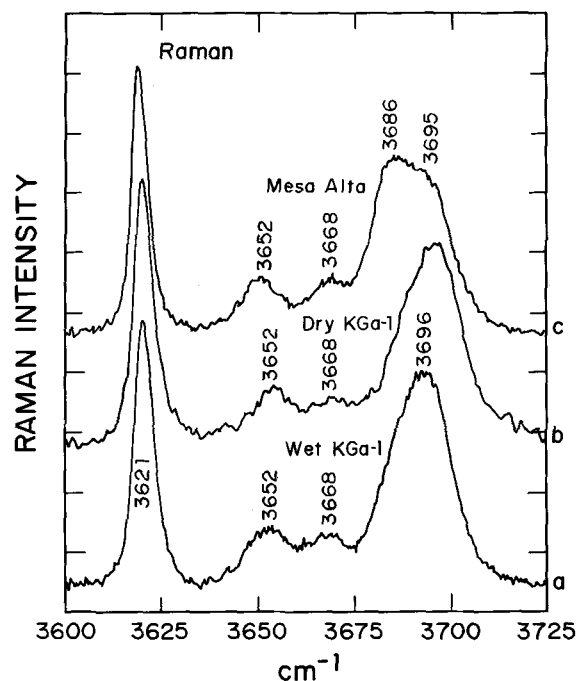


Figure 4. Raman spectra of (a) KGa-1 in aqueous suspension, (b) dry KGa-1, and (c) dry Mesa Alta kaolinite in  $3600\text{--}3725\text{-cm}^{-1}$  region.

Wiewiora *et al.* (1979) first reported a fifth band at  $3682\text{ cm}^{-1}$  in the Raman spectrum of dry Keokuk kaolinite. Deconvoluted Lorentzian band positions, widths, and relative intensities in the Raman spectra that support the five-band hypothesis are listed in Table 2.

The presence of five Raman bands in the OH-stretching region is difficult to reconcile with the fact that only four crystallographically distinct OH groups are present in kaolinite (Rouxhet *et al.*, 1977). The  $3620\text{-cm}^{-1}$  IR band has been assigned uniquely to the single inner-sheet hydroxyl (Ledoux *et al.*, 1964; Wada, 1967; White *et al.*, 1970; Rouxhet *et al.*, 1977). The integrated Raman intensity of the  $3620\text{-cm}^{-1}$  band is 25% of the total integrated Raman intensity for the OH-stretching region (Table 2). This correspondence between the integrated intensity and the relative inner-OH population (one-fourth of the total OH population) suggests that the Raman scattering cross sections are similar for the inner and inner-surface OHs. The inner-sheet OH should always represent one-fourth of the total OH population.

The problem thus is reduced to assigning the four Raman bands at  $3652$ ,  $3668$ ,  $3686\text{--}3688$ , and  $3695\text{--}3696\text{ cm}^{-1}$  to the three inner-surface OHs. Wiewiora *et al.* (1979) suggested that the  $3682\text{-cm}^{-1}$  band they observed in the Raman spectrum of Keokuk kaolinite resulted from the stretching vibrations of decoupled (i.e., isolated), perpendicular, inner-surface OHs; how-

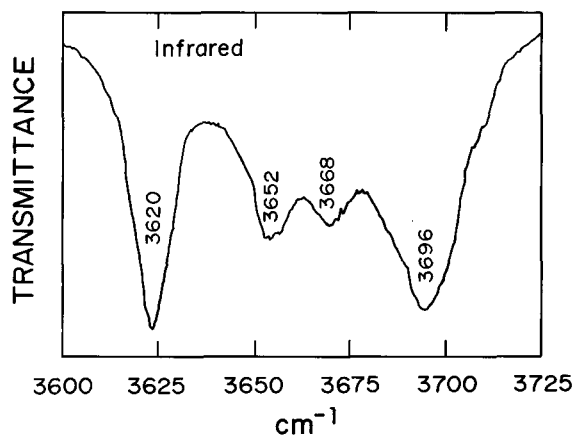


Figure 5. Infrared spectrum of dry KGa-1 kaolinite in 3600–3725-cm<sup>-1</sup> region.

ever, no direct evidence exists to confirm this proposed assignment. Future Raman investigations of selectively deuterated kaolinite samples may provide a clear-cut means of assigning the observed OH-stretching bands. Even for the IR bands at 3652, 3668, and 3696 cm<sup>-1</sup>, there is no consensus on assignment. In an isotope-dilution and pleochroic study of the IR spectrum of kaolinite, Rouxhet *et al.* (1977) observed that, at low levels of exchange with deuterium, the OH-stretching bands at 3696 and 3668 cm<sup>-1</sup> were represented by just one OD-stretching band (at 2714 cm<sup>-1</sup>) and that, as the degree of deuteration increased, two distinct OD-stretching bands appeared at 2723 and 2708 cm<sup>-1</sup>. The 3696-cm<sup>-1</sup> band was highly pleochroic, whereas the 3652-cm<sup>-1</sup> band was not. Rouxhet *et al.* (1977) assigned the 3696-cm<sup>-1</sup> band to the in-phase stretching vibration and the 3668-cm<sup>-1</sup> band to the out-of-phase stretching vibration of two similar, mechanically coupled, inner-surface OH groups oriented perpendicularly to the basal plane. The 3652-cm<sup>-1</sup> band was attributed to the stretching motion of an inner-surface OH group oriented parallel with the basal plane. Recent neutron (Adams, 1983) and X-ray (Suitch and Young, 1983) powder diffraction data of highly ordered kaolinite and a theoretical electrostatic calculation on kaolinite (Giese, 1982) are in conflict with this assignment because they suggest that all inner-surface OHs in kaolinite are oriented nearly perpendicularly to the basal plane.

The similarity between the Raman spectra of OH-stretching vibrations in “wet” KGa-1 (Figure 4a) and dry KGa-1 (Figure 4b) kaolinite can be attributed to the dominance of contributions from bulk OH groups. A similar result was reported in a study of the IR spectrum of deuterated kaolinite by Ledoux *et al.* (1964), who found that reacting kaolinite with deuterium oxide under ambient conditions did not yield OD-stretching bands. Bulk OH groups in kaolinite

Table 2. Measured positions, widths, and relative intensities of the OH-stretching bands in the Raman spectra of three kaolinites.

Position (cm <sup>-1</sup> )	Bandwidth FWHM <sup>1</sup> (cm <sup>-1</sup> )	Relative intensity (%)
“Wet” KGa-1 kaolinite		
3620.8 ± 0.1	5.7	25.7
3652.4 ± 0.2	13.8	12.2
3667.5 ± 0.2	8.7	3.7
3688.3 ± 0.3	13.8	26.9
3695.9 ± 0.2	12.0	31.6
Dry KGa-1 kaolinite		
3621	5.6	25.2
3652	14.3	10.1
3668	7.9	4.2
3688	13.6	27.0
3696	12.5	33.5
Dry Mesa Alta kaolinite		
3621	5.1	22.8
3652	11.3	10.4
3668	9.1	5.3
3686	13.5	34.9
3696	12.8	26.7

<sup>1</sup> FWHM = full width at half maximum intensity.

greatly outnumber the exposed surface OHs (Ledoux *et al.*, 1964; Johnston, 1983).

Although the positions, widths, and relative intensities of the 3621-, 3652-, and 3668-cm<sup>-1</sup> bands are essentially the same in the Raman spectra of Mesa Alta (Figure 4c), KGa-1 (Figures 4a, 4b), and Keokuk (Wiewiora *et al.*, 1979) kaolinite, the position and intensity of the 3686–3688-cm<sup>-1</sup> band differs significantly among the three kaolinite samples. Comparing the Raman spectra of dry Mesa Alta (Figure 4c) to dry KGa-1 (Figures 4a or 4b) kaolinite, one notes that the 3686–3688-cm<sup>-1</sup> band is considerably larger in the spectrum of the Mesa Alta sample. The calculated relative intensity of this band in the spectrum of the Mesa Alta sample was 35 ± 3%, as compared to 27 ± 3% in the KGa-1 spectrum (Table 2). The Raman spectra of Keokuk kaolinite was not deconvoluted by Wiewiora *et al.* (1979); however, the relative intensity of its 3682-cm<sup>-1</sup> band appears to be considerably larger than the intensity of the 3686-cm<sup>-1</sup> band in the Raman spectrum of Mesa Alta kaolinite. These comparisons indicate that the position and relative intensity of the 3686-cm<sup>-1</sup> band depend on the nature and origin of the particular kaolinite sample. The variability of the 3686–3688-cm<sup>-1</sup> band, which is not IR-active, indicates that the Raman technique may provide a unique tool to investigate and characterize OH groups in natural kaolins.

A series of KGa-1 kaolinite samples in aqueous suspension was prepared such that the equilibrium pHs ranged from 3 to 12. The positions, widths, and relative intensities of the OH-stretching bands in the Raman spectra of these samples were insensitive to the vari-

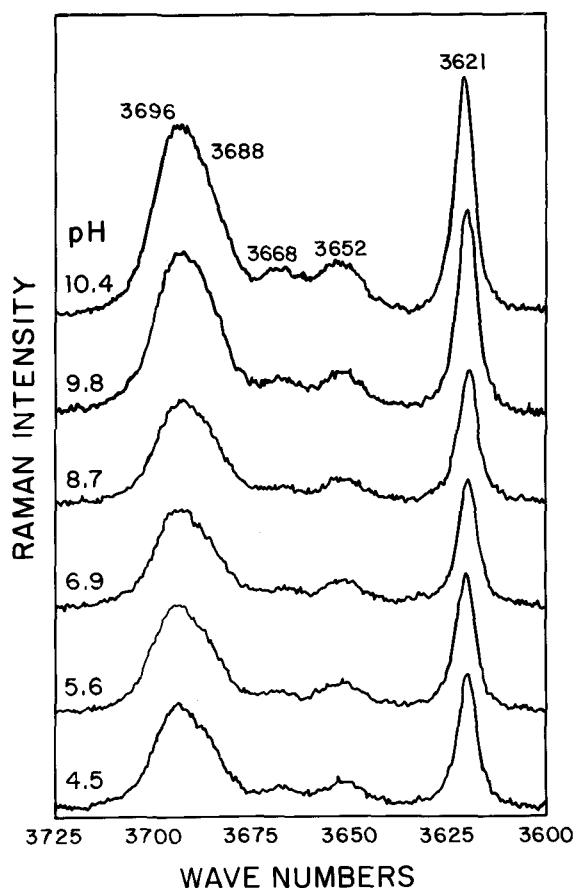


Figure 6. Raman spectra in 3600–3725-cm<sup>-1</sup> region of KGa-1 kaolinite in aqueous suspension as function of pH of supernatant solution.

ation in pH (Figure 6). This result is consistent with the fact that exposed surface OHs are greatly outnumbered by bulk OH groups. The total integrated intensity of the OH-stretching bands, however, increased significantly with increasing pH. A plot of the total intensity as a function of pH is shown in Figure 7. The total intensity reached a maximum at pH 10, then decreased at higher pHs. Note that at pH 10 the total intensity was 2.5 times greater than at pHs <7. The pH-enhancement effect is seen also in the increased signal-to-noise ratio of the spectra in Figure 6 at higher pHs. No conclusive explanation can be given for this observation at present; however, the conspicuous pH dependence of the Raman intensities has two related implications. First, it is evident that the Raman spectrum of kaolinite is sensitive to the type of interparticle interactions which occur in aqueous suspension. One important change that occurs on raising the pH of a kaolinite suspension (at low ionic strength) is the formation of a dispersed colloidal suspension (Rand and Melton, 1975; Schofield and Sampson, 1954). The Raman spectra indicate that enhanced Raman scattering

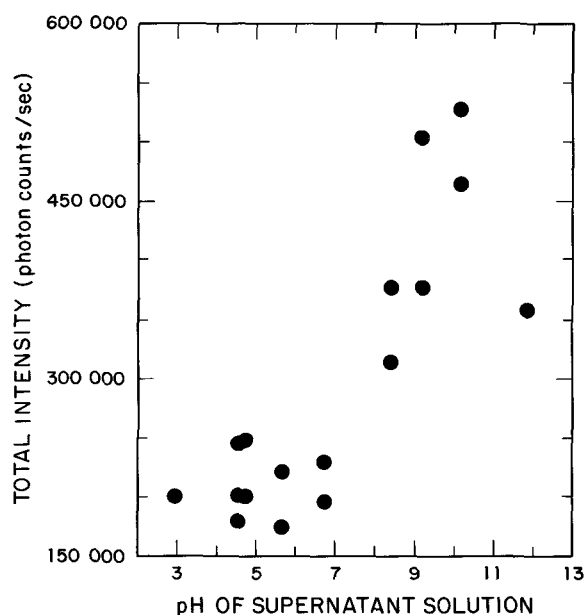


Figure 7. Sum of Raman intensities of 3621-, 3625-, 3668-, 3688-, and 3695-cm<sup>-1</sup> bands as function of pH of supernatant solution.

occurs in a dispersed suspension as opposed to a flocculated suspension. Second, it can be inferred that, for a more complete characterization of the Raman spectrum of kaolinite (or any other clay mineral) in aqueous suspension, spectra should be recorded for a range of pHs and ionic strengths because of the apparent strong dependence of the spectra on the colloidal properties of the clay.

## CONCLUSIONS

Raman spectroscopy is a useful technique for studying the vibrational spectrum of kaolinite. Its principal advantages are: (1) the study of the clay mineral in aqueous suspension, (2) the observation of low-wavenumber vibrational bands inaccessible to mid-IR range spectrometers, and (3) the observation of bands which are not IR-active. In this paper, the first Raman spectra of kaolinite in aqueous suspension have been reported. The low-wavenumber Raman spectrum of kaolinite was shown to be perturbed significantly by the presence of water, which suggests that Raman spectroscopy can provide a new method for studying the interactions between clay mineral surfaces and water molecules in the interfacial region.

Five Raman bands have been observed in the OH-stretching region of kaolinite, confirming similar findings of Wiewiora *et al.* (1979). Two prominent effects were observed in the Raman spectra of kaolinite in this region: First, the Raman scattering of dispersed aqueous kaolinite suspensions was considerably greater than for flocculated suspensions. Second, the relative intensity of the 3686–3688-cm<sup>-1</sup> band, which is not observed

in the IR spectrum of kaolinite, is larger in the Raman spectrum of Mesa Alta kaolinite than in the spectrum of the KGa-1 kaolinite. These observations suggest that Raman spectroscopy is sensitive to nuances of clay mineral structure and to interparticle interactions.

#### REFERENCES

- Adams, J. M. (1983) Hydrogen atom positions in kaolinite by neutron profile refinement: *Clays & Clay Minerals* **31**, 352–356.
- Bevington, P. R. (1977) *Data Reduction and Error Analysis for the Physical Sciences*: McGraw-Hill, New York, 237–245.
- Estep, P. A., Kouach, J. J., and Karr, C. (1968) Quantitative infrared multicomponent determinations of minerals in coal: *Anal. Chem.* **40**, 358–363.
- Farmer, V. C. (1974) The layer silicates: Ch. 15 in *The Infrared Spectra of Minerals*, V. C. Farmer, ed., Mineralogical Society, London, 331–363.
- Giese, R. F., Jr. (1982) Theoretical studies of the kaolin minerals: electrostatic calculations: *Bull. Soc. Fr. Mineral. Crystallogr.* **105**, 417–424.
- Ishii, M., Shimanouchi, T., and Nakahira, M. (1967) Far infra-red absorption spectra of layer silicates: *Inorg. Chim. Acta* **1**, 387–392.
- Johnston, C. T. (1983) A Raman spectroscopic study of kaolinite: Ph.D. dissertation, Univ. California, Riverside, California, 71–78.
- Johnston, C. T., Sposito, G., Bocian, D. F., and Birge, R. R. (1984) Vibrational spectroscopic study of the interlamellar kaolinite-dimethylsulfoxide complex: *J. Phys. Chem.* **88**, 5959–5964.
- Kerr, P. F. (1951) *Preliminary Reports, Reference Clay Minerals, American Petroleum Institute Project No. 49*: American Petroleum Institute, Columbia University, New York, 146 pp.
- Larson, S. J., Pardoe, G. W. F., Gebbie, H. A., and Larson, E. E. (1972) The use of far infrared interferometric spectroscopy for mineral identification: *Amer. Mineral.* **57**, 998–1002.
- Ledoux, R. L. and White, J. L. (1964) Infrared study of selective deuteration of kaolinite and halloysite at room temperature: *Science* **145**, 47–49.
- Maddams, W. F. and Mead, M. L. (1982) The measurement of derivative IR spectra. I. Background studies: *Spectrochimica Acta* **38A**, 437–444.
- Prost, R. (1984) Etude par spectroscopie infrarouge à basse température des groupes OH de structure de la kaolinite, de la dickite et de la nacrite: *Agronomie* **4**, 403–406.
- Rand, R. and Melton, I. E. (1975) Isoelectric point of the edge surface of kaolinite: *Nature* **257**, 214–216.
- Rouxhet, P. G., Samudacheata, N., Jacobs, H., and Anton, O. (1977) Attribution of the OH stretching bands of kaolinite: *Clay Miner.* **12**, 171–178.
- Schofield, R. K. and Samson, H. R. (1954) Flocculation of kaolinite due to the attraction of oppositely charged crystal faces: *Disc. Faraday Soc.* **18**, 138–145.
- Suitch, P. R. and Young, R. A. (1983) Atom positions in highly ordered kaolinite: *Clays & Clay Minerals* **31**, 357–366.
- van Olphen, H. and Fripiat, J. J. (1979) *Data Handbook for Clay Materials and Other Non-metallic Minerals*: Pergamon Press, New York, 346 pp.
- Wada, K. (1967) A study of hydroxyl groups in kaolin minerals utilizing selective deuteration and infrared spectroscopy: *Clay Miner.* **7**, 51–56.
- White, J. L., Laycock, A., and Cruz, M. (1970) Infrared studies of proton delocalization in kaolinite: *Bull. Groupe Franç. Argiles* **22**, 157–165.
- Wiewiora, A., Wieckowski, T., and Sokolowska, A. (1979) The Raman spectra of kaolinite sub-group minerals and of pyrophyllite: *Arch. Mineral.* **135**, 5–14.
- Wilson, E. B., Decius, J. C., and Cross, P. C. (1955) *Molecular Vibrations*: McGraw-Hill, New York, 34–53.
- (Received 28 January 1985; accepted 30 June 1985; Ms. 1448)