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# Electronic, Optical and Vibrational analysis of Nitrobenzene Adsorbed on Silver Cluster

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***Abstract:*** *Interaction between nitrobenzene and silver cluster is investigated using the Density Functional Theory (DFT) at the B3PW91 level of theory. Adsorption causes a variation in the structural parameters. The charge transfer from silver cluster to nitrobenzene is identified from the plot of the molecular electrostatic potential (MEP) surface and natural population analysis (NPA). A marked enhancement in the calculated polarizability values is also obtained. Enhancement in the first order hyperpolarizability of nitrobenzene-Ag3can find applications in the design of NLO devices. Red shift in C-N stretching vibration indicates that the nitrobenzene is attached to the cluster through the nitro group.*

***Keywords:*** *DFT, Natural Population Analysis, Non Linear Optics, Nitrobenzene, Molecular Electrostatic Potential.*

## I. Introduction

In recent years, organic molecular systems have attracted considerable interest because the delocalization of their π-electrons makes them more potent as candidates in organic field-effect transistors (OFETs), organic light-emitting diodes (OLEDs) and organic photovoltaics (OPVs). Special interest has been paid to molecular systems of two-dimensional (2D) nonlinear acenes due to their delocalized pi electrons [1]. Researchers are showing significant interest in the study of the materials with enhanced optical nonlinearity, due to their potential applications in telecommunications, optical computing and optical information processing [2].Noble metal nanoparticles (NPs) are known to exhibit unique electrical and optical properties, which lead to their potential application in the design of new materials. Adsorption of organic ligands on metal NPs induces changes in catalytic and optoelectrical properties [3].

Several researchers have reported that nanomaterials could enhance the nonlinear optical (NLO) behavior of the molecular system [4]. Computational modeling methods are excellent tools for investigating relationships between the properties of a system and for the interpretation of experimental data. Density functional theory (DFT) is an advanced modeling technique, which is used in analyzing optimized structures, NLO properties and vibrational frequencies of molecular systems [5].

A.G.Al-Sehemi et.al have synthesized and analyzed some N, N-diacylaniline derivatives using both theoretical and experimental FTIR and NMR techniques. The effect of different substituents has been analyzed with the aid of these techniques [6]. In the current work, adsorption behavior of nitrobenzene on silver cluster is investigated using DFT approach. The geometrical, electronic, linear and nonlinear optical properties are studied. In order to gain more understanding about the adsorption process, Raman spectra are also stimulated and analyzed.

## II. Computational Methods

Molecular geometrical properties were analyzed for nitrobenzene and its interactions with silver cluster using the DFT/B3PW91 implemented through the Gaussian 03 software [7]. The basis set 6-31G(d,p) was used for atoms in nitrobenzene. LANL2DZ was applied for Ag3 clusters, which is a well-known typical basis set for metal atoms and organometallic complexes [3]. Zero imaginary vibrational frequencies confirm a true local minimum on the potential energy surface. Investigations on the structural properties, molecular electrostatic potential (MEP), frontier molecular orbitals (FMOs) and Natural population analysis (NPA) gives an insight into the adsorption process. Further, theoretical NLO properties of the system were investigated. The Raman spectra are simulated for both nitrobenzene and nitrobenzene on silver cluster.

## III. Results And Discussion

### 3.1 Structural Analysis

Optimized geometries of nitrobenzene before and after adsorption on silver cluster are shown in Fig.1. The minimum energies of these geometries are calculated as -1.188 x 104 eV and -2.378 x 104 eV respectively. Adsorption on silver cause changes in the structural parameters (bond length, bond angle and dihedral angle) of nitrobenzene. The elongation of the bond lengths are mainly found at C1-C2 and C1-C6 bonds (1.391 Å to 1.414 Å), N12-O13 and N12-O14 (1.225 Å to 1.348 Å). However, the shortening of bond length at C1-N12 (1.468 to 1.412) is due to the withdrawal of electron density from silver to molecule. Significant variations in bond angles close to the cluster namely C1-C2-C6, C1-N12-O13 and C1-N12-O14 are identified. The results suggest that adsorption is due to an electrostatic interaction between nitrobenzene and the silver cluster.

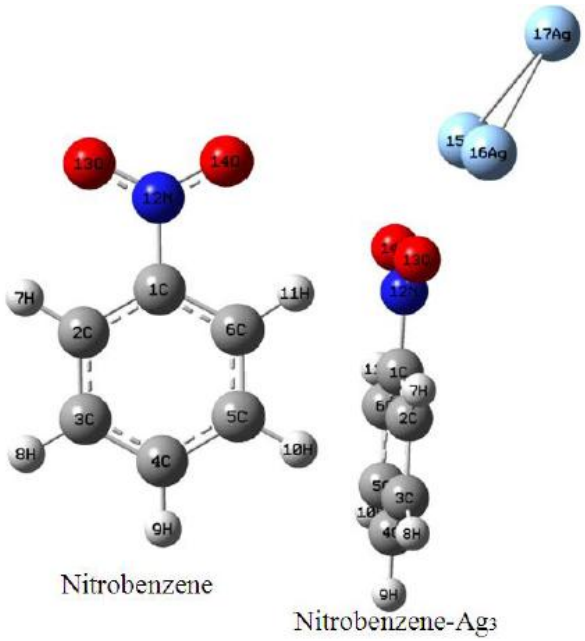


**Fig.1** Optimized Geometries

### 3.2 Molecular Electrostatic Potentials

MEP is used to predict the reactive behavior of a molecular system. In the MEP plot, the most electronegative potential is represented by red (electrophilic site), the most positive electrostatic potential is indicated by blue (nucleophilic site) and the region of zero potential is represented by green color [8]. In the case of nitrobenzene, the hydrogen atoms are enveloped by positive potential surface (Fig.2). While, the carbon and oxygen atoms are surrounded by negative region, which can be attributed to the delocalization of π electrons in the carbon ring and the lone pair of oxygen atoms respectively. Upon adsorption, changes in the potential of nitrobenzene are noticed. Interestingly, silver cluster is enveloped by positive electrostatic potential, which confirms the transfer of electronic charge from silver cluster to nitrobenzene.

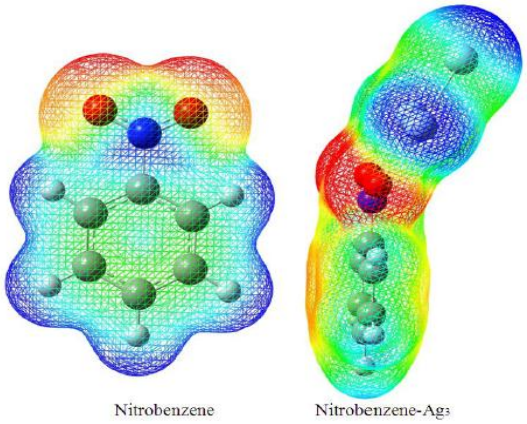


**Fig.2** Molecular Electrostatic Potential Surface

**3.3 NPA Analysis**

NPA is an effective tool used to explain the distribution of charges of a chemical system [9]. Table.1 shows the NPA analysis of the investigated molecules. In the case of nitrobenzene, all the carbon atoms carry a negative charge except C1 that is attached to the electronegative nitrogen atom. All the hydrogen atoms carry positive charges. Adsorption on the silver cluster leads to redistribution of charges that makes the –NO2 more negative. The above result correlates well with the plot of MEP.

**Table 1.** Charges

| Charges | Nitro benzene | Nitro benzene-$Ag_3$ | Charges | Nitro benzene | Nitro benzene-$Ag_3$ |
|---|---|---|---|---|---|
| C1 | 0.049 | 0.105 | H9 | 0.257 | 0.223 |
| C2 | -0.223 | -0.225 | H10 | 0.259 | 0.225 |
| C3 | -0.241 | -0.217 | H11 | 0.283 | 0.248 |
| C4 | -0.218 | -0.227 | N12 | 0.517 | 0.345 |
| C5 | -0.241 | -0.217 | O13 | -0.381 | -0.652 |
| C6 | -0.223 | -0.226 | O14 | -0.381 | -0.654 |
| H7 | 0.283 | 0.248 | Ag 15 | | 0.473 |
| H8 | 0.259 | 0.225 | Ag 16 | | 0.474 |
| | | | Ag 17 | | -0.150 |

**3.4 Optical Properties**

The linear (polarizability) and nonlinear (first order hyperpolarizability (βtot)) characteristics of nitrobenzene and nitrobenzene-Ag3 are computed in order to understand their optical properties. The mean polarizability α0 and the mean first hyper-polarizability βtot are defined as using the x, y, z components [10],

$$\alpha_0 = \frac{(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})}{3} \quad (1)$$

$$\beta_{tot} = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2} \quad (2)$$

where,

$$\beta_x = \beta_{xxx} + \beta_{xyy} + \beta_{xzz}$$
$$\beta_y = \beta_{yyy} + \beta_{xxy} + \beta_{yzz}$$
$$\beta_z = \beta_{zzz} + \beta_{xxz} + \beta_{yyz}$$

The calculated linear and nonlinear optical properties are tabulated in Table.2. Adsorption causes an increase in polarizability, which can be correlated with the plot of MEP and the distribution of charges from NPA analysis. Interestingly, the first order hyperpolarizability of nitrobenzene and nitrobenzene- Ag3 are respectively 5 and 240.33 times higher than that of urea suggesting there is a potential for application of the system under study in the field of NLO devices particularly after adsorption on Ag3.

**Table 2.** Linear and Nonlinear Optical properties

| **Molecules** | **Polarizability ($x10^{-23}$) esu** | **Hyperpolarizability ($x10^{-30}$) esu** |
|---|---|---|
| Nitrobenzene | 1.057 | 2.181 |
| Nitrobenzene -$Ag_3$ | 2.949 | 99.017 |

**3.5 Vibrational Analysis**

Theoretical Raman spectra were analyzed for nitrobenzene before and after adsorption on silver cluster. A change in polarizability of the molecule is responsible for the peak obtained in the Raman spectra. This is one of the methods to identify the site of adsorption [11].Fig.3and Table 3 shows that, upon adsorption, there is an enhancement in the intensity of some peaks of nitrobenzene, confirms the process of adsorption.

After adsorption on silver cluster, peaks identified at 172 cm-1and 217 cm-1confirms the metalmolecule interactions. Another noteworthy aspect is the downshifting of C-N stretching vibrational mode from 1428 cm-1 (Nitrobenzene) to 1342 cm-1 (Nitrobenzene-Ag3). The large magnitude of the red shift of this vibration indicates that nitrobenzene is attracted to the surface of silver through the nitro group [12].

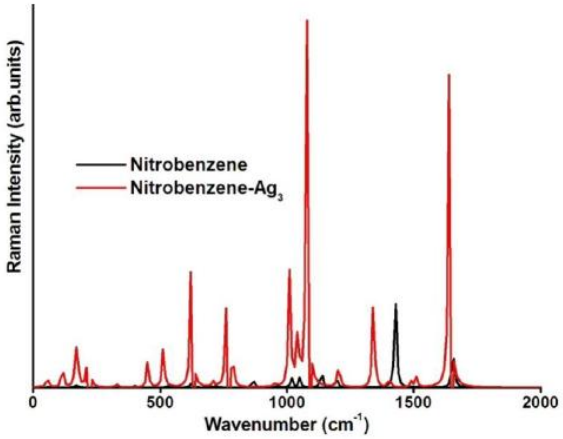


**Fig.3.** Simulated Raman Spectra

**Table 3.** Vibrational Assignments

| Nitrobenzene ($cm^{-1}$) | Nitrobenzene-Ag3 ($cm^{-1}$) | Assignments |
|---|---|---|
| | 172 | Ag-Nitrobenzene stretch |
| | 217 | Ag-Nitrobenzene stretch |
| 621 | 623 | Inplane Ring Deformation |
| | 765 | Inplane Ring Deformation |
| 1051 | | Inplane CH bending |
| | 1081 | Inplane CH bending,C-N Stretching, N-O Stretch |
| 1428 | 1342 | C-N stretching |
| 1657 | 1642 | C-C Stretching |

## IV. Conclusions

Based on the DFT calculations, optimized geometrical parameters, MEP plot and NPA of nitrobenzene and nitrobenzene-Ag3were analyzed. The Raman spectra were also simulated for the investigated molecules. The plot of the MEP surface and NPA analysis indicates that adsorption causes a transfer of charges from silver to nitrobenzene. Enhancement in the polarizability values was identified due to the adsorption process. Red shift of C-N stretching vibrations indicates that the nitrogen atom in the nitrobenzene is attached on the surface of silver. This study reveals that adsorption causes a increment in the first order hyperpolarizability suggesting its suitability in the design and development of NLO materials.

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