Control of atoms and molecules with shaped broadband pulses

by

Sergey Zhdanovich

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Abstract

The main goal of this PhD work is an experimental study of coherent excitation of atomic and molecular wavepackets, i.e. superpositions of many quantum eigenstates, by shaped femtosecond pulses. Approaches allowing nearly complete population transfer between quantum eigenstates were well studied in the past within the two level approximation. In this work we focus on adiabatic and non-adiabatic methods of population transfer beyond the two-level approximation. Excitation of multi-level target states is possible due to broad spectrum of an ultrashort pulse which contains frequencies needed for multiple transitions to different states in the final superposition. At the same time, the spectrum of an ultrashort pulse can be modified, or “shaped”, in order to affect the excitation process and control the amplitudes in the final superposition. Both non-adiabatic and quasi-adiabatic methods were first implemented and studied in electronic wavepackets in alkali atoms. The non-adiabatic approach revealed features linked to the strong-field perturbations of the energy level structure of the quantum system. An adiabatic method was implemented for the first time on a femtosecond time scale, and was thoroughly characterized. The control over complex amplitudes in the target superposition was demonstrated as well as completeness of the population transfer. In the second part of this work, we focused on coherent control of rotational wavepackets in diatomic molecules. Rotational excitation by a periodic train of femtosecond pulses was investigated in the context of “δ-kicked” rotor - a paradigm system for studying quantum chaos, and the effect of quantum resonance was demonstrated for the first time in a system of true quantum rotors.

Control of uni-directional molecular rotation was proposed and demonstrated with a novel “chiral pulse train” - a sequence of femtosecond pulses with polar-
ization rotating from pulse to pulse by a predefined angle. All the developed tech-
niques offer new tools in coherent control of atomic and molecular wavepackets on
an ultrashort time scale.
Preface

In the course of my Ph.D. work, I coauthored the following papers published in refereed journals:


In Papers 1, 2, 3 and 5 (numbers from the list above), I contributed by designing and building the experimental setup, collecting and analyzing experimental data,
and participating in writing up the manuscripts.

In Paper 4, I also suggested the main conceptual idea of the experiment.
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Glossary

AP       Adiabatic Passage
BBO      Barium Borate
CCD      Charge-Coupled Device
FROG     Frequency Resolved Optical Gating
FWHM     Full Width at Half Maximum
MCP      Micro Channel Plate Detector
MIIPS    Multiphoton Intrapulse Interference Phase Scan
OPA      Optical Parametric Amplifier
PAP      Piecewise Adiabatic Passage
RAP      Rapid Adiabatic Passage
REMPI    Resonance Enhanced Multi-Photon Ionization
RGA      Regenerative Amplifier
RWA      Rotating Wave Approximation
SH       Second Harmonic
SLM      Spatial Light Modulator
STIRAP   Stimulated Raman Adiabatic Passage
TL  Transform Limited

TOF  Time-of-Flight Apparatus
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Chapter 1

Introduction

1.1 Motivation for the development of excitation schemes with broadband shaped pulses

In 1917 Einstein postulated [47] that an atom interacts with radiation resonant with a Bohr transition frequency. As the result of the interaction, the atom may absorb or emit a photon and undergo the transition up or down respectively. This phenomena opens opportunity to study atomic energy structure, leading to the development of numerous spectroscopic applications. After the emergence of quantum theory, studies of Rabi [120] refined understanding of interaction between light and matter, paving the way for atomic wavefunction control with coherent electromagnetic field, now known as Coherent Control [135]. The term control implies the ability to transfer population between the states preserving the relative phase or modifying the phase at will. Parameters of the driving field, such as field strength, instantaneous frequency and polarization, each being a function of time, can be designed to guide the system to the target state via the desired path. After the invention of the laser, continuous efforts were devoted to the development of applications based on such control in physics, chemistry and many other branches of science and technology.

Nuclear magnetic resonance technique [120], design of atomic clocks [42] and fault tolerant quantum computing schemes [110] require reliable methods of control of two selected quantum states, usually the ground and one of the excited states.
of a real atom. The two-level approximation [2], in which only two states of interest are taken into account, is well suited and widely employed for theoretical studies. Dynamics of a two-level atom interacting with coherent light is well understood allowing design and experimental realization of efficient control schemes for a plain two-level atom [2]. Schemes involving an intermediate state or states were also explored [15, 20, 44].

At the same time, many applications require more complicated control with the target state being a coherent superposition of several exited states. For example, preparing a superposition or a wavepacket of vibrational states is essential for many spectroscopic techniques allowing the study of molecular vibrations [41, 143], defining the outcome of chemical reactions [23, 71, 79, 147] and used in the schemes of coherent control [135]. Another example is a superposition of rotational states used for controlling chemical reactions [135, 141], deflection of neutral molecules by external fields [58, 119, 142], enhancing high harmonic generation [66, 165], and controlling molecular collisions with atoms [151] and surfaces [62, 83, 137, 149, 182]. Preparation of a wavepacket is the subject of ongoing and active research [10, 24, 31, 109, 174, 180]. **Novel methods of quantum state preparation in multilevel systems is the main focus of this work.**

The big diversity of quantum systems as well as the large number of applications do not allow for a single universal method of control but dictate the necessity of different population transfer techniques, to which new methods are constantly added. Energy separation between the states in the system and the selection rules for the transitions, are the factors defining the possible population transfer techniques. Selection rules may not allow an electric dipole transition between the initial state and the target state, or the transition frequency may lie beyond the laser tunability region. In these cases, multi-photon transitions, i.e. transitions induced by simultaneous absorption and emission of several photons, can be used [33, 46]. Fig.1.1 shows three examples. Panel (a) shows a system with one ground state and several excited states. It is assumed that the selection rules allow for a one-photon transition between the ground state and any of the excited states. This is often the case for the transitions between different electronic states of an atom or a molecule. A transition can be executed with a monochromatic light source and a coherent superposition of excited states can be obtained with a number of light sources with
Figure 1.1: Examples of quantum systems and excitation methods. Dipole transitions between the ground and excited electronic states of an atom or a molecule are allowed, and a coherent superposition can be excited by several photons with resonant frequencies (a). Manipulation with vibrational energy levels of a molecule using Raman excitation with pump and Stokes laser fields (b). Ladder climbing process can be used to excite high rotational levels of a diatomic molecule (c).
be controlled by changing the laser pulse parameters \cite{23,71,147}. There are three main different strategies of finding the optimal control field. Brumer and Shapiro \cite{135} consider the interference of different optical transitions as the mechanism of control. The field should provide more than one way from the initial to each of the target states. If the paths interfere constructively for one of the reaction channels and destructively for the other, the reaction goes preferably towards the former product. The analysis is more natural to carry out in the frequency domain, and the goal is to find an optimal spectrum of the field. An alternative approach was taken by Tannor and Rice \cite{147}, who considered molecular fragmentation with a pair of laser pulses separated by a variable time interval. The first pulse creates a wavepacket in the excited electronic state. The wavepacket evolves in time, changing the Frank-Condon overlap with each of the reaction channels. At some later time, the second pulse causes stimulated emission and brings the system to a fragmented state. The probability of each reaction channel depends on the corresponding Frank-Condon factor and by choosing the proper time delay for the second pulse, one can maximize the yield of one of the products. The two approaches require detailed knowledge about the molecule for optimizing the driving field parameters. In contrast, Rabitz proposed \cite{71} the use of learning algorithms for finding the optimal field. The field is changed in an adaptive fashion while measuring the desired product yield. Employing genetic learning algorithm, the optimal field is usually found after several iterations. All three scenarios enjoyed numerous successful experimental realizations \cite{4,7,11,12,29,30,112,116,166}. This work is based on the first two approaches to Coherent Control, in which the control field is derived from the apriori knowledge about the quantum system of interest \cite{23,147}.

Fig.1.1 illustrates that control of multilevel systems requires photons of several different energies or, equivalently, electromagnetic waves of different frequencies. In order to preserve the coherence of a quantum system, the phases of the waves have to be well defined. This can be possible if all the photons are originated from a single laser pulse. Though the carrier frequency of a laser pulse is constant and well defined, the spectrum can be quite broad. An ultrashort pulse, or pulse of sub-picosecond ($10^{-15} - 10^{-13}$ sec) duration has a bandwidth comparable to the energy level spacing in many real quantum systems. In the time domain picture, it means
that this pulse is shorter than the characteristic time scale of the relevant molecular motion [37, 183]. In the frequency domain, broad spectrum implies the presence of photons of different colors allowing to execute several different transitions simultaneously [20, 69]. In the context of this dissertation, it is useful to compare the spacing for some particular molecules and the bandwidths of available laser pulses. For example, a pulse of duration of 150 fs with a central wavelength of 800 nm has a FWHM bandwidth of 140 wavenumbers. In comparison, the energy spacing between the vibrational states of iodine molecule is of the order of 200 wavenumbers, hence at least two of them lay within the bandwidth of a two-photon field of two 150 fs pulses. Another example is the hyperfine structure of Potassium 4P states. Separated by 3.5 nm (60 wavenumbers) at 768 nm, these two states can be populated from the ground state with a single 150 fs pulse since $4S \rightarrow 4P$ transition is dipole allowed. Therefore, both quantum systems can be controlled by a single 150 fs pulse. Laser sources with sub-picosecond pulse duration are commercially available, for example Titanium:Sapphire lasers and amplifiers provide laser pulses tunable within the range of 750-850 nm and with a pulse duration as short as 5 fs.

If the transitions of interest do not fall in the tunability range of the available laser, several techniques are available to extend this range. Optical parametric amplification enables one to tune ultrafast laser frequency from UV to far infrared.

The approach adopted in this work relies on controlling the target quantum state by tailoring the driving pulse spectrum. The spectral amplitude of a typical transform-limited (TL) pulse is close to a Gaussian, while the spectral phase is a linear function of frequency. These can be altered with the technique known as pulse shaping [167], which will be described in detail later in this Dissertation. Shaped pulses can be characterized by a number of pulse diagnostics methods such as FROG [157], spectral interferometry [175] and MIIPS [96]. Invented in early 1990’s, pulse shaping has become a versatile and powerful tool in experimental laser physics and chemistry [4, 97, 102, 171]. Control of the excitation field provided by the pulse shaping technique allows practical realization of many Coherent Control scenarios. This study aims at atomic and molecular control with shaped broadband pulses.

Use of ultrashort pulses as the tool to control atomic and molecular systems is attractive not only because of the great flexibility of pulse shaping, but also because
of its potential to avoid the decoherence effects found in virtually any quantum system. While spontaneous emission of an atom from an exited electronic state can take a few nanosecond, collisional decoherence in a liquid or dense gas sample can be of the order of a few picoseconds. If the excitation pulses are much shorter than the decoherence time scale, these effects can be safely neglected, facilitating theoretical investigation and interpretation of the experimental results.

For a spectroscopic technique it is usually enough to excite a small fraction of the molecular ensemble to the upper level of interest \[114, 115\]. In contrast, successful realization of a qubit gate would require a complete population transfer with high fidelity \[14, 110\]. In the first case, a quantum state preparation method developed using perturbation theory adequately describes the interaction. For a one-photon transition, the fraction of the transferred population is proportional to the amplitude of the resonant spectral component. This resembles the result of Einstein’s analysis and indicates that the quantum system interacts with photons of only one frequency. In this perturbative approximation, deriving analytical solution is often possible and this approach is well developed for many practical applications in spectroscopy, studies in nonlinear optics, and many proof-of-principle experiments in coherent control of chemical reactions \[17, 27, 111, 135\].

If a significant part of the population has to be transferred, perturbation theory is inapplicable and a different approach is required \[32, 46, 69, 70, 154\]. Only the simplest cases are analytically solvable and numerical integration of the time dependent Schrödinger equation is usually employed for theoretical studies, especially for multi-state systems. This work deals with a non-perturbative regime of excitation when significant part of population is transferred.

The semiclassical approach, in which an atom is treated as a quantum object interacting with a classical electro-magnetic field, is sufficient to model all phenomena studied here and is used throughout the study.

Coherent population transfer can be executed via adiabatic and non-adiabatic routes \[2, 136\]. During the interaction with the field, the eigenstates of the system are perturbed, and the states which diagonalize the time-dependent Hamiltonian are often referred as dressed sates or quasi-eigenstates. If the system stays in the same dressed state throughout the interaction the process is called adiabatic, and non-adiabatic otherwise. In the non-adiabatic case, the population oscillates be-
tween the ground and excited bare states with Rabi frequency proportional to the electric field strength and the dipole matrix element between the two states. The pulse duration and the light intensity can be adjusted to control the fraction of the transferred population. The same method can be utilized also for transferring population in multi-level systems. Using multiple frequencies resonant with the target states one can induce synchronous oscillations between the exited superposition and the ground state [56]. This phenomena were observed and studied in this work.

Non-adiabatic methods are known to be very sensitive to the laser parameters such as intensity and frequency. Sometimes, for example in quantum information processing, this sensitivity is detrimental and should be avoided by using composite pulse sequences [93, 153] or adiabatic methods [84, 100, 101, 163]. The adiabatic methods are based on an adiabatic evolution of a quantum system from the initial to the final state induced by specially designed laser fields. As described later in this Dissertation, laser pulses required for an adiabatic population transfer can be produced using the pulse shaping technique. This work is an experimental study of both non-adiabatic and adiabatic methods applied to single-photon electronic excitation [131] and multi-photon rotational ladder climbing [91].

1.2 Coherent population transfer

Since the original work of Rabi [120], coherent excitation of quantum systems was thoroughly studied. Many techniques of population transfer were proposed and realized experimentally. In this section we briefly review the theory of coherent population transfer in two-level approximation, considering two special cases of non-adiabatic and adiabatic population transfer. We mainly follow [2, 40, 163]. We then proceed by reviewing experimental work on coherent wavepacket excitation and detection. The theory of a novel method of Piecewise Adiabatic Passage which is behind this experimental work will be considered at the end of this Section.

1.2.1 Coherent population transfer in two-level systems

Let us consider a two-level system interacting with a pulse of nearly resonant light. The system is depicted in Fig. 1.2. It consists of the ground state $|i\rangle$ and the excited
state $|f\rangle$. The energies of the states are the eigenvalues of the system Hamiltonian, defined as:

$$ H_s|i\rangle = E_i|i\rangle $$
$$ H_s|f\rangle = E_f|f\rangle. \tag{1.1} $$

A general state of the system is a superposition of the two states:

$$ \psi(t) = a_i(t)|i\rangle e^{-iE_i\hat{t}/\hbar} + a_f(t)|f\rangle e^{-iE_f\hat{t}/\hbar}, \tag{1.2} $$

where $a_i$ and $a_f$ are complex amplitudes. The transition frequency is defined as:

$$ \omega_{fi} = \frac{E_f - E_i}{\hbar}. \tag{1.3} $$

The system is interacting with a pulse of light:

$$ \vec{E}(t) = \hat{\epsilon} E_0 f(t) \cos[\omega(t)t], \tag{1.4} $$

where $f(t)$ is a real, slowly varying electric field envelope, $E_0$ is the electric field strength and $\omega$ is the laser frequency, which is a real function of time. $\hat{\epsilon}$ is the vector of light polarization. Since a typical atom is much smaller than a typical wavelength, the electric dipole approximation can be used.

The interaction Hamiltonian in the dipole approximation [40] is written as:

$$ V(t) = -e\vec{r} \cdot \vec{E}(t), \tag{1.5} $$

where $e$ is the electron charge.
The system evolves according to the Schrödinger equation:

\[ (H_s + V(t)) \psi(t) = i\hbar \frac{\partial \psi(t)}{\partial t}. \]  \hspace{1cm} (1.6)

We can define the dipole matrix element:

\[ d = -e \langle i | \hat{\epsilon} \cdot \vec{r} | f \rangle, \]  \hspace{1cm} (1.7)

the Rabi frequency:

\[ \Omega = \frac{d |\vec{E}(t)|}{\hbar}, \]  \hspace{1cm} (1.8)

the detuning:

\[ \Delta = \omega_f - \omega, \]  \hspace{1cm} (1.9)

and, finally, introduce the Rotating Wave Approximation (RWA) [40]. In RWA all terms with \( \exp(i [\omega_f + \omega] t) \) in Eq.\( 1.6 \) are neglected as oscillating much faster than any relevant time scale, while the terms with \( \exp(i [\omega_f - \omega] t) \) are kept. In this work Rabi frequency was always much lower than the optical frequency, which justified the use of RWA. The Schrödinger equation under RWA results in the following set of equations:

\[ \frac{\partial a_i}{\partial t} = -i \Omega(t) a_t e^{-i\Delta t}, \]
\[ \frac{\partial a_t}{\partial t} = -i \Omega'(t) a_i e^{i\Delta t}. \]  \hspace{1cm} (1.10)

These equations can be solved for particular cases of \( E(t) \).

**Non-adiabatic population transfer**

Eq.\( 1.10 \) was first solved by I.I.Rabi, who showed that the population of the excited state of a two level atom subject to coherent light of constant intensity \( f(t) =
const) and constant frequency ($\omega = \text{const}$) is oscillating $[2, 40]$ as:

$$P_t(t) = |a_t(t)|^2 = \frac{\Omega^2}{(\Omega^2 + \Delta^2)} \sin^2 \left[ \frac{(\Omega^2 + \Delta^2)^{1/2} t}{2} \right]. \quad (1.11)$$

In the case of a time-dependent intensity the argument of the sin function is replaced with $A/2$, where the pulse area $A$ is defined as:

$$A = \int dt [(\Omega(t)^2 + \Delta^2)^{1/2}]. \quad (1.12)$$

According to Eq.1.11, the population is an oscillatory function of both time and pulse area.

The properties of non-adiabatic population transfer follow from Eq.1.11. If pulse area takes the value of $A = n\pi$ where $n$ is an odd number, the population of the excited state reaches its maximum. A pulse with the smallest possible area for transferring all the population into the excited state is called $\pi$-pulse. In the case of zero detuning, $\Delta = 0$, the population of the excited state reaches unity. The population transfer is extremely flexible e.g. it allows to transfer an arbitrary fraction of population into the excited state.

Eq.1.11 and 1.8 show that the time duration of a $\pi$-pulse can be shortened by increasing the strength of the driving field as long as RWA holds. By making it shorter than the spontaneous life time, spontaneous emission may be neglected and the excitation can be used in applications requiring high degree of coherence. From a practical standpoint however, the electric field strength is limited due to multiphoton ionization.

Eq.1.10 can be also solved $[56]$ when the target state is a superposition of several states (see Fig.1.1, (a)). In the case of two excited levels and perfect resonance of two CW lasers with the corresponding transitions, the populations of the two excited states $|f_1\rangle$ and $|f_2\rangle$ can be found:

$$P_{f1}(t) = \frac{\Omega_1^2}{\Omega_{\text{eff}}^2} \sin^2 (\Omega_{\text{eff}} t/2)$$

$$P_{f2}(t) = \frac{\Omega_2^2}{\Omega_{\text{eff}}^2} \sin^2 (\Omega_{\text{eff}} t/2). \quad (1.13)$$
where \( \Omega_i = E_i d_i / \hbar, E_i \) and \( d_i \) are the field strength and the dipole moment of the corresponding transition, and \( \Omega_{\text{eff}} = \sqrt{\Omega_1^2 + \Omega_2^2} \). As seen from equation Eq.1.13, populations of the two excited states are oscillating in sync with each other. The ratio between them is determined by the ratio of Rabi frequencies and therefore can be controlled by the intensities of the two CW lasers. If the phase between the states in the superposition is not important, phase locking of the laser fields is not required. We will refer to this ability to control the populations of different states independently as selectivity of excitation. The result of Eq.1.13 is obtained under the assumption that each laser interacts only with a corresponding single excited state.

From the above considerations, one may conclude that the non-adiabatic population transfer is fast, complete, selective and works in multilevel systems.

Rabi oscillations can be used for other purposes as well. An oscillatory shape of the population vs. pulse energy makes Rabi oscillations suitable for intensity calibration. The latter is usually estimated by measuring the pulse parameters such as the beam diameter, pulse energy and pulse duration. Experimental errors in determining these parameters prohibit accurate calculation of laser intensity. If, on the other hand, the dipole matrix element for the transition is known, and the dependence of population on pulse energy is obtained, the intensity in the interaction zone can be retrieved.

Quantifying a quantum state population is often based on measuring the fluorescence or ionization from the excited state. In both cases it is very difficult to estimate the absolute value of the excited state population as this would require knowledge about the density of atoms in the interaction zone, the interaction zone volume, the absolute number of detected ions or photons, and the detection efficiency. Rabi oscillations provide a convenient calibration tool for the excited state population vs. experimental signal, since the signal maximum implies a complete population transfer, provided that zero detuning from resonance can be achieved and the de-coherence is negligible. The amount of de-coherence in the quantum system of interest can be estimated from the contrast of Rabi oscillations.

While the non-adiabatic excitation of a multi-state target is possible, there are a few difficulties associated with the method. The first difficulty stems from its sensitivity to the pulse area and therefore, laser intensity and detuning. In the case
when population has to be switched with high fidelity, e.g. in the case of quantum information processing, using a $\pi$ pulse is not the optimal solution. A slight error in the pulse energy will result in an incomplete population transfer.

Second, since frequency detuning plays an important role in non-adiabatic excitation, Doppler shift should be taken into account. For a molecule moving at 500 m/s the Doppler shift is of the order of $2 \times 10^9$ Hz at 800 nm. Thus for a pulse of area $\pi$ and duration 1 ns, the maximum of transferred population would be only 60%. While shortening the pulse reduces the effect of the Doppler shift, it results in a higher peak intensity and therefore complications arising from non-linear effects.

Finally, for a given pulses area, the shorter the pulse the higher the intensity. High intensity may result in AC Stark shifts of non-resonant energy levels, expressed as:

$$\Delta \omega = \frac{1}{\Delta} \left( \frac{dE}{2\hbar} \right)^2,$$

where $d$ is the transition dipole moment, $E$ is the electric field strength and $\Delta$ is the frequency detuning [92]. If several lasers of different colors are used, shifts induced by the off-resonant frequencies would lead to incomplete population transfer.

Non-linear effects arising from the interaction of an atom with intense laser fields in non-adiabatic femtosecond population transfer were studied in this Dissertation.

**Rapid Adiabatic Passage (RAP)**

High sensitivity to laser parameters complicates experiments and served as a motivation for developing adiabatic methods. Adiabatic methods are based on the adiabatic theorem [104]. This theorem deals with quasi-eigenstates of a time-dependant Hamiltonian, known as "dressed states". The adiabatic theorem states that if the Hamiltonian changes slowly enough in time, the system stays in the initial dressed state. If before the interaction (when light intensity is zero) this dressed state is the same as the ground state of the system, whereas after the interaction it coincides with the excited state, the population will be transferred between the corresponding states.
Here we describe Rapid Adiabatic Passage \[15, 163\] executed in a two level system.

Eq.1.10 can be rewritten in a matrix form \[163\]:

\[
\frac{d}{dt} C(t) = H'(t) C(t),
\]

(1.15)

where:

\[
H'(t) = \begin{bmatrix}
0 & \frac{\Omega(t)}{2} \\
\frac{\Omega^*(t)}{2} & \Delta
\end{bmatrix},
\]

(1.16)

and

\[
C(t) = \begin{bmatrix}
1 & 0 \\
0 & e^{-i\Delta t}
\end{bmatrix} \begin{bmatrix}
a_i \\
a_f
\end{bmatrix}.
\]

(1.17)

Note that the detuning \(\Delta\) is time dependant. The problem is simplified if the dressed states are used as the basis states. These are defined as:

\[
\Phi_+ = \cos \theta |i\rangle - \sin \theta |f\rangle
\]

\[
\Phi_- = \sin \theta |i\rangle + \cos \theta |f\rangle,
\]

(1.18)

where the “mixing angle” \(\theta\) is defined as:

\[
\theta(t) = \arctan \left[ \frac{\Omega(t)}{\Delta(t)} \right]/2.
\]

(1.19)

By substituting the states of Eq.1.18 into Eq.1.17 one can check that \(\Phi_{\pm}\) are the instantaneous eigenstates of the Hamiltonian of Eq.1.16 with instantaneous eigenenergies given by:

\[
E_{\pm} = \frac{\Delta(t) \pm \sqrt{\Delta(t)^2 + \Omega^2(t)}}{2}
\]

(1.20)

In order to illustrate RAP we consider a pulse with a gaussian intensity envelope \(f(t) = \exp \left[ \frac{t^2}{2\sigma^2} \right]\), and a linear dependance of the instantaneous frequency on time \(\omega(t) = \omega_0 + t/(2\alpha)\), i.e. a frequency chirped pulse. In this case, the detuning is
Figure 1.3: Rapid adiabatic passage in two-level approximation.

given by: $\Delta = t/(2\alpha)$. The dressed state energies are plotted in Fig.1.3 (a) by solid blue lines. The Rabi frequency is shown by solid red line. On the diagram all the energies are shown with respect to the energy of the exited state. It can be seen that $\Phi_+$ state coincides with the ground bare state at the beginning of the interaction, and with the excited state when the pulse is over. Therefore, the population transfer is complete as long as the transition probability between states $\Phi_+$ and $\Phi_-$ is zero or negligible. The latter can be estimated using the Landau-Zener formula:

$$
P(\Phi_+ \rightarrow \Phi_-) = 1 - \exp\left(-\frac{\pi\Omega^2(t_0)}{2|\Delta(t_0)|}\right),
$$

(1.21)

where $t_0$ corresponds to the maximum Rabi frequency in the present case.

We notice that if the probability defined by Eq.1.21 is close to zero then the population transfer from the initial to the final state is complete. Because of the exponent in the Landau-Zener formula the population transfer between bare states is complete if the Rabi frequency is high or if the chirp rate $\Delta(t_0) = 1/(2\alpha)$ is slow. If these conditions are satisfied, the completeness of the population transfer does not depend on the central wavelength or the exact value of the intensity or the frequency chirp.

Frequency chirp defines how long is the pulse of a given bandwidth in the time domain. Higher chirps, i.e. higher values of $\alpha$ correspond to longer pulses. This is illustrated in Fig.1.3 (b). The bandwidth is shown by horizontal dotted lines, whereas two tilted lines illustrate an instantaneous frequency of two hypothetical pulses. The pulse corresponding to the dashed line has a higher chirp rate and spans longer time as compared to the pulse shown by the dash-dotted line. If shorter AP
is needed, the chirp rate can be lowered. However, preserving the fidelity of the process may require increasing the Rabi frequency. As in the non-adiabatic case, this is limited by the highest intensity which a system can tolerate.

As was shown by Melinger and co-workers [101] a single chirped pulse sweeping across several excited levels moves the population from the initial to a single excited state only, either the lower or the upper in the excited manifold, depending on the sign of the frequency chirp. Hence, the method does not allow to prepare a superposition target state.

Other than this inapplicability to multilevel target states, RAP is fast, complete and robust with respect to the laser parameters. Adopting the principle of adiabatic transfer to the case of a multilevel target is one of the main goals of this work.

1.2.2 Coherent population transfer with wavepackets: Piecewise adiabatic passage

As it was noted in the previous section, the idea of sweeping the frequency of the excitation pulse across several states leads to a selective excitation of a single state of an atom. Hence, the toolbox for controlling population transfer between quantum states lacks a method of adiabatic passage into a wavepacket. The theory of such method, called piecewise adiabatic passage (PAP) was developed in [131, 133]. The idea is to shape an ultrashort laser pulse in such a way as to execute several two-level adiabatic passages at once. Consider a quantum system consisting of the non-degenerate ground state \( |0\rangle \) and \( N \) excited states \( |1\rangle, |2\rangle, ..., |n\rangle, ..., |N\rangle \). The excited state manifold is coupled to the ground state with a laser field consisting of \( N \) modes of frequencies \( \omega_n \) close to the corresponding transition frequencies. The proposed PAP approach requires that the modes are chirped and therefore \( \omega_n \) are time dependent as shown in Fig.1.4(a).

Derivation similar to one presented in section 1.2.1 leads to the Schrödinger equation in the form:

\[
\frac{id}{dt}C(t) = H'(t)C(t),
\]

(1.22)
where $H'$ is:

$$H'(t) = \begin{bmatrix}
0 & \Omega_1'(t) & \Omega_2'(t) & \ldots & \Omega_N'(t) \\
\Omega_1(t) & \Delta_1(t) & 0 & \ldots & 0 \\
\Omega_2(t) & 0 & \Delta_2(t) & \ldots & 0 \\
\vdots & \vdots & \vdots & \ddots & \vdots \\
\Omega_n(t) & 0 & 0 & \ldots & \Delta_N(t)
\end{bmatrix}.$$  \hspace{1cm} (1.23)

The complex Rabi frequencies are defined as $\Omega(t) = d_{0n} E_n(t) \exp(-i\phi_n)/\hbar$ where $\phi_n$ is the phase of the $n$'th light mode. Note that the definition is different from the one used before by a factor of $1/2$. From Eq.1.23 one can see that the interaction between any excited state and “off-resonant” modes was omitted from the Hamiltonian. This is a valid approximation for the cases where the detuning between a state and the “off-resonant” mode is large in comparison to the corresponding Rabi frequency.

While it in not required by the general theoretical treatment, for the sake of simplicity, we will consider a particular field shape which can be achieved with the pulse shaping technique. The field can be written as $E(t) = \sum_n E_{0n} f(t) \cos((\omega_{0n} + t/(2\alpha))t)$. In this case, all detunings are equal, e.g. $\Delta_n(t) = \Delta(t) = t/(2\alpha)$, and the Hamiltonian can be diagonalized. There are $N-1$ degenerate quasi-eigenstates of energy...
Δ(t) and two eigenstates with energies given as:

\[ E_\pm = \Delta(t) \pm \sqrt{\Delta(t)^2 + 4\Omega_{\text{eff}}^2(t)} \],

(1.24)

where \( \Omega_{\text{eff}}^2(t) = \sum_{n=1}^{N} |\Omega_n(t)|^2 \). The eigenstates corresponding to the energies \( E_\pm \) are given by:

\[ \Phi_+ = \cos(\theta)C_i + \sin(\theta)C_f \]

(1.25)

\[ \Phi_- = \sin(\theta)C_i - \cos(\theta)C_f \]

(1.26)

with \( \tan \theta = E_+/\Omega_{\text{eff}} \) and \( C_i = [1,0,\ldots,0] \), \( C_f = [0,\Omega_1(t),\ldots,\Omega_N]/\Omega_{\text{eff}} \). In the case of our particular field, the Rabi frequencies exhibit identical time dependance expressed by \( f(t) \), and the vector of the target state amplitudes \( C_f \) does not depend on time.

Consider two time instances when \( \Delta \ll \Omega_{\text{eff}} \) and \( \Delta \gg \Omega_{\text{eff}} \), corresponding to times prior to the arrival of the laser pulse and after the pulse is gone. For \( \Delta \ll \Omega_{\text{eff}} \) the state \( \Phi_- \) coincides with \( C_i \) and for \( \Delta \gg \Omega_{\text{eff}} \) with \( C_f \). Similarly to the case of a two level adiabatic passage, if the Hamiltonian changes slowly, the system would stay in \( \Phi_- \) and therefore would be transferred from \( C_i \) to \( C_f \), with \( C_f \) being the desired target superposition state.

The spectrum required for PAP is depicted in Fig.1.4(b). It corresponds to a set of pulses centered at resonant frequencies and chirped individually, which results in simultaneous, parallel adiabatic passages. As in the case of a two-level system, the rate of the frequency chirp is an important parameter defining the adiabaticity of the process. From the definition of \( C_f \), one can see that the amplitudes in the target superposition are functions of the corresponding Rabi frequencies and therefore can be controlled by shaping the spectrum of the driving laser pulse.

PAP adopts principles of adiabatic population transfer to the case of a superposition of excited states. Experimental realization of PAP is the main goal of the first part of this work. It is interesting to compare piecewise adiabatic passage with more traditional non-adiabatic population transfer experimentally. It was noted that the latter allows transferring population into a wavepacket as well. Hence, the
direct comparison of the two techniques was included into this study.

1.2.3 Review of prior experimental work

Experimental development of the technique of Piecewise Adiabatic Passage requires a quantum system with suitable energy levels, a technique of quantum state detection and a technique of controlling the excitation field shape. This short review of a big body of experimental work on coherent population transfer is aimed to give a general idea of these aspects of the planned experiments.

Rabi oscillations in CW laser fields have been studied in [60] using the $D_1$ transition of Rb atom. Authors used magnetic field to shift the transition frequency in order to make it resonant with the frequency of a Hg laser. Rubidium atoms were excited to $4p_1/2$ state and the intensity of spontaneous emission back to the ground state was detected. Since the fluorescence intensity depends on the excited state population, the observed dependence of the fluorescence on light intensity exhibited Rabi oscillations. It was suggested that the obtained dependence could be used to calibrate the pulse area or to measure the dipole moment of the transition. Rabi oscillations between Rydberg states of atomic Rb were used in [123] to demonstrate experimentally the quantum collapse and revival predicted by Jaynes - Cummings model, emphasizing the deviation from the semiclassical predictions. Though the ultimate goal of the work is not related to this Thesis, the details are. The transitions between Rydberg states $63p_{3/2} \rightarrow 61d_{3/2,5/2}$ of atomic Rb were excited with a RF field.

Rabi oscillations excited with a femtosecond laser pulse were observed in quantum dots [77, 121], and in alkali atoms [169] using two different detection methods. If the photon was absorbed by the quantum dot the electron-hole was created. An electric potential was applied across the dot forcing the hole to move. The resulting current was detected and recorded as a function of the pulse energy. The curve unambiguously demonstrated up to three slightly damped oscillations. This very specific sinusoidal curve was used to calibrate the pulse area for the further experiments. The splitting of the excited electronic state of potassium atoms in the presence of strong laser field (Autler-Townes splitting) was measured using energy-resolved photo-electron spectroscopy [169]. This detection method enabled
to observe the oscillatory behavior of the dressed state population (equivalent to Rabi oscillations), but could not determine the final population of the bare atomic states.

In summary, these studies demonstrated Rabi oscillations, discussed technical challenges of the experiments and introduced a number of quantum state detection methods.

Frequency chirping - one of the simplest pulse shaping techniques, was used for excitation of atomic dressed states in adiabatic passage and Rabi regime [171]. Using energy-resolved photo-electron spectroscopy the authors showed that depending on the sign of the frequency chirp, different dressed states were populated. Importantly, a nearly transform limited (TL) pulse with a frequency chirp of up to \( \pm 100 \, \text{fs}^2 \) did not show the selectivity of excitation in the Rabi regime. This sets the lower chirp limit at which the excitation starts to show adiabatic features.

The ability of the broad spectrum of ultrashort pulses to cover several excited states simultaneously and to transfer population into a coherent superposition of states, was explored in a number of papers. In [16], excitation of a wavepacket by a femtosecond pulse and subsequent evolution of the \( 6p \) hyperfine states of Cs atom was studied. The wavepacket evolution was detected with a second, probe pulse. The second pulse interacts with the wavepacket, driving the system to the \( 7d \) state. It was shown that the probability to populate the final, \( 7d \) state depends on the relative phase of the wavepacket. In contrast with the presented work the wavepacket was excited in a weak field regime where only small fraction of the population was moved into the superposition.

The ability to control the target superposition state by means of pulse shaping was analyzed in [81, 172, 173]. These works confirmed again that a nearly transform limited pulse excites a coherent superposition of the neighboring states, while chirped pulses allow selective excitation.

In summary, prior experimental work demonstrated coherent control within two-level approximation, covered the possibility to create a wavepacket using ultrashort pulses, developed techniques of wave packet characterization and discussed the possibility of coherent control by shaping the spectrum of the excitation field. However, adiabatic population transfer to a coherent superposition was not considered or demonstrated.
1.3 Controlling molecular rotation with short laser pulses

Control of rotational motion of molecules is an interesting and important case of coherent control. A classical description of an excitation process is simple and illustrative. Here we briefly review the classical theory of interaction of a diatomic molecule with intense laser fields and the quantum theory of rotational excitation with short pulses. We then review recent most relevant works on laser control of rotational motion.

1.3.1 Theoretical background

Classical picture

For the sake of simplicity we start by considering the interaction of a classical diatomic molecule with a non-resonant intense laser field. The applied field polarizes the molecule and the resulting dipole interacts with the electric field. Potential energy of such molecule-laser interaction is given by [5]:

\[ U_0 = -\frac{1}{4} E(t) \left[ (\alpha_{||} - \alpha_{\perp}) \cos^2(\Theta) + \alpha_{\perp} \right], \]  

(1.27)

where \( \alpha_{||} \) and \( \alpha_{\perp} \) are the polarizabilities of the molecule along and perpendicular to the internuclear axis, \( \Theta \) is the angle between the internuclear axis and the polarization of the field, and \( E(t) \) is the electric field strength.

It is easy to see that if the polarizability difference \( \Delta\alpha = \alpha_{||} - \alpha_{\perp} \) is positive, the energy in Eq.1.27 is minimized at \( \cos(\Theta) = 1 \) corresponding to the potential well with a minimum at \( \Theta = 0 \). In other words, a molecule “feels” a torque towards the direction of the laser polarization. This classical torque is used to change the (initially random) orientation of molecules in a thermal ensemble and to control the speed of their rotation.

First, molecules can be aligned [54, 55, 141] along a certain direction using a long laser pulse with linear polarization. The value of \( \langle \cos^2(\Theta) \rangle \) averaged over the ensemble is used to measure the degree of molecular alignment. For an isotropic ensemble of three dimensional rotors this value is 1/3. During the laser pulse this
parameter changes towards $\langle \cos^2(\Theta) \rangle = 1$ which describes an ideal situation of perfect alignment. Second, if the polarization of the applied laser field rotates and the period of rotation is comparable with that of a molecule, an ensemble of molecules spinning in the same direction with the same angular velocity can be produced. The required optical field is known as an optical centrifuge [35, 72, 159, 161, 179]. Finally, if the pulse duration is short on the time scale of molecular rotation, the molecule receives a “kick” in angular momentum perpendicular to the laser polarization and the molecular axis [5, 49, 75]. Because the acquired momentum is proportional to the initial orientation of the molecule, different molecules in the ensemble rotate differently, resulting in the periodic dynamics of alignment and antialignment.

**Quantum picture**

From the quantum mechanical point of view, rotational excitation of a molecule by an off-resonant laser pulse is described by coherent population transfer into the higher states via rotational ladder climbing (see Fig. 1.1 (c)). In this context, the potential of Eq. 1.27 is added to the system Hamiltonian and the solution of the corresponding Schrödinger equation reveals the dynamics of the system. Depending on the amplitudes and phases of the excited rotational states, the resulting quantum wavepacket describes classically aligned or spinning molecules.

We consider here the quantum theory of non-adiabatic rotational excitation with short laser pulses following [91]. The Hamiltonian of a rigid rotor driven by a short pulse is given by:

$$H = \frac{L^2}{2I} + U_0,$$

where $L$ is the angular momentum operator, $I$ is the moment of inertia of the molecule and $U_0$ is defined by Eq. 1.27. The general solution of the unperturbed Hamiltonian (e.g. $U_0 = 0$) is a superposition of spherical harmonics:

$$\Psi = \sum_{m,n} c_{n,m} Y_n^m(\Theta, \varphi).$$

(1.29)
Starting with a single, ground state spherical harmonic:

\[ \Psi(\Theta, \varphi, t = 0) = Y_0^0(\Theta, \varphi), \]  

(1.30)

the interaction with a short pulse in impulsive approximation, i.e. when the pulse is much shorter than the period of molecular rotation, results in the following wavefunction:

\[ \Psi(\Theta, \varphi, t = 0^+) = \exp(iP \cos^2 \Theta) \Psi(\Theta, \varphi, t = 0), \]  

(1.31)

where:

\[ P = \frac{\alpha_{||} - \alpha_{\perp}}{4\hbar} \int dt E^2(t), \]  

(1.32)

describes the rotational kick strength measured by the amount of angular momentum transferred from the laser field to the molecule. The wavefunction of Eq. 1.31 can be written as a superposition of spherical harmonics by expanding the exponent:

\[ \Psi(\Theta, \varphi, t) = \frac{1}{\sqrt{4\pi}} \sum_{l=0}^{\infty} c_l \exp(-il(2l + 1)\hbar/\bar{\hbar}) Y_{2l}^0(\Theta, \varphi), \]  

(1.33)

where \( c_l \) are the expansion coefficients given by:

\[ c_l = \sqrt{\pi(4l+1)} (iP)^l \frac{\Gamma(l+\frac{1}{2})}{\Gamma(2l+\frac{3}{2})} \text{$_1F_1$} \left[ l+\frac{1}{2}, 2l+\frac{3}{2}, iP \right], \]  

(1.34)

where \( \text{$_1F_1$} \) is the confluent hypergeometric function.

Eq. 1.33 shows that a single kick results in a coherent superposition of rotational states evolving in time. All the states in the superposition have the same azimuthal quantum number which is inherited from the initial state. The time evolution results in a periodic alignment of the ensemble in space \([5]\). The period of this alignment is known as revival time and is equal to \( T_{\text{REV}} = 1/(2Bc) \), where \( B \) is the rotational constant expressed in wavenumbers and \( c \) is the speed of light. This evolution is illustrated classically in Fig. 1.5. Quantum mechanically, the revival time is an integer multiple of the period of the phase evolution of any rotational state and
Therefore any rotational wavefunction repeats itself after the revival period.

1.3.2 Review of prior work

In this work we study the excitation of rotational motion with a sequence of short pulses with polarization changing from pulse to pulse by a constant angle - a so-called chiral train. The resulting wavepacket should be characterized and compared to the results achieved by other methods described in Section 1.3.1. The review will focus on the experiments on rotational control and observation of rotational dynamics.

One of the first observations of molecules aligned by long intense laser pulses was spectroscopical [74]. The excitation of high rotational states was reflected by the change of rotational Raman spectrum. The assumed coherence of the resulting wave packet was not verified experimentally. The degree of alignment was retrieved from the obtained spectrum. Another approach to detecting molecular alignment was employed in [87, 88, 129]. The idea was to photodissociate a molecule with an ultrasort pulse. The fragments acquire momentum along the internuclear axis and fly away from each other. Using two-dimensional imaging the space distribution of the fragments was obtained. A non-uniform angular distribution of photofragments showed a preferred direction of the fragments velocities and
therefore preferred orientation of molecules prior to the dissociation. These studies showed that molecules subject to long, intense laser pulses exhibit narrowed angular distribution during the pulse. The degree of alignment depends on the laser intensity and is limited by the ionization threshold.

Optical centrifuge was proposed in [72]. In this method, the polarization of the electric field rotates with constant acceleration. A molecule is aligned along the direction of the field polarization and accelerates with it. It was shown that the maximum of transferred rotational energy is limited by the laser pulse bandwidth and can reach the dissociation threshold of molecules with high moment of inertia, such as Cl$_2$. If the dissociation threshold is not reached, the method produces an ensemble of molecules rotating in certain direction within a range of rotational velocities. Narrowing this range and creating a superrotor, a molecule occupying a single highly excited rotational state, was discussed theoretically [139, 160, 161], but no experimental results were reported.

Optical centrifuge was experimentally realized shortly after it was proposed [159]. Authors succeeded in exciting Cl$_2$ molecule to $J \approx 420$, as confirmed by detecting the dissociation fragments. It was suggested to use the dissociation to separate isotopes mixtures of molecules with different rotational constants [72]. We note that molecular centrifuge relies on an adiabatic process [161] and as such it requires high intensities of the laser field.

As it was mentioned before a short, intense laser pulse produces a coherent superposition of rotational states. The phase relation between the states is such, that the average over the ensemble expectation value of $\cos^2(\Theta)$ periodically exceeds the value for a uniform distribution in $\Theta$ - $\langle \langle \cos^2(\Theta) \rangle \rangle > 1/3$. Classically, an ensemble of molecules oriented randomly, subject to a short linearly polarized pulse, aligns shortly after the pulse because different molecules acquire different angular velocities, depending on their orientation with respect to the polarization of the kicking field. Later the ensemble dephases and rephases again. Therefore, this method allows to produce field free alignment as well as an ensemble of rotating molecules. This behavior is discussed in [5].

The dissociation method was used in [126] to observe non-adiabatic alignment. In this case the time delay between the ultrashort pump and the dissociating probe pulse was varied with controllable time delay and the dependence of $\langle \langle \cos^2(\Theta) \rangle \rangle$
on time showed clear revivals of the wavepacket. Different detection approach was used in [21, 50]. Authors used degenerate four wave mixing to observe the evolution of a rotational wavepacket.

The degree of molecular alignment resulting from the interaction with a short light pulse can be improved by applying several pulses [91]. The efficiency of excitation by a pulse train is maximized if the pulse train period is close to the molecular revival time as shown in [34]. In this case, the effect of quantum resonance in a system of periodically kicked quantum rotors leads to coherent accumulation of rotational energy. At resonance, the accumulative kick strength of a pulse train is equal to the sum of kick strengths of the individual pulses in the train. We note that using a train might be advantageous for samples with low ionization threshold due to a much lower peak power of pulses in the train. High sensitivity of rotational energy transfer to the time period of the pulse sequence enables isotope selective alignment [50] in a mixture of molecular isotopologues.

In contrast to optical centrifuge a single short pulse induces both clockwise and counter-clockwise molecular rotation. A scheme for exciting unidirectional motion with two short pulses was proposed theoretically [49] and demonstrated experimentally [75]. The idea is to apply the second pulse with polarization at 45° to the first pulse polarization (Fig.1.6). Unidirectional rotation is achieved when the time delay between the two excitation pulses matches the molecular revival time. In the experimental work [75] the excited sample was probed with a resonance enhanced multi-photon ionization (REMPI), a spectroscopic technique which provides information about the population of different rotational states. REMPI was executed by the pulses of left and right circular polarization. A non-zero difference in ionization signals for different photon helicities was attributed to preferred direction of molecular rotation.

Existing methods of rotational excitation allow to align, orient and spin molecules in certain directions. All these methods excite a large number of rotational states - a wavepacket. While some degree of control of the population distribution in the wavepacket is possible, selectivity of rotational excitation was not investigated in detail. In this work we attempt to design, realize and study rotational excitation with sequences of femtosecond pulses, exploring the effect of quantum resonance in a system of periodically driven quantum rotors.
Figure 1.6: “Double-kick” scheme of inducing a unidirectional rotation.

1.4 The goal of the present study

This work aims at studying coherent population transfer between quantum wavepackets with shaped femtosecond pulses. First part deals with a single-photon excitation of electronic wavepackets in atoms, outlined in section 1.2. Here, we develop, implement and study the technique of Piecewise Adiabatic Passage. We investigate its efficiency and robustness against laser parameters. We also perform thorough experimental comparison of adiabatic and non-adiabatic approaches, their respective properties and limitations.

The second part concentrates on exciting coherent rotational wavepackets in molecules, summarized in section 1.3. Here we focus on using femtosecond pulse shaping to improve selectivity of rotational excitation, as well as to induce unidirectional molecular rotation.
Chapter 2

One-photon excitation of a wavepacket

2.1 Experimental considerations

2.1.1 Atomic system

The choice of an atomic system for our experiments was dictated by the following requirements. First, a proof-of-principle experiment on PAP in a two-level system required an atom with well isolated excited electronic states, separated in frequency by more than an excitation laser bandwidth. Second, the main study of population transfer into a wavepacket required a system with a few closely spaced excited levels which would make up the excited wavepacket. In this case, the separation between the levels had to be smaller than the laser bandwidth. For both experiments the separation between the ground and the excited states had to be within the laser tunability range.

Another desired property of the quantum system is strong transition dipole moment, which allows achieving high pulse area even at relatively weak laser intensity, typically limited by the damage threshold of a pulse shaper.

Alkali atoms exhibit strong dipole transition, known as D-line, between the ground state $ns_{1/2}$ and the two fine-structure electronic states $np_{1/2}$ and $np_{3/2}$. 
Table 2.1: Properties of $^{85}$Rb and $^{39}$K

<table>
<thead>
<tr>
<th></th>
<th>Wavelength (nm)</th>
<th>Dipole matrix element (C·m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{85}$Rb, $5s_{1/2} \rightarrow 5p_{1/2}$</td>
<td>794.7603</td>
<td>$2.35 \times 10^{-29}$</td>
</tr>
<tr>
<td>$^{39}$K, $4s_{1/2} \rightarrow 4p_{1/2}$</td>
<td>769.8965</td>
<td>$2.46 \times 10^{-29}$</td>
</tr>
<tr>
<td>$^{39}$K, $4s_{1/2} \rightarrow 4p_{3/2}$</td>
<td>766.4899</td>
<td>$3.48 \times 10^{-29}$</td>
</tr>
</tbody>
</table>

Each of the two $np$ states is degenerate with respect to the projection of the total angular momentum. Hyperfine splitting due to the interaction of the total angular momentum with the nuclear spin is much smaller than the spectral resolution of the pulse shaper. Hence, both control and detection of individual hyperfine states is not possible with our optical setup. Rather, we were analyzing the total population of $np_{1/2}$ and $np_{3/2}$. The dipole matrix elements are large for both $ns_{1/2} \rightarrow np_{1/2}$ and $ns_{1/2} \rightarrow np_{3/2}$ transitions and are of the order of 1 Debye ($10^{-29}$ Cm) [1, 94]. The transitions are known as $D_1$ and $D_2$, respectively. The lifetime of the excited states is of the order of a few nanosecond which is much longer than our laser pulses. Therefore, spontaneous emission can be neglected. Furthermore, the transition wavelengths are in the visible and near infrared region which makes it convenient to use the available laser sources.

Rubidium (Rb) and Potassium (K) atoms were chosen for our experiments on single - and multi-level population transfer, respectively. Their relevant energy levels are shown in Fig.2.26. The separation between $5p_{1/2}$ and $5p_{3/2}$ levels of Rb atom is about 15 nm. This is larger than the pulse bandwidth (8.5 nm), allowing us to treat Rb as a two-level atom. The $D_1$ transition was used with an excitation wavelength of 794.76 nm.

The separation between $4p$ states in Potassium is about 3.5 nm. This is smaller than the laser bandwidth but still large enough to be resolved spectroscopically. The wavepacket, consisted of two $4p$ fine-structure states, has the period of evolution of 580 fs, which corresponds to the frequency of 1.73 THz. The duration of our pulses enabled us to resolve this evolution. Therefore K was used for the experiments on population transfer into a coherent superposition of states.

Relevant transition wavelengths and transition dipole moments for both atoms are given in Tab.2.1
Both atoms can be delivered inside a vacuum chamber using an atomic beam apparatus or by an alkali metal miniature dispenser. The latter is a small size metal container, filled with an intermetallic alkali compound. The compound has a relatively high boiling point in comparison to a pure alkali metal. This allows the dispenser to withstand a bakeout at high temperature. If heated with an electrical current passing through the container wall, the dispenser emanates a cloud of alkali atoms. This source is much simpler than an atomic beam apparatus, can be mounted close to the laser beam waist and it provides sufficient density of atoms in the interaction zone. We used dispensers manufactured by Alvatec.

2.1.2 Quantum state characterization methods

After the desired state or states are populated, the resulting superposition has to be characterized. Here we utilized the technique of multiphoton ionization of excited atoms and subsequent ion detection by a time-of-flight (TOF) apparatus. The excited state population is retrieved from the observed ion rate. In the case of an excited wavepacket, i.e. an excited coherent superposition state, the phases of the individual eigenstates have to be determined as well as the populations. These relative phases are reflected in the evolution of the excited wavepacket, which we observed by means of detecting the ion signal as a function of the probe delay time. Classically, the evolution of the wavepacket can be seen as a precession of the electronic orbital angular momentum and the spin vectors around the total angular momentum. Oscillations of the angle between the ionizing light polarization and the orbital angular momentum leads to the oscillation of the ionization probability. In both cases, the quantum state characterization requires a probe pulse source and an ion detector.

We used a vacuum chamber equipped with a TOF mass spectrometer schematically shown in Fig. 2.10. This apparatus allowed separating ions in arrival time according to their masses, detecting each type of ion with a microchannel plate detector (MCP) and measuring the ion yield for each ion type in a different time interval.

An OPA (TOPAS), manufactured by Light Conversion, pumped by a regenerative femtosecond Ti:Sapphire amplifier (Spitfire, Spectra-Physics) made a good
choice for the source of probe pulses due to its short pulse duration, wide wavelength tuning range and intrinsic synchronization with the excitation pulses. Because the OPA was pumped by the same amplifier which produced the excitation pulses, it was possible to control the time delay between the pump and the probe pulses precisely, by using an optical delay line. OPA pulses were much shorter that the period of evolution of the "spin-orbit wavepacket" (a superposition of $4p_{1/2}$ and $4p_{3/2}$ states) in Potassium. Broad wavelength tunability made it possible to use resonantly enhanced multiphoton ionization.

With a properly chosen probe wavelength the ionization from the excited state occurs through an intermediate resonance reducing the nonlinearity order of the ionization process. If the ionization by the probe pulses from the ground state has no intermediate resonances, the order of the nonlinearity is much higher, making this process negligible with respect to the ionization from the excited state. Therefore, the ion signal is proportional to the excited state population. 1300 nm wavelength was chosen for the excited state detection in Rubidium. The multiphoton ionization path is depicted in Fig.2.26 by red arrows. At this wavelength, the ionization from the excited $5p_{1/2}$ state occurs through an intermediate resonance $7p_{1/2,3/2}$ state, and requires three probe photons. Ionization from the ground state is a non-resonant five-photon process. In the limit of weak probe intensity the ionization from the ground state can be therefore safely neglected and the ion signal considered proportional to the $5p_{1/2}$ population.

The absolute value of the excited state population is difficult to measure since the density of atoms in the interaction region, the ionization cross-section and the ion detection efficiency are not known. Instead of measuring the absolute state population, we used a $\pi$-pulse excitation as a reference for complete population transfer, and determined the efficiency of population transfer in PAP excitation relative to that value.

To achieve a $\pi$-pulse excitation, light intensity has to be constant across the sample. We probed a small central volume of the gas sample where the excitation intensity profile is relatively flat, by making the probe beam diameter approximately three times smaller than that of the pump beam. We typically achieved this by increasing the probe beam diameter before the focusing lens. The nonlinearity of multi-photon ionization also contributes to effectively decreasing the probing
Figure 2.1: Scheme of weak field bichromatic coherent control. The population of the 5s\(_{1/2}\) results from interference between two transitions and therefore depends on the relative phase between 4p\(_{3/2}\) and 4p\(_{1/2}\) states.

Our detection method for a wavepacket is based on the weak field bichromatic coherent control scheme [134]. The 4p\(_{1/2}\) and 4p\(_{3/2}\) states are coupled to 5s\(_{1/2}\) with a weak (less than 0.3 \(\mu\)J) femtosecond pulse (Fig.2.1). The central wavelength of probe pulses is tuned in such a way as to drive both transitions at 1243 and 1252 nm with equal efficiency. Two more photons from the same probe pulse ionized the atoms. At such low probe energy, 5-photon ionization from the ground electronic state is negligible.

In order to understand the bichromatic control detection we write the wavefunction of the system as:

\[
\Psi(t) = \sum_i b_i(t) \psi_i \equiv b_0(t)|4S_{1/2}\rangle + b_1(t)|4P_{1/2}\rangle + b_2(t)|4P_{3/2}\rangle.
\]

Because of the low probe energy, the ionization probability is proportional to the population of the 5s\(_{1/2}\) state. In the perturbative regime of interaction, this probability can be calculated as [134]:

\[
P(t) \propto |b_1(t)|^2 |\epsilon(\omega_1)|^2 d_{11} + |b_2(t)|^2 |\epsilon(\omega_2)|^2 d_{22} + 2Re[b_1(t)b_2^*(t)\epsilon(\omega_1)\epsilon^*(\omega_2)d_{12}],
\]

where \(b_1(t)\) and \(b_2(t)\) are the excited eigenstate amplitudes (Eq.2.1), \(\epsilon(\omega_1)\) and \(\epsilon(\omega_2)\) are probe field amplitudes at the resonant probe transition frequencies of
$4p_{1/2} \rightarrow 5s_{1/2}$ and $4p_{3/2} \rightarrow 5s_{1/2}$, respectively, and $d_{ij} = \langle \psi_j | \hat{d} | 5S_{1/2} \rangle \langle 5S_{1/2} | \hat{d} | \psi_i \rangle$ with $\hat{d}$ being the dipole moment operator.

The last term in Eq. (2.2) is the interference term which depends on the difference between the relative phase of the excited wavefunctions $b_{1,2}$ and the relative phase of the two resonant probe field components $\epsilon(\omega_1, 2)$. Since the latter is constant, the ionization probability, and therefore the ion signal recorded as a function of the pump-probe time delay, oscillates as $\sin[(\omega_1 - \omega_2)t + \phi_{12}]$, where $\phi_{12} = \arg\{b_1^* b_2 d_{12}\}$. These oscillations indicate that two $4p$ states are populated coherently, whereas their relative amplitudes and phases can be extracted from the oscillation contrast and phase, respectively [180].

### 2.1.3 Femtosecond pulse shaping technique

In the present work we utilized a well developed technique of femtosecond pulse shaping [167]. We briefly review here the main principles of this technique. We then describe a few critical parameters for our pulse shaper and discuss its design, alignment and calibration.

**Principles of operation**

The general scheme of a "4f Fourier pulse shaper" implemented in this work, is presented in Fig. 2.2. The incoming pulse is dispersed in space by a spectrometer consisting of a diffraction grating and a lens. Its spectrum is modified by amplitude and phase masks according to the experimental requirements. The spectral components are recombined into a single beam by a second lens-grating pair.

The scheme presented in Fig. 2.2 may work with either cylindrical or spherical lenses. While using a spherical lens reduces the number of degrees of freedom, simplifies the alignment and improves the spatial profile of the outgoing beam, cylindrical lens reduces the light intensity at the Fourier plane. If the damage threshold of the mask is low it is preferable to use a cylindrical lens (as implemented in our pulse shaper) in order to achieve higher energy of the outgoing pulse.
Figure 2.2: Scheme of a "4f Fourier" pulse shaper (a). The left diffraction grating and the left lens constitute a spectrometer. Pulse spectral components are dispersed in the Fourier plane of the lens. A double-layer SLM serves as an amplitude-and-phase mask. The second lens-grating pair (right) recombines the pulse. The distance between each consecutive optical element in the shaper equals 1 focal length of the lens (hence the term "4f geometry"). Since in the time domain the pulse is completely defined by its spectrum, an arbitrary temporal profile can be obtained via spectral shaping. Examples of the pulse shapes often used in our excitation schemes are shown in (b, c). A sinusoidal phase modulation (middle left panel, red) produces a train of equidistant pulses (b). A parabolic phase modulation (lower left panel, red) produces a frequency chirped pulse with its instantaneous frequency changing linearly with time. The Gaussian spectral amplitude envelope was not changed in both cases (blue lines on the left). Blue (red) lines on the right panels represent the dependence of the shaped pulse intensity (phase) on time.

Spatial light modulator

The phase-and-amplitude mask can be realized with a number of methods. One of the most popular is the use of a double-layer spatial light modulator (SLM). SLM is based on a liquid crystal technology. A nematic liquid crystal exhibits optical
birefringence controlled by the electric potential across the medium. The refractive index for the light polarized along the extraordinary axis depends on the applied voltage. The refractive index for the orthogonally polarized light is not affected by the applied voltage. A linear array of such crystals constitutes a single one-dimensional mask of an SLM. The elements of the array are usually referred to as pixels.

A single-layer SLM allows to change either phase or polarization of light. In the first case, the incoming field is polarized along the extraordinary axis and the phase is controlled by the applied voltage. In the second case the polarization is at 45° to the extraordinary axis and the applied voltage results in a elliptical polarization of the output light. The change in polarization is used for controlling the amplitude of light by means of an output polarizer.

Simultaneous amplitude and phase control is achieved by using a double-layer SLM. Two liquid crystal arrays are bonded together. The pixels of the two arrays are aligned with respect to each other. The extraordinary axes of two arrays are orthogonal and are at ±45° to the incoming light polarization (see Fig 2.3). In the
analysis below, unit vectors along the two extraordinary axes are denoted as $\hat{e}_1$ and $\hat{e}_2$. Applying phase shifts $\delta_1$ and $\delta_2$ to the polarization components $\hat{e}_1$ and $\hat{e}_2$ of the initial field $E_{\text{in}}(t) = \hat{x}\cos(\omega t)$ results in the output field:

$$E_{\text{out}}(t) = \hat{x}\cos\left(\omega t + \frac{\delta_1 + \delta_2}{2}\right)\cos\left(\frac{\delta_1 - \delta_2}{2}\right) - \hat{y}\sin\left(\omega t + \frac{\delta_1 + \delta_2}{2}\right)\sin\left(\frac{\delta_1 - \delta_2}{2}\right)$$

(2.3)

If $\hat{y}$ component is blocked by a polarizer inserted in the outgoing beam, the remaining field becomes:

$$E_{\text{out}}(t) = \hat{x}\cos\left(\omega t + \frac{\delta_1 + \delta_2}{2}\right)\cos\left(\frac{\delta_1 - \delta_2}{2}\right)$$

(2.4)

Therefore, the phase of the shaped wave is $(\delta_1 + \delta_2)/2$ and the amplitude is controlled by the phase difference, as described by the factor $\cos((\delta_1 - \delta_2)/2)$.

**Optical design**

Designing a 4f shaper starts from calculating the focal length of the lens ($f$) and the diffraction grating density ($\rho$). Both depend on the required optical resolution and the SLM aperture. The technique of PAP developed in this work requires a pulse spectrum discussed in [133] and shown in Fig.1.4. In order to populate a wavepacket of $4p$ states of potassium the spectrum should consist of two peaks centered at the resonance frequencies of $D_1$ and $D_2$ transitions. The separation between the peaks is 3.5 nm, which dictates the width of the peaks to be less then 2 nm FWHM. The parabolic phase shape required for PAP has to be formed by at least 10-15 pixels. Therefore, the spectral resolution required by the experiment is around 0.13-0.20 nm/pixel. For this part of the work a 128 pixel SLM with a 100 $\mu$m pixel pitch and a 5 mm pixel height from CRi Inc. was used.

Two requirements should be fulfilled. First, the available excitation pulse bandwidth of $\approx 9$ nm FWHM at 800 nm should fit into the SLM window in the Fourier plane of the shaper. Second, the focal spot size of a monochromatic beam in the same plane should be smaller than the SLM pixel size (100 $\mu$m). We first calculate the focal length $f$. Aperture height of the SLM (5 mm) sets the upper limit on the
input beam diameter. The diffraction limited spot size in the Fourier plane is equal to:

\[ 2w_0 = \frac{4 \lambda f}{\pi D}, \]  

(2.5)

where \( f \) is the focal length of the lens, \( D \) is the input beam diameter and \( \lambda \) is the wavelength. From Eq.2.5 the focal length of the lens should be less than 500 mm. For the purpose of compactness, we chose \( f = 300 \) mm. For this focal length the depth of focus defined as:

\[ DOF = \frac{8 \lambda}{\pi} \left( \frac{f}{D} \right)^2, \]  

(2.6)

is equal to 7 mm. This number shows how precise should the SLM be positioned in the Fourier plane between the two lenses.

When the lens focal length is known, the required groove density of the grating is calculated as follows. The angular dispersion is:

\[ \frac{d\beta}{d\lambda} = \frac{n\rho}{\cos(\beta)}, \]  

(2.7)

where \( \beta \) is the angle of diffraction, \( n \) is the diffraction order (here, \( n = 1 \)). The relationship between the diffraction angle and the incidence angle \( \alpha \) is given by the grating formula:

\[ \sin(\alpha) + \sin(\beta) = n\rho\lambda. \]  

(2.8)

The angular dispersion introduced by the grating results in the following spatial dispersion in the focal plane of the lens:

\[ \frac{dx}{d\lambda} = \frac{fn\rho}{\sqrt{1 - \left( \frac{n\rho\lambda}{\sin(\alpha)} \right)^2}}. \]  

(2.9)

For the grating with a groove density of \( \rho = 1800 \) grooves per millimeter and an optimal angle of incidence of 46.5 degrees, the linear dispersion is equal to 770 \( \mu m/nm \). Given the available pixel size of 100 \( \mu m \) it results in the shaper resolution
of 0.13 nm/pixel, which is in the required range of 0.13-0.2 nm per pixel.

We used a transmissive grating from Kaiser Optical Systems.

**Mechanical design, assembly and alignment**

The simplest design of a 4f pulse shaper corresponds to the direct implementation of the scheme shown in Fig.2.2, with two gratings and two lenses. However, too many degrees of freedom due to the large number of optical elements makes it difficult to align. For instance, incorrect distance between the lenses leads to a diverging output beam. It can be easily adjusted by moving one of the lenses. The latter, however, results in the changing lens-to-grating distance, which introduces an undesired frequency chirp. Several simpler schemes were reported, for example in [117]. For our experiments we used a “folded configuration” with a single lens-grating pair. The layout is shown in Fig.2.4. Mirrors M1, M2, M3, M4 are mounted on a thin breadboard which is installed on a translation stage using two angle brackets. In this design the mirror assembly can be moved as a whole, enabling to change the distance between the two lenses with one adjustment knob. A single cylindrical lens is mounted on a separate translation stage and can be moved towards or away from a single diffraction grating. The scheme ensures the equality of the distance between the grating and the lens for the input and the output pairs. The SLM is mounted on yet another separate translation stage and can be moved into the focal plane of the lens.

The goal of the assembly and alignment procedures is to ensure that (i) the output beam is well collimated and free of spatial chirp, (ii) the phase of the output pulse is nearly the same as that of the input pulse, (iii) the energy of the output pulse is as high as possible.

First, all mounts are positioned at their approximate locations using a ruler. A mirror is installed into the grating mount and the beam trajectory is aligned along the shaper optical axis using mirrors M1-M4, in such a way as to be in one vertical plane parallel to the mirror plane. The output beam should be parallel to the table surface. Two irises are installed to define the beam path from the grating to mirror M1.

In the next step, the grating is installed into the mount. The angle of the inci-
Figure 2.4: Folded shaper layout (a) and design (b).

dence, and the point of incidence are adjusted in order to guide the first reflection through the irises. At this point, a spectrometer may help to ensure that the central frequency of the input pulse passes through the irises. All visible diffraction orders (e.g. 0 and 1) should be parallel to the table surface. This ensures that the incoming beam is perpendicular to the grating grooves.

Now, the irises are removed and the lens is installed into the mount. The optical axis of the lens is aligned along the beam propagation direction using the back reflection from the lens.

The position of the lens is changed with an increment of 0.25 mm. For every position of the lens, the output pulse duration is calculated from its auto-correlation trace. The position is set as to provide the shortest output pulse length. Then the mirror assembly position is changed with the same increment, in such a way as to minimize the output beam divergence and spatial chirp.

The position of the SLM is set by moving the SLM translation stage while monitoring the optical resolution of the shaper. This is done by closing all pixels except of the one near the center of the mask. The width of the transmitted spectrum is
measured with a spectrometer and minimized by adjusting the SLM position. The spectrum of a single open pixel is shown in Fig.2.6 by red line. The insert in Fig.2.6 shows the same spectrum (blue dots). The width of the fitted Gaussian (solid line) is 0.15 nm, in good agreement with the calculated value of the shaper resolution.

**Shaper calibration**

Shaper calibration consists of two parts. First, one needs to calibrate the phase shift vs. the voltage applied to a liquid-crystal pixel. The SLM is controlled using a computer program. The voltage settings are expressed in arbitrary units ("counts") ranging from 0 to 4095. The calibration is accomplished by the following procedure. The first mask voltage is set to its maximum value of 4095 counts. The voltage of the second mask is scanned from zero to maximum while transmission through each pixel is measured by a spectrometer equipped with a CCD camera. The central part of the resulting curve is fitted with the function:

\[ T(V) = A + B \sin(\arctan(CV + D)) \]  

(2.10)

The arc-tangent dependence is chosen empirically as giving the best fit in the range of 600-1500 counts. Parameters \( A, B, C \) and \( D \) are found by the least mean square method. The best fit is obtained within three or four maxima as shown in Fig.2.5 (a). Each period of oscillation corresponds to an additional \( 2\pi \) phase shift, resulting in the overall maximum phase shift of \( (6 - 8)\pi \). An example of the phase shift vs. voltage dependence is shown in Fig.2.5 (b).

The calibration quality is verified by setting the transmission to zero and monitoring the leakage of light through the shaper. Usually, about 3-4 percent of light passes through. This can be explained by a 3 \( \mu m \) gap between pixels of 100 \( \mu m \) width.

Second, the wavelength vs. pixel number calibration is performed. All pixels are shut except of three, one at the left end of the mask, one at the right end and one in the middle. Three open pixels manifest themselves as three spectral peaks in the spectrum of the transmitted light. Wavelength is assumed to change linearly with the pixel number and the exact functional dependence is obtained using the least mean square fit.
Figure 2.5: SLM voltage calibration. Transmission of an SLM pixel (a) as a function of voltage applied to the first mask while the voltage of the second mask is set to maximum (4095 counts). The retrieved phase shift induced by the pixel of the first mask as a function of applied voltage (b).

2.1.4 Ultra-short pulse characterization.

Experiments with shaped excitation pulses require accurate characterization of the field amplitude and phase as functions of both time and frequency. Intensity spatial profile of the excitation beam in the interaction zone was another important parameters for the planned experiments. Here we briefly review the used pulse characterization methods.

Spectral amplitude

Pulse spectrum was measured with a single-grating monochromator produced by McPherson Inc. (Model 2035) equipped with a linear charge-coupled device CCD camera. The spectrometer was also equipped with a rotatable 1800 grooves/mm diffraction grating resulting in a 0.08 nm optical resolution at 800 nm. The spec-
Figure 2.6: Spectrum of an excitation pulse (blue line), the best Gaussian fit (orange line) and the spectrum of light passing through a single SLM pixel (red line). The insert shows the latter (blue dots) together with its best Gaussian fit (yellow line).

Figure 2.7: Optical scheme of a FROG setup.

trometer was calibrated using rare gas discharge lamps.

An example of an excitation pulse spectrum is shown in Fig. 2.6 by blue line. The best fitted Gaussian shown by orange line has a width of 7 nm FWHM.

Frequency Resolved Optical Gating (FROG)

The technique of frequency resolved optical gating (FROG) [157] is one of the most standard approaches to ultrashort pulse characterization. It allows to characterize both the spectral amplitude and phase of the pulse.

FROG is based on the analysis of the spectrally resolved auto-correlation function of an unknown pulse. The pulse is split into two replicas, and these replicas are
overlapped on a nonlinear crystal as shown in Fig. 2.7. The time interval between
the pulses is scanned by means of an optical delay line. Recording the second har-
monic (SH) spectrum as a function of the time delay between the two replicas one
obtains a so called FROG trace. Such trace can be analyzed with an iterative genetic
algorithm retrieving the pulse spectral amplitude and phase.

A FROG setup was built using a 100 µm thick β-barium borate type I (BBO)
crystal and a spherical mirror of 300 mm focal length.

**Multiphoton Intrapulse Interference Phase Scan (MIIPS)**

A broadband pulse propagating through a dispersive media acquires phase distor-
tions. A perfectly compressed transform limited pulse would arrive to the interac-
tion zone chirped after propagation through glass elements and air. Imperfections
in the pulse compressor lead to phase distortion of phase of second and higher
orders. For the sensitive experiments on non-adiabatic excitation these phase dis-
tortions have to be compensated. Multiphoton intrapulse interference phase scan
(MIIPS) [96] is a method of pulse characterization allowing to compensate phase
distortions induced by the media dispersion, imperfect optical alignment of the
laser system, etc. *in situ*.

The idea is to use second harmonic generation obtained using a nonlinear crys-
tal placed in the point of interest. It was shown [96] that intensity of the second
harmonic at frequency 2ω is maximum if the phase of the fundamental spectrum
is flat around the frequency ω. Consider an arbitrary frequency component in the
pulse spectrum. If the spectral phase exhibits a non-zero curvature near this fre-
quency, the intensity of the corresponding second harmonic would be lowered.
Applying a phase mask compensating this curvature would increase the SH com-
ponent. Scanning the curvature of the applied mask one finds the second derivative
of the input pulse phase. Once the second derivative of the pulse phase is found for
every frequency, one can find the phase by integrating the second derivative twice,
assuming that the phase is smooth, continuous function of frequency.

Practically, the following phase mask is applied to the pulse by the shaper:

\[ \varphi(\omega) = A \sin((\omega - \omega_0)T + \delta_M), \]  

(2.11)
where $\omega_0$ is the central frequency of the pulse. Parameters $A$ and $T$ are kept constant while $\delta_M$ is scanned, usually within the range of $(2-3)\pi$. The curvature of the phase mask is equal to the second derivative of the function in Eq. 2.11:

$$\phi''(\omega) = -AT^2 \sin((\omega - \omega_0)T + \delta_M). \quad (2.12)$$

When the absolute value of $\phi''$ is equal to the local phase curvature at frequency $\omega$ and has the opposite sign, the SH of the corresponding frequency is maximized. For each value of $\delta_M$ the SH spectrum is taken. The spectra are combined into a two-dimensional trace. Examples of such trace are shown in Fig. 2.8 (b,f). MIIPS trace for a pulse with perfectly flat phase is a set of parallel, tilted stripes distributed evenly as shown in Fig. 2.8 (f). Phase distortions lead to an uneven distribution, different tilt angle and change of the stripes shape as can be seen in panel (b) of Fig. 2.8.

For each frequency the value of $\delta_M$ maximizing the SH is determined and the second derivative of the phase as a function of frequency is found. The integration yields the spectral phase of the pulse and the negative of that is applied through the pulse shaper to compensate phase distortions. The method requires a few iterations to achieve high precision of the retrieved phase. The quoted number is 0.013 radian within FWHM of a 80 nm pulse [177] bandwidth. We were able to achieve the precision of 0.25 radians.

In our work we implemented MIIPS technique using a 100 $\mu$m BBO crystal. The crystal was initially installed close to the FROG setup, and later inside of the vacuum chamber.

### Elimination of phase distortions

Fig. 2.8 shows the result of eliminating phase distortions of the excitation pulses by introducing a “compensation phase” with a pulse shaper. Panel (a) shows the FROG trace of an uncompensated pump pulse, i.e. when all SLM pixels were set to zero phase. The result of the FROG retrieval algorithm is shown in panel (c) by black dotted line (spectrum) and blue dashed line (phase). Green line shows the spectrum obtained directly with a spectrometer for reference. The phase was also determined by MIIPS and is shown by blue solid line. The difference between the
Figure 2.8: Pump pulse characterization. FROG trace of an uncompensated Spitfire pulse after the shaper (a), MIIPS trace of the same pulse (b), retrieved phase and spectrum (c), temporal autocorrelation functions of compensated (red) and non-compensated (blue) pulses (d), FROG trace of the pulse with the phase distortions corrected (e), MIIPS trace of corrected pulse (f). In panel (c) the spectrum of the pulse is shown by black dotted (FROG retrieval) and green (spectrometer) lines. The fitted Gaussian is shown by turquoise thin solid line and the thick line indicates FWHM of the pulse. The phase of original, uncompensated pulse is shown by dashed (FROG) and solid (MIIPS) lines. The phase of the compensated pulse is shown by solid (MIIPS) and dashed (FROG) red lines. In panel (d), red (blue) line shows the autocorrelation function of compensated (uncompensated) pulse.
Figure 2.9: Pump (a) and probe (b) intensity profiles at the interaction zone. The vertical (c) and horizontal (d) sections of the pump (blue) and the probe (red) profiles

two methods stems mainly from the high error of the FROG retrieval algorithm. FROG and MIIPS traces for the compensated pulse are shown in panel (e) and (f) respectively. The retrieved phase is shown in panel (c) by magenta dashed line (FROG) and by red line (MIIPS). It is clear that the compensated phase exhibits much lower distortion. Panel (d) shows the autocorrelation functions for uncompensated (blue) and compensated (red) pulses, emphasizing the same point.

Spatial profile of the beams

Spatial intensity profile in the interaction zone was obtained using model LBA-FW-SCOR CCD camera manufactured by Spiricon. Part of the pulse was picked by a fused silica plane window right before the interaction zone, attenuated and steered towards the camera as shown in Fig. 2.11

An example of measured beam profiles is shown in Fig. 2.9. Vertical and hor-
orizontal central cross-sections of the two-dimensional intensity distribution were fitted by Gaussians, resulting in the focal spot sizes of 260 $\mu m$ and 110 $\mu m$ for the pump and probe beams, respectively. The same camera was also used to spatially overlap the beams.

2.1.5 Experimental setup

The experimental setup consisted of two main parts: the optical setup and the vacuum chamber equipped with an atomic source and a time-of-flight apparatus.

Vacuum chamber

The vacuum chamber is shown in Fig.2.10. The TOF mass-spectrometer consists of three plates, which produce the extraction and acceleration electric fields, the free flight zone and the MCP assembly. The interaction zone is located in between the lower plates. The plates have a mesh in the center to let the ions pass through. The atoms were produced by a miniature alkali dispenser mounted underneath the TOF apparatus. This arrangement minimizes the distance from the atom source and the interaction zone and therefore maximizes the density of atoms in the interaction zone. The atoms were excited by the shaped pulses from the Ti:Sipphire amplifier and ionized by probe pulses from a tunable optical parametric amplifier (OPA). Motion of the atoms during a few picosecond time delay between pump and probe pulses was negligibly small. The ions were accelerated by the electric field produced by the TOF plates, underwent free flight and were detected by the MCP. The electrical signal from the MCP was gated and measured with model SR250 boxcar integrator from Stanford Research Systems Inc. The resolution of the TOF mass spectrometer allowed to separate $^{87}Rb$ from $^{85}Rb$. Only $^{85}Rb$ signal was recorded in the experiments on population transfer in a two-level system.

Optical setup

Our optical setup was modified throughout the course of this work. Important changes of the setup will be highlighted at the time of describing particular experiments. The basic setup is depicted in Fig.2.11. Pump pulses were produced by the regenerative amplifier (Spectra Physics, Spitfire). Spitfire beam had to be
Figure 2.10: Vacuum chamber equipped with the source of alkali atoms and TOF apparatus.

downsized from 15 mm to 5 mm diameter in order to fit into the SLM aperture. Small size of a compressed beam implies high intensities and potentially leads to undesired non-linear effects. These complications were avoided by using the following scheme. A fused silica wedge was installed inside the Spitfire amplifier. The wedge was inserted into the amplified beam right after the regenerative cavity. At this point, the pulse is stretched and its duration is tens of picoseconds, the beam diameter is about 1 mm and beam divergence is high. The beam was split by the wedge at 1/10 ratio. The high-energy part was sent via the usual path into the Spitfire compressor. The low-energy part was shaped and used as an excitation pulse.
Figure 2.11: Experimental setup for studying population transfer with shaped femtosecond pulses.
The energy of the pulse was approximately 200 µJ. The beam traveled about 1.5 m, and when its diameter reached 4-5 mm entered a collimating telescope of zero magnification. After the collimating telescope, pulses were shaped by the shaper and compressed by an external replica of the compressor. In this scheme, the beam is compressed at the very last stage, which minimizes all-possible non-linear effects. Also, from our experience, this scheme provides higher quality of spatial profile.

The energy of the excitation pulses was controlled by a variable neutral density filter installed after the compressor. The beam was either sent towards the vacuum chamber or deflected by a flipping mirror into the diagnostics setup consisting of FROG and MIIPS.

Probe pulses were produced by an OPA (TOPAS, Light Conversion) pumped by the high-energy part of the Spitfire beam. Signal and idler were separated by a pair of dichroic mirrors. Probe pulses were delayed with respect to the excitation pulses by a computer controlled delay line. Time resolution of the delay line was better than 1 fs.

Pump and probe beams were focused by lenses of 100 cm and 40 cm focal length, respectively, and combined on a polarizing beamsplitter cube. The probe beam was focused tighter than the pump so as to allow probing the atoms in the central part of the pump intensity profile, where the pump intensity is almost uniform. Tighter focusing was achieved by both increasing the beam diameter in front of the focusing lens and by using a lens with shorter focal length. A telescope consisting of positive and negative lenses was used to increase the probe beam diameter. One of the telescope lenses was mounted on a translation stage which allowed matching the divergence of the probe and pump beams and ensured that they are focused in the same plane.

Small part of the pump/probe beam pair was reflected by a plane fused silica window towards a CCD camera for spatial beam characterization and overlap control.

The power of probe pulses was below 0.1 µJ which produced no detectable ionization from the atomic ground state. The energy of excitation pulses inside the chamber was about 0.5-1 µJ.

Pulse to pulse energy fluctuations result in the fluctuations of the excitation
pulse area, detrimental to observing clear Rabi oscillation. To eliminate this problem, the energy of each excitation pulse was measured with a fast photodiode (DAT410 from Thorlabs Inc.) along with the ionization signal. After acquiring data from about 30,000 laser pulses, the data points were binned according to the pump energy, and averaged within corresponding bins. This binning procedure proved crucial for observing high-contrast Rabi oscillations.

**Optical alignment**

As a first step of the alignment procedure, all parts of the optical setup: the regenerative femtosecond amplifier, the pulse shaper, the OPA and the external compressor were aligned individually. The next step was to align the beams on the target and find the exact time overlap between the excitation and probe pulses. The following alignment procedure was used. Probe pulses were delayed by approximately 400 ps (long enough to be measured with a fast photodiode) with respect to the pump using a motorized delay line. The ion signal from the excitation pulses alone (with no probe pulses present) was observed and maximized by changing the position of the pump focusing lens. This ionization signal was detected at the highest MCP voltage. After that, the two focal spots from the pump and probe beams were overlapped on the CCD camera, ensuring good beam overlap in the interaction zone. At this point, the MCP voltage was lowered so as to have no detectable signal from either pump or probe beam alone. However, if both beams were sent to the chamber the atoms were transferred to the excited electronic state by pump pulses and ionized by the probe, resulting in high ionization signal proportional to the population of the excited state.

To find the temporal overlap between pump and probe pulses, the ionization signal was recorded as a function of the probe time delay. A typical dependence of the ionization signal on the probe time delay is shown in Fig.2.12. In this particular case, the pulses overlapped at 1.7 ps. At shorter delays, probe pulses arrive prior to pump pulses, resulting in zero ionization signal.
2.2 Population transfer between two quantum states by piecewise chirping of femtosecond pulses: Theory and experiment

We propose and experimentally demonstrate the method of population transfer by piecewise adiabatic passage between two quantum states. Coherent excitation of a two-level system with a train of ultrashort laser pulses is shown to reproduce the effect of an adiabatic passage, conventionally achieved with a single frequency-chirped pulse. By properly adjusting the amplitudes and phases of the pulses in the excitation pulse train, we achieve complete and robust population transfer to the target state. The piecewise nature of the process suggests a possibility for the selective population transfer in complex quantum systems.

The existence of robust and selective methods of executing population transfer between quantum states is essential for a variety of fields, such as precision spectroscopy and atomic clocks [42], quantum computing [110], control of molecular dynamics and chemical reactions [135]. Traditionally, population transfer between
two quantum states has been achieved by either executing a half-cycle Rabi flop-
ing, i.e. by applying a “π-pulse”, or by optically inducing an adiabatic passage
(AP) between the states of interest [2]. Though the application of a π-pulse can be
implemented on a very short time scale, it is far from being robust, as it is highly
sensitive to fluctuations in the laser power, phase, and pulse duration. In contrast,
AP, which for example can be executed by the STIRAP technique [162], or by
slowly chirping the instantaneous frequency of the pulse, exhibits high degree of
robustness against the fluctuations of many of the laser field parameters [2, 162].
Because of this property, AP with chirped pulses has been widely employed for
controlling atomic [20, 26] and molecular [28, 101] systems.

Though well suited for two-level systems, population transfer with chirped
pulses in multilevel systems becomes sensitive to the exact value of the chirp
and field strength [24, 99], thus losing some of its appeal as a robust way of ef-
ciently manipulating populations. When used with spectrally broad strong ultra-
short pulses, frequency chirping can no longer selectively populate a pre-chosen su-
perposition of states [99, 101], and other methods of adiabatic [80] or non-adiabatic
strong-field excitation must be employed. In the latter case, the problem can be
treated in a purely empirical way by designing feedback-controlled experiments
with genetic search algorithms [71, 156]. Notably, the solution of Ref.[156], as
well as the alternative approaches of strong-field population transfer [46, 170] in-
volve an accumulative action of sequences of laser pulses [113]. Yet the robustness
and efficiency of the AP method has not been fully achieved.

Recently, we have demonstrated theoretically that one can implement AP with
ultra-short pulses by executing the transfer of population in a piecewise manner
[131, 132]. The original work on Piecewise Adiabatic Passage (PAP) [131] pro-
posed using two temporally overlapping pulse trains. It was shown that one can
bring about a complete population transfer between two quantum states through a
third intermediate level. In this Thesis we present the first experimental demon-
stration of the PAP method with a single pulse train by introducing the technique of
“piecewise chirping”. We show that the piecewise population transfer reproduces
an AP process executed with a continuous frequency-chirped pulse, achieving com-
parable level of robustness and efficiency.

Consider a system of two states, $|1\rangle$ and $|2\rangle$, of energies $E_1$ and $E_2$, driven
by a near-resonant field with a frequency detuning $\Delta$ relative to the transition frequency $\omega_0 = (E_2 - E_1)/h$. An arbitrary coherent superposition of these states can be written in the “laser” reference frame in terms of two angles, $\theta$ and $\phi$, as

$$\psi = \cos \frac{\theta}{2} \exp[-iE_1 t/\hbar] |1\rangle + \sin \frac{\theta}{2} \exp[-i(E_2/\hbar - \Delta)t + i\phi] |2\rangle,$$

This state can be represented as a unit Bloch vector pointing along the $(\theta, \phi)$ direction. The Rotating Wave Approximation results in two eigenstates, $\psi_+ \text{ and } \psi_-$, which constitute two stationary points on the Bloch sphere, $(\theta_\pm, \phi_\pm)$. Here, $\tan \theta_\pm = \pm \Omega/\Delta$ and $\phi_\pm = \pm \pi/2$, $\Omega$ being the Rabi frequency. All other solutions of the time dependent Schrödinger equation precess around the axes defined by the above stationary points, displaying periodic trajectories of the familiar Rabi oscillations [2].

In conventional AP with chirped pulses, $\Delta$ and $\Omega$ are slowly varied in time. If initially $\Delta \ll |\Omega|$, and at the end of the process $\Delta \gg |\Omega|$, there is an interchange of populations between state $|1\rangle$ and state $|2\rangle$. This is reflected on the Bloch sphere as a movement of the stable points from the $\theta = 0$ direction to the $\theta = \pi$ direction and vice versa. The above behavior holds as long as the adiabaticity condition is maintained:

$$|\dot{\theta}(t)| \ll \sqrt{\Delta^2(t) + \Omega^2(t)} \quad (2.13)$$

In the “transition” frame, which rotates around the $z$-axis with the angular velocity $\Delta(t)$ relative to the laser frame, the Bloch vector during AP proceeds via a spiral trajectory, as shown in Fig.2.13(a) (see also Ref.[171]).

We now consider the evolution of the Bloch vector in the transition frame under the action of a train of short, mutually coherent, laser pulses. Each pulse, centered at the transition frequency $\omega_0$ and of duration $\tau$, generates a rotation $\hat{P} \equiv R(\alpha_P)$ of the Bloch vector by an angle $\alpha_P = \int_\tau \Omega(t) dt$ around an axis lying in the $(x,y)$ plane. If the relative phase of the carrier oscillations of two pulses is zero, the corresponding rotation axes coincide. To account for the change in the carrier phase between consecutive pulses, instead of changing the rotation axis each time, we fix it along $y$, but introduce an additional $z$-rotation of the Bloch vector between the pulses, $\hat{F} \equiv R_z(\alpha_F)$. The overall evolution may be represented by a sequence
Figure 2.13: Two calculated sample trajectories of the Bloch vector (thick gray arrow) during the AP process implemented in atomic Rb with a single continuous chirped pulse (a), and a train of 20 ultra-short pulses (b)(see text).

of rotations \( \hat{U} = \ldots \hat{\Phi} \hat{P} \hat{P} \ldots \) The product \( \hat{\Phi} \hat{P} \) of two rotations is an overall rotation by an angle \( \alpha_0 \) about an axis defined by the \((\theta_0, \phi_0)\) angles, given to lowest-order expansion in \( \alpha_p, \alpha_F \) as

\[
\begin{align*}
\alpha_0 &= \sqrt{\left(\frac{\alpha_p^2 + \alpha_F^2}{2}\right)}, \\
\phi_0 &= \pm \frac{\pi}{2} - \frac{\alpha_F}{2}, \\
\tan \theta_0 &= \pm \frac{\alpha_p}{\alpha_F}.
\end{align*}
\]

By maintaining the same value of \( \alpha_F \) and \( \alpha_p \) throughout the pulse train we induce piecewise rotations of the Bloch vector around the closest stable point \((\theta_0, \phi_0)\). By slowly varying the values of \( \alpha_p, \alpha_F \) we can make the stable points move and the Bloch vector, captured near one of them, follow. Intuitively, the conditions of such piecewise following are: (i) the y- and z-rotations should be small (i.e. each pump pulse should induce an angular change much smaller than \( \pi \) and each increment in the carrier phase should be small too), and (ii) \((\theta_0, \phi_0)\) should not move much from pulse to pulse, i.e.

\[
\Delta \theta_0 \ll \sqrt{\frac{\alpha_p^2 + \alpha_F^2}{2}}.
\]
If initially $\alpha_p \ll |\alpha_F|$, the two stationary points, $\theta_0 = 0$ and $\theta_0 = \pi$, correspond to the bare states $|1\rangle$ and $|2\rangle$. As $\alpha_p$ increases and $|\alpha_F|$ decreases, the states originating in $|1\rangle$ and $|2\rangle$ move towards the equator of the Bloch sphere. They cross the equator as soon as $\alpha_F$ changes sign, and finally interchange with each other. Depicted in the original transition frame, the trajectory of the Bloch vector is a piecewise spiral, as shown in Fig.2.13(b).

The above analysis shows that the adiabatic following, similar to that implemented with the continuous chirped pulse, can be executed by a sequence of pulses with slowly varying amplitudes, and with the absolute carrier phase changing from pulse to pulse in a non-linear way (i.e. decreasing $\alpha_F$ in the first half of the process and increasing $\alpha_F$ in the second). An example of such AP, corresponding to the piecewise population transfer in atomic Rb, is shown in Fig.2.14. Here, the field is given by a sequence of 20 femtosecond pulses. For the $k$-th pulse ($k \in [0, 20]$)

$$E_k(t) = A_k \cos [\omega_0 t + \Phi_k] \times \sin^2 \left[ \frac{\pi t - t_k}{\tau} \right] \quad (2.18)$$

where $t_k$ marks the beginning of the $k$-th pulse, with $\tau = 300$ fs being its full duration. The $A_k$ amplitude represents the train envelope parametrized as a Gaussian of 3 ps width (FWHM), and $\omega_0$ is the transition frequency between the states $|1\rangle = 5s_{1/2}$ and $|2\rangle = 5p_{1/2}$ of Rb. The “piecewise chirp” of the pulse train is determined by the extra phase factor $\Phi_k = \bar{\alpha} (k - k_0)^2 / 2$, where $k_0 = 11$ and $\bar{\alpha} = 0.2$. As the pulse sequence proceeds, the pulse-to-pulse phase change, $\alpha_F = \bar{\alpha} (k - k_0) + \bar{\alpha} / 2$,

![Figure 2.14](image_url)

**Figure 2.14:** (a) The amplitudes (oscillatory, blue) and phases (piecewise parabola, red) of the driving field. (b) The populations of states $|1\rangle$ (falling, blue) and $|2\rangle$ (rising, green) during the PAP process.
smoothly evolves from large negative values to large positive values. Our simulations show that as long as the conditions of piecewise adiabaticity (2.17) are maintained, the population transfer is robust with respect to the pulse shapes, their intensities, and the exact value of the piecewise chirp $\bar{\alpha}$.

The population transfer by piecewise chirping described here is a particular example of the Piecewise Adiabatic Passage (PAP) concept introduced in Ref.[131]. In the limit of infinitesimal rotations, the present process becomes equivalent to the usual continuous frequency chirping, associated with the quadratic phase change of the carrier phase in time. In this limit, the coarse-grained adiabaticity condition (2.17) reduces, up to a numerical factor, to the familiar quantum adiabaticity condition (2.13).

In the proof-of-principle experiment, we studied one-photon excitation of atomic rubidium ($^{85}$Rb) from the ground to the excited electronic state, $5s_{1/2}$ to $5p_{1/2}$, respectively. The effect of a single frequency-chirped laser pulse was compared with the effect of a short pulse train described above. The pulses were produced by a Ti:Sapphire regenerative amplifier and had a spectral width of 7.1 nm (FWHM). We tuned the central wavelength of the laser to 795 nm, resonant with the $5s_{1/2} \rightarrow 5p_{1/2}$ transition. To generate a continuous or a piecewise chirp, the original pulse was spectrally shaped using a home made pulse shaper based on a double-mask liquid crystal spatial light modulator in the 4-$f$ configuration [167]. The excitation beam was focused with a long focal length lens ($f = 100$ cm) onto a cloud of rubidium atoms continuously evaporated from the rubidium dispenser in a vacuum chamber equipped with the time-of-flight ion detector.

To determine the population of the excited state, we ionized the atoms by a second, probe pulse tuned to 1300 nm and arriving in the chamber 2.5 ps after the excitation pulse (Fig.2.15(a)). The ion signal provides good selectivity between the ground and excited state Rb atoms because the ionization of $5s_{1/2}$ requires two more probe photons than that of $5p_{1/2}$. The power of the probe pulse was lowered to less then 0.1 $\mu$J so as to produce no detectable ions from the atoms in the ground state. To ensure ion sampling from the region of uniform excitation field strength, we confined the interaction region in the longitudinal direction by a 3 mm aperture placed between the rubidium dispenser and the laser beam. We suppressed the transverse spatial averaging by focusing the probe beam to a smaller...
Figure 2.15: (a) Experimental setup. Ion signal is measured for each excitation pulse (wide blue) followed by an ionizing probe (narrow red); (b) Amplitude (solid blue) and phase (dashed red) mask for generating a train of 9 pulses from a transform-limited pulse (dash-dotted black line). (c) FROG retrieval for the above pulse train with the temporal field amplitude (solid blue) and phase (dashed red), compared with the target quadratic phase of the pulses, $\Phi_k$ (black dots). All amplitudes are shown in arbitrary units.

spot size than the size of the 795 nm beam ($1/e^2$ beam diameters of 180 and 470 $\mu$m, respectively). The effect of the laser power fluctuations was eliminated by recording the energy of each excitation pulse together with the corresponding ion count.

The resolution of our spectral pulse shaper of 0.17 nm per pixel allowed us to split the original pulse into a sequence of up to 9 well separated pulses. Continuous chirping was applied by means of the quadratic phase-only modulation, $\phi(\omega) = \alpha(\omega - \omega_0)^2$, where $\alpha$ is the linear chirp and $\omega_0$ is the center frequency of the pulse. Generation of a pulse train requires both the amplitude and phase modulation of the field spectrum. A sequence of $N$ replicas of the original transform-limited pulse
with the real amplitudes $A_k$ and phases $\omega_0 t + \Phi_k$, separated by the time interval $\tau$ were obtained with the following complex spectral mask:

$$S(\omega_n) = \sum_k A_k e^{-i(k\omega_n \tau + \Phi_k)} / |S|,$$

(2.19)

where the frequency $\omega_n$ corresponds to the $n$-th pixel of the pulse shaper, and the normalization factor $|S|$ was used to satisfy $|S(\omega_n)|^2 \leq 1 \forall n$. Examples of the applied spectral shaping and the corresponding pulse train, characterized by the method of frequency resolved optical gating (FROG), are shown in Fig. 2.15(b,c).

In Fig. 2.16 we show the measured ion count corresponding to the population of the $5p_{1/2}$ state of rubidium for various parameters of the excitation field. The oscillatory (blue) curve in plot (a) represents the well known Rabi oscillations as a function of the energy of a single transform-limited pulse. This and all other experimental data points were normalized to the first maximum of this curve at around 0.1 $\mu$J. Similar oscillatory dependence in plot (b) corresponds to the train of 7 pulses with Gaussian envelope of amplitudes and zero piecewise chirp, namely $A_k = \exp(-k^2 \ln 2/4)$ and $\Phi_k = 0$ where $-3 \leq k \leq 3$. The temporal separation between the pulses in the train was 400 fs. As expected, the integrated pulse area of the train is larger than the corresponding area of a single pulse with the same total energy. The difference stems from the different scaling of the pulse area and pulse energy with the field amplitude (first and second power, respectively), resulting in the smaller period of Rabi oscillations for the piecewise excitation.

When either continuous or piecewise chirp is applied to a single excitation pulse or a series of pulses, respectively, the amount of excited Rb atoms ceases to oscillate with the pulse energy. In both cases it saturates at the maximum value and becomes insensitive to the excitation field strength in the typical AP way (red circles in Fig. 2.16(a,b)). We attribute the decay of both the amplitude of the Rabi oscillations and the saturated signal to the weak pre-pulse generated by our laser system 3 ns prior to the main pulse. To demonstrate the significance of the quadratic phase in the piecewise excitation, Fig. 2.16(b) also shows one example of the observed signal for a pulse train with randomly chosen $\Phi_k$ (black crosses). Different sets of random $\Phi_k$ produced different shapes of the energy dependence, but none of them resulted in the AP-like saturation of the population of the excited state close to the
Figure 2.16: Measured (dots) and calculated (lines) population of the excited state for a single pulse (a,c) and a train of 7 pulses (b,d). In (a) and (b), the efficiency of the population transfer is shown as a function of the integrated pulse energy. Blue diamonds and solid lines represent Rabi oscillations; red circles and dashed lines correspond to continuously (a) and piecewise (b) chirped excitation with $\alpha = 20 \times 10^3$ fs$^2$ and $\bar{\alpha} = 1$ radian, respectively. Black crosses in (b) represent an example of random distribution of phases $\Phi_k$. In (c) and (d), the efficiency of the population transfer is shown as a function of the continuous and piecewise chirp, respectively. In both cases, the energy of the excitation field corresponds to the first minimum of the respective Rabi oscillation. Experimental signals on all 4 plots are normalized to the maximum of Rabi oscillations in plot (a).
maximum value.

The stability of the adiabatic passage is reflected in the dependence of the transfer efficiency on the magnitude of the chirp. In both the continuous and piecewise scheme, we set the unchirped pulse area to $2\pi$ (energy of 0.31 and 0.07 $\mu$J, respectively). The result of scanning the conventional chirp from $-10^4$ to $+10^4$ fs$^2$ is similar to scanning the piecewise chirp $\bar{\alpha}$ between -1.5 and +1.5 radians, attesting to the similar mechanisms of the two processes. Note the decay of the excited state population at $|\bar{\alpha}| > 1.5$ rad in plot (d), caused by the breakdown of the piecewise adiabaticity due to the increasingly high phase increments from pulse to pulse in the pulse train. Fig.2.16 also shows the results of numerical simulations. The only fitting parameter was the area of the excitation beam. FROG traces were used to define the temporal profile of the pulses.

Unlike the adiabatic transfer with continuously chirped pulses, PAP can be easily generalized to a wide class of cases. One can consider replacing states $|1\rangle$ or $|2\rangle$ by wave packets composed of many individual eigenstates, with the population transfer executed with a train of pulses separated in time by the wave packet’s vibrational period. The ability to control the shape of the wavepacket by shaping the pulses in the train positions PAP as a powerful tool in controlling molecular dynamics.

### 2.3 Complete transfer of populations from a single state to a pre-selected superposition of states using Piecewise Adiabatic Passage: Experiment.

#### 2.3.1 Remarks

Experimental work reported in the previous section demonstrated the validity of PAP and some of its properties. The goal of the next experiment was to observe PAP into a wavepacket, and to study its properties further.

Significant satellite pulses about 2.8 ps prior to the main pulse of the amplifier were detected during the previous experiment. The existence of these pre-pulses can be seen in Fig.2.12. Even when the probe pulse arrives earlier than the excitation pulse, i.e. at times earlier than 1.5 ps, the ionization rate is not zero. In
that figure, zero ion rate was detected at 0.5 ps, by blocking the excitation pulse completely.

The origin of the observed pre-pulses was traced to a leakage of light through the Pockel’s cell in the regenerative amplifier. This mechanism means that a pre-pulse and the main pulse are not coherent, which lowers the degree of coherence of the excited target state. To mitigate this problem, in the following experiment we used an OPA as a source of excitation pulses. Due to the non-linearity of optical parametric amplification, pre-pulses were completely eliminated.

We demonstrate a method of adiabatic population transfer from a single quantum state into a coherent superposition of states. The transfer is executed with femtosecond pulses, spectrally shaped in simple and intuitive manner, which does not require iterative feedback-controlled loops. In contrast to non-adiabatic methods of excitation, our approach is not sensitive to the exact value of laser intensity. We show that the population transfer is complete, and analyze the possibility of controlling the relative phases and amplitudes of the excited eigenstates. We discuss the limitations of the proposed control methods due to the dynamic level shifts and suggest ways of reducing their influence.

2.3.2 Motivation

Population transfer from one energy state to a coherent superposition of states (i.e. a “wavepacket”) is an important tool in atomic and molecular physics and chemistry. Preparation of a wavepacket with well defined amplitudes and phases of the constituent eigenstates is the starting point for many techniques in precision spectroscopy [41, 143], coherent control of molecular dynamics and chemical reactions [135], in the design of atomic clocks [42] and fault tolerant quantum computing schemes [110]. Non-adiabatic Rabi cycling can be extended to the case of a multilevel target state [187], but suffers from the following complications.

Because of the difference in transition dipole moments to different excited eigenstates, a single transform-limited pulse can not, in general, serve as a $\pi$-pulse for all transitions simultaneously. Recently, we have shown that such non-uniformity of dipole moments can be compensated using the technique of spectral pulse shaping [187]. Rabi frequencies, and therefore pulse areas, for each transi-
tion can be equalized by adjusting the amplitudes of the corresponding frequency components of the excitation pulse. The required amplitudes are, however, not easy to find due to the dynamic Stark shifts of the energy levels. As illustrated in Fig. 2.17(a), strong polychromatic field changes the instantaneous resonant frequencies of atomic transitions, making the necessary (for a $\pi$-pulse) resonance condition hard to satisfy throughout the whole excitation process. Similar scenario has been considered in a two-photon excitation scheme, where the required pulse shaping has been found by means of iterative feedback controlled loops [155].

In contrast to the above, the method of Adiabatic Passage (AP) is less sensitive to the parameters of the driving field, transition dipole moments and resonant frequencies [57, 99, 163]. In AP, the dynamics of a quantum system is described by a time-dependent Hamiltonian, whose instantaneous “adiabatic” eigenstates are essentially decoupled from one another as long as the field is strong and its parameters are changing slowly [104]. Each adiabatic state is a coherent superposition of bare eigenstates of a field-free Hamiltonian. As the parameters of the interaction field change in time, projections of each adiabatic state on the bare-state basis set are evolving accordingly. By making one of the adiabatic states coincide with the initial state of an atom at the beginning of the interaction, and with the target excited state - at the end, one can achieve robust and complete transfer of population as long as the adiabaticity conditions are satisfied throughout the interaction.

Adiabatic passage between two states is most commonly executed by sweeping, or “chirping”, an instantaneous frequency of the driving field across a resonance. Adiabatic crossing of the excited state by the ground state dressed with a photon field results in complete population transfer between those two states. AP into multi-level wavepackets have been recently considered in two distinct interaction scenarios: with multiple phase-locked narrowband laser fields [80, 85, 150], and a single spectrally shaped broadband pulse [133]. The latter approach provides a simple strategy of shaping the pulse in accord with the energy level structure of the system of interest. Introducing local frequency chirp around each resonant transition frequency (Fig. 2.17(b)), simultaneous AP is initiated into multiple target states which make up the final wavepacket. Figure 2.17(b) provides an intuitive illustration of the robustness of the method, not only with respect to the field amplitude and frequency, but also with respect to the dynamic level shifts associated
Figure 2.17: Illustration of the interaction of a multilevel system with polychromatic coherent radiation consisting of a number of discrete spectral components (red vertical arrows). Dashed lines represent the ground state “dressed” with a photon. Bare excited states of the system (solid lines) are dynamically shifted in energy due to the presence of non-resonant components of the laser field. This results in incomplete population transfer via non-adiabatic process (a). When the spectral components are simultaneously chirped in frequency (b), adiabatic transfer into a coherent superposition of excited states is executed. Different timing of the level crossings (gray arrows) complicates the control over the resulting wavepacket, but does not affect the completeness of excitation.

with the presence of a strong polychromatic field. Indeed, crossings of the dressed ground state with multiple excited states will occur even if the latter are heavily perturbed by the off-resonance components of the driving field. Dynamic shifts of transition frequencies result in a slightly different timing of each adiabatic crossing. As we show here, this lack of synchronism between multiple APS slightly complicates the control of the makeup of the target wavepacket, but does not reduce the efficiency of population transfer.
In the time domain, the interaction picture is especially intuitive when the target states are equidistant in energy. In that case, shaping a pulse with multiple local frequency chirps results in a train of mutually coherent ultrashort pulses, separated by the evolution period of the wavepacket. Though each pulse in the train transfers only a small amount of population to the target superposition state, population of that state coherently accumulates [41, 144, 148] piece by piece, reaching 100% at the end of the interaction regardless of the total energy of the pulse train [133]. Shown in Fig 2.18 is an example of numerically calculated dynamics of such Piecewise Adiabatic Passage (PAP) into a wavepacket consisting of only two levels and driven by a train of ultrashort pulses.

The population transfer technique we are studying here can be viewed as a practical application of the $1 + N$-level control schemes, based on the Morris-Shore transform [108] and discussed in [85]. The selectivity of the transfer is obtained by tailoring the temporal and spectral profiles of the train of pulses to the target wavepacket dynamics [38, 39, 41, 170]. The correspondence between the properties of the pulse train and the target wavepacket dynamics has also been noted in the optimization studies aimed at either maximizing population transfer into a wavepacket [61, 86, 156] or stabilizing such transfer against the wavepacket spreading and decoherence [18]. Our method provides an alternative to the “multi-RAP” pulse sequences of [13] and "molecular π-pulses” used in exciting molecular wavepackets [8, 9, 24, 178]. The difference with the latter methods is manifest when the target wavepacket consists of more than two eigenstates [133].

Recently, we have demonstrated experimentally the method of piecewise adiabatic passage into a single excited state [185]. Here, we extend this method to the multi-level target states case, by exciting the fine-structure doublet in atomic Potassium. We show experimentally that one can achieve complete population transfer into such “spin-orbit” wavepacket with high degree of robustness. We also present a simple and intuitive approach to controlling the phases and amplitudes of the constituent eigenstates of the final superposition, and address its limitations.
Figure 2.18: Results of numerical simulations of piecewise adiabatic passage for Potassium atom. Population transfer is shown in (a) as a function of time. Blue solid line represents the ground state population while red dashed and green dotted lines correspond to the populations of $4p_{1/2}$ and $4p_{3/2}$ excited states, respectively. Excitation field amplitude is plotted in (b) on the same time scale.

2.3.3 Experimental setup and detection method

The relevant levels of Potassium atom are shown in Fig.2.19(a). Two fine-structure levels, $4p_{1/2}$ and $4p_{3/2}$, make up the target wavepacket, which is populated from the initial ground state $4s_{1/2}$. The $D_1$ ($4s_{1/2} \rightarrow 4p_{1/2}$) and $D_2$ ($4s_{1/2} \rightarrow 4p_{3/2}$) transitions at 769.9 and 766.5 nm, respectively, are excited by a single broadband laser pulse of 9.5 nm full width at half maximum (FWHM) centered at 768.2 nm. The latter (“pump”) pulse is produced by a traveling wave optical parametric amplifier (Fig.2.19(c)), pumped by a Ti:Sapphire femtosecond regenerative amplifier. The
Figure 2.19: (a) Relevant quantum states of Potassium. Blue double-peak curve represents the shaped spectrum of pump pulses, whereas red arrows depict possible channels of ionizing the atoms with probe pulses. (b) Spectral shaping of pump pulses with local frequency chirping around two electronic resonances at 766.5 and 766.9 nm: intensity (solid black) and phase (dashed red). Dash-dotted green line represents flat spectral phase used for a non-adiabatic excitation scheme. (c) Experimental setup. Two Optical Parametric Amplifiers (OPA) are pumped by a Ti:Sapphire regenerative amplifier (RGA) producing 130 fs 2 mJ pulses at 1 KHz repetition rate. One OPA is used to generate pump pulses of variable energy, controlled by an attenuator and measured by a fast photodiode. Pump pulses are shaped with a Pulse Shaper and are weakly focused on a cloud of Potassium atoms inside a vacuum chamber. Probe pulses are delayed by a variable time delay and tightly focused on the atomic cloud. Potassium atoms, ionized by probe pulses, are accelerated towards and detected by a multichannel plate based Ion Detector.
energy of pump pulses are attenuated and recorded with a fast photodiode prior to shaping. Hereafter, the reported pulse energies always correspond to the energy of unshaped pulses.

To apply spectral shaping, we use a home-made pulse shaper implemented in 4f geometry and based on a double-layer liquid-crystal spatial light modulator (SLM) [167]. The shaper controls both the phase and the amplitude of a pulse with spectral resolution of 0.14 nm. The amplitude is shaped by applying two Gaussian windows of variable relative height and width, each centered at one of the resonant frequencies (Fig.2.19(b)). Blocking of the non-resonant spectral components is important for achieving control over the target wavepacket, as discussed below. As shown in the figure, quadratic spectral phase is added to each Gaussian window, producing variable linear frequency chirp around the corresponding resonance. Prior to applying any spectral shape described below, the phase of pump pulses is flattened using the technique of multi-photon inter-pulse interference phase scanning (MIIPS [95]). Flat spectral phase is also used to drive Rabi oscillations as described below. The shaped pump pulses are then focused on a cloud of Potassium atoms evaporated from a Potassium dispenser inside a vacuum chamber.

The population of the excited coherent superposition state is detected by photoionizing the atoms with a second (“probe”) pulse. In order to probe the region of uniform pump intensity, the probe beam is focused much tighter than the pump pulse (beam diameters of 135 and 460 µm, respectively). The details of a wavepacket detection was discussed earlier in this Dissertation, see section 2.1.2.

2.3.4 Results

We first execute population transfer into each of the 4p states separately. Non-adiabatic interaction results in familiar Rabi oscillations which serve as a convenient tool for calibrating both the excitation pulse area and excited state population. The original spectrum and the two Gaussian windows of 1.8 nm FWHM used for amplitude shaping are shown in Fig.2.20(a). To drive Rabi oscillations on a selected transition, a single Gaussian filter was applied around the resonant frequency of $D_1$ or $D_2$ transition. Hereafter, we refer to the corresponding narrow-band pulses
as “$D_1$ pulse” and “$D_2$ pulse”, respectively. In both cases, the spectral phase was kept flat across the whole spectrum of a pulse. Rabi oscillations are shown in Fig. 2.20 for both $D_1$ (b) and $D_2$ (c) lines. Given the available laser power, we were able to reach pulse areas of up to $3\pi$ on each transition. By fitting the data with a $\sin^2 A_{1,2}$ function, we calibrate the areas of $D_1$ and $D_2$ pulses ($A_1$ and $A_2$, respectively) versus their energy. Simultaneously, we calibrate the magnitude of the ion signal corresponding to the pulse area of $\pi$. These calibrations are later used for assessing the completeness of the population transfer. The reasons for an incomplete return to the ground state, manifested as a non-zero ion signal at $2\pi$ pulse area, will be considered in the next section.

In order to execute an adiabatic passage into a single excited state, a frequency chirp is introduced by applying quadratic spectral phase shaping around one resonant frequency $\omega_{1,2}$, i.e. $\phi(\omega) = \frac{\alpha}{2}(\omega - \omega_{1,2})^2$ (Fig. 2.19(b)), while blocking the Gaussian window around the other resonance. The frequency chirp is gradually increased by the shaper until the population transfer shows AP-like saturation with intensity, such as that shown in Figs. 2.20(b,c) by open circles for both $D_1$ and $D_2$ transitions. Independent measurement of the applied chirp yields $\alpha = 270 \times 10^3$ fs$^2$. For both transitions, the ion signal reaches its maximum at a pulse area of $\approx \pi$ and stays relatively flat with increasing pulse energy. The maximum in the AP efficiency is seen to coincides with a maximal number of Rabi oscillations, attesting to nearly complete population transfer. The residual oscillations, reproduced in our numerical simulations (not shown), are due to the pixelization of the spatial light modulator which limits the maximum chirp value we can apply.

Once the pulse area and chirp required to satisfy adiabaticity conditions are determined, we can execute complete population transfer into a superposition of $4p_{1/2}$ and $4p_{3/2}$ states. If both states are populated coherently, quantum beats should be observed in the ionization signal as a function of the probe pulse delay according to the interference term in Eq.(2.2). In both the non-adiabatic and adiabatic approaches, the amplitude of the spectrum of the pump pulses is shaped by opening both the $D_1$ and $D_2$ Gaussian windows simultaneously. Interference of the $D_1$ and $D_2$ pulses in the time domain results in a train of pulses separated by a period of the quantum evolution of the wavepacket. The latter is inversely proportional to the fine-structure splitting of $4p$ state (1.73 THz) and equals 578 fs. A
Figure 2.20: Adiabatic and non-adiabatic excitation of a single ($4p_{1/2}$ or $4p_{3/2}$) excited state. (a) Pump pulse spectra used to excite either $D_1$ or $D_2$ transitions separately (solid blue and dashed red lines, respectively). Spectral profile of the initial unshaped femtosecond pulse is shown as dashed black curve. (b, c) Non-adiabatic (blue diamonds) and adiabatic (red circles) population transfer into $4p_{1/2}$ (b) and $4p_{3/2}$ (c) states. Ion signal, proportional to the target state population, is plotted as a function of the corresponding pulse area, $A_{1,2}$. Solid lines show the anticipated $\sin^2(A_{1,2})$ dependence fitted to the experimental data.
A numerical example of such pulse train is shown in Fig.2.18(b).

First, the spectral phase of pump pulses is kept flat across the whole double-peak spectrum. In the time domain, flat spectral phase translates into a train of pulses with constant carrier oscillation frequency and no extra phase shift between consecutive pulses [133]. The resulting Rabi oscillations between the ground state and the excited wavepacket are shown in Fig.2.21(a). The two-dimensional plot shows the ion signal as a function of the time delay (vertical axis) and effective pulse area (horizontal axis), which in the case of multiple excitation channels can be used as a convenient scale of the interaction strength. It is defined as:

\[ A_{\text{eff}} = \sqrt{A_1^2 + A_2^2} \quad (2.20) \]

where \( A_i \equiv \int_{-\infty}^{\infty} \Omega_i(t) \, dt \), with \( \Omega_i \) being the time dependent Rabi frequencies for the \( i \)-th transition.

Oscillations along the vertical axis indicate quantum beating between \( 4p_{1/2} \) and \( 4p_{3/2} \) states. Both the experimental and numerical plots (Fig.2.21(a,c)) demonstrate strong dependence of the result of the excitation on the effective pulse area. Rabi oscillations between the ground state and the excited wavepacket are manifested by the periodic re-appearance of the beat signal. Thus, high beating contrast at \( A_{\text{eff}} = \pi \) disappears almost completely at \( A_{\text{eff}} \approx 2\pi \), as shown by the vertical cross-sections of the two-dimensional data (white dashed lines) in plot (b).

We note that both the contrast of the beat signal and its phase are affected by an increase in the pulse energy. We attribute this phase change to the energy-dependent AC Stark shifts of the levels, caused by the strong non-resonant components of the polychromatic excitation field (see schematic illustration in Fig.2.17). In the case considered here, the \( 4p_{1/2} \) level is shifted due to the presence of an off-resonant \( D_2 \) pulse, whereas the \( 4p_{3/2} \) level is shifted by an off-resonant \( D_1 \) field. Since the shifts are in general unequal, the accumulated quantum phase of the two wavefunctions, \( |4S_{1/2}\rangle \) and \( |4S_{3/2}\rangle \), depends on the energy of both pulses. The effect is reproduced by the numerical calculations shown in Fig.2.21(c).

For pulse areas of order \( \pi \) and higher, typically needed for significant population transfers, such dynamic cross-talks between simultaneously driven transitions become substantial when the pulse bandwidth approaches the energy separation
Figure 2.21: Non-adiabatic population transfer into a superposition of $4p_{1/2}$ and $4p_{3/2}$ states. The two-dimensional plots (a: experiment, c: calculation) show the ion signal (color coded) as a function of the effective pulse area and pump-probe time delay. Oscillations along the vertical (time) axis reflect quantum beating due to the time evolution of the wavepacket. The quantum beats are shown in (b) for pulse areas of $\pi$ (solid blue) and $2\pi$ (dashed red), corresponding to the dashed vertical white lines in (a). In plot (d), we present the calculated populations of the two excited states, $4p_{1/2}$ (dash-dotted blue) and $4p_{3/2}$ (dashed green), and the relative phase (red dots) between the corresponding wavefunctions (in $2\pi$ units), as a function of the effective pulse area of the excitation field. The ground state population is shown as a solid black line.
between the levels. In this case, dynamic Stark shifts cannot be neglected and multiple interaction channels cannot be treated independently. This significantly complicates the non-adiabatic dynamics, making controlled and complete population transfer hard to achieve. Fig. 2.21(d) demonstrates the degree to which the dependence of the $|b_1(t)|^2$ and $|b_2(t)|^2$ populations on pulse energy deviates from the periodic Rabi oscillations behavior, once the effective pulse area exceeds $\pi$.

In striking contrast to Rabi flopping, when local chirp is added to both the $D_1$ and $D_2$ spectral windows (Fig. 2.19(b)), the observed quantum beats become insensitive to the pulse area (Fig. 2.22(a,c)). Using our experimental observation of separate adiabatic passages into each level (Fig. 2.20), we set the frequency chirp to $270 \times 10^3$ fs$^2$, for both the $D_1$ and $D_2$ pulses. As seen in Fig. 2.22(b), the contrast of the experimentally observed quantum beating changes only little throughout the wide range of pulse areas, $A_{\text{eff}} \approx \pi$ to $A_{\text{eff}} \approx 3\pi$. This demonstrates the stability of the population transfer against pulse energy in agreement with the adiabatic passage scenario.

Though clearly more stable than in the non-adiabatic regime, the beat signal gives only indirect evidence of the measure of the robustness of the population transfer. Unfortunately, extracting the absolute values of the population transferred to $4p_{1/2}$ and $4p_{3/2}$ from the measured beat signal proved inaccurate. We therefore calculate these populations numerically. The results, presented in Fig. 2.22(d), show that the population ratio varies with the excitation pulse energy. A number of simple approaches to controlling this ratio are discussed later in the text. For the time being we note that an increase in the pulse area leaves the phase of the excited wavepacket intact. This statement is confirmed experimentally and theoretically, as shown in panels (b) and (d), respectively.

In contrast to the non-adiabatic dynamics, AP exhibits a threshold at $A_{\text{eff}} \approx \pi$, beyond which the ground level remains empty, even though the population ratio between the excited levels may vary. This stability of the completeness of population transfer against variations in pulse energy is best demonstrated by comparing the numerical results of Figs. 2.21(d) and 2.22(d). It also forms the basis for the proposed schemes of controlling the population distribution among excited states. We therefore seek an independent experimental confirmation of the completeness of population transfer.
Figure 2.22: Adiabatic population transfer into a superposition of $4p_{1/2}$ and $4p_{3/2}$ states. The two-dimensional plots (a: experiment, c: calculation) show the ion signal (color coded) as a function of the effective pulse area and pump-probe time delay. The oscillations along the vertical (time) axis reflect quantum beating due to the time evolution of the wavepacket. The quantum beats are shown in (b) for pulse areas of $\pi$ (solid blue) and $2\pi$ (dashed red), corresponding to the dashed vertical white lines in (a). In plot (d), we present the calculated populations of the two excited states, $4p_{1/2}$ (dash-dotted blue) and $4p_{3/2}$ (dashed green), and the relative phase (red dots) between the corresponding wavefunctions (in $2\pi$ units), as a function of the effective pulse area of the excitation field. The ground state population is shown as a solid black line.
Figure 2.23: Demonstration of the population transfer completeness. (a) Ion signal as a function of the pump-probe time delay for a sequence of frequency chirped $D_1$ and $D_2$ pulses separated by 8 ps (The time when the second pulse is present is between two dashed vertical lines). Filled black (red or gray) dots correspond to the signal before (after) the arrival of the second pulse. (b) Fourier transform of the ion signal before (solid blue) and after (dashed red) the arrival of the second pulse (log scale). The frequency of the quantum beating (1.73 THz) is where a strong peak is expected in the case when both states are populated.
In the experiments described above, we have used Rabi oscillations between the ground state and one of 4\(p\) excited states for calibrating the population transfer efficiency, assuming that the first maximum of these oscillations corresponds to a complete transfer. However, even though a \(\pi\)-pulse is expected to drive the whole population to the excited state, it is conceivable that completeness is not fulfilled due to the sensitivity of the latter to frequency detuning. In order to perform an independent check of the completeness of the population transfer, we have carried out the following experiment: We delay the \(D_1\) pulse by approximately 8 ps with respect to the \(D_2\) pulse by inserting a thin piece of glass in front of the corresponding spectral window in the Fourier plane of the pulse shaper. If the \(D_2\) pulse, arriving first, drives all the atoms to \(p_{3/2}\) state and depletes the ground state, the \(D_1\) pulse, arriving second, will leave the system unchanged. As all atoms are residing in a single \(p_{3/2}\) state, no quantum beats would be observed. Alternatively, if the excitation driven by the first pulse is not complete, the second pump pulse would move the remaining ground state population to \(p_{1/2}\) state, resulting in the appearance of quantum beating.

To verify this, we set the areas of both \(D_1\) and \(D_2\) pulses (now separated in time) to \(\pi\), and their frequency chirp to \(270 \times 10^3\) fs\(^2\). As can be seen in Figs. 2.20(b,c), these parameters are sufficient for reaching maximum population transfer to either \(p_{1/2}\) or \(p_{3/2}\) when the corresponding pulse is acting alone. The results of the interaction with a sequence of two pulses are presented in Fig. 2.23. The first pulse arrives at approximately 0 ps, while the time of arrival of the second pulse is about 8 ps. Fourier analysis of the ion signal after the arrival of the second pulse (Fig. 2.23(c)) shows essentially no quantum beating, ensuring that the population of 4\(p_{1/2}\) state is below 3%.

As pointed out by us in the past [133], piecewise adiabatic passage potentially combines the efficiency and robustness of AP with the ability to excite complex superposition states (e.g. wavepackets) and control the makeup of the excited state wavefunction [133]. Control over the phase of a spin-orbit wavepacket in Potassium has been previously demonstrated experimentally in the weak field regime [27]. Here we show that the relative phase between the two eigenstates of the target superposition can be controlled even when the field is strong enough to ensure the adiabaticity of process. Control over the phase is implemented by adding an
**Figure 2.24:** Experimental control over the quantum phase of an excited wavepacket. (a) To control the relative phase of the eigenstates in the target superposition state, an extra constant phase shift of 0 (red), \(\pi/2\) (green) and \(\pi\) radian (blue) is added to the spectral phase of \(D_1\) pulses. Black dashed line shows the double-peaked spectral amplitude of the pulse. The introduced phase shift results in a corresponding vertical shift of the detected quantum beats shown in (b). (c) Vertical cross-sections of the two-dimensional scans in (b) at pulse area of \(\pi\). Blue (diamonds), red (squares) and green (circles) corresponds to 0, \(\pi/2\) and \(\pi\) phase shifts of \(D_1\) pulse.
Figure 2.25: Quality of population control with piecewise adiabatic passage. Numerical simulations demonstrate possible discrepancy between the achieved population ratio $\beta$ of two $4P$ states (vertical axis) and its target value (horizontal axis), for different control methods (see text for symbol description).

extra constant phase to one of the pulses, $D_1$ or $D_2$, on top of the local frequency chirp in the respective spectral window. The resulting phase profile, attained using the pulse shaper, is shown in Fig.2.24(a) for a relative phase of 0, $\pi/2$ and $\pi$ radian. Two-dimensional energy-time scans for these three phase shifts are shown in panel (b). The vertical cross-sections of each two-dimensional plot, displaying quantum beat patterns corresponding to $\approx \pi$ pulses, are plotted in panel (c). The phase of the oscillations, which directly reflects the relative phase of $p_{1/2}$ and $p_{3/2}$ eigenstates, closely follows the extra phase shift introduced via the pulse shaper.

One may expect that the amplitudes of the eigenstates in the target superposi-
tion can be controlled individually, similarly to the phase control described above. As was shown in [133] for the case of negligible Stark shifts, the state amplitudes at the end of the interaction are simply proportional to Rabi frequencies of the corresponding transitions. Thus, the distribution of populations among excited states (here, 4p_{1/2} and 4p_{3/2}) can be controlled by changing the relative strength of the corresponding spectral components of the excitation field (here, the energies of D_1 and D_2 pulses). This simple strategy fails, however, once the dynamic Stark shifts become comparable to the energy bandwidth of the laser pulses. This situation is illustrated in Fig.2.17(b), where one can see that unequal Stark shifts effectively change the time at which each adiabatic passage is executed. The farther these APs from being simultaneous, the bigger the deviation of the population distribution from the expected one.

In principle, the ratio between the populations in a wavepacket can be retrieved from the contrast of the quantum beats and the total population of the wavepacket can be retrieved from the ion rate averaged over time. However, poor accuracy of this retrieval did not allow us to investigate the possibilities of amplitude control experimentally. Here, we present numerical analysis of various ways of achieving reasonably high degree of control over the excited state populations by either avoiding, or compensating for the detrimental effects of the Stark shifts. The results are summarized in Fig.2.25 in which the calculated ratio $\beta \equiv |b_1|^2 / |b_2|^2$ is plotted versus its target value for different control methods. In all calculations, the effective pulse area was set to $\pi$, and the local spectral chirps near D_1 and D_2 lines was equal to $270 \times 10^3$ fs$^2$.

We first note that for the parameters used in our experiments, calculated values of $\beta$ (red circles) lie within 37.5% of those expected from a simple model which does not take Stark shifts into account (diagonal dashed line). Assuming the correct phases of the state amplitudes, this corresponds to the transfer fidelity (projection on the target wavepacket) varying between 1 and 0.997. The discrepancy can be further reduced by narrowing the spectral bandwidth of the excitation pulses. Decreasing it from 1.8 nm (as used here) to 0.18 nm, dramatically improves the quality of amplitude control, marked as blue diamonds. It is important to note that such improvement comes at the expense of much longer (by a factor of 10) interaction time, and higher spectral resolution of a pulse shaper, which will be
necessary for the frequency chirping of a spectrally narrower pulse.

Unlike the case of independent adiabatic passages, i.e. when Stark shifts can be ignored, the Stark-induced dynamical cross-talk between different AP channels makes $\beta$ sensitive not only to the ratio of $D_1$ and $D_2$ pulse energies, but also to their sum. This certainly reduces the robustness of the proposed method of amplitude control, though not the robustness of PAP itself. In other words, in PAP, the population transfer remains complete, even though the shape of the excited wavepacket may change in response to changes in the overall pulse energy. Utilizing this important property of piecewise adiabatic passage, we suggest a simple adaptive strategy of controlling the eigenstate amplitudes in the excited superposition state. By accurately measuring populations of the excited states (not available in our current experimental setup), a correction can be introduced into the relative energy of each spectral component of the excitation field, proportional to the deviation of the observed population distribution from its target shape. The numerical results of such an iterative procedure appear as green triangles in Fig. 2.25. After only two iterations, the calculated ratio between $|b_1|^2$ and $|b_2|^2$ is brought within 0.2% of its target value! Unlike the more general schemes of adaptive control [71], the present technique involves only as many control variables as there are excited states (in our case, two), and converges very quickly due to the inherent robustness of AP.

2.3.5 Conclusion

We have presented experimental and numerical studies of the population transfer using piecewise adiabatic passage from a single ground state to a superposition of excited states. As in conventional adiabatic population transfer into a single state, our method of piecewise adiabatic passage into a wavepacket is insensitive to the driving field amplitude. The method allows for complete population transfer and offers control of both the phase and amplitudes of the eigenstates composing the target superposition state. The latter are retrieved by applying bichromatic control to the process of photoionization.
2.4 **Strong-field effects in Rabi oscillations between a single state and a superposition of states**

Rabi oscillations of quantum population are known to occur in two-level systems driven by spectrally narrow laser fields. In this work we study Rabi oscillations induced by shaped broadband femtosecond laser pulses. Due to the broad spectral width of the driving field, the oscillations are initiated between a ground state and a coherent superposition of excited states, or a “wavepacket”, rather than a single excited state. Our experiments reveal an intricate dependence of the wavepacket phase on the intensity of laser field. We confirm numerically that the effect is associated with the strong-field nature of the interaction, and provide a qualitative picture by invoking a simple theoretical model.

Efficient transfer of population from one energy eigenstate of a quantum system to another eigenstate is an important tool in many fields of physics and chemistry such as control of molecular dynamics and chemical reactions [135], quantum computing and information processing [110], precision spectroscopy [41], cold and ultra-cold chemistry [43] and nanoscience [80]. In the simplest case of a two-level atom interacting with a resonant electro-magnetic field, the dynamics of the atomic population, described by Maxwell-Bloch equations, exhibit well known periodic Rabi oscillations [2, 136]. The phase of these oscillations is directly related to the notion of “pulse area”. When the latter assumes the value of $\pi$ (so-called “$\pi$-pulse”), the transfer of quantum population between the two levels is complete.

Rabi oscillations serve as a convenient calibration tool for measuring the pulse area and excited state population. Being a function of the pulse duration, intensity, detuning from resonance, and the transition dipole moment, an experimentally measured pulse area enables retrieving one of these parameters if the others are known. The contrast of Rabi oscillations reflects the degree of coherence of an atom-photon interaction, and can be utilized for assessing the coherence properties of either the atomic (molecular) system or the applied electromagnetic field.

Although $\pi$-pulses and Rabi oscillations between metastable states of atoms and molecules are observed and exploited quite routinely, e.g. between Rydberg states [123, 138] or spin states in Bose-Einstein condensates [176], population oscillations between two electronic states are much harder to detect due to quick,
typically nanosecond, spontaneous decay of electronic coherence [122]. Shortening the excitation pulses beyond this time scale results in two complications. First, nonlinear effects, such as AC Stark shift and multi-photon ionization, become non-negligible as their efficiency increases with decreasing length of a π-pulse [156]. Second, the spectral width of short pulses becomes comparable with the energy level spacing in the atomic or molecular spectrum, making the two-level approximation invalid. In the regime when the population of the quantum states participating in the interaction changes substantially, the perturbative approach, often invoked in ultrafast quantum electronics [44, 118], is not applicable [32, 154]. Hence, multiple excited states cannot be treated as independently driven by separate resonant frequency components of an excitation pulse.

Coherent population transfer with broadband laser pulses has been the focus of much experimental and theoretical work in the last two decades. The population dynamics and the origin of population oscillations are qualitatively different in weak and strong laser fields. In the case of an excitation by weak laser pulses (i.e. with pulse areas much smaller than π) driving a single photon transition, the final quantum state of an atomic system is defined solely by the resonant spectral component of the applied laser field, and the population of the target excited state is linearly proportional to the spectral power density at the transition frequency [46]. In this perturbative regime of interaction, oscillatory dynamics of the excited state population have been observed and attributed to coherent transients [181]. The latter have been used for quantum state reconstruction [106] and for enhancing the excited state population by means of femtosecond pulse shaping [45].

Two-photon weak-field transitions offer another mechanism of population oscillations due to the presence of resonant intermediate states. Quantum interferences arising from the evolution of the intermediate wavepacket have been studied and used for temporal control of an atomic population [16]. Weak shaped femtosecond pulses have also been utilized to control two-photon transitions without a resonant intermediate state [102, 103, 118]. Similarly to weakly driven single-photon transitions, the final excited state population in the case of a two-photon resonance is described by the second order perturbation theory, and is proportional to the resonant spectral component of the second harmonic. The latter depends on the phase shaping applied at the fundamental frequency, which may therefore lead
to the population oscillations of the target state.

In this work we discuss the oscillations of atomic population in strong fields, governed by the non-perturbative regime of atom-photon interaction. Two-level atoms in strong laser fields have been thoroughly studied in a series of works on selective population of dressed states (SPODS! [169-171]) both with transform-limited and shaped femtosecond pulses. An oscillatory behavior of the excited state population as a function of the laser intensity has been observed in atomic Potassium [169] and Rubidium [185] providing direct evidence of femtosecond Rabi oscillations in a two-level system. Frequency chirping has been used to selectively populate dressed states of an atom subject to a strong laser field [13, 171]. Pulse trains have also been utilized for controlling population transfer in the strong-field interaction regime. Relative phase between the pulses in the train has been shown to control the adiabaticity of the population transfer process [153, 185] and to provide selectivity in populating a single dressed state [170, 174].

When applied to multi-level systems, strong laser fields often shift the energy of near-resonant atomic levels, creating a number of time-dependent dressed states evolving on a femtosecond time scale [78]. When the energy of two such states become equal, the quantum system undergoes an avoided crossing. Quantum interferences between adiabatic and non-adiabatic routes through the avoided crossing result in the oscillations of the target state population [6, 20, 68, 81, 98]. In this strong-field interaction regime, frequency chirping and adaptive feedback loops have been exploited for increasing the population of a single target state [156] up to a complete population transfer [81].

The ability to cover several target states simultaneously by the broad spectrum of an ultrashort laser pulse offers an opportunity to transfer population into a coherent superposition of states, or a “wavepacket”, rather than a single target state. The oscillatory dynamics of the electronic wavepackets created by weak ultrashort pulses have been observed in a number of femtosecond pump-probe experiments [31, 109, 180]. In these studies, the perturbative regime of interaction ensures that the wavepacket dynamics are independent on the strength of the applied laser field. Control of the wavepacket phase by means of a spectral phase shaping of pump pulses has been demonstrated [26, 27].

In a series of recent works [133, 186], we have demonstrated how a complete
population transfer can be executed between a single state and a wavepacket. The method is based on a quasi-adiabatic evolution of the system in strong laser fields, as confirmed by the demonstrated robustness of the population transfer against uncertainty in laser intensity and wavelength. Surprisingly, despite the strong applied fields needed for the adiabatic passage, the phase of the excited wavepacket has been shown to obey the rules dictated by the perturbation theory. That is, similar to [26, 27], changing the phase of the resonant spectral components of the excitation pulse resulted in the corresponding change of the wavepacket phase [186]. The effect stems from the following argument. For the adiabatic passage to work in the case of a multi-level target state, it has to be carried out in a piecewise manner with a train of mutually coherent femtosecond pulses. Even though the accumulative pulse area of the whole train is high (> 4\pi), individual pulses in the train are relatively weak, which enables the perturbative control scheme of the target wavepacket.

The situation is qualitatively different if the wavepacket is created by a single strong laser pulse. Dynamic Stark shifts of the atomic levels forming the wavepacket result in an intensity dependent phase, which has to be taken into account on any route to strong-field coherent control [154]. In this paper, we present an experimental observation of Rabi oscillations between a single ground state and a spin-orbit electronic wavepacket, initiated by a strong unshaped laser pulse. We study the dependence of the wavepacket phase on the applied pulse area, and discuss the observed non-trivial step-like phase behavior using a simple model.

Our experimental setup, shown in Fig.2.26, has been described in our earlier paper [185] (see Fig.2.26(a)). Briefly, it consists of a regenerative femtosecond Titanium-Sapphire amplifier producing 2mJ, 130 fs pulses at 1 KHz repetition rate and central wavelength around 800 nm. The laser beam is split into two parts. The first (“excitation”) beam is used to drive Rabi oscillations of atomic population between the ground and excited electronic state(s) (thick blue arrows in Fig.2.26(b,c)). In some cases, an optical parametric amplifier (OPA, not shown) has being used for generating excitation pulses as described in [186]. Excitation pulses are spectrally shaped with a home made liquid crystal based pulse shaper [167], and weakly focused onto a vapor cloud of either Rubidium or Potassium atoms inside a vacuum chamber (shaded blue beam in Fig.2.26(a)). To determine the ex-
cited state population, we ionize the atoms with a weak 120 fs infrared “probe” pulse, generated by an OPA pumped with the second part of the 800 nm beam. Probe pulses follow excitation pulses with a variable time delay, and are focused much tighter on the central part of the interaction region (unshaded red beam in Fig.2.26(a)). We are able to detect the excited state population with good selectivity because the ionization of the ground state requires two more photons and is therefore negligibly weak (Fig.2.26(b,c)).

In the case of a resonant excitation by a laser pulse with the electric field envelope $\varepsilon(t)$, the final population of the excited state oscillates as $\sin^2\left(\frac{A}{2}\right)$ [2], where $A := \int_{-\infty}^{+\infty} dt |\Omega_0(t)|$ is the pulse area, $\Omega_0(t) := \varepsilon(t) \mu / \hbar$ is the time dependent Rabi frequency, and $\mu$ is the transition dipole moment. Since $A$ scales linearly with the field amplitude, the excited state population is expected to oscillate with pulse energy for a given pulse duration.

Figure 2.26: (Color online) (a): Experimental setup (see text for details); (b) and (c): relevant energy levels and excitation paths for Rb and K, respectively. Thick blue and thin red lines denote excitation and probe photons, respectively.
We first observed Rabi oscillations in a two-level system in order to test our experimental setup, and calibrate the pulse area. We used the $D_1$ transition ($5s_{1/2} \rightarrow 5p_{1/2}$) of atomic Rb at 794.75 nm. Initial bandwidth of our excitation pulses was narrowed from 10.3 nm to 6.2 nm full width at half maximum (FWHM). At this bandwidth the neighboring $5s_{1/2} \rightarrow 5p_{3/2}$ transition at 780 nm can be safely disregarded (as confirmed by our numerical analysis). Pulse energy was attenuated and scanned by a variable neutral density filter. The probe wavelength was tuned to 1300 nm. The observed dependence of the ionization rate, and therefore population of the $5p_{1/2}$ state, on the excitation energy is shown in Fig. 2.27. As expected, the excited state population exhibits oscillatory behavior, representative of Rabi oscillations. The intensity of pump pulses at the first minimum of oscillations, calculated from the measured energy and beam diameter, was about $2.1 \times 10^9$ W/cm$^2$. Given the transition dipole moment of $2.53 \times 10^{-29}$ Cm [1], this intensity corresponds to the pulse area of $2.2\pi$ (main uncertainty associated with the beam diameter value), in reasonable agreement with the experimental value of $2\pi$.

We have found that successful observation of femtosecond Rabi oscillations depends critically on the following conditions. First and most important, the pulse area of any unknown field preceding the excitation pulse (so-called “pre-pulse”, often generated by regenerative amplifiers) must be much smaller than $\pi$. Even a relatively weak pre-pulse will transfer some population to the excited state, preparing atoms in a superposition state. In the event that the optical phase of such a pre-pulse differs from that of the main excitation pulse, the contrast of Rabi oscillations will degrade with increasing pulse energy. Though we managed to suppress the energy of a pre-pulse (found in our case 2.8 ns ahead of the main pulse) to less than 1% of the main pulse energy, this proved satisfactory only for observing the first two periods of Rabi oscillations. We attribute the decay of the oscillation amplitude with increasing pulse energy (clearly seen in Fig. 2.27) to the presence of a residual pre-pulse.

The second critical point of concern is related to the spectral phase distortions of the excitation pulse which result in a time-dependent instantaneous frequency and hence affect the dynamics of Rabi oscillations. Though the lowest-order (quadratic with frequency) distortions can be eliminated by means of a pulse compressor, higher orders have to be compensated with an external pulse shaper.
Figure 2.27: \( \text{Rb}^+ \) ion signal (blue dots), proportional to the population of \( 5p_{1/2} \) state of Rb, as a function of the excitation pulse energy \( E \). Red solid line shows the best fit by \( \sin^2(A/2) \), with \( A \) being the pulse area calculated for a given pulse energy.

We carried out such compensation using the technique of multi-photon intra-pulse interference phase scans (MIIPS) [96], achieving the spectral phase flatness of better than 0.25 radian across FWHM of the excitation spectrum. Decreasing contrast of Rabi oscillations is partly attributed to the residual phase distortions.

Finally, the non-uniform spatial distribution of laser intensity in a focused Gaussian beam results in smearing out Rabi oscillations when the effect is averaged over the full beam profile. We minimized such averaging by tightly focusing our probe beam into the central part of the excitation region (ratio between the beam diameters of 0.4 and 0.3 for experiments with Rb and K, respectively) and therefore sampling the population in the region of relatively uniform intensity. In addition, multiphoton nature of ionization from the excited state effectively reduces the spatial area of probing.

To demonstrate Rabi oscillations between a single ground state and a coherent superposition of several excited states, we used the D lines of atomic potassium,
$4s_{1/2} \rightarrow \{4p_{1/2}, 4p_{3/2}\}$, with transition wavelengths of 769.9 nm and 766.5 nm, respectively. The difference between these wavelengths was well within the bandwidth of our laser pulses, which allowed simultaneous excitation of both transitions. The central wavelength of the excitation pulse was tuned to 768.2 nm. The superposition of $4p_{1/2}$ and $4p_{3/2}$ was probed by the subsequent photo-ionization with a broadband probe pulse at 1254 nm. The probe central wavelength was tuned on resonance with an intermediate state $5s_{1/2}$ (Fig. 2.26 (c)). The interference of two interaction paths, $4p_{1/2} \rightarrow 5s_{1/2}$ and $4p_{3/2} \rightarrow 5s_{1/2}$, results in the appearance of quantum beating in the ionization signal as a function of the time delay between the excitation and probe pulses, as discussed below. The dipole moments for the $4p_{1/2} \rightarrow 5s_{1/2}$ and $4p_{3/2} \rightarrow 5s_{1/2}$ transitions are different so the probe wavelength was varied in order to equalize the transition probabilities and therefore to maximize the contrast of quantum beatings.

Using the pulse shaper, we blocked all frequencies in the excitation spectrum except for two windows around 766.5 nm and 769.9 nm (Fig.2.28). Each spectral window of 1.2 nm FWHM corresponded to a transform limited pulse of about 0.75 ps length. The contrast of the observed quantum beats was maximized by varying the amplitude ratio of the two resonant spectral peaks.

The main result of this work is shown in Fig.2.29 (a). Color coded normalized ion signal is plotted as a function of the effective pulse area (horizontal axis) and time delay between the excitation and probe pulses (vertical axis). The effective pulse area is defined as $A_{\text{eff}} = \sqrt{A_1^2 + A_2^2}$ where $A_{1,2}$ are the pulse areas for the two individual transitions $4s_{1/2} \rightarrow 4p_{1/2}$ and $4s_{1/2} \rightarrow 4p_{3/2}$, respectively (for reasons behind this definition of $A_{\text{eff}}$, see [133]). As expected, the ionization signal exhibits oscillations along the vertical axis, indicative of quantum beats between the $4p_{1/2}$ and $4p_{3/2}$ states of Potassium. Repetitive appearance and disappearance of the quantum beat signal with changing excitation energy (horizontal axis) is the result of Rabi oscillations between the ground state and the coherent superposition of two excited states. This can be seen more clearly by examining the beating signal at two different excitation energies corresponding to pulse areas of about $\pi$ and $2\pi$, shown in Fig.2.30 by thin blue and thick red curve, respectively. Relatively high contrast of the quantum beats attests to the efficient population transfer to both excited states. The Fourier spectrum of the beat signal shows a strong peak at 1.77
Figure 2.28: Pulse spectrum for exciting a coherent superposition of $4p_{1/2}$ and $4p_{3/2}$ states of Potassium (thick blue), obtained by means of spectral pulse shaping of the original broadband pulse (thin red). Two main peaks are centered at the corresponding resonant frequencies. A weak line at 772 nm is due to the imperfections of the pulse shaper. It has been included in our numerical analysis and resulted in less than 5% change in the final state populations for the pulse energies used in the experiment.

$\text{THz}$, in close agreement with the fine structure splitting of 1.73 THz. Non-zero signal at negative time delays, clearly seen in the case of a higher energy excitation ($2\pi$), is due to the laser pre-pulse discussed above. Note that the detrimental effect of these pre-pulses, demonstrated in Fig.2.30, has been eliminated in the data of Fig.2.29 by means of an additional OPA [186], resulting in a much better contrast of oscillations.

We calculated the wavefunction amplitudes of $4s_{1/2}$, $4p_{1/2}$ and $4p_{3/2}$ by numerically solving the Schrödinger equation (for details, see [186]). In Fig.2.29(b), the numerical results are plotted in a two-dimensional form equivalent to that used in panel (a). The effective pulse area is scanned along the horizontal axis, whereas the relative phase between the two excited states changes along the vertical axis,
Figure 2.29: Experimental results (a) and numerical simulations (b) of Rabi oscillations between a single state and a wavepacket. The two-dimensional plots show the ion signal (color coded) as a function of the effective pulse area and probe delay.

and their total population is color coded. Good agreement between the measured and calculated signals enabled us to utilize the latter for better understanding of Rabi oscillations which involve multiple excited states.

Two effects, observed in the experiment and confirmed by the numerical calculations, are seen in Fig. 2.29(b). First, the ionization signal does not drop to zero after one full oscillation. Second, the phase of a wavepacket depends on the excitation energy. Both effects can not be explained by a simplified picture in which each excited state interacts only with the corresponding single resonant component of the driving field while being insensitive to the off-resonant part.

Fig. 2.31 shows the calculated populations of the two quantum states, composing an excited wavepacket, together with their relative phase as a function of the
Figure 2.30: Quantum beating of the excited wavepacket for two excitation pulse areas, $\pi$ (thin blue) and $2\pi$ (thick red).

effective pulse area. Panel (a) corresponds to the experimentally used excitation spectrum with two resonant peaks being 1.8 nm broad. In panel (b), the spectral peaks were narrowed to 0.36 nm. Narrower bandwidth implies longer pulse and weaker electric field for a given pulse area. Since the Stark shift scales quadratically with the amplitude of the off-resonant electric field, narrowing bandwidth effectively decreases the shift of $4p_{1/2}$ caused by the spectral peak resonant with $4p_{3/2}$, and vice versa. Hence, the result of panel (b) can be easily explained by a simplified interaction picture in which off-resonant coupling is neglected [56]. Excited state populations oscillate in-phase and return to zero at $2\pi$ pulse area. In contrast, panel (a) shows more complex oscillatory dynamics, which result in an incomplete return of population to the ground state, as observed in our experiment. This strong-field effect may prove especially important in the case when the contrast of Rabi oscillations is utilized for assessing the degree of coherence of an atom-photon interaction.

The relative phase between the two excited states in a wavepacket (solid red line in Fig. 2.31) deserves a closer look, since many applications of Rabi oscilla-
Figure 2.31: Numerical simulations of the interaction of Potassium with broadband laser pulses. Similarly to our experimental conditions, the excitation spectrum consists of two separate resonant peaks (Fig.2.28). The spectral width of each peak is 1.8 nm (a) and 0.36 nm (b). Populations of the two excited states, $4p_{1/2}$ (dash-dotted blue) and $4p_{3/2}$ (dashed green), and their relative phase (thick solid red) are plotted as a function of the effective pulse area of the excitation field. Ground state population is shown as a solid black line.
tions, e.g. in quantum computing, rely heavily on this phase behavior. The latter can be described by the following qualitative picture. Consider a system of two levels, $|g\rangle$ and $|e\rangle$, interacting with a cw laser field. At any given time, the wavefunction of this system can be expressed as:

$$\Psi(t) = a(t)|e\rangle e^{-i(\omega_0 t + \delta(t))} + b(t)|g\rangle,$$

(2.21)

where $a(t)$ and $b(t)$ are real amplitudes, $\delta(t)$ is the time dependent relative phase between the two quantum states, and $\omega_0$ is the transition frequency. By solving Maxwell-Bloch equations describing the dynamics of this system in the laser field [2], one finds for the excited state population $a^2(t)$ and relative phase $\delta(t)$:

$$a^2(t) = \frac{\Omega_0^2}{\Omega^2} \sin^2 \frac{\Omega t}{2},$$

$$\delta(t) = -\arctan\left(\frac{\Omega t}{\Delta}\cot\left(\frac{\Omega t}{2}\right)\right) - \Delta t,$$

(2.22)

where $\Omega_0$ is the intensity dependent resonant Rabi frequency, $\Delta$ is the detuning of the excitation field frequency from $\omega_0$, and $\Omega = \sqrt{\Omega_0^2 + \Delta^2}$. One can see from Eq. (2.22) that every time the excited state population passes through zero, the relative phase between the two states undergoes a jump by $\pi$ radian. From our numerical analysis, we conclude that similar behavior holds for a system of multiple (in our case, two) excited states. Namely, when the population of any of the excited states reaches zero, the phase of the corresponding wavefunction and therefore the phase of a wavepacket exhibits a “$\pi$-jump” (e.g. at pulse areas of $1.7\pi$ and $1.9\pi$ in Fig.2.31). When two zero crossings coincide (here, at approximate pulse area of $3.5\pi$) the phase jumps add up resulting in a larger overall change of the wavepacket phase.

In summary, we have experimentally demonstrated Rabi oscillations of atomic population between a single ground electronic state and a coherent superposition of two excited states, executed with broadband ultrashort pulses. Our results confirm the feasibility of applying $\pi$-pulses to multi-level systems for efficient population transfer on a femtosecond time scale. We illustrate, both experimentally and numerically, the limitations of ultrafast population transfer due to the Stark shifts resulting from strong off-resonant interactions. We analyze the phase of an excited
wavepacket and present a simple picture explaining its complex dependence on the excitation pulse area.
Chapter 3

Rotational excitation of molecules with femtosecond pulse trains

3.1 Outline of the idea

As briefly described in Chapter 1, a molecule with non-zero polarizability anisotropy experiences torque towards the direction of laser polarization (see Fig. 3.1). This phenomena gives rise to a number of scenarios of rotational motion control. In this work we studied rotational excitation of molecules with sequences of ultrashort pulses. First, we proposed, implemented and studied a technique based on the interaction of molecules with a sequence of short pulses separated by a constant time interval - a pulse train, with the field polarization changing from pulse to pulse by a constant angle. The polarization of the pulse train is “rotating” with the angular speed given by $\Omega = \frac{\delta}{\tau}$ where $\delta$ is the angle between the polarization of the consecutive pulses and $\tau$ is the train period. The periodicity of the pulse train enables selectivity in rotational frequency while the rotating polarization results in the ability to excite a certain direction of rotational motion. Because of the polarization rotation, we call this pulse sequence a “chiral pulse train”.

In the second part, we explored the phenomenon of quantum resonance occurring when the period of the pulse sequence matches the revival time or a fraction of the revival time of molecular dynamics. The effect was explored in the context of the periodically kicked quantum rotor - a paradigm system for studying classical
Figure 3.1: A molecule with a non-zero polarizability anisotropy experiences a torque towards the laser polarization.

and quantum chaos.

Classically, the interaction of a molecule with a chiral pulse train is closely related to a $\delta$-kicked rotor problem [25, 67]. For a high kick strength the excited rotational motion is known to be chaotic. As we demonstrated in this work, in the case of a low kick strength, a fraction of the molecular rotors in the ensemble can exhibit coherent accumulation of rotational energy in the quantum state with angular momentum “matched” to the rotating laser polarization. Theoretical treatment of this phenomenon is yet to be developed.

We consider two molecules rotating at almost the same velocity and phase as light polarization (see Fig. 3.2). If the molecular angular velocity is higher than the velocity of the polarization after the $(N-1)^{th}$ kick, the $N^{th}$ kick would slow the molecule down, as illustrated in Fig. 3.2(a). An initially slower molecule would be accelerated by the $(N+1)^{th}$ kick (Fig. 3.2(b)). Intuitively, more and more molecules will oscillate around the field polarization with their average velocity close to the speed of polarization rotation.

Of course, the molecular rotation obeys quantum dynamics, and the above described classical picture serves only as an illustration. From the quantum mechanical point of view, the population will be transferred from the initial, lower state to a coherent superposition of higher rotational states. In this work we would like
to demonstrate that if the period of the polarization rotation matches the period of molecular rotation defined as:

\[ T_{\text{rot}}(N) = \frac{2\pi I}{\hbar N}, \]  

where \( I \) is the molecular moment of inertia, the population is transferred to this state more efficiently.

**Figure 3.2:** Excitation of rotational motion with chiral pulse trains.
3.2 Experimental considerations

3.2.1 The method of creating a chiral pulse train

A pulse train with field polarization rotating from pulse to pulse can be obtained with little modification to the standard shaping technique (see Section 2.1.4). Consider a pulse propagating in \( \hat{y} \) direction and polarized along \( \hat{z} \) axis (see Fig. 3.3). The two shaper masks are changing the spectral phase of the two polarization components along \( \hat{e}_1 \) and \( \hat{e}_2 \). If \( \varphi_{1,2} = A \sin[(\omega - \omega_0)T + \delta_{1,2}] \), where \( \omega_0 \) is the carrier frequency, the resulting field in the time domain is:

\[
E(t) = \sum_{i=1,2} \hat{e}_i \sum_{n=-\infty}^{\infty} J_n(A) \epsilon(t+nT) \cos[\omega_0 t + n\delta_i],
\]

where \( \epsilon(t) \) is the electric field envelope of the original pulse, \( T \) is the train period and \( \delta_{1,2} \) are two arbitrary values. Eq. 3.2 describes two pulse trains polarized along \( \hat{e}_1 \) and \( \hat{e}_2 \) with the time delay between the pulses equal to \( T \). Consider the \( n^{th} \) pulse:

\[
E^n(t) = J_n(A) \epsilon(t+nT) \sum_{i=1,2} \hat{e}_i \cos[\omega_0 t + n\delta_i]
\]

\[
= J_n(A) \epsilon(t+nT) \times \{ \hat{z} \cos(\omega_0 t + n\delta_1) + \hat{x} \cos(\omega_0 t + n\delta_2) - \hat{x} \cos(\omega_0 t + n\delta_2) \}.\]

A quarter-wave plate inserted into the beam with its optical axis oriented along the initial field polarization (\( z \)-direction), would delay the \( \hat{z} \) components by \( \pi/2 \) with respect to the \( x \) component. The resulting field can be written as

\[
E^n(t) = -2J_n(A) \epsilon(t+nT) \sin(\omega_0 t + \left( n \frac{\delta_1 + \delta_2}{2} \right)) \times \left[ \hat{z} \sin \left( n \frac{\delta_1 - \delta_2}{2} \right) + \hat{x} \cos \left( n \frac{\delta_1 - \delta_2}{2} \right) \right].
\]

The term in the square brackets defines linear polarization of the \( n^{th} \) pulse, which is rotated by an angle \( n(\delta_1 - \delta_2)/2 \) with respect to the input polarization. We can therefore create a pulse train with the polarization of each pulse rotated with respect to the previous pulse by a certain constant arbitrary angle. In all
Figure 3.3: Polarization shaping. Input polarization $E_0$ can be decomposed into $\hat{e}_1$ and $\hat{e}_2$. Two different phase mask can be applied to the components.

experiments described in this Thesis, we took $\delta_1 = -\delta_2 = \delta$, with $\delta$ defining the polarization rotation angle.

3.2.2 Pulse train characterization

A chiral pulse train produced by the shaper was characterized using polarization sensitive cross-correlation method. The setup is depicted in Fig.3.4. The original laser beam of vertical polarization is split into two with the power ratio $\approx 10:1$. The smaller part is used as a reference pulse. The more intense part is shaped with the polarization shaper described in the previous section. The two beams are focused and overlapped on a nonlinear crystal with a 500 mm focal length lens. A polarization cube ensures that only vertically polarized light passes through. A $\lambda/2$ plate is mounted on a computer controlled rotational stage. A delay line allows to overlap in time any pulse in the train with the reference pulse. A photo-diode measures the cross-correlation intensity as a function of the time delay and the
To characterize a pulse train two measurements were done. First, a pulse train with constant vertical polarization is created by the shaper. The $\lambda/2$ plate is set to have no effect on this state of polarization. The cross-correlation of the pulse train and the TL reference pulse of the same polarization was obtained. An example of a pulse train with a period of about 8 ps is shown in Fig. 3.5, upper panel.

Pulse shaping was then applied to obtain a train with the same train period and rotating polarization. The time delay of the reference pulse was set to overlap with the angle of the half-wave plate.

Figure 3.4: Polarization sensitive cross-correlation setup.

Figure 3.5: Cross-correlation of a pulse train (top) and polarization graph for a $\delta = 45$ deg train (bottom).
a particular single pulse in the train and the $\lambda/2$ plate was rotated while the cross-correlation signal was measured. The result for a pulse train with the polarization rotation angle set to 45 degrees is shown in the lower panel of Fig.3.5 where the color coded cross-correlation signal is plotted as a function of the waveplate angle and the pulse number. It can be seen that maximizing the cross-correlation signal for each consecutive pulse requires the plate rotation by about 22 degrees, which means that the pulse polarization is indeed turning by about 45 degrees from pulse to pulse.

3.2.3 Jet-cooled oxygen molecules

Oxygen molecules were used in the experiments with a chiral train. For efficient laser-induced rotational excitation, a molecule has to have high polarizability anisotropy and long, as compared to the pulse duration, rotational period. Oxygen molecules possess moderate polarizability anisotropy of 7.26 atomic units [140] and rotational constant of 1.44 cm$^{-1}$ [63], which results in the revival time equal to 11.6 ps, which is much longer than our laser pulses.

The rotational structure of the ground electronic state $X^3\Sigma_g^-$ of oxygen is discussed in detail in [22, 82, 152]. Briefly, this is a Hund’s case (b) molecule, with a total electronic spin $S=1$ and zero electronic orbital angular momentum. Because the orbital angular momentum is zero, the angular momentum of the nuclei $R$ is equal to $N$ - the total angular momentum excluding spin. Spin $S$ and rotational angular momentum $N$ add up to the total angular momentum $J$. Only odd rotational states are allowed, $N=1,3,5,...$ due to the nuclear spin statistics. The rotational energy level structure is depicted in Fig.3.6. In the presented experiments we attempt to control the total populations of the rotational states $N$ without resolving their fine structure splitting into $J$’s.

The lower the initial rotational temperature of a molecule, the more pronounced the effects of the laser-induced rotational excitation. Molecular ensembles with low rotational temperature are typically obtained by means of seeded or pure supersonic gas expansions. Therefore a source of jet cooled oxygen was designed. The source chamber is shown in Fig.3.7. It consists of a vacuum chamber, a pulsed valve with a nozzle, a skimmer, and vacuum pumps. A pulsed valve is used instead of
a continuous jet in order to decrease the vacuum pump load and the background pressure. We used a valve manufactured by General Valve, which produced pulses of 250 µs duration, and had an orifice diameter of 200 µm. The valve was placed in a vacuum chamber equipped with a 1000 l/sec turbomolecular pump backed with an oil rotary pump (Edwards 40, pumping speed of 74 m³/hr). This pumping speed was sufficient to maintain 10⁻⁴ Torr pressure in the source chamber at 10 Hz valve repetition rate and 6-8 bar of back pressure.

The jet exits the source chamber through a 1 mm diameter skimmer and enters the detection chamber. The skimmer reflects the molecules, which do not go through the orifice, outwards from the upcoming jet and prevents reheating the jet by collisions. The nozzle was movable and the distance between the nozzle and the

Figure 3.6: $X^3\Sigma_g^-$ state of oxygen.
skimmer was controlled from outside the chamber. The temperature of molecules in the jet depends on the back pressure, type of the buffer gas, the ratio between the nozzle-skimmer distance and the nozzle diameter. In our setup all these parameters were tuned to achieve the temperature as low as 7-8K.

### 3.2.4 Laser power consideration

The goal of this work is to study laser excitation of higher rotational levels with chiral pulse trains. The idea is to excite the states selectively by matching the rotational speed of a molecule with the speed of rotating polarization. To see the effect, one needs to populate higher rotational levels than those covered by the initial thermal distribution. To determine how high the system will climb the rotational ladder one needs to calculate the kick strength of an excitation pulse (see Section 1.3.1). Roughly speaking, the kick strength is the amount of angular momentum in units of $\hbar$ supplied to the rotor [59]. Here we estimate the kick strength corresponding
to the laser power available in our experiments.

We start with the kick strength definition

\[ P = \frac{\Delta \alpha}{4\hbar} \int \varepsilon^2(t) dt, \]  

(3.5)

where \( \varepsilon(t) \) is the electric field amplitude, \( \Delta \alpha \) is the polarizability anisotropy. Assuming Gaussian pulse profile the former is written as:

\[ \varepsilon(t) = \varepsilon_{\text{max}} \exp \left( -\frac{t^2}{2\sigma^2} \right). \]  

(3.6)

where \( \varepsilon_{\text{max}} \) is the maximum field strength at \( t=0 \) and \( \sigma \) is the pulse envelope width (\( 1/e^2 \) in field).

Given that:

\[ \varepsilon_{\text{max}}^2 = \frac{2I_0}{\varepsilon_0}, \]  

(3.7)

where \( I_0 \) is the peak intensity, one can write:

\[ \varepsilon^2(t) = \frac{2I_0}{\varepsilon_0} \exp \left( -\frac{t^2}{\sigma^2} \right). \]  

(3.8)

Substituting (3.8) into (3.5) we arrive at:

\[ P = \frac{I_0 \Delta \alpha}{2\varepsilon_0 \hbar} \sqrt{\pi} \sigma. \]  

(3.9)

With a pulse of 150 fs duration, 150\( \mu \)J and moderate focusing we were routinely achieving intensities on the order of \( 10^{13} \text{W/cm}^2 \). This results in the kick strength for oxygen (\( \Delta \alpha=1.31 \times 10^{-40} \text{Cm}^2/\text{V} \)) of about 10.

### 3.2.5 Resonance enhanced multiphoton ionization (REMPI)

The rotational state distribution of the molecular ensemble after the excitation with a femtosecond pulse train was probed using REMPI [145, 146]. Briefly, one of the rotational states of the electronic ground state is coupled with two photons to a rotational state of an excited electronic state and then to the continuum with another
photon from the same probe pulse. The bandwidth of the probe pulse is narrow enough to resolve the rotational structure of the molecule. Selection rules limit the number of the spectral lines originated from any given rotational state which makes it possible to associate each line with a limited number of initial states.

We used the following two-photon resonance: \( C^3\Pi_g (v' = 2) \leftarrow X^3\Sigma_g^{-} (v'' = 0) \). Here we briefly review the rotational energy structure of the \( C^3\Pi_g \) state only, since \( X^3\Sigma_g^{-} \) was discussed earlier (section 3.2.3). \( C^3\Pi_g \) is a Hund’s case (a) state with an electronic orbital momentum coupled to the the electronic spin to form the total electronic angular momentum \( \Omega \). The latter is coupled to the nuclear angular momentum \( R \) to form the total angular momentum \( J \). Spin-orbit coupling produces three fine-structure components \( F_1 \), \( F_2 \) and \( F_3 \), corresponding to \( J=N+1 \), \( N \), \( N-1 \), where \( N \) is the rotational quantum number of the nuclei. The structure is depicted in Fig. 3.8. As shown in [146], rotational lines can be resolved only for

**Figure 3.8:** \( C^3\Pi_g \) state of oxygen.
the transitions involving $F_3$ spin-orbit components and only for $v' = 2 \leftarrow v'' = 0$ vibrational transitions.

The selection rules are $\Delta J = 0, \pm 1, \pm 2$ as follows from the fact that this is a two-photon process. An example of transitions between the ground and the excited electronic states allowed by the selection rules and originated from $N = 5$ is depicted in Fig.3.9. In general, there are up to 15 transitions allowed by the selection rules. Different $J$ states in the ground state were not resolved in our experiments due to a relatively broad laser spectrum, but different rotational states $N$, were clearly resolved. In figure 3.9 all possible transitions are grouped according to $\Delta N$, and it can be seen that there are up to seven transition observable with $\Delta N=-2, -1, 0, 1, 2, 3, 4$.

REMPI spectrum of Oxygen can be simulated using the constants for $C^3\Pi_g$ given in [146]. The spectroscopic constants for the ground state are readily available [63]. The equations for the states energies are obtained from [63]. The result of the simulations for 8K is shown in Fig.3.10 by blue dashed line. Good agreement between the experimental and the simulated spectra ensures correct lines assignment.

Probe pulses are produced by frequency doubling a tunable, YAG pumped dye laser (QuantaRay Pro, Sirah Presicion Scan). The beam was focused with a 150 mm focal length lens, down to an estimated beam diameter of 20-30 $\mu m$.

REMPI spectra of 300K and jet-cooled molecules were obtained and are shown in Fig.3.10. The spectrum of cold molecules indicates very little population above $N=1$. Simulated for 8K spectrum is shown by the dashed line and agrees well with the experiment.

3.2.6 Detection chamber

The REMPI technique requires detection of molecular ions. A TOF apparatus was built for this purpose. It is depicted in Fig.3.11. A focused laser beam (shown in red) crosses the molecular beam (shown in blue) in the center of the chamber. In general, the TOF apparatus is similar to the one described earlier in Chapter 2. The main difference is a smaller chamber size, which allowed us to use a shorter focal length lens for achieving higher laser intensities. The interaction zone is
Figure 3.9: Allowed two-photon transitions form $N = 5$ grouped according to $\Delta N$. The numbers on the left label the levels by their $N$ (left column) and $J$ (right column) quantum numbers.
Figure 3.10: Example of REMPI spectrum of 300K oxygen (top) and cold oxygen (bottom).

The intersection of the two beams, the laser beam and the molecular beam. The diameter of the molecular beam is estimated from a simple geometrical line-of-sight approximation at approximately 10-15 mm. The Rayleigh length of the laser beam is shorter that that. The middle TOF plate has a small, 1.5 mm orifice to limit the size of the sampling zone along the laser beam direction.

The chamber is pumped by a turbo-molecular pump at 210 l/sec pumping speed, which provides pressure of the order of $10^{-9}$ Torr without a pulsed beam, and $10^{-6}$ Torr when the beam was present.

After being extracted from the interaction region, the ions undergo a free flight before reaching the MCP. Since the molecules have substantial longitudinal velocity prior to the ionization the ions follow a trajectory deviating from a straight line perpendicular to the plates and going through the center of the 1.5 mm hole. The MCP detector is 18 mm in diameter and is centered on this line. Therefore if the time of flight is large enough the ions would miss the active area of the MCP. In our experiments the time of flight was less than 5 $\mu$s, making the molecules with the speed of up to 1800 m/s detectable.

The energy of probe pulses was 0.6-1.2 mJ. The detected ion signal was gated and integrated with a boxcar. Typically, an average over 10-100 probe pulses was performed with a data acquisition circuit.
3.2.7 Synchronization of the excitation laser, REMPI laser and pulsed valve

One of the technical challenges was to synchronize the timing of the molecular and laser pulses (both pump and probe). The valve and both lasers can be triggered by an internal or an external trigger and exhibit different trigger-to-fire time delays. In addition, the femtosecond laser operates at 1 kHz repetition rate, while the rest of the devices work at 10 Hz.

We first estimate how accurate the devices should be synchronized. Molecules are moving with a speed of about 1000-1500 m/s. The expected size of the focal spots of the laser beams is of the order of $10^{-5}$ m and therefore an average molecular transit time through the interaction zone is about 10 ns. This sets an upper limit on the pump-probe time delay uncertainty. The jet valve produces gas pulses which are much longer in duration than laser pulses (250 µs) and therefore its time jitter with respect to the laser pulses can be tolerated within 20-30 µs.

Fig. 3.12 shows the synchronization scheme based on two pulse generators and
Fig. 3.12: Scheme of time synchronization between the lasers and the pulsed valve.

Fig. 3.13 shows the time diagram of the control pulse sequence. The femtosecond system is triggered by its internal trigger at 1 kHz, which serves as a master trigger for the whole sequence (dashed lines in Fig. 3.13). The BNC pulse generator, triggered by the master trigger, divides the master frequency by 100. At t=0 the BNC pulse generator starts the sequence of pulses with ±5 ns time uncertainty. Channel A provides the trigger signal for the valve driver, channel B - for the ns system flashlamps. Channel C provides the gate signal for the second QC pulse generator. The gate pulse coincides in time with the third pulse from the fs system (counted from the master trigger event), and the effect of that pulse on the rotational distribution of molecules is analyzed with a ns probe. Triggered and gated QC generator produces the trigger for the Q-switch of the ns system with accuracy of 800 ps with respect to the trigger. The second channel of the QC generator is used to trigger the boxcar integrator.

In the resulting sequence, pump and probe laser pulses are separated by a controllable time delay of 0-1 μs±0.8 ns, while the valve can be opened 0.2-0.7 ms±5
ns prior to the laser pulses and the boxcar integration window is set with a ±0.8 ns accuracy with respect to the pump laser. To verify this time sequence, laser pulses were detected by a fast photodiode and monitored by an oscilloscope.

### 3.2.8 Experimental setup and experimental strategy

**Experimental setup**

The experimental setup is depicted in Fig.3.14. The beam of cold oxygen is produced in the source chamber and enters the detection chamber. The background pressure in the detection chamber measured with ion gauges was of the order of $10^{-9}$ Torr with non-operating valve and about $10^{-7}$ Torr when the valve was turned on. In order to obtain REMPI spectrum of room temperature molecules, the chamber can also be filled with gas through a bypass line. In general, higher molecular
density results in higher signal to noise ratio of the spectrum, however the pressure is limited by the functionality of the MCP detector by about $10^{-5}$ Torr.

The chiral pulse train is produced with a pulse shaper as described in section 3.2.1 and characterized according to section 3.2.2. The probe beam is produced by a doubled nanosecond dye laser, and is separated from the residual fundamental radiation with a dichroic mirror. The telescope is used to increase the beam diameter in order to avoid damaging the polarization optics. In addition, the telescope is used to equalize the divergencies of the two beams so as to have the corresponding beam waists in the same plane, resulting in probing the molecules from the center of the interaction region. The polarizing cube ensures linear polarization of the probe which is then modulated with the Pockel’s cell between left and right
circularly polarized, as required for the directionality measurement.

The two beams are combined on a dichroic mirror and sent to the detection chamber. The two beams are focused with a 150 mm focal length lens. The focal spot is located inside the chamber between the extraction plates of the TOF. The focal spot can be moved along the molecular beam with a steering mirror. A thin, fused silica plane window is inserted into the beams after the lens. This window splits a small fraction of both beams and is used for monitoring the overlap in the interaction zone. The main beams are separated at the exit from the chamber by another dichroic mirror. The energy of the two pulses is measured by photodiodes, boxcars and data acquisition system.

**Optical alignment and timing calibration procedure**

First, it is necessary to calibrate the probe laser wavelength. To do that, the chamber is filled with room temperature oxygen. The fundamental wavelength of the probe laser is set slightly below 575 nm (see Fig.3.10(a)). In this region REMPI spectrum is dense and molecules will be ionized regardless of the exact probe wavelength. With this wavelength setting, the ionization signal is found by scanning the probe beam in space. The position is optimal when the beam is exactly underneath the small orifice in the middle TOF plate. Once found, the ion signal is maximized by moving the lens along the optical axis for best focusing. At this point, the spectrum looks like the one in Fig.3.10(a). The spectrum is compared with the calculations and the wavelength of the transition originated from $N'' = 1$ is found.

Next, the valve should be synchronized with the laser pulses. The probe wavelength is set to 574.65 nm ($N'' = 1$ line) as seen in Fig.3.10. The ion signal is measured as a function of the time delay of the channel A of the BNC pulse generator. A typical result is shown in Fig.3.15. The horizontal axis represents the time delay between the master trigger and the opening of the valve. The quick rise at 2.4 ms indicates the leading edge of the gas pulse. The valve stays open for about 200-250 $\mu s$. The gas pulse is reflected by the chamber walls and the signal between 2.2 and 1.4 ms indicates the ionization of the reflected molecules. The signal decays due to the constant pumping by the turbomolecular pumps. The level of the background signal can be estimated from the data between 2.5-2.65 ms. At this time
window probe pulses arrive just before the cold beam reaches the interaction zone and the signal originates from the background molecules. The data at 2.68-2.72 ms shows the absolute zero of the ion signal because it was obtained without the probe beam. The final valve timing was set at the leading edge (2.35 ms in Fig.3.15).

Once the valve timing is set, REMPI spectrum of cold oxygen Fig.3.10(b) can be successfully obtained.

The next step is to position the pump beam in space. Once the pump focal spot is within 1 mm range from the probe on the external screen, the ion signal from the pump beam becomes observable. With the probe beam blocked, the ion signal from the pump pulse alone is maximized by moving the focusing lens along the optical axis. This ensures that the pump focal plane is right below the small hole in the middle TOF plate. Probe focusing is readjusted by changing the telescope in the probe beam line. Now both the probe and the pump beams are focused in the same plane. At this moment the screen is moved again to the focal plane of the beams. The probe beam has enough power to burn a small hole in the screen. The pump beam is directed through the hole in the screen by adjusting the steering mirror.

Pump pulses can efficiently ionize oxygen via non-resonant multiphoton process. The ion signal from the pump beam is very unstable because of the high non-linearity of this multiphoton ionization and therefore it has to be separated from the ion signal due to the probe beam. The two signals can be separated in time. The width of the signals is about 20-30 ns, so the time delay between the pump and
probe pulses of 100 ns is sufficient. However, because of the molecular motion in the jet, this should be compensated by moving the pump upstream from the probe. In order to do that the probe wavelength is set to $\lambda_{PR}=574.5$ nm, corresponding to the non-populated state N”=3. Without the rotational excitation by pump pulses, the ion signal is essentially zero. By slowly adjusting the horizontal knob on the pump steering mirror the pump focal spot is moved towards the source chamber. At the correct position of the pump focus the ion signal appears. With this position of the laser beams, REMPI spectrum of rotationally excited molecule is recorded (see Fig[3.17]).

3.3 Control of molecular rotation with a chiral train of ultrashort pulses

Trains of ultrashort laser pulses separated by the time of rotational revival (typically, tens of picoseconds) have been exploited for creating ensembles of aligned molecules. In this work we introduce a chiral pulse train - a sequence of linearly polarized pulses with the polarization direction rotating from pulse to pulse by a controllable angle. The chirality of such a train, expressed through the period and direction of its polarization rotation, is used as a new control parameter for achieving selectivity and directionality of laser-induced rotational excitation. The method employs chiral trains with a large number of pulses separated on the time scale much shorter than the rotational revival (a few hundred femtosecond), enabling the use of conventional pulse shapers.

Control of molecular rotation with strong non-resonant laser fields has become a powerful tool for creating ensembles of aligned [5, 54, 126, 141], oriented [5, 128, 164] and spinning molecules [49, 65, 72, 75]. Numerous applications of rotational control in molecular systems include control of chemical reactions [135, 141], deflection of neutral molecules by external fields [58, 119, 142], high harmonic generation [66, 165], and control of molecular collisions with atoms [151] and surfaces [62, 83, 137, 149, 182]. Alignment of molecular axes has been implemented with transform-limited and shaped laser pulses using various approaches (see, e.g. [36, 54, 64, 90, 141, 158]). Increasing the degree of molecular alignment has been achieved by employing a sequence of laser pulses (a “pulse
train”), separated by the time of rotational revival [34, 91, 184]. Such timing ensures that the accumulative effect of consecutive pulses is equally efficient for all molecules in the ensemble, regardless of their angular momentum.

Creating molecular ensembles with a preferred direction of rotation has been reported in both adiabatic (“optical centrifuge”) [35, 72, 159, 161, 179] and non-adiabatic [49, 75] regimes of excitation using a pair of laser pulses with different polarization. In this work we demonstrate an alternative way of exciting unidirectional rotational motion with a “chiral pulse train”, in which the polarization of the excitation field rotates from pulse to pulse by a controllable angle, in either clockwise or counter-clockwise direction. The time delay between the pulses is much shorter than the revival period. We show that by varying the train parameters using the technique of polarization shaping [19, 168], one can achieve selectivity in the rotational excitation and control its directionality. By matching the rotational period of the field polarization to the period of molecular rotation, molecules in a particular angular momentum state can be excited more efficiently than others. The chirality and the period of the pulse train define the direction of rotation.

Our experimental setup, rotational state detection technique and the method to produce a chiral pulse train were described earlier in this chapter. Fig.3.16 shows an example of a chiral pulse train with the modulation amplitude $A = 2$, train period $\tau = 1$ ps, and polarization rotation period $T_p = 8$ ps.

REMPI technique was modified in order to measure directionality of molecular rotation with high accuracy and low susceptibility to the power fluctuations of the nanosecond dye laser. A Pockels cell is used to alternate circular polarization of the consecutive probe pulses between left and right. A molecular state with a certain value $M_J$ of the projection of its total angular momentum on the laser beam axis, is coupled to the ionization continuum by a left circularly polarized probe field with an equal strength to that of a right circular polarization acting on a state with an opposite projection $-M_J$. Hence, the difference in the ionization rate between left and right circularly polarized probe pulses reflects the asymmetry in the $M$-distribution, or equivalently, the directionality of the induced rotation [75].

We estimate the intensity of pump pulses of the order of $10^{12}$ W/cm², which results in a dimensionless spatially-averaged “rotational kick strength” of $P \approx 7$. The latter parameter characterizes the amount of angular momentum (in units of $\hbar$)
Figure 3.16: Example of an intensity envelope and polarization of a chiral pulse train implemented in this work. Linear polarization of each pulse is shown in the circles above.

transferred from the laser field to the molecule [5, 91].

The observed REMPI spectrum of cold oxygen is shown in Fig. 3.17, together with a calculation (carried out similarly to [105]) for the rotational temperature of 8 K. The majority of molecules is in the lowest rotational state $N'' = 1$. Application of a pump pulse train changes the spectrum dramatically by increasing the intensity of lines originated from $N'' > 1$. REMPI spectrum of the excited molecules, obtained with the maximum available pulse energy of 300 $\mu$J, shows populated peaks for the rotational number as high as $N'' = 19$. Unfortunately, different rotational transitions in O$_2$ overlap with one another and it is generally difficult to have a REMPI line corresponding to a single initial state (see line assignments in Fig. 3.17). We use two spectral lines at 287.25 nm and 287.14 nm, for which the majority of ions originates from $N'' = 3$ and $N'' = 5$ rotational states, respectively. Even though the individual lines are not resolved, the relative contribution of the neighboring states to the total ion signal in both cases is estimated as $< 18\%$.

Our main results are shown in Figs. 3.18 and 3.19. With the probe wavelength set to 287.25 nm ($N'' = 3$) and 287.14 nm ($N'' = 5$), we vary $\delta$ and $\tau$ while keeping the pulse train envelope and energy (140 $\mu$J) constant. We record the total ionization signal for left and right circularly polarized probe, $S_L$ and $S_R$, respectively. The sum of the two signals, $S = S_L + S_R$, is plotted in Fig. 3.18 and represents the average total efficiency of exciting the molecules to $N'' = 3$ and 5 as a function of
Figure 3.17: REMPI spectrum of cold oxygen: experimental results (lower solid curve) and calculations (lower dashed line). Upper solid curve shows the spectrum of rotationally excited by a laser pulse molecules (shifted up for clarity). Dashed vertical lines indicate the frequencies of transitions originated from a certain rotational state, labeled with the corresponding $N''$ numbers. Thick vertical arrows point at the two peaks which correspond mostly to $N''=3$ (right), and $N''=5$ (left) initial rotational states.

Figure 3.18: Total excitation efficiency of oxygen molecules excited to $N''=3$ (a,c) and $N''=5$ (b,d) rotational state (note the difference in time scale). (a,b) - experimental data, (c,d) - numerical calculations. Each experimental data point represents an average over 150 probe pulses. Grayscale coding: (a,b) min: $S = 0$, max: $S = 1$ (arb.units); (c) min $P = 0.1$, max $P = 0.6$; (d) min: $P = 0$, max: $P = 0.35$. 
The experimental results are compared with a theoretical analysis of the population distribution of various rotational states of oxygen excited by the chiral train. In our model, the pulses were considered as $\delta$-kicks, and the molecular wavefunction was expanded in the Hund’s case (b) basis. The non-perturbative modification of the expansion coefficients due to the interaction with every pulse was determined with the help of the numerical procedure described in [49]. Thermal averaging over initial molecular states was done to account for thermal effects. As the observables related to the measured signals, we calculated $P_L$ ($P_R$) - the total population of the $N$-states with positive (negative) projection $M_J$ of the total angular momentum $J$ onto the propagation direction of the chiral pulse train. The population of the $M_J = 0$ state was equally divided between $P_L$ and $P_R$. The sum of these calculated populations ($P$) for $N'' = 3$ and $N'' = 5$ is shown in Panel (c) and (d), respectively.

Both experimental (a) and theoretical (c) plots of Fig.3.18 show that for $\delta = 0$, $\pi$ (non-rotating polarization) the total signal exhibits well pronounced maxima at $\tau \approx 2400$ fs and $\tau \approx 4700$ fs. As expected, these times correspond to one and two periods of “rotation” for $N'' = 3$, defined as $T_{N=3} = h/(E_{N=3} - E_{N=1}) = 2340$ fs. Of course, the picture of classical rotation is not applicable for such low rotational numbers, and the “period of rotation” simply means the evolution period of a rotational wavepacket consisting of only two states, $N'' = 1$ and $N'' = 3$. Similar maxima are observed in panels (b) and (d) for about twice lower values of $\tau$ corresponding to the faster evolution of a higher angular momentum state, $N'' = 5$.

All panels of Fig.3.18 show a characteristic “X” pattern with clear diagonal lines. Their slope defines a constant period of polarization rotation in the chiral train, $T_p = 2\pi \tau / \delta$. Diagonals with a positive slope, e.g. from point ($\tau = 0$, $\delta = 0$) to point ($\tau = 2400$, $\delta = \pi$) in plots (a,c), correspond to the polarization rotating clockwise, while a negative-slope diagonal corresponds to counter-clockwise polarization rotation. The population of the corresponding state is clearly higher along these diagonal lines, reflecting a higher degree of rotational excitation by a pulse train whose polarization is rotating in sync with the molecules. Note that the lines of enhanced excitation correspond to the train polarization rotating twice slower than the molecules, e.g. $T_p = 2T_{N=3}$. The effect is reproduced in the numerical calculations shown in panels (c,d), and can be attributed to the inversion
Figure 3.19: Directionality of molecular rotation for $N'' = 3$ (a,c) and $N'' = 5$ (b,d) state (note the difference in time scale). Grayscale coding: (a) min: $\varepsilon = -0.2$, max: $\varepsilon = +0.2$; (b) min: $\varepsilon = -0.4$, max: $\varepsilon = +0.4$; (c) min: $\varepsilon = -0.7$, max: $\varepsilon = +0.7$; (d) min: $\varepsilon = -0.8$, max: $\varepsilon = +0.8$. 

Aside from the diagonals, the plots of Fig.3.18 exhibit rich two-dimensional structure with notably more features visible in the case of lower ($N'' = 3$) rotational excitation. Our numerical analysis attributes this difference to the following two reasons. First, the spin-rotation splitting of the $N'' = 3$ state is more than 7 times that of $N'' = 5$, which makes a simple two-level wavepacket model less applicable. Second, with an estimated rotational kick strength of $P \approx 7$, the lower state undergoes stronger perturbation than the upper one. Theoretical calculations with neglected spin-rotation coupling and weaker field strength result in a higher degree of similarity between the $N'' = 3$ and $N'' = 5$ cases.

Fig.3.19 shows the degree of rotational directionality, defined as $\varepsilon = (S_L - S_R)/(S_L + S_R)$ or $\varepsilon = (P_L - P_R)/(P_L + P_R)$ for the experimental observations and numerical calculations, respectively. Similar “X” pattern can be recognized on all panels, confirming the directionality of molecular rotation along the “resonant” diagonals. Indeed, the dark positive-slope traces correspond to $\varepsilon < 0$ (clockwise rotation), whereas the bright ones with a negative slope - to $\varepsilon > 0$ (counter-clockwise rotation).

The end and center points of the “X” pattern in Fig.3.18 (i.e. at $\delta = 0, \pi/2$ and $\pi$) exhibit higher signal in comparison to the intermediate values of $\delta$. This is the result of a bi-directional rotational excitation at those points, where the pulse train
is resonant with both clockwise and counter-clockwise rotating molecules, and the total number of excited molecules is therefore higher. This conclusion is evident in Fig.3.19 where no circular anisotropy ($\varepsilon = 0$) is observed and calculated around $\delta = 0, \pi/2, \pi$.

An interesting increase in the directionality of the excited rotation is observed for low train period ($\tau = 100$ fs) and polarization rotation angle $\delta \approx \pi/2$. In this case, pulses of the chiral train are overlapping in time, forming a single pulse with gradually rotating polarization. Fig.3.20 shows the spectrum of the two polarization components in the case of a low train period. The period of the sinusoidal phase modulation is larger than the pulse bandwidth and two orthogonally polarized pulses are essentially linearly chirped. After the conversion to left and right circular polarization the pulses form almost the centrifuge field of $[35, 72, 159, 179]$, with the main difference being a non-zero initial rotational speed of the centrifuge. In contrast to the latter, here the polarization rotation is fast at the beginning of the pulse; it then slows down to zero in the middle, and accelerates in the opposite direction towards the end of the pulse. Even though our pulse is of much lower strength and duration than that needed for spinning molecules to high angular frequencies, its effect on low rotational state is quite evident for both $N'' = 3$ and $N'' = 5$ (Figs.3.19(a,b)). The centrifuge effect is not observed in the numerical calculations, which assume an infinitely short duration of pulses in the chiral pulse train.

In summary, we have proposed and implemented a new method of exciting uni-directional molecular rotation with polarization-shaped femtosecond laser pulses. The technique of generating a sequence of pulses with field polarization rotating from pulse to pulse by a predefined constant angle - a chiral pulse train, has been demonstrated and utilized for the rotational control of molecular oxygen. Tuning the parameters of the chiral pulse train enabled us to control both the frequency of excited molecular rotation and its directionality.
Figure 3.20: Low frequency phase modulation produces two linearly and oppositely chirped pulses. The resulting field polarization continuously rotates with a constant angular acceleration, starting from fast rotation in a certain direction, then slowing down, crossing zero angular velocity, and finally accelerating to fast rotation of an opposite sign with respect to the initial motion.

3.4 Quantum resonances in selective rotational excitation of molecules with a sequence of ultrashort laser pulses

In the following work, we introduced a few changes in our experimental setup. First, nitrogen was used instead of oxygen. Nitrogen REMPI spectrum is less complicated which enabled us to detect the populations of rotational states up to N=7. Availability of two isotopologues, \(^{14}N_2\) and \(^{15}N_2\), made it possible to study selective excitation of molecules with different moments of inertia. Second, the optical resolution of our pulse shaper was improved in order to produce pulse sequences with a longer period comparable to the revival period of nitrogen (8.3 ps).

We investigate experimentally the effect of quantum resonance in the rotational excitation of the simplest quantum rotor - a diatomic molecule. By using the techniques of high-resolution femtosecond pulse shaping and rotational state-resolved detection, we measure directly the amount of energy absorbed by molecules interacting with a periodic train of laser pulses, and study its dependence on the train period. We show that the energy transfer is significantly enhanced at quantum resonance, and use this effect for demonstrating selective rotational excitation of two nitrogen isotopologues, \(^{14}N_2\) and \(^{15}N_2\). Moreover, by tuning the period of the pulse
train in the vicinity of a fractional quantum resonance, we achieve spin-selective rotational excitation of para- and ortho-isomers of $^{15}\text{N}_2$.

The periodically kicked rotor is a paradigm system for studying classical and quantum chaos [25]. In the quantum regime, the dynamics of the kicked rotor exhibit such fundamental phenomena as suppression of classical chaos [25], Anderson localization in angular momentum [48] and quantum resonances in the accumulation of rotational energy [67]. Even though these effects have been thoroughly studied with ultracold atoms in optical fields [107] and Rydberg atoms in microwave fields [76], they have never been observed experimentally in a real rotational system.

It has been recently indicated [52] that quantum resonances can be detected in a system of true quantum rotors - an ensemble of diatomic molecules subject to periodic rotational kicking by ultrashort non-resonant laser pulses. It has been also proposed to use this quantum effect for selective laser manipulation of molecular mixtures [52]. Here, we demonstrate for the first time the fundamental phenomenon of quantum resonance in a real rotational system by studying the transfer of energy from a femtosecond pulse train to the rotation of different isotopologues of molecular nitrogen. We start with rotationally cold molecules and measure the energy transfer directly by means of a state-resolved detection of the rotational population in the excited molecular ensemble. To generate a train of ultrashort pulses, we employ a high-resolution femtosecond pulse shaper which enables us to scan the train period on the revival time scale. In our experiments, quantum resonance is manifested by a strong dependence of the population distribution width and the acquired rotational energy on the pulse train period with a sharp maximum at the rotational revival time.

Following the proposal of [52], we also demonstrate isotope-selective rotational control in a mixture of $^{14}\text{N}_2$ and $^{15}\text{N}_2$ by tuning the train period near the quantum resonance, and spin-selective control in a mixture of different spin isomers of $^{15}\text{N}_2$ by kicking the molecules near the fractional quantum resonance.

Strong laser fields affect molecular rotation by exerting an angle dependent torque on the field induced molecular dipole [54, 130, 158, 190]. In the limit of ultrashort laser pulses, the pulse acts on a molecule as an instantaneous rotational “$\delta$-kick”. In the quantum picture, a laser kick induces multiple Raman transitions
between the rotational states of the molecule, transferring population from lower to higher rotational states and creating a coherent rotational wavepacket - a quantum-mechanical analogue of the ensemble of classical rotors. Because of the discrete energy spectrum of the rotational wavepacket, its dynamics is periodic in time, with a period known as the rotational revival time $[125]$. Rotational revivals have been thoroughly studied in the context of molecular alignment $[127]$ - the appearance of a preferential direction in the distribution of molecular axes $[141]$.

Quantum periodicity of the rotational dynamics raises the question about the ability to enhance, and possibly control, molecular rotation with a periodic sequence of laser pulses (a “pulse train”) $[91]$. An accumulative effect of a pulse train on the degree of molecular alignment has indeed been observed when a train period exactly matched the revival time $[34]$, yet the direct measurement of the degree of rotational excitation and its dependence on the train period have not been studied. Here, we detect the total energy transfer between the optical field and the molecules, showing that the accumulation of rotational energy in the molecular species resonant with the applied pulse train is substantially higher than in the off-resonance molecules.

Understanding the dynamics of molecules driven by periodic laser fields in the context of periodically kicked rotor may offer new tools in numerous schemes of coherent control of chemical reactions $[135, 182]$, laser cooling and trapping of molecules $[53]$, control of molecular collisions $[151]$, deflection of molecular beams $[58, 119]$, high harmonic generation $[66, 165]$ and molecular scattering from surfaces $[73, 83]$. Being proportional to the molecular moment of inertia, the rotational revival time is different for different molecules, even if their chemical structures are identical as in the case of molecular isotopologues. Differences in revival times have been used to selectively align a single species in a mixture of molecular isotopologues $[50]$ by utilizing constructive and destructive interference in rotational excitation by a pair of short laser pulses $[89]$. Longer pulse trains significantly increase the degree of selectivity, for example enabling one to excite predominantly a single angular momentum $J$-state $[188]$. The effect of quantum resonance provides an alternative approach to selective coherent control of molecular rotation in mixtures $[52]$.

Our experimental setup is depicted in Fig.3.21(a). Cold nitrogen was produced
Figure 3.21: (a) Experimental setup. Cold nitrogen molecules from a supersonic expansion enter the detection chamber through a 1 mm-diameter skimmer. The rotational temperature, calculated from the REMPI spectrum, is 6.3 K. The molecules are excited by a femtosecond pulse train produced with a pulse shaper (red beam) and ionized 100 ns later with a narrowband UV pulse (blue beam) shifted downstream with respect to the excitation pulse. The ions are extracted and detected with a standard time-of-flight (TOF) apparatus. (b) Example of the intensity envelope of a pulse train implemented in this work ($A = 2.5, \tau = 8.5$ ps). Measured (red solid line) and calculated (green dashed line) intensity profile. The insets show the discrepancies attributed to the finite optical resolution of the shaper.
by a supersonic expansion from a pulsed valve nozzle (Even-Lavie valve, EL-5-C-S.S.-2010). After entering the second chamber through a 1 mm-diameter skimmer, the molecules were excited by a femtosecond pulse train and probed by a resonance enhanced multi-photon ionization (REMPI) with a second narrowband pulse. Probe pulses were focused downstream from the excitation region and timed in such a way as to account for the molecular motion between the two spots. The ions were extracted with a time-of-flight (TOF) apparatus and the total ion signal was measured with a microchannel plate detector. The ion signal was averaged over 20 pulses.

The excitation pulse train was obtained by phase-only shaping of a linearly polarized 600 µJ pulse originated from a regenerative amplifier (Spectra-Physics, Spitfire, 2 mJ at 1 KHz repetition rate). We used a home built 4f Fourier pulse shaper [167] based on a 640-pixel liquid crystal spatial light modulator (CRi). To avoid strong multi-photon ionization of nitrogen by the femtosecond train, the shaper was slightly misaligned for stretching the pulses from 150 fs to about 500 fs. Sinusoidal phase modulation \( \phi(\omega) = A \sin((\omega - \omega_0)\tau) \) was introduced to the input pulse spectrum to create a pulse train in the time domain, \( E(t) = \sum_{n=-\infty}^{\infty} J_n(A) \varepsilon(t + n\tau) \cos(\omega_0 t) \), where \( \varepsilon(t) \) and \( E(t) \) represent the electric field envelopes of the input and output pulses, respectively, \( A \) is the spectral phase modulation amplitude, \( J_n(A) \) are the Bessel functions of the first kind, \( \tau \) is the train period and \( \omega_0 \) is the carrier frequency of the input field. High resolution of the shaper (\( \Delta \lambda = 0.04 \text{nm/pixel} \)) allowed us to produce pulse trains of seven pulses with periods of up to 10 ps. An example of a pulse train (both calculated and measured) with \( A = 2.5 \) and \( \tau = 8.5 \) ps is shown in Fig.3.21(b). Due to the finite resolution of the shaper, the end pulses at \( \pm 17, \pm 26 \) ps are slightly distorted, but are still shorter than the rotational period of N\(_2\) in the highest rotational state \( (J = 7) \) accessible with the available total pulse energy of 190 µJ after the shaper. To achieve high intensity of the laser field, required for driving multiple Raman transitions between the rotational levels, pump and probe beams were focused by a 150 mm focal length lens. After measuring the focal spot size, the pump laser intensity was estimated on the order of \( 5 \times 10^{12} \) W/cm\(^2\). This corresponds to the dimensionless total kick strength \( P \approx 7 \). The latter corresponds to an average amount of angular momentum (in units of \( \hbar \)) transferred from the field to the molecule, and is defined
Figure 3.22: REMPI spectra of $^{14}\text{N}_2$. Relevant peaks of the S-branch are labeled by the corresponding $N''$ numbers. Prior to the application of a femtosecond pulse train, the distribution of rotational population is thermal and corresponds to 6.3K (lower solid blue line - experiment, dashed green line - calculations [63]). At this temperature, only $N'' = 0, 1$ and 2 are populated significantly. An example of the REMPI spectrum of rotationally excited molecules is shown by upper solid red line. For a total laser kick strength used in our experiments, states up to $N = 7$ are populated.

as $P = \Delta \alpha / (4\hbar) \int \varepsilon^2 dt$, where $\Delta \alpha$ is the anisotropy of the molecular polarizability, and $\varepsilon$ is the electric field strength [5].

The rotational distribution was probed by narrowband nanosecond pulses from a tunable dye laser (Sirah, Precision Scan, 2 mJ at 283 nm and 10 Hz repetition rate). Nitrogen molecules were ionized via a “2 +2” resonance enhanced multi-photon ionization, with a two-photon resonant transition $a^1\Pi_g (v' = 1) \leftarrow X^1\Sigma_g^+ (v'' = 0)$. The frequencies of the S-branch transitions ($\Delta N = 2$) are well separated, allowing us to detect the population of the first eight rotational levels $N'' = 0, 1, ..., 7$ of the ground electronic state. REMPI spectrum of $^{14}\text{N}_2$ molecules before and after the application of the excitation laser field is shown in Fig.3.22.

To measure the total rotational energy absorbed by the molecules, we detected the transfer of population from the initially populated ($N'' = 0, 1, 2$) to higher
(N'' ≤ 7) rotational states as a function of the pulse train period. REMPI signal was measured by tuning the probe wavelength to the corresponding peak of the REMPI spectrum, and recording the ion signal while scanning the train period with the pulse shaper. To determine the relative population of each rotational level, \( S_{N''} \), REMPI signals were scaled with the corresponding two-photon line strength factors for the \( N' \leftarrow N'' \) rotational transitions and the nuclear spin degeneracy weights \([3]\). The results are shown on the logarithmic scale in Fig.3.23(a). One can see that the highest increase of rotational energy (i.e. the most efficient population transfer up the rotational ladder) occurs around 8.4 ps - the revival time of \( ^{14}N_2 \), where the population is efficiently transferred from the lower to higher angular momentum states, as indicated by the dips and peaks in \( S_{0,1} \) and \( S_{2,...,7} \), respectively. Small drop of the total population (\( \sum_{N''} S_{N''} \)) below unity away from quantum resonance can be attributed to the resonance-enhanced anisotropy of the spatial distribution of the molecular angular momentum, which was not taken into account in our conversion of the REMPI signal to the relative populations. In panel (b), the population distribution is converted to the scaled total energy absorbed by the molecules and plotted as a function of the dimensionless detuning from quantum resonance, \( \varepsilon = 2\pi[t/T_{\text{rev}} - 1] \). The plot shows good qualitative agreement with a characteristic oscillating behavior predicted in \([52]\).

To emphasize the resonant nature of the rotational energy accumulation by the molecules, we normalized the ion signal for each \( N'' \) separately (i.e. divided each curve in Fig.3.23(a) by its maximum value) and plotted the results as a two-dimensional map in Fig.3.24(a). The effect of quantum resonance is clearly demonstrated by the significantly enhanced population transfer to higher \( J \)-states in the case when the period of the femtosecond pulse train matches the rotational revival time. Remarkably, even for a relatively small number of pulses in the train (see Fig.3.21), the observed resonance is quite narrow and can be used for selective rotational excitation of molecular mixtures. We demonstrate this by performing the same measurement with two isotopologues of nitrogen, which have identical chemical structure but different rotational properties, reflected by the difference in the revival time. The detected population transfer efficiency for \( ^{14}N_2 \) (\( T_{\text{rev}} = 8.38 \) ps) and \( ^{15}N_2 \) (\( T_{\text{rev}} = 8.98 \) ps) is shown in Figs.3.24(a) and (c), respectively. By tuning the pulse train period to 8.4 or 9.0 ps, one can induce the rotation of a selected
dependence on detuning, population and scaled energy (no re-scaling).

Train period (ps) 7.5 8.0 8.5 9.0 9.5
Rotational Population 0 1 2 3 4 5 6 7
Scaled Absorbed Energy (a) 0.05 0.1 0.2 0.3 0.4 0.5
(b)

Figure 3.23: (a) Relative populations $S_{N''}$ of the rotational levels of $^{14}N_2$ as a function of the pulse train period. Each curve is labeled with the corresponding rotational quantum number $0 \leq N'' \leq 7$. Vertical dashed line marks the rotational revival time, at which the efficiency of the rotational excitation by a periodic train of pulses is significantly enhanced. Total population, $\sum_{N''} S_{N''}$, is depicted by the upper dash-dotted line.

(b) Total absorbed energy, normalized by its resonant value, as a function of the dimensionless detuning from quantum resonance (see text).
Figure 3.24: Experimental results (upper row) and numerical simulations (bottom row) of a normalized REMPI signal (color coded) for different $N''$ states as a function of a pulse train period. Left and middle columns correspond to $^{14}N_2$ and $^{15}N_2$, respectively. For a pulse train period equal to the revival time (white vertical lines) the population is efficiently transferred from the initial states $N'' = 0, 1, 2$ to higher states $N'' = 3, 4, ..., 7$. Right column shows the rotational population distribution for $^{15}N_2$ as a function of the pulse train period around $3/4T_{\text{rev}}$.

The results of numerical calculation of the rotational population transfer for both isotopologues are shown in the bottom row of Figure 3.24 (panels (b) and (d)). In our simulations, we averaged over the fast oscillations of the electric field, expanded the wave function in the spherical harmonics, and solved numerically the time-dependent Schrödinger equation to obtain the expansion coefficients [52]. The actual shape of the generated pulse trains has been included in the calculations. To take into account thermal effects, we averaged over the initial states, where each result is weighted by the Boltzmann coefficient (including nuclear spin statistics) of the initial state.

Molecular spin isomers, such as para- and ortho-isomers of $^{15}N_2$, exhibit identical revival times yet different structure of rotational levels. Paranitrogen (total nuclear spin $I = 0$) does not have odd $N$ states in its rotational spectrum, whereas even $N$’s are missing in the spectrum of orthonitrogen (total nuclear spin $I = 1$). In this case, coherent control of molecular rotation can be based on fractional, rather
than full, rotational revivals. An example is shown in Figure 3.24(e) and (f) (experiment and theory, respectively), where selective population transfer into even (odd) excited rotational states of para (ortho) nitrogen is achieved by tuning the period of the femtosecond pulse train slightly below (above) $3/4T_{\text{rev}}$.

We note that unlike the selectivity of molecular alignment demonstrated with a sequence of two pulses [51, 124], our results suggest that pulse trains may offer a new way of state selective rotational excitation.

With a relatively small number of pulses used here, the selectivity is limited to low lying $N''$ states (e.g. $N'' = 4$ at $t \approx 6.3$ ps or $N'' = 5$ at $t \approx 7.1$ ps). Longer pulse trains, however, may lead to narrower resonances and enable population transfers into single states of high angular momentum. This would require a sequence of pulse trains with decreasing train period. While it is not clear if such combinations are practical, the possibility is evident.

In summary, periodically kicked quantum rotor was studied experimentally and theoretically, using nitrogen molecules and a train of ultrashort laser pulses. Quantum nonlinear resonances have been demonstrated in the efficiency of rotational excitation as a function of the pulse train period. Enhancement of the rotational energy transfer has been observed at and around full and fractional revivals of the molecular quantum wavepacket. The ability to utilize quantum resonances for the selective excitation of different molecular isotopologues and nuclear spin isomers has been shown.
Chapter 4

Conclusions

In the presented work we experimentally realized and studied several scenarios of coherent control of electronic and rotational quantum states using shaped broadband laser pulses.

We demonstrated that coherent superpositions of states can be efficiently created and controlled. This paves the way for experiments on coherent control of chemical reactions and more efficient time resolved spectroscopic methods. One of the promising application can be control of photo-association of cold atoms into an ultracold molecule. After the molecule is formed, excitation of a vibrational wavepacket of an excited electronic state and subsequent stimulated emission might be used to transfer the molecule to the ground vibrational state. Excitation of a wavepacket is essential in a popular spectroscopic technique of coherent antistokes Raman scattering. Promoting the excitation of a wavepacket beyond the limits of the perturbative regime one can achieve higher sensitivity and lower acquisition times.

As we described in Chapter 2, while the chosen wavepacket detection method allowed quantitative characterization of wavepacket populations, the uncertainty is high. Improving the wavepacket detection and accurate verification of the target states’ population discussed here would be an interesting and important direction for the future study.

As we demonstrated in the second part of the present dissertation, rotational states of a diatomic molecule can be effectively excited using trains of short pulses.
Using this system one can study the fundamental problem of the quantum-classical correspondence in chaotic systems. Studies of collisions of a rotating molecule with neutral atoms and solid surfaces were proposed theoretically and can benefit from the developed excitation methods.

Experimental comparison of different techniques such as optical centrifuge, double-kick scheme, etc. with the excitation by pulse trains was out of scope of this dissertation. Such study is currently underway in our research group at UBC.
Bibliography


→ pages [115]


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[95] V. V. Lozovoy and M. Dantus. Laser control of physicochemical processes; experiments and applications. Annual Reports Section "C" (Physical Chemistry), 102, 227, 2006. → pages 67


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Physical Journal D - Atomic, Molecular, Optical and Plasma Physics, 12, 255, 2000. → pages 2, 32, 82


