Raman structural studies of phthalocyanine thin solid films.

Carol Ann Jennings

University of Windsor

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RAMAN STRUCTURAL STUDIES OF PHTHALOCYANINE THIN SOLID FILMS

by

Carol Ann Jennings

A Thesis submitted to the
Faculty of Graduate Studies and Research through the Department of Chemistry and Biochemistry in Partial Fulfillment of the requirements for the Degree of Master of Science at the University of Windsor

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ABSTRACT
RAMAN STRUCTURAL STUDIES OF PHTHALOCYANINE THIN SOLID FILMS
by Carol Ann Jennings

Raman spectra of evaporated thin solid films (200nm thickness) have been studied using excitation frequencies in resonance and near resonance with the red absorption band of chloroaluminum (AlPcCl), chlorogallium (GaPcCl), and chloroindium (InPcCl) phthalocyanine. Molecular orientation of these films have been probed by polarization techniques. Expressions have been developed for SS, SP, PS and PP polarizations of A, B and E symmetry types for $C_{4v}$ molecules such as AlPcCl, GaPcCl and InPcCl. Experimentally the angle $\beta$ (between the laser beam and the normal to the substrate) can be varied and values obtained for the angle $\theta$ which describes the stacking of molecular columns on a substrate. Correlation field splitting (Davydov) of non-degenerate vibrational fundamentals were observed using polarization techniques with these thin solid films. The Davydov splitting pattern permits assignment of the crystallites in the AlPcCl film to a monoclinic system as opposed to a triclinic system.

Surface-enhanced Raman scattering (SERS) has been observed for a Langmuir-Blodgett monolayer of tetratertiarybutyl metal-free phthalocyanine ($t$-bu)$_4$H$_2$Pc on silver and indium island films.
Langmuir-Blodgett films or arachidic acid have been used as spacer layers to control the separation distance between evaporated Ag or In metal island films and the LB monolayer of (t-bu)$_2$H$_2$Pc. The distance dependence of the SERS enhancement factor was established and results support an electromagnetic mechanism rather than a short-range chemical mechanism.
DEDICATION

To my family and friends
ACKNOWLEDGEMENTS

I would like to express my sincere thanks to Dr. R. Aroca for his constant encouragement and advice during this project.

I would like to thank the following people from Xerox Research Centre of Canada located in Mississauga: Dr. R.O. Loutfy, Dr. A. Hor and Dr. G. Kovacs. Their suggestions and the opportunity to work in the Xerox laboratory on several occasions was appreciated.

Finally, I would like to thank my friends in the department and others who have made my stay in Windsor an enjoyable one.
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LIST OF ABBREVIATIONS

Pc - phthalocyanine
LB - Langmuir-Blodgett
(t-bu)_4H_2Pc - tetratertiarybutyl metal-free phthalocyanine
CuTSPc - 4,4',4'',4''' tetrasulfonated copper phthalocyanine
MPc - metallated phthalocyanine
NR - normal Raman
RR - resonance Raman
SERS - surface enhanced Raman scattering
CHAPTER 1: APPLICATIONS

Phthalocyanines (Pcs) in general are very stable, resistant to heat and light, fairly insoluble in water and organic solvents. Pcs are widely used as colorants. The pigments have been dispersed in paints, inks and plastics. They have been used as indicators, parts of lasers, catalysts and lubricants. Phthalocyanines have medical applications as stains for electron microscopy. Thin films of Pcs and derivatives are used in photography, semiconductor applications and xerography.

The laser properties of some phthalocyanines have been reported. Chloroaluminum phthalocyanine (AlPcCl), chlorogallium phthalocyanine (GaPcCl), magnesium phthalocyanine (MgPc) and zinc phthalocyanine (ZnPc) were dissolved in a number of solvents and pumped with a nitrogen laser. Two wavelength lasing was observed for AlPcCl in solution with lines separated by 70nm. The other phthalocyanines GaPcCl, MgPc and ZnPc lased at only one wavelength which was below 700nm.

An electrophotographic camera film consisting of X-metal-free phthalocyanine (X-H_2Pc) or vanadyl phthalocyanine (VOPc) has been described. Special features of the film include: handling in light prior to charging, high sensitivity in the visible and near IR, inexpensive raw materials, ease of fabrication, dry development and high resolution. The film is selectively erasable when developed using heat. The X-H_2Pc film could be
used for digital recording and one suggested application of the film would be "photography in the dark" where the "flash" is imperceptible to the subject.

Vanadyl phthalocyanine has been studied as a high density optical storage material\(^2\). The VOPc films were prepared by vacuum vapor deposition onto polymethylmethacrylate substrates and then annealed. A laser of wavelength in the region of 800nm evaporates the organic material and forms a pit (writing). The optical defects are detected or "read" a later time. Double and triple layer structures containing VOPc have also been tested. Metal-free phthalocyanine has been considered as a material for archival data storage using a krypton ion laser line of 647.1nm for pit formation\(^4\). Experimental conditions must be manipulated to obtain the smallest pit and thus increase the storage capacity.

Argon ion beams interact with organic materials such as nickel phthalocyanine (NiPc) and 3,4,9,10-perylene tetracarboxylic dianhydride\(^5\). The organic solids turn optically dense and conductivity is greatly increased. Nearly amorphous carbon is formed with high doses and this technique could have lithographic applications.

Gas sensors have been fabricated from Langmuir-Blodgett (LB) monolayers of phthalocyanines. A chemiresistor consisting of microelectrodes and a LB film of copper tetra cumylphenoxy Pc has
been tested. The conductivity of the film changes with the amount of ammonia vapor or nitrogen dioxide in contact with the device. Desirable properties of the chemical sensor are high sensitivity, fast response, selectivity, reproducibility and stability.

Phthalocyanines have photovoltaic and photoelectrolytic applications. Solar cells composed of thin films offer two advantages over other choices: (1) material costs can be reduced as the thickness of the active material is small and (2) thin films can be produced continuously on a large scale. The presence of metal phthalocyanine as dopants within metal-free phthalocyanine photovoltaic cells has been discussed. Heterojunction solar cells have been prepared consisting of cadmium sulfide and a phthalocyanine such as HPC, ZnPc, MgPc, CuPc, MnPc, PbPc, VOPc, chloroaluminum chlorophthalocyanine (ClAlClPc), ClAlPc and ClInPc.

Photoelectrochemical properties of X-HPC and VOPc coated tin oxide (SnO₂) electrodes coupled with Fe(CN)₆⁴⁻/₃⁻ and I₂/I₃⁻ have been optimized and reported. Tri- and tetravalent Pc electrodes have been studied. The crystallite size within the films influences the photoelectrochemical behavior. Hydrogen evolution was observed for GaPcCl/Au films coated with small amounts of platinum.
Electrochemical studies have been carried out on water-soluble tetrasulfonated phthalocyanines. The previous examples are not a complete list of Pc applications but illustrate their widespread use.
In this discussion of structure, Pcs are arbitrarily divided according to symmetry:

(i) $D_{2h}$: H$_2$Pc

(ii) 4,4',4''',4'''-tetratertiarybutyl metal-free phthalocyanine ((t-bu)$_4$H$_2$Pc)

(iii) $D_{4h}$: BePc, CoPc, CuPc, FePc, MgPc, MnPc, ZnPc, hexadecachloro-copper phthalocyanine ($\text{Cl}_{16}\text{CuC}_{32}\text{N}_8$)

(iv) $C_{4v}$: PbPc, SnPc, VOpc, AlPcCl, GaPcCl, InPcCl

(v) 4,4',4''',4'''-tetrasulfonated copper phthalocyanine (CuTSPc)

Data obtained from x-ray crystallography is used in structure determination. Phthalocyanines and metallated phthalocyanines occur in various polymorphic forms. A section is devoted to this topic. Molecular symmetry (point group) and crystal symmetry (space group) are mentioned.

There are two types of symbols used to represent the two-hundred and thirty space groups. Hermann-Mauguin symbols are frequently encountered in crystallographic reports and the other system is Schönhflies notation. The notation to be adopted here is the Schönhflies symbol is followed by the Hermann-Mauguin symbol, for example: $C_5^5(P2_1/a)$.
Phthalocyanines are structurally related to compounds of biological interest\(^2\). Figure 1 gives the structures of porphyrin, chlorophyll a and hemin. All these compounds have four pyrrole units. Porphyrins can contain four bridging methine groups or from one to four aza groups. Chlorophyll a has a central magnesium atom and is a photosynthetic pigment. Hemin contains iron and combines with protein to give hemoglobin.

**Metal-free phthalocyanine (H\(_2\)Pc) structure:**

Robertson has determined the structure of H\(_2\)Pc and a number of MPcs by x-ray crystallography\(^3\)-\(^7\). The skeleton of H\(_2\)Pc is given in figure 2. The first striking feature of this compound is its extensive conjugation which leads to a planar structure. It is convenient to discuss H\(_2\)Pc in terms of subunits. The core consists of a macrocycle of sixteen alternating carbon and nitrogen atoms. The interatomic C-N distance in the macrocycle has a constant value of 1.34\(\text{\AA}\) indicating a single-bond double-bond resonance\(^3\)-\(^4\). There are four isoindole groups in H\(_2\)Pc each consisting of a benzene and pyrrole ring. Four aza groups (-N=) bridge the isoindole moieties. The two imino hydrogens lie in the plane of the molecule and are shared by the nitrogens\(^8\). Peripheral hydrogens can be replaced by other atoms or groups. Metalated phthalocyanines (MPcs) are synthesized by substituting the two central hydrogens.
Figure 1. Structures of porphine, chlorophyll a and hemin$^2$. 
Polymorphs:

Metal-free Pc and metallated Pcs exist in various polymorphic forms\textsuperscript{9-12}. The polymorphic phase is determined by the orientation of adjacent molecules. A number of crystal packing arrangements are possible. Under a given set of conditions (pressure, temperature, solvent) there is only one stable phase which has the lowest free energy\textsuperscript{13}. All other phases under the set of conditions are metastable. Metastable phases can exist for long periods of time.

Three polymorphic forms of H\textsubscript{2}Pc (\(\alpha, \beta, \chi\)) have been qualitatively identified based on their IR and visible spectra\textsuperscript{9,14}. \(\beta\) and \(\chi\)-H\textsubscript{2}Pc polymorphic forms are more crystalline than the \(\alpha\) form. All the crystals studied by Robertson\textsuperscript{3-7} were long needles that had been sublimed and corresponded to the \(\beta\) polymorph. The x-ray diffraction results for \(\chi\)-H\textsubscript{2}Pc have been reported\textsuperscript{15}. \(\alpha\)-H\textsubscript{2}Pc is metastable and less ordered than \(\beta\)-H\textsubscript{2}Pc\textsuperscript{9}. The method of preparation determines which polymorphic form is present.

Intramolecular hydrogen bonding in \(\beta\)-H\textsubscript{2}Pc is extensive due to the presence of parallel molecular stacks\textsuperscript{4}. Each imino hydrogen is shared by nitrogen atoms of adjacent molecules\textsuperscript{9}. One nitrogen of an isoindole group lies directly above the hydrogen, while the other isoindole nitrogen is directly below. The bands of
Figure 2. Skeleton of metal-free phthalocyanine ($H_2Pc$).
FIGURE 2
the IR spectra that are used to identify various polymorphs are mainly C-H deformations, N-H deformations and N-H stretching\textsuperscript{9,14}. The x-H\textsubscript{2}Pc polymorph has a greater density and less hydrogen-bonding than β-H\textsubscript{2}Pc\textsuperscript{14}.

4,4',4'',4'''-tetratertiary butyl phthalocyanine, ((t-bu)\textsubscript{4}H\textsubscript{2}Pc) structure:

The structure of (t-bu)\textsubscript{4}H\textsubscript{2}Pc is given in figure 3. It is possible to prepare Langmuir-Blodgett films\textsuperscript{16} and this will be discussed in greater detail.

Planar divalent phthalocyanines, structure:

Early work on the structure of CuPc was done by Robertson\textsuperscript{3-5}. Further studies of β-CuPc were carried out by Brown\textsuperscript{17}.

The β-CuPc is monoclinic with space group C\textsubscript{5}\textsubscript{2h}(P2\textsubscript{1}/a) and there are two molecules per unit cell\textsuperscript{3,5,17}. Within the molecule, the Cu-N distance is 1.934Å and there is square planar coordination\textsuperscript{17}. The geometry of the copper can also be thought of as a distorted octahedral if one includes interaction with nitrogens of neighboring Pc molecules. Brown\textsuperscript{17} suggests that the difference between various polymorphs is due to the coordination of copper with different neighboring nitrogens and certain polymorphs could be selected by blocking specific nitrogen atoms with residues.
Figure 3. Skeleton of the most common type isomer of $(t$-bu)$_4$H$_2$Pc. 

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FIGURE 3
X-ray diffraction data for ZnPc reveals that the zinc is centrosymmetric and the molecule is essentially planar\textsuperscript{18}. The mean Zn-N distance is $1.980\text{\AA}$ with a monoclinic structure and space group $C_{2h}^5(P2_1/a)$\textsuperscript{18}. Additional planar compounds studied by Robertson were: NiPc, PtPc, BePc, CoPc, FePc, and MnPc\textsuperscript{3,5-7}. These compounds are all monoclinic, space group $C_{2h}^5(P2_1/a)$, and have two molecules per unit cell\textsuperscript{5}. The PtPc is somewhat anomalous based on the fact that for nearest neighboring molecules there are no atoms vertically over each other and the distance between molecular planes is much smaller, $3.41\text{\AA}$. Brown\textsuperscript{19} reinvestigated the structure of PtPc and found the original preparation by Linstead\textsuperscript{5} actually contained two polymorphs to be called $\alpha$ and $\gamma$. Both polymorphs were monoclinic and the space groups were $C_{2h}^6(C2/c)$ and $C_{2h}^5(P2_1/a)$ for $\alpha$ and $\gamma$ forms respectively\textsuperscript{19}. These planar divalent phthalocyanines belong to the point group $D_{4h}$.

Tetravalent phthalocyanines which have two equal axial ligands and distorted octahedral coordination about the central metal will also belong to the point group $D_{2h}$. Hexadecachlorocopper phthalocyanine (Cl$_{16}$CuC$_{32}$N$_8$) has all the peripheral hydrogens substituted with chlorine atoms. This compound also has $D_{4h}$ symmetry.
Non-planar divalent phthalocyanines, structure:

Lead phthalocyanine is not a planar molecule\textsuperscript{20}. Its shape can be described as that of a "shuttlecock". The lead atom is displaced from the plane defined by the four nitrogen atoms of the isoindole units. The lead atom sits above a concave structure formed by the Pc ligand. The molecular symmetry is \( C_{4v} \).

Monoclinic and triclinic crystal forms of lead phthalocyanine have been identified by x-ray diffraction\textsuperscript{20,21}. Iyechika\textsuperscript{23} obtained monoclinic and triclinic crystals by heating PbPc powder to 723\textdegree{}K and transporting the vapor by nitrogen to a tube with a controlled temperature gradient. The triclinic crystals grew at a region of the tube kept at 593\textdegree{}K while the monoclinic crystals grew at 523\textdegree{}K\textsuperscript{21}. The space groups of the monoclinic form and triclinic forms were found to be \( C_{2h}^{5}(P2_{1}/c) \) and \( C_{i}^{1}(P\overline{1}) \) respectively\textsuperscript{20,21}. In both cases there were four molecules in the unit cell. Monoclinic PbPc is a better electrical conductor than the triclinic form\textsuperscript{23}. The monoclinic form is a one-dimensional conductor due to a stacking of the PbPc molecules. It can be seen that if the crystal structure of a compound is modified, electrical and other properties change.

A triclinic form of tin phthalocyanine (SnPc) was studied by x-ray diffraction\textsuperscript{22}. The space group was \( C_{i}^{1}(P\overline{1}) \) with two
molecules per unit cell. The tin atom is out of the plane of the four isoindole nitrogens, the inner macrocycle is puckered and the Pc ligand is "saucer" shaped\textsuperscript{22}.

**Vanadyl phthalocyanine (VOPc), structure:**

Three polymorphic forms (phase I, II, III) have been observed for vanadyl phthalocyanine (VOPc)\textsuperscript{12}. These three phases are not isomorphous with α, β and x polymorphs of other phthalocyanines. X-ray diffraction data has been reported for phase II and suggests the crystals are triclinic with $C^1_i(P\overline{1})$ symmetry\textsuperscript{12}. The oxovanadium cation lies above the plane defined by the four isoindole nitrogens. The preparation of the three phases is given\textsuperscript{12}. Phase I occurs if VOPc is vacuum deposited onto fused quartz at $10^{-5}$ torr. Phase II is obtained by crystal growth from solvents such as quinoline and 1-chloronaphthalene, by crystal growth from vapor or by heating phase I to 200°C and above. Phase III occurs if a melt at 610°C is quenched. The point group of VOPc is $C_{4v}$.

**Trivalent phthalocyanines (AlPcCl, GaPcCl, InPcCl), structure:**

Single crystal x-ray analysis has been reported for AlPcCl and ClGaPc\textsuperscript{23}. These trivalent phthalocyanines belong to the point group $C_{4v}$. Chloroaluminum phthalocyanine as a single crystal is triclinic and of space group $C^1_i(P\overline{1})$ with four molecules per unit cell\textsuperscript{23}. The coordination geometry of AlPcCl is square.
pyramidal and the Al-Cl bond length is 2.179\text{Å} with Al 0.410\text{Å} above the plane defined by the four isoindole nitrogens$^{23}$. A crystal of chlorogallium phthalocyanine has the following properties: triclinic, space group $C_{2h}^{1}(P\bar{1})$, two molecules per unit cell, square pyramidal coordination, Ga-Cl=2.217Å and the gallium atom is 0.439Å above the plane of the four isoindole nitrogens$^{23}$.

4,4',4'',4'''-tetrasulfonated copper phthalocyanine (CuTSPc), structure:

The presence of sulfate groups makes this compound water-soluble.

Lattice parameters for the various phthalocyanines are summarized in table 1.
<table>
<thead>
<tr>
<th>Compound</th>
<th>Space Group</th>
<th>(a(\text{Å}))</th>
<th>(b(\text{Å}))</th>
<th>(c(\text{Å}))</th>
<th>(\alpha(\text{°}))</th>
<th>(\beta(\text{°}))</th>
<th>(\gamma(\text{°}))</th>
<th>(Z)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\chi)-H_2Pc(^3,4)</td>
<td>(C_{2h}(P2_1/a))</td>
<td>19.85</td>
<td>4.72</td>
<td>14.8</td>
<td>122.25</td>
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<tr>
<td>PbPc(^{20,21})</td>
<td>(C_{2h}(P2_1/a))</td>
<td>24.48</td>
<td>25.48</td>
<td>3.73</td>
<td>90</td>
<td>4</td>
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<tr>
<td>SnPc(^{22})</td>
<td>(C_{2h}(P2_1/a))</td>
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<td>16.131</td>
<td>12.889</td>
<td>94.22</td>
<td>96.20</td>
<td>114.19</td>
<td>4</td>
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<tr>
<td>VOPc(Phase II)(^{12})</td>
<td>(C_{2h}(P2_1/a))</td>
<td>12.060</td>
<td>12.618</td>
<td>8.675</td>
<td>95.89</td>
<td>95.08</td>
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<td>(\beta)-ZnPc(^{18})</td>
<td>(C_{2h}(P2_1/a))</td>
<td>19.274</td>
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<td>14.553</td>
<td>120.48</td>
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<td>(\beta)-CuPc(^{17})</td>
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<td>14.628</td>
<td>120.56</td>
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<td>(\beta)-NiPc(^3,5-6)</td>
<td>(C_{2h}(P2_1/a))</td>
<td>19.9</td>
<td>4.71</td>
<td>14.9</td>
<td>121.9</td>
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<td>(\beta)-BePc(^5)</td>
<td>(C_{2h}(P2_1/a))</td>
<td>21.2</td>
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<td>14.7</td>
<td>121.0</td>
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<td>(\beta)-CoPc(^5)</td>
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<td>4.77</td>
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<td>(\alpha)-PtPc(^{19})</td>
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<td>135.6</td>
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<td>(\gamma) triclinic</td>
<td>(C_{2h}(P2_1/a))</td>
<td>23.16</td>
<td>3.969</td>
<td>16.62</td>
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<td></td>
<td>a(Å)</td>
<td>b(Å)</td>
<td>c(Å)</td>
<td>α(°)</td>
<td>β(°)</td>
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<tr>
<td>AlPcCl$^{23}$</td>
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<td>triclinic</td>
<td>13.776</td>
<td>13.775</td>
<td>14.059</td>
<td>98.36</td>
<td>108.60</td>
<td>90.16</td>
<td>4</td>
<td>$C_1'i(P1)$</td>
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<tr>
<td>GaPcCl$^{23}$</td>
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<tr>
<td>triclinic</td>
<td>9.301</td>
<td>11.272</td>
<td>13.143</td>
<td>105.46</td>
<td>105.61</td>
<td>96.80</td>
<td>2</td>
<td>$C_1'i(P1)$</td>
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CHAPTER 3: NORMAL RAMAN, RESONANCE RAMAN AND SURFACE-ENHANCED RAMAN SCATTERING

Normal Raman

A laser beam strikes a sample and light is scattered. If the scattered light has the same frequency as the incident light we have elastic or Rayleigh scattering. Inelastic or Raman scattering arises when scattered light has a different frequency from the laser beam and there are two possibilities, Stoke's and anti-Stoke's. For Stoke's scattering the frequency of scattered light is less than the frequency of the incident light. Molecules are excited from a ground vibrational state (v=0) to a higher energy level (virtual state). The molecules leave this virtual state and return to an excited vibrational state (eg. v=1). In the anti-Stoke's case, molecules start in an excited vibrational state (eg. v=1), are excited to a higher energy state and then return to the ground vibrational state (v=0). The frequency of anti-Stoke's scattering is greater than the frequency of the incident light. Stoke's scattering is much more intense than anti-Stoke's because few molecules start out in an excited vibrational energy level.

A laser source has an oscillating electric field which interacts with molecules to induce a dipole moment $\mu$. The magnitude of $\mu$ depends on the amplitude of the light wave and the molecular polarizability $\alpha$. The molecular polarizability describes the ease of electron deformation in the molecule.

$$\mu = \alpha E \quad (3.1)$$
The components of the induced dipole moment are given by a polarizability tensor where $\alpha_{yx} = \alpha_{xy}$, $\alpha_{zx} = \alpha_{xz}$ and $\alpha_{yz} = \alpha_{zy}$.

$$
\begin{pmatrix}
\mu_x \\
\mu_y \\
\mu_z
\end{pmatrix} =
\begin{pmatrix}
\alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\
\alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\
\alpha_{zx} & \alpha_{zy} & \alpha_{zz}
\end{pmatrix}
\begin{pmatrix}
E_x \\
E_y \\
E_z
\end{pmatrix}
$$

Any or all of the six polarizability components can be modulated by a molecular vibration. Components which have a polarizability change are Raman active. From this point on the symbol $\alpha$ represents the polarizability derivative.

In this case:

$$
\alpha = \alpha_0 + \left(\frac{\delta \alpha}{\delta Q_V}\right)_0 Q_V
$$

The equilibrium configuration is $\alpha_0$. $Q_V$ is the vibrational coordinate and $\left(\frac{\delta \alpha}{\delta Q_V}\right)_0$ is the rate of change of the polarization.

**Number and types of IR and Raman active modes**

The number of infrared and Raman active modes for any molecule can be calculated using the character table of the appropriate point group. For example, AlPcCl has $C_{4v}$ molecular symmetry. This molecule possesses a fourfold axis of symmetry and vertical planes of symmetry. For a non-linear molecule, the total number of vibrations is $3N - 6$. AlPcCl has 58 atoms giving a total of 171 vibrations.

The total number of fundamentals of each type is calculated using the following equation:

$$
N_t = \frac{1}{N_G} \sum N_e(R) \Theta(R) \chi(R) \quad (3.2)
$$
\( N_G \) is the number of elements in the group.

\( N_e \) is the number of elements in each class.

\[
\Theta(R) = (\mu-2)(1+2\cos\phi) \quad (3.3)
\]

or \( = (\mu)(-1+2\cos\phi) \quad (3.4) \)

Equation (3.3) is used for PROPER ROTATIONS which include the identity \( E \) and rotations. Equation (3.4) applies to IMPROPER ROTATIONS which include reflections, inversion and rotation followed by reflection.

\( \chi_i(R) \) is the character of the vibration species, \( \mu_R \) is the number of atoms left unchanged by the operation and \( \phi \) is the angle associated with the rotation.

Infrared-allowed fundamentals can be calculated using the formula:

\[
N_l = \frac{1}{N_G} \sum N_e \chi_M(R) \chi_i(R) \quad (3.5)
\]

\[
\chi_M(R) = +/- 1+2\cos\phi \quad (3.6)
\]

The positive sign is for proper rotations, the negative for improper rotations. Raman allowed fundamentals are given by:

\[
N_l = \frac{1}{N_G} \sum N_e \chi_\alpha(R) \chi_i(R) \quad (3.7)
\]

\[
\chi_\alpha(R) = 2 +/- 2\cos2\phi \quad (3.8)
\]

The total number of fundamentals of each type have been calculated for three examples \( H_2Pc \), \( CuPc \) and \( AlPcCl \) and are given in table 3.1.
### TABLE 3.1: TOTAL NUMBER OF FUNDAMENTALS OF EACH TYPE FOR REPRESENTATIVE PHTHALOCYANINES OF $D_{2h}$, $D_{4h}$ AND $C_{4y}$ MOLECULAR SYMMETRY

<table>
<thead>
<tr>
<th>Symmetry</th>
<th>Fundamentals</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_{2h}[H_{2}Pc]$</td>
<td>$29A_g^* + 13A_u + 13B_{1g}^* + 28B_{1u} + 14B_{2g}^* + 28B_{2u} + 28B_{3g}^* + 15B_{3u}$</td>
</tr>
<tr>
<td>$D_{4h}[CuPc]$</td>
<td>$14A_{1g}^* + 6A_{2u} + 13A_{2g}^* + 8A_{2u} + 14B_{1g}^* + 7B_{1u} + 14B_{2g}^* + 7B_{2u} + 13E_{g}^* + 28E_{u}$</td>
</tr>
<tr>
<td>$C_{4y}[AlPcCl]$</td>
<td>$23A_{1}^* + 19A_{2} + 21B_{1}^* + 21B_{2}^* + 42E$</td>
</tr>
</tbody>
</table>

* indicates Raman active  
___ indicates IR active
Resonance Raman Scattering

Resonance Raman (RR) scattering is observed if the excitation frequency i.e. laser line coincides with the frequency of an electronic transition of the molecule. The intensity of RR scattering is much greater than that observed with normal Raman (NR) scattering. The total scattering $I_S$ for a ground state $G$ to final state $F$ is given by $^3, ^4$:

$$I_S = \frac{8\pi \omega I_L}{9c^4} \sum_{\rho \sigma} |(\alpha_{\rho \sigma})_{GF}|^2 \quad (3.9)$$

$\omega$ is the frequency of scattered light, $c$ is the speed of light and the intensity of the incident laser beam is $I_L$. $(\alpha_{\rho \sigma})_{GF}$ is the $\rho \sigma$th component of the Raman scattering tensor and $\rho, \sigma = x, y$ or $z$.

The elements of the polarizability derivative tensor $(\alpha_{\rho \sigma})_{GF}$ are given by $^3-^5$:

$$(\alpha_{\rho \sigma})_{GF} = \frac{1}{\hbar} \sum_{I} \left( \frac{<F|r_{p}|G> <I|r_{\sigma}|G> + <I|r_{p}|G> <F|r_{\sigma}|I>}{\omega_{GI} - \omega_L - i\Gamma_I} \right) \left( \frac{1}{\omega_{IF} + \omega_L - i\Gamma_I} \right) \quad (3.10)$$

$I$ = robovibronic excited electronic states

$r$ = electron position operator

$\Gamma_I$ = damping term
The main reason for introducing equations 3.9 and 3.10 is to show why resonance Raman bands are intense. When $\omega_L$ approaches $\omega_G$ the left hand term of the summation in equation 3.10 becomes very large for an allowed electronic transition. The term cannot reach infinity because of the damping $\Gamma_I$ which is related to the bandwidth of the electronic transition.

In resonance Raman, the polarizability derivative tensor may become asymmetric, i.e. $\alpha_{xy} \neq \alpha_{yx}$, etc. This introduces a new term in intensity and the depolarization expression.

$$(\alpha_{ps})_{GF}$$ is divided into two terms described by Albrecht\textsuperscript{3,4}. The first term in equation 3.10 is Albrecht's A term involves Franck-Condon factors. Only totally symmetric terms are enhanced in the RR spectrum. Albrecht's B term is important in RR by the Herzberg-Teller mechanism. Electronic states are mixed and asymmetric modes can be observed in the RR spectrum. Porphyrins and heme proteins which contain the porphyrin chromophore are molecules which produce RR scattering of the Herzberg-Teller type\textsuperscript{5}.

Resonance Raman scattering can be compared with normal Raman scattering. NR follows a $\omega^4$ dependence on excitation frequency whereas RR scattering varies greatly with the excitation frequency. The RR scattering time can be much slower than off-resonance or NR scattering. Overtones can be quite intense in RR spectra while they are weak in NR Raman spectra. The ratio of Anti-Stoke's to Stoke's
scattering for NR is given by the Boltzmann distribution which considers the ground state population. This is not the case for RR and the intensities of Anti-Stoke's lines can exceed the intensity of Stoke's.
Surface-enhanced Raman scattering

Surface-enhanced Raman scattering (SERS) is a phenomenon which involves molecules on or close to metal surfaces. A number of reviews and books have appeared in the literature on SERS\textsuperscript{6-12}. The Raman cross section of a molecule can be increased by a factor as large as $10^6$ by a "SERS-active surface"\textsuperscript{6,7}. A distinction is made between two types of adsorption processes. Chemisorbed molecules have strong interactions with the metal surface and Raman frequencies are shifted. Direct contact with the metal surface is necessary for chemisorption. Physisorbed molecules have Raman frequencies which coincide with those of the pure compound.

The type of metal surfaces that have been studied by SERS include electrode surfaces\textsuperscript{13,14}, island films\textsuperscript{15-22}, cold-deposited films\textsuperscript{10,23}, lithographically produced assemblies such as gratings\textsuperscript{7}, metal colloids\textsuperscript{24}, metal deposits on the top of CaF\textsubscript{2}\textsuperscript{25-28}, ion bombarded metals\textsuperscript{7}, acid etched material\textsuperscript{7}, particles supported on an oxide\textsuperscript{29} and metal on latex spheres\textsuperscript{29}. Seki\textsuperscript{31} has compiled a list of metals which give SERS and the environment in which the measurements were taken. Silver is the most studied metal and is a very efficient "SERS" material\textsuperscript{7,31}. Work in our laboratory has been done on silver and indium island films\textsuperscript{15-18}. 

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There are a number of reasons why the mechanism(s) for SERS must be found. We have a sensitive technique but interpretation of results is sometimes difficult. From an analytical point of view, one would like to optimize experimental conditions\textsuperscript{32} to get the highest sensitivity possible, identify adsorbates\textsuperscript{3}\ and allow geometries of adsorbates to be elucidated. Many theoretical models have been presented concerning the origin of SERS and no consensus regarding the mechanism has been achieved\textsuperscript{6-12,23-48}.

There are two electromagnetic models\textsuperscript{6}, one for continuous surfaces (extended surface plasmons) and another for discontinuous metals (localized particle plasmons). A model which considers the increased formation of electron-hole pairs on roughened surfaces was proposed by Burstein et al\textsuperscript{49}. The adatom model of Otto\textsuperscript{10} requires the adsorption of molecules at active sites and surface roughness increases the number of these sites. A mechanism has been suggested which has the metal altering and broadening energy levels of adsorbed molecules\textsuperscript{50-52}. Large intensities would be observed when the frequency of the laser line was in resonance with one of the molecular transitions. This resonant Raman mechanism\textsuperscript{50-52} requires direct contact of the adsorbate with the metal and surface roughness is not essential. One group\textsuperscript{53} discusses the effect of the formation of surface complexes consisting of metal atoms, ions, adsorbate and solvent molecules. In specific geometries, the electronic transitions of the complex are altered and a resonant
Raman effect is observed\textsuperscript{58}. Another model of Otto\textsuperscript{59} is modulated reflectance. A vibrating molecule has a charge density that fluctuates and is propagated to the metal surface either directly (chemisorption) or via Coulombic interactions (physisorption). One model for SERS is the image dipole mechanism\textsuperscript{6}. A molecular dipole induces an image dipole on the metal and the molecular-metal distance is critical.

SERS mechanisms can be tested by posing the following experimental questions. Is surface roughness required? A particular adsorbate could be added to smooth and rough metals. Is direct contact between the molecule and metal necessary? Spacer-type experiments are useful in checking this point. What is the effect of changing the incident photon energy? Excitation profiles are constructed using an internal standard and observing how intensities change with different laser lines. For island films, what is the optimum size of islands and best aspect ratio? How are results affected by changing the identity of the adsorbate or the metal (dielectric constant)? Optical absorption spectra can be taken of colloids and metal island films. Is aggregation mandatory and must the laser line fall within the absorption of the metal to observe intense Raman signals? The experimenter should attempt to determine the magnitude of the enhancement. For example, in the case of colloids one could obtain a Raman spectrum of adsorbate molecules.
only. The intensities and frequencies are compared with a spectrum of adsorbate with metal. Both solutions are run with identical conditions.
CHAPTER 4: POLARIZATION TECHNIQUES IN RAMAN SPECTROSCOPY

Nomenclature, Definition of Laboratory, Substrate and Molecular Coordinates

Three sets of cartesian coordinates must be considered in order to develop the theory for polarization ratios of phthalocyanines. The laboratory coordinates are given in figure 4 showing the laser and collection of scattered light. The incident laser line is always along the positive Z-axis, while scattered light is collected along the X-axis. The angle $\beta$ is defined as the angle the laser beam makes with the normal to the substrate. Therefore, the ZX plane is the incident and scattering plane.

The electric field of the laser beam is perpendicular to the direction of propagation. The two possible polarizations of the incident laser beam are X and Y. An analyzer placed after the sample has two positions allowing either X or Y polarizations to pass. A scrambler depolarizes light before it enters the monochromator. Since the laser beam has two positions and the analyzer has two positions, there are four polarizations of scattered light that can be measured and these are shown in figure 5.

The notation used here for polarized spectra in terms of Porto's notation is:

$$Z(YY)X = SS$$
$$Z(YZ)X = SP$$
$$Z(XY)X = PS$$
$$Z(XZ)X = PP$$
Figure 4. a) Laboratory coordinates showing the incident laser beam along the Z-axis and collection of scattered light at 90° along the X-axis. The angle between the laser beam and the normal to the substrate (C-axis) is the β angle. The Y-axis goes into the plane of the paper. b) Substrate coordinates. Substrate and laboratory have a common Y-axis. The substrate can be experimentally rotated by β about the Y-axis. c) Molecular coordinates. Phthalocyanine skeleton shown. z-axis out of the plane of the paper.
FIGURE 4

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Figure 5. Four polarizations of laser light obtained by two positions of the rotator on the laser and an analyzer after the sample. Propagation of the laser beam along the Z-axis, collection along the X-axis.
FIGURE 5

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The first letter indicates the direction of propagation of the laser beam (Z) while the second letter is the polarization of the laser beam. The third letter gives the polarization of light passed by the analyzer. The last letter (X) describes the collection direction.

The symbols S and P are also used to describe polarized light. S represents an electric field perpendicular to the scattering plane and P is parallel. One letter gives the incident laser beam polarization, the other the analyzer.

The second set of coordinates (x', y', z') is related to the glass substrate and is shown in figure 4. The Y-axis is the same as in the case of lab coordinates. Figure 4 also gives the molecular coordinates which provide the third cartesian set. x and y axes are in the molecular plane and z is along the C₄ axis of metallated phthalocyanines.

Random-orientation versus oriented films and polarization values

Amorphous or randomly oriented films give polarization ratios similar to liquids. However, oriented "crystal-like" films behave quite differently. Specific components of the polarizability tensor can be probed with the appropriate polarized radiation. Let us first consider the case of random orientation. The molecular axes were described by x, y, z and the laboratory coordinates by X, Y, Z. The average of the squares of the polarizability derivative tensor components must be calculated for all possible molecular orient-
tations relative to the laboratory coordinate system. The Raman intensities depend only on two parameters, the mean polarizability $\alpha$ and the anisotropy $\gamma^2$.

Expressions for the mean polarizability $\alpha$ and the anisotropy $\gamma$ are:

$$\alpha = \frac{1}{3} (\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \quad (4.1)$$

$$\gamma = \frac{1}{2} \left[ (\alpha_{xx}-\alpha_{yy})^2 + (\alpha_{yy}-\alpha_{zz})^2 + (\alpha_{zz}-\alpha_{xx})^2 \right] \quad (4.2)$$

The depolarization ratio $\rho$ or $SP/SS$ is given by:

$$\rho = \frac{3(\gamma)^2}{45(\alpha)^2+4(\gamma)^2} \quad (4.3)$$

An example of randomly oriented molecules would be carbon tetrachloride liquid. The minimum value of $\rho=0$ would occur for the totally symmetric vibration at 459 cm$^{-1}$ and only polarized radiation is scattered with $\gamma=0$. A maximum of $\rho=3/4$ is expected for a depolarized band such as 218 cm$^{-1}$ with $\alpha=0$.

Expression (4.3) does not hold for materials with preferred molecular orientations. The most ordered system would be a single crystal. Raman depolarization ratios have supplied information concerning the short-range order in liquid crystals$^3-6$. Silver tetracyanoquinodimethane (AgTCNQ) films have been prepared by vapor deposition of alternating layers of metal and TCNQ followed by heating to 100$^\circ$C$^7$. Raman polarization results indicated the
TCNQ units were oriented at approximately 45° to the substrate but domains were not oriented with respect to each other\textsuperscript{7}.

Electron micrographs have shown block-like crystallites in AlPcCl, GaPcCl and InPcCl films\textsuperscript{8}. These trivalent phthalocyanines have a preferred orientation that can be probed using Raman polarization techniques. The next section derives polarization expressions for compounds of $C_4v$ molecular symmetry. Information can be obtained about the angle the Pc stacks make with the substrate. Experimentally one can vary the angle the laser beam makes with the substrate and the polarizations of light.

**Transformations from molecular coordinates to laboratory coordinates**

The purpose of considering the transformation of cartesian coordinates is to convert from molecular coordinates to substrate coordinates. Once the substrate system is established, a transformation to laboratory coordinates is required. Theoretical expressions for polarization ratios $SP/SS$, $PS/SS$ and $PP/SS$ can be obtained.

Transformation from one set of coordinates to another is obtained by three successive rotations involving three Euler angles illustrated in figure 6. Right-handed coordinate systems are used which is also the convention adopted by Goldstein\textsuperscript{9}.

The first step in the calculations is to transform from molecular to substrate coordinates. A counterclockwise rotation
Figure 6. Transformation from cartesian coordinates \(x,y,z\) to \(x',y',z'\) by three successive rotations involving Euler angles \(\phi, \theta, \psi\). a) rotation by \(\phi\) about \(z\)-axis. b) rotation by \(\theta\) about \(\xi\)-axis. c) rotation by \(\psi\) about \(\xi'\) axis.
FIGURE 6
about the z-axis by the angle \( \phi \) transforms from \( x,y,z \) to \( \xi,\eta,\zeta \) and is described as:
\[
\xi = Dx \quad (4.4)
\]
\( \xi \) and \( x \) are column matrices while \( D \) is a \( 3 \times 3 \) matrix.

The next rotation is about the \( \xi \) axis by the angle \( \theta \) to go from axes \( \xi,\eta,\zeta \) to \( \xi',\eta',\zeta' \):
\[
\xi' = \mathbf{C}\xi \quad (4.5)
\]
The final rotation about \( \zeta' \) by \( \psi \) converts \( \xi',\eta',\zeta' \) to \( x',y',z' \):
\[
x' = B\xi' \quad (4.6)
\]
The three successive rotations can be described by:
\[
A = BCD \quad (4.7)
\]
The column matix \( x_s \) describes substrate coordinates and the molecular coordinates are given by \( x_m \). The transformation from molecular to substrate coordinates is:
\[
x'_s = Ax_m \quad (4.8)
\]
According to Goldstein\(^9\), the product matrix \( A \) is:
\[
\begin{vmatrix}
\cos\psi\cos\phi & \cos\psi\sin\phi & \sin\psi\sin\theta \\
-cos\theta\sin\phi\sin\psi & +cos\theta\cos\phi\sin\psi & \\
-sin\psi\cos\phi & -sin\psi\sin\phi & cos\phi\sin\theta \\
-cos\theta\sin\phi\cos\psi & +cos\theta\cos\phi\cos\psi & \\
-sin\theta\sin\phi & -sin\theta\cos\phi & cos\theta
\end{vmatrix} = A
\]
The polarizability component will be transformed according to:
\[
\alpha'_s = A\alpha_m A^{-1} \quad (4.9)
\]
\( A^{-1} \) is the symbol for the transpose matrix. The angle \( \phi \) represents a rotation about the \( z \) molecular axis and is set equal to zero in this particular problem. The molecular-substrate
angle is given by $\theta$, representing the angle between $z_\text{S}$ and $z_\text{M}$ axes. If $\theta=0^\circ$, the molecule is flat on the substrate. $\theta=90^\circ$ indicates a perpendicular stacking to the substrate. Finally the $\psi$ angle should be averaged between 0 and $2\pi$. The transformation $A$ is reduced to:

$$
\begin{pmatrix}
\cos\psi & \cos\theta \sin\psi & \sin\psi \sin\theta \\
-\sin\psi & \cos\theta \cos\psi & \cos\psi \sin\theta \\
0 & -\sin\theta & \cos\theta \\
\end{pmatrix}
= A
$$

The second transformation is from substrate to experimental coordinates:

$$
x_L = T x_S \quad (4.10)
$$

The glass slide containing the thin film is located on the $yz$ plane, with the laser beam along the $z$ direction and observation is along the $x$ axis. Therefore, the transformation is reduced to a counterclockwise rotation about the $y$ axis. In this case:

$$
\begin{pmatrix}
\cos\beta & 0 & \sin\beta \\
0 & 0 & 0 \\
-\sin\beta & 0 & \cos\beta \\
\end{pmatrix}
= T
$$

The polarizability components are finally obtained from the relation:

$$
\alpha_L = T \alpha_S T^{-1} \quad (4.11)
$$

Experimentally, spectra can be recorded for different values of the angle $\beta$. Specific expressions are obtained for the average of the squared polarizability derivatives of each symmetry type as a function of the angle $\beta$ (laser beam-normal to the surface of slide) and $\theta$ (molecular-substrate angle). In particular equa-
tions were derived for \( \alpha^{2}_{YY} \), \( \alpha^{2}_{YZ} \), \( \alpha^{2}_{XZ} \) and \( \alpha^{2}_{XY} \) which correspond to polarized spectra SS, SP, PP and PS respectively. For all symmetry type vibrations the \( \alpha^{2}_{YY} \) expression is only a function of the \( \theta \) angle. This indicates that the SS spectrum should remain unaffected by changes in the experimental geometry (\( \beta \) angle).

\( A_{1}(A'_{1}) \) type vibrations:

According to Loudon\(^{10}\) the diagonal tensor of \( A_{1} \) type vibrations has \( \alpha_{XX} = \alpha_{YY} = a \) and \( \alpha_{ZZ} = b \). Conventionally the \( z \) axis is chosen along the \( C_{4} \) symmetry element. It is reasonable to assume that \( a > b \) for this nearly planar molecule, and for practical considerations we take \( b = 0 \).

Results for \( A_{1}(A'_{1}) \) type vibrations going from molecular to laboratory coordinates follow. Expressions are obtained for SS, SP, PP and PS polarizations.

For \( A_{1}(A'_{1}) \) type vibrations\(^{10}\):

\[
\begin{pmatrix}
a & 0 & 0 \\
0 & a & 0 \\
0 & 0 & 0 \\
\end{pmatrix} = \alpha_{m}
\]
Using equation 4.11, one determines the laboratory values for $\alpha_{XY}$, $\alpha_{YY}$, $\alpha_{XZ}$ and $\alpha_{YZ}$. The calculated average of the squared polarizability derivatives are given:

\[
PS = <\alpha^2_{XY}> = \frac{1}{4} a^2 \cos^2 \beta (1 + \cos^4 \theta - 2 \cos^2 \theta)
+ \frac{1}{2} a^2 \sin^2 \beta \sin^2 \theta \cos^2 \theta
\]  
\[\text{(4.12)}\]

\[
SS = <\alpha^2_{YY}> = \frac{3}{8} a^2 + \frac{1}{2} a^2 \cos^2 \theta + \frac{3}{8} a^2 \cos^4 \theta
\]  
\[\text{(4.13)}\]

\[
PP = <\alpha^2_{XZ}> = \frac{1}{2} a^2 \sin^2 \theta \cos^2 \theta \left(\sin^4 \beta + \cos^4 \beta\right) + a^2 \sin^2 \beta \cos^2 \beta \left(\frac{3}{8} + \sin^4 \theta\right)
+ \frac{3}{8} \cos^4 \theta + \frac{1}{2} \cos^2 \theta - \sin^2 \theta - 2 \sin^2 \theta \cos^2 \theta
\]  
\[\text{(4.14)}\]

\[
SP = <\alpha^2_{YZ}> = \sin^2 \beta \left(\frac{1}{4} a^2 + \frac{1}{4} a^2 \cos^4 \theta - \frac{1}{2} a^2 \cos^2 \theta\right)
+ \frac{1}{2} a^2 \cos^2 \theta \sin^2 \theta \cos^2 \theta
\]  
\[\text{(4.15)}\]
The SS = $<\alpha^2_{YY}>$ expression is only a function of $\theta$ angle therefore, the SS spectrum should be unaffected by changes in experimental geometry ($\beta$ angle). The SS spectrum for $A_g$ would have a maximum intensity when $\theta = 0^\circ$ and a minimum for $\theta = 90^\circ$.

$B_g$ type vibrations:

The molecular polarizability tensor for $B_g$ type vibrations is

\[
\begin{pmatrix}
  c & 0 & 0 \\
  0 & -c & 0 \\
  0 & 0 & 0
\end{pmatrix}
\]

$\alpha_m$

\[
\begin{align*}
PS = <\alpha^2_{XY}> &= c^2 \cos^2 \beta (1/4 + 1/2 \cos^2 \theta + 1/4 \cos^4 \theta) \\
&+ 1/2 c^2 \cos^2 \theta \sin^2 \theta \sin^2 \beta & (4.16)
\end{align*}
\]

\[
SS = <\alpha^2_{YY}> = c^2 (3/8 - 1/2 \cos^2 \theta + 3/8 \cos^4 \theta) & (4.17)
\]

\[
\begin{align*}
PP = <\alpha^2_{XZ}> &= c^2 \cos^2 \beta \sin^2 \beta (3/8 + 3/8 \cos^4 \theta + \sin^4 \theta - 1/2 \cos^2 \theta \\
&+ \sin^2 \theta - 2 \sin^2 \theta \cos^2 \theta + 1/2 c^2 \sin^2 \theta \cos^2 \theta (\sin^4 \beta + \cos^4 \beta)) \\
& (4.18)
\end{align*}
\]
\[ SP = \langle \alpha_{YZ}^2 \rangle = c^2 \sin^2 \beta \quad (4.19) \]

\textbf{B}_2 \text{ type vibrations:}

The molecular polarizability tensor and equations for the average of the squared polarizability derivatives for B\textsubscript{2} vibrations are:

\[
\begin{bmatrix}
0 & d & 0 \\
d & 0 & 0 \\
0 & 0 & 0
\end{bmatrix}
= \alpha_m
\]

\[ PS = \langle \alpha_{XY}^2 \rangle = d^2 (1/4 \cos \theta \cos^2 \beta + 1/2 \sin^2 \beta \sin^2 \theta) \quad (4.20) \]

\[ SS = \langle \alpha_{YY}^2 \rangle = d^2 \cos^2 \theta \quad (4.21) \]

\[ PP = \langle \alpha_{XZ}^2 \rangle = 1/2 d^2 \sin^2 \theta (\sin^2 \beta + \cos^2 \beta) + d^2 \sin^2 \beta \cos^2 \beta (\cos^2 \theta - \sin^2 \theta) \quad (4.22) \]

\[ SP = \langle \alpha_{YZ}^2 \rangle = d^2 (1/4 \sin^2 \beta \cos^2 \theta + 1/2 \sin^2 \theta \cos^2 \beta) \quad (4.23) \]
$E_x$ type vibrations:

The molecular polarizability tensor $\alpha$ and equations for the average of the squared polarizability derivatives:

\[
\begin{bmatrix}
0 & 0 & e \\
0 & 0 & 0 \\
e & 0 & 0 \\
\end{bmatrix}
= \alpha_m
\]

PS = $<\alpha_{XY}^2>$ = $e^2(1/4 \sin^2 \theta \cos^2 \beta + 1/2 \sin^2 \beta \cos^2 \theta)$ \hspace{1cm} (4.24)

SS = $<\alpha_{YY}^2>$ = $e^2 \sin^2 \theta$ \hspace{1cm} (4.25)

PP = $<\alpha_{XZ}^2>$ = $e^2 \sin^2 \beta \cos^2 \beta + 1/2 e^2 \cos^2 \theta (\sin^4 \beta + \cos^4 \beta)$ \hspace{1cm} (4.26)

SP = $<\alpha_{YZ}^2>$ = $e^2(1/2 \cos^2 \beta \cos^2 \theta - 1/4 \sin^2 \theta \sin^2 \beta)$ \hspace{1cm} (4.27)

$E_y$ type vibrations:

The molecular polarizability tensor $\alpha$ and the equations for the average of the squared polarizability derivatives follow:

\[
\begin{bmatrix}
0 & 0 & 0 \\
0 & 0 & e \\
e & e & 0 \\
\end{bmatrix}
= \alpha_m
\]
Expressions have been derived for various symmetry types of a $C_{4v}$ molecule; $A_1(A_{1g})$, $B_1(B_{1g})$, $B_2$, $E_x$ and $E_y$. For each symmetry type, the four laboratory expressions were given; $SS,SP,PP$ and $PS$. For all symmetry type vibrations, the SS expression is only a function of the $\theta$ angle. The SS spectrum should remain unaffected by changes in the experimental geometry ($\beta$ angle). Experimentally relative intensities are remarkably constant for different values of the $\beta$ angle ($45^0, 60^0$ and $75^0$).

$A_1(A_{1g})$ type vibrations. The SS spectrum of $A_1$ would have a maximum intensity when the molecular-substrate angle equals zero and a minimum intensity for $\theta=90^0$. If the molecules were flat on the
surface ($\theta=0$), there would be zero intensity for $A_I$ types in the SP and PS spectra. The depolarization ratios $SP/SS$ and $PS/SS$ have maximum values (0.66) for $\theta=90^\circ$. Measurements of all depolarization ratios with three different experimental geometries for typical $A_I$ type vibrations (macrocycle breathing at 671 cm$^{-1}$, pyrrole stretching at 1338 and 1503 cm$^{-1}$) agree well with these findings. Experimental measurements for the 1338 cm$^{-1}$ vibration of InPcCl (200nm film on corning glass) indicate molecular stacks with $\theta=75^\circ$.

$B_1$, $B_2$ and $E$ type vibrations. Calculations show all three depolarization ratios can be found with values greater than 0.7. For instance, for $SP/SS$ and $PS/SS$ ratios of $B_I$ species a maximum of four could be observed in the case of a perfectly oriented film. The $PP/SS$ ratio should reach a maximum value of 1.58. Figure 7 gives the calculated depolarization ratio $PP/SS$ versus experimental angle for $B_I$ type and three stacking angles ($\theta=30, 55, 80^\circ$). Figure 8 presents the $PP/SS$ depolarization ratio versus stacking angle $\theta$ for three experimental $\beta$ angles.

Some examples of how polarization ratios can be used to assign vibrations follow. For a 200nm film of AlPcCl on NaCl, the resonance Raman spectrum has bands at 1525 cm$^{-1}$ and 1541 cm$^{-1}$. Recall, totally and non-totally symmetric bands can appear in resonance Raman spectra.
The NR spectra show 1541 cm$^{-1}$ as the predominant signal. The polarization ratio SP/SS is about 0.1 for the 1541 cm$^{-1}$ band but 0.7 for the 1525 cm$^{-1}$ band. Polarization ratio calculations for a C$_{4v}$ molecule indicate the polarization ratio for an A$_{1}$ type vibration should not exceed 0.66. All polarization ratio measurements for the 1541 cm$^{-1}$ band support its assignment as A$_{1}$. The 1525 cm$^{-1}$ band would be B$_{1}$, B$_{2}$ or E. Polarization ratios of Raman bands measured for a film grown on quartz are given in table 4.1.

Differences in relative intensities between the two bands 1525 cm$^{-1}$ and 1541 cm$^{-1}$ can now be explained. The intensity of an A$_{1}$ vibration in the SS spectrum is independent of the experimental angle $\beta$ but a function of the molecular-substrate angle $\theta$, with a maximum intensity at $\theta=0^\circ$ and a minimum value at $\theta=90^\circ$. Therefore, the low intensity of the 1541 cm$^{-1}$ band in the NaCl sample could be correlated with an angle $\theta$ close to a right angle. According to the data for polarization ratios the 1525 cm$^{-1}$ band can be assigned to a B$_{1}$ symmetry type.

The assignment of other observed fundamentals can be advanced by comparing results from RS, RRs and the infrared spectra of the film on NaCl substrate. For instance, the Raman band at 752 cm$^{-1}$ is seen in the SP, PS and PP spectra only, indicating that it could be a B$_{1}$, B$_{2}$ or E type vibration. Since this frequency is also seen in the i.r. it can be assigned to an E representation (A$_{1}$ and E only are
i.r. active). Similarly, the 785cm$^{-1}$ band with PR higher than 1, and also active in the i.r. spectra, could be assigned to an E symmetry type. Molecular vibrations that were assigned to the $A_g$ representation (see table 1) can be active in both RS and i.r.. However, they are not seen in the i.r. spectra, indicating that the change in dipole moment with these modes is negligible, instead these vibrations produce a significant change of the molecular polarizability.
Figure 7 Calculated PP/SS polarization ratio curves for experimental angle $\beta=0$ to $90^\circ$ and molecular-substrate stacking angle $\theta=30^\circ, 55^\circ$ and $80^\circ$ for $B_j$ symmetry type of a $C_{4v}$ molecule.
Figure 8  PP/SS polarization ratio curves for molecular-substrate angle $\theta = 0$ to $90^\circ$ and experimental angle $\beta = 45^\circ$, $60^\circ$ and $75^\circ$ for $B_1$ symmetry.
Figure 9  Normal Raman PS and SS spectra for a 200nm film of AlPcCl on quartz.
### Table 4-1
Polarization ratios measured on a 200nm film of AlPcCl

<table>
<thead>
<tr>
<th>Wavenumbers</th>
<th>514.5nm</th>
<th>488nm</th>
<th>Interpretation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PS/SS</td>
<td>PP/SS</td>
<td>PS/SS</td>
</tr>
<tr>
<td>559 (16)</td>
<td>0.5</td>
<td>0.5</td>
<td>-</td>
</tr>
<tr>
<td>591 (70)</td>
<td>0.1</td>
<td>0.5</td>
<td>0.1</td>
</tr>
<tr>
<td>681 (93)</td>
<td>0.1</td>
<td>0.6</td>
<td>0.1</td>
</tr>
<tr>
<td>752 -</td>
<td>$\infty$</td>
<td>$\infty$</td>
<td>$\infty$</td>
</tr>
<tr>
<td>785 (30)</td>
<td>0.6</td>
<td>3.7</td>
<td>1.4</td>
</tr>
<tr>
<td>831 (55)</td>
<td>0.2</td>
<td>0.5</td>
<td>-</td>
</tr>
<tr>
<td>1009 (14)</td>
<td>-</td>
<td>0.4</td>
<td>-</td>
</tr>
<tr>
<td>1038 (11)</td>
<td>0.8</td>
<td>0.4</td>
<td>1.2</td>
</tr>
<tr>
<td>1063 -</td>
<td>$\infty$</td>
<td>$\infty$</td>
<td>$\infty$</td>
</tr>
<tr>
<td>1107 (14)</td>
<td>0.9</td>
<td>0.9</td>
<td>1.2</td>
</tr>
<tr>
<td>1131 (11)</td>
<td>0.2</td>
<td>0.5</td>
<td>-</td>
</tr>
<tr>
<td>1147 (7)</td>
<td>1.0</td>
<td>0.8</td>
<td>-</td>
</tr>
<tr>
<td>1169 (8)</td>
<td>-</td>
<td>0.7</td>
<td>-</td>
</tr>
<tr>
<td>1191 (14)</td>
<td>0.7</td>
<td>0.5</td>
<td>0.7</td>
</tr>
<tr>
<td>1212 (9)</td>
<td>0.5</td>
<td>0.6</td>
<td>0.8</td>
</tr>
<tr>
<td>1303 (9)</td>
<td>0.6</td>
<td>0.5</td>
<td>0.9</td>
</tr>
<tr>
<td>1339 (100)</td>
<td>0.2</td>
<td>0.6</td>
<td>0.1</td>
</tr>
<tr>
<td>1407 (17)</td>
<td>-</td>
<td>0.4</td>
<td>-</td>
</tr>
<tr>
<td>1425 (28)</td>
<td>0.2</td>
<td>0.4</td>
<td>0.1</td>
</tr>
<tr>
<td>1450 (14)</td>
<td>-</td>
<td>0.5</td>
<td>-</td>
</tr>
<tr>
<td>1501 (10)</td>
<td>2.5</td>
<td>0.7</td>
<td>1.6</td>
</tr>
<tr>
<td>1525 (27)</td>
<td>0.7</td>
<td>0.9</td>
<td>0.7</td>
</tr>
<tr>
<td>1543 (71)</td>
<td>0.1</td>
<td>0.6</td>
<td>0.1</td>
</tr>
<tr>
<td>1598 (34)</td>
<td>0.3</td>
<td>0.5</td>
<td>0.3</td>
</tr>
<tr>
<td>1612 (19)</td>
<td>0.9</td>
<td>0.6</td>
<td>-</td>
</tr>
</tbody>
</table>

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CHAPTER 5: LANGMUIR-BLODGETT FILMS

Introduction

Early work (1930's) concerning the preparation of monolayer films on solid substrates was carried out by Irving Langmuir and Kathleen Blodgett of General Electric\textsuperscript{1-4}. Presently, there is renewed interest in Langmuir-Blodgett (LB) films\textsuperscript{5-23} with possible applications as solar cells, gas sensors, superconductors, magnetic storage media, biological sensors and as microelectronic components.

The LB technique in many cases, allows one to assemble monolayers in a well-defined geometry. Kuhn\textsuperscript{7} has used the phrase "synthetic molecular organize" to describe the preparation of molecules to form a functional unit. Rather than attempting the task of finding systems which self-assemble in solution, the LB approach is favored where layers of different composition can be deposited on one another\textsuperscript{7}.

Our interest in the LB technique has been to prepare a monolayer of (t-bu)\textsubscript{4}H\textsubscript{2}Pc which has been described by Kovacs\textsuperscript{11} and obtain Raman spectra. The main objective was to deposit a monolayer of (t-bu)\textsubscript{4}H\textsubscript{2}Pc on silver and indium island films. Would surface enhanced Raman scattering (SERS) be observed and would frequencies be shifted due to an interaction with the metal? Further, what would happen to the Raman spectra if monolayer spacers were placed between the metal island and the (t-bu)\textsubscript{4}H\textsubscript{2}Pc monolayer?
LB trough, material, solvent and subphase

A schematic diagram of a Langmuir-Blodgett trough is given in figure 10. Usually the molecules to be deposited as LB films have a hydrophilic group and a hydrophobic part but this is not a mandatory prerequisite. Fatty acids have been the subject of numerous LB experiments. Other types of materials such as porphyrins, anthracenes, and phthalocyanines\textsuperscript{10-19} have been prepared as LB films. The molecules are dissolved in an appropriate solvent with a typical concentration being $5 \times 10^{-4}$M for \((t\text{-}bu)_{2}H_{2}Pc^{11}\).

A number of properties of the solvent must be considered. The solvent must dissolve the molecules of interest and be sufficiently volatile to evaporate after drops are placed on the subphase. The solvent should be very pure as any remaining impurities could be incorporated in the LB film. One problem in preparing phthalocyanine LB films has been their lack of solubility in organic solvents. Derivatives have been prepared with various peripheral groups\textsuperscript{10-19}.

Drops of the LB material are placed on the subphase which is usually purified water. The solvent evaporates and the molecules remain on the surface of the water. It can be seen that the LB material must not dissolve in the subphase. The hydrophilic end of the molecule orients so that it is adjacent to the water surface. The hydrophobic or aliphatic region is positioned away from the water. One barrier of the LB trough is fixed while the other
Figure 10. A schematic of a Langmuir-Blodgett trough.
FIGURE 10

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barrier can be motor driven. The barrier is moved until the desired surface pressure is reached. The surface pressure is monitored by the Wilhelmy or Langmuir method. The Wilhelmy method determines the surface tension on a partially immersed plate and the Langmuir method compares the surface tension of a clean part of the substrate and a coated portion of the substrate. It is common to plot the surface pressure against the area occupied by the monolayer on the trough. These plots are called "pressure-area isotherms". A feedback system is required to maintain constant pressure as the LB film is deposited on a substrate.

The dipping assembly can raise or lower a substrate. Its motion must be smooth and different speeds can be selected. Many materials are used as substrates for LB deposition. Clean glass slides are hydrophilic and can be made hydrophobic by depositing a monolayer of arachidic acid. For metal layers, vacuum deposited on clean glass slides, Au, Cu and Ag result in a hydrophobic surface, whereas Al and Pb produce hydrophilic surfaces due to formation of oxides. Subsequent deposition of other monolayers on the metal is possible. LB material can be transferred to a solid substrate at constant pressure in a few ways. X-deposition takes place if the substrate is immersed only. Y-deposition involves immersion followed by withdrawal. Z-deposition requires withdrawal only. Two other less common methods are "touching" and "lifting" of the substrate. The orientation of adjacent monolayers depends on the deposition technique selected.
Specific phthalocyanine LB studies can now be discussed. Yamamoto\textsuperscript{12} prepared LB films of H\textsubscript{2}Pc and observed color changes in aqueous KCl solutions. A comparison of absorption spectra leads one to conclude the film goes from a monomeric structure to a dimeric structure after thermal annealing at 300\textdegree{}C for a few hours. No information was available on the stacking of the H\textsubscript{2}Pc molecules in this film. Yamamoto\textsuperscript{12} concluded that the electrochromic color changes correlate with the degree of molecular association.

Snow and Jarvis\textsuperscript{10} prepared LB films of the type MPcX\textsubscript{4} where M = H\textsubscript{2}, Co, Cu, Ni, Pd, Pt and X represents the cumylphenoxy group \((-\text{O}-(\text{CH}_3)_2-\text{C}_6\text{H}_5)\). The presence of cumylphenoxy peripheral groups improves the solubilities of Pcs in organic solvents. The association of MPcX\textsubscript{4} compounds was studied in solution. Most compounds were dimeric, PbPcX\textsubscript{4} was monomeric and PtPcX\textsubscript{4} displayed the highest degree of association. The packing efficiency of LB monolayers correlated with the size of the Pc aggregate in solution\textsuperscript{10}. The area/molecule at a constant film pressure for dimeric CuPcX\textsubscript{4} was less than the area/molecule for PtPcX\textsubscript{4}.

Barger\textsuperscript{14} also examined LB films of metal-substituted tetracumylphenoxy phthalocyanines MPcX\textsubscript{4} with M = Fe, Co, Ni, Cu, Zn, Pd, Pt and Pb. Other metallated derivatives prepared had pendant groups: phenoxy \((-\text{O}-(\text{C}_6\text{H}_5))\), octadecoxy \((-\text{O}-(\text{CH}_2)_{17}-\text{CH}_3)\)
and neopentoxy (-O-CH₂-C(CH₃)₂-CH₂). Pressure-area isotherms gave small areas compared to the known size of the Pc molecule.

Two conclusions drawn from the data by Barger was that classical monomolecular films were not observed and stacking was likely but the stack axis was not parallel to the plane of the film. In the experiments by Snow more highly associated Pcs gave larger areas/monomer. This observation cannot be explained by simple vertical stacking and Barger suggests a tilting of stacks and variation of tilt angles with different metals.

DiLella prepared tetracumylphenoxy Pc derivatives in 1:1 mixtures with stearyl alcohol. LB monolayers were deposited on Au, Ag and Pd vacuum evaporated films. A high degree of aggregation for LB films was inferred from the electronic spectra. The Raman results of this study will not be discussed in this section but for tetracumylphenoxy cobalt phthalocyanine [CoPc(Cp)₄] on gold, an adsorbate-substrate interaction was apparent. Results are consistent with a stacking of CoPc(Cp)₄ molecules with the bottom member of the stack in contact with the surface.

Roberts worked with LB films of (t-bu)₂ZnPc, (t-bu)₂CuPc, and an asymmetric compound CuPc tris(CH₂NHC₃H₇-isopropylidene). With an appropriate solvent cross-sectional areas were obtained which corresponded to molecules sitting vertically edge-on in the liquid.

Hann performed experiments on (t-bu)₄ZnPc and (t-bu)₄CuPc. A sample
was prepared for electron microscopy (EM) by horizontally lifting a (t-bu)$_4$CuPc monolayer onto an amorphous-carbon coated grid. EM on (t-bu)$_4$CuPc indicated short range order but most of the film was amorphous\textsuperscript{15}. Closest packing of tetra-tert-butyl phthalocyanine molecules is possible if the tert-butyl groups are interleaved\textsuperscript{11,15}.
CHAPTER 6  
EXPERIMENTAL

Vacuum Evaporation

Thin solid films were prepared either by vacuum evaporation or as Langmuir-Blodgett films. A schematic diagram is given in figure 11 of a typical vacuum evaporation system. Three different types of vacuum systems were used: a Varian NRC3115, Balzers and Vacuum Generators DPUHV. The rate of evaporation was 0.5nm for trivalent phthalocyanines (AlPcCl, GaPcCl, InPcCl) monitored with an Inficon XTM quartz crystal oscillator. Total thicknesses were 100nm or 200nm. A typical pressure before evaporation was $1.0 \times 10^{-6}$ torr or lower. A tantalum boat was used to contain the phthalocyanine material.

A number of different substrates have been used for vacuum evaporation. Quartz was preferable for red laser lines as it gave a low background. Other substrate materials were Corning 7059 glass, a cleavage face of NaCl and conductive tin-oxide (NESA) plates from the Pittsburg Glass Company.

Chemicals

The AlPcCl was purchased from Eastman Chemicals. The InPcCl and GaPcCl were provided by C.K. Hsiao and P. Kazmaier respectively of Xerox Research Centre of Canada. The InPcCl and GaPcCl were synthesized by reacting the metal chloride with phthalonitrile in quinoline. The Pcs were purified by the train sublimation procedure.
Figure 11. A schematic of a typical vacuum evaporation system.
Figure 11

Bell Jar

Substrate

Thicknes Monitor

Shutter

Evaporation Source

Diffusion Pump

Liq N₂ Trap

Rotary Pump

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Synthesis of (t-bu)$_4$H$_2$Pc, preparation of monolayers and their characterization have been reported previously$^2$. The purified (t-bu)$_4$H$_2$Pc was supplied by Xerox and was synthesized by refluxing 4-t-butyl phthalonitrile in amyl alcohol with sodium amylate present$^3$ and purification was by acid pasting$^4$. The solution of (t-bu)$_4$H$_2$Pc for spreading on the Langmuir Blodgett trough was $5 \times 10^{-4}$M in Eastman Kodak Reagent ACS Spectro Grade toluene. The water used in the trough was milli-Q followed by another distillation and kept at room temperature. A Fromherz$^5$ trough was used for preparation of the LB films. The trough was enclosed in a cabinet to exclude dust and was on a Terrazzo vibration-free table. The compression speed was 0.06 to 0.15 A$^2$/molecule/second and the lifting of the substrate was done at 3.8mm/min with pressures of 8-10 dynes/cm. The substrate was immersed before spreading the (t-bu)$_4$H$_2$Pc and the film was transferred to the glass on withdrawal. In the case of multilayers, the surface of the water was cleaned and this process repeated.

Mono and multilayer films of (t-bu)$_4$H$_2$Pc were deposited on the corning slides. Metal island films of silver and indium were deposited on corning to a thickness of 15nm measured by the quartz crystal thickness monitor at a rate of 0.1nm/sec. Subsequently a LB film of (t-bu)$_4$H$_2$Pc was deposited on the metal slides. One region of the slide had metal plus Pc while another region had Pc only. Absorption spectra were recorded on a HP8450 photodiode array spectrophotometer.
Samples were prepared for spacer studies by first depositing a region of 15nm silver or indium on Corning 7059 glass. The metal island films were then coated with close packed arachidic acid monolayers(s) (0,1,3...) on different regions of the slide. The \((t\text{-}bu)_4H_2Pc\) monolayer was then deposited on top of the arachidic acid. Figure 12 shows the metal islands with a spacer layer of arachidic acid and a phthalocyanine monolayer.

**Raman system**

The microcomputer controlled Raman system used to study the thin films has been described elsewhere. An IBM PC microcomputer was used to drive the stepper motor connected to the two 1800 grooves/mm holographic gratings. The microcomputer also acquired the signals from a Hamatsu R955 multialkali photomultiplier tube followed by conventional photon counting. Two software programs were used, one for data acquisition, another for data manipulation. Polarization measurements were carried out using a polarization rotator (Spectra Physics model 310-21) mounted on the 164 argon and krypton ion lasers. Scattered light was analyzed using a linear polarizer and scrambled before entering the Spex 1403 spectrophotometer. A RG375 dye laser has been used and was pumped by the model 164 argon ion laser. Backscattering Raman spectra were recorded in a Ramanor U-1000 instrument with microscope attachment.

The laser beam propagated along the Z-axis and the angle the laser beam made with the normal to the film was adjusted using the
Figure 12. Cross-sectional schematic view of metal island (modelled as a hemispheroid) coated with one spacer layer of arachidic acid and a phthalocyanine monolayer.
sample holder. The four polarizations (SS, SP, PP, PS) of light were obtained by moving the rotator on the laser and the analyzer. A quartz cell containing BDH spectroscopic grade carbon tetrachloride was used periodically to check the accuracy of Raman frequencies and polarization ratios. A more extensive calibration of the system was occasionally done with a capillary of distilled indene.

There are four slits present in the 1403 monochromator and settings are reported with the spectra. Other details given with the spectra are time delay and laser power. The laser lines used from the argon ion laser had wavelengths of 488.0nm (blue) and 514.5nm (green). A number of laser lines were available from the krypton ion laser and the most commonly used were 568.2nm (yellow), 647.1nm (red) and 676.1nm (red). A solution of rhodamine 6G pumped through the dye laser gave lines tunable over the region 580nm to 620nm.

Infrared spectra of 200nm films of AlPcCl, GaPcCl and InPcCl on NaCl were run using a Nicolet SDX FTIR spectrophotometer. Other substrates were not suitable for IR study. Uv-visible spectra were run on a HP 8450 spectrophotometer.
CHAPTER 7: SPECTRA AND RESULTS

Figures 13 to 15 are a few of the many spectra obtained for the trivalent Pc films. The laser line was 647.1nm so these are resonance Raman spectra. The assignment of the various bands follows in Chapter 8. Figures 16 to 18 are the uv-visible spectra for 100nm films of AlPcCl, GaPcCl and InPcCl.

Uv-visible absorption spectra

There are two main bands in the uv-visible region of phthalocyanines. A Soret band is present in the region 300 to 400nm and is associated with a $\pi$ to $\pi^*$ transition of the Pc ring.

The Q-band observed in the region 600 to 800nm is also a $\pi$ to $\pi^*$ transition, can have features from metal to ligand or ligand to metal charge transfer and is sensitive to the molecular environment.

All of the trivalent phthalocyanines (AlPcCl, GaPcCl, InPcCl) are blue in colour and the uv-visible spectra are red-shifted when compared with films of planar divalent Pcs such as CuPc, MgPc and ZnPc. The uv-visible absorption maxima for 100nm evaporated films were 344nm, 751nm (AlPcCl); 375nm, 750nm (GaPcCl) and 369nm, 732nm (InPcCl). Shoulders were also present in these spectra.

A compound which has its absorption bands into the IR is VOPc. Klofta concluded that the Q-band red shift in VOPc, AlPcCl and GaPcCl was due to a slip-stack orientation in the films. As mentioned earlier in the section on structure, the oxyvanadium
Figure 13. Resonance Raman spectrum of 200nm AlPcCl on quartz. Total S polarization, slits 800μm and laser line 647.1nm.
Figure 14. Resonance Raman spectrum of 200nm GaPcCl on quartz. Total S polarization. slits 800µm and laser line 647.1nm.
Figure 15. Resonance Raman spectrum of 200nm InPcCl on quartz. Total s polarization. slits 800μm and laser line 647.1nm.
cation lies above the plane of the four isoindole nitrogens\(^2\). Likewise the metal is displaced from the Pc plane in AlPcCl and GaPcCl\(^4\). The axial chlorine and oxyvanadium cation make cofacial stacking difficult. The bands of a film of AlPcF are not red-shifted like AlPcCl, GaPcCl and InPcCl films compared to planar divalent Pcs. AlPcF absorption bands occur at 328nm and 624nm in a 100nm film. The AlPcF molecules are cofacially aligned with a somewhat ionic structure\(^5\).

A number of Pc films (MgPc, ZnPc, VOPc, AlPcCl, ClAlPcCl and InPcCl) undergo a solvent-induced structural change\(^6,7\). The films have been either dipped in a solvent such as CH\(_2\)Cl\(_2\) or exposed to the vapor in a covered beaker. The solvent-induced changes in the absorption spectra of MPcs are due to molecular stacking changes which occur on dissolution and reorganization. Another way of inducing structural changes in Pc films is by annealing.

Uv-visible absorption spectra provide information concerning the angle Pc molecular stacks make with the substrates. As Pc molecules are stacked like pancakes with the plane of the molecule perpendicular to the substrate, the intensity of the Soret band decreases.

The argon ion laser lines 488.0nm and 514.5nm gave rise to normal Raman (NR) because of the valley in the trivalent Pc absorption spectra. The rhodamine 6G laser lines and the red laser lines of the krypton ion laser excited into the Q-bands of the Pcs.
Figure 16. Uv-visible absorption spectrum of 100nm film of AlPcCl on quartz.
Figure 17. Uv-visible absorption spectrum of 100nm GaPcCl film on quartz.
Figure 18. Uv-visible absorption spectrum of 100nm InPcCl film on quartz.

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A single Langmuir-Blodgett monolayer of (t-bu)$_4$H$_2$Pc is visible to the naked eye and is blue in colour. The absorption spectra have been reported for two LB monolayers of (t-bu)$_4$H$_2$Pc and an evaporated film. The evaporated (t-bu)$_4$H$_2$Pc film can be transformed by annealing to give a similar absorption spectrum to the LB film. The sharpness of the long-wavelength band of the LB film compared to an evaporated film indicated a well-defined ordered structure. There is a Soret band and a red band in the UV-visible absorption spectrum of the LB (t-bu)$_4$H$_2$Pc film. Thus, laser excitation at 488.0nm and 514.5nm was in the region of normal Raman while red laser excitation was in the region of resonance Raman.
DAVYDOV splitting

Figure 19 gives Raman spectra for a 200nm film of GaPcCI. Laser excitations of 488nm and 514.5nm would be in the preresonance region while the 609nm line is in the resonance region. Totally symmetric vibration modes dominate the preresonance region and are also seen in the RR spectrum. Non-totally symmetric vibrations also appear in the RR spectrum by the Herzberg-Teller mechanism. More detail on assignment follows in Chapter 8.

Figures 20 and 21 illustrate how different vibrational bands of InPcCl are observed depending on the polarization of light used. It was noted for trivalent Pcs that a number of Raman bands displayed splitting. For instance, the Raman band of AlPcCl that was observed at 1339cm$^{-1}$ in the SS spectrum using preresonance laser lines (488 and 514.5nm) appeared at 1344cm$^{-1}$ for PS or SP and in resonance Raman spectra. Polarization studies of components with different symmetry properties allow experimental observation of splitting when frequency differences are equal or less than the bandwidth of the Raman band. Nedungadi$^9$ probed intramolecular vibrations of a napthalene crystal using Raman polarization techniques and observed splitting differences of 4 to 5 cm$^{-1}$ for four bands.

The AlPcCl film behaves like a molecular crystal with Davydov (correlation field) splitting of non-degenerate vibrational energy levels of the free molecule. Molecular crystals have weak forces
Figure 19. Preresonance Raman (488 and 514.5nm) and resonance Raman spectra of a 200nm film of GaPcCl.
Figure 20. SP and SS polarized spectra for 200nm InPcCl using 514.5nm laser excitation.

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Figure 21. PS and PP polarized spectra for 200nm InPcCl using 514.5nm laser excitation.
between molecules of the van der Waals type. Davydov\textsuperscript{10} has pointed out that the magnitude and width of splittings is greatest for vibrations which have large changes in the molecular dipole moment. These vibrational frequencies appear in the infrared spectrum. This fact would suggest future work on $Pc$ films or any oriented film could be done using a NaCl substrate with a polarizer inside a high resolution IR spectrophotometer.

Vibrations in molecular crystals are of two types, internal vibrations and external or lattice vibrations. The internal vibrations generally occur in the region 100$\text{cm}^{-1}$ to 3600$\text{cm}^{-1}$ while lattice vibrations appear at low frequencies usually below 200$\text{cm}^{-1}$. We previously observed low frequency vibrations for solid 2,4-dithiobiuret (DTB) and the deuterated derivative DTB-$d_5$\textsuperscript{11}. Translational and rotational frequencies of molecular crystals of DTB are sensitive to changes in temperature and when cooled by liquid nitrogen all frequencies below 200$\text{cm}^{-1}$ shifted to higher values due to a compression of the crystal structure. In some cases, the crystalline lattice influences the internal vibrations, changes selection rules for polarization and splits internal vibrational frequencies\textsuperscript{10}.

Crystal symmetry and group theory are invoked to calculate the symmetry types which are active in Raman spectra. The symmetry of an individual molecule is described by its point group and the
symmetry of an array of molecules (molecular crystal) is given by the space group. The symmetry of a molecule can be changed by placing it in a crystal environment. Site groups contain operations that simultaneously leave the molecule and the crystal unchanged. It is helpful to consult correlation tables for irreducible representations of molecular point groups and crystal site groups.

Molecular crystals of Pc complexes have been found to be monoclinic of factor group $C_{2h}^{5}(P2_1/c)$ or triclinic; factor group $C_{1}^{1}(P1)$\textsuperscript{12}. For PbPc both monoclinic and triclinic forms were identified\textsuperscript{14}.

The number of Davydov components $N(\mu,\nu)$ for a molecular crystal with $m$ molecules per unit cell, factor group symmetry $\mu$ and site group symmetry $\nu$ is given by\textsuperscript{13}:

$$N(\mu,\nu) = \frac{m}{h} \sum \chi_{\mu}(R) \chi_{\nu}(R)$$

where $h$ is the order of the factor group, $\chi_{\mu}(R)$ and $\chi_{\nu}(R)$ are the characters of the irreducible representations $\mu$ and $\nu$ under an operation of the $R$ class of the factor and site group respectively.

Assuming a $C_{4v}$ point group for AlPcCl, a triclinic crystalline system and factor group $C_{1}$, the possible site symmetry is $C_{1}$. Davydov components for two molecules per unit cell are $1A_{g}$ and $1A_{u}$. The $A_{u}$ vibrations are not Raman active so
singlets would be observed. If there were four molecules per unit cell, $2A_g$ Raman active vibrations are suggested. Experimentally, doublets of different symmetries were observed for AlPcCl films. This observation can be best explained by a monoclinic system of factor group $C_{2h}^5(P2_1/c)$ with four molecules per unit cell. The calculated Raman active Davydov components for a $C_1$ site symmetry are $1A_g$ and $1B_g$. Table 7.1 correlates molecular symmetry and factor group with site symmetry. We have published more details concerning Davydov splitting\textsuperscript{13} and the reader is referred to this article for further information.

**TABLE 7.1: GROUP THEORY OF A 200NM ALPCCl FILM WITH FOUR MOLECULES PER UNIT CELL**

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Site</th>
<th>Factor Group</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{4v}$</td>
<td>$C_1$</td>
<td>$C_{2h}$</td>
</tr>
<tr>
<td>23A$_1$</td>
<td></td>
<td>$1A_g$</td>
</tr>
<tr>
<td>19A$_2$</td>
<td></td>
<td>$1B_g$</td>
</tr>
<tr>
<td>21B$_1$</td>
<td></td>
<td>$1A_u$</td>
</tr>
<tr>
<td>21B$_2$</td>
<td></td>
<td>$1B_u$</td>
</tr>
<tr>
<td>42E</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
SERS of tetratertiarybutyl phthalocyanine [(t-bu)$^4H_2$Pc]

We have published results for SERS observed from LB monolayers of (t-bu)$^4H_2$Pc on metal island films$^{15}$ and reported results for the distance dependence of the SERS enhancement factor$^{16}$. The molecules of (t-bu)$^4H_2$Pc as LB films are oriented with their molecular planes perpendicular to the metal surface$^{17}$. The type of interaction of the Pc with the metal was physisorption since Raman frequencies were not shifted from (t-bu)$^4H_2$Pc alone.

Figure 22 is the Raman spectrum of four LB monolayers of (t-bu)$^4H_2$Pc. Figures 23 and 24 show SERS enhancement against the distance of the (t-bu)$^4H_2$Pc from the surface of the metal for silver and indium.

The intensity of the 686cm$^{-1}$ line of (t-bu)$^4H_2$Pc was used to generate these plots. The enhancement factor was calculated by comparing the intensity of the 686cm$^{-1}$ line of a (t-bu)$^4H_2$Pc LB monolayer in the presence of metal to the intensity of the 686cm$^{-1}$ line for a single LB monolayer of (t-bu)$^4H_2$Pc on glass. The results suggest that an electromagnetic mechanism is operating since long range enhancement of signals was observed. Higher enhancements were obtained for Ag than In and greater enhancement in the green (514.5nm) than the red (647.1nm). These results are attributed to differences in the dielectric constant at appropriate frequencies.
Figure 22. Resonance Raman spectrum of four LB monolayers of (t-bu)$_4$H$_2$Pc on corning with laser line 647.1nm.
Figure 23. Enhancement factor versus distance from a Ag surface for a LB monolayer of \((t\text{-}bu)_{4}H_{2}Pc\).
**FIGURE 23**

The graph illustrates the relationship between the number of spacer layers and the distance from the metal surface, showing how the enhancement factor and intensity change as the number of layers increases.
Figure 24. Enhancement factor versus distance from an In surface for a LB monolayer of (t-bu)$_4$H$_2$Pc.
FIGURE 24

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CHAPTER 8:
ASSIGNMENT OF PHTHALOCYANINE VIBRATIONAL BANDS USING MODEL COMPOUNDS

There are a number of small molecules which are similar in structure to the subunits of phthalocyanine. These model compounds are useful in identifying vibrational bands of Pcs. The list of model compounds includes benzene, 1,3-diiminoisoindoline, imidazole, indole(isoindole), pyrrole and porphyrins.

The Raman spectrum has been reported for benzene\(^1\). The most intense band occurs at 992 cm\(^{-1}\) and is a ring breathing mode. This band is polarized, totally symmetric and is due to the in-phase motion of the six carbon atoms. The high Raman intensity arises because of the large deformation of the electron cloud (polarizability). Carbon-hydrogen bending vibrations were observed at 849 cm\(^{-1}\) and 1178 cm\(^{-1}\). Bands at 1326 cm\(^{-1}\), 1585 cm\(^{-1}\) and 1606 cm\(^{-1}\) were attributed to ring stretching. The band at 606 cm\(^{-1}\) is caused by a ring deformation.

The Raman spectrum of solid 1,3-diiminoisoindoline run in our lab is shown in figures 25 and 26. 1,3-diiminoisoindoline can be used as a starting material when synthesizing phthalocyanines\(^2,3\). An interesting feature of 1,3-diiminoisoindoline is the presence of intense bands in the low frequency region where lattice vibrations occur.
Figure 25. Raman spectrum of solid 1,3-diiminoisindoline using a 568.2nm laser line.
Figure 25

1,3-diminoisoindoline solid

LL=568.2 nm

WAVENUMBERS (cm⁻¹)

COUNTS/SEC

<655

80000

354

287

1014

1188

1600

538.0

592.0

1314.0

150.0
Figure 26. Low frequency lattice vibrations of solid 1,3-diimino-isoiindoline using 568.2nm laser line.
Many studies have been carried out yielding IR and Raman results for imidazole$^4$-$^9$. The Raman spectrum from our lab is given in figure 24. According to Cordes$^8$ imidazole has $C_{2v}$ symmetry with equivalent nitrogens and the carbons at 4- and 5-positions. Intermolecular hydrogen bonding in solid imidazole is strong. Imidazole with $C_{2v}$ symmetry should have a total of 9$A_g$, 8$B_g$, 3$A_2$ and 4$B_2$ IR and Raman active modes. Imidazole has a number of bands due to lattice vibrations below 150 cm$^{-1}$.

The Raman spectrum of indole has been run in our lab and was reported in the literature$^{10}$. A large number of bands are present due to the low symmetry of the molecule. No Raman data has been found for isoindole which is unstable.

Raman data has been reported in the literature for pyrrole. Figure 27 is the spectrum of liquid pyrrole obtained in our lab showing SP and SS polarizations. Carbon-hydrogen and nitrogen-hydrogen stretching vibrations are in the region above 3100 cm$^{-1}$. The ring breathing vibration occurs at 1148 cm$^{-1}$ and is very intense. Other ring type vibrations have been assigned$^{11}$ to 1472 cm$^{-1}$, 1416 cm$^{-1}$, 1384 cm$^{-1}$, 883 cm$^{-1}$, 870 cm$^{-1}$,
Figure 27. Raman spectrum of imidazole solid obtained using 608.9nm laser line.
Figure 28. SS & SP polarized Raman spectra of liquid pyrrole.
Figure 28

liquid pyrrole
LL=514.5 nm

COUNTS/SEC

800.0  849  1076
710  869  1049
649  869  1049
1238

WAVENUMBERS (cm⁻¹)

1480 1468
1380
1145>
649 cm\(^{-1}\) and 615 cm\(^{-1}\). The remaining vibrations are carbon-hydrogen bending and out of plane deformations.

Resonance Raman (RR) spectra have been reported with normal coordinate analysis for metallooctaethylporphyrins M(OEPs)\(^{12-14}\). These porphyrins are useful for assigning phthalocyanine bands because they lack benzene rings. The phthalocyanines have four bridging aza groups (-N=) while M(OEPs) have bridging methine groups (-CH=). A large number of Raman studies have been done on metallo-porphyrins including chlorophylls and heme proteins\(^{15-19}\).

Tables have been prepared from our Raman data\(^{20-25}\) and that of others\(^{26-28}\) summarizing frequencies of phthalocyanine vibrations. Table 8.1 compares Raman frequencies for macrocycle breathing and stretching vibrations. Recall the macrocycle is the inner ring of sixteen alternating carbon and nitrogen atoms. Analogous porphyrin frequencies are also listed in the table. The breathing vibration at approximately 680 cm\(^{-1}\) in phthalocyanines is a totally symmetric \(A_g\) vibration. The 720 cm\(^{-1}\) band is a \(B_{1g}\) mode which increases in intensity as the laser line approaches resonance.
TABLE 8.1: A COMPARISON OF MACROCYCLE RAMAN FREQUENCIES FOR VARIOUS PHThALOCYANINES

<table>
<thead>
<tr>
<th></th>
<th>Macrocycle Breathing (cm$^{-1}$)</th>
<th>Macrocycle Stretching (cm$^{-1}$)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Porphyrin</td>
<td>670</td>
<td>---</td>
<td>751</td>
</tr>
<tr>
<td>$\alpha$ - H$_2$Pc</td>
<td>682</td>
<td>720</td>
<td>---</td>
</tr>
<tr>
<td>$\beta$ - H$_2$Pc</td>
<td>678</td>
<td>720</td>
<td>---</td>
</tr>
<tr>
<td>$\chi$-H$_2$Pc</td>
<td>678</td>
<td>720</td>
<td>---</td>
</tr>
<tr>
<td>VOPc</td>
<td>681</td>
<td>723</td>
<td>747</td>
</tr>
<tr>
<td>MgPc</td>
<td>682</td>
<td>---</td>
<td>744</td>
</tr>
<tr>
<td>CuPc</td>
<td>678</td>
<td>---</td>
<td>743</td>
</tr>
<tr>
<td>ZnPc</td>
<td>678</td>
<td>---</td>
<td>748</td>
</tr>
<tr>
<td>SnPc</td>
<td>680</td>
<td>722</td>
<td>749</td>
</tr>
<tr>
<td>PbPc</td>
<td>672</td>
<td>---</td>
<td>744</td>
</tr>
<tr>
<td>(t-bu)$_4$H$_2$Pc</td>
<td>682</td>
<td>723</td>
<td>745</td>
</tr>
<tr>
<td>AlPcCl</td>
<td>678</td>
<td>---</td>
<td>752</td>
</tr>
<tr>
<td>GaPcCl</td>
<td>678</td>
<td>719</td>
<td>750</td>
</tr>
<tr>
<td>InPcCl</td>
<td>671</td>
<td>---</td>
<td>747</td>
</tr>
<tr>
<td>FePc</td>
<td>683</td>
<td>---</td>
<td>755</td>
</tr>
<tr>
<td>PtPc</td>
<td>679</td>
<td>---</td>
<td>755</td>
</tr>
<tr>
<td>PdPc</td>
<td>679</td>
<td>---</td>
<td>755</td>
</tr>
</tbody>
</table>

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Pyrrole rings move in and out of phase. In general, totally symmetric modes prevail in normal Raman (off-resonance) while non-totally symmetric modes can be more noticeable in RR spectra. The Pc band at 796 cm\(^{-1}\) is the analog of the 795 cm\(^{-1}\) porphyrin band\(^{14}\).

Table 8.2 compares Pc Raman frequencies for vibrations associated with pyrrole subunits. The ring breathing mode of pyrrole\(^{11}\) itself appears at 1148 cm\(^{-1}\). The frequencies for Pcs are remarkably constant at 1141 +/- 5 cm\(^{-1}\). A ring stretching mode of pyrrole occurs at 1384 cm\(^{-1}\). With the exception of \((t\text{-}bu)_{4}\text{H}_{2}\text{Pc}\), this pyrrole stretching mode is present at 1340 +/- 3 cm\(^{-1}\) in phthalocyanines. The 1384 cm\(^{-1}\) pyrrole band is due mainly to C\(\alpha\)-C\(\beta\) stretching and is observed in other model compounds, isoindole\(^{10}\) (1352 cm\(^{-1}\)) and Ni(OEP)\(^{13}\) (1383 cm\(^{-1}\)). The CN stretching mode in pyrrole is observed at 1530 cm\(^{-1}\). The band at 1513 cm\(^{-1}\) has been assigned to CN pyrrole stretching in \(H_{2}\text{Pc}\)\(^{20}\). DiLella\(^{29}\) has observed Raman vibrations with a large degree of pyrrole CN stretching character for tetracumylphenoxy phthalocyanine \([\text{Pc(Cp)}_{4}]\) Langmuir-Blodgett derivatives \(\text{PbPc(Cp)}_{4}\) (1530 cm\(^{-1}\)), \(\text{CuPc(Cp)}_{4}\) (1530 cm\(^{-1}\)) and \(\text{NiPc(Cp)}_{4}\) (1555 cm\(^{-1}\)).
TABLE 8.2: A COMPARISON OF PYRROLE RAMAN FREQUENCIES FOR VARIOUS PHTHALOCYANINES

<table>
<thead>
<tr>
<th></th>
<th>Ring Breathing (cm⁻¹)</th>
<th>Ring Stretching (cm⁻¹)</th>
<th>CN Pyrrole Stretching (cm⁻¹)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrrole</td>
<td>1148</td>
<td>1384</td>
<td>1530</td>
<td>11</td>
</tr>
<tr>
<td>α - H₂Pc</td>
<td>1140</td>
<td>1337</td>
<td>1513</td>
<td>20</td>
</tr>
<tr>
<td>β - H₂Pc</td>
<td>1138</td>
<td>1337</td>
<td>1513</td>
<td>20</td>
</tr>
<tr>
<td>x-H₂Pc</td>
<td>1140</td>
<td>1337</td>
<td>1513</td>
<td>20</td>
</tr>
<tr>
<td>VOPc</td>
<td>1140</td>
<td>1340</td>
<td>1527</td>
<td>21</td>
</tr>
<tr>
<td>MgPc</td>
<td>1141</td>
<td>1340</td>
<td>1506</td>
<td>22</td>
</tr>
<tr>
<td>CuPc</td>
<td>1140</td>
<td>1341</td>
<td>----</td>
<td>22</td>
</tr>
<tr>
<td>ZnPc</td>
<td>1143</td>
<td>1341</td>
<td>1512</td>
<td>22</td>
</tr>
<tr>
<td>SnPc</td>
<td>1141</td>
<td>1342</td>
<td>1513&amp;1519</td>
<td>24</td>
</tr>
<tr>
<td>PbPc</td>
<td>1137</td>
<td>1337</td>
<td>1505</td>
<td>24</td>
</tr>
<tr>
<td>(t-bu)₄H₂Pc</td>
<td>---</td>
<td>1330</td>
<td>1520</td>
<td>23</td>
</tr>
<tr>
<td>AlPcCl</td>
<td>1147</td>
<td>1343</td>
<td>----</td>
<td>25</td>
</tr>
<tr>
<td>GaPcCl</td>
<td>1147</td>
<td>1341</td>
<td>----</td>
<td>25</td>
</tr>
<tr>
<td>InPcCl</td>
<td>1142</td>
<td>1340</td>
<td>1497</td>
<td>25</td>
</tr>
<tr>
<td>FePc</td>
<td>1147</td>
<td>1343</td>
<td>----</td>
<td>26</td>
</tr>
<tr>
<td>PtPc</td>
<td>1145</td>
<td>1343</td>
<td>----</td>
<td>27</td>
</tr>
<tr>
<td>PdPc</td>
<td>1146</td>
<td>1338</td>
<td>----</td>
<td>28</td>
</tr>
</tbody>
</table>
Table 8.3 compares Raman frequencies of Pc vibrations associated with isoindole ring stretching. The band at 1534 cm\(^{-1}\) arises from C-C stretching of the bond common to pyrrole and benzene rings of isoindole groups. This band is absent in Ni(OEP) because this porphyrin does not have benzene ring. Other isoindole stretching vibrations appear at 1406 cm\(^{-1}\), 1428 cm\(^{-1}\) and 1450 cm\(^{-1}\) in H\(_2\)Pc\(^{20}\). The molecule indole \(^{10}\) has Raman bands at 1412 cm\(^{-1}\), 1455 cm\(^{-1}\) and 1487 cm\(^{-1}\).

Three Raman vibrations associated with benzene subunits of Pcs are summarized in table 8.4. Benzene\(^{1}\) itself has Raman bands at 606 cm\(^{-1}\), 1585 cm\(^{-1}\) and 1606 cm\(^{-1}\). Excitation profiles exhibit a steep side toward higher frequencies for H\(_2\)Pc 571 cm\(^{-1}\) and 1618 cm\(^{-1}\) bands\(^{20}\). The benzene groups are largely responsible for the electronic Soret band.

Carbon-hydrogen deformations occur in the range 1000 cm\(^{-1}\) to 1350 cm\(^{-1}\). The Raman bands for Pcs are given in table 8.5. It would be useful to have Raman data for a Pc derivative which has all peripheral hydrogens substituted. One such compound would be metal-free hexadecachlorophthalocyanine. Benzene\(^{1}\) has C-H deformations at 1038 cm\(^{-1}\), 1150 cm\(^{-1}\), 1178 cm\(^{-1}\) and 1326 cm\(^{-1}\). Table 8.6 gives Raman frequencies for isoindole ring deformations.
TABLE 8.3: A COMPARISON OF ISOINDOLE RING STRETCHING RAMAN FREQUENCIES FOR VARIOUS PHTHALOCYANINES

<table>
<thead>
<tr>
<th></th>
<th>WAVENUMBERS (cm(^{-1}))</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Indole</td>
<td>1412 1455 1534 10</td>
<td></td>
</tr>
<tr>
<td>(\alpha - H_2 P_c)</td>
<td>1406 1428 1450 1534 20</td>
<td></td>
</tr>
<tr>
<td>(\beta - H_2 P_c)</td>
<td>1408 1428 1450 1536 20</td>
<td></td>
</tr>
<tr>
<td>(x-H_2 P_c)</td>
<td>1408 1428 1450 1536 20</td>
<td></td>
</tr>
<tr>
<td>VOPc</td>
<td>1406 1428 1450 1534 20</td>
<td></td>
</tr>
<tr>
<td>MgPc</td>
<td>1408 1428 1450 1536 20</td>
<td></td>
</tr>
<tr>
<td>CuPc</td>
<td>1408 1428 1450 1536 20</td>
<td></td>
</tr>
<tr>
<td>ZnPc</td>
<td>1393 1429 1451 1527 24</td>
<td></td>
</tr>
<tr>
<td>SnPc</td>
<td>1393 1423 1444 1460 24</td>
<td></td>
</tr>
<tr>
<td>PbPc</td>
<td>1393 1423 1444 1460 24</td>
<td></td>
</tr>
<tr>
<td>(t-bu)(_2)H_2 P_c</td>
<td>1390 1428 1532 23</td>
<td></td>
</tr>
<tr>
<td>AlPcCl</td>
<td>1404 1450 1520 26</td>
<td></td>
</tr>
<tr>
<td>GaPcCl</td>
<td>1404 1450 1520 26</td>
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</tr>
<tr>
<td>InPcCl</td>
<td>1404 1450 1520 26</td>
<td></td>
</tr>
<tr>
<td>FePc</td>
<td>1404 1450 1520 26</td>
<td></td>
</tr>
<tr>
<td>PtPc</td>
<td>1404 1450 1520 26</td>
<td></td>
</tr>
<tr>
<td>PdPc</td>
<td>1404 1450 1520 26</td>
<td></td>
</tr>
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TABLE 8.4: A COMPARISON OF BENZENE RING RAMAN FREQUENCIES FOR VARIOUS PHTHALOCYANINES

<table>
<thead>
<tr>
<th></th>
<th>(cm⁻¹)</th>
<th>(cm⁻¹)</th>
<th>(cm⁻¹)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>606</td>
<td>1585</td>
<td>1606</td>
<td>1</td>
</tr>
<tr>
<td>(\alpha - H_2 \text{Pc})</td>
<td>570</td>
<td>1584</td>
<td>1618</td>
<td>20</td>
</tr>
<tr>
<td>(\beta - H_2 \text{Pc})</td>
<td>564</td>
<td>1584</td>
<td>1618</td>
<td>20</td>
</tr>
<tr>
<td>(x-H_2\text{Pc})</td>
<td>564</td>
<td>1584</td>
<td>1618</td>
<td>20</td>
</tr>
<tr>
<td>VOPc</td>
<td>590</td>
<td>1588</td>
<td>1614</td>
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<tr>
<td>CuPc</td>
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<td>ZnPc</td>
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<td>1590</td>
<td>1617</td>
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<tr>
<td>PbPc</td>
<td>590</td>
<td>1580</td>
<td>1610</td>
<td>24</td>
</tr>
<tr>
<td>(t\text{-bu})_2H_2\text{Pc})</td>
<td>588&amp;611</td>
<td>1581</td>
<td>1616</td>
<td>23</td>
</tr>
<tr>
<td>AlPcCl</td>
<td>591</td>
<td>----</td>
<td>1614</td>
<td>25</td>
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<td>GaPcCl</td>
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<td>----</td>
<td>----</td>
<td>25</td>
</tr>
<tr>
<td>InPcCl</td>
<td>589</td>
<td>1585</td>
<td>1613</td>
<td>25</td>
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</tr>
<tr>
<td>PdPc</td>
<td>600</td>
<td>----</td>
<td>----</td>
<td>28</td>
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</tbody>
</table>
### Table 8.5: A Comparison of C-H Deformation Raman Frequencies for Various Phthaloxyanines

<table>
<thead>
<tr>
<th>Compound</th>
<th>Wavenumbers (cm⁻¹)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>1038 1150 1326 1178</td>
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