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Molecular Orbital Calculation on the Configuration of Hydroxyl Group in Hexagonal Hydroxyapatite

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ABSTRACT

The possible configurations of hydroxyl group in hexagonal hydroxyapatite were identified through molecular orbital calculation. The molecular orbital interaction between O and H in hydroxyl column was analyzed using charge variation and Bond Overlap Population (BOP). We supposed 5 kinds of O-H bond configurations as cluster types of I, II, III, IV, and V. Mulliken's population analysis was applied to evaluate ionic charges of O, H, P, and Ca ions, and BOPs (Bond Overlap Populations) in order to discuss the bond strength change by the atomic arrangement. The stability of each O-H bond configuration was analyzed using bond overlap and ionic charge.

Key words : Hydroxyapatite, Molecular orbital, Bond configuration

1. Introduction

Through molecular orbital calculations using Discrete Variational (DV)-Xα method the possible configurations of hydroxyl groups in hexagonal hydroxyapatite were identified, and the molecular orbital interaction between O and H in hydroxyl column was analysed using charge variation and Bond Overlap Population (BOP).

Hydroxyapatite[HAp], with composition of $Ca_{10}(PO_4)_6(OH)_2$, is of considerable interest as an excellent material for artificial bone and teeth because of its biocompatibility.[1] In general apatites can incorporate numerous impurities of F, Cl, CO_3, Zn, Fe, and so on., and have various degree of nonstoichometry such as $Ca_{10-x}(HPO_4)_x(PO_4)_{6-x}(OH)_{2-x} \cdot nH_2O$, Ca/P = 1.67.[2] The biological bone is known as a dirty structure material, but the above incorporated impurity and the nonstoichiometry is intimately related with the characteristics of each bone component such as long bone, jaw bone and tooth. The structure of HAp has been well studied[2,3] for several decades and especially the hydroxyl group has an important property in biological aspect. In hexagonal HAp there is a long range disordering of the hydroxyl groups along the c-axis of hexagonal lattice[3] and a short range ordering is expected.[3,4] In monoclinic phase of HAp the hydroxyl ions are ordered in the c-axis. So, the phase transition of triclinic phase to hexagonal phase is said to the order-disorder transition. We have tried to figure out the possible configurations of O-H in hydroxyl column of hexagonal phase through the molecular orbital energy calculation. Recently some possible configurations of the hydroxyl groups in hexagonal HAp were proposed using density functional theory calculations.[5] Here we report some additional considerations.

2. DV-Xα Calculation and Cluster Model

Molecular Orbital (MO) calculation is one of the effective methods to analyze the chemical property of HAp by simulating the electronic states of a system having three-dimensional atomic arrangement. The electronic states of the figured model clusters of hexagonal hydroxyapatite crystal were calculated by using a DV-Xα method.[6-9] The net charge and Bond Overlap Population (BOP), which were derived by Mulliken population analysis, give the useful information to evaluate the bond formation. We used a PC-version software for DV-Xα calculation, which was supplied by DV-Xα Association Japan (http://dvworld.northwestern.edu/).

The crystal structure of hexagonal HAp has been described in the space group P63/m (No. 176) with lattice parameters $a = b = 9.432$ Å and $c = 6.881$ Å. Hydrogen atoms are located on the triangle of O atoms, which belong to PO_4^{3-} ions. Based on the reported data as shown in Table 1, we built up a cluster model as shown in Fig. 1. Because of the crystallographic mirror symmetry imposed by the space group, each OH ion has to be considered at statistically disordered positions (4e) both above and below the mirror planes at z = 1/4 and 3/4. An averaged structure could imply that in approximately half the unit cells the OH ions are pointed upward from the mirror plane and in the remaining unit cells they are pointed downward. It has been shown by neutron diffraction studies[4] that the oxygen atoms in

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Table 1. The Symmetry Data for Hydroxyl Group Configuration in the Hexagonal Hydroxyapatite Structure[10]

Space group	x	y	z	Note
Parameter, site				
Ca1, 4f	1/3	2/3	z	(z=0.0012)
Ca2, 6h	u	v	1/4	(u=0.2471)(v=0.9926)
O1, 6h	u	v	1/4	(u=0.3289)(v=0.4848)
O2, 6h	u	v	1/4	(u=0.5858)(v=0.4649)
O3, 12i	x	y	z	(x=0.3424)(y=0.2587)(z=0.0688)
O4(H), 4e	0	0	0.1964[10]	(z; O:0.2008, H:0.0617)[5]
P, 6h	u	v	1/4	(u=0.3986)(v=0.3682)

[a]We used two kinds of data[5,10] for O4(H). The O-O distances were 0.682 Å and 0.738 Å, respectively.

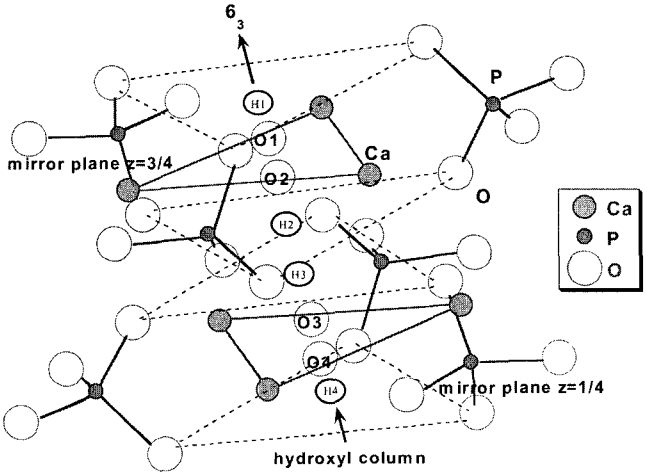

Fig. 1. Cluster structure of the hexagonal hydroxyapatite, showing the positions of the hydrogen and oxygen in the c-direction.

hydroxyl ions are 0.34 Å away from the mirror plane with the O-H direction pointing away from the mirror planes.

We supposed five kinds of O-H bond configurations as cluster types of I, II, III, IV, and V, shown in Table 2. The type VI cluster is a modification of type I cluster. The energy levels for all supposed cluster models were smoothly converged and the calculation was highly sensitive to the initial condition of input data. We put the initial charges of O (O1 – O3 in Table 1), Ca and P as –2, +2, and +5, respectively. On the other hands, the charges of O and H in hydroxyl column were given as –1 and zero, respectively.

The discrete variational Xα (DV-Xα) method, based on the first principle, is one of the MO calculation methods using an Xα potential for the estimation of exchange interaction between atomic orbitals. The Atomic Orbitals (AO) were numerically calculated by the self-consistent charge atomic Hatree-Fock method. Mulliken's population analysis was applied to evaluate ionic charges of O, H, P, and Ca ions, and BOPs (Bond Overlap Populations) in order to discuss the bond strength change by the atomic arrangement. The sign of a total BOP indicates the chemical bonding feature: that is, large positive BOP means the formation of stable and strong covalent bonding, while large negative BOP means the unstable chemical bonding, being impossible to form in a real material. The BOP is a good measure to evaluate the contribution of covalent bonding on the structural stability.

Table 2. O-H Configuration and the Resultant Net Charge

Cluster type	O-H configuration	Net charge		
		O	H	Ca
I	HOOH ■□□■	-0.70	0.61	1.44
II	HO□■ HO□■	-1.31	0.45	1.71
III	□■OH HO□■	-1.27	0.41	1.67
IV	H□O HO□■	-1.12	0.31	1.69
V	HO□■ ■□OH	-1.28	0.42	1.67
VI	HOOH ■□OH	-0.80	0.56	1.44

[a]The symbols of ■ and □ represent a vacancy of hydrogen and oxygen atom, respectively.

3. Results and Discussion

Table 2 shows the resultant net charge after the calculation and Fig. 2 shows BOP values for each of O-H bond and O-Ca bond. A column O ion is coordinated with both of O-H bond having covalent character and O-Ca bond having ionic character. A part of O2p orbital in the O column is hybridized with H1s orbital to make hydroxyl ion, while the other part of O2p orbital is localized in O atom for an ionic interaction with Ca3s/3p orbitals. That is, the column O atom has both character of covalency and ionicity. The charge variation of column O is intimately related with the formation of O-H bond and O-Ca bond. The charge variation for Ca ion is pretty small except type-I cluster showing lower charge value. Type II, III, and V clusters have similar charges for each of O and H. On the other hands, the charge variation of O and H in type I cluster is pretty big and the variation is intermediate in type IV cluster. The column O in type I and type IV clusters has a less amount of electrons in comparison with the afore-mentioned three clusters (II, III, V). Type I cluster has a peculiar charge variation for the related atom species. The electron charge density is largely reduced for each atom of O, H, and Ca.

From Fig. 2 type II, III, and V clusters show the nearly

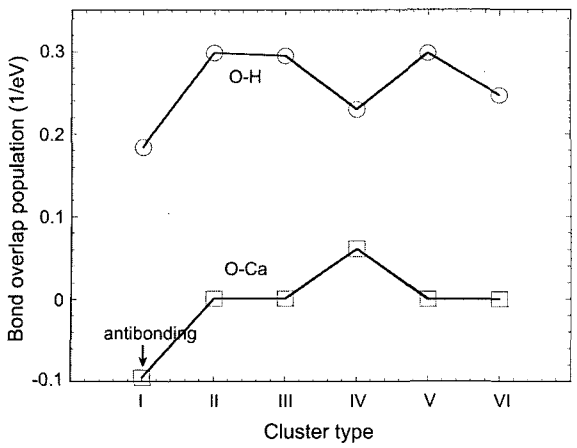

Fig. 2. Bond overlap population for O-H bond and O-Ca bond.

same BOP values for each of O-H bond and O-Ca bond. Type I and type IV clusters show the relatively weak BOP values for O-H bond. Normally negligible BOP values are appeared for Ca-O bond as shown in type II, III, and V cluster, because the main bond character is ionic. However, type IV cluster shows some covalent bond character for O-Ca bond and type I cluster shows an anti-bonding character for O-Ca bond. In type IV cluster the covalent character of O-H bond is weakened and the O-Ca bond contains a covalent character in its ionic orbital. That is, we can say that a part of electrons taken from O and H atoms contributes to form a covalent bond between O and Ca atoms. The covalent character of O-H bond for type I cluster is more weakened and the O-Ca bond shows a little bit of anti-bonding character.

The bond character of O-Ca bond is very sensitive to the O-O distance. When we changed the O-O distance in oxygen column from 0.682 to 0.738 Å (Table 1), the BOP values for O-Ca bond were changed from 0.012 to −0.095, respectively. If the distance was close to 0.68 Å the BOP value approached to zero. Type VI cluster contains a configuration feature of type I cluster and it shows a full ionic character for the O-Ca bond. The net charge of O, H, and Ca is very close to the value of type I cluster and the BOP value for O-H bond is lower.

From the above results all proposed cluster model of type I to type V can be one of hydroxyl ion configurations in the hexagonal hydroxyapatite. It seems that type II, III, and V clusters belong to the regular configurations. The formation of type I and IV clusters in hydroxyl column is accompanied by the bigger change of molecular orbitals. It may be hard to say that type I and type IV clusters are less stable. However, we can say that the molecular orbital change in type I and type IV clusters are more severe, leading to the modification of covalent bond and ionic bond for O-H and O-Ca, respectively.

If a monoclinic HAp is heated to 1000°C, the crystal type is changed to hexagonal phase (a = b = 9.4646, c = 6.9100).[10] The calculation result for the type-I cluster showed an anti-bonding character from the BOP value (−0.010). The expansion of the crystal led to the formation of anti-bonding orbital in O-Ca bond, which is only favorable under an activated condition. A part of the O2p orbital in hydroxyl column may be overlapped with Ca3s/3p orbitals through the orbital hybridization. This orbital overlap leads to the bonding hybridization in type IV cluster and the anti-bonding hybridization in type I cluster at high temperature. At least the stability of type-I cluster highly depends on the crystal property of HAp and the environment.

There has been some experimental works on the hydroxyl ion vacancies in the apatites using deuteration and ESR technique.[11,12] The OD ions can diffuse into the OH- ions along hydroxyl column in hyroxyapatite and the disordering of hydroxyl ions is well influenced by the environment such as temperature and atmosphere. The type of hydroxyl ion configuration seems to be changed by the environment, and the combination of the cluster types in a short range may also be sensitively influenced. The ordering combination by the proposed clusters will be more important to understand the property of hydroxyapatite. In these calculations the model clusters were limited on the pure hydroxyapatite crystal, but the apatite crystal in a biological bone is a dirty component, which may contain various kinds of cation substituents, anion defects and anion substituents. Acid dissolution in dental caries in human tooth enamel takes place preferentially along the c-axis direction,[13] because the vacancies and the disorder of OH ions in the hydroxyl ion channel are expected to provide easier passing site for diffusion. Especially CO_3^{2-} can replace OH^- (A-type carbonate) and PO_4^{3-} (B-type carbonate), and the substitution may be directly related with the local ordering of hydroxyl ion configuration.

4. Conclusions

The calculation result for the type-I cluster showed an anti-bonding character from the BOP value (−0.010) and the expansion of the crystal led to the formation of anti-bonding orbital in O-Ca bond. The bond stability of the above clusters by the introduction of substitutional ions such CO_3^{2-} for OH^- (A-type carbonate) and PO_4^{3-} (B-type carbonate) will be discussed further.

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