On the Hydroxyl Ions in Apatites

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The possible mechanism originating the stretching and librational bands of the OH groups in ir spectra of various apatites are discussed. On the basis of relating the v_s frequency of the V_3 hindered potential barrier, it is deduced that hydrogen bonds between the OH groups and the nearest O's of PO_4^{3-} ions exist, and that they are responsible for the observed frequencies of the stretching and librational modes. The additional ir OH bands of heated nonstoichiometric hydroxylapatites are also discussed.

1. Introduction

Although the vibrational spectra of calcium hydroxylapatites have been studied by several authors (*1–6*) and appropriate assignments have been made of the bands of the PO_4^{3-} groups, some doubts still remain about the interpretation of the bands of the OH group. In fact, the bands at 3572 and 630 cm^{-1} in ir spectra of calcium hydroxylapatite can be unequivocally assigned to the OH stretching mode and to the OH librational mode, respectively (*1–5*). The shift of the former with respect to the OH stretching mode in Ca(OH)$_2$ ($v_s = 3644$ cm^{-1}) seems to indicate the existence of a hydrogen bond either between adjacent OH in the unit cell or else between the OH and the nearest O's of PO_4^{3-} ions. The O$\cdots$O distance (3.44 Å) between adjacent reticular planes is too long to be compatible with the first mechanism, whereas the O(OH)$\cdots$O(PO$_4$) (3.068 Å) is short enough for a hydrogen bond if this is assumed to be linear. However, this last possibility has also been questioned on the ground that the expansion of the unit cell when passing from the hydroxylapatite of Ca to that of Pb to that of Sr, and to that of Ba does not correspond to the values of the corresponding OH stretching frequencies, so that a more complex model is needed. One possible model could be the existence of nonlinear hydrogen bonding in these compounds, although other questions may arise such as the fact that the metal might form bonds with the neighboring OH groups.

The possibility that the OH$\cdots$OPO$_3$ hydrogen bonding is bent is mainly grounded on polarized infrared measurements (*3*) that have shown that the OH ion is oriented approximately parallel to the apatic c axis in calcium hydroxylapatites. However, the existence of a librational OH band at high frequency indicates that the OH group cannot be situated parallel to the c axis.

Since no systematic relationship between the stretching and librational motions of Ca, Sr, Ba, Pb, and Cd hydroxylapatites exists, Engel and Klee (*7*) have suggested that the effects determining the stretching modes are not identical to those determining the librational modes.

In this paper we discuss the problem of the OH retention in the apatitic lattice of Ca, Sr, Pb, and Ba on the basis of assuming an additional degree of freedom for the motion of the OH group. Some effects of heating on the crystal structure of nonstoichiometric calcium apatite are also dealt with.

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2. Experimental

Stoichiometric Ca, Sr, Ba, and Pb hydroxyl-apatites were synthesized by the method of Winand (8), but either $(NO_3)_2Ca$, $(NO_3)_2Sr$, $(NO_3)_2Pb$, or $(NO_3)_2Ba$ was used in each case. X-Ray diffraction analysis indicated that all the samples were one-phased apatitic specimens.

Middle ir absorption spectra were recorded on a Perkin–Elmer 457 spectrophotometer. For the recording of the far infrared spectra a Fourier spectrometer Polytec FIR-30 was used.

Deuterated analogs were prepared by treating the previously degassed apatites with excess D_2O vapor in a glass cell at 250°C during 8 hr.

3. Results and Discussion

Besides the PO_4^{3-} vibrational modes, the Ba, Sr, Ca, and Pb hydroxylapatites are characterized by the position of their OH bands in the ir spectra. In these compounds the OH groups give a stretching band in the range 3650–3500 cm^{-1} and two librational bands, one in the range 700–400 cm^{-1} and the second in the range 100–200 cm^{-1} (far ir). Table I shows the positions (cm^{-1}) of these bands for the Ba, Sr, Ca, and Pb hydroxylapatites here studied and the v_s/v_1 and v_s/v_1' ratios for each case. Confirmation of the assignments of these bands has been made through deuteration or by dehydration or halogenation (7, 9, 11, 12) tests. The $v_1'(OH)$ librational mode of Table I arises from the fact that in the rotation of the OH ions around the c axis of the hexagono–helicoidal channels of apatites (12, 13). Two

positions have maximum probability of occurrence.

Most of the present assignments coincide with those given by Engel and Klee (7). These authors make no mention of the $v_1'(OH)$ bands. In the case of Pb hydroxylapatite, Engel and Klee attribute the band at 550 cm^{-1} to the $v_1(OH)$ mode. We assign this band to a v_4 mode of the PO_4^{3-}, while the band at 610 cm^{-1} is attributed to the $v_1(OH)$ mode.

Table I shows an apparent relationship between the value of the v_s and the value of the v_s/v_1 (or v_s/v_1' ratio for the hydroxylapatite of Ba, Sr, and Ca, which, however, is not maintained for the case of Pb hydroxylapatite. This fact is significant and may be interpreted as indicating that the effects determining the stretching modes are not identical with those determining the librational modes, as Engel and Klee have pointed out.

The stretching frequency depends on the bond order between the atoms involved; it is determined by the value of the force constant and the reduced mass and does not depend on other factors. On the other hand, the librational frequency depends on the relative geometry of the OH groups with respect to the surrounding atoms of the crystal structure.

Table II gives the lattice parameters of the above apatites derived from the X-ray diffraction data obtained by us (14–16). It may be observed that these values are directly related to the ionic radii of the respective cations: Thus, the c/a ratio decreases from Ba to Ca and increases from Ca to Pb, indicating that the angle between the O–H bond and the a axis in the hindered OH rotation is different for each of the apatites. Therefore, one should

TABLE I

STRETCHING AND LIBRATIONAL FREQUENCIES OF THE OH GROUP IN SOME APATITES

Cation	v_s (cm^{-1})	v_1 (cm^{-1})	v_s/v_1	v_1' (cm^{-1})	v_s/v_1'
Ba	3606	430	8.38	—	—
Sr	3593	539	6.66	145	24.7
Ca	3572	630	5.66	180	19.8
Pb	3559	610	5.83	—	—

TABLE II

IONIC RADII AND LATTICE PARAMETERS FOR SOME APATITES

Cation	Ionic radii (Å)	$a = b$ (Å)	c (Å)	c/a	V (Å³)
Ba	1.35	10.178	7.730	0.759	800.764
Sr	1.13	9.764	7.260	0.744	692.137
Ca	0.99	9.418	6.883	0.731	610.513
Pb	1.20	9.886	7.302	0.739	713.646

TABLE III

GEOMETRIC PARAMETERS (FIG. 1) AND ROTATION CONSTANT OF THE OH GROUP IN THE UNIT CELL OF SOME APATITES

Cation	d (Å)	R (Å)	s (Å)	(°)	B (cm⁻¹)
Ba	3.507	3.293	0.05	20.2	18.93
Sr	3.340	3.088	−0.02	22.5	19.53
Ca	3.068	2.915	0.30	18.2	18.45
Pb	3.065	3.060	1.08	3.3	16.75

not expect either a constancy of the v_s/v_1 (or v_s/v_1') ratio or a direct relationship between these ratios and the values of v_s frequencies for the different hydroxylapatites.

If the reference value of the OH stretching frequency is taken as 3644 cm⁻¹, then the equation (17)

$$\log d = \log 3.35 - \tfrac{1}{6} \log (\Delta v/50) \qquad (1)$$

relating the shift on the stretching frequency with $O \cdots O$ distance, d, in hydrogen bonds, reproduces well the observed $O(H) \cdots O$ distance of 3.068 Å for calcium hydroxylapatite, and this has been claimed as evidence of the existence of hydrogen bond mechanism (1, 18).

Since the probability of the formation of linear hydrogen bonding between the OH group and each of the three surrounding OPO_3 groups is the same, the average result is to have the OH situated parallel to the c axis (11, 18), such as indicated by polarized infrared measurements (3).
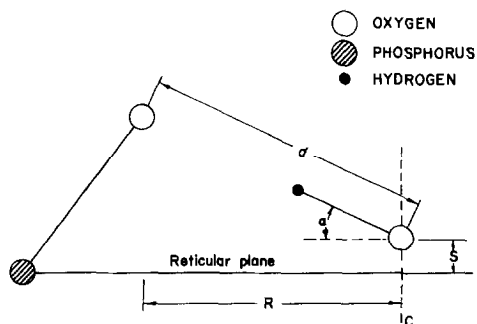

○ OXYGEN
▨ PHOSPHORUS
● HYDROGEN

FIG. 1. Geometric parameters of the apatitic channels with respect to the hindered rotation of the OH group around the c axis.

Because the main objective of the present study is to compare the different apatites to each other, and the OH stretching reference value of 3644 cm⁻¹ reproduces well the stretching OH frequency in calcium hydroxylapatite, the most consistent way for operating is to select this reference value for all apatites.

The geometric parameters of the channels with respect to the rotation of the OH group around the c axis (Fig. 1) may be so obtained from the values of d calculated from Eq. (1) for the different hydroxylapatites. These are given in Table III together with the values of the OH rotation constant given by

$$B \text{ (cm}^{-1}) = h^2/(8\pi^2 c I_r),$$

where h is the Planck's constant, c is the velocity of light in vacuum, and I_r is the reduced inertia moment of the OH rotor.

In order to calculate the reduced inertia moment I_r, it is necessary to know the O–H distance. This may be estimated using the CNDO/2 method (19, 20): Values of the bond order, N, are computed for a series of given O–H distances. Next, the force constant, K, is obtained from the empirical relation (21),

$$K \text{ (dym/cm)} = 1.67 N (E_O E_H/d_{OH}^2)^{3/4} + C, \qquad (2)$$

where E_O and E_H are the electronegativities of the oxygen and the hydrogen, respectively. The value of C is derived from the v_s(OH) frequency (3572 cm⁻¹) and the O–H distance ($\cong 1$ Å) for calcium hydroxylapatite. Finally, the values of the stretching frequencies are computed for each of the above O–H distances by means of the Hooke's law, which are plotted against the O–H distances (Fig. 2).
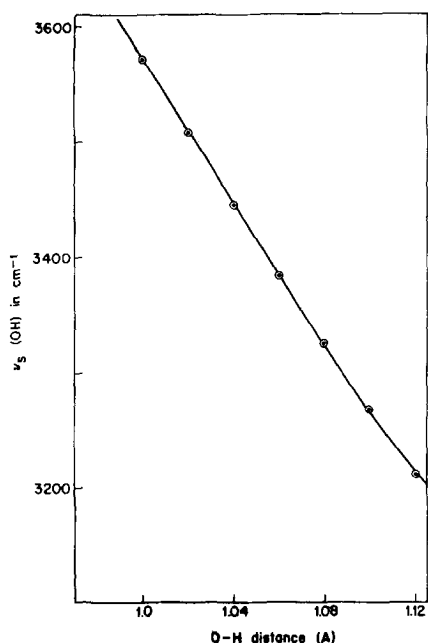
FIG. 2. ν_s(OH) frequencies against the interatomic O–H distances calculated by the CNDO/2 method for apatite-like structures.

Thus, calculated O–H distances for different hydroxylapatites are read in this plot for the observed ν_s(OH) values.

The values of the parameters of Table III have a certain degree of uncertainty because of the uncertainty of the selected reference value of the OH stretching frequency. These parameters are only used here in order to establish a consistent way of comparison between the different apatites.

The relative geometry of the OH group with respect to the surrounding atoms of the crystal is rather represented by the potential functions of the all-allowed motions of this group. In the present case, only a rotation around the c axis is possible. The hindered rotation of the OH group in apatites has periodicity 3; therefore, the potential function corresponding to this rotation is

$$V = V_3/2 \, (1 - \cos 3\phi), \qquad (3)$$

where ϕ is the rotation angle and V_3, the rotation barrier, is directly related to the strength of the bonds which are formed

between the OH group and the surrounding atoms of the crystal. Thus, V_3 is inversely related to the ν_s stretching frequency.

The Hamiltonian operator for hindered rotation can be written

$$\mathcal{H} = T + V, \qquad (4)$$

where T is the kinetic energy operator and V, the potential energy operator, is given by Eq. (3). When T is expressed as a momentum function (23), the Hamiltonian of Eq. (4) becomes

$$\mathcal{H} = -(d/d\,\phi)\left(B_0 + \sum_n \cos n\phi\right)(d/d\phi) \\ + \sum_n V_n^{\text{eff}}\,(1 - \cos n\phi), \qquad (5)$$

where V_n^{eff} is defined, for convenience, as an effective potential and B_0 and B_n are coefficients of a trigonometric expansion of the B.

Different values of V_3 have been tested for each of the values B of Table III using a FORTRAN IV program with 50 trigonometric base functions, in which $B_0 = B$ and, therefore, $B_n = 0$. In this way, the potential term V_3 has been optimized for each type of hydroxylapatite. Results are given in Table IV, where the dimensionless ratio ν_s/V_3 is also shown. It can be observed that the values of ν_s/V_3 are not constant, but vary inversely with V_3. Since the values of B given in Table III have been calculated under the hypothesis that only a hydrogen bonding mechanism takes place, it can be concluded that hydrogen bonds exist in the structure of the apatites, and that they are responsible for the observed values of the stretching and librational modes.

TABLE IV

V_3 POTENTIAL TERM AND ν_s/ν_3 RATIO IN SOME APATITES

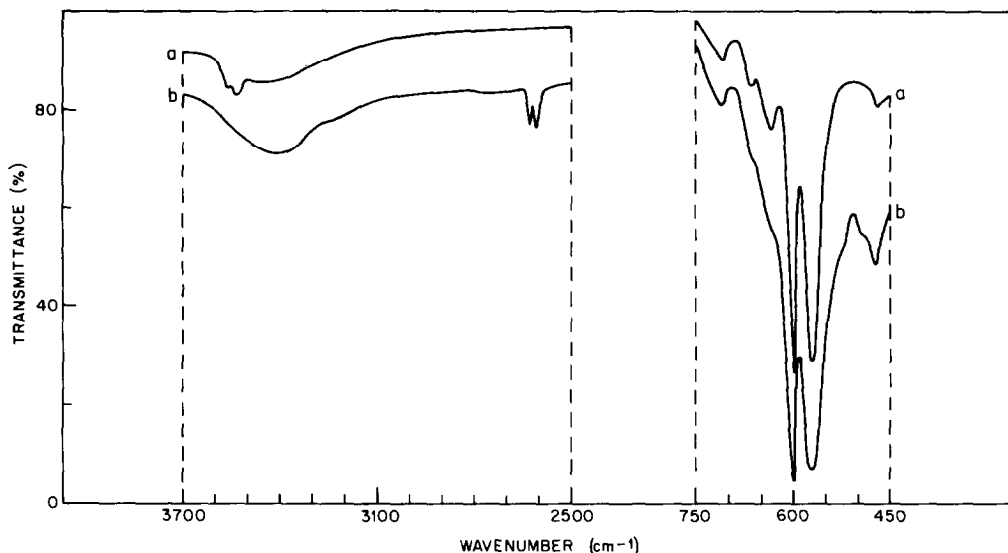| Cation	ν_3 (cm^{-1})	ν_s/V_3
Ba	1335	2.70
Sr	2000	1.79
Ca	2750	1.29
Pb	2775	1.27

FIG. 3. Infrared spectra of (a) a nonstoichiometric calcium hydroxylapatite heated 2 hr at 750°C.(b) The same sample after deuteration. Bands at 715 cm^{-1} in these two spectra are due to a P–O–P vibration of the $P_2O_7^{4-}$ ions.

4. Heating of Nonstoichiometric Calcium Hydroxylapatites

Nonstoichiometric hydroxylapatites mainly differ from stoichiometric hydroxylapatites in that the former contain variable amounts of HPO_4^{2-} ions replacing PO_4^{3-} ions in the structure and smaller Ca/P and OH/P ratios (24). By heating between 200 and 700°C HPO_4^{2-} ions are transformed to $P_2O_7^{4-}$ ions, which remain included within the crystal lattice of the apatite. As a result, two new bands appear in the ir spectrum (Fig. 3), at frequencies of 3540 and 670 cm^{-1} that are assigned, through deuteration, to the stretching and librational modes of the OH groups. The location of these groups should obviously differ from that of the OH groups in stoichiometric hydroxylapatites.

Since the channel symmetry is conserved through heating, the presence of the two new OH bands may be only justified by either of
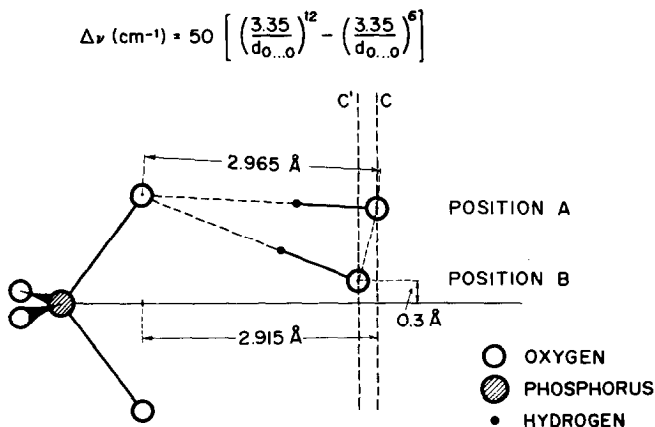
$$\Delta\nu \; (cm^{-1}) = 50 \left[\left(\frac{3.35}{d_{O\cdots O}}\right)^{12} - \left(\frac{3.35}{d_{O\cdots O}}\right)^{6} \right]$$

FIG. 4. Positions of the OH group justifying the $\nu_s(OH)$ band at 3540 cm^{-1} in heated nonstoichiometric calcium hydroxylapatites.
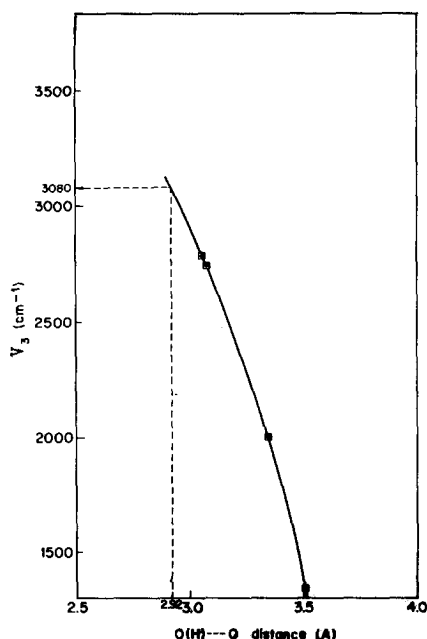
FIG. 5. V_3 potential term against $O(H) \cdots O$ distance for various apatites.

the two following mechanisms (Fig. 4): (A) OH groups are displaced along the c axis (25); (B) the average cross section of the hexagono–helicoidal channels is reduced when $P_2O_7^{4-}$ ions are formed within the three-dimensional structure (26).

Since the hindered rotation of the OH group takes place around the c axis, formation of the

linear hydrogen bond between adjacent OH groups displaced along the c axis cannot justify the existence of the librational band at 670 cm^{-1}. On the other hand, the presence of the bands at 3540 and 670 cm^{-1} in some, partially fluorated calcium hydroxylapatites, rather has to be attributed to the existence of certain amounts of $P_2O_7^{4-}$ ions in the samples, and cannot be claimed as evidence that the bands at 3540 and 670 cm^{-1} of heated nonstoichiometric calcium hydroxylapatites are originated from OH ions hydrogen bonded to F$^-$ ions. Moreover, no presence of F$^-$ ions has been detected in our samples.

From Eq. (1) an $O(H) \cdots O$ distance of 2.965 Å is computed for $\nu_s = 3540$ cm^{-1} and, therefore, a value for the potential term V_3 of 2990 cm^{-1} results for a librational frequency $\nu_1 = 670$ cm^{-1} from the curve in Fig. 5.

The values of the rotation constant B for the two positions given in Fig. 4 are derived from the geometric parameters deduced from this figure following the above described procedure. The values found are: $B_A = 16.93$ cm^{-1}; $B_B = 18.27$ cm^{-1}. Then, one obtains that the values of V_3 for the band at 670 cm^{-1} are $V_{3A} = 3327.5$ cm^{-1} and $V_{3B} = 3102.5$ cm^{-1} (Fig. 6). Since the value V_{3B} agrees better with 2990 cm^{-1} than does V_{3A}, it may be concluded that mechanism B is more consistent with the ir data.
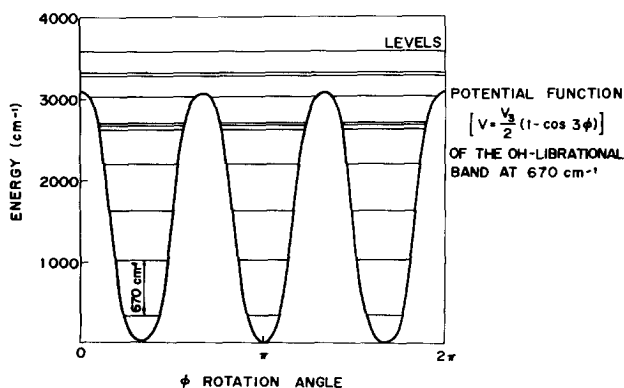

FIG. 6. The rotation potential function and the rotation levels of the OH group in heated nonstoichiometric hydroxylapatite.

Acknowledgments

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