

Chapter 10

Concluding Remarks

The goal of this work was to analyze and control ultrafast laser-induced processes occurring in model species, like the organometallic molecule $\text{CpMn}(\text{CO})_3$ and alkali systems. The control experiments were performed by employing the adaptive feedback-loop scheme. The analysis of the optimal pulses demonstrated that intrinsic information about the control process itself can be gained.

In order to analyze the molecular dynamics of the presented species by means of femtosecond transient spectroscopy, a few pump-probe experimental setups employing the two femtosecond laser systems, FS I and FS II, respectively, were constructed.

The wave packet dynamics on electronic excited states of the organometallic $\text{CpMn}(\text{CO})_3$ was studied by employing femtosecond laser pulses. The pump-probe experiments together with *ab initio* quantum mechanical analysis performed in the group of Manz allowed us to explain for the first time the ionization mechanism performed by the optimal pulse obtained for maximization of $\text{CpMn}(\text{CO})_3^+$. The optimized laser field avoided intelligently any fragmentation channels favorizing exclusively the ionization pathway. The fragmentation times of the organometallic molecule and its fragment ions were extracted from the pump-probe traces. Oscillations of the parent molecule with a period of $T_{osc} \sim 85$ fs were resolved. This dynamical behavior is reflected also in the pump-probe trace of the first fragment ion $\text{CpMn}(\text{CO})_2^+$. At higher peak intensities of the pump pulse, the time-resolved kinetic traces showed a different pattern, which could be due to dynamics in the ion states. Mass spectrometric investigations were made in order to support the statement that the ultrafast processes manifest on electronic excited states when low laser intensities are used. An attempt to decipher the optimal pulse obtained for optimization of the photo-ionization of the first fragment $\text{CpMn}(\text{CO})_2$ was proposed as well.

A method of producing sodium-fluoride clusters in a molecular beam was elaborated. For the Na_2F trimer, geometric rearrangement between the linear and triangular configurations with a period of ~ 185 fs was successfully observed with the help of pump–probe spectroscopic technique. This occurs after the Na–Na bond breaks. Motivated by the theoretical calculations from the group of Bonačić-Koutecký a pump–probe setup consisting of two optical parametric amplifiers was developed. The two lasers were tuned in the wavelength region predicted by the theory and the experiments were found to be in conformance with the *ab initio* simulations. This experiment was the first step in femtosecond investigations on ultrafast intramolecular processes on the non-stoichiometric sodium-fluoride clusters.

Characteristic motions of the involved wave packets were proposed as an attempt to explain the optimized dynamics in NaK. Hereby the central frequency of the laser was tuned in the 760–790 nm spectral range. This is similar to a laser scan of the potential energy curves. The measured optimization factors allowed a qualitative interpretation of the associated ionization pathway during the control process. From the acquired optimal pulses, information about wave packet propagation at the ionization path, oscillation periods and potential energy curves was gained. In almost all experiments the optimal pulses reveal three subpulses, whereby the most intense is situated at the central position. This allowed us to observe the number of subpulses, their relative temporal separation and their intensities necessary for the optimized process. A scheme of the ionization pathway was proposed in order to decipher the attributes within the pulse forms. The proposed scheme is in good agreement with the developed theoretical model for the ionization mechanism [153].

Furthermore, a technique advanced in this work allowed the control of isotope ionization ratio [164]. This approach was first demonstrated for the potassium dimer isotopes. It was possible to maximize and to minimize the ratio $\mathfrak{R} = I(^{39,39}\text{K}_2^+)/I(^{39,41}\text{K}_2^+)$ by a surprisingly high overall factor of 141 between maximization and minimization. The laser wavelength was centered around 833 nm. By analyzing the optimal pulse spectra, information about the chosen ionization path in which three electronic states participate (the ground state $X^1\Sigma_g^+$, the electronic excited state $A^1\Sigma_u^+$ and the higher lying excited state $2^1\Pi_g$) was collected. One was able to learn about the optimized process (the transitions involved on the way to the ion states) from the acquired optimal pulses, in particular their spectra. The studies were extended to the comparison between phase and amplitude modulation and phase-only or amplitude-only modulation. Since the wave packet can not evolve in time the amplitude-only modulation experiment can be considered as a restricted optimization. In the amplitude-only experiment some frequency lines are

missing, indicating a different ionization path compared to the combined phase and amplitude modulation. Successful optimizations were observed also for phase-only modulation where the frequency modulation was hindered. In this case the selectivity may be achieved by constructive/destructive interferences between wave packets and by optimal time evolution of the wave packets on the involved electronic excited states. By changing the central wavelength, the isotope ratio could be also controlled, yet the observed optimization factors between maximization and minimization were lower than at 833 nm. The peaks in the optimal spectra at other wavelengths (820 nm and 810 nm) correspond to particular transitions as well. The control of isotope ratio demonstrated for K_2 can be very well seen as a new spectroscopic approach of a distinct frequency pattern on femtosecond time scales due to the superposition of the spectral components.

