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EFFECT OF CHEMICAL POTENTIAL ON SURFACE CHEMİSTRY OF TITANIUM IMPLANTS: A FIRST PRINCIPLES STUDY

Metin Çalışır[1]*, Salih Akbudak[2]

1. Department of Periodontology, Faculty of Dentistry, Adıyaman University, Adıyaman, Turkey
2. Department of Physics Department, Adıyaman University, Adıyaman, Turkey

ABSTRACT: First principle density functional theory (DFT) calculations about TiSe2, TiO2, TiCa2, TiMg2, TiH2O, TiF4, TiCa3(PO4)2 have been carried out using b-p exchange correlation method. Total energy, spectroscopic constants such as entrophy, inner energy, enthalphy and chemical potential of the system have been obtained. Infrared Raman (IR) spectrums of these systems have been observed. Geometry relaxations have been performed to get the atomic positions of the molecules in equilibrium. Since titanium is very largely used in implant technology, we have interpretted our results according to applicability of these compounds to dental implants. We have seen that TiCa2, TiMg2, TiF4, TiCa3(PO4)2 have close chemical potential values which make these compounds promising in dental implant technology.

KEYWORDS: Ab-İnitio, Density-Functional Theory, Surface Modification, Biomaterials, Nanotec hnology

***Corresponding Author: Dr. Salih Akbudak** Ph.D.
Department of Physics, Faculty of Science and Letters, Adıyaman University, Adıyaman 02040, Turkey * Email Address: sakbudak@adiyaman.edu.tr

1. INTRODUCTION

DFT calculations have gained immense attention in different fields of science such as physics, chemistry, materials science, engineering, biology, dentistry and nanotechnology recently [1-5]. This is due to applicability of DFT to large systems including thousands of atoms as well as nanosystems. Preparing experimental setup for different systems including many atoms is very expensive. So, theoretical studies shed light onto studying different characteristics of the system with expense of computation time [6]. Nowadays, improvements in computer technology and DFT made theoretical studies more appealing. It opens new doors to experimental researchers.DFT is the mostly used theoretical method in Nanotechnology [7]. Nanotechnology can be defined as the science and engineering involved in the design, synthesis, characterization and application of materials and devices whose smallest functional organization in at least one dimension is on the nanometer scale [8]. In nanoscale, surface morphology of materials shows different characteristics compared to bulk size [9].The particle size of biomaterials used in the field of dentistry is decreased to below 100nm [10]. So, nanotechnology will have future medical applications in the field of nanodentistry [11]. The surface properties of biomaterials have a crucial role on the biomaterials and the surrounding host tissue [12]. Interactions between the biomaterials and cells mainly depend on surface features of biomaterials, such as surface topography, physical and chemical characteristics [13].Especially surface morphology of titanium is very important in implant technology which increases the importance of nanotechnology. Titanium (Ti) is used for implantable devices because of its biocompatible oxide surface layer. TiO_2 surfaces have a complex microtopography which increase the bone-to-implant contactand induce osteoblast differentiation *in vitro*. Researches examining the osteoblast response to implant surface showed that hydrophilic surfaces are osteogenic, but TiO_2 surfaces exhibit low surface energy because of adsorbed hydrocarbonsfrom the ambient atmosphere [14]. Surface topography, physical and chemical characteristics of biomaterials are important forbone-to-implant contact. Therefore, studies since the late 1980s have also focused on the osteoconductive nature of hydroxyapatite coatings [15]. The significance of surface chemistry is defined by the specific cellular responses to different bulk metals [16,17]. Some of the newer approaches to changing the reactivity of the pure(c.p.) titanium endosseous implant surface include direct chemical modification of titanium surface [18]. Some of ion treatment, such as flouride, calcium, calcium phosphate etc.,increase the bone-to-implant contact [19,20]. The aim of the study is to determine the effects of different elements on the chemical characteristics of the titanium surface. This will enable us to find a new parameter or molecule that will affect titanium implants positively.

2.MATERİAL AND METHOD

We have carried out self-consistent DFT calculations at b-p level for $TiSe_2$, $TiMg_2$, TiO_2, $TiCa_2$, TiH_2O, TiF_4 and $TiCa_3(PO_4)_2$ molecules. For all calculations def-SV(P) basis sets were used. The vibrational frequency calculations were carried out to obtain Infrared Spectrum of these molecules. For all molecules symmetry group was chosen to be c2v. And convergence criteria for total energy was set to 10^{-6}. Thermodynamic properties such as inner energy, enthalphy, entrophy and chemical potential were obtained. For these thermodynamic calculations initial conditions like temperature, pressure and symmetry were set to 298,15 K, 0,1 MPa and C1 respectively. Before running the self-consistent energy calculations geometry relaxation was done to observe the bond length in equilibrium. For all calculations ORCA program was used [21].

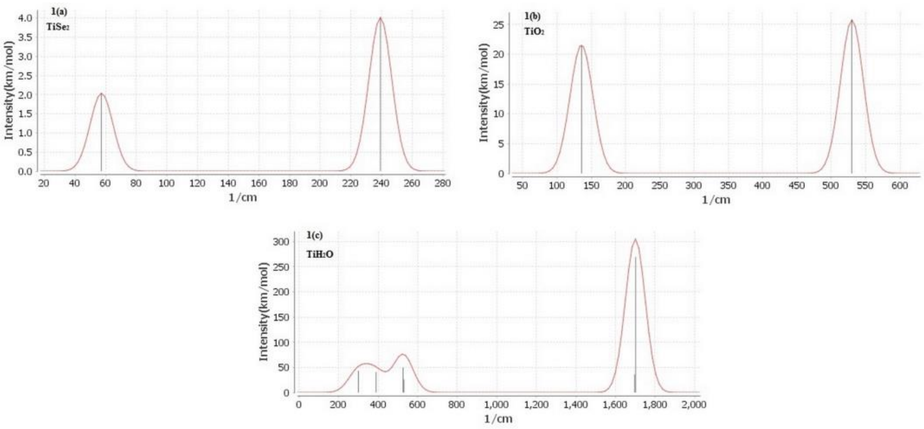
3.RESULTS AND DISCUSSION

Inner energy of $TiSe_2$, $TiCa_2$ and $TiMg_2$ molecules are very close to each other as shown in table 1.

Molecules	Inner Energy kJ/mol	Entalphy kJ/mol	Entrophy kJ/(molK)	Chemical Potential kJ/mol
$TiSe_2$	15.33	17.81	0.28	-64.4
TiO_2	17.33	19.81	0.22	-46.22
$TiCa_2$	15.1	17.58	0.34	-82.68
$TiMg_2$	15.09	17.57	0.33	-80.37
TiH_2O	41.2	43.68	0.28	-40.3
TiF_4	29.58	32.06	0.37	-79.44
$TiCa_3(PO_4)_2$	20.15	22.63	0.39	-93.69

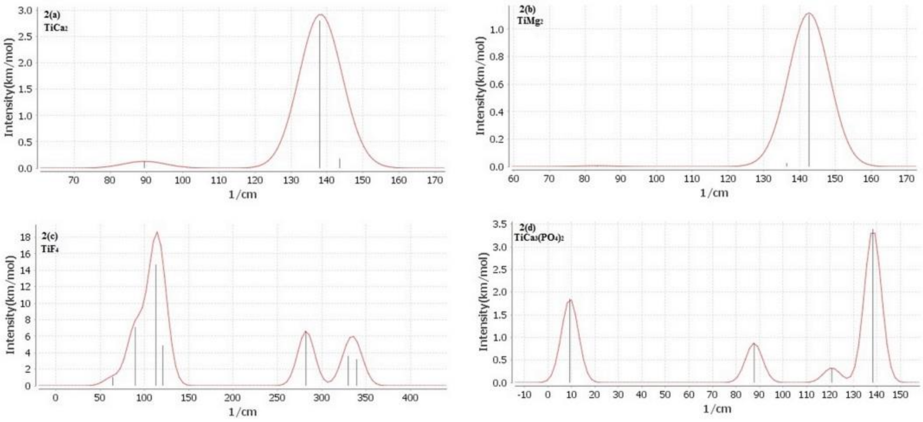
Table 1: Calculated Inner energy, enthalpy, entropy and chemical potential values for $TiSe_2$, TiO_2, $TiCa_2$, $TiMg_2$, TiH_2O, TiF_4, $TiCa_3(PO_4)_2$molecules using DFT at b-p level of theory.

And at the same time from our observation we can conclude that enthalphy values are directly proportional to inner energy values. So corresponding enthalphy values for $TiSe_2$, $TiCa_2$ and $TiMg_2$ molecules are again very close to each other. Chemical potential values for $TiCa_3(PO_4)_2$ and TiF_4 molecules are -79.44 and -93.69 kJ/mol. Chemical potential of $TiCa_2$ and $TiMg_2$ molecules are also close to each other having values -82.68 and -80.37 kJ/mol.



Figs. 1(a)-(c) Relation of intensity with respect to wavelength for $TiSe_2$, TiO_2 and TiH_2O.

Fig. 1(a)-(c) shows the relation of intensity with respect to wavelength for $TiSe_2$, TiO_2 and TiH_2O. In Fig 1(a) there are two peaks at 60cm^{-1} and 240cm^{-1}. Corresponding intensities at these wavelengths are 2.0 and 4.0 (km/mol) respectively. Fig. 1(b) is the graph of intensity with respect to wavelength for TiO_2. In this figure there are two peaks which occur at nearly 140cm^{-1} and 530cm^{-1}. Corresponding intensities at these wavelengths are approximately 22 (km/mol) and 25(km/mol). And wavelengths values are between 0-600cm^{-1}. Fig. 1(c) shows the relation of intensity with respect to wavelength for TiH_2O. There are two small peaks which occur at 300cm^{-1} and 520cm^{-1} and one sharp peak at $1700cm^{-1}$.Approximate intensity values at these peaks are $60cm^{-1}$, $75cm^{-1}$ and $300cm^{-1}$ respectively.



Figs. 2 (a)-(d) Relation of intensity with respect to wavelength for $TiCa_2$, $TiMg_2$, TiF_4, $TiCa_3(PO_4)_2$ molecules. Intensities are in (km/mol) and wavelengths are in (cm^{-1}).

Fig. 2 (a)-(d) shows the relation of intensity with respect to wavelength for $TiCa_2$, $TiMg_2$, TiF_4, $TiCa_3(PO_4)_2$ molecules. Intensities are in (km/mol) and wavelengths are in (cm^{-1}). Fig. 2(a) is the sketch of intensity versus wavelength for $TiCa_2$. From this figure, it is clearly seen that there is one very small peak and one sharp peak. Small peak is observed at approximately $90cm^{-1}$ and has an intensity of 0,2 (km/mol). On the other hand sharp peak occurs at nearly $138cm^{-1}$ and has approximately 3,0 (km/mol) intensity. Fig. 2(b) is the graph of intensity with respect to wavelength for $TiMg_2$. There is only one peak that occurs at $142cm^{-1}$. Intensity at these wavelength is approximately 1,2 (km/mol).Fig. 2(c) is the sketch of intensity with respect to wavelength for TiF_4. There is one sharp peak and two small peaks. These peak occurs at $120cm^{-1}$, $275cm^{-1}$ and $325cm^{-1}$. Corresponding intensities are 18, 6,1 and 6 (km/mol) respectively.Fig. 2(d) is the graph of intensity versus wavelength for $TiCa_3(PO_4)_2$. There are four peaks which ocur at 10, 88, 120 and $138cm^{-1}$. Intensities at these wavelengths are 1,8, 0,8, 0,2 and 3,3 (km/mol) respectively. Based on these results, there was no correlation between intensities and molecules. A rapid progress in Nanotechnology has been seen in the past several decades. Nanomaterials include basic structural units, grains, particles, fibers or other constituent components smaller than 100nm in at least one dimension [22]. Nanotechnology is a multidisciplinary field including the engineering, physics, chemistry and biology. The developing new field of nanotechnology creates various new opportunities for advancing medical science and disease treatment in human health care [23]. Nanotechnology will offernew medical applications in the nanodentistry. Some nanomaterials are investigated in the field of nanodentistry [11]. A new nanodentistry approach isabout the surface modifications of titanium dental implants [24]. A lot of dental implant procedures and types have increased steadily worldwide. Nearly, more than one million dental implantations are applied per year. The clinical success of dental implants is related to early osseointegration [25]. Bone accumulation onto the surface of the titanium is critical for the short- and long-term success of dental implants. There are two types of response after implantation, fibro-osseointegration and osseointegration. The first type leads to clinical failure of the dental implant. The second type of bone response is related to direct bone–implant contact. The second response is desired for the success of implantation. The rate and quality of osseointegration in titanium implants are related to their surface properties as successful as complete surgical procedure [26]. Geometry and surface topography are crucial for the short- and long-term success of oral implants [25]. The chemical composition and features of the materials on the surface of titanium implants are different, depending on their bulk composition. The surface features of implants are critical for protein adsorption and cell attachment [27]. After implantation, dental implants interact with oral biological fluids and tissues [26]. Dentalimplants are usually made from commercially pure titanium (cpTi; graded from 1 to 4) or titanium alloys(Ti6Al4V; grade 5 titanium alloy) [27]. Poor biomaterial may cause implant failure or infection of surrounding tissue [28]. For this reason, some strategies have been investigated in order to improve both the short- and long-term osseointegration of titanium oral implants [26]. Bone surface is highly mineralized with hydroxyapatite (HA) crystals. The surface topography of the bone may be counted as the optimal environment for cellular cells and component [29]. Therefore, investigations since the late 1980s also focused on the osteoconductive structure of hydroxyapatite coatings [15]. Calcium phosphates are composed on titanium and titanium alloys by being implanted in bone [30]. The ability of titanium to form calcium phosphate on itself is one of the reasons for its better hard-tissue compatibility than the other metals [31]. So, there were some studies which show that calcium phosphate coating implants have beter bone-to-implant contact [26, 32, 33]. Dental implants with fluoride-modified titanium dioxide show improved bone response and clinical performance. Therefore,fluoride is proposed to play a role in the chemical bonding between the newly formed bone and the modified dental implant surface. The presence of fluoride ions in titanium implant surfaces is suggested to enhance osteogenesis as well as to increase the rate of apatite seeding crystals [34-37].Changes in implant surface chemistry have increased bone formed around the implants [38].Thus, surface chemistry may provide important and possibly synergistic effects for bone formation around the dental implants. Nowadays, recent investigation focuses on the surface chemistry changes in many surface topographic modifications [39]. Calcium and vitamin D have an important role to get better bone health. Several additional food constituents, such as flavonoids, vitamins A, B, C, E, folate and minerals among which copper, zinc, selenium, iron fluoride and magnesium, are known to be crucial for bone regeneration [40]. Therefore, In recent study we investigated the effects of some new minerals such as selenium, magnesium and calcium on the titanium surface chemistry. We found same chemical potential values among $TiCa_3(PO_4)_2$, TiF_4, $TiCa_2$ and $TiMg_2$ molecules. So we could say that when magnesium and calcium are coated onto implant surface, we could get beter bone-to-implant contact.

4. CONCLUSION

This study is hypothesized that chemical potential may have an effect on the bone-to-implant contact. This hypothesis is not yet verified, and is under current investigation. If our theory is proven to be true, chemical potential which is a surface chemical property would be a crucial feature for upcoming implant surface modification parameter. We obtained the same chemical potential values in $TiCa_2$, $TiMg_2$, TiF_4, $TiCa_3(PO_4)_2$. Therefore, Ca_2 and Mg_2 may have beneficial effects on implant surface modifications and may trigger the production and mineralization of newly formed bone apposed to the implant's surface structure. But this hypothesis has to be proven by further experimental and clinical investigations.This is the first study that investigate the effect of chemical potential on the surface chemistry of titanium implants using DFT. We believe that this study will shed light onto new theoretical studies using DFT in the field of Nanodentistry.

CONFLICT OF INTEREST

The authors have stated explicitly that there are no conflicts of interest in connection with this article.

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