

## THEORETICAL STUDY ON SURFACE-ENHANCED RAMAN SPECTRA OF WATER ADSORBED ON NOBLE METAL CATHODES OF NANOSTRUCTURES

DE-YIN WU<sup>a</sup>, RAN PANG<sup>b</sup>, ZHONG-QUN TIAN, *College of Chemistry and Chemical Engineering, Xiamen University, Xiamen, China.*

The observed surface-enhanced Raman scattering (SERS) spectra of water adsorbed on metal film electrodes of silver, gold, and platinum nanoparticles were used to infer interfacial water structures. The basis is the change of the electrochemical vibrational Stark tuning rates and the relative Raman intensity of the stretching and bending modes. How it is not completely understood the reason why the relative Raman intensity ratio of the bending and stretching vibrations of interfacial water increases at the very negative potential region. Density functional theory calculations provide the conceptual model. The specific enhancement effect for the bending mode was closely associated with the water adsorption structure in a hydrogen bonded configuration through its H-end binding to surface sites with large polarizability due to strong cathodic polarization. The present theoretical results allow us to propose that interfacial water molecules exist on these metal cathodes with different hydrogen bonding interactions, the HO-H...Ag(Au) for silver and gold. In acidic solution, a surface electron-hydronium ion-pair was proposed as an adsorption configuration of interfacial water structures on silver and gold cathodes based on density functional theory (DFT) calculations. The EHIP is in the configuration of  $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n\text{e}^-$ , where the hydronium  $\text{H}_3\text{O}^+$  and the surface electron is separated by water layers. The electron bound in the EHIP can first be excited under light irradiation, subsequently inducing a structural relaxation into a hydrated hydrogen atom. Thus, Raman intensities of the interfacial water in the EHIP species are significantly enhanced due to the cathodic polarization on silver and gold electrodes.

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<sup>a</sup>State Key Laboratory of Physical Chemistry of Solid Surfaces and Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen, 361005, China

<sup>b</sup>State Key Laboratory of Physical Chemistry of Solid Surfaces and Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen, 361005, China