Chapter 7

Conclusions and Outlook

This thesis has considered the interaction of moderately intense femtosecond laser pulses with the C_{60} molecule. The fundamental concepts of energy absorption and its subsequent redistribution in complex molecules have formed the framework of investigation. The results of the experimental work are summarized with three questions.

- *How is the incident laser radiation energy absorbed by C_{60}?*

This question has been investigated through the rich electronic structure observed in photoelectron spectra that has been identified to be that of Rydberg series [BHS01]. Excitation of neutral C_{60} with moderate laser intensities (10^{12} W/cm^2-10^{13} W/cm^2) has illuminated this distinctive structure, which has been found to be excited and ionized within one laser pulse duration. The Schödinger equation has been solved for the binding energy for several electronic levels of C_{60} using a spherically symmetric jellium potential and accurately identifies three Rydberg series. Further experimental studies have shown the influence of several parameters, including the wavelength, chirp, and laser polarization [BHS02], as well as the internal energy dependence on their excitation [BHS04]. Time-resolved photoelectron spectroscopy has illuminated the relaxation dynamics of these states, which show a short lifetime, followed by a long-lived state. The excitation of these states is believed to be a manifestation of multiple active electrons / non-adiabatic multi-electron dynamics (MAE/NMED) which take place in an intermediate "doorway" state [BHS04], from which the excitation into high lying electronic states is best described with a single active electron, leading to the clearly assigned levels.

The MAE/NMED concept has far reaching implications in the field of molecular and cluster physics. Essentially, it shows that the single active electron approach

to the interpretation of the laser-matter interaction with strong laser fields fails. Excitation of multiple active electrons allows for the absorption of significant amounts of energy leading to substantial fragmentation. MAE/NMED are of great interest for understanding the interaction of laser radiation with complex systems.

- *What are the fragmentation dynamics after femtosecond excitation and to which extent can they be described by statistical models?*

One-color and two-color time-resolved pump-probe spectroscopy were performed to study the fragmentation dynamics of C_{60} after irradiation with moderately intense femtosecond laser pulses. The fragmentation pattern is dramatically influenced by the order of two unequal pulses. For the larger fragments, C_{60-2n}^{z+}, and the mother ions, C_{60}^{z+}, the dynamics are nearly step functions occurring near the overlap of the two pulses. For these heavy, fullerene-like fragments, statistical unimolecular fragmentation dominates the formation. This can be further observed in the spatial distribution of fragmentation measured with a position sensitive detector.

In contrast, the small fragments, for example, C^+ and C_2^+, show dynamics of the ion yield on the femtosecond and picosecond time scale. The increase in yield is significantly faster than the known statistical fragmentation which occurs on the nanosecond or even on the microsecond timescale. The measured kinetic energy of these fragments is peaked for short time delays and exponentially decreases with time, which can be explained by a Coulomb repulsion. The increase of kinetic energy due to Coulomb repulsion supports an ultrafast fragmentation. Simultaneous to the increase in yield for the small fragments is a decrease in yield for the middle sized fragments, e.g., C_7^+, which indicates that the predominant formation mechanism of the small fragments is a multiple cage fragmentation of C_{60}.

Three fragmentation mechanisms are intertwined in the fragmentation of C_{60} and each one's importance depends on the amount of internal excitation and the charge state. For low internal excitation energies (<80 eV) and for singly and doubly charged states, C_{60} undergoes neutral, sequential C_2 loss. As the charge state increases, asymmetric fission becomes more probable than unimolecular dissociation. For extremely high excitation energy >80 eV, the fullerene is likely to undergo multiple fragmentation of the cage. The ultrafast timescale of these observations pushes the statistical theories and perhaps indicates a nonstatistical fragmentation channel of C_{60} [BLS05]. However, the fragmentation primarily occurs through statistical fragmentation.

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

The femtosecond pulse shaping technique has been combined with an evolutionary algorithm to explore the possibility of whether the enhancement of fragmentation of C_{60} can be achieved through tailored electrical fields.

The enhancement of the large, singly charged fullerene fragments (C^+_{60-2n}) has been achieved by exciting first into the ionic state, followed by efficient energy absorption, leading to enhanced fragmentation. The resulting pulse form concurs with the pump-probe results where an increase in fragmentation occurs with a strong leading pulse.

The complexity of C_{60} hinders a detailed quantitative interpretation of the resulting optimal pulse shape. However, present development of multi-electron models will certainly improve and may possibly incorporate a shaped pulse experiment.

In this thesis, many new results on the interaction of C_{60} with femtosecond laser radiation have been found, from the observation of Rydberg series to ultrafast fragmentation. These phenomena are understood to be manifestations of multi-electron dynamics upon intense, ultrafast laser excitation followed by primarily statistical fragmentation mechanisms.

The study of laser-matter interaction in strong laser fields is presently a very hot topic. C_{60} is an ideal molecule for studying intense laser fields in isolated, complex systems and significant theoretical efforts are underway to describe such multi-electron and multi-atom systems.

Outlook

As with all scientific work, the investigation is never really finished, but the questions become more refined. These new questions continue to arise with each measurement and demand further measurements and/or further analysis.

The results from this work have sparked many new questions which will be further investigated at the Max Born Institute in the coming years. Below are several of these new questions:

The initial internal energy of C_{60} clearly affects the formation of Rydberg series [BHS04], however, it remains unclear why this occurs. Is the coupling between vibrational levels hindered? Is there a better Franck-Condon overlap? Or is the excitation

to the "doorway" state with 800 nm, which is two photon forbidden, allowed due to the extra vibrations (Jahn-Teller coupling)? A measurement of the influence of internal temperature on excitation would elucidate this finding.

The doorway state is thus far energetically poorly defined. What is the energy bandwidth of this intermediate state? A measurement of the influence of the wavelength could define excitation into the "doorway" state and determine the energy width of this state.

Does non-statistical fragmentation of C_{60} exist? Experimental evidence for non-statistical photo-fragmentation of C_{60} is elusive. In combination with newly developed position sensitive detection and a better defined laser-molecule interaction, this may be a possibility. Deviations from a statistical fragmentation could be evidenced, for example, by asymmetric fragmentation patterns, aligned along the laser polarization axis. Further studies of the kinetic energy release plus Coulomb repulsion will further clarify the fragmentation processes.

Temporal manipulation of the electric field is a new tool for investigating the reaction dynamics of molecules. With the initial success of enhancing fragmentation of C_{60}, further optimization can be envisioned, and the typical question is: "What pulse shape optimizes X ?", where X in this case may be the small fragments or the Rydberg states.

More general questions are : How does the C_{60} respond in higher intensities? or with shorter pulse durations?

These exciting questions, although presented here for C_{60}, can be generalized for other complex systems. The common goal is to understand the complicated dynamics underlying the laser-matter interaction. C_{60} provides an ideal testing ground for such experiments, and it will be interesting to follow the experimental and theoretical progress in this field.