O9 Frequency shift on the potential-dependent surface-enhanced Raman scattering of pyridine: simplified models for metal and solvent effects

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The electronic structure of adsorbates is altered when it interacts with a surface, modifying the properties of both entities and giving rise to interesting phenomena related to heterogeneous catalysis or molecular electronics. If such surface is a metallic substrate, the electrode potential can be used to tune this interaction. Potential-dependent Surface-Enhanced Raman Scattering (SERS) is a particularly useful technique to study the induced effects on the molecule when the metal-adsorbate surface complex is formed, as the observed frequency shifts of the vibrational modes can provide information about it. However, from the computational point of view, these systems are difficult to model, because the macroscopic metal cannot be modelled easily using quantum mechanics. As an approach, we propose a simple model using silver atomic wires with different size and charge bonded to the molecule (Ag_nPy^q, n = 2,3,5,7 and q = 0 and ±1 for n even and odd, respectively) which has been developed by the group and provides a good description of the effect of the electrode potential on the chemical enhancement mechanism of SERS.[1-3] Electronic calculations were performed using Density Functional Theory (DFT). In order to study the frequency shifts, solvent effects have been taken into account by using the Polarizable Continuum Model (PCM). We have used three different functionals (B3LYP, PW91 and M06HF) and two basis sets (LANL2DZ for
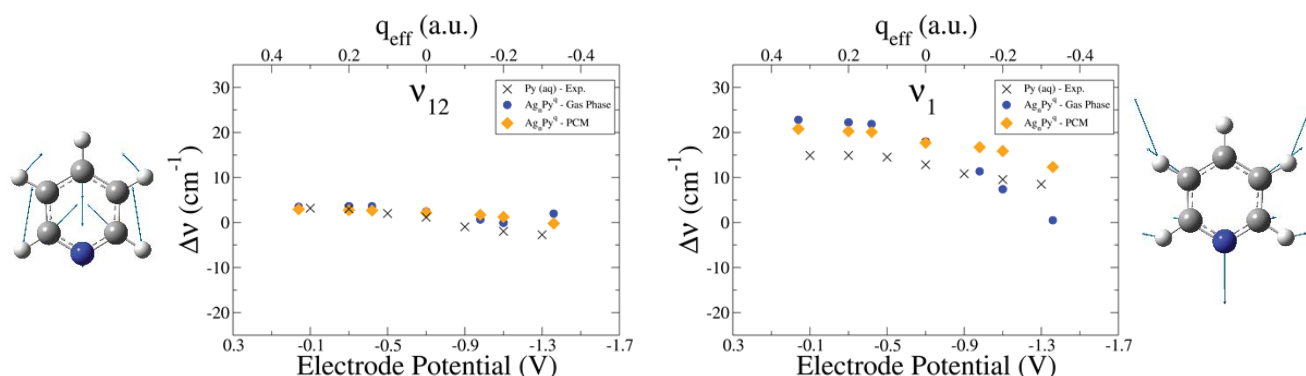

Figure 1. Frequency shifts comparison between experimental (black x) SERS of aqueous pyridine solution and calculated Ag_nPy^q in gas phase (blue circles) and in solution (orange diamonds) for trigonal deformation (v_{12}) and the breathing (v_1) vibrational modes.

all atoms and LANL2DZ for Ag and 6-31G(d) for C,N,H) and, in all cases, a good agreement is achieved in terms of amplitude and trend of the frequency shift for most of the vibrational modes, especially when solvent interactions are included (Figure 1). The method was extended to other metals and solvents giving results in agreement with the available experimental data.

References

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