Detection of different species of p-aminothiophenol on silver nanoparticles by Surface-Enhanced Raman Spectroscopy (SERS)

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Abstract: In the present work we have analyzed the experimental and theoretical SERS spectra of the organic compound p-aminothiophenol (pATP, HS-Ph-NH_2) recorded on silver nanoparticles. DFT calculations have been performed to support the experimental results in order to estimate the adsorption specie and the corresponding Raman bands assignment. It is found a different adsorption behavior of pATP not only by changing the concentration of the adsorbate but also by exciting the sample at different wavelengths.

Depending on the particular molecule-metal system and on the experimental conditions different Surface-enhanced Raman Scattering (SERS) mechanisms can operate simultaneously or separately. Therefore systematic interpretations of SERS spectra can be a challenge, given that complex selection rules are derived from these enhancement mechanisms related to electromagnetic properties of the nanoparticles or resonance Raman effects involving the molecule-metal complex.[1]

In the present work we have focused the discussion on the experimental and theoretical SERS spectra of the organic compound pATP recorded on silver colloids. The huge SERS of pATP on metal substrates is significantly different from its ordinary Raman spectra due to the formation of a new specie namely p,p' –dimercaptoazobenzene (DMAB). The features of the SERS spectra of pATP are strongly dependent on many factors as i.e. the laser power density or the laser wavelength [2] but there are still important aspects to understand as, for example, the effect of the concentration that has already been studied before by our group.[3] In this case we have analyzed the effect of the concentration at different wavelengths on the SERS spectra of pATP on silver nanoparticles.

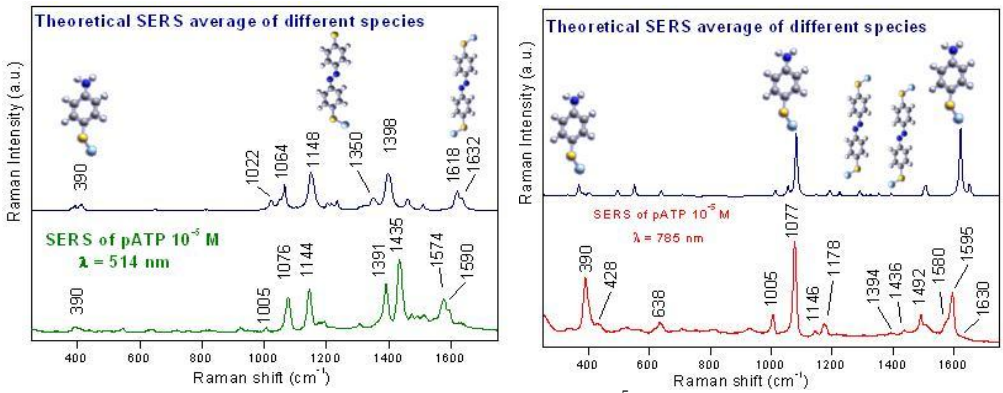

Figure 1. Theoretical and experimental SERS spectra of 10^{-5} M pATP at different wavelengths.

We have found that the Raman signals of the SERS of pATP arise from at least three different molecular species. At any concentration or wavelength we are able to detect SERS bands of pATP bonded to silver nanoparticles through sulfur atom (Agn-S^--Ph-NH_2). However we can only observe significant SERS bands from pATP bonded through both sulfur and nitrogen atoms (Ag_n-S^--$PhNH_2$-Ag_m) and the azo derivative in specific conditions.

Referencias:

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