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SURFACE ENHANCED RAMAN SCATTERING SPECTRA OF 2,2'-BIPYRIDINE ADSORBED ON AN Ag ELECTRODE FROM ITS KCl SOLUTION

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The surface enhanced Raman scattering (SERS) study indicates that 2,2'-bipyridine (bpy) molecules adsorb to an Ag electrode surface taking a nearly planar cis conformation. The potential-dependence of the interaction between the adsorbates and the Ag electrode was elucidated from the analysis of the spectra.

Surface enhanced Raman scattering (SERS) spectroscopy has now been established as one of the most powerful tools for studies on metal-electrolyte and metal-vacuum interfaces. In this letter the SERS spectra were reported for 2,2'-bipyridine (bpy) adsorbed on an Ag electrode. Bpy has interaction sites with the electrode similar to that of pyridine, whose SERS spectra have extensively been studied in terms of adsorbed species.[1] Further, since bpy has a possibility of taking a cis and/or a trans conformation, the spectra may reveal conformational changes of the adsorbate caused by the interaction with the electrode surface.

Bpy was of commercial origin. Bis(2,2'-bipyridine)silver(I) nitrate (Ag(I)-$(bpy)_2NO_3$) was synthesized in the usual way.[2] A Raman spectrophotometer and an electrochemical cell used in this study are similar to those of the previous study.[3] Sample solutions, 0.1 mol dm^{-3} KCl + 5 mmol dm^{-3} bpy, were deaerated before use by bubbling with high-purity argon gas. A silver electrode, which was used as a working electrode, was anodized by the following procedure. The electrode was potentiostated at +0.2 V (vs. Ag/AgCl). After 75 mC cm^{-2} of charge was passed through the electrode, the potential was altered slowly to a value at which a spectrum of the surface was taken. Raman spectra of bpy and Ag(I)$(bpy)_2NO_3$ in a crystalline state, and an aqueous solution of bpy were observed by using a spinning cell.

At first, the Raman spectrum was taken at +0.05 V, the result being shown in Fig. 1(A). At this potential, an electrochemical reduction of an AgCl layer formed during the anodization step is not completed. According to Fleischmann and Hill,[4] exposure of the AgCl layer to an Ar^+ laser light during the Raman measurement causes the formation of atomic clusters. As in the case of Ag-pyridine systems, it is expected that these clusters make an appreciable effect on the potential dependence of the SERS spectra in negative potential ranges ($\leq$+0.05 V). Therefore, the potential was slowly swept in the dark directly to -0.2 V after the anodization and successively to -0.5 V and -1.0 V in order to measure the spectra at these potentials. The results are given in Figs. 1(B), (C), and (D) in the 1540-900 cm^{-1}

region, where several bands clearly change their intensity and position with the electrode potential. The SERS spectrum recorded at +0.05 V gives rise to prominent peaks at 1484 cm^{-1}, 1306 cm^{-1} and 1061 cm^{-1}, which are attributable mainly to a ring stretching mode, a ring stretching mode coupled with a C-H in-plane deformation and a C-H in-plane deformation mode, respectively.[5,6] In the ring breathing region a well-defined band at 1011 cm^{-1} and a shoulder at 999 cm^{-1} are observed. On changing the potential to -0.2 V (Fig. 1(B)), the breathing mode gives a new band at 1024 cm^{-1} together with the 1012-cm^{-1} band. At -0.5 V the 1012-cm^{-1} band almost disappears and a strong and sharp band is observed at 1025 cm^{-1}. On sweeping the potential to -1.0 V the 1025-cm^{-1} band decreases its intensity and a new band appears at 1003 cm^{-1} accompanying a shoulder in its lower frequency side. The above-mentioned results clealy indicate that, on changing the electrode potential to negative values, the manner in which bpy molecules adsorb on the electrode surface changes appreciably. Further, it should be noted that, when the potential is scanned to -0.2 V, the 1488-cm^{-1} band - a higher frequency component of a doublet near 1485 cm^{-1} in Fig. 1(B) - appears simultaneously with the 1025-cm^{-1} band. At -0.5 V (Fig. 1(C)) only a higher frequency component at 1492 cm^{-1} is observed together with the prominent band at 1025 cm^{-1}. This result can be explained by considering that a C=N stretching vibration appreciably contributes to the doublet near 1485 cm^{-1} and the change in the interaction manner causes the frequency shift of this vibration.

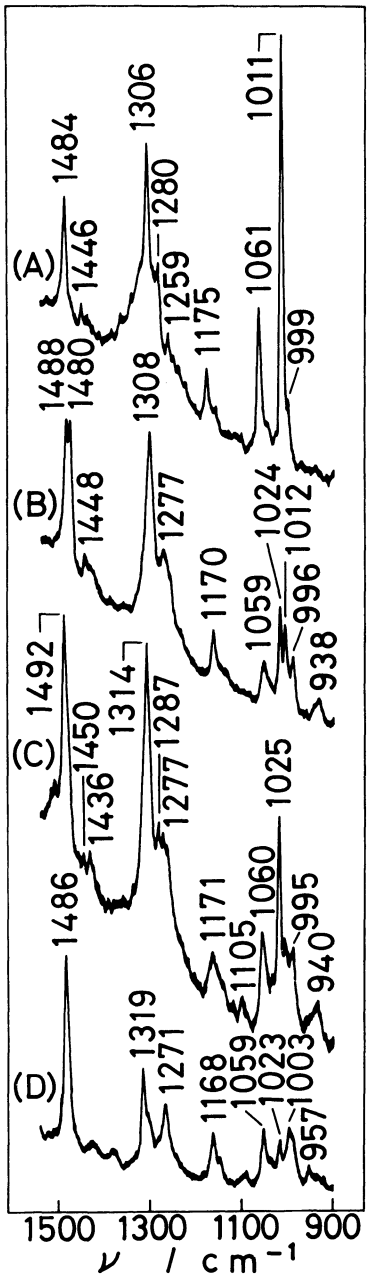

Fig. 1. SERS spectra of bpy adsorbed on an Ag electrode at various potentials: (A) +0.05 V, (B) -0.2 V, (C) -0.5 V, (D) -1.0 V (vs. Ag/AgCl). Excitation wavelength: 514.5 nm. The laser power is (A) 50, (B) 25, (C) 25, (D) 40 mW. The slit width is 4 cm^{-1}.

Figures 2(A) and (B) illustrate the cyclic voltammograms recorded for 0.1 mol dm^{-3} KCl + 5 mmol dm^{-3} bpy by using the same electrochemical cell as that used by the SERS measurement. After passing 75 mC cm^{-2} of charge at +0.2 V, the potential was swept from +0.2 V to -1.0 V and back to +0.05 V. During this cycle the voltammetry gave the solid curve in Fig. 2(A). Then the second potential cycle (+0.05 V → -1.0 V → +0.05 V) was given to the electrode and the cyclic voltammogram was recorded (Fig. 2(B)). The dashed curve in Fig. 2(A) is the voltammogram mearsured for an aqueous solution containing only 0.1 mol dm^{-3} KCl. The peak b in Fig. 2 (A) corresponds to a reduction process of the AgCl layer formed during the anodization at +0.2 V. The other peaks, a and c, were observed only in the presence of bpy. As the AgCl layer was completely reduced after the first cycle, the current peak b was not recorded in Fig. 2(B). Instead, two sets of oxidation-reduction waves, the half-wave potential of which are -0.03 V (d-g) and -0.35 V

(e-f), were found in Fig. 2(B). These waves could not be observed without the anodization process at +0.2 V even if bpy was present in the bulk solution. Therefore, two sets of waves reflect some electrochemical properties of the adsorbed bpy molecules. The arrows in Fig. 2(B) denote the potentials at which the SERS spectra were recorded. Probably the observed spectral changes caused by the potential sweep from +0.05 V to -0.2 V and that from -0.2 V to -0.5 V (Figs. 1(A), (B), and (C)) can be explained on the basis of the reduction processes around -0.03 and -0.35 V, respectively. The spectra change reversibly with the electrode potential in the -0.2 - -1.0 V region. On the other hand, the spectral change between Figs. 1(A) and (B) is not reversible. As described previously, the irradiation of 514.5-nm laser light during the SERS measurement at +0.05 V (Fig. 1(A)) modifies the electrode surface to an appreciable extent. This may be one of the main reasons for the above-mentioned irreversibility.

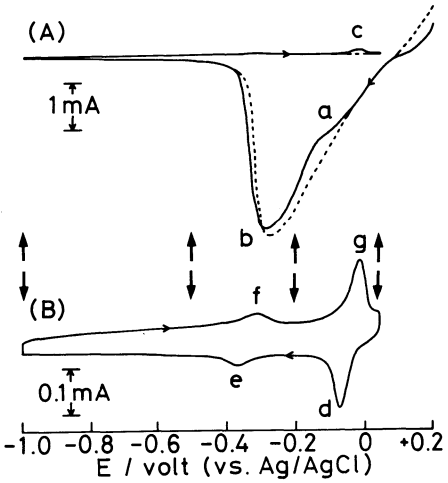

Fig. 2. Cyclic voltammogram for an Ag electrode. (A) The first scan voltammogram. The solid curve is the voltammogram for 0.1 mol dm^{-3} KCl + 5mmol dm^{-3} bpy and the dashed curve is that for only 0.1 mol dm^{-3} KCl. (B) The second scan voltammogram for 0.1 mol dm-3 KCl + 5mmol dm^{-3} bpy. The potential scanning rate is 50 mV/s.

Figures 3(A), (B), and (C) are the normal Raman spectra of bpy in a crystalline state and in an aqueous solution, and Ag(I)$(bpy)_2NO_3$ in a solid state, respectively. The crystalline bpy exists in a coplanar conformation.[7] Almost all the Raman bands in Fig. 3(B) have the counterparts in Fig. 3(A), suggesting that most of bpy molecules in the aqueous solution also take the trans conformation. The ring breathing vibrations are observed at 996 cm^{-1} for the crystalline bpy and at 1004 cm^{-1} for the aqueous solution. This result proves that, as in the case of pyridine,[1] the frequency of the breathing vibration reflect a difference in the environment of the molecule. Although detailed structural data have not yet been given to Ag(I)$(bpy)_2NO_3$, it can be concluded, on the analogy of the crystal structures of other metal-bpy complexes, that the bpy molecules in the argentous complex are fixed in a cis conformation. The spectrum of the complex in Fig. 3(C) does not show any bands which correspond to the 1450- and 1238-cm^{-1} bands in Figs. 3(A) and (B). Presumably the latter two bands can be ascribed to the trans conformation. Here, it should be noted that in the 1540-900 cm^{-1} region the Raman spectrum of Ag(I)$(bpy)_2NO_3$ (Fig. 3(C)) is quite similar to the SERS spectrum at +0.05 V (Fig. 1(A)). Especially the ring breathing vibrations are observed at an almost identical frequency; 1011 cm^{-1} in Fig. 1(A) and 1012 cm^{-1} in Fig. 3(C). Therefore, on adsorption to the electrode surface at +0.05 V, the bpy molecules are fixed in a cis conformation and form Ag(I)-N coordination bonds similar to those of Ag(I)$(bpy)_2NO_3$. The half-wave potentials ($E_{1/2}$=-0.03 and -0.35 V) observed in Fig. 2(B) are not negative enough to ascribe the oxidation-reduction processes to the bpy molecules itself.[8] Presumably, these waves correspond to the oxidation-reduction processes of the Ag atoms (Ag(I) $\rightleftarrows$ Ag(0)) participating in the formation of the adsorbed species at +0.05 V. Figure 1(B) indicates that, on reduction of a part of the silver ions having the half-wave

potential of -0.03 V, the adsorbed bpy molecules are converted to a species which gives rise to a breathing vibration near 1024 cm^{-1}. From Fig. 1(C) it is clear that, on reduction of the other part of the silver ions with $E_{1/2}$ of -0.35 V, the conversion of the adsorbates to the 1024-cm^{-1} species goes to completion. The frequency of 1024 cm^{-1} is almost identical with that observed for the breathing vibration of pyridine chemisorbed (a Lewis acid coordination) to an Ag electrode surface. According to Fleischmann and Hill,[4] pyridine oxide is a useful model for the chemisorbed pyridine. 2,2'-bipyridine N,N'-dioxide also gave the breathing vibration at 1023 cm^{-1} in our preliminary experiment. Therefore, the 1024-cm^{-1} band in Figs. 1(B) and (C) can be assigned to a strongly bound Lewis acid coordination structure. As already mentioned, bpy in an aqueous solution gives the breathing vibration at 1004 cm^{-1} (Fig. 3(B)). In the case of pyridine adsorbed on an Ag electrode the breathing vibration is observed also near 1004 cm^{-1}, which has been explained as arising from a physisorbed species.[4] On the basis of these results the 1003-cm^{-1} band in Fig. 1(D) can be ascribed to bpy physisorbed to the Ag electrode surface. Figures 1(C) and (D) do not show any bands near 1450 and 1238 cm^{-1}. Then during the conversion from the chemisorbed species to the physisorbed one the conformation of bpy adsorbed at the Ag electrode remains unaltered (or in the cis conformation). A shoulder band near 995 cm^{-1} observed in all the spectra in Fig. 1 suggests that there exists an adsorbed species, as a minor component, which has an environment around the nitrogen atoms similar to those of the crystalline bpy.

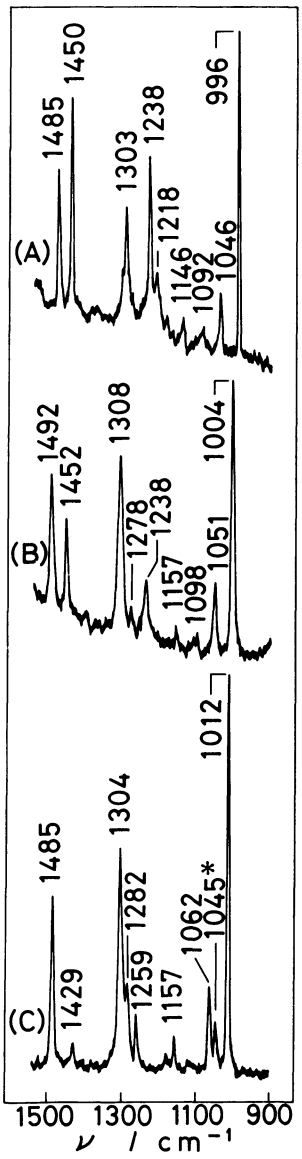

Fig. 3. Raman spectra of bpy in a crystalline state (A), bpy in an aqueous solution (B), and $Ag(I)(bpy)_2NO_3$ in a solid state (C). Excitation wavelength: 514.5 nm. The slit width is 4-6 cm^{-1}. The asterisk denotes the band due to ν_1 of NO_3^-.

The potential dependence of the SERS spectra proves that the bpy molecules on the Ag electrode show a series of transformations (from a species coordinated to Ag(I) to a more strongly bound chemisorbed species and from the chemisorbed species to a physisorbed one). It is presently unknown why there exist, for the adsorbates at +0.05 V, two kinds of interaction sites, in which the silver ions participating in the interaction have the redox half-wave potentials of -0.03 and -0.35 V. The detailed analysis of the SERS spectra will be needed to elucidate this point.[9]

References 1) M. Fleischmann and I.R. Hill, "Electrochemical effects," in "Surface Enhanced Raman Scattering," ed by R.K. Chan and T.E. Furtak, Plenum Press, New York (1982), p.275. 2) G.T. Morgan and F.H. Burstall, J. Chem. Soc., 1930, 2594. 3) M. Itabashi, K. Kato, and K. Itoh, Chem. Phys. Lett., 97, 528 (1983). 4) M. Fleischmann and I.R. Hill, J. Electroanal. Chem. Interfacial Electrochem., 146, 353 (1983). 5) E. Castellucci, L. Angeloni, N. Neto, and G. Sbrana, Chem. Phys., 43, 365 (1979). 6) A. Basu, H.D. Gafney, and T.C. Strekas, Inorg. Chem., 21, 2231 (1982). 7) L.L. Merritt, Jr. and E.D. Schroeder, Acta Crystallogr., 9, 801 (1956). 8) C. Creutz, Comments Inorg. Chem., 1, 293 (1982). 9) M. Kim and K. Itoh, to be published.

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