

## FT Raman spectrum and band assignments for metal-free phthalocyanine ( $H_2Pc$ )

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### ABSTRACT

Metal-free phthalocyanines ( $H_2Pc$ ) and its derivatives are an important organic electro and photo active material with remarkable chemical stability and flexibility offering considerable interest for many intensive applications. The complexity of the molecule makes the vibrational study of the Raman spectrum difficult. A vibrational assignment of the frequencies in the F.T Raman spectrum of  $H_2Pc$  has been made in comparison with its metal derivatives, other related porphyrin, pyrrole, indole and ortho-substituted benzene structures.

**Keywords:**  $H_2Pc$ , Raman spectrum, vibrational assignment.

### INTRODUCTION

Phthalocyanines are porphyrin derivatives that are characterized by a high degree of symmetry, planarity and electron delocalization. Phthalocyanines, has received considerable attention as charge generating materials in electrophotographic receptors, in solar cells, as organic semiconductors, in optical-data storage and in non-linear optics. Phthalocyanines are a class of materials which is most extensively investigated because of their great structural flexibility, and can host ~70 different elements in the central phthalocyanine cavity and also a large range of peripheral substituents of phthalocyanines is known to improve the poor solubility of the unsubstituted phthalocyanine. They consist of isoindole rings at the four corners linked together by four nitrogen atoms. The middle is a 16 membered ring called the macrocycle in which the two imino-hydrogen atoms are replaceable by metal. The space within the four central nitrogen atoms when occupied by hydrogen atoms become metal-free phthalocyanine or  $H_2Pc$  and when by metallic ions having coordination number greater than four to become metal substituted phthalocyanine or MPc. The metal

atom is held by the two isoindole N atoms of  $H_2Pc$  by primary valencies and is coordinated by the other two N atoms of the macrocycle to form four chelate rings adding greater stability to the structure than  $H_2Pc$ . Metal-free phthalocyanine ( $H_2Pc$ ) is known to exist in polymorphic forms of the types; face centred monoclinic  $\beta$ - $H_2Pc$ , the tetragonal  $\alpha$ - $H_2Pc$ , and the hexagonal  $\chi$ - $H_2Pc$  and  $\tau$ - $H_2Pc$  which are intermediate between  $\alpha$  and  $\beta$   $H_2Pc$ , all differing substantially in electronic conductivity and photoactivities. The structure of  $H_2Pc$  is presented in Fig.1. The polymorphs have different stack arrangement and different stacking overlap of adjacent molecules. The electronic properties are related to the overlap of electron wavefunctions and the stacking habit of molecules. The  $\alpha$ - $H_2Pc$  has a large intermolecular P wavefunction overlap resulting in a large carrier mobility. The intermolecular interaction and the stacking habit of molecules are considered to affect low wave-number Raman spectra in  $\alpha$ - $H_2Pc$  which exhibits two peaks at  $90\text{cm}^{-1}$  and  $132\text{cm}^{-1}$  while other polymeric forms of  $H_2Pc$  have only one band at  $132\text{cm}^{-1}$  that have not been identified with a characteristic vibrational mode.<sup>1</sup>

## EXPERIMENTAL

H<sub>2</sub>Pc crystals were prepared by vacuum sublimation under a pressure of about 10<sup>-5</sup> torr and at a temperature of about 460°C. The crystals are formed as whiskers having dimensions of 15-20x0.3x0.13 mm. The FT Raman spectrum of H<sub>2</sub>Pc was recorded on Bruker IFS 66v spectrophotometer using a FRA106 Raman module and a 200mW YAG laser is presented in Fig. 2.

## RESULT AND DISCUSSIONS

The molecular symmetry of H<sub>2</sub>Pc is D<sub>2h</sub> while its metal derivatives have D<sub>4h</sub> symmetry. The reduced symmetry of H<sub>2</sub>Pc is concluded on the

basis of E<sub>u</sub> mode of vibration which is infrared active for the D<sub>4h</sub> symmetry cases. The E<sub>u</sub> mode splits into two other infrared active modes B<sub>2u</sub> and B<sub>3u</sub> without too much change in the peak position when the molecule assumes D<sub>2h</sub> symmetry. The rule of mutual exclusion applies and only the gerade modes appear in the Raman spectrum.

The vibrations of phthalocyanines are regarded as complex but can be divided into two main types; higher frequency vibrations mainly due to the motion of the isoindole rings modified by the macrocycle and the other low frequency vibrations of the metal-nitrogen bonds of MPC's. It has been observed that absorption bands change with the coordination of the metal ion with the four nitrogen

**Table 1: Raman band assignments for H<sub>2</sub>Pc**

| Frequency(cm <sup>-1</sup> ) | Assignment                                                                                                 |
|------------------------------|------------------------------------------------------------------------------------------------------------|
| 3420 (2)                     | $\nu_{OH}$ , O-H stretch (water of crystallization)                                                        |
| 3058 (5)                     | $\nu_{CH}$ , C-H stretch (benzene)                                                                         |
| 1614 (6)                     | $\nu_{C\gamma C\delta}$ , ring stretch (benzene)                                                           |
| 1540 (84)                    | $\nu_{CaNa}$ , $\nu_{CaNB}$ , CNC group stretch (pyrrole)                                                  |
| 1508 (39)                    | $\nu_{CaC\beta}$ , C=C stretch (pyrrole)                                                                   |
| 1449 (27)                    | $\nu_{CaNB}$ , $\nu_{CaC\beta}$ , isoindole stretches                                                      |
| 1425 (10)                    | $\nu_{C\beta C\beta}$ , $\nu_{CaC\beta}$ , isoindole stretches                                             |
| 1339 (52)                    | $\nu_{C\beta C\beta}$ (mainly), $\nu_{CaNa}$ , pyrrole stretches                                           |
| 1311 (32)                    | $\nu_{C\gamma C\delta}$ , $\nu_{CaC\beta}$ , ring stretch (benzene), pyrrole stretch                       |
| 1179 (13)                    | $\delta_{CH}$ , C-H i.p.b (benzene)                                                                        |
| 1141 (45)                    | $\nu_{CaNB}$ , $\delta_{CH}$ , isoindole breathing, C-H i.p.b (benzene)                                    |
| 1113 (12)                    | $\nu_{CaNB}$ , $\nu_{CaNa}$ , pyrrole stretch                                                              |
| 1083 (4)                     | $\delta_{CH}$ , C-H i.p.b (benzene)                                                                        |
| 1025 (8)                     | $\pi_{CH}$ , C-H o.p.b (benzene)                                                                           |
| 1007 (9)                     | $\pi_{CH}$ , $\delta_{NH}$ , C-H o.p.b (benzene), N-H i.p.b                                                |
| 794 (8)                      | $\delta_{C\beta CaNB}$ , macrocycle ring deformation                                                       |
| 722 (38)                     | $\delta_{C\beta CaNB}$ , $\pi_{NH}$ , macrocycle ring deformation, N-H o.p.b                               |
| 681 (13)                     | $(N_{\alpha} C_{\alpha} N_{\beta} C_{\beta})_4$ , macrocycle breathing                                     |
| 567 (5)                      | $\delta_{CaNaCa}$ , $d_{C\gamma C\delta C\delta}$ , isoindole ring deformation, ring deformation (benzene) |
| 542 (5)                      | $\delta_{C\gamma C\delta C\delta}$ , ring deformation (benzene)                                            |
| 480 (15)                     | $\delta_{CaC\beta C\gamma}$ , isoindole ring deformation (complex)                                         |
| 231 (10)                     | $\delta_{CaNB Ca}$ , macrocycle ring deformation                                                           |
| 189 (9)                      | $\delta_{NaCaNB}$ , in phase motion of isoindole group                                                     |
| 132 (10)                     | $\pi_{C\beta CaNB}$ , macrocycle ring deformation                                                          |

values within parentheses are the relative intensities

n-stretching d-in-plane deformation p-out-of-plane deformation

i.p.b-in-plane bending o.p.b-out-of-plane bending

atoms of the macrocyclic ring leading to a classification of vibrations as metal dependent and metal independent. The probable assignments of Raman frequencies for the H<sub>2</sub>Pc is given in Table 1.

The characteristic frequencies for the inner macrocycle are observed at 132 cm<sup>-1</sup>, 231 cm<sup>-1</sup>, 681 cm<sup>-1</sup>, 722 cm<sup>-1</sup> and 794 cm<sup>-1</sup> in the Raman spectrum. The 681cm<sup>-1</sup> corresponds to a motion in which the co-ordinated nitrogen atoms breathe symmetrically in a typical macrobreathing vibration while all the other vibrations correspond to a macrocycle ring deformation. The vibrations of isoindole group have been assigned in comparison with the vibrations of pyrrole and indole groups<sup>2-4</sup>.

The isoindole and pyrrole stretches have been assigned to 1449cm<sup>-1</sup>, 1425cm<sup>-1</sup> and 1540 cm<sup>-1</sup>, 1508cm<sup>-1</sup>, 1339cm<sup>-1</sup>, 1141cm<sup>-1</sup>, 1113cm<sup>-1</sup> respectively. The motions of the isoindole rings have a greater effect on the macrocycle. The CNC group stretch at 1540cm<sup>-1</sup> is the most intense bands arising from C<sub>α</sub>-N<sub>α</sub> and C<sub>α</sub>-N<sub>β</sub> stretches that cause a significant alterations of the macrocycle. This Raman band is highly sensitive to the metal ion and the cavity size in MPC's. In ZnPc the metal ion is greater than the cavity size (3.96Å) and the CNC stretch

occur at 1505 cm<sup>-1</sup> while the cavity size for NiPc is 3.66Å giving the corresponding peak position at 1545cm<sup>-1</sup> and being the highest in all phthalocyanines. There are a number of in-plane skeletal pyrrole ring vibrations in the porphyrin system which are analogous to the phthalocyanine isoindole ring vibrations. The frequencies at 567cm<sup>-1</sup>, 480cm<sup>-1</sup>, and 189cm<sup>-1</sup> have been assigned to the isoindole ring deformations. The 480cm<sup>-1</sup> frequency is a complex vibration involving the isoindole rings.<sup>5-10</sup>

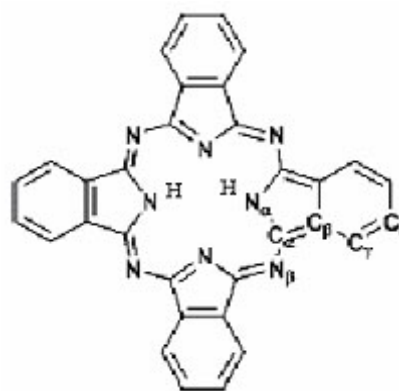


Fig.1: The structure of H<sub>2</sub>Pc

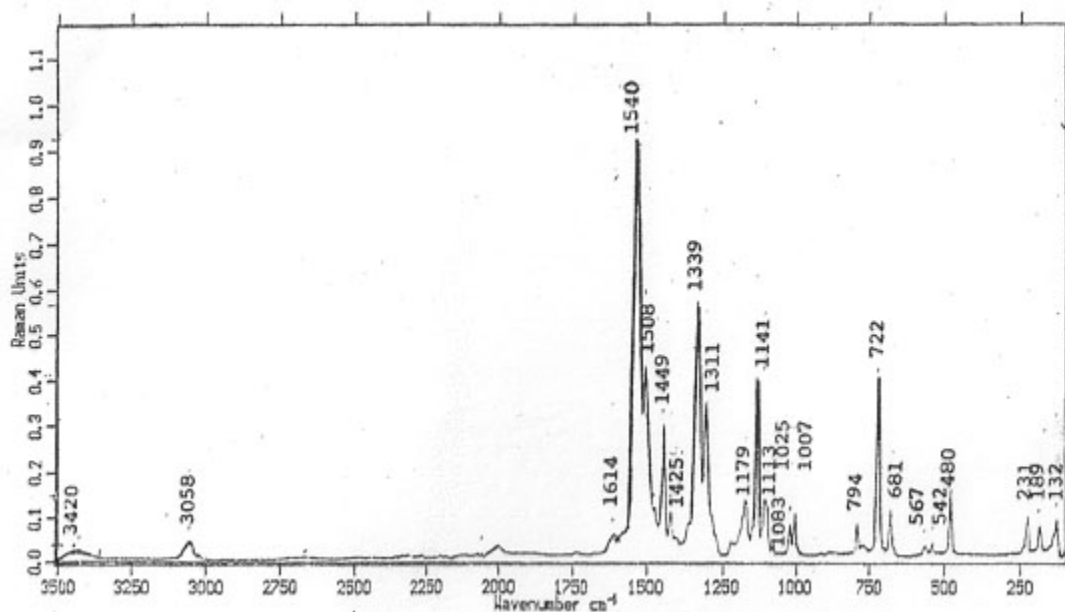


Fig. 2: FT Raman Spectrum of metal-free phthalocyanine (H<sub>2</sub>Pc)

Boucher and Gatz<sup>11</sup> have reported that the N-H deformations of photoporphyrins give rise to sharp absorptions bands at 1110cm<sup>-1</sup> and 740cm<sup>-1</sup> which have been observed in the Raman spectrum of H<sub>2</sub>Pc at 1007cm<sup>-1</sup> and 722cm<sup>-1</sup> respectively. The significant comparative shift in the frequencies is attributed to the effect of C-H bending and macrocycle deformation vibrations of H<sub>2</sub>Pc. A very broad band of low intensity has been observed at 3420 cm<sup>-1</sup> and has been assigned to the weakly bonded O-H stretching of crystalline water which usually give weak Raman bands .

The stretching and deformation vibrations of the C-C and C-H bonds of the external rings are metal independent and they have been assigned in comparison with ortho- substituted benzene<sup>12,13</sup>. The 3058cm<sup>-1</sup> band is assigned to all C-H stretchings while the band at 1614 cm<sup>-1</sup> is assigned to C-C ring stretches. The C-H in-plane bendings occur at frequencies 1179cm<sup>-1</sup>, 1141cm<sup>-1</sup> and 1083cm<sup>-1</sup> while the C-H out-of-plane bendings occur

at 1025cm<sup>-1</sup> and 1007cm<sup>-1</sup>. The vibrations at 567cm<sup>-1</sup> and 542cm<sup>-1</sup> have been assigned to C-C ring in-plane deformations.

In crystalline naphthalene which belongs to the same space group, lattice vibrations were observed below 100cm<sup>-1</sup> and so the vibration at 132cm<sup>-1</sup> is a macrocycle ring deformation mode. Further the Raman spectra shows no combination bands in the region 1800-3000 cm<sup>-1</sup> whereas all metal Pc's exhibit overtone and combination bands in this region.

### CONCLUSION

The Fourier Transform Raman spectrum of H<sub>2</sub>Pc has been investigated in comparison with other metal phthalocyanines, porphyrin, pyrrole, indole and benzene derivatives for the observed frequencies in the spectrum and a complete assignment of Raman bands is proposed for H<sub>2</sub>Pc.

### REFERENCES

1. Leznoff C.C, Lever A.B.P, Phthalocyanines- Properties and Applications, vol.1, VCH New York, (1989): vol.3 (1993).
2. Suiwaiyan A. and Zwarich R., *Spectrochim Acta*, **42A**: 1017 (1986).
3. Majaoube M., Vergoten G., *J. Raman Spectrosc.*, **28**(8): 431 (1992).
4. Takeuchi H. and Harada I., *Spectrochim Acta*, **42A**: 1069 (1986).
5. Nakamoto K., *Infrared and Raman Spectra of Inorganic and Coordination compounds (PartB)*, P-41, Wiley-VCH New York, (2009).
6. Shruvell H.F and Pinzuiti L., *Can. J. Chem.*, **44**: 125 (1966).
7. Aroca R., Dilella D.P and R.O Loutfy, *J. Phys.Chem.(solids)*, **43**(8): 707 (1982).
8. Jennings C.A, Aroca R., Kovacs G.J, Hsaio C., *J.Raman spectrosc.*, **27**: 867 (1996).
9. Tackley D.R, Dent G. and Smith W.E, *Phys.Chem.Chem. Phys.*, **2**: 3949 (2000).
10. Dent G. and Farell F., *Spectrochim Acta*, **53A**: 21 (1997).
11. Boucher L.J and Katz J.J, *J.Am.Chem. Soc.*, **89**: 1340 (1967).
12. Green J.H.S, Kynaston W. and Paisley H.M, *J. Chem. Soc.*, 473 (1963).
13. Scherer J.R and Evans J.C, *Spectrochim Acta*, **19**: 1739 (1963).