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Potential Dependence of the Orientation of Thiocyanate Adsorbed on an Iron Electrode as Probed by Surface-Enhanced Raman Spectroscopy

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Surface-enhanced Raman spectroscopy has been extended successfully to the study of a bare iron electrode (without any deposition of other noble metals) exposed to the neutral solution containing thiocyanate over a wide potential range from -1.8 to -0.4 V. The applied potential has a significant influence on the Raman frequency shift of SCN^- as a result of the electrochemical Stark effect. Both N- and S-coordination modes were observed. Results show that at large negative potentials N-bound SCN^- is favored, whereas at relatively positive potentials, S-bound thiocyanate predominates the iron surface. A sudden change in the $d\nu_{\text{CN}}/dE$ value is observed at potentials from ca. -0.75 to -1.1 V and is evidenced for the transition from N-bound thiocyanate to S-bound species.

Introduction

The development of surface-enhanced Raman scattering (SERS) spectroscopic techniques over the last two decades has led to a better understanding of the electrode/electrolyte interface.^{1,2} The intrinsically large surface enhancement factors (SEF) enable one to extract the “absolute” SERS spectra with virtual freedom from bulk-phase interferences. However, the breadth of applications of SERS in surface science has been limited heretofore, as we know, to Group IB metallic substrates (Cu, Ag, and Au). Several strategies have been developed to extend SERS to other surface materials, particularly the transition metals of Pt, Ni, and Fe which are widely used in industry. These strategies involve (i) deposition of an ultrathin transition metal, e.g., Fe film with several atomic monolayers onto a SERS active Ag (or Au) electrode,^{3–6} (ii) deposition of SERS active Ag microislands onto Fe substrates, which has been applied in the study of the passive film of iron,^{7–10} (iii) deposition of a rough and thick Fe film of few micrometer thickness at non-SERS active substrates such as glassy carbon electrodes.¹¹ However, the ultrathin Fe film with good uniformity on a rough surface used in strategy i is relatively difficult to prepare. The existence of “pinholes” in the films complicates both the vibrational spectroscopic interpretation and the electrochemical behavior. For the second method, it is difficult to distinguish the Raman signal from molecules bound to the Fe substrates and those to the Ag islands. In addition, the electrochemical deposited Fe films for the third method may differ in properties of crystalline structure from the bulk phase.

Recently, however, Weaver and co-workers^{12,13} have found that ultrathin (3–5 monolayer) films of Pt-group metals on gold can be prepared by judicious modification in the electrodeposition procedures. These deposited films are both essentially pinhole-free and exhibit near-optimal SERS properties. The

strategy has been applied to the study of adsorption of carbon monoxide on rhodium,¹⁴ thiocyanate on platinum, and palladium¹⁵ electrodes. Recent studies in our laboratory have found that by using an iron electrode subject to an oxidation–reduction cycle in sulfuric acid one can obtain the significant SERS signal of pyridine from bare iron surfaces.^{16,17} The inducement of the SERS-active metals is unnecessary now. The significance of this development is that it enables rich vibrational spectra to be obtained for a myriad of adsorbates, particularly organic inhibitors, on electrochemical bare iron interfaces. This strategy has been used to examine the chemisorption of benzotriazole¹⁸ on Fe. We aim to give insight to the nature of the surface bonding and molecular orientation by means of this strategy.

In the present study, thiocyanate was chosen as a candidate adsorbate not only for its simple molecular structure but also for its particular spectroelectrochemical interest and inhibitive action for iron.¹⁹ It is necessary to investigate the interactions between thiocyanate and iron for a better understanding of the inhibition mechanism. On the other hand, although thiocyanate adsorption on Ag and Au has been studied extensively using SERS technique, there is to date no consensus on the potential-dependent orientation behavior of this species.^{15,20,21} A study on the adsorption and coordination behavior of SCN^- on Fe may deepen our understanding of the general surface bonding of SCN^- on metals.

Experimental Section

Raman spectra were recorded using a confocal microprobe Raman system (LabRam I). The excitation line of 632.8 nm was used from an internal He–Ne laser with a power of ca. 12 mW on the electrode surface. The working electrode was a polycrystalline iron rod (99.99%) embedded in a Teflon sheath with a geometric surface area of 0.1 cm². Before the surface roughening pretreatment, the Fe electrode was mechanically polished with 0.3 and 0.05 μm alumina powder to a mirror finish followed by ultrasonic cleaning with Milli-Q water. An oxidation–reduction cycle (ORC) was employed to yield a roughened iron electrode surface prior to the Raman measurement.¹⁷ A

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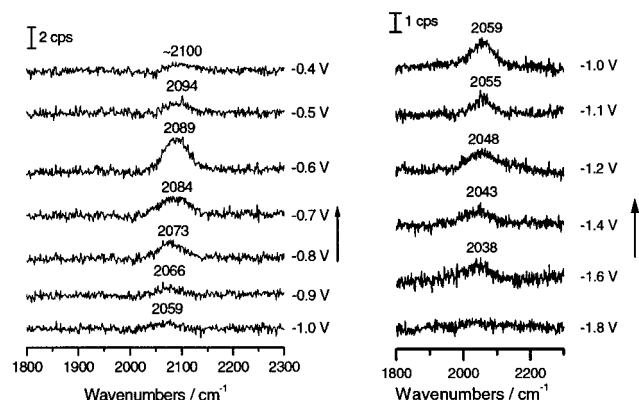


Figure 1. Potential-dependent SERS spectra of thiocyanate adsorbed on an iron electrode in 0.01 M SCN^- + 0.1 M KCl. Laser line: 632.8 nm. Acquisition time: 100 s. Accumulations: 4.

large platinum ring served as the counter electrode. All of the potentials, unless specified, were quoted versus a saturated calomel electrode (SCE). All of the chemicals used were of analytical reagent and the solutions were prepared using Milli-Q water.

Results and Discussion

Representative potential-dependent SERS spectra for the frequency region 1800–2300 cm^{-1} are shown in Figure 1. The electrolyte was 0.01 M NaSCN in 0.1 M KCl. 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. To the best of our knowledge, it is the first time that one is able to observe the SERS spectra of thiocyanate adsorbed on a bare iron electrode surface as a function of potential. It should be emphasized that the observation of the SERS spectra is attributed greatly to a proper surface pretreatment. As we know, a roughening procedure is necessary to observe the SERS phenomenon for Ag, Au, and Cu. Similar electrochemical roughening pretreatments were carried out for iron except the use of a different electrolyte. Scanning tunneling microscopic studies in our laboratory¹⁷ have shown that the iron electrode subject to an ex situ ORC cycle displays many bumps with a diameter of 10–100 nm on the surface. Strong SERS spectra of pyridine were observed on this surface. Given an in situ ORC cycle employed to the iron electrode, even more intense SERS spectra will be obtained. In this study, such an in situ ORC cycle was avoided in order to eliminate some unexpected impurities while recording the Raman spectrum. The SEF was calculated to be 10^2 – 10^3 by using the unique method for calculating SEF based on the confocal Raman system.²² The detailed discussion of the enhancement mechanism at an iron surface can be found in ref 17.

It can be seen from Figure 1 that no signal is observed when the iron electrode is polarized at -1.8 V. By adjusting the potential to -1.6 V, a broad band appears at ca. 2038 cm^{-1} , although the signal-to-noise is rather poor. This band is apparently attributed to the CN stretching mode of thiocyanate. On scanning potential to more positive values, the spectral quality improves gradually, and the CN band increases slightly in intensity but greatly in frequency, indicating that it may be due to surface species rather than those from the bulk solution. The intensity maximizes at -0.6 V. A review of the orientation of thiocyanate adsorbed on metals is necessary before the detailed analysis of the surface coordination behavior of thiocyanate on iron. It is generally agreed that thiocyanate is adsorbed via the sulfur atom at all potentials within the double

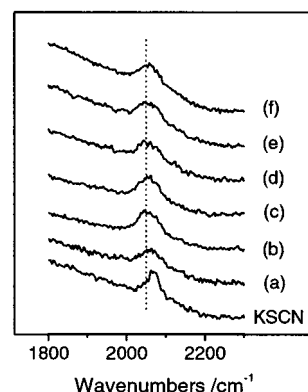


Figure 2. Normal Raman spectra of 0.1 M KSCN and bulk iron-thiocyanate complexes with different coordination numbers: (a) $n = 1$, (b) 2, (c) 3, (d) 4, (e) 5, and (f) 6. Excitation line: 1064 nm. Scans: 1024.

layer region on most electrode materials,¹⁵ but contentions regarding the existence of other surface binding thiocyanate species, including N-bound and bridge-bound, have been contradictory.²⁰ The frequency shift on coordination of CN stretching has been considered diagnostic of the different possible modes of coordination characteristic of the ion.²¹ Bonding through the nitrogen atom leads to little change or to a decrease in frequency below that of the free ion at ca. 2065 cm^{-1} , whereas the S-bound one results in an increase to ca. 2100 cm^{-1} . Also, it has been observed that the bridge-bound thiocyanate exhibits this line well above 2100 cm^{-1} .²⁰ Investigations of the potential-dependent SNIFTIR spectra by Ashley et al.²³ assigned a positive peak at ca. 2050 cm^{-1} of a bipolar band to N-bound adsorbed thiocyanate and a negative peak around 2135 cm^{-1} to S-bound thiocyanate at platinum. The former is favored at far negative potentials, whereas the latter predominates at more positive potentials.

In the present study, at far negative potentials, the CN band with a frequency far below that of a free ion may be suggestive of predominantly N-bound coordination. Comparisons with the bulk-phase–metal–thiocyanate complexes support this assignment. It is generally agreed that bulk iron–thiocyanate complexes are formed via the N coordination according to the theory of hard and soft acids and bases.²⁴ Figure 2 shows the normal Raman spectra of a series of bulk iron–thiocyanate complexes $\text{Fe}(\text{SCN})_n$ ($n = 1\sim6$), along with the spectra of the bulk KSCN solution. By adjusting the molar ratio of FeCl_3 to KSCN from 1:1 to 1:6, six complexes of iron with different coordination numbers were synthesized. The CN band frequency lies in the range of 2050–2058 cm^{-1} , which is below that of a free SCN^- ion and is in good agreement with the literature.²⁵ The coexisting band ca. 2065 cm^{-1} with the complex bands comes from the uncoordinated SCN^- in the solution. The analogous spectral characteristic of the bulk-phase complex with that on the iron surface was clearly observed except that the CN band frequency for the iron surface extends to smaller values at large negative potentials. Therefore, the N-bound coordination mode of thiocyanate may predominate on the iron surface in this potential region. This assignment is also consistent with electrostatic considerations, given the higher positive charge on the nitrogen atom.²⁶

Upon scanning the potential to more positive values, in particular positive to -0.75 V, the CN stretching mode is observed at frequencies well above 2065 cm^{-1} . Although the normal Raman spectrum of S-binding the bulk iron–thiocyanate complex cannot be obtained, the assignment of the S-bound coordination mode of thiocyanate on iron surface is still not

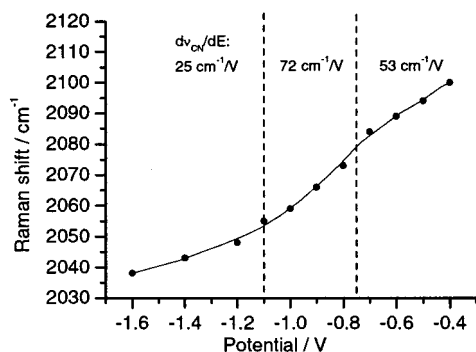


Figure 3. ν_{CN} frequency–potential profile of the SERS spectra of SCN^- adsorbed on an iron surface in a solution containing 0.01 M NaSCN and 0.1 M KCl.

unreasonable. It may be indicative of the difference between the charged iron surface and the Fe cation in solution. Then, a transitive potential region should exist for the changes of the surface coordination modes of thiocyanate, which is discussed further below. It should be noted here that the aforementioned assignment of the surface coordination modes is somewhat risky, especially for the CN band above 2065 cm^{-1} because exceptions were reported that the N-bound species may be high and the CN mode of bridge-bound thiocyanate may also appear in this region.²⁷ Unfortunately, the band reflecting the metal–adsorbate interactions in the low-frequency region, which may help one to distinguish the aforementioned coordination modes clearly, was not observed because of the poor enhancement factors of iron.

Further study of the change of the frequency with applied potentials provided us more insightful information. The relationship between them is depicted in Figure 3. As we know, the variation of the CN band frequency with potentials can be interpreted in terms of an electrochemical Stark effect. Usually, the band frequency varies linearly with potentials and yields a constant value $d\nu_{\text{CN}}/dE$. The magnitude of the value is controlled by the influencing extent of the band under the external electric field.²³ The striking feature of Figure 3 is that three potential regions with different values of $d\nu_{\text{CN}}/dE$ are observed clearly. The maximum value appears at the potential region: ca. -1.1 to ca. -0.75 V. Observation of different $d\nu_{\text{CN}}/dE$ values may indicate different configurations of thiocyanate on the iron electrode surface. We have assigned two different coordination modes, i.e., N-bound and S-bound thiocyanate at far negative and far positive potentials, respectively. It is apparent that a transition potential region should coexist. The potential of zero charge (pzc) in a neutral solution for iron was reported at ca. -0.73 V (vs SHE).²⁸ It is reasonable to assume that the adsorption of thiocyanate should not alter the pzc of the system studied in this paper significantly. That is to say, the pzc of the present system is assumed to be slightly negative to -0.73 V (vs SHE) for the special adsorption characteristic of thiocyanate anion. Therefore, the transition of the N-bound to S-bound thiocyanate is assumed to occur at potentials ($-1.1 \sim -0.75$ V) near pzc. As was studied by Ashley et al., the $d\nu_{\text{CN}}/dE$ value caused by the Stark effect may be high if the related band is experienced in a more intense electric field.²³ That is, in this study, when the CN triple bond approaches nearest to the iron surface, the related band frequency should be most susceptible to the change of the electrode potential. As a result, a high value of $d\nu_{\text{CN}}/dE$ should then be observed. This happens in the transition potential region because a flat configuration of thiocyanate is necessary for the transition of N-bound to S-bound species in this region. Thus, the CN triple bond should parallel

the surface and is easily influenced by the external electric field. So, we observed a high $d\nu_{\text{CN}}/dE$ of $72\text{ cm}^{-1}/\text{V}$ in comparison with other two potential regions.

A contradictory phenomenon was also observed in our laboratory. That is, the $d\nu_{\text{CN}}/dE$ value of the N-bound region is smaller than that of the S-bound potential region, which is contrary to observations on Pt by Ashley et al.²³ We cannot give a good explanation for these contradictory observations till now. More systematic investigations both experimentally and theoretically are necessitated for a better understanding of the orientation of thiocyanate on iron. Although the interpretation of different $d\nu_{\text{CN}}/dE$ values at far negative and positive potential regions is still not unambiguous, the chemisorption of thiocyanate on iron is evident for the frequency shift of the CN band with potentials. The success in obtaining the SERS spectra of thiocyanate stimulates us to further probe the inhibitive action of thiocyanate for iron at a molecular level in combination with the electrochemical measuring techniques.

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