

Chapter 1

An Overview

Atoms and molecules are the most fundamental building blocks of all the matter that surround us. Biomolecules like amino acids, DNAs, RNA etc. are considered to be the basic building blocks of life, which are available in the terrestrial medium. Interestingly, their presence has been confirmed in the interstellar environment as well [1]. Interstellar molecular clouds and circumstellar envelopes act as factories of complex molecular synthesis. Moreover, a high number of molecules that are used in contemporary biochemistry on the Earth is found in the interstellar medium, planetary atmospheres and surfaces, comets, asteroids and meteorites and interplanetary dust particles. Therefore monitoring the formation and evolution of organic matter in space is crucial in order to determine the prebiotic reservoirs available on the prehistoric Earth [2]. In past centuries, researchers tried to explore the structure and dynamics of atoms and molecules [3–5]. When the molecules are exposed to the charged particle or photon interaction, they absorb energy in their internal degrees of freedom and become unstable. These energetically excited molecules will find different pathways to reduce the energy content either by ionizing themselves or by breaking them into pieces. A number of processes are available for the parent molecular ions to relax into a stable configuration. The understanding of such processes is important in wide areas of physical sciences, ranging from planetary and interstellar space [6, 7]. The main goal of this work is to investigate the structure and dynamics of a class of large molecules called PAHs and its derivatives named as PANHs by probing their dissociation pathways. These molecules show similarity to bio-molecules and are considered as a model system which helps in designing the tools and methods, which on longer time scale can be applied to more complex and important systems like biomolecules, aggregates, and clusters.

1.1 Collision Processes and Energy Loss Mechanisms

Generally, molecular ions are produced by using photon or charged particle interaction. For charged particle-molecule interaction, depending upon the projectile velocity as well as the impact parameter, there are two types of interactions. First, in the case of typical projectile velocities lower than 1 a.u., the interaction is more effective to perturb the nuclear coordinates of the molecule, where electrons in the target molecule accommodate the changing field due to the projectile adiabatically. Second, in the case of the projectile with velocities higher than this, which interact with the target faster than the vibrational time scale so that the energy exchange to the target will happen only within the electronic cloud. Electron, as well as the proton, are used as the projectile in this work. In the case of electron impact, when the energy of the electron is very low (e.g. thermal electrons), it could be captured by the neutral molecule to form a negative radical ion. If the energy is sufficient to excite one of the electrons of a molecule to any higher electronic state, the process is termed as electronic excitation. When the energy of an electron is high enough, it can ionize the molecule by removing an electron from it and is possible to have single, double and higher degree of ionization. Similarly, depending on the target and the energy of the primary electrons, various other processes can take place like molecular dissociation/fragmentation, ion-pair (positive and negative ions) formation and dissociative re-arrangement processes [8].

The projectile energy dependence of the electron impact ionization process is very commonly known to peak at about 70 eV to 100 eV, particularly for low-Z targets like hydrocarbons. At higher energy, the cross section varies as $\ln E/E$. Electron impact studies on PAHs in the low energy regime (energy lower than 100 eV) have been reported for few PAHs and PANHs [9–13]. But a detailed and higher energy electron impact study has not been done for PAHs and PANHs. Heavy charged particle-molecule collisions at intermediate velocities (velocity comparable to less tightly bound target electron) is relatively complex due to competing magnitudes of ionization and electron transfer cross section in this regime. Interaction of intermediate velocity (~ 1 a.u.) charged particle like proton with molecules will give the possible understanding of how the low-energy cosmic ray charged particle interacts with PAHs or PANHs in the interstellar medium.

In this type of collision, the energy deposited into the molecule due to a light ion (e.g. proton) is dominated by electronic processes since the electronic stopping power is much larger than the nuclear one. In ion-molecule collision experiments, the impact parameter and the molecular orientation cannot be controlled experimentally. To understand projectile velocity dependence and the orientation of target molecule, both theoretical and experimental studies have been performed in the case of proton-naphthalene collision [14]. Charged particle interaction with atoms and molecules are extensively studied so far at various impact energy regime [15–26]. Such kind of study is rarely performed for PANHs but few experimental studies have been done for PAHs at low and high projectile velocity [27–31]. Photoionization studies have shown that in PAHs the collective excitation plays an important role and it is unexplored in the case of charged particle interaction except naphthalene and fullurene [32–35].

1.2 Plasmon or Collective Excitation

When projectile interacts with the dense cloud of electrons in the molecule with low impact parameter, the energy is transferred to the electrons locally, since the other charges will be screened by Coulomb screening effect. At higher impact parameters the screening effect is less significant and the delocalized electron cloud of the molecule responds to the Coulombic interaction collectively. Such excitation is often observed not only in molecules but also in metallic, non-metallic clusters and some atomic species as well. Fundamentally, similar oscillation is also very common in nuclei. These excitations are characterized by integrated oscillator strength well beyond one. C_{60} , for example, is known to have a 21 eV plasmon excitation with an integrated oscillator strength of effective participation of 71 electrons in the collective excitation [36]. Thus the excitation process deposits very small amount of energy per electron but the total energy deposited is much larger than the ionization potential of the species. Such collective excited states were first discovered in nuclei (proton-neutron oscillation) [37] and were called giant dipole resonances [38, 39].

The energy of giant resonance peaks varies from 2 eV in metal clusters to 20 MeV in nuclei making it 7 orders of magnitude higher. In the case of C_{60} , an analogous feature

appears nearly at 21 eV with width 11.5 eV, close to the one observed in graphite at about 25 eV [36]. Considering the two-dimensional structure of PAHs, this feature is expected nearly at 17 eV and has been observed in electron energy loss spectroscopy studies of PAH films and photoion yield studies in the gas phase [36,40]. The collective excitations are of interest, because of their very large cross sections compared to typical single particle processes and to know what follows after such excitations. In the case of molecules, this kind of excitation not only leads to single ionization but it also causes a significant amount of evaporation of smaller neutral fragments from the parent molecule [41]. Collective excitation is shown to play a major role in the photoionization of naphthalene and related compounds [32]. Similarly, it is very significant in the case of fullerene under charged particle interaction [42]. Plasmon excitation on PAHs has been less explored, whereas, in the case of PANHs such studies have not been reported till date to the extent of our knowledge.

1.3 Statistical and Non-statistical Decay Processes

In a charged particle-molecule collision, energy deposited by the projectile will be stored in the molecular internal rotational-vibrational mode [8,43]. Once the molecular ion is formed, the electron charge generally gets localized over the whole molecular ion [44–46]. So molecular ions are not generated with a specific internal energy but have a broad energy distribution. There will be a randomization of internal energy over all the vibrational modes of a molecular ion prior to any fragmentation and the resulting mass spectra would show a statistical bond breaking. Such processes favor the lowest-energy dissociation channels. The timescale of internal rotational-vibrational oscillation of the molecules is in picoseconds, with respect to which the unimolecular dissociation time scale is considerably larger, and will decide whether the process is a statistical or non-statistical one and which decides the survivability of these molecules. Typically, non-statistical fragmentation processes are fast (femtosecond time scales) and there is no time for the excitation energy to re-distribute itself over all the degrees of freedom of the molecule before the initial fragmentation step. Statistical and non-statistical fragmentation processes often compete. After a non-statistical fragmentation, the molecule may still have high enough

internal energy to decay further via secondary statistical fragmentation. In general, the balance between processes in which energy is transferred to the electronic degrees of freedom (electronic stopping processes) and processes in which energy is transferred directly to the vibrational modes (nuclear-stopping processes) affects the balance between statistical and non-statistical fragmentation processes. Few studies on statistical and non-statistical process has been reported in the case PAHs [47–52]

Larger molecules generally produce a very complex mass spectrum, mainly due to (i) the numerous possible dissociation channels and (ii) the complex isomerization followed by unimolecular dissociation which is statistical in nature with a variable decay constant. The decay constant itself is governed by the internal energy of the molecule which is strongly dependent on the collision parameters. These statistical processes make the molecular dynamics very significant in areas like biochemistry, astrochemistry, life sciences, etc. For the dissociation product ion to appear in the mass spectrum, they must have a very specific range of dissociation time constant for the parent ion. For linear time-of-flight mass spectrum (ToFMS), it is typically 10^6 s^{-1} . For PAHs and PANHs, specific channels like C_2H_2 loss and HCN loss occur with time constants of the order of 10^6 s^{-1} . In this work, the focus is to investigate the statistical processes since the molecular dynamics of our interest is in this regime.

1.4 Theoretical Methods

The understanding of high energy-molecule collision processes and chemical reactions/pathways will be an incomplete study without a complementary contribution from experimental and theoretical work. The theoretical calculation of molecules must address two parts. One is the static part, i.e. structure calculation, and the other is its dynamics. Structure calculation includes bond structure, binding energies, wave function and so on. Generally, such calculations are very accurate for small molecules (molecules having few atoms). But for larger molecules, it is difficult to get very accurate estimation due to the large basis sets. Still, fairly accurate estimations are possible for the ground state of large molecules as well, particularly for PAHs it is easy, because of the symmetries. It also calculates electron affinity, proton affinity with fairly good accuracy. But when it comes to

calculating transition strength, transition probabilities that are for the spectroscopy, mass spectroscopy, and fragmentation, the calculations of the transition states and the Arrhenius parameters becomes extremely difficult, because the excited states involved in such processes are not stable.

In statistical dissociation experiment, it is important to understand first, what particular dissociation channel one is interested in, followed by the different ways in which a system can go into a state of that fragmentation channel. Thus, for example, there could be two ways in which C_2H_2 loss can happen in the case of naphthalene and azulene as reported [53]. From these kinds of transition state calculations, one gets the probabilities and lifetimes/decay constants. Photon interaction with molecules gives photoelectron spectrum (PES) and the peaks represent the binding energy for molecular orbitals (MOs) in which the measured electron is coming out. Such interaction also alters the nuclear coordinates upon removal of an electron and hence gives rise to vibrational transitions due to Franck-Condon (FC) overlap. The PES of a molecule is typically associated with a broadening due to Franck-Condon overlap of vibrational states. Advanced calculations that take care of the electron-electron correlation as well as the relaxation energy correction to represent the PES peak positions with a reasonable accuracy include configuration interaction techniques, perturbation techniques, and Green's function methods like outer valence Green's function (OVGF) [54–56]. Such calculation is done for few PAH molecules in the case of photoionization spectra [29, 57, 58]. But in the case of charged particle interaction, such calculations have not been done in which the electron spectra have broad energy distribution, and additionally, configuration integral calculation make it more complex. In the present case to obtain various stability parameters for PAHs and PANHs the structure calculation has been performed. There are different methods in quantum chemistry to find the molecular properties like Hartree-Fock self-consistent, density functional theory (both are *ab initio* methods), semiempirical method etc.

1.5 Experimental Techniques

Typically in an ionization process, an electron and recoil ion are formed. The energetics of the ionization process can be traced back by measuring the properties of recoil ion as well as the properties of the outgoing electron. Energy and angular distribution of the outgoing electron carry the information of the structure of the target. Due to the low mass of electron even the smallest amount of stray magnetic/electric fields like earth magnetic field or stray electric field due to charges sitting on the insulating surface or even the insulating patch on the conducting surface itself will completely distort the information carried by the secondary electron. Moreover, while trying molecular studies, the outgoing electron will typically have few electron volts of kinetic energy. Therefore these electrons are more prompt in responding to the stray electric field. In the case of photoionization, a known energetic photon is used and the outgoing electron energy is predicted. But when it comes to charged particle interaction, the energy transfer to the outgoing electron is decided not only by the initial energy of the particle but also by the impact parameter.

Photoionization using synchrotron sources radiation is now a very commonly used technique and a lot of experimental as well as theoretical analysis for most of the molecules are already done. In fact, the technology is even commercialized. Most commonly known techniques for such measurements are the photoelectron-photoion coincidence (PEPICO) and the threshold photoelectron-photoion coincidence (T-PEPICO) spectroscopy [36]. In this experiment, with the help of the energy analysis of emitted electrons, a precise value of the internal energy and therefore a very narrow range of decay constants can be experimentally obtained. On the other hand charged projectiles would deposit a broad range of energies, hence making the process of estimating the internal energy very complex, even if the secondary electron energy is tracked. In the context of PEPICO spectroscopy, the excess energy left in the molecule after the photo-ionization process plays a vital role in deciding the decay pathways of the molecular ions [59]. Similarly, in the case of charged particle interactions, the mechanism of energy loss decides the internal energy of the recoil ions and possible decay channels [14, 60]. The sensitivity of the spectrometer is more critical in the case of charged particle interaction because the electron from the same molecular orbital can come at variable energies and the spectrometer should have

uniform sensitivity over this energy range.

It is equally important to understand the details of the recoil ion produced in such collision process. There it is also essential to thoroughly analyze the properties of the emitted ion which itself adds complication since these ions are heavy and cannot use their kinetic energy to analyze. Moreover, the change in their recoil kinetic energy will be comparable to the thermal energies, and negligible in comparison to their original momentum. An extremely cooled target can be used so that such recoil effects will be studied. But such a technique cannot be used for large molecules since these molecules can't really cool them down to such an extent to see the recoil effects. When the mass is so large, the momentum transfer will have an even lower change in their velocity. In case of a molecule, only when a multiply charged molecules fragments are produced the Coulomb repulsion between them only give rise to substantially a large momentum. So for singly charged molecular ion or a molecular fragment which is produced due to a monocation, one has to really rely on the mass detection. The detection of mass is perhaps the most important task to start, and the other measurements like momentum recoil ion momentum spectroscopy (RIMS) [61] and cold target recoil ion momentum spectroscopy (COLTRIMS) [62] are not really applicable here. For such mass measurement various techniques can be used like quadrupole mass analyzer, Penning trap, Paul's trap [63–65]. Penning trap and Paul's would make it is difficult to measure the electron energy due to the permanent magnetic field, closed geometry and RF field. Whereas the linear ToFMS is easy to build and it offers a possibility of having a completely field-free region for the electron emission [66]. It gives 2π accessibility for the emitted electron in principle so that a suitable electron spectrometer can be placed on the other side of ToFMS. In that sense, time-of-flight (ToF) is a very convenient technique for the recoil ion measurement. It measures the ToF of the particle after imparting an equal amount of energy per charge state. A two-stage Wiley-Maclaren geometry tries to correct for the spread due to velocity and spatial distribution [67]. But this comes at the cost of having some electric field in the interaction region. Therefore if any electron spectroscopic measurement is to be done then it is essential to do pulsing of the extraction field for the recoil ion.

Generally, such experiments utilize electrostatic and in some rare cases magnetic electron energy analyzer. The sensitivity of the measurement techniques requires very accu-

rate geometry and field free interaction region. Since the electron spectrometers provide angle and energy differential yields, it can detect an extremely small fraction of the total number of the electrons produced in the target.

A combination of a secondary electron spectrometer and a recoil ion mass spectrometer gives much more detailed information compared to the separate use of these instruments. Thus energy selective secondary electron-ion coincidence technique is an extremely powerful tool. The energetics in this whole process is very accurately known if it is due to photoionization. The major issue with such measurement is the very strong dissimilarity in the count rates, which causes extremely demanding conditions on the coincidence rate. A large count rate for ions is found compared to extremely low electron count rate. Generally, for any good quality electron spectrometer, the acceptance will be of the order of 10^{-3} , depending on the resolution of the spectrometer and will be able to detect 10^{-4} . That is, the total rate dissimilarity will be of the order of 10^{-6} or so. Moreover, for such a large dissimilarity in count rate and cannot afford to have large ion production rate. This increases the probability of chance coincidence detection for the uncorrelated event. Therefore such experiments are generally very long experiments and very focused. In case of photoionization, at least state selectivity can be assured by knowing what would be the energy of electron coming from a given molecular orbital by knowing the photon energy. State selectivity in case of charged particle collision becomes extremely complicated, so the experiment will be much more time-consuming than PEPICO. Therefore even though such a measurement is though expected to be very rewarding, it is very challenging by itself.

Since electrons are very sensitive to the stray field the instrument should make sure that no electric field is in the interaction region when the electron beam is interacting with molecules. But if the interaction region is kept field free and allow the recoil ion to slowly drift into the acceleration region (where a constant potential is applied) it will lead to delay in detection of recoil ion in the coincidence. For example, at thermal velocities (for naphthalene ~ 100 meters per second), the molecular ion will take hundreds of microseconds if not milliseconds to cross the distance of 1 cm field free interaction region and enter into the acceleration region. Moreover, before the extraction of the molecular ion from interaction region for the corresponding electron detection, further ionization

causes false coincidence. Adding to this, with overall collision rate of 1kHz, are producing one electron per millisecond ($1/10^{-6}$), which means that one out of 10^6 electrons produced will be detected on average and in 1000 seconds and get one true coincidence for the electron. To speed up the process for increasing the true coincidence rate, that means one has to accelerate the ions by applying potential in the interaction region. If a constant electric field is used in the interaction field for this purpose, it will affect the primary as well as the secondary electron. So the only way to solve this problem is to have an electron spectrometer and detect the electron till that time so as to ensure the electric field in the interaction region is zero (i.e, interaction region should be field-free during interaction and till detection of a secondary electron). After detecting the electron, switch the projectile electron beam OFF and field in the interaction region ON before the ion gets too much drift, otherwise, the resolution will be spoiled. Now how fast this is done is decided by the electronics entirely and therefore designing such electronics, pulse processing electronics and high voltage switches put a very demanding condition on such instruments.

Though the photoionization is a very powerful technique, considering there are several environments where charged particles are interacting with the molecule, that understanding is also very important. Investigations using such techniques are very rare due to the extreme complication resulting due to such conglomeration. The first and foremost is the contradictory requirement of the extraction fields in the interaction region for the instrument which forbids the use of constant voltages onto the extraction electrodes. At the same time, pulsed electric field affects the mass resolution adversely. Moreover, the double differential nature of secondary electron detection gives orders of the magnitude of dissimilarity in the count rate on electron and ion detector and therefore demands extremely low count rate resulting in an extension of data acquisition time.

1.6 Polycyclic Aromatic Hydrocarbons and their Derivatives

Polycyclic aromatic hydrocarbons (PAHs) are a group of organic compounds consisting of two or more fused aromatic rings. These are a family of hydrocarbons consisting of molecules where carbon (C) atoms are arranged in a honeycomb lattice type structure of fused six-member aromatic rings with H atoms located at the periphery of the ring, on the other hand polycyclic aromatic nitrogen heterocycles (PANHs) are species with one or more CH groups substituted by a nitrogen atom in PAHs. The proposed widespread existence of PAHs in the interstellar medium (ISM) has driven recent investigations of their spectroscopic and photophysical attributes [68,69]. Cations or protonated species of PAHs have been linked with the diffuse interstellar bands (DIBs) [70]. Since nitrogen is the fourth most abundant element in space, it has been proposed that PANHs should also be present in the ISM [68]. The spectroscopy of PANHs is motivated by their possible involvement in pre-biotic chemistry as well as eventual transformation into the nitrogen-containing aromatic systems that are essential ingredients in biomolecules apart from an astrobiological importance [71–76]. The presence of PANHs has been reported in the extraterrestrial meteoroids, in the atmosphere of Titan and they could be involved in the chemical origin of life [77, 78]. Small PANHs like quinoline readily dissociate under exposure to interstellar radiation [79]. Moreover, it produces reactive photo products that may contribute to the composition of the ISM; of particular significance is the HCN loss in these systems [80]. The incomplete combustion of fossil fuels, coal, wood, cigarette smoke etc generates PAHs on earth environment and it is carcinogenic [81,82]

Considering the abundance of high-energy radiation in the interstellar medium, it remains an interesting endeavor to understand the mechanisms behind the survivability of PAHs and PANHs in such harsh environments. The molecular structure of PAHs is strongly affected by shock processing in the interstellar medium [83, 84]. Micelotta *et al* demonstrated that the interstellar PAHs (with the number of carbon atom = 50) do not survive in shocks with velocities greater than 100 km s^{-1} and larger PAHs (with the number of carbon atom = 200) are destroyed for shocks with velocities 125 km s^{-1} [85]. Electronic excitation by impacting ions or electrons may lead to isomerization into stable

pure-C species such as fullerenes. But, nuclear interactions in interstellar shocks may be a viable pathway to the formation of nitrogen-containing PAHs [85]. Amongst the numerous interaction mechanisms between energetic radiation and PAHs, plasmon excitation dominates due to its large oscillator strength. With intermediate velocity proton impact on naphthalene, it has been shown that the plasmon excitation mode in PAHs contributes almost exclusively to the evaporation of H or C₂H₂ [86]. The existence of plasmon excitation in PANHs has not been investigated so far. In addition, PANHs have been associated with functional materials such as organic photovoltaics, where a clear understanding of their photochemistry and spectroscopy is necessary [87]. Very few investigations have been carried out in the context of HCN formation apart from the formation and dissociation of quinoline and isoquinoline [88]. The other ionization and dissociation channels have been largely ignored. In this work, statistical and non-statistical processes in these molecules have been focused on charged particle interaction.

1.7 Electron-Ion Coincidence Measurements on PAHs and PANHs

Considering the complexities involved in the case of electron-ion coincidence studies for molecules, it has been very difficult to make a focused study of large molecules like PAHs using such a technique, particularly while using charged particle as a projectile. If charged particle interaction has to be studied spectrometrically, it is very important that the particular channel is identified and is used as a tool to understand the dynamics of these molecules. It is also important that such an identified channel should have no cross channels because multiple processes give rise to same products and using such coincidence techniques to separately study each channel is impractical. Moreover, it will not be possible to do a very large set of measurements at many different ranges of electron energies and many different projectile configurations.

For PAHs and PANHs, it is known that the H₂ loss and the C₂H₂ loss channels are the important statistical channels. Due to the limited resolution of the spectrometer one can have due to pulsed extraction, it is hard to detect the H₂ and H loss process in a simple lin-

ear ToFMS, but C_2H_2 loss is clearly separable. An instrument with provisions to perform electron spectroscopy and simple ToF spectroscopy separately along with electron-ion coincidence measurement is a very useful tool for electron impact studies. Moreover, since the extraction and the excitation process is also pulsed, then by varying the delay between the excitation pulse and extraction pulse, the statistical nature of fragmentation process can be probed. Generally, high energy photon source facility like synchrotron facilities are large facilities and not easily available. High energy ion beam facilities are also sufficiently large that they are also not easily accessible or they have restricted access. An electron gun, on the other hand, is a very convenient tool while designing a setup of this kind of experiment. Moreover, the setup with such excitation source like electron gun makes whole instrument compact and portable. After completion of the development, of course, the setup can be installed at the facilities like Synchrotron Radiation Source (SRS) or at high energy ion beam facility. Then they can be used to study the different modes like electron emission mode pure ionization modes like ToF mode or coincidence mode. The sensitivity of the electron to the electric or magnetic field causes additional complications in the experiment. Therefore while using electron beam it becomes imperative that one should pulse the electron beam. This automatically provides an opportunity to study a special technique called delayed extraction time-of-flight mass spectrometry.

Typically the development of a mass spectrometry and electron spectrometry setup involves a substantial amount of simulation and design followed by a planning of the instrument, all the while keeping in mind various considerations which have mechanical engineering aspects as well as vacuum technology, after which the instrument has to be fabricated, integrated, tested and calibrated for its performance for all the different modes. Only after successful completion of such calibration and testing the instrument can be used to perform the physics experiment of interest. Pulse processing electronics in general plays very significant role in the performance of the instrument of this nature. Moreover, since one expects to use a pulsed extraction and pulsing of the electron beam itself, that means it involves not only the regular analog and digital pulse processing of low amplitude pulses but also high voltage extremely fast pulses which in itself is a complicated task. Generally, such instrumentation is extremely expensive and very specialized.

Such electron-ion coincidence studies under electron impact have been done mainly

in the case of atoms, where the Auger electron-ion coincidence measurements have been done extensively [89]. But for molecules, such studies are done under photon interaction using techniques like PEPICO [36, 90]. In the case of molecules, this kind of study was mainly focused on the dicationic states of molecules like N_2 , CO_2 and their dissociation dynamics [91–93]. Even though such studies are limited in the case of electron impact experiments on nitrogen, tetrachloromethane molecules have been reported [94, 95] by using Auger electron-ion coincidence measurements. These kinds of molecular, structural or dynamical studies are very rare in the case of large mole molecules like PAHs and PANHs.

1.8 Thesis Outline

This thesis concerns the electron and mass spectroscopy of large molecules under charged particle interaction. A very energy selective secondary electron-ion coincidence setup is designed, fabricated and tested. The instrumentation is then used to study electron impact ionization and statistical dissociation dynamics of three basic types of PAHs and PANHs. These dynamics are then compared with proton impact on the same set of molecules.

Chapter 1: An Overview:- In this chapter, a brief introduction to collision process and energy loss mechanism in charge particle-molecule collision is given. Various theoretical and experimental techniques are discussed briefly to understand the importance and role of PAHs and PANHs of the terrestrial and extraterrestrial environment. Further, this chapter explains the significance of plasmon/collective excitation (a peculiar property associated with PAHs and PANHs), dissociation process and their importance in statistical and non-statistical decay processes.

Chapter 2: Theoretical Methodology:- In this chapter, the various theoretical calculation methods used in this work have been discussed to understand the molecular, structural and dynamical properties. The quantum chemistry *ab initio* calculations performed to study the structural variations of PAHs and PANHs and their relevance under charged particle-PAH/ PANH interaction described in detail.

Chapter 3: Principles of Electron Spectroscopy and Ion Mass Spectrometry :-

This chapter introduces the basics of experimental techniques used in electron and ion spectroscopy. A detailed study on different experimental components is described including various spectrometric techniques, detection mechanism, and data acquisition system.

Chapter 4: Experimental Methodology:- This chapter describes the development of experimental setup at Atomic and Molecular Physics Laboratory, IIST, Thiruvananthapuram for electron impact ionization and electron-ion coincidence measurement. The simulation, instrumentation, and construction of e, 2e setup in detail is described.

Chapter 5: Testing and Calibration:- This chapter presents the testing for the functionality of individual components of the experimental setup including spectrometers and detectors. Further, calibration of spectrometers and detectors are discussed. Demonstration of electron spectra, mass spectra, electron-ion coincidence spectra of various atomic and molecular targets are shown as the preliminary test results.

Chapter 6: Electron Impact on PAHs and PANHs:- This chapter explains the interaction of the electron with PAHs and PANHs and the statistical dissociation process. The delayed extraction time-of-flight mass spectrometric technique is used in this work to study the statistical dissociation and neutral evaporation mechanisms.

Chapter 7: Ion impact on PAHs and PANHs:- This chapter discusses the interaction of the ion with PAHs and PANHs and the related structural effects. It also focuses on energy deposition and the effects of collective/ plasmon excitation in PAHs and PANHs. Further, metastable decay dynamics studies on dicationic molecules are discussed.

Chapter 8: Conclusion and Future Scope:- This chapter summarizes and concludes the work performed. The setup built under this work has excellent potential in molecular physics studies. This chapter also discusses the further possible extension of the work.