

## EFFECT OF THE ELECTRODE POTENTIAL ON SURFACE-ENHANCED RAMAN INTENSITIES OF 2-METHYLPYRAZINE


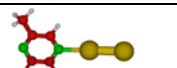

I. López-Tocón, S. Centeno, J. Román-Pérez and J.C. Otero.

*Department of Physical Chemistry, Faculty of Science, University of Málaga, Andalucía Tech E-29071 Málaga, Spain.*

The effect of the electrode potential on Surface Enhanced Raman Scattering (SERS) intensities of 2-methylpyrazine (2MP) recorded under resonant charge transfer (CT) conditions is analyzed by using a simple theoretical model [1] in which the macroscopic surface charge in the metal is modeled by several metallic clusters with different number of silver atoms ( $n$ ) and charges ( $q$ ),  $[\text{Ag}_n]^q$ . Two and three linear silver atoms with zero and positive and negative charges, respectively, bounded to the 2MP through the nitrogen atom, have been taking into account.

In this way, a new microscopic parameter called the effective atomic surface charge ( $q_{\text{eff}}$ ) is introduced being defined as the ratio between the charge and the number of silver atoms ( $q_{\text{eff}}=q/n$ ). This parameter is directly related to the macroscopic charge excess in the electrochemical experiences. The selected charge excess range ( $q_{\text{eff}} = \pm 0.33$ ) covers the usual experimental potential electrode range of 0-1.5 V [2]. Due to the non equivalent aromatic nitrogen atoms in 2MP, two different complexes have been considered,  $[\text{Ag}_n\text{-N1}]^q$  and  $[\text{Ag}_n\text{-N4}]^q$ . Time-dependent density functional theory (TDDFT) with the M06HF/LanL2DZ level of calculation has been used in order to identify the CT states of the  $[\text{Ag}_n\text{-2MP}]^q$  systems. After that, the SERS-CT spectra of these superficial complexes have been calculated by the independent mode displaced harmonic oscillator (IMDHO) method.

Table 1: Theoretical results for the  $[\text{Ag}_n\text{-N4}]^q$  complex

$q_{\text{eff}}$	Model $[\text{Ag}_n\text{-N4}]^q$	DFT Calculations (M06HF/LanL2DZ)				Experimental		
		CT <sub>0</sub> /eV Energy	$\Delta q$	Intensity		Potential Electrode	Intensity	
				8a	8b		8a	8b
-0.33		1.142	0.84	100	26	-0.75V	100	31
0.00		2.933	0.69	100	49	-0.50V	100	51
+0.33		5.324	0.51	100	12	-0.25V	100	20

The theoretical results (Table 1) reproduce satisfactorily the main experimental behavior, that is, the strong enhancement of the totally symmetric 8a ring-stretching mode, being the most enhanced band at any electrode potential. On the contrary, the weaker band corresponding to the other ring-stretching 8b mode reaches the maximum intensity at -0.50V and decreases at more negative or positive potentials.

*Keywords: SERS spectroscopy; 2-Methylpyrazine; Charge transfer mechanism.*

### References

- [1] F. Avila, D.J. Fernández, J.F. Arenas, J.C. Otero, J. Soto, Chem. Commun. 47 (2011) 4210.  
 [2] J.Román-Pérez, C. Ruano, S.P. Centeno, I. López-Tocón, J.F. Arenas, J. Soto, J.C. Otero, J. Phys. Chem. C 118 (2014) 2718.