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Structural and spectroscopic study of adsorption of naphthalene on silver

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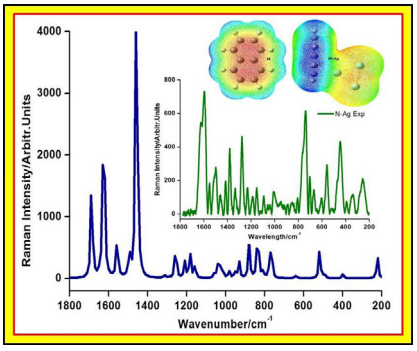
HIGHLIGHTS

- Adsorption characteristics of naphthalene on silver documented using DFT and SERS.
- Binding of π electrons of naphthalene with valence electrons of silver established.
- SERS studies infer tilted orientation of naphthalene on the silver surface.
- Lower bandgap of naphthalene on adsorption and localization in electron density.
- Utility in the design of electro active organic molecular devices.

GRAPHICAL ABSTRACT



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ABSTRACT

Adsorption characteristics of naphthalene on silver are investigated using methods based on Density Functional Theory (DFT) and Surface Enhanced Raman Spectroscopy (SERS). Variations in bond angles and dihedral angles of the optimized geometry of naphthalene after adsorption on silver indicate distorted hexagonal structure of the ring nearer to Ag atoms and deviations in co-planarity of carbon atoms. Theoretical computations establish binding interactions through π electrons as natural bond orbital analysis confirms intramolecular charge transfers originating from the orbital overlap between π(C—C) to π^*(C—C) and π(C—C) to σ^*(Ag—Ag) orbitals. Higher polarization values resulting from charge transfers on adsorption, indicated by DFT calculations, account for Raman enhancement of selective vibrational modes and band shifts. Silver nanoparticles (Ag NPs) were prepared using solution combustion method and were characterized by X-ray diffraction (XRD) and High Resolution Transmission Electron Microscopy (HRTEM). Surface plasmon resonance peak observed around 412 nm in the optical absorption spectrum of Ag NPs after adsorption of naphthalene is in good agreement with the theoretically simulated UV spectra derived using Time-Dependent Density Functional Theory (TDDFT) calculations. Theoretical and experimental SERS are correlating well, strongly confirming the process of adsorption, the tilted orientation of naphthalene on silver surface and the adsorption mechanism reported. Localization of electron density resulting from redistribution of electrostatic potential after adsorption on silver together with the reduction in bandgap of naphthalene suggests its utility in the design of electro active organic molecular devices.

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Introduction

Aromatic hydrocarbons constitute an important class of organic compounds because of their unique properties and ubiquitous nature. The scientific interest in organic compounds adsorbed onto the metal surfaces has long been of significance, as the adsorption studies of these compounds play a vital role in establishing the modifications in their catalytic and opto-electrical properties. Adsorption of organic ligands on a metallic surface induces changes in their shape or aggregation and accounting for the effects of any surface – adsorbed molecule is crucial to understanding of behavior of metal clusters observed experimentally [1,2]. The catalyzing efficiency of the metal substrates is related to their chemical characteristics. These can be monitored by observing the vibrational behavior of the adsorbate as their vibrational modes are largely dependent on the changes in symmetry on adsorption and the orientation of the adsorbate on to the surface [3,4]. Hence the interaction mechanism of adsorbed molecules on the surface of the substrate can be analyzed based on the shift of Raman Bands and the changes in their intensity [5,6]. Raman scattering cross sections can be greatly enhanced when the analyte molecule is adsorbed on metallic surfaces and in particular on silver nanoparticles [7,8]. The adsorption of aromatic compounds onto Ag NPs has been investigated extensively in the recent years due to their useful physical and chemical properties as the substrates for Surface Enhanced Raman Spectroscopy (SERS) applications in optoelectronics and biomedical science [9].

Structural properties of several biological systems are greatly influenced by their interaction with aromatic compounds [10]. The nature of metal – molecule adsorption and the subsequent electronic structure of the molecules reveal critical factors that determine their conductivity [11,12]. Research focusing on the interactions of aromatic compounds with metals is gaining momentum recently because of their potential applications in the design of devices based on electro active organic molecules and their promising role in molecular electronics [13–15]. Naphthalene is the simplest Polycyclic Aromatic Hydrocarbon (PAH) with a fused pair of benzene rings. Although the reactions involving naphthalene have been reported to be less aromatic in nature, they have been proved to be more reactive than benzene. Naphthalene is of recent scientific interest because of its extensive industrial applications. It is widely used as a precursor for many other chemicals and in the industrial production of several synthetic dyes. It finds application in the manufacture of plastics, resins, fuels, and insecticides and is used in the synthesis of photo multiplier tubes, synthetic resins, coatings, tanning agents and celluloids. Naphthalene and its derivatives are also biologically and pharmaceutically useful compounds [16,17].

Quantum Mechanical Modeling methods are among the most efficient tools of investigations of the adsorption characteristics of nano structured systems and are useful in predicting and interpreting the characteristics of their theoretical vibrational spectra [18]. Density Functional Theory (DFT) is an efficient Quantum Mechanical Modeling approach in analyzing the molecular structures, energies and vibrational frequencies using theoretical computations. DFT has also been reported to provide excellent vibrational frequencies of organic compounds if the computed frequencies are scaled to compensate for the electron correlation; basis set deficiencies and anharmonicity [19]. Surface Enhanced Raman Spectroscopy (SERS) is a powerful technique for studying the adsorption behavior of the molecules on the substrates and for identifying the molecular orientation and interaction mechanism of the molecules with the surface of the substrate. Enhancement of selective vibrational modes and band shifts observed in SERS are explained in terms of the charge-transfer model and are sensitive to the orientation of the molecules with respect to the surface [9].

The efficient fabrication of transition metal nanoparticles is of particular importance because of their unique properties and fascinating applications in optoelectronics and biomedical science. The synthesis of metal nanoparticles especially silver, based on solution combustion method is an already established method to prepare nanosized metal particles as it involves a high level of molecular mixing of the components resulting in higher chemical homogeneity of the synthesized products with high purity in a rapid and comparatively less expensive operation. Geetha et al. had presented an SERS spectral analysis of 1,4-dibromonaphthalene (1,4-DBrN) on silver surface [9]. Prabhu et al. had carried out a spectroscopic (FTIR and FT Raman) analysis and vibrational study on 2,3-dimethyl naphthalene using HF and DFT calculations [16]. Arivazhagan et al. had recorded the solid phase FTIR and FT-Raman spectra of 1,5-dinitronaphthalene and the findings were further interpreted based on computational methods using DFT [17]. Tsikritzis et al. had investigated the electronic and interfacial properties of naphthalene bisimide derivatives on gold using photoelectron spectroscopic techniques [20]. Schnockelborg et al. had studied the electronic structures of low-valent naphthalene and anthracene iron complexes using X-ray, spectroscopic and DFT methods [21]. In the current work, adsorption of naphthalene on silver is investigated using DFT methods and SERS.

Computational methods

In the present investigation, adsorption of naphthalene on silver is studied to analyze and understand the optimized geometries, charge transfers and vibrational modes using the commercially available software package Gaussian 03 [22]. The simulated spectrum is then compared with experimental observations. This model of study can be effective in estimating the changes in energetics, structural and electronic characteristics of metal cluster systems induced by the adsorption of polycyclic aromatic hydrocarbons. Computational study was carried out at the Density Functional Theory (DFT) level using B3PW91 functional and LANL2DZ basis set. LANL2DZ basis set uses an effective core for heavier atoms and is an established standard choice for the theoretical methods involving transition metals and organometallic complexes [23–27]. Silver cluster, Ag_3, identified to be stable and reactive has been considered in this study for the theoretical analysis of adsorption characteristics. To identify the theoretical configuration on adsorption, computations were performed using identical functional and basis set for multiple initial orientations. Irrespective of the initial geometry orientations of naphthalene and silver, the adsorption geometry was the one with the naphthalene in a tilted orientation with respect to the silver cluster. All optimized geometries were derived without imposing any symmetry constraints. Convergence of all the calculations together with the absence of imaginary vibrational frequencies confirms the attainment of a local minimum on the potential energy surface [28–31]. Time-Dependent Density Functional Theory (TDDFT) computations are employed to derive the optical absorption spectral values and the corresponding theoretical absorption spectra were simulated using the SWizard program [32].

Experimental methods

Synthesis

Silver nitrate and Glycine were purchased from MERCK and were used in experiments as purchased without further purification. All