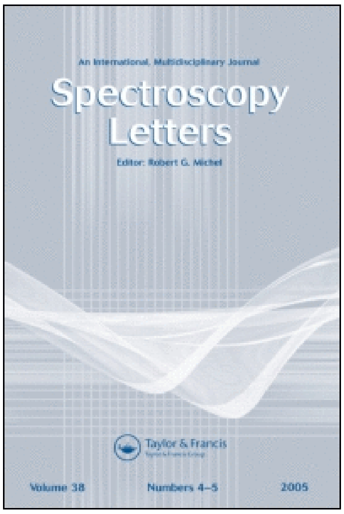

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ENHANCED RAMAN SCATTERING FROM PYRAZINOIC ACID ON SILVER AND GOLD SOLS.

Key Words : Raman, SERS, Pyrazinoic acid, Sols.

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ABSTRACT

We report the SERS of pyrazinoic acid on silver and gold sols. The assignments are consistent with bidentate bridging and unidentate coordinations of carboxylate group,respectively.

INTRODUCTION

The SERS of carboxylic acids adsorbed on various substrates have been extensively studied and are known to adsorb on metal surfaces as carboxylate ions [1-8] .The structures and orientation of these species have been discussed mainly trough the assignment of the stretching vibrations of the carboxylate groups.On this basis, the three structures, namely bidentate chelating, bidentate bridging and unidentate may done in the metal-carboxylate coordination.

In this work we report our results on SERS of pyrazinoic acid adsorbed on aqueous silver and gold sols.The study is interesting because this molecule possess other sites for linkage to the surface: can adsorb by the Π-electrons of aromatic ring and also by the lone electron pairs of the nitrogen atoms. And, on the other way, for to ascertain to what extent the adsorbate-surface interaction are perturbed by the addition of ring substituents to the pyrazine. This, links to the metal through one of the nitrogens atoms, leaving the aromatic ring perpendicular to the surface [9].

We give a complete assignment of the SER spectra and discuss the possible structure and orientation of the surface species. For this purpose we started with the assignment proposed by us of the vibrational spectra of pyrazinoic acid and its potassic salt [10].

EXPERIMENTAL

Pyrazinoic acid, (Ega-Chemie), was purified by dissolving it in an aqueous solution of KOH and treating it several times with active charcoal. Then the solution was acidified with hydrochloric acid to precipitate the acid which was then separated by filtration and dried in a vacuum oven.The potassic salt was synthesized by neutralization with KOH as described in ref.11. Silver sols were prepared in triply distilled water by reduction of $AgNO_3$ with an excess of $NaBH_4$ according to the method described by Creighton et al [12]. To prevent further reductions of the samples the silver sols prepared in this way were aged for at least 1 week before use to allow for the decomposition of $NaBH_4$. Gold sols were prepared similarly by reduction of $K(AuCl_4)$. Pyrazinoic acid was adsorbed onto the silver and gold particles by adding a dilute solution to the colloidal suspension, the final pyrazinoic acid concentration in the sol being 10^{-4} M.

Raman spectra were obtained with a Jobin-Yvon *U-1000* spectrometer fitted with a cooled Hamamatsu R943-02 photomultiplier tube, using 514.5 nm exciting radiation from a Spectra-Physics Model 2020 argon ion laser and 647.1 nm from a Spectra-Physics Model 2016 kripton ion laser. Spectra were recorded with an effective power of 60 mW at the sample.

RESULTS

Figures 1(a),(b) and (c) show the Raman spectrum of a 0.1 M aqueous solution of potassium pyrazinoate and the SER spectra of pyrazinoic acid adsorbed on silver and gold sols, respectively. Summarized in Table 1 are the band frequencies and the proposed asignments for the SER spectra.The assignments are described by Wilson's notation with an approximate mode description. Table 1 contains integrated band intensities (in parentheses) and values of the relative surface enhancement factor, SEF, for each vibration normalized to that for the 12 mode for the silver sol. These values are simply ratios of the relative integrated SERS intensities to those for the corresponding bands in 0.1 M aqueous solution of potassium pyrazinoate.

DISCUSSION

Silver Sol.

The SER spectrum of pyranizoic acid , Fig.1.(b) has a great similarity to the Raman spectrum from an aqueous solution of potassium pyrazinoate, shown for comparison in Fig.1(a). At frequencies higher than about 800 cm $^{-1}$ there is almost a one to one correspondence between the bands in the two spectra.

In addition to the corresponding modes of the solution spectrum new bands are seen in SERS at 1565, 783, 545, 451 and 232 cm $^{-1}$.The bands at 783, 545 and 451 cm $^{-1}$ correlate straighforwardly with those at 789, 535 and 448

TABLE 1.- Assignment of the observed SER bands of pyrazinoic acid on silver and gold sols in comparison with the Raman bands of a aqueous solution of potassium pyrazinoate.

Solution	SERS-Ag		SERS-Au	Assignment
		SEF		
	232		238	ν (M-O)
401(5)	392(5)	1.0		δ(CX)
	451(13)		439	r(OCO)
	545(3)		544	6a;δ ring
633(7)	641(6)	0.9	675	6b;δ ring
733(3)	731(34)	11.3		δ(OCO)
	783(4)		798	11;γ(CH)
858(23)	852(42)	1.8	838	1;ν ring
1028(100)	1032(100)	1.0	1046	12;δ ring
1060(49)	1056(29)	0.6		15;δ(CH)
1175(6)	1163(10)	1.7		14;ν ring
	1189(23)	3.8	1179	18a;δ(CH)
1294(3)	1288(7)	2.3	1292	ν(CX)
1388(47)	1376(45)	1.0	1350	ν_s(OCO)
1417(27)	1411(30)	1.1		19b;ν ring
1481(12)	1473(23)	1.9	1467	19a;ν ring
1533(37)	1525(60)	1.6		8b;ν ring
	1565			ν_{as}(OCO)
1585(9)	1591(48)	5.3	1597	8a;ν ring
			1631	ν_{as}(OCO)
3070(>100)	3072(5)			ν (CH)

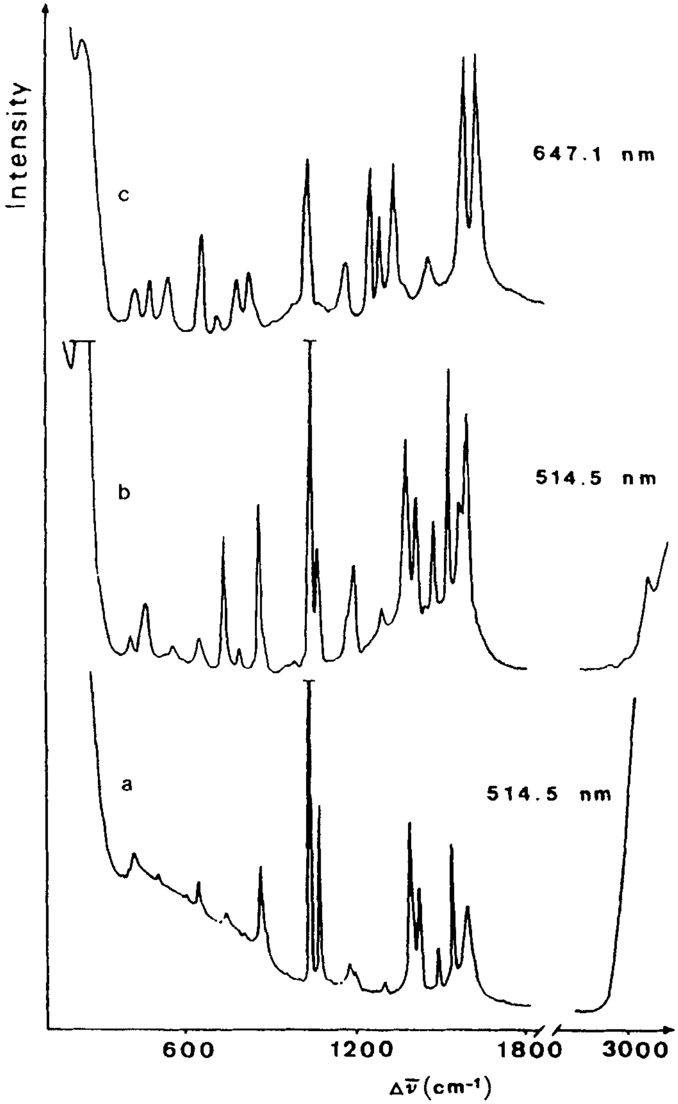

FIG.1.(a).Raman spectrum of a 0.1M aqueous solution of potassium pyrazinoate;(b).SERS of pyrazinoic acid,10^{-4} M, on silver sol;(c).SERS of pyrazinoic acid,10^{-4} M,on gold sol.

cm^{-1} assigned as 11;γ(CH), 6a;δring and r(OCO), respectively in the infrared and Raman spectra of the pyrazinoic acid solid [10]. The band at 232 cm^{-1}, with very strong intensity, is assigned to an Ag-O stretching vibration indicative of the adsorbate-metal bonding, in correspondence with the benzoic acid [2] and is a evidence that the bonding to the surface occurs through the carboxylate group and not with the pyrazine ring.

The shoulder on the low frequency side of the 8a;ν ring vibration, at 1565 cm $^{-1}$, can be assigned to the asymmetric OCO stretching mode, ν_{as}(OCO), because published studies[13] show that this vibration in bidentate bonding carboxylate-metal complexes occurs near 1580 cm^{-1}.

The ν_s(OCO) band at 1388 cm^{-1} in the ordinary Raman spectrum is red shifted by 12 cm^{-1} to 1376 cm^{-1} in the SER spectrum. Such a red shift is know for other carboxylic acids and shows that the two carbon-oxygen bonds are tending to become identical.

The frecuency difference of the stretching vibrations of the carboxylate group: 1565-1376 = 189 cm^{-1}, is also near the corresponding values for the bidentate bridging complexes.

The evaluation of adsorbate orientation can be obtained from surface vibrational band intensities by utilizing so-called "surface selection rules" [14]. We have found, with the results in Table 1.,that the enhancement of the characteristic bands of carboxylate group: r(OCO),δ(OCO) and ν_s(OCO) togheter with the SEF values for in-plane vibrations, and the significative intensity of ν(CH) bands point out to a standing-up orientation of the molecular anion with respect to the surface.This orientation is analogous to that proposed by us for pyrazinecarboxamide [15].

Finally, the blue-shift of the vibration 12 when going from the solution of the anion to the SERS conditions shows some involvement of N_1 in the coordination with the silver atoms.

Gold Sol.

The SER spectrum, Fig.1(c), at first sight, looks very different of the SERS on silver sol and the solution but the main differences are in relative intensities, band broadening and the shift in frecuency of some modes.

The most enhanced bands are those at 1597 and 1631 cm^{-1} have been assigned to vibrations 8a;ν ring and νas(OCO) respectively. The remaining bands are due to in-plane vibrations except the band recorded at 798 cm^{-1} assigned to 11;γ(CH).

The r(OCO) and 1;ν ring modes at 439 and 838 cm^{-1} are red shifted by 12 and 14 cm^{-1} respect the SERS on silver sol. The region of 3000 cm^{-1} has not been recorded when using the 647.1 nm exciting line because it is almost in the mechanical limit of our monochromator.

Information on the bonding geometry can be obtained from the bands at 238, 1046, 1350 and 1635 cm^{-1}.The band at 238 cm^{-1} is assigned as the metal-adsorbate stretching. Vibration 12 is assigned at 1046 cm^{-1}, 18 cm^{-1} higher than in the normal spectrum of solution and 14 cm^{-1} than in the SERS on silver sol.. This blue-shift indicates that the heteroatom takes place directly in the adsorption.

The bands at 1350 and 1631 cm^{-1},stretching vibrations of COO group, indicate that the acid bond to the gold surface as anion and that the two oxygen atoms are not identical. The COO group shows some C=O features in concordance with a unidentate coordination [13], in which the ν_{as}(OCO) increases,the ν_s(OCO) decreases and the separation between both increases because of the equivalence of two oxygen atoms is removed.The difference between the frequencies of two COO stretching is now about 100 cm^{-1} higher to the silver case.

In summary, the experimental results are consistent with a geometry for the adsorption analogous to described to silver sol but in this case only a oxygen atom link directly to the metal.

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