How the Electrode Potential Controls the Selection Rules

of the Charge Transfer Mechanism of SERS

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SERS-CT spectra have been calculated according with the independent mode displaced harmonic oscillator (IMDHO) method,^{1,2} where it is assumed that the excited-state displacements with respect to the ground state geometry are proportional to the gradient of the excited state potential energy surface. To be specific, it is assumed that the intensity of a Raman band in preresonance conditions is proportional to the dimensionaless shift parameter of Manneback³ [Eq. (1)] and this shift parameter is calculated within the harmonic approximation¹ [Eq. (2)].

$$I_i \propto \gamma_i \omega_i^2 \tag{2}$$

$$\gamma_i = B_i^2 \tag{3}$$

where B_i is the adimensional shift parameter given by [Eq.(3)]

$$B_{i} = \frac{1}{\sqrt{2}} \left(\frac{c}{4\pi^{2}h} \right)^{1/2} \frac{1}{c^{2}} \nu^{-3/2} f \cdot \mathbf{M}^{-1/2} \mathbf{L}_{i}$$
(4)

f is the gradient vector of the excited state evaluated at the Franck-Condon geometry, M is the diagonal matrix of atomic masses and L_i is the eigenvector of the Hessian matrix associated with the *i*-normal mode.

1. F. Zerbetto and M. Z. Zgierski, J. Chem. Phys. 1994, 101, 1842.

2. F. Avila, J. Soto, J. F. Arenas, J. A. Rodríguez, D. Peláez and J. C. Otero, *J. Phys. Chem. C*, 2009, **113**, 105.

3. C. Manneback, *Physica*, 1951, **17**, 1001.



Fig S1 Botton: Calculated SERS-CT spectra of a) silver pyridine $[Ag_n-A=Py]^q$ (left) and b) silver pyrazine $[Ag_n-A=Pz]^q$ (right) complexes in preresonance with their respective S_0 -CT₁ transitions. Top: Calculated SERS-CT spectra for the S_0 -D₁ "transition" between the isolated neutral Py and Pz (S₀) and their respective radical anions in the D₁ state. The bands are positioned at the M06-HF/LanL2DZ unscaled frequencies.



Fig S2 Botton: Calculated SERS-CT spectra of a) silver pyridine $[Ag_n-A=Py]^q$ (left) and b) silver pyrazine $[Ag_n-A=Pz]^q$ (right) complexes in preresonance with their respective S_0 -CT₀' transitions. Top: Calculated SERS-CT spectra for the S_0 -D₀ "transition" between the isolated neutral Py and Pz (S₀) and their respective radical anions (D₀). The bands are positioned at the M06-HF/LanL2DZ unscaled frequencies.



Fig S3 Botton: Calculated SERS-CT spectra of a) silver pyridine $[Ag_n-A=Py]^q$ (left) and b) silver pyrazine $[Ag_n-A=Pz]^q$ (right) complexes in preresonance with their respective S_0 -CT₁' transitions. Top: Calculated SERS-CT spectra for the S_0 -D₁ "transition" between the isolated neutral Py and Pz (S₀) and their respective radical anions (D₁). The bands are positioned at the M06-HF/LanL2DZ unscaled frequencies.