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Surface enhanced Raman scattering of 2-cyanopyridine adsorbed on silver colloidal particles

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Abstract. Surface-enhanced Raman scattering (SERS) spectra of 2-cyanopyridine (2CP) adsorbed on silver colloidal particles have been investigated. The prominent SERS bands are observed at 556, 612, 778, 1002, 1060, 1072, 1150 and 1240 cm^{-1}. The absolute enhancement factor of the Raman signals in SERS studies has been estimated to be of the order of 10^2–10^5 for various bands. The 2CP molecules have been ascribed to adsorb on colloidal particles in standing up fashion.

Keywords. Raman spectroscopy; surface enhanced Raman scattering; surface processes; adsorption; silver colloids; cyanopyridine.

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1. Introduction

Surface-enhanced Raman scattering (SERS) is a useful technique for the study of molecular adsorption on metal surfaces. Especially, information of the adsorbed species and its structure can be obtained from the SERS spectra. It allows good and intense Raman spectra to be obtained from minimal quantities of the samples. A lower concentration of the sample down to 10^{-6} mol/l is sufficient to record the Raman spectra. Fleischmann *et al* (1974) were the first to record the SERS spectra of adsorbed species from high surface area electrode. They investigated pyridine spectra adsorbed on a silver electrode that had been roughened by electrochemical oxidation reduction process. Since then SERS of molecules adsorbed on rough noble-metal surfaces has been extensively studied, both experimentally and theoretically (Gersten and Nitzan 1980; Moskovits 1980; Liao *et al* 1981). Creighton and his coworkers were the pioneers in investigating SERS of pyridine in colloidal particles (Creighton *et al* 1979). Later on, many investigations have been performed using silver, gold, iron and copper sol (Chang and Furtak 1982; Zhang *et al* 1988; Sánchez-Cortés and Garcia Ramos 1980).

The surface-enhanced Raman study of 2-cyanopyridine (2CP) adsorbed on electrode surface was investigated by Allen and van Duyne (1979). They studied the competitive adsorption of cyanopyridines on silver electrode surface. In the present work we have investigated the SERS of 2-cyanopyridine (2CP) adsorbed on silver colloidal particles. The absolute enhancement factor of the SERS signals has been estimated to be of the order of 10^2–10^5 for various bands.

2. Experimental

2.1 *Materials and colloid preparation*

$AgNO_3$ (BDH), $NaBH_4$ (Ubichem, UK), 2-cyanopyridine (Sigma Chemicals, USA) were of highest purity commercially available and were used as received. Water was deionized and triply distilled. The silver colloidal solution was prepared according to the procedure described by Creighton *et al* (1979): Briefly, a $1{\cdot}0 \times 10^{-3}$ M aqueous solution of $AgNO_3$ was mixed with $2{\cdot}0 \times 10^{-3}$ M aqueous solution of $NaBH_4$ in the volume ratio 1:3. $NaBH_4$ solution was maintained at ice-temperature and the mixture was stirred vigorously during the preparation of colloidal solution. A yellowish coloured silver colloidal solution thus prepared was stable for two months without any stabilizing agent. The pH of the colloidal solution was in between 7 and 8.

2.2 *Instrumentation*

The UV/visible extinction spectra of the colloidal solution were recorded on a Milton Ray Spectronic 1001 (Japan) absorption spectrophotometer using a cell of 1 cm thickness. The Raman spectra were recorded with RAMANOR U1000 double monochromator (Jobin Yvon, France). The 514·5 nm line of an Ar^+ laser (Spectra Physics, Model 171) was used as excitation light source. Glass capillary tube was used as a sampling device. Scattered light was collected at 90° to the excitation beam. The laser power was 300 mW.

3. Results

Absorption spectrum (figure 1a) of the Ag colloidal solution showed a single visible extinction band near 385 nm which indicates that the size of the particles is of the

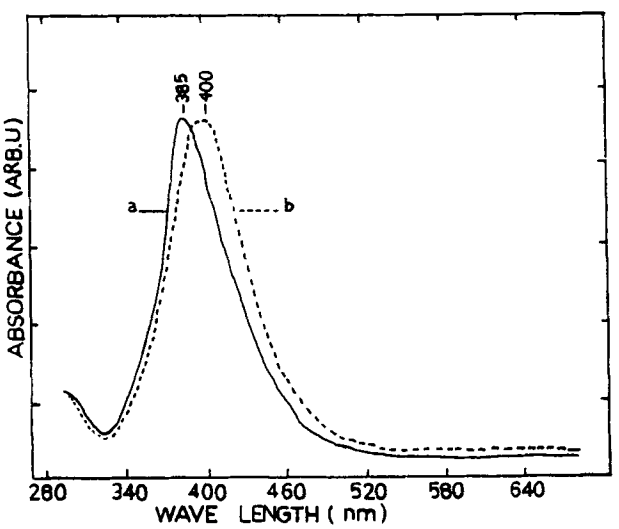

Figure 1. Extinction spectra of silver colloidal solution (a) before the addition of 2CP and (b) after the addition of 2CP.

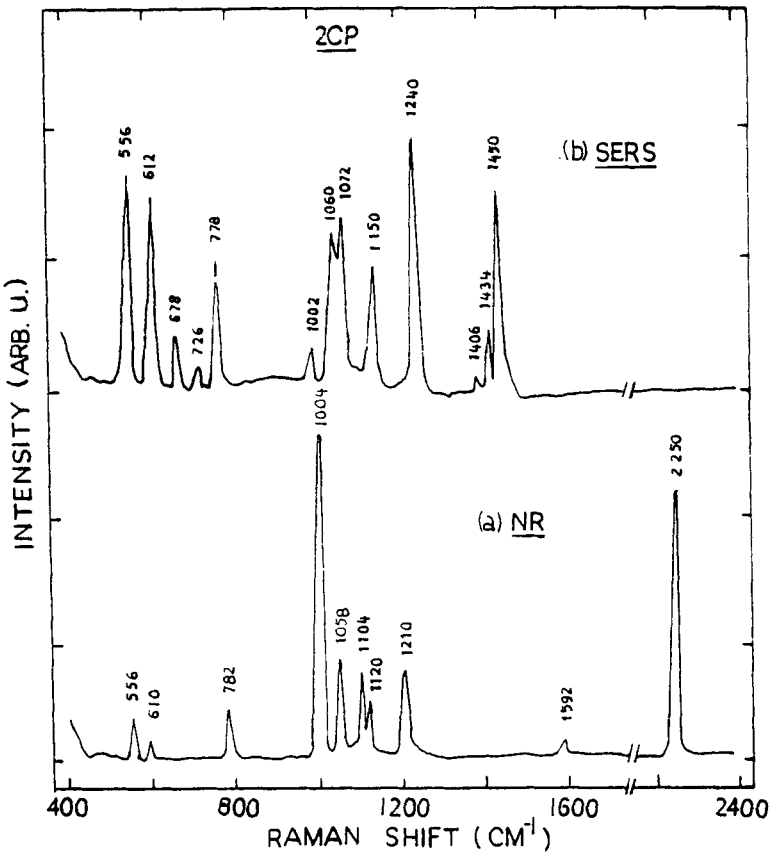

Figure 2. (a) Normal Raman spectrum of 2 CP. Laser power 300 mW, scan inc. 2 cm^{-1}/step, FS CNT 3000. (b) SERS of 2 CP, Laser power 300 mW, scan inc. 2 cm^{-1}/step, FS CNT 3000.

order of 1·0–50·0 nm (Wenning *et al* 1980). The absorption spectrum (figure 1b) was also recorded after adding 2 CP in the same colloidal solution. In the later case, the colour of the sol was changed and the extinction band was shifted to 400 nm which is an indication of growing particle size due to adsorption.

Figure 2a shows the normal Raman (NR) spectrum of 0·75 M aqueous 2 CP solution. Figure 2b is the SERS spectrum of 2 CP with colloidal solution in which the concentration of 2 CP was $7{\cdot}5 \times 10^{-5}$ M. The NR spectrum of 2 CP solution at $7{\cdot}5 \times 10^{-5}$ M conc. was not possible to record due to weak signal but the SERS spectrum of the same was possible. So, we have compared the NR spectrum of 2 CP at 0·75 M conc. to the SERS spectrum of 2 CP at $7{\cdot}5 \times 10^{-5}$ M conc. The bands at 556, 610, 782, 1004, 1058, 1104, 1120, and 1210 cm^{-1} are common in both the NR and SERS spectra although there is a shift in their frequencies.

4. Discussion

The C–C out-of-plane band at 726 cm^{-1} is active only in IR, but in our SERS studies it has appeared. So it can be concluded that the Raman selection rules are not being strictly followed in the SERS spectra. The relaxation of the Raman selection rule has

Table 1. Vibrational frequencies (cm^{-1}) observed in the normal Raman (NR) and SERS spectra of 2-cyanopyridine.

			Assignment		
NR[a]	SERS[b]	Abs. Enh[c]	Species (Cs)	Description of modes	Wilson no.
556	556	$1{\cdot}3 \times 10^5$	a'	C–C i.p.b.	6a
610	612	$1{\cdot}2 \times 10^5$	a'	C–C i.p.b.	6b
—	678	—	—	—	—
—	726	—	a''	C–C o.p.b.	4
782	778	$3{\cdot}0 \times 10^4$	a'	C–C i.p.b.	12
1004	1002	$5{\cdot}6 \times 10^2$	a'	C–C ring br.	1
1052	1060	$4{\cdot}0 \times 10^4$	a'	C–H i.p.b.	18a
1104	1072	$2{\cdot}0 \times 10^4$	a'	C–H i.p.b.	18b
1120	1150	$2{\cdot}8 \times 10^4$	a'	C–H i.p.b.	9a
1210	1240	$4{\cdot}7 \times 10^4$	a'	C–H stretch	13
—	1406	—	—	678 + 726 = 1404	—
—	1434	—	a'	C–C, C–N stretch	19b
—	1450	—	a'	C–C, C–N stretch	19a
1592	—	—	a'	C–C stretch	8a
2250	—	—	a'	C ≡ N stretch	—

a) 2CP conc. was 0·75 M; b) 2CP conc. was $7{\cdot}5 \times 10^{-5}$ M; c) estimated as by Kerker *et al* (1982) method.
i.p.b. = in-plane-bending, o.p.b. = out-plane-bending.

also been established by Muniz-Miranda *et al* (1988) in the SERS of pyrazine. We are not able to assign the band at 678 cm^{-1}, which might be due to a complex formed by the absorbed species with the silver substrate. The band at 1406 cm^{-1} is a combination of 678 cm^{-1} and 726 cm^{-1} bands. The appearance of combination band in SERS has also been predicted by Takahashi *et al* (1985). The 1434 and 1450 cm^{-1} bands are too weak to be observed in the NR of 2CP at 0·75 M concentration but the same bands come out in the SERS spectrum with considerable intensity. On the other hand the nitrile stretching band around 2250 cm^{-1} and C–C stretching band at 1592 cm^{-1} have not been observed in the present study. The maximum enhancement has been observed in the C–C in-plane bending modes (table 1). This is an indication of the 2CP molecules adsorbed on silver sol particles being in the standing-up orientation (Moskovits 1982). King *et al* (1978) also suggested that stronger signals are observed for the vibrations which generate a large image field. As a vibration perpendicular to metal surface generate a large image field, the signals of in-plane vibrations should be enhanced more if the molecules are adsorbed on the sol particles in standing-up orientation. Therefore, the adsorbed 2CP molecules form a σ-complex through its ring N atom to the Ag.

5. Conclusion

We have recorded the ordinary Raman and the surface enhanced Raman spectra of 2CP in the spectral range 400 cm^{-1}–2400 cm^{-1}. The enhancement factors of different SERS bands have been estimated to be $\sim 10^2$–10^5 times than the intensity of the

corresponding NR bands. We have also established that the 2CP molecules adsorb on silver in standing-up position forming a σ-bond through the lone pair N atom to the Ag. Moreover, the shifts in the Raman peaks might be attributed to the charge transfer effect (Chou and Liang 1984). Also it has been found that the SERS can relax the Raman selection rule.

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References

Allen C S and van Duyne R P 1979 *Chem. Phys. Lett.* **63** 455
Chang R K and Furtak T E (eds) 1982 *Surface enhanced Raman scattering* (New York: Plenum Press)
Chou Y C and Liang N T 1984 *Chem. Phys. Lett.* **106** 472
Creighton J A, Blatchford C B and Albrecht M C 1979 *J. Chem. Soc. Faraday Trans. II* **75** 790
Fleischmann M, Hendra P J and McQuillan A J 1974 *Chem. Phys. Lett.* **26** 163
Gersten J I and Nitzan A 1980 *J. Chem. Phys.* 73 3023
Kerker M, Wang D S, Chew H, Siiman O and Bumm L A 1982 *in surface enhanced Raman scattering* (eds) R K Chang and T E Furtak (New York: Plenum Press) p. 109
King F W, van Duyne R P and Schatz G C 1978 *J. Chem. Phys.* **69** 4472
Liao P F, Bergman J G, Chemla D S, Wokaun A, Melngailis J, Hawryluk A M and Economou N P 1981 *Chem. Phys. Lett.* **82** 355
Moskovits M 1980 *J. Chem. Phys.* **69** 4159
Moskovits M 1982 *J. Chem. Phys.* 77 4408
Muniz-Miranda M, Neto N and Sbrana G 1988 *J. Phys. Chem.* **92** 954
Sánchez-Cortés S and García-Ramos J V 1990 *J. Raman Spectros.* **21** 679
Takahashi M, Goto M and Ito M 1985 *Chem. Phys. Lett.* **121** 458
Wenning U, Pettinger B and Wetzel H 1980 *Chem. Phys. Lett.* **70** 49
Zhang P, Wang Y, He T, Zhang B, Wang X, Xin H and Liu F 1988 *Chem. Phys. Lett.* **153** 215