

Aggregate model for the vibrational properties of hydroxyapatites

M. Vallejo¹, M. Rada², L. Buelta³, I. Cabria⁴, F. Rodríguez⁵, and A. Mañanes¹

¹Departamento de Física Moderna, Universidad de Cantabria, 39005 Santander, Spain

²Instituto Cántabro de Estadística ICANE, 39008 Santander, Spain

³Departamento de Ciencias Médicas y Q., Universidad de Cantabria, 39011 Santander, Spain

⁴Departamento de Física Teórica, Atómica y Óptica., Universidad de Valladolid, 47011

Valladolid, Spain

⁵Departamento CITIMAC, Universidad de Cantabria, 39005 Santander, Spain

angel.mananes@unican.es

The infrared spectrum, IR, of the relevant biological material hydroxyapatite HA, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, is calculated using Density Functional Theory DFT to describe the electronic structure of the compound. The inorganic component of human bone is not pure HA but a poorly crystalline biological apatite containing numerous trace ions, the most abundant of which are carbonate, $(\text{CO}_3)^{2-}$ and acid phosphate, $(\text{HPO}_4)^{2-}$. It is then relevant to characterize the changes in the infrared spectra of pure HA due to the substitution of some phosphate groups by carbonate, for example, a process which is related with bone maturity.

As has been indicated in previous works [1, 2], the crystalline solid HA can be considered as a solid “made of clusters”, like for example some intermetallic compounds [3]. In the case of HA, the relevant structures are the, approximately tetrahedral, phosphate groups, with a charge $-3e$ and that maintain their structure inside the crystal, which are surrounded by the Ca^{2+} ions and the hydroxyl groups, OH^- . Following this suggestion, we have considered different finite clusters, which involve always six phosphate groups but different numbers of Ca and OH ions, to calculate the vibrational spectrum to be compared with the measured infrared spectra. To calculate the vibrational properties, a complete relaxation of the geometrical structure of the clusters has been performed by steepest descent methods.

The electronic structure is calculated by solving the Kohn-Sham equations of DFT, within the Local Spin Density Approximation, LSDA, for the exchange-correlation energy, using the Amsterdam Density Functional, ADF 2008.01, code [4]. This method uses Slater type orbitals localized at the atoms of the aggregate as basis sets, and it calculates bonding energies with respect to restricted atomic fragments. The dynamical matrix is obtained using analytical first derivatives of the binding energy.

Firstly, we have calculated the electronic structure of the cluster $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, in the geometry of the unit cell, and with a field of point charges located at the lattice points of the nearest 26 unit cells of hydroxyapatite surrounding the cluster, and considering in these extra unit cells charge $+2e$ at the Ca atoms, charge $-3e$ at P and charge $-1e$ at the O atom of the OH group. The electronic density of states DOS shows in this model the same main features which have been obtained in DFT calculations of the crystalline solid [1]. Secondly, the following free clusters have been considered as a model for the vibrational properties of HA: c1) $\text{Ca}_{24}(\text{PO}_4)_6(\text{OH})_4$, c2) $\text{Ca}_{14}(\text{PO}_4)_6(\text{OH})_4$, c3) $\text{Ca}_{12}(\text{PO}_4)_6(\text{OH})_4$, c4) $\text{Ca}_{12}(\text{PO}_4)_6(\text{OH})_2$ and c5) $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$. From larger to smaller clusters, we have chosen the six phosphate groups which are closer to the axis of the hexagonal channel formed by Ca atoms. The OH groups are located in this axis [1]. In each cluster, they are retained only those Ca atoms which remain closer to the six phosphate groups. For each aggregate, a complete optimization of the geometry is performed before the calculation of the electronic and vibrational densities of states. The clusters considered have always an inversion centre, so the calculation clearly separates infrared modes from the Raman active frequencies.

Charge population analysis, including Mulliken, Hirshfeld and Voronoi charges, and the study of the geometrical parameters allow for the comparison of the structure of the phosphate groups in the different clusters considered, and also with the free, neutral and charged, phosphate. The results indicate that, as expected, the structure is quite stable and rather

independent of the actual environment in the finite cluster. However, some distortions and differences are found when compared with the free phosphate structure.

The structure of the calculated electronic DOS for all the clusters resembles that of the HA crystal (Ca and phosphate dominated bands of electronic states). However, finite size effects show up at the Fermi level, producing a smaller band gap.

The calculated infrared vibrational spectra of all the clusters show the two bands associated to the normal modes of the free phosphate: One band around $\nu=1000\text{ cm}^{-1}$, associated to the asymmetric stretching mode, and another one at $\nu=500\text{ cm}^{-1}$, corresponding to the bending mode. Furthermore, the high frequency stretching mode of the OH group is also obtained at $\nu=3500\text{ cm}^{-1}$. The infrared spectrum of the smaller cluster c5 is given in Figure 1.

The biological processes induce the substitution of some phosphate groups of the HA by carbonate CO_3 groups. Alternatively, the carbonate group can also substitute the OH group. The influence of these two substitutions in the vibrational infrared spectrum of the HA has been analyzed in our case using the smaller cluster c5, and the infrared spectrum is given in Figure 2.

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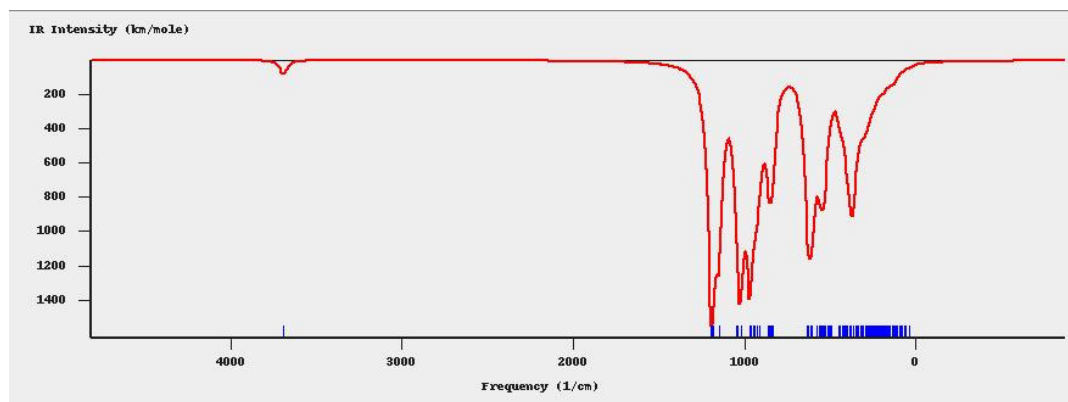


Figure 1: Calculated infrared spectrum for the cluster c5 $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$.

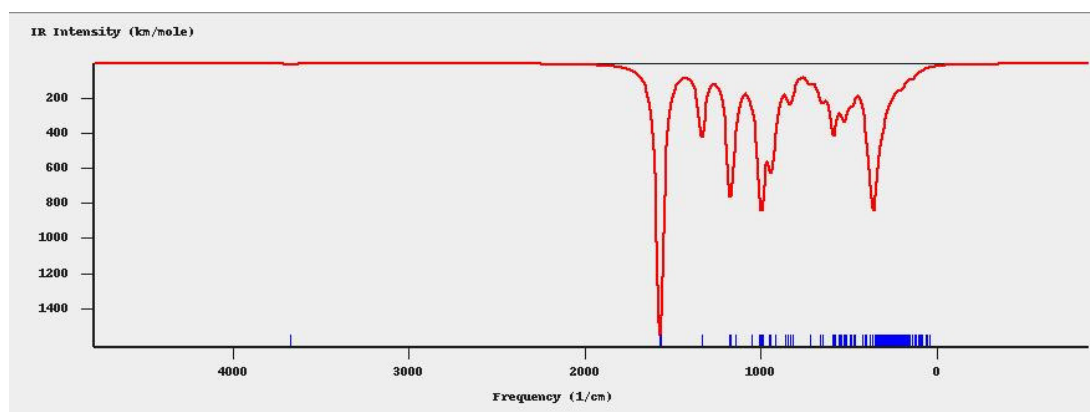


Figure 2: Calculated infrared spectrum for the cluster $\text{Ca}_{10}(\text{PO}_4)_4(\text{CO}_3)_2(\text{OH})_2$.