

Extending Surface Raman Spectroscopy to Transition Metal Surfaces for Practical Applications. 1. Vibrational Properties of Thiocyanate and Carbon Monoxide Adsorbed on Electrochemically Activated Platinum Surfaces

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By using confocal microprobe Raman spectroscopy and a unique electrochemical pretreatment procedure for the Pt surface, we are able to extend the detailed surface Raman studies, for the first time, to bare Pt electrodes in a wide potential region (e.g. -1.0 to $+1.4$ V vs SCE) and to more general adsorbates such as SCN^- and CO having small Raman scattering cross sections. Taking advantage of being capable of observing the adsorbate–metal vibrational bands in the low-frequency region over IR and SFG techniques, the surface Raman spectroscopy has demonstrated the virtues of yielding detailed information on the surface bonding affected by surface coverage, coadsorbate, electrolyte ions, and electrode potential. The potential-dependent Raman spectra of SCN^- reveal that the N-bound adsorbate is favored at the more negative potentials. The orientation conversion to the S-bound species occurs in the more positive region, depending on the SCN^- concentration. In a solution of 10^{-5} M NaSCN and 0.1 M NaClO_4 , a new C–N stretching band at ca. 2010 cm^{-1} was assigned to the bridge-bound SCN^- due to the low surface coverage. A preliminary study on CO irreversibly adsorbed on Pt, from -1.4 to 0.2 V in 0.1 M NaOH, infers that the interactions of CO with adjacent coadsorbed oxygen-containing species and with the surface are even more complex. At -0.8 V, the hydroxyl species starts to coadsorb with CO to the surface, then is partially oxidized at more positive potentials, and finally forms the oxidized sites at potentials positive of 0.0 V. In comparison with the roughened Ag, Cu, and Au electrodes, the dispersed Pt surface by electrochemical activation has shown better stability and reproducibility for the Raman measurements. This further provides a good reason to be optimistic that surface Raman spectroscopy will contribute on an increasingly broad frontier to the development of a true molecular-level probe of interfaces, particularly for practical applications. Finally, it is worth emphasizing that the present results could promote new efforts to sort out the surface selection rule and SERS mechanism(s).

Introduction

In the past two decades, in situ surface vibrational spectroscopies, including infrared (IR), Raman, and sum frequency generation (SFG) techniques have been applied more and more extensively at metal–solution as well as other types of interfaces in order to identify adsorbed species and provide insight into the nature of interactions of adsorbates with substrate and coadsorbates.^{1,2} So far, however, most studies have been focused on vibrational frequency shifts of adsorbate internal modes rather than the adsorbate–metal surface modes. This is mainly due to the difficulty in obtaining sufficient sensitivity for IR in the low-frequency region such as below 700 cm^{-1} , where metal–adsorbate vibrations are located.^{2,3a,b} It is even more difficult for SFG in detecting such low-frequency modes as it requires a tunable IR laser working in this specific frequency region.^{3c} Nevertheless, Raman spectroscopy can more readily detect such modes, even for surface–adsorbate bonds with frequencies below 300 cm^{-1} such as those involving heavy metal atoms. However, the application of Raman spectroscopy to metal–solution interfaces has been hampered because of the poor sensitivity inherent in the Raman scattering phenomenon. In the absence of any resonance Raman or surface-enhanced Raman effects, the differential Raman cross sections are only about or below $10^{-29}\text{ cm}^2\text{ sr}^{-1}$.⁴ The corresponding surface Raman intensities expected for a monolayer of adsorbates are less than 1 count per second (cps) when using conventional Raman spectrometer systems.⁵ As coinage

metals such as Ag, Au and Cu have been reported to exhibit large surface enhancements, i.e. the rough metal surface morphology can produce surface enhancements of up to a factor of 10^6 , surface-enhanced Raman scattering (SERS) has been widely used to investigate various interfaces of these metals in the past two decades.^{5,6,7a} Of particular interest in further developing surface Raman spectroscopy for the study of surface phenomena is the extension to the study of transition metal surfaces used as electrocatalysis in many technologically important processes. Therefore, great efforts have been made by many groups including our laboratory in order to extend surface Raman spectroscopic study to other metals and conducting polymers.^{7b–15} Successful approaches involve coating onto SERS active Ag or Au electrodes with ultrathin films of metals such as Ni, Co, Zn, Fe, Pb, Ti,^{7b–8a} Pt, Pd, Rh, and Hg^{8b–9} by electrochemical deposition, with a stainless steel film by laser ablation method,⁹ or with a polypyrrole film by electropolymerization.¹⁰ This unique method gives a way to extend Raman spectroscopy to the study of various metal and nonmetal surfaces other than Ag, Cu, and Au. This approach has yielded much valuable information about various interfaces.^{7b–10} However, the ultrathin film with only one to five monolayers in general has to be used in order to gain the relatively strong SERS effect by the electromagnetic (EM) enhancement created from the SERS active substrate underneath.^{7b–10} As a consequence, some residual substrate sites are usually exposed, which is discerned by the cyclic voltammograms. So it is extremely difficult, at least in some cases, to eliminate entirely the possibility that the adsorbate is bound to the exposed substrate

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or to the boundary of the two metals rather than to the overlayer sites. Furthermore, metal-chloride complexes are frequently used because they are favorable or indispensable for the electrodeposition of many transition metals; consequently, the residual chloride is retained at the metal surface in the subsequent SERS measurements. This specifically adsorbed species could affect more or less the adsorbate-surface interaction of interest, and in some cases, it may lead to the misinterpretation of results. The most essential, and also the most difficult, approach would be to obtain surface Raman spectra directly from the bare metal surface without the complexity of the sandwiched configuration (adsorbate/transition metal/SERS active metal). This important goal has attracted many groups since the early stage of surface Raman spectroscopy in 1977 when Cooney et al. observed the C—O stretching band of very low intensity from the system of CO adsorbed on a platinized Pt electrode.¹¹ After more than 10 years, Bilmes et al. reported a very interesting approach to obtain weak SERS signals of pyridine at electrodispersed Pt electrodes by using a unique roughening procedure to get a higher surface area.¹² Furthermore, with recent advances of Raman instrumentation, three groups attempted to make a more straightforward way to observe normal or resonance Raman signals from organic molecular layers on mechanically polished Pt electrodes.^{13–15} Pettinger et al. reported surface resonance Raman spectra for crystal violet^{13a} and normal Raman spectra of perchlorate ions at smooth Pt electrodes.^{13b} Fleischmann et al. reported a FT-Raman spectrum for surface pyridine at smooth Pt electrodes in 0.1 M KCl.¹⁴ Bryant et al. have performed measurements with a Raman triple monochromator with a CCD detector of very high sensitivity and acquired good quality surface Raman spectra of monolayer films of thiophenol and 4-mercaptopyridine.¹⁵ Unfortunately, in all of those works on bare Pt electrodes,^{11–15} the surface spectrum had to be obtained under optimized conditions or by the difference spectrum method due to the insufficiency of signal intensity. Indeed, the signals were too weak to be investigated as a function of electrode potential. As a consequence, there have been no continuous reports on bare Pt electrodes in the past 4 years, indicating the extreme difficulty for the practical application.

Fortunately, the problem of the low sensitivity of Raman spectroscopy has been solved at least partially by the latest advances in Raman instrumentation with the advent of the CCD cameras having essentially photon-noise-limited signal detection, the confocal microscope, and the holographic notch filter.¹⁶ The Raman experiment, which has historically used high-dispersion double or triple monochromators to filter out the elastically scattered laser radiation, can now be performed simply with a single spectrograph together with a holographic notch filter. This approach to Raman spectroscopy provides considerable benefits. The throughput efficiency of a single-grating system is far higher than, for example, a triple monochromator. This is certainly a great help for detecting a relatively weak surface Raman signal, e.g. from Pt electrodes, below the limit accessible with conventional instrumentation. Taking this advantage together with that of a confocal Raman microprobe¹⁷ and especially a unique ORC procedure to get an electrochemically activated Pt electrode surface,¹² we are able to extend, for the first time, the detailed surface Raman studies to bare Pt electrodes in a wide potential region (e.g. -1.0 to $+1.4$ V vs SCE) and to more general adsorbates such as SCN[−] and CO having smaller Raman scattering cross sections.

The main reason we chose SCN[−] as the first try in the present work is its particular specioelectrochemical interest as a specific adsorbate on Pt, which is advantageous for investigating the

dynamics of the electrical double layers because of their simple molecular and electronic structures. It also allows clear assignments of measured spectroscopic bands to molecular vibrations. Shifts of these bands caused by adsorption and their potential dependence can be detected and allow statements to be made about the nature of the adsorption mode and about the surface-adsorbate interaction. Although specifically adsorbed SCN[−] on Au, Ag, and Pt surfaces has been studied by IR¹⁸ and SFG¹⁹ extensively and many SERS investigations have been reported on Ag and Au but not Pt,²⁰ there is to date no consensus on the potential-dependent orientational behavior of this species on the electrode surface. Both S- and N-bound thiocyanate exhibit a C—N stretching vibration in the range 2050–2165 cm^{−1};^{18–20} therefore, use of the position of this band alone as a criterion of bonding could be somewhat risky. The clear analysis of the IR spectra is not an easy task at all because the spectra are obtained as a difference between two applied potentials. It is highly desirable to obtain the corresponding information of the surface-adsorbate interaction using surface Raman spectroscopy. In this article, it is shown that the surface spectra of reasonably good quality, in a wide frequency region down to 200 cm^{−1}, for SCN[−] at Pt electrodes can be obtained as a function of potential and electrolyte concentration.

In the final part of this paper, we will demonstrate that the surface Raman studies can even be extended to more practical applications. We will present a preliminary but even more interesting result, particularly from the view of electrocatalysis, about CO coadsorbed with oxygen containing species at a roughened Pt electrode in 0.1 M NaOH. The Pt—CO and Pt—OH/Pt—O vibration modes in the low-frequency region which change with the potential are observed and discussed along with the potential dependent C—O stretching bands in a wide potential range from -1.4 to 0.2 V.

Experimental Section

Raman spectra were obtained using a confocal microprobe Raman system (LabRam I from Dilor, France).²¹ The microscope attachment is based on an Olympus BX40 system and uses a 50× long working-length objective (8 mm) so that the objective will not be immersed in the electrolyte. A holographic notch filter was equipped to filter the exciting line, and two selective holographic gratings (1800 g/mm and 300 g/mm) were employed for different purposes of work. An air-cooled 1024 × 256 pixels CCD (Wright, England) operating in the MPP mode at -60 °C was used as the detector. The exciting wavelength was 632.8 nm from an air-cooled He—Ne laser with a power of 16 mW and a spot of ca. 3 μm on the surface. The slit and pinhole in experiment were 100 and 400 μm, respectively. With the 1800 g/mm holographic grating, the spectral resolution is 1.5–3.0 cm^{−1}, varying with the spectral region. PAR 173 potentiostat was employed for potential control. A polycrystalline Pt rod was embedded in a Teflon sheath and used as the working electrode with a geometric surface area of 0.1 cm². A large Pt ring served as the counter electrode. The surface pretreatment to get a highly dispersed Pt surface will be described below. All the potentials are quoted vs a saturated calomel electrode (SCE). All the chemicals used are of analytical reagent grade, and the solutions were prepared using triply distilled water.

Results and Discussion

Obtaining Surface Raman Spectra from Electrochemically Activated Pt Electrodes Using the Confocal Microprobe Raman System. Three sets of Raman spectra are presented in

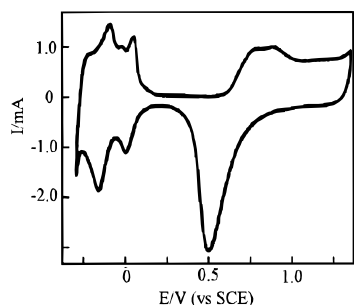


Figure 1. A typical cyclic voltammogram of a roughened Pt electrode in 0.5 M H_2SO_4 with the electrochemical roughening time of 10 min under the control of the 2 kHz square wave with the upper and lower potentials of 2.4 and -0.2 V. Sweep rate: 50 mV/s.

Figures 2–4 respectively for SCN^- adsorbed at the Pt electrode from solutions varying from 0.1 down to 10^{-5} M NaSCN in a wide potential range. The measurements were carried out stepwise from the negative extremity of the potential to more positive potentials with the spectral acquisition time of 100 s for the former two systems (0.1 and 10^{-3} M NaSCN) and 200 s for the 10^{-5} M NaSCN system. The results demonstrate clearly the advantage for the confocal microprobe Raman system over conventional Raman spectrometers. It is made evident by showing significantly high sensitivity for detecting the surface Raman signal. To our knowledge, it is the first time that one is able to study surface Raman spectra as a function of potential for bare Pt electrodes. The confocal optical configuration plays

a key role, particularly to eliminate the interference of strong Raman signal from the bulk solution phase. In the present study, although the electrolyte layer is as thick as 1 mm, the band of the C–N stretching from bulk electrolyte located at ca. 2065 cm^{-1} was hardly detected. This is because the confocal microscope has a good vertical spatial resolution so that only a very small amount of the solution (about $3 \times 3 \times 3\text{ }\mu\text{m}^3$) was sampled even using the long working-length objective. It means that the thin-layer cell is unnecessary, which is vitally important to the spectroscopic time-resolved measurement combined with the electrochemical transient measurement. However, it is necessary to note that there is one disadvantage for this type of Raman system (which may be overcome in the near future), i.e. there are some difficulties in analyzing the weak vibrational bands in the low-frequency region below 300 cm^{-1} due to the edge effect of the notch filter, i.e. there are some signals from the filter overlapping with Raman bands in this frequency region; see Figure 2a. Accordingly, the difference spectrum method had to be employed for the low-frequency region to remove these artificial bands. For example, the spectrum recorded at -1.4 V was subtracted from each spectrum for this study; see Figure 2b. For the high-frequency region, it is unnecessary to do so and the absolute spectra are shown in Figure 2c. It should be noted that the laser power density used in our experiment is as high as $2 \times 10^8\text{ mW/cm}^2$, which is much higher than that used in the conventional Raman spectroscopy. One must be very careful about the thermal effect and the possible photolysis process that can occur due to the strong laser irradiation.

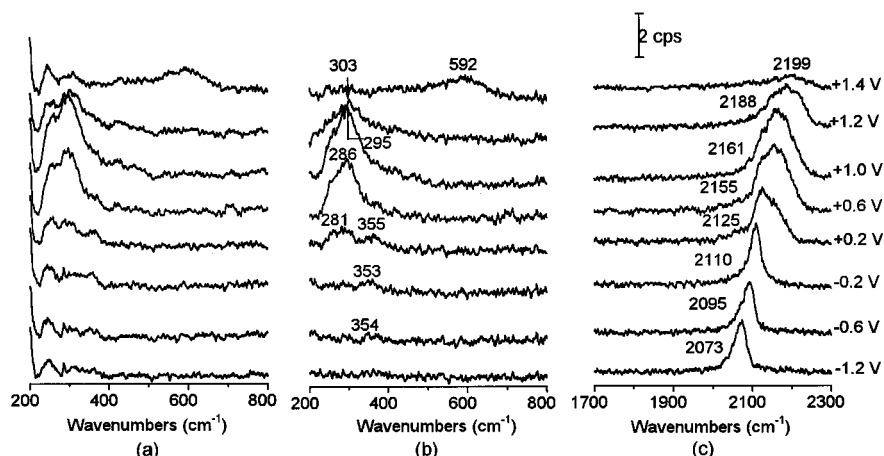


Figure 2. Potential-dependent surface Raman spectra from SCN^- adsorbed at a roughened Pt electrode in 0.1 M NaSCN. Excitation line: 632.8 nm. Acquisition time: 100 s.

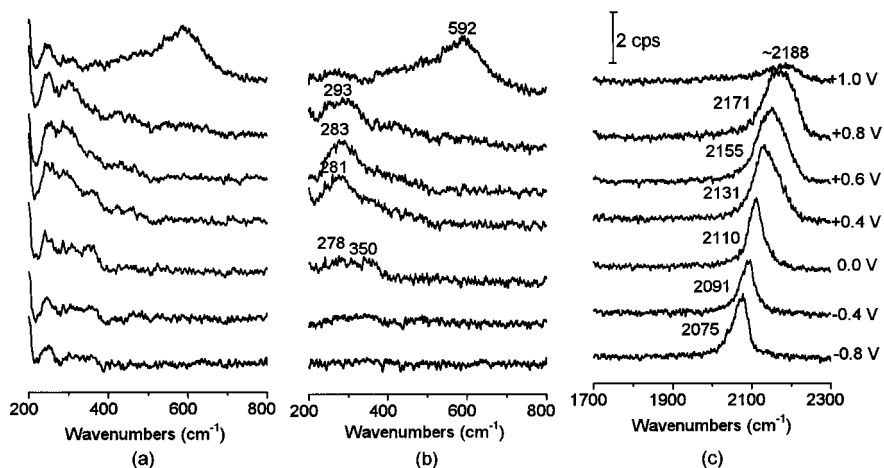


Figure 3. Potential-dependent surface Raman spectra from SCN^- adsorbed at a roughened Pt electrode in 10^{-3} M NaSCN + 0.1 M NaClO_4 . Excitation line: 632.8 nm. Acquisition time: 100 s.

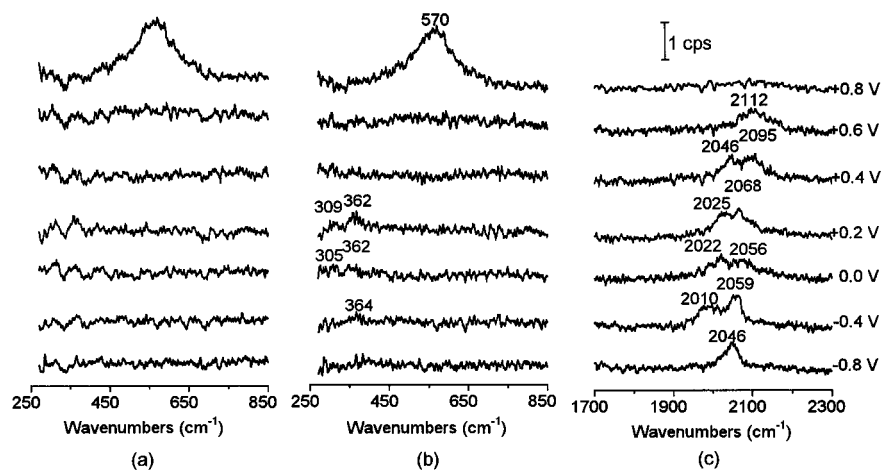


Figure 4. Potential-dependent surface Raman spectra from SCN^- adsorbed at a roughened Pt electrode in 10^{-5} M NaSCN + 0.1 M NaClO_4 . Excitation line: 632.8 nm. Acquisition time: 200 s.

Fortunately, the present study on the adsorption of organic and inorganic species on Pt surface has revealed that the Pt surface was very stable even in such a high laser power density.

It should be emphasized that the observation of good quality surface Raman spectra is attributed greatly to a proper surface pretreatment. A series of interesting papers by Arvia and co-workers demonstrates that a remarkable advance has been made recently in the development of metal electrode surfaces with preferred crystallographic orientation and different roughness through the application of periodic potential treatments. They found that these electrodispersed Pt electrodes of large surface area, which have very good electrochemical activity and behave highly reproducibly over a wide potential range, can be obtained in acid electrolytes via the electroreduction of a previously formed thick hydrous platinum oxide layer by applying a repetitive periodic potential. These electrochemically activated surfaces offer large catalytic activity very close to that of the starting material for electrocatalytic processes.²² In the present study, the Pt electrode was first mechanically polished with 0.3 and 0.05 μm alumina powder to a mirror finish, ultrasonically cleaned with triply distilled water, and then roughened by the procedure similar to that reported by Arvia et al.^{22a} In our case, a mild modification was made to get better surface Raman signal, e.g. a square wave of 2 kHz with upper and lower potentials of 2.4 and -0.2 V was applied to the electrode in 0.5 M H_2SO_4 for 5–10 min, and then the potential was held at -0.2 V until the electroreduction of the surface was completed. The electrode was then subjected to potential cycles between -0.25 and $+1.2$ V at 0.5 V/s until all unstable atoms or clusters were removed and a reproducible hydrogen adsorption/desorption peak was obtained, shown in Figure 1. The surface area can be estimated by the charge of hydrogen adsorption/desorption in the cyclic voltammogram. In our cases, the real surface area is ca. 400 times larger than that of the single crystal. Finally the electrode was rinsed thoroughly and transferred to the spectroelectrochemical cell for measurement. This electrodispersed Pt electrode has been found to be much better than that of roughened Ag, Cu, and Au in terms of the stability and reversibility for electrochemical and Raman measurements. It is well-known that the in situ ORC roughening process is generally required for Ag and Cu electrodes to obtain reasonably good SERS signals. Accordingly, problems of the irreversibility and instability in the SERS measurements arise. In particular, at more negative potentials adsorbates are desorbed or partially desorbed, leading to a sharp decrease or irreversible vanishing in SERS intensity, and even at more positive potentials the intensity could also decrease with time.^{5,6} Therefore, a method

named DESERS has to be used to remove those metastable SERS active sites at the cost of loss of the intensity substantially.^{7a} An alternative method named PASERS has been developed in our laboratory recently to overcome this problem. In the PASERS method, the SERS activity even at very negative potentials can be maintained more than 70%, but the experimental procedure becomes more sophisticated.²³ Ex situ roughening procedure is applicable to Au. In a method developed by Gao and Weaver, the Au electrode can be activated in one electrolyte, typically in 0.1 M KCl, and then be measured in another electrolyte.^{20e} However, one must still be very careful due to the possible effect by the residual Cl^- in the very porous surface which is loose and can be removed easily by a slight touch.

In the present study, the roughened Pt shows very good stability and reversibility after the extensive surface pretreatment mentioned above. Moreover, the Raman signal could be recovered completely upon returning to more positive values after a very negative potential excursion. Even more, the electrode can be reused over a long time period as long as it is subjected to an electrochemical cleaning procedure of cycling in a H_2SO_4 solution before each new experiment. The above advantage ensures the vibrational properties of the adsorbate probed by surface Raman spectroscopy to be reasonably representative of those for the entire surface rather than for some SERS active sites. Accordingly, this development in surface Raman spectroscopy may further prove it to be a general and reliable technique with the capability for more wide and practical applications. In the end of this section it is necessary to point out that Pt and Ni have been predicted theoretically to yield the SERS effect with an enhancement factor of about 10–100.²⁴ But in practice it is not easy to calculate the enhancement factor based on the previous experimental results due to the poor detecting sensitivity. Very recently we have been able to extend successfully the detailed surface Raman studies to molecules such as pyridine on smooth Pt and Ni electrodes in a wide potential region.²⁵ It is possible for us to calculate the very small enhancement factor. After considering the contribution of surface roughness to the increase of Raman intensity, we have calculated the surface enhancement factor by comparing the surface Raman signals from the Pt surfaces of different roughnesses with the bulk solution signal of the same vibration mode of pyridine. Due to the special optical configuration for sampling the solution species in the confocal microscopic measurements, a relevant model for the calculation was proposed and an enhancement factor of 10–120 for Pt was estimated, depending on the different surface roughness factors ranging

from about 20 to 400. A surface of moderate roughness could give a factor as high as 120.^{25c} A systematic study on the intensity dependence on the surface morphology and surface pretreatment and laser excitation line is being carried out, and the detailed discussion on the enhancement factor will be presented elsewhere.^{25c}

Potential Dependency of the Surface Raman Spectra of SCN⁻. As is pointed out in the Introduction, the assignment of the orientation for SCN⁻ on Pt in a wide potential range has been rather controversial in the literature. Before we discuss the present results in detail and compare the results with those obtained with other spectroscopic methods, it is worthwhile to look at the bonding mode of SCN⁻ with metal ions as complexes, which has been investigated intensively and proven to be very complicated.^{26a} Since the bonding behavior can be influenced by other coordinated ligands or even noncoordinated ions, the bonding to be expected in a given case is not always obvious. Either the nitrogen or the sulfur atom may be bonded to the metal ion. Further, bridging of two metal ions in the form M–NCS–M' is well-known, while alternate types of bridging, >SCN⁻ or >NCS⁻, are also possible. Nevertheless, the C–N stretching frequency shifting on coordination has been considered diagnostic. N-bonding generally leads to little change or to a decrease below the “free” ion value at around 2065 cm⁻¹, while S-bonding results in an increase to near 2100 cm⁻¹. It has been observed that bridging thiocyanate (–NCS–) exhibits this band well above 2100 cm⁻¹. It is known, however, that some of the above criteria have exceptions. In particular, N-bonded examples may be high (e.g. Cr³⁺ and Mo³⁺ which are near 2090 cm⁻¹),^{26b} and therefore use of the position of the C–N stretching alone as a criterion of bonding must be considered endangered.

In the surface vibrational spectroscopic studies, it is also very hard to assign the orientation of the adsorbed SCN⁻ unambiguously based only on the frequency of the C–N stretching vibration because the spectral band is broad under some conditions and both S-bound CN and N-bound CN could contribute to it. It is generally agreed that thiocyanate is adsorbed via a sulfur atom in a wide potential range within the double layer region at Ag and Au electrodes, but contention regarding the presence (or absence) of the other adsorbed orientations, including N-bound and bridge-bound have been contradictory, especially for Pt electrode systems.^{18f–19a,20f,g} According to the potential-dependent SNIFTIR spectra, Ashley et al. have assigned the positive peak at ca. 2050 cm⁻¹ of a bipolar band to N-bound adsorbed SCN⁻ and the negative peak around 2135 cm⁻¹ to S-bound SCN⁻ at Pt. The former is favored at far negative potentials, while the latter predominates at more positive potentials.^{18f} Taking advantage of the inherent surface sensitivity of SFG at the interface, which makes the band assignment more straightforward than in SNIFTIRS, Tadjeddine et al. have assigned the band appearing at –1.0 V at ca. 2070 cm⁻¹ to N-bound adsorbed SCN⁻ with the slope of $d\nu_{\text{CN}}/dE$ of 60 cm⁻¹/V. The other band appeared at 2140 cm⁻¹ at –0.4 V during the positive scan with a much smaller slope and was assigned to S-bound adsorbed SCN⁻. They further claimed the formation of thiocyanate bilayer adsorbed on Pt.^{19a} However, neither the IR nor the SFG experiments could provide the corresponding bands in the low-frequency region that would yield the direct information of the adsorbate–metal interaction. On the other hand, there have been no reports, unfortunately, about surface Raman studies on SCN⁻ adsorbed at Pt electrodes before. It is desirable, therefore, to carry out the surface Raman spectroscopic study to answer more clearly the question concerning the orientation of adsorbed SCN⁻.

Figure 2 shows potential dependent spectra of SCN⁻ in 0.1 M NaSCN in the low-frequency region as well as at higher frequencies where the internal C–N stretching mode is observed. It can be seen that the adsorption of SCN⁻ at Pt occurs throughout the double-layer region corresponding to a potential span between the onset of oxidation of SCN⁻ at ca. 0.5 V and hydrogen evolution at ca. –1.1 V. In fact, we can find clearly in Figure 2c that the SCN⁻ is already adsorbed at –1.2 V on the Pt surface, giving an intense band of the C–N stretching mode centered at 2073 cm⁻¹ with full width at half-maximum (fwhm) of about 40 cm⁻¹. The intensity and the fwhm of this band kept almost constant upon the increasing of potential to –0.2 V, while the frequency changed quite dramatically with potential with a band frequency–potential slope $d\nu_{\text{CN}}/dE$ of ca. 40 cm⁻¹/V. As shown in Figure 2b, a weak band appeared at ca. 350 cm⁻¹ around –0.6 V, which is reasonably attributed to the Pt surface–nitrogen stretching, $\nu_{\text{Pt–NCS}}$. This assignment is based on the calculations of $\nu_{\text{Pt–NCS}}$ and $\nu_{\text{Pt–SCN}}$ according to the relative masses of sulfur and nitrogen atoms together with the expectation that binding via the more positively charged nitrogen atom could dominate at potentials far negative of the potential of zero charge. Because the potential of zero charge (pzc) of Pt is very close to that of Au (ca. 0.1 V), the comparison of the potential dependent adsorption behavior between these two electrodes would be suitable and helpful. Gao and Weaver have studied the potential-dependent SERS spectra of SCN⁻ adsorbed at a Au electrode in a solution containing 2 mM NaSCN and 0.1 M NaClO₄. They assigned two bands at 295 and 237 cm⁻¹ to $\nu_{\text{Au–NCS}}$ and $\nu_{\text{Au–SCN}}$, respectively. According to their SERS result, the N-bound SCN⁻ on Au exists at the far negative potentials and coexists with the S-bound SCN⁻ in the potential region from –0.3 to 0.1 V, while the S-bound species dominates at more positive potentials such as +0.5 V.^{20e}

For the Pt electrode the $\nu_{\text{Pt–NCS}}$ vibration mode occurs at a higher frequency than that for Au, indicating a stronger surface bonding covalency for N-bound SCN⁻ at Pt. Furthermore, in our previous work on SCN⁻ adsorbed at a Ag surface, a quantum chemical calculation using self-consistent charge discrete vibrational X α (SCC-DV-X α) method was employed to investigate the charge transfer between the Ag surface and the S-bonded SCN⁻.^{20h} The model of linear adsorption of SCN⁻ at the Ag electrode imitated a pyramidal “metallic state” cluster Ag₄. The interaction between Ag and SCN⁻ ion can be described as follows: On shifting the potential toward a direction that diminishes the charge transfer from the adsorbed SCN⁻ ion to the surface atom of electrode, the adsorption of S-bound SCN⁻ is weakened and the desorption occurs as the potential reaches a critical potential, which is close to the pzc of the Ag electrode.^{20h} Unfortunately, we have not calculated the N-bound adsorption mode yet, but one cannot rule out such a possibility, particularly in the potential region negative of the pzc. Indeed, the surface vibrational band of SCN⁻ was detected at potentials from –0.3 V –1.2 V in the present work, illustrating that SCN⁻ may adsorb preferentially through the nitrogen atom in this potential range. It should be noted that the fwhm of the Raman band in Figure 2c negative of –0.2 V is quite narrow (ca. 40 cm⁻¹), revealing that the N-bound species SCN⁻ is the only dominating species at the surface at potentials negative of –0.2 V. At –0.2 V a weak band appeared as a tail in the higher frequency part of the intense band of 2110 cm⁻¹, and then this new band at 2145–2165 cm⁻¹ grew rapidly to become a strong band at 0.2 V. In the same potential region, a broad low-frequency band around 281 cm⁻¹ was observed starting at +0.2 V and positive of it, characterizing the presence of S-bound

SCN⁻ at the surface and providing evidence of orientation change around the pzc.

With further positive moving of the potential, the stretching band of C–N increased steadily in intensity, frequency, and bandwidth and reached a maximum at ca. 0.6 V, but decreased gradually at more positive potentials. The band of Pt–SCN vibration at low frequency increased in intensity and bandwidth even more markedly. As shown in Figure 2, there is no doubt that these two broad and unresolved bands exhibit more than two components respectively, which is mainly due to the more complicated surface process that took place by the oxidation of SCN⁻. The onset potential of SCN⁻ oxidation was found at about +0.5 V in the present study. The large band frequency–potential slope of the stretching mode C–N in the potential positive of 0.4 V indicates more effective contribution of the charge transfer of the applied potential. Ashley et al. have proposed the band at 2165 cm⁻¹ to be dissolved thiocyanogen as the electro-oxidation product.³⁶ However, it is hard, in the present study, to attribute the band at 280 cm⁻¹ which was simultaneously observed with the higher frequency band to any bondings of (SCN)₂ or (SCN)₃⁻ as the products.²⁷ Since the low-frequency band is very close to the $\nu_{\text{Pt-SCN}}$ of the complex of K₂[Pt(SCN)₄] at the position of 283 cm⁻¹,²⁸ it is more reasonable to ascribe it to be from the intermediates of the oxidation such as a surface complex. Since the spectra appeared upon scanning to positive potentials after the onset of the anodic faradaic current, they could be normal (or resonance) Raman spectra of electrogenerated bulk phase platinum–thiocyanate complexes. The nearly identical spectra reported in the literature for the bulk phase complies²⁶ support for this contention. It may be also necessary to consider an additional enhancement component arising from charge transfer processes associated with the adsorbate bound to specific metal sites having oxidized states. Further work is required in order to make a definite conclusion on this aspect.

Concentration Dependency of the Surface Raman Spectra of SCN⁻. As shown clearly in Figure 2b,c, the distinct change of the surface spectra can be detected in a wide potential range from -1.2 to 1.4 V, which can be divided into four regions: (i) -1.2 to -0.3 V, the N-bound SCN⁻ is dominated on the surface; (ii) -0.2 to 0.3 V, the two orientations N-bound and S-bound SCN⁻ coexist; (iii) 0.4 to 1.2 V, some surface complexes and/or intermediate products are formed; (iv) 1.4 V, platinum oxide film is formed. The boundaries of regions are changed significantly with the concentration of SCN⁻ from 0.1 to 10⁻⁵ M. For example, the potential where the band at ca. 592 cm⁻¹, corresponding to the formation of platinum oxide,²⁹ decreased from about 1.4 to 1.0 V and then to 0.8 V upon decreasing the concentration of SCN⁻ from 0.1 to 10⁻³ M and then down to 10⁻⁵ M. It means the oxidation of the Pt surface is prevented by the adsorption of SCN⁻. While the band with higher frequency up to ca. 2200 cm⁻¹ could probably be from the bridged mode of SCN⁻ interacting with the platinum oxide surface. The comparison of observed metal–ligand stretching frequencies for a given adsorbate in different concentrations can yield valuable information on possible variations in the surface bonding.

To our knowledge, the lowest concentration reported in the surface vibrational spectroscopic studies on SCN⁻ was 10⁻³ M^{18–20} in consideration of signal intensity. While in the present study, reasonably good quality Raman spectra could be obtained with solution concentration as low as 10⁻⁵ M, illustrating the strong capability of detecting the weak surface Raman signal from a submonolayer of the adsorbate, provided that an adequate surface pretreatment and a highly sensitive Raman microscope

were employed. In the potential regions (i) and (ii), the intensity of the C–N stretching band is independent (less than 5%) of the SCN⁻ concentrations equal to or higher than 10⁻³ M; see Figures 2 and 3. It reveals that the SCN⁻ can be adsorbed as a saturated monolayer on the surface. In the potential region (iii) the intensity of the metal–ligand stretching band is significantly dependent on the concentration. This band together with the broad band located at around 2150 cm⁻¹ even disappeared when the concentration was decreased to 10⁻⁵ M. It is likely that the surface concentration of the oxidation intermediates, products, and/or the surface complexes is too low to be detected because of the dissolution and diffusion of species into the solution.

It is especially important to emphasize that the extension to the lower concentration of 10⁻⁵ M explores a possibility of finding some interesting adsorbate–metal interactions. There are three interesting features in the surface Raman spectra as shown in Figure 4. Firstly, the frequency of the C–N stretching band for the N-bound SCN⁻ at 2046 cm⁻¹ is greatly lower than that at 2075 cm⁻¹ for the 10⁻³ M solution and that at 2085 cm⁻¹ for the 0.1 M solution at the same potential of -0.8 V. It is well-known that the factors affecting the frequency shifts include changes in the bond strength and lateral interactions of the coadsorbates. It was also shown in the previous SNIPTIRS studies that the frequency of the C–N stretching mode is dependent upon the nature of the supporting electrolyte cations particularly at the far negative potentials.^{18f} Therefore the remarkable down shift of the frequency in 10⁻⁵ M solution could be reasonably attributed to the effect of the coadsorbed cations. Secondly, the intensity of the surface Raman signal from the adsorbed SCN⁻ in 10⁻⁵ M solution is weaker than that of the higher concentrations. Meanwhile, a very weak band at 934 cm⁻¹ from totally symmetric vibrational mode of the electrolyte anion ClO₄⁻ was observed. This infers that surface coverage of SCN⁻ is only of submonolayer quantity which is in coadsorption with the electrolyte ions. Thirdly, which is the most interesting, in the potential region from -0.4 to 0.4 V one can observe a new C–N stretching band having extremely low frequency appearing at ca. 2010 cm⁻¹, which has never been reported previously. Taking into account the low surface coverage of SCN⁻, one can assume that the bridge-bound SCN⁻ is responsible for this band. Since this bridge-bound SCN⁻ has a relatively weak interaction with the surface, it can be either excluded by the coadsorbed cations at sufficiently negative potentials such as -0.8 V or converted to the terminal species at potentials positive of 0.4 V.

Potential Dependency of the Surface Raman Spectra of CO. As has been shown above, some uncertainties of the assignments of the bands of SCN⁻ remain, especially for the frequencies lower than 300 cm⁻¹, which is mainly due to the weak signal and the interference of the notch filter. Therefore, it may be of interest at this stage to find another adsorbate having a higher frequency of the adsorbate–Pt interaction in order to avoid the uncertainties that might arise in the interpretation of results. From the point of view of special interest in electrocatalysis and spectroelectrochemistry,^{30–32} there are many well-known reasons to choose CO. Detailed discussion of this system will be described elsewhere,^{25d} but here, we are just going to demonstrate that a more clear spectral band relating to the adsorbate–metal vibration can be obtained if it is located above 300 cm⁻¹. Prior to the discussion, it is of interest to notice that in 1977 Cooney, Fleischmann, and Hendra claimed their observation of surface Raman signal of CO at a platinized Pt electrode by showing poor quality spectra having extremely low S/N.¹¹ Ten years later, two interesting papers of good quality

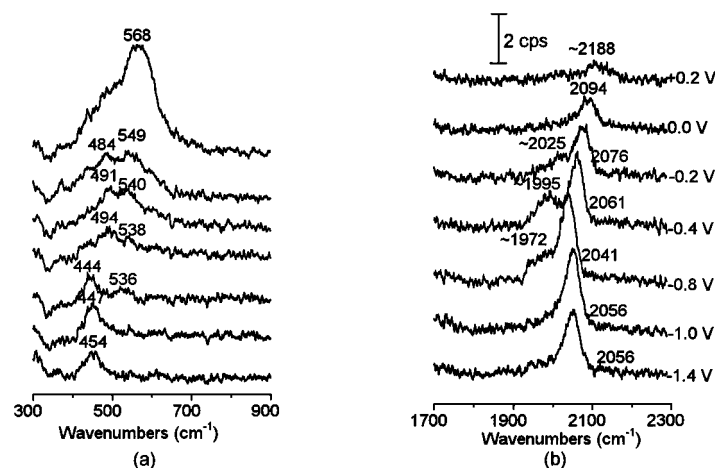


Figure 5. Potential-dependent surface Raman spectra from CO adsorbed irreversibly at a roughened Pt electrode in 0.1 M NaOH containing no CO. Excitation line: 632.8 nm. Acquisition time: 200 s.

SERS of CO adsorbed at Pt-coated Au electrodes were reported by Weaver and co-workers. But, two C–O stretching bands were observed simultaneously, one of which was from CO bound to residual uncovered Au sites.^{30b,32a}

We have also noticed that in most previous reports, studies are restricted in a relatively narrower potential range of about 0.7 V or less. This is partially because of the inevitable limitation in potential due to the common use of acidic aqueous media despite that a direct fuel cell based on an alkaline electrolyte seems to be more promising. Therefore, a basic aqueous solution was chosen in the present study so that the potential range studied was from -1.4 to 0.2 V, which is more or less overlapped with that of the SCN^- system and thus suitable for comparisons between these two systems. On the basis of the fact that CO is a sufficiently strong adsorbate at Pt electrodes, the study was carried out by immersing the Pt in a CO-saturated 0.1 M NaOH solution for 10 min so that a monolayer of CO is irreversibly adsorbed onto the Pt. This was followed by transferring the Pt into the cell containing only 0.1 M NaOH for Raman measurements. Figure 5 shows a pair of surface Raman spectral sequences in the high-frequency and low-frequency regions, obtained in a similar way to those of SCN^- mentioned above. As the Raman scattering cross section for CO is smaller than that for SCN^- , the spectral data acquisition time was as long as 200 s to produce surface spectra of reasonably high signal to noise (S/N) ratio. Figure 5 appears to be the first report in the vibrational spectroscopic studies on adsorbed CO at Pt in such a wide potential range in aqueous solutions.

According to the potential dependencies of the spectra, we could divide the potential into three regions: (i) -1.4 to -0.9 V, (ii) -0.8 to -0.2 V, and (iii) -0.1 to 0.2 V. At the far negative potentials of region (i), it can be seen that the low-frequency region contains a pronounced band at around 450 cm^{-1} . In comparison with the SERS result of CO at Pt-coated Au electrodes^{32a} as well as electron energy loss spectra (EELS) obtained from the Pt(111)/CO system under ultrahigh vacuum [68], this band can be attributed confidently to the $\nu_{\text{Pt-CO}}$ stretching associated with the terminal CO. The C–O stretching band at 2056 cm^{-1} has a relatively narrower bandwidth. Both C–O and Pt–CO stretching bands remain at approximately constant frequency and intensity at far negative potentials. This may indicate a very weak Stark effect and the involvement of inhibition of the charge transfer process between CO and the surface. By carefully examining the C–O band shape, one can find that this band consists of one dominant peak in the high-frequency part with a small tail in the low-frequency part. When

the potential was made more positive to ca. -0.8 V into the potential region (ii), a distinct change was observed, particularly in the high-frequency part. The tail grew remarkably as a broad shoulder at around 1972 cm^{-1} and then became a clear peak at -0.4 V. Iwasita et al.^{30f} and Peremans and Tadjeddine³¹ have assigned a very weak band at ca. 1970 cm^{-1} to be the 2-fold bridge-bound CO in their IR and SFG studies, respectively. However, many other authors have attributed the band in the frequency region of $1800\text{--}1900\text{ cm}^{-1}$ to the 2-fold bridge-bound CO.^{1d–3} According to our and the previous EELS³³ and SERS^{32a} data in the low-frequency region, we prefer to assume that this new band is from another type of the terminal CO because the corresponding new band in the low-frequency region appeared at ca. 536 cm^{-1} rather than at ca. 390 cm^{-1} due to the bridged one.^{32a,33} It seems to be more reasonable to ascribe the 536 cm^{-1} band to the Pt–OH $^-$ stretching and attribute the distinct change of the spectra to the coadsorption of OH $^-$. It should be noted that the dominant peak had a considerable downshift from 2056 to 2041 cm^{-1} , and then it increased in frequency as the potential was made more positive. The downshift of adsorbed CO on metal surfaces has generally been explained in terms of the electron donation from CO(5σ) to the metal d -band and back-donation from the metal d -band to CO-($2\pi^*$).^{30e} The remarkably lower frequency of CO observed in the present study may be attributed to the presence of electrolyte anions OH $^-$ near to or touching the Pt surface. For instance, in the potential region (i), OH $^-$ could be repulsed by the strong electrostatic field and only small amount of OH $^-$ can be close enough to touch the surface. In the potential region (ii), a considerable amount of OH $^-$ may be able to influence the adsorbed CO by binding to the surface directly, as evidenced in the band at 536 cm^{-1} . The adjacent coadsorption of an oxygen-containing species could be an important clue to the reason for the marked behavioral difference for the frequency dependency of the C–O stretching band in regions (i) and (ii).

With the molecular orbital (MO) calculations for CO on Pt-(111), Mehandru and Anderson predicted that the negative potential shifting will stabilize 2-fold and 3-fold bridging with a decrease of the $d\nu_{\text{CO}}/dE$ slopes toward more positive potentials.³⁴ This prediction results from the progressively greater extent of $d\pi-2\pi^*$ surface CO back-donation as the surface charge is made more negative. It has been demonstrated that the prediction fits quite well to the experimental data in the nonaqueous system reported by Roth et al.^{30b} However, it is in contrast to the present result at least to some extent, particularly for the region (i). The controversy could be caused by the presence or absence of oxygen-containing species such

as hydroxyl that can coadsorb strongly at Pt electrodes. Therefore, it seems to be highly desirable to consider the lateral interaction of adsorbates and effects of the electrolyte ions and even the solvent molecules so that the theoretical predictions can be in more quantitative agreement with the experiment. It is hoped that such experimental efforts made in our laboratory can spur further experimental and theoretical work.

As has been found that the electro-oxidation of solution CO on Pt is generally triggered only at potentials close to the onset of surface oxidation. Therefore, it could be of interest to find out whether the electro-oxidation of adsorbed CO and the Pt surface itself are interconnected. Our present result further confirms the relation between CO electro-oxidation and surface oxide formation. In potential regions (ii) and (iii) from -0.8 to -0.2 and to 0.2 V, the substantial upshift for the C–O stretching frequency from 2041 cm^{-1} to ca. 2110 cm^{-1} and the oxygen-containing species—surface stretching bands at around $540\text{--}568\text{ cm}^{-1}$ are a clear indication of the complicated change upon the potential mainly due to changes of the CO surface coverage and the nature of the coadsorbed oxygen-containing species. One may assume that at -0.8 V the hydroxyl species^{32a} start to coadsorb with CO to the surface and influence the charge distribution in the region (ii). The surface is partially oxidized at more positive potentials and finally forms the full oxidized sites at potentials positive of 0.0 V in the region (iii). Since the strong and broad band in the low-frequency region exhibits several components, the spectral bands of adsorbate–metal interaction still remain somewhat uncertain in this preliminary study. Accordingly, the isotopic method using ^{13}C and ^{18}O would be very helpful in giving a more definite interpretation. Research along these avenues, including more practical applications such as the electrocatalytic oxidation of many organic fuels, is currently being pursued in our laboratory.^{25d}

Concluding Remarks

It has been shown that by using confocal microprobe Raman spectroscopy and a unique electrochemical pretreatment procedure for Pt we are able to extend the detailed surface Raman studies, for the first time, to bare Pt electrodes in a wide potential region (e.g. -1.0 to $+1.4$ V vs SCE) and to more general adsorbates such as SCN^- and CO having small Raman scattering cross sections. The accessibility of the low-frequency Raman spectrum together with the sensitivity available in the present work make this technique of great power. The potential-dependent Raman spectra of SCN^- reveal that the N-bound adsorbate is favored at the potentials negative of the pzc. The orientation conversion to the S-bound species occurs in a more positive region, depending on the SCN^- concentration. In a solution of 10^{-5} M NaSCN and 0.1 M NaClO_4 , a new C–N stretching band at ca. 2010 cm^{-1} is observed and assigned to the bridge-bound SCN^- at Pt. A preliminary study on CO irreversibly adsorbed on Pt, from -1.4 to 0.2 V in 0.1 M NaOH, infers the interaction of CO with the surface is more complex, mainly due to the coadsorbed oxygen-containing species, the nature of which is dependent critically on the potential. Although the structural information discerned from the present results is incomplete and rather qualitative in nature, it demonstrates the virtues of surface Raman spectroscopy for yielding information on surface bonding relating to the surface coverage, coadsorbate, electrolyte ions, and electrode potential, which will contribute on an increasingly broad frontier to the development of a true molecular-level understanding of interfacial systems. It should be emphasized that the extremely stable and reproducible dispersed Pt surface for the Raman measurements also offers high electrocatalytic activity and

negligible distribution of active sites very close to that of the catalytic materials.²² Therefore, it could be very promising to extend the study of surface Raman spectroscopy together with such electrodes to ultrahigh vacuum environments for “UHV electrochemical modeling” systems^{32b,35} and to gas–metal interfaces. Furthermore, it would be of special importance to extend the surface Raman spectroscopy to the studies of other metals, semiconductors, and dielectric films with the further technical developments of the surface pretreatment procedure and Raman instrumentation. These could be good reasons to be optimistic that Raman spectroscopy will prove to be a surprisingly versatile means of characterizing interfacial processes on a variety of surfaces in electrochemical and other surface environments for both fundamental and practical applications.

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