

THEORETICAL STUDY OF SURFACE-ENHANCED RAMAN SPECTRA OF WATER AND IONIC COMPLEXES IN ELECTROCHEMICAL INTERFACES

RAN PANG, DE-YIN WU^a, ZHONG-QUN TIAN, *College of Chemistry and Chemical Engineering, Xiamen University, Xiamen, China.*

Water plays a very important role in surface science of electrochemical interfaces, closely associated with energy source, environment, our living, and life processes. However, it is very difficult to be observed from normal Raman spectra of water in electrochemical interfaces. Although the surface-enhanced Raman scattering effect can have million-fold Raman signal enhancement for molecules on adsorbed silver and gold electrodes of nanostructures, the surface-enhanced Raman spectrum of water is hard to be measured due to its very small Raman scattering cross section, weak adsorption ability, and very few surface molecular number relative to the bulk. Thus only electrochemical SERS spectra of water have been observed in electrode/electrolyte interfaces so far. Our present work focuses on the chemical enhancement from hydrogen bonding interaction, surface adsorption, halide ions, interfacial electric field effects on SERS signals of water adsorbed on silver electrodes, by combining the metallic cluster model and hybrid density functional theory (DFT-B3LYP) methods. The interfacial structures, binding interactions and the anion effect from different halides including chloride, bromide, and iodide ions have been analyzed and compared with experimental measurements in literatures. Then the excited states of halide ions modified active sites on roughened silver electrode have been discussed. Especially, our time-dependent DFT (TD-DFT) calculations predicted that halide ions can form low-lying excited states of surface complexes, like the photon-induced electron transfer states, and finally contribute to the chemical enhancement of SERS signals of water. Furthermore, we proposed that the halide effect on the relative SERS intensities of water is a good example for understanding the chemical enhancement of SERS active sites modified by halide ions in electrochemical systems.

^a*Email: dywu@xmu.edu.cn