Effects of Cu, Ag, Au, & Pd Nanocluster Loading on Acetone & Ethanol Sensing Performance of ZnO: A DFT Study

The thesis submitted in partial fulfillment of the requirements for the degree of

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by

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CERTIFICATE

It is certified that the work contained in this thesis, titled "*Effects of Cu, Ag, Au, & Pd Nanocluster Loading on Acetone & Ethanol Sensing Performance of ZnO: A DFT Study*" by Oishika Pradhan, has been carried out under my supervision and is not submitted elsewhere for a degree.

Date:

Advisor: Prof. Tapan Kumar Sau

To my parents

Acknowledgments

Five years ago, I entered IIIT Hyderabad as a starry-eyed teenager, and I honestly am shocked how fast time flew by. This thesis marks the end of a very significant chapter in my life.

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ABSTRACT

Gas sensors find widespread applications from healthcare to industrial safety. The detection of volatile organic compounds like acetone and ethanol in their gaseous state is very important, especially in the biomedical field. SMO-based gas sensors, which have simple architecture and several favorable features, require additional treatments like noble metal loading onto the SMOs like ZnO surface for superior performance. Experimental trial-and-error approach to performance improvement has been the prevalent practice due to the lack of knowledge of the electronic and chemical properties of such systems. Computational studies can play significant roles as predictive tools in this field. In this work, by using DFT study, we explore how Cu, Ag, Au, or Pd nanocluster loading onto ZnO cluster affects acetone vs. ethanol sensing performance of ZnO semiconductor. DFT simulations have been used obtain the chemical and electronic properties of various nanoclusters systems, which have been associated with sensor performances. First, we have studied the binding of acetone and ethanol to pristine (ZnO)₂ cluster which explains how ZnO show better sensor response to acetone than ethanol. Next, we have explored the metal nanocluster M_6 (where M = Cu, Ag, Au, and Pd) loading onto ZnO. Since the actual working motifs in the nanostructured sensor materials could be a small cluster of few atoms, we have taken M_6 nanocluster as a model for the metal nanoparticle. Finally, we have investigated acetone vs. ethanol sensing performance of the metal nanocluster loaded ZnO systems. For each system, we have calculated various parameters like the binding energy, HOMO-LUMO energy and bandgap, Mulliken charge distributions, bond distance, etc. The study shows that the electronic structure effects of M_6/ZnO nanoclusters can be used to understand the molecular level mechanism of sensor activation by metal nanoclusters and explain their acetone vs. ethanol sensing performance. A better understanding of the roles of various components of the sensor materials will help in better selection of sensor materials and develop efficient, low cost and portable sensors.

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Chapter 1

Introduction

1.1. Gas Sensors

Now-a-days sensors are everywhere. Sensors are used in wearables, house-hold appliances, healthcare, bioengineering, industrial manufacturing, automotive and aerospace industry, environmental protection, ocean exploring, and so on. [1] A sensor is a device that responds to a signal and then converts it into a readable signal. Physical signals-based sensing technology has a long history and has been well established. In comparison, chemical signals-based sensing technology that involves chemical substances is less developed and has an enormous potential. [2] "A gas sensor is a device that detects the presence of various gases, including combustible, flammable, and toxic gases." [3]

Gas sensors are used for detection and monitoring of various gases, e.g., CO, CO₂, SO₂, NOx, H₂S, NH₃, HCN, etc. and volatile organic compounds (VOCs), e.g., ethanol, acetone, CH₄, C₃H₈, etc. These sensors are used for both predictive and preventive measures in the fields of environmental monitoring, human safety, healthcare, etc. Vehicles and various industry processes produce harmful gases like NH₃, SO₂, CO₂, NO_x, etc. [1] They pose danger to life and working environment even at very low concentrations. Historically, gas sensors were developed to detect the presence of toxic and combustible gases in coal mines to save workers. [4] In addition to the work-place safety, gas sensors are used in commercial greenhouse agriculture for keeping optimal temperature and CO₂ for crop growth. [1]

VOCs, which are often toxic and flammable, are the most common indoor air pollutants. Paints, varnishes, various activities like oil refining, vehicular emission, cooking, etc. are the sources of the VOCs in the environment. VOCs can cause mild irritation to severe effects like cancers. Gas sensors are essential for indoor air quality monitoring. [1] Recently, VOCs detection in human body fluids is emerging as a promising new frontier in gas sensing applications. [5, 6] Detection of VOCs in body fluids shows exciting potential for the diagnosis and monitoring of human metabolism and health conditions, adding/complementing the conventional diagnostic

methods. VOCs act as the molecular biomarkers for various biochemical processes occurring in both healthy and diseased individuals. VOCs in human body fluids like breath air have been shown to be related to health conditions like diabetes to cancers. For example, breath carbon monoxide has been used for neonatal jaundice diagnosis, ammonia test for asthma and hemodialysis assessment, nitric oxide to monitor the asthma therapy process, and so on. [7] Similarly, an abnormal level of ethanol has been observed with head and neck cancer, liver cancer, colorectal cancer, and acute kidney injury (AKI). Breath-acetone level has been linked to health conditions like physical activities and diet, diabetes, acute kidney injury, lung cancer, colorectal cancer, etc. [8, 9]

Breath sensors can be used for inexpensive and noninvasive sampling and analysis of breath in real-time (even during sleep). Furthermore, the discomfort/inconvenience of interventional sampling techniques, sample treatment, etc. can be avoided with such breath sensors. Therefore, VOC sensors will be an integral part of the next-generation medical technologies for early diagnosis and monitoring of various pathological and physiological processes in the human body. Furthermore, acetone and ethanol are highly volatile and flammable organic solvents. They tend to ignite at room temperature, and even dilute solutions in water can be flammable. They are also used as synthetic raw materials in the laboratories and industrial sectors. Long term exposure to only 173 ppm or higher acetone vapor has been reported to be toxic to human health. [10, 11] Therefore, VOCs like acetone/ethanol detections are of paramount importance.

1.2. Gas Sensor Performance Parameters

There are a few parameters that are used to measure a sensor's performance at the macroscopic level. They are sensor response (sensitivity), selectivity, response time, recovery time, detection limit, etc. A gas sensor's 'sensor response' (S, detection sensitivity) is the relative change in the sensor's output signal in response to (a) given target gas(es) exposure. Different ways are employed to define measure S. For example, in semiconductor metal oxide-based gas sensors, S is often taken as the ratio of the sensor resistance in ambient air (R_a , in the absence of target gas) to the sensor resistance in the target gas (R_g). The sensitivity refers to the change in signal per gas unit. On the other hand, when a sensor preferably responds to a specific gas or

targeted set of gases over the other gases, the sensor is considered to be selective. For instance, if an acetone sensor shows only insignificant response or no response to other gases such as ethanol (C_2H_5OH), H_2O , CO_2 , etc., the sensor is said to have good acetone selectivity. Selectivity is measured by the ratio of the sensor responses between the target gas(es) and the non-target gas(es) at equivalent concentrations. Thus,

Selectivity Factor (k) = (sensor response of gas1/ sensor response of gas2) = (S_1/S_2) Selectivity and sensitivity are two most important characteristics of sensors. A sensitive gas sensor makes the detection possible even in the presence of a small quantity of the gas. On the other hand, selectivity allows detection of a (set of) gas(es) in the presence of other interfering gases.

Response time is defined as the time required for a sensor to reach the total response signal upon exposure to a given concentration of the target gas. On the contrary, recovery time is defined as the time required for the sensor signal to drop to the baseline value upon removal of the target gas. However, they are taken experimentally as the signal values of 90% rise or drop of the maximal signal, respectively. A good sensor should produce high response, fast response/recovery of the sensor (i.e., short response/recovery times), and acceptable selectivity, among other factors.

1.3 Gas Sensing Materials and Sensor Performance Improvement

In recent years, the new generation of advanced and smart sensors demands accuracy with faster transmission and real-time data, and so on. Therefore, sensor performance is a crucial factor in the design of future generation of sensors. Improvement of the sensor performance depends on various factors depending on the kinds of sensors and their v14arious components. In sensors, the sensing matrix (materials) plays a vital role because the signal transduction principles depend on the sensor materials. Based on various kinds of transduction principles, different kinds of sensors viz., electrochemical, optical, thermometric, gravimetric sensors, etc. have been designed. A range of solid materials like metal oxides, standard semiconductors, zeolites, carbon-based structures, polymers and composites, bulk metals, metal nanoparticles, etc. have been used as gas sensing materials. [4]

Gas sensors based on the electrochemical transduction principles are among the most commonly used gas sensors. In these sensors, physical property (e.g., electrical conductivity,

permittivity, and work function) of the sensor material undergoes a change upon interaction with the analyte gas, which is converted to measurable electrical signal. [4] To obtain the electrical signal from the gas-solid interaction, chemiresistive materials-based gas sensors offer simple working principle and architecture. Chemiresistive materials show a change in the electrical resistance (or conductance) depending on the quantity of the adsorbed or desorbed target gas. Among various chemiresistive sensor materials, semiconductor metal oxides (SMOs) are one of the most investigated systems due to their favorable semiconducting properties. [12,13] Furthermore, SMOs offer high chemical and thermal stability, non-toxicity, good sensitivity, greater lifetime, broad range of operating temperatures and prospects for low-cost miniaturization. [12, 13] SMOs of both n-type (e.g., ZnO, SnO₂, TiO₂, WO₃, MoO₃, Nb₂O₅, etc.) and p-type (PdO, CuO, NiO, Co₃O₄, Cr₂O₃, etc.) have been used as chemiresistive gas sensing materials. [13] d^0 transition metal oxides (e.g., TiO₂, V₂O₅, WO₃) and d¹⁰ post-transition metal oxides (e.g., ZnO, SnO₂) have been found to better suited as the chemiresistive gas sensor materials. Although transition-metal oxides with favorable energy difference between a cation d^n and a d^{n+1} or d^{n-1} configurations are sensitive to gas binding but their structural instability, etc. limit their applications. [13] On the other hand, pre-transition-metal oxides (viz., MgO), which have large band gaps, make them quite inert for gas sensing applications.

A commonly accepted gas sensing mechanism of SMOs-based chemisresistive sensors involves a receptor process or the analyte gas binding process and a transduction process or analyte reactions process. [3] In the receptor process, physisorption and chemisorption of the gas molecules occur at the surface of SMO via van der Waals and dipole interactions and further chemical interactions and the temperature. Upon exposure to air, oxygen gets adsorbed onto the surface vacancies of the SMOs. Surface adsorbed oxygen withdraw electrons from the conduction band of a n-type SMOs and will create a zone nearby the surface with low electron density, known as the electron depletion layer (EDL). The EDL depth is called as Debye length (L) which is typically \sim 20–22 nm for ZnO at in the 250 °C–300 °C range. [14]

The formation of an EDL on the SMO surface leads to a decrease in its electrical conductivity or increase in its resistance. In the transduction process, the analyte gas reacts with chemisorbed oxygen on the surface of the SMO. If the SMO is exposed to a reducing target gas (e.g., H₂, CO, NH₃, H₂S, H₂O, CH₄, and VOCs like ethanol, acetone), the reducing gas will be

oxidized by the surface-adsorbed oxygen species or replace the adsorbed oxygen by a competitive adsorption by other molecules. This process will release the withdrawn electrons to the SMO conduction band. Thus, there will be a decrease in the depletion layer and hence an increase in the conductance or decrease in the resistance. On the other hand, an oxidizing gas (e.g., NO₂, NO, SO₂, O₃) will gain electrons from the surface-adsorbed oxygen species. It will further increase EDL and a further decrease in electrical conductivity. The change in resistance is measured as the output signal. Briefly, the increase or decrease of the resistance depends on the type of semiconductor and the nature of the gas. For an n-type SMO, reducing gases decreases the resistance (increase the conductance) while oxidizing gases increase the resistance (decrease the conductance). One observes the reverse mechanisms for a p-type materials.

Despite various favorable characteristics, the SMOs-based sensors also have several limitations. Therefore, researchers have explored various ways to improve the sensor performance of the SMOs-based sensors. Various strategies adopted tried to improve the adsorption of target gases, selective binding, charge separation in the SMOs, catalytic activity, etc. via modulation in the nature, composition, surface area, microstructure, surface additives, etc., of the SMOs. For example, researchers have employed binary, ternary, quaternary, or complex hetero metal oxides, metal oxides with organic and carbon nanotubes, etc. in place of single oxides to obtain a synergistic effect of the components. [1]

The other approach that is being explored intensely in recent years is the use of nanomaterials-based sensors. Nanomaterials offer multiple ways to tailor sensor performance. In addition to composition, properties of nanomaterials can be tailored by varying their nanoscale particle/grain size, morphology, structure and crystallographic facets, order of arrangement, etc. [17] Furthermore, nanomaterials and nanotube arrays, nanoporous structures, hierarchical nanostructures, etc. are outstanding candidates for gas sensing applications. [15-24] Nanomaterials have large surface area to volume ratio, plenty of corners, vertices, edges, etc. which play favorable roles in surface reactions, catalysis, diffusion, etc., in turn, in the transducer function of the sensors while converting the chemical interactions into an electrical signal. The unique chemical and physical properties of nanoparticles make them extremely useful for designing improved sensors, especially biosensors and electrochemical sensors. Using nanomaterials, the performance of these sensors has been enhanced greatly.

A popular approach for the sensor performance improvement is the modification of SMOs surface by noble metals (viz., Pd, Pt, Au), carbon materials, metal oxides, etc. [1,14] Noble metal loading onto SMOs has a long history. SMOs like ZnO, SnO₂, TiO₂, etc. show very poor sensitivities towards gases without any additives like noble metals (viz., Pd, Pt, and Au). The exact mechanisms of metal additives' actions are yet to be known. However, noble metals loading onto SMOs are considered to improve sensor performance via interfacial electronic redistribution and chemical sensitization. [25] The electronic sensitization arises from the electronic interaction of the loaded metal with the SMO. The state of oxidation of metal depends on its surroundings. Often the metals form oxides in the air but get reduced by the reducing analyte gas. The oxidation of metal forming metal oxide increases the depth of EDL. Thus, loaded metal aids in the receptor process. [26, 27] The surface-loaded metals also considered to aid the transduction process via the chemical sensitization process. In the chemical sensitization process, the metal catalyzes the oxygen and analyte gas dissociation providing a greater number of active sites and favorable interactions. for resulting in faster catalysis. The loaded metal activates the spillover effect of the gas which get oxidized by the surface-adsorbed oxygen near the SMO-loaded metal junction. [28]

1.4 Problem Statement

We have seen above that improving SMO-based sensor performance like sensor response, recovery, selectivity, etc., requires additional treatments like noble metal loading onto the SMO surface. SMO-based sensors also inherently show poor selectivity due to their sensitivity to broad range of reducing or oxidizing gases. For instance, acetone and ethanol both are reducing gases and are structurally and chemically similar. Achieving selectivity is a challenging task in such cases. The simple solution to the problem of selectivity is to tailor the material characteristics that can specifically bind the target gas. However, an improvement in selectivity could result in a stronger binding to a gas that could compromise the reversibility of the sensor. Several experimental studies have been carried out to improve upon these limitations by understanding the microstructural and electrical properties levels. However, the design of the metal-loaded SMOs mostly depends on the trial-and-error kinds of approach because a detailed knowledge of their electronic and chemical properties is largely missing. Although only a limited number of studies have been conducted, computational studies can play significant roles as predictive tools in this field. [29-35]

Developing novel smart future sensors requires a thorough understanding of electronic and chemical properties of the sensor materials. Further theoretical studies will be of paramount importance to understand and manipulate the sensing properties and performance of such nanostructured sensor materials.

In this work, by using DFT study we compare the acetone vs. ethanol sensing performance of Cu, Ag, Au, Pd nanocluster (NC) loaded n-type semiconductor ZnO. DFT simulations have been used to get an insight into the effects of chemical and electronic properties changes arising from acetone/ethanol binding to NC-loading onto ZnO sensor materials. We have taken M₆ (where M = Cu, Ag, Au, Pd) nanocluster as a model for metal nanoparticle with an assumption that the actual working motifs in the nanostructured sensor materials will be a small cluster of few atoms, not an extended surface. Furthermore, since the spill-over zone, the preferred sites for coadsorption of reducing gas and oxygen, lies in the vicinity of nanostructured ZnO, it appears practical to consider M₆/ZnO nanocluster systems for the studies. The broad goal is to study effects of electronic structure effects of M₆/ZnO nanoclusters on the acetone vs. ethanol sensor performance and to understand the mechanism of sensor activation at molecular levels. A better understanding of the roles of various components of the sensor materials will help in better selection of sensor materials and develop efficient, low cost and portable sensors.

We have chosen ZnO because it is a highly stable, non-toxic, and inexpensive metal oxide. ZnO, a wide-band-gap n-type SMO ($E_g = 3.37 \text{ eV}$), finds many technologically promising applications in areas like photovoltaics, optoelectronics and spintronics, solid-state lasers, besides sensing and detection. It has been extensively used to detect a number of oxidizing and reducing gases and VOCs. [15, 17-19, 21-23, 36-38] We have also seen above, in addition to various other applications, detection of chemical biomarkers like acetone and ethanol in body fluids is of paramount importance. [5]

1.5 Scope of The Thesis

The structure and scope of the thesis are as follows. After an introduction to the thesis topic in Chapter 1, we describe the fundamentals of computational methodologies applied in our calculations in Chapter 2. DFT theoretical studies of acetone vs. ethanol binding to pristine ZnO cluster and how their electronic properties affect the sensing performance of pristine ZnO are described in Chapter 3. Next, we have explored the interactions of different metal nanoclusters with ZnO cluster in Chapter 4. Chapter 5 presents how the metal nanoclusters loading onto zinc oxide cluster affects acetone vs. ethanol sensing performance. Finally, Chapter 6 gives general conclusions.

Chapter 2

Computational Methodology

2.1. Computational details

It has been established that the exchange correlation DFT functional of Becke, 3 parameter, Lee-Yang-Parr (B3LYP), [39] is suitable for representing nanosystems. The B3LYP functional is also considered suitable for representing organic molecules like acetone and ethanol. All the reactions modelled and reported in this work have been done using the Gaussian 09 suite of programs, using the B3LYP functional. The Los Alamos National Laboratory 2 Double-Zeta (LanL2DZ), [40] which is a double- ζ basis set, was used to model the metal atoms. The valence electrons of the metal atoms were modelled explicitly, and the core electrons were modelled using the LanL2DZ effective core potential. Effective core potential (ECP) reduces the basis set superposition error (BSSE). [41] The 6-311++G(d,p) split valence Pople basis set was used for atoms like oxygen, carbon and hydrogen. This includes a set of polarization and diffusion functions. The nature of stationary points was verified using frequency calculations. Each of the stationary point structures has minimum energy with no imaginary frequency.

2.2. Density Functional Theory (DFT)

Density functional theory is a sufficiently accurate and successful theory to replicate the electronic structures of atoms and molecules. DFT aims to understand material properties using the fundamental laws of quantum mechanics. [42] The traditional methods of estimating electronic structures try to solve the Schrodinger equation of *N* interacting electrons, moving in an external electrostatic potential, typically generated by the atomic nuclei in the form of Coulombic potential. This is not an extremely useful or appropriate method because of the following reasons:

a. The wave functions become extremely complex and difficult to solve even for small values of *N*.

- b. The computational costs for solving such complex equations increase exponentially with increasing value of *N*.
- c. These wavefunctions are not quantities that one can record and observe physically. Wave functions are more of a mathematical concept.

A modified and more refined version of this theory is used to formulate the principles of DFT. Instead of considering wave functions for each electron (thus creating a many-body wave function), DFT considers the one body density as the primary variable. DFT is feasible even for large systems, because the density is a function of only three spatial coordinates (not 3N wave functions). Some of the popular DFT methods are listed below in [Table 2].

Method	Туре	Abbreviation
Hartree-Fock Slater functional	Hartree-Fock with local density	HFS
	approximation exchange	
Vosko, Wilks and Nusair	Local Density Approximation (with	VWN
	emphasis on electron correlation	
	approximation)	
Beck correlation functional; Lee,	Gradient-corrected LDA functional	BLYP
Yang, Parr exchange terms		
Becke 3-term correlation	Hybrid DFT	B3LYP
functional; Lee, Yang, and Parr		
exchange functional		
Perdew 1986 functional	Gradient-corrected LDA functional	P86
Becke 3-term correlation	Hybrid DFT	P3P86
functional; Perdew correlation		
term		
Modified Perdew-Wang one	Hybrid DFT	MPW1K
parameter hybrid for kinetics.		

[Table 2]: Description of DFT methodologies

Mathematically, the B3LYP functional can be represented as:

$$E_{xc} = (1 - a_0)E_x (LDA) + a_0E_x (HF) + a_xE_x (B88_x) + a_cE_c (LYP88_c) + (1 - a_c)E_c VWN80_c$$

where $a_0 = 0.2$, $a_x = 0.72$, and $a_c = 0.81$. [43]

The existing B3LYP functional is being improved repeatedly to obtain more accurate results against experimental data. The parameters, a_0 , a_x , a_{c_1} are refined using experimental and a more improved version of the B3LYP functional is obtained. This functional is called the OpB3LYP functional. [44]

B3LYP is considered a suitable functional to represent metal oxide systems. Multiple groups have confirmed that the optimized structures obtained by B3LYP faithfully reproduce the X-Ray crystal structures of these systems. B3LYP functional is also suitable in reproducing the chemical kinetics of different systems. [44a]

2.3. Basis Sets

What are basis sets? Basis sets in computational chemistry are combined linearly to obtain molecular orbitals. [45] To describe electronic states of molecules, wavefunctions are constructed using these electronic states. These wavefunctions are approximate solutions to the Schrodinger equation. A mathematical function for molecular orbitals, ψ i is constructed, which is a linear combination of other functions. The main aim of basis sets is to provide a mathematical representation of electrons in a molecular system that enables scientists to understand bonding, reactivity and thus make suitable predictions like for useful applications like drug design. [46]

Usually, Slater and Gaussian functions are used for the representation of molecular orbitals. Slater functions provide describe an atomic wavefunction very accurately, but the computational costs of solving these equations are extremely high. A single Gaussian function is often not suitable for describing these complex electronic systems. However, a linear combination of Gaussian functions can be considered as an approximation of Slater functions. Even though there are a greater number of functions, this can be solved more easily. Gaussian basis sets are represented as N-MPG*. N is the number of Gaussian primitives used; the hyphen indicates the number of split basis sets where the valence electrons are double zeta. There are some primitive basis functions also, like the STO-

nG basis functions. These are considered as primitive basis sets, because they only provide very basic information about the systems being studied.

There are more advanced basis sets called extended basis sets (split valence, polarised sets, diffuse sets), which give greater information about the charge distributions, shape and size of atoms and so on.

2.4. Split Valence Pople Basis Sets (sub section of basis sets)

Since valence electrons participate in bonding, these electrons are often represented using separate functions. These are usually represented by a fixed number of Gaussian functions. Some split valence basis sets, where the valence orbitals two functionals are used for each valence orbital instead of one, are the 4-31G, 5-31G and the 6-31G basis sets. These basis sets have some limitations which have been discussed by Krishnan and coworkers, [47] in great detail. A more efficient basis set can be used in place of this, the 6-311G basis set. This has a triple split for valence basis functions. This basis set provides more accurate results as compared to other basis sets. [48] In our study of acetone sensing, we use the 6-311++G(d,p) split valence basis set for non-metal atoms, which includes polarization and diffusion functions.

2.5. Los Alamos National Laboratory (LanL) basis sets

The Los Alamos National Laboratory basis sets, known as the LanL2DZ basis sets have been developed by Hay and Wadt. [40, 49, 50] This is a double zeta basis set and when used with the hybrid B3LYP functional, it can act as a suitable basis set for heavy metals. This basis set employs an ECP basis for transition metals and uses an all-electron basis for other elements. The LanL2DZ basis set is becoming increasingly popular for ab initio calculations of transition metal complexes and compounds. As every other basis set, this too does have limitations and there are improved methods to obtain the best results out of the LanL2DZ basis set. [51]

2.6. Polarization Functions

The concept of polarization comes into play when the atoms are brought close to each other during various chemical reactions. This causes a distortion of atomic orbitals. This phenomenon is accounted for by the use of polarization functions. The specific polarization functions are added

to the original basis sets, by suffixing them in brackets after the original basis set. For example, when 6-311++G upon addition of a polarization function becomes 6-311++G(d,p).

2.7. Diffuse Functions

Diffuse functions are used to model molecules with heteroatoms, electronic excitation. Electrons in such cases are very loosely bound to the nuclei. [52] Diffuse functions are represented using the '+' symbol. They are appended to basis sets, in a similar fashion as the polarization functions. A single '+' symbol implies addition of diffuse functions to heavy metal atoms and the '++' symbol implies addition of diffuse functions like hydrogen and helium. For example, when we want to add diffusion functions to 6-311G basis set, it becomes 6-311++G(d,p).

2.8. Effective Core Potential (ECP)

For elements with atomic numbers greater than 11, (Na and beyond), have a large number of electrons. In such cases, it is important to consider the Effective Core Potential (ECP), which considers the valence electrons separately as opposed to all-electron basis sets. ECP accounts for the effect of the nucleus on the chemically reactive valence electrons. ECP also takes into account the relativistic effects of transition metals.

Even though inclusion of ECP increases computational load, the results show greater accuracy. ECP also includes the non-reacting valence electrons of the system into the calculations for the core of the atom.

2.9. Applications of DFT

DFT can provide insight into a wide range of chemical phenomena, which in turn can help us understand and eventually design better performing systems for sensors. DFT calculations provide us with valuable data like identifying the site of reaction, the configuration of very small molecular clusters, bond distances, charge distribution, band gaps. This provides fairly accurate and important information that can be used to design sensors.

Chapter 3

Acetone and Ethanol Sensing Performance of ZnO Nanocluster

3.1. Zinc Nanostructures and Their Applications

ZnO is one of the most attractive SMO gas sensing materials due to its high chemical and thermal stability, low cost, non-toxic and biosafe nature, good mobility of conduction electrons, and many other excellent material properties. [53, 54, 55, 56, 57]

ZnO-based sensors have also considerable attention for acetone and ethanol gas sensing. Like many other SMOs, ZnO also exhibits poor sensor response and selectivity, long response/recovery times, and high operation temperature. Several demanding applications like breath acetone sensing require faster response and recovery along with high sensor response and low temperature of operations. Experimentalists have been exploring the compositions, nanomaterials morphologies, surface area, etc. to improve the sensor performance of ZnO and other SMOs. Among various approaches, metal nanoparticles decorated nanostructured ZnO have been reported to show enhanced sensor performance for acetone and/or ethanol gas sensing. However, we are far away from developing a comprehensive understanding of the factors that affect the sensor material properties of the pristine zinc nanocluster using density functional theory (DFT). Earlier, properties of zinc oxide nanostructures [(ZnO)_n] have been studied in detail using DFT. [58] In the following we calculate the adsorption and interaction parameters of acetone and ethanol gases with gaseous zinc oxide nanoclusters and explore how electronic properties of such systems affect the sensing behavior.

3.2. Computational Details

The Gaussian 09 software was used for these DFT calculations. [59] The adsorption energies, charge distribution and other parameters were calculated using the same models. The geometries of all the structures were optimized using the Becke, 3 parameter, Lee-Yang-Parr (B3LYP) density functional. The atoms O, C and H were optimized using the B3LYP/6-311++G(d,p) basis set and the heavy metal atoms like Zn were optimized using the Los Alamos National Library Double Zeta basis set (also known as LanL2DZ), considering the effective core potential (ECP). Frequency calculations were performed to ensure that there are no imaginary frequencies. The zinc oxide nanoparticle structure was optimized using tight optimization criteria which implies that the RMS force criterion is set to 10^{-5} Hartree/Bohr to get structures of reliable accuracy. The tighter convergence criterion implies more accurate results but requires more computational power. The systems were modelled at a temperature of 298.15 K and 1 atm pressure.

The organic compounds like acetone and ethanol are adsorbed onto the zinc oxide molecule via the oxygen atom of the organic compound. For the ethanol molecule, the functional group of the molecule is the –OH group, which is the most reactive part of the ethanol molecule. According to various previous studies conducted on adsorption of ethanol, the ethanol molecule is adsorbed on to the zinc oxide molecules via the hydroxyl group. [60, 61] Similarly, for the acetone molecules, the most reactive part of the molecule is the carbonyl oxygen of the acetone molecule. Since oxygen is more electronegative than carbon, the carbonyl bond of acetone is extremely polar, with a partial positive charge on the carbonyl carbon and a partial negative charge on the oxygen and carbon. The oxygen atom, as a result, pulls two pairs of electrons towards itself. [62] In most cases, acetone adsorption on zinc oxide nanoparticles, the acetone molecule gets adsorbed through the oxygen of the acetone molecule.

3.3 **Results and Discussion**

3.3.1 Zinc oxide nanocluster structure

The optimized structure of the zinc oxide nanocluster of formula $(ZnO)_2$ with the lowest energy s shown in [Figure 3.1]. As seen in the structure above, $(ZnO)_2$ has a planar structure, which

has D_{2h} symmetry. The bond lengths were found to be as follows: Zn-Zn bond length is 2.47 Å and the Zn-O bond length is 1.93 Å. These values obtained are agreement with the values reported by other similar studies. [63]



[**Figure 3.1**]: Optimized lowest energy structure of $(ZnO)_2$. The basis set used for oxygen atoms is 6-311++G(d,p) while the zinc atoms were optimized using the LanL2DZ basis set.

3.3.2 Acetone and ethanol molecules

Similarly, acetone and ethanol molecules were optimized using the B3LYP/6-311++G(d,p) appropriate level of computation. The optimized lowest energies structures [Figure 3.2] of both acetone and ethanol were considered for further calculations. The double bond between oxygen and carbonyl carbon, C-C-C bond angle of acetone are determined as 1.21 Å, 116.5° respectively. Similarly, the bond distance of C-O and C-C-O bond angle of ethanol are determined as 1.43 Å and 113° respectively. They agree well with previously reported values.[64, 65]



[Figure 3.2] Optimized and lowest energy structures of acetone [a] and ethanol [b]. Structures have been optimized using B3LYP/6-311++G(d,p) level of theory.

3.3.3 Adsorption of acetone and ethanol on zinc oxide nanocluster

Using the optimized structures of acetone, ethanol, and zinc oxide nanocluster, the adsorption process was modelled. The oxygen atom of acetone and hydroxyl group of ethanol interact with the zinc atom of (ZnO)₂. The resultant optimized interactive structures shown in [Figure 3.3]. The optimized lowest energy structures of (ZnO)₂–acetone and (ZnO)₂–ethanol will be henceforth referred to as ZnO-Act and ZnO-Eth respectively.



[Figure 3.3] Binding of $(ZnO)_2$ to acetone [Top] and ethanol [Bottom] gases. Acetone binds via the oxygen atom and ethanol via the hydroxyl oxygen atom. The resulting structure has been obtained as a result of optimization using B3LYP exchange functional, with 6-311++G(d,p) as basis set for H, C, O atoms and LanL2DZ as basis set for the Zn atoms.

The summary of bond lengths and the shortest distance between the ligand oxygen (O_L) and Zn atom of zinc oxide cluster are given in [Table 3.1]. The distance between the bonded zinc atom and the oxygen atoms of acetone and ethanol were calculated to be 2.075 Å and 2.088 Å respectively. There was a small change in the (ZnO)₂ structure. In the ZnO-Act system, the (ZnO)₂ structure loses its symmetry. The Zn1-O3, Zn1-O4, Zn2-O3, Zn2-O4 bond lengths change from the common value of 1.931 Å to 1.909 Å, 1.921 Å, 1.986 Å and 1.935 Å respectively. The Zn-Zn bond length increased from 2.470 Å to 2.494 Å. For the ZnO-Eth system, the Zn1-O3, Zn1-O4, Zn2-O4 bond lengths change to 1.894 Å, 1.930 Å and 1.918 Å. It is interesting to note that the Zn2-O3 bond was broken in the ZnO-Eth system. The Zn-Zn bond length was found as 2.506 Å which is longer than the ZnO-Act case.

[Table 3.1]: The bond lengths and distances (Å) of the ZnO, ZnO-Act and ZnO-Eth systems.

Bonds	Acetone	Ethanol	ZnO	ZnO-Act	ZnO-Eth
C-0	1.211	1.431	-	1.239	1.441
Zn-Zn	-	-	2.470	2.494	2.506
Zn1-O3	-	-	1.931	1.909	1.894
Zn1-O4	-	-	1.931	1.921	1.930
Zn2-O3	-	-	1.931	1.986	bond broken
Zn2-O4	-	-	1.931	1.935	1.918
Shortest Zn-OL distance	_	-	-	2.076	2.089

Systems

Further, we can see that the symmetry of the zinc oxide nanoparticle was broken for both ZnO-Act and ZnO-Eth systems and the distortion was less in the ZnO-Act system. The C-O bond slightly stretched in both acetone and ethanol upon binding to ZnO cluster. The C-O bond length increased by ~2.3% for the acetone case while ~0.70% for the ethanol case. It suggests the C-O bond weakened more in the case of ZnO-Act system. Similarly, the distance between the ligand and zinc oxide cluster was shorter in case of the ZnO-Act than ZnO-Eth. The C-C-C bond angle in acetone changes from 116.55° to 119.16° when acetone adsorbed onto zinc oxide cluster. Similarly, the C-C-O angle in ethanol changes from 107.81° to 109.25°.

3.3.4 Binding energy

Binding energy is defined as the energy that is required to separate a particle from a group of particles or even disperse the group of particles. [66] In designing the sensors, it is important to understand the binding process and hence the binding energy. It is a measure of the stability of the system that is formed after the adsorption of the ligand molecule. It is particularly important

because it indicates how sensitive a sensor material is to a particular chemical compound binding and whether the ligand adsorbate gets desorbed easily or not. The binding energy of a system can be measured as:

$$E_{ads} = E_{system} - (E_{ZnO} + E_L)$$

Here, E_{ZnO} and E_L are the energies of ZnO and the ligand (acetone/ethanol) of the system respectively. If $E_{ads} < 0$, then the reaction is exothermic, and the binding of ligand is said to be favorable. On the contrary, if $E_{ads} > 0$, then the ligand will not bind to the substrate. The comparison of the binding energies of the ZnO-Act and ZnO-Eth systems shown in [Figure 3.4]. From the Figure, it is evident that the zinc oxide cluster binds more strongly to acetone than ethanol.



[Figure 3.4] A comparison of binding energies of ZnO-Act and ZnO-Eth systems. We can see a large difference in binding energies between the two systems, with ZnO-Act having a larger binding energy

The adsorption energy, E_{ad} , is related to the recovery time, t_r , for gas desorption from the sensor surface as follows:

$$t_{\rm r} \propto V_0^{-1} \cdot \exp(\frac{-E_{\rm ad}}{kT})$$

where k is for the Boltzmann's constant, T is the Kelvin temperature of the system, and v_0 stands for the attempt frequency of the gas molecule. It shows that a higher negative value of E_{ad} results in longer sensor recovery time. Thus, ethanol will have a shorter recovery time than acetone.

3.3.5 Charge distributions

The Mulliken charge distribution was determined using the respective basis sets for each atom. The detailed charge distribution and charge transfer values are listed in [Table 3.2 and 3.3]. Since oxygen is an electronegative element and zinc is electropositive, the Mulliken charges are found to be negative and positive on oxygen and zinc respectively on ZnO cluster. Thus, the zinc atoms act as donor atoms for the oxygen atoms, in the zinc oxide system. For the acetone molecule, the oxygen atom is negatively charged, while the carbon attached to it is positively charged. Since carbon is more electronegative than hydrogen, [67] both carbons attached to hydrogens are negatively charged, while the hydrogens are positively charged. Considering the ethanol molecule, the oxygen atom is negatively charged as is expected. The hydrogen atom of the hydroxyl group has a positive charge, due to the electronegativity difference with oxygen. When the acetone and ethanol molecules adsorbed onto the ZnO cluster, there were charge redistributions due to the interactions between the ligand molecule and the cluster. Such charge transfer has a great impact on the sensitivity of the sensor substrate for the corresponding ligand molecule being sensed. [68-70] One can see that the charge transfer occurs from the ligand molecule to the sensor material, ZnO cluster. More importantly, the charge transfers from acetone to zinc oxide is greater than the charge transfer from ethanol. There is a transfer of 0.176e from acetone to zinc oxide and 0.104e from ethanol to zinc oxide. These values agree well with the previously reported values. [71, 72] It can be said that a higher charge transfer implies better sensitivity of sensor. [73-76] Metal oxide semiconductor-based chemoresistive sensors follow oxygen-related gas-sensing mechanism, where the adsorption of oxygen molecules from the air onto SMO surface is an important step for the sensing process. Oxygen molecules generate various chemisorbed oxygen species (viz., O_2^- , O⁻, O²⁻) on the oxide surface by capturing electrons from its conductance band. Formation of various anionic oxygen species may be facilitated by the oxide donor.

ZnO		Ac	etone	Etl	nanol	Zn	O-Act	Zn	D-Eth
Atom	Charge								
Zn1	0.831	C1	0.276	C1	-0.402	Zn1	0.666	Zn1	0.727
Zn2	0.831	O2	-0.276	C2	-0.219	Zn2	0.797	Zn2	0.884
03	-0.831	C3	-0.469	H3	0.126	03	-0.882	O3	-0.921
O4	-0.831	H4	0.171	H4	-0.15	O4	-0.757	O4	-0.794
		H5	0.148	H5	0.15	C5	0.609	C5	-0.459
		H6	0.15	H6	0.127	O6	-0.397	C6	-0.102
		C7	-0.469	H7	0.127	C7	-0.546	H7	0.144
		H8	0.15	08	-0.311	H8	0.175	H8	0.137
		H9	0.171	H9	0.253	H9	0.177	H9	0.161
		H10	0.148			H10	0.187	H10	0.136
						C11	-0.673	H11	0.17
						H12	0.18	012	-0.471
						H13	0.305	H13	0.388
						H14	0.159		

[Table 3.2] The individual Mulliken charges of all atoms are listed for the respective systems.
System	Charge on (ZnO) ₂	Charge on ligand		
ZnO-Act	-0.176	0.176		
ZnO-Eth	-0.104	0.104		

[Table 3.3] Charges on individual parts of the sensor system

3.3.6 Electrostatic potential (ESP) maps

Electrostatic potential (ESP) maps are particularly important because they help us visualize the charge distribution of molecules and estimate the charge related properties of said molecules. ESP measures the strength of close by charges, both nucleic and electronic charges. For the most accurate results, a lot of potential values need to be calculated. These values can be displayed in the form of a map to make interpretation easy. These calculations are based on the fundamental law of nature, Coulomb's Law. [77] A color spectrum is used to denote the different intensities of electrostatic potential values. The red color denotes the most negative electrostatic potential values while the blue color denotes the most positive values. [78] The electrostatic potential (ESP) maps of the lowest energy optimized structures of ZnO, acetone, ethanol, ZnO-Act, and ZnO-Eth can be seen in [Figure 3.5].



[Figure 3.5a]: ESP map of ZnO



[Figure 3.5b]: ESP map of acetone (left) and ethanol (right)



[Figure 3.5c]: ESP map of ZnO-Act system (left) and ZnO-Eth system (right)

[Figure 3.5] ESP maps of ZnO, acetone, ethanol, ZnO-Act, and ZnO-Eth

In [Figure 3.5a], a high negative electron density associated with the two oxygen atoms, while there is high positive electron density associated with the two zinc atoms. Since the zinc oxide structure is symmetrical, the ESP map also follows the symmetry. In [Figure 3.5b], a high negative electron density can be observed due to the oxygen atom, while the hydrogen atoms show

some positive electron density. However, in [Figure 3.5c], the hydrogen atom of the hydroxyl group has a high positive electron density. The oxygen atom has a high negative electron density. These electrostatic potential maps are in agreement with the acetone and ethanol molecules binding to the zinc oxide cluster and Mulliken charge distribution values given above.

3.3.7 HOMO-LUMO orbitals

Molecular orbital theory was introduced to explain those phenomena that could not be explained by the valence bond theory. It serves as a basis for most quantitative calculations.[79] There are a lot of complex mathematical calculations involved in accurate calculation of molecular orbitals, but the concept behind molecular orbitals is easily understood. The simple Lewis and VSEPR models considered that the atoms had one center orbitals. It wasn't considered that these orbitals will be modified upon interaction with other atoms. These 'valance bond' models are usually not very good at prediction, as they do not consider multiple aspects of electronic interactions with other atoms. Molecular orbital theory can be used to explain why certain molecules like He₂ do not exist. [80]

Chemical bonding occurs when the net attractive forces between two nuclei and an electron are greater than the repulsion between the two nuclei. The electron must be present in the binding region for the bonding to occur. If the electron is in the antibonding region, then the electron adds to the repulsive forces. We try to picture the individual orbitals and then eventually try to predict how these orbitals would behave when they react with each other, as the orbitals are moved close to each other. Finally, when the orbitals are at the appropriate bond distance, then the orbitals take the form of the actual orbitals that we are studying. We considered the interaction of two orbitals and got a single resultant orbital, but that doesn't add up. Hence like regular waves, the orbitals produce an additive result, known as bonding orbital and a subtractive result, known as antibonding orbital. When the two orbitals combine in phase, they produce a bonding orbital and when they combine out of phase, they produce an antibonding orbital. [81] We can say that the resultant number of molecular orbitals is the number of molecular orbitals that combine to form them.

The most important molecular orbitals in terms of reactivity are the frontier molecular orbitals. The orbitals at the 'frontier' of electron occupation are the highest energy occupied

orbitals and the lowest energy unoccupied orbitals (HOMO and LUMO respectively). The HOMO is electron donating, while the LUMO is electron accepting. [82, 83] The difference between HOMO and LUMO is regarded as the band gap. [84] The spatial distribution of the frontier orbitals of the studied systems are shown in [Figure 3.6]. It should be noted that in (ZnO)₂ cluster all the atoms contribute to HOMO and LUMO. On the other hand, although primarily ZnO contributes to HOMO but both ZnO and Act contribute to LUMO in ZnO-Act. In ZnO-Eth, majority contribution is observed from ZnO and a smaller contribution from Eth.





[Figure 3.6]: HOMO-LUMO frontier orbitals diagrams of zinc oxide, acetone, ethanol, ZnO-Act and ZnO-Eth

Next, we have calculated the energy values of the HOMO-LUMO orbitals and the HOMO-LUMO energy gaps (E_g) which are given in [Table 3.4]. The HOMO-LUMO energy values of ZnO were consistent with that reported by Chandraboss and coworkers. [63] Similarly, the HOMO-LUMO energy values of acetone and ethanol also were in agreement with the previously reported values. [85] The HOMO-LUMO energies of the clusters and molecules give an idea about their properties like the local chemical reactivity, electrical conductivity, etc. [29, 31]

Chemical hardness, $\eta \approx (E_{LUMO} - E_{HOMO})/2 = E_g/2$, is considered as the reactivity descriptor of a cluster or a molecule. Therefore, the HOMO–LUMO gap, E_g , values indicate the reactivities

and chemical stabilities of clusters and molecules. The molecules with lower chemical hardness (or smaller E_g value) are softer and more polarizable molecules. Since their electron density changes easily, softer molecules or systems show higher chemical reactivity (or lower chemical stability) than harder systems. Thus, ZnO-L systems were more reactive than the ligand (L) molecules and ZnO-Act was more reactive than ZnO-Eth.

[**Table 3.4**]: HOMO-LUMO values for all systems, where $E_g =$ HOMO-LUMO gap and $\Delta E_g =$ [$E_g(ZnO-L) - E_g(ZnO)$]

System	HOMO (eV)	LUMO (eV)	Eg (eV)	ΔE_g (in eV)
(ZnO) ₂	-6.291	-3.717	2.574	
Acetone	-7.053	-0.783	6.270	
Ethanol	-7.636	-0.339	7.297	
ZnO-Act	-5.517	-2.542	2.974	0.400
ZnO-Eth	-5.958	-2.947	3.011	0.437

The E_g value gives a measure of the electrical conductivity of the sensor material. The electrical conductivity, (σ) is given by the formula: [86, 87, 88]

$$\sigma \alpha \exp(-E_g/2KT)$$

Here, E_g , *K* and *T* are the HOMO-LUMO gap (band gap), Boltzmann constant, and absolute temperature, respectively. One can see a change in E_g values upon adsorption of gas molecules. We can see here that the acetone adsorption onto ZnO cluster produces better conductivity change than the ethanol adsorption process.

Next, we try to understand how the electrons are being transferred, i.e., who the electron donor is: the ligand (acetone/ethanol) or the ZnO cluster. [Table 3.5] shows the corresponding

calculated HOMO-LUMO energies. From [Table 3.5], we can see that for both the cases, based upon frontier molecular orbital theory, [89, 90] the ligands (acetone and ethanol) act as electron donors and ZnO cluster acts as the electron acceptor. This is consistent with the Mulliken charge transfer values obtained above. More importantly, one can see that electronic charge transfer is easier in ZnO-Act as compared to ZnO-Eth.

[**Table 3.5**]: HOMO-LUMO energy (eV) gaps of ligand molecules and zinc oxide and the energy gaps between Act/Eth and ZnO.

System	HOMO	LUMO	HOMO-	HOMO-	HOMO-	HOMO-
			LUMO	LUMO	LUMO	LUMO
			(ZnO→Act)	(Act→ZnO)	(ZnO→Eth)	(Eth→ZnO)
Acetone	-7.053	-0.783				
Ethanol	-7.636	-0.339				
(ZnO) ₂	-6.291	-3.717	5.508	3.336	5.952	3.919

3.3.8 Characteristics of a good sensor and how ZnO performs

For a nanocluster to be considered as an efficient gas sensor, it needs to have the following characteristics: [29, 91]

- 1. The gas molecule should adsorb onto the nanocluster with a high binding energy so that it stays bound to the sensor nanocluster and does not get desorbed easily.
- There is a significant charge transfer between the sensor nanocluster and the analyte gas molecule resulting in significant change in the electrical conductivity. According to our previous discussions, acetone can be sensed better than ethanol by the zinc oxide nanocluster.

Therefore, considering parameters like the binding energy, charge transfer, and variation of band gap energy, etc. we can say that the zinc oxide nanocluster will produce better sensor performance in terms of sensor response and selectivity for acetone as compared to ethanol. However, to improve the sensor performance further, researchers have decorated ZnO with noble metal nanoparticles. We shall attempt to explore these systems in detail in the next chapter.

Chapter 4

Acetone vs. Ethanol Binding to Metal Nanoclusters

4.1 Metal Nanoparticles and Ligand Gas Interactions

Loading/decorating ZnO surfaces with noble metals has been one of the favorite approaches in improving sensor performance. Prior to our DFT study of the metal nanocluster loaded ZnO systems, we have first explored the individual metal nanocluster-ligand gas systems. It gives us an idea about the interaction properties of acetone and ethanol with the individual metal nanoclusters and then we compare their properties with the ZnO-loaded systems, which is discussed in the next Chapter. The loaded noble metal on the sensor substrate has been proposed to influence the sensing process via "electronic" and "chemical" mechanisms. [57]

In other words, the loaded metal acts as an electron acceptor and catalytically activates the molecular oxygen adsorption, dissociation, and sensing reactions on the SMO surface. We explore here the individual interactions of ligand-metal nanoclusters interactions in order to understand the above mechanisms at the molecular level.

4.2 Computational Details

As given in the previous Chapter for the study of zinc oxide nanoclusters, we use the same basis set LanL2DZ for optimizing the metal clusters of Cu_6 , Ag_6 , Au_6 and Pd_6 using the electron core potential (ECP) as the noble metals especially require the use of ECP. To mimic the coating of the zinc oxide nanoclusters, we let the optimized metal nanoclusters interact with the zinc oxide nanoclusters and optimize the resulting structure.

4.3 **Results and Discussion**

The optimized structures of the Cu₆, Ag₆, Au₆, and Pd₆ nanoclusters were obtained which are shown in [Figure 4.1]. The structures are all planar, except Pd₆, as reported by earlier by others

have been observed in previous studies. [92-95] All the metal nanoclusters are planar, and the energies and bond lengths are listed below in [Table 4.1].



[Figure 4.1] The lowest energy optimized structures of Cu_6 , Ag_6 , Au_6 and Pd_6 nanoclusters.

[**Table 4.1**]: Average metal bond length (in Å) and scaled energies E_s (in kcal/mol). E_s is the scaled energy where $E_s = E_{system}/n$; E_{system} is the energy of the nanocluster system; *n* is the number of metal atoms in the nanocluster

	Cu ₆	Ag ₆	Au ₆	Pd ₆
Average M-M bond length	2.409	2.758	2.703	
	2.700			
Energy (Es)	-123101.864	-91492.617	-85024.433	-79541.069

4.3.1 Electrostatic potential maps

The electrostatic potential maps (ESP) can be seen in [Figure 4.2]. From all the ESP maps, we can see that all the corner atoms have positive charge, so the acetone and ethanol molecules are most likely to interact with the corner atom positions.



[Figure 4.2] Electrostatic potential map of Ag₆ Au₆ Cu₆ Pd₆ nanocluster (left to right)

4.3.2 HOMO-LUMO and HOMO-LUMO gaps

The frontier HOMO-LUMO's diagrams of all the metal nanoclusters are shown in [Figure 4.3]. We can see that Ag_6 and Cu_6 have similar HOMO-LUMO structure while Au_6 has a completely different frontier orbital structure. In [Table 4.2], we compare the HOMO-LUMO energies of these nanoclusters. From [Table 4.2], we find that $E_g(Cu_6) > E_g(Ag_6) > E_g(Au_6) > E_g(Pd_6)$. A similar trend has been reported by Jorge and coworkers. [96]



[Figure 4.3] [a]: HOMO of Cu₆



[Figure 4.3] [b]: LUMO of Cu₆





[**Figure 4.3**] [**c**]: HOMO of Ag₆

[**Figure 4.3**] [**d**]: LUMO of Ag₆



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[**Figure 4.3**] [e]: HOMO of Au₆

[Figure 4.3] [f]: LUMO of Au₆



[**Figure 4.3**] [**g**]: HOMO of Pd₆

[**Figure 4.3**] [**h**]: LUMO of Pd₆

[Table 4.2]: Calculated HOMO, LUMO and HOMO-LUMO gap (E_g) energies of the metal nanoclusters

	HOMO (eV)	LUMO (eV)	E _g (eV)
Cu ₆	-5.499	-2.253	3.245
Ag ₆	-5.458	-2.459	2.998
Au ₆	-7.838	-5.839	1.998
Pd ₆	-5.100	-3.811	1.289

4.4 Interaction of Acetone and Ethanol with Metal Nanoclusters

The acetone and ethanol molecules bind with the metal atom via the oxygen atoms of the acetone and ethanol molecules. As we have seen from the ESP maps of the metal nanoclusters, the corner atoms have positive charge and are most likely to interact with the organic molecules. The lowest energy optimized structures are shown in [Figure 4.4]. We have also performed optimizations, where the organic molecules interact with the metal atoms that are not in the corner. In case of palladium nanocluster, we consider only one position of interaction, as all the positions on the cluster can be considered equivalent. However, as expected, those interactions were not as favorable as they are with the corner atoms. We consider the average of all the possible sites of interactions while calculating the binding energies, bond distances, HOMO-LUMO gaps.



[Figure 4.4] [a]: Acetone on Cu₆

[Figure 4.4] [b]: Ethanol on Cu₆



[Figure 4.4] [c]: Acetone on Ag₆



[Figure 4.4] [d]: Ethanol on Ag₆





[Figure 4.4] [e]: Acetone on Au₆

[Figure 4.4] [f]: Ethanol on Au₆



[Figure 4.4] [g]: Acetone on Pd₆

[Figure 4.4] [h]: Ethanol on Pd₆

[Figure 4.4]: Optimized lowest energy structures of acetones and ethanol interacting with different metal nanoclusters.

4.4.1 Binding energies and bond distances

The binding energy (interaction energy) is calculated as given in the previous Chapter,

$$E_{ads} = E_{M-L} - (E_L + E_M)$$

where E_L and E_M are the energies of the ligand system (acetone or ethanol) and the energies of the

metal systems (M = Cu, Ag, Au, or Pd). The binding energies of these complexes are listed in [Table 4.3]. From the Table, we can find that all the interactions are favorable with negative energy values. For both acetone and ethanol, the strength of the (-ve) binding energy decreases in the order: Cu > Pd > Au > Ag. However, the ethanol binding energy was less than that of acetone one: M_6 -Act > M_6 -Eth. Their binding energy difference was more in the cases of Cu_6 and Pd_6 cases.

[**Table 4.3**]: Average binding energies (kcal/mol) of acetone and ethanol with respective metal nanoclusters

For Gas	Cu ₆	Ag ₆	Au ₆	Pd ₆
Acetone	-9.993	-4.298	-6.543	-8.477
Ethanol	-9.164	-4.036	-6.406	-7.687

The distances between the ligand oxygen atom and the binding metal atom (M-O_L) in the nanocluster cluster are listed below in [Table 4.4]. The M-O_L distance decreases in the order: Pd < Cu < Ag < Au. The C-O bond length of acetone increases from 1.212 Å to 1.227 Å, 1.225 Å, 1.221 Å and 1.222 Å for interactions with Cu, Ag, Au and Pd respectively. Similarly, the C-O bond length of ethanol increases from 1.431 Å to 1.446 Å, 1.443 Å, 1.440 Å and 1.445 Å for interactions with Cu, Ag, Au and Pd respectively. It shows that the C-O bond weakens in the ligand molecules upon binding with metal nanoclusters.

[**Table 4.4**]: The average distance (Å) between the ligand oxygen atom to the binding metal atom $(M-O_L)$ in the nanocluster

For Ligand Gas	Cu ₆	Ag ₆	Au ₆	Pd ₆
acetone	2.133	2.570	2.632	2.076
ethanol	2.168	2.584	2.596	2.089

4.4.2 Mulliken charge analysis

The Mulliken charge analysis is performed using the LanL2DZ basis sets, with ECP for heavy metals and 6-311++G(d,p) basis set for the H, C and O atoms. The individual charge distribution of all the atoms is listed in [Table 4.5]. From the Mulliken charge analysis, it is found that after the adsorption of the ligand onto the metal cluster, there is charge transfer from the ligand to the metal nanocluster. Thus, the metal atom can act as the active center for adsorption.

[**Table 4.5**] [a]: Mulliken charges on individual atoms of the M_6 -L systems (M = Cu, Ag, Au or Pd) and L= Acetone (Act) or Ethanol (Eth)

Cu	1-Act	Cu	ı-Eth	Ag-Act		Ag-Eth	
Atom	Charge	Atom	Charge	Atom	Charge	Atom	Charge
Cu1	0.027	Cu1	0.062	Ag1	-0.099	Ag1	-0.089
Cu2	0.059	Cu2	0.085	Ag2	0.079	Ag2	0.132
Cu3	-0.128	Cu3	-0.071	Ag3	0.087	Ag3	0.110
Cu4	0.040	Cu4	0.029	Ag4	-0.087	Ag4	-0.088
Cu5	-0.085	Cu5	-0.106	Ag5	0.069	Ag5	0.043
Cu6	0.061	Cu6	-0.033	Ag6	-0.081	Ag6	-0.142
C7	0.353	C7	-0.418	C7	0.358	C7	-0.369
08	-0.198	C8	-0.261	08	-0.220	C8	-0.243
C9	-0.642	H9	0.133	C9	-0.429	H9	0.135

H10	0.169	H10	0.159	H10	0.099	H10	0.144
H11	0.167	H11	0.129	H11	0.153	H11	0.133
H12	0.167	H12	0.143	H12	0.168	H12	0.143
C13	-0.449	H13	0.158	C13	-0.593	H13	0.142
H14	0.168	014	-0.263	H14	0.167	O14	-0.279
H15	0.123	H15	0.252	H15	0.171	H15	0.229
H16	0.167	•		H16	0.158		
Αι	ı-Act	Αι	ı-Eth	Pd	l-Act	Pd	l-Eth
Atom	Charge	Atom	Charge	Atom	Charge	Atom	Charge
Au1	-0.224	Au1	-0.215	Pd1	-0.009	Pd1	-0.006
Au2	0.008	Au2	0.059	Pd2	-0.025	Pd2	-0.032
Au3	0.027	Au3	0.081	Pd3	0.010	Pd3	0.003
Au4	-0.208	Au4	-0.196	Pd4	-0.007	Pd4	-0.007
Au5	0.147	Au5	0.088	Pd5	0.008	Pd5	0.001
Аиб	-0.102	Аиб	-0.073	Pd6	-0.101	Pd6	-0.068
C7	0.501	C7	-0.478	C7	0.461	C7	-0.419
08	-0.193	C8	-0.036	08	-0.264	C8	-0.148
C9	-0.515	H9	0.148	C9	-0.552	H9	0.138
H10	0.167	H10	0.217	H10	0.206	H10	0.146
H11	0.159	H11	0.112	H11	0.148	H11	0.172
H12	0.172	H12	0.134	H12	0.165	H12	0.147
C13	-0.671	H13	0.132	C13	-0.535	H13	0.140
H14	0.150	014	-0.254	H14	0.169	014	-0.341
H15	0.438	H15	0.281	H15	0.169	H15	0.273
H16	0.147			H16	0.158		

	Cu-Act	Ag-Act	Au-Act	Pd-Act
Charges on Metal	-0.025	-0.031	-0.353	-0.125
Charges on Ligand	0.025	0.031	0.353	0.125
	Cu-Eth	Ag-Eth	Au-Eth	Pd-Eth
Charges on Metal	-0.033	-0.035	-0.256	-0.109
Charges on Ligand	0.033	0.035	0.256	0.108

[Table 4.5] [b]: Charge distribution on ligand and metal nanoclusters after the ligand adsorption process

4.4.3 Frontier orbital analysis

The visualizations of the frontier orbitals were carried out using the Gaussian 09 suite of programs. We have considered only one position of interaction of the organic compounds with Pd nanocluster as the structure is completely symmetric in nature. Since the metal clusters are all symmetrical, all the corner atoms have the same visualization for the HOMO-LUMO orbitals upon interacting with the ligand, while the rest of the atoms have again similar visualization ([Figure 4.5 through 4.12]. It is evident that the metals have maximum contribution to HOMO. In some cases, like in Au-Act and Au-Eth there is some contribution to the HOMO from the ligand as well. Another interesting observation is that in Cu-Act, the entire LUMO contribution comes from the ligand.



[Figure 4.5][a]

[Figure 4.5][b]

[Figure 4.5] LUMO diagrams of Cu-Act



[Figure 4.5][c]

[Figure 4.5][d]







[Figure 4.6][a]



[Figure 4.6] LUMO diagrams of Cu-Eth



[Figure 4.6][c]

[Figure 4.6][d]

[Figure 4.6] HOMO diagrams of Cu-Eth



[Figure 4.7][a]

[Figure 4.7][b]

[Figure 4.7] LUMO diagrams of Ag-Act



[Figure 4.7][c]



[Figure 4.7][d]

[Figure 4.7] HOMO diagrams of Ag-Act





[Figure 4.8][a]

[Figure 4.8][b]

[Figure 4.8] LUMO diagrams of Ag-Eth



[Figure 4.8][c]



[Figure 4.8][d]

[Figure 4.8] HOMO diagrams of Ag-Eth







[Figure 4.9] HOMO diagrams of Au-Act



[Figure 4.10][a]











[Figure 4.10] HOMO diagrams of Au-Eth



[Figure 4.11] [a] LUMO diagram of Pd-Act



[Figure 4.11] [b] LUMO diagram of Pd-Eth



[Figure 4.12] [a] HOMO diagram of Pd-Act



[Figure 4.12] [b] HOMO diagram of Pd-Eth

Next, we consider the HOMO, LUMO, and HOMO-LUMO gap energies [Table 4.6]. From all the values listed above in [Table 4.6], we see that the band gap (E_g) values decrease as follows: Au-L > Cu-L > Ag-L > Pd-L. Therefore, the chemical hardness decreases in the same order. In other words, the chemical reactivity increases in the reverse order from Au-L through Pd-L. There is a substantial change in HOMO-LUMO gap in the gold clusters upon interaction with the ligands.

[**Table 4.6**]: HOMO, LUMO, HOMO-LUMO gap energies of the metal-ligand systems ($\Delta E_g = E_g$ (metal) - E_g (metal-ligand))

System	HOMO (eV)	LUMO (eV)	$\mathbf{E}_{\mathbf{g}}(\mathbf{eV})$	$\Delta E_g(eV)$
Cu-Act	-4.897	-1.961	2.936	0.309
Cu-Eth	-4.943	-1.885	3.057	0.188
Ag-Act	-5.003	-2.109	2.894	0.104
Ag-Eth	-5.088	-2.190	2.898	0.100
Au-Act	-6.283	-3.009	3.274	-1.276
Au-Eth	-6.376	-3.101	3.275	-1.277
Pd-Act	-4.708	-3.442	1.266	0.023
Pd-Eth	-4.748	-3.478	1.269	0.020

In the following, we also try to analyze whether the electron transfer occurs from the ligand to the metal nanocluster or vice versa. The data are listed in [Table 4.7]. From the Table, one can see that the electron transfer happens from ligand to metal nanocluster for both the ligands, acetone and ethanol for both gold and silver nanoclusters. The electron transfer is easier in both cases for acetone. Comparing the electron transfer of acetone with the two metals, the transfer of electrons is easier with gold than with silver nanoclusters. On the contrary, in the case of copper nanocluster systems, electron transfer occurs from the copper nanocluster to the ligands. Here also, the electrons transfer from the copper nanocluster to acetone molecule is easier than to ethanol molecule.

System	HOMO	LUMO	HOMO-	HOMO-	HOMO-	HOMO-
			LUMO	LUMO	LUMO	LUMO
			(Act→M)	(M→Act)	(Eth→M)	(M→Eth)
Act	-7.053	-0.783				
Eth	-7.636	-0.339				
Cu	-5.499	-2.253	4.800	4.716	5.383	5.160
Ag	-5.458	-2.459	4.594	4.675	5.087	5.119
Au	-7.838	-5.839	1.214	7.055	1.797	7.499
Pd	-5.100	-3.811	3.242	4.317	3.825	4.761

[Table 4.7] HOMO and LUMO energy (eV) values of Act, Eth and M₆.

4.4.4 Electrostatic potential maps

We generated the electrostatic potential maps of the M-L (M=Ag/Au/Cu, L=Act/Eth) systems using Gaussian 09 suite of programs. The basis sets remain the same, B3LYP/6-311++G(d,p) for the H, C and O atoms and B3LYP/LanL2DZ with electron core potential for the heavy atoms. The ESP maps for all the systems M-L (M = Cu, Ag, Au, or Pd, L = Act or Eth) are shown in [Figure 4.13 through 4.20]. From the ESP maps, we can see that there is a strong negative charge associated with the oxygen atoms of the acetone molecule. The hydrogen atoms of the acetone molecule have a strong positive charge. The metal clusters show a greater amount of charge in case of adsorption of acetone as compared to adsorption of ethanol.



[Figure 4.13] ESP maps of Cu-Act system



[Figure 4.14] ESP maps of Cu-Eth system



[Figure 4.15] ESP maps of Ag-Act system



[Figure 4.16] ESP maps of Ag-Eth system



[Figure 4.17] ESP maps of Au-Act system



[Figure 4.18] ESP maps of Au-Eth system



[Figure 4.19] ESP maps of Pd-Act system



[Figure 4.20] ESP maps of Pd-Eth system

Chapter 5

Acetone vs. Ethanol Sensing Performance upon Metal Nanocluster Loading onto ZnO Cluster

5.1 Sensor Performance Improvement by Addition of Metal Nanoparticles

ZnO-based gas sensors have been employed to detect various gases and VOCs like acetone, ethanol, humidity (moisture), O₂, CO₂, CO, H₂, NH₃, H₂S, NO, NO₂, SO₂, CH₄, etc. Since a wide range of gases can interact with chemisorbed oxygen species on to the surface of SMOs, detection of a given or a set of gas(es) in the presence of other interfering gases (i.e., selectivity) is a great challenge, in addition to other sensing parameters like the sensor response, response/recovery speed, operation temperature, etc. A number of approaches are being explored to improve the response and selectivity of the SMOs like ZnO. For examples, doping of metal oxide with metals, employing hybrid binary or ternary phase metal oxides, loading/decorating with noble metals, using filtering layers, modulating operating temperature, and using nanostructured oxides and/or additives are a few common approaches to cite. However, decorating/loading with (noble) metals has been a popular, simple, and effective method to increase the sensor performance of SMOs like ZnO. [97-108]

A sensing matrix (materials) has three key roles in the gas sensing process: (i) receptor function, (ii) transducer function, and (iii) utility factor. [109] The utility factor is associated with the gas accessibility issues due to the diffusion, chemical reaction, etc. of the target gas molecules inside a porous sensing matrix. The receptor function involves the interactions and adsorptions/binding of oxygen molecules and the target gases onto SMOs surface. The transducer function comprises of conversion of these surface chemical interactions (e.g., charge carrier mobility, resistance change) into an electrical signal (sensor response). One can find that metal nanoparticle loading has a great role in the receptor function. The improvement of sensing

performance due to metal loading have been generally explained by the "electronic" and "chemical" mechanisms. [110]

According to the "electronic" mechanism, the noble metal acts as the electron acceptor on the SMO surfaces and enhances the depletion layer thickness compared to the pristine SMO. In the "chemical" mechanism, it is proposed that the noble metal catalytically activate the molecular oxygen dissociation, their adsorption, and reactions on the SMO surface. However, despite many reports, we have limited understanding of the origins of these "electronic and chemical" mechanisms due to lack of molecular level information. It is essential to explore the molecular level origin of these mechanisms. To evaluate the molecular level impact of metal nanoclusters loading onto SMO surface on the sensing behavior, we have performed a systematic DFT study at nanoclusters levels involving ZnO loaded with Cu, Ag, Au, Pd for acetone and ethanol sensing.

5.2 Computational Details

As given in the previous Chapter for the study of zinc oxide nanoclusters, we use the same basis set LanL2DZ for optimizing the metal clusters of Ag_6 , Au_6 and Cu_6 using the electron core potential (ECP) as the noble metals especially require the use of ECP. To mimic the coating of the zinc oxide nanoclusters, we let the optimized metal nanoclusters interact with the zinc oxide nanoclusters and optimize the resulting structure.

5.3 **Results and Discussion**

5.3.1 Loading of zinc oxide with metal nanocluster

The lowest energy optimized structures are obtained using the same basis sets as given in the earlier Chapter. We use electron core potentials (ECP) for all the heavy metal atoms. The resultant optimized structures can be seen in [Figure 5.1]. One can find that the metal nanocluster binds to the zinc oxide nanoparticle via a Zn atom (in the case of Ag, Au) or oxygen atom (in the case of Cu) or both Zn and oxygen atom (in case of Pd). The binding of Cu to oxygen atom in place of Zn could be due to similar electronegativity of Cu and Zn [Table 5.1].

Table 5.1]: Allred Rochow	^v Electronegativity	of the elements
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Element	0	Zn	Cu	Ag	Au	Pd
Allred Rochow Electronegativity	3.50	1.66	1.75	1.42	1.42	1.35



 $[Figure \ 5.1] \ [a]: Optimized structure of \ Cu_6 \ nanocluster \ bound \ (ZnO)_2$



[Figure 5.1] [b]: Optimized structure of Ag_6 nanocluster bound (ZnO)₂



[Figure 5.1] [c]: Optimized structure of Au₆ nanocluster bound (ZnO)₂



[Figure 5.1] [d]: Optimized structure of Pd₆ nanocluster bound (ZnO)₂

5.3.2 Binding energy (E_{ads}) and bond lengths

The binding energies of M_6 -(ZnO)₂ systems are captured in [Figure 5.2]. E_{ads} (Pd-ZnO) > E_{ads} (Cu-ZnO) > E_{ads} (Au-ZnO) > E_{ads} (Ag-ZnO). It shows that the palladium nanocluster binds most strongly to the zinc oxide nanoparticle. This can be attributed to the fact that there are multiple bonds being formed. The bond lengths of Zn-Ag, Zn-Au and O-Cu are 2.737 Å, 2.679 Å and 1.897 Å, respectively. Pd on the other hand binds to both Zn and O. O-Pd bond length is 1.957 Å and Zn-Pd bond length is 2.666 Å. According to studies by Alsalmi and group, the M-Zn bond strength (M = Au, Cu, Ag) followed the order Cu-Zn > Au-Zn > Ag-Zn. This is attributed to the weakening of the M-Zn bond due to atomic size. However, for Ag and Au, the effect of d-orbitals being larger in size overcomes the earlier effect and increases the bonding as we go from Ag to Au. According to our study, since the bond length of Ag-Zn > Au-Zn, it indicates that Au-Zn is a more stable bond than Ag-Zn. [111] The Cu-O bond length calculated here is comparable to the bond length of Cu-O reported by others. [112]



[Figure 5.2]: Comparison of binding energies of metal clusters with zinc oxide
5.3.3 Mulliken Charge distribution

We calculated the Mulliken charges using the same basis sets as we had in the previous case. Using the Mulliken charges, we analyze electron donor and electron acceptor systems. The individual charges of the Cu/ZnO, Ag/ZnO, Au/ZnO and Pd/ZnO systems are listed in [Table 5.2]. Even though it's not very evident, we can understand that there has been some charge transfer in each of the M-ZnO clusters. A clear picture of charge transfer can be found from [Table 5.3]. We can see that there is a charge transfer from zinc oxide nanocluster to the metal nanocluster in case of silver and copper. However, for the gold nanocluster, the charge transfer occurs from zinc oxide to gold nanocluster. According to Perumal and coworkers, the energy level of defect states of ZnO and the Fermi level of Au are very close to each other. [113] The electrons from the defect level of ZnO can transfer very easily to the surface plasmons of Au. This causes a significant increase in electron density.

[**Table 5.2**]: Describing the charges of the individual atoms of the Cu/ZnO, Ag/ZnO, Au/ZnO and Pd/ZnO clusters

/ZnO	Ag	/ZnO	Au	/ZnO	Pd	/ZnO
Charge	Atom	Charge	Atom	Charge	Atom	Charge
0.765	Zn1	0.749	Zn1	0.863	Zn1	0.736
0.746	Zn2	0.821	Zn2	1.234	Zn2	0.789
-0.803	O3	-0.848	O3	-0.814	03	-0.833
-0.795	O4	-0.798	O4	-0.823	O4	-0.678
0.155	Ag5	0.163	Au5	-0.004	Pd5	-0.013
-0.007	Ag6	-0.169	Аиб	0.007	Pd6	-0.087
-0.36	Ag7	0.061	Au7	-0.065	Pd7	-0.020
-0.007	Ag8	-0.023	Au8	-0.178	Pd8	0.068
0.18	Ag9	0.137	Au9	-0.05	Pd9	-0.012
0.125	Ag10	-0.093	Au10	-0.17	Pd10	0.050
	ZnO <i>Charge</i> 0.765 0.746 -0.803 -0.795 0.155 -0.007 -0.36 -0.007 0.18 0.125	ZnO Ag Charge Atom 0.765 Zn1 0.746 Zn2 -0.803 O3 -0.795 O4 0.155 Ag5 -0.007 Ag6 -0.36 Ag7 -0.007 Ag8 0.18 Ag9 0.125 Ag10	ZnOAg/ZnOChargeAtomCharge0.765Zn10.7490.765Zn20.8210.746Zn20.821-0.803O3-0.848-0.795O4-0.7980.155Ag50.163-0.007Ag6-0.169-0.36Ag70.061-0.007Ag8-0.0230.18Ag90.1370.125Ag10-0.093	ZnO Ag/ZnO Au Charge Atom Charge Atom 0.765 Zn1 0.749 Zn1 0.765 Zn2 0.821 Zn2 0.746 Zn2 0.821 Zn2 -0.803 O3 -0.848 O3 -0.795 O4 -0.798 O4 0.155 Ag5 0.163 Au5 -0.007 Ag6 -0.169 Au6 -0.36 Ag7 0.061 Au7 -0.007 Ag8 -0.023 Au8 0.18 Ag9 0.137 Au9 0.125 Ag10 -0.093 Au10	ZnOAg/ZnOAu/ZnO $Charge$ $Atom$ $Charge$ $Atom$ $Charge$ 0.765 $Zn1$ 0.749 $Zn1$ 0.863 0.746 $Zn2$ 0.821 $Zn2$ 1.234 0.803 $O3$ -0.848 $O3$ -0.814 0.795 $O4$ -0.798 $O4$ -0.823 0.155 $Ag5$ 0.163 $Au5$ -0.004 -0.007 $Ag6$ -0.169 $Au6$ 0.007 -0.36 $Ag7$ 0.061 $Au7$ -0.065 0.18 $Ag9$ 0.137 $Au9$ -0.05 0.125 $Ag10$ -0.093 $Au10$ -0.17	ZnOAg/ZnOAu/ZnOPd/ $Charge$ $Atom$ $Charge$ $Atom$ $Charge$ $Atom$ 0.765 $Zn1$ 0.749 $Zn1$ 0.863 $Zn1$ 0.746 $Zn2$ 0.821 $Zn2$ 1.234 $Zn2$ 0.803 $O3$ -0.848 $O3$ -0.814 $O3$ 0.795 $O4$ -0.798 $O4$ -0.823 $O4$ 0.155 $Ag5$ 0.163 $Au5$ -0.004 Pd5 -0.007 $Ag6$ -0.169 $Au6$ 0.007 Pd6 -0.36 $Ag7$ 0.061 $Au7$ -0.065 Pd7 -0.007 $Ag8$ -0.023 $Au8$ -0.178 Pd8 0.18 $Ag9$ 0.137 $Au9$ -0.05 Pd9 0.125 $Ag10$ -0.093 $Au10$ -0.17 Pd10

[Table 5.3]: Values of charge transfer from metal to zinc oxide nanoparticles or vice versa.

System	Cu/ZnO	Ag/ZnO	Au/ZnO	Pd/ZnO
Charge on Metal Nanocluster	0.086	0.076	-0.46	-0.014
Charge on ZnO	-0.087	-0.076	0.46	0.014

5.3.4 Frontier orbital analysis

The frontier orbitals of the Cu/ZnO Ag/ZnO, Au/ZnO, and Pd/ZnO systems have been visualized using the Gaussian 09 suite of programs. The visual representation of frontier HOMO-LUMO's are shown in [Figure 5.3]. From the HOMO-LUMO diagrams, one can see that both the metal nanoclusters and zinc oxide contribute to the resultant orbitals.





[Figure 5.3] [a]: HOMO diagram of Cu/ZnO

[Figure 5.3] [b]: LUMO diagram of Cu/ZnO





[Figure 5.3] [c]: HOMO diagram of Ag/ZnO

[Figure 5.3] [d]: LUMO diagram of Ag/ZnO



[Figure 5.3] [e]: HOMO diagram of Au/ZnO



[Figure 5.3] [g]: HOMO diagram of Pd/ZnO



[Figure 5.3] [f]: LUMO diagram of Au/ZnO



[Figure 5.3] [h]: LUMO diagram of Pd/ZnO

The calculated HOMO-LUMO energy levels and the energy gaps are given in [Table 5.4]. One can find that ZnO has the largest energy gap, E_g . The HOMO energy values of Ag/ZnO and Cu/ZnO systems are very close to each other. The E_g energy values follow the order: $E_g(Au/ZnO) > E_g(Ag/ZnO) > E_g(Pd/ZnO)$. We know that the larger the HOMO-LUMO gap (E_g), the greater is the chemical hardness of the chemical species, the greater is the stability. [114–116] A larger HOMO-LUMO gap implies a low chemical reactivity and high chemical stability. Thus, we can see that the Au/ZnO system is the least chemically reactive and most stable, followed by Cu/ZnO, Ag/ZnO and finally Pd/ZnO.

[**Table 5.4**]: HOMO-LUMO energies, HOMO-LUMO energy gap (E_g) and the change in HOMO-LUMO gap upon interaction of metal cluster with zinc oxide nanoparticles ($\Delta E_g = E_g(ZnO) - E_g(ZnO-M_6)$)

System	HOMO (eV)	LUMO (eV)	Eg (eV)	$\Delta E_{g} (eV)$
ZnO	-6.291	-3.717	2.574	
Cu/ZnO	-5.526	-3.410	2.116	0.431
Ag/ZnO	-5.539	-3.507	2.032	0.542
Au/ZnO	-6.377	-4.165	2.212	0.362
Pd/ZnO	-5.514	-4.233	1.282	1.292

We also use the frontier molecular orbital theory to analyze the electron donor and acceptor species. Relevant calculations are given in [Table 5.5]. We know from frontier molecular orbital theory. [117, 118] that the Ag cluster and the Cu cluster, both act as electron donors, while the ZnO molecule acts as the electron acceptor. Au on the other hand acts as the electron acceptor while ZnO is the electron donor in this case. It is consistent with the Mulliken charge analysis, where the charge transfer occurs from Cu, Pd and Ag to ZnO whereas it occurs from ZnO to Au.

[**Table 5.5**]: HOMO-LUMO energy gaps of metal clusters and zinc oxide and the energy gaps between ZnO and the ligand (Act or Eth)

	Cu ₆	Ag ₆	Au ₆	Pd ₆	ZnO
HOMO (eV)	-5.499	-5.458	-7.838	-5.100	-6.291
LUMO (eV)	-2.253	-2.459	-5.839	-3.811	-3.717
HOMO-LUMO (eV)					1.782
(Cu→ZnO)					
HOMO-LUMO (eV)					4.038
(ZnO→Cu)					
HOMO-LUMO (eV)					1.741
(Ag→ZnO)					
HOMO-LUMO (eV)					3.832
(ZnO→Ag)					
HOMO-LUMO (eV)					4.121
(Au→ZnO)					
HOMO-LUMO					0.452
(ZnO→Au)					
HOMO-LUMO (eV)					1.383
(Pd→ZnO)					
HOMO-LUMO (eV)					2.480
(ZnO→Pd)					

5.3.5 Electrostatic potential maps

We can visualize all the ESP maps for the systems: Cu/ZnO, Ag/ZnO, Au/ZnO and Pd/ZnO. A closer inspection of the diagrams shows that the zinc atoms on all the maps have a positive charge, whilst the oxygen atoms have a negative charge. The cluster metal atoms have slight negative charges as well, but less than that of oxygen.



[Figure 5.4] [a]: ESP map of zinc oxide coated with copper nanocluster



[Figure 5.4] [b]: ESP map of zinc oxide coated with silver nanocluster



[Figure 5.4] [c]: ESP map of zinc oxide coated with gold nanocluster



[Figure 5.4] [d]: ESP map of zinc oxide coated with palladium nanocluster

5.3.6 Performance of ZnO coated with metals as an acetone sensor

Next, we try to explore how these metal cluster loaded ZnO materials would perform in the acetone vs. ethanol sensing. The acetone and ethanol molecules were allowed to interact with

the M/ZnO (M = Cu, Ag, Au, Pd) nanocluster and they are optimized to understand the resultant interactions. We assume that the gas molecule interacts with the metal nanocluster, since the "electronic" mechanism of the SMO surface-loaded metals work. The optimized structures are shown in [Figure 5.5 through 5.12].



[Figure 5.5] Optimized structures of acetone interacting with Cu₆-(ZnO)₂



[Figure 5.6] Optimized structure of ethanol interacting with Cu₆-(ZnO)₂



[Figure 5.7] Optimized structures of acetone interacting with Ag₆-(ZnO)₂



[Figure 5.8] Optimized structure of ethanol interacting with Ag₆-(ZnO)₂



[Figure 5.9] Optimized structure of acetone interacting with Au₆-(ZnO)₂



[Figure 5.10] Optimized structures of ethanol interacting with Au₆-(ZnO)₂



 $[Figure \ 5.11] \ Optimized \ structure \ of \ acetone \ interacting \ with \ Pd_6\text{-}(ZnO)_2$



[Figure 5.12] Optimized structures of ethanol interacting with Pd_{6} -(ZnO)₂

[Figure 5.5—5.12]: Optimized structures of M-ZnO-L structures upon optimizing with LanL2DZ basis set with ECP for heavy atoms and 6-311++G(d,p) for H, C, O atoms. The ligand is shown to attach in three different positions only because corner atoms have proven to have the strongest interactions. From all the optimized structures, one can see that the geometry of the nanocluster sensor material changes substantially. Upon analyzing the Cu/ZnO-acetone structures, we can see those five atoms from the copper cluster breaking and forming a separate cluster and one atom of copper gets attached to the zinc oxide molecule. We can see that copper cluster breaks away from the zinc oxide and the acetone molecule binds to the zinc atom of zinc oxide. Next, there is a formation of Zn-Cu bond and the formation of a Cu-Cu bond. We see that a pseudo-hexagonal geometry has formed by the copper nanocluster. However, there is no bond of copper

with the zinc atom. The average C-O bond length of acetone is 1.235 Å. The average Cu-O bond length is measured as 2.018 Å.

The silver cluster gets separated from the zinc cluster and binds at the zinc atom. The geometry of the silver nanocluster takes up a pseudo-hexagonal shape. One bond of the silver nanocluster breaks. The average C-O bond length of acetone for all the above-described systems is 1.231 Å. This is much greater than the original C-O bond length in acetone. [119] The average Ag-O distance for these interactions is 2.428 Å. This is less than the Ag-O distance we had observed, when acetone had adsorbed onto only the silver nanocluster.

Considering the Ag/ZnO-ethanol interactions, we see that there is some breaking and making of bonds. The silver nanocluster breaks into two parts, five atoms form a cluster and the remaining silver atom attached to the zinc oxide molecule and the ethanol molecule attaches to the zinc oxide molecule as well. Next, the silver nanocluster breaks off from the zinc oxide cluster and acetone molecule binds to zinc oxide. Unlike the interaction with acetone, we see a major and visible change in the geometry of the silver nanocluster as well. We can see that the silver nanocluster forms a pseudo-hexagonal shape that is similar to the geometry of silver in Ag/ZnO-Act. One can see that the sensor material remains largely unchanged geometrically, except the breaking of one bond. The average C-O bond length for ethanol becomes 1.449 Å. The average Ag-O distance is measured as 2.463 Å. This is also less than the Ag-O distance observed when acetone had adsorbed only onto the silver nanocluster.

Considering the geometry of the Au/ZnO-acetone, the geometry of the sensor material stays the same. The acetone assumes a slightly different form, a double bond is formed between C-C. Oxygen and zinc form a partial double bond. The gold nanocluster detaches from the zinc oxide nanoparticle. The gold nanocluster assumes a pseudo-hexagonal shape. The sensor material geometry doesn't change from that of the original cluster geometry. The average Au-O_L bond distance is measured as 2.494 Å, which is a decrease from 2.632 Å and the average C-O distance is 1.228 Å.

Analyzing the geometry of the Au/ZnO-ethanol systems, we find that the geometry of the sensor system remains the same as the original sensor system. The zinc oxide and gold nanocluster

detach and the ethanol binds to the zinc oxide cluster. An extra Au-Au bond is formed. The rest of the sensor remains the same. The C-O bond length increases from 1.43 Å to 1.447 Å and the average Au-O_L distance decreases from 2.596 Å to 2.511 Å.

5.3.6.1 Adsorption energy

Next, we compare the average ligand binding (adsorption) energies (E_{ads}) of the metal nanocluster loaded systems. The binding energies are calculated using the following definition:

$$E_{ads} = E_{M/ZnO-L} - (E_L + E_{M/ZnO})$$

where M = Cu, Ag, Au or Pd; and L = acetone or ethanol. The average binding energies of these systems are given in [Table 5.6]. We can find that for a given metal system, the binding energy for acetone is greater than ethanol. This difference between binding energies between acetone and ethanol is most prominent in the ZnO-Au system. The binding energies of acetone decreases in the order: Cu/ZnO > Ag/ZnO > Au/ZnO > Pd/ZnO

[Table 5.6]: Binding energy (kcal/mol) of the ligands with M/ZnO (M = Cu, Ag, Au or Pd).

System	Binding energy
Cu/ZnO-Act	-24.048
Cu/ZnO-Eth	-21.897
Ag/ZnO-Act	-18.762
Ag/ZnO-Eth	-16.520
Au/ZnO-Act	-18.264
Au/ZnO-Eth	-12.252
Pd/ZnO-Act	-13.330
Pd/ZnO-Eth	-13.282

5.3.6.2 Mulliken charges

We have used the same Mulliken charge calculation procedure like the earlier basis set calculations. The charges of all individual atoms are listed below in [Table 5.7 and 5.8]. The charges on each individual cluster for all the systems are calculated and listed in [Table 5.9]. As we have seen earlier that the ligand transferred charge to zinc oxide, here [Table 5.9] also, the ligands transfer charge to the sensor cluster. [120] Charge transfer is responsible for optimum adsorption strength. The lesser the charge transfer, the weaker the adsorption strength. [121] Comparing the charge transfer values, we find the following orders:

Cu/ZnO-Act > Cu/ZnO-Eth Ag/ZnO-Act > Ag/ZnO-Eth Au/ZnO-Act > Au/ZnO-Eth Pd/ZnO-Act < Pd/ZnO-Eth

It can be seen that acetone binding leads to greater charge transfer in all the systems, except Pd/ZnO systems. A comparison of the charge transfer values upon acetone binding to different metal nanocluster-loaded sensor systems gives the following order:

$$Au/ZnO-Act > Pd/ZnO-Act > Ag/ZnO-Act > Cu/ZnO-Act$$

Thus, based on the charge transfer values, one expects the same decreasing order of acetone sensor response. Moreover, acetone response is expected to be more than ethanol.

Atoms	Cu/ZnO-Act	Atoms	Ag/ZnO-Act	Atoms	Au/ZnO-Act	Atoms	Pd/ZnO-Act
Zn1	0.725	Zn1	0.738	Zn1	0.852	Zn1	0.738
Zn2	0.768	Zn2	0.805	Zn2	1.171	Zn2	0.765
O3	-0.841	O3	-0.815	O3	-0.833	O3	-0.819
O4	-0.752	O4	-0.844	O4	-0.779	O4	-0.681
Cu5	0.132	Ag5	0.149	Au5	-0.027	Pd5	-0.045
Cu6	0.010	Ag6	-0.062	Au6	-0.051	Pd6	-0.124
Cu7	-0.220	Ag7	0.026	Au7	-0.01	Pd7	-0.053
Cu8	-0.031	Ag8	-0.088	Au8	-0.229	Pd8	0.039
Cu9	0.077	Ag9	0.073	Au9	-0.163	Pd9	-0.031
Cu10	0.055	Ag10	-0.092	Au10	-0.192	Pd10	0.027
C11	0.454	C11	0.488	C11	0.571	C11	0.416
012	-0.26	O12	-0.268	O12	-0.254	O12	-0.212
C13	-0.587	C13	-0.599	C13	-0.576	C13	-0.572
H14	0.134	H14	0.193	H14	0.179	H14	0.197
H15	0.165	H15	0.226	H15	0.145	H15	0.165
H16	0.185	H16	0.159	H16	0.249	H16	0.166
C17	-0.587	C17	-0.573	C17	-0.612	C17	-0.500
H18	0.157	H18	0.178	H18	0.149	H18	0.177
H19	0.257	H19	0.143	H19	0.251	H19	0.186
H20	0.161	H20	0.164	H20	0.159	H20	0.161

[**Table 5.7**]: Average charges of each atom of Act-M/ZnO (M = Cu, Ag, Au, Pd) calculated using Mulliken charge analysis

[**Table 5.8**]: Average charges of individual atoms of all the Eth-M/ZnO (M = Cu, Ag, Au, Pd), calculated using Mulliken charge analysis

Atoms	Cu/ZnO-Eth	Atoms	Ag/ZnO-Eth	Atoms	Au/ZnO-Eth	Atoms	Pd/ZnO-Eth
Zn1	0.738	Zn1	0.724	Zn1	0.774	Zn1	0.716
Zn2	0.805	Zn2	0.854	Zn2	1.178	Zn2	0.772
O3	-0.834	O3	-0.844	O3	-0.793	O3	-0.816
O4	-0.759	O4	-0.806	O4	-0.778	O4	-0.680
Cu5	0.096	Ag5	0.139	Au5	-0.019	Pd5	-0.049
Cu6	0.063	Ag6	-0.046	Au6	-0.115	Pd6	-0.124
Cu7	-0.141	Ag7	0.031	Au7	-0.083	Pd7	-0.041
Cu8	-0.029	Ag8	-0.142	Au8	-0.147	Pd8	0.029
Cu9	0.034	Ag9	0.093	Au9	-0.074	Pd9	-0.022
Cu10	-0.046	Ag10	-0.093	Au10	-0.178	Pd10	0.025
C11	-0.439	C11	-0.420	C11	-0.464	C11	-0.430
C12	-0.242	C12	-0.248	C12	-0.073	C12	-0.122
H13	0.139	H13	0.139	H13	0.149	H13	0.145
H14	0.194	H14	0.205	H14	0.127	H14	0.160
H15	0.177	H15	0.138	H15	0.172	H15	0.166
H16	0.155	H16	0.155	H16	0.153	H16	0.141
H17	0.142	H17	0.142	H17	0.165	H17	0.145
O18	-0.314	O18	-0.376	O18	-0.272	O18	-0.313
H19	0.262	H19	0.355	H19	0.278	H19	0.299

Systems	ZnO	Μ	M/ZnO	L
Cu/ZnO-Act	-0.101	0.022	-0.078	0.079
Cu/ZnO-Eth	-0.051	-0.023	-0.074	0.075
Ag/ZnO-Act	-0.116	0.005	-0.111	0.111
Ag/ZnO-Eth	-0.072	-0.019	-0.091	0.090
Au/ZnO-Act	0.409	-0.672	-0.262	0.262
Au/ZnO-Eth	0.381	-0.615	-0.234	0.234
Pd/ZnO-Act	0.002	-0.187	-0.185	0.185
Pd/ZnO-Eth	-0.008	-0.182	-0.190	0.190

[Table 5.9]: Average charges of different clusters where L=Ligand and M = Cu, Ag, Au, Pd

5.3.6.3 Frontier Orbital Analysis

We have visualized the HOMO, LUMO of these systems and have obtained the energy values of the same using the Gaussian suite of programs. The frontier HOMO-LUMO diagrams of the studied systems are shown in [Figure 5.13 - 5.24]. It is evident that the metal atoms have the greatest contribution to the HOMO of these systems. There is some contribution from the zinc oxide system as well. On the other hand, the ligand molecules contribution was comparatively smaller.



[Figure 5.13] LUMO of Cu/ZnO-Act



[Figure 5.14] HOMO of Cu/ZnO-Act systems



[Figure 5.15] LUMO of Cu/ZnO-Eth systems



[Figure 5.16] HOMO of Cu/ZnO-Eth systems









[Figure 5.18] HOMO of Ag/ZnO-Act



[Figure 5.19] LUMO of Ag/ZnO-Eth systems



[Figure 5.20] HOMO of Ag/ZnO-Eth systems



[Figure 5.21] LUMO of Au/ZnO-Act



[Figure 5.22] HOMO of Au/ZnO-Act systems





[Figure 5.23] LUMO of Au/ZnO-Eth systems



[Figure 5.24] HOMO of Au/ZnO-Eth systems



[Figure 5.25] LUMO of Pd/ZnO-Act systems



[Figure 5.26] HOMO of Pd/ZnO-Act systems



[Figure 5.27] LUMO of Pd/ZnO-Eth systems



[Figure 5.28] HOMO of Pd/ZnO-Eth systems

As explained previously, there are three points of interaction considered with each of the metal loaded ZnO cluster as the corner atoms have been observed to have the best interactions with the ligand.

The average HOMO, LUMO energy levels of all the systems are listed in [Table 5.10]. Interestingly, it can be found that the HOMO and LUMO energy levels of the L-M/ZnO systems are comparable. Therefore, the systems have similar responses in terms of their reactivity.

[**Table 5.10**]: Calculated HOMO, LUMO and HOMO-LUMO gap energies (eV) for various systems. $E_g = E(HOMO) - E(LUMO)$; $\Delta E_g = E_g(M/ZnO) - E_g(L-M/ZnO)$ (where M = Cu, Ag, Au, Pd); and L = Act or Eth)

System	HOMO (eV)	LUMO (eV)	Eg (eV)	$\Delta E_{g}(eV)$
Cu/ZnO-Act	-5.002	-2.784	2.218	-0.102
Cu/ZnO-Eth	-5.051	-2.813	2.238	-0.122
Ag/ZnO-Act	-5.115	-2.906	2.209	-0.177
Ag/ZnO-Eth	-5.095	-2.980	2.115	-0.083
Au/ZnO-Act	-5.923	-3.639	2.284	-0.072
Au/ZnO-Eth	-6.038	-3.761	2.277	-0.065
Pd/ZnO-Act	-5.220	-3.824	1.396	-0.114
Pd/ZnO-Eth	-5.306	-3.889	1.417	-0.135

Next, we shall the electron transfer effects using frontier orbital molecular theory. [122, 123] The analysis is given in [Table 5.11]. From the data listed, we can say that the ligand acts as the electron donor and the sensor cluster acts as the electron acceptor. [124] It is in agreement with the data obtained by the Mulliken charge analysis. Comparing the ease of transfer of electrons in the frontier orbitals, we obtain:

Cu/ZnO-Act > Cu/ZnO-Eth Ag/ZnO-Act > Ag/ZnO-Eth Au/ZnO-Act > Au/ZnO-Eth Pd/ZnO-Act < Pd/ZnO-Eth Thus, based on the charge transfer values, it can be said that all the sensor materials, except palladium, display better sensitivity towards acetone compared to ethanol.

[**Table 5.11**] HOMO and LUMO energy (eV) levels of Act, Eth, and M/ZnO systems and the electron transfer energies

	Act	Eth	Cu/ZnO	Ag/ZnO	Au/ZnO	Pd/ZnO
HOMO (eV)	-7.053	-7.636	-5.526	-5.539	-6.377	
LUMO (eV)	-0.783	-0.339	-3.410	-3.507	-4.165	
HOMO-LUMO (eV)			3.643			
(Act→Cu/ZnO)						
HOMO-LUMO (eV)			4.743			
(Cu/ZnO→Act)						
HOMO-LUMO (eV)			4.226			
(Eth→Cu/ZnO)						
HOMO-LUMO (eV)			5.187			
(Cu/ZnO→Eth)						
HOMO-LUMO (eV)				3.546		
(Act→Ag/ZnO)						
HOMO-LUMO				4.801		
(Ag/ZnO→Act)						
HOMO-LUMO (eV)				4.129		
(Eth→Ag/ZnO)						
HOMO-LUMO				5.200		
(Ag/ZnO→Eth)						
HOMO-LUMO (eV)					2.888	
(Act→Au/ZnO)						
HOMO-LUMO (eV)					5.594	
$(Au/ZnO\rightarrow Act)$						

HOMO-LUMO (eV)		3.471	
(Eth→Au/ZnO)			
HOMO-LUMO (eV)		6.038	
(Au/ZnO→Eth)	 	 	
HOMO-LUMO (eV)			2.850
(Act→Pd/ZnO)			
HOMO-LUMO (eV)			4.848
(Pd/ZnO→Act)			2 4 2 2
HOMO-LUMO (eV)			3.433
(Eth→Pd/ZnO)	 	 	
HOMO-LUMO (eV)			5.292
(Pd/ZnO→Eth)			

5.3.6.4 Electrostatic potential (ESP) maps

The ESP maps of all the L-M/ZnO (M = Cu, Ag, Au or Pd; L = Act or Eth) systems are generated using Gaussian 09 and are shown in [Figure 5.29 – 5.36]. One can see a general trend where the oxygen atoms of zinc oxide show very prominent negative charge. When this oxygen interacts with hydrogen from the ligand, the negative charge gets dispersed and indicates the possibility of a hydrogen bonding. [125, 126] It causes a stronger ligand-sensor interaction and strengthens the adsorption. This stabilization is observed for both ligands, acetone and ethanol. The metal clusters do not show significant charge on them after the ligand adsorption. The hydrogen atoms show some positive charge, and the hydroxyl hydrogen shows higher positive charge density.



[Figure 5.29] ESP maps of Cu-ZnO/Act systems



[Figure 5.30] ESP maps of Cu-ZnO/Eth systems



[Figure 5.31] ESP maps of Ag-ZnO/Act



[Figure 5.32] ESP maps of Ag-ZnO/Eth



[Figure 5.33] ESP maps of Au-ZnO/Act



[Figure 5.34] ESP maps of Au-ZnO/Eth



[Figure 5.35] ESP maps of Pd/ZnO-Act systems



[Figure 5.36] ESP maps of Pd/ZnO-Eth systems

5.3.6.5 Assessment of sensor performance of metal nanocluster-loaded zinc oxide

In an earlier Chapter, we have discussed the criteria of the efficiency of a sensor. Briefly, we need to consider the following two points:

1. The energy of adsorption should be large enough to prevent the molecule from getting desorbed immediately. [127, 128]

We find that:

 $E_{ads} (Cu/ZnO-Act) > E_{ads} (Cu/ZnO-Eth)$ $E_{ads} (Ag/ZnO-Act) > E_{ads} (Ag/ZnO-Eth)$ $E_{ads} (Au/ZnO-Act) > E_{ads} (Au/ZnO-Eth)$ $E_{ads} (Pd/ZnO-Act) > E_{ads} (Pd/ZnO-Eth)$

It shows that the selectivity of the sensor materials towards acetone is higher than ethanol.

2. The adsorption of gases onto the sensor material should cause significant changes in the conductivity of the sensor material. This property is determined by the E_g and the charge transfer values of the nanocluster-loaded system. The conductivity can be estimated using the formula: [129, 130]

 $\sigma \alpha \exp(-E_g/2KT)$, where the terms bear their usual meaning as given in the earlier Chapter.

DFT the calculated data gives us the following relation with respect to Eg:

 $\Delta E_{g} (Cu/ZnO-Act) < \Delta E_{g} (Cu/ZnO-Eth) \Delta E_{g} (Ag/ZnO-Act) > \Delta E_{g} (Ag/ZnO-Eth), \Delta E_{g} (Au/ZnO-Act) > \Delta E_{g} (Au/ZnO-Eth) \Delta E_{g} (Pd/ZnO-Act) < \Delta E_{g} (Pd/ZnO-Eth)$

Therefore, we obtain the following conductivity relationship:

 $\sigma (Cu/ZnO-Act) < \sigma (Cu/ZnO-Eth)$ $\sigma (Ag/ZnO-Act) > \sigma (Ag/ZnO-Eth)$ $\sigma (Au/ZnO-Act) > \sigma (Au/ZnO-Eth)$ $\sigma (Pd/ZnO-Act) < \sigma (Pd/ZnO-Eth)$

We can see that although binding energy favors acetone over ethanol for Cu/ZnO and Pd/ZnO, but conductivity does not follow it.

The other important sensor performance parameter is the 'recovery time'. Recovery time is the time required to reach the baseline value of the sensor output signal (experimentally 90% of the max. signal) after the removal of the target gas (here, acetone or ethanol). [131-133] In other words, it is the time taken for the gas desorption process. Recovery time (τ) can be estimated form the following expression: [134-136]

$$\tau = \upsilon_0^{-1}(\exp(-E_{ads}/kT)).$$

Here, v_0 is the attempt frequency, *k* is the Boltzmann constant and *T* is the absolute temperature. It is essential to have a modest adsorption energy and not extremely large, so that desorption can occur with relative ease. [137, 138] Experimentally, the sensor can be recovered by exposing it to UV light. [139] Taking the vacuum UV light ($v \sim 3 \times 10^{14} \text{ s}^{-1}$) for the recovery of acetone from the surface of adsorbents, we see that pristine sensor material, (ZnO)₂, has an extremely high recovery time. Since these sensors find practical applications in room temperatures, we consider room temperature for calculating the recovery time. We have tabulated [Table 5.12] the calculated approximate recovery times of the three model sensor materials systems for acetone sensing: ZnO-Act, Ag/ZnO-Act and Au/ZnO-Act.

[**Table 5.12**]: Calculated recovery times (seconds) of ZnO-Act, Ag/ZnO-Act, and Au/ZnO-Act systems

System	Recovery time (s)
ZnO-Act	5.434×10 ⁷
Ag/ZnO-Act	0.191
Au/ZnO-Act	2.449×10 ⁻⁵

We can find that pristine zinc oxide has an extremely large recovery time compared to the metal nanocluster systems. Therefore, it can be concluded that Ag, Au metal nanocluster loading onto ZnO improves acetone sensor response, selectivity, and the recovery of the sensor materials compared to ethanol. Now considering the aspect of detection limit, even though we cannot come to a very definite conclusion, about the detection limit factor, we can guess that with higher change in conductance, the detection limit performance also improves.

Chapter 6

General Conclusions

Semiconducting metal oxide (SMO)-based gas sensors offer various favorable features stability, low cost, ease of fabrications and simple sensor architecture, etc. To improve sensor performance like the sensor response, speed of recovery, target gas selectivity, and low operation temperature, surface additives like metal nanoparticles are loaded onto the surface of SMOs. Often trial-and-error approaches are employed to improve the SMO-based sensor performance due to the lack of molecular-level knowledge of such systems. Computational studies can play significant roles in providing information regarding the electronic and chemical properties of the systems. The thesis work involves a DFT study to explore the electronic and chemical properties of the SMO, pristine ZnO cluster, and Cu, Ag, Au, or Pd nanocluster loaded ZnO systems and the effects of acetone and ethanol binding to these properties to develop a molecular-level understanding of their sensing behavior. Acetone and ethanol are highly volatile and flammable organic solvents, and they are also biomarkers of several health conditions. Therefore, detections of VOCs like acetone and ethanol are of paramount importance. However, acetone and ethanol are both reducing gases and are structurally and chemically similar. Selective detection of such gases is a challenging task.

The present study aims to understand how different metal loading affects the sensing behavior towards acetone and ethanol. Towards this end, we have studied the binding of acetone and ethanol to pristine $(ZnO)_2$ cluster, which explains how ZnO shows a better sensor response to acetone than ethanol. Next, we have explored the metal nanocluster loading onto ZnO. Since the actual working motifs in the nanostructured sensor materials could be a small cluster of few atoms, we have taken M₆ (where M = Cu, Ag, Au, and Pd) nanocluster as a model for the metal nanoparticle. Finally, we have investigated the acetone vs. ethanol sensing performance of the metal nanocluster-loaded ZnO systems. We have calculated various parameters for each system like the binding energy, HOMO-LUMO energy and bandgap, Mulliken charge distributions, bond

distance, etc. The study shows that the electronic structure effects of M_6/ZnO nanoclusters can be used to understand the molecular level mechanism of sensor activation by metal nanoclusters and explain their acetone vs. ethanol sensing performance. A better understanding of the roles of various components of the sensor materials will help in the better selection of sensor materials and inspire the development of high-performance, low-cost, and portable and practical gas sensors.

Also from our studies, one can see that pristine ZnO shows a decent sensing performance in regard to acetone and ethanol. However, ZnO does not impart desired selectivity in their detection. However, loading of metal nanoclusters onto ZnO drastically improves the selectivity. Also, there is a substantial improvement in key parameters like the recovery time. The recovery time decreases significantly upon metal nanoclusters loading. The conductivity also improves. However, the sensing parameters depend on the nature of the metals loaded. For example, the loading of metals like Pd and Cu improves a few sensing parameters, but fails to improve parameters like the conductivity. It has been observed that loading ZnO cluster with noble metal nanoclusters like Ag and Au improve the selectivity of acetone gas sensing over ethanol.
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