

# Surface-Enhanced Raman Scattering Spectra of Thiourea Adsorbed at an Iron Electrode in NaClO<sub>4</sub> Solution

Peigen Cao,<sup>†</sup> Jianlin Yao,<sup>‡</sup> Bin Ren,<sup>‡</sup> Renao Gu,<sup>\*,†</sup> and Zhongqun Tian<sup>\*,‡</sup>

Department of Chemistry, Suzhou University, Suzhou 215006, People's Republic of China, and State Key Laboratory for Physical Chemistry of Solid Surfaces, Department of Chemistry and Institute of Physical Chemistry, Xiamen University, Xiamen 361005, People's Republic of China

Received: March 7, 2002; In Final Form: July 30, 2002

Surface-enhanced Raman scattering (SERS) spectra of thiourea at an electrochemically activated iron electrode have been investigated as a function of applied potential. The marked downshift of the CS stretching and upshift of the NCN symmetric stretching by comparison of the SERS with the normal Raman spectrum of thiourea are clearly observed and interpreted by coordination of thiourea with the iron surface through sulfur atom. The appearance of the low-frequency mode at ca. 283 cm<sup>-1</sup> assigned to the Fe–S vibration supports the assumption of S-coordination of thiourea. The orientation of thiourea molecules is assumed to be slightly inclined to the iron surface at an intermediate angle due to the observation of the SCNN out-of-plane bending band. Potential dependence of the SERS spectra shows that thiourea may interact more strongly with the iron surface at relatively positive potentials. Coadsorption of the supporting electrolyte anion ClO<sub>4</sub><sup>-</sup> with thiourea has also been confirmed by the SERS spectra.

## Introduction

The electrochemical adsorption behavior of thiourea on various metals has been studied extensively for its wide application as an additive in electroplating and refining, e.g. for the electrodeposition of copper and silver.<sup>1–3</sup> The reagent is introduced to promote deposit smoothness and luster. Thiourea has also been known as an inhibitor for the corrosion of iron, steel, and other metals.<sup>4</sup> The information about the interaction between thiourea and metals is quite important for a better understanding of the particular influencing effect of thiourea on the metal inhibition and electrodeposition. A variety of techniques, including cyclic voltammetry, polarography, and polarization measurements, have been employed to obtain such information.<sup>5,6</sup> Some ex situ microscopy and surface analytical techniques (XPS, XRD, FT-IR) are also often applied to investigate the adsorption behavior of thiourea on electrode surfaces.<sup>7</sup>

Surface-enhanced Raman spectroscopy (SERS), since its advent in the middle 1970s, has been used to probe in situ the interaction between thiourea and metals such as copper,<sup>8</sup> silver,<sup>9,10</sup> and gold<sup>11</sup> in aqueous solution. Because of its surface sensitivity, SERS can provide a more complete picture of the metal–adsorbate interaction than comparable techniques such as IR or second harmonic generation (SFG). However, the application of SERS has been limited to the above three coinage metals. Both experimental and theoretical efforts have been spent on the extension of SERS to other transition metals, in particular the iron and platinum series metals. For instance, the electrodeposition of ultrathin films of transition metals onto SERS-active Ag or Au electrodes has been adopted by Fleischmann and co-workers<sup>12</sup> to obtain the SERS spectra of organic

adsorbates. However, problems still exist for the “pinholes” in the ultrathin deposition film, which may complicate the interpretation of the spectra. Recently Weaver and co-workers<sup>13,14</sup> 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 for some organic and inorganic adsorbates.

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 well resolved SERS signal of pyridine from bare iron surfaces.<sup>15</sup> The surface enhancement factor (SEF) for iron was calculated experimentally in the range of 10<sup>2</sup>–10<sup>3</sup>.<sup>16</sup> The significance of this development is that it enables rich vibrational spectra to be obtained for a number of adsorbates, particularly organic inhibitors, on electrochemical bare iron surfaces. Tian et al. used this strategy to examine the chemisorption of benzotriazole<sup>17</sup> and thiocyanate<sup>18</sup> on Fe. This study is aimed at the elucidation of the structure, orientation, and conformation of the surface species and the nature of the chemical bonding between the adsorbate and the substrate.

As part of these ongoing studies, the SERS results on adsorption of thiourea at iron electrodes are presented in this work. The motivation for the choice of this system is based on the following facts. First, most of the related SERS studies were performed on the above three coinage metals.<sup>8–11</sup> The SERS data from iron should provide a better understanding of the general surface interaction between thiourea and metals. Second, the inhibition properties of thiourea for iron have been characterized by many traditional electrochemical measurements. However, controversy still exists on the inhibition mechanism, particularly the surface bonding and the influencing environmental factors, including inhibitor concentration, solution pH, coadsorbed anion, electrode potential, etc.<sup>5,6</sup> The present SERS investigation is expected to give insight into the surface coordination and orientation of thiourea. The coadsorption of

\* Corresponding authors. Primary contact, R. Gu. Tel: 86+512+65112813, 65112645. Fax: 86+512+65231918. E-mail: ragu@suda.edu.cn. Secondary contact, Z. Tian. Tel: 86+592+2181906. E-mail: zqtian@xmu.edu.cn.

<sup>†</sup> Suzhou University.

<sup>‡</sup> Xiamen University.

thiourea with perchlorate anions and the related surface conformation is also analyzed.

## Experimental Section

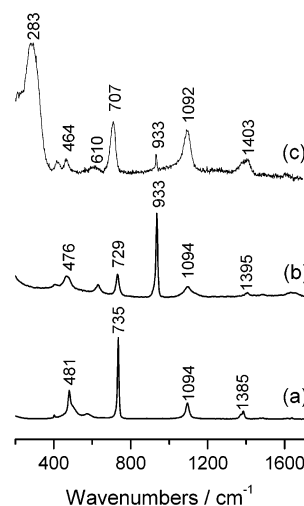
A confocal microprobe spectrometer (LabRam I from Dilor, France) was used to record the in situ Raman spectra. The excitation wavelength was 632.8 nm from an inner air-cooled He–Ne laser with a power of 10 mW and a spot of size 3  $\mu\text{m}$  at the sample surface. The slit and pinhole used were 200  $\mu\text{m}$  and 800  $\mu\text{m}$ , respectively. The acquisition time was 10 s and the accumulation was four times for each spectrum. With a holographic notch filter and a CCD detector, the spectrometer has an extremely high detecting sensitivity. A 50 $\times$  long working-length objective (8 mm) was used so that it was not necessary for the objective to be immersed in the solution.

A three-compartment spectroelectrochemical cell was also used while recording the in situ Raman data. The working electrode (WE) was a polycrystalline iron (99.99%) rod embedded in a Teflon sheath, with a geometric surface area of 0.1  $\text{cm}^2$ . A large Pt ring served as the counter electrode. All the potentials, unless specified, are reported versus a saturated calomel electrode (SCE). An EG&G model 173 potentiostat was employed to control the applied potentials. The WE was electrochemically roughened so as to obtain a SERS-active surface for the Raman measurements. Before the surface roughening pretreatment, the iron electrode was mechanically polished with 0.3 and 0.05  $\mu\text{m}$  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. The WE was first prepolarized at a negative overpotential of ca.  $-1.0$  V in 0.5 M  $\text{H}_2\text{SO}_4$  electrolyte to reduce any surface oxides present. Then the potential was changed to  $-0.7$  V for a few seconds and stepped to  $-0.35$  V where the potential was held for 15 s. After that, the potential was stepped back to  $-0.7$  V for ca. 20 s so that the oxidized iron surface was reduced sufficiently to yield a SERS-active iron surface. The roughened electrode was then rinsed with Milli-Q water and transferred to the spectroelectrochemical cell for the Raman measurements.

All chemicals used were of analytical reagent grade, and the electrolyte solutions were prepared using Milli-Q water.

## Results

Figure 1(a–c) compares the normal Raman spectra of solid thiourea, 0.1 M thiourea solution, and the typical SERS spectrum obtained at  $-0.6$  V at an electrochemically activated iron electrode in 0.1 M TU and 0.1 M  $\text{NaClO}_4$ . Assignment of the different vibrational bands is performed by combining the information from the spectra and from the literature.<sup>8,10,19–21</sup> The Raman spectrum of solid thiourea exhibits four strong bands in the frequency region 200–1700  $\text{cm}^{-1}$ . Specifically, the main Raman bands are observed at 481, 735, 1094, and 1385  $\text{cm}^{-1}$ . These bands, corresponding to the vibrational transition frequencies for thiourea, are assigned to NCN bending, CS stretching, strong coupling of NCN stretching with the  $\text{NH}_2$  group rocking, and NCN symmetric stretching modes, respectively. Of the four main Raman bands, the CS stretching mode gives the strongest band intensity, followed by the NCN bending mode. In addition, minor bands are also evident at 403  $\text{cm}^{-1}$  ( $\text{NH}_2$  torsion) and 1614 and 1637  $\text{cm}^{-1}$  ( $\text{NH}_2$  deformation). Note that the SCNN out-of-plane bending mode was not observable because of low polarizability and hence low intensity in the present Raman spectrum of solid thiourea, but it does exist at ca. 629  $\text{cm}^{-1}$  in



**Figure 1.** (a) Normal Raman spectrum of solid thiourea; (b) Normal Raman spectrum of thiourea in 0.1 M thiourea and 0.1 M  $\text{NaClO}_4$ ; (c) SERS spectrum of thiourea adsorbed on an electrochemically activated iron electrode in 0.1 M thiourea and 0.1 M  $\text{NaClO}_4$ . Laser line: 632.8 nm; acquisition time: 10 s; accumulation: 4.

the infrared spectrum of thiourea<sup>22</sup> (this vibrational mode appears as a weak band in the SERS spectrum, see later).

Although the normal Raman spectrum of thiourea in solution (see Figure 1b) shows good agreement with that of solid thiourea, some minor changes in the band frequency can also be observed. For instance, The CS stretching and NCN symmetric modes are observed to shift to 729 and 1395  $\text{cm}^{-1}$  respectively. This may be caused by the perturbation of the solvent and also probably by the supporting electrolyte. The Raman lines at ca. 630 and 933  $\text{cm}^{-1}$  come from the electrolyte anion  $\text{ClO}_4^-$ . The 1638  $\text{cm}^{-1}$  band can be attributed to the combination of the  $\text{NH}_2$  deformation of thiourea and the bending mode of water.

A typical in situ SERS spectrum of thiourea on iron is also presented in Figure 1c. It should be noted here that the observation of the SERS spectrum of thiourea is mainly due to the use of a confocal Raman system and a proper surface roughening pretreatment for the iron electrode, which is described in the Experimental Section. To the best of our knowledge, it is the first time that one is able to obtain the SERS spectrum of thiourea at a bare iron electrode. The proper roughening method plays a key role in the observation of SERS effect of iron. Four roughening pretreatments, including chemical etching, deposition of iron on an iron electrode, and ex situ and in situ electrochemical orc have been tried to obtain the SERS spectra.<sup>15</sup> The ex situ orc employed in the presently studied system was responsible for the resulting high intensity in the spectrum. The calculated SEF was enhanced 2- to 3-fold using the unique method for calculating SEF based on the confocal Raman system.<sup>16</sup> The lightning rod effect was proposed to give interpretation to the enhancement effect.<sup>23</sup> Briefly, the polarization of the metal in the external electric field produces a strong local field in the vicinity of the sharpest surface feature, such as an ellipsoid. Molecules adsorbed on the tip of such an ellipsoid experience this field and hence give out enhanced Raman scattering. The detailed discussion of the enhancement mechanism for iron can be found in ref 16. For comparison purposes, the experiment concerning the surface Raman spectrum of thiourea adsorbed on a smooth iron electrode was also performed. The reason is that the adsorption characteristics of organic molecules on electrochemically roughened electrodes are substantially different from those on smooth electrodes, as

**TABLE 1: Assignment of Vibrational Bands in the Normal Raman Spectrum of Thiourea and the SERS Spectra for Adsorption of Thiourea and Perchlorate Species at an Iron Electrode<sup>8,10,19–21</sup>**

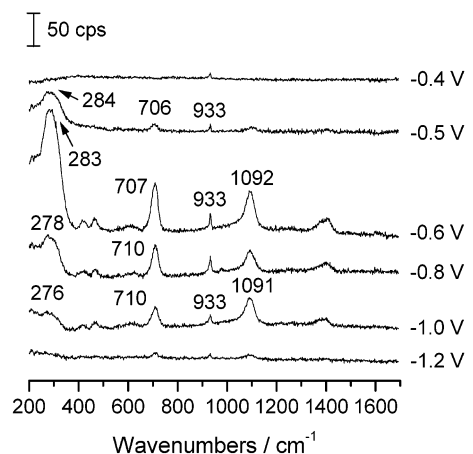
assignments	normal Raman (solid)	normal Raman (solution)	SERS on iron (−1.0 V)	SERS on iron (−0.6 V)
Fe–S stretching			276 <sup>w</sup> <sup>a</sup>	283 <sup>vs</sup>
NH <sub>2</sub> torsion	403 <sup>w</sup>	406 <sup>w</sup>	413 <sup>w</sup>	413 <sup>w</sup>
NCN bending	481 <sup>s</sup>	476 <sup>s</sup>	465 <sup>w</sup>	464 <sup>w</sup>
deformation of ClO <sub>4</sub> <sup>−</sup>		630 <sup>s</sup>		
SCNN out-of-plane bending			611 <sup>w</sup>	610 <sup>w</sup>
CS stretching	735 <sup>vs</sup>	729 <sup>s</sup>	710 <sup>s</sup>	707 <sup>s</sup>
totally symmetric stretching of ClO <sub>4</sub> <sup>−</sup>		933 <sup>vs</sup>	933 <sup>m</sup>	933 <sup>s</sup>
NH <sub>2</sub> rocking and NCN stretching	1094 <sup>s</sup>	1094 <sup>s</sup>	1091 <sup>s</sup>	1092 <sup>s</sup>
NH <sub>2</sub> rocking	1371 <sup>m</sup>	1380 <sup>m</sup>	1372 <sup>m</sup>	1375 <sup>m</sup>
NCN symmetric stretching	1385 <sup>s</sup>	1395 <sup>m</sup>	1394 <sup>s</sup>	1403 <sup>s</sup>
NCN antisymmetric stretching	1471 <sup>w</sup>	1482 <sup>w</sup>		
NH <sub>2</sub> deformation	1614 <sup>w</sup>			1609 <sup>w</sup>
NH <sub>2</sub> deformation	1637 <sup>w</sup>	1638 <sup>m</sup>		

<sup>a</sup> Wavenumbers (in cm<sup>−1</sup>) followed by relative intensities (vs, very strong; s, strong; m, medium; w, weak).

suggested by Stolberg for pyridine adsorption on gold.<sup>24</sup> However, the surface spectra obtained under the present conditions did not exhibit any characteristic of thiourea at a smooth iron electrode. Consequently, all further discussion will be confined to the SERS spectra obtained from the roughened iron electrodes.

The SERS spectrum in Figure 1c presents new bands and some frequency shifts of vibrational modes in relation to the normal Raman spectrum of thiourea in solution. For instance, the NCN bending is shifted from 476 to 464 cm<sup>−1</sup>, indicating some structural changes after adsorption of thiourea molecules onto the iron surface. The intense band of CS stretching observed in the spectrum of thiourea in solution has the largest frequency shift from 729 to 707 cm<sup>−1</sup>, which is in good agreement with those observed at other metal electrodes such as copper,<sup>8</sup> silver,<sup>9,10,25</sup> and gold.<sup>26</sup> This marked red shift of frequency may be indicative of a large weakening of the CS double bond. It can be seen from Figure 1 that the decrease in frequency of the CS band is also accompanied by the increase of the frequency of NCN symmetric stretching mode. The latter is blue-shifted from 1395 to 1403 cm<sup>−1</sup> in the SERS spectrum. The detailed analysis of these two bands will be given in the Discussion. Additionally, a shift of the 1094 cm<sup>−1</sup> band frequency is small and within 5 cm<sup>−1</sup>. Changes of the relative band intensity have also been observed. For instance, the ratio of the integrated intensity of the 729 cm<sup>−1</sup> band to that of the 1094 cm<sup>−1</sup> band changes from ca. 1.8 to 1.2. Another interesting feature in Figure 1c is that the NCN bending mode decreases significantly in intensity compared to other vibrational modes.

One of the most striking features is the observation of a new band located at ca. 283 cm<sup>−1</sup> in the low-frequency region. It does not correlate with any intramolecular vibrational bands of thiourea but relates to the metal–adsorbate vibrations, which is indicative of the strong interaction of thiourea with iron surface. This again shows the advantage of the confocal Raman technique over infrared and SFG. Additionally, a new band, albeit rather weak, was also detectable and observed at ca. 610 cm<sup>−1</sup>. As was mentioned above, it can be designated to the SCNN out-of-plane bending mode. Analysis of this band as a function of applied potential gives useful information about the orientation changes of thiourea on iron. The SERS spectrum in Figure 1c also shows a very intense band at 933 cm<sup>−1</sup> that arises from the totally symmetric stretching mode of the electrolyte anion ClO<sub>4</sub><sup>−</sup>. Despite no changes of the frequency of this band compared to the free anion, the enhanced band intensity is also indicative of coadsorption of this species with thiourea. Similar observations have been obtained in previous SERS studies of



**Figure 2.** Representative potential-dependent surface Raman spectra for thiourea adsorbed onto a roughened iron electrode in the same solution with that in Figure 1b in the frequency region 200–1800 cm<sup>−1</sup>. Potentials were changed stepwise positively (see text). Laser line: 632.8 nm; acquisition time: 10 s; accumulation: 4.

thiourea on copper and silver.<sup>8</sup> Some minor bands at ca. 413 cm<sup>−1</sup> (NH<sub>2</sub> torsion) and 1609 cm<sup>−1</sup> (NH<sub>2</sub> deformation) are also detected in the SERS spectra. A summary of the normal Raman and SERS vibrational frequencies for thiourea together with ClO<sub>4</sub><sup>−</sup> is presented in Table 1.

To facilitate the analysis of the interaction of thiourea with the iron surface and also the coadsorption with perchlorate anions, the potential dependency of the SERS spectra of thiourea was investigated. A representative series of potential-dependent SERS spectra of thiourea on an electrochemically activated iron electrode is shown in Figure 2. The electrolyte solution was the same as that used in Figure 1c. The measurements were carried out stepwise from the negative extremity of the potential to more positive values with the spectral acquisition time of 10 s. Prior to the Raman measurement, the iron electrode was polarized at −1.4 V for 5 min to reduce any possible contamination from surface oxides. Note that each spectral line has been obtained by subtraction of that acquired at −1.4 V (not shown here), where all the Raman bands are rather weak and arise mainly from the interference of solution thiourea and perchlorate anion. The subtraction method hence eliminated such interference from bulk solution.

As can be seen from Figure 2, the SERS spectrum of thiourea obtained at −1.2 V is rather poor, indicating also weak interaction of thiourea with iron. The signal-to-noise of the spectrum is enhanced greatly when the electrode is polarized at −1.0 V. Most of the characteristic bands of thiourea together



with a low-frequency mode at ca.  $276\text{ cm}^{-1}$  appear at this potential. The SERS intensity is seen to reach a maximum near  $-0.6\text{ V}$ , which is inconsistent with the results from copper and silver.<sup>27</sup> It is possibly caused by the different natures of the substrate. The use of halide as supporting electrolyte can also alter the potential value for maximum intensity, as was found by Loo and co-workers.<sup>8</sup>

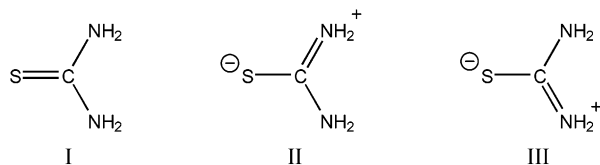
The SERS spectra in Figure 2 also shows some frequency shifts of vibrational modes with variation of applied potential. For instance, the CS stretching mode is shifted to lower frequencies when the potential becomes more positive, while the  $1091\text{ cm}^{-1}$  band ( $-1.0\text{ V}$ ) shows no apparent shift of frequency. More interestingly, the two bands reverse in intensity on scanning potential from  $-1.0$  to  $-0.6\text{ V}$ . The low-frequency mode revealing the metal-adsorbate interaction and the NCN symmetric stretching is also observed to shift to higher frequency values when the potential is changed to more positive values. This may be suggestive of stronger interaction of adsorbate with the substrate. Additionally, other minor bands including the  $\text{NH}_2$  torsion, NCN bending and the SCNN out-of-plane bending remain almost constant in frequency with positive-going potentials.

Another interesting feature in Figure 2 is the observation of the constant frequency of the  $933\text{ cm}^{-1}$  band, arising from the totally symmetric stretching mode of  $\text{ClO}_4^-$ , indicating no direct interaction or rather weak interaction of this anion with the iron surface. However, the band intensity rises simultaneously with those characteristic of thiourea with increasing positive potential less than  $-0.6\text{ V}$ . This is good evidence that  $\text{ClO}_4^-$  is coadsorbed with thiourea on iron. The potential dependency of the  $\text{ClO}_4^-$  band at  $933\text{ cm}^{-1}$  in the SERS spectra suggests further interesting characteristics of the adsorption of thiourea at the iron surface in sodium perchlorate solution.

## Discussion

As is mentioned in the Introduction, thiourea has been known as a highly efficient inhibitor for iron.<sup>4</sup> However, little direct information at the molecular level related to the thiourea-iron interaction has been obtained heretofore, despite much information obtained from copper and silver SERS.<sup>8-10</sup> The present communication provides direct evidence for the adsorbate-iron interaction. Specifically the ability to detect the low-frequency vibrations is very helpful to the detailed analysis.

The large red shift of the frequency of the CS stretching mode from  $729\text{ cm}^{-1}$  in the bulk solution to ca.  $710\text{ cm}^{-1}$  in the SERS spectrum has been observed for copper and silver by many researchers<sup>8-10</sup> and has been interpreted as adsorption of thiourea via the sulfur atom on the metal surface.<sup>25</sup> It is hence reasonable to assume that the similar observation of such marked shifting of the frequency of the CS stretching also suggests S-coordination of thiourea with the iron surface. It is well-known that thiourea has equal contributions from the following cononical forms:



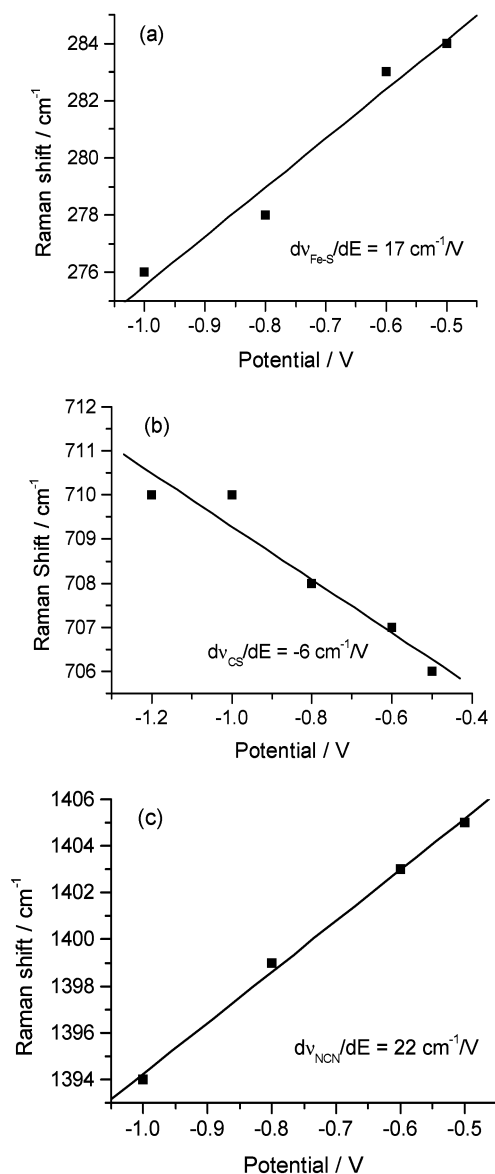
Provided that thiourea is bonded to metal surface through the sulfur atom, the contributions from the canonical forms II and III will increase, resulting in a decrease in CS and an increase in CN bond order for the coordinated species. A

corresponding weakening and strengthening of the CS and CN bonds respectively should be obtained. The above red shift of the CS stretching and blue shift of the NCN symmetric stretching from  $1395\text{ cm}^{-1}$  in the solution to  $1403\text{ cm}^{-1}$  in the SERS spectrum (see Table 1) support these changes. In the studies of the interaction of thiourea with a copper electrode by Brown and co-workers, even the absence of the CS double bond and the appearance of the CS single bond stretching located at ca.  $466\text{ cm}^{-1}$  were observed.<sup>28,29</sup> This may be indicative of the stronger interaction of thiourea with copper.

The low-frequency mode observed at  $283\text{ cm}^{-1}$  ( $-0.6\text{ V}$ , Figure 1) could then be assigned to Fe-S stretching, confirming the above assumption of S-coordination of thiourea. In a previous study of adsorption of pyridine on iron, we observed a band at ca.  $240\text{ cm}^{-1}$  arising from Fe-N stretching.<sup>15</sup> Note that the frequency is much less than the present observation, indicating no direct Fe-N interactions existing in the case of thiourea. Further, if thiourea adsorbs via nitrogen atom, the NH bond would be weakened. This is apparently inconsistent with the slight blue shift of the NH torsion mode (see Table 1). Additionally, a decrease in relative intensity of the NH torsion mode would also be expected for N adsorption. In fact, the relative intensity of this mode to the CS stretching is enhanced greatly (see Figure 1). Therefore, any direct interaction of the nitrogen atom with the surface can be ruled out in the case of thiourea. The vibration revealing the direct interaction of thiourea with a metal surface was also observed by researchers at ca.  $197\sim 220\text{ cm}^{-1}$  for gold,<sup>11,26</sup>  $240\text{ cm}^{-1}$  for silver,<sup>30</sup> and ca.  $280\text{ cm}^{-1}$  for copper,<sup>8,28</sup> depending on the different atomic mass of the substrate. Consequently, the above assignment of the Fe-S stretching is quite reasonable, since the atomic mass of iron approaches that of copper but is far less than that of silver and gold.

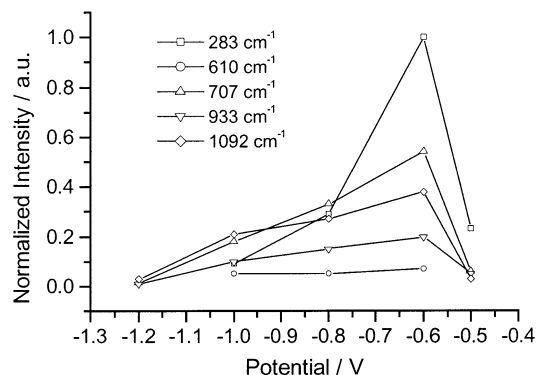
All these results suggest that the thiourea molecule is coordinated through sulfur atom and is probably oriented perpendicular to the iron surface. However, a band arising from the SCNN out-of-plane bending mode was also observed at ca.  $610\text{ cm}^{-1}$  in the SERS spectrum (see Figure 1). This band is detectable in the infrared spectrum but not observable in the normal Raman spectrum of thiourea because of low polarizability.<sup>22</sup> It was considered by some authors as an indication of orientation of the adsorbed thiourea.<sup>31,32</sup> For instance, in a previous study Fleischmann and co-workers<sup>31</sup> reported that this band, appearing at  $612\text{ cm}^{-1}$ , rose in intensity with increasing negative potential. They attributed it to a change in the orientation with respect to the surface, from essentially perpendicular to parallel orientation. A possible explanation for the great enhancement in intensity of this band in the SERS spectrum could be the image field effect,<sup>33,34</sup> as proposed by Fleischmann et al.<sup>31</sup> Briefly, if the image of the dipole perpendicular to the surface inside the metal is considered, the molecular polarizability should increase when thiourea is lying flat on the surface. The appearance of the SCNN band in the presently studied system facilitates the parallel orientation of thiourea on iron. However, this explanation is apparently in conflict with the assumption that the CS bond is perpendicular to the surface (see above). Therefore, given the rather weak intensity of the SCNN band observed in the SERS spectrum, a slight departure from perpendicular orientation of thiourea on the iron surface is assumed, to reconcile the above two explanations.

Further information regarding the interaction between thiourea and the iron surface can be obtained by detailed analysis of the potential dependency of the SERS spectra (see Figure 2). As is



**Figure 3.** Dependence of the band frequency upon applied potential for (a)  $\nu_{\text{Fe-S}}$ , (b)  $\nu_{\text{CS}}$ , and (c)  $\nu_{\text{NCN}}$  (see text).

described in the Results section, several SERS bands of thiourea exhibit frequency shifts with increasing positive potential. To facilitate the following discussion, such relationships between band frequency and applied potential for the Fe–S stretching, CS stretching, and NCN symmetric stretching modes are represented respectively in Figure 3(a–c). The variations of the frequency of the three bands with potential ( $d\nu_{\text{Fe-S}}/dE$  and  $d\nu_{\text{CS}}/dE$ ), usually designated as a Stark tuning rate,<sup>35</sup> were then calculated. The rate value for the CS stretching is relatively small ( $-6 \text{ cm}^{-1}/\text{V}$ ) compared with the other two modes. More interestingly, the CS stretching exhibits a negative Stark tuning rate, as is seen from Figure 3b. These observations could be interpreted well based on the proposition of S-coordination of thiourea on iron. As was proposed for the silver–thiourea interaction,<sup>31</sup> we assume that the strong iron–thiourea bond probably arises from  $\sigma$  donation from the ligand to empty metal d orbitals, along with back-donation from filled metal d orbitals to antibonding ligand orbitals. As the potential is made more negative, the iron–sulfur  $\sigma$  bond is weakened and hence the CS bond strengthened. At the same time there is increased back-donation from the filled iron d orbitals to the ligand antibonding orbital resulting in a weakened CS band and weakened CN



**Figure 4.** Dependence of the normalized Raman intensity upon applied potential for the major bands of thiourea together with the Fe–S and  $\text{ClO}_4^-$  vibrational bands as indicated.

bands. Therefore, an appreciable decrease in frequency for both the Fe–S and NCN stretching modes but little shift for the CS stretching with increasing negative potential should be observed. The experimental results support this behavior. These results above also show that the thiourea molecule may interact more strongly with the iron surface with positive-going potential. When the iron electrode is polarized at potentials positive to  $-0.5 \text{ V}$ , the thiourea molecule desorbs from the surface and hence the interactions also decrease for the oxidation of the surface, as is indicated by the increasing current flow from electrochemical measurements.

Figure 4 shows the dependence of the normalized integrated SERS intensity of the bands at 283, 610, 707, 933, and  $1092 \text{ cm}^{-1}$  respectively on the applied potential obtained from data of Figure 2. It is interesting to find that most of the bands, including the tetrahedral  $\text{ClO}_4^-$  band, exhibit the maximum intensity at the same potential  $-0.6 \text{ V}$ , which approaches the open circuit potential of the studied system ( $-0.58 \text{ V}$ ). According to the literature, the potential of zero charge (pzc) in a neutral solution for iron was reported at ca.  $-0.73 \text{ V}$  (vs SHE).<sup>36</sup> It is reasonable to assume that the adsorption of thiourea should not significantly alter the pzc value of the system studied in this paper. That is to say, the appearance of the SERS spectra of thiourea obtained at potentials particularly positive to  $-1.0 \text{ V}$  occurs mainly at the potential region positive to pzc. The positively charged iron surface, in particular at  $-0.6 \text{ V}$  where the maximum Raman intensity occurs, is then expected to facilitate the adsorption of anion. This behavior concurs with the known fact that when adsorbed onto Hg electrodes, thiourea behaves more like a surface active anion than as a neutral molecule.<sup>37</sup> Therefore, a surface coverage increase may contribute to the increase of Raman intensity as potential is shifted to more positive values. Additionally, the potential dependence of the Fe–S and CS stretching bands also support this point. As we know, when a neutral molecule is adsorbed onto the electrode surface, it would be expected to flip over as the potential of pzc is traversed, leading to large frequency shifts (especially for the CS band in this case). However, no such behavior is observed for thiourea, and hence a strong metal–sulfur bond should be expected to exist. The rather strong SERS intensity of this band, particularly at  $-0.6 \text{ V}$  compared with other bands (see Figure 4), is consistent with the above assumption.

It is also found from Figure 4 that although the absolute Raman intensity of the SCNN out-of-plane bending mode changes little in the potential range negative to  $-0.6 \text{ V}$ , the relative intensity of this band to that of the CS stretching decreases significantly with increasing positive potential. Based

on the aforementioned discussion, more thiourea molecules are then expected to be oriented perpendicular to the iron surface. The surface coverage increase with positive-going potential supports this for a more packed adsorption layer. The abrupt decrease in Raman intensity of all the bands as the potential is changed from  $-0.6$  to  $-0.5$  V, as is seen from Figure 4, can be explained by desorption of thiourea from the surface.

Another characteristic feature observed in Figure 4 is that the  $933\text{ cm}^{-1}$  band increases simultaneously in intensity with the bands related to thiourea, as is depicted in the Results section. It indicates coadsorption of this anion with thiourea, and this behavior has also been observed on other metals such as copper and silver. However, in the previous study of Fleischmann et al.,<sup>31</sup> the SERS band arising from  $\text{ClO}_4^-$  was observed only from acidified solution and there was no SERS signal of this anion from neutral solution. Upon lowering the pH, the SERS band of the coadsorbed anion was also observed to enhance greatly in intensity. This has been explained by protonation of the  $\text{NH}_2$  group, facilitating the electrostatic attraction of anions such as  $\text{ClO}_4^-$ . In the present neutral system, we assume that the  $\text{ClO}_4^-$  anion may be bonded to the H atom of the  $\text{NH}_2$  group.<sup>32</sup> However, this interaction would be expected to weaken compared with that formed in the acidified solution. Therefore, more thiourea molecules would be expected to be adsorbed onto the iron surface to facilitate the coadsorption of  $\text{ClO}_4^-$  and hence the observation of the SERS spectrum of the anion. The experimental results support this assumption. The ability to detect the coadsorbed  $\text{ClO}_4^-$  on iron in the neutral solution compared with copper and silver may also suggest a stronger interaction of thiourea with the iron surface. It is consistent with the higher inhibiting efficiency of thiourea for iron measured by the traditional electrochemical techniques.

## Summary

By using a confocal microprobe Raman system and the proper surface roughening pretreatment, the surface-enhanced Raman scattering spectra of thiourea on a bare iron electrode in  $0.1\text{ M NaClO}_4$  solution were observed for the first time. The interactions between anions, thiourea, and iron surfaces were established based on the analysis of the potential dependency of the SERS spectra. The main observations and conclusions have been summarized as follows.

1. The surface-enhanced Raman scattering spectra of thiourea adsorbed onto a roughened iron electrode in  $0.1\text{ M NaClO}_4$  ( $-0.6\text{ V}$ ) have been observed. The main Raman bands are observed clearly at ca.  $283$ ,  $707$ ,  $933$ ,  $1092$ , and  $1403\text{ cm}^{-1}$  and compared with the normal Raman spectrum of thiourea in solution. The electrochemical roughening pretreatment for the iron electrode plays a key role in obtaining the SERS spectra of thiourea.

2. The marked red shift of the CS stretching and blue shift of the NCN symmetric stretching by comparison with the normal Raman spectrum of thiourea in solution are clearly observed and interpreted by coordination of thiourea with the iron surface through sulfur atom.

3. The appearance of the low-frequency mode at ca.  $283\text{ cm}^{-1}$  assigned to the Fe–S vibration supports the assumption of S-coordination of thiourea with iron. The ability to detect the metal–adsorbate vibration in the present study owes mainly to the proper surface roughening pretreatment for iron and highlights again the advantage of Raman techniques. In combination with the detected SCNN out-of-plane bending mode at ca.  $610\text{ cm}^{-1}$  in the SERS spectrum ( $-0.6\text{ V}$ ), the thiourea molecule is expected to be inclined to the iron surface at an intermediate angle.

4. Different potential dependence of frequency of the Fe–S stretching, CS stretching and NCN symmetric stretching modes are observed. The corresponding Stark tuning rate for the three bands are calculated to be  $17$ ,  $-6$ , and  $22\text{ cm}^{-1}/\text{V}$ , respectively. These results show that as the potential is made more positive, thiourea may interact more strongly with the surface in the potential range negative to  $-0.6\text{ V}$ .

5. The SERS intensity of thiourea is found to reach a maximum near  $-0.6\text{ V}$ , which approaches the open circuit potential of the studied system and is far positive to the pzc. It suggests that thiourea may behave more like an anion than a neutral organic molecule. Changes of the relative intensity of the SCNN to the CS stretching band with increasing positive potential suggest that more thiourea molecules would be expected to be orientated perpendicular to the iron surface.

6. Coadsorption of the supporting electrolyte anion  $\text{ClO}_4^-$  with thiourea has been confirmed by the dependence of the SERS spectrum of the totally symmetric stretching band of  $\text{ClO}_4^-$  on the applied potential. The perchlorate anion is assumed to be bonded to the H atom of the  $\text{NH}_2$  group in the neutral solution.

**Acknowledgment.** This work was supported by the Science Foundation of Jiangsu Province and the financial support of State Key Laboratory for Physical Chemistry of Solid Surfaces of Xiamen University. The Raman spectroscopy experiments were carried out in Xiamen University. The authors thank the co-workers there for helpful discussions.

## References and Notes

- (1) Reents, B.; Plieth, W.; Macagno, V. A.; Lacconi, G. I. *J. Electroanal. Chem.* **1998**, *453*, 121.
- (2) Suarez, D. F.; Olsen, F. A. *J. Appl. Electrochem.* **1992**, *22*, 1002.
- (3) Szymaszek, A.; Biernat, J.; Pajdowski, L. *Electrochim. Acta* **1977**, *22*, 359.
- (4) Ateya, B. G.; El-Anadouli, B. E.; El-Nizamy, F. M. *Corros. Sci.* **1984**, *24*, 497.
- (5) Stankovic, Z. D.; Vukovic, M. *Electrochim. Acta* **1996**, *41*, 2529.
- (6) Frumkin, A. N.; Grigorev, N. B. *J. Electrochem. Soc.* **1972**, *119*, 1695.
- (7) Bockris, J. O'M.; Habib, M. A.; Cabarjal, J. L. *J. Electrochem. Soc.* **1984**, *131*, 3032.
- (8) Loo, B. H. *Chem. Phys. Lett.* **1982**, *89*, 346.
- (9) Tian, Z. Q.; Li, W. H.; Mao, B. W.; Gao, J. S. *J. Electroanal. Chem.* **1994**, *379*, 271.
- (10) Macomber, S. H.; Furtak, T. E. *Chem. Phys. Lett.* **1982**, *90*, 439.
- (11) Gao, P.; Patterson, M. L.; Tadayoni, M. A.; Weaver, M. J. *Langmuir* **1985**, *1*, 173.
- (12) Fleischmann, M.; Tian, Z. Q.; Li, L. J. *J. Electroanal. Chem.* **1987**, *217*, 397.
- (13) Zou, S.; Williams, C. T.; Chen, E. K-Y.; Weaver, M. J. *J. Am. Chem. Soc.* **1998**, *120*, 3811.
- (14) Zou, S.; Williams, C. T.; Chen, E. K-Y.; Weaver, M. J. *J. Phys. Chem. B* **1998**, *102*, 9039.
- (15) Gu, R. A.; Cao, P. G.; Yao, J. L.; Ren, B.; Xie, Y.; Mao, B. W.; Tian, Z. Q. *J. Electroanal. Chem.* **2001**, *505*, 95.
- (16) Cao, P. G.; Yao, J. L.; Ren, B.; Gu, R. A.; Tian, Z. Q. *Chem. Phys. Lett.* **2000**, *316*, 1.
- (17) Cao, P. G.; Yao, J. L.; Zheng, J. W.; Gu, R. A.; Tian, Z. Q. *Langmuir* **2002**, *18*, 100.
- (18) Cao, P. G.; Yao, J. L.; Ren, B.; Gu, R. A.; Tian, Z. Q. *J. Phys. Chem. B* **2002**, *106*, 7283.
- (19) Yamaguchi, A.; Penland, R. B.; Mizushima, S.; Lane, T. J.; Curan, C.; Quagliano, J. V. *J. Am. Chem. Soc.* **1958**, *80*, 527.
- (20) Dollish, F. R.; Fateley, W. G.; Bentley, F. F. In *Characteristic Raman Frequencies of Organic Compounds*; John Wiley: New York, 1974.
- (21) Ishiguro, T.; Suzuki, E.; Hirakawa, A. Y.; Tsuboi, M. *J. Mol. Spectrosc.* **1980**, *83*, 360.
- (22) Stewart, J. E. *J. Chem. Phys.* **1957**, *26*, 248.
- (23) Gersten, J.; Nitzan, A. *J. Chem. Phys.* **1980**, *73*, 3023.
- (24) Stolberg, L.; Lipkowski, J.; Irish, D. E. *J. Electroanal. Chem.* **1991**, *300*, 563.

- (25) Reents, B.; Plieth, W.; Macagno, V. A.; Lacconi, G. I. *J. Electroanal. Chem.* **1998**, 453, 121.
- (26) Holze, R.; Schomaker, S. *Electrochim. Acta* **1990**, 35, 613.
- (27) Macomber, S. H.; Furtak, T. E. *Chem. Phys. Lett.* **1982**, 90, 59.
- (28) Brown, G. M.; Hope, G. A.; Schweinsberg, D. P.; Fredericks, P. M. *J. Electroanal. Chem.* **1995**, 380, 161.
- (29) Brown, G. M.; Hope, G. A. *J. Electroanal. Chem.* **1996**, 413, 153.
- (30) Joy, V. T.; Srinivasan, T. K. K. *Spectrochim. Acta* **1999**, 55, 2899.
- (31) Fleischmann, M.; Hill, I. R.; Sundholm, G. *J. Electroanal. Chem.* **1983**, 157, 359.
- (32) Tian, Z. Q.; Lian, Y. Z.; Fleischmann, M. *Electrochim. Acta* **1990**, 35, 879.
- (33) King, F. W.; Van Duyne, R. P.; Schatz, G. C. *J. Chem. Phys.* **1978**, 69, 4472.
- (34) Schatz, G. C. In *Surface Enhanced Raman Scattering*; Chang, R. K., Furtak, T. E., Eds.; Plenum Press: New York, 1982; p 35.
- (35) Lambert, D. K. *Electrochim. Acta* **1996**, 41, 623.
- (36) Rybalka, L. E.; Leikis, D. I.; Zelinskii, A. G. *Elektrokhim.* **1976**, 12, 1340.
- (37) Parsons, R. *Proc. R. Soc.* **1961**, A261, 79.