

# SERS study of thiocarbonyl compounds adsorbed on metal nanoparticles

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Thiocarbonyl compounds have been reported to exhibit interesting biological and pharmacological properties but they are many often characterized by their toxicological effects. However the chemistry of thiobenzoic acid (TBA) and thiobenzamide (TB) has not been fully studied yet. Some of the biological studies of TBA are related to the tautomerism of thiocarboxylic acids and the important role that the  $-C(=O)-S$  and  $-C(=S)-O$  functional groups play in the catalytic activities of enzymes such as cysteine or serine proteases.<sup>1</sup> On the other hand, TB and derivatives are well known hepatotoxins and have been used as inhibitor in enzymatic reactions and in pharmacy due to their microbial activity.<sup>2</sup>

From a chemical point of view, thiocarboxylates are an interesting type of molecules having two different donor atoms, a soft sulfur donor atom and a hard oxygen donor one. The presence of these unlike groups can lead to the bonding with metal surfaces. Likewise the interaction of thiobenzamide and their derivatives with metals is of great interest because both the sulfur and nitrogen atoms are also able to coordinate with the surface. Therefore the high affinity of these molecules for metal surfaces makes them suitable SERS target adsorbates. Taking advantage of the fact that SERS spectroscopy is both surface selective and highly sensitive we have attempted to determine the molecular structure of TBA and TB once they are adsorbed on the metal.

The main objective of this work is focussed on discussing the observed vibrational wavenumber shifts of TBA and TB upon adsorption on silver nanoparticles. In this work the SERS substrates have been prepared by using different colloidal silver solutions according to the method described by Creighton et al.<sup>3</sup> and Leopold and Lendl.<sup>4</sup>

The analysis of the vibrational wavenumbers shifts of the Raman and SERS spectra allow us to know the adsorption process (Figure 1). In the case of TBA, the wavenumber of the SERS band assigned to  $\nu(C=O)$  vibrational mode shows an important blue shift up to  $40\text{ cm}^{-1}$  with respect to the Raman whereas the  $\nu(C-S)$  band undergoes a red shift up to  $40\text{ cm}^{-1}$ . These results suggest a unidentate coordination of TBA to the silver surface through the sulfur atom.

On the other hand, the SERS band assigned in the case of TB to Amide III (mainly  $\nu(CN)$ ) exhibits a significant blueshift up to  $41\text{ cm}^{-1}$ , and the SERS band assigned to Amide I (mainly  $\nu(CS)$ ) shows a red shift up to  $11\text{ cm}^{-1}$ . These wavenumber shifts indicate that TB interacts to the silver surface through the sulfur atom. Interestingly, in previous SERS studies of pyridinecarboxamides and benzamide we have observed that some SERS bands assigned to  $1;\nu_{ring}$ , Amide I (mainly  $\nu(C=O)$ ) and Amide III (mainly  $\nu(C-N)$ ) show wavenumber shifts of  $+50$ ,  $-50$  and  $+10\text{ cm}^{-1}$ , respectively, which were attributed to the deprotonation of carboxamide group.<sup>5,6</sup>

Finally, in order to verify experimental results DFT calculations have been carried out for different silver complexes of TBA and TB concluding that the unidentate

coordination is the most likely interaction of both of them.

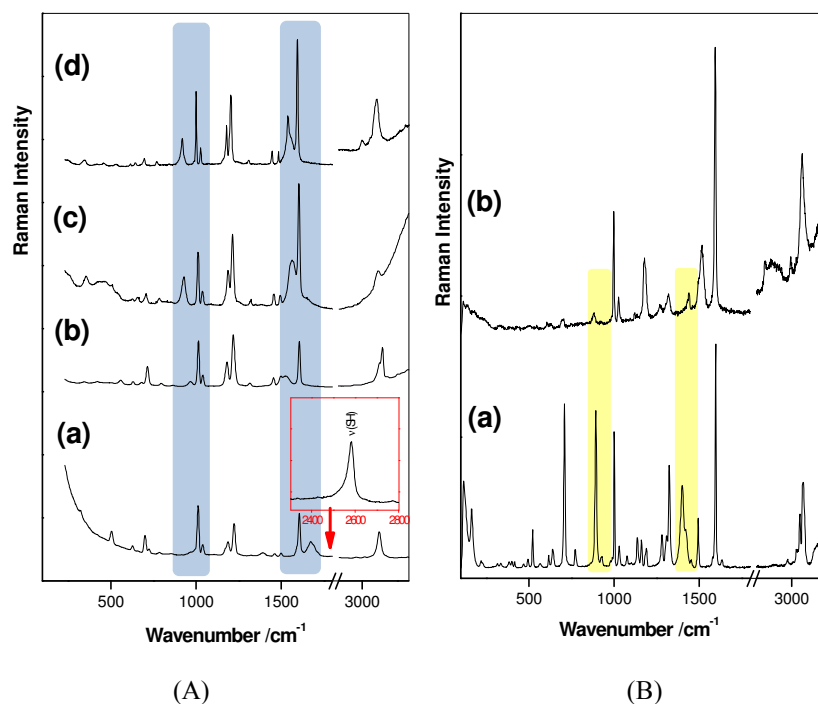


Figure 1.(A) Raman spectra of TBA in the neat liquid (a) and 1 M aqueous solution at pH 14 (b); SERS spectra of  $5 \times 10^{-4}$  M of TBA on Ag NPs obtaining by reduction with sodium borohydride (c) and by reduction with hydroxylamine hydrochloride (d); (B) Raman spectra of solid TB (a), SERS spectrum of  $5 \times 10^{-4}$  M of TB on Ag NPs obtaining by reduction with hydroxylamine hydrochloride (b). An excitation wavelength of 514.5 nm was used.

- <sup>1</sup> Carey P.R. Eds. (1982). *Biochemical Applications of Raman and Resonance Raman Spectroscopy*. Academic Press: London.
- <sup>2</sup> Yu K.L., Torri A.F., Luo G., Cianci C., Grant-Young K., Danetz S., Tiley L., Krystal M., Meanwell N.A. (2002), *Bioorg. Med. Chem. Lett.* 12, 3379-3382.
- <sup>3</sup> Creighton J.A., Blatchford C.G., Albrecht M.G. (1979), *J. Chem. Soc. Faraday Trans. II*, (75), 790-798.
- <sup>4</sup> Leopold N., Lendl B. (2003), *J. Phys. Chem. B*, 107 (24), 5723-5727.
- <sup>5</sup> Castro J.L., Lopez-Ramirez M.R., Arenas J.F., Soto J., Otero J.C. (2012), *Langmuir*, (28) 8926-8932.
- <sup>6</sup> Castro J.L., Arenas J.F., Lopez-Ramirez M.R., Soto J., Otero J.C. (2013), *J. Colloid Interface Sci.*, 396, 95-100.