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6. Conclusion:

Our short journey through different routes in the world of halogen bonded charge transfer complexes of n-donor Pyridines with Iodine monochloride and Iodine molecule unveiled many interesting facts, some known and some new; which we hope to become a topic of interest to other workers in this field. Science is an eternal journey of learning new facts. To wind up; we would like to share with others what we learnt through this conclusive chapter. We have discussed our findings related to every technique in the respective chapters of this thesis. In this final chapter we would mention the most significant findings and would try to correlate the experimental findings to the computational ones; which was the basic target of our work. And it occurred like, every tiny piece of thread is somehow attracted with a large gravitational pull by other objects; theory and experiment defends each other and proved to be the two sides of the same coin.

Basic findings of UV-Vis study revolved around the fact that the experimental CT complexes are 1:1, n→σ* CT complexes, and these complexes are stabilized by the dielectric enrichment of the solvents. The Gibbs free energy values obtained from the spectroscopic data shows that the CT complexes are stable at room temperature. However the dependence of the CT band was not satisfactorily explained alone by the dielectric constant value of the solvents. The multiple linear regression technique then comes to rescue. It shows that the bulk parameter, dielectric constant; alone is not enough to explain the behaviour of the CT band. The donor-acceptor bond largely depends on microscopic interactions at the molecular level. The successful
multiple linear regressions considering the microscopic parameters together with the bulk parameters helped us to propose a series of new linear form of equations. Moreover we examined the validity of two equations namely, Buckingham and Lippert Mataga equations in the context of our CT complexes. When we could relate the position of the CT band and the CT interaction with different solvent parameters; we applied DFT to observe if any relation of molecular structure with dielectric constant exists. And it is seen that equilibrium molecular geometry is governed by the dielectric behaviour of the solvents leading to stronger donor acceptor interaction in polar media. We observed it in the form of lengthening of I-Cl and I-I bonds and shortening of the N-I bond. This helped us to design a logarithmic relation between the solvent dielectric constants and these significant bond lengths which are strongly related to the strength of the donor acceptor bond. Besides the donor acceptor bond lengths, NBO, NEDA, NRT and QTAIM analyses supported the fact found experimentally that CT interaction in our complexes under study, increases with the solvent polarity.

Dipole moment values of the complexes show a gradual increase in their values with increasing solvent dielectric constant. It suggests stabilization of the complexes in polar media due to increasing favourable solvation of the CT complex by the media. The computation of energy of the molecular orbitals involved in CT interaction by DFT also clearly shows the formation of energetically favourable CT complexes from their respective donors and acceptors. It also shows that if we consider the molecular orbitals of the individual donors and acceptors which are
involved in the charge transfer interaction, we can arrive at a qualitative equivalence between theory and experiment regarding the trend of blue shift observed for CT bands in polar media. The quantitative equivalence is however not obtained and the reason may be due to the consideration of dielectric constant alone as the dominating solvent parameter and ignoring the other important solute solvent interactions in the theoretical study which are elaborately discussed during regression analysis.

The challenge or rather we should say the problem started at the last part when we tried to study the CT transitions with the help of TDDFT. We are trying to give a brief explanation regarding this anomalous finding of TDDFT study here on experimental grounds.

Direct transition refers to the vertical transition of electrons between the molecular orbitals involved following the Franck Condon principle. But the indirect transition is not so. Tauc plots clearly prove the CT transitions in the complexes as indirect allowed. While our experimental findings conclude the CT transitions as indirect transitions, we followed the TDDFT study for the direct transitions not knowing the fact earlier. So it leads to the conclusion that it has to be the reason of anomalous finding during TDDFT since we have also tried with different functional to obtain experimentally equivalent CT transitions by TDDFT. Although our inquisitiveness forced us enough to follow another route regarding our TDDFT study; which is that of adiabatic transitions; but time has been a constraint on the
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way. We are leaving it as our future prospect. **Fig: F.6.1** shows the difference which has been encountered when relating theory and experiment considering TDDFT.

![Diagram of electronic transition](image)

**Fig: F.6.1: Electronic transition studied experimentally Vs computationally**

Moreover in our TDDFT chapter we have elaborately discussed how we ignore the equilibrium between the CT complex and the component donor and acceptors in solution while we perform TDDFT calculations and it is worth mentioning that this equilibrium situation is of vital importance for studying donor acceptor interaction in solution using UV-Vis spectroscopy. Thus the discrepancy between the TDDFT and experimental results is unavoidable in the present situation.

If we do not mention the limit upto which our propositions are valid and claim them to be universally applicable then it would be wrong in our part. Because science; as always has been a field of specifications and our case is not an indifferent one. Since we took solvents of dielectric constant value within a range of 10, we can claim our propositions to be valid in this range only. To study the donor acceptor


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behaviour beyond dielectric constant value of 10 is one of our future prospects. Thus we wind up our journey with the following *new findings* during our research which we consider to be the major ones.

- High extinction coefficient values and regression analysis suggest that the charge transfer band is largely dependent on micro level solvent parameters. Solvatochromism is thus best explained by specific interaction between donor and acceptor molecules.
- Among the solvent parameters Hansen parameter stands best to explain solvatochromism.
- Multiple linear regression method shows that there exists linear relation of the following types between the CT band and solvent parameters mentioned therein.

\[
\begin{align*}
\Delta \lambda_{\text{max}} &= \Delta \lambda_0 + a\varepsilon + bn e^{0.6.1} \\
\Delta \lambda_{\text{max}} &= \Delta \lambda_0 + a\varepsilon + nb + s\pi e^{0.6.2} \\
\Delta \lambda_{\text{max}} &= \Delta \lambda_0 + a\partial d + b\partial p + c\partial h e^{0.6.3} \\
\Delta \lambda_{\text{max}} &= \Delta \lambda_0 + aSP + bSp + cSA + dSB e^{0.6.4}
\end{align*}
\]

- Charge transfer interaction between n-donor Pyridines with Iodine and Iodine monochloride increases with solvent polarity *within our experimental range of dielectric constant values.*
- DFT shows the formation of energetically favourable CT complexes from their constituent donors and acceptors.
- DFT qualitatively explains the experimental blue shift of the CT band with solvent polarity provided the donors and acceptors are considered alone.
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- DFT study helps us to propose a logarithmic relation between the important bond lengths associated with donor acceptor interaction and the dielectric constant of the experimental solvents as in equations e.6.5 and e.6.6

\[ r_{N-1} = a \ln \varepsilon + C \]  
\[ r_{1-cr} = a' \ln \varepsilon + C' \]  

- Theoretical red shift is attributed to the increase of energy of (HOMO-n) orbital of the CT complex more as compared to that of LUMO of the CT complex by DFT.
- Ignoring the specific solute solvent interaction and the equilibrium between the CT complex and the component donor and acceptor molecules present in solution at the theoretical level leads to the discrepancy in the experimental and theoretical results; besides the fact that the CT transitions studied are indirect allowed in reality and during TDDFT study they are regarded as direct transitions.

So, with the hope of contributing something interesting fundamental scientific research; as a tiny part to the vast world of scientific adventure; we conclude with the future prospect of studying beyond the limitations we were bound within, during this journey.

Future Prospect:
Learning is an eternal process and we are keen to know what happens beyond the dielectric constant value of 10 to our donor acceptor systems and what if we had considered the CT transitions as adiabatic transition during TDDFT study. If it is the method that failed to give experimentally obtained result or the reason lies somewhere else? We hope we can carry on with this future project.