

Charge-Transfer Surface Enhanced Resonance Raman: Effective Factor in Understanding the Selection-rules

Sahar Ashtari-Jafari ^a and Zahra Jamshidi ^{a,b*}

^a Chemistry & Chemical Engineering Research Center of Iran (CCERCI), Pajohesh Blvd, 17th Km of Tehran-Karaj Highway, P. O. Box 1496813151 Tehran, Iran.

^b Chemistry Department, Sharif University of Technology, Tehran 11155-9516, Iran.
njamshidi@sharif.edu, na.jamshidi@gmail.com

Surface-enhanced resonance Raman (SERS) is a powerful technique for ultrasensitive analysis and single-molecule detection. Since the discovery of SERS, elucidating the origin and selection rules of peak enhancements are the challenging and controversial process.¹ Different experimental and theoretical groups have tried to propose the unified model for variation of signal based on the two main mechanisms, electromagnetic (EM) and charge-transfer (CT) chemical.² The charge-transfer mechanism is associated with the resonance of the incident light with the CT states and plays a crucial role on the relative intensity and pattern of spectra. In our previous work,³⁻⁵ the validity of time-dependent excited-state gradient approximation⁶ to calculate the SERS-CT spectra of pyridine that adsorbed on the metal clusters has been demonstrated (in comparison to the experiment), and the controlling effects of ground-state and excited-state on the pattern of spectra has been justified. As the SERS intensity depends on the factors that modify the Raman tensors of different modes and the local fields polarization at the molecules, herein, we try to investigate the effect of adsorption site, molecular symmetry and orientation, and also the direction and amount of finite field on the pattern of SERS-CT spectra. We try to extend such an interpretation as a promising investigation that satisfactorily explain the experiment and propose the selection-rules for SERS-CT.

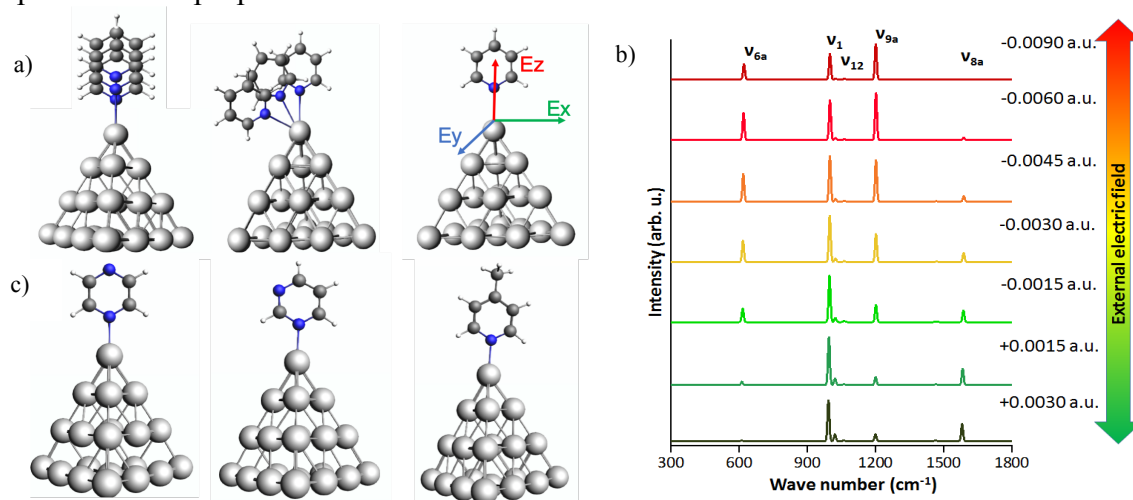


Figure 1: a) Changing the orientation of molecule and direction of applied field for Pyridine–Ag₂₀, b) SERS-CT spectra under the effect of external electric fields, c) benzenlike molecules with different symmetry adsorbed on Ag₂₀.

References

1. M. Moskovits, *Phys. Chem. Chem. Phys.* **15** (2013), 5301.
2. J. R. Lombardi and R. L. Birke, *Acc. Chem. Res.* **42** (2009), 734.
3. M. Mohammadpour and Z. Jamshidi, *J. Chem. Phys.* **144** (2016), 194302.
4. M. Mohammadpour, M. H. Khodabandeh, L. Visscher and Z. Jamshidi, *Phys. Chem. Chem. Phys.* **19** (2017), 7833.
5. M. Mohammadpour and Z. Jamshidi, *J. Phys. Chem. C*, **121** (2017), 2858.
6. T. Petrenko and F. Neese, *J. Chem. Phys.* **137** (2012), 234107.