



Theoretical studies of Raman scattering properties of methylphosphine and methylamine adsorbed on gold clusters



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ABSTRACT

Recent reports have demonstrated that nanoclusters of silver and gold can act as substrates for Raman signal enhancements. This article presents a density functional theory (DFT)-based study to explore how the variations in the nature of the cluster-binding heteroatom in the ligand molecule and the relative orientation of the alkyl group attached to the heteroatom affect the Raman signal enhancement in the ligand molecules. Our calculations involved nitrogen and phosphorus heteroatoms in two simple model molecules, methylphosphine and methylamine, as ligands and four small gold clusters, Au_n ($n = 6-9$). In order to understand the interactions in the cluster-molecule systems, we have calculated various geometrical parameters such as Au-X ($X = P, N$) distances, $\angle C-X-Au$ angles and different bond lengths of free and cluster-bound molecules as well as various interaction energies. We have performed natural bond order (NBO) analysis and have calculated second order stabilization energies for the molecules bound to the gold clusters from the NBO analysis. In addition, we have performed detailed calculations pertaining to the change in polarisability, quantity of molecule to cluster charge transfer as well as molecular orientations relative to the clusters and have studied how these factors influence the Raman scattering cross-sections and vibrational frequency shifts. The quantity of charge transfer and the orientation effect have been found to be important contributors in the chemical Raman enhancement mechanism of the ligand molecules.

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1. Introduction

Raman spectroscopy is an analytical tool that can provide information about molecular structure, conformation, dynamics and interactions relatively easily and quickly for a wide variety of samples and media, including IR-opaque aqueous media. Since, Raman spectroscopy measures the spectrum of photons inelastically scattered by molecules and materials [1,2], the low efficiency of inelastic photon scattering from most of the molecules, particularly under low concentration conditions, leads to weak Raman signals. This limits wide applications of Raman technique [3]. Surface-enhanced Raman scattering (SERS) technique has emerged as one of the simplest techniques that can greatly enhance the Raman signals of molecules present in contact/proximity of plasmonic particles or rough metal surfaces [4–7]. SERS technique couples the large signal enhancement and the

suppression of fluorescence to the high molecular specificity of conventional Raman spectroscopy. These features have made SERS a powerful technique for ultrasensitive chemical analysis down to single molecule detection [8,9]. After its observation on roughened metal electrodes, a variety of substrates such as metal colloids and nanoparticles, metal island films, etc., have been observed to show SERS [10–12]. Experimental and theoretical studies demonstrated that the SERS enhancements have mainly two kinds of enhancement mechanisms—chemical and electromagnetic [13]. The chemical enhancement mechanism involves an increase in the polarisability of the substrate-adsorbed molecules due to interactions between the adsorbed-molecule electronic states and the substrate-metal electrons [5,6]. It has been, however, observed that such chemical effects are of short-range and they enhance the signal by a factor of $\sim 10-1000$. The dominant contribution to the SERS enhancement (enhancement factor of $\sim 10^6-10^{10}$) comes from the electromagnetic effects. The electromagnetic enhancement is believed to be a result of enhanced local electric field caused by the excitation of localized surface plasmon resonance (LSPR) in the substrate with nanoscale surface features [7]. The

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enhanced local field leads to the amplification of both the incident and scattered radiations for analyte molecules residing within the enhanced local field range [7].

The strength of local electromagnetic field depends on factors such as the nature, size, shape, orientation, and extent of aggregation of plasmonic nanosystems. Substrates that have sharp nanoscale surface features or nanoscale gaps can concentrate the electromagnetic field in a very small volume (creating so-called “hotspots”) which gives rise to large enhancements in Raman scattering intensity [14]. However, the magnitude of enhancement is extremely sensitive towards the geometrical details in the nanostructures [15]. It is practically challenging to produce these substrates with precisely controlled size, shape, and surface features or aggregation leading to the formation of hotspots. This results in irreproducibility in SERS spectra. Therefore, preparation of reproducible and stable SERS substrates still remains challenging. Developments in the fabrication of periodic metallic nanostructures have led to high reproducibility in SERS spectra of some samples. However, fabrication of such patterned substrates is tedious and the substrates are often large compared to nanoscale. Therefore, the quest for developing alternative, reproducible Raman substrates continues unabated.

Recent reports demonstrate that nanoclusters of silver and gold can be used as viable Raman substrates [16–18]. Nanoclusters have molecule-like fixed compositions and have sizes less than that of typical nanoparticles. The small size could make the clusters suitable for various biological applications. Recently we have demonstrated how the variation in gold cluster size (Au_n , $n = 3–13$) modulates the electronic properties (viz., HOMO–LUMO gaps, dipole moments, etc.) of the cluster–proline complexes [19,20]. Molecule-like compositions of clusters and the specificity of cluster–molecule interactions can, in principle, give stable and reliable Raman spectra. Further, reproducible synthesis methods for the preparation of stable clusters of definite compositions and various sizes have started to appear. This provides us an opportunity to use various nanoclusters as controllable Raman substrates. For example, Pradeep and co-workers used Ag_{55} and Ag_{152} clusters as SERS substrates and observed a Raman enhancement factor of $\sim 10^8$ which were higher than that for 3–4 nm Ag nanoparticles [16]. Paramanik and Patra reported use of nanoclusters of Au as well as Au–Ag alloy for SERS of methylene blue [17]. Based on the computational study on a pyridine– Ag_{20} cluster model system, Schatz and co-workers predicted a cluster-mediated Raman enhancement comparable to findings on single nanoparticles [18].

Schatz and co-workers had performed a series of computational studies exploring various aspects of SERS spectroscopy [18,21–23]. For example, they studied the influence of the nature of metal substrates on SERS of pyridine by taking gold and silver clusters as model systems [21]. In a novel study they compared the effects of interaction sites – vertex orientation vs. surface orientation – of pyridine molecules on the Ag_{20} cluster-enhanced Raman scattering [18]. In another study they investigated how the absorption and Raman properties of pyridine molecule depend on the size of the clusters [23]. Cabalo et al. also reported a computational study on the orientation effects of analyte molecules, benzenethiol and 4-mercaptophenol, with respect to Ag, Ag_3 , Ag_5 and Ag_7 clusters as SERS substrates and compared their results with that of experimental study by using 36 nm Ag nanoparticles [24]. You et al. showed the importance of both the bonding and configuration effects of 4,4'-thiobisbenzenethiol molecule with respect to silver clusters [25]. Saikin et al. investigated both off-resonant and resonant enhancements and benzene ring–cluster orientation as well as proximity effects of analyte molecule, benzenethiol, on Ag_n ($n = 6–11$) clusters as substrates [26]. Huang et al. reported a similar study involving neutral adenine – Ag_n ($n = 4, 7, \text{ and } 9$) complexes

[27]. Similarly, Fleming et al. and Wu et al. reported a few studies on silver and gold systems [28–30]. Muniz-Miranda et al. demonstrated how the electric charge on metal cluster affects the charge transfer between the ligand, pyrazolide anions, and the metal cluster, $(Ag_4)^{+2}$, and hence affects the spectral frequency and intensities [31]. By using density functional calculations, Lang et al. studied SERS of adenine and 2'-deoxyadenosine 5'-monophosphate (dAMP) adsorbed on Ag_{20} cluster [32].

In most of the cases of SERS, the actual signal enhancement is a result of combined chemical and electromagnetic effects. However, both the chemical and the electromagnetic enhancement mechanisms can operate independently. Nanoclusters consisting of only a few atoms are unable to support plasmon resonances and hence show hardly any electromagnetic enhancement effect. In order to explore the chemical enhancement effect, researchers had investigated a number of silver and gold clusters as SERS substrates for several analyte molecules and their derivatives. For example, recently Valley et al. investigated how the chemical enhancement varies with various substituents on benzenethiol in a combined experimental and computational study involving Au_{19} cluster and immobilized silver and gold nanorod assemblies [22]. Jensen and co-workers reported systematic studies on the effects of charge transfer in chemical enhancement mechanism of SERS by using Ag_{20} cluster as model substrate and various pyridine derivatives as analyte molecules [33,34]. Similarly based on the calculations using dimercaptoazobenzene – Au_n ($n = 3, 5, 19$) clusters along with experiments using Au nanoparticles, Lang et al. concluded that the trend in chemical enhancement could be governed by the difference between the HOMO of the analyte molecule and the LUMO of the gold cluster [35]. From the experimental measurements on only a few atoms–Ag clusters with no plasmon resonances, Peyser-Capadona et al. concluded that only the chemical enhancement might be strong enough to allow single molecule detection [36]. By using time-dependent density functional theory, Schatz and co-workers obtained similar large chemical enhancement factors (10^5) for Raman scattering of pyrazine molecule complexed to the vertices of two Ag_{20} clusters [37]. All these studies suggest that small clusters of silver and gold can be an important class of Raman signal enhancement substrates. In the present study we have used density functional theory (DFT) to explore how variations in the nature of the heteroatoms in the ligand molecule and the relative orientation of alkyl group attached to the heteroatom influence the Raman signal of the cluster-bound ligand molecules. We have chosen two simple molecules, namely methylphosphine ($MePH_2$) and methylamine ($MeNH_2$), as model ligands for our calculations, because each one of them has only one functional group with one heteroatom and the smallest possible alkyl group, methyl, attached to the heteroatoms. Recent reports on SERS involve mostly silver and a very few gold nanoclusters. Therefore, we have chosen small gold clusters, Au_n ($n = 6–9$), as Raman substrates. The variation in cluster size enables us also to study the effects of differing cluster properties on the Raman scattering behaviour of cluster-bound ligand molecules.

2. Computational details

In the following, L represents one of the ligands whereas L^1 and L^2 , represent methylphosphine and methylamine, respectively. The interactions of methylphosphine and methylamine with four Au_n ($n = 6–9$) clusters were studied using Gaussian/09 suite of programs [38]. All the calculations were performed in gas phase using B3LYP (Becke three parameter Lee–Yang–Parr) hybrid exchange correlation functional [39–41]. The SDD (Stuttgart–Dresden) [42–44] basis set was used for Au atoms which utilizes the 19 electron effective core potential (ECP) and Pople's 6-311 + +G

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