Distribution of Fluorine in Hydroxyapatite studied by Infrared Spectroscopy

By **Friedemann Freund** * and **Rolf M. Knobel**, Mineralogisches Institut der Universität, Zülpicher Str. 49, D-5000 Köln-1, West Germany

In pure hydroxyapatite the O–H stretching and librational modes give rise to i.r. bands at 3 573 and 631 cm^{-1}. On introduction of F, the band at 631 cm^{-1} shifts to higher wavenumbers, ultimately to 641 and 647 cm^{-1}, and decreases in intensity. This shift can be correlated with the number n of OH groups in the chain sections between F which have the generalised form ··· F HO $(HO)_n$ HO:OH $(OH)_n$ OH F ···. The ' tail-to-tail ' configuration, ··· HO:OH ···, gives rise to bands at 680 (bending) and 3 643 cm^{-1} (stretching). The OH bonded to one F gives rise to bands at 720 and 3 546 cm^{-1}. If OH is dispersed in a chain composed mainly of F, the configuration ··· F OH F ···, the O–H stretching and bending bands lie at 3 540 and 747 cm^{-1} respectively.

HYDROXYAPATITE, $Ca_5(OH)(PO_4)_3$, is the main constituent of dental enamel and has received much attention in recent years. The incorporation of fluoride ions into the structure of hydroxyapatite is thought to help prevent caries.[1-3] The degree of fluorination has been studied by many different methods, although surprisingly not by i.r. spectroscopy. Only the end members, hydroxy- and fluoro-apatite, have been studied extensively by both i.r. and Raman spectroscopy.[4,5] Their vibrational spectra were unambiguously assigned by Fowler,[5] using isotopic substitution. Fowler's results can be used to study and to assign the i.r. spectra of solid solutions between hydroxy- and fluoro-apatite.

EXPERIMENTAL

Eleven samples of apatite solid solutions were prepared by Schaeken *et al.*[6] from $Ca[HPO_4]$, $Ca[CO_3]$, and CaF_2 reaction grade chemicals. The chemicals were thoroughly mixed as acetone slurries in an agate ball mill, then dried, pelletised, heated in open platinum crucibles to 1 000 °C, and held at this temperature for 3 h in a stream of nitrogen which had passed through 2 mol dm^{-3} Na[OH] at 0 °C to remove CO_2 and to provide $p_{H_2O} = 4$ Torr.† The samples were cooled slowly, crushed, and again powdered in the ball mill. Three heating and homogenisation cycles were necessary in order to attain complete or nearly complete reaction. The fluorine content of the samples was determined using the methods of Ingram and May [7] and Duff and Stuart.[8] The samples were analysed by X-ray diffractometry. The results are given in the Table.

The samples were dried in air at 120 °C for several days. Three milligrams of each were then mixed with KI (750 mg; Uvasol, Merck) in an agate mortar and compressed in an evacuated 13-mm die at *ca.* 5×10^7 N m^{-2}. Potassium bromide pellets gave identical i.r. results. The i.r. spectra were recorded on a conventional Perkin-Elmer 225 and on a Digilab FTS-14 Fourier-transform spectrometer using 1 000 scans at a resolution of 1 cm^{-1}. A Globar heater was used as a source instead of the standard Nichrome coil.

† Throughout this paper: 1 Torr = (101 325/760) Pa.

[1] G. N. Jenkins, *Sci. Basis Med. Ann.*, 1971, 365.
[2] G. S. Ingram, *Caries Res.*, 1973, **7**, 315.
[3] O. Baker-Dirks, *Caries Res. Suppl.*, 1974, **8**, 215.
[4] D. M. Adams and I. R. Gardner, *J.C.S. Dalton*, 1974, 1505.
[5] B. O. Fowler, *Inorg. Chem.*, 1974, **13**, 194.
[6] H. G. Schaeken, R. M. H. Verbeek, F. C. M. Driessens, and H. P. Thun, *Bull. Soc. chim. belges*, 1975, **84**, 881.
[7] B. L. Ingram and I. May, Geological Survey Research, U.S. Geol. Survey Prof. Paper 750–B, 180, 1971.

STRUCTURE OF APATITE

The structures of hydroxyapatite and of fluoroapatite have been determined by X-ray diffraction; that of hydroxyapatite has also been determined by neutron diffraction.[9,10] The unit cell is hexagonal. The space group is $P\ 6_3$ for hydroxyapatite and $P\ 6_3/m$ for fluoroapatite. The structure contains linear chains of $[OH]^-$ or F^- ions parallel to the

Composition of $Ca_5F_x(OH)_{1-x}(PO_4)_3$ solid solutions after Schaeken *et al.*[6]

x		Percentage of CaO present as second phase [a]
Found	Calc.	
b	0.00	1.0
b	0.03	0.9
b	0.06	0.9
0.097	0.10	0.7
0.191	0.20	0.7
0.31	0.30	0
0.38	0.40	0.6
0.51	0.50	0
0.66	0.65	0
0.76	0.80	0.4
0.95	1.00	0.3

[a] As determined by X-ray analysis. [b] Not determined.

c axis.[11] The distribution of $[OH]^-$ and F^- along these chains in apatite solid solutions is the main topic of the present paper.

Figure 1 shows a side view of the linear chain with the ionic radii of the $[OH]^-$ and the F^- to scale. Neutron-diffraction studies [10] have shown that the $[OH]^-$ is *ca.* 0.3 Å off the plane of the three Ca^{2+}. If an F^- is included in the chain, ^{19}F n.m.r. data show [12,13] that both adjacent $[OH]^-$ ions orientate themselves in such a way that their protonic ends point towards the F^-. This gives one type of configuration ··· OH F HO ···. The interatomic distances O–H ··· O and O–H ··· F as derived from the combined neutron diffraction and ^{19}F n.m.r. results are also indicated

[8] E. J. Duff and I. L. Stuart, *Analyt. Chim. Acta*, 1970, **52**, 155.
[9] A. S. Posner, A. Perloff, and A. F. Dioro, *Acta Cryst.*, 1958, **11**, 308.
[10] M. I. Kay, R. A. Young, and A. S. Posner, *Nature*, 1964, **204**, 1050.
[11] D. McConnell, 'Apatite,' Springer, New York, 1973.
[12] R. A. Young, W. Van der Lugt, and J. C. Elliott, *Nature*, 1969, **223**, 729.
[13] W. Van der Lugt, D. I. M. Knotnerus, and R. A. Young, *Caries Res.*, 1970, **4**, 89.

in Figure 1. In the undisturbed OH chain, schematically · · · OH OH OH · · · , the O–H distance within the $[OH]^-$ is 0.96 Å, while the distance H · · · O to the next $[OH]^-$ is 3.45 Å. The symmetrical H · · · F distances in the configuration · · · OH F HO · · · are much smaller, 2.19 Å.[13] This

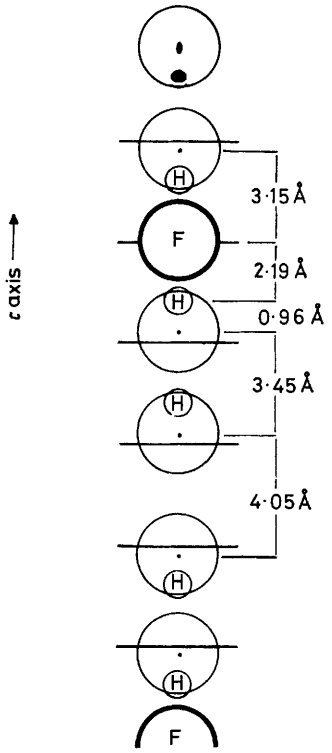

FIGURE 1 Side view of the (OH, F) chain in the apatite structure with the vertical 0.3 Å displacement of the $[OH]^-$ off the plane of the Ca^{2+} (indicated by the bar). In the uppermost $[OH]^-$ the anisotropic thermal motions of O^{2-} and H^+ at 300 K are shown (ref. 10)

H · · · F distance is very close to that expected if the F^- remains in the plane of the three Ca^{2+} and both $[OH]^-$, being 0.3 Å off the plane, orientate themselves as indicated. This particular OH F HO configuration should lead to another distinct O–H vibrational and OH librational mode of two $[OH]^-$ bonded to F.

If one considers a larger section of an $[OH]^-$ chain containing a few F^-, it becomes evident that somewhere between two F^- the dipole orientation of the $[OH]^-$ chain must reverse. This reversal will occur preferentially halfway between both F^-. This introduces a new configuration, · · · HO:OH · · · , which is expected to exhibit a different vibrational and librational spectrum. This configuration will be called ' tail-to-tail '. The ' head-on ' configuration · · · OH HO · · · is unlikely due to electrostatic repulsion.[10] It would lead to a marked deviation from the OH dipole alignment parallel to the *c* axis which was excluded by single-crystal i.r. studies using polarised radiation.[14]

In summary, on the basis of structural data, the (OH, F) chain of apatite should contain at least three types of $[OH]^-$, possibly four, with distinguishable vibrational energies: (1) the ' normal ' $[OH]^-$ in an extended $[OH]^-$ chain, schematically · · · OH OH OH · · · ; (2) the ' tail-to-tail ' configuration, · · · HO:OH · · · ; and (3) the F-bonded $[OH]^-$ in the symmetrical configuration · · · OH F HO · · · . In F^--rich chains containing only a few $[OH]^-$ one anticipates a fourth distinguishable situation, (4), in which the F-bonded $[OH]^-$ is in an asymmetrical configuration, · · · F F OH F F · · · .

RESULTS

Figure 2 illustrates the changes occurring in the O–H stretching region at *ca.* 3 600 cm^{-1} when increasing amounts of F^- are introduced into hydroxyapatite. The first set (*a*) of five spectra from hydroxyapatite containing 0, 3, 6, 10, and 19% F was normalised to the height of the component at 3 573 cm^{-1}. The second set (*b*) of spectra from hydroxyapatite with 31, 51, 66, 76, and 95% F was normalised to the height of the component at 3 540 cm^{-1}. As the OH content decreased (sample weight constant at 3.0 mg), the noise level increased noticeably for the last spectrum of nearly pure fluoroapatite containing only 5% OH).

While pure hydroxyapatite has only one O–H stretching band at 3 573 cm^{-1} as predicted by the factor-group analysis,[5] the introduction of F^- caused two new bands to appear at 3 643 and 3 544 cm^{-1}. Already at 31% F, the latter band,

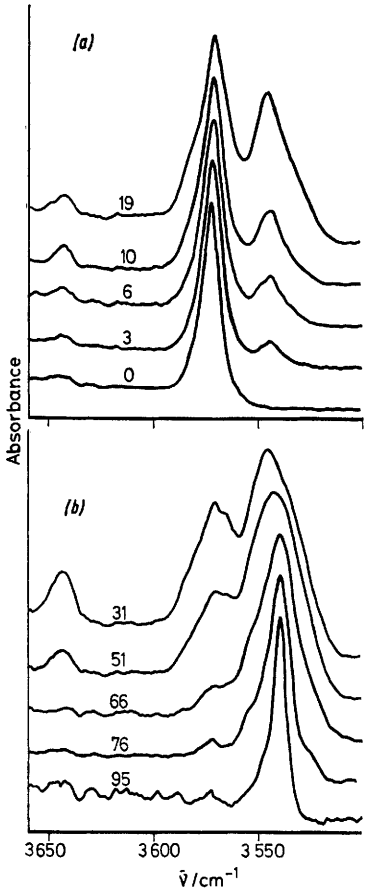

FIGURE 2 The OH stretching-band region of apatite solid solutions. For normalisation of (*a*) and (*b*) see text

now lying at 3 546 cm^{-1}, had a larger relative intensity. It was a comparatively broad band and appears to be composed of at least two unresolved components. As the amount of F was further increased so that finally only a few $[OH]^-$ will be dispersed in a chain composed mainly of F^-, this band sharpened and shifted again to lower wavenumbers, 3 540 cm^{-1} for 95% F. The behaviour of the

[14] J. C. Elliott, *J. Dent. Res.*, 1962, **41**, 1251.

weak band to higher wavenumber at 3 643 cm^{-1} is peculiar. It was present only in the solid-solution spectra, going through an intensity maximum at *ca.* 31% F.

Figure 3 gives a compilation of the spectra in the 500—800 cm^{-1} region showing the complexity for the various apatite solid solutions. All the spectra in Figure 3 are on an identical intensity scale, so that the areas under the bands can be directly compared. The two strong bands at 601 and 571 cm^{-1}, which are purposely off scale, are due to the ν_4 mode of the PO_4 tetrahedra. They are quite obviously unaffected by the OH/F substitution along the chains. The valley · · · OH OH OH OH OH · · ·. The continuous displacement and intensity decrease of this band on introduction of F is shown in Figure 4, which is an enlargement of the 620—655 cm^{-1} region in Figure 4. In the range 0—19% F this band shifts continuously from 631 to 637 cm^{-1} without apparent change in shape or half-width ($\nu_{\frac{1}{2}} \simeq 15$ cm^{-1}). The constant half-width shows that the F^- are more or less evenly distributed along the OH chains with no tendency to form clusters. For the sample containing 31% F this band seems to split into two maxima at

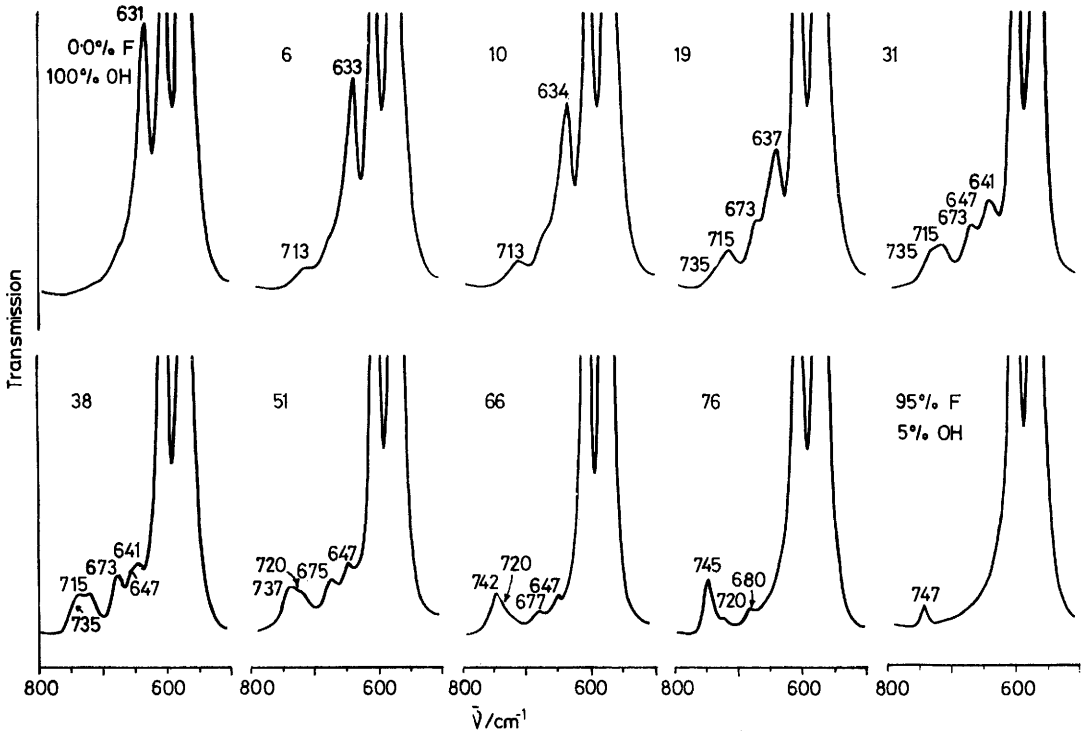

FIGURE 3 The OH librational-band region assigned to the Ca_3–OH bending mode for apatite solid solutions

between the two bands may serve as a convenient internal intensity reference. The most prominent feature of Figure 3 is that the band at 631 cm^{-1} assigned to the Ca_3–OH librational mode markedly shifts to higher wavenumbers and decreases in intensity as more F is introduced. Other weak bands appear, but only one survives in the 95% F spectrum, the weak band at 747 cm^{-1}. A detailed discussion of these spectra is given in the next section.

DISCUSSION

The Ca_3–OH *Librational Mode.*—The spectra in Figure 3 show that the band at 631 cm^{-1} shifts, and new bands appear nearby, when F^- ions are introduced into the OH chain of hydroxyapatite. These bands are related to the three or four distinguishable type of $[OH]^-$ predicted above. First we discuss the behaviour of the band at 631 cm^{-1}.

This band in pure hydroxyapatite is due to the OH librational mode where the $[OH]^-$ forming the apex of the flat Ca_3–OH trigonal pyramid executes a bending motion. The band is characteristic of the undisturbed OH chain, 641 and 647 cm^{-1}, of which only that at 647 cm^{-1} survives until 66% F.

The fact that the band at 631 cm^{-1} reacts so sensibly to the presence of F^- in the $[OH]^-$ chain indicates strong coupling between the OH dipoles along the OH chain. Three percent F means that, on average, about every 30th $[OH]^-$ is replaced by an F^-. This corresponds to a mean distance between fluorines of *ca.* 100 Å. The band at 631 cm^{-1} is undoubtedly due to the librational mode of the $[OH]^-$ surrounded by $[OH]^-$ in an infinitely long OH chain. As this chain decreases in length, the band at 631 cm^{-1} shifts. We can write down the shortest possible chain sections which still contain three, two, or one $[OH]^-$ ions in an OH surrounding: (*a*) · · · HO:OH *OH OH OH* OH F · · ·; (*b*) · · · HO:OH *OH OH* OH F · · ·; and (*c*) · · · HO:OH *OH* OH F · · ·. The italicised $[OH]^-$ are the only ones in these chain sections which are neither bonded to an F (right) nor part of a ' tail-to-tail ' configuration (left).

We assign the band at 647 cm^{-1} to the central $[OH]^-$

in the chain section (*c*), that at 641 cm^{-1} to the two central $[OH]^-$ in the section (*b*), possibly that at 637 cm^{-1} to the three central $[OH]^-$ in the section (*a*), and so on with increasing chain length and decreasing relative shifts. An analogous case would be the wavenumber dependence of the CH_2 rocking mode in paraffin chains $R[CH_2]_nR$. For long chains, $n \geqslant 4$, the CH_2 rocking lies at or slightly

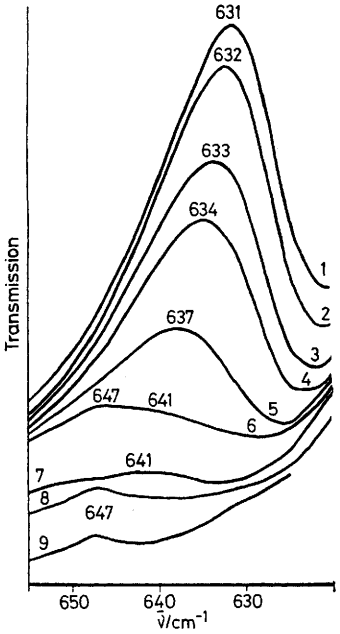

FIGURE 4 Change and shift of the band at 631 cm^{-1} of hydroxyapatite on introduction of F^- (0—66%) into the linear $[OH]^-$ chains

below 724 cm^{-1}, for $n = 3$ it shifts to 726—729 cm^{-1}, and for $n = 2$ it falls between 734 and 785 cm^{-1} depending on the nature of R.[15]

The next band in the spectra of Figure 3 which is rather easily assigned is that of 747 cm^{-1} of the apatite containing 95% F. In this case one may rightly assume that the last few $[OH]^-$ ions are evenly dispersed in the F chain. This gives the configuration · · · F F OH F F · · · and, hence, the assignment of the band at 747 cm^{-1} to single $[OH]^-$ in an extended F chain. The relatively high intensity of this band, noticeable also in the spectrum of the 76% F sample, supports this assignment. A single $[OH]^-$ between two F^- may adopt two orientations, · · · F OH F · · · or · · · F HO F · · ·, and may switch from the one to the other with a comparatively low energy barrier. Consequently the oscillator strength for the OH librational mode will be increased due to the large change in dipole moment when the librational quantum number increases. The band at 747 cm^{-1} also shifts as a function of the F^- content, going as low as 735 cm^{-1} in the samples containing <50% F. In this case the length of the F sections along the chains seem to cause the shift.

The spectra in Figure 3 also show that with decreasing F content a band at 720 cm^{-1} appears, overtakes the band at 735 cm^{-1}, and then disappears again for vanishing F contents. Its position varies from 713 cm^{-1} for low to 720 cm^{-1} for high F contents. Another band which shows the same behaviour is a shoulder which develops at *ca.* 673 cm^{-1} at low F content, becomes a band shifting to 680 cm^{-1}, and disappears at high F content. Both bands, at 720 and 680 cm^{-1}, have therefore to be assigned to configurations present only in apatite solid solutions of intermediate compositions. The proximity of the band at 720 cm^{-1} to that at 735—747 cm^{-1} which is due to the · · · F OH F · · · configuration suggests that the former band arises from the first step towards chain formation, · · · F OH:OH F · · ·, with a pair of $[OH]^-$ ions bonded directly to two F^-.

The last band to be assigned is that at 673—680 cm^{-1}. The only configuration which is still available is the ' tail-to-tail ' · · · HO:OH · · · in an OH chain of variable length.

In Figure 5 the possible chain configurations are schematically represented omitting all non-symmetrical arrangements except for · · · F OH F · · ·. The assignments discussed in this section are indicated. The range of the band position is given in cm^{-1} such that the last number refers to the band position in the sample with the higher F content. It should be noted that, even in pure hydroxyapatite, bands at *ca.* 675 and 715 cm^{-1} can be seen as very weak features, especially if one takes difference spectra

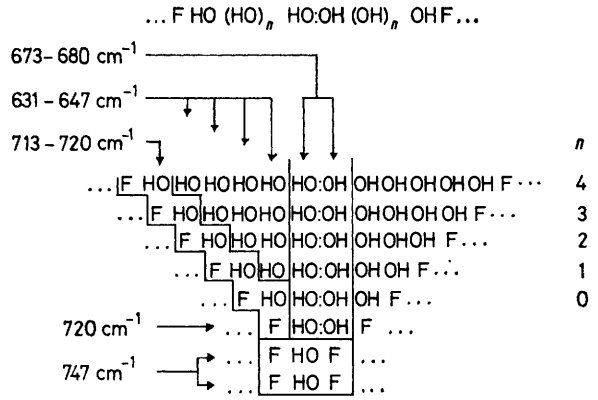

FIGURE 5 Schematic representation of the different possible types of (OH, F) configurations along the linear chains of the apatite structure, with band assignments

by subtracting the spectrum of pure hydroxyapatite from that of fluoroapatite. Those very weak bands might be due to the presence of O^{2-} ions which are likely to behave like F^- ions in the chain, causing ' tail-to-tail ' configurations and giving $[OH]^- \cdots O^{2-}$ interactions.

The OH *Stretching Vibration.*—As shown in Figure 2, the complexity of the Ca_3–OH librational modes has its counterpart in the O–H stretching region. Both pure hydroxyapatite and fluoroapatite containing only a few $[OH]^-$ have one sharp OH stretching band at 3 573 and 3 540 cm^{-1} respectively. The band at 3 573 cm^{-1} is of course the one i.r.-active O–H stretching mode predicted by the factor-group analysis for the undisturbed OH chain · · · OH OH OH OH OH · · ·. The band at 3 450 cm^{-1} must be due to the O–H stretching of an

[15] N. B. Colthup, L. H. Daly, and S. E. Wiberley, ' Introduction to Infrared and Raman Spectroscopy,' Academic Press, New York, 1964, p. 197.

isolated $[OH]^-$ dispersed in a F chain, · · · F F OH F F · · ·.

At low F contents (0—19%) one new band grows at 3 643 cm^{-1}, shifted to higher wavenumbers. This indicates a stiffening of the O–H bond such as one might expect for the ' tail-to-tail ' configuration, · · · HO:OH · · ·. Indeed, this band at 3 643 cm^{-1} first increases in intensity with increasing F content, then decreases again, and vanishes above 50% F as one would expect for the · · · HO:OH · · · configuration. Yet, there is some discrepancy in comparison with the band at 680 cm^{-1} which was also assigned to the ' tail-to-tail ' configuration: the band at 680 cm^{-1} remains as a shoulder up to 76% F.

The band at 3 540 cm^{-1} is sharp and narrow only for the 95% F sample. Its half-width is *ca.* 9 cm^{-1}, but increases rapidly to 30 cm^{-1} at 51 and 31% while at the same time the maximum shifts to 3 546 cm^{-1}. This indicates that the band at 3 540—3 546 cm^{-1} has at least two components, probably more. It appears to be safe to assign this band to $[OH]^-$ bonded directly to F^- in any of the OH F^- configurations shown in Figure 5. The band at 3 573 cm^{-1} on the other hand, which shifts slightly to 3 571 cm^{-1} with increasing F content, may be assigned to $[OH]^-$ ions which are not directly adjacent to either F^-, or to a ' tail-to-tail ' configuration. This band is broadened from 10-cm^{-1} halfwidth at 0% F to 15 cm^{-1} at 19% F. The band shape suggests some further components which, however, cannot be resolved.

In conclusion, the three most distinguishable configurations derived for the OH–F chain [(1) undisturbed OH, (2) OH bonded to F, and (3) ' tail-to-tail '] can also be found in the region of the O–H stretching vibration, however with less resolution than in the region of the Ca_3–OH librational modes.

Conclusions.—Both the Ca_3–OH librational and the O–H stretching band of hydroxyapatite at 631 and 3 573 cm^{-1} respectively sensibly react to the introduction of F^- into the linear OH chains. In particular, the band at 631 cm^{-1} shifts markedly to higher wavenumber, ultimately to 647 cm^{-1}, and decreases in intensity. In addition, new bands appear nearby. Three, possibly four, bands or band components can be distinguished. They have been assigned to different configurations expected to be present in the chains containing $[OH]^-$ and F^- in various proportions. The four types are: (1) OH with OH neighbours only, · · · OH OH OH · · ·; (2) OH in the ' tail-to-tail 'configuration, · · · HO:OH · · ·; (3) OH bonded to one F, · · · OH OH F · · ·; and (4) OH surrounded by F only, · · · F OH F · · ·. The shifts observed mainly for the band at 631 cm^{-1} can be correlated with the average number of OH of the same configuration in the chain section between F ions, generally · · · F HO $(HO)_n$ HO:OH $(OH)_n$ OH F · · ·. The partly resolved bands at 647 and 641 cm^{-1} have been assigned to chain sections with $n = 1$ and 2 respectively.

We thank Dr. R. M. H. Verbeek of the Rijksuniversiteit in Ghent, Belgium, who kindly provided the samples, and the Bayer AG, Leverkusen, in particular to Dr. G. Bayer and H. Devrient who ran the i.r. spectra.

[6/2151 *Received*, 22*nd November*, 1976]