In this thesis the fragmentation of molecules of biological interest and their clusters after collisions with keV ions and neutral particles has been studied in detail by means of high resolution coincidence TOF spectrometry. In the context of radiation damage to biological systems these studies are of relevance because they provide an insight into the very first steps of heavy ion damage in biological media.

The experiments presented in this thesis are not limited to the experimental setup at KVI in Groningen but they are also the fruit of collaborations with two different groups in France: the experiments with clusters were performed at GANIL/CIRIL in Caen and the experiments on energy loss of the projectile ion were performed at LASIM in Lyon. During this thesis period, also a neutralization chamber was added to the existing CHEOPS setup at KVI and pioneering experiments with neutral projectiles were carried out.

The first experiments during this research period were performed with water: the most common molecule in biological environments. In chapter 4 fragmentation channels for water molecules upon interaction with protons, He$^+$ and He$^{2+}$ projectiles in the energy range of 4-24 keV are treated. The corresponding KER distributions for a variety of dissociation channels are shown and the underlying fragmentation processes identified. In particular, a new dissociation channel for the water molecule which was predicted in the year 2000 was observed experimentally for the first time and is reported in this chapter. It was also found that when a water molecule dissociates, its fragments can have energies higher than 10 eV.

The interaction of ions with different nucleobases has been an emerging topic of study in the last years. Very significant dependence of the fragmentation patterns on the projectile electronic structure has been found. Also a relatively strong dependence of the fragment production on the different target molecules is found when comparing the pyrimidines thymine and uracil with the purine adenine. In this thesis, pioneering experiments with neutral projectiles and the nucleobase adenine were carried out. In chapter 5 new results on the fragmenta-
tion processes for the nucleobase adenine after collisions with neutral and charged projectiles are shown. The experiments were performed for different projectiles: \(H^+\) and \(H^0\), \(He^+\) and \(He^0\), and \(C^+\) and \(C^0\). The largest charge-state effect is observed for the \(C^0\) projectiles in comparison with \(C^+\). Delayed fragmentation of adenine fragments on \(\mu s\) timescales is observed for fragments usually assigned to the loss of the HCN group. This effect is particularly pronounced for neutral He projectiles but is also observed on a smaller scale for the other neutral projectiles.

For nucleobases in general the spectrum is very structured with well defined groups of peaks and in particular a strong surviving parent ion. These features indicate characteristic break-up processes for these molecules. The damage induced to nucleobases can be quantified according to the relative fragmentation cross sections: the number of fragments formed as compared to the number of surviving molecules. However, for deoxyribose molecules studied in chapter 6 virtually complete disintegration of the molecule is observed. The deoxyribose parent molecule has a very low intensity. The fragment distribution is found to follow a power law: a fingerprint of statistical fragmentation. These results might indicate that within the DNA, the deoxyribose molecule is more fragile than the nucleobases. The characteristic exponent of the power law fit is obtained for each different projectile as a function of velocity. For \(H^+\) and \(He^{2+}\), low exponents are observed which linearly increase with projectile \(v\). For \(He^+\), the characteristic exponent is larger and decreases with \(v\). These findings can be explained in the framework of charge exchange and electronic stopping. It is shown that the characteristic exponent is a suitable parameter for quantitative studies of deoxyribose fragmentation. Also, it is shown that this exponent can be related to the energy deposited in the molecular target.

All the above mentioned studies deal only with isolated molecules. In real biological environments, molecules are surrounded by many other molecules. The first step towards more realistic biological systems are studies of radiation damage on clusters. In this thesis for the first time the cluster approach is used to surround radiobiologically relevant molecules such as DNA building blocks by a realistic chemical environment and still be able to investigate the dynamics of a single biomolecule, the results are presented in chapter 7. A comparison between fragmentation patterns of isolated uracil, thymine, cytosine and adenine molecules with the corresponding data obtained for clusters of these molecules is made. For all systems except cytosine, characteristic additional fragmentation channels are observed in the cluster case. The strongest of these channels are loss of O and H (thymine and uracil) or of N and H (adenine). For thymine, the fragmentation was studied by means of coincidence techniques and it is compared to existing data on condensed phase thymine, where the respective characteristic channels observed in the cluster case are observed as well. The characteristic channels already open up for the smallest clusters but become relatively more important with increasing cluster size. These channels are probably due to the hydrogen bonding between O and H atoms in thymine, i.e. the clusters apparently favor planar geometries over stacked ones.

Preliminary studies on ion induced dissociation of Watson-Crick pairs in the gas phase have been performed. Preferential formation of clusters containing \(n\) thymine molecules is observed. When substituting thymine molecules for cytosine, the distribution is found to be statistical. According to spectroscopic and theoretical studies, several nucleobases tautomers can be present in the gas phase; therefore it is of importance to spectroscopically investigate the clusters formed with our technique to clearly identify the present tautomers.
In the context of biological radiation damage, the results presented in this thesis have the following implications:

- Surprisingly high intermediate charge states of the water molecule leading to fragment proton energies which often exceed 10 eV are observed. This is particularly interesting since these energetic protons have the potential to induce further damage in a cellular environment.

- The assumption that all physical processes take place on femtosecond time scales after the interaction might be wrong in view of the fact that delayed fragmentation processes taking place µs after the collision have been observed.

- The energy deposition by a particle on a fragile molecule can be estimated from the basic concept of statistical fragmentation. The measurement of the deposited energy has given an idea of the range of energies needed to inflict damage on the molecular level, which is usually well below the ionization potential of the molecules. For track calculations ionization potentials of the molecules involved are often used as threshold for damage.

- The results with clusters confirm the idea that it is very important to include the effects of the environment in assessing molecular damage induced by ionizing radiation.