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ORIGINAL RESEARCH PAPER

Adsorption of Vitamin C on a Fullerene Surface: DFT Studies

Rezvan Baniasadi [1], Kun Harismah [2], Maryam Sadeghi [3], Mahmoud Mirzaei [4]*

[1] Department of Pharmaceutical Chemistry, Pharmaceutical Sciences Branch, Islamic Azad University, Tehran, Iran
[2] Department of Chemical Engineering, Faculty of Engineering, Universitas Muhammadiyah Surakarta, Surakarta, Indonesia
[3] Department of Chemistry, Central Tehran Branch, Islamic Azad University, Tehran, Iran
[4] Bioinformatics Research Center, School of Pharmacy and Pharmaceutical Sciences, Isfahan University of Medical Sciences, Isfahan, Iran

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ABSTRACT
Density functional theory (DFT) calculations were performed to investigate adsorptions of vitamin C (Vit) on the surface a fullerene structure (Ful) in gas and water–solvated systems. Two models of Vit including OVit and MVit were created based on the original structure of Vit for OVit and mutilation of all hydroxyl groups for MVit. All singular and hybrid structures were optimized and the molecular properties were then evaluated for them. Binding energies and dipole moments indicated that the formation of MVit-Ful hybrid could be more favourable than OVit–Ful hybrid. Molecular orbital properties of hybrid systems demonstrated almost similarity to each other and similarity to the singular Ful model; however, they are completely different from both of singular Vit models. It could be mentioned that the Vit counterparts miss their contributions to molecular orbital distributions in the hybrid systems. Quadrupole coupling constants (CQ) have been also evaluated for oxygen atoms of Vit counterparts in both singular and hybrid models, in which they demonstrated the effects of interactions on the atomic scale properties of Vit counterparts. The evaluated results indicated the solvent effects on all molecular and atomic scale properties of Vit and Ful structures in both of singular and hybrid situations.

Keywords: *Fullerene; Vitamin C; Adsorption; Density functional theory.*

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INTRODUCTION

After the pioneering discovery of C_{60} fullerene structures [1], several attempts have been dedicated to exploring the existence of other nano–allotropes of carbon atom [2]. A few years later, discovery of nanotubes by Iijima [3] has modified the direction of research attempts from exploring carbon allotropes to exploring carbon nanostructures [4]. For this time, numerous research activities have been done to investigate the stabilities and properties of nanostructures created by either carbon atoms or non–carbon atoms [5–10]. Since the early days of nanostructures inventions, a major question was about how to employ the novel structures in living systems to increase the life quality [11]. In

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* Corresponding Author Email: mdmirzaei@pharm.mui.ac.ir, Tel: +98 (31)37927101

this case, it is very much important to know how the interactions could be taken placed between nanostructures and biological counterparts [12–14]. To achieve reasonable answers for this major question, the researchers have performed several computational and experimental activities; however, because of complexity of both biological and nonstructural systems, there is no clear answer yet. Therefore, performing further studies are still required in this field.

Within this work, we have employed quantum chemical computations to systematically investigate the absorption of vitamin C (Vit), or ascorbic acid, (Fig. 1) on a fullerene surface (Ful) (Fig. 2). To this aim, we have considered molecular systems for both of Vit and Full structures to see the physical interactions between them in the hybridized structural situations (Fig. 3). Possibilities of both physical and chemical interactions between biological molecules and nanostructures have been examined by earlier works [15,16], in which the initial properties of counterparts could be expected to be seen again in the physically interacted systems [17]. However, chemical interactions almost yield single standing new structures, in which the properties of counterparts could be very much different from their singular situations [18]. As a result, physical interactions between biological and nonstructural counterparts could be considered especially for those situations that the counterparts should be separated again to show their own properties, e.g., drug delivery systems [19]. To run such research works, performing quantum computations could help to either predict or interpret the complicated experimental results [20]. Avoiding the crowded molecular populations of experimental works, molecular or atomic scale studies could be performed in the computational works to see the chemical systems in their smallest possible scales, which is an advantage of quantum computations to generate properties for ultra pure materials. Based on these advantages, we have employed quantum chemical computations to investigate the properties of Vit adsorption on a representative Ful nanostructure.

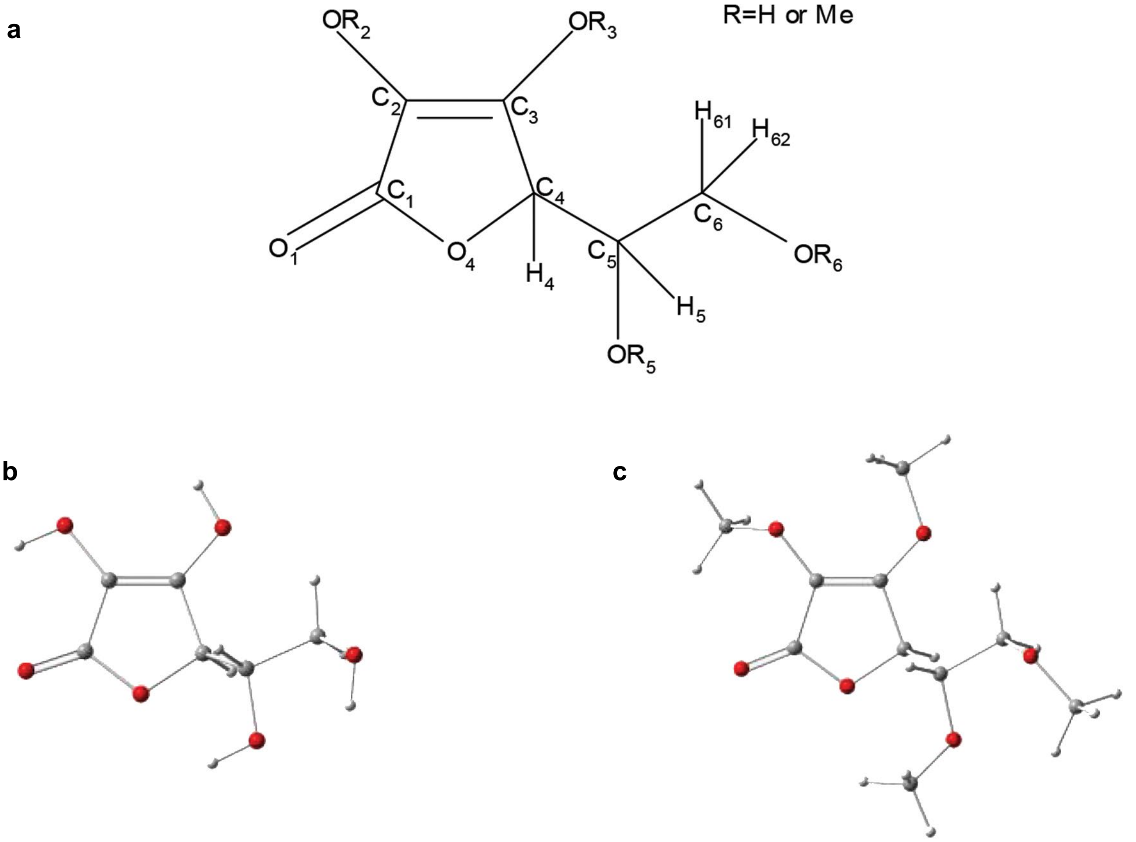

Fig. 1. (a) 2D representation of Vit (vitamin C). (b) 3D representation of OVit (original Vit). (c) 3D representation of MVit (methylated Vit).

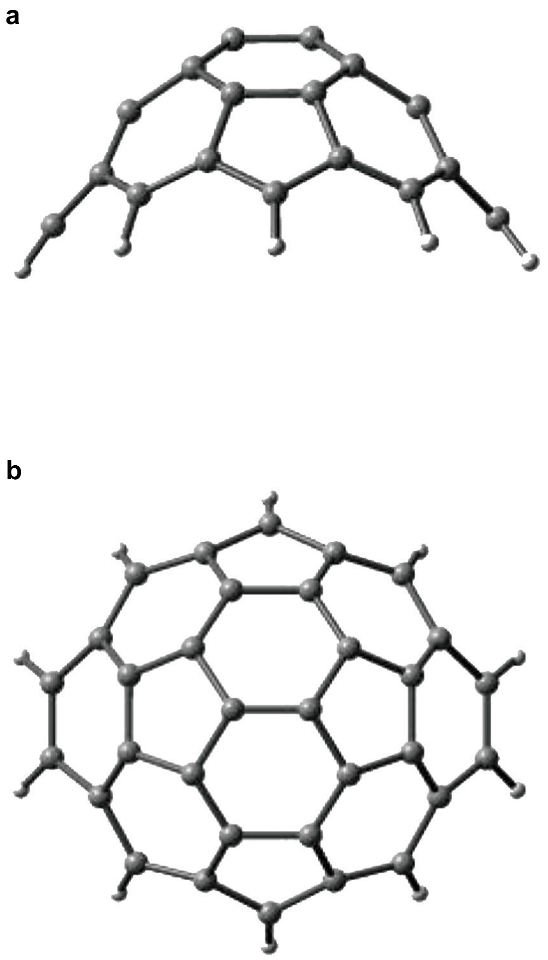

Fig. 2. Side and Up views of Ful (fullerene surface).

COMPUTATIONAL METHODS

Molecular systems of this work, including singular Vit and Ful structures and their hybrids (Figs. 1–3) have been investigated based on density functional theory (DFT) calculations. For Vit models, there are OVit and MVit models, in which the OVit model has the original structure of ascorbic acid ($C_6H_8O_6$) [21] whereas all hydroxyl groups are methylated in the MVit model ($C_{10}H_{16}O_6$), O and M indicate original and methylated (Fig. 1). To make a Ful surface, a half structure of C_{60} fullerene ($C_{32}H_{10}$) has been considered with the hydrogenated tips (Fig. 2). First, all singular molecules were optimized employing the B3LYP exchange–correlation functional and the 6–31G* standard basis set as implemented in the Gaussian 09 program [22]. Frequencies were also calculated to validate the global minimization points for the optimized structures. Subsequently, hybrid structures (Fig. 3) Were created using the available optimized counterparts and they were re–optimized to find the minimized energy structures. In this case, because of the existence of physical interactions, we employed IOp(3/124=3) to include dispersion corrections in our calculations [23]. It is very much important to mention here that the reliability of B3LYP functional versus other functionals for predictions of interactions between biological and nano structures has been examined by earlier works [24]. Moreover, the existence of basis set superposition errors (BSSE) [25] was examined for the hybrids, in which the results for energy differences were almost negligible. The optimization processes yielded properties such as optimized geometries, interaction distances (D_i), binding energies (E_b), energies for the highest occupied and the lowest unoccupied molecular orbital (HOMO and LUMO), energy gaps (E_g), and dipole moments (D_m), which are all summarized in Table 1. The energy differences between singular and hybrid structures were considered as binding energies. The energy differences between HOMO and LUMO levels were considered as energy gaps. Time–dependent (TD) DFT calculations were also performed to visualize HOMO and LUMO distribution patterns (Fig. 4). For further analysis of the investigated systems, quadrupole coupling constants (C_Q) were also evaluated for the oxygen atoms of Vit counterparts in both optimized singular and hybrid systems (Table 2). To this aim, electric field gradient (EFG) tensors were directly calculated and they were converted to C_Q; C_Q(MHz)= $e^2Qq_{zz}h^{-1}$, e is the electric charge, Q is the nuclear electric quadrupole moment, q_{zz} is the main EFG eigenvalue ($|q_{zz}|>|q_{yy}|>|q_{xx}|$) and h is the Planck's constant [26]. All mentioned calculations have been performed for gaseous and water–solvated systems, in which the polarizable continuum model (PCM) has been employed for the latter system [27].

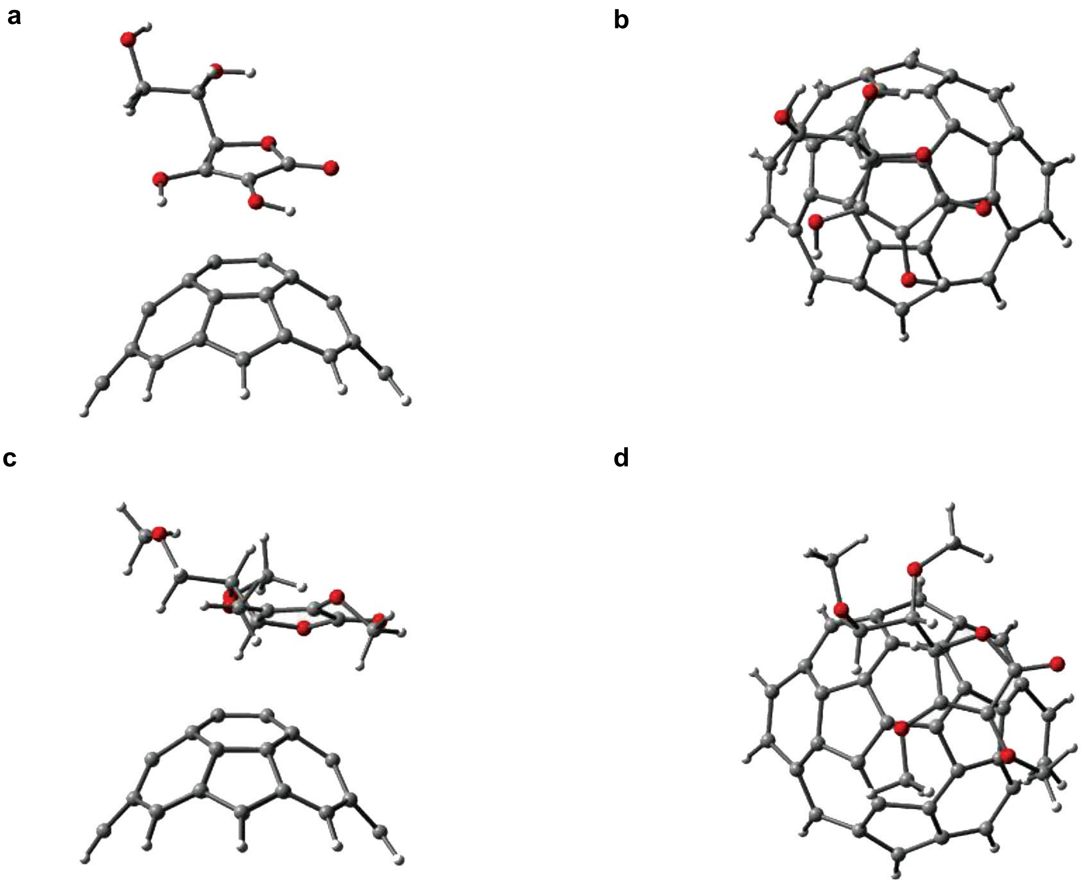

Fig. 3. (a) and (b) Different representations of OVit–Ful hybrid. (c) and (d) Different representations of MVit–Ful hybrid.

Table 1. Optimized molecular properties*

Property	OVit	MVit	Ful	OVit–Ful	MVit–Ful
Interaction Distance (Di: Å)	-	-	-	3.289	3.313
				[3.292]	[3.342]
Binding Energy (E_b: kj/mol)	-	-	-	−5.953	−13.803
				[−4.397]	[−9.931]
LUMO (eV)	−0.997	−0.724	−2.920	−3.064	−3.077
	[−0.784]	[−0.616]	[−2.879]	[−2.890]	[−2.905]
HOMO (eV)	−6.516	−6.245	−4.842	−4.980	−4.975
	[−6.145]	[−6.050]	[−4.770]	[−4.777]	[−4.782]
Energy Gap (E_g: eV)	5.519	5.521	1.922	1.916	1.898
	[5.361]	[5.434]	[1.891]	[1.887]	[1.877]
Dipole Moment (D_m: Debye)	2.297	3.753	4.266	7.180	6.822
	[3.227]	[6.052]	[6.620]	[9.868]	[9.351]

*See Figs. 1-3 for the models. The [brackets] include the parameters for water–solvated system. All other parameters are in the gaseous system.

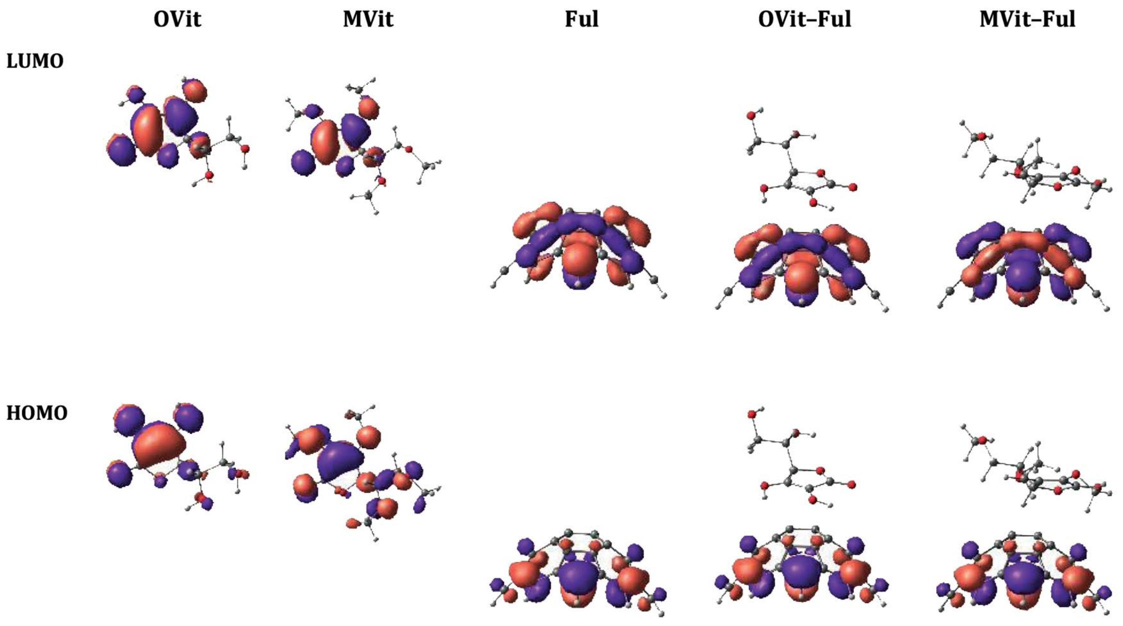

Fig. 4. HOMO and LUMO Distribution patterns. There were no significant changes between the distribution patterns in gaseous and water–solvated systems. See Figs. 1-3 for the models.

Table 2. Quadrupole coupling constants (C_Q: MHz)

Atom	OVit	MVit	OVit–Ful	MVit–Ful
O_1	8.047	8.582 {0.535}	8.119 (0.072)	8.603 (0.021)
	[7.910]	[8.194 {0.284}]	[8.006 (0.096)]	[8.204 (0.010)]
O_2	9.798	10.911 {1.113}	9.738 (–0.060)	10.805 (–0.106)
	[9.707]	[10.794 {1.087}]	[9.730 (0.023)]	[10.705 (–0.089)]
O_3	9.397	10.196 {0.799}	9.333 (–0.064)	10.058 (–0.138)
	[9.078]	[9.750 {0.672}]	[9.019 (–0.059)]	[9.731 (–0.019)]
O_4	9.148	9.225 {0.077}	9.059 (–0.089)	9.129 (–0.096)
	[8.905]	[8.912 {0.007}]	[8.856 (–0.049)]	[8.848 (–0.064)]
O_5	10.814	10.960 {0.146}	10.845 (0.031)	10.993 (0.033)
	[10.419]	[10.906 {0.487}]	[10.427 (0.008)]	[10.910 (0.004)]
O_6	11.099	11.174 {0.075}	11.121 (0.022)	11.040 (–0.134)
	[10.664]	[10.868 {0.204}]	[10.666 (0.002)]	[10.856 (–0.012)]

[*] See Figs. 1–3 for the models and Fig. 1, panel (a) for atoms numbers. To better show the changes of properties, differences of values (Δ) between hybrid and singular systems are in the parentheses (OVit–Ful – Ovit and MVit–ful – Mvit) and differences of values between Mvit and OVit are in the braces {MVit – OVit}. The [brackets] include the parameters for water–solvated system. All other parameters are for the gaseous system.

RESULT AND DISCUSSION

The models of this work include OVit, MVit, and Ful singular molecules (Figs. 1 and 2) and OVit–Ful and MVit–Ful hybrids (Fig. 3). Examining the optimized molecular properties of Table 1 reveals that the HOMO and LUMO levels and the corresponding energy gaps are almost similar for both singular Vit models. Comparing the mentioned properties with the singular Ful and hybrids indicates that the magnitudes are all reduced in the presence of Ful counterpart, in which the magnitudes of energy gaps are all reduced to around 1.9 eV in all three Ful systems. It could be mentioned that the role of Ful counterpart has significant effects on the MO properties of the Vit counterparts. As could be seen by the HOMO and LUMO distribution patterns (Fig. 4), all MOs are located on the surface of Ful counterpart in both OVit–Ful and MVit–Ful hybrids. This trend approves the important influence of Ful counterparts on the electronic properties of Vit–Ful hybrids. The magnitudes of dipole moments also indicate that the polarizations are significantly increased in the hybrids in comparison with all three singular models. Interestingly, the magnitude of the dipole moment for MVit–Ful hybrid is smaller than OVit–hybrid, in which it is in agreement with the results of binding energies for a better stability; binding energy of MVit–Ful is larger than OVit–Ful. It is shown in Fig. 3 that the orientation of MVit ring structure is almost parallel to the Ful surface; however, the orientation of the OVit ring structure has a different relaxation of the Ful surface. The interaction distance has been measured between O_4 of Vit and the nearest C atom of Ful surface, in which the distance of MVit–Ful is somehow longer than that of OVit–Ful whereas the molecular orientation of MVit on the Ful surface is more favorable than that of OVit. Therefore, a larger value of binding energy has been evaluated for the MVit–Ful hybrid than the OVit–Ful hybrid. As a conclusion of this section, both hybrid systems of this work could be achievable regarding the values of binding energies but the orientations of molecular ring of Vit on the Ful surface are different in the OVit–Ful and MVit–Ful hybrids, which lead to different magnitudes of dipole moments for the mentioned systems. Comparing the obtained optimized properties between the gaseous and water–solvated systems indicates that the solvent effects could be detected by these properties. As could be seen by interaction distances, they are increased in the solvated systems with the corresponding lower binding energies. Interestingly, the magnitudes of energy gaps have been all decreased in the water–solvated systems in comparison with the gaseous systems. The values of dipole moments have been all increased in the water–solvated systems referring larger polarizations for the molecular systems in the presence of water solvent versus the isolated gaseous systems.

Atomic scale properties including C_Q (quadrupole coupling constants) have been evaluated for oxygen atoms of Vit counterparts in both singular and hybrid systems (Table 2 and Figs. 1–3). C_Qs, which are evaluated from EFG tensors, are very much important parameters to investigate the electronic properties of matters at the atomic scales [28–30]. These parameters are very much sensitive to the electronic environments of atoms and they could detect any effects to their environments [31]. Regarding the purpose of this work to investigate the adsorptions of OVit and MVit counterparts on the Ful surface, the magnitudes of C_Q parameters indicate that the atomic environments of Vit counterparts detect the effects of hybridizations in both of OVit–Ful and MVit–Ful hybrids. Differences of values of C_Qs between hybrid and singular models of each system shows that the changes of properties for MVit–Ful are somehow more significant than the changes for OVit–Ful from singular to hybrid system. It is remembered here that the binding energy was larger for MVit–Ful than OVit–Ful, in which the changes of atomic properties also approve the earlier trend of more variability of formation of MVit–Ful than OVit–Ful regarding the binding energies. Comparing C_Q values between singular OVit and MVit models also indicates the influence of methylation on the atomic properties of Vit counterparts. Since C_Q values are very much sensitive to the electronic environments, both physical and chemical interactions could be detected by tracking changes of C_Q values from original to function molecular systems. It is worth to note that the C_Q values are more valid for those atoms with nuclear spin angular momentum (I) greater than one–half; they are very much useful for the ^{17}O isotope [32]. Hence, we have employed this parameter to investigate atomic scale electronic properties of the singular and hybrid systems of this work. The results indicated that the atomic scale properties also detect the effects of interactions between Vit counterparts and Ful surfaces, in which the interaction was somehow more highlighted for the MVit–Ful system than the OVit–Ful system. Comparing the results for the gaseous and water–solvated systems indicates that the solvent effects could be observed for the atomic scale C_Q properties in both of singular and hybrid systems, in which the achievements by solvated results are almost similar to the gaseous results. However, the exact magnitudes for the parameters are different in two computational systems.

CONCLUSION

We have performed DFT calculations to investigate adsorptions of Vit counterparts on the Ful surface based on molecular and atomic scale properties in gaseous and water–solvated systems. The results indicated different molecular orientations of Vit on the Ful surface for OVit and MVit models. Based on binding energies, formation of the MVit–Ful hybrid was somehow more favorable than the OVit–Ful hybrid. Dipole moments and atomic scale C_Q values approved the obtained trend formation favorability. Energy gaps and HOMO–LUMO distribution patterns indicated that the major MO contributions belong to the Ful surface whereas the Vit counterparts almost miss their MO roles in the hybrid systems. All obtained molecular and atomic properties indicated the solvent effects for the molecular counterparts in singular and hybrid systems. As a final trend, the Ful surface could be proposed as a surface for adsorption of Vit counterparts, in which both molecular and atomic scales properties approved the trend.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

REFERENCES

1. R.E. Smalley, Rev. Mod. Phys. 69, 723 (1997).
2. F. Cataldo, Carbon 40, 157 (2002).
3. S. Iijima, Nature 354, 56 (1991).
4. S. Iijima, Physica B 323, 1 (2002).
5. M.S. Lakmehsari and T. Kalateh, J. Nanoanalys. 3, 86 (2016).
6. M. Mirzaei and R.S. Ahangari, Int. J. Nano Dimen. 7, 284 (2016).
7. M. Rezvani, M.D. Ganji, and S. Jameh–Bozorghi, Appl. Surf. Sci. 360, 69 (2016).
8. B.B. Kadhim and H.O. Muhsen, Nanosci. Nanotechnol. 7, 9 (2017).
9. H. Mirzaei and M. Darroudi, Ceramics Int. 43, 907 (2017).
10. N. Hiremath, Polymer Rev. 57, 339 (2017).
11. P. Sharma, N.K. Mehra, K. Jain, and N.K. Jain, Cur. Drug Delivery 13, 796 (2016).
12. M.D. Ganji, Diamond Rel. Mater. 18, 662 (2009).
13. M. Rezvani, I. Ahmadnezhad, M.D. Ganji, and M. Fotukian, J. Nanoanalys. 3, 69 (2016).
14. A. Kouchaki, O. Gülseren, N. Hadipour, and M. Mirzaei, Phys. Lett. A 380, 2160 (2016).
15. M. Mirzaei, H.R. Kalhor, and N.L. Hadipour, J. Mol. Model. 17, 695 (2011).
16. L.K. Singh, A. Maiti, R.S. Maurya, and T. Laha, Mater. Manufact. Proc. 31, 733 (2016).
17. G. Jiang, S. Song, Y. Zhai, C. Feng, and Y. Zhang, Compos. Sci. Technol. 123, 171 (2016).
18. G. Charrier, A. Desrues, C. Barchasz, J. Leroy, R. Cornut, B. Jousselmea, and S. Campidelli, J. Mater. Chem. A 4, 15036 (2016).
19. N.K. Mehra and S. Palakurthi, Drug Discovery Today 21, 585 (2016).
20. H. Ström, Appl. Energy 185, 2224 (2017).
21. J. Hvoself, Acta Cryst. B 24, 1431 (1968).
22. M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, et al., Gaussian 09, Revision A.01 (Gaussian Inc., Wallingford CT, 2009).
23. S. Grimme, WIREs 1, 211 (2011).
24. H.T. Larijani, M. Jahanshahi, M.D. Ganji, and M.H. Kiani, Phys. Chem. Chem. Phys., 19, 1896 (2017).
25. L. Turi and J.J. Dannenberg, J.Phys. Chem. 97, 2488 (1993).
26. P. Pyykkö, Mol. Phys. 99, 1617 (2001).
27. J. Tomasi, B. Mennucci, and R. Cammi, Chem. Rev. 105, 2999 (2005).
28. H. Behzadi, N.L. Hadipour, and M. Mirzaei, Biophys. Chem. 125, 179 (2007).
29. Z. Bagheri, M. Mirzaei, N.L. Hadipour, and M.R. Abolhassani, J. Comput. Theor. Nanosci. 5, 614 (2008).
30. M Mirzaei, O Gülseren, and N Hadipour, Comput. Theor. Chem. 1090, 67 (2016).
31. M. Mirzaei, N.L. Hadipour, and M.R. Abolhassani, Z. Naturforsch. A 62, 56 (2007).
32. T. Partovi, M. Mirzaei, and N.L. Hadipour, Z. Naturforsch. A 61, 383 (2006).