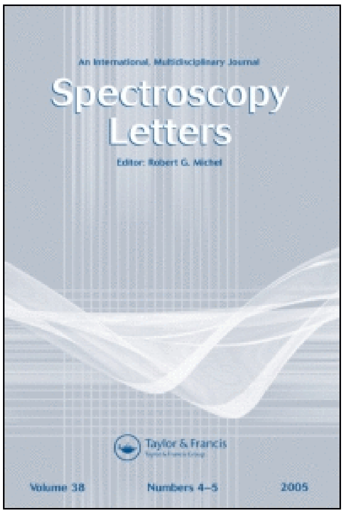

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

FT-Raman Surface Enhanced Scattering Study of the Adsorption of 10-Mercapto-1-decanol and Cefazolin Sodium on Chemically Reduced Silver Film

Zuoying Xue[a]; Jiacai Wang[a]; Jianghua Zhang[a]; Yanli Yu[a]; Cheng Yuan[a]
[a] Chinese PLA Jinan General Hospital, Jinan, R.P. China

To cite this Article Xue, Zuoying , Wang, Jiacai , Zhang, Jianghua , Yu, Yanli and Yuan, Cheng(1997) 'FT-Raman Surface Enhanced Scattering Study of the Adsorption of 10-Mercapto-1-decanol and Cefazolin Sodium on Chemically Reduced Silver Film', Spectroscopy Letters, 30: 8, 1649 — 1654
To link to this Article: DOI: 10.1080/00387019708006749
URL: http://dx.doi.org/10.1080/00387019708006749

SPECTROSCOPY LETTERS, 30(8), 1649-1654 (1997)

FT-RAMAN SURFACE ENHANCED RAMAN SCATTERING STUDY OF THE ADSORPTION OF 10-MERCAPTO-1-DECANOL AND CEFAZOLIN SODIUM ON CHEMICALLY REDUCED SILVER FILM

Key words: Fourier transform Surface Enhanced Raman Scattering spectroscopy (FT-SERS), 10-mercapto-1-decanol, Cefazolin sodium, silver mirror, self-assembled monolayer film.

Zuoying Xue*, Jiacai Wang, Jianghua Zhang, Yanli Yu and Cheng Yuan

Chinese PLA Jinan General Hospital, Jinan, 250031, R.P. China.

ABSTRACT

Chemisorption and conformation of 10-mercapto-1-decanol and Cefazolin sodium on chemically reduced silver film have been observed by Fourier transform Surface Enhanced Raman Scattering spectroscopy (FT-SERS). These compounds can easily be chemisorbed on silver film by the cleavage of S-H or nitrogen and sulfur coordination to form self-assembled monolayers.

INTRODUCTION

Organic sulfur derivatives coordinate strongly to some metal surfaces and form monomolecular films. Nuzzo, et al. showed that dialkyl disulfides formed oriented monolayers on metal from solutions [1]. The monolayer was well organized and endowed the metals attached many special properties such as wetting, adhesion, anti-corrosion. The discovery of SERS served to stimulate extensive interest in characterization of adsorbed organic compounds on metals such as silver , copper and gold owing to its very high spectral resolution and excellent sensitivity[2,3]. Now many studies have used SERS as spectroscopic tool [4,5]. The application of conventional laser Raman spectroscopy has been greatly limited by laser-induced fluorescence. A modified Fourier transform near IR Raman Scattering spectrometer with a near-infrared excitation can circumvent this problem.

The first reported SERS study of disulfide and thiols on a electrochemically roughened silver surface was by Sandroff and Herschbach[4]. They found that the surface products of thiophenol and phenyl disulfide on silver were identical and they were adsorbed in the same state. Sobocinske and co-workers have studied alkylthiols at electrode surfaces using SERS and they made comparisons between the surface interactions of alcohols and thiols[5].

In this study a fluorescence-free FT-SERS investigation was carried out on 10-mercapto-1-decanol and Cefazolin sodium adsorbed on silver film.

EXPERIMENTAL

The sampling methods of chemicals 10-mercapto-1-decanol can be easily synthesized as described previously [6,7]. Cefazolin sodium was supplied by Fuzhou Anti-biotic Co., China. Tollen's test was widely used in the identification of aldehyde[8]. Here it was used to prepare fine silver film which can react with sulfide. In a 10 ml beaker were a few of $10\times10\times1$ mm glass plates, which were washed with water and acetone. 5 ml 0.2 M silver ammonia complex and 5 ml 5% D-glocuse aqueous solution were mixed in the beaker. During heating at 50°C, the solution turned to milk and the silver ions were reduced and deposited on the glass plate to form fine silver film. After withdrawing the plates were washed with distilled water and then dipped in 0.001 M 10-mercapto-1-decanol solution or 0.001 M Cefazolin sodium aqueous solution for five minutes. The treated samples were washed with alcohol or water and ready for FT-SERS spectrum measurement.

FT-Surface-Enhanced Raman Scattering spectroscopy The FT-SERS spectra were recorded with a Bruker model RFS 100 Fourier Raman spectrometer with an air-cooled diode pumped Nd-YAG laser and Ge-detector, cooled to liquid nitrogen temperature. The incident laser excitation was 1064 nm. The outputs are 300 and 50 mW, respectively, for FT-SERS and regular FT-Raman measurement. The resolution was 4.0 cm^{-1}. The scattered light was collected at 180°.

RESULTS AND DISCUSSION

Alkanethiols can easily form monolayer at silver surface by the chemisorption of the S head group to the metal substrate, resulting the formation of Ag-S bond[1]. Evidence for this bonding could be observed in the FT-SERS spectra of their films. Spectrum B in Fig.1 showed the normal FT-Raman spectrum of 10-mercapto-1-decanol and B was the spectrum of neat silver film.. Spectrum 1C showed the FT-SERS spectrum of 10-mercapto-1-decanol on silver mirrors. Fig. 1A exhibited an intense band due to S-H vibration at 2574 cm^{-1}. A few spectral changes occurred, following the adsorption of 10-mercapto-1-decanol on the silver surface. First, the bands assigned to S-H vibration disappeared in Fig.1C. This observation indicated that they were chemisorbed dissociatively on the silver surface by the capture of their S-H groups. In addition, the absence of S-H intensity in the self-assembled monolayer film suggested that there was no free thiol present. The bands related to trans and gauche conformations could be observed at 718, 663 cm^{-1} in Fig.1 A and 699,631 cm^{-1} in Fig.1 C respectively[9,10]. As in the liquid state molecules moved easily and were disordered, and the band at 653 cm^{-1} corresponding to gauche conformation dominated the spectra Fig. 1A. Comparing Fig.1A and Fig.1C, we found that the trans (T) and gauche (G) C-S vibration bands of liquid compound, had shifted to low frequency in FT-SERS spectra. In the previous SERS investigation of $HO(CH_2)_{11}SH$, similar results were the thiolate on the copper electrode in a spectroelectrochemical cell [11]. Because of electrodonation from sulfur to silver, the C-S bond weakened, resulting the red shift of their stretching frequency. In Fig. 1B the band at 245 cm^{-1} perhaps, which was due to silver oxide on the silver film, was so intense that it could cover the band assigned to the weak Ag-N and Ag-S bands of the adsorbed chemicals.

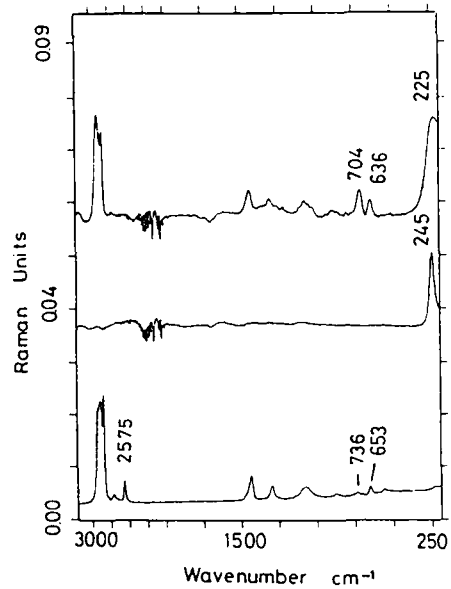

FIG.1 The FT-Raman spectra of 10-mercapto-1-decanol (A) and the FT-SERS of silver film (B), 10-mercapto-1-decanol adsorbed on silver film (C).

The chemically reduced silver film is very active to sulfur-containing or nitrogen-containing compounds. Fig. 3 shows the regular Raman (A) and SERS (B) spectra of Cefazolin sodium which is N and S-containing compound as shown in Fig.2. It
The chemically reduced silver film is very active to sulfur-containing or nitrogen-containing compounds. Fig. 3 shows the regular Raman (A) and SERS (B) spectra of Cefazolin sodium which is N and S-containing compound as shown in Fig.2. It
adsorption depended on the coordination of nitrogen and sulfur in the molecule. As in Cefazolin sodium molecule there are many nitrogen atoms and sulfur atoms, we proposed it was adsorbed by several "points." When the silver film pretreated with Cefazolin sodium was dipped in 0.001 M 2-mercaptoethanol aqueous solution, no signals of adsorbed 2-mercaptoethanol were observed except that of adsorbed Cefazolin sodium. Because of the steric volume, the small molecule, 2-mercaptoethanol could not go through the adsorbed Cefazolin sodium film.

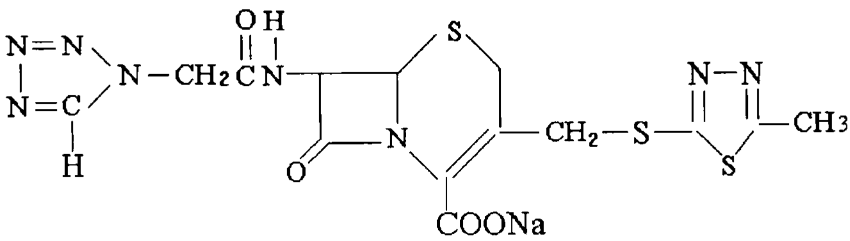

FIG. 2 The molecular structure of Cefazolin sodium.

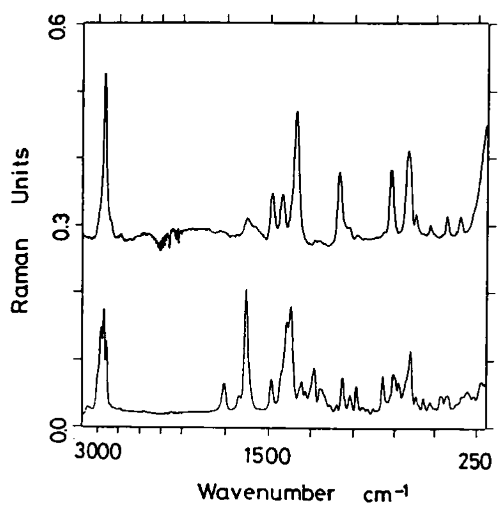

FIG. 3 The FT-Raman spectra of Cefazolin sodium (A) and its FT-SERS on silver film (B).

CONCLUSION

Fourier transform surface enhanced Raman scattering spectroscopy (FT-SERS) was used to characterized 10-mercapto-1-decanol and Cefazolin sodium self-assembled monolayer on chemically reduced silver film. The normal FT-Raman and FT-SERS spectra led the conclusion that by the split of S-H bond, or nitrogen-silver and nitrogen-silver coordinate above compounds could be adsorbed on the silver film to form self-assembled monolayers.

REFERENCES

1. Nuzzo R.G, and Allara D.L., *J. Am. Chem. Soc.* **1987,** *109*,733.
2. Albrecht M.G. and. Creighton J. A., *J. Am. Chem. Soc.* **1977,** *99*, 5215.
3. Chang R.K., Furrak T.E., Eds., *Surface Enhanced Raman Scattering*, Plenum, New York, 1982.
4. Sandroff C., and Herschbach D. R., *J. Phys. Chem.* **1992,** *86*, 3277.
5. Sobocinske R., Bryant M. A., and Pemberton J. E., *J. Am. Chem. Soc.*, **1990,** *112*, 6177.
6. Suk-Ku Kang, Won-Sup Kim and Byoung-Ho Moon., *Synthesis* **1985,** 1161.
7. Pattison F.L.M., Stothers J.B., and Woolford R.G., *J. Am. Chem. Soc.*, **1956,** *78*,2255.
8. Wingrove A. S., Caret R.L., Organic Chemistry (Harper & Row, Publisher, London, 1981),p867.
9. Scott D.W., and. El-Sabban M.Z., *J. Mol. Spectry.* **1969,** *30*, 317.
10. Hayashi M., Shiro Y., and Murata H., *Bull. Chem. Soc. Japan.*,**1966,** *39*, 112.
11. Yuichi Yamamoto, Hiroshi Nishihara and Kunitsgu Aramaki. *J. Electrochem. Soc.*, **1993,** *40*(2), 436.

Date Received:May 20,1997
Date Accepted:June 30,1997