RAMAN SPECTRA OF ION INTERCALATED VERMICULITES

H.X. JIANG,* S.A. SOLIN,* H. KIM** and T.J. PINNAVAIA**
*Department of Physics and Astronomy
**Department of Chemistry
Center for Fundamental Materials Research
Michigan State University, East Lansing, MI 48824-1116

ABSTRACT

The Raman spectra of ion intercalated Vermiculites have been studied. The torsional mode frequencies exhibit a shift to higher energy with increasing basal spacing d. Using a van der Waals type force model, and the nearest neighbor approximation, we have successfully derived the formula for the torsional mode frequency as functions of basal spacing d and other physical parameters. The calculation results are quite consistent with the experimental observations.

INTRODUCTION

Clay Intercalation Compounds (CIC's) have recently drawn attention in solid state physics because of their interesting physical properties. [1-3] One of the most important features of CIC's is that they can be used as an ideal quasi-two-dimensional system with which to investigate 2-D physical and chemical processes. One of the common CIC's is vermiculite which is classified as a 2:1 layered silicate due to its structure. [4, 5] In the interlayer galleries of vermiculite as well as other clays, chemical reactions can be selective, specific, and quite distinct compared with the corresponding reaction in free space. [6]

It is always important to understand the physical properties of CIC's for different intercalated ions. The most important properties for CIC's are layer rigidity, the structure (such as basal spacing), and the distributions of intercalated ions in the galleries all of which are heavily influenced by the guest - guest and guest - host interactions. Extensive work on graphite intercalation compounds [7, 8] and other layered solids has shown that Raman spectroscopy is an effective tool with which to study these interactions.

In this paper, we present the results of the torsional Raman mode of ion intercalated vermiculites. The detailed results and composition dependence of the Raman frequency of this mode of $[(CH_3)_4N^+]_{1-x}$ $[(CH_3)_3NH^+]_x$-Vermiculites will be published elsewhere. [9] The distinct behaviors of these systems suggests the importance of the ion size. The different force constants between guest ions and the basal oxygens also plays an important role. Using a van der Waals type force model and the nearest neighbor approximation, we have successfully derived a formula for the Raman frequency of the torsional mode as a function of basal spacing d, force constants and other physical parameters.

EXPERIMENTAL

For this study, M^+-V(ermiculites) samples were made from Mg-Vermiculite using an ion exchange method [10] with M^+=Rb^+, Cs^+, $(CH_3)_3NH^+$ and $(CH_3)_4N^+$, respectively. The samples were made of powder in which each crystallite was a few microns in size. The samples are well ordered and water free. Highly oriented films were prepared from powdered natural vermiculite. The water was removed by heating the samples in an oven for 12 hours at a temperature of 100 ^oC. Film samples formed on glass slides exhibited mosaic spreads of $\Omega \sim 5^o$ [2] indicating an oriented morphology with the silicate layers parallel to the slide surface.

Raman spectra were measured using the 5145 Å line of an argon laser, a Spex 1402 double spectrometer and a photon counting detection system. All measurements were made with the scattered light collected at 90^o to the direction of propagation of the laser light which was incident at an angle of about 45^o to the sample plane and polarized in the plane of incidence.

RESULTS AND DISCUSSIONS

The Raman frequencies of the torsional mode of M^+-V [M^+=Rb^+, Cs^+, $(CH_3)_3NH^+$ and $(CH_3)_4N^+$)] are at about 106 to 118 cm^{-1}. The torsional mode is an interlayer mode of the C_s symmetry group and is the vibration of oxygens in the basal plane. [1] A few other high frequency modes have also been observed which correspond to intralayer modes of the host layer. These high frequency modes will not be discussed here. In Fig. 1, we plot the Raman shift as a function of basal spacing d for M^+-V with M^+ = Rb^+, Cs^+, $(CH_3)_3NH^+$, and $(CH_3)_4N^+$, respectively. The basal spacing d was measured from x-ray experiments. [1, 2] In the figure, the Raman frequencies are normalized to the frequency of Rb-V, which is 106cm^{-1}, $\nu_{norm} = \nu/\nu_{Rb}$ and d_{norm} is the normalized basal spacing distance. $d_{norm} = (d_{obs} - d_{min})/(d_{max}$

$- d_{min})$ where d_{obs} is the observed basal spacing, and d_{min} and d_{max} are the basal spacing of Rb-V and $(CH_3)_4N^+$-V, which are 10.23Å and 13.3Å, respectively.

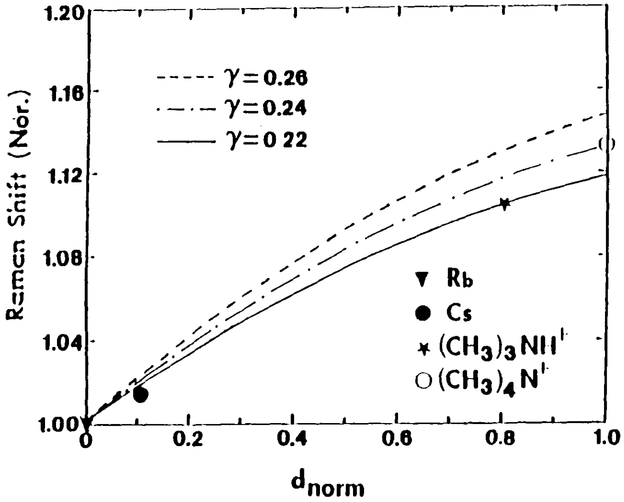

Fig. 1. Calculation results of Raman shift of torsional mode (normalized) as a function of basal spacing (normalized) of M^+-V with three different values of Υ, the ratios of force constants between oxygen-guest ion to oxygen-oxygen. The experimental results are shown in the figure with M^+ being Rb^+, Cs^+, $(CH_3)_3NH^+$ and $(CH_3)_4N^+$, respectively. The basal spacingsd were measured from x-ray experiments.(1),(2)

From Fig. 1, we can see that the Raman frequency of the torsional mode increases with the basal spacing d, which increases with the size of the guest ions. The connection between the Raman frequency and the basal spacing d is very clear. This implies that the basal spacing d is one of the most important parameters for the torsional mode. As we will see, the force constants between oxygen-oxygen and guest ions-oxygen are also important for the torsional mode.

The Raman frequency of the torsional mode as a function of the basal spacing and other physical parameters can be calculated under the following assumptions. First, we assume that the interaction between the oxygen-oxygen and oxygen-guest ion are of the van der Waals type, [11] Second, the guest ions are located in the centers of the hexagonal pockets of the Kagome lattice of the bounding oxygen planes. This should be true if we consider the minimum energy of the system or the equilibrium position of the guest ions. One should notice that when the system vibrates in the torsional mode, the position of each oxygen in the basal plane is determined uniquely, since we know the eigenvector of the mode (guest ions are motionless in the torsional mode).

Under the nearest neighbor approximation, the relation between the Raman frequency of the torsional mode, basal spacing and other physical parameters can be derived as

$$\tilde{\nu}^2 = (-2b^{n-1}/m)(\alpha/4\pi^2c^2)\{3 + \Upsilon(1 + h^2/b^2)^{(n-3)/2}(n + h^2/b^2)\}, \qquad (1)$$

where h=(d - 6.42/2 (Å) is the distance between the center of the guest ion and the basal plane and 6.42Å is the distance between the top and bottom layers of the basal planes in each period. In Eq.(1), b is the lattice parameter, b = 2.67Å, m is the mass of the oxygen atom, c is the speed of light, and $n = -7$ represents the van der Waals type force. The parameters α and $\beta < 0$ correspond to the attractive force constants between oxygen-oxygen and oxygen-guest ion while $\Upsilon = \beta/\alpha$ is the ratio of these force constants.

Equation (1) connects the Raman shift of the torsional mode with the physical parameters of M^+-V. From the parameters b, h, and m, we can calculate the Raman shift of torsional mode as a function of the basal spacing. In Fig.1, we have plotted the calculated results of Eq.(1), Raman shift of the torsional mode (normalized), $\tilde{\nu}_{norm}$, as a function of basal spacing d (normalized), d_{norm}, for three different values of Υ.

The calculated results are quite consistent with experimental observations. For a fixed value of Y, the Raman shift of the torsional mode increases with basal spacing d. The force constant for the oxygen-guest ion interaction is in the order of about 0.2 to 0.3 of the oxygen-oxygen interacton. The same method can also be used for other vibrational modes of CIC's. By comparing calculation and experimental results for other modes, we can derive the force constants between oxygen-oxygen and oxygen-guest ion in CIC's.

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