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Spectroscopic investigations on the orientation of 1,4-dibromonaphthalene on silver nanoparticles



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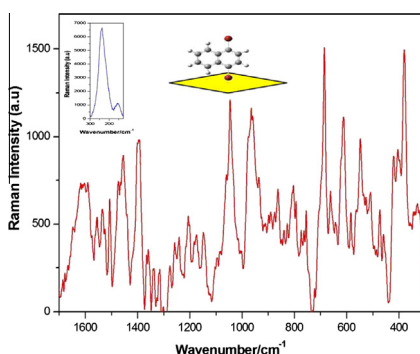
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HIGHLIGHTS

- Silver nanoparticles were synthesized by solution combustion method.
- Prepared silver nanoparticles are fcc structure with SPR at 380 nm.
- nRs and SERS studies were performed for 1,4-DBrN.
- Higher enhancement observed for C–H out-of-plane and C–Br stretching modes.
- Orientation of 1,4-DBrN on silver nanoparticles is 'stand-on'.

GRAPHICAL ABSTRACT



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ABSTRACT

Silver nanoparticles (Ag NPs) have been prepared by solution combustion method with glycine as fuel. Silver nanoparticles were characterized by X-Ray Diffraction (XRD), High Resolution Transmission Electron Microscopy (HRTEM) and UV–visible spectroscopy. The prepared silver nanoparticles exhibit cubic crystalline structure with grain size of 59 nm. HRTEM image shows that the silver nanoparticles have strain and four-fold symmetry formed by twinning in the crystal structure. The optical adsorption spectrum shows that the surface plasmon resonance peak of silver is observed at 380 nm. The orientation of 1,4-dibromonaphthalene (1,4-DBrN) on silver nanoparticles has been inferred from nRs and SERS spectral features. The absence of a C–H stretching vibrations, the observed high intense C–H out-of-plane bending modes and high intense C–Br stretching vibration suggest that the 1,4-DBrN molecule may be adsorbed in a 'stand-on' orientation to the surface.

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Introduction

Naphthalene derivatives have a wide range of applications in biology, pharmacology and material science. They are present in different families of plants, which have been used in diverse cultures such as colorants for cosmetics, fabrics, foods, and for medicinal purposes, including antitumor, anti-inflammatory and antimicrobial agent's medicine of diseases, especially cancer [1].

1,4-Dibromonaphthalene (1,4-DBrN) has become increasing important as a triplet excitation acceptor with useful phosphorescent properties. It is also useful as a precursor for other 1,4-dibromonaphthalene derivatives such as enzyme-inhibitory, antifungal, antibacterial, anticancer, antiproliferative, antiviral, trypanocidal, antiplatelet, anti-inflammatory, antiallergic, antimalarial, phenols, amines, aryl ethers, alkyl ethers and organ metallic's [2,3]. The treatment of 1-bromonaphthalene with bromine in dichloromethane at -30°C yielded the formation of 1,4-dibromonaphthalene in excellent yield (91%).

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Nanoparticles of metals have been investigated extensively in recent years. Among them, Ag NPs have been widely studied due to their useful physical and chemical properties and as the substrates for Surface-Enhanced Raman spectroscopy (SERS) [4]. Ag NPs show remarkable optical properties that depend on their size and shape. Ag NPs are widely used for medical applications especially for cancer treatment. When gold or silver nanoparticles are conjugated to cancer antibodies, cancer cells are marked with those particles and every cell can be detected under a simple microscope due to their enhanced scattering properties [5].

The fabrication of transition metal oxides with nanostructure has been the target of scientific interests in recent years because of their unique properties and fascinating applications in optoelectronics and biomedical science. Along this line, synthesis of silver nanoparticles with smaller sizes based on simple chemical reduction is highly demanded. The solution combustion synthesis of metal nanoparticles is being considered to be a promising method to obtain nanosized metal particles as it involves a high level of molecular mixing of the solution components leading to chemical homogeneity of the synthesized product with high purity in a rapid, inexpensive single step operation. The most important fact about solution combustion synthesis is that it is a short duration process and the various gasses formed during the process inhibit particle size growth, which favors the formation of nanosized powders [6].

Surface Enhanced Raman Spectroscopy (SERS) is a Raman Spectroscopic (RS) technique that provides greatly enhanced Raman signal from Raman-active analyze molecules that have been adsorbed onto certain specially prepared metal surfaces. Increases in the intensity of Raman signal have been regularly observed on the order of 10^4 – 10^6 , and can be as high as 10^8 and 10^{14} for some systems [7,8]. The importance of SERS is that it is both surfaces selective and highly sensitive where as RS is neither. RS is ineffective for surface studies because the photons of the incident laser light simply propagate through the bulk and the signal from the bulk overwhelms any Raman signal from the analyses at the surface. SERS selectivity of surface signal results from the presence of surface enhancement mechanisms only at the surface.

SERS using silver, gold or other noble metals as substrates, [9–11] is a powerful technique for studying the adsorption behavior of molecules on substrates, revealing the molecules' orientation and the mechanism of interaction of the molecules with the surface of the substrate in which researchers are interested [12,13]. SERS is widely used to elucidate information about the behavior of biomolecules adsorbed at the metal surfaces, orientation of adsorbed species and the changes in the orientation induced by external factors. In addition, the adsorption of molecules on metal particles reduces the fluorescence background and hence the technique is useful in the study of biological samples [14–16]. The enhancement of selective vibrational modes and band shifts observed in SERS have usually been explained in terms of the charge-transfer model and are found to be sensitive to the orientation of the molecules with respect to the surface [17–19]. The technique is therefore expected to provide interesting information on the sites through which the interaction takes place and also the molecular orientation with respect to the metal surfaces.

In this present investigation, SERS spectral analysis of 1,4-dibromonaphthalene (1,4-DBrN) on silver surface were studied.

Experimental

Materials

Silver nitrate (AgNO_3) and Glycine ($\text{C}_2\text{H}_5\text{NO}_2$) were purchased from MERCK. 1,4-Dibromonaphthalene were synthesized accord-

ing to the literature [20]. All the chemicals were of analytical grade and were used as purchased without further purification. Double-distilled water was used throughout the experiment.

Calculation of stoichiometry

The stoichiometry of the redox mixture used for combustion process was calculated using the total oxidizing and reducing valencies of the ingredients which serve as numerical coefficients for the stoichiometric balance so that the equivalence ratio (Φ_e) is unity and the energy released by the combustion is maximum [21]. According to the concept used in propellant chemistry the valence of C = +4, H = +1, Ag = +1 divalent metal ions = +2, trivalent metal ions = +3 and so on and O = −2. The valence of nitrogen is considered to be zero. Based on these considerations, silver nitrate has an oxidizing valence of −5 and Glycine a reducing valence of +9. For the preparation of solution combustion synthesis, the required mole ratio of $\text{AgNO}_3:\text{C}_2\text{H}_5\text{NO}_2$ becomes 1:0.5.

$$\Phi_e = \frac{\sum (\text{Coefficient of oxidizing elements in specific formula}) \times (\text{oxidizing valency})}{(-1) \sum (\text{Coefficient of reducing element in specific formula}) \times (\text{reducing valency})}$$

$$\Phi_e = \frac{[(1\text{Ag} \times +1) + (1\text{N} \times 0) + (3\text{O} \times -2)]}{(-1)[(2\text{C} \times -4) + (1\text{N} \times 0) + (5\text{H} \times -1) + (2\text{O} \times 2)]}$$

$$\Phi_e = 0.5$$

Preparation of Ag NPs using solution combustion method

Silver nanopowdered sample was prepared by solution combustion method, in which different precursors are used in stoichiometric amounts of taken as ratios. Fuel (organic compound) and Oxidizer (metal nitrates) compositions were calculated using reducing valences of fuel compounds and of oxidizing valences of metal nitrates. The materials are AgNO_3 and glycine mixed in 1:0.5 ratio and added to 25 ml distilled water in a crucible. The ratio of the fuel to oxidizers is taken as one ($\Phi_e = 1$). The entire mixture were mixed on a magnetic stirrer up to 30 min. It formed completely aqueous solution, after that the mixture of solution is placed on hot plate at 300 °C. After the solution reached the point of spontaneous combustion, it began to burn and released much heat, vaporizing the entire solution instantly and the combustion reaction was completed in 20 min. Finally loose greyish black color powder was formed which was crushed and ground thoroughly.

Preparation of 1,4-dibromonaphthalene

To a solution of 1-bromonaphthalene (1.0 g, 4.8 mmol) in CH_2Cl_2 (5.0 ml) cooled (−30 °C) was added bromine (0.85 g, 5.3 mmol) in dichloromethane (3.0 ml). The reaction mixture was kept in freezer at −30 °C for 2 days. After removal of the solvent at reduced pressure, the crude product was crystallized in CH_2Cl_2 /hexane (1/4) to give 1,4-dibromonaphthalene (1.25 g, 91%). ^1H NMR (400 MHz, CDCl_3): δ 8.81–8.19 (4H, AA'BB' system, ArH), 8.18 (2H, s, ArH). ^{13}C NMR (100 MHz, CDCl_3): δ 134.9, 132.1, 130.2, 130.1, 124.9. Anal. Calcd. for $\text{C}_{10}\text{H}_6\text{Br}_2$: C, 42.00; H, 2.11%; Found: C, 42.08, H, 2.16% [20].

Instrumentations and characterization

The X-Ray Diffraction (XRD) patterns were recorded on PANalytical X-ray diffractometer using Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) operated at 50 kV and 100 mA. The experiments performed in the diffraction angle range of $2\theta = 20$ – 80° . Transmission electron microscopy (TEM) analysis was done using a JEOL JEM 2100 High

Resolution Transmission Electron Microscope, operating at 200 kV. The optical measurements were carried out using Shimadzu UV-1700 pharmaspec UV–visible spectrophotometer. The Raman spectra were obtained by micro Raman system from Jobin Yvon LABRAM-HR with He-Ne laser. The excitation wavelength was 632 nm for 1,4-DBrN.

Result and discussion

XRD studies

The XRD pattern of prepared Ag NPs were compared and interpreted with standard data (PCPDF#870720). Fig. 1 shows the XRD pattern of the prepared silver nanoparticles which shows four different peaks at $2\theta = 38.16^\circ$, 44.37° , 64.47° and 77.46° with corresponding to (111), (200), (220) and (311) Bragg's reflection of the cubic structure of metallic silver respectively. The peak line width in the XRD spectra is broadened due to smaller particles sizes since the number of planes available is too small. Peaks of impurities not detected, indicating that the silver nanoparticles are pure and well crystalline. This XRD line width can be used to estimate the size of the particles by using the Debye–Scherrer formula as $D = 0.9\lambda/\beta\cos\theta$ where D is the particle size (nm), λ is the wavelength of X-ray radiation (1.5406 Å), β is the full-width at half maximum (FWHM) of the peak (in radians) and 2θ is the Bragg angle ($^\circ$). The calculated average particle size is found to be in the range of 59 nm. The lattice constant values were also calculated and agree well with the standard data. The sample exhibit smaller cell volumes than that of bulk.

TEM studies of Ag NPs

The morphology and internal crystalline structure of obtained nanoparticles was studied by High Resolution Transmission Electron Microscopy (HRTEM) shown in Fig. 2 and indicates dispersed particles which are more or less spherical. The TEM image illustrate silver nanoparticles are spherical in shape (Fig. 2). The spherical shape silver nanoparticles are found to be ranging from 13 to 53 nm these size of silver particle confirms the nanoparticles. This is in accordance with the XRD result. HRTEM studies confirm that glycine was the suitable and effective fuel for the formation of finer silver nanoparticles.

The prepared silver nanoparticles show twinning in the crystalline structure. Twinning is the planar defect in nanocrystals of face

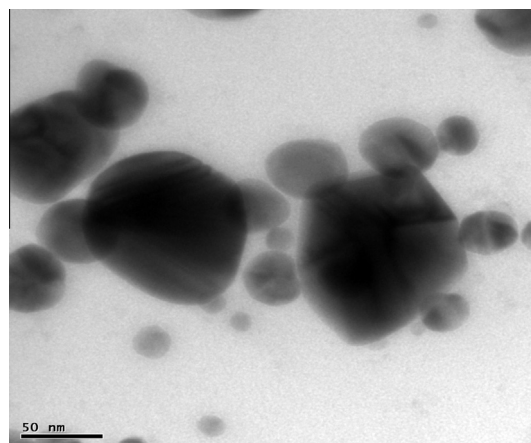


Fig. 2. TEM image of silver nanoparticles.

centre cubic (fcc) structure. It occurs when two subgrains share a common crystallographic plane. So the structure of one sub grain is the mirror image of the other by the twin plane [22]. The prepared silver nanoparticles are multiply twinned particles and have

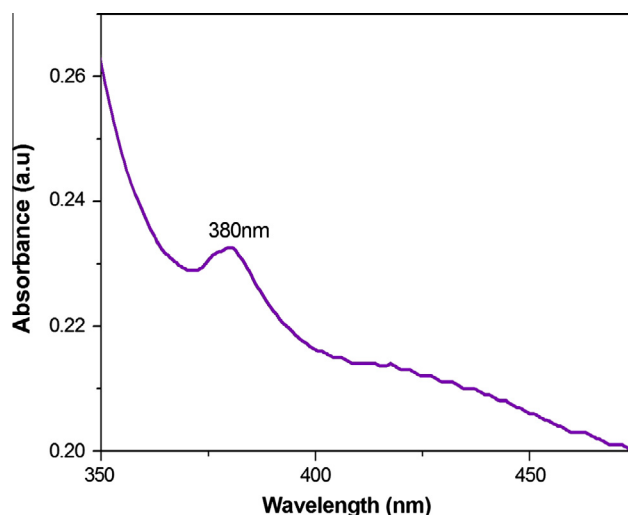


Fig. 3. Optical absorption spectrum of silver nanoparticles.

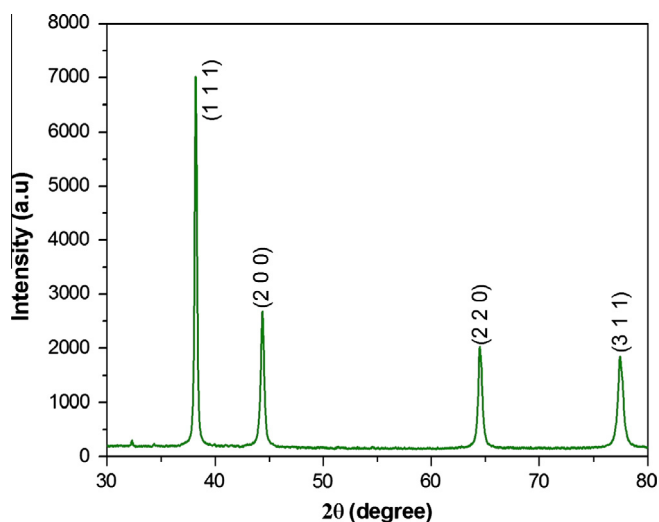


Fig. 1. X-ray diffraction pattern of silver nanoparticles.

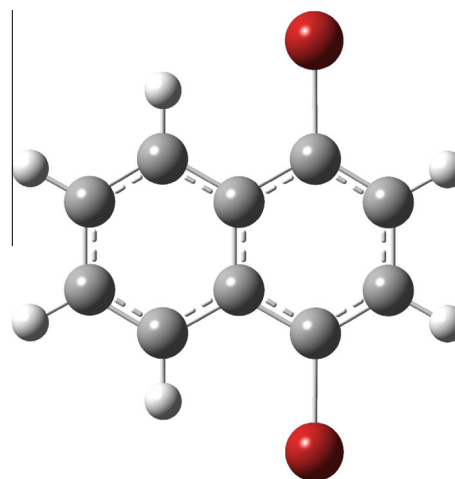


Fig. 4. Structure of 1,4-dibromonaphthalene.

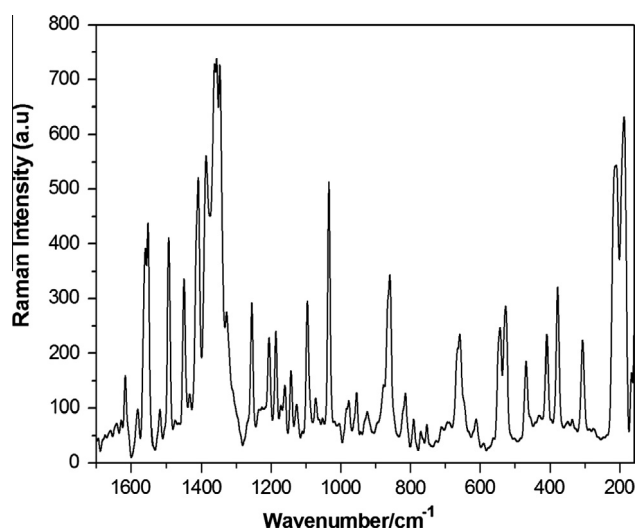


Fig. 5. Normal Raman spectra of DBrN molecule.

four-fold axis. Because of this four-fold axis, strain was induced in the particle to fill the gap. When the particles are smaller in size, the multiple twinning is the favorable structural configuration. It may be due to the smaller surface and volume energies [22].

Optical studies of Ag NPs

Fig. 3 shows the optical absorption spectrum of silver nanoparticles in the region 350–700 nm. The absorption spectra show one prominent symmetric peak around 380 nm, which is due to the characteristic surface plasmon resonance of spherical silver nanoparticles. This absorption band results from interactions of free electrons confined to small metallic spherical objects with incident electromagnetic radiation. Electronic modes in silver nanoparticles are particularly sensitive to their shape and size, leading to pronounced effects in the visible part of the spectrum. The observed plasmon band shows that the silver nanoparticles are spherical in shape [23]. The full width at half maximum (FWHM) is reported

to be quite useful in understanding the particle size and their distribution within the medium. In the present case, the FWHM of the silver nanoparticles is 14 nm.

Surface Enhanced Raman Spectral studies

The structure of 1,4-DBrN molecule is shown in Fig. 4. The normal Raman spectrum (nRs) and Surface Enhanced Raman Spectrum of 1,4-DBrN is shown in Figs. 5 and 6 respectively. The observed vibration modes and its corresponding assignments are listed in Table 1. The 1,4-DBrN molecule is assumed to be planar and belongs to the C_{2v} point group. The equilibrium geometry and vibration wave numbers of the 1,4-DBrN molecules in the electronic ground state have been computed at B3LYP/6-311G level using the Gaussian 03. The calculated normal mode wave numbers of DBrN are listed in the Table 1. In Table 1 the description of vibration motion, such as bending, deformation, and stretching, is on the basis of the vibration animations in the Gaussian view.

In bromobenzene the band occurs at 377 and 243 cm^{-1} are due to C–Br stretching modes [23]. In the title molecule, the nRs band at 383 and 214 cm^{-1} and SERS at 381 and 237 cm^{-1} are assigned to C–Br stretching mode. The C–C stretching mode occurs in the region 1600–1250 cm^{-1} [24]. In the present case C–C stretching are observed in the region 1616–1244 cm^{-1} in both nRs and SERS. In benzene-like molecules C–H in-plane bending vibrations are observed in the region 1300–1000 cm^{-1} and are usually weak. The C–H out-of-plane bending modes of usually medium intensity arises in the region 900–677 cm^{-1} [25]. In the present case C–H in-plane bending are observed in the region 1206–1144 cm^{-1} in both nRs and SERS. The out of plane bending observed at 892 and 640 cm^{-1} in both nRs and SERS are assigned to C–H out-of-plane bending. The other modes of vibration of carbon atom in the ring such as C–C–C in-plane bending and C–C–C out of plane bending vibrations are presented in the Table 1. The above assignment agrees well with literature values [26].

Orientation of adsorbed molecules

The adsorption mechanism of an adsorbate can be deduced from its SERS spectrum. The orientation of the adsorbate on the

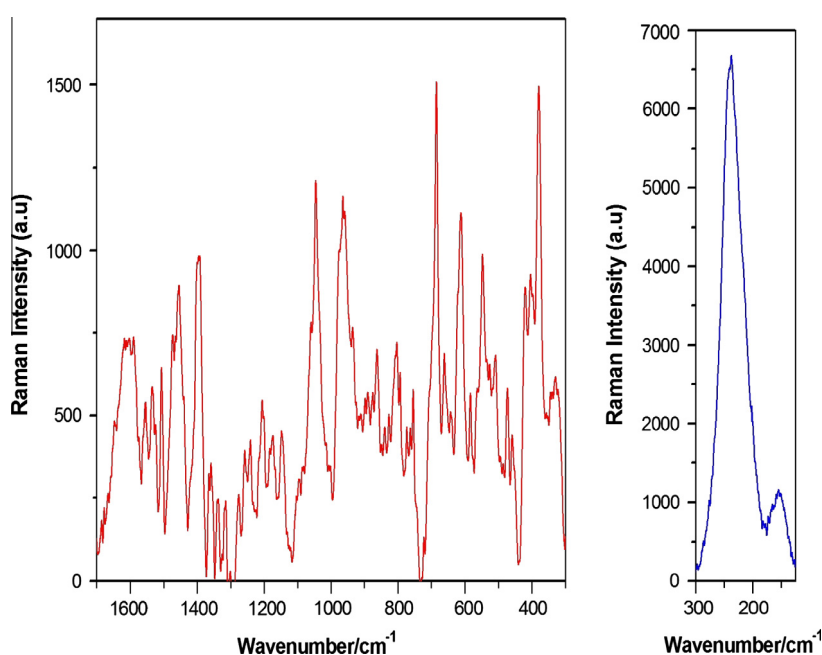


Fig. 6. SERS spectrum of 1,4-DBrN on silver nanoparticles.

Table 1
Vibrational assignments of 1,4-DBrN and 1,4-DBrN adsorbed on the silver nanoparticles.

Calculated wavenumber (cm ⁻¹)	Observed wavenumber (cm ⁻¹)		Band assignments
	nRs	SERS	
1617	1616	1604	C–C stretching
1578	1583	1587	C–C stretching
–	1549	1555	C–C stretching
1524	1521	1534	C–C stretching
–	1494	1508	C–C stretching
–	–	1475	C–C stretching
–	1541	1456	C–C stretching
1436	–	–	C–C stretching
1417	–	–	C–C stretching
1403	1409	–	C–C stretching
–	1389	1396	C–C stretching
1364	1357	1358	C–C stretching
1339	–	1337	C–C stretching
–	–	1314	C–C stretching
1299	–	1279	C–C stretching
–	1256	1258	C–C stretching
1244	–	1244	C–C stretching
1212	1206	1206	C–H in-plane bending
1195	1185	1176	C–H in-plane bending
1170	–	–	C–H in-plane bending
1158	1162	–	C–H in-plane bending
1134	1126	–	C–H in-plane bending
1097	1097	–	C–H in-plane bending
1089	1070	–	C–H in-plane bending
1033	1035	1045	C–H in-plane bending
1007	–	–	C–H out-of-plane bending
–	979	–	C–H out-of-plane bending
960	957	962	C–H out-of-plane bending
–	–	935	C–H out-of-plane bending
905	–	–	C–H out-of-plane bending
–	–	892	C–H out of plane bending
–	–	888	C–H out-of-plane bending
877	–	872	C–H out of plane bending
–	–	837	C–H out-o-plane bending
–	–	827	C–H out of plane bending
–	–	804	C–H out of plane bending
–	793	792	C–H out-of-plane bending
–	–	774	C–H out-of-plane bending
–	–	764	C–H out-of-plane bending
752	752	755	C–H out-of-plane bending
711	–	–	C–H out-of-plane bending
–	–	687	C–H out-of plane bending
–	657	659	C–H out-of-plane bending
649	–	640	C–H out-of-plane bending
–	610	612	C–C–C in-plane bending
580	589	582	C–C–C in-plane bending
551	545	547	C–C–C in-plane bending
539	533	–	C–C–C in-plane bending
–	–	509	C–C–C in-plane bending
479	468	474	C–C–C in-plane bending
–	412	420	C–C–C in-plane bending
–	–	404	C–C–C in-plane bending
–	383	381	C–Br stretching
346	–	330	C–C–C out-of-plane bending
–	309	–	C–C–C out-of-plane bending
252	214	237	C–Br stretching

metal surface will depend on the active sites through which the interaction takes place. The chemically possible orientations of the 1,4-DBrN molecular ion with respect to the silver surface can be envisaged: 'flat' or lying down on the metal surface through bonding with the ring system or 'standing up' (end-on) with bonding through the lone pair of the oxygen atom with silver [27–30]. The orientation of the molecule on the silver surface can be inferred from aromatic C–H stretching vibrations, in-plane and out-of-plane vibrations, in-plane bending and the SERS surface selection rule.

There are two possibilities for molecule adsorption on metal surface namely physisorption and chemisorptions. The spectrum of physisorbed molecules is practically the same as that of free

molecules with only changes being observed for bandwidth along with intensity enhancement. This situation corresponds to a relatively large distance between metal surface and adsorbed molecules [31]. When the molecules are chemisorbed, there is an overlapping of the molecular and metal orbital; the molecular structure the adsorbate being modified [32].

The surface geometry of compounds with a planar structure can be determined from the relative magnitude of the intensity of C–H stretching bands in their SERS spectrum. In case of benzene, the C–H stretching vibration significantly contributes only to the α_{zz} , α_{xz} , and α_{yz} polarizability components, when the molecule is lying up 'stand-on' to the surface. If it is flat on the surface, the C–H stretching vibration would contain their intensities from α_{yy} , α_{xx} ,

α_{xy} resulting in lower SERS intensity for these bending. The observation of a strong or weak band due to C–H stretching mode would constitute a simple rule for determining the surface geometry of planar molecule being adsorbed on the silver surface [33]. Generally C–H stretching vibrations are observed in the long wave number region. The present molecule does not show any C–H stretching vibration modes (not shown in figure). Therefore prediction of orientation from C–H stretching vibration cannot be made.

The intensity of out-of-plane vibrational modes decreases substantially relative to the in-plane vibrational modes when the adsorbate orientation is altered from vertical to 'stand-on' orientation. The in-plane vibrational modes occur both in Raman spectrum and SERS spectra in the region 1300–1000 cm^{-1} . The C–H out-of-plane vibration observed in the region 980–640 cm^{-1} . By comparing the observed intensities of in-plane and out-of-plane vibration in SERS indicates that 1,4-DBrN is adsorbed in 'stand-on' orientation.

'Stand-on' orientation of the title molecule on the silver nanoparticles may be through the bromine atom. In the present case the band at 237 and 214 cm^{-1} in SERS and nRs respectively are due to C–Br stretching vibrational. This mode is enhanced in SERS and shifted by 23 cm^{-1} . SERS intensity can be derived from the polarizability tensor components, which are tangential and normal to the surface. Considering the 1,4-DBrN molecule oriented 'stand-on' to the silver surface, the C–Br bond and the normal to the surface are parallel. In this configuration, the vibrational modes are predominantly excited by the normal component of the field resulting in an induced dipole with strong component normal to a surface. In the present case the SERS intensity of the above vibrational mode is arising due to the α_{zz} , α_{xz} and α_{yz} polarization components.

The determination of orientation is also based on SERS 'Surface selection rule'. It stresses that the vibrational modes possessing polarizability tensor in the direction of the surface normal should commonly experience the greater intensity enhancement. Modes where the bond axis is perpendicular as well as parallel to the surface often contain substantial polarizability components [34]. So if the molecule has stand-on orientation the vibrational modes possessing polarizability tensor normal to the surface will be enhanced. In the present case C–H out-of-plane mode, and C–Br stretching modes are normal to surface and enhanced.

Conclusion

Silver nanoparticles were synthesized by solution combustion method. The optical and structural properties of Ag NPs have been

assessed via UV–visible and XRD studies respectively. The XRD and TEM result confirms that the particles have a cubic crystalline structure. The enhanced out-of-plane vibrational modes and C–Br stretching vibration indicates that the 1,4-DBrN oriented in 'stand-on' orientation on Ag NPs.

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