Chapter 1
Introduction

When an energetic charged particle collides with an atom or molecule different processes can occur between the two collision partners resulting in changes either to the projectile or target or both of them. The projectiles that are used to probe the neutral target atoms/molecules can vary from mass less photons to negatively charged electrons to highly charged positive ions. If an electron (e^-) collides with a target atom/molecule (T), then different processes like elastic collision, target excitation, target ionization, electron attachment etc. can take place. On the other hand, if a positively charged ion collides with an atom/molecule, then in addition to excitation and ionization of target, there can be transfer of one or more electron(s) from the target to the projectile ion, known as electron capture. Further, along with capture, the target can also lose one or more electron(s), termed as transfer ionization.

Among the different processes mentioned above, the dominance of a particular mechanism over the others depend on the velocity of the projectile (v_p) and its charge state (q_p). By varying these two parameters, the collision characteristics could be changed. For a given charge state (q_p), if the projectile velocity (v_p) is much higher than the orbital velocity of the electrons in the target atom/molecule, then ionization will be one of the most dominant channel. However, if v_p is smaller than the orbital electron velocity, then, in case of ions as projectile, electron capture is dominant whereas for electrons as projectile, elastic scattering, electron attachment etc. would prevail. Along with q_p and v_p, their ratio i.e., q_p/v_p or perturbation strength is another important parameter for characterizing any collision mechanism. In the present thesis work, we have dealt with the studies on ionization of different target atoms and molecules when collided with electrons and positively charged ions. In case of ionization, a large amount of energy is transferred from the projectile to the target leading to the emission of free electrons from the target species.

Figure 1.1 shows the basic mechanisms involved during the collision when an electron is emitted from the target due to the perturbation caused by the incident projectile ion. In this situation, the impact parameter plays a crucial role in determining the amount of momentum transferred from the projectile to the ionized electron. If the outgoing electron is considered to have negligible interaction with the target nucleus, to which it was initially bound, then the ionization process is determined by a two body mechanism between the projectile and the outgoing target electron and is referred to as binary-encounter (BE) emission. Now for sufficiently fast bare projectile, the interaction with the target electron is very weak and this gives rise to the Zero center electron emission phenomenon. Here the target nucleus is only responsible for the initial velocity distribution of the electrons. Binary collisions are associated

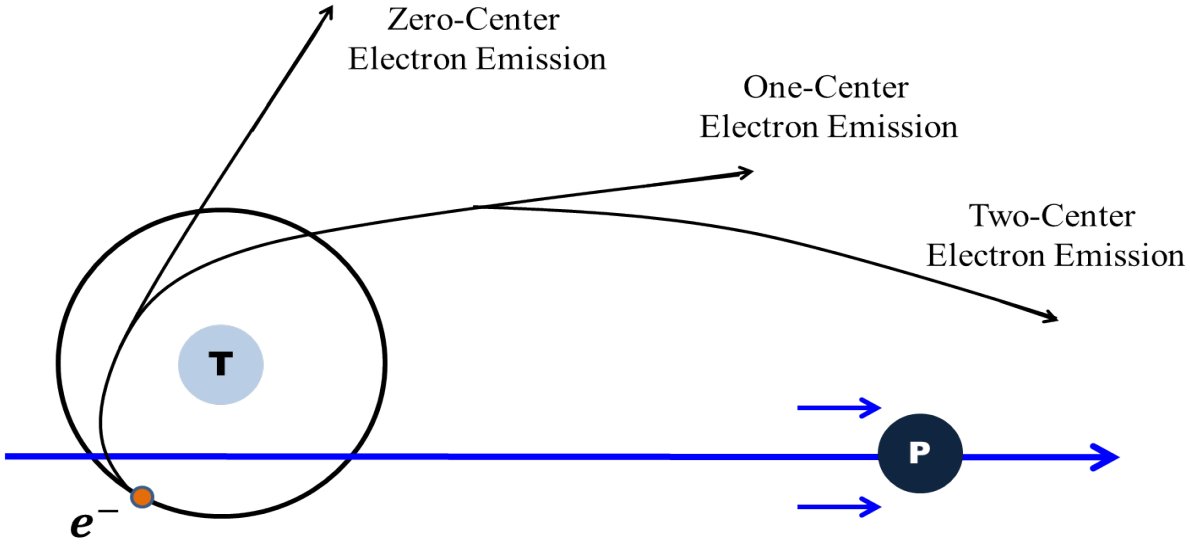

Figure 1.1: Schematic diagram of different mechanisms involving electron emission during ion-atom collision. Here 'P' denotes the projectile, 'T' the target nucleus and e^- stands for the active electron. Figure adapted and redrawn from [1].

with the projectile center. Thus, a violent binary collision, involving a bare projectile center yields the same result as the zero center case. The binary collision mechanism gives rise to a pronounced BE peak that can be observed in the double differential ionization cross section spectrum. The location of the BE peak is a function of electron emission angle determined by two body kinematics. The peak shape is determined by the Compton profile which, in turn, is governed by the initial velocity distribution of the ejected electron.

Single center phenomena may be associated either with the projectile center or with the target center [1]. In the above paragraph we have seen that binary encounter electron emission is associated with the projectile center. However, if the outgoing electron is strongly influenced by the Coulomb field of the target nucleus then the target center is dominant. The influence of the target nucleus increases with decreasing electron energy. At the low-energy limit, the interaction of the target nucleus with the active electron may be stronger than the interaction between the active electron and the projectile. This occurs for glancing collisions giving rise to the soft-collision (SC) maximum. In a soft collision, energy and momentum transfer is small, and hence the trajectory of the bare projectile hardly deviates from a straight line. Due to the large impact parameters involved in case of soft collision processes, the cross-sections reach a maximum.

Two center effect is important when the outgoing electron is influenced by both the fields of the residual target ion and projectile nucleus. Here the electron may undergo simultaneous or successive deflections in the two-center field of the heavy particles. Two center electron emission is expected to be observed in the electron spectra between soft collision and binary encounter maximum. The lowest energy electrons are assumed to be less affected by the two-

center effect, because the velocities are very small compared to the velocity of the projectile ion. This effect is dominant particularly for heavy ions.

In case of simple target systems like H, He, H_2, there is an overall and reasonable understanding of the reaction dynamics. All the basic mechanisms of electron emission discussed above are well understood for these target systems. The two-center mechanism has been found to influence the angular distribution of emitted electrons, producing an enhancement in electron yield for the forward angles [2, 3, 4, 5]. However, as more number of electrons are added to the target system, the complexity increases further and particularly for theoretical models, several approximations come into picture. In such cases accurate experimental measurements are required to test the efficacy of the different theoretical models.

Typically, using the traditional electron spectroscopy technique one can measure the double differential cross section (DDCS) of the electrons emitted from the target. In this approach, the spectra are measured as differentials in both the electron emission energy and solid angle. The DDCS measurements provide a much detailed understanding of the collision mechanism than the total cross sections. The two center electron emission is observed predominantly in the DDCS spectra and is known to influence the angular distribution appreciably for protons and highly charged ions as projectiles. In the present thesis work we have measured the absolute DDCS of electron emission from different targets when bombarded by keV energy fast electrons, keV energy protons and MeV energy C^{6+} ions. The range of targets studied here varied from atoms like helium to small molecules like N_2, O_2 and CH_4 and further to large biomolecules, uracil ($C_4H_4N_2O_2$) and bromouracil ($C_4H_3BrN_2O_2$). These experiments were performed using the 14 MV Pelletron accelerator and the 14.5 GHz electron cyclotron resonance ion accelerator (ECRIA), both existing at TIFR, Mumbai. In addition, a keV energy electron gun was also used to perform the experimental studies involving electron impact ionization. From the measured DDCS, the single differential cross section (SDCS) were obtained by performing numerical integration over the emitted energy or angle and upon further integration, the total ionization cross section (TCS) was derived for each collision system. The measured DDCS, SDCS and TCS for all the collision systems were critically compared with different state-of-the-art theoretical calculations like the CB1, CTMC and CDW-EIS approximations.

A part of this thesis was devoted to the understanding of the collision dynamics from the target ionization by changing the projectile velocity and charge state. In this regard, asymmetry parameter served as an important tool to gain insight about the collision dynamics and to study it's dependence by varying the molecular species. This study also provided a stringent test of the theoretical models to check their efficacy over a widely varying regime of projectile velocity. Further, molecular ionization studies have wide scale applications both fundamentally as well as for other fields of research. For example, studies on N_2 and O_2 provided valuable inputs regarding interference (see below), the studies on methane and biomolecules have certain specific applications as discussed below. Methane is one of the important molecules which is

present in the interstellar medium, circumstellar environment, surface of the Titan and also on the surfaces of several icy bodies of the solar system [6, 7]. These methane-containing surfaces when exposed to the energetic protons and other ions from the cosmic rays lead to the ionization and fragmentation of the molecules. Further, very fast electrons having energies from few keV to hundreds of keV are present in the interplanetary medium, which can ionize the surrounding molecules. Thus accurate collision measurements are useful for various astrophysical applications. Further, some of the basic quantum mechanical aspects can also be addressed from ionization cross section studies.

1.1 Interference oscillations

Electrons have both particle and wave like properties. A manifestation of this effect can be observed during the ionization of molecules. Diatomic molecules like H_2, N_2, O_2 have special interest since they act like a "molecular double slit" which are employed for investigating the Young type interference oscillations, initially proposed by H. Cohen and U. Fano in 1966 [8]. For homonuclear diatomic molecules, the two atomic centers are indistinguishable and hence the probability of electron emission from either atom can add coherently, resulting in an interference pattern. The two atoms of the diatomic molecule are analogous to the two slits of Young's double slit experiment on light scattering. In the last two decades there have been significant progress in this field. Extensive studies have been performed (both experimentally and theoretically) for the simplest diatomic molecule H_2 in collisions with ions, electrons and photons [9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22]. Further, a double collision model was employed to explain the double frequency component in the oscillatory structure arising due to higher order scattering processes [23, 24]. Such studies were then extended for multielectronic homonuclear diatomic molecules N_2 and O_2. For either molecules, there was an ambiguity in the experimental results obtained from heavy ion collisions [25, 26]. A theoretical study [27] suggested that it might not be possible to extract information about interference oscillations for multielectronic diatomic molecules, N_2 and O_2 when collided with heavy ions. However, photoionization studies on N_2 and O_2 have shown nice oscillatory structures in individual orbitals of the target molecules [28]. In this regard, electrons serve as an elegant probe. A systematic study has been carried out in the present thesis to investigate for the evidence of interference oscillations in O_2 and N_2 under the impact of fast (keV energy) electrons. The evidence of oscillations were studied in detail by looking into the DDCS ratios between the molecular system and its atomic counterpart (obtained from theoretical calculations). Further, the asymmetry in the cross section between forward and backward angles, giving rise to the angular asymmetry parameter, derived entirely from experimental measurements provided an excellent evidence of interference oscillations. Such an unambiguous evidence of the interference oscillations along with excellent agreement with the Cohen-Fano model for electron impact on multi electronic

diatomic molecules O_2 [29] and N_2 [30] were reported for the first time.

1.2 Ionization of biomolecules

Ionization studies of biomolecules have emerged as a new field of research over the past decade due to it's application in cancer treatment. In radiation therapy the malignant tumors are exposed to high energy photons or X-rays or ions like protons and heavy ions. In such mode of treatment, the main challenge lies in the fact that along with malignant cells several surrounding healthy tissues are also affected by the high energy radiation beam. This problem cannot be avoided completely due to the dose deposition of the incoming beam on the biological media, but, can be reduced by choosing the accurate mode of radiation therapy which in-turn depends on the location of the tumor.

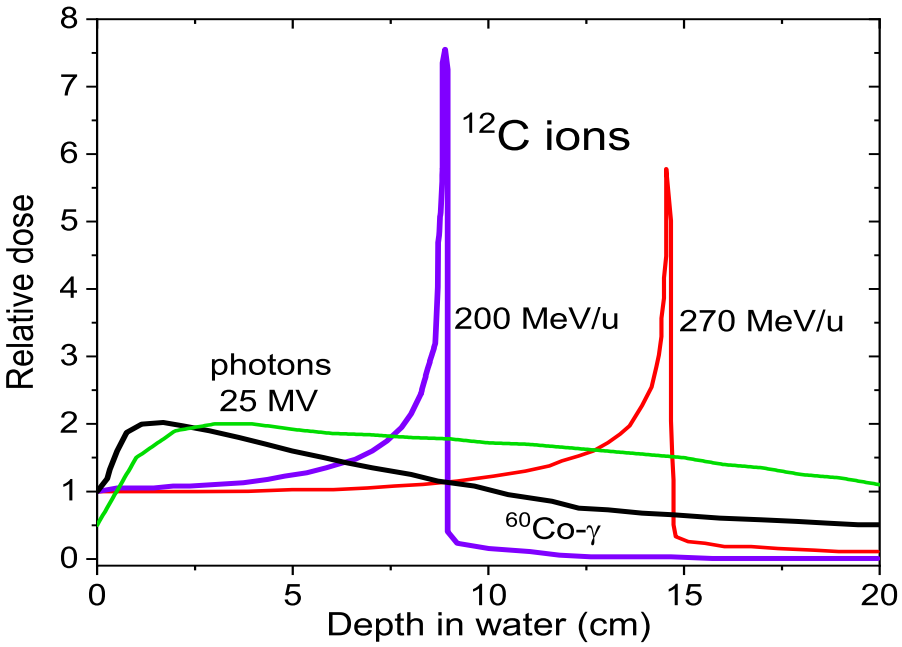

Figure 1.2: Relative depth dose profiles of ^{12}C ions, megavolt photons and ^{60}Co γ radiation in water. Figure adapted and redrawn from [31].

In case of deep seated tumors, ions are beneficial compared to photons because they exhibit favourable dose-depth distribution. This phenomena can be understood from Figure 1.2 which shows the manner in which the incoming beam deposits it's energy while passing through the medium. In case of megavolt photons and X-rays, it is observed that there is an exponential decrease in energy with increase in depth of the medium. Thus photons or X-rays deliver their maximum energy at the entrance of the target medium within few centimeters. On the other hand, it is seen that ^{12}C ions have a completely different depth-dose profile while passing through the medium. Although at the entrance some energy is deposited, but maximum energy

loss of the ions take place almost at the end of their path which is seen as a distinct sharp peak, known as the Bragg peak. This is a characteristic feature observed for both protons and heavy ions. As a result, in case of tumors which are located deep inside the body, radiation therapy using ions are more beneficial. The position of the Bragg peak can be adjusted depending on the depth at which the tumor is located by varying the kinetic energy of the incident beam. The sharpness of this peak varies between protons and heavy ions [32]. At this stage it is important to understand at the fundamental level the manner in which the radiation beam interacts with the target medium and deposits energy. Boudaiffa *et. al.* [33] had shown that the incident radiation beam while passing through the biological media leads to the generation of abundant low energy electrons. Single and double strand breaks of DNA/RNA induced by direct ionization and by secondary particles, such as low energy electrons, ions and free radicals, are the main causes of radiation damage. Thus the radiation damage on biological media is initiated by elementary processes which take place at very short time scale and at the nanoscopic level mostly dealing with the molecular constituents of the nucleobases, the building blocks of DNA and RNA. A large number of studies have been carried out in case of photons and charged particles interacting with the biomolecules [34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47, 48, 49]. Clustered strand breaks, localized along the DNA/RNA strands are the major source of lethal events leading to cell death. So far it is well understood that ions are preferential due to the utilization of maximum energy transfer at the Bragg peak and low energy electrons are the main driving agent for damaging the DNA and RNA of cells. In this context of cancer treatment using radiation therapy, radio-sensitization is emerging as a new technique to increase the killing efficiency of malignant cells. Au, Pt and Gd nanoparticles when inserted in the DNA/RNA and then irradiated by high energy ion beams have shown an increase in the number of strand breaks [50]. Halouracils are also known to exhibit such radio-sensitizing properties [51, 52].

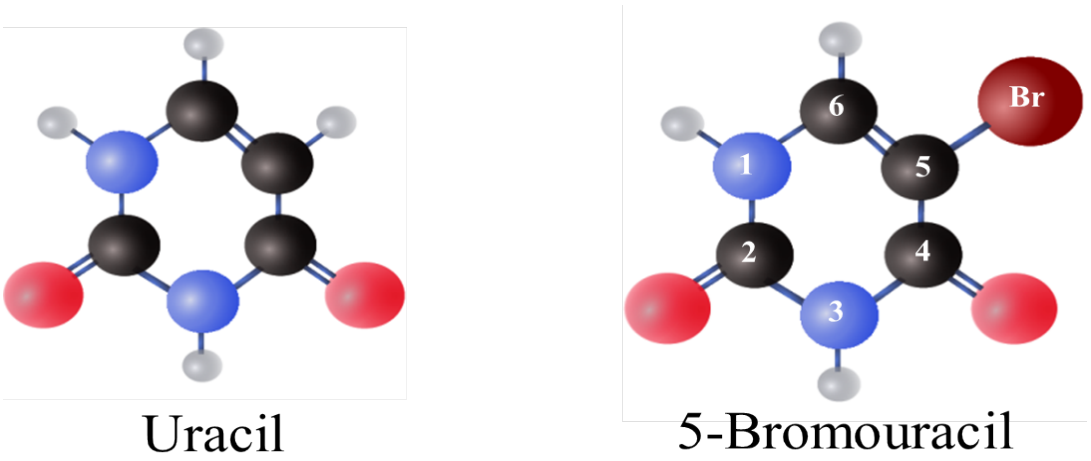

Figure 1.3: Molecular structure of uracil ($C_4H_4N_2O_2$) and 5-bromouracil ($C_4H_3BrN_2O_2$). Figure drawn using Inkscape.

In this thesis we have performed extensive experimental studies on the ionization of uracil, a nucleobase of RNA. For the ionization of uracil, the projectile beams chosen were keV energy protons and MeV energy C^{6+} ions. The DDCS for low energy electron emission were measured over various emission angles to understand the angular dependence of the yield of low energy electrons (if any). The second part of the study was focussed on measuring the production of low energy electrons from 5-bromouracil, a halouracil. The molecular structure of uracil and bromouracil have been shown in Figure 1.3. It is seen that the hydrogen atom attached to the 5^{th} position in uracil is replaced by Br atom for bromouracil. The projectiles were kept same for both the targets. Due to the presence of a high $Z-$ atom (Br in present case), it is expected that a large number of low energy electrons would be generated from bromouracil compared to that for uracil. From these studies we aim to provide a quantitative estimate of the enhancement in electron emission from bromouracil. The DDCS measurements were further compared with the state-of-the-art CDW-EIS calculations. To the best of our knowledge, no such work has been reported in the literature which provides a quantitative estimate of enhancement in electron production at the microscopic level due to the radio-sensitization effect, until very recently a similar kind of study has been reported on iodouracil from our group [53]. The CDW-EIS calculations were also extended for the first time for such a large molecule like bromouracil.

Table 1.1: The collision systems studied in the present work : e^- collisions and heavy ion collisions

Target	Projectile	Energy	Source
N_2	e^-	3 - 8 keV	Electron gun
O_2	e^-	7 keV	Electron gun
He	H^+	150 & 200 keV	ECRIA
O_2	H^+	200 keV	ECRIA
CH_4	H^+	200 keV	ECRIA
Uracil	H^+	200 keV	ECRIA
Bromouracil	H^+	200 keV	ECRIA
O_2	C^{6+}	66 MeV	Pelletron
Uracil	C^{6+}	66 MeV	Pelletron
Bromouracil	C^{6+}	42 & 66 MeV	Pelletron

1.3 Overview of the thesis

The present thesis has been divided into eight chapters including the current one. This thesis describes the different aspects of fast electron and ion collisions with atoms, small molecules and large biomolecules. Table 1.1 shows a list of all the different collision systems that have

been studied in this thesis. One of the main goal was to understand the basic mechanisms for electron emission from target atoms and molecules. Additionally, investigations were carried out to look for potential signature of Young-type interference oscillations from the electron emission spectra of multi electronic diatomic molecules, N_2 and O_2 under the impact of fast electrons. Further, measurements were performed for the ion impact ionization of uracil and bromouracil. The double differential cross section for electron emission from uracil and bromouracil were measured for keV energy proton impact. This study was further extended for MeV energy highly charged ions like C^{6+} ions. Apart from obtaining the absolute DDCS, we have investigated the amount of enhancement in electron emission from bromouracil compared to that for uracil. The details of existing experimental setup comprising of the scattering chamber, the electron spectrometer, detector, the data acquisition system along with the beamlines and its components have all been described in the second chapter. The development and testing of various components which were used during the course of this work have also been described in the second chapter. The third chapter deals with the theoretical models used to compare and interpret the experimental data. In the fourth chapter we have presented the absolute electron DDCS for N_2 and O_2 in collisions with 7 keV electrons. The experimental-to-theoretical DDCS ratios revealed evidence of interference oscillations for all the different emission angles. The variation in the frequency of oscillation over the emission angles have also been shown in the chapter. The forward-backward angular asymmetry also showed clear signature of interference oscillations for either molecules, N_2 and O_2. The fifth chapter deals with the detailed measurements of DDCS, single differential and total ionization cross sections for electron impact on N_2 over an energy range from 3 -to- 8 keV. The experimentally measured DDCS were compared with two ab-initio models, namely the CB1 model and the CTMC model. The total ionization cross section obtained from the DDCS were further compared with the semi-empirical CSP-ic model. In the sixth chapter, we move from electron impact to ion impact ionization studies. This chapter focuses on the ionization of atoms like helium and small molecules like CH_4 and O_2 in collisions with keV energy protons and MeV energy bare C ions. Here the projectiles were chosen with completely different q_p and v_p but nearly same perturbation strength (q_p/v_p). Such a choice was made to understand how the collision dynamics changes by tuning the projectile parameters whereas keeping the target fixed. The asymmetry parameter $\alpha(k)$ emerged as a strong tool for understanding the collision dynamics over widely varied projectile energy and charge state. In the seventh chapter we have discussed about the ionization of uracil and bromouracil in collisions with keV energy protons and MeV energy bare C ions. The experimental data were compared with the CDW-EIS model. The enhancement in electron emission from bromouracil was predicted from the experimental data as well as the theoretical calculations of the two projectiles. Finally, in the eighth chapter we have provided a summary of the work presented in this thesis.