Manarat International University Studies, 2 (1): 177-182, December 2011
ISSN 1815-6754

Surface-enhanced Raman Scattering (SERS) Studies of 2-Aminopyridine in silver colloids

Ekram Ali shaikh* and Y. Kumar **

ABSTRACT

Surface-enhanced Raman Scattering (SERS) has been established as a powerful method for elucidating the structure of adsorbed molecules and their interaction with the surfaces. In the present communication ordinary Raman spectrum of 2-Aminopyridine (2AP) aqueous solution (conc.1M) and surface-enhanced Raman spectra (SERS) of the same 2AP adsorbed on silver colloidal particles (2AP conc. 1.0 x 10^{-4}M) has been studied. It has been established, that the 2AP molecules have been adsorbed on the surface of silver sol particle in the edge-on (i.e. standing-up) position making a chemisorbed bond with the silver substrate.

Keywords: Surface-enhanced Raman Scattering (SERS), Surface science, Adsorption, Raman scattering.

1. INTRODUCTION

The discovery of the surface-enhanced Raman scattering (SERS) by Fleischman et el[1] had opened a wide research field both in physics and in chemistry [2,3]. SERS has played an increased role in studies of the behavior of molecules adsorbed on metal surfaces. It allows good Raman spectra to be obtained from a minimal quantities of the sample. Even a lower concentration of the sample down to 10^{-6} mol/litre is sufficient to record the Raman Spectra. SERS has attracted considerable interest largely because of its application in the study of interfacial processes and molecular structure [3,4,5]. While an intense efforts in this field concentrates on adsorbates on electrode surfaces, increased attention is presently drawn to adsorbates on colloidal particles. Following Creighton et al's [6] observations of SERS from pyridine adsorbed on silver and gold sols, several other investigations have been performed using iron and copper sols also [7,8].

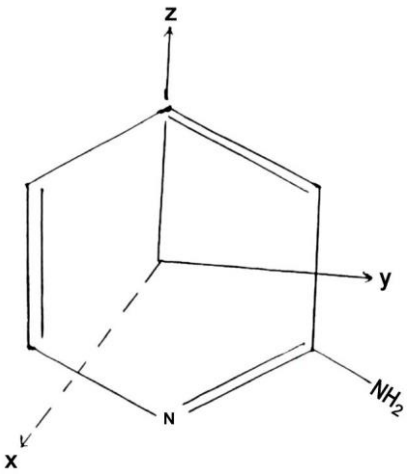

Fig. 1: Structure of 2-aminopyridine molecule

In the present study, the surface-enhanced Raman spectroscopic (SERS) investigations of 2-aminopyridine (2AP) adsorbed on silver colloidal particles have been performed. The absolute enhancement factors have been estimated to be of the order of 10^3-10^6 for various bands. The results have been analyzed in terms of current models for the enhancement mechanism of SERS.

2. EXPERIMENTAL

2.1 Materials

All chemicals used in this study were purchased at their highest purity commercially available. The silver nitrate, sodium borohydride and 2-aminopyridine were obtained from the sigma chemicals , U.S.A. Water used throughout this study was deionized and triply distilled.

2.2 Preparation of Colloidal Solution

The aqueous silver sol used in these experiments was prepared from a recipe described by Creighton et al [6]. 20 ml of 1.0 x 10^{-3}M aqueous solution of silver nitrate was added with 60ml of 2.0x10^{-3} M aqueous solution of sodium borohydride with uniform stirring. Both the solutions have been chilled to ice-temperature before hand. A light yellow coloured Ag sol thus obtained was stable for a new months. The pH paper was used to check the approximate pH of the sol and was found to be in between 7 and 8.

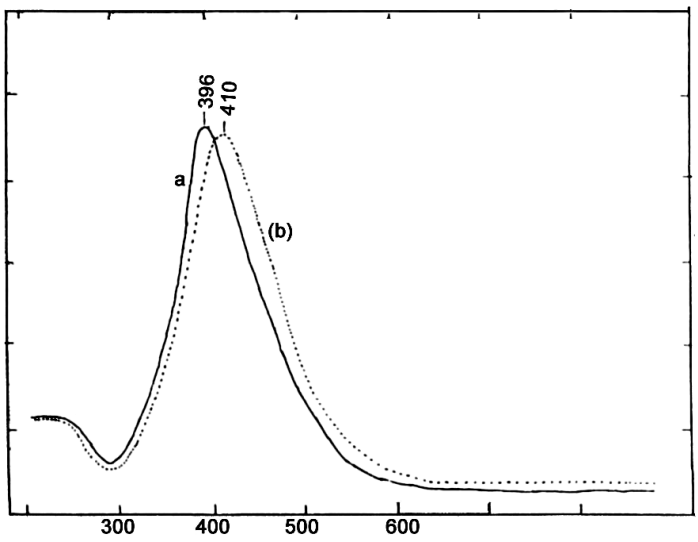

Fig. 2 : Absorption spectrum of Ag sol : (a) before addition of 2AP (b) After addition of 2AP.

2.3 Instrumentation

The UV/VIS absorption spectra of the silver sol were recorded on a Spectronic 1001 (Milton Roy, Japan) absorption spectrophotometer using cells of 1 cm thickness. Raman scattered light was analyzed with a Ramanor U1000. (Jobin Yvon, France) double monochromator equipped with 1800 grooves/mm holographic gratings, followed by a

thermoelectrically cooled RCA/C 31034 photomultiplier tube. The 514.5 nm exciting line was employed from an Ar^+ laser with a typical laser power of approximately 200 mW at the sample.

3 RESULTS AND DISCUSSIONS

The structure of 2-aminopyridine is shown in Fig. 1. The 2AP molecule is having C_S symmetry. The in-plane and out-of-plane vibrations are designated by the species a' and a" respectively. Fig. 2a shows the absorption spectrum of the Ag sol before addition of 2AP. It has been extinction band at 396 nm which is the characteristic of the sol particles being almost spherical in shape. The sizes of all the particles are not uniform. The diameter of the particles range form 1-50 nm in case of the extinction band of the sol appears near 390 nm [9,10]. After addition of 2AP in silver sol (overall 2AP conc. 1.0 x 10^{-4}M) the absorption spectrum was again recorded and it was found that the extinction band got shifted to the longer wavelength, at 410 nm (Fig. 2b). This implies that after adsorbing the 2AP molecules, the sol particles become neutral and due to vander Waals' forces the particles aggregate and thus grow in size. Yet coagulation was not found and the sol (with 2AP) was sampled for recording the Raman spectrum.

The ordinary Raman spectrum of 2AP aqueous solution (conc.1M) in the spectral range of 200-1650 cm^{-1} is shown in Fig. 3B. The surface-enhanced Raman spectra (SERS) of 2AP adsorbed on silver colloidal particles (2AP conc. 1.0 x 10^{-4}M) is shown in Fig. 3A. Table 1 lists the band positions, their vibrational assignments and absolute enhancement factors.

Normal Raman Spectrum (NRS) of 2AP at 1M conc. have been compared with the SER spectrum of the same at 1.0 x 10^{-4}M conc. as the NRS bands were too weak to be observed at such lower concentration (i.e. at 1.0 x 10^{-4}M).

The ring deformation mode *v*16a, *v*6a, *v*6b and *v*12 of 2AP are shifted in the SERS spectrum. From the Fig. 3 and Table 1 it is clear that the positions of those bands in NRS are 376, 590, 630, 594, 612, 760 and 824 cm^{-1}. So, all the bands have been shifted to higher frequency except ע6b. It has also been observed that the ring breathing mode has been shifted to higher frequency by 32 cm^{-1} (i.e. form 1000 to 1032 cm^{-1}). Hence it can be said that the 2AP molecule has been adsorbed through its ring N-atom which forms a bond between silver and the 2AP molecule. The formation of such bond limits the freedom of deformation of some of the modes. Thus the blue-shifting of the ring bending modes, observed in this study, is consistent with the formation of Ag-N bond. A new band has been observed at 330 cm^{-1} in the SERS spectrum which is absent in the normal Raman spectrum. This band is being assigned to Ag-N stretching vibration [11] confirms the formation of Ag-N bond. The formation of this bond arises due to chemisorption. The shift of position of some of the bands may be accounted for chemisorbed bonds.

The absolute enhancement factors of different bands have been estimated as by Kerker et al [12]. The maximum enhancement factors have been observed for the in-plane bending modes. The C-NH_2 in-plane bending (i.e. aromatic ring-NH_2 bending) mode at 440 cm^{-1} and C-C in-plane modes at 590 and 820 cm^{-1} have been enhanced up to the order of 1.2 x

10^4, 8.1 x 10^5 and 1.0 x 10^6 respectively. Creighton [13] had emphasized that, due to the electromagnetic effect Raman lines whose scattering tensor elements have components perpendicular to the metal surface exhibit relatively lager intensities in the SER spectrum than those in the bulk. According to this predication, in-plane bending modes will exhibit relatively large intensity enhancement when an adsorbed molecule takes-up an edge-on (i.e. standing-up) orientation. In the present study in has been found that the in-plane modes are getting more enhanced and thus supporting the standing-up orientation of the adsorbed molecule

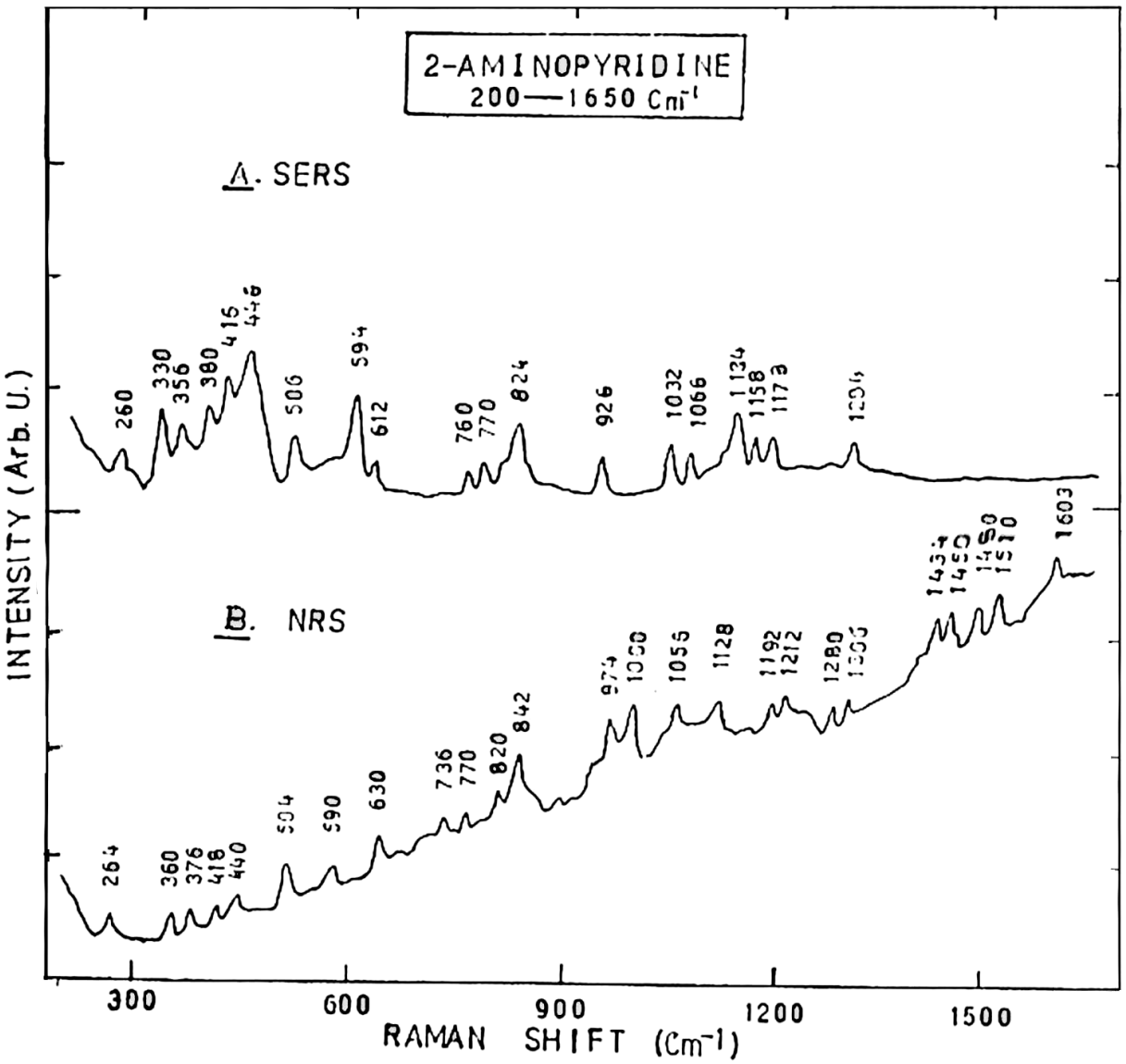

Fig. 3 : (A) : Normal Raman spectrum of 2-aminopyridine solution (conc. 1 M)
B) : SERS Spectrum of 2-Aminopyridine adsorbed on silver colloidal particles (2AP conc.
1.0 x 10^4) Laser power 200mW, scan inc. 2cm^{-1}/step, FS CNT 2000.

Table 1: Vibrational frequencies (cm^{-1}) observed in the normal Raman and SERS spectrum of 2-aminopyridine.

NRS [a]	SERS [b]	Wilson mode	Species	Abs. enh. Factor [c]	Tentative assignment [d]	
264	260	-	-	1.2 x 10^4	C-NH_2	o.p.b.
-	330	-	-	-	Ag-N	Str.
360	356	15	a’	1.3 x 10^4	C-H	i.p.b.
376	380	16a	a”	1.1 x 10^4	C-C	o.p.b.
418	416	16b	a”	2.5 x 10^4	C-C	o.p.b.
440	446	-		1.2 x 10^6	C-CH_2	i.p.b.
504	506	11	a”	1.0 x 10^4	C-H	o.p.b.
590	594	6a	a’	8.0 x 10^5	C-C	i.p.b.
630	612	6b	a’	6.5 x 10^3	C-C	i.p.b.
736	760	4	a”	1.0 x 10^4	C-C	o.p.b.
770	770	10b	a”	1.4 x 10^4	C-H	o.p.b.
820	824	12	a’	1.0 x 10^6	C-C	i.p.b.
842	-	10a	a”	-	C-H	o.p.b.
974	926	17a	a”	1.4 x 10^4	C-H	o.p.b.
1000	1032	1	a’	1.0 x 10^4	Ring Breathing	
1056	1066	18a	a’	1.5 x 10^4	C-H	i.p.b.
1128	1134	18b	a’	6.0 x 10^4	C-H	i.p.b.
1192	1158	9a	a’	2.0 x 10^4	C-H	i.p.b.
1212	1178	-		3.5 x 10^4	HNH sym. Bending	
1280	1284	3	a’	1.1 x 10^4	C-H	i.p.b.
1306	-	14	a’	-	C-C, C-N	Str.
1434	-	19b	a’	-	C-C, C-N	Str.
1450	-	-			C-NH_2	Str.
1480	-	19a	a’	-	C-C, CN	Str.
1510	-	8b	a’	-	C-C	Str.
1603	-	-	-	-	HNH Assym. bdend	

a) 2AP conc. 1M b) 2AP conc. 1.0 x 10^{-4}M c) Estimated as by Kerker et al [10]
d) o.p.b = out-of-plane bending, i.p.b. = in-plane bending Str. = stretching Sym = symmetric Assym = asymmetric

4 CONCLUSION

The spectral features indicate that the SERS spectrum is having less background whereas the NRS in having more background. It has been established, that the 2AP molecule have been adsorbed on the surface of silver sol particle in the edge-on (i.e. standing-up) position making a chemisorbed bond with the silver substrate which is also confirmed by the appearance of the Ag-N stretching band in the SERS spectrum. This is further in agreement with the observed enhancement factor which corresponds to Creighton's surface selection rules. The role of both chemical and electromagnetic effects has been observed to contribute in the overall enhancement in the SERS phenomenon.

REFERENCES

Chang R.K. and Furtak T.E. (Eds), *Surface-Enhanced Raman Scattering*, Plenum Press, New York .1982,

Creighton J.A., Blatchford C.G. and Albrecht M.G., *J. Chem. Soc. Faraday Trans II* 1979 *75* pp 790-795 (1).

Creighton J.A.; *Surface Science* 1983 *124* pp 209-213 .

Dines T.J. and Peacock R.D.; *J. Chem. Soc. Faraday Trans. I* 1988 *84* pp 3445-3449.

Fleishmann M., Hendra A.J. and McQuillan P.J..; *Chem. Phys. Lett.* 1974, *26* pp 163-170.

Kerker M., Wang D.W., Chew H., Siiman O. and Bumm L.A.; in: *Surface Enhanced Raman Scattering, R.K.* Chang and T.E. Furtak Eds, New York, Plenum Press, 1982. pp. 109.

Moskovits M ; *J. Raman Spectroscopy*, 2005; *36* pp 485-496

Sanches-Cortes S. and Garcia-Ramos J.V.; *J. Raman Spectros.* 1990 *21* pp 679-685.

Sanchez A.L., Lombardi J.R. and Birke R.L.; *Chem. Phys. Lett.* 1984 *108* pp 45-48.

Van Duyne R.P., in: *Chemical and Biochemical Applications of Lasers, Vol. IV*; C.B. Moore ed. (Academic Press, New York) pp. 101-110.

Wanning U., Pettinger B. and Wetzel H.; *Chem. Phys. Lett.* 1980 *70* pp 49-54.

Wu yuan, Ho Pui Ho, Rebecca K.Y. Lee, Siu Kai Kong,. J Applied Optics, Vol. 48, *Issue 22, pp. 4329-4337*

Zhang P., Wang Y.. He T., Zhang B., Wang X., Xin H. and Liu F.; *Chem. Phys. Lett* 1988 *153* pp 215-217.