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Investigating the Adsorption, Stability, and Electronic Properties of Silver–Citric Acid Nano complexes Utilizing DFT

Qasim Hassan Ubaid [1] *, *Walaa Sarhan Sarhan* [2]

[1] *Department of Physics, College of Sciences, University of Kerbala, Karbala 56001, Iraq*

[2] *Department of Medical Physics, College of Applied Medical Sciences, University of Kerbala, Karbala 56001, Iraq*

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ABSTRACT

This study uses density functional theory (DFT) to investigate the electronic interaction and molecular structure of a citric acid system with adsorbed silver as a nano complex. It emphasizes how silver adsorption affects the system's electronic and chemical properties, and evaluates the potential relevance of these changes to medical applications. We analyzed the geometric structure, Ag–O bond distance, HOMO–LUMO energy gap, molecular electrostatic surface potential (MESP), chemical hardness, and chemical softness. The silver atom positions itself near the electron-rich region associated with the oxygen atoms of citric acid, at an Ag–O distance of approximately 2.6 Å, indicating a favorable interaction between silver and the oxygen-containing site. Following adsorption, the system exhibited changes in its electronic distribution and a reduced HOMO–LUMO gap; this reduction correlates with decreased chemical hardness and increased softness, enhancing the system's susceptibility to electron-density redistribution and interaction with the surrounding medium. These properties are pivotal to the medical applications of silver nanomaterials, particularly antibacterial uses, because surface modification with citrate-like agents can alter surface properties, particle size, dispersion, and surface charge all of which govern interactions with bacterial cells and antimicrobial efficacy. The calculated electronic changes in the Ag–citric acid system, specifically the narrowed energy gap and increased chemical softness, therefore provide a theoretical basis for understanding the interaction between silver and the organic medium.

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INTRODUCTION

Researchers have recently turned to nanotechnology, particularly metallic nanoparticles, for applications in the field of medicine and treatment, owing to their unique physical and chemical properties [1]. Silver nanoparticles and their compounds possess well-known antimicrobial properties; silver nitrate solution, for instance, is used to treat bacterial infections [2]. Silver nanoparticles exhibit antimicrobial activity against a broad range of bacteria, fungi, and viruses; however, their safety and therapeutic efficacy depend on the concentration, route of administration,

* *Corresponding Author Email: qasim.hassan@uokerbala.edu.iq*

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and biological context [3, 4]. Attention has also turned to organic materials well tolerated by the human body, such as carbohydrates, doped with nano-silver and used as nano-components in anti-cancer applications [5]. Citric acid is a major acid found in the bodies of living organisms. It oxidizes glucose and releases energy, and it acquires important properties upon binding to metal ions; consequently, it is used in the food and pharmaceutical industries [6, 7]. Given the properties of hybrid nanocomposites, their use has become widespread. One group of researchers reduced silver ions using citrates in three ionic liquids. They characterized these compounds using analytical techniques and found them consistent with These substances demonstrated potent antibacterial action against three different kinds of bacteria after they were analyzed using analytical methods and found to be congruent with theoretical findings utilizing density functional theory [8]. Nanoparticle size also plays an important role in reactivity: a study combining the reduction of silver nitrate with environmentally friendly citric acid and a gelatin stabilizer, alongside density functional theory, concluded that smaller nanoparticles were more effective as antibiotics [9]. Raman spectroscopy combined with density functional theory calculations was used to study chlorpyrifos (CPF) with silver nanoparticle clusters adsorbed on the surface, and the results showed that silver nanoparticles are a strong reducing agent [10]. The alcoholic groups in lemon peel extract are responsible for stabilizing silver nanoparticles and exhibit the highest reaction energy according to density functional theory [11]. One study found citric acid to be a good reducing agent for silver nanoparticles adsorbed onto its surface; vibrational measurements and infrared spectroscopy indicated weak chemisorption, and the citrate could be removed from the surface [12]. An environmentally friendly bio-nanomaterial can be synthesized using water-soluble chitosan (as a stabilizer) and citric acid (as a reducing agent). A laboratory simulation revealed that the hydroxyl group in citric acid is responsible for stabilizing the silver nanoparticles, and the compound demonstrated antibacterial activity for 12 hours [13]. A separate study examined ascorbic acid with silver nanoparticles using a density functional theory approach; adsorption of ascorbic acid onto silver nanoparticles is accompanied by charge transfer from silver to ascorbic acid, as analyzed through the electrostatic surface potential [14]. Beyond the properties noted in previous studies,

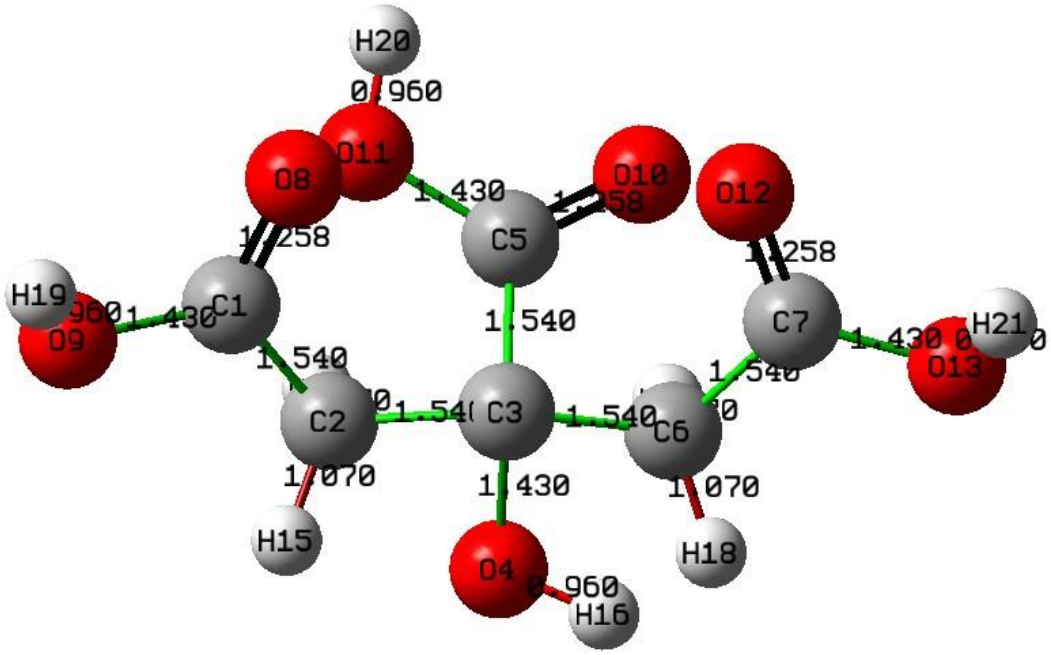

Fig. 1. The final geometric optimization of critic acid molecule – where red indicates oxygen atoms and white and gray indicate hydrogen and carbon atoms, respectively – was performed using the 6-311++G(d,p) basis.

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silver nanoclusters exhibit nonlinear optical behavior, as evidenced by comparisons of their electronic and vibrational patterns; the primary reason is increased polarization [15]. This study examines the pair values of silver nanoparticles (AgNPs) and their effect on the citric acid molecule, considering the stability and adsorption energies between molecular levels as hybrid nanomaterials, by analyzing surface charge distributions and using computer modeling to assess molecular levels and related physical properties.

COMPUTATIONAL PROCEDURE

The molecular structure and electronic

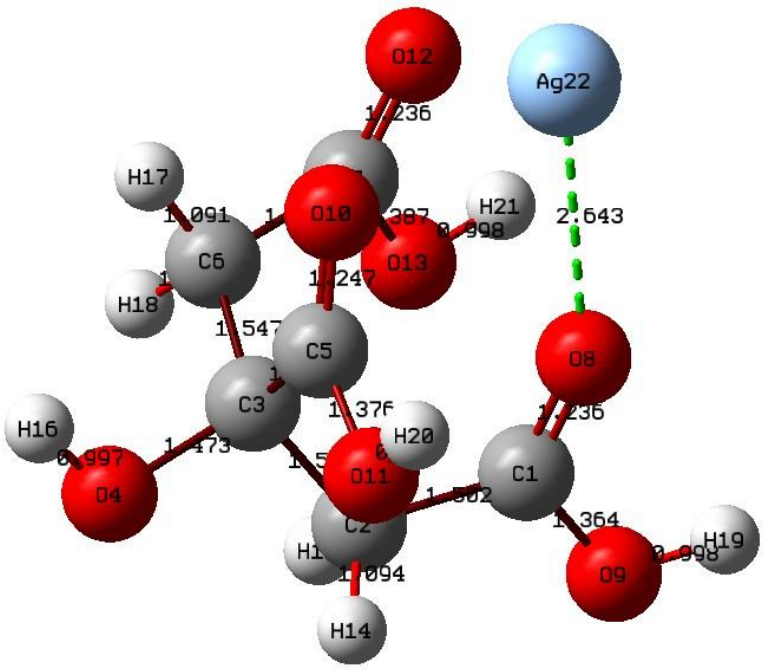

Fig. 2. The final optimized geometric structure of the of critic acid molecule including one sliver nanoparticles, where red indicates oxygen atoms and white, gray, and blue indicate hydrogen, carbon, and sliver atoms, respectively. Optimization was performed using the 6-311++G(d,p) basis and LAN2DZ for AgNPs.

Table 1. Electronic energy and adsorption energy after geometric optimization, calculated using density functional theory with a hybrid functional

Molecular structure	Total electronic energy (Hartree)	Adsorption energy Hartree)
$C_6H_8O_7$	760.309	-------
$C_6H_8O_7Ag$	5932.159	11864.3

Table 2. Calculations of interatomic bonds and surface angles using the 6-311++G(d,p) basis set and LAN2DZ for AgNPs.

Bound	Bound length A° (19, 20)	Angle	Value
C1=O8	1.236	C1=O8-Ag22	152.64
C7-C6	1.505	C7-C6-H17	107.8
C2-H15	1.09	C2-H15-C3	41.23
O4-H16	0.997	O4-H16-C3	44.36
O8-Ag22	2.643	O8=C1-O9	122.16

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properties of pure citric acid and its interaction with a single silver nanoparticle were studied using density functional theory with the B3LYP functional, as implemented in the Gaussian 09 software package. To accurately describe light atoms (C, O, H), ground- and excited-state computations were carried out using the 6-311++G(d,p) basis set, and LANL2DZ for the Ag adsorption system, to account for relativistic effects and effectively simulate transition metals. This combination is frequently used in research on metal–molecule interactions [14, 16, 17]. To identify the geometry of every citric acid system under study, all geometrical variables were optimized without symmetry constraints. The absence of imaginary frequencies indicated minimal energy structures. Water was employed as a solvent within the self-consistent reaction field framework. Gaussian 09 and GaussView 6.0 were used for all calculations and procedures [18]. Geometric optimization of the molecules was the initial step in producing a stable molecule with lower energy convergence thresholds. As shown in Fig. 1, the geometric optimization of a pure citric acid molecule ($C_6H_8O_7$) was performed, followed by the geometric optimization of a single silver nanoparticle with citric acid salt. The adsorption of the single silver nanoparticle onto the acid surface was evaluated. This design showed strong agreement with previous studies by determining the stable energy levels, calculating the energy gap between the highest and lowest energy levels, and calculating the physical parameters ordered by those energy levels.

RESULTS AND DISCUSSION

Fig. 2 displays the final product of the geometric optimization of the citric acid ($C_6H_8O_7Ag$) molecule with silver nanoparticles. This structure is considered the optimal geometric optimization for the nanocomposite ($C_6H_8O_7Ag$) for two main reasons: first, it satisfies the four criteria for geometric optimization and achieves ideal values; second, no imaginary frequencies appear.

After optimizing the molecular geometry of the compound and achieving the lowest electronic stability and adsorption energies (Table 1), where negative values indicate electronic stability between the primary and secondary energy orbitals, electronic transitions between the silver atoms and citric acid were observed.

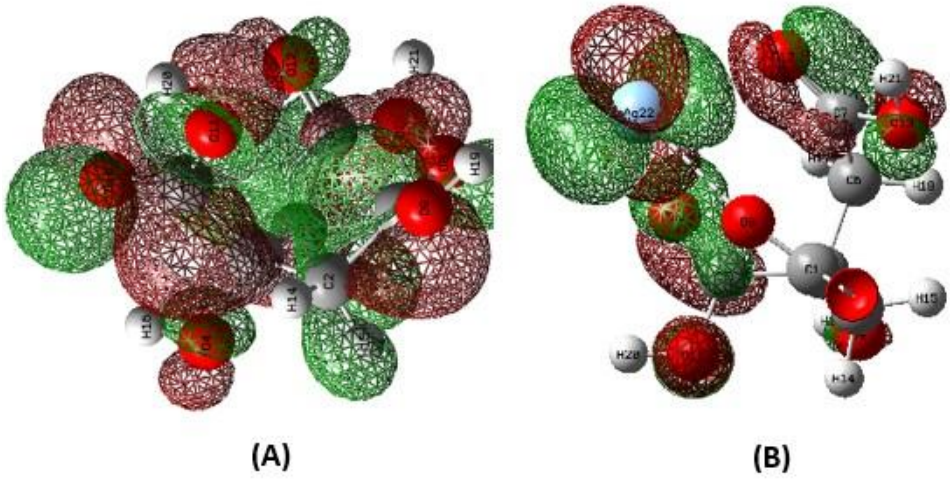


Fig. 3. HOMO- LUMO state A refers to citric acid $C_6H_8O_7$ before the addition of silver nanoparticles, and B refers to the acid after the addition of silver nanoparticles $C_6H_8O_7$, Ag using hybrid functionals 6-311++G(d,p) basis and LAN2DZ.

Table 3. The energy gap of the (HOMO- LUMO) level before and after the addition of a silver nanoparticle to citric acid.

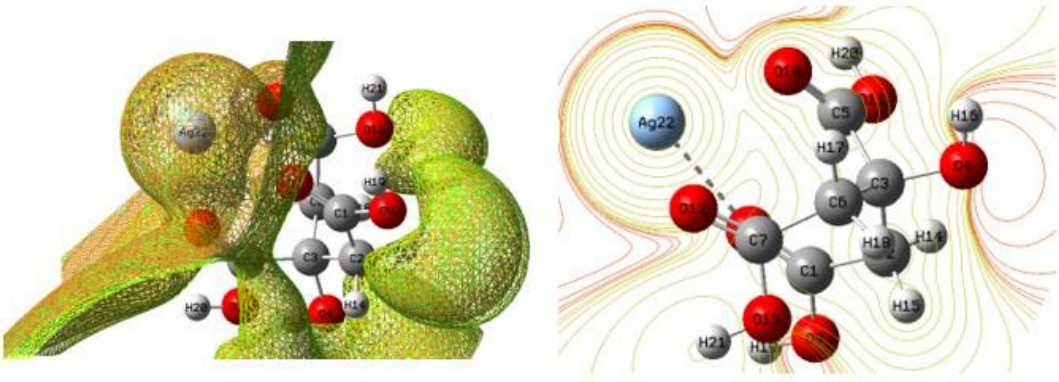
Structure	E LUMO (eV)	E HOMO (eV)	Eg = ELUMO – EHOMO (eV)
$C_6H_8O_7$	0.866	8.003	7.13
$C_6H_8O_7$/Ag	1.205	6.505	5.3

Following the geometric optimization of the complex at the true minimum of electronic and adsorption energy, Fig. 2 shows that the bonds between carbon, oxygen, and hydrogen atoms are colored red, clearly indicating a short distance between the bonded atoms. In contrast, the bond between the Ag22 silver atom and the O8 oxygen atom is colored green, indicating a longer bond distance of 2.643 Å. Table 2 details the bond lengths between the atoms.

In Fig. 2, we wish to illustrate that the bonding between the silver nanoparticle and the carboxyl group (COOH) is weak—specifically, a type of physical adsorption (van der Waals)—and that this interaction plays a significant role in forming a charge cloud on the surface of the citric acid [21]. The increase in bond length facilitates active participation in interactions between the adsorbent and adsorbate surfaces (such as electron gain or loss), thereby enhancing the stabilizing interactions of the nanocomposite [15].

Furthermore, to assess the stability of the citric acid molecular structure after adding a single silver nanoparticle, energy levels were calculated. The frontier molecular orbital (FMO) hypothesis holds that when the molecular orbitals of two reactants begin to interact and overlap, two new molecular orbitals form: one bonding orbital of lower energy and one antibonding orbital of higher energy [22]. We demonstrate this in a reaction following the second-order nucleophilic substitution mechanism, in which the reaction begins with an interaction between a higher-energy occupied orbital (HOMO, highest occupied molecular orbital)—containing the electron pair that will be donated to the acceptor—and the substrate's lower-energy unoccupied molecular orbital (LUMO, lowest unoccupied molecular orbital). Consequently, the HOMO energy (EHOMO) and LUMO energy (ELUMO) are related. Fig. 3 shows the structure's LUMO and HOMO distributions of citric acid before and after the addition of silver nanoparticles.

Fig. 3 illustrates positive charges in red and negative charges in green, indicating electron transitions between molecular orbitals; the energy gap between electron-poor and electron-rich levels was also calculated, as shown in Table 3



A B

Fig. 4. A) Molecular electrostatic potential (MEP) isosurface diagram and (B)) Molecular electrostatic potential (MEP) contour surface for critic acid /Ag

Table 4. Calculated physical parameters for citric acid after the addition of silver nanoparticles using density functional theory.

Structure	Physical parameter	Value (ev)
$C_6H_8O_7$/Ag	I	6.505
	A	1.205
	X	3.855
	η	2.650
	σ	0.377

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Table 3 shows a decrease in the energy gap upon adding silver atoms to citric acid. This decrease can be explained by the fact that silver nanoparticles possess abundant electronic levels capable of interacting with the molecular levels of the attached carboxyl (COOH) groups, even when the bonding is weak (adsorption). This interaction facilitates electronic activity, charge redistribution, and the overlapping of electronic orbitals between the two surfaces. These calculated values match the empirical values reported in previous studies [14, 23].

$$I = - E_{HOMO} \qquad A = - E_{LUMO}$$

$$X = I+A/2 \qquad \eta = I-A/2 \qquad \sigma = 1/\eta$$

The physical parameters referred to above are directly related to the surface electrostatic potential (ESP), and their values are presented in Table 4.

The parameter values calculated in Table 4 indicate the system's capacity to accept electron density; the higher the electron affinity, the greater the compound's tendency to acquire electrons [24, 25]. Chemical hardness represents a compound's resistance to the exchange of electron density; softness is the reciprocal of hardness, and the lower a compound's hardness, the softer it appears and thus the more susceptible it is to changes in electron density [26].

However, these characteristics may relate to a theory that describes the inhibitors' bonding tendencies with respect to the metal atom using the Hard–Soft Acid–Base (HSAB) and frontier-controlled interaction concepts [27]. According to the general principles of the HSAB theory, hard acids typically coordinate with hard bases, whereas soft acids typically coordinate with soft bases. Metal atoms are classified as soft acids. Hard molecules have a large HOMO-LUMO gap, whereas soft molecules have a small one [28]. For citric acid with adsorbed Ag, the reduction in the energy gap can be interpreted as an indication of decreased chemical hardness and increased chemical softness, thereby enhancing the system's susceptibility to electron-density redistribution or exchange and its reactivity with the medium [29].

Fig. 4 shows the electrostatic potential map of citric acid with silver nanoparticles.

The molecular electrostatic potential (MESP) map provides a visualization technique that helps identify the chemical interactions of compounds [30]. It aids in finding the optimal interaction sites between biomolecules and receptors through electron transitions between molecular orbitals, and in identifying nucleophilic and electrophilic sites which, combined with energy gap calculations, can be used to predict types of intermolecular reactions [31, 32]. The electrostatic potential map in Fig. 4 shows a significant redistribution of electron density after silver nanoparticles adsorb onto the citric acid surface. The electrostatic potential color scale indicates negatively charged (electron-rich) regions in red and positively charged (electron-poor) regions in green. The red regions are clearly concentrated around the oxygen atom; this is logical, as the oxygen atoms in the carboxyl group possess high electron density, producing a negative electrostatic potential. Conversely, green regions appear around the silver nanoparticle, representing areas that are electron-poor relative to the regions surrounding the oxygen.

Furthermore, the difference in surface potentials within the complex leads to electrostatic attraction between the silver nanoparticle core and the oxygen atom of the carboxyl group; this aligns with the explanation for the weak adsorption between the silver nanoparticles and citric acid [33].

CONCLUSION

According to the DFT results, adsorption of Ag onto citric acid changes the molecule's electronic structure, as seen in the decrease in the HOMO–LUMO energy gap. Conceptual density functional theory states that a decrease in the energy gap is linked to increased chemical softness and decreased global chemical hardness.

This indicates that the Ag–citric acid system becomes more electronically responsive and more susceptible to changes in its electron density. The calculated Ag–O separation of approximately 2.6 Å, together with the electrostatic potential distribution, indicates a favorable interaction between the Ag center and the oxygen-rich region of citric acid. In conjunction with the calculated adsorption energy, these results support the formation of a stable adsorbed Ag–citric acid configuration. However, the reduced HOMO–LUMO gap and the MESP distribution should be interpreted as evidence of electronic interaction and adsorption rather than, by themselves, as definitive proof of a covalent Ag–O bond.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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