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Spectroscopy Letters

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597299>

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To cite this Article Cao, Qing , Li, Fengting , Lu, Yun and Xue, Gi(1998) 'The Adsorption of 2-Mercaptoethanol on Silver Mirror and HCl-Etched Iron', *Spectroscopy Letters*, 31: 1, 167 — 175

To link to this Article: DOI: 10.1080/00387019808006770

URL: <http://dx.doi.org/10.1080/00387019808006770>

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THE ADSORPTION OF 2-MERCAPTOETHANOL ON SILVER MIRROR AND HCl-ETCHED IRON

Key words: 2-mercaptoethanol, HCl-etched iron surface, silver mirror;
Fourier transform surface enhanced Raman scattering

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ABSTRACT

The direct chemical deposition of silver on HCl-etched iron surface was first found to be able to present a SERS-active iron substrate. This method was used to study the adsorption of 2-mercaptoethanol on iron surface. For the propose of comparison, the adsorption of this substance on silver mirror was investigated. The results compounds could be chemisorbed HCl-etched iron plate and silver mirror surface in similar state and form a self-assembled monolayer of their thiolates.

INTRODUCTION

Surface-enhanced Raman scattering (SERS) has enjoyed widespread interest since its discovery in 1977, many researches were reported in the following years¹⁻². Organosulfur derivatives coordinate strongly to many metal surfaces and form

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monomolecular films. In 1983 Nuzzo, et al., first reported the organic surface phase by the immersion of a clean gold substrate in a solution of a long chain ω -substituted alkylthiol or dialkyldisulfide³. Porter, et al., presented data on monolayers of alkanethiols adsorbed on gold, using optical ellipsometry, infrared spectroscopy, and electrochemistry to characterize the monolayers⁴. These thiols and disulfides are adsorbed on metal surfaces from solution by the formation of covalent-like bond between metal and sulfur atoms following the cleavage of a sulfur-hydrogen bond or sulfur-sulfur bond. So far, a lot of SERS investigations have focused the preparation methods and characterization of the self-assembled layer of above compounds on noble metals. These methods include metal sols⁵, metal island films⁶, and HNO_3 etched metal foils⁷.

Up to now, there are a few of reports about adsorption of organic sulfide on noble metal surface. About the SERS on non-noble metal such as iron, aluminum, there is little reports. Most SERS spectra of some organic compounds adsorbed on iron in NaCl solution were recorded in situ by a SERS-active silver electrode coated with a suitable amount of deposited iron⁸. The overpotential deposition technique has also made it possible to obtain the SERS spectra of species adsorbed on such metals other than iron as lead, thallium, zinc, nickel, and cobalt⁹⁻¹¹. Because of the wide application of non-noble metals, now it is paid more attention to the methods to obtain surface information on these SERS-nonactive metal surface.

The work present here described that 2-mercaptoethanol on HCl-etched iron plates from ethanol solution. For the propose of compasion, FT-SERS spectra of them on silver mirror are also investigated.

EXPERIMENTAL

Materials: 2-mercapto-ethanol was obtained as high-grade commercial reagent and was used without further purification. Iron plates were available commercially (composition: C<0.08%; Mn:0.25-0.50%; Si<.03%; S<0.03%; P<0.02%). All chemicals except the iron plates, were analytical grade from a commercial source.

Solutions were made with distilled, deionized water. Silver foil (0.025mm, 99.99% pure) was purchased from Aldrich Co.

The sampling methods of 2-mercapto-ethanol and ferric hydroxide: The iron plate was cut into pieces of 10-mm×10-mm and immersed into 10-20% HCl solution (weight percent) at room temperature. After several minutes, a number of tiny bubbles had formed near the surface of iron. A light gray and sponge-like surface with substantial roughness was created. The etched iron plates were thoroughly rinsed with distilled water and then dipped into 2-mercapto-ethanol solution in ethanol at room temperature for five minutes. In every sampling procedure the plates were kept wet. After being withdrawn, they were washed with alcohol, and then dipped in 0.001 M AgNO₃ solution for a minute and the excess liquid was washed with water. The samples were dried in air and were ready for FT-SERS measurement. Details of the preparation of the silver mirror for SERS studies have already been described previously¹². Briefly, in a 10 mL beaker were a few of 10mm×10mm×1mm glass plates, which had been washed with water and acetone. We mixed 5 mL 0.1 M silver ammonia complex and 5 mL 5% formaldehyde in the beaker. A few of seconds later, the solution turned gray and black. Meanwhile the silver ions were reduced and deposited on the glass plates to form a fine silver film which was called a silver mirror. After withdrawing the silver mirror was washed with distilled water and then it was dipped in 2-mercaptoethanol solution. For comparison, the adsorption of Fe(OH)₃ from solution was investigated. The pH values of solution was adjusted by adding dropwise a aqueous 0.001 M KOH or 0.001 M HCl solutions. Under stirring, when the pH value approached to about 6.0, the ferric hydroxide precipitated as floc and was adsorbed to the silver mirror surface. After being withdrawn, the silver mirror dried in air and then measured.

Instrumentation: The samples were investigated on a Bruker model RFS 100 Fourier Raman spectrometer, consisting of an air-cooled diode pumped Nd-YAG laser and Ge-detector, which was cooled to liquid nitrogen temperature. The incident laser excitation was 1064 nm with an output of 50, 150, and 350 mW for 2-mercaptoethanol, iron samples and silver mirror, respectively. The spectral resolution was 4.0 cm⁻¹. The 2-

mercaptoethanol liquid is sealed in glass capillaries and measured. The scattered light was collected at the angle of 180° .

RESULTS AND DISCUSSION

Fig.1 presented the FT-SERS of the adsorbed ferric hydroxide on the silver mirror surface. The intense band at about 555 cm^{-1} and weak band at 1079 cm^{-1} were assigned to this hydroxide. The depositing process of Ag^+ on freshly etching iron surface is a redox in neutral solution as shown in following equation. The reduced silver was attached to the surface, meanwhile, iron was oxidized to ferrous and ferric ions and they dissolved in the solution and diffused off the surface. In neutral medium, ferrous ion was easily oxidized by the oxygen dissolved in the solution or distilled water to ferric ion, which hydrolyses easily to form ferric hydroxide and can adsorb on the tiny silver particles on the iron surface. When measured, the iron surface deposited with silver present distinct ferric hydroxide band, which was usually in the region of $550\text{--}570\text{ cm}^{-1}$. In the SERS spectra of iron surface covered with sulfide, it was difficult to identify the weak band at 1079 cm^{-1} . From the comparison of Fig.1 A, B, and C, we can conclude the chemically reduced silver can effectively enhance the signals of adsorbates.

ω -Substituted alkanethiols easily react with freshly polished silver surface and silver sols to form monolayer by the chemisorption of the S head group to the metal substrate¹. Of particular interest for our study are those spectral regions sensitive to the presence of trans and gauche conformation of the adsorbed 2-mercaptoethanol, the C-S stretching region ($600\text{--}750\text{ cm}^{-1}$)^{14,15}, the C-H stretch region ($2800\text{--}3000\text{ cm}^{-1}$), and the weak S-Ag stretch mode ($200\text{--}250\text{ cm}^{-1}$)¹⁶. In some cases the S-Ag band is so weak that it is difficult to identify it. The chemisorption can be confirmed by the formation of metal-sulfur bond, the disappearance of S-H bands and the shift of C-S bands in FT-SERS spectra. The C-S modes are interesting of the spectral signals they can tell us the molecular conformation of the adsorbed molecules.

Fig.2 showed: A, the normal FT-Raman spectrum of 2-mercapto-ethanol; B: FT-SERS spectrum of 2-mercapto-ethanol adsorbed on the silver mirror surface and C:

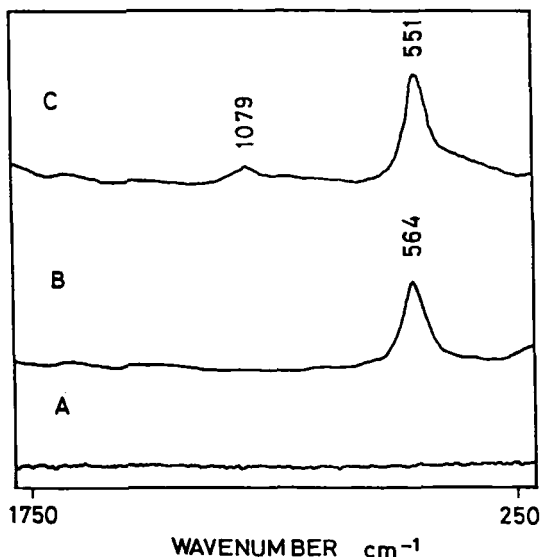


FIG.1 FT-SERS spectra of (A) neat HCl etched iron plate, (B) HCl etched iron coated with Ag by immersion in silver nitrate solution for 60s (There is no organic samples adsorbed on the specimen surface), (C) Ferric hydroxide adsorbed on silver mirror.

FT-SERS spectrum of 2-mercapto-ethanol adsorbed on the iron surface. The outstanding features in going from A to B and C were the disappearance of the S-H stretching band at 2557 and significant broadening and wavenumber lowering of the trans and gauche S-C stretching bands. Fig.2C also exhibited an intense vibration band of ferric hydroxide at 560 cm^{-1} . The missing S-H stretching band around 2566 cm^{-1} for the surface species indicates the expected covalent bonding of the sulfur atoms to silver surface and iron surface. In addition, the absence of S-H intensity in the self-assembled monolayer films from solution suggested that there was no free 2-mercapto-ethanol present. Being bonded to the metal surface through the S atom, the 2-mercapto-ethanol would be changed to 2-hydroxyethanethiolate.

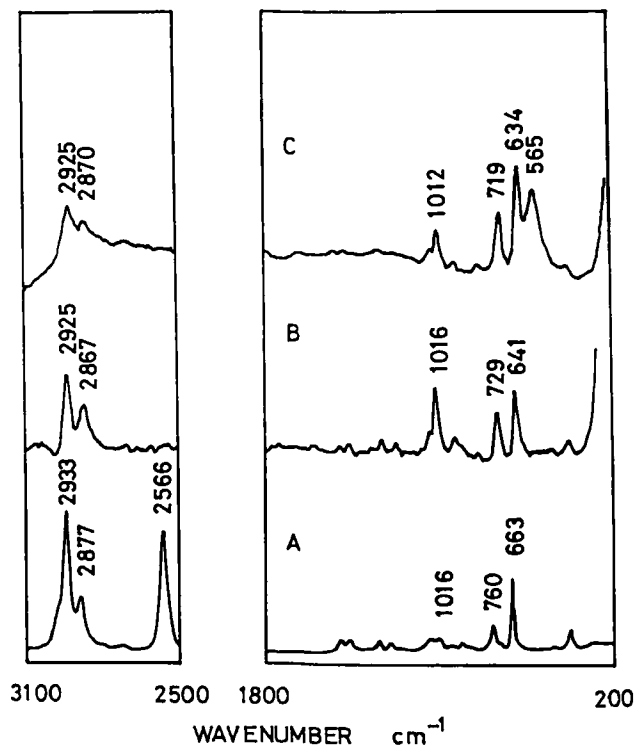


FIG. 2. Normal Raman spectrum of liquid mercaptoethanol(a), SERS spectra of the same substance adsorbed on silver mirror surface(b), and on HCl-etched iron surface.

For short-chained alkyl thiols, vibrational spectra and force field calculations indicate that the 650 cm^{-1} stretch originates from gauche rotamers while the 700 cm^{-1} stretch originates from trans rotamers¹⁷. The C-S stretching vibrations belong to the strongest bands in both spectra. They are characteristic for gauche (bands at 663 , 641 cm^{-1} and 634 cm^{-1} A through C) or trans conformation (bands at 760 , 729 cm^{-1} and 719 cm^{-1}) of 2-mercaptoethanol and its species on silver and iron surface. The trans (T) and gauche (G) C-S vibration band intensities were taken as a measure of actual number of trans bonds and gauche bands in the molecule or in adsorbed one. Table 1

Table 1. The relative intensity ratios $I_{TC(C-S)}$ of 2-mercaptoethanol and its thiolate adsorbed on silver mirror surface and HCl-iron surface

liquid state	on silver mirror	on iron
0.32	0.75	0.58

summarizes the intensity ratios $I_{TC(C-S)}$ of trans rotamers over gauche rotamers. The appearance of both C-S bands for the adsorbed 2-mercaptoethanol with large trans/gauche intensity ratio than for the liquid 2-mercaptoethanol shows that the adsorbed layer exhibits mixed conformation with a large portion of trans-conformed molecules, which may be related to ordering processes at the surface.

The shift of the C-S bands of the surface species towards lower wavenumber should be related to withdrawal of electron density from the C-S bond due to bonding of the sulfur to silver or to iron. The different shifts of C-S band in the SERS spectra of silver and iron from normal 2-mercaptoethanol confirmed that 2-mercaptoethanol were adsorbed on iron surface, not on the deposited silver particles. The deposited silver induced the iron surface electric field under incident laser.

The significant increase in intensity ratio for the FT-SERS spectra over the liquid spectra suggested that the C-S bond had a significant component perpendicular to the surface and they were ordered on the surface in more trans conformations than them in liquid form.

CONCLUSION

The adsorption on 2-mercaptoethanol on silver mirror surface and HCl etched iron surfaces were characterized by Fourier transform surface enhanced Raman scattering spectroscopy (FT-SERS). The normal FT-Raman and FT-SERS spectra led the conclusion that by the split of S-H bond, 2-mercaptoethanol could be adsorbed on the silver and the iron surface to form their thiolates and the iron substrate chemically deposited with silver exhibited relative significant Raman enhancement. The thiolates

were ordered in trans and gauche conformation. On the iron surface, the most thiolates were packed in gauche conformation as they in liquid state, while on the silver surface the thiolates tended to order in trans conformation.

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Date Received: June 25, 1997

Date Accepted: August 3, 1997