



Effect of mechanical stress on the Raman and infrared bands of hydroxylapatite: A quantum mechanical first principle investigation



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ABSTRACT

The calcium apatite minerals are among the most studied in the biomaterial field because of their similarity with the mineral phase of bone tissues, which is mainly the hexagonal polymorph of hydroxylapatite. Given the growing interest both in the microscopic processes governing the behaviour of these natural biomaterials and in recent experimental methods to investigate the Raman response of hydroxylapatite upon mechanical loading, we report in the present work a detailed quantum mechanical analysis by DFT/B3LYP-D* approach on the Raman and infrared responses of hydroxylapatite upon deformation of its unit cell. From the vibrational results, the piezo-spectroscopic components $\Delta\nu = \Pi_{ij}\sigma_{ij}$ were calculated. For the first time to the authors' knowledge quantum mechanics (QM) was applied to resolve the piezo-spectroscopic response of hydroxylapatite. The QM results on the uniaxial stress responses of this phase on the piezo-spectroscopic components Π_{11} and Π_{33} of the symmetric P–O stretching mode were $2.54 \pm 0.09 \text{ cm}^{-1}/\text{GPa}$ and $2.56 \pm 0.06 \text{ cm}^{-1}/\text{GPa}$, respectively (Raman simulation) and $2.48 \pm 0.15 \text{ cm}^{-1}/\text{GPa}$ and $\Pi_{33} = 2.74 \pm 0.08 \text{ cm}^{-1}/\text{GPa}$, respectively, of the asymmetric P–O stretching (infrared spectroscopy simulation). These results are in excellent agreement with previous experimental data reported in literature. The quantum mechanical analysis of the other vibrational bands (not present in literature) shed more light on this new and very important application of both Raman and IR spectroscopies and extend the knowledge of the behaviour of hydroxylapatite, suggesting and addressing further experimental research and analytic strategy.

1. Introduction

The calcium apatite phases are the most studied in the biomaterial field because of their similarity with the mineral phase of human hard tissues, which is mainly made of the hexagonal polymorph of hydroxylapatite (OHAp, space group $P6_3/m$) (Corno et al., 2010; Dorozhkin, 2009). From the geo-mineralogical point of view, as an earth crust mineral, OHAp occurs as a thermodynamically more stable monoclinic structure [space group $P2_1/b$] (Suda et al., 1995). In theoretical analysis of the hexagonal polymorph, the unphysical replica of the hydroxyl groups due to the mirror plane requires to reduce its internal symmetry from $P6_3/m$ to $P6_3$ (see Fig. 1) (Corno et al., 2006; Ulian et al., 2013a). Aside from the different internal symmetry and the doubled b parameter, the hexagonal polymorph presents columns of hydroxyl groups aligned along the c -axis with O–H bonds facing the same direction, while the monoclinic cell exhibits O–H columns with alternated orientations (Ma and Liu, 2009).

In recent years, several studies were conducted to investigate the structure of hydroxylapatite-based biomaterials as a function of their stoichiometry (Ulian et al., 2013a, 2014a; Fleet and Liu, 2007, 2003, 2005; Kovaleva et al., 2009; LeGeros, 2002; Morris and Mandair, 2011; Paschalis et al., 1997) and their mechanical properties (Dubey and Tomar, 2008, 2009a, 2009b, 2010; Haverty et al., 2005; Hearmon, 1961; Snyders et al., 2007; Ulian and Valdrè, 2017a). Although the knowledge of this material in the biomedical field is constantly growing, few works were devoted to investigate the nano-microscopic processes governing the behaviour of natural biomaterials (i.e., bone and teeth tissues) and how the microstructure of synthetic biomaterials (for example, ceramic oxides) affects the failure of artificial joints (Pezzotti, 2005a, 2005b; Pezzotti et al., 2017).

The macroscopic phenomenology of the structural evolution of natural and synthetic biomaterials, for example bone remodelling and demineralization, surface wear, or delamination in prosthetic joints, can be easily observed and classified, but only in recent years the nano-

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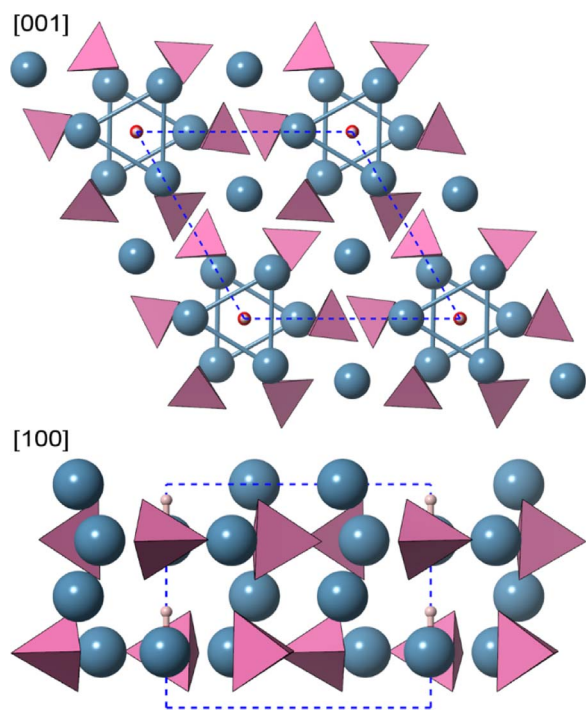


Fig. 1. Hydroxylapatite unit cell (space group $P6_3$) viewed along the [001] and [100] directions. Colour coding for atoms/groups: Ca – cyan, PO_4 – magenta, O – red, H – white.

microscopic factors behind these processes began to be rationalized in a satisfactory extent. To this aim, Raman spectroscopy was employed by an increasing number of researchers in the study of biomaterials, for instance (Bertoluzza et al., 1994; Penel et al., 2005, 1998; Tsuda and Arends, 1994; Tsuda et al., 1996). Furthermore, very recently innovative Raman imaging of local spectroscopic changes was used with considerable advantage in analysing the elementary mechanical processes behind the macroscopic structural behaviour of both natural and synthetic biomaterials (Pezzotti, 2005a, 2005b, 2005c, 2008; Pezzotti et al., 2017). The Raman spectroscopic tool has the considerable advantage of being sensitive to both the mineral and organic components of natural biomaterials, thus allowing the assessment of each individual component's properties. Many synthetic biomaterials of wide usage (e.g., hydroxylapatite, zirconia, polyethylene, etc.) possess a good Raman sensitivity and their vibrational spectra present useful bands that can be used to obtain structural information at the molecular level. Finally, being Raman (and infrared) spectroscopy extremely sensitive to variations in the local environment of vibrating molecular groups, it can be used to understand both stoichiometry and deformations due to stress in natural and synthetic biomaterials. By employing automatized procedures for promptly obtaining maps of piezo-spectroscopic ultra-structures of biomaterials, Raman piezo-spectroscopy has been elevated to the level of a tool for “stress microscopy” (Pezzotti, 2005c).

However, this novel approach needs several information at atomic level to effectively calibrate the Raman (and infrared, IR) spectroscopic response for each (natural/synthetic) biomaterial under “stress” investigation.

To extend the knowledge of the mechanical behaviour of hydroxylapatite, to suggest and foster further experimental research and to help the experimentalist interested in this kind of Raman/IR investigation on both natural and synthetic biomaterials, we report in the present work a detailed quantum mechanical analysis of the Raman and infrared responses of hydroxylapatite upon deformation of its unit cell. The quantum mechanical tools have proven their capability in dealing with structural, vibrational and mechanical analyses of different solid systems (Pierre et al., 2013; Perger, 2010; Tosoni et al., 2005; Ulian et al., 2014b, 2013b; Ulian and Valdrè, 2015a). The presented results

could be of great help for experimental researchers to clarify how the vibrational modes answer to the mechanical loading applied to hydroxylapatite and, ultimately, for calibrating the methods to analyse the residual stress in this kind of (bio)material.

2. Computational approach

This study was conducted by first principle simulations on periodic systems, using the CRYSTAL14 code (Dovesi et al., 2014), which implements the Hartree–Fock and Kohn–Sham self-consistent field method. The graphical drawings have been carried out with the molecular graphics software VESTA (Momma and Izumi, 2011). The analysis of the vibrational (IR and Raman) modes has been conducted using the MOLDRAW software (Ugliengo et al., 1993).

2.1. Basis set

Multielectron wave functions are constructed as an antisymmetrized product (Slater determinant) of mono-electronic crystalline orbitals (CO) that are linear combination of local functions (atomic orbitals, AO) centred on each atom in the system. In turn, atomic orbitals (basis set) are linear combinations of Gaussian-type functions (GTF). We employed the same all-electron basis sets adopted in our previous work on the bulks of OHAp and carbonated hydroxylapatite (Ulian et al., 2013a, 2014a, 2016; Peccati et al., 2014), which provided structural and vibrational (IR and Raman) results in very good agreement with the experimental findings. The calcium has been described with a 86–511 G(2d), with outer shell exponents $\alpha_{sp} = 0.453 \text{ bohr}^{-2}$, $\alpha_{d1} = 3.1910$ and 0.8683 bohr^{-2} and $\alpha_{d2} = 0.2891 \text{ bohr}^{-2}$. The phosphorus atom is described by the basis 85–21 G(d), $\alpha_{sp} = 0.48105 \text{ bohr}^{-2}$ and $\alpha_d = 0.135$ and $0.74583 \text{ bohr}^{-2}$, respectively. Oxygen and hydrogen are both represented by a 6–31 G* basis set with the outer shell exponents $\alpha_{sp} = 0.2742$ and 0.190 bohr^{-2} and $\alpha_d = 0.538 \text{ bohr}^{-2}$; and $\alpha_{sp} = 0.1613$ and $\alpha_p = 1.1 \text{ bohr}^{-2}$, respectively.

2.2. Hamiltonian and computational parameters

The Becke (Becke, 1993) three-parameter (B3LYP) hybrid exchange functional in combination with the gradient-corrected correlation functional of Lee et al. (1988) has been adopted for all calculations and is already widely and successfully used, especially in solid state calculations (Dovesi et al., 1991; Pascale et al., 2004; Prencipe et al., 2004). The presence of some fraction of exact exchange increases the electronic localisation, which in turn increases the ionic nature of the materials, causing a systematic decrease of the lattice parameters and an increase of the elastic constants and bulk moduli. The exchange–correlation contribution is performed over a grid of points and is the result of a numerical integration of the electron density and its gradient. The adopted pruned grid is given by 75 points and 974 angular points (XLGRID) and obtained from The Gauss–Legendre quadrature and Lebedev schemes (Prencipe et al., 2004). This is a good compromise between accuracy and cost of calculation for geometry optimization and vibrational frequencies. The tolerance thresholds that control accuracy of the Coulomb and exchange integrals were set to 10^{-7} and 10^{-16} , respectively (Dovesi et al., 2014). The Hamiltonian matrix has been diagonalized using a shrinking factor that leads to 12 reciprocal lattice points (k-points). The convergence on total energy was reached when the difference between the energy of two subsequent self-consistent field cycles was less than 10^{-8} Hartree.

A general drawback of all common generalized gradient approximation functionals, including hybrid ones, is their lack of adequate description of van der Waals (dispersive) forces. Since dispersion plays an important role in several chemical systems, in this work we included a semiempirical approach (DFT+D) suggested by Grimme (2006), which adds the following contribution to the calculated DFT energy, used to evaluate dispersive forces:

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