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EXPERIMENTAL AND THEORETICAL STUDY OF ADSORPTION OF 1, 2 DIHYDROXY ANTHRAQUINONE ON SILVER NANOPARTICLES

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ABSTRACT- An experimental study on the adsorption of 1, 2 Dihydroxy anthraquinone (1,2DHAQ) on biosynthesized nanoparticles has been investigated. It is compared with theoretically modeled surface complex using DFT calculation. 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 1,2DHAQ in NBO analysis have been associated with the redistribution of charges between silver and 1,2DHAQ. Reduction in the band gap of 1,2DHAQ 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. Based on the Time-Dependent Density Functional Theory (TDDFT), UV-Visible spectra is derived which is in agreement with the experimental one. Theoretical and experimental FTIR spectrum is compared. Enhancement in the first order hyperpolarizability of 1,2DHAQ -Ag complex suggests its potential applications in the design of NLO devices.

Keywords- [1, 2 Dihydroxy anthraquinone, DFT, Silver nanoparticles, Adsorption, TDDFT, NLO]

1. INTRODUCTION

Adsorption of organic molecules on metal surfaces makes technical attention in the optical and catalytic properties of the substrate. Organic or inorganic compounds that can be adsorbed on a metallic surface generally induce changes in the particle shape or aggregation [1]. Because of large surface to volume ratio, nanoparticles serve as good adsorbents. Use of biological organisms such as microorganism, plant extracts and biomass could be a best alternative method of physical and chemical method for synthesis of nanoparticles because the biological or green synthesis route is very spontaneous, economic, environmental friendly and non-toxic. Quantum mechanical modeling methods are among the most efficient tools of investigation available to study the adsorption characteristics of nanostructured systems. Silver Nanoparticles are of interest because of the unique properties (*e.g.*, size and shape depending optical, electrical, and magnetic properties) which can be incorporated into antimicrobial applications, biosensor materials, composite fibers, cryogenic superconducting materials, cosmetic products, and electronic components. 1, 2 dihydroxyanthraquinone (Alizarin/1,2 DHAQ) is the most important constituent of the madder lake dye. It has remarkable antigen toxic activity and is highly fluorescent. M.V.Canamares et al. applied FT-Raman and surface-enhanced Raman scattering (SERS) spectroscopy for vibrational characterization and to study the adsorption and acidity behavior of the highly fluorescent anthraquinone dye [2]. T.N.Rekha et al. investigated the adsorption of naphthalene on Silver using methods based on Density Functional Theory (DFT) and Surface Enhanced Raman Spectroscopy (SERS)[3]. Rajkumar swarnkar et al. carried out the surface enhanced Raman scattering (SERS) study of an organic dye Alizarin Red on colloidal silver nanoparticles[4].In this study, we attempted to synthesize the silver nanoparticles biologically from leaf extract and compared the adsorption of 1,2 DHAQ on silver nanoparticles experimentally and computationally.

2. MATERIALS AND METHODS

1, 4 Diamino anthraquinone and acetonitrile were purchased from National Scientific company. All chemicals were used as received without further purification. Deionized water was used throughout this study. Analytical grade silver nitrate ($AgNO_3$), a costly chemical, was purchased from local laboratory chemical suppliers.

3. SYNTHESIS OF SILVER NANOPARTICLES

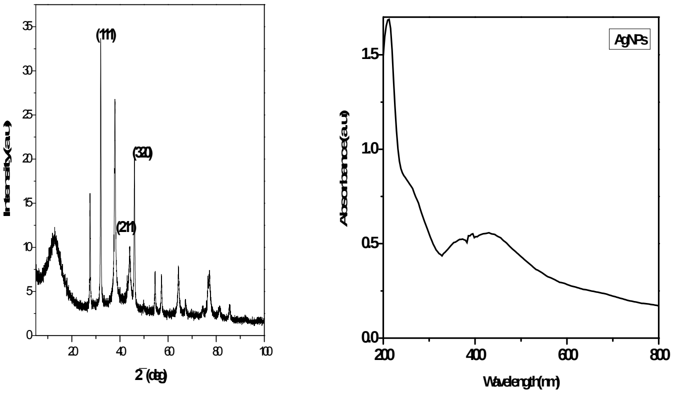
Terminalia arjuna leaves were collected from our College campus in the month of January.The fresh leaves were washed several times with running tap water and after that with distilled water. Around 20g of leave were weighted and boiled for 1h in 100ml double distilled water at 60^0C and then the extracts were filtered through whatman filter paper. Then the filtered extract was stored in refrigerator at 4^0C for further use in synthesis of silver nanoparticles. 1mM solution of alizarin (1,2 DHAQ) in DMF was prepared. Silver nanoparticles (AgNPs) were added into 1,2 DHAQ solution for further study.

Density functional theory was carried out to study the optimized geometry, structural properties, electronic property, charge transfer property and vibrational properties of 1,2 DHAQ before and after adsorption on silver.

4 RESULTS AND DISCUSSION

4.1 SILVER NANOPARTICLE

Powder XRD of the biosynthesized silver nanoparticles were recorded by PANalytical X-ray diffractometer with CuKα radiation (λ=1.54A^0).X-RD spectrum of synthesized AgNPs (Fig 4.1) showed distinct diffraction peaks around 38^0, which are indexed by the (100) of the cubic face-centered silver. Intense Bragg reflections suggested that strong X-ray scattering centers in the crystalline phase. A comparison of observed X-RD spectrum with the Standard one confirmed that the silver particles formed in our experiments were in the form of nano crystals of , as evidenced by the peaks at 2θ values of 31.92°, 44.03°, and 46.00°corresponding to (111),(211), and (320) planes for silver, respectively. The optical absorption spectrum of synthesized AgNPs was determined using UV-visible spectrophotometer UV-JASCO V-630. The spectrum was recorded in the wavelength range between 200nm and 800nm. Figure 4.2 displays an optical absorption band peak at about 440 nm typical of absorption for metallic Ag nano cluster. Thus, the above characterizations confirmed the biologically synthesized silver nanoparticles.



(a) (b)

Figure 4.1- (a) X-RD Pattern Of Silver Nanoparticles (b) UV-visible Spectra Analysis of AgNPs

4.2 COMPUTATIONAL METHODS

4.2.1 OPTIMIZED GEOMETRIES

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 (Fig 4.2). In the benzene ring C_4-C_5 bond length is about 1.396 Å. The optimized gas –phase geometry of 1,2 DHAQ is of C_1 symmetry and its carbon –carbon bonds were not of the same length. The geometrical parameters of 1,2 DHAQ-Ag complex were calculated using B3PW91 functional and LANL2DZ basis set. The highest bond length of the Atom C_{15} carbon atom to Ag 28 silver atom (3.260 Å). The carbon-carbon bonds in 1,2 DHAQ were calculated to be 1.38 Å (C_1-C_2, C_5-C_6, C_{10}-C_{11}, C_{13}-C_{14},) and 1.4Å (C_9-C_{10}, C_{14}-C_{15}); after adsorption the C-C bonds nearer to the silver cluster were significantly deformed with bond lengths measuring 1.39Å (C_5-C_6) and 1.45Å (C_9-C_{10}). However the C-H bond lengths remained unchanged after adsorption. The shortest computed C_9-Ag_{28} distance was 2.50Å. Silver cluster, Ag_3 maintains the same geometry after adsorption as original cluster although its bond lengths undergo some change. Bond angles of 1,2 DHAQ nearer to the Ag atoms were computed to be 118° (C_3-C_2-H_{17}, C_4-C_5-H_{18}, C_4-C_8-C_9, C_8-C_9-C_{15}, C_{10}-C_{11}-H_{12}, C_9-C_{15}-C_{14}) with 119° (C_9-C_{15}-C_{14}) with corresponding the dihedral angles at 179° (C_8-C_9-C_{15}-C_{14}) and 174° of adsorption of 1,2 DHAQ on silver. These bond angles and dihedral angles value clearly indicated that the regular hexagonal structure of the ring nearer to the Ag cluster was distorted on adsorption and there were deviations in the co-planarity of the corresponding carbon atoms which can be correlated to the chemical interactions resulting from adsorption. Many authors have been explained the changes in frequency or bond length of the C-H bond on substitution are due to change in the charge distribution on the carbon atom of the benzene ring.

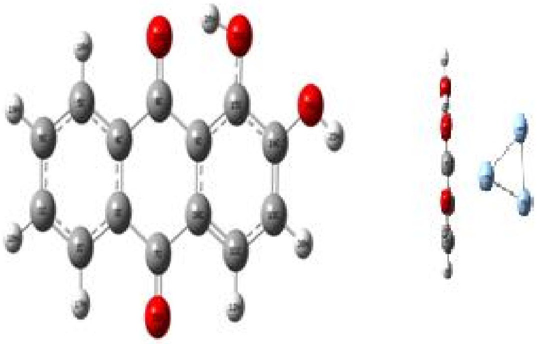


Figure 4.2- Optimized structure of 1,2 DHAQ, 1,2 DHAQ-Ag

4.2.2 ELECTRONIC PROPERTIES 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 1,2 DHAQ and the 1,2 DHAQ adsorbed on silver were presented in figures 4.3. HOMO of 1,2 DHAQ was located mainly around the carbon atoms excluding a couple of atoms, while the LUMOs tend to form specific antibonding orbitals around the carbon atoms. However, in the case of 1,2 DHAQ-Ag, the anti banding LUMOs extend to the silver cluster atoms too , where as the HOMOs were mainly spread over a couple of Ag atoms alone and carbon atoms of 1,2 DHAQ. 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 alizarin (3.275eV) is significantly reduced after adsorption on silver (0.83eV) and the shifting of MOs can be correlated to the transfer of charge associated with processes of adsorption.

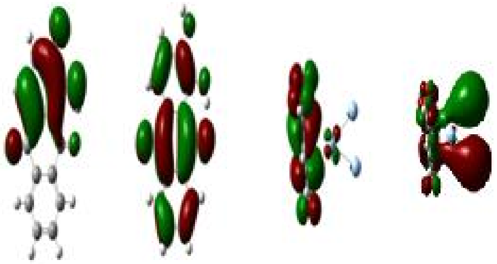


Figure 4.3- HOMO, LUMO of 1,2DHAQ and HOMO, LUMO of 1,2DHAQ-Ag

4.2.3. 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 [5-7]. 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 4.4. After adsorption redistribution in the electrostatic potential was clearly indicated with a decrease in negative potential around the oxygen atom and the silver atoms belong to the regions of positive potential .This can be associated to the interactions between the molecule and silver and the charge transfers.

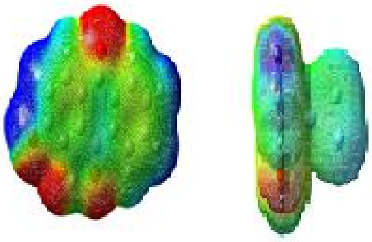


Figure 4.4- MEP of 1,2 DHAQ and 1,2 DHAQ-Ag

4.3 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 1,2 DHAQ were calculated by finite field method using DFT/6311G++(d,p) basis set. This result indicated the good non linearity of the title molecule.

	µ(Debye)	α(esu)	β(esu)
1,2DHAQ	0.4473	27.452×10^{-24}	
1,2DHAQ-Ag	2.45	64.76×10^{-24}	2.89×10^{-28}

Table 4.1- Dipolemoment , Polarizability, Hyperpolarizability

4.4 NATURAL POPULATION ANALYSIS

Natural population analysis of a molecular system describes the distribution of charges among the various subshells of their atomic orbitals [8]. The atomic charges on 1,2 DHAQ and the 1,2 DHAQ adsorbed on Ag are calculated based on NPA using the B3PW91/6-311G + + (d,p) method is presented in table 4.2. Among the ring carbon atoms C7, C8, C14, C15 have positive charges (0.53337e, 0.54427e, 0.29127e, 0.35955e) while others have negative charge. It may be the reason of the substitution of highly electronegative oxyzen atoms (O23 & O24). All hydrogen atoms have positive charge in 1,2 DHAQ. O23 Oxyzen atom has the highest negative charge (-0.63912e) when compare to other oxygen 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(in e)	
	1, 2 DHAQ	1, 2 DHAQ-Ag
C 1	-0.18474	-0.19564
C 2	-0.14441	-0.17228
C 3	-0.10977	-0.10092
C 4	-0.11791	-0.10609

C 5	-0.15518	-0.17241
C 6	-0.18432	-0.19683
C 7	0.53337	0.52218
C 8	0.54427	0.48609
C 9	-0.18953	-0.25939
C 10	-0.13386	-0.12952
C 11	-0.15899	-0.16384
H 12	0.23913	0.25463
C 13	-0.25403	-0.27247
C 14	0.29127	0.32316
C 15	0.35955	0.29763
H 16	0.21521	0.22814
H 17	0.2377	0.24695
H 18	0.23719	0.24641
H 19	0.21553	0.22842
H 20	0.21128	0.22649
O 21	-0.60193	-0.63209
O 22	-0.54772	-0.57229
O 23	-0.63912	-0.67512
O 24	-0.63568	-0.67703
H 25	0.47151	0.49498
H 26	0.50136	0.518
Ag 27		0.11785
Ag 28		-0.01917
Ag 29		0.15416

Table 4.2- Natural Population Analysis

4.5 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

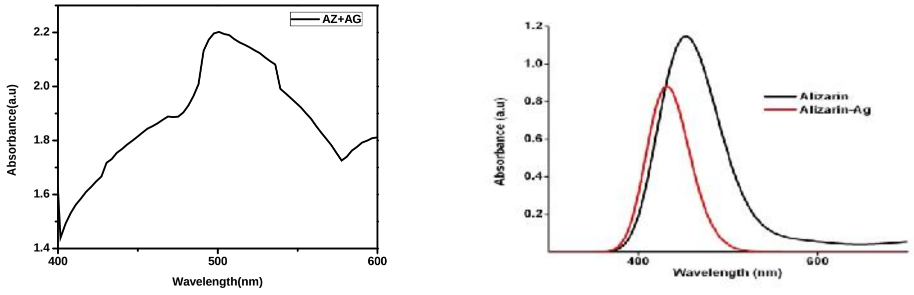
$E_2 = \Delta E_{ij} = q_i F(i,j)^2 / \varepsilon_i - \varepsilon_j$; q_i is the donor orbital occupancy, E_i and E_j are the diagonal elements(orbital energies) and F_{ij} is the off diagnol NBO fock matrix element. The energy value for the interaction between the filled (donors) i and vacant (acceptors) orbital j calculated by the second order perturbation theory have been tabulated table 4.3. 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.

	Donor NBO (i)	Acceptor NBO (j)	E(2) kcal/mol	E(j)-E(i) (a.u)	F(i,j) (a.u)
1,2DHAQ	π C1 - C2	π* C3 - C4	3.69	1.13	0.058
	π C3 - C4	π* C1 - C2	2.44	1.23	0.049
	π C3 - C4	π* C8 - O21	9.62	1.93	0.122
	π C5 - C6	π* C3 - C4	17.27	0.28	0.064
	π C 10 - C 11	π * C 7 - O 22	37.74	0.22	0.083
	π C 3 - C 4	π * C 7 - O 22	29.27	0.25	0.078
	π C 3 - C 4	π * C 1 - C 2	21.57	0.31	0.077
	π C 13 - C 14	π * C 10 - C 11	19.14	0.56	0.092
	π C 1 - C 2	π * C 3 - C 4	18.32	0.28	0.066
	LP (3) O 23	π * C 1 - C 2	10.13	0.79	0.082
	π C 9 - C 15	π * C 13 - C 14	2.87	2.07	0.07
	LP (3) O 21	π * C 13 - C 14	3.23	2.08	0.074
	π C 9 - C 15	π * C 13 - C 14	2.87	2.07	0.07
	LP (2) O 21	π * C 1 - C 2	2	0.49	0.028
1,2DHAQ-Ag	π C9 - C10	π* C8 - O21	14.98	0.26	0.08
	π C3 - C4	π* C8 - O21	14.31	0.23	0.073
	π C3 - C4	π* C7 - O22	11.27	0.26	0.07
	π C5 - C6	π* C3 - C4	10.89	0.29	0.073
	π C1 - C2	π* C5 - C6	10.68	0.29	0.072
	π C1 - C2	π* C3 - C4	10.53	0.29	0.072
	π C9 - C10	π* C11 - C13	10.5	0.31	0.072
	π C3 - C4	π* C1 - C2	10.09	0.3	0.071
	π C5 - C6	π* C1 - C2	9.93	0.29	0.069
	π C9 - C10	π* C7 - O22	9.81	0.29	0.069
	π C11 - C13	π* C9 - C10	9.63	0.27	0.069
	π C3 - C4	π* C5 - C6	9.47	0.3	0.069
	π C8 - O21	π* C9 - C10	2.38	0.4	0.046
	π C8 - O21	π* C3 - C4	2.26	0.43	0.044
	σ* Ag28 -Ag29	LP* Ag27	1.87	0.22	0.083
	LP (6) Ag27	LP*(6) Ag28	39.33	0.19	0.127

Table 4.3- NBO Analysis

4.6 UV-VIS SPECTRA

Optical absorption spectra of 1, 2DHAQ-Ag (Figure 4.13) along with theoretically simulated spectra are presented in figure 4.14. Differences in intensities of theoretical absorption spectrum and that of experimental one is mainly because the calculated spectrum is based on a single isolated 1, 2DHAQ-Ag which consists of a single 1, 2DHAQ and a single Ag_3 cluster, while the measured spectrum is obtained from many 1, 2DHAQ-AgNPs in the solid state.

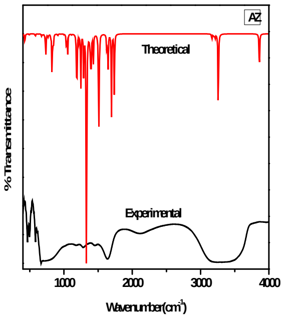


(a) (b)

Figure 4.5(a)- Optical absorption spectrum of 1, 2DHAQ-Ag (Experimental) and (b)Theoretically stimulated spectra of 1,2 DHAQ and 1,2DHAQ-Ag

4.7 VIBRATIONAL ANALYSIS: FTIR ANALYSIS

Theoretical and experimental FTIR data of 1,2 DHAQ and 1, 2 DHAQ-Ag were presented in figures 4. It confirms that the presence of C=C ($1637.56cm^{-1}$), C-O ($1178cm^{-1}$). The broadband in 3200-$3600cm^{-1}$and a band in 1660-$1820cm^{-1}$, confirm the presence of O-H , C=O respectively. The band at $1363cm^{-1}$ in . (Figure 4.16) 1,2DHAQ-Ag corresponds to nitro N-O bending which indicates one of the reducing agent present in leaf extract. After adsorption of 1, 2 DHAQ on Ag, the intensity of the peaks had been enhanced and slight shift in the bands also observed. The shift of peaks to lower wave number side correlated with the increase in bond length



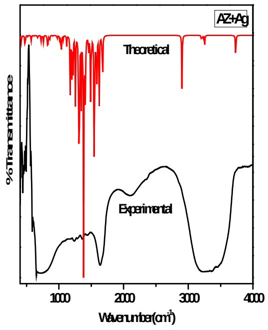


Figure 4.15- FTIR (Theoretical and experimental) spectrum of 1,2 DHAQ Figure 4.16 FTIR (Theoretical and experimental) spectrum of 1, 2 DHAQ-Ag

CONCLUSION

Geometry optimizations, frontier molecular orbitals, molecular electrostatic potential, NPA and NBOs of 1, 2 DHAQ and 1, 2 DHAQ -Ag were analyzed based on DFT calculations. The optical absorption spectrum was simulated for 1, 2 DHAQ –Ag and it is compared with experimental spectrum. The plot of the MEP surface indicates that adsorption causes a redistribution of the electron density and the calculated ESP charge identifies those atoms, which are closer to silver cluster, has more negative. 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.

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