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SERS Spectra of 2-Aminophenol in Silver Colloids

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Raman, IR, and SERS spectra of 2-aminophenol are recorded and analyzed. Strong intramolecular hydrogen bonding is noticed between NH_2 and OH groups in the compound. As bands due to CC stretching, in-plane CH bending, and in-plane and out-of-plane CCC bending modes are enhanced in the SERS spectra, it is inferred that the molecule assumes a tilted "side on" orientation with respect to the silver surface. The OH out-of-plane bending mode is enhanced in one type of silver colloid, while the twisting mode of NH_2 is enhanced in the other one. Also, the substituent-sensitive CX in-plane bending mode shows different frequencies in the two colloids. These differences in the spectra of the two colloids are interpreted as due to distinct orientations.

INTRODUCTION

Surface enhanced Raman scattering (SERS) spectroscopy is a very powerful technique for studying the symmetry, coordination, and orientation of molecules adsorbed on metal surfaces. Several vibrational analysis of aminophenols have been reported (1–4). Among them 2-aminophenol is of importance as the NH_2 and OH groups are very close, leading to strong intramolecular hydrogen bonding. This paper deals with the results of the analysis of the SERS spectra along with Raman and IR spectra.

EXPERIMENTAL

The Raman spectrum of the compound was excited with 488-nm radiation (power 200 mW) from an argon ion laser and recorded on a Dilor GMBH Z 24 spectrometer. Bruker IFS 66 V FT-IR (4000–400 cm^{-1}) and PE 983 (4000–200 cm^{-1}) spectrophotometers were used to record the IR spectrum.

Greenish-yellow silver colloid (colloid 1) having a sharp absorption band at 390 nm and greenish-grey colloid (colloid 2) with a broad absorption band around 430 nm were prepared by the standard procedures (5, 6). A 10^{-4} M solution of silver nitrate (10 ml) was added dropwise to 30 ml of 2×10^{-4} M sodium borohydride solution with uniform stirring to get colloid 1. Both the solutions were chilled prior to mixing. To obtain colloid 2,250 ml of 10^{-3} M silver nitrate solution was heated to boiling and then 5 ml of 1% sodium citrate solution was added dropwise. The solution was stirred and boiled for 10 min. Absorption spectra of silver colloids, 2-aminophenol, and adsorbed aminophenol were recorded on a UV-240 Shimadzu UV–Visible recording spectrophotometer. To obtain samples for SERS measurements equal volumes of colloid 1/colloid 2 and 10^{-5} M aminophenol were mixed. SERS spectra were recorded on the Dilor spectrometer, keeping the experimental conditions the same as in the case of the normal Raman spectrum with the sample in capillary tubes.

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RESULTS AND DISCUSSION

2-Aminophenol has characteristic absorption bands at 210, 245, 270, 285, and 435 nm. In colloid 1, it has a green color and absorbs at 396 nm. The other absorptions occur at 210, 240, 275, and 280 nm. In colloid 2, the low wavelength absorptions coalesce to give a broad shoulder around 260 nm and the maximum at 210 shifts to 205 nm. Further, a broad asymmetric band with maximum around 445 nm having a very broad shoulder (~600 nm) on the long wavelength side is also observed.

IR AND RAMAN SPECTRA

The observed Raman and IR bands together with their relative intensities and vibrational assignments are given in Table 1. The numbering of the modes is as suggested by Miller (7). The assignments are based on the literature data (1, 4) for molecules with similar functional groups.

In crystalline phenols Green *et al.* (2) observed that the OH in-plane bending mode (δ_{OH}) contributes two bands; one around 1220 cm^{-1} and the other around 1380 cm^{-1}. In the present case, CC stretching (vibration 9) and CH in-plane bending (vibration 3) also fall in the region 1250 to 1330 cm^{-1}. The medium band (1, 2, 4) at 1217 cm^{-1} in IR is due to δ_{OH}. The position of the OH out-of-plane bend (γ_{OH}) could not be identified. The NH_2 group has four bending modes (1), scissoring (δ^s), rocking (r), wagging

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TABLE 1
Spectral Data (cm^{-1}) and Band Assignments of 2-Aminophenol

Deuterated IR	IR	Raman	SERS *in* colloid 1	SERS *in* colloid 2	Assignments
3376 m					ν^{as} NH_2/ν^{as} ND_2
3351 m					$\nu^{s}NH_2$/$\omega^{s}ND_2$
3327 w	3376 vs				
3305 m	3305 vs	3071 s			1,12b (νCH)
3058 w	3052 mbr				
2526 m					15b (νCH)
2479 w					
2413 m					
2185 mbr	2714 mbr	2724 vsbr			νOH, overtones,
		2585 brsh			combinations
1990 mbr	2580 mbr				
	1877 vw				
	1762 vw				
		1590 mbr	1626 w	1626 w	δ^{s} NH_2
1594 vs	1604 vs		1575 m	1579 w	16a, 16b (νCC)
1506 s	1512 s		1489 m	1485 vs	13b (νCC)
1453 m	1471 s		1453 vs	1463 vs	13a (νCC)
1404 w	1403 vs		1398 s	1400 s	νC–N(H_2)/νC–N(D_2)
1019 m					
			1327 w	1333 m	δOH
1280 vs	1282 vs	1275 m	1264 m		3 (CH ipb)
	1268 vs		1231 s	1237 s	9 (νCC)
	1217 m		1204 m		δOH
1151 vw	1157 w	1150 m	1152 s	1157 s	10 (CH ipb)
1117 vw	1142 m				15a(νC–X), 17b(CH ipb)
	1085 m				5 (νC–C)
1038 m	1031 m	1030 s			14b (CH ipb)
921 w	924 s	932 s			11a (CH opb)
667 m					$\nu$$NH_2$/r$ND_2$
895 w	897 s				
849 w	847 m				11b (CH opb)
	803 m				
748 vs	765 m	765 s			6 (CC band), 4 (umbrella)
	743 vs				2 (breathing)
					8 (CCC puckering)
					wNH_2
531 vw	568 vw		586 s	600 sh	18a (CCC opb)
	549 w			593 m	
	496 w		484 vs	489 mbr	20a, 20b(CCC opb)
					18b(CCC ipb)
457 w	448 w		376 m	398 wbr	14a(CX ipb)
	421 w				17a (CX ipb)
	340 w	212 m		248 wbr	t NH_2, 19b(CX opb)
		151 s			19a (CX opb)
		104 s			
		80 vs			External modes
		56 s			

Note. ν = stretching, δ = bending, v = very, s = strong, m = medium, w = weak, sh = shoulder, br = broad. Comparison of peaks is with those of similar compounds reported in literature (1, 4, 7).

(ω), and twisting (t), which occur in the regions 1615–1630, 1040–1055, 600–800, and 190–250 cm^{-1}, respectively. The wagging mode usually overlaps (1) with the umbrella vibration—CH out-of-plane bend (vibration 4)—in the 735–770 cm^{-1} region.

As expected (1), in the 1700–2000 cm^{-1} (IR) region the so-called benzene fingers are observed (Table 1). Most of the bands in the 2000–3000 cm^{-1} region in the IR may also be due to overtones and combinations. However, the very large intensity of the Raman bands (Fig. 1) at 2724 and 2585 cm^{-1} is quite unusual. In 3-aminophenol the OH was observed as a strong IR band at 2850 cm^{-1} and no band corresponding to this mode appeared in the Raman spectra. In the present case, as the NH_2 and OH groups are very close, very strong intramolecular hydrogen bonding is expected which will shift the OH to very low frequencies. Hence the Raman band at 2724 with a shoulder at 2585 cm^{-1} is assigned to OH. The IR spectrum (Fig. 2) of the deuterated sample correlates well with this argument. The large broadening of the band (FWHM = 425 cm^{-1}) also supports the idea of strong intramolecular hydrogen bonding.

SERS SPECTRA

According to the surface selection rule (8, 9), when a molecule is adsorbed flat on the silver surface its out-of-plane bending (opb) modes will be more enhanced when compared with its in-plane bending (ipb) modes and vice versa when it is adsorbed perpendicular to the surface. Further, vibrations involving atoms that are close to the silver surface will be enhanced. In the present case, the vibrations 10 (CH ipb), 20 (CCC opb), 18a (CCC ipb), and 14a (CX ipb) are enhanced (Table 1) in both the colloids. Therefore, it is reasonable to assume that the molecule is adsorbed in a geometry other than flat or perpendicular, possibly in a tilted orientation. The substituent-sensitive 14a mode is observed (Fig. 3) as a medium intensity band at 376 cm^{-1} in colloid 1 and as a weak broad band at 398 cm^{-1} in colloid 2. Further, a weak broad band at 248 cm^{-1} corresponding to the twisting mode (1) of NH_2 appeared in colloid 2. Therefore, it may be inferred that NH_2 is close to the silver surface in colloid 2. The observation of the medium intense band at 1204 cm^{-1} corresponding to the OH in-plane bending mode in colloid 1 suggests that the OH group is close to the silver surface. The CC stretching modes are also enhanced in both the colloids. Therefore, the 2-aminophenol molecule assumes a "side on" orientation tilted with respect to the silver surface with OH close to silver in colloid 1 and NH_2 in colloid 2. The possible orientations are shown in Fig. 4.

It is reported (10) that when the frequency difference between normal and SERS spectra is not more than 5 cm^{-1}, then the molecular plane will be perpendicular to the silver surface. In the present case, the shifts observed for the vibrations 14a, 18a, 10 (ipb modes) and CC modes (vibrations 16, 13, 9) are more than 5 cm^{-1}, which further supports our conclusion that the molecule is in a tilted "side on" orientation. In the region 1400–1600 cm^{-1} changes in intensity distribution (Fig. 3) and frequency values (Table 1) are observed. The bands at 1204 and 1264 cm^{-1} (colloid 1) are not observed in colloid 2. Fur-

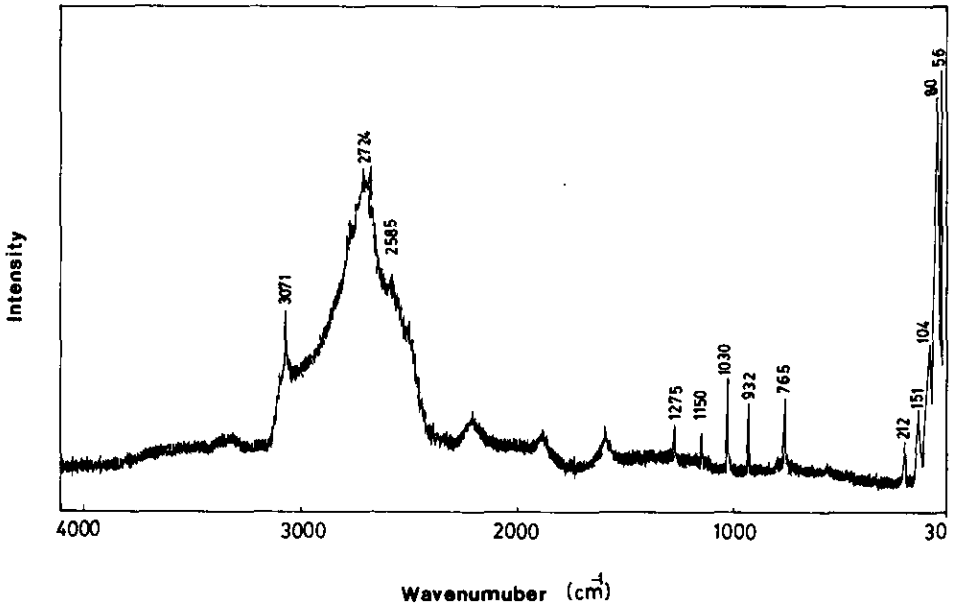

FIG. 1. Raman spectrum of 2-aminophenol.

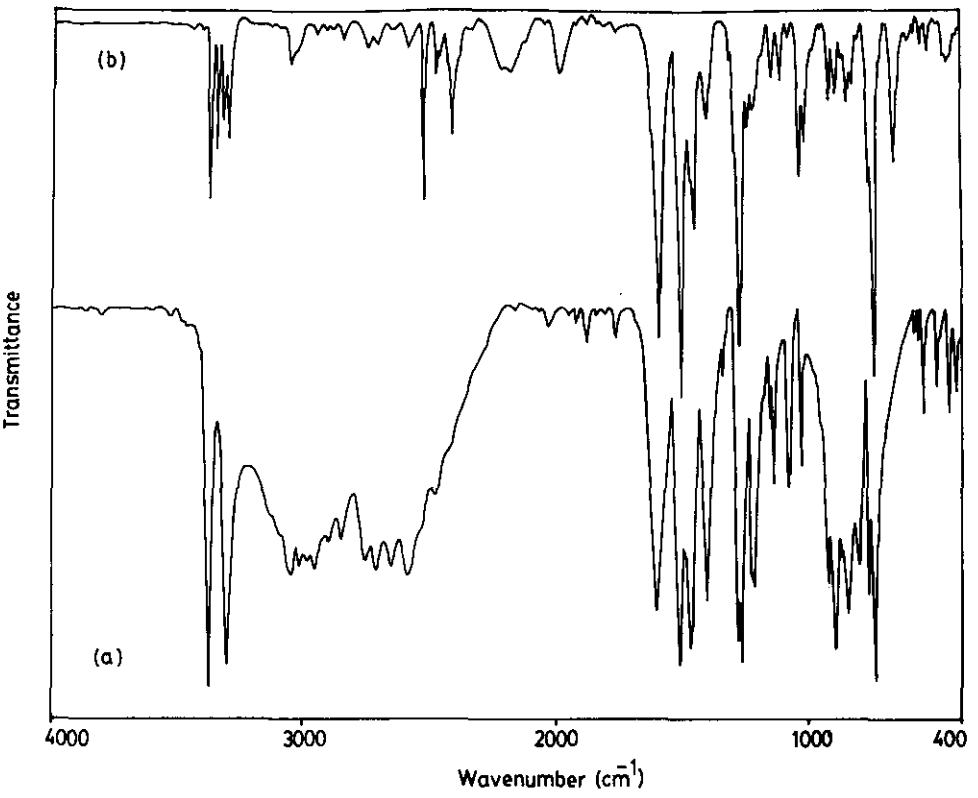

FIG. 2. IR spectrum of (a) 2-aminophenol, (b) deuterated 2-aminophenol.

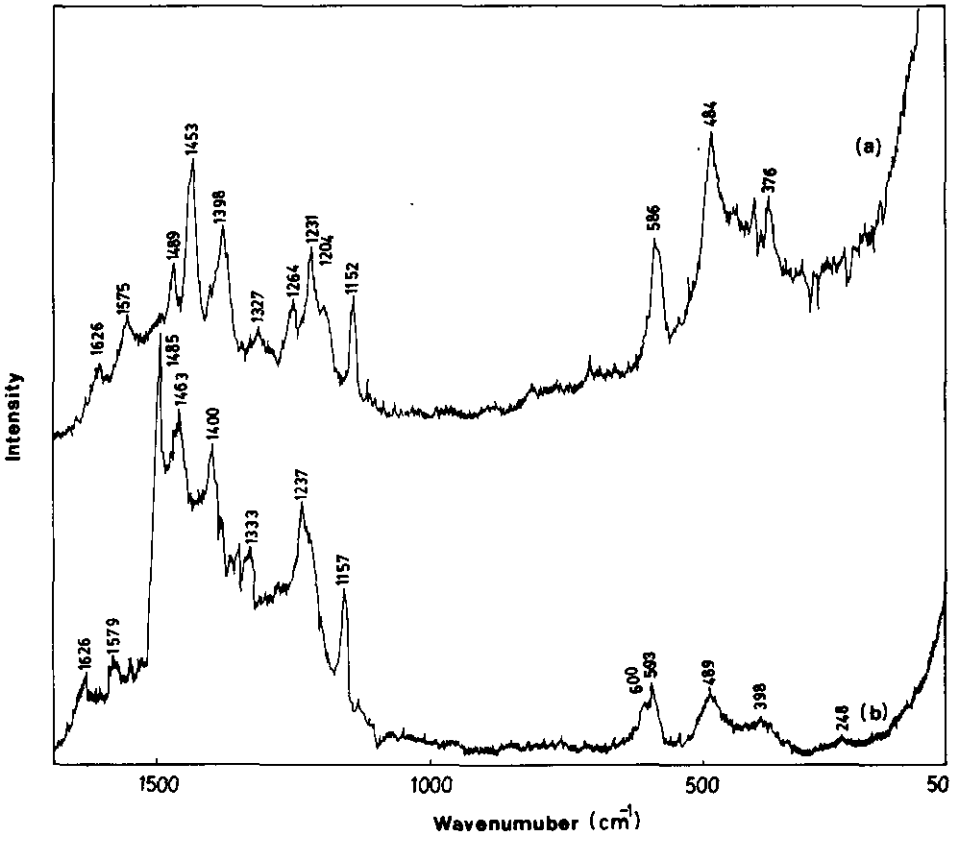

FIG. 3. SERS spectrum of 2-aminophenol (a) in colloid 1, (b) in colloid 2.

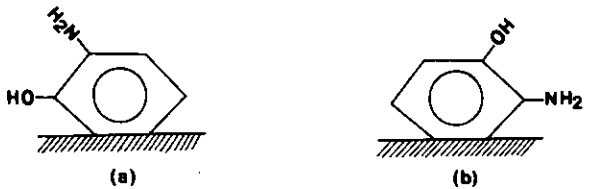

FIG. 4. Orientation of 2-aminophenol molecule on the silver surface (a) in colloid 1, (b) in colloid 2.

ther, the bands between 300 and 600 cm^{-1} show noticeable differences in the two colloids. These differences are due to the distinct orientations (Fig. 4) of the molecule on the silver surface.

CONCLUSIONS

The unusually low frequency (2724 cm^{-1}) of the OH stretching mode is due to the strong intramolecular hydrogen bonding between NH_2 and OH groups. The molecule assumes a tilted "side on" orientation with respect to the silver surface. Differences observed in the SERS spectra in the two colloids are due to distinct orientations of the molecule on the silver surface.

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