



**SYNTHESIS AND GROWTH DYNAMICS STUDY OF SILVER
NANOPARTICLES**

A thesis presented by

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Certification

I hereby certify that this thesis is a record of original research carried out under my supervision by Mr. Phumlane Selby Mdluli (19990010) of the Chemistry Department, University Of Zululand, South Africa.

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Abstract

The concept of shape-controlled synthesis of metal nanoparticles is investigated by considering the growth mechanism of metal nanoparticles. This thesis is divided into four chapters, chapter one presents a general introduction about various physiochemical aspects of nanomaterials. The different characteristic properties of nanomaterials, their chemically synthesized protocols, characterization techniques, and their applications are discussed in brief. Based on these reviews, the context scope and objective of the present work are outlined.

Chapter two deals with the theory of kinetically growth of nanoparticles. The basic optical properties of metal nanoparticles as well as the structural evolution of nanoparticles are also mentioned in this chapter

In Chapter three the synthesis of silver nanoparticles with varying morphologies using different synthetic routes are described in detail. Silver nanowires were synthesized by an aqueous route using dimethyl formamide (DMF) as the reducing agent in the presence of poly (*N*-vinylpyrrolidone) (PVP) without the addition of seeds. The products were characterized by UV-visible spectroscopy and transmission electron microscopy (TEM). This work was followed by a profound dig-out, to try and comprehend the mechanism for reduction and the kinetics of the reduction of silver nitrate to silver nanoparticles. It was established that in the alkaline medium the reduction of AgNO_3 is enhanced, which resulted to the formation of rod-like silver nanoparticles which were confirmed by TEM and UV-visible spectroscopy.

Silver nanodendrites, with an elongated central backbone and distinguished branches were synthesized by the reduction of silver nitrate with formamide using polyvinyl pyrrolidone (PVP) as the surfactant. The drastic evolution of the dendritic nanostructures was due to the variation of the concentration of the reactants. At low PVP concentration isotropic silver nanoparticles are visible in the transmission electron microscopy (TEM) images. The morphological evolution is confirmed by the optical measurements. The growth mechanism for the nanodendrites is discussed in some detail.

The use of single molecular precursors is a common route to synthesize nanostructured materials. There have been relatively few reports for the use of sophisticated precursors to synthesize metal nanoparticles at high temperatures. The N-(Diisopropylthiophosphoryl) thiourea complexes of silver were synthesised using a previously reported literature method. The complexes were then used as single molecule precursors for the synthesis of hexadecylamine (HDA) and tri-octylphosphine oxide (TOPO) capped silver nanoparticles. The absorption spectra of the HDA and TOPO-capped silver nanoparticles exhibit surface plasmon resonance (SPR) absorption in 400–420 nm regions.

In chapter four, the morphological evolution of silver nanoparticles prompted the development of a Density Function Theory (DFT) model to understand the adsorption of Pyrrolidinone on the surface of silver and gold nanoparticles. The interaction between PVP and the metal atoms on the surface of silver and gold nanoparticles, was studied using Surface Enhanced Raman Spectroscopy (SERS) and modeled using

Density Function Theory (DFT). The SERS analysis was carried out on pyrrolidinone and N-methyl pyrrolidinone in silver and gold colloids, whereas the assignments of bands in the pyrrolidinone molecules were performed by density function theory (DFT) quantum chemical calculations.

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List of Abbreviations

AAS	Atomic Absorption Spectroscopy
BOA	Born-Oppenheimer Approximation
CDBA	Cetyldimethylbenzylammonium
CMC	Critical Micelle Concentration
CVD	Chemical Vapour Deposition
∇^2	Laplacian Operator
DDA	Discrete Dipole Approximation
DFT	Density Functional Theory
DMF	Dimethyl formamide
DNA	Deoxyribonucleic acid
E_b	Binding Energy
EG	Ethylene Glycol
EHT	Extended Huckel Theory
E_k	Kinetic Energy
FIB	Focus Ion Beam
FTIR	Fourier Transform Infrared
GTO	Gaussian-Type Orbital
h	Plank constant
$\hat{H}$	Hamiltonian Operator
HDA	Hexadecylamine
HF	Hartree Fock
HT	Huckel Theory
KE	Kinetic Energy

LCAO-MO	Linear Combination of Atomic Orbital-Molecular Orbital
Me ₂ NCOOH	Carbamic Acid
MINDO	Modified Intermediate Neglect of Differential Overlap
MPPT	Møller-Plesset Perturbation Theory
MP	Second order Møller-Plesset model
MP4	Fourth order Møller-Plesset model
MTP	Multiple twinned nanoparticles
MW	Molecular Weight
NDO	Neglect of Differential Overlap
PPh ₃	Triphenylphosphine
PVP	Poly(<i>N</i> -vinylpyrrolidone)
RHF	Restricted Hartree Fock
SAD	Selected Area Diffraction
SCFT	Self Consistent Field Theory
SEM	Scanning Electron Microscopy
SERS	Surface Enhance Raman Spectroscopy
SPR	Surface Plasmon Resonance
STO	Slater-Type Orbital
TEM	Transmission Electron Microscopy
TEOS	Tetraethylorthosilicate
TOP	Tri-octylphosphine
TOPO	Tri-octylphosphine Oxide
UHF	Unrestricted Hartree Fock
UV-Vis	Ultraviolet Visible

V	Potential Energy
XPS	X-ray Photoelectron Spectroscopy
XRD	X-ray Diffraction
ψ	Wavefunction Describing Motion Of Electrons
ν_{max}	Frequency Of Maximum Absorption

CHAPTER ONE : GENERAL INTRODUCTION

1.1 Background

Over the last few years, the scientific and engineering communities have been witnessing extraordinary progress in the field of nanoscience and nanotechnology. Nanotechnology deals with small structures and materials of dimensions in the range of a few nanometers to less than 100 nanometers. One nanometer (10^{-9} m) is roughly the distance of five silicon or ten hydrogen atoms aligned in a line. For comparison, the hydrogen atom is ~ 0.1 nanometers, a virus is ~ 100 nanometers, a red blood corpuscle is approximately 7,000 nanometers in diameter and an average human hair is 10,000 nanometers wide.

Nanoscience is the study of the phenomena exhibited by materials at the nanoscale. In chemistry, this size-range is associated with colloids, micelles, polymer molecules and very large molecules or aggregate molecules. In physics and electrical engineering, nanoscience is most often associated with quantum behavior, and the behavior of electrons in nanoscale structures. Biology and biochemistry have also been closely associated with nanoscience since cellular structures, such as DNA, RNA and sub cellular organelles can be considered as nanostructures [1].

Nanotechnology is the application of science to control matter at the molecular level. At this level, the properties of matter are significantly different to that of bulk materials. It is also used as the term for the design, characterization, production and application of

structures, devices and systems by controlling the shape and size at the nanometer size regime [2]. In other words, nanoscience and nanotechnology are fields that focus on: (i) the development of synthetic methods and surface analytical tools for building structures and materials, (ii) the changes in chemical and physical properties due to miniaturization, and (iii) the use of such properties in the development of novel and functional materials and devices [3]. Nanoscience offers the exciting opportunity to study a state of matter that is intermediate between bulk and isolated atoms or molecules, as well as the effect of spatial confinement on electron behavior. It also provides an opportunity to explore the problems related to surfaces or interfaces because of their interfacial nature. It has been well known that living cells are the best examples of machines that operate at the nano level by performing a number of functions ranging from generation of energy to extraction of targeted materials at very high efficiency. The ribosome, histones and chromatin, the Golgi apparatus, the interior structure of the mitochondrion, the photosynthetic reaction center, and the ATPases that power the cell are all examples of nanostructures that work quite efficiently [4]. The ancient Indian medicinal system, *Ayurveda*, has been using gold in different formulations for curing acute diseases such as rheumatoid arthritis [5]. Thus, the fusion of ancient wisdom and present understanding of nanoscience imparts more light on the future development of medical sciences. The research field of nanotechnology is as diverse as physics, chemistry, material science, microbiology, biochemistry and also molecular biology. The nanotechnology interface between biotechnology and biomedical engineering is developing through the use of nanoscale structures in diagnosis, gene sequencing, and drug delivery. Nanotechnology holds promise for enabling us to learn

more about the detailed operation of individual cells and neurons, which could help us to re-engineer living systems.

The first so-called scientific study of nanoparticles took place in 1831, when Michael Faraday investigated the ruby-red coloured colloids of gold and made public the finding that the colour was due to the small size of the metal particles. Gold and silver have found their way into glasses for over 2000 years, usually as nanoparticles. They have most frequently been employed as colorants, particularly for church windows. Until 1959, nobody had thought of using atoms and molecules for fabricating devices. It was first proposed by Nobel Laureate Physicist Richard Feynman at a lecture entitled “There is plenty of room at the bottom”. It was much later in 1974 that Norio Taniguchi, a researcher at the University of Tokyo, Japan used the term “nanotechnology” while engineering materials precisely at the nanometer level. The primary driving force for miniaturization at that time came from the electronics industry, which aimed to develop tools to create smaller electronic devices on silicon chips of 40–70 nm dimensions.

The use of the term “nanotechnology” has grown to include a whole range of technologies: material sciences, where the design of new materials for wide-ranging applications are concerned; to electronics, where memories, computers, components and semiconductors are concerned; to biotechnology, where diagnostics and new drug delivery systems are concerned [6].

1.2 Consequences of Miniaturization

Every material, regardless of composition, exhibits new properties when its size is reduced to less than 100 nm. The electronic structure of a nanocrystal critically depends on its size. For small particles the electronic energy levels are not continuous as in bulk materials, but discrete. This arises primarily due to confinement of electrons within particles of dimensions smaller than the bulk electron delocalization length, this process is termed quantum confinement [7]. Noble metal and semiconductor nanoparticles are unique examples of this principle (Figure 1), where Φ_s is semi-conductor junction, Φ_m is the metal junction, and E_{fs} is the energy required for diffusion.[8].

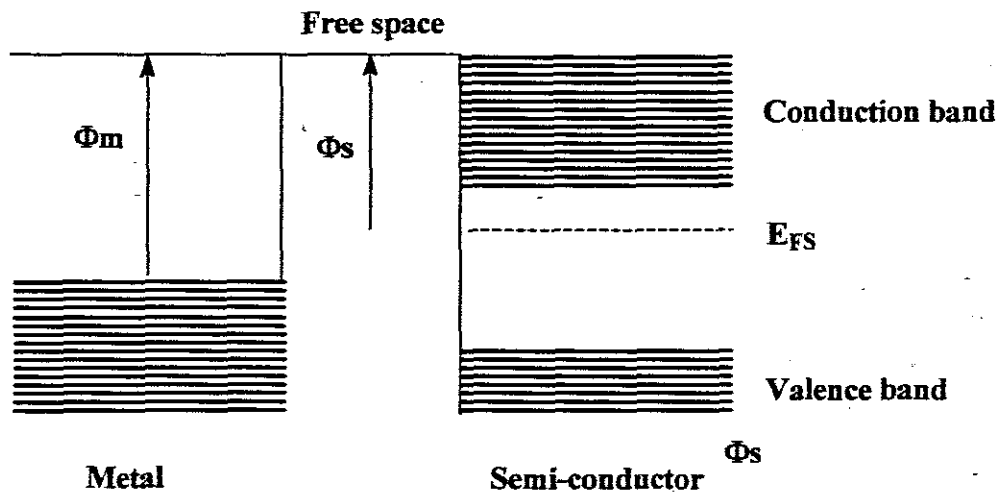


Figure 1 : Depiction of the fermi level for a metal and a semiconductor where .

Diodes junctions may be formed with n-type and p-type semiconductors. When the metal and semiconductor are brought together, excess electrons diffuse from the semi-conductor

to the metal until the fermi levels are equal. As electrons diffuse from the semiconductor to the metal, they leave behind their donor atoms. This depletes the region near the interface of charge carriers and hence this region does not conduct well. Thus for charges to diffuse across this region, they require additional energy. Since the extent of the depletion of charges is some function of distance, the conduction band is bent to represent the energy required for diffusion in that region, (**Figure 2**). Since the thermal energy (kT) at room temperature is $kT \cong 25 \text{ meV}$ (k is Boltzmann's constant), a 3 nm particle would be metallic ($kT > \delta$). However, at low temperatures the energy level spacing, especially in small particles, may become comparable to kT , rendering them nonmetallic [9]. Therefore the properties such as electrical conductivity and magnetic susceptibility exhibit quantum size effects due to the presence of the Kubo gap in individual nanoparticles [10].

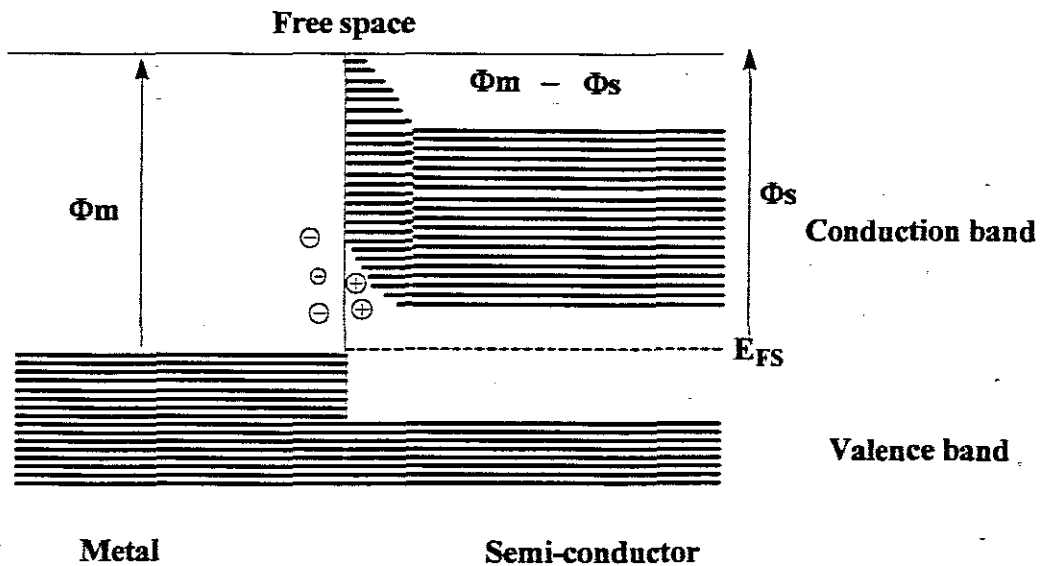


Figure 2 : The bending of the conduction band to acquire nano-structural properties

Electrons diffuse from the metal to the semiconductor over the barrier induced by the depletion region. Electrons diffuse from the semiconductor over this barrier in the opposite direction. When there is no externally applied voltage, this current will be equal and opposite. Thus, the properties of materials change at the nano-level due to the quantum effects, and the behavior of surfaces start to dominate. The optical, electrical, mechanical, magnetic, and chemical properties can be systematically manipulated by adjusting the size, composition, and shape of the nanoscale materials.

1.3 Methods for the Synthesis of Nanomaterials

Nanoparticles are viewed as the fundamental building blocks of nanotechnology. They are the starting point for preparing many nanostructured materials and devices. Their synthesis forms an important component of the rapidly growing research efforts in nanoscale science and engineering. The nanoparticles of a wide range of materials can be prepared by a variety of methods. In synthesis and assembly strategies of nanoparticles or nanomaterials, precursors in the form of liquids, solids or in the gas phase are used. They employ both a chemical and physical deposition approach, and rely on either chemical reactivity or physical compaction to integrate nanostructured building blocks. Generally the manufacturing techniques fall under two categories: the 'bottom-up' and the 'top-down' approach. The bottom-up approach refers to the build-up of a material from the 'bottom', i.e. atom-by-atom, molecule-by-molecule or cluster-by-cluster. The colloidal dispersion is a good example of a bottom-up approach in the synthesis of nanoparticles. Nanolithography and nanomanipulation techniques are also examples of the bottom-up

approach. The top-down approach involves starting with a block bulk material and designing or milling it down to the desired shape and size. This technique is similar to the approach used by the semiconductor industry in forming devices by utilizing pattern formation (such as electron beam lithography). Both approaches play very important roles in modern industry and most likely in nanotechnology as well. There are advantages and disadvantages in both approaches. The main challenge for the top-down approach is the creation of increasingly small structures with sufficient accuracy whereas in the bottom-up approach, the main challenge is to make structures large enough and of sufficient quality to be useful as materials [11]. The bottom-up approach has a better chance to generate or create nanostructures with less defects, more homogeneous chemical composition and, better short and long range ordering. This is because the bottom-up approach is driven mainly by the reduction of the Gibbs free energy, so that nanostructures and materials are produced in such a way that they are in a state closer to thermodynamic equilibrium. In comparison, the top-down approach most likely introduces internal stresses, in addition to surface defects. A select few methods for the synthesis of nanoparticles will be discussed.

1.3.1 Sol Process

In this approach, the reagents (metal ion solution) are rapidly added into a reaction vessel containing a hot coordinating solvent such as alkyl phosphate, alkyl phosphite, pyridine, alkyl amine, furan etc. The quick addition of reagents to the reaction vessel raises the precursor concentration above the nucleation threshold and the solution becomes supersaturated due to the high reaction temperature. As a result, a short nucleation burst

occurs and consequently the concentration of these species in solution drops below the critical concentration for nucleation. If the time for nanocluster growth during the nucleation period is short compared to the subsequent growth processes, the nanoclusters can become more uniform and monodispersed [12]. An alternative synthetic approach involves the mixing of the reagents in a vessel at a low temperature to prevent any appreciable reaction [12, 13]. A controlled rise of the solution temperature accelerates the chemical reaction and produces the required super saturation, which is then relieved by a burst of nucleation and particle growth. In either approach, the size distribution of the nanocluster sample is limited primarily by the short time interval in which the initial crystallites form and begin to grow. In general, nanocluster size increases with an increase in reaction time as more material is added to the nanocluster surfaces, and also with increasing temperature [12,13]. The systematic adjustment of the reaction parameters, such as reaction time, temperature, concentration, and the selection of reagents and surfactants, can be used to control the size, shape and quality of nanoclusters. There are a number of reports in the literature on the synthesis of nanoparticles, using this approach. A wide range of nanoparticles have been successfully synthesized by this method, such as CdSe [12,13,14], CdS [15], CdTe [16], ZnSe [17], ZnO [18], InP [19], InAs [20], PbSe [21], bimetallic nanoclusters such as AuAg and FePt [22]. CoPt [23], core/shell nanoclusters such as CdSe/ZnS [24], CdSe/CdS [25], metal oxides nanoclusters such as Fe₃O₄ [26], TiO₂ [27] and BaTiO₃ [28] have also been reported. Yu and Peng [16b] demonstrated the one-pot synthesis of high quality cadmium telluride nanoclusters by heating a mixture of CdO as the cadmium precursor, trioctylphosphine oxide and tetradecylphosphonic acid at 300–320 °C and then injecting the tellurium solution into the reaction mixture. Recently,

Alivisatos *et al.* [14d] reported the synthesis of nanorods, as well as arrow-, tetrapod- and branched tetrapod-shaped nanocrystals of CdSe by growing the nanoparticles in a mixture of hexylphosphonic acid and trioctylphosphine oxide at around 300 °C.

1.3.2 Micelles

A micelle is an aggregate of amphipathic molecules in water, with the nonpolar portions in the interior and the polar portions at the exterior surface, exposed to water (**Figure 3**). Amphiphilic molecules form micelles above a particular concentration which is called the critical micelle concentration (CMC). Micelles are known to have an anisotropic water distribution within their structure, which means the water concentration decreases from the surface towards the core of the micelle, with a completely hydrophobic (water-excluded) core. Hence hydrophobic nanoparticles can be encapsulated/solubilized within the inner core. Consequently, the spatial position of a solubilized nanoparticle in a micelle will depend on its polarity, the non-polar molecules will be solubilized in the micelle core and substances with intermediate polarity will be distributed along the surfactant molecules in certain intermediate positions.

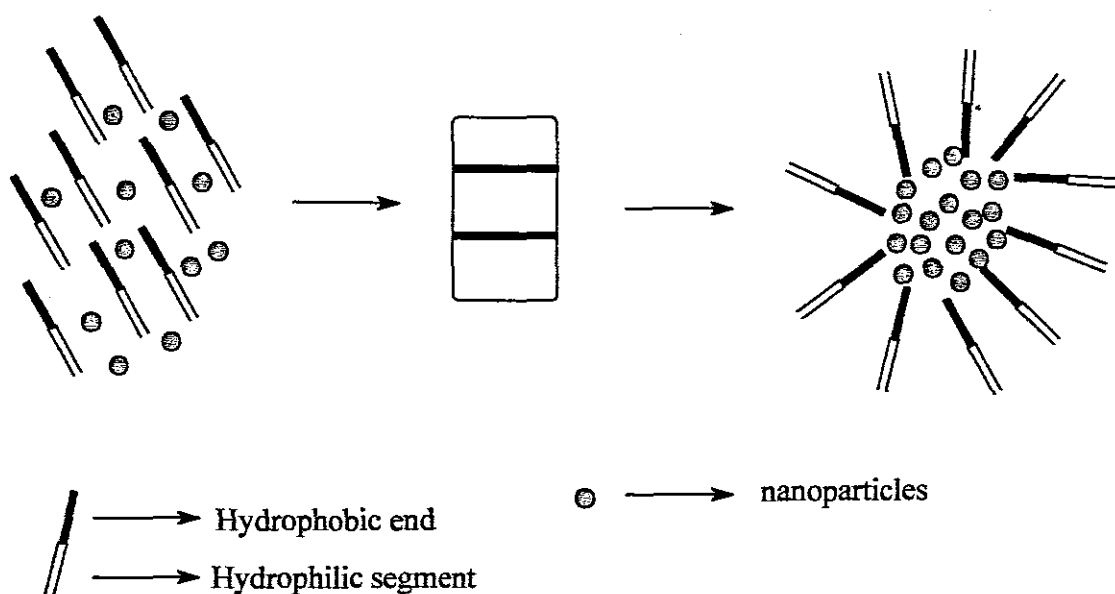


Figure 3 : Synthesis of nanoparticles using micelles

Recently, Taleb *et al.* [29] have shown that synthesis in reverse micelles combined with precipitation can lead to highly monodispersed metal and semiconducting nanoparticles and their spontaneous formation of 2D or 3D networks. They demonstrated the organization of silver particles in 2D and 3D super lattices using N_2H_4 as a reducing agent [29]. Sangregorio *et al.* [30] reported the synthesis of Cu_3Au alloy nanoclusters by the chemical reduction of the cations in water with isooctane as the microemulsion. A wide variety of nanoparticles have been synthesized using this process. The nanoparticles of Ir, Ag, Au, Cu, Co, Ni, FeNi and CoNi have been effectively synthesized by this route [31,32,33,34,35,36,37]. Metal oxide nanoparticles can also be prepared inside reverse micelles by the hydrolysis process where metal alkoxide dissolved in oil, reacts with water inside the droplets. Joselevich and Willner [38] reported the synthesis of ultrasmall TiO_2

particles *in situ* in a water/oil microemulsion composed of water, cetyldimethylbenzylammonium chloride (CDBA) and benzene by the controlled hydrolysis of TiCl_4 . Chhabra *et. al.* [39] demonstrated the use of water/triton X-100/hexanol/cyclohexane microemulsions for the preparation of TiO_2 nanoparticles in the size range of 20–40 nm. Chang and Fogler [40] reported the synthesis of silica particles from the hydrolysis of tetraethylorthosilicate (TEOS) in a non-ionic water/oil (W/O) microemulsion. Metal oxide nanoparticles such as ZrO_2 [41], TiO_2 [42], SiO_2 [43, 44] and Fe_2O_3 [45] have been prepared in this manner. Metal sulfate [46], metal sulfides [47], metal carbonates [48] and silver halides can be produced by the precipitation reaction between reactants in reverse micelles. It has been observed that the water content in the micelles greatly affects the shape of the nanoparticles. Nanowires such as BaCO_3 and BaSO_4 have been synthesized using reverse micelles with different water concentrations [49].

1.3.3 Sol-Gel Process

The sol-gel method is based on inorganic polymerization reactions. The sol-gel process includes four steps: hydrolysis, polycondensation, drying and thermal decomposition (Figure 4). The size of the sol particles depends on the solution composition, pH and temperature. By controlling these factors, one can tune the size of the particles. This method has been used to synthesize metal oxide nanostructures, such as TiO_2 , CeO_2 , and other nanostructures [50,51].

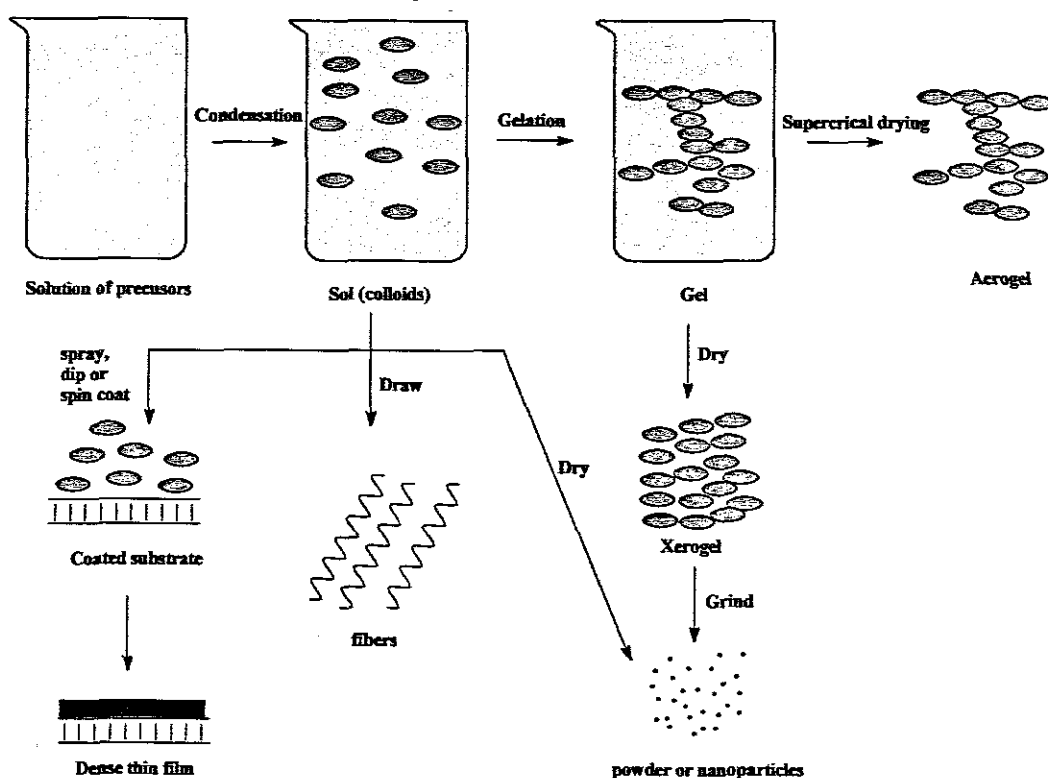


Figure 4 : Schematic representation of the sol gel synthesis of nanoparticles

1.3.4 Chemical Precipitation

This method uses the kinetics of nucleation and particle growth in homogeneous solutions, which can be adjusted by the controlled release of anions and cations. Careful control of the kinetics of the precipitation can result in monodisperse nanoparticles. It is therefore essential to control the factors that determine the precipitation process, such as the pH and the concentration of the reactants and ions. Organic molecules are used to control the release of the reagents and ions in the solution during the precipitation process. The particle size is influenced by the reactant concentration, pH, and temperature. By engineering these factors, nanoparticles with narrow size distributions can be synthesized.

It has been reported that urea can be utilized to control the nucleation process in the synthesis of $\text{Y}_2\text{O}_3\text{:Eu}$ nanoparticles [52,53,54,55,56,57]. Although the method of using precipitation to prepare nanoparticles is very straightforward and simple, very complicated nanostructures can also be constructed using these methods such as CdS/HgS/CdS and HgTe/CdS quantum well systems and other core/shell structures [58,59,60].

1.3.5 Hydrothermal Method

Hydrothermal synthesis is a common method to synthesize zeolite/molecular sieve crystals. This method exploits the solubility of almost all inorganic substances in PbS , water at elevated temperatures and pressures, and the subsequent crystallization of the dissolved material from the fluid. Water, at elevated temperatures, plays an essential role in the precursor material transformation, because the vapor pressure is much higher and the structure of water at elevated temperatures is different from that at room temperature. The properties of the reactants, including their solubility and reactivity, also change at high temperatures. The changes mentioned above provide more parameters to produce different high-quality nanoparticles and nanotubes, which are not possible at low temperatures. During the synthesis of nanocrystals, parameters such as pressure, temperature, reaction time and the respective precursor-product system, can be tuned to maintain quite high rates of simultaneous nucleation and therefore narrow particle size distribution. Different types of nanoparticles such as Bi_2S_3 nanorods and SiC nanowires have been successfully synthesized using this methodology [61,62]. Different types of nanostructures have also been obtained by solvothermal synthesis using supercritical fluids as solvents. Ji *et al.* [63]

described a method to synthesize metallic silver nanoparticles having diameters between 5–15 nm in supercritical CO₂ using water in CO₂ microemulsions. Cu, Ni, PdS, ZnS, CdS nanoparticles, nanowires and carbon nanotube have also been synthesized [64,65,66,67,68]. In addition, a new approach named solventless synthesis has recently been developed [80, 81].

1.3.6 Pyrolysis

This synthesis is a chemical process in which chemical precursors decompose into solid compounds and the unwanted waste evaporates. Generally the pyrolytic synthesis of compounds leads to powders with a wide size distribution in the micrometer regime. To get a uniform nanosized material, some modifications or revisions of the pyrolytic preparation procedure and reaction conditions need to be modified, such as slowing of the reaction rate or decomposition of the precursor in an inert solvent. Pyrolysis can be used to prepare different kinds of nanoparticles including metals, metal oxides, semiconductors and composite materials such as ZnS and carbon nanotubes [69,70]. The pyrolysis of organic precursors seems to provide a direct and effective method of producing nanotubes of various kinds, such as the one-step synthesis of aligned carbon nanotubes and Y-junction nanotubes. Carbon nanotubes produced from organometallic precursors can be used to further prepare gallium nitride nanowires, silicon nitride nanotubes and boron nitride nanotubes [71].

1.3.7 Chemical Vapor Deposition

In chemical vapor deposition (CVD), the vaporized precursors are introduced into a CVD reactor and adsorb onto a substance held at an elevated temperature. These adsorbed molecules will either thermally decompose or react with other gases/vapors to form crystals. The CVD process consists of three steps: (a) mass transport of reactants to the growth surface by diffusion through a boundary layer, (b) chemical reactions on the growth surface and, (c) removal of the gas-phase reaction by-products from the growth surface (Figure 5).

There are many examples of the application of this method in recent literature. Ostraat *et al.* [72] have demonstrated a two-stage reactor for producing oxide-coated silicon nanoparticles that have been incorporated into high-density non-volatile memory devices. This is one of the relatively few examples of a working microelectronic device in which vapor-phase synthesized nanoparticles perform an active function.

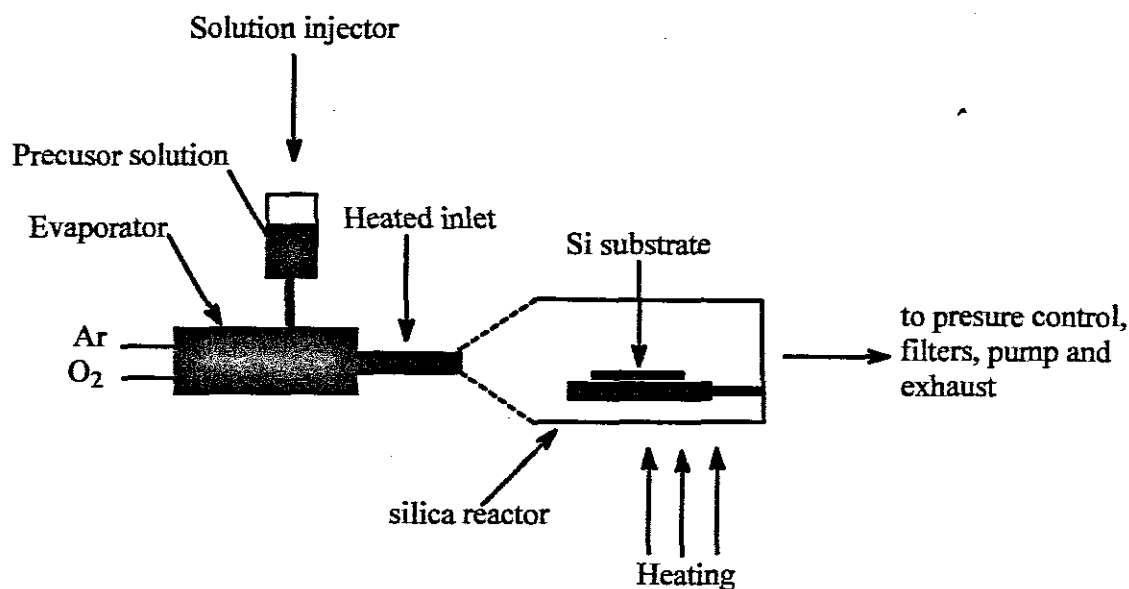


Figure 5 : Chemical vapor deposition

In other recent examples of this approach, Magnusson *et al.* [73] produced tungsten nanoparticles by the decomposition of tungsten hexacarbonyl. Another key feature of CVD is that it allows the formation of doped or multi-component nanoparticle by using multiple precursors. Schmechel *et al.* [74] prepared nanocrystalline europium-doped yttria (Y₂O₃:Eu) from organometallic yttrium and europium precursors. Senter *et al.* [75] incorporated erbium into silicon nanoparticles using disilane and an organometallic erbium compound as precursors. A particularly promising approach to this is the sodium metal/metal halide chemistry used by Ehrman *et al.* [76]. In this approach, a halide, such as SiCl₄, is reacted with sodium vapor in a heated furnace to produce NaCl-encapsulated particles. For example, SiCl₄ reacts with sodium to produce NaCl-encapsulated Si particles. The salt-encapsulation can potentially be used to prevent agglomeration of particles, and

the salt can then be washed away in a post-processing step. A wide variety of nanoparticles can be synthesized using other techniques which fall under the vapor phase process, namely inert gas condensation, pulsed laser ablation, ion sputtering, thermal plasma synthesis, and flame synthesis [77].

1.3.8 Bio-based Protocols

The utilization of microorganisms, such as bacteria and yeast, in the synthesis of nanoparticles is a relatively recent phenomenon [78]. The microorganisms minimize the toxicity within their cells by the reduction of the metal ions or by the formation of insoluble complexes with metal ions (e.g. metal sulfides) in the form of colloidal particles. An amalgamation of curiosity, environmental compulsions and understanding that nature has evolved the processes for synthesis of inorganic materials on nano- and micro-length scale, has created great interest among material scientists in the utilization of microorganisms for the synthesis of nanomaterials. Some of the examples include magnetotactic bacteria, which synthesize magnetite nanoparticles [79], diatoms and radiolarians that synthesize siliceous materials and S-layer bacteria that produce gypsum and calcium carbonate as surface layers [80,81]. These bioinorganic materials can be extremely complex in both structure and function, and also exhibit exquisite hierarchical ordering from the nanometer to the macroscopic length scale, which has not even remotely been achieved in laboratory based syntheses.

1.4 Properties of Nanomaterials

The reduction of a materials dimension has pronounced effects on its physical properties, which may be significantly different from the corresponding bulk material. Some of the physical properties exhibited by nanomaterials are due to: (i) the large number of surface atoms, (ii) large surface energy, (iii) spatial confinement and, (iv) reduced imperfections.

A few properties of nanomaterials are discussed below:

1.4.1 Optical

For the last few decades, metallic nanoparticles have fascinated researchers due to their colorful colloidal solutions. Mie was the first to explain the red color of gold nanoparticles (in 1908) by solving Maxwell's equation for an electromagnetic light wave interacting with small metallic spheres. The color exhibited by metallic nanoparticles is due to the coherent excitation of all the "free" electrons within the conduction band, leading to an in-phase oscillation that is known as the surface plasmon resonance (SPR). Thus, the color of metallic nanoparticles may change with their size due to surface plasmon resonance. The unique optical properties of nanomaterials may also be due to quantum size effects, which arise primarily due to confinement of electrons within particles with dimensions smaller than the bulk electron delocalization length. This effect is more pronounced for semiconductor nanoparticles, where the band gap increases with a decrease in size. The same quantum size effect is also shown by metal nanoparticles, when the particle size is greater than 2 nm.

1.4.2 Magnetic

Magnetic properties of nanostructured materials are distinctly different from that of bulk materials. Ferromagnetic particles become unstable when the particle size reduces to below a certain size, as the increase in surface energy provides sufficient energy for domains to spontaneously switch polarization directions and become paramagnetic. But this transformed paramagnetism is different from the conventional paramagnetism and thus is referred to as superparamagnetism [82]. In other words, ferromagnetism of bulk materials disappears and is replaced by superparamagnetism in the nanoscale due to the high surface energy.

1.4.3 Mechanical

The mechanical properties of nanomaterials increase with a decrease in size. Most recent studies have been focused on the mechanical properties of one dimensional structure such as nanowires. The enhanced mechanical strength of nanowires or nanorods is due to the high internal perfection of the nanowires. In general, imperfections such as dislocations, micro-twins, impurities, etc. in crystals are highly energetic and should be eliminated from crystal structures to enhance its mechanical properties. Due to the small cross-section of nanowires, the probability of finding any imperfections is reduced.

1.4.4 Thermal

Metal and semiconductor nanoparticles are found to have a significantly lower melting point or phase transition temperature as compared to their bulk counterparts. The lowering

of the melting points is observed when the particle size is less than 100 nm and is attributed to increase in surface energy with a reduction of size. The decrease in the phase transition temperature can be ascribed to the decrease in the ratio of surface energy to volume energy as a function of size.

1.5 Applications of Nanomaterials

Nanotechnology can be used in a broad range of potential applications from electronics, optical communications and biological systems to new smart materials. The wide range of applications are due to (i) the unusual physical properties exhibited by nanosized materials, e.g. gold nanoparticles used as an inorganic dye for coloration of glass, (ii) the large surface area, such as gold nanoparticles supported on metal oxides are used as low temperature catalyst and for various sensors, and (iii) the small size. For many applications, new materials and new properties have been introduced. Some of the applications of nanostructures and nanomaterials are highlighted.

1.5.1 Molecular Electronic and Nanoelectronics

The last few years have been witness to tremendous progress in the science of molecular electronic and nanoelectronics [83]. In molecular electronics, single molecules are designed to control electron transport, which offers the promise of exploring the vast variety of molecular functions for electronic devices. The control over electronic energy levels at the surface of conventional semiconductors and metals is achieved by assembly on the solid surfaces. Molecules can be designed into a working circuit. If molecules are

biologically active, then bio-electronic devices could be developed [84]. Many nanoelectronic devices have been developed which include tunneling junctions, electrically configurable switches, carbon nanotube transistors and single molecular transistors [85,86]. Various techniques have been used in the fabrication of nanoelectronics such as the focused ion beam (FIB) technique, electron beam and imprint lithography [87,88]. Gold nanoparticles have been extensively used in nanoelectronics and molecular electronics using the unique surface property and uniform size of the particles. For example, gold nanoparticles function as a carrier by attaching various functional organic molecules or biocomponents [89]. Gold nanoparticles can also be used as a mediator to connect different functionalities together in the construction of nanoscale electronics for the applications of sensors and detectors [90].

1.5.2 Nanorobots

Applications of nanotechnology in medical science also referred to as nanomedicine, have been promising. One of the attractive applications of nanomedicine is the creation of nanoscale devices for improved therapy and diagnostics. Such nanoscale devices are known as nanorobots [91]. These nanorobots have the potential to serve as vehicles for the delivery of therapeutic agents and detectors against early disease.

1.5.3 Biological Applications

One of the important biological applications of colloidal nanocrystals is molecular recognition [92]. Certain biological molecules can recognize and bind to other molecules

with extremely high selectivity and specificity. For molecular recognition applications, antibodies and oligonucleotides are widely used as receptors. If, for example, a virus enters an organism, antibodies recognize the virus as a hostile intruder, or antigen, and bind to it in such a way that the virus can be destroyed by other parts of the immune system. Antibodies and oligonucleotides are typically attached to the surface of nanocrystals via (i) thiol-gold bonds to gold nanoparticles, (ii) covalent linkages to silanized nanocrystals with biofunctional crosslinker molecules and (iii) a biotin-avidin linkage, where avidin is adsorbed on the particle surface [93,94,95,96]. Nanocrystals thus conjugated or attached to receptor molecules can be directed to bind to positions where ligand molecules are present, which 'fit' the molecular recognition of the receptor [97]. This facilitates a set of applications including molecular labeling [98]. For example, the change in color of gold nanoparticles from ruby-red to blue due to aggregation has been exploited for the development of very sensitive colorimetric methods of DNA analysis [99]. Other potential biological applications of nanomaterials include the use of colloidal semiconductor nanocrystals as fluorescent probes to label cells and chemical libraries, and the use of nanostructured materials as artificial bones [100,101].

1.5.4 Catalytic Applications

For a material to show good catalytic activity, it must possess high surface area. Nanomaterials have tremendous potential in catalysis since the surface area of nanomaterials markedly increases with a reduction in their size. For example, a nanocrystal of 10 nm diameter will have ~15 % of its atoms on the surface while nanocrystal of 1 nm

diameter will have ~100 %. Thus, a small nanocrystal with a higher surface area would be more catalytically active. Furthermore, the change in electronic properties arising from quantum confinement in small nanocrystals will also bestow unusual catalytic properties on these particles [102]. Yates *et al.* [103] demonstrated the decrease in catalytic activity per unit surface area of nickel with an increase in particle size in the hydrogenation reaction of ethane. In a series of papers, Corrolleur, Gault and their co-workers demonstrated the effect of particle size on mechanisms and product distributions of hydrogenolysis reactions over platinum catalysts [104]. There have been quite a few interesting examples of nanostructured metal oxides and sulfides exhibiting unusual catalytic properties [105]. Ying *et al.* [106] reported the use of cerium oxide nanoparticles in the selective reduction of SO₂ by CO with excellent poisoning resistance towards H₂O and CO₂. Very recently, Liu *et al.* [107] developed a highly efficient catalyst system for CO oxidation with Au-Ag alloy nanoparticles supported on the mesoporous MCM-41, and observed that the size effect is no longer a critical factor with Ag believed to play a key role in the activation of oxygen. Surface science investigations and theoretical calculations have proven that the smooth surface of gold is catalytically inactive for both hydrogenation and oxidation reactions [108,109]. It is due to the absence of characteristic dissociative absorption of H₂ and O₂ over the smooth surface of gold at a temperature below 473 K. However, in a series of papers, Bond and Sermon [110] and Haruta *et al.* [111] demonstrated the nanoscale effect of gold particles in heterogeneous catalysis. They have reported that nanosized gold (>10 nm) deposited on certain metal oxides exhibits surprisingly high catalytic activity in hydrogenation reactions and oxidation of carbon monoxide. Bond and Sermon demonstrated the hydrogenation of linear alkenes over a Au/SiO₂ catalyst [110]. Haruta *et*

al. [112] showed that gold nanoparticles, if deposited on partly reactive oxides, such as Fe_2O_3 , Co_2O_3 , NiO , MnO_2 , γ -alumina and titania, was found to be extremely reactive in the oxidation of carbon monoxide even at -70°C . The enhanced catalytic activities are due to the combined effect of the gold particle size and the selection of appropriate transition metal oxide supports. Parravano and his coworkers dispersed small gold particles over MgO and Al_2O_3 for oxygen and hydrogen transfer reactions [113]. Recently, Mukherjee *et al.* reported the catalytic activity of gold nanoparticles supported on fumed silica in the hydrogenation of cyclohexane [114]. Zhao *et al.* [115] reported the liquid phase oxidation of cyclohexane over Au/ZSM-5 and Au/MCM-41 . Thiol-stabilized gold nanoparticles have also been exploited for catalysis applications. Examples include asymmetric dihydroxylation reactions, carboxylic ester cleavage, and electrocatalytic reductions by anthraquinone functionalized gold particles. Thus, these observations clearly suggest that the smaller gold particles can exhibit appreciable catalytic activity and particle-bound ring opening metathesis polymerization [116,117,118,119].

1.6 Physiochemical Characterization

The nanomaterials can be characterized by various techniques, which provide important information for the understanding of different physiochemical features. The most extensively used techniques can be categorized into the following:

- a) X-ray diffraction (XRD)
- b) Scanning electron microscopy (SEM)

- c) Transmission electron microscopy (TEM)
- d) Ultraviolet-visible (UV-Vis) spectroscopy
- e) Fluorescence spectroscopy
- f) Fourier transform infrared (FTIR) spectroscopy,
- g) X-ray photoelectron spectroscopy (XPS)
- h) Atomic absorption spectroscopy (AAS)

1.6.1 X-Ray Diffraction

X-ray diffraction is a very important technique that has been used to determine the crystal structure of solids, lattice constants, geometry, identification of unknown materials, orientation of single crystals and defects [120]. The X-ray diffraction spectra are obtained by the measurement of the angles at which an X-ray beam is diffracted by the crystalline phases in the specimen. Bragg's equation relates the distance between two hkl planes (d) and the angle of diffraction (2θ) by: $n\lambda = 2d\sin\theta$, where, λ is the wavelength of X-rays and n is an integer known as the order of reflection (h , k and l represent Miller indices of the respective planes) [121]. From the diffraction spectra, the uniqueness of nanocrystal structure, phase purity, degree of crystallinity and unit cell parameters of the nanocrystalline materials can be determined. The X-ray diffraction technique is non-destructive and does not require elaborate sample preparation, which partly explains the wide use of XRD methods in material characterization. X-ray diffraction broadening analysis has been widely used to determine the crystal size of nanoscale materials. The average size of the nanoparticles can be estimated using the Debye-Scherrer equation: $D =$

$k\lambda / \beta \cos\theta$, where D is the thickness of the nanocrystal, k is a constant, λ is the wavelength of X-rays and β is the full width at half maxima of (111) reflection at Bragg's angle 2θ [122].

1.6.2 Scanning Electron Microscopy

Scanning electron microscopy (SEM) is one of the most widely used techniques for characterization of nanomaterials and nanostructures. The resolution of high-resolution SEM approaches a few nanometers and the instruments can operate at magnifications that are easily adjusted from ~ 10 to over 300,000. This technique provides not only topographical information like optical microscopes do, but also information of chemical composition near the surface. A SEM generates an electron beam that is scanned back and forth over a solid sample. The interaction between the beam and the sample produces different types of signals providing detailed information about the surface structure and morphology of the sample. When an electron from the beam encounters a nucleus in the sample, the resultant coulombic attraction leads to a deflection in the electron's path, known as Rutherford elastic scattering. A fraction of these electrons will be completely backscattered, re-emerging from the incident surface of the sample. Since the scattering angle depends on the atomic number of the nucleus, the primary electrons arriving at a given detector position can be used to produce images containing topological and compositional information [123]. The high-energy incident electrons can also interact with the loosely bound conduction band electrons in the sample. However, the amount of energy given to these secondary electrons as a result of the interactions is small and so they

have a very limited range in the sample. Hence, only those secondary electrons that are produced within a very short distance from the surface are able to escape from the sample. As a result, high-resolution topographical images can be obtained in this detection mode [123].

1.6.3 Transmission Electron Microscopy (TEM)

Transmission electron microscopy (TEM) is typically used for the high resolution imaging of thin slices of a solid sample for nanostructural and compositional analysis. The technique involves: (i) irradiation of a very thin sample by a high-energy electron beam, which is diffracted by the lattices of the crystalline or semicrystalline material and propagated along different directions, (ii) imaging and angular distribution analysis of the forward-scattered electrons (unlike SEM where backscattered electrons are detected) and, (iii) energy analysis of the emitted X-rays [124]. The information obtained by TEM can be utilized in structural characterization and identification of various phases of nanomaterials, namely hexagonal, cubic or lamellar [124]. One shortcoming of TEM is that the electron scattering information in a TEM image originates from a three-dimensional sample, but is projected onto a two-dimensional detector. Therefore, structural information along the electron beam direction is superimposed at the image plane. Selected area diffraction (SAD) can be used to determine the crystal structure of individual nanomaterials, such as nanocrystals and nanorods and, the crystal structures of different parts of the sample. In SAD, the condenser lens is defocused to produce parallel illumination at the specimen and a selected-area aperture is used to limit the diffracting volume. SAD patterns are often used

to determine the Bravais lattices and lattice parameters of crystalline materials by the same procedure used in XRD [125]. In addition to the capability of structural characterization and chemical analyses, TEM has also been explored for other uses in nanotechnology characterization. Examples include the determination of melting points of nanocrystals, in which an electron beam is used to heat up nanocrystals and the melting points are determined by the disappearance of electron diffraction [126]. Another example is the measurement of mechanical and electrical properties of individual nanowires and nanotubes [127].

1.6.4 Optical Spectroscopy

Optical spectroscopy has been widely used for the characterization of nanomaterials and the technique can be broadly categorized into (i) absorption (UV-Vis), (ii) emission (fluorescence), and (iii) vibrational (infrared) spectroscopy. Absorption and emission spectroscopy determines the electronic structures of atoms, ions, molecules or crystals by exciting electrons from the ground to excited states (absorption) and thereafter relaxation from the excited to ground states (emission) occurs. The vibrational technique involves the interactions of photons with species in a sample that results in energy transfer to or from the sample via vibrational excitation or de-excitation. The vibrational frequencies provide the information of chemical bonds in the detecting samples.

1.6.4.1 UV-Vis Spectroscopy

This technique deals with the study of electronic transitions between orbitals or bands of atoms, ions or molecules in the gaseous, liquid and solid state. The metallic nanoparticles are known to exhibit different characteristic colors. As mentioned earlier, Mie was the first to explain the origin of this color theoretically in 1908, after solving Maxwell's equation for the absorption and scattering of electromagnetic radiation by small metallic particles. This absorption of electromagnetic radiation by metallic nanoparticles originates from the coherent oscillation of the valence band electrons induced by an interaction with the electromagnetic field. These resonances are known as surface plasmons, which occur only in the case of nanoparticles and not in the case of bulk metallic particles. Hence, UV-Visible studies can be utilized to determine the unique optical properties of nanoparticles [128].

1.6.4.2 Fluorescence/Emission Spectroscopy

In this technique, light of a particular wavelength is directed onto a specimen, prompting the transition of electrons from the ground state to an excited state, which then undergoes an irradiative internal relaxation and the excited electrons move to a more stable excited level. After a characteristic lifetime in the excited state, the electrons return to the ground state by emitting the characteristic energy in the form of light. This emitted energy can be

used to provide qualitative and sometimes quantitative information about chemical composition, structure, impurities, kinetic processes and energy transfer.

1.6.4.3 Fourier Transform Infrared (FTIR) Spectroscopy

Fourier Transform Infrared (FTIR) spectroscopy deals with the vibration of chemical bonds in a molecule at various frequencies, which depends on the elements and types of bonds. After absorbing electromagnetic radiation, the frequency of vibration of a bond increases, leading to a transition between the ground state and several excited states. These absorption frequencies represent excitations of vibrations of the chemical bonds and thus are specific to the type of bond and the group of atoms involved in the vibration.

The energy corresponding to these frequencies correspond to the infrared region ($4000\text{--}400\text{ cm}^{-1}$) of the electromagnetic spectrum. The term Fourier Transform (FT) refers to a recent development in the manner in which the data are collected and converted from an interference pattern to an infrared absorption spectrum, which is like a molecular "fingerprint" [129]. The FTIR technique can be utilized to study the presence of protein molecules in the solution, as the FTIR spectra in the $1400\text{--}1700\text{ cm}^{-1}$ region provides information about the presence of --CO-- and --NH-- groups.

1.6.5 X-Ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) is widely used for probing the electronic structure of atoms, molecules and condensed matter. When an X-ray photon of energy $h\nu$ is incident

on solid matter, the kinetic energy (E_k) and the binding energy (E_b) of the ejected photoelectrons can be related as follows: $E_k = h\nu - E_b$. This kinetic energy distribution of the photoelectrons produces a series of discrete bands, which represents the electronic structure of the sample [130]. The core level binding energies of all the elements (other than H and He) in all different oxidation states are unique, which provides instant detection of the chemical composition of the sample after a full range scan. However, to account for the multiple splitting and satellites accompanying the photoemission peaks, the photoelectron spectra should be interpreted in terms of many-electron states of the final ionized state of the sample, rather than the occupied one-electron states of the neutral species.

1.6.6 Atomic Absorption Spectroscopy

The phenomenon of atomic absorption is based on the energy absorbed during transitions between electronic energy levels of an atom. When an amount of energy is provided to an atom in the ground state by a source such as a flame (temperature ranging between 2100–2800 °C), the outer-shell electrons are promoted to a higher energy excited state. The radiation absorbed as a result of this transition between electronic levels can be used for quantitative analysis of metals and metalloids present in solid matrices, which have to be dissolved by appropriate solvents before analysis. The basis of quantitative analysis depends on the measurement of radiation intensity and the assumption that radiation absorbed is proportional to atomic concentration. Comparison of relative intensity values for reference standards is used to determine elemental concentrations [131].

1.7 Scope and Objectives of the Study

One important area of nanotechnology is the development of reliable processes for the synthesis of nanomaterials over a range of sizes which have good monodispersity and chemical composition. Hence, current research is directed towards the development of different experimental protocols for the synthesis of nanomaterials of variable sizes and shapes. A number of reports prevail in the literatures that are eco-unfriendly and expensive. It is therefore very important to develop eco-friendly processes that are simple. This has led researchers to look at room temperature synthetic methods as well as to study the growth dynamics of metal nanoparticles. In-depth characterizations of these nanoparticles need to be highlighted in order to understand the stability of nanoparticles and the probable pathways of their formation. The main challenges frequently encountered by the researchers who are doing nanoparticle synthesis are (i) control of particle size and shape and (ii) achieving the required monodispersity. The synthesis of nanoparticles with controlled monodispersity is a recent demand by materials developers for the advancement of nanotechnology.

The specific problems chosen are:

- ✱ Synthesis of anisotropic silver nanoparticles at room temperature without the addition of seed particles,
- ✱ Synthesis of nearly monodispersed silver nanoparticles using biphenylphosphine silver complexes, and

- * Use of Density Functional Theory (DFT) and Surface Enhanced Raman Spectroscopy (SERS) for understanding the regioselective adsorption of N-methyl pyrrolidinone and pyrrolidinone to acquire a clear insight into the growth of metal nanoparticles.

1.8 Outline of the Thesis

The thesis will be presented in four chapters, a brief summary of which is given below.

Chapter One : Introduction and Literature Survey

Chapter 1 as shown in the previous pages presents a general introduction about various physicochemical aspects of nanomaterials. The different characteristic properties of nanomaterials, their chemically synthesized protocols, characterization techniques, and their applications are discussed in brief. Based on these reviews, the context, scope and objective of the present work are outlined.

Chapter Two : Growth of Anisotropic Silver Nanoparticles

Chapter 2 deals with the theory of kinetically growth of nanoparticles. The basic mechanisms involved in the reaction kinetics of PVP with silver salt are discussed as well as the structural evolution of nanoparticles are also mentioned in this chapter

Chapter Three : Synthesis of Anisotropic Silver Nanoparticles

Chapter 3 presents an improved DMF reduction method for the synthesis of anisotropic metal nanoparticles. The synthesis of silver nanowires and nanodendrites are described. Finally the synthesis of hexadecylamine (HDA) and tri-n-octylphosphine oxide (TOPO)-capped silver nanoparticles using biphenyl phosphine silver complexes as single molecule precursors is presented. The particles synthesized by all methods are characterized mainly by UV/Vis spectroscopy and TEM techniques.

Chapter Four : Computational Chemistry Mechanism and Regioselective

Adsorption of PVP on Metal Facets

Chapter 4 deals with Surface Enhanced Raman Spectroscopy (SERS) for understanding the regioselective adsorption of pyrrolidinone on metal nanoparticles. The probable mechanism helps to understand the structural orientation of pyrrolidinone on metal nanoparticles. This chapter also focuses on a Density Functional Theory (DFT) for understanding the regioselective adsorption of pyrrolidinone on the surface of gold and silver nanoparticles. Comparative experimental results are drawn in order to gain a thorough insight of the influence of PVP towards the growth behavior of metal nanoparticles.

CHAPTER TWO : PROPERTIES AND GROWTH OF METAL NANOPARTICLES

2.1. Optical Properties of Metal Nanostructures

Metal nanostructures have optical properties that are strikingly different from those of bulk materials. For example deep-red and yellow colours are indicative of small metal particles of gold and silver respectively (Figure 6 and 7). These colours are due to a strong interaction between light and the conduction electrons, which are confined to the small volume of the metal nanostructures.

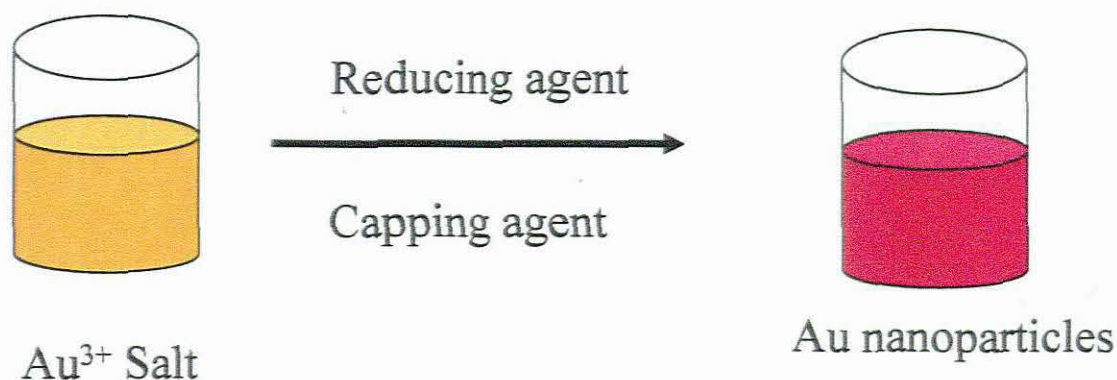


Figure 6 : Color change in gold nanoparticles.

Surface plasmons (SPs) are waves that propagate along the surface of a conductor or metal. SPs are trapped on the surface of a metal as they interact with free electrons. When these interactions occur, the free electrons on the surface of the metal respond collectively by

oscillating in resonance with the light waves. Silver nanoparticles give different colours in solution depending on their morphology (**Figure 7**).

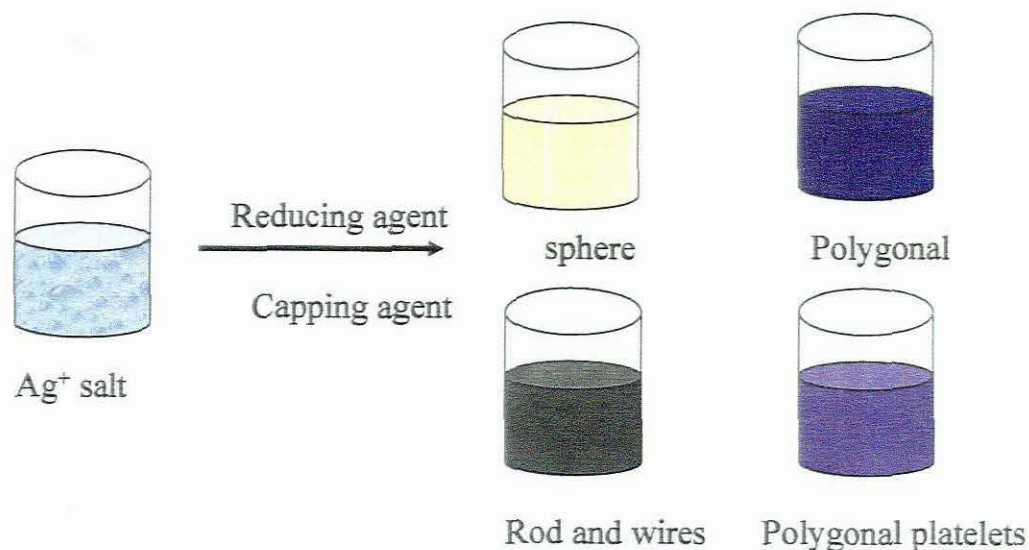


Figure 7 : Colors of silver nanoparticles with different morphologies

This kind of interaction between the surface charge oscillation of the metals and the electromagnetic field of light constitutes surface plasmons and, gives rise to the metal's unique optical properties. These very complex and interesting optical properties are due to the collective oscillation of the electrons on the metal's surface and are known as the surface plasmon resonance (SPR).

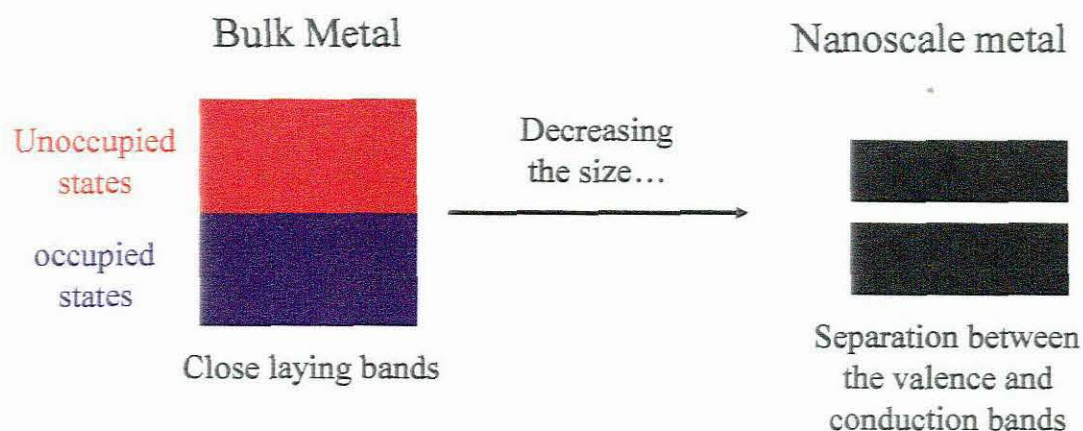


Figure 8 : Schematic of the energy levels in metal nanoparticles.

The optical properties of metals are influenced by the contribution of electrons and the dielectric function as it is reduced in size (**Figure 8**). As the optical properties have been defined to involve the oscillation of electrons on the surface of metal due to the electromagnetic field, when this phenomenon occurs it gives rise to the transformation of energy from the incident electromagnetic wave into thermal energy in the so called absorption process. These electrons can be accelerated and then radiated in a scattering process (**Figure 9**). The sum of this effect (absorption and scattering) is called the extinction of light.

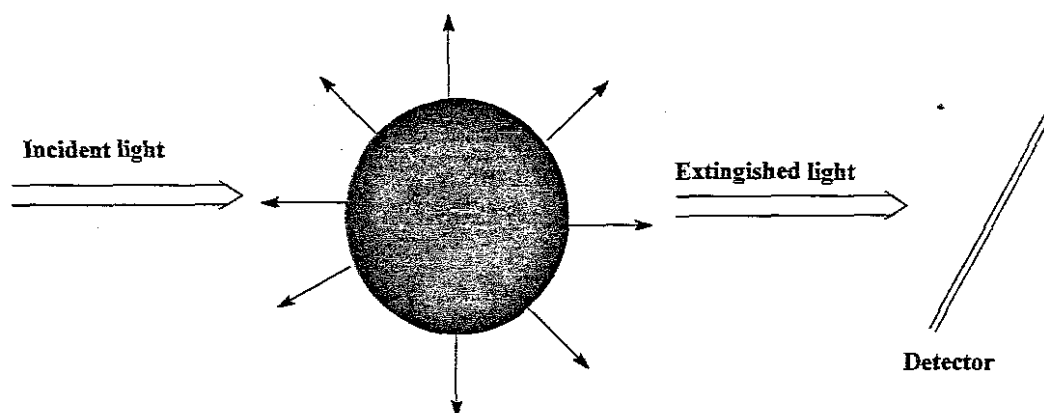


Figure 9 : Scattering of absorbed light

The optical properties of nanoscale metals depend strongly upon the particle size and shape. Bulk gold appears yellowish in reflected light whereas gold nanocrystals are red in transmitted light. However, bulk silver appears grayish while silver nanoparticles are yellow (**Figure 7**). These effects are due to the result of the surface plasmon resonance and can be exhibited only by metals with free electrons such as gold, silver, copper and alkali metals. The surface plasmon resonance can also depend on the nature of the surrounding molecule adsorbed on the surface of the metal. The optical properties of metal nanostructures can be understood by the following model:

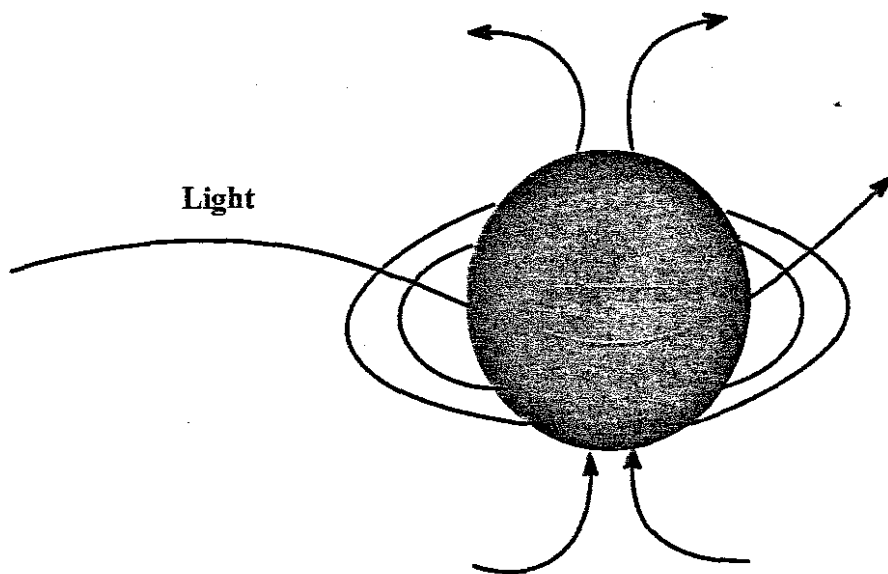


Figure 10 : Scattering of light due to the formation of dipole.

The excited light is able to penetrate the particle. The electric field inside the particle shifts the conduction electrons collectively with respect to the fixed positive charge of lattice ions (Figure 10). These electrons build up a charge on the surface of one of the particles. The attractive character of this negative and the positive charge of the remaining lattice ions on the opposite side result in the formation of the restoring force. This collective phenomenon is the most striking consequence of the particle plasmon excitation and gives the strong colour that noble metals exhibit.

2.2. UV- visible Absorption of Metal Nanoparticles with Different Geometries

The surface plasmons of metal nanospheres in water are explained by strong resonance. (Figure 11). The metal nanospheres primarily absorb blue light, letting the red and green wavelengths combine to give the appearance of a yellow colour. The absorption spectrum of metal nanospheres should show the presence of resonance peaks between 300 nm and 450 nm. These resonance peaks arise from one side of the sphere surface being positively charged while the opposite side is negatively charged. The shift in the blue region depends on the size of the spherical metal nanoparticles.

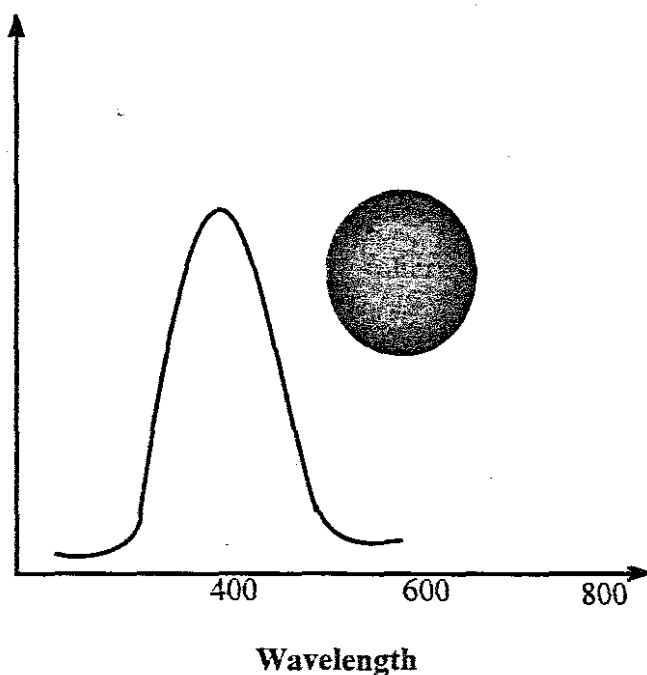


Figure 11 : Absorption of spherical shaped nanoparticles

The appearance of more than one peak in cubic metal nanoparticles is attributed to the presence of several distinct resonances when compared with metal nanospheres (**Figure 12**). This observation is further attributed to metal nanostructures with sharp corners. The surface charges accumulate at the sharp corners of metal nanostructures, and the most intense absorption peak is red-shifted compared to that of the metal nanosphere.

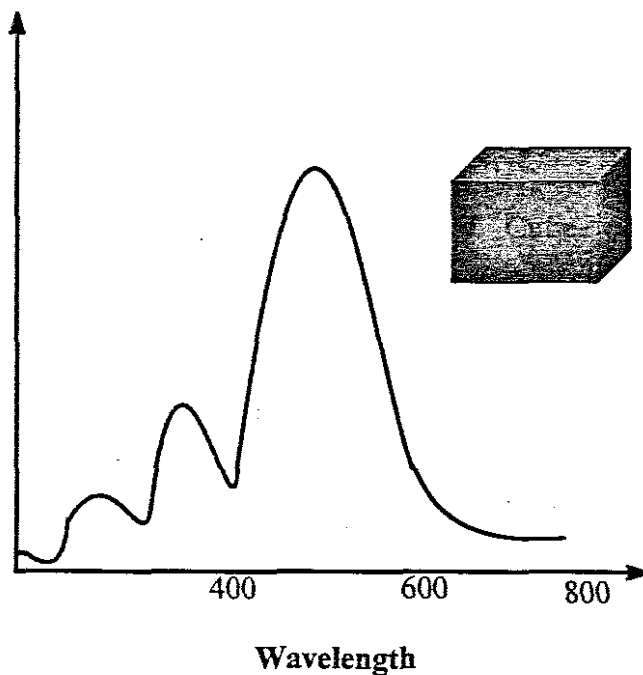


Figure 12 : Absorption of cubic shaped nanoparticles

Similar trends can be observed for tetrahedron and octahedron nanostructures (**Figure 13**). The tetrahedron is characterized by a red-shifted resonance peak due to the sharpest corners. The theoretical bases of this phenomenon have been shown by Discrete Dipole Approximation (DDA) calculations [132].

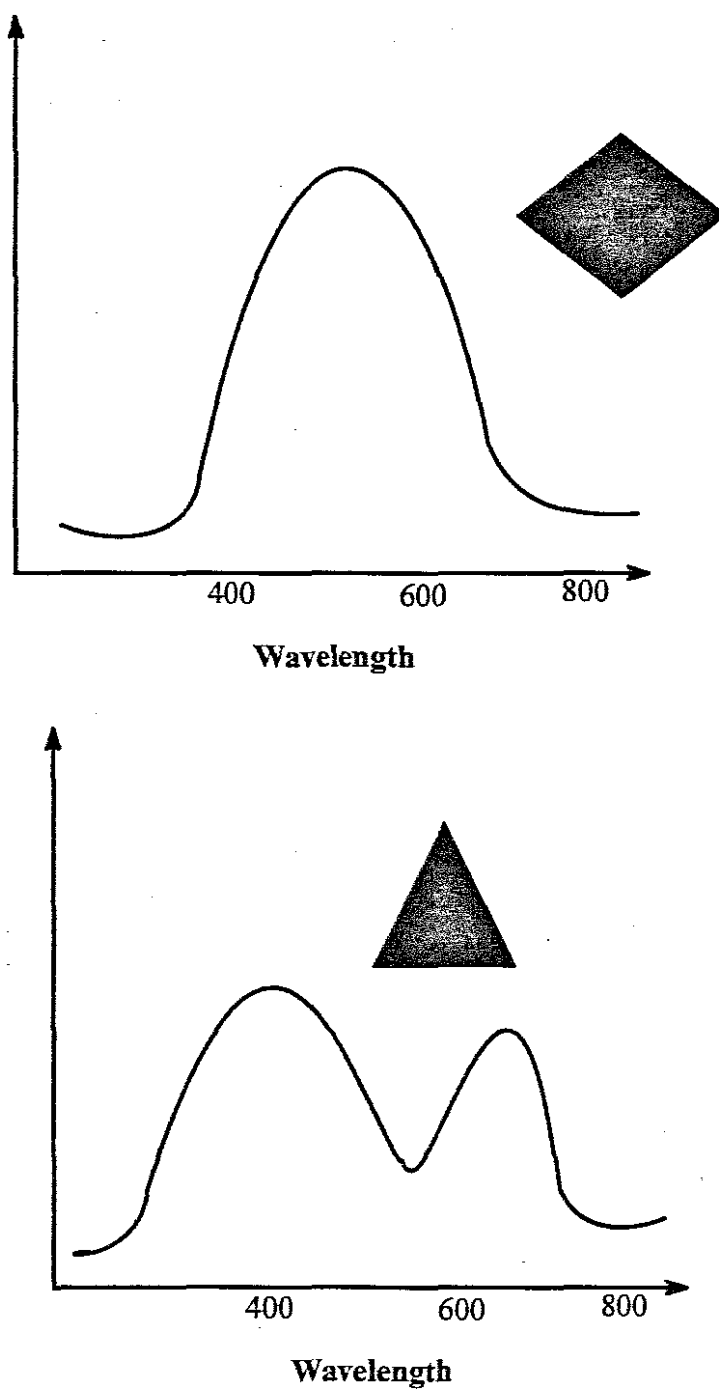


Figure 13 : Absorption peaks of triangular and octahedron shaped nanoparticles

In nanorods (Figure 14), two distinct peaks are present. These two plasmon peaks are due to the contribution of the transverse oscillation of electrons in the blue region and the longitudinal oscillation of electrons at a longer wavelength. The transverse oscillation does not depend on the aspect ratio, therefore it constitutes the same plasmon resonance as spherical nanoparticles. However, the longitudinal oscillation depends on the aspect ratio of nanorods which contribute to the red-shift of the longitudinal oscillation resonance peak.

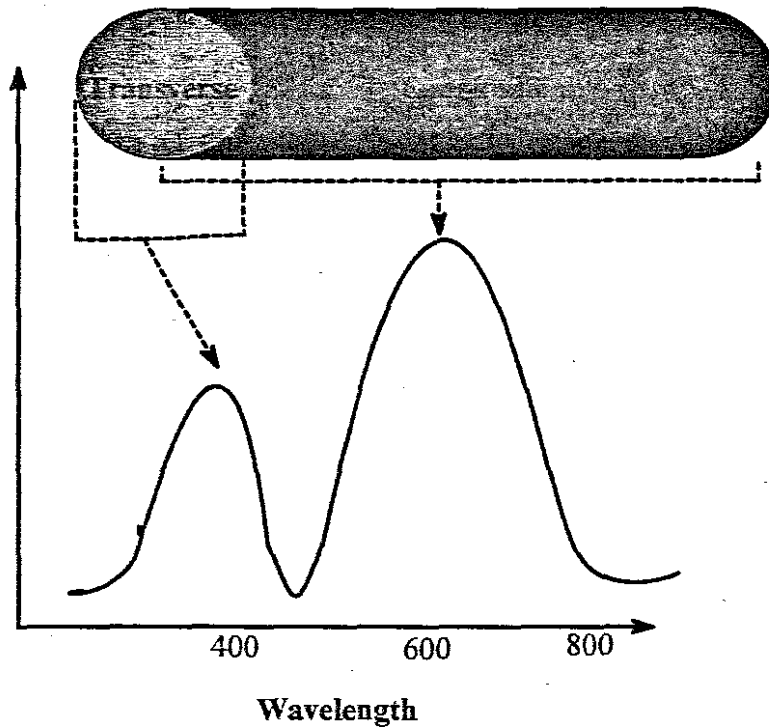


Figure 14 : Absorption spectrum of nanorods

The two absorption bands that appear in the UV-visible spectrum of metal nanorods are due to the oscillation of electrons along the transverse and the longitudinal region as explained above. The appearance of these two peaks depends on the aspect ratio (length divided by width of nanorods).

2.3 Growth of Anisotropic Metal Particles

2.3.1 Polyhedral nanocrystals

Most metal nanoparticles with sizes ranging from 10 to 20 nm are spherical, but their surfaces contain high-index crystallography planes that results in higher surface energy. These particles are therefore termed polyhedrons (**Figure 15**). These shapes vary based on the facet growth rate. In octahedrons, the growth rate is along the $\{100\}$ planes. The octahedron shaped nanoparticles have eight $\{111\}$ facets, with four $\{111\}$ facets on the edge when viewed along the $\{110\}$ plane. Most of these nanoparticles are spherically shaped when viewed in low resolution TEM.

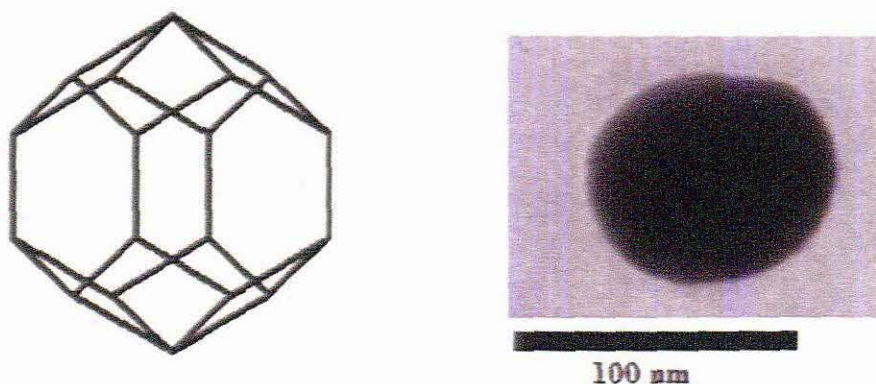


Figure 15 : Structure of polyhedron shaped nanoparticles

2.3.2 Twinned and multiply twinned nanoparticles

Twinning is considered as one of the most common planar defects in nanocrystal growth. Twinning results when two sub-grains share one crystallographic plane, and the structure of one subgrain is the mirror image of the other (Figure 16).

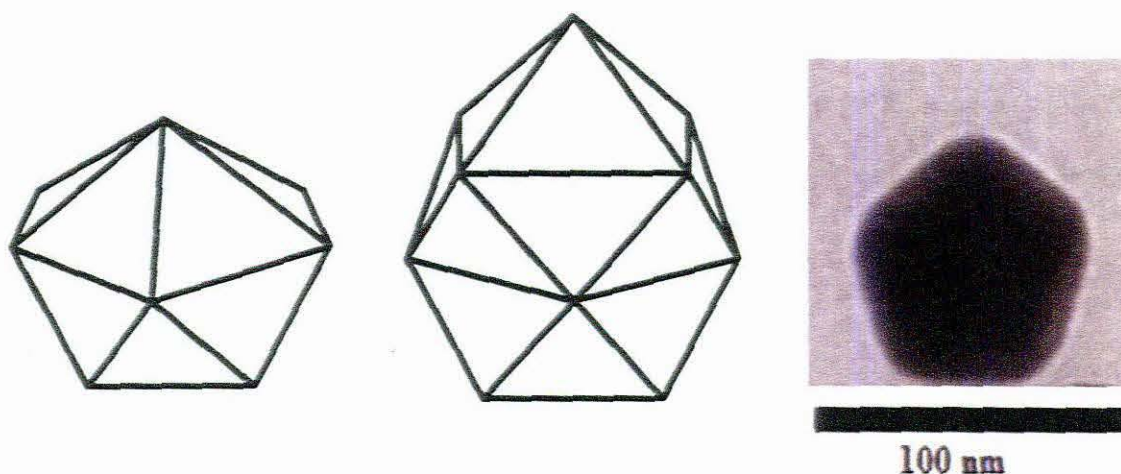


Figure 16 : Structure of pentagonal shaped silver nanoparticles

The most prominent multiply twinned particles (MTP) are decahedron and icosahedron-shaped nanoparticles. The presence of faults and twins in nanoparticles has a significant effect on their optical properties.

2.3.3 Rod-shaped nanoparticles

It is understood that by lowering the precursor concentration, the driving force for nanoparticle growth is reduced. It has been theoretically proven that the multiply twinned

decahedra is the most thermodynamically stable seed particle as it is bound entirely by the lower energy $\{111\}$ crystallographic plane. The low precursor concentration enhances the elongation along the MTP, the thermodynamically stable crystallographic plane (**Figure 17**). Poly(*N*-vinylpyrrolidone) (PVP) is adsorbed onto metal ions first and then acts as an anisotropic confiner to induce and maintain anisotropic crystallography by selective passivation of certain facets. The adsorption depends on the availability of the monomer units (polyvinyl skeleton) with polar groups. The presence of PVP also ensures that the Ag-PVP complex rather than single silver ions are reduced. PVP can also act as a weak reducing agent to reduce silver ions.

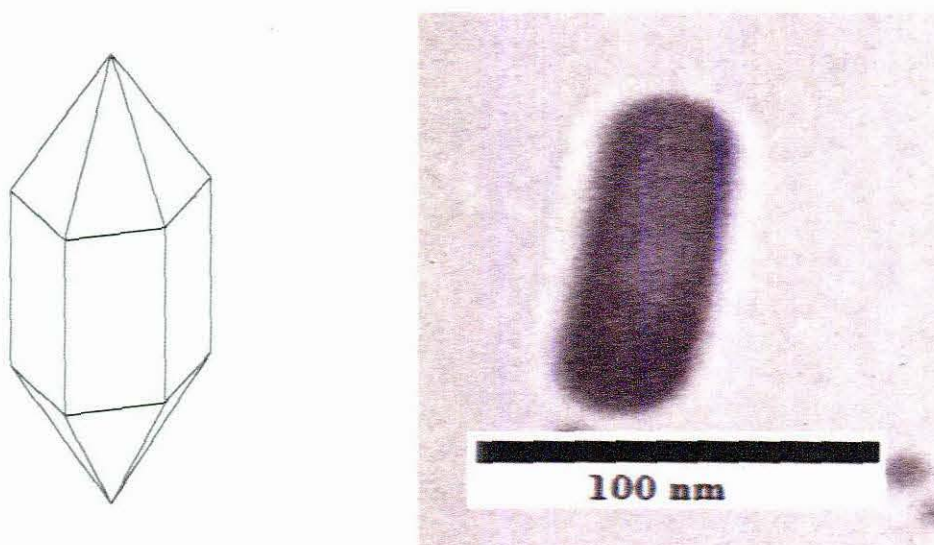


Figure 17 : Structure of rod-like silver nanoparticles

2.4 The Role of PVP in determining Particle Shape

Poly(*N*-vinylpyrrolidone), $(C_6H_9NO)_n$, according to the Sigma-Aldrich database is a component of Denhardt's solution. Throughout the literature, it is employed as a surfactant assisting in the formation of silver nanoparticles. As a surfactant, it has the ability to form micelles whose size is dictated by concentration. This confines and directs nanowire growth. PVP has a polyvinyl skeleton with polar groups (**Figure 18**). The lone pairs of electrons from the nitrogen and oxygen atoms can be used to reduce Ag^+ and form intra- and inter-chain interactions between the PVP and Ag.

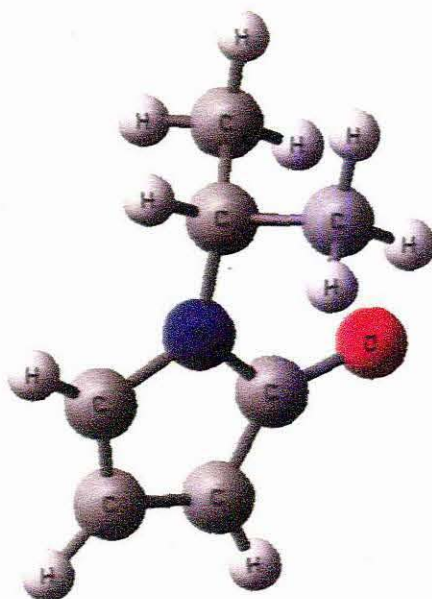


Figure 18 : Structure of the PVP monomer.

Dimethylformamide is a slow reducing agent at room temperature. When DMF is added to a Ag^+ -PVP complex, it reduces silver ions to silver atoms. The silver atoms do not form a strong interaction with the PVP molecule. Due to force fields which exist between atoms, the atoms begin to agglomerate to form colloidal silver particles which are dominated by the $\{110\}$ facet. The $\{110\}$ facet forms a weak interaction with the PVP molecules, resulting in a low binding energy. Silver nanoparticles with a bimodal size distribution will begin to be generated in the reaction. The silver nanoparticles with larger sizes will be able to grow at the expense of smaller ones through agglomeration and Ostwald ripening. As growth continues polygonal particles begin to form which have both $\{100\}$ and $\{111\}$ facets. In the literature [133] it is reported that the PVP molecule can bind more strongly with $\{100\}$ facets and relatively low with $\{111\}$ facets. Since there will be competition between the $\{111\}$ and the $\{100\}$ facets to absorb PVP molecules, certain amounts of PVP molecules will be absorbed on each of the facets, in this case $\{100\}$ facets will absorb more PVP molecules. In the case where a certain amount of PVP is absorbed on the $\{111\}$ facets, a polygonal particle will appear in solution as growth occurs on the $\{100\}$ facets but to a lesser extent than nanowires. In comparison, the interaction between PVP and the $\{111\}$ facets should be much weaker to enable the two ends of the nanorods to grow continuously throughout Ostwald ripening. Once the nanorods form, it can readily grow into long nanowires because its side surfaces are highly passivated by PVP and its ends are largely uncovered and are attracted to new silver atoms or particles.

A high concentration of PVP does not favour the formation of pentagonal and trigonal shaped particles, since a high concentrations leads to the formation of a thick coating over

the entire surface of the spherical particles, including the twin boundaries [134]. This leads to the selective interaction between PVP and various crystallographic planes being lost and thus no anisotropic growth can be induced.

2.5 Shape Evolution of Metal Nanoparticles

There are four main mechanisms involved in the shape evolution of nanoparticles. The four mechanistic stages are sintering, coagulation, particle inception and particle growth. These stages depend on the concentration of the reactants, temperature and surfactants. The surfactant is the most important factors due to its selective adsorption.

2.5.1 Sintering

This is the mechanism by which aggregate particles reduce their surface area while retaining their total mass. This is normally a fast mechanism which gives kinetically favorable nanoparticles.

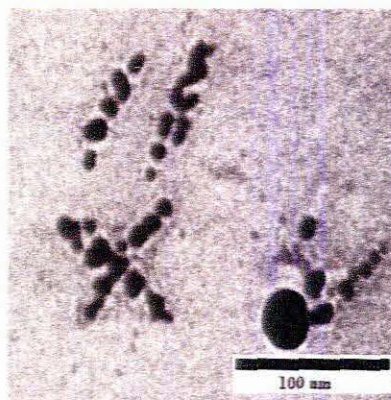


Figure 19 : TEM micrograph showing the sintering growth of silver nanoparticles

The TEM micrograph (**Figure 19**) shows that during sintering, small particles were attracted towards each other. This was prominent with metal nanoparticles synthesized using PVP, as it formed a weak compact layer around the spherical nanoparticles leaving out the metal nanoparticle susceptible to growth. Small particles are involved in this stage of growth as they can easily diffuse through the weak compact interaction of PVP to stimulate kinetic growth.

2.5.2 Coagulation

This mechanism involves two large and unstable metal nanoparticles that come together to form one larger metal nanoparticle. The unavailability of strong surface to PVP interaction contributes to this growth (**Figure 20**).

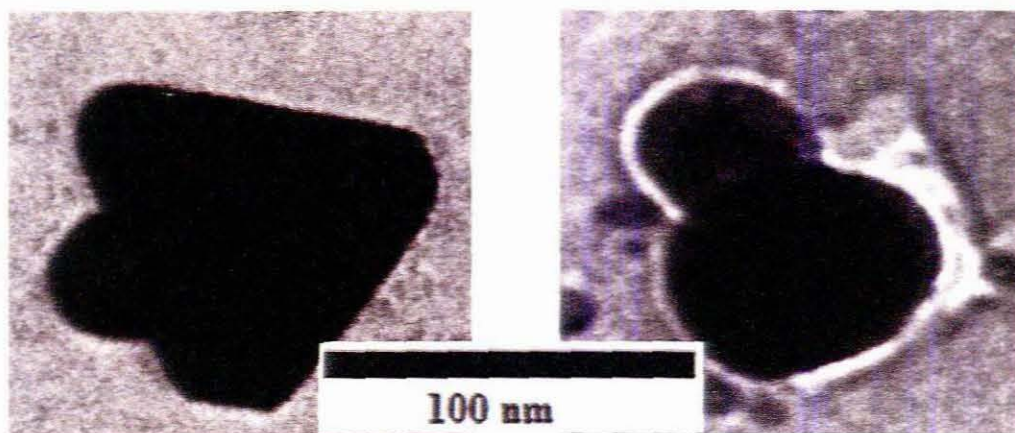


Figure 20 : TEM micrograph showing the coagulation of silver nanoparticles

2.5.3 Particle Inception and Particle Growth

Particle inception is the addition of new smaller particles on grown particles in the form of coagulation. This is the final step where thermodynamic growth becomes prominent (**Figure 21**). In this final stage of growth, the development of geometric nanoparticle shapes appears due to the development of facets which introduce selective interaction with the surfactant. This final stage is very important in nanoparticles synthesis as the morphology is the vital aspect which influences the optical properties.

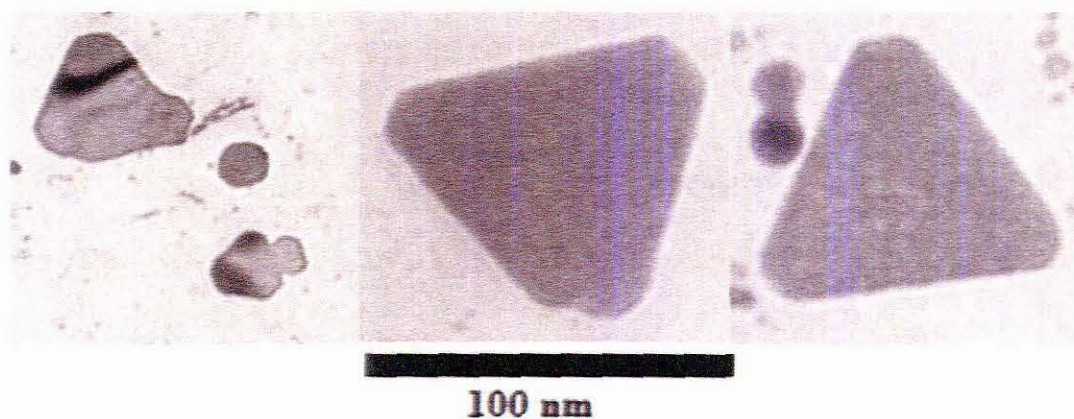


Figure 21 : TEM micrograph for Inception of silver nanoparticles

CHAPTER THREE : SYNTHESIS OF SILVER NANOPARTICLES

3.1 AN IMPROVED N,N-DIMETHYLFORMAMIDE AND POLYVINYL PYRROLIDONE APPROACH TO SYNTHESISE LONG SILVER NANOWIRES

3.1.1 Introduction

Silver, element 47 in the periodic table, is a white lustrous metal. Its inherent properties, such as electrical and thermal conductivity, make it an attractive element for nanotechnology research. Silver nanowires show promise as interconnects in microelectronics, optical, electronic, and magnetic devices [135]. The problem with the synthesis of silver nanowires is the current inability to effectively reproduce the morphology of nanoparticles consistently. The problem is two-fold, (a) the selection of proper reactants in the correct quantities and (b) the technique with which one executes such a procedure. The search for a less expensive, straightforward procedure to synthesize silver nanowires continues with each successive approach leading to silver nanoparticles with higher aspect ratios, greater lengths and smaller diameters.

Liu, *et al.* [136] reported that the formation of silver nanowires could not be completed without a template. Their investigations led them to believe that 1D silver nanostructures needed physical templates, such as carbon nanotubes or zeolites, to define the desired morphology of the nanowire. Their approach used AgBr crystals containing AgNO₃ along with a gelatinous template. Using XRD and TEM, they obtained nanoparticles and

nanowires (30 % yield by weight) with diameters of 80 nm and lengths of 9 μm . They theorized that the gelatin provided the reduced silver with preferential growth direction leading to anisotropic growth. Interestingly, they discovered that the silver comprised of the nanowire originated from the silver nitrate and not the silver bromide crystals. In 2002 Y. Sun, *et al.* [137] described a soft and solution-phase approach that did not require the need to dissolve and disintegrate hard templates that could potentially lead to diminished results. In their experiment, they reduced silver nitrate with ethylene glycol (EG) at 160 $^{\circ}\text{C}$ and subsequently added solutions of silver nitrate and PVP leading to nanowires with diameters between 30–40 nm and lengths up to 50 μm . The formation of silver nanowires centered on preformed seeds from the initial reduction of AgNO_3 in EG which served as both the reducing agent and solvent. PVP served to control the growth directions of the crystalline faces; therefore its concentration was critical to the final morphology. Too high a concentration could lead to isotropic growth. The order in which the PVP and AgNO_3 solutions were supplemented also had an effect on the morphology. Additionally, they reported that seeding with Pt or Ag led to nanowires with larger diameters while longer reaction times enhanced the morphology as well. Finally, they singled out certain variables which affected the growth of silver nanoparticles. Firstly, the ratio between PVP and AgNO_3 was critical. As previously mentioned in Chapter 2, a high ratio between these two components would lead to isotropic growth while a low ratio would lead to an increase in the yield of the final product. Additionally, they proposed that it was advantageous to use only slightly soluble silver salts such as AgBr, AgCl, and AgOH rather than AgNO_3 , since a delayed reaction would support anisotropic rather than isotropic growth. Thus far they have been able to produce nanowires and nanofibers. However, they hit a stumbling block

when it came to reproducibility and finding the proper technique. The dimethylformamide reduction method is a well published route to silver nanoparticles with different morphologies [138,139,140]. Recently, Zhou and co-workers [141] reported the formation of silver nanorods by a solid-liquid phase arc-discharge method and an ultraviolet irradiation-photoreduction method. The microwave polyol reduction method in which the molecular weight of PVP is varied in the presence of nucleation agents such as $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, also produces nanowires [142].

Murphy and co-workers [143] have also synthesized silver nanorods and nanowires by using a rod-like micelle template of cetyltrimethylammonium bromide (CTAB). In this method silver nanoparticles (3-5 nm) were added as seeds to a solution containing silver salt and CTAB. When a weak reducing agent such as ascorbic acid is added, the seeds serve as nucleation sites for the growth of nanorods under the confinement of CTAB. The synthesis of silver nanowires in the absence of seed particles remains a challenge. In this part of the thesis, the synthesis of silver nanoparticles with a variety of shapes ranging from spheres to triangular prisms and wires are reported. The silver nanowires were synthesized by allowing the reactants to stand at room temperature for 30 days without any addition of seed particles. This synthetic method may represent the most promising route to nanostructures in terms of cost, throughput, and the potential of high-volume production.

3.1.2 Experimental

3.1.2.1 Chemicals

Tri-*n*-octylphosphine (TOP) (95 %) and hexadecylamine (97 %), were obtained from Sigma Aldrich. Analytical grade silver nitrate (AgNO_3), dimethylformamide (DMF), formamide and poly(*N*-vinylpyrrolidone) (PVP, MW 30k) were purchased from Merck and used as starting materials, without further purification. All solutions were made up in conductivity water which was purified by a Milli-Q water purification system. Methanol and toluene (analytical grade) were obtained from Sigma Aldrich. All reagents were used as received. Reactions were carried out under nitrogen.

3.1.2.2 Optical properties

A Perkin Elmer Lambda 20 UV-visible spectrophotometer was used for the optical measurements. The analysis was done in silica cuvettes (1 cm path length), using conductivity water as a reference solvent.

3.1.2.3 Electron microscopy

The transmission electron microscopy (TEM) images were obtained using a Philips CM 120 Biotwin TEM. The samples were prepared by placing a drop of dilute sample in conductivity water on a copper grid (400 mesh, agar). The samples were allowed to dry completely at room temperature.

3.1.3.4 Synthesis of Silver Nanowires

In a typical experiment, a measured amount of PVP, and AgNO_3 were separately dissolved in 250 mL of deionised water (see Table 1). Each solution (10 mL) was mixed in a 50 mL vial to form a homogeneous mixture. DMF (10 mL) was then added, and the resultant mixture was left unstirred in the absence of light for 30 days. Excess acetone was added to precipitate the silver nanoparticles followed by centrifugation at 6000 rpm for 10 minutes. Optical and structural analysis was performed on Ag-PVP nanoparticles. The resultant mixture was then refluxed at 100 °C for 1 hour. Visual observation showed that during refluxing the color changed from reddish yellow to dark brown and a further change from dark brown to violet after one hour of reflux. Details on the quantities of reactants used are given in Table 1. The reaction was monitored by UV-visible spectroscopy.

Table 1 : Quantities of the reactants used during synthesis of silver nanoparticles

Sample before reflux	Sample after reflux	Conc. AgNO ₃ (mol/dm ³)	Conc. PVP (g/ml)
Ag-1	Ag-a	0.1	0.005
Ag-2	Ag-b	0.1	0.010
Ag-3	Ag-c	0.1	0.015
Ag-4	Ag-d	0.1	0.020

3.1.3 Results and discussion

For their effective use in applications, the morphology of nanoparticles is as important as the particle size. The particle shape depends on the reaction conditions such as concentration of reagents, reaction temperature and time. A combination of these reaction parameters can result in a variety of particle shapes. In this study we have investigated the role of PVP in the control of particle shape. Spherical silver nanoparticles exhibit a surface plasmon resonance (SPR) band at 350-500 nm with a distinct peak at about 410 nm [144].

In the case of nanowires, two SPR bands occur above and below 400 nm. As the aspect ratio of the rods increases the major longitudinal band shifts to red. When the shape changes to triangular plates or polygonal shaped particles, the SPR band appears in the 550-700 nm region. The occurrence of particles with varying morphologies produced in this study was confirmed by their UV-visible absorption spectra (**Figure 22**).

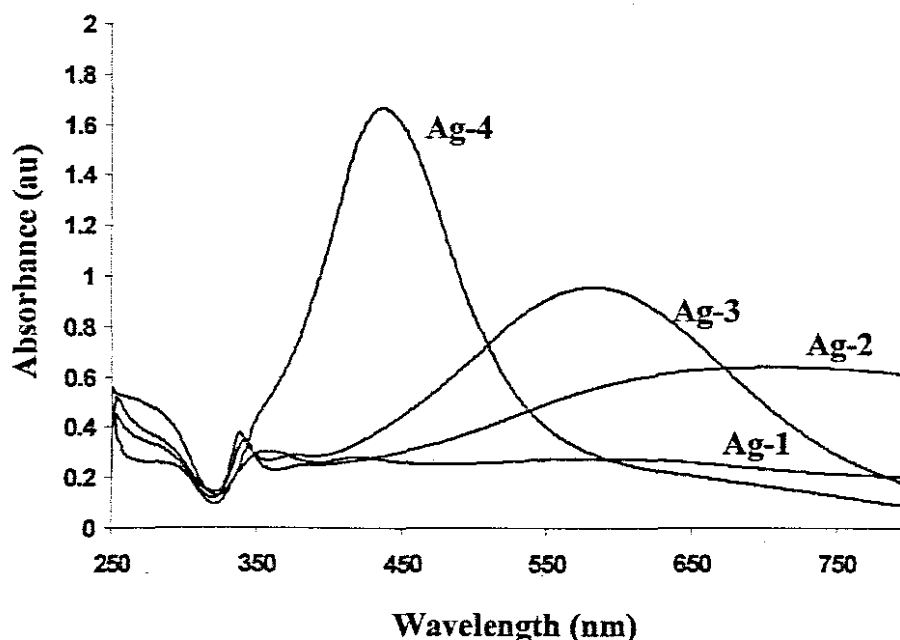


Figure 22 : UV-visible spectra of silver nanoparticles (Ag-1 to Ag-4) before reflux.

It is evident that the shape of the particles varies with the concentration of PVP. **Figure 23 (Ag-1)** shows silver nanoparticles with an anisotropic morphology. The image shows a predominance of particles in the shape of triangular platelets which are interspersed among nanowires with varying widths. For the Ag-1 sample the distinct absorption peak at 354 nm is due to the presence of nanowires. There was also evidence of spherical particles due

to the weak absorption at 413 nm. The broad absorption band in the 550-750 nm regions is typical of polygonal-shaped nanoparticles.

When the concentration of PVP was increased, the presence of triangular shaped particles along with nanowires was observed (**Figure 23, Ag-2**). For Ag-2, the absorption peak (339 nm) due to nanowires was more pronounced. However the broader peak in the 550-750 nm regions provides further evidence for triangular shaped particles. As the concentration of PVP was further increased (Ag-2 and Ag-3) the appearance of isotropic particles was prominent along with the triangular plated particles (Ag-2 and Ag-3). The spherical particles had an average size of $20 \text{ nm} \pm 11\%$. For Ag-3, the prominent peak at 581 nm was due to absorption by triangular shaped particles as confirmed by the TEM image (**Figure 23**). However for the highest concentration (Ag-4) the prominent SPR band at 380-500 nm was indicative of spherical particles. The TEM image of the Ag-4 validates the UV data with spherical nanoparticles clearly visible (**Figure 23, Ag-4**). Particle size distribution graphs were difficult due to the anisotropic shape of the particles. The shape and size of silver nanowires depend upon the adsorption of PVP on the surface of the silver particles. Previous studies have also found that increasing the chain length of PVP resulted in a change of shape of silver nanostructures from 2D plane structures to 1D rod and wire structures [134]. The PVP plays an important role in controlling the growth rate between the {100} and {111} plane directions.

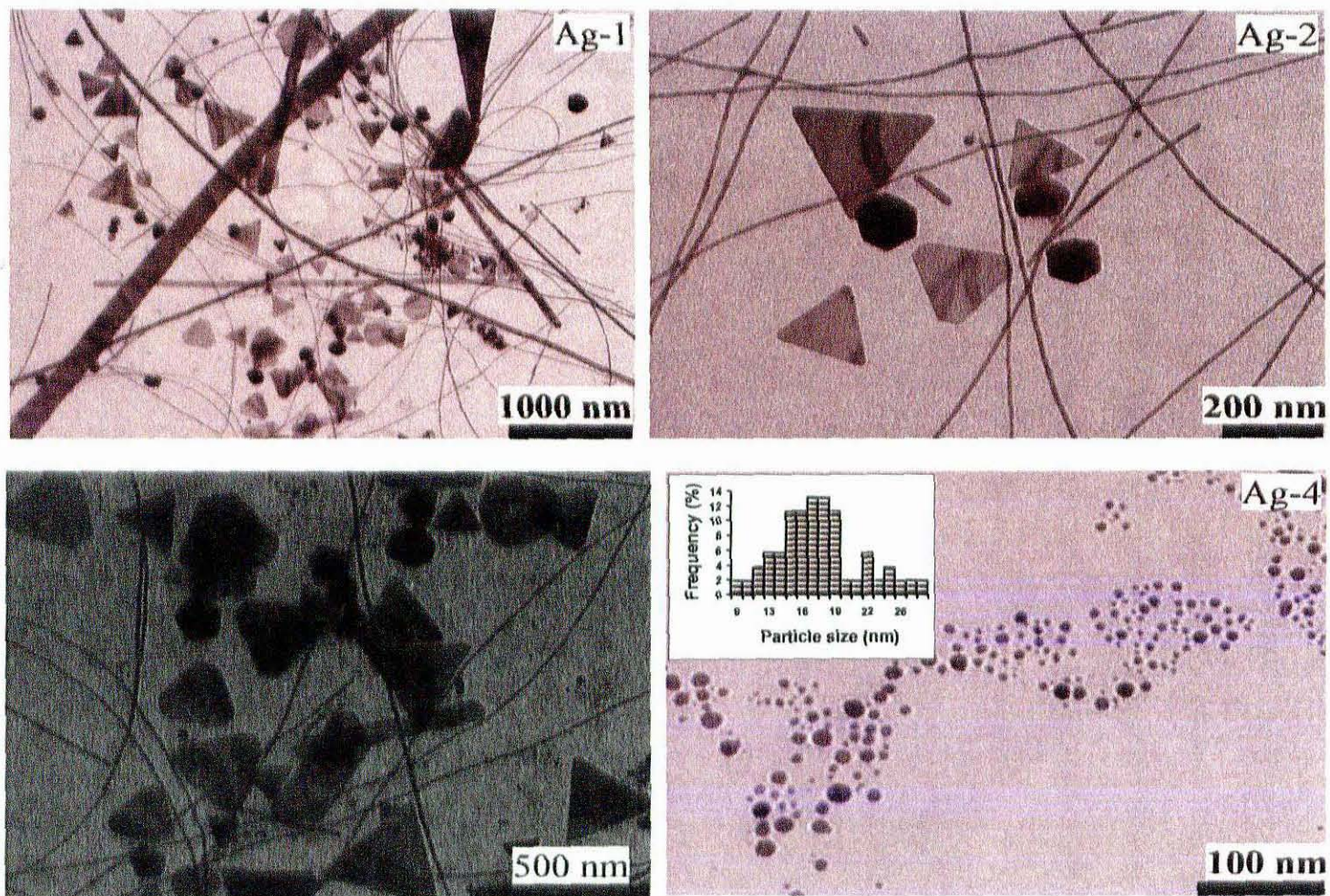


Figure 23 : TEM images of silver nanoparticles before refluxing

Reyes-Gasga *et al.* have proposed that nanowires evolve from a multiply twinned nanoparticle (MTP) of silver with the help of PVP at the initial Ostwald ripening stage [222]. The growth of the nanowires is facilitated by PVP selectively covering the {100} facet. This is done through chemical interactions with the nitrogen and oxygen atoms of the pyrrolidinone units of PVP. On the other hand the interaction between PVP and the {111} facet is weaker when compared to {100} facet, allowing the nanowires to grow continuously during the Ostwald ripening process.

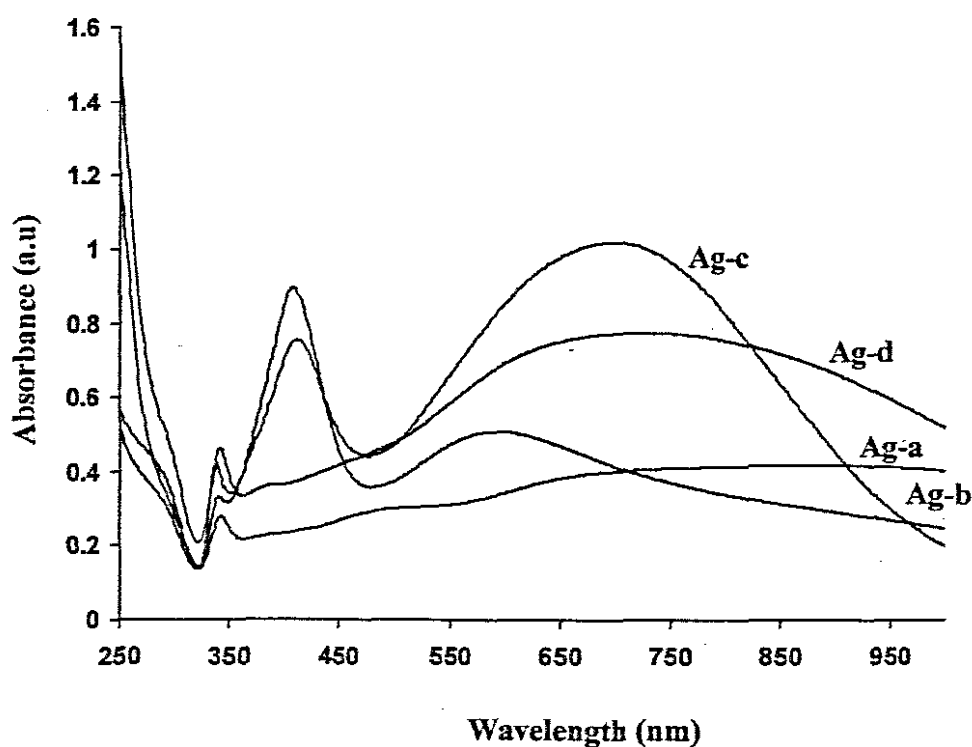


Figure 24 : UV-visible of silver nanoparticles (Ag-a-Ag-d) after reflux.

The rod shaped nanoparticles then grow into wires as new silver atoms continuously join the ends of the nanowire through diffusion. In this study the increase in concentration of

PVP results in a compact layer around the silver atoms which prevents agglomeration thereby favouring the formation of isotropic silver nanoparticles. The mechanism for the formation of silver nanowires is kinetically favourable yet the reaction for the formation of silver nanoplates is both thermodynamically and kinetically favourable. This could be attributed to the formation of silver nanoplates at both room temperature and under reflux conditions, while long silver nanowires are formed at room temperature. The selective adsorption of PVP on the surface of the silver nanoparticles is enhanced at high temperatures and when the reaction was left to proceed for a long time. In order to speed up the growth of silver nanowires, the solution was refluxed. The refluxing of the solution of silver nanoparticles for one hour resulted in subtle changes in the absorption spectra (**Figure 24**). The band at 350 nm, which is as a result of the coherent oscillation of the conduction band electrons when interacting with electromagnetic radiation, is typical of spherical nanoparticles [145]. The broad SPR bands in the 550–700 nm ranges, typical of polygonal shaped particles is observed for the Ag-b to Ag-d samples. The TEM images of all the refluxed samples (**Figure 25**) show the presence of polygonal shaped particles. In particular, triangular-shaped particles were observed in all samples while nanowires were also present in the Ag-c and Ag-d samples.

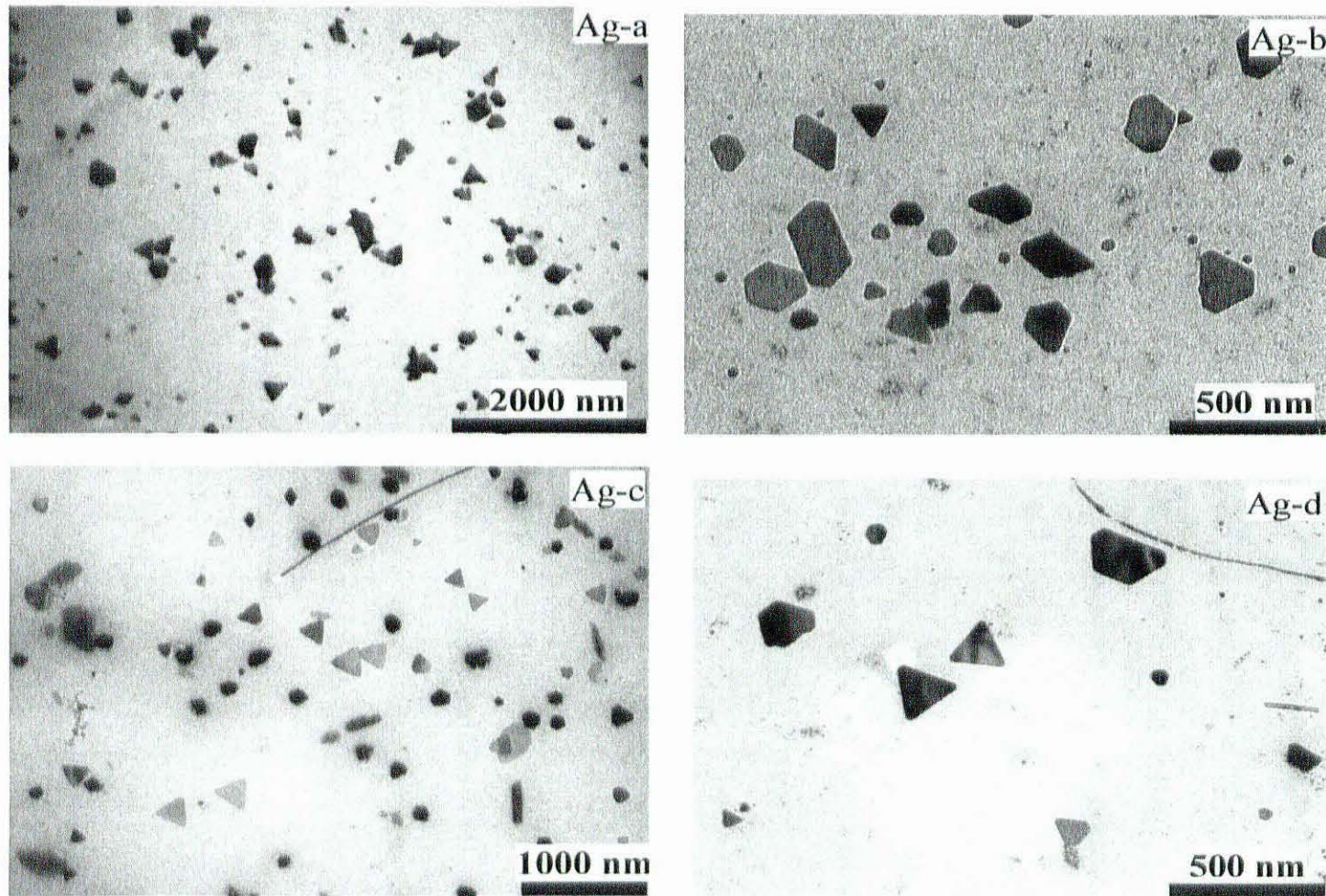


Figure 25 : TEM images of silver nanoparticles (Ag-a-Ag-d) after refluxing

3.1.4 Conclusions

A simple solution method for the synthesis of silver nanowires in PVP is reported. This method proved to be effective in controlling the growth of silver nanoparticles in solution. The study reveals that the PVP and reaction parameters play a vital role in the final shape of the particles. The variation in reaction parameters such as concentration and the refluxing of the reaction solution also results in changes in the optical properties and shape of particles.

3.2 SYNTHESIS OF SILVER NANOPARTICLES IN ALKALINE MEDIUM USING DIMETHYLFORMAMIDE AS THE REDUCING AGENT

3.2.1 Introduction

Among the synthetic methods reported to date, many reducing agents have been exploited which gave silver nanoparticles with variable morphology and size [146]. These reducing agents have been shown to be very active without any promoter to hasten the reduction of silver salt to silver nanoparticles. Depending on the effectiveness of these reducing agents, most of the reactions were carried out at various temperatures and times to achieve reasonable reduction rates. The photo-reduction method has also been utilized as an alternative method to activate the reduction of metal salts to metal nanoparticles [147]. Yet in all these reduction methods, few reports have highlighted the mechanism and kinetics which leads to the reduction of silver salt to silver nanoparticles. In general, it has

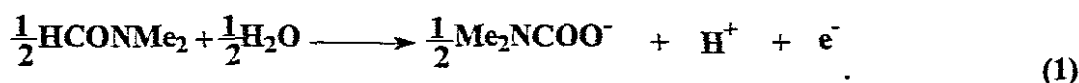
been reported by Lee and co-workers [148] that an increase in the pH could lead to the increase of the aspect ratio of silver nanorods, and this indicated that the pH played an important role in the reduction of silver nanoparticles. A report by Fukuyo and Imai [149] further highlighted this finding that the reduction of silver salt by ascorbic acids is also pH dependant and they confirmed a change in the morphology of silver nanoparticles when the pH of the system was varied. This variation in the morphology was proposed to be the dissociation of ascorbic acid when the pH of the system was varied. Further evidence of the mechanism for formation of silver nanoparticles was revealed by Haung and co-workers [150] when they studied the formation mechanism of silver nanoparticles in a basic 2-propanol system in which they detected the presence of Ag_2O . With all these systems in mind, this part of the work highlights the synthesis of silver nanoparticle with NaOH as a promoter where DMF was used as reducing agent and PVP as a stabilizer.

3.2.2 Experimental procedure

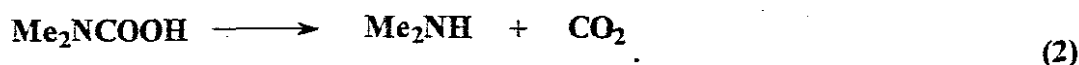
AgNO_3 (2 mL, 0.1 M) was mixed with 2 mL of PVP (0.1 g/mL, MW=30k) and 10 % DMF (V/V), and 0.5 mL of NaOH (0.1 M) was added as a promoter. Conductivity water (10 mL) was added to the reaction mixture. The mixture was then refluxed at 75 °C for half an hour. The solution changed from colourless to blue. The mixture was allowed to cool and three times the volume of acetone was added to precipitate nanoparticles. The precipitated solution was centrifuged at 6000 rpm for 15 minutes, and washed three times with acetone. The precipitate was dissolved in conductivity water for optical property measurements.

3.2.3 Results and discussion

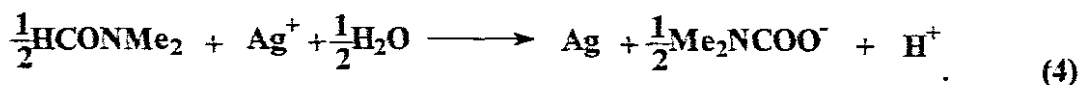
It has been demonstrated that the addition of alkaline solution is vital for the reduction process of numerous metallic ions [151]. It is believed that from the thermodynamic point of view, the reducing power of a reagent can be compared to the fundamental principle of its reducing potential [152]. The addition of NaOH can enhance the reduction power of DMF. It has also been reported that the reduction power of formaldehyde can be increased by the addition of NaOH [151]. The half reactions which are involved in the reduction of silver nitrate using DMF as a reducing agent are as follows:



The carbamic acid can easily decompose as:



The overall reaction for (1) to (3) is,



According to (4) the rate of change of silver ions can be expressed as follows:

$$-r_{\text{Ag}^+} = -\frac{d[\text{Ag}^+]}{dt} = k[\text{Ag}^+][\text{HCONMe}]^{1/2} \quad (5)$$

Since the concentration of the reducing agent varies proportionally with the silver ions can be simplified to :

$$-r_{Ag^+} = k[Ag^+]^{3/2}. \quad (6)$$

After integration, one then obtains the working equation as:

$$1/[Ag^+]^{0.5} = kt + a \quad (7)$$

The rate constant k can be obtained from the slope of a plot $1/[Ag^+]^{0.5}$ versus time. The reduction can be achieved in the presence of a strong base (NaOH) that acts as a promoter. When this reaction occurs there is the immediate formation of dark unstable colloids which are attributed to Ag_2O (8). This reduction gives silver nanostructures which exhibit anisotropic shapes which were confirmed by the TEM measurements as shown in **Figure 26**. At the initial stage (5 minutes) of the reduction of silver nitrate in the presence of NaOH, the TEM micrograph in **Figure 26A** revealed that the silver nanoparticles were in the shape of dendritic structures which were unstable. The UV-visible of silver nanoparticles prepared showed a broad plasmon resonance at 440 nm (**Figure 26C**) which symbolized the reduction of the silver ion to silver nanoparticles, confirmed by the quick appearance of the yellow color. Upon leaving the reaction from 20 to 30 minutes there was the slow appearance of silver nanorods (**Figure 26C**). The presence of anisotropic particles was further proved by the appearance of two absorption peaks, one blue-shifted and other red-shifted, this was an important indication of rod-like silver nanoparticles as discussed in Chapter 2, where the two peaks at 430 nm and 700 nm indicated absorption of the transverse section and the longitudinal section respectively. When the same solution was

refluxed for 30 minutes, there was further development of the clear rod silver nanoparticles. The formation of these nanoparticles is clearly shown in TEM image in **Figure 26D**. More evidence was revealed by UV-visible spectrum, which again showed two surface Plasmon resonance peaks at 425 nm and 560 nm, both these peaks again were the representation of the plasmon resonance of the transverse and longitudinal sectional part of the nanorods respectively.

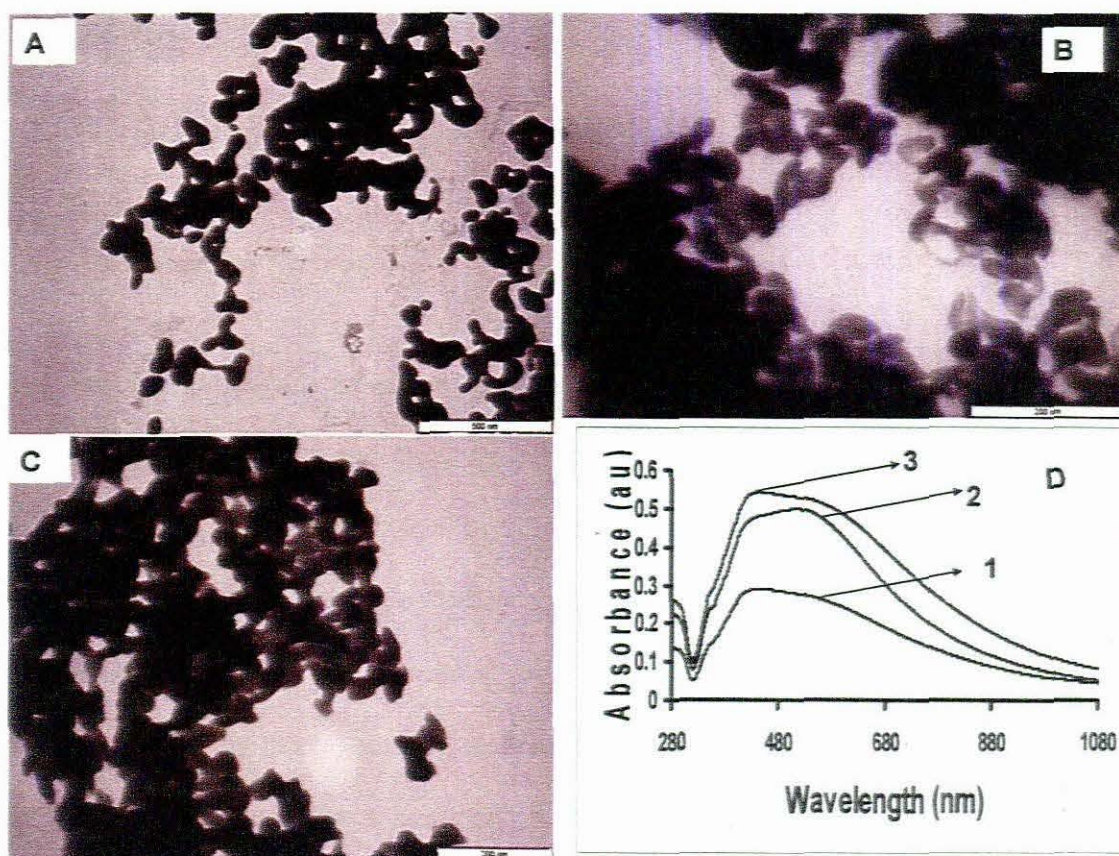


Figure 26 : TEM micrograph of silver nanorods formation, A = after 5 min, B after 20 min, C after 30 minutes and D is the UV-visible spectra for 1=A, 2=B and 3=C.

3.2.4 Conclusions

The addition of NaOH helped to speed up the reduction of silver ions which led to the formation of anisotropic silver nanoparticles. The amount of alkaline materials influenced the speed of the reduction process. It can also be suggested that the alkaline material may be involved in three reaction steps: (a) reduction of silver ions, (b) water hydrolysis and (c) dissociation of PVP molecules.

3.3 SYNTHESIS OF SILVER NANODENDRITES

3.3.1 Introduction

The intrinsic properties of metal nanoparticles are determined by their size, shape, composition, crystallinity and structure. In principle, one could control any one of these parameters to fine tune the properties of these nanoparticles. The various reported methods for metal nanoparticle synthesis employ surface passivation reagents such as polymers to prevent aggregation. The shape of the particles can be controlled by varying the concentration of the parent starting reagents and passivation agents. Silver nanodendrites are of considerable interest because of their large surface area that provides good connectivity, which makes them useful in applications such as biosensors, chemical sensors, plasmonics and superhydrophobic films [153,154,155]. Qiu *et al.* [156] demonstrated the fabrication of Ag dendrites by an aqueous chemical route based on the spontaneous galvanic displacement between Ag ions and metal solids under hydrothermal conditions. Ye and co-workers [157] reported the fabrication of silver dendrites on silicon

wafers via an electroless metal deposition technique. A very interesting technique for the synthesis of silver dendrites by an electrochemical approach in aqueous solution in the presence of DNA was reported by Chen and co-workers [158]. The dispersion property of DNA enhanced the stability of silver dendrites with the basic units of DNA reportedly interacting with the silver particles to enhance the surfactant properties [158]. A mixed surfactant system of cetyltrimethylammoniumbromide (CTAB) and sodium dodecyl sulfate (SDS) was reported by Zheng and co-workers for the synthesis of silver nanowires and silver dendrites in an aqueous medium [159]. This part of the thesis reports the solution synthesis of silver nanotrees in the presence of PVP at room temperature using formamide as the reducing agent.

3.3.2 Experimental Procedure

The procedure as reported by Mdluli and Revaprasadu [160] was adapted to synthesize silver nanodendrites. In a typical experiment, a measured amount of PVP, and AgNO_3 were separately dissolved in 250 mL of deionised water. Each solution (10 mL) was mixed in a 50 mL vial to form a homogeneous mixture. Formamide (10 mL) was then added, and the resultant mixture was left unstirred in the absence of light for 30 days. Excess acetone was added to precipitate the silver nanoparticles, followed by centrifugation at 6000 rpm for 10 minutes. Optical and structural analyses were performed on the solution sample of the particles. The solution was not refluxed further. Details on the quantities of reactants used are given in Table 2. The growth of nanoparticles was monitored by UV-visible spectroscopy.

Table 2 : Quantities of the reactants used during synthesis of silver nanotrees

Samples	Conc. of AgNO ₃ (mol/dm ³)	Conc. of PVP (g/ml)
Ag-1a	0.1	0.005
Ag-2b	0.1	0.010
Ag-3c	0.1	0.015
Ag-4d	0.1	0.020

3.3.3 Results and discussion

We have previously reported the synthesis of silver nanowires in PVP using DMF as a reducing agent [160]. The nanowires formed after a long period (30 days) when the reaction mixture was left to stand at room temperature and the concentration of PVP is varied. In this work, by replacing DMF by formamide we observed a similar trend whereby silver nanodendrites are formed after a period of time by varying the concentration

of PVP. At a low concentration of PVP we observed isotropic silver nanoparticles. The particles were in the 20-30 nm size range (Figure 27, NTa). When the concentration of PVP is increased from 0.05 to 0.01 g/mL, hexagonally shaped particles appear.(Figure 27, NTb). At the PVP concentration of 0.015 g/mL, there is further evidence of anisotropic nanoparticles, with isotropic particles also present (Figure 27, NTc). The anisotropic coagulate with the isotropic nanoparticles. At a high concentration (0.020 g/mL, PVP) after 30 days dendritic or tree-like structures are observed (Figure 28, NTd). The nano-trees are composed of a long central trunk and numerous rows of secondary branches which are interconnected to the central trunk. These secondary branches are approximately 100 nm in length. The branches are equivalently separated at an angle of 65° with respect to the central trunk. The particles are very stable at room temperature and can be redispersed in aqueous media without losing their shape.

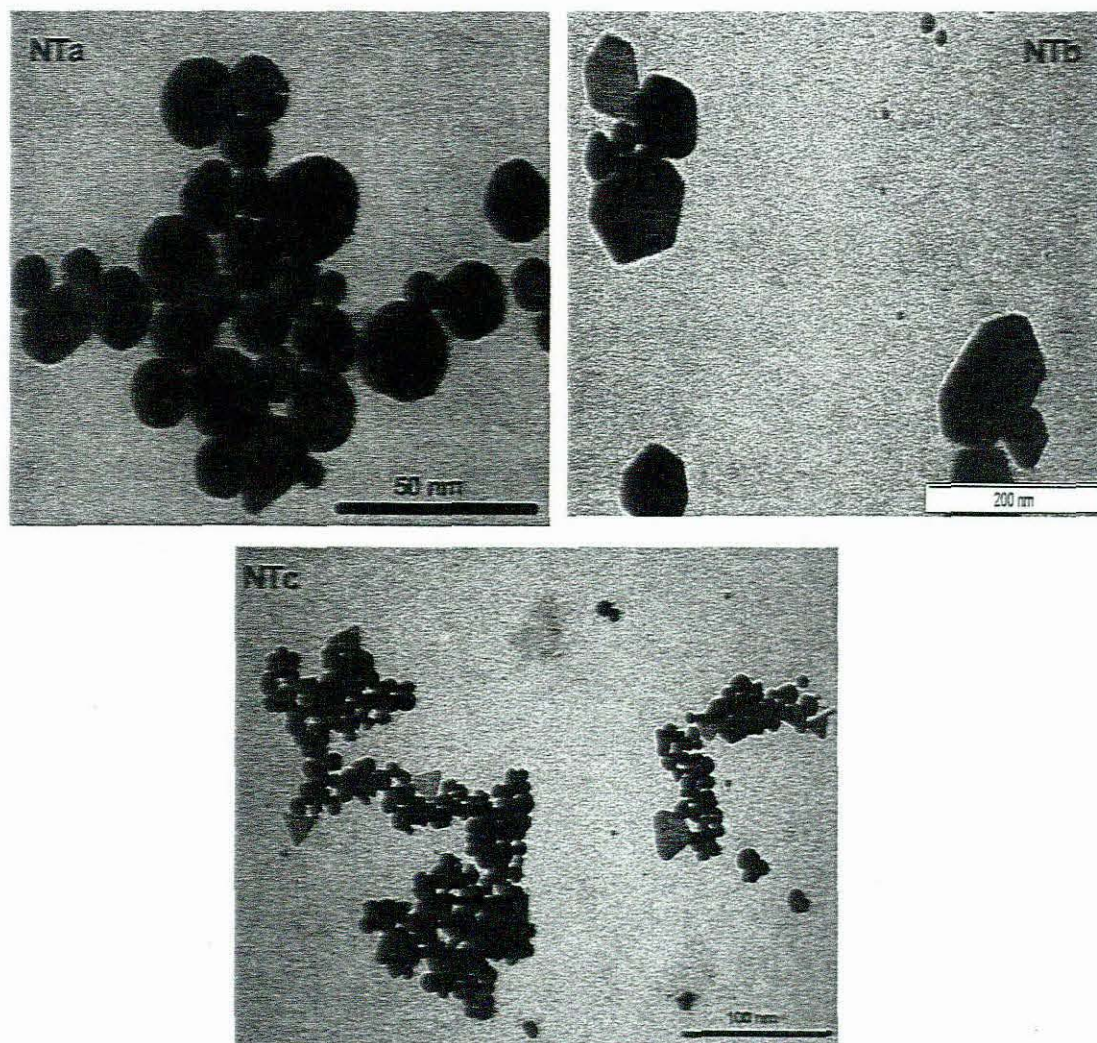


Figure 27 : TEM images of silver nanoparticles at PVP concentrations of (NTa) 0.005 g/mL, (NTb) 0.010 g/mL and (NTc) 0.015 g/mL

It is believed that the growth mechanism of the dendritic or tree-like structures follows a diffusion-limited aggregation (DLA) mode [161]. Cluster formation occurs by particles sticking together along a random path to a selected seed in allowing the particles to form a growing structure. The PVP provides significant control over the nucleation and directional aggregation which gives rise to a non-equilibrium system thereby favouring the

formation of silver dendrites [162,163]. Dendritic growth occurs at the tips and stem of branches. As the stem grows in length new shorter branches are formed continuously at the tips.

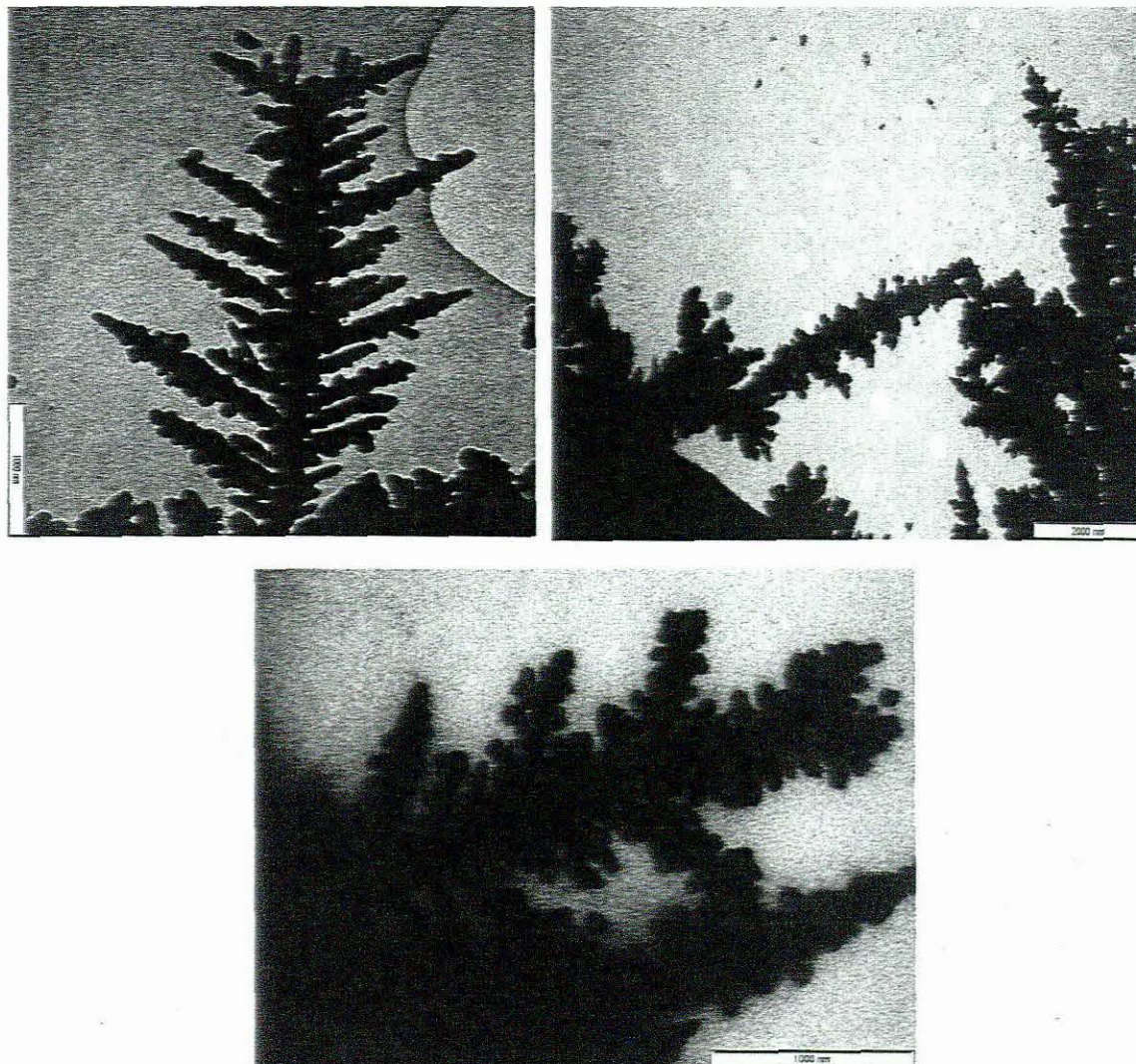


Figure 28 : TEM images of silver nanoparticles at PVP concentration of 0.020 g/mL (NTd)

Formamide is a very slow reducing agent which is expected to favour the formation of dendritic structures. The growth of silver nanodendrites is obtained when silver precursor is reduced to form silver isotropic nanoparticles which coagulate to form anisotropic structures, as the concentration of the PVP is increased (**Figure 29**). The anisotropic silver nanoparticles arrange themselves in a linear shape which provides the reaction environment for the formation of a trunk. As thermodynamic growth occurs there is physical adsorption of the diffusing nanoparticles once they are in contact with each other. The PVP forms a very weak interaction with the isotropic nanoparticles which influences the gradual growth of silver nanoparticles either in the form of nanowires or nanodendrites depending on the strength of the reducing agents used. The interaction of PVP with the surface of silver nanoparticles should be strong so that any diffusion of silver atoms is prevented from enhancing growth of silver nanoparticles. The PVP does not execute its role as a surfactant very efficiently allowing diffusion of new particles into the surface of the existing particles thereby allowing formation of the new tree-like structures when the reaction is left unstirred for a long period.

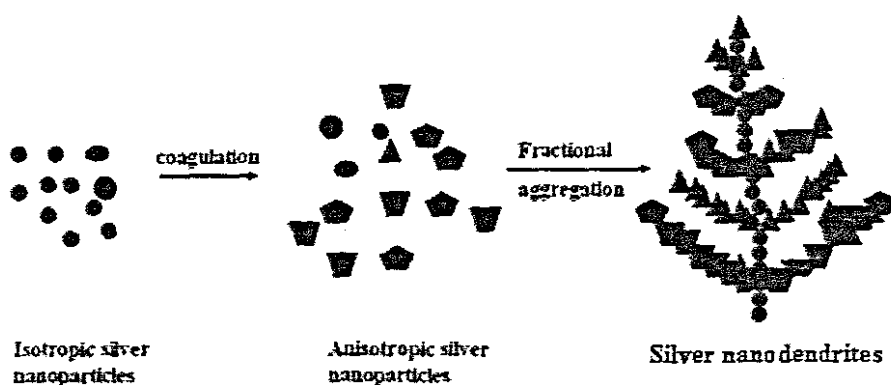


Figure 29 : Proposed route to formation of silver nanodendrites

It is known that the main optical response of plain spherical silver nanoparticles is often

shown by a single absorption band attributed to the surface plasma resonance, whereas, the absorption band of 1D silver or silver nanostructures splits into two resonance bands and as the aspect ratio increases, the long wavelength plasmon band exhibits a red shift [160].

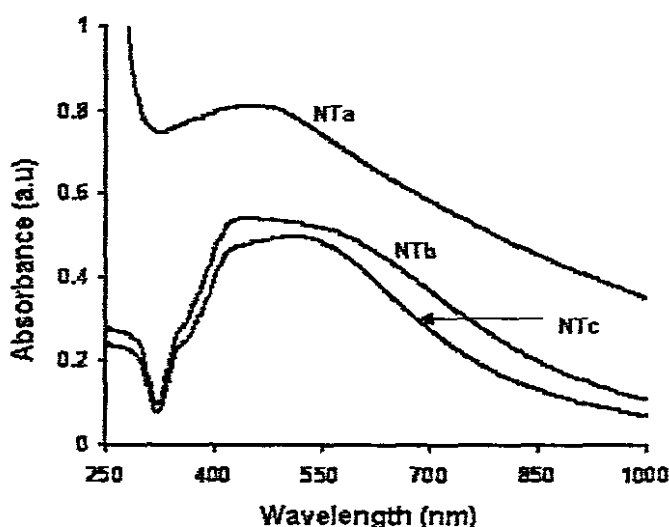


Figure 30 : Absorption spectra of silver nanoparticles at PVP concentrations of (NTa) 0.005 g/mL, (NTb) 0.010 g/mL and (NTc) 0.015 g/mL

The absorption spectrum of the silver nanoparticles synthesized at low concentration of PVP (0.010 g/mL) shows a broad band around 420 - 450 nm with a tail (Figure 30, NTb). The absorption band at *ca.* 520 nm becomes broader and more distinct as the concentration is increased. The broad absorption peak has two maxima, one at 420 nm indicative of spherical silver nanoparticles and a second peak at *ca.* 550 nm due to the presence of, anisotropic particles (Figure 31, NTc). The two resonance bands at 450 nm and 569 nm indicate that both isotropic and anisotropic particles are present.

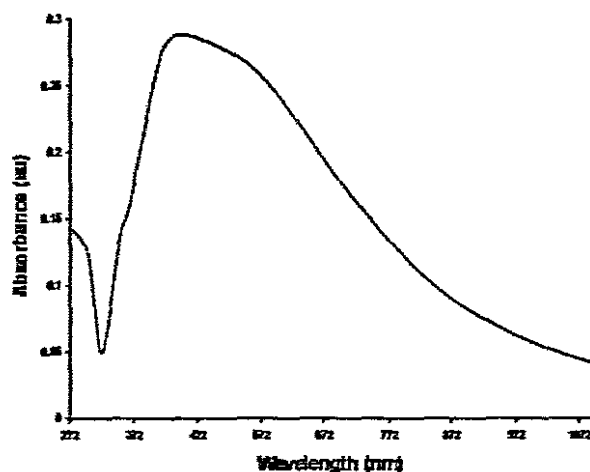


Figure 31 : UV-visible spectrum of PVP-capped silver at concentration of 0.020 g/mL.

3.3.4 Conclusions

A simple solution synthesis of silver nanodendrites in which silver nitrate is reduced by formamide in PVP is reported. It is found that time and the concentration of PVP play an important role in controlling the growth morphology of the silver particles. Low concentrations of PVP yield isotropic particles whereas high concentrations of PVP after an extended period gives particles in the shape of dendrites. The role of the PVP and the reducing agent is critical in the evolution of the particle shape. The UV/Vis spectra of the particles at various concentrations confirm the existence of particles with varying morphologies.

3.4 SYNTHESIS OF TOPO- AND HDA-CAPPED SILVER NANOPARTICLES USING COMPLEXES OF N-(DIISOPROPYLTHIOPHOSPHORYL) THIOUREA DERIVATIVES

3.4.1 Introduction

The use of single molecular precursors is a common route to synthesize nanostructured materials. Various semiconductor nanoparticles have been synthesized from precursors containing both the elements of the final compounds. [164,165,,166] The reactions are typically carried out at high temperatures, whereby the precursors are decomposed in high boiling point solvents. Examples of these coordinating solvents include alkyl phosphates, alkyl phosphites, pyridine, alkyl amines and furans. [59] The systematic adjustment of the reaction parameters, such as reaction time, temperature, concentration, and the selection of reagents and surfactants, can be used to control the size, shape and quality of the nanoparticles. [167,168,169] There have been relatively few reports for the use of sophisticated precursors to synthesize metal nanoparticles at high temperatures. Solution based routes whereby readily available metal salts are reduced at room temperature in the presence of stabilizing agents to give surface stabilized metal particles is the most commonly reported route to metal particles. The dimethylformamide reduction method is a well published route to silver nanoparticles with different morphologies [138,139,140,160]. Recently, Zhou and co-workers [141] reported the formation of silver nanorods by a solid-liquid phase arc-discharge method and the ultraviolet irradiation-photoreduction method.

The microwave polyol reduction method, in which the molecular weight of PVP is varied in the presence of nucleation agents such as $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, also produces nanowires [142]. Murphy and co-workers [143] have also synthesized silver nanorods and nanowires by using a rod-like micelle template of cetyltrimethylammonium bromide (CTAB).

Green and co-workers [170] reported the synthesis of trialkyl-phosphine oxide/amine stabilized silver nanocrystals. Recently, Nath *et al.* [171] have reported the synthesis of hexadecylamine (HDA)-capped silver organosols which were reproducibly stable for over a year. A well developed synthesis for monodispersed silver nanoparticles has been the focus for many chemists such as Chen *et al.* [172], who developed a very important method for the synthesis of monodispersed silver nanoparticles using tri-octylphosphine (TOP) as a reducing agent, solvent, and surfactant.

There have been many complexes of *N*-(thio)phosphorylated (thio)amides and (thio)ureas $\text{RC(X)NHP(Y)R}'_2$ ($\text{X, Y} = \text{O, S}$) (**HL**) with various metal cations previously reported [173,174]. However, only several studies about complexes of **HL** with coinage metals were published [175], and references therein, [176,177,178,179,180]. Among the reported coinage metal complexes, those containing the silver(I) cation are however scarcely represented [175]. This could be due to the propensity of Ag(I) to reduce up to Ag(0) and thus special methods need to be used especially for polynuclear Ag(I) complexes synthesis with **HL**. However, mononuclear Ag(I) complexes with the same type of ligands are easy to synthesize and isolate. Additional donor ligands associated with these complexes (e.g. PPh_3) prevent reduction of Ag(I) . Thus, Ag(I) complexes of **HL** (**Figure 32**) might be

good precursors for silver nanomaterial synthesis because they contain both the metal and chalcogenide in one molecule. But the **HL** ligand composition and structure [173], in turn, could lead to different nanomaterials formation. In this part of the work the synthesis of HDA-capped nanoparticles and thin films of silver using Ag(I) complexes of **HL** complexes as single-molecule precursors is described. The nanoparticles synthesized using this method have the desired properties of good stability and lack of aggregation.

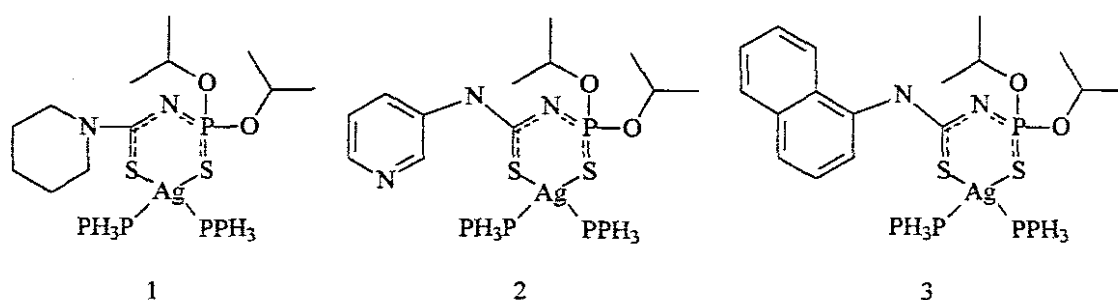


Figure 32 : N-(diisopropylthiophosphoryl)thiourea complexes

3.4.2 Experimental

3.4.2.1 General Synthesis of Silver Complexes (1, 2 and 3)

Silver complexes (1, 2 and 3) as shown in Figure 32 were synthesized following a general method reported by Sokolov *et al* [181]. In this synthesis, [Ag(PPh₃)₂NO₃] was used as a silver source which is prepared by reacting silver nitrate with triphenyl phosphine in acetonitrile, followed by recrystallization in chloroform [182]. The [Ag(PPh₃)₂NO₃] is then coordinated with N-thiophosphorylated thioureas to form silver complexes (Figures 33) in an alkaline medium.

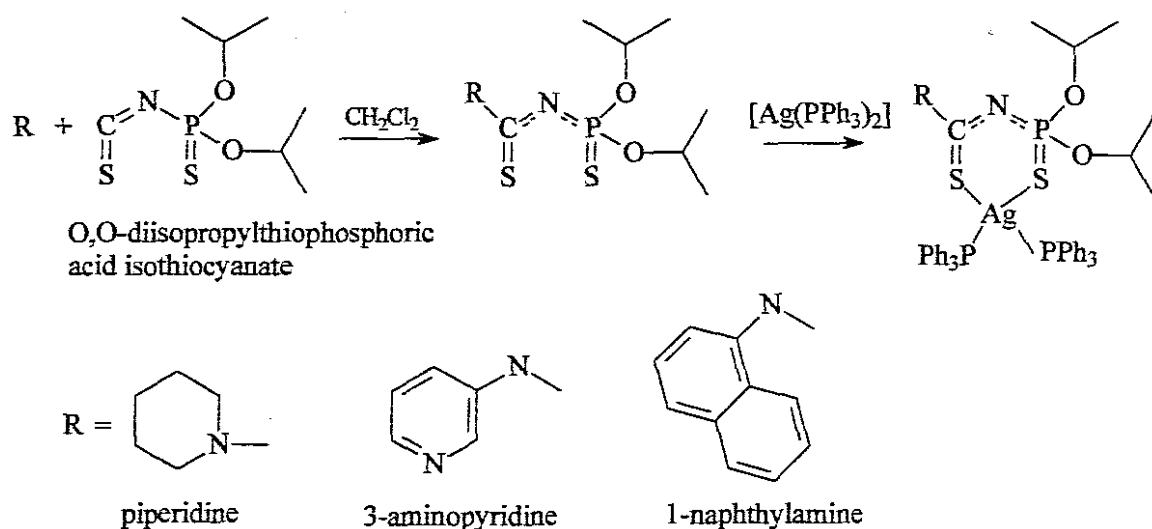


Figure 33 : Scheme for the synthesis of N-(diisopropylthiophosphoryl)thiourea complexes

3.4.2.2 Synthesis of ligand 1 from piperidine

A solution of piperidine (1.0 g, 12 mmol) in chloroform (25 mL) was added dropwise to a solution of O, O-diisopropylthiophosphonic acid isothiocyanate (3.1g, 13 mmol) in the same solvent (15 mL). The mixture was stirred at room temperature for 5 hours. The solvent was then removed *in vacuo*. The residue was recrystallized from dichloromethane-*n*-hexane mixture 1:5 (v/v). The product was obtained as colorless crystals. Yield: 3.2 g, 80 %. m.p. = 84 °C. Anal. Calculated for $\text{C}_{12}\text{H}_{24}\text{N}_2\text{O}_2\text{PS}_2$ (Mr = 323.1): C 44.56; H 7.48; N 8.66. Found: C 44.45; H 7.73; N 8.59.

3.4.2.3 Synthesis of ligand 2 from 3-aminopyridine

This complex was prepared in a similar manner to that described for ligand 1 but with 3-aminopyridine (1.02 g, 12 mmol). The product was obtained as colorless crystals. Yield: 2.6 g, 87 %. m.p. = 112 °C. Anal. Calculated for $C_{12}H_{18}N_3O_2PS_2$ (331.3): C 43.49; H 5.47 N; 12.68. Found: C 43.50; H 5.43; N 12.65.

3.4.2.4 Synthesis of ligand 3 from 1-naphthylamine

This complex was prepared in a similar manner to that described for ligand 1 and 2 but with 1-naphthylamine (1.05 g, 12 mmol). The product was obtained as colorless crystals. Yield: 2.9 g, 86 %. m.p. = 120 °C. Anal. Calculated for $C_{21}H_{21}N_2O_2PS_2$ (380.5): C 53.67; H 5.56; N 7.36. Found: C 53.70; H 5.59; N 7.33.

3.4.2.5 Synthesis of Complex 1

A suspension of ligand 1 (0.978 g, 3 mmol) in ethanol (25 mL) was mixed with an ethanol solution of KOH (0.185 g, 3.3 mmol). A dichloromethane (25 mL) solution of $[Ag(PPh_3)NO_3]$ (2.93 g, 3 mmol) was added drop-wise under vigorous stirring to the resultant potassium salt. The mixture was stirred at room temperature for a further one hour and the precipitate was filtered off. The filtrate was concentrated until crystallization began. The residue was recrystallised from a dichloromethane-*n*-hexane mixture 1:5 (v/v). Complex 1 was obtained as colorless crystals. Yield: 1.917 g, 72 %, m.p. = 148 °C. Anal.

Calculated for $C_{48}H_{54}AgN_2O_2P_3S_2$ (955.88): C 60.31; H 5.69; N 2.93. Found: C 60.30; H 5.68; N 2.89.

3.4.2.6 Synthesis of Complex 2

Complex 2 was prepared in a similar manner to that described for complex 1 but with ligand 2 (0.768 g, 3 mmol). Complex 2 was obtained as colorless crystals. Yield: 2.074 g, 80 %, m.p. = 120 °C. Anal. Calculated for $C_{48}H_{48}AgN_3O_2P_3S_2$ (963.84): C, 59.82; H, 5.02; N, 4.36. Found: C, 59.80; H, 5.03; N, 4.34.

3.4.2.7 Synthesis of Complex 3

Complex 3 was prepared in a similar manner to the method that is described for complex 1 but with ligand 3 (1.038 g, 3 mmol). Complex 3 was obtained as colorless crystals. Yield: 2.186 g, 75 %, mp = 121 °C. Anal. Calculated for $C_{53}H_{51}AgN_2O_2P_3S_2$ (1012.91): C, 62.85; H, 5.07; N, 2.77. Found: C, 62.83; H, 5.08; N, 2.73.

3.4.2.8 Synthesis of HDA-capped silver nanoparticles

Silver complexes (1, 2 and 3) (0.03 mol) were each dissolved in TOP (6 mL) and injected into hot HDA (6 g) at 150 °C. An initial decrease in temperature from 150 °C to 130 °C, was observed. The solution was then allowed to stabilize and reaction was then allowed to continue for 45 minutes at 150 °C. After the reaction was completed, it was allowed to cool down to 70 °C, and methanol added to precipitate the nanoparticles. The solid was separated by centrifugation, and washed three times with methanol. The resulting solid

precipitates of HDA-capped silver nanoparticles were dispersed in toluene for further analysis.

3.4.2.9. Synthesis of TOPO capped silver nanoparticles

Silver complexes (**1, 2 and 3**) (0.3 g) were each dissolved in TOP (6 mL) and injected into hot TOPO (6 g) at 150 °C. An initial decrease in temperature from 150 °C to 130 °C was observed. The solution was allowed to stabilize, and then allowed to continue for 45 min at 150 °C. After completion of the reaction, it was allowed to cool down to (70 °C) and methanol was added to precipitate the nanoparticles. The solid was separated by centrifugation, and washed three times with methanol. The resulting solid precipitates of TOPO-capped silver nanoparticles were dispersed in toluene for further analysis.

3.4.3 Results and Discussion

3.4.3.1 HDA and TOPO-capped Silver Nanoparticles

The reduction of silver complexes (**Figures 34A-36A**) at 150 °C in HDA resulted in the fast reduction of the silver complexes and growth of silver nanoparticles. The HDA acts as the capping agent, which gives the silver nanoparticles stability over time. The absorption spectra of all HDA capped silver nanoparticles (**Figures 34B-36B**) exhibit a strong absorption band in between 400 - 420 nm region. The appearance of this light absorption of metallic nanoparticles is due surface plasmon resonance (SPR) as discussed in Chapter 2. The resonance can be influenced by the size shape and dielectric constant of the medium in

which the nanoparticles are dissolved [143]. This SPR phenomenon has been extensively studied in other related papers and can be predicted by the Mie theory [183,184,185].

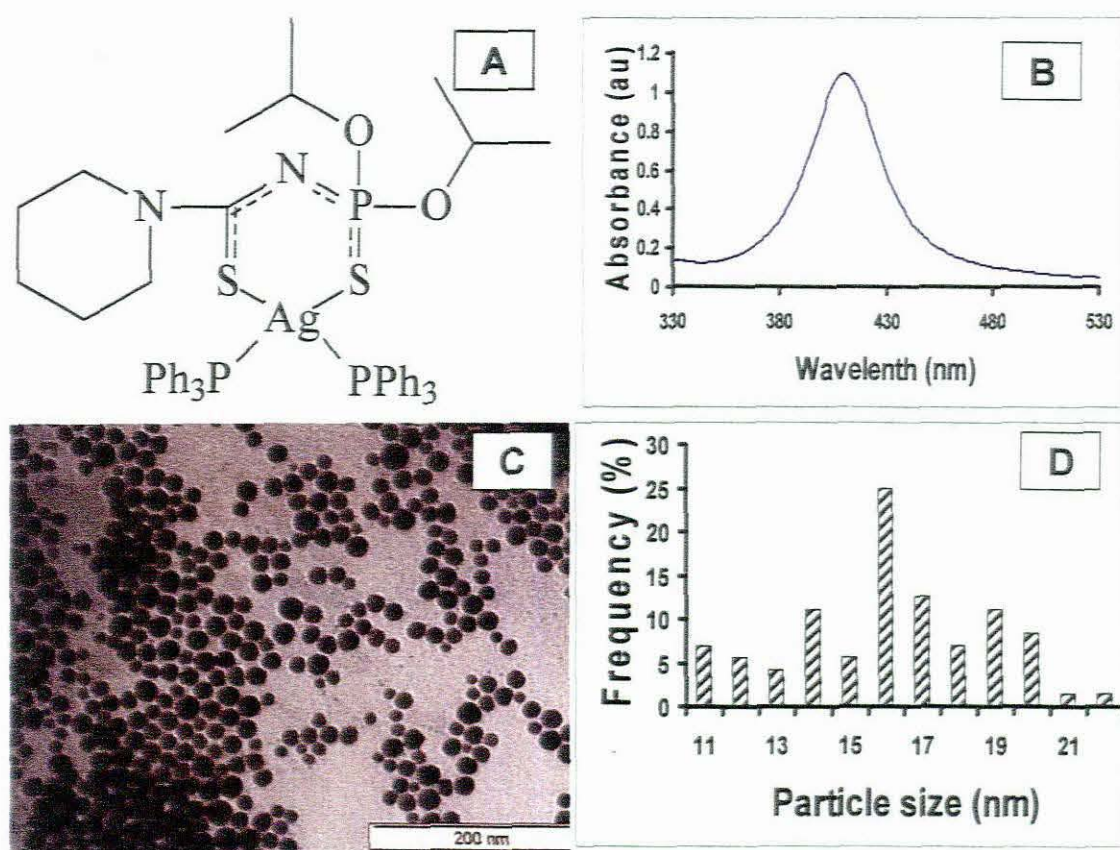


Figure 34 : HDA capped silver nanoparticles from (A) Complex 1, (B) Absorption spectrum, (C) TEM image and (D) particle size distribution

From their TEM images (Figures 34C-36C) the HDA-capped silver nanoparticles obtained from all complexes are close to spherical in shape. The average particle sizes (Figures 34D-36D) as determined from the TEM images are 16 ± 2 nm (complex1), 14 ± 2 nm (complex 2) and 20 ± 2 nm (complex 3). The particles obtained from complex 1 are evenly distributed over the TEM grid. There is evidence that the particles are more polyhedral

than spherical in shape (Figure 34C). The particles obtained from complex 2 show some degree of aggregation (Figure 35D) with particles obtained from complex 3 showing a linear arrangement of particles.

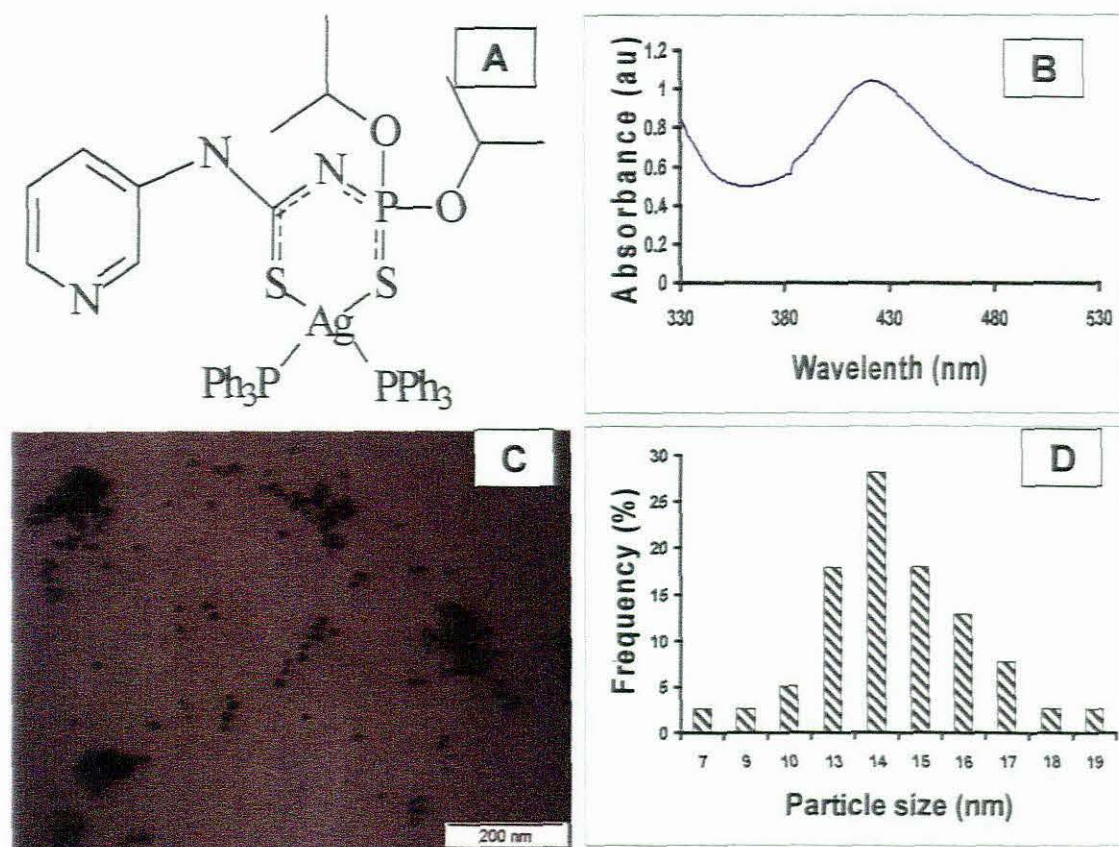


Figure 35 : HDA capped silver nanoparticles from (A) Complex 2, (B) Absorption spectrum, (C) TEM image and (D) particle size distribution

It was also shown that a compact layer of HDA is formed in between the silver nanoparticles that prevents them from aggregating, confirming HDA as a good surfactant for producing well dispersed metal nanoparticles. The formation of nearly monodispersed silver nanoparticles could be attributed to the balance between stabilization and

nanoparticle growth in solution. The HDA-capped silver nanoparticles retain the same morphology over a long period when compared to PVP capped silver nanoparticles. In the case of the HDA-capped silver nanoparticles, the amine functional group is adsorbed on the surface of silver nanoparticles and the long hydrophobic hexadecyl chains leads to a big compact environment around silver nanoparticles which leads to steric stabilization and therefore isotropic growth is favoured.

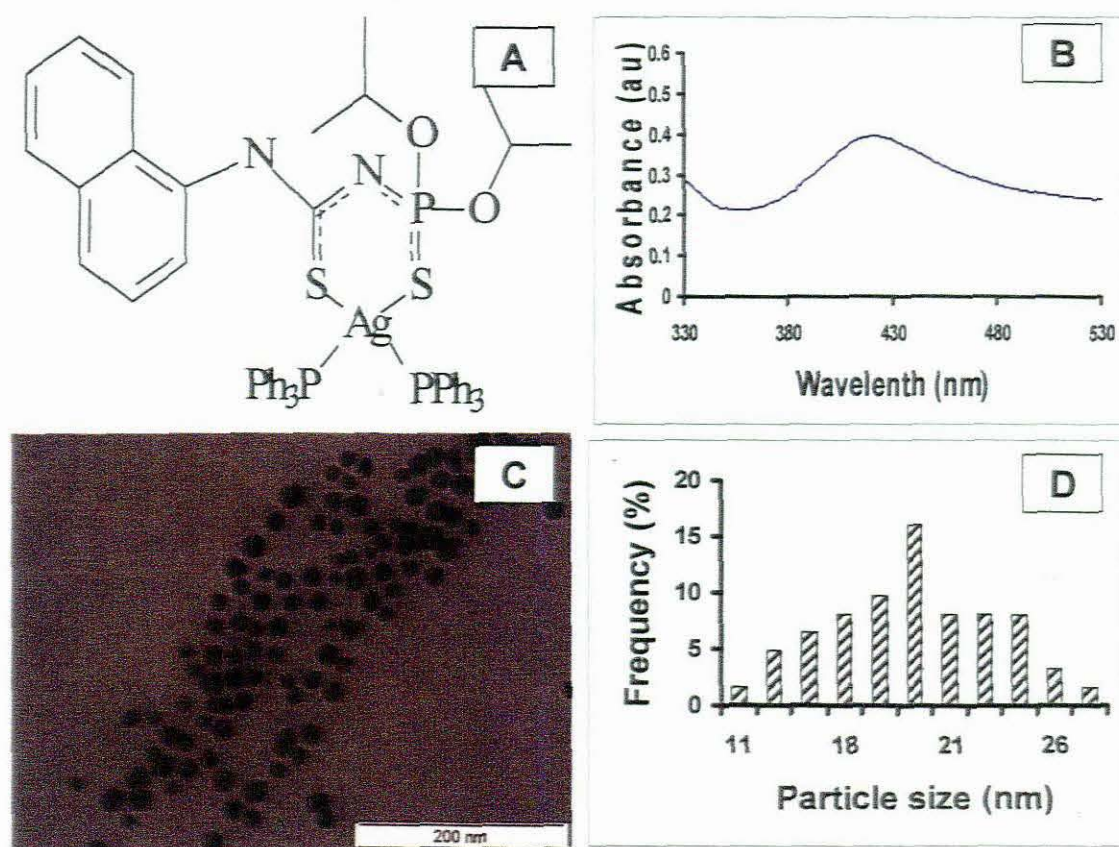


Figure 36 : HDA-capped silver nanoparticles from (A) Complex 3, (B) Absorption spectrum, (C) TEM image and (D) particle size distribution

The X-ray diffraction patterns of the HDA-capped silver nanoparticles are shown in **Figure 37**. The four diffraction peaks (111, 200, 220 and 311) above $2\theta = 30^\circ$ are distinctive of face centered cubic silver.

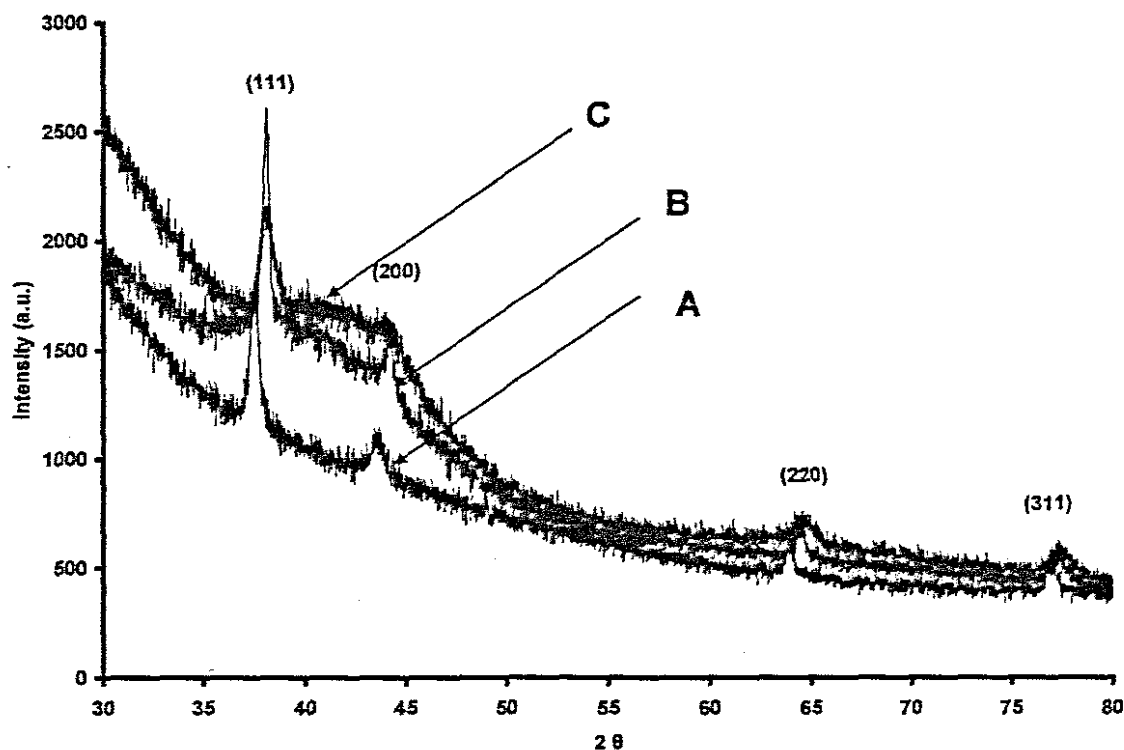


Figure 37 : Powder X-ray diffraction patterns of HDA capped silver nanoparticles synthesized from complexes 1-3.

Figure 38A is the representative scanning electron microscopy image of HDA-capped, silver nanoparticles deposited on the glass substrate activated by PVP. Isotropic HDA-capped silver nanoparticles are formed on the surface of glass substrate. Further elucidation of the HDA-capped silver nanoparticles distribution was achieved by EDAX

(Figure 38B). The EDAX revealed that about 60% of glass substrate constitutes silver nanoparticles and the other 40 % is shared by carbon. This can be attributed to carbon-coated glass subtracted for SEM analysis.

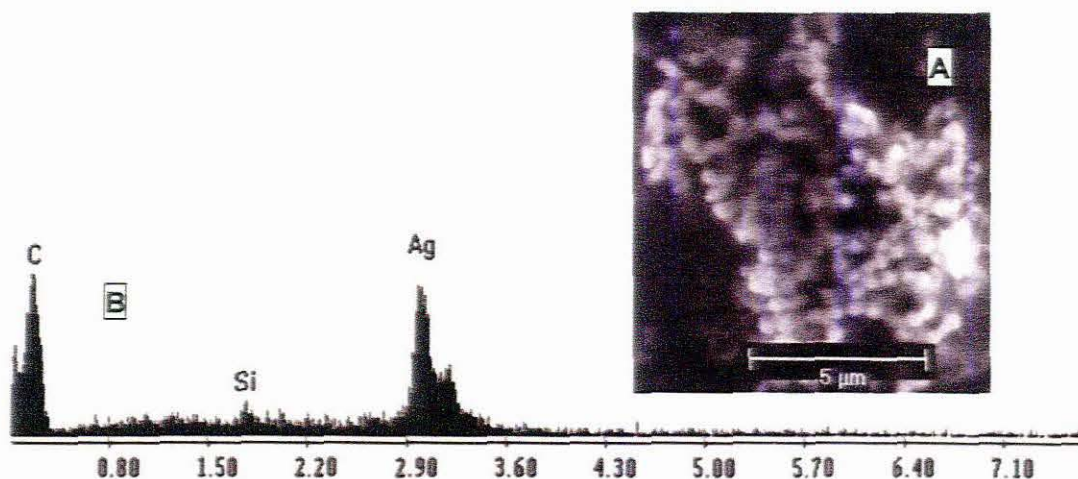


Figure 38 : HDA-capped silver nanoparticles (A) SEM image and (B) EDAX spectrum

The decomposition of silver complexes follows the Chugaev mechanism [186] as shown in Figure 39. There are two possible decomposition pathways involved during the decomposition of the complexes, the first gives Ag_2S . The second decomposition pathway is considered to be viable as it gives silver metal nanoparticles, which are observed in the TEM micrographs. It is therefore appropriate to study the time dependent decomposition pathway. In this experiment, the time dependent growth of silver nanoparticles was examined.

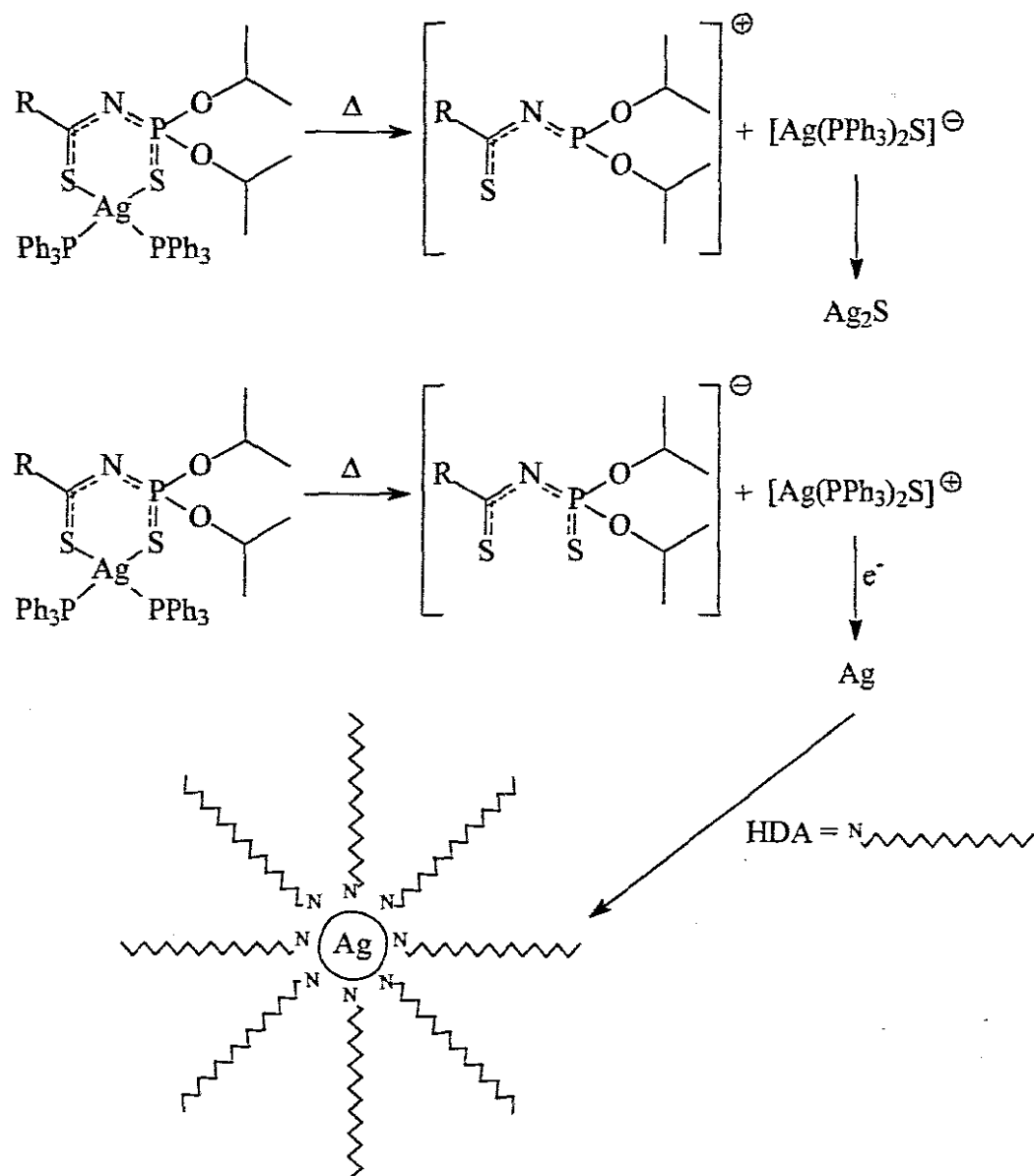


Figure 39 : Decomposition mechanism of silver complexes

The induction time was 5 minutes and the absorbance was observed to gradually increase with time. This could be attributed to an increase in the amount of silver nanoparticles as indicated in the UV-visible spectra at different time intervals. These spectra did not show

any trace of silver sulfide nanoparticles. At the elapsed time the absorption bands narrowed and shifted continuously to longer wavelengths, which could be attributed to the growth of silver nanoparticles (Figure 40).

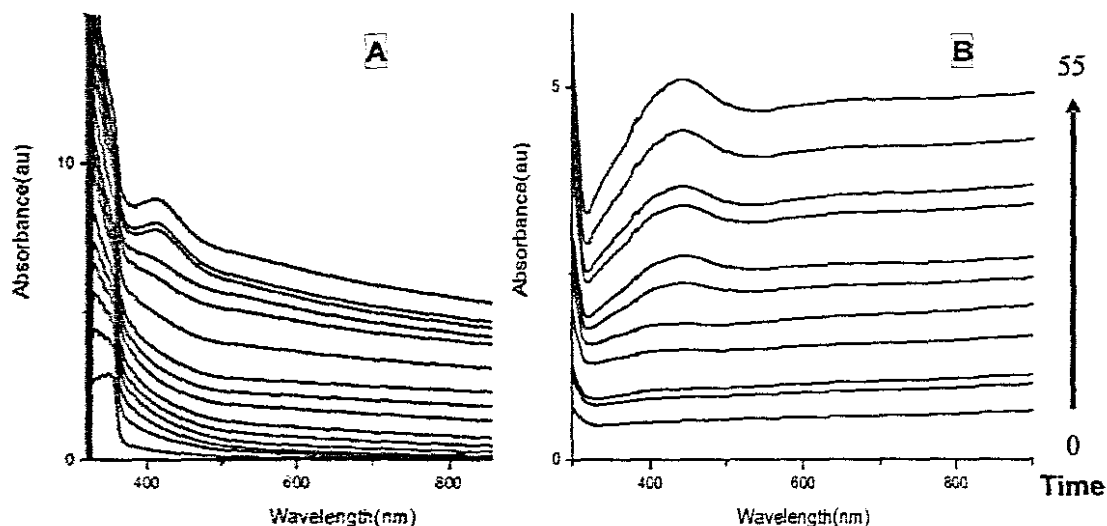


Figure 40 : UV-visible spectra of HDA-capped nanoparticles synthesized from (A) complex 1 and (B) complex 2, obtained between 5-55 minutes.

The TOPO on the surface of silver nanoparticles is attached to the Ag atoms via the lone pair on the oxygen. The bulkiness of the tri-octylphosphine (TOP) contributes to the bulk layer and prevents any diffusion of Ag atoms and thereby hindering any agglomeration (Figure 41). Since there was no subsequent addition of reducing agent, TOPO acts as both surfactant and reducing agent. The lone pair on the oxygen of TOPO forms a very labile bond with the surface of silver nanoparticles and thereby enhances the growth morphology of silver nanoparticles. However, the length of the alkyl group further contributes to fine-tune the shape and size of silver nanoparticles. Although TOPO is a good capping agent,

its contribution towards controlling the morphology of silver nanoparticles is still a challenge when compared to HDA.

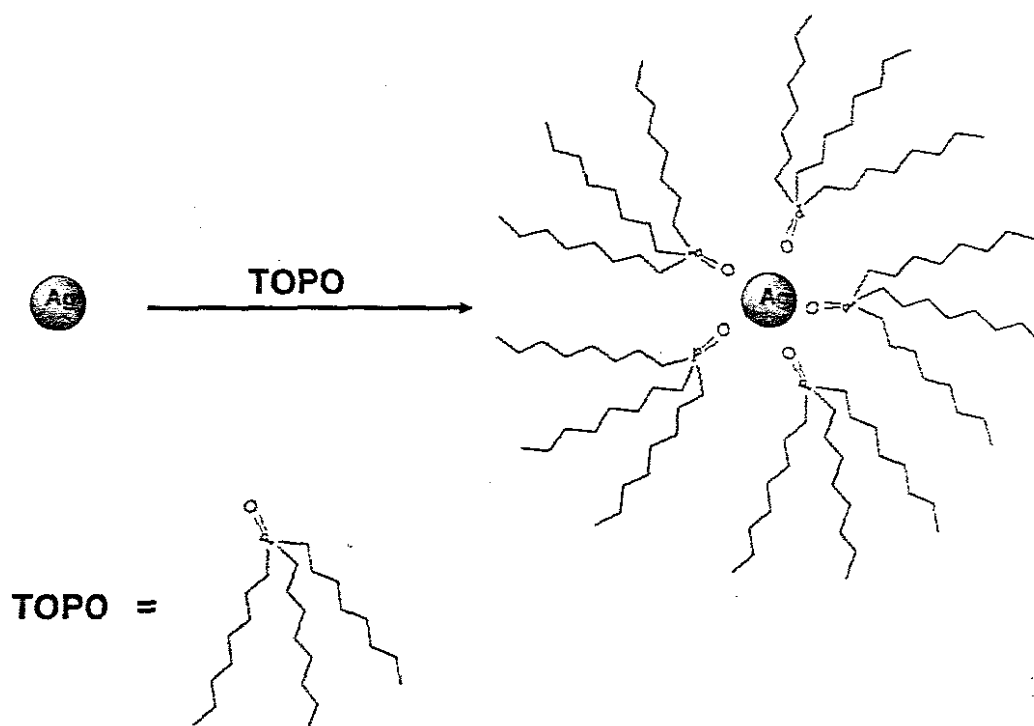


Figure 41 : TOPO capped silver nanoparticles

The UV/Vis spectra of TOPO-capped silver nanoparticles synthesized from complexes 1-3 show distinct SPR absorption bands at *ca.* 420 nm (**Figures 42B-44B**). The shape of the SPR bands suggests that all the particles are spherical. There is no evidence of secondary absorption peaks which indicate the presence of anisotropic particles. The TEM images (**Figures 42C-44C**) of the TOPO capped particles confirm their spherical shape. The

average particle sizes as determined from the TEM images are 18 ± 3 nm (Complex 1), 18 ± 3 nm (Complex 2) and 21 ± 1 nm (Complex 3). The decomposition of complex 2 in the presence of TOPO is shown by the TEM image in Figure 43C which reveals silver nanoparticles with different sizes, evidence of uncontrollable growth. There are no distinct changes on the morphology of silver nanoparticle prepared from complex 3, the particles are generally spherical in shape (Figure 44C).

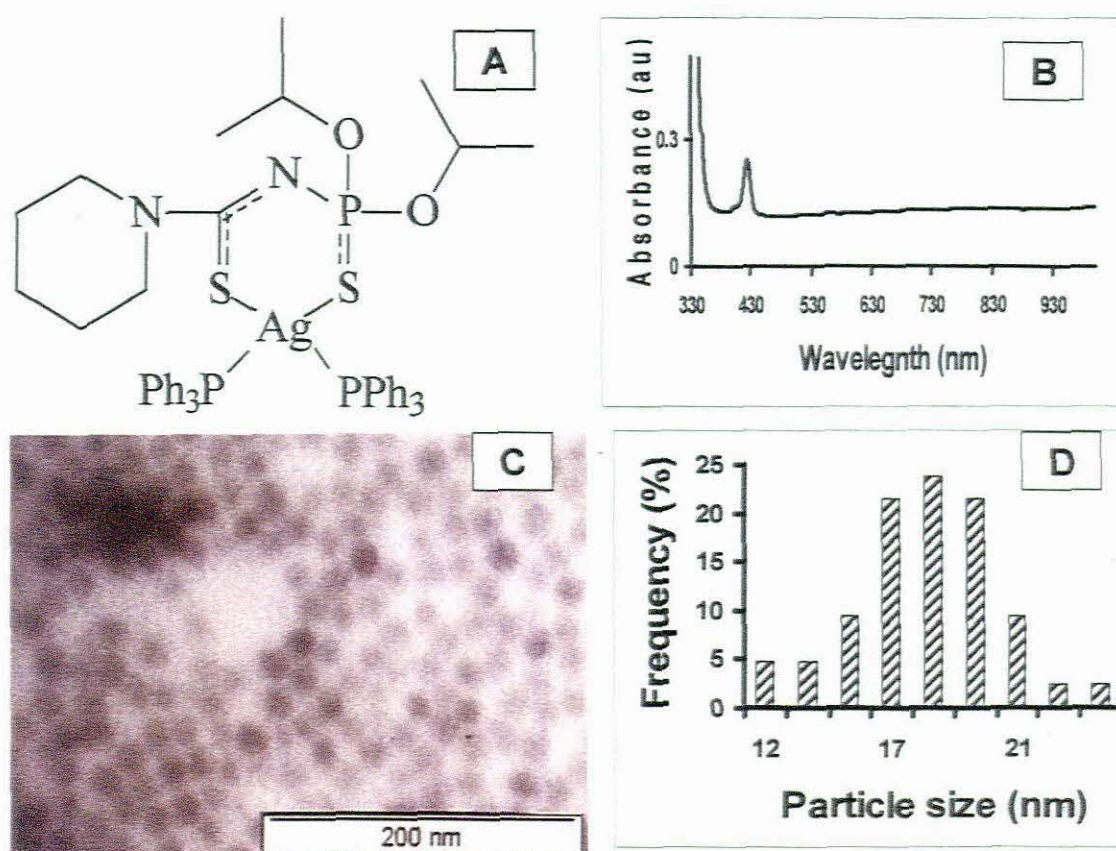


Figure 42 : TOPO capped silver nanoparticles from (A) Complex 1, (B) Absorption spectrum, (C) TEM image and (D) particle size distribution

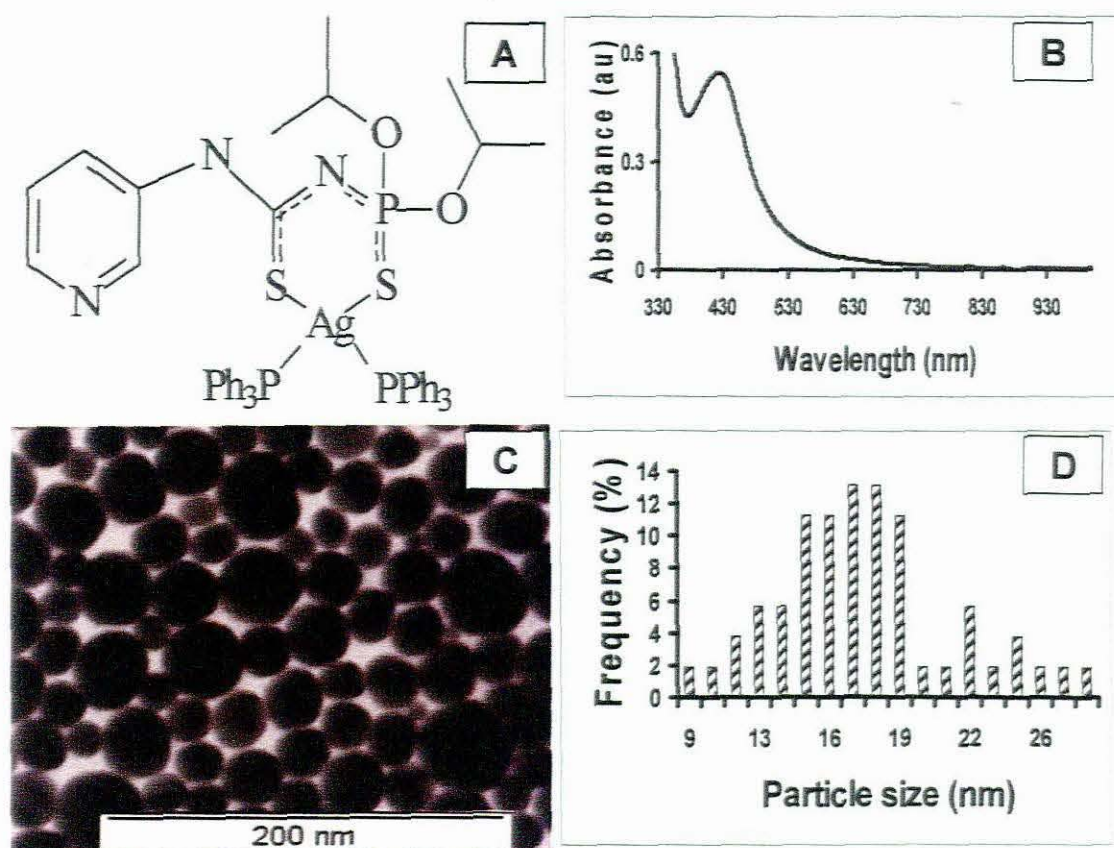


Figure 43 : TOPO capped silver nanoparticles from (A) Complex 2, (B) Absorption spectrum, (C) TEM image and (D) particle size distribution

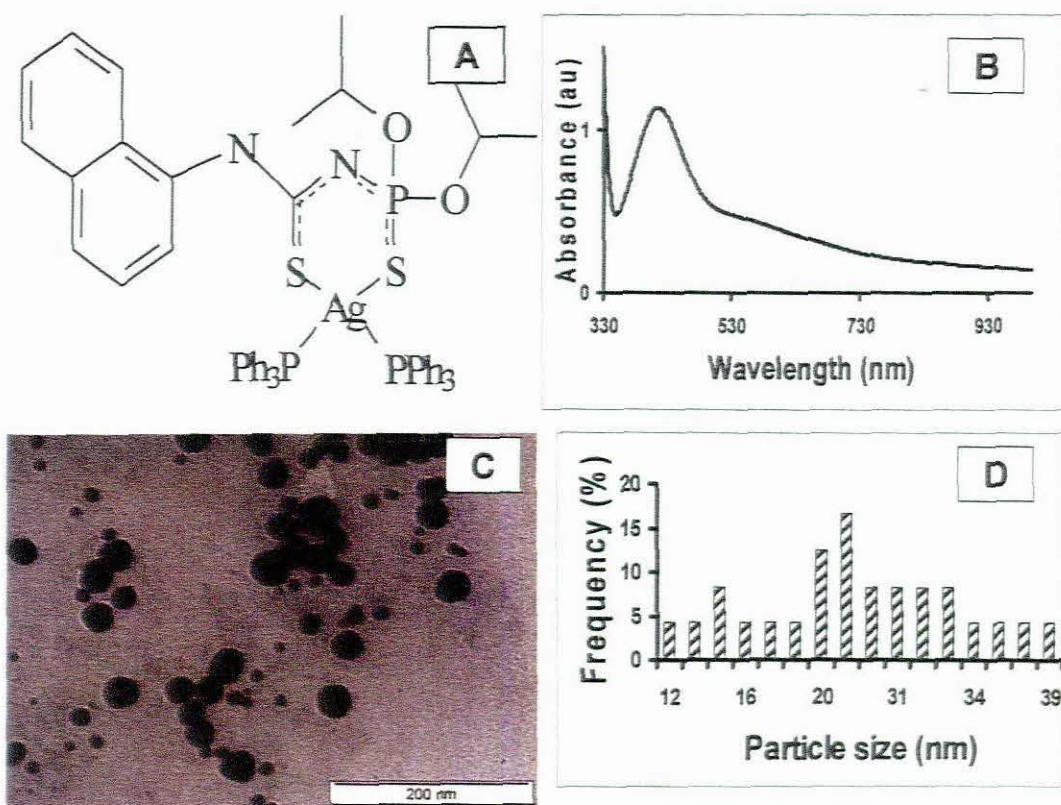


Figure 44 : TOPO capped silver nanoparticles from (A) Complex 3, (B) Absorption spectrum, (C) TEM image and (D) particle size distribution

3.4.4 Conclusions

A route to synthesize stable TOPO and HDA-capped silver complexes as single-molecule precursors has been described. The procedure is simple, reproducible and could be a general method for the direct synthesis of metal nanoparticles. Although both surfactants (HAD and TOPO) are considered good for stabilizing silver nanoparticles in solution, a thorough study on the effect of the concentration, time and mole ratio of silver complex to

surfactant needs to be undertaken for a complete understanding of the mechanism involved during this synthesis.

4. CHAPTER FOUR : DFT AND SERS STUDIES OF METAL NANOPARTICLES

4.1 Introduction

For centuries, quantum chemistry has been at an almost prenatal stage, staying in the womb of quantum mechanics [187]. From its early origins in theoretical chemistry, quantum chemistry has matured into a robust field with many different features and research areas like quantum chemistry, computational chemistry, molecular modeling and even interdisciplinary specialization such as structural biology and bioinformatics [188,189]. Recently quantum chemistry has been used to describe the chemical adsorption of molecules on the surface of metal nanoparticles. This is based on the reactive intermediates formed during the chemical orientation of the reactive species on the surface of metal nanoparticles.

Historically, quantum chemistry had to do with the prediction of structures and properties of a molecule, and was based on quantum theory and not on parameterization and empirical correlation, however accurate they may appear to be [187,188,189,190]. This sentiment has dramatically changed as the problems have become more complicated. This is clearly apparent in the computational results of this research. Regardless of the approximation being made now or in future, there will always be a difference of opinion as to what constitutes a large molecule, such as poly (*N*-vinylpyrrolidone). The *status quo* has an artificial barrier between various sizes of molecules and the level of detail in their structures and the property predictions. It is necessary to strike a balance between accuracy of results

and speed of computation. In order to understand electron behavior in molecular systems, quantum mechanics provides a good platform to begin with. A history of the development of quantum mechanics in relation with classical mechanics is presented. This mathematical model forms the fundamental basis for simulations in order to understand the mechanisms involved in the regioselective interaction of complexes on the surface of metal nanoparticles.

4.2 A Historical Prelude to density functional theory

4.2.1 Bohr (1913)

The Density functional theory originates from the following quantum mechanic principles. In looking at descriptions of hydrogen atom behavior, Bohr observed that the current models of that time did not work. He then decided to introduce the assumption that electrons moved in fixed orbits around the nucleus [191]. This led to the idea that the angular momenta of electrons in atoms were quantized rather than continuous:

$$\ell = n \frac{h}{2\pi} \quad n=1,2,3,\dots \quad (1)$$

This simple assumption led to an improved model of the hydrogen atom with constrained electron orbits. Bohr was followed by de Broglie in 1924, who made a very important observation which revealed that classical particle mechanics did not describe the behavior

of electrons, he thus introduced the principle of wave-particle duality for high-energy particles such as electrons [191].

4.2.2 The Schrödinger Equation

Based on de Broglie's wave-like description of electrons, Schrödinger combined the quantum assumptions of Bohr with the wave equations of classical mechanics to yield a new description of electrons. In mechanics, the total energy of a system of particles can be described in terms of particle momenta and coordinates. For time-independent systems in classical motion [192]

$$H = KE \text{ (kinetic energy)} + V \text{ (potential energy)}. \quad (2)$$

Consider an electron moving along the x-axis. Its kinetic energy is given by

$$KE = \frac{1}{2}mv_x^2 = \frac{p_x^2}{2m} \quad (3)$$

where m is the particle's mass, v_x is the particle's velocity, and p_x is the particle's momentum. Thus, the total energy along the x-axis is

$$E_x = \frac{p_x^2}{2m} + V \quad (4)$$

Equation (4) can be converted to a form suitable for use in quantum mechanics by replacing the momentum with an operator derived from Bohr's quantized orbits:

$$E_x = -\frac{h^2}{8\pi^2 m} \frac{d^2}{dx^2} + V \quad (5)$$

The problem with equation (5) is that it gives an indication that the operation should be performed, namely derivitization with respect to x , on something but not what that something should be, then it is necessary to give a brief background of the definition of operators.

4.2.3 Operators

Mathematical instructions to perform a task are conveyed in terms of operators [193]. In the expression $3xa$, the symbol " x " is an operator which symbolizes to multiply a by 3. Thus, an operator is simply a symbol which symbolizes to perform an operation. Similarly, in the expression

$$\frac{d}{dx} e^{\alpha} = \alpha e^{\alpha} \quad (6)$$

the (d/dx) symbol is an indication to perform the differentiation.

4.2.4 Eigenvalues and eigenfunctions

The special form adopted in equation (6) is an example of what's called an eigenvalue problem [193]. In eigenvalue problems, some function undergoes an operation that results in the formation of the function multiplied by a constant. The special function is called an eigenfunction and the constant is called an eigenvalue. Thus, from equation (6), the operator is (d/dx) , the eigenfunction is e^{ax} , and the eigenvalue is a . The Schrödinger equation is an eigenvalue problem. The something that is operated on by the operator in the right-hand side of equation (5) is a wavefunction that describes the wave-like nature of an electron. The wavefunction is represented by Ψ . When applied to equation (5) to complete the mathematical expression, the following result is obtained:

$$E_x \psi = \left(-\frac{h^2}{8\pi^2 m} \frac{d^2}{dx^2} + V \right) \psi \quad (7)$$

The operator from the right-hand side of equation (5) has a special name; it is called a Hamiltonian operator which is symbolized by H . In condensed form, the Schrödinger equation is written as

$$H\psi = E\psi \quad (8)$$

Where Ψ is a wave function, H is the Hamiltonian operator (the right-hand side of equation (5)), E is a constant. Therefore, the Schrödinger equation is an eigenvalue problem, Ψ is an eigenfunction, and E is an eigenvalue. This indicates immediately that the wave function must behave as an eigenfunction with respect to the operator H

4.2.5 The Total Hamiltonian

Before going any farther, it should be remembered that it is possible to derive equations (7) and (8) by considering the time-independent motion of a classical particle moving in one dimension. What is very interesting in this case is the behavior of electrons in organic molecules. What is needed is information about electrons in the presence of a nucleus and other electrons moving in three dimensions. Recalling the derivation of equation (5), it can be seen that the Hamiltonian simply represents the operations necessary to evaluate the kinetic and potential energy of the system. Thus, the Hamiltonian will have six terms comprising kinetic and potential energies [194]:

- ❖ Kinetic energy
- ❖ Electrons
- ❖ Potential energy
- ❖ Nuclear-nuclear repulsions
- ❖ Nuclear-electron attraction
- ❖ Electron-electron repulsion

So the Total Hamiltonian, H is given by

$$-\sum_{I=1}^N \frac{p_I^2}{2M_I} + \sum_{I=1}^{N-1} \sum_{J=I+1}^N e^2 Z_I Z_J R_{IJ}^{-1} - \frac{\hbar^2}{8\pi^2 m^2} \sum_{i=1}^n \nabla_i^2 - \sum_{i=1}^n \sum_{I=1}^N e^2 Z_I r_{iI}^{-1} + \sum_{i=1}^{n-1} \sum_{j=i+1}^n e^2 r_{ij}^{-1} \quad (9)$$

UPPER CASE = NUCLEI, lower case = electrons; $N(n)$ = number of particles; m = mass; Z = nuclear charge; e = electron charge; r_{ij} = distance between particles i and j . Because the electrons move in three dimensions, we have to resort to partial differentiation, so equation (9) contains the symbol ∇^2 which is the Laplacian operator (kinetic energy operator), which is given by the following equation [191, 195]:

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \quad (10)$$

Equation (8) can be solved exactly when using the total Hamiltonian of equation (9). Hence, a series of approximations should be considered to simplify this task. The wavefunction is referred as Ψ , and the approximate wavefunctions as Φ .

4.2.6 Simplifying Approximations: The Born-Oppenheimer Approximation (BOA)

It is known that the ratio of nuclear to electron masses is at least 1820/1. Thus, electrons move much faster than nuclei. This introduces the Born-Oppenheimer Approximation that assumes stationary nuclei [194,196]. Using this approximation $-\sum_{I=1}^N \frac{p_I^2}{2M_I}$ is zero and

$\sum_{I=1}^{N-1} \sum_{J=I+1}^N e^2 Z_I Z_J R_{IJ}^{-1}$ is a constant which can be easily calculated. Thus, only the electrons

can be considered, giving an Electronic Hamiltonian:

$$H_{el} = -\frac{\hbar^2}{8\pi^2 m^2} \sum_{i=1}^n \nabla_i^2 - \sum_{i=1}^n \sum_{I=1}^N e^2 Z_I r_{iI}^{-1} + \sum_{i=1}^{n-1} \sum_{j=i+1}^n e^2 r_{ij}^{-1} \quad (11)$$

Note that in equation (11), terms $\frac{\hbar^2}{8\pi^2 m^2} \sum_{i=1}^n \nabla_i^2$ and $\sum_{i=1}^n \sum_{I=1}^N e^2 Z_I r_{iI}^{-1}$ depend only on the coordinates of one electron. Using this fact, the equations can be rewritten in the form of electronic Hamiltonian as

$$H_{el} = \sum_i H_i + \sum_{i=1}^{n-1} \sum_{j=i+1}^n e^2 r_{ij}^{-1} \quad (12)$$

where H_i is the one-electron Hamiltonian (the core Hamiltonian) and is given by

$$H_i = -\frac{\hbar^2}{8\pi^2 m^2} \nabla^2 - \sum_{I=1}^N e^2 Z_I r_{iI}^{-1} . \quad (13)$$

It should be emphasized that the operation involves a one-electron wavefunction by using a lower case letter. NOTE: The Born-Oppenheimer approximation does not imply that the nuclei are not moving, but rather that the electronic distribution responds instantaneously to changes in the nuclear positions. To determine molecular geometry, H_{el} can be evaluated

and then added to the second term in equation (9) to approximate E_{tot} . Then a new geometry can be chosen, H_{el} re-evaluated in the second term in equation (9), with this process repeated until any geometrical changes raises the energy.

4.3 The Orbital Approximation

The total wave function for a molecule is generally approximated as a series of one-electron wave functions [197]:

$$\Phi_{tot} = \phi_a(1).\phi_b(2).\phi_c(3)..... \phi_n(i). \quad (14)$$

Thus, Φ is a product of one-electron functions, ϕ , each of which is called an orbital. The lower-case Greek symbols are one-electron wavefunctions. NOTE: Because Φ is essentially a probability, this approximation defines a total probability as a product of individual probabilities. This assumption can only be true in probability theory if the events are independent. Thus, this is an independent electron theory.

4.3.1 The Determinant Wavefunction

Electrons are Fermions. The minimum requirements for a many-fermion wavefunction are anti-symmetry with respect to interchange of electrons and indistinguishability of the electrons. Thus, no physical property of the system can change if the electrons are simply

renamed or renumbered. Mathematically, Φ must be antisymmetric with respect to an exchange of the coordinates of two electrons:

$$P_{1,2}(\Phi) = -\Phi \quad (15)$$

where $P_{1,2}$ is an operator that permutes the positions of electrons 1 and 2. For example, consider the total wavefunction of a two-electron molecule:

$$\Phi = \phi_a(1) \cdot \phi_b(2) \quad (16)$$

$$P_{1,2}(\Phi) = \phi_a(2) \cdot \phi_b(1) \neq \Phi \quad (17)$$

Thus, Φ is not an acceptable wave function for Fermions. If an alternative wave function is considered that is comprised of a linear combination of the one-electron orbitals, the following is obtained:

$$\Phi' = \phi_a(1) \cdot \phi_b(2) - \phi_a(2) \cdot \phi_b(1) \quad (18)$$

$$P_{1,2}(\Phi') = \phi_a(2) \cdot \phi_b(1) - \phi_a(1) \cdot \phi_b(2) = -\Phi' \quad (19)$$

Therefore, Φ' is an acceptable wave function. Notice that Φ' is the determinant of a simple matrix. Thus, Φ' can be written in determinantal form as:

$$\Phi' = \begin{vmatrix} \phi_a(1) & \phi_b(1) \\ \phi_a(2) & \phi_b(2) \end{vmatrix} \quad (20)$$

The matrix operation of finding the determinant has the net effect of producing an antisymmetrized sum of products of one-electron orbitals, f . Thus, any acceptable wavefunction can be written as a Slater determinant as follows:

$$\Phi' = \begin{vmatrix} \phi_a(1) & \phi_b(1) & \phi_c(1) & \vdots & \phi_n(1) \\ \phi_a(2) & \phi_b(2) & \phi_c(2) & \vdots & \phi_n(2) \\ \phi_a(3) & \phi_b(3) & \phi_c(3) & \vdots & \phi_n(3) \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ \phi_a(i) & \phi_b(i) & \phi_c(i) & \vdots & \phi_n(i) \end{vmatrix}. \quad (21)$$

A Slater determinant describes a single electronic configuration for a molecule.

4.3.2 Orbital Overlap : Normalization & Orthogonality

From the previous discussion the wavefunctions must be antisymmetric with respect to electron exchange. In addition, there are two other constraints on the orbitals. Recall that the independent electron nature of the theory defined that the products of wavefunctions produce probabilities. Consider the following two integrals:

$$\int \phi_a(i) \phi_a(i) d\tau \equiv 1 \quad (22)$$

$$\int \phi_a(i) \phi_b(i) d\tau \equiv 0 \quad (23)$$

where the integration is over all possible values of the three spatial coordinates, x , y , and z , as well as s , the “spin coordinate”. The symbol $d\tau$ represents the volume element of all electron-space. The integrals of equations (22) and (23) are called overlap integrals because they give the extent of spatial overlap of the two orbitals. The integral in equation (22) is called a self-overlap integral, and this integral over all space is actually just the probability of finding the electron in the orbital ϕ_a somewhere in space. Of course, this probability is exactly unity. This is only true for select wavefunctions. Such wavefunctions are said to be normalized. As an example, consider the following normalized determinant wavefunction based on equation (21):

$$\Phi_{nom} = \frac{1}{\sqrt{n!}} \begin{vmatrix} \phi_a(1) & \phi_b(1) & \phi_c(1) & \vdots & \phi_n(1) \\ \phi_a(2) & \phi_b(2) & \phi_c(2) & \vdots & \phi_n(2) \\ \phi_a(3) & \phi_b(3) & \phi_c(3) & \vdots & \phi_n(3) \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ \phi_a(i) & \phi_b(i) & \phi_c(i) & \vdots & \phi_n(i) \end{vmatrix} \quad (24)$$

Hereafter, it is assumed all relevant wavefunctions must be normalized, and it is a relatively straightforward mathematical chore to normalize a determinantal wavefunction. The integral of equation (23) is equal to zero, because the one-electron orbitals must be orthogonal (orthonormal) to one another. This is required by the Pauli Principle.

4.4 The Hartree-Fock (HF) Approximation

Equation (24) has the inherent restriction that other wavefunctions of the same form are possible if other orbitals are selected. Since there are an infinite number of arbitrary, one-electron orbitals, an infinite number of determinant wavefunctions in the form of equation (24) can be generated. The exact wavefunction can be expressed as a linear combination of the approximate determinant wavefunctions as follows:

$$\Psi = \sum_{i=0}^{\infty} d_i \Phi_i. \quad (25)$$

Equation (25) shows that in principle it is possible to obtain an exact wavefunction by considering the infinite number of determinant wavefunctions. Unfortunately, such consideration would require an infinite amount of time. Using the Hartree-Fock approximation [198,199,200], it can be assumed that the summation in equation (25) may be approximated by a single term, namely the single determinant wavefunction represented by the first term in equation (25) with $d_0 = 1$ (i.e., Φ_0). It is known that Φ_0 is an approximation of Ψ , so optimization of Φ_0 is required so that it matches Ψ as closely as possible. How can this be achieved without knowing Ψ in advance?

4.4.1 The Variational Theorem

The energy term of the Schrödinger equation can be extracted by multiplying both sides by Ψ , integrating over all coordinates involved, and rearranging:

$$\Phi H_{el} \Phi = \Phi E_{el} \Phi \quad (26)$$

$$E_{el} = \frac{\int \Phi H_{el} \Phi d\tau}{\int \Phi \cdot \Phi d\tau} \quad (27)$$

When the integration is over all electron-space, it should be remembered that the Hamiltonian operator means taking a derivative of the wavefunction. Therefore, to solve for the total Energy, it is required to integrate the effect of operating on the wavefunction. Why can a simple division by Φ not be performed? Among other reasons, Φ cannot be zero, so dividing by Φ can make the expression go to infinity.

As a quick aside, consider one of the postulates of quantum mechanics: for every observable quantity, o , of a system, there is a corresponding operator, O , such that an average or expectation value of the observable may be obtained by evaluating the expression

$$o = \frac{\int f(x) O f(x) dx}{\int f(x) \cdot f(x) dx} \quad (28)$$

Thus, equation (28) provides the expected electronic energy of the wavefunction, Φ . Despite all the approximations, equation (28) indicates the electronic energy can be estimated based on Φ . Equation (27) can be simplified ever so slightly by considering the integral in the denominator. This is a self-integral over all space which, as it can be seen in equation (22), is just the probability of finding the electron somewhere in space. Of course, this probability is exactly unity for normalized wavefunctions. Using the equality of equation (22), the equation for the expectation value of the electronic energy of the system is given by

$$E_{el} = \int \Phi H_{el} \Phi d\tau \quad (29)$$

The Variational Theorem states that, for a molecule in its electronic ground state, E from equation (29) is always greater than or equal to the exact energy, E and, that the two are equal only if $\Phi = \Psi$ [191, 201].

4.4.2 The Method of Variations

Applying the simplest statement of the Variational Theorem (i.e., E should be as low as possible) to the determinant wavefunction, Φ , produces a procedure known as the method of variations: (1) construct a determinant wavefunction that describes the system; (2) vary E with respect to each of the orbitals, in turn, and set the resulting equations to zero to

determine the minimum of E , and (3) solve the resulting set of simultaneous equations to obtain the optimum set of orbitals which give the lowest energy (i.e., closest to the exact energy) [201].

4.4.3 The Hartree-Fock Equation

If the Variational Theorem is used in conjunction with equation (29) and the simple antisymmetric determinant wavefunction for the two-electron system is described as in equation (18), the wavefunction should be normalized. Normalization using the simple relationship of equation (22) gives

$$\Phi = \frac{1}{\sqrt{2}} \cdot [\phi_a(1)\phi_b(2) - \phi_a(2)\phi_b(1)] \quad (30)$$

and substituting for Φ in equation (29) gives

$$E_{el} = \frac{1}{2} \int [\phi_a(1)\phi_b(2) - \phi_a(2)\phi_b(1)] H_{el} [\phi_a(1)\phi_b(2) - \phi_a(2)\phi_b(1)] d\tau \quad (31)$$

Using equation (12), the following can be derived

$$E_{el} = \frac{1}{2} \int [\phi_a(1)\phi_b(2) - \phi_a(2)\phi_b(1)] \left[\sum_i^n H_i + \sum_{i=1}^{n-1} \sum_{j=i+1}^n e^2 r_{ij}^{-1} \right] [\phi_a(1)\phi_b(2) - \phi_a(2)\phi_b(1)] d\tau \quad (32)$$

which can be rearranged to give

$$E_d = \frac{1}{2} \int [\phi_a(1)\phi_b(2) - \phi_a(2)\phi_b(1)] \cdot \sum_i^n H_i [\phi_a(1)\phi_b(2) - \phi_a(2)\phi_b(1)] d\tau$$

$$+ \frac{1}{2} \int [\phi_a(1)\phi_b(2) - \phi_a(2)\phi_b(1)] \cdot \sum_{i=1}^{n-1} \sum_{j=i+1}^n e^2 r_{ij}^{-1} [\phi_a(1)\phi_b(2) - \phi_a(2)\phi_b(1)] d\tau \quad (33)$$

Equation (33) looks complicated, but it can be simplified in a way that will allow identification of the key parts. It can be recognized that equation (33) comprises of two terms. The first term involves the coordinates of only a single electron. The second term involves the coordinates of two electrons. Thus, one-electron and two-electron components of the energy can be reported [202].

4.4.3.1 The One-electron Contribution

Consider the first term (the one-electron term) in equation (33):

$$E_d = \frac{1}{2} \int [\phi_a(1)\phi_b(2) - \phi_a(2)\phi_b(1)] \cdot$$

$$\{H_1 [\phi_a(1)\phi_b(2) - \phi_a(2)\phi_b(1)] + H_2 [\phi_a(1)\phi_b(2) - \phi_a(2)\phi_b(1)]\} d\tau \quad (34)$$

Notice that the expansion gives eight terms, each of which is a product of two integrals. If the identity of the electron is ignored, 1 or 2, for a moment, we see that there are really four types of terms

$$\int \phi_a(i) \phi_a(i) d\tau \equiv 1 \quad (35a)$$

$$\int \phi_a(i) \phi_b(i) d\tau \equiv 0 \quad (35b)$$

$$\int \phi_a(i) H_i \phi_a(i) d\tau \quad (36a)$$

$$\int \phi_a(i) H_i \phi_b(i) d\tau \quad (36b)$$

The integrals of equations (35a) and (35b) are the now familiar overlap integrals described by equations (22) and (23). Equation (35a) is equal to one because the orbitals are normalized. Equation (35b) is equal to zero, because the one-electron orbitals is orthogonal. Equations (36a) and (36b) can be easily simplified because they contain the one electron Hamiltonian operator. However, upon first noting that both equations (35a) and (36a), and equations (35b) and (36b) are found as products and then using the equalities expressed in equation (35), the first term of equation (33) can be simplified as:

$$E_d = \frac{1}{2} \int [\phi_a(1)\phi_b(2) - \phi_a(2)\phi_b(1)] \cdot \sum_{i=1}^n H_i [\phi_a(1)\phi_b(2) - \phi_a(2)\phi_b(1)] d\tau \quad (37)$$

Remembering that electrons are Fermions and therefore indistinguishable (i.e., electron 1 = electron 2), equation (37) can be simplified further in terms of the orbital as:

$$E_d = \sum_{i=1}^n H_i \quad (38)$$

where

$$H_i = \int \phi_i(1) \left(-\frac{h^2}{8\pi^2 m} \nabla^2 - \sum_{I=1}^N \frac{e^2 Z_I}{r_{1I}} \right) \phi_i(1) d\tau \quad (39)$$

This result is obtained using the definition of the one-electron Hamiltonian (h) from equation (12). Equation (39) is the energy of a single electron in the orbital ϕ_i . Equation (38) is the total one-electron contribution to the total electronic energy (i.e., the sum of the single electron terms). It can be noticed that equations (38) and (39) contain the original terms from the overall Hamiltonian in equation (9) [191].

4.4.3.2 The Two-electron Contribution

The form of the second term is the same as that of the first term, except that the one-electron Hamiltonian operator is replaced by $e^2 r^{-1}$. Therefore, a second term can be derived in an analogous manner:

$$E_{el} = \frac{1}{2} \iint [\phi_a(1)\phi_b(2) - \phi_a(2)\phi_b(1)] \cdot \{ e^{-2} r_{1,2}^{-1} [\phi_a(1)\phi_b(2) - \phi_a(2)\phi_b(1)] + e^2 r_{1,2}^{-1} [\phi_a(1)\phi_b(2) - \phi_a(2)\phi_b(1)] \} d\tau \quad (40)$$

The double integral has to be used because the r^{-1} operator involves the coordinates of two electrons. Inspection of equation (40) reveals two types of terms:

$$\iint \phi_a(i)\phi_b(j) \frac{e^2}{r_{i,j}} \phi_a(i)\phi_b(j) d\tau_i d\tau_j \quad (41)$$

$$\iint \phi_a(i)\phi_b(j) \frac{e^2}{r_{i,j}} \phi_a(j)\phi_b(i) d\tau_i d\tau_j \quad (42)$$

Equation (41) is called the Coulomb integral. They are relatively straightforward: they also represent the classical Coulomb (electrostatic) repulsion between two electrons, $\phi_a(i)$ and $\phi_b(j)$. These terms are destabilizing and positive in sign. They are referred to as J below. Equation (42) is an exchange integral. They are non-classical and arise as a consequence of the Pauli Principle (i.e., the determinant wavefunction). These terms are stabilizing and negative in sign. These integrals are called K below. Gathering like terms, the following can be deduced:

$$E_{el} = \sum_{i=1}^{n-1} \sum_{j=i+1}^n (J_{ij} - K_{ij}) \quad (43)$$

where

$$J_{ij} = \iint \phi_a(i)\phi_b(j) \frac{e^2}{r_{i,j}} \phi_a(i)\phi_b(j) d\tau_i d\tau_j \quad (44)$$

$$K_{ij} = \iint \phi_a(i)\phi_b(j) \frac{e^2}{r_{i,j}} \phi_a(j)\phi_b(i) d\tau_i d\tau_j \quad (45)$$

Note that equations (44) and (45) contain the original term from the overall Hamiltonian. Now the equation for the electronic energy of the molecule can be rewritten as (Equation (33)):

$$E_{el} = \sum_{i=1}^n h_i + \sum_{i=1}^{n-1} \sum_{j=i+1}^n (J_{ij} - K_{ij}) \quad (46)$$

This is an expression of the Hartree-Fock equation. It indicates that the electronic energy of the molecule is given by the sum of three components: (1) the total one-electron contribution, h , that is comprised of the kinetic energy of the electrons and the electron-nucleus attractions; (2) the Coulomb repulsion between electrons, J and (3) the non-classical Exchange energy between pairs of electrons, K [201].

4.4.3.3 The Fock Operator

Now that a workable definition of the electronic energy has been indicated, the variational method to optimize the wavefunction can be applied. This is done by varying the one-electron orbitals until the energy is minimized. Variation of the orbitals is carried out as follows (47):

$$\delta E = \sum_{i=1}^n \delta h_i + \sum_{i=1}^{n-1} \sum_{j=i+1}^n (\delta J_{ij} - \delta K_{ij}) = 0 \quad (47)$$

Since the variations of the orbitals are linearly independent, one can derive a related equation for a single electron (1) in a single orbital (i)

$$\left\{ h(1) + \sum_{j=1}^n [J_j(1) - K_j(1)] \right\} \phi_i(1) - \varepsilon_i \phi_i(1) = 0 \quad (48)$$

where ε_i is the electronic energy of the electron in orbital i . Notice the similarity between equation (48) and the Schrödinger equation (8). The quantity in large curly brackets is the Fock operator, $F(1)$. From equation (48), the orbitals are optimized and the electronic energy is minimized when each orbital is an eigenfunction of the Fock operator, with an associated orbital energy ε as follows,

$$F(1)\phi_i(1) = \varepsilon_i \phi_i(1) \quad (49)$$

In order to obtain a many-electron wavefunction of the determinant form which has the lowest electronic energy, one-electron wavefunctions (orbitals) which are eigenfunctions of the one-electron Fock operator are used (Equation (49)). When the n orbitals of minimum energy satisfy equation (48), then $\Phi = \Psi$ [201].

4.4.3.4 Electron Spin : Restricted Hartree-Fock (RHF) Theory

So far, the spin of the electrons has not been considered. This version of Hartree-Fock Theory is called Unrestricted Hartree-Fock (UHF) theory [198,199], and is appropriate for all molecules, regardless of the number of electrons and the distribution of electron spins. The total wavefunction includes not only a spatial part, but also electron spin ($-\alpha$ or β). The spin must be taken into account when the two-electron exchange integrals are being evaluated. For the Coulomb integral, J , there are four possible spin combinations ($\alpha(1)\alpha(2)$, $\alpha(1)\beta(2)$, $\beta(1)\alpha(2)$, and $\beta(1)\beta(2)$) for electrons 1 and 2, while for the Exchange integral, K , there are only two possible spin combinations ($\alpha\alpha$ and $\beta\beta$). To see this, the $\alpha\alpha$ and $\alpha\beta$ terms for each are:

$$J_{ij} = \iint \phi_i(1)\alpha(1)\phi_j(2)\alpha(2) \frac{e^2}{r_{i,j}} \phi_i(1)\alpha(1)\phi_j(2)\alpha(2) d\tau_1 d\tau_2 \quad (50)$$

$$J_{ij} = \iint \phi_i(1)\alpha(1)\phi_j(2)\beta(2) \frac{e^2}{r_{i,j}} \phi_i(1)\alpha(1)\phi_j(2)\beta(2) d\tau_1 d\tau_2 \quad (51)$$

$$K_{ij} = \iint \phi_i(1)\alpha(1)\phi_j(2)\alpha(2) \frac{e^2}{r_{i,j}} \phi_i(2)\alpha(2)\phi_j(1)\alpha(1) d\tau_1 d\tau_2 \quad (52)$$

$$K_{ij} = \iint \phi_i(1)\alpha(1)\phi_j(2)\beta(2) \frac{e^2}{r_{i,j}} \phi_i(2)\alpha(1)\phi_j(1)\beta(1) d\tau_1 d\tau_2 \quad (53)$$

Note the differences for the spin integrals of J and K . The fact that the $\alpha\beta$ and $\beta\alpha$ spin combinations are not possible for K , is derived from the fact that the integral value is zero by virtue of the orthogonality of the electron spin functions:

$$\int \alpha(1)\alpha(1)d\tau_1 = \int \beta(1)\beta(1)d\tau_1 = 1 \quad (54)$$

$$\int \alpha(1)\beta(1)d\tau_1 = \int \beta(1)\alpha(1)d\tau_1 = 0 \quad (55)$$

The application of electron spin in this analysis has two major consequences. First, all four spin combinations are allowable for J . However, only the parallel spin combinations are allowable for K . This introduces a factor of two into the Hartree-Fock equation. The second consequence is that K is a stabilizing factor only for the parallel electron spin functions. This is the origin of the more common statement of the Paul Principle where electrons of like spin cannot occupy the same region of space (i.e., the same orbital). If a molecule has the same number of electrons with spin up (α) as with spin down (β), the solution of the Hartree-Fock equation yields the result that the spatial part of the orbitals, describing α and β electrons, are equal in pairs. This yields the familiar picture of orbitals occupied by two electrons of opposite spin. This result can be used to simplify the discussion further. If it is assumed that half the number of orbitals can be filled with electrons with paired spins, then only half the orbitals are needed. This approach is called Restricted Hartree-Fock (RHF) theory and the RHF electronic energy is given by

$$E_{RHF} = 2 \sum_{i=1}^{n/2} h_i + \sum_{i=1}^{n/2} \sum_{j=1}^{n/2} (2J_{ij} - K_{ij}). \quad (56)$$

Note that the RHF electronic theory is not simply twice the sum of the orbital energies from UHF theory. That is because two of the K terms are eliminated when the spin functions are included. RHF theory is applicable for the ground state of closed shell molecules. The reduction in the number of orbitals offers considerable computational advantages. Therefore, RHF is a reasonable starting point unless one has reason to believe that UHF theory is necessary.

4.4.4 Self-Consistent Field Theory (SCFT)

Equation (46), provides a means of calculating the electronic energy for a determinant wavefunction is as follows. First, a guess is made as to what Φ is, then h , J and K are evaluated in order to calculate a new Φ . This process is continued iteratively until there is no change in Φ between iterations. The orbitals are then said to be self consistent with the field generated by electrons. Hence, this process is called Self-consistent Field (SCF) calculation [203,204].

4.5 Putting It All Together

In order to determine what the quantum particles (the electrons) are doing, there is a need to evaluate the Hamiltonian that describes them. Recall that the total Hamiltonian is comprised of five terms: the kinetic energy of the nuclei, the potential energy of nuclear-

nuclear repulsions, the kinetic energy of the electrons, the potential energy of nuclear-electron attraction, and the kinetic energy of electron-electron repulsions. The total Hamiltonian is simplified by the Born-Oppenheimer approximation and gives an electronic Hamiltonian, H_{el} , which can be calculated using the following steps:

Step 1: Choose a molecular geometry (i.e., build a model that provides the nuclear coordinates) and then construct a determinant wavefunction, Φ , that describes the molecule. Remember that Φ is comprised of a set of orthogonal one-electron orbitals, ϕ .

Step 2: Evaluate the electronic energy of the system (H_{el}) using the one electron Hartree-Fock equations for the $n/2$ molecular orbitals that are eigenfunctions of the Fock operator:

$$\left\{ h(1) + \sum_{j=1}^{n/2} [2J_j(1) - K_j(1)] \right\} \phi(1) = \varepsilon_i \phi_i(1). \quad (57)$$

Remember that the electronic energy of the molecule is given by the sum of three components: (1) the total one-electron contribution, h , that is comprised of the kinetic energy of the electrons and the electron-nucleus attractions; (2) the Coulomb repulsion between electrons, J and (3) the nonclassical exchange energy between pairs of electrons, K .

Step 3: Vary the wavefunction of the system with respect to the orbitals, ϕ , in order to find the $n/2$ orbitals of minimum energy that satisfy equation (57). Remember that in order to evaluate the K and J terms of H_{el} , calculating the electrostatic field generated by the electrons is needed, which means Φ must be known. Therefore, Step 3 involves an iterative calculation wherein we evaluate h , J , and K for each Φ in order to calculate a new Φ . The iteration is continued until self-consistency is reached, i.e., there is no change in Φ (or E_{el}) between iterations. By the Variational Theorem, when we obtain $n/2$ orbitals that provide a minimum in E_{el} , then $\Phi = \Psi$.

Step 4: After evaluating E_{el} , the potential energy arising from nuclear-nuclear repulsions is added to approximate E_{tot} . Then Step 1 is repeated with a new chosen geometry, E_{el} is re-evaluated and, this process is repeated until any geometrical changes raise the energy.

4.6 Molecular Orbitals

Thus, for all equations were derived without needing to specify what the one-electron orbitals are. Now is the time to look at the effect of orbitals.

4.6.1 Linear Combination of Atomic Orbitals

One-electron (molecular) orbitals can be expanded as a linear combination of atomic orbitals (AO's) [191]:

$$\phi_i(1) = \sum_{j=1}^n c_{ij} \chi_j(1) \quad (57)$$

where χ is an atomic orbital and c_i is a scalar coefficient. This approach is called the Linear Combination of Atomic Orbitals-Molecular Orbital (LCAO-MO) method. Each ϕ is therefore a molecular orbital (MO) or, more precisely, an LCAO-MO. This approach has the advantages because the atomic orbitals are known (e.g., s, p, and d orbitals), which describe the correct distribution of electrons near the nucleus and, they are simple enough to be integrated. Moreover, if there is a need to vary E_{el} by varying the MO's, ϕ , the coefficients in equation (57) give one a handle: the coefficients are changed for each AO until the total wavefunction, Φ , is optimized with respect to one-electron wavefunction, ϕ .

4.6.2 Basis Sets

The AO's used for the LCAO-MO procedure form the basis set of the calculation. Selecting the correct basis set is an important decision because it dictates the accuracy and computational difficulty of the calculation. In general the more inaccurate the basis set, the more computation, storage and retrieval of integrals are required. Three general types of basis sets are typically used [205,206,207,208,209,210,211]:

- (1) Valence: only valence orbitals (e.g., 2s and 2p on C),
- (2) Minimal: all orbitals up to and including valence orbitals (1s, 2s, and 2p on C), and
- (3) Extended: extra functions added to the Minimal set (e.g., d on C).

4.6.2.1 Functional Representations of Minimal Basis Set Atomic Orbitals

There are three general types of functions that are used to make up the basis sets. The best description of electron density near the nucleus is provided by hydrogen-like atomic wavefunctions, because the solutions to the Schrödinger equation for one-electron atoms are exact. These orbitals are called Slater-type Orbitals (STO's) and have the radial form

$$\chi^{STO}(l) = r^{n-1} e^{-\zeta r}. \quad (58)$$

The problem with STO's is that, evaluating the integrals is exceedingly difficult because of the exponential radial dependence [212]. For this reason, another set of functions can be considered. These are called nuclei-centered Cartesian Gaussian functions (or Gaussian-type Orbitals, GTO's). The radial distribution of these orbitals is given by

$$\chi^{GTO}(l) = X^l Y^m Z^n e^{-\zeta r^2}. \quad (59)$$

These functions are not a good match for the hydrogen orbitals, but the integrals are much easier to evaluate. In order to combine the ease of manipulation with accuracy, a third set of functions has been considered. These functions are simply a least squares expansion of an STO in terms of several GTO's. For example, the STO-nG basis sets mimic the radial behavior of STO's by using a linear combination of nGTO's

$$\chi^{STO-nG}(l) = \sum_{k=1}^n d_k \chi_k^{GTO}(l). \quad (60)$$

The STO-nG expansion is now universally adopted and the STO-3G is a common minimal basis set. As an example, consider the electrons around a carbon nucleus (i.e., the 1s, 2s, 2px, 2py, and 2pz AO's) for which the following LCAO-MO's is adopted as a STO-3G basis set :

$$\phi_i(l) = \sum_{j=1}^5 c_{ij} \sum_{k=1}^3 d_k \chi_k(l) \quad (61)$$

In equation (61), each electron's MO is described by a linear combination of one 1s AO, one 2s AO and three independent 2p AO's and, each AO is mathematically represented by a three-term Gaussian expansion.

4.6.2.2 Extended Basis Set Atomic Orbitals

An alternative approach to describe the AO's is the Split Valence approach. In a split valence basis set, core electrons are described by a simple GTO expansion while valence electrons are described by two independent functions, one of which is another GTO expansion and the other an independent single, diffuse Gaussian. An example of a split valence basis set is the 3-21G basis set where carbon core 1s atomic orbital is expanded as three (3) GTO's and each of its valence 2s and 2p orbitals are described by an expansion of

two (2) GTO's plus a single (1) independent Gaussian function. Hydrogen atoms are not considered to have a core, so the basis of H consists of two 1s functions. Hence, the 3-21G basis set and the STO-3G basis set are essentially identical. The advantage of the split valence approach is that it allows, for example, different p orbitals on the same nucleus to have different sizes. Common split valence basis sets are designated 3-21G, 4-31G, and 6-31G. Clearly, the more functions (GTO) and the more accurate and the more time consuming the calculation will be [213].

4.6.2.3 Extending Basis Sets : Polarization Functions

The next level of improvement of the basis set involves the addition of polarization functions to the split valence basis set. Generally, these functions are only added to the 6-31G basis set. These extended basis sets are designated 6-31G* and 6-31G**. The first asterisk denotes the inclusion of d-type orbitals on heavy atoms such as C, N and O. The second asterisk, if there is one, denotes the addition of p-type orbitals on H. Mixing of these functions produces wavefunctions with lower overall symmetry, thereby allowing the orbitals not to be centered on the nucleus. These functions thus provide better descriptions of hybridization or polarization of orbitals in the molecular environment. The better the basis set (i.e., the more Gaussian functions it includes), the better the calculation. However, the more functions to integrate, the harder the calculation becomes, and the more processor power (time), RAM and hard drive space is required.

Optimization of the nuclear coordinates as well as the electronic energy in order to get the best possible wavefunctions and molecular properties, is required. A common trade-off is to optimize the geometry (this is the changing of the coordinates) using a smaller basis set and then do a final electronic calculation at the optimum geometry, using a larger basis set. Such calculations are reported as, for example, 6-31G*//STO-3G. This means that an STO-3G (minimal) basis set was used to optimize the geometry and, then a 6-31G* (extended, split-valence with polarization) basis set was used to do the final energy/property calculations [214,215,216,217].

4.7 A Brief Glimpse beyond HF Theory

The central approximation involved in the derivation of HF theory, namely that a single determinant many-electron wavefunction can be constructed of one-electron orbitals, has one serious drawback. The electron-electron interactions in J and K are treated in an average way.

4.7.1 Correlation Energy

More specifically, in SCF theory, one electron moves in an average field created by all the other electrons. In reality, the motions of electrons are correlated pair-wise to keep electrons apart. This is a stabilizing effect and thus the electronic energy calculated by SCF methods is always too high:

$$E_{SCF} = E^o + E_{correlation} \quad (62)$$

The difference between the best guess (E_{SCF}) and reality (E^o) is called the correlation energy. This problem is most important for single-electron processes such as oxidation and reduction, photochemistry and hemolytic bond dissociation. For the ground state of most closed shell organic molecules, this isn't a major problem.

4.7.2 Configuration Interaction

One way to evaluate the correlation energy and obtain a better calculated result is to consider not just a single determinant wavefunction, but to consider a linear combination of determinant wavefunctions. Previously, it was argued that the exact wavefunction could be expressed as a linear combination of the determinant wavefunctions:

$$\Psi = \sum_{i=0}^{\infty} d_i \Phi_i \quad (25)$$

The simplest method to evaluate the correlation energy is to calculate Ψ in this way. Because each determinant wavefunction represents a single electronic configuration, this method is called Configuration Interaction (CI). A common way to approach the problem of choosing another configuration (Φ ; i.e., another set of MO's (ϕ)), is to include unoccupied or virtual orbitals in the configuration. CI theory is very expensive to implement, but the results are usually very good, especially for photoexcited states.

4.7.3 Many-Body Perturbation Theory

Alternative methods to estimate the correlation correction include the perturbation methods. Perturbation theory attempts to describe differences between systems, rather than to describe the systems separately and then take the difference. The most commonly used version is the Møller-Plesset (MP) variation of Rayleigh-Schrödinger perturbation theory. Møller-Plesset Perturbation Theory (MPPT) defines the perturbation as the difference between the sum of Fock operators and the exact Hamiltonian. One can calculate a complicated multi-term perturbation equation that accounts for the correlation energy. Because the contributions of the terms to the energy get smaller and smaller, one can limit the computational expense by truncating the perturbation after a few terms. One of the most commonly used perturbation methods is MP2 which includes perturbations up to second order (i.e., second-order MPPT). In addition to those single-electron processes mentioned above, MP2 calculations also improve the calculation of secondary molecular properties such as dipole moments, vibrational frequencies and infrared and Raman absorption intensities.

4.8 Real Methods of the Present and Recent Past

4.8.1 *Ab initio* Methods

The name *ab initio*, comes from Latin that roughly translates as “from the beginning”. The approach involves solving the HF equations essentially as described above with as few

short-cuts as possible. Because everything is calculated based on simple physics, the results are “from first principles”. Although these are computationally intensive, recent advances in desktop computational power have brought *ab initio*, calculations into the everyday realm of the organic chemist. This is where essentially all current research occurs. Much of the research involves better, and by that “faster and more accurate”, approaches to solving all the integrals involved.

4.8.2 Semi-empirical Methods

Because of the computer expense involved in doing rigorous *ab initio* calculations, alternative strategies have been widely applied to solving quantum mechanical problems. Probably the most widely used methods have been the semi-empirical methods. These methods are based on the observation that the vast majority of computer time is spent dealing with integrals and, to the use of two simplifying procedures to solve the problem.

4.8.2.1 Parameterization

The first was that the integrals could be solved in advance and plugged into programs designed to use the HF equations. Because the values of the integrals are unknown, they were adjusted until the results of the calculations matched the empirical properties of various test molecules. The name “semi-empirical method” opposes those based exclusively on “first principles”. This procedure of optimizing the integrals to match experimental data is called parameterization and the integral values are called parameters. Much of what separates the different semi-empirical methods involve the test molecules

used in parameterization and the exact properties chosen for emulation. Thus, one has to be careful that the parameter set of the method chosen matches the types that would be seen in one's molecule of interest before applying the method.

4.8.2.2 Neglect of Differential Overlap (NDO) Methods

The second key realization was that the really expensive part of *ab initio* HF methods is solving all the two-electron integrals in the exchange terms. The differential overlap (DO) is defined as

$$DO = \int \int \phi_i(1)\phi_j(2)d\tau_1d\tau_2. \quad (63)$$

These are particularly numerous in large molecules where there are many orbitals and many electrons to consider. The NDO methods assume

$$\int \int \phi_i(1)\phi_j(2)\frac{e^2}{r_{1,2}}\phi_k(1)\phi_l(2)d\tau_1d\tau_2 = 0. \quad (64)$$

for certain orbitals. This assumption greatly reduces the number of integrals, thereby reducing the computational intensity. These methods start with a single determinant wavefunction using the LCAO-MO-SCF approach with an STO basis set (note that the Gaussian expansion isn't needed because the orbital integrals are pre-solved rather than solved on-the-fly), but then neglects the overlap in solving the HF equation.

4.8.2.2 CNDO and INDO (C = complete; I = intermediate)

The most simplifying assumption one can make is that all overlap integrals described by equation (64) are zero except where $i = j$ and $k = 1$, and where all orbitals reside on the same atom. This approximation is the complete neglect of differential overlap (CNDO). Methods employing CNDO do introduce electron-electron repulsions but they do not handle the interactions between electrons accurately. As a correction, DO between electrons on the same atom was reintroduced. This intermediate neglect of differential overlap (INDO) results in assuming that all overlap integrals described by equation (64) are zero except where $i = j$ and $k = 1$, or where all orbitals reside on the same atom. Overall, INDO produces better results with only a slight increase in computational cost. These methods have integrals that are parameterized to reproduce *ab initio* results. Parameter sets include CNDO, CNDO/2, CNDO/3, CNDO/3S, INDO and INDO/S, where the higher numeral indicates a better parameterization and “S” designates parameterization to predict molecular spectra. Geometry calculations are not very good; however, these methods do produce accurate orbitals, primary properties like charge densities and secondary properties like dipole moments.

3.8.2.3 MINDO; MNDO and AM1

Modified intermediate neglect of differential overlap (MINDO) is an altered version of INDO that is parameterized to reproduce experimental heats of formation, a quantity that

chemists generally find more useful than total energies. The most commonly used version is MINDO/3. An improvement to the complete and intermediate NDO approximations is the NDDO (neglect of diatomic differential overlap) method, where the only overlap integrals ignored are those arising from orbitals on different atoms. These reductions in the original C/INDO assumptions allow for the inclusion of lone pair repulsions. MNDO is parameterized to reproduce experimental heats of formation and is generally superior to MINDO and, only slightly more expensive. One area where MNDO fails is the description of the hydrogen bond. AM1 (Austin Model 1) is a more recently parameterized update of the MNDO concepts that does successfully treat hydrogen bonds. In the process of improving the accuracy however, the number of parameters required to describe each atom effectively doubled. These methods are very efficient and even produce accurate geometries. In general, the results with MNDO/AM1 are comparable to *ab initio* STO-3G calculations, but the computation is much less expensive. Because MNDO/AM1 has been parameterized based on a set of standard structures, some caution must be used when applying the method to new, unusual structures [218].

4.8.3 Hückel Theory (HT)

In the early 1930s, Hückel published the first applications of quantum mechanics to large molecules. Given the state of the art then, some rather drastic approximations were required. Hückel's method applies to planar, conjugated systems and depends immediately on the assumption that s- and p-electrons in bonds act independently. Surprisingly, this assumption does not greatly influence many calculations of interest.

4.8.3.1 Hückel Molecular Orbital Method

The Hückel Molecular Orbital (HMO) method is the fastest and most simple method because it contains the most drastic approximations. Only p electrons are considered (i.e., a highly simplified valence basis set). This method totally ignores electron-electron repulsions; orbital overlap is completely neglected and electron-electron repulsion is not considered. Therefore, HT requires no J or K calculations and does not require iteration to give SCF (no field is necessary). Interaction energies (Coulomb terms) are further simplified by considering only the nearest eight interactions between particles. HT is fast, and can be done by hand; however, ignoring electron repulsions is a huge disadvantage for accuracy. Basically, Hückel theory is only useful for analyzing molecular topology. However, the orbitals (p-type only) and orbital energy patterns are qualitatively useful for understanding aromaticity and orbital symmetry arguments.

4.8.3.2 Extended Hückel Theory (EHT)

When computers started to be used for HMO, work began on extending quantum mechanical calculations to many-electron problems, involving both s and p electron systems no longer constrained to planar conjugated molecules. In general, these methods are referred to as Extended Hückel Theory (EHT) methods. EHT ignores electron-electron repulsions. Therefore, EHT requires no J or K calculations and does not require iteration to give SCF (no field is necessary). Unlike NDO methods, overlap is not neglected. Valence basis sets using STO's are used (inner shell electrons are often averaged with the nuclear

charge in the core approximation). EHT is very fast; however, ignoring electron repulsions is a disadvantage for accuracy. The method is good for visualizing orbitals and qualitative diagrammatic analysis. Geometries are satisfactory for nonstrained molecules, although geometry optimization is not reliable, requiring a good starting geometry.

4.9 Practical Matters

Quantum mechanical calculations usually provide total energies in atomic units. A key question is then: what does one do with this information?

4.9.1 What's a hartree?

Ab initio calculations give results in atomic units. The atomic unit for energy is called a hartree. The Hartree is defined as the energy of Coulombic repulsion between two electrons separated by a distance of one Bohr radius ($r_0 = 0.529 \text{ \AA}$); i.e.,

$$1 \text{ hartree} = \frac{e^2}{r_0} = 627.51 \text{ kcal/mol.} \quad (65)$$

Semi-empirical programs usually give total energies in electron volts (eV). A table of conversion factors between units used by different chemists is shown in Table 3.

Table 3 : Conversion Table

	Kcal/mol	KJ/mol	eV	Hartree	cm ⁻¹
1 Kcal/mol =	1	4.184	4.335×10^{-2}	1.292×10^{-3}	19.98
1 KJ/mol =	0.2390	1	1.036×10^{-2}	3.089×10^{-4}	83.60
1 eV =	23.06	96.48	1	3.675×10^{-2}	8065
1 Hartree =	627.5	2625	27.21	1	2.195×10^5
1 cm ⁻¹ =	2.859×10^{-3}	1.196×10^{-2}	1.240×10^{-4}	4.556×10^{-6}	1

4.9.2 What does the Total Energy mean?

The total energy includes electron repulsion, nuclear repulsion and electron-nuclear attraction. In addition to total energies, semi-empirical programs usually present the heat of formation (ΔH_f), which can be directly compared with experimental measurements. In contrast, *ab initio* results are calculated at absolute zero (0 K). In order to get a room temperature energy, it is necessary to carry out a frequency calculation and use the partition functions found there to approximate the value at room temperature. Furthermore, these values need to be corrected for zero-point energy vibrations, a value which is also obtained from the frequency calculation. These matters are handled internally as part of the parameterization of semi-empirical integrals. The relationships are:

$$\Delta H_f = 590.577436.E^{6-31G*} + 22373.755.N_C + 337.107.N_H \quad (66)$$

$$\Delta H_f = 589.754489.E^{6-31G^*/STO-3G} + 22340.834.N_C + 336.590.N_H \quad (67)$$

This empirical relationship means that ΔH_f of hydrocarbon molecules can actually be compared with something experimentally determined. However, for non-hydrocarbons, estimating ΔH_f from *ab initio* calculations is still problematic.

4.9.3 Surface Enhanced Raman Spectroscopy (SERS)

Surface enhance raman spectroscopy (SERS) is a well-known technique which gives information on molecular vibrations. SERS was accidentally discovered when researchers tried to do Raman spectroscopy on the electrode [219]. The original idea of SERS was to generate a high surface area on the roughened metal. After this trial it was realized that the roughened silver electrode produced a Raman spectrum that was more intense than what was expected. This enormously strong signal debuted the surface enhance Raman scattering. The key features of SERS occur when the molecules are brought to the surface of metal. Large enhancements are observed in silver, gold and copper. If the metal nanoparticle are used in the system, the particle size for enhancement of Raman ranges between 20 nm and 300 nm.

4.10 COMPUTATIONAL SIMULATION

4.10.1 Introduction

In order to acquire a detailed and effective mechanism to understand the steric effect of PVP molecules on the growth behavior of metal nanoparticles, the computational models were designed based on the mechanism shown in **Figure 45**. The models were based on introducing the steric group into the PVP monomer as discussed. Monomers are the only parts of PVP which are involved in the chemical interaction with metal nanoparticles; therefore a better understanding of this chemical reaction would give a better insight on the growth behaviour of metal nanoparticles.

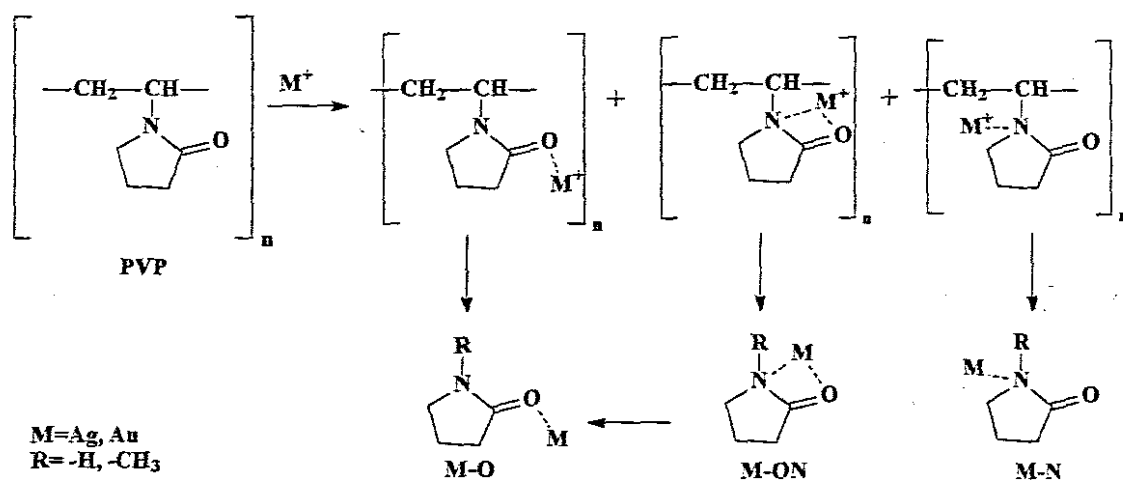


Figure 45 : Possible Mechanisms for the adsorption of PVP on Metal nanoparticles

Figure 46 shows the model optimized structure showing the chemical interaction of PVP with silver atoms; Ag-N-H and Ag-O-H were two models which were designed to show the chemical interaction of silver nanoparticles with the PVP monomer without the influence of

the steric group. Ag-N-Me and Ag-O-Me were models designed to represent the chemical interaction of silver nanoparticles with PVP monomer by imposing the steric effect with the methyl group. Ag-N-Propyl and Ag-O-Propyl represent the silver to PVP monomer interaction where steric hindrance is enhanced by the propyl group.

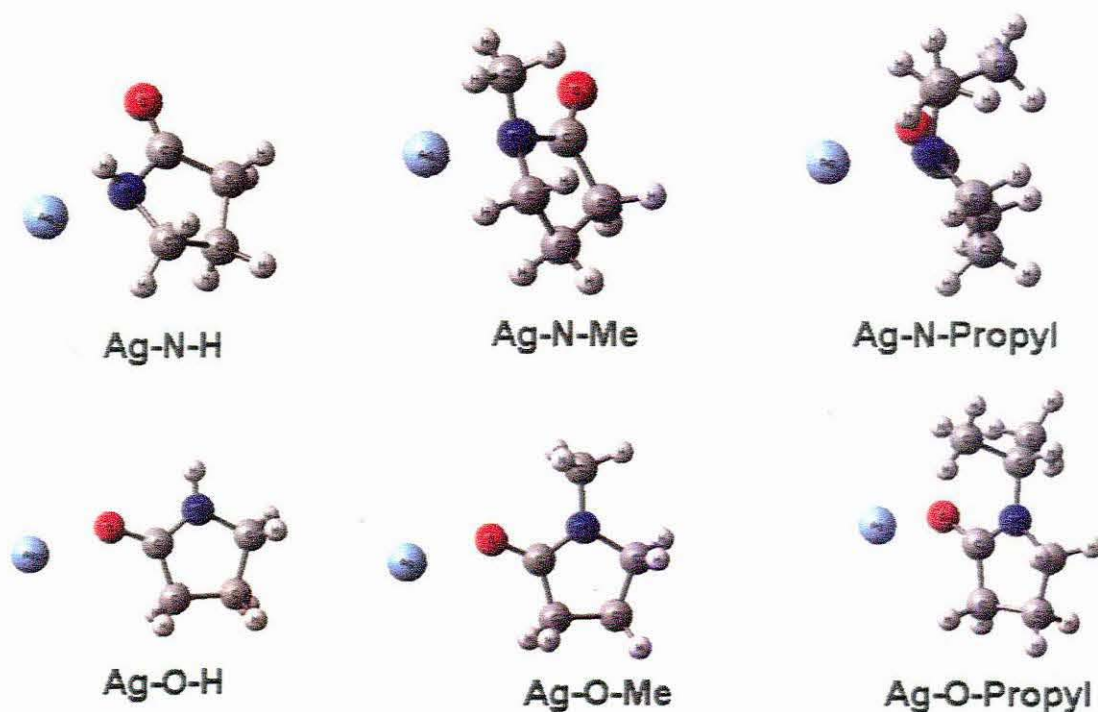


Figure 46 : Optimized silver complexes

The same interaction was repeated for gold where the steric effect of the methyl and propyl group (**Figure 47**). In the gold model, an interesting property was observed in terms of the bond length between the PVP monomer ring and the Au; it showed that there was a strong interaction as the bond length was shorter than the optimized silver models (**Table 4**).

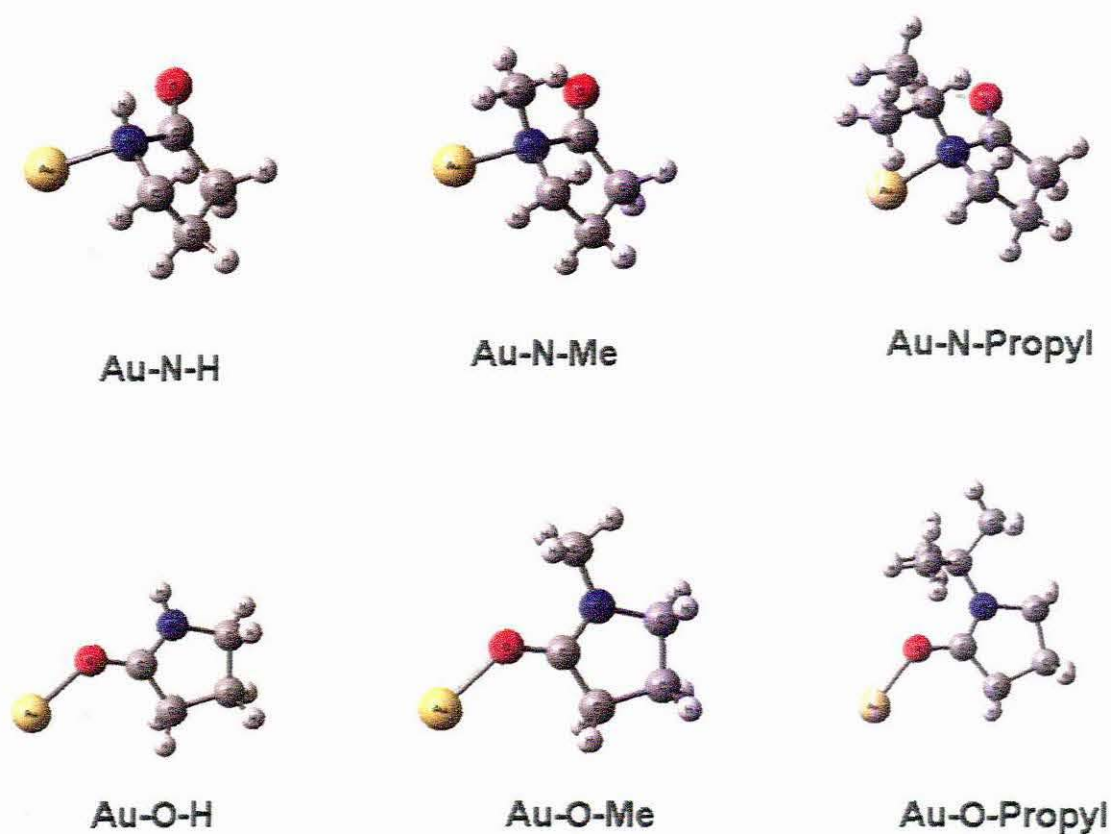


Figure 47 : optimized complexes of gold

The capping action of PVP on the surface of metal nanoparticles is still a challenge, since PVP, has been shown as a viable method of producing nanoparticles of tunable morphological and subsequently optical properties [220]. One such method involves the reduction of silver nitrate with dimethyl formamide (DMF) in the presence of PVP, which has been investigated in recent times [139,140,142]. Studies have shown that the interaction of silver nanoparticles and PVP can be associated with the selective growth of silver nanoparticles, when the polymer resides on the surface, and this creates a need to study the mechanism of such an interaction [134,221,222]. Since PVP is a large molecule,

a need for simplifying the interaction was adopted in this study. Wang *et al* [223] has studied the interaction of silver colloids with PVP but further computational studies have never been reported thus far. This prompted this investigation by synthesis and computational studies of the interaction of silver and gold nanoparticles with pyrrolidinone. It was believed that by looking at the interaction of pyrrolidinone with silver and gold nanoparticles, the mechanism for the interaction of these nanoparticles with PVP would be clarified. In the PVP molecule, the pyrrolidyl group is a suitable molecular system since it has greatly different electrostatic properties (Figure 48).

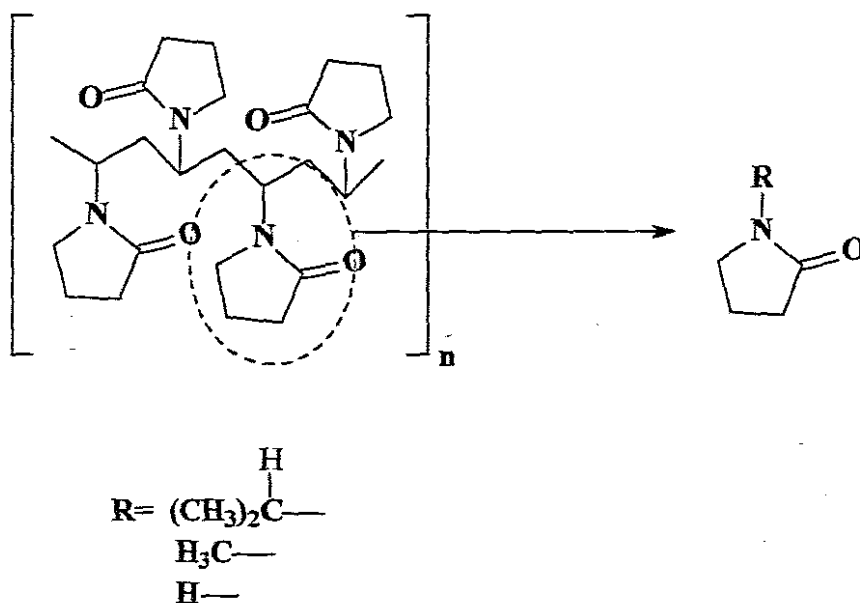


Figure 48 : The PVP monomer extraction

It is believed that during the synthesis of silver or gold nanoparticles in the presence of PVP, the first interaction is between the pyrrolidyl group of PVP and silver/gold ions. This is followed by the reduction process and the reaction is the growth of the nanoparticle,

which predominantly depends on the ratio of the metal ions to PVP in solution. To our knowledge no reports have been made available using the combination of experimental results and, density functional theory (DFT) methods to understand the complex formation on the surface of silver or gold by PVP molecules. This was done by looking at the interaction of silver or gold with N-methyl-2-pyrrolidinone and 2-pyrrolidinone respectively.

In order to acquire more detail regarding the interaction between PVP and the metal atoms on the surface of silver and gold nanoparticles, Surface Enhanced Raman Spectroscopy (SERS) and DFT had been employed to assist in the elucidation of the possible mechanisms. SERS is a powerful tool used to characterize the chemical state of bonds formed on metal surfaces and the subsequent molecular conformation on the specific metal surfaces [224]. This technique has been successfully applied in many systems designed to understand the adsorption of molecules on the surface of silver and gold colloids [225,226,227,228,229].

4.10.2. Experimental

4.10.2.1 Chemicals

Silver nitrate, tetrachloroauric acid trihydrate, N-methyl-2-pyrrolidinone, anhydrous (99.5 %), 2-pyrrolidinone (99 %) and trisodium citrate (99 %) were purchased from Sigma-Aldrich, and were used without any further purification unless otherwise stated. Double distilled water was used throughout the experiments.

4.10.2.2. Synthesis and functionalization of gold and silver colloids

Silver or gold colloids with the average size of 14 nm were prepared according to the method outlined in the literature [230]. Briefly, 10 mL of silver nitrate or tetrachloroauric acid trihydrate (0.25 mM) was heated to boiling point, followed by the addition of 10 mL of 1% trisodium citrate aqueous. The mixture was allowed to boil for a further 20 minutes under reflux. The green-grey silver and deep red-gold colloidal solutions were obtained for silver and gold nanoparticles respectively. Aqueous solutions (0.5 mL) of pyrrolidinone and N-methyl-2-pyrrolidinone (0.01 M) was mixed with 6 mL silver/gold colloidal suspensions which were then used for spectroscopic analysis.

4.10.2.3. Instrumentation

The Raman spectra were obtained from a Spex 1877 triple spectrometer with a CCD detector. The operating wavelength was set at 647.1 nm. The resolution was 2 cm^{-1} and a 180° geometry was used. The output laser power was 150 mW and 200 mW for colloidal solutions, which does not induce any changes in the adsorbate-substrate systems.

The optical absorption measurements were done using the Perkin Elmer Lambda 20 UV-vis spectrophotometer. The samples were measured in a quartz cell of 1 cm path length with water as a solvent or reference.

4.10.2.4. DFT calculations and models

All calculations were performed using the Gaussian 03 software program [231] within the density functional theory (DFT) framework.. All molecule-Ag or Au system structures were optimized and the corresponding Raman frequencies for the optimized structures were calculated. Calculations based on DFT have been applied in many different studies [225,226,227,228,229], with a reasonable measure of agreement between the theoretical and experimental data. In this study, the calculations were carried out with Beck's three-parameter hybrid method using the Lee, Yang and Parr [232] (B3LYP) correlation functional employed with electron core potential basis set LANL2DZ developed by Hay and Wadt [233]. For Ag and Au the LANL2DZ set the electron core potential simulates the 28 and 60 of their total 47 (Ag) and 79 (Au) electrons, respectively. For both heavy

elements the remaining 19 electrons are described by all electron basis sets consisting of a (8s6p4d) set of primitive Gaussian type functions contracted to the [3s3p2d]. For C, N and O the LANL2DZ basis consists of a (10s5p) set contracted to the [3s2p] set, while, for H a (4s) set contracted to the [2s] basis set is used. Each stationary point has been characterized by harmonic frequency calculations at the same level of theory (B3LYP/LANL2DZ) and the Raman active harmonic frequencies have been indentified.

4.10.2.5. Results and discussion

4.10.2.5.1. Optical absorption studies

The UV-vis absorption spectra of silver and gold colloids are presented in **Figures 49** and **50** respectively. The absorption spectra of the original silver colloids (**Figure 49**) showed a sharp peak located at 411 nm, attributed to the surface plasmon resonance (SPR) of the silver colloids [7d].

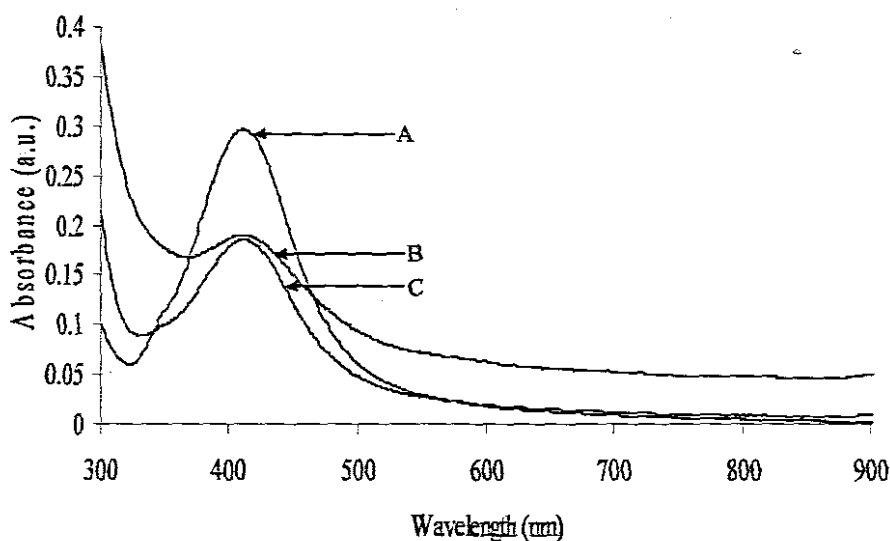


Figure 49 : Optical absorption spectra of (A) original silver colloids, (B) mixed with N-methyl-2-pyrrolidinone and (C) 2-pyrrolidinone mixture with the colloids.

Figure 49 shows the spectra after the addition of 2-pyrrolidinone and N-methyl-2-pyrrolidinone. The apparent loss of the sharpness and intensity of the spectra showed an onset of aggregation as a result of the multifunctional mode of the ligands adsorbed on the surface of the silver particles. The same phenomenon was observed for the gold colloids (Figure 50), with an absorption maximum of 525 nm observed, typical of a colloidal gold SPR absorption. Figure 50 shows the absorption after the ligands were mixed with the colloids. A secondary peak could also be observed at around 620 nm, signifying the aggregation of the gold particles. This observation can be attributed to the aggregation process of both silver and gold colloids. Longer reaction times were expected to allow for severe aggregation and therefore to push the secondary peak to higher wavelength for the

newly formed larger particles; at the same time diminishing the original SPR intensity of the smaller particles.

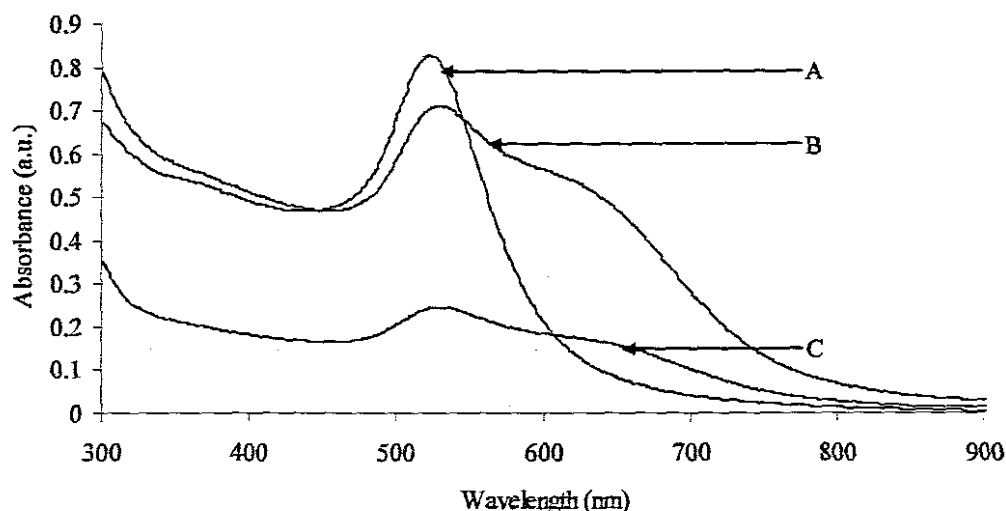


Figure 50 : Optical absorption spectra of A. original colloidal gold, B. N-methyl-2-pyrrolidinone mixture and C. 2-pyrrolidinone mixture.

4.10.2.5.2. Adsorption of N-methyl-2-pyrrolidinone and 2-pyrrolidinone on Ag/Au surfaces

The calculated Raman frequencies were found to be in good agreement with the experimental results as shown in Table 4. Practically, the molecules are adsorbed onto the surface of the silver and gold nanoparticles, and it is possible to calculate the vibration spectra in such a case. A postulate model, M-ON (Figure 51), that uses both oxygen and nitrogen as “substrates” is not observed [234].

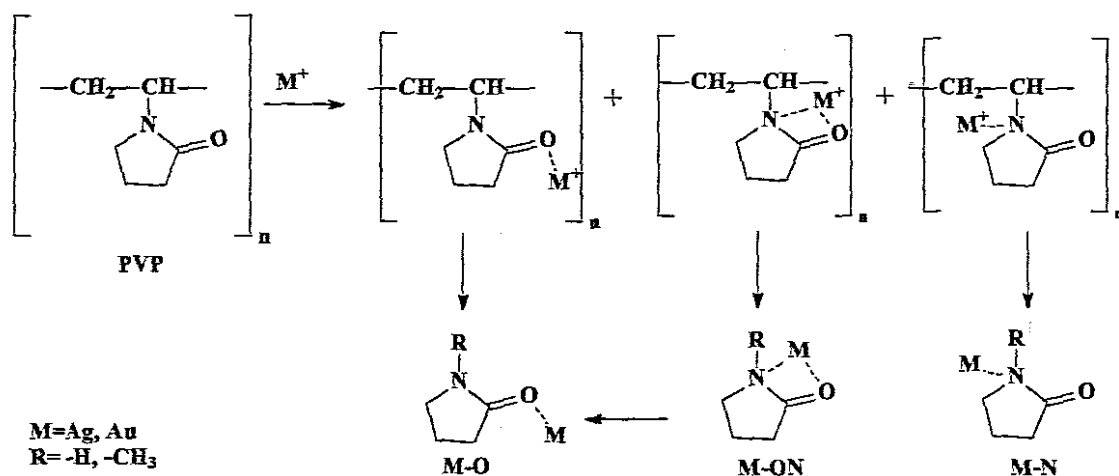


Figure 51 : Mechanism for metal nanoparticle interaction with PVP

The mass of a silver or gold atom is relatively large making the approximation reasonable, on the other hand in silver, the ligand molecule may not be fixed strongly onto the whole silver particle. Table 4 shows the results of the experimental SERS spectra of 2-pyrrolidinone on silver and gold colloids and the calculated Raman spectra with reference to the model in Figure 46 and 47. Figures 46 and 47 show models for the optimized interaction of silver and gold with 2-pyrrolidinone and N-methyl-2-pyrrolidinone respectively. The molecule-metal system shown in Ag-O, Ag-O-Me, Au-O and Au-O-Me (Figures 46 and 47) designated that the orientation of the ligand molecule adsorbed onto the surface of Ag and Au nanoparticles is through the carbonyl group. The system shown as M-ON (Figure 52) showed the gradient orientation of the ligand molecule adsorbed onto the surface of silver and gold both via the carbonyl and the nitrogen atom.

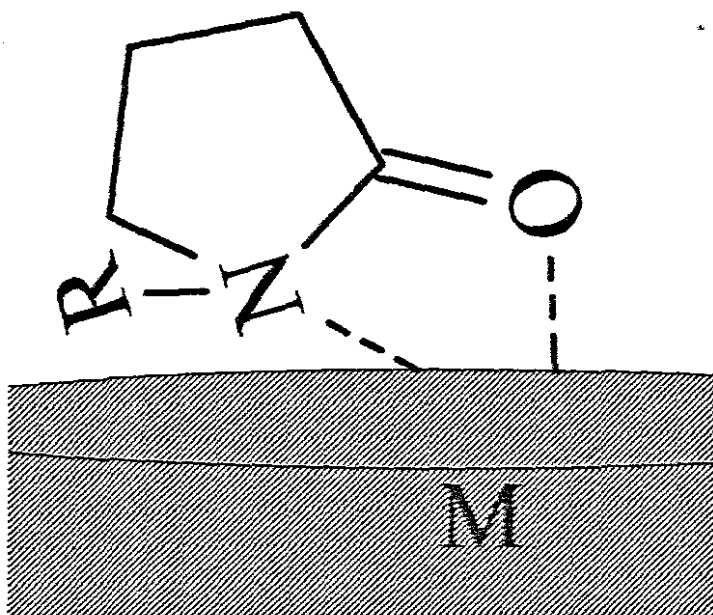


Figure 52 : Possible orientation of the pyrrolidinone on a colloidal metal surface

As shown in **Table 4**, it was found that the calculated Raman frequencies of a model in **Figure 46** are in accordance with the experimental values, thereby consistent with the predicted model. The results suggest that the nitrogen has a weak interaction with the metal surface. For the structures Ag-O, Ag-O-Me, Au-O and Au-O-Me (**Figures 46 and 47**), the frequency analysis showed a new band at about 223 cm^{-1} , which was absent in the Raman spectra of the isolated pyrrolidinone, with experimental limitations prohibiting measurements at frequencies below 200 cm^{-1} . Additionally, the geometry optimisation of the structure with a bonding capacity in both positions CO and N has shown that this structure is not stable and that it transforms into structure M-N (**Figure 52**). In brief, it is concluded that pyrrolidinone is perpendicularly adsorbed onto the surface of the metal nanoparticles mainly via the carbonyl group.

Table 4: Experimental and Raman frequencies of pyrrolidinone, NMP, Au-O, Au-O-Me, Ag-O and Ag-O-Me

Pyro (theory)	Pyro (SERS)	NMP (theory)	NMP (SERS)	Au-O (theory)	Au-O (SERS)	Au-O-Me (theory)	Au-O-Me (SERS)	Ag-O (theory)	Ag-O (SERS)	Ag-O-Me (theory)	Ag-O-Me (SERS)	Tentative assignment *
				226	224	225	219	223	223	227	221	Ag-N/O stretching
654	666	677	655	676	700	654	669	668	634	670	845	CCC in plane bend
823	841	843	847	756	820	799	829	756	760	777	756	Ring torsion, out of plane
888	880	867	899	913	900	920	888	887	887	893	871	Ring breathing, in plane
918	931	929	920	936	923	944	925	933	916	945	922	CH out plane bend
1015	1023	1030	1022	999	978	974	980	1010	963	1023	955	Breathing
1295	1276	1280	1266	1054	1111	1076	1090	1096	1099	1098	1111	β (CN), in plane
1287	1291	1299	1290		1188		1170	1213	1210	1224	1223	β (C-C=O)
1344	1355	1350	1348	1255	1257	1237	1259	1251	1277	1263	1287	CH in plane band
1370	1371	1377	1369	1348	1399	1350	1379	1343	1355	1341	1344	Ring breathing, antisymmetric
1381	1397	1399	1389	1488	1512	1479	1530	1467	1411	1472	1416	(CC, CN)
1443	1465	1450	1447	1559	1566	1580	1578	1533	1560	1540	1545	(CC)
1708	1715	1720	1711	1650	1646	1699	1700	1657	1740	1643	1733	(C=O)

* Assignments consult to theoretical results calculated at B3lyp/LANL2DZ level. Abbreviations: Pyro, pyrrolidinone; NMP, N-methylpyrrolidinone.

The appearance of the Ag-O stretching vibrations at 223 cm^{-1} is consistent with the pyrrolidinone molecule coordinated to the Ag-surface through the non-bonding electrons of oxygen in the carbonyl group. This could be compared to the observed result by Gao *et al* [134] who showed an Ag-O vibration at 233 cm^{-1} (Table 4 and Figure 53). The Raman spectral data of the silver complexes are given in Table 4; the peak at 854 cm^{-1} was assigned to the pyrrolidinone ring which exhibits a moderate Raman enhancement. From

the analysis of pyrrolidinone, the molecule was found to adsorb onto the silver surface mainly through the carbonyl group. **Table 4** displays the experimental SERS data for the gold colloid-pyrrolidinone complex and the calculated Raman spectra based on the model in **Figure 47**.

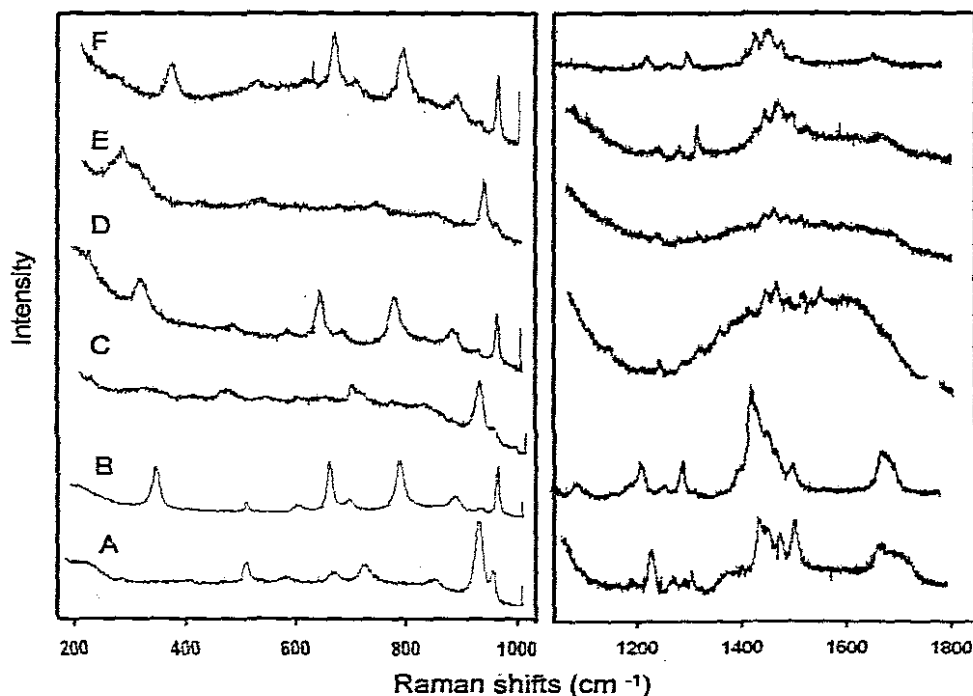


Figure 53 : SERS spectra of pyrrolidinone (A), methyl-pyrrolidinone (B), pyrrolidinone (C) in silver and (D) in gold colloids and methyl pyrrolidinone (E) in silver and (F) in gold colloids

Table 4 contains the experimental SERS spectral data for of pyrrolidinone and N-methyl-2-pyrrolidinone and the calculated Raman spectra. From **Table 4**, it can be seen that the calculated frequencies are close to the experimental Raman frequencies. **Figure 54** illustrates the compact layer formed by pyrrolidinone on the surface of metal nanoparticles indicating that there are three possible modes of interaction which may result from the adsorption of pyrrolidinone on the surface. In Cpl (**Figure 54**) the pyrrolidinone can

adsorb via the non-bonding electrons of oxygen from the carbonyl group to form a compact layer around the metal colloid. It is through this bonding or interaction where upon the kinetically favourable interaction is achieved. This interaction is also favored by the steric effect imposed by the pyrrolidinone ring to the metal. The other interaction is possible via the nitrogen of the pyrrolidinone ring (Cp2). This interaction arises from the charge-transfer between the low electronegative nitrogen with the metal, which renders nitrogen to attach preferably over the oxygen, although oxygen attachment is kinetically favoured.

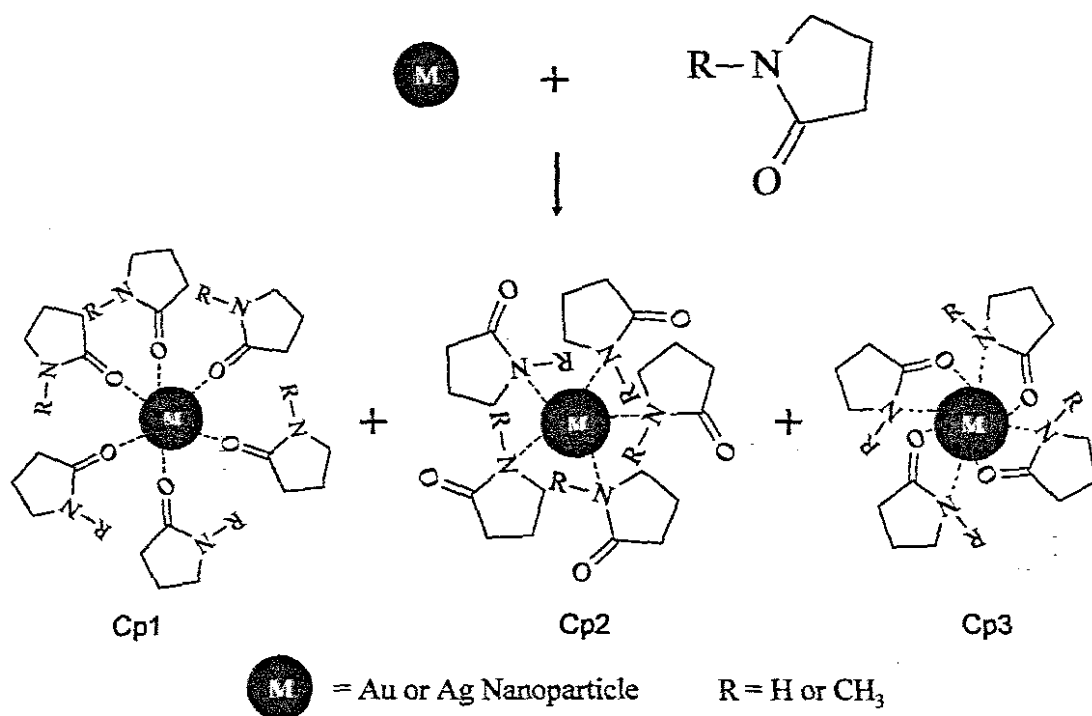


Figure 54 : Interaction of pyrrolidone with metal colloid

In Cp3, the simultaneous interaction of both nitrogen and oxygen on the surface of the metal nanoparticle may seem reasonable; however, all computational attempts to obtain the corresponding stable complex were unsuccessful. Failure to obtain Cp3 was due to the fact that, for both groups to simultaneously interact with the metal surface, the pyrrolidinone

ring has to bend to compensate for the steric effect of the pyrrolidinone ring as shown in **Figure 52**. The possibility of all complexes to be there in solution is subjective to the controlled size and shape of the metal nanoparticle; this has been shown through the consideration of the orientation of PVP on metal nanorods [134]. The influence of the steric factor is indicated by the change in bond length between the metal and the pyrrolidinone molecule. This effect is tabulated in **Table 5**, with the results demonstrating that the bond distance between the metal and pyrrolidinone increases as the steric factor is imposed on the metal nanoparticle. The widening of the Ag14-N5-H13 angle from 99.56° to that of Ag13-N5-C14 (106.55°) is an indication of the steric factor as a result of the replacement of a proton with a methyl group (**Table 5 and Figure 55**). The change of Au14-N5-H13 angle from 103.65° to Au13-N15-C14 (109.41°) angle in gold is minimal and this is attributed to the strong interaction of pyrrolidinone with gold.

Table 5 : Angles of Au-O, Au-O-Me, Ag-O, Ag-O-Me, Au-N, Au-N-Me, Ag-N and Ag-N-Me.

Complexes	Bonds	Parameters ^a
		Bonds (Å)
Ag-O	Ag10-O9	2.15
Ag-N	Ag14-N5	2.27
Ag-O-Me	Ag10-O9	2.15
Ag-N-Me	Ag13-N15	2.28
Au-O	Au10-O9	2.08
Au-N	Au14-N5	2.11
Au-O-Me	Au10-O9	2.08
Au-N-Me	Au13-N15	2.12
		Angles (°)
Ag-O	Ag10-O9-C1	143.26
Ag-N	Ag14-N5-H13	99.56
Ag-O-Me	Ag10-O9-C1	138.44
Ag-N-Me	Ag13-N15-C14	106.55
Au-O	Au10-O9-C1	130.2
Au-N	Au14-N5-H13	103.65
Au-O-Me	Au10-O9-C1	124.63
Au-N-Me	Au13-N15-C14	109.41

^a Bond angles were obtained from the optimized structures in figure 46 and 47

The calculated stability (E_s) of silver to pyrrolidinone (Ag-N) is 19.53 kcal/mol lower than that of the corresponding complex (Ag-O). This trend in stability is eminent for gold to pyrrolidinone complex (Au-N), which is 12.47 kcal/mol lower than that of the corresponding Au-O. The comparative stability of gold and silver proved that they are different and their reactivity towards the surfactant is also different; a fact also confirmed

by the appearance of the secondary peak in the UV-visible absorption of gold (**Figure 50**). However, there is no imminent appearance of a secondary peak for the silver colloids, with only a subsequent diminishing of the absorption maximum. This proved the slow interaction of silver with the surfactant. The shorter bond length of gold-pyrrolidinone complex compared with silver complex showed the higher reactivities of gold towards the surfactant (**Table 5**). The subtle changes in bond angles and lengths due to the imposed steric effects from the interactions of gold and pyrrolidinone are not enough to deduce the differences in reactivities of these metals. Therefore, there is a strong indication that PVP does not interact significantly with the surface of the metal nanoparticle surface, but most likely, it forms a compact layer around the metal colloids preventing any agglomeration which may arise from the selective adsorption of the pyrrolidinone.

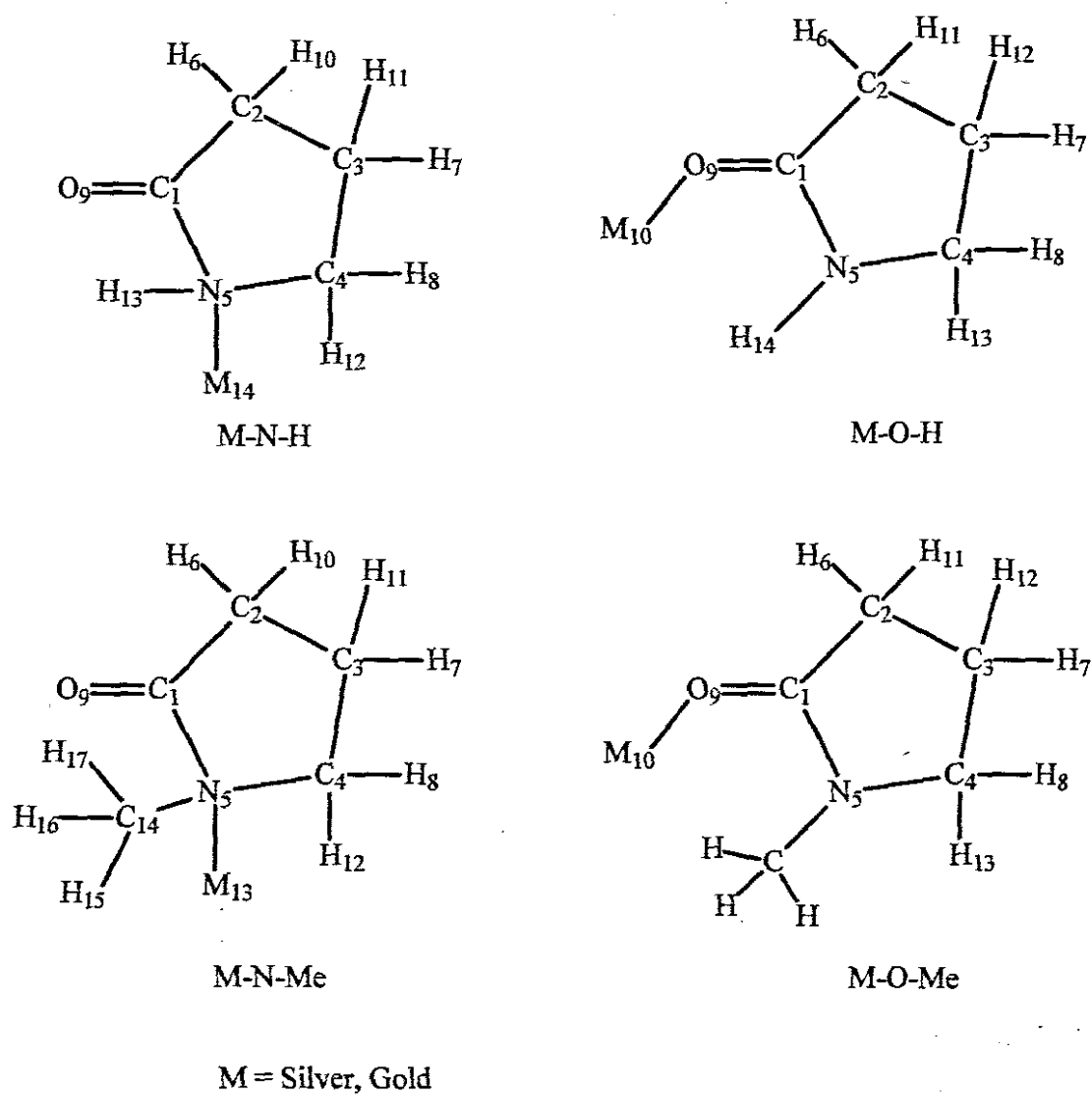


Figure 55: The numbering of atoms of gold and silver to pyrrolidone molecules

4.11. CONCLUSIONS AND FUTURE WORK

From the adsorption behavior, it was concluded that both functional groups may be coordinated to the metal surface. The more powerful the coordinating effect between functional groups and substrate, the easier the charge transfer. Pyrrolidinone, it had two potentially adsorbing groups: a carbonyl group and a pyrrolidinone nitrogen atoms. The carbonyl and the pyrrolidyl nitrogen were active atom or atomic groups that tend to interact with the metal surface. Therefore, two models were hypothesized for the interaction process between the pyrrolidinone molecule and the silver surface: (1) one pyrrolidinone molecule adsorbed on an Ag or Au atom through carbonyl; and (2) one pyrrolidinone molecule adsorbed on two Ag or Au atoms through both carbonyl and nitrogen atoms.

The future prospects for adsorption of PVP on the surface of the crystallographic planes of the metal nanoparticles can be examined. The model for the adsorption of pyrrolidinone and methyl pyrrolidinone on the surface of silver (110) and gold (110) is shown in **Figures 56 and 57**. This method could be useful to calculate the binding energy of PVP on the surface of the facet of silver and gold. The binding energy would explain the selective adsorption of PVP on the surface metal nanoparticles. This is the measure derivitization to explain the growth dynamics in metal nanoparticles. The selectivity toward the adsorption of PVP gives rise to morphologically evolution in metal nanoparticles. The frontier orbital for the interaction of silver with pyrrolidinone depends on the Highest Occupied Molecular Orbital (HOMO) and Lowest Occupied Molecular Orbital with the lowest energy

separation. More detailed work on the involvement of orbital would be looked at for both gold and silver systems. The silver molecular orbital diagram is shown in Figure 58.

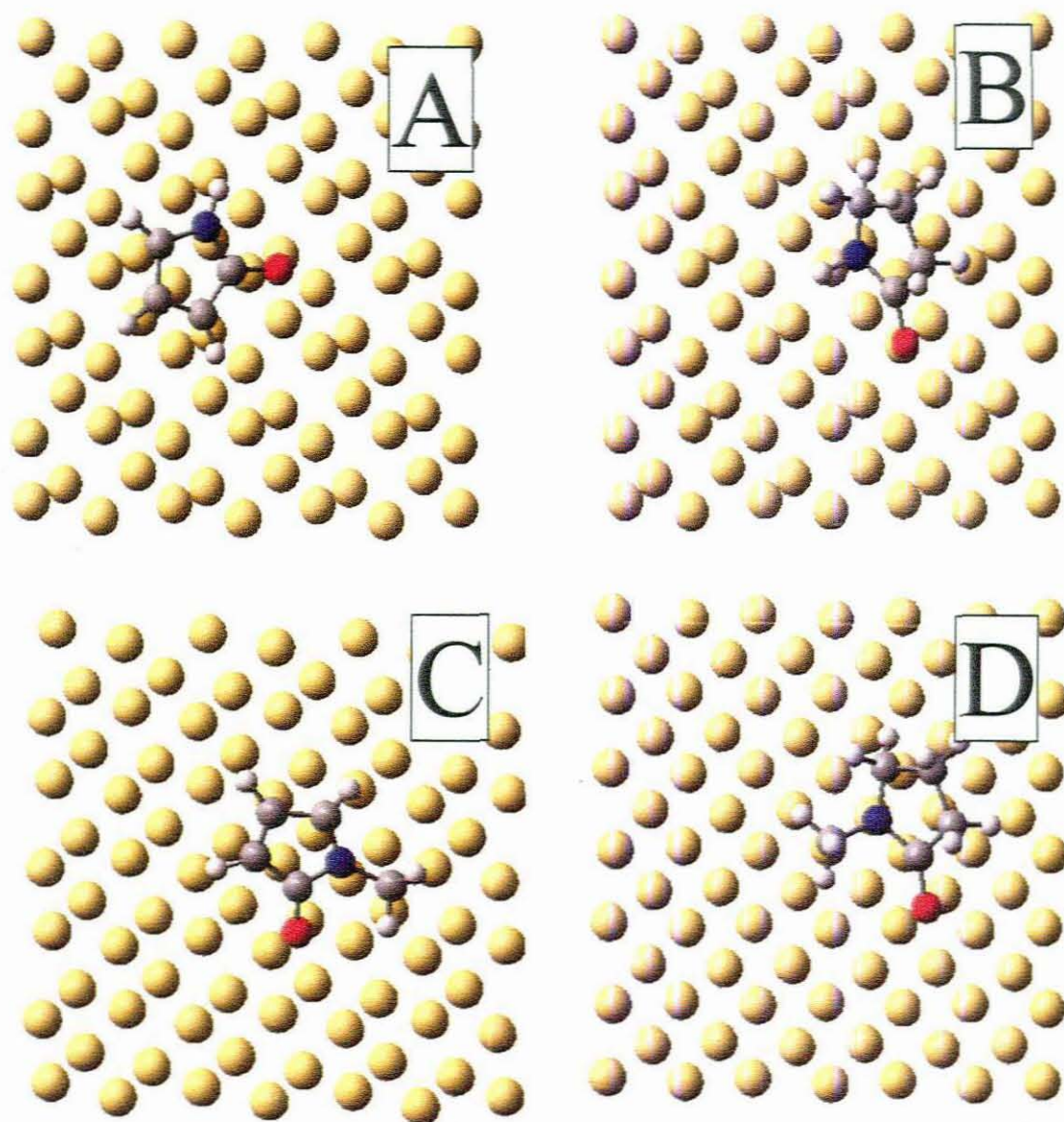


Figure 56: Au(110)-A-pyrrolidinone adsorbed on Ag(110) by nitrogen, B-pyrrolidinone adsorbed on Au(110) by oxygen, C –methyl pyrrolidinone adsorbed on Ag(110) by nitrogen, C-methyl pyrrolidinone adsorbed on Au(110) by oxygen

separation. More detailed work on the involvement of orbital would be looked at for both gold and silver systems. The silver molecular orbital diagram is shown in Figure 58.

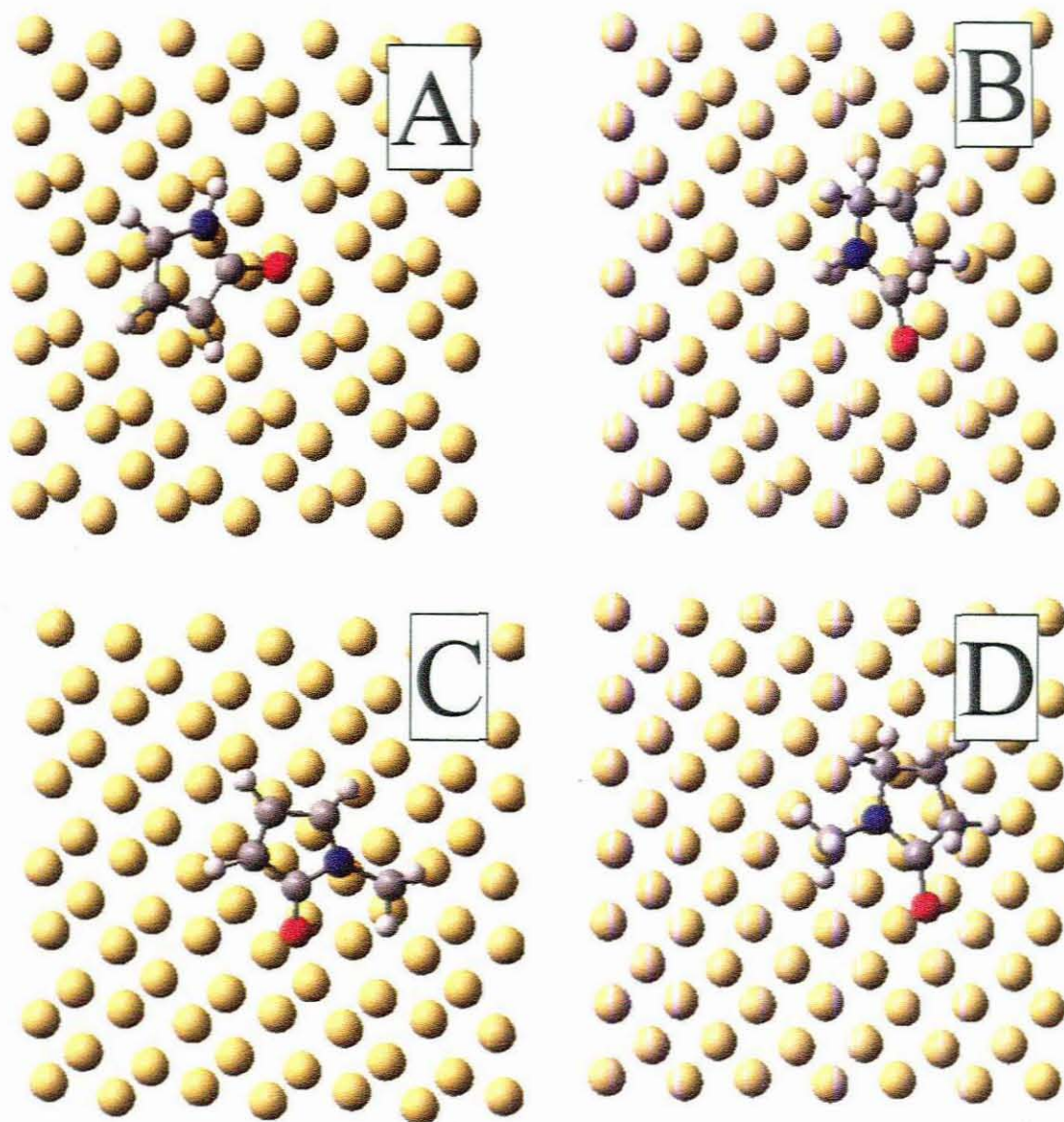


Figure 56: Au(110)-A-pyrrolidinone adsorbed on Ag(110) by nitrogen, B-pyrrolidinone adsorbed on Au(110) by oxygen, C –methyl pyrrolidinone adsorbed on Ag(110) by nitrogen, C-methyl pyrrolidinone adsorbed on Au(110) by oxygen

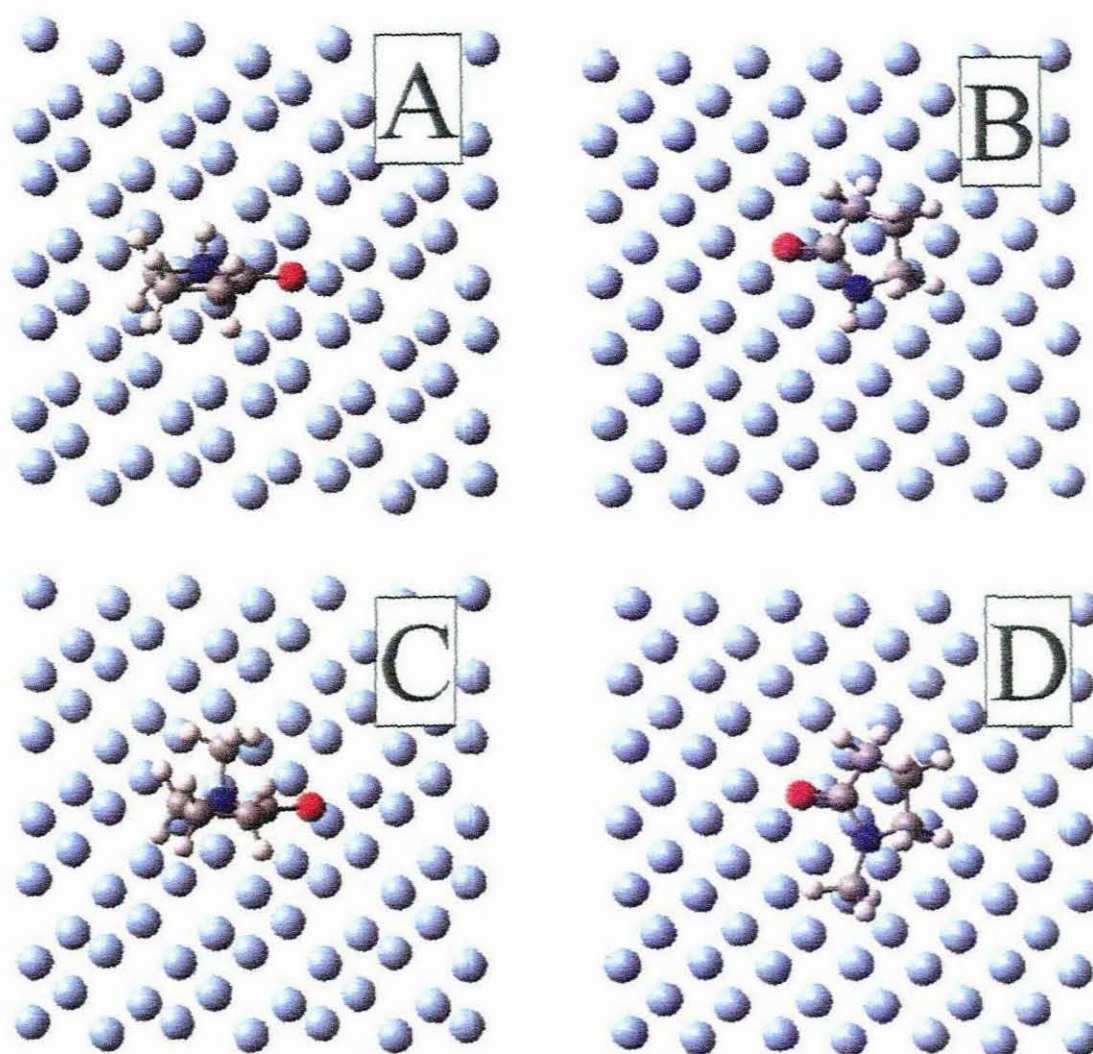


Figure 57: Ag(110), A -pyrrolidinone adsorbed on Ag(110) by nitrogen, B-pyrrolidinone adsorbed on Ag(110) by oxygen, C -methyl pyrrolidinone adsorbed on Ag(110) by nitrogen, C-methyl pyrrolidinone adsorbed on Ag(110) by oxygen

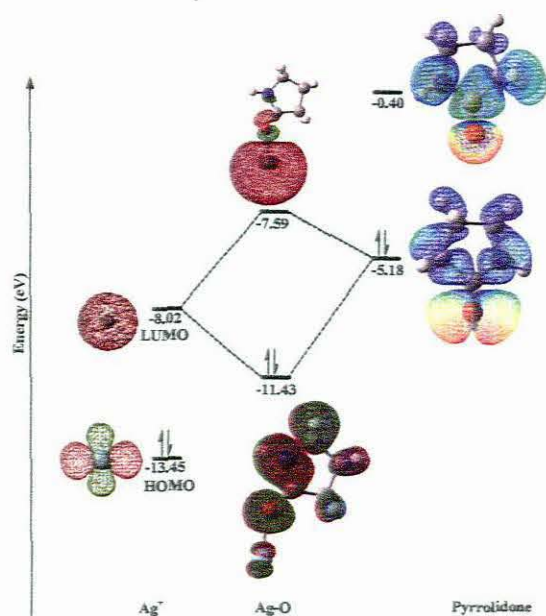


Figure 58: Orbital representation of silver to pyrrolidinone interaction

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List Of Published and Ready For Publication Papers

1. Mdluli PS, ^a Revaprasadu N* "Improved N,N-dimethylformamide And Polyvinylpyrrolidone Approach For Synthesis Of Long Silver Nanowire, . J. Alloys Compd., 469, 2009, 519
2. Mdluli PS, Sosibo NM, Revaprasadu N "Surface Enhanced Raman Spectroscopy and Density functional Theory study for understanding the regioselective adsorption mechanisms of methyl-pyrrolidone and pyrrolidone on the surface of silver and gold nanoparticles", Theochem, submitted
3. P.S. Mdluli, N. Revaprasadu, Damir A. Safin, M. Afzaal, M. Helliwell, P. O'Brien, E. R. Shakirova, M. G. Babashkina, A. Klein "Synthesis of HDA capped silver nanoparticles and thin film using complexes of N-(Diisopropylthiophosphoryl) thiourea derivatives" Journal of Material Science, Submitted.
4. Mdluli PS, Revaprasadu N. "A time dependant evolution of silver nanotrees in solution using formamide as reducing agent" Material letters 63, 2009, 447-450.

Contributions to National and International Symposia or Conferences

1. *Summer school on modelling and theories of nanomaterial held in Port Elizabeth (2006)*
2. *37th International Conference in Coordination Chemistry, ICCC (2006) in Cape Town Poster Phumlane Mdluli and Revaprasadu entitled "Synthesis and the growth dynamics of silver nanoparticles"*
3. *Post Graduate Symposium at University of Zululand (2006) Poster Phumlane Mdluli and Nerish Revaprasadu entitled "Synthesis and the growth dynamics of silver/Gold nanoparticles"*
4. *South African Nanotechnology Institute, SANI (2006) in Cape Town: Poster Phumlane mdluli and Neerish Revaprasdu entitled "Synthesis and the growth dynamics of silver nanoparticles"*
5. *Workshop on structure and properties of nanomaterials in partnership with ICMR (2007), Richards Bay Mdluli and Nerish Revaprasadu entitled "Synthesis and the regioselective adsorption of pyrrolidone on silver/Gold nanoparticles"*
6. *Summer institute on modeling and theories of nanomaterials, from June to July 2006 in Jackson State University, Computational Center for Molecular Structure and interactions (CCMSI)*
7. *Atmospheric Dispersion Project, Summer Field Session/Symposium 27 July 2007, Jackson State University, USA.*

8. ICMAT 2007 — Symposium :New Routes to Inorganic Materials, Films and

Nanocrystals: N. Revaprasadu, N. M. Sosibo and P. S. Mdluli entitled Synthesis

and Functionalisation of Isotropic and Anisotropic Silver and Gold Nanoparticles

Cartesian coordinate of all optimized complexes

Au-N-H

#P b3lyp/lanl2dz opt(tight) freq=raman

1,1

C,1.7459534247,0.9778182014,0.0959103937

C,2.7806784674,0.1738132023,-0.6668681294

C,2.3472489713,-1.3048101766,-0.5446655247

C,1.5836739603,-1.3638754799,0.7959593881

N,0.8368560202,-0.0320251519,0.8334265005

H,2.8520046169,0.5411342763,-1.6954614368

H,1.6916787462,-1.5908750082,-1.3758121157

H,2.274796754,-1.3770142411,1.6487685675

O,1.5631619776,2.1761153944,0.2196768941

H,3.7592370217,0.3562869352,-0.2003552827

H,3.1971508923,-1.9908373079,-0.5430132993

H,0.8941519813,-2.2034933426,0.8832615348

H,0.6501378998,0.3088894492,1.7874427085

Au,-1.0679867338,-0.0270197507,-0.0796431985

HF=-421.7746361

Au-O-H

#P b3lyp/lanl2dz opt(calcfc,tight) freq=raman

1,1

C,1.3020921447,1.0413661791,-0.0000110557

C,2.3022051623,-0.0957197458,0.0000303189

C,3.6951273559,0.6065126069,-0.0000293429

C,3.4067441901,2.1436691354,0.000022459

N,1.9211974191,2.2192718729,-0.0000189928

H,2.143567393,-0.7258442732,0.8837399878

H,4.2756810936,0.3250687629,0.8812082259

H,3.7991240902,2.6479083029,-0.8883354716

O,0.0000091239,0.9770863477,-0.0000318392

H,2.1435413592,-0.7259436868,-0.8836026214

H,4.2755750418,0.3251123388,-0.8813511792

H,3.7990687023,2.6478395911,0.8884446278

H,1.4092021994,3.0987817344,-0.0000373602

Au,-1.2597542756,-0.6724401664,-0.0000277564

HF=-421.7945092

Au-N-Me

#P b3lyp/lanl2dz opt freq=raman

I,1

C,1.6901528967,0.5851699454,-0.687922809
C,2.5043928278,-0.6803409984,-0.8788869977
C,2.0301892341,-1.6637111511,0.2153992722
C,1.5125393804,-0.7443740991,1.3401942883
N,0.8483517024,0.4158415385,0.6006261382
H,2.3884692066,-1.0506790948,-1.9023914722
H,1.2294088734,-2.3134828943,-0.1578582671
H,2.3446614906,-0.3191001065,1.9183326744
O,1.6472699938,1.6250185145,-1.3243541542
H,3.5644244158,-0.4145282095,-0.7623208635
H,2.8359097798,-2.308193682,0.5744020341
H,0.8112418855,-1.2172533531,2.0284511087
Au,-1.0814838065,-0.1205133371,-0.1066075312
C,0.7534870466,1.7043799828,1.398716941
H,0.0982588343,1.5538068746,2.258609903
H,1.757822255,1.9788077765,1.743138377
H,0.3676839837,2.4978272937,0.7565403577

HF=-461.0785375

Au-O-Me

#P b3lyp/lanl2dz opt

1,1
C,1.042539,-0.015775,0.025501
C,1.332187,-1.506783,0.112693
C,2.857779,-1.612399,-0.161506
C,3.401538,-0.17629,0.083157
N,2.186657,0.68176,-0.000453
H,1.063036,-1.861917,1.116891
H,3.345984,-2.343057,0.487033
H,4.129534,0.13707,-0.671763
O,-0.121961,0.547626,0.000494
Ag,-2.188936,-0.034724,-0.005654
H,0.726488,-2.065068,-0.609134
H,3.036684,-1.911893,-1.198333
H,3.860311,-0.059624,1.073145
C,2.279262,2.149355,-0.029957
H,1.273123,2.571804,-0.061582
H,2.796987,2.511615,0.865865
H,2.837112,2.471108,-0.916488

HF=-471.4571396

Au-N-Propyl

#p b3lyp/lanl2dz opt

1,1
C,1.9228709123,0.0720509287,-0.8938080173
C,2.8173286864,-1.0496383499,-0.3943731156
C,2.2406914808,-1.4781748113,0.9703711787

C,1.5158490485,-0.2155144921,1.4699277815
 N,0.8875707854,0.3903424203,0.2103735955
 H,2.8644340441,-1.8491791307,-1.1404834566
 H,1.5366011765,-2.3122673613,0.8589444539
 H,2.2330562122,0.519996907,1.8600624253
 O,1.9720463895,0.6990441516,-1.9407899114
 H,3.8358628181,-0.6473610405,-0.3047292669
 H,3.0149658236,-1.7925432648,1.6742969331
 H,0.7563685921,-0.404628628,2.2268750828
 Au,-0.8454107934,-0.7511403098,-0.343748567
 C,0.5055732705,1.8901193492,0.3289036948
 H,1.4762936956,2.4106758456,0.3510599522
 C,-0.2523711454,2.1449999837,1.6424033766
 H,-0.5305039178,3.2035442757,1.6841589241
 H,-1.1819238915,1.5591757539,1.6846648427
 H,0.3405605529,1.9293412139,2.5361365304
 C,-0.2975250083,2.3827563369,-0.8871826958
 H,-1.2824295841,1.8895168461,-0.9303073782
 H,-0.4829285735,3.4567316218,-0.7709125867
 H,0.2241154255,2.2255267541,-1.831559776

HF=-539.7007415

Au-O-Propyl

#p b3lyp/lanl2dz opt freq=raman

1,1

C,1.1256211093,0.5256186416,0.0000696489

C,1.0766001896,2.0393249567,0.0000296661
C,2.5703718863,2.4773075682,0.0003166628
C,3.3927021845,1.1535929344,-0.000823851
N,2.3690309456,0.0630386869,-0.0005775535
H,0.5298663202,2.3904988122,-0.8843160689
H,2.8042117255,3.0795242838,-0.8804955246
H,4.0263900405,1.0464130216,0.8860496816
O,0.0904968307,-0.288261633,0.0007805511
H,0.5294744762,2.3905914205,0.8840984639
H,2.8042508386,3.0779933253,0.88216618
H,4.0252222911,1.0471813046,-0.8886184982
Au,-1.9005295386,0.2651479949,0.0033084245
C,2.7927667623,-1.3834910859,-0.000533836
H,3.8886352717,-1.3429667832,-0.0025760265
C,2.3230280445,-2.0937033689,-1.2872870128
H,1.2312665635,-2.1620067109,-1.3262736887
H,2.6800493842,-1.5756481502,-2.1854411296
H,2.7289803356,-3.1112405828,-1.3024378839
C,2.3276172102,-2.0918467809,1.2889226978
H,2.6910462794,-1.5747117427,2.1850311488
H,1.2358403474,-2.1565635287,1.3336453726
H,2.7302435019,-3.1107275833,1.3022345757

HF=-539.7217592

Ag-N-H

#P b3lyp/lanl2dz opt(tight) freq=raman

l,1
C,1.2634548696,0.9878504639,0.1583448802
C,2.4788241824,0.4519026093,-0.5748567711
C,2.2804770429,-1.0820446944,-0.6086628123
C,1.4630767807,-1.3853330348,0.6712858585
N,0.5791417806,-0.16015465,0.8215519029
H,2.5726385154,0.9221483631,-1.5574352199
H,1.7233310268,-1.3815193257,-1.5046938192
H,2.1156011912,-1.4601955691,1.549905318
O,0.8054586396,2.1277695342,0.2363457682
H,3.3731521954,0.7336668469,-0.0004935066
H,3.2267546418,-1.6273647421,-0.6119725089
H,0.8649100021,-2.2951329507,0.600765965
H,0.339173714,0.067257424,1.7945085235
Ag,-1.4932985825,-0.0843032747,-0.1057615782

HF=-432.1195219

Ag-O-H

#P b3lyp/lanl2dz opt(calcfc,tight) freq=raman

l,1
C,1.2299738375,0.2673915319,-0.0375888022
C,1.7499172994,-1.1543145389,0.1260382114
C,3.2803859704,-1.0278760127,-0.1199697441
C,3.5967088266,0.483933869,0.0868632607
N,2.2637289683,1.1220605037,-0.0680688313
H,1.5174550634,-1.4992499635,1.1427999226

H,3.8630745565,-1.6549089515,0.5582068115
H,4.2950414488,0.8753510804,-0.6579626629
O,0.0052431722,0.6529570319,-0.120075291
Ag,-2.0277991407,-0.0530380096,-0.1359259835
H,1.2553031826,-1.8341157556,-0.5751824312
H,3.5236838726,-1.32519749,-1.1443508362
H,3.9953480719,0.6967664053,1.0855336011
H,2.1307798703,2.1268922996,-0.140317225

HF=-432.1506524

Ag-N-Me

#p b3lyp/lanl2dz opt freq=raman

l,l
C,1.2506859624,0.6287702953,-0.6754451547
C,2.2208420533,-0.5119648835,-0.9394236172
C,1.8810309163,-1.5851539846,0.1205531504
C,1.3079333549,-0.7618437524,1.2951519975
N,0.5519485228,0.3647988309,0.6176566026
H,2.1487255798,-0.8505116287,-1.9768141917
H,1.1359612301,-2.2948086898,-0.2630328056
H,2.1159810047,-0.3200841273,1.8954186633
O,1.0074278637,1.6317625186,-1.3472986768
H,3.2394932531,-0.1204241961,-0.8069382
H,2.754569513,-2.1641532308,0.4284514036
H,0.6539485773,-1.3276031331,1.9616213041
Ag,-1.4993411164,-0.2516483288,-0.1683110908
C,0.3357261771,1.5960717159,1.4654144284

H,-0.1078022837,2.3853151848,0.8538094549
H,-0.3183697148,1.3573014776,2.3078002702
H,1.2988401065,1.9523419319,1.8521854618

HF=-471.420761

Ag-O-Me

#p b3lyp/lanl2dz opt freq=raman

l,l
C,1.0559053861,-0.0434830852,-0.0422689922
C,1.4219038731,-1.5159205599,0.0698719682
C,2.9665837917,-1.5353766662,-0.0955233522
C,3.410202713,-0.0711715641,0.1824122556
N,2.1580287496,0.7172908572,0.0104734942
H,1.1027749169,-1.8864515589,1.0536604349
H,3.447949044,-2.237966539,0.588188692
H,4.1710195319,0.2832426904,-0.5201724873
O,-0.1336972064,0.4535808456,-0.1512634514
Ag,-2.1591050444,-0.2440448481,-0.3015905562
H,0.9010631938,-2.1067789303,-0.6911785291
H,3.2348901978,-1.8234844683,-1.1161702179
H,3.7905447829,0.0702869803,1.2019657037
C,2.1699566712,2.1877949668,-0.0170439759
H,1.1464483135,2.5530379497,-0.1210068009
H,2.601882114,2.5778494901,0.9119686933
H,2.7701579712,2.5411314399,-0.8629588787

HF=-471.4571396

Ag-N-Propyl

#P B3LYP/LANL2DZ OPT

1,1

C,0.975547691,1.2352351734,-0.4733238836
C,2.0838574808,0.7793415804,-1.4100450127
C,2.1014360512,-0.7615995591,-1.2862111122
C,1.577090839,-1.0117198166,0.1457550996
N,0.5353064125,0.0727614037,0.3392695854
H,1.9194948994,1.1586437137,-2.4224445147
H,1.4387165798,-1.2221384837,-2.0319527824
H,2.3802133602,-0.868638217,0.8779626401
O,0.464880666,2.3514189425,-0.3504166811
H,3.0254370526,1.2227315857,-1.0560296307
H,3.0979578742,-1.1861789953,-1.4277620955
H,1.1456938723,-2.0032156958,0.2933245051
Ag,-1.4129590973,-0.4651547914,-0.7330884874
C,0.0993936621,0.4189133263,1.7688257434
H,-0.5357061229,1.3046525218,1.6495457951
C,1.3009280405,0.8105378355,2.6564535498
H,1.9094454063,1.5948660963,2.1921745304
H,0.9214256978,1.2141743946,3.6018447107
H,1.9400971318,-0.0453767195,2.9010194049
C,-0.7181638501,-0.7317424534,2.3771311371
H,-1.0796531648,-0.4437107889,3.3702356161
H,-1.6130784077,-0.9696472666,1.7728887408

H,-0.127696308,-1.6483648329,2.4912852119

HF=-550.043421

Ag-O-Propyl

#p b3lyp/lanl2dz opt freq=raman

1,1

C,-0.7463998812,-0.5869592583,-0.0205891129

C,-0.9187271927,-2.0969897665,-0.1071351383

C,-2.4308346947,-2.3193084655,0.1644808378

C,-3.078728822,-0.9317568335,-0.095378418

N,-1.9359156532,0.0259280576,-0.0058556228

H,-0.62173759,-2.429544534,-1.1115629041

H,-2.8608028534,-3.0925014947,-0.4762241134

H,-3.8367666929,-0.6726457072,0.6501570675

O,0.3833130987,0.0496060068,0.0102715178

Ag,2.4755230207,-0.4051773442,0.0113135425

H,-0.2718003179,-2.6062804504,0.6154478661

H,-2.5889322273,-2.6200599049,1.2045782338

H,-3.5357067083,-0.8579995244,-1.0902830762

C,-2.1753917267,1.5084973691,0.0090537287

H,-3.2675777677,1.6108287909,0.0013867186

C,-1.6156240146,2.1761020571,-1.2651213901

H,-1.8927958846,3.2363703204,-1.2698631266

H,-0.523666728,2.1071618982,-1.2981732372

H,-2.0276874151,1.7164431816,-2.1717343952

C,-1.6361282288,2.1428297371,1.308232471