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Femtosecond pump–shaped-dump quantum control of retinal isomerization in bacteriorhodopsin

G. Vogt, P. Nuernberger, T. Brixner, G. Gerber *

Universität Würzburg, Physikalisches Institut, Am Hubland, D-97074 Würzburg, Germany

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Abstract

We experimentally demonstrate molecular quantum control on the photoisomerization of retinal in bacteriorhodopsin with pump and shaped-dump femtosecond laser pulses. The objective is a reversion of regular control schemes for optimal excitation in which the pump pulse is shaped. Instead, we seek optimal de-excitation with a shaped-dump pulse. The pump–shaped-dump–probe scheme allows control of molecular systems away from the initial Franck–Condon window in regions of the potential-energy landscape where the decisive reaction step occurs. In addition, this method has the potential to provide information on wave packet evolution and underlying potential-energy surfaces.

1. Introduction

Quantum control with shaped femtosecond laser pulses has become a well-established technology [1–8]. In adaptive control, a learning algorithm and experimental feedback are employed to find optimized electric field shapes [9]. In the usual situation a control field is desired that optimally and selectively excites a given quantum system, starting from the ground state, in order to reach a predefined target state such as a certain dissociative product channel. This method is well suited for controlling a large variety of quantum phenomena. On the other hand, it is often difficult to interpret optimal field shapes. One of the reasons is the generally complex interplay of several intermediate steps, i.e., population/depopulation processes of intermediate states, during the course of the photoreaction.

Since the characteristics of excited-state potential-energy surfaces (PESs) determine both photophysical and photochemical processes, it would be desirable to use the power of pulse-shaping technology for specifically studying excited-state dynamics. In order to facilitate such analysis despite the problem mentioned above, we here reverse the usual quantum control procedure: instead of looking for optimal excitation starting from the ground state, we seek optimal *de-excitation* starting from the excited state. This offers the opportunity to study the properties of the excited system more directly, retaining the capabilities of shaped-pulse analysis. The idea is that shaped de-excitation pulses (dump pulses) should contain information on the propagating excited-state wave packet and thus on the shape of the excited-state PES.

Specifically, we are interested in molecular reactions that involve non-radiative transitions to a lower-lying PES. These processes are often thought to proceed via a conical intersection (CI) [10]. In the example of Fig. 1 the molecule is excited by a pump pulse resulting in a wave packet in the Franck–Condon region of the first excited-state (S_1) PES. This wave packet evolves under the influence of the excited-state Hamiltonian. At the CI the wave packet can propagate back to the ground state (S_0). The probability for populating different product configurations on the ground-state PES is directly related to the dynamics at the CI. In the displayed example, the decay occurs with a certain probability either to the right or to the left well of the ground-state PES, such as *cis* or *trans* structures in

* Corresponding author. Fax: +49 931 888 4906.
E-mail address: gerber@physik.uni-wuerzburg.de (G. Gerber).

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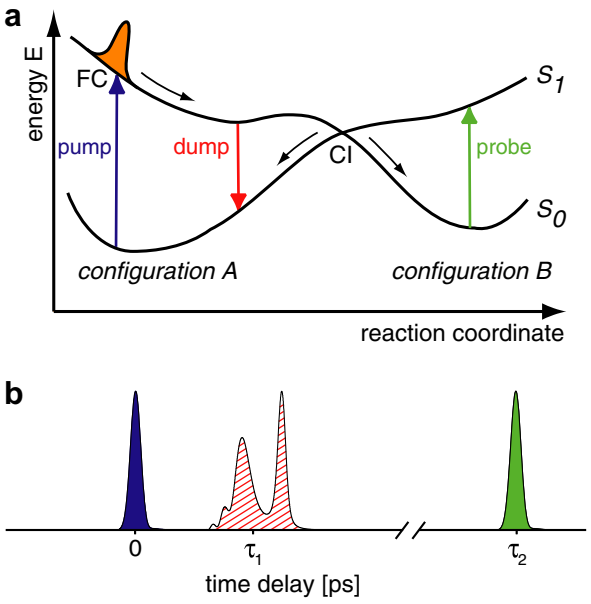

Fig. 1. (a) PES scheme for a typical molecule. After $S_0 \rightarrow S_1$ excitation by a pump pulse, the induced wave packet moves from the Franck–Condon region (FC) to the conical intersection (CI), where it can decay back to the S_0 PES. With a certain probability, either molecular configuration A or B is populated. (b) Pump–shaped-dump–probe sequence. In this example, the shaped-dump pulse (red/hatched) is delayed by τ_1 with respect to the pump pulse (blue/dark gray). The impact of the dump pulse, i.e. the final population in configuration B, is monitored by the probe pulse (green/light gray), which arrives at a time delay $\tau_2 \gg \tau_1$ after the pump pulse. (For interpretation of the references in colour in this figure legend, the reader is referred to the web version of this article.)

the case of an isomerization reaction. The shape and the velocity of the wave packet close to the CI depend on the nature of the S_1 PES.

In addition, a suitable electric dump field can influence the evolution of the wave packet. For many molecular systems, the excitation wavelength for the $S_0 \rightarrow S_1$ transition is in the UV region. If we desire to study and influence the wave-packet evolution further away from the initial Franck–Condon region, near the CI where the decisive step of the reaction occurs, then the control field is required in a lower frequency region than the pump pulse. This concept was realized with unshaped pulses in conventional pump–dump or pump–repump schemes with differing central wavelengths [11–13]. Also, shaped Stokes pulses were used in the context of achieving selective ground-state population within coherent anti-Stokes Raman spectroscopy [14,15]. For processes on electronically excited surfaces, it was suggested by theory that pump–dump–repump interactions are able to influence the dynamics in the vicinity of CIs, and that it would be useful to employ electric control fields that accompany the wave packet all the way to the product state [10,16–19].

In order to study the excited-state evolution, we here implement quantum control with a *shaped* dump pulse. This has the potential of influencing the dynamics in the vicinity of a CI, which is of essential importance to the final reaction outcome. The end result is measured by an additional time-delayed probe pulse. With adaptive quantum control the optimal shape for the dump pulse can be obtained, and together with systematic variations of parameterized dump pulse shapes, information on the PESs close to the CI may be deduced.

This concept is used to study the isomerization of retinal embedded in the protein bacteriorhodopsin. This molecular system has been intensively investigated (see, e.g. Refs. [11–13,20–27]) and it represents an important isomerization reaction in nature, where the isomerization triggers a proton pump process in bacteria that flourish in gruffy salt marsh environments [24]. The thermodynamically most stable configuration exhibits *all-trans* geometry and is commonly labeled bR_{568}. The subscript denotes the wavelength of the maximum of the absorption band connected with the $S_0 \rightarrow S_1$ transition. After excitation and wave-packet propagation on the S_1 PES, the decay to the ground state, where two isomers are accessible, is assumed to occur through a CI. The early-time dynamics on the S_1 PES are under discussion and it is still an issue whether it exhibits a small barrier or not [27]. The shape of the propagating wave packet would be affected by the presence of such a barrier and therefore a tailored dump pulse for most effective dumping should reflect this situation in a corresponding pulse shape. For bacteriorhodopsin, it has already been shown that one can influence the molecular dynamics with traditional pump–dump–probe schemes [11,13]. Therefore, the molecule is ideal to test the potential of the concept in which the dump pulse is shaped adaptively on the one hand and systematically on the other hand.

2. Experimental

The laser system delivers 80 fs, 800 nm, 800 μJ pulses. In the experimental setup (Fig. 2) one fraction is frequency-doubled in a 400 μm lithium triborate (LBO) crystal and is used as unshaped pump pulse, its energy attenuated to

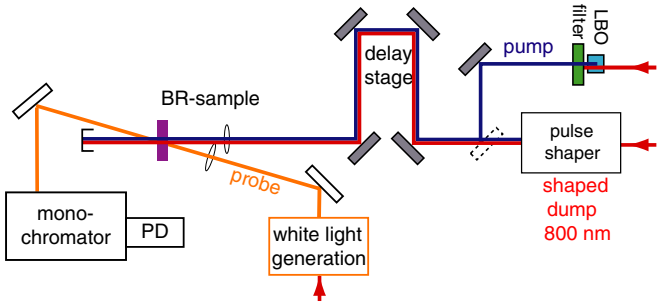

Fig. 2. Experimental setup. The 800 nm dump pulse is phase-modulated in the pulse shaper, and combined collinearly with the pump pulse that is frequency-doubled in a nonlinear LBO crystal. A probe-pulse white-light continuum is generated by focusing a small fraction of the 800 nm beam into a sapphire plate. All three pulses overlap spatially in the bacteriorhodopsin (BR) sample, and a monochromator with photodiode (PD) detects the desired (spatially separated) probe wavelength at an adjustable delay.