Surface-enhanced Raman Spectroscopy of Ethephone Adsorbed on Silver Surface

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We investigated the Surface-enhanced Raman Spectroscopy (SERS) spectrum of ethephone (2-chloroethylphosphonic acid). We observed significant signals in the ordinary Raman spectrum for solid-state ethephone as well as 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 that were prepared by the γ-irradiation method. The influence of pH and the influence of anion (Cl^-, Br^-, I^-) on the adsorption orientation were investigated. Two different adsorption mechanisms were deduced, depending on the experimental conditions. The chlorine atom or the chlorine and two oxygen atoms were adsorbed on the colloidal silver surface. Among halide ions, Br^- and I^- were more strongly adsorbed on the colloidal silver surfaces. As a result, the adsorption of ethephone was less effective due to their steric hinderance.

Key Words : Surface-enhanced Raman spectroscopy, Pesticide, γ-Irradiation, Ethephone

Introduction

Generally, molecules adsorbed on appropriately prepared metal surfaces exhibit a Raman scattering cross section that are several orders of magnitude greater than the corresponding quantity from the isolated molecule. This effect, called 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.[3-7] In general, the observation of the SERS effect requires the presence of nanometer-scaled roughness (10-500 nm) on the metal surface. The analytical applications employ metal-coated microspheres,[8] silver thin film (by silver mirror reaction), LB film,[9] and metal colloids[10,11] as the SERS-active substrates. Because the colloidal silver surface has been reported to be easily obtained by the γ-irradiation method and has superior surface enhancement on the Raman signal,[12] it was used in the present study. The 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.[13] Additionally, pest and disease resistance affecting crop protection capability and environmental pollutions produced by some agrochemicals are important growing concerns.[14] Thus, there have been many studies about crop protections for their wide applications. Many researchers have investigated spectroscopy with limited regard to agricultural medicines. Ethephone is a toxic chemical used as an insecticide in vegetables and fruits.[15] Thus, it is very important to observe the SERS spectra of ethephone, an agricultural insecticide. The current research elucidates the character and the adsorption mechanism of ethephone on silver colloids. The pH and anion effects were also investigated.

Experimental Section

Analytical-reagent grade ethephone was purchased from Aldrich Co. and used without further purification. All solutions were prepared with triply distilled water. Aqueous silver sol was prepared with 10.0 mM of analytical grade $AgNO_3$ in distilled water. 2.0% PVP was used as the stabilizer and 6.0 M isopropanol was used as a scavenger for hydroxyl radicals. All solutions were deaerated by bubbling with argon gas for 1 hour and then irradiated in the field of 20 KGy ^{60}Co γ-ray source. The absorption spectra were recorded on UV-240 shimadzu UV-VIS spectrophotometer using quartz cells. The aqueous solution of ethephone was mixed with the silver sol at a volume ratio 1 : 10. The SERS spectra were obtained with a SPEX 1403 scanning double monochromator, an RCA C31034 PMT detector, and SPEX DM 3000R software. Coherent Innova 90-5 argon ion laser (514.5 nm) was used as an excitation source. The laser power and the spectral slit widths used were 100 mW and 600 μm, respectively. The sample was placed in a 3 mm diameter glass tube and radiated, and the scattered light was collected at 90° geometry. The pH of the solutions was adjusted by injecting the necessary amounts of reagent grade H_2SO_4 and NaOH solutions and was checked before each day's experiments. The halide solution was prepared with 0.5 M of analytical grade KCl, KBr and KI in distilled water. The normal-mode calculations of ethephone were performed with the program HyperChem (release 7.0). PM3 hamiltonian was used to calculate the Raman frequencies of ethephone in this program.

Results and Discussion

Figure 1 shows the molecular structure of ethephone. Generally, the lone-pair electron and aromatic π system were easily bound to a metal surface. In the case of ethephone, chlorine or three oxygen atoms have lone-pair electrons. Therefore, ethephone involves four available adsorption
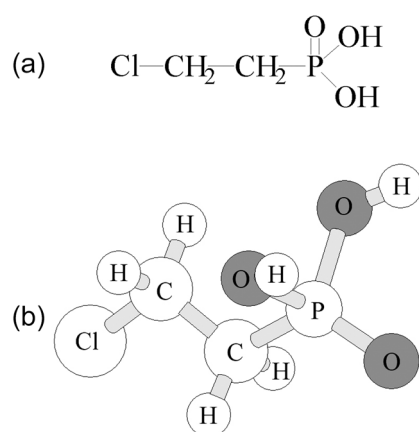
Figure 1. Chemical structure of ethephone: (a) two dimensional structure (b) balls and cylinders model. (geometry optimized from HyperChem 7.0 program)
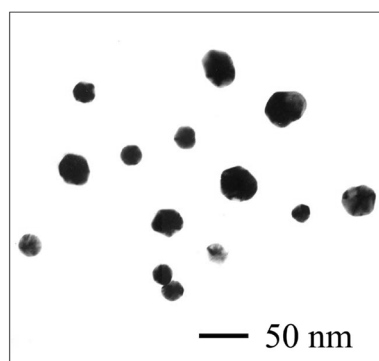

Figure 2. TEM image of silver sol.

Figure 3. UV-visible absorption spectrum of silver sol.
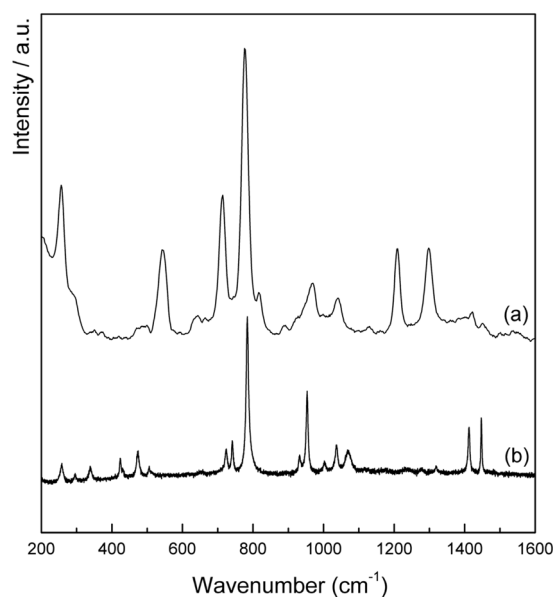
Figure 4. (a) SERS (1.0×10^{-4} M) and (b) ordinary Raman (solid state) spectra of ethephone.

atoms on colloidal silver surfaces. Figure 2 shows a TEM image of silver colloid particles prepared by the γ-irradiation method. The average size of the silver colloid particles was 35 ± 7.5 nm. The UV-VIS spectrum of the silver colloid particles is displayed in Figure 3, where the peaks at 403 nm is the surface plasmon band of the silver colloid particles synthesized by the γ-irradiation methods. It is well known that a surface plasmon band of spherical silver nanoparticles appears at around the 400 nm region. This explains the characteristics of aggregated silver particles are in good aggrement with previous studies of many researchers.[16,17] The ordinary Raman spectrum of solid-state ethephone is shown in Figure 4(b). In the SERS spectra, despite the lower concentrations, the vibrational peaks are clean and intense. Figure 4(a) shows the SERS spectrum obtained from 1.0×10^{-4} M aqueous solution of ethephone. In Table 1, the vibrational assignments of ethephone in the SERS and ordinary Raman spectra are summarized with reference to the literatures and values calculated using the HyperChem PM3 method.[18]

The following experiments were performed in order to investigate the pH effect of ethephone on the SERS spectrum. Solutions were prepared with various pH ranging from acidic to alkali conditions. As shown in Figure 5, an equilibrium structures of ethephone have been displayed
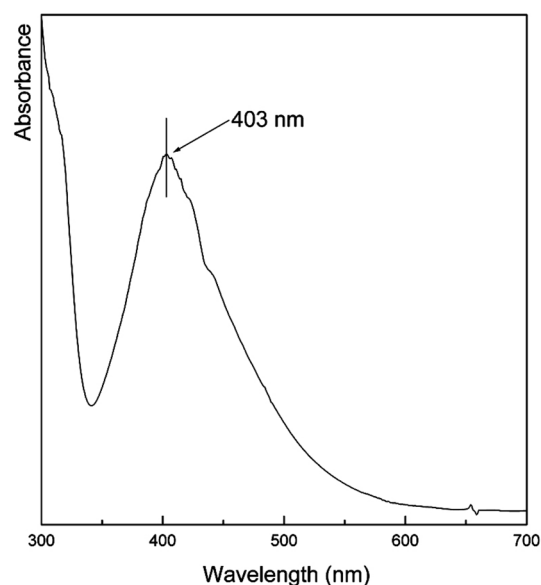
with different pH conditions. The hydroxyl group of ethephone is deprotonated in the alkali condition. However, in acidic condition, the P=O group of ethephone were protonated. Thus, the adsorption site of ethephone are three oxygen atoms and a chlorine atom in the alkali condition. On the other hand, the chlorine atom is mainly the adsorption site in acidic condition. The SERS spectra shown in Figure 6, for silver sol in acidic, neutral, and alkali conditions are little different. Three distinct peaks at 256, 776, and 972 cm^{-1} were observed in the SERS spectrum for ethephone on the colloidal silver surface. The strong bands of intensity appearing at 256 and 776 cm^{-1} in the SERS spectrum may be assigned to ν(Ag-Cl), ν(P-C), respectively, as shown in Table 1. In particular, the peak intensity at 256 cm^{-1} shown

Table 1. Details of assignment of ethephone
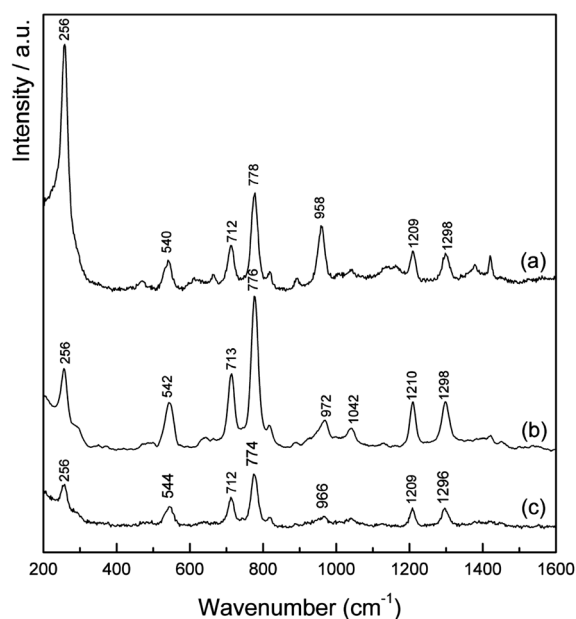
Calculation	Raman	SERS	Assignment
–	–	256(m)	ν(Ag-Cl)
654	657(w)	542(m)	ν(Cl-C)
711	741(ms)	713(ms)	ν(P-C)
778	783(s)	776(s)	ν(P-C), ν(P-O)
958	953(ms)	972(w)	ν(P-O)
1051	1036(w)	1042(w)	ν(P-O-C)
1195	1229(w)	1210(w)	ν(CH$_2$)
1293	1318(w)	1298(m)	ν(CH$_2$)
1366	1412(m)	1378(w)	ν(CH$_2$)
1410	1447(m)	1421(w)	ν(CH$_2$)

abbreviations: s = strong; m = medium; w = weak; ν = stretching; γ = bending; ω = scissoring; δ = deformation
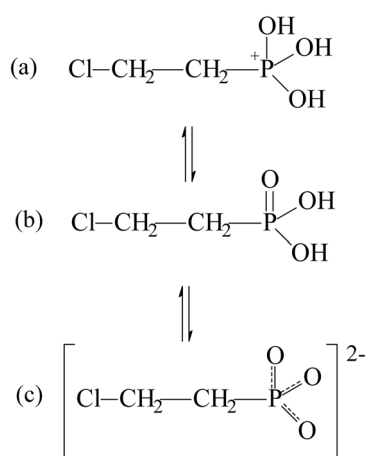
Figure 5. Equilibrium structures of ethephone as pH condition: (a) acidic (b) neutral (c) alkali

Figure 6. SERS spectra of 1.0×10^{-4} M ethephone in silver sol at (a) pH=2.0 (b) pH=7.0 (c) pH=12.0

the most intense in the SERS spectrum.[19,20] Moreover, the red-shift of the ν(P-C) band from 778 to 774 cm^{-1} are caused by increase pH. On the other hand, the peak position at 256 cm^{-1} was not changed as the pH increased. It can be assumed from the above results that the adsorption orientation of ethephone, under the neutral and acidic conditions, are similar with each other. As the pH increased, however, its adsorption process is different. In neutral and acidic conditions, ethephone interacts with the chlorine atom and the orientation of this molecule is nearly perpendicular to the colloidal silver surface. In alkali conditions, however, the interaction takes place through the chlorine and two oxygen atoms tilted to the colloidal silver surface. From the above result, we suggest the adsorption configuration of ethephone on the colloidal silver surface shown in Figure 7. To investigate the coverage degree of anions on colloidal silver surface, the SERS spectra of ethephone adsorbed on a

in Figure 6, was decreased as the pH increased. On the other hand, the peak intensity at 766 cm^{-1} was increased. In general, the determination of adsorption orientation was based on the SERS "surface selection rules", which stated the vibrations that derived their intensities from the large value of α_{zz} (z being the local surface normal) would become
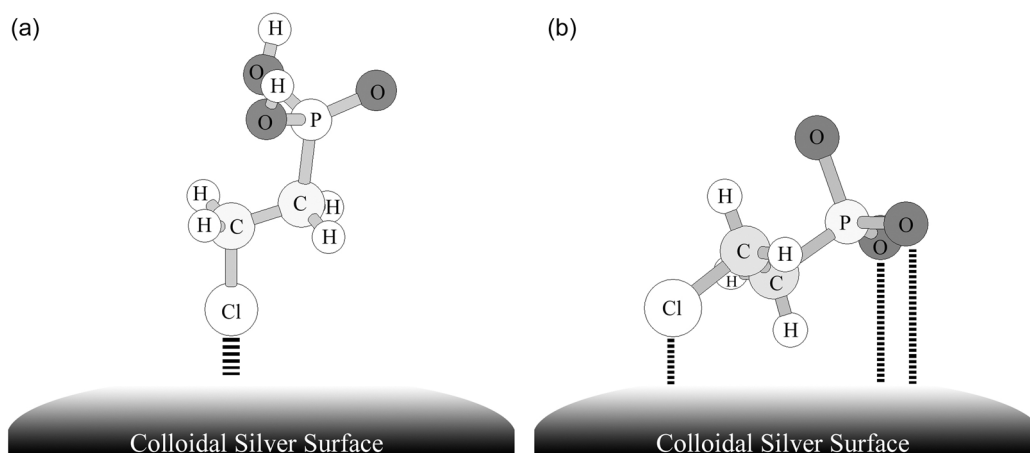
Figure 7. Adsorption configuration of ethephone on silver surface *via* (a) Cl atom (b) Cl and two O atoms.
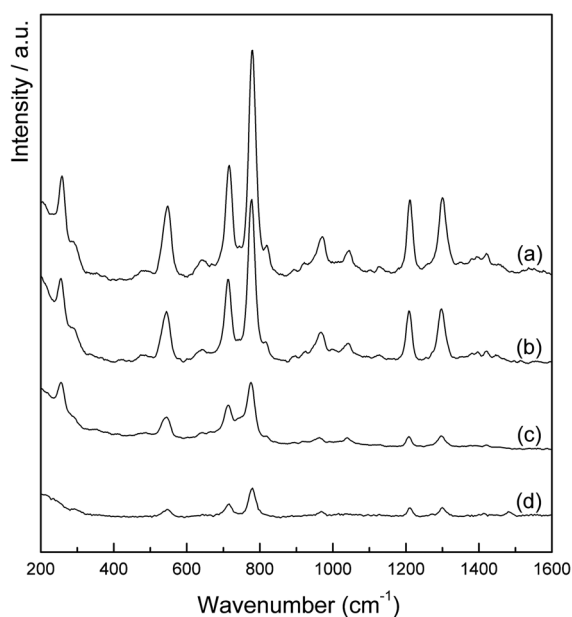
Figure 8. SERS spectra of 1.0×10^{-4} M ethtphone in silver sol containing (a) pure (b) 0.5 N Cl$^-$ (c) 0.5 N Br$^-$ (d) 0.5 N I$^-$ at pH=7.0.

colloidal silver surface have been observed from a series of aqueous solutions containing Cl$^-$, Br$^-$, and I$^-$ as electrolyte. Generally, it is known that the cation has no effect on the spectrum. The important role of anion adsorption has been discussed.[21] To investigate the degree of coverage of anions on colloidal silver surfaces, several different anions (Cl$^-$, Br$^-$, I$^-$) were used. As shown Figure 8, the SERS spectrum containing Cl$^-$, Br$^-$, and I$^-$ were reduced by indicating their order of peak intensity. In the presence of a halide ion, competitive adsorption occurred between the ethephone molecule and the halide ions on the colloidal silver surface. This results from the order of adsorption intensity of halide ion. We concluded from the above phenomena that Br$^-$ and I$^-$ were more strongly adsorbed on colloidal silver surfaces. Therefore, adsorption sites of colloidal silver surfaces for ethephone were reduced.[22] Additionally, from the point of view of steric hindrance the ionic radius of Cl$^-$, Br$^-$, and I$^-$ are 181, 195, and 216 pm, respectively. For that reason, Br$^-$ and I$^-$ ion were more sterically hindered between ethephone molecules and colloidal silver surface. However, pure ethephone (without a halide ion) exhibited the greatest intensity, as shown in Figure 8(a). Thus, only pure ethephone molecule was adsorbed on the colloidal silver surface. Finally, we conclude that bromide and iodide ions are more strongly adsorbed on colloidal silver surfaces and that steric hindrance occurs. Therefore, the rate of ethephone adsorption on the colloidal silver surface was very slow. Hence, to obtain useful SERS spectra, specifically adsorbed ethephone molecules revealed stronger Raman peak intensities than the other halide ions in the current experiment.

Conclusion

SERS spectroscopy is a very useful tool for detecting agrochemical-like pesticides and fungicides. In the case of ethephone, different adsorption mechanisms are possible, depending on the pH values. In acidic conditions, ethephone interacts with the chlorine atom and the orientation of this molecule is nearly perpendicular to the colloidal silver surface. In netural and alkali conditions, the interaction takes place through the chlorine and two oxygen atoms tilted to the colloidal silver surface. The roles of halide ion adsorption have been discussed. Among the halide ions, Br$^-$, and I$^-$ resulted in poor SERS spectra. Thus, we conclude that Br$^-$ and I$^-$ are more strongly adsorbed on colloidal silver surfaces and cause more strongly steric hindrance for ethephone.

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