Summary

The study of isolated atoms and molecules in the gas phase and their interaction with light constantly requires advanced techniques to obtain a more detailed understanding of the properties of these particles. After the absorption of a photon, also called excitation, the atoms and molecules are in an energetically higher state. This research focuses on understanding what is happening to these excited particles. For example, atoms can only lose their excess energy by emitting a photon, while molecules can dissociate if the energy of the absorbed photon is above the binding energy. By use of ultrashort femtosecond laser pulses in the excitation, the various processes can be investigated in a time-resolved manner. In such an experiment, the particles absorb one or more photons from a first laser pulse and subsequently the state of the particle is investigated or probed by the second laser pulse. The time between the pulses can be varied and, in this way, the dissociation and relaxation processes which are longer than the pulse duration can be studied. The second pulse causes an electron to be liberated in a process called ionization. An ion is formed as well and both the ion and electron can easily be detected.

In this thesis, the development of a new technique is described in which one electron and one ion are detected in coincidence on two different position sensitive detectors. The apparatus is extensively discussed in chapters 2, 3 and 4 of this thesis. The construction and optimization of the equipment have taken most of the time of my PhD period. In the remaining time, measurements on various atoms and molecules have been performed. The results of these measurements are described in the rest of the chapters.

Various aspects of the coincidence machine have been developed. Electric lenses which can be switched are implemented to accelerate the electrons first and subsequently the ions towards the two different detectors. Moreover, the lenses are made such that the initial velocity of the electrons and ions is projected onto the position sensitive detectors. This technique is called velocity map imaging and has not been previously employed in a coincidence measurement. Also, the flight time of the electrons can be determined with a very high temporal resolution of 50 ps, which was not obtained with such detectors before. The new apparatus and the developed technique allow for the determination of both the magnitude of the velocity and direction with high precision of the recoiling fragment ions and their partner electrons.

With the coincidence imaging technique, it is possible to determine how the energy of the absorbed photons is used. Besides the energy required for the dissociation and ionization, the electrons and fragment ions can obtain kinetic energy after the excitation. The velocity or kinetic energy of both the electron and ions can be determined by use of coincidence imaging. In general, the various ions can be distinguished by their difference
in masses, which affect the flight times of these particles. The flight time is the same for all the electrons and these electrons can only be distinguished by coincidence detection with the corresponding ion. In a coincidence measurement, the kinetic energy distribution can be obtained for each ion independently.

One of the results, which can only be obtained by use of the coincidence imaging technique, is the correlation between the kinetic energy of the electron and the kinetic energy of the ion. With this correlation, it is possible to determine the total kinetic energy due to the excitation process and to distinguish the different dissociation and ionization processes. The total kinetic energy is limited by the total energy of the absorbed photons and the number of absorbed photons can be deduced with knowledge of the total kinetic energy. This is important because femtosecond laser pulses have high peak intensities and simultaneous absorption of multiple photons is easily achieved. The interpretation of results from time-resolved experiments in combination with other techniques can be complicated, because the number of absorbed photons has to be determined first. This is relatively easy in a coincidence measurement and subsequently, conclusions can be drawn about which excited states are involved in the dissociation of a molecule.

Chapters 5, 6 and 7 describe the use of coincidence imaging in the study of the dissociation of molecules after the excitation by one or two laser pulses. In chapter 5, an experiment on the nitrogendioxide molecule, NO$_2$, is discussed, which is a frequently studied molecule due to its complicated electronic structure. The electrons are observed in coincidence with the parent ion, NO$_2^+$, or with the only fragment ion, NO$^+$, where one oxygen atom is split off. Various dissociation mechanisms have been observed and unambiguously assigned. The dissociation can take place after or before ionization. The ionization and dissociation are two processes induced by the excitation, which can occur in different order. That is, the ionization occurs first and the ion subsequently dissociates or the neutral molecule dissociates and the fragment is ionized. The distinction between the processes can be made by use of time-resolved coincidence imaging, but might be complicated in case of ionization and dissociation after excitation by a single laser pulse.

Chapter 6 describes an experiment in which a single pulse is used to excite the CF$_3$I molecule and both ionization as well as dissociation occurs. The results show that the ionization precedes the dissociation after absorption of four photons. The molecular parent CF$_3$I$^+$ ion is formed, and it can dissociate to form the CF$_3^+$ ion plus the iodine atom. Moreover, an additional fifth photon can be absorbed by the parent ion and dissociation can occur from the excited state of the parent ion. Via this process, also I$^+$ plus the neutral CF$_3$ fragment can be formed. Similar to the CF$_3$I molecule, ionization is the first process to occur for the CF$_2$Br$_2$ molecule. This molecule is investigated, which is described in chapter 7. The CF$_2$Br$_2$ molecule has many dissociation mechanisms and six different fragment ions are observed. These fragment ions are formed after absorption of one or more photons by the parent ion, similar to CF$_3$I. In a time-resolved experiment, a dominant channel is observed where a dissociative excited state of the neutral parent molecule results in the formation of a bromine atom and the CF$_2$Br fragment.

Besides the velocity of the electrons and ions, also the direction of the electrons and ions can be determined. Moreover, the coincidence imaging technique allows for the correlation between the direction of the electron and the ion. This correlation is discussed for nitromethane, CH$_3$NO$_2$, in chapter 8. After excitation, ionization occurs and the resulting
parent ion subsequently dissociates at the central C-N bond. Two different fragmentation processes are observed. The first process is the formation of the CH$_3^+$ ion together with the NO$_2$ fragment and the second process corresponds to the formation of the NO$_2^+$ ion and a CH$_3$ fragment. In both cases, the emission direction of the electron is predominantly in the same direction as the CH$_3$ fragment. Calculations of the electron charge distribution of the ground state of the molecule show that the electrons are located on the CH$_3$ moiety of the molecule. This makes a correlation between the electron charge distribution and the experimental results possible.

In the last two chapters, 9 and 10, describe the investigations of the ionization of rare gas atoms krypton and xenon, where multiple photons are absorbed by these atoms. The emission direction of the electrons is determined by the properties of the (excited) atoms and the polarization direction of the laser light. The polarization is easily adjusted in an experiment and the effects of varying the polarization on the angular distribution of the emitted photoelectron is investigated for various excitation schemes. For example, asymmetric angular distribution in the laboratory frame are observed in case of elliptical laser polarization. The manipulation of the laser polarization can be used in experiments to optimize particular atomic or molecular processes, like the dissociation of a particular bond in a molecule. The combination of coincidence imaging with the optimization of the laser polarization will provide new insights into the mechanism of selective dissociation.

This thesis describes the development of the coincidence imaging technique and the possibilities it provides for the interpretation of experiments on atoms and molecules with ultrashort laser pulses. From the various experiments discussed in this thesis, it is clear that this technique will improve the understanding of the interaction of atoms and molecules with light.