



Outer-Valence Green's Function Study on Small Biomolecules

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Abstract

Here, a theoretical study of electronic structures of conformers of vitamin C was studied in the gas phase. Outer-Valence Green's Function (OVGF) methodology employing with 6-311g++(d,p) basis set was used for the calculations. The stable conformers were selected by thermochemistry calculations and the ionization energies were obtained for them. Also, these results have been compared with another ionization method, for example, SAC-CI calculations. The comparison of two spectra shows that OVGF results are in better with experimental data for moieties of vitamin C. So the SAC-CI spectra were shifted along the ionization energy scale to enable the first band in SAC-CI spectrum to match the first band in corresponding OVGF spectrum. . Natural Bonding Orbital (NBO) study was performed for analyzing each band of ionization. NBO calculations showed that the first ionization band of vitamin C was related to the π electrons of C=C bond of the ring in the structure of the molecule.

Keywords: Ionization Energy, ionization site; OVGF, DFT, NBO.

Introduction

Antioxidant properties of vitamin C have been known for long times [1] but many of its properties have been unknown for scientists. Vitamins have many isomers which include conformers and tautomers with different biological properties. Therefore, conformational analysis of vitamins is very important. For example, the ionization energies and photoelectron spectra of vitamin C have not yet been reported. Based on the literature, there is no experimental data on the ionization of vitamin C. One of the best methods for measuring ionization energies of free molecules in gas phase photoelectron spectroscopy. Recently Abyar et al computed ionization energies of conformers of vitamin C by high-level computation such as SAC-CI study. The most challenging part of the gas phase photoelectron spectroscopic measurements, especially for large biomolecules, is the decomposition and degradation of the sample upon transfer to the gas phase. In this work, the relative abundance of conformers was obtained from conformational analysis using Boltzman population weighting (BPW). Moreover, to understand the nature of different ionization events, natural bonding orbital analysis (NBO) has been performed in order to assign orbitals to specific ionization events (bands in the photoelectron spectrum). Therefore, the calculation of gasphase valence ionization energies and simulation of photoelectron spectra of biomolecules by accurate computational methods is a useful substitute



when experimental spectra can not be obtained. High-level ab initio calculations using methods such as outer-valence Green's function (OVGF) can help in the analysis of the electronic structure and for simulation of UV photoelectron spectra by providing values of valence ionization energies.

Methodology

The geometries of all possible conformers of vitamin C were taken from literature[2]. Then optimization structures were obtained using density functional theory (DFT) method employing wb97-xd functional and 6-31+G(d) basis set. The frequency calculations were also performed, at the same level of theory, on the optimized structures to check the intrinsic of the obtained potential energy minima and determine the standard Gibbs free energies of conformers in the gas phase. The optimized structures of stable conformers have been shown in Figure1. The OVGF [3] level of theory was used for calculating the ionization energies and their intensities. The 6311++ g (d,p) basis set was used for the OVGF calculations. The use of the OVGF method is well established in UV photoelectron spectroscopy and provides the ionization energies which agree with experimental results to better than ± 0.5 eV.

Canonical molecular orbitals were performed at the Hartree-Fock (HF) level of theory using a 6-311++g(d, p) basis set to determine the contribution of different natural bonding orbitals in involving in the ionization processes for spectral band assignment [4]. The natural bonding orbital (NBO) calculations were also performed at the DFT level of theory using 6-311++G(d,p) basis set to determine contributions of different natural bonding orbitals in the canonical molecular orbitals involved in the ionization processes which is required for spectral band assignment. The NBO calculations were performed using NBO NBO (version 6) [5]. All calculations were performed using the Gaussian 09 Quantum Chemistry Package [4].

Results and discussion

The simulated photoelectron spectra for SAC-CI [6-10] and OVGF methods can be seen in Figures.2a also OVGF simulated spectra have been shown in Figure. 2b. In the Figure 2, solid lines indicate OVGF and dash lines SAC-CI results. Ionization bands in the spectra of conformers contain vertical lines which correspond to calculated vertical ionization energies. Results show that there is a difference between the SAC-CI and OVGF in the total number of ionizations. Tabel. 1 shows ionization energies and intensities for each conformer have been obtained by two methods. Also, ionization maybe take place from which orbitals in the ionization process.

The spectrum calculated with the SAC-CI method has been shifted towards higher binding energies by 0.6 eV that its HOMO ionization matches the OVGF simulated spectrum (Figure. 2.a). Relative band intensities in the two spectra are different, for conformer II, the intensity ratio 1:2:1:1 was predicted by the SAC-CI method while in the OVGF spectrum the predicted ratio is 1:3:1. Therefore, the SAC-CI result predicts the existence of four features in the simulated photoelectron spectrum, while OVGF predicts only three. Generally, the features of calculated spectra for conformers are different in two methods. The first ionization energy band is related to ionization from HOMO orbital (No:46) which has a π character corresponding to removal of an electron from C=C bond. Table 2 also shows that ionization occurs from the lone pairs on oxygen atoms.

Koopmans approximation says that ionization energy approximately equals the negative value of canonical HF orbital energy. If ionization corresponds to a linear combination of HF



determinants so it exhibits non-Koopmans behavior. Koopmans approximation is valid for first ionization band for all cofomers. But second and third ionization bands have different behaviour in the validation Koopmans approximation. The ionic states for fourth and fifth ionization bands have a linear combination of canonical HF determinants which indicate the breakdown of Koopmans approximation.

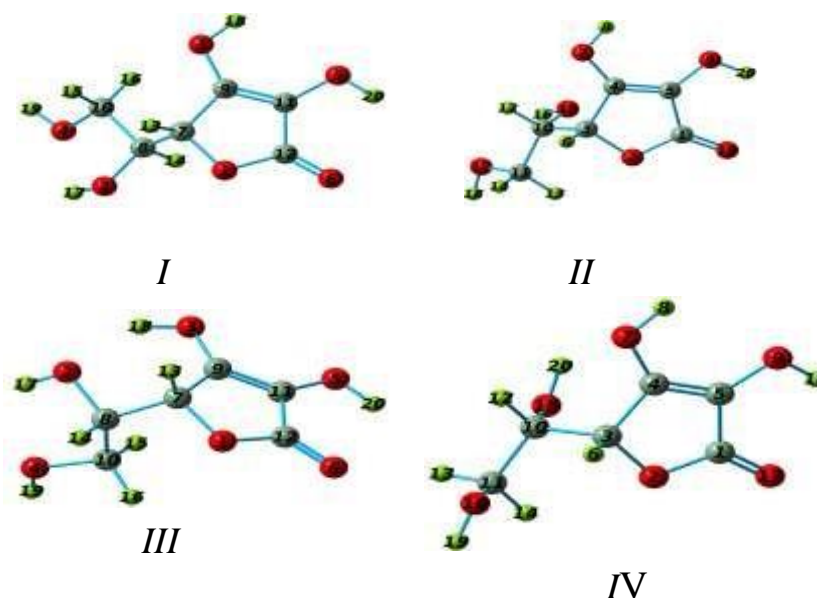


Figure.1 The most stable optimized structures of vitamin C in the gas phase.

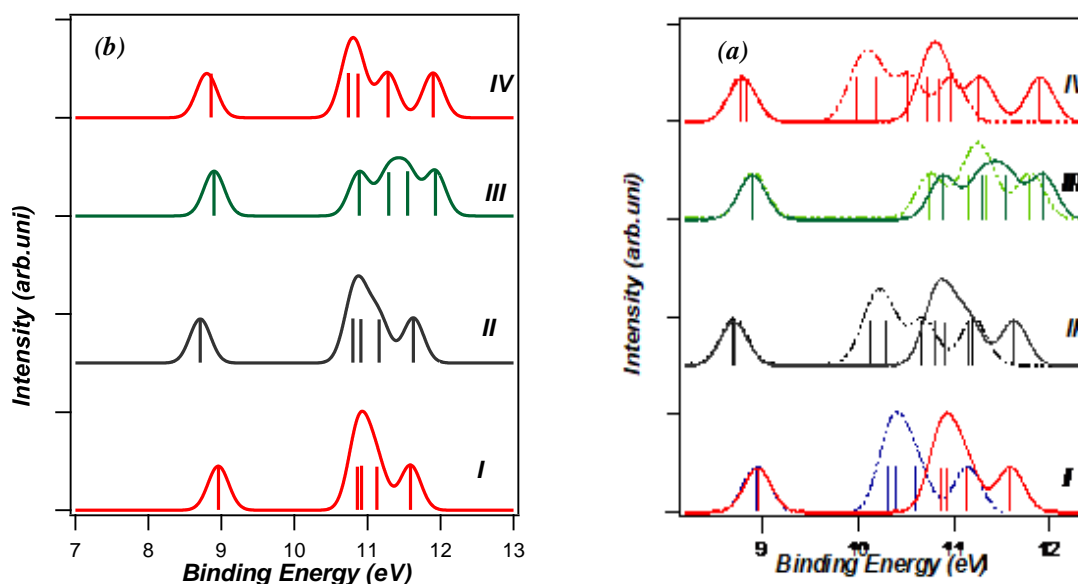


Figure. 2 (a). Comparison of simulated photoelectron spectra obtained with the SAC-CI and OVGf methods which solid lines OVGf indicate and dash lines SAC-CI results. (b). the computed photoelectron spectra by OVGf.



Table 1. The main electronic configuration, ionization energies (IE) and intensities of conformers of vitamin C calculated by ^aSAC-CI and ^bOVGF with the same basis set.

	<i>Ionic State</i>	<i>Main electronic configuration</i>	<i>Ionization energy (eV)/ Intensity^a</i>	<i>Ionization energy (eV)/ Intensity^b</i>
I	1	0.97(HOMO)	8.363 (0.954)	8.958 (0.90)
	2	-0.9(HOMO-2)- 0.3(HOMO-1)	9.742(0.931)	10.92(0.91)
	3	0. 91(HOMO-1)+ 0.3(HOMO-2)	9.817(0.933)	10.86(0.89)
	4	0.94 (HOMO-3)+0.13 (HOMO-4)- 0.10 (HOMO-2)	10.021(0.936)	11.13 (0.89)
	5	-0.12 (HOMO-3)-0.94(HOMO-4)	10.559(0.946)	11.59 (0.92)
II	1	0.97(HOMO)	8.045(0.953)	8.71(0.90)
	2	0. 95 (HOMO-1)	9.476 (0.926)	10.80(0.91)
	3	0.95 (HOMO-2)	9.646(0.936)	10.91 (0.9)
	4	-0.14 (HOMO-4)- 0.93(HOMO3)+0.27(HOMO-5)	10.020 (0.934)	11.16 (0.89)
	5	-0.23(HOMO-6)+ 0.91(HOMO-4)	10.542(0.946)	11.63 (0.92)
III	1	-0.97(HOMO)	7.885(0.951)	8.62 (0.91)
	2	-0.95 (HOMO-1)	9.727(0.916)	10.89(0.89)
	3	0.95 (HOMO-2)	10.138(0.931)	11.29(0.89)
	4	0.93 (HOMO-3)+0.17 (HOMO-4)- 0.10 (HOMO-7)	10.314 (0.938)	11.55(0.91)
	5	0.85 (HOMO-5)+0.31 (HOMO- 4)+0.26(HOMO-6)-0.11(HOMO-3)	10.772 (0.942)	11.92(0.91)
IV	1	-0.97(HOMO)	8.241(0.952)	8.88 (0.90)
	2	-0. 95 (HOMO-1)	9.456(0.935)	10.74(0.91)
	3	+ 0.11 (HOMO-3) -0.94 (HOMO- 2)	9.646(0.926)	10.87(0.9)
	4	- 0.93 (HOMO-3) -0.19 (HOMO4)- 0.1(HOMO-2)	9.985(0.942)	11.28(0.91)
	5	-0.91 (HOMO-4)+0.15(HOMO-3)- 0.11(HOMO-5)-0.11(HOMO-2)	10.426(0.933)	11.90(0.91)



Table 2. The HF energies, type of orbitals and the dominant natural bonding orbital contributions in the molecular orbitals involved in the ionization for all conformers.

	E (eV)	Type	Main characters
I	-9.767	π (HOMO)	(59.6%) π (C9- C11); (15.1%) LP (2) O 5; (11.2%) LP (2) O 3
	-12.299	n	(18.6%) σ (C8- H14); (57.6%) LP (2) O 2; (10.9%) σ (C8- C10);
	-12.460	n	(64.2%) LP (2) O 6 ; (9.3%) σ (C11- C12); (5.4%) σ (O1- C12)
	-12.609	n	(37.9%) LP (2) O 1 ; (24.5%) π (O6- C12); (7.5%) σ (C 7- C8) (7.1%) σ (C 7- H 13)
	-12.920	n	(57.6%) LP (2) O 4 ; (18.9%) σ (C 10- H16) (14%) σ (C 10- H 15);
II	-9.472	π (HOMO)	(59.8%) π (C4- C5) ; (11.3%) LP (2) O 7;(15.2%) LP (2) O 9
	-12.279	n	(10.9%) σ (C10- H12); (25.9%) LP (2) O 15 ; (34.8%) LP (2) O 19
	-12.421	n	(26.2%) LP (2) O 15 ; (29.2%) LP (2) O 19 (7.8%); σ (C10- H12);(7.7%) σ (C10- C11); (5.3%) σ (C1- C5)
	-12.662	n	(38.3%) LP (2) O 2 ; (28.6%) π (C1- O19););(7.7%) σ (C 3- C10) ; (5.6%) σ (C3- H6)
	-12.885	n	(55.4%) LP (2) O 17 ; (18.7%) σ (C11- H14); (14.6%) σ (C11H13)
III	-9.401	π (HOMO)	(57.8%) π (C 9- C11) (12.2%) LP (2) O 3 +(15.9%) LP (2) O 5
	-12.506	n	(57.7%) LP (2) O 6 ;(9.1%) σ (C11- C12); (5.5%) σ (O1- C12)
	-12.827	n	(36.1%) LP (2) O 1 ;(8.5%) π (C6- C12); (9.3 %) σ (C7- H13);(5.4%) σ (C 7- C8);(5.2%) LP (2) O 4
	-12.999	n	(34.5%) LP (1) O 2;(6.9%) LP (2) O 6; (10.7%) σ (C 8C10);(19.9 %) σ (C8- H14););(9%) σ (C 10- H15)
	-13.353	n	(52.5 %) LP (2) O 4;(16.8%) σ (C 10- H16); (9.2%) σ (C 10-H15)
IV	-9.767	π (HOMO)	(59.4%) π (C4- C5); (15.2%) LP (2) O 9; (10.9%) LP (2) O 7
	-12.250	n	(14.7%) σ (C3- C10); (17.5%) LP (2) O 2; (18.9%) LP (2) O 15 ; (6.6%) σ (C11- H13) ; (.4%) σ (C 10- C11);(6.8 %) σ (C1- O17); (5.6%) σ (C 10- H12) ; ; (8%) LP (2) O 16
	-12.525	n	(54.4 %) LP (2) O 17 ; (10.4%) LP (2) O 16; (7.7%) σ (C 1- C5)
	-12.730	n	(42.2 %) LP (2) O 16 ; (9.3%) LP (2) O 2; (10.5%) σ (C 11- H14);(9.9%) σ (C 11- H13); (6 %) LP (2) O 15 ;(6.2 %) LP (2) O 17
	-13.357	n	(34.6 %) LP (2) O 15 ; (7.4%) LP (2) O 2; (17.8%) σ (C 10- H12);(4%) σ (C 10- C11);(9.9 %) σ (C1- O17)

Conclusions

In this work, ionization energies and photoelectron spectra for most stable conformers for vitamin C have been calculated by SAC-CI and OVGf methods. Results show that there is a small energy difference between SAC-CI and OVGf simulated spectra. The comparison of two spectra shows that OVGf results are in better with experimental data for moieties of vitamin C. So the SAC-CI spectra were shifted along the ionization energy scale to enable the first band in



SAC-CI spectrum to match the first band in corresponding OVGF spectrum. NBO calculations show that each band of ionization occurs from what part of vitamin C.

Acknowledgments

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References

- [1] Lutsenko, E. A., Carcamo, J. M. and Golde, D. W. , " Vitamin C prevents DNA mutation induced by oxidative stress", *J. Biol. Chem.*, 277, 16895-16899 (2002).
- [2] Abyar, F. and Farrokhpour, H. , " Ionization of vitamin c in gas phase: Theoretical study", *J. Photoc, Photobiology B: Biology.*, 160, 11-17 (2016).
- [3] Niessen, W. V., Schirmer, J. and Cederbaum, L. S. , " Computational Methods for the OneParticle Green's Function", *Computer Physics Reports.*, 1, 57-125 (1984).
- [4] Frisch, M. J., Trucks, G. W., Schlegel, H. B., Scuseria, G. E., Robb, M. A., Cheeseman, J. R., Scalmani, G., Barone, V., Mennucci, B., Petersson, G. A., Nakatsuji, H., Caricato, M., Li, X., Hratchian, H. P., Izmaylov, A. F., Bloino, J., Zheng, G., Sonnenberg, J. L., Hada, M., Ehara, M., Toyota, K., Fukuda, R., Hasegawa, J., Ishida, M., Nakajima, T., Honda, Y., Kitao, O., Nakai, H., Vreven, T., Montgomery, J. A., Jr., Peralta, J. E., Ogliaro, F., Bearpark, M., Heyd, J. J., Brothers, E., Kudin, K. N., Staroverov, V. N., Kobayashi, R., Normand, J., Raghavachari, K., Rendell, A., Burant, J. C., Iyengar, S. S., Tomasi, J., Cossi, M., Rega, N., Millam, J. M., Klene, M., Knox, J. E., Cross, J. B., Bakken, V., Adamo, C., Jaramillo, J., Gomperts, R., Stratmann, R. E., Yazyev, O., Austin, A. J., Cammi, R., Pomelli, C., Ochterski, J. W., Martin, R. L., Morokuma, K., Zakrzewski, V. G., Voth, G. A., Salvador, P., Dannenberg, J. J., Dapprich, S., Daniels, A. D., Farkas, Ö., Foresman, J. B., Ortiz, J. V., Cioslowski, J., Fox, D. J., Gaussian, Inc., Gaussian 09, revision b.01, Vol. Wallingford CT, (2009).
- [5] Glendening, D., Badenhoop, J. K., Reed, A. E., Carpenter, J. E., Bohmann, J. A., Morales, C. M., Landis, C. R. and Weinhold, F. , " Theoretical Chemistry Institute, University of Wisconsin, Madison, 2013.
- [6] Nakatsuji, H., Kitao. O., Yonezawa, T., "Cluster Expansion of the Wave Function Valence and Rydberg Excitations and Ionizations of Pyrrole, Furan, and Cyclopentadiene". *J. Chem. Phys.*, 83, 723-734(1985).
- [7] Ehara, M., Nakatsuji, H., "Outer- and Inner-Valence Ionization Spectra Of N₂ And CO : SAC-CI (General-R) Compared with the Full-CI Spectra". *Chem. Phys. Lett.*, 282, 347354(1998).
- [8] Nakatsuji, H., Ehara, M., Palmer, M.H., Guest, M.F., "Theoretical Study on The Excited and Ionized States of Titanium Tetrachloride". *J. Chem. Phys* 1992, 97, 2561-2570.
- [9] Nakatsuji, H., Ehara, M., "Symmetry Adapted Cluster-Configuration Interaction Study on Excited and Ionized States of TiBr₄ and TiI". *J. Chem. Phys*, 101, 7658-7671. (1994).
- [10] Nakatsuji, H., Hasegawa, J., Hada, M., "Excited and ionized states of free base porphyrin studied by the Symmetry Adapted Cluster Configuration Interaction (SAC-CI) method", *J. Chem. Phys.*, 104 , 2321-2330(1996).