

Electrochemical SERS spectra of isonicotinic acid analyzed under a photoinduced charge-transfer mechanism.

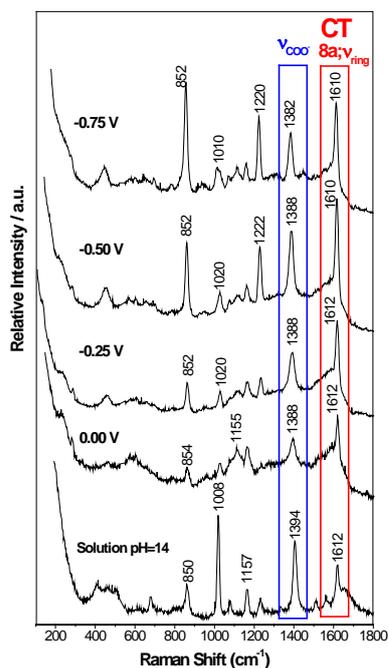
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Isonicotinic (IN) acid is one of the three monocarboxylic derivatives of pyridine in which the acid group is located in para-position of the heterocyclic ring. It is a weak acid ($pK_2=4.86$) and therefore, it is not completely ionized in neutral aqueous solutions, being the zwitterion and the anion the majority chemical species at neutral pH. In acidic solutions ($pK_1=1.84$) the pyridinic nitrogen atom can be protonated yielding a third chemical species with positive charge [1].

In addition, IN acid shows two functional centres that can interact with the silver metallic surface such as the carboxylate group and the aromatic nitrogen atom. Therefore, the analysis of the SERS spectra of IN has been focused on identifying the chemical species adsorbed on the silver surface and its centre of interaction by considering the participation of a photoinduced charge-transfer (CT) mechanism in each particular SERS record as we have previously detected in the SERS of pyridine derivatives [2].

SERS spectra of the IN acid (5×10^{-3} M) have been recorded on silver at electrode potentials ranging from 0.00 up to -1.00 V and at different pH by using 0.1 M Na_2SO_4 aqueous solution as electrolyte. The figure shows the SERS recorded at basic pH. The experimental set up is described elsewhere and the excitation line of 514.5 nm wavelength was used. [2]. The detection of the presence of CT processes, which are similar to resonance Raman, requires to carry out quantum mechanical calculations [2].



A simple Ag_2 -IN model for the surface complex involving two silver atoms with the IN linked through two possible groups to the metal, $\text{Ag}_2\text{-N(IN)}$ and $\text{Ag}_2\text{-O}_2(\text{IN})$, has been taken into account.

Time-dependent density functional theory (TDDFT) has been employed in order to identify the CT states of the studied $[\text{Ag}_2\text{-IN}]$ systems at the M06HF/LanL2DZ level of calculation. After that, the intensities of the theoretical SERS-CT spectra have been calculated by independent mode displaced harmonic oscillator (IMDHO) method.

The results yield that the isonicotinate ion adsorbs on silver at any pH with an almost perpendicular orientation with respect to the metallic surface, given that the carboxylate band is observed in all SERS spectra and only bands assigned to totally symmetric modes are enhanced. The vibrational frequency does not shift in the whole electrode potential range and therefore, a reorientation of the isonicotinate with the electrode potential is discarded.

The calculated SERS-CT spectra predict the enhancement of the 8a:ring stretching band recorded at 1600 cm^{-1} in agreement with the experimental results what demonstrates once again the participation of resonant CT processes in SERS of pyridine derivatives.

Acknowledgements

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References

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