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Halogen Doping to Control the Band Gap of Ascorbic Acid: A Theoretical Study

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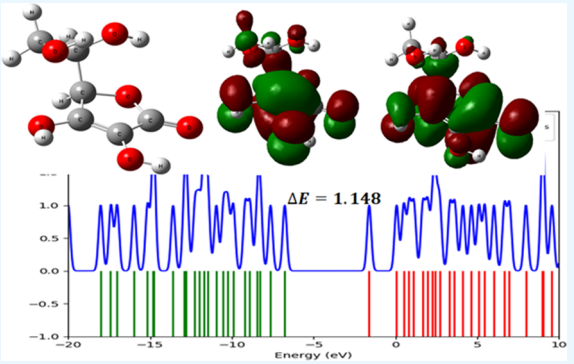
ABSTRACT: Ascorbic acid is an important antioxidant agent that acts as an electron donor and is involved in many physiological processes. Structural modification in ascorbic acid is a subject of extensive biochemical research due to its involvement in a variety of relevant phenomena including electron transport, complex redox reactions, neurochemical reactions, enzymatic reactions, and chemotherapeutic potential. In this work, the structure of ascorbic acid is modified via doping with the first three members of the halogen group to investigate the changes in the electronic structure and spectroscopic parameters using first-principles methods. To obtain the lowest-energy structures, different basis sets in density functional theory (DFT) and Hartree−Fock approaches were employed in the geometry optimization process. The potential energy maps of the structures were computed to study the molecular orientations and their optical and electrical properties. The spectroscopic properties were computed via UV−vis and nuclear magnetic resonance (NMR) spectroscopies to study the effects of doping into the compound. To obtain further insights into the chemical structure, the Fourier transform infrared (FT-IR) spectra of the materials were theoretically investigated. It was found that the band gap is sensitive to doping as we moved from fluorine to chlorine and then to bromine.



1. INTRODUCTION

Ascorbic acid (vitamin C) is a crucial natural organic compound that is present in the majority of fruit and some specialized vegetables.[1] It is an organic compound with the chemical formula $C_6H_8O_6$ that is chiral with six carbon atoms and has four stereoisomers.[2] Since the human body cannot indigenously produce vitamin C just like other animals, we have to obtain it from our diets or alternate sources.[3] Humans require vitamin C as a micronutrient.[4] It has been classified as an antioxidant. When oxidative stress is elevated, the effects of vitamin C may be more pronounced. With some infections in humans and other higher animals, the body releases an oxidizing agent that causes phagocyte activation (i.e., reactive oxygen species). These reactive species play a very important role in the deactivation of viruses and the killing of bacteria.[4−6] Analytical forensic studies have revealed that vitamin C can be used as a protective agent and remedy against stress as a result of an environment that is cold or hot.[7−10] The presence of ascorbic acid in blood plasma is 10 times lower than that in white blood cells, which is clear evidence that it plays an important role in the immune system of the body in the cells. Vitamin C also influences virus replication, interferon production, T-lymphocyte maturation, and phagocyte maturation in the laboratory.[11−15]

The fact that the human body is unable to produce ascorbic acid on its own makes the study and understanding of the acid (i.e., pharmacological, chemical, and biochemical importance) necessary and important for spectroscopic analysis.[16] The consumption of the acid on a regular basis through vegetables and fruits is very beneficial for the synthesis of some biological processes in the body. Analyses such as neutron and x-ray diffraction have been used to determine the spatial arrangement of atoms in ascorbic acid. The vibrational spectra of the compound in the range of 4000−900 cm^{-1} in the solid phase have been studied by Hvoslef and Klaeboe.[17,18]

In another study conducted by Panicker et al., it was discovered that the main bands in ascorbic acid are the bands of the lactone ring when FT-IR and SERS spectra have been analyzed.[19] In different studies, the vibrational spectra of vitamin C in diethylsulfoxide and dimethylsulfoxide solutions were analyzed. It has been found that the majority of the

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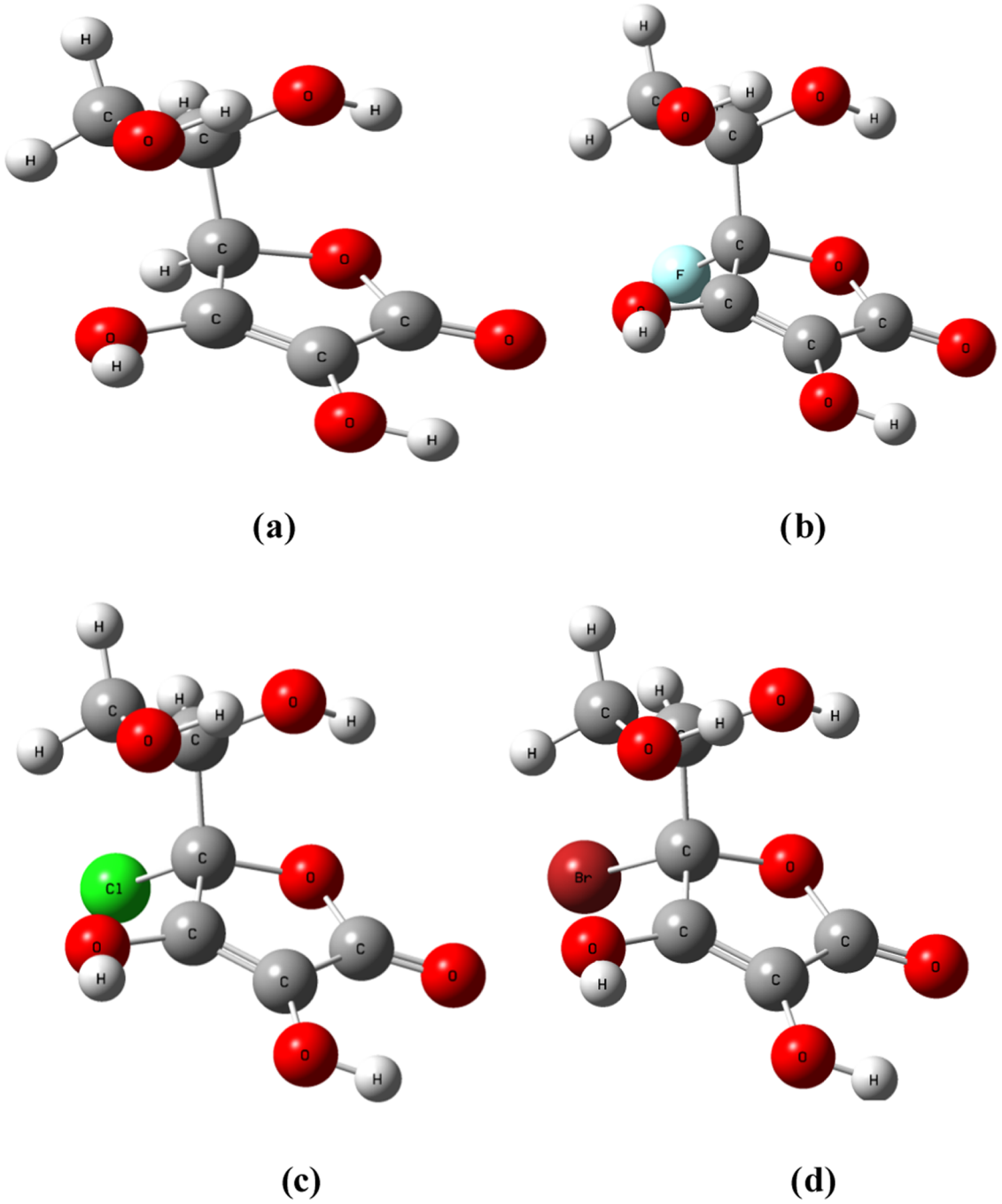

Figure 1. Geometrical structure of ascorbic acid, (a) pure, (b) with F (c) with Cl, and (d) with Br.

vibrational bands are a result of the enol group, which makes the compound a strong reducing agent. Hence, degradation of biologically active ascorbic acid is associated with changes in the juice flavor and color; as a matter of fact, it is extremely useful in nutrition.

Furthermore, a comprehensive characterization of vibrations in vitamin C is critical for determining the degree of decomposition and quantifying ascorbic acid in pharmaceutical and food products.[20]

Disease is always present in the human body and other animals due to broken bonds in the molecules, which result in the formation of radicals that cause the disease. Ascorbic acid is well known for washing away these radicals from the body. In this research, the band gap of ascorbic acid is analyzed to make it more effective by doping it with the first three members of the halogen family. With this work, we present a fresh method for calculating the band gap when some halogen atoms are added to the ascorbic acid. The impact of halogens on the band gaps, which are crucial for understanding how ascorbic acid transfers electrons, remained unclear until recently. We investigated ascorbic acid as a particular possibility for this goal as a new step to address this issue.

2. COMPUTATIONAL PROCEDURE

In this work, the DFT calculations were implemented using the Gaussian 09 package.[21] The B3LYP functional was used to achieve title molecular optimization along with the 6-311G basis set.[22−24] The method was implemented by different

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Table 1. Comparison Showing the Optimization of Basis Sets for Hartree−Fock Versus DFT

basis set	Hartree−Fock (eV)	DFT (eV)
STO-3G	0.801	0.700
3-21G	6.254	4.895
6-31G	7.050	5.146
6-31G	7.050	5.146
6-311G	7.286	1.147
LanL2DZ	7.272	5.129
LanL2MB	0.806	1.674
SDD	7.459	5.247

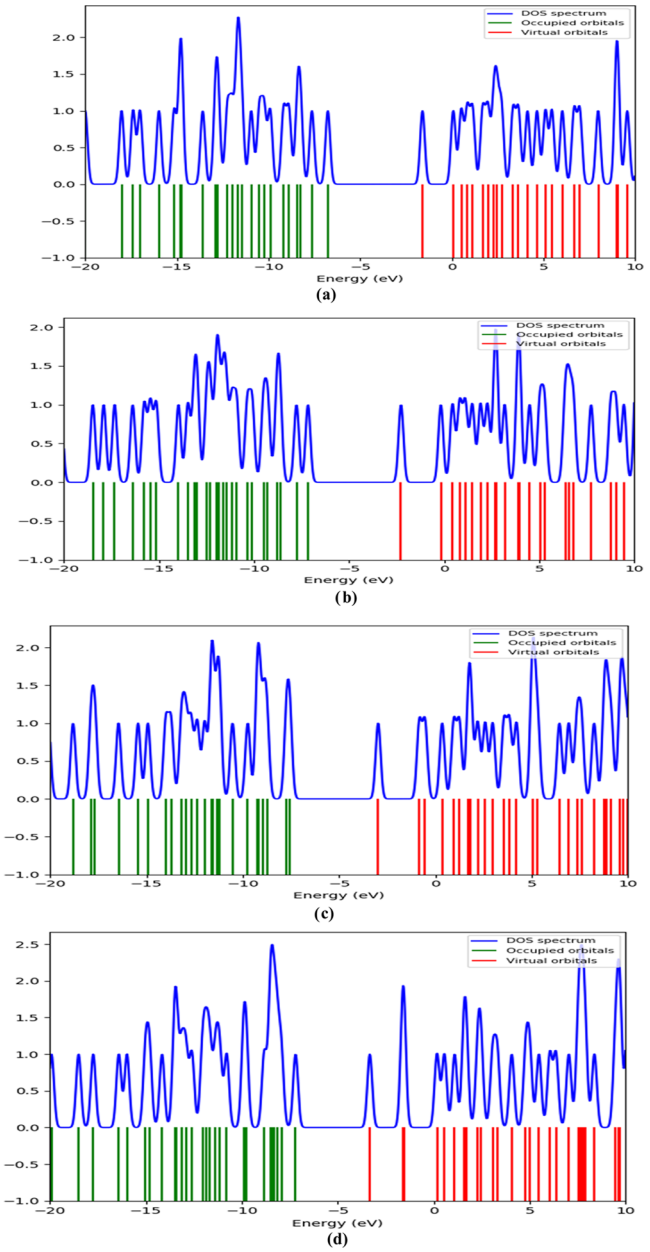

Figure 2. Density of states of (a) ascorbic acid, (b) ascorbic acid doped with fluorine, (c) ascorbic acid doped with chlorine, and (d) ascorbic acid doped with bromine.

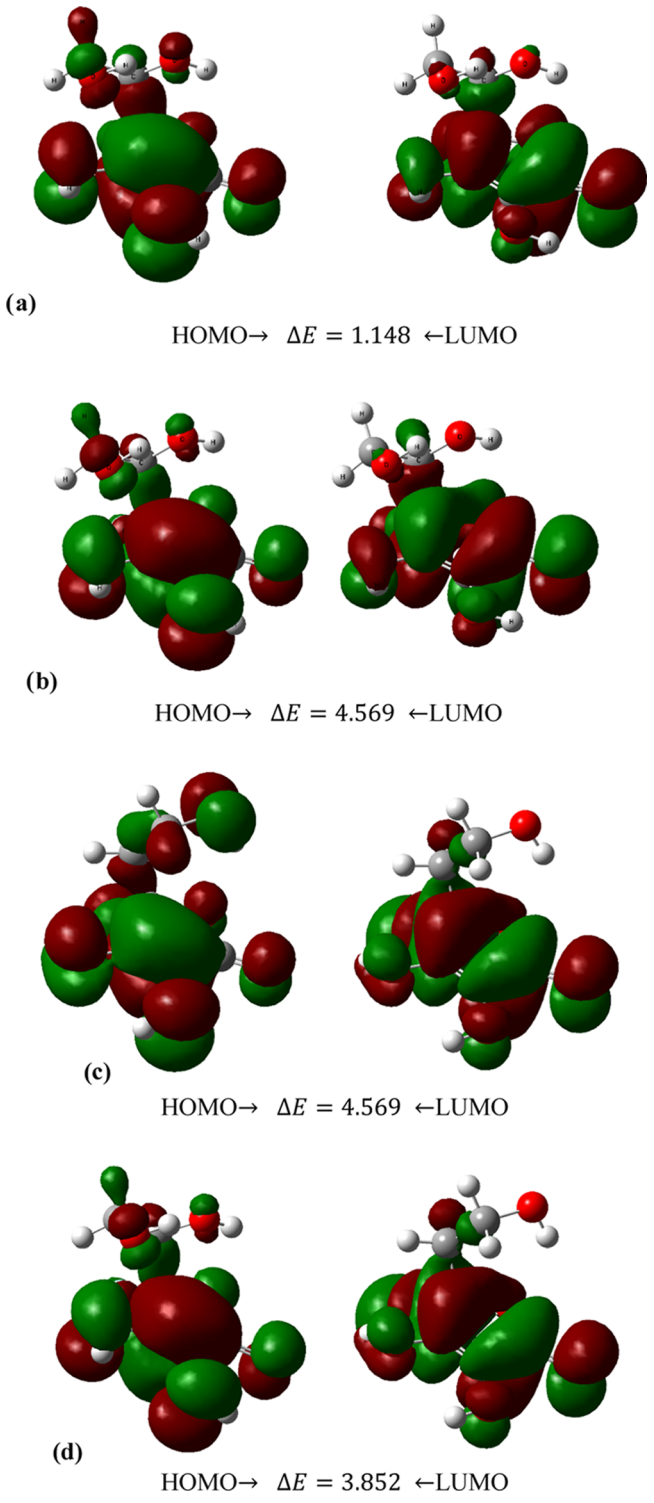

Figure 3. Frontier molecular orbital of ascorbic acid and ascorbic acid doped with the halogens, (a) ascorbic acid, (b) ascorbic acid doped with fluorine, (c) ascorbic acid doped with chlorine, and (d) ascorbic acid doped with bromine.

papers to describe the geometries and energies of noncovalent systems. The ground-state geometry optimization of ascorbic acid was done with DFT using the hybrid functional B3LYP at various basis sets: STO-3G, 3-21G, 6-31G, 6-31G*, 6-311G, LanL2MB, LanL2DZ, and SDD. The frequency calculation was performed using the optimized structure to obtain the minimum on the potential energy surface.[25] Furthermore, the UV is also determined using the optimized structure. The plotting of the three-dimensional mapping of the molecular orbitals is done using the B3LYP/6-311G basis set.[26] At the

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B3LYP/6-311G basis sets, the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energies are calculated (Figure 1). All calculations in this paper are performed using the Gaussian 09 program.[27−30]

3. RESULTS AND DISCUSSION

The ascorbic acid structure was designed using GaussView, and then, two models were used to optimize the structure (Hartree−Fock and DFT) using a different set of eight basis sets to find the suitable basis set (i.e., basis set with the lowest energy) for the following calculations (Table 1). During the stability check, there is an appearance of a bond from the ascorbic acid ring to the halogen group, and this shows that there is a strong bond between the atoms in the molecules and the structure is stable as well.[31]

Table 2. Comparison of the Band Gaps of Ascorbic Acid Doped with the First Three Members of the Halogen Group

S/N	atom doped with ascorbic acid	energy of the 6-311G basis set (eV)
1	fluorine	4.875
2	chlorine	4.569
3	bromine	3.852

3.1. Molecular Orbitals. The molecular orbital is one of the crucial factors that determine some spectroscopic, optical, and electrical properties such as UV−Vis spectra and chemical reactions.[32] Figure 2 depicts the precise information of distributions and energy levels of the HOMO, HOMO1, LUMO, and LUMO + 1 orbitals of ascorbic acid and that doped with the first three members of the halogen family at the B3LYP/6-311G basis set.

The calculation shows that normal ascorbic acid has 47 molecular orbitals that are occupied. The highest occupied molecular orbital (HOMO) is localized on the lactone ring, while the lowest unoccupied molecular orbital (LUMO) is not localized on the lactone ring but is very close to it. As seen in Figure 3, both the HOMO − 1 and LUMO + 1 are delocalized on the oxygen atom. The HUMO−LUMO energy values of ascorbic acid and ascorbic acid doped with the first three members of the halogen family are shown in Figure 3. In the attempt to create a close relationship between the biochemical system and chemical reactions, the band gap energy of the HOMO−LUMO is always used as a factor (i.e., quantum

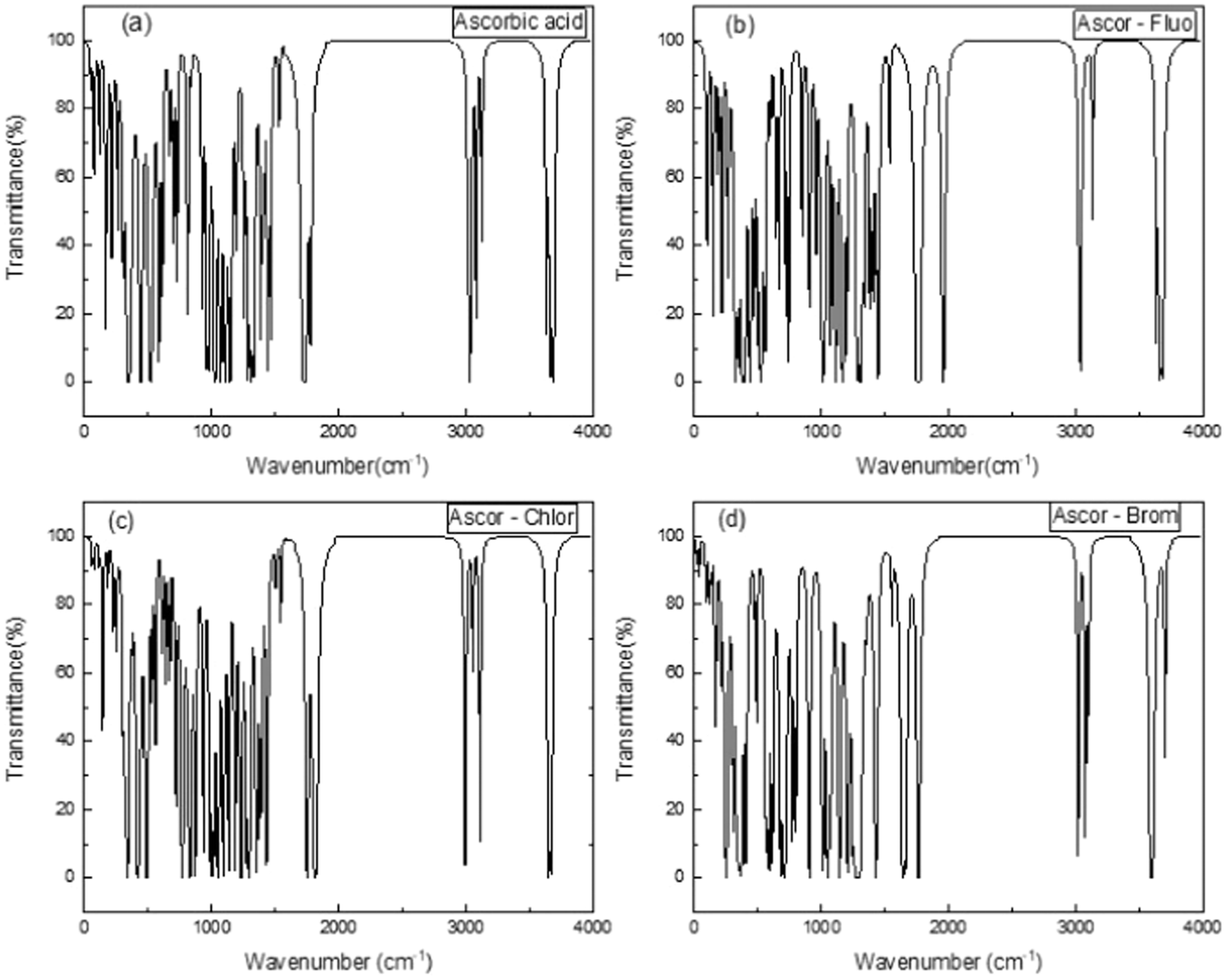

Figure 4. Comparison of FT-IR absorbance spectra of the ascorbic acid and then that with the first three members of the halogen group, (a) ascorbic acid, (b) ascorbic acid doped with fluorine, (c) ascorbic acid doped with chlorine, and (d) ascorbic acid doped with bromine.

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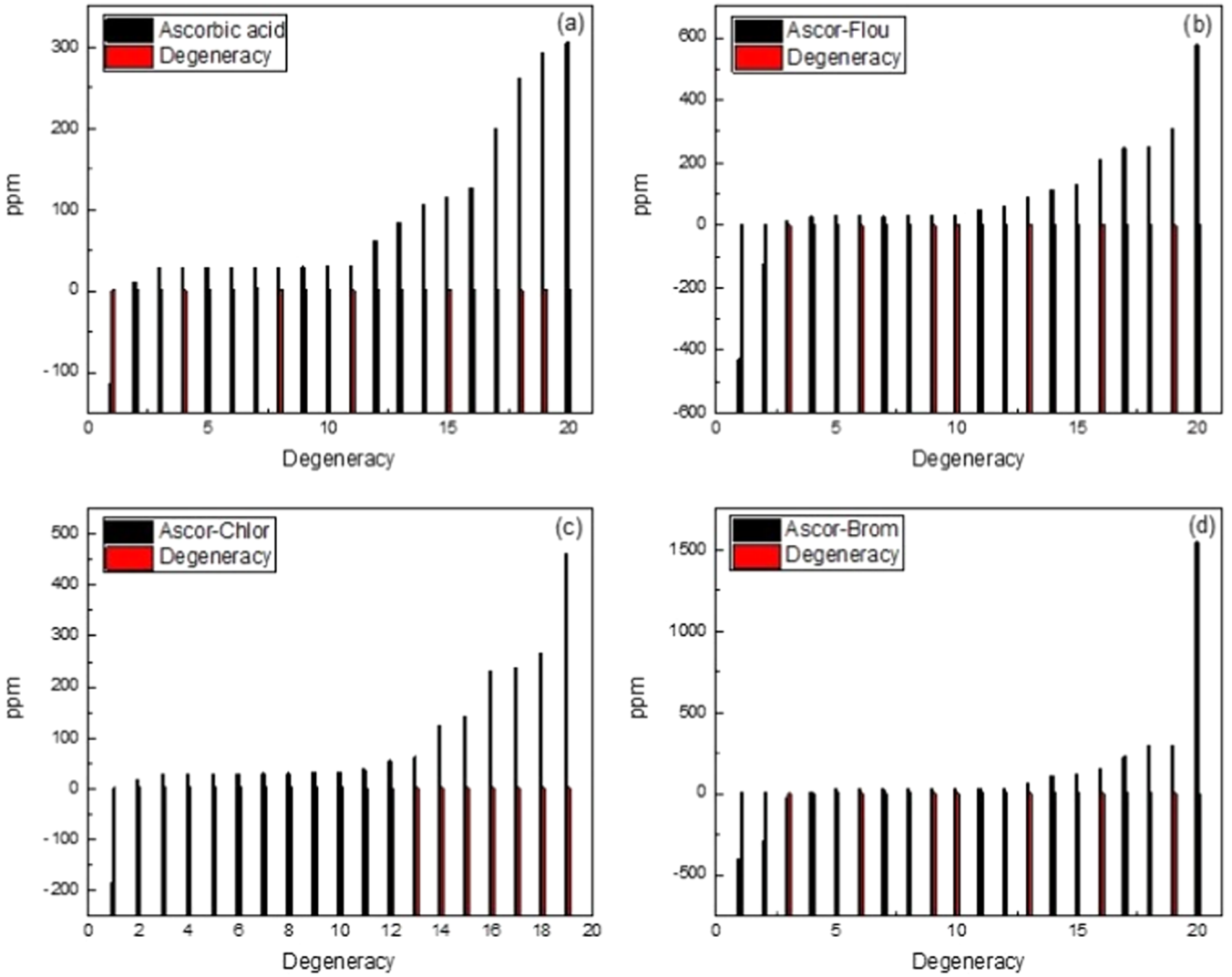

Figure 5. NMR of (a) undoped ascorbic acid, (b) ascorbic acid doped with fluorine, (c) ascorbic acid doped with chlorine, and (d) ascorbic acid doped with bromine.

Table 3. Computed NMR in ppm for Halogen Members Doped in Ascorbic Acid

S/N	doping atom	NMR (ppm)
1	fluorine	461.5714
2	chlorine	579.5031
3	bromine	1549.4873

chemical descriptor).[33] The wide difference in the energy band gaps indicates the high stability of the complex compound under investigation. There is another property associated with the band gap energy, i.e., polarizability. Soft molecules are less polarizable than hard molecules. The difference in the HOMO−LUMO band gap energy in normal ascorbic acid in the gas phase is 3.478 eV (Table 2).

3.2. Electronic and Optical Properties. The vibrational frequencies of ascorbic acid in this research were investigated using the DFT/B3LYP method incorporated with a 6-311G basis set. The infrared spectroscopy vibrational band assignments were plotted using the GaussView molecular visualization program, and Fourier transform infrared spectroscopy vibrational bands were characterized.[34] The correspondence between the pure ascorbic acid and then the ascorbic acid doped with the first three members of the halogen group frequency calculations can be seen from the plots presented in Figure 4.

The presence of the lactone ring in the ascorbic acid structure can be easily determined from the C−H and C═C−H ring vibrations. The C−H stretching vibrations of ascorbic acid occur at about 3000 cm^{-1}, and there is also the presence of weak to moderate bands (multiplicity) when compared with normal C−H stretching.[31] In this work, the vibrational modes are calculated theoretically in the range of 3065−3124 cm^{-1}. This shows an excellent and precise agreement with the experimental results.[18,35]

The normal aliphatic C−H stretching was detected experimentally at about 2867−2973 cm^{-1}.[32] In the work, C−H stretching in ascorbic acid was calculated at 2979−3046 cm^{-1} for B3LYP, while 1259, 1193, and 1147 cm^{-1} bands are ascribed to the C−H in-plane bending vibration in the ascorbic acid. The theoretical results obtained from the B3LYP model are close to the true value, which is an indication of the accuracy of the model. The C−C stretching vibration in the ring has different values due to the nature of the ring, but in most cases, it ranges from 1600 to 1350 cm^{-1}.[33] The value has

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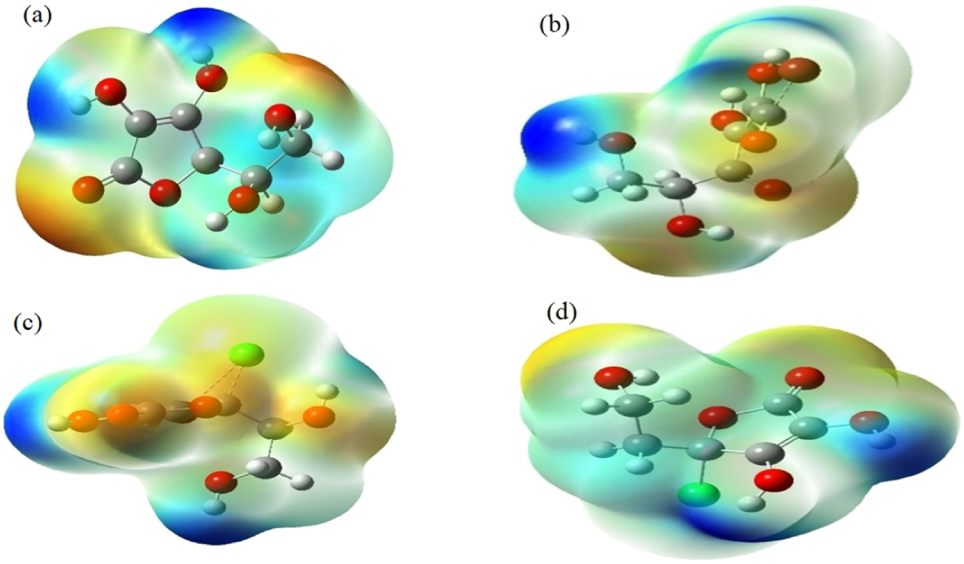

Figure 6. Potential energy maps for (a) ascorbic acid, (b) ascorbic acid doped with fluorine, (c) ascorbic acid doped with chlorine, and (d) ascorbic acid doped with bromine.

a little increase due to the DFT method approximation in this work and is found to be at 1680, 1444, and 1365 cm^{-1}.

3.3. Nuclear Magnetic Resonance (NMR). Figure 5 gives the theoretically computed H-NMR and C-NMR structures of normal ascorbic acid and that doped with the first three members of the halogen group. The Gaussian 09 software package was used to calculate the NMR. The figures show that the shielding for the normal ascorbic acid is from −100 to 300 ppm.[36] There was a shift in ppm when fluorine was introduced into the compound from −600 to 600 ppm. The changes in ppm also continued when fluorine was replaced with chlorine from −200 to 500 ppm. The changes in ppm were intense when bromine was introduced from −500 to 1500 ppm. This was a clear indication that the shielding range increased with an increase in the electronegativity of the halogen family.[37]

Figure 5 shows the normal NMR peaks of the undoped ascorbic acid with more carbon at the upfield and less carbon at the downfield. The entire orientation of the molecules changed when fluorine was introduced. A sharp medium peak of fluorine appears at 461.5714 ppm, and also the carbon atoms and the hydrogen atoms changed their chemical environment due to the inductive and neighboring effects. The same trend occurred when fluorine is replaced with chlorine and later bromine; they have peaks at 579.5031 and 1549.4873 ppm, respectively. This proves that the NMR peaks generated by the members of the halogen family in ascorbic acid have a close linear relationship with their electronegativity.[38] Table 3 gives the precise individual positions of the halogen members in terms of ppm.

3.4. Potential Energy Map (PES). The potential energy map plays a vital role in the explanation of the orientation of the molecule and also in determining the optical and electrical properties of the molecules.[39] In the normal ascorbic acid, as per Figure 6a, the electrons are concentrated toward oxygen (the blue portion) because oxygen is more electronegative than both carbon and hydrogen.

The orientation of the said molecule (i.e., ascorbic acid) has changed when fluorine is doped. Fluorine has a higher electron affinity than that of carbon and hydrogen, and electrons migrate toward the fluorine atom in the molecule.[40] The same trends occurred with chlorine and bromine as well. This makes the blue portion of Figure 6b−d the most reactive part of the doped ascorbic acid.

4. CONCLUSIONS

In this research, the main properties of ascorbic acid were calculated (including band gap, density of states, and spectra), and it is then doped with the first three members of the halogen group to compare many different properties including the change in the band gap energy and other spectroscopic parameters. Different basis sets in DFT and Hartree−Fock were used in the optimization process to determine the lowest energy and suitable basis set for the whole calculation of ascorbic acid, and then, later, the compound was doped with the first three halogen members separately. Spectroscopic properties were determined such as UV−vis and NMR for both the doped and undoped ascorbic acid. Finally, the FT-IR spectra of the ascorbic acid doped with different members of the halogen group were investigated by the theoretical method. It was found that the band gap is sensitive to the doping as we moved down the group members (the band gap depends on the electronegativity of the halogen members).

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Notes

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