Photoassociation and coherent control of ultracold molecules by femtosecond pulses

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Chapter 1

Introduction

Even though the interaction of two individual atoms might seem to be a system of low complexity, a closer look reveals a vast realm of exciting physics which gives rise to new knowledge whenever it is viewed from a new perspective. An ongoing flow of exciting observations was propelled by cooling techniques [9, 16, 18, 61] which now allow to reach temperatures down to a billionth of a degree above absolute zero. In this regime, the particles de-Broglie wavelength exceeds by far the characteristic interaction distances and the diatomic encounter is fully governed by quantum mechanics. Since the discovery of atomic Bose-Einstein Condensation (BEC) [16] in particular the quest for molecular quantum gases ignited a large number of projects, propelled by the search for new physics [27, 39], but also for future applications e.g. by quantum computing.

Whereas the formation of ultracold atomic gases became a standard technique, the creation of stable molecular samples at large numbers poses a problem still to be solved. The direct application of laser cooling to molecules is generally inhibited by their dense level structure. Leakage from the trapping cycles has to be compensated by repumping lasers which is, within reasonable practical limits, only possible for a limited number of molecules [5]. To date, the paths which are pursued can be divided into two directions: The formation of a molecular gas of the desired species and subsequent cooling in a buffer gas [17,67] or Stark deceleration [9] in a molecular beam. So far, the temperatures which can be achieved this way are limited above 1 mK.

The second approach is to create molecules form an ultracold atomic gas. An efficient method here for example is using Feshbach resonances [25, 27], resulting in long range pairs, bound in the last vibrational state of their interaction potential. The track we follow in this work is to create molecules from an atomic gas by means of photoassociation in laser fields (see fig. 1.2). Thereby, a pair free atoms in their electronic ground state is excited by a laser field to bound states in a higher lying potential manifold. The formation of bound ground state molecules then proceeds by spontaneous



Figure 1.1: Temperature regimes for cold atomic encounters and scattering wavefunctions. The figure on the left side shows the temperature regimes achieved by means of different cooling techniques, together with the associated thermal deBroglie wavelengths. In the regime of optical cooling techniques, these assume macroscopic values. On the right side, the s-wave scattering wavefunctions which describe ultracold atom pairs are shown. The upper panel shows such a wavefunction at large internuclear distances which are comparable to the thermal wavelength. The lower panel shows the wavefunction at small internuclear distances, where atomic interaction effects dominate. Taken from [82]



Figure 1.2: Scheme of the production of ultracold molecules by means of cw photoassociation. Indicated are the potential curves for one electronic ground and excited state, and the initial continuum, intermediate excited state and final ground state wavefunctions. Note that the spontaneous decay step can also lead to other states, especially back into continuum states.

or stimulated decay to the electronic ground state. The concept was first proposed by H.R. Thorsheim *et al.* in 1987 [72] and was successfully realized in the production of Na₂ in the excited state using cw-lasers by P.D. Lett *et al.* in 1993 [41]. The first observation of bound ground state molecules was achieved by A. Fioretti *et al.* [21]. Since then, tremendous research has been done on photoassociation. Homo- and hetero-nuclear molecules could be created from nearly any atomic species which is accessible to laser cooling [31, 40, 46, 66]. Extended reviews are available which give a good overview on the topic [28, 49].

An standing problem so far is the transfer of the such created ultracold molecules to their absolute ground state. So far only one experiment by J. Sage *et al.* succeeded to transfer a small number of RbCs dimers to v=0 [63]. Recently, A. Winkler *et al.* [85] reported on the coherent transfer of Feshbach created molecules to a lower vibrational state. However, in order to achieve efficient transfer from the an atomic gas to ultracold molecules in their absolute ground state, new concepts are required which might be found by exploiting the dynamics of coherent nuclear wavepackets which are created by specially tailored fields of shaped laser pulses.

In this respect the physics of ultracold gasses can benefit form another area of atomic and molecular physics, were comparable successes could be celebrated in the past decades. This is the field of quantum control of physical and chemical processes by ultrashort laser pulses [87]. With the advent of femtosecond lasers it became possible to intervene with molecular quantum systems on their intrinsic time scale and thereby manipulate their dynamics. Popular systems of study are, for example, the control of nuclear wavepacket dynamics in small molecules. This occurs by excitation of an initially well defined quantum state in an ultrashort laser pulse which creates a coherent wavepacket on a higher lying potential manifold. By tailoring the excitation pulses in amplitude, phase or polarization one can manipulate the wavepacket dynamics at will, which allows to steer the system towards a desired final state. This is the basic idea of the quantum control scheme by Tannor, Kosloff and Rice [71]. Another control scheme by Brumer and Shapiro [69] exploits the interferences of alternative pathways in multi-photon excitations. Both schemes rely on the control of constructive and destructive interferences to manipulate reaction dynamics. Experimental implementations of these schemes were successful in a large number of different systems e.g. the control of chemical reactions [4, 12], in isotope selective ionization [7,75] or selective bond breaking of molecules [42]. In many cases, where the systems are too complex to find the ideal pulse shape from first principles, quantum control experiments are combined with adaptive learning algorithms as proposed by R.Judson and H.Rabitz [29]. Here the excitation pulse parameters are controlled by a computer based learning algorithm which iteratively optimizes their composition to drive the examined physical system towards the desired goal. Effectively, all these developments provide a number of highly sophisticated tools for the manipulation of quantum systems. For our problem concerning the formation of stable, ultracold molecular samples one may now choose the appropriate tools for this purpose.

A first proposal on photoassociation by ultrashort laser pulses was published already in 1994 by M. Machholm et al. [45]. They describe a pumpprobe scheme where a nuclear wavepacket is created from a colliding atom pair. The wavepacket subsequently propagates in the attractive potential and is finally excited to the molecular ion at the inner turning point. The advantage of this scheme is that the free-bound transition occurs at large internuclear distances, where high excitation efficiency is provided due to large free-bound Franck-Condon overlaps. The transition to another molecular state occurs with good efficiency at short distances. The transfer of the wavepacket from long to short ranges is accomplished via the internuclear attractive force. A large number of publications followed this first one, examining various prospects of such a scheme: C. Koch et al. [35, 36] suggest a pump-dump scheme for the population of the deeply bound ground state molecules. A process for efficient de-excitation of Feshbach molecules using the pulse-to-pulse coherence in femtosecond pulse trains is suggested by A. Peer et al. [54].



Figure 1.3: Result of the pulsed PA experiment of Fatemi et al. The figure shows the ion signal produced by autoionizing molecules versus the delay between pump an probe pulses. The initial increase can be attributed to an inward spreading of the excited state wavepacket, while the decreasing slope for long delay times is due to dephasing. From [19]

Early experiments by Marvet and Dantus in 1995 [48] succeeded in photoassociating molecules from a hot gas of mercury atoms and were also able to observe wavepacket dynamics. The first experiments on an ultracold sample was carried out by Fatemi *et al.* [19] who followed a scheme closely related to the proposal by M. Machholm *et al.*. They performed a pump-probe experiment on ultracold sodium with two picosecond pulses tuned below the D2 transition. Depending on the pulse delay, an increase in molecular ions was observed with a maximum at 4 ns (see fig. 1.3) which can be understood in terms of flux enhancement [24], however no nuclear wavepacket dynamics were found.

Another issue in the application of pulsed lasers is the increase in electronic excitation efficiency by adiabatic transfer in chirped¹ laser pulses. Such concepts were proposed by Vala *et al.* [76]. Corresponding experimental work was published recently by Wright *et al.* in ultracold diatomic collisions in the presence of chirped laser fields. They observed significant dependencies on linear chirp direction which occurs when the nuclear wavepacket interacts with the laser field as it is accelerated in the attractive potential.

We present in this work the first experiments on the application coherent manipulation techniques to ultracold molecules and to the photoassociation of collision pairs. In chapter 5 we show an experiment on the optimization of ultracold molecule excitation and fragmentation by shaped femtosecond pulses in a closed loop experiment. These are among the first experiments [13, 64] to apply the repertory of coherent control to ultracold gases and, by verify its feasibility, represent the first step to a larger number of experiments. Chapter 6 reports on the photoassociation and ionization of ultracold molecules by shaped femtosecond pulses in a pump-probe scheme. We observe the formation of molecules in an excited state potential and, after spontaneous decay, also the population of bound ground states. During the formation process, the evolution of the molecular electronic dipole is observed as it interacts with the field of the photoassociation pulse.

 $^{^{1}}$ chirp = temporal variation of instantaneous light frequency

Chapter 2

Light matter interaction with femtosecond pulses

The central topic of this work is the application of shaped ultrashort laser pulses to the photoassociation of molecules from ultracold collision pairs and to the excitation of diatomic molecules from their electronic ground state. This chapter shall therefore review the theoretical background of the diatomic interaction in the presence of an arbitrary, time dependent light field, following the discussion in [60].

2.1 Diatomic encounters in the presence of laser pulses

The system under consideration is a pair of interacting atoms in the presence of a dependent optical field. The systems Hamiltonian therefore consist of distinct parts that describe the Coulomb interactions between the nuclei, labeled as V_{NN} , the electron-nucleus interactions V_{eN} and the electron-electron interaction V_{ee} . The action of the optical field on the system is modeled by via the electronic dipole operator \vec{D} :

$$H(\vec{r}, \vec{R}, t) = T_e(\vec{r}) + T_N(\vec{R}) + V_{NN}(\vec{R}) + V_{ee}(\vec{r}) + V_{eN}(\vec{r}, \vec{R}) + \vec{D} \cdot \vec{E}(\vec{r}, t).$$
(2.1)

Here, \vec{r} and \vec{R} denote the position operators of electrons and nuclei, $T_e(\vec{r})$ and $T_N(\vec{R})$ are the corresponding kinetic energy operators. For simplicity only the valence electrons are considered here. In the absence of light, electronic and nuclear motion can be decoupled due to the large difference in inertia. This is the so-called Born-Oppenheimer approximation which allows the definition of a Hamiltonian for the electronic motion:

$$H_{el}(\vec{r}, \vec{R}, t) = T_e(\vec{r}) + V_{NN}(\vec{R}) + V_{ee}(\vec{e}) + V_{eN}(\vec{r}, \vec{R}), \qquad (2.2)$$

from which we obtain a set of electronic eigenfunctions by solving the timeindependent Schrödinger equation (TISE):

$$H_{el}|\chi_n\rangle = E_n^{el}(\vec{R})|\chi_n\rangle.$$
(2.3)

Note that \vec{R} enters here only as parameter, since the differential operator $T_N(\vec{R})$ is not contained in H_{el} , which makes this equation much easier to solve. The eigenvalues and eigenfunctions in eqn. 2.3 then depend parametrically on the nuclear coordinates \vec{R} . We can now expand the total molecular wavefunction in these basis states:

$$|\Phi(t)\rangle = \sum_{m} \phi_m(\vec{R}, t) |\chi_m\rangle$$
(2.4)

The approximation now consists of neglecting the action of $T_N(\vec{R})$ on the electronic basis states, justified by the much larger inertia of the nuclei. We can therefore give a time dependent Schrödinger equation (TDSE) eqn. 2.1 with a Hamiltonian where the electronic coordinates are adiabatically eliminated:

$$i\hbar\frac{\partial}{\partial t}\phi_n(\vec{R},t) = (T_N + E_n^{el}(\vec{R})) \ \phi_n(\vec{R},t) - \sum_m \langle \chi_n | \vec{D} \cdot \vec{\epsilon} | \chi_m \rangle \ E(t) \ \phi_m(\vec{R},t) \ (2.5)$$

Here, the first part models the nuclear motion under the influence of the valence electron interaction $E(\vec{R})$. For fully separated atoms, $E(\vec{R})$ corresponds to the electronic energy levels of the individual atoms. As the atoms approach each other, the energy levels are shifted, depending on the separation R. The sign of the shift results from the relative electronic configurations of the approaching atoms, resulting in attractive (neg. shift) or repulsive (pos. shift) interaction. The second part in eqn.2.5 describes the interaction of the valence electrons with the optical field via the dipole operator \vec{D} .

We now change into the center-of-mass (cm) frame in order to obtain a one-dimensional differential equation. This is done by separating the cmmotion from the total wavefunction. The wavefunction in the cm-frame can now be written as the product of a one dimensional function depending only on the internuclear distance R and an angular part given by spherical harmonics. The transformed kinetic energy operator reads

$$T = -\frac{\hbar^2}{2\mu} \left(\frac{\partial^2}{\partial R^2} + \frac{2}{R} \frac{\partial}{\partial R} \right) + \frac{\hbar^2 l(l+1)}{2\mu R^2}$$
(2.6)

where μ is the reduced mass and the second term stems from the angular momentum of the colliding atom pair. In the ultracold regime, the relative kinetic energies are low and we can approximate the collision by considering only s-wave scattering with l = 0. Redefining the wavefunction as $\psi(R, t) = R \phi(R, t)$, one arrives at

$$i\hbar\frac{\partial}{\partial t}\psi_n(R,t) = \left(-\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial R^2} + V_n(R)\right) \ \psi_n(R,t) - \sum_m D_{mn} \ E(t) \ \psi_m(R,t)$$
(2.7)

where the notation for the electronic eigenvalues was changed to $V_n(R)$ since they act as a potential energy for the nuclear motion.

For photoassociation of two ground state atoms we need to consider only the two lowest electronic states, denoted as ground (g) and excited (e) state. The matrix element of the dipole operator is denoted as D_{eg} , its R-dependence is neglected in the following.

$$D_{eg} = \langle \chi_e | \vec{D}_{eg} \cdot \vec{e} | \chi_g \rangle, \qquad (2.8)$$

where the nuclear functions $\psi_{g,e}$ are taken at a specific *R*-value, i.e. $R \to \infty$. We can now write down the TDSE in a concise matrix form:

$$i\hbar \frac{\partial}{\partial t} \begin{pmatrix} \psi_g(R,t) \\ \psi_e(R,t) \end{pmatrix} = \begin{pmatrix} T + V_g(R) & D_{eg} \cdot E(t) \\ D_{eg}^* \cdot E(t) & T + V_e(R) \end{pmatrix} \begin{pmatrix} \psi_g(R,t) \\ \psi_e(R,t) \end{pmatrix},$$
(2.9)

We can separate the time evolution of the electronic states from the wavefunctions:

$$\psi_g(R,t) = \tilde{\psi}_g(R,t) e^{-i\frac{E_g(R\to\infty)}{\hbar}t} = \tilde{\psi}_g(R,t) e^{-i\omega_g t}, \qquad (2.10)$$

$$\psi_e(R,t) = \tilde{\psi}_e(R,t) e^{-i\frac{E_e(R\to\infty)}{\hbar}t} = \tilde{\psi}_e(R,t) e^{-i\omega_e t}.$$
(2.11)

Inserting this into the TDSE 2.9 and multiplication with $e^{i\omega_{g/e}t}$ gives:

$$i\hbar \frac{\partial}{\partial t} \begin{pmatrix} \tilde{\psi}_g(R,t) \\ \tilde{\psi}_e(R,t) \end{pmatrix} = \begin{pmatrix} T + \bar{V}_g(R) & D_{eg} \cdot E(t) e^{i(\omega_g - \omega_e)t} \\ D_{eg}^* \cdot E(t) e^{-i(\omega_g - \omega_e)t} & T + \bar{V}_e(R) \end{pmatrix} \begin{pmatrix} \tilde{\psi}_g(R,t) \\ \tilde{\psi}_e(R,t) \end{pmatrix};$$
(2.12)

where the potentials are shifted with respect to each other such that the asymptotic values coincide if the laser frequency matches the asymptotic transition frequency, i.e.

$$V_g(R) = V_g(R) - V_g(R \to \infty)$$

$$\bar{V}_e(R) = V_e(R) - V_e(R \to \infty)$$
(2.13)

For the real electric field we can write

$$E(t) = \frac{1}{2} E_0(t) \left(e^{i\omega_L t} + e^{-i\omega_L t} \right), \qquad (2.15)$$

where $E_0(t)$ is the time dependent envelope, for example of a Gaussianshaped laser pulse. By inserting the field into the Hamiltonian in eqn. 2.12, the off diagonal elements read:

$$H_{12} = \frac{1}{2} D_{ge} \cdot E_0(t) \left(e^{i(\omega_L + \omega_{eg})t} + e^{-i(\omega_L - \omega_{eg})t} \right)$$
(2.16)

$$H_{21} = \frac{1}{2} D_{ge} \cdot E_0(t) \left(e^{-i(\omega_L + \omega_{eg})t} + e^{i(\omega_L - \omega_{eg})t} \right)$$
(2.17)

Usually, the counter-rotating part is omitted and only the co-rotating term $\Delta = \omega_l - \omega_{eg}$ is considered which is called the rotating wave approximation (RWA). The oscillatory part in the coupling terms can be avoided by another transformation of the wavefunction:

$$\bar{\psi}_g = \tilde{\psi}_g e^{-i\frac{\Delta}{2}t}
\bar{\psi}_e = \tilde{\psi}_e e^{i\frac{\Delta}{2}t}$$
(2.18)

leading to the simplified version of the TDSE

$$i\hbar \frac{\partial}{\partial t} \begin{pmatrix} \bar{\psi}_g(R,t) \\ \bar{\psi}_e(R,t) \end{pmatrix} = \begin{pmatrix} T + \bar{V}_g(R) - \frac{1}{2}\hbar\Delta & \frac{1}{2}\hbar\Omega(t) \\ \frac{1}{2}\hbar\Omega^*(t) & T + \bar{V}_e(R) + \frac{1}{2}\hbar\Delta \end{pmatrix} \begin{pmatrix} \bar{\psi}_g(R,t) \\ \bar{\psi}_e(R,t) \end{pmatrix}$$
(2.19)

where the coupling matrix elements are given by the Rabi frequency:

$$\Omega = \frac{D_{eg} \cdot E_0(t)}{\hbar} \tag{2.20}$$

The full dynamics of the nuclear wavefunctions occupying the two electronic states and interacting with an arbitrary laser pulse can now be derived by integrating Eqn. 2.19. The distinction between photoassociation or molecule excitation only enters by choosing the initial nuclear state, either as a scattering state of free particles or a bound molecular state. Eqn. 2.19 can be solved by various methods which are summarized in [38] and [23]. For the treatment of ultracold molecules the state-of-the-art technique to integrate the TDSE is a combination of the Mapped Fourier Grid Hamiltonian (FGH) and a Chebychev propagator method. Reviews on these techniques can be found in [11,37,84]. Such an algorithm is used for the simulation of photoassociation by shaped femtosecond pulses which is presented in combination with the corresponding experiments in chapter 6. Its implementation and properties are discussed in detail in [60].

2.2 Potential Curves, Energy Levels and Franck-Condon Factors

The essential ingredient for both analytical and numerical solutions of the TISE 2.2 and TDSE 2.9 are accurate potential curves, V(R), for all involved

electronic states. These potential curves can either by obtained by ab-initio calculations or by inversion of spectroscopy data. The latter technique is especially efficient for large values of R, where the potentials typically display a $\Sigma_n C_n/R^n$ behavior. For instance, if we consider an atom pair where one of the atoms is found in an atomic *s*-state and the other one in an excited *p*-state, the dominant interaction is the resonant dipole-dipole interaction leading to a long-range C_3/R^3 behavior. The interaction potentials can be determined with high accuracy from PA spectroscopy data with the RKR technique [20]. In our case, the potential curves stem from ab-initio calculations by Park et al. [53]. These, however, totally neglect spin-orbit coupling, which was also neglected in our basic Hamiltonian eq. 2.1. For heavier alkali atoms, spin-orbit coupling plays an important role and must therefore be taken into account. This is done by changing the basis of electronic state from Hund's case(a) to Hund's case(c). In Hund's case(a), the electronic states are identified in molecular Russel-Saunders notation according to

$$^{2S+1}\Lambda_{\Omega},$$
 (2.21)

Here, Λ is the projection of the total orbital angular momentum onto the internuclear axis, S is the total spin and:

$$\Omega = |\Lambda + \Sigma| \tag{2.22}$$

where Σ is the spin analogue of Λ . In our case, we deal with ground and first excited electronic states where $\Lambda = 0$ or $\Lambda = 1$, respectively. These are called Σ and Π states in analogy to atomic notation. Additional quantum numbers that distinguish the electronic states are the mirror symmetry +/with respect to a plane perpendicular to the internuclear axis, and g/u the wavefunction symmetry under the exchange of electrons.

If there is considerable spin-orbit coupling present, Λ and Σ are no good quantum numbers. We therefore have to change the basis to Hund's case(c), where the states are denoted by the total angular momentum J. The potential curves for Hund's case(c) are obtained from the curves in Hund's case(a) by a transformation in the space of electronic states, i.e. a diagonalization. For instance, two different 0_q^- states are obtained by Guterres *et al.* [26]:

$$V_{0_g^-}(R) = \left| \begin{array}{cc} V^{\Pi}(R) - \Delta^{\Pi\Pi}(R) & \Delta^{\Sigma\Pi}(R) + \sigma(R) \\ \Delta^{\Sigma\Pi}(R) + \sigma(R) & V^{\Sigma}(R) \end{array} \right|,$$
(2.23)

where $\Delta^{\Pi\Pi}(R)$ and $\Delta^{\Sigma\Pi}(R)$ are the position-dependent matrix elements of the spin-orbit coupling operator and $\sigma(R)$ is a further relativistic correction. For our calculations, we used Hund's case(a) potentials that were transformed to Hund's case(c) with the atomic, i.e. asymptotic values for the spin-orbit matrix elements, since the position-dependent values would require a fully relativistic ab-initio calculation. The transformation was done



Figure 2.1: Potential curves for the ground and first excited states of Rb_2 .

by C. Koch [33], who also modified the potentials so that their long range behavior agrees with experimentally derived dispersion coefficients [20, 47]. The curves are shown in fig. 2.1.

From the potential curves, the energy levels, corresponding wavefunctions and Franck-Condon factors (FCF) can be numerically calculated by solving eqn. 2.2, for example by means of finite differences method, e.g. a Numerov algorithm. Accurate FCF for bound-bound as well as free-bound transitions are computed with the more advanced mapped Fourier-Grid-Hamiltonian (FGH) method [38], the results for the ⁸⁵Rb₂ ${}^{1}\Sigma_{g}(5s+5s) \rightarrow 0^{+}_{u}(5s+5p^{1/2})$ transition are shown in fig. 2.2.

2.3 Photoassociation of by laser pulses and wavepacket preparation

For photoassociation, the initial state is pair state of free atoms and the goal is to transfer it into a final bound state by means of the laser excitation. We describe in this section the formation of molecules from an ultracold colliding atom pair by a short laser pulse. Short means, in this context, that the relevant timescales are short compared to the lifetime of the excited state. We follow the treatment in [69]. Although the dynamics of the system is well described in position space by the TDSE (eqn. 2.9), we use an equivalent approach in the Hilbert space of static eigenfunctions here. Doing so delivers an expression for the final molecular state in the basis of the vibrational eigenstate spectrum. If the perturbation by the laser pulse is small, this approach is particularly useful in combination with frequency-domain pulse shaping as it gives a direct relation between the spectral pulse composition and the final amplitudes and phases of the basis states.

Therefore we first expand the the total state vector in the basis of solu-



Figure 2.2: Franck-Condon factors for the $X^{-1}\Sigma_g \to 0^+_u$ transition. The overlap integrals for bound-bound transitions are presented on the left, where μ denotes the vibrational levels of the ground state and ν the levels of the excited state. Note the alternating sign of the integrals. On the right, the FCF for the corresponding free-bound transition are plotted logarithmically due to their variation by several orders of magnitude. The inset shows the dependence of the free-bound FCF from the energy of the initial continuum wavefunction for three different excited vibrational levels. The kink in these curves stems from the avoided crossing in the 0^+_u potential curve.

tions of the time-independent Schrödinger equation (TISE):

$$\Psi(t) = \sum_{g,e} \left[\sum_{n} b_{n}^{g,e}(t) e^{-i E_{n}^{g,e} t/\hbar} |\psi_{n}^{g,e}\rangle + \int c^{g,e}(E,t) e^{iE^{g,e} t/\hbar} |E^{g,e}\rangle dE \right]$$
(2.24)

where g and e denote the two electronic manifolds and $b_n^{g,e}(t)$ and $c^{g,e}(E,t)$ are the expansion coefficients for bound and continuum eigenstates of the TISE. For the description of photoassociation, the continuum of nuclear states is included here.

The coupled equations of motion, resulting from the time dependent Schrödinger equation (TDSE) consist of a set of differential equations for the expansion coefficients $b_n^{q,e}$ and $c_{q,e}(E,t)$. If we neglect transitions into and between the continua, these equations read:

$$\frac{db_m^{g,e}}{dt} = \frac{1}{i\hbar} \sum_n b_n^{e,g}(t) e^{i\omega_{mn}^{g,e}t} E(t) \left\langle \psi_m^{g,e} | \vec{D} \cdot \vec{\epsilon} | \psi_n^{e,g} \right\rangle$$
(2.25)

+
$$\int c^{e,g}(E,t)e^{i\omega_{m,c}t}E(t)\langle \psi_m^{g,e}|\vec{D}\cdot\vec{\epsilon}|E^{e,g}\rangle dE.$$
 (2.26)

(2.27)

In an ultracold gas, the energy of the initial continuum state is generally well defined so that its distribution can be approximated by a delta function $c_{g,e}(E, t \to -\infty) = \delta(E - E_{init}^g)$, where E_{init}^g is given by the average thermal energy in the trap. If we further assume a weak perturbation by the light field¹ and that no bound states are initially populated, such that $b_n^{g,e}(t \to -\infty) = 0$. We can then obtain upon integration:

$$b_m^e(t) = -\frac{d_{m,c}}{i\hbar} \int_{-\infty}^t dt' \, e^{i\omega_{m,c} \, t'} E_0(t)$$

$$= -\frac{d_{m,c}}{i\hbar} \int_{-\infty}^\infty d\omega \, \tilde{E}_0(\omega) \int_{-\infty}^t dt' \, e^{i(\omega_{m,c}-\omega)t'}$$
(2.28)

where $E_0(t)$ and $\tilde{E}_0(\omega)$ are the temporal and spectral envelope functions of the pulse, and

$$d_{m,c} = D_{eg} \left\langle \psi_m^e | E_{init}^g \right\rangle \tag{2.29}$$

is the effective dipole matrix element for the free-bound transitions, which is essentially the product of the atomic dipole moment and the free-bound Franck-Condon factors. If we are interested only in the superposition coefficients after the pulse is off, we can extend the upper integration limit to infinity and simply obtain the coefficients from the spectral envelope function of the excitation pulse:

$$b_m^e(t \to +\infty) = \frac{2\pi i}{\hbar} d_{m,c} \tilde{E}_0(\omega_{m,c})$$
(2.30)

It is important to notice at this point that $\mathscr{E}(\omega)$ can be complex valued, and that the pulse therefore imparts both its phase and its amplitude on the expansion coefficients. As will be discussed in chapter 4 both parameters can be varied with high accuracy by using femtosecond pulse shaping techniques [80]. According to eqn. 2.30 the pulse shape is directly imprinted into the resulting nuclear wavepacket by means of the complex expansion coefficients. Also the temporal propagation in the potential well may be influenced by the phases of the pulse. Appropriate choice of the pulse shapes may then be used to create a desired wavepacket at a particular time. One of the principle goals here is to create a nuclear wavepacket for optimized and coherent transformation from a continuum pair state to bound molecules in a pump-dump scheme [35]. Pulse shaping here is also useful in the regime of strong coupling to the laser pulse where chirped laser pulses can achieve highly efficient transfer from the initial continuum state to bound molecular states by adiabatic transfer [76].

Eqn. 2.28 assumes a weak interaction with the laser field and represents a first order, perturbative approach. In experiments with ultrashort laser pulses this condition is easily violated. For the correct treatment of the problem then the full TDSE has to be solved numerically.

¹which is not necessarily true as will be seen in the following experiments

For the actual experiment it is also useful to view the problem on a macroscopic scale. The formation of molecules here is described using rate equations, where photoassociation enters with the term

$$R_{PA} = \int_{V} d^{3}r \ \beta \ n^{2}(\vec{r})$$
(2.31)

The parameter β here incorporates all parameters like spectral dependence and Franck-Condon factors, which have to be derived from the microscopic treatment. Here, β also includes the power dependence of the process and is therefore position dependent due to the spatial profile of the photoassociation beam.

For a rough, upper estimation of rates one can calculate the number of pairs within the Condon radius that may be converted to molecules as:

$$N_{pairs}(r) = \int_{0}^{r} n_{pairs}(r') \, dr'$$
(2.32)

Here, $n_{pairs}(r')$ is the density of pairs in the trap. It describes the probability to find two atoms at a distance r and is therefore the classical envelope to the quantum mechanical probability distribution, given by the absolute square of the continuum pair wavefunction. Assuming a gaussian distribution of atoms in the trap with a peak density n_0 , $n_{pairs}(r')$ is given by:

$$n_{pairs}(r) = 2\pi n_0^2 r^2 e^{-\frac{r^2}{2\sigma}}$$
(2.33)

A precise calculation on the formation rates requires details of the ground state scattering wave function for a given pair distribution. By using the excitation formalism discussed above, one can then derive a photoassociation rate per pulse from the calculated free-bound transfer efficiency. For the photoassociation of rubidium molecules by picosecond pulses this has been done and recently published by Christiane Koch *et al.* [34].

Chapter 3

A transportable high density magneto-optical trap

For our experiments we use an ultracold gas of 85 Rb atoms which is confined in a magneto-optical trap [61]. In order to maximize the photoassociation rate of molecules, a dark SPOT configuration was chosen to increase the number density of atoms in the trap. For detection of molecules, we use two different schemes: In experiments in chapter 5 molecules are ionized by nanosecond laser pulses in a REMPI¹ scheme [22] and mass selectively detected by time-of-flight. For the photoassociation experiments in chapter 6 molecules are ionized by femtosecond pulses for which a new ion detection system was developed, based on continuous mass filtering in an RF quadrupole.

The trap setup was designed to be fully transportable so it could be moved to the femtosecond laser laboratory at the FU Berlin, where the experiments where carried out. Atoms are trapped in an ultra high vacuum (UHV) vessel which is equipped with all necessary components for operation and diagnostics of the trap and for mass selective, single ion detection. Trapping lasers are situated on a separate optics table together with all tools for frequency stabilization and beam control. Electronic equipment for the laser system and trap control is mounted separately in 19" racks. Optical fibres between the laser table and the vacuum vessel allow to place the table at some distance from the chamber. All components are mounted on mobile racks so they can easily be moved and positioned. After transport, usually some adjustments have to be made to the lasers and magnetic fields, however full operation can be achieved after 2-3 days.

¹REMPI = Resonance enhanced multi-photon ionization

3.1 Density increase in a dark SPOT

One of the outstanding features of the mobile MOT setup is its operation in a dark SPOT configuration, which provides high atomic densities of up to $10^{11} \,\mathrm{cm}^{-3}$. In standard MOTs, the trap density is limited by scattering and re-absorption of trap light by atoms. The re-scattering of photons causes an outward directed force on the atoms which counteracts the compressive magneto-optical force [55, 70, 73]. This process can be avoided by storing trapped atoms in their lower hyperfine state which is, far off-resonant² with the trapping light and therefore called a dark state [3, 32]. The mechanism shall be briefly discussed in this section, a detailed analysis can be found in Townsend *et al.* [74]. Atoms in the trap are continuously pumped between the hyperfine ground states. In the trapping cycle they undergo continuous transitions between F=3 and the excited F'=4 state (see Rb level scheme fig. 3.2). Population of the lower F=2 hyperfine ground state occurs either by offresonant excitation to the F'=3 state, or by a depumping laser, resonant with F=3 to F'=2. By subsequent spontaneous decay both leads to population the lower hyperfine state. A repump laser on the F=2 to F'=3transition returns the atoms to the upper state. The distribution among the hyperfine ground states is given by the re- and depumping rates between the two states:

$$\frac{N_u}{N_d} = \frac{R_{rep}}{R_{dep}} = \frac{\tau_u}{\tau_d};\tag{3.1}$$

where $N_{u/d}$ is the number of atoms in the upper and the lower hyperfine ground state respectively. The time constants $\tau_{u/d}$ characterize the dwell times for an atom in one of the two states. A central parameter in a dark SPOT is the bright state fraction (BSF) parameter p:

$$p = \frac{N_u}{N_d + N_u} \tag{3.2}$$

which represents the fraction of atoms in the upper F=3 hyperfine state which participate in the trapping cycle. In analogy to a standard MOT, in a dark SPOT, one can distinguish between a temperature limited and a density limited regime [73]. In the range of small upper state populations, p is well approximated by $p \approx \tau_u/\tau_d$.

In the temperature limited regime, the interaction between atoms via re-scattering is low and the trap density is defined by the temperature and the effective spring constant κ . The trap radius $r_{x,y,z}$ along each spatial direction is given by the equipartition theorem:

$$\frac{1}{2}\kappa_{i\,i}r_i = \frac{1}{2}k_BT\tag{3.3}$$

 $^{^{2}3.1}$ GHz in case of $^{8}5$ Rb

where κ_{ii} is the effective spring constant tensor. As the total number of atoms in this regime is independent on the radius, the trap density is given by:

$$n_T = \frac{N}{2(\sqrt{2\pi}\,r)^3} \tag{3.4}$$

In this regime, the ultracold gas is compressible as n can be increased by a higher spring constants κ_{ii} , e.g. due to an stronger magnetic field gradient. In a dark SPOT, atoms spend only fractions of their time in the upper state which decreases the spring constant κ by p, effectively leading to a decrease in atom density as more atoms are transferred to the lower state. The density is then given by:

$$n_T^{DS} = \frac{N}{(\sqrt{2\pi})^3} \left(\frac{\kappa}{k_B T}\right)^{3/2} p^{3/2}$$
(3.5)

In larger, standard MOTs the interaction between atoms by reabsorption of scattered trap light limits the density to typically 10^{10} 1/cm³. Townsend *et al.* [73] give a scaling law for the density dependence in this regime on various trapping parameters.

$$n_{DL} = C_{DL} \frac{\kappa_0}{\lambda \hbar \Gamma} \frac{b}{b_0} \frac{\delta \Gamma^{\frac{1}{2}}}{\Omega^2}, \delta < 2\Gamma$$
(3.6)

where C_{DL} is a dimensionless constant (~50), κ_0 is an experimentally measured proportionality constant for the spring constant, b/b_0 the magnetic field gradient in units of G/cm, Γ is the natural line width and Ω the trap light Rabi frequency. The density here is proportional to the effective spring constant, which reduces in a dark SPOT as p drops. The density limitation by re-scattering, however is a two-body effect which scales with the square of p resulting in an effective inverse proportional relation of n_{DL} and p,

$$n_{DL}^{DS} = \frac{n_{DL}}{p} \tag{3.7}$$

. which causes the density increase in the dark SPOT.

A typical dependence of the trap density on p, shown in fig.3.1 is taken from Townsend *et al.* [74] where is was measured in a cesium trap. One can clearly distinguish between the two density regimes discussed above. As p is reduced from 1, which corresponds to a standard, density limited trap, the density increases due to the reduction of re-scattering forces. A maximum is reached at p=0.1 at a density about a factor of eight higher than at p=1. For smaller p, no further increase can be achieved as the trap already became transparent³ for scattered photons resulting in a full suppression of the rescattering forces. The trap then enters the temperature limited regime where

³mean free path \gg cloud size



Figure 3.1: Atomic density versus BFS in a dark SPOT. Density increase due to reduction of rescattering effects. Highest densities achieved when 90% of atoms are ketp in lower hyperfine state. Taken from Townsend *et al.* [74]

the density drops due to decreasing effective trapping force. The validity of this picture is also confirmed by the two lines in fig.3.1 which represent model calculations of the density in both regimes.

3.2 The mobile trap setup

3.2.1 Diode laser system

The laser system for the transportable MOT is mounted on a mobile laser table. It provides laser light for trapping and cooling of rubidium atoms in a high density, dark SPOT configuration [32], for optical hyperfine pumping and absorption imaging of the trap. Laser light is produced by three home built diode lasers which are actively stabilized to the relevant rubidium transitions within a few MHz bandwidth. Two extended-cavity grating lasers (ECL) [62] are actively stabilized to rubidium hyperfine transitions, the high power trapping laser itself is stabilized via injection seeding. Most parts of the setup consist of standard, commercial opto-mechanical components, custom made parts were used where alternatives were expensive or unavailable. The setup for the ECL lasers and the frequency stabilizations are described in detail in the appendix A and A.2. All laser beams are coupled into polarization maintaining optical fibres which guide them to the trapping chamber.

The operation of the dark spot magneto-optical trap requires laser light on resonance or close to several rubidium hyperfine transitions as they are



Figure 3.2: Hyperfine level scheme of ⁸⁵Rb D2 line. Right hand side: Hyperfine transitions required for operation and diagnostics of dark SPOT

shown in fig. 3.2. Trapping and cooling of atoms is provided by laser light which is tuned several line widths below $F=3 \rightarrow F'=4$ transition [61]. Optical pumping between two hyperfine ground states is provided by repump light for the $F=2 \rightarrow F'=3$ transition, and depump light, resonant with the $F=3 \rightarrow F'=2$ transition. Atoms in the trap are detected in the F=3 hyperfine state by absorption from a beam resonant with the closed $F=3 \rightarrow F'=4$ transition.

To provide the relevant beams, the laser system consists of three diode lasers (see fig. 3.3). One ECl diode laser is operated on resonance with the $F=3 \rightarrow F'=2$ transition and serves as master laser for the injection locked trap laser and as depump laser for optical pumping. The frequency reference for the active stabilization is taken from doppler-free frequency modulation (fm) spectroscopy in a rubidium vapor cell. In the obtained fm-spectra, the F'=3/F'=4 crossover resonance is, due the large signal, a preferable reference for active frequency stabilization strength. To operate the master laser on the the $F=3 \rightarrow F'=2$ transition while locking it to the F'=3/F'=4 crossover, its spectroscopy beam is shifted upwards in frequency by 124 MHz by a single pass acousto-optical modulator (AOM).

Laser light for the trapping beams is produced by an additional single mode laser diode which is injection locked to the narrow band ECL master laser. The amplification of the narrow band grating laser such a masterslave configuration increases the available intensity for the trapping beams to 110 mW under conservation of the master laser bandwidth. The slave laser consists of a temperature stabilized laser diode which is mounted and collimated in a Thorlabs collimation tube. Its output beam passes a single stage optical isolator. The master laser beam is injected into the diode via an exit port of the optical isolator (see fig.3.3). To operate the trap,



Figure 3.3: Scheme of dark SPOT laser setup. Relevant laser beams are produced by two ECL diode lasers and one injection seeded diode. Rubidium FM spectroscopies act as frequency references for active stabilization of ECL lasers. Fabry-Perot resonators are used to monitor narrow-band, single mode operation

the frequency of slave laser is tuned $3\Gamma = 18$ MHz below the F=3 \rightarrow F'=4 resonance by frequency shifting the injection beam in a double pass AOM. The slave laser beam are then split into the three trapping beams, one for each spatial direction. They are coupled into polarization maintaining optical fibres which guide them to the UHV⁴ vacuum vessel where the rubidium trap is produced. For mode matching with the optical fibres, the slave beam passes a telescope. The traplight is switched by a fast mechanical shutter which is positioned at the focus of the mode-matching telescope. Opening of the shutter takes 200 μ s closing about 500 μ s. The master laser also provides the depumper beam for the dark SPOT. Therefore a beam is split off, attenuated to 0.1 mW and passes an electro-optical modulator (EOM) for beam switching. The EOM swaps from 100% to 2% transmission in 5 μ s. Subsequently, this beam is also coupled into an optical fibre and transferred to the trap setup.

The second grating diode laser is locked to the $F=2 \rightarrow F'=3$ hyperfine transition and is used as repump laser 3.3. The frequency reference is also a doppler-free fm spectroscopy. For the optimization atom density in the dark spot configuration, it proved advantageous to detune the repump laser from the $F=2 \rightarrow F'=3$ resonance (fig. 3.2) [3,74] by locking it to the F=2/F'=3crossover resonance which occurs 31 MHz below the atomic resonance. The repump laser output is split into two parts: 90% is used for the two hollow dark spot beam, which are described in detail in section 3.2.3. The remainder of 10% serves as a fill-in beam which is needed for the detection of atoms in dark spot (see B.1). It passes an EOM-switch before it is overlapped with the depump beam and coupled into a polarization maintaining optical fibre.

3.2.2 Vacuum system and UHV chamber

The vacuum chamber is mounted on a mobile rack as shown in fig.3.4. The trap section provides optical access for the trapping beams via four CF40 viewports in the horizontal plane and two CF100 ports in the vertical direction. The larger aperture of the vertical ports is also used for trap diagnostics via fluorescence detection and for additional laser beams for optical pumping and absorption imaging (see appendix B.1). UHV conditions are provided by two pumping systems: Molecular gases like H₂, N₂ and water are pumped by a titanium sublimation pump (Ti:Sub). It is combined with a so-called cryo shield by Varian (TSP Cryopanel) which allows flushing with cooling water or liquid nitrogen to increase the pumping speed. At 20 ° C This combination provides pumping speeds up to 12501/s (for H₂). The Ti:Sub is supported by an ion getter pump (Varian StarCell 55) of $501/s^5$ which is particularly well suited for pumping of rare gases like helium and argon. After breaking the vacuum the setup has to be baked at 130 ° C for about 48 hours. Dur-

⁴Ultra high vacuum

 $^{{}^{5}}N_{2}$ nominal speed for saturated diode



Figure 3.4: Transportable vacuum chamber for dark SPOT: Optics assemblies for trapping beams are attached to vacuum chamber via welded and bolted bread boards at the traplight view ports. Ion or laser beams for scattering experiments pass the chamber along the short axis. Ion detectors are mounted perpendicular to beam direction. Setup contains ion getter and Ti:Sub vacuum pumps to provide UHV conditions

ing bake-out, pumping down to 10^{-8} mbar is provided by an external turbo pump. The base pressure achieved this way is $8 \cdot 10^{-11}$ mbar, measured by a vacuum ion gauge (Pfeiffer IKR 270). The rack which holds the chamber supplies three 19 inch slots to carry electronics and controllers for vacuum pumps and gauges, for the MOT magnetic quadrupole and compensation coils and for the ion detection systems.

3.2.3 Compact optics assemblies for dark spot trap

The fully operational system as it was set up during the experiments at FU Berlin is shown in fig. 3.5. A major contribution to the compactness of the MOT setup arises from the use of concise optics assemblies which couple the trapping and repumping beams into the chamber. Trapping beams are guided to the chamber in three optical fibres. For each beam, the optics assembly consists of an fibre receptacle, a plano-convex lens of 25 mm diameter and 100 mm focal length (see fig. 3.6) and a 50 mm quatre-waveplate. From the end of the single mode fibre, the linear polarized beam expands freely for 100 mm, thereby increasing its sigma width to 22 mm ⁶. The plano-convex lens collimates the beam, which passes the waveplate before it enters the chamber. The three trapping beams are retro-reflected after passing the chamber and are overlapped in the geometric center of the trap section.

With an output power of 100 mW from the trapping laser and a fibre coupling efficiency of 70% the resulting light intensity in the trap center is $I = 18 \text{ mW/cm}^2$. At a laser detuning of $\delta = 18 \text{ MHz} = 3 \Gamma$ and assuming a resonant saturation intensity for rubidium of $I_{sat} = 1.6 \text{ mW/cm}^2$ ⁷, the saturation parameter for on the trapping transition is [51]:

$$S = \frac{S_0}{1 + 4\delta^2 / \Gamma^2} = 0.3, \tag{3.8}$$

with $S_0 = I/I_{sat}$. The corresponding population in the excited F'=4 state of:

$$\rho_{22} = \frac{S}{2(1+S)} = 0.12\tag{3.9}$$

The dark SPOT is implemented, according to Ketterle *et al.* [32], by two hollow beams of repump light which intersect in the the trap center. A shadow is cast in the central region of both beams by passing through a glass slide which holds circular pieces of black insulation tape of 3mm in diameter. In order to avoid diffraction at the edges, these black spots are imaged by a lens onto the position of the trap. The optical system for beam collimation and spot imaging is shown in fig.3.7. It consists of a two plano-convex lenses

⁶Numerical aperture of single mode fibre NA=0.11

⁷Theoretical saturation intensity for pure two level system



Figure 3.5: Operational trap chamber at FU Berlin femtosecond photoassociation experiments.



Figure 3.6: Trap light assembly for expansion, collimation and coupling of vertical trapping beam into vacuum chamber.

L1 and L2 and a glass slide holding the black spot. The expanding beam from the optical fibre is collimated by the lenses, the dark spot is mounted between the two lenses and imaged onto the trap by L2. With the boundary values for α , B and w, which are defined by the setup, all other parameters can be calculated. For a 1:1 imaging of the spot and b=350 the focal length of L2 is defined as f2=175 mm and with the relations

$$\tan(\alpha) = \frac{a}{b} \qquad \tan(\beta) = \frac{a}{c} = \frac{w}{2f_2} \qquad \beta = \alpha(\frac{b}{f_1} - 1) \tag{3.10}$$

we derive f1=100 mm, b=165 mm, c=254 mm and the total length of L = b + c + f2 = 594 mm.

The optical system for the repump beams is implemented in a similar manner as the trapping beams as an assembly where all elements are held in position by 4 steel rods and which is directly attached to the trap chamber (fig. 3.9). Before entering the chamber, the two collimated hollow repump beams are collinearly overlapped with the two horizontal trapping beams. This is done via large aperture polarizing beam splitters (PBS) where the trapping beams are back-reflected, as shown in fig. 3.8.



Figure 3.7: Expansion and collimation of repump beams for dark SPOT. hollow beams are created by beams casting a shadow in the beam center by passing black spots of circular pieces of insulation tape. Spots are imaged onto trap location to avoid diffraction.

3.2.4 Bright state fraction measurements

For the characterization of the dark SPOT, the distribution of trapped atoms among the two hyperfine ground states is of particular interest. It largely influences the traps properties, e.g. its density (see section 3.1) but also



Figure 3.8: Vertical plane: Repump beams pass the dark spots on glass slides which creates hollow beams. Overlap with trap light beams on polarizing beam splitter (PBS). Imaging of dark spot onto trap location avoids diffraction of repump light into trap volume. Horizontal plane: Overlapping of two hollow beams ensures dark region (no repump light) at trap location, which is fully enclosed by region with repump light.



Figure 3.9: Implementation of repump expansion, collimation and dark spot imaging system into transportable trap setup.

the photoassociation of molecules by the trapping light (see 6.4.9). The characteristic parameter for the trap here is the bright state fraction (BSF)

$$p = \frac{N_u}{N_d + N_u} \tag{3.11}$$

describing the population ratio between the upper and the lower hyperfine ground state. In our experiments we approximate p by fluorescence measurements of the dark and a fully repumped trap, where all atoms are in the F=3 state [32,74]. For optical pumping between the hyperfine ground states, additional fill-beams of repumper and depump light illuminate the dark trap volume where the atoms are kept to pump atoms out of or into the dark F=2 state. Detuning of the repumping laser from the F=2 \rightarrow F'=3 transition by 30MHz and no fill-beams results in a BSF of p=0.1 [3,74]. For larger p additional repumping light is added to the trap with the repump fill beam, smaller p is achieved by additional depumping light. For measurements of p, under conservation of the total number of atoms, the depump fill beam is blocked and the the repump fill beam is set to maximum intensity for typically 30 ms. This results in a flash of fluorescence light as shown in fig.3.10, which is detected on a photodiode.

In our BSF measurements we assume that the major contribution to the fluorescence P_d of a dark SPOT containing N atoms is due to population in the F=3:

$$P_d \simeq pN \tag{3.12}$$

Comparing this with the signal P_b from a bright trap with p=1 gives:

$$\frac{P_d}{P_b} \simeq p \tag{3.13}$$

We hereby neglect contributions by repump excitation from F=2. This overestimates the F=3 population and therefore also the BSF p. A more detailed discussion of the dark SPOT fluorescence in given in the appendix B.1.

Certainly, a better method to determine the hyperfine populations in the dark SPOT should be sensitive to exclusively one hyperfine state. This could be achieved by absorption imaging of the dark SPOT on the closed transition and comparison with absorption images of the fully repumped trap.

3.3 A mass selective detector for ultracold molecules

For the experiments on photoassociation with femtosecond laser pulses, presented in chapter 6, a novel scheme for mass selecitve detection of ultracold molecules was developed and implemented into the mobile trap setup. In most photoassociation experiments to date molecules are detected in their electronic ground state by resonant-multi-photon-ionization (REMPI) by



Figure 3.10: Fluorescence progression during repumping of a dark SPOT by fill beams: (1) Depump light off, (2) Repump light on, (3) Repump light off, (4) Depump light on. P_d and P_b indicate the fluorescence levels of the dark and the bright trap.
nanosecond laser pulses. Here, atomic and molecular ions are detected and subsequently mass selected by time-of-flight. In experiments involving photoassociation and ionization by femtosecond pulses this is not possible anymore due to the much higher pulse repetition rates. At rates of 80 Mhz the pulse repetition time of 12.5 ns is much smaller than the temporal resolution of ion detection systems (typically some hundreds of nanoseconds) resulting in a continuous signal of ions. Also at lower repetition rates of Kilohertz fs-pulse systems, time-of flight mass selection is problematic. Atomic ions strongly dominate the total ion yield and, even though their time-of-flight peaks can be well resolved, large numbers of temporally uncorrelated atomic ions where observed at all times. These occur also in the time range where molecules are expected such that no clear identification of molecular ions is possible. In the presented setup this problem is avoided by mass selection by a radio frequency quadrupole (RFQ) before ions hit the detector such that each individual count can be attributed to a specific species.

The novel ion detector is based on a commercial RFQ restgas analyzer which was modified to extract, mass analyze and detect single ions from a magneto-optical trap. For ion extraction the RFQ is equipped with a set of electrodes, held by an open structured assembly to allow optical access with the trapping beams (see fig.3.11 a.). Ions produced in the trap are accelerated towards the RFQ by a push electrode on positive voltage. An additional, ring-shaped pull electrode directs the ions towards the 4 mm RFQ entrance aperture. Simulations of the extraction fields and Rb/Rb₂ ion trajectories, using the Simion software, are shown in fig. 3.11 b. and c. The voltages in these simulations were set to of +10 V for the push and -50 V for the pull electrode. To simulate the perturbation of the extraction by external fields, a transverse field (x-direction) is also included into the simulation and causes the asymmetry of potential lines in fig.3.11 b. With the chosen voltages, ions are injected into the RFQ with 100% efficiency up to transverse fields of 0.4 V/cm.

The realization of this concept is shown in fig. 3.12. The push electrode is at a distance of 70 mm from the RFQ by 4 insulated rods. The pull electrode is in front of the RFQ and surrounds its entrance aperture. Special care has been taken to ensure that all surfaces which are in the line of sight of the ionization volume are metallic and are kept on defined potentials. The RFQ itself it left unmodified. It consists of four stainless steel rods which are connected to the RF oscillator which was supplied with the control electronics of the restgas analyzer. The rods are enclosed by a stainless steel tube shielding the radio frequency from the environment. For ion detection the RFQ was initially equipped with a Faraday cup. To attain efficient detection for single ions, the cup was replaced by a compact channeltron (Sjuts, KBL510) which is positioned at the exit aperture of the RFQ. The whole assembly is mounted on a CF63 flange which is attached to the vacuum system and also contains feedthroughs for the required voltages.



Figure 3.11: Simion simulation of ion extraction. a.) Full setup of extraction electrodes and RF quadrupole mass filter rods. b.) Ion trajectory simulation for atomic and molecular ions created in the trap area. Perturbation by external fields is simulated by transverse electric field of 0.4 V/cm. Molecular ions are guided towards detector whereas atomic ions are deflected. c.) Circular pull electrode on negative potential improves efficiency of insertion into RF mass filter in presence of transverse fields.



Figure 3.12: Realization of RF quadrupole mass filter for magneto-optical trap. Ions are inserted into mass filter by push and pull electrodes. After passing the filter ions are detected on channeltron with single ion efficiency. The full setup is held by CF63 flange which is attached to UHV chamber.S



Figure 3.13: Implementation od RF mass filter and ion extraction into trap setup.

The implementation of the RFQ assembly into the mobile MOT setup is shown in fig.3.13. The ion extraction is placed in between the magnetic quadrupole coils and surrounds the central volume where the trap is created. Trap laser beams can pass the assembly unobstructed from all three spatial directions. The channeltrons front end is on negative potential of 3 kV, its rear exit at 300 V so electrons are accelerated to the anode, which is on ground potential. The signal is then extracted via a 100 nF capacitor. Electronic single ion pulses are further processed in order to determine their detection rate. RF pickup at 1.9 MHz from the RFQ is high pass filtered before the ion signals are amplified by a Timing filter amplifier (Ortec TFA474). Analog ion pulses are then converted to digital NIM pulses by a constant fraction discriminator (CFD). A fast digital counter acquires the pulses and integrates over intervals of 100 ms. The resulting averaged count rate is then read via a GPIB connection by the data acquisition computer. In order to avoid counter triggers due to noise signal the CFD discriminator level is adjusted to transmit ion signals well above noise only. The resulting dark count rate of the system is ~ 0.1 counts/s.

A mass spectrum of ions form the ultracold gas is shown in fig. 3.14. Here, rubidium atoms and dimers were ionized from their the $5p_{3/2}$ or $5s+5p_{3/2}$ excited state by femtosecond laser pulses centered at 19700 cm⁻¹. The mass scan shows the two ion peaks which are well separation by a region where only the noise level is present. In the experiments presented in chapter 6 the precise mass filtering was one of the central features which allowed the identification of photoassociation of ultracold molecules by on femtosecond laser pulses.



Figure 3.14: Mass spectrum of ions produced in trap by 496 nm femtosecond pulses taken with RF mass filter. The peak close to 0 amu is caused by rubidium ions and arises from bad mass selection properties in this region.

Chapter 4

Production and shaping of ultrashort laser pulses

A central issue of the experiments discussed in this work is the manipulation of femtosecond laser pulses in order to control their action on ultracold atomic and molecular systems. The manipulation is carried out by decomposing the pulses into their spectral components, which are then modified in phase and amplitude. This chapter gives a review on the formalisms to describe laser pulse shaping in the frequency domain as well as the technical implementation as described in [8]. In the last section, the femtosecond laser system, which is situated in the AG Wöste at the FU Berlin is presented in more detail.

4.1 Formalism of pulse shaping

The electric field of a laser pulse may by expressed in the time or frequency domain. The spectral composition of an arbitrary laser pulse, represented by a real function E(t) can be derived by Fourier transformation (FT):

$$\tilde{E}(\omega) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} E(t) \, \mathrm{e}^{-i\omega t} \, \mathrm{d}t.$$
(4.1)

In this form the spectral electric field is, in general,¹ a complex function which fulfills $E(\omega) = E^*(-\omega)$. The real electric field in the time domain is related to the spectral field via the inverse Fourier transform:

$$E(t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \tilde{E}(\omega) e^{i\omega t} d\omega.$$
(4.2)

 $^{{}^{1}}E(\omega)$ is real if E(t) is a symmetric function

For practical purposes it is sufficient to consider the positive frequency part only and to define:

$$E^{+}(t) = \frac{1}{\sqrt{2\pi}} \int_{0}^{\infty} \tilde{E}(\omega) \mathrm{e}^{i\omega t} \mathrm{d}\omega.$$
(4.3)

$$\tilde{E}^{+}(\omega) := \begin{cases} \tilde{E}(\omega), & \omega \ge 0\\ 0, & \omega < 0 \end{cases}$$

$$(4.4)$$

$$\tilde{E}^{-}(\omega) := \tilde{E}^{+*}(-\omega).$$
(4.5)

 $E^+(t)$ and $\tilde{E}^+(t)$ are related via eqns. 4.1 and 4.2. The full expressions for the real electric field and its spectrum can be reconstructed from these and the corresponding negative frequency functions $E^-(t)$ and $E^-(\omega)$ with $E(t) = E^+(t) + E^-(t)$ and $E(\omega) = E^+(\omega) + E^-(\omega)$.

The function $E^+(t)$ is complex valued due to omitting the counter-rotating frequency part. Therefore, it corresponds to the temporal field function with is inserted into the Hamiltonian of the TDSE after the rotating wave approximation 2.19, where only co-rotating frequencies are considered. In the proceeding discussion we shall consider the electric fields in time and frequency to be fully complex such that:

$$E(t) := E^+(t)$$

$$\tilde{E}(\omega) := \tilde{E}^+(\omega).$$
(4.6)

We can express this temporal field using real functions by writing:

$$E(t) = E_0(t) \ e^{i \Phi(t)}$$
(4.7)

where $E_0(t)$ is the pulse envelope and $\Phi(t)$ describes the phase of the field. The spectral amplitude of a laser pulse is centered around a specific carrier frequency and drops quickly to zero outside the spectral width. Therefore, $\Phi(t)$ can be decomposed into a carrier frequency ω_0 and a temporal, relative phase function $\phi(t)$, such that

$$E(t) = E_0(t) e^{i\omega_0 t - i\phi(t)}$$
(4.8)

The instantaneous frequency of the oscillating electric field in the pulse is given by the temporal derivative of $\Phi(t)$:

$$\frac{d}{dt}\Phi(t) = \omega(t) = \omega_0 - \frac{d}{dt}\phi(t).$$
(4.9)

A constant time derivative $\frac{d}{dt}\phi(t)$ results in a frequency shift of the pulse carrier, whereas time-dependent derivatives imply temporal variations of $\omega(t)$



Figure 4.1: Zero dispersion compressor.

which are usually referred to as "chirps". In order to characterize the phase modulation it is useful to expand $\phi(t)$ in a Taylor series:

$$\phi(t) = a_0 + a_1(t - t_0) + \frac{1}{2}a_2(t - t_0)^2 + \dots$$
(4.10)

The coefficient a_0 defines the field's phase relative to the envelope, a_1 is the frequency shift relative to the pulse carrier frequency ω_0 and a_2 characterizes the linear frequency chirp which is a linear variation of the instantaneous frequency during the pulse.

In our experiments, the pulses are shaped in the frequency domain by a double grating 4f-pulse shaper [7, 79, 81] as shown in fig. 4.1. The pulse's spectral components are separated spatially in the shapers Fourier plane. They pass through a filter mask which modifies the frequency components in amplitude and phase with a certain spectral resolution. Similar as in the time-domain the electric field entering the pulse shaper can be decomposed into spectral amplitude and phase:

$$\tilde{E}_{in}^{+}(\omega) = \tilde{E}_{0}(\omega) \cdot e^{-i\,\varphi(\omega)} \tag{4.11}$$

where the envelope can be derived from the spectral intensity by $\tilde{E}_0(\omega) = \frac{1}{\sqrt{2\epsilon_0}}\sqrt{I(\omega)}$. The action of the dispersive filter can be expressed as a linear transform of the spectral field $\tilde{E}(\omega)$ by a complex function $\tilde{H}(\omega) = \tilde{R}(\omega) e^{-i\psi}$:

$$\tilde{E}_{out}(\omega) = \tilde{H}(\omega) \cdot \tilde{E}_{in}(\omega) \tag{4.12}$$

$$= \tilde{R}(\omega) e^{-i\psi(\omega)} \cdot \tilde{E}_0(\omega) e^{-i\varphi_0}.$$
(4.13)

 $R(\omega)$ corresponds to a pure amplitude filter, while ψ represents the phase modulation of the laser pulse. Again it is helpful to expand $\psi(\omega)$:

$$\psi(\omega) = b_0 + b_1(\omega - \omega_0) + \frac{1}{2}b_2(\omega - \omega_0)^2 + \frac{1}{6}b_3(\omega - \omega_0)^3 + \dots$$
(4.14)

In a pulse shaper setup as in fig. 4.1, the laser beam, leaving the Fourier plane, passes the second lens and grating which effectively perform the backwards Fourier transform on the pulses into the time-domain. Taking eqns. 4.3 and 4.14 the temporal output field then reads:

$$E_{out}(t) = \frac{1}{2\pi} \mathrm{e}^{-i(b_0 - \omega_0 t)} \int_0^\infty R(\omega) \tilde{E}_{in}(\omega) \mathrm{e}^{i(\omega - \omega_0)(t - b_1)} \prod_{n=1}^\infty \mathrm{e}^{-i\frac{1}{n!}b_n(\omega - \omega_0)^n} \mathrm{d}\omega.$$
(4.15)

Doing so shows the meaning of the spectral expansion coefficients: b_0 defines a general phase relative to the envelope and b_1 corresponds to a shift of the pulse in time. The coefficients $b_n = \frac{\mathrm{d}^n \psi}{\mathrm{d}\omega^n}\Big|_{\omega_0}$ for $n \ge 2$ are the chirp parameters in frequency space.

4.2 Pulse manipulation with a LCA

Femtosecond pulse shaping in the manner discussed above is implemented into the experimental setup by a zero dispersion double grating setup as in fig. 4.1. A liquid crystal array (LCA) is placed in the shapers Fourier plane and acts by performing the linear transform $H(\omega)$ on the transmitted light field. The basic working principle of an LCA is shown in fig. 4.2. The



Figure 4.2: Principle of a double layer LCA. Cooperative delay and polarization rotation allows for independent phase and amplitude shaping. Alternatively, by removing the linear polarizers, phase and polarization shaping can be performed

spectrally decomposed light field enters the LCA through a polarizer, then

passes two subsequent liquid crystal pixel masks and exits again through a polarizer oriented in the same direction as the entrance one. For the independent manipulation of phases and amplitudes, each shaper pixel consists of two layers of liquid crystals.

In the mask, each pixel can be controlled individually. The pulse shaper we used in our experiments is a CRI SLM-640, possessing 640 pixels with each 12 bit voltage resolution. The with of the pixels is 98μ m, the spectral resolution is 2.2 cm^{-1} per pixel.

If voltage is applied to a specific pixel, it becomes birefringent, therefore acting as a Pockels cell. The linearly polarization of the spectral component passing through this pixel is rotated and phase delayed. The subsequent pixel can be used to compensate for this rotation, thereby admitting full transmission, but doubling the phase lag. Alternatively, the polarization can be altered overall, therefore also attenuating the spectral component after it passed the exit polarizer. Effectively, this allows for independent control the phase and amplitude of each component. For a specific spectral component ω this can by expressed explicitly: Each of the two pixels causes a voltage dependent phase shift:

$$\Delta\phi_{1,2}(\omega) = \frac{2\pi}{\lambda_0} n(V_\omega) d, \qquad (4.16)$$

where λ_0 is the central wavelength of the pulse, $n(V_{\omega})$ is the voltage dependent birefringence and d is the length of the medium. We can now account for both the total phase lag and attenuation in terms of the components of the filter function $\tilde{H}(\omega)$:

$$\tilde{R}(\omega) = \cos((\Delta\phi_1(\omega) - \Delta\phi_2(\omega))/2)
\psi(\omega) = \Delta\phi_1(\omega) + \Delta\phi_2(\omega).$$
(4.17)

If we give the desired phase and transmission values $\psi(\omega)$ and $R(\omega)$, we can solve this to attain the phase shifts:

$$\Delta \phi_1 = \frac{\pi}{2} + \frac{\psi(\omega)}{2} + \arccos(\tilde{R}(\omega))$$

$$\Delta \phi_2 = \frac{\pi}{2} + \frac{\psi(\omega)}{2} - \arccos(\tilde{R}(\omega)).$$
(4.18)

A global phase of $\pi/2$ was added to avoid negative phase retardances. If we know the voltage dependent birefringence of the pixels, we can achieve any desired phase and amplitude of each spectral component.

The shaper can then be used to obtain any desired pulse shape in time and frequency. A fairly simple example are gaussian pulses which are modified by quadratic spectral phase. This results in a linear temporal frequency chirp with $a_2 = 1/b_2$ and an increase in pulse duration by:

$$\tau_c = \sqrt{1 + \frac{b_2^2}{\tau^4}} \tau, \tag{4.19}$$

where τ is the duration of the transform limited pulse.

The full potential of this technique, however, can be exploited in combination with closed loop optimization algorithms where complicated pulse shapes are produced with the goal to direct a quantum system into a desired final state [4, 12, 75]. Extended reviews on such experiments can be found in [8, 58, 78].

In general, the resulting spectral pulse compositions are very complicated and the temporal pulse field cannot be calculated analytically. The Fourier transform then has to be performed numerically which is done most efficiently by using FastFourierTransform (FFT) algorithms, as they are supplied by most mathematical software.

4.3 Pulsed femtosecond system

The shaped femtosecond pulse system, which we used for our experiments, is situated in the group of Ludger Wöste in the Physics Institute at the FU Berlin. The system represents a state-of-the-art setup for production and manipulation of fs pulses and was used in a number of exciting experiments [7,15,58,75].

Femtosecond pulses are created (see fig. 4.3) by passive mode-locking of a Ti:Saphire oscillator (Coherent Mira), yielding pulses of 76MHz repetition rate and energies of 10 nJ per pulse. They pass a grating based pulse stretcher and seed a regenerative Ti:Saphire amplifier (Coherent RegA 9050). Output pulse repetition rate can be varied between 10 and 300 kHz and it provides transform limited pulses of 6μ J energy and Fourier limited durations of 80 fs. For pulse shaping, the system features a zero-dispersion grating-based pulse shaper in a linear 4f configuration. In its Fourier plane a liquid crystal array (CRI SLM 640) is positioned which facilitates pulse shaping of phases and amplitudes with 2.2 cm⁻¹ resolution. A novel scheme also allows the simultaneous manipulation of the pulses amplitude, phase and polarization [58].

The Ti:Saphire oscillator operates at central wavelengths between 700 and 950 nm. Pulses at shorter wavelengths can be created by optical mixing in a non-colinear optical parametric amplifier (NOPA) [57] which allows continuous tuning of central wavelengths between 460 nm to about 650 nm with pulse energies up to 500 nJ

Experiments with shaped laser pulses can also be carried out in a closed optimization loop [4, 75] using evolutionary strategies. Here, a computer based genetic algorithm administrates a certain population of pulse shapes



Figure 4.3: Pulsed femtosecond laser, consisting of fs-oscillator, stretcher/compressor and regenerative amplifier

which are implemented by the pulse shaper. In an iterative scheme, the effect of the resulting pulses on a particular quantum system, e.g. a molecular ionization process, is optimized towards the desired result. An extensive discussion of the closed loop setup can be found in [8,77].

For the experiments presented in this work most of the described features were used in combination with ultracold molecules. Chapter 5 describes the excitation and dissociation of ultracold molecules in a closed loop coherent control experiment. The femtosecond photoassociation presented in chapter 6 was performed in a pump-probe scheme, using a sequence of a shaped photoassociation pulse and an ionization probe pulse, created in the NOPA.

Chapter 5

Coherent control of ultracold molecule excitation

This chapter reports on the excitation and dissociation of ultracold dimers by shaped femtosocond laser pulses. The experiments presented here are among the first studies [13, 64] on the interaction of ultrashort laser pulses with ultracold matter. The beginning of the chapter discusses the loss of atoms from the trap caused by femtosecond pulses. For our principle interest of photoassociation by ultrashort pulses, spectral intensity close to atomic resonances is reqired. In the interaction of such pulses with an ultracold gas we observe strong losses from the trap by light scattering forces and ionization. We show that this can be avoided by filtering narrow frequency bands containing the atomic resonances from the pulse spectra which contain the atomic resonances. The work, presented in this chapter, has been published in [64].

In this chapter, we investigate the interaction of fs pulses with ultracold molecules. Weakly bound rubidium molecules are produced in a magnetooptical trap and detected from their electronic ground state by 2 photon ionization. Excitation by femtosecond pulses leads to subsequent fragmentation or ionization and is measured as a reduction of the ground state molecule signal. An increase in excitation efficiency is demonstrated in a feedback loop experiment where evolutionary strategies are used to optimize the femtosecond pulse shape. The efficiency of the resulting pulses exceeds unshaped, transform limited pulses by a factor of 3 and is attributed to an optimal distribution of pulse energy among specific spectral components. Regarding the goal of creating large numbers of molecules in bound ground states by fs pulses, the excitation of molecules by the pulses may pose a problem as molecules are effectively destroyed by the very pulses that were used to produce them. For an efficient accumulation of molecules, pulses need to be created which specifically enhance the formation process and simultaneously suppress all unwanted effects. In an ideal experiment this might be achieved by a pulse which steers the quantum mechanical system towards a desired bound molecular state and all alternatives are avoided by destructive interference. This problem is well suited to be solved in a closed loop optimization experiment. The experiments discussed in this chapter follow this line and show that such manipulation is indeed possible.

5.1 Ultracold molecules formed by trapping light

The molecular sample, which is used for the closed loop optimization experiments, is created by photoassociative processes in the magneto-optical trap. As these molecules play a central role for the experiments presented here, their formation and detection shall be discussed in more detail. The trapping light photoassociates molecules in bound states closely below the $5s+5p_{3/2}$ asymptote from where they spontaneously decay to loosely bound vibrational states in the electronic ground state. The precise formation mechanism and final vibrational distribution are unknown, so far, however, some assumptions can be made, according to other photoassociation experiments [14, 20, 22, 43]. A likely scenario is the photoassociation via the 0_a^- or 1_u potential due to their $1/r^3$ character at long distances. From here, both the X ${}^{1}\Sigma_{a}^{-}$ and a ${}^{3}\Sigma_{u}^{+}$ potentials in the electronic ground state can be populated, according to selection rules. In particular the 0_a^- has, due to its inner turning point at comparatively large distances, good Franck-Condon overlap with the triplet ground state potential which leads to the assumption that trap light photoassociated molecules predominantly populate the ${}^{3}\Sigma_{u}^{+}$ state. Franck-Condon factors here suggest population of states with binding energies of not more than 10 cm^{-1} [43]. Earlier publications discuss three-body processes as the origin for dimer formation in the MOT [22], however this is in disagreement with the dependence of formation rates on atom density and trap light intensity as shown by Caires et al. [14]. In this paper also experimental rate coefficients are given for the dimer production, which, for our trap, predict formation rates of about 500 s^{-1} .

Detection of molecules from the electronic ground state is done by resonant two-photon ionization. The resonant intermediate states lie in the socalled diffuse bands of the rubidium dimer. In rubidium, the diffuse bands are located between 16400 to 16800 cm⁻¹ above the ground state and originate from a large number of intersecting molecular potential curves, resulting in a dense spectrum of vibrational states [56]. For the two photon ionization the intermediate states lie below the 5s+4d potential asymptote. In tentative assignments by Lozeille *et al.* [43], ionization resonances in the diffuse bands are attributed to vibrational levels in the $(2)^{3}\Pi_{g}$, $^{3}\Delta_{g}$, $^{3}\Sigma_{g}^{+}$ and $^{1}\Sigma_{g}^{+}$ potentials. Even though molecular ionization is enhanced by the resonant intermediate state, atomic ionization is still strong which requires a mass selective detection system.



Figure 5.1: Experimental setup for iterative closed-loop maximization of ultracold Rb_2 excitation from the ground electronic singlet or triplet states by shaped femtosecond laser pulses. The ultracold molecules are formed in a magneto-optically trapped gas of rubidium atoms. The laser pulse shapes represent individuals of an evolutionary algorithm. Their fitness is evaluated by the reduction of the Rb_2^+ signal resulting from resonantly enhanced photoionization of the Rb_2 molecules.

5.2 Experimental procedure

In our experimental setup (Fig. 5.1), about 10^{7-85} Rb atoms are captured in a standard magneto-optical trap (MOT) at a density of 10^{10} atoms/cm³ and temperatures of $100 \,\mu$ K. The Rb₂ molecules are detected in the electronic ground state via resonant two photon ionization and time-of-flight mass analysis. Signals from the MCP ion detector are therefor acquired by a fast digital oscilloscope (Tektronix, 500MHz bandwidth) which is read out by a computer. The data acquisition software then integrates the timeresolved ion signals in the range where molecular ions are expected. The ionization laser is a 15 Hz Nd:YAG pumped dye laser that has a spectral width of $0.5 \,\mathrm{cm}^{-1}$ and a pulse energy of 20 mJ. Rb₂⁺ molecules are observed at dye laser wavelengths between 600 and 610 nm with a maximum count rate of 0.5 molecules per pulse at 602.5 nm.

The femtosecond (fs) laser pulses are generated in a Ti:Sapphire oscillator (Tsunami; Spectra Physics) that provides pulses of 120 fs duration (FWHM) at a rate of 80 MHz, a spectral width of $\Delta \lambda = 10$ nm and an energy up to 18 nJ per pulse. Low pulse energies ensure that the laser-molecule interaction is well described in a perturbative picture and no high intensity effects have

to be considered. To modify the spectral components of the pulses we use a pulse shaper that allows independent phase and amplitude modulation [79]. It consists of a liquid crystal modulator (CRI; SLM-256) [81] with 2x128 pixels, placed in the Fourier plane of a double grating zero dispersion compressor. A lens focuses the beam to a spot of $150 \,\mu\text{m}$ diameter at the center of the trap, illuminating about 10% of the cloud volume. For the experiments the fs-laser is tuned in the range between 780 and 820 nm.

5.3 Femtosecond pulse induced trap loss

Transform-limited fs-pulses that are focused into the MOT strongly interact with the trapped atoms, as we observe through a significant decrease of MOT fluorescence. At small pulse energies, the trap loading rate outside the femtosecond beam can partly compensate for the losses in the focus, resulting in an area of reduced fluorescence predominantly where the beam is passing, whereas for high energies the trap is completely depleted. We attribute this to photon scattering from the femtosecond pulses, which causes a light force on the atoms which is directed along the fs beam and leads to trap loss. The effect is significantly stronger when the D2 atomic resonance at 12816 cm⁻¹ (780 nm) is part of the pulse spectrum than for the D1 resonance at 12578 cm⁻¹ (795 nm), reflecting the higher transition dipole moment of the D2 line.

The effect of individual frequency bands on the trap loss is investigated by scanning a narrow slit through the Fourier plane of the pulse shaper, representing a bandpass of 4.5 cm^{-1} (0.3 nm) width, as shown in fig. 5.2 a. The spectral width of the bandpass was calculated from the slit width and the resolution in the Fourier plane. Atomic loss from the trap was measured through reduction of trap fluorescence. Fig. 5.2 b. shows two data curves from such measurements: The upper curve represents the direct photodiode signal. As the filter crosses the D1 resonance, strong trap loss is observed, leading to a nearly complete depletion. The width of the fluorescence dip is with 7 cm^{-1} significantly wider than the slit width of 4.5 cm^{-1} which we attribute to saturation effects of the D1 transition by the fs beam. For higher precision in close proximity to the D1 transition, a lock-in measurement was performed on the trap fluorescence. The fs beam was shuttered using a chopper wheel and the fluorescence variation was measured by a lock-in amplifier. The lock-in data in fig.5.2 b. (lower curve) shows the modulation amplitude on the trap fluorescence as the bandpass is scanned. The measurable trap loss occurs within 10 $\rm cm^{-1}$ to both sides of the D1 resonance whereas all other frequency components show no effect on the trapped atoms.

The trap loss can be understood as a light pressure force along the fs beam direction. Singly-charged rubidium ions have been detected when the central pulse frequency was resonant with one of the atomic transitions,



Figure 5.2: a.) Spectra of laser pulses after band pass for three slit positions. Peak widths are limited by the spectrometer resolution. b.) Trap fluorescence as function of bandpass position. Spectral width of bandpass $4.5 \text{ cm}^{-1} \blacktriangle$: Photodiode signal, \bullet : Lock-in fluorescence signal of chopped fs beam



Figure 5.3: $\rm Rb_2^+$ signal as function of detection laser wavelength and femtosecond beam intensity. Black: 0 mW/cm², blue: $6\cdot10^7~\rm mW/cm^2$, red: $12\cdot10^7~\rm mW/cm^2$

indicating that resonant three-photon ionization contributes to the loss of atoms from the MOT. To study the laser pulse interaction with rubidium molecules, the atomic resonance components were removed from the pulse spectrum by a notch filter, realized by a physical block in the shaper's Fourier plane. This way atomic losses from the MOT could be reduced below the detection threshold.

5.4 Molecule dissociation by femtosecond pulses

The interaction of ultracold rubidium molecules with fs pulses is investigated as an excitation efficiency from the ground state for different fs pulse parameters. This is measured as a decrease of the molecular ion signal resulting from two photon ionization and is sensitive to the electronic ground state only. Fig. 5.3 shows scans of the detection dye laser frequency for different fs pulse energies. The variation of the ion signal reflects the change in ionization efficiency by going through different intermediate states and agrees with spectra taken by Gabbanini *et al.* [22] and Kemmann *et al.* [30]. For increasing fs pulse energies the overal signal decreases, caused by loss of ground state molecules due to excitation, ionization or fragmentation.

The rubidium dimers interact with the fs-pulses over the entire accessible range of central wavelengths from 780 nm to 820 nm. As shown in Fig. 5.4, the molecular signal decreases rapidly at small pulse energies and levels off to 25% at a pulse energy of 0.6 nJ. As only molecules in the electronic ground state are detected, the signal reduction can be attributed to excitation by



Figure 5.4: Reduction of the Rb_2^+ molecular ion signal as function of transform limited femtosecond pulse energy. The pulses have a central wavelength of 800 nm and 10 nm FWHM. The D1 atomic resonance at 795 nm is filtered out of the pulse. The ionization laser for REMPI is set to 602.6 nm.

the fs-pulses. The process can be modelled by a simple rate equation for the number of ground state molecules:

$$\frac{dN_{Mol}}{dt} = -R_{fs}N_{Mol} - R_{loss}N_{Mol} + R_{PA}N_{Atoms}^2 \tag{5.1}$$

where R_{fs} is the excitation rate by the fs-laser, R_{loss} the molecular loss rate from the detection volume and R_{PA} the production rate of molecules from trapped atoms. Assuming that R_{fs} is proportional to the fs-laser intensity I_{fs} , the steady state dependence $\left(\frac{dN_{Mol}}{dt} = 0\right)$ of N_{Mol} on this intensity is of inverse proportional character:

$$N_{Mol} \sim \frac{R_{PA} N_{At}^2}{R_{loss} + \alpha I_{fs}},\tag{5.2}$$

where α is a constant. The curve in fig. 5.4 represents a fit to the data based on this model indicating that, in this regime of pulse energies, the interaction with the molecules has the character of a one-photon excitation [6]. As discussed in section 5.1, the molecules produced by the MOT initially populate the highest levels in the $a^{3}\Sigma_{u}^{+}$ state. Due to selection rules and Franck-Condon factors, they are preferably excited to the 0_{g}^{-} and 1_{g} 5s5p_{1/2} states (see Fig. 5.6). After spontaneous decay it is very likely, due to the large number of accessible states, that the molecules will end up in the ground state outside the detection bandwidth of the REMPI dye laser, effectively leading to a reduced molecular count rate. Scans of the detection laser from 600nm to 610nm (fig. 5.3) show that this is the case for all ground state molecules accessible in this range. At high energies all molecules in the laser focus are excited or dissociated and the residual signal in Fig. 5.4 is due to molecules that did not interact with the femtosecond laser, indicated by the dashed line. This shows that most of the molecules are produced within a small volume inside the MOT, where the fs beam passes, which is consistent with the picture that they form at the MOT center where the atom number density is at its maximum [73].

5.5 Coherent control of molecule dissociation

In order to demonstrate the practical applicability of coherent control concepts to ultracold molecules, the Rb_2^+ signal acts as an input for the self-learning optimization algorithm which autonomously programs the pulse shaper in a closed loop experiment. The algorithm is based on evolution strategies and is described in detail in [7]. Because of the small molecular ion count rate and hence the low signal-to-noise ratio the signal is averaged over 128 dye laser pulses for each individual of the algorithm. To reduce the search space for the learning algorithm we chose a scheme of parametric optimization where the algorithm tries to find the optimal pulse shape under the restriction that only a few sharp spectral peaks are allowed. During an optimization these spectral peak positions, amplitudes and temporal succession (spectral phases) are altered to find the best fitting combination of frequencies. The evolutionary algorithm administrates 31 individuals, each representing the pulse shaper parameters to produce pulses consisting of not more than eleven Gaussian peaks of 7 cm⁻¹ FWHM.

The adaptive algorithm was applied to manipulate the excitation pulses with the aim of minimizing the molecular signal from the MOT. For each iteration the ion signals corresponding to the best and worst individuals are protocolled together with the mean fitness of the whole generation. As depicted in fig. 5.5 a, all three signals decrease during the optimization to about 70% of the initial value after 20 iterations. The spectra of the final best individuals of two successive runs are shown in Fig. 5.5 b display several peaks which coincide in some but not all spectral positions. The frequency span of the fs-pulse supports our assignment of excitation to the 0_g^- and $1_g 555p_{1/2}$ states (see Fig. 5.6). By comparing the excitation yield of the best individuals with transform-limited pulses of the same energy, it is observed that the optimized pulse excites the molecules on average 25% more efficiently, which demonstrates the feasibility and potential of adaptive control.

We attribute the observed excitation enhancement to an increased spectral intensity at particular molecular resonances found by the evolutionary



Figure 5.5: (a) Molecular ion signal resulting from the best, the worst and the mean individual of the population for each generation during a closed loop experiment. (b) Femtosecond laser pulse spectrum of the final best individuals of two successive optimization runs under equal conditions with similar final optimization result.



Figure 5.6: Potential curves of the rubidium dimer including spin-orbit interaction. Initially, the molecules are expected to populate the highest levels in the $a^3\Sigma_u^+$ state [22, 30]. The molecular excitation by the femtosecond pulses is indicated by the arrow. The shaded areas show the initial and final distribution of molecular vibrational states.

algorithm. Starting from a narrow band in the $a^{3}\Sigma_{\mu}^{+}$ state [22,30], molecules are excited into bound states below the D1 resonance. By shifting the peak positions, the algorithm finds transition frequencies from this band to certain vibrational states, thereby sharing the pulse energy more efficiently than a broad Gaussian pulse. The algorithm therefore has a large number of possible solutions to choose from and so the final pulse shapes after an optimization are not identical. Another possible reason for the differences in the final pulse shapes is the high noise level on the molecular signal. The algorithm may therefore converge to pulses which are of different shape but of similar fitness within the noise level. In the spectral region between 12000 and 12500 cm⁻¹, the vibrational level separation is about 10 cm⁻¹ in the $0_q^$ and 1_q 5s5p_{1/2} states, respectively. The high density of states also explains the limited potential of the optimization because the optimization factor depends on the chosen peak width, which is limited by the shaper resolution. The Franck-Condon factors may also be relevant for the excitation process since they differ for different vibronic transitions and favor particular frequencies which are enhanced in the experimentally acquired spectra. As the initial ground state population distribution in the vibrational states is not known accurately, no quantitative treatment or assignment can be made.

To conclude, we show the application of iterative adaptive control techniques to the manipulation of ultracold molecules. The minimization of the molecular signal from a rubidium magneto-optical trap results in pulse shapes that significantly excite more Rb_2 molecules than transform-limited pulses of the same energy. The resulting pulse spectra are not unambiguous because of the large number of possible optimal solutions within the experimental accuracy. For further applications of shaped fs-pulses in photoassociation experiments, the dissociative effect of the pulses has to be suppressed. On one hand, photoassociated cold molecules may be dissociated by subsequent femtosecond pulses. Therefore, photoassociated molecules have to be detected directly after their formation by increasing the repetition rate of the detection system, ideally matching the rate of the photoassociating beam. On the other hand, the excitation of ground state molecules may be coherently suppressed while enhancing the molecule formation through actively shaping the pulses.

Chapter 6

Photoassociation of ultracold molecules with shaped femtosecond pulses

The following chapter presents the first experimental realization of ultracold molecule photoassociation by shaped femtosecond laser pulses. Using a pump probe-scheme, molecules are produced in their first excited state by a shaped femtosecond pulse and are ionized for detection after a few picoseconds. Pulse shaping reduces atomic trap loss by removing atomic resonant components from the pump pulse. The photoassociation signal is accompanied by characteristic dynamics on a picosecond timescale, caused by interactions of the induced molecular dipole with transients of the shaped pump pulse. Excited state molecules, which are not directly ionized by the probe laser, decay to bound ground states from where they can be detected by a subsequent pulse pair at negative delays in the pump-probe measurements. The photoassociation step is simulated by solving the corresponding time-dependent Schödinger equation. The results reproduce the experimental data with very good accuracy and give detailed insight into the relevant processes. These experiments were designed to investigate the free-bound transition by femtosecond pulses, beeing the bottleneck for the coherent formation of ultracold molecules in their electronic ground state.

6.1 Pump-probe photoassociation - the concept

The formation and detection of molecules in the present experiment proceeds in a sequence of two laser pulses as shown in fig. 6.1. Starting from an ultracold gas of rubidium atoms in a magneto-optical dark SPOT trap, molecules are created from colliding pairs by a pump pulse. The center frequency of the pump pulse is tuned below the dissociation limit of the 5s+ $5p_{1/2}$ first electronically excited state. Femtosecond pulse shaping is applied



Figure 6.1: Scheme of pump-probe photoassociation. Formation of molecules in 1st excited state by shaped pump pulses. Transfer to molecular ion by probe pulses. Inset: Pulse shaping removes atomic resonances from pump pulses to prevent strong trap loss.

to reduce the loss of atoms from the trap due to interactions with resonant pulse components, as discussed in section 5.3. Such losses lead to strong reduction in atomic density within the laser overlap which will inhibit successful photoassociation. This effect can be limited to an acceptable level by blocking the relevant frequencies in the pump pulse spectrum with a pulse shaper. In the present case the D1 (12578 cm^{-1}) and D2 (12816 cm^{-1}) are covered by the pulse spectrum and need to be removed. Excitation by frequencies blue to atomic resonances can address anti-binding potential branches leading to radiation shielding effects which can also interfere with photoassociation. However, photoassociation requires high spectral intensity closely below the molecular dissociation limit where high excitation efficiency is provided by large Franck-Condon overlaps between initial continuum pair state and bound molecular states. The desirable pulse spectrum then has a step-like characteristic with a sharp spectral cutoff closely below the atomic D1 dissociation limit (see inset fig. 6.1). Such spectral composition is attained by applying an optical low pass filter to the pump-pulse spectrum using pulse shaping techniques.

Furthermore, we use pulse shaping to apply linear frequency chirps to the pump pulses. This is to investigate the effect of spectral phases on the free-bound transition. The benefits of linear chirps were proposed theoretically as an increased excitation efficiency due to adiabatic following [76]. Experimentally, the effect of chirped nanosecond pulses on inelastic trap loss collisions in a MOT has been investigated by Write *et al.* [86]. They observe a significant difference in the inelastic collision rates for positive and negative chirps which they attribute to the propagation of a nuclear wavepacket on an attractive potential and which causes a break in time-symmetry for the coupling to the laser field. Another experiment by Brown *et al.* [13] reports on increased excitation efficiency of ultracold molecules by chirped femtosecond pulses. All this work, and the experiments presented here, aim on the principal goal of coherently control the diatomic interaction and the efficient formation of ultracold molecules by manipulation of laser fields.

The femtosecond photoassociation experiments required some modifications on the setup as compared to the closed loop setup. The magneto-optical trap ins constantly operated in a detuned dark SPOT configuration. The density increase of one order of magnitude which raises the photoassociation rate by two orders of magnitude, due to the increase in density of pairs. The dark SPOT trap furthermore allows to distinguish femtosecond photoassociation from the ever present process of trap light photoassociation by tuning the distribution of rubidium atoms among the two hyperfine ground states.

The scheme of a pump-probe experiment was chosen to directly detect the ultracold molecules after formation in order to prevent their destruction by successive pulses as it was observed in the experiments presented in chapter 5. Ionization could be very efficiently implemented by using frequency conversion of femtosecond pulses by a NOPA 1 (see section 4.3).

The experiences in the coherent control experiments (chapter 5) showed that atomic ionization by the femtosecond pulses dominates the detected ion signal. In the pump-probe experiments described below, this problem becomes even more evident as the experimental repetition rate is increased from 10 Hz to 100 kHz. As a result the total rate of ions produced in the pump-probe experiments increases dramatically and reaches up to 200 kHz. Not only that such amounts of ions become harmful for the ion detection devices, but it also prohibits reliable identification of molecular ions by time-of-flight analysis of the detector signals. To improve the performance of the mass analysis, we use radio-frequency quadrupole mass analyzer in these experiments which is described in detail in section 3.3.

6.2 Quantum dynamical simulations

In order to gain detailed insight into the mechanisms of femtosecond photoassociation, the pump excitation was simulated in a quantum dynamical calculation of the light-molecule interaction. This is done by numerically solving the time-dependent Schrödinger equation (TDSE, eqn. 2.19) for the system of two colliding ultracold atoms and their interaction with the field of a shaped fs laser pulse which was derived in chapter 2. The corresponding Hamilton operator is given by:

$$\mathbf{H} = \begin{pmatrix} T + V_g(R) & \hbar\Omega(t) \\ -\hbar\Omega(t)^* & T + V_e(R) + \Delta \end{pmatrix}$$
(6.1)

Here, T is the kinetic energy operator, $V_g(R)$ and $V_e(R)$ are potential energy curves of ground and excited electronic states and R is the internuclear distance. The parameter Δ in eqn. 6.1 describes the frequency detuning of the pulse center frequency with respect to the 5s+5p_{1/2} asymptote. The coupling between the electronic states is given by:

$$\Omega = \frac{d}{\hbar} E_0(t), \tag{6.2}$$

where d is the transition dipole matrix element and $E_0(t)$ the complex, time-dependent electric pump-pulse field envelope. The time-dependent Schrödinger equation is solved by an numeric algorithm using a combination of a Mapped Fourier Grid Hamiltonian method and a Chebychev propagator method as described in [38] and [11]. The algorithm calculates the eigenstates for the internuclear potential curves $V_g(R)$ and $V_e(R)$ by solving the time-independent Schrödinger equation (TISE). By taking an arbitrary complex electric field and a defined initial state, the algorithm then integrates the

¹non-linear optical parametric amplifier

TDSE, thereby deriving the full nuclear dynamics on the two potential manifolds and their couplings by the light field. The two nuclear wavefunctions are finally transformed to a spacial grid for output. Wavefunctions as well as their projections of TISE eigenfunctions can be thereby derived at any desired instant of time during the interaction. For photoassociation, the initial state of the colliding ground state atoms is represented by a continuum nuclear wavefunction on the 5s+5s manifold with the kinetic energy that corresponds to the 100 μ K trap temperature. The potential curves which were used in the simulations are the ${}^{1}\Sigma_{g}^{-}$ 5s+5s for the ground and the 0_{u}^{+} 5s+5p_{1/2}for the excited state and were taken from [33, 53].

Parameters which characterize the pump-pulse spectrum, like cutoff position or arbitrary spectral phases and amplitudes enter implicitly into the simulations via the temporal complex pulse field. The function $E_0(t)$ is derived from converting the pump-pulse spectrum into the time domain via Fast-Fourier-Transform. The temporal behaviour of the cut spectrum pump pulse strongly deviates from a transform limited profile. The pulse is accompanied by long tails which reach out to a few picoseconds before and after the maximum as shown in fig.6.2 a. Within these tails, the optical field oscillates with a frequency that matches the spectral cutoff frequency (see fig.6.2). It shall be discusses below, how the specific shape of the pump pulses in time and frequency domain influences the interaction with atoms and photoassociated molecules.

The total population in bound $5s+5p_{1/2}$ state depends on the amplitude of the initial ground state continuum wavefunction at the Condon point. In order to derive excitation rates that can be compared to the experiments it is necessary to adjust the probability distribution in the ground state to fit the actual distribution of pairs in the trap. In the simulations this has not been done, therefore the $5s+5p_{1/2}$ is only accurate up to a constant scaling factor.

6.3 Experimental procedure

Our experiments on femtosecond photoassociation are carried out in a collaboration project between the Freie Universität Berlin and the University of Freiburg. The joined experimental setup consists of a shaped femtosecond laser system, situated at the Institut für Experimentalphysik at the FU Berlin, and a transportable, high density magneto-optical trap for rubidium atoms (see chapter 3), which was shipped from the Physikalische Institut Freiburg. The femtosecond laser pulses are produced by a Coherent Mira oscillator and amplified by a Coherent RegA 9050, yielding pulses of $6 \,\mu J$ energy and 80 fs FWHM at 100 kHz repetition rate. Output pulses have a spectral width of 390 cm⁻¹ FWHM and are centered around 12500 cm⁻¹ (800 nm), which is $78 \,\mathrm{cm}^{-1}$ below the dissociation limit of the first elec-



Figure 6.2: Pump pulses in the time domain are derived from Fourier transforms of the corresponding spectra. A gaussian spectrum, representing the transform limited laser pulse is multiplied by a step function to model the spectral cutoff. For transformation the Mathematica FFT algorithms is used to calculate the complex time dependent field function. The instantaneous field frequency is given by the time-derivative of the argument (= temp. phase) of this function. a. Temporal field envelope of cut spectrum pump pulse. b. Instantaneous frequency of the resulting pulse. In the pulse transients the field oscillates with the frequency at the cutoff



Shaped Femtosecond laser system

Figure 6.3: Experimental setup for pump-probe photoassociation



Figure 6.4: Measurement for calibration of cutoff detuning: Atomic resonance fluorescence increases as cutoff position is scanned across D1 resonance in pump pulse spectrum (squares). Errorfunction fit (red line) delivers position of D1 resonance and cutoff resolution of 1.8 cm^{-1}

tronically excited $5s+5p_{1/2}$ state. 10% of the laser output beam is split off to create the pump-pulse beam. The pulses pass a zero dispersion, double grating pulse shaper equipped with a liquid crystal array (LCA) (CRI, SLM 640) to manipulate spectral phases and amplitudes with a spectral resolution of $2.2 \,\mathrm{cm}^{-1}$ (see also section 4.3). Using the LCA for attenuation of spectral components on resonance with rubidium transitions proved to be insufficient as the 2% residual transmission still causes significant atom loss from the magneto-optical trap. Therefore, undesirable spectral components are removed by an additional physical block in the pulse shapers Fourier plane, which fully suppresses spectral intensity above a well determined and adjustable cutoff frequency. Such an optical low pass filter is realized by a simple razor edge (see fig. 6.3) which is mounted on a precision stage to adjust the cutoff frequency. The position of the cutoff in frequency space is determined by measuring the resonance fluorescence of rubidium atoms in the magneto-optical trap caused by the shaped pump-pulse beam. As the cutoff is scanned across an atomic resonance, the trap fluorescence steeply increases which is detected on a photodiode. An error function fit to the resulting data delivers precisely the cutoff position with a resolution of about $1.8 \, {\rm cm}^{-1}$.

Ionization probe-pulses are produced by frequency conversion of the RegA output in a non-linear optical parametric amplifier (NOPA) which uses the remaining 90% of the RegA output power. The probe-pulses are centered at 20160 cm^{-1} (496 nm) and have a spectral FWHM of 1000 cm^{-1} (25

nm), pulse energies of 50 nJ and non-transform limited durations of 600 fs. The time delay between the pump and the probe-pulses is scanned by an optical delay stage with a speed of typically 15 fs/s. Before the magneto-optical trap, both beams are spatially overlapped and focussed into the trap to waists of 150 μ m, resulting in peak intensities of 2.5 × 10⁴ MW/cm² for the pump and 1.4 × 10³ MW/cm² for the probe pulses.

The magneto-optical dark SPOT trap and the ion detection system are described in detail in chapter 3, so we only give a brief summary here. The trap captures 10^{8} 85 Rb atoms at densities of 10^{11} cm⁻³ and temperatures of $100 \,\mu$ K. Highest densities are achieved in a detuned dark SPOT configuration [3, 32, 74] when 90% of the atoms are kept in the lower F=2 hyperfine state. The trap fluorescence is continuously measure with a photodiode. Trap densities and sizes are measured by absorption imaging on a CCD camera (see B.2). Atomic and molecular ions produced in the trap are extracted by an electric field of 40 V/cm and are mass selectively detected by a RFquadrupole and a channeltron. Electronic ion signals from the channeltron are high pass filtered to remove residual quadruople RF before they are amplified and digitized by a constant fraction discriminator. Digital pulses are acquired by a fast counter and integrated over 100 ms. The noise count rate of the ion detection system is 0.1 counts/s. In the pump-probe scans, ion counts, trap fluorescence and the actual pulse delay stage are gathered by the data acquisition computer.

When the magneto-optical trap is loaded, a constant rate of about 30Hz of atomic Rb ions is detected which is caused by three photon ionization of Rb by the trapping lasers. When the femtosecond beams pass the trap and no mass filtering is applied, large total numbers of ions are detected. From the ion signal here no reliable ion production rates for atomic can be derived because the large signals saturate the detection system. From the reduction in trap fluorescence we can estimate, a loss rate of $6 \cdot 10^5 \, 1/s$ due to the ionization probe beam. The pump pulses cause, despite the blocking of the atomic resonances a loss of $2 \cdot 10^6$ atoms/s from the trap at $6 \,\mathrm{cm}^{-1}$ cutoff detuning. When the quadrupole mass filter is set to the ⁸⁵Rb₂ mass and only the ionization beam hits the trap, a molecular ion signal of typically 300-500 Hz is detected. This signal is correlated to the presence of the trapping light and vanishes if the trapping beams are switched off while a fs pulse hits the trap. We identify this Rb_2^+ signal to originate from Rb_2 molecules which are photoassociated in the $5s+5p_{3/2}$ state by the trapping light and are ionized by the fs probe-pulses. In our pump-probe experiments, this signal causes a constant background which is subtracted form the data.

6.4 Pump-probe experiments

In the following section the results of the pump-probe experiments are presented together with the corresponding quantum dynamical simulations. A detailed discussion of the molecule formation in the pump-probe experiments is given. The dynamics observed on the pump probe data is analyzed according to the calculations. Contributions of molecules photoassociated by the trap light on the pump-probe signals is estimated by investigating their formation rate depending on the trap configuration.

In the pump-probe scans the trap is subjected to both pulses. While the relative pulse delay is varied from -20 to +20 picoseconds, the molecular ion rate and the trap fluorescence are protocolled. As shown in fig. 6.5, the detected molecular ion rate in the pump- probe experiments depends strongly on the pulse delay and the pump pulses spectral cutoff detuning from the D1 potential asymptote. For negative delays, when the ionization probe pulse precedes the pump pulse, we observe a constant rate of molecular ions. At t=0 both pulses coincide in time and the count rate increases strongly, forming a peak of 1 ps width. For positive delays, a clear increase in the molecular ion signal is observed, compared to negative delays. Here, the signal is modulated by characteristic oscillations with periods of a few picoseconds and which are fully damped after a few periods. In order to extract quantitative information form the data for further analysis we take a time average of the signal at t < 0 and fit an oscillatory function to the data at t>0 to extract the average level, modulation frequency, amplitude and damping constant.

Going from top to bottom in fig. 6.5 the spectral cutoff detuning from the D1 asymptote is increased form 6 cm^{-1} to 12 cm^{-1} in steps of 2 cm⁻¹ which results in reduction of the pump-probe signal for all delays. Significant pump-probe signals are observed in the experiments only for cutoff positions closer than 20 cm⁻¹ to the D1 asymptote. Also the the modulation frequency varies characteristically as the cutoff detuning is changed: Fig. 6.6 shows that the modulation frequency always matches the cutoff detuning if both are expressed in the same units.

The simulation curves in fig. 6.5 represent the temporal progression of the total population in bound vibrational states in the $5s+5p_{1/2}$ potential while the pump pulse interacts with the system. For comparison with the data, simulation results were convoluted with the temporal width of the probe pulses. To compensate for the unknown ionization efficiency by the probe pulses and the incorrect excitation efficiency predicted by the model (see section 6.2), the calculated excited state population was adjusted by one scaling parameter to fit the pump-probe data. For positive delays the simu-


Figure 6.5: Black line: Pump-probe Rb_2^+ data for cutoff detunings of 6 cm⁻¹ (top) to 12 cm⁻¹ (bottom) from the $5s+5p_{1/2}$ asymptote. Red line: Total $5s+5p_{1/2}$ population from simulations. For comparison, simulation data is scaled and convoluted with the 600 fs probe-pulse duration



Figure 6.6: Frequencies of modulations on pump-probe ion signals at t > 0 versus cutoff position.

lations are in very good agreement with the experimental data and reproduce the variations in the signal level, modulation periods and amplitudes with good accuracy. It can be therefor concluded, that from t=0 onwards, the ion signal also reflects the population of molecules in in their first excited state. The action of the ionization pulse is then to probe this population by transfer to the molecular ionic state, thereby converting the dynamics in the total $5s+5p_{1/2}$ population into a temporal variation of the molecular ion yield. However, fig. 6.5 also shows that at negative delays, the simulations predict no population in the excited state, whereas the experiments show a clear molecular signal. It shall be seen below that signals in both time ranges are closely related which can be understood from the formation and detection processes of molecules in their electronic ground state.

6.4.1 Cutoff detuning

Fig.6.7 a. displays the variation of the time-averaged pump-probe signals with the spectral cutoff detuning which shows an increase in Rb_2^+ rate as the cutoff approaches the potential asymptote. The simulations reproduce this behavior with good accuracy, as shown by the curves in fig. 6.7 a. Molecular ion levels at positive and negative delays show similar behavior, which can be seen from their relative variation as the cutoff is changed. The inset in fig. 6.7 a. shows that the ratio of both levels is fairly constant at





Figure 6.7: a.) Pump-probe Rb_2^+ average rates versus spectral cutoff position and simulation results. \blacktriangle : Rb_2^+ at positive delays, solid line: Simulated $5s+5p_{1/2}$ population. \forall : Rb_2^+ at negative delays, Dashed line: Simulated $5s+5p_{1/2}$ population. Inset: Constant ratio of ~ 0.3 between time-averaged levels at negative and positive delays for different cutoff detunings. b.) Pump-probe Rb_2^+ average rates pump-pulse energy and simulation results. \blacktriangle : Rb_2^+ at positive delays, solid line: Simulated $5s+5p_{1/2}$ population. \forall : Rb_2^+ at negative delays, solid line: Simulated $5s+5p_{1/2}$ population. \forall : Rb_2^+ at negative delays, solid line: Simulated $5s+5p_{1/2}$ population. \forall : Rb_2^+ at negative delays, Dashed line: Simulated $5s+5p_{1/2}$ population. \forall : Rb_2^+ at negative delays, Dashed line: Simulated $5s+5p_{1/2}$ population, scaled a factor of 0.3 to model formation of ground state molecules. Inset: Constant ratio of ~ 0.3 between time-averaged levels at negative and positive delays for different pump-pulse energies

0.3.

As we saw above the signal at t>0 represents the population in the 5s5p manifold. For smaller detunings the coupling of the electronic system to the pump pulse increases, resulting in a higher excitation efficiency. In the pump-probe scans, this results in a higher ionization rate by the probe pulses. The experimental data rises steeper than predicted by the simulations. This may be due to discrepancies of the actual ground and excited state wavefunction overlaps and those used in the calculations where only transition between ${}^{1}\Sigma_{a}^{-}$ 5s5s and 0_{u}^{+} 5s5p_{1/2} are considered.

From constant ratio of ion levels at positive and negative delays (see inset fig. 6.7 a.) it can be deduced that also the signal at t<0 is related to the 5s5p population and therefore originates in the pump excitation. As a consequence, the simulated excited state populations at t>0 are able to reproduce the molecular signal at t<0 when the simulations are scaled down by the level ratio. Doing so delivers the dashed curve in fig.6.7 a. which is also in good agreement with the data.

6.4.2 Pulse energies

Fig. 6.7 b. shows the variation of the time- averaged Rb_2^+ rates as a function of pump-pulse energy. The signal levels rise strongly non-linear with the pump pulse energy for both delay ranges. This behavior is also predicted by the simulations, represented by the lines in fig.6.7 b., and indicates that the excitation into the 5s5p states is dominated by non-linear effects. The constant ration of 0.3 between the levels at both delay ranges is also observed for the energy dependence (see inset fig. 6.7 b.). In a similar manner as discussed for the cutoff detunings, the simulation here can be scaled by the ratio to fit the negative delay data.

6.4.3 Discussion: Positive delays

At positive delays, the probe succeeds the pump pulse by a few picoseconds. Collision pairs on the 5s+5s potential can be excited to bound molecular states and directly ionized. The signal from t=0 onwards represents the total population in the $5s+5p_{1/2}$ potential which is found by comparison with the corresponding simulation results.

The pump pulse creates a coherent superposition of the two electronic molecular states. When both pulses coincide in time at t=0, the coupling between these states is strongest and causes the peak in the excited state population. At later times, a significant population of pairs remains in the 5s5p state, which is ionized and detected. The modulations on the pump-probe signal and on the simulations are caused by the interaction of the induced electronic dipole with the declining pump pulse. After the pump pulse maximum the dipole continues to oscillate with its intrinsic frequency



Figure 6.8: Simulated population distribution in 0_u^+ 5s+5p_{1/2} state. The solid line displays the spectral pump pulse amplitude at the transition energy from the continuum ground state to bound excited states. Inset: Distribution in v=200 - 300 shows excitation into short range states.

and exchanges energy with the declining pump pulse field, according to their relative phase difference. This leads to a modulation in the excitation efficiency which will be discussed in more detail in section 6.4.6. The observation of the electronic dipole dynamics on the pump probe signal, however, shows the coherent character of the excitation by the pump pulse.

In the following we shall concentrate on the excitation mechanisms which lead to the detected molecular ion signal. In a simplified, perturbative model for the pump excitation, one would expect only excitation into states which lie energetically within the pulse spectrum. For the present case, this would allow the population of vibrational eigenstates only up to the transition energy that corresponds to the spectral cutoff. However, as shall be seen from the simulation, the nuclear wavefunction, created in the the 5s+5p potential, consists of bound and continuum components of nuclear eigenstates, both lying above the spectral cutoff. Fig. 6.8 displays a calculated population spectrum of vibrational states in the $5s+5p_{1/2}$ potential, resulting from the the projection of the excited state wavefunction. Vibrational states around the maximum of this population distribution at y=400 are characterized by large internuclear distances on the order on 1000 a_0 and low binding energies of about $1 \,\mathrm{GHz}$ ($0.03 \,\mathrm{cm}^{-1}$). As they lie energetically above the cutoff, their population arises from off-resonant excitation due to the high peak intensities of the pump pulses. The distribution among the states around v=400corresponds to the free-bound FCF with the initial continuum wavefunction.



Figure 6.9: Calculated wavefunctions in ground and excited state. Major contributions to pump-probe molecular ion signals due to off-resonant excitation of ground state wavefunction to weakly bound, long-range and continuum states. Ionization occurs by transfer to long range molecular ionic states by probe pulses.

Only a small fraction of the population is excited to states within the pump pulse spectrum. For a spectral cutoff detuning of -15 cm^{-1} , this population is restricted to states below v=290 (see inset fig. 6.8). Compared to the weakly bound, long range states, their population is suppressed by two orders of magnitude, due to the lower FCFs.

The total population of bound molecular states is therefore dominated by the weakly bound long range states. The characteristic variation of the total excited state population with pulse energy, cutoff detuning (see fig. 6.7) or the oscillatory dynamics in time (fig. 6.5) are due to these off-resonantly populated states.

Calculated wavefunctions on the ground and excited state potentials, at 2 ps after the pump pulse maximum, are displayed in fig. 6.9. The wavefunction consists of a tightly bound part below $60 a_0$ and of a long range, sinusoidal part which incorporates the continuum part of the wavepacket. Referring to fig. 6.8, the part below R=60 a_0 corresponds to states below v=290. The dominant fraction in the population arises from the projection of the long range, sinusoidal part onto vibrational eigenstates. The full decomposition of the excited state wavepacket, created by the pump pulse, into eigenfunctions of the 5s5p potential also incorporates continuum states. Population of these, however, cannot be regarded as a photoassociation process.

The formation of molecular ions proceeds by transfer of the excited state wavepaket to the ionic potential manifold. The range of internuclear distances for which this is possible is given by the Franck-Condon overlaps with the addressed ionic vibrational states. With the center frequency of 20160 cm^{-1} and a width of 1000 cm^{-1} about 10% of the probe pulse spectrum reaches across the ionic dissociation limit. Therefore its spectrum addresses vibrational states up to the ionic dissociation limit which provides efficient ionization from the 5s5p state also at large internuclear distances. Effectively, the pump-probe Rb_2^+ signal represents the photoassociative ionization of colliding atom pairs from their electronic ground state. This occurs by including bound, long-range and continuum states on the 5s5p manifold, which are both off-resonantly excited by the intense pump laser pulses.

In these experiments one could in principle expect to observe the propagation of a nuclear wavepacket which is created by the pump pulse and subsequently oscillates in the excited state potential. However, the vibrational time constants of the long range nuclear states that principally contribute are in the range of several hundreds of picoseconds. On the timescale of the pump probe delays of several picoseconds this part of the nuclear wavefunction is stationary and no evolution in the potential is expected.

6.4.4 Discussion: Negative delays

We showed above that the molecular ion signal at negative pulse delays is closely related to the population created by the pump pulse first excited state. At negative delays the probe- precedes the pump pulse, so any signal related to a 5s+5p excitation must be due to a previous pair of pulses. The temporal separation between pulse pairs of $10 \,\mu s$ is much longer than the 12 ns spontaneous lifetime of the $5s+5p_{1/2}$ state. Any population created by a pump pulse will have decayed before a successive pair of pulses interacts with the trap. The ionization of residual population in the excited state can therefore be excluded as the origin of the negative delay signal. However, the molecular ions detected here can be attributed to molecules in the electronic ground state. These are formed by spontaneous decay of bound excited states, previously photoassociated by a pump pulse. As discussed in the previous section, the pump pulse excitation results in a considerable population in bound vibrational states. These may either dissociate or decay to bound molecular states. Vibrational ground states are populated according to their Franck-Condon overlaps with the intermediate 5s5p vibrational state. As these are loosely bound and of long range character, ground state molecules can also be expected to populate the uppermost vibrational states in the ground state potential. In cw-photoassociation experiments [22, 43] such a process is well known and the major formation process of ultra-



Figure 6.10: Coherent population of bound ground state molecules, resulting from simulation

cold molecules in their electronic ground state. For detection, ground state molecules are excited to an intermediate state below the 5s+4d asymptote by a probe- and subsequently ionized by a pump-pulse. The ratio of 0.3 between the time-averaged levels at positive and negative delays then represents the efficiency ratio for direct pump-probe ionization and the ionization via formation of ground state molecules.

6.4.5 Coherent formation of ground state molecules

The simulations also predict the coherent formation of molecules in the electronic ground state by multi-photon processes. Compared to the population in bound excited states the production is about three orders of magnitude smaller (see fig.6.10). These molecules are formed within the pump-pulses, directly from the colliding atom pair. The distribution concentrates to the uppermost vibrational ground states with binding energies of not more than $1cm^{-1}$. In our experiments, this formation process can be expected to occur, regarding the good agreement of the simulations with other data. However, it can not be identified in the pump -probe Rb₂⁺ signals and is dominated by the signal of molecules formed by spontaneous decay.



Figure 6.11: Details of ultrafast dipole dynamics: a. Black line: Instantaneous frequency of pump-pulse. Red line: Frequency of induced dipole. b. Relative phase between dipole and light field. c. Black line: Electric field envelope of pump-pulse. Red line: Population in 0_u^+ 5s+5p_{1/2} state

6.4.6 Ultrafast molecular dipole dynamics

The oscillatory modulation on femtosecond photoassociation originates form the interaction of the molecular dipole with the transient field in the pumppulse tails. These interactions are governed by the relative phases between the induced molecular dipole and optical field as shall be discussed with fig. 6.11. Experiments showing closely related processes in the interactions of induced dipoles with femtosecond pulses have been presented recently by Monmayrant *et al.* [52].

The instantaneous frequency of the cut spectrum pump-pulse is shown by the black curve in fig. 6.11 a. Due to the spectral manipulation, the optical field oscillates with the cutoff frequency before and after the pulse maximum and dips to 12450 cm^{-1} during the pulse maximum. The red curve in fig.6.11 a. shows the frequency of the molecular dipole during the interaction with a pump pulse. During the pulse maximum at t=0, a dipole is induced, which is, at first, driven by the strong electric field and follows its oscillation. As the field declines for t > 0, also the coupling is reduced and the dipole continues to oscillate with its intrinsic frequency. We discussed in section (6.4.3), that the population in the $5s+5p_{1/2}$ state is dominated by long range states which concentrate closely below the potential asymptote. Hence, the eigenfrequency of the molecular electronic dipole is given by the mean of this distribution and is therefore only by a few Gigahertz different from the atomic D1 resonance frequency. The dipole dynamics are governed by the relative phase between dipole and field which is plotted in fig. 6.11 b. Depending on this phase difference energy is exchanged between dipole and field, resulting in an increase in dipole moment when both are oriented parallel, and decrease when they are antiparallel. The red curve in fig. 6.11 c. shows the modulation of the excited state projection of the dipole as a measure of the induced dipole amplitude. The modulation performs one period as the phase difference between dipole and field changes by 2π . In the pulse tail, the modulation occurs from a beat between dipole and field oscillating with the cutoff frequency, resulting in the coincidence shown in fig. 6.6. As the pump pulse transients decline (black curve in c.) also the interactions with the dipole abate causing the appearance of damping on the modulation amplitude and the energy exchange vanishes.

6.4.7 Atomic dipole dynamics

Also the trap fluorescence changes under variation of the pump-probe delay and shows a dependence closely related to the molecular ion signal. As shown in fig. 6.12 the ionic pump-probe signal is mirror-imaged in the trap fluorescence. The trap loss rate at t> 0 is estimated to about $4 \cdot 10^6$ atoms/s which exceeds femtosecond photoassociation signal by 3 orders of magnitude. The atomic trap loss is caused by pump-probe excitation and ionization of



Figure 6.12: [Pump-Probe signals of trap fluorescence] Pump-Probe signals of trap fluorescence (upper curve) and molecular ion rate (lower curve). Trap loss due to atomic pump-probe excitation or ionization, modulation from atomic dipole dynamics

trapped atoms. Similar to the collision pairs, single atoms are off-resonantly excited to the $5p_{1/2}$ state by the pump laser. Trap loss occurs by the subsequent probe pulse excitation. The probe pulse spectrum reaches from low lying Rydberg states at n=8 up to the ionization threshold. Atoms may either be directly ionized or excited to Rydberg states, the decay of which also results in trap loss.

The oscillatory modulations on the trap loss shows that large numbers of atoms interact with the pump pulse field via their induced electric dipole, in the same manner as discussed for the photoassociated molecules in section 6.4.6. The large loss rates of atoms as compared to the molecular ion count rates shows that atomic excitation is by far the dominant process in the trap during the pump-probe experiments. However, due to the mass selection by the RF quadrupole, the ion detection is restricted to molecular ions, which can only be formed from atom pairs in close proximity where bound molecules can be formed in the intermediate and in the ionic state.

6.4.8 Phase modulation of pump pulses

A topic of great interest in photoassociation by femtosecond pulses is the proposed possibility to coherently manipulate the process by impressing the pulses phases on the molecular quantum state. The application of linear chirps, for example, is proposed to increase the excitation efficiency of the free bound transition [34,44,68,76,86] by adiabatic transfer. Also the nuclear dynamics can be influenced as can be seen e.g. from the dependence of TISE eigenstate expansion coefficient on the field phase which was derived in eqn. 2.30. As demonstrated by Koch *et al.* [35] or Poschinger *et al.* [59] this may allow to optimize the coherent formation of bound ground states in pump-dump experiments.

In the pump-probe photoassociation experiments presented here, the nuclear wavepacket detected by the probe pulse is stationary in the examined time range. Variations on the signal due to phase modulations in the pump pulses can therefore be attributed to the electronic degree of freedom of the detected quantum state.

In the experiments presented in this section, we modify the pump pulses phases by applying quadratic spectral phase shifts in order to investigate the effect on the pump-probe signal.. Therefore, a phase pattern is written onto the LCD array in the shaper where also the spectral cut is applied. The phase pattern corresponds to a quadratic function according to eqn. 4.14 which is centered at the pulse carrier frequency and characterized by the parameter b_2 . Without the spectral cutoff, a finite value of b_2 results in a linear frequency chirp². The pulses temporal duration is increased and maximum field amplitude decreased by a factor $\sqrt{1 - \frac{b_2^2}{\tau^4}}$. The temporal field of a chirped cut spectrum pulse is derived by FFT of the corresponding complex function $E^+(\omega)$. The resulting pulses are depicted in amplitude and frequency figs. 6.13 and 6.14 for $b_2 = \pm 25000 \, \text{fs}^2$. Again, at times far from the pulse maximum, the field oscillates with the cutoff frequency. Compared to an unchirped pump pulse (fig. 6.2), the maximum in field strength is reduced by a factor of ~ 2 and its duration is increased to 1.2 ps FWHM. The spectral cutoff, in combination with the quadratic phase, causes strong distortions of amplitude and frequency behavior during the pulse (figs. 6.13 and 6.14). During the pulse, the instantaneous frequency varies strongly on a short timescale and only the time-averaged slope within $t = \pm 1$ ps shows the linear progression which corresponds to $b_2 = \pm 25000 \, \text{fs}^2$. The simulation data, using the chirped pulses, reproduce the temporal behavior of the pump-probe signal with good accuracy as shown in figs. 6.15 and 6.16. The major effect of the quadratic phases is a strong reduction of the excited state population, i.e. the molecular ion signal, both for positive and negative parameters b_2 . A progression of calculated excited state populations as a function of b_2 is plotted in fig. 6.17 showing strong suppression in the excitation for both chirp directions from for b_2 larger than ± 10000 fs². This can be expected as the off-resonant excitation of the 5s5p state discussed above, requires high peak intensities during the pulse maximum. The crosses in fig. 6.17 indicate the change in peak intensity which shows a similar behavior as the excited state population and can therefor be considered as the major cause for the

²Which is a linear variation of the instantaneous field frequency



Figure 6.13: Cut pulse with positive Figure 6.14: Cut pulse with negative chirp. $b_2 = +25000 \text{fs}^2$, cutoff -8 cm⁻¹

chirp. $b_2 = -25000 \text{fs}^2$, cutoff -8 cm⁻¹



Figure 6.15: Pump-probe and simulation for pos. chirp $b_2 = +25000 \text{fs}^2$ and cutoff -8 cm⁻¹



Figure 6.16: Pump-probe and simulation for neg. chirp $b_2 = -25000 \text{fs}^2$ and cutoff -8 cm⁻¹

signal reduction by chirps. The spectral composition of the pulses, however, is conserved as b_2 changes, so the induced electronic dipole can still interact with the same electric field after the pulse maximum passed. The oscillatory modulations caused by this interaction are therefor observable also for large values of b_2 where they only change in amplitude whereas their frequency, being defined by the cutoff, remains unchanged. The contrast between these



Figure 6.17: ■5s5p population predicted by simulations.× Peak intensity in pump pulse. Reduction of population results from decrease in peak intensity under conservation of bandwidth

results and the proposed efficiency increase by chirped pulses, e.g. in [76] arises from the fact that these proposals consider resonant³ excitation to bound levels in the free bound transitions. As discussed above this is not the case in our photoassociation experiments.

6.4.9 Competing processes

The magneto-optical trap itself produces a certain rate of molecules in the electronic ground state (see also chapter 5), which can in principle be ionized by the femtosecond pulses. The contribution of these molecules to the pump-probe signal shall be discussed in this section. Excited state molecules are photoassociated by the trapping light below the $5s+5p_{3/2}$ potential asymptote. After a lifetime of 12 ns they spontaneously decay to their electronic ground state, thereby populating the uppermost levels of the ${}^{3}\Sigma_{u}^{+}$ 5s+5s metastable state [14, 22]. For detection, these molecules are ionized in a

³within pulse spectrum



Figure 6.18: Molecules produced by trapping light, ionized from 5s+5s ground state by nanosecond dye laser pulses

resonant 2 photon excitation (REMPI) by a 10Hz pulsed dye laser tuned to 602 nm and about 10mJ pulse energy. Observed rates for molecular ions are on the order of 0.5 per pulse.

In a dark SPOT magneto-optical trap, the formation of ground state molecules by trapping light varies characteristically with the distribution of trapped atoms among their two hyperfine ground states. This distribution can be characterized by the ratio p of atoms in the upper F=3 state, which participate in the trapping cycle, and atoms in the off-resonant F=2 hyperfine state. The density of atoms varies over about one order of magnitude as p changes and reaches its maximum around p=0.1 (see section 3.1). As p is varied, the photoassociation rate changes due to its dependence on the density squared. Because of the tight bandwidth of the trapping lasers, photo association by trap light is also sensitive to the hyperfine configuration of the colliding pairs which is directly influenced by p. The formation of ground state molecules as a function of p is shown in fig. 6.18. The molecular signal is low at small p, reaches its maximum at about p=0.6 and drops again for p=1. The trap density peaks around p=0.1, so the comparatively slow rise in fig.6.18 to p=0.6 can be attributed to a photoassociation process that requires at least one of the colliding atoms to be in the F=3 hyperfine state. A similar dependence on p is observed for the signal which is caused when the ionization probe pulses alone interact with the trap laser (fig. 6.19). As explained in the experimental setup section (6.3), this signal is due to photo association by trap light below the the $5s+5p_{3/2}$ asymptote, being in the



Figure 6.19: Molecules produced by trapping light, ionized from $5s+5p_{3/2}$ excited state by femtosecond probe pulses

intermediate state before forming ground state molecules by spontaneous decay.

In contrast to trap light photoassociation, the photoassociation by femtosecond pulses can only be influenced by the trap density, i.e. when p is changed because their enormous bandwith prohibits the resolution of hyperfine effects and a significantly different behavior is found for the pump-probe signals compared to figs. 6.18 and 6.19. Fig. 6.20 shows the variation of the time-averaged Rb_2^+ rate at positive delays under variation of p. The signal shows a steep increase from p=0, reaches its maximum at about p=0.2 and drops for p approaching unity. Such behavior is similar to that of the atomic density (see section 3.1) and characterizes a process which is only sensitive to the change in density as p rises. All pump-probe data presented in this work where taken at p=0.1 where photoassociation rates by trapping light are small according to fig. 6.18 so that their contribution is, if present, of minor importance. The major fraction of the pump-probe signal can therefore be attributed to the photoassociation by the shaped femtosecond pump-pulses.

To conclude, we presented the formation of ultracold molecules by shaped femtosecond laser pulses in a pump-probe experiment. The experimental setup features a magneto-optical dark SPOT trap and a continuously operating mass selective ion detection system. Both components proved to be essential to achieve the experimental results. A molecular wavepaket is



Figure 6.20: Pump-Probe signals levels for different bright state fractions p)

formed by the pump-pulse and ionized for detection by the subsequent probe pulse. Femtosecond photoassociated molecules which are not ionized by the probe pulses, spontaneously decay to their electronic ground state. They are ionized by subsequent pulse pairs and cause the molecular ion signal at negative pulse delays. Within the pump excitation coherent dynamics of the molecular dipole are observed. They result from the periodic energy exchange of the induced electronic dipole with the electric field in the tails of the shaped pump laser pulse. Femtosecond photoassociation is verified experimentally by showing that the only alternative process of molecule formation by trapping light cannot serve as a satisfactory explanation for the observed effects. 6.4. Pump-probe experiments

Chapter 7 Conclusion and outlook

This work presents experiments on the creation and manipulation of ultracold molecules by shaped femtosecond laser pulses. They represent the first steps towards a new realm where two fruitful fields of physics are merged with the goal to efficiently form ultracold molecules in their absolute ground state by coherently controlling their internal dynamics.

In the first experiment, we successfully optimized the excitation and fragmentation of ultracold molecules in the scheme of a closed loop coherent control experiment. It shows that iterative pulse shape optimization, one of the powerful tools in the field of coherent control, is applicable to the manipulation of ultracold molecules. Complications in these experiments arise from the low signal to noise ratio, but also from the not well defined initial state and the high density of states in the region where molecules are excited to. The optimization algorithm therefore did not converge to a particular pulse shape, but to pulses with a similar excitation efficiency which is increased by a factor of three compared to transform limited pulses.

Furthermore, we learned about the interaction of femtosecond pulses and ultracold gases in magneto-optical trap where spectral pulse components on resonance with atomic transitions are identified as the source of severe trap losses. Avoiding these losses by pulse shaping techniques proved to be vital for the successes of later experiments.

We successfully photoassociated and detected excited state rubidium dimers in a pump-probe experiment and found indications for the formation of molecules in the electronic ground state by spontaneous decay. The coherent interaction between the induced molecular dipole and the electric field of the shaped photoassociation pulse causes modulations on the pump-probe signals on a picosecond time scale. The photoassociation is governed by the proximity of the molecular dissociation limit and proceeds by the non-linear, off-resonant excitation of weakly bound, long-range vibrational states which exhibit large Franck-Condon factors with the initial continuum state. Due to the long vibrational time constants of these states the excited state nuclear wavepacket shows no propagation in the attractive potential during the observed range of delays. Chirped pump-pulses result in a decreased photoassociation efficiency due to lower peak intensities and the non-linear character of the excitation.

For future experiments, the present expertise on the topic will be used to develop improved schemes for the formation and detection of ultracold molecules. A next step is to observe the propagation of nuclear wavepackets in the excited state potential. Therefore, excitation has to occur into more strongly bound states to reduce the time scales of vibrational motion, but also to avoid rapid wavepacket dispersion due to the potentials anharmonicity close to the dissociation limit. The application of adiabatic following schemes with chirped pulses will provide increased excitation efficiency [76]. This requires the resonant excitation of bound vibrational states, so offresonant excitation, as observed by excitation with cut femtosecond pulses, has to be avoided.

For pulsed photoassociation close to the dissociation limit, the use of picosecond pulses represents a promising approach [36]. Compared to femtosecond pulses, they concentrate their energy in a smaller spectral range and have lower peak intensities, which allows for better control over the addressed vibrational states close to the dissociation limit. On the other hand, pulses with 1-2 ps duration are still short enough to resolve nuclear dynamics in the range of binding energies where good free-bound FCFs are expected. In order to preserve the tools for coherent control experiments, also for the narrow bandwidth picosecond pulses, a new scheme for a pulse shaper is required which allows to manipulate the picosecond pulses with high spectral resolution and, alternatively, may be used for the manipulation of femtosecond pulses.

For the observation of nuclear wavepacket dynamics, new detection schemes need to be developed. The required temporal resolution still advises a pumpprobe scheme. For experiments with picosecond pulses, no frequency mixing unit, like a NOPA, is available, so ionization of molecules will occur in scheme of stepwise excitation by laser pulses and cw-fields to the molecular ionic state. Alternatives to ionization for the observation of wavepackets may be found by inducing inelastic collision with the laser pulses which can be detected by measuring two-body loss rates from the trap [86].

Once detailed knowledge of the nuclear dynamics in the excited state is available, we will use this in a pump-dump experiment for the coherent population of bound molecular ground states. In particular rubidium represents an interesting system for such experiments, as the specific structure of excited state potentials results in wavefunctions which are well suited for photoassociation due to their large free-bound FCFs, but also feature good Franck-Condon overlap with low lying vibrational ground states [35]. This property may allow to perform two-color pump-dump experiments, which directly produce deeply bound molecules in the electronic ground state.

Finally, we will also take advantage of the pulse-to-pulse coherence of the mode-coupled laser source. Such schemes were recently presented by E. Shapiro *et al.* [68] and propose the accumulative de-excitation of weakly bound ground state molecules by coherently adding single-pulse effects over trains of many pulses.

The technique of closed loop optimization may be used to any of the mentioned steps to increase their efficiency or to direct it towards a particular vibrational state for detection. The implementation of a pulse optimization algorithm and its combination with the femto- and picosecond pulse shaper in Freiburg is projected for this purpose.

The precise control over dynamics in nuclear and electronic degrees of freedom shall then be used to efficiently create molecules from an ultracold gas and transfer them to their lowest vibrational ground state.

Appendix A

Transportable trap system: Details

A.1 Extended cavity grating diode laser

The operation of a magneto-optical trap involves optical pumping of atoms between two atomic hyperfine states and requires stable operation of the trapping laser at a frequency a few MegaHertz below the resonance. Laser sources for this purpose are tunable single mode cw lasers which are actively stabilized to some external frequency reference ,typically to dopplerfree spectroscopy signals, to achieve stabilities of about 1 MHz. Depending on which element shall be trapped, different types of active laser media are used. For alkali elements, cost efficient semiconductor laser sources are available to date. Also Ti:Saphire lasers are used because of their high powers. For sodium and lithium cw dye lasers are used when there are no or insufficient alternatives.

For rubidium, to date there is good supply of high power semiconductor lasers as the relevant spectral range is used in important commercial applications e.g. telecommunication and CD- writers. Turn-key commercial systems of single mode lasers are a available with output powers up to 1 Watt for less than 25 000 euros and are frequently used for rubidium traps. These mostly consist of narrowband external cavity grating diode lasers, DFB or DBR diodes ¹, high output powers are achieved by injection seeding of tapered semiconductor diodes.

For matters of cost efficiency, the narrow band diode lasers for the transportable MOT are home built and consist of an external cavity diode laser (ECL) setup which is designed in Littrow configuration [62]. The laser is mounted inside a solid aluminium holder which carries the laser diode and a collimation lens (see in figs. A.1 and A.1). Opposite to the diode output is a holographic grating and a deflection mirror, both mounted in a separate

 $^{^1\}mathrm{DFB}$ = distributed feedback, DBR = distributed Bragg reflection

aluminium block, which is attached to the main holder via springs and three precision screws.

The laser diode (Sharp GH0781JA2C, 5.6 mm case, 120mW cw output power, not AR coated) itself is mounted inside a so-called collimation tube (by Thorlabs) together with the collimation lens which ensures stable and precise relative position of diode and collimation lens. The lenses aperture and focal length are adapted to the opening angles of the diode output beams. A special tool was designed which is attached to the collimation lens and which allows the optimization of its focus when the external cavity is closed by the grating. The grating is a holographic sine grating with a grating constant of 1800/mm to fulfil Littrow conditions. For good grating illumination, the diodes orientation is adjusted such that its elliptic beam profile is perpendicular to the groove orientation (i.e. polarization parallel). The laser frequency is scanned by a vertical tilt of the grating holding block, which is done by the corresponding precision screw for coarse adjustments or by a piezo crystal which is attached to the tip of this screw. The stacked piezo crystal (Piezomechanik PSt150/2x3/5) maximum stroke of 5μ m and facilitates tuning of ?? MHz per Volt in this configuration. The mirror below the grating deflects the 0th order to the laser output. Under frequency tuning, the mirror co-rotates with the grating and ensures stable beam pointing (up to small parallel shift). The whole setup is temperature stabilized by a Thorlabs temperature controller (TED200) and a Peltier element. For shielding against convection the laser is mounted in a sealed box with is bolted to the optics table.

The laser diode current is supplied by a commercial diode current controller (Thorlabs LDC2000). Before entering the diode, the current passes a small electronics board, mounted inside the laser box (see fig.A.1) which serves a number of purposes. The circuit board features components for protection of the laser diode. A choke and smoothes the diode current to prevent harmful voltage spikes. A frequent reason for laser diode destruction is false connection or high voltages. Therefore a Schottky diode is used against accidental reversed voltages and three safety diodes, in parallel with the laser diode, avoid over-voltages across the laser diode. Two parts on the platina serve for modulation of the laser current. A bias-T (MiniCircuits JEBT-4AR2GW, 4.3GHz bandwith) allows for voltage modulation up to a few tens of MegaHertz which is used to create frequency sidebands on the laser field. These sidebands are needed for the active stabilization via frequencymodulation spectroscopy. A so-called current eater is implemented on the board with a JFET- transistor for modulation of the laser current up to 1MHz. In the closed servo loop that stabilizes the laser frequency, the JFET acts as fast bipolar current source that modulates the diode current according to the P-share of the analog PID control signal. Frequency control with the grating only is band limited mechanically to about 20 Hz due to the inertia of the setup. The current-eater largely increases the bandwidth of



Figure A.1: Compact design for extended cavity grating diode laser based on precision mirror mount design. Diffraction rating is held in separate block opposite to diode output. Frequency control via rotation of grating with piezo element. Zeroth order output beam is deflected to avoid beam walk under frequency tuning. Temperature control ensures stable operating conditions



Figure A.2: Front and rear view of ECL setup. Alignment of external cavity and coarse frequency adjustment by precision screws.



Figure A.3: Front and rear view of operational ECL setup

the servo loop resulting in a reduced noise level on the laser frequency. This also results in a better performance of the loop as the shorter response time causes less failures under acoustic disturbance.

For frequency scans of the diode laser over the range of several gigahertz with the grating only, the geometry of the setup is not ideal. As the grating is rotated, frequency feedback and the change in cavity length are not synchronized which causes mode hopping [50]. This, however can be compensated for by tuning the diode current as the grating is rotated to conserve the resonance condition for the laser mode as the frequency feedback changes. For such a current feed-forward, the correct ratio between piezo voltage and current change is adjusted using an operational amplifier circuit, which varies the diode current, according to the piezo voltage via the modulation input of the LDC200. This way, single mode frequency scans over 25GHz can be achieved with this setup. A very helpful and instructive review on building ECL lasers and their properties was published by Wieman and Hollberg [83]

A.2 Frequency stabilization & FM spectroscopy

Frequency references for the stabilization of master and repump laser are taken from doppler-free frequency modulation (FM) spectroscopies in rubidium vapor cells. FM spectroscopy is chosen because it is a fairly simple technique to produce strong (~ 1 V), dispersion shaped signals which can be

directly used as input signal for a analog PID² controls. Compared dichroism locks, ³ this technique insensitive against ambient magnetic fields and other disturbances and provides high stability of the lock signals. The general technique of FM spectroscopy is described in detail in by Björklund etal. [10] and shall be only briefly discussed here. FM spectroscopy is closely related Lock-In techniques where the detected signal is only analyzed within a small spectral range which is defined by a local master oscillator. The laser beam used for spectroscopy is phase-modulated by a RF-oscillator to create sidebands on the laser spectrum. When the laser is scanned across an atomic resonance, differential absorption from the sidebands causes amplitude modulations on the laser beam with the RF-oscillator frequency. This modulation is detected by a fast photodiode and the resulting electronic RF signal is merged with the original oscillator signal in a RF mixer. After low-pass filtering, the mixer signal varies proportional to the derivative of the absorption profile, resulting in a dispersion shaped curve with the zero crossing at the atomic resonance.

A schematic of the FM spectroscopy is shown in fig. A.2 and represents the locking scheme for both grating diode lasers. The lasers are RF- modulated via the Bias-T frequency modulation input by a Hameg HM8032 (f < 20 MHz) sine generator. For resolution of rubidium hyperfine structure, the spectroscopy is configured for doppler-free detection with a double passage through the vapor cell. The amplitude modulated beam is detected on a photodiode (Hamamatsu, S1223), electronic signals are amplified by two RF amplifiers (MiniCircuits, ZFL500LN). The phase analysis of the electronic RF spectroscopy signals is done by RF mixing (MiniCircuits). After lowpass filtering, the resulting FM spectroscopy signals (see fig. A.2 directly enter an analog PID controller which is used for active frequency stabilization of the grating laser. In a closed servo loop the PID controller takes the FM spectroscopy signal as input and seeks to keep it at the zero crossing by controlling the laser frequency, thereby effectively stabilizing the laser to the atomic resonance. Working principles shall of PID controllers shall not be discussed here, details of circuits and their adjustment can be found in [65]. The PID controllers used in the experiments for master and repumper stabilization follow designs which were developed for laser cooling experiments in the group of M. Weidemüller at the MPI-K Heidelberg and the Physics Institute Freiburg. They consist of three parallel operational amplifier circuits in amplifier- (P-share), integrator (I-share) and differentiator (D-share) configuration, such that each parameter can be adjusted individually. For the frequency stabilization servo loop, the PID controls the grating position of ECL laser by tuning the piezo voltage. The PID control also provides a separate output of the p-share only, which is connected to the current-eater

²P=proportional, I= integral, D= differential

³magnetically induced dichroism close to hyperfine resonances



Figure A.4: Frequency modulation spectra of the Rb D2 line hyperfine structure. Transitions from the upper (top graph) and the lower (bottom graph) hyperfine ground states of $^{87}\rm{Rb}$ and $^{85}\rm{Rb}$



Figure A.5: Setup for frequency locking by FM spectroscopy and closed servo loop: Laser HF-modulation via Bias-T input, FM spectroscopy signal is detected by fast photodiode. Mixing with HF oscillator signal delivers analog locking signal for servo loop. Low frequency drifts are compensated via optical grating, high frequency noise is compensated via diode current.

input of the diode laser for compensation of frequencies above the bandlimit of the grating setup (see appendix A).

A.3 Magnetic quadrupole field & rubidium source

The vacuum camber to create the Rb dark SPOT was explained in detail in section 3.2. For completeness we give a brief description of the arrangements of magnetic field coils and rubidium sources.

The coils to produce the quadrupole magnetic field for the magneto-optical trap consist of Capton insulated copper wire of 2.6mm diameter which is wound around two copper coil formers. Each coilformer carries two coils of 40 turns each, an inner coil of 30 mm radius, and an outer coil of 40 mm radius. The coilformers are mounted inside vacuum to the top and bottom CF200 flanges of the vacuum chamber (fig.A.3).

In the experiments, the inner 40 windings on both formers are used to



Figure A.6: View into vacuum setup: Quadrupol field coils are held by massive copper coil formers to provide sufficient heat dissipation. Rubidium vapor to fill trap is created by current heated alkali dispensers.

produce the magnetic quadrupole, whereas the outer windings create a homogenous field to compensate the vertical components of ambient magnetic fields. In this configuration, a current of 1 A the quadrupole coils produce linear gradients of 1 G/cm along the vertical and 0.5 G/cm along the radial direction (see fig. A.3). The resistance of each of the coils is $7 \text{ m}\Omega$. With a typical operating current of 15 A the electrical power consumption of two MOT coils is 3 W which has to dissipate via the copper coil formers. During standard operation (15 A, no field switching) heating of the trap chamber by the coils occurs after several hours of operation effectively increasing the pressure to about $3 10^{-10}$ mbar which was so far considered to be tolerable. If higher powers have to be dissipated, arising from higher currents or eddy currents due to repetitive switching, the top and bottom flanges of the chamber provide cooling rings which may be flushed with cooling water.

The rubidium vapor to load the trap is produced by current heated dispenser sources (SAES Getters, Length = 25 mm (see fig. A.3). They are continuously operated at currents of 3.5 A which, in combination with trapping beam sizes and powers results in loading rates of $3 \, 10^7$ atoms per second.



Figure A.7: Magnetic quadrupole fields for 1 A current: a.) Radially in horizontal symmetry plane (z=0). b.) axially along symmetry axis (R=0)

Appendix B

Details on trap characterization

B.1 Fluorescence in a dark SPOT

The detected fluorescence signal P, is at any time, proportional to the population in the excited hyperfine states which are addressed by the laser fields 3.2:

$$P \sim \Gamma \left(N_{F'=4} + N_{F'=3} + N_{F'=2} \right) \tag{B.1}$$

where Γ is the excited state spontaneous decay rate.

Fluorescence form the F'=4 state is caused by absorption from the traplight. The steady state population of the F'=4 state can be approximated by a two level formalism [51]. With the trap laser intensity of 18 mW cm^2 and 3Γ detuning this gives a saturation parameter of

$$S_{3 \to 4} = \frac{S_0}{1 + \frac{4\delta^2}{\Gamma^2}} = 0.3 \tag{B.2}$$

which corresponds to a excitation of

$$\rho_{22}^{\prime 4} = \frac{S_{3 \to \prime 4}}{2(1 + S_{3 \to \prime 4})} = 0.11 \tag{B.3}$$

and trap light scattering rate per atom of

$$R = \rho_{22}^{\prime 4} \Gamma = 4.4 \ 10^6 1/s \tag{B.4}$$

The F'=3 state is populated by off-resonant excitation by trap light and by repump light from the F=2 state. Compared to the trapping transition, this is suppressed by the larger detuning of $\delta_{F'=3} \approx 17\Gamma$. The relative excitation rate can be estimated by

$$R_{off} \approx \frac{\delta_{F'=3}^2}{\delta_{F'=4}^2} R = 0.03R = 1.3 \ 10^5 1/s \tag{B.5}$$



Figure B.1: Collimation of absorption beam after optical fibre. 2σ waist after lens is 8.8 mm, beam is clipped to 10 mm diameter by quatre-waveplate

Fluorescence from the F'=3, due to excitation by repump light, depends on the population in the F=2 state and can be considerable. In a steady state, the repumper compensates the off-resonant excitation rate, so the excitation rate is on the order of R_{off} or less. However, when the trap is repumped by an intense flash of the fill beam as in fig.3.10, up to 99% of the atoms are transferred via the F'=3 state which strongly contributes to the fluorescence as long as the F=2 population is depleted.

Also the depuming process causes fluorescence by population of the F'=2 state. Typical depumper intensities are below $1 \,\mathrm{mW/cm^2}$ which is much weaker than the trap light, however, as the depumper is on resonance with the transition the excitation probabilities can be comparable. In our measurements, this effects the BSF measurements of so-called forced dark SPOT with p< 0.1, as only here the depumper is used to actively depopulate the F=3 state.

B.2 Absorption imaging of the dark SPOT

Measurement of the traps atom numbers and densities was done by absorption imaging of the trap on a CCD camera.

The absorption beam is created by collimating the output beam to a diameter of 10 mm as shown in fig. B.2. After picture of the trap is imaged by a 4-f setup onto a CCD camera (fig.B.2). Taking absorption pictures has to follow a precise temporal procedure for switching of lasers and magnetic fields which is done in a computer controlled sequence using LabView and a hardware programable I/O-card (NiDAQ M6259) which processes defined sequences for a number of digital channels (fig. B.2). As the imaging occurs on the closed $F=3\rightarrow F'=4$ transition, all atoms in the dark SPOT have to be transferred to the upper hyperfine state by the repump fill beam before the absorption beam passes.

In the limit of small intensities (no saturation) absorption from a gaussian



Figure B.2: Imaging system for absorption measurements on trap with CCD camera



Figure B.3: Timing scheme for absorption imaging. Sequence starts at t=0, times in ms

shaped beam after passing a cloud of atoms is derived from Lambert-Beers' law:

$$I(x,y) = I_0(x,y) \cdot \exp\left(-\sigma_{\rm abs}(\omega) \int n(x,y,z) dz\right),\tag{B.6}$$

where $I_0(x, y)$ is the intensity distribution of the absorption beam, which is considered to be Gaussian:

$$I_0(x,y) = I_{\max} \exp\left(-\frac{(x-x_0)^2}{2\sigma_{\text{beam},x}^2}\right) \exp\left(-\frac{(y-y_0)^2}{2\sigma_{\text{beam},y}^2}\right)$$
(B.7)

For the MOT we assume a 3-dimensional density distribution:

$$n(x, y, z) = n_0 \cdot exp\left(-\frac{x^2}{2\sigma_{MOT,x}^2} - \frac{y^2}{2\sigma_{MOT,y}^2} - \frac{z^2}{2\sigma_{MOT,z}^2}\right)$$
(B.8)

The absorption cross section in eqn. B.6 is frequency dependent and, for the closed transition F=3, $m_F=3\rightarrow F'=4, m'_F=4$ can be approximated by the Two level formalism, giving:

$$\sigma(\omega) = \frac{\sigma_0}{1 + 4\left(\delta/\Gamma\right) + I/I_{sat}}, \ \sigma_0 = \frac{\hbar\omega\Gamma}{2I_{sat}} \tag{B.9}$$

After integration along the beam direction through the cloud, the absorption of the atomic cloud is given by

$$I(x,y) = I_0(x,y) \cdot \exp\left[-n_0 \cdot \sqrt{2\pi} \cdot \sigma_{abs}(\omega) \cdot \sigma_z \cdot \exp\left(-\frac{x^2}{2\sigma_{MOT,x}^2} - \frac{y^2}{2\sigma_{MOT,y}^2}\right)\right]$$
(B.10)

For analysis and fitting of absorption images it is useful to take the logarithm of eqn. (B.10):

$$\ln \frac{I}{I_0} = -n_0 \cdot \sqrt{2\pi} \cdot \sigma_{\rm abs}(\omega) \cdot \sigma_z \cdot \exp\left(-\frac{x^2}{2\sigma_{MOT,x}^2} - \frac{y^2}{2\sigma_{MOT,y}^2}\right).$$
(B.11)

In the absorption measurements at least three pictures have to be acquired:

- Absorption image: Image of absorption beam with MOT to acquire I(x, y)
- Flatfield image: Image of absorption beam without MOT (e.g. magnetic field turned off) to obtain $I_0(x, y)$
- Background image: Image without absorption beam or MOT.
To derive the trap density n_0 from the pictures eqn. B.11 can be fitted to a logarithmic image which is calculated from:

$$LogImage = ln\left(\frac{pic_{Absorption} - pic_{Background}}{pic_{Fflatfield} - pic_{Background}}\right)$$
(B.12)

Another method to obtain the density in a MOT are detuning scans of the absorption laser. In this case a whole sequence of pictures is taken, each with a different detuning for the absorption beam. The detuning is scanned across the atomic resonance and for each picture the absorption maximum in the center of the cloud is measured. Plotting the absorption maximum against the detuning, the theoretical expectation deduced in (B.11) and (B.9) can be used to fit the data:

$$I(\delta) = I_0 \exp\left(-\sqrt{2\pi}\,\sigma_{MOT,z}\,n_0\,\sigma_{\rm abs}(\omega_0)\frac{1}{1+4\left(\frac{\delta}{\Gamma}\right)^2}\right).\tag{B.13}$$

The images for each detuning also have to be background subtracted and normalized by a flatfield. After taking the logarithm, the pixel values at the trap center can be fitted by:

$$\ln\left(\frac{I(\delta)}{I_0}\right) = \left(-\sqrt{2\pi}\,\sigma_{MOT,z}\,n_0\,\sigma_{\rm abs}(\omega_0)\frac{1}{1+4\left(\frac{\delta}{\Gamma}\right)^2}\right) \tag{B.14}$$

This technique does not necessarily require a CCD camera as the peak density in the trap center can also be measured by a focussed absorption beam and a photodiode.

The whole procedure of taking absorption images is very accident-sensitive. Especially the timing of the switching of the several components is very crucial. The last density measurements were performed at the fs-laboratory of the group of Prof. Wöste at the Freie Universität Berlin. During this measurements severe problems concerning the acquisition of background pictures occurred. As usual the absorption beam was blocked with the EOM, but the additional shutter was missing. This lead to a leakage of the absorption beam of $\approx 2\%$, causing a significant signal integrated over the exposure time on the CCD chip.

Another problem with the missing shutter is, that the background measurments become very sensitive to fluctuations of the transmitted absorption beam, resulting in a large number of corrupted data sets. Only for a bright MOT with p=1 data quality was sufficient to produce reliable 2 dimensional fits to the images. A detailed analysis of the density measurements presented here, together with an extended theoretical discussion of absorption imaging can be found in a Diploma theses by Magnus Albert [1,2].

For density measurements of a bright MOT six divided and background subtracted pictures were evaluated. Due to insufficient flat field normalization a model had to be used for the 2D fitting which incorporates the absorption beam profile. The results of the six fits are comparable and lead to a mean peak density of $n = (1.9 \pm 1.0) \cdot 10^{10}$.





Figure B.4: x-cross-section through Figure B.5: y-cross-section through the centre of the atomic cloud.



the centre of the atomic cloud.



Figure B.6: Absorption image, Figure B.7: 2D-fit to the absorption smoothed with 9x9 median filter. data.

Density measurements for the configurations of a detuned and a forced dark SPOT with p=0.1 and p=0.01 respectively, densities were derived from detuning scan measurements. These measurements suffer from strong drifts in the background signal. The background subtracted pictures therefore exhibit pixelvalues below zero. For analysis, we assume that the trap optically dense on resonance, set the pixel values here to zero and shift the absorption data for other detunings according to this level. The data for measurements on the detuned dark SPOT are presented in figs. B.8-B.11. For the peak density we get $n_0 = (1.4 \pm 0.7) \cdot 10^{11} \text{ cm}^{-3}$. A similar procedure was applied to the data for the forced dark SPOT at p=0.01 gives values for the peak density of $n_0 = (5.5 \pm 2.8) \cdot 10^{10} \text{ cm}^{-3}$. The data resulting from the detuning scans are collected in figs. B.12-B.15.

In figs. B.16 the results of the absorption measurements at different BSFs are collected. For the three measurements the trap density peaks for p=0.1, in agreement with the measurements by Townsend *et al.* [74]. The total number of atoms drops strongly as p in increased. This is caused by light assisted two-body collisions in the trap (see Anderson *et al.*) which effectively limit the size of large traps. The collision loss is induced by the trap light and its rate coefficient therefore rises as more atoms participate in the trapping cycle.





Figure B.8: Detuning scan for the de- Figure B.9: Centre of cloud, detuned tuned dark SPOT. The rescaling fac- dark SPOT. The Centre was chosen tor was utilized as a fitting parame- interactivly. ter.



Figure B.10: x-cross-section detuned Figure B.11: y-cross-section detuned dark SPOT. The values were chosen dark SPOT interactivly (background value with uncertainty, centre value with uncertainty, left and right postion of FWHM).







Figure B.12: Detuning scan for the Figure B.13: Centre of cloud, forced forced dark SPOT. The rescaling fac- dark SPOT. The centre was chosen tor was utilized as a fitting parame- interactivly with the mouse from the ter.



plot. Y cross sections Y=532



Figure B.14: x-cross-section forced Figure B.15: y-cross-section forced dark SPOT. The values were chosen dark SPOT interactivly (background value with uncertainty, centre value with uncertainty, left and right postion of FWHM).



Figure B.16: Variation of trap density (a.) atom number(b.) and sigma radius (c.) under variation of BSF parameter p.

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