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Spectroscopic and Electrochemical Studies of Transition Metal Tetrasulfonated Phthalocyanines

2†—Resonant Raman Spectra of Aqueous Solutions of Cobalt and Iron Tetrasulfonated Phthalocyanines

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Raman spectra of the polarized and depolarized light scattered from cobalt and iron tetrasulfonated phthalocyanines in aqueous media at various pH values are discussed and correlated with previously obtained data. The Raman vibrational modes from pyrrole and benzene were used for a tentative band assignment in the frequency range from 200 to 1700 cm⁻¹.

INTRODUCTION

It has been shown by various research groups¹⁻³ that transition metal phthalocyanines exhibit catalytic activity when absorbed on various electrode surfaces. However, the physico-chemical behavior of water soluble tetrasulfonated phthalocyanines (TSPc) in aqueous media is not well explained.

The influence of the sulfonic acid groups on the overall behavior of the metallo-phthalocyanines and specific differences between sulfonated and non-sulfonated macrocyclic species are of particular interest. The experimental evidence obtained in the study of the absorption spectra from H₂-, Co- and Fe-TSPc in aqueous media^{4,5} indicates that sulfonation does not affect molecular symmetry. Prior Raman⁶ and infrared⁷ studies of phthalocyanines provided some basic information on their vibrational modes when these molecules were in their crystalline and solution phases.

This paper reports resonant Raman spectra of the tetrasulfonated cobalt and iron phthalocyanines in aqueous solutions at various pH values as a prerequisite to studies of the adsorbed macrocyclics on electrode surfaces by Raman spectroscopy. Raman spectra were recorded between 200 and 1700 cm⁻¹ of the polarized and depolarized laser light scattered from phthalocyanines in acidic (0.05 M H₂SO₄, pH ≈ 1), neutral (pH ≈ 7) and alkaline (0.1 M NaOH, pH ≈ 13) solution phases with the objective of observing the fundamental vibrational properties of TSPc in aqueous media.

EXPERIMENTAL

Cobalt and iron tetrasulfonated phthalocyanines (Co- and Fe-TSPc) were synthesized and purified according

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to the method of Weber and Busch.⁸ The electrolytes with pH ca 1, 7 and 13 were prepared from ultrapure grade sulfuric acid and sodium hydroxide (J. T. Baker) and triply distilled water. The detailed solution phase preparations were described elsewhere.⁵

The aqueous solution phases contained 5 × 10⁻⁵ M of M-TSPc. All Raman experiments were performed at room temperature and aerobic atmosphere.

The source of light was the Spectra-Physics Model 125 He-Ne laser operating at 632.8 nm with an output power of 50 mW. The laser light was filtered in order to eliminate plasma lines. The effective power at the sample was about 20 mW. The He-Ne laser excitation line falls within the visible Q absorption bands of Co- and Fe-TSPc and provides pre-resonant and resonant Raman excitation, respectively. Some measurements were conducted with argon-ion excitation lines at 488.0 and 514.5 nm but these spectra will be omitted in this discussion. It has also been shown that the intensities and shapes of the Raman bands are highly sensitive to the laser excitation.⁶

The plane of polarization of the laser incident light was rotated with the Spectra-Physics wide-band polarization rotator. The Raman polarized and depolarized spectra from aqueous solutions of M-TSPc were obtained using a Spex 1400 double monochromator, FW 130 photomultiplier and photon counting electronics. The resolution of the monochromator was 2.5 cm⁻¹ in all experiments. The scanning speed was 0.2 cm⁻¹ s⁻¹ and the accuracy of the band position was ± 5 cm⁻¹.

RESULTS AND DISCUSSION

Metallo-phthalocyanines (M-Pc) belong to D_{4h} symmetry point groups⁹ and that symmetry appears to remain for cobalt and iron tetrasulfonated phthalocyanines (Co- and Fe-TSPc) in aqueous media. This conclusion is reached after a comparative analysis of the UV-visible absorption spectra of the Co- and

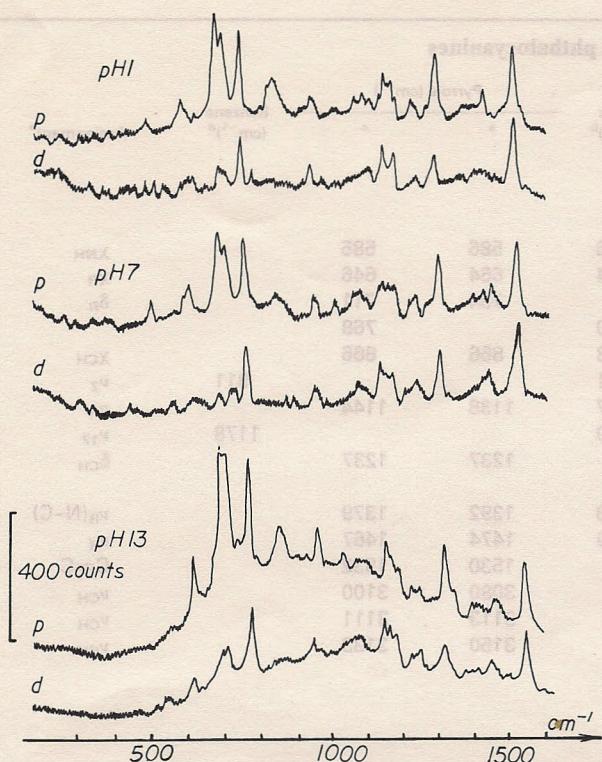


Figure 1. Raman spectra of (p) the polarized and (d) the depolarized light scattered from 5×10^{-5} M of cobalt tetrasulfonated phthalocyanine in aqueous solutions at pH ca 1, ca 7 and ca 13. A relative intensity scale is indicated in counts s⁻¹ and spectra are twice more intense for alkaline solution; resolution is 2.5 cm^{-1} and the laser excitation is at 632.8 nm with 20 mW output power.

Fe-TSPc in aqueous media⁵ with the previously obtained data from Co- and Fe-Pc in the vapor phase.⁹

The absorption spectrum from Co- and Fe-TSPc is principally due to $\pi-\pi^*$ electronic transition and the visible portion of the absorption spectrum is due to $a_{2u}(\pi) \rightarrow e_g(\pi^*)$ electronic transition with the corresponding $Q(0, 0)$ and $Q(1, 0)$ absorption bands positioned at ca 680 and ca 630 nm, respectively.⁵ The He-Ne laser excitation at 632.8 nm falls in the region of the Q absorption bands and therefore provides resonant Raman scattering.

Resonant Raman spectra of the polarized and depolarized light scattered from aqueous solutions of Co-TSPc and Fe-TSPc at various pH values are displayed in Figs 1 and 2. It was found experimentally that a 5×10^{-5} M concentration of the macrocyclic molecular species dissolved in aqueous media produced the optimal Raman signal when the He-Ne laser line at 632.8 nm was used for the excitation. Higher concentrations of the phthalocyanines increased self-absorption of the scattered light and lowered the Raman signal. The lower concentration also produced weaker Raman signals.

Raman spectra from Co- and Fe-TSPc could be obtained with the other laser excitations at 488.0 and 514.5 nm but required a much higher concentration of the phthalocyanines in aqueous media, usually of the order of 10^{-2} M.

The resonant Raman spectra from Co- and Fe-TSPc in aqueous solutions are similar to those obtained in prior studies⁶ of the Raman spectra from Co- and Fe-Pc in crystalline form and in tetrahydrofuran solutions.

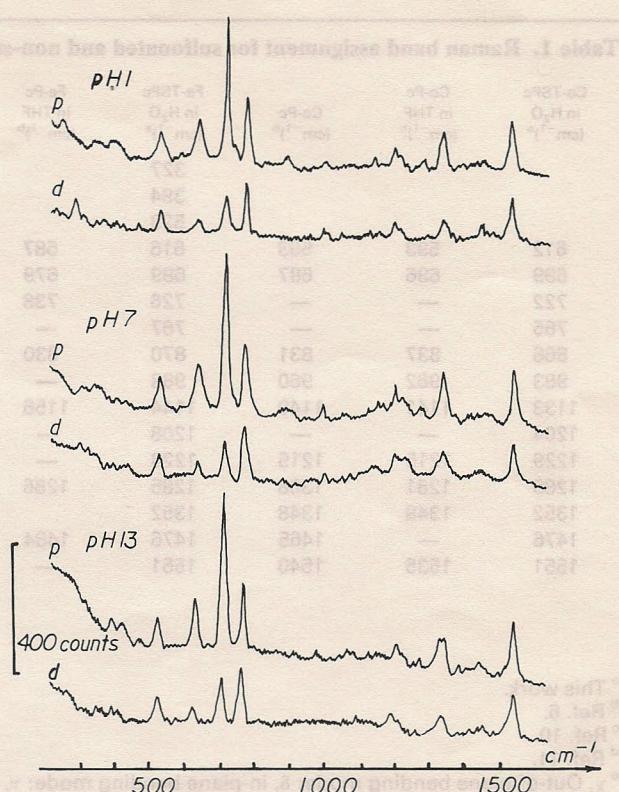


Figure 2. Raman spectra of (p) the polarized and (d) the depolarized light scattered from 5×10^{-5} M of iron tetrasulfonated phthalocyanine in aqueous media. A relative intensity scale is indicated in counts s⁻¹; resolution is 2.5 cm^{-1} and the laser excitation is 632.8 nm with 20 mW output power.

The positions of the Raman bands from Co- and Fe-TSPc in aqueous media together with previously obtained data⁶ are shown in Table 1. The Raman bands did not show a frequency shift as a function of pH with the exception of the Fe-TSPc 1352 cm^{-1} band. The experimental error was $\pm 5 \text{ cm}^{-1}$.

A tentative band assignment of the vibrational modes of the phthalocyanines was made through a comparative analysis and band assignment for the pyrrole and benzene rings. It was assumed that the active resonant chromophore associated with the nitrogen atom in the pyrrole ring would be the most predominant factor in the resonant Raman scattering, and that the corresponding comparison of the vibrational modes could be deduced most adequately on this assumption. The Raman spectrum from freshly distilled liquid pyrrole was recorded (see Fig. 3), analyzed and compared with the values previously reported and was correlated with the phthalocyanines Raman bands as shown in Table 1. Table 1 also contains the band assignments already made in great detail for pyrrole in the liquid state by Lord and Miller¹⁰ and the band assignments for benzene molecules.

The origin of the vibrational modes in the low-frequency range below 500 cm^{-1} is most controversial. Aleksandrov *et al.*⁶ suggest that metal-nitrogen stretching vibrations are responsible for these Raman bands. In a study of metallo-porphyrins by infrared spectroscopy, Boucher and Katz¹² also indicate that the low-frequency bands are metal sensitive. Ogoshi *et al.*¹³ in a similar study suggested that the band at ca 200 cm^{-1}

Table 1. Raman band assignment for sulfonated and non-sulfonated phthalocyanines

Co-TSPc in H ₂ O (cm ⁻¹) ^a	Co-Pc in THF (cm ⁻¹) ^b	Co-Pc (cm ⁻¹) ^b	Fe-TSPc in H ₂ O (cm ⁻¹) ^a	Fe-Pc in THF (cm ⁻¹) ^b	Fe-Pc (cm ⁻¹) ^b	Pyrrole (cm ⁻¹) ^a ^c	Benzene (cm ⁻¹) ^d	Assignment ^e
			327					
			394					
			523					
612	593	593	616	587	596	586	585	XNH
699	686	687	699	679	644	664	646	XR
722	—	—	726	738	—	734	711	δ _R
765	—	—	767	—	780	—	768	
866	837	831	870	830	833	866	866	XCH
983	962	960	983	—	951	—	911	ν ₂
1133	1141	1140	1144	1156	1147	1138	1144	ν _R
1204	—	—	1208	—	1200	—	1178	ν ₁₇
1229	1215	1215	1223	—	—	1237	1237	δ _{CH}
1289	1281	1308	1285	1286	—	—	—	
1352	1348	1348	1352	—	1343	1392	1379	ν _R (N-C)
1476	—	1465	1476	1484	1450	1474	1467	ν _R
1551	1535	1540	1551	—	—	1530	1532	C=C
						3080	3100	ν _{CH}
						3113	3111	ν _{CH}
						3150	3133	ν _{CH}

^a This work.^b Ref. 6.^c Ref. 10.^d Ref. 11.^e X, Out-of-plane bending mode; δ, in-plane bending mode; ν, stretching mode.

is responsible for Zn-N stretching in zinc octaethylporphyrin (ZnOEP). This band shifts toward lower values for NiOEP. In a subsequent report, Ogoshi *et al.*¹⁴ suggested that the bands at 605, 277 and 266 cm⁻¹ are sensitive to the ⁵⁴Fe/⁵⁶Fe isotope which causes a frequency shift of about 3 cm⁻¹. The most probable explanation was given by Kobayashi,¹⁵ who assumes that the origin of the low-frequency bands is metal-dependent isoindole ring deformations. In this case direct metal nitrogen vibrations should be well below 200 cm⁻¹.

Unfortunately, this frequency region was obscured with a strong Rayleigh scattering in the studies of Co- and Fe-TSPc dissolved in aqueous media. An attempt was made to record Raman spectra from H₂-TSPc in aqueous media but an intense fluorescence masked the Raman spectra and a comparative analysis could not

be performed. However, H₂-TSPc adsorbed on a silver electrode produced clearly resolved Raman spectra⁴ and produced the Raman band at 366 cm⁻¹. Hence, the Raman bands at 327 and 394 cm⁻¹ for Fe-TSPc in aqueous solvents most probably originate from isoindole ring deformation.

The region between 500 and 800 cm⁻¹ is dominated by the pyrrole vibrational modes. The intensity of these bands may represent an influence of the metal atom on the vibrational amplitude of the pyrrole modes rather than on their frequency change and band positions.

The strong Raman bands at 699 and ca 760 cm⁻¹ are probably due to out-of-plane deformations of the pyrrole rings. A special feature for Co-TSPc is the strong shoulder at 722 cm⁻¹ and the much broader linewidth of the band at 699 cm⁻¹. Sidorov and Kotlyar⁷ believe that the origin of these bands is due to the deformation of the benzene ring. This appears very unlikely, as shown in Table 1 and previously reported critique.¹⁶

The spectral region between 800 and 1600 cm⁻¹ is characterized by weaker Raman bands which are probably due to C-H vibrational modes, with the exception of the two strong bands at about 1352 and 1550 cm⁻¹ which are due to =C-N- and C=C stretching modes, respectively.¹⁷ These two prominent Raman bands are also observed in pyrrole, porphyrin,¹⁸ ferrocytocrome-c¹⁷ and hemoglobin,¹⁹ but slightly shifted in frequency.

The Raman band at 1352 cm⁻¹ from Fe-TSPc in acidic and neutral solutions shows interesting behavior. This band shows a frequency shift of about 11 cm⁻¹ and appears at 1363 cm⁻¹ when Fe-TSPc is in an alkaline medium (pH 13). In a study of porphyrins by Spiro and Strekas,¹⁷ this kind of frequency shift is assigned to Fe(II) → Fe(III). Spiro and Strekas proposed that the frequency shift of this band may be used to characterize

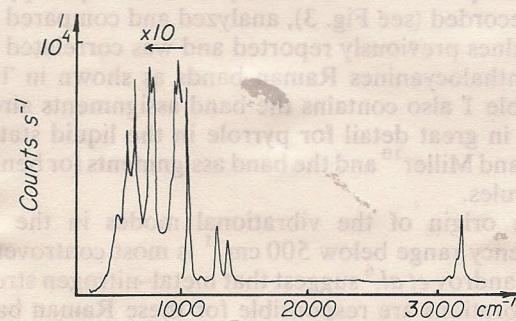


Figure 3. Raman spectrum of the polarized light scattered from pyrrole in the liquid state. Resolution is 2.5 cm⁻¹ and the laser excitation is at 514.5 nm with 100 mW output power. The low-frequency part of the spectrum is magnified 10 times.

oxidation-reduction states of the iron ion; however, it is not sensitive to replacement of iron by other ions.²⁰

It is interesting that the Raman spectrum from pyrrole in the liquid state shows three bands at 3080, 3113 and 3150 cm⁻¹ due to hydrogen vibrations. This was also reported by Lord and Miller.¹⁰ Similar Raman bands were recorded from the solutions of Co- and Fe-TSPc and no significance was given to that spectral region. However, Sharp and Lardon,²¹ in a study of metal-free phthalocyanine by infrared spectroscopy, assumed that these high-wavelength bands are associated with polymorphic forms of H₂-Pc.

The interaction of the solvent molecules with Co- and Fe-TSPc may have profound effects. The odd electron in the d_{z²} orbital¹⁶ interacts easily with the solvent molecules and the six-coordinated complexes of the phthalocyanine molecule may affect the overall molecular behavior. This effect probably accounts for the frequency differences observed in crystalline phthalocyanines, phthalocyanines dissolved in tetrahydrofuran and tetrasulfonated phthalocyanines dissolved in aqueous media.

The Raman spectra of the depolarized light scattered from aqueous solutions of Co- and Fe-TSPc show a normal depolarization ratio $\rho < 3/4$ for all Raman bands except for the band at 523 cm⁻¹ recorded in the Fe-TSPc spectra. This depolarization ratio is close to 0.9 and indicates anomalous depolarization which may be

closely associated with a peculiar iron vibration in and out of the inner ring. A theoretical study by Schaffer *et al.*²² allows for the iron atom to be displaced out-of-plane as much as 0.49 Å, hence forming a domed structure where the iron ion assumes high spin state. The iron ion assumes the low spin state when it is in the plane of the inner ring. This peculiar iron vibration in the iron-octaethylporphyrin complex, according to Spaulding *et al.*,²⁰ produces an anomalous depolarization in the high frequency region around 1568 cm⁻¹. In some iron-octaethylporphyrins the iron ion can be displaced between 0.21 and 0.475 Å.²⁰ Therefore, it is conceivable that the vibration of the iron ion promotes the anomalous depolarization in macrocyclics.

In conclusion, the Raman spectra from metallo-tetrasulfonated phthalocyanines are very similar to these Raman spectra obtained from phthalocyanines in the crystalline form and when dissolved in organic solvents. This suggests that the influence of the sulfonic acid groups on the overall structure of the macrocyclic molecule is minimal. However, a specific metal vibration could not be definitely assigned.

Acknowledgments

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