Earthline Journal of Chemical Sciences
E-ISSN: 2581-9003; CODEN: EJCSB4
Volume 13, Number 4, November 2026, Pages 399-408
https://doi.org/10.34198/ejcs.13426.28.399408

Effect of zinc cation on PABA – A DFT treatment

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Abstract

p-Amino benzoic acid (PABA) should be considered a pseudo vitamin because it has no role in human nutrition. It is in fact, a chemical that bacteria use it a part of folic acid synthesis. So PABA should be considered as a vitamin for bacteria. The only substantiated use of it, is the best available sunscreen and has been included in almost in every suntan products. Presently, interaction of zinc cation with PABA have been investigated within the constraints of density functional theory (DFT) theory at the level of B3LYP/6-31++G(d,p). The collected data have revealed that the optimized structures of PABA and PABA+Zn^{+2} have exothermic heats of formation and favorable Gibbs free energy of formation values. They are thermally favored and electronically stable at the standard states. Various structural and quantum chemical data have been collected and discussed, including bond densities and time dependent density functional UV-VIS spectra.

1. Introduction

Para-aminobenzoic acid (4-aminobenzoic acid, PABA) is an aromatic structure having molecular formula $C_7H_7NO_2$ [1,2]. PABA has been extensively used in the chemical industry as a starting material for the preparation of folate, which a crucial vitamin required for DNA synthesis and replication [3]. The deficiency of PABA leads to several disorders like erratic white areas of skin, grey hair, fatigue, depression and irritability. It is also used for the production of hair dyes and sunscreens due to its ability to absorb UV radiation [4]. Furthermore, the PABA is a non-toxic molecule, easily absorbed in the intestine, and its derivatives are capable of broad biological activities [5]. The drugs containing PABA scaffolds are believed to be well tolerated [6]. In folic acid synthesis, para-aminobenzoic acid is a necessary and irreplaceable vitamin of group B [7] and PABA is found in various foods such as grains, milk, eggs, and meat. Through folic acid breakdown, it is also produced in the human body [8]. Besides its medicinal importance, PABA has been used in the synthesis of various biologically active heterocyclic nuclei like benzimidazoles, azitidinones, thiazolidinones, pyrazoline, etc. [9]. PABA fits well as a building block for a general chemical library of “drug-like” molecules with a wide range of functional and structural diversity [10,11].

In recent years many publications on usage of PABA have emerged in the literature [12-16].

On the other hand, zinc is one of the most abundant and nutritionally essential elements in the human body. In general, it is found in all body tissues (such that with 85% of the whole body zinc is in muscle and bone, 11% in the skin and the liver and the rest remains in all the other tissues [17]). Virtually all zinc in multicellular organisms, is intracellular, 30–40% of it is located in the nucleus, 50% in the cytoplasm, organelles and specialized vesicles including digestive enzymes or hormones and the remainder in the cell membrane [17,18]. Zinc is essential for the structure and function of a large number of macromolecules and for over 300 enzymic

Received: August 23, 2026; Accepted: September 22, 2026; Published online: September 24, 2026

Keywords and phrases: para-aminobenzoic acid, 4-aminobenzoic acid, PABA, zinc cation, DFT calculations, UV-VIS spectra.

reactions [19]. It has both catalytic and structural roles in enzymes, it provides a scaffold that organizes protein sub-domains for the interaction with either DNA or other proteins [17,19]. It is critical for the function of a number of metalloproteinase, and has coactivating functions with copper in superoxide dismutase or phospholipase C. The zinc ion (Zn++) does not participate in redox reactions, thus it is a stable ion in a biological medium whose potential is in constant flux. Zinc ions are hydrophilic and do not cross cell membranes by passive diffusion [17,18]. Zinc ions exist primarily in the form of complexes with proteins and nucleic acids and participate in all aspects of intermediary metabolism [17]. The body tightly regulates homeostasis through two specific transporter families: ZIP proteins (which move zinc into cells) and ZnT proteins (which move zinc out of cells or into organelles) [20]. Zinc and some human diseases are interrelated in many respects [21,22].

2. Method of Calculations

In the present study, all the initial optimizations of the structures leading to energy minima have been achieved first by using MM2 method which is then followed by semi empirical PM3 self consistent fields molecular orbital method [23-25]. Afterwards, the structure optimizations have been achieved within the framework of Hartree-Fock and finally by using density functional theory (DFT) at the level of B3LYP/6-31++G(d,p) [26,27]. Note that the exchange term of B3LYP consists of hybrid Hartree-Fock and local spin density (LSD) exchange functions with Becke's gradient correlation to LSD exchange [28]. The correlation term of B3LYP consists of the Vosko, Wilk, Nusair (VWN3) local correlation functional [29] and Lee, Yang, Parr (LYP) correlation correction functional [30]. In the present study, the normal mode analysis for each structure yielded no imaginary frequencies for the $3N–6$ vibrational degrees of freedom, where N is the number of atoms in the system. This search has indicated that the structure of each molecule considered corresponds to at least a local minimum on the potential energy surface. Furthermore, all the bond lengths have been thoroughly searched in order to find out whether any bond cleavages occurred or not during the geometry optimization process. All these computations were performed by using SPARTAN 06 program [31].

3. Results and Discussion

Figure 1 shows the optimized structures of the systems of consideration. The arrows stand for the direction of calculated dipole moment vectors. One must keep in mind that the resultant dipole moment vector of a molecule is the vectorial sum of the individual bond dipoles, thus location of the heteroatoms and the conjugation present greatly affect both the magnitudes and the directions.

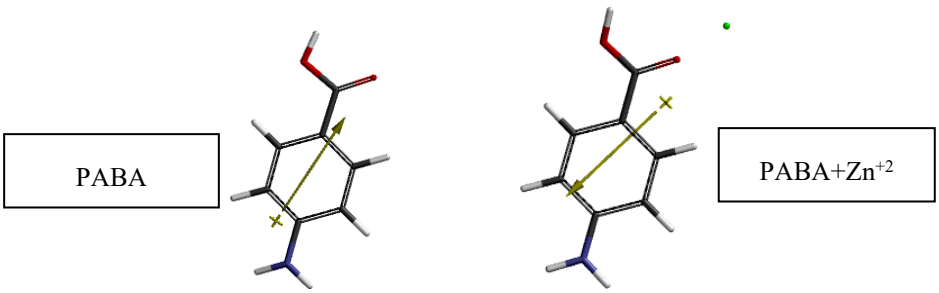


Figure 1. Optimized structures of the species of interest.

Figure 2 displays the calculated bond lengths of the species considered. The figure reveals that most of the bond lengths (rings C-C as well as C-H bonds) and carboxylic acid C-O bonds are affected by the presence of

the zinc cation. In general, ring C-C bonds are longer in PABA+Zn^{+2}. It should be because of the reshuffling of electron population of PABA under the influence zinc cation.

Figure 2 shows the calculated bond lengths of the species presently considered. Note that not only the bond lengths but also some respective bond angles vary between the two figures.

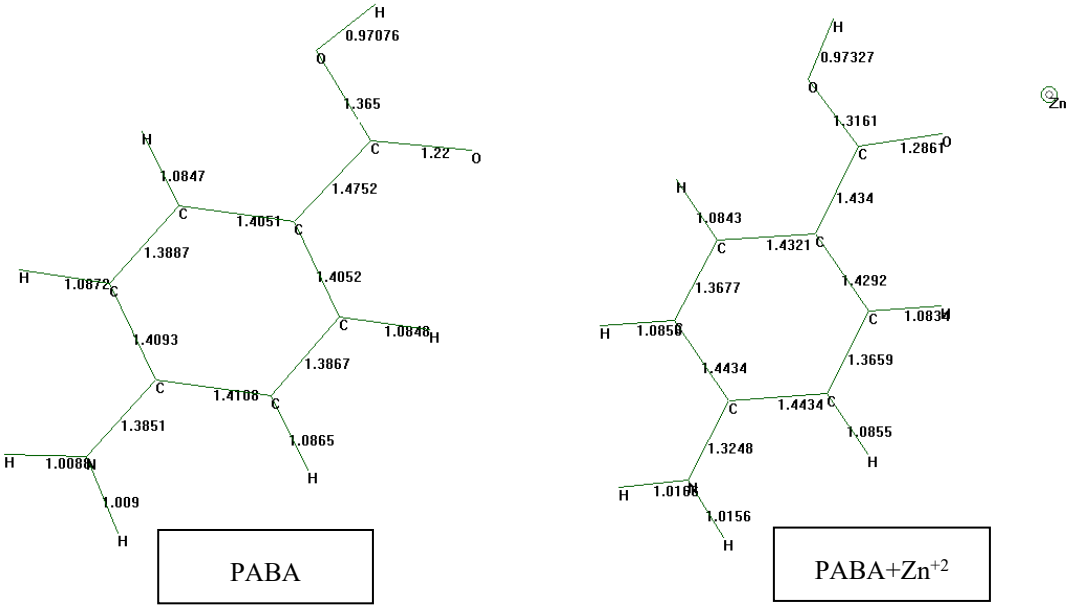


Figure 2. The calculated bond lengths of the species considered.

Some thermo chemical properties and energies of the species presently considered are listed in Tables 1 and 2, respectively. The data presented in the Table 1 reveal that the standard thermo chemical formation data of all the species considered are exothermic (H^o values) and they are favored according to their G^o (Gibbs free energy of formation) values. In Table 2, E, ZPE and E_C stand for the total electronic energy, zero point vibrational energy and the corrected total electronic energy, respectively. According to the data, all the structures are electronically stable.

Table 1. Some thermo chemical properties of the the species considered.

Species	H^o	S^o (J/mol^o)	G^o
PABA	-1249963.06	365.57	-1250072.053
PABA+Zn^{+2}	-5919307.772	396.53	-5919425.973

Energies in kJ/mol.

Table 2. Some energies of the species considered.

Species	E	ZPE	E_C
PABA	-1250321.46	346.47	-1249974.99
PABA+Zn^{+2}	-5919630.56	351.47	-5919279.09

Energies in kJ/mol.

Figure 3 shows the electrostatic potential maps of the species considered. It is noteworthy that electro static potential is the energy of interaction of a positive charge with the nuclei and fixed electron distribution of a molecule [31]. In an electrostatic potential map negative potential regions reside on red/reddish and positive ones on blue/bluish parts of the maps. As seen in the figure, in case of PABA+Zn^{+2}, the positive charge of the zinc cation, affects the whole system, thus the local effects are veiled.

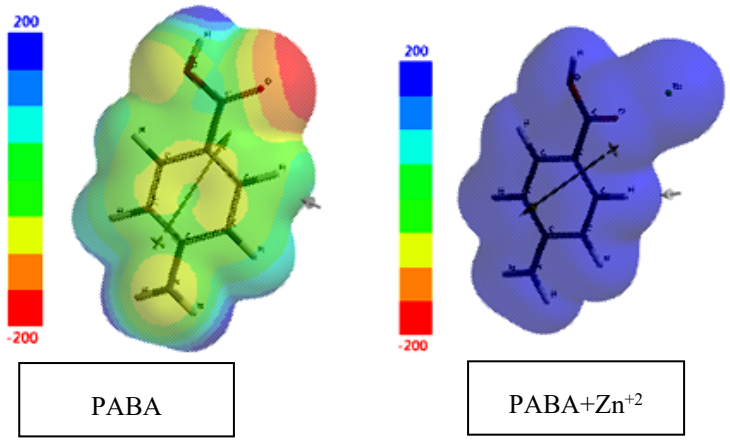


Figure 3. Electrostatic potential maps of the species considered.

Figure 4 shows the distribution of the ESP charges of the species considered. The ESP charges are obtained by the program based on a numerical method that generates charges that reproduce the electrostatic potential field from the entire wavefunction [31].

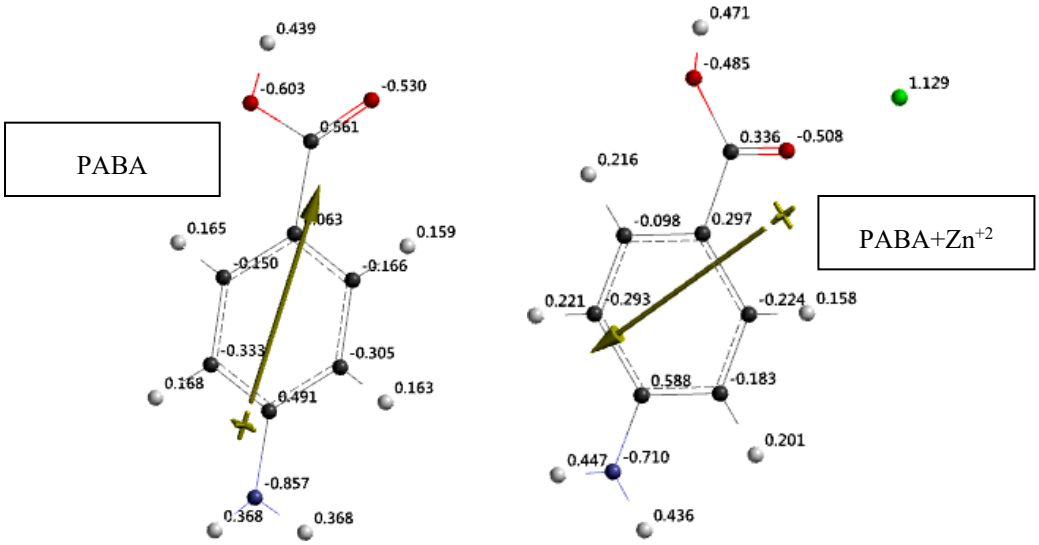


Figure 4. Distribution of the ESP charges of the species considered.

The zinc cation redistributes the ESP charges of PABA, and some decrease and some increase. It is evident from Figure 4 that some π-population of ring is donated to the zinc cation so that its initial +2 charge decreases in PABA+Zn^{+2}.

Figure 5 displays the local ionization potential maps of the species considered, where conventionally, red/reddish regions (if any exists) on the density surface indicate areas of which electron removal is relatively

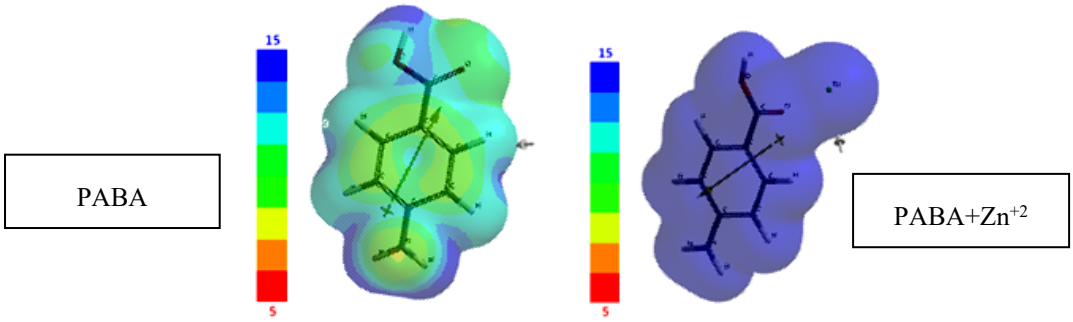


Figure 5. Local ionization potential maps of the species considered.

easy, meaning that they are subject to electrophilic attack. Note that the local ionization potential map is a graph of the value of the local ionization potential on an isodensity surface corresponding to a van der Waals surface [31,32]. The positive charge of the zinc cation veils the local effects.

Figure 6 stands for the bond density maps of the species considered. The bond density contains fewer electrons in total and demarks atomic connectivity.

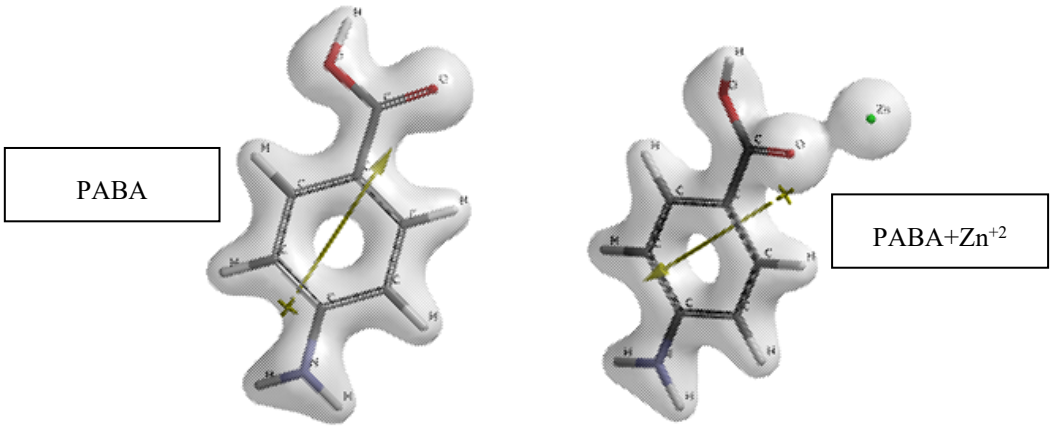


Figure 6. Bond density maps of the species considered.

Figure 6 reveals that there exists an interaction between the organic moiety (PABA) and the zinc cation. The interaction is at the site of C=O moiety, where the oxygen atom is more negative than O-H oxygen atom (see Figure 4).

Figure 7 shows some of the molecular orbital energy levels of the species. The cation lowers all the molecular orbital energy levels, however lowering on the HOMO and LUMO energy levels are unequal extents, thus the interfrontier molecular orbital energy gap ($\Delta\varepsilon = \varepsilon_{LUMO}-\varepsilon_{HOMO}$) of PABA+$Zn^{+2}$ is much less than the respective value of PABA.

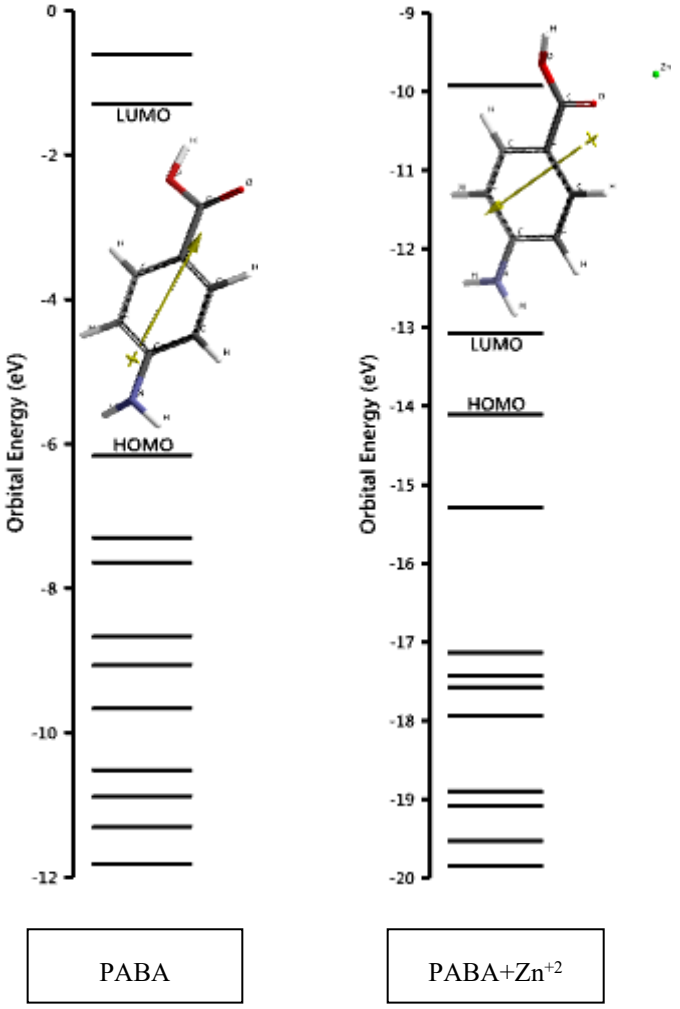


Figure 7. Some of the energy levels of the species considered.

Table 3 lists the HOMO, LUMO energies and Δε values (frontier molecular orbital energy gap, $\Delta\varepsilon = \varepsilon_{LUMO} - \varepsilon_{HOMO}$) values of the species considered.

Table 3. The HOMO, LUMO energies and Δε values of the species considered.

Species	HOMO	LUMO	Δε
PABA	-594.15	-124.96	469.19
PABA+Zn^{+2}	-1361.24	-1261.37	99.87

Energies in kJ/mol.

Figure 7 and the data of Table 3 clearly indicate that the presence of the cation substantially lowers both the LUMO and HOMO energy levels. Consequently, PABA+Zn^{+2} possesses a Δε value much smaller than the respective value of PABA.

Figure 8 shows the HOMO and LUMO patterns of the species considered. They generally possess π-type symmetry. In PABA the carbonyl group contributes the HOMO less than its contribution to the LUMO. There exists strong conjugation with ring orbitals which is apparently reflected in the LUMO pattern. Those effects arise from the electron donating effect of p-amino substituent, whose contribution to the HOMO is greater than its contribution to the LUMO. The HOMO and LUMO patterns of PABA+Zn^{+2} have been perturbed to a great extent and large contribution of the cation in to both of the frontier orbitals are noticeable.

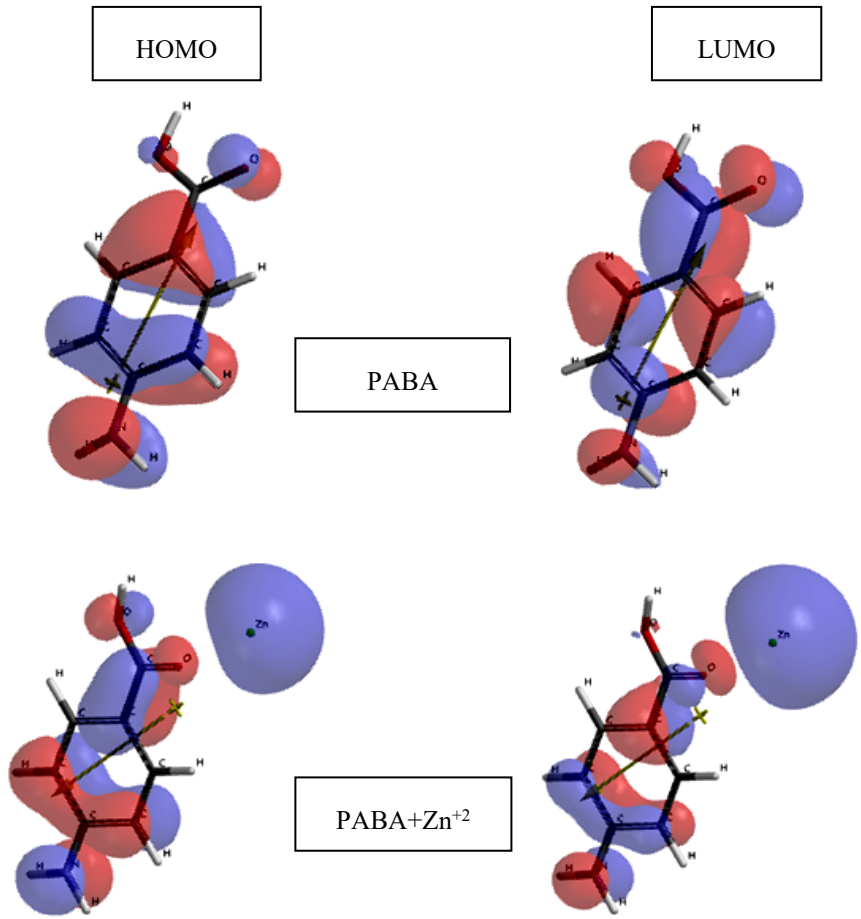
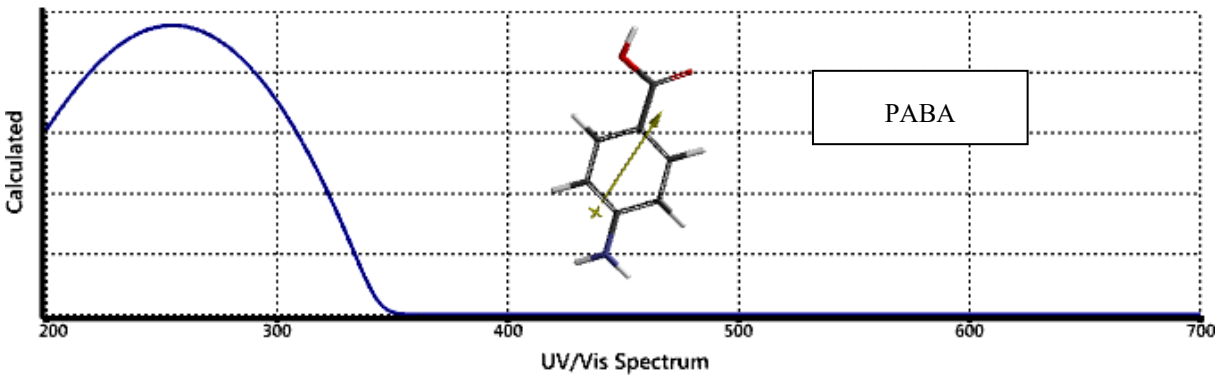


Figure 8. The HOMO and LUMO patterns of the species considered.

Figure 9 shows the UV-VIS (time dependent density functional) spectrums of the species considered. According to the data obtained PABA absorbs in the UV region of the spectrum, in contrast to PABA+Zn^{+2} case which covers the visible region as well. The bathochromic effect exhibited is due to the effect of the zinc cation. Also, in the later case absorptions at 300.30(0147), 333.36(0.161), 3444.48(0.428), 356.93(0.277), and 411.97(1.106) emerge. The calculated intensities of the peaks (which are in parenthesis, raw data) are related to magnitudes of the electronic transition moments between the orbitals involved in the transitions which vary from structure to structure [33,34].



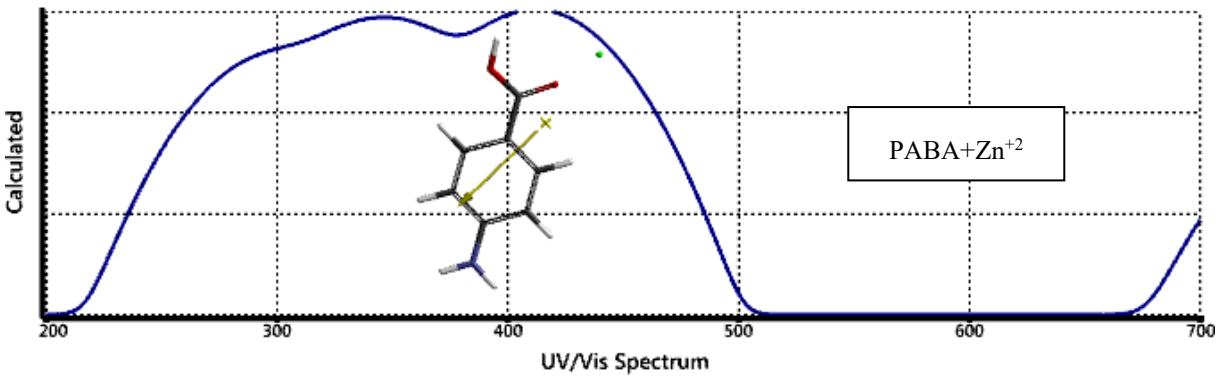


Figure 9. The UV-VIS spectrums of the species considered.

PABA has been included in almost in every suntan products and according to the present DFT study, the zinc cation extends its absorption spectrum towards the visible region. Note that human sweat contains various zinc products which may be producing zinc cation.

4. Conclusion

The present study considers interaction of zinc cation and PABA leading to PABA+Zn^{+2} and has been subjected to DFT treatment at the level of B3LYP/6-31++G(d,p). The species of interest have exothermic heats of formation and favorable Gibbs free energy of formation values and are thermally favored and electronically stable at the standard states. Most of the properties of PABA, including molecular orbital energy and UV-Vis spectrum are affected by the zinc cation, producing a strong bathochromic effect due to much smaller interfrontier molecular gap of PABA+Zn^{+2}.

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