In this chapter, we present the experimental methods of the Fourier Transform-Infrared and Raman spectral measurements, a brief description of the electronic structure methods and normal mode calculations.
2.1 Experimental details

2.1.1 Introduction

IR spectroscopy is generally considered to be able to provide only qualitative and semi quantitative analyses of samples, using the conventional dispersive instruments such as a high quality monochromator. However, the development of FTIR instrumentation and computerized data-processing capabilities have greatly improved the performance of quantitative IR work.

The Fourier transform infrared (FTIR) spectrometers are based on an interferometer such as Michelson interferometer that produces an interferogram of the sample from which the absorbance spectrum can be calculated. The interferogram contains information over the entire IR region to which the detector is responsive. A complete spectrum can be obtained during a single scan. The FTIR approach has number of advantages in terms of speed, accuracy, reproducibility and sensitivity. FTIR has revolutionized IR spectroscopy by allowing a range of sampling techniques to be used, so that a useful and reproducible spectrum of almost any sample can be obtained with relative ease. The sampling techniques are generally employed with sample holders, such as liquid or gas cells with NaCl or KBr windows for liquid or gas samples and KBr pellets or nujol mulls for solid samples.

Raman spectroscopy technique gives complementary information to IR spectrum, but has the advantage that sampling can be very simple since glass is an acceptable optical material for Raman spectra and water is the preferred solvent. Typically, Raman scattering has been excited by visible (occasionally
UV) lasers and the light analyzed by a dispersive system including a high 
quality monochromator and photomultiplier tube as detector. The development 
of Fourier Transform Raman (FT-Raman) spectrometers have overcome to a 
large extent the problem of fluorescence which has always plagued Raman 
measurements. The central idea behind FT-Raman is to move the exciting line 
from the visible to the near-IR (typically a Nd-YAG laser of wavelength 1064 
nm). The lower energy of this light reduces fluorescence in most cases, and 
also has the advantage of reducing both self-absorption of the Raman signal by 
dark coloured samples and photodegradation of the sample. The main benefit 
of FT-Raman is that a much wider range of sample types can be examined 
[128,129].

All the compounds chosen for study were procured from Aldrich 
Chemical Company and were used as received. All the compounds of 
benzaldehyde derivatives and 2-Chloro-5-bromopyridine are solid samples, and 
2-Chloro-4-methoxypyridine and 3-Bromo-5-methylpyridine are liquid 
samples.

2.1.2 Fourier Transform Infra Red spectral measurements

*Nicolet’s Impact 410 FT spectrometer* was used for the infrared spectral 
measurements at room temperature in the range of 4000-400 cm\(^{-1}\). The 
instrument was provided with a ETC Ever-Glo\textsuperscript{TM} Mid IR source, a deuterated 
Lanthanum triglycine sulfate (DLaTGS) solid state detector and Germanium on 
KBr as beam splitter. The solid sample was grinded in KBr to form a pellet 
,and liquid sample was smeared between cells of KBr window. The signals
were collected for 100 scans with a scan interval of 1 cm\(^{-1}\) and at optical resolution of 0.4 cm\(^{-1}\).

2.1.3 Fourier Transform Raman spectral measurements

The Fourier-Transform Raman Bruker-FRA 106/RFS 100 spectrometer was used for the Raman spectral measurements at room temperature in the range of 3500-50 cm\(^{-1}\). The spectrometer consisted of a quartz beam splitter and a high sensitive Germanium diode detector (D 418) cooled to the liquid nitrogen temperature. The sample was packed in a quartz tube of about 5 mm diameter and excited in the 180° geometry with 1064 nm laser beam from a diode pumped-air cooled-cw Nd:YAG laser. The power of the laser beam was varied between 75-150 mw depending on the sample. Rayleigh scattering was avoided by using Notch filters. The signals were collected for 300 scans at the interval of 1 cm\(^{-1}\) and optical resolution of 0.1 cm\(^{-1}\).

2.2 Computational details

2.2.1 Electronic structure calculation methods

The development of theoretical methods and in particularly quantum chemistry, allowed not only an interpretation of the experimental observations, but also made it possible to predict molecular properties and processes. Computational chemistry is simply the application of quantum mechanical and computing skills to the solution of physical, chemical, biological and even medical problems. Here, one uses computer softwares to generate information such as properties of molecules or simulated experimental results. Some
common computer softwares used for computational work includes: GAUSSIAN, GAMESS, MOPAC etc. It helps physicists/chemists to make predictions before running the actual experiments so that they can be well prepared for making observations. The Schrödinger equation is the basis for the computational methods. With these methods we can calculate: electronic structures, frequencies, transition structures, electron and charge distributions, potential energy surfaces (PES), rate constants for chemical kinetic reactions, thermodynamic properties—heat of reactions, energy of activation, and protein calculations, etc [130-135]. Calculating Schrödinger’s equation for systems with more than one electron is quite difficult. However, by using a number of approximations, coupled with the ever-increasing number-crunching modern computers, it is now possible to solve Schrödinger’s equation for multiple-electron systems. The Born-Oppenheimer approximation is the first of several approximations made while trying to solve Schrödinger’s equation for more complex systems with more than one or two electrons. A few electronic structure computation methods are discussed in brief as follows.

In the ab initio Hartree-Fock self-consistent field (HF-SCF) method, the wave function is an antisymmetrized determinantal product of one-electron orbitals (the "Slater" determinant). Schrödinger’s equation is transformed into a set of Hartree-Fock equations. The wavefunction of each electron is optimized under the mean potential averaged over all the other electrons in the system, as well as the electrostatic potential generated by the fixed nuclei. In another words, during the Hartree-Fock calculation, the electron cannot ‘see’
other electrons, instead of averaged ‘electron gas’. The primary deficiency of Hartree-Fock method is that the correlation of electron motion cannot be accounted adequately.

The semi-empirical methods replace the computationally expensive Hartree-Fock integrals with parameters chosen to fit experimental data. The most common semi-empirical methods are: modified neglect of differential overlap (MNDO) algorithm, the Austin Model 1 (AM1), Parameterized Model 3 (PM3).

Density Functional Theory (DFT) method is one of the most popular approaches to quantum mechanical many-body electronic structure calculations of molecular and condensed matter systems. It has been proved that for molecules, the ground-state molecular energy is uniquely determined by the ground-state electron probability density. Therefore, all the ground-state molecular properties can be calculated from the electron density, without having to find the molecular wave function. In addition, according to the Hohenberg-Kohn variational theorem, the true ground-state electron density minimizes the energy functional [130]. The DFT method is variational. Although the present form of DFT computation was proposed by Kohn-Sham in 1965 [131,132], it is fair to say that DFT has been taken seriously as a tool for solving physical/chemical problems only since the mid 1980s [133-139]. A number of density functional theoretical methods have been developed, namely, B-LYP (Becke’s exchange functional with Lee Yang Parr correlation
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functional), B-P86 (Becke's exchange functional with gradient-corrected Perdew correlation functional), B3-P86 (Becke's three parameter mixing of exchange functional with gradient-corrected Perdew correlation functional), B3-PW91 (Becke's three parameter mixing of exchange functional with gradient-corrected Perdew and Wang correlation functional), B3-LYP (Becke's three parameter mixing of exchange functional with Lee Yang Parr correlation functional) and S-VWN (Slater exchange functional with local Vosko-Wilk-Nusair correlation functional) [130-138].

There are several multiple determinant methods, where multiple Slater determinants are formed, two of them are:

**Configuration Interaction (CI) methods** proceed by constructing more than one determinants by replacing one or more occupied orbitals in Hartree-Fock determinant with a virtual orbital. The wave function of the system is represented as the linear combination of these multiple determinants.

**Møller-Plesset perturbation theory** is also an electron correlation method. Closely related to many-body perturbation theory, this method introduces correction of Hamiltonian corresponding to the perturbation of the system. Actually, the Hartree-Fock energy is the energy correct through first-order in Møller-Plesset perturbation theory. With the energy the correct through second order, it is called MP2 level of theory. Similarly, MP3 level of theory includes the correction through the third order, and so on. All orders of MPn theory are size-consistent, but not variational [138].
2.2.2 Basis functions and Basis sets

The basis set is the set of mathematical functions from which the wave function is constructed. The molecular orbitals are expanded as a linear combination of one-electron functions known as basis functions. Basis functions are usually centered on the atomic nuclei, hence are called linear combinations of atomic orbitals (LCAO). An individual molecular orbital is defined as

$$\phi_i = \sum_{\mu=1}^{N} C_{\mu i} \chi_{\mu}$$

where $\chi_1, \chi_2, \chi_3, \chi_4, \ldots$ are known as basis functions and are collectively called as basis set and the equation as the 'linear combination of atomic orbitals' (LCAO). There are mainly two types of atomic basis functions: Slater type atomic orbitals (STO) and Gaussian type atomic orbitals (GTO). In practice, the Gaussian-type atomic orbitals are commonly used because evaluation of integrals is easier over Slater-type orbitals. In above equation, if $\chi_1, \chi_2, \chi_3, \chi_4, \ldots$ are Cartesian Gaussians, the coefficients remain constant during calculation, then, $\phi_i$ is called a contracted Gaussian–type function (CGTF) and $\chi_1, \chi_2, \chi_3, \chi_4, \ldots$ are called primitive Gaussians. One can have any number of basis functions in a basis set. If the minimum required numbers of basis functions are used, it is a minimal basis set. For increase of accuracy in results we can have more number of the basis functions per atom: it is known as split valence basis set. The basis set formed by doubling all the functions of a minimal basis set is called double zeta basis set, similarly triple zeta basis set. When contracted Gaussian are used, a minimal basis set consists of one contracted
Gaussian function for each inner-shell and valence atomic orbital, a double zeta basis set consists of two contracted Gaussian for each such atomic orbitals and a double zeta+polarization basis set adds polarization functions apart from of two contracted Gaussian for each such atomic orbitals. Therefore, 6-31*G basis set is a split valence polarization basis set; it uses a linear combination of six primitives in each inner-shell atomic orbital, represent each valence-shell atomic orbital by one CGTF with three primitives, one Gaussian with one primitive and adds a single set of six d-type Cartesian polarization functions for each nonhydrogen atom. 6-31+G* basis set is formed from 6-31G* basis set by the addition of four highly diffuse functions (s, p_x, p_y, p_z) on each nonhydrogen atom (a highly diffuse function is one with a very small orbital exponent) Similarly triple zeta basis set 6-311G* and 6-311+G* can be described. Split valence basis set allows orbital to change size but not shape. The polarization basis set is included to allow change in shape [130]

2.2.3 Computational levels and Basis sets

In order to model structures and vibrational spectral properties, we performed calculations with the ab initio and DFT methods using the Gaussian 03W suite of programs [140]. For all the compounds selected for study, we started with following methods: RHF, BLYP, SVWN, BP86, B3LYP, B3P86 and B3PW91 were combined with the 6-31G* basis set, to see the performance of levels, but these results are not presented and discussed in the thesis. Conformational analysis that is, geometry optimization for all the compounds is carried out with B3LYP/6-31G*. For the compound, 5BMeB, the levels RHF and B3LYP
combined with 6-311G* basis set were used for frequency calculation. For the compounds 2CFB, 3CFB and 3MFB, the levels, RHF, B3LYP and B3P86 combined with 6-311G* basis set were used for frequency calculations. For the remaining compounds, the levels RHF, B3LYP and B3PW91 combined with 6-311G* basis set were used for frequency calculations. Molecular electronic energies, equilibrium geometries, IR and Raman spectra have been computed. All the computed harmonic frequencies have been scaled with suitable scale factors [141].

The available experimental bond lengths [from ref.] and computed bond lengths are compared using the following formula and corresponding graphs are plotted.

$$\%\text{error} = \frac{0_{\text{exp}} - 0_{\text{cal}}}{0_{\text{exp}}} \times 100$$

Similarly the available experimental bond angles [from ref.] and computed bond angles are calculated using the following formula. As there is no experimental data available for some bond angles, we have chosen not to plot the corresponding graphs, but errors are discussed in the respective chapters.

$$\%\text{error} = \frac{A_{\text{exp}}^\circ - A_{\text{cal}}^\circ}{A_{\text{exp}}^\circ} \times 100$$

The experimental and computed frequencies are compared using the following formula and corresponding graphs are plotted.

$$\%\text{error} = \frac{v_{\text{exp}} - v_{\text{cal}}}{v_{\text{exp}}} \times 100$$
In 3CMeB, we examined the performance of B3LYP level combined with different basis sets. The basis sets include: split valence basis sets; 3-21G*, 6-31G*, 6-31G**, 6-311G*, 6-311G+(d,p), 6-311G++(d,p) and correlation-consistent polarized split valence basis sets-ccpVXZ (X=D for double, T for triple), but, the results are not presented. In BHB, we modeled dimer structure to account for the hydrogen bonding at B3LYP/6-31G*.

2.2.4 Normal mode calculations

Normal Coordinate Analysis plays an important role in understanding vibrational and thermal properties of molecular structures at the atomic level. Around 1970 Gwinn developed a program for normal coordinate analysis using mass-weighted Cartesian coordinates, which eliminates the redundancy problems arising when internal valence coordinates are used, as in the GF-method [142]. Gwinn’s methods have subsequently been improved. MOLVIB is based on the same fundamental idea. In the harmonic approximation, the potential energy may be expressed as,

\[ V = \frac{1}{2} \sum_{i,j} f_{ij} x_i x_j \]

where the coefficients \( f_{ij} \), the second order partial derivatives of the potential energy in equilibrium, form a square-symmetric matrix of order 3N, called the force constant matrix \( F \).

Frequently force constants are expressed in terms of internal coordinates. \( L\)-matrix gives the transformation from normal to internal coordinates. The normal modes can be characterized by means of the Potential
Energy Distribution (PED), which is calculated from $L$-matrix and the $F$-matrix in internal coordinates according to the formula.

$$P_{ij} = (L_{ij})^2 F_{ij} / \lambda_i$$

Hence Potential Energy Distribution (PED), which gives the fractional contribution of the diagonal matrix elements of $F$ to the normal modes.

MOLVIB is a FORTRAN program for the calculation of harmonic force-fields and vibrational modes of molecules upto 50 atoms [143]. To aid the vibrational assignments, we carried out normal coordinate calculations using MOLVIB package [144]: force fields and PEDs have been computed for B3LYP/6-311G* results for all the compounds. We have calculated the PEDs as in the following way. Using the optimized geometries and cartesian force constants from B3LYP/6-311G* archive file is created and used as input in the MOLVIB package. The package generated the internal coordinates via a transformation, which in the second stage computed internal force constants from a similarity transformation of the DFT force constant matrix (the Hessian). Finally, PEDs were calculated in terms of symmetry coordinates (internal coordinates are symmetry coordinates for low symmetry molecules). All the vibrational normal modes were visualized by the MOLDEN package, which uses the Gaussian results for displaying animated normal modes [145].