8 June 2001

ELSEVIER

Chemical Physics Letters 340 (2001) 425–430

CHEMICAL PHYSICS LETTERS

www.elsevier.nl/locate/cplett

Temperature dependence of adlayers on Pt(1 1 1) and Au(1 1 1) in a sulfuric acid solution studied by in situ IRAS

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Received 14 September 2000; in final form 13 March 2001

Abstract

Temperature dependence studies of adsorption of sulfuric acid species on Pt(1 1 1) and Au(1 1 1) electrodes were carried out using in situ infrared reflection absorption spectroscopy. A temperature-dependent shift of the interconversion potential between HSO_4^-/H_3O^+ and H_2SO_4 on a Pt(111) electrode was observed. A temperature-dependent frequency shift of the absorption bands of HSO_4^- was also observed on both Pt(1 1 1) and Au(1 1 1) electrodes in the potential region where a $\sqrt{3} \times \sqrt{7}$ structure evolved. Modelling experiments in ultrahigh vacuum revealed that ordering of the overlayer water molecules played an important role in the frequency of the absorption bands of HSO_4^-. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

A Pt(1 1 1) electrode in an aqueous H_2SO_4 solution is one of the fundamental systems in electrochemistry and has been studied widely [1–16] since Clavilier published a characteristic cyclic voltammogram (CV) in the system [1,2]. It is well known that the CV profile is ascribed to adsorption and desorption of both hydrogen and anions [14–16]. The adsorption of sulfuric acid species on Pt(1 1 1) has been studied by in situ measurements such as IR [3–9], scanning tunneling microscopy (STM) [10,11], radiochemistry [12] and chronocoulometry [13]. Sulfuric acid species on Pt(1 1 1) have also been observed under UHV conditions using IR [17–21], low-energy electron diffraction (LEED) [20–22], Auger electron spectroscopy (AES) [22], thermal desorption spectroscopy (TDS) [17–19] measurements. The results show that bisulfate species are adsorbed at potentials more positive than 400 mV and form an ordered $\sqrt{3} \times \sqrt{7}$ structure in the potential range between 500 and 700 mV [19]. Despite the thorough studies of the system, almost nothing was known about the temperature dependence of the CV. Recently, Zolfaghari et al. reported a quite interesting temperature dependence of the CV profile for a Pt(1 1 1) electrode in a 0.5 M H_2SO_4 solution [23]. In this Letter, it is shown that current peaks corresponding to hydrogen adsorption or desorption shift to a negative direction and that sharp spikes at around 450 mV shift to a positive direction with a rise in temperature. It is also reported that asymmetric peaks at around 700 mV shift to a negative direction with a rise in temperature.

In this Letter, we discuss the influence of temperature changes on the adlayer of sulfuric acid species on Pt(1 1 1) and Au(1 1 1) electrodes using

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PII: S0009-2614(01)00374-8

in situ infrared reflection absorption spectroscopy (IRAS). A UHV modelling technique is also executed in order to discuss structure of water layers on the adsorbed HSO_4^-/H_3O^+ species.

2. Experimental

In situ IRAS measurements were carried out using a FTS-45RD Fourier transform infrared spectrometer (BIO-RAD) with a liquid nitrogen cooled MCT detector. CaF_2 was used as a prism window and an incident angle of IR beam was 65°. IRAS measurements were carried out with a kinetic sampling method with 4 cm^{-1} resolution during a potential sweep of 5 mV/s. Six consecutive spectra were co-added, and the interval of the electrode potentials between co-added spectra was 10 mV. The temperature of the system was controlled with an electric heater which was wrapped around the IR cell. The reference electrode was $Hg/Hg_2SO_4/0.5$ M H_2SO_4, but values of electrode potential are quoted versus the standard hydrogen electrode (SHE) in this Letter. The reference electrode was maintained at room temperature.

The experimental details of the UHV modelling technique were described elsewhere [19]. A home-made UHV apparatus was used. The Pt(1 1 1) surface was prepared by a conventional cleaning method. The adsorbed sulfuric acid species were formed from H_2O and SO_3 in the UHV chamber. IRAS measurements under UHV conditions were carried out using a system 2000 Fourier transform infrared spectrometer (Perkin-Elmer).

3. Results and discussion

3.1. Temperature dependence of in situ IRA spectra from a Pt(1 1 1) electrode in a sulfuric acid solution

A large temperature dependence of asymmetric current peaks was reported at around 700 mV in a CV of a Pt(1 1 1) electrode in a 0.5 M H_2SO_4 solution [23]. We paid attention to this point. We reported previously that the current peak was ascribed to the current associated with the interconversion between the HSO_4^-/H_3O^+ ion pair and the H_2SO_4 adlayer on a Pt(1 1 1) electrode [17]. Therefore, it is expected that the potential at which the interconversion occurs shifts upon a variation in temperature. In situ IRAS measurements were carried out at various temperatures in order to investigate the temperature dependence of the interconversion. Fig. 1 shows in situ IRA spectra from a Pt(1 1 1) electrode in a 0.5 M H_2SO_4 solution obtained at 297 K (solid line), and 350 K (dotted line), respectively. The spectra were obtained with 4 cm^{-1} resolution and 6 scans co-addition during an anodic potential sweep of 200–800 mV. The spectrum at 200 mV was referred to the background and the sweep rate was 5 mV/s. Absorption bands in the spectra are

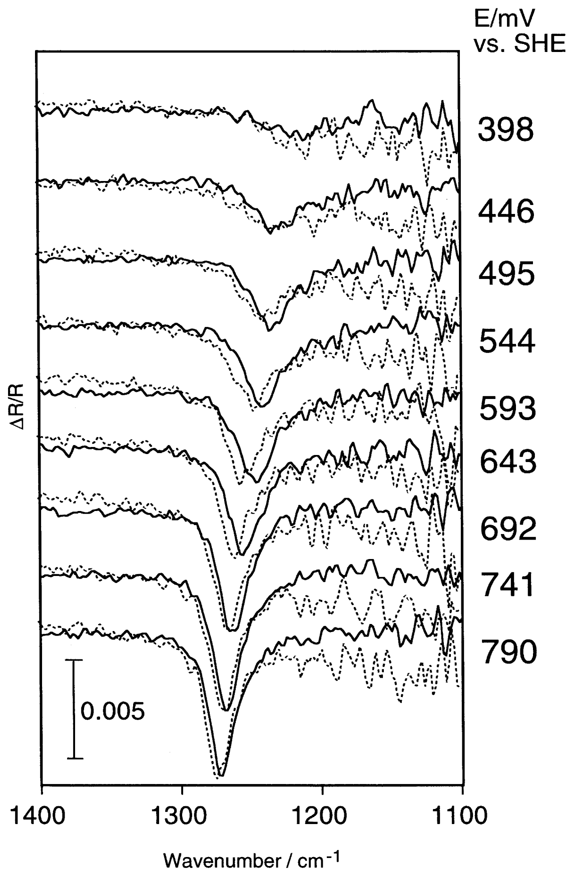

Fig. 1. In situ IRA spectra from a Pt(1 1 1) electrode in a 0.5 M H_2SO_4 solution. The spectra were obtained at 297 K (solid line) and 350 K (dotted line).

assignable to the SO_3 symmetric stretching of HSO_4^- and the SO_2 symmetric stretching of H_2SO_4 [19]. The spectral features of both temperatures resemble each other in both frequency and intensity on the whole.

We reported the frequency shift of S–O stretching band of HSO_4^- adsorbed on electrode surface is related to an electronic state of the metal and an orientation of hydration water molecules on the surface [24]. It is interesting to note that the deviation of the peaks from lower (solid line) and higher (dotted line) temperature phases is largest at potential ranges where a $\sqrt{3} \times \sqrt{7}$ structure is formed and smallest at negative potential ranges where the coverage of sulfuric acid species on the surface is not enough to form ordered adlayer. Since a discontinuity in the band center frequency vs. potential plot appeared at the potential where the interconversion between HSO_4^-/H_3O^+ and H_2SO_4 occurs at room temperature [17], the band center frequency was plotted as a function of potential as shown in Fig. 2. The upper and lower plots represent the anodic and cathodic sweeps, respectively. In the graphs, it is shown that the discontinuous points of the frequency shift toward negative potentials as the temperature increases. This means that the potential at which the interconversion between HSO_4^-/H_3O^+ and H_2SO_4 adlayer takes place depends on temperature. This finding coincides with the result of the CV.

This temperature dependence of the interconversion potential can be explained as follows. We reported previously that the HSO_4^-/H_3O^+ adlayer forms a hydrogen bonding network as shown in Fig. 3. The model is based on UHV modelling of the HSO_4^-/H_3O^+ adlayer on Pt(1 1 1) [19]. The fact that the asymmetric bending mode of H_3O^+ appeared in the IRA spectrum while the symmetric mode was missing indicates that the molecular C_3 axis of the adsorbed H_3O^+ is parallel to the surface [19]. TDS measurements of water molecules showed the existence of one additional hydration water in the adlayer. However, the bands of hydration water were absent in the IRA spectrum. The results indicate that the hydration water is adsorbed in a molecular plane parallel to the surface as shown in the figure. It is clearly shown that the $\sqrt{3} \times \sqrt{7}$ structure was stabilized through the

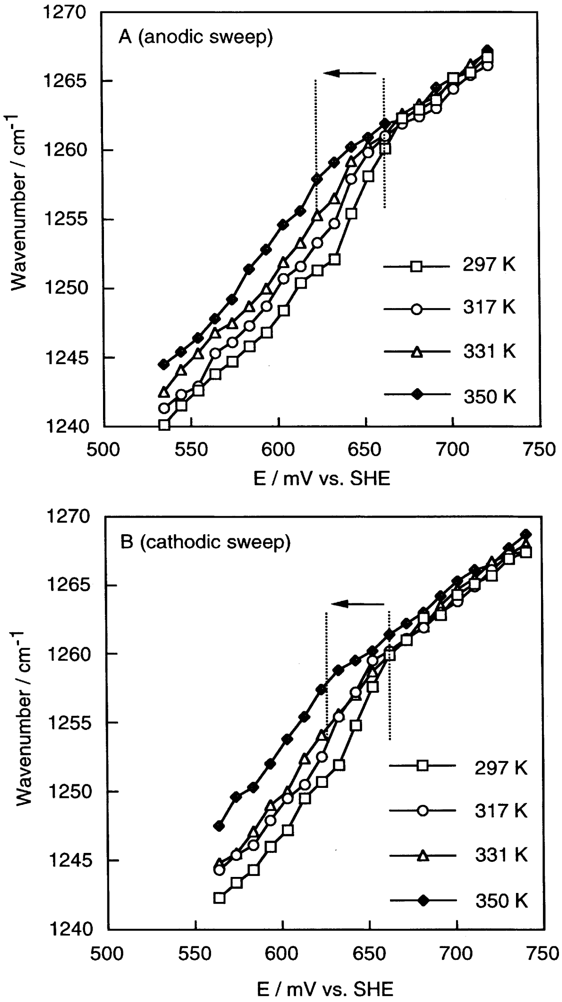

Fig. 2. The band center frequencies of adsorbed sulfuric acid species as a function of the electrode potential: (A) anodic sweep, (B) cathodic sweep. The spectra were obtained at 297, 317, 331 and 350 K.

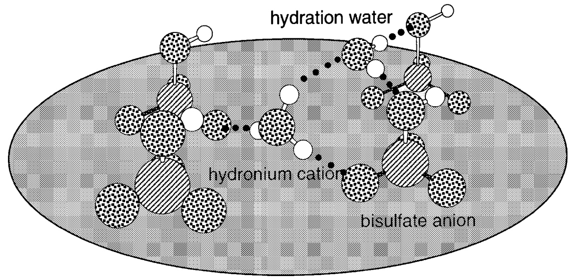

Fig. 3. A schematic diagram of HSO_4^-, H_3O^+ and H_2O on Pt(1 1 1).

hydrogen bonding network between the ion pairs and the water molecule. The network structure is unfavorable as far as entropy is concerned. Density functional molecular orbital calculations also indicate that formation of a hydrogen bonding network in ionic $HSO_4^-/H_3O^+(H_2O)_n$ clusters is accompanied by destabilization due to entropy factors [25]. On the contrary, the H_2SO_4 adlayer does not form a hydrogen bonding network and an adsorbed H_2SO_4 may translate or rotate on the surface, so that an H_2SO_4 adlayer can benefit from the entropy factor due to a temperature rise. Therefore, the HSO_4^-/H_3O^+ adlayer becomes unstable as temperature increases and the equilibrium potential between HSO_4^-/H_3O^+ and H_2SO_4 adlayer shifts toward the negative.

Another finding in Figs. 1 and 2 is that while the frequency of the SO_2 symmetric stretching of H_2SO_4 is almost independent of temperature, the frequency of the SO_3 symmetric stretching of HSO_4^- increases with rising temperature. In the UHV measurements, the frequency of the SO_2 symmetric stretching of H_2SO_4 adsorbed on Pt(1 1 1) is independent of temperature, which is in good agreement with the result of in situ IRAS for H_2SO_4 and is quite reasonable. The frequency shift of the HSO_4^- band upon variation in temperature is about 0.085 cm^{-1}/K. Since the integrated intensity of the band is almost the same, a dipole–dipole coupling effect is excluded from the reason of the frequency shift. One of the candidates is the effect of the hydronium (oxonium) cation as a counter cation. The oxonium perchlorate crystal has a layer structure similar to that of the HSO_4^-/H_3O^+ adlayer. And it has been reported that the H_3O^+ orientations in the hydrogen bonding network of oxonium perchlorate became disordered at high temperatures [26]. Therefore, one possible reason for the frequency shift might be a change in the conformation of the HSO_4^-/H_3O^+ adlayer.

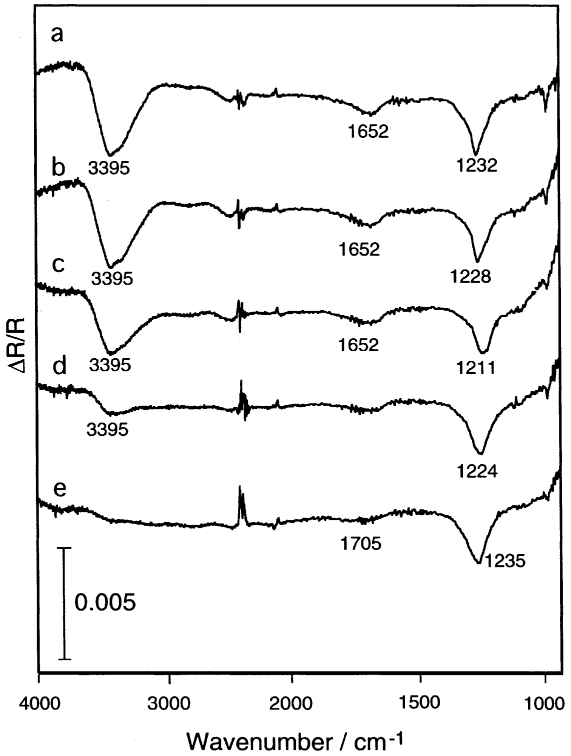

Fig. 4. IRA spectra of adsorbed HSO_4^- and 2 ML H_2O on Pt(1 1 1) in UHV at 110 K (a). After annealing at (b) 138 K, (c) 151 K, (d) 162 K, (e) 186 K.

3.2. UHV modelling of HSO_4^- and H_2O on Pt(1 1 1)

A more reasonable explanation for the temperature-dependent frequency shift of the adsorbed HSO_4^- can be given from the results of UHV modelling experiments. The structure of the water layer on top of the HSO_4^-/H_3O^+ adlayer would become important. Fig. 4 shows IRA spectra of adsorbed HSO_4^- and H_2O on the Pt(1 1 1) surface obtained under UHV conditions. Spectrum (a) was obtained by the formation of about a 1 ML HSO_4^-/H_3O^+ adlayer followed by the addition of 2 ML H_2O at 110 K. The adsorption bands at 1232 and 3395 cm^{-1} can be assigned to the SO_3 stretching mode of the adsorbed HSO_4^- and to the OH stretching mode of the H_2O molecules in the hydration layer on top of the HSO_4^-/H_3O^+ adlayer, respectively. Spectra (b) to (e) were obtained by heating the sample stepwise to 138, 151, 162 and 186 K. The absorption bands of the HSO_4^- and H_2O adlayer change together by annealing. While the intensity of the H_2O band decreases at annealing temperatures higher than 151 K because of thermal desorption, the frequency of the HSO_4^- band shifts continuously to lower values up to 151 K then at still higher annealing temperatures, the band shifts back to the original frequency value.

These results arise from the behavior of the H_2O on top of the HSO_4^-/H_3O^+ adlayer. At 110 K, the H_2O molecules would exhibit relatively random orientations. Since the HSO_4^-/H_3O^+ adlayer forms $\sqrt{3} \times \sqrt{7}$ structure which has a hydrogen bonding network, the water on top of the layer should form an ordered layer affected by the underlying ordered layer (HSO_4^-/H_3O^+) through hydrogen bonding. The ordered water layer extends gradually by annealing the sample. The remarkably large frequency shift of the HSO_4^- band observed at 151 K is ascribed to the ordered H_2O layer. The preferential orientation of H_2O molecules which have a permanent dipole moment would induce a charge in the first adlayers on Pt(1 1 1). As a result, the absorption band of HSO_4^- shifts to lower frequency. The preferential orientation of the overlayer water induced by adsorbed Br in the first layer on Ag(1 1 0) was also shown by Bange et al. [27] under UHV conditions. A negative frequency shift was also observed in the case of CO co-adsorbed with water on Pt(1 1 1) by annealing the sample under UHV conditions [28]. The disappearance of the H_2O band at higher temperatures indicates that the H_2O molecules are desorbed from the surface. Since the H_2O layer does not affect the HSO_4^-/H_3O^+ adlayer and substrate any more, the frequency of the HSO_4^- band recovers a value close to spectrum (a).

The explanation for the water-induced frequency shift can hold for the case of temperature variations. A continuous frequency shift of the SO_3 symmetric stretching mode of the adsorbed HSO_4^- towards higher value was observed with increasing temperature as shown in Figs. 1 and 2. The ordered H_2O layer which should be on top of the HSO_4^- layer, would fall into disorder with increases in temperature because of thermal motion. Therefore, the in situ IRA spectra obtained at higher and lower temperatures correspond to spectra (a) and (c), respectively, in Fig. 4. In the case of H_2SO_4, which is adsorbed at potentials higher than 700 mV, the frequency would be temperature independent because of the lack of a hydrogen bonding network.

3.3. Temperature dependence of in situ IRA spectra from an Au(1 1 1) electrode in a sulfuric acid solution

The $\sqrt{3} \times \sqrt{7}$ structure has been observed on an Au(1 1 1) electrode in a sulfuric acid solution at potentials more positive than that of the sharp spike found around 1050 mV in a CV and various structural models was proposed [29–31]. Since a temperature dependence of the IRA spectra was expected, we carried out in situ IRAS measurements of an Au(1 1 1) electrode in a 0.5 M sulfuric acid solution as a function of temperature. The spectra were obtained by the same method as in the case of Pt(1 1 1). The range of the potential sweep was 700–1300 mV, and background spectra were obtained at 500 mV. Fig. 5 shows the band center frequencies of adsorbed sulfuric acid species plotted as a function of electrode potential which were observed at 296, 311, 331 and 341 K. In this figure, the temperature dependence of the frequency is clearly shown. While there is almost no temperature dependence at potentials more negative than 1000 mV, in the positive potential region,

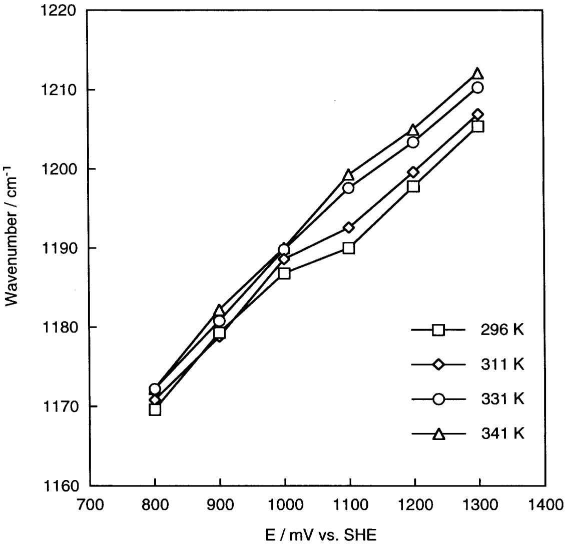

Fig. 5. The band center frequencies of adsorbed sulfuric acid species on a Au(1 1 1) electrode as a function of the electrode potential. The spectra were obtained at 296, 311, 331 and 341 K.

the frequencies shift to higher values with temperature increases.

These results coincide well with the case of Pt(1 1 1), and the temperature-dependent frequency can be ascribed to the behavior of the water adlayer as well. Since in situ STM measurements show that the $\sqrt{3} \times \sqrt{7}$ structure forms at potentials more positive than 1050 mV, the divergence in Fig. 5 is ascribed to temperature-dependent ordering of the water layer affected by the $\sqrt{3} \times \sqrt{7}$ structure. The rate of the frequency shift of 0.15 $\mathrm{cm^{-1}/K}$ is larger than that on Pt(1 1 1). Information regarding the structural details of the water layer is needed to reach a quantitative explanation of the frequency shift.

4. Conclusion

A temperature-dependent shift of interconversion potential between HSO_4^-/H_3O^+ and H_2SO_4 on a Pt(1 1 1) electrode was observed using in situ IRAS. We propose that the negative shift of the interconversion potential on an increased temperature arises from destabilization of the HSO_4^-/H_3O^+ layer because of the entropy factor. The temperature-dependent frequency shift was also observed both on Pt(1 1 1) and Au(1 1 1) electrodes in the potential region where $\sqrt{3} \times \sqrt{7}$ structure evolved. The higher frequency shift due to rising temperature is ascribed to disordering of the overlayer water which has a preferential orientation at room temperature (lower temperature).

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