# DFT Chemical Reactivity Analysis of Biological Molecules in the Presence of Silver Ion

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Abstract

Silver ion oxidation process was studied in different biological molecules by Density Functional Theory; this by using the Becke three parameter Lee, Yang, and Parr functional and the Pople 6-31G (d) and Los Alamos LANL2DZ basis sets. The calculation was used to find the lowest energy molecular structure, molecular orbitals, and chemical reactivity parameters. Chemical hardness showed that the oxidation process begins in the purine and pyrimidine bases. The frontier orbitals electronic density distribution were analyzed in the biological molecule-silver ion complex. This distribution clearly revealed the transfer of electrons from highest occupied molecular orbital to lowest unoccupied molecular orbital indicating an oxidation process.
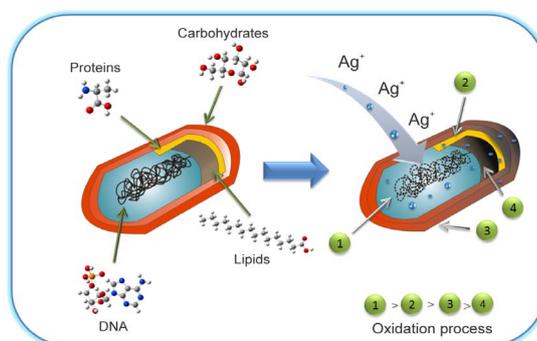
Keywords: Silver ion; DFT; Oxidation process

Introduction

Because of its diverse properties silver is a versatile and safe agent with different uses. Silver ions had been used in biosensors [1], clothing [2], food industry [3-5], stainless steel coatings [6], beauty products [7], and in medical devices [8]. Silver is usually inert in its metallic form; however, it ionizes when in contact with skin moisture or fluids from a wound. As a result, it becomes highly reactive leading into an antibiotic behavior [9-12]. Studies of the inhibitory mechanism of silver ions on gram-positive and gram-negative bacteria have been reported [13,14], showing morphological changes in cytoplasm, cell membrane, and wall.

Currently, there is few information about how silver becomes bioactive. Some authors have reported that silver ions act when they penetrate the cell and get between purine and pyrimidine bases; thus, denaturing the deoxyribonucleic acid (DNA) [15]. Other authors indicate that bioactivity comes from deactivation of respiratory enzymes; this by forming complexes with the sulfur of the thiol group of cysteine [16,17]. It is also been reported that silver can be involved in catalytic oxidation reactions resulting from the formation of disulfide bonds (R-S-S-R). It catalyzes the reaction between oxygen molecules in the thiol groups. In such reaction, water is released as a by-product and two thiol groups are covalently joined through a disulfide bond [18]. The catalyzed form of silver in disulfide bonds might possibly change the three-dimensional structure of cell enzymes, and thus change their function. The effect of silver ions on bacteria can be difficult to understand. However, observation of morphological and structural changes can yield useful information for understanding the antibacterial effect and the inhibitory process of silver ions. Theoretical studies about the affinity of silver ions with DNA at a molecular level were performed to determine the interaction of silver ions with a cytosine and an adenosine basis, using ab initio calculations and Density Functional Theory (DFT) [19]. Another quantum chemical study, focused to shed light on the electronic and energetic properties of silver upon DNA adenosine and cytosine bases, was performed through DFT using the Becke three parameter Lee, Yang, and Parr functional (B3LYP) and the Minnesota family M06-L functionals [20]. According with the generated results with previous theoretical calculations and the experimental information mentioned above, it is considered imperative to extend the study of biological molecules in presence of silver ion, in an attempt to define the antibacterial mechanism, so, the aim of this research is the study of a silver ion antibacterial mechanism through an oxidation in the presence of biological molecules such as proteins, polysaccharides, lipids, and nucleic acids. In the particular case of biopolymers, they were analyzed according to their constituent monomers through a theoretical study; aiming to determine which parts of the bacterium cell react in the presence of the silver ion. To accomplish this goal, the calculation of the chemical reactivity parameters was done, among them: chemical potential (I), electron affinity (EA), electronegativity

(χ), electrophilicity (ω), chemical hardness (η), and electron donor potential (ω-), which aid in understanding the oxidation process between silver ions and biological molecules. Also, highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), which allow to observe electron transfer. All these parameters were determined through DFT.

Materials and Methods

The studied biological molecules were selected considering them as representative of each group of the different kind of components of the bacterial cell structure: proteins, carbohydrates, lipids and DNA basis.

Proteins

From the non-polar aliphatic R group, alanine was used, since it is abundant in living matter and it is the smallest chiral amino acid [21]. From the aromatic R group, the phenylalanine, since its structure contains an aromatic ring which allows to see its interaction with the silver ion. From the uncharged polar R group, cysteine and its structure contains sulphur and it has a high presence in peptides and proteins. It also has a reactive nature, and its inclusion of a thiol group has a preponderant role in the synthesis of proteins. Moreover, it is known that the thiol group interacts strongly with noble metals such as gold, silver, and cooper [22]. From the negatively charged R group, aspartic acid, since it contains dicarboxylic acids. Also, from the positively charged R group histidine was selected; it contains an imidazole functional group, and this feature will allow to evaluate interactions with the silver ion.

Carbohydrates

Among monosaccharides, D-glucose was analyzed since it has dramatic effects on carbon metabolism regulation and it is responsible for cellular respiration regulation. Also, it has an effect on gluconeogenesis, making it capable of transporting and catabolizing sugars [23]. From polysaccharides, sucrose was analyzed because it has a high molecular weight and it is constituted by glucose and fructose. Also it is certainly involved in metabolic processes. Polysaccharides interfere in adenosine triphosphate (ATP) synthesis, and according to some researchers, silver ions inhibit oxidation of glycol, glucose and other molecules.

Lipids

Lipids are fundamental structural components of cell membranes, they are little oxidizable molecules, and they serve as an energy reservoir for the cell. It is important to analyze the constituting elements of bacterial cell membranes for when there is an attack by foreign agents they become injured. The lipids analyzed in this research were palmitic acid, a saturated lipid, and palmitoleic acid, an unsaturated lipid. Palmitic acid promotes cell cycle progression, it accelerates cell proliferation, and it induces a transient and sequential activation of a series of kinases [24]. Palmitoleic acid is to be analyzed because it is biosynthesized through palmitic acid.

DNA basis

In DNA, purine and pyrimidine bases (adenosine and cytosine) were analyzed. Adenosine monophosphate (AMP) was selected because it has an important role in energy metabolism. Through enzymatic reaction AMP forms bonds with other phosphate groups and plays an important role in incorporating amino acids into proteins [25]. Cytosine monophosphate (CMP) was selected since it is involved in the biosynthetic processes of phospholipids and uracil for carbohydrates [26]. There have been research papers that state silver ions bind to DNA transcription, while in the blocks they bond to the cells of the surface, thus disrupting bacterial respiration, and also they cause interference in ATP synthesis.

Computational methods

Calculations were made using Density Functional Theory, DFT [27-29] to find the geometry in the minimum energy state in the gas phase of L-Alanine (Ala), L-Aspartic acid (Asp), L-Cysteine (Cys), L-Phenylalanine (Phe), L-Histidine (His), Adenosine, Cytosine, D-Glucose, Sucrose, palmitic acid, and palmitoleic acid, with functional B3LYP [30]. All calculations were performed with the Gaussian 09 software [31]. For carbon (C), Hydrogen (H), Oxygen (O), Nitrogen (N) and Phosphorus (P), the Pople 6-31G (d) [32] basis set was assigned, whereas Los Alamos LANL2DZ [33-35] basis set was elected for silver (Ag). The DFT approach has been successful in presenting a theoretical basis for chemical descriptors such as ionization potential (I), electron affinity (EA) which are defined by the energy difference $E_{(N)} - E_{(N-1)}$ and $E_{(N)} - E_{(N+1)}$, where N indicates the parent molecule, N-1 and N+1 correspond to the cation and anion radicals generated after electron transfer. Global hardness (η) [36], electronegativity (χ) [36], electrophilicity (ω) [37], indexes related to electronic structure and chemical reactivity; and the electron donor potential proposed by Gázquez et al. [38], which measures the capability to donate fractioned charges.

Results and Discussion

The geometry optimization of the biological molecules in gas phase and frequency calculation were performed to make sure molecules were in their lowest energy level, Figure 1 shows the optimized geometries of the studied molecules. Condensed Fukui functions are mathematical expressions that define the sensitivity a molecular system has to experience changes in its electronic density, in different points of its structure. In a chemical reaction, a change in the number of electrons involves the addition or subtraction of at least one electron in the frontier orbitals [39]. Thus, calculating Fukui functions helps us determine the reactive sites of a molecule, based on the electronic density changes experienced by it during a reaction. The dual descriptor for nucleophilicity and electrophilicity was defined in terms of the variation of hardness with respect to the external potential; such dual descriptor was defined as the difference between nucleophilic and electrophilic Fukui functions, allowing to characterize both reactive behaviors [40]. The dual descriptor predicted the site reactivity induced by different donor and acceptor groups of the biological molecules. The condensed results of the Fukui indexes and dual descriptor showed which atoms are most susceptible to an electrophilic attack, see Table 1. These results were obtained with the Hirschfeld charge distribution [41]. The definition for these atoms was performed to establish the zone where the silver ion attraction was more likely to create the biological molecule-silver ion complex. Also, energy calculations were performed to obtain the most stable structure of the complex at a specific point, such as exemplified with the Ala-Ag$^+$ amino acid. Figure 2. Qualitative chemical concepts such as electronegativity and hardness have been widely used in understanding various aspects of chemical reactivity. The theoretical basis for these concepts has been provided by DFT [42]. These reactivity indices are better appreciated in terms of the associated electronic structure of atoms and molecules such as electronegativity and hardness [38]. The obtained chemical reactivity parameters for the biological molecules are: ionization potential (I), which is defined as the energy needed to remove an electron from a molecule; electron affinity
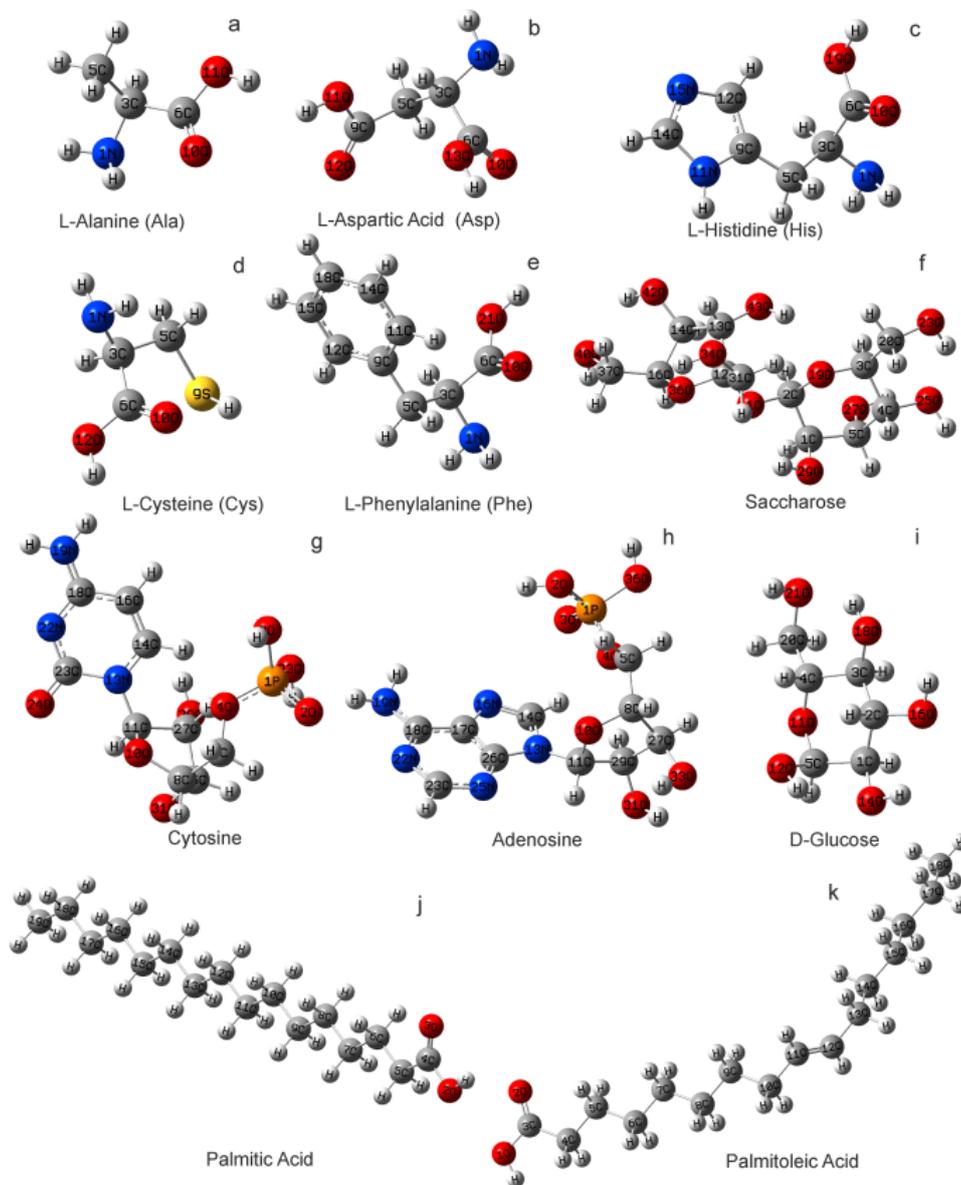
Figure 1: Optimized molecular structure of the minimum energy structure of biological molecules in the gas phase with the level of theory B3LYP/6-31G(d). (a) Ala, (b) Asp, (c) His, (d) Cys, (e) Phe, (f) Saccharose, (g) Cytosine, (h) Adenosine, (i) D-Glucose, (j) Palmitic Acid, (k) Palmitoleic Acid.

Biological Molecules	f_k^-	f_k^2
Ala	N1	N1
Asp	N1	N1
Cys	S9	S9
Phe	N1	N1
Hys	C12	C12
Adenosine	N19	N19
Cytosine	O24	O24
D-Glucose	O16	O12
Saccharose	O43	O43
Palmitic Acid	O3	C12
Palmitoleic Acid	C11	C11

Table 1: Electrophilic attack site and dual descriptor in biological molecules obtained with B3LYP/6-31G(d).

(EA), which measures the ability of a molecule to accept electrons and form anions; electronegativity (χ), representing the tendency of atoms or molecules to attract electrons; electrophilicity (ω), that gives an idea of the stabilization energy when the system acquires electrons from the environment up to saturation; and electron donor potential (ω-). These reactivity information shows if a molecule is capable of donating charge. The reactivity parameters mentioned above were obtained using vertical approximation, in which the energy of the molecule in its anionic, cationic, and neutral states is calculated, keeping in mind the geometry of the fundamental state. Results are shown in Table 2. According with these results, the biological molecule Ala showed the highest ionization potential value, thus showing this amino acid would require the highest amount of energy to rip an electron off its structure, and therefore this amino acid will not oxidize easily in the presence of silver ions. On the other hand, Adenosine and Cytosine show the lowest

Figure 2: Approximation of silver ion in the site susceptible to electrophilic attack of Ala.
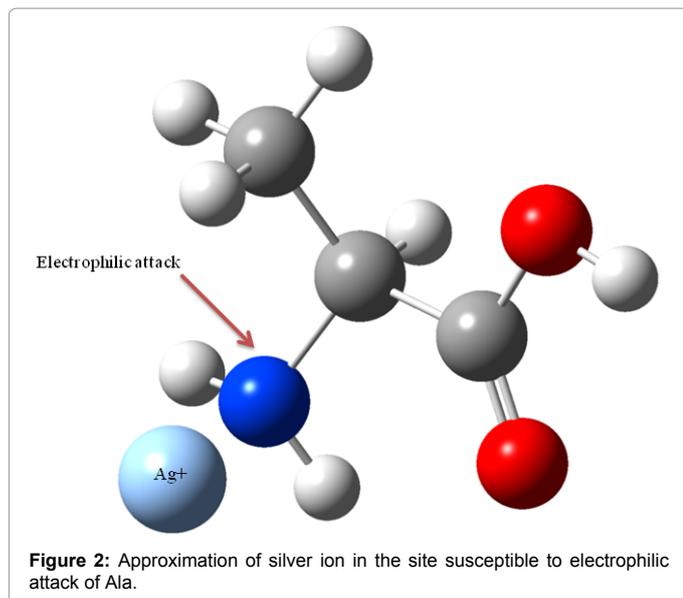
Biological Molecules	I (eV)	AE (eV)	X (eV)	η(eV)	ω (eV)	ω⁻ (eV)
Ala	9.27	-2.76	3.26	6.02	0.88	3.26
Asp	9.14	-1.96	7.71	5.55	1.16	3.65
Cys	8.71	-2.11	3.30	5.41	1.01	3.33
His	8.18	-2.14	3.02	5.16	0.88	3.04
Phe	8.18	-1.70	3.24	4.94	1.06	3.30
Adenosine	8.06	-0.95	3.56	4.51	1.41	3.75
Cytosine	7.98	-1.04	3.47	4.51	1.34	3.64
D-Glucose	9.02	-2.86	3.08	5.94	0.80	3.08
Saccharose	8.51	-2.16	3.17	5.34	0.94	3.20
Acid Palmitic	8.87	-2.57	3.15	5.72	0.87	3.16
Acid Palmitoleic	8.19	-2.07	3.06	5.13	0.91	3.08

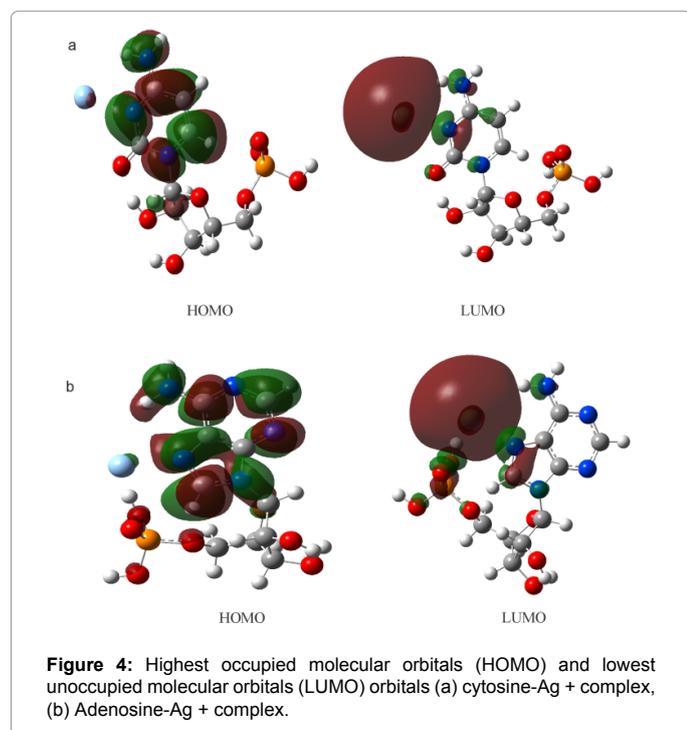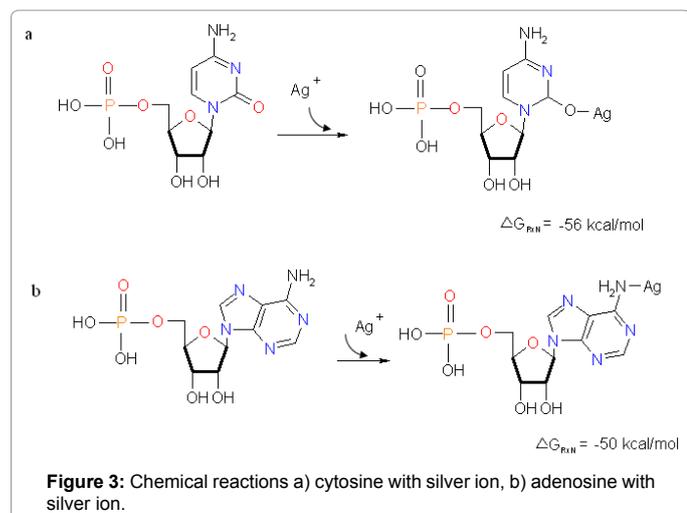**Table 2:** Reactivity parameters of biological molecules calculated with B3LYP/6-31G(d).

ionization potential value, which indicates they will oxidize more easily in the presence of the silver ion [43]. There are some EA negative values because the energy of biological molecules is not absorbed, but released in the process of electron acceptance, namely it is required to supply energy in order to form the anion [43]. Biological molecules adenosine and cytosine are capable of donating electrons, getting oxidized more easily in contact with the silver ion. According to the electronic affinity results, biological molecules are more capable of donating electrons and therefore, more prone to oxidization. Agreeing to Dunning et al. [44], in order to obtain a reliable calculation of electronic affinity, it is necessary to use base complexes with high angular momentum scattered functions. In order to discard that the 6-31G (d) were the cause of the negative electron affinity results, the scattered function 6-31++G(d) was used on the Ala biological molecule. This calculation yield to -0.4479 eV EA result, a value that corroborates that even using a scattered function that allowed changing the angular momentum and the shape of the orbital, EA still results in a negative value. Regarding electronegativity, the highest value was 7.71 eV for Asp, this means that Asp presented the highest difficulty to be oxidized in the presence of the silver ion, since this amino acid tends to attract electrons more strongly. On the other hand, the purine and pyrimidine bases (adenosine and cytosine) show electronegativity values of 3.56 eV and 3.47 eV respectively, which indicates they can be oxidized more easily in the

presence of the silver ion. The chemical hardness values (η), one of the reactivity parameters considered to determine the oxidation process (namely a measure of the resistance of a system to transfer charge), are higher in D-Glucose and sucrose with 5.94 eV and 5.34 eV respectively. This indicates that D-Glucose and sucrose are not prone to yield charge. Adenosine and cytosine show the lowest η values (4.51 eV), which makes them the molecules more prone to yield electrons, thus being the molecules that are more easily oxidized in the presence of the silver ion. According to the results obtained, the reactivity order, expressed as the ease to be oxidized, as for value η is: DNA>Proteins>Carbohydrates>Lipids

Adenosine, cytosine and Asp show the highest (ω) value. About the electron donor potential, low values indicate an antioxidant behavior, thus, results show that lipids tend to stabilize the electron loss in the other parts of the bacterium. The analysis of the reactivity results confirm that the DNA is the effortlessness bacterium fragment to be oxidized. Figure 3 shows the proposed chemical reaction of the adenosine and cytosine basis interaction with silver ion through the heterocycles. This proposed is based in the Jeffrey et al. [45] work where they found that silver ions favor bonding strongly with heterocyclic bases and not with the phosphate groups. The association of silver with the purine base (adenosine) forms complexes via the N19, while with the pyrimidine bases (cytosine) the complex is formed by the O24. These sites agree with the electrophilic attack sites defined in this work. Also, the reaction with oxygen in the heterocycles is an association confirmed as well by the Jeffrey et al. in the cited paper above. A distribution analysis of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of complexes of biological molecules-silver ion was performed in an attempt to observe the difference of this frontier orbitals distribution in presence of the silver ion. In all cases studied, the HOMO is localized over the structure of the amino acids, lipids, sugars, and purine and pyrimidine bases and the LUMO is found over the silver ion. If we also take into account that a global reaction called oxide reduction takes place (in every chemical reaction, the electrons one molecule loses, another must gain; in other words, one molecule is oxidized whereas the other one is reduced) [26], then we propose that the LUMO distribution over the silver ion, indicates an oxidation process, in which the biological molecules are oxidized and the silver is reduced. Figure 4 shows HOMO and LUMO orbitals for cytosine-Ag⁺ and adenosine-Ag⁺ complexes.

Conclusions

The oxidation process of the silver ion upon the parts that constitute a bacterium were analyzed in this work, considering the analyzed amino acids as part of a protein, the purine and pyrimidine bases as part of DNA, D-glucose and sucrose as carbohydrates, and palmitic and palmitoleic acids as the lipids. The molecular characterization of the biological molecules includes the calculation of the molecular structure and chemical reactivity parameters, also the calculation of the complexes biological molecule-silver ion reactivity properties. Low chemical hardness values indicate which constitutive parts are more prone to yield electrons, thus generating an oxidation process. The results show that the process order is: DNA>Proteins>Carbohydrates>Lipids. In all the cases, the HOMO orbital is found in the biological molecules, whereas the LUMO orbital is found in the silver ion, indicating there is a HOMO to LUMO electron transfer, suggesting an oxidation process.

Figure 3: Chemical reactions a) cytosine with silver ion, b) adenosine with silver ion.

Figure 4: Highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbitals (LUMO) orbitals (a) cytosine-Ag + complex, (b) Adenosine-Ag + complex.

Acknowledgements

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