

# Infrared Reflection Absorption Spectroscopy of the Sulfuric Acid Anion on Low and High Index Planes of Palladium

Nagahiro Hoshi,\* Makiko Kuroda, Osamu Koga, and Yoshio Hori

Department of Applied Chemistry, Faculty of Engineering, Chiba University, 1-33, Yayoi-cho, Inage-ku, Chiba 263-8522, Japan

Received: April 3, 2002; In Final Form: June 18, 2002

The sulfuric acid anion ( $\text{HSO}_4^-$  or  $\text{SO}_4^{2-}$ ) adsorbed on Pd single-crystal electrodes was studied using infrared reflection absorption spectroscopy (IRAS) in 0.05 M  $\text{H}_2\text{SO}_4$  solution. Surfaces examined are flat ones (Pd(111) and Pd(100)) and stepped ones (Pd(110) (= 2(111)–(111)) and Pd(311) (= 2(111)–(100))). All of the surfaces give a single IRAS band around  $1200\text{ cm}^{-1}$  that is assigned to S–O stretching vibration. The integrated band intensity depends on the crystal orientation significantly, i.e.,  $\text{Pd}(311) \sim \text{Pd}(110) \ll \text{Pd}(100) < \text{Pd}(111)$ , showing that the flat surfaces adsorb more sulfuric acid anion than the stepped ones. Magnitude of the band shift ( $\text{d}\nu/\text{d}E$ ) on the flat surfaces is nearly twice as high as that on the stepped ones.

## Introduction

Single-crystal electrodes provide well-defined surfaces on which the structure of adsorbates and active sites can be scrutinized on the atomic scale. Many papers have reported the structural effects on electrochemical reactions using single-crystal electrodes of Pt,<sup>1,2</sup> since Clavilier reported the simple method for preparing a single-crystal bead from Pt wire.<sup>3</sup> The catalytic activity of Pd is as high as that of Pt, but fewer papers have reported electrochemistry on Pd single crystals because of the difficulty in preparation of a Pd single crystal with Clavilier's method. We recently established a method to prepare a single-crystal bead of Pd and studied the structural effects on the voltammogram on stepped and kinked-stepped surfaces of Pd in 0.5 M  $\text{H}_2\text{SO}_4$ .<sup>4,5</sup> Pd electrodes with wide terraces give redox peaks around 0.25 V (RHE) that may correlate with the adsorption and desorption of sulfuric acid anion ( $\text{HSO}_4^-$  or  $\text{SO}_4^{2-}$ ).

The adsorbed sulfuric acid anion is known to affect the electrochemical reactions on Pt single crystals significantly, such as hydrogen adsorption,<sup>6–9</sup> oxidation of hydrogen<sup>10</sup> and methanol,<sup>11</sup> and reduction of oxygen<sup>12</sup> and  $\text{CO}_2$ .<sup>13</sup> Infrared reflection absorption spectroscopy (IRAS) is one of the useful methods to detect adsorbed anions sensitively.<sup>14,15</sup> Some papers reported IRAS spectra of sulfuric acid anion on low<sup>16–25</sup> and high index planes of Pt.<sup>26</sup> Pt(111) gives a single IRAS band around  $1200\text{ cm}^{-1}$  that is assigned to S–O stretching vibration of the sulfuric acid anion adsorbed with 3-fold geometry (through three oxygen atoms of the anion).<sup>16–23</sup> Pt(100) and Pt(110) provide two bands around 1100 and  $1200\text{ cm}^{-1}$ ; a model is proposed that the sulfuric acid anion is adsorbed with 2-fold geometry (through two oxygen atoms of the anion).<sup>24,25</sup> IRAS spectra of Pt(S)-[ $n(111) \times (111)$ ] and Pt(S)-[ $n(100) \times (111)$ ] also give two bands around 1100 and  $1200\text{ cm}^{-1}$ , suggesting that the anion is adsorbed with 2-fold geometry.<sup>26</sup>

IRAS spectra of sulfuric acid anions were also reported on low index planes of Au and Rh. Au(111)<sup>27–29</sup> and Rh(111)<sup>30</sup>

provide IRAS spectra similar to Pt(111). The (100) and (110) surfaces of Au and Rh present a single band around  $1200\text{ cm}^{-1}$ , which suggests that the anion is adsorbed with 1-fold geometry (through 1 oxygen atom of the anion).<sup>29,30</sup>

No paper, however, has reported the IRAS spectra of the sulfuric acid anion on Pd single-crystal electrodes. In this paper, we present the IRAS spectra of the anion adsorbed on flat (Pd(111) and Pd(100)) and stepped surfaces (Pd(110) and Pd(311)) and discuss the nature of the anion adsorbed on Pd.

## Experimental Section

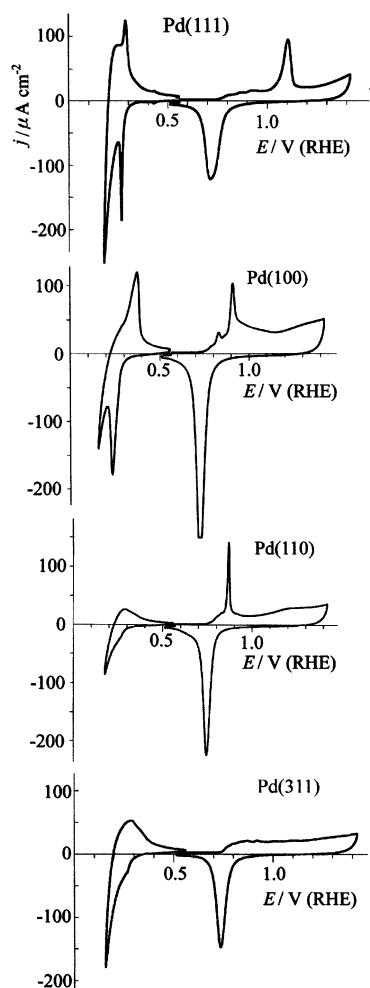
A single-crystal bead of Pd in about 3 mm diameter was prepared from Pd wire (1 mm diameter, 99.99% purity) according to the method described previously.<sup>4</sup> Larger surface area is necessary for measuring IRAS spectrum with a good signal-to-noise ratio. We melted the lower half of the bead with an  $\text{H}_2/\text{O}_2$  flame, added Pd little by little, and finally obtained a large single crystal in teardrop shape with a cross section between 0.30 and  $0.35\text{ cm}^2$ .<sup>31</sup>

The crystal was oriented using the reflection beam of a He–Ne laser from (111) and (100) facets on the crystal<sup>32,33</sup> and then mechanically polished with diamond slurries down to  $0.125\text{ }\mu\text{m}$ . Surfaces examined were Pd(111), Pd(100), Pd(110) (= 2(111)–(111)), and Pd(311) (= 2(111)–(100)). Pd(111) and Pd(100) are composed of flat terraces, whereas the first layers of Pd(110) and Pd(311) consist of only step atoms. The polished surface was annealed in an  $\text{H}_2/\text{O}_2$  flame about  $1300\text{ }^\circ\text{C}$  for removing the distortion caused by the mechanical polishing and then cooled in Ar atmosphere (99.9999%).

The annealed surface was protected with ultrapure water and transferred to the working electrode compartment of an electrochemical cell. We measured a voltammogram in 0.05 M  $\text{H}_2\text{SO}_4$  in order to confirm that the surface was correctly oriented. Then, the surface was protected with ultrapure water again and inserted into an IRAS cell.

IRAS spectra were measured in 0.05 M  $\text{H}_2\text{SO}_4$  saturated with Ar using JIR-6000M spectrometer (JEOL) with p-polarized light with a resolution of  $4\text{ cm}^{-1}$ . The window for the IRAS measurement was a  $\text{CaF}_2$  plate with a thickness of 2 mm.

\* To whom correspondence should be addressed. Fax: +81–43–290–3384. E-mail: hoshi@faculty.chiba-u.jp.



**Figure 1.** Voltammograms of flat (Pd(111) and Pd(100)) and stepped surfaces (Pd(110) (= 2(111)–(111)) and Pd(311) (= 2(111)–(100)) in 0.05 M H<sub>2</sub>SO<sub>4</sub> saturated with Ar. The scanning rate is 0.02 V s<sup>-1</sup>.

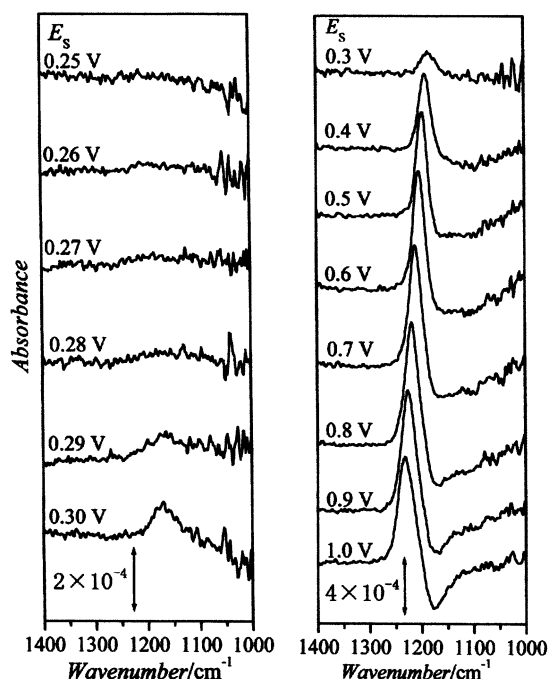
Reflected IR light was detected with an MCT detector cooled by liquid nitrogen. The spectra were averaged over 1000 scans using SNIFTIRS (subtractively normalized interfacial FT-IR spectroscopy). The reference spectra were measured at 0.20 V (RHE) ( $E_R$ ), whereas the sample spectra were collected at the potentials ( $E_S$ ) up to the onset of the oxide film formation. IRAS spectra are displayed in the form of absorbance ( $= -\log(R(E_S)/R(E_R))$ ) vs wavenumber. Positive-going bands arise from the adsorbates at  $E_S$ . We prepared two sets of electrodes examined and obtained reproducible results.

The electrolytic solution was prepared with suprapur grade chemicals (Merck) and ultrapure water treated with Milli Q plus low TOC system (Millipore). All of the potentials are shown with respect to a reversible hydrogen electrode (RHE).

## Results and Discussion

**Voltammograms.** Figure 1 shows voltammograms of the large single-crystal electrodes for IRAS measurement. Sharp redox peaks appear around 0.25 V on Pd(111) and Pd(100) electrodes. These peaks may correlate with the adsorption and desorption of sulfuric acid anion, because no redox peak appeared in HClO<sub>4</sub> solution in which the anion does not adsorb on electrodes at this potential range. The stepped surfaces (Pd(110) and Pd(311)) give no redox peaks around 0.25 V.

Sharp anodic peaks above 0.85 V arise from the oxide film formation. Previous papers report that the peak potentials



**Figure 2.** IRAS spectra of sulfuric acid anion adsorbed on Pd(111) in 0.05 M H<sub>2</sub>SO<sub>4</sub>. Sample potentials  $E_S$  are shown in the figure. The reference potential  $E_R$  is 0.20 V (RHE). Resolution: 4 cm<sup>-1</sup>. The spectra were averaged over 1000 scans.

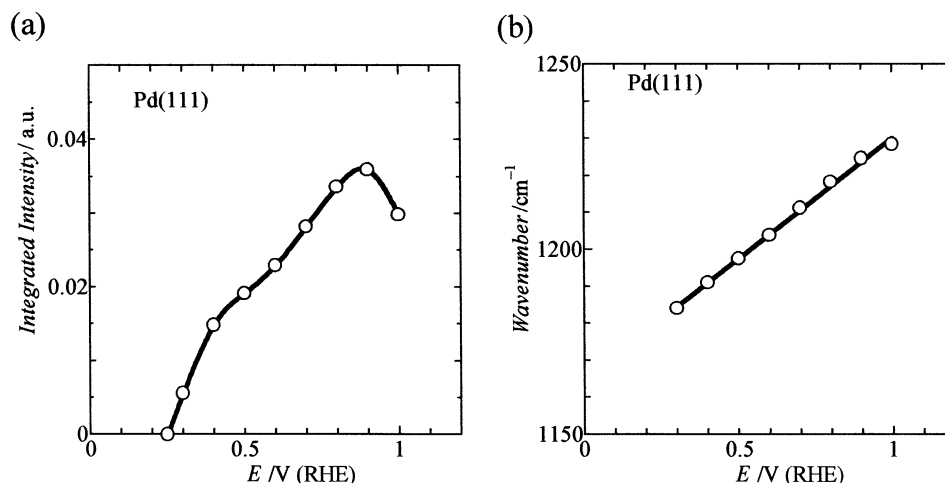
increase positively as (110) structure < (100) terrace < (111) terrace,<sup>4,5,34,35</sup> and the step sites provide no sharp peak due to the oxide film formation except (110) site.<sup>4,5</sup>

The voltammograms in Figure 1 agree with those reported previously,<sup>4,5,34,35</sup> and we judge that the surfaces are correctly oriented.

**IRAS Spectra on the Pd(111) Electrode.** Figure 2 shows IRAS spectra of the sulfuric acid anion adsorbed on the Pd(111) electrode in 0.05 M H<sub>2</sub>SO<sub>4</sub>. A single band appears around 1200 cm<sup>-1</sup> above 0.29 V, which is almost identical with the positive end of the sharp anodic peak around 0.25 V in the voltammogram (Figure 1). The band intensity is enhanced, and the peak position shifts to higher wavenumber with the increase of  $E_S$ . These features are identical with those of the IRAS band of the sulfuric acid anion adsorbed on Pt(111) with 3-fold geometry.<sup>16–23</sup>

Wan and Itaya reported the in-situ STM image of the sulfuric acid anion with  $\sqrt{3} \times \sqrt{7}$  superstructure between 0.5 and 0.9 V on Pd(111).<sup>36</sup> Below 0.4 V, however, no image of the sulfuric acid anion was obtained. They conclude that the sulfuric acid anion diffuses on the surface below 0.4 V. The small redox peaks at 0.42 V in Figure 1 indicate that order–disorder phase transition of the anion occurs at this potential.<sup>36</sup> IRAS spectra detect the adsorbed sulfuric acid anion at 0.3 and 0.4 V (Figure 2), verifying that Pd(111) does adsorb sulfuric acid anion below 0.4 V.

Kim and Soriaga reported the in situ STM image of the sulfuric acid anion at lower potential (0.35 V) than Itaya's report.<sup>37</sup> The voltammogram of Kim and Soriaga, however, gave no redox peaks caused by the order–disorder transition of the adsorbed anion. The redox peaks due to the phase transition are very sensitive to the annealing and cooling condition in our experience, and thus, the potential of the phase transition may change significantly according to the experimental conditions. Because our IRAS spectra are measured with Pd(111) electrode



**Figure 3.** Potential dependence of the IRAS band around  $1200\text{ cm}^{-1}$  on Pd(111) in  $0.05\text{ M H}_2\text{SO}_4$ : (a) integrated intensity and (b) band peak position.

giving the redox peaks due to the phase transition, we discuss the IRAS results on the basis of the Itaya's report.

IRAS spectra give a negative-going band above  $0.8\text{ V}$ . This band may be assigned to the  $\text{SO}_3$  stretching vibration of the  $\text{HSO}_4^-$  anion ( $\sim 1200\text{ cm}^{-1}$ ) in the solution phase.<sup>38,39</sup> A negative-going band arises from the decrease of  $[\text{HSO}_4^-]$  at a sample potential: a positively charged surface removes a significant amount of  $\text{HSO}_4^-$  from the solution phase. The peak of the negative-going band locates below  $1200\text{ cm}^{-1}$ , probably because the positive-going band hides the real peak of the negative band. In this paper, we focus our attention to the positive-going band.

We separated the bipolar bands using two Gaussian curves to evaluate the integrated band intensity and the peak position precisely. Figure 3 depicts the integrated intensity and the peak position of the IRAS band at various potentials after the peak separation. The integrated band intensity is enhanced with the increase of the potential up to  $0.9\text{ V}$  (Figure 3a), showing the monotonic increase of the coverage of the sulfuric acid anion. The enhancement of the band intensity is not attributed to the anion in solution phase that is accumulated near the electrode at positive potentials, because the IRAS band locates at higher wavenumber than that in the solution phase. The peak shift with the potential also supports that the band arises from the adsorbed species. The decrease of the intensity at  $1.0\text{ V}$  may result from the oxide film formation that removes a part of the adsorbed anion.

The gradual enhancement of the coverage at positive potentials might be due to the slow transport process of the sulfuric acid anion in the thin layer; measurement of SNIFTIRS keeps an electrode pushed to the window. The IRAS spectra on Pt(111) also show a monotonic increase of the coverage at positive potentials.<sup>16–23</sup> The radiotracer method on Pt(111), in which sulfuric acid anion is adsorbed without the transport process prevented, shows the same potential dependence of the coverage as IRAS spectra.<sup>40</sup> Thus, the gradual increase of the IRAS band intensity may arise from the nature of the sulfuric acid anion on Pt(111) and Pd(111) electrodes.

The variation of the coverage contradicts the results of the in situ STM: the  $\sqrt{3}\times\sqrt{7}$  superstructure is invariant between  $0.5$  and  $0.8\text{ V}$ .<sup>36</sup> If IRAS observes only the sulfuric acid anion with  $\sqrt{3}\times\sqrt{7}$  structure, the band intensity will be constant at this potential range. STM observes only stable and immobile adsorbates and cannot detect mobile ones. The enhancement of

**TABLE 1: IR Band of the Cobalt Complex with  $\text{SO}_4^{2-}$  Reproduced from Ref 44<sup>a</sup>**

$C_{3v}$ Point Group ( $[\text{Co}(\text{SO}_4)(\text{NH}_3)_5]\text{Cl}$ )				
	$\nu_s(\text{SO})$	$\nu_{as}(\text{SO})$	$\nu_s(\text{SO}^*)$	
wavenumber/ $\text{cm}^{-1}$	1044	1135	974	
irreducible	$A_1$	E	$A_1$	
$C_{2v}$ Point Group ( $[(\text{NH}_3)_4\text{Co}(\text{NH}_2)(\text{SO}_4)\text{Co}(\text{NH}_3)_4](\text{NO}_3)_3$ )				
	$\nu_s(\text{SO})$	$\nu_{as}(\text{SO}^*)$	$\nu_{as}(\text{SO})$	$\nu_s(\text{SO}^*)$
wavenumber/ $\text{cm}^{-1}$	1109	1064	1171	997
irreducible	$A_1$	$B_1$	$B_2$	$A_1$

<sup>a</sup>  $\nu_s$ , symmetric stretching vibration;  $\nu_{as}$ , asymmetric stretching vibration; SO, S–O bond uncoordinated to metal;  $\text{SO}^*$ , S–O bond coordinated to metal.

the IRAS band suggests that Pd(111) adsorbs the mobile sulfuric acid anion as well as the rigidly adsorbed one with  $\sqrt{3}\times\sqrt{7}$  structure.

The peak of the IRAS band depends linearly on the potential as shown in Figure 3b. The slope of the linear line gives the band shift ( $d\nu/dE$ ) of  $65\text{ cm}^{-1}\text{ V}^{-1}$ . This value is lower than that of Pt(111) ( $\sim 100\text{ cm}^{-1}\text{ V}^{-1}$ )<sup>16–23</sup> and as high as those of Rh(111)<sup>30</sup> and Pd/Pt(111) ( $\sim 70\text{ cm}^{-1}\text{ V}^{-1}$ ).<sup>41</sup>

The band shift is generally caused by the following mechanisms: donation and back-donation of electrons between adsorbate and surface,<sup>16,42</sup> Stark effect,<sup>43</sup> and dipole–dipole interaction among adsorbates.<sup>44</sup> The intensity of the dipole–dipole interaction depends on the coverage of the adsorbate. The coverage of the sulfuric acid anion increases up to  $0.9\text{ V}$  and then decreases at  $1.0\text{ V}$  as shown in Figure 3a. On the other hand, the band position ( $\nu$ ) depends linearly on the applied potential ( $E$ ) up to  $1.0\text{ V}$  (Figure 3b). These facts suggest that the other factors affect the band shift more dominantly than the dipole–dipole interaction.

**Geometry of the Adsorbed Sulfuric Acid Anion on Pd(111).** IRAS bands of the sulfuric acid anion have been assigned according to the IR absorption spectra of  $\text{SO}_4^{2-}/\text{HSO}_4^-$  in aqueous solutions<sup>37,38</sup> and metal complexes with sulfate.<sup>45,46</sup> Table 1 summarizes the IR bands of the Co complexes with sulfate above  $950\text{ cm}^{-1}$ .<sup>45</sup> The  $C_{3v}$  complex gives three IR bands, whereas the  $C_{2v}$  complex provides four bands. According to the surface selection rule, only vibrations of which dipole moments have a  $z$  component ( $A_1$ ) are observable on an



electrode surface. Sulfuric acid anions adsorbed with 1- and 3-fold geometry belong to the  $C_{3v}$  point group, whereas the anion with 2-fold geometry belongs to  $C_{2v}$ . All of the geometries have two  $A_1$  bands above  $950\text{ cm}^{-1}$ , according to Table 1. There have been, however, several arguments on the band assignments as follows.

Previous papers reported an IRAS band around  $1200\text{ cm}^{-1}$  on Pt(111) in  $\text{H}_2\text{SO}_4$  solutions.<sup>16–23</sup> All of the papers conclude that the sulfuric acid anion is adsorbed on Pt(111) with 3-fold geometry. The assignments of the band around  $1200\text{ cm}^{-1}$ , however, contradict one another. Faguy and Yeager et al. assigned the band to the asymmetric stretching vibration of the S–O bond of  $\text{HSO}_4^-$  ( $\sim 1200\text{ cm}^{-1}$ ) that is forbidden on the surface, suggesting that surface selection rule is broken on the electrode surface.<sup>16</sup> Ito et al. assigned the band to the symmetric stretching vibration of S–O bond of  $\text{HSO}_4^-$ , which locates around  $1050\text{ cm}^{-1}$  in solution phase, according to the surface selection rule.<sup>18</sup> Ito et al. showed that the band shifts significantly to higher wavenumber on the positively charged surface on the basis of the MO calculation. Nart and Iwasita et al. interpreted that the band around  $1200\text{ cm}^{-1}$  is composed of the symmetric stretching vibrations of uncoordinated S–O ( $\nu_s(\text{SO})$ ) and that of coordinated S–O ( $\nu_s(\text{SO}^*)$ ) which shift to higher wavenumber on Pt(111).<sup>19</sup>  $\text{SO}_4^{2-}$  adsorbed with  $C_{3v}$  symmetry would give two IRAS bands above  $950\text{ cm}^{-1}$  according to Table 1. Pt(111), however, gives a single IRAS band in the solution containing only the  $\text{SO}_4^{2-}$  ion;<sup>19</sup> it is probable that  $\nu_s(\text{SO}^*)$  shifts in the vicinity of  $\nu_s(\text{SO})$  on an electrode surface.

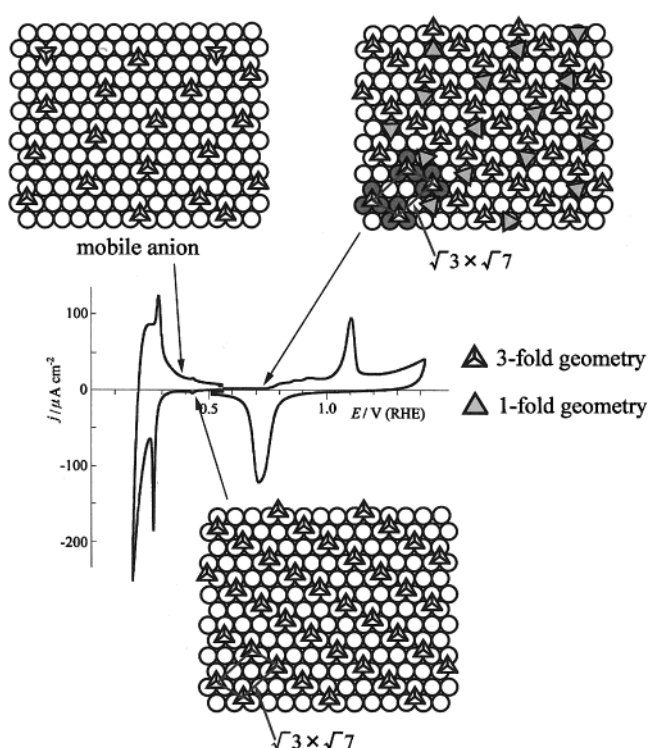
Pt(100) and Pt(110) give two IRAS bands around 1200 and  $1100\text{ cm}^{-1}$ , which arise from the sulfuric acid anion adsorbed with 2-fold geometry.<sup>24,25</sup> The higher and the lower frequency modes are assigned to  $\nu_s(\text{SO})$  and  $\nu_s(\text{SO}^*)$ , respectively. Corresponding bands of the Co complex, 1109 and  $997\text{ cm}^{-1}$ , may shift to higher wavenumber on the electrode surface.

There is another contradiction as to which  $\text{SO}_4^{2-}$  or  $\text{HSO}_4^-$  anion is adsorbed on Pt electrodes in  $\text{H}_2\text{SO}_4$  solutions. Some papers reported a weak IRAS band around  $950\text{ cm}^{-1}$ .<sup>17,18,20,21</sup> Some of them assigned it to S–OH stretching vibration, suggesting that the  $\text{HSO}_4^-$  anion is adsorbed on Pt(111).<sup>17,18,20</sup> However, Faguy et al. assigned the band to the stretching vibration of the ion pair of  $\text{SO}_4^{2-}$  and  $\text{H}_3\text{O}^+$ .<sup>22,23</sup> Nart and Iwasita et al. reported no peak around  $950\text{ cm}^{-1}$  in the solution in which the  $\text{HSO}_4^-$  anion is the predominant species.<sup>19</sup> Kolics and Wieckowski claimed that the adsorbate is a partially discharged  $\text{SO}_4^{2-}$  anion.<sup>40</sup> There is no general consensus on the adsorbed species on Pt electrodes in  $\text{H}_2\text{SO}_4$ ; thus, we will not discuss which anion is adsorbed on Pt electrodes in this paper.

Taking the former reports into account, we discuss the IRAS results on the basis of the following assumptions:

1. The surface selection rule is valid for the IRAS of sulfuric acid anion.
2. IR bands of the sulfuric acid anion adsorbed on electrodes locate at higher wavenumber than those of metal complexes with sulfate.
3. When the sulfuric acid anion is adsorbed with  $C_{3v}$  symmetry,  $\nu_s(\text{SO})$  locates near  $\nu_s(\text{SO}^*)$ .
4. Adsorbed  $\text{HSO}_4^-$  approximately has the same symmetry as adsorbed  $\text{SO}_4^{2-}$ .

The single band around  $1200\text{ cm}^{-1}$  on Pd(111) may arise from symmetric S–O vibrations of 1- and 3-fold sulfuric acid anion. The sulfuric acid anion giving  $\sqrt{3}\times\sqrt{7}$  superstructure may be adsorbed with 3-fold geometry; the symmetry and the atomic distance of the Pd(111) surface are almost identical with

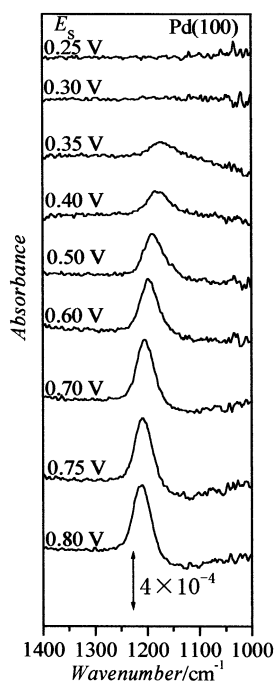


**Figure 4.** Models of the sulfuric acid anion adsorbed on Pd(111) at various potentials. Pyramid like and shaded triangles show the sulfuric acid anion adsorbed with 3-fold and 1-fold geometry, respectively. The sulfuric acid anion with 1-fold geometry moves on the surface; thus, the adsorption site is not fixed. Shaded circles represent the area of the steric hindrance because of the anion adsorbed with 3-fold geometry.

those of the bottom plane of the tetrahedral sulfuric acid anion. The 3-fold sulfuric acid anion will be adsorbed more tightly than the 1-fold sulfuric acid anion. The mobile anion that is adsorbed above 0.5 V may have 1-fold geometry, because the 3-fold sulfuric acid anion cannot be adsorbed in the unit cell of  $\sqrt{3}\times\sqrt{7}$  structure because of the steric hindrance. Figure 4 summarizes the models of the sulfuric acid anion adsorbed on Pd(111).

STM studies propose a model that  $\text{H}_2\text{O}$  is coadsorbed with the sulfuric acid anion on (111) surfaces of Pt group metals.<sup>36,47–49</sup> Surface enhanced infrared absorption spectroscopy (SEIRAS) verifies the coadsorption of  $\text{H}_2\text{O}$  on Au(111).<sup>28</sup> Some IRAS studies show that  $\text{H}_3\text{O}^+$  is also coadsorbed on the Pt(111) electrode.<sup>22,23,50,51</sup> The 1-fold anion would move among the stable adsorbates on Pd(111).

**Relation between IRAS Spectra and the Voltammogram of Pd(111).** In the former papers, we attributed the cathodic peak around 0.25 V to the desorption of the sulfuric acid anion from Pd(111) electrodes, because the charge of the peak almost agrees with that of  $\text{SO}_4^{2-}$  adsorbed with  $\sqrt{3}\times\sqrt{7}$  structure.<sup>4,5</sup> The IRAS band intensity at 0.3 V, however, is 1/4 as high as that at 0.5 V at which the  $\sqrt{3}\times\sqrt{7}$  structure is completed. IRAS band intensity depends linearly on the coverage according to the study of on-top CO adsorbed on Pt(111)<sup>52</sup> and Pt(110),<sup>53</sup> and the results of Pd(100) described in the next section support that IR absorptivity of the 1-fold anion is close to that of the 3-fold anion. Thus, the coverage of the sulfuric acid anion may be 1/4 of the  $\sqrt{3}\times\sqrt{7}$  structure. This result suggests that all of the cathodic charge at 0.25 V does not originate from the desorption of the sulfuric acid anion. The redox peaks of the



**Figure 5.** IRAS spectra of the sulfuric acid anion adsorbed on Pd(100) in 0.05 M  $\text{H}_2\text{SO}_4$ . Sample potentials  $E_s$  are shown in the figure. The reference potential  $E_R$  is 0.20 V (RHE). Resolution:  $4\text{ cm}^{-1}$ . The spectra were averaged over 1000 scans.

voltammogram around 0.25 V may be also related with the adsorbed hydrogen on Pd(111).

There is another controversy between the voltammogram and IRAS spectra of Pd(111): the coverage of the sulfuric acid anion increases above 0.5 V according to the IRAS results, but no apparent current from the anion adsorption appears in the voltammogram above 0.5 V. The same phenomenon occurs in iodine adsorption on Au(111): the electrochemical quartz crystal microbalance (EQCM) method shows the increase of the iodine coverage at positive potentials, whereas no corresponding current appears in the voltammogram.<sup>54</sup> We estimate the maximum current density due to the adsorption of the sulfuric acid anion according to the following assumptions: (a)  $\text{SO}_4^{2-}$  is adsorbed; (b) two electron transfer during the adsorption; (c) the sulfuric acid anion forms a  $\sqrt{3}\times\sqrt{7}$  structure at 0.5 V, giving the coverage of 0.22.

The IRAS band intensity at 0.7 V is 1.4 times as high as that at 0.5 V, giving the coverage of 0.31. The charge due to the

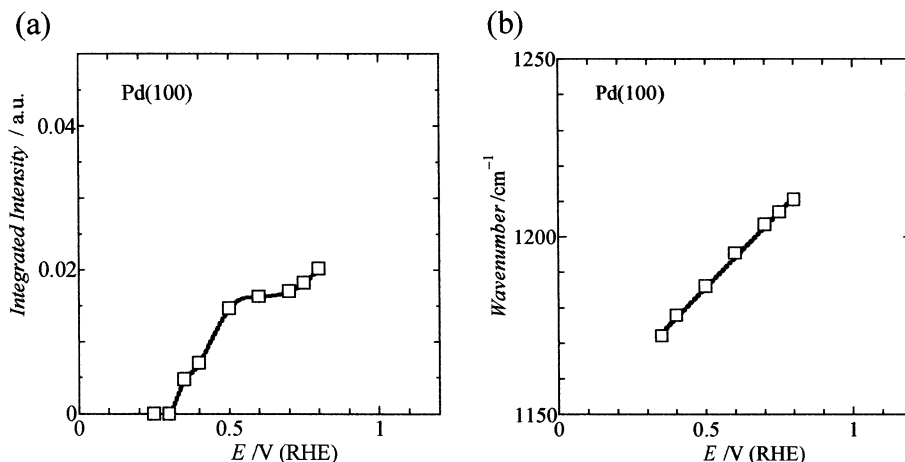
increase of the coverage is  $44\text{ }\mu\text{C cm}^{-2}$  according to the assumptions. It takes 10 s to scan from 0.5 to 0.7 V with the rate of  $0.02\text{ V s}^{-1}$ , giving the current density of  $4.4\text{ }\mu\text{A cm}^{-2}$ . This current density is comparable to the double layer charging current of Pd(111) in Figure 1. If the anion is coadsorbed with  $\text{H}_3\text{O}^+$  for reducing the repulsive coulomb interaction among anions as is the case of Pt(111),<sup>22,23,50,51</sup> the current density will be lower. Thus, the anion adsorbed above 0.5 V will hardly provide observable current in the voltammogram.

**IRAS Spectra on the Pd(100) Electrode.** Figure 5 depicts IRAS spectra of the Pd(100) electrode in 0.05 M  $\text{H}_2\text{SO}_4$ . A single band appears around  $1200\text{ cm}^{-1}$  above 0.35 V, which is almost identical with that of the anodic peak of the voltammogram in Figure 1.

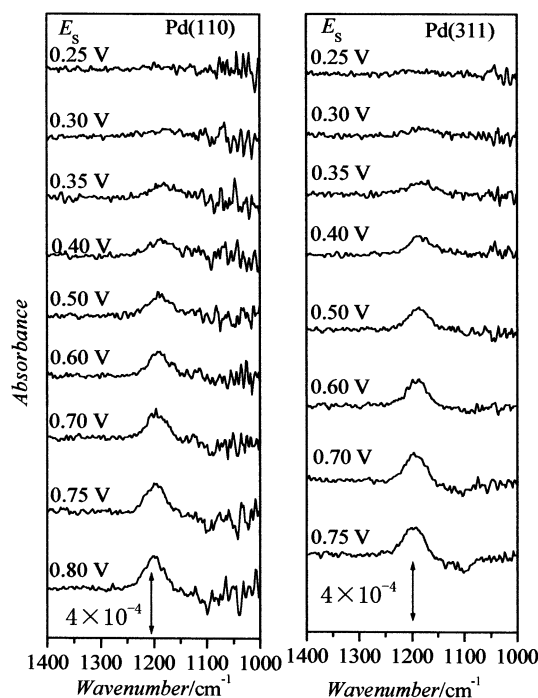
The feature of the IRAS band on Pd(100) differs significantly from that on Pt(100). The IRAS spectra of Pt(100) gives two IRAS bands around  $1200$  and  $1100\text{ cm}^{-1}$ , indicating that the sulfuric acid anion is adsorbed with 2-fold geometry.<sup>24,26</sup> The IRAS spectra of Pd(100), however, provide a single band. This fact suggests the following possibilities: (a) sulfuric acid anion is adsorbed on the surface with 1-fold or 3-fold geometry and (b) the sulfuric acid anion is adsorbed with 2-fold geometry as is the case of Pt(100), but the lower frequency band shifts out of the observable range of  $\text{CaF}_2$  window ( $<1000\text{ cm}^{-1}$ ).

The (100) surface cannot adsorb the sulfuric acid anion with 3-fold geometry; the 4-fold symmetry of the surface does not match with the triangle bottom plane of the anion. The position of the IRAS band of the sulfuric acid anion may not depend on metals remarkably, because the wavenumber of the IRAS band on Pd(111) is only  $30\text{ cm}^{-1}$  lower than that on Pt(111). Therefore, it is plausible that Pd(100) adsorbs the sulfuric acid anion with 1-fold geometry, as is the case of Au(100)<sup>29</sup> and Rh(100).<sup>30</sup> A single IRAS band supports that the anion is adsorbed upright on Pd(100). If the anion is tilted, the IRAS spectra will give the forbidden band  $\nu_{\text{as}}(\text{SO})$  as well as the symmetric vibrations, according to Table 1.

Figure 6 shows the potential dependence of the integrated band intensity and the position of the IRAS band on Pd(100). The integrated band intensity is enhanced monotonically with the increase of the potential (Figure 6a), but the maximum intensity is half as high as that on Pd(111) (Figure 3a). That is because the coverage of the sulfuric acid anion on Pd(100) is lower than that on Pd(111); the intensity of the negative-going band on Pd(100), which shows the decrease of the anion in the solution, is about half as high as that on Pd(111) at 0.7 V. These



**Figure 6.** Potential dependence of the IRAS band around  $1200\text{ cm}^{-1}$  on Pd(100) in 0.05 M  $\text{H}_2\text{SO}_4$ : (a) integrated intensity and (b) band peak position.



**Figure 7.** IRAS spectra of the sulfuric acid anion adsorbed on Pd(110) and Pd(311) in 0.05 M H<sub>2</sub>SO<sub>4</sub>. Sample potentials  $E_s$  are shown in the figure. The reference potential  $E_R$  is 0.20 V (RHE). Resolution: 4 cm<sup>-1</sup>. The spectra were averaged over 1000 scans.

results also suggest that IR absorptivity of the 1-fold sulfuric acid anion approximately equals that of the 3-fold anion. Pd(111) adsorbs the 3-fold sulfuric acid anion as well as the 1-fold one, accommodating more anions than Pd(100).

The band position depends linearly on the potential (Figure 6b), as is the case of Pd(111). The band shift ( $d\nu/dE$ ) is 75 cm<sup>-1</sup> V<sup>-1</sup>, which is a little bit larger than that of Pd(111).

**IRAS Spectra on the Pd(110) and Pd(311) Electrodes.** Pd(110) (2(111)–(111)) and Pd(311) (2(111)–(100)) electrodes also give a single IRAS band around 1200 cm<sup>-1</sup> in 0.05 M H<sub>2</sub>SO<sub>4</sub> solution as shown in Figure 7. The (111) terrace widths of these surfaces are too narrow to accommodate a sulfuric acid anion with 3-fold geometry; the sulfuric acid anion will be adsorbed with 1-fold geometry on the step site of the surfaces. Rh(110) also gives a single IRAS band around 1200 cm<sup>-1</sup> in

the solution containing SO<sub>4</sub><sup>2-</sup>.<sup>30</sup> Pt(110)<sup>25</sup> and Pt(311),<sup>26</sup> however, provide two IRAS bands around 1100 and 1200 cm<sup>-1</sup>, suggesting that the sulfuric acid anion is adsorbed with 2-fold geometry on the step.

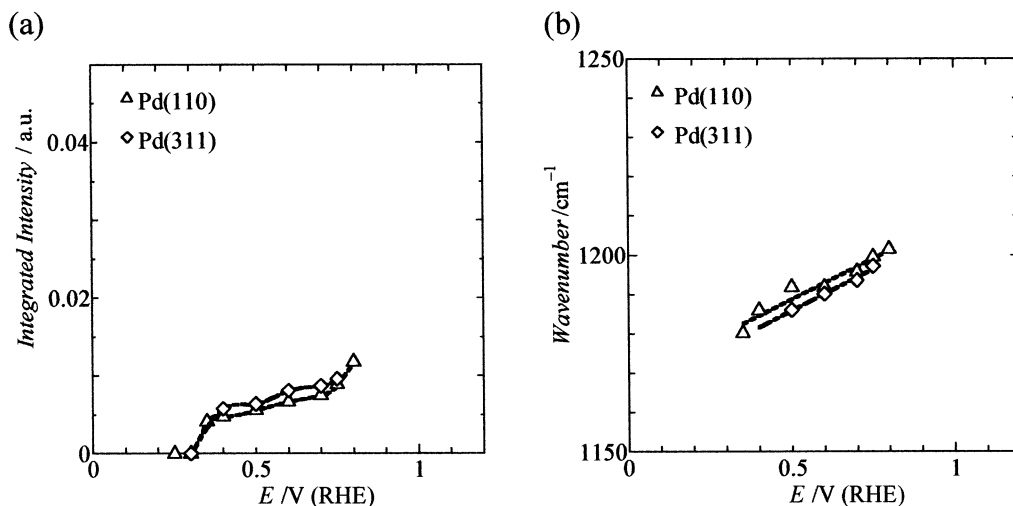
The integrated band intensity of Pd(110) is as high as that of Pd(311) (Figure 8a), increasing monotonically at positive potentials, as is the case of the other surfaces. The intensities of the stepped surfaces are, however, much lower than those of the flat surfaces. These facts suggest that the step site of Pd hardly adsorbs the sulfuric acid anion.

The IRAS spectra show that a trace of the sulfuric acid anion is adsorbed around 0.30 V. Voltammograms, however, show no peak due to the anion adsorption on Pd(110) and Pd(311). The coverage of the anion is too low to give peaks in the voltammogram.

The values of the band shift ( $d\nu/dE$ ) of the stepped surfaces (41 cm<sup>-1</sup> V<sup>-1</sup>) are lower than those on the terrace surfaces. This result differs from that of Pt single crystal electrodes: the IRAS band of the sulfuric acid anion on the step shifts more steeply than that on the terrace of Pt.<sup>26</sup> Some models are proposed for explaining the higher band shift on the step site of Pt,<sup>55,56</sup> but they cannot be applied to Pd. The difference of coverage between the stepped and the terrace surfaces will not affect the band shift, because the band shift does not correlate with the coverage as shown in Pd(111). The discrepancy between Pd and Pt stepped surfaces may be attributed to the difference of the donation and back-donation of the electron between the anion and the surface: a local electron orbital at Pd step might differ from that of the Pt step considerably. More IRAS data and a theoretical treatment of stepped surfaces are necessary for revealing this problem.

## Conclusion

1. IRAS spectra of the sulfuric acid anion give a single band around 1200 cm<sup>-1</sup> on Pd(111), Pd(100), Pd(110), and Pd(311) electrodes.
2. Onset potentials of sulfuric acid adsorption are close to the anodic bands of the voltammogram on Pd(111) and Pd(100).
3. Coverage of the sulfuric acid anion on the flat surfaces is higher than that on the stepped surfaces.
4. The flat surfaces give higher values of the band shift ( $d\nu/dE$ ) than the stepped surfaces.



**Figure 8.** Potential dependence of the IRAS band around 1200 cm<sup>-1</sup> on Pd(110) and Pd(311) in 0.05 M H<sub>2</sub>SO<sub>4</sub>: (a) integrated intensity and (b) band peak position.

**Acknowledgment.** This study was partially supported by grant-in-aid of scientific research from Ministry of Education and Science of Japan No. 12650805.

## References and Notes

- (1) Adzic, R. In *Modern Aspects of Electrochemistry* Vol. 21; White, R. E., Bockris, J. O'M., Conway, B. E., Eds.; Plenum Press: New York, 1990; Chapter 5.
- (2) Lamy, C.; Leger, J. M. *J. Chim. Phys.* **1991**, 88, 1649 and references therein.
- (3) Clavilier, J.; Faure, R.; Guinet, G.; Durand, R. *J. Electroanal. Chem.* **1980**, 107, 205.
- (4) Hoshi, N.; Kagaya, K.; Hori, Y. *J. Electroanal. Chem.* **2000**, 485, 55.
- (5) Hoshi, N.; Kuroda, M.; Hori, Y. *J. Electroanal. Chem.* **2002**, 521, 155.
- (6) Clavilier, J.; Armand, D.; Wu, B. L. *J. Electroanal. Chem.* **1982**, 135, 159.
- (7) Ross, P. N. *J. Chim. Phys.* **1991**, 88, 1353.
- (8) Marković, N. M.; Marinković, N. S.; Ažić, R. R. *J. Electroanal. Chem.* **1988**, 241, 309.
- (9) Marković, N. M.; Marinković, N. S.; Ažić, R. R. *J. Electroanal. Chem.* **1991**, 314, 289.
- (10) Kita, H.; Gao, Y.; Nakato, T.; Hattori, H. *J. Electroanal. Chem.* **1994**, 373, 177.
- (11) Marković, N. M.; Ross, P. N. *J. Electroanal. Chem.* **1992**, 330, 499.
- (12) Kita, H.; Gao, Y.; Ohnishi, K. *Chem. Lett.* **1994**, 73.
- (13) Hoshi, N.; Suzuki, T.; Hori, Y. *J. Electroanal. Chem.* **1996**, 416, 61.
- (14) Kunimatsu, K.; Samant, M. G.; Seki, H.; Philpott, M. R. *J. Electroanal. Chem.* **1988**, 243, 203.
- (15) Kunimatsu, K.; Samant, M. G.; Seki, H. *J. Electroanal. Chem.* **1989**, 258, 163.
- (16) Faguy, P. W.; Marković, N. M.; Ažić, R. R.; Fierro, C. A.; Yeager, E. B. *J. Electroanal. Chem.* **1990**, 289, 245.
- (17) Nichols, R. J. In *Adsorption of Molecules at Metal Electrodes*; Lipkowski, J. L., Ross, P. N., Jr., Eds.; VCH: New York, 1991; Chapter 7.
- (18) Sawatari, Y.; Inukai, J.; Ito, M. *J. Electron Spectrosc.* **1993**, 64/65, 515.
- (19) Nart, F. C.; Iwasita, T.; Weber, M. *Electrochim. Acta*, **1994**, 39, 961.
- (20) Shingaya, Y.; Ito, M. *Chem. Phys. Lett.* **1996**, 256, 438.
- (21) Thomas, S.; Sung, Y.-E.; Kim, H. S.; Wieckowski, A. *J. Phys. Chem.* **1996**, 100, 11726.
- (22) Faguy, P. W.; Marinković, N. S.; Ažić, R. R. *Langmuir* **1996**, 12, 243.
- (23) Faguy, P. W.; Marinković, N. S.; Ažić, R. R. *J. Electroanal. Chem.* **1996**, 407, 209.
- (24) Nart, F. C.; Iwasita, T.; Weber, M. *Electrochim. Acta* **1994**, 39, 2093.
- (25) Iwasita, T.; Nart, F. C.; Rodes, A.; Pastor, E.; Weber, M. *Electrochim. Acta* **1995**, 40, 53.
- (26) Hoshi, N.; Sakurada, A.; Nakamura, S.; Teruya, S.; Koga, O.; Hori, Y. *J. Phys. Chem. B* **2002**, 106, 1985.
- (27) Edens, G. J.; Gao, X.; Weaver, M. J. *J. Electroanal. Chem.* **1994**, 375, 357.
- (28) Ataka, K.; Osawa, M. *Langmuir* **1998**, 14, 951.
- (29) Moraes, I. R.; Nart, F. C. *J. Electroanal. Chem.* **1999**, 461, 110.
- (30) Moraes, I. R.; Nart, F. C. *J. Braz. Chem. Soc.* **2001**, 12, 138.
- (31) Hoshi, N.; Tanizaki, M.; Koga, O.; Hori, Y. *Chem. Phys. Lett.* **2001**, 336, 13.
- (32) Furuya, N.; Koide, S. *Surf. Sci.* **1989**, 220, 18.
- (33) Motoo, S.; Furuya, N. *J. Electroanal. Chem.* **1984**, 172, 339.
- (34) Solomun, T. *J. Electroanal. Chem.* **1987**, 217, 435.
- (35) Sashikata, K.; Matsui, Y.; Itaya, K.; Soriaga, M. P. *J. Phys. Chem.* **1996**, 100, 20027.
- (36) Wan, L.-J.; Suzuki, T.; Sashikata, K.; Okada, J.; Inukai, J.; Itaya, K. *J. Electroanal. Chem.* **2000**, 484, 189.
- (37) Kim, Y.-G.; Soriaga, J. B.; Vigh, G.; Soriaga, M. P. *J. Colloid Interface Sci.* **2000**, 227, 505.
- (38) Clarke, J. H. R.; Woodward, L. A. *Trans. Faraday Soc.* **1961**, 57, 1286.
- (39) Dawson, B. S.; Irish, D. E.; Toogood, G. E. *J. Phys. Chem.* **1986**, 90, 334.
- (40) Kolics, A.; Wieckowski, A. *J. Phys. Chem. B* **2001**, 105, 2588.
- (41) Alvarez, B.; Climent, V.; Rodes, A.; Feliu, J. M. *J. Electroanal. Chem.* **2000**, 497, 125.
- (42) Holloway, S.; Korsknov, J. K. *J. Electroanal. Chem.* **1984**, 161, 193.
- (43) Lambert, D. K. *Phys. Rev. Lett.* **1983**, 50, 2106.
- (44) Person, B. N. J.; Ryberg, R. *Phys. Rev. B* **1981**, 24, 6954.
- (45) Tanaka, N.; Sugi, H.; Fujita, J. *Bull. Chem. Soc. Jpn.* **1964**, 37, 640.
- (46) Chia, P. S. K.; Lindoy, L. F.; Livingstone, S. E. *Inorg. Chim. Acta* **1968**, 2, 459.
- (47) Wan, L.-J.; Yau, S.-L.; Itaya, K. *J. Phys. Chem.* **1995**, 99, 9507.
- (48) Funtikov, A. M.; Stimming, U.; Vogel, R. *J. Electroanal. Chem.* **1997**, 428, 147.
- (49) Wan, L.-J.; Hara, M.; Inukai, J.; Itaya, K. *J. Phys. Chem. B* **1999**, 103, 6978.
- (50) Shingaya, Y.; Hirota, K.; Ogasawara, H.; Ito, M. *J. Electroanal. Chem.* **1996**, 409, 103.
- (51) Shingaya, Y.; Ito, M. *Chem. Phys. Lett.* **1996**, 256, 438.
- (52) Leung, L.-W. H.; Wieckowski, A.; Weaver, M. J. *J. Phys. Chem.* **1988**, 92, 6985.
- (53) Chang, S.-C.; Weaver, M. J. *Surf. Sci.* **1990**, 230, 222.
- (54) Lei, H.-W.; Uchida, H.; Watanabe, M. *J. Electroanal. Chem.* **1996**, 413, 131.
- (55) Greenler, R. G.; Dudek, J. A.; Beck, D. E. *Surf. Sci.* **1984**, 145, L453.
- (56) Wang, H.; Tobin, R. G.; Lambert, D. K.; Fisher, G. B.; DiMaggio, C. L. *J. Chem. Phys.* **1995**, 103, 2711.