

SERS of Dithiocarbamate Pesticides Adsorbed on Silver Surface; Thiram

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In the present work, we studied thiram on silver surface by SERS. Investigations of disulfides with SERS revealed that the molecules undergo a surface reaction on silver, namely easy cleavage of the S-S bond. We believe that the two S atoms of resonance formed from the thiram may be chemisorbed strongly on Ag sol. This resonance form adheres perpendicularly to the Ag surface via the two S atoms, since the $\delta(\text{CII}_3)$ and $\nu(\text{CN})$ mode perpendicular to the surface showed strong enhancement. The important roles of halide anion adsorption have been discussed and the pH effects of thiram on Ag sol in acidic, neutral, and alkaline conditions were examined.

Key Words : Surface-enhanced Raman scattering, Thiram, Silver sol

Introduction

Many molecules adsorbed on appropriately prepared metal surfaces exhibit a Raman scattering cross section which is several orders of magnitude greater than the corresponding quantity for the isolated molecules. This effect, surface enhanced Raman scattering (SERS),^{1,2} provides a sensitive method for observing vibrational excitations of molecules that interact with metal surfaces. After the pioneering efforts by Fleischman, Van Duyne, Creighton and their co-workers, SERS spectroscopy has been extensively employed and is now established as a powerful and widely used method for studying vibrational spectra of a monolayer or submonolayer of adsorbed molecules on metal surfaces.^{3,4}

Since the initial discovery of SERS from pyridine adsorbed on a silver electrode, a number of investigations for pyridine-silver systems have been reported and information about the mechanism of SERS has been obtained. SER spectra are obtained on a limited number of metal substrates such as Ag, Au, Cu, Pt, and alkali metals.⁵ Metal substrates generate intense SERS spectra comparable to those from the electrode systems and uniquely advantageous for theoretical analysis.^{6,7} The most often used as an active surface are silver sols, which possess several distinct advantages over silver electrodes. SERS spectroscopy has been successfully used to investigate the geometry, conformation, and chemical reaction of molecules adsorbed on metal surfaces.⁸⁻¹¹ Even though the origins of the SERS phenomenon have still to be clearly defined, SERS nonetheless provides a powerful means for studying the in situ adsorption of a range of molecules onto an ever-increasing number of metal substrates.

The modern history of crop protection is little more than one hundred years old, but over this period enormous advances and some notable mistakes have been made.¹² Unfortunately, fungicide has been used intensively. Additionally, pest and disease resistance affecting our crop protection capability and environmental pollutions produced by some agrochemicals are important growing concerns.¹³

So far, there have been many studies of variety agricultural fields. Additionally, many researchers have investigated spectroscopy with limited regard to agricultural medicines. Thus, we will observe SER spectra of thiram(tetramethylthiuramdisulfide)bis(dimethyl-thiocarbonyl)disulfide as an agricultural fungicide. Thiram is used to deal with weeds, apple anthrax, polymerization initiators, vulcanization accelerators, and verticillium of alfalfa.

The effects of solution pH, anions, and solvents on the SERS behavior of adsorbates have been investigated by numerous researchers.¹⁴ Therefore, the overall aim of this paper is to outline the character and orientation of the thiram adsorbed on silver sol. The orientation of adsorbate-metal interaction is the principal focus of the present paper.

Experimental Section

Analytical-reagent grade thiram was purchased from Aldrich Co. and used without further purification. All procedures were accomplished with sonication. The solutions were prepared with triply distilled water and acetonitrile as an organic solvent.

The aqueous silver sol used in these experiments was prepared by reduction of AgNO_3 with excess NaBH_4 at room temperature as described in Creighton *et al.*'s method.¹⁵ Briefly, a 1.0×10^{-4} M aqueous solution of thiram was mixed with the silver sol in a volume ratio of 1 : 10. A 0.1 mL volume of 0.5 M KCl solution was added to silver sol to prolong the silver colloid activity. Immediately after addition of thiram into the sol, the silver sol changed its color from greenish yellow to blue-gray due to aggregation. This blue-gray colloid showed intense Raman scattering by adsorbed thiram in excitation at 514.5 nm. The UV-VIS spectra prepared is displayed in Figure 1 and shows a maximum at 398nm, with a shoulder peak at about 450 nm. This result explains the characteristic of aggregated silver particles, in agreement with previous studies of many researchers.

The Raman instrument was equipped with a SPEX 1403 scanning double monochromator, an RCA C31034 PMT

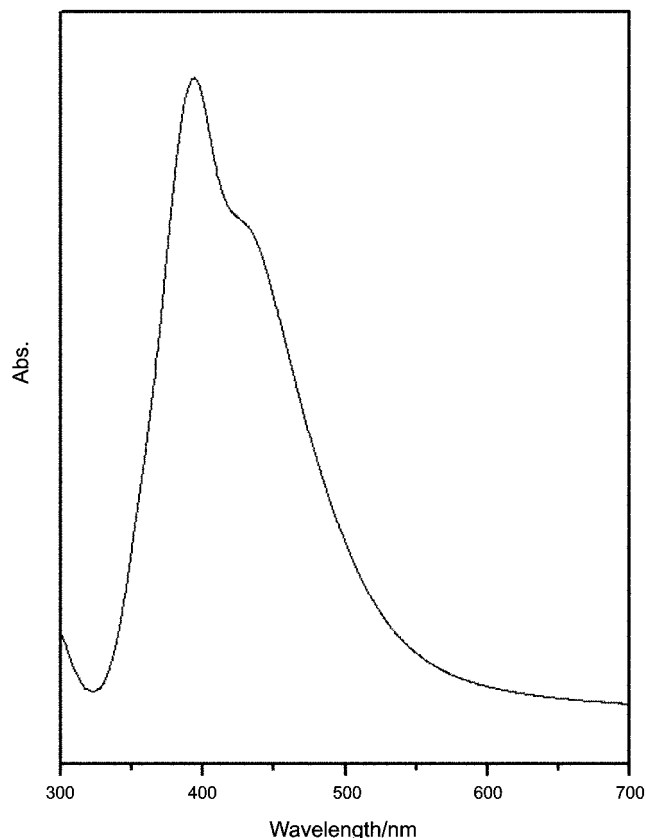


Figure 1. UV-Vis spectrum of silver sol.

detector, and SPEX DM 3000R software. Coherent Innova 90-5 argon ion laser (514.5 nm) excitation was used. The laser power and the spectral slit widths used were 100-150 mW and 600-800 μm , respectively. The Raman in situ measurements were performed in the conventional way for samples with the observation direction perpendicular to the exciting light. UV-visible absorption spectra were measured using a Shimadzu UV-360 pc instrument. Infrared spectra were measured in KBr pellets with the aid of a Galaxy series FT-IR 7000.

The pH of the solutions was adjusted by injecting the necessary amounts of H_2SO_4 and NaOH solutions of reagent grade and was checked before each day's experiments. We examined SER spectra of thiram containing F^- , Cl^- , Br^- , and I^- ions.

Results and Discussion

The Orientation of Adsorbates to the Metal. First of all, it is necessary to determine the molecular configuration and the resonance structures of thiram. According to the various IR, Raman spectra of the thiocarbonyl compounds which are linked to one or two nitrogen atoms, strong vibrational coupling effects are possible and the C=S vibration is not localized. The IR and Raman spectra of thiram are shown in Figure 2.

Thiram consists of two planar C_2NCS_2 units with a dihedral C-S-S-C angle of 88.3° . The most important bond

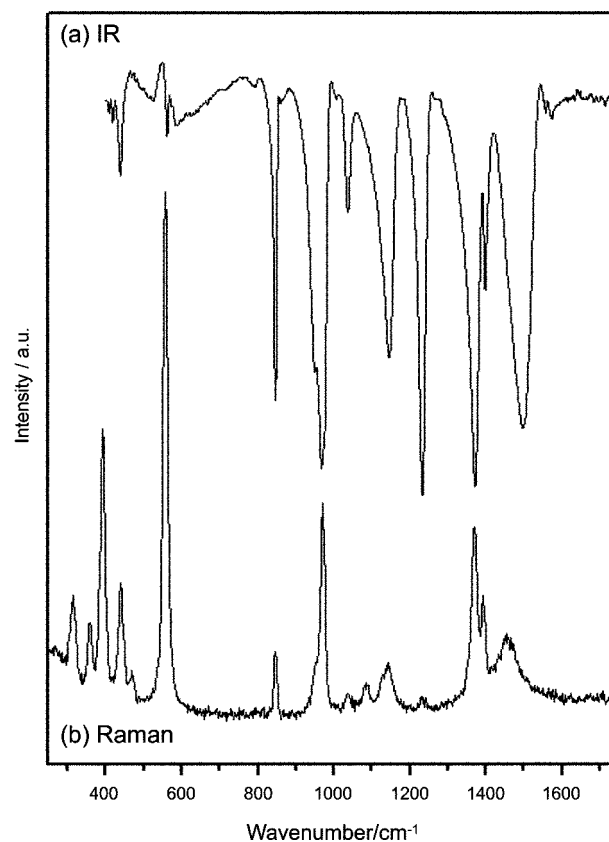


Figure 2. (a) IR and (b) Raman spectra of thiram (pure).

distances are CH₃-N: 1.483 and 1.506 Å, C-N: 1.319 Å, C=S: 1.634 Å, C-S: 1.829 Å, and S-S: 2.005 Å. Therefore, thiram can be considered as two planar dimethyl-dithiocarbamate units joined by an S-S bond; *i.e.*, the C₂-symmetry is retained. Thiram exhibits C₂-symmetry so that all IR modes are also Raman active, as shown in Figure 2.

For the disulfides, a report of SERS revealed that molecules with cleavage of the S-S bond undergo a surface reaction on silver.^{16,17} Additionally, we can easily understand the above bond distances. With the studies of reactions of sulfur compounds on various metals, investigations have shown that sulfur compounds are chemisorbed dissociatively on the metal surface by cleavage of S-S bonds. These conclusions are reasonable given the adsorption of thiram on silver surface. Thus, it is explained in terms of resonance structures, as described in Figure 3. These compounds are stabilized by electron delocalization.

If bonding to the metal substrate is through the S atom, contributions from the resonance form will be increased. In this case, it is expected that the S-S bonding is divided, the $\nu(\text{C}=\text{S})$ and $\nu(\text{C}-\text{S})$ mode is decreased, and the $\nu(\text{C}-\text{N})$ mode is enhanced. However, if the bonding is through the N atom, opposite results are expected.

In this paper, the IR, Raman, and SER spectra of thiram were measured in the solid and solution state in the region below 1800 cm^{-1} . The IR spectrum of thiram in the range $4000\text{-}250\text{ cm}^{-1}$ has been reported for use as a reference spectrum in pesticide research.¹⁸ The ordinary Raman and

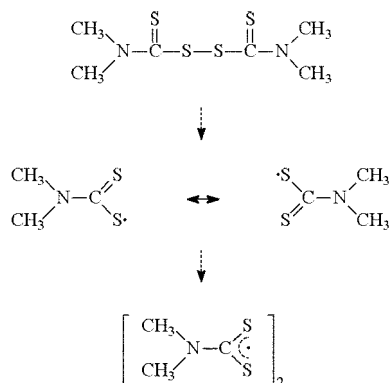


Figure 3. Structure and resonance structure of thiram.

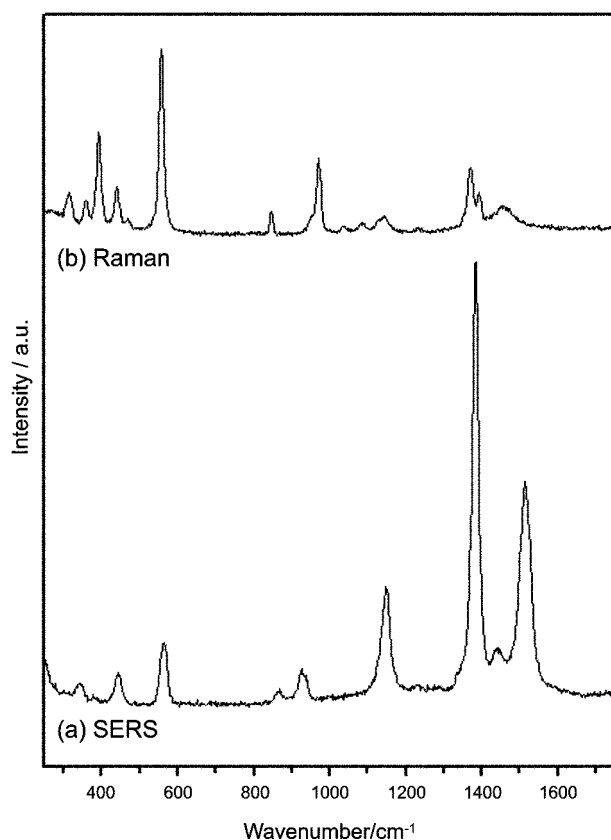


Figure 4. (a) SERS (1.0×10^{-4} M) and (b) Raman (pure) spectra of thiram.

SERS spectra of thiram are shown in Figure 4 and the major bands of the spectra are listed in Table 1. The vibrational assignments shown in Table 1 for thiram have been made on the basis of assignments reported in the literature for the Raman and IR spectra of thiram, and by comparison with the thiram structure of similar thioureas and thioamides.^{19,20}

By comparison of the above results, the orientation of metal-thiram interaction can be described approximately. The most prominent peak of the Raman spectrum is the 558 cm^{-1} mode in the ordinary Raman spectrum. The strong intensity band at 558 cm^{-1} is attributed mainly to the $\nu(\text{S-S})$ mode of thiram. It is the band having the lowest depolarization ratio (0.14). The counterpart in the IR spectrum (Fig.

Table 1. Details of assignment of thiram

IR	Raman	SERS	Assignment
		226(vw)	$\nu(\text{Ag-S})$
		236(vw)	$\nu(\text{Ag-Cl})$
	316(ms)	342(m.br)	$\delta(\text{S-C-S}), \delta(\text{CSS})$
	360(m)		$\nu(\text{CH}_3\text{NC}), \nu(\text{CS})$
	394(vs)		$\nu_s(\text{CSS}), \delta(\text{CH}_3)_2\text{N}, \nu(\text{C-S})$
441(w)	440(ms)	446(m)	$\delta(\text{CH}_3\text{NC}), \nu(\text{C-S})$
563(vw)	558(vs)	564(ms)	$\nu(\text{SS})$
847(s)	848(m)	870(vw)	$\nu(\text{CH}_3\text{N})$
951(sh)	955(w.sh)	928(m)	$\nu(\text{CH}_3\text{N}), \nu(\text{C-S})$
969(s)	972(s)		$\nu_{as}(\text{CSS})$
1038(w)	1038(w.br)		$\rho(\text{CH}_3), \nu(\text{CH}_3\text{N})$
	1088(w.br)		$\rho(\text{CH}_3)$
1147(m)	1144(w.br)	1150(ms)	$\rho(\text{CH}_3), \nu(\text{CN})$
1235(s)			$\nu(\text{CH}_3\text{N}), \delta(\text{CH}_3\text{NC})$
1373(s)	1372(s)	1386(vs)	$\delta_s(\text{CH}_3), \nu(\text{CN})$
1400(m)	1396(s)		$\delta_s(\text{CH}_3)$
	1456(m.br)	1444(m.br)	$\delta_{as}(\text{CH}_3)$
1498(s.br)		1514(ms)	$\nu(\text{CN}), \delta(\text{CH}_3), \rho(\text{CH}_3)$

s - strong, w - weak, m - medium, sh - shoulder, v - very, ν - stretching, δ - deformation, ρ - rocking.

4) is only of weak strength, indicating that the change of dipole moment during the vibration is small. Then we will see that this band undergoes dramatic changes in both the relative intensity and frequency in the SER spectra. Additionally, two bands at 316, 394 cm^{-1} decrease in intensity. Thus, it is expected that the divided S atom of thiram chemisorbs strongly on Ag surfaces.

It should be noted that the SER spectra of thiram between 1350 and 1550 cm^{-1} regions are not found in the ordinary Raman spectrum. Three distinct peaks at 1386, 1444, and 1514 cm^{-1} were observed in the SER spectrum of thiram on the Ag surface. The strong bands of intensity appearing at 1386, 1444 cm^{-1} in the SER spectrum may be assigned to $\delta_s(\text{CH}_3)$, $\delta_{as}(\text{CH}_3)$, respectively, as shown in Table 1. Especially, the band at 1386 cm^{-1} which is assigned to the $\delta_s(\text{CH}_3)$ weakly coupled to the $\nu(\text{CN})$, increased strongly. Moreover, the most dramatic difference was exhibited by the 1514 cm^{-1} line which didn't appear in the ordinary Raman spectrum. This new band is assigned to the $\nu(\text{CN})$ mode by the IR and Raman spectra of thiram. The appearance of a 1514 cm^{-1} line reflects enhancement of the $\nu(\text{CN})$ mode which is perpendicular to the Ag surface. Evidently, this mode has a low polarizability that is greatly enhanced after adsorption.

It can be assumed from the above results that the thiram molecule of resonance form having the cleavage of S-S is bonded to perpendicularly to the metal.

It is suggested that the Raman lines near 316 and 394 cm^{-1} in Figure 4 are due to the $\delta(\text{S-C-S}), \nu_s(\text{CSS})$ mode decrease in the SERS. Joo *et al.* concluded that the C-S bonds did not cleave easily on SERS investigation of aliphatic sulfides adsorbed on silver.^{19,20} Therefore, the reduction of the intensity and the largest frequency shift at these peaks indicate that the two S atoms of thiram are bonded to the Ag surfaces. Thus, it can be concluded that the $\nu(\text{C-S})$ and ν

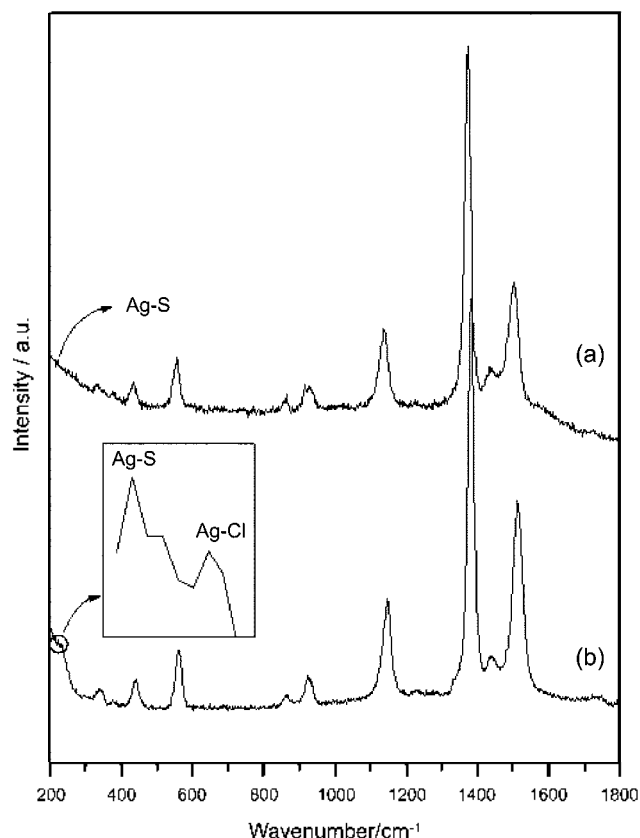


Figure 5. SER spectra of 1.0×10^{-4} M thiram in silver sol containing (a) 0.5 N KBr (b) 0.5 N KCl.

(C=S) modes were strongly affected in the SER spectrum.

Several researchers have studied the metal-sulfur stretching bands between 200 and 250 cm^{-1} .²¹⁻²³ In this paper, new bands at 220-240 cm^{-1} in the SER spectrum of thiram were found. It is supposed that this peak at around 226 cm^{-1} can be attributed to the silver-sulfur stretching vibration. Figure 5 shows SER spectra of thiram containing 0.5 M KCl and 0.5 M KBr as electrolyte. According to previous investigators, the silver-chloride stretching vibration is shown around 240 cm^{-1} . Additionally, the silver-sulfur stretching vibration at around 220 cm^{-1} is indistinct.²⁴ The 226 cm^{-1} band was observed on silver in solution containing 0.5 M KBr and 1.0×10^{-4} M thiram (Fig. 5a). Thus, it can be assumed that the line at 226 cm^{-1} is due to the silver-sulfur stretching mode because of the presence of an identical peak in both chloride and bromide anion. In addition, it can be assumed that the line at 236 cm^{-1} (Fig. 5b) is due to the silver-chloride stretching mode.

Therefore, experimental observations suggest that only a single thiram molecule will bond to the silver surface *via* the two S atoms, and that halide ions in the interface near the silver surface affect the silver adsorbate vibration which will form a stable complex formation.

The Influence of Anions. SER spectra of thiram adsorbed on a silver surface have been observed from a series of aqueous solutions containing F^- , Cl^- , Br^- and I^- as electrolyte.²⁵⁻²⁷ It is known that the cation has essentially no

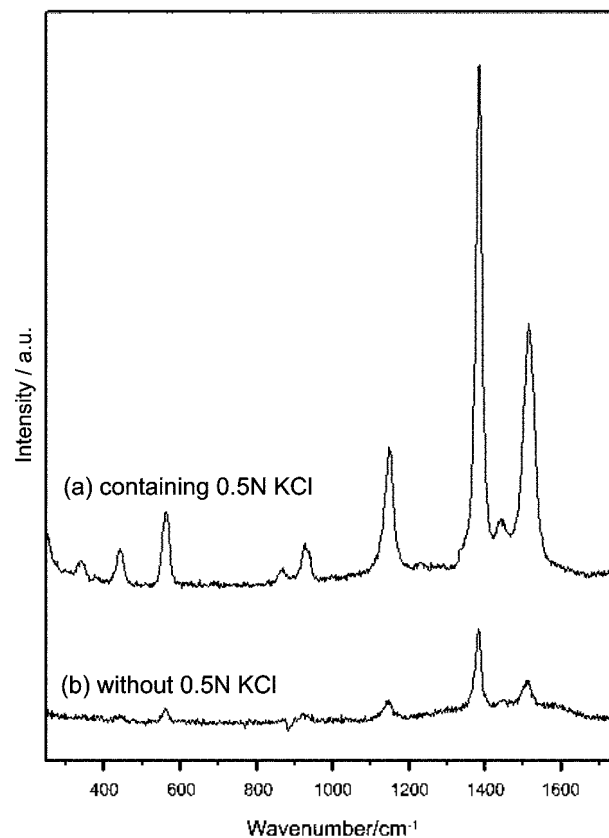


Figure 6. SER spectra of 1.0×10^{-4} M thiram in silver sol (a) containing 0.5 N KCl (b) without 0.5 N KCl.

effect on the spectrum. The important role of anion adsorption has been discussed. Generally, it increases the intensity of the Raman signal of the adsorbed molecule. Studies by Pettinger, Roy, Furtak, Fleischman, and Watanabe have shown that an electrochemically roughened silver electrode presents a surface containing Ag^+ ions that are stabilized by coadsorbed Cl^- ion, a constituent of the electrolyte.²⁸ The roles of stabilizing Cl^- ions or other coadsorbed species on a positively charged Ag ion have been predicted and then experimentally verified.

First of all, we are going to investigate the influence of surface Cl^- ions on the SER spectra of thiram. Figure 6 shows the SER spectra of thiram in the presence and the absence of Cl^- . The SER spectra of thiram containing a Cl^- ion are stronger and sharper than in the absence of Cl^- . It is important to point out that the presence of Cl^- ions increase reproducibility of the SER spectra of thiram. This enhancement may originate from the induction of positive charges by the coadsorbed chloride ion that leads to an increase in the interaction between thiram and the silver surface.

To better understand the underlying mechanism, we investigated UV-visible spectra of sol containing Cl^- . After addition of Cl^- ion, the aggregation peak at *ca* 450 nm was reduced and broader than that of sol without Cl^- . Cortes showed that this causes a breakup of the loose aggregates of elementary colloidal particles.²⁹ Thus, Cl^- addition leads to a small degree of dispersion from the aggregated surface, and

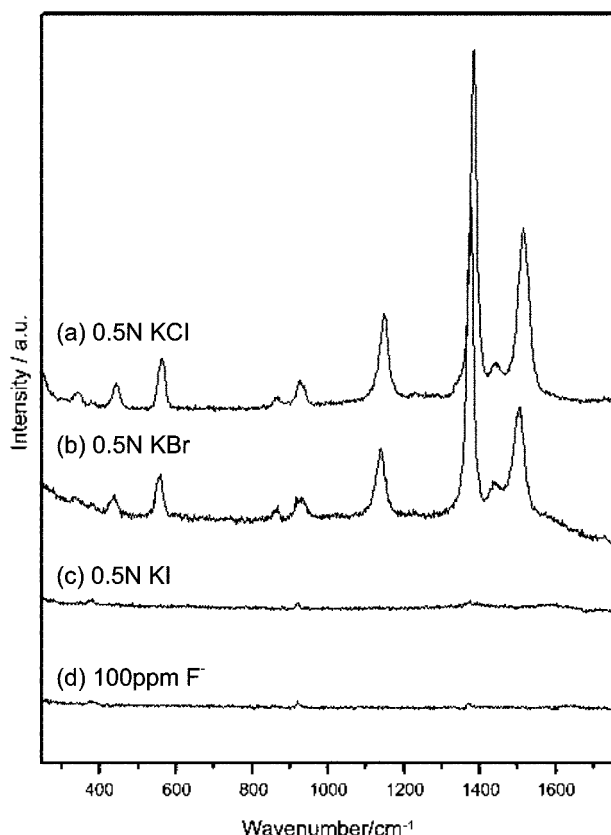


Figure 7. SER spectra of 1.0×10^{-1} M thiram in silver sol containing (a) 0.5 N KCl (b) 0.5 N KBr (c) 0.5 N KI (d) 100 ppm F^- .

the formation of Ag^+Cl^- on substrate offers proper active sites.

Additionally, these observations provide more evidence for the importance of surface complexes in the SER process on sol. When a complex forms between the active site and a probe molecule this involves a bond that is stimulated by the number of adsorbed Cl^- ions around the Ag sol. Thus, this bond leads to modifications in the relative Raman polarizabilities. Desorbing of Cl^- ions on the Ag surface bring about unstable surface complexes, which are deactivated by being left with insufficient Cl^- ions to hold the Ag^+ on the surface. The inactive sites do not contribute to SERS, leading to a decrease in the scattering intensity. Therefore, only pertinent Cl^- ion coverage on Ag surfaces is important. Finally, a Cl^- ion is necessary to enhance Raman scattering and prevent photoreaction of the silver surface.

To understand the coverage degree of anions on silver surface, the SER spectra of aqueous solutions containing F^- , Cl^- , Br^- , and I^- ions are exhibited in Figure 7. These results are in good agreement with some of the predictions of previous researchers. The SER spectrum from the Br^- solution in Figure 7b is quite similar to that from the Cl^- solution in Figure 7a. In this case, the overall spectral feature hardly changed except for some noise from the Br^- solution in Figure 7b. Therefore, it is supposed that bromide ions are more strongly adsorbed than chloride ions on silver. UV-visible absorption experiments suggest that Br^- and Cl^- ions

are similar in their influence on the substrate.³⁰ Figures 7c and 7d show similar SER spectra for F^- and I^- ions as electrolytes. For silver halide systems, the surface concentrations of specifically adsorbed anions were reported by Hupp *et al.*^{22,30} I^- ion is tenaciously adsorbed on a silver surface and an F^- ion is adsorbed very weakly, so that the SER spectrum is very poor. An increase in spectral intensity is associated with fitting in the surface coverage of the specifically adsorbed anions. Thus, a Cl^- ion is very pertinent among anions. The presence of halide ions was a prerequisite for the observation of SERS using hydrosol.

The Effect of Solution pH. The following experiments were performed in order to investigate the pH effect of thiram on the SER spectrum. Solutions were prepared with various pH ranging from acidic to alkali conditions. Many researchers have investigated the effect of solution pH on the SERS behavior of adsorbates in order to determine the adsorption mechanism or the orientation of adsorbates.^{31,32}

The SER spectra in Figure 8 are for silver sol in acidic, neutral, and alkali conditions. In acidic and neutral conditions, similar SER spectra are shown. This shows that adsorption in acidic and neutral conditions is about the same. In spite of a various range of acidic conditions, peak patterns did not differ, as shown in Figure 9.

Figure 10 shows SERS of thiram in alkali condition. Most of all, all peaks decreased on a large scale in intensity. In

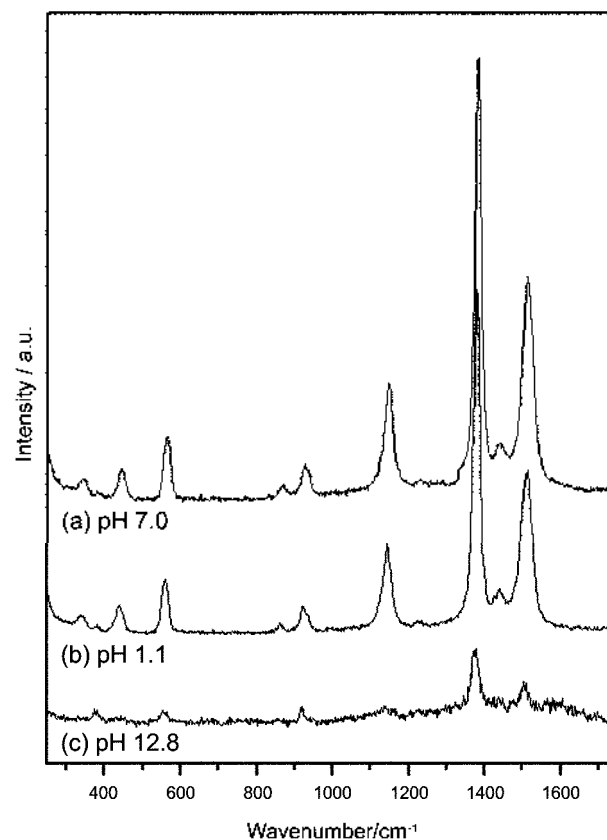


Figure 8. SER spectra of 1.0×10^{-1} M thiram in silver sol containing 0.5 N KCl at (a) neutral (pH = 7.0) (b) acidic (pH = 1.1) (c) alkali (pH = 12.8).

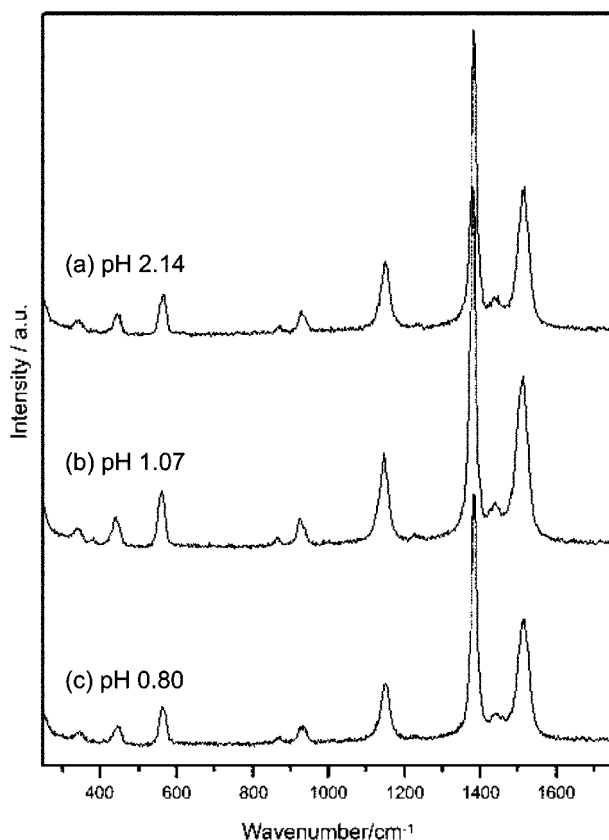


Figure 9. SERS spectra of 1.0×10^{-4} M thiram in silver sol containing 0.5 N KCl at (a) pH = 2.14 (b) pH = 1.07 (c) pH = 0.80.

particular, the peaks around $370\text{--}390\text{ cm}^{-1}$ in Figure 10 increased as the pH increased. In light of the above results, it can be concluded that the bonding of two S atoms on Ag sol is weak; thus, the intensity of (CH_3) and (CN) modes which are perpendicular to the substrate decreased. Thus, for the higher pH (11 to 14), orientation of thiram on the Ag sol is more tilted on the Ag surface.

As the pH is increased from 11 to 14, the peaks at $1300\text{--}1500\text{ cm}^{-1}$ are broader than in acidic conditions. The competitive adsorption of the OH^- ion and Cl^- ion on silver surface has been reported.³² As the pH is increased, surface sites are occupied by the OH^- ion rather than the Cl^- ion. A strong influence of OH^- ion on this competitive adsorption is seen in Figure 10. A broad band around $1300\text{--}1500\text{ cm}^{-1}$ is very likely caused by reduction of the extent of the surface coverage of Cl^- ions.

Finally, this experimental study shows that adsorption patterns in neutral and acidic conditions are similar, but as the pH is increased thiram is bonded to tilted stances on the Ag surface via the two S atoms. It can be suggested that the change of adsorption orientation in alkalic conditions is explained by inactive sites that are left with insufficient Cl^- ions due to the competitive adsorption of OH^- ions.

Conclusion

The Raman process is associated with a low photon

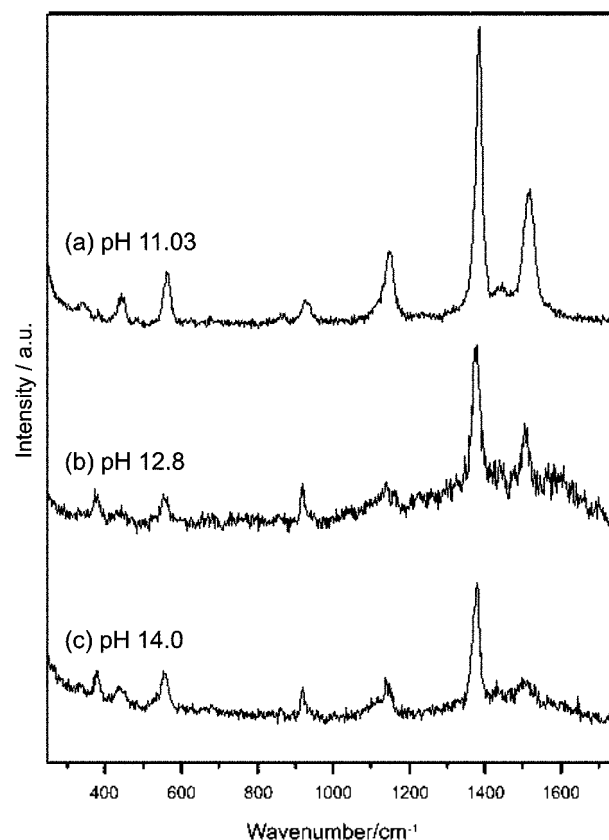


Figure 10. SERS spectra of 1.0×10^{-4} M thiram in silver sol containing 0.5 N KCl at (a) pH = 11.03 (b) pH = 12.8 (c) pH = 14.0.

scattering efficiency. Although multichannel photon detectors have enhanced Raman sensitivities, the technique is still limited in surface studies and at low concentrations. In the present work, we studied thiram on silver surface by SERS. Investigations of disulfides with SERS revealed that the molecules undergo surface reaction on silver, namely easy cleavage of the S-S bond. We believe that the two S atoms of resonance formed from the thiram may be chemisorbed strongly on Ag sol. This resonance form is adhered perpendicularly to the Ag surface via the two S atoms, since the (CH_3) and (CN) mode perpendicular to the surface showed strong enhancement. The important roles of halide anion adsorption have been discussed. Among the halide anions, addition of F^- and I^- ions resulted in very poor spectra of SERS. In the case of Br^- and Cl^- ions, good results were obtained, excepting minute noise from the Br^- solution. Thus, Cl^- ion has a proper coverage and stability on Ag surface. The pH effects of thiram on Ag sol in acidic, neutral and alkali conditions were examined. For acidic and neutral conditions, orientations of thiram on Ag sol are perpendicular to the silver surface, showing good SERS spectra. However, for the alkali conditions, orientations of thiram on Ag sol are slightly tilted on the silver surface. As the pH increased from 11 to 14, the peaks at $1300\text{--}1500\text{ cm}^{-1}$ were broader than in acidic conditions. This shows the competitive adsorption of the OH^- ion and Cl^- ion on the silver surface.

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