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In situ Infrared Reflection Absorption Spectroscopy at an Electrode-Electrolyte Interface in the Fingerprint Wave-Number Region

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Abstract

In order to extend the wave number to the fingerprint region in *in situ* infrared spectroscopy for an electrode system, new techniques were developed. First, a new test cell equipped with a micrometer attached to the test electrode and an O-ring for setting an optical window was made of Kel-F. The cell prepared a thin electrolyte layer imposed between the window and the test electrode, as a stable state during experiments. Next, a new manipulation system for treating the piston attached to the test electrode was devised. This made it possible to manipulate the piston without any interference with the purging effect of N₂ gas. With these new techniques we succeeded in the acquisition of significant signals of monolayer-adsorbed aromatic thiols in the fingerprint region.

The spectra showed that both 2,5-dihydroxythiophenol (DTH) and p-mercaptophenol (MP) adsorbed on the surface of gold with the molecular plane nearly perpendicular to the electrode surface and that the oxidation states changed with the potential changes.

1. Introduction

Infrared spectroscopy of molecules adsorbed on a metal surface provides fundamental information about the modification of metal surfaces and electrocatalytic reactions. Since the Southampton group succeeded in the application of infrared spectroscopy to an electrode system, by the *in situ* outer reflection absorption technique^{1,2}, this method has become one of the most powerful techniques to elucidate electrode kinetics and to develop modified electrodes, and many groups around the world have applied the technique to electrode systems. Even though great efforts have been made to improve the technique, the wave number region where significant peaks can be obtained is still limited and vibration modes are also limited to very strong signals such as the C-O stretching of carbon monoxide, the C=O stretching of aldehyde, the C≡N stretching of cyanide and so on.

We developed new techniques in order to extend the applicable wave number to the fingerprint region^{3,4}, where the signals contain much information about organic molecules adsorbed on electrode surfaces. The objective of this study is to report these new techniques and to demonstrate some results for 2, 5-dihydroxythiophenol (DTH) and p-mercaptophenol

(MP) adsorbed on polycrystalline gold surfaces.

2. Experimental

Application of *in situ* infrared spectroscopy to an electrode system involves special difficulties, since the signals from monolayer-adsorbed molecules are very small and water strongly absorbs infrared light. To overcome these difficulties, the electrolyte layer between a working electrode and an optical window should be made as thin as possible, only a few microns thick, and should be stable during a series of experiments. Therefore it is essential to set the working electrode strictly parallel to the optical window.

The test cell prepared for both electrochemical and spectroscopic experiments and the reservoir for solutions are schematically presented in Fig. 1.

The cell is composed of a body block and a piston made of Kel-F rods and an optical window made of a 65° calcium fluoride dove prism connected with the body by using an O-ring. The window plane can be set strictly parallel to the electrode surface by setting the three screws of the window holder (not shown in the figure) with the guidance of interference rings formed in the thin electrolyte layer. The working electrode is pushed against the window or withdrawn from it by manipulating the micrometer, which fixes the thickness of the electrolyte film stably. This was accomplished by using the O-ring and the micrometer. Usually we carried out both spectroscopic and electrochemical experiments while pushing the electrode surface against the window.

The reservoir, made of pyrex glass, has a compartment for a reference electrode, and is electrically connected with the test cell through an electrolyte in a thin teflon tube.

The test electrode was prepared by molding a gold plate (99.99 %, Johnson Matthey Co.) in Kel-F powder at 300 °C under high pressure⁵⁾ and working it with a lathe. The counter electrode was a platinum wire, and a saturated calomel electrode or a silver-silver chloride electrode was employed as a reference electrode. The potential is described by referring to NHE in this work.

Solutions were made with Ultrex grade HClO₄ (Baker) and triply distilled water and were thoroughly deaerated with high-purity N₂ gas. In this study, 0.1 M HClO₄ was used throughout all experiments as a base electrolyte. DHT was synthesized by the method of Alcalay⁶⁾, and later extracted and recrystallized in ether. MP of reagent grade was used as received (Wako Pure Chemical Ind. Ltd.).

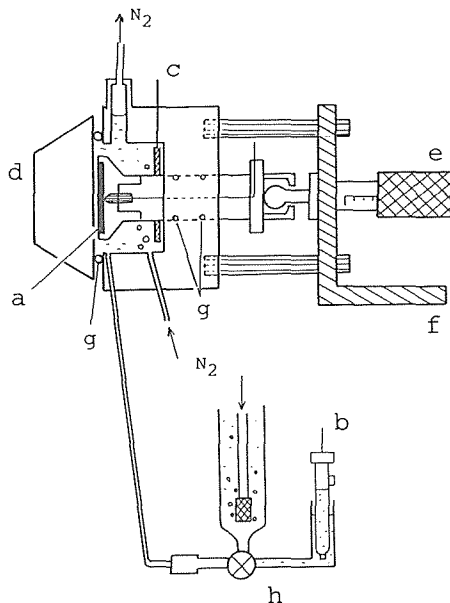


Fig. 1 Schematic diagram of a spectroelectrochemical cell and a reservoir. a: test electrode (Au plate), b: reference electrode, c: counter electrode (Pt wire), d: CaF₂ window, e: micrometer, f: cell holder, g: o-ring, h: reservoir.

The optical arrangement in the sample room of the Fourier transform infrared spectrometer (IR/98, IBM Instruments, Inc. or FT/IR 8000, Japan Spectroscopic Co., Ltd.) and the measurement apparatus are shown in Fig. 2.

A p-light selected by a polarizer radiated to the electrode with an incident angle of 65° and went into a liquid-nitrogen-cooled HgCdTe detector. During the measurements, the piston was manipulated from outside the sample room, which was purged continuously with N_2 gas throughout all experiments. This manipulation did not interfere with any purging effect of the sample room, and it led to success in the acquisition of spectra in the fingerprint region. This is the other main point of this technique, because atmospheric water also hides most of the significant peaks in this wave-number region.

The test electrode was polished to an mirror finish with a series of alumina powders of successively smaller size down to $0.3 \mu\text{m}$. After rinsing with alcohol and distilled water, the electrode was cleaned by ultrasonic waves for a short time. Before every experiment the electrode was cleaned by cycling potential between hydrogen evolution and oxygen evolution in 0.1 M HClO_4 , until the characteristic features of clean surfaces appeared.

After cleaning the electrode, the electrolyte was replaced with a solution containing 10 mM organic materials several times, finally keeping the solution in the cell for 10 minutes to place organic materials in contact with the electrode. Next, the solution was replaced with neat perchloric acid several times to remove the organic materials remaining in the electrolyte without adsorption to the electrode. Then, the electrode was pushed against the window and the spectroscopic or electrochemical experiments were carried out.

In the optical experiments, the spectra were acquired and plotted by SNIFTIRS (subtracted normalized interfacial Fourier transform infrared spectroscopy). By this technique a reference spectrum is acquired at a special value as a reference potential and sample spectra are measured at the desired sample potentials. The reflectivity difference between the sample and the reference is divided by the reference reflectivity for normalization, which can make a small signal originating from a monolayer substance very clear. In the spectra plotted by this formula, positive-going peaks come from the sample and negative-going peaks come from reference states.

The interferograms between 1000 and 2000 were collected and co-added at each potential to improve the S/N ratio.

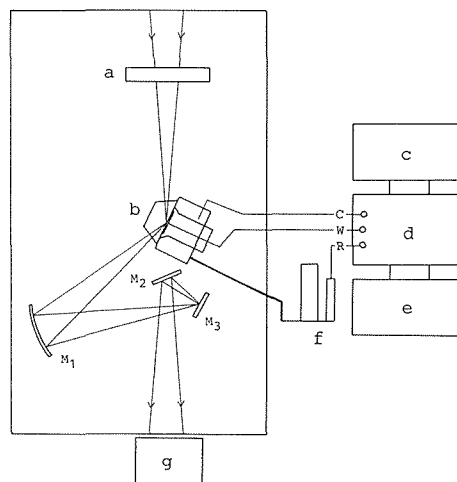


Fig. 2 Optical arrangement and measurement apparatus. a: polarizer, b: spectroelectrochemical cell, c: function generator, d: potentiostat, e: recorder, f: reservoir, g: HgCdTe detector, M₁: spherical mirror, M₂, M₃: plane mirror.

3. Results and discussion

A cyclic voltammogram of DHT and that of MP are shown in Fig. 3 and Fig. 4, respectively. As shown in the figures, there is one peak on the oxidation wave and one on the reduction wave for both compounds. Neither the positions nor the heights of these peaks change with repetitions of the cycling potential and replacements of the electrolyte.

Since DHT adsorbs to Au electrodes forming a mercaptide bond between S and Au⁷, it is concluded from Fig. 3 that DHT adsorbs irreversibly on the surface of gold and the redox reaction occurs reversibly as it adsorbs; the reduced state is the hydroquinone-type and the oxidized state is the quinone-type.

The quantities of electricity shown by the peak areas in Fig. 3 are nearly the same and equal to ca. 1.4×10^{-4} coulomb/cm² (7.3×10^{-10} mol/cm²). According to Soriaga and co-workers⁸, this value corresponds to the full monolayer coverage of DHT when the roughness factor of the electrode is 1.3, which is a reasonable value for the mirror-finished surface of gold.

The quantity of electricity for MP is, on the other hand, 3.7×10^{-5} coulomb/cm². The coverage is calculated to be nearly 0.5 by assuming that the occupation area of MP is nearly equal to DHT, since we do not have any data about the occupation area of MP.

A series of spectra were measured by SNIFTIRS in the DHT system and the results are presented in Fig. 5. As indicated in Fig. 5, first, a number of positive- and negative-going peaks could be clearly identified at the potential of +0.84 V, after which they disappeared at +0.34 V. This is consistent with the cycling voltammogram in Fig. 3, that is, the materials were in the oxidized state at +0.84 V, and at +0.34 V, they returned to the reduced state and the peaks disappeared, since the reference spectrum is for the reduced state. The rather strong signals observed suggest that the various normal vibration modes have dynamic dipole moments with components along a direction perpendicular to the electrode surface and that the modes are capable of interacting with the electric field vector for light polarized parallel to the plane of incidence. This provides evidence that the adsorbate, both in the

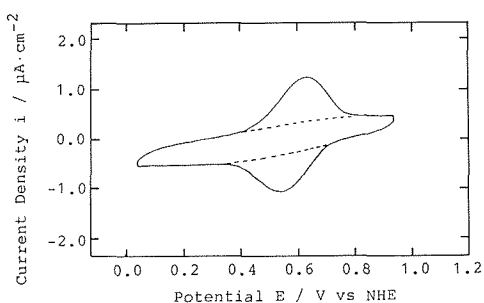


Fig. 3 Cyclic voltammogram of monolayer-adsorbed DHT on a Au electrode (surface area is 1.7 cm²). Scan rate is 1 mV/sec. The dashed lines represent the capacitive contribution of the interface.

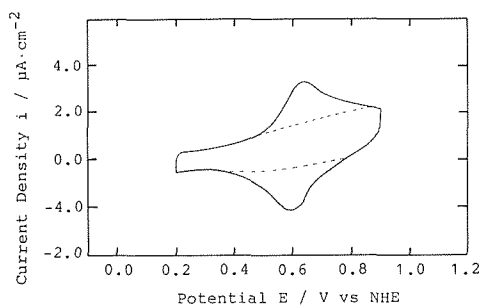


Fig. 4 Cyclic voltammogram of monolayer-adsorbed MP on a Au electrode (surface area is 1.6 cm²). Scan rate is 10 mV/sec. The dashed lines represent the capacitive contribution of the interface.

reduced and oxidized forms, is coordinated to the surface with the molecular plane perpendicular, rather than parallel to, the substrate.

Considerable insight into the nature of these spectrum features could be obtained from FTIR reflection absorption experiments involving a thicker layer of a DHT solution interposed between the window and the electrode surface. Figure 6 shows the spectrum obtained with unpolarized light for a solution of 50 mM DHT in 0.1 M HClO₄ that was electrolyzed for 150 min at a potential of 0.5 V. This spectrum displays a number of prominent features: (i) a negative-going band at 1211 cm⁻¹, which is characteristic of C-O stretching arising from the hydroquinone form of the compound,⁹ (ii) two positive-going bands at 1277 and 1319 cm⁻¹ associated with C-C stretching modes,¹⁰ (iii) two negative-going bands at 1501 and 1454 cm⁻¹, which may be assigned to C=C skeletal deformation of the benzene ring.^{10,11} These observations are consistent with a hydroquinone-quinone-type redox process.

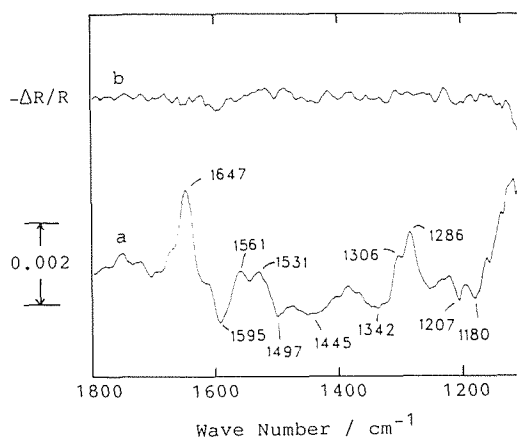


Fig. 5 Normalized difference IRRAS spectra of DHT adsorbed on a Au electrode. The spectrum obtained at +0.34 V was used as a reference. The curve a at +0.84 V was recorded first and next the curve b at +0.34 V was recorded.

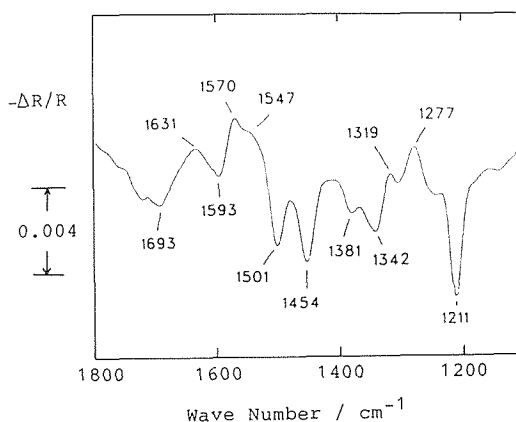


Fig. 6 Normalized difference IRRAS spectrum of a solution of 50 mM DHT in 0.1 M HClO₄ electrolyzed for 150 min at a potential of +0.74 V with the spectrum obtained at +0.34 V as a reference.

On the other hand, the increase in intensity of the difference spectrum in the wave-number region below 1150 cm^{-1} is due to the existence of a peak from perchlorate ions at 1107 cm^{-1} .¹²⁾ The perchlorate ions diffuse into the thin electrolyte layer to hold the electric neutrality in the course of electrolysis.¹³⁾

Although the similarities between the spectra obtained in solution and on the surface *in situ* are marked, there are some differences that deserve further attention. These include the much-decreased relative intensity of the peak at about 1211 cm^{-1} for the surface-bound species compared with those at 1319 and 1277 cm^{-1} and the slight shifts in energies. In fact, a careful inspection of Fig. 5 affords some evidence for a splitting of the 1211 cm^{-1} peak into two bands. This effect may be related to the inequivalency of the two C-O bonds, which may become particularly pronounced upon adsorption of DHT to the surface.

The same experimental procedure was carried out in the MP system as in the DHT system, and the spectra of MP adsorbed and in electrolyte are shown in Fig. 7 and Fig. 8.

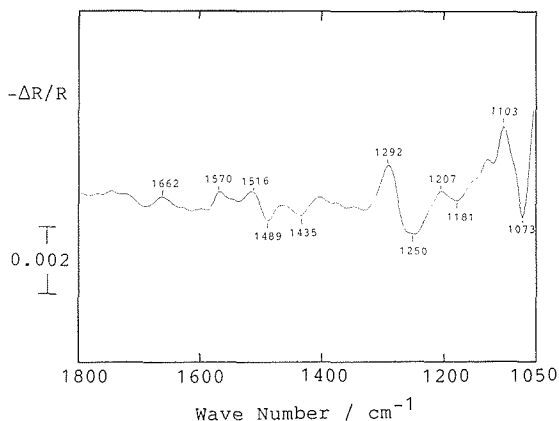


Fig. 7 Normalized difference IRRAS spectrum of MP adsorbed on a Au electrode. The spectrum was measured at $+0.9\text{ V}$ with the spectrum obtained $+0.2\text{ V}$ as a reference.

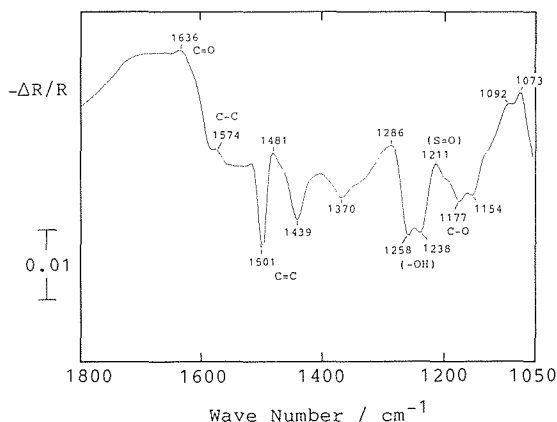


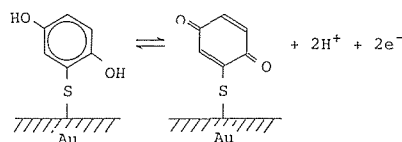
Fig. 8 Normalized difference IRRAS spectrum of a solution of 20 mM MP in 0.1 M HClO_4 electrolyzed for 15 min at a potential of $+0.9\text{ V}$ with the spectrum obtained at $+0.2\text{ V}$ as a reference.

The vibration modes were investigated as in the case of DHT and the assigned modes are presented in Fig. 8. In this figure, the positive-going peak of 1636 cm^{-1} associated with C=O stretching vibration is apparently very small due to overlapping of the deformation vibration peak of water. Two large negative-going bands of 1258 and 1238 cm^{-1} may be assigned to C-O stretching.¹⁴⁾ It was very difficult to assign a C=S stretching mode in the figure, since the intensity was usually low and it easily changed position depending on the substituents.¹⁴⁾ But the band of 1211 cm^{-1} may be associated with the C=S stretching vibration. The band from the C-S bond was positioned at lower than 1000 cm^{-1} and we could not detect the band due to the usage of the CaF_2 window. Although no modes related to sulfur could be clearly assigned in this experiment, MP also changed the oxidation state between the hydroquinone type and the quinone type with potential change as DHT did, since C=O and C-O modes were observed.

By comparing Fig. 7 with Fig. 8, the spectra of MP adsorbed on the electrode surface were seen to be similar to those in solutions such as DHT, the peak shifts were very small, but some peaks changed their relative heights. Further investigations of these changes remain to be carried out.

The bands associated with the skeletal deformation of the benzene ring were observed in the spectra shown in Fig. 5 and Fig. 7. This concludes that both DHT and MP adsorb to the gold surface with the molecular plane nearly perpendicular to the electrode surface. The schematic diagrams of the adsorbed DHT and MP with their redox changes are presented in Fig. 9.

2,5-Dihydroxythiophenol



p-Mercaptophenol

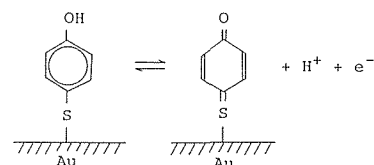


Fig. 9 Schematic diagram of the oxidation and reduction of the adsorbed DHT and MP.

4. Conclusions

As shown in this report, we succeeded in the acquisition of significant signals of monolayer-adsorbed aromatic thiols in the fingerprint region by using a new cell and arrangement in the sample room. The spectra show that both DHT and MP adsorb to the surface of gold with the molecular plane nearly perpendicular to the electrode surface and change the oxidation states with the potential changes.

Acknowledgment

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