Abstract

The objective of the present thesis is focused on the Surface Enhanced Raman Spectroscopic (**SERS**) study of different arylazo imidazole (AAI) molecules adsorbed on colloidal silver nanoparticles (SNPs). The AAIs have two N heteroatoms and a pendant azo group and show significant chemical interaction **(chemisorption)** with Ag nano particles through exchange of electronic charge. These five membered N-heterocycles are poor π-acceptors and hence good π-donors. Thus there is a possibility of charge transfer between the AAIs and the Ag-particles which has been probed by SERS. The significant modification of the physical and chemical properties of the complexes due to presence of different substituents in the heterocyclic ring and side arm to azo functions has also been investigated by a comparative SERS study. The present work gives information for better understanding of the mechanism involved in SERS and finds the possibility of some AAIs of being used as organic semiconducting material.

The thesis consists of nine chapters and an outline of each of them is given below:

In **Chapter 1**, the mechanisms involved in Raman scattering as well as in the enormous enhancement of Raman signal of the molecules adsorbed on suitable metal surfaces due to SERS effect are discussed. At the beginning the classical and quantum theories of Raman effect are presented. In the following sections, advantages and limitations of normal Raman spectroscopy are illustrated. Although Raman signals can be used as a fingerprint for a given structure of molecule as different structures exhibit characteristic Raman spectra, normal Raman signals are very weak. That SERS effect enhancing the Raman signal by a factor of 10^{10} to 10^{11} overcomes the weak scattering cross-section of normal Raman spectroscopy is discussed in the subsequent sections of this chapter in different sub-sections:

Discovery of SERS, Key features of SERS, SERS substrates, Mechanisms involved in SERS and Application of SERS.

Chapter 2 gives a brief description of the materials and methods of study along with the experimental details. The instrumentation for the related experiments is also discussed in a nutshell. This chapter consists of sections presenting an overview of the functional properties of the arylazo heterocyclic molecules, preparation of colloidal SNPs and recording of UV−Vis spectra, Raman spectra and Transmission Electron Micrograph (TEM). The computational details for the simulation of Raman and SER spectra for comparison with experimental results are presented in the concluding section.

In **Chapter 3,** the Raman spectra and SERS of 1H-2(phenylazo) imidazole (PaiH) adsorbed on SNPs are presented. A *trans*-to-*cis* isomerization of PaiH is suggested by the appearance of the *cis*-signature peak at 570 cm^{-1} for a monomolecular layer coverage at a concentration of 5×10^{-6} M. This hypothesis is further substantiated by the shifting of the π–π^* band from 358 nm, in methanol solution to 370 nm, in silver sol along with the appearance of the n–π^* band, in silver sol at the optimum concentration, as observed by UV-vis spectroscopy. The excellent agreement of the SER spectra obtained experimentally with that simulated by DFT calculations indicates that electronically, biologically as well as optically important PaiH molecule undergoes chemical interaction with SNPs possibly through the imidazole nitrogen atom. A gradual *trans*-to-*cis* dark isomerisation of PaiH is suggested with lowering of concentration: the *trans*-isomers being the majority and hence predominant at higher concentrations whereas almost all the molecules are present as *cis*-isomer at monomolecular layer coverage.

Chapter 4 presents a pH dependent SERS study of 1H-2(phenylazo) imidazole (PaiH) adsorbed on SNPs. A combination of different conformations of PaiH is evident where majority of the molecules prefer a particular conformation at a given pH. It is revealed that most of the PaiH molecules are in *cis*-form in the concentration range from 10^{-6}M–10^{-5} M at pH = 7. In alkaline pH, majority of the molecules undergoes azo to hydrozone conformation whereas at acidic pH the azo-Ns participate in the electronic interaction with silver. Significant reduction of HOMO–LUMO gap indicates the possibility of PaiH of being used as an organic semiconductor

In **Chapter 5,** Raman and SER spectra of 1-H-2 (tolylazo) imidazole (TaiH) are reported. It is observed that monomolecular layer of TaiH is formed on SNPs at a concentration of 4.93×10^{-6} M in Ag-sol which is less than the concentration required for monomolecular layer coverage of PaiH which is indicative of the effect of the substituent methyl group on the electronic interaction with the metal nanoparticles. Plasmon induced *trans*-to-*cis* dark isomerization of TaiH molecules is evidenced by the appearance of signature *cis*-peaks in SERS and the UV-Vis absorption spectra. Fragmentation of SNPs with significant reduction in the particle size is revealed by the interaction of TaiH. Large SERS enhancement is observed by these uncoupled plasmons. DFT calculations based on single Ag-atom model are in excellent agreement with experimental observations.

Chapter 6 highlights the significant changes observed in the SER spectra of 1-H-2(parachloro phenylazo) imidazole (pClPai-H) molecule with respect to those of PaiH molecules. Monomolecular layer of pClPaiH is formed on SNPs at a concentration of 10^{-5} M. A moderate dark *trans*-to-*cis* isomerization of pClPai-H molecule is indicative with lowering of concentration. The influence of the presence of the chlorine atom at the para position of the phenyl ring is discussed. The pClPaiH molecule undergoes chemical interaction with SNPs possibly through azo N atoms.

In **Chapter 7**, Raman spectra and SERS of two larger arylazo imidazole compounds 1-(CH2)17CH3-2(phenylazo) imidazole (Pai-C18) and 1-(CH2)17CH3-2(tolylazo) imidazole (Tai-C18) adsorbed on SNPs are reported. The Pai-C18 molecules which are known to demonstrate some liquid crystal properties show monomolecular layer coverage at a concentration of 10^{-7} M in Ag-sols, whereas, the first layer coverage of Tai-C18 is observed at a higher concentration

of 10^{-6} M in Ag-sols. Higher concentration for monomolecular layer formation indicates smaller effective coverage of the metal surface by Tai-C18 molecules as compared with Pai-C18 molecules.

Chapter 8 illustrates a comparative study of SERS on different arylazo imidazole molecules. The substituents on the imidazole ring as well as on the phenyl ring are observed to change the electron density in the rings significantly. Consequently, the extent of adsorption of the molecules on the metal surface is modified by the presence of these substituent groups. SERS of 1-methyl-2-(phenylazo) imidazole (PaiMe),1-ethyl-2-(tolylazo) imidazole (TaiEt) and 1-H-2-(napthylazo) imidazole (NaaiH) is reported and the substituent effect on the SER spectra of these molecules is also presented in this chapter.

Chapter 9 summarizes the experimental results described in chapters 3-8. It is revealed that AAI molecules undergo chemical interaction with the SNPs mainly through the imidazole N atom and/or azo N atoms. Also the π-electron system of the aryl group significantly contributes to the charge transfer between the AAI molecules and the SNPs depending on the side group attached to it and the concentration in Ag sol. It is inferred that because of the presence of π-electron system of the aryl group, imidazole N atoms and azo N atoms the arylazo imidazole molecules may find significant use as prospective smart molecules to show various functionality.