Probing Interfacial Electronic and Molecular Structures of CO Absorbed on Pt Surface in Electrochemical Environment by Double-resonant Sum Frequency Generation Spectroscopy

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The adsorption and oxidation of CO on Pt electrode have been intensively studied as an important model system of fuel cell catalysis. Information of molecular and electronic structures of CO/Pt interface is essential to understand the role of adsorbed CO in catalytic reactions to improve the efficiency. Although structural information of CO/Pt interface under ultrahigh vacuum (UHV) condition is well established by previous studies, electronic structure of CO/Pt in electrochemical environment is not well understood because of the lack of techniques for determining it in solution. Double-resonant sum frequency generation (DR-SFG) spectroscopy, which utilizes resonant enhancement of SFG intensity with two incident fundamental lights, i.e., visible and IR, and has been utilized to detect the electronic structure at CO/Pt interface in UHV, can be used in elucidating both molecular and electronic structures at electrochemical interface.

In the present work, potential-dependent molecular and electronic structures of CO-Pt electrode/electrolyte interface is investigated by DR-SFG spectroscopy. A vibrational band due to C-O stretching on Pt atop site dominates the SFG spectra and shows a Stark shift of 30 cm⁻¹/V, which is in good agreement with previous reports. An enhancement of the SFG signal of CO is also observed at certain input visible energy. This enhancement is considered to be due to the resonance of visible energy with that of an electronic state of absorbed CO, i.e., double resonance effect. Resonant visible energy is found to linearly depend on electrode potential, indicating the electronic resonance is caused by the transition from the Fermi energy of Pt to the unoccupied 5σₐ anti-bonding state of adsorbed CO.

References