

Charge Transfer mechanism in the Surface Enhanced Raman Scattering of 2,2'-bipyridine recorded on a silver electrode

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Nowadays, Surface Enhanced Raman Spectroscopy (SERS) has become a powerful technique to investigate the electronic structure of surface-molecule hybrid systems due to the huge enhancement of the Raman signal. It is established that the origin of this enhancement has two main contributions; the electromagnetic (EM), related to surface plasmons, and the chemical mechanism, due to resonant charge transfer (CT) processes between the adsorbate and the metal. With the aim to investigate the SERS-CT of bipyridine and to identify charge transfer process, the spectra were recorded on silver electrode by using three different wavelengths (473, 532 and 785 nm) in a range from 0.0 up to -1.4 V electrode potential. The electrode potential was modelled in the calculations with atomic silver wires of different size and charge attached to the BPy molecule (Ag_nBPy^q , with $q = 0$ for $n = 2$ and $q = \pm 1$ for $n = 3, 5, 7$) and were computed with Density Functional Theory (DFT). Although BPy shows a trans conformation in solution, a cis conformation was chosen for its chelating properties. The results indicate that the intensification of the $\sim 1550 \text{ cm}^{-1}$ band at negative potentials is due the Franck-Condon factors related to the resonant CT process from the metal to the BPy molecule (Figure 1).

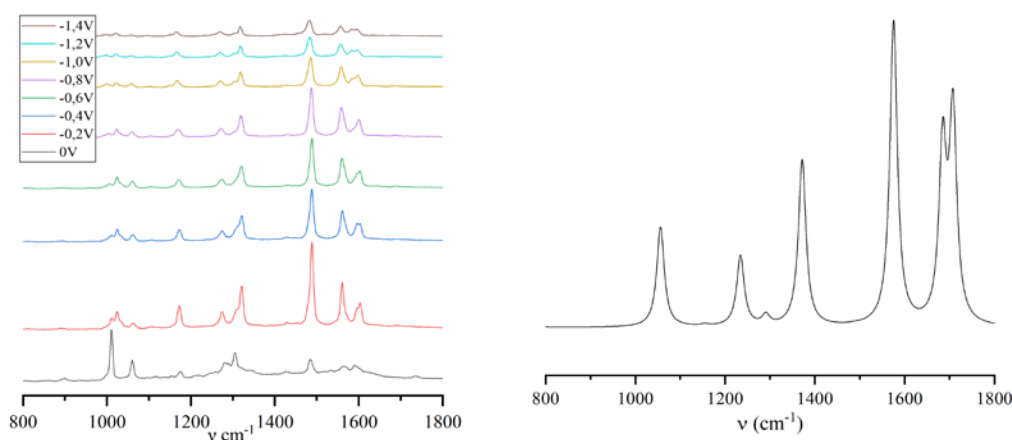


Figure 1: Experimental SERS Spectra of 10^{-3} M aqueous bipyridine solution at 532 nm (left), and calculated $S_0\text{-CT}_0$ resonant Raman spectrum (right).

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