

# Electrochemical and Surface Enhanced Raman Scattering Spectroelectrochemical Study of Phytic Acid on the Silver Electrode

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Phytic acid (IP<sub>6</sub>) and its salts are promising reagents to alleviate corrosion of metals, which are environmentally friendly and highly efficient, compared to some traditional inhibitors toxic to environment. This paper reports the studies of the structure and anticorrosion features of two kinds of the self-assembled monolayers (SAMs) of IP<sub>6</sub> at the silver surface under various pH values, 1.27 and 13, by using electrochemical and surface enhanced Raman scattering (SERS) spectroelectrochemical measurements. On the basis of recorded *ex situ* SERS spectra, different adsorption modes of both resulted SAMs of IP<sub>6</sub> at the silver surfaces have been postulated. In addition, based on *in situ* SERS electrochemical measurements, a tentative explanation for the difference in corrosion potentials of two kinds of the silver surfaces in the presence of SAMs formed from completely protonated or deprotonated IP<sub>6</sub> molecules has also been presented.

## I. Introduction

The protection of metal from corrosion draws increasing attention due to the severity of corrosive environment increase. Benzotriazole, imidazole, chromates, etc. have been extensively and successfully used for anticorrosion.<sup>1</sup> However, environmental restrictions to the above-mentioned inhibitors due to their toxicity such as carcinogenic effects of chromates require the development of more efficient and environmentally friendly anticorrosive agents.<sup>2</sup>

Inositol hexakisphosphoric (IP<sub>6</sub>) acid known as phytic acid, a naturally derived material, has been investigated for corrosion prevention of metal and attracted increasing interest for reasons including the following:

(1) IP<sub>6</sub> is an economical reagent as it can easily be produced from many plant sources, including corn, wheat, rice, soybean, sesame, and oat.

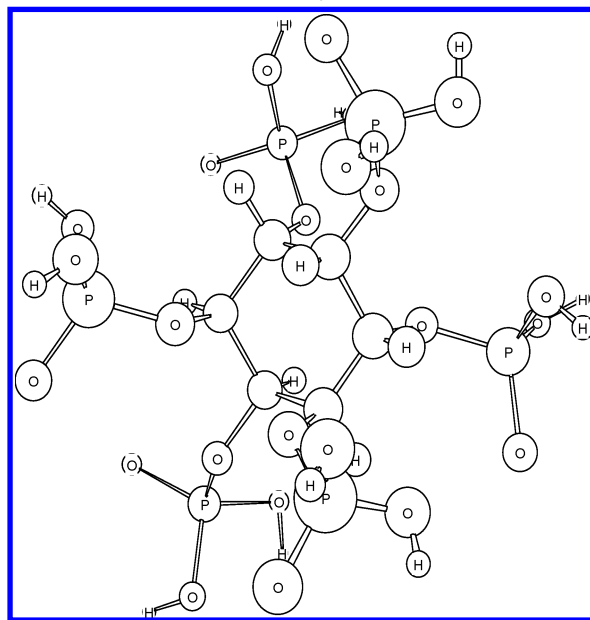
(2) IP<sub>6</sub> is safely used as an oral cleansing agent, water treatment agent, food additive, and cosmetic additive as it is nontoxic and “green” to the environment.

(3) Owing to its structure containing 12 acid groups (see Scheme 1), IP<sub>6</sub> and its salt are liable to interact with metal ions as a result of formation of complexes at the metal surface for antirust and anticorrosion.

(4) Water is a good solvent for IP<sub>6</sub>.

Electrochemical and spectroelectrochemical methods have been employed to elucidate the inhibition mechanism and efficiency.<sup>4–9</sup> To our knowledge, though some anticorrosion agents containing IP<sub>6</sub> or its salts are patented or available commercially,<sup>10–12</sup> up to date, little work has been published on the investigation of the interaction between phytic acid and metal at a submolecular or molecular level.

## SCHEME 1: Structure of Phytic Acid



Silver as a noble metal which is made into silver jewelry, silverware, silver solder, dental alloys, coins, etc. plays an important role in human life, but silver and all of its alloys are also very susceptible to tarnish and corrosion. Taking advantage of the excellent Raman enhancement caused by silver of a factor even greater than 10<sup>6</sup>,<sup>13</sup> in the present paper, *in situ* surface enhanced Raman scattering (SERS) experiments were conducted to observe the self-assembled monolayers of phytic acid formed at the surface of silver under various pH conditions. Their polarization behaviors were also examined.

## II. Experimental and Methods

**Materials.** Aqueous phytic acid (70%) was purchased from Jiashan Jufeng Chemicals Inc. (Jiangsu, China). Two stock

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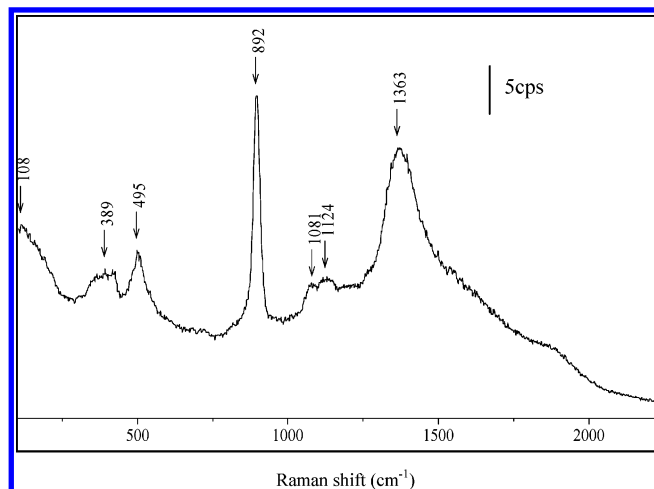


Figure 1. Normal Raman spectrum of IP<sub>6</sub> in aqueous solution.

TABLE 1: Tentative Assignments<sup>a</sup> of the Raman Spectra of IP<sub>6</sub> in an Aqueous Solution and SERS Spectra of SAMs of IP<sub>6</sub> on the Silver Electrode at pH 1.27 and 13

IP <sub>6</sub> /aq	IP <sub>6</sub> SAMs on the silver electrode		calculated	assignments
	pH 1.27	pH 13		
		571 <sup>m</sup>	584	O–P–O deformation
		705 <sup>w</sup>	695	cyclohexyl ring breath
892 <sup>vs</sup>		922 <sup>m,br</sup>	902	P–O(H or Ag) stretch
	1006 <sup>m</sup>		1007	P–O–C stretch
1081 <sup>w,br</sup>		1083 <sup>m,br</sup>	1074	P=O stretch
1124 <sup>w,br</sup>		1	139	P=O stretch
	1133 <sup>w</sup>			P=O–Ag stretch( <sup>s</sup> )
	1236 <sup>m</sup>			P=O–Ag stretch(as <sup>b</sup> )
1363 <sup>s,br</sup>	1389 <sup>m,br</sup>		1375	C–H deformation

<sup>a</sup> Wavenumbers (in cm<sup>-1</sup>) followed by superscripted relative intensities (vs, very strong; s, strong; m, medium; w, weak; br, broad). <sup>b</sup> s, symmetric; as, asymmetric.

solutions of 10<sup>-2</sup> mol/L IP<sub>6</sub> of different pH value, 1.27 and 13, were prepared by adjusting the pH with dilute NaOH or HCl, monitored by a pH meter. Doubly distilled water was freshly prepared and bubbled with nitrogen for ~15 min in order to remove oxygen. All other reagents were of analytical grade.

**Electrochemical Cell and Electrode Treatment.** A lab-made cell with an end of quartz window (0.5 mm thickness) for in situ Raman spectral measurement was employed. A silver disk electrode (1 mm diameter) was constructed from a polycrystalline silver rod (a purity of 99.99%) imbedded in a Teflon shroud. Prior to formation of IP<sub>6</sub> layers at the surface of the silver electrode, it was polished successively with emery paper and 1 and 0.3 μm Al<sub>2</sub>O<sub>3</sub> powder to a smooth mirror and then rinsed with distilled water followed by oxidation–reduction cycle (ORC) treatment. The ORC procedure was much the same as that reported in the literature<sup>14</sup> except that the reduction was performed at –0.25 V for 120 s and then at –0.5 V for 60 s in 0.1 mol/L KCl solution. Pt wire and a saturated calomel electrode (SCE) were employed as counter and reference electrodes, respectively. During this pretreatment and all other electrochemical process, the experiments were performed by a potentiostat (model 283 EG&G).

**Self-Assembled Monolayers.** The freshly roughened silver electrode was flushed with doubly distilled water and installed in the cell, and then 10<sup>-2</sup> mol/L aqueous IP<sub>6</sub> was injected into the cell to form self-assembled monolayers (SAMS) on the surface of silver after a quiet time of 0.5 h at room temperature. Two kinds of IP<sub>6</sub> SAMs formed at the silver surface under the

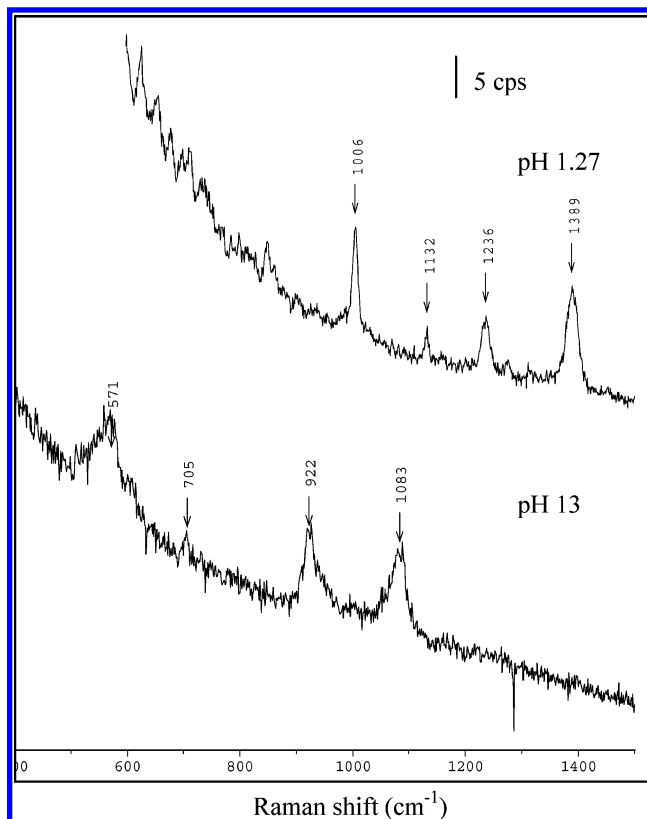


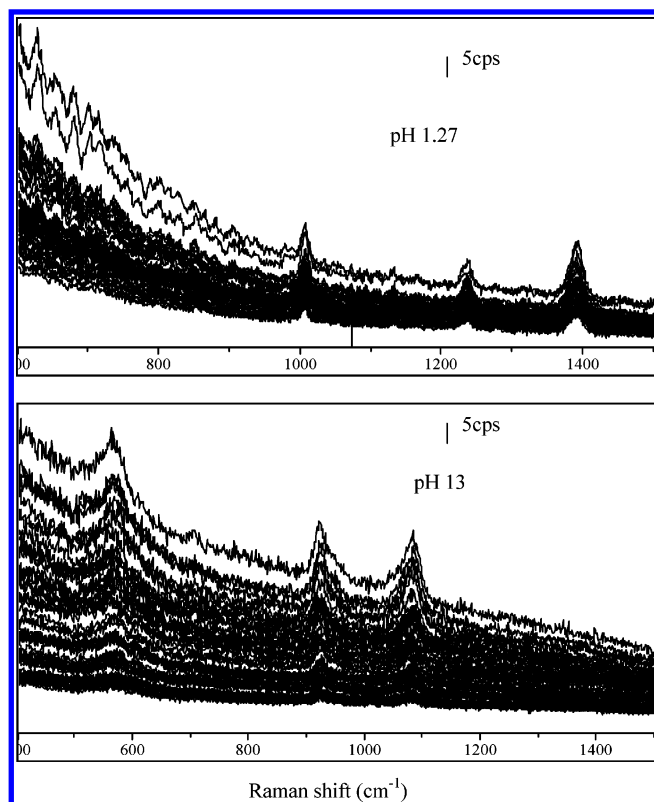
Figure 2. SERS spectra on IP<sub>6</sub> adsorbed at the silver surface at pH 1.27 and 13.

above-mentioned two various pH values were investigated by Raman mapping and in situ SERS spectroelectrochemical technique, respectively.

**Raman Spectroscopy and Raman Mapping.** Raman spectra were recorded with a confocal Raman system (SuperRamLab II, Dilor). It comprises an integral Olympus BX40 microscope with a 50× objective (8 mm), which can focus the laser onto the sample to collect the backscattered radiation, a notch filter to cut the exciting line, a holographic grating (600 g/mm), which provides a spectral resolution of 4 cm<sup>-1</sup>, and a liquid-nitrogen-cooled 1024 × 800 pixels CCD detector. The exciting wavelength of 785 nm from a semiconductor laser tube with a power of ca. 1 mW and a spot of the diameter ca. 3 μm on the silver surface were used not only to avoid destroying the sample but also to eliminate the effects of fluorescence. The slit and pinhole were respectively set at 100 and 500 μm in a confocal configuration to increase the spatial resolution. The collection time was 50 s, and for each spectrum, there were 2 accumulations. Especially for in situ SERS electrochemical measurement, each spectrum was acquired several times at the same biased voltage. A motorized translator XY stage with the capability of moving automatically one step for 1 μm was utilized to perform Raman mapping. The mapping area of ca. 64 × 40 μm<sup>2</sup> was squared randomly on an image of the surface, which was obtained by the use of optical axis conjugate camera and white light source. Calibration was done referring to the 519 cm<sup>-1</sup> line of silicon.

**Polarization Measurements.** Measurements of Tafel curves of the silver electrodes, in the presence and absence of IP<sub>6</sub> SAMs, were carried out in 0.1 mol/L KCl solution at 25 °C. The scan rate was set at 10 mV/s.

**Calculations.** Full geometry optimization was performed with Polak-Ribiere method and vibrational spectra of IP<sub>6</sub> were calculated with CNDO method<sup>15–17</sup> by using the Hyperchem



**Figure 3.** Raman mapping of SAMs of IP<sub>6</sub> at the silver surface formed under pH 1.27 and 13.

7.5 package of programs. The vibrational modes were also visualized by using the Hyperchem release 7.5 programs.

### III. Results and Discussion

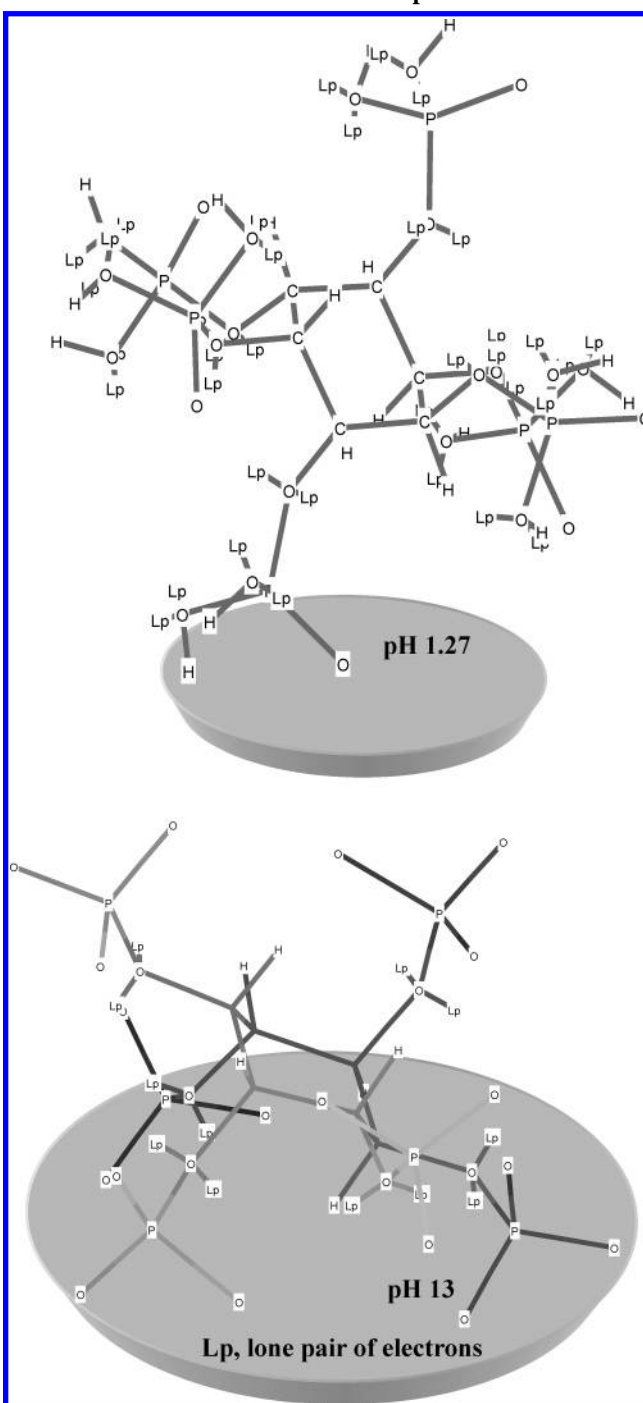
**Normal Raman Spectra, SERS, and Raman Mapping Measurement.** A normal Raman spectrum of IP<sub>6</sub> in aqueous solution is represented in Figure 1. Based on the results of normal mode calculation for vibrational spectra of IP<sub>6</sub>, the tentative assignments of bands are tabulated in Table 1 together with the assignments of the surface enhanced Raman spectra (Figure 2) on IP<sub>6</sub> monolayers self-organized at the silver surface at pH 1.27 and 13.

It is well-known that the sterically stable conformation of IP<sub>6</sub> adopts one phosphate in the axial (ax) position and five phosphates in the equatorial (eq) position and all of 12 acid groups of six phosphates are of protonated forms at low pH less than 1.5.<sup>18</sup> It can be seen clearly from the structure of IP<sub>6</sub> (Scheme 1) that four phosphates in the eq position are involved in strong H-bond formation and two free phosphates (one in the ax position and another in the eq position) remain on either side of the cyclohexyl ring.

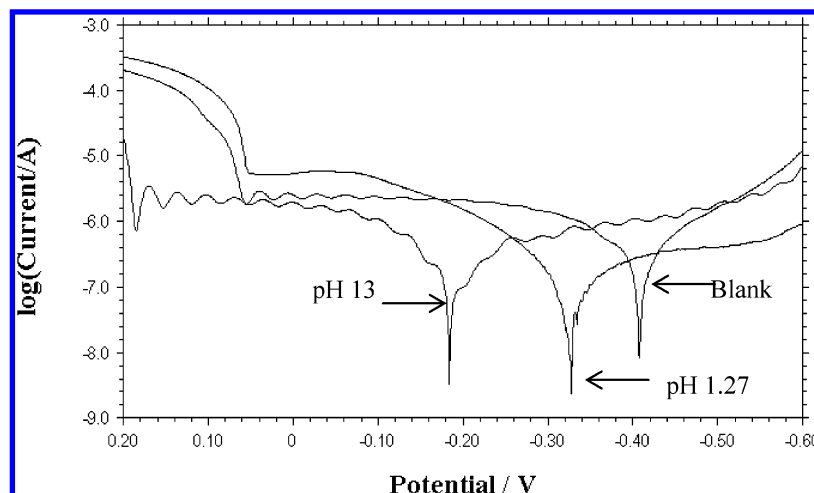
It is widely recognized that Raman signals from the SERS active surface illustrate that chemical moieties or groups of species closely access or directly adsorb on the surface.<sup>19</sup> In Table 1, in the pH 1.27 column, two peaks at 1133 and 1236 cm<sup>-1</sup> are attributed to symmetric and asymmetric stretching vibration of P=O- -Ag, respectively. It is suggested that IP<sub>6</sub> molecule self-assembled into monolayers at silver surface via P=O of either of two free phosphates, which is also supported by the observation of the P-O-C stretching vibrational mode near 1006 cm<sup>-1</sup>.

Brown and co-workers<sup>20</sup> reported that above pH 9.0 IP<sub>6</sub> undergo conformational inversion from the 1ax/5eq form to the 5ax/1eq according to their study on pH-dependent NMR

### SCHEME 2: Proposed Adsorption Modes of IP6 SAMs Formed at the Silver Surface under pH 1.27 and 13



spectroscopy of IP<sub>6</sub>. Under base condition of pH 13 in this experiment, phosphates of IP<sub>6</sub> are completely ionized or deprotonated. As shown in Figure 2 and Table 1, for pH 13, a broad band near 922 cm<sup>-1</sup> due to P-O stretching vibration blue-shifted by about 30 cm<sup>-1</sup> compared to the Raman spectrum recorded from IP<sub>6</sub> in aqueous solution was observed. It indicates that some phosphates of IP<sub>6</sub> tend to be absorbed on the silver surface through their P-O bonds to form SAMs. P=O groups of those phosphates could closely approach the surface according to the observed stretching vibrational mode near 1083 cm<sup>-1</sup>. Considering the occurrence of the enhanced band of 705 cm<sup>-1</sup> assigned to the breathing vibration of cyclohexyl ring, which is too weak to be seen in normal Raman spectrum of IP<sub>6</sub>, an



**Figure 4.** Tafel curves recorded in 0.1 mol/L KCl solution for blank silver electrode and the presence of IP<sub>6</sub> SAMs formed at the silver surface under pH 1.27 and 13.

**TABLE 2: Corrosion Potential, Corrosion Current Densities and Inhibition Efficiencies in 0.1 mol/L KCl Solution for a Blank Silver Electrode and in the Presence of IP<sub>6</sub> SAMs on the Silver Surface Formed under pH 1.27 and 13**

silver electrodes	$E_{\text{corr}}$ (mV)	$I_{\text{corr}}$ (mA/cm <sup>2</sup> )	$\eta$ (%)
blank	-408	$1.16 \times 10^{-5}$	
IP <sub>6</sub> SAMs (pH1.27)	-327	$3.27 \times 10^{-6}$	71.8
IP <sub>6</sub> SAMs (pH 13)	-183	$4.42 \times 10^{-6}$	61.2

adsorption mode of coplanar four phosphates in the axial position is postulated.

Raman mapping measurements were carried out to examine the IP<sub>6</sub> SAMs at the surfaces of silver electrodes formed under pH 1.27 and 13, and the results are depicted in Figure 3. It is very obvious that either of the two kinds of IP<sub>6</sub> SAMs demonstrates relatively ordered uniform features. Scheme 2 shows the proposed adsorption modes of IP<sub>6</sub> SAMs formed under pH 1.27 and 13.

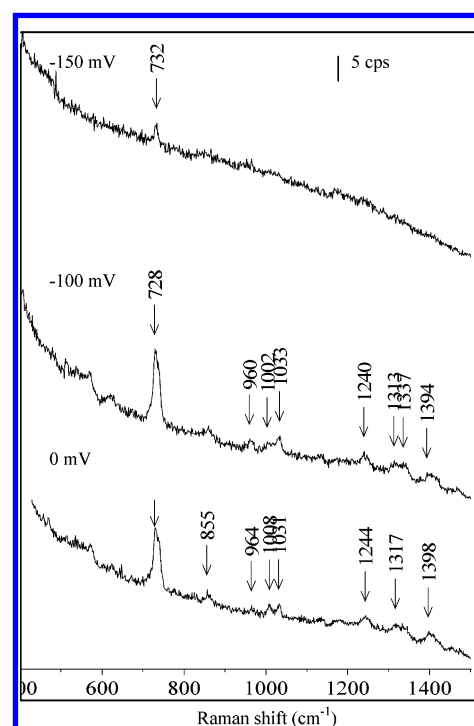
**Polarization Measurements.** Typical Tafel curves recorded at 25 °C for the above resulted SAMs of IP<sub>6</sub> at silver surface and a blank silver surface in 0.1 mol/L KCl solution are shown in Figure 4. The dynamic parameters of the corrosion potential ( $E_{\text{corr}}$ ) and the corrosion current ( $I_{\text{corr}}$ ) are listed in Table 2, together with the inhibition efficiency  $\eta$ ,<sup>21</sup> which is defined by

$$\eta = 1 - I_{\text{corr}}(2)/I_{\text{corr}} \quad (1)$$

where  $I_{\text{corr}}(1)$  and  $I_{\text{corr}}(2)$  refer to corrosion current densities in the absence and presence of IP<sub>6</sub> SAMs at the silver surface, respectively.

It is easy to find out that the corrosion potential of IP<sub>6</sub> SAMs formed at the silver surface under pH 13 is more positive than that under pH 1.27, and the later is more positive than the corrosion potential of the blank silver electrode. The variations between the corrosion potentials of two kinds of IP<sub>6</sub> SAMs at the silver surfaces and that of the blank silver are respectively 81 mV (pH 1.27) and 225 mV (pH 13), which suggest strong inhibitor to corrosion of the surfaces of silver electrodes.

From the proposed adsorption mode mentioned above, due to IP<sub>6</sub> SAMs formed at the silver surface under pH 1.27 by only one phosphate, it can be evaluated that the density of resulted monolayers is greater than that of SAMs formed at pH13. It is likely to be a sound explanation for the difference of inhibition efficiencies between two IP<sub>6</sub> SAMs at silver surfaces with the similar ordered uniformity.

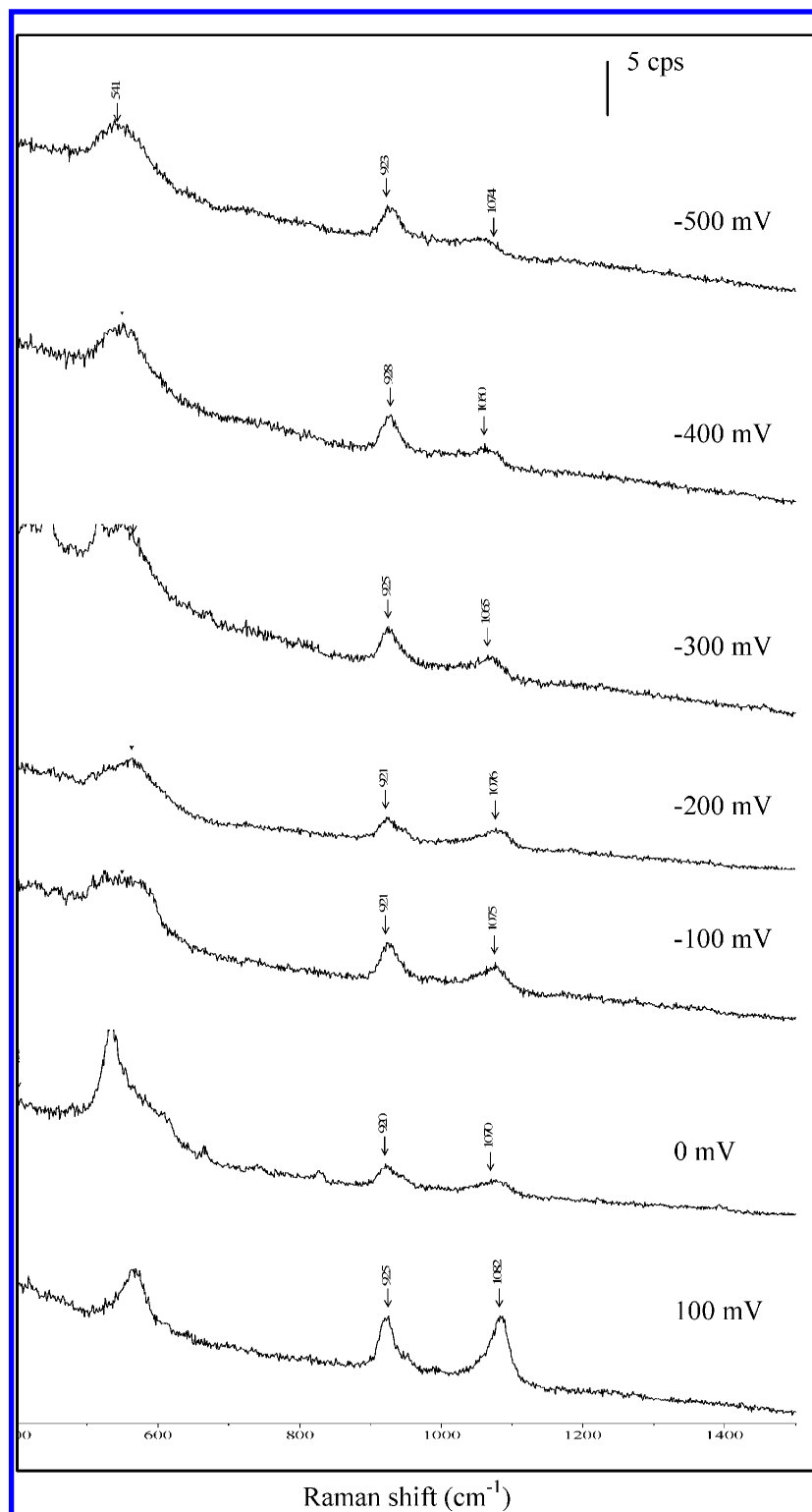


**Figure 5.** In situ SERS electrochemical spectra of SAMs of IP<sub>6</sub> at the silver surface formed under pH 1.27.

For further understanding the anticorrosive features of the SAMs of IP<sub>6</sub> on the silver surface, they were investigated by in-situ SERS electrochemical method.

**In Situ SERS Electrochemical Measurements.** In situ SERS electrochemical spectra of two kinds of SAMs of IP<sub>6</sub> at the silver surfaces were obtained and shown in Figures 5 and 6, respectively.

As shown in Figure 5, when the potential was applied at 0 mV or -100 mV vs. SCE, a novel band was observed around 728 cm<sup>-1</sup>. It could be tentatively attributed to the combination of deformation vibrations of O=P=O and deformation vibrations of O-P-O, referred to the results of above-mentioned calculations for vibration modes of IP<sub>6</sub>. Additionally, a peak at about 1031 cm<sup>-1</sup> originating from the combination of stretching and deformation vibrations of P-O also occurred. Aforementioned results indicate that it was undergoing the change of adsorption mode of IP<sub>6</sub> SAMs at the silver surface with the potential moving, compared to its results of Raman spectra



**Figure 6.** In situ SERS electrochemical spectra of SAMs of IP<sub>6</sub> at the silver surface formed under pH 13.

recorded without applied potential. Up to the holding potential at  $-150$  mV, the Raman spectra changed dramatically and no clear signal could be seen except a band near  $732\text{ cm}^{-1}$ . It displays that molecules of IP<sub>6</sub> tended to detach from the silver surface, which could be attributed to increasing electrostatic repulsion force between the negatively charged silver surface and P=O moiety as an anchoring site. It has been suggested that the difference in the surface charge should be of the dominating factor leading to different SERS spectra to some extent and especially IP<sub>6</sub> may just be physically adsorbed onto

the silver surface by electrochemical static interaction under such strong acidic solution.

It is interesting to note from Figure 6 that only slight alternations of Raman spectra of IP<sub>6</sub> SAMs at the silver surface formed under pH 13 were observed with potential shifting in the range  $+100$  to  $\sim -500$  mV. It reveals that the IP<sub>6</sub> SAMs at the silver surface formed under pH 13 are more stable than those under pH 1.27 owing to a strong reaction of molecules of completely deprotonated IP<sub>6</sub> with the silver surface via the P–O moieties of four phosphates. The conclusion is in agreement



with the fact of corrosion potential of the silver surface in the presence of IP<sub>6</sub> SAMs formed under pH 13 occurring at more positive voltage than in the presence of IP<sub>6</sub> SAMs formed under pH 1.27.

#### IV. Conclusions

The investigations and evaluations of two kinds of SAMs of IP<sub>6</sub> at the silver surfaces formed under various pH values, 1.27 and 13, have been performed by using SERS techniques, Raman mapping, electrochemical polarization measurements, and in situ SERS electrochemical measurements. Some conclusions can be reached as follows:

(1) Either completely protonated IP<sub>6</sub> molecules under strong acid condition of pH 1.27 or completely deprotonated IP<sub>6</sub> molecules could form dense and efficiently anticorrosive monolayers at the silver surface by a self-assembled way.

(2) Two adsorption modes for formation of SAMs of IP<sub>6</sub> at the silver surfaces under various pH, 1.27 and 13, were suggested that for completely protonated IP<sub>6</sub> molecule, either of P=O moieties in two free phosphates served as an adsorbing site and IP<sub>6</sub> molecule after completely deprotonated preferred to adopt P–O moieties in coplanar four phosphates of IP<sub>6</sub> attaching at the surface.

(3) The relatively strong interaction between the completely deprotonated IP<sub>6</sub> and the silver surface arising from its adsorption mode could be the reason the corrosion potential of the silver electrode in the presence of SAMs of such IP<sub>6</sub> molecules occurred at a more positive voltage than in the presence of SAMs from completely protonated IP<sub>6</sub> molecules.

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