Chapter 1
Introduction

The interaction of strong laser fields with matter is a challenging topic in modern science and has a long history. The possibility of multiphoton transitions was theoretically predicted by Maria Göppert-Mayer in 1931 [Goe31]. The invention of the laser has opened new horizons for experimental and theoretical studies on nonlinear interaction of laser fields with atoms, molecules, and clusters. In 1965 G. S. Voronov and N. B. Delone investigated multiphoton ionisation (MPI) of xenon with a ruby laser [VDe65]. In 1979 above threshold ionisation (ATI) was observed [AFM79], where a photoelectron absorbs more photons than the minimum required for MPI. Under certain conditions the ionisation can occur by tunnelling of an electron through the potential barrier created by an intense laser field. This process is known as “tunnelling ionisation” [GHa98]. If the laser intensity is high enough, the laser radiation suppresses the potential barrier so far that the electron is able to escape freely from the atom. This is called “over the barrier” ionisation (OTBI) or the “barrier suppression ionisation” (BSI) [BRK93]. In addition, strong laser fields allow one to investigate intramolecular dynamics for molecules and clusters. The dynamics takes place on the time scale of the atomic motion. Therefore, laser radiation with pulse durations on the fs time scale is required for such investigations.

The aim of this thesis is to investigate the interaction of large but finite systems with moderately intense femtosecond laser radiation using methods of photoion and photoelectron spectrometry. In context of the present work “moderately intense radiation” implies laser intensities strong enough to modify potential surfaces (in particular, if they are close to resonances) but far below the onset of relativistic effects. To separate energy deposition into the system from energy redistribution among the various electronic and nuclear degrees of
freedom ultrashort laser pulses with a duration as short as 9 fs have been used. Combination of different laser parameters i.e. intensity, pulse duration, and light ellipticity as well as the use of time resolved measurements with the pump-probe technique provide powerful tools to study fundamental photoinduced processes. Two different systems were studied: C$_{60}$ fullerenes and model peptides.

The discovery of carbon fullerenes by H. R. Kroto and co-workers [KHO85] opened for science a new class of materials with very interesting physical and chemical properties. For this discovery R. F. Curl, H. R. Kroto, and R. E. Smalley received the 1996 Nobel Prize in Chemistry. The most stable member of fullerene family, C$_{60}$, has a highly symmetric structure built out of 12 pentagons and 20 hexagons, it has 174 nuclear degrees of freedom, 60 essentially equivalent delocalised $\pi$- and 180 structure defining, localised $\sigma$-electrons. The C$_{60}$ molecule can be considered as a model of a large but finite system. Experimental investigations of isolated C$_{60}$ have revealed both atomic properties, such as above threshold ionisation (ATI), and bulk properties, such as thermionic emission (delayed ionisation) [CHH00]. The exploration of the electronic and nuclear dynamics in C$_{60}$ has a long history. One early observation was the delayed ionisation on a microsecond time scale upon irradiation with nanosecond laser pulses [CUH91] due to thermionic electron emission from vibrationally excited C$_{60}$. Strong electron-phonon coupling leads to efficient heating of the nuclear degrees of freedom during laser excitation, and the subsequent ionisation in turn is one important energy relaxation channel [RHB01]. Another significant relaxation channel is the fragmentation due to the sequential loss of C$_2$ units [SDW96]. It has been found that the ionisation and fragmentation behaviour depends sensitively on the excitation time scale, i.e. on the laser pulse duration $\tau$ [CHH00]. For pulse durations above 1 ps one observes a characteristic bimodal fragmentation pattern of heavy fullerenes C$_{60-2n}$ separated by C$_2$ units ranging down to 60 $-$ 2$n$ $>$ 32 and a series of small carbon clusters C$_n$ below $n$ $<$ 28. In contrast, for laser pulse durations below 500 fs the excitation energy tends to remain in the electronic system, and multiply charged clusters C$_{60}^{q+}$ are observed. Direct multiphoton ionisation dominates for very short laser pulses $\tau$ $<$ 70 fs [THD00]. As a fingerprint of the multiphoton process the photoelectron spectra of C$_{60}$ exhibit a characteristic ATI structure [CHH00] in which the active electron absorbs more photons than necessary to overcome the ionisation potential. Additionally, sharp peaks attributed to the population of several Rydberg series were found in the photoelectron spectra of C$_{60}$ on
top of the ATI series [BHS01].

The study of the interaction of intense laser radiation with clusters is a rapidly expanding field of research due to its fundamental and practical importance in many areas of physics, chemistry, and material science. Nevertheless, knowledge about the energy absorption, ionisation and fragmentation pathways of large systems is still limited. Initially, the theoretical description of the interaction with laser radiation has been considered through the perturbation approach with a single active electron (SAE) [JBF07]. However, with increasing complexity of molecules and increasing laser intensities, the limitations of this approximation become obvious, indicating that multiple active electrons (MAE) are necessary to explain the observed phenomena [BCM01, TNE01, ZSG03]. The following questions are answered in this work: (i) How does \( \text{C}_{60} \) absorb the incident laser radiation? (ii) How is the absorbed energy redistributed among various degrees of freedom? (iii) Can these processes be controlled with temporally shaped laser pulses?

Peptides, which are building blocks of proteins, are very interesting objects for investigations. So far, little is known about their interaction with laser pulses. Such investigations may help to understand processes within a living cell which have a high importance for biochemistry. Femtosecond, temporally shaped laser pulses may possibly open the door to selective peptide bonds breaking and provide a new way compared to the well established methods of protein sequencing such as chemical analysis by enzymatic digestion (Edman degradation reaction) and ionic fragmentation in connection with mass spectrometry. Femtosecond pulse shaping as an analytic tool for laser induced protein sequencing is considered in this work. Results of the utilisation of ultrafast, shaped laser pulses picked by an evolutionary algorithm inside a learning control loop to break specific, pre-selected bonds in the model peptides Ac–Phe–NHMe and Ac–Ala–NHMe are discussed. These model peptides are not building blocks of proteins but something similar to the real peptides in proteins which can be handled with relative ease.

This thesis has the following structure:

In Chapter 2, the physical properties of the objects of interest, namely, \( \text{C}_{60} \) fullerene and model peptides are discussed. Chapter 3 discusses a general theoretical background concerning the interaction of strong laser fields with matter. Direct multiphoton ionisation, non-statistical fragmentation, energy redistribution, delayed ionisation, and statistical fragmentation are considered in detail. Chapter 4 consists of a record of the experimental apparatus
utilised in this work. Chapter 5 is dedicated to methods of the femtosecond as well as sub-10 fs laser pulses generation, laser intensity and polarisation control, and a temporal manipulation of laser pulse shape with a pulse shaper technique. In Chapter 6, experimental techniques used for the laser pulse characterisation both temporal and spatial are discussed. Chapter 7 presents a description of optimisation methods, especially concentrates on the method used in present work. Chapter 8 gives a detailed description and shows experimental results on $C_{60}$ excitation in moderate strong laser fields. Chapter 9 reports and discuss experimental data on the dynamics of ultrafast energy redistribution in $C_{60}$ fullerene. In Chapter 10, the experimental results of detailed mass spectroscopic investigations of model peptides with shaped laser pulses are presented. Finally, Chapter 11 outlines the most important conclusions of this study.