Comparative study of different theoretical approaches for modeling the dependence of the SERS vibrational wavenumbers on the electrode potential

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Keywords: SERS, Raman, vibrational Stark effect, wavenumber shifts, electrode potential.

Surface-enhanced Raman scattering (SERS) is a powerful technique to study the electronic structure of charged metal-molecule interfaces, which are relevant in many fields like electrochemistry, heterogeneous catalysis or molecular electronics. When electrochemical SERS experiments are carried out two main features are observed: a selective enhancement of the intensity of some bands and a shift of the vibrational wavenumbers. Both characteristics are very often dependent on the applied electrode potential. The first of them has been widely discussed and is related to different SERS enhancement mechanisms,[1,2] while the second one reflects changes of the electronic structure of the adsorbate in the ground electronic state. The theoretical modelling of the effect of the electrode potential in electronic structure calculations is a challenge due to the large number of factors to be considered such as the adsorption on a particular site of the metal surface, the way to take into account the role of the electrode potential on the calculations or the electrolyte or solvent effects. In this work we discuss two different approaches to compute the wavenumber dependence of the vibrational modes of pyridine adsorbed on silver at different electrode potentials (Figure 1). On the one hand, the effect of the electrode potential has been modelled by means of simple linear metal-pyridine complexes[3] $[Ag_nPy]^q$ where the metal cluster has variable size (n) and charge (q) what allows for defining the $q_{eff} = q/n$ parameter, which quantifies the mean density of charge of the cluster (Figure 1A). On the other hand, an external electric dipole field has been applied on the $[Ag_2Py]^0$ neutral complex as an alternative model for simulating the effect of the electrode potential (Figure 1B). The calculations were performed using Density Functional Theory (DFT) and several variables have been considered like the level of theory, solvent effects and the size or shape of the metal cluster. A good agreement is achieved for the main A_1 vibrations observed in the SERS experiments of pyridine and the main advantages and drawbacks of each approach are discussed.

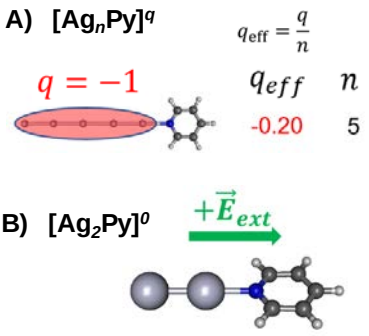

Figure 1. Theoretical approaches to simulate the effect of the electrode potential in the vibrational wavenumbers: A) Charged metal clusters and B) External electric fields.

References:

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