Spectroscopy of Surfaces and Interfaces

The effect of concentration on the *Surface-Enhanced Raman Scattering* of *p*-Aminothiophenol

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The organic compound *p*-aminothiophenol (*p*ATP, HS-Ph-NH_2) has become very popular because it is often used for checking the enhancement capability of each new SERS substrate due to its very intense SERS spectra. SERS of pATP on silver electrode is significantly different from its ordinary Raman spectra and it is very dependent on the particular conditions of the SERS experiment. In this work the effect of adsorbate concentration on the potential dependent SERS spectra of *p*ATP recorded on a silver electrode has been studied using $NaClO_4$ as electrolyte. On the other hand, MS-CASPT2 have been performed in order to help the analysis of the experimental results by computing resonance Raman spectra of selected structural models of the metal−adsorbate surface complex.

It is found that the spectra are dependent on adsorbate concentration and dominated by a resonant charge transfer (CT) mechanism, where the charge is always transferred from the adsorbate to the metal. The relative SERS enhancements are due to Franck−Condon factors related to the CT process, and there are not intensified bands through Herzberg−Teller contributions. Furthermore, the Raman signals of the SERS recorded at low concentration arise from at least three different molecular species: (i) *p*ATP bonded to silver electrode through sulfur atom (Ag_n-S^--Ph-NH_2); (ii) *p*ATP bonded to silver electrode through both sulfur and nitrogen atoms (Ag_n-S^--PhNH_2-Ag_m); (iii) The azo derivative p,p′-dimercaptoazobenzene (or its nitrene precursor).

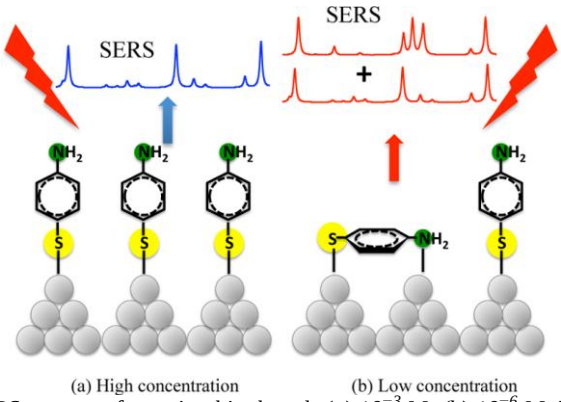

Fig. 1. Potential dependent SERS spectra of p-aminothiophenol: (a) 10^{-3} M; (b) 10^{-6} M, in $NaClO_4$ on silver electrode at excitation wavelength of 785 nm.

Keywords: p-aminothiophenol, SERS, silver electrode, ab initio calculations.

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References

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