

# Coherent control of electrons, atoms and molecules with intense shaped light pulses

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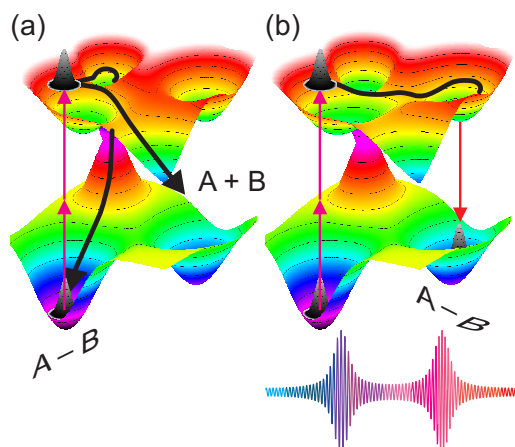
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**Abstract.** We report on a physical mechanism of coherent control with intense shaped femtosecond laser pulses. We study photoelectron spectra from multi-photon ionization of potassium atoms and dimers using tailored femtosecond laser pulses. Our results are interpreted in terms of Selective Population of Dressed States (SPODS). Two realizations of SPODS by Photon Locking (PL) via pulse sequences and Rapid Adiabatic Passage (RAP) via chirped pulses are discussed. New physical mechanisms arise, when both PL and RAP are at play simultaneously. Control by the combined effect of PL and RAP is studied by mapping out a two-parameter Quantum Control Landscape (QCL) for selective population of dressed states.

## 1. Introduction

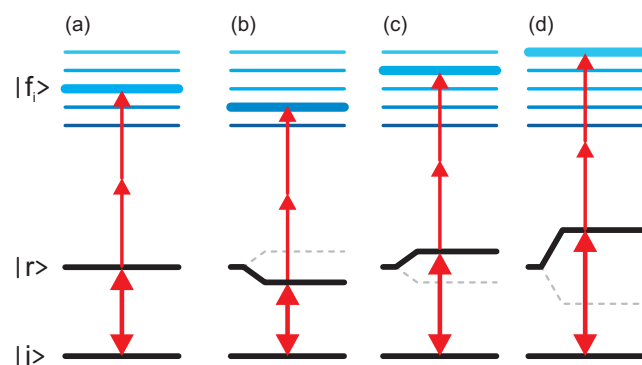
Quantum control deals with the design of suitably shaped laser pulses in order to guide a quantum system from an initial quantum state to a preselected final target state with high efficiency. Quantum control strategies making use of tailored ultrashort light pulses are enormously successful to manipulate a great variety of physical and chemical properties of matter. Applications range from basic research, non-linear optics, materials processing, quantum computing to coherent control of chemical reactions [1]. The operating principle of chemical reaction control is shown in Fig. 1. Upon excitation, a wave packet is created in the excited Potential Energy Surface (PES) of a molecule A–B. Multiple pathways (Fig. 1(a)) such as dissociation or relaxation via conical intersections are available to form – sometimes unwanted – reaction products or dissipate the excitation energy. To steer this process, coherent control schemes have been devised to manipulate the initial position and momentum of the excited state wave packet in order to select one of the accessible pathways [2, 3] via shaped laser pulses [4, 5]. Strong shaped laser pulses open new pathways by modifying the excited state PES via AC Stark-shifts as shown in Fig. 1(b). These pathways on the light-induced potentials open new reaction channels which are inaccessible in weak laser fields. The combination of pulse-shaping techniques with closed loop adaptive feedback learning algorithms [6, 7, 8, 9] allows to optimize virtually any conceivable observable as reviewed for example in [10, 11]. However, in many cases the underlying physical processes are not very well understood – particularly when shaped *resonant intense* pulses are applied. This class of pulses is of general importance because resonant control scenarios will be the dominant pathways as shorter and shorter pulses with ultra broad spectra become available.

Fig. 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  $|r\rangle$ . In general, strong



**Figure 1.** (Colour online) Operating principle of coherent control exerted on a photochemical reaction involving the ground and excited state Potential Energy Surface (PES) of the molecule A-B. (a) examples of reaction pathways on the unperturbed excited state PES. (b) a new pathway on the PES modified by the interaction with a shaped strong laser field (bottom) gives rise to a reaction channel inaccessible in weak laser fields.

laser fields give rise to an energy splitting of the resonant state into two (so called dressed) states in the order of  $\hbar\Omega$ , where  $\Omega$  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 one of these two (dressed) states [12], 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) for the lower and upper dressed state respectively. By variation of the laser intensity the energy splitting can be controlled and thus a particular target state among the manifold of final states is addressed (cf. Fig. 2(d)) providing tunability. In this contribution, we combine femtosecond laser



**Figure 2.** (Colour online) Quantum control of multi-photon processes via intermediate resonant states: (a) shaped resonant laser pulses steer the population from the initial state  $|i\rangle$  via an intermediate resonant state  $|r\rangle$  to a single target state  $|f\rangle$  within a manifold of final states  $|f_i\rangle$ . (b) and (c) selectivity in the population transfer is obtained by manipulating the energy and population of the dressed states. (d) shows tunability among the target states.

techniques with atomic- and molecular beam techniques and photoelectron detection techniques [13, 14, 15] in order to investigate the physical mechanism of strong field quantum control on simple systems (potassium atoms and dimers) with well characterized shaped pulses.

## 2. Theoretical description

In order to study the control scenario shown in Fig. 2, we use potassium atoms as a model system providing the one-photon resonance  $4p \leftarrow 4s$  and a manifold of final target states  $|f_i\rangle$  in the ionic continuum (cf. Fig. 4). In this section we summarize the theoretical description of photoelectron spectra obtained from resonant  $4p$  excitation and simultaneous two-photon ionization detailed in [16] (and references therein). Making use of the fact that the coupling among the initial state  $4s$  and the resonant intermediate state  $4p$  is much stronger than the coupling of either state to

the continuum, the numerical calculation of the total photoionization process is divided into two steps. At first, the strong field interaction of the shaped laser pulse with the neutral system is treated by solving the time-dependent Schrödinger equation

$$i\hbar \frac{d}{dt} \begin{pmatrix} c_{4s} \\ c_{4p} \end{pmatrix} = -\frac{\hbar}{2} \begin{pmatrix} 0 & \Omega \\ \Omega^* & 0 \end{pmatrix} \begin{pmatrix} c_{4s} \\ c_{4p} \end{pmatrix} \quad (1)$$

in the interaction picture, applying the rotating wave approximation and using the short time propagator method. Herein,  $c_{4s}$  and  $c_{4p}$  are the time dependent probability amplitudes of the corresponding quantum states. In the second step, the two-photon ionization starting from the  $4p$  state is evaluated in the framework of second order perturbation theory. The final photoelectron amplitude then reads [17, 18, 19]

$$c(\omega_e) \propto \int_{-\infty}^{\infty} c_{4p}(t) \Omega^2(t) e^{i(\omega_e + \omega_{IP} - \omega_{4p})t} dt \quad (2)$$

with  $\hbar\omega_e$  being the kinetic excess energy of the emitted electron,  $\hbar\omega_{IP}$  the potassium ionization potential and  $\hbar\omega_{4p}$  the eigenenergy of the  $4p$  state.

### 3. Experimental

The experimental implementation of SPODS is based on a combination of femtosecond pulse shaping techniques [20] with atomic/molecular Time-Of-Flight (TOF) photoelectron spectroscopy. In our experiment (cf. Fig 3) the spectrum of a femtosecond laser pulse (790 nm, 30 fs, 0.35 – 2  $\mu$ J) is phase-modulated in frequency domain by applying a spectral phase function  $\varphi(\omega)$  to the Liquid Crystal Spatial Light Modulator (LC-SLM). In the experiments with atoms (Sec. 4.1) we study the effect of chirps by quadratic phase modulation

$$\varphi(\omega) = \varphi_2 \cdot (\omega - \omega_0)^2 \quad (3)$$

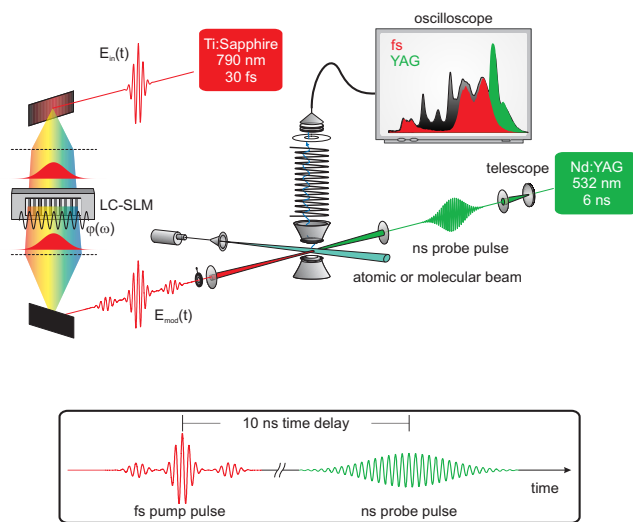
and pulse sequences by sinusoidal phase functions

$$\varphi(\omega) = A \sin[(\omega - \omega_0) \cdot T + \phi]. \quad (4)$$

Linear combinations of both types of modulation, i.e.  $\varphi(\omega) = \varphi_2 (\omega - \omega_0)^2 + A \sin[(\omega - \omega_0) \cdot T + \phi]$  are employed to measure quantum control landscapes discussed in Sec. 4.2. The shaped pulses are focused by a 300 mm focal length lens into a vacuum chamber, where they intersect a beam of potassium atoms or molecules. Photoelectron spectra for different pulse shapes are measured using a magnetic bottle TOF spectrometer. We make use of a 1+2 REMPI (Resonance Enhanced Multi-Photon Ionization) process (see Fig. 4). The fs-laser couples coherently the  $4s$  and  $4p$  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 [15]. 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) doublet [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.

Control of molecular dynamics (Sec. 4.3) is carried out exclusively by sinusoidal phase modulation (Eq. 4). In these experiments the final state population of the  $5^1\Sigma_g^+$  and the  $2^1\Pi_g$

states is probed by a 532 nm, 6 ns Nd:YAG laser separated from the shaped femtosecond pulse by 10 ns. In order to probe only the most intense part of the fs-laser focus, the ns-laser beam is expanded by a telescope and focused by a lens of 250 mm focal length. The resulting two-colour photoelectron spectra is illustrated in Fig. 3 (black spectrum). Beside the one-colour signals of the fs-laser (red spectrum) and the ns-laser (green spectrum) two-colour signals originating from the ionization of the atomic excited state  $4p$  and the molecular excited states  $2^1\Pi_g$  and  $5^1\Sigma_g^+$  show up in addition.



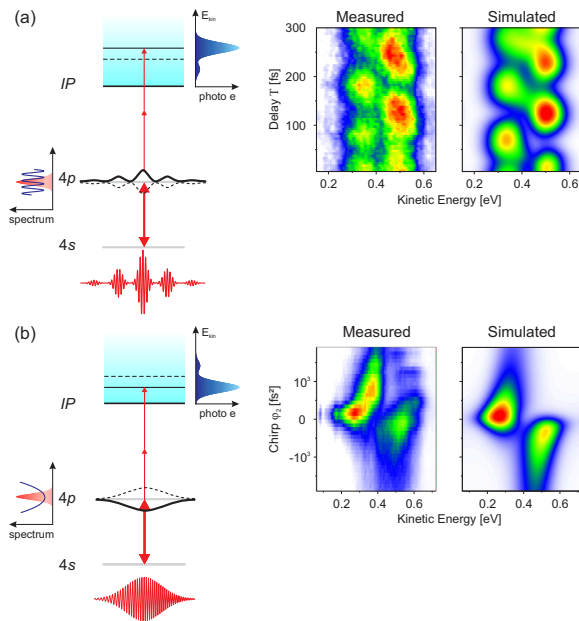
**Figure 3.** (Colour online) Schematic of the experimental set-up for SPODS (Selective Population of Dressed States) experiments on potassium atoms and dimers. The spectrum of our femtosecond laser pulse is phase-modulated in frequency domain to produce complex shaped output pulses which are focused on potassium atoms or molecules in a beam. In the experiments on molecules the final state population is probed by a time delayed nanosecond pulse (lower panel). The resulting photoelectrons are detected with a magnetic bottle TOF photoelectron spectrometer giving rise to a one-colour signal of the pump laser (red), a one-colour signal of the probe laser (green) and a two-colour signal (black).

## 4. Experimental results

In this section we first describe the experimental results to exert control on atoms by one parameter schemes (see Sec. 4.1), i.e. either phase jumps in a pulse sequence or continuously varying phases by chirped pulses. In Sec. 4.2, simultaneous variation of both parameters yielding quantum control landscapes are shown. In Sec. 4.3, we extend our studies on atoms to control of molecular dynamics by SPODS.

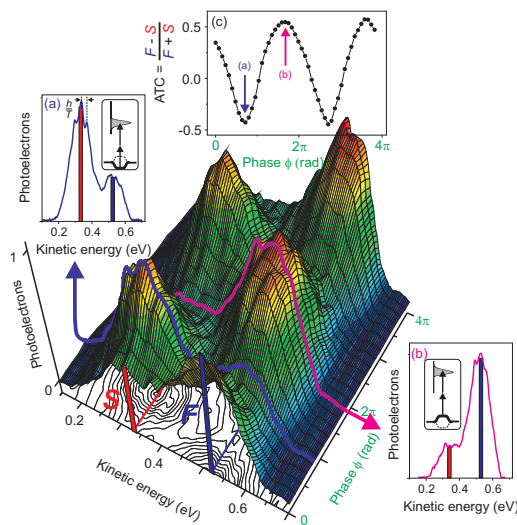
### 4.1. SPODS on atoms: One-parameter control

Fig. 4 shows two realizations of SPODS on potassium atoms using (a) pulse sequences and (b) chirped femtosecond laser pulses. In both cases the experimentally observed photoelectron spectra are in good agreement with our simulations. The results shown in Fig. 4(a) have recently been discussed with the help of dressed states in [16]. Briefly, the pre-pulses in the sequence creates a coherent electronic superposition. The pulse separation  $T$  in the sequence controls the relative optical phase of the central sub-pulse. Depending on this relative phase 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 (PL) [22]. An alternative realization of SPODS shown in Fig. 4(b) is based on Rapid Adiabatic Passage (RAP) [23, 24] by chirped laser pulses. 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 an adaptive feedback learning

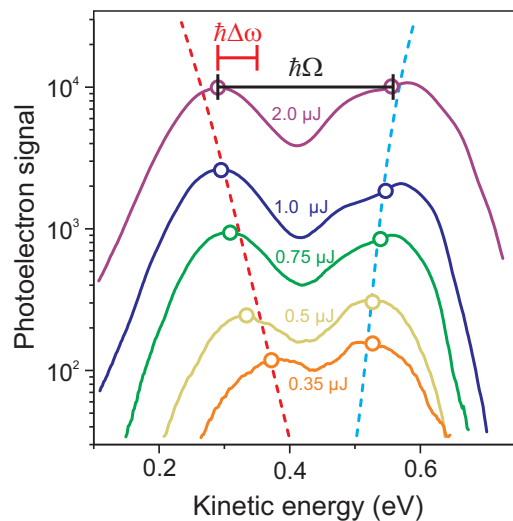


**Figure 4.** (Colour online) SPODS on potassium atoms by (a) Photon Locking (PL) and (b) Rapid Adiabatic Passage (RAP). PL is realized by pulse sequences generated by sinusoidal spectral phase modulation. Population of the upper dressed state is shown. RAP is realized by chirped pulses generated by quadratic spectral phase modulation. Up-chirped pulses populate the lower dressed state. Measured photoelectron spectra (false colour representation) as a function of the pulse parameters delay ( $T$ ) and chirp ( $\varphi_2$ ) are in good agreement with the simulated results.

algorithm we are able to control the dressed state population by more than 90% as demonstrated in [12]. With the help of tailored pulse trains we demonstrate that SPODS is highly selective,



**Figure 5.** (Colour online) Selective population of dressed states using pulse sequences generated by sinusoidal phase modulation  $\varphi(\omega) = A \sin[(\omega - \omega_0) \cdot T + \phi]$ . The photoelectron spectra in (a) and (b) show selective population of the lower and upper dressed states, respectively. The selectivity is measured by the AT contrast  $ATC = (F - S)/(F + S)$  (upper panel).

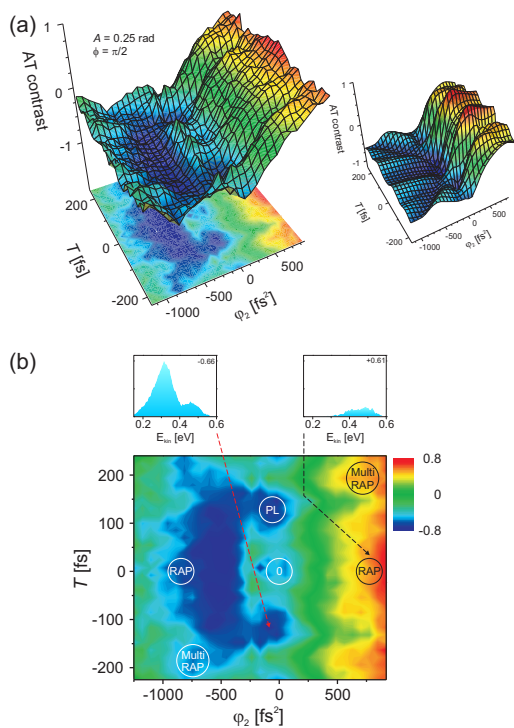


**Figure 6.** (Colour online) Photoelectron spectra as a function of the laser pulse energy ranging from  $0.35 \mu\text{J}$  to  $2.0 \mu\text{J}$  plotted on a logarithmic scale. AT splittings up to  $\hbar\Omega = 270 \text{ meV}$ , corresponding to 4.5 times the laser spectral bandwidth  $\hbar\Delta\omega = 60 \text{ meV}$ , are observed and can be tuned via the laser intensity.

tunable (up to 270 meV) and robust [25]. Fig. 5 shows that SPODS is directly mapped into the

measured photoelectron spectra. These results are obtained by variation of the phase  $\phi$  within the sinusoidal spectral phase modulation function. A section through the distribution along the energy axis at  $\phi = 0.7 \pi$  yields the photoelectron spectrum in which the lower dressed state is selectively populated (Fig. 5(a)). Selective population of the upper dressed state at  $\phi = 1.7 \pi$  is shown in Fig. 5(b). The selectivity is measured by the AT Contrast  $ATC = (F - S)/(F + S)$  (upper panel in Fig. 5) of fast (F) and slow (S) photoelectrons showing up to 80% selectivity. Tunability of the population transfer is demonstrated by the control of the AT splitting as shown in Fig. 6. By variation of the laser intensity electron energy splittings up to  $\hbar\Omega = 270$  meV are observed. As a matter of fact, this exceeds the laser spectral bandwidth ( $\hbar\Delta\omega = 60$  meV) by a factor of 4.5 indicating the strong field character of our control scheme.

#### 4.2. SPODS on atoms: Quantum control landscapes



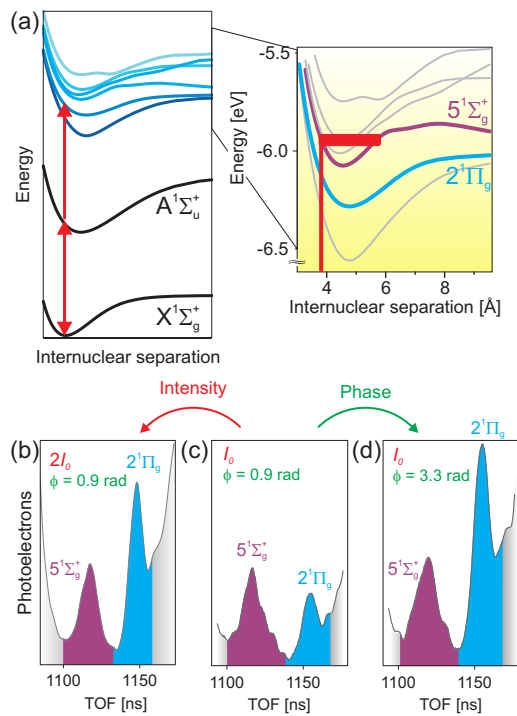
**Figure 7.** (Colour online) (a) measured Quantum Control Landscape (QCL) of selective population of the upper dressed state population. Shaped laser pulses are parameterized by the spectral phase function  $\varphi(\omega) = \varphi_2 (\omega - \omega_0)^2 + A \sin[(\omega - \omega_0) \cdot T + \phi]$ . Variation of  $T$  and  $\varphi_2$  defines a two-dimensional parameter space  $\{T, \varphi_2\}$ . The AT Contrast obtained from the photoelectron spectra from the modulated pulses are plotted for each value of the parameter space. ATC's from simulated photoelectron spectra (right side) reproduce the experimental observations. (b) analysis of the physical mechanisms realized by different parameter combinations within the QCL. Underlying phototelectron spectra for two selected points of efficient SPODS realization via PL (red arrow) and RAP (black arrow) respectively are shown in addition.

So far, one-parameter control of SPODS was demonstrated, introducing the two control mechanisms PL and RAP. A more comprehensive picture of the attainable control is obtained by the investigation of multidimensional Quantum Control Landscapes (QCL) introduced by Rabitz [26] and demonstrated experimentally in [27]. Since PL and RAP are based on *complementary* approaches to control the temporal phase – and thereby exerting control on the dressed state populations – we studied the combined effect of PL and RAP by mapping out a two-parameter QCL of the upper dressed state population. The pulse parametrization is given by a linear combination of chirp and sinusoidal phase modulation:  $\varphi(\omega) = \varphi_2 (\omega - \omega_0)^2 + A \sin[(\omega - \omega_0) \cdot T + \phi]$ . This produces a sequence of chirped laser pulses separated by  $T$  and chirped according to the value of  $\varphi_2$ . Simultaneous variation of these *orthogonal* parameters, which control PL and RAP respectively, defines a two-dimensional parameter space. Scanning the parameter space and measuring the  $ATC$  for the combinations  $(T, \varphi_2)$  yields the two-dimensional QCL shown in Fig. 7(a). Comparison with simulation results (right panel) shows good agreement indicating reliably shaped pulses in the interaction region and demonstrating the feasibility of strong field control using shaped pulses. Fig. 7(b) shows a contour plot of the QCL. Here,

prominent points corresponding to certain physical mechanisms can clearly be identified. At the center  $(T, \varphi_2) = (0 \text{ fs}, 0 \text{ fs}^2)$  the unmodulated pulse produces a medium *ATC* indicating no dressed state control. However, at  $(140 \text{ fs}, 0 \text{ fs}^2)$  an efficient population of the lower dressed state via PL is observed whereas at  $(0 \text{ fs}, 800 \text{ fs}^2)$  the upper dressed state is populated selectively via RAP. Finally, at diagonal points such as  $(200 \text{ fs}, 800 \text{ fs}^2)$  a combined mechanism based on multiple sequential realizations of RAP (Multi-RAP) is at play, also showing significant effect on the dressed state population.

#### 4.3. SPODS on molecules

Fig. 8(a) shows the excitation scheme of near resonant multi-photon excitation of potassium dimers. Control of the dynamics in  $K_2$  is analogous to the resonant strong field control scenario depicted in Fig. 2 and was recently studied theoretically in [28]. Molecules in the vibrational eigenstate  $v'' = 0$  of the  $X^1\Sigma_g^+$  electronic ground state are excited by a pre-pulse with a pulse area of approximately  $\pi/2$  to the near resonant  $A^1\Sigma_u^+$  state to create an *electronic* coherent superposition. Depending on the relative phase, the intense central pulse of the sequence selectively populates one dressed state. This dressed state is shifted in energy such that a single target state within the excited state manifold is selectively excited via resonance. The magnified region in Fig. 8 shows the Franck-Condon region for a 30 fs pulse at an excitation wavelength of 795 nm. At this wavelength the population is switched between the  $5^1\Sigma_g^+$  and the  $2^1\Pi_g$  states. In the experiment, the final state population of the  $5^1\Sigma_g^+$  and the  $2^1\Pi_g$  states



**Figure 8.** (Colour online) (a) Excitation scheme of potassium dimers. The magnified region shows the Franck-Condon window within the excited state manifold. At an excitation wavelength of 795 nm, population is switched between the  $5^1\Sigma_g^+$  and the  $2^1\Pi_g$  states. Molecular dynamics is controlled by the intensity  $I$  of the pulse and the phase  $\phi$  in the spectral phase function  $\varphi(\omega) = A \sin[(\omega - \omega_0) \cdot T + \phi]$ . (b–d) two-colour photoelectron spectra from Nd:YAG probing of the final state population in the  $5^1\Sigma_g^+$  and the  $2^1\Pi_g$  states. (c) shows the reference measurement at intensity of  $I_0 = 2 \times 10^{11} \text{ W/cm}^2$  and a phase of  $\phi = 0.9 \text{ rad}$ . (b) variation of the intensity by a factor of two and (d) by changing the phase to  $\phi = 3.3 \text{ rad}$ .

is controlled by the intensity  $I$  of the pulse and the phase  $\phi$  in the sinusoidal spectral phase function Eq. (4) and probed by Nd:YAG photo-ionization. Fig. 8(b–d) show the two-colour photoelectron spectra resulting from the Nd:YAG probing of the final state population. The reference measurement at an intensity of  $I_0 = 2 \times 10^{11} \text{ W/cm}^2$  and a phase of  $\phi = 0.9 \text{ rad}$  is depicted in Fig. 8(c). By changing the phase to  $\phi = 3.3 \text{ rad}$ , the population in the  $2^1\Pi_g$  state is enhanced by more than a factor of three indicating population of the lower dressed  $A^1\Sigma_u^+$  state. Intensity dependent control as observed in strong field control of atoms [14] and molecules [28]

provides a critical test to discriminate weak field control scenarios such as spectral interference from strong field control. As an evidence of strong field control, we varied the intensity by a factor of two (Fig. 8(b)) resulting in a significant enhancement of the population in the  $2^1\Pi_g$  state (relative to the  $5^1\Sigma_g^+$  population).

## 5. Conclusion

In this contribution we discussed a physical mechanism of coherent control with intense shaped femtosecond laser pulses. We studied the effect of chirped pulses and pulse sequences to manipulate the photoelectron spectra from multi-photon ionization of potassium atoms. Results were discussed in terms of the Selective Population of Dressed States (SPODS). SPODS provides a unifying framework for the observed strong field control schemes Photon Locking (PL) and Rapid Adiabatic Passage (RAP). Combined effects which arise when both mechanisms are at play simultaneously were investigated by mapping out a two-dimensional Quantum Control Landscape (QCL). Applying the principles of dressed state control to potassium dimers we demonstrated experimentally that SPODS is operative in quantum control of molecules as well. Since switching of the dressed state population occurs within a few femtoseconds, this technique is also interesting for applications in the presence of decoherence processes. Because SPODS combines high selectivity and tunability (several hundred meV) with efficient population transfer, relevant applications to chemistry are within reach.

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