



DFT COMPUTATIONS OF SOME MOLECULAR AND PHYSICAL PROPERTIES OF GLUTAMINE-TEMPLATED NOBLE METAL NANOCLUSTERS FOR APPLICATION IN BIOSENSING



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Abstract: The molecular geometry of Glutamine derived nanoclusters with Gold carriers for Biosensing are studied using ab-initio Quantum Chemical calculations. Density functional calculations at the Becke3LYP (B3LYP) are carried out using LANL2DZ basis set. The molecular structure, dipole moment, quadrupole moment, charge transfer, polarizability and energy are studied. It is predicted that the properties of pure Glutamine are affected when attached with Gold nanoclusters. The predicted dipole moment is high indicating that the nanocluster molecules are polar and the charge distribution is not symmetrical. The quadrupole moment predicts that the molecules are slightly elongated along the ZZ axis. Using the total energies, it is predicted that the Glutamine molecules are slightly more unstable with increase in the molecular size.

Keywords: Glutamine, gold, biosensing, molecular, physical

Introduction

Ab-Initio Molecular Theory is concerned with predicting the properties of atomic and molecular systems. It is based upon the fundamental laws of Quantum Mechanics and uses a variety of mathematical transformations and approximation techniques to solve the fundamental equations (Alzate *et al.*, 2005).

Noble metal nanoclusters are collections of small numbers of gold or silver atoms (2-30 atoms) with physical sizes close to the Fermi wavelength of an electron (~0.5 nm for gold and silver). Providing the missing link between atomic and nanoparticle behavior in noble metals, these nanoclusters exhibit optical, electronic, and chemical properties dramatically different from those of much larger nanoparticles or bulk materials. Among the water-soluble noble metal nanoclusters newly developed, DNA-templated silver nanoclusters (DNA/Ag NCs) have attracted great interest in biosensing owing to a number of useful photophysical and photochemical properties (Levine, 1991; Ma, 2004; Liu *et al.*, 2007).

Gold is one of the most extensively studied materials due to some of its properties e.g. stable chemical property, facile synthesis and nontoxicity, high stability etc. Furthermore, gold nanoparticles (NPs) portray unique properties which differ from nanoparticles such as their surface Plasmon resonance (SPR) effect, size-dependending electronic properties and their photothermal effect in biological therapy (Lee *et al.*, 1988). The properties of nanoparticles depend on many controllable, variable parameters. The use of a control of synthesis of nanoparticles of noble metals having engineered properties is determined by the strong influence of their size, shape, structure and aggregates on their physiochemical properties as well as on their resonance and spectral characteristics (Stancheva, 2012).

The mini-type sensor in nanoscale is of interest in the wide array of biomedical applications and environmental science for detection of metal ions and biomolecules possessing high sensitivity and low cost. The surface modified AuNCs can be utilized as biosensors with the fluorescent AuNCs core as transducer and the surface functionalized molecules as recognition component (Coates, 2000; Clarkson, 2003).

For these fascinating aspects, goldNPs have been considered as the key materials of nanoscience and nanotechnology in recent years. AuNCs can be used in a wide range of applications, such as biodetection, biosensing, biological labeling and bioimaging (Xiaochao *et al.*, 2015).

This work examines some of the most promising molecular materials known as noble metal nanoclusters. The aim of this study is to determine the molecular, opto-electronic and vibrational properties of a DNA-templated noble metal nanocluster (Glutamine) for application in biosensing.

Materials and Methods

Materials

The following materials were used for this research work

- Gaussian Software with specification Gaussian 09 Revision-A.02-SMP (09W), 2009
- Gauss View software with specification Gauss View 5.08, 2008
- Pavilion HP laptop with specification Intel (R) Core (TM) i5 4210U CPU@ 1.70GHz 2.40GHz 12.0GB 64-bit Operating System x64-based processor Windows 8.1

Methods

Gaussian package

The Gaussian package is a computational Physics and Chemistry program. The name comes from the fact that it uses Gaussian type basis functions (Kimberly and Ernest, 2011). It is used for electronic and geometric structure optimization (single point calculation, geometry optimization, transition states and reaction path modeling); and molecular properties and vibrational analysis (IR, Raman, NMR vibrational frequencies and normal modes; electrostatic potential, electron density, multipole moments, population analysis, natural orbital analysis, magnetic shielding induced current densities, static and frequency-dependent polarizabilities and hyperpolarizabilities) using both DFT and ab-initio methods (Kukhta *et al.*, 2011).

Geometry and vibrational frequency optimization

Geometry optimization was carried out by locating both the minima and transition states on the potential surface of the molecular orbital (Ochterski, 1993). It was optimized in Cartesian coordinates that are generated automatically from the input Cartesian coordinates. It also handles fixed constraints on distances, bond angles and dihedral angles in Cartesian or (where appropriate) internal coordinates (Lee and Parr, 1988; Makashir and Kurian, 1999). The process is iterative, with repeated calculations of energies and gradients and calculations or estimations of Hessian in every optimization cycle until convergence is attained.

One of the most computationally demanding aspects of calculating free energy using electronic structure theory is the

calculation of the vibrational energy and entropy contributions. The computational expense was incurred by the calculation of the matrix of second energy-derivatives (i.e. the Hessian or force constant matrix) which yields harmonic vibrational frequencies upon diagonalization (Parr and Yang, 1989; Anderson, 2012).

Computation of molecular properties

The molecular structures and geometries of the organic semiconductor material anthracene and some of its derivatives was completely optimized using ab-initio quantum mechanical calculations at the Restricted Hartree-Fock (RHF) level of theory without using any symmetry constraints. Geometry optimization was performed using the ab-initio RHF method with 6-31G basis set. The structures were refined further using Density Functional Theory which is a cost effective method for inclusion of electron correlations with the three-parameter density functional generally known as Becke3LYP (B3LYP), which includes Becke's gradient exchange corrections (Becke, 1993), the Lee *et al.* (1988) correlation functional and the Vosko, Wilk and Nusair correlation functional with suitable basis sets. At the first step, geometry optimizations are carried out then, the IR and Raman frequencies are calculated using the Hessian which is the matrix of second derivatives of the energy with respect to geometry.

The optimized molecular structures will be tested by computing the second derivatives and checking that all the harmonic vibrational frequencies are found to be real at all level of calculations. All calculations will be performed using Windows version of Gaussian 03W suit of ab-initio Quantum Mechanical Software (Gaussian 03 Revision C.02, 2004).

Nanoparticle and nanocluster considerations

Research has been intensified to seek ways of developing and synthesizing novel gold nanostructures with improved characteristics or new properties. Over the past few decades, small gold clusters protected by various types of ligands have attracted much attention. Ligands allow obtaining the gold nanoclusters with given size, shape and properties (Hinchliffe, 1988; James, 2007). Three main families of organic ligands are usually used for stabilization of the gold nanoclusters: phosphine, thiolate ligands and DNA. These ligands are essential in the creation of highly stable gold nanoparticles and nanoclusters (Perdew and Wang, 1992).

Stability of small gold nanoclusters protected by thiolate (SR) or phosphine (PR₃) and halide ligands can be predicted in the terms of "Superatom Electronic Theory". According to this theory, valence electrons of the metal core can be transferred to suitable ligands, opening the possibility to achieve a noble-gas-like electronic configuration in the formation of stable complexes (Foresman, 1996; Colon *et al.*, 2004).

Gold and silver nanoparticle structures with a helical arrangement are very interesting areas of research (Friedrich *et al.*, 2004). The most popular methods of synthesis of this type of nanoparticles are based on the assistance of biological molecules such as peptides and DNA molecules. These assemblies have potential applications in photonics and as optical polarizers, sensors, catalysts, *etc.* During the interaction of noble metal nanoparticles with biomolecules, formation of two types of nanostructures are possible (Herbert, 2002):

- i. metal clusters are nested on the outside of the biomolecule and arrange in external helical chains around these peptide or DNA molecules with production of Plasmonic helical metal nanoparticle assemblies.
- ii. a few to tens of metal atoms are located inside the DNA molecule, between two polynucleotide strands.

In this research work, small gold nanostructures are attached to a DNA basis (Glutamine) and studied for possible application as biosensing material. Stability, opto-electronic, chemical and vibrational properties of these potential nanomaterials are also studied.

Results and Discussion

Optimized molecular structure and bond lengths

In Gaussian, a geometry optimization begins at the molecular structure specified at the input and steps along the potential energy surface. It computes the energy and gradient at that point, and determines which direction to make the next step. The optimized parameters are the bond lengths (in Armstrong), the bond angles and the dihedral angles for the optimized molecular structure (Ochterski *et al.*, 2007; Naoto *et al.*, 2007).

The optimized molecular structures of various Glutamine and Gold derived nanocluster molecules are shown in Fig. 1. The optimized bond lengths of various Glutamine and Gold derived nanocluster molecules in gas phase are presented in Table 1.

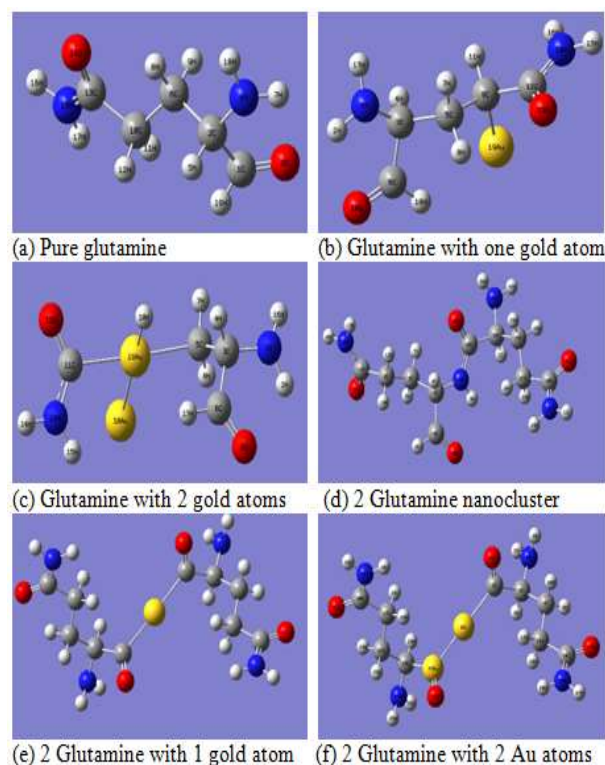


Fig. 1: Optimized structures of various glutamine and gold derived nanoclusters

The predicted bond lengths for Glutamine derived nanoclusters shows that generally the N–H bond is the strongest with the least values for the bond length. For pure Glutamine nanoclusters, the weakest bond is the C–C bond. Introduction of Gold into the Glutamine changes the trend as the Au–C, Au–Au and Au–H bonds become the weakest. The mean C–C bond length reduces with the introduction of Gold into Glutamine and for a double Glutamine molecule it increases. Glutamine derived nanoclusters studied in this work have shorter bond length for C–C bond compared to TNT (Clarkson *et al.*, 2003).

Table 1: Optimized mean bond lengths (Å) of glutamine and gold derived nanoclusters

Bond type	G1	Au1G1	Au2G1	AuG2	G2	AuG2	Au2G2
Au – C	-	2.0955	2.1790	2.1092	-	2.1092	2.1091
Au – O	-	-	-	2.9527	-	2.9527	1.2326
Au – H	-	2.797	2.9053	3.2810	-	3.2810	2.1788
C – C	1.5416	1.5385	1.5353	1.5054	1.3450	1.5054	1.5498
C – O	1.2503	1.2503	1.2435	1.2443	1.2555	1.2443	1.2482
C – N	1.4147	1.4548	1.4039	1.4242	1.4114	1.4242	1.4131
N – H	1.0116	1.0122	1.0133	1.0137	1.0132	1.0137	1.0132
C – H	1.1017	1.1027	1.0995	1.0973	1.0991	1.0973	0.9757
Au – Au	-	-	2.6605	-	-	-	2.1091

Table 2: Optimized mean bond angles degree of glutamine derived nanoclusters

Bond type	G1	Au1G1	AuG2	G2	Au2G1	Au2G2
C – Au – H	-	82.4810	100.0042	-	109.7470	-
C – Au – C	-	-	177.2696	-	177.0661	-
O – Au – H	-	-	82.8530	-	-	147.6531
O – Au – C	-	-	157.4541	-	-	120.4565
Au – C – C	-	110.4872	177.6053	-	116.3860	117.6061
C – C – O	123.3629	123.0682	121.3506	122.4789	123.2103	122.2429
C – C – N	112.9662	113.1980	112.0953	112.9959	109.6038	114.1171
C – C – H	108.0729	109.6219	109.1750	109.3523	110.8508	109.7440
C – C – C	112.4228	112.6713	110.4455	111.6966	110.3720	111.3093
N – C – H	111.4751	112.8464	112.1778	108.7451	112.0504	109.2271
C – N – H	118.8568	117.4509	119.0280	118.5195	119.0508	115.3660
H – N – H	118.1691	117.7272	117.5700	117.4914	119.2775	116.7613
H – C – H	107.0276	105.1278	107.8785	107.3766	111.5345	107.5121
C – H – H	-	-	109.6442	-	-	109.8480
H – H – H	-	-	106.4842	-	-	-
Au – H – H	-	-	108.4987	-	-	-
H – C – O	120.4986	120.8066	123.1334	120.8795	121.6316	-
O – C – N	121.6611	121.6760	121.7237	121.7103	125.7376	-
Au – C – O	-	-	121.9340	-	-	121.9338
Au – H – C	-	125.4568	108.4793	-	-	108.1217
H – C – Au	-	101.2248	-	-	-	-
N – C – Au	-	-	-	-	117.7880	-
H – Au – Au	-	-	-	-	96.7700	89.6860
C – Au – Au	-	-	-	-	91.4276	117.6091
H – Au – H	-	-	-	-	74.2227	-
C – H – N	-	-	-	-	-	111.0936
Au – H – N	-	-	-	-	-	112.0768
Au – Au – O	-	-	-	-	-	121.9340

Optimized bond angles

The optimized mean bond angles of Glutamine derived nanoclusters are shown in Table 2. It can be seen that most of the bond angles range between 100 and 120 degrees with very few exceptions below 100 degrees which is agreement with that of Ochterski *et al.* (2007).

Dipole moments, quadruple moments and energies

The dipole moment of the nanoclusters gives the strength of the polarity of the molecules. In case of Glutamine, the predicted dipole moment shown on Table 3 indicate that all the molecules are polar and the charge distribution is not symmetrical. Glutamine with one gold atom has the highest dipole moment. As the nanocluster molecule grows from one Glutamine to a cluster of two Glutamine molecules, there is an increase in dipole moment and hence the molecule becomes more polar. Addition of a second gold atom to Glutamine decreases the dipole moment in both cases and hence gold has the effect of reducing the polarity of the molecule.

Table 3: Total Dipole moments (in Debye) of glutamine derived nanoclusters

G1	Au1G1	AuG2	G2	Au2G1	Au2G2
4.2722	6.1979	4.2552	5.3543	6.5656	3.4026

Table 4: Predicted thermal energies (kcal/mol) for glutamine derived nanoclusters

Parameter	G1	Au1G1	AuG2	G2	Au2G1	Au2G2
Electronic	0.000	0.000	0.000	0.000	0.000	0.000
Translational	0.889	0.889	0.889	0.889	0.889	0.889
Rotational	0.889	0.889	0.889	0.889	0.889	0.889
Vibrational	104.108	97.922	198.899	198.903	91.534	196.819
Total	105.885	99.699	200.676	200.680	93.312	198.596

The total energies are shown in Table 4. The translational energy relates to the displacement of molecules in space as a function of the normal thermal motions of matter. Rotational energy is observed as the tumbling motion of a molecule as a result of the absorption of energy within the microwave region. The vibrational energy component is a higher energy term and corresponds to the absorption of energy by a molecule as the component atoms vibrate about the mean center of their chemical bonds. The electronic component is linked to the energy transitions of electrons as they are distributed throughout the molecule, either localized within specific bonds, or delocalized over structures, such as an aromatic ring (Wilson, 1955).

It is seen that the Glutamine molecules are less stable with the introduction of Gold molecules as the total energy decreases. This agrees with findings by Young (2001).

Charge transfer and polarizabilities

The Mulliken population analysis partitions the charges among the atoms of the molecule by dividing orbital overlap evenly between two atoms. Whereas the electrostatic potential derived charges assign point charges to fit the computed electrostatic potential at a number of points on or near the Van Der Waal surface. Hence, it is appropriate to consider the

charges calculated by CHelpG scheme of Breneman instead of Mulliken population analysis. The mean electrostatic potential derived charges on different atomic species for Glutamine derived nanoclusters is shown in Table 5. It is seen that the bulk negative charge goes to Nitrogen atoms. Carbon atoms are also electronegative. Gold and Hydrogen atoms carried the net positive charge.

Table 5: Mean electrostatic potential derived charges on different atomic positions for glutamine nanoclusters

Atom	G1	Au1G1	AuG2	G2	Au2G1	Au2G2
N	-0.643104	-0.647467	-0.606459	-0.558336	-0.589858	-0.600192
H	0.248458	0.257789	0.281473	0.256076	0.252443	0.299393
C	-0.135453	-0.139429	-0.164501	-0.116604	-0.124053	-0.175053
O	-0.260552	-0.254132	-0.231997	-0.379302	-0.198581	-0.358112
Au	-	0.141603	0.201857	-	-0.151695	0.159504

Table 6: Polarizabilities of glutamine derived nanoclusters

Orientation	G1	Au1G1	Au1G2	G2	Au2G1	Au2G2
XX	86.717	124.715	365.358	164.312	282.174	366.563
XY	1.382	-1.074	121.648	-2.612	-37.726	5.920
YY	73.256	120.420	243.776	140.968	197.067	215.780
XY	-3.517	-5.602	0.180	-6.399	-23.151	-26.093
YZ	-1.296	-0.460	0.134	5.427	4.304	17.414
ZZ	48.980	82.977	156.781	111.809	116.561	158.278

The polarizability tensor components of the nanocluster molecules are shown in Table 6. All the six polarizability tensor components (XX, XY, YY, XZ, YZ and ZZ) increases significantly on the addition of gold atoms to Glutamine molecules. The polarizability along the off-diagonal axis XZ, YZ and XY is very minimal in both cases.

Conclusion

In this study, the predicted dipole moment is high indicating that the nanocluster molecules are polar and the charge distribution is not symmetrical. The quadrupole moment predicts that the molecules are slightly elongated along the ZZ axis. Using the total energies, it is predicted that the Glutamine molecules are slightly more unstable with increase in the molecular size.

Conflict of Interest

Authors have declared that there is no conflict of interest reported in this work.

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