Spectroscopic Characterization Of Polycyclic Aromatic Hydrocarbons and Their Radical Ions Trapped in Glasses

Author
Md.Naziruddin Khan

Supervisor
Prof. Z H Zaidi
Department of Physics
Faculty of Natural Sciences, JMI

Human population is exposed to large variety of natural and synthetic chemical compounds from various environmental sources such as air, water and food. Polycyclic aromatic hydrocarbons (PAHs), which comprise a major class of environmental contaminants, are predicted as potent carcinogens. They are the dominant component of coals, coal derived liquids and an important by product of petroleum manufacture. PAHs are also found in the burning of tobacco as wenll as during incomplete combustion of organic matter in wood and fossil fuels. PAHs have been the subject of several classic investigations in molecular spectroscopy. Despite the considerable interest that attaches to the condensed aromatic hydrocarbons, the treatment of their molecular vibrations has been largely neglected. During the past decade evidences have been mounting that (P AHs) are important components of the interstellar medium. Polycyclic aromatic hydrocarbons (PAHs) have often served as leading examples for understanding spectroscopic and photophysical phenomena in larger molecules and are central knowledge of such properties. Accurate understanding of the radiative properties of PAHs is also fundamental importance to the modeling of the interstellar environment. Therefore, the importance of IR spectrometry as a tool of the practicing organic chemist is readily apparent from the number of literatures. Since IR spectrum of each molecular species is unique, IR is a powerful tool for the identification organic compounds. To properly address the astrophysical problem, a number of works of both theoretical and experimental (gas-phase) effort has been brought over the last several years. While this body of information has been invaluable in establishing the interstellar PAH hypothesis, there are important differences in detail between the laboratory and interstellar spectra. Therefore, the infrared spectroscopic data for PAHs that are free from the perturbations of intermolecular interactions are still very important.

The aim of the present work is to study some small and large non-linear PAHs in solid isolated matrix and investigate the individual characteristic band in neutral and cations. A complete assignment of these molecules through theoretical values is one of the objectives in this work. Further, to understand the spectral behaviour of neutral and cation PAHs in this solid film and minimize the number of fundamental vibrations and spectral complexity of PAHs. Structure and size influence the infrared spectra of small PAHs in their neutral and cations are also studied. To reduce the conspiracies among the different workers reported in earlier. Finally, it is very important to identify changes in between the band positions of solid film spectra and gas-matrix spectra. All these results are to be made a detail discussion to the interstellar emission problems.

For this, a suitable matrix at low temperature is needed. In this work, solid wax film is employed and found excellent matrix for the infrared study and able to make at low temperature, which also can prepare easily. No one has ever been used such matrix, we are using this technique for the first time and the task is found satisfactory. Some small and large P AHs (linear and non-linear) are logically selected and investigated systematically their individual vibrational bands. The characteristic of individual bands for P AHs are assigned through theoretical (DFT) values and the effects on spectra due to change of matrix is also being discussed. The selection P AHs in this thesis work are as follows:

1. Anthracence and Phenanthrene
2. Pyrene and 3.4-benzopyrene
3. Chrysene and 1.2-benzantharacene

The thesis as a whole is divided into six chapters. The chapter wise break up of the present work is as follows:

CHAPTER- 1: INTRODUCTION

To introduce the subject. in the first chapter contains enough backgroW1d and the cuaent status in the literature on Polycyclic Aromatic hydrocarbot1S in general, their importance and its use. A detailed description on historical background of Unidentified Infrared Bands and how these are related to PAHs spectra with Interstellar. Further, an extensive summary on Diffuse Interstellar bands (DIB) and its correlation with PAH are also discussed. It contains enormous experimental study reports on infrared spectroscopic of neutral and cations ofP ARs at low temperature matrix. A few probable IR matrix at low temperature obtain ftom the literature survey is discussed. The motivations behind the selection of the molecules for the present investigations and the objective of the present work are discussed.

Chapter- 2: EXPERIMENTAL DETAILS

The second chapter deals with basic electromagnetic radiation and preparation of solid film in the present study. A brief history of the doping and formation of cations of PAH species in the film is also explained. Detailed information of some probable matrix and their method in literature are reported in this chapter. The background history of wax film technique and preparation method is explained. It provides a short note of preparation of sample in the liquid phase (mull).

CHAPTER- 3: THEORETICAL METHOD AND ITS APPLICATIONS

Third chapter reports the basic foundation, Evolution and development of density functional theory (DFT) calculations method from the very beginning stage and how the quantum chemists had developed for the investigation of structural and vibrational properties of the molecules.

CHAPTER- 4: INTERPRETATION OF INFRARED SPECTRA OF NEUTRAL PAHs

In chapter fourth, a systematic characterization of experimental results is presented and described the effects on spectra due to size and structure differences of PAHs. A brief discussion on individual spectra of all molecules as to changes matrix are also expressed. All neutral spectra of P AHs are compared with the theoretical values obtained by DFT values, previous gas-phase spectra and discussed the differences in band positions.

Chapter- 5: INTERPRETATION OF INFRARED SPECTRA OF CATIONS

All cation spectra positions and intensities are listed together with their relative neutral and described the differences in spectral positions and intensities. Further, it is also discussed that how P AHs spectra are resembled with the interstellar spectra.

Chapter- 6: CONCLUSIONS

An overview of results and conclusions obtained from the present investigation has been given. Suggestions in view of the limitation of the present work and towards the improvements of some of the aspects have been made for future work.