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The Raman Spectrum of Monetite, $CaHPO_4$

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The Raman spectrum was measured for monetite, $CaHPO_4$. A consistent set of band assignments were made for both the Raman and infrared spectra. The effects of factor group and two-site effect are discussed.

The structure of anhydrous dicalcium phosphate (monetite), $CaHPO_4$, has been studied extensively using diffraction (*1–4*) and infrared spectroscopy (*5, 6*) techniques. However, no Raman spectra have been investigated for monetite. In this paper, we will present and analyze the Raman spectrum of monetite along with its infrared spectrum using factor group analysis.

Monetite powders were prepared by a precipitation technique described by Tovborg-Jensen and Rathlev (*7*). The precipitation was conducted at 90–95°. The filtration, washing and drying *in vacuo* of the samples was also conducted at 90°. Single crystals of monetite were prepared using a method described by Smith *et al.* (*8*). This method involved a slow interdiffusion process of calcium and phosphate ions through nitric acid during which the solutions were maintained at 83°C. Wet chemical and trace emission analysis indicated high-purity, stoichiometric materials. The X-ray diffraction patterns were characteristic of monetite.

Raman spectra were measured for powdered samples in capillary tubes and pressed pellets using a Spex Model 1401 Spectrophotometer and a CRL Model 54 Argon Ion Laser. The 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. Indene and the plasma lines of the laser were used for calibration of the instrument.

The monetite structure has triclinic symmetry with space group C_i^1–$P\bar{1}$ (*1–4*). Four molecular units are contained in a unit cell. Two distinct sets of pairs of PO_4 units are found in each primitive cell. Each member of a pair is related to the other member by a center of symmetry. Coupled vibrational motions of the pair of PO_4 units related by the center of symmetry causes factor group splitting of site group bands. Further splitting also occurs because of two-site effect due to two distinct sets of pairs. Differences in the bonding between H ions and the phosphate ions of the two different sets will further perturb the band splitting pattern of the vibrational spectra. Table I illustrates the correlation of the internal vibrational modes for the PO_4 units of monetite from the free PO_4^{3-}-ion group to the factor group with two-site effect. Because the unit cell of monetite possesses a center of symmetry, no coincidences are expected between bands observed in the infrared and Raman spectra. Also, two-site effect should double

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TABLE I

CORRELATION OF THE INTERNAL VIBRATIONAL MODES FOR PO_4 UNITS IN MONETITE

Free PO_4^{3-} in solution (T_d) (*9*)	C_{3v} in solution (*9*)	Site group (C_1)	Factor group (C_i)	Factor group with two-site effect
P–O str. ν_1A_1 (936)[a]	P–O str. ν_2A (988)	$A\nu_1$	Ag + Au	2Ag + 2Au
OPO bend ν_2E (420)	OPO bend ν_8E (394)	$A\nu_2'$	Ag + Au	2Ag + 2Au
		$A\nu_2''$	Ag + Au	2Ag + 2Au
	PO str. ν_3A (862)	$A\nu_3'''$	Ag + Au	2Ag + 2Au
P–O str. ν_3F_2 (1004)	PO str. ν_6E (1076)	$A\nu_3''$	Ag + Au	2ag + 2Au
		$A\nu_3'$	Ag + Au	2Ag + 2Au
OPO bend ν_4F_2 (573)	OPO bend ν_4A (537)	$A\nu_4'''$	Ag + Au	2Ag + 2Au
	OPO bend ν_7E (537)	$A\nu_4''$	Ag + Au	2Ag + 2Au
		$A\nu_4'$	Ag + Au	2Ag + 2Au

[a] In units of cm^{-1}.

the number of bands if adequate resolution is present. Disorder is introduced into the crystal structure of $CaHPO_4$ which may also perturb the observed vibrational spectra. One hydrogen atom in its unit cell is statistically distributed between two centrosymmetric positions.

The Raman spectrum of monetite is illustrated in Fig. 1. The band assignments for the Raman fundamentals along with the infrared fundamentals are listed in Table II.

Simple site models are insufficient to interpret the observed vibrational spectra without the inclusion of factor group and two-site effects. Too many bands are observed to be explained with only these simple models. The noncoincidences between many infrared and Raman bands associated with various site group modes are consistent with the factor group for space group C_i^1–$P\bar{1}$. Such noncoincidences which are beyond the limitations of experimental er-

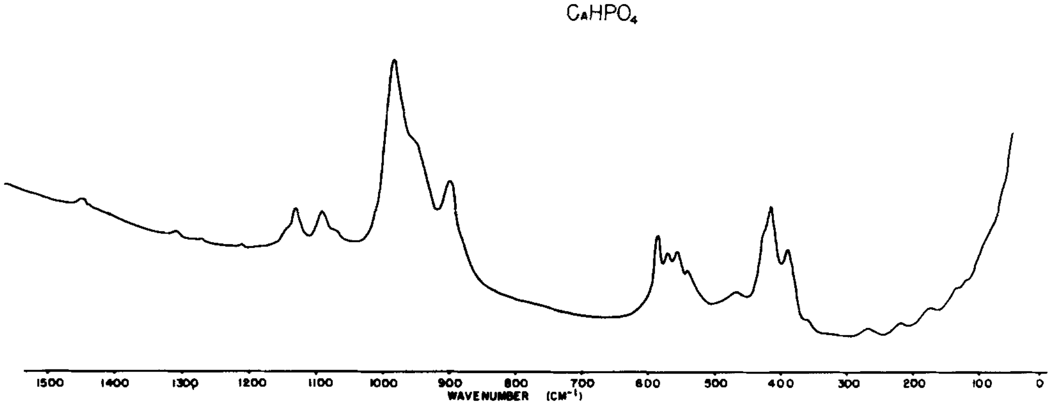

FIG. 1. The Raman spectrum of powdered $CaHPO_4$.

TABLE II

FUNDAMENTAL FREQUENCIES (cm^{-1}) AND BAND ASSIGNMENTS FOR $CaHPO_4$

	Raman	Infrared (*5*)
ν(OH)	3300 vw	3200 vw
	2800 vw	2820 w
	2300 vw	2400 m
combination		1650 w
δ(POH)	1447 vw	1400 m
	1434 vw	1350 m
	1415 vw sh	
	1300 vw	
	1257 vw	
	1200 vw	
ν_3'	1140 sh	1170 sh
	1126 w	1130 s
ν_3''	1086 w	1070 s
	1060 sh	
ν_1	983 vs	1000 m
	946 sh	
ν_3'''	895 m	900 m
δ(POH)		790 vw[a]
ν_4'	583 m	581 m
ν_4''	569 m	566 sh
ν_4'''	553 m	530 m
	539 m	
combination	463 wb	480 sh
ν_2'	423 sh	428 w
	413 m	
ν_2''	390 m	405
		398
lattice modes	353 vw	(285)[b]
	264 w	(255)
	214 vw	
	173 vw	
	135 vw	

[a] Measured at 77°K.

[b] Infrared bands in parentheses were obtained in this study.

ror or solid-state effects may be particularly noted for modes associated with ν_1, ν_3', ν_3'', ν_4''' and ν(OH). Two-site effect is noted for most factor group fundamentals, especially in the Raman spectrum. Cases for which this effect is not observed probably involve overlapped bands.

The band locations of the observed peaks for the P–O stretching and OPO bending modes for monetite occur in the same regions of the vibrational spectra as those observed for free PO_4^{3-}-ion and HPO_4^{2-}-ion groups which correlate to them. The relative intensities of these bands are consistent with those observed for correlated modes. These vibrational bands are also consistent on the basis of band locations and relative intensities with those observed for brushite ($CaHPO_4 \cdot 2H_2O$) (*10*). For instance, the most intense Raman bands (983 and 946 cm^{-1}) correlate to the symmetrical P–O stretching mode of the free PO_4^{3-} ion which occurs at 936 cm^{-1} in solution. Its infrared counterpart occurs as a broad band at 1000 cm^{-1} which is probably indicative of more than one band component. This type of mode is seen as a strong Raman band at 984 cm^{-1} with a shoulder at 1005 cm^{-1} in the case of brushite.

Three weak bands (3200, 2820, and 2400 cm^{-1}) have been assigned by earlier investigators to the (P)O–H stretching modes (*2, 5, 6, 11*). However, the explanations differ concerning the number of observed infrared bands. Blinc and Hadzi (*11*) have interpreted the observed spectra using proton tunneling. In their model, the hydrogen atom is placed between two oxygen atoms in a double minimum potential well. The oxygen atoms in question would not be crystallographically equivalent and therefore the O–H bonds formed with each of them would account for the number of OH stretching bands. On the other hand, Jones and Cruickshank (*2*) interpreted the infrared data from another point of view. Their NMR data indicated that the protons in the crystal were stationary. Their structural study also indicated that three short O–O distances occurred for the phosphate ions in the unit cell which could accommodate hydrogen bonds. They suggested that at least three different types of hydrogen-bonded OH bonds should exist in the monetite structure accounting for the number of OH stretching bands. A recent neutron diffraction study has shown that hydrogen bonding plays an important role with respect to the structure of monetite (*4*). Catti *et al.* have shown that three different O–H---O bonds occur within its structure. Disorder is introduced into the crystal structure of monetite because one of the O–H---O bonds has two choices in location of centrosymmetric positions within the unit cell. The observed number of different O–H--O bonds would generate the number of bands observed for ν(OH). The number of Raman bands observed in this study for ν(OH) is consistent with this interpretation of the infrared bands. As mentioned earlier, differences in band location of infrared and Raman bands is due to the centrosymmetric nature of the crystal. Normal coordinate analysis with isotropic substitution will be necessary to determine which O–H---O bonds generate each band. It is interesting to note that δ(POH) occurs as a group of bands between 1200–1450 cm^{-1}. Again, hydrogen bonding apparently generates the range of vibrational bands for δ(POH) as for ν(OH).

References

1. G. MacLennan and C. A. Beevers, *Acta Crystallogr.* **8,** 579 (1955).
2. D. M. Jones and D. W. J. Cruickshank, *Z. Kristallogr.* **116,** 101 (1961).
3. B. Dickens, J. S. Bowen, and W. E. Brown, *Acta Crystallogr. Sect. B* **28,** 797 (1971).
4. M. Catti, G. Ferraris, and A. Filhol, *Acta Crystallogr. Sect. B* **33,** 1223 (1977).
5. I. Petrov, B. Šoptrajanov, N. Fuson, and J. R. Lawson, *Spectrochim. Acta Part A* **23,** 2637 (1967).
6. B. Šoptrajanov and I. Petrov, *Croat. Chem. Acta* **39,** 37 (1967).
7. A. Tovborg-Jensen and J. Rathlev, *Inorg. Syn.* **4,** 19 (1953).
8. J. P. Smith, J. R. Lehr, and W. E. Brown, *Amer. Mineral.* **40,** 893 (1955).
9. A. C. Chapman, D. A. Long, and D. T. L. Jones, *Spectrochim. Acta* **24,** 633 (1965).
10. F. Casciani and R. A. Condrate, Sr., *Spectrosc. Lett.* **12,** 699 (1979).
11. R. Blinc and D. Hadzi, *Spectrochim. Acta* **16,** 852 (1960).