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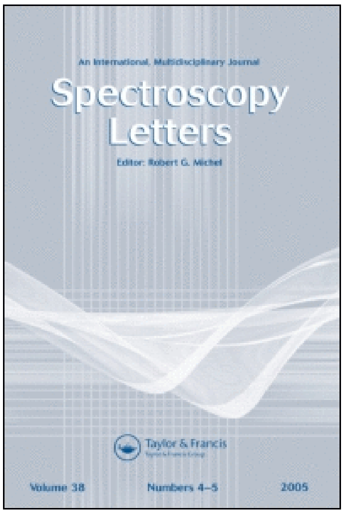

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FT-Raman Surface Enhanced Scattering Study of the Adsorption of Ω-Mercaptoalkanols on Different Silver Surface

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FT-RAMAN SURFACE ENHANCED SCATTERING STUDY OF THE ADSORPTION OF ω-MERCAPTOALKANOLS ON DIFFERENT SILVER SURFACE

Key words: FT-SERS spectroscopy (FT-SERS), ω-mercaptoalkanols, HNO_3 etching silver surface, silver mirror.

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ABSTRACT

Chemisorption and conformation of ω-mercaptoalkanols ($HO(CH_2)_nSH$, n=2, 6, 10) on silver mirror and HNO_3 etched silver foils have been observed by Fourier transform Surface Enhanced Raman Scattering spectroscopy (FT-SERS). The conformations of these adsorbates were affected by molecular chain length and surface roughness. In the adsorption state most of adsorbates inclined to be in trans conformation and ratio of trans to gauche conformation increased with the chain length.

INTRODUCTION

It is well-known that organic sulfur derivatives coordinate strongly to some metal surfaces and form monomolecular films, just as Nuzzo reported in 1987 [1]. The monolayer was well-organized microscopic characteristics and endowed the attached metals many special properties such as wetting, adhesion, anti-corrosion. Since then, the

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aspects of these monolayers have been the subjects of intensive academic and industrial researches. In their studies the surface enhanced Raman scattering (SERS) have been used as a powerful spectroscopic tool [2-3]. 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 [4, 5].

Sobocinske and co-workers have studied the alkylthiols on electrode surfaces using SERS and they made comparisons between the surface interactions of alcohol and thiols[3]. Meanwhile some studies indicating the existence of surface-enhanced photochemistry was reported [6]. Most SERS spectra were obtained on noble metals such as silver, gold by metals island films, metal films deposited on quartz or Teflon particles. However, these substrates are not quite stable for long periods of time or at elevated temperature. It's difficult to obtain reproducible enhancement. The problem hinders widespread acceptance of SERS as a technique for mechanistic investigations. Recently, stable substrate prepared by the nitric acid etching method for SERS study has been developed in this laboratory [7]. Silver foils etched with nitric acid exhibited excellent enhancement factor, and showed extraordinary stability under various environmental conditions. In this study a detailed fluorescence-free FT-SERS investigation was carried out on ω-mercaptoalkanols adsorbed on silver mirror and HNO_3 etched silver surface.

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EXPERIMENTAL

2-Mercapto-ethanol was obtained as high-grade commercial reagent and was used without further purification (purity 99.9%). 6-Mercapto-1-hexanol and 10-mercapto-1-decanol can be easily synthesized as described previously [8,9].

Silver foils of 0.025 mm thickness purchased from Aldrich Co. were immersed into 5-6 M HNO_3 solution at room temperature. After several seconds, a number of tiny bubbles were formed near the surface of the silver. A milky and sponge-type surface with substantial roughness was created a few minutes latter. The roughness of etched metal surface was about 10-100 nm as measured by electron microscopy. The etched silver foils were thoroughly rinsed with water and dried in air. The etched silver substrates and chemically deposited silver films were dipped into the solution at room temperature for several minutes. After withdrawing, the excess liquid was blown off with nitrogen and the samples were dried under air [10]

The preparation procedure of silver mirror was as described previously [10]. First, ω-mercaptoalkanols were dissolved in ethanol to make a 0.001 M solution, respectively. The silver mirror or etched silver substrates were then dipped into the solution at room temperature for several minutes. After withdrawing, the excess liquid was washed with alcohol. The treated samples were ready for FT-SERS spectrum measurement. The liquids were sealed in glass capillaries and determined.

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 30 and 50 mW for FT-SERS and normal FT-Raman measurement respectively. The resolution was 4.0 cm $^{-1}$.

RESULTS AND DISCUSSION

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Alkanethiols were first reported to form monolayer at silver surface by the Chemisorption of the S head group to the metal substrate, resulting in the formation of Ag-S bond. Evidence for this bonding could be seen in the FT-SERS spectra of their films. Spectra A in Fig. 1 through Fig. 3 showed the normal FT-Raman spectra of 2-mercapto-ethanol; 6-mercapto-1-hexanol and 10-mercapto-1-decanol. They exhibited strong vibration of S-H bond at 2566, 2569 cm^{-1} and 2574 cm^{-1}, respectively. Spectra B and C in Fig. 1 through Fig. 3 showed the FT-SERS spectra of 1-mercaptoethanol; 6-mercapto-1-hexanol and 10-mercapto-1-decanol on HNO_3 etched silver foils and silver mirrors. A few spectral changes occurred, following the adsorption of $HO(CH_2)_nSH$ on the silver surface. First, the bands assigned to S-H vibration all disappeared in FT-SERS spectra. This observation indicated that they were chemisorbed dissociatively on the silver surface by the capture of their S-H bonds. In addition, the absence of S-H intensity in the self-assembled monolayer films suggested that there was no free ω-mercapteralkanol present. Once bonded to the silver surface through the S atom, the ω-hydroxyalkanethiolate would interact through the Van der Waals forces and were ordered in different conformations. As the intensity of Raman spectra can be taken as the measure of molecules of different conformation. Of these signals, the most telling of the molecular conformation was the C-S stretching modes (600-750 cm $^{-1}$) [11, 12]

The bands related to trans and gauche conformations could be observed at 757, 663 cm $^{-1}$; 729, 641 cm^{-1}; 718, 663 cm $^{-1}$ in A through C of Fig. 1, 733, 654 cm $^{-1}$; 703,

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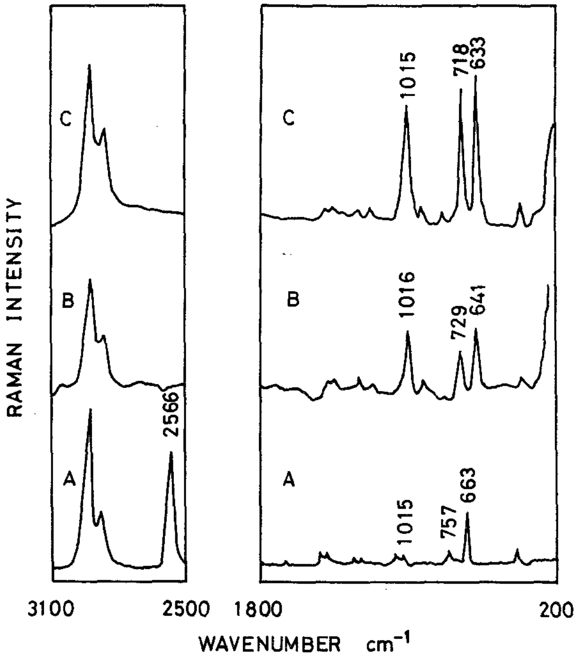

Fig. 1 The FT-Raman spectra of 2-mercaptoethanol $HO(CH_2)_2SH$,
(A) neat compound; (C) FT-SERS on silver mirror;
(B) FT-SERS on HNO_3 etched silver.

630 cm^{-1}, 692, 627 cm^{-1} in A through C of Fig. 2 and 737, 653 cm^{-1}; 693, 622 cm^{-1}; 699, 631 cm^{-1} in A through C of Fig. 3 respectively. As in the liquid state molecules moved easily and were in disorder, and the gauche conformation corresponding to the bands at 663, 654 and 653 cm^{-1} dominated the spectra A, Fig. 1 through Fig. 3. Comparing Fig. 1 and Fig. 2, we found that the trans (T) and gauche (G) C-S vibration bands of the above liquid compounds, had red shifted about 2-50 cm^{-1} 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 [13]. Because of electron-donation from sulfur to silver the C-S bond weakened, resulting in a red shift of their stretching frequency.

For ω-hydroalcanoathiolate adsorbed on different silver surface, the extent of order and conformation appeared to be somewhat different because of the complexity

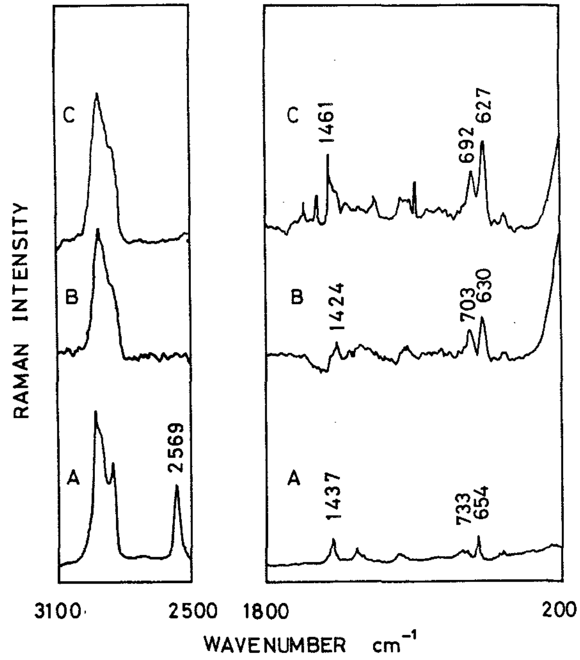

Fig. 2 The FT-Raman spectra of 6-mercaptohexanol $HO(CH_2)_6SH$,
(A) neat compound; (C) FT-SERS on silver mirror;
(B) FT-SERS on HNO_3 etched silver.

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of molecular structure and morphology. The ratios of the intensity of T (C-S) to G (C-S) were calculated and given in Table 1. The significant increase in intensity ratio of the FT-SERS spectra over the spectra of the liquid 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 when in liquid form. With the increasing of chain length, molecules were inclined to be more ordered. These results were consistent with some work published previously on n-alkylthiol monolayer on gold [14].

Comparing spectra B and C, Fig. 1 through Fig. 3, we found that the adsorbates on silver mirrors were more organized than that on HNO_3 etched silver surface. It could be firmed by the clear bands at 1015, 1461, 1437 cm^{-1} in C, Fig. 1 through Fig. 3, which were assigned to the C-O stretching vibration and CH_2 bending vibration. These results suggested that the mirror surface favored ordered organization of adsorbates,

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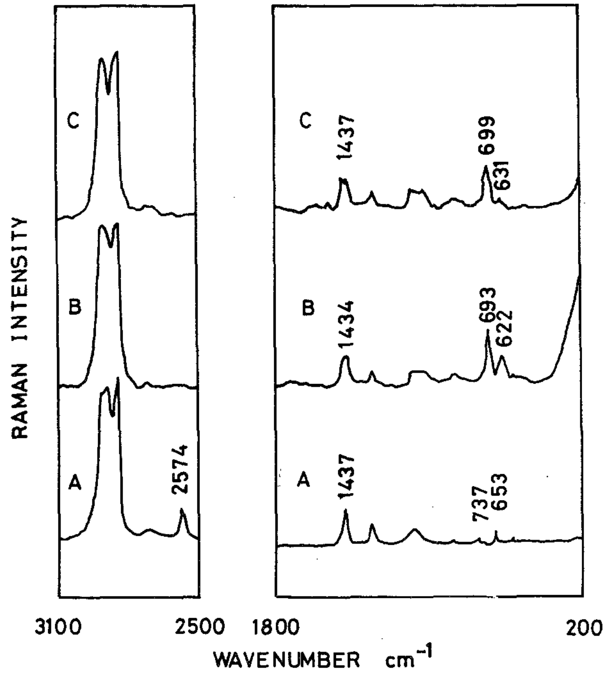

Fig. 3 The FT-Raman spectra of 10-mercapto-1-decanol $HO(CH_2)_{10}SH$,
(A) neat compound; (C) FT-SERS on silver mirror;
(B) FT-SERS on HNO_3 etched silver.

Table 1 The relation of sulfide state to their trans/gauche conformer intensity

compound	liquid state	adsorbed state	
		on silver mirror	on etched silver foil
n=2	0.32	0.90	0.72
n=6	0.36	0.64	0.63
n=10	0.33	4.58	1.40

perhaps it was caused by the surface roughness. The roughness of HNO_3 etched silver is 10-100 nm, however the average roughness of silver mirror is finer than that of HNO_3 etched silver. The same molecules easily cut the thinner roughness surface than the thicker one to form monomolecular film, especially for the longer chain molecules.

CONCLUSION

Fourier transform surface enhanced Raman scattering spectroscopy (FT-SERS) was used to characterize ω-mercaptoalkanols self-assembled monolayer on HNO_3 etching silver surface and silver mirror. The normal FT-Raman and FT-SERS spectra led the conclusion that by the split of S-H bond, the mentioned compounds could be adsorbed on the silver mirror and HNO_3 etched silver surface to form their thiolates. The thiolates were ordered in trans and gauche conformation. The ratio of trans over gauche conformation increased with the alkyl chain's getting longer and decreased with surface roughness. The trans conformation was conjectured to be more favorable on the basis of closed-packed structure.

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