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Orientation and Motion of Interlamellar Water: An Infrared and NMR Investigation of Water in the Galleries of Layered $Cd_{0.75}PS_3K_{0.5}(H_2O)_y$

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Abstract: The motion of water in the galleries of layered $Cd_{0.75}PS_3K_{0.5}(H_2O)_{1.2}$, prepared by the ion-exchange intercalation of hydrated potassium ions into $CdPS_3$, have been investigated using a combination of orientation dependent NMR and infrared (IR) spectroscopies as a function of temperature. Within the galleries of the intercalated compound the potassium ions are displaced toward the layers and are immobile, while the water molecules form monolayer-thick two-dimensional islands. Two types of interlamellar water are distinguishable by both NMR and IR spectroscopy. A loosely bound isotropically tumbling water which is easily lost on mild evacuation and a more tightly bound water with restricted degrees of rotational freedom. The angular dependence of the NMR and IR spectral features of the latter indicate that their $\vec{C}_2$ symmetry axis is at a fixed orientation with respect to the interlamellar normal and rotate rapidly about it. In analogy with bulk aqueous solutions these two types of interlamellar water may be considered as two-dimensional solventlike water and water coordinated to the potassium ion forming part of its hydration shell. A remarkable feature of the water in the galleries of $Cd_{0.75}PS_3K_{0.5}(H_2O)_{1.2}$ is the extremely slow rate of exchange ($\tau \gg 10^{-5}$ s) between the two-dimensional solventlike water and the coordinated water, in direct contrast to the rapid exchange observed for K ions in bulk aqueous solutions. The present experimental results provide the first observation of the effect of confinement on solvation shell exchange. It is suggested that the slowing down could be the effect of confinement in two dimension which would strongly inhibit any mechanism involving transition or intermediate states which require an expansion of the coordination shell around the potassium ion.

Introduction

The layered divalent metal thiophosphates MPS_3, where M = Mn, Fe, or Cd, undergo an unusual ion-exchange intercalation reaction in which solvated cationic guest species from solution insert into the interlamellar space with an equivalent loss of the divalent ion from the layer.[1,2] Intercalation occurs with a dilation of the host lattice, the extent of which depends on the nature of the guest species. For cadmium thiophosphate the reaction may be written as

$$CdPS_3 + 2xK^+(aq) \rightarrow Cd_{1-x}PS_3K_{2x}(H_2O)_y + xCd^{2+}(aq)$$
$$x = 0.26, y = 1.2$$

where the guest species hydrated K ions reside in the interlamellar space. The above reaction was first reported by Clement and co-workers[3] who observed that the interlayer distance, d, varied continuously from 9.2 to 9.45 Å depending on the ambient humidity. On closer examination we find that there are two discrete phases of the intercalated $Cd_{0.75}PS_3K_{0.5}(H_2O)_y$; a phase with interlayer distance $d = 9.45$ Å which on partial loss of water, on mild evacuation, gives a phase with $d = 9.25$ Å, with all other structural parameters remaining identical. The concentrations of the two phases depend on the ambient humidity. The results are interesting since for the two phases the values of the lattice expansion on intercalation (Δd), 2.9 Å and 2.7 Å, are in one case comparable and in the other slightly smaller than the van der Waals diameter of a water molecule.[4] This suggests that there are two types of interlamellar water. Our studies show that in the $d = 9.45$ Å phase they coexist and in analogy with bulk aqueous solutions may be considered as water molecules which are coordinated to the potassium ion forming its hydration shell and free or solventlike water. The water molecules are, however, confined in the galleries of $Cd_{0.75}PS_3K_{0.5}(H_2O)_y$ and hence restricted to move in two dimensions. The negatively charged $Cd_{0.75}PS_3$ layers themselves do not significantly influence the organization of interlamellar water.[5] This system therefore allows one to address the important question as to how confinement affects hydration dynamics and how far it differs from the dynamics in bulk aqueous solutions.

The structure of the host lattice, cadmium thiophosphate, may be viewed as being formed by the stacking of $CdPS_3$ layers, which in turn have been built from edge-sharing CdS_6 and P_2S_6

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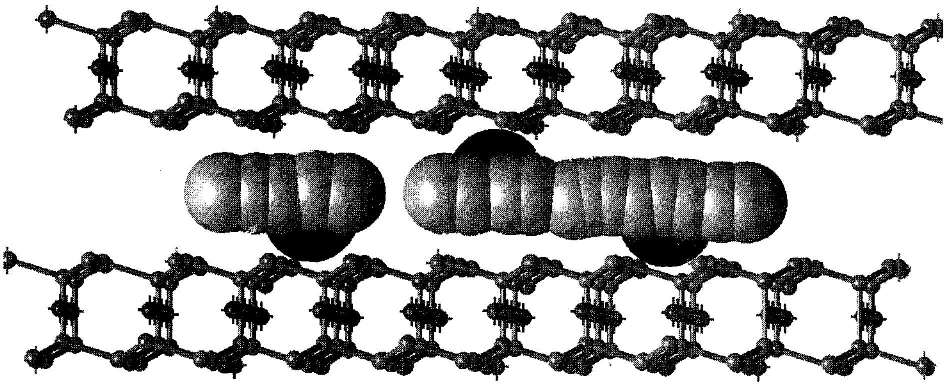

Figure 1. A schematic cartoon of the arrangement of water molecules and potassium ions in the interlamellar region of $Cd_{0.75}PS_3K_{0.5}(H_2O)_{1.2}$. The host lattice is shown in the ball-and-stick representation; cadmium ion vacancies are not shown. The potassium ions (dark circles) are displaced toward the sulfur atoms of the $Cd_{0.75}PS_3$ layer. The water molecules(shaded circles) of the solvation shell form monolayer-thick islands at the center of the van der Waals gap.

polyhedra.[6] On ion-exchange intercalation of hydrated K ions, an equivalent amount of Cd ions are lost from the layer, leaving random immobile vacancies. The projected one-dimensional electron density map constructed from a Fourier transform of the X-ray 00*l* reflections of $Cd_{0.75}PS_3K_{0.5}(H_2O)_y$ indicates that in the interlamellar space, K ions are displaced from the center toward the layer.[7] The K ions are coordinated only on one side by water molecules and on the other side by S atoms of the layer and are consequently immobile, a fact confirmed by conductivity measurements.[7] Within the galleries potassium ions have equal probability of being bound either to the top or bottom $Cd_{0.75}PS_3$ layer with H_2O molecules forming a "mono layer" in the center of the van der Waals gap (Figure 1). Detailed dielectric measurements in the audio frequency range on $Cd_{0.75}PS_3K_{0.5}(H_2O)_y$ have been reported.[5] Two phenomena are observed, an anomalous low-frequency dispersion of the dielectric permittivity at low frequencies and a dielectric relaxation at acoustic frequencies at low temperatures. In addition, a drop in the magnitude of the relative dielectric permittivity on evacuation was also observed. These features have been interpreted by considering the intercalated water molecules as forming a two-dimensional (2D) network. The density of the intercalated water molecules is such that connectivity of this network is below the percolation threshold for a 2D close-packed lattice so that finite clusters are realized. The anomalous dispersion in the permittivity at low frequencies arises from proton-hopping on these clusters, while the dielectric loss arises from the fact that the water molecules possess a permanent dipole moment. The dielectric relaxation in $Cd_{0.75}PS_3K_{0.5}(H_2O)_y$ has relaxation times and activation energies comparable to that in ice. However, in contrast to ice where the dielectric relaxation is almost Debye-like,[8] in $Cd_{0.75}PS_3K_{0.5}(H_2O)_y$ a distribution of relaxation times is observed.[5]

We have used a combination of infrared (IR) spectroscopy and NMR to probe the orientation and motion of interlamellar water in $Cd_{0.75}PS_3K_{0.5}(H_2O)_y$. This material offers the advantage of large lamellar crystals, allowing for orientation-dependent spectroscopic measurements. In the interlamellar region we are able to distinguish "bound" and "free" water molecules by the fact that restriction on the degrees of motion of the former allows only certain orientations of these water molecules with respect to the layer. In contrast to most bulk solutions where rapid exchange makes the bound and free water spectroscopically indistinguishable, confinement in two dimensions causes a dramatic slowing down of this exchange so that the two are observed as distinct spectroscopic species over a wide temperature range.

Experimental Section

Preparation. The host compound cadmium thiophosphate, $CdPS_3$, was prepared from the elements following the procedure reported in ref 9. Cadmium metal powder, phosphorus, and sulfur in stoichiometric amounts were sealed in quartz ampules at 10^{-5} Torr and heated at 650 °C for a period of two weeks. The formation of $CdPS_3$ was confirmed by powder X-ray diffraction; the pattern could be indexed in the *C*2/*m* space group with lattice parameters $a = 6.313$ Å, $b = 10.787$ Å, $c = 6.906$ Å, and $\beta = 108.35°$, similar to that reported in the literature.[6] Single crystals of $CdPS_3$ were grown by chemical vapor transport using excess sulfur as a transporting agent. The charge end of the evacuated ampule was maintained at 650 °C while the cooler end at 600 °C. Platelet-like, transparent crystals of hexagonal morphology were obtained with typical size 6 × 6 × 0.1 mm.[3] The potassium ion-exchange intercalated compound $Cd_{1-x}PS_3K_{2x}(H_2O)_y$ was obtained by stirring $CdPS_3$ powder (without stirring for crystals) in an aqueous solution of 4 M KCl along with a complexing agent EDTA. The pH of the solution was maintained at 10 using a 1 M $K_2CO_3/KHCO_3$ buffer. Cadmium and alkali metal stoichiometries were established by atomic absorption spectrometry after dissolving a weighed amount of the intercalated compound in aqua-regia. Phosphorus and sulfur stoichiometries were not estimated but assumed to be identical to those in the starting host compound. The extent of hydration was determined by thermogravimetry. The stoichiometry of the as-prepared intercalated compound is $Cd_{0.74}PS_3K_{0.52}(H_2O)_{1.2}$. The powder XRD of the intercalated compound could be indexed in the same space group *C*2/*m* as that of the host $CdPS_3$.[6] The lattice parameters of $Cd_{0.75}PS_3K_{0.5}(H_2O)_y$ are $a = 6.722$ Å, $b = 10.344$ Å, c = 10.024 Å, and $\beta = 108.76°$.

Measurements. Powder X-ray diffraction was recorded on a Shimadzu-XD-D1 diffractometer using Cu Kα radiation. The 00*l* reflections of the crystals were recorded after mounting on a sapphire disk using silicone grease. The arrangement also allowed for the recording of the XRD of samples under dynamic vacuum. The crystals of $Cd_{0.75}PS_3K_{0.5}(H_2O)_y$ showed considerable mosaic. The Weissenberg photographs showed spots only for the 00*l* reflections, whereas all other reflections appeared as streaks. In these crystals it is only the *c* axis which can, morphologically, be accurately defined. In the subsequent IR and NMR experiments the orientational dependence referred to, is with respect to the $\vec{C}^*$ axis, the axis normal to the plane of the layers.

Thermogravimetric (TG) measurements were carried out in air using a Cahn 2000 microbalance. The isothermal weight change on evacuation could also be recorded.

Static ^{1}H NMR spectra of powder and single-crystal samples of $Cd_{0.75}PS_3K_{0.5}(H_2O)_y$ were recorded on a Bruker DSX-300 solid-state

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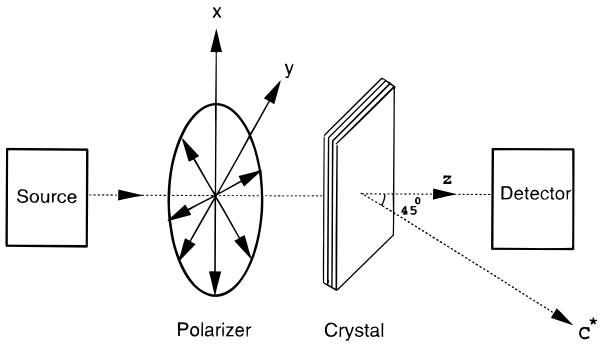
Scheme 1



FT-NMR spectrometer at a Larmor frequency of 300.13 MHz. Temperature variation studies on both single crystal and powder samples were done using the Bruker variable temperature accessory (B-VT 2000). Angular variation of the crystal spectra was studied using an assembly similar to that in ref 10. The ^{1}H NMR spectra were obtained by a Fourier transform of the free induction decay (FID) following a single $\pi/2$ pulse. Spectra were also recorded using the solid echo sequences but the line shapes were found to be essentially the same as those recorded using a single pulse.

IR spectra of crystals of $Cd_{0.75}PS_3K_{0.5}(H_2O)_y$ were recorded in the transmission mode in the spectral range 400−4000 cm^{-1} on a Bruker IFS55 spectrometer equipped with a polarizer accessory. The crystals were mounted on a hollow copper block and cooled using a CTI-Cryogenics closed cycle cryostat. Sample temperature could be varied from 300 to 40 K. The cryostat was evacuated at 10^{-2} Torr to prevent condensation on the crystals. The spectra for different orientations of the electric field vector, $\vec{E}$, of the incident IR with respect to the $\vec{C}$* axis of the crystals (the axis normal to the layers) was obtained using the arrangement shown in Scheme 1. Such an arrangement was necessary because of the platelet-like nature of the crystals of $Cd_{0.75}PS_3K_{0.5}(H_2O)_y$.

In this arrangement the crystals are held in the sample block of the cryostat in such a way that the $\vec{C}$* axis of the crystal is at an angle of 45° with respect to $\vec{z}$, the propagation vector of the incident IR beam, and lying in the *yz* plane. The electric field vector $\vec{E}$ of the incident IR lies in the *xy* plane. In Scheme 1 for an "*x*" polarization of the IR beam the $\vec{E} \perp \vec{C}^*$ spectra is obtained, whereas for the "*y*" polarization the spectra is a combination of the $\vec{E} \parallel \vec{C}^*$ and $\vec{E} \perp \vec{C}^*$ spectra. Since the angle between the $\vec{C}$* and $\vec{z}$, the propagation vector, is known (45°), the individual contributions may be obtained. The intensity for *x* polarization, $I_x(\nu)$, is given by

$$I_x(\nu) = I(\nu,\vec{E} \perp \vec{C}^*)$$

while for *y* polarization

$$I_y(\nu) = \cos^2 45\ I(\nu,\ \vec{E} \perp \vec{C}^*) + \cos^2 45\ I(\nu,\ \vec{E} \parallel \vec{C}^*)$$

For any angle, θ, of the polarization of $\vec{E}$ in the $x-y$ plane

$$I_\theta(\nu) = \cos\theta\ I_x(\nu) + \sin\theta\ I_y(\nu)$$

$$= \cos\theta\ I(\nu,\ \vec{E} \perp \vec{C}^*) + \sin\theta[\cos^2 45\ I(\nu,\ \vec{E} \perp \vec{C}^*) + \cos^2 45\ I(\nu,\ \vec{E} \parallel \vec{C}^*)]$$

Thus, from a measurement of the IR spectrum at two different angles of polarization of the electric field vector, $\vec{E}$, the spectra for $\vec{E} \perp \vec{C}^*$ and $\vec{E} \parallel \vec{C}^*$ can be recovered, and subsequently, the spectrum for any orientation, ϕ, of $\vec{E}$ with respect to $\vec{C}$* can be calculated. The accuracy in the determination of ϕ is ±5°, the uncertainty arising from errors in positioning the $\vec{C}$* axis of the crystals at precisely 45° with respect to the propagation vector of the IR irradiation.

Results

Thermal Analysis and X-ray Diffraction. Thermogravimetric (TG) measurements were carried out on the as-prepared air-dried intercalated compound $Cd_{0.75}PS_3K_{0.5}(H_2O)_y$. The TG recorded in air showed (Figure 2) a weight loss of 9.2% per formula unit of $Cd_{0.75}PS_3K_{0.5}(H_2O)_y$. In this temperature range the host $CdPS_3$ shows no weight loss. The isothermal (300 K) weight loss as a function of time under a dynamic vacuum of 10^{-2} Torr is also shown in Figure 2. The weight loss stabilizes after an hour of pumping. Evacuation at 300 K leads to a loss of about half the number of water molecules from $Cd_{0.75}PS_3K_{0.5}(H_2O)_{1.2}$ (weight loss = 4.3%). This weight loss is reversible; the original weight is regained on exposure of the evacuated sample to the atmosphere.

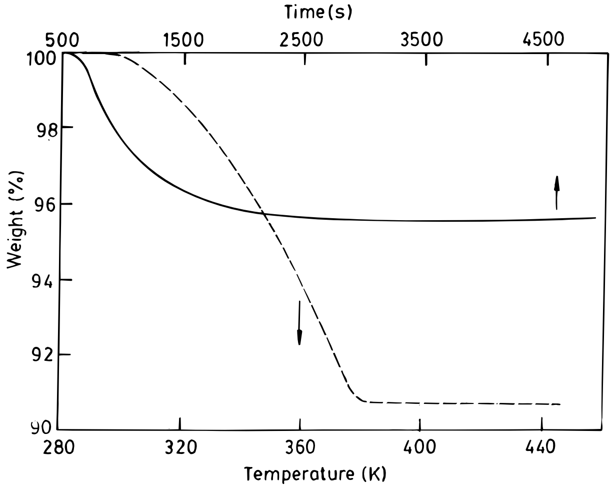


Figure 2. Isothermal (300 K) weight loss of $Cd_{0.75}PS_3K_{0.5}(H_2O)_y$ as a function of the evacuation (10^{-2} Torr) time. The dotted line shows the thermogram (TG) in air.

The effect of pumping on the XRD pattern of $Cd_{0.75}PS_3K_{0.5}(H_2O)_{1.2}$ is shown in Figure 3. The diffraction patterns are for crystals mounted flat on a sapphire disk so that only 00*l* reflections are observed. The interlayer spacing as calculated from the X-ray 00*l* reflections of the as-prepared $Cd_{0.75}PS_3K_{0.5}(H_2O)_{1.2}$ is 9.45 Å corresponding to a lattice expansion on intercalation, Δd, of 2.9 Å. On evacuation a reduction in the interlayer spacing may clearly be seen from the shift in the 2θ values of the 00*l* reflections. The interlayer spacing of 9.25 Å, on evacuation, corresponds to a Δd of 2.7 Å. The XRD of the evacuated powders showed that the *a* and *b* as well as the β lattice parameters are unaffected on evacuation. On exposure to the atmosphere the original phase with d = 9.45 Å is recovered.

Nuclear Magnetic Resonance. The proton NMR spectra of $Cd_{0.75}PS_3K_{0.5}(H_2O)_{1.2}$ powders and crystals were recorded as a function of temperature. Figure 4 shows the ^{1}H NMR powder spectra of the as-prepared $Cd_{0.75}PS_3K_{0.5}(H_2O)_{1.2}$ as a function of temperature. The room temperature spectrum consists of a well-resolved Pake powder pattern and a narrow central component. The separation between the singularities and the shoulders are 32 and 65 kHz, respectively. For different batches of $Cd_{0.75}PS_3K_{0.5}(H_2O)_{1.2}$ there were variations in the relative intensities of the central component with respect to the Pake doublet, but in all samples the positions of the singularities and the shoulders were identical. On cooling there is, at first, a small decrease in the intensity of the central component with an increase in intensity of the Pake doublet. On further cooling, however, the decrease in intensity of the central component is accompanied by the appearance of a new Pake pattern with an inner singularity of 40 kHz (these are marked by arrows in Figure 4). The above-mentioned features are more clearly seen in the spectra of the single crystals. The ^{1}H NMR spectra of an

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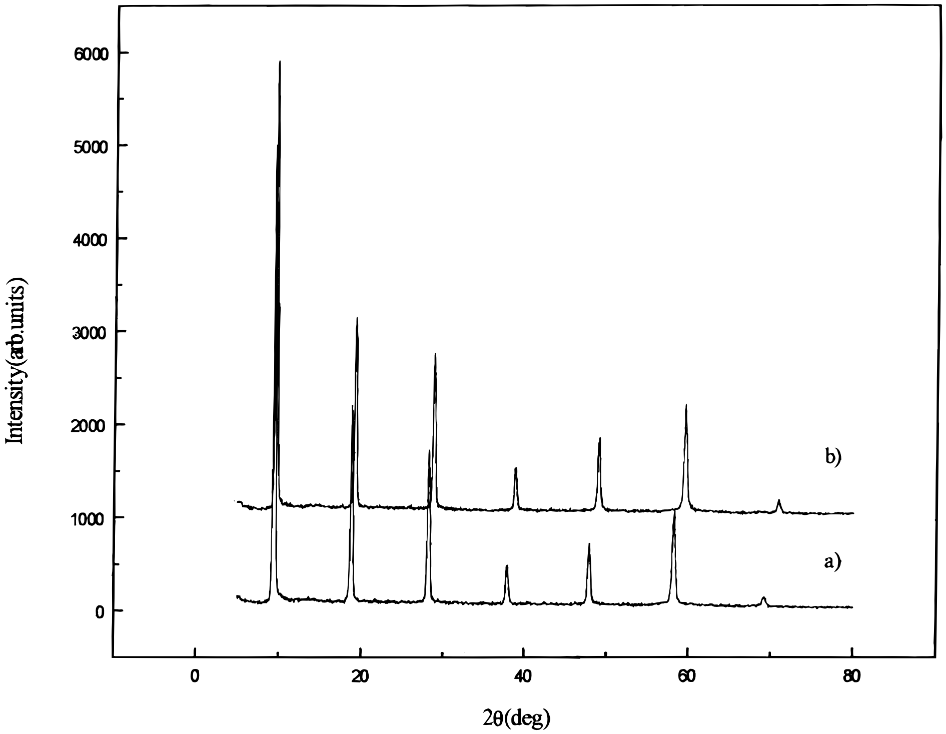

Figure 3. 00*l* reflections in the room temperature XRD pattern of (a) $Cd_{0.75}PS_3K_{0.5}(H_2O)_{1.2}$ and (b) after evacuation at 10^{-2} Torr for 60 min.

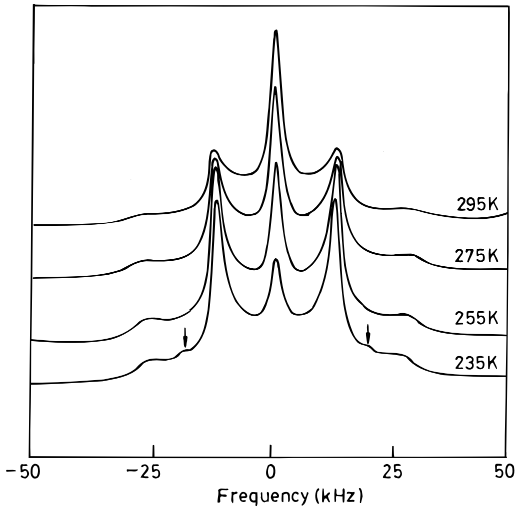

Figure 4. ^1H NMR powder spectra of the as-prepared $Cd_{0.75}PS_3K_{0.5}(H_2O)_{1.2}$ as a function of temperature.

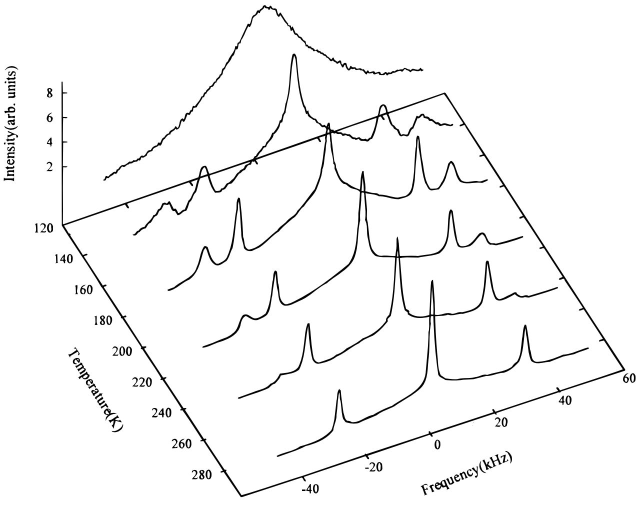

Figure 5. ^1H NMR spectra of $Cd_{0.75}PS_3K_{0.5}(H_2O)_{1.2}$ crystal for $\delta = 0°$ at different temperatures (δ is the angle between the interlamellar normal, $\vec{C}^*$, and the external magnetic field, $\vec{H}_o$.).

oriented crystal of $Cd_{0.75}PS_3K_{0.5}(H_2O)_{1.2}$ were recorded as function of the angle δ between the $\vec{C}^*$, the vector normal to the layers, and $\vec{H}_0$ the external magnetic field. The spectra were also recorded as a function of temperature. Spectra at some typical temperatures are shown in Figure 5. The spectra shown are for $\delta = 0°$. The temperature variation of the ^1H NMR spectra of crystals is broadly similar to that observed in powders (Figure 4); the notable differences being the sharpness and the better resolution available due to the absence of orientational distribution. The spectrum at room temperature has a narrow central component and a well-resolved doublet, observed for all values of δ (Figure 5). The variation of the doublet separation, Δ, as a function of δ at 298 K is shown in Figure 6 and follows the relation $\Delta = 65\ (3\cos^2\delta - 1)/2$ kHz. It may be seen from Figure 5 that, although the intensity of this doublet varies with temperature, neither the position nor separation of the doublet changes with decreasing temperature. The line width (fwhm) shows no variation between 298 and 218 K, remaining constant at 2.3 kHz, and it is only below 218 K that a broadening of the components of the Pake doublet is observed. This feature will henceforth be referred to as the 65 kHz doublet. On cooling there is a decrease in intensity of the narrow central component with the appearance of a second doublet with $\Delta = 80$ kHz at $\delta = 0°$. The separation of this doublet shows a small variation with temperature. At 272 K, when it is just discernible, the separation is 72 kHz. At 218 K the separation is 80 kHz, and there is no further change in separation below this temperature. Although a detailed angular variation for this doublet was not carried out, the values of the doublet separation for $\delta = 0$, 45, and 90° at 218 K, 80, 20, and 40 kHz, respectively, suggest a $(3\cos^2\delta - 1)/2$ angular dependence for this doublet as well, just as in the case of the 65 kHz doublet. The intensity of the 80 kHz doublet increases with decreasing temperature down to

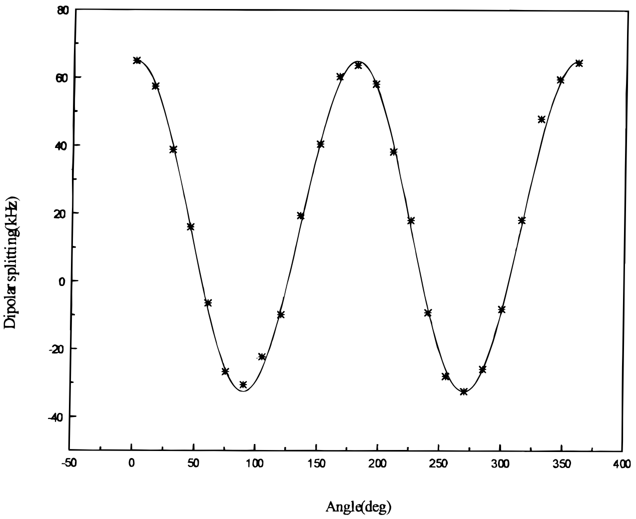

Figure 6. Variation of the separation between the doublets observed in the ^1H NMR spectrum at room temperature as a function of the angle, δ, between, $\vec{C}^*$, the normal to the layers of $Cd_{0.75}PS_3K_{0.5}(H_2O)_{1.2}$ and the external magnetic field, $\vec{H}_o$. The solid line is a plot of the function $\Delta = 65(3\cos^2\delta - 1)/2$.

218 K below which the only change is an increase in line width. This feature will henceforth be referred to as the 80 kHz doublet. The other notable feature is the change in the central component with temperature. At room temperature it consists of a single Lorentzian component; however, on cooling its intensity decreases, and a broad Gaussian-like component develops whose contribution increases with decreasing temperature. All four features—the 65 kHz doublet, the 80 kHz doublet, the narrow Lorentzian component, and the broad Gaussian-like central component— may clearly be seen in the spectra at 218 K. Below 180 K there is a broadening in the line width of both doublets, and by 170 K there is a merging of these features with the broad central Gaussian component.

The effect of evacuation on the ^1H NMR spectra of $Cd_{0.75}PS_3K_{0.5}(H_2O)_{1.2}$ has also been studied. It was not possible to carry out in situ evacuation studies, and the NMR spectra were recorded on sealed powders, evacuated at 10^{-2} Torr for different periods of time. The room temperature spectra for different periods of evacuation time are shown in Figure 7. It may be seen that on evacuation the intensity of the central component drops rapidly and is nearly absent after about an hours pumping. The other interesting feature is that the Pake powder pattern after evacuation is different. Figure 7a shows the spectrum of the as-prepared $Cd_{0.75}PS_3K_{0.5}(H_2O)_{1.2}$. The Pake powder pattern has an inner singularity separation of 32 kHz with shoulders separated by 65 kHz. After an hour of evacuation (Figure 7d), the separation between the inner singularities of the Pake pattern is 40 kHz and the outer shoulders 80 kHz (The spectra are not typical Pake powder patterns because the powders of $Cd_{0.75}PS_3K_{0.5}(H_2O)_{1.2}$ were packed prior to evacuation leading to a pronounced preferred orientation of the flaky crystallites). Evacuation thus leads not only to a decrease in intensity of the narrow central component but also to the disappearance of the 65 kHz doublet with the appearance of the 80 kHz doublet. The spectrum after 5 min of evacuation shows the presence of both the 65 and 80 kHz doublets.

Broad Pake doubletlike spectra usually in association with a narrow central component have been reported in a number of hydrated layered intercalates especially clays,[11] layered hydrated chalcogenides,[12] and thiophosphates.[13] The broad component has usually been assigned to water molecules in the immediate vicinity of the alkali ion (i.e., the hydration shell), while the narrow component, to isotropically tumbling water molecules which lie outside the shell or to proton exchange.

The 65 kHz Pake doublet as well as the 80 kHz doublet correlate fairly well with the spectra expected of a solid in which nuclear spins occur in isolated pairs. In the case of isolated water molecules it is well-known[14] that intramolecular dipolar interaction gives rise to a doublet with separation, $\Delta = \alpha(3\cos^2\delta - 1)/2$ where $\alpha = 3\gamma^2\hbar/r^3_{H-H}$ and θ is the angle between the inter-proton vector and the magnetic field and r_{H-H} the inter-proton distance. For r_{H-H} of 1.58 Å, corresponding to water molecules in their equilibrium geometry, $\alpha_{equil} = 91$ kHz. We shall at first consider the 65 kHz doublet. Assuming that the water molecules maintain their equilibrium geometry even after intercalation, the observed dipolar splitting would require an interpretation based on the motion of water molecules which partially averages dipolar interactions.

The model proposed here is one in which the $\vec{C}_2$ axes of the water molecules in the hydration shell rotate about the $\vec{C}^*$ axis at a rate much greater than the frequency corresponding to the dipolar splitting ($\tau \ll 10^{-5}$ s). The Legendre polynomial $P_2(cos\ \theta)$ must then be averaged for this rotation such that $P_2(cos\ \theta) = P_2(cos\ \delta)P_2(cos\ \beta)$ where β is the angle between the $\vec{C}^*$ axis and the H−H vector and δ, the angle between the $\vec{C}^*$ axis and $\vec{H}_o$, is the experimental variable (The definition of the angles is indicated in Figure 8). The NMR spectra would therefore consist of two lines with separation

$$\Delta = \alpha_{equil}((3\cos^2\delta - 1)/2)((3\cos^2\beta - 1)/2) \qquad (1)$$

The experimentally observed angular dependence $\Delta = 65(3\cos^2\delta - 1)/2$ then requires that β in eq 1 be 26°. Correspondingly, ψ, the angle between the $\vec{C}_2$ axis of the water molecule and the $\vec{C}^*$ axis, will have a value of 64°.

This rotational motion could correspond to any one of the following: (i) a collective motion of the hydration shell as a whole, that is, the water molecules rotate about an axis parallel to the $\vec{C}^*$ axis and passing through the K ion, (ii) a motion involving 60° or 120° jumps of the water molecules about the K ion, or (iii) a spinning motion of individual water molecules in which the $\vec{C}_2$ axis rotates about an axis parallel to $\vec{C}^*$ and passes through it as shown in Figure 8. All of these three models would be able to account for the observed NMR results. A collective motion similar to the possibility (i) has been invoked for water molecules in the hydration shell of the alkali ion within the galleries of mica type silicates.[11] In $Cd_{0.75}PS_3K_{0.5}(H_2O)_{1.2}$, however, it is difficult to reconcile such a rotational motion involving the hydration shell as a whole with the fact that the stoichiometric ratio of K to coordinated H_2O requires sharing of water molecules between neighboring K ions. The TG experiments showed that about half the water is lost on mild evacuation which leaves the above ratio as 1:1.2, implying that coordinated water molecules are part of the hydration shell of more than one K ion. Similar considerations would also apply to the rotational jump model (possibility (ii)) making such a motion unlikely. The large number of bridging water molecules

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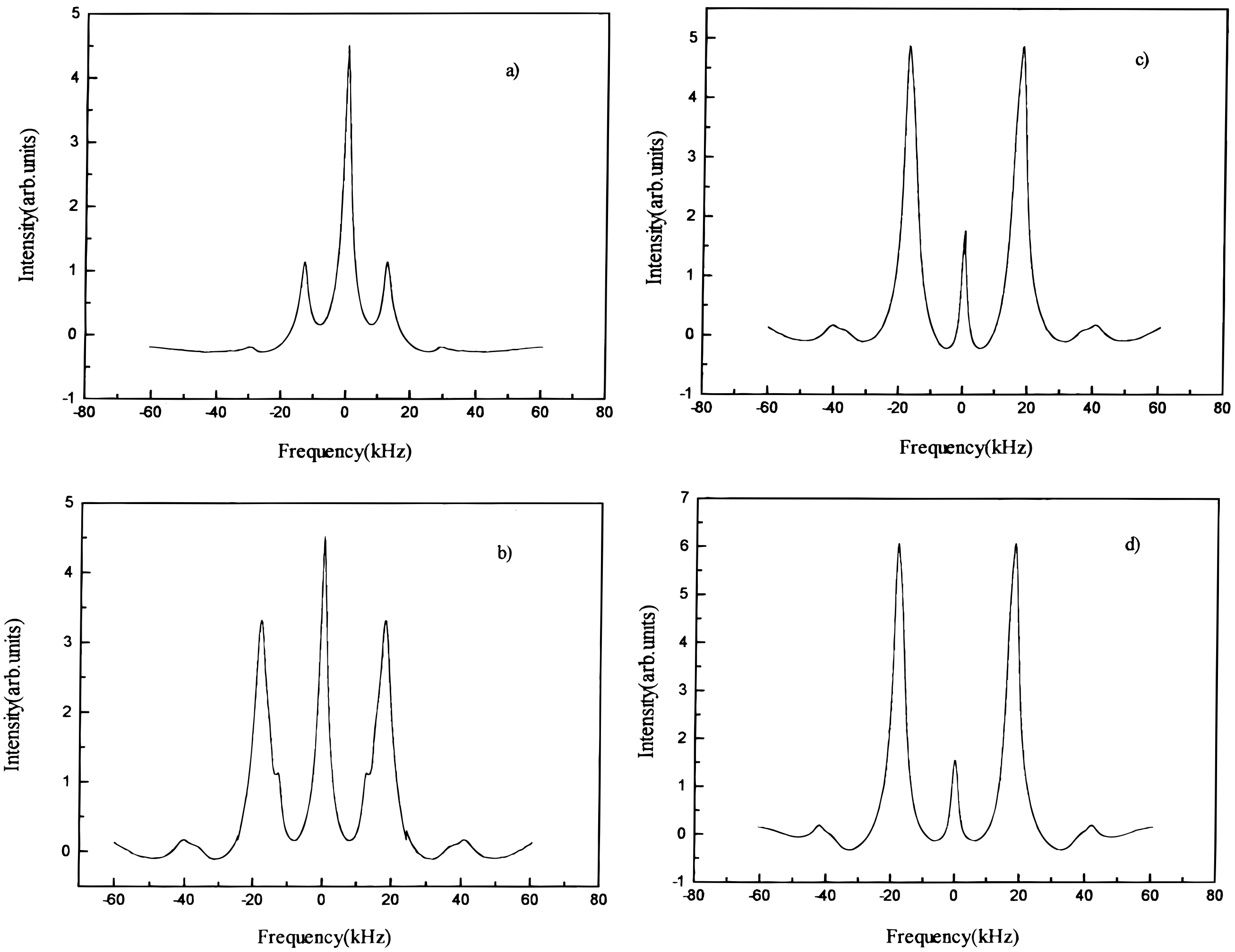

Figure 7. ^{1}H NMR spectra of $Cd_{0.75}PS_3K_{0.5}(H_2O)_{1.2}$ powder for different periods of evacuation time: (a) unevacuated, (b) 5 min, (c) 15 min, (d) 60 min.

would favor a spinning motion of individual water molecules (possibility (iii)) since it would allow the water molecules to maintain an identical time averaged orientation toward neighboring K ions (Figure 8) while at the same time satisfying the requirements for the observed ^{1}H doublet splitting.

Additional degrees of freedom for the interlamellar water can be ruled out since it would cause further averaging of the dipolar interaction. If, for example, the H−H vector of the water molecule were to precess freely about the $\vec{C}_2$ axis, the maximum possible doublet splitting is 45 kHz, half of 91 kHz expected for a static water proton pair, compared to the observed value of 65 kHz.

Using a similar argument the 80 kHz doublet may be assigned to water molecules for which the $\vec{C}_2$ axis is oriented at an angle of 74° to the $\vec{C}^*$ axis and rotates rapidly about it. For these water molecules, too, additional degrees of freedom can be ruled out.

The validity of eq 1 rests on the assumption that the H−H vector of the water molecules undergo rapid rotation ($\tau \ll 10^{-5}$ s) around the $\vec{C}^*$ axis. The intramolecular dipolar splitting, thus provides an internal probe for the motion of the water molecules as well as their orientation. The fact that the dipolar splitting does not change with temperature implies from the above analysis that the orientations of the water molecules do not change, and the assumption of fast rotation of the H−H vector about the $\vec{C}^*$ holds good in the range of temperatures investigated.

The narrow central component is primarily due to isotropically tumbling water and the fact the intensity drops rapidly on evacuation indicates that these are more loosely bound as compared to the water molecules contributing to the Pake doublets. The reason as to why the intensity of the 65 kHz doublet too decreases on evacuation will be discussed in a subsequent section. A contribution from proton hopping to the central component cannot, however, be ruled out since this process, too, could average out dipolar interactions leading to a narrow Lorentzian line. On cooling, the intensity of the narrow component decreases while the intensity, at first, for the 65 kHz and later the 80 kHz doublet increases suggesting that at least some of the loosely bound water is now more strongly held and in the process, loses some of its degrees of freedom. In addition, the growth of the broad, Gaussian-like central component indicates freezing of the motion of these isotropically tumbling molecules in random orientations. This freezing occurs over a broad temperature range as expected for a two-dimensional system.[15]

IR Spectroscopy. The mid-IR spectra of $Cd_{0.75}PS_3K_{0.5}(H_2O)_{1.2}$ crystals were recorded in the transmission mode. Crystals, rather than powders, were preferred to minimize the contribution of water on the external surface and micropores. The room temperature IR spectrum recorded with the electric

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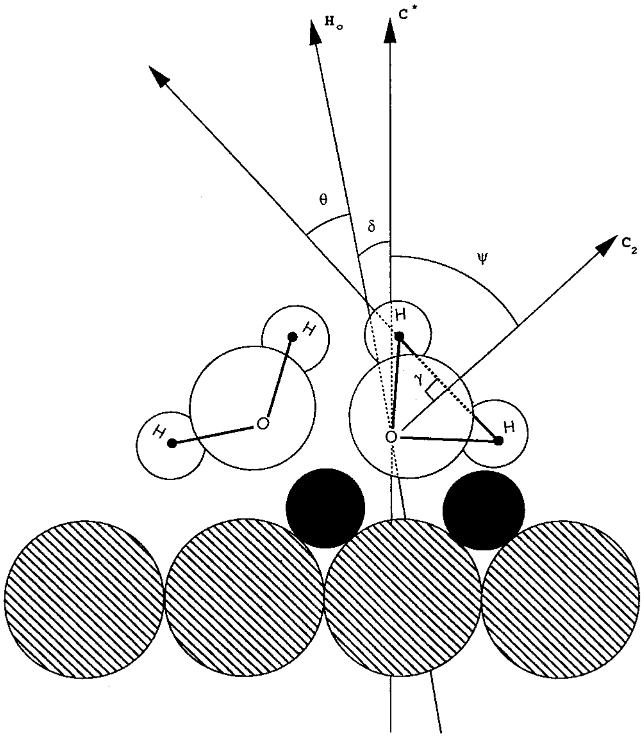

Figure 8. Definition of the angles used in the analysis of the ^{1}H NMR spectra of $Cd_{0.75}PS_3K_{0.5}(H_2O)_{1.2}$. The potassium ion is shown as the filled circle, and sulfur atoms of the layer, as dashed circles.

field vector of the incident radiation perpendicular to the interlayer normal, $\vec{E} \perp \vec{C}^*$, is shown in Figure 9a. The spectrum shows a broad band at 3500 cm^{-1} and an intense band at 1600 cm^{-1}, which in comparison with the vibrational frequencies of water[16] may be assigned to the stretching (symmetric (ν_1) and asymmetric (ν_3)) and bending (ν_2) modes, respectively, of interlamellar water. The vibrational modes of the host lattice appear below 1000 cm^{-1}.[17] The spectrum of the as-prepared $Cd_{0.75}PS_3K_{0.5}(H_2O)_{1.2}$ in the mid-IR region is similar to that reported for water in clays[18] and the broad feature at 3500 cm^{-1} typical of hydrogen-bonded water. Figure 9b shows the spectrum of the same crystal after evacuation at 10^{-2} Torr at 300 K for a period of 10 min. It may be recalled, from the previous section, that evacuation leads to a partial loss of water and a contraction of the lattice by 0.2 Å. (An evacuation time of 10 min was chosen so that the conditions would be as close to those for the sample whose NMR is shown in Figure 7b while at the same time prevent condensation on initial cooling.) Evacuation lifts the broad envelope centered at 3500 cm^{-1}, and resolved features at 3450 cm^{-1} and 3200 cm^{-1} are observed. In addition the feature at 1600 cm^{-1} is considerably narrowed and shows a splitting. These features are more clearly seen on cooling. Figure 9c shows the spectrum ($\vec{E} \perp \vec{C}^*$) of the evacuated crystal (10^{-2} Torr, 10 min) at 15 K. The spectral features are sharp and almost gas-phase-like, the main features being a well-resolved doublet at (1580 and 1620 cm^{-1}) and bands at 3200 cm^{-1} and 3400 cm^{-1} both of which show well-resolved features.

The splitting of the vibrational bands of the interlamellar water (Figure 9c) suggests that there are more than one type of interlamellar water, but the splitting could also arise from intermolecular interactions between similar or dissimilar water molecules.[16] The latter interaction is the origin of the correlation or factor group splitting commonly observed in the solid state.[19] The fact that in the bending region one of the bands (1580 cm^{-1}) appears at a frequency lower than that for the vibrational bending mode of water in the gas phase (1595 cm^{-1})[20] suggests that the origin of the splitting in this region is probably due to intermolecular interactions.

The bending mode frequencies of water unlike the stretching modes are, however, not too sensitive to the environment,[19] and consequently the above observations do not exclude the presence of more than one type of interlamellar water. The feature at 3200 cm^{-1} is due to the symmetric stretching mode (ν_1). Assignment of features in this region is not straightforward because of possible Fermi resonance between the first overtone of the bending mode ($2\nu_2$) and the symmetric stretch (ν_1). This has been commonly observed in water. A characteristic feature of the Fermi resonance in water is that it can give rise to unusual band shapes.[21] In situations where a broad distribution of fundamental transitions interacts with a narrow overtone band, sharp holes termed "Evans holes" are produced which appear as transmission spikes in the IR spectra or intensity spikes in the Raman.[21a,b] The sharp transmission spike at 3200 cm^{-1} (marked with an arrow) in the low-temperature spectrum of $Cd_{0.75}PS_3K_{0.5}(H_2O)_{1.2}$ which appears at $2\nu_2$ may be assigned to such a feature. Similar features have been observed in the IR spectrum of inorganic hydrates and have been used as evidence for the Fermi resonance interaction between ν_1 and $2\nu_2$.[16,21]

In the asymmetric stretch region (~3400 cm^{-1}) multiple features are clearly seen. These cannot all be accounted by intermolecular interactions and, therefore, suggest the presence of more than one type of water in the galleries of the partially evacuated $Cd_{0.75}PS_3K_{0.5}(H_2O)_{1.2}$. The assignment and interpretation of these features is made easier by examining the IR spectra for different orientations of the electric field vector $\vec{E}$ of the incident IR radiation with respect to the $\vec{C}^*$ axis of the crystal. Figure 10a shows the IR absorption spectrum for evacuated crystals of $Cd_{0.75}PS_3K_{0.5}(H_2O)_{1.2}$ at 15 K for different orientations of the $\vec{C}^*$ axis with respect to $\vec{E}$. It may be seen that orientational dependence of the four bands, 3576, 3534, 3454, and 3417 cm^{-1}, are quite explicit and different. The orientational dependence has been more quantitatively examined by plotting $I(\phi)/I(\phi + 90°)$ as a function of ϕ for the four bands (Figure 10b); ϕ is the angle between $\vec{E}$ and $\vec{C}^*$ and $I(\phi)$ the absorption intensity of the vibrational mode for an orientation with angle ϕ. The function would peak for a value of ϕ at which $\vec{E}$ is parallel to the transition dipole moment vector of the vibrational mode. Figure 10b shows that the orientational dependence behave in pairs; the bands at 3576 and 3534 both peak at $\phi = 35 \pm 5°$, while the 3454 and 3417 cm^{-1} bands peak at $10 \pm 5°$. It may be noted that the separation of peaks for both pairs is ~40 cm^{-1} which is similar in magnitude to the doublet separation in the bending region and suggests a common origin viz. intermolecular interaction. The orientational dependence of the bands indicate that in the evacuated $Cd_{0.75}PS_3K_{0.5}(H_2O)_{1.2}$ there are two types of interlamellar water molecules which differ in their orientation with respect to the $\vec{C}^*$ axis. For the asymmetric stretching mode of water the transition dipole moment is perpendicular to the $\vec{C}_2$ symmetry axis, and therefore

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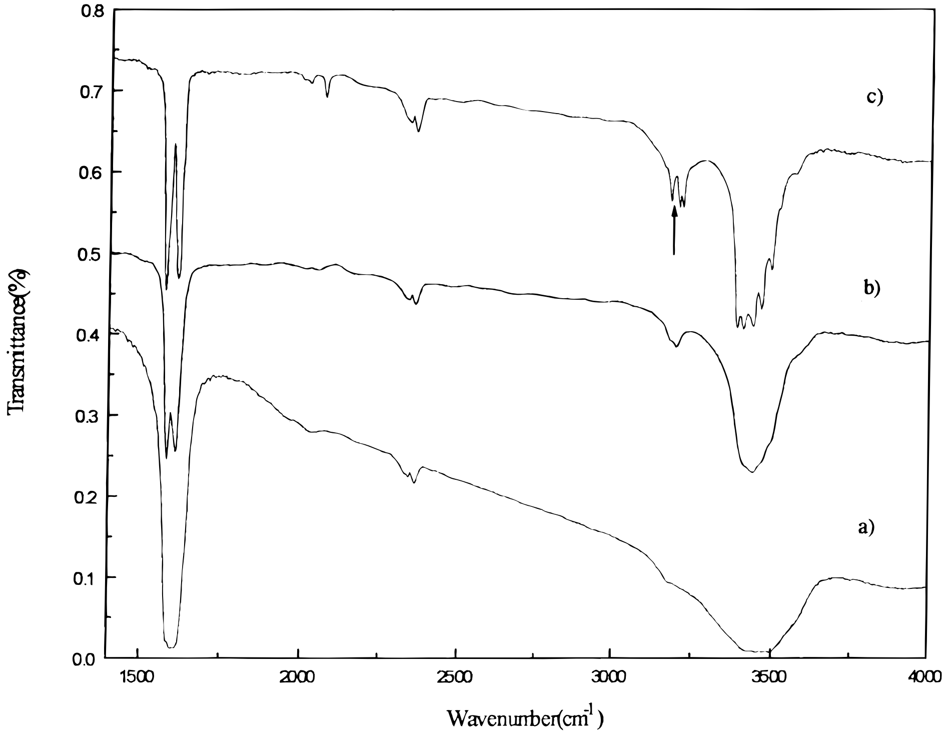

Figure 9. (a) The room temperature IR spectrum of $Cd_{0.75}PS_3K_{0.5}(H_2O)_{1.2}$ crystal. The electric field vector of the incident radiation is perpendicular to the interlamellar normal, $\vec{E} \perp \vec{C}^*$. (b) IR spectrum ($\vec{E} \perp \vec{C}^*$) of the crystal after evacuation at 10^{-2} Torr at room temperature for a period of 10 min. (c) IR spectrum ($\vec{E} \perp \vec{C}^*$) of the evacuated crystal (10^{-2} Torr, 10 min) at 15 K.

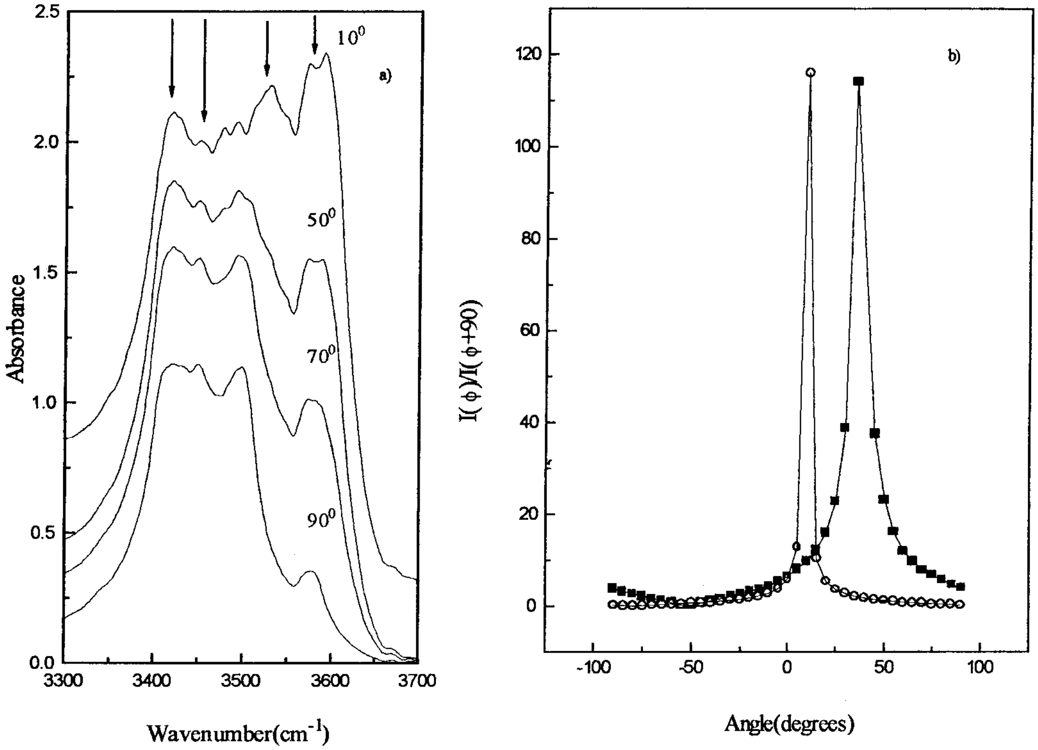

Figure 10. (a) IR absorption spectra for evacuated crystals of $Cd_{0.75}PS_3K_{0.5}(H_2O)_{1.2}$ at 15 K for different values of, ϕ, the angle between the electric field vector, $\vec{E}$, and the interlamellar normal, $\vec{C}^*$. (b) The dichroic ratio $[I(\phi)/I(\phi + 90°)]$ as a function of ϕ, the angle between $\vec{E}$ and $\vec{C}^*$. The ratio is plotted for the bands in the asymmetric stretch region; 3576, 3534, 3454, and 3417 cm^{-1}. $I(\phi)$ is the absorption intensity of the vibrational mode for an orientation with angle ϕ.

the orientation of the $\vec{C}_2$ axes of the two types of interlamellar water are 55 ± 5° and 80 ± 5°, respectively, with respect to the $\vec{C}^*$ axis. These values are in good agreement with the values obtained from the analysis of the NMR Pake doublet pattern, 74° and 64°. These results provide additional evidence for the validity of the interpretation of the NMR spectra. The reason as to why the asymmetric stretching frequencies for the two orientations are different will be deferred to a later section.

Discussion

The IR and NMR results are in good agreement with each other as well as the observation of weight loss and lattice

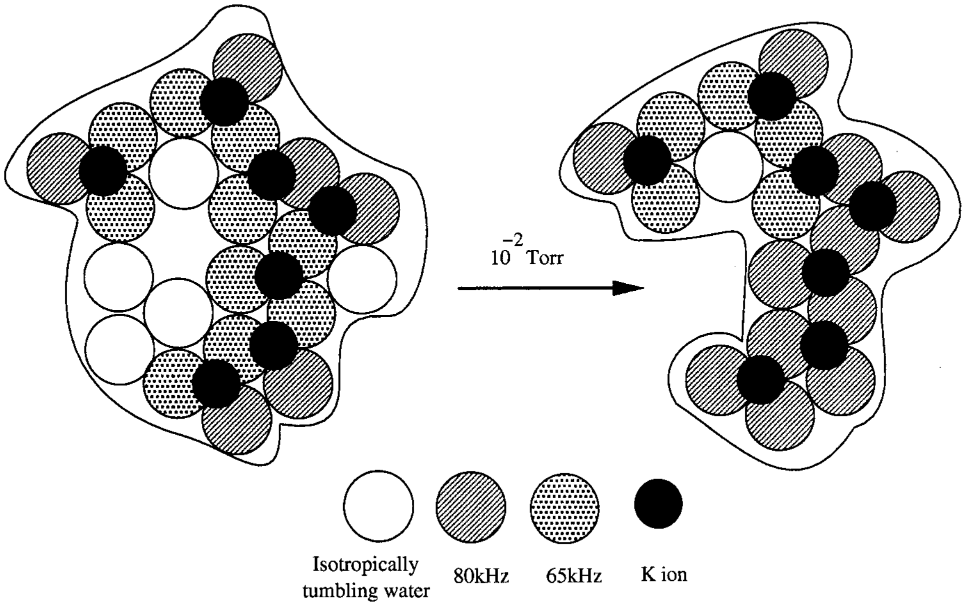

Figure 11. A possible scenario of the effect of evacuation on the interlamellar water in $Cd_{0.75}PS_3K_{0.5}(H_2O)_{1.2}$. The cartoon depicts a view down the $\vec{C}^*$ axis. The two types of coordinated water are shown as circles shaded differently, dotted (65 kHz) and dashed (80 kHz). The isotropically rotating water are shown as empty circles. The potassium ions, filled circles, could lie either above or below the plane of the water molecules.

contraction on evacuation of $Cd_{0.75}PS_3K_{0.5}(H_2O)_{1.2}$. On evacuation ($10^{-2}$ Torr) at ambient temperatures, close to half of the interlamellar water molecules are lost. This loss manifests in the NMR spectra as a decrease in the contribution of the isotropically tumbling water. (The contribution of the 65 kHz doublet, too, decreases, but we shall comment on this at a later stage.) The contraction in the X-ray lattice expansion value of Δd from 2.9 Å to 2.7 Å, a value less than the van der Waals diameter of H_2O, is a consequence of the loss of this freely tumbling water. IR spectroscopy indicates that these less tightly bound water molecules are hydrogen-bonded probably forming a 2D network as suggested by earlier dielectric studies.[5]

The NMR spectra of the as-prepared $Cd_{0.75}PS_3K_{0.5}(H_2O)_{1.2}$ with $\Delta d = 2.9$ Å (Figures 4 and 5) show that two types of water, distinguishable by their differing degrees of freedom, coexist. As already mentioned, the isotropically tumbling water is responsible for the central peak. The more strongly bound water molecules have their $\vec{C}_2$ symmetry axis at a fixed orientation, 64°, with respect to the interlamellar normal, $\vec{C}^*$, and the only motion allowed is a rapid rotation of the H−H vector of the water molecules about the $\vec{C}^*$ axis. The observation of a second Pake doublet with a different splitting but similar angular variation, on cooling as well as on evacuation, requires that the orientation of the $\vec{C}_2$ axis for some of the water molecules be 74° with respect to the $\vec{C}^*$ axis. Supporting evidence for two different orientations for the interlamellar water comes from the orientation-dependent IR spectra. The values of 55 ± 5° and 80 ± 5° for the angles between the $\vec{C}_2$ symmetry axis and the $\vec{C}^*$ axis obtained from the IR dichroic ratios are in reasonable agreement with the values obtained from the NMR measurements. The value of 64° for ψ is similar to that reported in other hydrated layered intercalates.[11,13] In the corresponding Na ion compound,[13] $Cd_{0.75}PS_3Na_{0.5}(H_2O)_2$, where Na ions occupy the octahedral sites of a close-packed bilayer array of water molecules the value of ψ is 67.8°, while in the mica-type silicates[11] in which the alkali ions have a similar octahedral coordination the reported value of ψ from ^1H NMR measurements is 65°. These values have been interpreted as indicating a trigonal compression of the octahedra. In comparison the K ions in $Cd_{0.75}PS_3K_{0.5}(H_2O)_{1.2}$ are coordinated only on one side to water molecules. The vibrational frequencies and line widths in the IR spectra (Figure 9) indicate that the coordinated water molecules do not interact with the layers and hence the angle ψ remains essentially unchanged from that for the bilayer compounds.

In analogy with bulk aqueous solutions we can assign the water molecules with restricted degrees of freedom as those belonging to the hydration shell of the potassium ion and the less tightly bound, isotropically tumbling, water as a 2D "bulk" or "solventlike" water. Such a model would still require an explanation as to why the water molecules in the hydration shell have two different orientations with respect to the $\vec{C}^*$ axis. The fact that only the 65 kHz doublet is seen in the room temperature NMR spectrum of $Cd_{0.75}PS_3K_{0.5}(H_2O)_{1.2}$ with the 80 kHz doublet appearing only on cooling might suggest that the water molecules contributing to the 80 kHz doublet are part of a second hydration shell of a potassium ion. Such a possibility may, however, be clearly ruled out since the NMR spectra on evacuation at room temperature shows a decrease in the intensity of the 65 kHz doublet with the appearance of the 80 kHz doublet, so much so that after an evacuation of 1 h only the 80 kHz doublet is seen. A more likely explanation is that, since the interlamellar water molecules do not form a continuous sheet but are broken up into 2D islands (or clusters), the water molecules of a hydration shell at the perimeter of such an island would have a different orientation from those within the island (An island consists of both bulklike water as well as coordinated water molecules.). In such a model the 80 kHz doublet arises from oriented water molecules at the perimeter of an island, while the 65 kHz doublet are due to those within the island. Alternatively, the 65 kHz doublet could originate from coordinated water molecules which have isotropically tumbling or solventlike water as neighbors. The loss of the isotropically tumbling water on evacuation leads to an increase in the ratio of the bound water molecules at the perimeter to bound water molecules within an island. This manifests in the ^1H NMR spectra as an increase in the intensity of the 80 kHz doublet at the expense of the intensity of the 65 kHz doublet. A schematic cartoon for such a process is shown in Figure 11. Support for such an assignment comes from the values of the asymmetric stretching frequencies in the IR spectra. The stretching frequencies of the water molecules oriented at an angle of 74° with respect to the $\vec{C}^*$ axis (3576 cm^{-1}) are ~100 cm^{-1} higher than those oriented at an angle 64° with respect to the $\vec{C}^*$ axis (3454 cm^{-1}). It is known that association among water molecules causes a red-shift in the stretching frequencies.[22] Therefore, an assignment of the water molecules oriented at 74° with respect to the $\vec{C}^*$ axis at the perimeter could explain the difference in the stretching frequencies. The model, however, cannot offer an explanation as to why the presence of neighboring water molecules causes a "relaxation" in the orientation of a coordinated water molecule.

After the temperature is lowered, the isotropic tumbling motion of the free or solventlike water freezes in random orientation, giving rise to the broad Gaussian-like central component. The fact that the contribution of the broad component increases with decreasing temperature while the intensity of the narrow Lorentzian-like component decreases suggests a distribution of correlation times for the freezing of the tumbling motion. This is expected since in two dimensions a thermodynamic freezing temperature is not defined.[15] The formation of this "2D ice" due to the freezing of motions of the solventlike interlamellar water would also explain the origin of the dielectric relaxation at acoustic frequencies observed at low temperatures in the as-prepared $Cd_{0.75}PS_3K_{0.5}(H_2O)_{1.2}$ with relaxation times and activation energies similar to that for the dielectric relaxation at acoustic frequencies in ice.[5] Unlike the relaxation in ice which has an almost Debye-like relaxation, the relaxation in $Cd_{0.75}PS_3K_{0.5}(H_2O)_{1.2}$ exhibits a symmetric distribution(Cole−Cole) of relaxation times.[5]

The most remarkable feature of the NMR spectra is the temperature dependence, or rather the lack of it, in the position and the values of the Pake doublet separation. This, of course, requires that the orientation of the bound water molecules do not change, and the assumption of fast rotation of their H−H vectors about the $\vec{C}^*$ axis holds good over the entire range of temperatures investigated. More importantly, in the context of the above model for the interlamellar water it implies that exchange between the free or solventlike water and coordinated water molecules in the hydration shell of the K ion is extremely slow on NMR time scales. Exchange between the free solventlike water with water of the hydration shell at rates faster than the intramolecular dipolar interactions would destroy the Pake doublet. If the rates were comparable, then a broadening of the components of the doublet as well as of the central line would be observed.[14] In addition a decrease in the doublet separation due to a shift in the position of the components of the doublet toward the center may also be observed.[14] It may be seen from the NMR spectra of Figures 4 and 5 that position and line width of the components of the 65 kHz doublet show no variation in the temperature range studied, indicating that exchange between the water molecules contributing to the doublet and the free tumbling water molecules responsible for the central line is much slower than 65 kHz. Fast exchange between water molecules contributing to the 65 kHz and 80 kHz doublets may also be ruled out by a similar argument. The intensities of the Pake doublets and the central component in the ^1H NMR spectra at various temperatures, therefore, reflect on the near-equilibrium population of the various species contributing to these features (provided, of course, that the T_1's are comparable).

NMR has been widely used to study the static and dynamic structure of hydrated metal ions.[23] Depending on the metal ion, water molecules in the coordination sphere can, in principle, be distinguished from those in the bulk from their differing ^1H and ^{17}O chemical shifts.[24] This has been demonstrated for the larger, inert metal ions where large diamagnetic or paramagnetic shifts can be expected. In such situations coordination numbers may also be determined from an integration of the NMR intensities.[23] In most cases, however, rapid exchange between coordinated and solventlike water makes spectroscopic distinction between them impossible. Even in situations where they may be distinguished by NMR the temperature range over which it is possible is limited to low temperatures. In aqueous solutions this is usually achieved by adding organic solvents so that the freezing point of the solution becomes low enough to slow the rate of exchange.[24] In contrast for the two-dimensionally confined water molecules in layered $Cd_{0.75}PS_3K_{0.5}(H_2O)_{1.2}$ we are able to distinguish between bound or coordinated water and free or solventlike water, spectroscopically over a wide temperature range. The obvious question that arises is why in the "flatland"[25] of the interlamellar region the rates of exchange between coordinated and free water are so slow. In bulk aqueous solutions the residence time of water molecules in the hydration shell of monovalent cations is typically ~10^{-11} s[4b,26] (see also Figure 1 in ref 27). A possible reason is that confinement in two dimensions inhibits formation of intermediate or transition states which involve an increase in the coordination number of the K ion. Solvation shell exchange reactions are known to proceed via a nucleophilic mechanism that may involve an expansion of the coordination shell of the metal ion.[24] The $Cd_{0.75}PS_3$ layers are rigid, and therefore any mechanism which invokes an intermediate state with increased volume of the hydration shell (positive ΔV) would require a localized dilation of the interlamellar region which is highly unlikely. Our results are probably the first observation of the effect of confinement in two dimensions on solvation shell exchange rates. We believe that our observations are universal, and similar effects should be observed for confined aqueous solutions irrespective of whether the rigid confining environment is an inorganic layered solid or a micro- or mesoporous solid or even biological systems.

Conclusions

A combination of IR and NMR spectroscopy has been used to probe the orientation and motion of interlamellar water in $Cd_{0.75}PS_3K_{0.5}(H_2O)_{1.2}$ prepared by the ion-exchange intercalation reaction of layered $CdPS_3$. In this compound potassium ions reside in the gallery; they are displaced from the center toward the layers and are immobile, while the water molecules form a monolayer. The number of interlamellar water molecules are inadequate to form a continuous sheet and consequently are broken up in 2D islands or clusters. Evacuation of $Cd_{0.75}PS_3K_{0.5}(H_2O)_{1.2}$ at 10^{-2} Torr leads to a partial loss of water (about 50%), accompanied by small contraction of the interlayer distance. The Δd value decreases from 2.9 to 2.7 Å, suggesting that more than one type of water may be present in the galleries.

IR and NMR are able to distinguish two types of interlamellar water in $Cd_{0.75}PS_3K_{0.5}(H_2O)_{1.2}$ by their differing degrees of freedom. An isotropically tumbling, solventlike water which forms a loosely bound hydrogen-bonded network and a more tightly bound water which is coordinated to the K ion forming a part of its hydration shell. The latter water have their $\vec{C}_2$

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symmetry axes at a fixed orientation with respect to the interlamellar normal and have restricted degrees of rotational freedom and hence exhibit a well-defined dipolar split doublet in the ^{1}H NMR.

A remarkable feature of the ^{1}H NMR of $Cd_{0.75}PS_3K_{0.5}(H_2O)_{1.2}$ is the absence of any significant variation in the position or separation of the Pake doublet with temperature. The sharpness of the features of the ^{1}H spectrum is also quite informative. The obvious conclusion is that the rate of exchange between the 2D bulk or solventlike water and the coordinated water of the hydration shell is extremely slow as compared to the strength of the dipolar interactions. Consequently, the two show up as distinct spectroscopic species over the entire temperature range studied. The results are interesting since in most NMR studies on bulk aqueous solutions spectroscopic distinction between bulk and coordinated water, for example on the basis of chemical shift differences, is limited to a narrow temperature range. It is suggested that these slow exchange rates in $Cd_{0.75}PS_3K_{0.5}(H_2O)_{1.2}$ could arise because the rigid confining environment of the layers inhibits the formation of an intermediate or of transition states which may involve an expansion of the hydration shell around the potassium ion.

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