Chapter 9
Conclusion

This thesis presents a thorough analysis of the Infrared and Raman spectra of certain groups of phosphorus compounds in the solid state. The IR and Raman spectra of all the compounds were recorded using a Bruker IFS 66V FT-IR/FT-Raman Spectrometer employing a globar source and an Nd:YAG laser at 1.064 μm wavelength, respectively. The polarized Raman spectra was recorded using a Nicolet 950 FT-Raman Spectrometer. Raman spectra of some deuterated samples as well as their aqueous solutions are used inorder to understand and remove the ambiguity regarding certain vibrations. Effects due to lower site symmetry, correlation field and hydrogen bonding are observed in most of the compounds.

Strong hydrogen bondings characterised by the appearance of ABC bands is observed in the compounds C₆H₅NH₃⁻HPO₃H⁻, Pb(O₃PC₆H₁₅) and bis(2-diethoxyphosphonyl-2-phenyl-ethenolate)zinc(II) 1½hydrate. In the case of C₆H₅NH₃⁻HPO₃H⁻, this observation supports the structural report on the compound. In the case of the latter two compounds, however no such hydrogen bonding is reported in their structures. The vibrational spectra reveals that, in both these compounds the hydrogen bond exist as C-H---O. In the case of Pb(O₃PC₆H₁₅), the phosphoryl oxygen is hydrogen bonded to the hydrogen atom at a corner of the benzene ring, and in the case of the zinc complex it is between the phosphoryl oxygen and the hydrogen atom in the ethene group. Hydrogen bonds of varying strength involving water molecules are observed in all the four cyclo-hexaphosphates, hydrated
tri and tetra- metaphosphimates and Co(en)$_3$Al$_2$P$_4$O$_{16}$·3H$_2$O. The NH$_4^-$ ion in (NH$_4$)$_4$(PO$_2$NH)$_4$·4H$_2$O and (NH$_4$)$_3$[Co(NH$_3$)$_6$]$_3$[Al$_2$(PO$_4$)$_4$]$_2$·2H$_2$O are hydrogen bonded. In the former the ion exhibits hindered rotation and in the latter the ion is in the locked-in position and is not free to rotate.

The lifting of degeneracy, shifting of frequency and activation of inactive modes due to lower site symmetry of the vibrating unit in the crystal lattice are observed. The lower site symmetry of the monosubstituted benzene rings, viz., phenyl phosphonate (O$_3$PC$_6$H$_4$) and anilinium (C$_6$H$_5$NH$_3^-$) in their respective lattice make the IR inactive A$_2$ modes active and also lifts the degeneracy of the degenerate modes. The intramolecular vibrations of NH$_3^-$ ligand in Co(NH$_3$)$_6^{3+}$ ion are distributed in the IR active F$_{1u}$ mode. However, the lower site symmetry of the ion in the lattice has made these modes active in the Raman and the degeneracy of the v$_3$Co-N (F$_{1u}$) mode is lifted. The NH$_4^-$ ion in the (NH$_4$)$_4$(PO$_2$NH)$_4$·4H$_2$O and (NH$_4$)$_3$[Co(NH$_3$)$_6$]$_3$[Al$_2$(PO$_4$)$_4$]$_2$·2H$_2$O also shows site symmetry effects. In the study of cyclohexaphosphates, the splitting of the v$_{as}$PO$_2^-$ mode into a larger number of components in the spectra of magnesium and calcium compounds, indicates distorted P$_6$O$_{18}^-$ anion ring in them.

Splitting of non-degenerate modes due to correlation field effect are observed in the case of 3 and 8 modes of the phenyl ring in Pb(O$_3$PC$_6$H$_4$). In the aluminium phosphate ions Al$_3$P$_4$O$_{16}^-$ and Al$_2$(PO$_4$)$_4^-$ the stretching modes of PO$_3$ and PO$_2^-$, respectively shows multiplicity of bands due to correlation field splitting.
In the study of nickel(II) and zinc(II) complexes of diethyl(2-oxo-1-phenyl)ethylphosphonate, a strong interaction between the 16b mode of the benzene ring and νC=C of the ethene group is revealed by the increased intensity and the shifting of the frequency of the former mode. The analysis of the spectra of the Co(en)₃⁺ complex reveals a Fermi resonance between the overtone of CH₂ deformation and the CH₂ symmetric stretching mode in the compound.

It has been reported earlier that the monosubstituted benzene ring has C₂ᵥ symmetry, when the substituent is monoatomic or linear and the symmetry is lowered if the substituent is other than monoatomic or linear (McWhinnie & Poller, 1966). However, Gao et al., (1977) have assigned C₂ᵥ symmetry to toluene, benzonitrile and benzoic acid to interpret their SERS spectra. In the present work, the polarized Raman spectra of C₆H₅NH₃⁺ HPO₃H⁻ is consistent with the C₂ᵥ symmetry of C₆H₅NH₃ group. The vibrational spectra of Pb(O₃PC₆H₅) are also interpreted by assigning C₂ᵥ symmetry to the phenylphosphonyl, O₃PC₆H₅ group.

The correlation between the asymmetric and symmetric stretching frequencies of PNP group and the angle PNP are reported for the first time. Both the correlations (i) νₛPNP - νₛPNP as a function of θ PNP and (ii) νₛPNP - νₛPNP/νₛPNP + νₛPNP as a function of θ PNP, shows a definite pattern, as in the case of POP bridge. These correlations can therefore be used to predict the PNP angles of compounds whose structures are not investigated.