

# Chapter 1

## Introduction

The interaction of light with matter is among the most important physical processes that occur. Every day, the earth is bombarded with radiation from the sun, which may be converted to a type of energy that plants and animals can use, as in, for example, photosynthesis. Therefore, both the absorption of energy and its subsequent redistribution are of great interest for the understanding of the functionality of various systems. The example of photosynthesis concerns weak radiation fields, however, it is also interesting to study systems in significantly stronger electric fields to learn about damaging processes, such as fragmentation. Energy redistribution and fragmentation are expected to proceed on the time scale of the motion of atoms. Thus, to study the dynamics of these fundamental processes the use of ultrashort laser pulses is necessary.

Clusters define the transition from atomic and molecular physics to bulk physics and can be described as large but finite systems, consisting of two to several thousand atoms or molecules (monomers). Physical properties are found to be strongly size dependent [Jor92] and investigations of the size dependence aim to link the microscopic and macroscopic properties of matter. An additional advantage of clusters is that the environment of the cluster can be controlled in gas phase experiments by microsolvation, thus providing ideal testing grounds for intermolecular processes in isolated clusters or effects of an environment by addition of a solvent, e.g., water. The present thesis focuses on the laser interaction with the isolated carbon cluster  $C_{60}$ .

Carbon is the fundamental building block of life and one of the most abundant elements on earth and in space. Pure carbon is known to exist in four allotropic forms: as an amorphous solid, as graphite, as diamond, and as fullerenes.  $C_{60}$  is one species of a larger family of fullerenes, whose cage-like structure is reminiscent of the geodesic

dome, which was brought to popularity by the architect R. Buckminster Fuller and is considered the lightest, strongest and most cost-efficient structure ever devised. Discovered in 1985 by Kroto and co-workers [KHB85], fullerenes have captured the imagination of scientists due to their unique structure and extraordinary stability. R.F. Curl, H.R. Kroto, and R.E. Smalley won the 1996 Nobel prize in chemistry for their discovery of fullerenes.

The structure of  $C_{60}$  is special even among fullerenes. It is a truncated icosahedron belonging to the  $I_h$  symmetry point group, composed of 12 pentagons and 20 hexagons, and is a perfect microscopic model of a soccer ball. This unique structure makes  $C_{60}$  the most stable of the fullerenes. The breakthrough in  $C_{60}$  science came when macroscopic amounts (grams) were produced by W. Krätschmer and colleagues [KLF90] by the carbon arc method in 1990. Today,  $C_{60}$  can be bought from several chemical companies with a purity greater than 99%. The study of  $C_{60}$  and the other fullerenes remains important since they form the basis of carbon nanotubes and are model systems for other large molecules.

$C_{60}$  is a particularly interesting system to study because of its large number of electrons (240 valence electrons, of which there are 60 delocalized  $\pi$ -orbitals), its large number of vibrational modes (174), and because of its high symmetry. Experiments on isolated  $C_{60}$  have revealed atomic and molecular properties, such as above threshold ionization [CHH00], and bulk properties, such as thermionic emission (delayed ionization) [CUH91]. Despite nearly 20 years of intensive research, several fundamental questions about energy absorption and its subsequent redistribution are without definitive answers.

A surprisingly rich electronic structure has been observed in photoelectron spectra of  $C_{60}$  under moderate laser intensity ( $10^{12}$  W/cm<sup>2</sup>) [BHS01]. This structure has been attributed to the population of Rydberg states, which is inherently linked to the absorption of energy from the electric field of the laser. Historically, the interaction of laser radiation with molecular systems has been considered through the perturbation (weak field) approach with a single active electron. However, with increasing complexity of molecules and increasing laser intensities, the limitations of these approximations become obvious, indicating that multiple active electrons (MAE) are necessary to explain the observed phenomena. MAE dynamics have even been observed in atoms with non-sequential ionization. Presently, there is great interest to investigate multi-electron dynamics experimentally in larger systems [MSR03, LBI02] and to develop the theoretical models [FKM03, BCM01] to describe MAE.  $C_{60}$  pro-

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vides an ideal testing ground to study the effects of MAE dynamics and to explain the population mechanism of excited states.

There are three energy release channels for isolated particles: ionization, photon emission, and fragmentation. The photo-fragmentation of  $C_{60}$  under nanosecond laser irradiation exhibits a very interesting structure which indicates a sequential loss of  $C_2$  units down to a size of 32 carbon atoms and has been explained through statistical models, indicating an efficient energy coupling between electronic and vibrational modes. Under intense femtosecond laser irradiation, however, these statistical pictures may not hold, since the deposition of energy is faster than the energy redistribution. To monitor the ultrafast electronic and vibrational redistribution processes such as internal conversion, internal vibrational redistribution, and dissociation, short laser pulse durations are necessary.

Femtosecond laser pulses have opened the door to monitoring molecular processes of absorption and fragmentation in real time. The Ti:Sapphire laser, being the first stable, “easy-to-use” femtosecond light source, has triggered an explosion of research done in the femtosecond time regime. Experiments and visualization of these processes have garnered the 1999 Nobel prize in chemistry for Ahmed Zewail.

Active control of molecules has been the dream of chemists and physicists for decades. Recent advances in ultrashort laser technology have developed liquid crystal modulators to manipulate the temporal form of femtosecond laser pulses, thereby creating the possibility to control molecular processes or population of desired states. Temporal shaping is based on the modulation of the amplitude and/or the phase of individual frequency components, which translates to a temporal modulation of the electric field. Incorporation of these modulators into a feedback loop has generated a powerful tool to search unknown potential energy surfaces for global minimum or maximum for a particular product.

Despite the nearly parallel growth in the interest of fullerenes and femtosecond laser technology, there are surprisingly few experiments performed combining the two disciplines. This thesis investigates gas phase  $C_{60}$  with femtosecond laser irradiation to answer the following questions:

- *How is the incident laser radiation energy absorbed by  $C_{60}$ ?*
- *What are the fragmentation dynamics after femtosecond excitation and to which extent can they be described by statistical models?*

- *Can the fragmentation be controlled and enhanced with temporally shaped pulses despite the large number of photons and electrons involved?*

This work is organized as follows:

In **Chapter 2**, the experimental apparatus and techniques are described, with a concentration on the details important for understanding the interpretation of measured quantities.

**Chapter 3** discusses a general theoretical background concerning laser interaction with molecules, with a particular focus on atoms, molecules, and clusters in the gas phase. This chapter is meant to be a brief overview of concepts central to all topics covered in the subsequent sections.

The following three chapters present the experimental results obtained. The contents of these chapters will present an introduction to each topic, the experimental observations, the interpretation of these results, and finally will close with a summary.

**Chapter 4** concerns the absorption of femtosecond laser radiation. The results are presented through investigations of the excitation of Rydberg states observed in photoelectron spectroscopy. The identification, ionization characteristics, and excitation mechanisms of these Rydberg states will be discussed in detail.

In **Chapter 5**, experimental results concerning energy redistribution in  $C_{60}$  will be presented. One-color and two-color time-resolved pump-probe spectroscopy have been used to study the fragmentation dynamics after femtosecond laser excitation. Three fragmentation mechanisms will be discussed: sequential  $C_2$  loss, fission, and multiple fragmentation of  $C_{60}$ . The time scales associated with the observed fragmentation dynamics push statistical models to their limits. The spatial distribution of fragmentation after femtosecond laser irradiation is also investigated.

**Chapter 6** will address the question of whether the absorption of energy or the relaxation pathway can be controlled to enhance the  $C_{60}$  fragmentation signal. Control is attempted with temporal modification of a femtosecond laser pulse in combination with an evolutionary optimization algorithm. The resulting optimal pulse shape will be qualitatively analyzed and the stability of this result will be tested.

Finally, a summary will highlight the experimental results, answer the posed questions, and provide an outlook for future studies of  $C_{60}$ .