

Chapter 1

Introduction

This work contributes to two of the most recent fields in physics and chemistry: *femtochemistry* and *femtocontrol* of molecular processes with femtosecond¹ laser pulses. The experiments were carried out in the research group of Prof. Dr. Ludger Wöste at Institut für Experimentalphysik at Freie Universität Berlin.

The development of the femtosecond lasers in the 80's made possible the study of chemical processes in *real-time*. This is because the chemical reactions occur on the femtosecond time scale. One can simply imagine a very fast photo-camera (the femtosecond laser) which takes pictures or makes a film of the molecular processes. Many pioneering experiments were devoted to real-time observation of molecular dynamics with femtosecond pulses [1–3].

The method, known as *pump-probe spectroscopy*, implies an ultrashort laser pulse (pump) which excites the investigated system into a non-stationary (excited) state. Due to the broad spectrum of the femtosecond pulse several vibrational levels from that particular excited state are coherently excited. Their coherent superposition is also known as a *wave packet*. The propagation of the wave packet corresponds to the movement of the nuclei. An oscillation is described by the periodical (classical) motion of the wave packet back and forth in the molecular potential well. In order to monitor the molecular dynamics a second pulse (probe) is required. This probe pulse scans the potential surface of the molecule and where the wave packet is most localized (inner or outer turning point) one expects to see a change in the measured signal. In this way, vibrational dynamics on bound-bound states can be investigated, whereby a succession of minima and maxima of the measured signal is observed. Moreover molecular dynamics on dissociative states can be also examined, whereby an exponential decay is expected.

¹1 fs = 10⁻¹⁵ s.

The efforts of physicists and chemists in fundamental understanding of elementary molecular processes, like bond breaking, making and shaking by using femtosecond laser pulses (*femtochemistry*) are mirrored in the Nobel prize for chemistry awarded to A. H. Zewail in 1999.

Understanding chemical reactions has been in the attention of scientists for many centuries, yet their influence has gained more interest in a variety of fields. By changing macroscopical parameters like temperature, pressure, concentration, pH, or solvent one can control the ratio/quantity of the desired chemical products. However the employed methods are based on incoherent collisions between the molecules and do not allow an active control of microscopic processes. An active control would imply the use of external fields, whose intensity, phase and frequency distribution can vary in time leading to a modification of molecular dynamics by influencing the evolution of the reactant(s) and thereby generating a higher yield of the desired product. Minimizing the undesired products and increasing the reaction effectiveness are only two of the goals of industrial chemistry which can be achieved by the understanding and controlling of microscopic processes.

The breaking of a chemical bond due to the irradiation with light, particularly with laser light, leads to a separation of the products caused by the repulsive potential. The recoil speed is around 1 km/s, implying transitions from the bound state to the isolated species with a duration of hundreds of femtoseconds. Indeed, by choosing the appropriate photon energy (using the monochromatic cw² laser radiation), a chemical bond breaks due to the localized excitation. This happens after the laser induces oscillations of high amplitude which cause the bond rupture. However, in most cases this *bond-selective chemistry* fails because of the IVR (Internal Vibrational energy Redistribution); hereby the energy given to the molecule after the optical excitation redistributes throughout the internal vibrational modes, due to the coupling of different degrees of freedom before any reaction can take place.

Optimal Control Theory brought an important aspect in control of chemical reactions with laser light. Based on intrinsic molecular properties it was possible to calculate the form of femtosecond laser pulses, which can drive the reaction dynamics in a particular direction. The coherence of the laser light is transmitted to the molecule and is followed by a coherent molecular motion. Although IVR is always present and sometimes fragmentation can take place, these theoretically proposed laser fields can localize the photon energy in a particular bond on a particular place on the potential energy surfaces. Quantum mechanical constructive or destructive interferences caused

²cw = continuous wavelength.

by the coherent radiation can be used to direct a population toward a desired pathway. Advances in femtosecond laser techniques and in pulse shaping methods [4] have allowed the experimental realization of a long-standing dream: *laser control of chemical reactions*.

However, these optimal laser fields can be only approximated, since precise theoretical calculations of potential energy surfaces of larger molecules are difficult to perform. The major part of the results presented in this work are based on an idea of Judson and Rabitz [5] which suggested the use of a self-learning optimization method to allow the laser itself to find the optimal pulse shape. In other words, the lasers are taught to control molecules. The optimal pulse form is iteratively found by an evolutionary algorithm in a feedback loop, which changes the properties of the laser field so that the selected molecular process arrives at a terminus point. All of this is achieved without any prior knowledge of the process to be controlled.

The acquired optimal pulse form contains information about the photo-induced process itself [6]. Thus the mechanism of the controlled reaction dynamics can be decoded by examining the optimal laser field. This is, however, not a trivial task, since complex pulses can be obtained for large molecular systems. Even for small molecules the manipulated processes do not appear to be simple [7]! In this work a special attention is given to the measured optimal pulses and their interpretation.

The investigation of clusters – small particles consisting of several atoms or molecules – has known an important increase in the past 20 years. They exhibit interesting properties, not only bulk-related (latent heat, melting point, surface composition, etc.), but also their real-time behavior has caught the attention of many physicists and chemists. In order to understand the elementary processes occurring in unimolecular reactions it is useful to start with small molecules. Alkali metal clusters are excellent model systems for time-resolved investigations on a femtosecond time scale. They exhibit absorption bands well-located within the operating range of commercial femtosecond laser sources. Their photo-ionization energies are relatively low and their vibrational dynamics can be resolved with the available photon energies [8] and femtosecond pulse durations, respectively. Organometallic molecules are also good prototype species for investigating the dynamics during laser-induced fragmentation. Their dissociative property is a significant feature which can be of an advantage in optimal control of fragmentation channels in unimolecular reactions.

The systems investigated in here are different in many aspects, but the central aim of this work is to study, influence and understand their chemical and photo-physical properties. The present work is structured as follows:

Chapter 2 consists of a short introduction into the world of femtosecond

laser pulses. The basics of their generation, amplification and measurement, together with elements of nonlinear optics are briefly described.

The following chapter focuses on shaping of femtosecond laser pulses. Shaped pulses represent the hot topic inhere, since their interpretation gives the possibility of understanding the mechanism of the controlled process. A concise theoretical introduction of shaped fs pulses is given, but the attention is directed to the central element, which is a liquid crystal modulator. The construction of the pulse shaping apparatus was a part of the present work.

The experimental setup is detailed in Chapter 4. A general description of the molecular beam apparatus is given, but details regarding generation of particular cold molecules are outlined in each corresponding chapter. Production of a continuous jet of cold molecules is essential, since in this way molecules in their electronic ground state are prepared for the experiment. For an enhanced flexibility in the experiments, two laser systems were employed during this work. Modifications in laser layout and molecular beam setup allowed a significant improvement in their operation.

Theoretical concepts used in the experiments are outlined in Chapter 5. A description of analysis of molecular processes by means of pump–probe spectroscopy is briefly given. Examples of wave packet dynamics as well as their influence are illustrated in the first part. The second part of the chapter touches theoretical considerations of selective control of molecular processes based on different proposed control schemes.

The results obtained on the organometallic compound cyclopentadienyl manganese tricarbonyl – $\text{CpMn}(\text{CO})_3$ – are presented in Chapter 6. The mass spectrometric analysis together with pump–probe spectroscopy of the molecular dynamics is performed at different central laser wavelengths and intensities for both parent and fragment species. Femtosecond pump–probe experiments together with theoretical *ab initio* quantum calculations of the Manz group were carried out in order to decipher the ionization mechanism performed by the optimal laser field obtained for maximizing the $\text{CpMn}(\text{CO})_3^+$ ion yield.

The next chapter describes the results obtained on Na_2F , the smallest species from the family of sodium-fluorides. Details on the production of sodium-fluorides in a molecular beam are also presented. Based on previous theoretical predictions of the Bonačić-Koutecký group, pump–probe experiments were performed. The obtained results are discussed and compared with the theory.

Optimization experiments on the NaK dimer, performed at different laser wavelengths, are shown in Chapter 8. Hereby the transient three-photon ionization of $\text{NaK} \rightarrow \text{NaK}^+$ is controlled. A qualitative analysis of the measured optimization factors based on the potential energy curves of NaK is given.

Information about the optimized process could be gained from the acquired optimal pulse shapes recorded in the 760–790 nm spectral region.

Chapter 9 presents details about the results obtained on isotope ratio control of the potassium dimers ($^{39,39}\text{K}_2^+$ vs. $^{39,41}\text{K}_2^+$) by means of shaped laser pulses. Hereby, optimally chosen transitions between the vibrational levels within the electronic excited states during the ionization path are found, which lead to a pronounced isotope ratio control. The phase-only and the amplitude-only modulation experiments are compared with combined phase and amplitude modulation for both cases of the maximization and minimization of the aforementioned ratio. The optimization method is continued at other central wavelengths. From the optimal laser fields, particularly their spectra, detailed information about the isotope enhancement compared to the other and vice versa could be extracted. Thus, again a fingerprint of the molecular dynamics on the involved electronic states could be found in the optimal pulse shape.

The last chapter summarizes the results presented in this work. At the end of each experimental chapter an outlook at possible future experiments is given.

