

Observation of Water/Deuterium Molecules on Hydrogen Evolution Process via Surface Enhanced Raman Scattering Measurements

Hiro Minamimoto, Kei Murakoshi

Department of Chemistry, Faculty of Science, Hokkaido University,
Sapporo, Hokkaido 060-0810, Japan

E-mail: minamimoto@sci.hokudai.ac.jp

The strong optical field generated by the excitation of the localized surface plasmon resonance (LSPR) under the light illumination leads several interesting phenomena such as chemical reactions, or surface-enhanced Raman Scattering (SERS).^[1] SERS is a very promising tool for observing a small number of molecules on the progress of the electrochemical reactions due to its high sensitivity. Especially for water molecules which are Raman in-active molecules, it has been reported that SERS of water can be obtained only on the progress of the electrochemical hydrogen evolution reaction (HER). Usually, SERS intensity of water depends on the metal species, electrode potentials, and the supporting electrolyte species. In terms of the isotope effect for HER process, there is a still room for the discussion about the factor for the control of the reaction ratio of H₂ and D₂. In this study, we have investigated the isotopic effect for HER process via *in-situ* electrochemical SERS measurements.

Electrochemical SERS spectra from the mixed solutions of H₂O and D₂O at the Ag electrode surface were shown in the Figure. The electrode potential was scanned from -2.0 to -1.0 V. As can be seen in the figure, the sharp band for OH (OD) bending mode at 1600 (1400) cm⁻¹ which is the representative Raman band for SERS of water can be observed only in HER potential region. The origin for this can be thought as the charge transfer effect to induce effective resonance of the scattering. The broad bands at around 500 and 3400 (2400) cm⁻¹ are corresponding to the libration and OH (OD) stretching mode (σ (OH)). Generally, the scattering intensity of each Raman band depends on the mixed ratio of the bulk solutions. However, in the present result, the scattering intensity for σ (OH) is not agreement with the mixed ratio of the bulk solution. From this, it can be expected that the composition of the interfacial water structure is quite different from that of the bulk solution. Through the use of various mixed ratio and electrode potential, we have confirmed that the very unique behavior of the deuterium oxide at the strong optical field during HER process. The present results would indicate that the strong optical field could be key for the control of the isotopic effect for HER process.

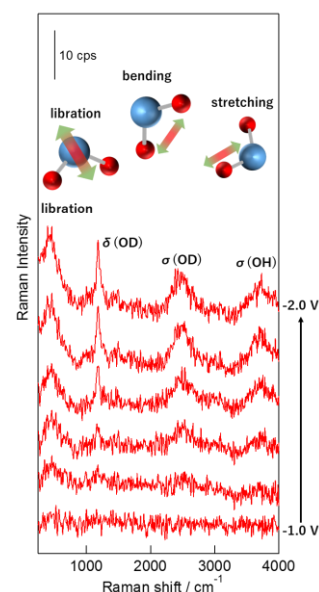


Figure. *In-situ* electrochemical SERS spectra obtained from mixed solution. The ratio of H₂O and D₂O was 1 to 10. The electrode and the excitation wavelength were Ag and $\lambda_{\text{ex}} = 514$ nm, respectively.

References:

- [1] H. Minamimoto, K. Murakoshi *et al.*, *J. Phys. Chem. C*, **2016**, 120(29), 16051, and *J. Electroanal. Chem.* in revision.