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Raman, SERS and DFT study of chemically-adsorbed thiobenzoic acid on silver nanoparticles

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Abstract

Thiocarboxylic acids are organosulphur compounds with general formula $RC(O)SH$. They are related to carboxylic acids by the replacement of one oxygen by sulphur. Two tautomers are possible, written as $RC(S)OH$ and $RC(O)SH$. The second one is the majority species in solid state and solution of thiobenzoic acid (TBA) at room temperature [1], but derivatives from both tautomers are known so that the SERS spectrum can be originated by either one. 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 once it is adsorbed on the metal surface. To accomplish this SERS spectra of TBA have been recorded on different silver colloids. A combination of layer-by-layer method with spin-coating deposition of silver nanoparticles have been used to prepare SERS active substrates on which the homogeneity of the SERS signal of TBA has been analyzed.

Fig. 1 (I) shows the Raman spectra of TBA in the neat liquid (a), 1 M aqueous solution at pH 14 (b), SERS spectrum of a 5×10^{-4} M silver colloid prepared by reduction of silver nitrate with sodium borohydride at pH 7 (c) and SERS spectrum of a 5×10^{-4} M silver colloid prepared by reduction of silver nitrate with hydroxylamine hydrochloride (d). The assignment of the Raman spectra has been based on the present work as well as on previous studies [2-4]. The two bands recorded at 1662 and 2572 cm^{-1} in Fig.1a, are assigned to $\nu(C=O)$ and $\nu(SH)$ modes, what confirms that the Raman spectrum in the neat liquid is due to the thiolic specie of TBA, $RC(O)SH$. In the Raman spectrum of the solution (Fig. 1b) a significant redshift of $\nu(C=O)$ mode of 52 cm^{-1} and the absence of the $\nu(SH)$ band are detected in agreement with the behavior observed in the SERS spectrum (Fig. 1c). The latter confirms that the thiol tautomer of thiobenzoate anion, $RC(O)S^-$, is adsorbed on silver nanoparticles. Other important SERS enhancements have been registered for the following vibrational modes: $8a_1 \nu_{ring}$, $\nu(C=O)$ and $\nu(CS)$ recorded at 1592, 1554 and 928 cm^{-1} in Fig. 1c and 1d, respectively. The last two modes, $\nu(C=O)$ and $\nu(CS)$, undergo wavenumber shifts of +40 and -40 cm^{-1} respectively, which are closely related with the coordination of thiobenzoate anion to the metal surface [5]. The analysis of the vibrational wavenumber of these modes suggests that this molecule shows unidentate coordination through the sulphur atom to the metal surface. In order to confirm this fact DFT calculations have been carried out for different silver complexes: I) bridging bidentate ligand, II) chelating ligand and III and IV) unidentate ligand (Fig. 2). Theoretical wavenumber of representative bands of these compounds have been compared to the experimental one concluding that the behavior of the unidentate ligand (III) is the most probably coordination type of TBA on the metal surface.

In order to confirm these conclusions the SERS spectra of TBA on silver colloid prepared by reduction of silver nitrate with hydroxylamine hydrochloride at different concentration of analyte have been recorded as well (Fig. 1 (II)). It is well known that the SERS enhancement factor depends strongly on different factors and in particular on the adsorption properties of the probe and the analyte concentration on the surface coverage. In this sense TBA has shown a very good detection level for this particular silver colloid it being a highly SERS active molecule. The detection limit is estimated to be 0.01 μ molar.

Finally, Fig. 3 shows a representative Raman mapping of TBA adsorbed on a silver substrate prepared by spin-coating. Generally speaking, the image represents a fairly homogeneous distribution of the SERS intensity highlighting some points where the intensity is stronger as is expected in areas with heterogeneous coverage. The reproducibility of this type of substrate is under study focusing their application as reproducible and ultrasensitive sensing assemblies by using TBA as the target molecule due its good SERS sensitivity.

References

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Figure 1. (I) Raman spectra of TBA in the neat liquid (a), 1 M aqueous solution at pH 14 (b), SERS spectrum of 5×10^{-4} M of TBA on Ag NPs obtaining by reduction with sodium borohydride (c) and SERS spectrum of 5×10^{-4} M of TBA on Ag NPs obtaining by reduction with hydroxylamine hydrochloride (d). (II) SERS spectrum of TBA on Ag NPs obtaining by reduction with hydroxylamine hydrochloride at different concentration of this molecule.

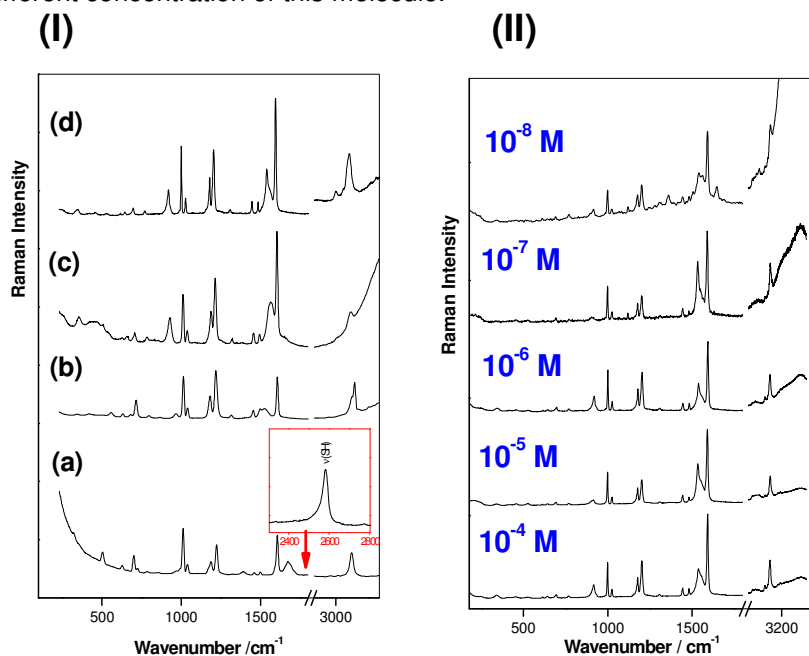


Figure 2. Optimized geometries of TBA Ag-complexes calculated at B3LYP/LanI2dz level of theory.

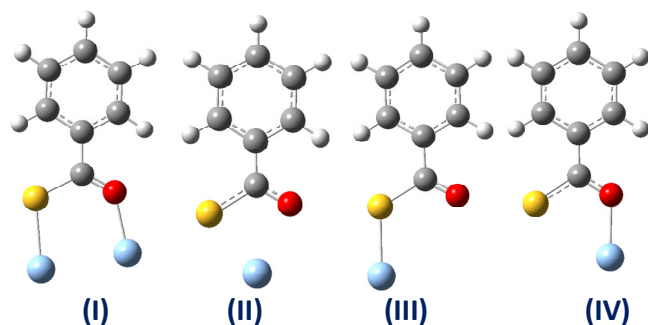


Figure 3. Raman mapping image (30x40 μm) of TBA on silver substrate prepared by spin-coating.

