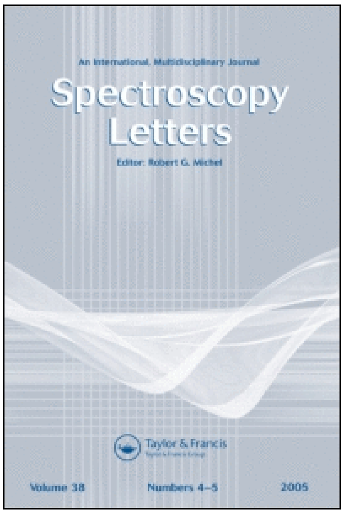

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Near Infrared Excited Surface Enhanced Raman Scattering on HNO_3 Etched Metals by Using Fourier Transform Technique

Jian Dong[a]; Zhihao Sheng[a]; Gi Xue[a]
[a] Department of Chemistry, Nanjing University, Nanjing, P.R.China

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NEAR INFRARED EXCITED SURFACE ENHANCED RAMAN SCATTERING ON HNO_3 ETCHED METALS BY USING FOURIER TRANSFORM TECHNIQUE

Keywords: Fourier transform Raman spectroscopy, surface enhanced Raman scattering, surface reaction

Jian Dong * , Zhihao Sheng and Gi Xue

Department of Chemistry, Nanjing University,
Nanjing 210008, P.R.China

ABSTRACT

Surface enhanced Raman scattering (SERS) has been produced on HNO_3 roughened silver and copper foils using near infrared excited Fourier transform (FT) Raman spectroscopy. The FT-SERS spectra obtained from 4-aminophenyl disulfide reveal the S-S bond fission of the molecule upon adsorption both on Ag and Cu surfaces. The spectra of acrylamide on Ag indicate that a relatively complete polymerization has occurred on Ag. The SERS technique on such metal substrates, in combination with FT instrumentation, shows fair simplicity, high sensitivity and great promise as a general analytical tool for surface reaction studies.

INTRODUCTION

Observation of surface enhanced Raman scattering (SERS) using near infrared (NIR) excitation at 1064 nm has been demonstrated recently, using new-generation Fourier transform Raman spectrometers. Although only a few observations by this technique have been published [1-10], a number of experimental advantages are already apparent. These include the speed of data acquisition and the ease of sample alignment when using the back-scattering geometry, which is the usual scattering configuration with this type of instrumentation. Although the work at present has been largely confined to observations at electrode surfaces and on metal colloidal particles, SERS excited in the NIR region appears to have larger enhancement factors than that excited in the visible spectral region [1,9].

The preparation of surfaces from which SERS may be observed has been the subject of many investigations. One of the aim of such work has been simply to identify SERS-active surfaces which may be easily and reproducibly prepared and which may be stored without degradation. If SERS is to find widespread use as an analytical tool, such preparation techniques are essential. Several types of SERS substrate have been suggested as having utility for analytical applications: these include sols [11], evaporated [12] and chemically deposited films [13,14], Ag and Au particles coated on metal substrates or filter paper [9,15], and compacted powders [16]. This paper presents some results of FT-SERS observations on metal foil surfaces prepared by HNO_3 etching method. We have shown previously that such SERS active substrates are reproducible and stable in storage under severe conditions [17,18]. The overall procedure is perhaps the simplest of any yet described for general SERS observations. From the electromagnetic mechanism, a prerequisite for producing SERS effect is to couple the incident electromagnetic field and Raman-scattered light with the metal surface plasmon enhancing the local electric field. What will happen then to HNO_3 etched metal surfaces if the excitation line changes from the visible to NIR spectral region? In this paper, we will show that SERS on such substrates can be extended to NIR region. Such work will be helpful for understanding the SERS mechanism. In combination with the recently developed FT-Raman techniques, the HNO_3 roughening method becomes particularly efficient for the purpose of surface analysis.

EXPERIMENTAL

Raman spectra were collected using a Bruker RFS 100 Fourier transform Raman spectrometer equipped with an air-cooled diode-pumped Nd-YAG laser (ADLAS, DPY 301) at 4 cm^{-1} resolution. A back scattering collecting optics in conjunction with an InGaAs detector was used for room temperature operation for all samples. Fourier transformation was carried out with the four-term Blackman-Harris apodization function and a zero-filling factor of 2. The HNO_3 roughening procedure is similar to that previously reported [17,18]. Briefly, Ag and Cu foils were immersed in concentrated HNO_3 solutions for etching, and after withdrawal, rinsed with copious amount of distilled water before drying. The roughened Ag and Cu foils were dipped into the adsorbate solutions in ethanol for sample doping and dried in air before measurement.

RESULTS AND DISCUSSION

1. Adsorption of 4-aminophenyl disulfide on Ag and Cu

In order to assess the potential of performing SERS on nitric acid etched metals in NIR region, we present first the results from the adsorption and reaction studies of 4-aminophenyl disulfide (APDS). This kind of molecule is particularly useful in building up supramolecular structures on metals by self-assembly. Chemisorption studies of disulfide compounds by LEED, FT-IR, XPS, *etc.*, have elucidated the binding and fission of the S-S bond on the metal surfaces like Au, Ag, Ni, etc. [19]. A question still exists whether the reaction will be interfered when an amino group with strong coordination tendency to metals is introduced on the phenyl ring.

Excellent FT-SERS spectra have been obtained from monolayer APDS on HNO_3 roughened Ag and Cu foils, as shown in FIG.1B and 1C, respectively. For comparison, FIG.1A displays the FT-Raman spectrum of neat APDS. Based on the reported infrared spectrum and comparison of the Raman spectrum with its diselenide counterpart, the 461 cm^{-1} band in FIG.1A may be assigned as the stretching vibration of the S-S bond [20,21]. The strong 1083 cm^{-1} bands can be attributed to phenylene-S stretching mode [22]. Most of the other vibrational bands in FIG.1A can be attributed to various ring vibrations, whereas vibrations originated from the NH_2 group appear very weak in the FT-Raman though they are quite apparent in its FT-IR spectrum (not shown here). In the FT-SERS spectrum on Ag, band frequencies due to ring vibrations are shifted, for instance, the bands at 1489, 1174, 1003 and 821 cm^{-1} in FIG.1A have shifted to 1486, 1177, 999 and 812 cm^{-1}, respectively, in FIG.1B. From the frequency shift of the strong phenylene-S stretching band (from 1083 cm^{-1} to 1077 cm^{-1}), one can induce that a sulfur-silver bond has been formed. The most remarkable changes in FIG.1B or FIG.1C are the disappearance of the S-S band. The phenomenon that the

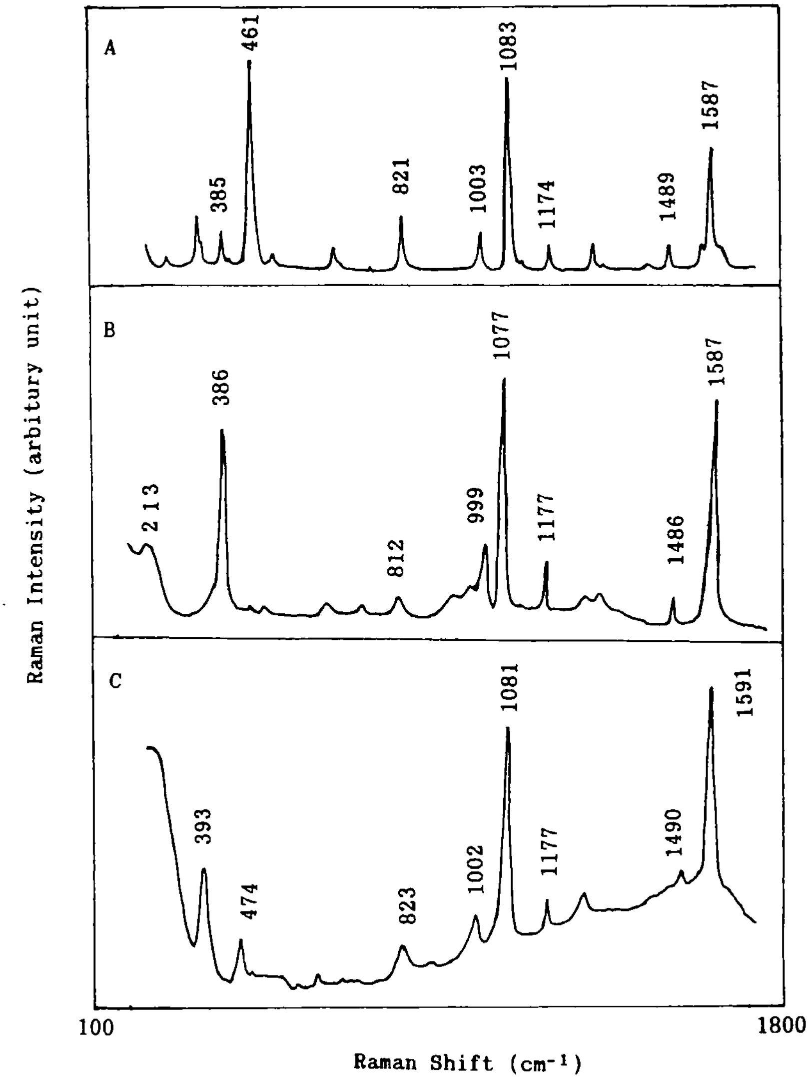

FIG.1 (A) FT-Raman spectrum of neat APDS; (B) FT-SERS spectrum of APDS on Ag; (C) FT-SERS spectrum of APDS on Cu. The spectra were collected after 100 scans under a laser power of about 200 mW at the samples.

S-S stretching mode of a disulfide molecule disappeared in its SERS spectrum on silver was first reported by Sandroff and Herschbach [23]. By comparing the SERS spectra excited in the visible region with the normal Raman spectra, they proposed that the S-S linkage was readily cleaved to form mercaptide species on Ag surfaces. It was, however, argued that the reaction may be a laser light induced but not a spontaneous process upon adsorption, since photochemistry is enhanced on SERS substrates. The present FT-SERS results support the viewpoint that APDS undergoes a adsorption-induced reaction on Cu or Ag since there's rare possibility of a photochemical process under NIR radiation. The enhancement of the 386 cm^{-1} band in FIG.1B, as well as that of the 393 cm^{-1} band in FIG.1C also implies chemisorption via S atom since this band is due to a ring in-plane bending mode sensitive to S atom. The appearance of the new band at 213 cm^{-1} in FIG.1B can be attributed to Ag-S bond. K.Kim, *et al.* assigned the new band at 237 cm^{-1} to Ag-S stretching in the SERS spectrum of benzenethiol on Ag [24]. The Ag-S stretching has been reported to lie within the 150-250 cm^{-1} range in several alkyl and aryl silver thiolates [25]. The Cu-S stretching is not obvious in FIG.1C since it's obscured by the substrate background.

When the concentration of the dipping solution is varied, the molecules adsorbed may have different orientation on the surface, resulting possible changes of the relative intensity of peak signals in SERS spectra. We have compared the FT-SERS spectra obtained from Ag substrates coated with a series of solutions of APDS with concentrations from 1% to 0.04% wt. The multilayer spectra were exactly similar to FIG.1B. This not only demonstrated that the observed SERS signals were characteristic of the chemisorbed layer restricted on the SERS active sites (short-range effect), but also implied that the amino group on the phenyl ring does not interfere with the adsorption fashion in which the sulfur atom dominates the bonding with the surface. The latter feature is important since the remaining NH_2 group may be bonded with tailored functionality to form a self-assembled structure on the surface.

2. Polymerization of acrylamide on Ag

An FT-SERS spectrum of acrylamide (AM) adsorbed on Ag is shown in FIG.2B. For comparison, FT-Raman spectra of neat AM and polyacrylamide (PAM) solid are listed in FIG.2A and 2C, respectively. Comparison of the SERS and normal Raman spectrum of AM in FIG.2 reveals many differences. For neat AM, strong bands arising from CH bending, C-N stretching (and CH_2 bending) and C=C stretching at 1283, 1433, 1636 cm^{-1}, respectively, are

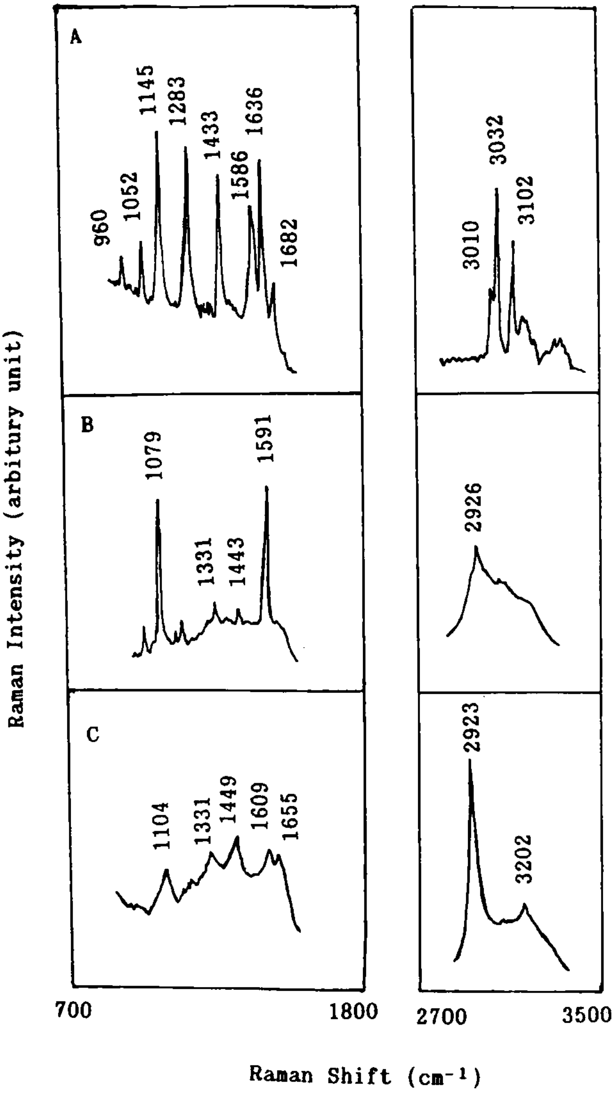

FIG.2 (A) FT-Raman spectrum of neat AM (recording condition: 200 mW, 100 scans); (B) FT-SERS spectrum of AM on Ag(recording condition: 200mW, 1000 scans); (C) FT-Raman spectrum of PAM (recording condition: 200mW, 800 scans).

observed; other bands due to H-C=C-H out-of-plane bending, NH_2 twisting, NH_2 bending (amide II) and C=O stretching (amide I), are found at 960, 1145, 1586 and 1682 cm^{-1}, respectively. Strong bands at 3102 and 3032 cm^{-1} are due to CH_2 asymmetric and symmetric stretching, respectively, while a shoulder at 3010 cm^{-1} is due to CH stretching. In the Raman spectrum of solid PAM, there are strong bands at 1104, 1331, 1449 and 2923 cm^{-1} which are the C-C skeletal stretching, CH bending, CH_2 bending and CH_2 stretching, respectively, while bands due to NH_2 bending (amide II), and C=O stretching (amide I) are observed at 1609 and 1655, respectively. These spectra are in general agreement with previously published data [26]. The SERS spectrum of AM, contains strong bands at 1079, 1591 cm^{-1}, and weak bands at 1331, 1443, 2926 cm^{-1}, indicating that AM polymerizes on the surface of HNO_3 roughened Ag. The CH stretching frequency clearly corresponds to that of PAM; the 1331 and 1443 bands are very close to the C-H bending, CH_2 bending modes of PAM. Another indication of polymerization is the disappearance of the C=C band near 1636 cm^{-1} in FIG.2B. The amide II band (NH_2 bending) in FIG.2B shifts to 1591 cm^{-1}, while the weak amide I band (C=O stretching) is not observed. The strong 1079 cm^{-1} band in FIG.2B corresponds to the broad 1104 cm^{-1} band in FIG.2C which contains C-C skeletal stretching and NH_2 vibration after peak deconvolution [26].

Suh and Michaelian also found the polymerization of AM on silver sol particle surfaces by using conventional dispersive SERS excited in the visible spectral region [27]. However, the polymerization was incomplete since the SERS spectrum of AM on silver sol still exhibited strong C=C stretching vibration. Furthermore, there was much difference between the SERS spectrum of AM on Ag sol particle and the normal Raman of PAM or the SERS spectrum of PAM on silver sols [27]. The present FT-SERS of AM on HNO_3 roughened Ag indicates no vibrational signals arising from AM monomer are observable, implying the polymerization is nearly complete. This also excludes the possibility that polymerization might be initiated by laser light.

CONCLUSIONS

The performance of presenting SERS on HNO_3 roughened metal foils excited at NIR 1064 nm has been illustrated. Because of its simplicity, the FT-SERS procedure on such substrates is a good general surface-analytical tool for adsorption and reaction studies. As an example, we have shown that 4-aminophenyl disulfide undergoes a S-S bond fission on Ag and Cu surface without the interference from the possible bonding formation between the amino group and the surface; a more complete polymerization of acrylamide occurs on HNO_3 etched Ag than on Ag sol particles. Due to the low energy of NIR radiation, the FT-SERS results further confirm that both of the surface reactions were not photon-induced.

Up to now, most FT-SERS studies were conducted in electrochemical cells or metal sols. Since some chemicals don't dissolve in water and many reactions don't occur in aqueous media, these FT-SERS techniques are apparently inadequate. In contrast, the FT-SERS based on HNO_3 etching method is a convenient approach with few limitations. On the other hand, it must be pointed out that the metal substrates can be used as electrodes for observations at imposed electrode potentials though the results given here are for direct adsorption from solutions.

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