SERS analysis of a bioactive isomer of pyridinecarboxamide: picolinamide

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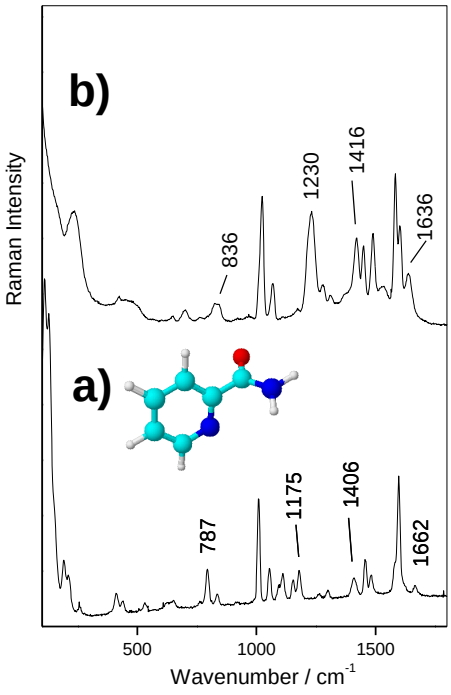
SERS phenomenon (Surface-enhanced Raman scattering) has been widely used to study the adsorption on some metallic roughed surfaces, mainly of Ag, Cu and Au, of many organic molecules. The high sensitivity of this effect allows an accurate structural study of adsorbates at very low concentrations. This technique can be used to gain information concerning the adsorbed species and the functional groups which are in contact with the metal surface and in many cases, concerning the conformation of the adsorbate [1,2].

In this work we have recorded the Raman and SERS spectra of picolinamide (PIA) recorded on silver colloids. PIA is one of the three bioactive isomers of pyridinecarboxamide and it shows an important biological activity with the NAD coenzyme (nicotinamide adenine dinucleotide) [3] which plays important roles in more than 200 aminoacid and carbohydrate metabolic reactions [4].

Raman and SERS spectra were recorded with a Jobin-Yvon U-1000 double monocromator spectrometer fitted with a cooled Hamamatsu R943-02 photomultiplier, using the 514.5 nm exciting line from a Spectra Physics 2020 Ar^+ gas laser. In the case of liquid samples a quartz cell with a 1cm path length was used, whilst a glass capillary was used for the microcrystalline solids. Colloidal silver solutions have been prepared in deionized and triply distilled water according to the method described by Creighton et al.[5].

Fig.1.a shows the Raman spectrum of solid crystalline PIA and Fig.1.b the SERS spectrum of a 10^{-4} M solution of PIA adsorbed on silver colloids, both in the range 100-1800 cm^{-1}.



EXPERIMENTAL WAVENUMBERS			
Mode	**Solid**	**SERS**	**Δν (cm^{-1})**
Amide I	1662	1636	-26
Amide III	1406	1416	+10
ν (CX)	1175	1230	+55
1; ν_{ring}	787	836	+49

Fig. 1. a) Raman spectrum of solid PIA; b) SERS spectrum of a 10^{-4} M solution of PIA. Table: Experimental wavenumbers of the Raman and SERS spectra of PIA and wavenumber shifts between them.

This region of the Raman spectrum of the solid (Fig. 1.a) is dominated by two very strong bands at 1004 and 1594 cm^{-1}. These bands are assigned to the 12; δ_{ring} and 8a; ν_{ring} modes, respectively, and they don't experiment important changes in the SERS spectra. However there are some characteristic bands of this molecule associate with the amide and aromatic functional group that undergo significant wavenumber shifts in the SERS spectra. Therefore the Raman vibrational modes related to the amide I, amide III, ν(CX) and 1;ν_{ring} recorded at 1662, 1406, 1175 and 787 cm^{-1}, respectively, undergo important wavenumber shifts of -26, +10, +55 and +49 cm^{-1} when PIA is adsorbed on the nanostructures. The shift undergone by the mode 1;ν_{ring} is very similar to that observed in the SERS spectra of aromatic molecules as benzamide which indicates the adsorption on silver nanoparticles as azanions linking to the metal through both the nitrogen and the oxygen atoms of the ionized carboxamide group. The delocalization of the negative charge in the whole molecule originates changes in the molecular structure affecting to these vibrational modes.

Finally, the enhancement of the SERS bands attributed to amide I, amide III and ν(CX) vibrations is due to the fact that PIA interacts to the metal through both the nitrogen and the oxygen atoms of carboxamide group and the aromatic ring is orientated approximately perpendicular to the mentioned surface.

References

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