

Selection rules of surface-enhanced Raman scattering: the role of the out-of-plane vibrations

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The origin of the selective enhancement of a band in surface-enhanced Raman scattering (SERS) is a controversial question since the discovery of the phenomenon.¹ The electromagnetic/plasmonic (SERS-PL) and the chemical (usually involving resonant photoinduced metal-adsorbate (M-A) charge transfer processes (SERS-CT: $M-A+h\nu \rightarrow M^+-A^-$)) mechanisms are recognized as the two main contributions to the enhancement of a particular band in a SERS record. The key problem is to know which mechanism dominates the spectrum and to apply the corresponding selection rules. Many spectra have been analyzed according to the so-called "SERS propensity rules"² of the PL mechanism: only normal modes vibrating perpendicular to the surface should be observed. In this way, it would be possible to get information about the perpendicular/parallel orientation of the adsorbate on the nanoparticle if in-plane/out-of-plane vibrations of planar aromatic molecules show relative enhancement.

The SERS of pyridazine (Pdz) on a silver electrode (Figure 1) is a very special case where the relative intensities are tuned by the electrode potential. Three different types of spectra are recorded showing no selective intensification (0 V) or in-plane (-0.5 V) and out-of-plane (-0.75 V) enhancements. The relative activity of both in-plane (8a and 19b modes) and out-of-plane (16b mode) vibrations can be explained under the same resonant SERS-CT chemical mechanism due to Franck-Condon factors related to differences between the equilibrium geometries (A_1 vibrations, $\Delta Q \neq 0$) and gradients (B_1 vibrations, $\Delta v \neq 0$ and $\Delta Q \neq 0$), respectively, of the potential energy surfaces of the involved ground and photoinduced CT electronic states. Therefore, it is not necessary to resort to any change in the orientation of the adsorbate, which is the standard explanation based on the propensity rules of the SERS-PL mechanism. This conclusion is supported on the basis of electronic structure calculations of the properties of Ag_2 -Pdz clusters in the ground ($S_0; A_1$) and excited states with CT characteristics ($CT_0; A_2$ and $CT_1; B_1$).³ As a conclusion, Pdz (A) is very similar to the corresponding radical anion Pdz^- (A^-) in the respective M^+-A^- ;CT states.

This methodology is able to explain the differences found between the results obtained for related molecular systems⁴ and to extract a very detailed information on the subtle electronic structure of molecules bonded to charged metallic surfaces/nanostructures, which controls fundamental processes in electrochemistry, heterogeneous adsorption, catalysis or molecular electronics.

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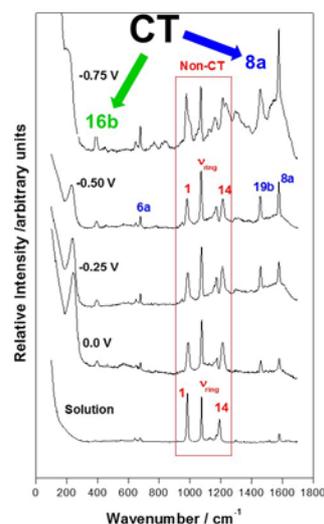


Figure 1. Aqueous solution Raman and SERS spectra of pyridazine on silver surface at different electrode potentials (514.5 nm excitation).