

# Chapter 11

## Summary and Outlook

The main goal of this work was to investigate the interaction of moderately intense femtosecond laser pulses with free clusters and molecules. Processes of energy absorption and redistribution within various electronic and vibrational degrees of freedom in large, complex systems have been studied within the framework of this thesis.

First, the response of  $C_{60}$  fullerenes upon excitation by intense laser pulses of 9 fs duration has been investigated with photoion spectroscopy. Using a laser pulse duration below the characteristic time scale for electron relaxation allows one to separate the energy deposition processes into the electronic system from the energy redistribution among the various electronic and vibrational degrees of freedom. From an analysis of the resulting mass spectra as a function of laser intensity information on the dynamics of the ionisation and fragmentation has been obtained. The experimental data suggest that ionisation processes do not occur sequentially and that the relevant mechanisms can not be considered in a single active electron (SAE) picture. Both, the slopes of the ion yields for the final charge states  $q$  as well as the unexpected behaviour of the saturation intensities appear to indicate that for  $q > 1$  the giant plasmon resonance may be involved in the energy deposition processes, while for  $q = 1$  the results may be viewed as essentially adiabatic and dominated by SAE behaviour. A barrier suppression ionisation model with an appropriate, jellium type potential and centrifugal term can qualitatively account for the observed saturation intensities. Nevertheless, many important details of their relative magnitude at different laser parameters and charge states remain unexplained and contradict such quasi-static model. Time resolved pump-probe experiments with 9 fs pulses also indicate the presence of multielectron effects. In addition to the direct multiphoton ionisation process, a small contribution ( $< 25\%$ ) to the total ion yield is attributed

to energy stored intermediately in an excited doorway state ( $t_{1g}$ ) which relaxes on a time scale of about 50 fs. A more rigorous theoretical effort is needed taking into account multiphoton excitation of the giant plasmon as well as possible other intermediate resonances, non-adiabatic multielectron excitation (NMED/MAE), and dynamic polarisation.

A significant influence of ellipticity on ionisation and fragmentation processes in  $C_{60}$  fullerene in intense fs laser pulses was observed. The decrease of ion yields at lower intensities gives strong evidence for the crucial role of the  $t_{1g}$  state as a doorway state for energy deposition, followed by efficient multielectron dynamics. In contrast, at higher intensities a remarkable increase of fullerene-like fragments is observed in circularly polarised light. This might be caused by closed loops of recolliding electrons in circularly polarised light due to the particular structure of  $C_{60}$ .

The detailed study of energy redistribution dynamics in  $C_{60}$  has been performed with time resolved two colour pump-probe mass spectrometry. The role of intermediate excited states as rate limiting step in energy deposition into the molecular system was addressed by resonant pre-excitation of  $C_{60}$  fullerene with 399 nm laser pulses of 25 fs duration via the first dipole allowed  $t_{1g}$  state. Characteristic electron relaxation times are derived by probing the initially neutral many-body system with delayed 27 fs pulses at 797 nm. Detailed information on the relaxation process is obtained from the analysis of singly and multiply charged parent and fragment ion signals formed by the probe pulse as a function of pump-probe delay and pulse intensities. Three different trends were identified and characterised : (i) Electron relaxation times in the neutral precursor decrease with increasing charge state  $q$  of the eventually detected  $C_{60}^{q+}$ ,  $q = 1 - 5$ . The lowest relaxation time observed for  $C_{60}^{3+}$  is  $\tau_{el} \simeq 60$  fs. (ii) Fragments that have evaporated the largest number of  $C_2$  units arise from pre-excited species showing the slowest electronic thermalisation. These fullerenes are vibrationally hot but electronically rather cold. (iii) Electronic relaxation times observed in the fragment channels  $C_{60-2n}^{q+}$  increase with decreasing charge states and with increasing number of  $C_2$  losses. This corresponds to more and more vibrational excitation at the cost of electronic excitation energy. The longest relaxation times  $\tau_{el} \simeq 400$  fs are observed in the singly charged fragment ion channels.  $C_{60-2n}^+$  can apparently only be formed when the electron energy is particularly low, thus avoiding multiple ionisation via quasi-resonant multiphoton ionisation (MPI) through the plasmon resonance. This also solves the long standing puzzle why only spurious amounts of singly charged large

fragment ions are observed in mass spectra created by very short laser pulses. The particularly low electronic excitation combined with substantial vibrational excitation as intermediate neutral precursor required for the formation of  $C_{60-2n}^+$  occurs only with a very low probability. Ensembles with higher electronic pre-excitation are much more abundant and lead to multiply charged ions by MPI via the plasmon resonance.

To control the enhancement of  $C_{60}$  fragmentation the femtosecond pulse shaping technique has been combined with an evolutionary algorithm. A characteristic pulse sequence was found to excite large amplitude oscillations by coherent heating of nuclear motion and to enhance a formation of large, singly charged fullerene fragments  $C_{60-2n}^+$ . The resulting pulse form concurs with the two colour pump-probe results, where the  $t_{1g}$  state was identified to play the key role in the energy deposition process. With the help of time dependent density functional theory (TDDFT) the experimentally observed periods can be connected to the calculated, laser induced giant vibrational motion. A strong optical laser field excites many electrons in  $C_{60}$  via the  $t_{1g}$  doorway state. The almost homogeneously distributed excited electron cloud couples to the radially symmetric  $a_g(1)$  breathing mode. The observed periodicity (80 – 127 fs) depends on the number of excited electron (deposited energy) and the degree of ionisation. Despite various electronic and vibrational degrees of freedom, this essentially one dimensional motion prevails for up to 6 cycles with an oscillatory amplitude of up to 130% of the  $C_{60}$  diameter.

This work has also generated a lot of new questions which have to be investigated in future. These further investigations require new high power lasers and new experimental methods such as a two colour (400 nm/800 nm) pump-probe techniques with sub-10 fs laser pulses to continue the investigation of energy redistribution pathways in  $C_{60}$ , a two colour (800 nm/VUV) pump-probe technique to study electronic structure of excited  $C_{60}$ , measurements of electron-ion coincidence which would allow to gain important information about photochemical reactions. In future strong field pulse shaping technique could also be applied to optimise the population of the Rydberg states, the formation of small fragments, and even spatial distribution of ions.

Finally, this work presents first experimental data using pulse shaping technique embedded in an adaptive feedback loop to provide an additional dimension for mass spectrometric studies of the primary structure of peptides. It was found that specific pulse sequences are able to break pre-selected bonds in the amino acid complexes Ac-Phe-NHMe and Ac-Ala-NHMe. During

the strong field and highly nonlinear excitation of the presumably neutral molecule with shaped laser pulses cleavage of the N1-C3 peptide bond in Ac-Phe-NHMe is enhanced. Monitoring the fragmentation pattern with the parameterised phase function indicates sensitivity of the formation of fragment mass 43 u as a function of the phase parameter. The observed mass spectra in the optimisation experiment on Ac-Ala-NHMe with additional peaks of protonated species suggest that this technique may even be useful to elucidate intramolecular reaction channels such as excited state hydrogen transfer which plays an important role in efficient deactivation of DNA base pairs irradiated by UV light. The plans for further investigations should include pulse shaping experiments with larger polypeptides and hopefully even small proteins.