

Diabatic Approach for SERS: From Quantum Dynamics to Spectra

Francisco García-González,^{*a} Daniel Aranda,^a Francisco Ávila,^a J. C. Otero,^a Fabrizio Santoro^b

a) Facultad de Ciencias, Departamento de Química Física, Universidad de Málaga, Blvr. Louis Pasteur, 31, 29010, Málaga, Spain.

b) Istituto di Chimica dei Composti Organo Metallici, Consiglio Nazionale delle Ricerche, Via G. Moruzzi 1, I-56124, Pisa, Italy.

*fgarciag@uma.es

SERS (Surface-Enhanced Raman Spectroscopy) has established itself as an important characterization technique, owing to both its characteristically high intensities and the large amount of information it is capable of yielding;¹ however, this high sensibility also implies intrinsic complexity when it comes to extracting valuable information from the spectra. Electrochemical SERS (EC-SERS), in which the substrate is a nanostructured electrode for which the electrode potential (V_{el}) can be tuned, poses further challenge given the sensibility of SERS spectra of certain molecules to V_{el} . This is the case for Pyridine, the most emblematic SERS molecule, for which the interaction between Charge-Transfer (CT) states and Plasmons has been proven to play a crucial. In this work, we have performed full diabaticizations for systems consisting of Pyridine attached to different silver clusters, giving the possibility to readily define CT states, whose energy is tunable by an applied external field E , a microscopic analogous to V_{el} . Nuclear wavepacket propagations on the coupled potential energy surfaces including both local excitations of the metal and CT states were performed to retrieve Resonance Raman spectra. Our results show that the population transfer from bright metal states to CT states plays a most pivotal role when it comes to the shape and absolute intensities of EC-SERS spectra of Pyridine.²

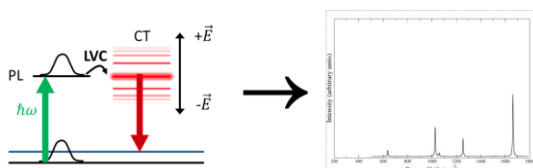


Figure 1. Scheme for a diabatic SERS mechanism.

References

1. Langer, J. et al., *ACS Nano*, 2019, **14**, 28.
2. Morton, S. M.; Silverstein, D. W.; Jensen, L., *Chem. Rev.*, 2011, **111**, 3962.