J. Am. Chem. Soc. 1982, 104, 6528–6532

Surface-Enhanced Resonance Raman Scattering from Water-Soluble Porphyrins Adsorbed on a Silver Electrode

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Abstract: Resonance Raman (RR) and surface-enhanced resonance Raman (SERR) spectroscopy have been used to study two water-soluble porphyrins, tetrasodium *meso*-tetrakis(4-sulfonatophenyl)porphine (TSPP) and *meso*-tetrakis(4-carboxyphenyl)porphine (TCPP). Both compounds were found to adsorb spontaneously at a silver electrode and exhibit intense SERR spectra. The combination of the surface-enhanced and resonance effects allows the observation of high-quality spectra of the adsorbed porphyrins using bulk solution concentrations of only 10^{-6} M. Evidence which supports a surface-enhancement process includes the increase in signal intensity by a factor of approximately 10^5 above that observed under resonance conditions alone, depolarization ratios greater than 0.5 for all of the Raman vibrations, and the dependence of signal intensity on the anodization step and the static electrode potential during data acquisition. An analysis of the vibrational spectra of the adsorbed porphyrins shows that both undergo partial metal incorporation during the electrode anodization step. However, the two exhibit marked differences in photostability and adsorption behavior. The differences are discussed in terms of the possible effects of the sulfonate and carboxylate groups on the porphyrin–electrode interactions.

Introduction

There have been a number of electrochemical studies of porphyrins immobilized at electrodes, the objectives of which have included the development of models for the more rigid environment of porphyrins in their biological matrix,[2a] as well as the practical application of porphyrin-coated electrodes as catalysts or sensitizers in photoelectrochemical cells.[2b–m]

In these examples an empirical approach was used to prepare the immobilized porphyrins and detailed structural information concerning the porphyrin–electrode interaction was not available. The type of information which would be most useful in this respect includes the following: (1) the nature of the porphyrin-electrode bond (covalent or coordinate) and the atoms involved; (2) the orientation of the porphyrins at the electrode surface; (3) the surface coverage; (4) the identification of any chemical interactions between the porphyrin and the electrode, solvent, electrolyte, or other species in solution (e.g., protonation and axial ligand coordination to the metal atom site in the porphyrin); and (5) the effect of electrode potential on each of the above as well as the redox state of the attached porphyrin. A correlation of information with electrochemical parameters such as redox potentials, electron transfer kinetics, and reversibility would identify those parameters which are most important for efficient electron transfer between the porphyrin and the electrode. Such knowledge would enable a more rational approach to the design of porphyrin-coated electrodes for specific applications.

Several recent publications indicate that resonance Raman spectroscopy (RRS) and its variant surface-enhanced resonance Raman spectroscopy (SERRS) have considerable potential for providing structural data of the type outlined above for molecules adsorbed on electrodes. In one of the first applications of RRS to this problem, Fujihara and Osa[3] studied monolayers of the dye methylene blue adsorbed on SnO_2 electrodes by an internal reflectance method. Their results showed that the electrode surface coverage was potential dependent and that methylene blue could be reduced to its colorless form on the electrode at sufficiently negative potentials. Yamada et al.[4] followed the changes in RR intensity of another dye, rose bengal, on ZnO electrodes. A decrease in RR intensity was observed to correlate with a decrease in photocurrent and the author postulated that rose bengal was forming a reaction product on photooxidation which did not absorb strongly at the laser excitation wavelength. The original RR intensity could be restored by poising the electrode at negative potentials, which presumably reduced the reaction product to rose bengal. Melandres and Cafasso[5] used RRS to study iron phthalocyanine at a glassy carbon electrode in an effort to determine the structural basis for differences observed in photocatalytic oxygen reduction as a function of electrode preparation. The RR spectra showed that two different forms of the phthalocyanine resulted when the electrode was coated by an evaporation procedure or by vapor deposition of the phthalocyanine. In addition, the RR spectrum indicated that hydration of the bridge nitrogen atoms in the phthalocyanine occurred on placing the electrode in aqueous electrolyte. In the first application of SERRS to molecules adsorbed on Ag electrodes, Jeanmaire and Van Duyne[6] found that the resonance and surface-enhancement effects were multiplicative and RR spectra of crystal violet were obtained with only a few milliwatts of laser power. Kötz and Yeager have used SERRS recently to probe the orientation and potential dependence of cobalt phthalocyanine at Ag electrodes.[7] The SERR effect can also be used to study large molecules containing a chromophore as observed by Cotton et al.[8] for cytochrome *c* and myoglobin spontaneously adsorbed on Ag. The oxidation-state marker bands for the heme chromophore in the surface-bound proteins suggest that they undergo reduction at negative potentials. Finally, Pemberton and Buck[9] have exploited the high sensitivity

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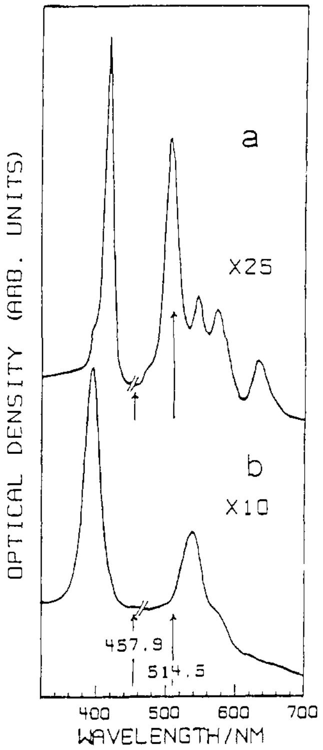

Figure 1. Porphyrin visible absorption spectra: (a) 1 × 10^{-4} M *meso*-tetrakis(4-sulfonatophenyl)porphine (TSPP) in water. (b) Ag(II) metallated porphyrin in part a. The ×25 and ×10 are the scale factors used for Q bands.

of surface-enhanced resonance Raman spectroscopy to detect dithizone anion adsorbed on Ag from solution concentrations as low as 10^{-9} M.

In the results to be presented SERRS has been used to study two water-soluble porphyrins spontaneously adsorbed on Ag electrodes. The data are interpreted in terms of potential dependence, mode of interaction, and photostability. The RR data were also used to identify an interesting and unexpected reaction of the porphyrins at the electrode or within the diffusion layer near its surface.

Experimental Methods

The water-soluble porphyrins, *meso*-tetrakis(4-carboxyphenyl)porphine (TCPP) and tetrasodium *meso*-tetrakis(4-sulfonatophenyl)porphine (TSPP) were purchased from Strem Chemicals, Inc., Newburyport, MA, and used as received. Tetraphenylporphine was purchased from Aldrich Chemical Co., Milwaukee, WI, and purified according to published procedures.[10] Metal incorporation was accomplished with silver acetate solutions in pyridine in the case of TPP.[11] Water-soluble porphyrins were also metallated with silver acetate, but water was used as the solvent. The reaction progress was monitored spectroscopically on a Cary 14 spectrophotometer.

Solutions of the water-soluble porphyrins were prepared in distilled and deionized water (Milli-Q, Millipore Corp.) at a concentration of 1 × 10^{-4} -1 × 10^{-6} M. The electrolyte was 0.1 M Na_2SO_4 and all solutions were thoroughly degassed by purging with high-purity nitrogen. Since TCPP is insoluble in the electrolyte in the acidic form, the sodium salt was prepared by adding carbonate-free NaOH. This was not necessary in the case of TSPP, however, which is supplied as the sodium salt.

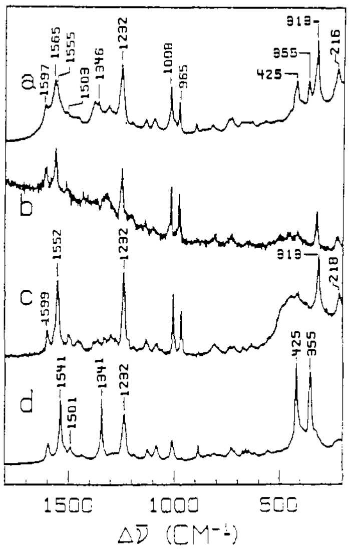

Figure 2. Resonance Raman spectra of TSPP, 457.9-nm excitation: (a) SERR spectrum on Ag at 0.0 V vs. SCE from a 1 × 10^{-6} M solution. (b) RR solution spectrum of 1 × 10^{-3} M TSPP in a 3-mm sample tube. (c) RR spectrum of solid TSPP. (d) RR solution spectrum of 1 × 10^{-4} M Ag^{II}TSPP. The excitation wavelength was 457.9 nm and the laser power was (a) 25, (b) 30, (c) 30, and (d) 9 mW. The monochromator slit width was 2 cm^{-1}. Unlabeled peaks correspond with those in spectra above or below.

The Raman apparatus and cell used in these experiments have been described.[6] A bulk Ag wire working electrode was used for all the surface experiments. The wire was flattened at the end with pliers and masked with Torr Seal to provide a flat rectangular working electrode area of approximately 3 × 10 mm. Finally, the Ag surface was mechanically polished and electrochemically anodized according to established procedures. The anodization consisted of an oxidation step at +0.45 V vs. SCE, followed by a reduction step at 0.0 V vs. SCE. The total charge passed in the oxidation step was equivalent to 25 mC/cm^2 (approximately 100 monolayers of Ag).

Results and Discussion

Porphyrins and metalloporphyrins absorb strongly in the visible spectral region and are therefore ideal candidates for study by resonance Raman methods. When the resonance enhancement is coupled with that observed at Ag electrodes, it appears probable that even submonolayers of porphyrins will be detectable. The absorption spectrum of one of the porphyrins used in this study, TSPP in water, is shown in Figure 1a. Arrows indicate the two laser excitation wavelengths, 457.9 and 514.5 nm, used in the SERR experiments to be discussed. Also shown is the absorption spectrum of the Ag derivative of TSPP (Figure 1b). As may be seen, only the 514.5-nm line is close in resonance with an absorption band in metal-free TSPP, yet excellent spectra were observed at both wavelengths for TSPP when adsorbed on a Ag electrode. The absorption spectra of the metal-free TCPP and its Ag salt are not shown since they are nearly identical with those of TSPP.

RR and SERR Spectroscopy of TSPP. Figure 2a shows the RR spectrum obtained for TSPP using 457.9-nm excitation. This spectrum was recorded by using a bulk solution concentration of only 1 × 10^{-6} M. No RR spectrum was observable for the solution species at this concentration using 457.9- or 514.5-nm excitation. An increase in concentration of TSPP by 1000-fold produced the solution spectrum shown in Figure 2b, where it is obvious that even at this concentration the solution spectrum does not exhibit a signal-to-noise ratio comparable to that observed for TSPP on the electrode. An approximate estimate of the enhancement resulting from the surface effect can be made by assuming monolayer coverage of the electrode with TSPP. A comparison of the 1555-cm^{-1} band intensity with that expected for an equal number of TSPP molecules in the solid state under similar experimental conditions (but not adsorbed on the electrode) indicates that a factor of approximately 10^5 is attributable to the surface-enhancement effect. This value is comparable to that observed in the nonresonance case for small molecules adsorbed at Ag electrodes.[6,12]

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Table I. Raman Frequencies (cm^{-1}) of TSPP, TPP, and Their Ag Salts

solid TSPP	TSPP at 0.0 V[a]	AgTSPP[b]	AgTPP[c]	assignment[d]
1599	1597	1594		phenyl
1566 (sh)	1565		1553 (sh)	$\nu(C_\beta\text{-}C_\beta)$ + $(C_\beta\text{-}H)$
1552	1555	1541	1536	$\nu(C_\alpha\text{-}C_m)$
1502	1503	1491	1487	$\nu(C_\beta\text{-}C_\beta)$
1454	1456, vw			$\nu(C_\alpha\text{-}C_\beta)$ + $\delta(C_\beta\text{-}H)$
1440		1435		
1377				
1358	1362	1360 (sh)	1360 (sh)	$\nu(C_\alpha\text{-}N)$ + $\delta(C_\beta\text{-}H)$
1331	1346	1341	1343	$\nu(C_\alpha\text{-}C_\beta)$ + $\delta(C_\beta\text{-}H)$
1297	1295	1292, vw	1296	
1278		1273, vw		$\nu(C_\alpha\text{-}N)$
1236	1232	1232	1236	$\nu(C_\alpha\text{-}N)$
1196	1185	1190, vw	1175	
1134	1127	1121	1122	
1084	1080	1081	1076	$\delta(C_\beta\text{-}H)$
1004	1008	1007	1012	$\nu(C_\alpha\text{-}C_m)$
965	965	964, vw		
884	886	887	885	phenyl
811	807	811	806	
	425	422		
410				
			400	
	355	355		
313	313			
216	216			

[a] TSPP spontaneously adsorbed at Ag; bulk concentration = 1×10^{-6} M. [b] AgTSPP in water; concentration = 1×10^{-2} M. [c] AgTPP in CH_2Cl_2; concentration = 1×10^{-2} M. [d] Assignments are based upon those for FeTPP in ref 25. sh = shoulder; w = weak; vw = very weak.

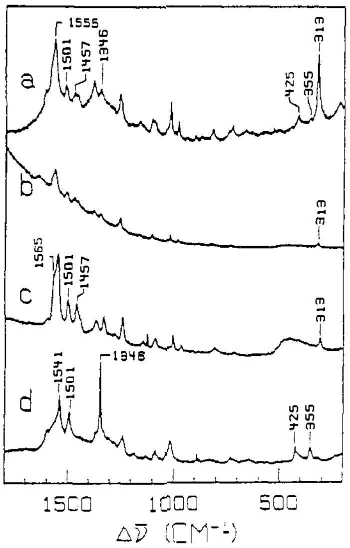

Figure 3. Resonance Raman spectra of TSPP, 514.5-nm excitation: (a) SERR spectrum on Ag at 0.0 V vs. SCE from a 1×10^{-6} M solution. (b) RR solution spectrum of 1×10^{-3} M TSPP in a 3-mm sample tube. (c) RR solid spectrum of solid TSPP. (d) RR solution spectrum of 1×10^{-4} M Ag^{II}TSPP in a 3-mm sample tube. The excitation wavelength was 514.5 nm and the laser power was (a) 30, (b) 600, and (c) 30 mW. The monochromator slit width was 2 cm^{-1} for all spectra. Unlabeled peaks correspond with those in spectra above or below.

Several other criteria which are important in distinguishing the spectrum of a surface-bound species from its solution counterpart were also met by TSPP. These are dependence of the signal intensity on the anodization step and the electrode potential, as well as the observation of depolarization ratios near 0.5 or greater for all of the RR bands. (Obviously the changes in depolarization ratio for the vibrations in the surface-bound species could result from a number of different causes and these are not considered here. Rather depolarization ratios are used solely as a diagnostic for surface-bound species.) Only very weak RR spectra were observed when no anodization step was performed on the working electrode and changing the electrode potential to more negative values (−0.3 V and beyond) resulted in a substantial decrease in the signal intensity for anodized electrodes. The intensity could be restored by returning the electrode to a potential of 0.0 V. Thus, maximum intensity was observed near 0.0 V. However, it is important to note that the intensity of the SERR signal as a function of electrode potential is strongly dependent upon both the anodization conditions and the laser excitation wavelength. Recent studies[13] indicate that, when 530.9-nm excitation is used to excite SERR scattering from TSPP adsorbed at a Ag electrode, strong spectra are obtainable even at potentials as negative as −0.6 V.

The SERR spectrum of TSPP is substantially different from that observed in solution or in the solid state as shown in Figure 2a–c and Table I. (Bands are listed for the solid spectrum in Table I because the better signal-to-noise ratios allow more accurate determination of their values; no appreciable differences are observed between the solid and solution spectra.) New peaks are observed in the surface spectrum at 1346, 425, and 355 cm^{-1}. There are also intensity differences, with the bands at 1555, 1503, 1456, and 965 cm^{-1} appearing somewhat weaker at the surface. The new bands are similar to those observed in other porphyrins which are metallated, which suggests that TSPP may undergo Ag incorporation during the anodization step. To test this possibilty we prepared the Ag derivative of TSPP and recorded its RR spectrum. The results, as shown in Figure 2d and Table I, indicate that TSPP is indeed partially metallated during the anodization step. Excellent correspondence is observed between the new bands on the surface and those in AgTSPP. Furthermore, when TSPP is added after anodization of the Ag electrode, metal incorporation is much less (ca. a factor of 4) as shown by the decreased intensity of the metal-sensitive bands.

The RR spectrum of silver tetraphenylporphyrin (TPP) was recorded and compared to that of AgTSPP to determine whether any vibrations could be assigned to the sulfonate group. Also, Burke et al.[14] have interpreted the RR spectrum of FeTPP recently and their results can be used to make tentative assignments in the water-soluble porphyrins used in this investigation. The values for AgTPP are listed in Table I and, as may be seen, the major differences between its spectrum and that of AgTSPP are in the low-frequency region. The band at 400 cm^{-1} in AgTPP is at 425 cm^{-1} in AgTSPP and a new band is observed in the latter at 355 cm^{-1}. This new band is close to the 363-cm^{-1} vibration in $(FeTPP)_2O$ which has been assigned to an out-of-plane symmetric Fe–O–Fe stretch. Thus, it may arise from an out-of-plane mode in AgTSPP (e.g., ligand mode involving water or the sulfonate group of another TSPP molecule). No vibrations are observed in the spectra of AgTSPP in solution at the excitation wavelengths used here, which are assignable to the sulfonate group. This is in contrast to the results reported for cobalt tetrasulfonated phthalocyanine (TSPc) in which a vibration at 1275 cm^{-1} was assigned to the sulfonate group.[7] Other plausible assignments which can be made for the silver porphyrins are based on FeTPP results.[14] The bands at 1541, 1341, and 1236 cm^{-1} were found to be anamolously polarized in spectra recorded by using the 530.9-nm line of a Kr^+ laser as the excitation source (not shown).[13] The appearance of anomalously polarized bands in porphyrins is generally observed on excitation into the α and β bands.[15] These correspond to the 1510-, 1338-, and 1225-cm^{-1} bands in FeTPPCl which are composed of C_α–C_m, C_α–C_β, and C_α–N stretching vibrations, respectively, with some contribution of C_β–H bending

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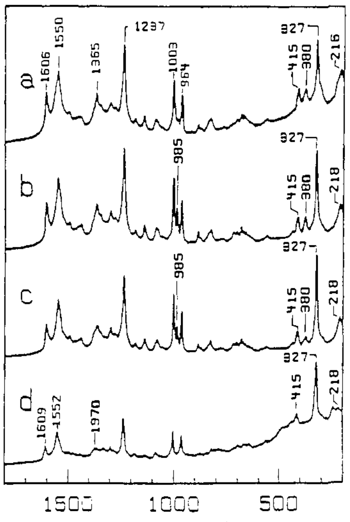

Figure 4. Resonance Raman spectra of TCPP, 457.9-nm excitation: SERR spectra from 1 × 10^{-6} M solution of TCPP on a Ag electrode at (a) 0.0, (b) −0.4, and (c) −0.6 V; (d) RR spectrum of solid TCPP. The laser power was 10 mW for surface spectra and 30 mW for spectrum d. Unlabeled peaks correspond with those in spectra above or below.

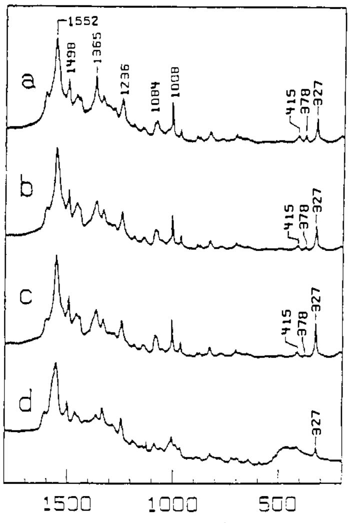

Figure 5. Resonance Raman spectra of TCPP, 514.5-nm excitation: SERR spectra from a 1 × 10^{-6} M solution of TCPP on a Ag electrode at (a) 0.0, (b) −0.4, and (c) −0.6 V; (d) RR spectrum of solid TCPP. The laser power was 60 mW in all cases. Unlabeled peaks correspond with those in spectra above or below.

Table II. Raman Frequencies ($\mathrm{cm^{-1}}$) of TCPP

solid TCPP	TCPP at 0.0 V[a]	solid TCPP	TCPP at 0.0 V[a]
1609	1606	1131, w	1140
1566, sh	1567, sh	1084	1087
1552	1550	1004	1003
1498, vw	1497, w, sh		985, w
1477, vw	1452	965	964
1440		889, vw	888
1370, w, br	1365	822	829
1331, w	1348, sh	415	415
1297	1297		380
1283, sh	1277	327	327
1238	1237	244	
1185	1181	220	216

[a] TCPP spontaneously adsorbed at Ag; bulk concentration = 1 × 10^{-6} M. sh = shoulder; w = weak; vw = very weak; br = broad.

modes to the latter two bands as well.

Results obtained by using 514.5-nm excitation to produce the SERR spectrum of TSPP agree for the most part with those summarized above. Once again the most intense spectra are observed at 0.0 V (Figure 3a) and a comparison of the surface spectrum with that of AgTSPP shows bands characteristic of the metal derivative (1346, 425, and 355 $\mathrm{cm^{-1}}$). The strong 313-$\mathrm{cm^{-1}}$ band is characteristic of this wavelength, since 514.5 nm is very close to the maximum in its Q_{y1} transition (See Figure 1a). Differences between the spectra obtained with 457.9 and 514.5-nm excitation include relative intensity variations as well as a much weaker solution spectrum (Figure 3b) in the 514.5-nm case. In addition, the RR spectrum for TSPP in solution is superimposed on background fluorescence, which is quenched at the electrode. The quenching of fluorescence from chromophores at the electrode appears to be another important advantage of SERRS.

RR and SERR Spectroscopy of TCPP. The sodium salt of TCPP was chosen for study at Ag electrodes in order to determine the effect of a different functional group on the surface behavior of a water-soluble porphyrin. As will be seen, the carboxylate has a markedly different effect on the adsorption properties of this porphyrin as compared to those of the sulfonate in TSPP. Figure 4, a and d, depict the spectra resulting from 457.9-nm excitation of surface-adsorbed TCPP at 0.0 V and the solid, respectively (see also Table II). The solution spectrum of TCPP is not shown, but substantially higher concentrations are needed than those used for SERR spectroscopy (1 × 10^{-6} M). No differences are observed between the solution and solid spectra. A comparison of the surface spectrum with that of the solid, on the other hand, shows several differences. Bands at 1606, 1365, 1140, 1088, 829, 415, and 216 $\mathrm{cm^{-1}}$ are more intense on the surface. A new band is also present at 380 $\mathrm{cm^{-1}}$ in the adsorbed TCPP, which is analogous to that at 355 $\mathrm{cm^{-1}}$ in AgTSPP. This observation, together with the increased intensity of the other bands which are characteristic of AgTSPP (1365, 415 $\mathrm{cm^{-1}}$), indicates that a fraction of the surface-bound TCPP is also metallated at, or near, the electrode surface. Preparation of the AgTCPP has verified these assignments.[13]

The adsorbed TCPP responded to changes in electrode potential in a dramatically different manner than TSPP. It was possible to observe intense SERR spectra at very negative potentials as shown in Figure 4, b and c, where spectra are displayed at −0.4 and −0.6 V. As may be seen, the overall intensity in these spectra is equal to that for the 0.0 V spectrum, but differences exist in relative band intensities as the potential is changed to more negative values. Bands at 1365, 415, and 380 $\mathrm{cm^{-1}}$ decrease somewhat in relative intensity as the potential is made more cathodic, whereas the band at 327 $\mathrm{cm^{-1}}$ increases with these changes. These first three bands are metal sensitive and that at 327 $\mathrm{cm^{-1}}$ is characteristic of the free-base porphyrins. Thus, the intensity changes suggest that some demetallation is occurring at the electrode with cathodic shifts. Silver porphyrins have been observed to lose their central Ag atom under reducing conditions.[16] Besides these intensity changes, a new band is observed at 985 $\mathrm{cm^{-1}}$, which increases in intensity as the electrode potential is made more negative. This band can be assigned to a phenyl-ring mode,[14] and its appearance at more negative potentials implies either a conformation change in the adsorbed porphyrin and/or a change in its mode of interaction with the electrode. For example, increased phenyl interaction in the excited state of the porphyrin at negative potentials should lead to increased intensity in the phenyl modes. Or, closer contact of the phenyl groups with the electrode surface as a result of a potential-dependent reorientation of the porphyrin should also lead to increased intensity, but in this case the enhancement results from the surface effect. These two possibilities cannot be distinguished at present.

The SERR and RR spectra of TCPP produced by excitation at 514.5 nm are very intense (Figure 5). The potential-dependent behavior is similar to that discussed for 457.9 nm. At more negative potentials the spectra indicate some demetallation of the Ag derivative which is formed at the electrode surface (bands at

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1365, 415, and 380 cm^{-1} decrease in intensity). The 327-cm^{-1} band increases considerably with a decrease in electrode potential. A comparison of the −0.6-V spectrum with that of solid TCPP (Figure 5, c and d, respectively) shows that this mode is one of the most strongly enhanced at the electrode surface. Other modes which are more intense relative to those in the solid are at 1497, 1365, 1140, 1087, and 1003 cm^{-1}. Note that the 985-cm^{-1} band is not observed at 514.5 nm, which suggests that it is a resonance-enhanced phenyl mode.

Comparison of the RR and SERR Spectra of TSPP and TCPP. The RR spectra of TSPP and TCPP were found to be quite similar in the solid state, as would be expected since they differ only in the para substituent on the meso phenyl group. The major differences in the metal-free compounds are seen in the 1599-cm^{-1} band of TSPP which is at 1609 cm^{-1} in TCPP, and the 314-cm^{-1} band of TSPP which is at 327 cm^{-1} in TCPP. In the Ag complexes, the low-frequency modes at 425 and 355 cm^{-1} in TSPP are at 415 and 380 cm^{-1} in TCPP.

The behavior of TSPP and TCPP at Ag electrodes, however, is markedly different. First, the TSPP displayed photoinstability when irradiated at 457.9 or 514.5 nm at the electrode. An exponential decrease in overall signal intensity was observed with time. The photoinstability is attributed to desorption of surface-bound TSPP since the original signal intensity could be recovered by allowing the electrode to remain in the dark for several minutes followng intensity loss. Also, no photoinstability was detected in the solution studies of TSPP. The signal recovery in the dark illustrates the dynamic nature of the adsorption process; i.e., irreversible adsorption is not involved. The SERR spectra of TCPP, on the other hand, were photostable indefinitely. No change was observed in the SERR spectrum of TCPP when irradiated with 100 mW of 457.9-nm light for as long as 4 h. Second, SERR spectra could only be observed at potentials near 0.0 V in the case of TSPP, whereas intense SERR spectra of TCPP were observable over the entire available potential span. These results show that the functional groups attached to the porphyrins are extremely important in their adsorption behavior. A comparison of their surface spectra suggests the possible origins of the different adsorption properties. At 0.0 V the 1605-cm^{-1} phenyl and 1365-cm^{-1} (C_α–N) modes of TCPP are more intense than in TSPP. A band at 829 cm^{-1} in TCPP is not observed in the surface spectrum of TSPP. This band is in the region where out-of-plane bending modes of the phenyl group should occur. Thus, the increase in intensity of the phenyl and C_α–N modes together with the appearance of a new band would imply that TCPP has a somewhat different orientation or at least a stronger interaction at the electrode. The photostability of TCPP would support the latter interpretation.

A coherent explanation for the differences in the surface behavior of TSPP and TCPP must rationalize the photostability and potential dependence of the basis of the possible interactions of these porphyrins with the electrode. The explanation must consider that the only chemical difference between TSPP and TCPP is the substitution of a sulfonate group for a carboxylate. In considering the possible modes of interaction of the porphyrins with the electrode, there are two sites which might be expected to interact with Ag. These are the sulfonate or carboxylate substituents and the porphyrin core, which either is present as the Ag derivative or exists as a free base. With these criteria in mind, the following hypothesis is offered to rationalize the surface behavior of these porphyrins. At 0.0 V it appears that the interaction between TCPP and the electrode is stronger than that of TSPP based on the enhancement of the phenyl stretching vibrations and the 1365-cm^{-1} mode. This suggests that the site of interaction involves the carboxylate groups, in agreement with previous results obtained for aromatic carboxylic acids.[16] Sulfonate groups are known to interact only weakly with Ag electrodes from other studies of small molecules in this laboratory. Nonetheless, there is some interaction between the TSPP, through either its sulfonate group or the core nitrogens, which are partially metallated. However, it is much weaker than the carboxylate and leads to desorption of the porphyrin under irradiation. A change in electrode potential to more negative values appears to favor the interaction of the porphyrin core nitrogens with the Ag electrode. In the case of TSPP this interaction is inhibited and the porphyrin is desorbed, no doubt because of Coulombic repulsion between the sulfonate groups and the negatively charged electrode. With TCPP, on the other hand, enhancement of metal-free modes is observed together with out-of-plane bending modes in the phenyl groups as the potential is made more negative. This suggests that the macrocycle is bonded in a more parallel orientation with respect to the electrode surface. Apparently, the carboxylate ion does not interfere with this interaction to as great an extent as the sulfonate. This could be due to the strong interaction between the carboxylate and Ag^+ ions formed during the anodization procedure, since silver carboxylates are very insoluble and hence little dissociated.

The results obtained in this study for TSPP are somewhat different from those reported for cobalt tetrasulfonated phthalocyanine (TSPc) adsorbed on a Ag electrode.[7] The latter was found to adsorb weakly at anodic potentials, with little difference between the surface spectrum and that in solution, in agreement with what has been observed here for TSPP. However, unlike TSPP, the CoTSPc was found to remain adsorbed on the electrode at negative potentials. Moreover, the SERR spectra changed considerably with a decrease in potential, with modes in the 1550–1600- and 1100–1200-cm^{-1} regions undergoing greater enhancement at −0.2 V. Based on the above argument for TCPP, we might interpret these data to indicate a change in orientation of the CoTSPC at the negative potentials, although the authors suggest another possible interpretation.[7] If our interpreation is accepted, it would appear that the sulfonic group on CoTSPc does not interfere with adsorption at the negative potentials. The electrolyte in the CoTSPc experiments was 0.05 M H_2SO_4, which should result in protonation of a significant fraction of the sulfonic groups. This, together with the difference in a the macrocyclic structure of the phthalocyanine as compared to the porphyrin, might explain the decreased repulsion. However, the CoTSPc intensity was observed to decrease as the electrode potential was changed to −0.4 V, so some repulsion is present in this compound as well.

In conclusion, the results presented have illustrated the application of SERRS to the study of two water-soluble porphyrins at a Ag electrode. The data have shown how the vibrational spectra can be used to suggest the possible mode of interaction between the porphyrins and the electrode as well as their potential-dependent behavior and photostability. The RR data indicate that metallation of the porphyrins occurs at the electrode, a fact which would have been difficult to determine by other spectroscopic methods. Finally, the results show that the substituent groups of these porphyrins have a profound influence on their adsorption behavior as well as their photostability. Thus, the use of the SERR effect for the study of immobilized porphyrins at electrodes should be useful in evaluating structural modifications which stabilize these systems for practical applications.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Reseach Fund, administered by the American Chemical Society, for partial support of T.M.C.'s work. T.M.C. also gratefully acknowledges support from Research Corp. Additional support was provided by the National Institutes of Health (Grant no. GM 27498), National Science Foundation (Grant no. CHE78-24866), and the Office of Naval Research (Contract no. N00014-79-C-0794).

Registry No. TSPP, 39050-26-5; TCPP, 14609-54-2.