ABSTRACT

Vibrational spectroscopy is a valuable tool for the elucidation of molecular structure. Vibrational spectra can be utilized directly and simply as molecular fingerprints to characterize and identify a molecule. Recent developments in Fourier Transform Spectrometers have led to higher resolution, total wavelength coverage, higher accuracy in frequency and intensity measurements. Moreover, sophisticated computational methods of theoretical chemistry have also been developed by powerful personal computers. This has made it possible to perform a complete vibrational analysis on relatively large polyatomic molecules.

Statement of Problem

For a proper understanding of IR and Raman spectra, a reliable assignment of all vibrational bands is essential. For this purpose, quantum chemical methods are invaluable tools. Among them, Density Functional theory (DFT) methods have evolved as powerful quantum chemical tool for the determination of the structure of molecules. In the frame work of DFT approach, different exchange and correlation functionals are routinely used. Among these, the B3LYP combination is the most used since it proved its ability in reproducing various molecular properties, including vibrational spectra. In the present investigation, various compounds of some specific application have been chosen for vibrational spectroscopic analysis. The chosen compounds were purchased from Sigma Aldrich with high purity of 99% as well as synthesized and taken up for further investigations. The experimental FTIR, FT-Raman and UV-Vis spectra of all the chosen compounds were recorded in the condensed phase and the vibrational wavenumbers thus obtained were used for comparison with their calculated counterparts.

Literature survey

Density Functional Theory (DFT) based conformational analysis and vibrational studies have been carried out on 2,4-dihydroxy-4-methyl-acetophenone and 2,4-dihydroxy-3-acetyl-6-methyl-acetophenone by Saiket K. Seth et al. The conformational equilibrium of the monooximes of 1,2-naphthoquinone and their Nuclear magnetic resonance (NMR) reports have been extensively carried out previously. The density functional studies on 1-napthol have been extensively carried out by Raja et al., The spectroscopic studies including IR mass
spectrometry, EPR & x-ray were reported earlier on DPC by Fouda et. al. Also, determination of metal complex using ERS was reported by Laszlo Szabo et. al.

**Research methodology and tools used**

In the present work, DFT has been effectively utilized in analyzing the molecules in following aspects:

1. Energy optimization,
2. Conformal stability,
3. Potential Energy Surface scan analysis,
4. Hydrogen bonding,
5. S-cis and S-trans conformers.

The energy optimization was performed on all the chosen compounds using suitable combination of DFT methods and basis sets. During the optimization procedure, all the geometrical parameters were relaxed and the true energy minimum was identified. In some compounds, to identify the most stable geometry among the different conformers taken up, the energy optimization was performed on all the assumed conformers and from the results obtained, that conformer which was having the global minimum energy was identified to be the most stable one. In the potential energy surface scan analysis, the selected dihedral angle of the chosen molecule was rotated and the most stable geometry was ascertained. The presence of intra molecular hydrogen bond in some of the chosen compounds was identified. From the changes that occur in molecular geometry, deviations in the vibrational wavenumbers due to the formation of intra molecular hydrogen bond was investigated. The analysis of the existence of rotational isomers namely S-cis and S-trans among one of the chosen compound was also investigated with the aid of DFT.

To predict the charge transfer that takes place within the molecule, Natural Bond Orbital analysis has been utilized. The intramolecular interactions, delocalization of electrons and stabilization energy of the title compounds were investigated by performing NBO analysis using NBO 5.1 program as implemented in the Gaussian 09W package. The NBO analysis gives the information about the interactions both in filled and virtual orbital spaces which could enhance the analysis of intra and intermolecular interactions. The second order Fock matrix
was carried out to evaluate the donor-acceptor interactions in the NBO analysis. The energy gap of the chosen compounds was obtained from HOMO-LUMO analysis.

The Gaussian 09w version along with Gauss view 5 software package was used for the above investigations. The Density Functional Theory calculations were carried out with B3LYP/B3P86 methods and 6-31G*, 6-31G**, 6-31+G** and 6-31++G** basis sets.

The DFT computations provide vibrational frequencies usually in fair agreement with experiment. However, for a reliable vibrational analysis, scaling of the compound harmonic force field is required. In the present study, the scaling of vibrational frequencies was done using Scaled Quantum Mechanical (SQM) method. Three types of scaling procedure namely uniform scaling, initial scaling and final scaling were adopted to achieve a close agreement between the experimental and calculated vibrational wavenumbers. For visual comparison the calculated graphical spectra were compared with the experimental counterparts. The least square refinement of scale factors, calculation of potential energy distribution, prediction of IR and Raman spectra were performed using the software package MOLVIB version 7.0.

**Arrangement of chapters**

The proposed thesis is organized in nine chapters.

**Chapter one** deals with preliminary concepts of vibrational spectroscopy and its applications to polyatomic molecules.

The procedure of quantum chemical calculations, normal coordinate analysis, potential energy surface scan analysis, Natural bond orbital analysis, Homo-Lumo analysis and Mulliken charge analysis of the vibrational spectra form the subject matter for **chapter two**.

The instrumentation aspects, sample handling techniques and the advantages of FT techniques are to be briefly discussed in **chapter three**.

In **chapter four**, an insight into the conformal flexibility and vibrational behavior of 2-nitroso-1-naphthol using density functional theory approach has been analyzed. In order to carry out a detailed vibrational spectroscopic analysis of 2-Nitrosol-1-naphthol, Fourier Transform Infrared and Fourier Transform Raman spectra have been recorded in condensed phase. Density functional theory calculations in the B3LYP/6-31G** level have been carried out followed by scaling using the SQM methodology. Substitution of nitroso group into the 1-
napthol has produced remarkable changes in the structural parameters. The ultraviolet visible spectra of the title compound dissolved in various solvents were recorded in the range of 300-500 nm. The Natural bond orbital analysis, frontier molecular orbital analysis and thermodynamic features were also performed using B3LYP/6-31G** method.

**Chapter five** is devoted to the effect of hydrogen bonding, the conformational stability and vibrational analysis of 2,6- and 3,5-Dihydroxyacetophenone. The experimental (FT-IR and FT-Raman) spectra were recorded in the condensed phase. The optimized geometry and vibrational wavenumbers were determined by using B3LYP/6-31G** level Density Functional Theory calculations. The effect of scaling on the calculated wavenumbers was analyzed by employing unscaled, uniform scaling and selective scaling procedures. A detailed comparative analysis on the effect of hydrogen bonding on the geometry, structural parameters and vibrational wavenumbers has been carried out using the results obtained from PES scan and DFT level calculations.

Analysis of S-cis & S-trans conformers and vibrational Spectroscopic studies of 2-Methoxy benzoic chloride by quantum chemical calculations forms the subject matter for **chapter six**. The experimental spectra were recorded in the condensed phase. The optimized geometry and vibrational wavenumbers were determined by using different sets of DFT method and basis sets. The presence of intra molecular hydrogen bond in the S-cis conformer was identified from the changes observed in the molecular geometry and vibrational wave numbers. This S-cis conformer with the hydrogen bond makes it as a most stable conformer. In addition this, comparative NBO and Homo-Lumo analysis were carried out.

The Molecular Structure and vibrational spectroscopic (FT-IR, FT-Raman & DFT based) analysis of Diphenyl Carbazide was discussed in **chapter seven**. To carry out a detailed vibrational spectroscopic analysis of the title compound, FT-IR and FT-Raman spectra of DPC have been recorded in the condensed phase. Density Functional Theory calculations in the B3LYP/6-31G* level have been carried out to determine the optimized geometry and vibrational frequencies. The SQM treatment was done on the calculated frequencies. The NBO analysis shows that change in electron density (ED) in the σ* and π* antibonding orbitals and second order delocalization energies E(2) confirms the occurrence of intramolecular charge transfer (ICT) within the molecule. The calculated Homo and Lumo energies show that charge transfer occurs within the molecule.
In the **chapter eight**, the synthesis procedure, preparation, spectral characterization and vibrational analysis of Semi cinnamalydene acetone using DFT calculations acetone have been discussed. Different conformers of the title compound were assumed and the most stable conformer was identified with the help of DFT calculations. A detailed study on the natural bond orbital analysis, Homo-Lumo analysis were also done on the title compound.

The **final chapter** summarizes the results of works presented in the thesis about the different compounds taken up for study and suggestions, scope for the future works. At the end of thesis, publications of the work and conference presentation details were mentioned.

**Summary of findings**

The various possible conformers, their respective energies, optimized geometry, vibrational wavenumbers and the intramolecular interactions of the title compounds were investigated with aid of Density Functional Theory. The most stable conformers were identified using DFT optimization procedure. The results of different scans (2D and 3D), using potential energy surface scan analysis, have been effectively used to confirm the choice of the most stable conformer of the titled compounds. From the comparative study made on the geometrical parameters of some of the title compounds, the presence of a strong intramolecular hydrogen bond was confirmed. A satisfactory assignment of most of the fundamentals was provided using the scaling procedure. The vibrational wavenumber, IR and Raman intensities were calculated using DFT method and they were found to be in good agreement with the experimental values. The results from the frontier molecular orbital analysis establishes the energy gap of all the title compounds. The theoretical UV-Vis results agree very well with the experimental determinations in terms of absorption wavelength and their respective assignments were made for various solvents. The electron density changes in the bonding and antibonding orbitals and that of lone pairs due to the charge transfer of electrons between various bonds have been investigated by NBO analysis.