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THEORETICAL STUDY OF ADSORPTION OF L-CYSTEINE ON SILVER NANOPARTICLES

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ABSTRACT- Theoretical study on the adsorption L-cysteine on silver nanoparticles has been investigated. Theoretical computations on the shifting of frontier molecular orbitals from HOMO to LUMO, Natural population analysis (NPA) and the orbital overlapping between silver cluster and L-Cysteine in NBO analysis have been associated with the redistribution of charges between silver and L-Cysteine. Reduction in the band gap of L-cysteine after adsorption on silver combined with a redistribution of electron density in the molecular electrostatic potential (MEP) confirms the redistribution of charges resultant to the process of adsorption. In addition, an enhancement in the calculated dipole moment and polarizability values are also obtained. Enhancement in the first order hyperpolarizability of L-cysteine -Ag complex suggests its potential applications in the design of NLO devices.

Keywords- [L-cysteine, DFT, Silver nanoparticles, Adsorption, NLO]

1. INTRODUCTION

Amino acids are the molecular building blocks of peptides and proteins. L-Cysteine is sulphur-containing amino acid which is characterized by the presence of a mercaptogroup (-SH). The mercapto group has a high affinity for heavy metals. In the cysteine molecule, the function groups, such as –NH2, –COOH and –SH, have a strong tendency to coordinate with inorganic cations and metals, which has been demonstrated by Burford and co-workers on the basis of the observations of mass spectrometry [1-3]. The DFT method allows us to calculate the structures, electrostatic properties and optical properties of Molecules which can help us study the adsorption of molecules better.

The aim of the present communication is to study the influence of silver nanoparticles on the electrostatic and optical properties of L-cysteine.

2. COMPUTATIONAL STUDY

All Density functional theory calculations computations were carried out with Gaussian03 software. The molecular structure of L-cysteine was optimized using the B3PW91 and the LANL2DZ basis set of vibrational frequencies.

3. RESULTS AND DISCUSSION

The optimized geometric parameters such as bond lengths, bond angles and dihedral angles of the title molecule were calculated using DFT method with 6-311G++(d,p) as a basis set. The optimized gas –phase geometry of L-Cysteine is of C_1 symmetry and its carbon –carbon bonds were not of the same length. The geometrical parameters of L-Cysteine -Ag complex were calculated using B3PW91 functional and LANL2DZ basis set. After adsorption (Fig 3.1) the C-C bonds nearer to the silver cluster were significantly deformed. These deviations in the bond angles and dihedral angles value clearly can be correlated to the chemical interactions resulting from adsorption. The highest bond length of the Atom S1 carbon atom to Ag 15 silver atom (2.65 Å). The shortest computed O2-H14 distance was 0.98Å. Ag_3 maintains the same geometry after adsorption as original cluster although its bond lengths undergo some change. Bond angles and dihedral angles of L-Cysteine nearer to the Ag atoms were deformed after adsorption of L-Cysteine on silver.

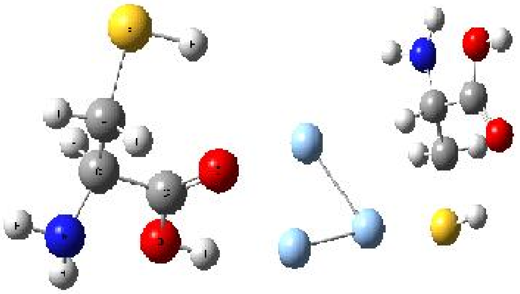
(a) (b)

Figure 3.1- Optimized structure of (a) L-Cysteine and (b) L-Cysteine-Ag.

4. HOMO AND LUMO

Analysing the structures of molecular orbitals in the ground and the excited state can help to identify the binding sites of specific electrophillic nucleophillic adsorbates. The smaller the energy gap, the greater is the reactivity. HOMO and LUMO of L-Cysteine and the L-Cysteine adsorbed on silver were presented in figures 3.2

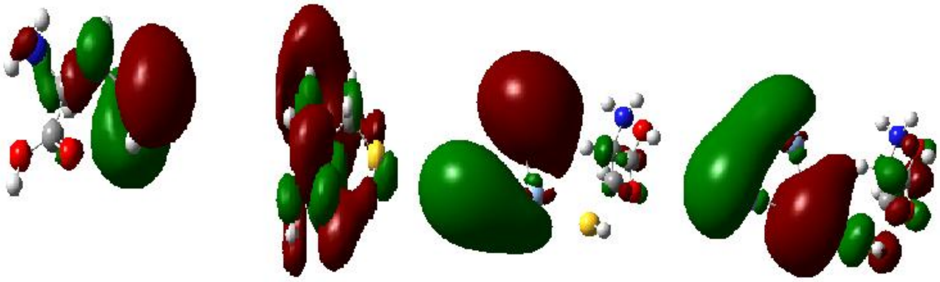
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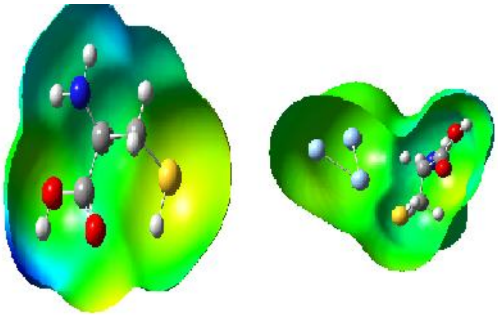
Figure 3.2 (a)- HOMO, LUMO of L-Cysteine and (b) HOMO, LUMO of L-Cysteine –Ag

HOMO of L-Cysteine was located mainly around the sulphur and the carbon atoms excluding oxygen atoms, while the LUMOs tend to form specific antibonding orbitals around the carbon atoms. However, in the case of L-Cysteine -Ag, the HOMOs were mainly spread over a couple of Ag atoms alone where as the anti banding LUMOs extend to the silver cluster atoms, carbon and sulphur atoms too. It accounts for the intramolecular charge transfer taking place from the π to the silver. It was also interesting to note that in the band gap of L-Cysteine (5.724eV) is significantly reduced after adsorption on silver (1.859eV) and the shifting of MOs can be correlated to the transfer of charge associated with processes of adsorption.

5. THE MOLECULAR ELECTROSTATIC POTENTIAL

An electron density iso-surface mapped with electrostatic potential surface provides the useful information about the size, shape, charge density and the site of chemical reactivity [4-6]. Hence the MEP surfaces (electron density isosurface value of 0.0004 a.u) had been plotted over the optimized geometries of the title compound and were presented in figure 3.3 After adsorption redistribution in the electrostatic potential can be associated to the interactions between the L-Cysteine and silver and the charge transfers.



(b)

Figure 3.3 MEP of L-Cysteine and L-Cysteine –Ag

6. STATIC POLARIZABILITY AND FIRST ORDER HYPERPOLARIZABILITY

Quantum chemical calculations have been shown to be useful in the description of the relationship between the electronic structure of the system and its NLO response. The polarizability (α), hyper polarizability (β) and the electric dipole moment (μ) of the L-Cysteine were calculated by finite field method using DFT/6311G++(d,p) basis set.

	μ(Debye)	α(esu)	β(esu)
L-Cysteine	2.8	$1.07x10^{-23}$	$9.24x10^{-31}$
L-Cysteine –Ag	3.61	$3.43x10^{-23}$	$1.85x10^{-25}$

Table 3.1 Dipolemoment , Polarizability, Hyperpolarizability

7. NATURAL POPULATION ANALYSIS

Natural population analysis of a molecular system describes the distribution of charges among the various subshells of their atomic orbitals [7]. The atomic charges on L-Cysteine and the L-Cysteine adsorbed on Ag are calculated based on NPA using the B3PW91/6-311G ++ (d,p) method is presented in table 3.2. Among the atoms C7, H8, H9, H10, H11, H12, H13, H14 have positive charges while others have negative charge. It may be the reason of the substitution of highly electronegative oxyzen, nitrogen and sulphur atoms. After adsorption on silver, the carbon atoms are identified to be more negatively charged and the hydrogen atoms are more positively charged. This shows the adsorption on silver causes a redistribution of charges.

Atom No	**Charge**	
	L-Cysteine	**L-Cysteine+Ag**
S 1	-0.05125	-0.12509
O 2	-0.69827	-0.73612
O 3	-0.59451	-0.63234

N 4	-0.83719	-0.93768
C 5	-0.12722	-0.12521
C 6	-0.49612	-0.50197
C 7	0.81624	0.84519
H 8	0.19512	0.22938
H 9	0.21127	0.26038
H 10	0.23141	0.25305
H 11	0.36835	0.41785
H 12	0.35323	0.40373
H 13	0.14139	0.19624
H 14	0.48754	0.52209
Ag 15		0.24005
Ag 16		-0.09519
Ag 17		-0.21436

Table 3.2 Natural population analysis of L-Cysteine and L-Cysteine-Ag

8. NBO ANALYSIS

The natural bond orbital (NBO) calculation is an essential tool for investigating charge transfer or conjugative interaction in molecular systems. The second-order fock matrix was carried out to evaluate the donor – acceptor or interaction in the NBO analysis. The strengths of these delocalization interaction, E_2, are estimated by second order perturbation theory as estimated by equation $E_2 = \Delta E_{ij} = q_i F(i,j)^2 / \varepsilon_i - \varepsilon_j$; q_i is the donor orbital occupancy, E_i and E_j are the diagonal elements(orbital energies) and F_{ij} is the off diagnol NBO fock matrix element. The energy value for the interaction between the filled (donors) i and vacant (acceptors) orbital j calculated by the second order perturbation theory have been tabulated table 3.3. The larger the E(2) value, the more intensive is the interaction between electron donors and acceptors ,i.e the more the electrons donating tendency from electron donors to acceptors.

L-Cysteine				
Donor NBO(i)	**Acceptor NBO (j)**	**E(2) kcal/mol**	**E(j)-E(i) a.u.**	**F(i,j) a.u.**
LP(2) O 2	π* O 3 - C 7	44.59	0.35	0.111
LP (2) O 3	σ^*O 2 - C 7	31.52	0.6	0.124
	σ^*C 5 - C 7	16.42	0.63	0.093
LP (1) O 2	σ^*O 3 - C 7	7.46	1.19	0.084
LP (1) N 4	σ^*C 5 - H 8	5.62	0.72	0.057
σ C 5 - H 8	σ^*O 3 - C 7	4.46	1.08	0.062
	σ^*C 6 - H 10	2.68	0.91	0.044
LP (2) S 1	σ^*C 5 - C 6	4.33	0.61	0.046
σ O 2 - H 14	σ^*C 5 - C 7	3.25	1.12	0.055
σ S 1 - C 6	σ^*N 4 - C 5	3.17	0.94	0.049
σ C 6 - H 9	σ^*C 5 - C 7	2.84	0.89	0.045

σ N 4 - H 11	σ*C 5 - C 6	2.75	0.98	0.046
σ C 6 - H 10	σ*C 5 - H 8	2.57	0.91	0.043
σ C 5 - C 7	σ*O 2 - H 14	2.53	1.01	0.045
	σ*N 4 - H 12	2.33	1.08	0.045
	σ*C 6 - H 9	1.54	1.05	0.036
LP (2) S 1	σ*C 6 - H 10	2.49	0.65	0.036
σ N 4 - C 5	σ*S 1 - C 6	2.42	0.89	0.042
	π*O 3 - C 7	1.93	0.73	0.035
σ N 4 - H 12	σ*C 5 - C 7	2.4	0.98	0.044
LP (1) O 3	σ*C 5 - C 7	2.13	1.08	0.043
σ S 1 - H 13	σ*C 6 - H 9	2.04	0.93	0.039
σ C 5 - C 6	π*O 3 - C 7	2.04	0.64	0.034
	σ*N 4 - H 11	1.83	1.06	0.039
L-Cysteine-Ag				
LP (2) O 2	π*O 3 - C 7	20.07	0.34	0.105
LP (2) O 3	σ *O 2 - C 7	16.15	0.56	0.121
	σ *C 5 - C 7	7.31	0.64	0.088
LP (2) S 1	σ *Ag 15 -Ag 16	11.47	0.35	0.082
LP (6)Ag 17	σ* Ag 15 -Ag 16	4.56	0.16	0.034
LP (1) N 4	σ *C 5 - H 8	3.95	0.68	0.066
	σ *C 5 - C 6	2.28	0.58	0.046
LP (1) O 2	σ *O 3 - C 7	3.28	1.06	0.075
σ C 5 - H 8	π * O 3 - C 7	3.26	0.49	0.053
π *O 3 - C 7	σ *O 3 - C 7	2.72	0.47	0.123
σ O 2 - H 14	σ *C 5 - C 7	2.17	1.12	0.063
σ C 6 - H 9	σ *C 5 - C 7	2.11	0.87	0.055
LP (1) O 3	σ *C 5 - C 7	1.97	1.06	0.058
σ N 4 - H 12	σ *C 5 - C 7	1.83	0.97	0.054
LP (2) O 3	σ *S 1 - H 13	1.82	0.5	0.039
σ C 5 - C 7	σ *O 2 - H 14	1.76	1.05	0.054
σ N 4 - C 5	σ *S 1 - C 6	1.72	0.86	0.049
LP (1) S 1	σ *C 5 - C 6	1.7	0.76	0.046
σ S 1 - C 6	σ *N 4 - C 5	1.68	0.88	0.049
σ C 5 - H 8	σ C 6 - H 10	1.67	1	0.052
σ C 5 - C 6	σ *O 2 - C 7	1.57	0.9	0.048

Table 3.3 - NBO analysis of L-Cysteine and L-Cysteine-Ag

CONCLUSION

NBOs of L-Cysteine and L-Cysteine - Ag were analyzed based on DFT calculations. The plot of the MEP surface indicates that adsorption causes a redistribution of the electron density. It has been shown that enhancement in dipole moment and polarizability values on adsorption. Studies reveal that after adsorption on silver cluster, there is a significant reduction in the bandgap and increase in the first order hyperpolarizability suggesting its suitability in the design and development of NLO materials. Geometry optimizations, frontier molecular orbitals, molecular electrostatic potential, NPA and

REFERENCES

[1]. Y.Yamada, G. Kutluk, H. Namatame,,M. Taniguchi , and S. Yagi , Spectroscopic Study on the Adsorption Reaction of L-Cysteine on Cu nanoparticle/Ag under in vivo conditionJournal of Surface Analysis Vol.17, No. 3 (2011) pp. 194-197

[2]. Cuiyu Jing, Yan Fang , Experimental (SERS) and theoretical (DFT) studies on the adsorption behaviors of L-cysteine on gold/silver nanoparticles, Chemical Physics 332 (2007) 27–32

[3]. P.V. Prasad, T.K.V. Rao, S. Rajya Lakshmi, B. Brahmaji et al., Spectroscopic Studies on Pure and Mn2^{+} Doped Nonlinear L-Cysteine Hydrochloride Monohydrate for Electro-optic Modulation, International Journal of ChemTech Research, CODEN (USA): IJCRGG ISSN: 0974-4290 Vol.7, No.01, pp 269-274, 2014-2015

[4]. N.R. Sheela, S. Muthu, S. Sampathkrishnan, Spectrochim. Acta, Part A 120237–251, (2014).

[5]. T. Karthick, V. Balachandran, S. Perumal, A. Nataraj, J. Mol. Struct.1005202– 213 (2011).

[6]. R. Gayathri, M. Arivazhagan, Spectrochim. Acta, Part A 81242– 250, (2011).

[7]. Rekha T.N., Beulah J.M. Rajkumar, “Nonlinear optical and charge transfer properties of tetracene adsorbed on silver”, A DFT approach Synthetic Metals 215 207–215, (2016).