

Surface-enhanced Raman Spectroscopy of Quinomethionate Adsorbed on Silver Colloids

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We have studied the surface-enhanced Raman spectroscopy (SERS) spectrum of quinomethionate (6-methyl-1,3-dithiolo[4,5-b]quinoxalin-2-one), which is an insecticide or fungicide used on vegetables and wheat. We observed no signals in the ordinary Raman spectra of solid-state quinomethionate, but when it was adsorbed on a colloidal silver surface, strong vibrational signals were obtained at a very low concentration. The SERS spectra were obtained by silver colloids prepared by the Creighton *et al.* method. The influence of pH and the aggregation inductors (Cl⁻, Br⁻, I⁻, F⁻) on the adsorption mechanism was investigated. Two different adsorption mechanisms were deduced, depending on the experimental conditions: The one N atom or two N atoms are chemisorbed on an Ag surface. An important contribution of the chemical mechanism was inferred when the one N atom was perpendicularly adsorbed on a surface. It is possible that quinomethionate can be detected to about 10⁻⁵ M.

Key Words : Surface-enhanced Raman spectroscopy, Insecticide, Quinomethionate

Introduction

The modern history of agricultural chemicals is little more than one hundred years old, but over this period enormous advances and some notable mistakes have been made. The extensive use of agricultural chemicals has caused environmental contamination, especially of the underground water system, which has been seriously polluted, leaving agrochemical residue in crops. Therefore, it is necessary to develop methods to detect these chemical holdouts.

Since its discovery by Fleischmann *et al.* in 1974,¹ surface-enhanced Raman spectroscopy (SERS) has become a common technique for analyzing the adsorption of molecules on metallic surfaces. The enhancement of the Raman signal induced by a roughened metal surface, which is the basis of SERS, can be understood as a contribution from two different mechanisms: Electromagnetic (EM) enhancement and charge-transfer (CT) enhancement. The CT mechanism is commonly attributed to a first layer effect, whereas the EM mechanism is also operative beyond the first adsorbed layer.²⁻⁵ Of the several different SERS active media, silver colloids have been widely used for the following reasons: The simplicity of preparation and characterization; the possible control of the size and shape, and the convenience of monitoring the colloids by UV-visible absorption spectroscopy.^{6,7}

Quinomethionate (6-methyl-1,3-dithiolo[4,5-b]quinoxalin-2-one) is a toxic chemical used as an insecticide or fungicide

in vegetables, fruits and wheat, and has a planar structure due to ring resonance.⁸

This research elucidates the character and the adsorption mechanism on silver colloids and investigates the detection limit in the best condition, according to the pH and anion effects.

Experimental Section

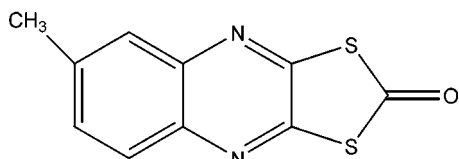
Quinomethionate of analytical reagent grade was purchased from Aldrich Co. and used without purification. Quinomethionate is insoluble in water and slightly soluble in acetone.

Two types of colloids were prepared, one by the Creighton *et al.*'s method,^{9,10} and the other by the Lee and Miesel's method.^{11,12} In the Creighton *et al.*'s method, silver nitrate is reduced by sodium borohydride, and the color of the colloid is greenish-yellow. In the Lee and Miesel's method, silver nitrate is reduced by sodium citrate, and the colloidal color is milky yellow. Both are stable at room temperature for a week. Ag colloids and a quinomethionate solution were used with a volume ratio of 10 : 1, and the pH of the solutions was adjusted with H₂SO₄ and NaOH.

The Raman and the SERS spectra were measured with a SPEX 1403 scanning double monochromator, RCA C31034 PMT detector and SPEX DM 3000R software. A Coherent Innova 90-5 argon ion laser was used as the source, and the wavelength was 514.5 nm. The laser power was 100 mW, and the spectral slit width was 800 μm. Data were taken at a scan rate of 2 cm⁻¹/0.3s.

UV-visible absorption spectra were measured using a Shimadzu UV-360 pc instrument and the IR spectra were measured with a Galaxy series FT-IR 7000.

The normal-mode calculations of quinomethionate were performed with the program package HyperChem[®] (release



Quinomethionate

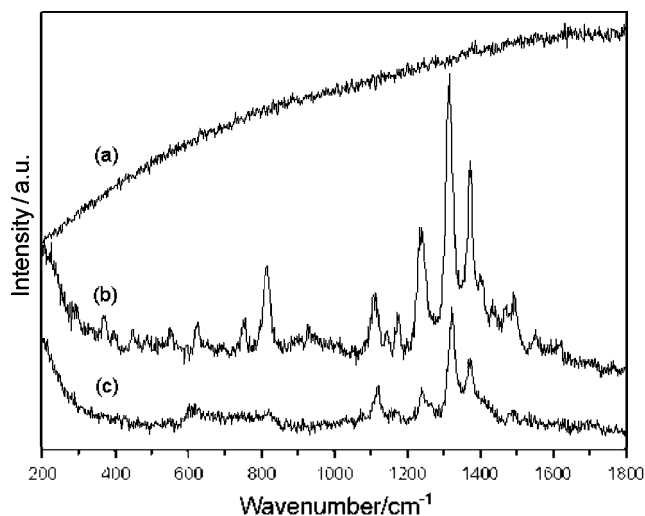


Figure 1. (a) Ordinary Raman spectrum of solid state. (b) SERS spectrum of quinomethionate (10^{-3} M) in acetone with Creighton *et al.*'s colloid and (c) with Lee and Meisel's colloid.

4.5). The program uses the PM3 Hamiltonian for the calculation of ground-state energies.

Results and Discussion

As shown in Figure 1, an ordinary Raman spectrum of solid-state quinomethionate, the vibrational peaks are superimposed on a strong yellowish fluorescent background. But in the SERS spectra, despite the lower concentrations, the vibrational peaks are clean and intense. Figure 1(b) and 1(c) are the SERS spectra obtained from solutions in which two types of colloids were added to a 0.5 M KCl solution. The shapes of the Raman bands coincide. The mechanisms of surface adsorption, therefore, are similar. It is evident that the SERS spectrum in Creighton *et al.*'s colloids has better resolution and stronger intensity. As shown in Figure 1(c), the C-S stretching vibration peaks at 622 cm^{-1} and 692 cm^{-1} disappeared and the entire peak intensity decreased when we used Lee and Miesel's method.

For a better understanding, we investigated the Raman spectra and UV-visible absorption spectra of the Ag colloid itself. In the Raman spectra of the Ag colloids, Creighton *et al.*'s colloid did not display a peak, but Lee and Miesel's colloid showed a weak peak around 1400 cm^{-1} , which can be attributed to citrate ions. In the UV-visible absorption spectra, Creighton *et al.*'s spectra showed a maximum absorption peak at 395 nm and a shoulder peak at 450 nm, whereas Lee and Miesel's colloid appeared at 453 nm, which is a longer wavelength than that of Creighton *et al.*'s colloid.

There are several kinds of sols, but their sizes, shapes and surface charge properties are a little different; therefore, the SERS effect is different as well. So compatible sols must be selected for the sample preparation. From a comparison of these two colloidal spectra, we conclude that Creighton *et al.*'s colloid is best suited for our research. We, therefore, will focus on the Creighton *et al.*'s colloids in the future.

Figure 2 shows the IR and the SERS spectra of 10^{-3} M

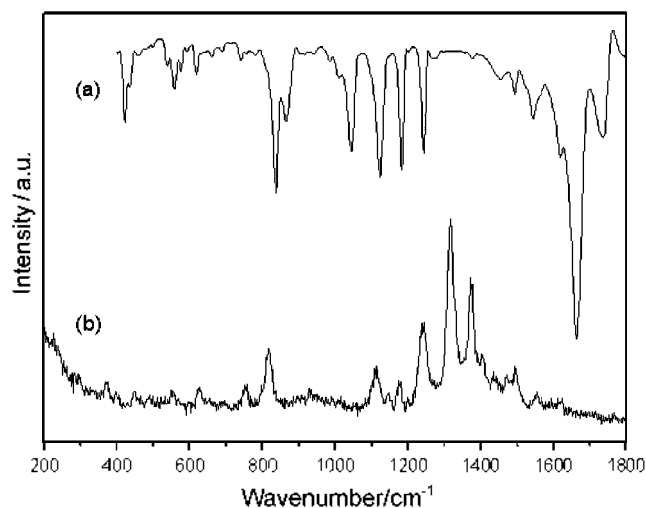


Figure 2. Comparison of (a) IR spectrum of quinomethionate with (b) SERS spectrum shown in Figure 1.

quinomethionate in acetone. In the IR spectra, the carbonyl stretching mode at 1699 cm^{-1} is very strong, but the SERS spectra show the enhanced (C-N) stretching mode to be around $1320\text{--}1370\text{ cm}^{-1}$. Skeletal vibrations of the quinoxaline ring are found at $1120\text{--}1250\text{ cm}^{-1}$. It is expected, therefore, that the N atom adsorbs strongly on the Ag surface. At 226 cm^{-1} , even if it is very weak, the (Ag-N) stretching mode appears.

The splitting of the enhanced (C-N) stretching mode is caused by adsorption changes in the molecular structural symmetry. The band at 1324 cm^{-1} is attributed to the (C-N) stretching mode of the adsorbed N atom and at 1368 cm^{-1} to the un-adsorbed N atom. This phenomenon becomes clear when the N atom is adsorbed to silver colloid particles. As a result, the (C-N) bond weakens because of a charge transfer from the molecule to the metal. Of the two N atoms, which is adsorbed? It is not clear, but we have inferred that the

Table 1. Details of assignment of quinomethionate

IR	SERS	Assignments
	226(w)	$\nu(\text{Ag-N})$
	254(w)	$\nu(\text{Ag-Cl})$
	376(m)	$\delta(\text{C-S})$
557(m)	546(m)	ring deformation
617(w)	622(m)	$\nu_s(\text{C-S})$
740(w)	692(m)	$\nu_{as}(\text{C-S})$
837(s)	818(s)	$\gamma(\text{C-H})$ benzene ring
1122(m)	1122(s)	skeletal vibration
1182(m)	1172(w)	skeletal vibration
1242(m)	1244(m)	skeletal vibration
	1324(vs)	$\nu(\text{C-N})$
1374(w)	1368(vs)	$\nu(\text{C-N})$
1493(w)	1486(m)	$\nu(\text{C-C})$
	1554(w)	$\nu(\text{C-C})$
	1618(w)	$\nu(\text{C-N})$
1662(vs)	1699(w)	$\nu(\text{C-O})$

vs - very strong, s - strong, m - medium, w - weak, ν - stretching vibration, δ - in-plane bending vibration, γ - out-of-plane bending vibration.

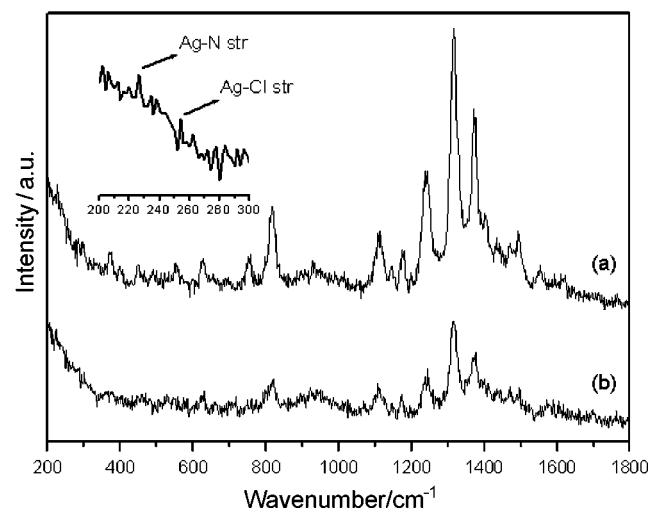


Figure 3. SERS spectra of quinomethionate (a) containing KCl and (b) without KCl.

methyl group is located in a direction opposite the surface because of steric hindrance.

In the IR spectra, the carbonyl stretching mode is very strong, and the skeletal ring vibration has a medium intensity. But in the SERS spectra, the (C-N) stretching vibration mode is the strongest. Even if they are very weak, the (Ag-N) stretching mode appears at 226 cm^{-1} , and the (Ag-Cl) stretching mode appears at 254 cm^{-1} . In Table 1, the vibrational assignments of quinomethionate in the IR and the SERS spectra are summarized with reference to the literatures^{13,14} and calculated values from the HyperChem[®] program.

The effect of anion as an electrolyte is shown in Figure 3. It is known that the cation has essentially no influence on the spectrum, hence the difference between the two spectra intensities is due to the presence of chloride ions. In the SERS spectrum, which contains chloride ion, the Raman signal is stronger and sharper than in the absence of chloride ion, and a (Ag-Cl) stretching peak at 254 cm^{-1} appears. The role of chloride or other co-adsorbed species on the positively charged Ag surface has been predicted and experimentally verified.^{15,16} This enhancement originates from the induction of positive charges on silver surfaces by the co-adsorbed chloride, which leads to an increase in the interaction between the molecule and the silver surface. Figures 4(b), 4(c) and 4(d) show that the relative intensities increase gradually with increasing concentrations of chloride. This is in agreement with the chloride-quenching effect observed by Wentrupt-Byrne *et al.* in their investigation of various organic molecules on silver colloids.¹⁷ If the chloride ion concentration is too high, the Ag-Cl⁻ interaction will induce the desorption of a sufficient amount of quinomethionate, and thus will reduce the SERS intensity as shown in Figure 4(a). Over a certain range of higher chloride ion concentrations, the enhancement effect is replaced by the quenching effect. Here the boundary is about 0.5 M.

For a better understanding, UV-visible spectra were obtained in the presence and absence of chloride ion. In the

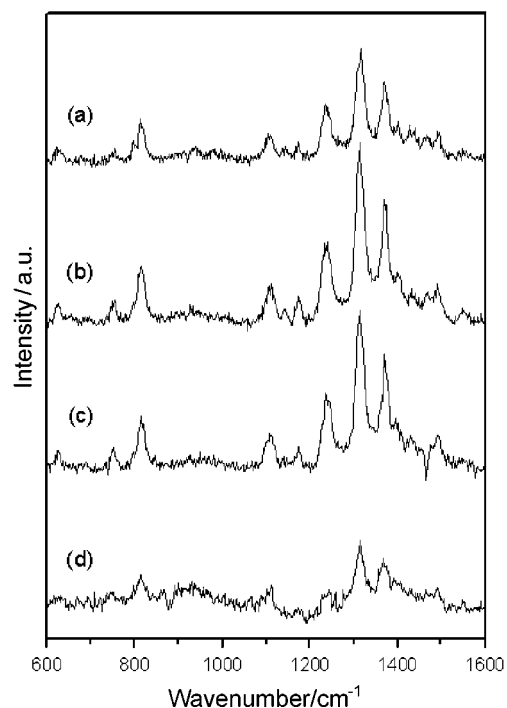


Figure 4. SERS spectra of quinomethionate at various KCl concentrations: (a) 5 M (b) 0.5 M (c) 0.1 M (d) 0.01 M.

spectrum of silver colloid, the maximum absorption band at 395 nm is a characteristic of the plasma resonance absorptions on silver spheres. The shoulder at 438 nm indicates the resonance of particles with non-spherical geometries or the presence of a slight coagulation of spherical particles in the colloid. When quinomethionate is added to the colloid, a

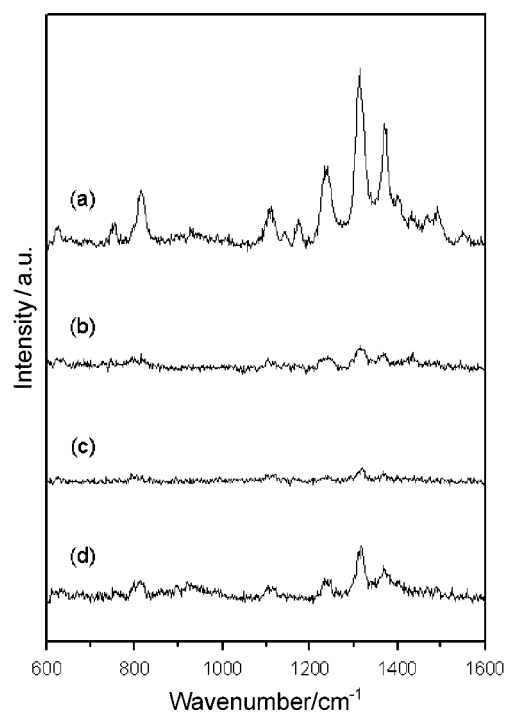


Figure 5. SERS spectra of quinomethionate containing various anions: (a) 0.5 M Cl⁻ (b) 0.5 M Br⁻ (c) 0.5 M I⁻ (d) 0.5 M F⁻

broad band at a longer wavelength appears. This behavior is believed to be due to the formation of a silver particle cluster with the adsorbate. After the addition of KCl, this band shifts to a longer wavelength. This shows that quinomethionate is strongly adsorbed on the silver sol.¹⁸

To investigate the degree of coverage of anions on silver surfaces, several different anions (Cl^- , Br^- , I^- , F^-) were used. As shown in Figure 5, the SERS spectrum containing chloride ion is largely enhanced when compared with other spectra. Since the characters of the spectra are entirely similar, we know from deduction that the cation has essentially no effect on the spectrum. So it is considered that iodide ion and bromide ion are tenaciously adsorbed on silver surfaces, and, thus, a little quinomethionate is adsorbed on the Ag surface. Fluoride ion is very weakly adsorbed, so it does not increase the interaction between the adsorbate and the silver surface. Hence, for obtaining a useful SERS spectra, specifically adsorbed anions are essential and the chloride ion is the best among the several anions examined in this experiment.

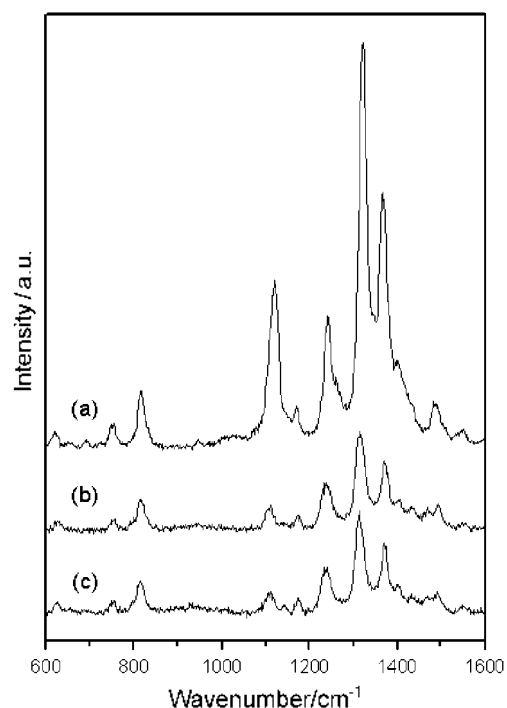


Figure 6. SERS spectra of quinomethionate containing KCl in different conditions: (a) acidic (b) neutral (c) basic.

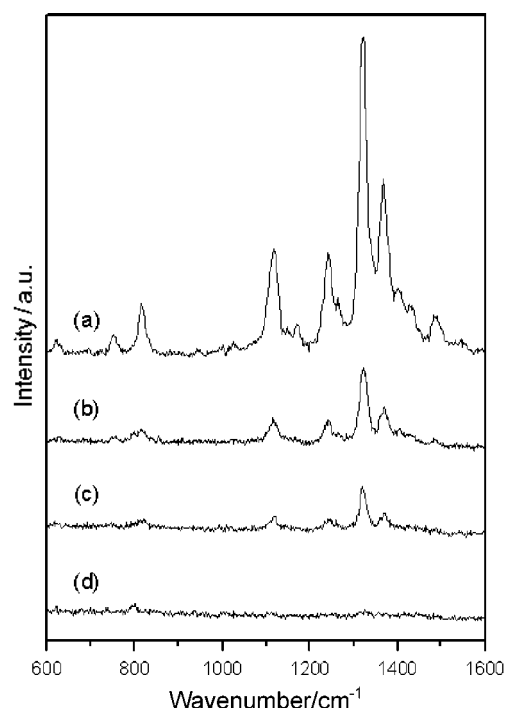
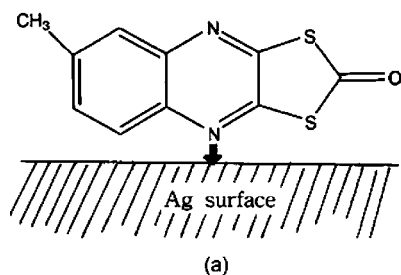


Figure 8. SERS spectra of different concentrated quinomethionate: (a) 10^{-3} M (b) 10^{-4} M (c) 10^{-5} M (d) 10^{-6} M.

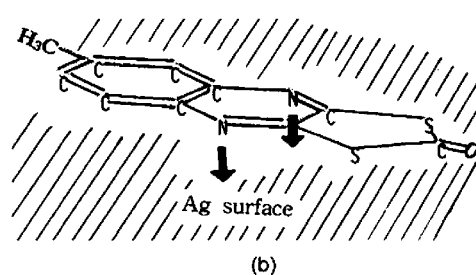


Figure 7. Adsorption configuration of quinomethionate on silver surface *via* (a) one N atom (b) two N atoms.

The pH effect is also important in the SERS spectra. In Figure 6, the SERS spectra are studied at different pH values. The acidic pH solution was achieved by adding H_2SO_4 to the mixture instead of HCl to avoid the influence of the chloride ion, whereas the basic pH was achieved by adding NaOH. The spectrum in neutral conditions was similar to that in basic (Figure 6(b), 6(c)). This shows that the adsorption configuration in both conditions are the same. In acidic conditions (Figure 6(a)), the intensities of all the peaks increased, especially the skeletal ring vibration peak at 1122 cm^{-1} largely increased in comparison with the other skeletal ring vibration peak at 1244 cm^{-1} . Their relative intensities were reversed against neutral and basic conditions. It is evident that quinomethionate is adsorbed by one N atom perpendicularly; the peaks at 1122 cm^{-1} and 1244 cm^{-1} are skeletal ring vibrations. The former may arise from symmetric vibrations, and the latter from asymmetric vibrations.

In acidic conditions, the protonated N atom is adsorbed to the silver surface perpendicularly (Figure 7(a)). In basic and

neutral conditions, however, the adsorption occurs dominantly via two N atoms in the parallel configuration (Figure 7(b)). According to the surface selection rule, the component of the transition dipole normal to the surface is excited more strongly than the tangential component.¹⁹ More enhancements, therefore, occurred in acidic conditions that adopt a perpendicular configuration to the surface (Figure 6(a)). Specifically, in basic conditions, the peak intensity decreased generally. This is because the hydroxide ion is adsorbed competitively on the Ag surface with chloride ion, so it prevents the interaction between the adsorbate and the silver colloids.²⁰ The opposite occurs in acidic conditions, because the positive ion pairs coordinated by the proton form a complex with chloride ion on the surface. This complex is good electromagnetic-field material, so the degree of adsorption is strong. The shapes of spectra obtained in a range of acidic conditions resembled one another. Only the intensity changed gradually. At pH=1, the spectrum was the best.

We have obtained the SERS spectra from various concentrations (Figure 8). All of these spectra were obtained in acidic solutions containing 0.5 M KCl. As the concentration decreased, the peak intensity diminished. The peak intensity can be detected at a lower concentration of 10^{-5} M.

Conclusion

SERS spectroscopy turns out to be a very useful tool for detecting agrochemical residue in crops and fruits. In the case of insecticides or fungicide quinomethionate, different adsorption mechanisms are possible, depending on pH values. In acidic conditions, this molecule interacts with the surface *via* the protonated nitrogen atom and the orientation of the planar molecule is perpendicular to the surface. In neutral and basic conditions, however, the interaction takes place through the two nitrogen atoms parallel to the surface in addition to the perpendicular adsorptions *via* one N atom. Two types of silver colloids, the Creighton *et al.*'s colloid and Lee and Miesel's colloid, were used in our present research. Since their charge properties are a little different, the peak intensity of one differs slightly from the other as well. Creighton *et al.*'s colloid performed better in our

present research. As shown in an ordinary Raman spectroscopy, the vibrational peaks are superimposed on the strong fluorescence background. When it is adsorbed on silver colloids containing chloride ion, however, the vibrational spectra can be obtained at a solution of 10^{-5} M.

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