# Vibrational Studies of Molecular Organization in Evaporated Phthalocyanine Thin Solid Films

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The molecular organization in evaporated submicron thin solid films of five phthalocyanine complexes and the metal-free phthalocyanine was studied using the propensity rules and the intensity theory of molecular vibrations in the electric dipole approximation. The spatial anisotropy was probed using transmission FTIR spectroscopy of films formed onto a KBr surface, and reflection absorption FTIR spectroscopy (RAIRS) of the films fabricated onto smooth silver and aluminum surfaces. The effect of the substrate and of the film thickness on molecular organization in the thin films is discussed. The vibrational IR and Raman (spontaneous, resonance Raman, and surface-enhanced resonance Raman SERRS) spectra of the fluorogallium phthalocyanine complex are also reported here for the first time.

## Introduction

Thin films of organic materials are being widely investigated for potential applications in numerous advanced technologies. Phthalocyanines (Pc) have received much attention due to their chemical and physical properties, and Pc derivatives are presently widely used and are expected to be significant in the development of thin film devices.[1-7] The properties of thin films are often dependent on the deposition conditions.[8] A great deal of effort has been directed to correlate the molecular orientation in films with specific fabrication conditions such as substrate material, substrate temperature, deposition rate etc. Evaporated films of CuPc have been recently studied by Dowdy *et al.*[10] They studied CuPc films (5–200 nm) on air-oxidized alumina and showed that the molecules in thinner films (5–100 nm) are preferentially oriented with the unique molecular axis ($C_4$) almost parallel to the substrate plane (edge-on orientation), while the thicker films (200 nm) consist of crystallites oriented with the molecular axis pointing away from the surface (face-on orientation). In an early study, Debe[11] illustrated that changing the substrate temperature during deposition of $H_2$Pc films (45–120 nm) on air-oxidized aluminum films leads to drastic differences in the relative intensities observed in the middle-IR spectrum. In addition to Debe's IR work[11-13] to determine molecular orientation, there were also similar attempts using Raman intensities.[14-16] Vincett[17] has discussed the singularities in the optical spectra of $H_2$Pc evaporated films formed on glass substrates under different evaporation conditions.

The present report focuses on the application of transmission and reflection absorption FTIR spectroscopy (RAIRS) to the study of the molecular organization in thin solid films of Pc materials formed by vacuum evaporation onto KBr and smooth surfaces of silver and aluminum. Using vibrational spectroscopy as a probe for molecular organization in thin solid films requires (i) a reliable assignment of characteristic normal modes with a well-defined direction of their transition dipole moment, (ii) measurement of the relative intensity of vibrational band in the transmission and reflection geometry, and (iii) for reference and comparison the transmission spectrum of solid matrices (KBr pellet or similar) where a random distribution of the material can be assumed. The latter spectrum represent the relative intensity given by spatial average of the allowed components of the transition dipole moment of each symmetry type. The study includes vacuum evaporated ultrathin films of previously studied CuPc and $H_2$Pc (for comparison with Dowdy's and Debe's work) and a group of $C_{4v}$ molecules TiOPc, VOPc, InClPc, and GaFPc (the vibrational spectra of GaFPc is given here for the first time). The data obtained show that film quality and molecular orientation may also be dependent upon the molecular point group symmetry and the ligand coordinating to the central dication.

The study also provides a testing ground to explain the operative selection rules or propensity rules for reflection absorption spectroscopy of vapor-deposited thin films on a smooth metal substrate in terms of film thickness and substrate material.

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## Experimental Section

CuPc and $H_2$Pc were purchased from Eastman Kodak Co. and purified by sublimation. The other Pc derivatives (VOPc, InClPc, TiOPc, and GaFPc) were kindly provided by Ms. C. Jennings from the Xerox Research Centre of Canada. Thin films of phthalocyanine complexes and smooth metal surfaces were vapor deposited in a high-vacuum chamber; the pressure before evaporation was $2 \times 10^{-6}$ mBar. Pc materials were resistively heated in a tantalum boat and deposited onto various substrates kept at room temperature (293 K), and the deposition rate was 0.35 ($\mp$0.05) nm/s, except for CuPc where the deposition rate was between 0.4 ($\mp$0.1) nm/s. Films for RAIRS were made by evaporating Pc derivatives onto glass substrates previously coated with a 100 nm smooth film of Ag or Al. Smooth metal films were grown at a rate of 0.5 nm/s onto the glass substrates maintained at ca. 473 K. An Inficon XTC crystal oscillator was used to monitor the rate and final mass thickness of the evaporated films. Aluminum-coated substrate was removed from the system when it was at 100 °C and was exposed to atmosphere for 4 h to obtain the air-oxidized aluminum substrate.

IR spectra were recorded using a BOMEM DA3 FTIR spectrometer equipped with mid- and far-IR accessories. A KBr beam splitter and liquid nitrogen cooled MCT detector were used to record mid-IR spectra. RAIR spectra were obtained with a SpectraTech Inc. specular reflectance accessory set to give an incident angle of 80°. A 6 $\mu$m stretched Mylar pellicle beamsplitter and DTGS detector were used to record far-IR spectra of samples dispersed in Nujol and pressed between polyethylene plates. Resonance and surface enhanced resonance Raman spectra (RRS and SERRS) were recorded with a Spex 1403 double monochromator using the 647.1 nm laser line from the Spectra-Physics 2020 $Kr^+$ laser. Spontaneous Raman (SR) scattering was produced with the 514.5 nm line of a Lexel (Model 95) $Ar^+$ laser and recorded on a Jobin Yvon ISA THR3000 spectrograph equipped with a charged-coupled detector (CCD). For data analysis, IR and Raman spectral files were imported to Spectra Calc software available from Galactica Ind. Corp.

## Results and Discussion

**Surface Selection Rules.** The theory on which the experimental reflection infrared and Raman techniques are based is well-known and was mainly developed by Greenler.[18,19] Greenler pointed out the advantage of using light at a high angle of incidence to probe molecules adsorbed onto metal surfaces. For metal surfaces, optimum excitation (maximum absorption in the IR) is obtained with P-polarized light (electric vector parallel to the plane of incidence) incident at ca. 80°. The rationalization of observed vibrational intensities for molecules near reflecting surfaces has been termed "propensity rules".[20,21] Assume, for example, that the $x,y$ plane lies on the metal surface and that $z$ is the perpendicular to the surface. In RAIRS experiments only the $E_z$ (P-polarization) component of the incident light can interact with the organic film, and the surface selection rule leads, exclusively, to the manifestation of molecular vibrations with a finite component of their dynamic dipole perpendicular to the metal surface. The propensity rules apply to monolayers as well as to thin solid films deposited onto highly reflecting metal surfaces and it has become a powerful tool for molecular orientation studies. Recently, the molecular orientation in Langmuir–Blodgett films has been determined quantitatively from the combined infrared spectral data obtained in a transmission geometry and in a reflection absorption geometry. This approach has been demonstrated by Umemura *et al.*,[22] and it has been tested by several groups on Langmuir–Blodgett films.[23,24] The number of applications in reflection Raman spectroscopy[19] are scarce, and the rules have been mainly used in surface-enhanced Raman scattering.

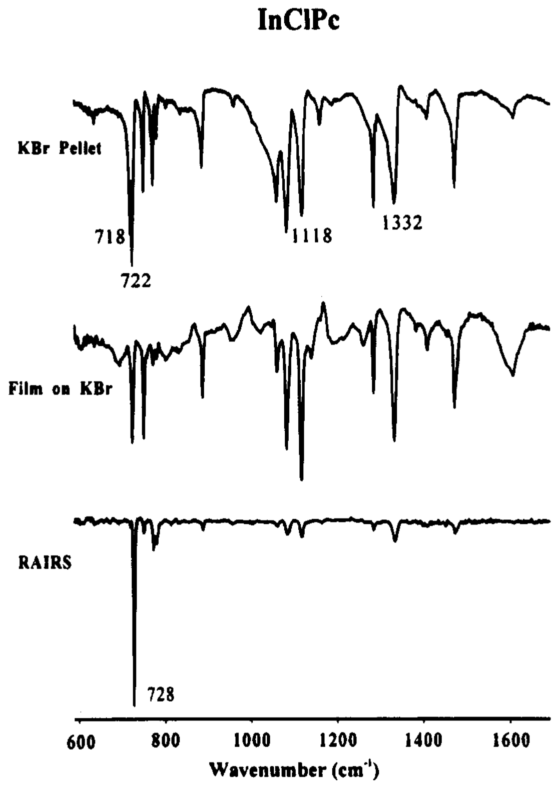

**Figure 1.** FTIR spectra of InClPc. Random orientation reference spectrum on KBr, transmission spectrum of a 25 nm film on KBr and RAIRS of 25 nm film on smooth silver.

In summary, the propensity rules in RAIRS can be used to determine the average molecular orientation provided that the assignment and symmetry of at least one of the normal modes is well established. Similarly, the molecular orientation can be probed in thin solid films formed onto flat IR-transparent surfaces in the transmission geometry. Light at normal incidence, with the electric vector parallel to the surface, will interact with vibrations which generates a change in the dipole moment along the $x$ or $y$ axes ($\mu_x \cdot E$ or $\mu_y \cdot E$), allowing us to predict average orientation if the direction of a well-assigned transition dipole moment is known in the molecular frame of reference. The reference for both the RAIRS and the transmission IR analyses is a random distribution of molecules in the sample, where the relative intensities can be considered to be the result of the spatial average of transition dipole moments interacting with the external electric field. The common dispersion of the materials in IR transparent matrices (KBr, NaCl, CsI, etc.) could be taken as such a reference point. The reference spectrum of InClPc in a KBr pellet, the transmission spectrum of a 25 nm thick film on KBr and the RAIR spectrum of a 25 nm thick film on silver, are given in Figure 1. The observed changes in relative intensity (frequencies remain unchanged) are due to molecular orientation in the thin solid film.

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**Table 1. Characteristic IR Frequencies ($cm^{-1}$) Used for Orientational Studies of Evaporated Pc Films**

| | CuPc | $H_2$Pc | VOPc | TiOPc | InClPc | GaFPc |
|---|---|---|---|---|---|---|
| C−H wagging ($z$) | 729 | 736 | 734 | 732 | 728 | 733 |
| C−H bending ($x,y$) | 1120 | 1119 | 1120 | 1119 | 1118 | 1120 |
| pyrrole stretch ($x,y$) | 1334 | 1333 | 1335 | 1333 | 1332 | 1334 |

**Characteristic Vibrational Frequencies and Molecular Orientation.** The first step for molecular organization studies is the reliable assignment of the characteristic frequencies to be used in the determination of molecular orientation. Totally symmetric vibrations of $D_{4h}$ and $C_{4v}$ Pc molecules including CuPc have been assigned.[25] For CuPc $D_{4h}$ ($3N - 6 = 165$), the infrared active vibrations are 8 $a_{2u}$ ($z$) and 28 $e_u$ ($x,y$). The direction of the transition dipole moment is given in parentheses ($z$ is along the $C_4$ symmetry axis). A strong characteristic $a_{2u}$ frequency is observed at 729 $cm^{-1}$, which is due to the out-of-plane C−H vibration with a transition dipole moment along the $C_4$ symmetry axis. Similar frequencies are observed in all the studied molecules as can be seen in Table 1. According to correlation for descent in symmetry the $a_{2u}$ modes become part of the $a_1$ modes of the $C_{4v}$ molecules, which have a nonzero $\mu_z$ component of the transition moment. Two characteristic $e_u$ or e modes, which have nonzero component of the transition dipole moment in the molecular plane are also included in Table 1.

The e modes given in Table 1 pertain to in-plane stretching vibrations of C=C or C=N bonds in the pyrrole ring and in-plane bending vibrations of the C−H groups. It can be seen that for a molecular orientation with the molecular plane lying flat on the $x,y$ metal surface (face-on orientation), a strong C−H wag in the RAIR spectrum is expected as seen in Figure 1 for InClPc, and the in-plane modes should be weak. The same trend was observed for GaFPc as can be seen in Figure 2. The opposite (weak wag and strong in-plane) should hold for the transmission spectra of a face-on orientation of InClPc and GaFPc films on the KBr surface. In fact, the wag is very weak in the transmission spectrum of InClPc and weak in the case of GaFPc, as shown in Figure 3.

Transmission electron microscopy (Hitachi 600 Electron microscope operating at 100 kV) was used to obtain the micrographs of the 25 nm thick vapor-deposited films. The TEM data showed that GaFPc formed needles, and consequently, the surface coverage was not continuous. The TEM micrograph of InClPc also revealed a discontinuous island film for the 25 nm thickness. However, the InClPc islands give a better surface coverage than the GaFPc needles. The CuPc island film presented a surface coverage similar to InClPc. The TiOPc island film structure seems to contain microcrystals producing a lower surface coverage.

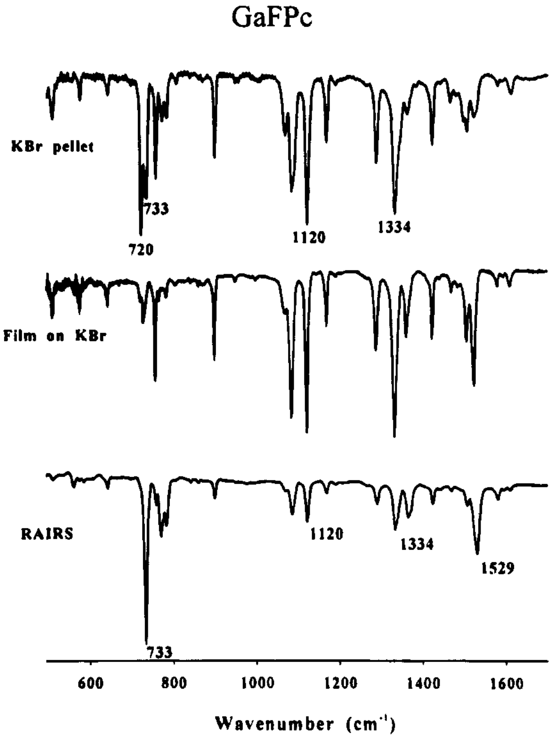

**Figure 2.** FTIR spectra of GaFPc. Random orientation reference spectrum on Kbr, transmission spectrum of a 25 nm film on Kbr and RAIRS of 25 nm film on smooth silver.

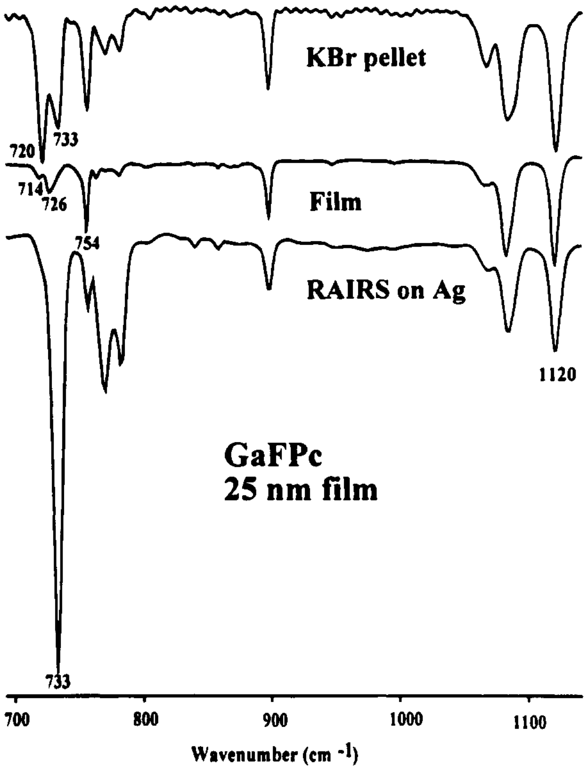

**Figure 3.** Relative intensity pattern observed in the FTIR spectra of GaFPc in the region of the C-H wagging vibration (733 $cm^{-1}$).

Examination of C−H out of plane and in-plane vibrational intensity in the spectra of TiOPc and VOPc (Figures 4 and 5) showed that the differences between the transmission and the RAIR spectra were not as pronounced as those observed in GaFPc and InClPc. The relative intensities of the spectra shown in Figures 4 and 5 exclude both a predominant face-on or edge-on organization. It can be concluded that the average orientation on the plane of the film is that of a molecular plane tilted with respect to the substrate. In a similar study performed with diphthalocyanine complexes, a

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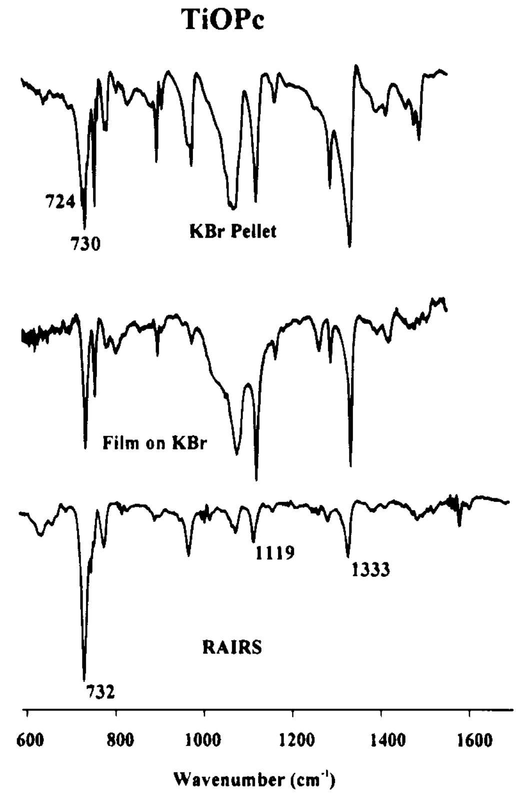

**Figure 4.** FTIR spectra of TiOPc. Random orientation reference spectrum on KBr, transmission spectrum of a 25 nm film on KBr and RAIRS of 25 nm film on smooth silver.

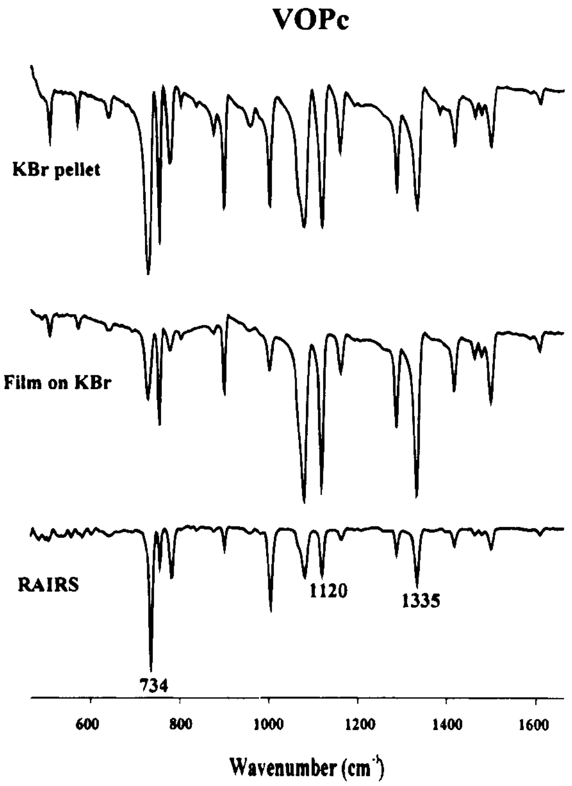

**Figure 5.** FTIR spectra of VOPc. Random reference spectrum on KBr, transmission spectrum of a 25 nm film on KBr and RAIRS of 25 nm film on silver.

tendency to a predominant edge-on orientation was observed for vapor deposited films.[26] Therefore, there are strong similarities in the structure and alignment of TiOPc and VOPc films formed under comparable conditions, in contrast with the properties of InClPc and GaFPc films. It may be speculated that oxygen coordination may contribute to a film morphology that can be associated with a tilted molecular orientation in the film.

**CuPc and $H_2Pc$ Films.** The question of change in the infrared relative intensities of CuPc as a function of the film thickness has been an outstanding problem. Dowdy *et al.*[10] have found a tilted molecular orientation for the first layers of CuPc films (5–20 nm) on air-oxidized Al surface, while a face-on organization prevails for thicker films (200 nm mass thickness). Our experiments with 25 nm CuPc film on 100 nm silver surface and on 100 nm Al gave transmission and RAIR spectra in agreement with those obtained by Dowdy *et al.* for the 200 nm films. The spectra of CuPc films (25 nm) on Ag and Al showed no considerable differences, an indication of substrate independence in the thin solid film morphology of the two samples. Further experiments with 50, 100, and 200 nm mass thickness films of CuPc on KBr and Ag produced equivalent infrared spectra. It can be concluded that a predominant face-on average orientation for CuPc films prevails for mass thickness ranging from 25 to 200 nm.

Evaporated films of $H_2Pc$ of 25 nm mass thickness were deposited onto KBr and Ag surfaces. The spectra of the $H_2Pc$ sample confirm the α-form in the film. The assignment of the N–H and C–H out-of-plane modes has been controversial. Shurvell and Pinzuti[25] assigned the N–H mode at 716 cm$^{-1}$ and the C–H wag at 736 cm$^{-1}$. Sammes[27] assigned the 735 cm$^{-1}$ band to the N–H out-of-plane vibration. In our spectra, we observed three bands in this spectral region at 716, 731, and 736 cm$^{-1}$. Examining the spectra in the sequence pellet, film on KBr, and film on Ag (RAIRS), the relative intensity of the 731 cm$^{-1}$ band follows the trend of the in-plane molecular vibrations of the macrocycle. However, the intensity of the 716 and the 736 cm$^{-1}$ bands is the opposite of the intensity trend observed for the in-plane modes: their relative intensity increases in the RAIR spectrum, while the relative intensity of the in-plane mode decreases. Therefore, both of these frequencies should be assigned to the out-of-plane vibrations, and we propose assigning the 736 cm$^{-1}$ band to the C–H wagging vibration, in agreement with what is observed for the metalated Pc molecules. At the same time, the relative intensity pattern in the transmission (strong in-plane, weak out-of-plane) and RAIRS (strong out-of-plane, weak in-plane modes), clearly indicate that the $H_2Pc$ film has an average molecular organization with the macrocycle close to a face-on orientation.

**Fundamental Vibrational Frequencies of GaFPc.** Since the detailed spectroscopic vibrational data for GaFPc are not available in the literature, the Raman, the resonance Raman and surface-enhanced resonance Raman spectra of GaFPc are presented in Figure 6. The total irreducible representation for a $C_{4v}$ molecule of GaFPc ($3N - 6 = 168$) is $\Gamma = \underline{23a_1(z)} + 19a_2 + 21b_1 + 21b_2 + \underline{42e(x,y)}$. Underlined irreducible representations are infrared-active vibrations. The 19 $a_2$ vibrations are the only Raman-silent modes. The

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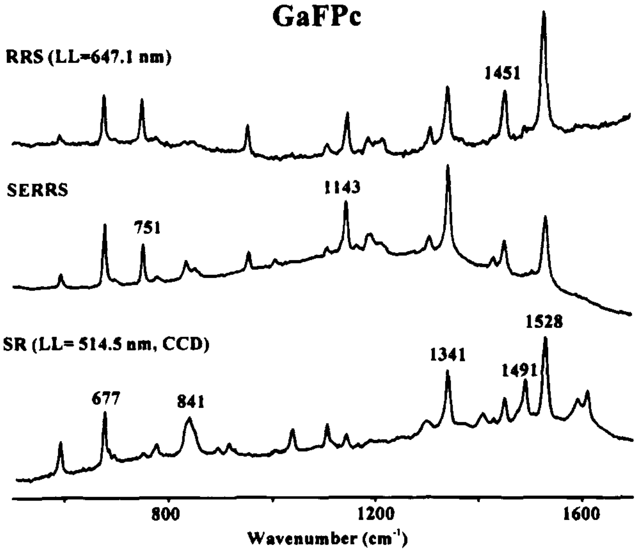

**Figure 6.** Spontaneous Raman (SR), resonance Raman (RRS), and surface-enhanced resonance Raman (SERRS on a gold island film) spectra of GaFPc.

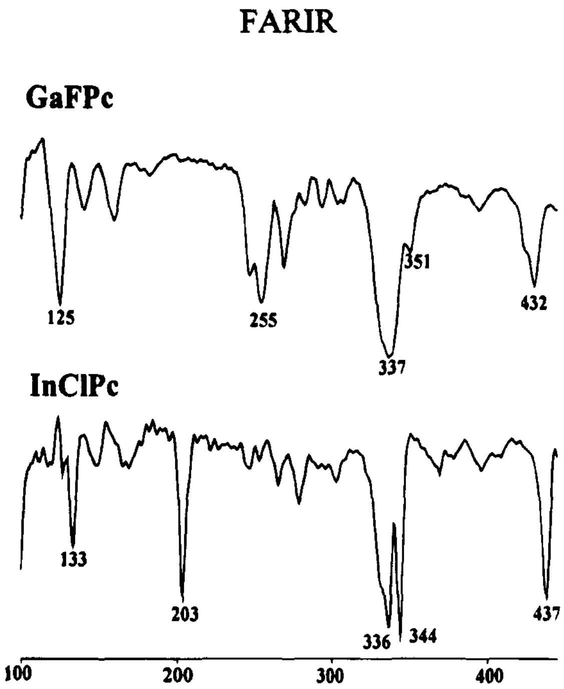

**Figure 7.** Far infrared spectra of GaFPc and InClPc.

assignment of characteristic vibrations for similar Pc molecules has been reported.[28,29] Although the $a_1$ and e are both IR and Raman active, there were few Raman bands with an IR counterpart. Therefore, the observed frequencies are separately listed in Tables 2 and 3. It seems reasonable to assume that fundamental vibrations observed in both IR and Raman should be assigned to the e type. The number corresponding to the vibration in the parent benzene molecule[30] has been added for completeness.

**Table 2. Observed Infrared Vibrational Bands (cm$^{-1}$) of GaFPc (Numbers in Parentheses Are Normalized Relative Intensities)**

| pellet | film | RAIRS | interpretation |
|---|---|---|---|
| 508(14) | 507(12) | | |
| 570(5) | 568(8) | | |
| 574(16) | 573(14) | | benzene ($\upsilon_6$) |
| 634(5) | 636(8) | 636(7) | Ga−F st. |
| 640(12) | 640(16) | | |
| 720(100) | 714(14),726(27) | | |
| 733(79) | 733(sh) | 733(100) | C−H wag |
| 753(75) | 755(56) | 756(17) | benzene ($\upsilon_1$) |
| | 763(12) | | |
| 770(28) | 770(5) | 769(36) | C−H wag |
| 781(28) | 780(11) | 781(30) | C−H torsion |
| 898(65) | 897(38) | 897(13) | C−H bend |
| 1068(38) | 1068(12) | | C−H bend |
| 1084(73) | 1082(87) | 1083(23) | C−H bend ($\nu_{18}$) |
| 1122(94) | 1120(96) | 1120(26) | C−H bend |
| 1168(38) | 1167(33) | 1168(10) | C−H bend ($\nu_{9a}$) |
| 1288(55) | 1289(48) | 1288(13) | benzene ($\upsilon_{14}$) |
| 1334(87) | 1333(100) | 1334(28) | pyrrole st |
| 1362(24) | 1361(40) | 1364(20) | isoindole st |
| 1423(44) | 1424(40) | 1423(13) | isoindole st |
| 1466(18) | 1469(43) | | benzene ($\nu_{19b}$) |
| 1498(26) | | | isoindole st |
| 1506(36) | 1506(43) | 1508(13) | benzene ($\nu_{19a}$) |
| 1525(26) | 1525(69) | 1527(42) | C−N pyrrole |
| 1580(7) | 1579(10) | 1579(10) | benzene ($\nu_{8b}$) |
| 1613(12) | 1610(10) | | benzene ($\nu_{8a}$) |

**Table 3. Observed Raman Bands (cm$^{-1}$) of GaFPc**

| RRS (LL = 647.1 nm) | SERRS (LL = 647.1 nm) | SR (LL = 514.5 nm) | interpretation |
|---|---|---|---|
| 168(10) | 169(4) | | |
| 234(14) | 246(8) | | |
| 485(14) | 484(9) | | |
| 592(10) | 593(9) | 592(47) | benzene radial |
| 676(40) | 677(65) | 677(58) | Pc breathing |
| | 686(8) | 686(14) | |
| 750(37) | 751(44) | 751(5) | benzene ($\nu_1$) |
| 778(5) | 778(8) | 778(16) | C−H torsion |
| 832(5) | 832(18) | 841(45) | |
| 851(5) | 852(7) | | |
| | | 896(5) | |
| | | 918(9) | |
| 952(24) | 954(20) | | |
| | 1007(7) | | C−H bend |
| | | 1040(20) | C−H bend |
| 1106(11) | 1105(5) | 1107(26) | C−H bend |
| 1144(27) | 1143(55) | 1144(12) | pyrrole breathing |
| 1187(14) | 1187(19) | | C−H bend |
| 1213(14) | 1212(8) | | C−H bend ($\nu_3$) |
| 1305(19) | 1304(18) | 1299(12) | C−H bend |
| 1340(44) | 1341(100) | 1341(56) | pyrrole stretch |
| | | 1409(7) | |
| | 1430(11) | 1431(6) | benzene ($\nu_{19b}$) |
| 1451(37) | 1451(31) | 1451(32) | benzene ($\nu_{19a}$) |
| | | 1491(45) | isoindole st. |
| 1526(100) | 1528(33) | 1528(100) | C−N pyrrole |
| | | 1590(26) | benzene ($\nu_{8b}$) |
| | | 1611(39) | benzene ($\nu_{8a}$) |

The far-infrared frequencies of GaFPc and InClPc (not previously reported) are listed in Table 4. Low-frequency vibrations of the macrocycle are highly coupled, and the assignment to a single internal coordinate is inadvisable. However, an attempt can be made to identify vibrations with a large contribution of the central metal atom. The bands at 337 cm$^{-1}$ in GaFPc and 336 cm$^{-1}$ in InClPc can be associated, by analogy with a series of MPc molecules,[31] with the fundamental

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**Table 4. Far-Infrared Frequencies ($cm^{-1}$) for GaFPc and InClPc**

| GaFPc | InClPc |
|---|---|
| 125(81) | 126(12) |
| 141(24) | 133(51) |
| | 148(31) |
| 160(28) | 167(28) |
| | 203(85) |
| 247(54) | 247(11) |
| 255(70) | 253(8) |
| 270(45) | 266(15) |
| 283(10) | 278(26) |
| 294(10) | |
| 306(10) | 303(15) |
| 337(100) | 336(92) |
| 351(32) | 344(100) |
| | 370(18) |
| | 379(8) |
| 395(5) | 396(18) |
| 432(46) | 437(77) |

frequency having a large contribution from the metal−N stretching mode. The strong band at 344 $cm^{-1}$ (close to the In−Cl diatomic frequency) in the far-IR spectrum of InClPc could be assigned to the In−Cl stretching vibration. The band at 203 $cm^{-1}$, present in the spectrum of the InClPc but absent in the spectrum of the GaFPc, could be due to the In−Cl bending vibration. Similarly, the Ga−F bending vibration could be assigned to the strong band at 255 $cm^{-1}$. The Ga−F stretching mode is expected in the 600−700 $cm^{-1}$ region. The infrared band at 637 $cm^{-1}$, that retains intensity in the RAIR spectrum, is assigned to the Ga−F stretching vibration.

## Conclusions

The average molecular organization in Pc films has been determined using the directional properties of the interaction between the molecular transition dipole moments and the electric field of the infrared radiation. Using transmission and reflection absorption spectroscopy, it was found that molecules in GaFPc and InClPc films are predominantly in a face-on orientation, while the average molecular orientation in VOPc and TiOPc films appears to be a tilted orientation with respect to the substrate plane. The organization in CuPc films from 25−200 nm mass thickness was also found to be a prevailing face-on molecular orientation. The vibrational characterization of GaFPc using Raman, surface-enhanced Raman, middle-infrared, and far-infrared spectra is also given. The results show once again that polarization infrared spectroscopy in transmission and RA geometry is a powerful analytical technique for a rapid determination of average molecular orientation in ultra-thin solid films.