

CHAPTER VI

SURFACE ENHANCED RAMAN SCATTERING OF 1,4-DIBROMONAPHTHLENE (1,4-DBrN) BY Ag NPs

Abstract

Ag NPs have been prepared by solution combustion method with glycine as fuel. Ag NPs were characterized by The orientation of 1,4-dibromonaphthlaene (1,4-DBrN) on Ag NPs has been inferred from nRs and SERS spectral features. The absence of a C–H stretching vibrations, observed high intense C–H in-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 Ag NPs. The HOMO-LUMO analyses explain the charge transfer taking place within the molecule.

6.1 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 fabrics and for medicinal purposes, including antitumor, anti-inflammatory and antimicrobial agent's medicine for diseases, especially cancer [1]. 1,4-DBrN has become increasingly 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]. In this present investigation, SERS spectral analysis of 1,4-DBrN on Ag NPs were studied.

6.2 Experimental

6.2.1 Materials

The details of the chemicals used are similar as discussed in chapter IV. 1,4-DBrN molecule was synthesized according to the literature [4].

6.2.2 Synthesis of Ag NPs using solution combustion method

Ag NPs used in this study were synthesized by solution combustion method as discussed in chapter II and IV.

6.2.3 Characterization

The details of the instruments used are similar as described in chapter III and V.

6.3 Result and discussion

6.3.1 SERS studies

6.3.1.1 Vibrational assignments

The structure of 1,4-DBrN molecule is shown in figure 6.1. The nRs and SERS spectrum of 1,4-DBrN is shown in figure 6.2 and 6.3 respectively. The observed vibration modes and its corresponding assignments are listed in table 6.1. 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 1,4-DBrN are listed in the table 6.1. In table the description of vibration motion, such as bending,

deformation, and stretching, is on the basis of the vibration animations in the Gaussian view.

The C–C stretching mode occurs in the region $1600\text{--}1250\text{cm}^{-1}$ [5]. In the present case C–C stretching were observed in the region $1616\text{--}1244\text{cm}^{-1}$ in both nRs and SERS. In benzene-like molecules C–H in-plane bending vibrations were observed in the region $1300\text{--}1000\text{cm}^{-1}$ and are usually weak. The C–H out-of-plane bending mode of usually medium intensity arises in the region $900\text{--}677\text{cm}^{-1}$ [6]. In the present case C–H in-plane bending are observed in the region $1279\text{--}1035\text{cm}^{-1}$ in both nRs and SERS. The out-of-plane bending observed at $979\text{--}640\text{cm}^{-1}$ in both nRs and SERS are assigned to C–H out-of-plane bending. In bromobenzene the band occurring at 377 and 267cm^{-1} was due to C–Br stretching modes [5]. In the title molecule, the nRs band at 383 and 214cm^{-1} and SERS at 381 and 237cm^{-1} were assigned to C–Br stretching mode. The other modes of vibration of carbon atom in the ring such as C–C in-plane bending and C–C–C out-of-plane bending vibrations are presented in the table 6.1. The above assignment agrees well with literature values [7].

6.3.1.2 Orientation of 1,4-DBrN molecule and 1,4-DBrN molecule on Ag NPs

The adsorption mechanism of an adsorbate can be deduced from its SERS spectrum. The orientation of the adsorbate on the metal nanoparticles 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 Ag NPs 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 [8-10]. The orientation of the molecule on the Ag NPs 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 physisorped 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 nanoparticles and adsorbed molecules [11]. When the molecules are chemisorbed, there is an overlapping of the molecular and metal orbital; the molecular structure the adsorbate being modified [12].

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 a_{zz} , a_{xz} , and a_{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 a_{yy} , a_{xx} , a_{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 Ag NPs [13]. 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 show 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. In the present case, the in-plane vibrational modes occur both in Raman spectrum and SERS spectra in the region $1279\text{--}1035\text{cm}^{-1}$. The C–H out-of-plane vibrational modes observed in the region $979\text{--}640\text{cm}^{-1}$ in both nRs and SERS. 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 Ag NPs may be through the bromine atom. In the present case the band at 237 and 214cm^{-1} in SERS and nRs respectively are due to C–Br stretching vibrations. This mode is enhanced in SERS and shifted by 23cm^{-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 Ag NPs, 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 arises due to the a_{zz} , a_{xz} and a_{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 [14]. 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 in-plane mode and C–Br stretching modes are normal to surface and enhanced.

The charge transfer mechanism of SERS can be explained by the resonant Raman mechanism in which charge transfer excitation from the metal to the adsorbed molecule or vice versa occurs at the energy of the incident laser wavenumber [15]. The frontier orbital theory plays a significant role in the understanding of the charge transfer mechanism of SERS [16]. Two types of charge transfer mechanisms are predicted. One is molecule to metal and the other is metal to molecule. Molecule to metal charge transfer excitation occurs when an electron is transferred from the HOMO of the adsorbate to the Fermi level of the metal. Conversely, transfer of an electron from the Fermi level of the metal to the LUMO results in metal to molecule charge transfer [17-19]. Figure 6.4 (a) and (b) shows the calculated HOMO-LUMO molecular orbitals for 1,4-DBrN and 1,4-DBrN molecule with Ag NPs at DFT/B3LYP. The calculated energy gap of 1,4-DBrN and 1,4-DBrN molecule with Ag NPs are 3.18eV and 1.46eV at DFT/B3LYP. By evaluating both case, energy band gap between HOMO-LUMO of 1,4-DBrN molecule on Ag NPs (1.46eV) is lower than that of 1,4-DBrN molecule (3.18eV) which leads to strong intermolecular interaction. The HOMO and LUMO energy gap explains the fact that final charge transfer interaction is taking place within the molecule.

6.4 Conclusion

SERS spectra of 1,4-DBrN molecule adsorbed on Ag NPs synthesized by solution combustion method with glycine as fuel were studied. The high intensity of C-H in-plane vibrational modes and C–Br stretching vibration indicates that the 1,4-DBrN oriented in ‘stand-on’ orientation on Ag NPs. The lowering of the HOMO-LUMO energy gap value has substantial influence on the intermolecular charge transfer and bioactivity of the molecule and Ag NPs has an attractively established constitution.

References

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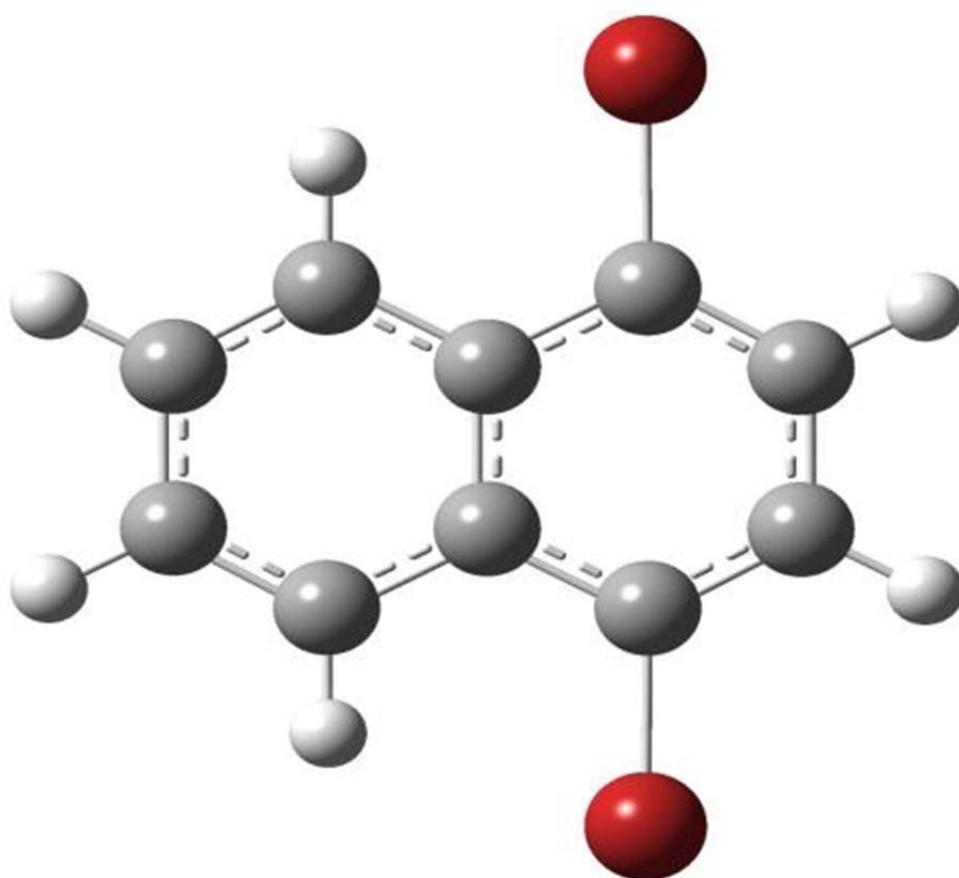


Figure 6.1 Structure of 1,4-dibromonaphthalene (1,4-DBrN).

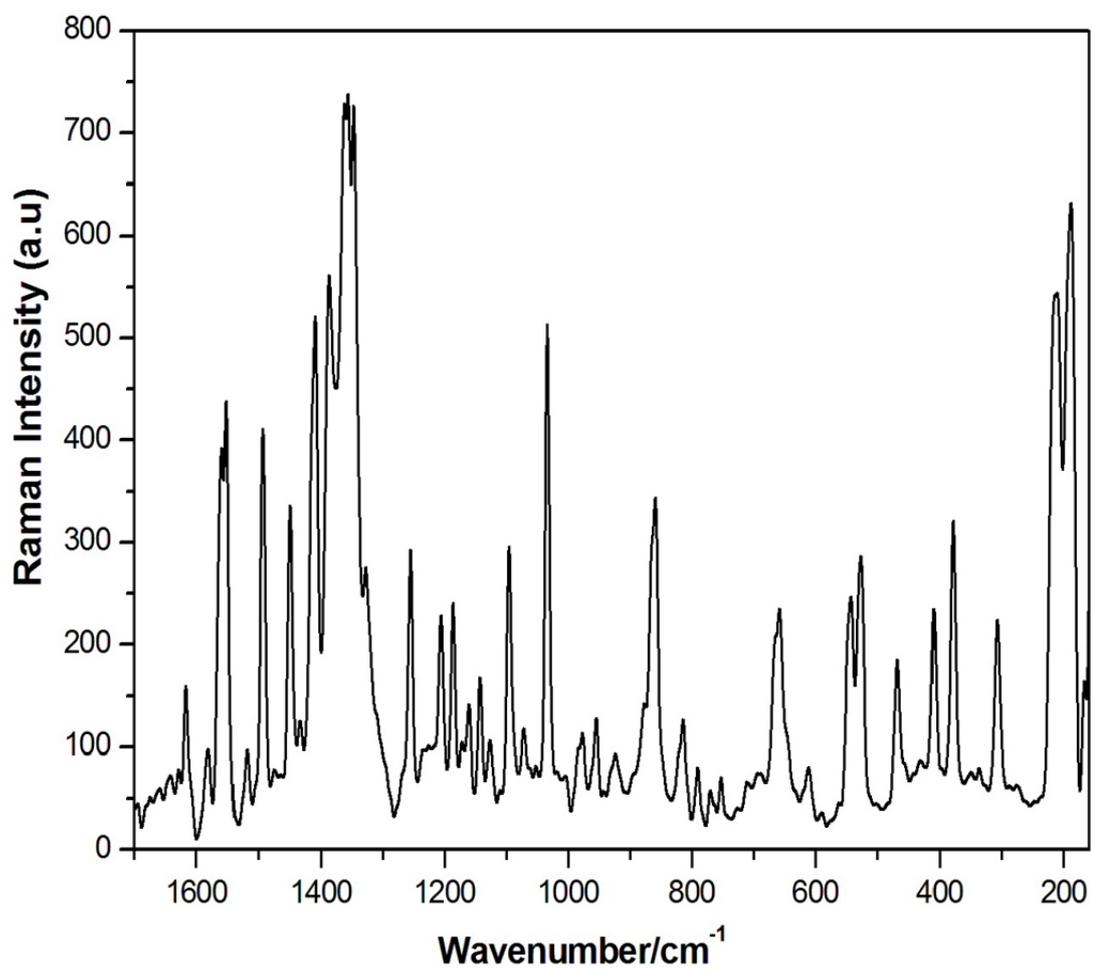


Figure 6.2 Normal Raman Spectrums of 1,4-DBrN molecule.

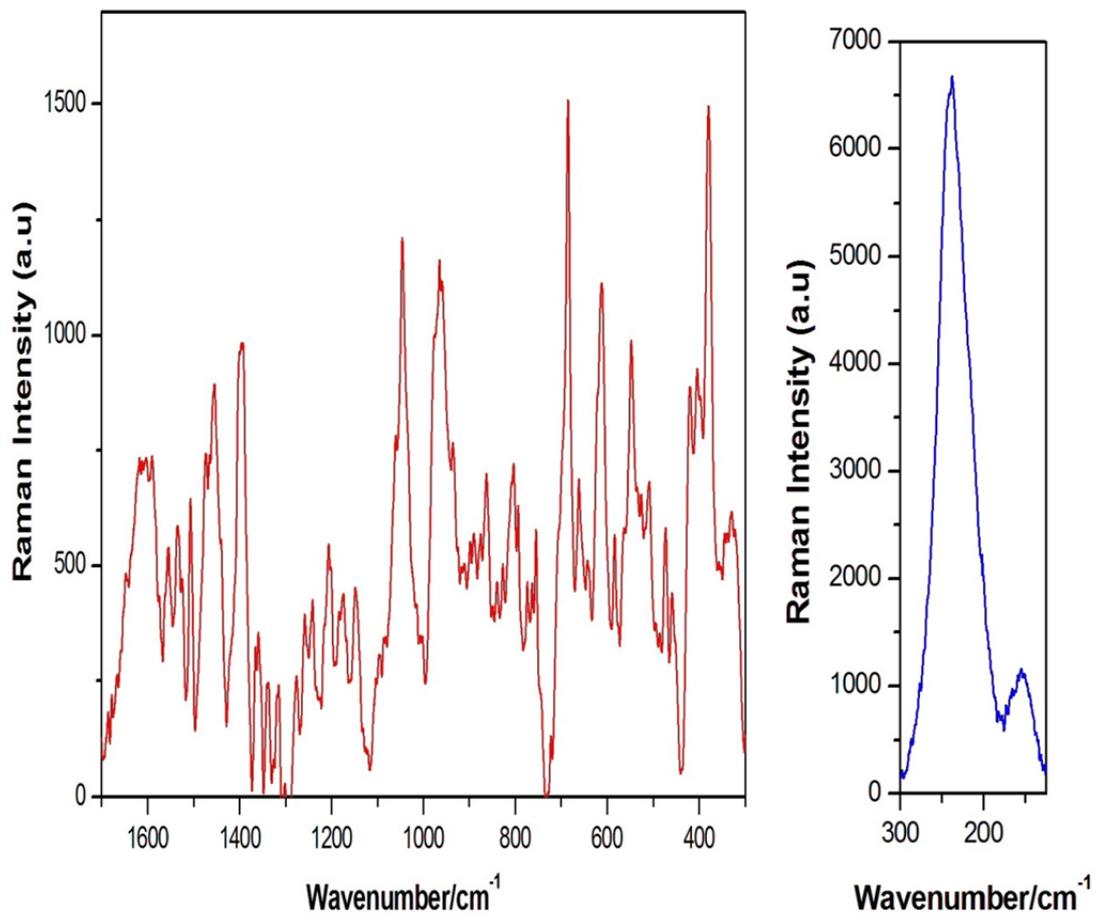


Figure 6.3 Surface Enhanced Raman Spectrums (SERS) of 1,4-DBrN on Ag NPs

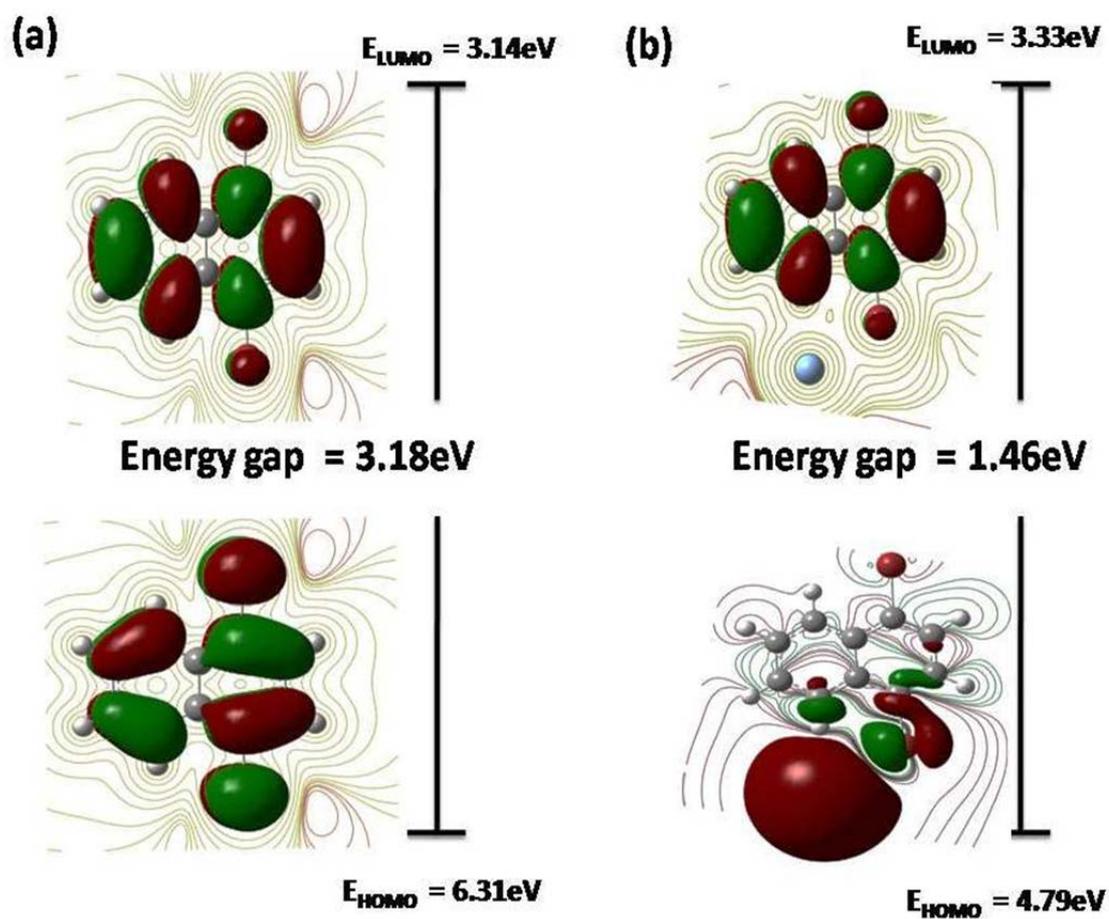


Figure 6.4 HOMO and LUMO plot of (a) 1,4-DBrNQ molecule and (b) 1,4-DBrNQ molecule on Ag NPs.

Table 6.1 Vibrational assignments of 1,4-DBrN molecule and 1,4-DBrN molecule on the Ag NPs.

Calculated wavenumber (cm^{-1})	Observed wavenumber (cm^{-1})		Band Assignments
	nRs	SERS	
1617	1616	1604	C-C str.
1578	1583	1587	C-C str.
	1549	1555	C-C str.
1524	1521	1534	C-C str.
	1494	1508	C-C str.
		1475	C-C str.
1436	1541	1456	C-C str.
			C-C str.
1417			C-C str.
1403	1409		C-C str.
	1389	1396	C-C str.
1364	1357	1358	C-C str.
1339		1337	C-C str.
		1314	C-C str.
1299		1279	C-C str., C-H i.p.
	1256	1258	C-C str., C-H i.p.
1244		1244	C-C str., C-H i.p.
1212	1206	1206	C-H i.p.

1195	1185	1176	C-H i.p.
1170			C-H i.p.
1158	1162		C-H i.p.
1134	1126		C-H i.p.
1097	1097		C-H i.p.
1089	1070		C-H i.p.
1033	1035	1045	C-H i.p.
1007			C-H i.p.
	979		C-H o.p.
960	957	962	C-H o.p.
		935	C-H o.p.
905			C-H o.p.
		892	C-H o.p.
		888	C-H o.p.
877		872	C-H o.p.
		837	C-H o.p.
		827	C-H o.p.
		804	C-H o.p.
	793	792	C-H o.p.
		774	C-H o.p.
		764	C-H o.p.
752	752	755	C-H o.p.

711			C-H o.p.
		687	C-H o.p.
	657	659	C-H o.p.
649		640	C-H o.p.
	610	612	C-C-C i.p.
580	589	582	C-C-C i.p.
551	545	547	C-C-C i.p.
539	533		C-C-C i.p.
		509	C-C-C i.p.
479	468	474	C-C-C i.p.
	412	420	C-C-C i.p.
		404	C-C-C i.p.
	383	381	C-Br str.
346		330	C-C-C o.p.
	309		C-C-C o.p.
252	214	237	C-Br str.

str.- stretching, def.- deformation, i.p.-in-plane bending, o.p.-out-of-plane bending.