Crystal structure, vibrational characteristics and vibronic coupling of some conducting organic molecules

ABSTRACT OF THE
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The invention of organic conductors in the beginning of seventh decade of the 20th century has played an important role in science. Hereinbefore, it was believed that majority of organic solids are electrical insulators and the idea that such traditional organic materials could exhibit electrical, optical and magnetic properties which are characteristics of metals, seemed to be completely unacceptable. The picture has, however, changed in recent years, as researches on organic conductors have now given rise to new classes of molecular and polymeric materials with properties analogous to those of metals. In the last four decades there has been a revolution in terms of electrical conductivity, with a progression from insulating and semiconducting behaviour to conducting and superconducting behaviour. A new field known as organic conductors/molecular conductors has emerged at the interface of chemistry, physics and materials science.

Conductive organic materials are lighter, more flexible, and less expensive than inorganic conductors. Also there are varieties to synthesize them and ease of processing. Unlike inorganic conductors, organic conducting materials are constructed from organic (carbon - based) small molecules. Superconductivity could be also achieved in these types of materials due to their highly crystalline nature. Organic superconductor may have more advantage over inorganic superconductor. For example, these have reduced weight and potential versatility having ability to modify their electrical attributes via chemical methods. Current applications of high temperature organic superconductors include; magnetic shielding devices, medical imaging systems, superconducting quantum interference devices (SQUIDS), IR sensors, analogue signal processing devices, and microwave devices. These materials are used in energy storage devices, particle accelerators, levitated vehicle transportation, rotating machinery, and in magnetic separators also. These properties make them desirable alternatives in many applications. These provide possibility of new applications that could have been impossible using copper or silicon devices. Organic conductors are expected to play important role in the emerging science of molecular computing.
Growing interest in the organic conductor stems from their functionalization which may potentially give rise to more complex structures and physical properties. The molecular, crystal and electronic structures help to understand the basic mechanism of the conductivity in organic materials. The knowledge of the vibrational characteristics for the organic conductor molecules is helpful to understand the mechanism of conductivity. In the crystals of conducting organic materials, molecular vibrations strongly interact with the electronic motions and therefore, are altered in their properties; due to electron-molecular-vibrational coupling (vibronic coupling). Therefore, it is worthwhile to undertake the molecular, crystal and electronic structures, vibrational characteristics and vibronic coupling investigations such molecules. In the present thesis we have selected five such molecules, namely, 2,3,5,6-tetrafluoro-7,7,8,8 tetracyanoquinodimethane (F$_4$-TCNQ), 2,3-dichloro-5,6-dicyano-p-benzoquinone (DDQ), tetramethyltetraselenafulvalene (TMTSF), Dibenzotetrathiafulvalene (DBTTF) and octamethylenetetrathiafulvalene (OMTTF). The results of these investigations are presented in this thesis.

The present thesis encompasses seven chapters. The introductory Chapter 1 outlines the aims and objectives of undertaking the present work. It also gives an account of the work accomplished on the charge transfer complexes.

Chapter 2 is divided in two parts. The first part (2a) describes the experimental details of the IR and Raman spectroscopies and X-ray diffraction technique. The second part of this Chapter (2b) includes brief introductory notes on the methods. DFT is a quantum mechanical theory used in physics and chemistry to investigate the electronic structure of many-body systems, in particular atoms, molecules, and the condensed phases. With this theory, the properties of a many-electron system can be determined by using functional, i.e. functions of another function (electronic charge density). Methodology of calculation of the potential distributions is also present in this part. Also a mathematical derivation for the vibronic coupling is given in this part.

Chapter 3 describes the molecular, electronic and crystal structures of the F$_4$-TCNQ molecule. The interpretations of the experimental single crystal XRD and IR and Raman spectra for F$_4$-TCNQ have been done. The normal mode analyses of F$_4$-TCNQ have been done in light of the observed IR and Raman spectra, DFT calculations and PEDs computations. Vibronic coupling constants (VCCs) for F$_4$-TCNQ, F$_4$-TCNQ$^*$ and F$_4$-TCNQ$^-$ have been determined and analyzed. The F$_4$-TCNQ molecule
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belongs to $D_{2h}$ point group symmetry. Changes in bond lengths are more prominent in going from neutral to its first excited state as compared to the neutral to its anionic state. Hence, the conjugation nature is dominating in case of the first excited state of $F_4$-TCNQ which is an important property for conductivity. More conjugation of a molecule means the molecule could accept an electron more easily. The structural parameters derived from the experimental XRD data agree quite well with the DFT optimized structural data. Crystal system of $F_4$-TCNQ is orthorhombic and it belongs to Pbca space group. In unit cell of $F_4$-TCNQ, the $C_1, C_3, C_4, C_6$ and all N atoms are interacting with the molecules of neighbouring and its own cell. The major change in frequency from neutral to the excited state for $\nu$(ring) under the $a_g$ species is noticed for $F_4$-TCNQ. In this $\nu$(ring) mode, contribution of $C=C$ motion is dominating. The magnitude of the VCC is maximum for the above $\nu$(ring) mode. Hence vibronic coupling of this mode gives an idea that the geometry of $F_4$-TCNQ under this mode resembles to that of the ion and vice-versa and charge transfer occurs. Thus large VCC of the mode shows that addition of an electron is much easier during this vibrational mode. From the present study one could conclude that in $F_4$-TCNQ the halogen atoms, cyano groups and phenyl ring participate in the charge transfer process.

Chapter 4 deals the experimental single crystal XRD, IR and Raman spectra for the DDQ molecule. The DFT computations have been carried out for the molecular structures and vibrational characteristics of the neutral (DDQ), anionic (DDQ-) and first excited state (DDQ*) of the DDQ molecule. In this chapter we have discussed the vibrational assignments of DDQ, DDQ- and DDQ* in light of the observed IR and Raman spectra, DFT calculations and potential energy distributions (PEDs). The short bond interactions of molecule with the molecules in the neighboring and its own unit cell have been discussed. VCCs in DDQ, DDQ- and DDQ* have been computed using the DFT/B3LYP results. The DDQ molecule belongs to $C_{2v}$ point group symmetry. Changes in bond lengths are more prominent in going from neutral to its first excited state as compared to the neutral to its anionic state. Hence, more conjugation is found in case of DDQ* means the DDQ* molecule could accept an electron more easily as compared to DDQ-. The structural parameters derived from the experimental XRD data agree quite well with the DFT optimized structural data. Crystal system of DDQ is orthorhombic and it belongs to Pbca space group. In unit cell of DDQ, except $C_1, C_2, C_{11}$ and $C_{12}$ atoms, all atoms are interacting with the molecules of neighbouring and its
own cell. The major change in frequency from neutral to the excited state for $\nu\ (\text{ring})$ is noticed whereas in going from the neutral to its cation the major change is noticed for the $\nu\ (\text{C}=\text{O})$ mode. Therefore, the magnitude of the VCC is maximum for the above $\nu\ (\text{ring})$ mode in the transition $\text{DDQ} \rightarrow \text{DDQ}^*$ and for the $\text{DDQ} \rightarrow \text{DDQ}^-$ transition, maximum VCC is calculated for the $\nu\ (\text{C}=\text{O})$ mode. From the present study one could conclude that in DDQ, the halogen atoms, O atoms, cyano groups and phenyl ring participate in the charge transfer process.

Chapter 5 deals the molecular, electronic and crystal structures of TMTSF. The experimental single crystal XRD and IR and Raman spectra for TMTSF have been interpreted in this chapter. Computations and interpretations of the vibrational characteristics and VCCs for the TMTSF and TMTSF$^+$ molecules have been presented in this chapter. In Chapter 6 of the thesis, interpretations of the experimental single crystal XRD and IR and Raman spectra for the DBTTF molecule have been presented. In order to facilitate this, computations have been carried out for the molecular structures and vibrational characteristics of the DBTTF molecule. The short bond interactions of molecule with the molecules in the neighboring and its own unit cell have been discussed. Vibronic coupling constants in DBTTF and DBTTF$^+$ have been computed using the DFT/B3LYP results. The TMTSF and DBTTF molecules belong to $C_{2v}$ point group symmetry. All the studied molecules exhibit partial double bond character as all the bond lengths are changed from their usual bond lengths. The partial double bond character has been found to be indicate that the conducting behaviour of these molecules. Crystal system of TMTSF is Triclinic whereas the crystal system of DBTTF is monoclinic. In unit cell of TMTSF, the H$_6$, H$_9$, H$_{14}$, H$_{16}$ and all Se atoms interact with the molecules of neighbouring and its own cell whereas in unit cell of DBTTF, only C$_7$ and S$_{23}$ atoms participate. The major changes in frequencies from neutral to the cationic state for $\nu\ (\text{ring})$ and $\nu(\text{C}=\text{C})$ are found in both molecules. The magnitude of the VCC is noticed to be maximum for the $\nu\ (\text{C}=\text{C})$. The geometry of the neutral molecule under this mode resembles to that of the ion and vice-versa. Thus large VCC of this mode shows that removal of an electron is much easier during the vibrational modes.

Chapter 7 embodies the results of our investigations on the molecular and electronic structures of the OMTTF molecule. The calculated optimized geometry of the OMTTF molecule is compared with the experimental XRD results. The X-ray
crystal structure of OMTTF has been used to analyze inter-molecular interactions. To make a complete analysis of the IR and Raman spectra of OMTTF the results obtained from the DFT calculations and the computed potential energy distribution (PEDs) have been used and normal mode assignments have been made. VCCs in OMTTF and OMTTF\(^+\) have been computed using the DFT/B3LYP results. OMTTF belongs to \(C_\text{s}\) point group symmetry. The OMTTF molecule exhibit partial double bond character as all the bond lengths are changed from their usual bond lengths. The crystal system of OHBTTF is Monoclinic. Again the major changes in frequencies from neutral to the cationic state for \(\nu\) (ring) and \(\nu(C=\text{C})\) are found for OMTTF. The magnitude of the VCC is found to be maximum for the \(\nu\) (C═C). Thus large VCC of this mode shows that removal of an electron is much easier during the vibrational modes. Hence vibronic interaction provides a direct link between the geometry and electronic structures and its transport properties in the material.

The references cited throughout the thesis are listed collectively after chapter 7.

**List of Publications**


- R.A. Yadav, **P. Rani**, M. Kumar, R. Singh, Priyanka Singh, N.P. Singh, “Experimental IR and Raman spectra and quantum chemical studies of molecular


➢ **Poonam Rani** and R. A. Yadav, “ab initio investigation for molecular behavior of building blocks of organic superconductors: 4,5-ethylenedithio-1,3-dithiole-2-thione and 4,5-ethylenedithio-1,3-dithiole-2-one”. Asian journal of Physics, 2015. Accepted.