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# Surface-Enhanced Raman Spectroscopy and Electrochemical Studies of 4-Phenylpyridine Adsorption at the Silver/Solution Interface

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The adsorption of 4-phenylpyridine (4-PhPy) on silver was examined using conventional electrochemical techniques: cyclic voltammetry, impedance measurements and surface enhanced Raman spectroscopy (SERS) in a wide range of electrode potentials. Electrochemical results indicate a weaker adsorption of 4-PhPy molecules on Ag than on Au electrode, but considerably stronger than adsorption of pyridine. For saturated solutions the Raman results point out the reorientation of the 4-PhPy molecules from more flat configuration at potentials more positive than –0.7 V *vs* SCE, to more perpendicular one at more negative potentials. This reorientation may be connected with the formation of stable surface complexes at potentials more positive than –0.7 V and of molecular stacks at more negative electrode potentials.

**Key words**: silver, 4-phenylpyridine, differential capacity, SERS, adsorption

Pyridine (Py) and some of its derivatives have been the subject of numerous studies on electrosorption at metallic electrodes (*i.e.* at gold [1–3], silver [1,4,5] or mercury [6–8]). Py has been used as a model compound for the bonding and coordination with metal surfaces. The data presented show that the orientation of these molecules depends strongly on the applied potential, but in the case of Py in a different way on gold and silver electrodes. On the Au surface the flat orientation appeared at negative charge densities, while on the Ag electrode it occurs in the region of positive charges [1], as was reported also for the mercury electrode [6].

The 4-phenylpyridine (4-PhPy) molecule has interesting properties owing to its molecular structure, which includes two aromatic rings: phenyl and pyridine (with N atom). This molecule contains a delocalized $\pi$-electrons system and a lone pair located on the N atom, both of which are able to participate in bonding with metal. Hence, 4-PhPy molecule may adsorb in different configurations with respect to the metal surface.

Previously we investigated the adsorption of 4-PhPy molecule on copper [9] and gold [10] electrodes by cyclic voltammetry, surface-enhanced Raman scattering (SERS) and additionally impedance measurements in the case of Au. The results obtained indicated that on copper the 4-PhPy molecules change their orientation with

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respect to the surface twice. At negative potential (E < –0.6 V *vs* SCE) and at the positive potential (E > +0.05 V) the adsorbed molecule adopts a vertical orientation, while at intermediate potential range the molecule is adsorbed rather in a more flat configuration. However, on gold electrode [10] it was found that the 4-PhPy molecule gradually changes its orientation from more vertical to more flat, with the potential changing towards more positive values. In order to know more about the role of the metal electrode in the electrosorption process of 4-PhPy molecule, we have performed similar investigations on a polycrystalline Ag electrode and in this paper we present results of these studies.

## EXPERIMENTAL

**Electrode and experimental technique**: The electrochemical experiments were carried out in a standard electrochemical cell with three electrodes. The reference electrode was a saturated calomel electrode (SCE). Before each experiment the working, smooth polycrystalline Ag electrode was mechanically polished and then chemically cleaned in the bath based on $CrO_3$ [11]. The quality of the silver electrode prepared in this way has been verified by cyclic voltammetry (CV). The adsorption equilibrium at the electrode/solution interface, in the measurements of impedance, was monitored by capacitance *versus* time in the concentration range examined. As found from that study, a time period of t = 900 s is long enough to achieve the equilibrium state at the interface for the smallest concentration of 4-PhPy. The time required to reach the steady state capacitance was significantly shorter in solutions of higher 4-PhPy concentrations. All capacitance measurements were carried out with the electrode being held at each potential until the adsorption equilibrium was established. The differential capacity was calculated on the basis of ac impedance measurements, assuming the simplest (RC) electric double layer model. The electrode impedance was studied as a function of frequency from 10 Hz to 200 Hz. The equilibrium capacity (zero frequency capacity) was obtained from the intercept of the $C = f(\omega^{1/2})$ dependence at $\omega = 0$ (where C is capacity and $\omega$ is the angular frequency). The roughness factor of the silver smooth electrode (R = 1.15) was derived from Parsons – Zobel's graph [12]. The same value of R was obtained by applying the method of Pb monolayer electrodeposition on the silver electrode from alkaline solution of $Pb^{2+}$. All zero frequency capacities were divided by product, R s, where s is the geometrical area of the electrode, and then presented in the figure. Cyclic voltammograms and impedance measurements were carried out with 0.1 M $LiClO_4$ as a supporting electrolyte using, as previously [4,13], AUTOLAB system with GPES and FRA modules (Eco Chemie, Netherlands).

For spectroscopic measurements the surface of polycrystalline Ag electrode was prepared in a different way. Before each experiment a polycrystalline Ag disc electrode was roughened by exposure to three oxidation-reduction cycles (ORCs) in a separate cell containing 0.1 M KCl. The potential was swept cyclically between –0.3 and +0.3 V *vs* SCE at a sweep rate of 5 mV $s^{-1}$. In order to achieve better understanding of the spectroscopic results, the cyclic voltammetry curves were also recorded on the roughened Ag electrode used in SERS experiments. Raman spectra were recorded with a Cary 82 spectrometer using a Lexel model 98 $Kr^+$ ion laser (647.1 nm). Each spectrum was recorded at a constant potential maintained by a potentiostat. The spectral band pass was 5 $cm^{-1}$. The spectroscopic set-up for SERS experiments and the electrochemical equipment for cyclic voltammetry of roughened electrode have been described elsewhere [14].

**Solutions**: 4-Phenylpyridine (Fluka p.a.), $LiClO_4$ (Merck p.a.) and KCl (Merck p.a.) were used without further purification. All the solutions were prepared using distilled and deionized water (from Q-Millipore) with a resistivity of 18 MΩ cm. The pH of the solution was adjusted using $HClO_4$, HCl or LiOH. All solutions were deareated with purified argon prior to the experiments. The measurements were carried out at 23°C.

## RESULTS AND DISCUSSION

### Electrochemistry of 4-PhPy at a silver electrode

**Cyclic voltammetry**: CV curves were recorded for the smooth and roughened Ag electrodes in a supporting electrolyte (0.1 M $LiClO_4$) and in respective solutions containing different concentration of 4-PhPy. In both cases, the addition of 4-PhPy shifts the potential of hydrogen evolution towards more negative values, pointing out to the inhibiting effect of adsorbed 4-PhPy molecules. This effect is illustrated in Fig. 1 by CV curves for a smooth Ag electrode. In comparison to the results obtained at the Cu electrode, the inhibiting effect is rather small and similar to that observed at the Au electrode [10]. The ideal polarization range (without 4-PhPy) was determined, from CV curves, as extending from –1.25 V to –0.2 V *vs* SCE in the neutral solutions and from –0.4 V to +0.2 V in acidic solutions. Since the hydrogen evolution, in acidic solutions, starts before attaining the potential of zero charge (pzc), further electrochemical study of adsorption of 4-PhPy molecules (by impedance measurements) were performed only in neutral solutions, where the ideal polarization range in the cathodic direction is greater. When the voltammetric response of a roughened Ag electrode was recorded in the presence of 4-PhPy in the potential range changed from –0.7 V to 0.1 V, the well established redox peaks were seen in CV curves (Fig. 2a). This redox pair can be probably ascribed to the oxidation/reduction of [Ag – 4-PhPy] complex, which is formed upon anodic polarization of the electrode. The complex is characterized by formal potential $E_f$ equal to –0.12 V *vs* SCE. The difference between the oxidation and reduction peak potentials ($E_{pa} - E_{pc}$ equal to ~ 60 mV) points out to the one electron redox reaction. The linear dependence of the oxidation and reduction peak

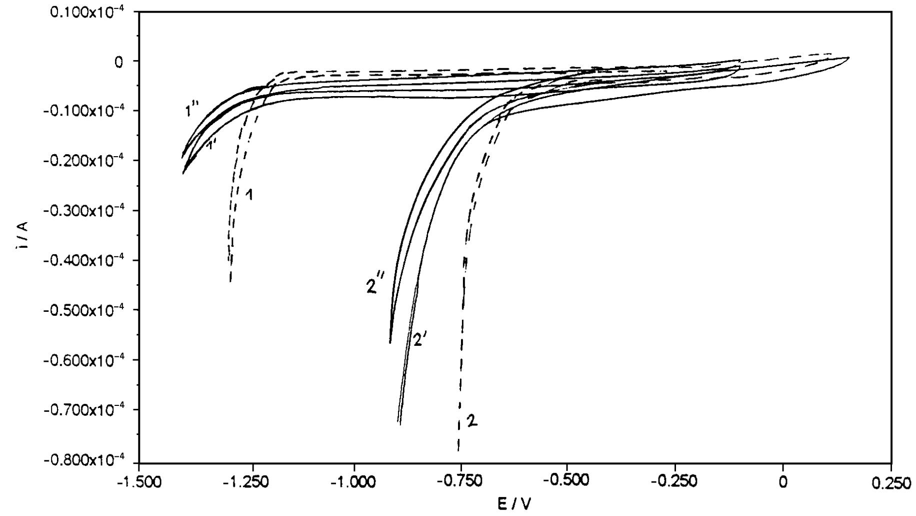

**Figure 1.** Cyclic voltammograms for the smooth Ag electrode for neutral (1) and acidic (2) solutions (pH = 2) of 0.01 mM of 4-PhPy (1′ and 2′) and 1.2 mM of 4-PhPy (1″ and 2″) in 0.1 M $LiClO_4$ as a supporting electrolyte.

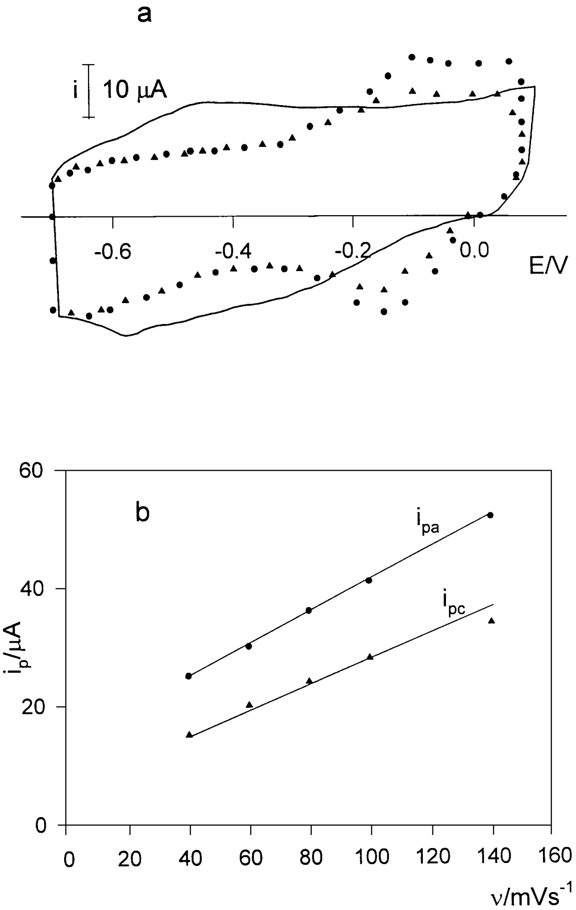

**Figure 2.** (a) Cyclic voltammograms for roughened Ag electrode in 0.1 M $LiClO_4$ solution containing different concentrations of 4-PhPy: (—) 0; (▲) 0.6 mM; (•) 1.2 mM. (b) Currents of the CV peaks (for saturated solution – 1.2 mM) as a function of scan rate.

currents ($i_{pa}$, $i_{pc}$) on the sweep rate (v) (Fig. 2b) indicates that this complex is surface attached. An increase of $i_{pa}$ and $i_{pc}$ caused by addition of 4-PhPy indicates that the amount of complex depends on the concentration of 4-PhPy.

**Capacity curves**: Differential capacity *versus* potential (C *vs* E) curves (Fig. 3) were measured for nine concentrations of 4-PhPy (from 0.01 mM to nearly saturated solution of 4-PhPy, *i.e.* to about 1.2 mM). The corresponding C *vs* E curve for pure supporting electrolyte (0.1 M $LiClO_4$) exhibits a minimum at the potential corresponding to pzc $E^0 = -0.975$ V *vs* SCE, being in a fairly good agreement with [15,16]. Contrary to the Au/4-PhPy system [10], the general shape of C *vs* E curves for Ag/4-PhPy practically does not change with increasing concentration of 4-PhPy in the bulk.

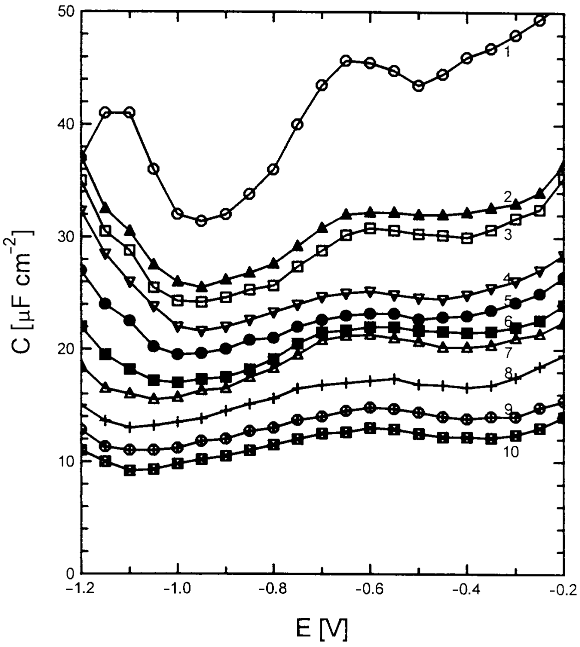

**Figure 3.** Differential capacity *vs* potential curves in solutions of 0.1 M $LiClO_4$ (1) containing different concentrations of 4-PhPy (mM): (2) 0.01; (3) 0.05; (4) 0.10; (5) 0.20; (6) 0.40; (7) 0.60; (8) 1.00; (9) 1.1; (10) 1.2.

As it is visible in Fig. 3, the capacity diffuse minimum (indicating the pzc value) has been shifted to the potential of about –1.1 V in the saturated 4-PhPy solution. Thus, the shift of the pzc, $\Delta E^0$, is equal to –0.12 V. This means that the contribution of 4-PhPy dipole potential to the potential drop across the inner layer is not great. However, since pzc moves towards negative values, it suggests that the 4-PhPy molecules are oriented with the nitrogen atom (negative end of this molecule) facing the metal surface, similarly as it was observed for adsorption of Py on Ag electrode [1,16]. Therefore, 4-PhPy adsorption also takes place predominantly at the positively charged Ag surface.

The potential corresponding to the maximum value of $\Delta C \equiv C^0 - C'$ (where $C^0 = 43$ μF cm$^{-2}$ is the capacitance of the electrode in the background electrolyte solution and $C'$ corresponds to the full coverage, $\theta = 1$) $E_{max}$ is equal to –0.65 V *vs* SCE being similar to that obtained for Py adsorption on Ag(110), where $E_{max} \approx -0.70$ V *vs* SCE for about 1.5 mM concentration of Py [16]. However, further changes of the polarization potential in anodic direction (to –0.25 V) does not significantly influence the $\Delta C$ value. $E_{max} = -0.65$ V indicates that maximal adsorption of 4-PhPy, according to charge density curve for supporting electrolyte [17], appears at the positively charged electrode (from $\sigma = 8 \div 10$ μC cm$^{-2}$), thus confirming the possibility of the surface orientation of 4-PhPy adsorbed molecules with the negative end towards the Ag electrode. The capacity $C'$, estimated from extrapolation of the plot $1/C$ *versus* $1/c_{4\text{-PhPy}}$ to 0 of $1/c_{4\text{-PhPy}}$, is relatively large and equals 11 μF cm$^{-2}$. It also should be stressed that this C′ value is very similar to that obtained for Py adsorbed on Ag (110) surface ($C' \approx 10.5\ \mu F\ cm^{-2}$), being, however, markedly greater than that of 4-PhPy adsorbed on Hg [7] or Au [10] electrode, where C′ was about 3.2–3.5 $\mu F\ cm^{-2}$. This fact may indicate a different surface orientation of adsorbed 4-PhPy molecules in the case of Ag electrode than in the case of Au or Hg. On the other hand, the relatively high C′ may result from the fact that water molecules remain in the surface layer at silver. It is probable, that the Ag electrode is only partly covered with adsorbate, even at saturation, on account of the difficulty for the organic molecule to displace water from the surface of the nonuniformly distributed Ag atoms on the polycrystalline surface (which is most similar to the stepped surface Ag(110) [1]). The presence of water in the adsorbed monomolecular 'film" may increase the capacity [17,18].

Since, the C *vs* E curves for different concentrations of 4-PhPy in the solution do not coincide with the respective curve for supporting electrolyte at either negative or positive ends of the polarization potentials for Ag electrode, the application of back-integration method to obtain the surface tension curves was not possible. Therefore, a tentative analysis of the data had to be applied to the capacitance versus potential data with the assumption that the adsorption is congruent with the potential and that the two parallel capacitors model according to the Frumkin-Damaskin theory [19] is approximately valid. Then, the individual values of degree of coverage, θ, for different concentration of 4-PhPy at the potential of maximal adsorption (E = –0.65 V), were calculated using

$$C = C^0 (1 - \theta) + C'\theta \qquad (1)$$

Although this procedure is based on the assumption that C is a linear function of θ, it has been shown [17,20,21] to yield essentially the same results as the back-integration method, when applicable. The standard Gibbs energy of adsorption, $\Delta G^0_{ads}$ and the interaction parameter A, were obtained from a linear test of the Frumkin isotherm according to

$$\ln (\beta c) = \ln [\theta/(1 - \theta)] + A\theta \qquad (2)$$

by plotting $\ln\{\theta/[(1 - \theta)c]\}$ as a function of θ (Fig. 4). $\Delta G^0_{ads}$ (for $\theta \to 0$) was calculated from the adsorption coefficient β, *i.e.* $\Delta G^0_{ads} = -RT \ln(55.5\beta)$ assuming as a standard state the unit molar fraction of the solute in the solution ($x^0 = 1$) and unit coverage ($\theta^0 = 1$) of the electrode. It was found that $\Delta G^0_{ads}$ is about –40 kJ $mol^{-1}$. This value is markedly larger than that obtained for Py adsorption on Ag electrode, which was about –21 kJ $mol^{-1}$ [1]. The slope of the line presented in Fig. 4 gives a value of interactions parameter A, which equals to 6 (positive value of A means repulsive interactions). Frumkin isotherm accounts separately for size and particle – particle interaction effects, where $A \equiv \Delta G^*/RT$ and $\Delta G^*$ means an extra free energy term, which can be re-

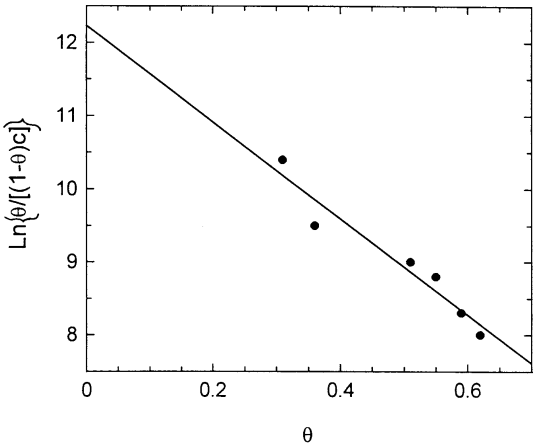

**Figure 4.** Linear test of the Frumkin isotherm for 4-PhPy on Ag electrode.

garded as a free energy of solution of adsorbate molecules in the solvent layer at the interface. If ($\Delta G^*/RT$) > 0, as here, particles of adsorbate tend to be bonded preferentially to solvent molecules. The effect is of particle – particle repulsion, but in fact it corresponds to surface miscibility with possible formation of ordered structures. Hence, the obtained value of A parameter indicates that this situation may appear in the case of 4-PhPy adsorbed on the Ag electrode.

Summarizing, the electrochemical results indicate a slightly weaker adsorption of 4-PhPy molecules on Ag than on Au electrode [10], being simultaneously markedly greater than in the case of Py and other derivatives of pyridine on Ag electrode [4]. However, from the presented results it is impossible to estimate clearly the interface structure or the adsorption geometry for 4-PhPy molecules. In order to determine the orientation of the adsorbate molecules we also applied surface-enhanced Raman scattering spectroscopy.

## SERS of 4-PhPy on the Ag electrode

The normal Raman (NR) spectrum of 4-PhPy powder exhibits several peaks (see Table 1 for their frequencies). The most intensive ones are due to totally symmetric $A_1$ modes, as follows from our previous assignment, based on *ab initio* calculations of the vibrational spectrum of this molecule [9]. We recorded the SERS spectra of 4-PhPy adsorbed at the Ag electrode from saturated (1.2 mM) solutions containing $LiClO_4$ or KCl at neutral and acidic pH.

**Table 1.** Selected NR and SERS vibrational frequencies (cm$^{-1}$) of 4-phenylpyridine.

| NR bands Solid 4-PhPy | Symmetry of modes | SERS bands 4-PhPy in 0.1 M LiClO$_4$ | $I_{405}/I_{1010}$ | | $I_{385}/I_{1010}$ | |
|---|---|---|---|---|---|---|
| | | | NR | SERS | NR | SERS |
| 331 m | $A_1$ | | | | | |
| | | 355 m* | | 0.39 (E = –0.4 V) | | 0.36 (E = –0.4 V) |
| ~385 vvw | $B_1$ | 385 w | 0.027 | | 0.021 | |
| ~405 vvw | $B_1$ | 405 w | | 0.12 (E = –0.8 V) | | 0.10 (E = –0.8 V) |
| 745 m | $A_1$ | 755 m | | | | |
| 995 vw | $B_1$ | ~1000 sh | | | | |
| 1002 vs | $A_1$ | 1012 s | | | | |
| 1019 w | $A_1$ | 1028 s* | | | | |
| | | 1036 s** | | | | |
| 1043 w | $A_1$ | | | | | |
| 1070 w | $B_2$ | 1073 m | | | | |
| 1223 w | $B_2$ | 1225 m | | | | |
| 1233 m | $A_1$ | 1235 sh | | | | |
| 1281 vs | $A_1$ | 1293 vs | | | | |
| 1587 s | $B_2$ | | | | | |
| 1598 vs | $A_1$ | 1600 s | | | | |
| 1610 s | $A_1$ | 1612 s | | | | |

*At E more negative than –0.7 V *vs* SCE. **At E more positive than – 0.7 V *vs* SCE. w – weak; m – medium; s – strong; vs – very strong; vvw – extremely weak; sh – shoulder.

**Neutral solutions:** The spectra in neutral solutions do not depend on the kind of anion in the supporting electrolyte, but exhibit a very strong dependence on the electrode potential (Fig. 5). As seen in Fig. 5, the SERS bands are shifted towards higher frequency as compared with the NR spectrum and their relative intensities are considerably changed. These effects are rather typical for SERS of chemisorbed molecules and point out to coordination of the molecule to the surface through nitrogen atom of the pyridine ring. Analyzing the potential dependence of the SERS spectra, one can notice that there are two types of spectra. One at potentials ranging from open circuit potential to about –0.65 V and the second one at more negative potentials. The most spectacular changes of the spectral pattern are observed within 900–1100 cm$^{-1}$ frequency range. Fig. 5 presents typical spectral patterns characteristic for these two potential ranges. The spectrum characteristic for potentials more positive than –0.7 V exhibits three bands of comparable intensity: at 1010, 1036 and 1073 cm$^{-1}$. At the vicinity of –0.7 V the spectrum abruptly grows in intensity, the band at 1036 cm$^{-1}$ disappears and a new band at 1028 cm$^{-1}$ appears instead. Also in the lower frequency range new bands emerge at 755 and 355 cm$^{-1}$ (the spectrum not shown here). The 755 cm$^{-1}$ band corresponds to shifted $A_1$ mode, that is observed at 745 cm$^{-1}$ in the NR spectrum (see Table 1). The second feature does not have its counterpart in the NR spectrum and, thus, may be tentatively assigned to the intermolecular stretching Ag-N vibration. This band should be considerably enhanced in vertical (or slightly tilted) coordination of 4-PhPy to the Ag surface, diminishing its intensity in a more flat configuration. The spectrum characteristic for more negative potentials remains extremely strong up to *ca.* –1.3 V. All spectral changes were totally reversible, *i.e.* if the spectra were collected in the positive-going potential sequence the 1028 $cm^{-1}$ band vanished at potentials more positive than –0.7 V and a new component at 1036 $cm^{-1}$ appeared instead. Interestingly, we previously observed almost the same potential dependence of the SERS spectrum of 4-PhPy for adsorption on the copper electrode [9].

In order to explain effects described above we suggest the following interpretations: (1) formation of a surface complex at an open circuit voltage, which remains at the surface at potentials ranging from –0.2 to –0.7 V and its subsequent reduction at more negative potentials, and/or (2) reorientation of adsorbed molecules at the vicinity of –0.7 V. Some information on the reorientation process may be inferred from the SERS spectra by discussing the relative intensities of the out-of-plane modes *versus* the in-plane ones. In SERS the high enhancement factors are observed for those modes, whose Raman tensor components involve axis perpendicular to the surface. Thus, if the out-of-plane modes are considerably enhanced in SERS, it is indicative of a flat-on or at least a tilted orientation of the molecular plane with respect to the surface.

In Table 1 selected frequencies of the SERS bands and their assignments are collected for two electrode potentials, corresponding to most typical spectra in two potential ranges. Moreover, the relative intensities of two low-frequency bands corresponding to the out-of-plane vibrations ($B_1$ or $A_2$) are given. As seen in Table 1, the

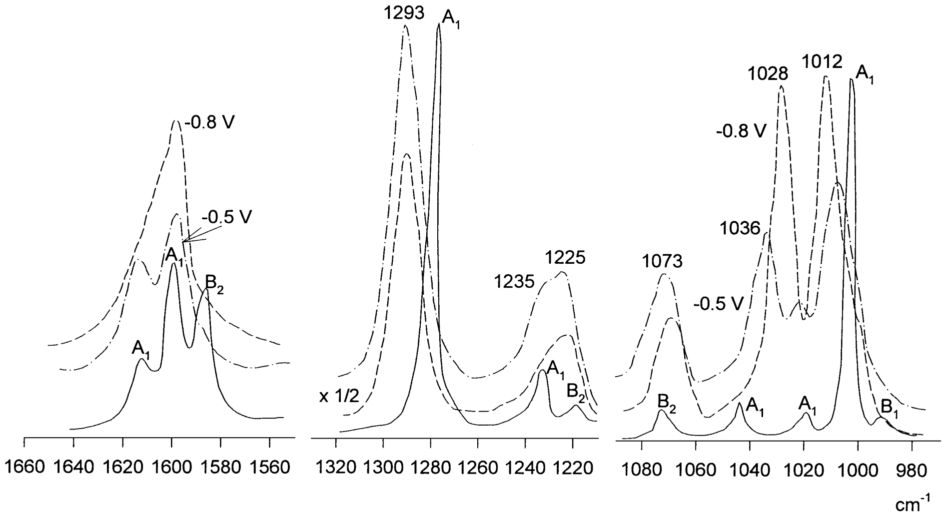

**Figure 5.** SERS spectra of 4-PhPy adsorbed on Ag electrode from saturated 4-PhPy solution (1.2 mM) in 0.1 M $LiClO_4$ at –0.5 V *vs* SCE (- • -) and -0.8 V *vs* SCE (---). Part of the normal Raman spectrum is shown for comparison (—).

relative intensity of the 405 and 385 $cm^{-1}$ bands, due to out-of-plane vibrations, considerably increases in the surface spectrum (*e.g.* $I_{405}/I_{1010} = 0.36$ at E = –0.4 V and 0.13 at –0.8 V) as compared with the NR spectrum ($I_{405}/I_{1010} = 0.027$). Other $B_1$ mode appears in the SERS spectrum as a shoulder on the low-frequency side of the 1010 $cm^{-1}$ band and could correspond to the weak feature observed at 995 $cm^{-1}$ in the NR spectrum. Relatively high intensity of the bands, due to out-of-plane modes, is an evidence of tilting of the molecular plane towards the Ag surface in the whole potential range, but greater at more positive potential values. The most spectacular changes of the spectra with the electrode potential are observed in the frequency range 900–1100 $cm^{-1}$. In this region the relatively strong band is observed at 1036 $cm^{-1}$ for potentials more positive than –0.7 V and respectively at 1028 $cm^{-1}$ for more negative electrode potentials. The interpretation of this part of the spectrum is difficult. In the NR spectrum two weak bands appear at 1019 and 1043 $cm^{-1}$, both assigned to totally symmetric $A_1$ modes. Taking into account that all the bands in the 4-PhPy spectrum shift to higher frequencies upon adsorption, the 1028 $cm^{-1}$ band could correspond to surface enhanced 1019 $cm^{-1}$ feature. An explanation of the origin of the 1036 $cm^{-1}$ bands needs some comment. As follows from our *ab initio* calculations [9] two out-of-plane modes of $B_1$ and $A_2$ symmetry are found in the vibrational spectrum of 4-PhPy at the vicinity of 1030 $cm^{-1}$. They are forbidden, in the normal Raman spectrum, but might become active in the surface spectrum when the molecular symmetry is lowered as a result of strong coordination to the surface. It should be mentioned that in the case of 3-phenylpyridine molecule ($C_s$ symmetry) the band at 1032 $cm^{-1}$ is relatively strong in the NR spectrum and even more strong in SERS [22,23]. Thus, in agreement with the electrochemical data we may assume that, at open circuit potential, 4-PhPy molecules form some kind of the surface complexes at the Ag surface, stable within –0.2 ÷ –0.65 V electrode potentials. In these complexes the molecular symmetry drops from $C_{2v}$ (characteristic for "free" molecule or bonded in the end-on configuration) to $C_s$, probably owing to simultaneous interaction of the phenyl ring with Ag in more tilted orientation. In this reduced symmetry, $B_1$ modes transform into totally symmetric ones ($A'$), thus contributing to a quite intense Raman band. At –0.7 V the surface complexes are reduced and the 4-PhPy molecules adopt a more vertical position, corresponding to $C_{2v}$ symmetry as in free molecule. The SERS spectrum at potentials more negative than –0.7 V is dominated by the totally symmetric modes ($A_1$). In the end-on configuration the stacking and lateral $\pi$-interactions between the aromatic rings can lead to an increased coverage at the vicinity of –0.7 V, as evidenced by the capacity data, which correspond to an increased total intensity of the spectrum.

Summing up, the Raman results point out to the reorientation of the 4-PhPy molecules from more flat configuration at potentials more positive than –0.7 V, to more perpendicular one at more negative electrode potentials. This reorientation may be connected with the formation of stable surface complexes at E > –0.7 V at the Ag surface and formation of molecular stacks at more negative electrode potentials.

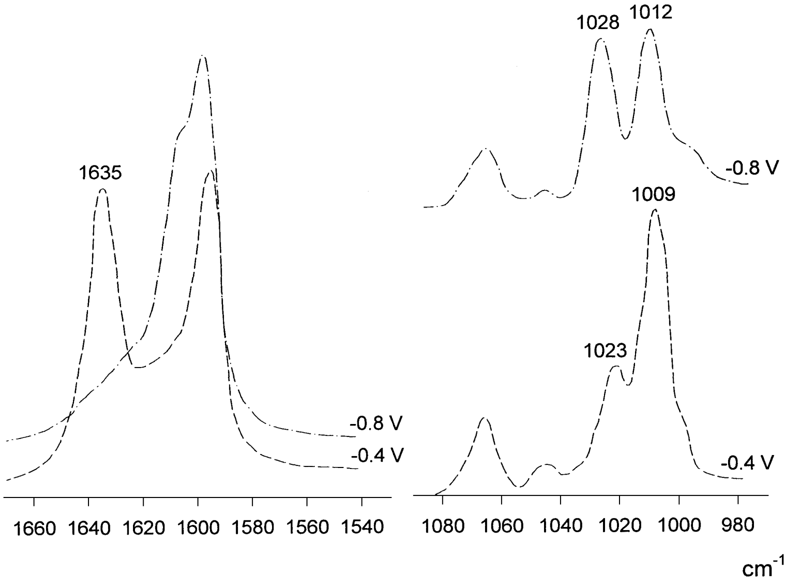

**Figure 6.** SERS spectra of 4-PhPy adsorbed from saturated solution of 4-PhPy in 0.1 M KCl (pH 4 adjusted by adding respective amount of HCl) at two electrode potentials *vs* SCE: (- - -) –0.4 V and (- • -) –0.8 V.

**Acidic solutions**: A similar SERS measurements were performed for acidic solutions of 4-PhPy, containing chlorides or perchlorates. As seen in Fig. 6, for potentials more positive than –0.8 V *vs* SCE, the SERS spectra recorded at low pH in presence of $Cl^-$ anions are changed, as compared with the respective spectra observed for the neutral solutions (*cf.* Fig. 5). Frequencies of the respective bands are slightly lower, the relative intensities are changed and, what is very important, a new band arises at 1635 $cm^{-1}$. The relative intensity of this band increases with decreasing pH values of the solution. This band is indicative of the presence of pyridinium-like species at the metal surface [24,25]. The same spectral pattern was previously reported by us for 4-PhPy adsorbed on the Cu electrode from acidic KCl solution [9] and reminds that observed by Cotton *et al.* [25] for 4, 4′-bipyridine at the Ag surface at low pH values. At potentials equal to and more negative than –0.8 V, the spectrum changes, the 1635 $cm^{-1}$ band corresponding to the protonated molecules vanishes and the spectrum becomes quite similar to that observed for a neutral medium. Unexpectedly, when lithium perchlorate is used as a supporting electrolyte, no bands characteristic for pyridinium-like cation have been found in the SERS spectra. Thus, we suppose that in presence of chlorides protonated 4-PhPy molecules are preferentially adsorbed as ion pairs with $Cl^-$ anions at potentials ranging from an open circuit potential up to –0.8 V. At –0.8 V, after desorption of the chloride ions, almost all adsorbed molecules deprotonate at the surface. In the case of perchlorate containing solution, 4-PhPy adsorbs at the Ag surface in non-protonated form, irrespective of the solution pH.

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