Therefore, it is concluded that the symmetry reduction of the excited complex is a matrix effect. According to this view, the symmetry reduction is induced by the interaction of the excited complex with the surrounding solvent sphere. Support for this argument comes from the observation that the electrons of the doubly reduced complex in solution can be described as being localized in bpy π^* orbitals, whereas in the corresponding solid this interpretation fails.[11]

Conclusion

This paper reports on the polarized emission of single-crystal $[Ru(bpy)_3](PF_6)_2$ at various temperatures in the range from 1.6 K to room temperature and presents a detailed energy-level diagram for the emitting states, which are assigned in the D_3' symmetry group. At $T \lesssim 2$ K an E′ state being mainly of triplet character is responsible for the emission. It gains its intensity through vibronic coupling. With a temperature increase to about 4 K the blue shift and the intensity increase of the emission spectra indicate that a second E′ state becomes dominant which has some more singlet character mixed in. According to the assignments of the two lowest excited states to E′, the low-temperature emission is characterized by dominating $\mathbf{E}\perp\mathbf{c}$-polarized components. For $T \gtrsim 4$ K the $\mathbf{E}\parallel\mathbf{c}$-polarized transition resulting from a A_2' state appears. At about 70 K this transition carries more than half of the total emission intensity. In the temperature range from 100 to 300 K an emission from a third E′ state (or states) leads to the dominance of the $\mathbf{E}\perp\mathbf{c}$-polarized component which takes about 95% of the total emission intensity near room temperature. A second A_2' state, gaining influence above 250 K and giving a blue shift of the $\mathbf{E}\parallel\mathbf{c}$-polarized component, is of minor importance for the emission spectrum at room temperature.

It is found that a description of the emitting states of single-crystal $[Ru(bpy)_3](PF_6)_2$ within the D_3' double group accounts very well for the symmetry properties of the excited states detected in the temperature-dependent polarized emission spectra. It is argued that there is no indication of a substantial symmetry reduction in the excited states for the $[Ru(bpy)_3](PF_6)_2$ single crystals compared to the ground-state symmetry. Therefore, it is concluded that the symmetry reduction as was determined in ref 9–12 cannot be accounted for as an intrinsic property of the excited complex. In contrast, the observed symmetry reduction might originate from the use of polar solvents in these investigations. It is proposed that the interaction of the excited complex with the surrounding solvent (respectively matrix) molecules induces the distortion of the excited complex.

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The Behavior of Pyridine, Pyridinium Ion, and Pyridinium Halide on a Ag Electrode and Their SERS Spectra

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Abstract: A newly developed electrochemically plated Ag electrode was used to study the surface-enhanced Raman scattering from pyridine adsorbed on the electrode. It was found that in basic and neutral solution, the adsorbed species on the electrode is pyridine. In acidic solution without chloride ion, the pyridinium ion turns to pyridine on the electrode. However, in an acidic solution with chloride ion both pyridinium and chloride ions are adsorbed together on the Ag electrode and pyridinium chloride forms, then the 1026-cm^{-1} Raman band appears for the ν_8 mode. At a potential of −0.45 V (SCE), chloride ion is driven away from the electrode and pyridinium ion decomposes immediately into pyridine. This potential is called the "driving-off potential". The effects of bromide and iodide ions were also studied. A model is proposed for the behavior of pyridine, pyridinium ion, and pyridinium chloride on the Ag electrode with and without applied potential.

The Raman spectra of pyridine (Py, hereafter) adsorbed on the silver electrode at different potentials were observed first by Fleischmann, Hendra, and McQuillan[1] in 1974. Three years later, Jeanmaire and Van Duyne[2] studied this new Raman scattering in great detail and found many fascinating phenomena, such as the enhancement in Raman signal, the effect of reduction and oxidation cycles, the effect of potential, the effect of metal and the condition of the metal surface, etc. The name surface-enhanced Raman scattering or SERS was given to this Raman scattering. Since then, many physicists and chemists devoted themselves to this field. Many reviews have appeared recently.[3,4] However, many phenomena are not fully understood yet.

One of the big problems is the metals properties and surface conditions. Silver is always used because it gives the best signals compared to the other metals, such as Au, Cu, etc. SERS has been observed on various metal surfaces prepared by various methods. These methods are oxidation- and reduction-cycled Ag electrodes.[5-12] (ORC Ag electrode, hereafter), metallic films,[13,14]

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gels,[15,16] anodized electrodes,[17-19] and electrochemically plated Ag electrodes[20,21] (EP Ag electrode, hereafter). Among those surfaces, the ORC Ag electrode was the most popular. The EP Ag electrode was developed recently.[20,21] Its properties have been studied thoroughly in Py solution.[21] In this work, the EP Ag electrode was used for the following reasons: it gives large enhancement, it behaves just as the ORC Ag electrode, and the interference from other ions can be avoided.

Although the mechanism for such large enhancement is very important, it is the species adsorbed on the surface that we are most concerned about. Several Raman bands at 235, 1008, 1026, and 1036 cm^{-1} are important in assigning the adsorbed species. Few of them are well-known; the 235-cm^{-1} band is due to the adsorbed chloride ion[3,4] (Cl^-, hereafter), and the 1008- and 1036-cm^{-1} bands are from the adsorbed pyridine molecules.[3,4] The corresponding normal modes are ν_9 and ν_8, respectively.[3,4] These are well-known from the studies of the adsorbates on the ORC Ag electrodes, metallic films, and gels. However, the 1026-cm^{-1} band was still in doubt. It appeared in some reports[1,6,7] and was not observed in others.[2,9,19] Fleischmann et al.[1] proposed that it was associated with Py coordinated to the Ag electrode through the nitrogen atom. Creighton, Albrecht, Hester, and Matthew[6] also found it and assigned it to the symmetric ring-stretching mode of Py bonded to the Ag surface through the nitrogen atom. Regis and Corset[7] also found it and proposed that it was due to the pyridinyl radical formed on the Ag electrode. That band should be identified.

The potential applied to the electrode also affects the intensity of the Raman signals. The intensities of a few bands decreased, but others increased when the potential was scanned to the negative side.[2,3] This reflected that some chemical or physical changes had occurred on the electrode at different potential. It would be interesting to follow those changes and also important to identify the adsorbates on the electrode at various potentials.

The decrease in Raman signals after the potential was scanned from a very negative one implied that some properties of the electrode surface had changed. Active sites or adatoms on which Py was adsorbed were suggested by many authors.[12,17] The loss of the active sites or adatoms caused the decrease of the Raman signals. However, the mechanism is not clear yet.

Our purposes for this work are following: to identify the species for the 1026-cm^{-1} band, to study the effect of the potential on the adsorbates or the chemical changes during scanning of the potential, and to understand the mechanism for the reduction in Raman signals.

In this work, the 1026-cm^{-1} band was observed from the EP Ag electrode immersed in an acidic Py solution prepared from HCl but not from H_2SO_4, HNO_3, or $HClO_4$. Strong evidences indicate that the adsorbate which gives the 1026-cm^{-1} band is pyridinium chloride (PyH^+Cl^-) formed on the Ag electrode (PyH^+Cl^-(Ag), and (Ag) represents the Ag electrode, hereafter). When the potential is scanned to the negative side, the 1026-cm^{-1} band disappears. This potential is named as the "driving off potential". The corresponding chemical change is suggested to be the decomposition of PyH^+Cl^-(Ag) into Py(Ag), H^+, and Cl^- on the electrode. The recovery of the 1026-cm^{-1} band intensity was only about one-third after the potential was scanned back from a very negative one. Here, we propose that the active sites or adatoms are lost by the formation of soluble compounds or complex ions. All the above-mentioned phenomena, the species adsorbed, and the chemical changes on the electrode can be summarized into a simple model which will be presented in detail in this work.

Experimental Section

In this work, two Ag electrodes were used. They were prepared by the following methods. The EP Ag electrode was prepared by oxidizing the polished Ag electrode in a 0.1 M $AgNO_3$ aqueous solution at +1.2 V (CE) (against the counter electrode) for 10 s and then electrochemically plating it in the same solution with a 6-mA current (fixed current) at about -0.4 V (CE) for 50 s.[21] The ORC Ag electrode was prepared by oxidizing and reducing the polished Ag electrode from -0.3 to +0.2 V (SCE) with a scanning rate of 0.5 V/s for 12 min in a 0.05 M Py + 0.1 M KCl aqueous solution of which the pH was adjusted to 4.38 by HCl. The solutions were prepared from pyridine (Aldrich, spectrophotometric grade), KCl, HCl, HBr, $HClO_4$, H_2SO_4 and HNO_3 (Merck, analytical grade), HI (Prolabo, analytical grade), and deionized water.

The Ag electrode was placed 1 cm from the front cell wall of a 2.5-cm-square electrochemical cell with different solutions. The counter electrode was a ring-shaped platinum wire, which was placed between the Ag electrode and the front cell wall. The saturated calomel reference electrode (SCE) was positioned beside the Ag electrode. The applied potential on the Ag electrode was controlled by a potentiostat against the SCE electrode.

The experimental equipment for the in situ Raman measurements had been described elsewhere.[21] The laser light from an argon ion laser was focused and reflected into the electrochemical cell on the Ag electrode surface with an incident angle of about 40°. The right-angle-scattered light was collected and focused at the slit of a Spex double spectrometer and detected by a cooled photomultiplier. The electric signal was processed by a photon counter and recorded on a strip-chart recorder.

Results and Discussion

All the spectra obtained in this work are similar in peak position, peak width, and peak intensity to those SERS spectra reported by pioneers.[1-21] The spectra reported here are in the ranges from 150 to 300 and from 950 to 1080 cm^{-1} with the band pass of the spectrometer of 2.5 cm^{-1}, because the important bands for various forms of adsorbed Py and Cl^- on the Ag electrode are in those ranges. The excitation light was 180 mW of 5145 Å except in part (section a below) where 4880 Å was used.

(a) Spectra of Py in Solution. The behavior of the 1026-cm^{-1} Raman band from the ORC Ag electrode was strange. It appeared in some experiments[1,6,7] but disappeared in others.[2,9,19] In order to study it in detail, we started with the Raman spectra of Py in solution. In aqueous solution, Py forms hydrogen bonds with water molecules through the nitrogen atom. Therefore the bands for ν_9 and ν_8 modes shift from 991 and 1030 cm^{-1} in liquid Py to 994 and 1030 cm^{-1} in an 8.3 M Py solution and shift further to 1003 and 1036 cm^{-1} in a 0.05 M Py solution, respectively.[3,22] No 1026-cm^{-1} band appears. In acidic solution pyridinium ion (PyH^+, hereafter) forms. In order to investigate the Raman bands of Py and PyH^+, eleven Py samples of different pH were prepared from HCl or NaOH. The ratios of Py to PyH^+ in those solutions varied from 1:2300 to 2.3×10^7:1 calculated from $k_b = 2.3 \times 10^{-9}$. Their Raman spectra in the range from 950 to 1100 cm^{-1} were measured and shown in Figure 1. The pH and the ratio of Py to PyH^+ were also marked to the corresponding spectrum in Figure 1. The spectra illustrate that, in acidic solution, the ν_9 and ν_8 modes shift from 1003 and 1036 cm^{-1} for Py to 1010 and 1029 cm^{-1} for PyH^+, respectively. The Raman cross section of the ν_8 mode of PyH^+ would be only about one-fifth of that of Py by comparing the intensities of the bands shown in Figure 1. Some results could be obtained from Py solutions whose pH were adjusted by H_2SO_4, HNO_3, or $HClO_4$ instead of HCl.

From the above spectra and also the spectra obtained hereafter, we found that the shift of the ν_9 mode was small: from 1003 to 1010 cm^{-1}, particularly around 1008 and 1009 cm^{-1}. In fact, sometimes only a broad band was observed. We could not get much information from this band. On the other hand, the ν_8 mode shifted much more: from 1036 to 1026 cm^{-1}. Definite and important information about the molecular structures of the ad-

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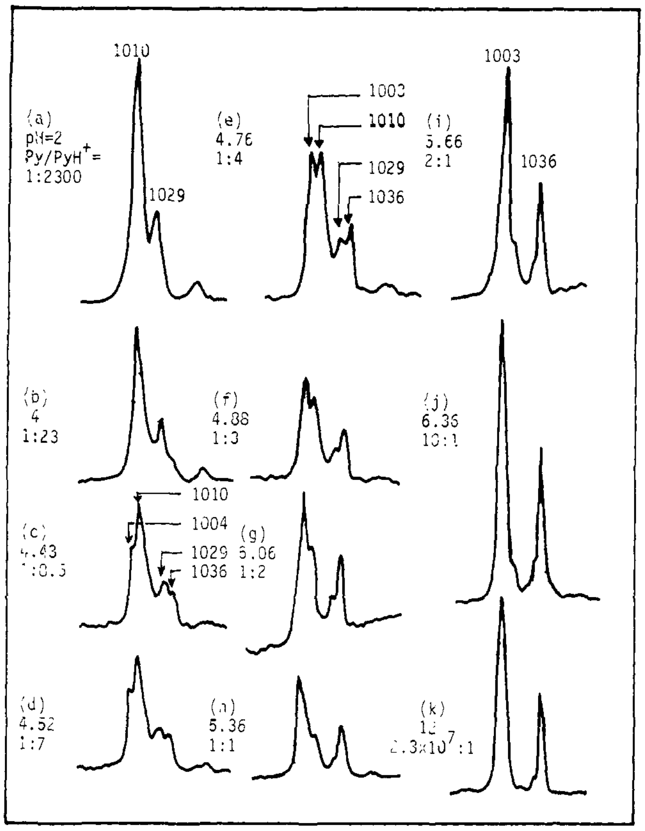

Figure 1. Raman spectra observed from eleven 0.05 M Py solutions of varying pH adjusted by NaOH or HCl. The pH value and the ratio between PyH^+ ion and Py are marked beside the spectrum.

sorbates could be obtained from the variation of the peak position of this mode.

(b) Spectra of Py Adsorbed on the EP Ag Electrode. On the basis of the above results, the spectra of the Py adsorbed on the EP Ag electrode at different pH were studied in an attempt to identify the species that was responsible for the 1026-cm^{-1} band. Raman spectra of the Py adsorbed on the Ag electrode in different solutions of pH 10.6, 4.13, 3.58, and 2.71 adjusted by HCl or NaOH were measured and shown in Figure 2. All the spectra were taken at open-circuit circumstances. Only 1008- and 1036-cm^{-1} bands are found at pH 10.6. To our surprise the 1026-cm^{-1} band appears and becomes larger and larger as the solution becomes more acidic. On the other hand, the 1036-cm^{-1} band becomes smaller and finally is replaced by the 1026-cm^{-1} band at pH 2.71. The Raman intensities of the adsorbed Py are about 150 times stronger than those in solutions as reported.[3,7] This indicates that the SERS effect is also observed here from the Py adsorbed on the EP Ag electrode in the acidic solutions at open-circuit circumstances.

From the intensity variation of the 1026- and 1036-cm^{-1} bands in different acidic solutions, we can conclude that H^+ should play an important role for the appearance of the 1026-cm^{-1} band and the diminution of the 1036-cm^{-1} band. The Raman spectrum of the Py adsorbed on the EP Ag electrode in a Py + KCl solution (pH was about 8.25) was also shown in Figure 2e for comparison. An amazing feature is that the intensity of the 1026-cm^{-1} band is very weak and the 1036-cm^{-1} band is very strong.

In order to make sure that the 1026-cm^{-1} band is due to PyH^+, a set of Py solutions was prepared of which pH was adjusted by $HClO_4$, H_2SO_4, or HNO_3, instead of HCl. The spectra of the Py adsorbed on the EP Ag electrode were measured. Only those spectra of the adsorbed Py in H_2SO_4 solution are shown in Figure 3. Other spectra are same and were not reproduced here. To our great surprise, the 1026-cm^{-1} band cannot be found at all. But the 1036-cm^{-1} band does appear in all spectra even in a strong acidic solution, such as pH 2.71, in which PyH^+ should be dominant. This set of spectra proves that the 1026-cm^{-1} band also has some connection with Cl^-. In other words, Cl^- is also necessary for the appearance of the 1026-cm^{-1} band. These three identical spectra shown in Figure 3 and other spectra taken from Py in the solutions with other acids imply that one, and only one, species is adsorbed on the EP Ag electrode, no matter what the pH of the solution is when Cl^- is absent. Because the Raman bands are at 1008 and 1036 cm^{-1}, it should be reasonable to infer that the adsorbed species is Py, not PyH^+, even in a very acidic solution such as pH 2.71 where PyH^+ is dominant in solution.

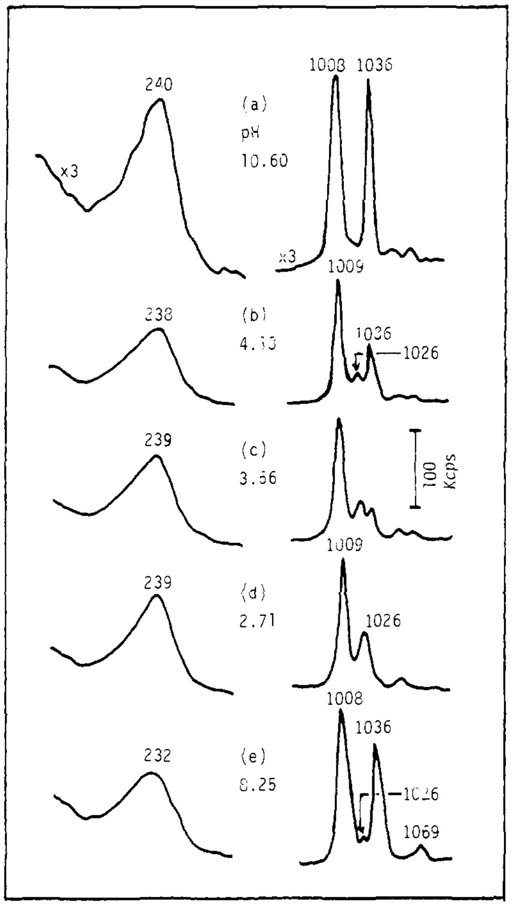

Figure 2. Raman spectra observed from the EP Ag electrode immersed in 0.05 M Py solution with pH values of (a) 10.6, (b) 4.13, (c) 3.58, and (d) 2.71 adjusted by NaOH or HCl and (e) in 0.05 M Py + 0.1 M KCl solution at the open-circuit condition.

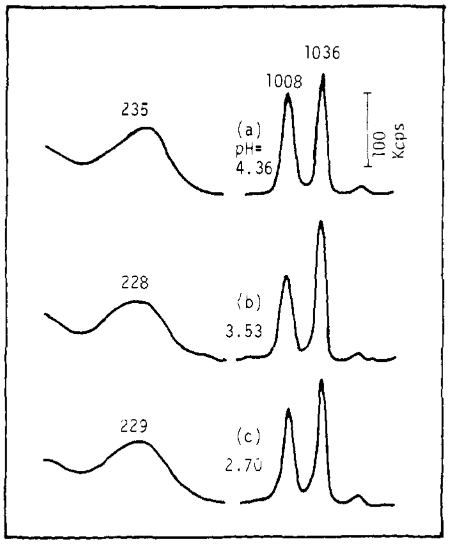

Figure 3. Raman spectra observed from the EP Ag electrode immersed in 0.05 M Py solution with pH values of (a) 4.36, (b) 3.53, and (c) 2.70 adjusted by H_2SO_4 at the opern-circuit condition.

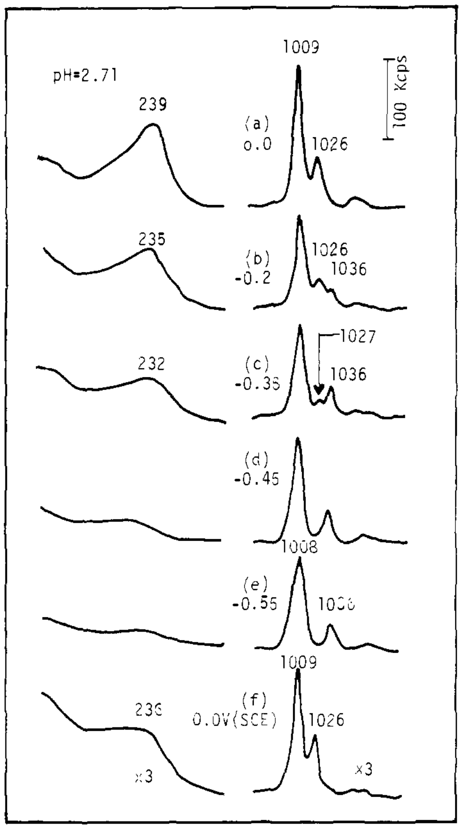

Figure 4. The Raman spectra observed from the EP Ag electrode immersed in 0.05 M Py + HCl solution with pH 2.71. The applied potential was (a) 0.0, (b) -0.2, (c) -0.35, (d) -0.45, (e) -0.55, and (f) 0.0 V (SCE) after keeping the open circuit for 10 min.

From the above results, the 1026-cm^{-1} band appears only when both Cl^- and H^+ are present in the solution. It vanishes completely when Cl^- is absent or it is weak while the solution is of low concentration of H^+, as shown in Figures 3 and 2e, respectively. This indicates that the 1026-cm^{-1} band is due to an adsorbed species which forms on the EP Ag electrode in the presence of both H^+ and Cl^-. This can explain why the 1026-cm^{-1} band is absent in some reports.[2,9,19]

The chemical properties of Py would be important and helpful in understanding its behavior while it is adsorbed on the EP Ag electrode. It is well-known that Py can form salts with strong acids such as HCl.[23] By bubbling dry HCl gas into liquid Py, white solid pyridinium chloride PyH^+Cl^- is formed. It dissolves in water and dissociates into PyH^+ and Cl^-. Raman peaks at 1009 and 1026 cm^{-1} can be observed from this white solid PyH^+Cl^- salt. They shift to 1010 and 1029 cm^{-1}, respectively, in aqueous solution. Obviously, the 1029-cm^{-1} band is due to the ν_8 mode of PyH^+ in solution, and it shifts to 1026 cm^{-1} in solid PyH^+Cl. From the spectra shown in Figures 2 and 3, it can be concluded that the species PyH^+Cl^- is formed on the EP Ag electrode because the 1026-cm^{-1} band is also observed from the EP Ag electrode in acidic solution with the presence of both Cl^- and H^+.

(c) Spectra of Py Adsorbed on the EP Ag Electrode at Different Potentials. In order to study the behavior of PyH^+Cl^- adsorbed on the Ag electrode, a set of Raman spectra was taken from the EP Ag electrode immersed in a HCl + Py solution of pH 2.71 and shown in Figure 4. Raman bands of 1009 and 1026 cm^{-1} are observed at 0.0 V (SCE) as in Figure 4a. It has the same pattern as that taken at open circuit as in Figure 2d. However, when the applied potential becomes negative, the intensity of the 1026-cm^{-1} band decreases and the 1036-cm^{-1} band appears. The former one vanishes completely at -0.45 V (SCE). It seems to be a reversible process, because after keeping it at open circuit for 10 min and applying a 0.0 V (SCE) potential, the 1036-cm^{-1} band turns back to 1026 cm^{-1} completely as shown in Figure 4f. However, the intensities of both 1009- and 1026-cm^{-1} bands reduce to about one-third. The intensity of the 235-cm^{-1} band is found to have the same variation pattern as that of the 1026-cm^{-1} band. The potential at which the 1026-cm^{-1} band disappears completely is called the "driving off potential" because the adsorbed PyH^+Cl^- is driven off from the electrode by the applied potential. This will be discussed later.

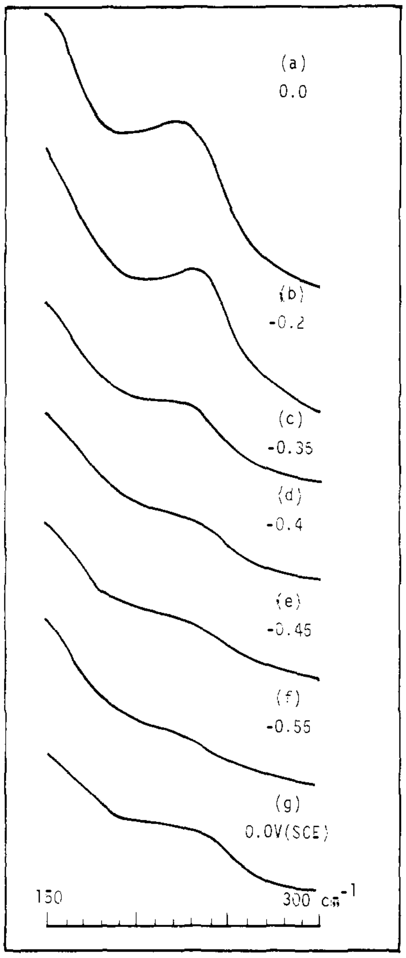

Figure 5. The Raman spectra observed from the EP Ag electrode immersed in 0.1 M KCl solution with the applied potential (a) 0.0, (b) -0.2, (c) -0.35, (d) -0.4, (e) -0.45, (f) -0.55, and (g) 0.0 V (SCE) after keeping the open circuit for 3 min.

The behavior of Cl^- on our EP Ag electrode was also studied in a 0.1 M KCl solution. The Raman spectra with various applied potentials are shown in Figure 5. The band for the ν(Ag–Cl) mode[16,17] at 239 cm^{-1} does become smaller gradually as the applied potential becomes more negative. It almost vanishes at -0.45 V (SCE) and comes back at open-circuit circumstances as shown in Figure 5, parts e and g; however, the intensity also reduces to about one-fourth of the original intensity as in Figure 5a. The behavior of the Cl^- on the EP Ag electrode is consistent with that of the 1026-cm^{-1} band as shown in Figure 4. So the assignment of the 1026-cm^{-1} band to a species with Cl^- on the Ag electrode is more encouraged.

(d) Spectra of Py Adsorbed on the EP Ag Electrode with HBr. For more confirmable evidence, Raman spectra of the adsorbed Py in an acidic solution of pH 2.73 adjusted by HBr, instead of HCl, were also measured at different applied potential and are shown in Figure 6. Instead of the 1009- and 1026-cm^{-1} bands, Raman peaks at 1007 and 1023 cm^{-1} were observed at open circuit. The intensity of the 1023-cm^{-1} band increases to a maximum at -0.05 V (SCE) and then decreases at more negative potentials. These two bands shift to 1010 and 1027 cm^{-1} when the applied potential is between -0.2 and -0.3 V (SCE). The 1036-cm^{-1} band

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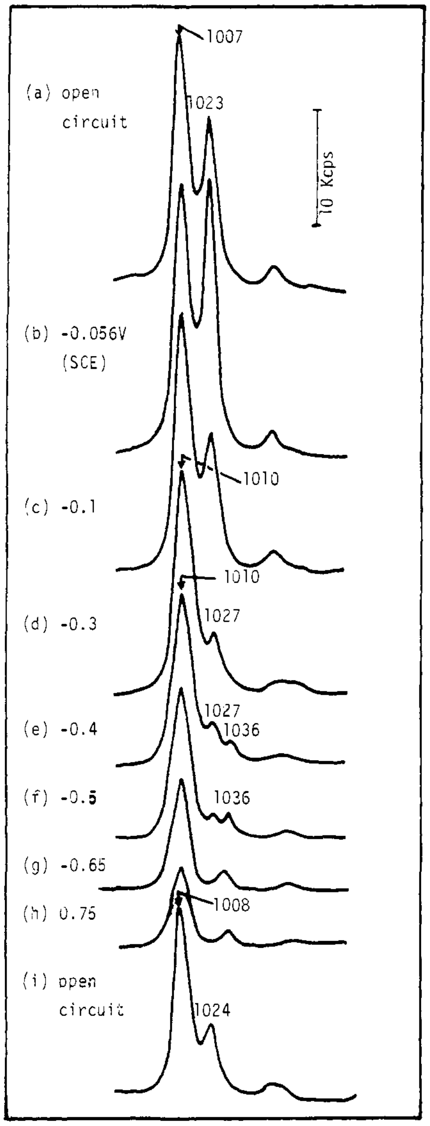


Figure 6. Raman spectra observed from the EP Ag electrode immersed in a 0.05 M Py + HBr solution with pH 2.73 at the potential of (a) open circuit, (b) –0.056, (c) –0.1, (d) –0.3, (e) –0.4, (f) –0.5, (g) –0.65, (h) –0.75, and (i) open circuit after keeping the open circuit for 5 min.

appears at –0.4 V (SCE), and its intensity increases gradually as the applied potential becomes more negative and finally replaces the 1027-cm^{-1} band at –0.65 V (SCE). The ν(Ag–Br) mode[16,17] is at 166 cm^{-1}. It was also studied in a 0.1 M KBr solution without Py. It decreases gradually as the potential scans to more negative, and it disappears at –0.65 V (SCE), just the potential where the 1027-cm^{-1} band vanishes. The intensity variation of the 166-cm^{-1} band is similar to that of the 1027-cm^{-1} band. The driving off potential for the adsorbed PyH$^+$Br$^-$(Ag) is –0.65 V (SCE), more negative than the –0.45 V (SCE) of the adsorbed PyH$^+$Cl$^-$. This indicates our suggestion that the appearance of the 1026- and 1023-cm^{-1} (or 1027-cm^{-1}) band is due to the formation of the PyH$^+$X$^-$ (X$^-$ = Cl$^-$ or Br$^-$) on the EP Ag electrode and that their disappearance is due to drive off of the halide ions from the electrode should be correct. From hereon, the species PyH$^+$Cl$^-$ formed on the Ag electrode will be represented as PyH$^+$Cl$^-$(Ag).

The formation of the PyH$^+$I$^-$(Ag) on the EP Ag electrode was also studied. The characteristic peaks of PyH$^+$I$^-$(Ag) are at 1004 and 1021 cm^{-1} which also shift a little from those of PyH$^+$X$^-$(Ag) (X$^-$ = Cl$^-$ or Br$^-$) at open circuit. They also shift to 1005 and 1024 cm^{-1} while a negative potential is applied. We failed to observe the driving off potential of the 1024-cm^{-1} band because of the bubbles generated on the electrode around –0.7 V (SCE). The driving off potential of the adsorbed I$^-$ is expected to be more negative than –0.7 V (SCE). The reasons for the shifts of 1023- and 1021-cm^{-1} bands to 1027 and 1024 cm^{-1} for PyH$^+$Br$^-$(Ag) and PyH$^+$I$^-$(Ag), respectively, are not known yet. It will be studied further.

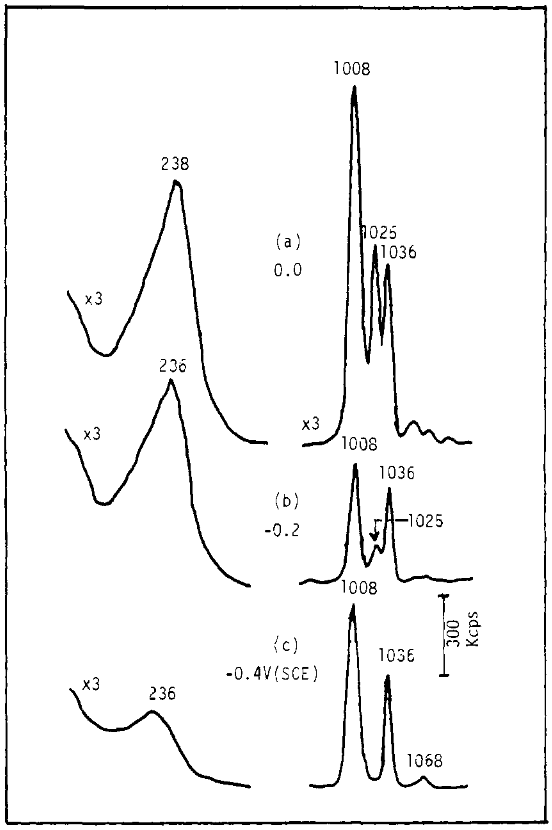


Figure 7. Raman spectra observed from the ORC Ag electrode immersed in a 0.05 M Py + 0.1 M KCl solution with pH 4.38 adjusted by HCl with the electrode at the potential of (a) 0.0, (b) –0.2, and (c) –0.4 V (SCE).

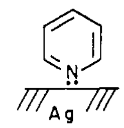
(e) Spectra of Py Adsorbed on the ORC Ag Electrode. Another trial was made to study PyH$^+$Cl$^-$(Ag) on the ORC Ag electrode which was prepared by cycling between –0.3 and +0.2 V (SCE) with a scanning rate of 0.5 V/s for 12 min in an acidic solution of 0.05 M Py + 0.1 M KCl. The acidity of the solution was adjusted by HCl to pH 4.38. The spectra at different applied potential are shown in Figure 7. As our expectation, all 1008-, 1026-, and 1036-cm^{-1} bands are observed at 0.0 V (SCE) as shown in Figure 7a. However, the 1026-cm^{-1} band intensity is very strong. This is different from that observed from the EP Ag electrode at the same pH as shown in Figure 2b. It indicates that the amount of PyH$^+$Cl$^-$(Ag) is much more on the ORC Ag electrode than on the EP Ag electrode. As expected, the intensity of the 1026-cm^{-1} band reduces, finally disappears, and is replaced by the 1036-cm^{-1} band when the applied potential is beyond –0.4 V (SCE), as shown in Figure 7c. In the meantime, the intensity of the 235-cm^{-1} band also decreases, as does that of the 1026-cm^{-1} band.

Model for Py Adsorbed on the Ag Electrode

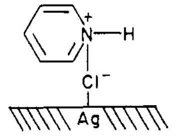
The shifts of the ν_9 and ν_8 bands of Py are interesting. They are 991 and 1030 cm^{-1} for Py in pure liquid, 1003 and 1036 cm^{-1} for hydrated Py in 0.05 M solution, 1008 and 1036 cm^{-1} for Py adsorbed on the Ag electrode in basic solution or in acidic solution without halide ion, 1010 and 1029 cm^{-1} for PyH$^+$ in acidic solution, and 1009 and 1026 cm^{-1} for both solid PyH$^+$Cl$^-$ salt and PyH$^+$Cl$^-$(Ag) adsorbed on the Ag electrode in a solution containing both Cl$^-$ and H$^+$. For different halide ions, these two modes have different positions: 1009 and 1026 cm^{-1} for PyH$^+$Cl$^-$(Ag), 1007 and 1023 cm^{-1} for PyH$^+$Br$^-$(Ag), and 1004 and 1021 cm^{-1} for PyH$^+$I$^-$(Ag).

In neutral or basic solution, Py is present in solution as hydrated Py. The ν_9 and ν_8 modes appear at 1003 and 1036 cm^{-1}, respectively. In acidic Py solution the Raman bands are at 1010 and 1029 cm^{-1}, no matter what the acid is. These are of PyH$^+$

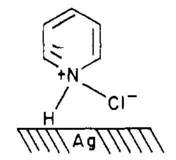
Scheme I



Scheme II



Scheme III



which are dominant in the solution.

When the Py solution is acidified by H_2SO_4, $HClO_4$, or HNO_3, Raman spectra from the EP Ag electrode show peaks at 1008 and 1036 cm^{-1}. This implies that the adsorbed species should be Py, not PyH^+ even in a very acidic solution such as pH 2.71 where PyH^+ is dominant. We suggest that PyH^+ turns to Py on the Ag electrode by releasing a H^+ into the solution. It can be described as follows:

$$PyH^+_{aq} + (Ag) \rightarrow Py(Ag) + H^+_{aq}$$

where aq represents aqueous solution. (Ag) represents the active site or the adatom on the Ag electrode.[12,17] The structures of the active sites are not clear yet. This also suggests that PyH^+ cannot be adsorbed or it is unstable on the Ag electrode. Here, Py may stand on and bond to the Ag electrode through the lone-pair electrons of the nitrogen atom as Fleischmann et al.[1] proposed. The adsorption of Py on the Ag electrode can be represented by Scheme I.

Our experimental results indicate that the 1026-cm^{-1} band appears only in the solution with both Cl^- and H^+ and it disappears gradually as the applied potential is scanned to more negative. We suggest that a species including Py, Cl^-, and H^+ forms on the Ag electrode. The species is inferred to be $PyH^+Cl^-(Ag)$ because same bands are found in solid PyH^+Cl^- prepared by bubbling HCl into Py liquid. The adsorption process can be described as follows: When Py dissolves in HCl solution, PyH^+ forms

$$Py_{aq} + H^+_{aq} + Cl^-_{aq} \rightarrow PyH^+_{aq} + Cl^-_{aq}$$

Both PyH^+ and Cl^- are adsorbed together onto the active sites on the Ag electrode and $PyH^+Cl^-(Ag)$ forms.

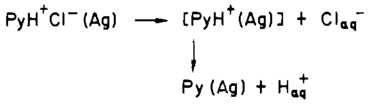
$$PyH^+_{aq} + Cl^-_{aq} + (Ag) \rightarrow PyH^+Cl^-(Ag)$$

This is why the observed band is at 1026 cm^{-1} of PyH^+Cl^- solid, not at 1029 cm^{-1} of PyH^+. The structure of that species on the Ag electrode is shown in Schemes II and III. H is bonded to the nitrogen atom just the same as in PyH^+. Cl^- could bond to both N and active site on the Ag electrode by Coulomb attraction. Py could lay on the Ag electrode through the interaction between the π electrons of the pyridine ring and the Ag electrode as in Scheme II. That interaction is weak, hence Py could stand slantwise on the Ag electrode as in Scheme III.

The salt PyH^+Cl^- formed by bubbling dry HCl gas into liquid Py dissociates into PyH^+ and Cl^- in aqueous solution. It would be reasonable to assume that the adsorption of PyH^+Cl^- on the Ag electrode provides an extra factor to stabilize it from dissociating into PyH^+ and Cl^-. One direct bit of evidence for the formation of the $PyH^+Cl^-(Ag)$ on the Ag electrode is that the same Raman peak at 1026 cm^{-1} was observed from both solid PyH^+Cl^- salt and the species on the Ag electrode. In H_2SO_4, $HClO_4$, or HNO_3 acidic solution, there would be no such $PyH^+Y^-(Ag)$ ($Y^- = HSO_4^-$, ClO_4^-, or NO_3^-) formed on the Ag electrode because they are not stabilized. Therefore, only 1008- and 1036-cm^{-1} bands are observed from the species on the electrode.

Several pyridinium silver halide iodide compounds, such as PyHI·5AgI and PyHI·8AgI, have also been reported.[24] These compounds could also be written as PyH^+I^-·5AgI or PyH^+I^-·8AgI because the ionic forms would be much better. This would not only support the formation of $PyH^+X^-(Ag)$ ($X^- = Cl^-$, Br^-, or I^-) on the Ag electrode but also give evidence that some kind of bond can be formed between PyH^+X^- and AgX. In other words, AgX can provide extra stabilization for $PyH^+X^-(Ag)$ from dissociating. The very intense 1026-cm^{-1} band found by Fleischmann et al.[1] and also observed by Creighton et al.[6] might be explained by the formation of similar compounds, $PyH^+Cl^-\cdot n$AgCl, with unreduced AgCl remaining on the Ag electrode after the oxidation and reduction cycles. Therefore we can conclude that the presence of AgCl on the ORC Ag electrode may further stabilize the adsorbed $PyH^+X^-(Ag)$ ($X^- = Cl^-$, Br^-, or I^-) by the formation of salts like PyH^+I^-·5AgI (or PyHI·5AgI) or PyH^+I^-·8AgI (or PyHI·8AgI).

The gradual diminution of the 1026-cm^{-1} band, while the applied potential becomes more negative, is due to the decomposition of $PyH^+Cl^-(Ag)$ on the electrode for Cl^- is repelled away from the electrode beyond the driving off potential. As mentioned above, PyH^+ is unstable on the Ag electrode without Cl^- and dissociates at once by releasing a H^+ into solution. This process can be represented by the following equation



$$\begin{tikzcd} PyH^+Cl^-(Ag) \arrow[r] & {[PyH^+(Ag)]} + Cl^-_{aq} \arrow[d] \\ & Py(Ag) + H^+_{aq} \end{tikzcd}$$

where $[PyH^+(Ag)]$ represents the unstable species PyH^+ on the Ag electrode. Therefore only the spectra of the adsorbed Py at 1008 and 1036 cm^{-1} are observed. Beyond the driving off potential of Cl^-, −0.45 V (SCE), most of Cl^- is repelled away from the Ag electrode. Of course, the 1026-cm^{-1} band should disappear and be replaced by the 1036-cm^{-1} band of the adsorbed Py.

One remaining problem is the reduction in SERS intensity after cycling to a very negative potential. This was also observed by many other laboratories.[10,17,25] It can be explained by losing and recovering active sites or adatoms on the electrode. Active sites or adatoms would be atoms or metal clusters sticking out of the electrode where Py or PyH^+Cl^- could be adsorbed on. This is also the reason why the Ag electrode should be roughened. At a potential more positive than the driving off potential, adsorbates cover the electrode and protect those active sites. At a potential more negative than the driving off potential, adsorbates can be driven away from the electrode. These active Ag atoms become unprotected and part of them lose with Cl^- as AgCl into the solution. Although K_{sp} of AgCl is small (2.8×10^{-10}), an extremely small amount of AgCl can dissolve into the solution and dissociate into Ag^+ and Cl^-. $AgCl_2^-$ may be the other species which can remove the active site on the Ag electrode. Then, the active sites or adatoms are lost. Ag^+ can be reduced and redeposit on the electrode after the potential is cycled back. If the Ag redeposits as an atom sticks out of the electrode, the active site recovers. If it redeposits in a cavity, then the electrode becomes smooth and the active site does not recover. The probability for recovering its activity may be only one-third because after it is returned to the original potential the band intensity is reduced to one-third. The mechanism is suggested as follows

$$Cl^-(Ag) \rightarrow AgCl(Ag) + e^-$$

$$AgCl(Ag) \rightarrow Ag^+_{aq} + Cl^-_{aq} + (Ag)$$

$$Ag^+_{aq} + e^- + (Ag) \rightarrow Ag(Ag) \quad \text{(active or inactive)}$$

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[24] Ferraro, J. R.; Walling, P. L.; Sherren, A. T. *Appl. Spectrosc.* **1980**, *34*, 570.

[25] Watanabe, T.; Pettinger, B. *Chem. Phys. Lett.* **1982**, *89*, 501.

or

$$2Cl^-(Ag) \rightarrow AgCl_2{}^-{}_{aq} + e^- + (Ag)$$

$$AgCl_2{}^-{}_{aq} \rightarrow Ag^+{}_{aq} + 2Cl^-{}_{aq}$$

$$Ag^+{}_{aq} + e^- + (Ag) \rightarrow Ag(Ag) \quad \text{(active or inactive)}$$

Where Ag (Ag) in the last equation represents the active or inactive Ag site on the Ag electrode. In this work, we cannot determine which mechanism is dominant.

Conclusion

Pyridine has a nitrogen atom which has large electronegativity. In aqueous solution, it can form a hydrogen bond with water, and its vibrational frequencies of ν_9 and ν_8 modes shift from 991 and 1030 cm^{-1} in liquid Py to 1003 and 1036 cm^{-1} in a very dilute aqueous solution. In acidic solution, Py forms PyH$^+$. The corresponding peaks of PyH$^+$ are at 1010 and 1029 cm^{-1}. In both acidic and basic solutions, Py is adsorbed on the Ag electrode and gives Raman peaks at 1008 and 1036 cm^{-1} in the absence of halide ion. Thus, it can be understood that the adsorbed species is Py, not PyH$^+$. Hence PyH$^+$ is unstable and turns to Py on the Ag electrode by losing a H$^+$.

In strong acidic solution, such as pH 2.7, Cl$^-$ and PyH$^+$ are adsorbed together on the Ag electrode to form PyH$^+$Cl$^-$(Ag), and the Raman peaks of PyH$^+$Cl$^-$(Ag) appear at 1009 and 1026 cm^{-1}. Therefore, the 1026-cm^{-1} band is due to PyH$^+$Cl$^-$(Ag). The corresponding modes are observed at 1023 (or 1027) and 1021 (or 1024) cm^{-1} for PyH$^+$Br$^-$(Ag) and PyH$^+$I$^-$(Ag), respectively. Apparently, the shift is due to the different halide ions.

Adsorbed Cl$^-$ on the Ag electrode can be driven away from the electrode beyond the driving off potential. As Cl$^-$ leaves from the Ag electrode, PyH$^+$ turns to Py on the electrode by releasing its H$^+$. Therefore, peaks at 1008 and 1036 cm^{-1} appear. The driving off potentials for different halide ions are also different. At the experimental conditions in this work, they are −0.45, −0.65, and <−0.7 V (SCE) for Cl$^-$, Br$^-$, and I$^-$, respectively. We also found that the driving off potential is dependent on the concentration of the given halide ion, concentration of the H$^+$, and surface characteristics of the electrode used.[26] The larger the halide ion is, the stronger is the affinity with the Ag electrode and the more negative should be the driving off potential.[10] The driving off potentials for PyH$^+$X$^-$(Ag) (X$^-$ = Cl$^-$, Br$^-$, or I$^-$) are consistent with those of the corresponding halide ions alone.

The behavior of the 1026-cm^{-1} band on the EP Ag electrode is similar to that on the ORC Ag electrode. It seems that the formation of PyH$^+$X$^-$(Ag) (X$^-$ = Cl$^-$, Br$^-$, or I$^-$) is easier on the ORC Ag electrode than on the EP Ag electrode at the same pH because the observed 1026-cm^{-1} band is stronger on the former one. On the ORC Ag electrode in Py + KCl solution, a small amount of AgCl is not reduced to the Ag atom during the reduction half-cycle. Because of the residual AgCl, PyH$^+$Cl$^-$ may be stabilized further by forming PyH$^+$Cl$^-$·nAgCl. In other words, the residual AgCl may increase the concentration of PyH$^+$Cl$^-$ on the ORC Ag electrode. This is why the intensity of the 1026-cm^{-1} band is much larger on the ORC Ag electrode.

The reduction of the intensity after cycling to a very negative potential can be explained as follows. When the protecting coating of the adsorbed Cl$^-$ or PyH$^+$Cl$^-$ is driven away, the active Ag atoms are lost by forming AgCl or AgCl$_2^-$ which dissociate into Ag$^+$. At reducing potential, Ag$^+$ may redeposit on the electrode as active or inactive sites during the reduction half-cycle. Hence part of the active sites are lost.

In summary, the model for the behavior of Py on the Ag electrode is the following:

(1) In neutral or basic solution, Py is adsorbed on the Ag electrode and gives 1008- and 1036-cm^{-1} bands.

(2) In acidic solution with no halide ion, PyH$^+$ is unstable and dissociates into Py on the electrode by releasing a H$^+$. So only 1008- and 1036-cm^{-1} bands are observed. The mechanism is

$$PyH^+{}_{aq} + (Ag) \rightarrow Py(Ag) + H^+{}_{aq}$$

(3) In acidic solution with Cl$^-$, PyH$^+$Cl$^-$(Ag) is formed on the Ag electrode. So 1009- and 1026-cm^{-1} bands of PyH$^+$Cl$^-$(Ag) are observed. The reaction is

$$PyH^+{}_{aq} + Cl^-{}_{aq} + (Ag) \rightarrow PyH^+Cl^-(Ag)$$

At the AgCl site on the ORC Ag electrode, PyH$^+$Cl$^-$ is stabilized further by forming PyH$^+$Cl$^-$·nAgCl (Ag) as follows,

$$PyH^+{}_{aq} + Cl^-{}_{aq} + n\text{AgCl}(Ag) \rightarrow PyH^+Cl^-\cdot n\text{AgCl}(Ag)$$

where AgCl remains on the ORC Ag electrode after the reduction half-cycle.

(4) Beyond the driving off potential, Cl$^-$ is driven away from the electrode and the remaining PyH$^+$ dissociates at once to Py which gives 1008- and 1036-cm^{-1} bands,

$$\begin{tikzcd} PyH^+Cl^-(Ag) \arrow[r] & {[PyH^+(Ag)] + Cl^-_{aq}} \arrow[d] \\ & {Py(Ag) + H^+_{aq}} \end{tikzcd}$$

where [PyH$^+$(Ag)] represents the unstable species PyH$^+$ on the Ag electrode which would dissociate at once.

(5) The active sites or adatoms on the Ag electrode expose and lose with adsorbates beyond the driving off potential as follows:

$$Cl^-(Ag) \rightarrow AgCl(Ag) + e^-$$

$$AgCl(Ag) \rightarrow Ag^+{}_{aq} + Cl^-{}_{aq} + (Ag)$$

$$Ag^+{}_{aq} + e^- + (Ag) \rightarrow Ag(Ag) \quad \text{(active or inactive)}$$

or

$$2Cl^-(Ag) \rightarrow AgCl_2{}^-{}_{aq} + e^- + (Ag)$$

$$AgCl_2{}^-{}_{aq} \rightarrow Ag^+{}_{aq} + 2Cl^-{}_{aq}$$

$$Ag^+{}_{aq} + e^- + (Ag) \rightarrow Ag(Ag) \quad \text{(active or inactive)}$$

Although Ag could redeposit on the electrode, only one-third of its activity would be recovered. That reduces not only the number of the active sites on the electrode but also the observed Raman intensities.

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Registry No. Py, 110-86-1; PyH$^+$, 16969-45-2; PyH$^+$Cl$^-$, 628-13-7; Ag, 7440-22-4; Cl$^-$, 16887-00-6; Br$^-$, 24959-67-9; I$^-$, 20461-54-5.

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(26) Chang, H.; Hwang, K. C., unpublished work.