ABSORPTION OF INFRARED RADIATION BY D₂O AND HDO MIXED WITH MONTMORILLONITE[1]

J. Sallé de Chou, P. F. Low, and C. B. Roth

Department of Agronomy, Purdue University
West Lafayette, Indiana 47907

Abstract—The frequency, ν, for O–D stretching in D_2O films between the superimposed layers of different micas and montmorillonites was measured at several film thicknesses and temperatures of 2° and 25°C by infrared spectroscopy. The molar absorptivity, ϵ, for O–D stretching in HDO films between the montmorillonite layers was also measured at different film thicknesses and 25°C. It was found that ν is related to m_w/m_m, the mass ratio of D_2O to mica or montmorillonite, by the equation $\nu = \nu^0 \exp \beta/(m_w/m_m)$ where ν^0 is the O–D stretching frequency in pure D_2O and β is a constant. Since m_w/m_m is proportional to a, the area under the absorption peak, m_w/m_m can be replaced by a in this equation. It was also found that ϵ decreased dramatically as the thickness of the water film between the montmorillonite layers decreased. These results were interpreted to mean that the structure of the interlayer water is perturbed by the interlayer cations and/or silicate surfaces.

Key Words—Absorption, Deuterium, Infrared, Molar absorptivity, Montmorillonite, Water.

INTRODUCTION

Infrared spectroscopy has been used to study the nature of hydrogen bonding in bulk water (Pimentel and McClellan, 1960; Walrafen, 1972; Luck, 1973) and in the interlayer water of clays (Serratosa, 1960; Fripiat *et al.,* 1960; Russell and Farmer, 1964; Jorgensen, 1968; Leonard, 1970; Low and White, 1970; Lerot and Low, 1976). However, most of the spectroscopic studies of interlayer water were conducted with relatively dry clays and were largely concerned with the frequency of O–H stretching. The frequency of O–H stretching increases as the length of the hydrogen bond increases (Nakamoto *et al.,* 1955; Pimentel and McClellan, 1960; Kamb, 1968; Bellamy and Pace, 1969). The present work is concerned with the nature of hydrogen bonding in the interlayer water of relatively wet clays. Also, since the frequency of the O–H stretching band is less sensitive to perturbations of the hydrogen bond than is the intensity (Swenson, 1965; Wall and Hornig, 1965), it was also of interest to examine the intensity of this band as a function of the ratio of water to clay.

MATERIALS AND METHODS

Dry, <2-μm, Na-saturated fractions of montmorillonites from Upton, Wyoming; Polkville, Mississippi; Otay, California; and Cameron, Arizona; were prepared as described by Davidtz and Low (1970). To examine O–D stretching in their interlayer water by infrared spectroscopy (IR), the clays were mixed with specific amounts of D_2O or a solution of D_2O in H_2O to form mixtures having different values of m_w/m_m, the mass ratio of water (i.e., D_2O or $D_2O + H_2O$) to mont-

morillonite. The O–D stretching frequency is lower than the O–H stretching frequency by a constant factor of 1.36 and cannot be confused with the stretching frequency of the hydroxyls in the montmorillonite crystal.

Infrared spectra were obtained with a Perkin-Elmer (Model 180) double-beam recording spectrometer. Sheets of freshly cleaved muscovite or phlogopite mica were used as windows. Neither mica absorbs IR radiation in the frequency range where absorption occurs due to O–D stretching, i.e., ~2500 cm⁻¹. Also, mica sheets are durable and inexpensive, unlike commercial windows of Irtran and AgCl. In addition to being recorded on the recorder chart, the output of the spectrometer was digitalized by an analog-to-digital converter, recorded on a cassette tape, and subsequently analyzed by a computer which was programmed to compute the area of the absorption peak, the center of the peak at half height, and the centroid of the peak. Also, the computer was programmed to smooth and replot the data.

In most of the experiments, the temperature of the sample was maintained at either 25° or 2°C by enclosing it in a Beckman (Model VLT 2) variable low-temperature unit. This unit could be cooled with ice and heated with heaters controlled by a thermoregulator activated by a thermocouple near the sample.

In one set of experiments, a film of D_2O was introduced between *freshly cleaved* mica sheets of comparable dimensions, and the frequency for O–D stretching was determined at several film thicknesses. The film thickness was varied either by allowing the D_2O to evaporate between measurements or by introducing different amounts of D_2O initially. In both cases, evaporation during the measurements was prevented by sealing the open edges of the windows with polyethylene wax.

111

In another set of experiments, 1:1 weight mixtures of montmorillonite and D_2O were squeezed between the mica windows until the O–D absorption peak was on scale. The frequency of this peak was then measured at successively lower D_2O contents at the desired temperature. The D_2O content was reduced between measurements by raising the temperature of the control unit to 80°–100°C and allowing evaporation to occur for about one-half hour. D_2O contents below the initial one were determined by assuming that the ratio of peak areas is the same as the ratio of D_2O contents.

The intensity of an absorption peak is supposed to be more sensitive to structural perturbations involving the absorbing dipoles than the frequency (Swenson, 1965; Wall and Hornig, 1965). Therefore, in a third set of experiments, the several montmorillonites were mixed in different proportions with a D_2O–H_2O mixture containing 3% D_2O by volume. The intensities of the respective peaks due to uncoupled O–D stretching were than determined by supporting the mixtures in a Beckman (Model AG-01) cell between AgCl windows separated by exactly 0.0025 cm, the depth of the recess for the sample in one of the windows. To insure that the separation between the windows was not changed by overfilling the recess, the surface of the sample was scraped level with the flat rim of the recess. Also, if the increase in weight of the cell due to the introduction of the sample did not approximate the calculated weight of the sample required to fill the recess, the recess was refilled.

It was assumed that Beer's law applies to the absorption of IR radiation by O–D stretching. This law can be written

$$A = \epsilon c \ell \qquad (1)$$

where A is the absorbance, ϵ is the molar absorptivity, c is the concentration of HDO and ℓ is the path length. The true value of A can be determined experimentally only if monochromatic radiation is used. However, even if monochromatic radiation is not used, a good approximation of A can be determined from the maximum height of the absorption peak provided the ratio of the spectral slit width of the spectrometer to the apparent half peak width is small (Ramsay, 1952). In our experiments, this ratio was <0.2. Therefore, the value of A was determined from the height of the absorption peak at its center (2500 cm^{-1}). The value of ℓ was 0.0025 cm. The value of c in moles/cm^3 of mixture was calculated by the equation

$$c = \frac{0.00322(m_w/m_w)}{[(m_w/m_m) + 0.3582]}. \qquad (2)$$

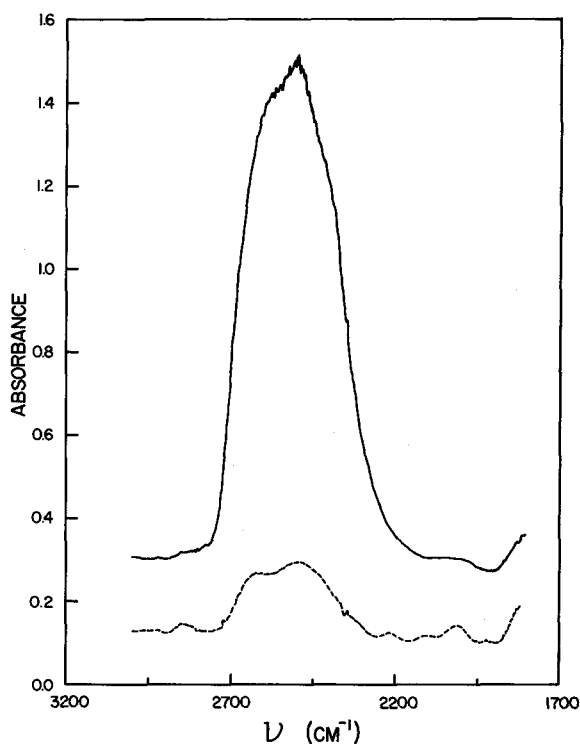In deriving this equation, the equilibrium constant for the reaction

$$D_2O + H_2O \rightleftharpoons 2HDO \qquad (3)$$

Figure 1. Characteristic infrared absorption peaks for O–D stretching in films of D_2O between phlogopite mica sheets at 25°C (——— relatively thick film; ------ relatively thin film).

was assigned a value of 3.96, the density of the D_2O–H_2O mixture was assigned a value of 1.0032 g/cm^3, and the density of the montmorillonite was assigned a value of 2.80 g/cm^3. The above value for the equilibrium constant was reported by Swenson (1965), that for the density of the D_2O–H_2O mixture was calculated from the proportions and densities of the pure components, and that for the density of the montmorillonite was reported by Low and Anderson (1958). Although interaction between the D_2O–H_2O mixture and the montmorillonite causes their respective densities to differ from those cited above (e.g., Anderson and Low, 1958; Ravina and Low, 1977) the differences do not introduce sufficient error into Eq. (2) to preclude its use for the present purpose.

RESULTS

Figure 1 shows characteristic O–D absorption peaks for a relatively thick film (solid line) and a relatively thin film (dashed line) of D_2O between phlogopite sheets at 25°C. Note that the latter absorption peak is at a higher frequency than the former. Also note that on either side of it there are small recurring peaks. These peaks became increasingly apparent as the film thickness decreased. They are probably due to interference effects arising from reflections from closely spaced interfaces.
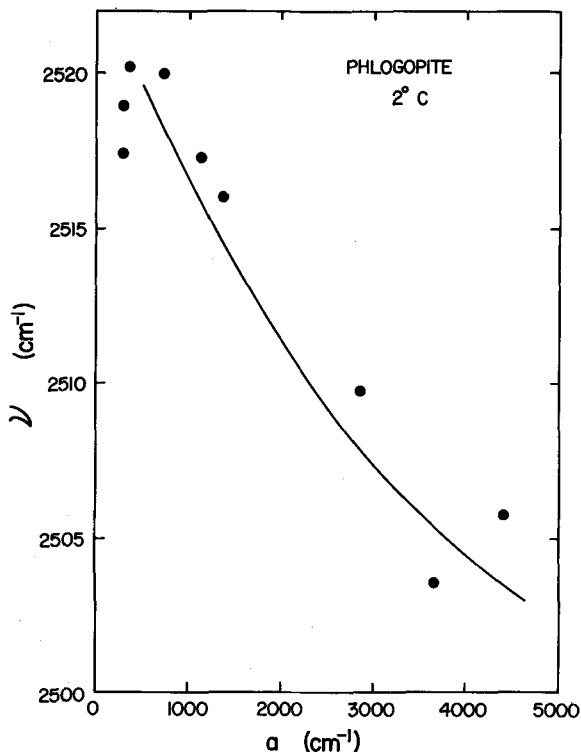
Figure 2.   The relation between the frequency, ν, of O–D stretching in films of D_2O between phlogopite mica sheets at 2°C and the area, a, under the O–D absorption peak.

Figure 3.   The relation between the frequency, ν, of O–D stretching in films of D_2O between muscovite and phlogopite mica sheets at 25°C and the area, a, under the O–D absorption peak (O, ●—film thickness controlled by evaporation; △, ▲—film thickness controlled by amount of D_2O introduced initially).

One of them may be responsible for the high-frequency shoulder on the main absorption peak. However, it is more likely that the development of this shoulder was caused by an increase in the proportion of O–D dipoles whose vibrations are influenced by surface forces. At the present time, no definite conclusion is possible in this regard.

Peaks of the kind shown in Figure 1 were obtained for different film thicknesses between both muscovite and phlogopite sheets at 2° and 25°C. The area of every composite peak (primary peak plus its high-frequency shoulder) and the frequency of its center at half-intensity were determined by means of the computer. Plots of frequency, ν, vs. peak area, a are presented in Figures 2 and 3. In both figures, the circles represent data obtained when the thickness of the D_2O film between the mica sheets was controlled by evaporation, and the triangles represent data obtained when the thickness of this film was controlled by varying the amount of D_2O introduced initially. Note from these figures that ν increases as a, the film thickness, decreases. Insufficient data were available at 2°C to obtain a reliable equation for the dependence of ν on a. However, the equation that describes the data at 25°C is
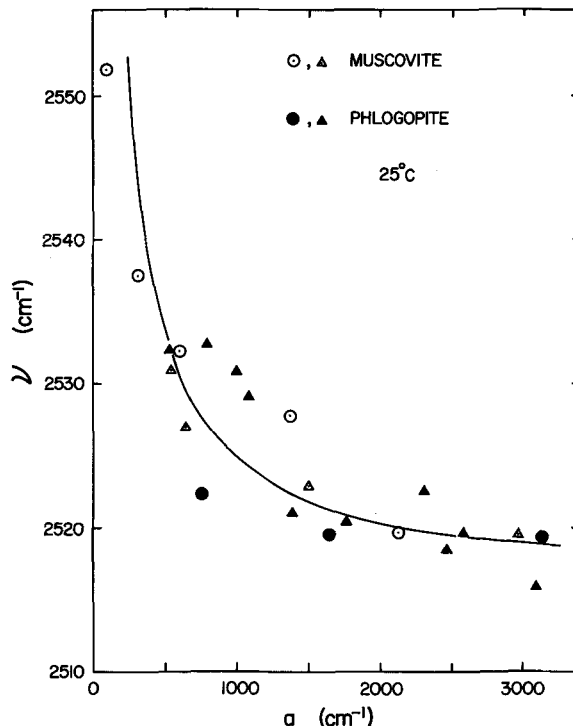
$$\nu = 2516 \exp 3.479/a. \qquad (4)$$

It is important to note that, within experimental error, the results for the phlogopite and muscovite mica were the same. However, their b dimensions are ~9.2 and 8.99 Å, respectively. This suggests that the surface geometry of the mica is not the primary factor influencing the perturbation of the vicinal D_2O.

Superimposed spectra in the region of O–D absorption for mixtures containing the Upton and Polkville montmorillonites at two D_2O contents and 2°C are presented in Figures 4 and 5. Similar spectra were obtained for mixtures containing each of the four montmorillonites at several D_2O contents and at temperatures of 2° and 25°C. Observe that the spectra in both figures indicate the existence of two closely spaced absorption peaks which are not resolvable at the higher D_2O content but are easily resolvable at the lower D_2O content. Also observe that the composite peak has shifted to a higher frequency at the lower D_2O content. Thus, the results for the montmorillonites are similar to those for the micas.

Figures 6 and 7 show plots of ν, the frequency of the composite peak, vs. m_w/m_m, the mass ratio of D_2O to montmorillonite, for the different montmorillonite-D_2O systems at 2° and 25°C, respectively. It is evident that
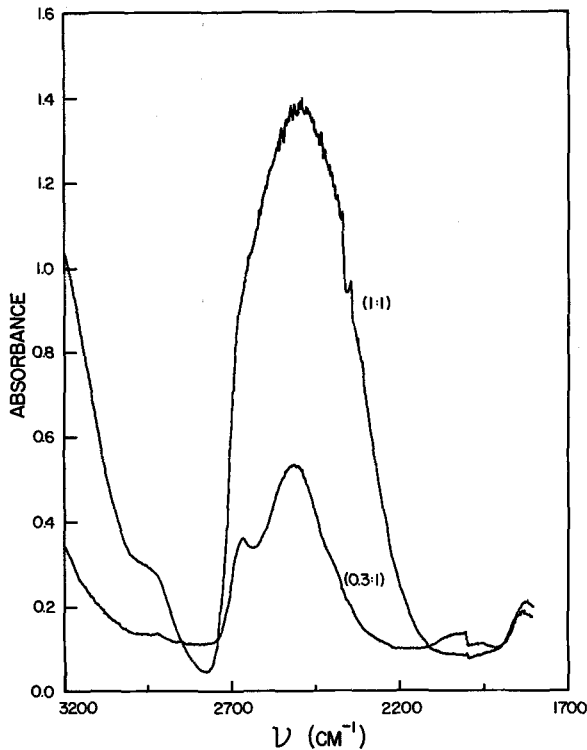
Figure 4. Characteristic infrared absorption peaks for O–D stretching in D_2O mixed with Upton montmorillonite at two different values (in parentheses) of the mass ratio of D_2O to montmorillonite.
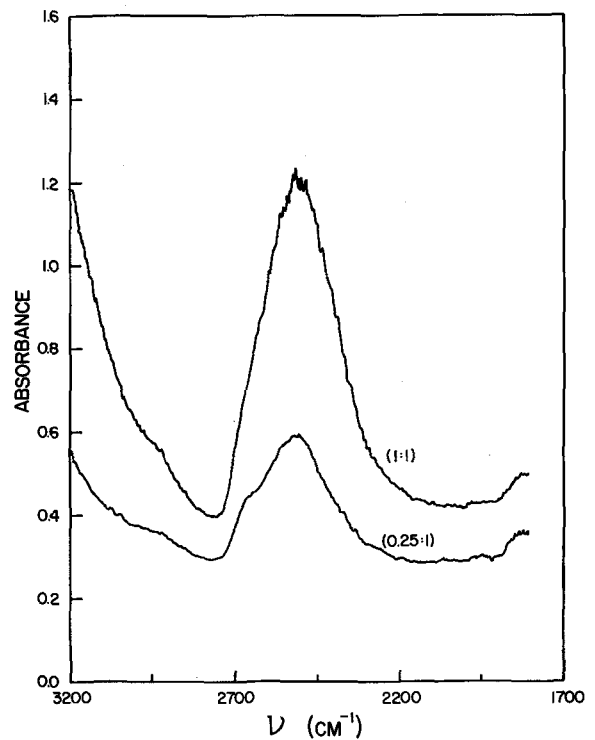

Figure 5. Characteristic infrared absorption peaks for O–D stretching in D_2O mixed with Polkville montmorillonite at two different values (in parentheses) of the mass ratio of D_2O to montmorillonite.

ν shifts to higher frequencies with decreasing m_w/m_m, i.e., with decreasing thickness of the film of interlayer D_2O. This shift, and the comparable shift in the micas, is attributed to an enhancement of the perturbing effects of the exchangeable cations and/or silicate surfaces on the associated D_2O. Farmer and Russell (1971) demonstrated that such effects exist at low water contents.

The best-fitting curves in Figures 6 and 7 are described by equations of the form

$$\nu = \nu^0 \exp \beta/(m_w/m_m) \qquad (5)$$

where ν^0 is the value of ν for pure D_2O ($m_w/m_m = \infty$) and β is a constant that is characteristic of the montmorillonite with which the D_2O is associated. Note that, since m_w/m_m is approximately equal to a, the form of the relation between ν and m_w/m_m (or a) is the same for the montmorillonites as for the micas. Values of ν^0 and β for the different montmorillonite systems were obtained by linear regression analysis with ln ν and m_m/m_w as variables. To improve the reliability of the regression analysis for any system represented by relatively few data points (e.g., the Cameron system at 2°C and the Otay and Cameron systems at 25°C), the average of the values of ν^0 calculated for the other sys-

tems at the appropriate temperature was included as the value of ν in the given system for $m_m/m_w = 0$. The results are presented in Table 1.

It has been shown recently by Low (1979) that such properties as viscosity, specific expansibility, specific heat capacity, and specific entropy of compression of the interlayer water in montmorillonites are described by the equation:

$$P_w = P^0_w \exp \gamma/(m_w/m_m) \qquad (6)$$

Table 1. Values of ν^0 and β in Eq. (5) for the different D_2O–montmorillonite systems.[1]

Montmoril-lonite	Temperature (°C)	ν^0 (cm⁻¹)	β
Upton	2	2501 ± 7	0.0042 ± 0.0010
Polkville	2	2498 ± 5	0.0045 ± 0.0008
Otay	2	2505 ± 7	0.0032 ± 0.0008
Cameron	2	2501 ± 10	0.0024 ± 0.0009
Upton	25	2511 ± 3	0.0042 ± 0.0005
Polkville	25	2511 ± 5	0.0039 ± 0.0006
Otay	25	—	—
Cameron	25	2508 ± 5	0.0031 ± 0.0007

[1] The confidence coefficient = 95% for the confidence intervals reported herein.
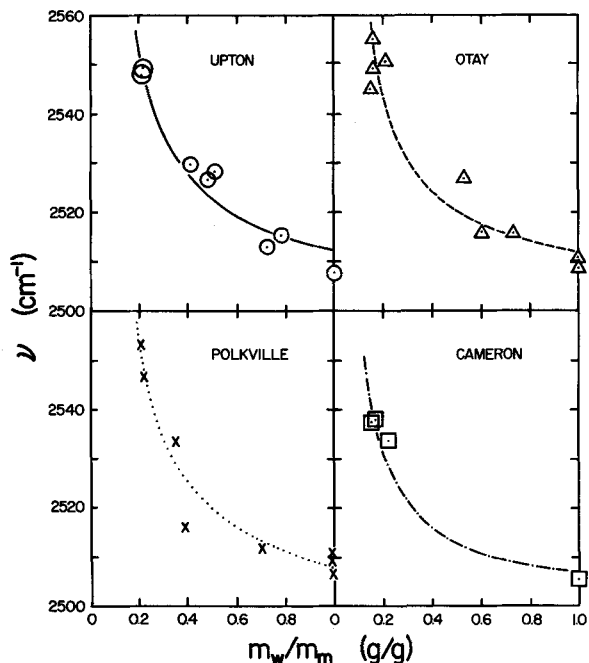
Figure 6.   The relation between ν, the frequency of O–D stretching, and m_w/m_m, the mass ratio of D_2O to montmorillonite, for different montmorillonites at 2°C.
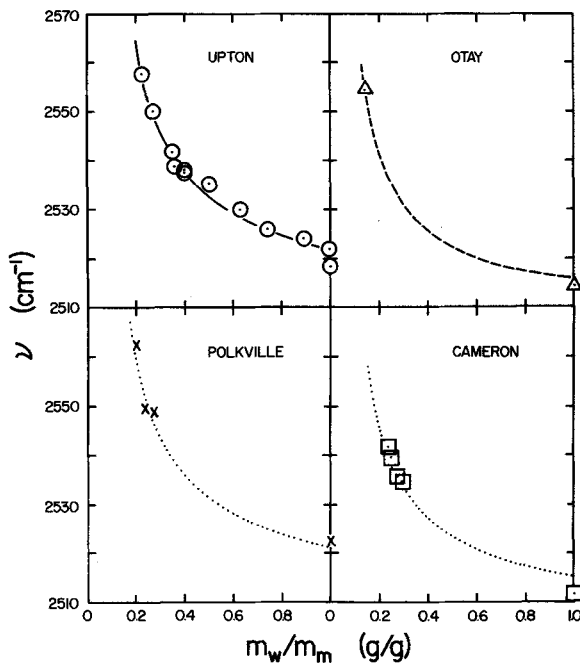

Figure 7.   The relation between ν, the frequency for O–D stretching, and m_w/m_m, the mass ratio of D_2O to montmorillonite, for different montmorillonites at 25°C.

where P_w is the average value of the property for the interlayer water, P^0_w is the value of the property for pure bulk water, and γ is a constant that depends on both the property under consideration and the nature of the associated montmorillonite. Attention is called to the fact that this equation with $P_w = \nu$ and $P^0_w = \nu^0$ is the same as Eq. (5). Evidently, perturbations in the water structure affect all structure-sensitive properties of the water in a similar way.

In other studies on interlayer water involving different montmorillonites (Low, 1976; Ruiz and Low, 1976) it was found that γ in Eq. (6) is a linear function of the b dimension and cation exchange capacity of the associated montmorillonite, the cation exchange capacity being of secondary importance. At first, the dependence of γ on b dimension was regarded as evidence in favor of epitaxy between the water and montmorillonite. Subsequently, however, it was found that the fraction of layers that expand (and, hence, the surface area available to the water) is linearly dependent on the b dimension (Odom and Low, 1978). Therefore, it is hypothesized that γ is essentially a linear function of S_m, the specific surface area of the montmorillonite.

To see if the present results are consistent with the foregoing hypothesis, values of S_m were obtained for the various montmorillonites from the report of Odom and Low (1978) and plotted against the corresponding values of β from Table 1. The resulting graph is shown in Figure 8. Evidently, β, like γ, is a linear function of

S_m. The regression equation relating β and S_m in cm^2/g is

$$\beta = 2.77 \times 10^{-10}S_m + 1.95 \times 10^{-3}. \qquad (7)$$

As mentioned above, the intensity of an absorption peak is usually more sensitive to structural perturbations than is the frequency. Therefore, the absorbance, A, for uncoupled O–D stretching was determined at different values of the concentration, c, of HDO in montmorillonite–water mixtures of constant thickness,
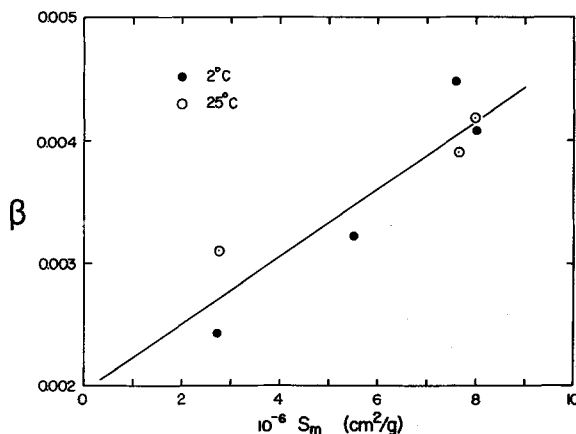

Figure 8.   Relation between the value of β in Eq. (5) and S_m, the specific surface area of the montmorillonite.
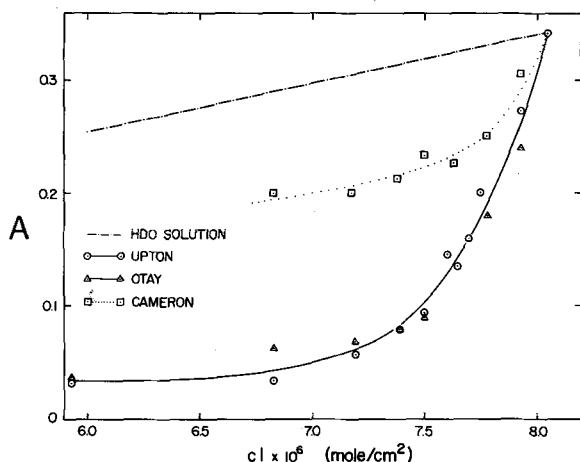
Figure 9. Relation between the absorbance, A, and the product of the HDO concentration, c, and the path length, ℓ.
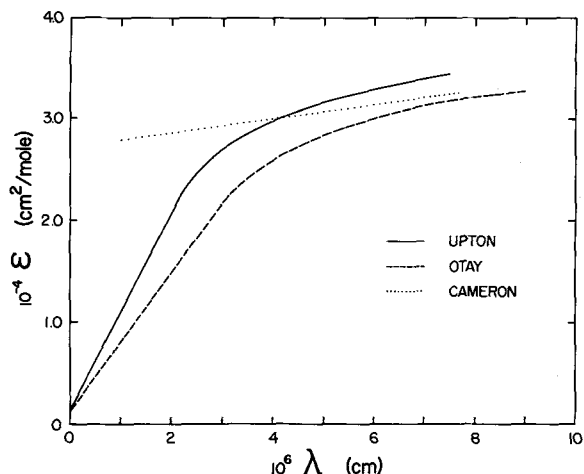

Figure 10. Relation between ϵ, the molar absorptivity for O–D stretching, and λ, the thickness of the film of water (HDO in H_2O) between the montmorillonite layers.

ℓ. The results are presented in Figure 9. Also included in this figure are results that would be expected for a solution of HDO in H_2O without montmorillonite. The latter results were calculated by using in Eq. (1) the experimentally determined value of ϵ for uncoupled O–D stretching in a solution of HDO in H_2O, namely, 4.232×10^4 cm^2/mole. This value of ϵ compares favorably with those obtained by Bayly *et al.* (1963) and Falk and Ford (1966). The values of A in the figure are regarded as approximate because the base line used in the determination of this quantity had a significant slope due to the absorption of H_2O in the spectral region of interest ($\sim$2500 cm^{-1}). Nevertheless, it is evident that values of A for the montmorillonite-water systems are appreciably smaller than those for the HDO solution and that the difference increases with decreasing c $\times$ ℓ. A decrease in c $\times$ ℓ corresponds to a decrease in the proportion of water in the montmorillonite-water system.

In order to obtain values of ϵ for the HDO in the interlayer water, the data in Figure 9 were used in Eq. (1). Corresponding values of λ, the interlayer distance or thickness of the film of water separating the layers, were than calculated by means of the approximate equation:

$$\lambda = 2m_w/\rho_w S_m m_m \qquad (8)$$

in which ρ_w is the density of the interlayer water ($\sim$1.0 g/cm^3). The applicability of this equation is indicated by the fact that it yields values for the c-axis spacing of montmorillonite (c spacing = $10^8\lambda$ + 9.8) which agree well with those measured at various water contents by Norrish (1954), Fink *et al.* (1968), Barclay and Ottewill (1970) and Ravina and Low (1972). Hence ϵ could be plotted as a function of λ as shown in Figure 10. It appears from this figure that ϵ is smaller for O–D absorp-

tion in the interlayer water than in the bulk solution ($\lambda = \infty$). Below $\lambda \approx 2 \times 10^{-6}$ cm, the relation between ϵ and λ is linear for the Upton and Otay systems. For the Cameron system, it is linear over the entire range of λ. Apparently, the different montmorillonites have different effects on ϵ at low values of λ.

DISCUSSION

In discussing these results, it is important to realize that inferences regarding the O–D dipole apply to the O–H dipole as well because the only difference between them is the reduced mass of the atoms involved. Likewise, inferences regarding D_2O apply to H_2O. Hence, the existing data can be used to elucidate the nature of the interlayer water in montmorillonites.

The frequency (expressed in wavenumbers) of an absorption band due to a stretching vibration is given by (e.g., Szymanski, 1964; Colthup *et al.*, 1975)

$$\nu = (f/u)^{1/2}/2\pi v \qquad (9)$$

where v is the velocity of light, f is the force constant, and u is the reduced mass. Different empirical formulas have been developed (Badger, 1934; Gordy, 1946) showing that f is inversely related to the internuclear distance of the vibrating atoms. The integrated intensity of such a band is proportional to the square of the change in the dipole moment caused by the vibration (Tsubomura, 1956; Colthup *et al.*, 1975), that is,

$$\int_{band} \epsilon \, d\nu \propto (d\mu/dr)^2 \qquad (10)$$

where μ is the dipole moment and r is the internuclear distance.

When hydrogen bonds form in bulk water, the frequency of the O–H stretching band shifts toward lower

wave numbers and the intensity of the band increases markedly (Pimental and McClellan, 1960; Vinogradov and Linnell, 1971). In keeping with Eq. (9), the downward shift in frequency is due to a weakening of the force constant, probably because the H atom is displaced along the $O–H \cdots O$ axis and the O–H distance is increased. In keeping with the proportionality expressed in Eq. (10), the increase in intensity is due to a change in $(d\mu/dr)$ which arises because of a redistribution of charge.

It should be recalled that an increase in ν and a decrease in ϵ for O–D stretching were observed as the thickness of the film of interlayer water decreased. In view of the above discussion, it can be concluded that the increase in ν is attributable to an increase in the magnitude of f and that the decrease in ϵ is attributable to a decrease in the magnitude of $(d\mu/dr)$. These changes could have been the result of a weakening of the hydrogen bonds in the interlayer water under the influence of the exchangeable cations and/or surfaces of the montmorillonite layers. However, it is conceivable that factors other than hydrogen bonding influenced the magnitudes of f and $(d\mu/dr)$ and, hence, of ν and ϵ. For instance, the strong electrical field emanating from the layer surfaces could have altered the charge distribution in the vicinal water molecules and, thereby, the magnitudes of both f and $(d\mu/dr)$. Consequently, it cannot be concluded unequivocally that there are fewer or weaker hydrogen bonds in the interlayer water than in bulk water. All that can be stated at the present time is that this water is perturbed relative to bulk water to a degree depending on its thickness.

ACKNOWLEDGMENT

REFERENCES

Anderson, D. M. and Low, P. F. (1958) The density of water adsorbed by lithium-, sodium-, and potassium-bentonite: *Soil Sci. Soc. Amer. Proc.* **22**, 99–103.

Badger, R. M. (1934) A relation between internuclear distances and bond force constants: *J. Chem. Phys.* **2**, 128–131.

Barclay, L. M. and Ottewill, R. H. (1970) The measurement of forces between colloidal particles: *Spec. Disc. Faraday Soc.* **1**, 138–147.

Bayly, J. G., Kartha, V. B., and Stevens, W. H. (1963) The absorption spectra of liquid phase H_2O, HDO and D_2O from 0.7 μm to 10 μm: *Infrared Physics* **3**, 211–223.

Bellamy, L. J. and Pace, R. J. (1969) The significance of i.r. frequency shifts in relation to hydrogen bond strengths: *Spectrochim. Acta* **25A**, 319–328.

Colthup, N. B., Daly, L. H., and Wiberley, S. E. (1975) *Introduction to Infrared and Raman Spectroscopy:* Academic Press, New York, 523 pp.

Davidtz, J. C. and Low, P. F. (1970) Relation between crystal-lattice configuration and swelling of montmorillonites: *Clays & Clay Minerals* **18**, 325–332.

Falk, M. and Ford, T. A. (1966) Infrared spectrum and structure of liquid water: *Can. J. Chem.* **44**, 1699–1707.

Farmer, V. C. and Russell, J. D. (1971) Interlayer complexes in layer silicates. The structure of water in lamellar ionic solutions: *Trans. Faraday Soc.* **67**, 2737–2749.

Fink, D. H., Rich, C. I., and Thomas, G. W. (1968) Determination of internal surface area, external water, and amount of montmorillonite in clay-water systems: *Soil Sci.* **105**, 71–77.

Fripiat, J. J., Chaussidon, J., and Touillaux, R. (1960) Study of dehydration of montmorillonite and vermiculite by i.r. spectroscopy: *J. Phys. Chem.* **64**, 1234–1241.

Gordy, W. (1946) A relation between bond force constants, bond orders, bond lengths, and the electronegativities of the bonded atoms: *J. Chem. Phys.* **14**, 305–320.

Jorgenson, P. (1968) I. R. study of water adsorbed on Wyoming bentonite: *Geol. Fören. Stockholm Förh.* **90**, 213–220.

Kamb, B. (1968) Ice polymorphism and the structure of water: in *Structural Chemistry and Molecular Biology,* A. Rich and N. Davidson, eds., Freeman and Co., San Francisco, 507–542.

Leonard, R. A. (1970) Infrared analysis of partially deuterated water adsorbed on clay: *Soil Sci. Soc. Amer. Proc.* **34**, 339–343.

Lerot, L. and Low, P. F. (1976) Effect of swelling on the infrared absorption spectrum of montmorillonite: *Clays & Clay Minerals* **24**, 191–199.

Low, P. F. (1976) Viscosity of interlayer water in montmorillonite: *Soil Sci. Soc. Amer. J.* **40**, 500–505.

Low, P. F. (1979) Nature and properties of water in montmorillonite–water systems: *Soil Sci. Soc. Amer. J.* **43**, 651–658.

Low, P. F. and Anderson, D. M. (1958) The partial specific volume of water in bentonite suspensions: *Soil Sci. Soc. Amer. Proc.* **22**, 22–24.

Low, P. F. and White, J. L. (1970) Hydrogen bonding and polywater in clay-water systems: *Clays & Clay Minerals* **18**, 63–66.

Luck, W. A. P. (1973) Infrared studies of hydrogen bonding in pure liquids and solutions: in *Water, a Comprehensive Treatise*, Vol. 2, F. Franks, ed., Plenum Press, New York, 235–321.

Nakamoto, K., Margoshes, M., and Rundle, R. E. (1955) Stretching frequencies as a function of distance in hydrogen bonds: *J. Amer. Chem. Soc.* **77**, 6480–6486.

Norrish, K. (1954) The swelling of montmorillonite: *Faraday Soc. Disc.* **18**, 120–134.

Odom, J. W. and Low, P. F. (1978) Relation between swelling, surface area and b dimension of Na-montmorillonites: *Clays & Clay Minerals* **26**, 345–351.

Pimentel, G. C. and McClellan, A. L. (1960) *The Hydrogen Bond:* W. H. Freeman and Co., San Francisco. 475 pp.

Ramsay, D. A. (1952) Intensities and shapes of infrared absorption bands of substances in the liquid phase. *J. Amer. Chem. Soc.* **74**, 72–80.

Ravina, I. and Low, P. F. (1972) Relation between swelling, water properties and b-dimension in montmorillonite-water systems: *Clays & Clay Minerals* **20**, 109–123.

Ravina, I. and Low, P. F. (1977) Change of b-dimension with swelling of montmorillonite: *Clays & Clay Minerals* **25**, 201–204.

Ruiz, H. A. and Low, P. F. (1976) Thermal expansion of interlayer water in clay systems. II. Effect of clay composition: in *Colloid and Interface Science,* Vol. 3, M. Kerker, ed., Academic Press, New York, 503–515.

Russell, J. D. and Farmer, V. C. (1964) I. R. spectroscopic study of the dehydration of montmorillonite and saponite: *Clay Minerals Bull.* **5**, 443–464.

Serratosa, J. M. (1960) Dehydration studies by i.r. spectroscopy: *Amer. Mineral.* **45**, 1101–1104.

Swenson, C. A. (1965) Absolute infrared intensities of HDO in aqueous solution: *Spectrochim. Acta* **21**, 987–993.

Szymanski, H. A. (1964) *Theory and Practice of Infrared Spectroscopy:* Plenum Press, New York, 375 pp.

Tsubomura, H. (1956) Nature of the hydrogen bond. III. The measurement of the infrared absorption intensities of free and hydrogen-bonded O–H bands. Theory of the increase of the intensity due to the hydrogen bond: *J. Chem. Phys.* **24**, 927–931.

Vinogradov, S. N. and Linnell, R. H. (1971) *Hydrogen Bonding:* Van Nostrand Reinhold Co., New York, 319 pp.

Wall, T. T. and Hornig, D. F. (1965) Raman intensities of HDO and structure in liquid water: *J. Chem. Phys.* **43**, 2079–2087.

Walrafen, G. E. (1972) Raman and infrared spectral investigations of water structure: in *Water, a Comprehensive Treatise,* Vol. 1, F. Franks, ed., Plenum Press, New York, 151–214.

Резюме—Инфракрасной спектроскопией замерялась частота ν для растягивания O–D в пленках D_2O между прилегающими слоями разных слюд и монтмориллонитов при нескольких толщинах пленки и температурах 2° и 25°C. Также замерялась молярная поглощаемость, ϵ, для растягивания O–D в пленках HDO между слоями монтмориллонита при разных толщинах пленки и 25°C. Было найдено, что связь ν с m_w/m_m, отношением массы D_2O к слюде или монтмориллониту, описывается уравнением $\nu = \nu^0 \exp \beta/(m_w/m_m)$, где ν^0 = частота растягивания O–D в чистом D_2O, а β = постоянная. Поскольку m_w/m_m пропорционально a, площади под пиком поглощения, вместо m_w/m_m в этом уравнении можно подставить a. Также было найдено, что ϵ резко понизилаςь, когда уменьшилась толщина пленки между слоями монтмориллонита. Эти результаты показывают, что структура межслойной воды искажается межслойными катионами и/или силикатными поверхностями. [N. R.]

Resümee—Die Frequenz, ν, für die O–D-Streckung in D_2O-Filmen zwischen den Schichten unterschiedlicher Glimmer und Montmorillonite wurde bei verschiedenen Filmdicken und bei Temperaturen von 2° und 25°C mittels Infrarot-Spektroskopie gemessen. Die molare Absorptivität, ϵ, für die O–D-Streckung in HDO-Filmen zwischen den Montmorillonitschichten wurde ebenfalls bei unterschiedlichen Filmdicken, bei 25°C gemessen. Es zeigte sich, daß ν mit m_w/m_m, dem Massenverhältnis von D_2O zu Glimmer oder Montmorillonit, durch die Gleichung $\nu = \nu^0 \exp \beta/(m_w/m_m)$ zusammenhängt, wobei ν^0 die O–D-Streckungsfrequenz in reinem D_2O und β eine Konstante ist. Da m_w/m_m proportional zu a ist, der Fläche unter dem Absorptionspeak, kann m_w/m_m in dieser Gleichung durch a ersetzt werden. Weiters zeigte sich, daß ϵ sehr stark zurückgeht, wenn die Dicke des Wasserfilms zwischen den Montmorillonitschichten abnimmt. Diese Ergebnisse wurden dahingehend interpretiert, daß die Struktur des Zwischenschichtwassers durch die Zwischenschichtkationen und/oder durch die Silikatoberflächen gestört wird. [U.W.]

Résumé—La fréquence, ν, de l'étirement de films D_2O entre les couches superposées de différents micas et de montmorillonites a été mesurée à plusieurs épaisseurs de films et à des températures de 2° et 25°C par spectroscopie infrarouge. L'absorptivité molaire, ϵ, pour l'étirement O–D dans les films HDO entre les couches de montmorillonite a aussi été mesurée à des épaisseurs de film différentes et à 25°C. On a trouvé que ν est apparenté à m_w/m_m la proportion de masse de D_2O au mica ou à la montmorillonite, par l'équation $\nu = \nu^0 \exp \beta/(m_w/m_m)$ où ν est la fréquence de l'étirement O–D dans D_2O pur et où β est une constante. Puisque m_w/m_m est proportionnel à a, la région sous le sommet d'adsorption, m_w/m_m peut être remplacé par a dans cette équation. On a aussi trouvé que ϵ a décru dramatiquement à mesure que l'épaisseur du film d'eau entre les couches de montmorillonite décroissait. On a interprété ces resultats comme signifiant que la structure de l'eau interfolaire est perturbée par les cations interfolaires et/ou par les surfaces silicées. [D.J.]