

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


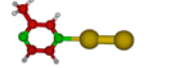
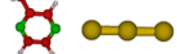
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The effect of the electrode potential on Surface Enhanced Raman Scattering (SERS) intensities of 2-methylpyrazine (2MP) recorded under resonant charge transfer (CT) conditions is analyzed by using a simple theoretical model [1] in which the macroscopic 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_{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_{eff}	Model	DFT Calculations (M06HF/LanL2DZ)				Experimental		
		CT ₀ /eV Energy	Δq	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.