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**Electronic Structure of CO/Pt Electrochemical Interfaces
Investigated by Potential Dependent Double Resonance Sum
Frequency Generation Spectroscopy**

（電位依存二重共鳴和周波発生分光法による CO/Pt 電極界面の電子構造解析）

Shuo YANG

*Graduate School of Chemical Sciences and Engineering
Hokkaido University*



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Chapter 1

Introduction

1.1 General Introduction

The term “catalysis” was first coined by Berzelius in 1836, and is defined as a process of increasing the rate of a chemical reaction by using a substance, a catalyst, which is not consumed by the chemical reaction.¹ Catalytic reactions exist in myriad ways of society and play an essential role in our daily lives. Examples include most biological reactions in our bodies, photosynthesis-related processes and many technologically important reactions utilized in the chemical industry. Given the immense importance of catalytic reactions, a tremendous effort has been expended by the scientific community toward understanding the catalytic processes.

Numerous important catalytic reactions occur at solid/liquid interfaces. A detailed understanding of in situ, real time information, including geometric structure, electronic structure and molecular structure, at solid/liquid interfaces, is essential to clarify the mechanism of various catalytic processes at interfaces and to develop new catalysts for meeting today’s challenges in environmental pollution and manufacturing.²

Modern surface science has long employed a variety of ultrahigh vacuum (UHV)-based surface analytical methods, such as low-energy electron diffraction (LEED), auger electron spectroscopy (AES), high-resolution electron energy loss spectroscopy (HREELS) and X-ray photoelectron spectroscopy (XPS), to monitor the catalytic processes at the solid/gas interfaces.^{3–7} A wealth of information has been obtained about surface structures, chemical compositions, bonding geometries, surface atom vibrations, reaction intermediates and oxidation states in the catalytic reactions.

While people have obtained great insights to model systems in ideal conditions, they often fall short in their relevance to real-world systems. Model system behavior for solid/gas interfaces under UHV does not always directly extrapolate to catalytic

reactions at solid/liquid interfaces, which closely resemble the catalysis environment in some realistic devices. Thus, in situ characterization of solid/liquid interfaces has become particularly valuable in the investigation of surface catalysis. However, one must realize that measurements of adsorbates on a solid surface in solution are more difficult than those carried out in UHV systems since many effects from the presence of the solvent and the supporting electrolyte must be considered. For example, an electrochemical system, i.e., an electrode/electrolyte interface, is more complicated to investigate owing to the effect of the strong electric field at the interface. However, most traditional vacuum surface techniques are not applicable to characterizing a solid surface in solution because these techniques often utilize electron beams as their probes, which interact strongly with the liquid, to determine surfaces. In order to understand what is happening at a catalytic reaction surface, scientists need to find techniques capable of investigating a solid surface exposed to solution.

Although many characterization techniques, such as scanning probe microscopy,⁸⁻¹⁰ surface X-ray scattering (SXS),^{11,12} infrared reflection absorption spectroscopy (IRAS),¹³⁻¹⁵ surface-enhanced Raman spectroscopy (SERS)¹⁶⁻¹⁸ and X-ray absorption fine structure (XAFS),^{19,20} have been developed for studying the geometric and molecular structures of solid/liquid interfaces in the last 30 years, techniques to probe the electronic structure at solid/liquid interfaces in situ are still limited. Second harmonic generation (SHG) spectroscopy is one solution to probe the surface electronic structure; however spectroscopic SHG study is rather limited, and the interpretation of the results is not straightforward.²¹⁻²³ X-ray absorption near edge structure (XANES) can probe the oxidation states of elements²⁴⁻²⁶ and electronic states at the electrode/electrolyte solution interfaces,²⁷ and recently an in situ electrochemical XPS system was developed by combining with a specially designed electrochemical cell with a thin (ca. 20 nm) Si window, which separates the solution from vacuum.²⁸ The latter two methods are useful, but of limited practical use because the synchrotron X-ray source is required.

IR/visible sum frequency generation (SFG) spectroscopy, which is based on a second order nonlinear optical effect, has the particular advantage of high intrinsic

interface sensitivity over classical vibrational spectroscopy techniques, such as IRAS^{13–15} and SERS.^{16–18} It is used to study molecular structures on a surface.^{29–32} On the other hand, in the SFG process, two photons at different frequencies generate one photon with a sum frequency of these two.^{33–37} Photons, in contrast to electrons, are not limited to UHV conditions and can readily probe surfaces in solutions. Consequently, as a photon-in photon-out technique, SFG spectroscopy has been applied to solid/liquid interfaces. More recently established double resonance (DR)-SFG spectroscopy, which utilizes resonant enhancement of SFG intensity with both frequency-tunable incident fundamental light, i.e., visible and IR, has been proved to be able to elucidate both molecular and electronic structures in vacuum conditions³⁸ and should be applicable to the electronic structure study of solid/liquid interfaces.

This project aims to elucidate the interfacial electronic structures in electrochemical environment by using DR-SFG spectroscopy.

1.2 Electrocatalysts

1.2.1 Review of Electrocatalysts

Electrochemical processes, such as fuel cell reactions, which consist of the anode reaction (hydrogen oxidation, methanol oxidation) and the cathode reaction (oxygen reduction), and the hydrogen evolution reaction (HER), play an important role in many energy conversion devices. These processes only take place at the electrocatalyst/electrolyte interfaces and affect the performance of the devices. Thus, developing efficient electrocatalysts for ideal electrode reactions is highly required.

In recent decades, there has been a rapid rise in fuel cell and HER electrocatalysts, generally, from precious metals to non-precious metal compounds, and finally to metal-free materials.

In the early stage of research, the most widely used electrocatalyst for both fuel cell and hydrogen production was Pt. The first proton exchange membrane fuel cell utilized finely divided Pt black (particle size is around 50–100 nm, Pt loading is >4 mgPt/cm²) as the anode and cathode electrocatalyst.³⁹ In 1800, Nicholson and Carlisle

observed that hydrogen gas was generated at the ends of Pt wires when they carried out a water decomposition experiment using a galvanic battery.^{40,41} After more than two centuries, Pt remains the most efficient electrocatalyst for fuel cell and HER because of its good stability and high activity.

Unfortunately, Pt is expensive and is relatively scarce on the earth, limiting the utilization of Pt in the global energy economy.⁴² Hence, there is a critical need for low-cost electrocatalysts for practical applications. One of the strategies to tackle this problem is to minimize the Pt content in electrocatalysts, whilst at the same time improving the electrocatalytic activity as much as possible. Examples include microstructured or nanostructured Pt electrocatalysts with a large surface-to-volume ratio,^{43,44} Pt alloys with different transition metals,^{45,46} and monolayer Pt supported on low-cost materials (Figure 1-1).⁴⁷⁻⁴⁹

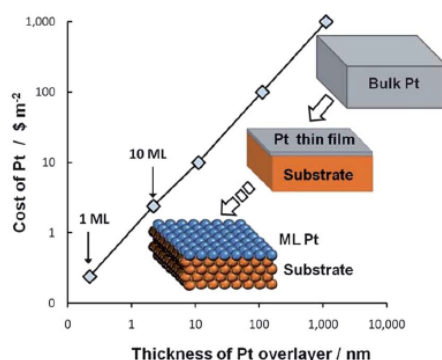


Figure 1-1. Relationship between cost of Pt and overlayer thickness for a planar catalyst configuration.⁴⁹

Noble metal-free compounds using nonmetals, mainly including B, C, N, P, S and Se, are the most common electrocatalysts for fuel cell reactions and HER. Some of them have high activity and stability for fuel cell reactions and HER, which approach or even surpass those of their Pt-based counterparts owing to their unique electronic structure.^{50,51} Metal-free carbon materials doped with N, B and/or P,⁵²⁻⁵⁴ particularly N- and B-doped carbon materials, are commonly employed as effective electrocatalysts for oxygen reduction reaction (ORR) and HER. A carbon electrode

codoped with B and N atoms has higher ORR catalytic activity than the same electrode doped with a single element.^{53,55,56} More recently, Uosaki's group demonstrated that BN nanosheets on Au substrate could act as good ORR⁵⁷ and HER active catalysts by combining theoretical and experimental study.

Looking ahead, there are a number of challenges in the future development of fuel cell and HER electrocatalysts. Although the ideal electrocatalyst for fuel cell reaction and HER should meet the requirements of lower cost, high efficiency, good durability and reliability, so far, no electrocatalysts have been found that can meet all the above advantages. Thus, exploring new fuel cell and HER electrocatalysts with improved performance is an important task in the following years. Considering that the reactivity of electrocatalysts depends on the fundamental understanding of the electronic structures at the electrode/electrolyte interfaces, in recent years, the combination of theoretical density functional theory (DFT) calculations and experimental data has increased tremendously.^{46,58,59}

1.2.2 Electrocatalytic Activities of Electrocatalysts Depend on Their Electronic Structures

Electrocatalytic reactions are significantly affected by the surface electronic structures of the electrocatalyst. Since the proposal by Taylor of the concept of the active site in 1925,⁶⁰ a large number of studies have been oriented to finding a relationship between the surface electronic characteristics of electrocatalysts and their electrocatalytic activity for certain reactions, such as the hydrogen evolution,⁶¹ molecular oxygen reduction⁶² and the electrooxidation of CO,⁶³ and understanding the effect of electrocatalyst electronic structures on their electrocatalytic activity has become one of the essential objectives in heterogeneous catalysis.^{7,64,65}

Bimetallic surfaces consisting of transition metals and foreign metals were found to have higher electrocatalytic activity toward ORR and methanol oxidation than that of the monometallic surfaces,^{66–69} as displayed in Figure 1-2. The substantial enhancement of electrocatalytic properties for the bimetallic electrocatalysts is believed to have resulted from the modification of surface electronic structure, in

which a metal–metal bond is formed, and therefore altering the d-band vacancy, in turn changing their electrocatalytic properties.^{70,71}

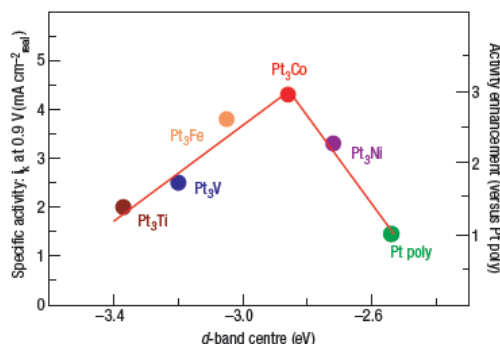


Figure 1-2. Relationships between electrocatalytic properties and electronic structure of Pt₃M alloys.⁷²

In addition, the electrocatalytic activities of the transition metal monolayers on various substrates were different from each other.⁷⁰ The difference was caused by the charge transfer because of the mismatch of crystal lattice between the thin layer and the substrate. Norskov and co-workers recently proposed a description of the electronic structure of metal monolayers and their electrocatalytic activity by using a d-band center model, in which the energy center of the d-band (ε_d) plays an important role in determining surface electrocatalytic activity.^{58,71} DFT calculations showed that the binding energies and reactivity of the small adsorption correlate well with the position of ε_d on metal monolayers,⁷³ in agreement with a large number of experimental results.^{74,75}

Recently, Kolb et al. investigated the electrochemical oxidation of formic acid on Pd ultrathin films electrodeposited on Au(111) and Au(100) and found that the activity of the electrode very much depended on the thickness of the Pd film. The cause of this effect was also related to the unique electronic properties of the deposited Pd layer.⁶⁷

For the last two decades, considerable efforts have been dedicated to optimizing the electronic structures of various electrocatalysts compatible with the highest

electrocatalytic activity. The knowledge on the surface electronic structure of electrocatalysts has become more and more important in electrochemical reactions for the application of energy conversion devices.

1.3 In Situ Techniques to Characterize Electrochemical Interfaces

To acquire the required information of electrode/electrolyte interfaces, electrochemists are searching for suitable techniques in the field of surface science.⁷⁶ However, most surface science techniques must be used in a vacuum, which cannot be applied to electrochemical interfaces. Accordingly, one of the main challenges in surface chemistry has been to develop characterization methods that enable in situ monitoring of electrochemical interfaces.

As a result of concentrated efforts in the past decades, remarkable progress has been made in the development of useful experimental methods applicable to solid/liquid interfaces.^{77–82} These techniques have the ability to examine electrode/electrolyte interfaces under potential control and, in general, can be classified into three categories: in situ techniques for geometric, molecular and electronic structure, as shown in Table 1-1.

Table 1-1. Typical techniques used for in situ evaluation of electrochemical interfaces.⁸²

Techniques		Note
➤ <u>Surface Geometric Structure</u>		
Scanning tunnelling microscopy	STM	Outermost layer of conductor only
Atomic force microscopy	AFM	Applicable to insulator but outermost layer only
Surface X-ray scattering	SXS	Very high resolution, long range order required
➤ <u>Surface Molecular Structure</u>		
IR reflection absorption spectroscopy	IRAS	Difficult to distinguish surface signal from bulk, IR adsorption by water
Surface enhanced Raman scattering	SERS	Limited substrates
Sum frequency generation	SFG	Surface-specific, IR adsorption by water
➤ <u>Surface Electronic Structure</u>		
X-ray absorption near-edge structure	XANES	Restriction by synchrotron X-ray probe
UV/visible electroreflectance	ER	Indirect evidence for the existence of surface states
Second harmonic generation	SHG	Complicated analysis and not straightforward
Double resonance SFG	DR-SFG	Surface-specific, simultaneous capture of electronic and molecular structure

1.3.1 Geometric Structure

Reactions at electrode surfaces are strongly dependent on geometric structures such as the orientation and atomic arrangement of the substrates. Prominent methods for studying geometric structures at electrochemical interfaces are scanning probe microscopy,⁸⁻¹⁰ e.g., scanning tunnelling microscopy (STM)^{9,10} and atomic force microscopy (AFM),⁸ and SXS.^{11,12}

In 1981, Binnig and Rohrer developed STM.⁸³ Within the first few years of its invention, STM has helped to provide a large number of atomic images of solid surfaces not only in UHV but also in an ambient atmosphere. Since Hansma et al.^{84,85} firstly reported that STM can be operated in electrolytes, much progress has been made in electrochemical exploration by STM. Especially, the development of a four-electrode configuration (Figure 1-3) for in situ STM measurements under potential control has enabled new perspectives for studying electrochemical processes at solid/liquid interfaces on a nanometer or even atomic scale.^{86,87}

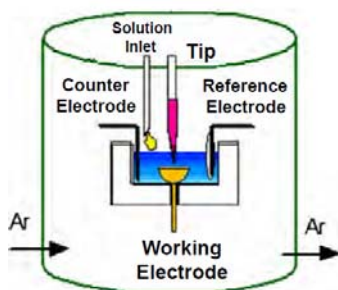


Figure 1-3. Schematic of electrochemical STM cell.⁸²

Despite the phenomenal success of STM, it has a serious limitation to sample materials. STM requires the sample to be electrically conductive because STM uses the tunnelling current, which flows between a tip and a sample. Subsequently, AFM was developed as a variant of STM. AFM can image virtually any flat solid surface without the need for a conductive sample⁸⁸ because in the AFM the interaction force between the tip and the sample surface is sensed by image surface topography. With the latest advances in AFM technology, imaging of the samples in electrolyte solution

can be carried out efficiently. Various electrochemical processes, such as corrosion, bioelectrochemical reactions, electroplating and charging and discharging of batteries, can be monitored in situ by using AFM.

Among the atomic-level structural probes, synchrotron X-rays, unlike electrons, are able to monitor the structure under well-controlled electrochemical conditions because of their penetrating nature. SXS is a technique used for probing the surface atomic structure at electrode/electrolyte interfaces. Many successful SXS studies of in situ structural evaluation at electrode/electrolyte interfaces have been carried out in the last 20 years.^{78,89} Among the earliest works, Ocko et al. for the first time investigated the structures of the reconstructed Au(111) and Au(100) surfaces using in situ SXS;^{11,90} in situ SXS measurements from a UPD monolayer at a metal/liquid interface was reported by Melroy's group;⁹¹ Dahn et al. employed in situ X-ray diffraction to monitor changes in lattice spacing of intercalation compounds with potential.⁹² As more innovative X-ray electrochemical cells are designed, SXS is now widely used for single crystal electrodes to study the metal deposition, anion adsorption and surface oxidation. Figure 1-4 shows a typical electrochemical cell used for SXS measurement,¹² in which an ultrathin polymer film (a few μm) was introduced as a window and sealed the cell, making a thin solution layer (10–20 μm) formed between the window and working electrode, to minimize the scattering of X-rays by the solution and window.

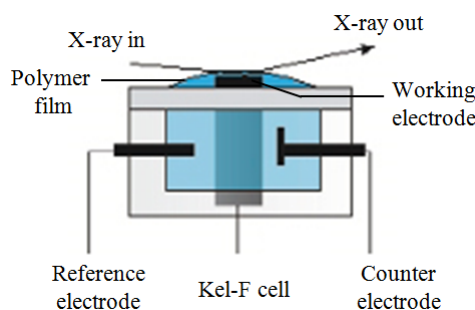


Figure 1-4. The electrochemical cell with a thin layer configuration for in situ SXS measurements.⁹³

1.3.2 Molecular Structure

Apart from the surface structures of an electrode itself, surface molecular structures are also important to understand the reactions at electrochemical interfaces. Such molecular structures are determined by using vibrational spectroscopy, comprising IRAS,^{13–15} SERS^{16–18} and IR/visible SFG.^{29–32} These three techniques have markedly different strengths and weaknesses.

Since the observation of unusually strong Raman signals for pyridine adsorbed on Ag electrode by Fleischmann et al. in the early 1970s,^{94,95} great interest has developed in SERS studies of adsorbed species on electrode surfaces. SERS provides high surface sensitivity over bulk-phase solution species, molecular vibrational information, orientation on surfaces and low Raman cross section for water, which has especially significant attributes for electrochemical systems. Despite the obvious advantages, SERS has limited application in the metals that have appreciable activity, for instance, Ag, Cu, Au.^{96–98} In addition, SERS is not applicable to single crystals because surface roughening is required for activation.

In contrast to SERS, IRAS spectroscopy offers the advantage of being applicable to a wide range of metal surfaces, including well-ordered single crystal surfaces. As first demonstrated by Bewick and co-workers in the early 1980s,⁹⁹ applications of IRAS in situ techniques for electrochemical interfaces study were made possible through potential-difference tactics in conjunction with thin layer electrochemical cells (typical thickness of the thin layer is 1–5 μm) to minimize the absorption of the IR beam by electrolyte solution.^{14,78,100} The technique they used is called electrochemically modulated (EM)-IRAS. Modulation of the electrode potential produces a difference spectrum of the electrode/electrolyte interface at two different electrode potentials. Accordingly, EM-IRAS is only useful when the structure of the adsorbate changes with applied potential. An alternative modulation scheme for IRAS is polarization modulation,¹⁰¹ which takes advantage of the fact that the absorption by a thin layer on an electrode is much greater for p-polarized infrared radiation than for s-polarized radiation. The orientation of adsorbed species can be determined with this

technique. In the last 20 years, it has been seen that both EM-IRAS and polarization modulated (PM)-IRAS have become increasingly popular as the research tools for molecular structure study of adsorbates in the electrochemistry field.

Some salient findings are summarized briefly for the illustrative electrochemical systems examined by IRAS. IRAS has been successfully used to characterize the electrooxidation of small organic molecules on metal electrode surfaces, in which the adsorption mode as well as the site geometry were determined, and the complex mechanistic pathways were more thoroughly evaluated. Beden et al.¹⁰² studied the adsorption of CO on smooth Pt electrodes using EM-IRAS and later Russell et al.¹⁰³ utilized PM-IRAS¹⁰¹ in a similar study. The C-O stretching mode of the linearly adsorbed CO was observed and its frequency shift with electrode potential was confirmed. Moreover, the behaviors of water molecules at the electrode/electrolyte interfaces are perhaps the most widely studied electrochemical processes. IRAS has provided an important contribution toward the understanding of water adsorption on different electrodes. Bewick et al. employed in situ EM-IRAS to study the interfacial behavior of water molecules at polycrystalline Pt^{104–106} and Au¹⁰⁷ electrodes in 1 M H₂SO₄ and 0.1 M HClO₄ aqueous solution, respectively. They also deduced the orientation of water molecules at the interface with water dimer hydrogen bonding to the weakly adsorbed hydrogen.

Unfortunately, IRAS measurements are troubled by an inability to remove the interfere of chemical species adsorbed on the electrode surface from those diffused in bulk electrolyte,^{108–110} necessitating the subtraction of the bulk-phase spectra from IR data to obtain surface information. As a consequence, a technique utilizing photons with surface specificity in solution was urgently required.

With the advent of ultrafast pulsed lasers, a new type of surface vibrational spectroscopy that uses a nonlinear optical phenomenon, IR/visible SFG spectroscopy, emerged and has been demonstrated to be a very powerful tool for investigating the vibrational transitions of molecules at electrochemical interfaces^{111–115} since it helps solve the two biggest problems of linear vibrational spectroscopy, sensitivity and selectivity. In SFG, two incident photons with frequencies ω_1 and ω_2 are combined to

create a third photon with $\omega_3 = \omega_1 + \omega_2$. SFG is especially interface-sensitive. As a second order nonlinear process, SFG is only generated in media without inversion symmetry.³³⁻³⁷ Since the inversion symmetry is present owing to the cubic structure of the electrode and the isotropy of the electrolyte, but not at the interface between them, SFG can selectively probe the molecules at the symmetry breaking the electrode/electrolyte interface and ignores molecules in the electrolyte. The SFG measurements for electrochemical systems are also based upon the formation of a thin layer electrolyte configuration to avoid the IR absorption by electrolyte. Furthermore, photochemical damage can be caused during SFG experiments if the laser is too strong.

1.3.3 Electronic Structure

In contrast to a number of methods for geometric and molecular structure studies of electrochemical interfaces, very little is known about their electronic structure details, although the knowledge of the surface electronic structure is vital for understanding electrochemical surface processes. Electron spectroscopy, which has proved so valuable to the study of surface electronic structure in vacuum, cannot be applied to electrochemical surfaces owing to the extremely low path length of electrons in condensed media. Thus, a specific surface technique that is capable of monitoring electronic structure at electrochemical interfaces is really needed.

XANES spectroscopy plays a very important role in monitoring the electronic structure, oxidation state and coordination environment of metal atoms.^{116,117} The energy range of XANES is from 0 to 50 eV. Using XANES, the transition of core electrons into unoccupied states of species can be successfully determined in electrochemical interfaces.²⁷ In spite of this, this approach is still of limited use owing to the synchrotron X-ray probe.

In recent years, there has been a major effort to develop spectroscopic methods for characterizing the electronic structures of the electrode/electrolyte interfaces since such methods with photons as the probe could be used in solutions.

In situ electroreflectance (ER) spectroscopy in UV/visible frequency range is one

method used to determine the electronic structure of electrode surfaces in electrolyte solution. The potential induces a strong electric field near the electrode surface. Therefore, the surface electronic states are affected by this field. By measuring the relative reflectance change of the electrode surface as a function of the potential, the surface electronic states of the electrode can be effectively detected. Kolb et. al successfully applied ER spectroscopy to monitor the electronic transitions from d-band into the unoccupied surface states on Au(100) surface in 0.01 M HClO₄ solution.¹¹⁸ The disadvantage of this technique is lack of surface specificity because it is a linear technique.

Optical SHG is recognized as a special case of SFG, where $\omega_1 = \omega_2 = \omega$ and therefore the frequency-doubled light ($\omega_3 = 2\omega$) is generated from the inversion symmetry broken interface.^{22,33,119–121} The resonant enhancement of the SHG signal arises when either the input fundamental photon or the output SH photon energetically couples with an electronic transition localized at the interfaces and, therefore, SHG spectroscopy is considered to be a powerful probe for interfacial electronic structures.^{22,121–123} The application of SHG spectroscopy to determine the surface electronic structures of various systems including electrochemical systems, has been carried out in both resonant and nonresonant conditions.^{22,119,121,123} Furthermore, the aqueous electrolyte is transparent for both incident light and the SH light in UV/visible range. Consequently, SHG can be used in a regular electrochemical experimental configuration without the need for a thin electrolyte layer configuration as with other spectroscopies. The disadvantage of this technique is lack of absolute molecular specificity and in nonresonant conditions, it cannot directly probe interfacial information via perturbation and redistribution of the surface electronic structure as a result of absorption and requires a complex analysis of the signal.^{124,125}

It has recently been demonstrated that a novel technique for SFG spectroscopy by tuning both incident visible and IR frequencies, i.e., DR-SFG spectroscopy, which is detailed in Section 1.5, can probe electronic and vibrational transitions of interfacial molecules simultaneously.^{38,126,127} With both tunable visible and IR, when IR light is resonant with the vibrational state and SF light is resonant with the electronic states of

molecules, so-called “double resonance”, the vibrational mode couples to the electronic transition between two electronic states at a surface, producing the doubly enhanced SFG signal. Obviously, by changing the wavelength of the visible light, the electronic spectra of the adsorbates on electrode surfaces can be obtained. This new technique could be valuable for studies of electronic structure at electrochemical interfaces.

1.4 CO/Pt Electrochemical Interfaces Studied by Spectroscopy

The adsorbed CO on a Pt surface is one of the most studied systems in surface science,^{5,7,128} catalysis¹²⁹⁻¹³¹ and electrochemistry,¹³²⁻¹³³ since CO is one of the simplest adsorbed molecules and is an intermediate and/or a poison of important interfacial processes. For example, in the direct methanol fuel cell (DMFC) (Figure 1-5), adsorbed CO is formed when the Pt anode is in contact with methanol solution and inhibits the methanol oxidation reaction, degrading the performance of the DMFC.^{134,135} Therefore, an understanding of the geometric, molecular and electronic information of CO/Pt interfaces, especially in electrochemical conditions, is essential to understand the role of adsorbed CO in the reactions and design new electrocatalysts for effective removal of CO from Pt surfaces and improve the efficiency of the reactions.

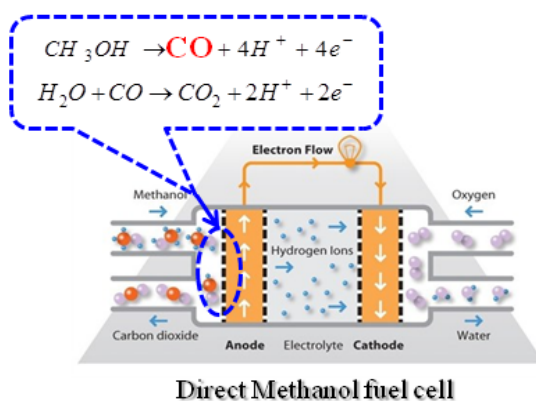


Figure 1-5. Schematics of a DMFC.

Adsorption of CO onto a metal surface is widely regarded as a chemisorption process. When CO is chemisorbed on a Pt surface, the interfacial electronic structure is significantly modified by the hybridization of electronic states of CO and Pt orbitals,

and as a result new energy states are formed at the interface.^{136,137} The adsorbed CO is considered to interact with the Pt surface through a 5σ donation- $2\pi^*$ back-donation model.¹³⁸⁻¹⁴⁰ The interaction between Pt and CO creates CO-derived antibonding states, $2\pi_a^*$ and $5\sigma_a$, above the Fermi level of Pt and bonding states, $2\pi_b^*$ and $5\sigma_b$, below the Fermi level.^{141,142} A large number of experiments in UHV environment¹⁴³⁻¹⁴⁶ and theoretical calculations^{136,137,147} have been carried out to clarify these hybridization states. Dose et al. reported that the unoccupied $5\sigma_a$ antibonding state of adsorbed CO at Pt(110) is located at around 2.0 eV above the Fermi level by using inverse photoemission spectroscopy.¹⁴⁵ The positions of unoccupied and occupied states of the atop CO band on Pt(111), $2\pi_a^*$ and $2\pi_b^*$, respectively, were determined as 4.3 eV above and 0.3 eV below the Fermi level by two-photon photoemission and photoemission measurements,¹⁴⁶ and photoemission measurement,¹⁴³ respectively. Based on these studies, an electronic structure model of CO/Pt system in UHV environment has been proposed, as shown in Figure 1-6.

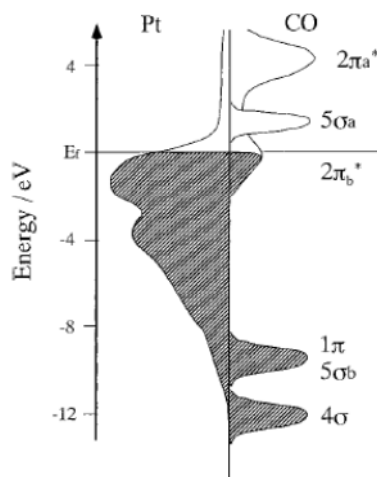


Figure 1-6. A schematic diagram for electronic structure of a CO/Pt interface (black indicates occupied states and white indicates vacant states).¹⁴⁸

However, the electronic structure of CO/Pt interfaces in an electrochemical environment is still less understood because the electron spectroscopy cannot be applied to electrochemical interfaces. Although SHG studies for the CO/Pt(111) system in electrolyte solutions were carried out,¹⁴⁹⁻¹⁵¹ application to probing the

electronic structure is limited.¹⁴⁸ Bae et al. applied XANES to the CO/Pt system in an acid electrolyte and suggested the transitions from the Pt 2p(3/2) orbital to unoccupied states above the Fermi level were localized predominantly on CO, but the resolution was not high enough to specify the CO states.²⁷ Recently, IR/visible SFG spectroscopy, although it was carried out in a UHV environment, to successfully probe the interfacial electronic structure of the CO/Pt was reported by Somorjai's group.³⁸ In this work, an SFG enhancement caused by the resonance of visible light with the electronic transition between $2\pi^*_b$ and $5\sigma_a$ states at the interface, i.e., DR-SFG, was observed.

The molecular structures of CO/Pt electrochemical interfaces have been investigated extensively by vibrational spectroscopy techniques, such as IRAS, SERS and SFG. Generally, three kinds of vibrational frequencies for CO species on Pt are well-known in these studies, i.e., atop, bridge and three-fold hollow site CO,¹⁵² as shown in Figure 1-7. Atop site CO is one CO molecule linearly adsorbed on a single “atop” Pt atom (Figure 1-7(a)) and is usually observed at 2000–2080 cm^{-1} in the IR and SFG spectra.^{153–155} Bridge-CO is formed when the CO coordinates in a “bridging” configuration to two Pt atoms (Figure 1-7(b)) and is commonly detected at 1800–1860 cm^{-1} .^{156,157} When a CO molecule is adsorbed at the three-fold hollow sites of Pt, as shown in Figure 1-7(c), it has frequencies lower than 1800 cm^{-1} .¹⁵⁸

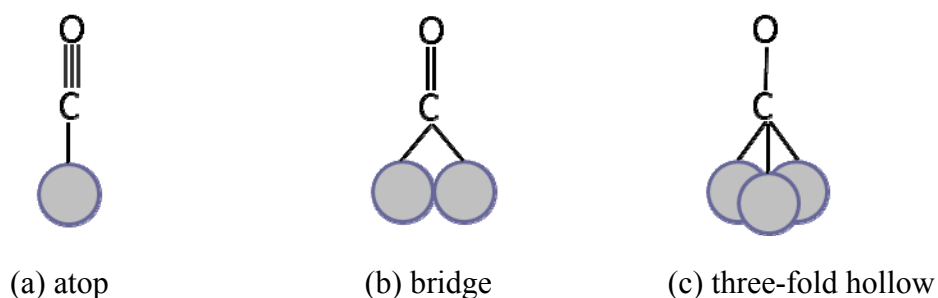


Figure 1-7. Schematic model of CO adsorption sites.

The potential dependence of the peak position for CO adsorbed on a Pt electrode in HClO_4 or H_2SO_4 aqueous solution was demonstrated by Russell et al.¹⁵⁹ The band

shifts to higher wavenumber as the potential becomes more positive. The linear relationship between electrode potential and CO peak position was confirmed in the work of Golden, Kunitatsu and Seki.¹⁶⁰ Kunitatsu et al. found that the rate of atop CO peak shift was ca. $30 \text{ cm}^{-1}/\text{V}$ in acid solutions (Figure 1-8(a)).¹⁶¹ Later, similar results were also observed in SERS and SFG measurements,^{162,163} as shown in Figure 1-8(b-c).

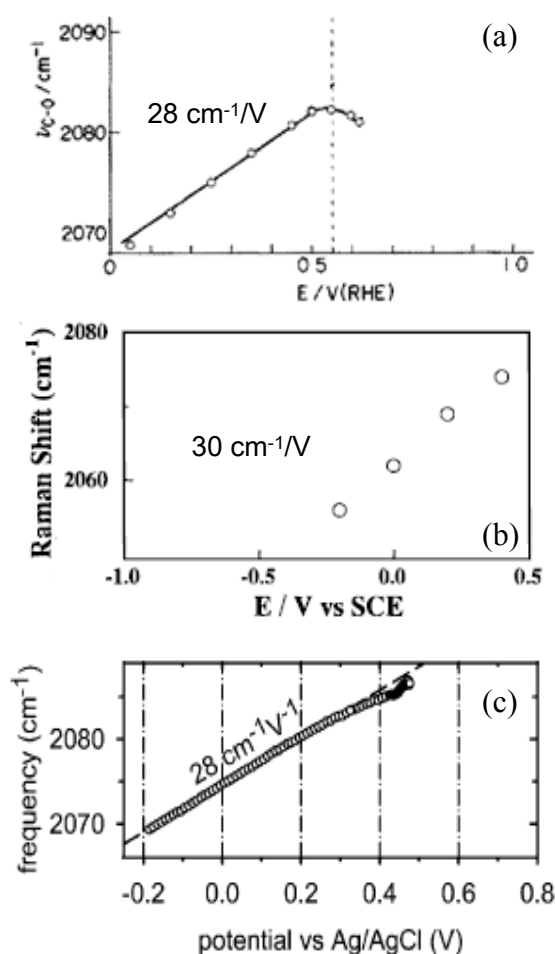


Figure 1-8. Potential dependence of the C-O stretching frequency of atop CO adsorbed on a Pt electrode in acid conditions measured by (a) IRAS,¹⁶⁴ (b) SERS¹⁶² and (c) SFG¹⁶³ spectroscopy.

Usually, there are two explanations for the frequency shift with potential: “chemical effect” and “electrochemical Stark effect”.

“Chemical effect” means the change of the degree of donation and back-donation

with applied potential. At more positive potentials, the Pt electrode accumulates positive charges on its surface, which induces an electric field extending above the electrode owing to the interfacial capacitance. Electrons on CO are electrostatically withdrawn into the Pt under this electric field, at the same time, electrons from the filled Pt orbital that overlaps with the CO π^* orbital are also moved toward the Pt, therefore weakening the back-donation of the metal electrons into the antibonding $2\pi^*$ orbital of the CO, causing the potential dependent frequency shift to the higher wavenumber as a result of CO bond strength enhancement. A change in the electrode potential to a more negative direction repels the electrons from σ donation and extends the electron cloud of its filled d orbital further into the CO π^* orbital. The increase in the donation to the C-O antibonding orbitals weakens the CO bond and shifts its vibration to lower frequency.

The “Electrochemical Stark effect” proposed by Lambert as an alternative theoretical explanation for the frequency shifts states that an electric field induces redistribution of the electrons within the adsorbed molecule, which changes at the vibrational frequency of a dipole whose direction of vibration is parallel to the surface normal.^{165,166} Lambert’s equations predict that, at constant surface coverage, the shift of the CO frequency, ν , under the influence of electric field E should be linear with respect to the field strength (Eq. (1-1)).

$$\delta_{\nu E} = \frac{\partial \nu}{\partial E} \quad (1-1)$$

Since it is necessary to apply a potential V to the electrode in order to produce the electric field E , the linear relationship between the strength of electric field and the applied electrode potential can be written as Eq. (1-2),

$$\frac{\partial E}{\partial V} = \frac{C}{\varepsilon} \quad (1-2)$$

where ε is the interfacial dielectric constant, C represents differential capacitance.

Eq. (1-2) is transformed as

$$\frac{\partial E}{\partial v} \frac{\partial v}{\partial V} = \frac{C}{\varepsilon} \quad (1-3)$$

$$\frac{\partial v}{\partial V} = \frac{\partial v}{\partial E} \frac{C}{\varepsilon} \quad (1-4)$$

$$\delta_{vV} = \delta_{vE} \frac{C}{\varepsilon} \quad (1-5)$$

where $\delta_{vV} = \frac{\partial v}{\partial V}$.

Eq. (1-5) indicates that a plot of the peak frequency ν versus electrode potential V ought to be linear with the slope being defined as the Stark tuning rate δ_{vV} . The differential capacitance C of a metal/electrolyte interface is approximately 10–20 $\mu\text{F}/\text{cm}^2$, and the dielectric constant ε of a water layer at a metal surface is in the range of 6–8, thus, $\partial E / \partial V$ is calculated to be 1.2×10^7 – 3.3×10^7 (V/cm)/V. The $\partial v / \partial E$ for a high coverage of atop CO on Pt(111) in electrolyte was reported as $1.2 \times 10^{-6} \text{ cm}^{-1}/(\text{V}/\text{cm})$.¹⁶⁷ Accordingly, the variation of CO vibrational frequency with potential on Pt is evaluated to be 15–40 cm^{-1}/V .

However, it is difficult to discriminate these two effects experimentally, the chemical and the Stark effects, as the origin of the CO band shift, so both of them should be considered.

UV/visible reflectance spectroscopy was historically one of the first methods applied to electrochemical interfaces. This technique is generally used to monitor the adsorbate-induced reflectance change on an electrode surface. Electroadsorption of CO on a Pt single crystal electrode has been studied by Lamy et al. with in situ UV/visible reflectance spectroscopy at a fixed wavelength since 1985.¹⁶⁸ In their work, two different CO species, i.e., atop and bridge CO, were detectable, depending on both electrode potential and CO coverage. The changes in relative reflectivity with CO coverage suggested that bridge CO is the main adsorbate at low coverage, in

contrast, atop CO predominates the Pt surface at high coverage. With the variety of experimental techniques, wavelength-modulated and potential-modulated UV/visible reflectance spectroscopy were developed and have shown the ability to determine the electron transfer rate of adsorbed species on electrode surfaces.¹⁶⁹

1.5 Second Order Nonlinear Spectroscopy

1.5.1 Nonlinear Optics^{35,170}

When an electric field $\mathbf{E}$ interacts with a matter, an induced dipole moment of the molecule of this matter $\boldsymbol{\mu}$ can be generated. In the presence of substantially intense electric fields, for example, under pulsed laser irradiation, the induced dipole moment $\boldsymbol{\mu}$ of the molecule can be expressed by Eq. (1-6) in the electric dipole approximation,

$$\boldsymbol{\mu} = \boldsymbol{\mu}^0 + \vec{\alpha} \cdot \mathbf{E} + \vec{\beta} : \mathbf{E}\mathbf{E} + \vec{\gamma} : \mathbf{E}\mathbf{E}\mathbf{E} + \dots \quad (1-6)$$

where $\boldsymbol{\mu}^0$ is the static dipole, and $\vec{\alpha}$, $\vec{\beta}$, $\vec{\gamma} \dots$ are the linear polarizability, the first and second ... hyperpolarizabilities of the molecule, respectively, and are represented by second, third and fourth ... rank tensors. These give rise to nonlinear optical effects that are known as second and third order nonlinear effects, respectively.

Since polarization $\mathbf{P}$ represents the total dipole moment per unit volume V in the material,

$$\mathbf{P} = \frac{\sum \boldsymbol{\mu}}{V} \quad (1-7)$$

in condensed phase, polarization $\mathbf{P}$ is usually introduced for a convenient description. According to Eq. (1-6) and (1-7), the following equation is obtained,

$$\mathbf{P} = \mathbf{P}^{(0)} + \mathbf{P}^{(1)} + \mathbf{P}^{(2)} + \mathbf{P}^{(3)} + \dots \quad (1-8)$$

where $\mathbf{P}^{(0)}$ is the static polarization, $\mathbf{P}^{(1)}$, $\mathbf{P}^{(2)}$ and $\mathbf{P}^{(3)}$... are the first, second and third ... order polarizations. Here, the first term $\mathbf{P}^{(0)}$ is supposed to be 0 because there is no static polarization in the materials. Thus, Eq. (1-8) can be written as

$$\mathbf{P} = \mathbf{P}^{(1)} + \mathbf{P}^{(2)} + \mathbf{P}^{(3)} + \dots \quad (1-9)$$

If the polarizabilities of molecule $\vec{\alpha}$, $\vec{\beta}$, $\vec{\gamma}$... are substituted by the susceptibilities $\vec{\chi}^{(1)}$, $\vec{\chi}^{(2)}$, $\vec{\chi}^{(3)}$..., respectively, according to the relationships shown in Eq. (1-10),

$$\vec{\chi}^{(1)} = N \langle \vec{\alpha} \rangle / \varepsilon_0, \vec{\chi}^{(2)} = N \langle \vec{\beta} \rangle / \varepsilon_0, \vec{\chi}^{(3)} = N \langle \vec{\gamma} \rangle / \varepsilon_0, \dots \quad (1-10)$$

in which $\vec{\chi}^{(1)}$ is the linear susceptibility, $\vec{\chi}^{(2)}$, $\vec{\chi}^{(3)}$... are the second, third ... order nonlinear susceptibility. N is the number of molecules per unit volume, ε_0 is dielectric constant in vacuum, $\langle \rangle$ denotes the ensemble average of the molecular orientation, the polarization $\mathbf{P}$ can also be rearranged by using the linear and nonlinear susceptibilities to form

$$\begin{aligned} \mathbf{P} &= \mathbf{P}^{(1)} + \mathbf{P}^{(2)} + \mathbf{P}^{(3)} + \dots \\ &= \varepsilon_0 (\vec{\chi}^{(1)} \mathbf{E} + \vec{\chi}^{(2)} : \mathbf{E}\mathbf{E} + \vec{\chi}^{(3)} : \mathbf{E}\mathbf{E}\mathbf{E} + \dots) \end{aligned} \quad (1-11)$$

Here, only the second order term of the polarization given by Eq. (1-11) is concerned

$$\mathbf{P}^{(2)} = \varepsilon_0 \vec{\chi}^{(2)} \mathbf{E}_1 \mathbf{E}_2 \quad (1-12)$$

because the SFG phenomenon, which is mainly discussed in this thesis, belongs to the

second order nonlinear optical process. When two input laser fields oscillating with frequencies of ω_1 and ω_2 irradiate on the sample surface,

$$\mathbf{E}_1 = E_1(\mathbf{r})\cos\omega_1 t, \mathbf{E}_2 = E_2(\mathbf{r})\cos\omega_2 t \quad (1-13)$$

where $\mathbf{r}$ and t represent a position vector and time, respectively. The second order nonlinear polarization $\mathbf{P}^{(2)}$ is induced at the surface of the sample.

$$\begin{aligned} \mathbf{P}^{(2)} &= \varepsilon_0 \overleftrightarrow{\chi}^{(2)} \mathbf{E}_1 \mathbf{E}_2 \\ &= \varepsilon_0 \overleftrightarrow{\chi}^{(2)} E_1(\mathbf{r})\cos(\omega_1 t) \cdot E_2(\mathbf{r})\cos(\omega_2 t) \\ &= 1/2 \varepsilon_0 \overleftrightarrow{\chi}^{(2)} E_1(\mathbf{r})E_2(\mathbf{r})\{\cos[(\omega_1 + \omega_2)t] + \cos[(\omega_1 - \omega_2)t]\} \end{aligned} \quad (1-14)$$

From Eq. (1-14), it is found that there is now an oscillating dipole emits four possible frequencies at $2\omega_1$ or $2\omega_2$ (in the case of $\omega_1 = \omega_2$), $\omega_1 + \omega_2$ and $\omega_1 - \omega_2$. These processes are known as SHG, SFG and difference frequency generation (DFG), respectively. In this thesis, since SFG spectroscopy was employed as the main experimental technique for investigating molecular and electronic structures at interfaces, the background of SFG will be mainly discussed, although DFG also occurs.

It is worth noting that the SFG process is highly interface selective. In the dipole approximation, SFG is forbidden in media with inversion symmetry. That is because, under an inversion operation, as displayed in Figure 1-9, the polarization $\mathbf{P}^{(2)}$ changes its sign as

$$-\mathbf{P}^{(2)} = \varepsilon_0 \overleftrightarrow{\chi}'^{(2)} (-\mathbf{E}_1)(-\mathbf{E}_2) \quad (1-15)$$

Then

$$\mathbf{P}^{(2)} = -\varepsilon_0 \overleftrightarrow{\chi}'^{(2)} (-\mathbf{E}_1)(-\mathbf{E}_2) = \varepsilon_0 \overleftrightarrow{\chi}^{(2)} (\mathbf{E}_1)(\mathbf{E}_2) \quad (1-16)$$

It is found that

$$-\vec{\chi}^{(2)'} = \vec{\chi}^{(2)} \quad (1-17)$$

For the materials with inversion symmetry, nothing should be changed under the inversion operation,

$$\vec{\chi}^{(2)'} = \vec{\chi}^{(2)} \quad (1-18)$$

The only possibility for obeying both Eq. (1-17) and (1-18) is $\vec{\chi}^{(2)} = 0$. Thus, for materials with inversion symmetry, SFG is inactive. In general, most bulk materials, including bulk solids, liquids and gases, do have inversion symmetry because various functional groups more or less are randomly oriented in these bulk materials and thus they would not make a contribution to SFG. However, when molecules reside on surfaces or at interfaces between two centrosymmetric bulk phases, where inversion symmetry is broken, the Eq. (1-18) is not valid anymore. Here, $\vec{\chi}^{(2)}$ does not need to be 0, and SFG process can occur. Briefly, SFG is surface specific. It is only active at interfaces or surfaces lacking inversion symmetry, whereas it is not allowed in bulk phases with inversion symmetry.

This unique property is directly responsible for the inherent surface sensitivity of the SFG process, which makes it such a powerful surface spectroscopic technique.¹⁷¹

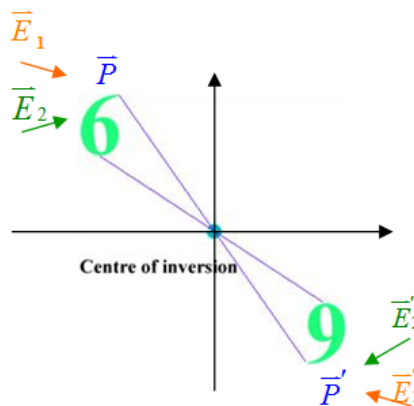


Figure 1-9. Schematic picture of inversion operation.

1.5.2 Sum Frequency Generation (SFG) Spectroscopy^{35,172}

1.5.2.1 Theory of SFG Spectroscopy

IR/visible SFG spectroscopy is based on a second order nonlinear optical phenomenon, SFG, in which two incident photons with frequencies of ω_1 and ω_2 are combined at an interface, producing an output photon with a sum frequency of the two incoming photons ($\omega_3 = \omega_1 + \omega_2$). In traditional SFG experiments, one of the incident photons comes from a narrow bandwidth picosecond laser pulse with tunable frequency in the IR region, while the other comes from a narrow bandwidth picosecond visible laser pulse with fixed frequency. As described in Figure 1-10, the IR beam is scanned across the region of interest, and when the frequency of IR beam is in resonance with specific vibrational mode of the molecules on the surface (ω_0), i.e., $\omega_2 = \omega_0$, the SFG signal can be significantly enhanced, and a vibrational spectrum of the molecules is observed. Therefore, the traditional SFG technique is sometimes called IR-resonant SFG vibrational spectroscopy.

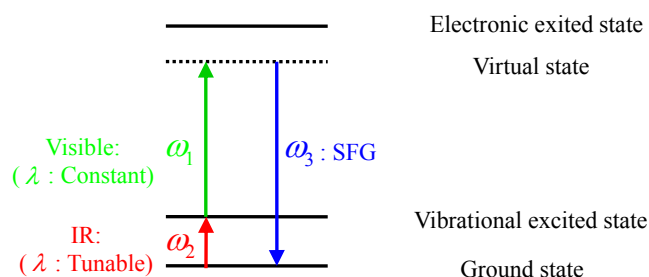


Figure 1-10. Energetic excitation diagram for IR-resonant SFG process.

The energy resolution of SFG signal is mainly determined by the frequency width of the IR laser pulses. In this thesis, a broad bandwidth femtosecond IR beam is used rather than a narrow bandwidth picosecond IR beam utilized in scanning mode SFG spectroscopy. Therefore, scanning of the IR frequency is not necessary, and measurements become more efficient. Employing the broadband femtosecond IR beam in SFG vibrational spectroscopy has exhibited the advantages of shorter

acquisition time, stronger SFG signals and better signal-to-noise ratios.

Figure 1-11 shows the most widely used optical configuration of an SFG interfacial system, in which visible (ω_1) and IR (ω_2) beams are incident from medium 1 and spatially and temporally overlapped at the interfacial layer sandwiched between medium 1 and medium 2, and the resulting SFG signal (ω_3) generated at the interface is reflected into medium 1 with a emission angle θ_{SFG} .

$$\theta_{SFG}(\omega_2) = \sin^{-1} \frac{\omega_1 \sin \theta_1 + \omega_2 \sin \theta_2}{\omega_1 + \omega_2} \quad (1-19)$$

where θ_1 and θ_2 are the incident angles of visible and IR light, respectively. Here, θ_{SFG} is as a function of IR frequency ω_2 , because the incident angles θ_1 , θ_2 , and visible frequency ω_1 are constant in SFG measurements.

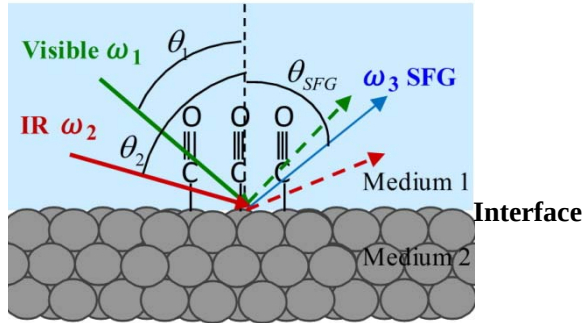


Figure 1-11. Experimental schematic of SFG spectroscopy.

According to the theory of surface SFG introduced in Section 1.5.1, the second order polarization $\mathbf{P}^{(2)}$ acts as the source term for the radiation of the SFG signal. Thus, the intensity of the SFG signal is given by

$$\begin{aligned} I_{SFG} &\propto \left| \mathbf{P}^{(2)} \right|^2 \\ &\propto \left| \epsilon_0 \chi^{(2)} \mathbf{E}_1 \mathbf{E}_2 \right|^2 \end{aligned} \quad (1-20)$$

Further, this equation can be transformed to

$$I_{SFG} \propto \left| \overleftrightarrow{\chi}^{(2)} \right|^2 I(\omega_1) I(\omega_2) \quad (1-21)$$

It can be seen that the SFG intensity is dependent upon the intensities of the input beams (visible, IR) as well as the absolute square of the macroscopic second order nonlinear susceptibility of the medium, $\overleftrightarrow{\chi}^{(2)}$. Since $\overleftrightarrow{\chi}^{(2)}$ is a property of the materials at the interface, it is composed of a nonresonant component $\overleftrightarrow{\chi}_{NR}^{(2)}$ and a resonant component $\overleftrightarrow{\chi}_R^{(2)}$.

$$\overleftrightarrow{\chi}^{(2)} = \overleftrightarrow{\chi}_{NR}^{(2)} + \overleftrightarrow{\chi}_R^{(2)} \quad (1-22)$$

In general, $\overleftrightarrow{\chi}_{NR}^{(2)}$ is made up of three parts, nonresonant contributions from molecules ($\overleftrightarrow{\chi}_{NR,mol}^{(2)}$) and the substrate ($\overleftrightarrow{\chi}_{NR,sub}^{(2)}$), and the interaction between the molecules and the substrate ($\overleftrightarrow{\chi}_{NR,s-m}^{(2)}$).

$$\overleftrightarrow{\chi}_{NR}^{(2)} = \overleftrightarrow{\chi}_{NR,mol}^{(2)} + \overleftrightarrow{\chi}_{NR,sub}^{(2)} + \overleftrightarrow{\chi}_{NR,m-s}^{(2)} \quad (1-23)$$

The nonresonant component $\overleftrightarrow{\chi}_{NR}^{(2)}$ is typically constant at the incident IR frequencies. In contrast to strong $\overleftrightarrow{\chi}_R^{(2)}$, $\overleftrightarrow{\chi}_{NR}^{(2)}$ is substantially smaller for dielectric substrates and it only contributes a small amount to the overall SFG signal. However, metal surfaces generally generate a very large nonresonant signal, which mainly arises from $\overleftrightarrow{\chi}_{NR,sub}^{(2)}$, i.e., $\overleftrightarrow{\chi}_{NR,sub}^{(2)} \gg \overleftrightarrow{\chi}_{NR,mol}^{(2)}, \overleftrightarrow{\chi}_{NR,s-m}^{(2)}$. Therefore, in the case of metal substrates, the nonresonant background cannot be negligible.

The resonant susceptibility $\overleftrightarrow{\chi}_R^{(2)}$ originates from the vibrational modes of

molecules adsorbed on the surface. It is related to the number density of surface oscillators N , their ensemble average orientation and the hyperpolarizability $\vec{\beta}$, as shown in Eq. (1-10).

If neither ω_{vis} nor ω_{SFG} is in resonance with the electric dipole transition in the material and only the electric dipole transition is considered, the microscopic hyperpolarizability, $\vec{\beta}_{ijk}$, near a vibrational transition in a molecule is given by^{35,173}

$$\beta_{ijk} = \frac{1}{2\hbar^2} \cdot \sum_s \left(\frac{\langle g | \mu_i | s \rangle \langle s | \mu_j | v \rangle}{\omega_{SFG} - \omega_{sg}} - \frac{\langle g | \mu_j | s \rangle \langle s | \mu_i | v \rangle}{\omega_{vis} + \omega_{sg}} \right) \left(\frac{\langle v | \mu_k | g \rangle}{\omega_{IR} - \omega_{vg} + i\Gamma} \right) + const. \quad (1-24)$$

where $\langle g |$ is the ground state, $\langle v |$ is the excited vibrational state, $\langle s |$ is any other state, ω_{sg} is the transition frequency from $\langle g |$ to $\langle s |$, ω_{vg} is the transition frequency from $\langle g |$ to $\langle v |$, Γ is the relaxation time of the excited vibrational state, $const.$ is off-resonant terms which can be considered as a constant and $\mu = er$ is the electric dipole operator. The first bracket is identified as Raman transition dipole moment $\mathbf{M}_{ij}$, and the term $\langle v | \mu_k | g \rangle$ as the infrared transition dipole moment μ_n^{vg} . If ω_{vg} is substituted to ω_n , Eq. (1-24) becomes

$$\beta_{ijk} = \frac{1}{2\hbar^2} \cdot \frac{\mathbf{M}_{ij} \cdot \mu_n^{vg}}{\omega_{IR} - \omega_n + i\Gamma} + const.$$

Thus,

$$\begin{aligned} \overleftrightarrow{\chi}_R^{(2)} &= \sum_n \overleftrightarrow{\chi}_{R,n}^{(2)} \\ &= \sum_n \frac{N}{\epsilon_0} \langle \vec{\beta}_{ijk} \rangle \end{aligned}$$

$$\begin{aligned}
& \propto \sum_n \frac{N}{\epsilon_0} \cdot \frac{\langle \mathbf{M}_{ij} \cdot \boldsymbol{\mu}_n^{\text{vg}} \rangle}{\omega_{IR} - \omega_n + i\Gamma_n} \\
& = \sum_n \frac{\vec{A}_n}{\omega_{IR} - \omega_n + i\Gamma_n}
\end{aligned} \tag{1-25}$$

where $\vec{A}_n = \frac{N}{\epsilon_0} \langle \mathbf{M}_{ij} \cdot \boldsymbol{\mu}_n^{\text{vg}} \rangle$ is introduced for a simple description of resonant susceptibility $\vec{\chi}_R^{(2)}$. $\vec{A}_n$, ω_n and Γ_n correspond to the oscillator strength, resonant frequency and half-width at the half-maximum of the n^{th} transition moment, respectively. Bracket $\langle \rangle$ denotes the ensemble average of the molecular orientation.

From Eq. (1-25), it is clear that

1. The SFG intensity, which is inherently dependent upon the resonant susceptibility $\vec{\chi}_R^{(2)}$, reaches a maximum when the frequency of the IR beam is equal to the vibrational level of surface molecules, i.e., $\omega_{IR} = \omega_n$.

2. SFG vibrational modes are only active when they are both IR and Raman active, confirming that only non-centrosymmetric surfaces or interfaces, which satisfy both IR and Raman selection rules, allow an SFG signal to be generated.

3. The intensity of the SFG signal is also dependent on the orientation or ordering of molecules on the surface. The more ordered the surface adsorbates are, the stronger the SFG signal will be generated because SFG spectroscopy probes an ensemble, so the average value of $\vec{\chi}_R^{(2)}$ is 0 even in randomly oriented SFG active materials.

To sum up, combining Eq. (1-23) and (1-25), Eq. (1-22) can be written as

$$\vec{\chi}^{(2)} = \vec{\chi}_{NR}^{(2)} + \sum_n \frac{\vec{A}_n}{\omega_{IR} - \omega_n + i\Gamma_n} \tag{1-26}$$

Finally, the intensity of the SFG signal can be expressed in terms of an effective

nonlinear susceptibility $\vec{\chi}_{eff}^{(2)}$ that incorporates Fresnel factors $\mathbf{F}$ into $\vec{\chi}^{(2)}$ as follows:

$$I_{SFG} \propto \left| \vec{\chi}_{eff,NR}^{(2)} + \sum_n \frac{\vec{A}_{eff,n}}{\omega_{IR} - \omega_n + i\Gamma_n} \right|^2 \quad (1-27)$$

where $\vec{\chi}_{eff,NR}^{(2)} = \mathbf{F} : \vec{\chi}_{NR}^{(2)}$ and $\vec{A}_{eff,n} = \mathbf{F} : \vec{A}_n$.

1.5.2.2 Peak Deconvolution and Effect of Interference between Resonant and Nonresonant Contributions on an SFG Spectrum

For a nonlinear technique, the SFG intensity dependence is more complicated¹⁷⁴ than with linear techniques such as SRES and IRAS.^{175,176} The usual way to interpret IRAS measurements in electrochemistry is to subtract off the background and measure the integrated area of the vibrational peak.^{175,176} In SFG, one ordinarily expects the integrated area of the resonant transition to be proportional to the square of the number density,¹⁷⁴ but in an electrochemical system there is an additional complication. Beside the resonant vibrational transition, the SFG signal at the interface also includes a broader nonresonant background from the metal electrode surface, which further complicates the analysis. Depending on the different ratios of resonant and nonresonant contributions, it is interesting to note the SFG spectral profile of a resonance can appear in various different forms. Thus, a direct comparison of the raw SFG spectra to Raman or IR spectra may be misleading because of interference effects between the resonant and nonresonant parts, and the SFG spectrum should be fit to Eq. (1-27), which combines both contributions in order to extract the characteristic parameters of the resonant transition.

Both $\vec{\chi}_R^{(2)}$ and $\vec{\chi}_{NR}^{(2)}$ are complex quantities and the total SFG signal primarily depends on the relative phases, ε and $\delta(\omega_{IR})$, of the two susceptibilities. $\delta(\omega_{IR})$ is the resonant phase, which depends on the IR frequency (ω_{IR}). ε is referred to as

the fixed nonresonant phase, which is approximately invariant with IR frequency and dependent on the intrinsic properties of the metal substrate.³⁵

If a single resonance is considered for simplification, Eq. (1-28) is obtained.

$$\vec{\chi}_R^{(2)} = \frac{\vec{A}}{\sqrt{(\omega - \omega_{IR})^2 + \Gamma^2} \cdot e^{i\delta(\omega_{IR})}} = \left| \vec{\chi}_R^{(2)} \right| e^{-i\delta(\omega_{IR})} \quad (1-28)$$

$$\delta(\omega_{IR}) = \tan^{-1} \frac{\Gamma}{\omega - \omega_{IR}} \quad (1-29)$$

When ω_{IR} is scanned from lower to higher frequency around ω , $\delta(\omega_{IR})$ changes its value from 0 to π continuously across at $\pi/2$, $\omega_{IR} = \omega$,

$$\vec{\chi}_{NR}^{(2)} = \left[\vec{\chi}_{NR}^{(2)} \right] e^{i\varepsilon} \quad (1-30)$$

ε is the constant. Using Eq. (1-28) and (1-30), Eq. (1-27) can be written as

$$\begin{aligned} I_{SFG} &\propto \left| \vec{\chi}^{(2)} \right|^2 = \left| \vec{\chi}_{NR}^{(2)} + \vec{\chi}_R^{(2)} \right|^2 \\ &= \left[\left| \vec{\chi}_{NR}^{(2)} \right| e^{i\varepsilon} + \left| \vec{\chi}_R^{(2)} \right| e^{i\delta(\omega_{IR})} \right] \times \left[\left| \vec{\chi}_{NR}^{(2)} \right| e^{-i\varepsilon} + \left| \vec{\chi}_R^{(2)} \right| e^{-i\delta(\omega_{IR})} \right] \\ &= \left| \vec{\chi}_{NR}^{(2)} \right|^2 + \left| \vec{\chi}_R^{(2)} \right|^2 + 2 \left| \vec{\chi}_{NR}^{(2)} \right| \left| \vec{\chi}_R^{(2)} \right| \cos[\varepsilon - \delta(\omega_{IR})] \end{aligned} \quad (1-31)$$

Since $\delta(\omega_{IR})$ in Eq. (1-31) is dependent on ω_{IR} , the spectral shape of SFG spectra is not simple. Eq. (1-31) shows that the profile of an SFG resonance consists of three parts. The first part is a pure background contribution from $\left| \vec{\chi}_{NR}^{(2)} \right|^2$. The second part is the resonant contribution $\left| \vec{\chi}_R^{(2)} \right|^2$. The first two parts of the susceptibilities are positive and the cross-term, as the third part, which comes from interference between the resonant and nonresonant parts, might have a positive or a

negative value. A positive cross-term forms constructive interference, thus giving rise to a peak. On the other hand, a negative cross-term forms a destructive interference, thus giving rise to a dip. Therefore, the relative phase difference in the cross-term between the two susceptibilities gives rise to peaks or dips or semi-interference peaks.

Figure 1-12 shows a series of simulated curves of $|\vec{\chi}^{(2)}|^2$ with different ω . When $|\vec{\chi}_{NR}^{(2)}|=0$, the $|\vec{\chi}^{(2)}|^2$ spectra are expressed by a Lorentz function centered at ω and independent of ε , whereas, if $|\vec{\chi}_{NR}^{(2)}|$ cannot be negligible ($|\vec{\chi}_{NR}^{(2)}| = |\vec{A}/\Gamma| > 0$), the spectral shape is not necessarily symmetric and dependent on ε . The spectral profile gives a Lorentz shape only when $\varepsilon = \pi/2$. Differential shape profiles are observed when $\varepsilon = 0$ and π , and even a negative peak profile is observed when $\varepsilon = 3\pi/2$. A non-Lorentz shape SFG spectrum indicates that there is measureable nonresonant contribution in the spectrum, but the opposite is not always true (in the case of $\varepsilon = \pi/2$ and $|\vec{\chi}_{NR}^{(2)}| > 0$). Note that the peak frequency in appearance is often different from that in truth, which must be obtained by peak fitting.

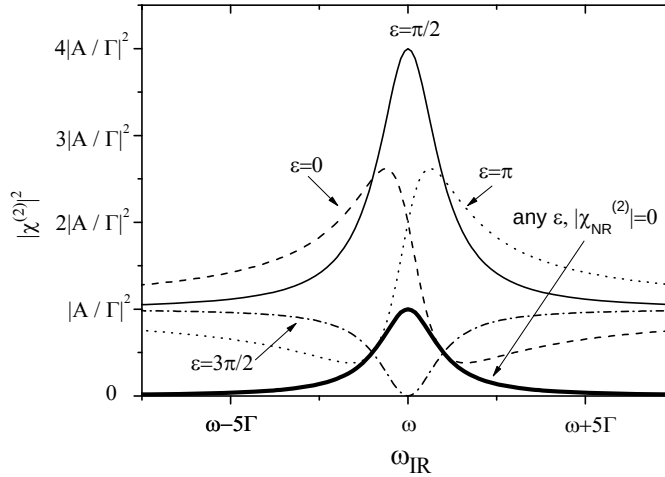


Figure 1-12. The effect of interference between resonant and nonresonant components on a spectral profile. In all cases, $|\vec{\chi}_R^{(2)}| = |\vec{A}/\Gamma| = |\vec{\chi}_{NR}^{(2)}|$. ε for each case is shown in the figure. The thick solid line shows a simulation with $|\vec{\chi}_{NR}^{(2)}|=0$, where the spectral shape is independent of ε .

In practical use, it is convenient to separate the real and imaginary parts in $\vec{\chi}_{NR}^{(2)}$ and $\vec{\chi}_{R,n}^{(2)}$.

$$\vec{\chi}_{NR}^{(2)} = \left| \vec{\chi}_{NR}^{(2)} \right| e^{i\varepsilon} = \left| \vec{\chi}_{NR}^{(2)} \right| \cos \varepsilon + i \left| \vec{\chi}_{NR}^{(2)} \right| \sin \varepsilon \quad (1-32)$$

$$\vec{\chi}_{R,n}^{(2)} = \frac{\vec{A}_n(\omega_n - \omega_{IR})}{(\omega_{IR} - \omega_n)^2 + \Gamma_n^2} + i \frac{\vec{A}_n \cdot \Gamma_n}{(\omega_{IR} - \omega_n)^2 + \Gamma_n^2} \quad (1-33)$$

where phase angle ε is introduced between them. Then Eq. (1-27) is written as

$$\begin{aligned} I_{SFG} &\propto \left| \vec{\chi}^{(2)} \right|^2 = \left| \vec{\chi}_{NR}^{(2)} + \vec{\chi}_R^{(2)} \right|^2 \\ &= \left\{ \sum_n \frac{\vec{A}_{eff,n}(\omega_n - \omega_{IR})}{(\omega_{IR} - \omega_n)^2 + \Gamma_n^2} + \left| \vec{\chi}_{eff,NR}^{(2)} \right| \cos \varepsilon \right\}^2 + \left\{ \sum_n \frac{\vec{A}_{eff,n} \cdot \Gamma_n}{(\omega_{IR} - \omega_n)^2 + \Gamma_n^2} + \left| \vec{\chi}_{eff,NR}^{(2)} \right| \sin \varepsilon \right\}^2 \end{aligned} \quad (1-34)$$

All the SFG spectra were fitted by Eq. (1-34) using Origin 6.1. An example of the fitting function by using Origin is shown as follows:

> Parameters=A1, B1, C1, A2, B2, C2, A3, B3, C3, A4, B4, C4, A5, B5, C5, NR, F, s0

[FORMULA]

```
> M1=A1/((B1-w)^2+C1^2);
> M2=A2/((B2-w)^2+C2^2);
> M3=A3/((B3-w)^2+C3^2);
> M4=A4/((B4-w)^2+C4^2);
> M5=A5/((B5-w)^2+C5^2);
> U=F*Pi/180;
> R=M1*(B1-w)+M2*(B2-w)+M3*(B3-w)+M4*(B4-w)+M5*(B5-w)+NR*cos(U);
> I=M1*C1+M2*C2+M3*C3+M4*C4+M5*C5+NR*sin(U);
> y=(R)^2+(I)^2+s0;
> INDEPENDENT VARIABLES: w
> DEPENDENT VARIABLES: y
```

1.5.2.3 Applications of SFG Spectroscopy to Electrochemical Interfaces

Owing to the ability to provide molecular-level information about surface species at all interfaces accessible by light, to date, SFG spectroscopy has already been successfully applied to analyzing a wide variety of interfacial problems. Many electrochemical interfaces have been investigated by in situ SFG technique and important molecular information on adsorbates has also been obtained. In this section, only a few examples are selected and briefly introduced.

SFG spectroscopy gives the freedom as to observe changes between crystal structures, like the Pt single/poly crystals (Figure 1-13), as well as the production of dissociative adsorption/reaction intermediates from fuel (e.g., methanol and ethanol) oxidation. Many groups have used this technique to study the adsorbed CO poisoning intermediate and its vibrational transitions which are surface-sensitive, potential dependent, and fuel concentration dependent.^{29,177,178} Monitoring adsorbates on the electrode surface with SFG can offer great insight as to reactions that would happen at fuel cell electrodes, including the reactions that cause poisoning or could help in the field of catalyst development.

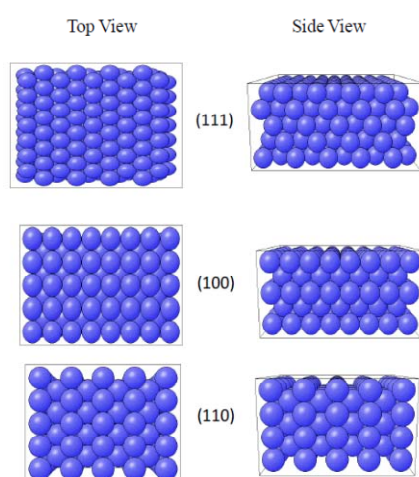


Figure 1-13. The surface structures of Pt(111), Pt(100) and Pt(110) single crystals.

Hydrogen is involved as a reactant or product in many fundamentally important surface-catalyzed reactions. SFG allows probing of absolute vibrational spectra, even

for a system like H-Pt with a very weak IR cross-section, without the need to extract the surface signal by taking a reference at a particular potential. Moreover, because of the use of a free electron laser (FEL) as the IR source, SFG is sensitive enough to record the vibrational signature of the hydride interface in the electrochemical environment.^{179–184} The absolute vibrational spectra of hydrogen on a polycrystalline and a single crystal Pt electrode in acid medium were measured both in the under and in the overpotential regions, providing new insights into the hydrogen adsorption and evolution processes. At underpotential, hydrogen occupies the atop site and forms hydrogen bonding with the water molecules located in the double layer region. The SFG fingerprint of the underpotential deposited hydrogen is structure-sensitive and is related to its bonding configuration to interfacial water molecules.¹⁸¹ At overpotential, a new H-Pt band was detected by SFG and it was found to be not sensitive to the surface structures of the electrode. This new hydrogen adspecies is presumed to be the intermediate of the hydrogen evolution reaction.¹⁸⁰

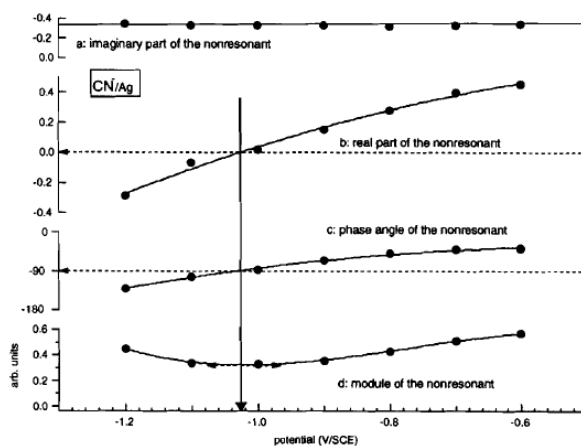


Figure 1-14. Potential dependence of imaginary part (a), real part (b), phase angle (c) and amplitude (d) of the nonresonant contribution to the SFG susceptibility of an Ag electrode in 0.1 M NaClO₄ + 0.025 M KCN electrolyte. The vertical arrow indicates the PZC.¹⁸⁶

The quantitative analysis of the structures of electrochemical interfaces requires information on surface charge, particularly point of zero charge (PZC). For a dilute

solution on nonadsorbing ions such as ClO_4^- on silver, the PZC is readily obtained from capacitance measurements. However, there is no electrochemical technique that is able to directly give the PZC in the presence of strongly adsorbed ions.^{181,185} An attempt has been made to derive the PZC from the nonlinear optical response.¹⁸⁶ As is known, the nonresonant SFG signal comes mainly from the substrate and closely depends on the surface electronic properties of the substrate. Not only the amplitude but also the phase of the nonresonant signal carry surface electronic information. Through analyzing these parameters as a function of potential, when the phase angle is equal to 90° and the amplitude of the nonresonant SFG component displays a well-defined minimum, the PZC can be located, as shown in Figure 1-14. Thus, SFG spectroscopy has become a valuable tool for direct determination of the PZC in concentrated electrolytes and in the presence of a strong ionic specific adsorption. The adsorption of CN^- on a silver electrode has been studied in 0.1 M NaClO_4 + 0.01 M KCN solution by potential dependent SFG technique, where the PZC at ca. -1.02 V (vs. SCE) and the adsorption behavior of CN^- on Ag were successfully detected.¹⁸¹

As shown above, SFG spectroscopy has provided valuable information on molecular structures at various electrochemical interfaces. However, most is static information, which can also be obtained by linear vibrational spectroscopy such as IRAS and SERS. Therefore, to acquire something specific, in recent years, scientists have devoted themselves to utilizing SFG techniques in some new ways.

SFG spectroscopy has the advantages of high spatial and temporal resolution over linear vibrational spectroscopy because it is conducted with ultrafast pulsed lasers. Thus, the time-resolved SFG technique was developed by using a pump-probe configuration. It provides the possibility to explore the ultrafast reaction kinetics and surface dynamics that occur on the time scale from picoseconds to femtosecond. Domen et al. employed time-resolved SFG spectroscopy to trace short lived intermediate species in thermal decomposition reactions.¹⁸⁷ The vibrational relaxation of CN^- on Pt(111) in D_2O solution was investigated with time-resolved SFG technique, and observed a life time from a few ps to 60 ps was observed for CN^- vibration with the effect of potential.¹⁸⁸ Noguchi et al. carried out time-resolved SFG measurements

on a Pt electrode/electrolyte interface covered with a CO adlayer.¹⁸⁹ By producing a transient temperature jump by irradiating the electrode with a picosecond visible pulse, a reversible transient migration of CO molecules on a Pt surface was monitored under electrochemical conditions.

1.5.3 Possibility of Double Resonance (DR)-SFG Spectroscopy for Probing Electronic Structure at Electrochemical Interfaces

Traditional SFG spectroscopy is performed by using the frequency-fixed visible and tunable IR beams and can provide the vibrational fingerprints of molecules at electrochemical interfaces. Recently, a newly developed SFG technique of tuning both incident visible and IR frequencies has attracted much attention.³⁸ As shown in Figure 1-15, with both frequencies of visible (ω_1) and IR (ω_2) tuned over surface vibrational and electronic resonance, respectively, doubly resonant enhancement in output SFG intensity occurs when the corresponding vibrational and electronic transitions are coupled. Such enhanced SFG process is called double resonance (DR)-SFG, which carries information on the interfacial electronic and molecular properties simultaneously.

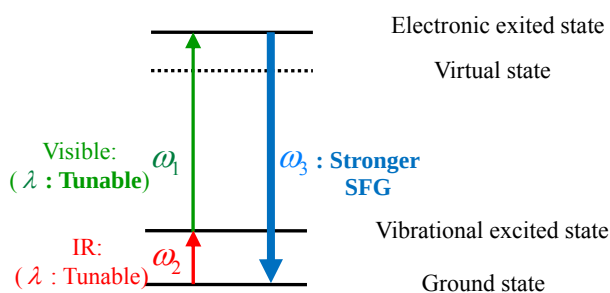


Figure 1-15. Energetic excitation diagram for IR/visible double-resonant SFG process.

With this advantage, DR-SFG has been used to probe the electronic properties of a buried interface,¹⁹⁰ organic light emitting diode interface,¹⁹¹ and a small amount of choral molecules in biological systems.¹⁹² More recently, Somorjai and his colleagues reported that DR-SFG spectroscopy could elucidate the electronic structure of the

CO/Pt(111) interface by showing that the intensity of the SFG band corresponding to C-O stretching is enhanced by the resonance of visible light with the electronic transition between the bonding $2\pi^*_b$ and $5\sigma_a$ states at the interface, i.e., IR/visible double resonance effect,³⁸ although the experiments were carried out in a UHV environment. Therefore, as a photon-in photon-out technique, DR-SFG spectroscopy is expected to be an extremely useful technique for probing the electronic transitions at electrochemical interfaces.^{38,126,127}

1.6 Objectives and Outline of the Present Thesis

The objective of this thesis is to determine the structural information of various electrochemical interfaces, including CO adsorbed on Pt single crystal electrodes, polycrystalline Pt electrodes and epitaxial Pt ultrathin films deposited on Au surfaces, by employing DR-SFG. Emphasis is placed on the study of interfacial electronic structures in electrochemical conditions, since these are less studied owing to the lack of suitable techniques for determining the electronic structures in solutions and are very vital to understanding the mechanism of catalytic reactions and designing high-efficiency electrocatalysts for fuel cell applications.

The outline of the present thesis is as follows:

Chapter 1 provides the introduction to the thesis, in which the background of surface catalysis, electrocatalysts and the related characterization techniques is reviewed. The fundamentals of SFG spectroscopy, which is utilized in later chapters to characterize electrochemical interfaces, is also introduced.

Chapter 2 presents the experimental details, including the information on materials, preparation procedures of samples, experimental setups and measurements.

Chapter 3 deals with the system of a CO adlayer adsorbed on a Pt(111) single crystal electrode surface in a CO-free 0.5 M H_2SO_4 electrolyte, where potential dependent DR-SFG spectroscopy was successfully applied to this electrochemical interface for probing interfacial electronic structures. The results of scanning and constant potential measurements concerning the potential dependence of the SF response of the CO/Pt(111) interface are present. When the experiments were further

carried out by using visible light of eight different incident energies, the SFG signal on Pt(111) was found to depend on visible energy, which is related to the unique electronic structure information reflected by the double resonance effect. Under the same experimental conditions, IRAS measurements were also performed for a comparative discussion.

In Chapter 4, the electronic structure of the CO/polycrystalline Pt electrochemical interface was studied by using the potential dependent DR-SFG technique. The potential dependent SFG measurements were carried out at different visible light energies under constant potential control. As already found on the Pt(111) surface, an anomalous SFG intensity increase and a linear potential shift of the SFG peak with visible and/or SF light energy were observed. The effect of substrate structure on the interfacial electronic structures of CO was discussed by comparing the widths of the SFG peak with potential on polycrystalline Pt with that on Pt(111) electrode.

Chapter 5 focuses on the investigation of a CO/bimetal system synthesized by electrochemically depositing a Pt ultrathin film on a polycrystalline Au substrate. With the use of the electrochemical technique, the electrocatalytic activity of the Pt-modified Au electrode toward CO oxidation was checked as a function of Pt thickness. Furthermore, potential dependent DR-SFG spectroscopic study was carried out at the CO/Pt-modified Au interface. An improved understanding of the interfacial electronic structures of CO on a Pt-modified Au surface is achieved by comparing the results to those of CO/Pt(111) (in Chapter 3) and CO/polycrystalline Pt (in Chapter 4) systems.

The most important conclusions are summarized in Chapter 6 together with a brief discussion of possible future work.

References

- (1) Berzelius, J. J. *Edinb. New Philos. J.* **1836**, *21*, 223–228.
- (2) Centi, G.; Ciambelli, P.; Perathoner, S.; Russo, P. *Catal. Today* **2002**, *75*, 3–15.
- (3) Woodruff, D. P.; Delchar, T. A. *Modern Techniques of Surface Science*, 2nd ed.; Cambridge University Press: Cambridge, U.K., 1986.
- (4) Somorjai, G. A. *Surf. Sci.* **1994**, *299–300*, 849–866.
- (5) Ertl, G. *Surf. Sci.* **1994**, *299–300*, 742–754.
- (6) Goodman, D. W. *Chem. Rev.* **1995**, *95*, 523–536.
- (7) Somorjai, G. A.; Li, Y. *Introduction to Surface Chemistry and Catalysis*, 2nd ed.; John Wiley & Sons: Hoboken, N.J., 2010.
- (8) Uosaki, K.; Koinuma, M. *J. Electroanal. Chem.* **1993**, *357*, 301–306.
- (9) Naohara, H.; Ye, S.; Uosaki, K. *J. Phys. Chem. B* **1998**, *102*, 4366–4373.
- (10) Takakusagi, S.; Kitamura, K.; Uosaki, K. *J. Phys. Chem. C* **2008**, *112*, 3073–3077.
- (11) Wang, J.; Ocko, B. M.; Davenport, A. J.; Isaacs, H. S. *Phys. Rev. B* **1992**, *46*, 10321–10338.
- (12) Kondo, T.; Morita, J.; Hanaoka, K.; Takakusagi, S.; Tamura, K.; Takahashi, M.; Mizuki, J.; Uosaki, K. *J. Phys. Chem. C* **2007**, *111*, 13197–13204.
- (13) Bewick, A.; Kunimatsu, K.; Pons, B. S.; Russell, J. W. *J. Electroanal. Chem. Interfacial Electrochem.* **1984**, *160*, 47–61.
- (14) Gale, R. J. *Spectroelectrochemistry: Theory and Practice*; Plenum Press: New York, N.Y., 1988.
- (15) Iwasita, T.; Nart, F. C. *Prog. Surf. Sci.* **1997**, *55*, 271–340.
- (16) Fleischmann, M.; Hendra, P. J.; McQuillan, A. J. *Chem. Phys. Lett.* **1974**, *26*, 163–166.
- (17) Koglin, E.; Schwuger, M. J. *Faraday Discuss.* **1992**, *94*, 213–220.
- (18) Zhang, B.; Li, J.-F.; Zhong, Q.-L.; Ren, B.; Tian, Z.-Q.; Zou, S.-Z. *Langmuir* **2005**, *21*, 7449–7455.
- (19) Dewald, H. D. *Electroanalysis* **1991**, *3*, 145–155.
- (20) McBreen, J.; Scherson, D. *Spectroscopic Tools for the Analysis of Electrochemical Systems: Proceedings of the International Symposium*; The Electrochemical Society: Pennington, N.J., 2002.
- (21) Guyot-Sionnest, P.; Tadjeddine, A.; Liebsch, A. *Phys. Rev. Lett.* **1990**, *64*, 1678–1681.
- (22) Corn, R. M.; Higgins, D. A. *Chem. Rev.* **1994**, *94*, 107–125.
- (23) Yang, D.; Bizzotto, D.; Lipkowski, J.; Pettinger, B.; Mirwald, S. *J. Phys. Chem.* **1994**, *98*, 7083–7089.
- (24) Tryk, D. A.; Bae, I. T.; Scherson, D.; Antonio, M. R.; Jordan, G. W.; Huston, E. L. *J. Electrochem. Soc.* **1995**, *142*, L76–L78.
- (25) Masuda, T.; Fukumitsu, H.; Fugane, K.; Togasaki, H.; Matsumura, D.; Tamura, K.; Nishihata, Y.; Yoshikawa, H.; Kobayashi, K.; Mori, T.; et al. *J. Phys. Chem. C* **2012**, *116*, 10098–10102.
- (26) Masuda, T.; Fukumitsu, H.; Takakusagi, S.; Chun, W.-J.; Kondo, T.; Asakura,

- K.; Uosaki, K. *Adv. Mater.* **2012**, *24*, 268–272.
- (27) Bae, I. T.; Scherson, D. A. *J. Phys. Chem.* **1996**, *100*, 19215–19217.
 - (28) Masuda, T.; Yoshikawa, H.; Noguchi, H.; Kawasaki, T.; Kobata, M.; Kobayashi, K.; Uosaki, K. *Appl. Phys. Lett.* **2013**, *103*, 111605.
 - (29) Dederichs, F.; Friedrich, K. A.; Daum, W. *J. Phys. Chem. B* **2000**, *104*, 6626–6632.
 - (30) Noguchi, H.; Okada, T.; Uosaki, K. *J. Phys. Chem. B* **2006**, *110*, 15055–15058.
 - (31) Lagutchev, A.; Lu, G. Q.; Takeshita, T.; Dlott, D. D.; Wieckowski, A. *J. Chem. Phys.* **2006**, *125*, 154705.
 - (32) Xiong, W.; Laaser, J. E.; Mehlenbacher, R. D.; Zanni, M. T. *Proc. Natl. Acad. Sci. U. S. A.* **2011**, *108*, 20902–20907.
 - (33) Ponath, H.-E.; Stegeman, G. I. *Nonlinear surface electromagnetic phenomena*; North-Holland: Amsterdam, Netherland, 1991.
 - (34) Miranda, P. B.; Shen, Y. R. *J. Phys. Chem. B* **1999**, *103*, 3292–3307.
 - (35) Bain, C. D. *J. Chem. Soc. Faraday Trans.* **1995**, *91*, 1281–1296.
 - (36) Shen, Y. R. *Proc. Natl. Acad. Sci.* **1996**, *93*, 12104–12111.
 - (37) Clark, R. J. H.; Hester, R. E. *Spectroscopy for Surface Science*; John Wiley & Sons: New York, N.Y., 1998.
 - (38) Chou, K. C.; Westerberg, S.; Shen, Y. R.; Ross, P. N.; Somorjai, G. A. *Phys. Rev. B* **2004**, *69*, 153413.
 - (39) Kordesch, K.; Simader, G. *Fuel Cells and Their Applications*, 1st ed.; VCH: Weinheim, Germany, 1996.
 - (40) Kreuter, W.; Hofmann, H. *Int. J. Hydrog. Energy* **1998**, *23*, 661–666.
 - (41) Santos, D. M. F.; Sequeira, C. A. C.; Figueiredo, J. L. *Quím. Nova* **2013**, *36*, 1176–1193.
 - (42) Gordon, R. B.; Bertram, M.; Graedel, T. E. *Proc. Natl. Acad. Sci.* **2006**, *103*, 1209–1214.
 - (43) Chen, J.; Lim, B.; Lee, E. P.; Xia, Y. *Nano Today* **2009**, *4*, 81–95.
 - (44) Koenigsmann, C.; Zhou, W.; Adzic, R. R.; Sutter, E.; Wong, S. S. *Nano Lett.* **2010**, *10*, 2806–2811.
 - (45) Toda, T.; Igarashi, H.; Uchida, H.; Watanabe, M. *J. Electrochem. Soc.* **1999**, *146*, 3750–3756.
 - (46) Greeley, J.; Jaramillo, T. F.; Bonde, J.; Chorkendorff, I.; Nørskov, J. K. *Nat. Mater.* **2006**, *5*, 909–913.
 - (47) Zhang, J.; Vukmirovic, M. B.; Xu, Y.; Mavrikakis, M.; Adzic, R. R. *Angew. Chem. Int. Ed.* **2005**, *44*, 2132–2135.
 - (48) Esposito, D. V.; Hunt, S. T.; Stottlemeyer, A. L.; Dobson, K. D.; McCandless, B. E.; Birkmire, R. W.; Chen, J. G. *Angew. Chem. Int. Ed.* **2010**, *49*, 9859–9862.
 - (49) Esposito, D. V.; Chen, J. G. *Energy Environ. Sci.* **2011**, *4*, 3900–3912.
 - (50) Chen, Z.; Higgins, D.; Yu, A.; Zhang, L.; Zhang, J. *Energy Environ. Sci.* **2011**, *4*, 3167–3192.
 - (51) Zheng, Y.; Jiao, Y.; Zhu, Y.; Li, L. H.; Han, Y.; Chen, Y.; Du, A.; Jaroniec, M.; Qiao, S. Z. *Nat. Commun.* **2014**, *5*, 3783.
 - (52) Sidik, R. A.; Anderson, A. B.; Subramanian, N. P.; Kumaraguru, S. P.; Popov,

- B. N. *J. Phys. Chem. B* **2006**, *110*, 1787–1793.
- (53) Ikeda, T.; Boero, M.; Huang, S.-F.; Terakura, K.; Oshima, M.; Ozaki, J.; Miyata, S. *J. Phys. Chem. C* **2010**, *114*, 8933–8937.
 - (54) Zheng, Y.; Jiao, Y.; Li, L. H.; Xing, T.; Chen, Y.; Jaroniec, M.; Qiao, S. Z. *ACS Nano* **2014**, *8*, 5290–5296.
 - (55) Yang, D.-S.; Bhattacharjya, D.; Inamdar, S.; Park, J.; Yu, J.-S. *J. Am. Chem. Soc.* **2012**, *134*, 16127–16130.
 - (56) Zhao, Y.; Yang, L.; Chen, S.; Wang, X.; Ma, Y.; Wu, Q.; Jiang, Y.; Qian, W.; Hu, Z. *J. Am. Chem. Soc.* **2013**, *135*, 1201–1204.
 - (57) Uosaki, K.; Elumalai, G.; Noguchi, H.; Masuda, T.; Lyalin, A.; Nakayama, A.; Taketsugu, T. *J. Am. Chem. Soc.* **2014**, *136*, 6542–6545.
 - (58) Jeff Greeley; Jens K. Nørskov; Mavrikakis, M. *Annu. Rev. Phys. Chem.* **2002**, *53*, 319–348.
 - (59) Stolbov, S.; Ortigoza, M. A.; Rahman, T. S. *J. Phys. Condens. Matter* **2009**, *21*, 474226.
 - (60) Taylor, H. S. *J. Phys. Chem.* **1925**, *30*, 145–171.
 - (61) Kessler, T.; Luna, A. M. C.; Triaca, W. E.; Arvia, A. J. *J. Appl. Electrochem.* **1986**, *16*, 693–702.
 - (62) Zinola, C. F.; Castro Luna, A. M.; Triaca, W. E.; Arvia, A. J. *Electrochimica Acta* **1994**, *39*, 1627–1632.
 - (63) Bilmes, S. A.; Arvia, A. J. *J. Electroanal. Chem. Interfacial Electrochem.* **1986**, *198*, 137–148.
 - (64) Henry, C. R. *Surf. Sci. Rep.* **1998**, *31*, 231–325.
 - (65) Yoo, S. J.; Jeon, T.-Y.; Lee, K.-S.; Park, K.-W.; Sung, Y.-E. *Chem Commun* **2010**, *46*, 794–796.
 - (66) Adžić, R. R.; Marković, N. M. *J. Electroanal. Chem. Interfacial Electrochem.* **1982**, *138*, 443–447.
 - (67) Baldauf, M.; Kolb, D. A. *Electrochimica Acta* **1993**, *38*, 2145–2153.
 - (68) Naohara, H.; Ye, S.; Uosaki, K. *Electrochimica Acta* **2000**, *45*, 3305–3309.
 - (69) Arenz, M.; Stamenkovic, V.; Schmidt, T. J.; Wandelt, K.; Ross, P. N.; Markovic, N. M. *Surf. Sci.* **2002**, *506*, 287–296.
 - (70) Rodriguez, J. *Surf. Sci. Rep.* **1996**, *24*, 223–287.
 - (71) Hammer, B.; Nørskov, J. K. *Impact of Surface Science on Catalysis* **2000**, *45*, 71–129.
 - (72) Stamenkovic, V. R.; Mun, B. S.; Arenz, M.; Mayrhofer, K. J. J.; Lucas, C. A.; Wang, G.; Ross, P. N.; Markovic, N. M. *Nat. Mater.* **2007**, *6*, 241–247.
 - (73) Xu, Y.; Ruban, A. V.; Mavrikakis, M. *J. Am. Chem. Soc.* **2004**, *126*, 4717–4725.
 - (74) Rodriguez, J. A.; Goodman, D. W. *Science* **1992**, *257*, 897–903.
 - (75) Buatier de Mongeot, F.; Scherer, M.; Gleich, B.; Kopatzki, E.; Behm, R. J. *Surf. Sci.* **1998**, *411*, 249–262.
 - (76) Yeager, E. *Surf. Sci.* **1980**, *101*, 1–22.
 - (77) Chang, S. C.; Weaver, M. J. *J. Phys. Chem.* **1991**, *95*, 5391–5400.
 - (78) Abruna, H. D. *Electrochemical Interfaces: Modern Techniques for In-Situ*

- Interface Characterization*; VCH: New York, N.Y. 1991.
- (79) Weaver, M. J.; Gao, X. *Annu. Rev. Phys. Chem.* **1993**, *44*, 459–494.
 - (80) Lipkowski, L. J.; Ross, P. N. *Structure of Electrified Interfaces*; VCH: New York, N.Y., 1993.
 - (81) Weaver, M. J. *J. Phys. Chem.* **1996**, *100*, 13079–13089.
 - (82) Uosaki, K. *Jpn. J. Appl. Phys.* **2015**, *54*, 030102.
 - (83) Binnig, G.; Rohrer, H.; Gerber, C.; Weibel, E. *Phys. Rev. Lett.* **1982**, *49*, 57–61.
 - (84) Sonnenfeld, R.; Hansma, P. K. *Science* **1986**, *232*, 211–213.
 - (85) Hansma, P. K.; Tersoff, J. *J. Appl. Phys.* **1987**, *61*, R1–R24.
 - (86) Lustenberger, P.; Rohrer, H.; Christoph, R.; Siegenthaler, H. *J. Electroanal. Chem. Interfacial Electrochem.* **1988**, *243*, 225–235.
 - (87) Itaya, K.; Tomita, E. *Surf. Sci.* **1988**, *201*, L507–L512.
 - (88) Haugstad, G. *Atomic Force Microscopy: Understanding Basic Modes and Advanced Applications*; John Wiley & Sons: New York, N.Y., 2012.
 - (89) Melendres, C. A.; Tadjeddine, A. *Synchrotron Techniques in Interfacial Electrochemistry*, 1st ed.; Springer: London, U.K., 1994.
 - (90) Wang, J.; Davenport, A. J.; Isaacs, H. S.; Ocko, B. M. *Science* **1992**, *255*, 1416–1418.
 - (91) Toney, M. F.; Gordon II, J. G.; Melroy, O. R. **1991**, *1550*, 140–150.
 - (92) Dahn, J. R.; Py, M. A.; Haering, R. R. *Can. J. Phys.* **1982**, *60*, 307–313.
 - (93) Zegenhagen, J.; Kazimirov, A.; Scherb, G.; Kolb, D. M.; Smilgies, D.-M.; Feidenhans'l, R. *Surf. Sci.* **1996**, *352–354*, 346–351.
 - (94) Fleischmann, M.; Hendra, P. J.; McQuillan, A. J. *J. Chem. Soc. Chem. Commun.* **1973**, *3*, 80–81.
 - (95) McQuillan, A. J. *Electroanal. Chem.* **1975**, *65*, 933–944.
 - (96) Rogers, D. J.; Luck, S. D.; Irish, D. E.; Guzonas, D. A.; Atkinson, G. F. *J. Electroanal. Chem. Interfacial Electrochem.* **1984**, *167*, 237–249.
 - (97) Kudelski, A.; Bukowska, J. *Vib. Spectrosc.* **1996**, *10*, 335–339.
 - (98) Brolo, A. G.; Irish, D. E.; Lipkowski, J. *J. Phys. Chem. B* **1997**, *101*, 3906–3909.
 - (99) Clark, R. J. H.; Hester, R. E. *Advances in Infrared and Raman Spectroscopy*; John Wiley & Sons: New York, N.Y., 1985.
 - (100) Bewick, A.; Kunimatsu, K.; Robinson, J.; Russell, J. W. *J. Electroanal. Chem. Interfacial Electrochem.* **1981**, *119*, 175–185.
 - (101) Golden, W. G.; Dunn, D. S.; Overend, J. *J. Catal.* **1981**, *71*, 395–404.
 - (102) Beden, B. *J. Electroanal. Chem.* **1982**, *142*, 345–356.
 - (103) Russell, J. W.; Overend, J.; Scanlon, K.; Severson, M.; Bewick, A. *J. Phys. Chem.* **1982**, *86*, 3066–3068.
 - (104) Bewick, A.; Kunimatsu, K. *Surf. Sci.* **1980**, *101*, 131–138.
 - (105) Bewick, A.; Russell, J. W. *J. Electroanal. Chem.* **1982**, *132*, 329–344.
 - (106) Bewick, A.; Russell, J. W. *J. Electroanal. Chem.* **1982**, *142*, 337–343.
 - (107) Kunimatsu, K.; Bewick, A. *Indian J. Technol.* **1986**, *24*, 407–412.
 - (108) Heinen, M.; Jusys, Z.; Behm, R. J. *J. Phys. Chem. C* **2010**, *114*, 9850–9864.

- (109) Gomes, J. F.; Busson, B.; Tadjeddine, A.; Tremiliosi-Filho, G. *Electrochimica Acta* **2008**, *53*, 6899–6905.
- (110) Camara, G. A.; de Lima, R. B.; Iwasita, T. *J. Electroanal. Chem.* **2005**, *585*, 128–131.
- (111) Zhu, X. D.; Suhr, H.; Shen, Y. R. *Phys. Rev. B* **1987**, *35*, 3047–3050.
- (112) Guyot-Sionnest, P.; Hunt, J. H.; Shen, Y. R. *Phys. Rev. Lett.* **1987**, *59*, 1597–1600.
- (113) Harris, A. L.; Chidsey, C. E. D.; Levinos, N. J.; Loiacono, D. N. *Chem. Phys. Lett.* **1987**, *141*, 350–356.
- (114) Shen, Y. R. *Nature* **1989**, *337*, 519–525.
- (115) Guyot-Sionnest, P.; Tadjeddine, A. *Chem. Phys. Lett.* **1990**, *172*, 341–345.
- (116) Xia, K.; Weesner, F.; Bleam, W. F.; Helmke, P. A.; Bloom, P. R.; Skyllberg, U. *L. Soil Sci. Soc. Am. J.* **1997**, *62*, 1240–1246
- (117) Kendig, M. W.; Davenport, A. J.; Isaacs, H. S. *Corros. Sci.* **1993**, *34*, 41–49.
- (118) Kolb, D. M.; Schneider, J. *Surf. Sci.* **1985**, *162*, 764–775.
- (119) Shen, Y. R. *Principles of Nonlinear Optics*; John Wiley & Sons: New York, N.Y., 1984.
- (120) Guyot-Sionnest, P.; Chen, W.; Shen, Y. R. *Phys. Rev. B* **1986**, *33*, 8254–8263.
- (121) Richmond, G. L.; Robinson, J. M.; Shannon, V. L. *Prog. Surf. Sci.* **1988**, *28*, 1–70.
- (122) Liebsch, A. *Surf. Sci.* **1994**, *307-309*, 1007–1016.
- (123) McGilp, J. F. *Prog. Surf. Sci.* **1995**, *49*, 1–106.
- (124) Lynch, M. L.; Barner, B. J.; Corn, R. M. *J. Electroanal. Chem. Interfacial Electrochem.* **1991**, *300*, 447–465.
- (125) Pettinger, B.; Lipkowski, J.; Mirwald, S.; Friedrich, A. *J. Electroanal. Chem.* **1992**, *329*, 289–311.
- (126) Raschke, M. B.; Hayashi, M.; Lin, S. H.; Shen, Y. R. *Chem. Phys. Lett.* **2002**, *359*, 367–372.
- (127) Li, Q.; Hua, R.; Chou, K. C. *J. Phys. Chem. B* **2008**, *112*, 2315–2318.
- (128) Morgan, A. E.; Somorjai, G. A. *Surf. Sci.* **1968**, *12*, 405–425.
- (129) Masel, R. I. *Principles of Adsorption and Reaction on Solid Surfaces*; John Wiley & Sons: New York, N.Y., 1996.
- (130) Jensen, J. A.; Rider, K. B.; Salmeron, M.; Somorjai, G. A. *Phys. Rev. Lett.* **1998**, *80*, 1228–1231.
- (131) Starr, D. E.; Liu, Z.; Hävecker, M.; Knop-Gericke, A.; Bluhm, H. *Chem. Soc. Rev.* **2013**, *42*, 5833–5857.
- (132) Marković, N. M.; Ross Jr., P. N. *Surf. Sci. Rep.* **2002**, *45*, 117–229.
- (133) Feliu, J. M.; Herrero, E. *Contrib. Sci.* **2010**, *6*, 161–172.
- (134) Chang, S. C.; Weaver, M. J. *J. Phys. Chem.* **1990**, *94*, 5095–5102.
- (135) Iwasita, T. *J. Braz. Chem. Soc.* **2002**, *13*, 401–409.
- (136) Bagus, P. S.; Nelin, C. J.; Bauschlicher, C. W. *Phys. Rev. B* **1983**, *28*, 5423–5438.
- (137) Föhlisch, A.; Nyberg, M.; Hasselström, J.; Karis, O.; Pettersson, L. G. M.; Nilsson, A. *Phys. Rev. Lett.* **2000**, *85*, 3309–3312.

- (138) Blyholder, G. *J. Phys. Chem.* **1964**, *68*, 2772–2777.
- (139) Sung, S. S.; Hoffmann, R. *J. Am. Chem. Soc.* **1985**, *107*, 578–584.
- (140) Ishi, S.; Ohno, Y.; Viswanathan, B. *Surf. Sci.* **1985**, *161*, 349–372.
- (141) Avouris, P. *Phys. Scr.* **1987**, *35*, 47.
- (142) Matsumoto, Y.; Watanabe, K. *Chem. Rev.* **2006**, *106*, 4234–4260.
- (143) Shirley, D. A.; Stöhr, J.; Wehner, P. S.; Williams, R. S.; Apai, G. *Phys. Scr.* **1977**, *16*, 398.
- (144) Dose, V.; Rogozik, J.; Bradshaw, A. M.; Prince, K. C. *Surf. Sci.* **1987**, *179*, 90–100.
- (145) Rangelov, G.; Memmel, N.; Bertel, E.; Dose, V. *Surf. Sci.* **1991**, *251–252*, 965–970.
- (146) Anazawa, T.; Kinoshita, I.; Matsumoto, Y. *J. Electron Spectrosc. Relat. Phenom.* **1998**, *88–91*, 585–590.
- (147) Grönbeck, H.; Andreoni, W. *Chem. Phys. Lett.* **1997**, *269*, 385–390.
- (148) Yagi, I.; Nakabayashi, S.; Uosaki, K. *J. Phys. Chem. B* **1997**, *101*, 7414–7421.
- (149) Akemann, W.; Friedrich, K. A.; Linke, U.; Stimming, U. *Surf. Sci.* **1998**, *402–404*, 571–575.
- (150) Pozniak, B.; Mo, Y.; Scherson, D. A. *Faraday Discuss.* **2002**, *121*, 313–322.
- (151) Fromondi, I.; Scherson, D. *Faraday Discuss.* **2008**, *140*, 59–68.
- (152) Ocko, B. M.; Wang, J.; Davenport, A.; Isaacs, H. S. *Phys. Rev. Lett.* **1990**, *65*, 1466–1469.
- (153) Severson, M. W.; Stuhlmann, C.; Villegas, I.; Weaver, M. J. *J. Chem. Phys.* **1995**, *103*, 9832–9843.
- (154) King, D. A.; Woodruff, D. P. *The Chemical Physics of Solid Surfaces and Heterogeneous Catalysis*; Elsevier: New York, N.Y., 1988.
- (155) Madey, T. E.; Jr, J. T. Y. *Vibrational Spectroscopy of Molecules on Surfaces*; Plenum Press: New York, N.Y., 1987.
- (156) Heyden, B. E.; Bradshaw, A. M. *Surf. Sci.* **1983**, *125*, 787–802.
- (157) Tüshaus, M.; Schweizer, E.; Hollins, P.; Bradshaw, A. M. *J. Electron Spectrosc. Relat. Phenom.* **1987**, *44*, 305–316.
- (158) Ibach, H.; Mills, D. L. *Electron Energy Loss Spectroscopy and Surface Vibrations*; Academic Press: New York, N.Y.; 2013.
- (159) Russell, J. W.; Severson, M.; Scanlon, K.; Overend, J.; Bewick, A. *J. Phys. Chem.* **1983**, *87*, 293–297.
- (160) Golden, W. G.; Kunimatsu, K.; Seki, H. *J. Phys. Chem.* **1984**, *88*, 1275–1277.
- (161) Kunimatsu, K.; Golden, W. G.; Seki, H.; Philpott, M. R. *Langmuir* **1985**, *1*, 245–250.
- (162) Zou, S. Z.; Weaver, M. J. *J. Phys. Chem.* **1996**, *100*, 4237–4242.
- (163) Lu, G. Q.; Lagutchev, A.; Dlott, D. D.; Wieckowski, A. *Surf. Sci.* **2005**, *585*, 3–16.
- (164) Furuya, N.; Motoo, S.; Kunimatsu, K. *J. Electroanal. Chem.* **1988**, *239*, 347–360.
- (165) Lambert, D. K. *J. Vac. Sci. Technol. B* **1985**, *3*, 1479.
- (166) Lambert, D. K. *J. Chem. Phys.* **1988**, *89*, 3847–3860.

- (167) Chang, S.-C.; Leung, L.-W. H.; Weaver, M. J. *J. Phys. Chem.* **1989**, *93*, 5341-5345.
- (168) Beden, B.; Enea, O.; Hahn, F.; Lamy, C. *J. Electroanal. Chem.* **1984**, *170*, 357-361.
- (169) Feng, Z. Q.; Sagara, T.; Niki, T. *Anal. Chem.* **1995**, *67*, 3564-3570.
- (170) Andrews, A. B.; McClelland, A.; Korkeila, O.; Demidov, A.; Krummel, A.; Mullins, O. C.; Chen, Z. *Langmuir* **2011**, *27*, 6049-6058.
- (171) Vidal, F.; Tadjeddine, A. *Rep. Prog. Phys.* **2005**, *68*, 1095.
- (172) ITO, M. Vibrational Spectroscopic Study on Structure and Reaction of Self-Assembled Monolayers, Ph. D. Thesis, Hokkaido University, 2011.
- (173) Ober, M. H.; Hofer, M.; Hofer, R.; Reider, G. A.; Sucha, G. D.; Fermann, M. E.; Harter, D.; Mendonca, C. A. C.; Chiu, T. H. *Opt. Lett.* **1995**, *20*, 2303.
- (174) Mukamel, S. *Principles of Nonlinear Optical Spectroscopy*; Oxford University Press: Oxford, U.K., 1999.
- (175) Corrigan, D. S.; Weaver, M. J. *J. Electroanal. Chem. Interfacial Electrochem.* **1988**, *241*, 143-162.
- (176) Leung, L. W. H.; Wieckowski, A.; Weaver, M. J. *J. Phys. Chem.* **1988**, *92*, 6985-6990.
- (177) Vidal, F.; Busson, B.; Six, C.; Pluchery, O.; Tadjeddine, A. *J. Surf. Sci.* **2002**, *502-503*, 485-489.
- (178) Lu, G. Q.; Lagutchev, A.; Dlott, D. D.; Wieckowski, A. *Surf. Sci.* **2005**, *585*, 3-16.
- (179) Peremans, A.; Tadjeddine, A. *Phys. Rev. Lett.* **1994**, *73*, 3010-3013.
- (180) Peremans, A.; Tadjeddine, A. *J. Chem. Phys.* **1995**, *103*, 7197-7203.
- (181) Tadjeddine, A.; Peremans, A.; Guyot-Sionnest, P. *Surf. Sci.* **1995**, *335*, 210-220.
- (182) Tadjeddine, A.; Peremans, A. *J. Chem. Phys.* **1996**, *93*, 662-672.
- (183) Tadjeddine, A.; Peremans, A.; Rille, A. L.; Zheng, W. Q.; Tadjeddine, M.; Flament, J.-P. *J. Chem. Soc. Faraday Trans.* **1996**, *92*, 3823-3828.
- (184) Tadjeddine, A.; Peremans, A. *J. Electroanal. Chem.* **1996**, *409*, 115-121.
- (185) Wieckowski, A. *Interfacial Electrochemistry: Theory, Experiment, and Applications*; Marcel Dekker: New York, N.Y., 1999.
- (186) Guyot-Sionnest, P.; Tadjeddine, A. *J. Chem. Phys.* **1990**, *92*, 734-738.
- (187) Domen, K.; Bandara, A.; Kubota, J.; Onda, K.; Wada, A.; Kano, S. S.; Hirose, C. *Surf. Sci.* **1999**, *427-428*, 349-357.
- (188) Schmidt, M. E.; Guyot-Sionnest, P. *J. Chem. Phys.* **1996**, *104*, 2438-2445.
- (189) Noguchi, H.; Okada, T.; Uosaki, K. *J. Phys. Chem. B* **2006**, *110*, 15055-15058.
- (190) Li, Q.; Hua, R.; Chou, K. C. *J. Chem. Phys. B* **2008**, *112*, 2315-2318.
- (191) Miyamae, T. *Vibrational Spectroscopy* **2012**, *5*, 115-140.
- (192) Ji, N.; Shen, Y. R. *Chirality* **2006**, *18*, 146-158.

Chapter 2

Experimental

2.1 Materials

Sulfuric acid (H_2SO_4 , 98%), hydrogen peroxide (H_2O_2 , 30%), perchloric acid (HClO_4 , 60%), chloroplatinic acid hexahydrate ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, 99.9%), sodium chloride (NaCl , 99.9%), were obtained from Wako Pure Chemical Industries. All chemicals were of analytical grade and used as received.

Ultrapure argon (Ar , >99.99%), nitrogen (N_2 , >99.99%) were purchased from Suzuki Shokan. High purity carbon monoxide (CO , >99.95%) gas was from Taiyo Nippon Sanso.

All aqueous solutions used in the experiments were prepared with ultrapure water ($\text{TOC} < 10$ ppb, electric resistivity $> 18 \text{ M}\Omega \cdot \text{cm}$) supplied by a Milli-Q water apparatus (WRX10, Yamato Scientific).

A commercial (111)-oriented Pt single crystal (diameter: 10 mm, thickness: 5 mm, 99.98%), polycrystalline Pt (diameter: 10 mm, thickness: 5 mm, 99.98%) and polycrystalline Au (diameter: 10 mm, thickness: 5 mm, 99.98%) disks as working electrodes were purchased from MaTeck GmbH. Pt wires (diameter: 0.5 mm, 99.98%), Ti (thickness: 15 mm, 99.5%) and Ag (thickness: 0.1 mm, 99.98%) plates were purchased from Nilaco.

Alumina slurries (1, 0.3 and 0.05 μm) were supplied by Baikowski International. Sapphire optical windows (30 mm in diameter) and calcium fluoride (CaF_2) prisms (12.5 mm in radius and 25 mm in long) were obtained from Edmund Optics and Pier Optics, respectively.

2.2 Electrode Preparation

2.2.1 Pretreatment of Pt(111) Single Crystal Electrode

The annealing of a Pt(111) single crystal electrode was carried out in order to obtain a reproducible and well-defined surface.^{1,2} A Pt wire (diameter: 0.5 mm) was

spot-welded to the unpolished face of the Pt(111) disk, and the polished face was used for electrochemical and spectroscopic characterizations. The crystal was annealed in a gas-oxygen flame and slowly cooled in Ar gas flow, succeeded by quenching the electrode in ultrapure water which was degassed with the Ar gas. The (111) surface, which was protected with a droplet of ultrapure water, was then immediately transferred to a standard three-compartment spectroelectrochemical cell (described in Figure 2-1) and immersed into the Ar-purged electrolyte under a potentiostatic control at 0 mV.³

2.2.2 Pretreatment of Polycrystalline Pt Electrode

The polycrystalline Pt electrode was successively polished with 1, 0.3 and 0.05 μm alumina slurries on a polishing cloth, followed by a 10 min sonication in the ultrapure water prior to use. Subsequently, the Pt electrode was embedded into a Kel-F holder (shown in Figure 2-2). An electrochemical cleaning of the electrode surface was carried out by repeating oxidation-reduction cycles between -150 and 1100 mV in Ar-saturated 0.5 M H_2SO_4 aqueous solution with a scan rate of 100 mV/s until the well-defined peaks due to hydrogen adsorption/desorption were evident.

2.2.3 Preparation of Pt-modified Au electrode

2.2.3.1 Pretreatment of Polycrystalline Au Electrode

The polycrystalline Au electrode was successively polished with the alumina slurries down to 0.05 μm and was sonicated for 10 min in the ultrapure water. The Au electrode was then embedded into the Kel-F electrode holder, as shown in Figure 2-2, and was electrochemically pretreated by cycling the potential in the range of -200 to 1450 mV in Ar-saturated 0.05 M H_2SO_4 aqueous solution at 100 mV/s until the reproducible cyclic voltammetry (CV) of a clean Au electrode, which is consistent with previous reports,^{4,5} was obtained.

2.2.3.2 Electrodeposition of Pt Thin Film on Au Surface

A Pt thin film was electrochemically deposited on a polycrystalline Au substrate by contacting the Au surface with a deaerated 0.1 M HClO_4 + 0.05 mM H_2PtCl_6

aqueous solution.^{6,7} The electrochemical cell employed in this experiment is shown in Figure 2-1. The electrode potential was started from open circuit potential (OCP), ca. 800 mV, and slowly scanned with 2 mV/s in the negative direction to the potential of 600, 500 and 450 mV, respectively, and kept at each potential to deposit Pt. Then, the electrode was rinsed with concentrated H₂SO₄ and ultrapure water to remove the adsorbed PtCl₆²⁻ ion.

2.3 Measurements

2.3.1 Spectroelectrochemical Cells

Electrochemical measurements were performed in a standard three-electrode spectroelectrochemical cell. The configuration of the cells used in the experiments is depicted as follows:

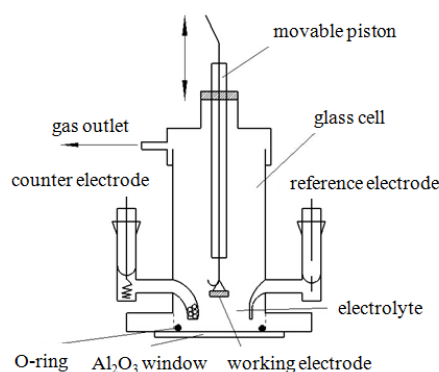


Figure 2-1. Spectroelectrochemical cell for the Pt(111) single crystal experiments.

Figure 2-1 represents the cell for the electrochemical and SFG experiments using a Pt(111) single crystal. The cell consists of a glass body and Teflon valves. The bottom of the cell was sealed with a sapphire plate which was sandwiched by an acid-proof O-ring to hold the electrolyte into the cell and also utilized as the optical window for SFG measurements because of its high transparency (200–7000 nm), unbreakable capability and good stability in acid electrolyte. The Pt(111) working electrode was hooked to the end of an airtight glass tube via a Pt wire which was welded onto the unpolished side of the Pt(111) disk. Since the glass tube is like a

piston which can be moved up and down in the cell, the Pt(111) electrode not only can be contacted with the surface of the electrolyte solution for CV characterization, but also can be immersed into the solution and pressed against the window for spectroscopic measurements. The electrical contact between the working electrode and the potentiostat was established by a conducting wire inside of the glass tube. The reference electrode and counter electrode were placed in two separate compartments. In order to minimize the IR drop, the reference electrode was set close to the surface of the working electrode via a Luggin capillary.⁸ To avoid O₂ during electrochemical reactions, Ar gas was continuously flowed into the cell from the gas inlet and disposed from the gas outlet, as indicated in the figure.

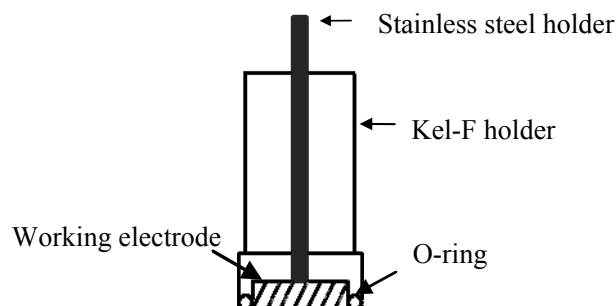


Figure 2-2. Schematic illustration of the Kel-F holder used in the polycrystalline working electrode experiments.

When polycrystalline Pt, polycrystalline Au and Pt-modified polycrystalline Au disks were used as working electrodes, a moveable Kel-F holder was employed, as shown in Figure 2-2, where the working electrode was embedded in one end of the holder, leaving only the polished surface exposed. The electrical contact between the electrode and the potentiostat was built by a stainless steel rod.

The configuration of the electrochemical cell used in Fourier-Transform (FT)-IRAS measurements is shown in Figure 2-3. The glassware and the electrode holder are as same as that employed in the SFG experiments. A hemicylindrical CaF₂ prism was used as the optical window to avoid a decrease of the incident angle which is caused by refraction, ensuring a strong absorption intensity of the surface species.

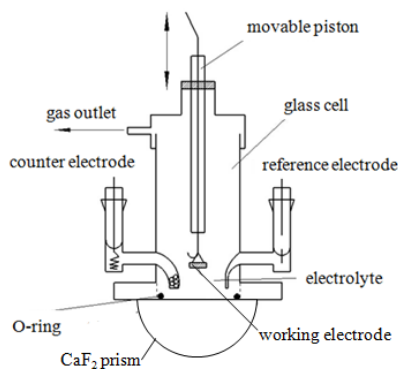


Figure 2-3. Spectroelectrochemical cell for FT-IRAS measurements.

The sapphire window, glassware and other parts of the spectroelectrochemical cells were cleaned in a freshly prepared piranha solution (2:1 concentrated H_2SO_4 : H_2O_2) in order to remove the organic contaminants, and then rinsed several times with ultrapure water. The CaF_2 prism was cleaned by 0.1 M HClO_4 aqueous solution for 10 min, followed by a rinsing cycle. The cells were rinsed with the electrolyte prior to use.

2.3.2 Electrochemical Measurements

A homemade NaCl-saturated Ag/AgCl was served as a reference electrode throughout all the experiments. A coil Pt wire (diameter: 0.5 mm) was used as a counter electrode to increase the area. All electrochemical measurements were carried out under a high purity Ar-protected atmosphere. The electrolyte solutions were deaerated with Ar gas by passing the gas through the electrolyte for at least 30 min before electrochemical measurements. The electrode potential was controlled by a potentiostat/galvanostat (HABF-501A, Hokuto Denko). Both potential and current were recorded by a data logger (GL900, Graphtec).

All the CV measurements were carried out with a hanging meniscus configuration, where only the polished surface was contacted with the electrolyte solution. Figure 2-4 shows the hanging meniscus configuration by using a Pt(111) electrode as an example.

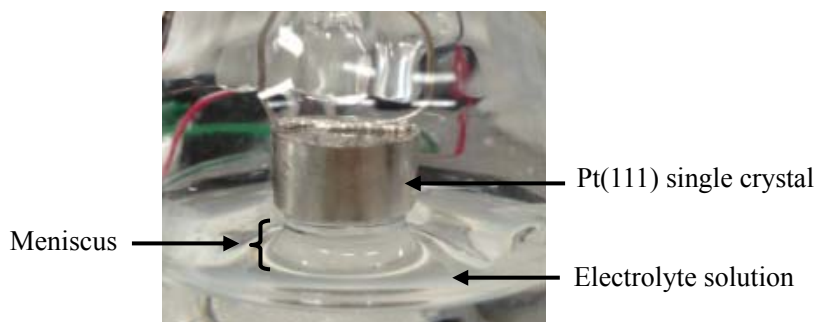


Figure 2-4. Hanging meniscus configuration for electrochemical measurements on a Pt(111) electrode surface.

The CO adsorption onto the electrode surface was performed by introducing the CO gas through the electrolyte solution at 0 mV.⁹ This procedure typically takes ca. 10 min of bubbling to obtain a good surface coverage. Then, by purging with Ar gas for another 40 min to remove the residual CO in the solution, a CO-free electrolyte solution was achieved.¹⁰ To maintain the O₂-free environment in the cell, the Ar gas was continued flowing during the subsequent electrochemical and spectroscopic measurements.

2.3.3 Spectroscopic Measurements

2.3.3.1 Fourier-Transform Infrared Reflection-Absorption Spectroscopy (FT-IRAS) Measurements

In situ FT-IRAS experiments were carried out by using a JASCO FT/IR-6200 Fourier transform infrared spectrometer. Figure 2-5 shows the experimental setup for FT-IRAS measurements. An IR beam was irradiated onto the sample after passing through a pulse motor-driven wire grid polarizer. The incident angle of IR was set at ca. 60° from the surface normal. The reflected beam from the electrode surface was detected via a highly sensitive mercury-cadmium-telluride (MCT) detector which was cooled with liquid nitrogen. The chamber was continuously purged with dry N₂ gas during measurements to avoid water vapor and CO₂.

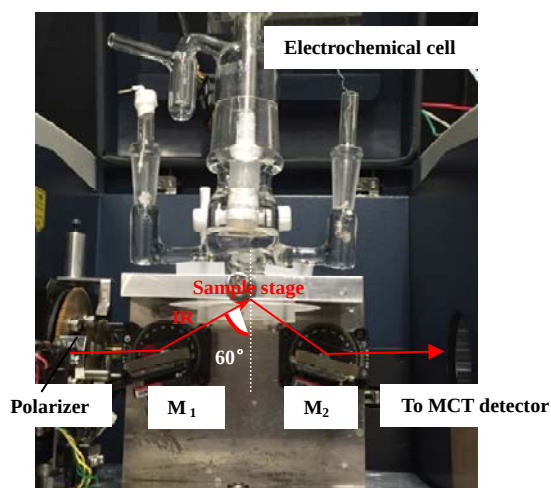


Figure 2-5. Experimental setup of FT-IRAS measurements. M_1 and M_2 are gold mirrors.

Prior to IRAS measurements, the electrode with preadsorbed CO was immersed into the solution and pressed against the CaF_2 prism at the bottom of the spectroelectrochemical cell, forming a thin electrolyte layer of ca. 1–2 μm thick between them to avoid the strong IR absorption by water. During the measurements, the electrode potential was positively changed from -150 to -100 mV, followed by 100 mV step increase to 900 mV, e.g., -150, -100, 0 ... 900 mV, while the single beam spectra were successively acquired at each potential. The data acquisition time for each single beam spectrum was ca. 1 min. In total, 128 interferograms at a resolution of 4 cm^{-1} were averaged for each single beam spectrum to enhance the signal-to-noise ratios. All spectra were recorded with p polarization. The spectral range was 1000–4000 cm^{-1} because the information below 1000 cm^{-1} could not be extracted owing to the strong absorption by the CaF_2 window. Finally, the results were given by absorbance units defined as $A = -\log(R/R_0)$, where R and R_0 represent the reflected IR single beam spectral intensities of the sample and reference, respectively. Here, the single beam spectrum taken at 900 mV was used as the reference.

2.3.3.2 DR-SFG Measurements

In the present thesis, a broadband femtosecond laser setup was employed for

DR-SFG measurements. An overview of this SFG system is illustrated schematically in Figure 2-6. In brief, a Ti:sapphire oscillator (Tsunami: 3960-L2S, Spectra-Physics), which was pumped by a Nd:YVO₄ laser (Millennia-Vs, Spectra Physics), delivered 790 nm, 90 fs seed pulses at 5 nJ energy per pulse with 82 MHz repetition frequency. The seed laser from the oscillator was amplified in a regenerative amplifier (Titan: model 4812RGA/4823S/C, Quantronix) pumped with a mode-lock Nd:YLF laser (Darwin 527-40-M, Quantronix). Finally, a pulse centered at 790 nm of 2.5 mJ energy, 120 fs duration and 1 kHz repetition rate was generated and used as the fundamental light source.

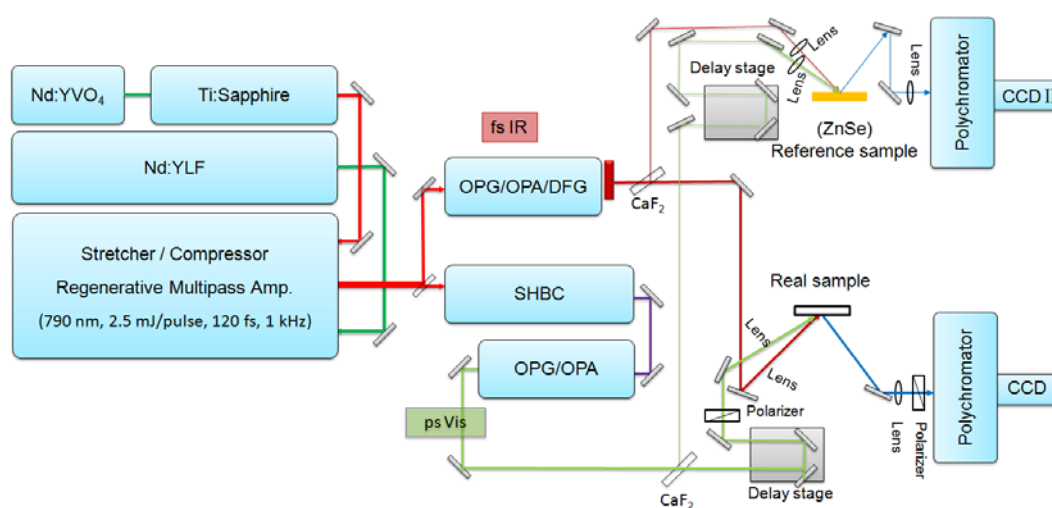


Figure 2-6. Schematic diagram of a femtosecond broadband SFG system.

The 40% of fundamental output from Titan was split to drive an optical parametric generation/optical parametric amplification/difference frequency generation (OPG/OPA/DFG) system (TOPAS 8034, Light conversion), yielding a broadband tunable femtosecond IR probe from 3 to 10 μm . The pulse energy and spectral width of the IR light depend on its wavenumber. Typically, an IR pulse has the energy of 5 μJ and the spectral width of ca. 200 cm^{-1} at 5 μm region.

For spectrally resolved SFG, a narrowband picosecond visible pulse (4 ps, ca. 10 cm^{-1} spectral width, 10 $\mu\text{J}/\text{pulse}@600\text{ nm}$) was produced from a second harmonic bandwidth compressor (SHBC, Light conversion) by using the residual of the

amplifier output. In the present study, in order to obtain a wavelength tunable visible probe, this output was used as the pump source of another OPG/OPA system (TOPAS 8034, Light conversion).

Both broadband femtosecond IR and narrowband picosecond visible beams were spatially and temporally overlapped on the surfaces of real and reference (ZnSe substrate) samples with the incident angles at ca. 60° and 70° relative to the surface normal, respectively. The polarization directions of SFG, visible and IR beams were all p. The generated SFG signals of the sample and reference (ZnSe substrate) were simultaneously detected by two spectrographs (Shamrock SR500i-A, Andor technology) coupled with cooled CCD multichannel detectors (iDus 420 DU420A-BU2, Andor technology), and the data acquisition was started with a common trigger to guarantee the synchronism of two CCD detectors.

For the electrochemical SFG measurements, the working electrode with preadsorbed CO was firmly pressed against the sapphire window on the spectroelectrochemical cell, forming a thin electrolyte layer of ca. 1–2 μm between the electrode and the window to avoid the strong IR absorption by water. The attenuation of the IR light before reaching the electrode surface by passing through the ca. 1–2 μm thick water with the angle at 60°, which is calculated by using the Lambert-Beer equation of $\exp(-\alpha L)$ with the absorption coefficient of water (α) as 400 cm^{-1} at 4.8 μm ,¹¹ is 0.88–0.94.¹²

A series of SFG spectra were acquired at the electrode with preadsorbed CO in solution with the accumulation time of 50 s for each spectrum using a certain visible light either during the positive potential scan of 1 mV/s or at a constant potential in the region of -150 to 900 mV. Simultaneously, for each spectrum of CO, the corresponding SFG spectra of the ZnSe substrate were also recorded with a 50 s interval. Finally, the SFG spectra of CO were normalized by dividing the CCD output of the sample by that of the ZnSe. The frequency was calibrated by the absorption bands of CO₂ within the IR beam path (4–5 μm region).

In the experiments, an Ag film as a helpful reference was sputtered at the edge of the inside face of the sapphire optical window, as shown in Figure 2-7, in order to

optimize the overlapping condition of IR and visible. Once the strongest SFG signal from the Ag film was found, the laser spot was switched to the electrode surface for probing CO by moving the X-Y sample stage.

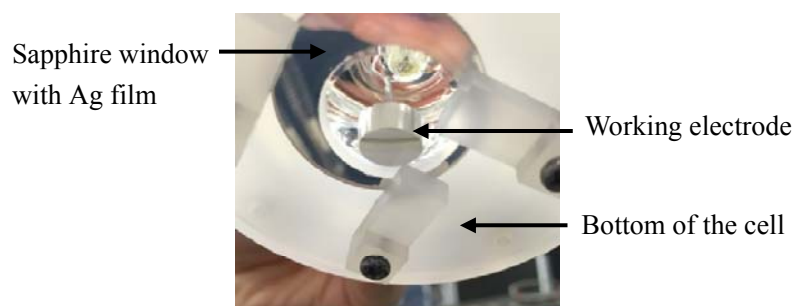


Figure 2-7. The picture of an Ag film sputtered on a sapphire window at the bottom of the spectroelectrochemical cell.

The detailed procedures for the Ag film preparation are described below:

After cleaning the sapphire window of the electrochemical cell by concentrated H_2SO_4 , ultrapure water, and drying it with N_2 gas, the successive evaporation of 5 nm Ti film as an adhesion layer and 25 nm thick Ag film on the window was carried out in a vacuum of 3×10^{-2} Torr by using ion sputter (JEOL, JFC-1200). Ti and Ag plates were used as metal sources for sputtering. The thickness of the deposited film was measured with a quartz crystal microbalance (5 MHz, AT-cut, JEOL, FC-TM10). The deposition rate was kept at 0.01 and 0.2 nm/s for Ti and Ag, respectively.

The SFG intensity is the most important parameter for the interfacial electronic structure study. Thus, it is necessary to estimate the SFG intensity error, which is caused by the laser pulse energy fluctuation. Before each DR-SFG experiment, a synchronism test of the two CCDs was performed under various visible energies by using the Ag film and ZnSe as a sample and a reference, respectively, and the results are presented in Figure 2-8 in the form of the integrated SFG intensity ratios between them. From Figure 2-8, it is obvious that the SFG intensity ratios between the sample and reference were always roughly equal to 1, which clearly demonstrates that the fluctuation of the SFG intensity owing to the laser intensity fluctuation was successfully removed in the present SFG apparatus by introducing the reference CCD

detector.

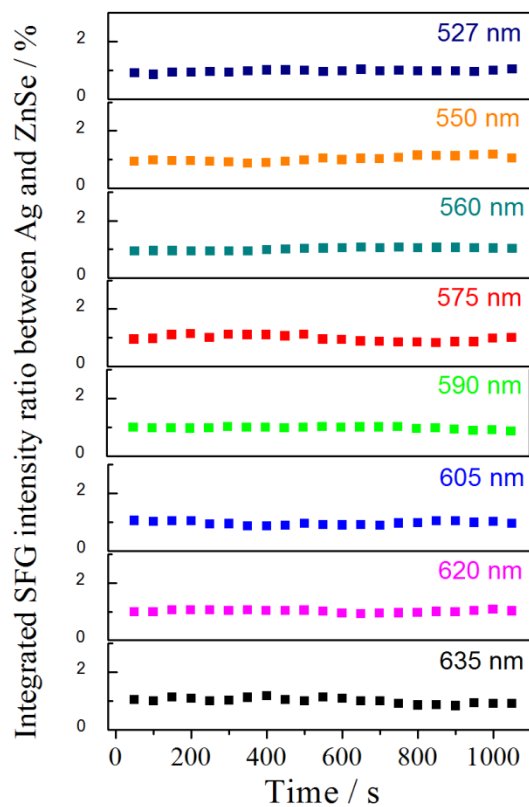


Figure 2-8. The integrated SFG intensity ratios between Ag and ZnSe as a function of time at visible light of different wavelengths.

All experiments were carried out at room temperature, ca. 24°C.

References

- (1) Motoo, S.; Furuya, N. *J. Electroanal. Chem. Interfacial Electrochem.* **1984**, *172*, 339–358.
- (2) Lebedeva, N. P.; Koper, M. T. M.; Feliu, J. M.; van Santen, R. A. *Electrochem. Commun.* **2000**, *2*, 487–490.
- (3) Jaaf-Golze, K. A.; Kolb, D. M.; Scherson, D. *J. Electroanal. Chem. Interfacial Electrochem.* **1986**, *200*, 353–362.
- (4) Ron, H.; Rubinstein, I. *Langmuir* **1994**, *10*, 4566–4573.
- (5) Tkac, J.; Davis, J. J. *J. Electroanal. Chem.* **2008**, *621*, 117–120.
- (6) Shibata, M.; Hayashi, N.; Sakurai, T.; Kurokawa, A.; Fukumitsu, H.; Masuda, T.; Uosaki, K.; Kondo, T. *J. Phys. Chem. C* **2012**, *116*, 26464–26474.
- (7) Kondo, T.; Shibata, M.; Hayashi, N.; Fukumitsu, H.; Masuda, T.; Takakusagi, S.; Uosaki, K. *Electrochimica Acta* **2010**, *55*, 8302–8306.
- (8) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods: Fundamentals and Applications*, 2nd ed.; John Wiley & Sons: New York, N.Y., 2000.
- (9) Kitamura, F.; Takeda, M.; Takahashi, M.; Ito, M. *Chem. Phys. Lett.* **1987**, *142*, 318–322.
- (10) Chou, K. C.; Markovic, N. M.; Kim, J.; Ross, P. N.; Somorjai, G. A. *J. Phys. Chem. B* **2003**, *107*, 1840–1844.
- (11) Wieliczka, D. M.; Weng, S.; Querry, M. R. *Appl. Opt.* **1989**, *28*, 1714–1719.
- (12) Seki, H.; Kunitatsu, K.; Golden, W. G. *Appl. Spectrosc.* **1985**, *39*, 437–443.

Chapter 3

Electronic Structure of CO/Pt(111) Electrode Interface Probed by Potential Dependent DR-SFG Spectroscopy

3.1 Introduction

The electronic structure information of CO adsorbed at Pt electrode/electrolyte interfaces is essential to understand the role of CO in many important electrocatalytic reaction processes. Among various Pt electrodes, Pt single crystal surfaces having well-defined spatial atom arrangement are more reproducible compared to polycrystalline, alloy, or codeposited systems.¹ Consequently, a plethora of electronic structure studies on the CO/Pt interfaces in UHV have been carried out with single crystal electrodes in order to gain clear electronic structure information and well understanding of the interfaces,²⁻⁴ although less is studied in electrochemical environments.

This chapter dealt with the system of CO adsorbed on a Pt(111) single crystal electrode surface in a CO-free 0.5 M H₂SO₄ aqueous solution for interfacial electronic structure study, where the broadband SFG measurements were carried out as a function of potential using visible light of eight different incident energies. The intensity of the bands observed in SFG spectra, which correspond to C-O stretching vibration, anomalously increased prior to anodic CO oxidation and the anomalous SFG peak potential linearly depended on the incident visible light energy with a slope of 1 V/eV. This result shows that the increase of SFG intensity is due to a surface electronic resonance, in which the energy of visible and/or SF light becomes equal to the energy of interfacial electronic transition from the Fermi level of Pt(111), which is tuned by the electrode potential, to the 5 σ_a antibonding state of the adsorbed CO.

3.2 Results and Discussion

3.2.1 Electrochemical Properties

Figure 3-1 shows CV of the freshly annealed Pt(111) electrode in a CO-free

Ar-saturated 0.5 M H₂SO₄ aqueous solution obtained by scanning the potential between -100 and 450 mV with a scan rate of 20 mV/s. The features of the CV of the Pt(111) electrode without preadsorbed CO, such as characteristic flat hydrogen adsorption/desorption waves between the -100 and 100 mV region and the sharp spikes at ca. 250 mV associated with adsorption/desorption of sulfate or bisulfate anions, are in good agreement with those previously reported for a clean and well-ordered Pt(111) electrode by other groups.⁵⁻⁷

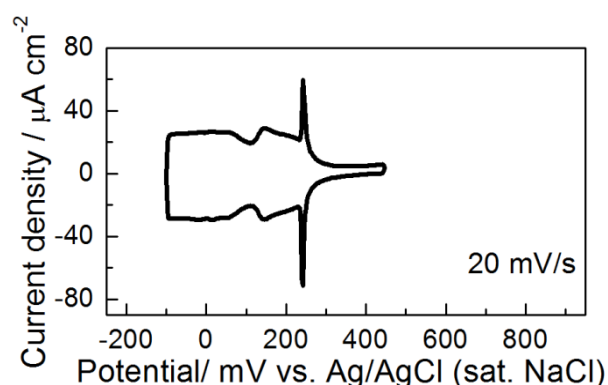


Figure 3-1. CV of the Pt(111) electrode in a CO-free Ar-saturated 0.5 M H₂SO₄ aqueous solution without preadsorbed CO between -100 and 450 mV with a scan rate of 20 mV/s.

Figure 3-2 shows the CV of the Pt(111) electrode with preadsorbed CO in the CO-free Ar-saturated 0.5 M H₂SO₄ aqueous solution obtained by scanning the potential positively from -150 to 900 mV and negatively to -150 mV (first cycle: black), and then positively to 900 mV and negatively to -150 mV (second cycle: red) with a scan rate of 1 mV/s. In the first positive going scan, the hydrogen desorption peak was completely suppressed by adsorbed CO; the anodic current started to flow when the potential became more positive than ca. 400 mV; and a sharp peak due to the stripping of adsorbed CO was observed at 500 mV.⁸ The current became nearly 0 at around 550 mV. The charge for CO oxidation obtained by integrating the area of the CO stripping peak was ca. 460 μC/cm², which is in good agreement with the previously reported value for the oxidation of the CO monolayer,⁸ confirming that the

CO monolayer was formed on the Pt(111) electrode. In the negative going scan of the first cycle, the current-potential relation was similar to that of the bare Pt(111) electrode, implying that the CO monolayer was fully removed by anodic oxidation and a clean Pt(111) surface was recovered. The recovery of the clean Pt surface was further proved by the CV of the second cycle, which is exactly the same as that of the clean Pt(111) electrode without the trace of the CO oxidation peak.

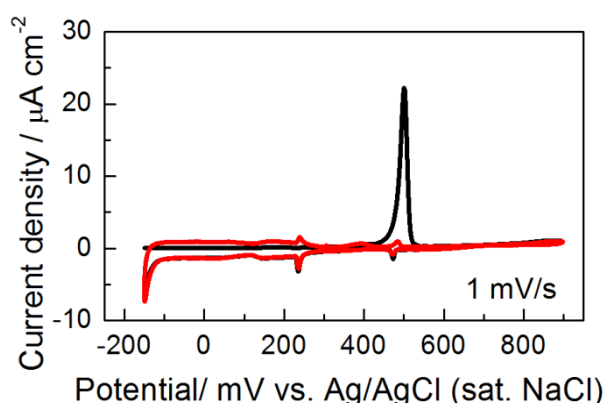


Figure 3-2. CV of Pt(111) electrode in the CO-free Ar-saturated 0.5 M H₂SO₄ aqueous solution with preadsorbed CO between -150 and 900 mV with a scan rate of 1 mV/s for the first (black line) and the second (red line) cycles.

3.2.2 Potential Dependent Spectral Features of CO on Pt(111) Surface

A series of SFG spectra were acquired at Pt(111) electrode with preadsorbed CO in 0.5 M H₂SO₄ aqueous solution with an accumulation time of 50 s for each spectrum by using a certain visible light while potential was scanned positively from -150 to 900 mV with a scan rate of 1 mV/s. Figure 3-3 shows typical potential dependent SFG spectra obtained by using visible light of 560 nm during potential scan between -150–100, -50–0, 50–100, 200–250, 300–350, 350–400 and 500–550 mV. All SFG spectra show a single band at 2066–2077 cm⁻¹, corresponding to C-O stretching of CO adsorbed on the atop site of the Pt(111) surface,⁸⁻¹⁰ which is caused by the resonance of IR with the vibration transition of C-O stretching.

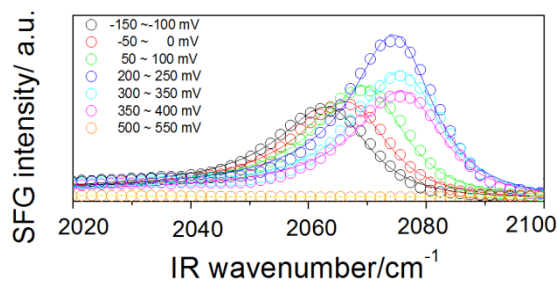


Figure 3-3. Typical potential dependent SFG spectra of the Pt(111) electrode with preadsorbed CO in the CO-free Ar-saturated 0.5 M H₂SO₄ aqueous solution obtained during potential scan by using visible light of 560 nm. Solid lines are the best fits according to Eq. (1-27).

For a comparative study, FT-IRAS measurements were also performed on the CO/Pt(111) system. In this experiment, the electrode potential was positively changed from -150 to -100 mV, followed by a 100 mV step increase up to 900 mV, while the single beam spectra were successively acquired at each potential. The single beam spectrum collected at 900 mV, at which CO adsorption is negligible owing to the oxidation, was used as the reference. Figure 3-4 shows the electrode potential dependence of IRAS spectra in 2020–2100 cm⁻¹ region obtained for CO adlayer on the Pt(111) surface in 0.5 M H₂SO₄ aqueous solution. Consistent with above SFG results and earlier studies,⁸⁻¹⁰ the potential dependent spectral feature observed near 2070 cm⁻¹ (Figure 3-4) is assigned to the C-O stretching of the adsorbed atop CO.

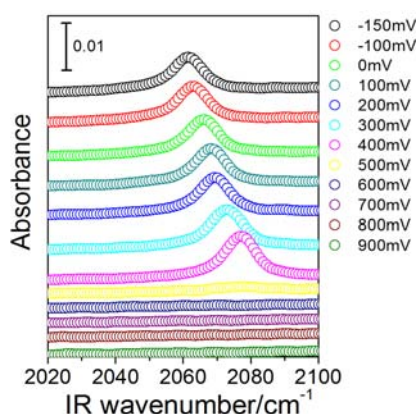


Figure 3-4. Potential dependent IRAS spectra in 2020–2100 cm⁻¹ region of CO adsorbed on the Pt(111) surface in a CO-free 0.5 M H₂SO₄ aqueous solution acquired under the constant potential control by using single beam spectrum taken at 900 mV as the reference.

The left hand side of Figure 3-5 shows the typical analysis results of the potential dependencies of (a) peak wavenumber, (b) full width at half-maximum (fwhm) of the CO band and (c) amplitude, derived from the fitting of the SFG spectra obtained by using visible light of 560 nm (Figure 3-3)). Since each SFG spectrum was obtained by 50 s accumulation during 1 mV/s potential scan, results are on average of 50 mV and are presented at the midpotential of the accumulated potential range, e.g., -125 mV for the data accumulated between -150 and -100 mV. The analysis results of the peak wavenumber, fwhm and integrated intensity as a function of potential for IR spectra (Figure 3-4) are presented in Figure 3-5 (d-f).

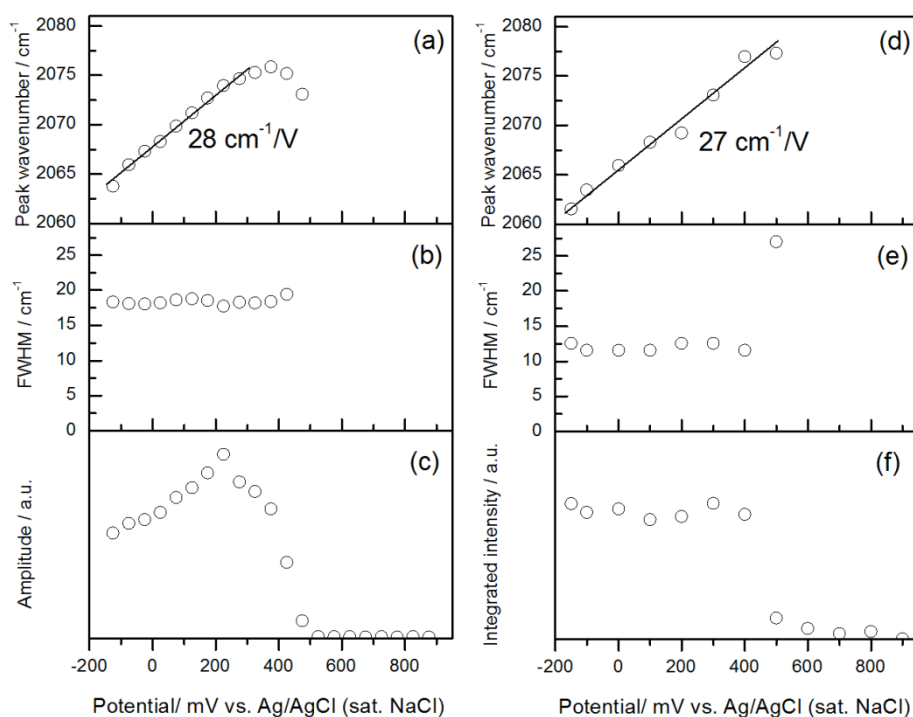


Figure 3-5. Potential dependencies of (a) peak wavenumber, (b) fwhm and (c) amplitude of the bands derived from the fitting of the SFG spectra obtained by using visible light of 560 nm (Figure 3-3); (d) peak wavenumber, (e) fwhm and (f) integrated intensity for IR bands obtained from Figure 3-4 as a function of the electrode potential.

Figure 3-5(a) shows that the position of the CO band shifted to higher wavenumber by ca. $28 \text{ cm}^{-1}/\text{V}$, which is attributed to the electrochemical Stark

effect¹¹ or weak electron back-donation to $2\pi^*$ orbital, as the potential became more positive up to ca. 375 mV and then to lower wavenumber. Such a downward shift can be explained by the reduction of the dipole–dipole interaction among CO molecules as a result of the decrease of CO coverage due to anodic oxidation, which started at around 400 mV (Figure 3-2).^{12,13} The IR band shows a shift with a slope of $27\text{ cm}^{-1}/\text{V}$ as compared with the value of $28\text{ cm}^{-1}/\text{V}$ obtained from the SFG experiment.

From Figure 3-5(b) and (e), it is found that the fwhm of both SFG and IR bands were almost constant but increased when the CO oxidation started as already reported for the CO stripping at the Pt(111) electrode in acidic solution by previous IRAS⁹ and SFG⁸ measurements, suggesting a constant coverage of the atop CO until the CO oxidation started. The broadening of the width when the CO oxidation started supports the disordered distribution of the CO molecular interaction upon oxidation of adsorbed CO.

The potential dependent intensity variation of atop C-O stretching band is shown in Figure 3-5(c) and (f). The increase of the SFG amplitude prior to CO oxidation was observed as shown in Figure 3-5(c), in agreement with the previous reports.^{8,14} During the positive going scan, the amplitude was almost constant up to 25 mV and then increased by 70% toward 225 mV, started to decrease, and finally disappeared completely at around 525 mV, as a result of the electrochemical oxidation of adsorbed CO, as proved by CV (Figure 3-2). However, in IRAS experiment, the intensity was almost constant without any significant increase up to 400 mV, then suddenly dropped due to CO oxidation, as shown in Figure 3-5(f), suggesting the number of the CO species on the Pt surface remained constant prior to CO oxidation. Thus, the increase of the SFG intensity was not caused by the changes in CO population.

3.2.3 Visible Energy Dependence of Spectral Results of CO on Pt(111) Surface

Further electrochemical SFG measurements at the CO/Pt(111) electrode were carried out by changing visible energy. Besides visible light of 560 nm, whose spectral results have already been shown in Figure 3-3, seven more visible light of different energies, i.e., 635, 620, 605, 590, 575, 550 and 527 nm, were employed for

the visible energy dependent investigation, and the SFG spectra obtained by using these seven visible light can be found in Figure 3-6. Obviously, the anomalous increase of the SFG amplitude was observed in all the cases except when visible light of 527 nm was used.

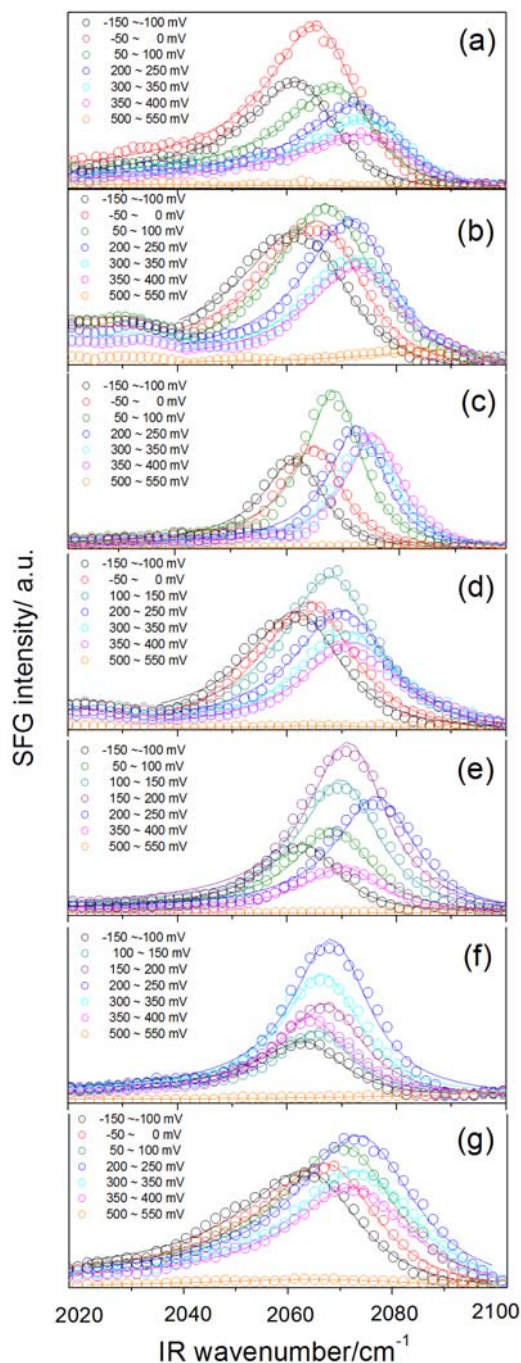


Figure 3-6. Typical potential dependent SFG spectra of the Pt(111) electrode with preadsorbed CO in the CO-free Ar-saturated 0.5 M H₂SO₄ aqueous solution obtained during potential scan by using visible light of (a) 635, (b) 620, (c) 605, (d) 590, (e) 575, (f) 550 and (g) 527 nm. Solid lines are the best fits according to Eq. (1-27).

Figure 3-7(a-h) shows the potential dependencies of normalized SFG amplitude obtained by using visible light of 635 nm (1.95 eV), 620 nm (2.0 eV), 605 nm (2.05 eV), 590 nm (2.10 eV), 575 nm (2.15 eV), 560 nm (2.21 eV), 550 nm (2.25 eV) and 527 nm (2.35 eV). Here the SFG amplitude was normalized by making that before the increase as 1, since the absolute values of SFG amplitude obtained by using visible light of different energies cannot be compared directly as they are dependent on the experimental conditions including intensities of visible and IR lasers. When visible light of 635 nm was used (Figure 3-7(a)), the intensity increased immediately after the potential scan was started from -150 mV, reached a maximum at -25 mV, decreased, reached a constant value at 75 mV, started to decrease again at 375 mV, and finally disappeared completely at around 525 mV, as a result of electrochemical oxidation of adsorbed CO. When visible light of 620, 605, 590, 575 and 560 nm were employed (Figure 3-7 (b-f)), the intensity gradually increased to a maximum at 25, 75, 125, 175 and 225 mV, respectively, then decreased and almost went back to the initial intensity before CO oxidation occurred, afterwards the CO intensities suffered a big drop and became 0 at around 525 mV, as a result of the electrochemical oxidation of the adsorbed CO. In contrast, when visible light of 550 nm was used (Figure 3-7(g)), the intensity stayed constant until the potential became as positive as 175 mV, reached a maximum at ca. 225 mV, and decreased gradually to become completely 0 at around 475 mV. When visible light of 527 nm was used (Figure 3-7(h)), the intensity stayed constant until the potential became as positive as 375 mV and then decreased without the increase. These results show that the potential dependencies of SFG characteristics of the CO/Pt(111) electrode are strongly affected by the energy of visible light. This is more clearly seen in Figure 3-7(i), which shows a contour map of the normalized SFG amplitude as functions of the potential and wavelength of visible light obtained by using the eight visible light. It is clear that the peak potential became more positive as the wavelength of visible light became shorter, except for the measurement using visible light of 527 nm.

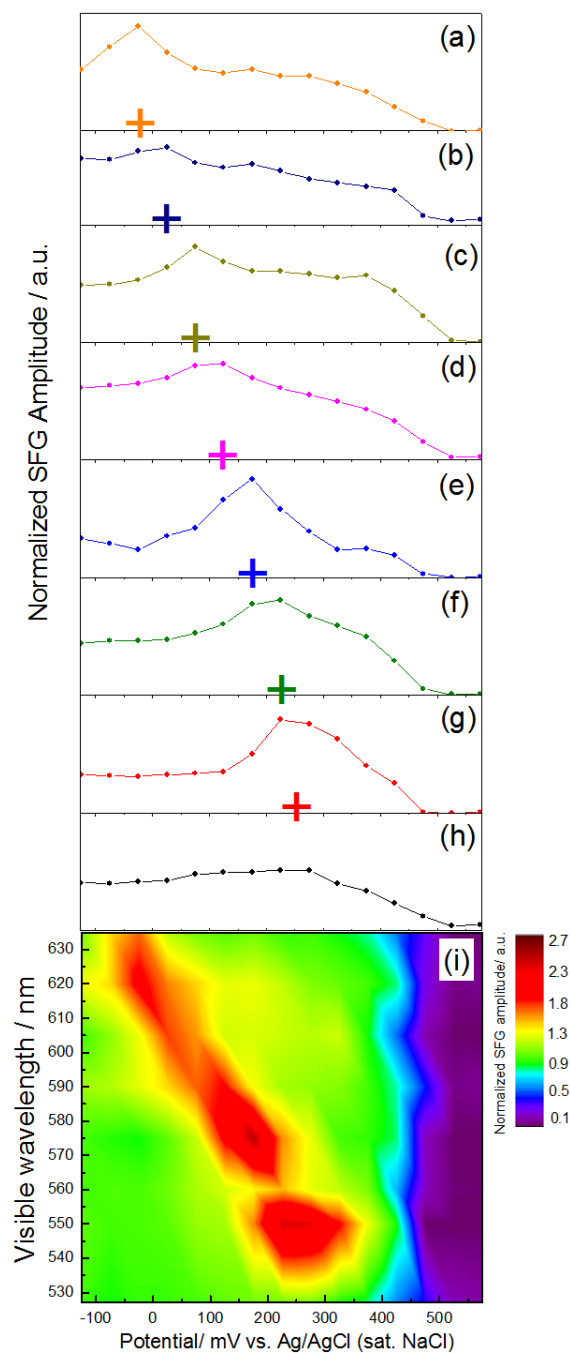


Figure 3-7. Normalized SFG amplitude as a function of potential obtained during potential scan by using visible light of (a) 635 nm (1.95 eV), (b) 620 nm (2.0 eV), (c) 605 nm (2.05 eV), (d) 590 nm (2.10 eV), (e) 575 nm (2.15 eV), (f) 560 nm (2.21 eV), (g) 550 nm (2.25 eV) and (h) 527 nm (2.35 eV). The cross in each figure is used to mark the peak center and baseline. (i) A contour map of the SFG amplitude as functions of the potential and wavelength of visible light obtained by using these eight visible light.

The relation between the SFG peak potential (observed in Figure 3-7) with the energy of both incident visible light and generated SF light is shown in Figure 3-8. The peak potential was obtained by fitting the SFG peak with a Gaussian function. It has an error bar of 25 mV since each data point is an average result of 50 mV. A linear dependence between the visible/SF light energy and electrode potential was observed with a slope of 1 V/eV. The reason why no peak was observed when visible light of 527 nm was used (Figure 3-7(h)) can be explained by this relation. The peak must be observed at 375 mV if visible light of 527 nm was used but the amount of adsorbed CO started to decrease already at this potential, which is quite close to CO main oxidation region; therefore, the SFG peak was not observed.

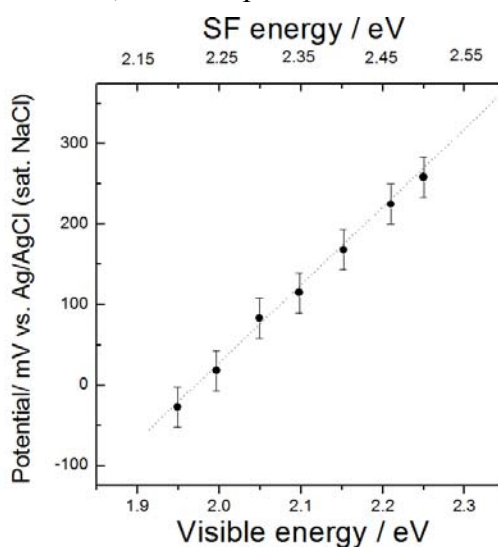


Figure 3-8. Peak potential observed in Figure 3-7 as functions of the input visible (bottom axis) and output SFG energy (top axis).

The effects of visible energy on the frequency and fwhm of the C-O stretching band on the Pt(111) in a given potential region are shown in Figure 3-9(a) and (b), respectively. It can be seen that, at all visible energies, with the potential became more positive the CO band shifted to higher wavenumber firstly due to electrochemical Stark effect or weak electron back-donation effect, then to lower wavenumber due to the reduction of dipole-dipole interaction among CO molecules, and the fwhm of the CO band kept almost constant prior to CO oxidation, as already found when visible light of 560 nm was used above. In a fixed potential region, the maximum difference

between the CO frequencies of different visible energies is ca. 5 cm^{-1} , which is smaller than the resolution of the SFG laser setup (ca. 10 cm^{-1}). Thus, the CO frequency is considered to not be affected by visible light. In contrast, as shown in Figure 3-9(b), the fwhm of various visible energies are more different and scattered at a given potential because of the different widths of visible light.

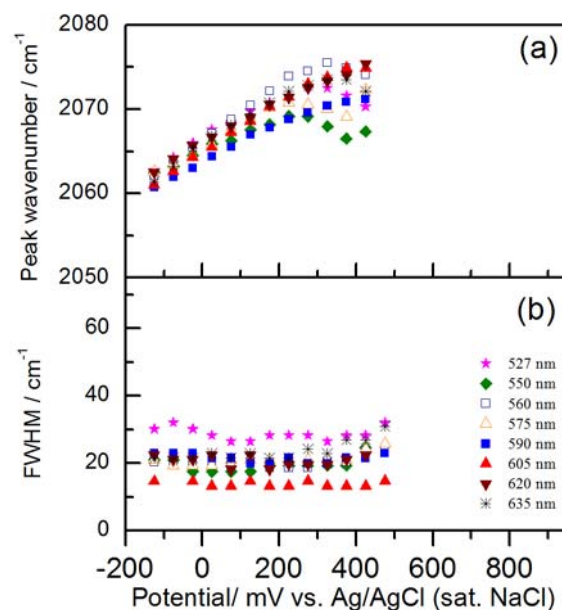


Figure 3-9. Potential dependencies of (a) peak wavenumber and (b) fwhm of the CO bands derived from the fitting of the SFG spectra obtained during potential scan by using visible light of 635, 620, 605, 590, 575, 560, 550 and 527 nm (Figure 3-3 and 3-6).

The each SFG spectrum above was obtained during the potential scan of 50 mV. To obtain the information at each exact potential, the potential dependent SFG measurements of CO adsorbed on the Pt(111) electrode in 0.5 M H_2SO_4 aqueous solution were also carried out at each constant potential by using these eight visible light. The potential was manually increased from -150 to 900 mV with a step of 25 mV. Each SFG spectrum is an average of three spectra recorded with a 50 s accumulation at a certain potential. Figure 3-10 and 3-11 are the typical SFG spectra and normalized SFG amplitude of CO/Pt(111) in 0.5 M H_2SO_4 aqueous solution at various constant potentials together with a contour map by using visible light of 635,

620, 605, 590, 575, 560, 550 and 527 nm, respectively.

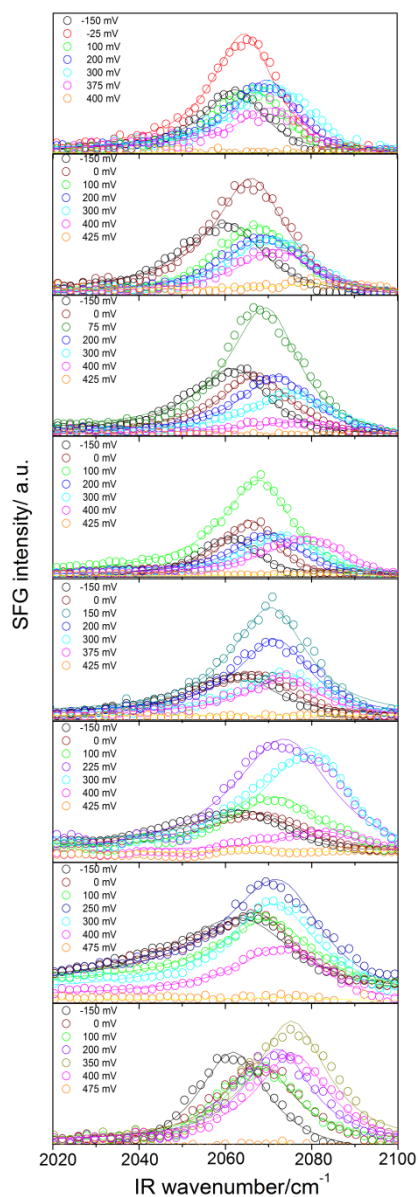


Figure 3-10. Typical potential dependent SFG spectra of the CO/Pt(111) in the CO-free 0.5 M H₂SO₄ solution obtained at constant potentials by using visible light of (a) 635, (b) 620, (c) 605, (d) 590, (e) 575, (f) 560, (g) 550 and (h) 527 nm. Solid lines are the best fits according to Eq. (1-27).

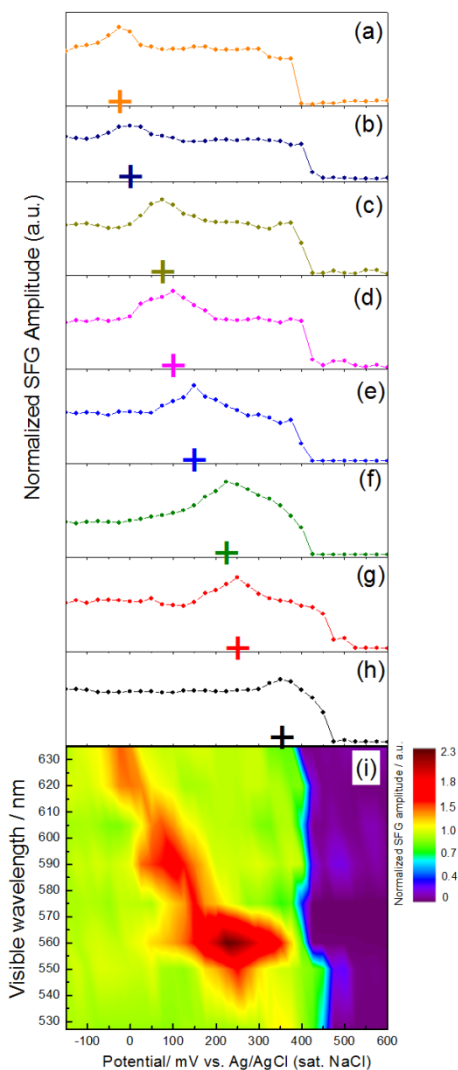


Figure 3-11. Normalized SFG amplitude as a function of potential obtained at constant potentials by using visible light of (a) 635, (b) 620, (c) 605, (d) 590, (e) 575, (f) 560, (g) 550, and (h) 527 nm. The cross in each figure is used to mark the peak center and baseline. (i) A contour map of the SFG amplitude as functions of the potential and wavelength of visible light obtained by using these eight visible light.

The bands observed at 2062–2075 cm^{-1} in Figure 3-10 are corresponding to C-O stretching of CO adsorbed on the atop site of the Pt(111). In agreement with the results of SFG measurements during potential scan as shown in Figure 3-3, 3-6 and 3-7, these bands strongly depended on both potential and visible energy, and the anomalous increase of the SFG amplitude prior to CO oxidation was observed in all the visible energies, as shown in Figure 3-11, the SFG peak potential became more positive as the wavelength of visible light became shorter. Through fitting the SFG peaks (in Figure 3-11) with the Gaussian function, the peak potential and its error bar for each visible energy can be known. As plotted with red squares in Figure 3-12, the relation between the SFG peak potential and visible/SF light energy in constant potential measurements was found to be near linear, and is almost in consistent with the relation of scanning potential measurements within the error bar.

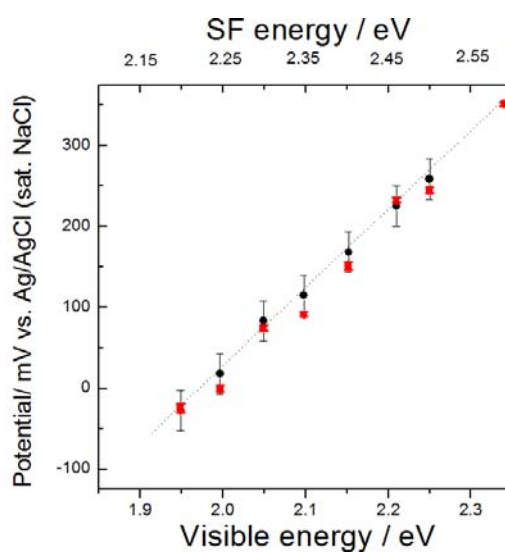


Figure 3-12. Peak potential in constant potential (red squares) and scanning potential (black circles) measurements as functions of the input visible (bottom axis) and output SFG energy (top axis).

3.2.4 Discussion for the Increase of SFG Intensity

The anomalous increase of the SFG intensity prior to CO oxidation was already reported by two groups. Somorjai and his colleagues showed the SFG intensity increased in CO-free solution by using visible light of 532 nm and suggested the

changes in the orientation and hyperpolarizability of adsorbed CO to be the possible reasons for the increase of SFG intensity.⁸ Wieckowski and his colleagues reported the increase of SFG intensity in CO-saturated and partially saturated 0.1 M H₂SO₄ aqueous solutions but not in CO-free solution by using visible light of 804 nm and proposed that the SFG intensity increase was caused by the potential-induced phase transition of the CO adlayer from (2 × 2) to (√19 × √19),¹⁴ which has been also accounted for by the increase of SHG intensity at CO/Pt(111) electrode prior to the anodic oxidation of adsorbed CO in CO-saturated solution.^{13,15} Neither the changes in the orientation and hyperpolarizability nor the phase transition of adsorbed CO can explain the present results of the visible light energy dependent peak potential as these are not be affected by visible light energy. Although the molecule hyperpolarizability of CO depends on visible light energy and a change in the hyperpolarizability might cause the increase of SFG intensity,⁸ the potential, at which the anomalous SFG peak (in Figure 3-7 and 3-11) is observed, should not be affected by visible light energy. It is also unlikely that the orientation of adsorbed CO is affected by visible light energy. The increase of SFG and SHG intensities due to the potential-induced phase transition of the CO adlayer from (2 × 2) to (√19 × √19) can be possible in fully or partially CO-saturated solution but not in CO-free solution where extra CO required for the transformation cannot be provided from the solution, although the surface structure of the CO adlayer in CO-free solution is not well-defined. Furthermore, the phase transition potential should not affect the visible light energy. The peaks (in Figure 3-7 and 3-11) were observed at potentials more negative than the phase transformation potential (ca. 300 mV vs. Ag/AgCl (sat. NaCl)).^{15,16}

Since the anomalous increase in CO-free solution has been observed only for SFG not for IR, Raman, or SHG, one may speculate that there is an SFG specific reason. In this respect, DR-SFG, which was reported by Somorjai and his colleagues for CO/Pt(111) in UHV,¹⁷ may be accounted for by the potential dependent behavior of the SFG intensity, although they did not mention their previous result of anomalous increase of SFG intensity in the electrochemical environment⁸ in their DR-SFG paper.¹⁷ DR-SFG, in which SFG intensity is enhanced not only by the vibrational

resonance but also by electronic resonance when the energy of input visible light or output SF light becomes equal to the transition energy of two electronic states at the interface, was first experimentally demonstrated by Raschke et al.¹⁸ Based on the electronic structure model of CO/Pt interface established in UHV studies as shown in Figure 3-12, in which $2\pi_a^*$ and $2\pi_b^*$ are two CO derived electronic states due to electron back-donation from d band of Pt to the vacant $2\pi^*$ orbital of CO, and $5\sigma_a$ is formed by the hybridization between 5σ orbital of CO and d band of Pt, Somorjai and his colleagues suggested that the electronic SFG enhancement at CO/Pt(111) in UHV is caused by the resonance of visible/SF light with the electronic transition from $2\pi_b^*$ to $5\sigma_a$. In the present study, SFG measurements were carried out with a visible light of a given energy as a function of potential. If one of the electronic states is varied with potential, the energy difference between the two states is also varied with potential and therefore, the SFG enhancement takes place at a specific potential where the energy difference between the two states becomes equal to the energy of visible/SF light. As a result, a peak should be observed in the SFG intensity-potential relation as experimentally observed in Figure 3-7 and 3-11. Taking into account the results of Somorjai and his colleagues for CO/Pt(111) in UHV, SFG enhancement at the CO/Pt(111) electrode in solution is proposed to be caused by the resonance of visible/SF light with the electronic transition from the Fermi level of Pt, which is varied linearly with potential, to the $5\sigma_a$ state of adsorbed CO as schematically shown in Figure 3-12. When the energy of visible light is increased, the Fermi level at which the resonance takes place becomes lower, and as a result the SFG peak potential is expected to become more positive. A linear dependence between the visible/SF light energy and the SFG resonance peak potential (i.e. intensity-potential relation peak in Figure 3-7 and 3-11) with the slope of 1V/eV observed experimentally in this study supports this model. Similar transition from the Pt 2p(3/2) orbital to unoccupied states at the CO/Pt system in an acid electrolyte has been suggested by Bae et al. using XANES¹⁹ as mentioned before. One must note that although the SFG enhancement is caused by the resonance of either the input visible photon (1.95–2.35 eV) or the corresponding output SF photon (2.2–2.6 eV) with the electronic transition between

two electronic states at the surface it is not possible to separate these two contributions since the energy difference between the visible and SF light is ca. 0.25 eV and the resolution of the present SFG setup is not high enough to distinguish this small energy difference. It must be also noted that the present results do not exclude the possible contribution of changes in the orientation and hyperpolarizability and the phase transition of adsorbed CO on the potential dependence of SFG intensity but show the major contribution is the potential dependent electronic transition.

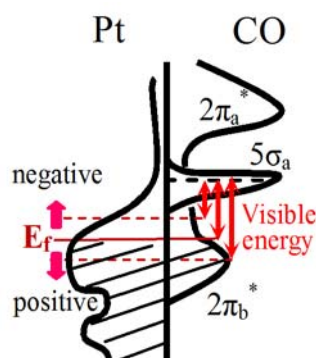


Figure 3-12. Model of electronic structure of the CO/Pt(111) electrode interface, showing the potential-induced Fermi level shift and electronic coupling of visible energy to the electronic transition between the Fermi level and $5\sigma_a$ state.

3.3 Conclusions

In this chapter, it was demonstrated that potential dependent DR-SFG spectroscopy can probe not only molecular structure but also the electronic state at the CO/Pt(111) interface in solution. SFG measurements by using eight different visible light energies showed that the intensity of the band corresponding to C-O stretching of preadsorbed CO on the Pt(111) electrode in H_2SO_4 aqueous solution increased anomalously prior to anodic oxidation of CO, and the anomalous peak potential shifted negatively when the visible light energy decreased with the linear relation by 1 V/eV, showing that the origin of the increase of SFG intensity is due to the resonance of visible and/or SF light with electronic transition from the Fermi level of Pt(111) to the $5\sigma_a$ antibonding state of adsorbed CO.

References

- (1) Spendelow, J. S.; Wieckowski, A. *Phys. Chem. Chem. Phys.* **2004**, *6*, 5094–5118.
- (2) Rangelov, G.; Memmel, N.; Bertel, E.; Dose, V. *Surf. Sci.* **1991**, *251/252*, 965–970.
- (3) Anazawa, T.; Kinoshita, I.; Matsumoto, Y. *J. Electron. Spectros. Relat. Phenomena.* **1998**, *88-89*, 585–590.
- (4) Chou, K. C.; Westerberg, S.; Shen, Y. R.; Ross, P. N.; Somorjai, G. A. *Phys. Review B.* **2004**, *69*, 153413.
- (5) Clavilier, J. *J. Electroanal. Chem. Interfacial Electrochem.* **1979**, *107*, 211–216.
- (6) Scherson, D. A.; Kolb, D. M. *J. Electroanal. Chem. Interfacial Electrochem.* **1984**, *176*, 353–357.
- (7) Jaaf-Golze, K. A.; Kolb, D. M.; Scherson, D. *J. Electroanal. Chem. Interfacial Electrochem.* **1986**, *200*, 353–362.
- (8) Chou, K. C.; Markovic, N. M.; Kim, J.; Ross, P. N.; Somorjai, G. A. *J. Phys. Chem. B* **2003**, *107*, 1840–1844.
- (9) Kitamura, F.; Takeda, M.; Takahashi, M.; Ito, M. *Chem. Phys. Lett.* **1987**, *142*, 318–322.
- (10) Leung, L. W. H.; Wieckowski, A.; Weaver, M. J. *J. Phys. Chem.* **1988**, *92*, 6985–6990.
- (11) Lambert, D. K. *Solid State Commun.* **1984**, *51*, 297–300.
- (12) Persson, B. N. J.; Ryberg, R. *Phys. Rev. B* **1981**, *24*, 6954–6970.
- (13) Akemann, W.; Friedrich, K. A.; Stimming, U. *J. Chem. Phys.* **2000**, *113*, 6864–6874.
- (14) Lagutchev, A.; Lu, G. Q.; Takeshita, T.; Dlott, D. D.; Wieckowski, A. *J. Chem. Phys.* **2006**, *125*, 154705.
- (15) Akemann, W.; Friedrich, K. A.; Linke, U.; Stimming, U. *Surf. Sci.* **1998**, *402-404*, 571–575.
- (16) Rodes, A.; Gómez, R.; Feliu, J. M.; Weaver, M. J. *Langmuir* **2000**, *16*, 811–816.
- (17) Chou, K. C.; Westerberg, S.; Shen, Y. R.; Ross, P. N.; Somorjai, G. A. *Phys. Rev. B* **2004**, *69*, 153413.
- (18) Raschke, M. B.; Hayashi, M.; Lin, S. H.; Shen, Y. R. *Chem. Phys. Lett.* **2002**, *359*, 367–372.
- (19) Bae, I. T.; Scherson, D. A. *J. Phys. Chem.* **1996**, *100*, 19215–19217.

Chapter 4

Electronic Structure of CO/Polycrystalline Pt Electrode

Interface Probed by Potential Dependent DR-SFG

Spectroscopy

4.1 Introduction

Although most electronic structure studies on CO/Pt interfaces have been carried out using single crystals because of their highly reproducible and well-ordered surfaces,¹⁻³ most practical electrocatalysts are polycrystalline. The information obtained from single crystal surfaces often falls short in its relevance to real systems. Hence, electronic structure study with polycrystalline electrodes especially at electrochemical interfaces becomes important.

In this chapter, the electronic structure of a CO/polycrystalline Pt electrochemical interface was studied by using potential dependent DR-SFG technique. The SFG measurements of CO on a polycrystalline Pt electrode surface in 0.5 M H₂SO₄ aqueous solution were carried out at various constant potentials by using different visible light energies. As already found on a Pt(111) surface (Chapter 3), an anomalous SFG intensity increase and a linear potential shift of the SFG resonance peak with the visible energy were observed. The substrate effect on the interfacial electronic structures of CO was discussed by comparing the width and potential of the SFG resonance peak on polycrystalline Pt with those on the Pt(111) electrode.

4.2 Results and Discussion

4.2.1 Electrochemical Behaviors of Polycrystalline Pt without and with CO in 0.5 M H₂SO₄

Figure 4-1 shows the CV for a bare polycrystalline Pt surface in 0.5 M H₂SO₄ recorded with a scan rate of 20 mV/s. The negative and positive potential limits are -150 and 1100 mV, respectively. At potentials more negative than 150 mV, when the

potential was scanned in the negative direction, the current owing to adsorption of hydrogen at the Pt surface was observed. In contrast, when the potential was scanned positively, the observed current is due to desorption of hydrogen from the Pt surface. The adsorption and desorption of hydrogen are reversible processes. The potential region between 150 and 600 mV is a double layer region, where the current only comes from charging of the double layer. At potentials more positive than 600 mV, Pt starts to oxidize and forms an oxide layer on the surface. The reduction of the Pt oxide happens at a more negative potential, indicating that Pt oxidation is an irreversible reaction. The features of this CV are in agreement with those reported by other electrochemists,⁴⁻⁶ suggesting a clean polycrystalline Pt surface is obtained.

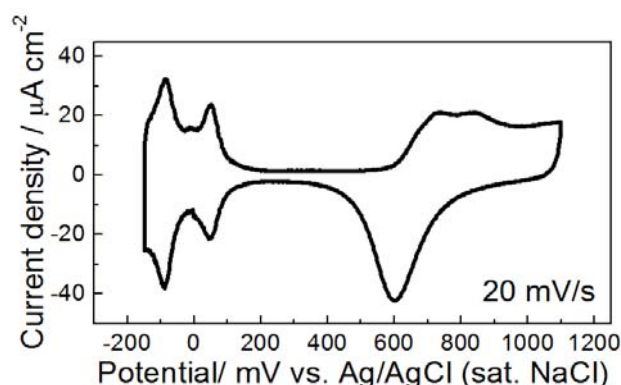


Figure 4-1. CV for the polycrystalline Pt electrode without preadsorbed CO immersed in 0.5 M H₂SO₄ aqueous solution. A scan rate of 20 mV/s was employed.

The real active surface area of the polycrystalline Pt electrode was able to be calculated from the hydrogen adsorption peaks in the CV. A charge of 400 μC is obtained by integrating the hydrogen adsorption peaks. Assuming that there is one hydrogen per surface Pt atom and a surface charge equals to 220 $\mu\text{C}/\text{cm}^2$, the real active surface area of the electrode is calculated to be 1.80 cm^2 . The active surface area is about two times larger than the geometrical area of the electrode surface.

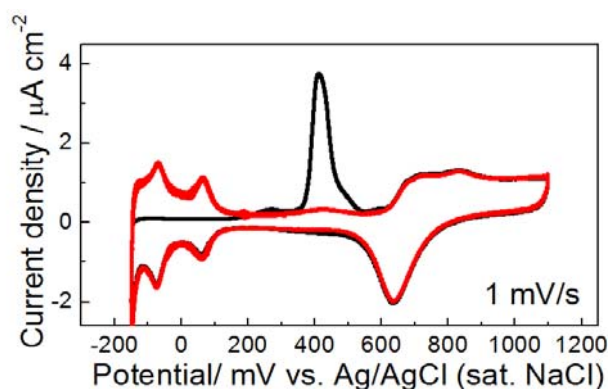


Figure 4-2. CV of the polycrystalline Pt electrode in CO-free Ar-saturated 0.5 M H_2SO_4 aqueous solution with preadsorbed CO between -150 and 1100 mV with a scan rate of 1 mV/s for the first (black line) and the second (red line) cycles.

Figure 4-2 shows two-cycle voltammetry of the polycrystalline Pt electrode with preadsorbed CO in CO-free 0.5 M H_2SO_4 aqueous solution obtained by scanning the potential between -150 and 1100 mV with a scan rate of 1 mV/s. For the first cycle (black line), the potential was positively scanned from -150 to 1100 mV, and then reversed to -150 mV. The second potential cycle (red line) was recorded in a similar manner to the potential scanned in the first cycle. In the first positive going scan, the current corresponding to the hydrogen desorption was not found due to the surface poisoning by adsorbed CO. The CO adlayer on the polycrystalline Pt electrode was stable from the hydrogen evolution potential to ca. 200 mV, then two distinct peaks were observed at ca. 260 and 410 mV. The small peak at ca. 260 mV and the big peak at ca. 410 mV are referred to as a preoxidation peak and a main oxidation peak of the CO adlayer, respectively.⁷ The integrated area from 200 to 550 mV represents the oxidation charge for the CO adlayer. This value is 630 μC and with the electrode area of 1.80 cm^2 corresponds to a charge density of 350 $\mu\text{C}/\text{cm}^2$. For the two-electron oxidation of CO to CO_2 , a full monolayer of CO on Pt would produce a charge density of 480 $\mu\text{C}/\text{cm}^2$. Therefore, by dividing the measured charge by the theoretic value for a full CO monolayer, a coverage corresponding to a 0.73 monolayer (ML) was obtained. This is close to the coverage of the $\text{p}(2 \times 2)\text{-3CO}$ structure (0.75 ML) determined from STM⁸ and X-ray scattering.⁹ The preoxidation peak accounts for

approximately 10% of the total oxidation charge generated in the CO oxidation.⁹⁻¹¹ After this CO stripping, a pair of Pt oxidation/reduction peaks followed by the hydrogen adsorption peaks appeared in the CV. When the electrode underwent the second cycle potential scan, there was no trace of the CO oxidation peaks and the hydrogen adsorption/desorption peaks were perfectly retraced, which became almost equal to the CV of the bare Pt in 0.5 M H₂SO₄ aqueous solution, as shown in Figure 4-1. This kind of CV was also observed in all subsequent cycles. The recovery of the CV indicates that most CO molecules on the Pt surface were oxidized to CO₂ during the first potential cycle.

It is noticeable that the features for the CO stripping on polycrystalline Pt surface are different from that of CO/Pt(111), as is already shown in Figure 3-2. Instead of a single and sharp CO oxidation peak at 500 mV on the well-ordered Pt(111) surface, the preoxidation peak and a ca. 100 mV negative shift of the main oxidation peak were observed on the polycrystalline Pt electrode.

4.2.2 Potential Dependent Spectra of CO/Polycrystalline Pt Interface

Figure 4-3 shows the in situ SFG spectra of CO adsorbed on a polycrystalline Pt electrode in 0.5 M H₂SO₄ aqueous solution at various constant potentials by using 560 nm visible light. Starting from -150 mV, the electrode potential was manually changed in the positive direction with a step of 25 mV and stopped at 900 mV. Thus, there are 43 spectra in total. Here, in order to clearly display the change of the SFG spectra as a function of potential, only a selective few spectra were put into the figure. Each SFG spectrum is an average of three spectra recorded with 50 s accumulation at each constant potential. The bands observed at 2055–2073 cm⁻¹ are attributed to the C-O stretching of CO adsorbed on atop site of the Pt surface.^{12,13} The peak wavenumber is lower than that of the atop CO adsorbed on the Pt(111) surface (2062–2075 cm⁻¹) as already shown in Chapter 3. It is obvious that both peak position and SFG intensity varied with the electrode potential. More details of potential dependencies of peak wavenumber, fwhm and amplitude, which were extracted from

the fitting result of each spectrum, are presented in Figure 4-4(a), (b) and (c), respectively.

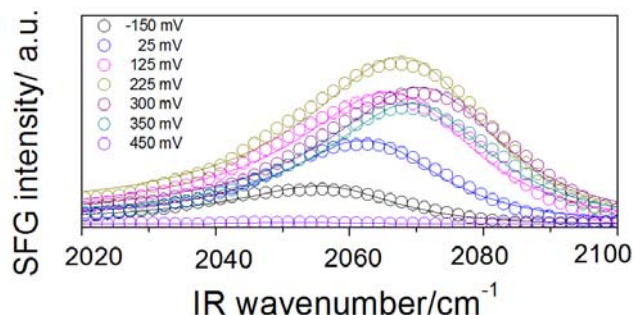


Figure 4-3. Typical potential dependent SFG spectra of the polycrystalline Pt electrode with preadsorbed CO in CO-free Ar-saturated 0.5 M H₂SO₄ aqueous solution obtained by using visible light of 560 nm. Solid lines are the best fits according to Eq. (1-27).

From Figure 4-4(a), it can be seen that the external electrode potential induced a change in the vibrational frequency of adsorbed CO. At the potentials more negative than 325 mV, the frequency of the CO band linearly exhibited a shift with a slope of 37 cm⁻¹/V^{14,15} owing to the Stark effect or weak electron back-donation effect. As the potential became more positive, the CO frequency had a significant decrease at around 350 mV. This unique phenomenon was consistent with that was observed at the CO/Pt(111) interface in Chapter 3, and is attributed to the reduced dipole–dipole interaction among CO molecules as a result of the decrease of CO coverage due to CO oxidation.^{16–18} Correspondingly, the fwhm in Figure 4-4(b) shows no substantial variation prior to CO oxidation, as found in the CO/Pt(111) system, implying a constant CO coverage.

In addition, the anomalous potential dependence of the SFG intensity was observed in Figure 4-4(c). During the positive going potential, the intensity of the atop CO band gradually increased and reached a maximum at 225 mV, then afterwards started to decrease. The intensity had an advanced drop from 350 mV and

completely disappeared at 450 mV. The loss of the SFG signal of the adsorbed CO on the polycrystalline Pt surface has been associated with the CO oxidation, which was proved by the CV results, as shown in Figure 4-2.

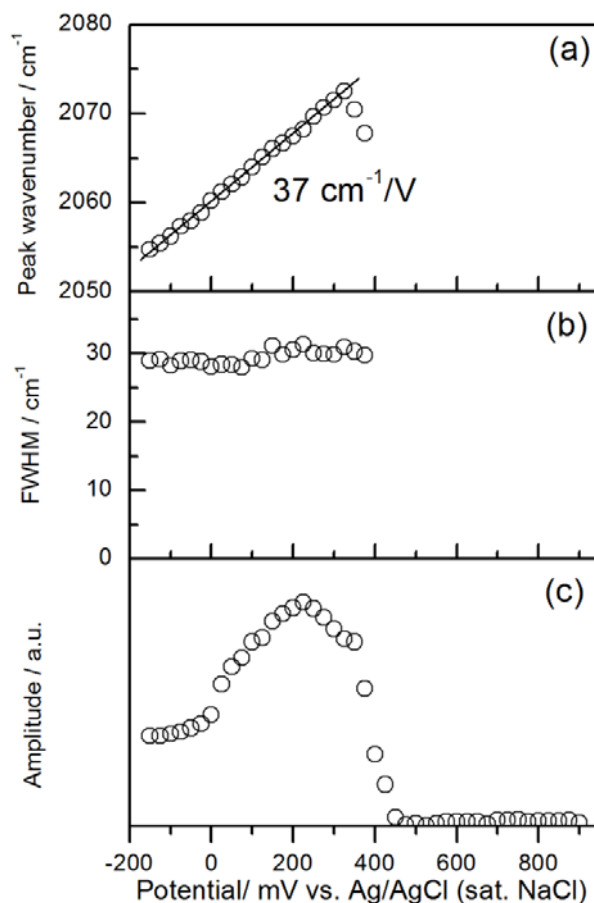


Figure 4-4. Potential dependencies of (a) peak wavenumber, (b) fwhm and (c) amplitude of the bands derived from the fitting of the SFG spectra obtained by using visible light of 560 nm (Figure 4-3).

4.2.3 Visible Energy Dependent Spectra of CO/Polycrystalline Pt Interface

To understand the origin of the SFG intensity increase, the potential dependent SFG measurements at the CO/polycrystalline Pt electrode were conducted with eight different wavelengths of visible light, including visible light of 635, 620, 605, 590, 575, 560, 550 and 527 nm. Since the results using 560 nm visible light have already been discussed in Section 4.2.2, the potential dependent SFG spectra from the other

seven visible probes are presented in this section (as shown in Figure 4-5).

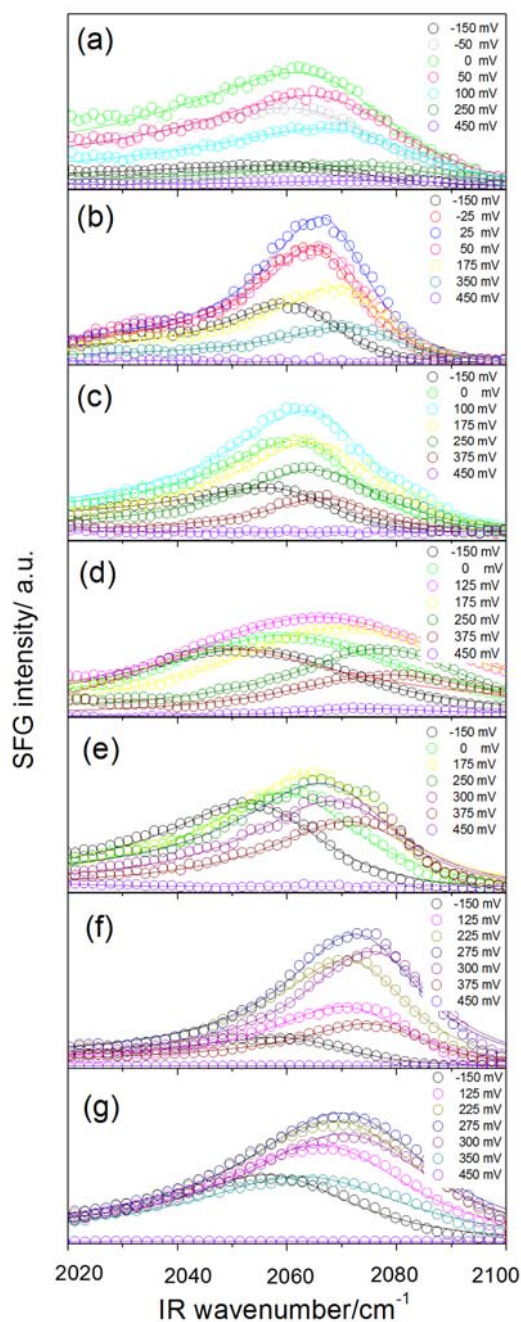


Figure 4-5. Representative potential dependent SFG spectra of the polycrystalline Pt electrode with preadsorbed CO in the CO-free Ar-saturated 0.5 M H₂SO₄ aqueous solution obtained by using visible light of (a) 635, (b) 620, (c) 605, (d) 590, (e) 575 (f) 550 and (d) 527 nm. Solid lines are the best fits according to Eq. (1-27).

The effect of visible energy on the SFG intensity is illustrated by the plots of the potential-normalized SFG amplitude relation at each visible energy in Figure 4-6.

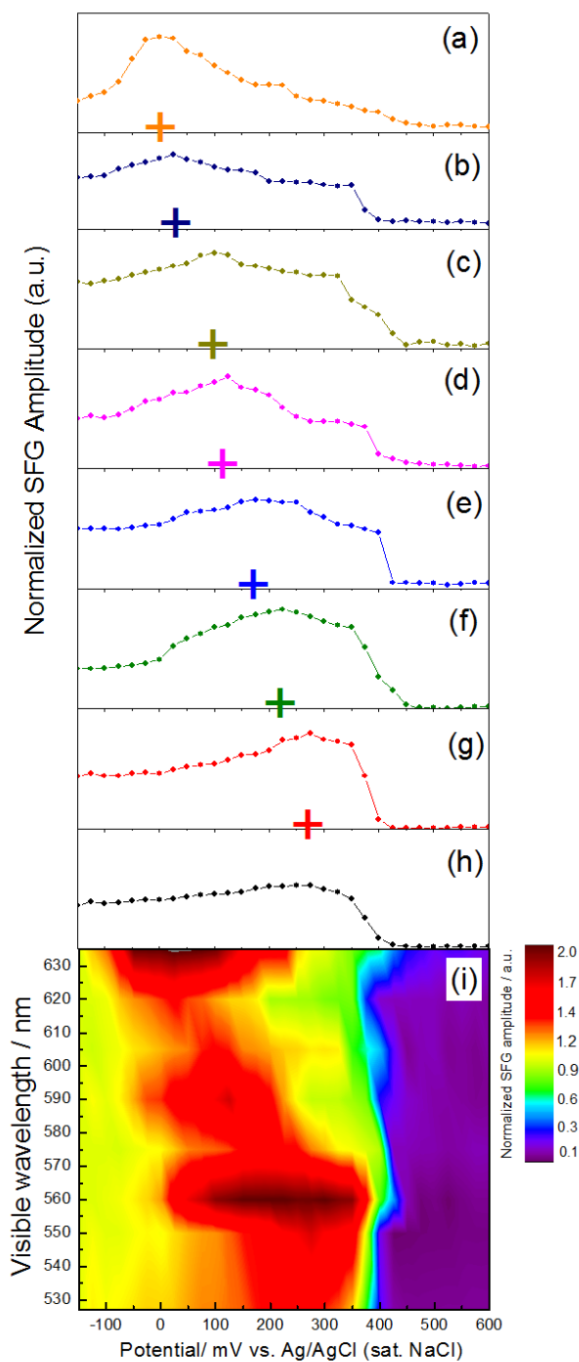


Figure 4-6. Normalized SFG amplitude as a function of potential obtained by using visible light of (a) 635 nm (1.95 eV), (b) 620 nm (2.0 eV), (c) 605 nm (2.05 eV), (d) 590 nm (2.10 eV), (e) 575 nm (2.15 eV), (f) 560 nm (2.21 eV), (g) 550 nm (2.25 eV) and (h) 527 nm (2.35 eV). The crosses are used to mark each peak's center and baseline. (i) A contour map of the SFG amplitude as functions of the potential and wavelength of visible light obtained by using these eight visible light.

In the limited potential range prior to CO oxidation, the anomalous SFG intensity increase can always be found at each visible energy except when 527 nm visible light was used. When visible light of 635, 620, 605, 590 and 575 nm were employed (Figure 4-6 (a-e)), the intensity increased from -150 mV, reached a maximum at 0, 25, 100, 125 and 175 mV, respectively, then decreased gradually to the initial intensity before CO oxidation occurred; afterwards the intensities suffered a big drop and became 0 at around 450 mV as a result of the electrochemical oxidation of the adsorbed CO. When visible light of 560, 550 and 527 nm was used (Figure 4-6 (f-h)), similarly, the intensity increase also took place in each case, where the maximum intensity was found at 225, 275 and 275 mV, respectively, decreased gradually until the potential became as positive as 350 mV and then dramatically decreased instead of returning to the initial intensity due to CO oxidation. From this figure, it can be seen that the SFG peak potential strongly depends on the energy of visible light. By fitting each SFG peak (in Figure 4-6) with a Gaussian function, the peak potential and its error bar were obtained and plotted as functions of visible and SF energy (indicated with black squares in Figure 4-7). It is shown that the peak potential positively shifted with decreasing the wavelength of the incident visible light, except for visible light of 527 nm. A near linear dependence between the visible/SF light energy and the SFG peak potential was observed as a slope of 1 V/eV, in agreement with the corresponding results for CO/Pt(111) in Chapter 3, which were also obtained by using constant potential measurements, as shown by red circles in the figure. However, there might be some differences owing to substrate effect between the two slopes. At the given potential, it seems that less visible energy of ca. 0.025 eV (as indicated in Figure 4-7) was needed for the CO/polycrystalline Pt interface to generate a resonance than that needed for the CO/Pt(111) interface. Furthermore, at a given visible energy, the peak potential at which electronic resonance took place of the CO/polycrystalline Pt shows slightly more positive (ca. 25 mV) than that of the CO/Pt(111).

Moreover, according to this slope, when 527 nm visible light was employed, the anomalous peak is expected at 375 mV, but now appeared at 275 mV. Here, CO oxidation could be the most probable reason to explain the present difference at 527

nm. By referring the CV as shown in Figure 4-2, it was found that there was a preoxidation peak of CO at ca. 300 mV, thus the amount of adsorbed CO has already started to decrease at this potential and 375 mV already entered the main CO oxidation region. That is why the SFG peak was observed at 275 mV.

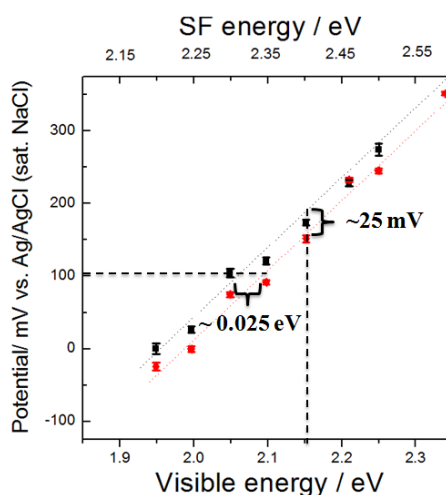


Figure 4-7. Peak potential for CO/polycrystalline Pt (black squares) and CO/Pt(111) (red circles) obtained by using constant potential measurements as functions of the input visible (bottom axis) and output SF energy (top axis).

Figure 4-8 gives the visible energy dependencies of the peak wavenumber and fwhm of CO band on the polycrystalline Pt electrode at each potential. Similar to the discussion for the case of CO/Pt(111) in Figure 3-9, the visible light should not affect the frequency of CO on the polycrystalline Pt, but should seriously affect its fwhm seriously. Despite the big differences between the fwhm for various visible light, the fwhm of CO bands on the polycrystalline Pt surface in all visible energies are generally broader than those on the Pt(111) (ca. 20 cm^{-1}) as shown in Figure 3-9(b). Furthermore, the peak wavenumbers of CO on the polycrystalline Pt electrode in all visible energies (ca. 2056 cm^{-1} @ -150 mV, Figure 4-8(a)) are lower than those on the Pt(111), ca. 2062 cm^{-1} @ -150 mV (Figure 3-9(a)).

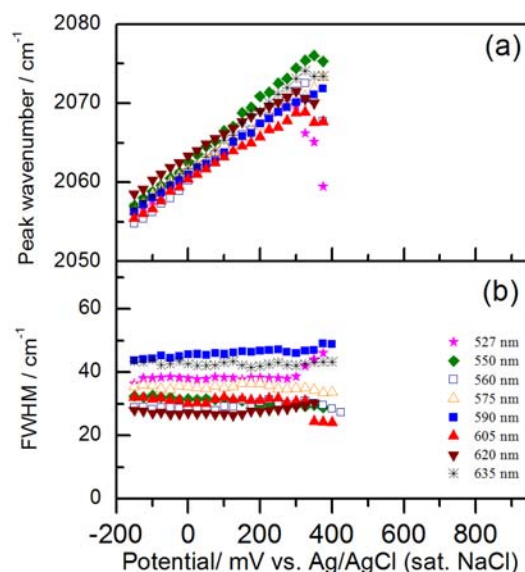


Figure 4-8. Potential dependencies of (a) peak wavenumber and (b) fwhm of the CO band derived from the fitting of the SFG spectra obtained by using visible light of 635, 620, 605, 590, 575, 560, 550 and 527 nm (Figure 4-3 and 4-5).

4.2.4 A Comparative Discussion of Double Resonance Effect on Polycrystalline Pt and Pt(111) Surfaces

It was found that in the present results, the SFG intensity increase depended on both potential and visible energy, which agrees with those observed at the CO/Pt(111) interface. Thus, the origin of the increase in the SFG intensity on the polycrystalline Pt electrode was also attributed to the resonance of visible and/or SF light with the electronic transition from the Fermi level of Pt to the $5\sigma_a$ antibonding state of adsorbed CO but not due to the potential dependent geometric structure change of adsorbed CO.

At a given potential, less visible energy seems to be needed for the CO/polycrystalline Pt interface to generate an electronic resonance than for the CO/Pt(111) interface, and at a given visible energy, the SFG resonance peak for CO on polycrystalline Pt was observed at slightly more positive potential, where the Fermi level was downward shifted, than that on the Pt(111), suggesting the energy of the $5\sigma_a$ antibonding state of CO adsorbed on the polycrystalline Pt electrode might be

slightly lower than that on the Pt(111) electrode, as illustrated in Figure 4-9. The slight downward shift of the $5\sigma_a$ antibonding state of CO on the polycrystalline Pt might be caused by the lower d-band energy of polycrystalline Pt than that of Pt(111).

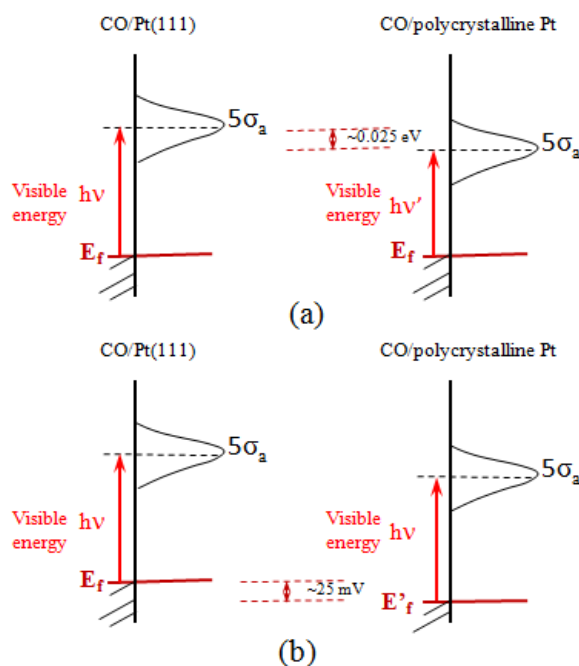


Figure 4-9. Schematic models for resonance of visible light with the electronic transition between the Fermi level (E_f) and the $5\sigma_a$ antibonding state of CO adsorbed on Pt(111) and on polycrystalline Pt (a) at a given potential and (b) at a given visible energy, showing that the energy of the $5\sigma_a$ antibonding state of CO adsorbed on polycrystalline Pt surface is slightly lower than that on the Pt(111) electrode.

Through fitting the SFG resonance peaks, which can be seen in Figure 4-6, with the Gaussian function, the width of the peak at each visible energy was extracted and plotted in Figure 4-11. The results of the widths of the SFG peaks obtained at the CO/Pt(111) in constant potential measurements are also shown in this figure. The fitting examples are given in Figure 4-10, where the potential widths of the SFG peaks for the CO/polycrystalline Pt and CO/Pt(111) are indicated by the arrows.

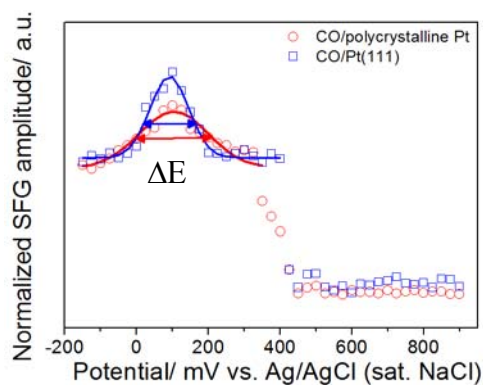


Figure 4-10. A schematic for fitting the SFG resonance peak for the CO/polycrystalline Pt and CO/Pt(111) with a Gaussian function to extract the half width of the peak as indicated by the arrows.

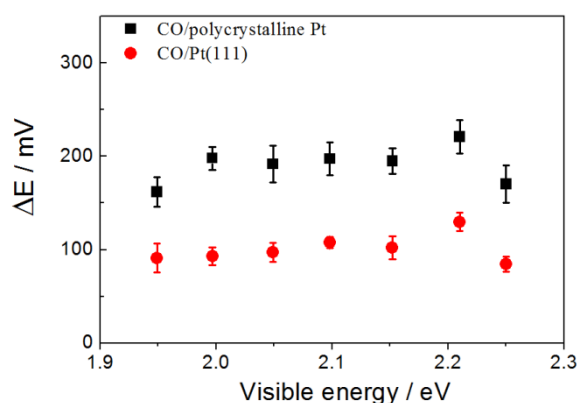


Figure 4-11. The width of the SFG peak obtained from constant potential SFG measurements of CO adsorbed on the polycrystalline Pt (black squares) and on the Pt(111) (red circles) as a function of visible energy.

It is worth noting that the widths of the peaks obtained from the CO/polycrystalline Pt results (indicated by black squares) are generally broader than those from the CO/Pt single crystal (indicated by red circles). The difference in the peak widths between CO/polycrystalline Pt and CO/Pt(111) is thought to be related to their different interfacial electronic structures. The interaction between the CO and the Pt surface depends on the face and terrace size of the surface, and many other factors. Comparing to the well-ordered Pt(111), the polycrystalline Pt electrode has many faces and the terrace size on polycrystalline surface can be small. Hence, when a CO

molecule is adsorbed on a polycrystalline Pt surface, many kinds of interactions between CO and Pt present on polycrystalline Pt electrode and, as a result, the energy distribution of the $5\sigma_a$ antibonding electronic state of CO on a polycrystalline surface is broader than that on a Pt single crystal, as shown in Figure 4-12. That is why such broader SFG peaks were observed on the polycrystalline Pt electrode. This result can also be confirmed by the broader fwhm of the atop CO band adsorbed on the polycrystalline Pt electrode (ca. 30 cm^{-1}), as shown in Figure 4-8(b), than that on the Pt(111) single crystal electrode (ca. 20 cm^{-1}), as shown in Figure 3-9(b).

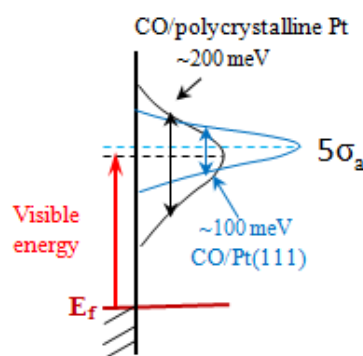


Figure 4-12. A model of the $5\sigma_a$ antibonding state of CO adsorbed on polycrystalline Pt and Pt(111) electrodes at a given potential, showing that the energy distribution of the $5\sigma_a$ states of CO adsorbed on a polycrystalline Pt is broader than that on a Pt (111).

Moreover, changes in the electronic structures of CO on the polycrystalline Pt as mentioned above can properly explain the more negative potential of CO oxidation and the lower wavenumber of the C-O frequency on the polycrystalline Pt surface, as revealed in Figure 4-2 and Figure 4-3, respectively, compared to the case of CO/Pt(111). As the d-band moves far from the Fermi level, the d-band becomes more diffused and the back-donation of the metal electrons into the $2\pi^*$ antibonding state of CO increases, giving rise to weaker strength and longer length of the C-O bond^{19,20} as well as lower activation energy for CO oxidation.²¹ Therefore, the frequency of CO was observed at a lower wavenumber on the polycrystalline Pt surface, and the CO

oxidation became easier and took place at a more negative potential on the polycrystalline Pt than on the Pt(111).

4.3 Conclusions

In this chapter, potential dependent DR-SFG spectroscopy was applied to study the electronic structures of the CO/polycrystalline Pt electrochemical interface. In the visible energy dependent SFG study, an anomalous increase of SFG intensity prior to oxidation was observed, and its peak potential was found to near linearly depend on the visible and/or SF light energy, which agrees with the results for the CO/Pt(111) interface, indicating the increase of SFG intensity on the polycrystalline Pt is also caused by the vibrational transition of CO followed by an electronic transition between the Fermi level and the $5\sigma_a$ state of CO. A slight positive shift of the SFG peak potential at a fixed visible energy and less visible energy used for a generation of the electronic resonance at a fixed potential show a downward shift of the $5\sigma_a$ antibonding state of CO on polycrystalline Pt due to the lower energy of the d-band center of polycrystalline Pt. A broadening of the SFG resonance peak on the polycrystalline Pt surface was also observed, indicating the energy distribution of $5\sigma_a$ antibonding electronic state of CO adsorbed on polycrystalline Pt is broader than that on single crystal Pt surface. This study has proved that potential dependent DR-SFG spectroscopy is a strong tool for characterizing the microscopic electronic structure of various interfaces in electrochemical environments.

References

- (1) Rangelov, G.; Memmel, N.; Bertel, E.; Dose, V. *Surf. Sci.* **1991**, *251/252*, 965–970.
- (2) Anazawa, T.; Kinoshita, I.; Matsumoto, Y. *J. Electron. Spectros. Relat. Phenomena.* **1998**, *88-89*, 585–590.
- (3) Chou, K. C.; Westerberg, S.; Shen, Y. R.; Ross, P. N.; Somorjai, G. A. *Phys. Review B.* **2004**, *69*, 153413.
- (4) Paulissen, V. B.; Korzeniewski, C. *J. Electroanal. Chem.* **1993**, *351*, 329–335.
- (5) Nakabayashi, S.; Sugiyama, N.; Yagi, I.; Uosaki, K. *Chem. Phys.* **1996**, *205*, 269–275.
- (6) Yagi, I.; Nakabayashi, S.; Uosaki, K. *J. Phys. Chem. B* **1997**, *101*, 7414–7421.
- (7) Sun, S.-G.; Lin, Y.; Li, N.-H.; Mu, J.-Q. *J. Electroanal. Chem.* **1994**, *370*, 273–280.
- (8) Villegas, I.; Weaver, M. J. *J. Chem. Phys.* **1994**, *101*, 1648–1660.
- (9) Marković, N. M.; Grgur, B. N.; Lucas, C. A.; Ross, P. N. *J. Phys. Chem. B* **1999**, *103*, 487–495.
- (10) Kunitatsu, K.; Seki, H.; Golden, W. G.; Gordon, J. G.; Philpott, M. R. *Langmuir* **1986**, *2*, 464–468.
- (11) Ikezawa, Y.; Saito, H.; Fujisawa, H.; Tsuji, S.; Toda, G. *J. Electroanal. Chem. Interfacial Electrochem.* **1988**, *240*, 281–289.
- (12) Kitamura, F.; Takahashi, M.; Ito, M. *Chem. Phys. Lett.* **1986**, *123*, 273–276.
- (13) Kitamura, F.; Takeda, M.; Takahashi, M.; Ito, M. *Chem. Phys. Lett.* **1987**, *142*, 318–322.
- (14) Bishop, D. M. *Rev. Mod. Phys.* **1990**, *62*, 343–374.
- (15) Lambert, D. K. *Electrochimica Acta* **1996**, *41*, 623–630.
- (16) Leung, L. W. H.; Wieckowski, A.; Weaver, M. J. *J. Phys. Chem.* **1988**, *92*, 6985–6990.
- (17) Lu, G. Q.; Lagutchev, A.; Dlott, D. D.; Wieckowski, A. *Surf. Sci.* **2005**, *585*, 3–16.
- (18) Stamenkovic, V.; Chou, K. C.; Somorjai, G. A.; Ross, P. N.; Markovic, N. M. *J. Phys. Chem. B* **2005**, *109*, 678–680.
- (19) Blyholder, G. *J. Phys. Chem.* **1964**, *68*, 2772–2777.
- (20) Sung, S. S.; Hoffmann, R. *J. Am. Chem. Soc.* **1985**, *107* (3), 578–584.
- (21) Meier, D. C.; Bukhtiyarov, V.; Goodman, D. W. *J. Phys. Chem. B* **2003**, *107*, 12668–12671.

Chapter 5

Electronic Structure of CO Adsorbed on Pt-modified Au

Electrode Probed by Potential Dependent DR-SFG

Spectroscopy

5.1 Introduction

In recent years, transition metal thin films on a second noble metal surface have received considerable interest because of their distinctive electronic and electrocatalytic properties for many reactions, such as ORR and electrooxidation of small molecules (methanol, formic acid, CO etc.).¹⁻⁴ For instance, when a monolayer of Pt is deposited on Pd(111) electrodes or Pd nanoparticles, the kinetics of ORR is enhanced significantly compared to that of either Pt(111) surfaces or Pt nanoparticles.² Naohara et al. deposited ultrathin Pd films on Au(111) and Au(100) surfaces, and reported that depending on the substrate and the thickness of the Pd film, different electrocatalytic activities for the oxidation of formaldehyde were observed.¹ The reasons for the electroactivity changes on the thin film-modified electrodes have been suggested as significant changes in electronic structures of the surfaces resulting from the interaction between the overlayer and metal substrate.⁵ Therefore, a deep understanding of the underlying electronic structure information at the thin film-modified electrode/electrolyte interfaces can be very essential for understanding electrocatalytic reaction processes and improvement of electrocatalysts.

Early studies were focused on the development of thickness dependent thin film electrocatalysts for tailoring the properties of catalysts. Transition metal thin films from one atomic layer to tens monolayers epitaxially deposited on various noble metal substrates have been achieved by a number of methods, such as electrochemical deposition,^{6,7} vapor deposition⁸ and molecular beam epitaxy (MBE).⁹ As compared to these efforts, however, studies of interfacial electronic structures of the thin film-modified electrodes in electrochemical conditions have not yet been exploited.

Hence, the work in this chapter is dedicated to probing the interfacial electronic structures of CO adsorbed on a Pt sub-monolayer electrochemically deposited on a polycrystalline Au electrode surface in acid solution by using potential dependent DR-SFG spectroscopy. The visible energy dependent study was carried out. In addition, the electrocatalytic activity of the Pt thin film-modified Au substrate toward CO oxidation was characterized as a function of the Pt thickness. The origin of the SFG intensity increase prior to CO oxidation and the Pt thickness dependent electrocatalytic activity are briefly discussed with comparison to the results obtained from Pt(111) and polycrystalline Pt electrodes.

5.2 Results and Discussion

5.2.1 Electrochemical Characterizations

5.2.1.1 Cyclic Voltammetry of Polycrystalline Au Surface in 0.05 M H₂SO₄

Figure 5-1 reveals the electrochemical behaviors for a bare polycrystalline Au electrode in 0.05 M H₂SO₄ between -200 and 1450 mV. During the positive going scan, the peaks found at ca. 1100 and 1330 mV are attributed to the Au oxide formation. The corresponding Au reduction peak develops at 910 mV when the potential was scanned negatively.¹⁰ The electrochemical active area of the surface was calculated by integrating the charge of this Au oxide reduction peak with a theoretical value of 444 $\mu\text{C}/\text{cm}^2$ required for reducing a monolayer of Au oxide as a reference.¹¹ The CV is in good agreement with those reported previously,^{12,13} reflecting a clean polycrystalline Au surface was achieved.

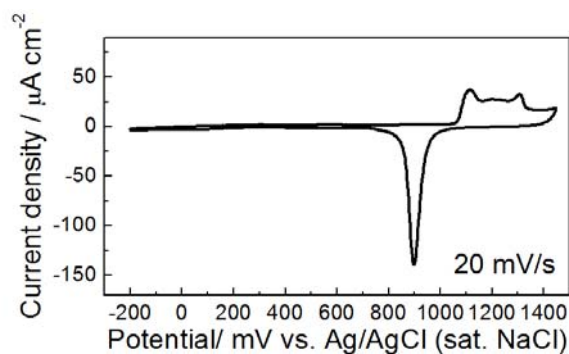


Figure 5-1. CV of a polycrystalline Au electrode in 0.05 M H₂SO₄ aqueous solution with a scan rate of 20 mV/s.

5.2.1.2 Electrochemical Behavior of Pt Thin Film on Au Surface

In order to find the ideal deposition rate, a potential dependent Pt deposition experiment was carried out. Figure 5-2 shows a linear sweep voltammogram of a polycrystalline Au electrode measured in a 0.1 M HClO₄ aqueous solution containing 0.05 mM H₂PtCl₆ scanned negatively from open circuit potential (OCP), ca. 800 mV, with a scan rate of 2 mV/s. The potential scan was stopped at 600, 500 and 450 mV, respectively, while the potential was maintained for 3500 s to deposit Pt.

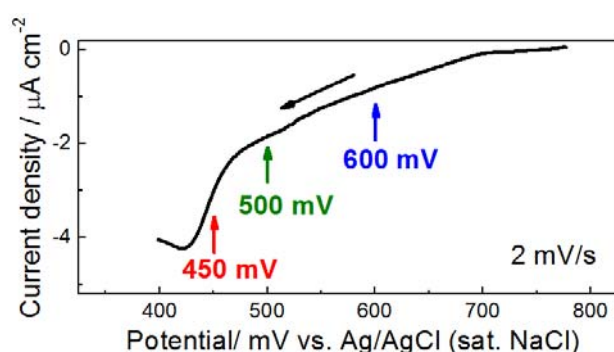


Figure 5-2. Linear sweep voltammogram of a polycrystalline Au electrode measured in 0.1 M HClO₄ containing 0.05 mM H₂PtCl₆ with a scan rate of 2 mV/s. Electrode potential scan was negatively started from OCP (ca. 800 mV). Arrows show the deposition potentials of 600 (blue), 500 (green) and 450 mV (red).

Figure 5-3 shows the time-current density relations during Pt deposition. When the potential scan was started, a cathodic current immediately flew. After the potential scan was stopped at (a) 600, (b) 500 and (c) 450 mV, the current gradually decreased and became almost constant at ca. -0.3 , -1.5 and $-2.5 \mu\text{A/cm}^{-2}$, respectively. Through integrating the area of each current-time curve in Figure 5-3, the total charge supplied during Pt deposition can be evaluated. The results are shown in Figure 5-5(d) for the following discussion.

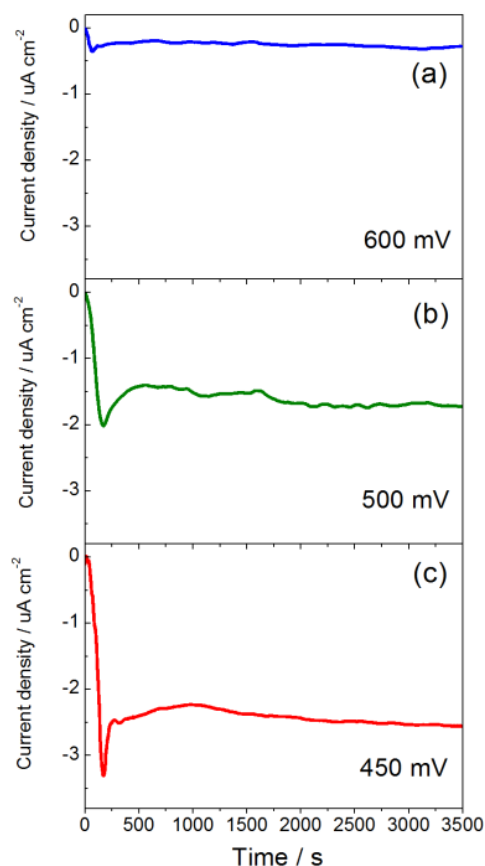


Figure 5-3. Time dependences of the current density when the Pt deposition was carried out at (a) 600, (b) 500 and (c) 450 mV.

After rinsing with concentrated H_2SO_4 and ultrapure water, the CVs of the Au electrodes after Pt was deposited at (a) 600, (b) 500 and (c) 450 mV for 3500 s were measured in 0.05 M H_2SO_4 , as presented in Figure 5-4.

Figure 5-4(a) reveals the CV of the Pt-modified Au electrode prepared at 600 mV. The broad and small peaks of Pt oxide formation/reduction occurring were found around 950 and 400 mV, respectively, and the weak hydrogen adsorption/desorption current more negative than 200 mV indicates the deposition of Pt. The Au oxide formation/reduction peaks (ca. 1300 and 900 mV) indicate that the Au surface had not been fully covered with Pt and still exposed to the solution even after 3500 s deposition time.

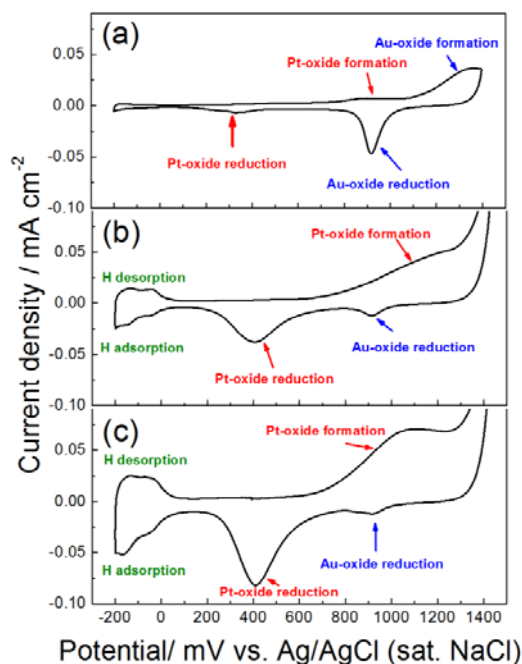


Figure 5-4. CVs of the Pt-deposited Au electrodes, which were prepared at (a) 600, (b) 500 and (c) 450 mV for a deposition period of 3500 s in 0.05 M H₂SO₄ with a scan rate of 20 mV/s.

Figure 5-4(b) shows the Pt-modified Au electrode prepared at 500 mV. In comparison to Figure 5-4(a), the Pt oxide formation/reduction and the hydrogen adsorption/desorption peaks increased, whilst at the same time the Au oxide reduction peak decreased, due to Pt deposition. However, the Au oxide reduction peak did not completely disappear, which suggests that a small fraction of Au surface was still exposed to the solution. The large anodic current observed at potentials more positive than 1350 mV is due to oxygen evolutions on Pt surface.

The result in Figure 5-4(c), which was obtained from the Pt-modified Au electrode prepared at 450 mV, was similar to that obtained from the Pt-modified Au electrode prepared at 500 mV (Figure 5-4(b)), although the peaks for Pt oxide formation/reduction and hydrogen adsorption/desorption continuously increased. The Au oxide reduction peak further decreased and became almost invisible, since the Au surface was fully covered with a Pt layer.

Figure 5-5 shows the charges for (a) Pt oxide reduction, (b) hydrogen adsorption

(c) Au oxide reduction, which were acquired from Figure 5-4 and (d) total charge flown during Pt deposition obtained from Figure 5-3, as a function of deposition potential.

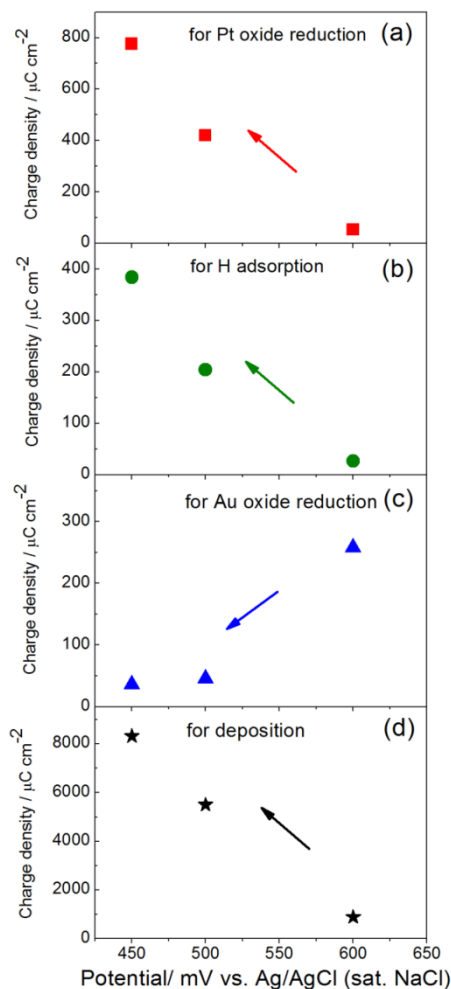


Figure 5-5. Deposition potential dependences of charge density for (a) Pt oxide reduction (red squares), (b) hydrogen adsorption (green circles), (c) Au oxide reduction (blue triangles), which were obtained from Figure 5-4 and (d) the total charge flown during Pt deposition obtained from Figure 5-3.

When Pt deposition was carried out at 600 mV (Figure 5-4(a)), small charges for Pt oxide reduction ($54 \mu\text{C/cm}^2$, Figure 5-5(a)) and the hydrogen adsorption ($27 \mu\text{C/cm}^2$, Figure 5-5(b)), which correspond to the amount of deposited Pt, were obtained, and the charge for Au oxide reduction, which corresponds to the amount of Au surface without Pt deposition, was ca. $260 \mu\text{C/cm}^2$, as shown in Figure 5-5(c),

suggesting a slower process of Pt deposition on the Au surface at 600 mV, where Pt stopped growing below the monolayer and left the Au surface uncovered by Pt.

When Pt deposition was performed at 500 mV (Figure 5-4(b)), charges for the Pt oxide reduction (Figure 5-5(a)) and hydrogen adsorption (Figure 5-5(b)) as well as the reduction of Au oxide (Figure 5-5(c)) increased and decreased, respectively. The charges for Pt oxide reduction, ca. 420 $\mu\text{C}/\text{cm}^2$ (Figure 5-5(a)), and hydrogen adsorption, ca. 204 $\mu\text{C}/\text{cm}^2$ (Figure 5-5(b)), are almost consistent with the charges expected for an epitaxial Pt monolayer on an Au surface of 222 and 444 $\mu\text{C}/\text{cm}^2$, respectively. Furthermore, the charge for the Au oxide reduction decreased to a very small value but did not become 0 (ca. 45 $\mu\text{C}/\text{cm}^2$, Figure 5-5(c)), indicating that ca. 10% of the Au surface remained uncovered by Pt even after 3500 s deposition time. All the information confirmed that the atomically flat Pt monolayer was epitaxially formed on the Au surface at 500 mV, although a small fraction of Au surface remained uncovered by Pt.

When Pt deposition was carried out at 450 mV (Figure 5-4(c)), charges for Pt oxide reduction (Figure 5-5(a)) and hydrogen adsorption (Figure 5-5(b)) continued to increase, exceeding the expected values for an atomically flat Pt monolayer, i.e., 222 $\mu\text{C}/\text{cm}^2$ for hydrogen adsorption and 444 $\mu\text{C}/\text{cm}^2$ for Pt oxide reduction. These indicate that too much Pt was deposited, and the Au surface was not covered by a Pt monolayer but multilayers with an increase in roughness. The charge for the reduction of Au oxide further decreased (ca. 36 $\mu\text{C}/\text{cm}^2$, Figure 5-5(c)) as the deposition potential was more negative but was still not 0, indicating that the Au surface was not fully covered by Pt. The possible reason is that, at relatively negative potential, Pt grew with a higher speed due to the big current density, easily forming rough Pt layers with defects.

Since Pt film was formed on Au by a four-electron reaction (Reaction 5-1),



the charge required to deposit a Pt monolayer on Au is $888 \mu\text{C}/\text{cm}^2$. Nevertheless, from Figure 5-5(d), it is worth noting that the total charge flown during deposition at each potential was always larger than that required to deposit a given Pt film, indicating that the current during deposition was not only due to the Reaction 5-1 but also due to other reduction reactions, such as ORR on Pt.

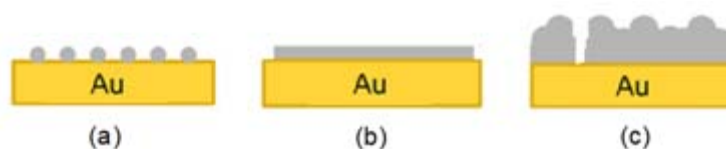


Figure 5-6. Schematically of deposition of Pt on Au surface with deposition potentials of (a) 600, (b) 500 and (c) 450 mV.

The results of Pt deposition at (a) 600, (b) 500 and (c) 450 mV are schematically summarized in Figure 5-6 based on the above discussions. Similar results were observed for the potential dependent growth mode observed by in situ STM for the electrochemical deposition of Ru on Au.¹⁴

5.2.1.3 Electrocatalytic Activity of Pt-modified Au surfaces

To help understand the electronic structure information of CO adsorbed on a Pt/Au electrode, the Pt thickness dependence on the electrocatalytic activities of Pt/Au electrodes toward CO oxidation was tested. In this experiment, 500 mV was chosen as the deposition potential since a Pt monolayer can be obtained with a mild deposition rate at this potential, as shown in Figure 5-4(b), and the different thicknesses of Pt were achieved by controlling the deposition time.

Figure 5-7 shows the CVs of the irreversibly adsorbed CO on Pt thin film-modified polycrystalline Au electrodes, which were prepared by supplying the deposition charges of (a) 380, (b) 1080 and (c) $3400 \mu\text{C}/\text{cm}^2$ in 0.5 M H_2SO_4 .

For the CV measurements, the potential was scanned between -150 and 1100 mV with a scan rate of 1 mV/s. Similar electrochemical behaviors can be observed on each electrode: in the first cycle (black line), no current due to hydrogen desorption was observed at the beginning of the positive going scan because of the surface

poisoning by the adsorbed CO, followed by a CO oxidation peak when the potential scanned more positively. Afterwards, the Pt oxidation/reduction peaks at ca. 800 and 450 mV as well as the hydrogen adsorption peaks at more negative potentials than 200 mV were observed in the CVs. In the second cycle (red line), no CO oxidation peak can be found and the hydrogen adsorption/desorption peaks appeared, indicating that CO was completely oxidized in the first cycle. The features of the negative going scan of the first cycle and the CV of the second cycle are close to the CV of the bare polycrystalline Pt electrode, as shown in Figure 4-1, suggesting that the Pt thin films formed on Au are polycrystalline. The current density was evaluated with respect to the real Au surface area.

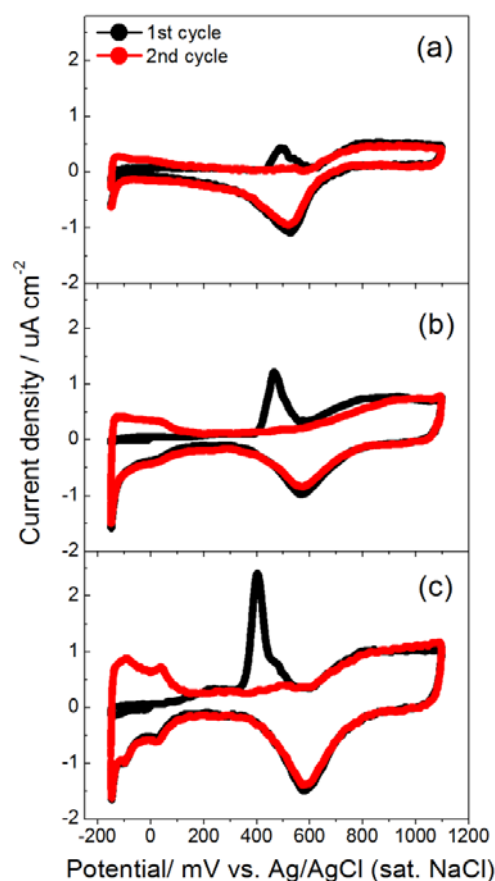


Figure 5-7. CVs of Pt thin film-modified polycrystalline Au electrodes, which were prepared by supplying the deposition charges of (a) 380, (b) 1080 and (c) 3400 $\mu\text{C}/\text{cm}^2$ in CO-free 0.5 M H_2SO_4 aqueous solution with preadsorbed CO between -150 and 1100 mV with a scan rate of 1 mV/s for the first (black line) and the second (red line) cycles.

The charge information for CO oxidation, hydrogen adsorption and Pt oxide reduction at each Pt-modified Au electrode was obtained by integrating the corresponding peaks in the CVs (Figure 5-7). The results are shown in Table 5-1. It was found that, in general, the CO oxidation charge and Pt oxide reduction charge as well as the hydrogen adsorption charge increase with increasing charge for Pt deposition.

Table 5-1. Charge information involved for Figure 5-7.

Deposition charge ($\mu\text{C}/\text{cm}^2$)	380	1080	3400
CO oxidation charge ($\mu\text{C}/\text{cm}^2$)	43	110	185
Pt oxides reduction charge ($\mu\text{C}/\text{cm}^2$)	90	162	240
hydrogen adsorption charge ($\mu\text{C}/\text{cm}^2$)	35	85	123
Pt thickness (ML)	0.15	0.38	0.55

The charges for hydrogen adsorption and Pt oxide reduction are direct indicators of the real Pt amount on Au. With them, how much Pt was deposited on Au surface can be evaluated. For 1 ML Pt on an Au surface, the expected charges for hydrogen adsorption and Pt oxide reduction are 222 and 444 $\mu\text{C}/\text{cm}^2$, respectively. Therefore, Pt oxide reduction charges of ca. 90, 162 and 240 $\mu\text{C}/\text{cm}^2$ and hydrogen adsorption charges of ca. 35, 85 and 123 $\mu\text{C}/\text{cm}^2$ indicate ca. 0.15, 0.38 and 0.55 ML Pt thickness, respectively.

The charges required to deposit 0.15, 0.38 and 0.55 ML Pt on Au are ca. 133, 337 and 488 $\mu\text{C}/\text{cm}^2$, respectively, which are much smaller than the supplied charge, again, showing that not all the supplied charge was involved in Reaction 5-1 during the deposition.

In order to reveal a clear Pt thickness dependent electrocatalytic activity for CO oxidation, the potential axis of Figure 5-7 was expanded to present only the segment of CO oxidation in Figure 5-8. The CO stripping voltammograms obtained on polycrystalline and single crystal Pt electrodes were also included for comparison. A broad ($\Delta E \approx 88$ mV) CO oxidation peak appeared at ca. 500 mV (black curve)

when the Au substrate was covered with 0.15 ML Pt. The oxidation current started to flow at ca. 440 mV, which is 100 and 20 mV more positive than that obtained on the bulk polycrystalline Pt (blue curve) and Pt(111) (pink curve) electrodes, respectively. On increasing the Pt thickness to 0.38 ML, the magnitude of the CO oxidation peak (red curve, $\Delta E \approx 76$ mV) increased and the potential at which current started to flow negatively shifted to ca. 400 mV. Upon further increasing the Pt thickness to 0.55 ML, the onset potential of CO oxidation (green curve) negatively shifted more and became as negative as that on a bulk Pt electrode (blue curve). Meanwhile, the peak gained intensity while the peak width ($\Delta E \approx 51$ mV) was much narrower than that of the former two.

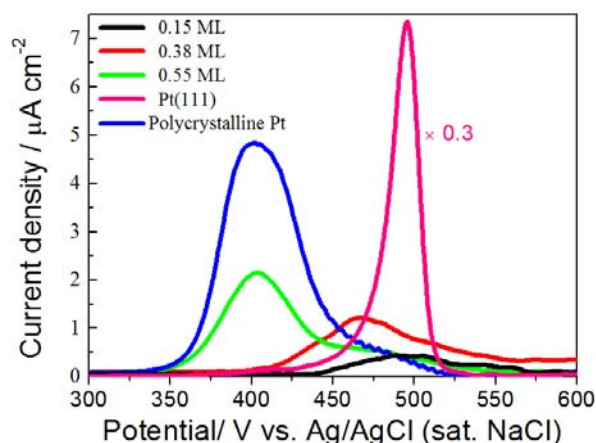


Figure 5-8. Selective CVs of CO stripping on Pt thin film-modified Au as a function of the film thickness and on bulk polycrystalline and single Pt electrodes in 0.5 M H_2SO_4 .

The film thickness dependent results in Figure 5-8 show that the adsorption properties and the reactivity of Pt thin films can be greatly influenced by the underlying Au substrate, as often observed for bimetallic surfaces,^{6,15} and this change can be related to the changes of the electronic structure at the interface, which are caused by the shift of the d-band center energy.^{16,17} Thus, it is attractive to probe the electronic structure of CO adsorbed on a Pt thin film-deposited Au surface by using potential dependent DR-SFG spectroscopy.

5.2.2 Visible Energy Dependent SFG Spectra of CO on Pt-modified Au Electrode

A series of SFG spectra of CO adsorbed on 0.15 ML Pt-modified polycrystalline Au electrode in CO-free Ar-saturated 0.5 M H₂SO₄ aqueous solution were recorded as a function of the electrode potential in a stepwise fashion and in 25 mV increments through the oxidation region by using visible light of 620, 605, 590, 575, 560, 550 and 540 nm. Typical SFG spectra are shown in Figure 5-9. A negative band at 2067–2085 cm⁻¹, which was based on a very strong and broad nonresonant SFG signal, was observed. The negative band is assigned to the C-O stretching of the CO adsorbed on the atop site of the Pt surface.^{18,19} The CO band presented at all potentials between -150 and 500 mV, and its frequency is generally higher than the frequency of the atop CO adsorbed on both the polycrystalline Pt electrode (2055–2073 cm⁻¹) and the Pt(111) electrode (2062–2075 cm⁻¹), as shown in the former two chapters. No band due to CO adsorbed on polycrystalline Au was observed in the spectra, which should be apparent at around 2100 cm⁻¹.²⁰

Compared to the SFG spectra obtained from CO/bulk Pt interfaces, the spectral shape of CO adsorbed on the Pt thin film-modified Au surface looks quite different. Instead of the positive bands observed on the bulk Pt surface, the negative bands were found in the SFG spectra of CO on Pt/Au. A similar phenomenon has already been shown by previous results and explained by the interference between resonant and nonresonant signals.^{21,22} Since the interband transition of Au lies in the visible range,²² as a consequence, there is a dominant contribution of the interband transition to the nonresonant Au signal. When the nonresonant Au signal interferes with the CO resonant signal, a destructive interference is formed and gives rise to a negative band. Therefore, the strong nonresonant SFG signal in the spectra mainly comes from Au.

Since the SFG spectrum is an admixture of the resonant CO vibrational transition and a broader nonresonant background from Au substrate, the SFG signal should be analyzed by fitting it to Eq. (1-27) with considering the effect of two contributions in order to extract the peak wavenumber, fwhm and amplitude of the resonant CO transition.

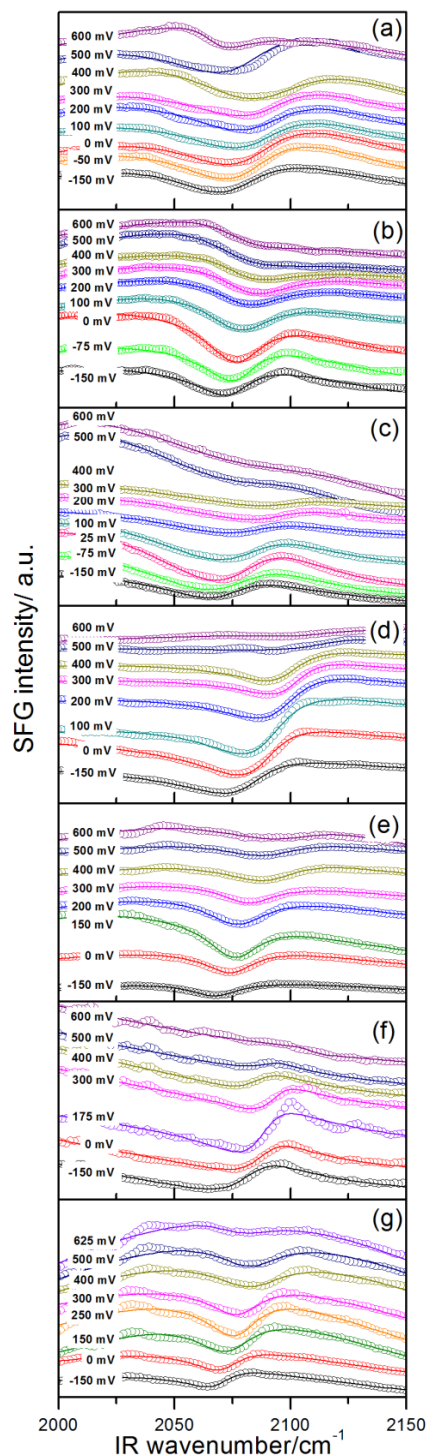


Figure 5-9. Typical potential dependent SFG spectra of the 0.15 ML Pt thin film-modified polycrystalline Au electrode with preadsorbed CO in the 0.5 M H₂SO₄ aqueous solution obtained by using visible light of (a) 620, (b) 605, (c) 590, (d) 575, (e) 560, (f) 550 and (g) 540 nm. Solid lines are the best fits according to Eq. (1-27).

Figure 5-10 shows the typical changes of peak wavenumber and fwhm of the CO

band as a function of potential by using 560 nm visible light as a respective. From Figure 5-10(a), it can be seen that the peak wavenumber for the C-O stretching band linearly shifted to a higher wavenumber with electrode potential up to 475 mV. The slope was determined to be $32 \text{ cm}^{-1}/\text{V}$ in the present study, as compared with the values in previous reports.^{23–25} A solid line with this slope was drawn in Figure 5-10(a). However, the slope was not constant when the potential scanned more positive than 475 mV, at which point the CO band began to shift to lower wavenumber as the oxidation reaction began. The downshift of the peak wavenumber accelerated above ca. 500 mV, which is consistent with its band intensity decrease in the same potential region shown in SFG spectra (Figure 5-9(b)) as CO was removed. Such a downshift of the C-O stretching frequency is typical for a CO stripping process accompanied by its coverage decrease, which gives rise to decreased dipole-dipole coupling in the CO adlayer.²⁶

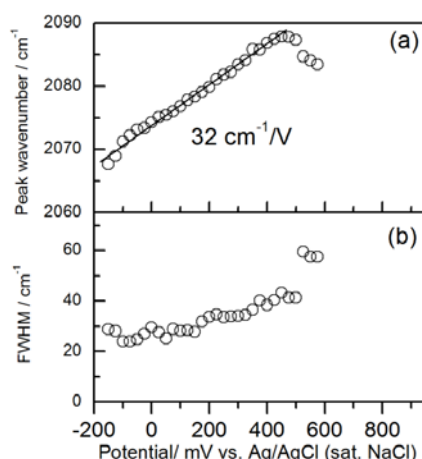


Figure 5-10. Potential dependencies of (a) peak wavenumber and (b) fwhm of the CO band derived from the fitting of the SFG spectra obtained by using visible light of 560 nm (Figure 5-9(b)).

The potential dependence of the fwhm of the CO band on the Pt thin film deposited Au shown in Figure 5-10(b) is qualitatively consistent with the results of the polycrystalline Pt surface in Chapter 4 but broader than the results of the Pt(111) in Chapter 3. The fwhm of the CO band increased slightly until CO oxidation began (at ca. 500 mV), then there is considerable broadening in the fwhm produced by CO

oxidation. For different visible light wavelengths, at a given potential, the frequency differences between them are within the resolution of SFG spectroscopy and, therefore the CO frequency should not be affected by visible energy, whereas the fwhms of the CO bands at various visible energies are distributed between 30 and 50 cm^{-1} depending on the different widths of visible light.

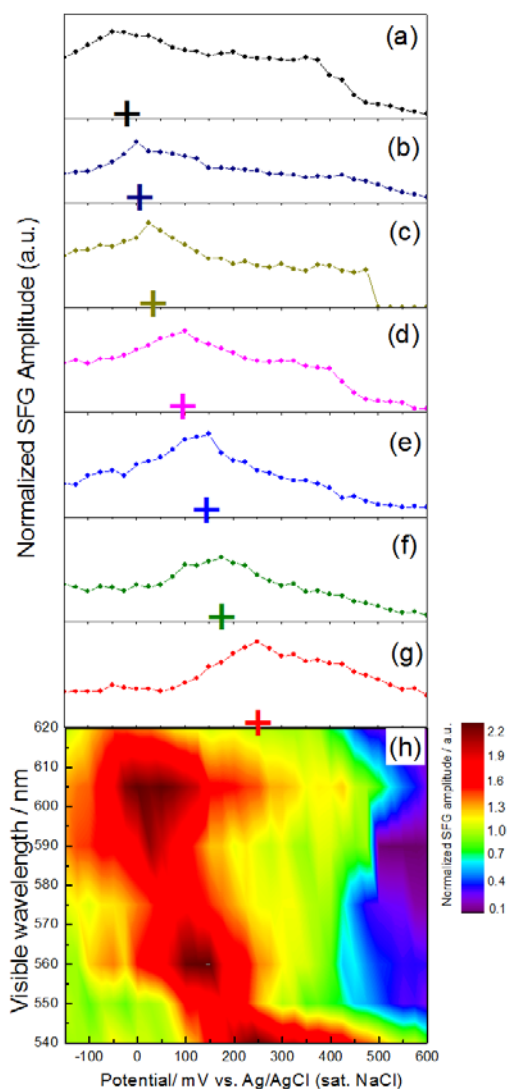


Figure 5-11. The normalized SFG amplitude as a function of potential obtained by using visible light of (a) 620 nm (2.0 eV), (b) 605 nm (2.05 eV), (c) 590 nm (2.10 eV), (d) 575 nm (2.15 eV), (e) 560 nm (2.21 eV), (f) 550 nm (2.25 eV) and (g) 540 nm (2.29 eV). The cross in each figure is used to mark the peak center and baseline. (h) A contour map of the SFG amplitude as functions of the potential and wavelength of visible light obtained by using these seven visible light.

Figure 5-11 shows the potential dependence of the normalized SFG amplitude for the SFG spectra obtained by using seven different visible light. Given that the absolute values of SFG amplitude obtained by using different visible light cannot be compared directly because of the differences in the intensities of visible and IR lasers, the additional normalization was carried out by making the amplitude before increase as 1. When visible light of 620, 605 and 590 nm were used (Figure 5-11(a-c)), the intensity started to increase from -150 mV and showed an increase when the potential moved toward -50, 0 and 25 mV, after which the intensity decreased and became almost constant at 175 mV; when the serious oxidation of CO began at around 500 mV, the SFG intensity dropped precipitously, indicating CO is removed, in good agreement with the CV given in Figure 5-7(a). When visible light of 575 and 560 nm were employed (Figure 5-11(d-e)), the amplitude remained constant up to ca. -100 mV, gradually increased and reached maximum at 100 and 150 mV, then decreased; as the potential approached a more positive value up to 500 mV, the amplitude was close to 0. When visible light of 550 and 540 nm were used (Figure 5-11(f-g)), the intensity was approximately constant up to 75 mV, then increased and reached maximum at 175 and 250 mV, respectively, then gradually decreased and disappeared at ca. 600 mV. It is obvious that the potential dependent SFG characteristics of the CO/Pt sub-monolayer-modified Au electrode strongly rely on the energy of visible light, as shown in the contour map (Figure 5-11(h)). When the wavelength of visible light became shorter, the SFG peak potential (observed in Figure 5-11) became more positive.

Figure 5-12 shows the visible and SF energy dependences of the SFG peak potential, which were obtained from the Gaussian function fitting. The fitting errors are also shown in this figure. In order to compare the present results with the those in preceding chapters, the relations between peak potential and the energy of visible and generated SF light for CO/polycrystalline Pt and CO/Pt(111) interfaces measured at constant potentials are also shown in this figure. It was found that the peak potential positively shifted with increasing the energy of visible/SF with a slope of ca. 1 V/eV in all systems. However, at a fixed visible/SF energy, the electronic resonance takes

place at a ca. 75 mV more negative potential on Pt-modified Au compared to the peak potentials for CO/polycrystalline Pt and CO/Pt(111). At the fixed potential, it shows that ca. 0.075 eV more visible energy is needed to generate an electronic resonance on Pt-modified Au than on bulk Pt.

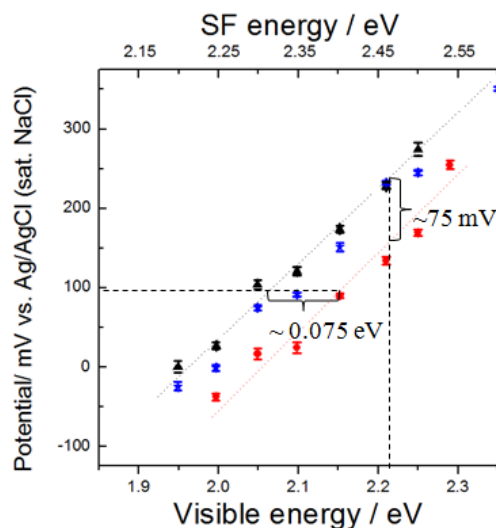


Figure 5-12. Input visible (bottom axis) and output SFG energy (top axis) dependences of the SFG peak potential for CO adsorbed on a Pt sub-monolayer deposited on Au (red circles), on polycrystalline Pt (black triangles) and on Pt(111) electrodes (blue stars).

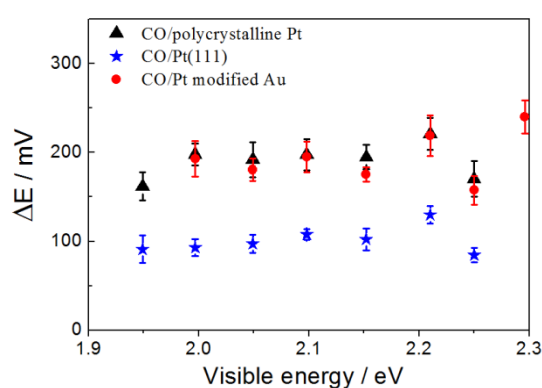


Figure 5-13. The width of the SFG peak obtained in constant potential measurements of CO adsorbed on 0.15 ML Pt thin film-modified Au (red circles), Pt(111) (blue stars) and polycrystalline Pt (black triangles) as a function of visible energy.

Besides the peak potentials, the widths of the SFG peaks observed in Figure 5-11 were also compared with the results of both CO/polycrystalline Pt and CO/Pt(111). The width of the SFG peak for the CO/Pt-modified polycrystalline Au electrode at each visible energy was extracted from the fits to the Gaussian function and plotted in Figure 5-13. It was found that the widths of the peaks obtained from CO/Pt-modified Au were qualitatively consistent with the results of CO/polycrystalline Pt surface, but generally broader than those from CO/Pt single crystal, reflecting the polycrystalline nature of the Pt thin film formed on the Au polycrystalline substrate.

5.2.3 In Comparison to Polycrystalline Pt and Pt(111) Substrates

An SFG intensity increase was observed on CO/Pt-modified Au at different visible energies and the SFG peak potential shifted with the visible light energy by ca. 1 V/eV, showing that the origin of the increase of SFG intensity is not due to the potential dependent geometric structure change of adsorbed CO as suggested before,²⁷ but rather is due to the resonance of visible and/or SF light with the electronic transition from the Fermi level of the Pt sub-monolayer, which is varied linearly with applied potential, to the $5\sigma_a$ antibonding state of CO, as already found at CO/Pt(111) (Chapter 3) and CO/polycrystalline Pt (Chapter 4) interfaces.

When the potential is fixed, more visible energy is needed to generate an electronic resonance, i.e., energy coupling between visible light and the electronic transition from the Fermi level of Pt to the $5\sigma_a$ antibonding state, at the CO/Pt thin film-modified Au than at the CO/bulk Pt, as shown in Figure 5-12, suggesting the energy level of the $5\sigma_a$ antibonding state is higher than that at the CO/bulk Pt, which is schematically drawn in Figure 5-14(a). When the energy of visible light is fixed, the electronic resonance at the CO/Pt thin film-modified Au takes place at more negative potential, where the Fermi level is lifted up, than the CO/bulk Pt, also indicating an upward shift of the $5\sigma_a$ state of CO on the Pt thin film-modified Au electrode, as shown in Figure 5-14(b).

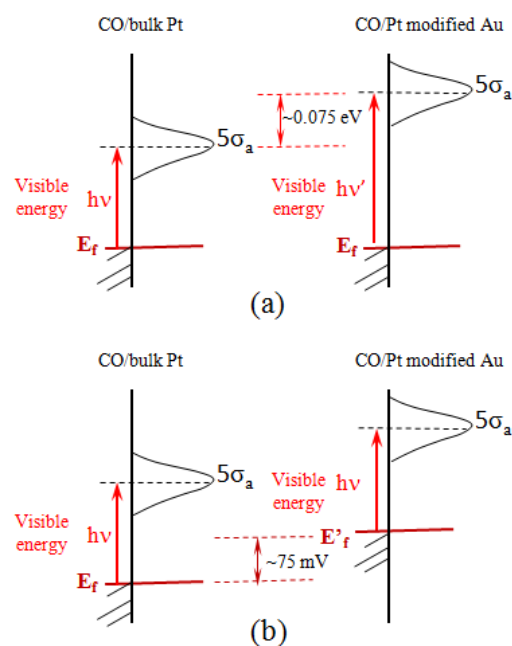


Figure 5-14. Schematic models for resonance of visible light with the electronic transition between the Fermi level (E_f) and the $5\sigma_a$ antibonding state of CO adsorbed on bulk Pt and on the Pt thin film-modified Au (a) at a given potential and (b) at a given visible energy, showing the energy of $5\sigma_a$ antibonding state of CO adsorbed on Pt thin film-modified Au surface is higher than that on bulk Pt electrodes.

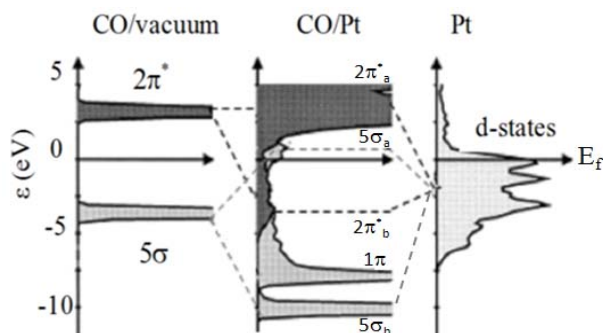


Figure 5-15. The electronic structures of the 5σ and $2\pi^*$ states of CO in vacuum and on a Pt surface.¹⁷

An upward shift of the $5\sigma_a$ antibonding state of CO is considered to be due to an upward shift of the d-band relative to the Fermi level since the $5\sigma_a$ antibonding state is related to the d-band of the Pt surface.¹⁷ Figure 5-15 shows that when CO is adsorbed on the Pt surface, the sharp states of CO in vacuum are seen to broaden and

shift down in energy, whilst at the same time the electronic states of CO hybridize with the d-band of the Pt surface, giving rise to a 5σ -d antibonding state, $5\sigma_a$, at the top of the d-bands and a $2\pi^*$ -d bonding state, $2\pi_b^*$, at the bottom.

A UPS study has shown the upward shift of the d-band center with the sub-monolayer deposition of Pd on the Au surface.²⁸ Very recently, according to theoretical calculations for a Pt monolayer on an Au(111) substrate by Taketsugu's group, Pt monolayer deposition on Au results in a shift of the d-band center toward the Fermi level, as shown in Figure 5-16.²⁹

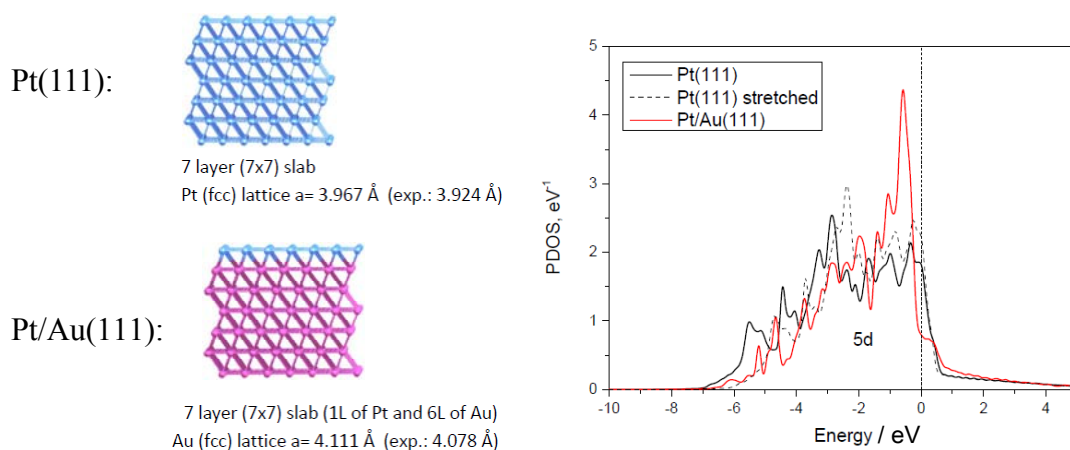
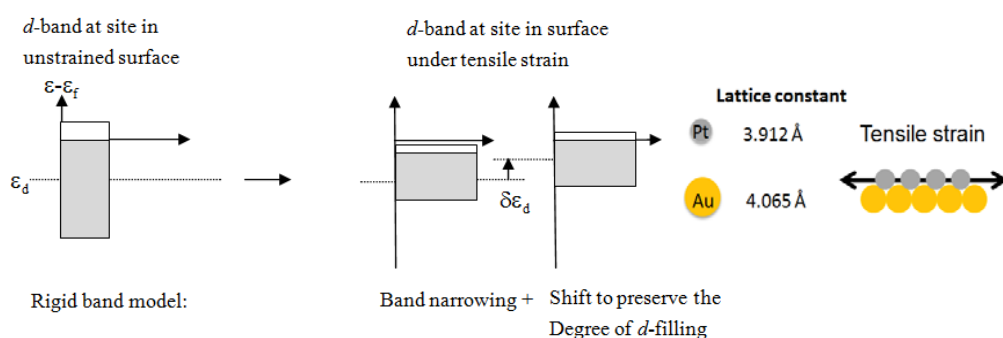


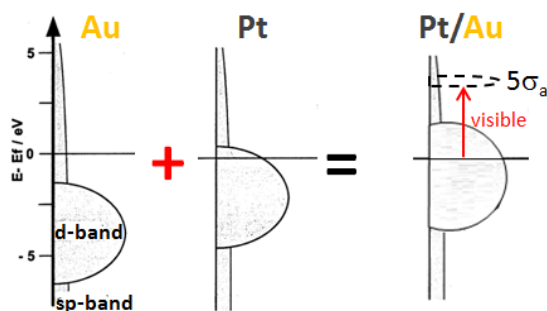
Figure 5-16. The projected density of states (PDOS) calculated for Pt(111) and Pt monolayer deposited on Au(111), showing the d-band position modulated by the Au substrate.²⁹ The Fermi level is 0 eV.

For the d-band shifting, there are generally two possible explanations proposed in previous reports. The first possibility to the d-band shifting is attributed to the tensile strain effect on the Pt thin film.^{17,30} When the Pt monolayer is deposited on the bulk Au electrodes since the lattice constant of Pt is smaller than that of Au,³¹ there is a significant tensile strain on the Pt film, in which the d-band width of the Pt film shrinks and becomes narrower than that of the bulk Pt, and in order to maintain the overall d-band filling, the d-band center has to move up in energy, as shown in Figure 5-17(a).

The other proposed possibility for the upward shift of d-band is the electronic structure coupling between Au and Pt, as illustrated in Figure 5-17(b).³² Due to the electronic interaction between Au and Pt thin film, some new electronic structures might be formed at the interface resulting in a shift of the d-band center toward the Fermi level. The origin for the d-band shifting is still speculative, whether it arises as a result of either tensile strain effect or electronic structure coupling between two metals. However, in either case, the change in the surface electronic structure with the d-band shift can explain the increase in the energy level of the $5\sigma_a$ antibonding state of CO with the decreased Pt thickness on the Au electrode.



(a) Tensile strain effect



(b) Electronic structure coupling between Au and Pt

Figure 5-17. Illustration of (a) tensile strain effect¹⁷ and (b) electronic structure coupling effect³² on the d-band center.

This d-band shifting can also explain the more positive onset potential of CO oxidation on the Pt sub-monolayer deposited on Au (ca. 440 mV) than that on polycrystalline Pt (ca. 340 mV) and Pt(111) (ca. 420 mV), shown by both CVs (Figure 5-8) and SFG spectral results (Figure 5-9), and the higher wavenumber of the

atop CO band on Pt/Au (2067–2085 cm^{-1}) than that on both the polycrystalline Pt (2055–2073 cm^{-1}) and Pt(111) electrodes (2062–2075 cm^{-1}). As the Pt film becomes thinner, the d-band shifts up in energy, moves toward the Fermi level and becomes less diffused, which repels back-donation of the metal electrons into the CO $2\pi^*$ antibonding state. As a consequence the length of the C-O bond is shortened and the strength of the C-O bond increases,^{33,34} thus increasing the activation energy for CO oxidation.³⁵ That is why the CO stripping peak shifts to a more positive potential and the C-O frequency shifts to a higher wavenumber compared to the case of CO on polycrystalline Pt. The stronger CO adsorption also introduces broadness to the CO stripping peak on the Pt monolayer and sub-monolayer (Figure 5-8). The broad width of the CO stripping peak can be attributed to the low mobility of the reactants, as demonstrated by the Monte Carlo simulations.^{36–38} Of course, more experimental proof is needed to support the present discussion. A Pt film thickness dependent electronic structure study of CO-Pt/Au electrochemical interface will be carried out in the future.

Moreover, since the Pt thin film was deposited on a polycrystalline Au electrode, the surface structure of the Pt thin film are polycrystalline, as proved by CVs (Figure 5-4 and Figure 5-7) in the hydrogen UPD region, the widths of the SFG peaks in Figure 5-11 and fwhm of CO band (Figure 5-10) obtained at the CO/Pt-modified Au interface are comparable to those from the CO/polycrystalline Pt surface, as shown in Chapter 3, but broader than those from CO/Pt single crystal, as revealed in Figure 5-13, in agreement with the results of Chapter 4, confirming that the energy distribution of the $5\sigma_a$ antibonding state of CO on the polycrystalline surface is broader than that on Pt single crystals.

5.3 Conclusions

In this chapter, potential dependent DR-SFG spectroscopy was successfully applied to the interfacial electronic structure study of CO adsorbed on a Pt sub-monolayer deposited on a polycrystalline Au electrode surface, which was prepared by electrochemical deposition method in acid solution. As on polycrystalline

Pt and Pt(111) surfaces, the SFG intensity increased prior to CO oxidation and the SFG peak potential linearly shifted with the visible and/or SF light energy. At a given visible light energy, the potentials of the SFG peak were more negative on Pt sub-monolayer-modified Au electrode than those on Pt(111) and polycrystalline Pt electrodes. In addition, at a given potential, to generate the electronic resonance on the CO/Pt sub-monolayer-modified Au surface needed more visible energy than on the other two bulk Pt electrodes, suggesting the energy of the $5\sigma_a$ antibonding state of CO adsorbed on the Pt sub-monolayer-modified Au electrode is higher than that on bulk Pt electrodes. This shift seems to be caused by the modulation of the d-band position by the Au substrate, as suggested by a theoretical calculation. The width of the anomalous SFG peak at the CO/Pt-modified Au were comparable with those at CO/polycrystalline Pt, but broader than those at CO/Pt(111), confirming that the energy distribution of the $5\sigma_a$ antibonding state of CO on the polycrystalline surface is broader than that on Pt single crystals, reflecting the polycrystalline nature of the Pt thin film formed on the Au polycrystalline substrate.

References

- (1) Naohara, H.; Ye, S.; Uosaki, K. *J. Electroanal. Chem.* **2001**, *500*, 435–445.
- (2) Zhang, J.; Mo, Y.; Vukmirovic, M. B.; Klie, R.; Sasaki, K.; Adzic, R. R. *J. Phys. Chem. B* **2004**, *108*, 10955–10964.
- (3) Zhang, J.; Vukmirovic, M. B.; Sasaki, K.; Nilekar, A. U.; Mavrikakis, M.; Adzic, R. R. *J. Am. Chem. Soc.* **2005**, *127*, 12480–12481.
- (4) Kumar, S.; Zou, S. *Langmuir* **2007**, *23*, 7365–7371.
- (5) Lin, W. F.; Zei, M. S.; Eiswirth, M.; Ertl, G.; Iwasita, T.; Vielstich, W. *J. Phys. Chem. B* **1999**, *103*, 6968–6977.
- (6) Uosaki, K.; Ye, S.; Naohara, H.; Oda, Y.; Haba, T.; Kondo, T. *J. Phys. Chem. B* **1997**, *101*, 7566–7572.
- (7) Kondo, T.; Shibata, M.; Hayashi, N.; Fukumitsu, H.; Masuda, T.; Takakusagi, S.; Uosaki, K. *Electrochimica Acta* **2010**, *55*, 8302–8306.
- (8) Argile, C.; Rhead, G. E. *Surf. Sci. Rep.* **1989**, *10*, 277–356.
- (9) Brune, H. *Surf. Sci. Rep.* **1998**, *31*, 125–229.
- (10) Bharathi, S.; Yegnaraman, V.; Rao, G. P. *Langmuir* **1993**, *9*, 1614–1617.
- (11) Angerstein-Kozłowska, H.; Conway, B. E.; Hamelin, A.; Stoicoviciu, L. *Electrochimica Acta* **1986**, *31*, 1051–1061.
- (12) Ron, H.; Rubinstein, I. *Langmuir* **1994**, *10*, 4566–4573.
- (13) Tkac, J.; Davis, J. J. *J. Electroanal. Chem.* **2008**, *621*, 117–120.
- (14) Strbac, S.; Maroun, F.; Magnussen, O. M.; Behm, R. J. *J. Electroanal. Chem.* **2001**, *500*, 479–490.
- (15) Rodriguez, J. *Surf. Sci. Rep.* **1996**, *24*, 223–287.
- (16) Hammer, B.; Morikawa, Y.; Nørskov, J. K. *Phys. Rev. Lett.* **1996**, *76*, 2141–2144.
- (17) Hammer, B.; Nørskov, J. K. *Advances in Catalysis*, **2000**, *45*, 71–129.
- (18) Kitamura, F.; Takahashi, M.; Ito, M. *Chem. Phys. Lett.* **1986**, *123*, 273–276.
- (19) Kitamura, F.; Takeda, M.; Takahashi, M.; Ito, M. *Chem. Phys. Lett.* **1987**, *142*, 318–322.
- (20) Zaera, F. *Chem Soc Rev* **2014**, *43*, 7624–7663.
- (21) Noguchi, H.; Ito, M.; Uosaki, K. *Chem. Lett.* **2005**, *34*, 950–951.
- (22) Wieckowski, A. *Interfacial Electrochemistry: Theory: Experiment, and Applications*; Marcel Dekker: New York, N.Y., 1999.
- (23) Kunimatsu, K.; Seki, H.; Golden, W. G.; Gordon, J. G.; Philpott, M. R. *Langmuir* **1986**, *2*, 464–468.
- (24) Furuya, N.; Motto, S.; Kunimatsu, K. *J. Electroanal. Chem. Interfacial Electrochem.* **1988**, *239*, 347–360.
- (25) Kunimatsu, K.; Sato, T.; Uchida, H.; Watanabe, M. *Electrochimica Acta* **2008**, *53*, 6104–6110.
- (26) Leung, L. W. H.; Wieckowski, A.; Weaver, M. J. *J. Phys. Chem.* **1988**, *92*, 6985–6990.
- (27) Lagutchev, A.; Lu, G. Q.; Takeshita, T.; Dlott, D. D.; Wieckowski, A. *J. Chem. Phys.* **2006**, *125*, 154705.

- (28) Sellid, A.; Koel, B. E. *Phys. Rev. B* **1994**, *49*, 8367–8376.
- (29) Lyalin, A.; Taketsugu, T. unpublished, **2016**.
- (30) Du, B.; Tong, A. *J. Phys. Chem. B* **2005**, *109*, 17775–17780.
- (31) Kittel, C. *Introduction to Solid State Physics*, 8th ed.; John Wiley & Sons: Hoboken, N.J., 2005.
- (32) Awatani, T.; Yagi, I.; Noguchi, H.; Uosaki, K. *J. Electroanal. Chem.* **2002**, *524-525*, 184–193.
- (33) Blyholder, G. *J. Phys. Chem.* **1964**, *68*, 2772–2777.
- (34) Sung, S. S.; Hoffmann, R. *J. Am. Chem. Soc.* **1985**, *107* (3), 578–584.
- (35) Meier, D. C.; Bukhtiyarov, V.; Goodman, D. W. *J. Phys. Chem. B* **2003**, *107*, 12668–12671.
- (36) Koper, M. T. M.; Jansen, A. P. J.; Santen, R. A. van; Lekkien, J. J.; Hilbers, P. a. *J. J. Chem. Phys.* **1998**, *109*, 6051–6062.
- (37) Saravanan, C.; Markovic, N. M.; Head-Gordon, M.; Ross, P. N. *J. Chem. Phys.* **2001**, *114*, 6404–6412.
- (38) Korzeniewski, C.; Kardash, D. *J. Phys. Chem. B* **2001**, *105*, 8663–8671.

Chapter 6

General Conclusion and Future Prospects

In the present thesis, potential dependent DR-SFG spectroscopy was employed to obtain the information of the electronic structures of CO adsorbed on various electrode surfaces, i.e., Pt(111) single crystal, polycrystalline Pt electrode and Pt-modified Au substrate, in electrochemical environment.

In Chapter 3, the electronic structure of a CO/Pt(111) interface was investigated by using potential dependent DR-SFG spectroscopy in 0.5 M H₂SO₄ aqueous solution. The SFG bands, which correspond to the C-O stretching of CO adsorbed on the atop site of the Pt(111), were observed both at constant potential and during potential scan using eight different visible light energies. The SFG intensity increased anomalously prior to CO oxidation and the anomalous SFG resonance peak potential shifted negatively when the visible light energy decreased linearly by 1 V/eV, indicating that the origin of the anomalous increase of the SFG intensity is due to the resonance of visible and/or SF light with the electronic transition from the Fermi level of Pt(111) to the 5 σ_a antibonding state of adsorbed CO.

In Chapter 4, potential dependent DR-SFG technique was employed to determine the electronic structure of a CO/polycrystalline Pt interface in CO-free acid solution. As on the Pt(111) surface, an increase of SFG intensity was found prior to CO oxidation. At a given visible energy, the SFG resonance peak on the polycrystalline Pt was observed at little more positive potential than those on the Pt(111), showing that the energy of the 5 σ_a antibonding state of CO on the polycrystalline Pt electrode is little lower than that on the Pt(111). The widths of the SFG resonance peaks on the polycrystalline Pt electrode with potential are broader than those on the Pt(111) electrode, showing the broader distribution of the 5 σ_a antibonding state of CO adsorbed on the polycrystalline Pt than that on the Pt(111) because of the presence of many kinds of atop sites on the polycrystalline surface.

In Chapter 5, the interfacial electronic structure of CO adsorbed on a Pt sub-monolayer deposited on polycrystalline Au electrode surface, which was prepared by an electrochemical deposition method, was investigated by the potential dependent DR-SFG spectroscopy. As on the Pt(111) and polycrystalline Pt electrodes, the SFG intensity increased prior to CO oxidation. At a given visible light energy, the potentials of the SFG resonance peaks on the Pt sub-monolayer-modified Au electrode are more negative than those on the Pt(111) and polycrystalline Pt electrodes, suggesting that the energy of the $5\sigma_a$ antibonding state of CO adsorbed on the Pt sub-monolayer-modified Au electrode is higher than that on the bulk Pt electrodes. This shift seems to be caused by the modulation of the d-band position by the Au substrate as suggested by a theoretical calculation. The widths of the SFG peaks on the Pt-modified Au are comparable to those on the polycrystalline Pt, but broader than those on the Pt(111), reflecting that the polycrystalline nature of the Pt thin film formed on the Au polycrystalline substrate.

In this thesis, potential dependent DR-SFG spectroscopy has been proved to be a strong tool for characterizing the microscopic interfacial electronic structure in electrochemical environments by using CO adsorbed on an electrode/electrolyte interface as a model system. The preliminary studies were performed on several different electrodes, i.e., Pt(111), polycrystalline Pt and Pt-modified Au electrodes, in CO-free acid solution.

In future, the effects of pH value of electrolyte solution, saturated CO solution, methanol solution, orientation of the single crystal face and thickness of the metal ultrathin layer on the electronic structure of CO will be systematically investigated not only at the Pt surfaces but also at the other substrates, such as Pd and its alloy in order to gain better understanding of the electronic structure of CO in electrochemical environments and develop new electrocatalysts to improve the efficiency of the electrochemical energy conversion processes. A theoretical calculation on the electronic structure of CO adsorbed at electrochemical interfaces will also be launched to confirm the present experimental results. After all, the potential dependent DR-SFG spectroscopy will be extended to the electronic property studies

of other interfaces involved in electrochemical reactions, such as ORR and HER, which could bring us better understanding of the electrochemical reactions for fuel cell application.