

SURFACE-ENHANCED HYPER RAMAN AND SURFACE-ENHANCED RESONANCE HYPER RAMAN SCATTERING FROM MOLECULES ADSORBED ON SILVER SOL AND SILVER SOL-IMMOBILIZED-ON-SMOOTH-ELECTRODES AT DIFFERENT POTENTIALS

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Keywords: *hyper Raman scattering, surface enhancement, resonance enhancement.*

Abstract: We report on the surface-enhanced hyper Raman (SEHR) and surface-enhanced resonance hyper Raman (SERHR) spectroscopic study of molecules adsorbed on Ag sol and Ag-nanoparticles-immobilized-on-smooth-electrode substrates, respectively. Molecules with and without an inversion centre in their free state, and with and without an electronic transition in resonance with the doubled-frequency of excitation wavelength were studied. For the purpose of comparison, we also carried out surface-enhanced Raman (SERS) and surface-enhanced resonance Raman (SERRS) spectroscopic study on the same molecules. For certain free molecules (not in the adsorbed state) with and without an inversion centre, we calculated the total as well as partial (directional) normal Raman and hyper Raman intensities using *ab initio*/DFT method, with the aim to evaluate the orientation of adsorbed molecules on substrate surface.

Since the observation of surface enhancement in hyper Raman scattering (SEHRS) in 80s of the last century [1-3], several groups, including ours, reported the SEHRS study of molecules adsorbed on different active substrates, including the randomly roughened electrode surfaces, the aggregated noble metal colloids, and the metal-nanoparticles-immobilized-on-smooth-electrodes, to improve the efficiency of SEHRS and to explore its application in chemical, biological and materials sciences [4-8]. After comparing the SEHRS efficiencies from the randomly roughened electrode and the aggregated metal colloids for different types of molecules [8a,b,c], we lately focused our attention on the study of SEHRS and SERHRS on molecules adsorbed on metal nanoparticles-immobilized-on-smooth-electrodes (NOSE) for its better stability and reproducibility in our SERS and SEHRS studies [8d,e].

We have chosen two groups of molecules in our SEHRS study. The first group of molecules include small heterocyclic rings with and without an inversion centre, such as pyridine vs. pyrazine, 4-phenyl-pyridine vs. 4,4'-bipyridyl, 1,2-bis(4-pyridyl)ethylene vs. 1,2-bis(4-pyridyl)acetylene vs. 1,2-bis(4-pyridyl)ethane, and other linear and branched bis-pyridyls linked with different spacers. These molecules do not possess electronic transitions in resonance with the doubled-frequency of the excitation used in hyper Raman excitation. The other group of molecules include linear and/or nonlinear optical dyes such as rhodamine-6G, crystal violet, basic fuchsin, metalloporphyrins, metallopolypyridyl complexes, as well as a series of two-photon octapolar dyes.

Figure-1 displays a set of typical SERS and SEHRS spectra observed from an octapolar two-photon dye T72 adsorbed on Ag sol. T72 has a large two-photon absorbance in near-UV and blue wavelengths. As expected, its SERS and SEHRS spectra contain both common and unique features. For example, bands at 1625, 1588, 1554 and 1176 cm^{-1} show comparable relative intensities in both SERS and SEHRS spectra. On the other hand, bands at 1550 and 653 cm^{-1} only showed up in SERS spectrum and bands at 1499 and 681 cm^{-1} are pronounced only in SEHRS spectrum. A careful study of the Raman excitation profile of this molecule reveals an interesting constructive interference effect between its $\pi-\pi^*$ and charge-transfer electronic transitions.

We will also show our systematic SEHRS and SERS studies of above mentioned molecules on NOSE substrate in this report, together with calculations of normal Raman and hyper Raman intensities using a method incorporated in *ab initio*/DFT package.

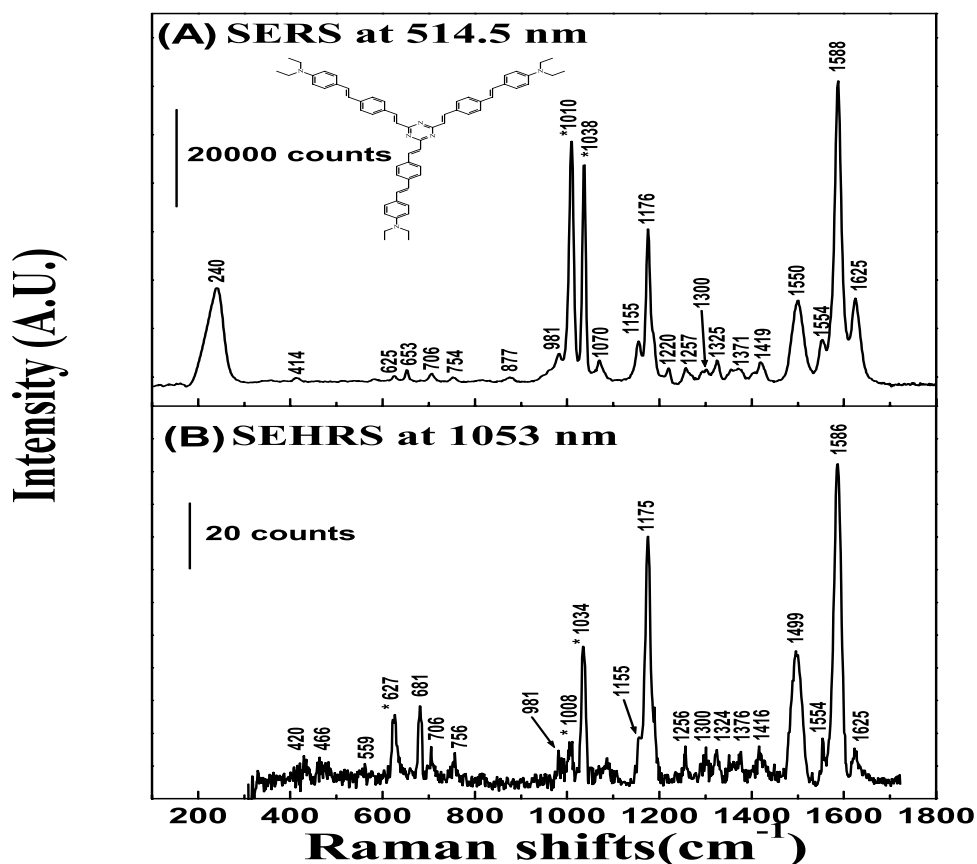


Fig. 1. (A) Observed SERS spectrum of T72 adsorbed on silver sol with excitation at 514.5 nm; (B) Observed SEHRS spectrum of T72 adsorbed on Ag sol with excitation at 1053 nm using pyridine as the carrying solvent for the sample; the insert shows the structure of T72 molecule.

Acknowledgements:

We acknowledge the financial support of this project from the Research Grants Council (RGC) of Hong Kong and HKUST.

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