Chapter 7

FTIR spectra of lead phthalocyanine hydrogen bonded with emeraldine, nigraniline and pernigraniline
7.1 Introduction:

Lead Phthalocyanine has lead chains in one crystallographic direction and acts as a one-dimensional conductor [1]. Thin films were found to be semi-metallic or metallic down to low temperature [2]. However, single crystals were found to be semiconducting [3]. The uv-visible and IR spectra also have been studied which show a band gap of 0.63 eV along the direction of lead chains. Recently charge transfer complexes of PbPc (lead phthalocyanine) have been studied which show allowed indirect transition in the infrared absorption edge [4]. Dielectric property of PbPc has also been studied which show Maxwell-Wagner effect in the nano-crystalline PbPc [5]. Polyanilines namely emeraldine, nigraniline and pernigraniline have also been studied using FTIR spectroscopy [6]. In the present work, these polyanilines are hydrogen bonded with lead phthalocyanine (PbPc). The molecular structures of PbPc and polyanilines are shown (Figure 1). FTIR spectra were recorded the hydrogen bonded molecular complexes which are studied in details.
7.2 Experimental Details:

Lead Phthalocyanine(PbPc) was prepared by refluxing lead monoxide with nitrobenzene solution of phthalonitrile. PbPc was obtained in this manner as a blue nanocrystalline material. This blue powder was mixed with polyanilines which were also prepared in laboratory by oxidation of aniline with different oxidizing agents [6]. The mixtures were ground till colours deepened and black powders of hydrogen bonded complexes were obtained. These black materials were mixed and grounded with anhydrous spectrograde KBr powder. Finally, round palates were made using a manually operated machine and a circular die which were semitransparent. These circular discs were placed in the dark chamber of a spectrophotometer.

The spectra in the range 400-4000 cm$^{-1}$ were recorded using a GX-FTIR single beam spectrophotometer manufactured by Perkin-Elmer company USA. It
was having a resolution of 0.15 cm\(^{-1}\), a scan range of 15600-30 cm\(^{-1}\), a scan time of 20 scan sec\(^{-1}\), an OPD velocity of 0.2 cm sec\(^{-1}\) and MIRGS and FIRTGS detectors. A beam splitter of opt KBr type was used having a range of 7800-370 cm\(^{-1}\). The spectra were recorded in purge mode.

**7.3 Results and Discussion:**

The FTIR spectrum of PbPc is shown (Figure-2a). There is monotonic increase in absorption in the range between 1780 cm\(^{-1}\) and 3000 cm\(^{-1}\) as the energy of infrared light increases. This shows that there is an infrared absorption edge with \(E_g = 0.223\) eV (1780 cm\(^{-1}\)) which is analyzed (Figure-2b). PbPc is a two-dimensional (layered) material perpendicular to lead chains. There is \(\pi-\pi\) stacking of benzene rings and the fine structure (a large number of weak absorption bands) of the absorption edge is because of non-degenerate ring puckering vibrations of benzene rings. The analysis \(\alpha h\nu\) vs \(h\nu\) shows that it is a two-dimensional conductor perpendicular to lead chains.
The infrared gap of 0.20 eV is between the planar rings of benzene and it is a gap in the phonon dispersion relation between acoustic and optical phonon modes. Rest of the bands below 1780 cm\(^{-1}\) are due to several intramolecular vibrations of organic network of phthalocyanine ligand around the lead chains. Some of the bands can be assigned LO and TO modes of lattice vibrations. Metal-ligand vibrations which give rise to allowed indirect transitions in charge transfer complexes of PbPc lie below 700 cm\(^{-1}\). These bands are also shifted by hydrogen bonding of polyanilines.

The FTIR spectrum of PbPc-emeraldine is shown (Figure-3a). The minimum absorption point remains at 1780 cm\(^{-1}\) (0.223 eV) but the nature of absorption edge is complicated by exciton-phonon emission band in this edge followed by a series of threshold energies of excitons. This is similar to what is observed in the absorption edge of GaP [7,8]. Gallium Phosphide (GaP) is an ionic semiconductor and has shown electron-hole liquid (EHL) below 45 K of temperature.
hole pairs form a gas at room temperature which condense into a liquid at low temperature [9]. Similarly in the present H-bonded complex of PbPc with emeraldine can also undergo a transition to electron-hole liquid phase at low temperature because emeraldine provides a high exciton density medium. The absorption edge of the emeraldine complex of PbPc has been analyzed and $(\alpha h\nu)^{1/2}$ vs $h\nu$ was found to be the best fit for absorption coefficient (Figure-3b). This shows that it is an allowed indirect transition in a disordered material. The material is disordered and so does not allow calculation of phonon energy from the absorption edge. Only a crystalline material shows a break in straight line in such a plot having two intercepts at $E_g + E_p$ and $E_g - E_p$. $(\alpha h\nu)^{1/2}$ vs $h\nu$ rather than crystalline case where $(\alpha)^{1/2}$ vs $h\nu$ is a straight line being a rectilinear plot shows that it is a disordered material. There are four phonon emission bands with four threshold energies of the formation of excitons. The band gap is obtained by extrapolation of straight line segment at higher energy as an intercept with energy axis. It is found to be about 0.26 eV (Figure 3b).
There is a shift of absorption edge of 0.200 eV to 0.260 eV in the emeraldine complex. This blue shift of PbPc absorption edge is related with Burstein-Moss shift in heavily doped PbPc with emeraldine. Instead of additional shrinkage of an indirect gap, the Burstein-Moss shift is pronounced. The Burstein-Moss shift parameter $\xi$ is of the order of 0.060 eV. Repulsive effects are dominant in PbPc because of two electrons vibrating across the ligand rather than only one electron found in Ni(Hdmg)$_2$-bis(dimethylglyoximato)Ni$^{II}$. The present case is an infrared analogy of what is found in gallium phosphide. In GaP threshold energies are found in visible range while here these energies lie in infrared range. There is photoluminiscense in GaP [9] while here there can be infrared luminescence. Electron-hole pairs are formed across a band gap lying in the infrared range and IR
luminescence can occur through recombinations of electrons and holes. In a hard material, IR luminescence can be absorbed but in a soft material there is re-absorption of emitted infrared radiation and phonons are emitted (local strains and thermal phonons) as found here. Probability of recombination is more when band gap is smaller, i.e. when exciton-phonon coupling is stronger. When this coupling is weak, more number of phonons are emitted and band gap is larger.

The FTIR spectrum of PbPc-nigraniline is shown (Figure 4a) and the absorption edge is analyzed similarly finding \((\alpha h\nu)^{1/2}\) vs \(h\nu\) as the best fit (Figure 4b). Again a Burstein-Moss shifted edge is found at 0.270 eV which is blue shifted due to heavy doping of nigraniline. The Burstein-Moss shift \(\xi\) is nearly 0.07 eV.
There are five phonon emission bands in the absorption edge corresponding to a weaker exciton-phonon coupling compared to emeraldine complex. Thus as this coupling weakens, more number of phonon emissions are found and simultaneously band gap increases. The number of threshold energies for the formation of excitons is the same as number of phonon emission bands. There are larger number of thresholds in a large band gap material. This shows that there is more probability of electron-hole droplet formation in materials with large band gap. This is consistent with the fact that electron-hole pairs are stable against recombination in a large band gap material.

The FTIR spectrum of PbPc-pernigraniline is also shown (Figure 5a) and the absorption edge is analyzed to be $\alpha h\nu = B(h\nu - E_g)^2$ as the best fit giving rise to $(\alpha h\nu)^{1/2}$ vs $h\nu$ as rectilinear plot at higher energy (Figure 5b). There are six phonon...
bands in the absorption edge and band gap is nearly 0.275 eV. The Burstein-Moss shift parameter $\xi$ is 0.075 eV. Electron-hole droplet formation at low temperature in this complex is more probable as compared to emeraldine and nigraniline complexes because of large number of excitons.

A comparison can be made with hydrogen bonded complexes of polyanilines with Ni(Hdmg)$_2$. The latter complexes have less band gap than even CTCS of Ni(Hdmg)$_2$ acceptors due to excitonic reduction of band gap. In the present cases of PbPc, band gaps are larger than CTCS of PbPc with acceptors [4] and larger than H-bonded Ni(Hdmg)$_2$ due to Burstein-Moss as a dominating effect. Infrared luminescence is more probable in H-bonded Ni(Hdmg)$_2$ while electron-hole droplets are more probable in H-bonded PbPc. Exciton-phonon coupling is weaker in PbPc complexes as compared to Ni(Hdmg)$_2$ complexes.
The number of phonon bands which is reciprocal to exciton-phonon coupling is plotted against the band gap and it is found to be nearly a rectilinear plot (Figure 6).
Conduction band or valence band edges may not be sharp and there are exponentially tailing states into the forbidden energy gap. In this case

\[ \alpha = \alpha_0 \exp \left\{ \frac{(h\nu-E_1)}{E_0} \right\} \]

leading to

\[ E_0 = \left[ \delta \ln \alpha / \delta (h \nu) \right]^{-1} \]

\[ = 1 / \text{slope} \]

\( \ln \alpha \) vs \( h\nu \) is straight line. \( E_0 \) is called the width of the tail and \( E_1 \) is called the focal point. In the present case, \( E_0 \) is determined by the dye added and \( E_1 \) is characteristic of the PbPc. \( E_0 \) is a measure of disorder. \( E_0 \) is large when disorder is more. \( \ln \alpha \) vs \( h\nu \) are plotted (Figure 7a) and \( E_0 \) and \( E_1 \) are found from these graphs. \( E_g \) vs \( E_0 \) is also
plotted (Figure 7b). As $E_0$ increases, $E_g$ decreases almost linearly. This is also theoretically established [10].

![Graph showing $E_g$ vs $E_0$](image)

[Figure 7(a) Band tailing analysis and focal point (b) $E_g$ vs $E_0$ i.e. band gap vs width of the tail]
7.4 Conclusions:

The hydrogen bonded complexes of polyanilines namely emeraldine, nigraniline and pernigraniline are formed with PbPc. These complexes show complicated absorption edge due to exciton-phonon coupling. The absorption edges are Burstein-Moss shifted with respect to only PbPc due to heavy doping of excitonic polyanilines. There is probability of formation of electron-hole liquid at low temperature as large number of excitons found in absorption edge can condense into liquid.
References: