Summary & Conclusion

The present investigation is undertaken with an aim to determine the distorted structure of porphyrin in Magnesium octaethyl porphyrin (Mg(OEP)), Copper tetraphenyl porphyrin cation radical (Cu(TPP)^+), Copper tetramesityl porphyrin (Cu(TMP)) and its cation radical (Cu(TMP)^+) in Dichloromethane (CH_2Cl_2) with the help of Resonance Raman (RR) spectroscopy, excited at 406.7 nm.

The results of the theory of distortion induced Resonance Raman intensities are applied to determine the distorted symmetry of porphyrin in Mg(OEP), Cu(TPP)^+, Cu((TMP) and Cu(TMP)^+. This theoretical investigation uses the principle of group theory and approximation method (c.f. Chapter 2).

The central idea of the work is that the electric field associated with the exciting Resonance Raman (RR) frequency serves as the
source of perturbation that distorts the molecule and hence, modifies its dynamics. In such a case, one has to use a set of "Propensity rules" (c.f. Chapter 2). The rules predict that for active modes:

(i) when the distortion is along x-direction, the $\alpha_{xx}$ modes of the molecules are more intense than the modes with $\alpha_{xy}$ or $\alpha_{xz}$ symmetry and the $\alpha_{yy}$ and $\alpha_{zz}$ modes have less intensity than $\alpha_{xy}$ or $\alpha_{xz}$.

(ii) In y-direction intensities of $\alpha_{yy}$ \( |(\alpha_{yx} \text{ or } \alpha_{yz}) \rangle \langle (\alpha_{xx} \text{ or } \alpha_{zz}) | \)

and

(iii) In z-direction, that is $\alpha_{zz}$ \( |(\alpha_{zx} \text{ or } \alpha_{zy}) \rangle \langle (\alpha_{xx} \text{ or } \alpha_{yy}) | \).

In case of forbidden modes, the forbidden transitions become active due to structural distortion of the molecular unit and they are ascribed as distortion induced transitions. Such transitions are of different orders i.e., DIA-I/DIA-II/.../DIA-h representing first/second/.../higher order effect of distortion (DIA, distortion induced activity). Normally, the transition occurring only in first order effect in the polar type of distortion are expected to gain observable intensity, others may result in perceptible intensity in exceptional situations. Therefore, for better understanding of the distorted structure of a molecular unit and the observed RR spectra it is highly desirable to know the type and order of DIA of the forbidden modes of a molecular unit.
Chapter 6

The results of the theory of distortion induced RR intensity help in understanding which of the forbidden modes of a molecular unit after being allowed will appear with observable intensity and allowed modes will have different intensities because of the propensity rules. Thus, it helps in correct determination of the symmetry of a distorted molecule.

Based on these results: In Chapter 3, we conclude that the Porphyrin in Mg(OEP) excited at 406.7 nm for RR study, in CH₂Cl₂ solution attains a polar type of distorted structure of C₂(X) symmetry.

In Chapter 4, we conclude that the porphyrin in Cu(TPP)⁺ in CH₂Cl₂ solution, excited at 406.7 nm for RR study, attains a polar type of distorted structure of C₂(X) symmetry. This observation is justified because the distorted structure of Cu(TPP) is also of C₂(X) symmetry.

In Chapter 5, we conclude that the porphyrin in Cu(TMP) and Cu(TMP)⁺ in CH₂Cl₂ solution, excited at 406.7 nm for RR study, attains a polar type of distorted structure of C₂(X) symmetry.

Moreover, from the shift in frequencies on the cation formation of Cu(TPP) and Cu(TMP) in Chapter 4 and Chapter 5 respectively, the ground state of Cu(TPP)⁺ and Cu(TMP)⁺ is found to be of a₂u character.

Finally, it is hoped that this work will serve as a good example of the application of the results of the theory of Distortion Induced Resonance Raman intensities for determination of distorted structure of molecular unit, particularly in biomolecular systems.