Ultrafast Switching of Coherent Electronic Excitation: Great Promise for Reaction Control on the Femtosecond Time Scale

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Abstract. We report on a physical mechanism of coherent control with shaped intense femtosecond laser pulses. To this end we study photoelectron spectra from the multi-photon ionization of potassium atoms using tailored femtosecond laser pulses. Our results are interpreted in terms of Selective Population of dressed states (SPODS). Two realizations of SPODS by Photon Locking and Rapid Adiabatic Passage are discussed. A physical picture of SPODS based on the interplay of the laser electric field and the atomic wave function is presented. In addition, coherent control of a larger molecule (isopropyl alcohol) by shaped femtosecond laser pulses is demonstrated experimentally.

1. Introduction

With the advent of femtosecond laser pulses the temporal aspect of the interplay of light and molecular dynamics came to the fore and became experimentally accessible. The beauty of femtochemistry lies in our ability to observe [1] and to manipulate [2,3] ultrafast processes as they occur. Shaped femtosecond optical laser pulses [4] are the suitable tools to exert microscopic control on molecular dynamics at the quantum level. Fig. 1 depicts the concept of quantum control exerted by suitably shaped femtosecond laser pulses.

Initially, the quantum system is in the ground state $|i\rangle$. The dynamics induced by specifically designed laser pulses (three examples of which are depicted in Fig. 1) drives the system towards one of the possible final states $|f_i\rangle$. This particular target state represents for instance a specific excitation in an atom or molecule which initiates a desired physical process or chemical reaction. Important require-ments for applications of quantum control are (1) the ability to address different target states, i.e. *tunability* among the manifold of final states, and (2) to ensure that only one of the final states is populated, i.e. high *selectivity* among the final states. The combination of pulse-shaping techniques with closed loop adaptive feedback learning algorithms [5–8] allows to optimize virtually any conceivable observable as reviewed for example in [9,10]. However, it is not always possible to deduce the underlying physical mechanism from the electrical fields obtained by this procedure. Therefore, the need to bridge the gap between the efficient ‘black box’ closed loop optimal control methods and detailed understanding of the physical processes especially in strong laser fields is quite

evident. To that end we combine femtosecond laser techniques with atomic-/molecular beam techniques and photoelectron-/ion detection techniques [11] in order to investigate the physical mechanism of strong field quantum control on simple systems with well characterized shaped pulses. So far we have extended weak field methods to free electrons [12]. New techniques making use of polarization control in molecular multi-photon excitation [13] and shaped intense laser pulses for molecular alignment [14,15] open further dimensions in this field.

Within this context, shaped *resonant* intense pulses are of special interest, as this class of pulses is of *general importance.* Resonant control scenarios will be the dominant pathways as shorter and shorter pulses with ultra broad spectra become available. Figure 2 shows the general picture of the physical principles of resonant strong field control. In this scenario, control is exerted via the intermediate resonant state |r>. In general, strong laser fields give rise to an energy

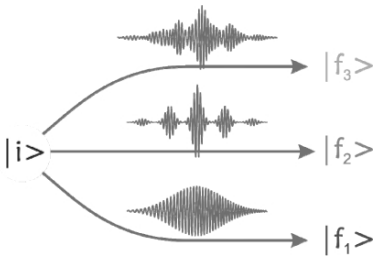

Fig. 1. Principle of quantum control by shaped femtosecond laser pulses: control is obtained by the design of pulse shapes that guide the quantum system from an initial state |i> to different final states $|f_i>$ with high efficiency and high selectivity

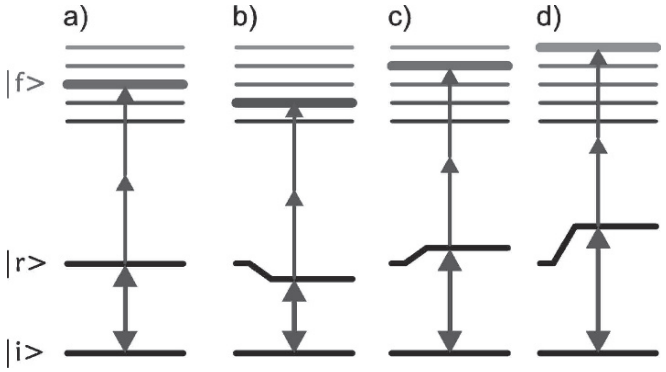

Fig. 2. Quantum control of multi-photon processes via an intermediate resonant state: (a) shaped resonant laser pulses are used to steer the initial population in state |i> via the intermediate resonant state |r> to an individual target state |f> within a manifold of final states. (b) and (c) selective population transfer is obtained by manipulating the energy of the resonant state |r>. (d) selection of a particular target state among the manifold of final states is achieved by tuning the intermediate resonant states into resonance with the desired target state

splitting of the resonant state into two (so called *dressed*) states in the order of $\hbar\Omega$, where Ω describes the Rabi-frequency. The decisive step in switching among different final electronic states is realized by manipulation of dressed state energies and dressed state populations. By suitable phase shaping of the driving laser field, it is possible to populate only one of these two (dressed) states [16], i.e., to realize *Selective Population of Dressed States* (SPODS). Effectively, population of a single dressed state corresponds to a controlled energy shift of the resonant state into a desired direction as illustrated in Fig. 2(b) and (c). In Fig. 4(b), a physical picture for population of a single dressed state is given. Generally, during laser *excitation* the driving laser field precedes the atomic dynamics by a phase of $\pi/2$. However, in the case of SPODS the wave function of the superposition state $|\psi(x,t)|^2$ and driving laser field are perfectly in-phase (no phase shift) or anti-phase (phase shift of π). This is exemplified in the upper (lower) panel of Fig. 4(b) for selective population of the upper (lower) dressed state. Depending on the orientation of the atomic dipole with respect to the laser field vector $\mathcal{E}$ the interaction between the atomic dipole and the laser field gives rise to a positive or negative energy contribution. By variation of the laser intensity the energy splitting can be controlled and thus a particular target state among the manifold of final states are addressed (cf. Fig. 2(d)) providing tunability.

2. Experimental

An experimental implementation of resonant strong field control is shown in Fig. 3(a). This approach makes explicit use of the manipulation of the temporal phase of a pulse sequence with attosecond precision [17]. Sequences of pulses are generated by sinusoidal phase modulation in frequency domain [4,18,19] with our home-built pulse shaper [20]. The shaped pulses are allowed to interact with potassium atoms in an atomic beam. Photoelectron spectra for different pulse shapes are measured using a Time-Of-Flight (TOF) electron spectrometer. Experimentally we make use of a 1+2 REMPI process on potassium atoms (see Fig. 3(b)). An intense fs-laser couples coherently the 4*s* and 4*p* states and at the same time ionizes the system in a two photon process. The shape of the photoelectron spectra reflects the temporal phase of the excited state amplitude [11]. In particular, the photoelectron spectra map the dressed state population. During the time evolution, the dressed states are characterized by a time-dependent energy splitting giving rise to the observed Autler-Townes (AT) splitting [21] in the photoelectron spectra. Employing two-photon ionization as the non-linear probe step precludes averaging over the intensity distribution within the laser focus since the ionization probability is highest in the spatial region of highest laser intensity. This technique permits us to overcome the common problem of washing out intensity dependent strong field effects.

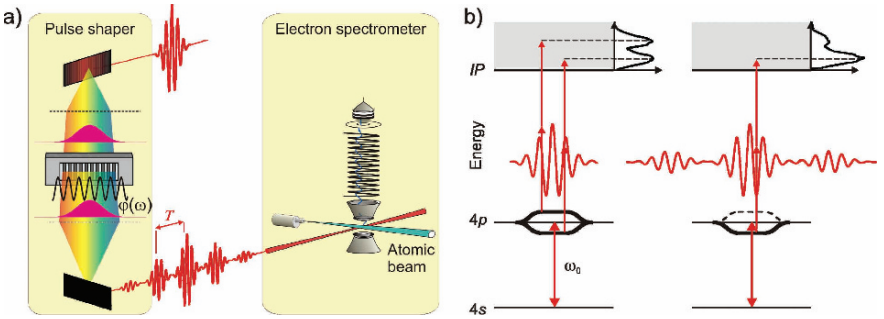

Fig. 3. (a) Schematic of the experimental set-up: tailored pulse trains are created via applying a phase mask in the Fourier plane of our pulse shaper [20]. In the case discussed here, the spectrum of our femtosecond laser pulse (785 nm, 30 fs, 0.35 – 2μJ) is phase-modulated in frequency domain with a sinusoidal phase function $\varphi(\omega) = A \sin[(\omega-\omega_0) T + \phi]$ with A = 0.2, T = 170 fs and $\omega_0 = 2.40$ fs^{-1} to produce a sequence of pulses in time domain separated by T. The pulses are focused on a potassium atomic beam. The resulting photoelectrons are detected with a magnetic bottle Time of Flight photoelectron spectrometer. (b) Schematic of the excitation scheme (potassium-atoms): The bare states are indicated with thin lines. Thick lines illustrate the dressed state splitting during the interaction giving rise to a symmetric Autler Townes splitting (left). Selective population of a dressed state with a tailored pulse train is shown in the right panel, leading to a strongly asymmetric Autler Townes doublet

3. Results and Discussion

Figure 4 shows two realizations of SPODS on potassium atoms using (a) phase-locked double pulses and (c) chirped femtosecond laser pulses. In both cases the experimentally observed photoelectron spectra are in good agreement with our simulations [19]. The results shown in Fig. 4(a) have been discussed in the bare state picture [17] and with the help of dressed states [16]. Briefly, the first pulse creates a coherent electronic superposition state. Depending on the relative optical phase of the second pulse either the upper or the lower dressed states are populated with high selectivity as seen in the alternating peaks in the photoelectron spectra. This realization of SPODS is based on Photon Locking [22]. An alternative realization of SPODS shown in Fig. 4(c) is based on Rapid Adiabatic Passage (RAP) [23,24] by chirped laser pulses. In our experiment chirped pulses are created by quadratic spectral phase modulation. By variation of the chirp parameter, we can switch between the population of the upper and the lower dressed state. Up-chirped pulses lead to population of lower dressed state and vice versa. Making use of adaptive feedback learning algorithms we are able to control the dressed state population by more than 90% as seen by the corresponding suppression of one AT component [16].

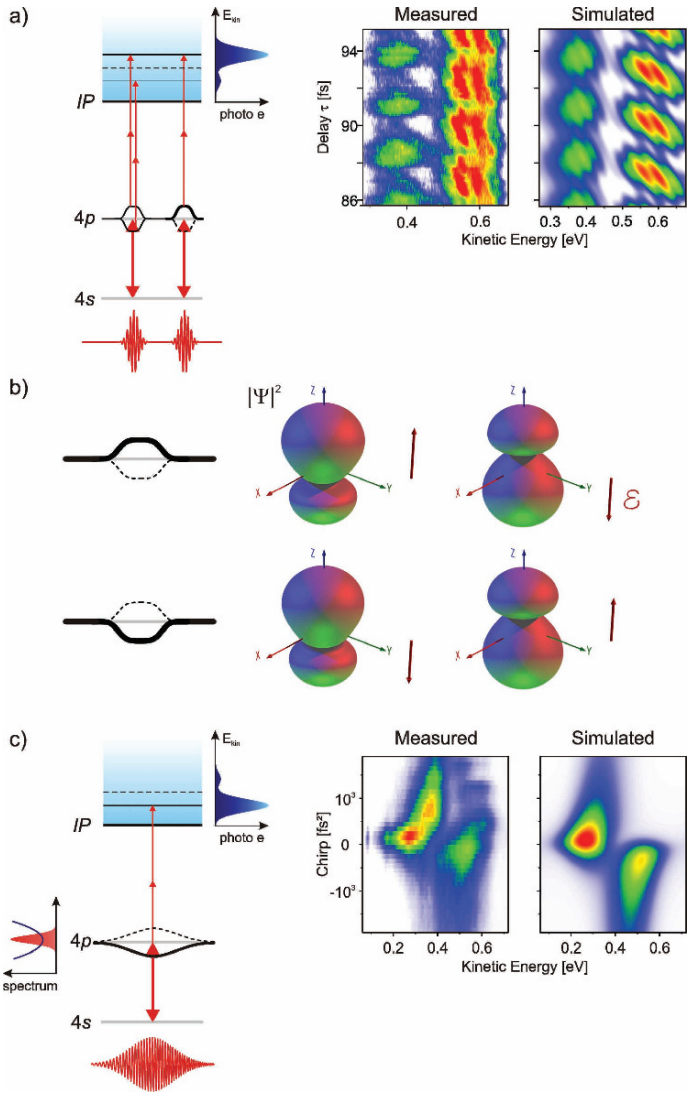

Fig. 4. Selective population of dressed states (SPODS) on potassium atoms via (a) Photon Locking in a two-pulse experiment and (c) Rapid Adiabatic Passage (RAP) using chirped pulses. Measured photoelectron spectra (false colour representation) as a function of the pulse parameters (a) delay and (c) chirp are in good agreement with the simulated results. (b) population of a single dressed state manifests itself by in-phase or anti-phase oscillations of the wave function of the superposition state $|\psi(x,t)|^2$ with respect to the driving laser field vector $\mathcal{E}$. Examples for two orientations of the electrical field vector $\mathcal{E}$ with respect to the wave function during selective population of the upper dressed state (upper panel) and lower dressed state (lower panel) are shown

With the help of tailored pulse trains we demonstrate that SPODS is highly selective, tunable (up to 250 meV) and robust [25]. In Fig. 5 experimental results – obtained with a pulse train created by applying a sine mask in the Fourier plane of the pulse shaper (see Fig. 3) – are displayed.

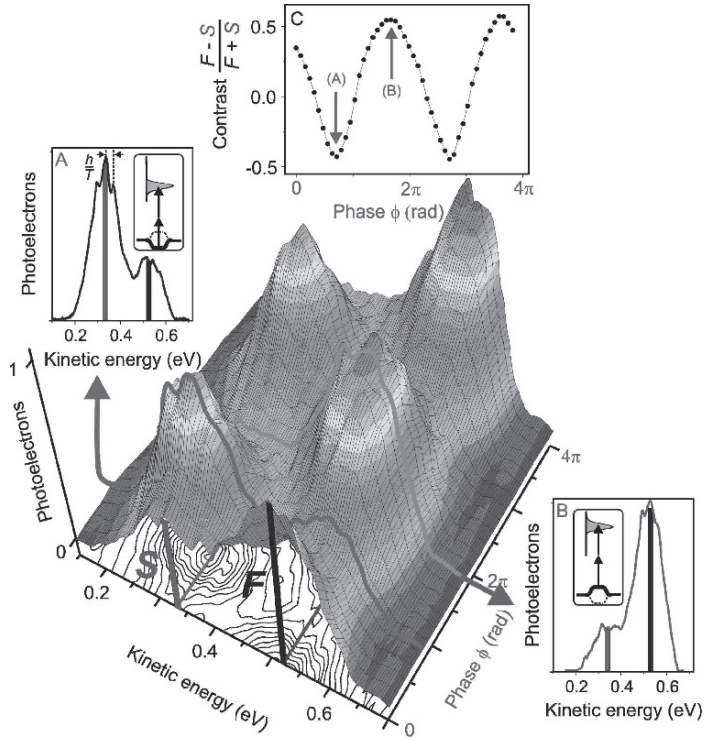

Fig. 5. The Selective Population of Dressed States (SPODS) is directly mapped into the measured photoelectron spectra by variation of the phase ϕ. The maximum of the asymmetric photoelectron distribution alternates between 0.33 eV and 0.52 eV. These results are obtained at a laser energy of W = 0.5 μJ. A section through the distribution along the energy axis at ϕ = 0.7 π – indicated with the violet trajectory – yields the photoelectron spectrum (A) where the lower dressed state is selectively populated as depicted in the inset to (A). Fringes in the spectrum with an energy separation of h/T arise from the interference of free electron wave packets [12] launched during the different pulses. Selective population of the upper dressed state is achieved at ϕ = 1.7 π as indicated with the magenta trajectory and plotted in spectrum (B). The signal of the slow photoelectrons at 0.33 eV (S) and the fast photoelectrons at 0.52 eV (F) – as indicated with the red and blue bars – is obtained as a function of the phase ϕ by taking a section through the distribution along the phase coordinate. The contrast of F and S, i.e., (F–S) / (F+S) as shown in (C) is a measure of the selectivity of dressed state population. The phases corresponding to the highest selectivity for population of the lower dressed state – spectrum (A) – and the upper dressed state – spectrum (B) – are indicated with violet and magenta arrows respectively

Besides the experimental demonstration of SPODS on atoms, theoretical studies on potassium dimers (K_2) have been performed [25,26]. These studies confirm the applicability of strong field control by SPODS to molecules. In particular, the insights into the physical mechanism of strong field control obtained on atoms can be used to design shaped laser pulses to efficiently switch the final population among different electronic states of a diatomic molecule. For applications to chemistry, it is particularly important to validate coherent control strategies on larger molecules. As a first step, we investigate the mass spectra – measured with a TOF spectrometer – from dissociation of isopropyl alcohol (C_3H_8O) using a pulse sequence. The results shown in Fig. 6 show pronounced variations in the molecular ion yield upon variations of the phase ϕ in the pulse sequence. In these experiments we simultaneously measured the atomic ion yield of K^{39} and K^{41} at about 7.8 µs and 8.1 µs respectively. Here no significant variations of the ion-yield with the phase ϕ were found as expected since ion detection integrates over all accessible final electronic states. This result confirms that neither scattering losses or spectral/spatial cross-sensitivities are introduced by our pulse shaper. These observations show that control on the molecular dynamics of isopropyl alcohol is exerted by the optical phase of the shaped pulse.

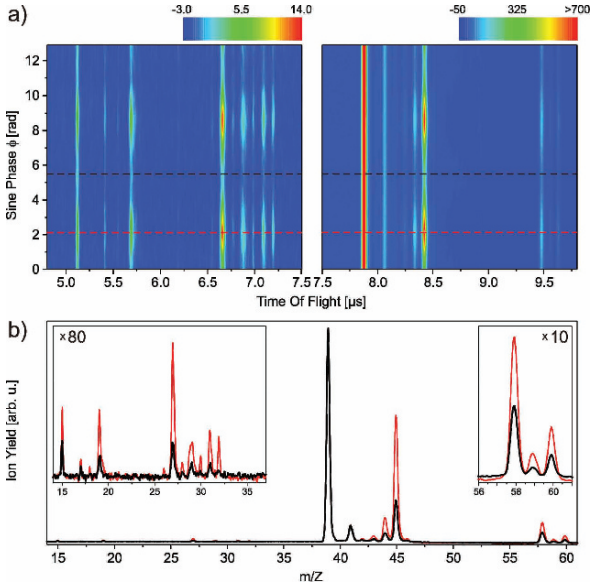

Fig. 6. (a) false color representation of TOF - mass spectra from the dissociation of isopropyl alcohol (C_3H_8O) using a pulse sequence. Shaped laser pulses are generated by sinusoidal spectral phase modulation of $E = 10$ µJ, $\lambda = 790$ nm, $\Delta t = 30$ fs pulses using a phase function $\varphi(\omega) = 0.5 \sin[50 \text{ fs } (\omega - 2.4 \text{ fs}^{-1}) + \phi]$. The phase ϕ is varied within 4π. (b) sections through the mass spectra at $\phi = 2$ rad (red) and $\phi = 5.5$ rad (black) exhibit a strong variation of the molecular ion yield. At m = 45 u ($C_2H_5O^+$) a variation in the molecular ion yield by a factor of 3 is observed. The insets show a magnification of the spectra. The atomic ion yield of K^{39} (7.8 µs) and K^{41} (8.1 µs) measured simultaneously shows no variation with the phase ϕ

However, so far it is not fully clear whether the physical mechanism underlying our observations on isopropyl alcohol is based on SPODS. Currently, other physical mechanisms such as spectral interference [27,28] can not be ruled out. In future we will carry out systematic studies on the intensity dependence of phase control of larger molecules. Intensity dependent phase effects as observed in strong field control of atoms [17] and molecules [26] provide a critical test to discriminate weak field control scenarios such as spectral interference from strong field control exemplified by SPODS.

4. Conclusions

Since switching between selective population of either dressed states occurs within a few femtoseconds, this technique is also interesting for applications in the presence of decoherence processes. SPODS can be realized with very different pulse shapes making use of diverse physical mechanisms ranging from Photon Locking [17,25,29] – to Rapid Adiabatic Passage [24]. In this sense, SPODS provides a unifying framework to describe resonant strong field control scenarios. We believe that SPODS is at play in many other circumstances as well, for instance in adaptive closed loop experiments [16,30,31]. Because SPODS combines high selectivity (more than 90% as observed in our experiments) and tunability (several hundred meV) with efficient population transfer, relevant applications to chemistry – so far investigated theoretically [25,26] – are within reach. Initial studies on mass spectra from dissociation of isopropyl alcohol using pulse sequences show pronounced phase effect.

Acknowledgements

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