SURFACE-ENHANCED RAMAN SPECTROSCOPY OF THIOBENZOIC ACID ON METAL NANOPARTICLES

M.R. Lopez-Ramirez, J.F. Arenas, J.C Otero and J.L. Castro

Universidad de Málaga, Facultad de Ciencias, Departamento de Química Física,

Campus de Teatinos s/n, 29071 Málaga, Españas

Molecules adsorbed on some metal surfaces such as silver, copper and gold, can exhibit enormous *Surface-enhanced Raman Scattering* (SERS). The SERS effect has historically been associated with substrate roughness on two characteristic length scales [1,2]. Surface roughness on the 10 to 100 nm length scale supports the electromagnetic resonances which are the dominant mechanism of enhancement. A second mechanism often thought to require atomic scale roughness, is referred to as the chemical enhancement mechanism. This second mechanism involves the creation of new electronic excited states which result from adsorbate–substrate chemical interactions. These two mechanisms operate simultaneously making it difficult to isolate the role and magnitude of each one.

In this work the SERS spectra of thiobenzoic acid (TBA) adsorbed on several silver colloids are recorded by using different excitation wavelengths. Taking advantage of the fact that SERS spectroscopy is both, surface selective and highly sensitive, we have attempted to determine the molecular structure of the surface complex once TBA is adsorbed on the metal. The analysis of the vibrational wavenumbers of the Raman and SERS spectra suggests that this molecule shows unidentate coordination to the silver surface through the sulphur atom. In order to confirm this conclusion DFT calculations have been carried out for different TBA-silver complexes concluding that the unidentate coordination is the most likely interaction of TBA on the metal surface.

Wavelength-scanned SERS excitation spectroscopy involves the measurement of SERS signal by using several excitation wavelengths and it was recognized as a useful tool for checking the mechanisms responsible for the SERS enhancement [3]. We have studied the effect of the wavelength within the SERS spectra of TBA on silver colloid prepared by different methods and we have analyzed the intensity of the 8a vibrational mode of TBA recorded at about 1590 cm^{-1}. The intensity of this mode is noticeably higher in the spectrum recorded with the 514.5 nm line (Fig. 1). This result is attributed to the presence of a resonant Raman effect associated to a photoinduced charge-transfer process when using the most energetic excitation line.

Finally, it is important to mention the high affinity of TBA for the silver surfaces what allows for a detection limit estimated to be 0.01 μM.

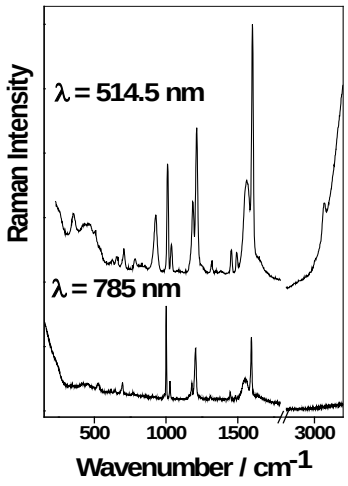

Fig.1. SERS spectra of TBA at different wavelengths.

Keywords: SERS, thiobenzoic acid, nanoparticles

References

[1] Moskovits, M., Rev. Mod. Phys. 57 (1985) 783.

[2] Campion, A., Kambhampati, P., Chem. Soc. Rev. 27 (1998) 241.

[3] Lopez-Ramirez, M.R., Garcia-Ramos, J.V., Otero, J.C., Castro, J.L., Sanchez-Cortes, S., Chemical Physics Letters 446 (2007) 380.