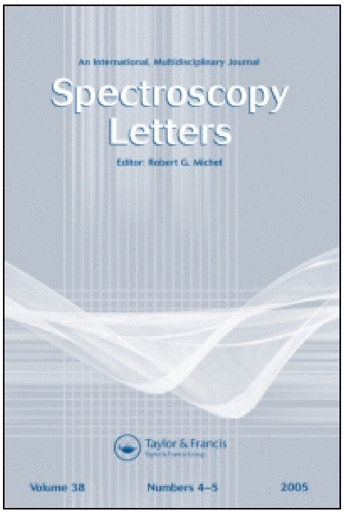

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# Dilution Effect on Surface Enhanced Raman Scattering for Organic Disulfide Adsorbed from Solutions

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# DILUTION EFFECT ON SURFACE ENHANCED RAMAN SCATTERING FOR ORGANIC DISULFIDE ADSORBED FROM SOLUTIONS

Keywords: Surface enhanced Raman scattering, Solution, Adsorption, 4-aminophyenyl disulfide, metal, surface.

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## Abstract

The concentration dependence of surface enhanced Raman scattering (SERS) of adsorbed 4-aminophenyl disulfide on surfaces of silver and gold has been investigated. It has been found that the spectral qualities are inversely proportional to the concentration of solutions applied. Excellent SERS spectral enhancement and perpendicular orientation could be achieved for the sample applied from $4 \times 10^{-6}$ *M* solution rather than that from 0.001 *M* solution. This

phenomenon was termed as "dilution effect" on SERS spectrum.

## Introduction

The adsorption of organicsulfur compounds on gold, silver, and copper metals represents a chemisorption system with unique and important properties. Recently, a general description of the chemisorption of organic isulfides (RSSR') from solution on noble metals was presented[1,2]. It was surprised to find that all of the disulfides under investigation formed very strong chemisorption bonds and that it is possible to prepare structurally and chemically complex organic surfaces with well-defined microscopic characteristics when an appropriate molecular structure in the adsorbate molecule was used[1,2].

There is considerable interest in the mechanism by which organic disulfides, thiols, and sulfides adsorbed to metal surfaces. More recently, they have become popular as anchors for constructing self-assembled organic layers on metals[3]. Since much of the work has been on noble-metal surfaces and the symmetric disulfide stretches are *IR* inactive. Many of the surface studies have used SERS as spectroscopic tool[4-9].

The first reported SERS spectra of disulfides on metal surface was by Sandroff and Herschbach[4]. They found that the surface products of thiophenol and phenyl disulfide on silver were identical. Sobocinski and co-workers have studied alkylthiols at electrode surface using SERS and have made comparisons between the surface interactions of alcohols and thiols[5]. While some studies indicating the existence of surface-enhanced photochemistry have been reported[9]. Takahashi et al. reported S-S bond cleavage and that 2,2'-dipyridyl disulfide and diphenyl disulfide could chemisorb dissociative on silver electrode surface, taking sticking-up configurations through S atoms[10]. More recently, Xue et al. reported the formation of monolayer films by the spontaneous assembly of thiophenol and 4-chlorothiophenol adsorbed from their gaseous state. SERS, XPS, and contact-angle measurements indicated that the films adsorbed from gaseous thiol are well oriented[9].

In our recent study we found a "dilution effect" on SERS spectral enhancement and on the molecular orientation when an organic disulfide was adsorbed onto silver surface from dilute solutions.

## Experimental

All reagents were purchased from Aldrich Chemical Corp. and were reagent grade. SERS active silver substrate (0.025 mm thick) was prepared by etching in nitric acid solution according to the procedure reported early[11].

4-aminophenyl disulfide was dissolved in ethanol to make solutions with various concentrations. The roughened silver substrates were dipped into these solutions at room temperature for approximately 10 min. After withdrawing, the excess liquid was blown off with nitrogen and the samples were dried under air.

The SERS spectra were measured with a backscattering geometry in air on a SPEX-1403 Raman spectrometer. Spectra were obtained with 647.1 nm laser irradiation from a $Kr^+$ laser source with output power of 20-100 mW, 3-$cm^{-1}$ band-pass, 2 $cm^{-1}$ step size, and 6-second integration. The Raman band intensities are reported in Counts-$mW^{-1}$-$Sec^{-1}$ to account for the different laser powers and integration times.

## Results and Discussion

Figure 1A and 1B show excellent SERS spectra of 4-aminophenyl disulfide on roughened silver applied from $4\times10^{-6}$ *M* and $8\times10^{-5}$ *M* solutions respectively. For comparative purpose, a SERS spectrum recorded from a solution with concentration of 0.001 *M* is shown in Figure 1C. By comparing SERS spectra for 4-aminophenyl disulfide adsorbed on silver from various solutions,

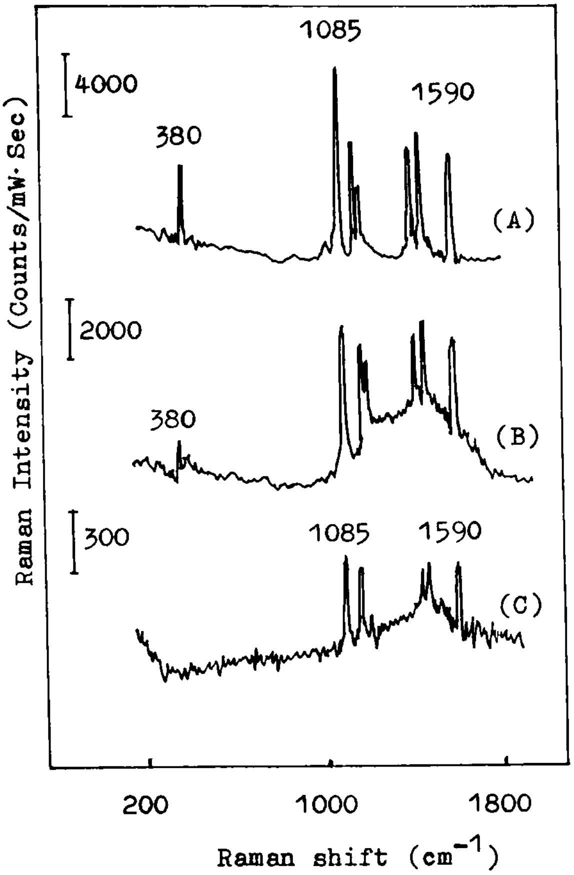

Figure 1. SERS spectra of 4-aminophenyl disulfide adsorbed on silver from $4 \times 10^{-6}$ *M* (A), $8 \times 10^{-5}$ *M* (B), and 0.001 *M* (C) solutions.

one can easily find a "dilution effect" on the spectral quality and on the orientation of adsorbate.

Good SERS spectra were illustrated in Figure 1A and 1B which were recorded from 4 $10^{-6}$ *M* and 8 $10^{-5}$ *M* solutions, respectively. As reported by Garoff et al.

dipping a metal substrate in 0.001 *M* solution for 30 seconds results in rather uniform coverage of the adsorbate[12]. The dipping technique has also been shown to yield reproducible coverage in the monolayer range. This method appeared to provide good SERS spectra for adsorbates that could be dissolved in volatile solvents. Figure 1A and 1B were recorded from the adsorbed 4-aminophenyl disulfide on silver surface applied from much dilute solutions, which shows even better enhancement factor than Figure 1C. Furthermore, Figure 1A clearly shows a large enhancement of the 380 $cm^{-1}$ band. This is to be expected since this mode is largely composed of the $\alpha_{zz}$ tensor[14]. The band at 1085 $cm^{-1}$ corresponding to $S-C_6H_4-$ stretching mode[9] is strongly enhanced in Figure 1A and 1B. Though more detailed studies are required to produce an accurate measurement of the surface enhancement factor, a semiquantitative estimate can be provided by comparing the intensity of the 1085-$cm^{-1}$ band of SERS spectra. When monolayer coverage at the surface was assumed, the surface Raman signal per adsorbed molecule for Figure 1A and 1B were approximately one to two orders higher than that in Figure 1C. A plot of Raman signal of SERS spectrum versus the concentration is shown in Figure 2.

One can easily find a turning point in the plot, which indicates that the maximum enhanced factor reached at the concentration of $6 \times 10^{-6}$ *M*.

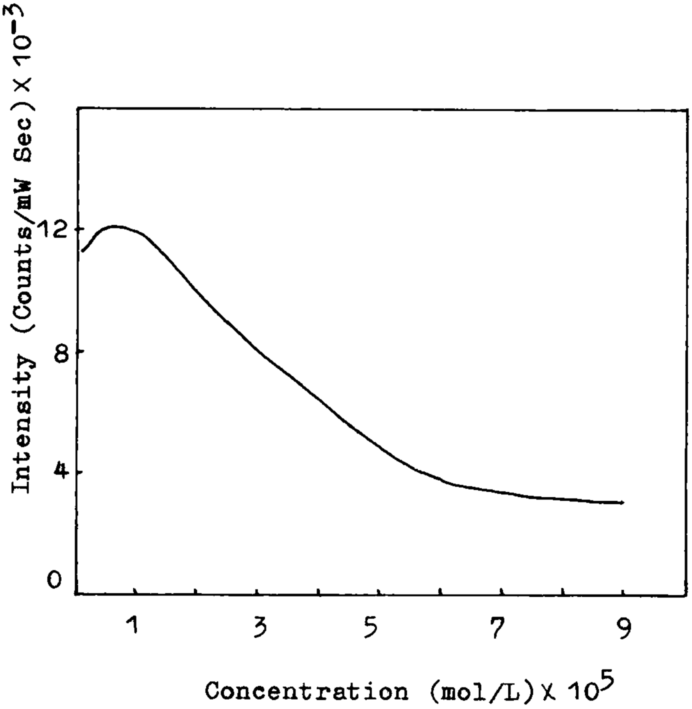

Figure 2. A plot of Raman intensities at 1085 $cm^{-1}$ versus concentration.

There are probably more than one mechanism responsible for the strong enhanced Raman scattering for adsorbed molecules on roughened surface of noble metals. And the observed enhancement factors might resulted from a combination of several contributions. One may not exclude the possibility that surface interactions, e.g. formation of charge transfer states of the metal-adsorbate complex, are effective at close range[13]. We propose that the geometry of the surface species for metal-adsorbate complex is related to the process of charge transfer, and thus to the enhancement. Proper orientation of the adsorbed molecule would produce strong enhancement. As the sample was adsorbed from very dilute solution (less than 0.00001 *M*), each molecule seems to has more chance to orient itself. While the solution is thick, molecules would collapse on the surface.

Changes in the relative intensity of each peak in Figure 1 should be related to the surface enhancement mechanism and molecular orientation. Clearly, the 380 and 1085 $cm^{-1}$ bands were enhanced in the SERS spectra in Figures 1A and 1B. A successful basis for analyzing SERS spectra with respect to orientation of adsorbates has been reported in the form of "surface selection rules" by Moskovits et al.[15] and others[16]. These rules are based on the electromagnetic theory of SERS intensity, which says that, via resonance interaction with surface plasmons of the metal, incident light increases in the electromagnetic fields are highest normal to the surface; normal modes of the adsorbed molecule involving changes in molecular polarizability with a component perpendicular to the surface are subject to the greatest enhancement. This same type of analysis has been successfully applied by Cotton [17] and by Strekas[18]. Based on these "surface selection rules" and the relative intensity changes in Figure 1, we conclude that as 4-aminophenyl disulfide was adsorbed from a very dilute solution, the molecules had more chance to orient themselves, resulting in more order surface species and thus a stronger enhancement on Raman scattering. This is the "dilution effect" on the SERS spectral quality and on the molecular orientation of disulfide on surface.

## Conclusion

We have demonstrated that SERS spectral quality and the molecular orientation of 4-aminophenyl disulfide on silver surface are inversely proportional to the concentrations in the range of investigation. This "dilution effect" could be also observed on gold substrate and for other organic disulfide.

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## References

[1] Nuzzo,R.G.; Allara,D.J. *J. Am. Chem. Soc.*1983, *105*, 4481.

[2] Nuzzo R.G.; Zegarskii,B.R.; and Dubois,L.H. *J. Am. Chem. Soc.*, **1987**, *109*, 733.

[3] DeLong H.C.; Buttery,D.A. *Langmuir*, **1990**, *6*, 1319.

[4] Sandroff, C. and Herschbach,D.R. *J. Phys. Chem.*, **1982**, 3277.

[5] Sobocinski, R.L.; Bryant,M.A.; and Pemberton, J.E. *J. Am. Chem. Soc.*, **1990**, *112*, 6177.

[6] Joo,H.J.; Kim,M.S.; and Kim, K. *J. Raman Spectrosc.*, **1987**, *18*, 57.

[7] Lee,T.G.; Yeom,H.W.; Oh,S.; Kim,K.; and Kim,M.S. *Chem. Phys. Lett.*, **1989**, *163*, 98.

[8] Xue, G.; Ma,M.; Zhang,J.; Lu,Y.; and Carron,K.T. *J. Coll. and Interf. Sci.,* **1992**, *150(1)* , 1.

[9] Carron, K.T. and Hurley,L.G. *J.Phys.Chem.*, **1991**, *95*, 9979.

[10] Takahashi,M.; Fujita,M.; and Ito,M. *Surface Science*, **1985**, *158*, 307.

[11] Xue, G. and Dong, J. *Polymer* , **1992**, *33(3)*, 643.

[12] Garoff,S.; Stephenes,R.B.; Hanson,C.D.; and Sorenson,G.K. *Opt. Commun.*, **1982**, *41*, 257.

[13] Gersten,J. and Nitzan,A. *J. Chem. Phys.*, **1980**, *73*, 3023.

[14] Dollish,F.R.; Fateley,W.G.; Bentley,F.F. *Characteristic Raman Frequencies of Organic Compounds*, John Wiley & Sons; New York, 1974, p172.

[15] Moskovits,M. and Suh,J.S. *J. Am. Chem. Soc.*, **1985**, *107*, 6826.

[16] Creighton,J.A. *Surf. Sci.*, **1983**, *118*, 415.

[17] Ni,F. and Cotton,T.M. *J. Raman Spectrosc.*, **1988**, *19*, 429.

[18] Strekas,T.C. and Diamandopoulos,P.S. *J. Phys. Chem.*, **1990**, *94*, 1986.

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