

Structure of Water Molecules on a Pt Electrode Surface Studied by Surface-Enhanced Infrared Spectroscopy

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Introduction

The structure and orientation of water molecules at the electrochemical interface has attracted much interest. It has been investigated using both theoretical and experimental approaches. In the present study, we used surface-enhanced IR absorption spectroscopy (SEIRAS) in the Kretschmann ATR mode to investigate the interfacial water molecule on a Pt electrode.

The ATR-SEIRAS is more convenient for this purpose than IR reflection-absorption spectroscopy (IRAS), commonly used in electrochemistry, due to the higher sensitivity and surface-selectivity than the latter. Even though, a potential difference tactic has been required to subtract the background absorption by bulk water,^{1,2} which have prevented the measurement of “absolute” spectrum of interfacial water. We solved this problem in this study by replacing interfacial water with CO in acquiring the reference spectrum. The results are compared with earlier IRAS studies on Pt and SEIRAS studies on Au,^{1,2} and the potential-dependence of the interfacial structure is discussed.

Experiment

Experimental details was described elsewhere.^{1,2} The Pt thin film (working electrode) was formed on the flat plane of a hemicylindrical Si prism using an electroless deposit method.³ A reversible hydrogen electrode (RHE) and a Pt mesh were used as the reference and the counter electrodes, respectively. The electrolyte was a 0.1M H₂SO₄ or 0.1M HClO₄. Infrared spectra were recorded with a Bio-Rad FTS-575C FT-IR spectrometer.

Results and discussion

CO is known to almost fully cover Pt surface (the coverage estimated from CV was about 0.9) and can be removed easily by oxidation. In addition, Adsorbed CO has no absorption bands in the spectral region of water. Therefore, the CO-covered Pt surface is suitable to be used as the reference. Figure 1 shows a set of SEIRA spectra of the CO-free Pt surface measured at several potentials in 0.1M H₂SO₄ by using the single-beam spectrum of the CO-covered Pt surface measured at each potential. As a result of the experimental procedure, the up-going bands at 2500-3600 and 1606 cm⁻¹ are assigned to $\nu(\text{OH})$ and $\delta(\text{HOH})$ of the interfacial water removed from the surface by the CO adsorption. The up-going bands at 950-1200 cm⁻¹ are of adsorbed (bi)sulfate. On the other hand, the down-going bands around 2000 cm⁻¹ are the $\nu(\text{CO})$ of CO adsorbed at atop and bridge sites. The down-going band at 3670 cm⁻¹ is the $\nu(\text{OH})$ of water molecules embedded in the CO adlayer.³

Figure 2 shows the $\nu(\text{OH})$ region after subtracting the sharp 3670- cm⁻¹ band numerically. Potential difference of the spectra were in good agreement with those measured in CO-free solution (not shown), which insures that the

effect of adsorbed CO on the spectral features are nearly completely removed.

The observed “absolute” spectrum of interfacial water is largely different from that of bulk water which is characterized by a very broad band centered around 3400 cm⁻¹. A single band with a tail in the lower wavenumber region is observed at potentials more negative than 0.1 V. The high wavenumber and narrow feature compared with those of bulk water indicate that water molecules are isolated from the hydrogen-bonded network in the bulk. At more positive potentials where (bi)sulfate is adsorbed (Figure 1), a very broad band centered around 3000 cm⁻¹ appears. This band has been attributed to strongly hydrogen bonded water molecules with a ice-like structure.^{1,2} We will discuss that the observations are consistent with the structural model of the Rh(111) and H₂SO₄ interface proposed by Itaya et al.⁴ to explain the *in situ* STM images they observed.

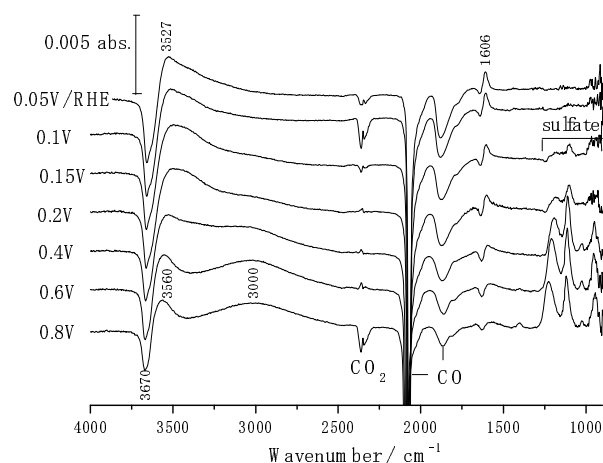


Figure 1. SEIRA spectra on Pt electrode in 0.1M H₂SO₄.

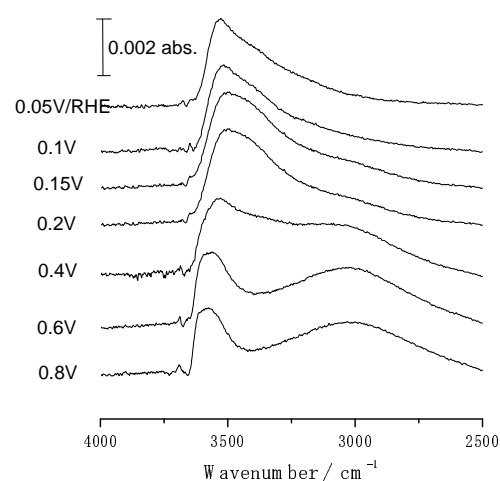


Figure 2. IR spectra of interfacial water obtained by subtracting the sharp 3670-cm⁻¹ band numerically from Figure 1.

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