

# Abstract

This thesis considers the interaction of large, finite systems with moderately intense femtosecond laser radiation up to  $4 \times 10^{14} \text{ W/cm}^2$  studied by the methods of photoion and photoelectron spectrometry.  $\text{C}_{60}$  fullerenes and amino acid complexes (Ac–Phe–NHMe and Ac–Ala–NHMe) were chosen as objects of investigations.

$\text{C}_{60}$  fullerene is an extremely interesting model system for studying the dynamics of photoexcitation, photoionisation, and photofragmentation in molecular systems with many degrees of freedom.  $\text{C}_{60}$  with its well defined, highly symmetric structure and the large number of electronic and nuclear degrees of freedom can be seen as an excellent prototype for both theoretical and experimental studies.

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 from 30 fs up to 9 fs have been utilised for investigations. The excitation time thus addressed lies well below the characteristic time scale for the electron relaxation. From a detailed analysis of the  $\text{C}_{60}$  mass spectra as a function of important laser parameters e.g. intensity, pulse duration, and time delay between pump and probe pulses insight into fundamental photoinduced processes such as ionisation and fragmentation is obtained. The observation of multiple charged fragments  $\text{C}_{60-2n}^{q+}$  ( $q > 1$ ) even with 9 fs pulses indicates direct non-statistical fragmentation of fullerenes on a femtosecond time scale through non-adiabatic multielectron dynamics (NMED), while singly charged ions are generated by an essentially adiabatic single active electron mechanism (SAE). Light ellipticity dependent studies can very sensitively distinguish between SAE and NMED. Time resolved mass spectrometry in a two colour fs pump probe setup provides direct information on the characteristic relaxation time. In all cases resonant multielectron excitation of the  $t_{1g}$  state was identified to play the key role in the energy deposition process.

The manipulation of molecules by temporally shaped laser pulses has become a standard technique for controlling and possibly analysing reaction pathways in complex systems. A closed feedback optimisation loop allows one to find optimal excitation schemes on potential energy surfaces of very complex systems without prior knowledge of their structure. First, this technique was applied to  $\text{C}_{60}$  fullerenes for studying the fragmentation processes. An optimal pulse sequence results in significant enhancement of  $\text{C}_2$  evaporation, a typical energy loss channel of vibrationally hot  $\text{C}_{60}$ , in comparison with the response to a single pulse of the same energy and overall width. Second, the same technique was utilised for selective bond cleavage in the amino acid complexes Ac–Phe–NHMe and Ac–Ala–NHMe that may be regarded as model peptides. Strong field excitation with shaped laser pulses allows one to cleave strong backbone bonds in the molecular system with high selectivity while keeping other more labile bonds intact. These results show that pulse shaping in combination with high resolution mass spectroscopy can be a first step towards creation of efficient tools for the chemical analysis of larger biomolecules or even proteins.

