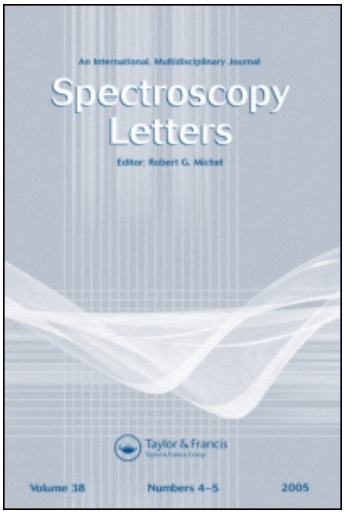

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The Vibrational Spectra of Brushite, $CaHPO_4 \cdot 2H_2O$

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THE VIBRATIONAL SPECTRA OF BRUSHITE, $CaHPO_4 \cdot 2H_2O$

KEY WORDS: Dicalcium phosphate dihydrate, brushite, DCPH, calcium phosphates, Raman spectra, infrared spectra

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INTRODUCTION

Brushite ($CaHPO_4 \cdot 2H_2O$) has been extensively studied using X-ray[1),2),3),4)] and infrared techniques[5),6),7),8)]. However, no Raman data have been reported in the literature for this phase. In this paper, we will present the nonpolarized and

polarized Raman spectra, and interpret them along with infrared spectra using factor group analysis.

EXPERIMENTAL

Brushite powder was prepared by the method of Tovborg-Jensen and Rathlev[9]. A solution containing 0.50 moles of $Na_2HPO_4 \cdot 8H_2O$ and 0.37 moles of KH_2PO_4 per liter of water, and a solution containing 0.50 moles of $CaCl_2 \cdot 6H_2O$ were prepared. These solutions were added simultaneously at the same rate to a constantly stirred solution containing 0.074 moles of KH_2PO_4 in 0.5 liters of water at 25°C. The addition rates were maintained in order to keep the PH at 4.8. The resulting powdered precipitate was filtered on a Buchner funnel, washed with 0.05% H_3PO_4 solution and dried in a vacuum at 60°C.

Single crystals of brushite were grown using a method described by LeGeros[10]. The procedure involves the slow interdiffusion of calcium ions from a 20% solution of $Ca(NO_3)_2 \cdot 4H_2O$ and acid phosphate ions from a 20% solution of $NH_4H_2PO_4$ through a barrier of dilute nitric acid solution, PH4. The system was maintained at room temperature during the crystallization. After approximately twenty days, crystals formed with suitable sizes for spectral

study. These crystals were washed in water and dried in vacuo at 50°C.

Wet chemical and emission spectrographic analyses indicated a high degree of stoichiometry and low concentrations of trace impurities for both the powders and crystals. The X-ray diffraction patterns were characteristic of brushite.

Infrared spectra were measured on a Perkin-Elmer Model 621 spectrophotometer using KBr pellet, and mineral oil and vaseline mull techniques. Raman spectra were measured for powders and crystals using a Spex Model 1401 Monochromator and a CRL Model 54 Argon ion laser. These spectra were obtained in the Stokes region of the blue line at 4880 Å. The double monochromator was oriented at 90° to the incident beam. Powder Raman spectra were obtained using both capillary tube and pressed pellet techniques. Single crystals were mounted onto glass capillary tubes with Duco cement, and the capillaries were attached to a goniometer on the goniometer frame of the Raman spectrophotometer. The polarized studies involved rotating the single crystal so that the plane polarized incident light was either parallel or perpendicular to the ac plane of the crystal.

RESULTS AND DISCUSSION

The brushite structure has monoclinic symmetry with space group Ia - C_s^4 [4]. Its crystallographic unit cell is body centered and contains four molecular units. In each primitive cell, a pair of HPO_4^{2-}-ions relate to each other by a glide plane. Therefore, the factor group modes involve coupled motions for the pairs of ions related by the mirror plane. In contrast, two different sets of pairs of water molecules occur in the unit cell which are crystallographically non-equivalent. Therefore, splitting is predicted by the two site effects for the fundamental modes of the water molecules but not for the modes of the HPO_4^{2-}-ions. Table 1 illustrates the predicted spectral correlations and changes in the selection rules for the phosphate ions of brushite as one proceeds from the PO_4^{3-} free ion to the HPO_4^{2-} free ion in solution to the HPO_4^{2-} site ion (C_s and C_1) to the factor group (C_s^4). One may note in Table 1 that each site group mode for the phosphate ion will split into fundamentals possessing A' - and A"- symmetry when one applies factor group analysis. Also, because the unit cell does not possess a center of symmetry, coincidences are predicted between bands observed in the infrared and Raman spectra.

TABLE 1

Correlation of the Vibrational Modes for Phosphate Ions in Brushite

Free PO_4^{3-} (T_d)	Free HPO_4^{2-} (C_{3v})	Site Group (C_s)	Site Group (C_1)	Factor Group (C_s)
P-O_4 str. ν_1 A_1 (936)*	P-O str. ν_2 A (988)	A'	A ν_2	A' + A"
OPO bend ν_2 E (420)	OPO bend ν_8 E (394)	A'	A ν_8	A' + A"
		A"	A $\nu_{8'}$	A' + A"
P-O_4 str. ν_3 F_2 (1004)	P-OH str. ν_3 A (862)	A'	A ν_3	A' + A"
	P-OH str. ν_6 E (1076)	A'	A ν_6	A' + A"
		A"	A $\nu_{6'}$	A' + A"
OPO bend ν_4 F_2 (573)	OPO bend ν_4 A (537)	A'	A ν_4	A' + A"
	OPO bend ν_7 E (537)	A'	A ν_7	A' + A"
		A"	A $\nu_{7'}$	A' + A"
	PO-H str. ν_1 A (2900)	A'	A ν_1	A' + A"
	POH bend ν_5 E (1230)	A'	A ν_5	A' + A"
		A"	A $\nu_{5'}$	A' + A"

* in units of cm^{-1}

The infrared and Raman spectra of brushite are illustrated in Figs. 1 and 2. Table 2 summarizes the assignments of the Raman and infrared fundamentals, and demonstrates within experimental limits the

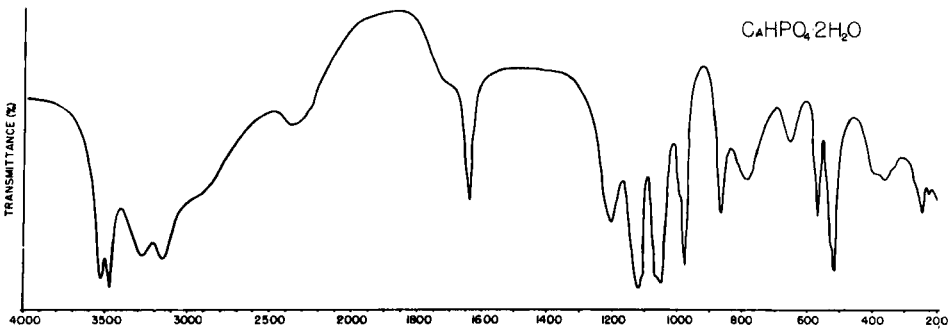

FIG. 1. The Infrared Spectra of $CaHPO_4 \cdot 2H_2O$.

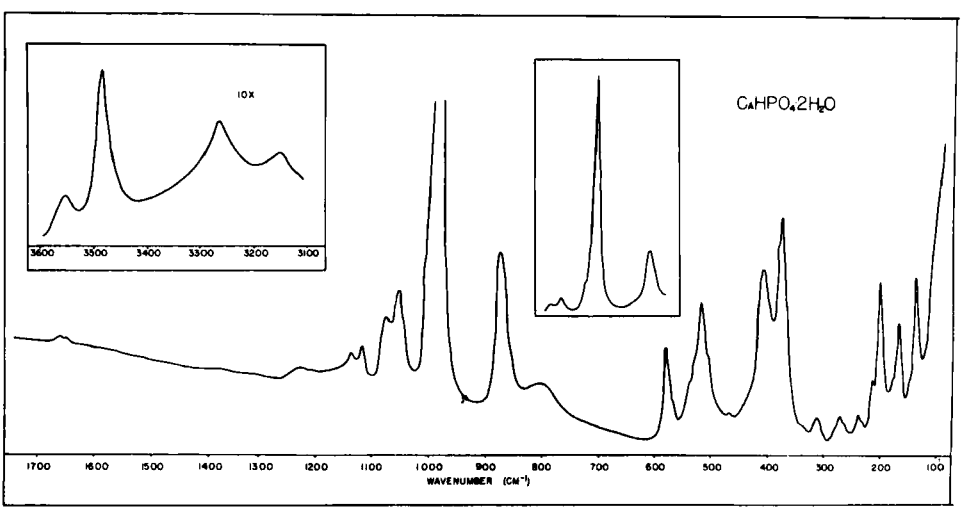

FIG. 2. The Raman Spectra of $CaHPO_4 \cdot 2H_2O$.

coincidences in wavenumbers due to the absence of a center of symmetry. The single crystal data are also correlated in this table to the powder data. All assignments are consistent with those observed for phosphate ions in solution[11].

As reported by other authors[5),6),7),8)] clear evidence exists for two crystallographically distinct types of molecules in the case of water (see Fig. 1). The pair of doublets in the infrared occurring at 3545 and 3490 cm^{-1} and at 3280 and 3160 cm^{-1} correspond to the Raman doublets at 3539 and 3473 cm^{-1} and at 3269 and 3159 cm^{-1}, and can be assigned to the stretching modes of water. The factor group splittings which Berry and Baddiel[5)] observed for the OH stretching modes of water are not observed in the present study, similarly to Petrov et al[6)]. In this study, the polarized Raman data is the only direct evidence for factor group splitting in the case of water-related bands.

The broad band with low intensity occurring in the infrared spectrum at 2930 cm^{-1} is assigned to the O_3PO-H stretching mode and shows no evidence of factor group splitting. This band is probably not observable in the Raman spectrum because it involves the motion of hydrogen atoms which possess low polarizabilities. Also, the Raman bands which correspond

TABLE 2

Band Assignments for $CaHPO_4 \cdot 2H_2O$ (cm^{-1})

	Raman			Infrared
	Single A'	Crystal A''	Powder	
$\nu_1(H_2O)$	3539 3482	3544 3486	3539 wb 3483 m	3545 s 3490 s
$\nu_3(H_2O)$	3270 3163	3270 3165	3270 w 3163 wb	3280 m 3160 m
ν_1				2930 w sh 2380 wb 2270 sh 2140 vwb
$\nu_2(H_2O)$			1647 vw 1635 vw	1650 m
ν_5	1226	1215	1220 wb 1210 vwb	1215 m 1200 w sh
ν_6	1140 1057	 1120 1079 	1140 w 1121 w 1079 m 1057 m	1140 s 1123 s sh 1075 s sh 1057 s
ν_2	 984	1005 	1005 sh 984 vs	1000 m sh 984 s
ν_3	 873	877 	 873 s	875 s
ν_5	 784	809 	 790 wb	 785 mb
water librations			678	 665 wb 663 sh
ν_4	586		585 m 574 sh	583
ν_7	 521 511	540 528 	545 sh 535 sh 521 s 508 sh	 535 sh 519 m

(continued...)

TABLE 2 (cont.)

Band Assignments for $CaHPO_4 \cdot 2H_2O$ (cm^{-1})

	Raman			Infrared
	Single A'	Crystal A''	Powder	
			460 vw	
ν_8		417		
	405		408 s	
				394
	381		381 sh	
		377	375 s	
lattice modes	364			363
			343 w sh	337
		315	316 w	
	274		276 w	
			259 vw	
	246		242 sh	
		220	217 w	
	207		205 m	
	183		184 w sh	
		175	173 m	
			153 w sh	
			140 m	
	141			
	118			

to the infrared bands at 2380, 2270 and 2140 cm^{-1} previously assigned to combination modes are not observed.

The bending modes for the water molecules in DCPH occur approximately in the vicinity of the bending mode for water in the liquid state. Two bands are observed in this region of both the infrared and Raman spectra. A broad weak shoulder and a sharp

band with medium intensity occurs in the infrared spectrum at 1720 and 1650 cm^{-1}, respectively. Berry and Baddiel assigned these bands to the bending modes for two distinct water molecules[5]. Petrov et al[6] assigned their band at 1720 cm^{-1} to a combination mode and their bend at 1652 cm^{-1} to a water bending mode. Analysis of the present Raman data indicates that the band which occurs in the water bending region is a doublet involving a very weak band at 1636 cm^{-1} with a slight shoulder at 1647 cm^{-1}. No evidence exists for a band in the vicinity of 1720 cm^{-1}, indicating that this band is probably a combination band, as suggested by Petrov et al.

The bands for the internal modes for the HPO_4^{-2} ion are also illustrated in the infrared and Raman spectra for powdered $CaHPO_4 \cdot 2H_2O$ (see Figs. 1 and 2). The most intense band in the Raman spectra originates from a P-O symmetrical stretching mode (ν_2). The band correlates to the symmetrical stretching mode from the A_1- species of a PO_4^{-3} ion with T_d symmetry. Factor group analysis predicts that this fundamental will split into two bands from the A'- and an A"- species. The Raman band corresponds to the infrared band at 984 cm^{-1} with its shoulder at 1000 cm^{-1}. Polarized Raman spectra confirm that the band at

984 cm^{-1} possesses A'- symmetry while the shoulder at 1005 cm^{-1} possesses A"- symmetry.

ν_3 which is assigned to the P-O(H) stretching mode occurs at 873 cm^{-1} in the Raman spectrum and at 875 in the infrared spectrum. Although Berry and Baddiel[5] reported a weak shoulder on the low wavenumber side of this band in the infrared spectrum, neither the present work or that of Petrov et al[6] observed a similar splitting. ν_3 occurs in the A'- spectrum at 873 cm^{-1}, while an additional band also occurs in the A"- spectrum at 877 cm^{-1}. The factor group splitting is not resolvable in either infrared or Raman spectra of the powdered sample.

ν_4 which relates to the O-P-O(H) bending mode derived from the F_2- species of the T_d- group was assigned by Berry and Baddiel[5] along with the ν_7 components to the bands of 580, 535 (sh), 530 cm^{-1} without distinction. Petrov et al[6] assigned the band which occurs at 577 cm^{-1} as a strong band maxima to ν_4. However, the same authors[6] did not assign a band with medium intensity at 526 cm^{-1}. Use of factor group analysis and single crystal Raman data clarify the assignments of ν_4 and ν_7. Factor group analysis predicts two fundamentals for ν_4 and four fundamentals for ν_7. All six bands are

observed in the single crystal Raman spectra. The band possessing A'- symmetry at 586 cm^{-1} and the band possessing A"- symmetry at 580 cm^{-1} can be assigned to ν_4, while the bands at 521 and 511 cm^{-1} with A'- symmetry and the bands at 540 and 528 cm^{-1} with A"- symmetry can be assigned to ν_7. On this basis, the band at 583 cm^{-1} in the infrared spectrum corresponds to ν_4, and the band at 519 cm^{-1} corresponds to ν_7.

The ν_5- components which involve the in-plane POH bending mode occur at 1215 and 1200 cm^{-1} in the infrared spectrum. Because of low Raman intensity expected for modes associated with the motions of hydrogen ions, these bands possessed the lowest intensities in the Raman spectra. These fundamentals occur in the Raman spectra as a very weak broad band at 1220 cm^{-1} with a shoulder at 1210 cm^{-1}. Single crystal Raman analysis indicates a band at 1226 cm^{-1} in the A'- spectra and a band at 1215 cm^{-1} in the A"- spectra. The ν_5- conponents which involve a rotation of the O-H bond about the P-O(H) axis occurs at 790 cm^{-1} in the powder Raman spectrum and is a very broad low intensity band. ν_5 occurs in the infrared spectrum as a single broad band with medium intensity at 785 cm^{-1}. The single crystal polarized Raman spectrum resolves the ν_5- component with A'- symmetry

at 784 cm^{-1} while the component with A"- symmetry occurs at 809 cm^{-1}.

ν_6 originates from the triply degenerate P-O stretching mode with F_2- symmetry for the T_d- group. The observed powder Raman spectrum is characterized by a pair of doublets in the appropriate spectral region. One pair occurs at 1140 and 1121 cm^{-1}, and the other pair occurs at 1079 and 1057 cm^{-1} with medium intensities. These bands correspond to the strong infrared band at 1140 cm^{-1} with a strong shoulder at 1123 cm^{-1}, and a strong infrared shoulder at 1075 cm^{-1} and a band at 1057 cm^{-1}. The single crystal Raman spectra separates these four bands into bands with A'- symmetry (1140 and 1057 cm^{-1}) and bands with A"- symmetry (1120 and 1079 cm^{-1}).

ν_8 originating from the doubly degenerate bending mode of the T_d- group split with C_1- site symmetry into two non-degenerate bands each of which should be further split by factor group into an A'- and A"- component. Berry and Baddiel[5] have assigned bands occurring in the far infrared spectrum at 256, 248 and 238 cm^{-1} to this mode while Petrov et al[6] have assigned a pair of bands at 418 and 400 cm^{-1} to ν_8. Berry and Baddiel made this assignment to lower wavenumber bands because of the weak intensity of the infrared bands around 400 cm^{-1}. However, it is

important to note that these modes correlated to the ν_2 (E-symmetry) of the PO_4^{3-}-free ion which is forbidden in the infrared spectrum. Therefore, they may appear only weakly in the infrared. The related Raman bands appear strongly in the Raman spectrum. This result would be expected because the ν_2- mode of PO_4^{3-} is allowed in the Raman spectrum. Consistent with these considerations, we have assigned the Raman peaks with A'- symmetry at 405 and 381 cm^{-1} and with the A"- symmetry at 417 and 377 cm^{-1} along with the related infrared band to ν_8. Bands below these wavenumbers should be lattice modes. Isotopic substitution will be necessary to determine their exact nature.

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