Polarized Raman Spectroscopy of Metallophthalocyanine Monolayers on Carbon Surfaces

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Metallophthalocyanines (MPc's) have sufficiently large Raman cross sections to obtain high S/N spectra when excited by a 691-nm laser. Both theory and experiment indicate that partial orientation of MPc molecules at solid/gas or solid/liquid interfaces yields depolarization ratios which are quite different from those in solution. For MPc monolayers adsorbed on graphite, the observed depolarization ratios lead to the conclusion that MPc (M = Co, Fe(II), Zn, Mg) molecules are uniaxially oriented upon adsorption with their molecular plane parallel to the graphite basal plane. The results also allow unambiguous assignment of MPc Raman mode symmetry.

I. Introduction

Raman spectroscopy has been used extensively as a probe of molecules adsorbed on surfaces, with particular emphasis on metals which support surface-enhanced Raman spectroscopy (SERS). Although the signals are much weaker than those from SERS, normal (*i.e.*, unenhanced) Raman has also been useful for examining monolayers on surfaces such as Ni, Pt, and Si. For adsorbates which are resonance Raman active, relatively strong surface Raman spectra may be obtained without SERS, even for monolayer coverage. While Raman spectroscopy has some advantages over IR absorption for many cases (e.g., aqueous solutions), IR is generally more sensitive and amenable to a wider range of conditions.

Although there is significant practical and economic driving forces, monolayers on carbon surfaces have not been examined in detail with spectroscopy. There is no evidence for the enhancement required for SERS on carbon, so sensitivity is usually inadequate to observe monolayers. Multilayer and, in a few cases, monolayer films have been observed on carbon surfaces but with limited success compared to studies of adsorption on metals.

The polarization properties of Raman scattered light distinguish the technique from IR absorption. Since the depolarization ratio (ρ) depends on the vibrational symmetry, ρ provides additional structural information about the molecules in question. Depolarization ratios are usually measured for randomly oriented molecules in solution, in which case the theory is straightforward. Raman scattering from crystals, in which the molecular orientation is known relative to the polarization of the light's electric field, is more complex but also more informative. Polarization information has not been used extensively for monolayer adsorbates for two reasons. First, the mechanisms underlying SERS are not yet completely clear, and enhancement effects do not have a firm theoretical basis. Second, since unenhanced surface spectra are generally very weak, ρ is hard to measure with good accuracy. Despite this difficulty, Raman polarization measurements have recently been used to determine the orientation of perfectly ordered monolayers on single-crystal surfaces.[1-3]
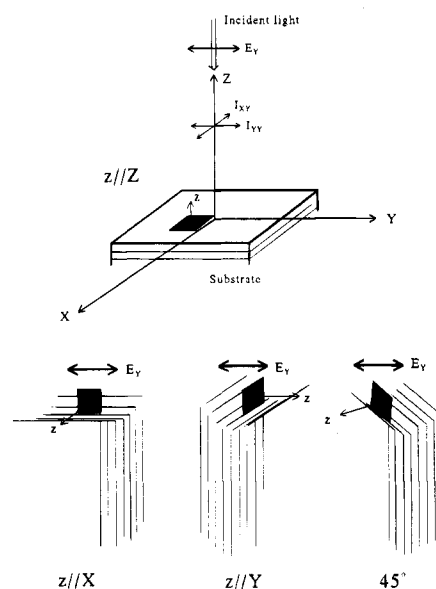

Figure 1. Schematic representation of the perpendicular and parallel components for back-scattering geometry; sample orientations relative to the laboratory fixed coordinate system. Black rectangles indicate MPc molecular plane.

The objective of the present effort is to demonstrate orientation effects on Raman depolarization ratios from a SERS inactive surface, carbon. The resonance Raman active metallophthalocyanines (MPc's), including CoPc, FePc, MgPc, and ZnPc, provide sufficiently strong signals to permit observation of monolayer coverages. By controlling the nature of the carbon surface, the effect of adsorbate orientation on observed ρ is obtained.

II. Experimental Section

CoPc, Fe^{II}Pc, MgPc, and ZnPc were purchased from Aldrich and used without further purification. HOPG was "ZYA" grade and was a gift from Union Carbide. It was cut into ca. 1- × 1- × 0.05-cm pieces. Polycrystalline ("spectroscopic") graphite rods

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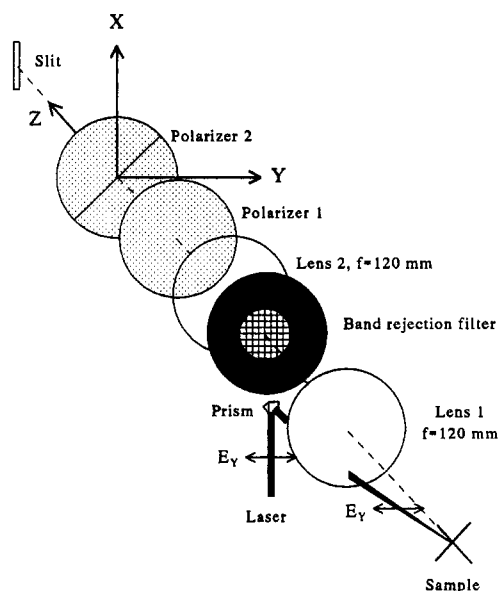
Figure 2. Optics for back-scattered polarization measurement in the laboratory fixed coordinate system $X-Y-Z$. Two-way arrows on the light path indicate the direction of the polarized electric field.

Table 1. Depolarization Ratios (ρ_Z) of CCl_4 and Benzene Liquids

band, cm^{-1}	pred	obsd
CCl_4		
222	0.75	0.741
316	0.75	0.749
459	0.00[a]	0.0087
760	0.75	0.767
790	0.75	0.769
benzene		
602	0.75	0.768
992		0.033
1173	0.75	0.748
1587	0.75	0.748
1608	0.75	0.764

[a] Minimum value presented in the literature is ca. 0.006.

(type U-5) were purchased from Carbone of America, Ultra Carbon Division. Glassy carbon (GC-20) was purchased from Tokai.

The collection geometry and measured intensities are shown in Figure 1. Lower case x,y,z refer to the molecular fixed coordinate system, while upper case X,Y,Z refer to a laboratory fixed coordinated system. A laser beam polarized in the Y direction is brought to the sample along the $-Z$ direction, the scattered light is collected in the Z direction (back-scattering), and the depolarization ratio is defined as

$$\rho_Z = \frac{I_{XY}}{I_{YY}} \qquad (1)$$

The optics for the polarization measurement are illustrated in Figure 2. A tunable Ti:sapphire laser (Coherent Model 890 pumped by an Innova 90) working at 691 nm was used as the laser source. The laser was passed through a 691-nm dielectric band-pass filter (Omega-691DF10-9227), reflected by a small prism, and then focused onto the sample by lens L1 (40-mm diameter, 120-mm focal length (FL)). The scattered light was collected by the same lens and sent through a dielectric band rejection filter (Omega-702 REFLP-9228) to remove the reflection and the Rayleigh scattering component. The light was then focused by a second lens L2 (120-mm FL) onto the entrance slit of a single-stage spectrograph (Instruments SA, HR640). The dispersed light was detected by an 1152 × 298 element CCD cooled to −110 °C. The effective collection aperture was limited by the band rejection filter and was *f*/8. The distance between the small prism and the optical axis was measured to be ca. 1.2 cm, yielding an angle between the incident laser beam and the
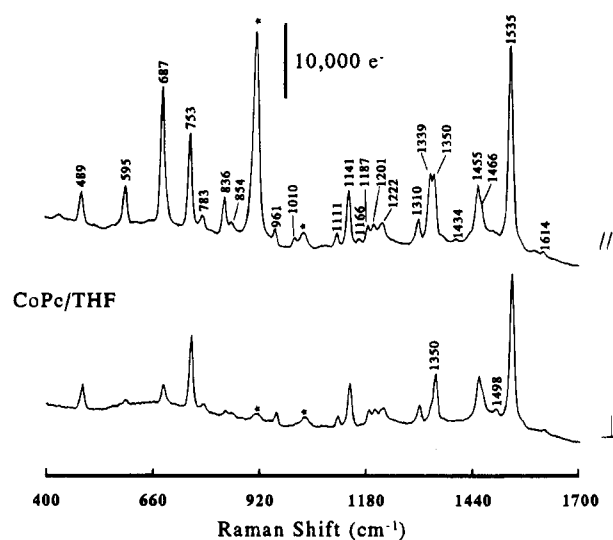

Figure 3. Polarized spectra of CoPc in 0.6 mM THF solution. Integrated 60 s with 20-mW 691-nm excitation. * indicates THF peaks.

optical axis at the sample of ca. 6°. The deviation from 180° collection angle imposes no error in the polarization measurement, since the prism was arranged such that the plane containing the optical axis and the laser path was perpendicular to Y, the direction of the laser polarization.

The laser itself was well polarized as indicated by the depolarization ratio of CCl_4 totally symmetric vibration; thus, no polarizer was used in the laser path. The scattered light was analyzed by polarizer P1, positioned after lens L2. An attempt was made to use a commercial depolarizer preceding the spectrograph, but it induced a small interference pattern in the spectra. The result was a severe oscillation in the observed depolarization ratios. An alternate approach involved a second, fixed polarizer P2 placed before the entrance slit, at 45° to both the X and Y axes. For either || or ⊥ polarization, the resulting spectrograph response function was equal, negating the requirement for a depolarizer. The observation of the expected depolarization ratios for known systems (Table 1) validates the procedure.

CoPc, MgPc, and ZnPc were dissolved in reagent-grade tetrahydrofuran (THF) to form 0.11, 0.26, and 0.21 mM solutions, respectively. Fe^{II}Pc was dissolved in methanol to yield a saturated solution, with its concentration well below 0.07 mM. A graphite rod (Ultracarbon U-5) was cut by knife into 1-mm-thick disks. GC disks (Tokai GC-20) were polished with 180-grit and then 600-grit silicon carbide paper followed by 1.0-, 0.3-, and 0.05-μm alumina on a polishing cloth and then sonicated in nanopure water for at least 5 min after each polishing step. A HOPG basal plane was obtained by cleaving with adhesive tape. HOPG edges were obtained by fracturing a 10-mm × 10-mm × 0.5-mm HOPG piece; the broken piece was then sonicated in water to remove the debris. The above carbon samples were immersed and sonicated in MPc solutions for 5 min, followed by sonication in 3 washes of 5 mL of pure solvent for 3 min each. The carbon samples were then dried and their Raman spectra obtained in air. All spectra were frequency calibrated using naphthalene and acetonitrile as standards, yielding ±2-cm^{-1} accuracy. Although not necessary for the purpose of ρ measurement, all spectra were intensity calibrated using a white light source.[4] Peak position and area were measured by peak fitting.

III. Results and Discussion

Metallophthalocyanines generally exhibit two absorption maxima in the UV−vis wavelength range, both due to ligand $\pi \to \pi^*$ transitions. The B or Soret band occurs at ca. 350 nm, while the Q band and associated vibronic

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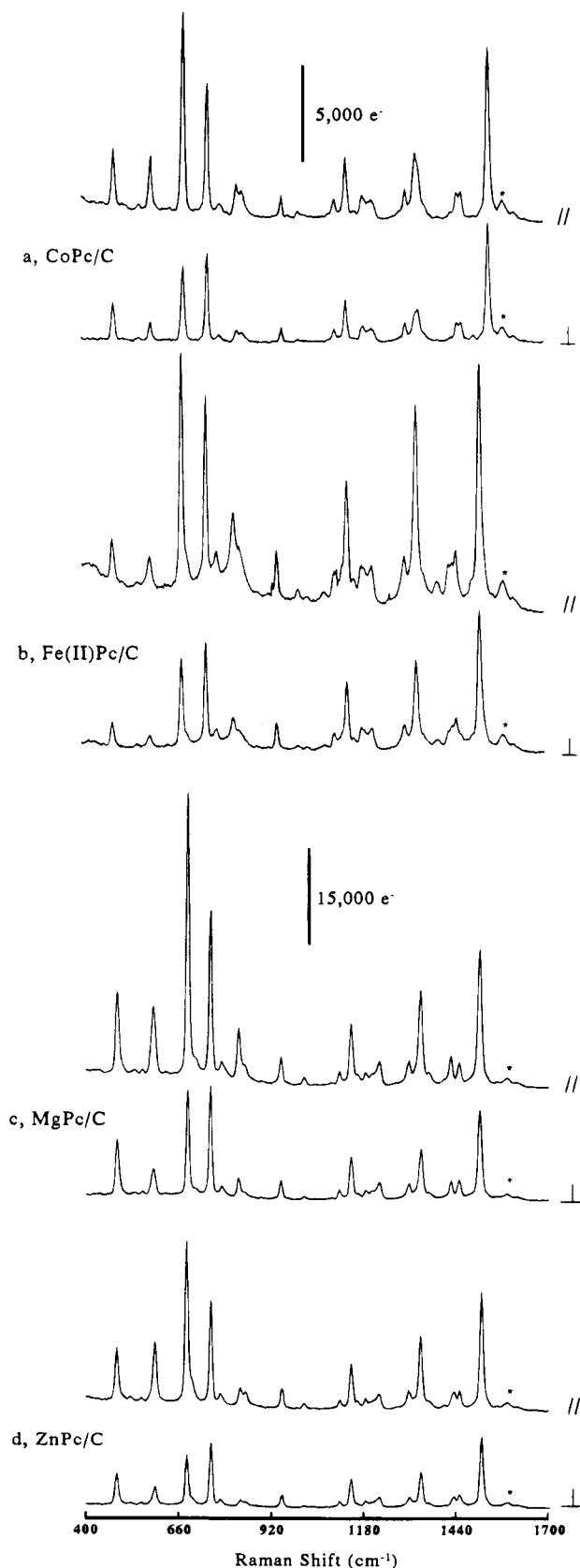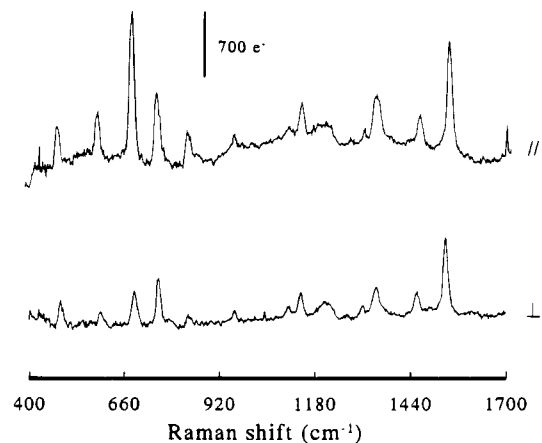
Figure 5. Polarization of Raman bands of CoPc monolayer on GC under water. Spectra of GC under water were subtracted. Integrated 30 min with a 4-mW 691-nm diode laser source.

cence has inhibited direct Raman investigation of most MPc's; thus, most Raman spectroscopy of these compounds involves SERS. For CoPc in THF, the Q-band maximum is at 656 nm, and at 691 nm, CoPc is preresonant with little fluorescence. By comparison to the 992-cm^{-1} band of benzene, the integrated Raman cross section for the 752-cm^{-1} band of CoPc is 7.0×10^{-26} cm^2 molecule^{-1} sr^{-1}, or 7800 times that of benzene. The preresonant Raman spectrum of CoPc in THF is shown in Figure 3. Raman spectra for FePc, MgPc, and ZnPc in solution were not observable due to sample fluorescence. In contrast, high S/N Raman spectra were obtained for monolayers of all MPc's adsorbed on the carbon materials studied here. Fluorescence quenching by graphitic carbon has been demonstrated previously.[9]

The depolarization ratio (ρ_Z) is well-known for different Raman active vibrations in the case of random molecular orientation.[10] Snyder considered two types of partial molecular orientation and their effects on depolarization ratios.[11] In the first type, the molecular z axis is parallel to a laboratory fixed axis ($z||Z$, $z||Y$, and $z||X$ in Figure 1), with all of the z axes parallel, and is said to be "uniaxially oriented". In the second type, z is perpendicular to a laboratory fixed axis ($z\perp Z$, $z\perp Y$, and $z\perp X$), and the molecules do not have parallel z axes. For $\mathscr{G}$-type molecules, defined as belonging to point groups C_n, C_{nv}, C_{nh}, D_n, D_{nh}, D_{nd}, S_{2n}, $C_{\infty v}$, or $D_{\infty h}$, with $n > 2$, excluding the possibility that the derived polarizability tensor can be asymmetric, we classify the vibrational modes into the following types: (a) totally symmetric modes, including a_1, modes that induce $\alpha_{xx} + \alpha_{yy}$ components, and a_2, modes that induce α_{zz} components; (b) nontotally symmetric modes that do not induce α_{xz} or α_{yz}; (c) modes that induce α_{xz} and/or α_{yz}. A reconstruction and simplification of Snyder's Tables IV–VI yields the predicted depolarization ratios for these vibrational modes for the two types of partial orientation, which are listed in Table 2. These are to be compared with the experimental results.

Figure 4 shows the polarized Raman spectra of MPc adsorbates on polycrystalline graphite rods. Figure 5 shows the spectra of a CoPc monolayer on GC immersed

Figure 4. Polarized Raman spectra of CoPc, Fe^{II}Pc, MgPc, and ZnPc monolayers on polycrystalline graphite surfaces. Integrated 10 min with 20-mW 691-nm excitation. * indicates graphite E_{2g} mode.

broadening occur in the 600–800-nm range.[5–8] Fluores-

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Table 2. Theoretical Depolarization Ratios, ρ_Z, of Different Types of Vibrations for Six Different Partial Orientations of $\mathscr{G}$-Type Molecules, Including Metallophthalocyanines of the D_{4h} Group and a Randomly Oriented System[a,b]

	$z\|\|Y$				$z\|\|Z$				$z\|\|X$				$z\perp Y$				$z\perp Z$			$z\perp X$			random	
	a_1	a_2	b	c	a_1	a_2	b	c	a_1	a_2	b	c	a_1	a_2	b	c	a	b	c	a	b	c	a	b, c
ρ_Z	×	0	×	∞	0	×	1	×	0	×	0	∞	0	×	½	∞	⅓	⅓	1	0	4/3	1	<3/4	3/4

[a] "×" indicates an indeterminate ratio of two negligible intensities. [b] Based on refs 10 and 11.

Table 3. Observed Depolarization Ratios and Induced Polarizability Tensor Components of CoPc Raman Bands with 691-nm Excitation

band, cm^{-1}	THF soln	on polycrys graphite	on GC	HOPG $z\|\|Z$	HOPG $z\|\|X$	HOPG 45°	symm[a]
489	0.69	0.60	0.65	0.87	0.09	1.1	b
595	0.21	0.37	0.34	0.11	0.05	0.96	a_1
687	0.16	0.37	0.24	0.06	0.02	0.96	a_1
753	0.69	0.66	0.62	0.85	0.09	0.99	b
836	0.14	0.44	0.3	0.0	0.0	0.96	a_1
854	0.29	0.44		0.0	0.0	0.96	a_1
961	0.80	0.60		1.0	0.08	0.93	b
1010	<0.3	0.36		0.0	0.0	0.96	a_1
1111	0.73	0.63	0.78	1.04	0.11	0.92	b
1141	0.73	0.66	0.73	0.92	0.12	0.96	b
1166	0	0.5		0		0.96	a_1
1187	0.84	0.64		0.95	0.10	0.92	b
1201	0.76	0.64		1.0	0.2	0.93	b
1222	0.76	0.64		1.0	0.2	0.93	b
1310	0.71	0.63		0.96	0.16	0.96	b
1339	0.22	0.46		0.1	0.01	0.96	a_1
1350	0.62	0.49		0.9	0.21	0.96	b
1371		0.73			0.12	0.96	b
1402	<0.5						a_1
1434							
1455	0.76	0.67	0.68	0.88	0.11	0.96	b
1466	0.79	0.71		0.96	0.15	0.96	b
1498	>3	>3		>6			d
1535	0.70	0.65	0.67	0.92	0.09	0.96	b
1586[b]		0.72		1.03	0.07	0.96	b
1614	0.8	0.8		0.0		1	b

[a] Symmetry: a_1 corresponds to $\alpha_{xx} + \alpha_{yy}$, b to $\alpha_{xx} - \alpha_{yy}$ or $\alpha_{xy} + \alpha_{yx}$, and d to $\alpha_{xy} - \alpha_{yx}$, where $\alpha_{xy} = \alpha_{yx}$. [b] Graphite E_{2g} mode.

Table 4. Correlation of Observed Raman Bands of CoPc in THF and CoPc, Fe^{II}Pc, MgPc, and ZnPc on Carbon with 691-nm Excitation

CoPc/THF	CoPc/C	FePc/C	MgPc/C	ZnPc/C	symm
489, m[a]	491, m	488, m	488, m	487, m	b
	520, vw		536, vw	524, vw	
	563, vw	557, vw	558, vw	555, vw	
595, m	596, m	592, m	588, m	593, m	a_1
687, s	688, s	682, s	685, s	682, s	a_1
753, s	755, s	751, s	749, s	750, s	b
783, w	790, 2	780, w	782, w	778, w	b
836, m	838, m	828, m	828, m	832, w	a_1
854, w	854, w	849, w	844, w	848, w	a_1
961, m	963, m	950, m	947, m	949, m	b
1010, w	1011, w	1010, w	1012, w	1012, w	a_1
1111, w	1111, w	1110, w	1112, w	1112, w	b
1141, m	1144, m	1146, s	1145, m	1145, m	b
1166, vw	1168, vw	1166, vw	1164, vw	1163, vw	a_1
1187, w	1190, w	1186, w	1186, w	1185, w	b
1201, w	1200, w	1200, w	1209, w	1207, w	b
1222, w	1218, w	1216, w	1225, vw	1223, w	b
1310, w	1312, w	1307, w	1307, w	1307, w	b
1339, m	1338, m	1336, s	1337, m	1338, m	a_1
1350, m	1348, m	1341, s	1342, m	1341, m	b
1371, vw,	1364, vw	1362, vw	1366, vw	1365, vw	b
1402, vw	1404, vw	1401, m	1409, vw	1407, vw	a_1
1434, vw	1438, vw	1430, m		1428, w	
1455, m	1456, m	1441, m	1426, m	1435, m	b
1466, m	1468, m	1453, m	1450, m	1450, m	b + d
1498, vw	1502, vw				d
1535, s	1545, s	1519, s	1508, s	1512, s	b
1614, vw	1618, vw	1617, vw	1612, vw	1615, vw	b

[a] s, strong; m, medium; w, weak; vw, very weak.

in water, where the spectra of pure GC substrate in water was subtracted. As noted in Table 3, the observed ρ_Z values for CoPc in solution and adsorbed on GC are similar, implying nearly random orientation of the adsorbed CoPc relative to the laser beam. Since polished GC is microscopically rough, this behavior is not surprising. ρ_Z values for CoPc on polycrystalline graphite are similar to those on GC, again because of random CoPc orientation. In contrast, MPc adsorbed on the HOPG basal plane exhibits ρ_Z values of either 0 or 1 (with the exception of the 1498-cm^{-1} band), as shown in Figure 6 and Table 3. Inspection of Table 2 indicates that such behavior is consistent with a uniaxially oriented system with $z\|\|Z$ and that all but the 1498-cm^{-1} band are either a_1 ($\rho_Z \approx 0$) or b ($\rho_Z \approx 1$) type vibrations. The doubly degenerate graphite E_{2g} mode at 1586 cm^{-1} behaves as expected ($\rho_Z = 1$) for a b-type vibration with $z\|\|Z$. We conclude, therefore, that all the MPc's studied here are adsorbed on the atomically flat HOPG basal plane with their z molecular axis parallel to the surface normal but their x, y axes freely distributed within the surface plane.

As indicated schematically in Figure 1, the $z\|\|X$ and $z\|\|Y$ orientations may be examined by rotating the HOPG specimen. Parts a and b of Figure 7 show the results for the CoPc monolayer oriented as $z\|\|X$ and $z\|\|Y$, respectively. Although the HOPG edge was macroscopically rough, it appeared to retain its crystallite orientation, as indicated by the negligible ρ_Z value of the graphite E_{2g} band when $z\|\|X$ (theoretically, $\rho_Z = 0$) and the negligible intensities of both components when $z\|\|Y$. When $z\|\|X$, all Raman bands become totally polarized, with typical ρ_Z near 0.1.

When $z\|\|Y$, however, both parallel and perpendicular components are nearly extinguished. These results are in excellent agreement with the theoretical values in Table 1. No a_2- or c-type vibrations are observed.

It is useful to consider an orientation in which the z axis is at 45° with respect to both X and Y, as shown in Figure 1. For this orientation, it can be shown that the parallel and perpendicular components for a- and b-type vibrations have equal intensities and $\rho_Z = 1$. Note that for CoPc in the 45° orientation (Figure 7c), both $\|\|$ and $\perp$ spectra have intensities equal to $^1/_4$ of the $z\|\|X$ parallel component (Figure 7a), and $\rho_Z \approx 1$ for all modes. All four MPc's behave similarly. Also note that the anomalously polarized band of CoPc/THF at 1498 cm^{-1} becomes inversely polarized on the HOPG basal plane. This behavior is predicted only for vibrations of the $\alpha_{xy} - \alpha_{yx}$ type, which is assigned as d type in Tables 3 and 4.

Several authors have assigned the Raman bands for MPc systems.[5,12-18] Because of strong fluorescence in-

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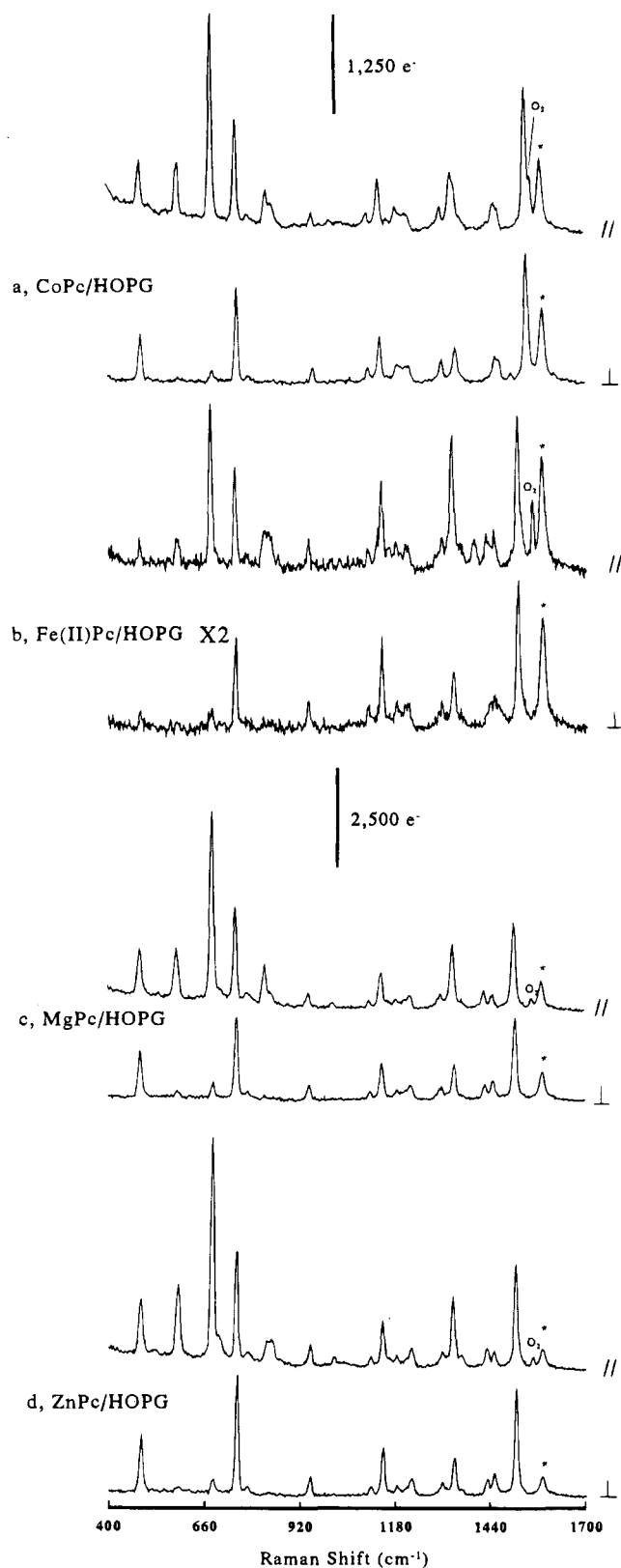(18) Masheder, D.; Williams, K. P. J. *J. Raman Spectrosc.* **1987**, *18*, 391.

Figure 6. Polarized Raman spectra of CoPc, Fe^IIPc, MgPc, and ZnPc monolayers on the HOPG basal plane. The basal plane normal was parallel to Z, the optical axis, as shown in Figure 1. CoPc and Fe^IIPc were integrated 20 min; MgPc and ZnPc were integrated 10 min. Laser power was 15 mW. * indicates graphite E_{2g} mode. O_2 is atmospheric oxygen.

terference, these investigations involved either MPc derivatives or SERS. The current observations permit unambiguous determination of the polarizability tensor components induced by each Raman vibrational mode.
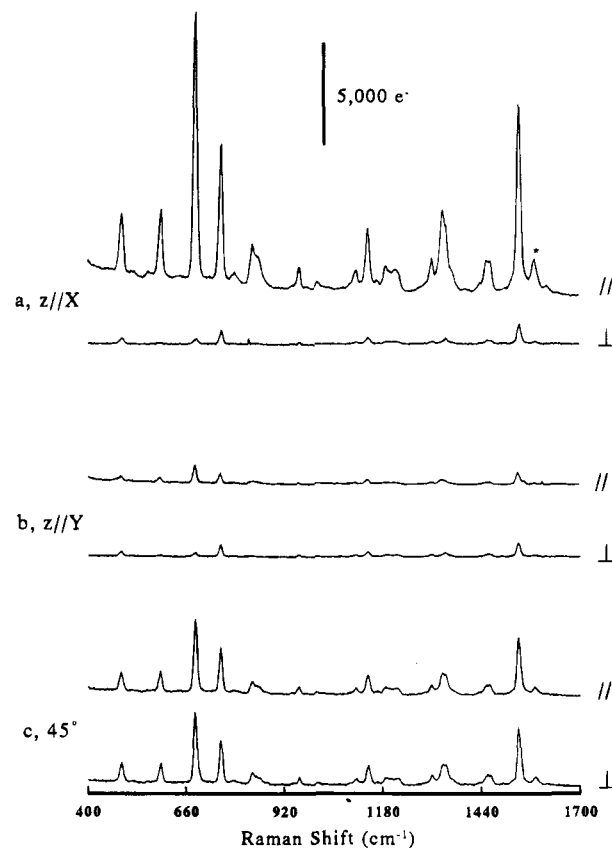

Figure 7. Polarized Raman spectra of CoPc monolayer on the HOPG edge. a, $z||X$; b, $z||Y$; and c, z is 45° between X and Y. Orientations of incident field and HOPG correspond to those shown in Figure 1.

Assuming the CoPc retains its D_{4h} symmetry upon adsorption to HOPG, modes with $\rho_Z \approx 0$ in Figure 6a correspond to $\alpha_{xx} + \alpha_{yy}$ and include the bands at 595, 687, 836, 854, 1010, 1339, and 1402 cm^{-1}. Ignoring vibrational mixing at resonance,[19] these should all be A_{1g} modes. All other Raman bands listed in Table 3 except 1498 cm^{-1} correspond to $\alpha_{xx} - \alpha_{yy}$ or $\alpha_{xy} + \alpha_{yx}$ modes and have B_{1g} or B_{2g} symmetry. Mode frequencies and symmetries are listed for all four MPc's in Table 4.

Assuming the cross section is the same for solution and adsorbed CoPc, an approximate surface coverage may be calculated by comparing solution and surface-integrated intensities. Based on the 755-cm^{-1} band in Figures 5 and 6a, the CoPc coverages on GC and HOPG are about 9.2 × 10^{13} and 7.7 × 10^{13} molecules/cm^2, respectively. Although this coverage should be considered approximate, it does indicate coverage of approximately a monolayer, which is 5.0 × 10^{13} molecules/cm^2, assuming a CoPc molecule has an area of 200 Å^2.[20,21] Similar coverages was determined voltammetrically.[20]

In summary, we have found that four metallophthalocyanines, namely, CoPc, Fe^IIPc, MgPc, and ZnPc, are adsorbed on HOPG and form stable monolayers, with their molecular plane parallel to the HOPG basal plane. All of the Raman bands observed with 691-nm excitation were unambiguously classified according to their contribution to the derived polarizability tensor.

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