

Infrared Spectroscopy of Water Adsorbed on M(111) (M = Pt, Pd, Rh, Au, Cu) Electrodes in Sulfuric Acid Solution

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Received: February 19, 2008; Revised Manuscript Received: April 8, 2008

Spectroscopic characterization of adsorbed water has been carried out on (111) surfaces of Pt, Pd, Rh, Au, and Cu in sulfuric acid solution using infrared reflection–absorption spectroscopy (IRAS). The absorption band of the HOH bending mode (δ_{HOH}) is measured below the onset potential of (bi)sulfate adsorption. The band frequency of δ_{HOH} of adsorbed water is lower than that of bulk water. The δ_{HOH} band shifts to higher frequencies with the increase of the positive potentials on Pt, Pd, and Rh, whereas the band intensity is unchanged between the potentials of hydrogen evolution and (bi)sulfate adsorption. This suggests that water is adsorbed through an oxygen lone pair, with its molecular plane slightly tilted from the surface. On Au(111), the δ_{HOH} band intensity decreases with the increase of the electrode potential. This result indicates that the orientation of water depends on the applied potential. No absorption band of water is found on Cu(111), which indicates different behavior of adsorbed water compared with the other metal electrode surfaces.

1. Introduction

It is one of the most important tasks in electrochemistry to elucidate the detailed adsorption structure of water at the solid–liquid interface. Water is the most convenient solvent used in electrochemistry, and furthermore, it plays a role as a reactant and a product in redox reactions. However, there are controversial and complicated issues regarding the structure of adsorbed water on metal electrodes in electrolyte solutions. The lack of effective experimental methods prevents the detailed investigation of adsorbed water on electrode surfaces. For interfacial water, experimental measurements in ultrahigh vacuum (UHV) and a theoretical approach have been developed by many researchers.^{1,2} Calculations based on ab initio method and density functional theory (DFT) have predicted that the nature of adsorbed water depends on the substrate materials and surface structures.^{3,4} Water preferentially binds at the atop sites of metal surfaces through the oxygen lone pair.⁵ On many surfaces, the molecular plane of water monomer is nearly parallel to the surface.⁵ Results obtained from scanning tunneling microscopy (STM) and vibrational spectroscopy in UHV also agree with the theoretical predictions.^{6,7}

During the past two decades, water adsorption on polycrystalline electrode surfaces of Pt and Au has been investigated using various surface-sensitive techniques.^{8–10} Infrared spectroscopic studies have revealed that the band intensity of water changes with electrode potential.⁸ Oxygen-up orientation was reported for adsorbed water on Au film by sum frequency generation (SFG) and surface-enhanced infrared absorption spectroscopy (SEIRAS).^{10,11} These results indicate that the molecular orientation of water is sensitive to the electric field in the electric double layer. Surface X-ray diffraction (SXD) of Ag(111) electrode in NaF solution suggests a change in the orientation of the first-layer water.¹² Iwashita et al. observed the frequency jump of the O–H stretching band on Pt(111) in perchloric acid, which was also assigned to the orientation change.¹³ For a more detailed discussion of adsorbed water, a systematic study is required using well-defined electrode surfaces.

In this study, water adsorbed on (111) surfaces of transition metal electrodes was studied using infrared spectroscopy. We focused on the bending mode of the first-layer water below the potential of (bi)sulfate anion adsorption. Specifically adsorbed anion inhibits water adsorption. Even if the electrolyte containing nonspecifically adsorbed anion is used, OH_{ad} and O_{ad} are adsorbed on Pt above 0.8 V.¹⁴ The coadsorption of anion and oxygen species with water may complicate the interpretation of the experimental results. The band shape of the bending mode is sharper than that of the stretching mode, and the detector has a much better sensitivity in the bending frequency range. The narrow width of the absorption band is convenient for the discrimination of the band frequency. There have been many studies of the OH stretching mode in adsorbed water; however, the OH stretching region includes the information of hydronium cation and hydroxyl species as well as water. The HOH bending band is also sensitive to the adsorption strength, orientation, and structure of water.

2. Experimental Section

Rh(111) and Au(111) single-crystal disks with diameters of 10 mm were purchased from MaTeck (Germany). Pt(111) and Pd(111) were prepared from single-crystal beads with the method of Clavilier et al.¹⁵ Cu(111) single crystal was prepared by the Bridgeman method. The detailed procedures for the preparation of each electrode are given in previous reports.^{16–18} The electrolyte was prepared from suprapure H_2SO_4 (Merck) and ultrapure water (Milli-Q Advantage). The Rh, Pt, Au, and Pd single-crystal electrodes were annealed in a hydrogen–oxygen flame and cooled in a stream of Ar. The Cu single electrode was electropolished in phosphoric acid and then rinsed with Milli-Q water. The reference electrode was Ag/AgCl, but potentials are quoted against the reversible hydrogen electrode (RHE) in this paper. IR spectra were measured using a spectrometer (FT/IR-6100, JASCO) equipped with a liquid nitrogen cooled MCT detector with 4 cm^{-1} resolution. A p-polarized infrared beam incident to the surface was directed through a CaF_2 or BaF_2 window at an angle of 60°. All spectra

TABLE 1: Data Accumulation of SNIFTIR Spectra^a

	Pt(111)	Pd(111)	Rh(111)	Au(111)	Cu(111)
N_c (cycle)	128	10	10	128	20
N_s (scan)	8	100	100	7	50
total (scan)	1024	1000	1000	896	1000

^a N_c , number of potential step cycles; N_s , number of scans in each potential.

were obtained using subtractively normalized interfacial Fourier transform infrared spectroscopy (SNIFTIRS). The procedure for the accumulation of spectra obtained is summarized in Table 1.

3. Results and Discussion

3.1. Cyclic Voltammetry of M(111) (M = Pt, Pd, Rh, Au, and Cu) in Sulfuric Acid Solution. Figure 1 shows the cyclic voltammograms (CVs) of M(111) (M = Pt, Pd, Rh, Au, and Cu) electrodes in sulfuric acid solution. The overall shape of each CV is similar to those reported previously.^{19–23} The CVs show the features of clean and well-defined surfaces. According to STM studies, a $\sqrt{3} \times \sqrt{7}$ structure of adsorbed (bi)sulfate anion is found on M(111) (M = Pt, Pd, Rh, Au, and Cu) electrodes.^{21–25} It is important for the IR experiments to select the appropriate reference potential. In order to observe the first water layer, reference potentials were selected at 0.50 V (Pt), 0.60 V (Pd), 0.65 V (Rh), 1.10 V (Au), and 0 V (Cu). The first layer is covered with (bi)sulfate anion forming the $\sqrt{3} \times \sqrt{7}$ structure at these potentials.^{21–25} The sample spectra were collected at potentials at which no (bi)sulfate anion is adsorbed. Previous IR studies selected the reference potential at the potential of zero charge (pzc).¹¹ If the reorientation and the coverage change of chemisorbed water do not occur between the reference and sample potentials, the absorption bands will be canceled out. Since the vibrational frequency of chemisorbed water differs from that of overlayer water,^{1,2} we select the reference potential at the potential where anion forms the well-known structure rather than the pzc.

The $\sqrt{3} \times \sqrt{7}$ structure of (bi)sulfate includes coadsorbed oxygen species, which is assumed to be either water or hydronium cation.^{21,23,26,27} Although it is difficult to identify these species from the STM image, Kolb et al. suggested that hydronium cation rather than water is incorporated in the $\sqrt{3} \times \sqrt{7}$ layer of (bi)sulfate on Au(111).²⁶ Recently, the coadsorption of hydronium cation and (bi)sulfate was confirmed using tunneling spectroscopy measurements.²⁸ UHV-IRAS study on Pt(111) also supports the incorporation of hydronium cation.²⁷ The OH stretching frequency of the adsorbed hydronium cation is almost the same as that of adsorbed water. On the other hand, the bending frequency of the adsorbed hydronium cation is different from that of adsorbed water. The IR bands due to asymmetric and symmetric bending modes of hydronium cation are observed around 1750 and 1200 cm⁻¹, respectively.²⁹

3.2. Infrared Spectra of Adsorbed Water on M(111) (M = Pt, Pd, Rh, and Au). Figure 2 presents the potential dependence of SNIFTIR spectra on Pt(111), Rh(111), Pd(111), and Au(111) electrodes in 0.5 M H₂SO₄. Positive-going bands arise from the increase of IR-active species at sample potentials. The negative-going band at 1200–1270 cm⁻¹ is assignable to the SO₃ symmetric stretching mode (ν_{SO_3}) of adsorbed (bi)sulfate anion at the reference potential. The band frequencies of (bi)sulfate anion are consistent with those reported previously.^{30–32} The mirror used in the spectrometer is coated with SiO₂; the IR intensity between 1000 and 1200 cm⁻¹ is too weak to detect

the ν_{SO_3} mode of (bi)sulfate anion on Au(111) that gives a band at 1180 cm⁻¹.³³ Therefore, (bi)sulfate adsorption on Au(111) was confirmed by the presence of the ν_{SO} band at 950 cm⁻¹ using a BaF₂ prism.³³

A broad band appeared at 1760 cm⁻¹ on Pt(111), Pd(111), and Au(111), which is assignable to the asymmetric bending mode of hydronium cation. Interestingly, the band intensity on Pd(111) gradually increases in the negative direction. This may be due to the decrease of proton in the double layer caused by hydrogen absorption into the metal bulk. It is well-known that Pd absorbs a large amount of hydrogen at room temperature. The spectral features of δ_{HOH} on Au(111) and Pt(111) are essentially identical to those from previous SEIRAS studies measured by the different reference potentials.^{11,34}

3.2.1. Pt(111), Pd(111), and Rh(111) Surfaces. The band at 1605–1620 cm⁻¹ can be assigned to the HOH bending mode (δ_{HOH}) of adsorbed water on the surfaces. These band frequencies are lower than those in the liquid phase (1645 cm⁻¹) and solid phase (1650 cm⁻¹) and shift with the increase of the electrode potential. IR spectra obtained in UHV have revealed that the δ_{HOH} band shifts to lower frequency by adsorption on metal surface.² The red shift from 1595 cm⁻¹ (isolated monomer) to 1560 cm⁻¹ (adsorbed monomer) has been observed on Ni(111), Rh(111), and Ru(001),^{7,35,36} and can be explained by the charge transfer accompanying the coordination through an oxygen lone pair of water.² DFT calculations have revealed that water monomer is preferentially adsorbed at atop sites on several closed-packed structure surfaces via the oxygen lone pair.⁵ Charge transfer from the oxygen lone pair to the metal causes a small expansion of the HOH angle, which means the decrease of the bending frequency.¹ The higher frequency (1605–1620 cm⁻¹) in solution compared to water monomer in UHV (1560 cm⁻¹) is due to the formation of hydrogen bonds with neighboring water molecules. It is well-known that the formation of hydrogen bonding increases the δ_{HOH} frequency of water.³⁷

The observed δ_{HOH} band has a small absorbance (A) < 0.0004, which is comparable to that of ice-like bilayer in UHV.³⁸ The weak band intensity of δ_{HOH} indicates that the molecular axis of adsorbed water is significantly inclined from the surface normal. The vibrational mode, of which the dynamic dipole moment is parallel to the surface, cannot be observed due to the surface selection rule. Since the binding to the surface through the oxygen lone pair is favorable, the molecular orientation of water is thought to slightly tilt from the surface as shown in Figure 3b. It is known that this nearly flat configuration is the most stable on various metal surfaces.⁵ There have been several arguments regarding water orientation at the solid–liquid interface: whether the OH bond is directed away from the surface (oxygen-down) or downward toward the surface (oxygen-up) as shown in Figure 3a and Figure 3c, respectively. The small band intensity on Pt(111), Rh(111), and Pd(111) in sulfuric acid solution indicates that adsorbed water is slightly tilted in the potential region examined as shown in Figure 3b.

At 0.05 V, the δ_{HOH} frequency of adsorbed water on Pd(111), Rh(111), and Pt(111) is 1617, 1616, and 1620 cm⁻¹, respectively. The frequency order of the bending mode is consistent with that in UHV: 1616 (Pd(111)), 1620 (Rh(111)), and 1630 cm⁻¹ (Pt(111)).^{39–41} The differences in the δ_{HOH} band frequencies may indicate that the adsorption of water on Pd(111) and Rh(111) is stronger than that on Pt(111) at 0.05 V. Stronger adsorption of water means more charge transfer from the oxygen lone pair to the substrate metal. The increase of charge transfer

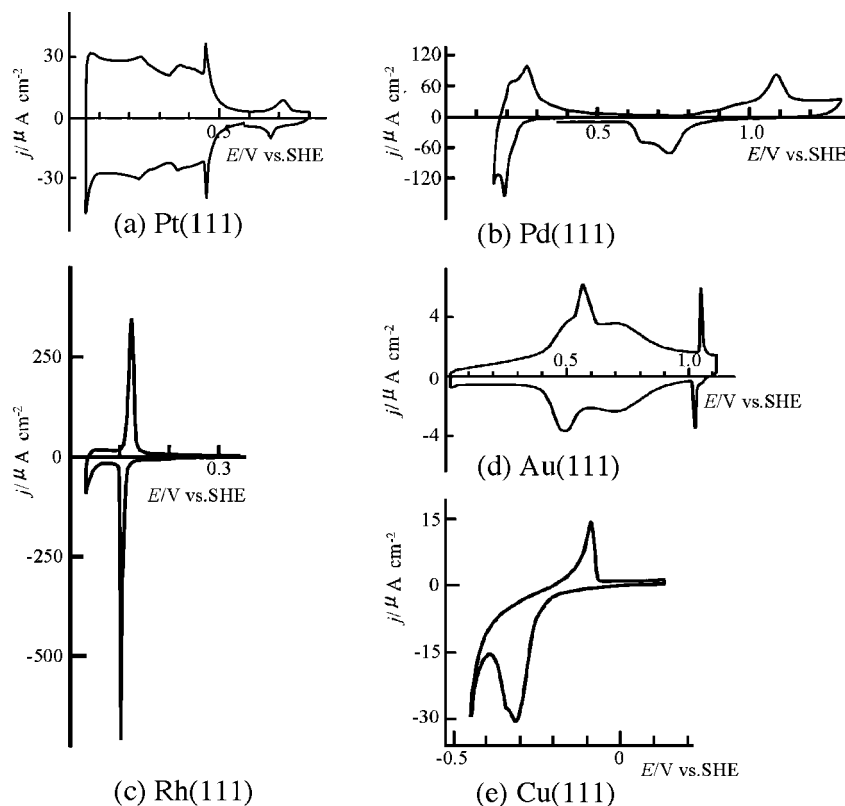


Figure 1. Cyclic voltammograms of M(111) (M = (a) Pt, (b) Pd, (c) Rh, (d) Au, and (e) Cu) electrodes in sulfuric acid solution in 0.5 M (a–d) and 0.005 M (e) H_2SO_4 . Scanning rate is 0.05 V s^{-1} (a–d) and 0.01 V s^{-1} (e).

from the oxygen lone pair tends to decrease the δ_{HOH} band frequency. This tendency is consistent with previous DFT calculations.⁴

It is known that underpotential deposition of hydrogen (H_{upd}) occurs on Pt and Rh.^{42,43} Overpotential deposition of hydrogen (H_{opd}) is also reported in hydrogen evolution regions. In SEIRAS study, a band appears at 2090 cm^{-1} below 0.05 V , which is assigned to ν_{PtH} of H_{opd} adsorbed at an atop site.⁴⁴ However, adsorbed hydrogen does not affect the structure of water adsorbed at the atop site because H_{upd} is located at a hollow site.⁴³ We do not observe the ν_{PtH} of H_{opd} in the potential region examined. SEIRAS on Pt shows that water does not interact with adsorbed hydrogen (H_{upd} and H_{opd}).³⁴

3.2.2. Comparison of Au(111) and Pt(111) Surfaces. In order to discuss the adsorption structure on Au(111), we compare the IR spectra on Au(111) with those on Pt(111). These metals have wider potential windows between hydrogen evolution and (bi)sulfate adsorption than Pd(111) and Rh(111). Figure 4 shows the IR spectra of δ_{HOH} on Pt(111) and Au(111). The potential dependence of the band frequency and intensity on Au(111) differs from those on Pt(111) remarkably. Figure 5 summarizes the potential dependence of the δ_{HOH} band frequency on M(111) (M = Pt, Pd, Rh, and Au). The δ_{HOH} bands for Pt, Pd, and Rh show the same band shift of about $50 \text{ cm}^{-1}/\text{V}$, whereas Au(111) gives a smaller band shift. This indicates that the interaction of water with Au is extremely weaker. The calculated binding energy of water monomer adsorbed on Au(111) is 1/3 the values on the platinum group;⁵ water adsorption on Au(111) is classified as physisorption rather than chemisorption. The chemisorption of water is mainly due to charge transfer from the oxygen lone pair to the metal d-band.^{1,45} The weak interaction between water and Au(111) can be explained by the full occupancy of electrons in the 5d-band of Au.

Figure 6 shows the potential dependence of the integrated band intensity of δ_{HOH} of water and ν_{SO} of (bi)sulfate on Pt(111) and Au(111). On Pt(111), the δ_{HOH} and ν_{SO} band intensities decrease drastically above 0.35 V . The decrease of the negative-going ν_{SO} intensity is due to (bi)sulfate adsorption at sample potentials, which gives the positive-going band. The decrease of δ_{HOH} above 0.35 V indicates a decrease of water coverage with substitution of (bi)sulfate at the sample potential. The potential independence of both band intensities below 0.35 V indicates that there is no significant change in water coverage and molecular orientation. However, the estimation of water coverage on the electrode surface is difficult; the coverage of adsorbed water on Pt(111) electrode is still unclear.

The δ_{HOH} band intensity on Au(111) decreases monotonically with the increase of the electrode potential, and then disappears around the pzc (around 0.5 V on Au(111) in sulfuric acid solution).⁴⁶ Since the ν_{SO} band intensity of (bi)sulfate anion is unchanged even at 0.50 V , (bi)sulfate anion is not adsorbed on Au(111) at sample potentials below 0.50 V . A previous study showed that the onset potentials of (bi)sulfate anion adsorption is 0.7 V on Au(111).³³ Thus, the decrease of δ_{HOH} intensity is not due to the decrease of water coverage due to the (bi)sulfate adsorption. The monotonic decrease of δ_{HOH} intensity on Au(111) is rationalized by the orientation change of water. The applied electric field at the interface can change the orientation of water because of the weak interaction of water with the Au surface. The tilt angle of water decreases with the increase of electrode potential and the molecular plane becomes parallel to the surface at the pzc of 0.5 V . SFG and SEIRAS studies of Au film in sulfuric acid came to the same conclusion: the orientation of water is flat at the pzc and oxygen-up at the potentials below the pzc.^{10,11} A previous SXD study of the Ag(111) electrode also revealed that the OH direction of water depends on the electrode potential: water changes the orientation

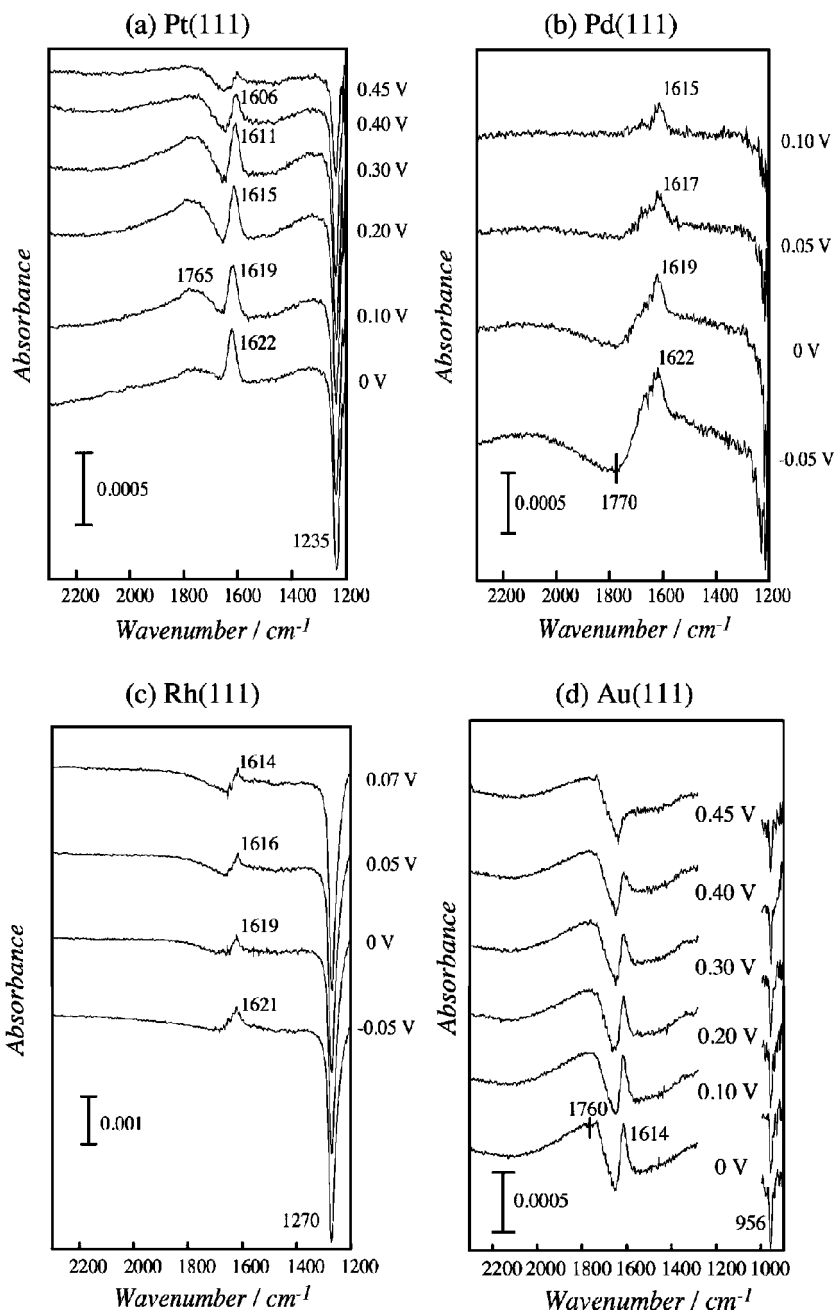


Figure 2. SNIPTIR spectra of water adsorbed on (a) Pt(111), (b) Pd(111), (c) Rh(111), and (d) Au(111) in 0.5 M H₂SO₄. The reference potentials are 0.50 V (Pt), 0.60 V (Pd), 0.65 V (Rh), and 1.10 V (Au).

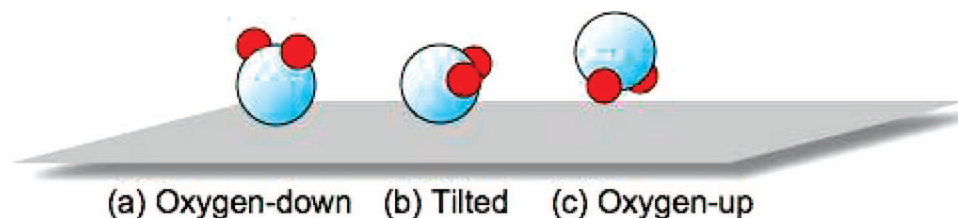


Figure 3. Schematic model of water adsorbed on the surface.

from oxygen-up to oxygen-down.¹² The orientation change of water is not observed on Pt(111) in the same potential region. This difference can be explained by the effect on the interaction of water with the surface. The chemisorption of water with Pt through the oxygen lone pair inhibits the reorientation.

Since the interaction between water and the Au surface is weaker than that of the platinum group, the frequency of the

δ_{HOH} band on Au will be higher than that on Pt (1620 cm⁻¹). However, the δ_{HOH} frequency on Au(111) is lower than that on Rh and Pd at 0 V. This discrepancy can be explained by the difference in the hydrogen bond strength. Adsorbed water at an atop site forms hydrogen bonds with water at neighboring atop sites. A typical OH...O hydrogen bonding distance matches the nearest-neighbor distances of M(111) (M = Pt, Rh,

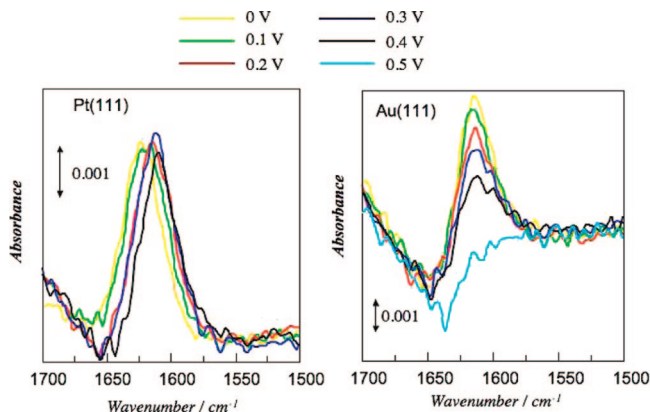


Figure 4. SNIFTIR spectra of the δ_{HOH} band on Pt(111) and Au(111) at various potentials in 0.5 M H_2SO_4 .

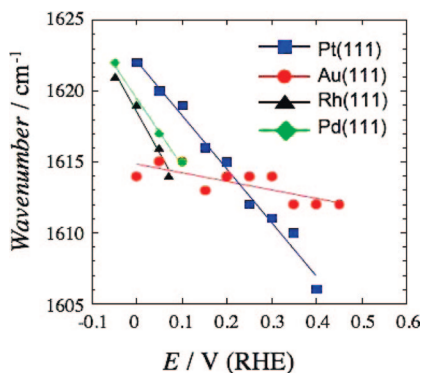


Figure 5. Potential dependence of the IRAS band frequency around 1620 cm^{-1} for Pt(111), Au(111), Rh(111), and Pd(111) in 0.5 M H_2SO_4 .

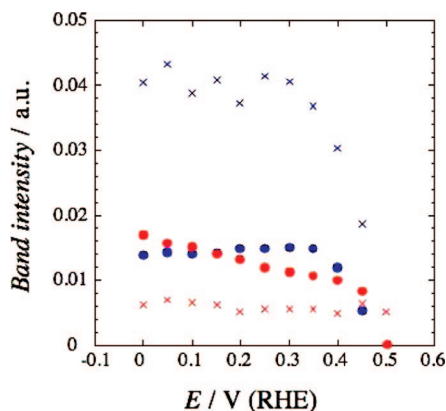


Figure 6. Potential dependence of the IRAS band intensity of δ_{HOH} and ν_{SO} on Pt(111) and Au(111). Blue and red circles indicate the δ_{HOH} intensity on Pt(111) and Au(111), respectively. Blue and red crosses indicate the ν_{SO} intensity at 1235 cm^{-1} on Pt(111) and at 950 cm^{-1} on Au(111), respectively.

Pd), but is shorter than that of Au.¹ Moreover, the reorientation of water on Au may not provide ideal hydrogen bonding geometry. Therefore, the decrease of hydrogen bonding strength causes the lower frequency shift of δ_{HOH} on Au(111).

3.3. Infrared Spectra of Cu(111). Figure 7 shows the infrared spectra of Cu(111) electrode in 5 mM H_2SO_4 as a function of electrode potential. The single negative-going band of adsorbed (bi)sulfate anion at 1223 cm^{-1} indicates that no (bi)sulfate anion is adsorbed on the surface between -0.30 and -0.43 V . Below -0.30 V , oxygen species such as adsorbed oxygen, water, hydronium cation, and hydroxyl species are expected to be adsorbed on the surface. However, the δ_{HOH} band

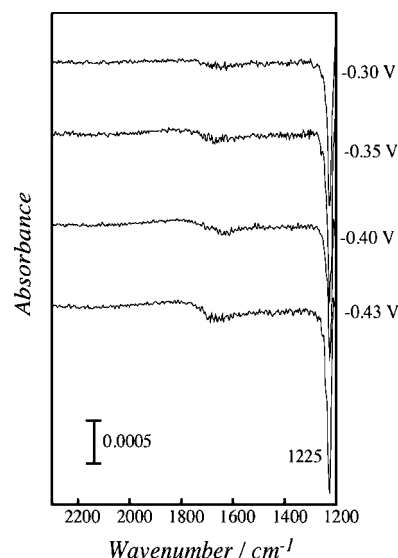


Figure 7. SNIFTIR spectra of Cu(111) in 0.005 M H_2SO_4 . The reference potential is 0 V.

of adsorbed water and hydronium cation, which has been observed on other metal surfaces, is not observed in the potential region examined. No band of δ_{HOH} may indicate that the surface is covered with adsorbed oxygen or hydroxyl species. Surface enhanced Raman scattering (SERS) of Cu electrode in sulfuric acid solution suggests the existence of a Cu_2O layer above -0.6 V vs SCE.⁴⁷

An STM study reported 4×4 and 5×5 superstructures on Cu(111) at negative potentials in sulfuric acid solution.⁴⁸ The coverage of the adsorbate increased with the decrease of potentials. The coverage of electronegative species such as OH_{ad} and O_{ad} should decrease with the decrease of potentials. They concluded that the adsorbate was water including cationic species. We cannot exclude the possibility that water is adsorbed on Cu(111). If hydrogen-bonded water molecules interact weakly with Cu, the band frequency of adsorbed water has the same value as that of the bulk phase. IR band will be canceled out in such a case. It is also probable that the molecular plane of adsorbed water is completely parallel to the surface. This geometry has no dynamic dipole moment perpendicular to the surface. It was reported that the adsorption energy of water monomer on Cu(111) is intermediate between that on Pt(111) and that on Au(111).⁵ The IR result on Cu(111) is different from those of both surfaces. This different behavior is attributed to the difference of atomic radius. The atomic radius of Cu is 8–11% smaller than those of Pt and Au; the interatomic distance of Cu is smaller than the $\text{OH}\cdots\text{O}$ hydrogen bonding distance. This large mismatch may affect the structure of water layer on Cu(111).

4. Conclusion

The δ_{HOH} band of adsorbed water on M(111) ($M = \text{Pt}, \text{Pd}, \text{Rh}, \text{and Au}$) was observed below the potential of (bi)sulfate anion adsorption. Water molecules are adsorbed on M(111) ($M = \text{Pt}, \text{Pd}, \text{and Rh}$) via the oxygen lone pair with its molecular plane nearly parallel to the surface. On Au(111), the tilt angle between the molecular plane and the surface decreases with the increase of the potential, giving a flat orientation at the pzc. On the other hand, Cu(111) gave no δ_{HOH} band of adsorbed water. The spectral features of water on Cu(111) are different from those on M(111) ($M = \text{Pt}, \text{Pd}, \text{Rh}, \text{and Au}$).

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JP801473G