

A Computational Study to Explore the Possibility of Doping in Ascorbic to Increase Its Efficiency: A Theoretical Study

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Abstract

As a result of continuous demand of ascorbic acid as oxidizing agent that can be used for radical ions scavenging cure in the body and other cold related diseases. The makes the researches in ascorbic acid molecule field become of utmost important. In this work, theoretical first principal method is implemented to analyze the effect of alkali-earth metal doping on the bandgap and electronic structure through structural modification to make the compound more effective. The ground state energy and geometry optimization is achieved by using trial and error between two method (Density functional theory and Hartree-Fock) and eight basis set. The molecular orientations were investigated using potential energy maps. To have an advance understanding of electrical and spectroscopic properties, UV-VIS, NMR, and FT-IR spectra were computed. It discovered that the ascorbic acid molecule responds to doping with halogens.

Keywords: Ascorbic acid, DFT; Hartree-Fock; Bandgap; HOMO-LUMO; Spectroscopy.

1. Introduction

For a more than a century dopamine molecules was known traditionally for busting the immune system of the body, pharmacological and other related properties[1-5]. This means it can be as a cure radical formation, neusea, influenza, and other cold related disease[6-9]. It can also be used as starting material in the pharmaceutical industries and it can sometimes combine with other species to form important biochemical synthesis[10-16]. The investigation of the structure of ascorbic acid, stable conformers, reactivities and other properties were studied extensively by many researches due to its importance[17-23]. II Nasidi et al study the doping of ascorbic acid with halogen to understanding the effect on the bandgap energy and found that the bandgap energy is sensitive to the doping[10]. As a result of the the titled molecules demand the study for the new methods to improve its effectiveness and at the same time reduce the side effect as well [24-29].

This paper has an insight into the way of improving the effectiveness of ascorbic acid by doping with the first three members of the alkali-earth metals group. The work is to analyze the effect of alkali-earth metals doping on the bandgap and electronic structure through structural modification to make the compound more effective.

The ground state energy and geometry optimization is achieved by using trial and error between two method (Density functional theory and Hatree-Fock) and eight basis set. The molecular orientations were investigated using potential energy maps. To have an advance understanding of electrical and spectroscopic properties, UV-VIS, NMR, and FT-IR spectra were computed. It was found that the ascorbic acid molecule respond to doping with halogens.

2. Computational method

The density functional theory (DFT) was implemented in this research using Gaussian 09 software package. The molecular optimization of the ascorbic acid is also achieved using B3LYP functional together with the 6-311G basis in the DFT method [30-36]. The method has been used by many researchers to explain the geometries and bandgap energies of the complex covalent molecular systems. Different basis set in both HF and DFT were explioted using trial and error to achieve the smallest energy possible (ground-state energy) for the rest of our calculation. It was found that the energy value for the 6-311G basis set is in agreement many reseach papers, which is the main incentive for the continuation for the rest of quantum mechanical calculations in this research. The ultraviolet spectroscopy (UV-VIS) was computed using the optimized structure. The Fourier transform infrared calculation was used to done using the optimized structure tu achieve the minimum potential energy surface and at the end of calculations FT-IR results have been multiplied by a factor of 0.2. The optimized structure was also computed to calculate theoretical nuclear magnetic resonance (NMR) to determine the chemical shift when the doping took place. The three-dimensional plotting of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) was carried out using the same functional and basis set. The bandgap energy is also achieved from the 3-D plot of the HOMO and LUMO. The theoretical calculations in this work is carried out by Gaussian software package.

The density of state (DOS) calculations has been achieved using the below equation

$$DOS(E) = \sum g(E - \varepsilon_i) \quad (1)$$

here g is a function dependent on energy E and ε_i , respectively. ε_i is the energy levels of the calculated system which is a function of electronic orbitals.

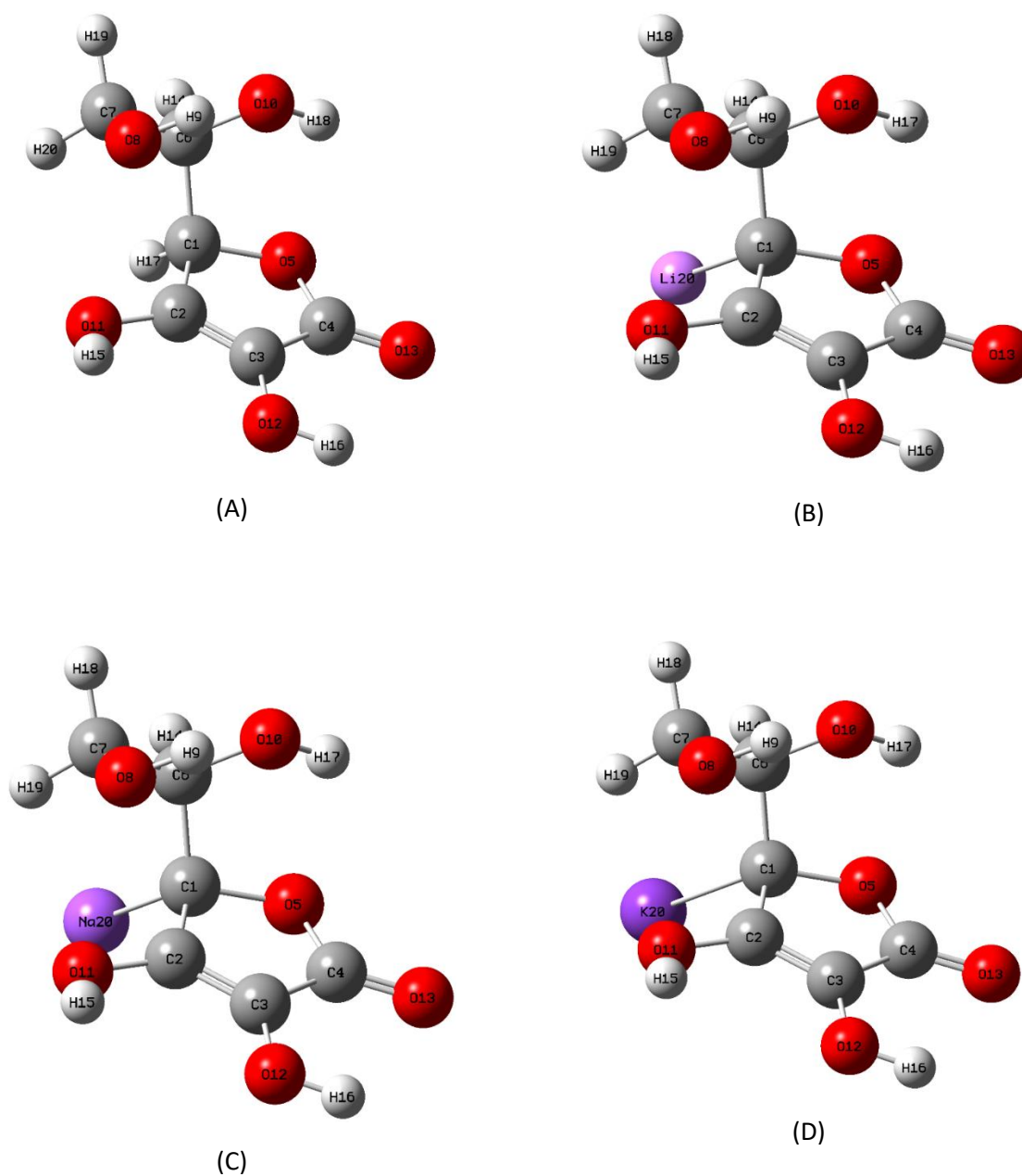


Figure 1. The geometry optimized structure of (A) ascorbic acid (B) ascorbic acid doped with lithium (C) ascorbic acid doped with sodium (D) ascorbic acid doped with potassium.

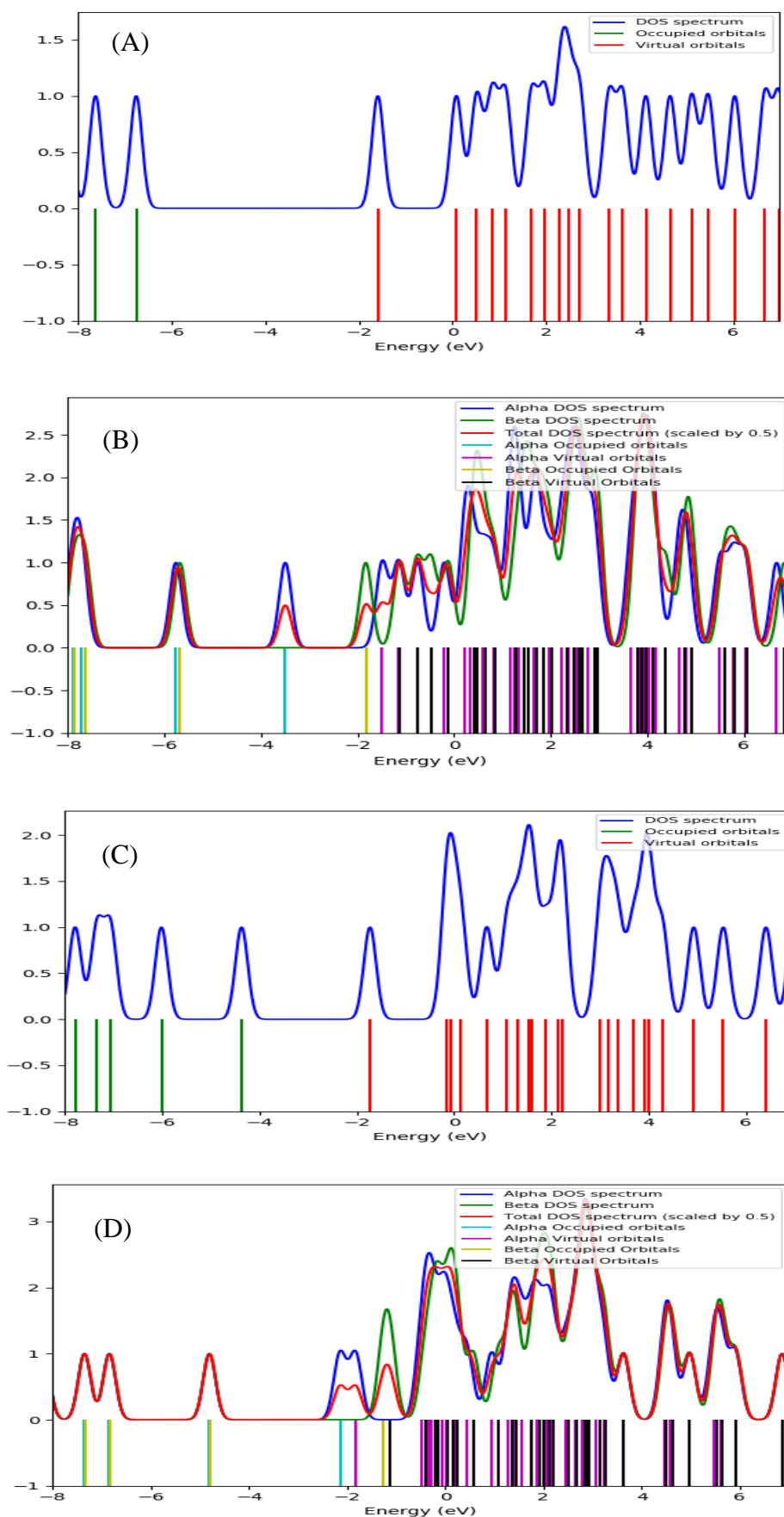


Figure 2. The density of states of (A) ascorbic acid (B) ascorbic acid doped with lithium (C) ascorbic acid doped with sodium (D) ascorbic acid with doped with potassium

3 Result and discussion

In this paper, two methods (Hartree-Fock HF and density functional theory DFT) were tested with eight basis set for the comparing of lowest ground-state energy and a suitable basis set for the remaining analysis. The analysis in this work include doping the titled compound with halogens to see their effective on the bandgap and density of states through spectroscopic analysis such as ultraviolet (UV), fourier transform spectroscopy (FT-IR), and nuclear magnetic resonance (NMR). Table 1 gives the values of the comparison between the methods. The calculation in this research were conducted using Gaussian 09 software program.

Table 1 Comparison showing the optimization of basis set for Hartree-Fock versus DFT in ascorbic acid. Basis

Basis set	Hartree-Fock (eV)	DFT (eV)
STO-3G	0.80	0.70
3-21G	6.25	4.90
6-31G	7.05	5.15
6-31G*	7.05	5.15
6-311G	7.28	1.15
LanL2DZ	7.27	5.13
LanL2MB	0.81	1.68
SDD	7.46	5.25

3.1 The molecular orbital

The titled compound is having forty seven (47) molecular orbitals which can be used to analyzed the bandgap and other important properties. The investigation of molecular orbital is very important because it explains the electrons distribution in the ascorbic acid molecule [37-40]. Figure 3 clearly shows the bandgap energy of normal ascorbic acid then doped with lithium, sodium, and potassium.

The orbitals in the ascorbic acid that are already occupied by the electrons are forty seven (47). It can be seen from figure 3 that the highest occupied molecular orbitals (HOMO) resided on the portion of the ring while at the same time the lowest unoccupied molecular orbital (LUMO) totally resides and localised on the ring part. The energy difference between the HOMO and LUMO can be describe as the bandgap energy. To form a correlation between the chemical reaction and biochemical systems, the bandgap energy is used as a pointer.

The heteroatoms that are used as doping agents in this research are lithium Li, sodium Na, and potassium P which have electronic configuration as $1s^2 2s^1$, $[\text{Ne}] 3s^1$, and $[\text{Ar}] 4s^1$ respectively. Due to the closeness in the number of electrons in the orbitals of sodium and potassium, there is a small effect and it was translated by small difference in their value but Li has the smallest energy which makes it more electronegative than the former. As a result, Li cause a big effect in the bandgap value. The high stability of ascorbic acid is indicated by the high energy bandgap. Another property associated with bandgap energy is polarizability. The bandgap energy in undoped ascorbic acid in this work is found to be 1.147 eV.

3.2 Ultraviolet spectroscopy (UV-VIS)

Ultraviolet spectroscopy (UV-VIS) is another tool use in spectroscopy for the structure determination of complex molecules because it can measure the absorption. In this work, the UV-vis is implemented to measure the wavelength and the intensity of ascorbic acid. Later, the comparison was made between the ascorbic acid and alkali-earth metals doped ascorbic acid to determine the highest peak present.

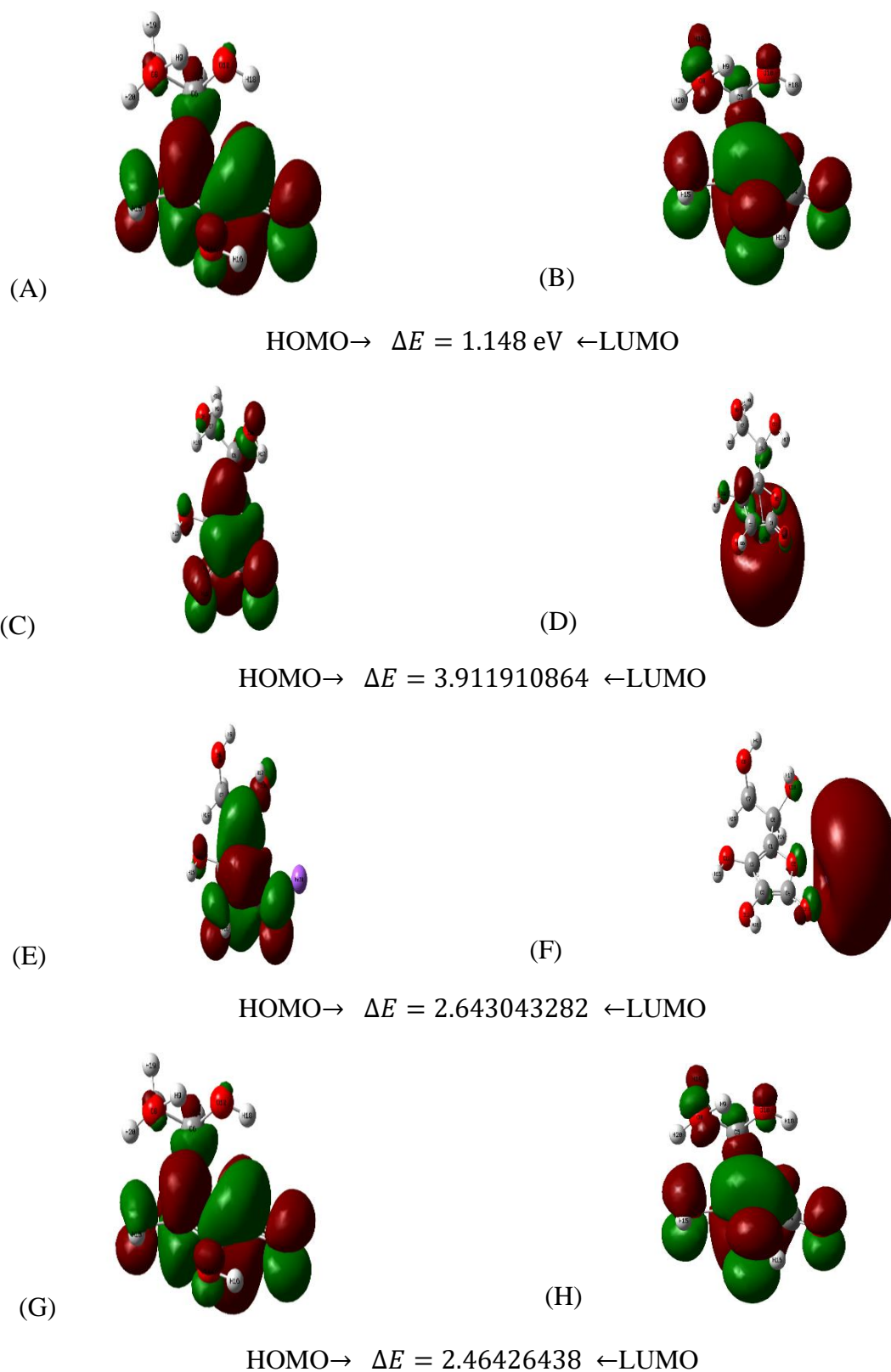


Figure 3. The homo and lumo of (A)(B) normal ascorbic acid (C)(D) ascorbic acid doped with lithium (E)(F) ascorbic acid doped with sodium (G)(H) ascorbic acid doped with potassium

In figure 4 the highest wavelength and intensity belong to sodium doped ascorbic acid with about 200 cm and 7250 eV respectively. The potassium doped ascorbic acid is with the second to the largest value at about 200 cm and 7200 eV respectively. The absorption in the intermediate is attributed to the lithium doped ascorbic acid at about 220 cm and 6500 eV. Table 2 shows a comprehensive data analysis of both the wavelength and intensity of the titled molecule. There is a second band at around 250 cm which may come from the higher excited states of the system (electrons migrating to another states of higher energy).

The changes that happened in the wavelengths and intensities of the ascorbic acid after been doped with the first three members of the halogen group are attributed to the electropositivity of the alkali-earth metals as arranged in the periodic table. Lithium is the most electropositive element, followed by sodium and then potassium. The increasing positivity of the group started from the top member down to the lowest member. Inductive and mesomeric effect can also be play a role in the variations in the movement of electrons in the molecule.

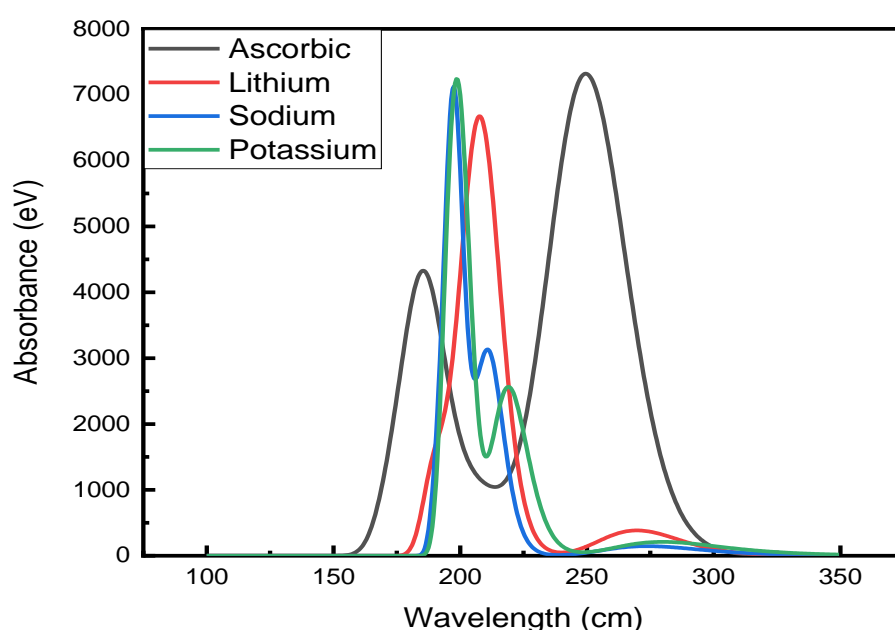


Figure 4 The comparison of simulated UV-vis absorption of ascorbic acid, doped with lithium, doped with sodium, and doped with potassium

3.3. Fourier transform infrared spectroscopy (FT-IR)

This section of the research focuses on the vibrational frequencies in the ascorbic acid before and after doped with first three members of the alkali-earth metals family. The frequency calculations were done using Gaussian 09 with DFT method and 6-311G/B3LYP basis set. Later the Origin is used to plot FT-IR after the IR was plotted in Gaussian. In figure 5, the benzene rings present can be investigated through C-C, C=C, and C-H bond. In literature, the normal carbon hydrogen (C-H) stretching vibrations of ascorbic acid occur at about 3000 cm^{-1} and moderate bands (multiplicity) can be present when compared to normal C-H stretching vibrations [16-18]. In this investigation, the modes of vibrational associated with C-H bond in ascorbic acid is present at about 3065-3124 cm^{-1} . This indicates the accuracy of the selected basis set due to its agreement with the literature. The stretching vibrations of aliphatic C-H is about 2750 cm^{-1} [] but it

was found to be about 2867-2973 cm^{-1} . The theoretical peaks at about 1259, 1193, and 1147 cm^{-1} bands are attributed to in-plane bending vibration in the ascorbic acid molecule.

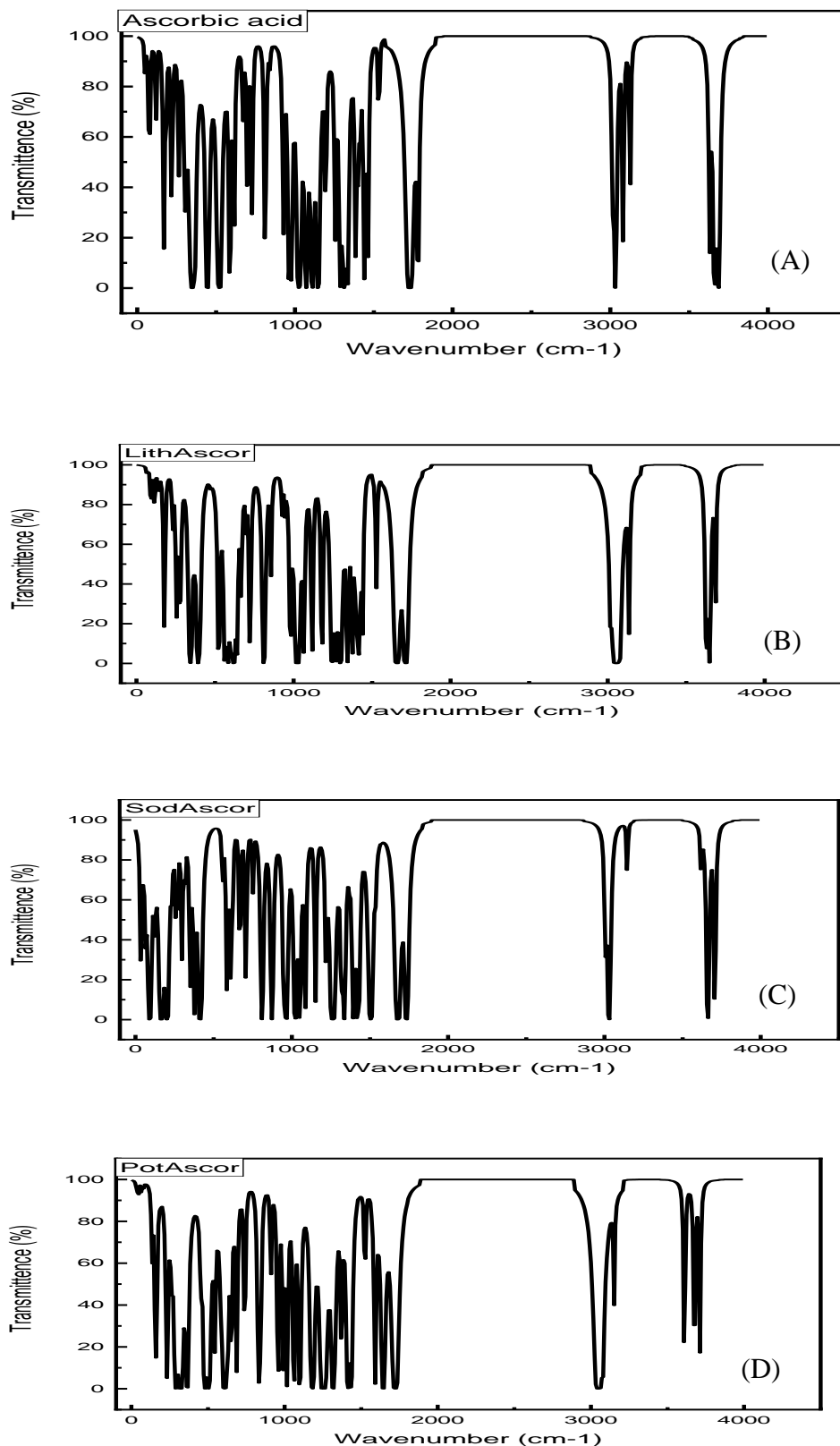


Figure 5. The simulated FT-IR of (A) ascorbic acid (B) ascorbic acid doped with lithium (C) ascorbic acid doped with sodium (D) ascorbic acid with doped with potassium.

The results obtained theoretically from this work is confirming the B3LYP model are close to the true value, which indicates the model is accurate for this molecule and result are outstanding. The C-C vibrations exhibited different due to the nature of the ascorbic acid as it has two benzene ring attached to it.

3.4. Ascorbic acid with alkali-earth metals (NMR)

This work centralizes on the chemical shifts of carbon and protons from one environment to another to analyse on the movements of electrons when the ascorbic acid is doped with the first three members of alkaline-earth metals group. Figure 6 gives a pictorial view of the theoretical result obtained when ascorbic acid has been doped with the alkali-earth metal group. Gaussian 09 was used for the theoretical calculations and Origin was used for the plotting of the NMR peaks. Il Nasidi et al investigated the halogen doping of ascorbic acid and discovered that there is always change in the orientation in carbon and proton of a complex molecule when the doped with the halogens [10].

The figures below (figure 6) depicts the shielding of the ascorbic acid before the doping and after the shielding effect is reduced depending on the electropositive of the incoming atom. The normal ascorbic acid has range 0-250 ppm but changes to 300, 700, and 2000 when doped with lithium, sodium, and potassium. The figures below (a, b, c, and d) is comparing the chemical shift that occur when ascorbic acid is doped with the first three members of the alkali-earth-metal group.

In fig b the peak with the highest value (lithium peak) is about 271 ppm and the carbons has little shift in the ppm due to the introduction of lithium atom. The same happened in fig c where the highest peak is attributed to the sodium atom at about 659 ppm and finally, the carbons also changed chemical environment due to deshielding by less electropositive atom. Finally, in fig d potassium have the highest peak about 1940 ppm due to shielding effect by more electrons in its outermost shells. In results, the trend follows that the more electropositive atom is the less absorption in chemical environment and the reverse is the case. This changes happened due to inductive and neighboring effect of the incoming electropositive atom. This indicates that NMR peaks generated by the halogens family in ascorbic acid molecule have a close linear relationship with the inductive effect of the incoming alkali-earth metal atom. Table 4 gives a precise individual position of the halogen members in terms of ppm.

3.5. Electrostatic potential surface (EPS)

The arrangement, distribution and orientation of the electrons in the molecules can be determined the electrostatic potential map [40-45]. In the electrostatic potential map, the electron rich area is denoted by the red colour while electron poor area is denoted blue color. This research focuses on the movement of electrons as the ascorbic acid molecule is doped with the first three members of the alkali-earth metal family. Before the doping took place, the electrons were distributed around the ring and also around nitrogen atom due to its electronegativity but as the compound was doped with the alkali-earth metal, the total orientation of the molecule change. The electrons shifted away from the group area due to its affinity as the most electropositive nature of the group figure 7. The electrons also shifted away from to lithium side but not as powerful as in sodium because it is less electropositive. The potassium is the least in electropositive among all the doping atoms and that is why it attracted less electrons than lithium and sodium. So it was found that the migration of the molecules depends on the electron affinity of the incoming alkali-earth metal atom.

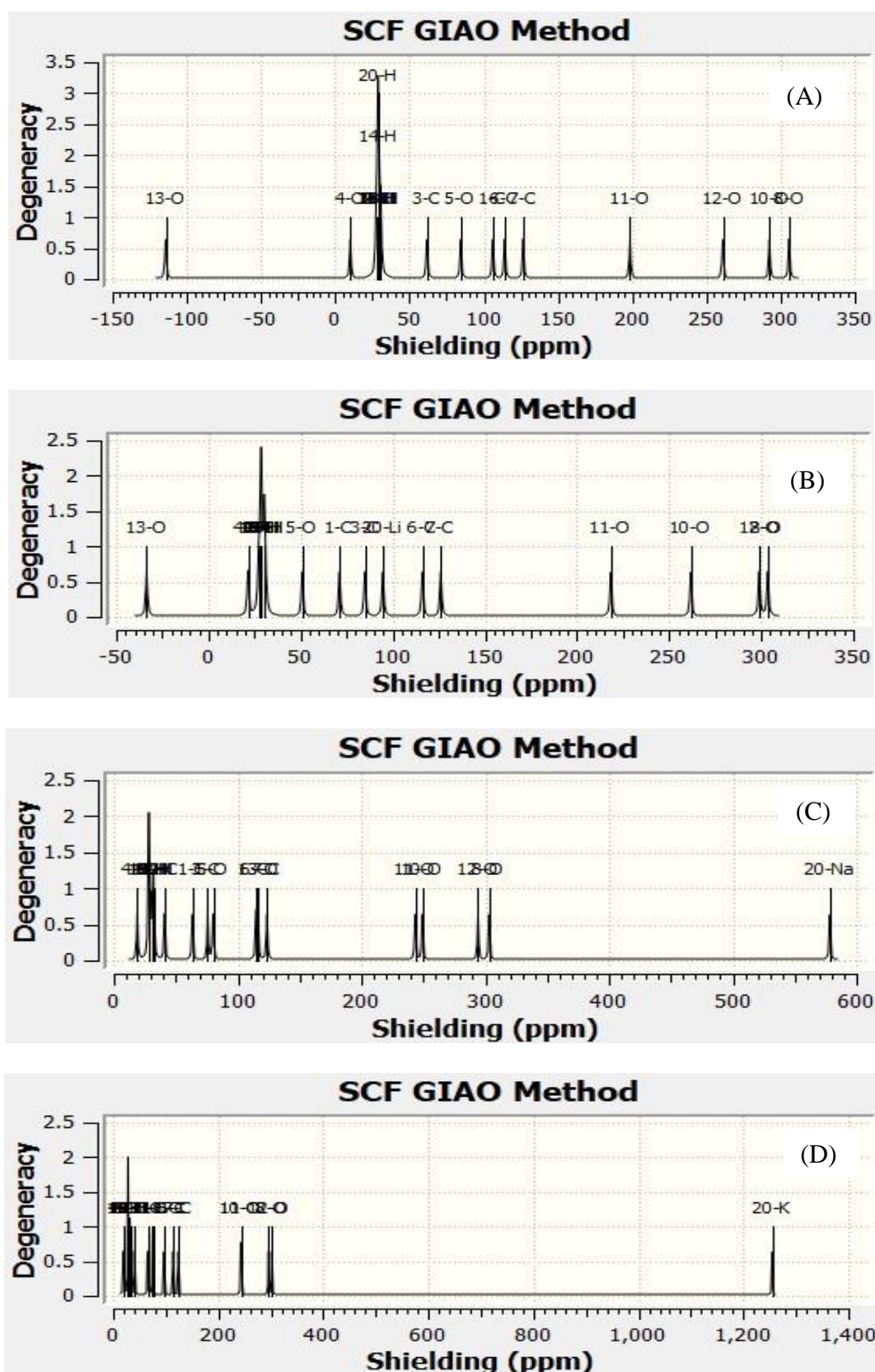


Figure 6. The simulated NMR of (A) ascorbic acid (B) ascorbic acid doped with lithium (C) ascorbic acid doped with sodium (D) ascorbic acid doped with potassium.

Table 3. The comparison of the simulated nuclear magnetic resonance of ascorbic acid doped with the first three members of alkali-earth metals group

S/N	Dopant atom	NMR (PPM)
1	Lithium	271.5
2	Sodium	659.0
3	Potassium	1940

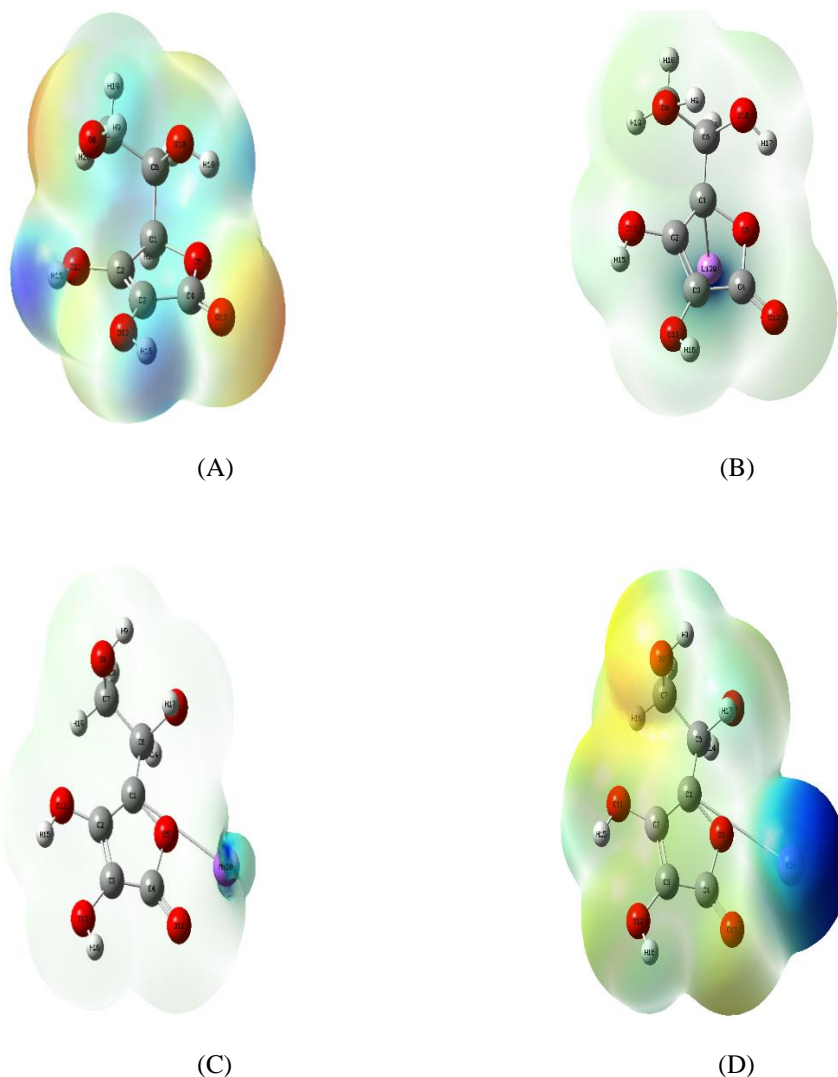


Figure 7. The PES of (A) ascorbic acid (B) ascorbic acid doped with lithium (C) ascorbic acid doped with sodium (D) ascorbic acid doped with potassium.

4. Conclusion

This research focuses on the increasing the medicinal effect of ascorbic acid through doping with alkali-earth metal family through change in the bandgap energy. Ascorbic acid is an oxidizing agent that can be to use medicine that can be use to bust the immune system of the body. The activity of the titled molecule can be increase through a better understanding of is bandgap and controlling it. The disease normally started in the body due to formation of ionic radicals which is caused by breaking of bonds in some molecules. As result of increasing the efficiency of the titled molecule through bandgap control the rate at which diseases in the body are spreading. This research analyzes the properties of ascorbic acid such

as bandgap, spectroscopic properties and density of states. These properties were investigated on the pure ascorbic acid and later investigated on the ascorbic acid doped with first three members of alkali-earth metal family (F, Cl, and Br) to check any change in the electronic structure. The 6-311G/B3LYP basis has been selected from DFT method after the optimization check. Spectroscopic structure determination analysis was conducted on the titled molecules and the doped titled molecules. The analysis include NMR, UV-VIS, and FT-IR. It was found that the ascorbic acid molecule is responding to doping through change in the bandgap.

Conflict of Interests

The authors declare no conflict of interest.

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