Thesis Synopsis

In this thesis, I report the gas phase infrared spectra of some polycyclic aromatic hydrocarbons (PAHs) namely 1, 5-, 1, 6-, and 2, 6-dimethyl naphthalenes (DMNs); 2, 4-, 2, 6-, 2, 7-, and 2,8-dimethyl quinolines (DMQs); and 1, 9-, 2, 4-, and 3, 9-dimethyl phenanthrenes (DMPs) and diols such as 1, 2-ethylene glycol (1,2-EG) and 1, 4-butanediol (1,4-BD). Assignment of the IR spectra has been done with the help of DFT calculations followed by scaled quantum mechanical force field calculations.

Chapter 1 gives a brief introduction to PAHs and diols. A brief survey of literature pertinent to their sources, their importance, experimental techniques for identification of PAHs and different conformers of diols and intramolecular interactions between the two hydroxyl groups in the diols are presented. The scope and motivation of the present investigation have been described at the end of the chapter.

In Chapter 2, I have discussed all the methods used in carrying out this work. The details of the experimental FT IR set-up and quantum-chemical calculations employed in this work have been elaborated in this chapter.

The subsequent chapters 3 - 5 deal with the experimental and theoretical results obtained for DMNs, DMQs, and DMPs. In chapter 3, infrared spectra of 1,5-, 1,6-, and 2,6-DMN have been described. The spectra have been recorded using a multi-pass gas cell coupled with Nexus-870 spectrometer (Thermonicolet, US). Qualitatively, spectral assignments have been made with the help of calculated doubly scaled (one scaling factor for the C-H stretching and another factor for the non C-H stretching frequencies) harmonic frequencies at the B3LYP/6-31G* level of theory. The spectral features to distinguish three different isomers of DMN have
been identified. In chapter 4, IR spectra of 2,4-, 2,6-, 2,7-, and 2,8-DMQ in the gas phase have been recorded using a high resolution Vertex-70 (Bruker Optics, Germany) FT-IR spectrometer. DFT calculations have been carried out in order to get harmonic and anharmonic frequencies and their intensities at the B3LYP/6-31G* level of theory. Unambiguous assignments of IR bands could not be made with the help of anharmonic or selectively scaled harmonic frequencies. Therefore, scaled quantum mechanical (SQM) force field calculations were performed where force fields in local coordinates were scaled for getting frequencies in close agreement with experiment. Potential energy distributions (PEDs) of the normal modes in terms of the local coordinates of the molecule using a modified UMAT program in the QCPE package were also obtained in order to identify the nature of the fundamental vibration modes. In chapter 5, I have presented the gas phase IR spectra of 1,9-, 2,4-, and 3,9-DMP. The harmonic and anharmonic frequencies and their intensities were obtained at the B3LYP/6-31G* and B3LYP/6-311G** levels of theory. I have carried out SQM calculations for the assignment of the experimental frequencies in a similar fashion as was done for the DMQs.

In chapter 6, IR spectra of two diols namely 1,2-ethylene glycol and 1,4-butane diol are reported and discussed. DFT calculations have been carried out for the harmonic fundamental frequencies and intensities at the experimental temperatures with 10 unique chosen conformers of the diols at the B3LYP/6-311++G** level of theory. Gas phase equilibrium population analysis has been done in order to generate the theoretical spectrum with the weighted average contributions from the 10 conformers to match the experimental spectrum. The hydrogen bond enthalpy, strength and nature have been investigated in details. From this experimental and theoretical studies, it has been concluded that the intramolecular hydrogen bond is absent in 1,2-EG at ordinary temperatures whereas it is present in 1,4-BD.
Chapter 7 is the concluding chapter where the main work done in this thesis is summarized and future direction is presented.